Characteristics of main research directions investigated at the institute and the achievements 2010−2014

Institute	Institute of Physics of the CAS, v. v. i.

Introduction – history and structure of the Institute

Fyzikální ústav AV ČR, v. v. i. (FZÚ; in English: Institute of Physics of the Czech Academy of Sciences) is a public research institute, oriented on fundamental and applied research in physics. The founder of the Institute is the Czech Academy of Sciences. The present research program of the Institute comprises five branches of physics: particle physics, physics of condensed matter, solid state physics, optics and plasma physics. This also corresponds to the way how the institute is divided into major research divisions.

The history of the FZÚ is rich, related to series of successive reconstitutions of various physical institutions. A crucial step in 1979 was the merging of the original Institute of Physics of the Czechoslovak Academy of Sciences (CSAS) at the Slovanka site with the Institute of Solid State Physics of the CSAS (ISSP). The germ of the ISSP was the Physical Research of Škoda Works, founded in 1932, transformed after nationalization into the Central Institute of Physics (CIP) in 1950. It was transferred to the premises at Cukrovarnická Street in Prague – Střešovice and in 1952 already as the Institute of Technical Physics it became one of the seven constituent institutes of the CSAS, in 1962 it was again renamed as ISSP. The Institute of Physics of the CSAS was established in 1954 by merging the Laboratory for Nuclear Physics (LNP), founded in 1946, with a newly founded Laboratory for Experimental and Theoretical Physics (LETP). In 1970 it moved to new buildings at Na Slovance Street in Prague – Kobylisy. In 1983 the department of the Applied Plasma Physics of the Institute of Plasma Physics CSAS was incorporated into the FZÚ, later giving rise to the Division of High Power Systems. In 1990 the Division of Optics was created, the important part of which has been since 1985 the Joint Laboratory of Optics of the FZÚ and Palacký University in Olomouc, one of the first joint laboratories between the FZÚ and the University.

Since January 1, 2007 the FZÚ has become a public research institution (v. v. i.). The Structural funds of the European Union significantly influence the research in the FZÚ, which is a coordinator of the greatest such project in the CR aimed at the Extreme Light Infrastructure (ELI). For its realization a new Division was created in 2012. The FZÚ is the largest institute of the Academy of Sciences of the CR, with more than 400 scientists.

FZÚ has always been an important center of international cooperation. Today, several of its laboratories are nodes in programs of European Community, and many more participate in international grant programs, bilateral co-operations, and the work of international research centers all over the word. A number of prestigious international conferences and schools organized by the Institute brought thousands of international experts to the Czech Republic. Within the country, the cooperation with other institutes of the Academy and with Czech universities has high priority. Traditionally, graduate studies in physics have been a joint effort of the universities and of the Academy. Presently, the Institute of Physics is accredited to educate students in a number of fields, with the PhD degree being granted by the Charles University, Palacký University, Czech Technical University as well as other Czech technical and

technological universities. Many of the graduate students nowadays come from abroad. Different supporting programs, including the Marie Curie Training Site, are available. In some areas, the needs of research cooperation prompted more profound steps towards uniting resources and coordinating the efforts. Within the Academy, and together with the universities, the Institute has helped to establish several Joint Laboratories, as well as several national Research Centers.

As we have stated above, FZÚ currently comprises six scientific divisions. We will describe them and their structure in more detail in following paragraphs:

Division of Elementary Particle Physics.

Teams: 1 - Astroparticle Physics, 17 - Experimental Particle Physics, 18 - Particle Physics Theory and Phenomenology

The research program of the Division is carried out mainly within large international collaborations which run their experiments in a few main research centres equipped with powerful accelerators or other large experimental facilities. The principal purpose of these experiments is to study the structure of matter on subnuclear scales and the properties of fundamental forces acting among its constituents. Particle physics is in many ways connected to various topics of modern astrophysics such as the structure and evolution of the early universe or the existence of extremely energetic cosmic rays.The Division consists of four departments.

The accelerator experimental program of the Division is conducted within the **Department of Experimental Particle Physics** as well as the **Department of Detector Development and Data Processing** which for the purpose of this evaluation form together Team 17. It is focused on the ATLAS experiment at the LHC collider at CERN and neutrino experiment NOvA at Fermilab. Activity of this team covers a wide range of areas – physics analyzes as well as design, development and production of detector components, data acquisition, software development, and distributed computing used for detector simulation and data analysis within the GRID project. Experimental activities of the Division exploit the facilities and personnel of our Laboratory for semiconductor detectors.

Program of the **Department of Particle Theory and Phenomenology** (Team 18) focuses on a range of topics from purely theoretical and formal subjects within string theory to the phenomenological aspects of real-world hadrons - strongly interacting particles. On the theoretical side a dominant subject of interest is string theory, conformal field theory, higher spin theory and quantum gravity, which are often interrelated. On the phenomenological side the research mostly deals with issues of direct experimental relevance. In fact, all four phenomenology researchers are members of major international high-energy particle physics collaborations at CERN (Atlas, Alice or Totem).

Department of Astroparticle Physics (Team 1) participates in the Pierre Auger Observatory to study particles with energies several orders of magnitude higher than those of the terrestrial accelerators. The observatory measures cosmic ray showers in the atmosphere. The team is involved in the operation of the fluorescence telescopes, the data analysis related to the characteristics of the hadronic interactions and the atmospheric monitoring that is essential for an unbiased shower reconstruction.

Since 2011 the Department has been active in the Cherenkov Telescope Array (CTA) a future generation observatory of high-energy gamma-rays. Other activities concern the LSST project, measurement of the fluorescence yield in air and the pioneering project attempting to detect cosmic ray showers at gigahertz frequencies.

Condensed Matter Physics Division.

Teams: 8 - Magnetic Nanosystems, 9 – Dielectrics, 10 – Nanocrystals and Grain Boundaries, 11 – Nanodiamond and Biointerfaces, 12 – Shape Memory Materials and Composites, 13 – Microscopic Theory of Manyparticle Systems

It is a dynamically evolving research division, dealing with physical properties of modern materials. It consists of 6 departments – Dielectrics, Advanced Structural Materials, Functional Materials, Magnetic Nanosystems, Condensed Matter Theory, and **Chemistry**, which focuses on materials technologies such as crystal growth, sample preparation, chemical analysis and synthesis of liquid crystals. This department is not evaluated as it serves as a support facilty, mainly for the Department of Dielectrics.

Department of Dielectrics (Team 9) has traditionally been connected to physics of ferroelectrics and structural phase transitions. It also represents a unique center of the dielectric spectroscopy carried out in the extremely broad frequency range of 1–10^{14} Hz. Current research concentrates mainly on ferroelectric and multiferroic substances in the form of solid and liquid crystals, thin films, ceramics, composites and nanostructured materials.

After finishing the period of studying plastic deformation of iron and iron-based alloys, the former Department of Metals - now renamed as the **Department of Advanced Structural Materials** (Team 10 - Nanocrystals and Grain Boundaries) – currently focuses on the development of new prospective bulk materials with controlled microstructure, including ultra-fine-grained metals with unique properties. This research requires modern equipment, enabling e.g. a preparation of precisely localized samples by means of the focused ion beam, (Dual Beam) and analytical transmission electron microscopes.

The **Department of Functional Materials** (Team 12 - Shape Memory Materials and Composites; Team 11 - Nanodiamond and Biointerfaces) focuses on studies of unique properties of materials exhibiting martensitic phase transformations, particularly NiTi shape memory alloys and ferromagnetic Heusler alloys, the main representative of which is the Ni-Mn-Ga alloy exhibiting the magnetic shape memory and magnetocaloric effects. NiTi(X) shape memory alloys are used in high temperature actuators or medical devices e.g. as braided NiTi stents or functional NiTi textile-polymer composites. Furthermore, the department researchers also grow and characterize CVD nanodiamond films and particles for a broad range of applications in engineering, energy and medical fields.

As a successor of the former Department of Magnetism and Low Temperatures, the newly established **Department of Magnetic Nanosystems** (Team - 8) is focused on studies of transition metals (magnetic nanoparticles, thin films, giant anisotropy materials) and carbon nanostructures in broad ranges of temperatures and magnetic fields. This Department actively participates in two Joint Laboratories with the Faculty of Mathematics and Physics, Charles University in Prague.

The research activity in the **Department of Condensed Matter Theory** (Team 13 - Microscopic Theory of Manyparticle Systems) is mainly focused on ab-initio calculations and modeling electron properties of metals, semiconductors, and other complex materials with non-trivial elementary cell or with enhanced electron correlation effects. Non-equilibrium and cooperative phenomena are studied in quantum and classical systems by means of advanced analytic and numerical simulation methods. Furthermore, unique material properties related to surfaces and interfaces are investigated.

Division of Solid State Physics.

Teams: 2 – Semiconductors, 3 – Spintronics and Nanoelectronics, 4 – Structural Analysis, 5 – Magnetics and Superconductors, 6 – Thin Films and Nanostructures, 7 – Optical Materials

It is the oldest and biggest division, comprised of 6 departments. The **Department of Structure Analysis** (Team 4) represents a longtime tradition of the X-ray physics where the understanding of atomic structure, electron states and hardness enables research into unique materials. The structure analysis by diffraction methods aims at so called aperiodic structures. Thanks to computing methods of the JANA program, the Department contributes to the methodology of this branch on a worldwide scale. The latest development concerns the precession electron diffraction tomography for investigation of submicroscopic amounts of samples.

Research into semiconductors has been an important subject of the Division from the very beginning. Ge and Si single crystals of extreme purity but also the III – V semiconductor lasers were prepared. The principal technology used in the **Department of Semiconductors** (Team 2) is the Metal-Organic Vapor Phase Epitaxy (MOVPE) which makes it possible to prepare unique nanostructures, such as quantum dots and wells. In these and other semiconductor systems quantum Hall effects, excitons in quantum dots and superconductivity of nanocrystalline diamond are studied experimentally as well as theoretically.

Molecular Beam Epitaxy (MBE) and Electron Beam Lithography (EBL) are two basic technologies of the **Department of Spintronics and Nanoelectronics** (Team 3) which enable, together with theoretical background, a study of a series of phenomena pertaining to a fast developing branch of so called spintronics. Spin transistors and spintronic magnetoresistent parts on the basis of ferromagnetic, antiferromagnetic and nonmagnetic semiconductors or metals, as well as optical spin-transfer and spin-orbit torques are studied in cooperation with Charles University, universities in Nottingham, Cambridge and other world laboratories.

This Division significantly contributed to the worldwide development of amorphous semiconductors, the **Department of Thin Films and Nanostructures** (Team 6) mainly by the study of amorphous silicon, used in flat screens or photovoltaic cells. Research into the surfaces and silicon nanocrystals naturally led to the development of nanotechnologies and/or nanophotonics. Atomic Force Microscopy and Scanning Tunneling Microscopy (AFM/STM) and unique methods of theoretical calculations enabled visualization, identification as well as targeted formation of nanostructures on an atomic level. Hybrid bio-interfaces with metals and semiconductors, such as diamond, are being developed.

Preparation and study of various forms of diamond are an important part of the research of the **Department of Optical Materials** (Team 7). A significant success is the preparation of large-area samples of nanodiamond by CVD method at low temperatures, their nanostructuralization and biofunctionalization. A considerable attention is paid to scintillation materials, studied in the frame of many national and international cooperations. Unique material compositions in various forms and morphologies enable a sensitive detection of ionizing radiation and are used especially in the medical, nuclear and security applications.

Experimental study of multifunctional magnetic materials, supported by top theory of the studied phenomena with first principle calculations is a foundation in the **Department of Magnetics and Superconductors** (Team 5). Internationally recognized are the results of the study of magnetic interactions, magnetic structures and limiting states under very high pressures. Unique methods of measurement both of magnetocaloric and of Seebeck effects contribute to the testing of materials suitable for magnetic cooling, and/or thermoelectric heat conversion. An important application is potential use of magnetic nanoparticles in magnetic fluid hyperthermia in oncologic diagnostics and therapy.

Division of Optics.

Teams: 19 – Optical and Biophysical Systems, 20 – Physical Processes in Low Temperature Plasma, 21 – Plasma-based Technologies and Analysis of Functional Materials, 22 – Classical and Quantum Optics

This division covers a wide range of research topics including optics, materials science and engineering, optical technology, and biophysics. It consists of one technical and four scientific departments. The **Department of Optical and Biophysical systems** (Team 19) is mainly focused on the research and development of optical materials and systems for micro-electronic, optoelectronic and biomedical applications. The spectroscopic ellipsometry and other optical techniques are used for the study of nanostructures, surfaces, and thin films, detection of surface, bulk and interface phase transitions, and dynamics of biological films and surfaces. The optical structures for the research are prepared by pulsed laser deposition technique. The important part of the research is focused on the field of X-rays optics, where new monochromators for synchrotron radiation sources are developed and investigated.

Four years ago, the new research area of biophysics in the framework of the department was established. The research comprised several lines: magnetic targeting of stem cells, magnetic hyperthermia, magnetically driven cellular endocytosis, stem cells networking with micro-magnet arrays, application of atmospheric low-temperature plasma for bacteria deactivation and regenerative medicine.

Quantum optics with cryptographic applications and nonlinear optical phenomena are investigated at the **Joint Laboratory of Optics** which is considered as a Department in the organizational scheme of the Institute (Team 22 – Classical and Quantum Optics). In the area of quantum and nonlinear optics, the research topics are mainly related to the generation, transmission, detection and quantum processing of information, using the fields of photon pairs obtained by parametric down conversion. The department for a long time deals with advanced approaches and applications focused on various areas of applied and technical optics and optoelectronics. In the

field of statistical and wave optics the researches are engaged in the development and applications of advances optical methods.

Advanced characterization of materials is performed at the **Department of Analysis of Functional Materials** (Team 21 – Plasma-based Technologies and Analysis of Functional Materials), which is a part of Center of Analysis of Functional Materials (SAFMAT). Sophisticated analytical instruments NanoESCA and EPR are used at the department. This combination is optimized for non-destructive analysis of chemical compounds (Imaging ESCA / XPS), imaging ultraviolet photoemission spectroscopy (UPS) and Angular Resolution UPS (ARUPS). The EPR laboratory is equipped by spectrometer Bruker ELEXSYS E580, which is a top-class scientific device to measure electron paramagnetic (spin) resonance in both modes – classic (CW) and pulsed (FT), in the common X-band as well as high-frequency Q-band.

The research of low-temperature plasma deposition processes at the **Department of Low-Temperature Plasma** (Team 20 – Physical Processes in Low Temperature Plasma) is oriented to the development of the plasma reactors, used for the deposition of advanced thin film structures. A hybrid deposition system based on the combination of pulsed high power magnetrons and pulsed hollow cathode plasma jets are developed for the deposition of high quality optical TiO2 thin films at low substrate temperature. UHV deposition systems with “in situ” advanced monitoring of deposition processes are developed for deposition of the self-organized nanostructures.

Division of High Power Systems.

Teams: 14 – Laser-Matter Interaction and Chemical Physics, 15 – Laser Development and Applications

The division is focused on experimental research of laser produced plasma and lasers. In the **Department of Radiation and Chemical Physics** we study phenomena on the edge of high energy density physics and also high energy chemistry, particularly the interaction of extremely intense ultraviolet and X-ray radiation with matter. The techniques of plasma spectroscopy, characterization of focussed beams of short-wave lasers, visualization of the local structure of atoms in crystals, development of chemical and plasma-chemical generators for chemical lasers, monitoring of laser-induced dielectric breakdown in molecular gases, theory and numerical simulations of hot dense plasmas, and laser acceleration of particles all play an important role in our studies.

The key project of strategic importance is the construction of a modern laser research centre HiLASE in Dolní Břežany pursued by **Department of Diode Pumped Lasers.** Project is focused on the experimental development of a new generation of diode-pumped solid-state lasers with high pulse energy and high repetition rate. The main applications of these lasers include laser induced damage threshold measurement of optical materials, laser shock peening, development of compact X-ray sources for lithography, and laser micromachining.

The detailed description of the achievements of the Department of Radiation and Chemical Physics is described in the report of the Team 14 (Laser-Matter Interaction and Chemical Physics) and the Department of Diode Pumped Lasers presents its results in the report of the Team 15 (Laser Development and Applications). In this case the main accomplishment is the succesfull completion of the HiLASE building in June 2014, moving the team to Dolní Břežany and restart of laser research.

ELI Beamlines Project Division.

Team: 16 – ELI Beamlines

This division has a very specific role. It has as the main goal preparation and realization of the **ELI** (Extreme Light Infrastructure) **Beamlines** project, which is the largest research initiative in the history of the Czech Republic. Therefore it is presented as one Team 16 (ELI Beamlines). The Institute of Physics of the Academy of Sciences acts as the coordinator of the ELI project in the Czech Republic and as a recipient of the structural funds grant from the Operational Program Research and Development for Innovations. The ELI project is part of the European plan to build a new generation of large research facilities selected by the European Strategy Forum for Research Infrastructures (ESFRI). The ELI will consist of three complementary facilities currently under construction in the Czech Republic, Hungary and Romania. The main goal of ELI is to create a **modern international laser infrastructure** with world-unique parameters that will be focused on user-oriented research.

The research projects at ELI will cover the area of interaction of matter with light at extreme intensities about 10 times higher than are current limits. ELI will provide **ultrashort laser pulses** of a few femtoseconds (10-15 fs) duration and give performance up to 10 PW. ELI will bring new knowledge and techniques applicable in astrophysics, for medical image-display, diagnostics and radiotherapy, in nanotechnologies, in construction of tools for development and testing of new materials, in X-ray optics, imaging in material sciences, chemistry and biology at various wave lengths, pump and probe experiments and further scientific and advanced aplied applications. ELI will also be an attractive platform for the education of a new generation of scientists.

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Astroparticle Physics

Astroparticle physics projects form a significant part of the scientific program of the Elementary Particle Physics division and Optics division of the Institute of Physics of the Academy of Sciences of the Czech Republic. Dedicated astroparticle physics department, which forms the evaluated team (scientific team No. 1 – astroparticle physics), was created in the division of Elementary Particle Physics in 2010 as a result of the long term and significant involvement of the Czech Republic at the Pierre Auger Observatory and other previous astroparticle physics projects. The personnel of the department currently consist of 7 researchers, 2 PhD students and 4 young technicians and the group is led by Petr Trávníček. The evaluated team includes also the director of the Institute of Physics Jan Řídký who is formally not a member of the department but he stays very active as a scientist and representative of the Czech Republic at the Pierre Auger Observatory. The department took over the responsibility for the operation and maintenance of the fluorescence detector and atmospheric monitoring devices of the Pierre Auger Observatory. Within the Institute the involvement in the Pierre Auger Observatory and now also in the Cherenkov Telescope Array (CTA) is based on a very close collaboration between the Department of Astroparticle Physics (in Prague - team No. 1 – astroparticle physics) and the Joint Laboratory of Optics of the Palacký University and the Institute of Physics ASCR (in Olomouc – team No. 22 - classical and quantum optics) where the technology for production of mirror segments and testing facilities of physics properties of optical samples is available. The team in the Department of Astroparticle Physics in Prague consists of particle physicists and astronomers, while the collaborating team from Olomouc is focused on optical problems related to the construction and operation of the observatories as part of its research program. It is the synergy of the two teams that makes the contribution of the Institute unique. If not stated and explained otherwise in more detail we have focused in the following text on the results that were achieved with major contributions specifically from the evaluated team.

Beyond its scientific activities at the Pierre Auger Observatory and since 2012 also in the Cherenkov Telescope Array, the Department of Astroparticle Physics serves also as a coordinating node of the national technical and scientific activities in the above-mentioned projects (i.e. it coordinates not only the involvement of the Institute of Physics but also the activities of other institutions from the Czech Republic). The Charles University and the Palacký University have been partner institutions for a long time in most of the activities and a steady flow of students to the team is established from these institutions as well as from the Czech Technical University in Prague.

Currently, the most important activities of the Department of Astroparticle Physics are focused on experimental studies of ultra-high energy cosmic rays (Pierre Auger Observatory) as well as high energy gamma rays (Cherenkov Telescope Array - CTA). Other activities in 2010-2014 consisted of laboratory measurements of the fluorescence yield in air (Air FLuorescence Yield - AirFLY), which is crucial for the precise energy reconstruction in fluorescence detectors, and of the participation in the pioneering project attempting to detect cosmic ray showers at gigahertz frequencies (Air Microwave Yield - AMY). Furthermore, the team takes part in the project of the new largest survey telescope (LSST), which among other priorities aims to determine properties of dark energy and dark matter.

In total, the team has co-authored during the evaluation period more than 50 refereed papers, the team members regularly participate as representatives of the international collaborations at important conferences or they present their original work done outside these collaborations (more than 15 conference talks during the evaluation period). The team members serve as supervisors of bachelor, master and doctoral students at the Palacký University, the Czech Technical University and the Charles University (during the evaluation period 3 bachelor theses, 6 master theses and 1 doctoral work were defended; another doctoral thesis was defended at the beginning of 2015). During the evaluation period, the team activities were financed by 8 research grants of the Ministry of Education, Youth and Sports of the Czech Republic (AUGER, CTA and LSST projects and bilateral projects between Czech Republic and Argentina), 1 project of the Grant Agency of the Czech Republic, 2 projects of the Grant Agency of the Academy of Sciences of the Czech Republic and 2 EU projects under FP7 (GLORIA – the network of robotic telescopes, ASPERA – AStroParticle ERA net). In all these grant projects one of our team members has been a principal investigator and the resources were distributed by our Institute typically also to the Charles University and to the Palacky University. Furthermore a member of our team coordinated another EU project related to access to Frascati accelerator via FP7 grant TARI (Transnational Access to Research Infrastructure) – see also description of the AMY experiment further in the text.

Ultra-high energy cosmic rays (Pierre Auger Observatory)

The highest energy cosmic rays coming to the Earth from the Universe remain one of the most intriguing puzzles of modern physics already for more than 40 years. These cosmic particles have an energy above 10 million trillions (10^19) electron volts. There is no scientific consensus on how or where cosmic rays with these ultra-high energies originate. Cosmic rays with energies above 10^19 eV arrive on Earth at a rate of only 1 particle per square kilometer per year. The especially interesting cosmic rays, which have energies of over 10^20 electron volts have an estimated arrival rate of just 1 per square kilometer per century. In order to record a large number of these events, the Pierre Auger Observatory has created a detection area in western Argentina of the size of 3 000 square kilometres.

With unprecedented collecting power and experimental controls, the Pierre Auger Observatory gathers the data needed to solve several important questions, namely: Where do these particles come from? What are they (composition)? How are they accelerated (source mechanism)? Does their energy spectrum end?

The Pierre Auger Observatory measures the so called cosmic ray showers, which develop in the atmosphere as a result of an interaction of a primary cosmic ray particle coming from the Universe with atomic nuclei of air gases. The Institute joined the international collaboration already in its early days in 1997 and participated in design, prototyping as well as construction of the observatory. The main hardware contribution of the Czech Republic was the design and production of 15 out of 27 (12 sq. m each) segmented mirrors of the fluorescence detector done in Olomouc (team No. 22 - classical and quantum optics) and coordinated at that time by the leader from the astroparticle physics team (No. 1) in Prague. The scientific topics related to the fluorescence detector have remained the main part of the department interest for many years. The department personnel is involved in the operation of the fluorescence telescopes, in the atmospheric monitoring and in the data analysis.

Operation of the fluorescence telescopes of the Pierre Auger Observatory
During the whole evaluation period (and also several years before) the scientists of the department were concentrated apart from other duties on the operation of the fluorescence telescopes. A member of the astroparticle physics team (Jan Řídký) served several years, including 2010, as the Fluorescence Detector Task Leader. Due to a huge amount of other responsibilities he was later replaced by other member of our team (Radomír Šmída - now

working from KIT Karlsruhe). The alarm system developed by the team in Prague as well as the online cloudiness cameras from Olomouc help to improve the data taking of the observatory. The essential summarizing paper concerning the fluorescence detector of the Pierre Auger Observatory was written under the leadership of the Prague team and was published in 2010 [1]. Another continuous contribution of our team during the evaluation period has been devoted to regular analysis of the calibration data of the fluorescence detector.

Atmospheric monitoring at the Pierre Auger Observatory

The monitoring of the atmosphere above the Pierre Auger Observatory is essential for an unbiased cosmic ray shower reconstruction. We have been working on the topic for many years. The journal paper with our significant contribution summarized the influence of the atmospheric conditions on the data reconstruction already in 2010 [2]. Our group has designed, developed and constructed the FRAM robotic telescope [3] located at the observatory. The main goal of the instrument is to determine atmospheric conditions, namely the transparency of the air and cloudiness using stellar photometry. The FRAM telescope is a part of an extensive system of devices for atmospheric monitoring as the knowledge of the state of the atmosphere with high temporal and spatial resolution is essential for precise interpretation of the Auger fluorescence data. The use of FRAM in this regard is twofold. Firstly, it is in principle able to provide a completely independent measurement of total atmospheric extinction (and thus the aerosol content of the atmosphere) in any given direction by comparing the measured light flux from a set of stars with catalogue values. This method, while straightforward in theory, comes with a plethora of practical issues, among which the most prominent are the deficiencies of the catalogues, variations in stellar spectra or long-term changes in the sensitivity of the device. As it turns out, an end-to-end solution that would allow us to simply convert the observed light fluxes into vertical aerosol optical depths does not exist yet and thus our ongoing work in an implementation of such an algorithm constitutes substantial original research.

The second application of the FRAM robotic telescope is in the so-called “rapid monitoring program” [4] which aims to characterize the atmospheric properties on very short timescales in response to an observation of a particularly interesting shower [5]. Of highest interest in this regard are showers with anomalous profiles, where the knowledge of presence or absence of clouds is indispensable for the assessment whether the cause of the profile anomaly is of atmospheric or particle-physics origin. The FRAM telescope is capable of a very fast reaction and within seconds after receiving a trigger it can start to take images of the sky along the apparent celestial path of the shower. By analyzing the zenith-angle dependence of observed stellar extinction, we are able to identify even very small clouds or aerosol layers as irregularities with regard to a smooth model curve. This data is regularly processed and a database is available to the members of the Auger Collaboration to help in their data analysis.

As a bonus, the robotic nature of the telescope allows for efficient use of any observing time that is not needed for atmospheric monitoring duties. In collaboration with both professional and highly advanced amateur astronomers from the Czech Republic, we have prepared a selection of astronomical programs that are carried out in this free time, such as photometry and astrometry of small solar system bodies (comets and asteroids) and photometry of variable stars [6]. The FRAM telescope is also part of the global detection network of robotic telescopes GLORIA financed by EU FP7 with our team members as significant part of the project.

Data analysis - Physics of Extensive Air Showers, primary cosmic ray composition and energy spectrum, cosmic ray sources and transport of cosmic rays in the Universe

The interaction of Ultra High Energy Cosmic Rays (UHECR) with the atmosphere leads to a development of the so-called Extensive Air Showers (EAS) – cascades of billions of elementary particles propagating through the atmosphere. The first stages of an EAS contain interactions at energies well beyond those achievable at accelerators and thus present a unique opportunity to study hadronic interactions, albeit indirectly by the means of observing the particles that reach ground or the longitudinal development of the showers via fluorescence

techniques. Multiple experiments have shown discrepancies with respect to predictions of the current generation of interaction models, in particular concerning production of muons.

In our research we have pursued two fundamental avenues of inquiry into possible explanations of these discrepancies. The first one was the study of scarce or outright exotic processes which may become relevant due to either the very large amount of interactions in one EAS or due to the large amount of center-of-mass energy (and thus phase space) available in the highest-energy interactions. Using theoretical calculations, we have identified two kinds of processes to be the most promising in this regard, namely the production of heavy flavors and the production of hypothetical weakly interacting massive spin 1 particles - the so-called “dark photons” – which inevitably appear in a plethora of plausible dark-matter models. These two options we have then explored using detailed Monte-Carlo simulations; in both cases we have shown that under any physically sound assumptions these mechanisms cannot provide the explanation for the observed muon excess [7, 8]. The second idea is in some sense orthogonal to the former – taking into account at the same time the muon excess at the Pierre Auger Observatory and the somewhat older observation of an excess of multi-muon cosmic-ray bundles at underground particle detectors at the DELPHI experiment in CERN, we have noticed that while these particles have very different kinematics at the observation level (the characteristic energy of DELPHI muons is at least an order of magnitude higher than of those observed by Auger), their parent particles are likely to occupy a similar phase-space region in the center-of-mass system at the point of their production. This simple observation, backed by exploratory simulations, has inspired the creation of our framework model, in which the original interaction models are slightly modified so that the most common particles (mainly pions) of low c.m.s. momenta are added through the high-energy parts of the showers (while retaining the conservation of energy and momentum). This second approach is being investigated by our team members right now.

Our group is also highly interested in related studies with respect to primary cosmic ray composition; these have been for long time among the priority topics of the department. Quantitative estimates of the mass composition of cosmic rays deduced from measured mass sensitive observables can be obtained only when distributions of these quantities are compared to predictions of hadronic interaction models for different primary particle types. The determination of the cosmic ray composition thus suffers from significant systematic errors mainly due to the uncertainty in Monte Carlo models describing the nucleusnucleus interactions during the air shower development in the Earth atmosphere. We address these questions in our studies and the team members are frequently nominated by the Pierre Auger Collaboration to present these issues at particle physics conferences (e.g. [9, 10]). The research in the field of cosmic ray composition is based not only on our contributions to the collaboration papers [11, 12]. Together with the group at the Charles University we investigate possible new parameters measurables in the cosmic ray shower that are sensitive to the type of the initial primary particle – not only the usual measurable such as position of the shower maximum or the number of muons. In our team we focus on studies of parameters that are related to the procedure of energy calibration. We have shown in several conference contributions [13, 14, 15] and very recently also in a journal paper [16] that for example the details of the so called Constant Intensity Cut procedure contain interesting information about composition of the primary particle beam. Furthermore we have strongly participated in studies that try to find out, which muon detection techniques are suitable extensions of the surface detector at the Pierre Auger Observatory. In particular, the Prague group was responsible for an examination of the detection capability of the MARTA detector (Muon Auger RPC for the Tank Array). A large amount of Monte Carlo simulations has been performed and analyzed in Prague with the aim to estimate sensitivity and resolving power of muon measurements collected by an array of segmented RPCs for the primary composition analysis. A member of our team (Jan Řídký) was also part of the expert panel evaluating the different options of the AUGER upgrade.

In the course of our research the group has developed tools for efficient simulations of the EAS using computer clusters and for analysis and visualization of their results, thus gaining a significant insight into the inner mechanisms of the EAS, which are – being multi-billion-particle phenomena – complex systems with non-intuitive behavior. This experience is then invaluable in any attempts to further interpret the data from the Pierre Auger Observatory that are available to our group. The Prague team initiated the usage of the grid computing for the observatory simulations. The grid has since become a major part of the official simulation production, where the Prague group is responsible for the central servers. The so called AUGER grid virtual organization (VO) is now supported by cca 20 computing centres all over the world. VO AUGER has been the largest computing organization in terms of computing time in astroparticle physics already for several years.

Scientists of the department are also studying the energy spectrum of the primary cosmic rays [17], sources and processes responsible for an origin of high-energy cosmic particles [18] and how these particles propagate through the universe to the Earth [19].

The involvement in the Pierre Auger Observatory is one of the key projects of the Institute and a successful example of the world-wide collaboration of our scientists with foreign institutions. This participation has in fact significantly broadened the new research field of astroparticle physics in the Czech Republic, it stimulated activities at the national level and it was instrumental in establishing several dedicated astroparticle physics courses at two universities.

AIR Fluorescence Yield (AIRFLY)

Fluorescence technique is one of the well-established methods to detect UHECR, where the emission from the nitrogen molecules in the atmosphere induced by the charged air shower secondary particles is detected. It is the only technique where the longitudinal profile of the shower development can be directly observed. This technique also allows us to minimize the model dependence of the energy reconstruction of the primary UHECR. The fluorescence emission is proportional not only to the energy deposited by shower particles but it is also affected by atmospheric conditions during emission and propagation of the light. These effects have to be carefully studied in a well-defined laboratory conditions.

The AIRFLY experiment represents more than ten years of efforts resulting in the most complete and precise model of the air fluorescence, which is now used by the Pierre Auger Observatory. Our group was involved in the construction, simulation, data acquisition and analysis since the very beginning.

The experimental apparatus of AIRFLY consists of a pressure chamber placed into a beam of relativistic particles with a photosensor placed perpendicularly to the beam, viewing the emission inside the chamber. The vacuum system allows to change the pressure, temperature and humidity inside the chamber and also to compare the emission from different gas mixtures. The data taking was performed using the Beam Test facility in Frascati, Italy, Argonne National Laboratory and Fermilab, USA.

In the last five years, with a very active involvement of our team, the most delicate measurement of the absolute emission was finalized using a new method of comparing the fluorescence emission to a well-known process, such as Cherenkov yield [20]. This procedure helps to eliminate the systematic effects of the measurement and allows us to lower the systematic uncertainty of the fluorescence yield from 15% to 4%, which in turn significantly improves the uncertainty of the energy reconstruction of the fluorescence technique.

Air Microwave Yield (AMY)

The disadvantage of the fluorescence method is that the measurement is disturbed by parasitic light (the Moon, towns, etc.) and weather conditions resulting in duty cycle of about 13%. Detection technique based on emission in the microwave region would keep the feature of viewing directly the shower longitudinal profile but the disturbance from weather conditions and parasitic light would be significantly reduced, resulting in enormously improved duty cycle and consequently increased statistics of detected UHECR.

The existence of the microwave molecular bremsstrahlung radiation (MBR) from air shower particles has been suggested by P. Gorham (Phys. Rev. D 78, 032007, 2008). Subsequently, several telescopes were built in order to verify the detection possibilities. Our group was involved in the construction and operation of the telescope MIDAS [21], first built on the campus of the University of Chicago and later moved to the far more radio quiet site of the Pierre Auger Observatory in Argentina. It consisted of a 5 meter dish with 53 GHz receivers in its focus. The trigger logic allowed us to autonomously recognize shower patterns. Several shower candidates have been found but the results were not convincing and called for further laboratory measurements of the phenomenon.

The main objective of AMY experiment is to make a precise measurement of the MBR absolute yield and to study the spectrum in frequency in the wide band between 1 and 20 GHz. The knowledge of the absolute yield is necessary to understand the feasibility and the best way to design an air shower detector. A detailed knowledge of the spectrum is also very important. In addition to the continuum bremsstrahlung emission, other processes can cause the production of microwave radiation. If bright spectral lines were found, the frequency band of an extensive air shower detector could be restricted around these lines in order to maximize the signal to noise ratio. The measurements are conducted at the Beam test facility of LNF, Frascati, Italy. The experimental apparatus of AMY includes an anechoic Faraday chamber with the dimensions around 2m x 2m x 4m made of copper and lined with RF absorbers. The electron beam of 510 MeV crosses the chamber along its axis and the produced emission is detected by a broad band antenna. To maximize the energy deposit or to modify the beam coherence, an alumina interaction target of a variable thickness can be placed in front of the chamber. Several measurement campaigns were realized in the past four years. Large amount of studies were performed and the data analysis is being finalized. The team member has been serving to the AMY collaboration as the coordinator for the measurement campaigns within the EU framework TARI (Transnational Access to Research Infrastructure). TARI is one of the three blocks of activities (networking, joint research and transnational access) that make up the Integrating Activity "Strongly Interacting Matter" (acronym: "HadronPhysics3"), financed by the European Commission and coordinated by INFN.

High energy gamma-rays from the Universe (Cherenkov Telescope Array)

Radiation at high gamma-ray energies differs fundamentally from that detected at lower energies. Energies of gamma rays of the order of GeV to TeV cannot conceivably be generated by thermal emission from hot celestial objects. Instead, we find that high-energy gamma-rays probe a "non-thermal" Universe and objects with the concentration of large amounts of energy onto a single quantum of radiation. These gamma-rays can be generated when highly relativistic particles - accelerated for example in the gigantic shock waves of stellar explosions - collide with ambient gas, or interact with photons and magnetic fields. High-energy gamma-rays can also be produced by possible decays of heavy particles such as the hypothetical dark matter particles or cosmic strings, both relics which might be left over from the Big Bang. Therefore, gamma-rays also provide a window to the discovery of the nature and constituents of dark matter. Cherenkov Telescope Array (CTA) will be a new generation observatory of (very) high-energy gamma-rays and as such it will allow discovery of a large number of new astrophysical sources of gamma rays and the determination of their characteristics [22]. It will

also address fundamental questions related to dark matter. CTA will consist of two sites, one located in the southern and one in the northern hemisphere, thus providing full-sky coverage. The observatory will use the technology of the imaging atmospheric Cherenkov telescopes, where the mosaic camera samples the incoming Cherenkov photons with frequency of tens of nanoseconds.

In 2011 the astroparticle physics group of the Institute joined the CTA consortium and initiated a substantial increase of the Czech involvement in CTA. Within few months the group from the Institute have become recognized and well visible in several CTA work packages. The intense involvement of the Institute in the CTA Observatory is a natural continuation of current involvement in the Pierre Auger Observatory both from the scientific as well as the technological point of view. Currently, the department is responsible for the analysis of satellite images used for a characterization of the long-term properties of the proposed sites of a CTA location. Olomouc laboratory (team classical and quantum optics) developed all-sky cameras, which monitor cloudiness above eight candidate sites [23, 24] and the laboratory also tests mirror samples. Based on the experience from the Pierre Auger Observatory, the astroparticle physics team in Prague is designing and developing a robotic telescope to be used as a monitoring instrument of the immediate observational conditions above the CTA Observatory [25] and we are establishing a team for physics analyses during CTA operational phase.

The participation in CTA is currently the second largest Czech participation in any astroparticle physics project so far (after the Pierre Auger Observatory). The Institute of Physics of the Academy of Sciences acts as the leading institution in the Czech Republic with the efforts being coordinated by the Astropaticle Physics Department. Our active role in CTA was supported and prioritized also by the outcome of the last evaluation process in 2010.

LSST

The Large Synoptic Survey Telescope (LSST) is the project of the future world largest ground-based survey telescope [26] that is currently under construction in Chile at Cerro Pachón and should be ready for scientific observations in 2022. With the 8.4 m primary mirror, the 3.2 Gpx mosaic camera and the field of view of 10 square degrees it will explore the observable sky into unprecedented depth. The telescope will be able to cover whole sky within 3 nights and thus return to study each location several hundred times during the expected 10 years of operation. The LSST will be able to observe an object of up to 24.5 magnitude in a single exposure and up to 27 magnitude in stacked images from the whole duration of the project. It will thus create “a movie of the deep universe”, enabling the precise measurement of 3 billion galaxies, detailed study of our own Galaxy, discovery of 250 thousands of supernovae and more than 90% of asteroids larger than 140 m potentially threatening the Earth. The LSST will be particularly sensitive to any transient sources, and all data will be made public. The largest catalogue and database of astronomical objects in the history of humankind will thus be created.

Our group participates in the LSST project since 2008, when we started a collaboration with the Brookhaven National Laboratory (BNL) in the area of CCD testing and characterization [27, 28]. More than 200 especially designed CCD sensors will compose the mosaic camera of the telescope. Each CCD sensor needs to be fully tested and characterized (quantum efficiency, linearity, point spread function, dark current, etc.). Such characterization consists of many thousands measurements under strictly controlled conditions.

The main contribution of our group was the creation of software that controls the testing process and enables its automation. This software [29, 30] is based on the RTS2 that our group uses and develops for robotic telescopes used within Pierre Auger Observatory and CTA projects. RTS2 system is used also by ca 30 dedicated astronomical telescopes all over the world and has helped to major discoveries such as e.g. [31]. We have participated not only

in the software development, but also in the testing campaigns directly at BNL and later also at IN2P3-CNRS institute in Paris, France.

Our participation in the project was formalized in 2012, when we have signed the Memorandum of Understanding, and Institute of Physics was approved as a third institutional member of the LSST Collaboration outside United States. In 2014 we have extended our LSST activities and we have entered the Dark Energy Science Collaboration (DESC), which currently involves more than 150 scientists. DESC is dedicated to one of the primary goals of the LSST project, which is the investigation of the observable effects of dark energy. Currently, we collaborate on this topic mostly with Argonne National Laboratory (ANL).

Please note that the supporting pictures and plots illustrating briefly the relevant projects and the involvement of the astroparticle physics team are available at http://cta.fzu.cz/evaluation/astroparticle_pictures_for_evaluators.pdf

Publications (underlined names are the members of the astroparticle physics team No 1 in Prague, the other names represent our collaborators from Olomouc – team No 22 – classical and quantum optics):

[1] J. Abraham et al. (AUGER Collaboration, from IP: M. Boháčová, J. Chudoba, T. Kárová, D. Mandát, P. Nečesal, L. Nožka, M. Nyklíček, M. Palatka, M. Pech, M. Prouza, J. Řídký, J. Schovancová, P. Schovánek, R. Šmída, P. Trávníček), The fluorescence detector of the Pierre Auger Observatory, Nucl. Instrum. Meth. A 620 (2010) 227 – 251.

[2] J. Abraham et al. (AUGER Collaboration, from IP:M. Boháčová, J. Chudoba, T. Kárová, D. Mandát, P. Nečesal, L. Nožka, M. Nyklíček, M. Palatka, M. Pech, M. Prouza, J. Řídký, J. Schovancová, P. Schovánek, R. Šmída, P. Trávníček), A Study of the Effect of Molecular and Aerosol Conditions in the Atmosphere on Air Fluorescence Measurements at the Pierre Auger Observatory, Astropart Phys. 33 (2010) 108 – 129.

[3] M. Prouza, M. Jelínek, P. Kubánek, J. Ebr, P. Trávníček, R. Šmída, FRAM - The Robotic Telescope for the Monitoring of the Wavelength Dependence of the Extinction: Description of Hardware, Data Analysis, and Results, Adv. Astron. 2010 (2010) 849382(1) - 849382(5).

[4] P. Abreu et. al. (AUGER Collaboration, from IP: M. Boháčová, J. Chudoba, J. Ebr, D. Mandát, P. Nečesal, L. Nožka, M. Palatka, M. Pech, M. Prouza, J. Řídký, J. Schovancová, P. Schovánek, R. Šmída, P. Trávníček, J. Vícha), The rapid atmospheric monitoring system of the Pierre Auger Observatory, Journal of Instrumentation 7 (2012), P09001.

[5] D. Mandát, M. Pech, J. Ebr, M. Hrabovský, M. Prouza,J. Ebr,P. Janeček, M. Prouza, P. Kubánek, M. Jelínek, M. Mašek, I. Ebrová, J. Černý for the Pierre Auger Collaboration:Shoot-the-Shower: real-time observations for astroparticle physics using the FRAM robotic telescope, III Workshop on Robotic Autonomous Observatories (Eds. Juan C. Tello, Alberto Riva, David Hiriart & Alberto J. Castro-Tirado) Revista Mexicana de Astronomía y Astrofísica (Serie de Conferencias) Vol. 45, pp. 53--56 (2014).

[6] D. Mandát, M. Pech, J. Ebr, M. Hrabovský, M. Prouza, P. Janeček, P. Kubánek, M. Jelínek, M. Mašek, I. Ebrová, J. Černý, FRAM: showers, comets, GRBs and popular science, III Workshop on Robotic Autonomous Observatories (Eds. Juan C. Tello, Alberto Riva, David Hiriart & Alberto J. Castro-Tirado) Revista Mexicana de Astronomía y Astrofísica (Serie de Conferencias) Vol. 45, pp. 114 – 117 (2014).

[7] J. Ebr, P. Nečesal, Effects of massive photons from the dark sector on the muon content in extensive air showers, Phys. Lett. B 725 (2013) 185 – 189.

[8] J. Řídký, D.Nosek, P. Trávníček, P. Nečesal, Prompt muons in extended air showers, arXiv:0706.2145, Contribution to the 30th International Cosmic Ray Conference, Merida, Mexico, 3-11 July 2007, Vol.4 (HE part 1), 605-608.

[9] P. Trávníček for the Pierre Auger Collaboration, Particle physics @ sqrt(s_pp) > 50 TeV with the Pierre Auger Observatory, EDSBlois 2013 56, arXiv:1310.5332.

[10] J. Ebr for the Pierre Auger Collaboration, Particle Physics at the Pierre Auger Observatory, Proceedings of the MESON2014 – 13th International Workshop on Meson Production, Properties and Interaction, held in Krakow, Poland, May-June 2014, EPJ Web of Conferences, 81 (2014) 01021.

[11] J. Abraham et al. (AUGER Collaboration, from IP: M. Boháčová, J. Chudoba, T. Kárová, D. Mandát, P. Nečesal, L. Nožka, M. Nyklíček, M. Palatka, M. Pech, M. Prouza, J. Řídký, J. Schovancová, P. Schovánek, R. Šmída, P. Trávníček), Measurement of the Depth of Maximum of Extensive Air Showers above 10^18 eV., Phys. Rev. Lett. 104 (2010) 091101(1) - 091101(7).

[12] P. Abreu et al. (AUGER Collaboration, from IP: M. Boháčová, J. Chudoba, J. Ebr, D. Mandát, P. Nečesal, L. Nožka, M. Nyklíček, M. Palatka, M. Pech, M. Prouza, J. Řídký, J. Schovancová, P. Schovánek, R. Šmída, P. Trávníček, J. Vícha), Anisotropy and chemical composition of ultra-high energy cosmic rays using arrival directions measured by the Pierre Auger Observatory, J. Cosmol. Astropart. Phys. 2011 (2011) 022(1) - 022(15).

[13] J. Vícha, P. Trávníček, D. Nosek, J. Ebr, On the methods to determine signal attenuation curve for different surface arrays, 33rd International Cosmic Ray Conference, Rio de Janeiro, Brazil, July 2013, arXiv:1310.0330.

[14] J. Vícha, P. Trávníček, D. Nosek, J. Ebr, Signal Attenuation Curve for Different Surface Detector Arrays, 14th ICATPP Conference on Astroparticle, Particle, Space Physics and Detectors for Physics Applications, arXiv:1408.1595, 23-27 Sep. 2013. Como, Italy, proceedings p.162-166.

[15] D. Nosek, J. Vícha, J. Nosková, J. Ebr, Testing chemical composition of highest energy cosmic rays, arXiv:1309.5924, Sep 23, 2013.

[16] J. Vícha, P. Trávníček, D. Nosek, J. Ebr, Study of Dispersion of Mass Distribution of Ultra-High Energy Cosmic Rays using a Surface Array of Muon and Electromagnetic Detectors, Astropart.Phys. 69 (2015) 11-17.

[17] J. Abraham et. al., (AUGER Collaboration, from IP: M. Boháčová, J. Chudoba, T. Kárová, D. Mandát, P. Nečesal, L. Nožka, M. Nyklíček, M. Palatka, M. Pech, M. Prouza, J. Řídký, J. Schovancová, P. Schovánek, R. Šmída, P. Trávníček), Measurement of the energy spectrum of cosmic rays above 10^{18}eV using the Pierre Auger Observatory,Phys.Lett. B685 (2010) 239-246.

[18] J. Abraham et al. (AUGER Collaboration, from IP: M. Boháčová, J. Chudoba, T. Kárová, D. Mandát, P. Nečesal, L. Nožka, M. Nyklíček, M. Palatka, M. Pech, M. Prouza, J. Řídký, J. Schovancová, P. Schovánek, R. Šmída, P. Trávníček), Update on the correlation of the highest energy cosmic rays with nearby extragalactic matter, Astropart Phys. 34 (2010) 314 – 326.

[19] P. Abreu (AUGER Collaboration, from IP: M. Boháčová, J. Chudoba, J. Ebr, D. Mandát, P. Nečesal, L. Nožka, M. Nyklíček, M. Palatka, M. Pech, M. Prouza, J. Řídký, J. Schovancová, P. Schovánek, R. Šmída, P. Trávníček, J. Vícha), Search for signatures of magnetically-induced alignment in the arrival directions measured by the Pierre Auger Observatory, Astropart Phys. 35 (2012) 354 – 361.

[20] M. Ave et. al., (AIRFLY Collaboration, from IP: M. Boháčová, L. Nožka, M. Palatka, J. Řídký, P. Schovánek), Precise measurement of the absolute fluorescence yield of the 337 nm band in atmospheric gases, Astropart Phys. 42 (2013) 90 - 102.

[21] J. Alvarez-Muniz et. al. (MIDAS Collaboration, from IP: M. Boháčová), Search for microwave emission from ultrahigh energy cosmic rays, Phys. Rev. D 86 (2012) 051104-1 - 051104-5.

[22] B. S. Acharya et. al. (CTA Consortium, from IP: J. Chudoba, J. Ebr, M. Hrabovský, D. Mandát, M Palatka, M. Pech, M. Prouza, J. Řídký, P. Schovánek, P. Trávníček), Introducing the CTA concept, Astropart Phys. 43 (2013) 3 - 18.

[23] D. Mandát et. al. (CTA Consortium, from IP: D. Mandát, M. Pech, J. Ebr, M. Hrabovský, M. Prouza), All Sky Cameras for the characterization of the Cherenkov Telescope Array candidate sites, Proceedings of the 33rd International Cosmic Ray Conference, Rio de Janeiro, Brazil, 2. – 9. July 2013.

[24] D. Mandát et. al. (CTA Collaboration, from IP: D. Mandát, M. Pech, M. Hrabovský, P. Schovanek, M. Palatka, M. Prouza, P. Trávníček, P. Janeček, J. Ebr), All Sky Camera for the CTA Atmospheric Calibration work package, EPJ Web Conf. 89 (2015) 03007.

[25] P. Janeček, J. Ebr, M. Prouza, FRAM for CTA, EPJ Web of Conferences 89, 03006 (2015).

[26] Z. Ivezic et al. (from IP: M. Prouza), LSST: from Science Drivers to Reference Design and Anticipated Data Products, 2008, living paper on arXiv.org; arXiv 0805.2366v4 - revision v4 from August 2014.

[27] I. V. Kotov, A. I. Kotov, J. Frank et al. (from IP: P. Kubánek, M. Prouza), Study of Pixel Area Variations in Fully Depleted Thick CCD,High Energy, Optical, and Infrared Detectors for Astronomy IV, Proceedings of SPIE, 774206, July 02, 2010.

[28] I. V. Kotov, J. Frank, A. I. Kotov et al. (from IP: P. Kubánek, M. Prouza), CCD characterization and measurements automation,Nuclear Instruments and Methods in Physics Research Section A Accelerators Spectrometers Detectors and Associated Equipment, 11/2011, pages: 188-192.

[29] M. Prouza, P. Kubánek, P. O'Connor et al., Software for automated testing and characterization of CCDs for Large Synoptic Survey Telescope (LSST), Software and Cyberinfrastructure for Astronomy, Proceedings of SPIE, 77403N, July 19, 2010.

[30] P. Kubánek, M. Prouza, I. Kotov et al., Use of RTS2 for LSST multiple channel CCD characterization, Software and Cyberinfrastructure for Astronomy II, Proceedings of SPIE, 84512T, July 1, 2012.

[31] C. C. Thöne et al, (from IP: P. Kubánek) The unusual gamma-ray burst GRB 101225A from a helium star/neutron star merger at redshift 0.33, Nature 480 (2011) 72 – 74.

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Semiconductors

The team of Semiconductors representing a part of the Section of Solid State Physics of the Institute of Physics AS CR consists of four collaborating groups, namely, technology group, photoluminescence group, transport group and group of theory. Between the years 2010-2014 the team reached numerous original results which were published in impacted journals (96) and in conference proceedings (36). Besides, the members of the team edited and contributed to a few books (22), organized international conferences (2) and produced patents (4). Our activities were focused mainly onto the following directions:

The principal common subjects of research of the technology and photoluminescence groups are InAs/GaAs based quantum dots prepared by MOVPE. Quantum dots (QD) are nanometric objects where the movement of electrons is confined in all three dimensions. This results in a robust discrete energy level structure which depends mainly on the size of QDs. Since the QDs imbedded in heterostructures can in principle control the optoelectronic properties of the whole system, the research in this direction is of primary importance for applications in tunable lasers, detectors, solar cells and possibly in the next generation optoelectronic devices with true quantum-mechanical functionality such as single-photon sources and quantum information processors. Reflecting thus practical demands, our research was primarily oriented to a reproducible preparation of MOVPE grown heterostructures with InAs based QD emitting at telecommunication bands of 1.3 μm and 1.55 μm.

In order to achieve this aim, it was necessary first to master the preparation of self-assembled (Stranski - Krastanow) InAs QDs monolayer surrounded by GaAs layers, emitting around ~ 1.2 μm (e.g. [1]). For the further red shift of wavelength, various strategies were used. Required increase of the QD size was achieved mainly by capping QDs by strain reducing layers (SRLs) of InGaAs or GaAsSb, effectively preventing the dissolution of QDs. However, the GaAsSb SRL offers several advantages compared to the InGaAs one, especially because it increases the PL

efficiency and widens the energy gap between the ground and the first excited states. As a result, we are able at present to prepare QD structures with wavelength emission from 1.2 μm to nearly 1.8 μm [2], which is to our knowledge the longest emitted wavelength ever reached in InAs/GaAs QD structure.

The use of GaAsSb SRL provided us also with a new tool for QD band structure engineering, enabling one to control type-I or type-II band alignment by GaAsSb composition and QD size. (Recall, in type-I electrons and holes are localized in QDs contrary to type-II, where electrons are localized in QDs and holes in SRL.) For example, the heterostructures operating at relatively long wavelengths can be intently grown also with more efficient PL type I band alignment. Such a possibility is due to the behavior illustrated in Fig. 1. Accordingly, the transition energy (or recombination wavelength) between the electron and hole ground states and the type of band alignment are sensitively dependent on both, Sb content and QD height, in other words, on technologically controllable parameters.

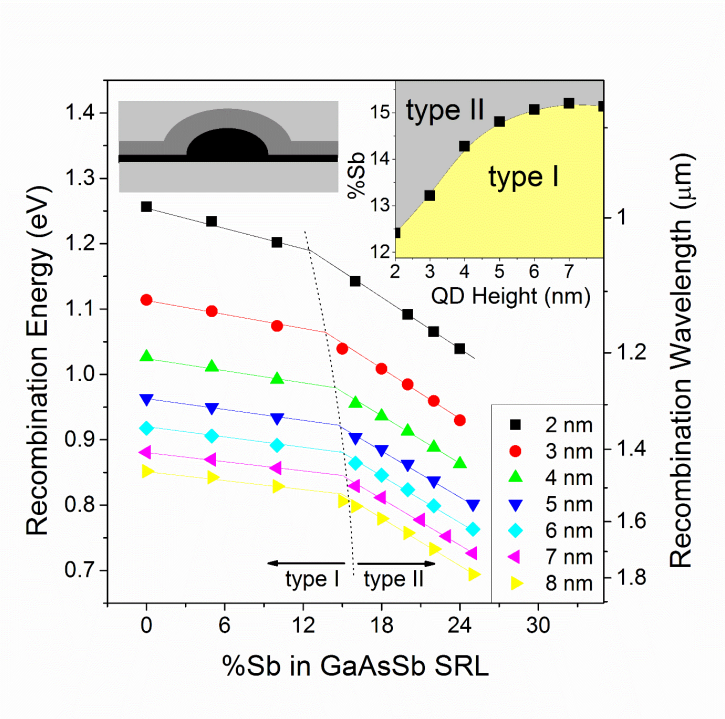


Fig. 1: Dependence of the recombination energy between ground states of electrons and holes on the composition of GaAsSb SRL for different heights of QDs. Dotted line represents the transition between type-I and type-II heterostructures. The inset shows the dependence of the type-I/type-II transition on the Sb content in the GaAsSb SRL and on the QD height [3].

As was shown later, the band alignment is influenced not only by the absolute Sb content but also by its profile [4]. The examples of three types of QD structures with different Sb profiles are shown in Fig. 2. Obviously, the most convenient profile for the wavelength prolongation is thus that with decreasing content of Sb, see Fig. 3.

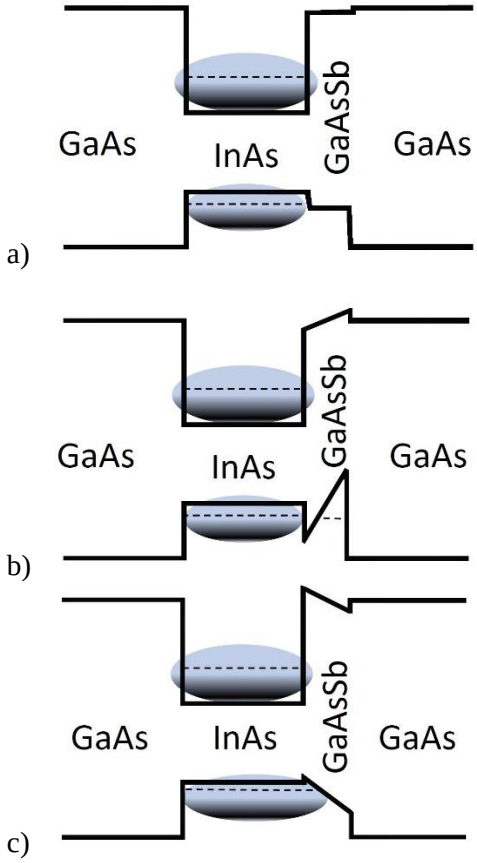


Fig. 2: Three types of QD structures with different Sb gradients: a) constant, b) increasing and c) decreasing.

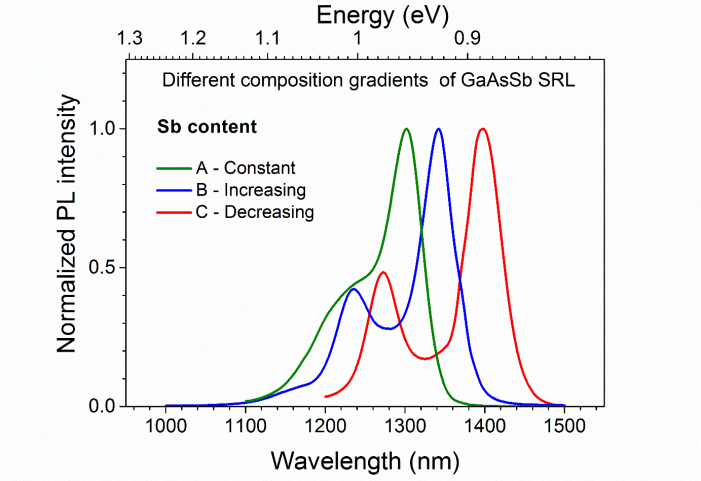


Fig. 3: Normalized room temperature PL spectra of QD structures with 5 nm GaAsSb SRL for all three types of composition gradient – constant, decreasing and increasing.

Tailoring of the Sb profile affords another promising application, a formation of vertically correlated combined InAs and GaAsSb QDs separated by a GaAsSb triangular barrier with increasing Sb concentration in the valence band (Fig. 4). The triangular GaAsSb barrier in the valence band separating the hole quantum states in InAs and in GaAsSb QDs, enabled us, namely, to change their mutual energy position and band alignment separately by tuning the structure parameters [5].

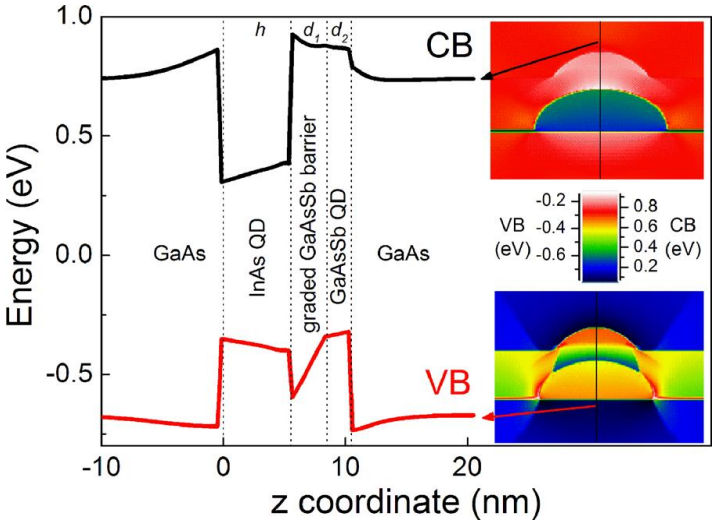


Fig. 4: Calculated band alignment in the axis of vertically correlated combined InAs and $GaAs_{0.76}Sb_{0.24}$ QDs, separated by a triangular GaAsSb barrier with graded Sb content from 10% to 24%. The insets demonstrate maps of the calculated valence (left scale) and conduction (right scale) band edge energies for InAs and $GaAs_{0.76}Sb_{0.24}$ QDs in (100) cross section, the corresponding values of band edge energies along QD axis are plotted in the graph on the left.

In the last year we were awarded by EU structural fund for the project LABONIT and purchased a new MOVPE apparatus for nitride based compounds and started the research in this field (see our future plans for years 2015-2019). In cooperation with Aixtron we prepared InGaN/GaN multiple quantum well (MQW) structure and characterized it by XRD measurements [6]. Since the observed decay characteristics of the excitonic emission in MQW were better than those of widely used single crystal YAP:Ce or YAG:Ce scintillators, we have demonstrated in this way the suitability of our structures to be efficient scintillator detectors.

Essential part of experiments performed in the transport group consists of the systematic measurement of the transport coefficients and deep levels in

semiconductor structures, which serves as a feedback information for technological group. However, the most valuable and interesting part of activities of the transport group concerned with the development of original techniques and methods for the investigation of semiconductor structures and, in cooperation with theoreticians, analysis of fundamental problems of physical measurement.

In the frame of contract with Kyma Technologies Inc. (see “Collaboration with other subjects”) a simple but very effective technique was developed for the characterization of semi-insulating GaN:Fe [7]. This promising substrate material for microwave devices and optoelectronics having extremely small intrinsic charge concentration and a conductivity of $<10^{-11}$ S/m, cannot be, namely, reliably characterized by standard magnetotransport methods. Enhancement of charge carrier concentration to the measurable level was achieved by means of charge injection from a tungsten point pressed against GaN:Fe single crystal. Such a charge injection (see Fig.5) results in space-charge-limited radial flow of carriers corresponding to the

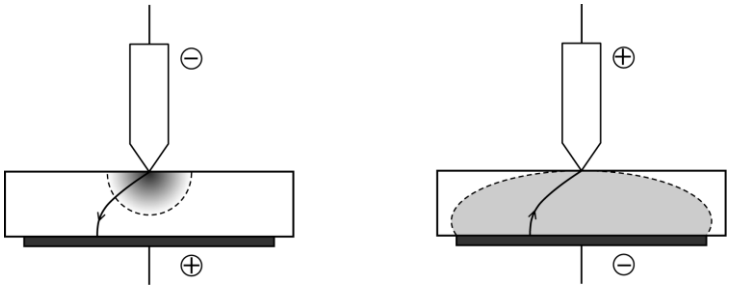


Fig. 5: Distribution of charge injected from point contact into the semi-insulating sample when the point contact is biased negatively and positively. Arrows on current lines indicate the direction of electron flow.

specific I-V curve. Among others a universal $I \sim V^{3/2}$ law was observed, which corresponds to the regime controlled by spreading of the space charge region inside the sample. It was theoretically predicted earlier but for the first time observed just by our group. As has been further shown, analysis of space charge limited I-V curves enables one to determine required transport parameters and local trap concentrations as well. A similar point contact method was successfully applied also to another insulating material, to single crystalline intently undoped diamond [8], where the dependence of charge injection from the point contact on the surface resistivity ($\rho^{\square}$) was discovered. This effect became a basis for a new technique of estimation of

surface resistivity in the range $\rho^{\square} \in (10^{12}–10^{17}\ \Omega)$ otherwise inaccessible by standard methods.

For our research into the diamond and related materials we have also suggested and experimentally verified a method of resistivity measurements of flat structures based on the application of Thompson–Lampard theorem, a lesser known theorem of 2-dimensional electrostatics. The method which was proved to be dual to the popular van der Pauw technique preserves some of its advantages and can work even in cases where the van der Pauw method fails. Our paper [9] (issued to the compilation of outstanding papers to the 90th anniversary of Meas. Sci. Technol. in 2012) contains the discussion on electrically dual systems and practical directions how to design a wide class of computable measuring structures.

In the group of theory, in close collaboration with the transport group, various aspects of quantum transport and related effects were systematically investigated in the years 2010-2014. For example [10], new results were obtained on anomalous Hall effect, which exists, in addition to the standard quantum Hall effect, in ferromagnetic materials even at zero magnetic fields. In connection with our previous experimental research into the superconductivity of nanocrystalline diamond we were also looking for various theoretical approaches to this effect. For a wide class of materials ranging from metallic alloys, high T_c ceramics and organic superconductors to Fermi gases and hypothetical condensate of quarks, we have thus developed a theory based on the description of multiple scattering in T-matrix approximation which enabled us to determine superconducting gap of the said systems [11]. In order to account for the observed dynamical behavior of very small quantum systems under the non-equilibrium conditions in time-dependent fields a special modification of technique of non-equilibrium many body Green's functions was worked out (e.g. [12]).

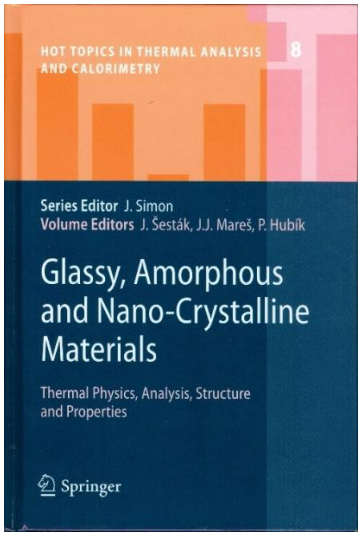


Fig. 6: Cover of the book [13] having in 2013 a total of 8799 recorded chapter downloads.

Besides the above mentioned theoretical approaches aiming at the establishment of *ab initio* microphysical models of reality, an attention was paid also to the classical phenomenology. The contribution [13] (see Fig. 6) deals with the systematic treatment of the central concept of thermal physics, phenomenological temperature. As far as we know, for the first time in terms of elementary set theory, we analyzed the mathematical structure of precursor of temperature, hotness manifold. Using then the results of this work, we have demonstrated [14] that the surviving antinomy between von Mosengeil's and Ott's formulae for relativistic transformation of temperature is actually an artifact, while the Kelvin temperature has to be Lorentz invariant. Somewhat controversial subjects also belonging to the classical phenomenology are discussed e.g. in papers [15] and [16]. In contribution [15] we discussed a class of linear phenomenological transport equations and their relation to the microphysical description of corresponding effects. The established congruence between Fick's law and Schrödinger equation (using Fürth's Ansatz) opened a new possibility to interpret the rather enigmatic quantum-like behavior of periodic chemical reactions as a special kind of diffusion. In paper [16] we have among others drawn attention to an astonishing fact that the experimental proof of identity between speed of light and Maxwell's constant in equations controlling electromagnetic interaction is lacking.

Our team is also a principal organizer of highly recognized series of international conferences "Frontiers of Quantum and Mesoscopic Thermodynamics (FQMT)" held

in Prague. (http://fqmt.fzu.cz) and regularly visited by many outstanding physicists, including Nobel Prize winners. The conference series is multidisciplinary, addressing hot topics from foundations of quantum physics to astrophysics.

Collaboration with other subjects

In collaboration with the Institute of Chemical Technology - Prague, we have started a research into the physico-chemical properties of toxic metal-organic substances which are used as precursors to MOVPE technology. During this project a prototype of apparatus for the measurement of the temperature dependences of vapour pressure was developed, a similar version of which was installed in 2011 in the NIST (formerly Bureau of Standards) as an étalon apparatus. The results of this research (e.g. [17]) were highly appreciated also by renowned producers of metal-organic compounds. In the frame of contract US MDA-HQ0147-09-C-0005 with Kyma Technologies Inc. from North Carolina USA, we have developed original transport and optical methods for characterization of semi-insulating GaN:Fe, namely, point-contact space-charge–limited method [7] and already patented modification of UV–vis /FIR transmission spectroscopy [18]. In cooperation with Crytur s.r.o. – Turnov very effective scintillators were prepared, the figure of merit of which exceeds parameters of most garnets (see patent application PV 2015-82, nitride scintillator – with Crytur. s.r.o.).

References

(The authors of the team of Semiconductors are written in red)

[1] A. Hospodková, J. Vyskočil, J. Pangrác, J. Oswald, E. Hulicius, K. Kuldová; Surface Science 604 (2010) 318–321.
[2] A. Hospodková, J. Pangrác, J. Oswald a, P. Hazdra, K. Kuldová, J. Vyskočil, E. Hulicius,; Journal of Crystal Growth 315 (2011) 110–113.
[3] A. Hospodková, M. Zíková, J. Pangrác, J. Oswald, J. Kubištová, K. Kuldová, P. Hazdra, E. Hulicius; J. Phys. D: Appl. Phys. **46** (2013) 095103.
[4] A. Hospodková, M. Zíková, J. Pangrác, J. Oswald, K. Kuldová, J. Vyskočil, E. Hulicius,; Journal of Crystal Growth 370 (2013) 303–306.
[5] A. Hospodková, J. Oswald, J. Pangrác, M. Zíková, J. Kubištová, Ph. Komninou, J. Kioseoglou, K. Kuldová, E. Hulicius; Journal of Aplied Physics 114, 174305 (2013).
[6] A. Hospodková, M. Nikl, O. Pacherová, J. Oswald, P. Brůža, D. Pánek, B. Foltynski, E. Hulicius, A. Beitlerová, and M. Heuken; Nanotechnology **25** (2014) 455501.
[7] J.J. Mareš, P. Hubík, J. Krištofik, L. Prušáková, Š. Uxa, T. Paskova, K. Evans J. Appl. Phys. **110** (2011) 013723(1) - 013723(6).
[8] J.J. Mareš, P. Hubík, Š. Uxa, J. Krištofik, H. Kozak

Semicond. Sci. Tech. **27** (2012) 065013(1) - 065013(4).
[9] J. J. Mareš, P. Hubík, J. Krištofik
Meas. Sci. Technol. **23** (2012) 045004(1) - 045004(5).
[10] P. Středa
Phys. Rev. **B 88** (2013) 134422(1) - 134422(5).
[11] B. Šopík, P. Lipavský, M. Männel, K. Morawetz, P. Matlock
Phys. Rev. **B84** (2011) 094529(1) - 094529(13).
[12] V. Špička, A. Kalvová, B. Velický
Physica **E42** (2010) 525 – 538.
[13] J. J. Mareš
Glassy, Amorphous and Nano-Crystalline Materials
Editors: J. Šesták, J. J. Mareš, P. Hubík ISBN 978-90-481-2881-5, e-ISBN 978-90-481-2882-2, Springer (Dordrecht) 2011, Chapter 20, pp. 327 – 346.
[14] J. J. Mareš, P. Hubík, J. Šesták, V. Špička, J. Krištofik, J. Stávek
Relativistic transformation of temperature and Mosengeil–Ott's antinomy.
Physica **E42** (2010) 484 - 487.
[15] J. J. Mareš, J. Šesták, P. Hubík
Glassy, Amorphous and Nano-Crystalline Materials
Editors: J. Šesták, J. J. Mareš, P. Hubík ISBN 978-90-481-2881-5, e-ISBN 978-90-481-2882-2, Springer (Dordrecht) 2011, Chapter 14, pp. 227 – 244.
[16] J. J. Mareš, P. Hubík, V. Špička, J. Stávek, J. Šesták, J. Krištofik
Phys. Scr. T**151** (2012) 014080(7).
[17] http://web.vscht.cz/~fulemm/index_soubory/Research.htm
[18] P. Gladkov, E.Hulicius, T. Paskova, E. Preble, K.Evans; Aplied Physics Letters **100**, 031908 (2012).

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Department of Spintronics and Nanoelectronics

The Department of Spintronics and Nanoelectronics was founded in 2007 with the aim to establish in the Institute of Physics a technological-experimental-theoretical center for spintronics research in nanostructured materials and devices. Between 2010-14, principal investigators from the Department have brought to the Institute 7 European grants, including a ERC Advanced Grant and a ERC Synergy Grant, a Center of Excellence of the Czech Science Foundation, and the Praemium Academiae and J. E. Purkyně Fellowship of the Czech Academy of Sciences. Between 2010-14, the Department has published 2 Reviews of Modern Physics, 1 Science, 17 Nature Publishing Group, 7 Physical Review Letters, and numerous other peer reviewed articles in the more specialized journals. Most of the works were performed within international collaborations with world-leading groups in the field. In all works, members of the department played the leading or key role. They presented the results at more than 50 invited talks at international conferences.

Spintronics, *Nature Mater. (Insight)* 11 (2012)

Figure 1 Front page of the special issue of Nature Materials journal on Spintronics.

Spintronics is the leading technology for magnetic storage and sensing. In the near futurte, it is expected to provide high density magnetic random access memories and logic-in-memory architectures, opening a route to the new generation of high-speed, low-power instant on-and-off computers. While the potential for applications has been a major drive for the field it would be a fallacy to consider the eventual applications more important than the fundamental insight provided by spintronics research. Spin is a purely quantum-mechanical entity and its interaction with the electron charge or the atomic environment provides a unique opportunity to understand the quantum nature of matter. The 2012 special issue of *Nature Materials* introduces in a comprehensive format several of the most prominent areas of current spintronics research. Fourteen scientists from Europe, United States, and Japan, including 4 memebrs of the Department, have joined forces to prepare the featured review articles.

The main focus of the research in the Department was on the following 3 areas:

I. Electrically generated non-equilibrium spin-polarization in relativistic materials, namely spin Hall and spin galvanic effects, and magnetic torques.

II. Materials research, nanodevices, and relativistic magneto-transport and magneto-optical phenomena in ferromagnetic semiconductors.

III. Spintronics in antiferromagnets.

In the following we introduce in more detail several of the results of the Department:

I.a. Spin Hall effect transistor, *Science* 330 (2010) 1801 – 1804

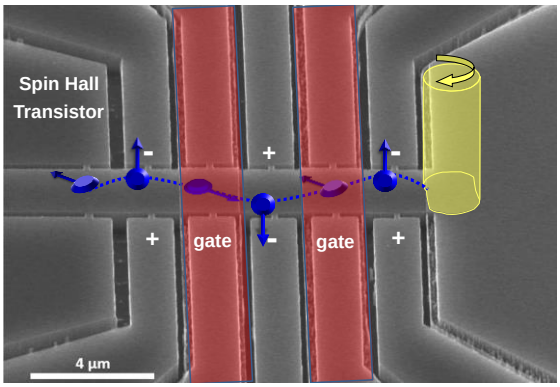


Figure 2 Electron microscopy image of the spin-Hall transitor structure with highlighted laser-beam (yellow), gate electrodes (red) and precessing injected spins (blue).

We reported an experimental demonstration of a transistor whose functionality is based on electron's spin. The work was performed in collaboration with the Charles University in Prague, the Hitachi Cambridge Laboratory, the University of Cambridge and Nottingham in the UK, and the Texas A&M University in the USA.

60 years after the discovery of a transistor its operation is still based on the same physical principle of electrical manipulation and detection of electron's charge in a semiconductor. The technology has focused on down-scaling the device size which has brought transistor dimensions from the original table-top size close to the inter-atomic-distance scale in an astonishingly short time of several decades. Since we are quickly approaching the ultimate down-scaling limit it is now an eminent task to establish new physical principles of transistor operation. One extensively studied possibility is utilizing electron spin.

Theoretical proposal of electrical manipulation and detection of electron spin in semiconductors is 20 years old. However, its experimental realization turned out to be unexpectedly difficult. We engaged recently discovered quantum-relativistic phenomena for both spin manipulation and detection to realize the spin transistor and to demonstrate spin-logic operation.

To observe the electrical manipulation and detection of spins we utilized a specially designed planar photo-diode placed next to the transistor channel. By shining light on the diode, photo-excited electrons are injected into the transistor channel. A circularly polarized light is used to generate spin-polarized electrons. The quantum-relativistic effects are employed to control the precession of spins by input gate-electrode voltages. Quantum-relativity, namely the spin Hall effect, is also responsible for the onset of transverse electrical voltages which depend on the local orientation of precessing electron spins in the transistor channel and represent the output signal.

The observed output electrical signals remain large at room temperature and are linearly dependent on the degree of circular polarization of the incident light. The device represents a realization of an electrically controllable solid-state polarimeter which directly converts polarization of light into electric voltage signals.

I.b. Electric control of spin-Hall effect by inter-valley transitions, *Nature Mater.* 13 (2014) 932 - 937

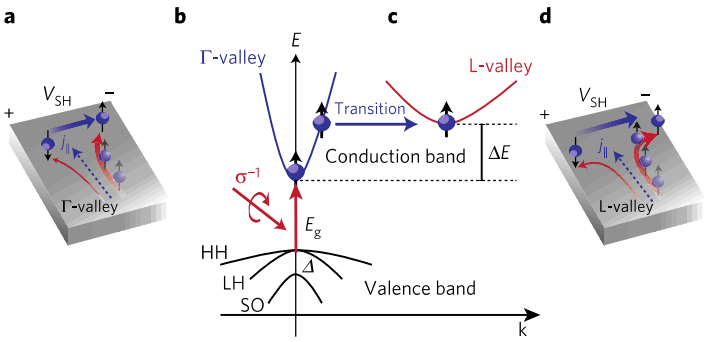


Figure 3 Schematics of optically induced intervalley spin Hall effect (SHE). (a) The optically induced SHE for Γ-valley electrons. (b) GaAs band structures and spin-polarized electrons generated by circularly polarized light absorption. (c) High electric field induces a transition of the spin-polarized electrons from the Γ-valley to the satellite L-valley with a larger spin-orbit coupling. (d) The optically induced SHE for L-valley electrons. Owing to the larger spin-orbit coupling of the L-valley, the efficiency of the charge–spin conversion is strongly enhanced.

Current information technologies are either charge-based or spin-based. Efficient spin-charge and charge-spin convertors are needed for future technologies allowing to integrate the so far isolated worlds of semiconductor charge-based and magnetic spin-based devices.

In collaboration with researchers from the UK, Germany, and Japan, we discovered an efficient spin-charge converter in a common semiconductor material GaAs. The device functionality is based on the relativistic phenomenon called the spin Hall effect which members of the Department discovered in 2004 and which since then has become a text-book tool for converting electrical to magnetic signals, and vice versa, in a broad class of metals and semiconductors. So far, the most efficient spin-charge converters have been identified among heavy-metal elements such as platinum. We found that one of the most common semiconductors GaAs can be turned into an as efficient spin Hall effect spin-charge converter as platinum. We utilized the property of semiconductors in which electrons can carry the current of their charge and spin in different conduction “valleys”. We discovered that by moving carriers in GaAs from one to another valley, the spin-charge conversion efficiency increases in this semiconductor forty-times.

II.a. Spin-dependent phenomena and device concepts explored in (Ga,Mn)As, *Rev. Mod. Phys.* 86 (2014) 855 - 896

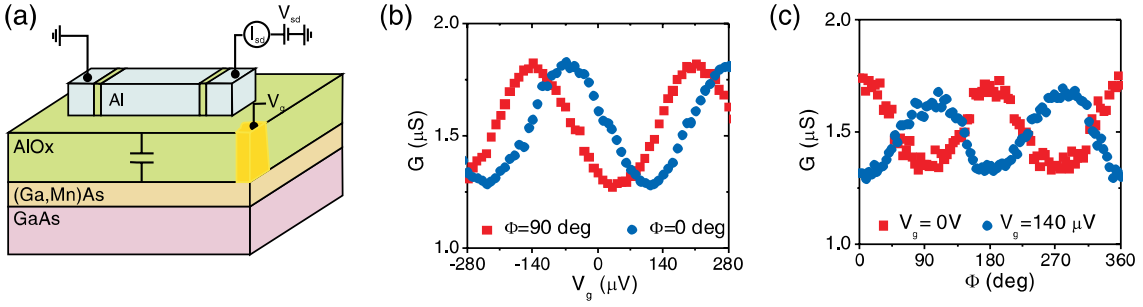


Figure 4 Transistor with a (Ga,Mn)As ferromagnetic-semiconductor gate electrode (a) which allows to open and close the transistor channel, in the same device, using either charge (b) or spin (c).

Over the past two decades, the research of ferromagnetic semiconductors, with (Ga,Mn)As as a prime example, has led to a deeper understanding of relativistic spin-dependent phenomena in magnetic systems. It has also led to discoveries of new effects and demonstrations of unprecedented functionalities in experimental micro-electronic and opto-electronic devices. In collaboration with researchers from the Charles University in Prague and from the UK we put together a comprehensive review of this field.

Ferromagnetic semiconductors represent a favourable class of materials integrating the charge-based and spin-based functionalities of micro-electronic and opto-electronic devices. Semiconductor silicon microprocessors are prime examples among the large variety of charge-based devices. They utilize the possibility offered by semiconductors to easily electrically manipulate and detect their electronic charge states representing the zeros and ones. Spin-based devices operate on an entirely distinct principle. In some materials, like iron, electron spins spontaneously align their direction, what subsequently generates magnetism of such material. The position of the north and south pole of the magnet can be used to represent the zeros and ones. This technology is behind memory applications such as computer hard disks. Ferromagnetic-semiconductors can simultaneously behave like silicon and iron which offers the unique possibility to investigate the charge and spin functionalities in one material. The leading position of the Department in the international research of ferromagnetic semiconductors, acknowledged by the invitation to prepare the comprehensive Reviews of Modern Physics article, is an outgrowth of the materials development and device nano-fabrication activities, magnetic, electrical, and optical experiments, and an extensive theoretical modeling in the Department.

II.b. Spin-orbit driven ferromagnetic resonance: A nanoscale magnetic characterisation technique, *Nature Nanotech.* 6 (2011) 413 – 417

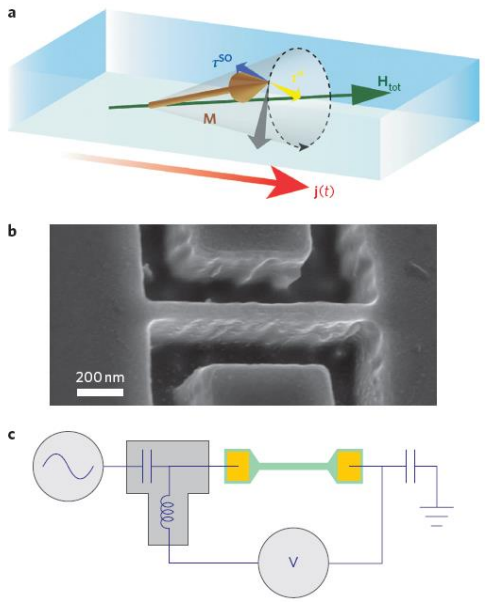


Figure 5 The figure shows (a) the principle of relativistic magnetic resonance, (b) the ferromagnetic semiconductor nanodevice and (c) electrical set-up used for the observaion.

We demonstrated that the relativistic behavior of electrons makes it possible to utilize magnetic resonance in electronic nanodevices. The discovery was a result of a collaboration with laboratories in Cambridge and Nottingham in the UK.

In physics, magnetic resonance represents one of the basic methods for investigating new magnetic systems. With the help of known magnetic elements it is also an indispenseble diagnostic tool utilized, e.g., in medicine. Our work introduced a new physical principle of magnetic resonance. The remarkable aspect of the principle is that the driving radiofrequency field is generated and acts directly inside the studied magnetic device, and the device itself serves also as the detector of the induced magnetic oscillations. We demonstrated that the method allows to perform detail investigation of magneto-electronic devices with dimensions of only several tens of nanometers.

Similar to conventional electronics, spintronics which utilizes both electrical and magnetic properties of electrons in e.g. new types of memories is approaching the tiny scales of sever hundreds or just tens of nanometers. The relativistic magnetic resonance may become an important tool for exploring and utilizing these ultrasmall spintronic devices.

II.c. An antidamping spin–orbit torque originating from the Berry curvature, *Nature Nanotech.* 9 (2014) 211 - 217

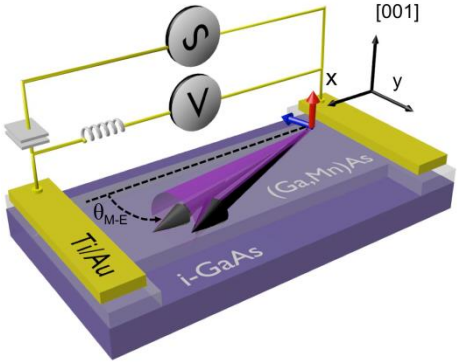


Figure 6 Schematics of electrical excitation of a ferromagnet.

The drawback of current magnetic memories is that in order to reverse the north and south poles of the magnet, i.e. flip the zero to one or vice versa, the magnetic bit has to be coupled to an electro-magnet or to another permanent magnet. If instead one could flip the poles by an electric field without involving another magnet, a new generation of memories can be envisaged combining the merits of both charge and spin-based devices.

In collaboration with researchers from Cambridge, Nottingham, and Mainz, we discovered a new physical phenomenon that allows us to manipulate the state of a magnet by electric fields.

In order the shake a magnet electrically without involving an electro-magnet or another permanent magnet one has to step out of the realm of classical physics and enter the relativistic quantum mechanics. It allows electrons accelerated in an electric field to order their spins, in other words, to become magnetic. We took a permanent magnet GaMnAs and accelerated some of the electrons inside the permanent magnet by electric field. These accelerated electrons created a new internal magnetic cloud which was able to shake the surrounding permanent magnet, and we detected that the poles of the permanent magnet moved.

The observed phenomenon is closely related to the relativistic spin Hall effect which has become a text-book demonstration how electrically accelerated electrons can magnetize any material, including common semiconductors. Earlier we tried to combine the merits of charge and spin-based devices by turning semiconductors into magnets through the spin Hall effect and in this work analogous physical phenomenon allowed us to also inverse the approach. We started from a magnet and made it sensitive to electric fields. Both approaches are promising for realizing a new generation of memories.

II.d. Experimental observations of optical spin torques, *Nature Phys.* 8 (2012) 411 - 415, *Nature Commun.* 4 (2013) 2322(1) - 2322(6), *Nature Photon.* 7 (2013) 492 - 498, interview at *Nature Photon.* 7 (2013) 500

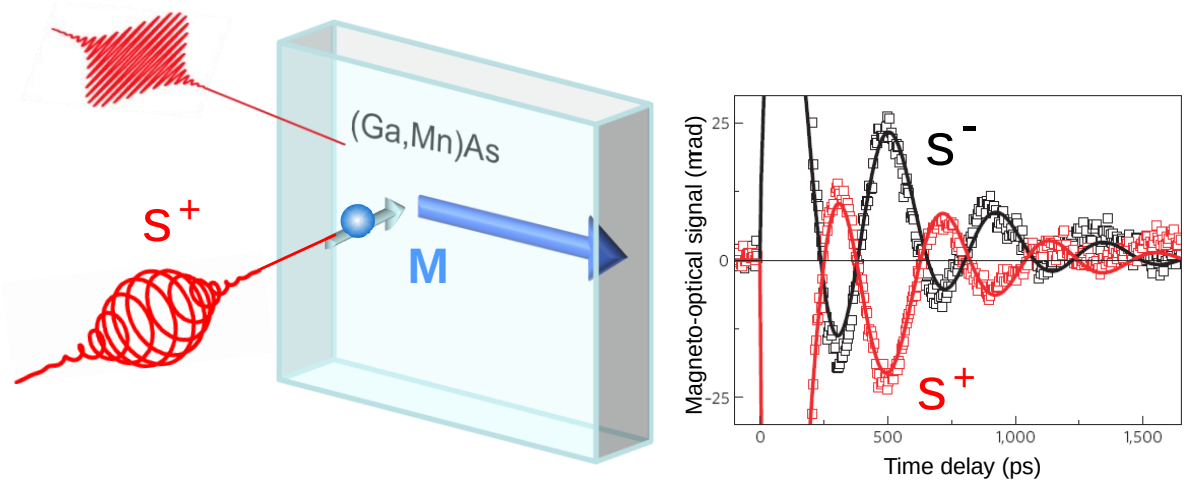


Figure 7 shows the physical principle of the optical spin-transfer-torque and the experimental observation of the optical excitation of the ferromagnetic semiconductor by short, circularly-polarized laser pulses allowed by the new phenomenon.

A direct transfer of angular momentum from a circularly polarized light to spins allowed us to excite a magnet from its equilibrium state at sub-picosecond time scales. This discovery, providing means to manipulate spins in a magnet by short laser pulses, was reported by the joint Laboratory of Opto-Spintronics of the Department and the Faculty of Mathematics and Physics, Charles University.

Angular momentum transfer from a spin-polarized electrical current to magnetization in a ferromagnet is the so called spin-transfer-torque phenomenon. The effect allows, for example, to write information in the latest generation of magnetic random access memories. The timescales for exciting magnetization by the current-induced spin-transfer-torque are typically nanoseconds. We observed an optical variant of the phenomenon, the so called optical spin-transfer-torque, in which magnetization is excited in a magnetic semiconductor by photo-carriers injected by circularly-polaized laser pulses at timescales which are several orders of magnitude shorter. The material for the experiment was a GaAs semiconductor doped with Mn, which was prepared by atomic layer-by-layer growth in the Department. Femtosecond pump-and-probe technique for optically exciting and detecting magnetization dynamics was employed by members of the joint Laboratory of Opto-Spintronics from the Faculty of Mathematics and Physics of the Charles University.

Electrical current can induce a rotation of the magnetization vector in a ferromagnet also due to a relativistic spin-orbit coupling effect and this recently discovered phenomenon is the so called spin-orbit-torque. We observed an optical variant of the phenomenon in which magnetization is excited in a magnetic semiconductor by photo-carriers injected by linearly-polarized laser pulses.

Our work on optical spin-torques combines the photo-effect, a phenomenon which is at the very heart of semiconductor opto-electronics, with the electrical spin-torques which are the key phenomenona for spintronics and magnetic memories. By this we built a new bridge between these two modern fields of research in microelectronics.

III.a. A spin-valve-like magnetoresistance of an antiferromagnet-based tunnel junction, *Nature Mater.* 10 (2011) 347 - 351

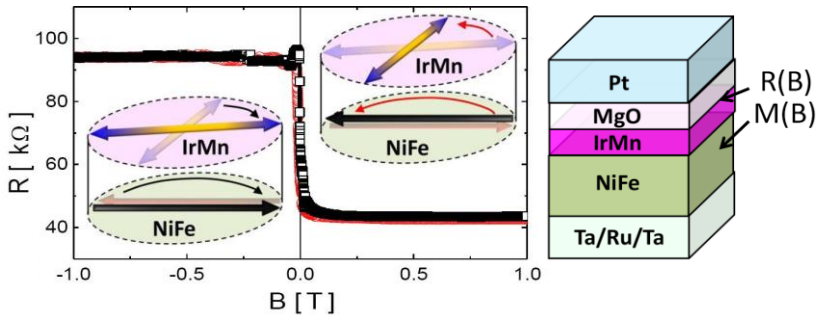


Figure 8 The antiferromagnetic tunneling device and its magentoresistive signal. Left pannel shows the measured tunneling resistance as a function of the applied magnetic field and schematic diagrams of rotating moments in the device. Right pannel shows the individual layers forming the studied tunneling device.

We demonstrated a new principle of operation of a spintronic device based on an antiferromagnet. The work was performed in collaboration with Hitachi laboratories in the UK and Japan, and with the Charles University in Prague.

All current spintronic devices used, e.g., in hard drive read-heads or magnetic random access memories are based on ferromagnets. In these materials, like iron or cobalt, spins have the natural tendency to orient in parallel and the materials then act as strong magnets.

There is, however, a large family of materials with ordered spins in which spins in the vicinity of one group of atoms in the crystal are orieneted in one direction while spins at another group of atoms have the oposite orientation. Besides the large number of these so called antiferromagnets, the materials are attractive because their magnetic behavior is felt only inside the crystal while for the outside world they appear as non-magnetic. They do not produce magnetic stray field that would influece the neighboring element which is a particularly useful property when considering the high density of elemenets in current integrated circuits. It has been, however, unknown to scientists on what physical principles a spintronic device can operate whose active magnetic electrode is made of an antiferromagnet.

We introduced not only the principle but also an experimental realization of such a device. When rotating the spins in an antiferromagnetic electrode, we observed a large change in the resistance of the studied device, comparable to resistance changes in conventional ferromagnetic spintronic devices. The effect is based on a quantum-relativistic phenomenon called tunneling anisotropic magnetoresistance.

III.b. Room-temperature antiferromagnetic memory resistor, *Nature Mater.* 13 (2014) 367 - 374

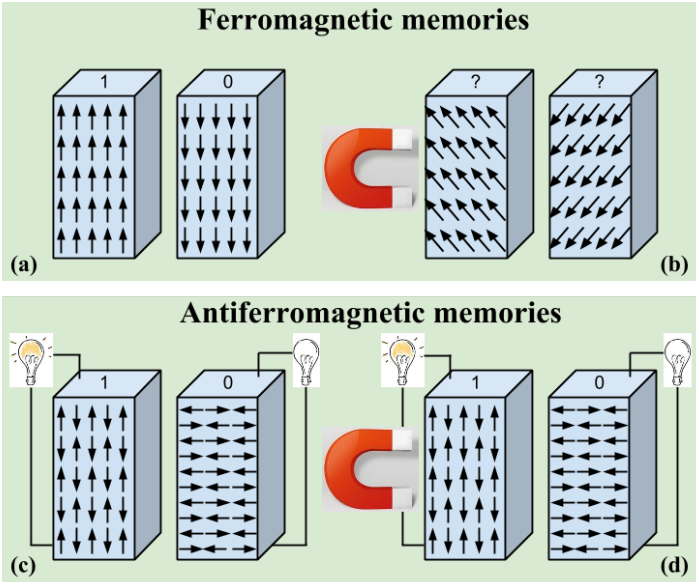


Figure 9 Schematics of the ferromagnetic memory sensitive to magnetic field perturbations (a,b) and antiferromagnetic memory insensitive to magnetic field perturbations (c,d).

In ferromagnetic materials, information can be stored in “zeros” and “ones” defined by the orientation of magnetic moments. This technology is behind a range of memory applications from kilobyte magnetic stripe cards to terabyte computer hard disks. It is dangerous to place a parking ticket or a hard disk next to another magnet or device generating strong magnetic fields because the magnetic moments of the memory can be unintentionally reoriented and the information lost. Moreover, being magnetic on outside, a ferromagnetic bit could disturb the neighboring one if the integration of bits in high-density memories was pushed to limits.

In collaboration with researchers from Berkeley and Barcelona, we demonstrated that it is possible to use antiferromagnets to store information. We used a special antiferromagnet FeRh which changes to a ferromagnet upon heating. To be able to select the magnetic moment direction of the antiferromagnet for encoding “zeros” or “ones”, it is heated up to bring the material into the ferromagnetic phase. A magnetic field pointing along one or another direction is then applied and the material is allowed to cool down back into the antiferromagnetic state where the direction of the antiparallel moments “freezes” along an axis determined by the magnetic field direction applied during cooling. Once in the antiferromagnetic state, the information is written and is no more sensitive to external magnetic fields. Information is subsequently read by measuring the electrical resistance which depends on the relative angle between the measuring current run through the antiferromagnetic bit and the direction of the antiferromagnetic moments in the bit.

III.c. Anisotropic magnetoresistance in an antiferromagnetic semiconductor, *Nature* Commun. 5 (2014) 4671(1) - 4671(7)

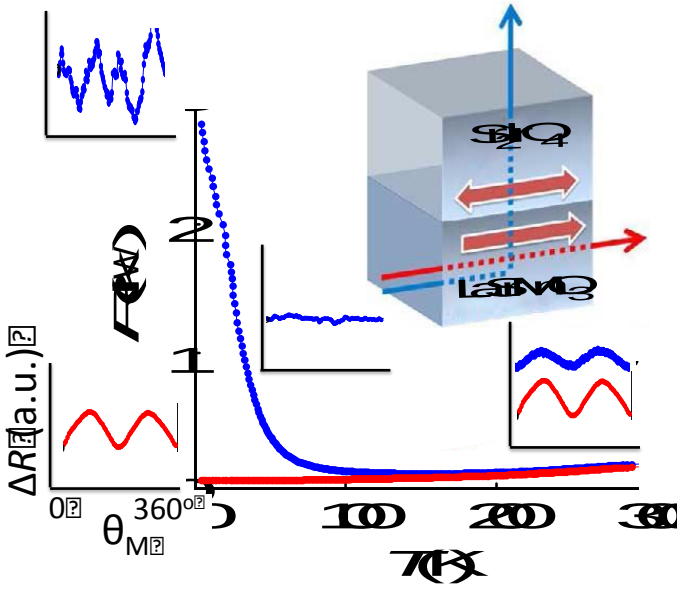


Figure 10 Main panel: Strongly temperature dependent resistance of the semiconductor Sr_2IrO_4 (blue) compared with the weak dependence in a metal $LaSrMnO_3$ (red). Insets: Resistance changes when changing angle of the spin magnetic-moment at corresponding temperatures. The magnetoresistance is again strongly temperature dependent only in Sr_2IrO_4.

Semiconductor transistors, which are the founding blocks of modern information processing technologies, allow for the control of the electrical current by temperature, light, or electrostatic gating. Metal ferromagnets like iron, used in information storage devices, allow for a complementary approach in which the electrical current is controlled by manipulating the orientation of electron spins. For more than a decade, the research towards merging the semiconducting and magnetic approaches to microelectronics in one material has focused on utilizing artificial ferromagnetic semiconductor materials, e.g. GaMnAs. These are, however, difficult to synthesize and so far have not met the requirements on material properties practical for microelectronic applications. Antiferromagnetic semiconductors are much more abundant than ferromagnetic semiconductors, and many of them have naturally the favourable properties required for microelectronics.

In collaboration with researchers from Barcelona, Berkeley, and Halle we demonstrated an experimental spin-based microelectronic device using an antiferromagnetic semiconductor compound Sr_2IrO_4. Experiments in the Sr_2IrO_4 device showed that the electrical current flow through the device can be controlled by the usual means provided by conventional semiconductors but, simultaneously, also by reorienting the electron spins in this antiferromagnet. Our findings open a route to integrate semiconducting and spin-based microelectronics by utilizing antiferromagnets.

III.d. Tetragonal phase of epitaxial room-temperature antiferromagnet CuMnAs, *Nature Commun.* 4 (2013) 2322(1) - 2322(6), *Physics* 4, 7 (2011)

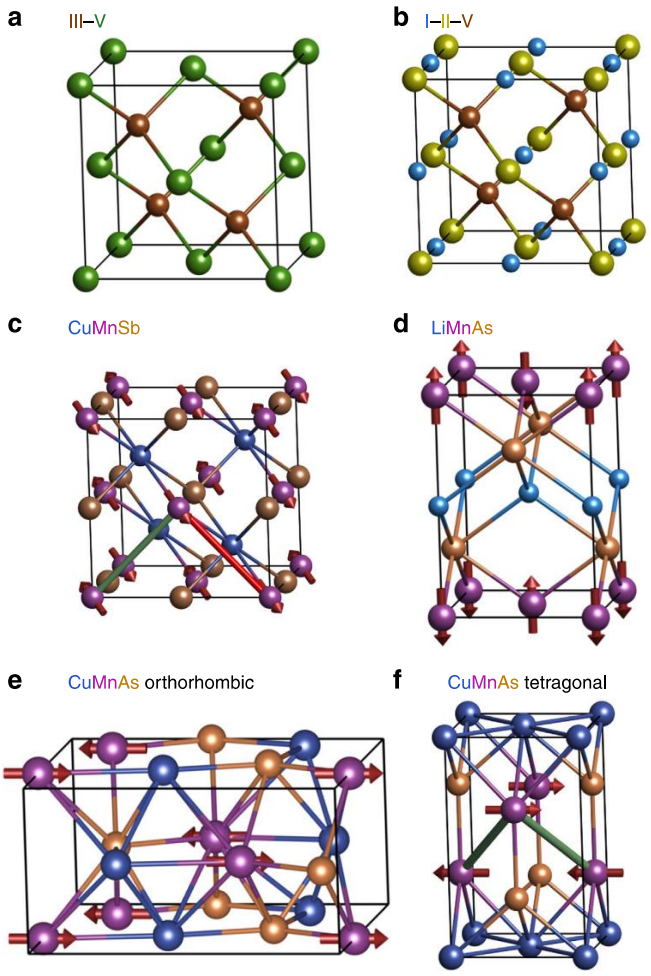


Figure 11 Unit cell structures of non-magnetic semiconductors and their magnetic counterparts. (a) III–V zincblende structure. (b) I–II–V half-Heusler structure. (c) Half-Heusler CuMnSb. (d) Tetragonal LiMnAs. (e) Orthorhombic CuMnAs. (f) Tetragonal CuMnAs.

We prepared single-crystal thin films of the LiMnAs antiferromagnetic semiconductor by molecular beam epitaxy (MBE). In terms of the crystal structure, the material is the antiferromagnetic counterpart of the common zinc-blende/half-Heusler non-magnetic semiconductors and ferromagnets. The inclusion of alkali metal elements represents, however, a challenge both in terms of the growth and the stability of devices. This motivated our interest in CuMnAs as a suitable antiferromagnetic material for spintronics which is structurally compatible with common semiconductors. We confirmed that the bulk equilibrium phase of CuMnAs displays room-temperature AFM ordering. However, the bulk orthorhombic crystal structure is not compatible with conventional compound semiconductor substrates. In our subsequent work we demonstrated that CuMnAs films can be prepared by MBE in the tetragonal form on GaP (Si) substrates. The functionality of this new antiferromagnetic compound was demonstrated in all-epitaxial CuMnAs/Fe antiferromagnet/ferromagnet bilayers.

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Structural analysis

2.1 Introduction

The research team “Structural analysis” corresponds to the Department of structure analysis, a unit established in the fifties of the last century for structure analysis of crystals using x-ray diffraction. Atomic structure has always been a necessary pre-requisite for chemical and material research. Therefore, the progress in crystal structure analysis is driven by growing demands in many scientific fields while conversely, the improvement of methods and instruments for structure analysis opens new possibilities in these related fields.

Throughout its long history, structure analysis of crystals was several times considered a closed story, an omen that a qualitative jump would come on the instrumental or methodological level. Technically, the upgrade came with the invention of automatic diffractometers in the seventies and CCD area detectors in the nineties. Methodologically, the formulation of the superspace theory in the eighties improved the understanding of aperiodic structures. Nowadays, we witness another turbulent period with considerable changes in technology (microfocus sources and new kinds of detectors) as well as in methodology (the advent of electron diffraction tomography). It seems that before stating once again that structure analysis of crystals is a closed story, a lot of work has to be done!

The department of structure analysis (head Michal Dušek, 19 researchers, and four students) has been always an important participant in the evolution of methods for structure analysis, especially in the field of aperiodic (modulated) structures. Here we earned reputation with the development of the universal crystallographic computing system JANA (Petříček et al., 2014), which is *de facto* world standard for calculation of aperiodic or otherwise difficult structures with 2000 users worldwide and about 250 citations per year (Fig. 1). JANA represents a platform for implementation of all new methods and improvements made by our team as well as of methods developed by others. Another success was the charge flipping program Superflip (Palatinus and Chapuis, 2007), a program for structure solution in arbitrary dimension cited more than 200 times a year. In the previous evaluation period 2005-2009 our team obtained a significant support from Praemium Academiae awarded by Academy of Sciences to Václav Petříček for development of the program JANA. This helped us to build three modern laboratories (single crystal x-ray diffraction, powder x-ray diffraction and electron diffraction), to attract several excellent young scientists, and to accelerate the development of methods for structure analysis.

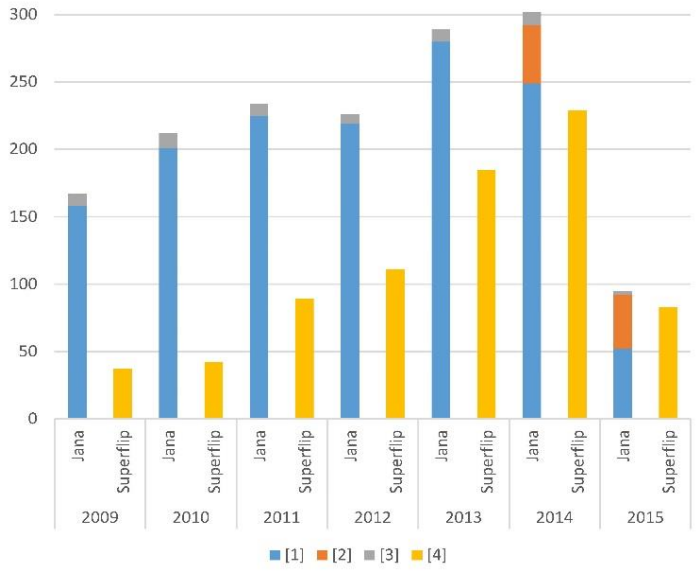


Figure 1: Citations of Jana and Superfip. [1] unpublished; [2] Petříček et al., 2014; [3] Dušek et al., 2001 + Petříček and Dušek, 2004; [4] Palatinus and Chapuis, 2007. Source: WOS, 25 April 2015

2.2 Outline

Our main concern in the current evaluation period 2010-2014, with respect to the excellent rating obtained in the previous evaluation, was to keep the exclusive position of the team in the field of development of methods for structure analysis. To this aim, we reinforced our traditional tools and

responded to the latest challenges in our field. At the same time, having access to the new experimental equipment, we decided to extend the scope of our diffraction experiments and build a team providing routine as well as a specialized structure analysis of all kinds of crystals except proteins. It is unquestionable that rich experimental background accelerates development of methods, therefore both aims were synergic. More specifically, our tasks in the current evaluation period were as follows:

1) Development of methods based on electron diffraction tomography. This is one of the most important challenges in the contemporary crystallography to perform accurate structure analysis of micro- and nanocrystals comparable with x-ray structure analysis.

2) Development of structure analysis of magnetic compounds. This method, based in low temperature neutron diffraction experiments, represents a direct link between crystallography and physical properties. The goal was to utilize directly the symmetry of the diffraction pattern.

3) Understanding the physical mechanisms leading to magnetic structures. The interplay between the crystal and magnetic structures is mediated by the spin-orbit coupling (SOC). Studying the effects of SOC on the electronic structure reveals links between the structure and properties of materials.

4) Further development of methods for modulated structures. Although this is our main specialization, the complexity of modulated structures is growing with the number of crystallographers trying to solve them, and the methods need continuous development.

5) Enhancement of mineralogical crystallography with special regard to uranium minerals. The research of uranium minerals is highly challenging due to the complexity of their modular crystal structures and connection with the environmental problematics.

6) Reinforcement of chemical crystallography. New equipment for single crystals and powders allowed us to expand our services in the field of chemical crystallography and to make corresponding development of JANA system focused on automatic features applicable to simple structures.

7) Dissemination of our methods. Development of methods requires user feedback, therefore considerable efforts have been undertaken to spread our methods, especially through workshops.

2.3 Results

2.3.1 Precession electron tomography and related computing methods

(leading scientist Dr. Lukáš Palatinus)

Electron diffraction is a technique that allows crystal structure analysis of extremely small crystals, down to just about 10nm in size. Until recently, electron diffraction was mostly used only as a qualitative tool, and structure solution or refinement remained the domain of a few specialists and special materials. The principal reason for the difficulties is the presence of dynamical diffraction effects, which complicate the relationship between the diffracted intensities and the crystal structure.

The situation changed in the year 2007, when it was shown (Kolb et al., 2007, 2008) that electron diffraction data can be used for *ab initio* structure solution of crystals, if the data are collected using the rotating crystal method, dubbed *electron diffraction tomography* (EDT). In this method the crystal is oriented randomly in the beam, rotated in small steps (from 0.05° to ~1°), and a diffraction pattern is taken at each step. With this approach a three-dimensional record of the diffraction can be collected and the data can be used for structure solution. Another technique used to collect electron diffraction data for structure analysis is *precession electron diffraction.* In this technique the electron beam is not stationary during the recording of the diffraction pattern, but performs a precession-like motion – moves on the surface of a cone with vertex on the sample and with an opening angle typically between 1°and 3°. This leads to the integration of the intensities of reflections and partial suppression of the dynamical diffraction effects.

The best results can be obtained by a combination of both techniques. This combination is used in our laboratory. The research projects focus on further development of the method, especially in the improvement of the accuracy of obtained structural information, and on the application of the method to specific materials. The data are collected in a transmission electron microscope equipped with a precession unit. We have developed (unpublished) software for automatic collection of the data. This software, after reading-in the parameters of the data collection, controls the movements of the goniometer of the microscope, the precession angle, exposure time etc. to perform either a semi-automatic or fully automatic mode. It is optimized so that a complete data collection takes typically only about fifteen minutes. This is globally one of the fastest EDT systems.

The recorded images must be processed to determine the unit cell dimensions, crystal orientation and to integrate the diffraction intensities. For this purpose we have developed a computer program PETS (Palatinus, 2011). The program performs all tasks necessary for the data processing. It extracts

the positions of reflections in the images, refines the centres of the diffraction patterns, calculates the three-dimensional coordinates of each peak in reciprocal space, completes the reciprocal space using the difference space approach and prepares the necessary input for the determination of the orientation matrix. This determination is carried out in the graphical interface of JANA2006. Using this orientation matrix, PETS integrates the diffracted intensities and produces a file suitable for structure analysis. Shortly after its development the program started to be used also by other researchers in the field. In an article (Gemmi & Oleynikov, 2013) it was shown that PETS yields results comparable and sometimes even better than other available software.

The current standard in the solution and refinement of structures from EDT data is to neglect the dynamical effects and consider the data as kinematical, *i.e.* consider the intensities proportional to the square of the amplitude of the Fourier coefficients of the electrostatic potential. This approximation allows for the building of structure models and approximate determination of the structure. For the structure solution step we use the software Superflip (Palatinus & Chapuis, 2007), which was developed by Dr. Palatinus, who continues its development. The program was optimized for the best performance against electron diffraction data and is now being successfully used for this purpose.

The suite of programs just described makes our laboratory one of three laboratories in the world developing a complete suite of programs for data collection and data reduction of EDT data, and the only laboratory that develops a whole system including a structure solution and refinement software. In addition to the software and methods' development we apply the methods to specific materials. We have solved the structure of copper silicide $Cu_{3+x}Si$ – the first incommensurately modulated structure solved solely from EDT data (Palatinus et al., 2011). This structure exhibits extreme modulations and it eluded proper structure description for more than 25 years. Further works in the analysis of modulated structure include the identification of modulated phase in $EuTiO_3$ (Goian et al, 2012) and the solution of $Bi_5Nb_3O_{15}$ (Boullay et al., 2013) in collaboration with the laboratory Cristmat (CNRS, Caen, France).

Further successes in the structure solution from EDT data include the elucidation of several mineral structures. Mineralogical samples are specific, because they often contain a mixture of phases and their analysis by powder diffraction techniques is challenging or impossible. The possibility of EDT to analyse a single grain allows a detailed analysis of any phase mixture. Using this approach, we could elucidate for example the structure of iron arsenate-sulphate (Paktunc et al. 2011), which was determined from a sample containing at least six different phases, or the structure of lead uranyl carbonate (mineral widenmannite, Plášil et al., 2014).

The most severe limitation in the use of electron diffraction for accurate structure determination has been the use of kinematical approximation in the calculations and neglecting the dynamical diffraction effect. In our laboratory we decided to tackle this problem and develop a method for accurate structure refinement against electron diffraction data using full dynamical calculation of diffracted intensities. This method has the potential of bringing structure analysis from electron diffraction to the similar level of accuracy as the x-ray-based methods, but from much smaller crystals.

The development of the method posed significant challenges. In the first important step it was shown on selected examples using oriented diffraction patterns that using precession electron diffraction yields better figures of merit, more stable refinements and more accurate results (Palatinus et al., 2013). The next step was to generalize the dynamical refinement to general, non-oriented diffraction patterns. Traditional approaches used in electron diffraction were of no use here, because they were developed for oriented patterns. Similarly, approaches used in x-ray diffraction data analysis could not be used directly, because the intensities in EDT depend on more parameters than x-ray diffraction intensities, especially on the exact orientation of the crystal to the incident beam and on the crystal thickness. A method had to be found to determine, which reflections should be included in the refinement process. A set of data selection criteria was devised for selection of such data points with good sensitivity to the structural details and limited sensitivity to crystal imperfection, mosaicity and thickness variation (Fig. 2). The selection criterion relating the excitation error of every reflection with the precession angle is a novel quantity, which does not have a precedent in other methods and which turns out to be of critical importance for the success of the whole procedure.

The method was implemented in the computer programs JANA2006 and DYNGO, which are closely interconnected. JANA2006 takes care of the structure refinement procedure and allows using all the advanced features of this computing system. DYNGO is a utility for calculating the dynamical diffraction intensities for a given set of parameters. It is a multithreaded program that allows performing the calculation on multiple processors in parallel. A summarizing article about the implementation of the method was submitted and accepted for publication by the end of the year 2014 and published at the beginning of 2015 (Palatinus et al., 2015). (Implementation of the dynamical refinement was partially supported by the Czech Science Foundation (CSF) project 13-25747S). The method was tested with several real data sets. The samples for testing were selected so that a reliable, good quality reference structure was available for all of them and, therefore, we could evaluate the accuracy of the refinement against EDT data. The results show (table 1) that an average deviation of atomic positions obtained by EDT refinement is in all cases close to or lower than 0.02Å, with the maximum less than 0.05Å. This exceeds the typical accuracy of refinements against powder x-ray diffraction data and approaches the accuracy of single crystal x-ray diffraction.

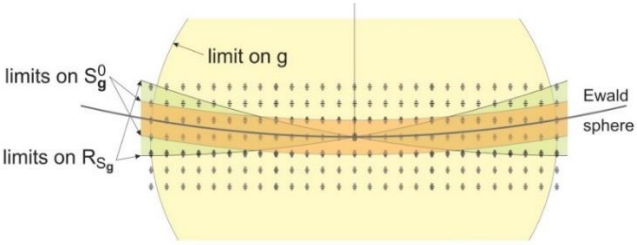


Figure 2: Schematic representation of the Ewald construction with different data selection criteria shown as filled areas of different colors. Yellow area: reflections passing the limit on the length of the diffraction vector. Orange area: reflections passing the limit on the maximum excitation error S_g^0. Green area: reflections passing the limit on the ratio between the excitation error and the amplitude of the precession motion R_{Sg}.

Table 1: Refinement results on selected structures. Comparison of kinematical refinement (column Kin) and dynamical refinement (column Dyn), showing refinement R-factors on observed reflections (R(obs)) , goodness of fit (GOF) and the mean and maximum deviation from the reference structure.

Sample	Ni_3Si_2		Ni_2Si		Orthopyroxene		Kaolinite		PrVO3	
Refinement	Kin	Dyn	Kin	Dyn	Kin	Dyn	Kin	Dyn	Kin	Dyn
R(obs) (%)	21.73	9.99	11.07	6.42	24.22	8.33	19.16	6.23	24.04	6.95
GOF(obs)	14.44	3.64	6.57	1.84	17.45	3.38	9.29	2.36	9.86	1.62
Mean/Max deviation (Å)	0.018/ 0.039	0.007/ 0.013	0.020/ 0.028	0.009/ 0.015	0.031/ 0.066	0.016/ 0.033	0.097/ 0.268	0.021/ 0.042	0.141/ 0.239	0.020/ 0.020

The development and successful testing of the method of dynamical structure refinement was the climax of the effort of the team at the Department of structure analysis to create a system for a complete structure analysis from electron diffraction data. This effort started in the year 2010 by installation of a transmission electron microscope with a precession unit, continued with the development of data collection software and data processing software, with the solution of first unknown structures, especially the modulated ones, and finished in the year 2014 by the development and testing of the structure refinement method. In these five years the group of electron diffraction became known world-wide as one of the leading groups in electron crystallography.

2.3.2 Magnetic structures (leading scientist Dr. Václav Petříček)

Neutron diffraction experiments reflect not only the nuclear structure but also the ordering of magnetic moments in crystals. The diffraction pattern is composed by two sets of sharp diffraction spots originating from the nuclear and the magnetic structures. The magnetic ordering for most of new materials occurs at low temperatures and the experiments are performed at neutron sources. Most of data are collected on powder samples but in cases, when a single crystal of reasonable size can be grown, single-crystal data collection allows more detailed analyses.

Ordering of magnetic moments is strongly affected by the original nuclear symmetry and therefore all possible symmetry characteristics of magnetic arrangements can be obtained by detailed analysis of the parent nuclear symmetry. For this, the analysis based on irreducible representations (Bertaut, 1968) plays a crucial role. It can be applied to two major cases: (1) when the translation symmetry remains the same as in the parent structure (i.e. the magnetic propagation vector **k**=**0**); (2) when the original translation symmetry is violated, either commensurately or incommensurately (i.e. **k≠0**). However, this approach does not show directly the resulting magnetic symmetry and its backward influence on the nuclear structure.

We decided to focus on an alternative, so far a less-used approach based on magnetic space groups, which shows directly the relationship between magnetic moments on symmetry related atoms as well as the relationship between the magnetic space group and the diffraction pattern. It follows the fact that the magnetic moment is an axial vector and introduces the so-called time inversion operator, which inverts the magnetic moments. This operation can be combined with standard space groups operations. Thus, each even order operator can exist in a pure and "primed" variant, the latter being combined with the time inversion. The magnetic space groups were introduced by Russian crystallographers and are named Shubnikov space groups. The symbols of magnetic space groups are usually described in BNS notations (Belov et al., 1957). Magnetic space groups cover not only cases when **k**=**0** but many other types of magnetic states found in materials, e.g., antiferromagnetic ordering which doubles the translation period in some crystallographic direction.

Magnetic space groups can be inferred from diffraction symmetry. Another advantage is that the magnetic symmetry together with nuclear symmetry can be described by the one set of symmetry operations which allow better prediction and understanding of changes in nuclear structure as induced by magnetic ordering. On the other hand, the representation theory gives all most probable basic magnetic arrangements induced by phase transitions. In our implementation we use advantages of both approaches and we relate any irreducible representation with a magnetic space group - kernel symmetry (Petříček et al., 2010), and with the system of the so-called epikernels. This approach is analogical to the one used in the program ISODISTORT (Campbell et al., 2012).

JANA2006 appeared to be an ideal platform for implementation of magnetic structure analysis because the formalism used for the magnetic **k** vector and for the description of spin waves is similar to that used for modulated structures. Furthermore, JANA2006 supports refinement against single crystal as well as powder data and allows for combination of data from different sources (x-ray, neutron and electron diffraction) offering a complex tool for structural studies of complicated multi-order systems.

The implementation into JANA was possible only after generalization of the original concept of magnetic space groups into magnetic superspace groups. For this reason a new operation, time inversion combined with a half period shift along an internal axis, has been introduced (Petříček et al., 2010; Perez-Mato et al., 2012). Similarly as for **k**=**0** and antiferromagnetic (AFM) cases, the new generalized magnetic superspace groups are connected with the representation analysis tool, which shows their relationship. It is now possible to describe magnetically modulated structures with an incommensurate propagation vector and study its possible influence on the nuclear modulations. Another important benefit is that we can describe magnetic ordering occurring in a nuclear structure, which became modulated even before the magnetic phase transition. This can be realized either by combination of magnetic space groups with the parent superspace group or by adding one or more additional modulation (propagation) vectors. One candidate for such considerations is the crystal of $BaCoX_2O_7$ (X=As, P) (David et al., 2013).

The generalized superspace approach was also used for the data reduction process, where the generalized Laue symmetry is applied to merge symmetrically related reflections for single crystal data collection or to generate the independent set of reflections for refining against powder diffraction data. Like for other crystallographic methods, using the symmetry in this way considerably improves the stability of the refinement process.

The magnetic option in JANA2006 attracted scientists specialized in physics as well as in crystallography. While physicists usually prefer the representation analysis and set of magnetic modes, crystallographers lean to the symmetry concept. For this reason a special wizard has been developed, which makes the process easier for both communities. The new option was presented by Dr. Václav Petříček as invited lectures at two most respected crystallographic conferences, ECM in Warwick, 2013, and IUCr Congress in Montreal, 2014. Several authors proved the applicability to different magnetic structures, with the most interesting example of the magnetic multiferroic structure $CaMn_7O_{12}$ with a helical screw type magnetic structure (Fig. 3) (Sławiński et al., 2012). During the last two years the magnetic option in JANA2006 earned reputation even among the users of other well established programs and at present 20 published magnetic structures were solved with JANA2006.

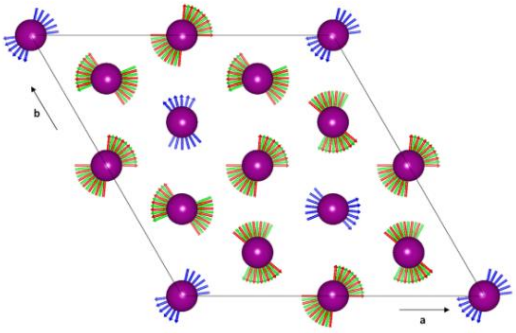


Figure 3: Circular magnetic ordering in $CaMn_7O_{12}$ (view of six unit cells along the modulation vector direction).Red and green arrows represent magnetic moments of two Mn^{3+} sublattices, blue arrows denote magnetic moments of Mn^{4+}.

2.3.3 Understanding physical mechanisms leading to magnetic ordering
(leading scientist Dr. Ondřej Šipr)

Magnetic properties of materials reflect their magnetic order. Two aspects of magnetic ordering can be distinguished according to the physical mechanism behind them. The first aspect concerns the magnitude of the moments and is governed by the so-called exchange interaction, which is generated by an interplay between the Pauli exclusion principle and the Coulomb interaction. The second aspect of magnetic order concerns the direction of magnetic moments with respect to the crystal lattice. It is manifested by the magnetic anisotropy and is linked to the crystal structure via the crystal electric field. This structure-related part of the magnetic anisotropy is usually called the magnetocrystalline anisotropy (MCA) to distinguish it from the shape anisotropy. The physical mechanism behind the MCA is the spin-orbit coupling (SOC). As the SOC is of paramount importance e.g., in the field of spintronics, studying the effect of the SOC on the electronic structure contributes to understanding the magnetic structure of materials and their properties alike.

During the 2010-2014 period, our in the area of understanding the magnetic order work (supported by the CSF project 108/11/0853) focused on selected problems concerning the MCA as well as on some aspects related to SOC-induced spectroscopies. One of the problems we addressed was related to calculations of the MCA for systems containing magnetic and non-magnetic atoms – which is a typical situation for magnetic nanostructures supported by non-magnetic substrates. We demonstrated that for accurate MCA calculations a much more careful treatment of the substrate is needed than what is necessary for magnetic moments and what had been common practice up to that time (Šipr et al., 2010). In particular, we found that reliable values of the MCA cannot be obtained if the substrate is represented by a slab of less than ten atomic layers. We supplemented this study by a systematic investigation of magnetic properties of transition metal clusters and monolayers on noble metal surfaces (Bornemann et al., 2012). Some unexpected trends for Ni clusters were found, especially regarding the Dzyaloshinski-Moriya interaction, which is another effect related to the SOC with consequences for the magnetic structure (leading, among others, to skyrmions). To learn more about structural aspects of the MCA, we investigated further to what extent the magnetic properties of nanostructures can be influenced by growing them on crystallographically different surfaces of the same substrate (Šipr et al., 2013). We found that changing the crystallographic orientation of the surface has a moderate effect on the spin magnetic moment, a larger effect on the orbital magnetic moment but sometimes a dramatic effect on the MCA and on the so-called magnetic dipole term, which is important in spectroscopic studies.

The ultimate goal of our research in this area is to get an intuitive understanding of the processes and mechanisms leading to the MCA. We started by analysing the substrate contribution to the MCA of supported nanostructures by a site-selective manipulation of the SOC and of the effective exchange field for adatoms and monolayers on Cu, Ag, Au, Pd and Pt surfaces (Šipr et al., 2014). We found that for adatoms, the influence of the substrate is relatively small while for monolayers, this influence can be substantial. The influence of the substrate SOC is much more important than the influence of the substrate exchange field, except for highly polarizable substrates with a strong SOC (such as Pt).

Another important effect associated with the SOC is x-ray magnetic circular dichroism (XMCD), i.e., the difference between the absorption of right-hand and left-hand circularly polarized x-rays in a magnetic sample. The XMCD spectroscopy is a complementary technique to neutron diffraction; it is not sensitive to long-range order but it carries chemically-specific information about local magnetic moments. Importantly, XMCD makes possible to study separately the spin magnetic moment, which is due to the exchange interaction, and the orbital magnetic moment, which is due to the SOC. Extracting this information from measured data can be substantially aided by an accurate calculation of x-ray absorption and XMCD spectra. One of areas where current computational procedures should be improved is many body effects beyond the local density approximation (LDA). We contributed to this by employing the LDA+DMFT many-body technique to calculate x-ray absorption and XMCD spectra of transition metals (Šipr et al., 2011). We found that LDA+DMFT improves the LDA results, in particular concerning the asymmetry of the spectral lines. Remaining differences with respect to the experiment concerning the ratio of the intensities of the peaks indicate that to get more accurate spectra, one has to treat the core hole beyond the final state approximation.

X-ray absorption and XMCD spectroscopy can be a useful tool to determine the atomic structure around an impurity by comparing measured spectra with spectra calculated for different structural models. An example of this approach is a study of Cu dopants in ZnO (Šipr et al., 2013) where a combined experimental and theoretical investigation shows that magnetic Cu impurities must be located in Zn-substitutional sites.

2.3.4 Modulated structures (leading scientist Dr. Václav Petříček)

The number of modulated structures solved with JANA2006 is continuously growing. Our laboratory practice shows one out of fifty new structures is modulated and in some classes of materials modulations appear regularly. This is also true worldwide and almost all modulated structures are solved with JANA2006. Tools for simple modulated structures are now expected to be user friendly and effective. For these reasons we revised, improved and simplified JANA2006 wizards for modulated structures and elaborated the interface for the Superflip program (Palatinus and Chapuis, 2007), which is the most effective way to obtain a reasonable starting point for refinement of modulated structures. On the other hand, in cases when satellite reflections are very weak and refinement thus depends strongly on a selected starting point, structure model of Superflip may converge into a false minimum. For this problem we developed a routine for random search of an optimal set of the starting modulation parameters.

Recently it has been shown that even such a complicated system like a protein crystal can be affected by modulations and the corresponding satellites can be measured. Solution of modulated proteins is not supported by JANA2006 because protein structures require quite different strategy and sophisticated procedures for keeping geometrical restrains. The simplest way to solve a modulated protein structure seems to be the implementation of selected procedures of JANA2006 into a program specialized to protein crystallography, e.g. REFMAC (Murshudov et al., 1997). First steps in that direction have been done in collaboration with the Eppley Institute for Research in Cancer and Allied Diseases in Nebraska (Lovelace et al., 2013).

While modulated structures described in (3+1) dimensional superspace are now common, there are also cases in which more modulation vectors are needed. Recently, we have solved the high-temperature cubic form of bismuth oxide, δ-Bi_2O_3, the best known intermediate-temperature oxide-ionic conductor, with three modulations vectors. For solution of this structure several data sets were used based on x-ray, synchrotron and neutron diffraction, and the solution took several years (Ling et al., 2013). It should be noted that this kind of structures cannot be solved without JANA.

2.3.5 Mineralogical crystallography (leading scientist Dr. Jakub Plášil)

Mineralogical crystallography has a very long tradition in our team, with emphasis on the description of twinning, polytypism, order-disorder (OD) phenomena and modulations. It benefits from the power of the computing system JANA2006, which has been specially developed for solving challenging structures. Another important advantage for this research is the possibility to combine experimental methods in order to obtain complementary data, especially the electron and x-ray diffraction.

During this evaluation period, owing to the previous support of Praemium Academie, we were able to start new research in mineralogical crystallography focused on the structure of uranyl oxysalts, namely uranyl sulfate minerals. These minerals represent widely occurring phases originating from alteration of natural source of uranium – mineral uraninite, under oxidizing conditions. They are responsible for retention or migration of U in the environment under low pH. Their crystal structures are usually quite complex and complicated, diffraction patterns often include twinning and diffuse scattering. The knowledge of structural properties, namely the weak bonding interactions in the crystals that hold together the entire structure, allow us to determine or at least to estimate mineral stabilities.

Uranyl sulfate minerals represent one of so far not widely studied mineral groups, mostly due to limitations of experimental equipment in the past, since uranyl sulfates usually crystallize in small and imperfect crystals. Our team contributed considerably to the research of uranyl sulfates during the last four years, especially to minerals of the zippeite-group, which contain sheet structures with hydrated mono-, di- or trivalent cations between the sheets. They are quite abundantly in nature, however, their structures remained unknown for a long time. Nowadays due to the successful structural characterizations (Plášil et al., 2011a,b, 2012a, 2013a; Burn at al., 2003; Peeters et al., 2008) we know far more about the complexity of the zippeite-group than previously thought based only on studies of synthetics. In the course of this research a detailed review and reinvestigation of known samples containing uranyl sulfate minerals were undertaken, which lead to the discovery of more than twelve new minerals (see below) and redefinition or refinement of already known uranyl sulfates (Plášil et al., 2012b, 2014a). Among the new minerals majority of them were found to contain new structure types or less frequently occurring structures, known previously only from analogous synthetics (Kampf et al., 2014; Plášil et al., 2013b, 2014b,c). The recent developments and discoveries were also referred and presented in two comprehensive reviews focused on mineralogy and crystallography of uranium (Krivovichev and Plášil, 2013) and mechanisms of formation of uranyl minerals from the primary uraninite (Plášil, 2014). These research studies were supported by the CSF project 13-31276P.

We also advanced in the research of the OD structures. We revised the structure of mineral kermesite Sb_2S_2O (Hybler and Ďurovič, 2013), which was interpreted as a strongly desymmetrized OD structure. Kermesite exhibits certain pecularities: although the structure is layered, the OD layers must be delimited differently from the structure building layers. These layers are parallel to one face of a non-standard octuple pseudomonoclinic cell, F-centred with extra centring points. The stacking rule was explained, and two possible MDO (*i.e.* Maximum Degree of Order) polytypes were derived. The structure studied represents one of them. Another successfully solved structure was the one of the rare 1M polytype of the mineral cronstedtite, $(Fe^{2+}_{3-x}\ Fe^{3+}_{x})\ (Si_{2-x}Fe^{3+}_{x})\ O_5(OH)_4$, (Hybler, 2014) obtained from a rare crystal from Eisleben, Germany.

2.3.6 Chemical crystallography and powder methods (leading scientist Dr. Michal Dušek)

One of our aims was to fully utilize the equipment acquired during the previous evaluation period and build a team providing specialized as well as routine structure analysis of all types of crystals. Routine structure analysis, sometimes called chemical crystallography, is important not only because a laboratory for structure determination is expected to make structure analysis for other teams. It also helps the team to gain experience based on thousands of measurements, and use this experience to develop methods towards everyday practical use. Moreover, among standard samples there is always a portion of difficult cases, which can be used for further methodological development.

For single crystal x-ray diffraction, using the new much faster four-circle diffractometer, a fruitful collaboration has been established with several institutes and universities worldwide, and nowadays the instrument is running at 100% of its capacity having a throughput about 400 samples every year. The most interesting results in this area were the determination of a novel In^{I} precursor for P_n ligand coordination chemistry (Welsch et al., 2010); determination of Bambus[n]urils, a new family of anionic receptors (Havel et al., 2011, Švec et al., 2011); determination of materials for second harmonic generation (Matulková et al., 2011); determination of luminescent molybdenum clusters (Kirakci et al. 2012, Kirakci et al., 2014); determination of regioselectively halogenated (Lukášek et al., 2014) and mercurated (Botha et al. 2014) thiacalix[4]arenes, etc. In summary, more than 150 papers from the field of chemical crystallography were published based on the structures determined by us. Our contribution to these publications was data collection, structure determination and crystallographic interpretation of the results. This work was accompanied with adding new features into the JANA2006 software based on the experience from the measurements. The most important was the full support for absorption correction based on the crystal shape as well as on the spherical harmonics, and scaling procedure for data acquired with area detectors (supported by the CSF project P204110809).

Although the program JANA supports calculation of powder structures since 2000, powder diffraction experiment itself was not available in our laboratory until 2010 when we obtained the necessary equipment. Our task was to master practical powder diffraction and establish collaboration with chemists and material scientists producing powder materials. This effort was successful and at the end of the current evaluation period, the powder diffractometer is running at 60% of its full capacity, producing about 100 powder profiles per year for the full structure determination and Rietveld refinement. The most important collaborating laboratories were at the University of Chemistry and Technology in Prague, University El Manar in Tunis and Golestan University in Iran. Due to the collaboration with these laboratories we published several articles based on the solved structures, e.g. Rohlíček *et al.*, 2013; Sládková *et al.,* 2014; Ouni *et al*., 2012; and Khalaji *et al.*, 2014.

The most difficult part of the powder structure analysis is the *ab initio* solution of crystal structures from powder data. To this point, in collaboration with the department of Computer Systems at the Technical University in Prague, we modified the TREOR-based indexing algorithm written for multi-core or graphic cards systems (Šimeček *et al.*, 2015) and improved the algorithms for powder data in the program Superflip (Palatinus and Chapuis, 2007). The most promising experimental strategy for the *ab initio* solutions seems to be combination with electron diffraction, where one grain of a powder may act as a single crystal. Electron diffraction thus provides unit cell parameters or a raw estimation of the structure model. This approach was successfully applied on the mineral widenmannite (Plášil et al., 2014). This mineral resisted to be solved from powder diffraction data due to the mixture of heavy (Pb, U) and light (C, O) atoms. The light atoms could not be found *ab initio* from powder diffraction data. However, the solution was possible from electron diffraction data. The initial structure model was then refined against powder diffraction data.

2.3.7 Training activities

In order to educate students, spread knowledge about our methods and attract young scientists, we organized so-called Ad Hoc Workshops on JANA2006 with topics selected by the users through the web page http://jana.fzu.cz. In the period 2010-2014, 250 people from many countries visited 23 such workshops. Apart from these events, we were invited to external workshops about JANA2006, e.g. four workshops at the Shanghai Institute of Ceramics (tot. of 200 participants), three crystallographic schools at La Valérane- Carqueiranne (France), Uberlandia (Brazil) and Bayreuth (Germany) (tot. of 140 participants), and many others. In summary, more than 1100 people visited JANA2006 workshops in the period 2010-2014, with clear impact to the visibility of our methods and citations of our programs. As a part of our training activities, we wrote JANA2006 Cookbook cumulating worked examples from all workshops. This book of 500 pages is available in the JANA web page.

2.4 Summary

As a first team in the world, we were able to utilize dynamical refinement method which allows us to refine crystal structures from electron diffraction tomography data with accuracy approaching that of single crystal x-ray diffraction. We mastered the related experimental methods, established the laboratory of electron diffraction and implemented electron diffraction tomography combined with precession electron diffraction as a tool for structure determination of micro- and nanocrystals.

We developed an original method to analyse magnetic structures, which is based on the magnetic space and superspace groups. The method has distinct advantages over the so far used method of representation analysis. Moreover, our implementation offered unique possibilities, e.g. to refine incommensurate magnetic structures together with incommensurate parent structures against combined data sets from various diffraction sources. Related research of magnetic ordering helped us to understand that the direction of magnetization and associated magnetic anisotropy in multicomponent systems depends on the spin-orbit coupling on magnetic atoms as well as on non-magnetic atoms; for nanostructures, there is additionally a complicated interrelation with the exchange field and the whole complex of phenomena strongly depends on the geometrical arrangement of the magnetic atoms.

Our experimental capabilities were considerably extended by the enhancement of the x-ray single crystal experiment and by mastering the powder diffraction method. Both laboratories are now well established, providing wide crystallographic services (several hundred structures per year and more than 150 papers in the field of chemical crystallography during 2010-2014). Good experimental background and original solution and refinement methods allowed us to start new research of uranyl sulphate minerals with considerable environmental importance, and we determined or redetermined fifteen new minerals of this group. First promising results were obtained with the combination of electron and powder diffraction as the most powerful solution procedure for complicated structures, which are not available as single crystals. We also continued our research of modulated structures, improved the related methods and solved several difficult structures.

All new methods and improvements were implemented or connected to our computing system JANA2006, which retained its position of the most general crystallographic system with steadily growing number of citations (1250 during 2010-2014). A review article about JANA2006 was cited more than 80 times in less than one year after its publication.

2.5 References

Bertaut, E.F. (1968). Acta Cryst., A**24**, 217-231

Belov, N.V., Neronova, N.N and Smirnova, T.S. (1957). Sov. Phys. Crystallogr., **2**, 311-322

Bornemann, S., Šipr, O., Mankovsky, S., Polesya, S., Staunton, J.B., Wurth, W., Ebert, H. and Minár, J. (2012). Physical Review B, **86**, 104436 (12 pages)

Botha, F., Böhm, S., Dvořáková, H., Eigner, V. and Lhoták, P. (2014). Org. Biomol. Chem., **12**, 5136 - 5143

Boullay, P., Palatinus, L. and Barrier, N. (2013). Inorg. Chem., **52**, 6127-6135

Burn, P.C, Deely, K.M. and Hayden, L.A. (2003). Canad. Mineral., **41**, 687-706

Campbell, B.J., Stokes, H.T., Tanner, D.E. and Hatch, D.M. (2006). J. Appl. Cryst., **39**, 607-614

David, R., Kabbour, H., Colis, S., Pautrat, A., Suard, E. and Mentre, O. (2013). Journal of Physical Chemistry, **117**, 18190-18198

Dušek, M., Petříček, V., Wunschel, M., Dinnebier, R.E. and van Smaalen, S. (2001). J. Appl. Cryst. **34**, 398-404

Gemmi, M. and Oleynikov, P. (2013). Z. Kristallogr., **228**, 51-58

Goian, V., Kamba, S., Pacherová, O., Drahokoupil, J., Palatinus, L., Dušek, M., Rohlíček, J., Savinov, M., Laufek, F., Schranz, W., Fuith, A., Kachlik, M., Máca, K., Shkabko, A., Sagarna, L., Weidenkaff A. and Belik, A.A. (2012). Phys. Rev. B, **86**, 054112

Havel, V., Švec, J., Wimmerová, M., Dušek, M., Pojarová, M. and Šindelář, V. (2011). Org. Lett., **13**, 4000-4003

Hybler, J. and Ďurovič, S. (2013). Acta Cryst., B**69**, 570–583

Hybler, J. (2014). Acta Cryst., B**70**, 963-972
Kampf, A.R., Plášil, J., Kasatkin, A.V. and Marty, J. (2014). Mineral. Mag., **78**, 639-649
Khalaji, A.D., Rohlíček, J., Machek, P., Das, D. (2014). J. Clust. Sci., **25**, 1425-1434
Kirakci, K., Fejfarová, K., Kučeráková, M. and Lang, K. (2014). Eur. J. Inorg. Chem, 2331 - 2336
Kirakci, K., Kubát, P., Dušek, M., Fejfarová, K., Šícha,V., Mosinger, J. and Lang, K. (2012). Eur. J. Inorg. Chem, 3107 - 3111
Kolb, U., Gorelik, T., Kübel, C., Otten, M.T. and Hubert D. (2007). Ultramicroscopy, **107**, 507-513
Kolb, U., Gorelik, T. and Otten, M. T. (2008). Ultramicroscopy, **108,** 763-772
Krivovichev, S.V. and Plášil, J. (2013). Mineralogical Association of Canada Short Course, **43**, 15-119
Ling, C.D., Schmid, S., Blanchard, P.E.R., Petříček, V., McIntyre, G.J., Sharma, N., Maljuk, A., Yaremchenko, A.A., Kharton, V.V., Gutmann, M. and Withers, R.L. (2013). JACS, **135**, 6477-6484
Lovelace, J., Simone, P.D., Petříček, V. and Borgstahl, G.E.O. (2013). Acta Cryst., D**69**, 1062-1072
Lukášek, J., Böhm, S., Dvořáková, H., Eigner, V. and Lhoták, P. (2014). Org. Lett., **16**, 5100 - 5103.
Ouni, S., Nouri, S., Rohlíček, J. and Ben Hassen, R. (2012). Journal of Solid State Chemistry, **192**, 132-138
Matulková, I., Cihelka, J., Fejfarová, K., Dušek, M., Pojarová, M., Vaněk, P., Kroupa, J., Šála, M., Krupková, R. and Němec, I. (2011). CrystEngComm **13**, 4131 - 4138.
Murshudov, G.N., Vagin, A.A. and Dodson, E.J. (1997). Acta Cryst., D**53**, 240-255
Palatinus, L. (2011). PETS – program for analysis of electron diffraction data. Institute of Physics of the AS CR, Prague, Czech Republic
Palatinus, L. and Chapuis, G. (2007). J. Appl. Cryst., **41,** 786–790
Palatinus, L., Klementová, M., Dřínek, V., Jarošová, M. and Petříček, V. (2011). Inorg. Chem., **50**, 3743–3751
Palatinus, L., Jacob, D., Cuvillier, P., Klementová, M., Sinkler, W. and Marks, L.D. (2013). Acta Cryst, A**69**, 171-188
Palatinus, L., Petříček, V. and Correa, C.A. (2015). Acta Cryst., A**71**, 235-244
Peeters, O.M., Vochten, R. and Blaton, N. (2008). Canad. Mineral., **46**, 173-182
Perez-Mato, J.M., Ribeiro, J.L., Petříček, V. and Aroyo, M.I. (2012). J.Phys.: Condens. Matter, **24,** 163201
Petříček, V. and Dušek, M. (2004). Z. Kristallogr. **219**, 692-700
Petříček, V., Dušek, M. and Palatinus, L. (2014). Z. Kristallogr., **229,** 345–352
Petříček, V., Fuksa, J. and Dušek, M. (2010). Acta Cryst., A**66**, 649–655
Plášil, J. (2014). J. Geosci., **59**, 99-114
Plášil, J., Dušek, M., Čejka, J. and Sejkora, J. (2014a). Mineral. Mag., **78**, 1249-1264
Plášil, J., Dušek, M., Novák, M., Čejka, J., Císařová, I. and Škoda, R. (2011a). Am. Mineral., **96**, 983-991
Plášil, J., Fejfarová, K., Škoda, R., Dušek, M., Marty, J. and Čejka, J. (2013a). Miner. Petrol., **107**, 211-219
Plášil, J., Fejfarová, K., Wallwork, K.S., Dušek, M., Škoda, R., Sejkora, J., Čejka, J., Veselovský, F., Hloušek, J., Meisser, N. and Brugger J. (2012a). Am. Mineral., **97**, 1796-1803
Plášil, J., Hauser, J., Petříček, V., Meisser, N., Mills, S.J., Škoda, R.. Fejfarová, K., Čejka, J., Sejkora, J., Hloušek, J., Johannet, J.M., Machovič, V. and Lapčák, L. (2012b). Mineral. Mag., **76**, 2837-2860
Plášil, J., Kampf, A.R., Kasatkin, A.V. and Marty J. (2014b). J. Geosci., **59,** 145-158
Plášil, J., Kampf, A.R., Kasatkin, A.V., Marty, J., Škoda, R., Silva, S. and Čejka, J. (2013b). Mineral. Mag., **77**, 2975-2988
Plášil, J., Mills, S.J., Fejfarová, K., Dušek, M., Novák, M., Škoda, R., Čejka, J. and Sejkora, J. (2011b). Canad. Mineral., **96**, 983-991
Plášil, J., Palatinus, L., Rohlíček, J., Houdková, L., Goliáš, V. and Škácha, P. (2014). Am. Mineral., **99**, 276-282.
Plášil, J., Veselovský, F., Hloušek, J., Škoda, R., Novák, M., Sejkora, J., Čejka, J., Škácha, P. and Kasatkin, A.V. (2014c). Am. Mineral., **99**, 625-632
Rohlíček, J., Ketata, I., Ben Ayed, T. and Ben Hassen, R. (2013). Journal of Molecular Structure, **1051**, 280-284,
Sládková, V., Cibulková, J., Eigner, V., Šturc, A., Kratochvíl, B. and Rohlíček, J. (2014). Crystal Growth & Design, **14**, 2931-2936
Sławiński, W., Przeniosło, R., Sosnowska, I. and Petříček, V. (2012). Acta Cryst., B**68**, 240-249
Šimeček, I., Rohlíček, J., Zahradnický, T. and Langr, D. (2015). J. Appl. Cryst., **48**, 166-170
Šipr, O., Bornemann, S., Ebert, H., Mankovsky, S., Vackář, J. and Minár, J. (2013). Physical Review B, **88**, 064411 (14 pages)
Šipr, O., Bornemann, S., Ebert, H. and Minár, J. (2014). J. Phys.: Condens. Matter, **26**, 196002 (12 pages)
Šipr, O., Bornemann, S., Minár, J. and Ebert, H. (2010). Physical Review B, **82**, 174414 (8 pages)
Šipr, O., Minár, J., Scherz, A., Wende, H. and Ebert, H. (2011). Physical Review B, **84**, 115102 (9 pages)
Šipr, O., Vackář, J., Vachhani, P.S., Ramamoorthy, R.K., Dalba, G., Bhatnagar, A.K. and Rocca, F. (2013). J. Phys.: Conf. Ser., **430**, 012128 (6 pages)
Švec, J., Dušek, M., Fejfarová, K., Štacko, P., Klán, P., Kaifer, A.E., Li, W., Hudečková, E. and Šindelář, V. (2011). Chem. Eur. J., **17**, 5605 - 5612
Welsch, S., Bodensteiner, M., Dušek, M., Sierka, M. and Scheer, M. (2010). Chem. Eur. J., **16**, 13041 - 1304

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Magnetics and Superconductors

During the years **2010-2014** we followed the historically successful lines of the experimental and theoretical research in the field of magnetic, magnetocaloric, thermal, electric and superconducting properties of novel intermetallic and oxide materials prepared under various morphologies. As nowadays the standard our research was significantly framed by awarded grants. These covered both the complex experimental research of magnetic systems, prepared either by us or by collaborating subjects, and the theoretical studies of the electronic structures of materials on a verge of metallic behaviour. Despite the fact that magnetism as a whole or its microscopic origin represents a common, but sometimes hidden meaning of our research, in sake of lucidity we structure the team-research into several sub-domains, where we describe concrete scientific topics.

The general focus of the **Electronic structure group** was on *materials with strong electronic correlation*s and on physical phenomena which make them unique both from the fundamental as well as the application point of view. The goal was to mathematically describe and understand the correlations related phenomena on the level of simplified models as well as to obtain quantitative results for specific materials. The basic tools represented the large scale computer simulations in the framework of dynamical mean-field (DMFT) and density functional theories. Integral part of the group was a **FIRM laboratory,** concentrated on both experimental and theoretical study of high frequency vortex dynamics.

The **Laboratory of magnetic oxides** focused its interest on fundamental research of *cobalt oxides* exhibiting spin state transitions, including materials prospective for *thermoelectric energy conversion,* and perovskite and spinel type *magnetic nanomaterials* targeted for medical and biological applications. The research methods of the laboratory comprised an advanced synthesis of the materials, their structural characterization, measurements and analysis of magnetic, electric and thermal properties. The team members have also developed and constructed several home-made apparatuses for transport measurements, including an equipment for the thermoelectric modules characterization.

The research of **High pressure laboratory** was focused both on experimental studies (magnetic, transport and magnetotransport properties) of ***intermetallic compounds at extreme conditions*** and the investigation of novel ***magnetocaloric materials*** and corresponding ***magnetocaloric effects***. The scope of the laboratory research included, among all, the design and construction of diamond anvil cell (DAC) for direct magnetization measurements under very high pressures.

The work of the **Electronic structure group** was focused on three general topics: spin-state transitions, strong spin-orbit coupling and crystal fields on rare earth ions.

The spin-state transition was investigated in materials of the $LaCoO_3$ family. In a series of DMFT calculations we were able to reproduce the thermally and doping induced spin-state transitions and explain their microscopic mechanism [1]. The example of the calculated density of states is shown in the Fig. 24-1. Simultaneously we have studied a much simplified model of spin-state transition materials – the two-band Hubbard model [2]. We have found that close to the transition the system, depending on its details, may become unstable towards long-range order (LRO). A particular type of LRO that can be described as a condensate of magnetic excitons has many peculiar and unexplored properties.

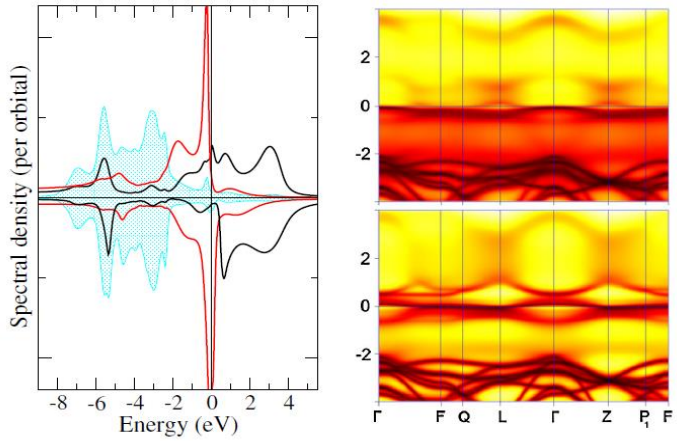


Fig. 24-1.*On the left, the spectral density of states of the magneticperovskite$La_{0.7}Sr_{0.3}CoO_3$: Co-3d t_{2g}(red), Co-3d e_g (black), O p (blue).Right, the same spectral density by symmetry directions in reciprocal space. The upper and lower panels in both cases correspond to two spin projections.*

Spin-orbit related phenomena have become very popular in the past ten years leading to a great interest in materials with 5d elements, iridium oxides in particular. We have participated in some of the first calculations that provided microscopic understanding of some of the physics of Na_2IrO_3 and Sr_2IrO_4 [3]. These studies have addressed two basic questions: How does spin-orbit coupling affect the topological properties of the band structures of the studied materials? To what extend are spin-orbit induced Mott insulators similar to cuprate high-temperature superconductors?

In most materials the 4f shells of rare-earth ions couple on weakly to their environment, which is thus essentially unaffected by their presence. This makes the rare-earth ions unique local probes as their optical or magnetic response carry information about the electronic structure of their surroundings and its changes with temperature or external fields. However, in order to extract this information one has to know to a great accuracy the coupling between the rare-earth ion and the rest of the crystal encoded in the so called crystal field. **Calculation of the crystal fields from first principles** has been a long standing problem. We have developed a method to calculate the crystal fields and demonstrated its accuracy and capabilities on series of diverse materials [4]. As the necessity to address new theoretical phenomena is mandatory conditioned by the development of **novel computational methods**, we must mention the development of three theoretical tools [5] that stand out in the past five years: (i) Wannier functions with Wien2k, (ii) Bethe-Salpeter formalism for linear response in DMFT and (iii) new measurement technique in quantum Monte-Carlo algorithm.

The research of the **Far-InfraRed Magnetospectroscopy** (FIRM) laboratory (see Fig 24-2), was concentrated on study of high frequency vortex dynamics in superconducting materials.

Fig.24-2*The FIRM laboratory*

The participation in the COST Action MP1201 enabled to study high quality NbN films. The terahertz thermal spectroscopy measurements [6] have been supplemented by a time-domain terahertz spectroscopy method in collaboration with the Terahertz Spectroscopy Group from our institute [7]. As an important result a full quantitative agreement between the experimental data, spanning broad ranges of temperature and frequency and the fundamental BCS-based microscopic theory, was reached without use of any fitting parameter. The experiments outlined, however, some contradictions in the state of art theory and thus motivated its improvements [8].

Literature 24 – Theory group and FIRM.

1. P. Augustinsky, V. Krapek, and J. Kunes, Phys. Rev. Lett. 110 (2013) 267204; V. Krapek et al., Phys. Rev. B 86 (2012) 195104; J. Kunes et al., Phys. Rev. Lett. 109 (2012) 117206.
2. J. Kunes and P. Augustinsky, arXiv:1405.1191; J. Kunes and P. Augustinsky, Phys. Rev. B 89 (2014) 115134; J. Kunes and V. Krapek, Phys. Rev. Lett. 106 (2011) 256401.
3. R. Arita et al., JPS Conf. Proc. 3 (2014) 013023; Li et al.,Sci. Rep. 3 (2013) 3073; R. Arita et al., Phys. Rev. Lett. 108 (2012) 086403.
4. P. Novak, J. Kunes, and K. Knizek, arXiv:1407.7669; P. Novak et al., J. Phys.: Condens. Matter 25 (2013) 446001; P. Novak, K. Knizek, and J. Kunes, Phys. Rev. B 87 (2013) 205139.
5. P. Augustinsky and J. Kunes, Comput. Phys. Commun. 184 (2013) 2119; J. Kunes, Phys. Rev. B 83 (2011) 085102; J. Kunes et al., Comput. Phys. Commun. 181 (2010) 1888.
6. R. Tesař, M. Šindler, K. Il'in, J. Koláček, M. Siegel, L. Skrbek, Phys. Rev. B 84, 132506 (2011)
7. M. Šindler, R. Tesař, J. Koláček, P. Szabó, P. Samuely, V. Hašková, C. Kadlec, F. Kadlec, P. Kužel,Superconductor Science and Technology 27 (2014) 055009
8. Pavel Lipavský, J. Bok, Jan Koláček, Physica C 492 (2013) 144-151

The research of **Laboratory of magnetic oxides** covered three fields: (i) thermoelectricity, (ii) physics of cobalt perovskites with spin state transitions and (iii) technology and magnetism of oxide magnetic nanomaterials. The field of **thermoelectricity**

comprised both the basic research focused on the optimization of the thermoelectric oxide based materials (aimed to high temperature applications)both the applied route exploring the possibility of the thermoelectric waste heat recovery from the exhaust gas of automobile heat engine. Here, due to the lack of commercial thermoelectric characterisation tools which are either unavailable or not trustworthy, we focused essentially on measurement automation and substantial thermoelectric metrology refinement in the evaluation of thermal, thermoelectric and electric power characteristics of newly developed materials and thermoelectric modules [1]. The detail of the measuring apparatus including thermography sensing surface temperature is shown in Fig. 24-3.

Fig. 24-3.*Automatedcharacterizationequipmentfortestingof thermoelectricmodulesandmaterials*.

As concerns the **cobalt perovskites with spin state transitions** the studies were directed to probe the magnetic, electric and thermal phenomena in the $LaCoO_3$ -type cobaltites and structurally related compounds with variable Co^{3+}/Co^{4+} valence. The interest in these systems was stimulated by a possibility of the octahedrally coordinated cobalt ions to attain different electronic configurations, characterized as the low, high or intermediate spin states. Such spin-state degree of freedom is at the root of very complex and often contradicting behaviors in dependence of temperature and actual composition. Numerous cobaltites were prepared and investigated by experimental and theoretical means, mainly those where lanthanum was substituted by magnetic rare earths. This research included both the single valence $LnCoO_3$ (Ln=Pr,Nd,Sm,Tb,Dy) and mixed valence $Ln_{1-x}Ca_xCoO_3$ (Ln=Pr, Nd) systems (see e. g. [2-4]).The attention was given to a peculiar metal-insulator (M-I) transition found for the first time in the calcium "half-doped" cobaltite $Pr_{0.5}Ca_{0.5}CoO_3$and, later on, to less doped systems like $(Pr_{1-y}Y_y)_{0.7}Ca_{0.3}CoO_3$. Our studies unveil that the transition is not due to a mere change in cobalt ions from the intermediate to the low- spin states, as previously speculated, but is associated with a significant electron transfer between Pr^{3+} and Co^{3+}/Co^{4+} sites. The Pr ions thus occur below T_{M-I} in a mixed Pr^{3+}/Pr^{4+} valence, and the significance of our work lies in an original method that evidences the Pr^{4+}states and quantifies their amount in rather simple and physically clear way [5-7]. The method is based on the observation of Schottky peak that governs specific heat in 1 K range and arises due to Zeeman splitting of the ground-state Kramers doublet of Pr^{4+}, while Pr^{3+} ions in singlet ground state do not contribute. The conclusions deduced from the specific heat measurements are supported by X-ray absorption spectroscopy [8] and band structure calculations, performed also in our department [9] managed to explain why, in the absence of magnetic ordering is observed splitting ion exchange Pr^{4+} [1]. The challenging issue appearing from the studies is the exchange splitting on Pr sites, clearly evident in the specific heat experiments, though

nomagnetic ordering is detected down to 2 K. Applying the dynamical mean-field model calculations, a new kind of order parameter which physics is related to the excitonic condensation has been suggested for $Pr_{0.5}Ca_{0.5}CoO_3$ and other systems in the proximity of spin-state transition [10].

As regards the **oxide magnetic nanomaterials,** major efforts were directed towards finding novel synthetic methods for magnetic nanoparticles and for modification of their surface by complex shells. At the same time, thorough characterizations were carried out addressing, foremost, magnetic and structural peculiarities of nano particles. Principal studies were focussed on monodisperse ferrite nanoparticles (Fig. 24-4) and nanocrystalline phases of ferromagnetic manganites $La_{1-x}Sr_xMnO_3$(Fig. 24-5), with respect to their use as labelling and contrast agents in biological research and heating agents in hyperthermia applications [11].

Following these aims, magnetic cores were synthesized either in a flux, by sol-gel methods, or via thermal decomposition of metalo-organic precursors, whereas elaborate fluorescent shells based on hybrid silica, gold nanolayers and biocompatible polymers were prepared for subsequent biological studies.

:

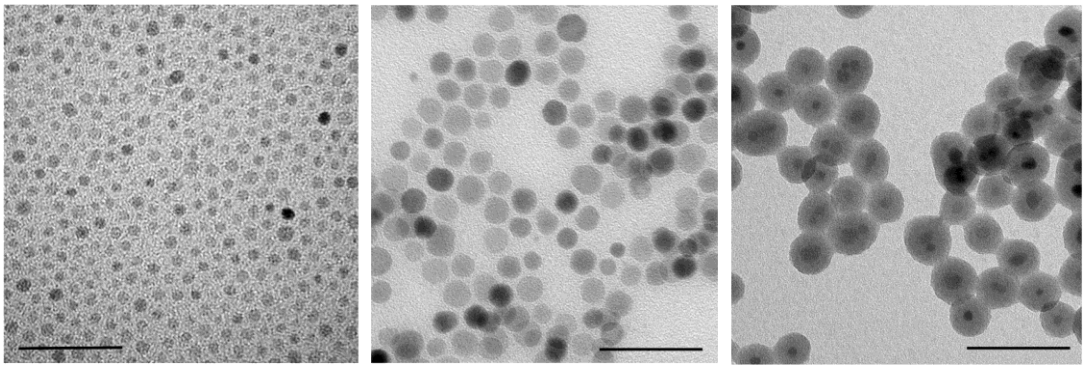


Fig. 24-4. *Examples of bare and silica coated cobalt-zinc ferrite nanoparticles possessing different size, the scale bar is 50 nm.*

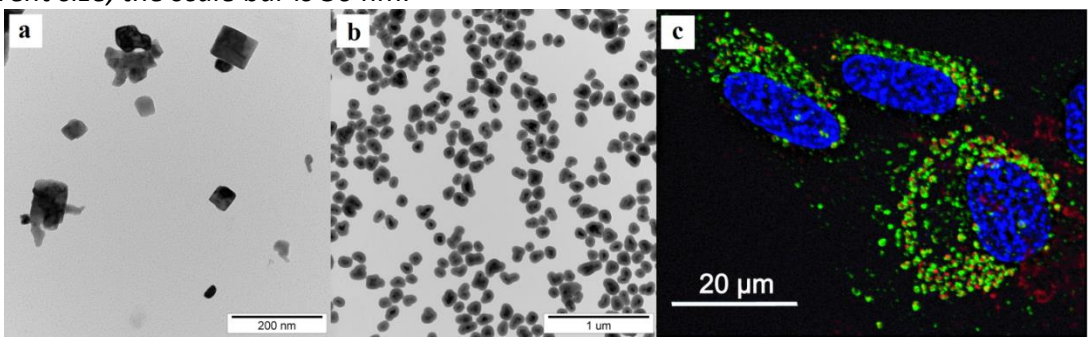


Fig. 24-5*. Magnetic nanoparticles $La_{1-x}Sr_xMnO_3$, as synthesised (a) and modified with bilayer fluorescent coating based on SiO_2 (b), which may be observed by fluorescent microscopy (c). It shows human desmocytes with nanoparticles (red) localised in lysosomes (green) outside cell nucleus (blue).*

New method for the synthesis of $La_{1-x}Sr_xMnO_3$ nanoparticles with impressive yield was developed using the growth of nanocrystals in the flux of $NaNO_2$ at temperature as low as ≈ 500 °C. An exciting advantage of this facile method is the morphology and size distribution of the resulting nanoparticles that do not require subsequent mechanical processing compared to the tedious preparation via sol-gel [12]. Importantly, complex structural and physical investigations performed on these products pointed to a decisive role of the surface. The uppermost surface layer is generally over-oxygenated since Mn ions at the surface of

manganite particles tend to complete the octahedral coordination [13]. This oxygen excess is responsible for a suppression of hole charge carrier doping close to surface, which diminishes the ferromagnetic double exchange interactions and is thus in the root of so-called magnetically dead layer in $La_{1-x}Sr_xMnO_3$ particles.

We addressed also the fundamental questions associated with Mn^{3+}/Mn^{4+} ordering in „half-doped" systems $Pr_{0.5}Ca_{0.5}MnO_3$ and $La_{0.5}Ca_{0.5}MnO_3$. By means of neutron diffraction and magnetic measurements, the particle size effects on the structure and low-temperature spin arrangement have been investigated [14]. The study shows that the Mn^{3+}/Mn^{4+} charge ordering and CE-type antiferromagnetic structure characteristic for bulk are completely suppressed when particle size is decreased down to 20 nm, and a ferromagnetic state is stabilized instead. The reason is not in a lower energy of the latter state, but in the hindering of displacive processes through which the charge ordering develops. Our results are of general importance for the perovskite manganites. In particular, the room temperature crystal structures in the particle cores are found not to deviate from the bulk material, disproving thus former speculations about enormous structural distortions due to surface effects. Another issue is the changing character of charge carriers in the particle shell, which is at the root of the size-dependent reduction of magnetization observed commonly in manganites possessing ferromagnetic state.

Literature24 – Laboratory of oxide materials.

1. J. Hejtmánek, K. Knížek, V. Švejda, P. Horna, M. Sikora, Journal of Electronic Materials 43, (2014) 3726
2. P. Novák, K. Knížek, M. Maryško, Z. Jirák and J. Kuneš, J. Phys.-Condens. Mat. 25 (2013) 4460001
3. K. Knížek, Z. Jirák, P. Novák, Clarina de la Cruz, Solid State Sciences 28 (2014) 26 - 30
4. Z. Jirák, J.Hejtmánek, K. Knížek, M. Maryško, P. Novák, E. Šantavá, T.Naito,H. Fujishiro, J. Phys.-Condens. Mat. 25 (2013) 216006.
5. J. Hejtmánek, E. Šantavá, K. Knížek, M. Maryško, and Z. Jirák, T. Naito, H. Sasaki, and H. Fujishiro, Phys. Rev. B 82 (2010) 165107.
6. J. Hejtmánek, Z. Jirák, O. Kaman, K. Knížek, E. Šantavá, K. Nitta, T. Naito, H. Fujishiro, Eur. Phys. J. B 86 (2013) 305.
7. K. Knížek, J. Hejtmánek, M. Maryško, P. Novák, E. Šantavá, Z. Jirák, T. Naito, H. Fujishiro, C. de la Cruz, Phys. Rev. B 88 (2013) 224412.
8. H. Fujishiro, T. Naito, S. Ogawa, N. Yoshida, K. Nitta, J. Hejtmánek, K. Knížek, and Z. Jirák, J. Phys. Soc. Jpn. 81 (2012) 064709.
9. K. Knížek, J. Hejtmánek, P. Novák, Z. Jirák, Phys. Rev. B 81 (2010) 155113.
10. J. Kunes and P. Augustinsky, Phys. Rev. B 90 (2014) 235140.

11. M. Kačenka, O. Kaman, J. Kotek , L. Falteisek, J. Černý, D. Jirák, V. Herynek, K. Zacharovová, Z. Berková, P. Jendelová, J. Kupčík, E. Pollert, P. Veverka, and I. Lukeš,.*Journal of Materials Chemistry* 21 (2011) 157
12. M. Kačenka, O. Kaman, Z. Jirák, M. Maryško, P. Žvátora, S. Vratislav and I. Lukeš, Journal of Applied Physics, 115, (2014) 17B525
13. P. Žvátora, M. Veverka, P. Veverka, K. Knížek, K. Závěta, E. Pollert, V. Král, G. Goglio, E. Duguet, and O. Kaman, Journal of Solid State Chemistry 204 (2013) 373.
14. Z. Jirák, E. Hadová, O. Kaman, K. Knížek, M. Maryško, E. Pollert, M. Dlouhá, and S. Vratislav, Phyical. Review B, 81, (2010) 024403.

Magnetic measurements at extreme conditions represent the essential characterizing tool of the **High pressure laboratory**. Therefore, the design of the new diamond anvil-type of pressure cell has been motivated by the need to extend available pressure range for magnetic measurements in order to investigate pressure induced phenomena in various types of novel magnetic materials. Diamond anvil cell (DAC) for direct magnetization measurements under very high pressures in the commercial SQUID magnetometer (Quantum Design) has been thus designed and built considering: (i) very limited available space (9 mm diameter), (ii) the need to support large forces (~ 10 kN) necessary for generating the high pressures and the (iii) specific geometric constrains needed to handle the background signal of the pressure cell [1]. The result of this engineering challenge is shown in Fig.24-6 (let us note that there is very few high pressure facilities in the world).

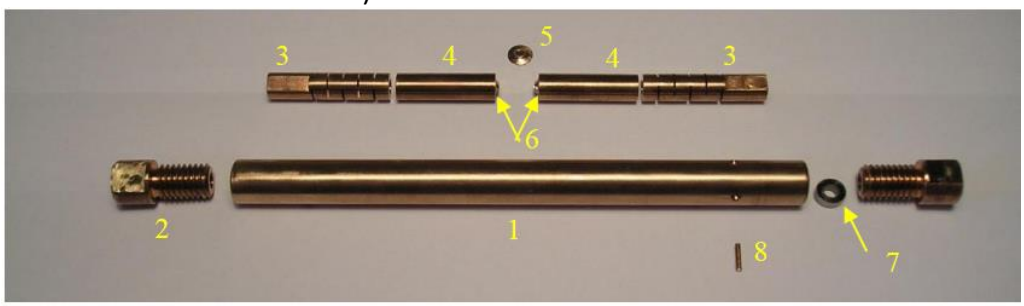


Fig.24-6.*DAC (Diamond Anvil Pressure Cell) for the SQUID magnetometer: 1) body of the cell, 2) bottom locking nut, 3) springs, 4) piston-guide for the diamond anvils, 5) gasket, 6) diamond anvils, 7) highly polished zirconia ceramic washer with a MoS lubricant, 8) position lock for the upper spring.*

In the field of **magnetocaloric materials** we followed a most recent trend where, due to their remarkable properties, Ni_2MnGa based Heusler alloys are often considered as promising prototypical materials for magnetic refrigeration. It has been previously shown that the magnetocaloric effect (MCE) can be substantially improved when the structural martensitic transformation and the Curie temperature of the austenitic phase are driven to coincidence by proper stoichiometric control. We have employed this coincidence by the synthesis off-stoichiometric variation of the alloy composition around the Mn-rich composition - $Ni_{50-x}Co_xMn_{30}Ga_{20}$. Here the saturation magnetization of austenite is strongly enhanced by Co with respect to the martensitic one (contrary to the Co-free alloys) and thus MCE turns from direct into inverse, i.e. a cooling is induced by a putting of the alloy into

external magnetic field and vice versa. By varying the composition, it is possible to tune the critical temperatures of martensitic transitions and the saturation magnetization jumps accompanied structural transitions. The remarkable values of the magnetic properties related to MCE, i.e., the high saturation magnetization jumps, the strong field dependence of the transformation temperature, $dT_{A,M}/dH$, were discovered determined and presented, together with high positive values of the isothermal magnetic entropy change, ΔS. This possibility to switch the direct MCE into the inverse one just by off-stoichiometric variation of composition of refrigerants gives new application ideas and opens new ways of a design of refrigeration devices [2–6].

Literature – 24 – Laboratory of high pressures.

1. J. Kamarád, J. Kaštil and Z. Arnold, Rev. Sci. Instrum. 83 (2012) 083902
2. S. Fabbrici, J. Kamarád, Z. Arnold, F. Casoli, A.Paoluzi, F.Bolzoni, M.Solzi, G.Porcari, F.Albertini, ActaMaterialia, 59, (2011) 412.
3. G. Porcari, S. Fabbrici, C. Pernechele, F. Albertini, M. Buzzi, J. Kamarad, Z. Arnold, and M. Solzi, Phys. Rev. B 85 (2012) 024414
4. J. Kaštil, J. Kamarád, K. Knížek, Z. Arnold, P. Javorský, J. Alloys and Comp.565(2013) 134
5. J. Kamarád, F. Albertini, Z. Arnold, S. Fabbrici, J. Kaštil , ActaMaterialia77(2014) 60–67
6. S.Fabbrici , G.Porcari , F.Cugini, M.Solzi, J.Kamarad , Z. Arnold , R.Cabassi and F.Albertini, *Entropy 16*(2014)2204

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Thin Films and Nanostructures

The origins of the **Department of Thin Films & Nanostructures** (**TF&N**) date back to the pioneering research of Jan Tauc devoted to amorphous semiconductors. The department is recognized as one of the pioneering labs in the field of amorphous and nanocrystalline hydrogenated silicon thin films, as evidenced by the invited Mott lecture by Jan Kočka, the former department head (until 2014). This highly prestigious plenary lecture was delivered at the 24th Int. Conference on Amorphous and Nanocrystalline Semiconductors [1].

In the last decade, the department expanded considerably both in size and research topics. The number of researchers has increased mainly because we have always tried to involve students. Some of these young researchers became new project leaders. Correspondingly, the research topics expanded to include silicon- and carbon-based nanostructures, molecular structures at surfaces or interfaces and 2D materials (graphene). We study physical properties of these materials using microscopic techniques, mostly scanning probe methods (SPM) with resolution down to the atomic scale. Bigger objects of study are silicon and diamond nanocrystals (~ 1 – 10 nm). The "largest" objects of study are silicon nanowires (~10 nm wide and ~ μm long) and thin (≤ μm) films. We are also involved in development of new imaging SPM techniques, e.g. simultaneous atomic force microscopy (AFM) and scanning tunnelling microscopy (STM), QPlus AFM or Kelvin probe force microscopy (KPFM). The experiments strongly benefit from activities of the theoreticians in the department, who are using and developing density functional theory (DFT), simulations of molecular transport phenomena etc.

TF&N consists of 5 groups centred around leading senior scientists:

1. **Nanosurf Lab** (group of Pavel Jelínek)
2. **Molecular Transport group** (group of Héctor Vázquez)
3. **Laboratory of Functional Nano-Interfaces** (group of Bohuslav Rezek)
4. **Nanocrystalline Silicon for Nanophotonics** (group of Ivan Pelant)
5. **Silicon Thin Films and Nanocharacterization** (group of Jan Kočka and Antonín Fejfar)

The description of the research activities and achievements of each of the groups is described below. The groups are ordered according to increasing size of the experimental objects. The description also progresses from fundamental towards application oriented research, revisiting thin films and their present role in the end.

1. Nanosurf Lab (http://nanosurf.fzu.cz) focuses on chemical, mechanical and transport properties of nanostructures at the atomic scale by both experimental and theoretical methods.

High-resolution AFM/STM images with functionalized tips: experiment and theory

High-resolution scanning probe images with functionalized tips belong to most significant advances in the field of SPM, but the detailed imaging mechanism was missing. To address this problem, we developed [2],[3] an efficient numerical model that for the first time clarifies main features of high-resolution scanning STM and AFM images measured with functionalized tips. We obtained perfect match between experiment and simulation, revealing that not all sharp edges in the images can be attributed to real chemical bonds. In particular, we demonstrated that the high-resolution images recently published by Zhang et al. in Science [4] were incorrectly attributed to the hydrogen bridge bonds but should be explained by probe particle relaxation driven by the potential energy landscape.

Very recently a new high-resolution imaging technique employing inelastic electron tunneling spectroscopy (IETS) acquired with STM has been introduced [5]. However an explanation of the imaging mechanism has been missing. We provided a detailed description of the IETS-STM imaging mechanism. Our numerical model provided simulated STM-IETS images in excellent agreement with the original experimental data. Thus we have shown that the mechanism is related to a variation of the frustrated translational mode of CO molecule placed at the tip apex, which reacts sensitively to the changes of a local curvature of the surface potential. The sharp sub-molecular contrast is closely related to a bending of a CO-probe in the repulsive regime.

This puts the IETS-STM imaging mechanism on common ground with already established high-resolution atomic force microscopy (AFM) and scanning tunneling microscopy (STM) mechanisms.

In addition, we proposed a novel route towards real-space imaging of submolecular charge distribution. We showed for the first time the effect of the electrostatic forces, originating from intramolecular charge transfer, has significant influence on the high-resolution AFM/STM/IETS images. We demonstrated the importance of the electrostatic interactions on the high-resolution contrast by achieving an excellent agreement between the experimental and simulated IETS-STM images of Cobalt-Phtalocyanine molecule deposited on Ag(110) surface [2]. We believe that this observation opens new possibilities for analysis of the intramolecular charge transfer in single molecules in real space. Namely it may be useful for estimating local electrostatic field or charge from AFM/STM or IETS-STM measurements with possibly better spatial resolution than in Kelvin probe force microscopy (KPFM) experiments.

2D materials: Doping of epitaxial graphene

We proposed a novel way [6] to achieve high-quality substitutional nitrogen and boron (co)doping of epitaxial graphene grown on silicon carbide. Graphene doping, and specifically doping with B and N, is generally a very hot topic of fundamental interest and with large potential applications (e.g. in electronics, sensing or even biochemistry). Our work brings following advances in the field (i) precise control of B,N doping on atomic scale; (ii) deeper understanding of scanning probe imaging and charge transport through N-dopant; (iii) new information about the nitrogen doping process by means of ion implantation; and (iv) B,N co-doping of epitaxial graphene grown on SiC surface for the first time. The precise control of the N doping concentration was achieved by changing the flux density and duration of the ion irradiation. For the B doping control, the crucial factor is the amount of deposited B on the sample surface before graphene growth. Our two-step methodology for B,N co-doping might open new perspectives in the graphene/SiC based electronics. By using a suitable masking technique for the doping process, control of dopant distribution can be achieved. In principle, a nanoscopic p-n junction device consisting of only single B and N dopants in graphene could be manufactured.

2D materials: Hydrogen adsorption on graphene

We developed a new theory of the origin of polyaromatic hydrocarbon molecules in the universe. According to the new theory, these molecules are formed by hydrogen etching of the graphitic surface of the stardust particles. These organic molecules, composed of carbon and hydrogen with two or more benzene rings, are key ingredients to understanding the origin of life in the universe, but their origin is still unclear. Current theories assume bottom-up chemical processes, where small molecules merge into larger units by mutual collisions. However, this cannot satisfactorily explain the large amount of these hydrocarbons in interstellar space in the vicinity of some stars observed by large radio telescopes.

As already happened in science many times, experimental observations in one discipline - in this case the physics of surfaces - can bring a whole new findings in a seemingly unrelated field like astronomy. The new theory of the origin of polyaromatic hydrocarbons was originated by experiments carried out using STM at Nanosurf Lab, which studied interaction of atomic hydrogen with the graphene grown on silicon carbide in conditions similar to those in the interstellar medium (i. e. ultra high vacuum and high temperature). Observation of the graphene surface after being exposed to a flux of atomic hydrogen at temperatures about 800 °C revealed significant changes of graphene layer accompanied by formation of graphene flakes passivated by hydrogen. These graphene flakes can be considered seeds of polyaromatic hydrocarbons. Based on these and other experimental observations, further supported by theoretical calculations performed in the Nanosurf Lab showing the decomposition of graphene with hydrogen at high temperatures, we proposed a new theory of the formation of polyaromatic hydrocarbons in interstellar space [7].

Single atom chemical identification and beyond

We have proved new possibility of the chemical identification of individual atoms in nanostructures and semiconductor surfaces by combined AFM measurements and DFT modeling [8]. The method extends our previous work [9]. We showed that combination of the measured and calculated short-range forces allows the identification of not only individual chemical species but also different chemical states of atoms determined by their hybridization. This aspect opens new possibilities to identify chemically active surface sites, where a chemical reaction can happen. We demonstrate the potential of the method by resolving chemical structure of 1D metallic chains grown on a semiconductor surface. We have investigated chemical identification of individual atoms in mixed In–Sn chains, grown on a Si(100)-(2 × 1) surface, by means of room temperature dynamic noncontact AFM measurements and DFT calculations. On the basis of this method, we have revealed incorporation of silicon atoms from the substrate into the metal chains, which has been ignored until now, but it has an important role in the formation and stability of 1D chains.

Fundamental relation between force and current in SPM

We established a fundamental correlation between the tunneling current and the chemical bond [10],[11],[12]. Both tunneling current and the chemical force between two bodies are driven by wave-function overlap between their outermost atoms. We demonstrated that the quantum degeneracy determines the fundamental relationship between the conductance (G) and the chemical force (F) acting between two bodies in atomic-sized contacts. Namely, depending on the contact conditions, the following proportionalities hold, either $G \sim F$ or $G \sim F^2$. We demonstrate that the presence of the latter one, $G \sim F^2$, is driven by the quantum degeneracy between frontier electronic states. To prove the presence of this quantum degeneracy phenomenon we have deliberately chosen the Si(111)-7x7 surface, which possesses strongly localized dangling bond states. By means of a careful combination of precise simultaneous AFM/STM measurements with DFT simulations, we showed that the $G \sim F^2$ relation holds in point contacts formed between scanning probe and silicon adatoms on the Si(111)-7x7 surface. The experimental part of this work was performed at Osaka University and IBM Almaden.

Development of simultaneous AFM/STM technique & installation of LT-SPM

Simultaneous Scanning Tunneling and frequency modulated dynamic Atomic Force Microscopy measurements with a qPlus setup is very progressive technique, which becomes frequently used in many laboratories. The qPlus sensor is a purely electrical sensor based on a quartz tuning fork developed by F. J. Giessibl. Despite its relatively simple design, it hides certain pitfalls. If stray capacitance between cables detecting the tunneling current and the force signal is present, a cross-talk of the tunneling current into the force signal can easily occur. Indeed many instrumental setups suffer by this problem, which makes the simultaneous AFM/STM measurements unreliable. We investigated in detail the origin and general features of the capacitive cross-talk in collaboration with Omicron Ltd. Based on our analysis, we modified an experimental setup of our VT-AFM/STM machine, which significantly improved the level of decoupling between the tunneling current and the deflection signal [13].

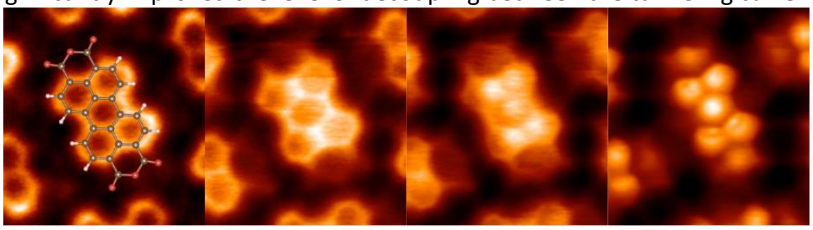


Fig. 1. Variation of high-resolution contrast of PTCDA molecule on Ag(111) surface with Xe-tip for varying tip-sample distance.

Installation of LT-AFM/STM machine equipped with magnetic field up to 3 Tesla in January 2014 opened new horizons in activities of the Nanosurf Lab. Early after the installation, we were able to achieve unprecedented high-resolution images of PTCDA molecule on Ag(111) surface with functionalized Xe-tip (see Fig.1). The capability to perform the high-resolution images ranked the Nanosurf Lab among the very few laboratories in the world where this kind of measurements can be achieved.

We have also done simultaneous AFM/STM measurements with a single PTCDA molecule lifted up from surface at different magnetic fields. The controlled lifting process allowed transits from strongly to weakly coupled Kondo regime by mechanical gating of the molecule. We also observed splitting of the Kondo peak in the weakly coupled regime when the magnetic field was applied (see Fig. 2).

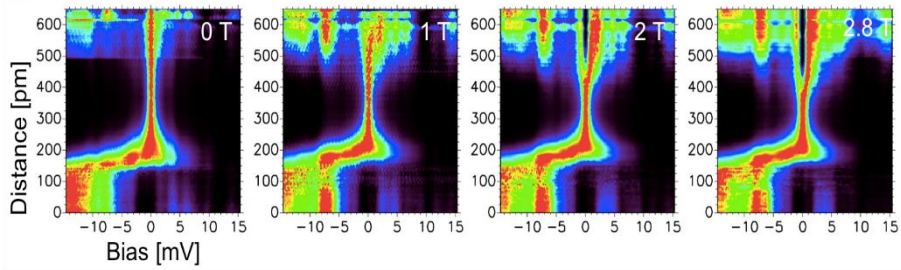


Fig. 2. Conductance variation during lifting up of a single PTCDA molecule at different magnetic fields. Splitting of the Kondo resonance is visible in far distance.

Further development of local orbital DFT Fireball code

Among other developments, we implemented molecular dynamics with electron transitions into a home-built local orbital DFT Fireball code in collaboration with colleagues from Spain and USA. The development of computationally efficient first-principles non-adiabatic molecular-dynamics techniques is the next step in computational physics [14]. In addition, we derived equation that allows the direct on-the-fly calculation of the non-adiabatic coupling vectors in a practical way [15]. This tool opens new possibilities for non-adiabatic MD simulations of large complex systems.

2. Molecular Transport Group (http:/www.fzu.cz/~vazquez/) was established in Oct. 2013 around Héctor Vázquez, awarded Purkyně fellowship. Main objective of the group is a theoretical description of electronic quantum transport processes at molecular nanojunctions: in particular metal-molecule linkers and tuning of

conductance by molecular structure design. This follows and extends the previous Vázquez's high-impact publications from abroad [16][17]. The group's main theoretical tools are first-principles methods based on Density-Functional Theory (DFT) and Non-Equilibrium Green's Functions (NEGF).

At molecular nanojunctions, the structure of the molecule and the metal-molecule interface strongly affects conductance, yet cannot be determined in experiment, and standard DFT-NEGF calculations are computationally costly. We have developed an approximate method for the molecular conductance calculations with a small computational cost and used it to for thousands of junction structures obtained from a molecular dynamics simulation, yielding the molecular conductance during junction evolution (see Fig. 3a).

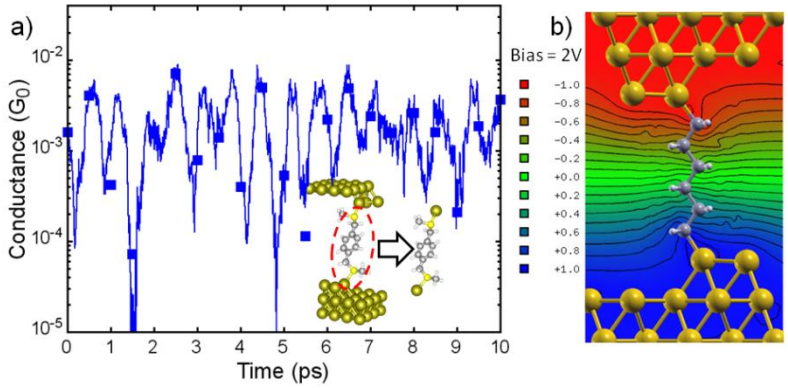


Figure 3(a) Molecular conductance during junction evolution (squares: exact; line: approximated), (b) Calculated self-consistent potential drop across a molecule with Au-C links for an applied bias of 2V.

Elastic and inelastic transport in alkanes with highly-conducting Au-C links

Molecular linker groups are necessary for the formation of stable and reproducible metal-molecule contacts in single molecule transport. Highly-conducting Au-C links between the tip and the molecular backbone result in a conductance much higher than with any other termination. The elastic and inelastic conduction properties of Au-C links were investigated by DFT-NEGF calculations [18]. The potential across an alkane junction was calculated self-consistently for an applied bias, providing a picture of the intramolecular potential drop (see Fig. 3b). Inelastic Electron Tunneling Spectroscopy (IETS) calculations were carried out for the different binding scenarios proposed for the formation of Au-C bonds, which is not yet well understood. The calculated vibrational modes in each scenario chemically characterize the metal-molecule junction, providing an unambiguous theoretical identification of different interface bonds.

3. Functional Nano-Interfaces (http://www.fzu.cz/~rezek/) laboratory has been established by B. Rezek, the previous Purkyně Fellow (2006-11). The Laboratory has a long-term focus on the research of semiconductor materials and physical phenomena in two, entangled directions: opto-electronics and bio-electronics. The research is devoted mainly to diamond, silicon, organic dyes, and proteins, in particular at their junctions and interfaces. Physical and chemical parameters are employed to merge these materials in a controlled way (physisorption or chemisorption, spatial localization, molecular conformations). Functionality (such as charge transport and transfer) is characterized with view to target applications in electronics, energy conversion, medicine, environment, and security.

Nanocrystalline diamond field-effect transistors or impedance sensors

By using selective nucleation and/or surface plasma treatment of nanocrystalline diamond films (methods developed with the group of Dr. Kromka) we prepared electrically conductive nanocrystalline **diamond microstructures that are fully operational as field-effect transistors** (FET). The transistor gate was insulated only by hydrogen atoms (no oxide) and it was controlled by a Schottky contact (aluminum) or by electrolyte [19]. We used these FETs as local amplifiers to characterize electronic effects at the diamond-protein-cell interface [20]. We showed that protein adsorption from cell medium with fetal bovine serum (FBS) leads to a characteristic 45 ± 10 mV shift of the FET transfer characteristics. This shift could not be attributed to the electrostatic field-effect as it had an opposite sign. We attributed this shift to a thin (< 10 nm) layer of proteins on the diamond gate (observed by AFM). We proposed a model where proteins replace ions adsorbed on H-terminated diamond gate, which modifies transfer doping of diamond. By characterizing FETs with various nanocrystal size (30 - 350 nm) and thickness (100 – 400 nm), we showed that the FET function and sensitivity is controlled by the H-terminated surface of diamond nanocrystals (i. e. even 30 nm nanocrystals function as single-crystal diamond) and grain boundaries are not detrimental [21]. Using Hall effect (measured in the group of Dr. Mares) we confirmed that the grain boundaries reduce only the carrier mobility in the FET channel, while carrier concentration remains as high as in the single-crystal diamond.

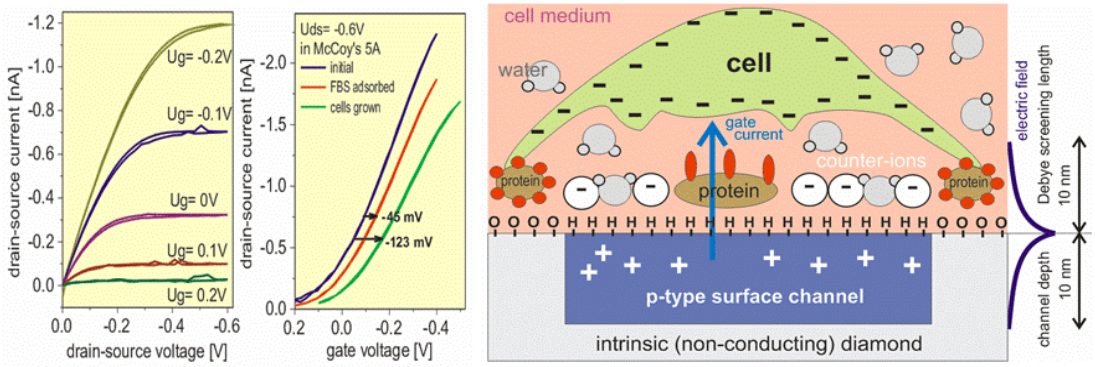


Fig. 4: Operational and transfer characteristics of bio-FET based on nanocrystalline diamond thin films, showing sensitivity of the gate interface to biological environment (protein and cell adsorption). The scheme shows microscopic model of electronic effects at the diamond-protein-cell interface.

Similarly to the diamond bio-FET we collaborated on the research of **nanocrystalline diamond chemical sensors using impedance** effects. The impedance elements coated by diamond were developed in Kromka's group. By impedance analysis we found that these sensors with H-terminated surface are able to resolve physisorbed molecules of Tröger's base (provided by Inst. of Chemical Technology) having pyrrole anchor groups, a foundation for electronically detected molecular tweezers. Oxidized diamond did not show such functionality. We proposed mechanism based on replacement of surface ions by Tröger's base, in similarity to proteins effects [22]. In addition, similar sensors have been used in Kromka's group for detection of phosgene, where they built upon the knowledge obtained in this study. The impedance sensing was also employed for real-time monitoring of cells and for active nanocrystalline diamond membranes in perfusion cell reactors (fabricated in collaboration with INESC-MN, Portugal).

We also continued our research of the interface between diamond and polypyrrole (PPy) from the optoelectronic point of view. Previously we observed efficient dissociation of excitons at PPy diamond interface. Recently we resolved another effect, where a thin, electrochemically synthesized **PPy film on nanocrystalline diamond (NCD) enabled extraction of photo-generated charge** carriers from as much as 200 nm depth of NCD films [23]. This effect was deduced from a change of decay kinetics (stretched exponential to power law) in time-resolved photoluminescence (PL) spectra at nanosecond scale. For the PL experiments we used expertise and facilities at Faculty of Mathematics and Physics, Charles University. The effect was not achieved by using common immersion oil or simply physisorbed PPy from solution. The covalent diamond-PPy bond thus plays a fundamental role in this effect.

For **recognition of bonding (physisorption or chemisorption) between diamond and organic molecules**, we previously developed a method combining molecular nanoshaving in AFM with surface work function measurement by Kelvin probe force microscopy (KPFM) as XPS was not conclusive in this all-carbon systems. Recently we have developed a novel method using scanning electron microscopy (SEM). When hydrogen or oxygen groups on original diamond surface are changed by chemical reaction, related electron affinity changes were reflected in a change of secondary electron emission. By using boron doped diamond (from Hasselt University, Belgium) we showed that PPy can be synthesized on both oxygen and hydrogen terminated surface, but covalent bond is created only on H-terminated diamond [24] where, surprisingly, the electron emission was increased. We proposed a new model that included also sub-surface band bending. With AIST (Japan), we found that this "side-effect" could be exploited for more efficient electron emission in electronics, power switching, and chemistry.

When we studied **work function of diamond nanoparticles** (DNPs) by using KPFM to resolve their surface termination we found that their potential is not fixed by material properties. Instead, it depends on their size (or size of their aggregates) up to at least 50 nm and the material of substrate they are deposited on [25]. The potentials of the same DNPs differ by up to 0.4 V. This phenomenon was independently confirmed by SEM. Moreover, by comparing potential-size trends we were able to resolve minute differences (< 50 mV) due to different surface terminations of DNPs (hydrogen, oxygen, graphite, all prepared in CEA Saclay). The same effect was observed also on metal (Au) nanoparticles. This seems to be a general phenomenon which has an impact on all nanoparticle properties (electron emission, light emission, chemistry, etc.). By applying voltage in AFM we confirmed that both diamond and gold nanoparticles can indeed retain and even reverse charge vs underlying substrate [26]. The charging was partially influenced by DNPs surface termination, an effect of which was

attributed to modified electronic states and conductivity of DNPs. The charging effects were further corroborated by electrostatic charge storage in ultrathin (70 nm) nano-crystalline diamond films [25].

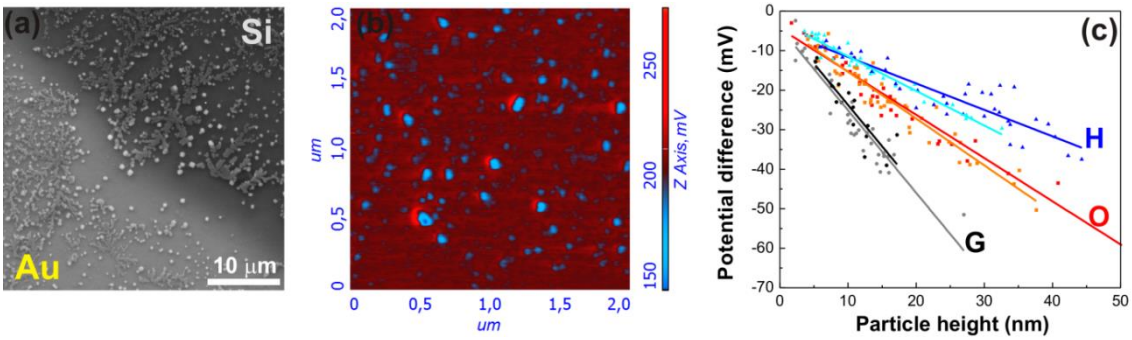


Fig. 6: (a) SEM image of diamond nanoparticle (DNP) aggregates showing different secondary electron emission on Au and Si substrates. (b) Typical KPFM image of oxidized DNPs on Si. (c) Extracted potential-size dependence of differently modified DNPs on Au and Si substrates.

4. Nanocrystalline Silicon for Nanophotonics **(NanoSilicon)** is a group of I. Pelant focusing on optoelectronic and quantum properties of silicon nanocrystals and other photonics structures.

Silicon in its bulk form is a very poor light emitter due to its indirect bandgap, therefore it is finding its way to light emitting applications only very slowly. This problem can be partly alleviated by using silicon in the form of silicon nanocrystals (SiNCs), which typically emit light much better in term of photoluminescence (PL) efficiency, but still with slow radiative rates (10^{-4} s). Improving this drawback, which goes hand in hand with better understanding of the physics underlying the light emission process, could lead to the possibility of integrating a silicon-based laser onto microelectronics circuits and thus lowering the excessive heat losses of current computers. A second application niche for light-emitting SiNCs opens up in luminescent bio-labels as a result of their low toxicity, making them an interesting and viable alternative to toxic cadmium-based direct-bandgap nanoparticles (CdS, CdSe, etc.).

Silicon nanocrystals for optoelectronic applications

The first project our group has undertaken in the last five years is actually disproving the general validity of the popular cliché of "the indirect bandgap of silicon" used in numerous textbooks and journal articles. We showed, both theoretically and experimentally, that properly passivated strain-engineered SiNCs *are a direct-bandgap material* with light-emission properties fully comparable with those of other direct-bandgap semiconductors. First of all, the concept of bandstructure for a SiNC, which consists of only a few hundreds of atoms at most and thus being very far from the infinite crystal, was revisited [27]. In this way we confirmed that the band structure of SiNC with sizes down to about 2 nm (see Fig. 7b on the left) is very close to that of bulk silicon. Then, as sketched in Fig. 7a, we proposed an idea [28] to switch the nature of the indirect and direct bandgap in Si, using a cooperation of quantum confinement and tensile strain. Our subsequent rigorous DFT calculations (done together with the Nanosurf group) backed-up this concept by showing that tensile strain does lead to the upshift of the corresponding Δ_1 valence-band minimum and simultaneously it creates a dip and lowers the Γ_{15} valence-band maximum [28]. We identified an agent enabling such bandstructure engineering in experiments by showing that a surface capping by $-CH_3$ methyl groups causes an elongation of the lattice constant and thus tensile strain [28]. Experimentally, methyl-capped SiNCs exhibit light-emission properties parallel to those of other direct-bandgap materials [29], most notably short radiative lifetimes (10 ns), see Fig. 7c. This work was chosen by the editors for the journal's cover and K. Kůsová was awarded the L'Oreal-UNESCO for Women in Science scholarship.

A second line of research was focused on a further study of the behaviour of oxidized indirect-bandgap SiNCs prepared in our laboratory. Here, the most interesting results are connected with the measurements of *ultrafast PL*. Our complex study of blue PL of these SiNCs combining picosecond temporal resolution and cryogenic temperatures [30], see Fig. 7d, demonstrates that the detected ultrafast PL signal comes from the core of the NC, arising from quasi-direct radiative recombination. This is an important result, because the link between blue PL and SiNCs is disputed in some publications. Also, by adapting a measurement method of optical gain, a prerequisite to lasing, to the ultrafast temporal regime, we revealed the existence of room-temperature transient (lifetime < 1 ps) optical gain in quasi-direct transitions in SiNCs at ~ 590 nm (hundreds of reciprocal centimetres) [31]. Some of the ultrafast measurements were performed at IPCMS, Strasbourg, France, sample preparation and data interpretation were carried out at our department.

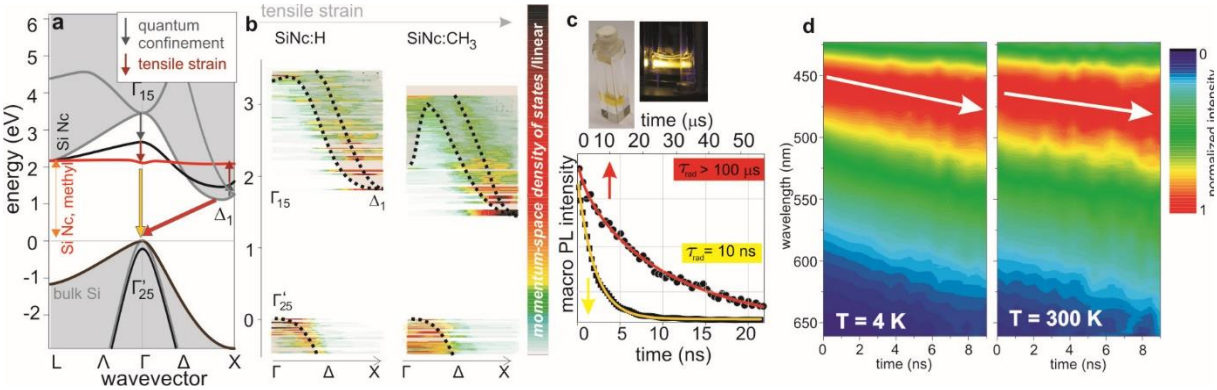


Fig. 7: (a) The concept of direct-bandgap silicon. (b) The calculation of the band structure of ideal, „bulk-silicon-like" SiNCs (on the left) and bandgap-engineered SiNCs (on the right). (c) Experimental realization of a colloidal dispersion of direct-bandgap SiNCs (photos under ambient light and under laser illumination) and the corresponding change in radiative lifetimes from indirect- (red) to direct-bandgap (yellow) transitions. (d) Blue luminescence of oxide-passivated SiNCs with picosecond temporal resolution at cryogenic and room temperatures.

Photonic structures for enhancing light extraction

A second project concentrates on the utilization of photonic crystals for enhancing light extraction. High refractive index of a matrix can significantly reduce the amount of light emanating from the sample due to internal total reflection. This drawback can be overcome with the aid of photonic crystal slabs, periodically patterned structures of tiny columns/holes of finite height. We verified the effect of photonic crystal slabs in the case of SiNCs embedded in a polished silica plate [32]. The sample was prepared by Si^+-ion implantation and annealing (ANU Canberra), resulting in a SiNC-rich luminescent layer, and subsequent periodical patterning using electron beam lithography and reactive ion etching. SEM image of the resulting structure is shown in the inset of Fig. 8a, PL spectra measured along the Γ–X direction are displayed as a function of the detection angle θ in Fig. 8a. The strongly enhanced directionality of PL can be clearly seen. In the normal direction (θ = 0), *8-fold enhanced extraction of SiNCs PL* compared to the reference bare planar layer was achieved (Fig. 8b).

We also succeeded in making unique **diamond photonic crystals** (with Kromka and Rezek groups) which provided up to 6-fold amplification of visible PL from nanocrystalline diamond (from embedded sp2 and color centers) in a broad spectral range [33]. The photonic structures were created by using careful calculations of required dimensions, precise electron beam lithography, and reactive ion etching.

Last but not least, we also assessed applicability of our SiNCs as fluorescent biological label. Our comparative study [34] thoroughly evaluates cytotoxicity and spectral suitability of PL of commercially available nanodiamond (ND) and oxidized SiNCs prepared in our department. Both types of nanoparticles were introduced into SAOS-2 human osteosarcoma cells and their PL was investigated using confocal fluorescence microscopy.

Fig. 8c, showing an example of confocal PL images in different depths (1, 2, 3) of live SAOS-2 cells incubated with SiNCs for 2 hours, clearly demonstrates that (red) PL of SiNCs located inside the cell can be easily distinguished from the cell autofluorescence background (green). The results of lactase dehydrogenase test of cytotoxicity after 48 hours, which indicates the level of cell damage, are shown in Fig. 8d. Significant difference in viability between SiNCs and ND incubated cells can be seen; higher cytotoxicity of ND is evident, which rather limits the use of ND for *in vitro* studies, while *SiNCs in usual concentrations do not cause any harm.* Bio-imaging and cytotoxicity tests were carried out at the Faculty of Medicine of Charles University in Prague.

During the period 2010–2014, we also devoted our time to preparing our textbook [35] for publication. The book had appeared originally in Czech in two volumes (2006, 2010) in the Academia Praha publishing house. During 2010–2011, we translated the text to English for a single-volume edition at Oxford University Press (2012). Besides, in the evaluation period we published two invited chapters in books [36],[37] and one invited review article [38].

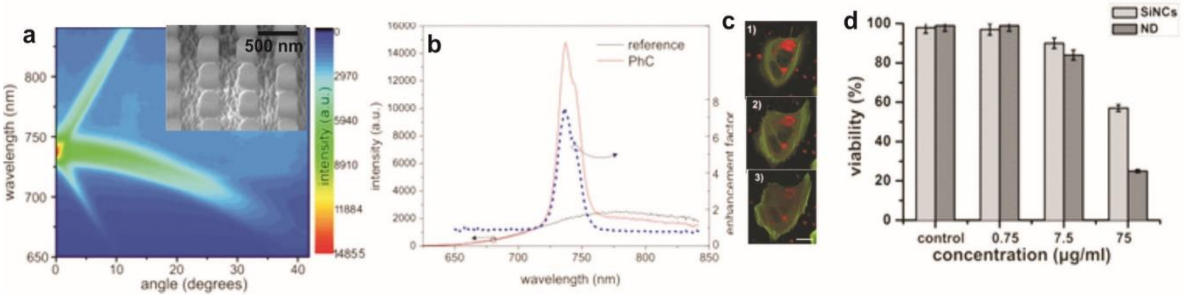


Fig. 8: (a) Angularly resolved photoluminescence along the Γ–X direction of a SiNC-rich layer with a photonic-crystal pattern. (b) 8-fold enhancement in the extraction of light in the normal direction. (c) Confocal luminescence images of live SAOS-2 cells incubated with SiNCs. (d) Cytotoxicity after 48 hours.

5. Silicon Nanostructures and Thin Films (http://thinfilms.fzu.cz/) is a group focusing on the growth of silicon nanostructures using plasma enhanced chemical vapour deposition (PECVD) and study of their electronic, optical and other physical properties.

We explored direct formation of ordered crystalline Si nano-objects at low temperatures, which are compatible with the CMOS process temperature limits. We have shown previously that amorphous silicon (a-Si:H) can be locally crystallized down to 60 nm by applying electrical current in AFM, allowing fabrication of arrays of Si nanocrystals. By adjusting this method we created nanopits (< 200 nm) in the thin film a-Si:H that served as a template for secondary nanocrystal growth in PECVD (with Rezek and Kromka groups). We achieved selective growth of Si nanocrystals from silane as well as of diamond nanocrystals from methane as detected by C-AFM, KPFM and Raman spectroscopy [39],[40].

As another possibility we have used the self-organized formation of dots of catalytic metals (Au for example) on surfaces and the Vapour–Liquid–Solid (VLS) mechanism for the growth of silicon nanowires (SiNWs) in PECVD [41]. By using plasma-enhanced process we have achieved a substantial decrease of the preparation temperature to about 250°C [42].

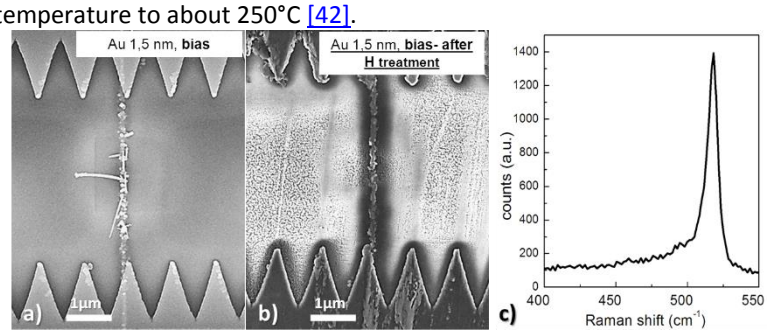


Fig. 9: a) SEM image of a strip of SiNWs grown from gold nano-islands from 1.5 nm thin film,
b) the same place after hydrogen plasma treatment and
c) Raman spectrum of treated strip of silicon nanowires. The thickness of original gold thin film was 1.5 nm.

The remaining problems of the SiNWs grown perpendicular to the substrate are to achieve 100% nucleation and a good control over the growth direction. In the area of SiNWs grown in the surface plane, we have demonstrated a possibility to prepare 30 nm wide crystalline "Lateral SiNWs", grown parallel to the substrate (Fig. 9) [43], which are more suitable for the preparation of electronic and light-emitting nanostructures. The revolutionary way of the preparation of lateral SiNWs with a high growth rate has been recently demonstrated by so called In Plane Solid-Liquid-Solid (IP SLS) process with In as a catalytic metal [44]. Recently we have achieved the similar growth with Pb as a catalytic metal.

SiNWs were also used for the fabrication of modern nanostructured thin film solar cells containing new designs of p-i-n radial junctions (RJs). Such solar cells achieved excellent light trapping and efficient photogenerated charge collection, reaching efficiencies close to 10% even with only ~100 nm thin a-Si:H absorber layers [45],[46]. We have established a fruitful cooperation with Ecole Polytechnique at Palaiseau, Paris, aimed at characterization of the photovoltaic conversion at the level of individual nanowire based junctions [47]. We studied influence of irregularities (e.g. SiNW lengths, orientations, shapes and mutual interactions) on the local photovoltaic performance. Direct measurements of these effects require microscopic techniques that provides information on photoresponse of individual nanocells. We have demonstrated that this is possible using a conductive atomic force microscopy (C-AFM) with a conductive cantilever which serves as a contact to individual radial junctions. This work led to invited talks at E-MRS in 2013 [47] and Int. Symposium on Nanowire Solar Cells [48] at FUTURE-PV in Fukushima.

Identification of the origin of variations of local photoresponse in nanostructured thin film solar cells requires correlating its maps with measurements of other physical properties, e.g. using scanning electron microscopy. We have developed a procedure (Fig. 10) for correlative microscopy using nanoindents as position markers [49], which is applicable to various types of nanostructures for photovoltaic solar energy conversion and which serves as a tool for investigating the role of disorder in nanostructured solar cells. The procedure for correlating different microscopies was originally designed for totally featureless structures, for example thin films of solid-phase crystallized silicon which we have investigated within the FP7 PolySiMode project.

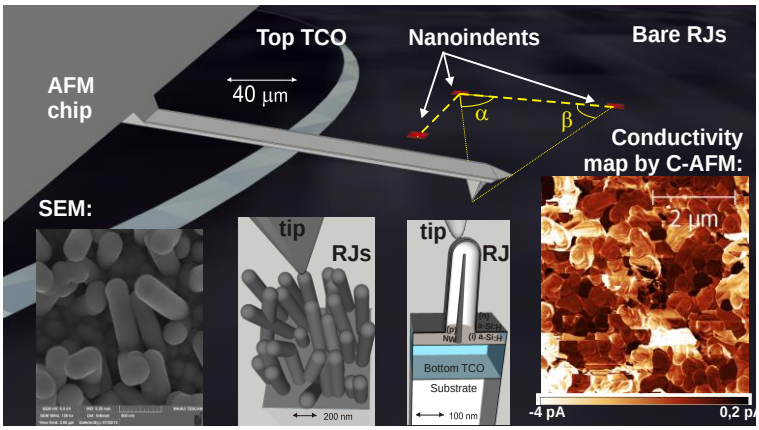


Fig. 10 Scheme of the correlated microscopic measurements of solar cells with radial junctions (RJ) based on Si nanowires (NW). Orientation on sample is provided by the three nanoindents. Circular top TCO is shown in blue below the AFM chip with the 200 μm long cantilever. Insets: SEM image of the RJs, schemes of the tip – RJ contact and Rj cross section and a local (photo)current map.

Summary

In the period 2010-14, the team of the TF&N department has achieved original and noteworthy results, published in total of 184 impacted journal papers, 2 books, 9 book chapters and 6 patents or utility designs, out of which 42 outputs were selected for the 1st round of the present evaluation. The research of the department was supported by 32 grant projects, including FP7 or 4 Czech Science Foundation Centres of Excellence. Several works were highlighted in Nature, Nature Materials and Nature Nanotechnology, APS Physics and Physical Review Letters Editor's suggestions. From the awards we point out:

- Literary prize of Josef Hlávka for Ivan Pelant (2010)
- Award of the Czech Academy of Sciences for Pavel Jelínek (2012)
- L'Oréal UNESCO award for Women in Science for Kateřina Kůsová (2014)
- Wichterle premium for Younger Scientists for M. Ledinský (2013) and M. Švec (2014)
- Josef Hlávka price for young scientists for L. Ondič (2013)
- Česká hlava Doctorandus for A. Fučíková (2012)
- Fellowship J. E. Purkyně H. Vázquez (2013 – 2017) and B. Rezek (2006 – 2011)
- Bolzano prize for L. Ondič (2015)
- SciEx fellowships for A. Vetushka (2012-13) at EMPA, M. Ledinský (2013-14) at EPFL Neuchatel and Š. Stehlík (2014-15) at Basel University.
- Invitation of A. Fejfar to Advisory Committees of Japanese NEDO and FUTURE-PV projects.

The members of the department have also reached out towards the scientific and general public at numerous occasions, organizing international conferences and schools as well as science popularization events.

References:

[1] J. Kočka, J. Non-Cryst. Solids 358 (2012) 1946.
[2] P. Hapala, R. Temirov, F. S. Tautz, P. Jelínek, Phys. Rev. Lett. 113 (2014) 226101.
[3] P. Hapala, G. Kichin, C. Wagner, F. S. Tautz, R. Temirov, P. Jelínek, Phys. Rev. B 90 (2014) 085421.
[4] J. Zhang, P. Chen, B. Yuan, W. Ji, Z. Cheng, X. Qiu, Science 342 (2013) 611.
[5] C. Chiang, C. Xu, Z. Han, W. Ho, Science 344 (2014) 885.
[6] M. Telychko, P. Mutombo, M. Ondráček, P. Hapala, F. C. Bocquet, J. Kolorenč, et al, ACS Nano 8 (2014) 7318.
[7] P. Merino, M. Švec, J. I. Martinez, P. Jelinek, P. Lacovig, M. Dalmiglio, et al. Nat. Commun. 5 (2014).
[8] M. Setvín, P. Mutombo, M. Ondráček, Z. Majzik, M. Švec, et al, ACS Nano 6 (2012) 6969.
[9] Y. Sugimoto, P. Pou, M. Abe, P. Jelinek, R. Perez, S. Morita, O. Custance, Nature 446 (2007) 64.
[10] M. Ternes, C. González, C. P. Lutz, P. Hapala, F. J. Giessibl, P. Jelínek et al, Phys. Rev. Lett. 106 (2011) 016802.
[11] P. Jelínek, M. Ondráček, F. Flores, J. Phys. Condens. Matter 24 (2012) 084001.
[12] Y. Sugimoto, M. Ondráček, M. Abe, P. Pou, S. Morita, R. Perez, et al. Phys. Rev. Lett. 111 (2013) 106803.
[13] Z. Majzik, M. Setvin, A. Bettac, A. Feltz, V. Chab, P. Jelinek, Beilstein J. Nanotechnol. 3 (2012) 249.

[14] E. Abad, J. P. Lewis, V. Zobač, P. Hapala, P. Jelínek, J. Ortega, J. Chem. Phys. 138 (2013) 154106.
[15] V. Zobač, J. P. Lewis, E. Abad, J. I. Mendieta-Moreno, P. Hapala, et al, J. Phys. Condens. Matter 27 (2015) 175002.
[16] Z.-L. Cheng, R. Skouta, H. Vazquez, J. R. Widawsky, S. Schneebeli, et al, Nat. Nanotechnol. 6 (2011) 353.
[17] H. Vazquez, R. Skouta, S. Schneebeli, M. Kamenetska, R. Breslow, et al, Nat. Nanotechnol. 7 (2012) 663.
[18] G. Foti, H. Vázquez, D. Sánchez-Portal, A. Arnau, T. Frederiksen, J. Phys. Chem. C 118 (2014) 27106.
[19] H. Kozak, A. Kromka, O. Babchenko, B. Rezek, Sens. Lett. 8 (2010) 482.
[20] B. Rezek, M. Krátká, A. Kromka, M. Kalbacova, Biosens. Bioelectron. 26 (2010) 1307.
[21] M. Krátká, A. Kromka, E. Ukraintsev, M. Ledinský, A. Brož, et al, Sens. Actuators B Chem. 166–167 (2012) 239.
[22] S. Stehlik, T. Izak, A. Kromka, B. Dolenský, M. Havlík, B. Rezek, ACS Appl. Mater. Interfaces 4 (2012) 3860.
[23] J. Čermák, Y. Koide, D. Takeuchi, B. Rezek, J. Appl. Phys. 115 (2014) 053105.
[24] E. Ukraintsev, Int. J. Electrochem. Sci. 8 (2013) 17.
[25] S. Stehlik, T. Petit, H. Girard, J.-C. Arnault, A. Kromka, B. Rezek, Langmuir 29 (2013) 1634.
[26] H. Kozak, Z. Remes, J. Houdkova, S. Stehlik, A. Kromka, B. Rezek, J. Nanoparticle Res. 15 (2013) 1.
[27] P. Hapala, K. Kůsová, I. Pelant, P. Jelínek, Phys. Rev. B 87 (2013) 195420.
[28] K. Kůsová, P. Hapala, J. Valenta, P. Jelínek, O. Cibulka, L. Ondič, et al. Adv. Mater. Interfaces 1 (2014) 1300042.
[29] K. Kůsová, O. Cibulka, K. Dohnalová, I. Pelant, J. Valenta, A. Fučíková, K. Žídek, et al, ACS Nano 4 (2010) 4495.
[30] L. Ondič, K. Kůsová, M. Ziegler, L. Fekete, V. Gärtnerová, V. Cháb, V. Holý, et al, Nanoscale 6 (2014) 3837.
[31] K. Žídek, I. Pelant, F. Trojánek, P. Malý, P. Gilliot, B. Hönerlage, J. Oberlé, et al, Phys. Rev. B 84 (2011) 085321.
[32] L. Ondič, M. Varga, K. Hruška, A. Kromka, K. Herynková, et al. Appl. Phys. Lett. 102 (2013) 251111.
[33] L. Ondič, K. Dohnalová, M. Ledinský, A. Kromka, O. Babchenko, B. Rezek, ACS Nano 5 (2011) 346.
[34] A. Fucikova, J. Valenta, I. Pelant, M. H. Kalbacova, A. Broz, B. Rezek, A. Kromka, et al, RSC Adv. 4 (2014) 10334.
[35] I. Pelant, J. Valenta, Luminescence Spectroscopy of Semiconductors, Oxford University Press, 2012.
[36] Kateřina Herynková, I. Pelant, in: Handbook of Porous Silicon Springer, 2014, pp. 345–354.
[37] J. Valenta, T. Ostatnický, I. Pelant, Handb. Nanophysics Nanoelectr. Nanoph, CRC Press, 2010, pp. 37–1 –37–15.
[38] K. Dohnalová, T. Gregorkiewicz, K. Kůsová, J. Phys. Condens. Matter 26 (2014) 173201.
[39] E. Ververiotis, B. Rezek, E. Šípek, J. Stuchlík, M. Ledinský, J. Kočka, Nanoscale Res. Lett. 6 (2011) 145.
[40] E. Ververiotis, E. Šípek, J. Stuchlík, J. Kočka, B. Rezek, J. Non-Cryst. Solids 358 (2012) 2118.
[41] J. Červenka, M. Ledinský, H. Stuchlíková, J. Stuchlík, et al, Phys. Status Solidi RRL - Rapid Res. Lett. 4 (2010) 37.
[42] J. Cervenka, M. Ledinsky, J. Stuchlik, H. Stuchlikova, S. Bakardjieva, et al, Nanotechnology 21 (2010) 415604.
[43] M. Müller, J. Kočka, H. G. El Gohary, J. Stuchlik, H. Stuchlikova, K. Hruška, et al, Can. J. Phys. 92 (2014) 819.
[44] L. Yu, P.-J. Alet, G. Picardi, P. Roca i Cabarrocas, Phys. Rev. Lett. 102 (2009) 125501.
[45] S. Misra, L. Yu, W. Chen, M. Foldyna, P. Roca i Cabarrocas, J. Phys. Appl. Phys. 47 (2014) 393001.
[46] S. Misra, L. Yu, M. Foldyna, P. Roca i Cabarrocas, IEEE J. Photovolt. 5 (2015) 40.
[47] A. Fejfar, M. Hývl, M. Ledinský, A. Vetushka, J. Stuchlík, et al, Sol. Energy Mater. Sol. Cells 119 (2013) 228.
[48] A. Fejfar et al: 2nd Int. Symp. Nano-Wire Si Sol. Cells, Japan Sci. & Tech. Agency (JST), MEXT, Kooriyama, 2014.
[49] A. Fejfar et al, Sol. Energy Mater. Sol. Cells 135 (2015) 106.

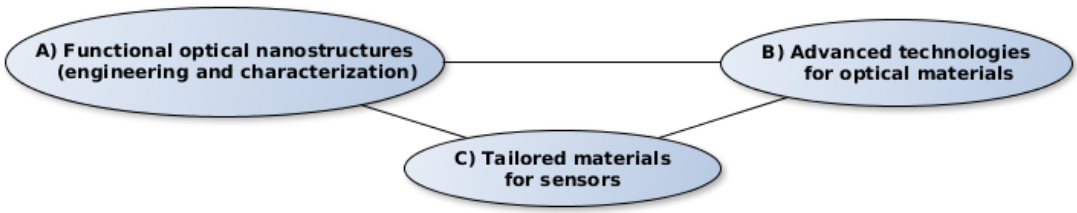
Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Department of Optical Materials

Summary 2010-2014 (following provided list of publications)

In the Department of Optical Materials (DOM) a wide range of functional materials (including composites, glasses, crystalline materials, nanofibers, diamond nanoparticles and biocompatible materials) are prepared using sophisticated advanced technologies (various forms of CVD and plasma techniques, nanosperical litography). Their properties are studied theoretically and experimentally (SEM, AFM, microRaman, thermal analysis, specialised spectrometers in a broad spectral range from 200 nm up to 20 μm, such as UV-visible-near infrared spectrometers and Fourier transform infrared spectrometers for transmittance and reflectance measurements, photocurrent metods, photothermal deflection method, time resolved UV/VIS luminescence and scintillation techniques, x-ray photoelectron spectroscopy, Auger electron spectroscopy, ultraviolet electron spectroscopy and low electron energy diffraction) and the convergence of such complementary methods amplifies a cooperative synergic effect between research teams in DOM resulting in multifaceted *processing-structure-properties-application* interactions. The long-standing strategy of DOM is to allow for effective collaboration between particular research teams applying different, but strongly interlinked concepts and methodologies to solve complex interdisciplinary problems with substantial application potential extending from quantum computation processing, advanced sensoric/scintillators techniques to medicine and solar energetics. The principal topics investigated in DOM are following:



In the **Laboratory of luminescent and scintillation materials** an extended set of experimental methods from the field of optical and time-resolved luminescence spectroscopies further correlated with magnetic spectroscopies and scintillation characteristics evaluation is applied to study in detail the luminescence and scintillation mechanism in solid state, influence of specific defects and irregularities in highly ordered single crystals, ceramic, powder or even glass material systems and relation of such defects and traps to the manufacturing technology. Quite several material systems have been systematically studied in 2010-2014 period, which belongs to to *A)* and *C) topics.*

Among the bulk materials the most intensive research and development (R&D) efforts were devoted to the garnet scintillators derived from Ce- and Pr-doped heavy aluminum garnet $Lu_3Al_5O_{12}$ (LuAG). The band-gap engineering strategy has been defined as a novel tool in wide band-gap materials and demonstrated for Ga-admixed $Lu_3Al_5O_{12}$:Ce(Eu) single crystals to tailor their scintillation characteristics [5].

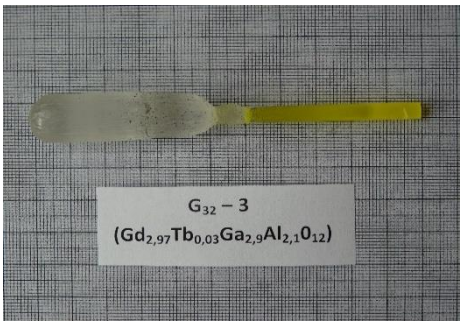


***Fig. 1**: Tb-doped multicomponent garnet single crystal grown by Czochralski method in Chemical department of the Institute.*

In collaboration with the group of Prof. A. Yoshikawa at Tohoku university, Japan, using the micro-pulling down crystal growth technology, the combinatorial study within the whole group of cerium-doped Ga- and Gd-admixed $Y_3Al_5O_{12}$ and $Lu_3Al_5O_{12}$ scintilllators resulted in the discovery of new class of ultraefficient, so called multicomponent, garnets [6,7], for review see [11]. Single crystals of $Gd_3Ga_3Al_2O_{12}$:Ce grown later by Czochralski method have shown light yield approaching 60 000 phot/MeV and energy resolution below 5% at 662 keV. These results belong to the most important discoveries in the field of scintillation materials in the last decade. In collaboration with the Chemistry department, the Czochralski growth of $Gd_3Ga_3Al_2O_{12}$ single crystals with various rare earth dopants has been recently accomplished also in the Institute of Physics ASCR, Fig. 1, which is one of the outcomes of the EC project Luminet carried out in the group (FP7, MC ITN no. 316906, 2012-2017).

Another optimization strategy of these cerium-doped garnet scintillators has been recently introduced by us in collaboration with the groups in Shanghai Institute of Ceramics, CAS and above mentioned Tohoku university. It is based on the stabilization of Ce^{4+} center by divalent Mg^{2+} codopant in Ce-doped LuAG optical ceramics or single crystals. The stable Ce^{4+} center introduces a complementary fast radiative recombination pathway efficiently enhancing the fast part of scintillation response at the expense of (unwanted) delayed radiative recombination processes [15]. Thus, a new optimization tool was found for the whole family of Ce-doped garnet scintillators which greatly improves their application important characteristics.

We have been studying garnet scintillators also in nanocrystalline form in the collaboration with the group of Prof. V. Čuba from Czech Technical university in Prague. Using newly developed radiation method for their preparation, the structurally perfect and well separated nanocrystals of $Lu_3Al_5O_{12}$:Ce were prepared, Fig. 2. They show potential for the application in modern photodynamical therapies for cancer treatment [9]. Preparation method is protected by the Czech national patent.

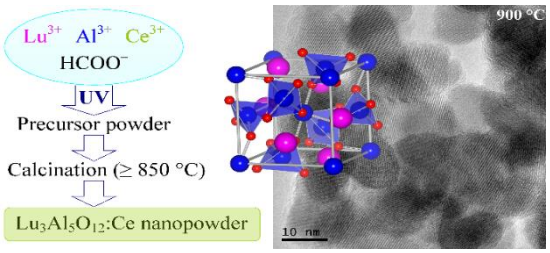


***Fig. 2**: Sketch of radiation method for Ce-doped $Lu_3Al_5O_{12}$ nanocrystals. Its structure and HRTEM photograph are displayed on the right.*

Systematic effort has been devoted to the study of single crystals based on ortho- and pyrosilicates which belong to commercially successful materials applied, for example, in the PET imaging. Two kinds of cerium emission centers were separated and comprehensively described in a wide temperature range in $(Lu,Y)_2SiO_5$ host [1]. Electron and hole traps, which can negatively influence scintillation performance, were studied in detail in Y_2SiO_5 and Lu_2SiO_5 hosts [13]. In a novel, very promising pyrosilicate host, namely La-admixed $Gd_2Si_2O_7$ host, luminescence characteristics of the Ce^{3+} center were described and scintillation performance compared with other commercial scintillators [14]. In the Ce-doped $Lu_2Si_2O_7$ pyrosilicate, in collaboration with the group of Prof. A. Vedda from University of Milano-Bicocca we have also developed and tested the model explaining the role of electron traps in, shaping the temperature dependence of the delayed radiative recombination processes following the ionization of the Ce^{3+} excited state [8]. Such a model is of general importance for all scintillator materials where the excited state ionization of emission centers is significant.

In collaboration with the IP Chemistry department we have developed a technology for crystalline rare earth-doped ternary sulfides $ALnS_2$ (A = Na, K, Rb, Cs; Ln = Lu, Y, Gd, La). Their

structural, luminescence and scintillation characteristics were studied in collaboration with already mentioned group of prof. V. Čuba [4]. They appear as novel and very attractive material group for both X-ray and white LED phosphors. The most interesting result consists in spontaneous stabilization of Eu^{2+} emission center in these hosts which, so far, has been studied in detail in $KLuS_2$ [12], Fig. 3. Given the broad excitation bands of Eu^{2+} center in near UV-blue spectra region and possibility to tune the position of Eu^{2+} emission in blue-green-red spectral region these materials show an application potential for white LED solid state light sources. Their preparation and application is also protected by the Czech national patent. Other powder phosphors developed in this collaboration belong to ternary hafnates and zirconates of general formula $Sr_iA_{2-i}O_{4-i}$, A = Hf, Zr. At room temperature the Sr-deficient (i < 1) materials of this kind show efficient emission in near UV, decay times well below 1 microsecond and very low afterglow which point to their potential in very fast imaging methods. An introductory study of their emission properties is reported in [2]. Their preparation and application is also protected by the Czech national patent.

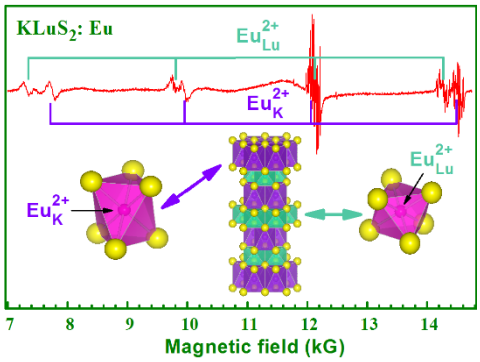


***Fig. 3**: Bottom part - structural units of hexagonal $KLuS_2$ and octahedral substituted by Eu^{2+} center. Upper part – electron paramagnetic spectra characterizing Eu^{2+} center at K^+ and Lu^{3+} sites.*

Taking advantage of our extended experience in the study of color centers and charge traps in oxide scintillators using correlated EPR and TSL experiments, we have accomplished the finding of paramagnetic hole centers in $PbWO_4$ single crystal host after more than a decade lasting efforts in which the nature of all dominating electron traps has already been clarified. Namely, the O^- character of these hole centers was found and their further stabilization by nearby defects was confirmed [3]. This finding thus allows to conclude the trapping mechanism of electrons and holes in a transfer stage of scintillation process. Practical importance of $PbWO_4$-based scintillator is given by the fact that it has been applied in LHC calorimetric detectors in CERN and is still considered for other projects in high energy physics (e.g. Panda in Germany).

Finally, an effort has been also devoted to the development of single crystal scintillators suitable for thermal neutron detection which is a hot topic in the latest R&D activities in the field of security techniques and anti-terroristic measures. In collaboration with the already mentioned group of Prof. A. Yoshikawa we have studied the characteristics of Ce- and Eu-doped $LiCaAlF_6$ single crystals [10] and pointed to large room for optimization of this promising material system. Photoelectron spectroscopy has been successfully applied (XANES method) to resolve two different charge states of the dopants which very suitably complement (and confirm) the results from optical experiments.

By the vertical Bridgman method single crystals of pure and doped ternary halides such as $RbPb_2Cl_5$ and $RbPb_2Br_5$ were grown in the **Laboratory of Crystal Growth and Thermal Analysis** in the period 2010 -2014 (*topic B*). When doped with rare earth (RE) elements, these crystals are prospective materials for solid state laser operation in mid-IR region. Influence of growth conditions, such as the temperature gradient in the furnace, position of the special quartz ampoule in the temperature gradient, and pulling rate, on the position and shape of the crystal/melt interface was studied. Obtained and recalculated data allowed the detailed analysis of heat transport in different experimental arrangements in the simulated growth system and optimization of growth conditions.

Core facilities of the **Laboratory of diamond thin films and carbon nanostructures** rely on two unique microwave (MW) deposition systems with ellipsoidal resonator cavity (i.e. focused microwave plasma with an egg-like resonator) and linear antenna arrangement (i.e. scaleable large area system). Both deposition systems represent a microwave plasma assisted chemical vapor deposition. Other facilities within the group include optical emission setup for plasma analysis, contact angle measurement setup, and standard semiconductor processing systems as reactive ion etching with capacitively coupled plasma or inductively induced plasma, surface microwave plasma –surfatron type, radio-frequency chamber for sputtering polymers, etc.

Both microwave plasma deposition systems are used for i) fundamental studies of plasmo-physic processes (plasma characterization), ii) plasma enhanced chemical vapor deposition of carbon

allotrope nano-forms (diamond, diamond nanoparticles, carbon and graphene sheets, CNTs), and ii) plasma-assisted functionalization of various materials (diamond films, ZnO, diamond nanoparticles, CNT, etc.). All produced materials are systematically investigated and the processes are optimized to tailor intrinsic properties of carbon nano-forms for inter-disciplinary oriented fields, such as plasma physics, opto-electronics, material engineering, plasmonics and photonic crystals, spintronics, bio-sensorics, drug delivery, tissue engineering, regenerative medicine and others. To achieve all these activities, fruitful cooperation within home departments, universities and institutes is actively running on both national and international levels. These studies include following topics:

A) Functional optical nanostructures: engineering and characterization

At present, the focused microwave plasma deposition system is routinely used for growth of nanocrystalline and microcrystalline diamond thin films, self-standing diamond mesh-like membranes or disks, etc., Fig. 4. Recently, the system is used for i) a controllable doping of diamond thin films by silicon atoms to fabricate optically active centers in diamond, and ii) a growth of thin films used in IS FETs and planar-impedance sensors (gas molecules, proteins, DNA, etc.). For the pulsed linear antenna microwave plasma working at low pressures (<100Pa) we made a breakthrough in the growth of nanocrystalline (grain size < 100 nm) and microcrystalline (grain size >500 nm) diamond films of optical and electronic quality over large areas (up to 20x30 cm^2) by employing pulsed linear antenna microwave plasma at low pressures (<100Pa) [36]. The CVD process is characterized by low temperature plasma (Te<2 eV) which allows the plasma assisted CVD deposition at temperatures as low as 250°C. So, the family of temperature sensitive substrates includes glass, gold, silver, germanium, etc. We discovered that process parameters, such as gas mixture (i.e. mainly adding CO_2 to the gas mixture CH_4+H_2) and process pressure (i.e. the range 6-100 Pa) are crucial for controlling the crystal size and film porosity.

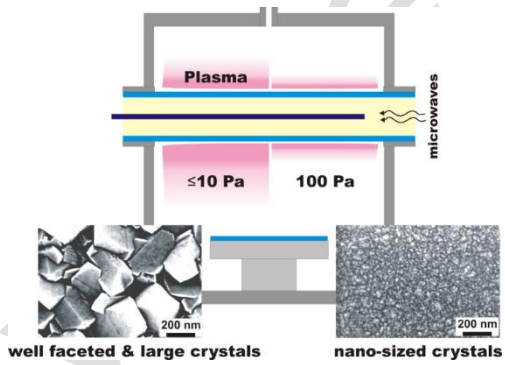


Fig. 4*: Schematic view of plasma kinetics and SEM surface morphologies of diamond films grown at low (10 Pa) and high (>100Pa) process pressure. Scale bar in SEM images is 200 nm.*

Our research activities also include studies on diamond nanoparticles (DNPs), i.e. manipulation with their surface, DFT calculations of surface chemistries and characterization by means of analytic techniques. These are well represented by the study on chemical modifications and stability of diamond nanoparticles resolved by infrared spectroscopy and Kelvin force microscopy [34]. IR spectra of the as-received DNPs were dominated by C-H bonds and carboxylic groups (COOH), probably related to the wet chemical treatment in acids. Annealing in air and oxygen plasma led to a significant enhancement of C=O groups and C-H groups vanishing. After short-term (10 min) oxygen plasma treatment, IR peaks changed their intensity and position indicating a spontaneous reactivity of DNPs, probably due to partial erosion of the graphitic shell. Prolonged oxygen plasma treatment (40 min) or annealing in air at 450°C for 30 min provided a stable DNPs surface. Surface potential measurements by KFM indicated that the pronounced C-H band was not related to H-termination of diamond core but rather to amorphous and/or graphitic shell of the as-received DNPs. The GAR-FTIR well resolved a complex structure and chemical moieties present on DNPs. Despite the DNP nanoscale dimensions and possible imperfections, their chemical stability in air was similar to bulk diamond. Aforementioned studies are presently correlated not only with results of analytic techniques but also with DFT calculations of neighboring atomic environment, surface coverage and orientation on the vibrations of particular functional group. For these calculations, small clusters representing a part of diamond surface and selected oxygen-containing groups with total number of 100 to 400 atoms were used.

As newly and highly attractive research field, we investigated antibacterial properties of diamond nanoparticles against the gram-negative model bacterium E. coli [31], Fig. 5. The antimicrobial potential of DNPs was studied as a function of DNP concentrations, i.e. from 5 to 60 μg per 1 ml of the diluted bacterial culture. After 16 h of cultivation at 37°C, vital cells gave rise to colonies on the surface of agar plate. From the average number of colonies, the proportion of cells survived in the presence of DNPs relative to negative control without DNPs was counted and expressed as colony forming ability (CFA).

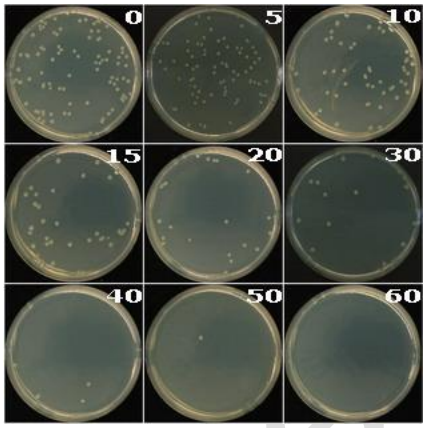


Fig. 5: *Growth of E. coli colonies on LB agar plates in the presence of different concentration of diamond nanoparticles. The numbers define the concentration in μg of DNPs per 1 ml of diluted bacterial culture inoculated on each plate.*

Our experiments confirmed the antimicrobial potential of DNPs which was nonlinearly concentration dependent. While the presence of DNPs at concentration of 5 $\mu g.ml^{-1}$ (cca. 4 ng of DNPs per 1 cell) gave rise to a 25% inhibition of bacterial growth, the concentration of 10–20 $\mu g.ml^{-1}$ (7–15 ng per cell) inhibited the bacterial counts by 85%. The DNP concentration higher than 50 $\mu g.ml^{-1}$ (37 ng per cell) caused a complete inhibition of bacterial growth (CFA ≤ 0.5 %). We proposed a model in which DNPs cluster around bacterial cells and thus, they block essential cellular functions. Moreover, we also found that this effect is considerably influenced by the chemical and physical properties of surface structures of particular bacterial cell.

Similarly to DNPs studies, in cooperation with a group of Dr. J. Mosinger (Charles University in Prague) we investigated the influence of oxygen plasma treated polystyrene (PS) nanofiber on the antibacterial properties [30]. The FTIR spectra of PS nanofibers reflected a decrease in the intensity of the CH bands at 2850-3080 cm^{-1} and an increase in the intensity of the OH-related band compared with the original PS materials. Moreover, the oxygen treated nanofibers revealed a new band at 1743 cm^{-1}, which was assigned to the stretching of carbonyl C=O groups. The spectrum also indicated the presence of a very broad band at 3100-3500 cm^{-1}, which most likely corresponds to hydroxyl groups from the oxygen species and/or adsorbed water. The original PS nanofiber exhibited hydrophobic properties (contact angle 130 ± 4°) and the plasma treated nanofibers changed to highly hydrophilic (contact angle <5°). It was confirmed that the increase in the surface wettability resulted in acceleration of the photo-oxidation of external substrates and an increase in the antibacterial activity of the nanofibers.

Except for the treatment of polymer nanofibers, we have also studied a dry treatment of the Single Wall Carbon Nanotubes (SWCNT) film in oxygen plasma at low rf power which resulted in a controllable initialization of defects over the SWCNT, as confirmed by Raman measurements [39]. Contact angle measurements showed that newly initialized defects changed the hydrophobic character of pristine SWCNT surface into hydrophilic. Significant changes in topography of SWCNT surface were found only for extensively treated SWCNT samples (>30 min). With the close cooperation with Dr. Kalbacova (Charles University in Prague) we proved the biocompatibility for pristine SWCNT and 1 and 5 min oxygen plasma treated SWCNT. The SWCNT sample treated for 5 min was found as the best for osteoblast adhesion followed by massive proliferation. On the other hand, strong changes in topography of the sample treated by oxygen plasma for 30 min reduced cell adhesion despite its hydrophilic character. These results demonstrated that both hydrophilic character and specific surface topography are important factors for cell adhesion and proliferation. Therefore the control of these factors is crucial for future design of implants and application of new materials in regenerative medicine.

Collaboration within EU photovoltaics and nanotechnology collaborative projects of 6 FP and 7 FP as well as national projects (Czech Science Foundation, KONTAKT) connected with ZnO hydrothermal growth, complex characterization of the ZnO nanostructures, a new class of absorbers with perovskite structure and various kinds of oxide and sulphide nanoparticles embedded in dielectric or semiconducting layer and quantum dot structures were in the focus of **Laboratory of optics and photovoltaics**. Specific optical, photoelectrical and luminescence methods, partly developed in our laboratory have been used for characterization. Together with Oerlikon Solar, Trubbach, Switzerland, we have applied for patents (USA, EU, China) on 3-dimensional design of amorphous and amorphous-microcrystalline solar cells, in order to solve the problem of metastability of amorphous Si and increased optical absorption in very thin silicon absorbers. This is needed for an increase of thin film silicon solar cells efficiency, which is now lacking behind other thin film solar cell technologies. Our 3-D design uses a weakly conductive nanostructured ZnO transparent electrode as a skeleton, see Fig. 6, upon which the very thin Si absorber layers are deposited.

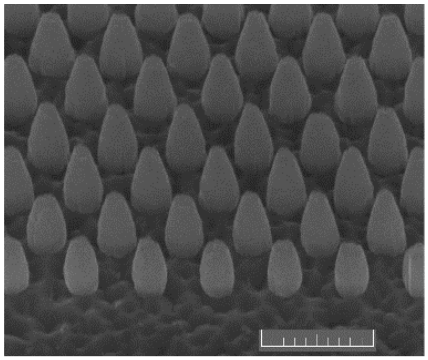


Fig. 6: *Arrays of ZnO nanocolumns for 3-D thin film silicon solar cells.*

B) Advanced technologies for optical materials

Diamond thin films have remarkable properties, especially optical, comparable with natural diamond. In a cooperation with Dr. Prajzler (Czech Technical University in Prague) we designed and fabricated optical planar waveguides from nanocrystalline diamond (NCD) thin films [35], Fig. 7. The waveguide structure was first calculated for various operating wavelengths for TE as well as TM polarizations by using modified dispersion equation. The nanocrystalline diamond planar waveguide was deposited by focused microwave plasma and was schemed for 632.8 nm, 964 nm, 1310 nm and 1550 nm wavelengths. Waveguiding properties of Si/SiO2/NCD planar optical element were confirmed by employing the prism-coupling technique. Even though our diamond film was thin (380 nm) and consisted of small grains, a high optical quality of diamond film was confirmed. This was in a good agreement with Raman measurements which detected a sharp diamond characteristic line centered at 1332.4 cm^{-1}. The Si/SiO2/NCD planar optical element revealed only one fundamental mode for all the measured wavelengths (473 nm, 632.8 nm, 964 nm, 1 311 nm and 1 552 nm). Values of the refractive indices of the prepared diamond thin films measured at various wavelengths were almost the same as those of natural diamond.

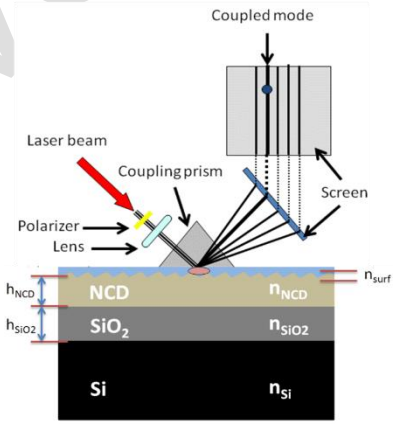


Fig. 7: *Schematic view of the dark mode spectroscopy measurement with the optical planar NCD waveguide structure.*

The diamond coated Au mirrors were used for the fabrication of optical elements for IR spectroscopy, Fig. 8. For this purpose, three different diamond morphologies were employed: flat, nanocolumnar, and nanoporous. Fabricated diamond coated optical elements were successfully used for the grazing angle reflectrance (GAR) Fourier transform infrared (FTIR) characterization of fetal bovin serum (FBS) proteins adsorbed on the O-terminated diamond surface [32]. Despite the different processing and structuring, all types of diamond layers showed good stability, uniformity, and optical properties, including good reflectivity of the gold mirrors. Gold mirrors coated with nanostructured diamond were sensitive optical elements for studying the interactions of small amount of organic molecules with the diamond surfaces in the immediate vicinity. Even 3-nm-thick layers of protein molecules adsorbed from FBS solution were well recognized. In fact, the thinner the adsorbed FBS layer, the higher the gain sensitivity. The enhanced sensitivity was attributed to the increased surface area of the nanostructured coating.

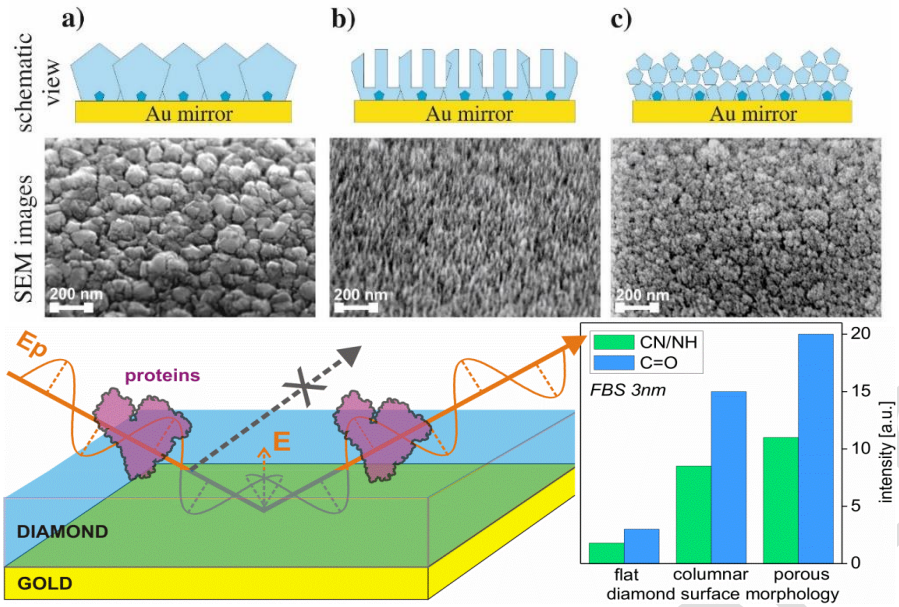


***Fig. 8**: Schematic drawing, SEM images of the diamond coated Au mirrors and corresponding IR intensities for CN/NH and C=O bonds. Diamond morphology was a) flat, b) nanocolumnar, and c) nanoporous.*

These results are promising for further studies of organic molecules on hydrophobic or hydrophilic diamond surfaces (achieved, for example, by hydrogen or oxygen plasma) and on diamond with various surface moieties as well as for monitoring chemical reactions between diamond and molecules. Moreover, optical elements based on electrically conductive yet fully transparent H-terminated diamond films could be used for the combined optical and electronic monitoring of ongoing electrochemical reactions at the diamond−molecule interface in real time.

C) Tailored materials for sensors

Nanocrystalline diamond film with a porous-like morphology was used as the functional part of a semiconductor gas sensor. The device function was based on the two-dimensional p-type surface conductivity of intrinsic diamond with an H-terminated surface. Metallic electrodes were buried beneath the diamond film. Therefore, these electrodes are protected from harmful substances, and the electronic connection is facilitated by grain boundaries [33]. The gas sensing properties of the sensor structure were examined using oxidising gases (i.e., phosgene, humid air) at various operating temperatures. A pronounced and selective increase by two orders of magnitude was found in the surface conductivity after sensor exposure to phosgene gas (20 ppm) at 140°C. Density functional theory calculations indicated no direct charge transfer between the phosgene molecule and diamond. We presented

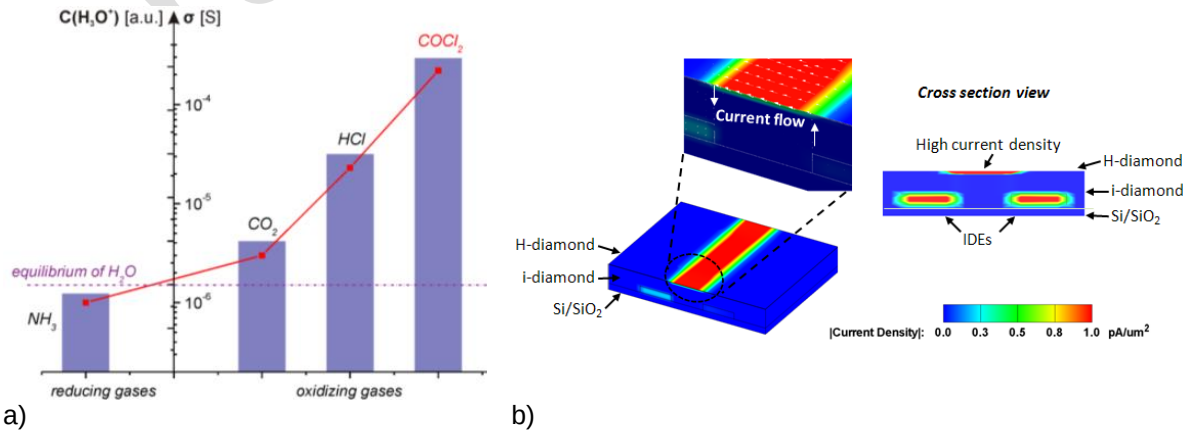


***Fig. 9**: a) Schematic diagram showing dependencies of $H3O^+$ ions concentration (columns), and surface conductivity (red curve) on the diamond surface covered by adsorbed water layer containing the dissolved reducing (NH_3) or oxidizing gases (CO_2, HCl, $COCl_2$) and b) current density profile for single pair of IDEs covered by intrinsic diamond with hydrogenated surface.*

a model in which phosgene indirectly yet efficiently increases the H_3O^+ concentration, which consequently leads to multiplied electron transfer and a pronounced sensor response, Fig. 9.

Our extended study confirmed the sensor sensitivity to NH_3 or CO_2 gases. A pronounced response of the sensor was observed for dense electrode arrays (50 μm). Moreover, the three-dimensional model of the current density distribution of the hydrogenated diamond described the transient flow of electrons between interdigitated electrodes and the hydrogenated diamond surface, i.e., the formation of closed current loop [21]. The concept of built (i.e. capped) metal electrodes in the diamond layer was also used for fabrication of a molecule sensitive transducer for Tröger's base derivative decorated with pyrrole groups. Impedance spectroscopy resolved that the transducer response is given by a change in longitudinal surface conductivity while transverse resistance of diamond cap layer remained constant under all conditions and surface terminations [37]. In contrast to this observation, the oxygen terminated diamond did not reveal any response or sensitivity to the molecule.

Within the frame of international collaboration with Prof. Szunerits (Université de Lille) we fabricated optically-based biosensors for sensing the detection of hydrogen peroxide - a crucial factor for monitoring toxic products in the living cells. First, planar diamond thin films grown by linear antenna microwave plasma system were grown on optically transparent substrates (glass), aminated and finally decorated with horseradish peroxidase enzyme (HRP) [38]. The enzymatic activity of immobilized horseradish peroxidase enzyme was determined by catalytically driven oxidation reactions. The dependence of optical absorbance (420 nm) on the concentration of hydrogen peroxide clearly confirmed the functionality of realized biosensors based on functionalized diamond surface with the detection limit as low as 39 nm and long-term stability.

Laboratory of electron spectroscopy (LES) is focused on characterization of the solid surfaces by electron spectroscopy methods, in particular the x-ray photoelectron spectroscopy (XPS). Furthermore, Auger electron spectroscopy (AES), ultraviolet electron spectroscopy (UPS) and low electron energy diffraction (LEED) can also be applied to study solid surfaces.

LES is equipped by two photoelectron spectrometers. The ADES 400 (VG Scientific, UK) photoelectron spectrometer was bought in 1980 but it has invariable importance for scientific research in LES. The new photoelectron spectrometer was bought in 2014. The ASIS Supra (Kratos Analytical, UK) instrument belong to the state of the art of the photoelectron spectrometers in the world. The AXIS Supra is designed for ease of use with automated sample loading, optical microscopes for sample identification and positioning and processing software. Co-axial electron charge neutralization system, high sensitivity, excellent energy resolution and fast, high resolution imaging ensure that photoelectron spectra can be collected for any vacuum stable materials including insulators. The AXIS Supra spectrometer is also equipped with a gas cluster ion source for depth profiling.

LES is focused on surface sample characterization of the various prepared functional nanostructures (*topic A*). During last years we reported our results on the chemical composition, chemical state and the C sp^2/sp^3 ratio of different carbon based materials. Interesting data were obtained on nanocrystalline diamond film surfaces [17]. The elastic peak electron spectroscopy (EPES) was used for surface H detection and quantification. By combination of XPS and EPES methods the full quantification of surface composition of nanocrystalline diamond films was shown. The work combines preparation of nanocrystalline diamond films, their chemical modification, hydrogenation in hydrogen plasma, surface characterization by XPS, and finally the hydrogen detection and quantification by EPES. All research was carried out in our department.

In LES the attention was also paid to the basic research concerning movement of medium energy electrons in the vicinity of polycrystalline or amorphous solid surface. In this field we have collaborated with the team of prof. Werner from the Vienna Technical University. New scattering process - supersurface electron scattering - was described within a joint research [16]. Supersurface electron scattering, i.e. electron energy losses and associated deflections in vacuum above the surface of a medium, is shown to significantly contribute to electron spectra. As can be seen from Fig. 10 when the contribution of supersurface scattering is removed from the raw data Fig. 10 (a), the resulting spectra, shown in Fig. 10 (c), are essentially in agreement with the Landau-Goudsmit-Saunderson theory,

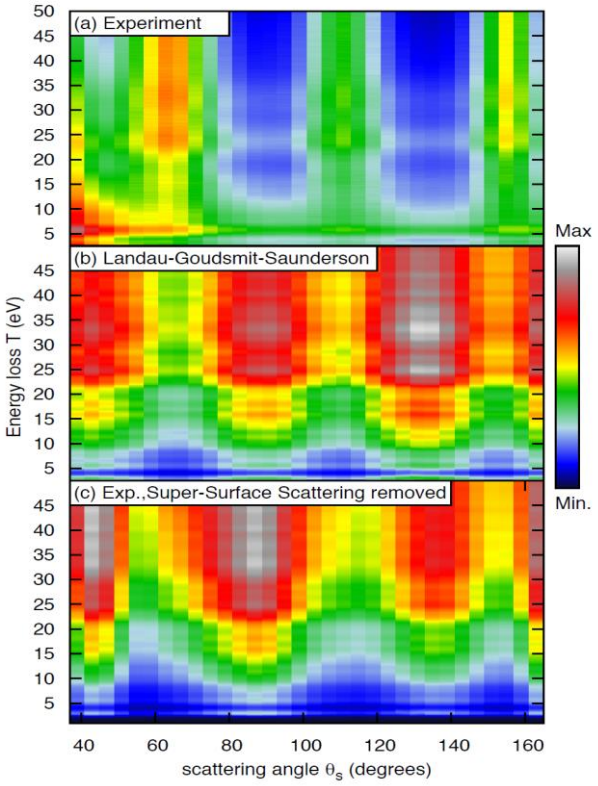


***Fig. 10**: Combined energy and angular spectrum of 500-eV electrons backscattered from an Au surface. The elastic peak has been removed from all data sets to improve contrast. (a) As measured; (b) Theoretical results according to the Landau-Goudsmit-Saunderson theory; (c) Experimental data after elimination of the supersurfaces scattering contribution.*

Fig. 10 (b). All experimental measurements presented in [16, 18] were performed at LES. The unique property of the ADES 400 photoelectron spectrometer, independent rotation of the energy electron analyzer around sample, was applied.

The most important material in science and technology is GaN. GaN has attracted a lot of attention because of its relevance for photoelectronics. For preparation of electronic elements based on GaN the knowledge of polarity of the grown layer surface (whether the sample surface is terminated by Ga or N atoms) is essential. In LES a new and very effective method for determination of the surface polarity was proposed [19]. This method is based on the photoelectron diffraction measurement. Based on theoretical calculations and experimental measurement it was demonstrated that a measurement of N 1s photoelectron line for two emission angles is sufficient to distinguish whether the GaN surface is terminated by Ga or N atoms. The proposed approach, experimental measurement, calculations and evaluation of the experimental and theoretical data were performed at LES.

Five research projects were successfully completed at LES in the period 2010 – 2014. The laboratory has a vivid collaboration with other domestic and international groups, such as the Institute of physical chemistry in Warsaw.

Recent advanced (nano)technologies are based on fundamental understanding of processes leading to formation of structured and distinct nanodomains of a new product phase within the metastable one. It is well recognized that nucleation theory plays a key role in description of the very first stage of the phase transformation at microscopic level and resulting knowledge allows to optimize/control characteristics of a product phase. In the research team of **Theory and Modelling of Phase Transitions** the scientific activities are focused both on study of thermodynamical aspects of nucleation process (formation energy of clusters, surface effects, nucleation barriers for various systems – gaseous, liquid, solid) and on modelling of homo/heterogeneous nucleation in both open and confined systems (formation of clusters on active sites, on strongly curved surfaces of polymeric nanofibers, within solid matrices). Kinetic equations are solved using numerical codes developed in the research team. Furthermore, certain modifications of Monte Carlo, or molecular dynamics methods have been adapted to model a formation of structured nanophases within solid matrices. In the Institute of Physics sufficiently efficient computational equipment is at hand to perform aforementioned time-consuming calculations.

Within the context of long-term collaboration with the group of *Laboratory of Diamond Thin Films and Carbon Nanostructures* (altogether with the *Joint Laboratory of Polymer Nanofibers of the Institute of Physics and the Czech Technical University*) the systematic effort is oriented to theoretical study of diamond nucleation on different substrates, using various deposition techniques and under variety of process conditions (*Topic A*). In particular, applying pulsed-linear antenna microwave plasma, the influence of CO_2 on the rate of nucleation process has been analyzed. An unexpected, bimodal distribution of diamond clusters for low ratios of CO_2/H_2 has been detected. It is possible that larger diamond clusters heterogeneously nucleate on the substrate while smaller nuclei form homogeneously

within the volume of plasma and the bimodal distribution function is closely connected with the structural/morphological difference between small and large clusters as well. Conceptually, our results indicate a promising way to balance nucleation/growth regimes and to optimize technological processes [43]. Following this methodology, hydrogenated nanocrystalline diamond layer of unique sensitivity to NH_3 has been prepared [21]. Such novel materials remarkably extend application potential in the field of sensoric techniques.

Another exciting and goal-directed problem promoted a teamwork with both the *Laboratory of Luminescent and Scintillation Materials (LLSM) and Laboratory of Crystal Growth and Thermal Analysis (LCGTA*)**:** formation of structured nanophases (quantum dots) via nucleation within halide matrices KCl (NaCl) slightly doped by $PbCl_2$ and prepared in LCGTA. Indeed, a phase transition begins to occur on the scale of individual to thousands atoms due to stochastic fluctuations. When these bunches of particles reach a certain critical size they become stable and further increasable. Using the lattice model for KCl-Pb system, the natural nucleation pathway from the single impurity-vacancy complex to Suzuki phase was identified, not demonstrated in previous analyses. Calculations in the case of NaCl-Pb suggest that from initially formed platelike nanophases of a certain critical thickness a nucleation readily proceeds to larger $PbCl_2$ clusters [24]. These unique results coincide with measurements of Pb in NaCl and KCl nucleation performed in LLSM. Deeper understanding of processes accompanying quantum dots formation of required properties within the bulk materials may contribute to optimization of hardware for quantum computing processing.

Nucleation in small confined systems is studied within cooperation with the *Graduate School of Biosphere Science at Hiroshima University, Japan* in response to the recent high interest in research on crystallization in emulsion and microemulsion droplets. In small volumes a higher supercooling is needed for the phase transition to occur. We have numerically solved kinetic equations to determine the conditions under which nuclei of new crystalline phase are formed by homogeneous and heterogeneous nucleation from supercooled melt and supersaturated solution. Standard nucleation models suppose unchanged conditions during the phase transition. However, depletion of parent phase leads to decrease of supersaturation in time as a consequence of the phase transition. We have determined conditions under which first nuclei are formed depending on the system volume [22]. Crystal nucleation kinetics in confined systems was presented as a keynote lecture in the Fourth European Conference on Crystal Growth (ECCG4) in Glasgow 2012 [23]. We have also determined the growth rate of nuclei from the size distribution of newly forming crystalline nuclei, Fig. 11. In the limit of a flat interface the growth rate v_∞ (analytical value from transient probabilities) is higher than the growth rate in a small volume. The growth of nuclei even stops (v=0) for small volumes ($V \leq 10^{-9}$) due to decrease of supersaturation.

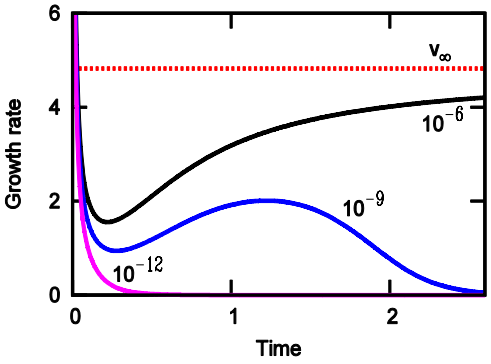


Fig. 11: *Schematic dependence of growth rate of nuclei on time.*

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Magnetic Nanosystems

The **Department of magnetic nanosystems** was established in January 2013 as a succesor of the Department of magnetism and low temperatures. MNS joins two research units**:** group of **Magnetic NanoSystems - MNS** and group of **SuperFluidity – SF**, the scope of the research falls in fields of solid-state magnetism, nanomagnetism and superfluidity, and resides mainly in experimental efforts with use of extreme enviroments (low temperatures, high magnetic fields). The key experimental centres of MNS are **the Joint laboratory for magnetic studies** (JLMS, http://kfkl.cz/jlms/) and **Joint laboratory of low temperatures** (JLLT). They are operated in close collaboration with several departments of the Faculty of Mathematics and Physics (FMP) and Faculty of Science (FS) Charles University in Prague (CU); the Mössbauer laboratory (part of JLLT) also joins Institute of Inorganic Chemistry AS CR, v.v.i. The department participates on operation of helium liquifier, which supplies cryoliquids for the CU and Institute of Physics (FZU).

The **MNS group** is a merge of the group of J. Vejpravová, which was transferred from FMP CU in 01/2011 and till 12/2012 was a part of the Department of functional materials, and group of A.V. Andreev oriented on *f*-electron magnetism. It is represented by two senior scientists (A.V. Andreev, J. Vejpravová – head of the department & author of the report), four postdocs/scientists (E. Tereshina, T. Verhagen, D. Gorbunov – from 12/2014 temporary at postdoc position in Dresden High-Field Laboratory, Z. Janů) and doctoral students (B. Pacáková, S. Kubíčková – from 04/2014 on maternal leave, A. Mantlíková). Beside its own research, most of the MNS members participate in routine operation of the large facilities in the JLMS, which is also the primary task of the skilled technical stuff (J. Šebek, M. Žáček, E. Šantavá – left in 03/2015, retired).

The **SF group** is currently represented by two scientists (S. Babuin, T. Chagovets), their research is coupled to the scientific activities of the Superfluidity group within the JLLT; the group also joins three technicians of the cryogenic unit working in the helium liquifier (P. Boháč, B. Vejr, P. Vacek – left in 01/2015, retired & replaced by D. Dlouhý, together 1.8 FTE) and one technician for development of electronics, namely for low temperature enviroment (F. Soukup, 0.3 FTE).

The age structure of the research team (presented in page 1) includes **3** Ph.D. students (in age category **25 – 30)** and technicians (**2** in 30-35, **1** in 55 – 60, **1** in 60 - 65 and **2** in > 70).

The main research activities within the period were related to the grant projects, obtained for the period 2010 – 2014 (summarized in section 2.1.a). As the final shape of the research team was consolidated in 2013, most of the activities were carried out independently within the original units and the research portfolio was rather fragmented. However, slowly graduating effort to make the research more compact has been already initiated (described in part 3.).

2.1.a Summary of grant project in the period 2010 – 2014 (title, leader in FZU, project no. & provider, period)

1. **Multifunctional Nanotechnology for selective detection and Treatment of cancer (MULTIFUN)**, J. Vejpravová - principal investigator (PI) at FZU, project no. 262943, 7th Framework Program, theme NMP-2010-4.0-1 (2011 – 2015)
2. **Magnetic and magnetoelastic properties of f-d intermetallics in extreme magnetic fields**, A. Andreev - PI, project no. M100101203 supported by the Ministry of youth, education and sports, program of interantional collaboration (2012 – 2015)
3. **Investigation of electric induction in He II using second sound generation**, T. Chagovets - PI, project no. 13-03806P supported by the Czech Science Foundation (2013 – 2015)
4. **Uranium-based multilayers: structure, magnetism and related electronic properties**, E. Tereshina - PI, project no. 13-25866P supported by the Czech Science Foundation (2013 – 2015)
5. **Magnetism of carbon nanostructures in the pure and doped state**, J. Vejpravová – PI at FZU, project no. P204/10/1677 supported by the Czech Science Foundation (2010 – 2014)
6. **Potencial oxide - diluted magnetic semiconductor nanostructures**, A. Mantlíková - PI, project guarantor J. Vejpravová, student project supported by Grant Agency of the Charles University (2010 – 2012)
7. **Magnetic and other electronic properties of intermetallic compounds RFe_xAl_{12-x} (R – Gd, Tb, Dy, Ho, Er, Tm, Lu a Y, $5 \leq x \leq 6$) with concurrent interactions**, D. Gorbunov - PI, project guarantor A.V. Andreev, student project supported by Grant Agency of the Charles University (2012 – 2014)
8. **Study of graphene-nanoparticle based systems**, B. Pacáková - PI, project guarantor J. Vejpravová, student project supported by Grant Agency of the Charles University (2013 – 2014)
9. **Multifuncional nanoparticles: advanced preparation methods and investigation of their physical properties**, J. Vepravova - PI, project no. P108/10/1250 supported by the Czech Science Foundation, affiliated to FS CU (2010 – 2014)

2.2. Research on magnetic materials (MNS group)

The most significant results were obtained in the field of strongly anisotropic *f*-electron materials and magnetic nanoparticles.

Studies of magnetic and other electronic properties of several groups of rare-earth and uranium intermetallic compounds were carried out with special attention to new and poorly-studied alloys. Results presented in most of the papers published in 2010-2014 were obtained on single crystals, grown for the first time. International cooperation with Dresden High Magnetic Field Laboratory (Germany) and Tokyo-Kashiwa (Japan) allowed us reaching magnetic fields up to 74 T. In the case of U compounds, we also continued our long-term fruitful collaboration with Institute for Materials Research, Tohoku University, Sendai, Japan. The contribution of the MNS members (Andreev, Gorbunov & Tereshina) is major and resides in crystal growth, sample characterization, measurement of magnetic and other properties in static magnetic fields, active participation on high-field experiments and interpretation of the results. Most of the manuscripts were also written by the MNS members (11, references [1-8, 12,13,15]).

Those with other corresponding authors, the MNS members formulated parts related to crystal growth and magnetic order (4, references [9,11,14,16]). The results were achieved within the grant projects of A. V. Andreev and D. Gorbunov as PI and represent substantial contribution in the field of strongly anisotropic *f*-electron magnets; we summarize the most important achievements below.

First, we prepared and studied series of RFe$_5$Al$_7$ compounds with tetragonal crystal structure of the ThMn$_{12}$ type with heavy rare-earths, R = Lu, Gd, Tb, Dy, Ho, Er, Tm [1-4]. RFe$_5$Al$_7$ with magnetic R exhibit complicated competition in exchange and anisotropic interactions contributed by the R and Fe sublattices. In order to distinguish between these contributions, we studied LuFe$_x$Al$_{12-x}$ with non-magnetic Lu and thus determined the properties of the Fe sublattice. In the homogeneity range $4 < x < 6$, exchange interactions and magnetic anisotropy are significantly modified.

Further we focused on compounds with "2-17" stoichiometry with hexagonal crystal structure of the Th$_2$Ni$_{17}$ type [5-12].

Er$_2$Co$_{17}$ and Tm$_2$Co$_{17}$ are ferrimagnets with rather similar magnetic properties. They have T_C = 1170 K and spontaneous magnetic moment M_s = 10.1 and 13.4 μ_B/f.u. for the Tm and Er compound, respectively. They both exhibit a large uniaxial magnetocrystalline anisotropy. We studied these compounds in detail on single crystals in ultrahigh fields (Figure 1). Both compounds exhibit field-induced transitions in vicinity of critical filed H_{cr} ~ 40 T. In Er$_2$Co$_{17}$, the transition is clearly of the first order and corresponds to sharp rotation of the Er sublattice by approx. 50 degrees with its further continuous alignment towards the collinear ferromagnet. For Tm$_2$Co$_{17}$, the transition is attributed to a direct ferri-to-ferromagnetic transformation by way of paramagnetic remagnetization of the Tm sublattice. Thus, despite the similarity of magnetic properties below 20 T, the field-induced transitions in Er$_2$Co$_{17}$ and Tm$_2$Co$_{17}$ are completely different. The crystal structure and temperature evolution of the magnetic structure of Lu$_2$Fe$_{16.5}$Ru$_{0.5}$ were studied using high resolution and high flux neutron powder diffractometers. In contrast to the parent Lu$_2$Fe$_{17}$, which transforms on cooling from AF to F state, Lu$_2$Fe$_{16.5}$Ru$_{0.5}$ is AF below 208 K down to the lowest temperatures. It transforms to F by metamagnetic transition at 1 T (at 2 K). The magnetic polarization at the Lu $L_{2,3}$, Fe K and Ru L_2 absorption edges was studied by x-ray magnetic circular dichroism (XMCD) on a single crystal of Lu$_2$Fe$_{16.5}$Ru$_{0.5}$ in a magnetic field up to 3 T, i.e., in both AF and F states. The Ru XMCD signal proves the existence of induced magnetic polarization parallel to the dominant Fe sublattice magnetization. Whereas in the R$_2$Fe$_{17-x}$Ru$_x$ (R = Y, Lu) systems F state transforms fast into AF with a field-induced metamagnetic transition, in Y$_2$Co$_{17-x}$Ru$_x$ only a monotonous decrease of magnetic characteristics is observed.

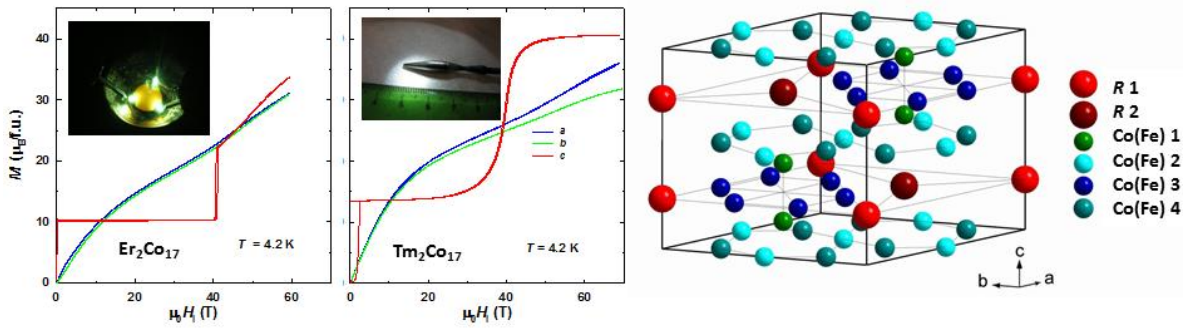


Figure 1. High-field magnetization curves of the Er_2Co_{17} and Tm_2Co_{17} compounds with the pulsed magnetic field applied along the principal crystal axes. The unit cell of the R_2Co_{17} demonstrates packing of the 4*f* and 3*d* elements in the crystal structure. The insets show a typical crystal growth by Czochralski method and the resulting ingot.

A magnetization study of a Tm_2Fe_{17} single crystal and aligned powder of the deuteride $Tm_2Fe_{17}H_{3.2}$ was carried out in steady and pulsed magnetic fields. Tm_2Fe_{17} is a ferrimagnet with T_C = 295 K and M_s = 22 μ_B/f.u. T = 4.2 K. Of particular interest are low-temperature magnetization curves along the *c* axis, which is an easy direction in Tm_2Fe_{17} and a hard direction in the deuteride [11]. We also succeeded in preparing a high-quality single-phase $Tb_2Fe_{17}H_3$ single crystal, which has the easy-axis anisotropy up to T_C = 560 K. At T = 300 K, $Tb_2Fe_{17}H_3$ has the spontaneous magnetic moment M_s of 22.5 μ_B per formula unit and anisotropy field of 2.5 T [12].

Other interesting results were obtained on single crystal of Kagome lattice $Dy_3Ru_4Al_{12}$ [13]. The onset of a long-range magnetic order of Dy moments occurs at 7 K through a first-order phase transition. The compound has a non-collinear AF structure with a propagation vector (1/2 0 1/2). The electronic specific-heat coefficient is strongly enhanced to 500 mJ/(mol K^2) taking into account the localized nature of Dy magnetism. In magnetic field $Dy_3Ru_4Al_{12}$ displays magnetization jumps along all crystallographic directions. All the metamagnetic transitions are accompanied by large positive magnetoresistance (up to 125-140%).

The most important results on uranium intermetallics are published in [14-16].

Studies of magnetic and magnetoacoustic characteristics of $UCu_{0.95}Ge$ (hexagonal structure) with AF ground state were performed on single crystals in pulsed fields up to 64 T applied along the main axes [14]. The results of our theoretical analysis within the framework of the mean-field approximation qualitatively agree with the observed behavior of magnetic and magneto-acoustic characteristics of $UCu_{0.95}Ge$. Also single crystals of UCo_2Si_2 were studied by magnetization and ultrasound measurements in pulsed fields up to 60 T and we concluded that the low-temperature changes in the sound velocity and attenuation are determined by exchange renormalization caused by the sound waves [15].

Magnetic properties of U_2Fe_3Ge (hexagonal structure, ferromagnet below T_C = 55 K) presents an exception to the Hill rule, as the nearest inter-uranium distances do not exceed 0.32 nm (it means, it should be non-magnetic). The spontaneous magnetic moment M_s = 1.0 μ_B/f.u. at T = 2 K is in the basal plane. The dominance of U in the magnetism of U_2Fe_3Ge is found by the ^{57}Fe Mössbauer spectroscopy, which indicates zero Fe moments. Crystal structure, magnetic and transport properties were studied under hydrostatic pressure. up to 27 GPa. The extrapolation indicates that the magnetic order will be completely suppressed between 3 and 4 GPa [16].

We also focused on aspects of reduced dimensions on *f*-electron systems. For the first time, we investigated of exchange bias (EB) effect in heterostructures of uranium-based antiferromagnets (UO_2 in our case) combined with ferro- (iron or permalloy) or ferrimagnets (magnetite). The anisotropy of an antiferromagnetic UO_2 (bulk Néel temperature T_N = 30.8 K) made it feasible to observe a large EB of the order of several kOe in UO_2/Fe_3O_4 bilayers [17]. Moreover, we have observed novel phenomena in the UO_2/Fe_3O_4 system, for instance, the blocking temperature, read exchange bias, above T_N of the antiferromagnet was reported for the first time. Our study revealed a complex nature of the effect: we suggested that it was provided both by strong exchange coupling between UO_2 and Fe_3O_4 and by exchange biasing

within magnetite. The work is a part of the postdoctoral project of E. Tereshina on UO_2/Fe_3O_4 multilayers. She performed magnetic measurements, participated in the XRD studies and sample preparation, interpreted the results and wrote the manuscript. Recently, the crystal structure and magnetic properties of $UO_2/Ni_{80}Fe_{20}$ (permalloy) thin film samples have been thoroughly investigated in 2014 (manuscript E. Tereshina et al., *Crystal structure and magnetic properties of UO_2/permalloy thin films* is currently under review in Thin Solid Films).

Finally, we also conducted research on multimodal magnetic carriers for biomedical theragnosis within the 7thFP project MULTIFUN (www.multifun-project.eu). The design and tuning of the particles for the proposed applications requires deep understanding of the relation of their magnetic properties to the internal crystallographic and spin structure (Figure 2), which are even strongly modified by mutual magnetic interactions. Therefore our studies were carried out with impact on limits of real systems including surface spin canting, inter-particle interactions, size distribution and collective response of nanoparticle ensembles.

For reliable classification of the spin canting, we proposed to determine the evolution of the hyperfine field with respect to the applied magnetic field by Mössbauer spectroscopy in order to obtain the complex response of the spins in individual sublattices. Finally, we have broken the myth that the spin canting is a general feature for all nanoparticles; it was recognized as negligible in highly crystalline particles with sizes larger than 6.5 nm. The investigation of the spin canting phenomena was summarized in 2 manuscripts written by the MNS members [18, 19].

Comparing results of structural and magnetic characterization, we also observed, that some level of internal particle spin and/or structural disorder is crucial for enhancement of the so-called specific absorption rate (SAR) – a measure of the particle performance in magnetic fluid hyperthermia. We introduced a model, which describes relative and absolute spin alignment within a single-domain nanoparticle, which scale the internal order to effective anisotropy (manuscript by Pacakova et al, *Universal Parameter of Spin and Structural Disorder of Single-Domain Nanoparticles for Biomedical Applications* has been recently submitted).

We also carried out systematic investigation of magnetic and structural properties of residual metal catalyst in single-wall carbon nanotubes (SWCNTs). It enabled us to decouple their magnetic response and optimize the purification procedure of the SWCNTs, which opens possibility of experimental detection of the carbon magnetic moments predicted theoretically. The investigations of the impurities in SWCNTs were summarized in several manuscripts written by the MNS members, e.g. [20,21].

We also participated on development of advanced preparation methods of monodisperse nanoparticles and multifunctional nanocomposites, mainly by characterization of magnetic properties and temperature-dependent Mössbauer spectroscopy studies under magnetic field [22, 23].

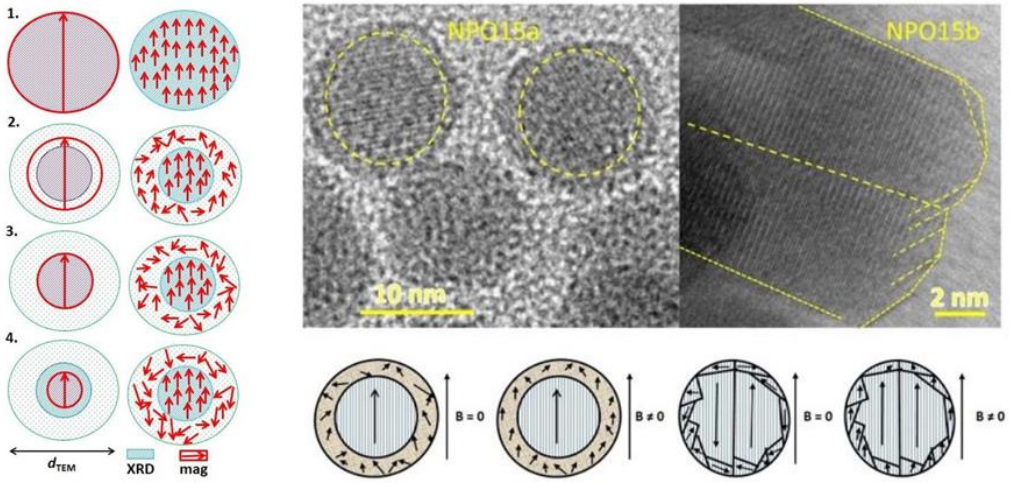


Figure 2 Illustration of the limiting cases of the internal structure of nanoparticles with particle size determined from transmission electron microscopy (TEM), X-ray diffraction (XRD) and magnetic measurements (mag). The large arrow represents the particle superspin, while the small arrows correspond to individual magnetic moments per unit cell. The figure on right represent TEM images of particles with identical TEM size, but very different XRD and magnetic sizes together with schematic response of the spin structure to the applied magnetic field.

2.3. Research on quantum turbulence and electric activity of Helium (SF group)

The research activities aimed to study a unique system where quantum effects have measurable consequences on large scales, and at applied level to contribute to the general understanding of the phenomenon of turbulence. We built a new low temperature system made up of a bellows for generating flows into channels of different dimensions, to realize flow studies which are typical of hydrodynamics, but using liquid helium instead. As a probe for these flows we use an acoustic technique where the attenuation of second sound mode existing in Helium was related to the density of vortices, *L* (Figure 3, left). Our measurements lead to a determination of *L* as a function of mean flow velocity *V*, temperature *T*, and time *t*, for turbulence decay. The first use of this apparatus was to demonstrate that the steady-state properties of the fully turbulent flow of superfluid Helium-4 in a channel are essentially the same as when the components move in opposite direction by thermal activation, i.e. Galilean invariance applies, except for some details near the transition to turbulence [24] (Figure 3, right). The temporal decay of this superflow is summarised in a manuscript, which is currently under review in Phys. Rev. B.

We then moved to studies of coflow, i.e. the simultaneous flow of superfluid and normal fluid components. The steady-state of such flow was used for a new independent determination of an important parameter of turbulent helium, i.e. its "effective viscosity" which results from the interaction of the two components [25]. In this work we also showed that quantum turbulence has an important formal equivalence with classical turbulence in terms of the scaling of the smallest dynamical scale of the system to the Reynolds number. These results were supported by numerical simulation from colleagues in Grenoble and Lyon. We studied also temporal decay of this coflow for the first time and with unprecedented accuracy, showing that the temporal scaling of vortex line density is the same as vorticity in classical homogenous turbulence [26,27].

Besides the collaboration with France [25], we participated in a program funded by a bilateral agreement of the Academy of Science of the Czech Republic with CONICET, Argentina, where we made new observations visualizing the motion of particles in the turbulent Helium flow caused by oscillating objects.

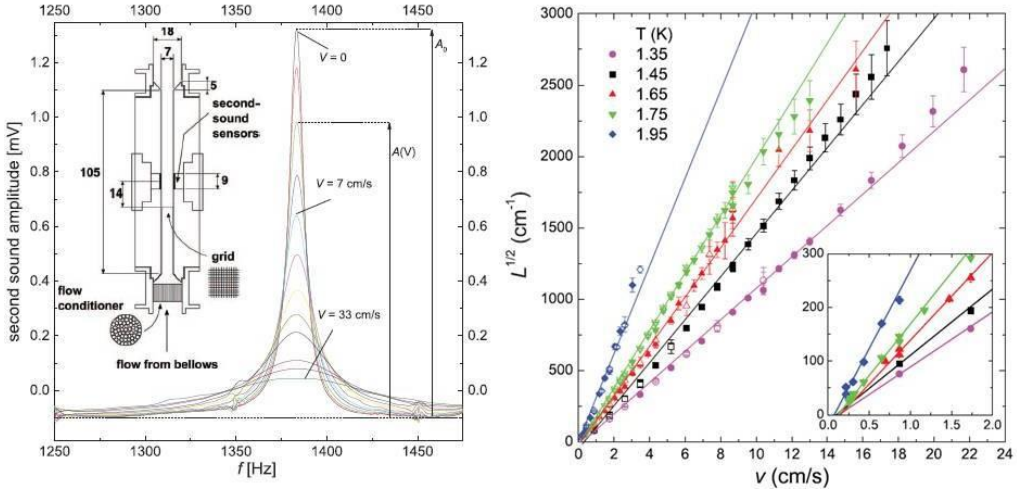


Figure 3: Apparatus for generation of the superfluid turbulence in ^{4}He together with demonstration of scaling laws for the turbulence intensity, *L*.

2.4. Novel themes profiled within the period

In order to formulate actual topics in the MNS group, we expanded our collaboration with the Department of Low-dimensional systems, Institute of Physical Chemistry JH (IPC JH) in the field of carbon nanostructures, initiated in the project *Magnetism of carbon nanostructures in the pure and doped state*. We focused on rigorous interpretation of the role of substrate on electronic structure of graphene and its modification by local variation of topography by nanoparticles. Our contribution resides in advanced characterization of the bare and decorated substrates, synthesis of modified nanoparticles and development of software for advanced analysis of Raman spectra maps [27-31]; the efforts recently resulted in a new project (described in part 3).

In the SF group, a new work on in-depth comparison of channel flows with three distinct configurations of motion of the two helium components relative to themselves and to the channel walls, with a potentially important new idea on how to determine the spatial distribution of quantum vortices, has been proposed.

2.5. Experimental facilities – status & progress

The research themes of MNS require extreme environment of low temperatures and high magnetic fields, available either in JLMS (0.3K@14T in Physical Property Measurement System, PPMS) and JLLT (^{3}He/^{4}He refrigerators, 6T cryomagnet for Mössbauer spectroscopy) or in collaboration with high field laboratories in Dresden and Kashiwa (up to 74 T). Except the PPMS devices in JLMS, various equipment for crystal and thin film growth, sample characterization (diffraction, spectroscopic and microscopic methods) and chemical synthesis is available only within external collaboration. Instrumentation for the SF activities is provided

exclusively by the partner in FMP (in spite of the fact that one of the projects is fully allocated in IP). However, thanks to collaboration and support of the Institute of Physical Chemistry JH of the AS CR, v.v.i. and FS CU, a world-wide unique magneto-Raman confocal microscope operating at two excitation energies has been set up in the PPMS 14 T in 02/2014. The system is customized for temperature-dependent and magneto-Raman studies of graphene, other 2D materials, multiferroics etc. and enables simultaneous measurements of electrical resistivity, magnetoresistance, Hall resistivity and/or electrical or electrochemical gating. In addition, reconstruction of chemical laboratory (with permission to handle uranium materials) is in progress.

2.6. Summary

The MNS team condensed in 2013 as a successor of the Department of Magnetism and Low Temperatures and currently involves 2 principal investigators, 4 scientists, 2 postdocs, 3 Ph.D. students and several technicians. In 2010 - 2014, the core research activities included studies of giant anisotropy intermetallics with *f*-electrons, nanomagnets targeting biomedical theragnosis, other magnetic nanomaterials, and quantum turbulence in superfluids. In 2010-2014, the research was supported by **9** projects, including large consortium project of the 7thFP – MULTIFUN. The MNS team is actively involved in two joint laboratories of IP and CU (JLMS and JLLT) and participates in operation of the helium liquefier. The JLMS, maintained by the MNS team, enables to study materials under combined extreme conditions in the temperature range 0.3 – 1000 K, magnetic fields up to 14 T with large spectrum of experimental methods. The MNS team has a strong link to the Dresden High Magnetic Field Laboratory, EuHIT network for turbulence and EU frontiers in biomedical applications of nanoparticles. Thanks to external collaboration and support, a world-wide unique magneto-Raman spectro-microscope has been set up in the PPMS 14 T in 02/2014. In 2010 – 2014, the team has published **94** papers **with IF** (28 with IF > 3.5, without output of J.V. et al. affiliated to CU in years 2010 - 2011).

References

[1] **D.I. Gorbunov**, **A.V. Andreev**, M.D. Kuz'min, Phys. Rev. B 86 (2012) Art. No. 024407 (8 pp.).
[2] **D.I. Gorbunov**, **A.V. Andreev**, J. Alloys Comp. 577 (2013) 203-210.
[3] **D.I. Gorbunov**, S. Yasin, **A.V. Andreev**, Y. Skourski, Z. Arnold, S. Zherlitsyn, J. Wosnitza, J. Phys.: Cond. Matter 26 (2014) Art. No. 136001 (11 pp.).
[4] **D.I. Gorbunov**, S. Yasin, **A.V. Andreev**, N.V. Mushnikov, E.V. Rosenfeld, Y. Skourski, S. Zherlitsyn, J. Wosnitza, Phys. Rev. B 89 (2014) Art. No. 2414417 (10 pp.).
[5] **E.A. Tereshina**, **A.V. Andreev**, Intermetallics 18 (2010) 641-648.
[6] **E.A. Tereshina, A.V. Andreev,** Intermetallics 18 (2010) 1205-1210.
[7] **A.V. Andreev**, M.D. Kuz'min, Y. Narumi, Y. Skourski, N.V. Kudrevatykh, K. Kindo, F. R. de Boer, J. Wosnitza, Phys. Rev. B 81 (2010) Art. No. 134429 (5 pp).
[8] **A.V. Andreev**, Y. Skourski, M.D. Kuz'min, S. Yasin, S. Zherlitsyn, R. Daou, J. Wosnitza, A. Iwasa, A. Kondo, A. Matsuo, K. Kindo, Phys. Rev. B 83 (2011) Art. No. 184422 (9 pp.).
[9] Y. Skourski, M.D. Kuz'min, **A.V. Andreev**, K.P. Skokov, J. Wosnitza, Phys. Rev. B 83 (2011) Art. No. 214420 (9 pp.).
[10] **E.A. Tereshina**, O. Isnard, A. Smekhova, **A.V. Andreev**, A. Rogalev, S. Khmelevskyi, Phys. Rev. B 89 (2014) Art. No. 094420 (10 pp.).

[11] O. Isnard, **A.V. Andreev**, M.D. Kuz'min, Y. Skourski, **D.I. Gorbunov**, J. Wosnitza, N.V. Kudrevatykh, A. Iwasa, A. Kondo, A. Matsuo, K. Kindo, Phys. Rev. B 88 (2013) Art. No. 174406 (10 pp.).
[12] **E.A. Tereshina**, H. Drulis, Y. Skourski, I.S. Tereshina, Phys. Rev. B 87 (2013) Art. No. 214425 (5 pp.).
[13] **D.I. Gorbunov**, M.S. Henriques, **A.V. Andreev**, A. Gukasov, V. Petříček, N.V. Baranov, Y. Skourski, V. Eigner, M. Paukov, J. Prokleška, A.P. Gonçalves, Phys. Rev. B 90 (2014) Art. No. 904405 (12 pp.).
[14] S. Yasin, **A.V. Andreev**, Y. Skourski, J. Wosnitza, S. Zherlitsyn, A.A. Zvyagin, Phys. Rev. B 83 (2011) Art. No. 134401 (5 pp).
[15] **A.V. Andreev**, S. Yasin, Y. Skourski, A.A. Zvyagin, S. Zherlitsyn, J. Wosnitza, Phys. Rev. B 87 (2013) Art. No. 214409 (8 pp.).
[16] M.S. Henriques, **D.I. Gorbunov**, **A.V. Andreev**, Z. Arnold, S. Surblé, S. Heathman, J.-C. Griveau, E.B. Lopes, J. Prchal, L. Havela, A.P. Gonçalves, Phys. Rev. B 89 (2014) 054407 (9 pp.).
[17] **E. A. Tereshina**, Z. Bao, L. Havela, S. Daniš, C. Kuebel, T. Gouder, R. Caciuffo, Appl. Phys. Lett. 105 (2014) 122405.
[18] **S. Burianova**, **J. Vejpravova**, P. Holec, J. Plocek, D. Niznansky, J. Appl. Phys. 110 (2011) 073902 - 073902-7.
[19] **S. Kubickova**, D. Niznansky, M. P. Morales Herrero, G. Salas, **J. Vejpravova**, Appl. Phys. Lett. 104 (2014) 223105(1) - 223105(4).
[20] **B. Bittova**, **J. Vejpravova**, M. Kalbac, **S. Burianova**, **A. Mantlikova**, S. Danis, S. Doyle, J. Phys. Chem. C 115 (35) (2011) 17303 - 17309.
[21] **B. Pacakova Bittova**, M. Kalbac, **S. Kubickova**, **A. Mantlikova**, S. Mangold, **J. Vejpravova**, Phys. Chem. Chem. Phys. 15 (2013) 5992 - 6000.
[22] **S.Kubickova**, J.Plocek, **A. Mantlikova**, **J. Vejpravova**: RSC Adv. 4 (2014) 5113 - 5121.
[23] A. Repko, D. Niznansky, **J. P. Vejpravova**, J. Nanoparticle Res. 10 (2011) 5021-5031.
[24] **S. Babuin**, M. Stammeier, E. Varga, M. Rotter, L. Skrbek, Phys Rev B 86 (2012)p 134515.
[25] **S. Babuin**, E. Varga, L. Skrbek, E. Leveque, P.-E. Roche, European Phys. Lett. 106 (2014) 24006.
[26] **S. Babuin**, E. Varga, L. Skrbek, J Low Temp Phys, 175 (2014) 324.
[27] **S. Babuin**, E. Varga, M. Stammeier, M. Rotter, L. Skrbek, J Low Temp Phys, 171 (2013) 551.
[28] V. Vales , **J. Vejpravova**, **B. Pacakova**, V. Holy, S. Bernstorff, M. Kalbac, phys. stat. solidi b 1 (2014) 1 - 6.
[29] M. Kalbac, V. Vales, **J. Vejpravova**, RSC Adv. 4 (2014) 60929 - 60935.
[30] O. Frank, **J. Vejpravova**, V. Holy, L. Kavan, M. Kalbac: Carbon 68 (2014) 440 - 451.
[31] **B. Pacakova**, **J. Vejpravova**, A. Repko, M. Kalbac, *Formation of wrinkles on graphene induced by nanoparticles: atomic force microscopy study*, arXiv:1503.08113. 2015; submitted.
[32] **J. Vejpravova**, **B. Pacakova**, J. Endres, **A. Mantlikova**, **T. Verhagen**, O. Frank, M. Kalbac, *Graphene wrinkling induced by monodisperse nanoparticles: facile control and quantification*; arXiv:1504.05495. 2015; submitted.

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Department of Dielectrics

The principal mission of the Department of Dielectrics (DD) is contributing to scientific understanding of insulating or semiconducting materials for which the frequency dependence of dielectric or conductivity function can be probed by capacitance, waveguide or optical techniques. The key research capital of the DD stems from the experience of its members with a range of experimental techniques including broad-band dielectric, infrared, time-domain THz, Raman and neutron spectroscopy and from their expertise in the physics and theory of about dozen currently studied subjects covering liquid crystals, ferroelectrics, multiferroics, piezoelectrics, low-loss materials, composites or nanostructured semiconductors.

Within the DD, the essential decisions, technical supervision and long-term research plans are realized by the **DD Head (Jiří Hlinka)** and the four experienced senior group heads: Petr Kužel – Terahertz and ultrafast spectroscopy, Vladimíra Novotná – Liquid crystals, Stanislav Kamba – Dielectric and phonon spectroscopy, Přemysl Vaněk – Ferroelectric and piezoelectric materials. Tight collaboration between these five leaders allows delegating coordination of a large portion of the actual research activities to other qualified DD members, which then act as *project principal investigators (PI)*. These internal PI's, often supported by 3–4 year funding of the Czech Science Foundation, are typically working with a group of 2–8 colleagues best suited for the particular research aim, which often implies that the team composition goes across the formal group divisions. In the end of 2014, DD operated with 31 scientists (FTE of 28.1), 7 PhD students and 3 technicians.

This flexible organization of the DD and the wide diversity of competences have allowed us maintaining parallel activity in a rich collection of subjects, often multidisciplinary, and targeting even quite challenging tasks of the fundamental research, for example tasks aimed to elucidate physical mechanisms of important material–property relationships. Most of the valid results of our research carried out in the **2010–2014 period** were published **in impacted peer-reviewed journals** (in 2010–2014, **298 articles** including **13 articles in Physical Review Letters and Nature group journals**, http://publikace.fzu.cz/indexfzu.php?odd=12&lang=en).

The priority topics and examples of outstanding results are highlighted below. Unless stated differently, all the selected **activities described here are chiefly realized within DD** and they *represent disciplines where DD is recognized as a world leader.*

Ultrafast Photoconductivity in Nanostructured Semiconductors

The ultrafast conductivity and charge transport in various semiconductor nanostructures (silicon nanowires, dye-sensitized nanoparticles, organic semiconductors, etc.) have been investigated in an effort to achieve low cost, easy

fabrication, and tunable elements for photovoltaic and optoelectronic applications (solar cells, thin-film transistors, light-emitting diodes). The microscopic mobility of carriers, which is deeply influenced by the sample morphology, plays the central role in applications and reflects the physical mechanisms of the charge transport. Nanoscale transport phenomena occurring shortly (< 1 ns) after carrier injection usually impose an upper limit on the drift mobility value. The diffusion length of carriers, $L \approx \sqrt{D/f}$, where D is the diffusion coefficient and f is the probing frequency, usually matches the characteristic dimensions of semiconductor nanoparticles (5–50 nm) if the terahertz (THz) frequencies are used. As a results, the transient THz spectroscopy permits non-contact probing of photo-carrier transport on nanometer distances with a time resolution in the range ps–ns.

During the last ten years the so-called Drude-Smith model of the charge carrier response became very popular because it was able to fit the observed complex-valued THz photoconductivity spectra in many cases. The charge carrier transport in the THz regime was then abundantly interpreted on this purely phenomenological basis without addressing the characteristic sizes of nanostructures. However, this model was frequently applied directly to the as-measured THz conductivity spectra without considering the depolarization fields developing in the structure. The Drude-Smith parameters then only serve to describe the spectral shape “by some numbers”; however, we do not believe that they provide a meaningful physical insight.

In a series of papers we proposed a new concept of analytical description and interpretation of THz conductivity spectra. This concept allows one to disentangle systematically the response function of the carriers $\mu(\omega)$ (called “microscopic mobility”) from the effect of the depolarization fields and we used this framework to interpret our experiments in various nanostructured systems. The proposed analysis involves a transformation of the incident THz probe field to the local electric field, which directly acts on charge carriers. This transformation is frequently non-linear and strongly depends on the sample morphology (percolation pathways, non-percolated parts, voids, etc.) and on the photo-carrier concentration.

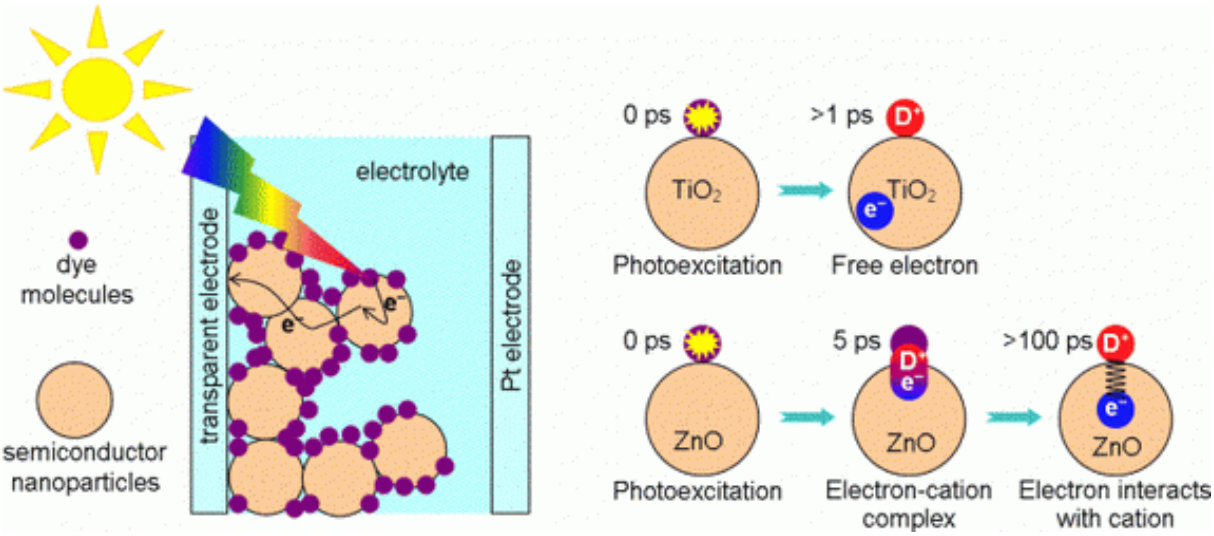


Fig. 1: *Left panel:* Scheme of a Grätzel photovoltaic cell. Incident radiation first excites dye molecules. Subsequently, the electron (e^-) is injected into a semiconductor nanoparticle and it is transported to the anode. The oxidized dye cation (D^+) is reduced by redox electrolyte. *Right panel:* In TiO_2, an electron is injected to the semiconductor nanoparticle in less than 1 ps after photoexcitation. After injection, the

electron is free to diffuse through the nanoparticle network to the electrode. In contrast, injection into ZnO occurs via an intermediate electron-cation complex in which the electron and cation are strongly bound to each other. This state is formed within 5 ps and it breaks within 100 ps. After that, the electron is released, but it remains weakly attracted by the cation which makes its transport to the electrode much slower [2].

We first developed a framework for Monte-Carlo simulations of charge carrier motion in nanostructures. This model provides us with the carrier response function based on microscopic properties: the mobility spectra are calculated using the Kubo formula from an autocorrelation function of thermal carrier velocity obtained in the simulations. Then, we stressed the requirement to complement such analysis by a suitable effective medium model [1]. Based on this approach we proposed microscopic models of the response of partly or completely localized charge carriers in a number of systems including CdS, TiO_2 and ZnO nanoparticles, in Sb-doped SnO_2 nanoparticles, and in various nanocrystalline silicon systems, see e.g. [2,3,4,5,6]. For example, in [2] we investigated dye sensitized TiO_2 and ZnO nanoparticles, which are used for Grätzel-type solar cells (Fig. 1). We discovered that in ZnO nanoparticles, where the bulk electron mobility is by more than an order of magnitude higher than in TiO_2, the initial mobility is dramatically reduced shortly after the electron injection from the photo-excited dye molecule. This is due to an electrostatic interaction of the injected electron with the dye cation. On the other hand, such an effect does not occur in TiO_2 nanoparticles owing to the screening related to the high permittivity of TiO_2.

In [5] we introduced a general model describing the effective medium effects in photo-excited nanostructured semiconductors. It is based on the Bergman representation of effective medium with a single dominant depolarization factor and it depends on three “morphological” parameters. Numerical calculations of the effective response of a large variety of structures strongly suggest that this three-parameter model can be applied to calculate the effective response in a very broad family of photoconductive structures.

Further, we solved the wave equation for the THz transient photo-induced field with an inhomogeneous current source term, which is defined by the photoconductivity issuing from the above mentioned effective medium model [6,7]. The results of our theoretical analysis compared to experiments in some nanostructured systems allow us to draw the following general conclusions. (1) The transient THz signal is determined by the transient sheet conductivity of the photo-excited sample; this quantity takes into account properly the inhomogeneity related to the in-depth variation of carrier concentration. (2) Any serious experiment must be carried out as a function of photo-carrier concentration (i.e., optical pump pulse fluence); this allows to separate effective medium effects from the local response function of carriers and to assess the sample morphology. (3) The nanocrystal size and morphology as inferred from optical measurements and from TEM do not necessarily match the morphology determined from THz experiments (item 2). Any real nanostructured sample contains a broad distribution of nanocrystals with different sizes. This distribution has to be carefully considered when comparing the THz conductivity and e.g. the optical luminescence [6]. Namely, the optical signals usually originate from small nanocrystals with strong optical confinement, whereas a long-range transport can be observed in parallel due to the presence or sparser large volume nanocrystals.

Ultra-broadband Spectroscopy of Ferroelectric Thin Films and Dielectric-Conductor Nanocomposites

One of the key opportunities in our DD is the possibility to perform dielectric spectroscopy investigations in an ultra-broad range of frequencies (1 mHz–100 THz). This is particularly useful in studying dielectric–conductor nanocomposites with concentrations of the conductive component near the percolation threshold. Examples of such systems are nanocomposites of polymers with carbon nanotubes (CNTs). A well electrically conducting CNT, due to its specific shape, enables processing composites with extremely low percolation threshold. Our colleagues in the UK [8] succeeded in preparation of well-dispersed composites of PET polymer with CNTs, which have been for the first time characterized by us (in DD, [8]) by broadband conductivity and dielectric spectroscopy, covering up to 17 orders of magnitude in frequency (10^{-4}–10^{13} Hz) from room temperature down to 5 K. We revealed the extremely low percolation threshold of 0.07 vol.% CNT as appearance of the low-frequency AC conductivity plateau (see Fig. 2a) corresponding to the DC conductivity, whose value increased with CNT concentration according to the power law with a high critical exponent of 4.3 – it is also the basis for our interpretation [8].

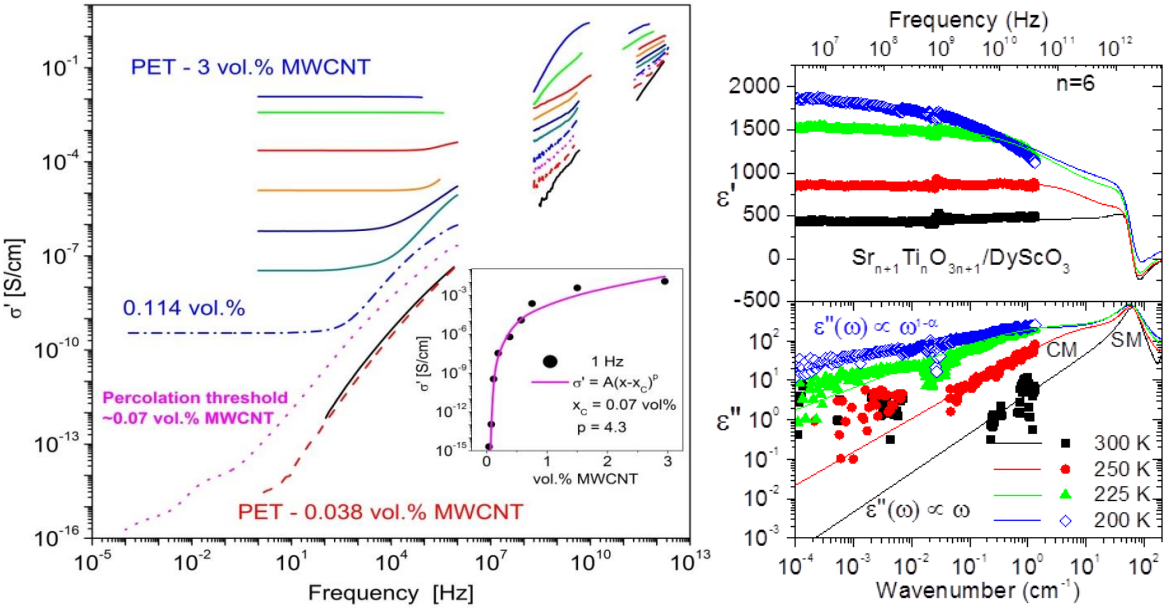


Fig. 2: *Left panel:* Room-temperature AC conductivity spectra dependent on the CNT concentration show that from the concentration of 0.114 vol.% up, CNT plateaus of low-frequency conductivity appear, which increase and broaden with the CNT concentration. The inset shows the critical power dependence of the conductivity at 1 Hz above the percolation threshold. At high frequencies the conductivity increases up to the THz range, which corresponds to the increase in localised conductivity due to the contributions of non-percolated CNT clusters [8]. *Right panel:* Complex dielectric function in $Sr_7Ti_6O_{19}$ thin film explaining the origin of microwave dielectric loss as contributions of central mode (CM) and ferroelectric soft mode (SM).

Microwave, THz and IR technique was also used for the discovery of strain-induced ferroelectric phase transition in $Sr_{n+1}Ti_nO_{3n+1}$ thin films [9] (grown by collaborators from the USA) and for our explanation of the anomalously high electric-field tunability of MW permittivity and extremely low MW dielectric loss [10].

New Liquid Crystalline Compounds with Multifunctional Character

The work of the liquid crystal group is mainly focused on structure–property relations of newly synthesized liquid crystalline compounds which are then investigated with respect to the length and/or character of chains, number of lactate units and the lateral substitutions in the molecular core. This research is carried out in a close collaboration with the Department of Chemistry of our Institute, which synthetized most of the liquid crystals studied in DD. Within the last 5 years, we studied physical properties of more than 20 homological series of liquid crystalline compounds with respect to the potential application aspect. The studied mesogenic molecules were for example rod-like, hockey-stick-like or bent-shaped ones. The asymmetry of the molecular structure was introduced by the type of the central core, by the differences in the arms, or by the orientation and the character of the linking group.

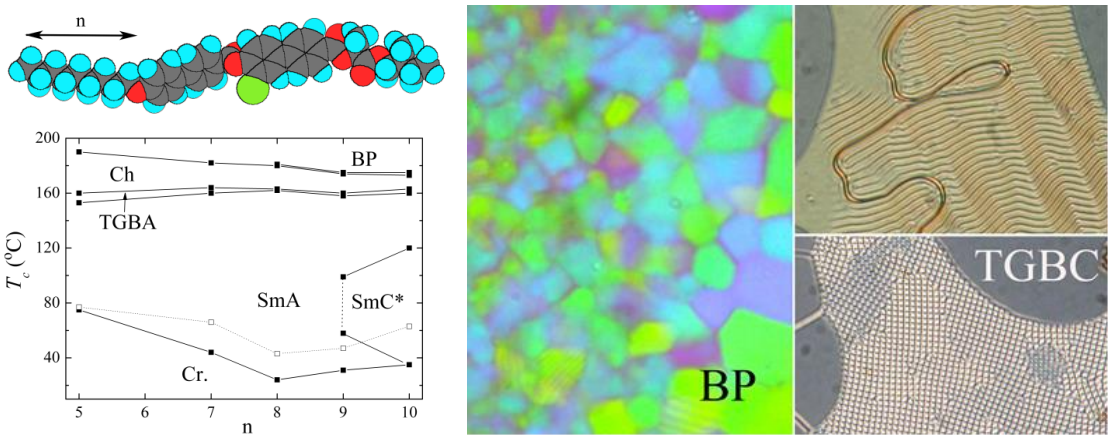


Fig. 3: *Left panel:* Liquid crystalline molecule of a compound exhibiting re-entrancy of the smectic A phase. The length of a non-chiral chain is connected with the number of carbon atoms *n*. Phase diagram shows the homologue series of lactic acid derivatives with respect to *n* [11,12]. *Right panel:* Liquid crystalline textures observed under polarizing microscope in a blue phase (BP) and at the cholesteric–TGBC phase transition [13].

An example of a new effect discovered in DD is the re-entrance of orthogonal paraelectric SmA phase below the ferroelectric tilted SmC phase accompanied with anomalies in dielectric, optical and switching properties. This unique behaviour was explained by non-monotonous temperature dependence of the principal coefficient in the free energy expansion induced by the occurrence of a lateral bulky group in the molecule. The re-entrant SmA phase can be easily influenced by electric field and it can exhibit strong electro-optic effect, which is promising for electro-optic applications [14]. Studies of binary mixtures exhibiting re-entrancy of the smectic A phase were carried out presenting a direct phase transition between A and re-entrant A phases [12].

Other kinds of unusual mesomorphic behaviours were observed in binary mixtures of liquid crystals. For example, mixtures of certain chiral and achiral mesogens produced complex phase diagrams of frustrated phases, showing interesting blue phases and smectic A and C twisted grain boundary phases (TGBA, TGBC), absent in starting compounds. We explained that the admixture of the hockey stick molecules to a chiral compound considerably changes the molecular interactions due to non-

trivial packing of both types of molecules, which have a significant impact on the mesomorphic properties as well as on macroscopic behaviour [13].

Several types of hybrid systems have been prepared by mixing of nanoparticles with liquid crystalline materials. We succeeded in preparation of a novel type of hybrid nanocomposite prepared by mixing maghemite nanoparticles and a chiral liquid crystalline compound. The multiferroic system exhibits the ferroelectricity as well as superparamagnetic properties. Among others, we were able to influence the ferroelectric properties by applying magnetic field [15]. We also studied hybrid nanocomposite made of functionalized gold nanoparticles embedded into a “de Vries” compound and proved the existence of a disordered tilt in the smectic A phase of “de Vries” type [16].

Dynamics of Polarisation Fluctuations in Relaxors and Ferroelectrics

Ferroelectrics and relaxor ferroelectrics are known for their extraordinary dielectric and electromechanical properties, widely used in industrial applications ranging from micro-capacitors and ferroelectric memories to transducers and actuators. Search for new materials, such as lead-free piezoelectrics, which should replace toxic lead-based compounds in the near future, typically requires a detailed insight in the nature of their material–property relationships. Spectral studies of polar fluctuations in these substances, and, in particular, those revealing the dynamical origin of the ferroelectric phase transitions, constitute often the most fundamental starting point for quantitative modelling or for the search of reasonable material design rules. The worldwide recognized expertise of DD in this field implies that studies of the dynamics of polarisation fluctuations remain one of our leading activities.

These tasks are particularly complex in partially disordered materials involving nanoscale structural correlations, such as relaxors. It is obvious that a full understanding of this kind of materials requires complementary experimental techniques such as inelastic neutron scattering, and therefore several members of DD are also keeping their experience with performing experiments on external large scale facilities like neutron and synchrotron sources. For example, using neutron diffuse scattering measured on a single crystal of $Sr_{0.61}Ba_{0.39}Nb_2O_6$ (uniaxial relaxor in the MHz–GHz range), we determined characteristic frequencies of polar fluctuations on the nanoscopic scale (see Fig. 4abcd). Comparison with dielectric measurements proved that these polar fluctuations are the source of giant dielectric response, whose temperature and frequency dependence is specific for relaxor ferroelectrics with glass-like ferroelectric phase transition [17].

DD is also involved in atomistic modelling. For example, we have noticed and quantitatively explained a Fano-resonance effect revealing the role of the sublattice interactions in the anomalous soft mode response of lead-free perovskite relaxor $Ba(Zr_{0.5}Ti_{0.5})O_3$ (see Ref. [18] and Fig. 4ef).

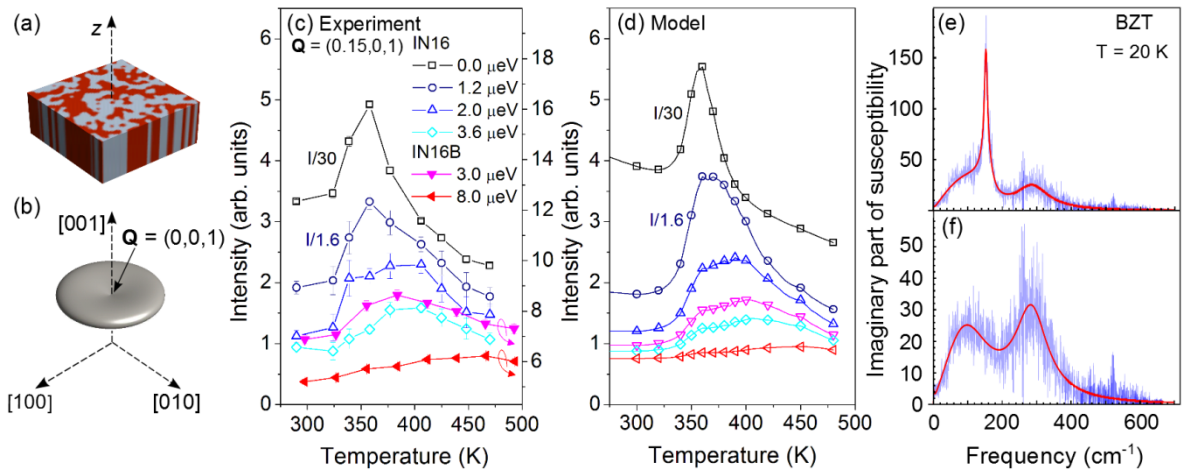


Fig. 4: (a) Typical domain structure of $Sr_{0.61}Ba_{0.39}Nb_2O_6$ relaxor ferroelectric with polar nanodomains and (b) characteristic diffuse scattering of a disk-like sample. Comparison of the temperature dependence of diffuse scattering (c) measured with neutron spectrometers at the Institut Laue Langevin (Grenoble) and (d) calculated from dielectric data for different energy transfers [17]. (e) Dielectric response of $Ba(Zr_{0.5}Ti_{0.5})O_3$ (BZT) relaxor and its part generated only by Ti ion displacements (f) (from Ref. [18]).

Single Phase Multiferroics

Strategic and successful topics of DD also involve studies of magnetoelectric materials. It is worth noting that we have been the first to demonstrate experimentally that new multiferroics with a high magnetoelectric coupling can be induced using an epitaxial strain in thin films [19]. The epitaxial films were prepared by our collaborators (USA, Spain). Our expertise consists in revealing ferroelectric phase transitions in strained ultrathin magnetic films by non-contact methods (microwaves, infrared spectroscopy). Critical temperatures in these samples are still low and their enhancement up to room temperature remains a challenge for the future. In this field we closely collaborate with theoreticians from the USA, Switzerland and Belgium.

We also study static and dynamic magnetoelectric effects in various bulk multiferroics. For example, we have used Raman spectroscopy to obtain the first experimental data of angular dispersion curves of the lattice vibrations in a model multiferroic $BiFeO_3$. This was furthermore the first experimental determination of dispersion curves using a polycrystalline material in general (see Fig. 5 [20]). This original technique developed in collaboration of DD (Raman spectroscopy expertise) and the University of Sheffield (synthesis and general characterization) also enabled us to clarify the long-standing controversy about the assignment of polar phonon modes.

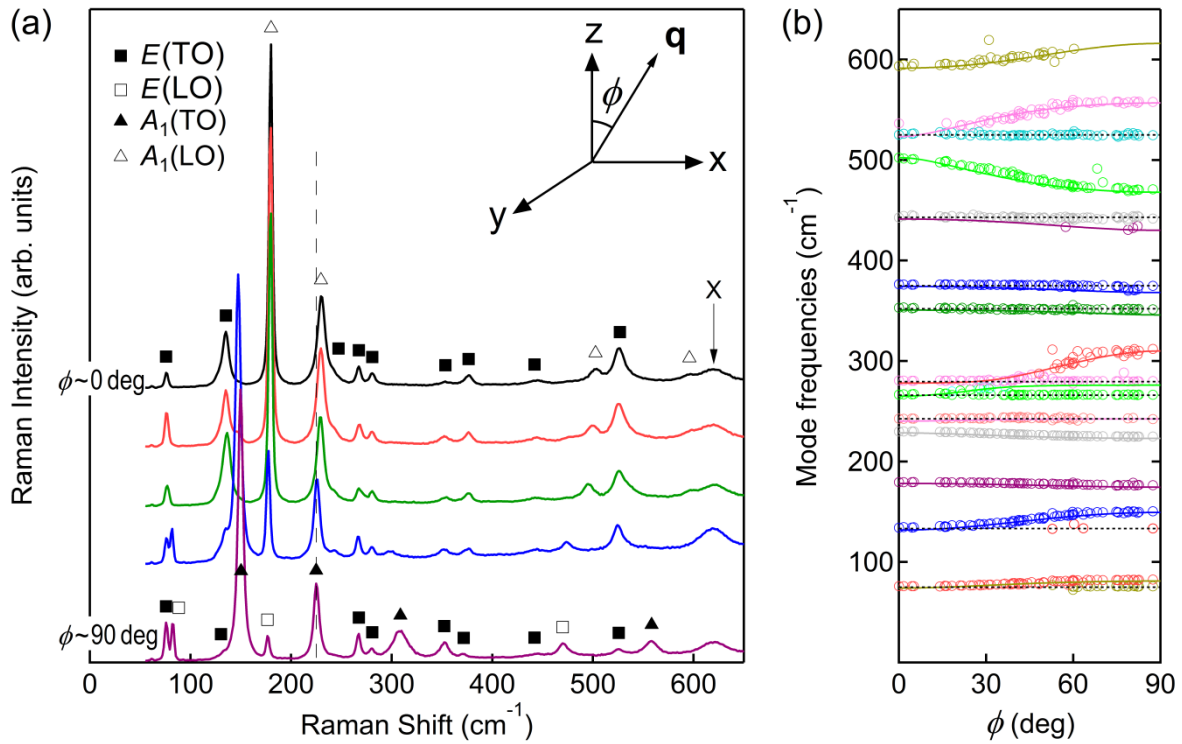


Fig. 5: Phonon spectra of multiferroic $BiFeO_3$. (a) Raman spectra from selected ceramic grains. Symbols indicate positions of the pure modes. (b) Angular phonon dispersion curves. Full lines represent oblique modes, dashed lines purely transverse E(TO) branches, open circles are frequencies determined from individual Raman spectra as a function of the angle between the phonon propagation vector and the optical axis [20].

A range of investigated multiferroic materials was prepared directly in DD (e.g. $EuTiO_3$, $Eu_{0.5}(Ba,Sr)TiO_3$, $Ca_3Mn_2O_7$, $Pb_2Fe_2O_5$, etc.) by the sol-gel technique and solid state synthesis using mechanochemical activation. Most remarkably, high purity and low electric conductivity $Eu_{0.5}Ba_{0.5}TiO_3$ ceramics were prepared and investigated in view of a search for the permanent dipole moment of the electron – see the Fig. 6 [21].

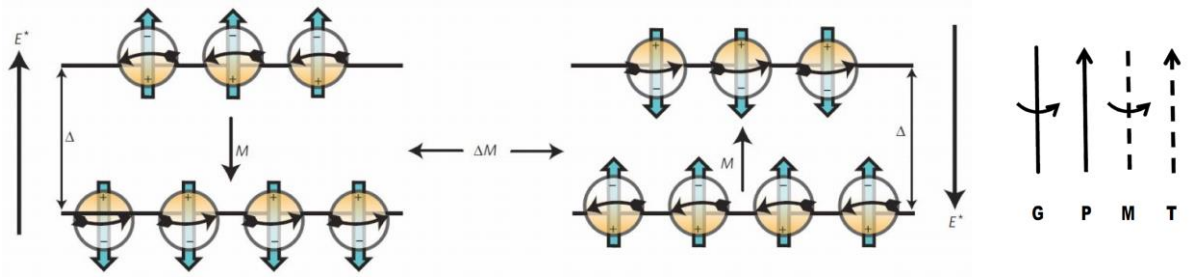


Fig. 6: *Left panel:* Scheme of the principle of measurement of a hypothetic electric dipole moment of the electron. Electric and magnetic moments of the electrons switch with switching of the electric field which leads to a change of the measured magnetization [21]. *Right panel:* Pictographs of 4 basic vectorial quantities used in the symmetry analysis of magnetoelectric phenomena in crystals [22].

Mechanism of Antiferroelectric Phase Transition

Example of a successful combined theoretical and experimental team work of DD (9 members involved) is a detailed analysis of the antiferroelectric phase transition in $PbZrO_3$ that resulted in revealing of the essential role of a coupling trilinear term involving ferroactive cation displacements and two oxygen octahedra tilt modes [23].

Domain Wall and Domain Structure Studies

Another topic strongly developed in DD during the last 5 years is the investigation of ferroelectric domain structures and domain walls. This is a fascinating subject fuelled by a collection of evidences for remarkable property variations achieved by intelligent domain engineering. Most of our results are theoretical predictions of properties related to domain walls and domain structures. Perhaps the most spectacular prediction [24] was that ferroelectric perovskites such as $BaTiO_3$ most likely support exotic domain walls, resembling Bloch walls known from ferromagnetism. Our later computer simulations based on the Ginzburg–Landau–Devonshire theory were used to study details of the phase transition between the Ising and Bloch types of a domain wall. Such a transition was predicted to appear for the 180° domain wall in the rhombohedral ferroelectric phase of $BaTiO_3$ at compressive stress of about 2 GPa [25]. We have also confirmed the hypothesis that the phase transition is of the second order and predicted corresponding divergent increase of the dielectric permittivity in the vicinity of the transition. In the case of a dense domain-wall pattern this effect can represent a substantial part of the dielectric response of the material [26]. Ferroelectric domain structures of numerous materials have been experimentally studied using piezoresponse force microscopy – see the right-hand panel of Fig. 7 [27].

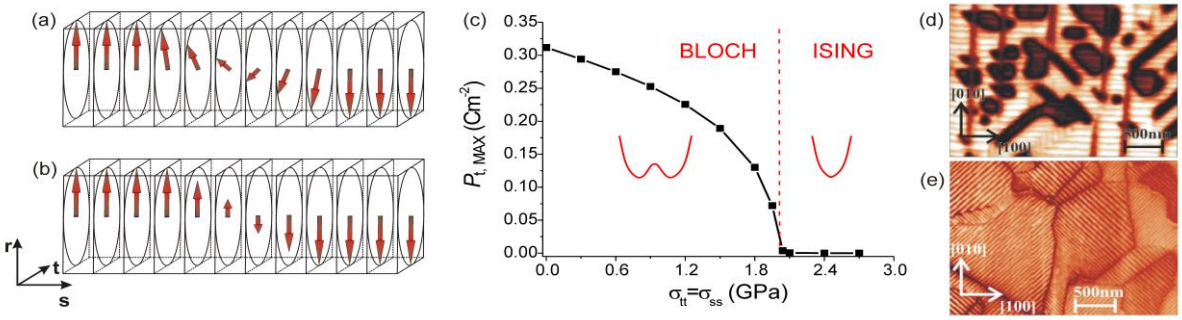


Fig. 7: *Left panel:* Variation of polarization within Bloch- and Ising-type domain walls. The Bloch-type structure (a) conserves the magnitude of the local vectorial order parameter. This is typically encountered in ferromagnetism. In contrast, the magnitude of the electric polarization can be more easily adjusted. Therefore, antiparallel walls in ferroelectrics usually correspond to the achiral Ising solution (b). *Middle panel:* Chiral order parameter. The extremal value of the polarization component in the core of the domain wall is plotted as a function of the epitaxial stress. This quantity can be taken as an order parameter of this chiral phase transition within the domain wall. For the wall under study, the phase transition is continuous and it can be associated with the Landau free-energy sketched in the Fig. [25,26]. *Right panel:* Our PFM images of thin $PbTiO_3$ films grown on (110)-oriented (d) $TbScO_3$ and (e) $SmScO_3$ single crystal substrates. $PbTiO_3$ film grown on $TbScO_3$ has preferentially $c/a/c/a$ polydomain structure, while the $PbTiO_3$ film deposited on $SmScO_3$ has $a_1/a_2/a_1/a_2$ domain pattern. The striking difference between the two domain structures is elucidated in Ref. [27].

References:

[1] H. Němec et al., J. Photochem. Photobiol. A **215**, 123–139 (2010).
[2] H. Němec et al., Phys. Rev. Lett. **104**, 197401 (2010).
[3] Z. Mics et al., Phys. Rev. B **83**, 155326 (2011).
[4] H. Němec et al., J. Phys. Chem. C **115**, 6968–6974 (2011).
[5] H. Němec et al., IEEE Trans. Terahertz Sci. Technol. **3**, 302–313 (2013).
[6] V. Zajac et al., New J. Phys. **16**, 093013 (2014).
[7] P. Kužel, and H. Němec, J. Phys. D: Appl. Phys. **47**, 374005 (2014).
[8] D. Nuzhnyy et al., Nanotechnology **24**, 055707 (2013).
[9] C. H. Lee et al., Nature **502**, 532 (2013).
[10] V. Goian et al., Phys. Rev. B **90**, 174105 (2014).
[11] V. Novotná et al., Phys. Rev. E **83**, 020701 (2011).
[12] N. Podoliak et al., Phys. Rev. E **84**, 061704 (2011).
[13] V. Novotná et al., Soft Matter **9**, 647 (2013).
[14] V. Novotná et al., J. Mater. Chem. **21**, 14807–14813 (2011).
[15] V. Novotná et al., RSC Adv. **3**, 10919 (2013).
[16] L. Lejcek et al., Phys. Rev. E **89**, 012505 (2014).
[17] P. Ondrejkovic et al., Phys. Rev. Lett. **113**, 167601 (2014).
[18] D. Wang et al., Nat. Commun. **5**, 5100 (2014).
[19] J. H. Lee et al., Nature **466**, 954 (2010).
[20] J. Hlinka et al., Phys. Rev. B **83**, 020101 (2011).
[21] K. Z. Rushchanskii et al., Nature Mat. **9**, 649 (2010).
[22] J. Hlinka, Phys. Rev. Lett. **113**, 165502 (2014).
[23] J. Hlinka, Phys. Rev. Lett. **112**, 197601 (2014).
[24] P. Marton et al., Phys. Rev. B **81**, 144125 (2010).
[25] V. Stepkova et al., J. Phys.: Condens. Matter **24**, 212201 (2012).
[26] P. Marton et al., Phase Transitions **86**, 103 (2013).
[27] F. Borodavka et al., J. Appl. Phys. **113**, 187216 (2013).

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Nanocrystals and Grain Boundaries

The team represents the scientific part of the Department of Advanced Structural Materials of the Institute of Physics, AS CR, http://www.fzu.cz/en/department/17, headed by P. Lejček (WOK: 171 publications, 1389 citations, h=19) (the other part of the Department, the Laboratory ROTAN, is the Institute's Central Laboratory providing predominantly service activity in the field of X-ray analysis).

The Ariadne's thread of our activity is the materials-science investigation of the behaviour of extended defects in metallic-based materials. This activity might be presently divided into two main directions, (i) the traditional studies of extended defects in crystallographically defined samples with focus on Grain Boundary Engineering; and (ii) the newly started studies of the role of grain boundaries in production and behaviour of ultra-fine-grained and nanocrystalline materials, mainly prepared by severe plastic deformation. Nevertheless, both these directions naturally complement each other and eventually form a base of fundamental knowledge. In this respect our activity is focused mainly on basic research and the problems are solved by both experimental and theoretical methods. Let us say that our group achieved numerous important and original results in the field of the study of extended defects which is developed in the Department for decades and is now renowned and respected in the world.

During the period 2010–2014 the team published numerous original results in impacted (60 papers) and other journals (11), and in conference proceedings (13). It also produced 1 author's monograph and 1 utility model.

In 2010–2014 the team solved numerous research projects, e.g.:

- *Multifunctional bulk metallic materials with nano- and ultra-fine-grained structure* (2008–2012, Program "Nanotechnology for Society", AS CR, KAN300100801, total amount of about 2.3 mil EUR, Cooperation with the Charles University (ChU), the Institute of Chemical Technology (ICT) and the Institute of Metals Research, Principal Investigator: P. Lejček);
- *Interface controlled properties of micro/nanocrystalline materials for advanced structural applications, biodegradable implants and hydrogen storage* (2012–2018, Grant of Excellence, Czech Science Foundation (CSF), P108/12/G044, total amount of about 2.2 mil EUR, Cooperation with ChU and ICT, Principal Investigator: P. Lejček);
- *Laboratory of Nanostructures and Nanomaterials* (2012–2016, Program of "Support for Research Infrastructures", Ministry of Education, Youth and Sport, LM2011026, total amount of about 2.3 mil EUR, Principal investigator: P. Lejček); and
- Numerous projects granted by CSF, COST actions and by ICT (for PhD students).

A. Grain boundaries and other extended defects in metallic materials (Group Head: Pavel Lejček)

I. Summary of the results in 2010–2014

The study of the extended defects has a long tradition in the Department. The main focus in the period 2010–2014 has been paid to attractive themes concerning the description of complex behaviour of (i) grain boundaries in crystallographically defined samples (bi- and tricrystals) as well as in coarse-grained polycrystals; and (ii) dislocations in intermetallic materials. The most important results are as follows:

1) Summary of the present knowledge on grain boundary segregation in metals;
2) Introduction of a new thermodynamic variable in segregation studies – segregation volume;
3) Explanation of the reversed anisotropy of grain boundary properties on basis of the enthalpy-entropy compensation effect;
4) Interpretation of the effect of stacking-fault-like interfaces on plastic deformation of B2 intermetallics;
5) Explanation of the behaviour of interfaces in disilicides, materials for applications at ultrahigh temperatures;
6) Generalization of displacive processes forming dislocations to diffusionless phase transformations.

II. The results obtained in 2010–2014

The main effort in elucidation of the role of grain boundaries (GBs) in materials properties was focussed on the structure-property relationship with the main attention paid to GB segregation of solutes, migration and corrosion and their consequences for materials behaviour. The main entry in this filed is represented by the monograph *Grain boundary segregation in metals* (Fig. 1) [13]. In this book, the fundamentals of GB segregation were summarized and documented. Besides thermodynamic description and gathered results of experimental investigation of solute segregation at individual GBs in bicrystals, non-equilibrium processes are described and the consequences of the phenomenon for material properties are also shown. This book thus representing a present overview of the phenomenon has been well accepted by the researchers in the field as it is documented by the number of citations which increases each year.

Further studies in this area were focussed on the effect of pressure and role of real behaviour of the systems on solute segregation. Chemical composition of interfaces – free surfaces and GBs – is generally described by the Langmuir-McLean segregation isotherm controlled by the Gibbs energy of segregation, or by the segregation enthalpy and entropy. In case of the segregation under pressure, new thermodynamic variable – segregation volume – must be considered. For the first time, we did define and evaluated the segregation volume for various systems. Main work published in [23] was done by P. Lejček. Additionally, we did clearly define individual contributions to the segregation enthalpy and entropy, especially the excess variables which strongly affect chemical composition of interfaces [13,22]. In this respect we modelled the effect of solute interaction on interfacial segregation and intergranular embrittlement on the basis of the combined Fowler and Rice–Wang approaches in a binary [14] and ternary [15] system using the chosen values of the standard thermodynamic parameters of interfacial segregation and varied values of the interaction coefficients. The results of this modelling clearly showed that attractive interaction strengthens interfacial segregation and substantially enhances intergranular embrittlement, while repulsive interaction exhibits an opposite effect in binary systems [14]. In ternary ones, in opposite, repulsive *I*-*J* interaction strengthens interfacial segregation of the impurity *I*, suppresses segregation of the solute *J*, and substantially enhances intergranular embrittlement. Attractive interaction exhibits the opposite effect [15]. Generally, the effect of the ternary interaction is weaker than that of the binary one. Although there are only rare experimental data in this respect, their comparison to model calculations shows a very good agreement.

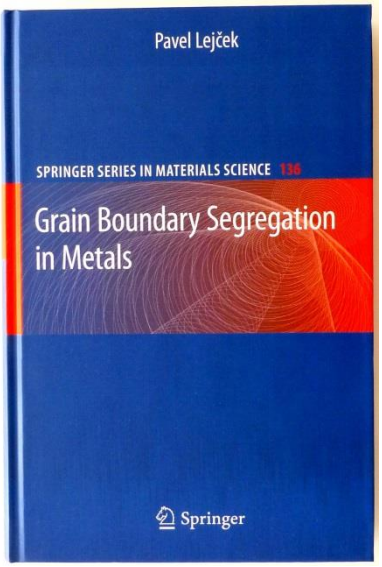


Figure 1. Cover of the book [13].

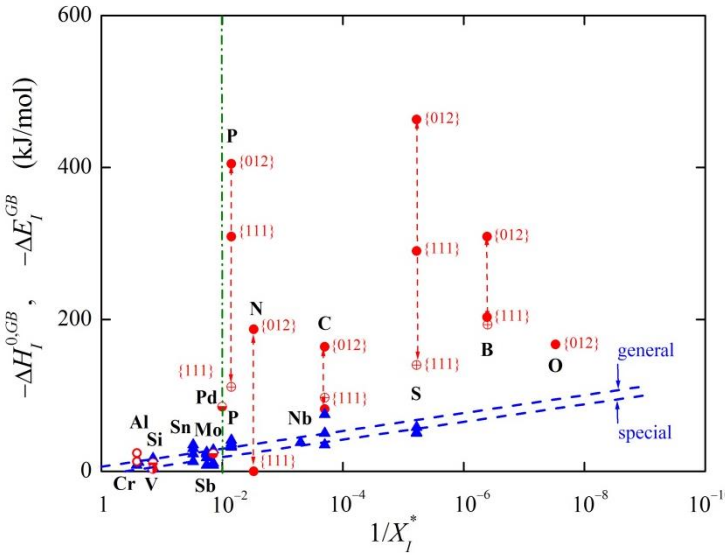


Figure 2. Energy, ΔE_I^{GB}, or enthalpy, $\Delta H_I^{0,GB}$, of GB segregation vs. reciprocal solubility, X_I^*, at 800 K for various impurities in α-Fe. Triangles: experiments, circles: DFT calculations. The blue dashed lines: predictions of $\Delta H_I^{0,GB}$ [22].

Auger electron spectroscopy (AES) study on chemistry of the 46.8°(111) twist GB of an Fe–2.3%V alloy doped by P showed an extended P enrichment but apparently independent segregation of V at temperatures in range of 500°C and 800°C. The standard enthalpy and entropy of GB segregation of P and V were determined according to the Guttmann model of multicomponent interfacial segregation. Obtained data clearly show that this boundary is special. The data also fit well with the predictive model of grain boundary segregation [13] and confirm that P segregates interstitially at the GB while V substitutes Fe atoms in the interface structure [19]: major work (sample preparation, interpretation of the results and thermodynamic calculations) was done by our team. The AES measurements were realised at IMT Ljubljana/Slovenia. Complementary fracture experiments on polycrystalline Fe–V–P alloy done at IT Brno, showed that the fracture mode is directly related to GB composition: the fracture spreads along those GBs, which contain more than 17at.% of segregated P [45]. We prepared all samples and contributed to interpretation of the segregation data.

Grain boundary migration has been widely studied in the past, however, we performed a new migration experiments under a magnetic field using Fe–3mass%Si alloy bicrystals with 36.9°[100],Σ5 coincidence-site-lattice (CSL) GB as well as on the 45°[100] general tilt GB at temperatures between 1223K and 1323K. A 6T magnetic field applied parallel to the [100] direction, which is one of easy magnetization directions, showed that magnetic field substantially increases the velocity of migration of both GBs. This means that magnetic field acts as a driving force for GB migration [49]. For this work we provided the samples and participated at interpretation of the results: all migration experiments were done in Japan.

An interesting study concerning the structure-property relationship of the GBs was performed on excavated archaeological silver objects. These objects exhibited extended intergranular degradation caused by the localised corrosion of highly Cu-segregated GBs in case of a Ag–Cu base alloy during burial for more than 1000 years in graves. (The tendency of Cu to segregate at GBs of Ag is hardly measurable experimentally but can be well deduced from the results of changed surface composition of this material [18] made on our samples at Jožef Stefan Institute in Ljubljana/Slovenia.) Detailed electron backscatter diffraction (EBSD) analysis of individual GBs showed that this corrosion degradation is controlled by the crystallography of the GBs: only the general GBs are prone to the corrosion while the special GBs are not attacked at all. We also showed that the orientation of the GB plane plays an important role in the selective corrosion attack [16]. Major part of this work was done by our

team. ICT provided us with the samples, some EBSD measurement were done at Czech Geology Service.

The goal of the experiments on growth and annealing of bi- and tricrystals of an Fe–3mass%Si model alloy intended to model the behaviour of the GBs in polycrystals: either of a free GB in a bicrystal or constrained GBs at a triple junction of a tricrystal. The results clearly show the tendency of GBs to incline to special orientations dominated mainly by the {011} and {112} planes. It supports our earlier proposal that GBs may reorient their planes during annealing and change their character from general to special [20]. Majority of this work was done by our team, some experiments and orientation determinations were done by Y. Kinoshita (and her colleagues from Kumamoto University) during her stay in our group.

We also applied nanoindentation of bi- and tricrystals to study incipient plasticity in vicinity of GBs with different character in an Fe–3mass%Si alloy. Pop-in events associated with the GBs in the load–displacement curves, their hardness and critical stresses required to propagate the yield were estimated to be in the range of approximately $\mu/400$– $\mu/130$ (μ is the shear modulus) depending on GB character: the special GBs usually had higher critical stresses than the general GBs. A Hall–Petch type relationship was found between the hardness and the distance of the indenter to the GB: its slopes were approximately one order-of-magnitude lower than the macroscopic value of those for bulk and were generally lower for general GBs than for special GBs [48]. We provided our Japanese colleagues with defined bi- and tricrystalline samples and participated at interpretation of the results.

We did also summarize numerous data on anisotropy of GB properties frequently published in literature. These data exhibit unexpectedly reverse course of structural dependence in some cases. We demonstrated that this “reversed anisotropy” of GB properties is caused by the enthalpy-entropy compensation effect and can result in serious consequences for the Grain Boundary Engineering concept for production of polycrystalline materials with optimum properties. The results of this analysis also prove unambiguously that GBs can be classified solely on the basis of well-defined thermodynamic parameters [17].

Further we found that density-functional-theory (DFT) based calculations often provide unreliable segregation energies at interfaces when the bulk solid solubility of the segregant is lower than that corresponding to one solute atom per computational repeat cell. In this case, the calculated energy of a solute in the bulk cannot be used when evaluating segregation energies. We document this problem by analysing the measured and calculated GB segregation energies in α-Fe available in literature (Fig. 2) [22]. We also thoroughly compared available experimental as well as theoretical values of the strengthening/ embrittling energy of numerous solutes at GBs in α-Fe and assessed their reliability. We did plot the strengthening/embrittling energy against the difference of corresponding sublimation enthalpies of the host and the solute as well as with regard to the position of the solute in the Periodic Table [21]. Our team made major part of the above work: other co-authors participated at discussions and finishing the manuscripts.

Finnis–Sinclair many-body interatomic potentials were applied to model the {231} type-II twin GB in orthorhombic 2H structure. All found types of configurations can be described as continuity of {121} planes, which cross the twin GB. We found that both faceted and non-faceted structures of GB are possible, but faceted structure of GB has the lowest energy [33].

The behaviour of dislocations and other extended defects was studied in complex materials such as intermetallic compounds and Si-based intermetallics. For example, the dominant slip directions in different intermetallic alloys with B2 structure are either ⟨001⟩ or ⟨111⟩. The elastic energy of ⟨111⟩ dislocations is usually significantly higher than that of ⟨001⟩ ones and it is commonly assumed that ⟨111⟩ slip occurs if ⟨111⟩ dislocations can dissociate on {110} planes into ½⟨111⟩ superpartials. However, we showed that ½⟨111⟩ anti-phase boundaries may not be metastable faults on {110} planes and the displacement vectors of metastable stacking-fault-like defects on these planes vary from material to material. This analysis involves calculations of {110} γ-surfaces for eight B2 alloys using a DFT based method. Since both ⟨111⟩ and ⟨001⟩ screw dislocations may possess non-planar cores if undissociated and will then control plastic properties analogously as ½⟨111⟩ screw dislocations in bcc metals, the

dissociations have been analysed for screw dislocations. Subsequently, we may assume that if the width of splitting in {110} planes exceeds the Burgers vector of the corresponding dislocation, the dislocation spreads in this plane and is glissile while undissociated dislocation is sessile. The ability to glide is then regarded as the determining factor for the choice of the slip direction. If no planar spreading occurs the dominant dislocations are determined by their energy. This analysis predicts the slip directions for all alloys studied and demonstrates that an interplay of elastic anisotropy, displacement vectors of metastable stacking-fault-like defects and their energies govern the choice of the slip direction in any specific B2 alloy [24]. V. Paidar made major part of the work concerning the dislocation reactions.

The slip system in FeAl at low temperatures is ⟨111⟩{110}. However, while in B2 compounds the slip plane is {110}, the slip direction is often ⟨001⟩ which is the shortest lattice vector in this structure. Differences among various B2 systems are obviously rooted in the nature of chemical bonds and it has often been assumed that it is the antiphase boundary energy that dictates the choice of the slip system. By comparing the three compounds CuZn, FeAl and CoTi we showed, however, that factors governing the choice of the slip direction are more varied. They are, in particular the elastic anisotropy, types of planar faults on {110} planes with which dislocations can dissociate and the energy of these faults that is not simply related to the order–disorder transition temperature. Analysis taking into account all these factors explains then different slip directions in FeAl and CoTi that have similar order–disorder transition temperatures and shows why in FeAl the slip system is the same as in CuZn [41]. V. Paidar made major part of the work concerning the dislocation reactions.

Recent experimental investigation of additional alloying of pseudobinary $(Mo_{1-x}Nb_x)Si_2$ showed surprisingly a similar effect of smaller and larger atoms (Cr and Zr) on the interface misfit. Nevertheless, we showed that the measured modifications of misfit at the interfaces between the $C11_b$ and C40 lattices in two-phase systems of transition metal disilicides can be in agreement with the measured or calculated values of lattice parameters of pure binary systems [42]. V. Paidar proposed the interpretation of the results obtained in Japan.

The sample shape can change during plastic deformation or in course of martensitic phase transformation. In both cases the mechanisms of atomic rearrangements are based on collective displacements of atomic aggregates. The internal structure of dislocations can be examined using the energies of generalized stacking faults displayed by so called γ-surfaces. This approach can be extended to the shuffling of atomic planes that plays a crucial role in martensitic phase transformations [40].

B. Severe plastic deformation and grain refinement processes of difficult-to-work materials (Group Head: Aleš Jäger)

I. Summary of the results in 2010–2014

One of the main scientific aims in this area was the study of grain refinement of difficult-to-work materials via severe plastic deformation (SPD) at low temperatures and subsequent elucidation of microprocesses of plastic deformation, and correlation of microstructures and properties of the processed materials. Special attention was dedicated to Mg and Mg based alloys, especially with biodegradable composition. The main effort was focused on analysis of the recrystallization processes, behaviour of both low- and high-angle grain boundaries (GBs) in ultra-fine-grained (UFG) materials, investigation of the mechanical properties, and analysis of the texture and microtexture formation. All these aspects were studied from both experimental and theoretical viewpoints. The most import results attained are:

1) Successful processing of Mg and binary Mg based alloys via equal channel angular pressing (ECAP) with back-pressure (BP) at room temperature;
2) Clarification of often observed, yet reasonably unexplained, 30° peak in the misorientation angle distribution in wrought Mg and its alloys;
3) Grain size reduction down to ~400nm in many Mg based alloys (biomedical Mg–6mass%Zn, WE43+12mass%Zn, Mg–0.3at%Y and others); and

4) Confirmation of a new double twinning mode {10−12}–{10−12} in Mg and proving of its occurrence at high temperatures.

II. The results obtained in 2010–2014

Attractiveness of Mg alloys for structural applications arises from their intrinsic properties such as low density. The main challenge in the development of Mg alloys is connected with requirement to fulfil the fundamental function of structural materials i.e. load bearing. Grain refinement of Mg alloys at temperatures below 200°C via deformation processes is a difficult task due to hcp structure. ECAP is one of the SPD techniques which can significantly refine grain size. Refined grains consequently improve (not only) mechanical properties.

Various processing routes were successfully applied to as-cast Mg during ECAP with BP at room temperature (RT). The most profound finding was high frequency of the formation of special Σ13a GBs and {10−12} twin boundaries during recrystallization at RT [6].

A Mg−3Al−1Zn (mass%; AZ31) alloy was also processed by different multi-temperature ECAP cycles down to 150°C. Shear bands were observed after ECAP finishing at temperatures of 175 and 150°C. Crystallographic analyses showed that (0001) and {11−22} planes in large elongated grains tend to be aligned parallel to the shear plane [27].

In order to explain GB formation and recrystallization during ECAP, Mg single crystals with different initial orientations were processed by single-pass at 503K [44]. The texture after ECAP was investigated and compared to texture simulations based on a visco-plastic self-consistent (VPSC) model. The results show that orientation of [0001] and ⟨10−10⟩ axes in single crystals with respect to the ECAP die geometry significantly affects activation of deformation modes and texture evolution.

ECAP processing of Mg single crystals also enabled to investigate formation of GBs from the boundary-free structure. After passing the shear plane, the {10−12} twinned microstructure was gradually fragmented via shear. Simultaneously, continuous dynamic recrystallization was observed, starting with formation of low-angle GBs with different misorientations [43]. The misorientation distribution of near-coincidence GBs that occur in magnesium single crystals during ECAP at 503K also exhibited a 30° peak. Crystallographic analysis enabled us to explain its existence by a relatively high frequency of Σ13a CSL GBs and partially by the appearance of Σ15a GBs [38]. Majority of this work was done by our team; a co-worker of Tata Steel participated at some discussions only.

To compare the results on Mg single crystals, the creep behaviour and microstructure changes were investigated in Al single crystal during ECAP [10]. Analysis showed an inhomogeneity of microstructure after ECAP and the increasing fraction of high angle GBs with increasing number of ECAP passes. It was also found that the creep behaviour is influenced by cooperative GB sliding along mesoscopic shear bands. We prepared oriented single crystals and participated in writing of the manuscript.

One of the most frequently studied Mg based alloy is AZ31 (Mg−3mass%Al−1mass%Zn alloy). ECAP processing of this material using route A at 150°C proved substantial grain refinement. Nonhomogeneous grain size distribution occurred during this process which promotes shear band formation. EBSD analysis of these shear bands revealed presence of frequent microcracks inside the material [28].

Low-angle GBs play a very important role in grain refinement of AZ31 Mg alloy at temperatures decreasing from 200°C to 150°C. Our studies revealed that low-angle GBs with misorientation angles <5° are surrounded by regions of increased strain gradients, which can stimulate the generation of non-basal slip dislocations during ECAP at temperatures of approximately 150°C [30].

To elucidate the process of the grain refinement during the ECAP of AZ31 Mg alloy, it is necessary to understand the nucleation of twins. We found that this process run at 200°C results in formation of a larger fraction of {10−12} twin boundaries in comparison to the as-rolled AZ31 material. The reason is that the preferential sites for the {10−12} twin nucleation were grain boundaries with misorientation angles ranging from 10° to 35° [31]. New {10−12}-

{10−12} double twinning mode was also proven experimentally during rolling of Mg single crystals (Fig. 3) and direct extrusion of the Mg–0.3at.%Al alloy at 433K [8].

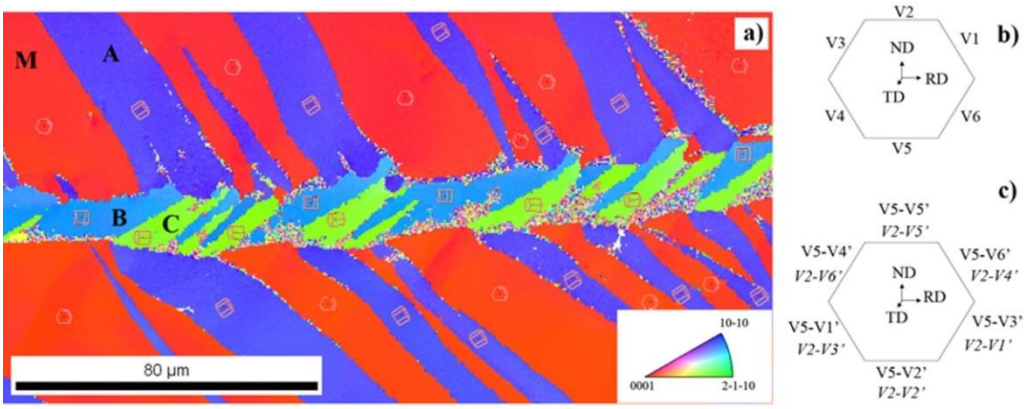


Figure 3. IPF map with superimposed hcp unit cells in the RD–ND plane of the rolled Mg single crystal. (a) Initial matrix M with primary {10−12} twins A and B, and secondary {10−12} twins C inside the primary twin B. (b) and (c) Schemas of twinning plane intersection with single-crystalline sample surface for primary twin variants V and double twin variants V', respectively. The orientations of the ND, RD and TD axes shown in hexagons are also valid for (a) [8].

To support our experimental results, we also performed several theoretical studies. Due to complex processes during SPD, VPSC model has been used to model the ECAP of Mg single crystals [39]. We developed a new misorientation scheme and included it in the model to reproduce texture, grain misorientation distribution and coincident site lattice distribution. The comparison of the model calculations with both the experimental data and the predictions of the VPSC model without grain interactions and considering a co-rotation scheme showed that our model reproduces the reality much better than traditional schemes.

Applications of VPSC model to an AZ31 alloy processed by ECAP was successfully used to reproduce a grain misorientation distribution and the distribution of CSL boundaries in the model framework. Co-rotation and a Mg misorientation scheme were employed together with the conventional VPSC model to improve its predictions [36].

As mentioned above, a 30° peak appears regularly on the misorientation angle distribution in ECAP processed metals and it has been explained by frequent occurrence of Σ13 CSL GBs in materials with hcp structure. In contrast to other works dealing only with this misorientation, we also analysed the GB *plane* distribution for these boundaries in Mg. We show that the most frequent plane in these GBs is (0001) basal plane. The experimental data obtained by stereological approach are in very good the agreement with the GB energies obtained by atomistic calculations [37].Our theoretical study was also focused on twinning in Mg. The concept of the "shuffling-dominated" mechanism of the {10−12} twinning mode in Mg calls into question about the importance of twinning dislocations. Nevertheless, this concept is still used as the basis for hypotheses concerning inclined twin GBs. In [35], we demonstrated that the effect of shear deformation cannot be neglected, even if atomic motions due to shuffling are larger than those due to shear. Consequently, a twin GB on the {10−12} plane is always expected due to strain compatibility conditions, and inclinations are possible only due to the presence of dislocations.

Recent experiments have revealed that the {10−12} twin boundaries in hcp materials are decorated by (0001)/{10−10} basal–prismatic facets. We investigated the mechanism that leads to the formation of these basal–prismatic interfaces using atomistic simulations and to carry out their stability analysis under an externally applied shear. We demonstrated that the stability of the basal–prismatic interface is a consequence of large capillary forces that are caused by differences of the energies of a perfect {10−12} twin boundary and the basal–prismatic interface [34]. In [34], A. Ostapovets simulated the interfaces and wrote the paper.

Since wrought Mg alloys possess strong basal texture which causes anisotropy of mechanical properties, we investigated the way how to benefit from this behaviour. Crystallographic analyses and calculations explain why reversible motion of twin GBs is more favourable than nucleation of other twin variants. The experiments profile wrought Mg alloys as smart materials and emphasize the importance of strong {0001} ⟨10–10⟩ texture and {10–12} twinning in obtaining the properties characteristic for smart materials [31].

In order to analyse grain refinement during industrial forming processes, coarse grained Mg–0.33mass%Al alloy was processed by direct extrusion at low temperature [7]. The extrusion remainder was analysed in three distinct zones: the cast billet, the conical zone of extrusion die, and the as-extruded rod. Complex networks of {10–12} twins produced a noticeable fragmentation even before the material reached the conical zone of the die. Twinning was followed by a continuous dynamic recrystallization that gradually changed low angle GBs to high angle ones. The Japanese co-author prepared suitable material, however, our team characterized microstructure and wrote the paper.

Influence of Zn in defect formation was investigated in Mg–Y–Nd–Zr (WE43) based alloys by positron lifetime spectroscopy combined with other techniques. While the vacancy-like defects were found in quasicrystalline WE43 with Zn, such defects were not present in in the alloy without Zn. This testifies that vacancy-like defects are associated with the quasicrystalline phase which can be created by Zn addition [3]. Our team prepared the sample, observed and interpreted microstructure in SEM.

Dynamic changes in microstructure of the superplastic UFG Al–3Mg–0.2Sc (mass%) alloy refined by ECAP were observed by in-situ transmission electron microscopy (TEM) during annealing at temperatures up to 300°C as well as during tensile deformation in order to simulate the initial stages of superplastic forming [4]. During the deformation at 300°C, high dislocation activity as well as motion of low-angle GBs was observed while high-angle GBs did not move due to the presence of Sc. However, considerable changes in the microstructure during preheating occur in Sc-free material before superplastic deformation: The apparent changes of the grain size seem to affect considerably the quantification of the superplastic deformation. The co-worker of ICT did complete the TEM measurements.

To compare the development of the microstructure of biomedical Mg–3.6Zn and Mg–3.6Zn–0.4Ca alloys (mass%), they were tested in compression at 200°C–280°C with various strain rates. Microstructure analyses showed that lower temperatures and lower strain rates initialize deformation-induced precipitation, which results in evolution of heterogeneous microstructure in the binary alloy and the addition of Ca is favourable to recrystallization occurring during the hot deformation [5]. The samples and ECAP processing was done in our laboratories, other experiments were done at ESMSE, St. Etienne, France, during the stay of M. Hradilová there.

C. Cooperation with other subjects

I) Summary of the results in 2010-2014

Integral part of a scientific work is collaboration on various problems with external subjects (i.e. out of the Department and/or Institute) and share both knowledge and instrumental background. The problems covered by this cooperation involve intermetallics, nanoparticles and thin layers. Some tasks are realised under the open-access program of the research infrastructure “Laboratory of Nanostructures and Nanomaterials” (LNSM), one part of which is our group and which is granted by the Ministry of Education, Youth and Sport (see above).

II) The main results obtained in 2010–2014

A set of $KTaO_3$ nanopowders has been prepared at 180°C using various aliphatic alcohols and water as solvents. Pronounced connection between the solvent type and $KTaO_3$ structures was found. Microstructure analysis has shown that the solvent dielectric constant ε is an important critical parameter [25]. Electron Paramagnetic Resonance and Nuclear Magnetic

Resonance spectra were used to determine defects and to tailor nanoparticles structure and crystallization processes based on solvothermal- and citrate sol–gel-grown (CSGG) $SrTiO_3$:Cr(0.1%) crystalline nanopowders [2]. Electron microscopy inspection of cubic perovskite $SrTi_{1-x}Mn_xO_3$ nanopowders of particles sizes of 10–80nm with x=0–0.5, which is much higher than the conventionally believed Mn incorporation limit, proved the potential of the citrate sol–gel method for their successful synthesis [47].

We cooperated on fabrication and characterization of amorphous Si (a-Si) thin layers by means of bombardment of a Si(100) surface using monoenergetic C60 cluster ions with energies ranging from 50keV to 400keV [12], and on physical interpretation of the F-band origin based on the results of an experimental study, in which we combined temperature (4K–296K), temporally (picosecond resolution) and spectrally resolved luminescence spectroscopy of free-standing oxide-passivated Si nanocrystals [32].

Deposition of nanocrystalline diamond (NCD) over large areas is of high interest for industrial applications. For instance NCD is an excellent substrate for cell growth but it is also interesting for photonic applications associated with nitrogen-vacancy centres. Using detail electron microscopy analyses we substantially contributed to characterization of materials and interpretation of the results in cases of preparation of ultra NCD (UNCD) type of morphology upon N_2 addition to H_2–CO_2–CH_4 plasmas at low pressures (0.3mbar) and low temperature (520°C) [9], B-doped NCD layers grown over large areas (up to 50cm×30cm) and at low substrate temperatures (<650°C) using microwave plasma enhanced linear antenna chemical vapour deposition apparatus (MW-LA-PECVD) [46], a series of NCD films were deposited by custom made MW-LA-PECVD apparatus with linear antenna delivery at different substrate temperatures and frequencies in a hydrogen rich working gas mixture of H_2–CO_2–CH_4 [26], B-doped NCD and crystalline silicon solar cell (c-Si SC) heterostructure designed for direct photoelectrochemical water splitting application [1] and a 300nm thick polycrystalline diamond layer has been used for protection of Zr alloy nuclear fuel cladding against undesirable oxidation with no loss of chemical stability and preservation of its functionality [11].

In the above works (Part C), our team participated at preparation of samples for electron microscopy (e.g. by focussed ion beam), conducted TEM and SEM investigations of the structures and cooperate during preparation of manuscripts.

References

(The authors of the Team are written in red)

1. P. Ashcheulov, M. Kusko, F. Fendrych, A. Poruba, A. Taylor, A. Jäger, L. Fekete, I. Kraus, I. Kratochvílová, *phys. stat. sol. a* **211** (2014) 2347–2352.
2. I. Bykov, M. Makarova, V. Trepakov, A. Dejneka, L. Yurchenko, A. Jäger, L. Jastrabik, *phys. status solidi b* **250** (2013) 821–824.
3. J. Čížek, M. Vlček, B. Smola, I. Stulíková, I. Procházka, R. Kužel, A. Jäger, P. Lejček, *Scripta Mater.* **66** (2012) 630–633.
4. K. Dám, P. Lejček, A. Michalcová, *Mater. Charact.* **76** (2013) 69–75.
5. M. Hradilová, F. Montheillet, A. Fraczkiewicz, Ch. Desrayaud, P. Lejček, *Mat. Sci. Eng. A* **580** (2013) 217–226.
6. A. Jäger, V. Gärtnerová, *Philos. Mag. Lett.* **92** (2012) 384–390.
7. A. Jäger, V. Gärtnerová, T. Mukai, *Mater. Charact.* **93** (2014) 102–109.
8. A. Jäger, A. Ostapovets, P. Molnár, P. Lejček, *Philos. Mag. Lett.* **91** (2011) 537–544.
9. M. Jakl Krečmarová, V. Petrák, A. Taylor, K. J. Sankaran, I-Nan Lin, A. Jäger, V. Gärtnerová, L. Fekete, J. Drahokoupil, F. Laufek, J. Vacík, P. Hubík, V. Mortet, M. Nesládek, *phys. stat. sol. a* **211** (2014) 2296–2301.
10. P. Král, J. Dvořák, P. Šedá, A. Jäger, V. Sklenička, *Rev. Adv. Mater. Sci.* **31** (2012) 138–144.
11. I. Kratochvílová, R. Škoda, J. Škarohlíd, P. Ashcheulov, A. Jäger, J. Racek, A. Taylor and L. Shao, *J. Mater. Process. Technol.* **214** (2014) 2600–2605.

12. V. Lavrentiev, V.Vorliček, A.Dejneka, D. Chvostova, A. Jäger, J. Vacik, L. Jastrabik, H. Naramoto, K. Narumi, *Vacuum* **98** (2013) 49–55.
13. P. Lejček, *Grain Boundary Segregation in Metals* (Springer, Berlin, 2010).
14. P. Lejček, *J. Mater. Sci.* **48** (2013) 2574–2580.
15. P. Lejček, *J. Mater. Sci.* **48** (2013) 4965–4972.
16. P. Lejček, V. Gärtnerová, A. Jäger, J. Vaníčková, J. Děd, J. Haloda, *Surf. Interface Anal.* **43** (2010) 1128–1133.
17. P. Lejček, A. Jäger, V. Gärtnerová, *Acta Mater.* **58** (2010) 1930–1937.
18. P. Lejček, J. Kovač, J. Vaníčková, J. Děd, Z. Samardžija, A. Zalar, *Surf. Interface Anal.* **42** (2010) 662–665.
19. P. Lejček, J. Pokluda, P. Šandera, J. Horníková, M. Jenko, *Surface Sci.* **606** (2012) 258–262.
20. P. Lejček, P. Šedá, Yu Kinoshita, V. Yardley, A. Jäger, S. Tsurekawa, *J. Mater. Sci.* **47** (2012) 5106–5113.
21. P. Lejček, M. Šob, *J. Mater. Sci.* **49** (2014) 2477–2482.
22. P. Lejček, M. Šob, V. Paidar, V. Vitek, *Scripta Mater.* **68** (2013) 547–550.
23. P. Lejček, L. Zheng, S. Hofmann, M. Šob, *Entropy* **16** (2014) 1462–1484.
24. Yi-Shen Lin, M. Čák, V. Paidar, V. Vitek, *Acta Mater.* **60** (2012) 881–888.
25. M. Makarova, P. Bykov, J. Drahokoupil, M. Čerňanský, Z. Dlabáček, A. Dejneka, L. Jastrabik, V. Trepakov, *Mater. Res. Bull*. **47** (2012) 1768–1773.
26. J. Mistrik, P. Janicek, A. Taylor, F. Fendrych, L. Fekete, A. Jäger, M. Nesladek, *Thin Solid Films* **571** (2014) 230–237.
27. P. Molnár, A. Jäger, *Philos. Mag.* **93** (2013) 3612–3626.
28. P. Molnár, A. Jäger, P. Lejček, *Acta Phys. Polon. A* **122** (2012) 461–464.
29. P. Molnár, A. Jäger, P. Lejček, *Scripta Mater.* **67** (2012) 467–470.
30. P. Molnár, A. Jäger, P. Lejček, *J. Mater. Sci.* **47** (2012) 3265–3271.
31. P. Molnár, A. Ostapovets, A. Jäger, *Mater. Design* **56** (2014) 509–516.
32. L. Ondič, K. Kůsová, M. Ziegler, L. Fekete, V. Gärtnerová, V. Cháb, V. Holý, O. Cibulka, K. Herynková, M. Gallart, P. Gilliot, B. Honerlage, I. Pelant, *Nanoscale* **6** (2014) 3837–3845.
33. A. Ostapovets, *Comput. Mater. Sci.* **49** (2010) 882–887.
34. A. Ostapovets, R. Gröger, *Model. Simul. Mater. Sci. Eng.* **22** (2014) 025015–025025.
35. A. Ostapovets, P. Molnár, *Scripta Mater.* **69** (2013) 287–290.
36. A. Ostapovets, P. Molnár, A. Jäger, *J. Mater. Sci.* **48** (2013) 2123–2134.
37. A. Ostapovets, P. Molnár, P. Lejček, *Mater. Lett.* **137** (2014) 102–105.
38. A. Ostapovets, P. Šedá, A. Jäger, P. Lejček, *Scripta Mater.* **64** (2011) 470–473.
39. A. Ostapovets, P. Šedá, A. Jäger, P. Lejček, *Int. J. Plast.* **29** (2012) 1–12.
40. V. Paidar, *Prog. Mater. Sci.* **56** (2011) 841–851.
41. V. Paidar, Yi-Shen Lin, M. Čák, V. Vitek, *Intermetallics* **18** (2010) 1285–1287.
42. V. Paidar, T. Nakano, *J. Alloy. Compd.* **607** (2014) 48–49.
43. P. Šedá, A. Jäger, P. Lejček, P.R. Triguero, *Philos. Mag.* **94** (2014) 1095–1111.
44. P. Šedá, A. Ostapovets, A. Jäger, P. Lejček, *Philos. Mag.* **92** (2012) 1223–1237.
45. P. Šandera, J. Pokluda, J. Horníková, B. Vlach, P. Lejček, M. Jenko, *Eng. Fract. Mech.* **77** (2010) 385–392.
46. A. Taylor, L. Fekete, P. Hubík, A. Jager, P. Janíček, V. Mortet, J. Mistrík, J. Vacík, *Diam. Relat. Mater.* **47** (2014) 27–34.
47. V. Trepakov, M. Makarova, O. Stupakov, E.A. Tereshina, J. Drahokoupil, M. Čerňanský, Z. Potůček, F. Borodavka, V. Valvoda, A. Lynnyk, A. Jäger, L. Jastrabik, A. Dejneka, *Mater. Chem. Phys.* **143** (2014) 570–577.
48. S. Tsurekawa, Y. Chihara, K. Tashima, S. Ii, P. Lejček, *J. Mater. Sci.* **49** (2014) 4698–4704.
49. S. Tsurekawa, K. Inoue, P. Lejček, *ISIJ Int.* **50** (2010) 591–595.

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Nanodiamond and Biointerfaces

Team overview

The research team **Nanodiamond and Biointerfaces (head as.prof. I. Kratochvílová** [1-4,6,9-11,14-16,19-22]**, author of the Report)** was created by merging two existing research teams from the **Department of Functional Materials** of the **Institute of Physics of the AS CR (FZÚ) – Materials for Nanosystems and Biointerfaces (MNB)** (head Dr. V. Mortet [5,13,18]) and **Physical Properties of Biomaterials Research (PPB)** (head as.prof. I. Kratochvílová). There are strong links between the scientific activities of both groups (MNB, PPB) based on the common characterisation techniques, technology equipment, projects, publications and patents [1-9, 14-16,19,20,22]. The team **Nanodiamond and Biointerfaces** (next labelled as team) combines variety of theoretical approaches and experimental techniques to explore the interaction between physical and chemical state of the nanomaterials[1,2,3] (particularly diamond [4-9]) and biomaterials for innovative applications[3,6,19-22].

Team laboratory is equipped with world unique facility: the low temperature linear antenna microwave plasma enhanced chemical vapour deposition (LA-MW-PECVD) reactor over general curved material surfaces is a unique technology developed jointly by prof. M. Nesládek[1,2,4,5,7,8,10], Dr. M. Lier[4], Dr. F. Fendrych[1,4] and A. Taylor[4,5] in 2009-12. At the same time, as. prof. I Kratochvílová and prof. M. Nesládek begun to investigate nanodiamond particles as optical markers for cellular imaging[1,2] and drug delivery complexes with liposomes[3,6]. Variety of new materials properties were explored in research projects. This is

---

[1] Petráková, A. J. Taylor, I. Kratochvílová, F. Fendrych, J. Vacík, J. Kučka, J. Štursa, P. Cígler, M. Ledvina, A. Fišerová, P. Kneppo, M. Nesládek, Adv. Funct. Mater. 22 (2012) 812

[2] Irena Kratochvílová, Alexander Kovalenko, František Fendrych, Vladimíra Petráková, Stanislav Záliš, Miloš Nesládek, J. Mater. Chem. (2011) 21, 18248

[3] **Josef Mašek,** Eliška Bartheldyová, Pavlína Turánek-Knotigová, Michaela Skrabalová, Zina Korvasová, Jana Plocková, Stěpán Koudelka, Petra Skodová, Pavel Kulich, Michal Křupka, Milada Horynová, Irena Kratochvílová, Andrew D Miller, Daniel Zýka, Jaroslav Michálek, Jana Vrbková, Marek Sebela, Miroslav Ledvina, Milan Raška, Jaroslav Turánek, Journal of Controlled Release (2011) 151, 193

[4] Frantisek Fendrych, Andrew Taylor, Ladislav Peksa, Irena Kratochvilova, Jan Vlcek, Vladimira Rezacova, Vaclav Petrak, Zdenek Kluiber, Ladislav Fekete, Michael Liehr and Milos Nesladek: J. Phys. D: Appl. Phys. (2010) 43 , 374018

[5] Andrew Taylor , Ladislav Fekete, Pavel Hubík, Aleš Jäger, Petr Janíček, Vincent Mortet, Jan Mistrík, Jiří Vacík Diamond and Related Materials (2014) 47, 27

[6] Josef Mašek, Eliška Bartheldyová, Zina Korvasová, Michaela Škrabalová, Štepán Koudelka, Pavel Kulich, Irena Kratochvílová, Andrew D. Miller, Miroslav Ledvina, Milan Raška, Jaroslav Turanek, Analytical Biochemistry (2011) 408, 95

where the high level team publications[1-6,7,8] and patents[9,22] come from. Since 2013, the team actively participates in the SAFMAT/ FUNBIO laboratory established in FZÚ to promote interdisciplinary research of interfaces among anorganic and organic materials involving physics, materials science, engineering and medicine. During the 2010-2014 period 3 PhD. students finished their doctoral thesis under leadership of the team members (prof. M. Nesládek, as.prof. I. Kratochvílová, Dr. F. Fendrych). At the end of 2014, team consisted of 4 full time scientists, 3 part-time scientists, 5 Ph.D. students and 2 technicians. Excellent research results of the team were published in top journals[1-6], highly cited, presented in the media and appreciated by the Czech society (nomination for Czech head 2014, award **Cooperation of the Year 2014)**. Also, Czech and European patents were filled[9]. Team cooperate with universities (Czech Republic, Belgium, USA), research institutes (Institute of Organic Chemistry and Biochemistry AS CR, J. Heyrovský Institute of Physical Chemistry AS CR, Institue of Macromolecular Chemistry AS CR, Nuclear Physics Institute, Veterinary Research Institute, large French research institutes LAAS and IEMN), and also industrial partners (Westinghouse, VÚHŽ a.s., Preciosa Team, ČZ a.s, Fill Factory s,r.o., ISCARE).

Key Persons:

As. prof. I. Kratochvilová[1-4,6,9-11,14-16,19-23] obtained experience with nanosystems during post-doc position at the Penn State University studying charge carrier transport through various materials, cooperated with teams from Penn State University, Rice University and Yale University. Her original publications[10,11] had strong impact.

Prof. Miloš Nesládek [1,**2,4-8,**12,**13**] came from the Institute for Materials Research, Hasselt University, Belgium as internationally recognized expert in carbon/diamond materials.

A.Taylor [4,5] that had been working for the leading international diamond company DeBeers from Great Britain joined the team in 2009. His expertise enabled important and fundamental diamond knowledge and technical support for chemical vapour deposition (CVD) apparatus.

Dr. Vincent Mortet [**5,**13,**18**] from France joined the team as an expert in CVD diamond synthesis and applications. He had been working in this research field in the Institute for Materials Research, Hasselt, Belgium for more than 7 years and at the Laboratoire d'analyse et d'Architecture des Systems, Toulouse, France, for 3 years. His work in team is supported by Purkyně Fellowship.

Dr. František Fendrych[**1**,4] and **Dr. Ladislav Peksa** [4], are deeply skilled and experienced in plasma CVD and ultra high vacuum apparatus constructions.

---

[7] Janssens, S.D. - Pobeidinskas, P. - Vacík, Jiří - Petráková, Vladimíra - Ruttens, B. - D´Haen, J. - Nesládek, M. - Haenen, K. Wagner, P. New Journal of Physics (2011) 13, 083008

[8] Havlík, Jan ; Petráková, Vladimíra ; Řehoř, Ivan ; Petrák, Václav ; Gulka, Michal ; Štursa, Jan ; Kučka, Jan ; Ráliš, Jan ; Rendler, T. ; Lee, S. Y. ; Reuter, R. ; Wrachtrup, J. ; Ledvina, Miroslav ; Nesládek, M. ; Cígler, Petr. Nanoscale (2013) 5, 3208

[9] Czech patent 305059 :Layer protecting the surface of zirconium alloys used in nuclear reactors
EU patent Layer for protecting surface of zirconium alloys, Patent Number: WO2015039636-A1

[10] J. K. N. Mbindyo, T. E. Mallouk, J. B. Mattzela, I. Kratochvílová, B. Razavi, T. N. Jackson, and T. S. Mayer: "", Journal of American Chemical Society (2002) **124**, 4020

[11] I. Kratochvílová , M. Kočiřík, A. Zambova, J. Mbindyo, T. E. Mallouk, and T. S. Mayer: Journal of Materials Chemistry (2002) **12**, 2927

[12] Lim Candy Haley Yi Xuan , Sorkin Anastassia , Bao Qiaoliang , Li Ang , Zhang Kai; Nesladek Milos; Loh Kian Ping, Nature Communications (2013) 4, 1556

[13] V. Mortet, O. Elmazria, M. Nesladek, M. B. Assouar, G. Vanhoyland, J. D'Haen, M. D'Olieslaeger and P. Alnot Appl. Phys. Lett. (2002) 81, 1720

Excellent results:

- Worldwide unique device **LA MW PECVD reactor was constructed** – this fact together with high-level experts makes the team excellent in nanodiamond area – beside high level research[4,5,14,15](protective polycrystalline diamond layers, photoelectrochemical cells for water splitting, sensors) team also cooperate with industrial partners (Solartech, Precioza, Fill Factory s,r.o., Westinghouse[15]) Czech and EU patents have been filed[9].
- **Nanodiamond particles as optical markers for cellular imaging** - a novel method for remote monitoring of chemical processes in biological environments was found and represents an important contribution to understending the nanodiamond luminiscence phenomenon[1,2,7,8]. Paper[1] was selected to **A Contribution in II Pillar Board by Czech Council for Research, Development and Innvovation**. **The whole work** attracted significant attention in media.
- Based on **theoretical modelling and analysis** of the drugs/vaccine complexes a new recombinant vaccine **against Lyme boreliosis** was prepared[3,6] and certified[22]. Due to these excellent results, as. prof. I. Kratochvílová and her colleagues were nominated for prestigious award Česká hlava 2014 (Czech Head 2014) and obtained award **Cooperation of the Year 2014**.

Research overview

Team members focused on preparation, characterization, and functionalization of

A. ***Polycrystalline diamond films*** for photoelectrochemical cells for water splitting, anticorrosion protection of zirconium alloys in nuclear reactors, MEMs devices and sensors.
B. ***Materials for bio applications*** such as intracellular markers, vaccines (nanodiamond particles, liposomes), protection of cells under extremely low temperatures (anti-freeze proteins), biosensors based on DNA charge transfer.

A.Polycrystalline diamond films

Using specific technology and analytical methods team is able to prepare and investigate different forms of diamond: nanocrystalline/polycrystalline and microcrystalline diamond layers and nanodiamond particles - Fig. 1. These materials were prepared in pure form or doped (e.g. Boron, Phosphorous and Nitrogen).

[14] P. Ashcheulov, J. Sebera, A. Kovalenko , V. Petrak, F. Fendrych, M. Nesladek, A. Taylor , Z. Vlckova Zivcova, O. Frank, L. Kavan , M. Dracinsky, P. Hubik, J. Vacik, I. Kraus , and I. Kratochvilova, Eur. Phys. J. B (2013) 86: 443

[15] I. Kratochvílová, R. Škoda, J. Škarohlíd, P. Ashcheulov, A. Jäger, J. Racek, A. Taylor and L. Shao, J. Mater. Process. Technol. (2014) 214, 2600

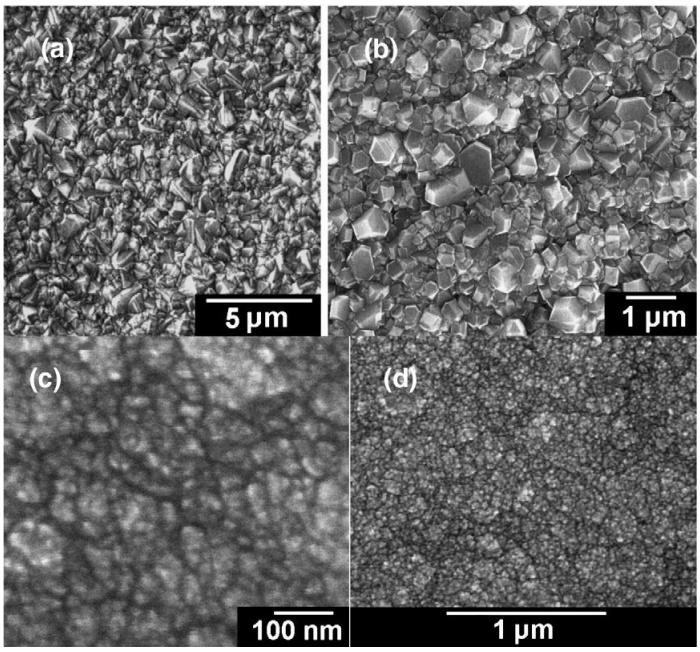


Fig. 1 SEM top view images of the surface of the three types of diamond film (a) microcrystalline diamond, (b) nanocrystalline diamond with grain sizes ~ 100-500 nm, (c) and (d) nanocrystalline diamond with grain sizes 20-100 nm.

A.1 Doped nano-crystalline and epitaxial diamond layers for photovoltaic applications

In order to realize the optimal diamond electrode performance on substrates with large area, a careful optimization of synthesis conditions was done to produce highly conductive layers with low impurity level. New surface modifications of diamond were investigated for their potential application in novel photo-electrochemical solar cells. Boron doped nano-crystalline diamond from low boron concentration with semiconducting properties to very high concentration with metallic conduction have been prepared as well as high quality epitaxial layer on (100) oriented substrates without surface defects.

Boron-doped nanocrystalline diamond coated silicon solar cells were prepared for direct photoelectrochemical water splitting. Photoelectrochemical (PEC) cells for water splitting can offer a potentially inexpensive route for molecular hydrogen fuel generation. In the frame of such applications, nanocrystalline diamond has a potential to be utilized in PEC systems as a protective and electrically active coating for water oxidation. Boron-doped diamond electrodes were responsible for water decomposition, i.e. oxygen generation and electrochemical degradation of environmental pollutants, whilst commercial crystalline Si solar cell is integrated as an efficient light absorber to drive the water splitting reaction without an external load from the electricity grid. Furthermore, cathodic production of molecular hydrogen during water decomposition enables use of solar fuel to power the electrolysis when the solar energy is in deficiency (Fig. 2).

The significance of such a concept is that it presents economically attractive, decentralized and viable resources of hydrogen fuel energy from water electrolysis by utilizing abundant and low cost materials. The goal was to identify the properties of diamond films suitable for PEC application and to reveal the influence of diamond deposition process on the quality of silicon solar cells. Work was supported by project MATCON – EU FP7-PEOPLE-ITN-2008, PITN-GA-2009-238201, Marie Curie Initial Training Networks, Materials and Interfaces for Energy Conversion and Storage and done by PhD. student P. Ashcheulov,

advisor as.prof. I. Kratochvílová and Dr. F. Fendrych in cooperation with company Solartech a.s. (Dr. A. Poruba).

In[16] team demonstrated the possibility of replacing indium tin oxide (ITO) with heavily boron-doped diamond (BDD). Plasma Enhanced Chemically Vapor Deposited BDDs layers containing various boron concentrations were prepared. The dependence of the above-mentioned parameters on the optical and electrical properties of each BDD was studied. Bulk-heterojunction polymer-fullerene organic solar cells were fabricated to test the potency of BDD application in photovoltaic devices. The obtained results demonstrated the possibility of the aforementioned application. Even though the efficiency of BDD-based devices is lower compared to those using regular ITO-based architecture, the relevant issues were explained.

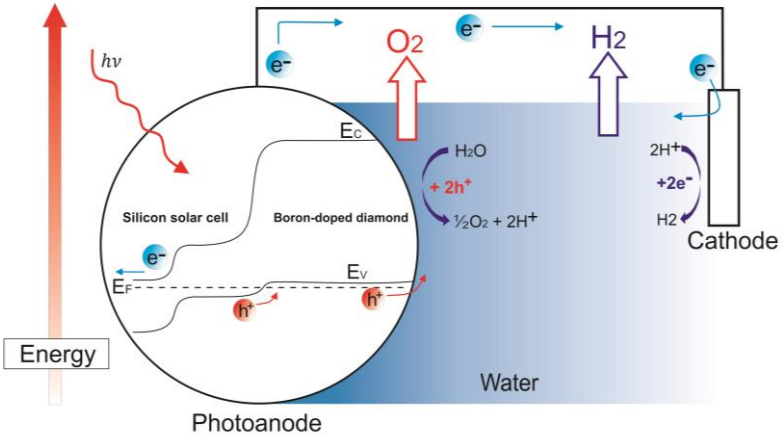


Fig. 2 Schematic representation of the water splitting system based on Si solar cell equipped with boron-doped diamond electrode deposited on the p-side of the Si solar cell with closed circuit on the externally wired cathode.

A.2 Polycrystalline diamond layer for protection of zirconium alloys for nuclear reactors

A polycrystalline diamond layer was used for protection of zirconium alloy nuclear fuel cladding against undesirable oxidation with no loss of chemical stability and preservation of its functionality [9,15]. Deposition of polycrystalline diamond layer was carried out using LA-MW PECVD apparatus. In our recent work we demonstrated success: 300 nm composite polycrystalline diamond layer with high crystalline diamond content and low roughness can protect zirconium alloys nuclear fuel cladding against undesirable oxidation and consolidate its chemical stability while preserving its functionality. After ion beam irradiation (10 dpa, 3 MeV Fe^{2+}) the diamond film still showed satisfactory structural integrity with both sp^3 and sp^2 carbon phases[9,15] (cooperation with Texas A&M University, Department of Nuclear Engineering TAMU-3133, U.S.A.). The zirconium alloys under the carbon-based protective layer after hot steam oxidation test (1100 °C, 30 min) differed from the original zirconium alloy's material composition only very slightly - the diamond coating increases the material resistance towards high temperature oxidation by forming a protective composite structure. We also found that the

[16] Petr Ashcheulov, Martin Kusko, František Fendrych, Aleš Poruba, Andrew Taylor, Aleš Jäger, Ladislav Fekete, Ivo Kraus, and Irena Kratochvílová, Phys. Status Solidi A,(2014) 211, 2347

presence of the PCD coating blocks hydrogen diffusion into the Zr surface and protects Zr material from degradation. By more closely monitoring the oxidation rate and phase change of PCD coated Zircaloy2 fuel cell rods as a function of temperature, we found that even at temperatures above 850 °C (Zr beta phase which is more opened for oxygen/hydrogen diffusion) Zircaloy2 surface could be effectively protected against hot steam corrosion. PCD anticorrosion protection of Zircaloy nuclear fuel rods can significantly prolong life of Zr material in nuclear reactors even above phase transition temperatures.

This investigation is currently supported by TACR project TA04020156 in cooperation with Westinghouse co and Faculty of Mechanical Engineering Czech Technical University in Prague and published in [15] and patented[9].

A.3 Nanodiamond films for MEMs devices and sensors

Recently, team begun with development of two important microfabrications processes which are necessary for the realization of diamond based MEMS: diamond etching by reactive ion etching and lithography using recently acquired laser writer with submicrometre resolution. In this frame, low temperature deposition conditions (< 500°C) of nanocrystaline diamond have been optimized to be compatible with substrates a piezoelectric quartz crystals and IC circuits. Theoretical study of shear horizontal surface acoustic wave sensor have been carried out and first diamond based surface acoustic wave sensors have been prepared[17,18]

A.4 Theory

Modelling of nanodiamond particles, molecules for organic electronics, parts of vaccination constructs, DNA, RNA by ab-initio quantum chemistry methods[19,20,21] - Density Functional Theory (DFT) and density-functional based tight-binding methods (DFTB) - Gaussian 09, Turbomole 6.3 program packages and molecular dynamics. Modelling was performed by team member Dr J. Šebera and PhD. student A. Kovalenko, Researchers focused on deep study of the connection between geometry, molecular orbitals, charge distribution, and charge transport conditions (molecules for organic electronics, DNA) or conditions for light absorption/emission in nanodiamnond particles[2] (PhD. thesis of Mgr. A. Kovalenko). Based on DFT modelling vaccine complexes against Lyme boreliosis were prepared[3,6] and certified.

[17] A. Talbi et al. “Simulations, fabrication and characterization of diamond coated Love wave SAW sensors” Submitted to Physica Status Solidi A

[18] Kirsch P; Assouar M.B., Elmazria O., Mortet V., Alnot P., **APPLIED PHYSICS LETTERS (2006)** 88, 223504

[19] I. Kratochvílová, J. Šebera, P. Ashcheulov, M. Golan, M. Ledvina, J. Míčová, F. Mravec, A. Kovalenko, D. Zverev, B. Yavkin, S. Orlinskii, S. Záliš, A. Fišerová, J. Richter, L. Šefc and J. Turánek J. Phys. Chem. C (2014) 43 25245

[20] I. Kratochvílová, M. Golan, M. Vala, M. Špérová, M. Weiter, O. Páv, J. Šebera, I. Rosenberg, V. Sychrovský,Y. Tanaka and F. M. Bickelhaupt J. Phys. Chem. B (2014) 22 5374

[21] Irena Kratochvílová, Martin Vala, Martin Weiter, Miroslava Špérová, Bohdan Schneider, Ondřej Páv, Jakub Šebera, Ivan Rosenberg and Vladimír Sychrovský, Biophysical Chemistry (2013) 180 127

B.Materials for biomedical applications

B.1 Nanodiamond particles for biological applications

Nanodiamond particles (ND) adjusted for application in optically-traceable intracellular nanodiamond sensors were investigated. Theoretical and experimental study of specific optical properties of high-pressure high-temperature nanodiamonds containing NV^- and NV^0 centers was performed. ND particles with a size range of 5 – 100 nm can serve as a new type of optical marker for cellular imaging (see Fig. 3). Strong ND photoluminescence originates from single photon producing nitrogen-vacancy (NV) color centers consisting of a substitutional nitrogen atom next to a vacancy, engineered artificially in the diamond lattice. High biocompatibility, variable size ranging from ~ 5 nm, stable luminescence from its color centers and simple carbon chemistry for biomolecule grafting make nanodiamond particles an attractive alternative to molecular dyes for drug-delivery.

Team presented[1] a principle of a novel method that can be used for remote monitoring of chemical processes in biological environment based on color changes from photo-luminescent NV centers in ND. We proposed to drive the NV luminescence chemically, by altering the surface chemical potential by atoms and molecules interacting with the diamond surface (PhD. thesis of excellent student ing. V. Petráková). The results of this research were published in high-impacted scientific journals [1,2,7,8] and attracted significant attention.

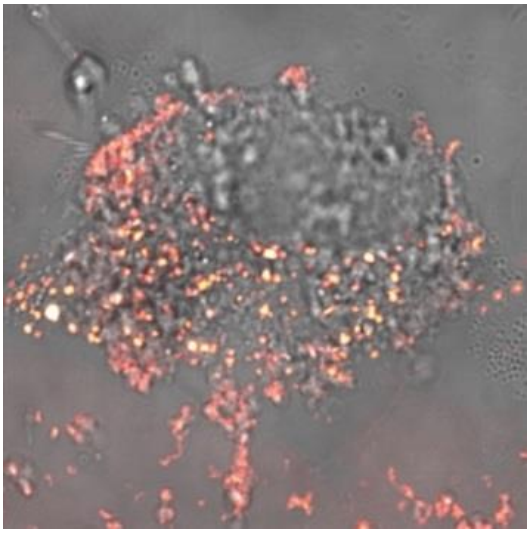


Fig. 3 Confocal microscopy analyses of localization of fluorescence nanodiamonds in HeLa cells. The image shows numerous clusters of ND particles within the cytoplasm, clearly demonstrating the absence of any particles within the nucleus.

B.2 Liposomes– drug carriers, vaccines

The team has participated in a national cooperation of academic and industrial groups from medicine, biology, chemistry and physics focusing on excellent investigation of recombinant vaccines and biocompatible drug carriers. Team from FZÚ made theoretical modelling of complexes (finding stable systems) and made selected analyzis of the final construct. A technology for preparation of corpuscular immunogens was discovered and certified. Corpuscular immunogens involve liposomal carrier, molecular adjuvants and antigen structures. At present, clinical evaluation of a liposomal recombinant vaccine against Lyme boreliosis combined with lipophilic derivatives of norAbuMDP/GMDP is under way on animals.

Safety and induction of immune response has been demonstrated. Excellent research results were publish in high impacted journals[3,6] and finally were successfully completed by

filing a national patent application. Discovery of the new vaccine against Lyme borreliosis[22] was widely presented in the media and highly appreciated by the Czech society.

B.3 Charge transfer DNA sensors

Based on team previous theoretical and experimental works on charge transfer through nanosystems containing biomolecules (DNA, RNA) we focus on charge transfer DNA sensors [20,21]. The ability of oligonucleotides to mediate charge transfer is the basis of novel molecular devices and plays a role in the processes of sensing and/or repair of molecular damage. Charge transfer through these molecules has been investigated by various theoretical (DFT, molecular dynamics) and experimental techniques – AFM, STM, time dependent/steady state fluorescence spectroscopy. DNA sensor could detect BRCA1 DNA. Both theory and experiment were done in the team[20,21].

B.4 Study of cryopreservated biological material

In 2013 we started (M. Golan, PhD. student, as.prof. I. Kratochvílová, advisor) with new topic: investigation of selected physical and chemical parameters (temperature, chemical composition of cell media) on biomolecules (DNA, RNA) and living cells. The state of the biological material was analysed using Raman spectroscopy, Scanning Differential Calorimetry and both standard and innovative biological methods. In particular, team focused on description of selected solutions (standard and novel cryoprotectants) phase change/ freezing (melting). The influence of cultivation and method of achieving extremely low temperature (-196 C) on the condition of cells was studied. In the scope of this work team strongly cooperate with 1 Faculty of Medicine and Faculty of Mathematics and Physics, Charles Univesity in Prague, University of Wyoming, USA and centers of reproduction medicine ISCARE, Arletta.

Awards

As. prof. I. Kratochviíová obtained award **Cooperation of the Year 2014** for the project "**Recombinant Vaccine against Lyme Borreliosis"** and was nominated for the prestigious award Česká hlava 2014.

Dr. V. Petráková obtained Price for perfect results in study and science work, 2013

Mgr. M. Golan obtained the **Price for the best work of young authors in the field of spectroscopy**, 2013

Excellent GACR project P304/10/1951 GA CR "*Nanoliposomes for development of recombinant vaccines and targetted immunotherapeutics*", 2014

Projects

Team members were responsible persons/leaders of 15 Czech and European projects.

Selected European projects:

2011-2013 DINAMO – EU FP7, KBBE-2009-3-6-01, EU FP7 *Development of Diamond Intercellular NAnoprobes for Oncogen Transformation Dynamics MOnitorig in Living Cells*

2009-2012 MATCON – EU FP7-PEOPLE-ITN-2008, PITN-GA-2009-238201, Marie Curie Initial Training Networks (ITN), *Materials and Interfaces for Energy Conversion and Storage*

[22] Czech patent PV 2014-320 Polyepitope recombinat vaccines for protection against Lyme borreliosis in human and veterinar medicine

2006-2010 COST, 137, MŠMT *Charge carrier transport in molecular solids and nanodevices*

Technical equipment

The team possesses world unique capabilities to deposit microcrystalline / nanocrystalline diamond layers at low temperature and over large areas by microwave plasma enhanced chemical vapour deposition – Fig. 4.. Low temperature NCD deposition uses linear antenna MW PECVD reactor with optimized doped and un-doped NCD layer properties (see Fig. 1). This technology can open many new applications due to large surface and low temperature of deposition as well as outstanding properties of the deposited diamond layer. Linear antenna MW PECVD offers many advantages over classical resonance cavity based **LA MW PECVD** systems, which require high growth temperatures (>600°C) and are fundamentally restricted in deposition area due to the incoming MW frequency and cavity design. Our system is not restricted by the incoming MW frequency and therefore can produce diamond (typically NCD) uniformly over large areas.

Another major difference compared with other classical MW PECVD techniques is the use of high-frequency pulsed microwaves, which due to nonlinear absorption enables an increase in the plasma concentration and thus maximizes growth rates and material quality. In addition to the aforementioned differentiating factors, the system operates at much lower pressures (<1mBar). When all the above factors are coupled together with a well-tuned chemistry, diamond growth at temperatures down to 150°C is enabled. The ability to deposit diamond at such low temperatures opens up the possible range of substrates which can be deposited on - such as plastics, which in a standard MW PECVD system is not possible. Also, due to the diffuse nature of the plasma, 3D objects can be coated. The system also allows the creation of oxygen and hydrogen plasmas for functionalization of diamond substrates that are important for diamond surface bio-functionalization (PhD. thesis of student ing. J. Vlček).

Another CVD reactor installed in the laboratory is the **Seki Technotron AX5010** Microwave Plasma CVD Reactor System. This commercially available 1.5 kW CVD reactor is used for the growth of high quality intrinsic and doped diamond films. The reactor is capable of producing nanocrystalline and microcrystalline diamond layers on a variety of substrates as well as monocrystalline diamond. The system also allows the creation of oxygen and hydrogen plasmas for functionalization of diamond substrates.

Atomic Force Microscopes (Bruker Dimension Icon and NT-NDT Ntegra Prima) enable 3D visualization of surfaces at the nanometre scale. AFM was used to study diamond layers, nanodiamond particles, liposomes and also living cells. Statistical methods were developed within the team, allowing evaluation of grain sizes of nanocrystalline layers or the number and size of nanoparticles. In addition to morphological studies the apparatus is also used to study conductive surfaces via scanning tunnelling microscopy, magnetic measurements and work function measurements.

Sample characterization is carried out not only within the team (AFM) but also in cooperation with other teams of FZÚ and other institutions. Typical techniques employed are: scanning and transmission electron microscopy, ellipsometry, neutron depth profiling, electrical transport measurements, Raman spectroscopy, photoluminescence spectroscopy, X-Ray diffraction, confocal microscope, electro-chemical spectroscopy and analysis.

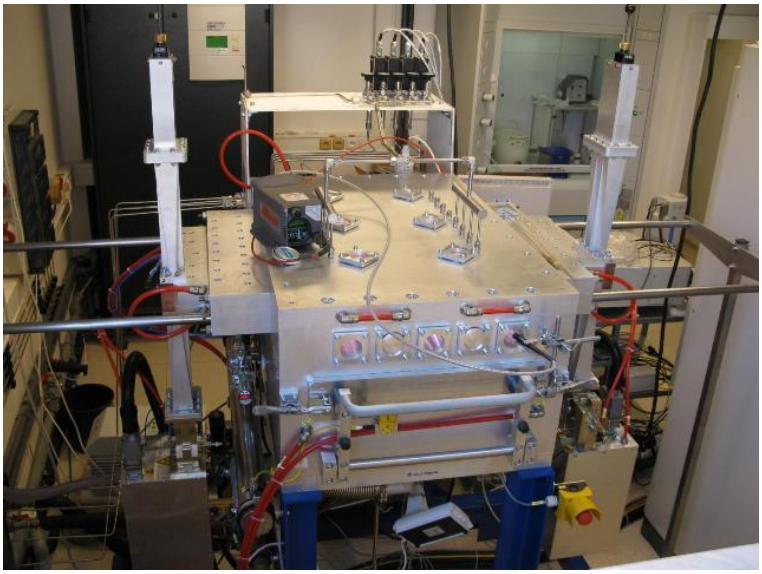


Fig. 4 Linear antenna microwave plasma enhanced chemical vapour deposition apparatus.

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Shape memory alloys and composites

Team overview

The research team **Shape memory alloys and composites** comprises two existing research groups from the ***Department of Functional Materials /OFM/*** of the **Institute of Physics of the Czech Academy of Sciences /FZÚ/** involved in the research of martensitic transformations /MT/ and shape memory alloys /SMA/. The research groups are the ***Functional Materials and Composites /FMC/*** (19 members, group leader **Luděk Heller**) and ***Magnetic Shape Memory Materials /MSM/*** (16 members, group leader **Oleg Heczko**). Both groups were established in 2009 together with the newly created department OFM. The staff of 35 group members currently consists of 12 scientists, 6 engineers, 2 technicians, 8 PhD students and 7 undergraduate students.

P. Šittner, the leader of the research team (WOK: 144 publications, 1710 citations, h-index=25), has been working in the SMA field since 1991, worked as research associate at Mie University Japan for 3 years, founded the FMC group together with V. Novák in 2005-10 within the Department of Metals. Currently, P. Šittner is the head of the Department of Functional Materials, vice director of the FZÚ and member of the group FMC. He lead the FZÚ team in 8 European projects, gave over 25 keynote/invited lectures at international conferences, is an associated editor of the Shape Memory and Superelasticity journal, member of international advisory committees of series of international conferences in materials physics and engineering fields ESOMAT, SMST, THERMEC, EUROMAT and CIMTEC, organized two major conferences in the field of martensitic transformations ESOMAT 2009 and SMST 2013 in Prague and several SMA symposia at international congresses.

Research activities of the FMC and MSM groups are planned and supervised independently by their group leaders, who bear responsibility for the results. The groups run independent experimental facilities, organize independent meetings and train students separately. They, however, share some experimental facilities, collaborate in research projects as well as organize jointly conferences and workshops. More information on the team activities can be found on the department website.

Genesis of the team

Department of Functional Materials, where the FMC and MSM groups belong to, was created in 2009 as a completely new research department of the FZÚ from mostly young researchers working on the FP6 European projects in the Department of Metals (see list of past international projects) supplemented with a newly created team of M. Nesládek, who returned from Belgium to start nanodiamond research in FZÚ and won several research grants for that. At present, 52 OFM staff members are organized within 4 research groups (FMC (19, L.Heller), MSM (16, O. Heczko), MNB (8, V.Mortet) and PPB (8, I. Kratochvílová)) dealing with different research topics mutually linked together by the idea of active functionality imprinted to the solids on the structural level. Since 2009, OFM researchers have built 5 new laboratories, moved to the new office and laboratory space and published over 170 publications in impacted journals. Experimental equipment was purchased partially using the budget of the projects (FP6 projects, Nanotechnology CAS project) and institutional budget. Department website, regularly updated by the group leaders, plays a central role in the management of the department and provides update information on staff, research topics, students, projects, patents, publications, conferences and news.

The FMC research group (6 scientists / 4 engineers / 5 PhD students / 4 undergraduate students) has formed gradually during the 2004-9 period mainly from young researchers (D. Vokoun), postdocs (L. Heller, I. Stachiv) and students (J. Pilch, S. Sedláková) who returned from abroad to join the team for working on the FP6 projects. L. Heller who joined FZÚ in 2004 as a postdoc who just finished PhD in LMARC Besancon in France, has been leading the FMC group since 2009. Senior researchers V. Novák and N. Zárubová left the group in 2011 and 2013, respectively. Later on, young engineers (D. Dostálová, J. Kadeřávek, M. Lamač) joined the group. Electron microscopist B. Bartova has been

staying for a long time in CERN. One competition for a postdoc position was organised in 2012 and won by J. Racek, who joined the team as a corrosion specialist to work on the newly launched research of superelastic fatigue of NiTi stent in biofluids.

The history of the MSM group (6 scientists / 2 engineers / 2 technicians / 3 PhD students / 3 undergraduate students) is closely related with activities of O. Heczko, who joined FZÚ as an experienced researcher (h-index=27) after returning to CR after 10 years in Finland and Germany. He was awarded Purkyně fellowship in 2008 and since that time he has gradually built his research team. In 2012, J. Kopeček, experienced metallurgist, who had returned from 2 years postdoc stay in Holland, joined the group. He has built technology lab, installed modern FIB-SEM electron microscope and, currently, he is building electron microscopy team within the SAFMAT laboratory (L. Klimša,A.Lančok). Later in 2014, in frame of the FZÚ reorganization having nothing to do with the OFM department, three senior scientists I. Tomáš, J Kadlecová and M. Jirsa (see figure) one postdoc (O. Perevertov) and one young engineer (M. Rameš) joined the group with their complementary expertise in magnetic NDT and superconductivity.

Research overview

Research activities of the team focus mainly on characterization and exploitation of unique properties of functional materials derived from martensitic phase transformations, particularly SMAs. The research covers theoretical studies [8,15,18], experimental characterization of physical properties [2,5-7,9,14,17,19], modelling of thermomechanical behaviors [15] and development of engineering applications [28].

As concerns phenomena, we have studied martensitic transformations [4,13,15], multiferroic effects combining ferro-elasticity and (ferro)magnetism [3,9,11,16], effect of stress on magnetic properties of ferromagnetic materials [12,44,45], magnetic interactions for functional materials [3,13], and magnetic high-Tc superconductive materials [1].

As concerns materials, we have investigated mainly superelastic NiTi SMAs for applications in medical devices and actuators for automotive and aerospace applications [5-7,20-22, 26, 30-32], Ni-Mn-Ga non-stoichiometric single crystals exhibiting MSM [3,4,9-11, 16,17], functional hybrid textiles with NiTi filaments [23], metal-polymers composites or electroactive polymers combined with NiTi sheets, filaments and textiles.

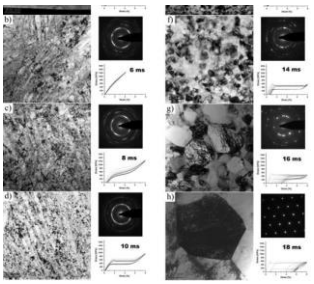
As concerns experimental methods, we have applied heat treatments to modify microstructures and functional properties of NiTi filaments [5,7,27], carried out wide range of thermomechanical testing using commercial as well as selfdesigned equipment [6,7], characterized physical properties [18,19], microstructures [5], and deformation processes [6] in those exciting materials. Since the unique functionalities of SMAs derive from mobile interfaces created by martensitic transformation, we have developed dedicated in-situ experimental methods, particularly in-situ X-ray [7] and neutron [25] diffraction, in-situ TEM straining of thin foils [2,14,17,29], in-situ SEM studies under thermomechanical loading [21], in-situ electric resistometry [5], in-situ electrochemical studies [21] during mechanical fatigue in liquids or digital image correlation mapping of surface strains during thermomechanical loads.

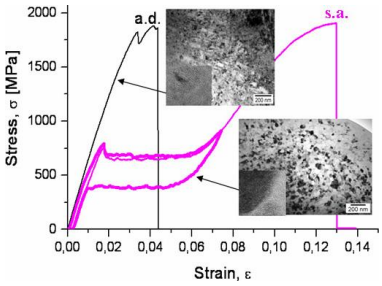
As concerns theory and modelling, we have calculated elastic moduli [18], magnetic forces between arrays of cylindrical permanent magnets [8], developed constitutive models of thermomechanical behaviour of SMAs [15, 24,31], numerically implemented these models into FE codes to simulate real components [20,22] and to design structures and/or composites [23,28] built from functional materials.

As concerns practical applications of our results, the area of smart engineering materials is a good example of the field in which oriented research in physics, materials and mechanics easilz finds engineering applications. We have collaborated with industrial partners on the development of range of engineering applications of functional materials, particularly with the Czech company ELLA-CS on development of braided NiTi esophageal stents [20], German company ITV-DITF Denkendorf on medical device-stentgraft, NiTi producers Fort Wayne Metals and SAES Getters on thin NiTi wire processing and with Czech producer of firefighter equipment THS Poličká on the design of SMA springs for thermostatic valves, US company DSI on the adaptation of the Gleeble simulator for ESS.

Research Results

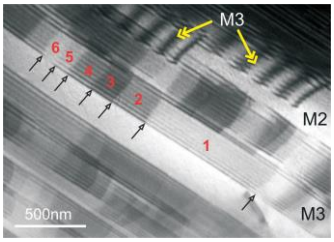
Electropulse treatment of SMA filaments: A talented PhD student J. Pilch developed a novel electropulse method for nonconventional heat treatment of metallic filaments. He has shown that the progress of the recovery and recrystallization processes conventionally proceeding during the heat treatments of metals in environmental furnaces, can be precisely controlled when the heat treatment is performed by joule heating using carefully programmed electric power pulse in millisecond range yielding the metal desired microstructure and properties (**right**). Compared to conventional methods, NiTi filaments with desired properties, gradients of properties or unique properties can be prepared. The method has been applied to very efficient processing of thin cold worked metallic filaments as a part of textile technologies [27] (**middle**). We have studied microstructures in electropulse treated NiTi filaments by TEM [5] and time resolved synchrotron X-ray methods [7]. L**eft figure** became iconic in the field. B. Malard worked at that time in Prague as experienced researcher of the MULTIMAT network. R. Delville and D. Schryvers (PhD student and his supervisor) are collaborators from EMAT Antwerps, who carried

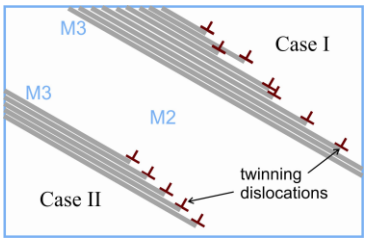




out the excellent TEM work. The research was coordinated from Prague, articles were written jointly by P. Šittner, J. Pilch and R. Delville. J. Pilch presented the method at SMST 2011 conference in Monterey, California, where it attracted attention of the representatives of the leading NiTi filament producer Fort Wayne Metals which initiated collaboration running till present. Thanks to the renewed interest in electroplastic processing of nanostructured metals, the published articles are frequently cited. The electropulse treatment research of the group set a new direction for the heat treating NiTi filaments for medical devices as stents, guide wires or dental wires (share 90%).

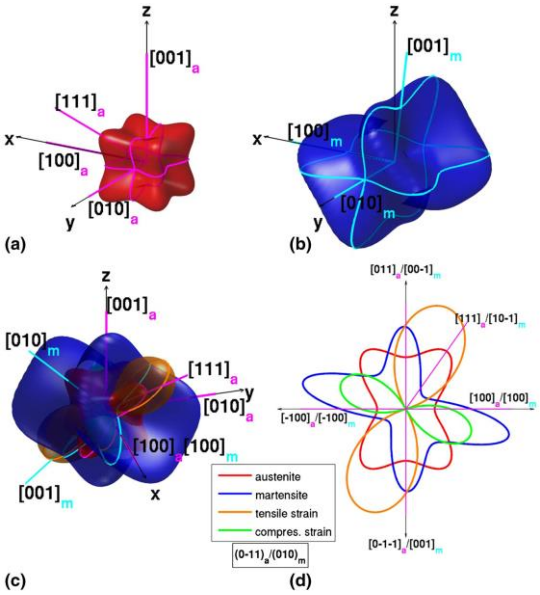
In-situ TEM analysis of mobile interfaces in SMAs: Interfaces created by martensitic transformation are responsible for unique thermo-(magneto-)mechanical behaviors of SMAs. However, not all the interfaces are mobile and there is very limited information about their internal structure and mobility. The problem is that we need to observe the moving interfaces under stress and temperature variation in transmission electron microscope. We performed this using a unique in-situ TEM holder for that purpose (designed and constructed Z. Dlabáček yet in the Department of Metals). We investigated moving martensitic interfaces in Cu-based [2], NiTi [6] and NiMnGa [14,17,29] alloys under tensile loading. **Figure** [17] shows twinning dislocations moving during reorientation of non-modulated martensite in NiMnGa (conversion between M3-M2 plates) moving upon straining in TEM. Since only few laboratories posses such holders, the results attracted attention in the field that resulted in several invitations to keynote lectures for Niva Zárubová, who did most of this excellent TEM work before her retirement in 2013. She collaborated with Yanling Ge from Aalto university in Finland, who did supplementary ex-situ TEM studies. Since these results continue to attract interest in the SMA field, we decided to launch a dedicated website popularizing the in-situ TEM results (share 80%).





D**eformation/transformation processes in NiTi:** Although the martensitic transformations in NiTi are theoretically reversible and recoverable, in reality the moving interfaces create slip dislocations and austenite twins, which remain in the microstructure, cause local plastic deformation, hysteresis and instability of cyclic stress-strain behaviors of NiTi. We have systematically investigated these processes and defects by TEM [6], X-ray diffraction [30] and micromechanics modelling [31]. The results were published in 22 scientific articles and PhD theses of students J.Pilch, B.Mallard, R. Delville and P.Sedmak who worked with the team for some period of time. It was found that major source of the irreversibility and cyclic instability are the incremental plastic strains resulting in internal stresses within the polycrystal microstructure developing upon the superelastic cycling [6,30]. This explains the functional fatigue of NiTi and irreversible processes upon overheating the actuator wires (LTSS processes introduced by the team). The results were presented at conferences and the team has gradually become famous for these unique results (share 80%).

Another successful recent result of the team in the area of deformation behavior of NiTi wires was the theoretical explanation of the curiously small Young's modulus of the stress induced martensite repeatedly measured on NiTi wires, which has puzzled the SMA community for 50 years [18]. The explanation is based on the unique coincidence of the elastic anisotropy of the B19' martensite (**figure**), austenite drawing texture and strong martensite texture due to the variant selection under tensile stress (share 80%).

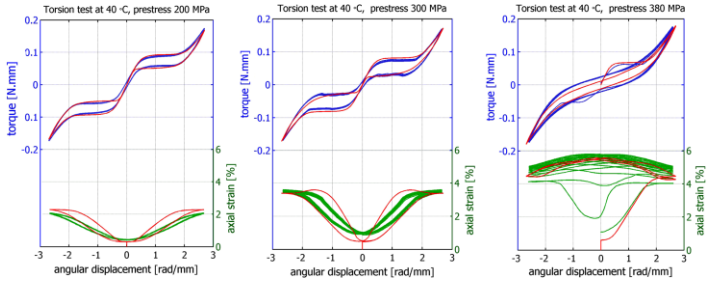


In-situ synchrotron X-ray and neutron diffraction studies of phase transforming solids: The team has applied neutron and x-ray diffraction methods to analyze internal stress, phase fractions and textures in SMAs and SMA composites (~15 articles). As an example of the recent results, research of thermally activated internal stresses around NiTi inserts embedded in a steel plate by combination with neutron diffraction and FE modelling [25] carried out on neutron engineering diffractometer SALSA at ILL Grenoble or time resolved synchrotron x-ray diffraction studies of fast recovery processes in metals during electropulse heat treatments on ID11 instrument at ESRF Grenoble [7] attracted attention in the field due to the innovative ideas (share 70%).

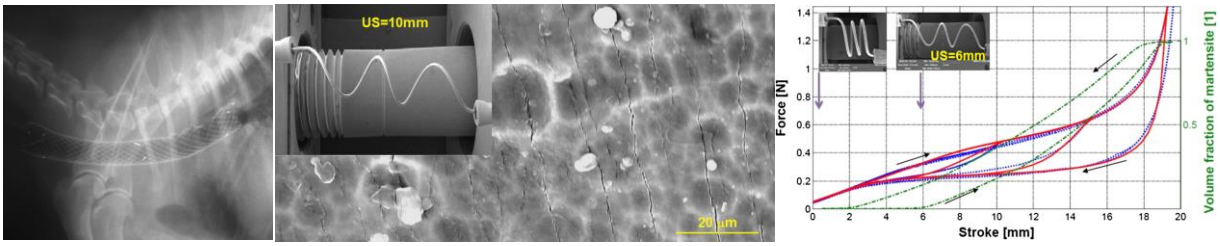
Main achievement in this area, however, is probably the extension of neutron engineering research towards the material processing at high temperatures and long time testing proposed to be performed in future on the neutron diffractometer BEER (figure) to be built at European Spallation Source/ESS/ in Lund, Sweden. Although, this is a wider collaboration with teams from NPI ASCR and HZG in Germany, in which our team plays only minor role, the central idea of material processing on neutron diffractometer has been initiated and promoted by P. Šittner and J. Pilch, who are coauthors of the Technical Design Report of ESS (share 10%).

Thermomechanical modelling of SMAs and numerical simulations for application design: Unique thermomechanical behavior of NiTi is due to several martensitic transformations and twinning processes, all reversible in complete thermomechanical cycles. There is a long history of the development of thermomechanical models of SMAs in the team dating back to pioneering work of P. Šittner in 1995 on experiments and modelling of combined tension-torsion of Cu-based SMA tubes, micromechanics crystallographic model of SMAs by P.Sittner and V. Novak [31], development of the RLoop algorithm for SMA composites in 2000 to 3D SMA model for NiTi [15] developed in 2012 by P. Sedlák and his colleagues from IT ASCR in collaboration with our team. With that latest model [15], the collaborating teams have finally made it to the "premier league of SMA modelling". **Figure 6** shows comparison of experimental data and simulation results of tension-torsion behavior of thin NiTi wire at various temperatures. The model was numerically implemented into FE code ABAQUS. It currently quickly spreads throughout the community and it was recently used to simulate practical NiTi applications as braided NiTi stents or NiTi actuator springs [20,22,23,28]. We have organized Roundrobin SMA modelling forum, where worldwide teams of SMA modelers simulated experimental

results on thin superelastic NiTi wires measured in our lab. Figure shows comparison of experimental and simulated results (red) using the model [15]. The Roundrobin results were published in a common article [32]. The experimental dataset has been frequently downloaded from our website by worldwide SMA modelers. Although the IT ASCR team recently took over initiative with the model development, overall share of both teams in this research can be estimated to ~ 50%.

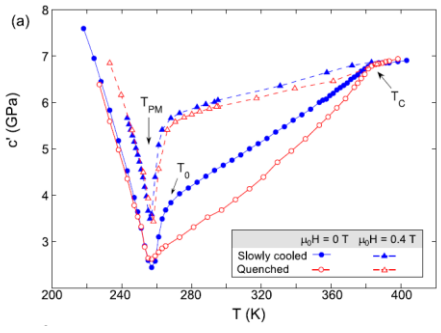


Environmentally assisted fatigue of NiTi stents: Superelastic NiTi technologies and implants exploiting the extreme recoverable deformability of NiTi enabled development of many microinvasive surgery techniques and further growth of superelastic technologies is expected. The problem is fatigue of NiTi, particularly if it transforms martensitically in the corrosive biofluids, as is the case e.g. for tracheal stents or esophageal stents in the stomach. In the last 10 years, we have been collaborating with Ella-CS company producing these stents. They are naturally afraid of unexpected failures of these stents (**left figure** in vivo fracture of NiTi wires of a tracheal NiTi stent implanted to a dog). Motivated by this, we have developed and employed a physical simulation method [20] to investigate environmentally assisted fatigue of NiTi. We have found that a mechanocorrosion processes taking place within the nanocracks of the surface TiO_2 oxide (**middle**) opening/closing cyclically upon mechanical loads (**right**) in biofluids are probably key to the problem. We have developed original in-situ electrochemical methods

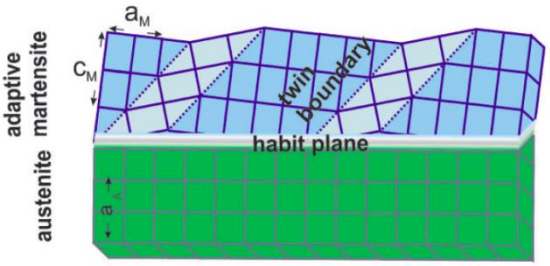


[33] to investigate these processes during cyclic mechanical loading of NiTi wires and springs. The results bring completely new dimension to the research of NiTi fatigue, since they support the view that surface processes are more important than bulk processes, which contradicts the state of art opinion in the field. The results were partially presented at the SMST 2013 conference in Prague, published in 3 articles in JMEP journal [20-22] and in an invited article [26] recently submitted to inaugural issue of the Shape Memory and Superelasticity journal (share 90%).

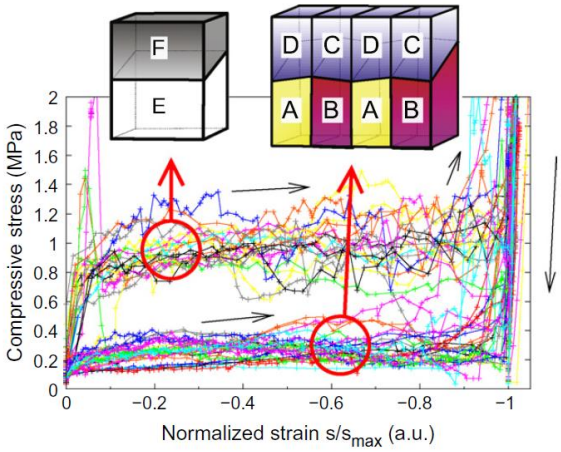
Lattice softening in SMAs: Anomalous lattice softening (**figure**) is expected to be closely related to the martensitic transformation. We have shown, for the first time, what is the effect of the magnetic field on the anomalous lattice softening by measuring elastic constants of the cubic Ni2MnGa austenite single crystal using ultrasound pulse-echo method and resonant ultrasound spectroscopy under magnetic field. The softening was attributed to the strong magnetoelastic coupling enhanced by the low magnetic anisotropy [34] and premartensitic transformation [35]. Limited softening in Co38Ni33Al29 [36] compared to Ni2MnGa [37] was suggested to be responsible for the lack of magnetic shape memory effect in Co-based alloys. The research work was carried out in collaboration with the team of M.Landa from IT ASCR (share 50%).



Concept of modulated martensite as an adaptive phase: Modulated phases frequently occur in functional materials like ferroelectrics and magnetic shape-memory alloys. The giant magnetically induced strain (magnetic shape memory effect) in Ni-Mn-Ga alloy is supposed to be determined by the presence of modulated martensite phase. We have shown for the first time [4] that this phase can be considered as adaptive phase. This dramatically changes the way how so called modulated phases are viewed in the field magnetic shape-memory research. Based on the analysis of the coexistence of austenite, adaptive 14M phase, and tetragonal martensite in Ni-Mn-Ga magnetic shape-memory alloy epitaxial films, we have shown [4] that the modulated martensite can be constructed from nanotwinned variants of the tetragonal martensite phase (**figure**). By combining the concept of adaptive martensite with branching of twin variants, we could explain key features of modulated phases [10], as e.g. the metastability, the experimentally observed sequence of 10M-14M-NM intermartensitic transitions or anomalous behaviour of premartensite phase [35]. We suggested one of the key indirect experimental evidence for the adaptive concept concerning magnetocrystalline anisotropy of martensite [3].The adaptive phase can be related to high mobility of interfaces [38] and can explain suppression of the magnetic shape memory effects in the vicinity of the intermartensitic transformation [39]. The sequence of these articles represents the key contribution of our team to the martensitic transformation research, particularly the role of the highly mobile twin structure crucial for the MSM effect. The work was done in cooperation between IFW Dresden and Institute of Physics, Prague (share 50%).



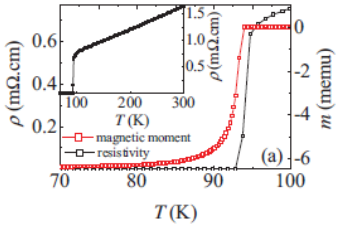
Hierarchy of martensitic structures and explanation of high twin mobility: Frequently observed variations in mobility of various twin boundaries represent one of the key issues in the research area of magnetic shape memory effect. In general, the understanding of twinned microstructures, which can rationalize the extreme mobility or low twinning stress of intervariant interfaces in ferroelastic martensite, is crucial for further development of magnetically induced reorientation. We were first to explain the puzzling experimental observations of different mobility of twin boundaries in Ni-Mn-Ga alloys. Combining dedicated experiments to probe the microstructure and mechanical properties with theoretical calculations using elastic continuum theory, we discovered the existence of Type I and Type II macrotwins having different mobility in magnetic field and twin microstructures in Ni-Mn-Ga [9]. Although initial observations were published by our coauthors L. Straka, Soroka and A. Sozinov from Aalto University in Helsinki in Finland, most of the identification and interpretation was done in IoP ASCR (experiments by O. Heczko, J. Drahokoupil and L. Straka on visit in Prague) in cooperation with the IT ASCR team (theory by H. Seiner). Further studies on the morphology and microstructure of different macroscopic twin interfaces have proven that there exist a large variety of different complex twin arrangements which can explain the previously mysterious observations of different behaviour in seemingly same or very similar materials [16]. Based on these unique experimental results, we have developed a continuum-based model and applied it to highly mobile interfaces in Ni–Mn–Ga martensite. We have shown that Type I and Type II macro-twins (**figure**) have different morphologies at all spatial scales considered. It directly explains their different twinning stress observed in experiments [40,41]. Motivated by this, we have searched for materials which exhibit magnetic shape memory effect in broad temperature range [11]. We have found that the effect can exist even in the vicinity of absolute zero temperature [42], which is fundamental for physical understanding of the effect and also for potential actuator applications, e.g. in space (share 50%).

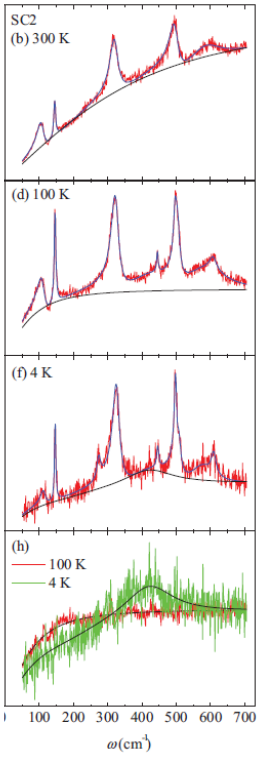


NDT for inspection of ferromagnetic steels: Mechanical stress affects magnetic properties of ferromagnetic materials. Traditionally, hysteresis loops of ferromagnetic materials were studied and modeled in the literature separately from the studies of magnetic domains. We have investigated and modeled bulk magnetic hysteresis loops of soft ferromagnetic materials exposed to compressive and tensile stress [12, 43] with high accuracy using an effective field concept. The observation of magnetic

domains (**figure**) helped us to understand the nature of that effective field. In connection with it, new revolutionary method for inspection fatigue damage in cyclically loaded ferromagnetic steel samples was proposed. The method relies on magnetic adaptive testing (MAT), which, in contrast to traditional magnetic hysteresis methods, picks up the relevant information from systematic measurement and evaluation of whole minor magnetic hysteresis loops and their derivatives. Correlations between non-destructively measured magnetic descriptors and actual fatigue lifetime of ferromagnetic steels were found [44]. The method was also applied for the investigation of flake graphite cast iron. A very good correlation was found between the magnetic descriptors and the graphite morphology. Based on this, the method was suggested as highly promising nondestructive alternative of destructive tests for monitoring structural changes in cast iron [45]. There is a patent application, collaboration with industrial partners interested in the application of the method is currently in progress (share ~100%).

Superconductivity: M. Jirsa has been investigating high-Tc superconductors in FZÚ since 1985 and developed extensive international collaborations. His most recent results concern vortex pinning properties and related utility parameters of GdBaCuO pellets, representing the currently most prospective bulk high-Tc superconductors [1] for practical use. Among other materials, the ternary (Nd,Eu,Gd)-123 type superconductors exhibit record values of electromagnetic parameters, Jc and Birr, allowing levitation up to 90,2 K (boiling point of liquid oxygen). This property is connected with a special type of pinning defects observed in these materials and with the doping by particles of refractory metals. Recently, the group has investigated charge carrier interactions with phonons in single crystals of these ternary compounds, prepared in KIT Karlsruhe [46]. Analysis of the Raman spectra (Eu enriched crystal, figure right) performed by our team showed that some of the phonons, namely the out-of-phase planar oxygen phonon and the Ba phonon, interacted not only with the charge carriers but also with the crystal field excitations. This is the first observation of this specific behavior of these complex superconductors, in simpler Y-123 compounds such an effect does not occur.





Current trend in the field is to utilize bulk high-Tc superconductors in a wide r**a**nge of levitation applications and as a compact source of very high magnetic fields. It was found that, despite the low-cost batch fabrication method, uniformity and high quality of GdBaCuO pellets can be achieved. The samples investigated in our Institute were prepared in the Railway Technical Research Institute in Tokyo, which is responsible also for testing MagLev trains, a typical product utilizing levitation principles. Dr. Jirsa participated in the research as an expert on magnetic properties of high-Tc superconductors (share ~30%).

Research Projects

The team participated in 12 national (CSF (10), MSMT KONTAKT (2)) and 6 international (FP6, FP7, ASCR international collaboration) research projects in the evaluation period 2010-14. Funding of the research of the team heavily relies on project budgets and half of the salaries of the team members is financed from personel budgets of the research projects. Since the topics of the research projects largely determine the research activities, careful project planning is necessary for the small team to remain competitive in the field. Research activities in selected key research projects are briefly introduced below to illustrate this point.

- ***Stability and elastic properties of martensitic phases in shape memory alloys*****,** CSF, V. Novák, 2006-10: This was extremely successful national research project coordinated by V. Novák carried out in collaboration with the team from IT ASCR. Though the overlap with the evaluation period is just one year, it is mentioned here among the key projects, since the FMC group and IT ASCR teams were born in that project. 58 publications in impacted journals were jointly published. PhD students and postdocs were trained within the exciting environment of the prestigious Marie-Curie

RTN network MULTIMAT running in parallel and the team organized one of the main conferences in the SMA field - the ESOMAT 2009 conference in Prague.

- ***Development and Characterization of Active Hybrid Textiles with Integrated Nanograin NiTi Micro Wires* NiTiTEX,** CSF, L. Heller, 2010-12: This was national collaboration project (TUL, FS CVUT) coordinated by L. Heller as a kind of continuation of the large scale FP6 integrated IP-SME project AVALON (2005-9), in which the idea of functional hybrid textiles with metallic NiTi filaments was first ever explored in collaboration of 32 research centers and innovation oriented European SMEs. However, the project finished before the elaborated applications could have been developed and industrially viable concepts. Taking this as a chance we continued this research in frame of the sequel national project NITITEX. We managed together with the textile researchers from TU Liberec to develop new textile processing technologies for production of NiTi textiles. Patent applications 1,3-6 listed below originate from the AVALON and NITITEX projects, the last one of them (6) was filed only in April 2015.
- ***Fatigue of high temperature SMA actuators /*FACT*/*, CSF, P. Šittner, 2012-15: This is an ongoing large scale national collaborative project (VUT Brno, UJF AVCR) coordinated by P. Šittner focusing development of novel high temperature SMA actuators. In frame of this project we developed close collaboration with ESRF in Grenoble France. PhD student P. Sedmák spent 18 months at ESRF where he together with the project team members performed unique in-situ synchrotron X-ray studies on thin NiTi filaments working as high temperature actuators.
- **Experimentally based multiscale modelling of shape memory alloys,** CSF, Petr Šittner, 2014-16 This is an ongoing collaboration project of three academic institutes in which theoretical models of SMAs are being developed, numerically implemented and applied to simulate and design engineering applications of SMAS.
- **SMARTNETS FP7-NMP-2010-SMALL,** collaboration project of R&D centers with SMEs, P. Šittner, 2011-13: This was an application oriented European project coordinated from DITF Denkendorf. FZÚ team worked together with Czech medical device company ELLA-CS and German textile company DITF-ITV Denkendorf within a small innovation oriented network purposefully created to develop a unique medical implant – Stentgraft.
- **Integrated Wind Turbine Design /UpWind/,** FP7 N-019945, integrated project, 2006-11, V. Novák. We participated in the development of smart rotor blades adjusting its shape depending on the wind condition with the help of integrated SMA actuators.
- ***Purkyne Fellowship, O. Heczko, 2008-13*** This project facilitated the return of O. Heczko to the FZÚ after 10 years working abroad in Finland and Germany. The project was instrumental for foundation of the MSM group.
- ***Materials exhibiting magnetic shape memory and related effects* CSF, O. Heczko, 2011-2015**, This is the main project of the MSM group, it enabled to start the research of magnetic shape memory effect.
- **Multidisciplinary research centre for advanced materials – AdMat, CSF, I. Tomáš**, **2014-2018**, Joint CSF Center of Excellence project of six teams (4 ASCR institutes and two Universities) focusing on advanced engineering materials research and joint PhD training.
- **Mechanical properties of functional layers of submicron thickness**, **CSF,** J. Kopeček, **2009-2014**, range of thin films was studies obtained within broad international cooperation
- **Cobalt-based ferromagnetic shape memory alloys, CSF, J. Kopeček, 2010-2012**, these alloys are considered as alternative to Ni-Mn-Ga.
- **ASCR international collaboration projects** supported cooperation of the MSM group with IFW (2010-11) and Aalto University (2012-13) and other outstanding of MSM research centers.

Experimental facilities

Since 2009 the team has built 4 new laboratories (metallurgy lab, thermomechanical testing lab, physical and magnetic properties lab, electron microscopy SEM/FIB+AFM lab). The team has actively participated in the development as well as in scientific activities of the FUNBIO-SAFMAT project. Safmat laboratory is a new FZU infrastructure built using two EU structural fund projects in the period 2011-14, currently offering research services in the area of characterization of material surfaces and biointerfaces. It is a shared activity between the Department of Analysis of Functional Materials and Department of Functional Materials. J. Kopeček is a Safmat deputy head and leader of the Electron microscopy team and P. Šittner is one of the scientific team leaders. The experimental equipment, which has become part of the SAFMAT laboratory, particularly the SEM and AFM microscopes, are operated by the members of the team (J. Kopeček, L. Klimša, A. Lančok) for other FZÚ teams as well as for external users.

BEER diffractometer for European Spallation Source

P.Šittner, J.Pilch and L. Kadeřávek collaborate with the teams at NPI ASCR and HZG on the design and construction of Material Engineering Diffractometer BEER for ESS in Lund. FMC group organized in Prague two ESS Science symposia in 2012 and 2014 focused on exploring the potential of the material processing reaser on neutron beamline. The proposal for construction of the diffractometer BEER was accepted in 2014. In the Czech Republic, it is going to be constructed as an in-kind participation of the CR in the ESS project in frame of the large scale research infrastructure initiative. P. Sittner acts as the Czech representative within the In-kind review committee of the ESS.

Research collaborations

The team collaborates with large number of academic as well as industrial partners. Selected key collaborators we have been interacting in the evaluation period are listed below

- **Prof. Sylvain Calloch, LBMS Brest, France:** collaboration on fatigue of SMAs, exchange stays, joint publications, projects, common PhD student E. Alarcon.
- **Prof. J. Van Humbeeck, Department MTM, KU Leuven, Belgium.** collaboration on metallurgy and martensitic transformations, joint projects, several months stays at MTM, joint publications
- **Prof. G. Eggeler, Ruhr-Universität Bochum, Germany.** Long term collaboration on SMAs, currently high temperature SMAs, exchange seminars,
- **Prof. D. Favier, Laboratory TIMC-IMAG, Grenoble, France**, thermomechanics of SMAs, medical applications of NiTi, common PdD student F.Tissot, joint publications
- **Prof. D.Schryvers, EMAT Antwerps, Belgium,** collaboration on TEM, students trained at EMAT, joint publications, conference organization activities Esomat 2009, Esomat 2015, IMC 2014
- **G. N. Dayananda, NAL Bangalore**, **India,** collaboration on aerospace applications of SMAs, common projects, 6 several months long exchange stays, joint publications
- **C. Curfs, ESRF,** common FZÚ/ESRF PhD project of P. Sedmák
- **B. Allen DSI Inc., producer of GLEEBLE simulators,** collaboration on installation at ESS.
- **J. Schaeffer, Fort Wayne Metals,** thin NiTi wire heat treatment and fatigue research
- **K. Volenec ELLA-CS**, collaboration of NiTi stent development, collaboration on EU projects
- **P. Lukáš NPI ASCR**, collaboration on the building of the diffractometer BEER at ESS
- **M. Landa IT ASCR**, collaboration on SMA modelling, collaboration in national and EU projects
- **J. Militký, TU Liberec,** collaboration of textile technologies, common patents
- **Dr. S. Faehler, IFW Dresden, Germany,** collaboration on adaptive model of martensite,
- **Prof. S.P. Hannulla, Y. Ge, Aalto University (previously Helsinki University of Technology)** structural studies (TEM, Xray) of MSM materials, microstructure of martensite, joint publications
- **K. Ullakko, A. Sozinov now in LUT, Finland**, New functionality of MSM materials
- **I. Škorvánek, Institute of Experimental Physics SAS, Kosice, Slovakia,** Magnetocaloric materials
- **P. Švec, Institute of Physics SAS, Bratislava, Slovakia,** rapidly quenched alloys with MT

Commercialization of research results

The team has been involved in contractual research, collaborative research with SMEs as well as in research commercialization activities, which lead to 3 awarded national patents and 3 international patent applications and 1 national patent applications.

Patents and patent applications

1. **Pressure and/or force sensor**, L.Heller CZ304873
2. **Quiet magnetic Velcro fastener**, D.Vokoun, CZ 26401 A44B
3. **Quiet velcro fastener**. D.Vokoun, D.Majtás, P. Šittner, CZ 304397 A44B
4. **A method of heat treatment and/or inspection of functional mechanical properties, particularly transformation strain and/or strength, of shape memory alloy filaments and apparatus for the application of this method**, J.Pilch, P.Šittner, US20120018413 A1
5. **Medical device**, P.Šittner, L.Heller US20120116492 A1, EP2434984 A1,
6. **3D textile fabric and its production technology**, L. Heller, P. Šittner, K. Janouchová, national patent application
7. **Composite material based on MSM element,** O.Heczko, A.Soroka, S.P.Hanulla, European patent application, PCT/FI2008/050260

References (*first 19 references are those submitted to the Evaluation*):

1. Muralidhar, M.; Tomita, M.; Suzuki, K.; Jirsa, Miloš; Fukumoto, .Y ; Ishihara, A., A low-cost batch process for high-performance melt-textured GdBaCuO pellets. *Superconductor Science and Technology* 2010, 23, 4,
2. Zárubová, Niva ; Gemperlová, Juliana ; Gemperle, Antonín ; Dlabáček, Zdeněk ; Šittner, Petr ; Novák, Václav. In situ TEM observation of stress-induced martensitictransformations and twinning processes in CuAlNi single crystals. *Acta Materialia* 2010, 58, 15, s. 5109-5119.
3. Heczko, Oleg ; Straka, L. ; Novák, Václav ; Fähler, S. Magnetic anisotropy of nonmodulated Ni-Mn-Ga martensite revisited. *Journal of Applied Physics* 2010, 107, 9,
4. Kaufmann, S. ; Roßler, U.K. ; Heczko, Oleg ; Wuttig, M. ; Buschbeck, J. ; Schultz, L. ; Fähler, S. Adaptive modulations of martensites. *Physical Review Letters*, 2010, 104, 14, 145702/1-4.
5. Delville, R. ; Malard, B. ; Pilch, Jan ; Šittner, Petr ; Schryvers, D. Microstructure changes during non-conventional heat treatment of thin Ni–Ti wires by pulsed electric current studied by transmissionelectron microscopy. *Acta Materialia* 2010, 58, 13, s. 4503-4513.
6. Delville, R. ; Malard, B. ; Pilch, Jan ; Šittner, Petr ; Schryvers, D. Transmission electron microscopy investigation of dislocation slip during superelastic cycling of Ni–Ti wires. *International Journal of Plasticity* 2011, 27, 2, s. 281-297.
7. Malard, B. ; Pilch, Jan ; Šittner, Petr ; Delville, R. ; Curfs, C. In situ investigation of the fast microstructure evolutionduring electropulse treatment of cold drawn NiTi wires. *Acta Materialia* 2011, 59, 4, s. 1542-1556.
8. Vokoun, David ; Tomassetti, G. ; Beleggia, M. ; Stachiv, Ivo. Magnetic forces between arrays of cylindrical permanent magnets. *Journal of Magnetism and Magnetic Materials* 2011, 323, 1, s. 55-60.
9. Straka, L. ; Heczko, Oleg ; Seiner, Hanuš ; Lanska, N. ; Drahokoupil, Jan ; Soroka, A. ; Fähler, S. ; Hänninen, H. ; Sozinov, A. Highly mobile twinned interface in 10 M modulated Ni-Mn-Ga martensite: Analysis beyond the tetragonal approximation of lattice. *Acta Materialia* 2011, 59, č., s. 7450-7463.
10. Kaufmann, S. ; Niemann, R. ; Thersleff, T. ; Roßler, U.K. ; Heczko, Oleg ; Buschbeck, J. ; Holzapfel, B. ; Schultz, L. ; Fähler, S. Modulated martensite: why it forms and why it deforms easily. *New Journal of Physics* 2011, 13, 5, 053029/1-053029/24.
11. Straka, L. ; Hänninen, H. ; Heczko, Oleg. Temperature dependence of single twin boundary motion in Ni–Mn–Ga martensite. *Applied Physics Letters* 2011, 98, 14, 141902/1-141902/3.
12. Perevertov, Oleksiy ; Schäfer, R. Influence of applied compressive stress on the hysteresis curves and magnetic domain structure of grain-oriented transverse Fe–3%Si steel. *Journal of Physics D-Applied Physics* 2012, 45, 13, "135001-1"-"135001-11
13. Heczko, Oleg ; Seiner, Hanuš ; Sedlák, Petr ; Kopeček, Jaromír ; Landa, Michal. Anomalous lattice softening of Ni2MnGa austenite due to magnetoelastic coupling. *Journal of Applied Physics* 2012, 111, 7, "07a929-1"-"07a929-3".
14. Zárubová, Niva ; Ge, Y. ; Gemperlová, Juliana ; Gemperle, Antonín ; Hannula, S.-P. Dislocation mechanism of twinning in Ni-Mn-Ga. *Functional Materials Letters* 2012, 5, 1, "1250006-1"-"1250006-4".
15. Sedlák, Petr; Frost, Miroslav; Benešová, Barbora; Zineb, T.B.; Šittner, Petr.Thermomechanical model for NiTi-based shape memory alloys including R-phase and material anisotropy under multi-axial loadings. *International Journal of Plasticity* 2012, 39, s. 132-151.
16. Heczko, Oleg ; Straka, L. ; Seiner, Hanuš. Different microstructures of mobile twin boundaries in 10 M modulated Ni-Mn-Ga martensite. *Acta Materialia* 2013, 61, 2, 622-631.
17. Zárubová, Niva ; Ge, Y. ; Heczko, Oleg ; Hannula, S.-P. In situ TEM study of deformation twinning in Ni-Mn-Ga non-modulated martensite. *Acta Materialia* 2013, 61, 14, s. 5290-5299.

18. Šittner, Petr ; Heller, Luděk ; Pilch, Jan ; Curfs, C. ; Alonso, T. ; Favier, D. Young´s modulus of austenite and martensite phases in superelastic NiTi wires. *Journal of Materials Engineering and Performance* 2014, 23, 7, s. 2303-2314.
19. Stachiv, Ivo ; Vokoun, David ; Jeng, Y.-R. Measurement of Young's modulus and volumetric mass density/thickness of ultrathin films utilizing resonant based mass sensors. *Applied Physics Letters* 2014, 104, 8, "083102-1"-"083102-4".
20. K. Hiřmanová, J. Pilch, J. Racek, L. Heller, P. Šittner, P. Sedlák, Physical Simulation of the Random Failure of Implanted Braided NiTi Stents, *J. of Material Eng. and Perform* , 2014, 23, p. 2650-2658
21. J. Racek, P. Šittner, L. Heller, J. Pilch, M. Petrenec, P. Sedlák, Corrosion of NiTi wires withy cracked oxide layer, *J. of Mater. Eng. and Perform*. 2014, 7, p. 2659-2668
22. P. Sedlák, M. Frost, K. Hiřmanová, P. Šittner, L. Heller, Simulations of Mechanical Response of Superelastic NiTi Helical Spring and its Relation to Fatigue Resistance, *J. of Mater. Eng. and Perform.* 2014, 7, p. 2591-2598
23. L Heller, D Vokoun, P. Sittner and H Finckh, 3D flexible NiTi-braided elastomer composites for smart structure applications*, Smart Mater. Struct.* 21 (2012) 045016,
24. M.Frost, P.Sedlak, M.Sippola, P.Šittner Thermomechanical model for NiTi shape memory wires *Smart Mater. Struct*. 19 (2010) 1 - 10.
25. B. Malard, J. Pilch, P. Sittner, V. Davydov, P. Sedlak, K. Konstantinidis, D.J. Hughes, Internal stresses in steel plate generated by shape memory alloy inserts, *Acta Materialia*. 60 (2012) 1378-1394
26. J. Racek, M. Stora, P. Šittner, L. Heller, J. Kopeček and M. Petrenec, Monitoring tensile fatigue of superelastic NiTi wire in liquids by electrochemical potential *Shape Memory and Superelasticity*, 1 (2015), 204-230
27. J. Pilch, L.Heller, P. Sittner, Thermomechanical treatment of thin NiTi filaments for textile applications by electric current, Materials & Processes for Medical Devices, 2009 August 10–12, 2009, Minneapolis, Minnesota, USA, J. Gilbert, Ed., p 232-237
28. D Vokoun, P Sedlak, M Frost, J Pilch, D. Majtas and P Sittner, Velcro-like fasteners based on NiTi micro-hook arrays, *Smart Mater. Struct*. 20 (2011) 085027 (13pp)
29. Y. Ge, N. Zarubova, O. Heczko and S-P. Hannula, Stress-induced transition from modulated 14M to non-modulated martensite in Ni–Mn–Ga alloy, *Acta Materialia* 90 (2015) 151–160
30. P. Sedmák, P. Šittner, J. Pilch, C. Curfs, Instability of cyclic superelastic deformation of NiTi investigated by synchrotron X-ray diffraction, *Acta Materialia*, 94 (2015) 257-270
31. V. Novák, P Šittner, J. Pilch and R. Delville, Proceedings of ESOMAT 2009, 03009 (2009), http://dx.doi.org/10.1051/esomat/200903009
32. P. Sittner, L. Heller, J. Pilch, P. Sedlak, M. Frost, Y. Chemisky, A. Duval, B. Piotrowski, T. Ben Zineb, E. Patoor, F. Auricchio, S. Morganti, A. Reali, G. Rio, D. Favier, Y. Liu, E. Gibeau, C. Lexcellent, L. Boubakar, D. Hartl, S. Oehler, D.C. Lagoudas and Jan Van Humbeeck Roundrobin SMA modeling , Proceedings of ESOMAT 2009, 08001, http://dx.doi.org/10.1051/esomat/200908001
33. J.Racek, P. Šittner, L. Heller, J. Pilch, L. Kadeřávek, Electrochemistry of NiTi Wires/Springs Subjected to Static/Cyclic Loadings, Materials Today Proceedings, 2S (2015) S965 – S969
34. Heczko, Oleg ; Seiner, Hanuš ; Sedlák, Petr ; Kopeček, Jaromír ; Landa, Michal. Anomalous lattice softening of Ni2MnGa austenite due to magnetoelastic coupling. Journal of Applied *Physics* 2012, roč. 111, č. 7, "07a929-1"-"07a929-3". ISSN 0021-8979.
35. H. Seiner, V. Kopecký, M. Landa, O. Heczko, Elasticity and magnetism of Ni2MnGa premartensitic tweed, *Phys. status solidi* b 251 (2014) 2097 - 2103.
36. H. Seiner, J. Kopeček, P. Sedlák, L. Bodnárová, M. Landa, P. Sedmák, O. Heczko, Microstructure, martensitic transformation and anomalies in c′-softening in Co–Ni–Al ferromagnetic shape memory alloys, *Acta Materialia*., 61:(15), 5869-5876, (2013)
37. O. Heczko, H. Seiner, P. Sedlák, J. Kopeček, V. Kopecký, M. Landa, Resonant ultrasound spectroscopy – a tool to probe magneto-elastic properties of ferromagnetic shape memory alloys, *Eur. Phys. J. B* 86: 62 (2013) 1 - 5.

38. R. Niemann, U.K. Rossler, M.E. Gruner, O. Heczko, L. Schultz, S. Fahler, The Role of Adaptive Martensite in Magnetic Shape Memory Alloys, Adv. Eng. Mater., 14, 562-581 (2012)
39. L. Straka, A. Sozinov, J. Drahokoupil, V. Kopecký, H. Hänninen, O. Heczko, Effect of intermartensite transformation on twinning stress in Ni-Mn-Ga 10 m martensite, *J. Appl. Phys*. 114 (2013) 063504-1-7.
40. H. Seiner, L. Straka, O. Heczko, A microstructural model of motion of macro-twin interfaces in Ni-Mn-Ga 10 M martensite, *J. Mech. Phys. Solids* 64 (2014) 198 - 211.
41. O. Heczko, Magnetic shape memory effect and highly mobile twin boundaries, Mater. Sci. Technol. 30 (2014) 1559 - 1578.
42. O. Heczko, V. Kopecký, A. Sozinov, L. Straka, Magnetic shape memory effect at 1.7 K, *Appl. Phys. Lett.* 103 (2013) 072405(1) - 072405(4).
43. O. Perevertov, R. Schafer, Influence of applied tensile stress on the hysteresis curve and magnetic domain structure of grain-oriented Fe–3%Si steel , *J. Phys. D-Appl. Phys*. 47 (2014) 185001 - 1815010.
44. I.Tomáš, O. Kovářík, G. Vértesy, J. Kadlecová, Nondestructive indication of fatigue damage and residual lifetime in ferromagnetic construction materials, *Meas. Sci. Technol*. 25 (2014) 065601(1) - 065601(10).
45. G. Vértesy, T. Uchimoto, T. Takagi, I. Tomáš, Flake graphite cast iron investigated by a magnetic method, *IEEE Trans. Magn*. 50 (2014) 1 - 4.
46. M. Rameš, V.Železný, I. Gregora, T. Wolf, M. Jirsa: Interaction of phonons with intraband electronic excitations and crystal field transitions in Raman spectra of (Nd,Eu,Gd)Ba2Cu3Oy crystals , *Materials Science and Engineering B* 197 (2015) 10–17

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Microscopic Theory of Many-Body System

Structure of the team and basic research orientation

The long-term research orientation of the team "Microscopic Theory of Many-Body System" is microscopic modelling of quantum and classical interacting many-body systems in solids in and out of equilibrium and under influence of external perturbations. The team consists of two groups with different principal research objectives, but with a partial methodologic and personal overlap. The core of the team (9 researchers) focuses on studying the impact of strong configurational disorder, electron correlations and time-dependent excitations on the electronic structure, low-temperature transport, magnetic and thermodynamic properties of metals, alloys and semiconductors. The other part (5 researchers) addresses non-standard collective, critical and out of equilibrium phenomena in macroscopic statistical and thermodynamic systems with interdisciplinary outreach. Both teams use and develop advance analytic and large-scale numerical methods.

Experience, knowledge base, and methods in use

Most of the senior researchers grew up or established themselves in the group of Prof. B. Velický and contributed to the fame of the Prague school of the coherent-potential (mean-field) approximation for disordered electron systems in solids. That is why the team masters techniques for the calculation of the electronic structure and transport properties of metallic allys. The methods cover a broad spectrum from fundamental model to realistic and materials specific calculations of electronic properties of solids. A number of programs from tight-binding to realistic ab-initio ones based on the density functional, or their combination, have been used for the calculation of the electronic structure. We can run various numerical codes such as modified versions of FLAPW (full potential linearized augmented planewave code) or TB-LMTO (tight-binding linear muffin-tin orbital package). In addition to this we can use advanced solvers from the dynamical mean-field theory so that to include dynamical corrections due strong electron correlations into large-scale calculations of the electronic structure of real materials. We also have acquired good knowledge and experience in the application of the Green-function and diagrammatic techniques including self-consistent calculations of vertex, correlation and response functions in disordered and correlated electron systems. Our study of thermodynamic properties of macroscopic systems is based on the application of techniques related to or derived from the mean-field theory of spin glasses, Monte-Carlo and multi-scale simulations and exact solutions of simplified models. The techniques used to study non-equilibrium phenomena include non-equilibrium Green functions for quantum systems, stochastic dynamics, diffusion and growth processes for temperature dominated situations. Members of our team participate in teaching at Charles University and within the given circumstances also strive to become supervisors of doctoral students.

A major recognition of our research activities before the year 2010 was participation in writing two review articles on the theory of dilute magnetic semiconductors [A0, E21]. We

contributed mostly to writing parts on ab-initio calculations of incorporated defects and the section on transport properties of these materials. Our own research results referred to in these highly cited reviews are calculations of the electronic structure and magnetic properties of magnetic semiconductors that allowed to clarify physical mechanisms relevant for the determination of the Curie temperature in a large class of diluted magnetic semiconductors. In particular, we were the first who showed the decisive role of magnetic percolation and the atomic ordering on the value of the Curie temperature.

Research activity

Our research activity covered several different groups of problems the discussion of which we devided into separate parts with each covering related topics. In each part we sketch the general trends in our research and select the noticeable advances we achieved there.

1. *Electronic structure of random alloys*

Due to the experience and available techniques a large part of our research was focused on electronic, magnetic, and transport properties of solids with configurational disorder that may be important for technological applications. We have tried to solve unresolved theoretical questions as well as attempted to explain experimentally observed phenomena or to perform unbiased, first-principles calculations for real materials.

We studied galvanomagnetic properties of magnetic alloys including anisotropic magnetoresistance and anomalous Hall effect (AHE). We were the first who found a consistent solution of AHE in disordered metallic alloys within a first-principles approach based on the Kubo-Bastin transport formula realistically describing the effects of disorder on the conduction electrons. Our construction was applied to a number of ferromagnetic and Heusler alloys. We analyzed the impact of the alloy ordering and spin disorder on the anisotropic magnetoresistance and the anomalous Hall effect. We found a good quantitative agreement with available experimental data that justified validity of our approach [E20,E11,E3,E2, A1].[1]

The behavior of magnetic systems above the Curie temperature is well characterized by the paramagnetic spin-disorder resistivity. We used the theory of disordered local magnetic moments to obtain reliable and conceptually simple estimates of the spin-disordered resistivity. We showed that the results from these estimates agree quite well with numerically more demanding supercell calculations for ordered and partially ordered ferromagnetic and Heusler alloys. We were among the first who calculated a broad range of physical properties of quaternary Heusler alloys $(Cu,Ni)_2MnSn$. We determined temperature dependence and the effect of pressure as a function of the chemocal composition on the magnitude of magnetic moments, exchange interactions, Curie temperature, spin-stiffness and residual resistivity. All these results were obtained within the same electronic-structure model. A similar study was also done for Fe_3Al/Fe_3Si alloys [E27,A2].

Transport properties of metallic alloys are still of interest from the general point of view, since a comprehensive picture of the effects of multiple scatterings on impurities is missing. There is a mean-field theory of alloys (coherent-potential approximation) that works astonishingly well for spectral one-electron properties, but it fails to capture back-scatterings that may lead in the extreme situation to vanishing of diffusion. That is why there are numerous attempts to calculate the electrical conductivity beyond mean-field and to incorporate the so-

[1] We denote references to the numbered list of selected excellent publications with letter E. We specify the attached references to this file with letter A.

called vertex corrections properly. We investigated back-scattering effects on the electrical conductivity in models where electron interactions are simulated by frozen, but thermally equilibrated, impurities. We showed that this static type of electron interactions has the same effect on the electrical conductivity as configurational randomness in the chemical composition, that is, they decrease the charge diffusion [E23]. Further on, we showed how to incorporate vertex corrections so that the reduced conductivity remains nonnegative in the whole range of disorder strength [A3]. We analysed the existing computational schemes for the electrical conductivity and diffusion and demonstrated that beyond the one-particle self-consistency of the mean-field theory one needs a two-particle self-consistency for the vertex functions so that one can reach vanishing of diffusion [A4]. In another study we answered the question about the character of the metal-insulator transition in disordered electron systems and/or in systems with local static electron repulsion. We showed that the transition is critical, with diverging imaginary part of the self-energy, only in specific situations that we analyzed in details. We demonstrated that the critical behavior is universal and the transition is preceded by a singularity in an irreducible two-particle vertex. We showed that the physical two-particle vertex remains non-singular and the observed two-particle singularity has no measurable consequences [E4].

2. *Magnetic properties of metals and semiconductors, spintronics*

There is also a long tradition in our team in using alloy analogies in simulating effects of electron interactions. This experience, combined with knowledge in the physics of semiconductors and small and large scale computational tools, proved useful in the recently fastly developed field – spintronics. We used our know how and started to collaborate with the group of T. Jungwirth in theoretical investigation of various groups of spintronic materials. A lot of effort was devoted to (Ga,Mn)As. Although this is already a traditional spintronic material, extensively studied for its interesting physical properties and perspective applications, there were several open fundamental question about its electronic structure and magnetic behavior. The main controversy we addressed was the character of the electronic states induced by the substitution of Mn atoms. Several authors claimed that the Mn-induced states remain localized and form a narrow impurity band up to typical Mn concentrations (5 %). Experiments, however, and also ab initio calculations, indicated that the "impurity" states are merged into the valence band, at least for the metallic samples. We used a tight-binding method to implement the ideas beyond various impurity-band models at the microscopic level and demonstrated that the concept of an impurity band is inconsistent: our calculations failed to dicern a distinct impurity band. This finding, together with a series of the DFT calculations and a careful interpretation of new optical data brought strong arguments in favor of the itinerant picture of magnetism in (Ga,Mn)As [E22].

The drop of the Curie temperatre when was observed experimentally in (Ga,Mn)As when co-doped with a small amount of phosphorus defects. We analyzed this effect and showed that the defects (inhomogeneities, clusters, and conventional compensating defects) reduce the hole concentration. This found that this ruduction causes the drop of the transition temperature and our results appeard in a reasonable agreement with experimental values for the critical temperature [E26].

Another unclear, yet important feature of (Ga,Mn)As is the uniaxial [110]/[1-10] magnetocrystalline anisotropy. We proposed a possible explanation of this property, based on an inhomogeneous distribution of Mn atoms due to the stacking faults. It is observed, that the concentration of the faults in (111) and (11-1) planes in (Ga,Mn)As is much higher than in pure GaAs. We used the total-energy calculations to study the interaction of Mn impurities with the

faults and showed that it is attractive. As a result, the faults are decorated by Mn impurities and their formation energy decreases, which explains a higher density of the faults in the mixed crystal. We suggested that the specific orientation of the resulting Mn-rich planes may be the reason for the observed anisotropy [A5]. Concerning GaAs-related materials, we also explained a strong enhancement of the spin Hall effect in GaAs due to a partial excitation of the conduction electrons to side energy minima. We showed that, in contrast to a common opinion, the spin-orbit coupling can be quite important also in the conduction band of GaAs due to the admixture of atomic p-states, making itself evident in peripheral parts of the Brillouin zone. We also predicted an even stronger effect in (Ga,Al)As semiconductor with a lower energy of the side-minima [A6]. A detailed analysis of the spin-orbit interaction around the side minima is still in progress.

Another direction of our spintronic research was searching for new materials combining semiconducting and magnetic properties. We were particularly interested in suitable antiferromagnets. We were the first to show that compounds from the family of I-Mn-V materials are semiconductors with the structure and bangaps compatible with traditional III-V materials [A7]. By using the total energy calculations we were able to determine details of the antiferromagnetic arrangement in different I-Mn-V compounds. The subsequent effort to prepare layers of the representative LiMnAs in our Institute was only partly successful and the related technological difficulties led us to other compounds containing monovalent copper instead of alkali metals. Our theoretical support helped establish the crystalline structure of a new, tetragonal phase of CuMnAs prepared by the molecular-beam epitaxy. We also showed that CuMnAs and related compounds have, in both tetragonal and orthorombic phases, a semimetallic band structure with a narrow overlap of the "valence" and "conduction" bands. Electronic structure calculations then resulted in a stable antiferromagnetic behavior with a high transition temperature, which was later confirmed by experimental measurements. Our theiory was in good agreement with the experimenatl observations [A8,A9].

It is still a problem to determine reliably magnetic properties of ultra thin overlayers, which are important for applications in spintronics. First-principles calculations are difficult to use, since the range of surface interactions is longer than in the bulk, which tremendously increases the numerical resources. We hence used a model of a magnetic monolayer of iron and cobalt adsorbed on the fcc-Cu(001) surface. We constructed an effective Heisenberg model with exchange interactions obtained from first principles. The mmodel was examined by means of Monte-Carlo simulations and the random-phase approximation combined with a virtual-crystal approximation from which we extracted the dependence of the Curie temperature on the alloying concentration. The highest Curie temperature appeared to be for an iron overdoping [E6]. Magnetic monolayers of iron on Ir(001) surface covered by adsorbed oxygen and hydrogen were also studied by ab-initio methods. We showed that the adsorption of oxygen, as well as hydrogen, leads to a p(2x1) antiferromagnetic order of magnetic moments of iron. Simulated scanning tunnelling images suggested that the proposed p(2x1) antiferromagnetic order should be detected even by non-magnetic tips [E7]. Such studies were pioneering in the field.

We further studied the so-called tunneling anisotropic magneto-resistance (TAMR) in anti-ferromagnetic materials. Magnetic anisotropy phenomena in bimetallic antiferromagnets Mn_2Au and MnIr were studied by first-principles, density-functional theory calculations. Large magnitude of the anisotropy we found can open a route towards spintronics in compensated

antiferromagnets without involving ferromagnetic elements [E19]. Later, this theory was applied to various types of novel tunnel junctions with antiferromagnetic materials [A10], which are potentially important for practical applications of the antiferromagnetic spintronics.

3. Strong correlations: Heavy fermions, actinide compounds, transuranium elements, cold atoms and correlation-driven phase transitions

Apart from the methods for disordered systems we also have experience in both analytic and numerical approaches to many-body quantum systems. In particular in the application of the methods connected with the so-called dynamical mean-field theory (DMFT). We continued research in this field on the model as well as in the combination of ab-initio calculations with DMFT. The latter in a collaboration with A. I. Lichtenstein (University of Hamburg). The actual implementation was, however, carried out by members of our team

Systems with f and d valence electrons, where electron correlations are strong, cannot be described by the standard ab-initio methods that neglect dynamical fluctuations. We have continued developing and implementing first-principles methods for an accurate description of the electronic structure of these materials in the framework often referred to as DFT+DMFT. These methods build on a material-specific multi-band models of Hubbard's type. These models re constructed on the top of the first-principles band structure from the density-functional theory (DFT). The Hubbard models are then solved by means of the dynamical mean-field theory (DMFT), which reduces the problem of interacting electrons in an extended system to a problem of interacting electrons on a single lattice site embedded in a non-interacting effective dynamical medium (dynamical mean field). We would solve the resulting many-body impurity problem by exact diagonalization of discrete states. It allowed us to take into account the full Coulomb interaction vertex, the spin-orbital coupling as well as the crystal field without any further approximations. When the correlated orbitals (such as 5f orbitals) hybridize mainly with uncorrelated orbitals (such as 6d orbitals or ligand states), the density-functional theory itself often provides a sufficiently accurate effective medium, which allows for a substantial reduction of the computational cost.

The DFT+DMFT method was applied to the electronic structure of elemental actinides as well as of actinide intermetallic compounds, in particular, members of the so-called 115 family of plutonium based superconductors ($PuCoGa_5$ and $PuCoIn_5$). We analyzed the origin of magnetism in these compounds, or its absence, and its connection with the intermediate valence of the plutonium 5f shell [E9,E10]. These findings are relevant for the ongoing search for the pairing mechanism responsible for occurrence of superconductivity in these materials. Furthermore, we demonstrated that many features observed in the photoemission spectra of the elemental actinide metals and actinide compounds originate in atomic-like multiplet transitions. These investigations were carried out in a close collaboration with the experimental groups at the Institute for Transuranium Elements (JRC-ITU) of the European Commission in Karlsruhe, and at the Charles University in Prague.

It turned out that our computational framework is particularly well suited for modeling of the electronic structure of Mott insulators. In plutonium dioxide, for instance, we were able to consistently bridge the correlated band-structure theory that rationalizes the formation of the band gap with the crystal-field theory that was used in the past to explain the quenching of magnetic moments on plutonium atoms [E5]. The progress in the description of bulk systems in the framework of the dynamical mean-field theory is beneficial also for first-principles

studies of magnetic impurities located in a bulk, or magnetic adatoms adsorbed on surfaces, as we have demonstrated on several applications to this type of systems [E18].

Despite decades of studies, certain aspects of the electronic structure of transition metals have not yet been fully understood. We contributed to this problem by analyzing many-body effects in the valence spectrum of nickel. The main focus was the on satellite observed around 6 eV below the Fermi level the origin of which has been under debate. Our theoretical estimates of the shape and spin polarization of the satellite corresponded well with the experimental data confirming thus accuracy of the model used [E12].

Although most of the correlated many-body systems relevant for condensed matter physics are systems of fermions (electrons), the interacting lattice bosons also drew considerable interest recently, since they are relevant for experiments with cold atoms in optical lattices. We adapted the dynamical mean-field theory to systems of strongly interacting bosons, within thebosonic Hubbrad model. In collaboration with K. Byczuk from Warsaw and D. Vollhardt from Augsburg, we developed a new semi-analytical method to solve the DMFT equations for correlated bosons [E13]. Motivated by a new experimental technique employed to probe excitations of bosons in optical lattices, the Bragg spectroscopy, we computed momentum-dependent spectral functions and dispersion relations of bosons in different parameter regimes, in both the Mott insulator and superfluid phases. For this purpose, we wrote our own codes that solve the DMFT equations and perform the analytic continuation using Pade polynomials and the maximum entropy method.

4. *Large-scale computational schemes*

Majority of calculations of realistic electronic structure of solids is based on the density-functional theory. Nevertheless, there are numerous situations where the accuracy of this approximation is insufficient to describe the physical phenomena of interest, such as strongly correlated electrons already discussed, open structures with a highly inhomogeneous electron density, or van der Waals molecular systems. One class of computational approaches that are able to address these issues are quantum Monte Carlo (QMC) methods. We participated in the develoment and extension of a particular variant of QMC, the so-called diffusion Monte Carlo method, build on explicitly correlated many-body wave functions, to large extended many-body systems. We show in an invited review article [E14], written in collaboration with L. Mitas form the North Carolina State University, that the diffusion Monte Carlo provides us with very accurate data on cohesion energies, structural characteristics, or equations of state. It was shown that the quality of the results does not depend much on the character of the chemical bonding. The weakly bound van der Walls crystals are described as accurately as covalent materials or metals. A large part of the results on the transition-metal compounds reported in the review were calculations done by the authors themselves. Recently, the QMC method was employed to estimate formation energies of substitutional defects in graphene [A11].

5. *Critical properties of interacting frustrated macroscopic systems with interdisciplinary applications*

Although the main interest of the team are quantum systems of interacting and disordered electrons we have pursued also more general topics in macroscopic interacting sytems. It is necessary to understand well simpler classical collective and critical phenomena before one can explore quantum phase transitions in interacting and disordered electron systems. That is why we have studied a class of classical macroscopic systems diplaying nontrivial critical behaviour

for which a number of analytic and numerical methods were developed. Phase transitions and critical behaviour caused by coherent cooperative, avalanche-like reaction of small external perturbations are generally very important macroscopic phenomena and stil studied in various circumstances.

We studied models and developed methods for describing the critical behaviour in interacting disordered systems with frustration that are related to or described by spin glass models. We succeeded to expand the hierarchical set of approximations to the full mean-field free energy functional for the Potts glass below the transition to the glassy phase. We showed that the Parisi-type continuous replica-symmetry breaking gives the equilibrium state in the whole spin-glass phase. It had been believed that due to missing spin-reflection symmetry of the Potts model, the Parisi construction does not apply. We demonstrated that the Parisi continuous solution exists, but the accepted interpretation of its continuous order-parameter function does not hold for the Potts model [A13,E16]. We also worked on the general theory of spin glasses with the full replica-symmetry breaking. We derived a first direct Landau-type approximation in the continuous order-parameter function determining the full Parisi solution. Moreover, we showed how to expand it in the continuous order-parameter function around the discrete first level of replica-symmetry breaking. The latter is not covered by the continuous solution. The first level of the replica-symmetry breaking allow to apply the expansion at very low temperatures. A non-self-consistent version of the derived expansion to second order was calculated explicitly [E8].

We analyzed models of random graphs, known in the physics of topologically disordered matter, glasses or granular assemblies. We concentrated, in particular, on the spectral and localization properties of these graphs. In granular assemblies we can describe with random graphs localization of classical or sound waves, microwaves, or light. Random graphs are also used to establish connections and build tight communities in social networks. We performed a more abstract analysis of localization in random graphs [E17]. We showed applicability of this phenomenon in general complex systems beyond the realm of physics [A14]. A long tradition and unique experience in the application of methods of statistical mechanics of disordered frustrated systems culminated in invitation to write a book for the prestigious Oxford University Press about modeling of economical and social processes [E1]. The book is a unique and exceptional overview of these methods. It covers a number of physical models and methods of statistical physics in economics and sociology. About one third of the book is based on the own results of the author. Among the topics contained in the book and based on results achieved by its author are deposition-evaporation models in 1+1 dimension simulating stock market transactions, analysis of the models with anomalous diffusion that as well apply to modeling the stock market, and reaction-diffusion models used for modeling the opinion spreading and consensus forming in society. The author received the Prize of the Academy of Sciences of the Czech Republic for results of great scientific importance ((2014).

6. *Microscopic and macroscopic systems far from equilibrium*

The last area of interest of our team are nonequilibrium, transient and growth processes in small nanoscopic as well as large macroscopic systems. We have studied thermodynamic processes described by classical dynamics as well as quntum time-dependent and relaxation phenomena. We applied advanced analytic theories and/or large-scale numerical calculations to reach new results.

Our research in the realm of quantum nonequilibrium systems focused on the effort to improve theoretical understanding of small (nanoscopic) systems arbitrarily far from equilibrium. In particular, the processes that are in non-stationary evolution from a general initial state. The main technical tool used was non-equilibrium Green's functions (NGF). Initial conditions at a given time play all an important role in the transient dynamics of open small quantum systems. We represented the studied open systems by a simple generic structure of a molecular island between two metallic leads. The physics of the model was controlled by tunneling functions of both lead-island junctions. The complex initial conditions were treated using our original method of time partitioning, linking the transient process with the Keldysh proces. This method was applied in particular to processes generated by sudden changes of connectivity of the model. We extended our construction to a series of on/off switching events. In this way a substantial progress was achieved in the comprehensive description of transient processes from the early coherent period to the phase controlled by a Generalized Master Equation (the so-called Bogolyubov decay of correlations) and further to the effective Master Equation [E24]. We summarized the methods and approximations we developed and used in studying quantum systems far from equilibrium in a review paper [A15].

We used a multiscale approach to study a lattice-gas model of submonolayer growth of Fe/Mo(110) by Molecular Beam Epitaxy. We constructed a two-dimensional lattice-gas model of Fe/Mo(110) derived from first-principles calculations of the monomer diffusion barrier and adatom-adatom interactions. We used the equilibrium kinetic Monte Carlo (KMC) simulations to calculate the diffusion coefficients of Fe islands of different sizes. These diffusion coefficients were used as input to the coarse-grained Kinetic Rate Equation (KRE) approach. We also estimated effects of the range of the Fe-Fe interactions with the restriction of interactions to third nearest neighbors. It allowed us to develop feasible atomistic KMC model. We calculated time evolution of the island size distributions by both KMC and KRE methods and find good agreement between the two methods [A15].

In genarla theory of nonequilibrium phenomena we focused on stochastic thermodynamics, which is a fast growing field of nonequilibrium statistical physics of open nanoscopic systems maintained out of equilibrium by, e.g., persistent driving forces or inhomogeneous boundary conditions. The results were mostly obtained in collaboration with the group of C. Maes (ITF, KU Leuven). We analyzed (stochastic) McLennan-Zubarev nonequilibrium ensembles that are known to suffer from generic divergences and interpretational problems from a mathematical point of view. We showed how the divergences can be removed so that the resulting non-Boltzmannian correction in stationary statistical weights retains its thermodynamic meaning. Thi feature is important for applications to heat processes. We applied our results to derive new variational potentials for nonequilibrium steady states which are also Lyapunov functions, i.e., monotonous along any relaxation and hence useful for stability analysis [E15]. We also critically analyzed other approaches to stability of stationary states, the Minimum entropy production principle and the Glansdorff-Prigogine stability criterion, for which we found new conditions of validity. Using a more standard heat renormalization framework we characterized behavior of nonequilibrium heat capacity in various nonequilibrium regimes, with emphasis on understanding its relation to the microscopic structure of the system. In particular, we demonstrated and explained how the nonequilibrium heat capacity can become negative. Beyond quasistatic processes, we also proposed a new approach to the problem of stochastic pumping by which some previous results could easily be derived and extended [E25].

Collaborations and outreach

We keep a number of collaborations with teams of theorists and experimentalists on national and international level. In the Institute, we collaborate extensively with spintronics department of T. Jungwirth on magnetic semiconductors, antiferromagnetic metals and problems related to spintronics. We supplied them with models based on first-principles calculations for understanding of different phenomena. There is a long-term productive collaboration with I. Turek from the Institue of Physics of Materials on the calculation of transport and magnetic properties of alloys. We also had collaboration with L. Havela of Charles University to whom we provided theoretical support of experimental measurements on transuranium compounds. We also had kept similar collaboration with the experimental group from the Institute for Transuranium Elements (JRC-ITU) of the European Commission in Karlsruhe led by R. Caciuffo. We are still collaborating on the problem of the implementation of correlation-induced dynamical fluctuations into ab-initio calculations with group of A. Lichtenstein from the University of Hamburg. Apart from less frequent and regular contacts with foreign researchers we have profited from collaboration with theoretical group of C. Maes from the University of Leuven on nonequilibrium thermodynamics.

References

[A0] T. Jungwirth, J. Sinova**, J. Mašek**, J. Kučera, A.H. MacDonald: *Theory of ferromagnetic (III,Mn)V semiconductors*, Rev. Mod. Phys. **78** (2006) 809 - 864.

[A1] X. Marti, I. Fina, C. Frontera, Jian Liu, P. Wadley, Q. He, R. Paull, J. Clarkson, **J. Kudrnovský**, I. Turek, J. Kuneš, D. Yi, J.-H. Chu, C. T. Nelson, L.You, E. Arenholz, S. Salahuddin, J. Fontcuberta, T. Jungwirth, and R. Ramesh: *Room-temperature antiferromagnetic memory resistor*, Nature Materials **13** (2014) 367-374.

[A2] S. K. Bose, **J. Kudrnovský**, **V. Drchal**, and I. Turek: *Pressure dependence of Curie temperature and resistivity in complex Heusler alloys*, Phys. Rev. B **84** (2011) 174422.

[A3] **V. Pokorný** and **V. Janiš**: *Vertex corrections to the mean-field electrical conductivity in disordered electron systems*, J. Phys.: Condens. Matter **25** (2013) 175502.

[A4] **V. Janiš** and **V. Pokorný**: *Renormalized perturbation theories of Anderson localization: Self-consistent two-particle vertices*, Ann. Phys. (Berlin) **523** (2011) 715-723.

[A5] M. Kopecký, J. Kub, **F. Máca**, **J. Mašek**, O. Pacherová, A. W. Rushforth, B. L. Gallagher, R. O. Campion, V. Novák, T. Jungwirth, *Detection of stacking faults breaking the [110]/[1-10] symmetry in ferromagnetic semiconductors (Ga,Mn)As and (Ga,Mn)(As,P)*, Phys. Rev. B **83** (2011) 235324(1)-235324(7).

[A6] N. Okamoto, H. Kurebazashi, T. Trypiniotis, I. Farrer, D. A. Ritchie, E. Saitoh, J. Sinova, **J. Mašek**, T. Jungwirth, C. H. W. Barnes, *Electric control of spin-Hall effect by inter-valley transitions*, Nature Materials **13** (2014) 932-937.

[A7] T. Jungwirth, V. Novák, X. Marti, M. Cukr, **F. Máca**, **A. B. Shick**, **J. Mašek**, P. Horodzska, P. Němec, V. Němec, V. Holý, J. Zemek, P. Kužel, I. Němec, B. L. Gallagher, R. P. Campion, C. T. Foxon. J. Wunderlich, *Demonstration of molecular beam epitaxy and a semiconducting band structure for I-Mn-V compounds*, Phys. Rev. B **83** (2011), 035321(1)-035321(6).

[A8] **F. Máca**, **J. Mašek**, O. Stelmakhovych, X. Martim K. Uhlířová, P. Beran, H. Heichlová, P. Wadley, V. Novák, T. Jungwirth, *Room-temperature antiferromagnetism in CuMnAs*, J. Magn. Magn. Mat. **324** (2012) 1606-1612.

[A9] P. Wadley, V. Novák, R. P. Campion, C. Rinaldi, X. Martí, H. Reichlová, J. Železný, J. Gazquez, M. A. Roldan, M. Varela, D. Khalyavin, S. Langridge, D. Kriegner, **F. Máca**, **J. Mašek**, V. Holý, A. W. Rushforth, K. W. Edmonds, B. L. Gallagher, C. T. Foxon, J.

Wunderlich, and T. Jungwirth: *Tetragonal phase of epitaxial room-temperature antiferromagnet CuMnAs*, Nature Commun. **4** (2013) 2322, p1-6.

[A10] I. Fina, X. Marti, D. Yi, J. Liu, J. H. Chu, C. Rayan-Serrao, S. Suresha, **A. B. Shick**, J. Železný, T. Jungwirth, J. Fontcuberta, R. Ramesh, Nature Communications **5**, 4671 (2014).

[A11] M. Telychko, P. Mutombo, M. Ondráček, P. Hapala, F. C. Bocquet, **J. Kolorenč**, M. Vondráček, P. Jelínek, and M. Švec: *Achieving high-quality single-atom nitrogen doping of graphene/SiC(0001) by ion implantation and subsequent thermal stabilization*, ACS Nano **8**, 7318 (2014).

[A12] V. Janiš and A. Klíč, *Equilibrium state of the mean-field Potts glass*, J. Phys.: Condens. Matter **23**, 022204 (2011).

[A13] F. Slanina: *Complex temporal structure of activity in on-line electronic auctions*, Adv. Compl. Syst. **15**, 1250053 (2012).

[A14] V. Špička, **B. Velický** and **A. Kalvová**: *Electron systems out of equilibrium: Nonequilibrium Green's function approach*, Int. J. of Modern Physics B, Vol. **28**, 1430013 (2014) 1–103.

[A15] M. Mašín, **M. Kotrla**, B. Young, M. Asta, M. O. Jahma, and T. Ala-Nissila: *Multiscale study of submonolayer growth for Fe/Mo(110)*, European Physical Journal B. **86**, 359 (2013).

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Laser-matter Interaction and Chemical Physics

Research activities of the **Department of Radiation and Chemical Physics IP-ASCR** are located at the frontier of high-energy-density physics and high-energy chemistry. Following research streams are elaborated: (a) interaction of intense extreme ultraviolet and soft X-ray radiation with matter of various kind, from elemental solids to biomolecular systems, (b) X-ray, extreme ultraviolet and optical emission spectroscopy of plasmas produced by focused beam of short-wavelength and conventional, long-wavelength lasers, (c) characterization and application of neutrons and charged particles emitted under these interaction conditions, (d) other advanced diagnostic techniques, incl. imaging and pump-and-probe, utilized to the study of laser-produced plasmas, (e) characterization and applications of focused beams of short-wavelength lasers, (f) X-ray holography with atomic resolution and related techniques, (g) chemical and plasma-chemical generators of atomic and excited species for chemical lasers and related purposes, (h) chemical consequences of laser-induced dielectric breakdown (LIDB) in molecular gases and their mixtures, and (i) theory and computer simulations of an interaction of intense radiation in different spectral ranges with matter (from isolated atoms to complex solids) and its consequences, i.e., hot dense plasmas (HDP) and warm dense matter (WDM) formed in that way. In above-mentioned areas, both fundamental and application-motivated research is conducted at large-scale facilities operated abroad (FLASH in Hamburg, LCLS at SLAC in Menlo Park - CA, LULI in Palaiseau, CELIA in Bordeaux, SCSS and SACLA in Japan, ELETTRA in Trieste, and many others) as well as at IP-ASCR using the PALS facility (kJ-class iodine photo-dissociation laser system providing sub-nanosecond pulses of near-IR radiation; PALS – Prague Asterix Laser System). The motivation comes mostly from inertial confined fusion (ICF) research and technology, laboratory astrophysics and astrobiology, materials science and processing, radiation chemistry and biophysics, and so on.

1. Interaction of intense short-wavelength radiation with matter, including characterization and application of focused XUV/x-ray laser beams

Interaction of extreme-ultraviolet radiation (XUV; 10 nm < λ < 100 nm) and soft x-rays (SXR; 0.2 nm < λ < 30 nm) with matter differs dramatically from that of the long-wavelength (i.e., UV-Vis-IR) radiation. The interaction of the short-wavelength radiation occurs mostly due to the photo-effect in atoms of the irradiated material. Valence electrons play in general a minor role in the interaction. Thus an absorption coefficient depends on the elemental composition and density of the irradiated material. Contrary to the long-wavelength radiation, there is a little influence of the fine chemical structure of the particular material chosen for an irradiation.

In addition to that, the short-wavelength radiation is deposited much effectively in the material because an effect of plasma reflection of laser light is reduced. It follows from the fact that in a certain spatial position in the plasma, where the oscillation frequency of plasma electrons (so called plasma frequency and/or Langmuir frequency) oscillating in the electromagnetic field is equal to the frequency of laser radiation, the index of refraction becomes zero and the electromagnetic wave is reflected. Langmuir frequency is a function of electron density (n_e)

$$\omega_e^2 = n_e\, e^2 / \varepsilon_0\, m_e\ .$$

Laser frequency is equal to the Langmuir frequency at the critical density which depends on the laser wavelength in the following way:

$$n_c\ [\text{electrons in cm}^3] = 10^{21} \times \lambda^{-2}\ [\mu\text{m}]\ .$$

Let compare a typical XUV and VUV laser from this point of view. A critical density $n_c = 5\text{x}10^{23}$ cm^{-3} can be expected for 46.9-nm radiation in the XUV spectral range. It means that the XUV-laser radiation can penetrate all the parts of the plasma formation volume with an electron density < $5\text{x}10^{23}$ cm^{-3}. This value is comparable to an electron density of solids. Therefore the sample can be heated by the short-wavelength radiation in the whole volume irradiated. Thus the technique is called a volumetric heating. In comparison, the critical density is at least 15x smaller for ArF excimer laser. Expanding ArF-laser-induced plasma plume begins to reflect the 193-nm laser radiation at a certain moment of the interaction

course. Therefore the volumetric heating of solids cannot be carried out with the VUV (and of course UV-Vis-NIR-IR) laser radiation.

1.1 Unique combination of plasma temperature and density achieved with focused beams of x-ray lasers

An international team of researchers created a unique state of matter due to the above-mentioned volumetric heating of aluminum induced by tightly focused beam of x-ray free-electron laser LCLS (Linac Coherent Light Source) in California. Solid-density plasmas at a temperature exceeding 10^6 K were produced under these irradiation conditions [1]. Researchers from our Department contributed mainly by an accurate and reliable determination of an irradiance reached in the focused beam. Their original techniques made possible to cope with this problem (details and references can be seen in part 1.2 of this report).

Matter with a high energy density (>10^5J/cm^3) is prevalent throughout the Universe, being present in all types of stars and towards the center of the giant planets; it is also relevant for inertial confinement fusion (ICF). Its thermodynamic and transport properties are challenging to measure, requiring the creation of sufficiently long-lived samples at homogeneous temperatures and densities. An understanding of the contrasting case of intense x-ray interaction with dense systems is important from a fundamental viewpoint and for applications.

Detailed simulations of the interaction process conducted with a radiative-collisional code showed good qualitative agreement with the experimental results. Insights into the evolution of the charge state distribution of the system, the electron density and temperature, and the timescales of collisional processes were obtained. The unique, but well-determined conditions were utilized for a systematic treatment of various particular phenomena occurring in the dense plasmas [2-4]. Presented results should inform future high-intensity x-ray experiments involving dense samples, such as x-ray diffractive imaging of biological systems, material science investigations, and the study of matter in extreme conditions with a motivation coming mostly from ICF, Earth, and Space sciences.

1.2 Characterizing the “strange” beams of XUV/x-ray lasers

In the physics of extreme states of matter, it is important not only to approach an appropriate high-energy-density level but also to diagnose and characterize the system investigated under the unsteady conditions. Therefore systematic experimental and theoretical works dealing with an accurate and reliable characterization of focused laser beams are conducted in our Department to carry out the short-wavelength laser-matter interaction research properly. The detailed knowledge of transverse energy distribution within the beam profile turns out to be essential for interpretation of the quite nontrivial experimental results obtained at an enormous irradiance. Non-Gaussian beams, which are typical of XUV/x-ray lasers, require a rigorous study as well as the interactions induced by them. Our recent work is therefore devoted to a detailed characterization of focused general laser beams [5, 6] extending the ablative imprint technique published earlier [7].

1.3 Damage to materials of optics designed for the new generation of XUV/x-ray sources: Diamond slabs and amorphous carbon-coated reflection gratings as examples

It follows from the above paragraphs that high-performance optics is needed to concentrate energy of the XUV/x-ray laser beam on solid targets to produce dense plasmas. Of course, an optical element itself is heavily exposed to the short-wavelength laser radiation. Any element of the beam guiding and focusing system should be constructed, manufactured and operated under conditions avoiding damage by laser pulses. We are systematically studying responses of a wide variety of XUV/SXR optical materials to intense short-wavelength radiation. Our Department organized a series of international SPIE conferences in this area. Proceedings of the fourth conference (XDam4) in the series appeared in 2013 [8]. The XDam5 Conference was held in Prague, 15-16 April 2015.

A typical element often considered for the surface coating of high-performance XUV/SXR optics is carbon. We have already investigated several allotropes of this light element, i.e., diamond, graphite, amorphous carbon, and fullerenes. For example, diamond samples were irradiated by free-electron laser femtosecond pulses at XUV/SXR photon energies ranging from 24 to 275 eV [9]. Micro-Raman analysis evidenced the graphitization of the irradiated diamond samples. The fluence threshold for graphitization was retrieved for all radiation photon energy using Nomarski (DIC - differential interference contrast) microscopy. A dedicated theoretical approach was applied to model the short wavelength laser-matter interaction. Comparison of the experimental and theoretical values shows their good agreement, indicating non-thermal nature of the graphitization process initiated by intense extreme ultraviolet and soft x-ray radiation.

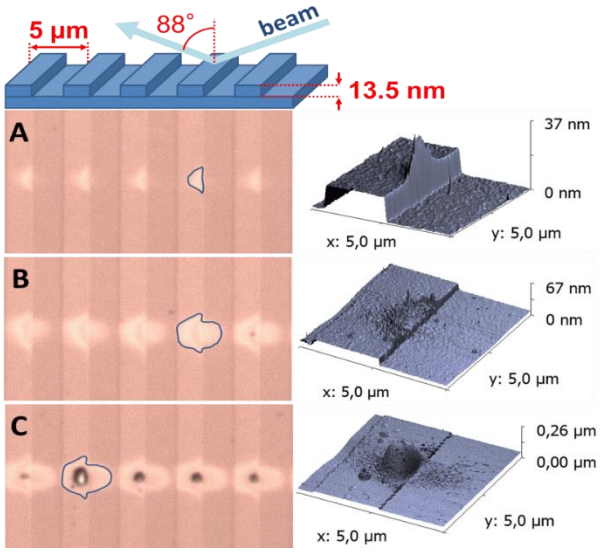


Fig. 1 Reflection grating (i.e., a structured silicon substrate covered by 45 nm thick layer of amorphous carbon; a grating profile and irradiation conditions are displayed at the top of the figure) irradiated by a single shot of SXR FEL radiation at a fluence of (A) 356 mJ/cm², (B) 806 mJ/cm², and (C) 1115 mJ/cm² [10].

Not only a particular material of the substrate and coatings, but also a spatial structure (i.e., single coating of different thicknesses, multilayer mirrors, grating-like structures, and so on) influences radiation resistance of optical elements. We studied an interaction of free-electron laser (FEL) pulses with a grating structure (Fig. 1, see, please, the top of the figure for the grating shape and dimensions) using 4.6-nm radiation generated at the FLASH facility in Hamburg. For fluences above 63.7 ± 8.7 mJ / cm², the interaction triggers a damage process starting at the edge of the grating structure as evidenced by Nomarski optical and atomic force microscopy (Fig. 1). Simulations based on solution of the Helmholtz equation demonstrate an enhancement of the electric field intensity distribution at the edge of the grating structure. The ratio of the maximum energy absorbed in the grating to the energy absorbed on the surface of a flat mirror is found to be $\gamma = 3.4$. This value is directly related to the ratio of damage thresholds of the mirror and the grating determined in our irradiation experiment carried out at the FLASH facility.

Researchers belonging to the Department contributed to above-mentioned papers by the determination of an effective beam area, damage thresholds and performing and interpreting the spectromicrochemical (Raman and ESCA) measurements on damage patterns.

2. Investigating photons, neutrons and charged particles emitted from laser-produced plasmas

2.1 Low- and high-energy photons

We are using optical, extreme ultraviolet and x-ray emission spectroscopy of plasmas produced by XUV/x-ray lasers ([11] and references cited therein) and conventional, long-wavelength lasers [12-20]. For example, several schemes of high-resolution x-ray spectroscopy was in our Department utilized for investigating phenomena occurring in colliding plasmas and during the plasma-wall interaction. Directional flows of energetic ions ([12]; for more details on ion emission see, please, the next paragraph of the report) produced by laser-exploded foils were used to investigate collisional effects in counter-streaming plasmas [13] and transient phenomena accompanying the plasma interaction with surfaces

of solid targets (walls). Macroscopic characteristics of optimized plasma jets launched from rear surfaces of double-foil targets [14] were studied using a diagnostic complex based primarily on high-resolution, high-dispersion X-ray spectroscopy and temporally-resolved x-ray imaging. The spatially variable, complex satellite structure observed in emission spectra of the H- and He-like ions proved a formation of relatively cold dense plasma at irradiated foil surfaces, an occurrence of the hot interpenetrating plasma in the inter-target region and subsequent thermalization, deceleration and trapping of ions in the colliding plasmas close to secondary targets [15]. The x-ray spectra interpretation based on the atomic and collisional-radiative codes was complemented by 1D and 2D hydrodynamic modeling of the plasma expansion and interaction of counter-propagating plasmas [16]. The radial expansion of ions back-scattered due to the plasma collision was directly observed from the Doppler-effect-induced splitting of x-ray lines [17]. Finally the charge exchange phenomena in the near-wall plasma region of secondary targets were characterized for the first time via analysis of local depressions (dips) identified in profiles of emitted x-ray lines [18-20]. Both last mentioned observations and their interpretation represent priority-character results.

2.2 Ions and neutrons

Since the first studies of laser interaction with solid targets, the efficient emission of energetic ions from laser-generated plasmas has been of special interest for ion sources, especially for bio-chemistry, high quality collimated ion beams for nuclear reactions and hadron-therapy as well as for material modification [21-25].

The expansion of ions into vacuum reflects the plasma evolution from the laser-target interaction up to the phase, where no collisions between ions occur and the charge-states of ions are frozen. Then the ion time-of-flight spectra exhibit a dependence on the detector's distance from the target. The easier way how to determine the main characteristics of ions may be through the analysis of the TOF signal $S(t)$ transformed into the velocity space $S(v)$ [26]. If an ion collector is used and ions have the shifted Maxwell-Boltzmann velocity distribution, than

$$S(v)\, v^{-3} = \sum S_{i,0} \exp\left[-\frac{(v - u_{i,q})^2}{2kT_i / m_i} \right], \qquad (1)$$

where v is the velocity, $u_{i,q}$ is the velocity of their center-of-mass motion directed to the ion collector, k is the Boltzmann constant, m_i is the ion mass and T_i is the ion temperature. The relationship (1) allows us to determine partial velocity spectra of ion groups emitted by the plasma, as Fig. 2 shows. For example, the energy distribution of alpha-particles from the $^{11}B(p; \alpha)2\alpha$ reaction driven by the laser system PALS were easily retrieved from the TOF signal using (1) [27]. Moreover, (1) makes it possible to transform observed ion currents $j(t)$ into the distance-of-flight (DOF) charge density profiles $q(x)$ where x is the flight distance [28]. A set of the density profiles allows to draw a map of ion charge density at a selected time τ after the end of the laser pulse, as Fig. 3 shows. These characteristics are especially relevant for implementation of beam-target nuclear fusion reactions driven by lasers.

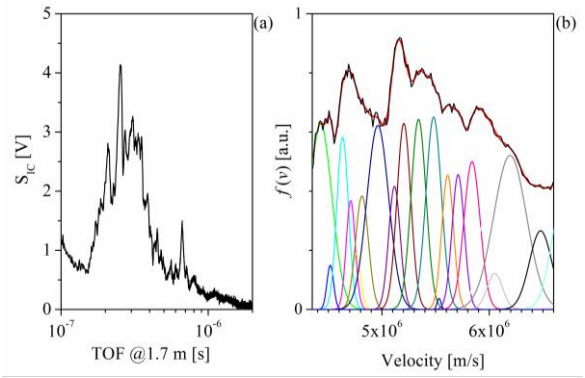


Fig. 2 Ion collector signal induced by ions from Ti target exposed to 2×10^{16} W/cm^2 intensity delivered by iodine laser system PALS operated at 1.315 μm wavelength (a). Deconvolution of selected part of velocity spectrum $f(v)\approx S(v)v^{-3}$ to spectra of partial ion groups, where $S(v)$ is the ion collector signal S_{IC} transformed into the velocity space (b).

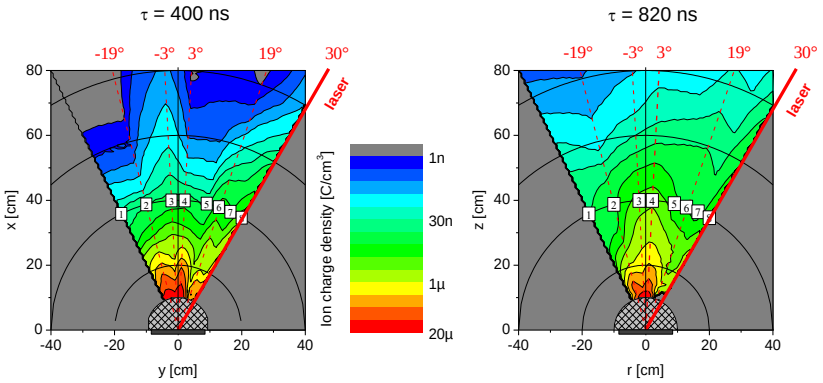


Fig. 3 Charge density maps of protons and carbon ions at time of 400 ns and 820 ns after the interaction of a PALS-laser beam with a $(CH_2)_n$ target. The labels indicate the directions of observation of ion currents with the use of eight ion collectors positioned at the distance of 40 cm from the target. The laser beam struck the target at the angle of 30°; target irradiation of 3×10^{16} W/cm^2.

Plasmas produced at the PALS facility are sources of a very high number of fast ions. This fact allowed us to produce a high yield of alpha particles of ~10^9 per steradian per shot from a well-defined layer of boron dopants in a hydrogen-enriched silicon target irradiated with an intensity of 3×10^{16} Wcm^{-2} triggering the fusion reaction $^{11}B + p \rightarrow 3\alpha + 8.7$ MeV [27]. Moreover, deuterons accelerated by the PALS facility are capable of initiating the $^7Li(d,n)^8Be$ reaction in a secondary LiF (catcher) target as well as the $D(d,n)^3He$, and $^{12}C(d,n)^{13}N$ reactions in the primary target [28,29].

The observed yield of neutrons from the D+D → ^{3}He (0.82 MeV) + n (2.45 MeV) nuclear reaction was of 2 × 10^8 neutrons per laser shot for the average laser energy of 550 J [28]. Fig. 4 shows a spread in the neutron yield dependence on the energy delivered on deuterated targets with the use of various fs-, ps- and sub-ns lasers. The spread can be limited by a baseline which was estimated to be $Y_{BL} = 2000\times E^{1.65}$ [29]. Deuterons with energy up to ~2.5 MeV accelerated from the front surface of a massive CD_2 target in the backward direction with respect to the laser beam impacted a thick natural LiF slab, as Fig. 5 shows. Neutrons produced through the fusion reaction $^7Li(d,n)^8Be$ had a mean energy of ~13.5 MeV. Only a minority of them reached up to ~16-MeV energy. The neutron yield obtained under these non-optimized reaction conditions reached a value up to 5×10^7 neutrons per shot [30].

The acceleration of ions by a double layer results in polarization of irradiated targets. A return current flowing through the target holder balances the positive charge occurred on the target [31]. We developed a new inductive target probe allowing us measuring the target current derivative in a kA/ns range [32]. Fig. 6 shows the scheme of this target probe and the laser pulse energy dependence of the maximum current flowing through copper, carbon, and polyethylene targets irradiated by the laser system PALS. The corresponding maximum target charge exceeded a value of 10 μC. The observation of the target polarization also shown a correlation between the electromagnetic pulse produced by the laser-target interaction and the return target current.

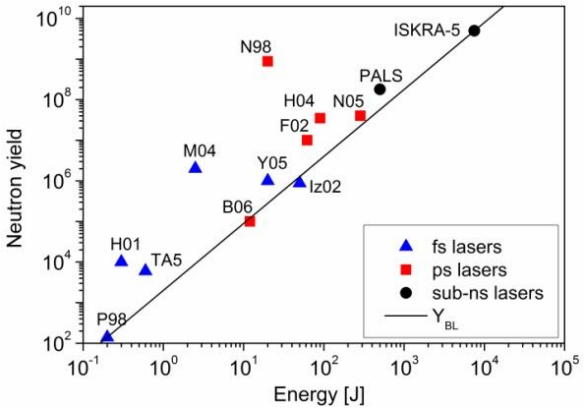


Fig. 4 Neutron yield per laser shot versus laser energy. Data from: P98 – Pretzler et al., 1998; H01 – Hilscher et al., 2001; TA5 – Ter Avetysian et al. 2005; M04 – Madison et al., 2004; Y05 – Youseff et al.,

2005; Iz02 – Izumi et al., 2002; B06 – Belyaev et al., 2006; F02 – Fritzler et al., 2002; N05 - Norreys et al., 2005; N98 – Norreys et al., 1998; H04 – Habara et al., 2004; PALS – presented experiment; ISKRA-5 – Bessarab et al. 1992, for more details, please, see ref. [29].

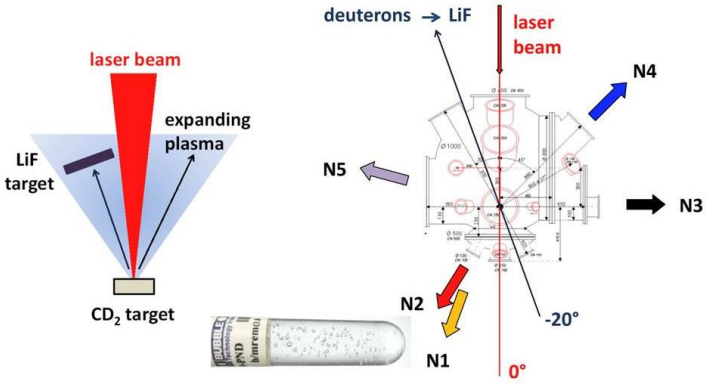


Fig. 5 Left: diagram of the dual target configuration. Right: configuration of scintillation detectors N1 to N5 around of the target chamber. Bottom: calibrated bubble dosimeter (BD-PND) used for measurement of the dose of neutrons.

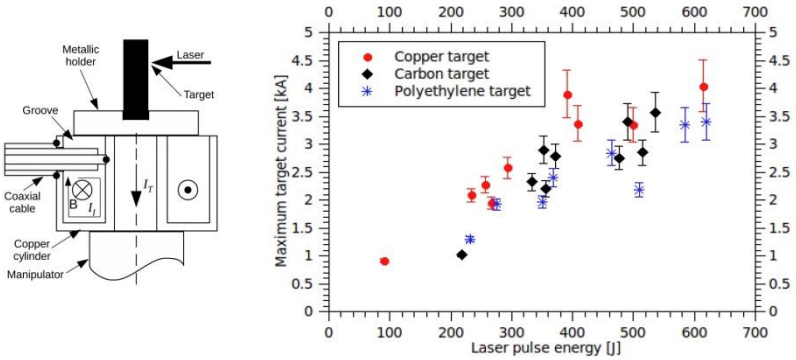


Fig. 6 Left: Schematic diagram of the target current probe. Right: Laser pulse energy dependence of maximum current flowing through copper, carbon, and polyethylene targets.

3. X-ray holography with atomic resolution and related techniques

Researchers of the Department are also working on the determination of local atomic structures of crystalline materials with short-range chemical and/or displacive disorder by means of x-ray diffuse scattering. The experiments are mostly carried out using powerful sources of synchrotron radiation in Trieste (Sincrotrone Trieste) and in Grenoble (ESRF). A large package of computer programs for experimental data processing has been developed on the platform of interactive data language (IDL). These codes make it possible to reconstruct a large volume of the reciprocal space of samples from sets of diffraction patterns collected on large position-sensitive detectors taking into account experimental conditions (absorption in the sample, scattering in air, x-ray fluorescence, geometrical conditions, detector efficiency etc.) in order to get very high precision of experimental data which is crucial for successful real-space reconstruction.

In co-operation with the Department of Spintronics and Nanoelectronics and Department of Condensed Matter Theory of IP-ASCR, we have studied the local atomic structure of diluted magnetic semiconductors [33]. On the basis of high-resolution x-ray diffraction measurements at Elettra synchrotron light source in Trieste, we have revealed the structural anisotropy on (Ga,Mn)As and (Ga,Mn)(As,P) epilayers in the form of anisotropic distribution of stacking faults. By numerical simulations of the measured diffraction patterns, we have determined the type of stacking faults. The relation of the observed structural anisotropy and magnetocrystalline anisotropy has been treated. Full-potential density functional calculations provided the evidence of enhanced density of Mn along the stacking fault planes. Anisotropic distribution of Mn produces a symmetry-breaking mechanism of strength which can explain uniaxial magnetocrystalline anisotropy of these ferromagnetic semiconductors.

We have also studied the diffuse scattering of strontium titanate [34]. By using a powerful synchrotron radiation, we have measured the scattered intensity in a large volume of the reciprocal space. This three-dimensional diffuse scattering pattern has been modeled using numerical simulation. In contrast to previous papers on similar perovskite materials, it has been shown that x-ray diffuse scattering pattern can be explained only when taking into consideration correlated displacements of both strontium and titanium cations. It also demonstrated that the diffuse scattering simulated on the bases of a structural model has to be compared to experimental data in a large volume of the reciprocal space in order to avoid some misleading conclusions.

4. Laser-plasma chemistry and generators of reactive species

To provide a unique way to mimic the chemical effects of high-energy-density events in planetary atmospheres (cometary impact, lightning) and related environments, single ≤1 kJ pulses from a high-power laser PALS have been focused into homogeneous and heterogeneous molecular systems to create large amounts of dense, chemically active plasma that closely matches their natural energy-density and plasma-volume in a fully-controlled laboratory environment. The many chemical reactions initiated by laser-plasma formation in systems containing condensed phases (fog, dust particles, ices, meteoritic and/or geological materials, etc.) and molecular gases with compositions relevant to the chemical evolution of the Earth's early atmosphere and some extra-terrestrial bodies will be systematically studied and the chemical action of laser plasmas generated in homogeneous and heterogeneous systems will be compared. The processes responsible for the chemical action of laser plasmas in these two cases will be identified and investigated. By conducting more realistic laboratory simulations in heterogeneous systems we are gaining a deeper understanding of naturally occurring mixed phase phenomena relevant to astrobiology. Our work done in the homogeneous systems is summarized in review articles [35,36]; results of recent PALS experiments focused on the heterogeneous systems can be found in refs [37,38]. In these studies, our Department is responsible for the laser plasma generation and revealing its characteristics by advanced plasma diagnostic techniques. Colleagues from the chemical institutions participating in these experiments are dealing with the chemical analysis of laser-plasma exposed samples.

Chemical and plasma generators of singlet oxygen [39,40] and other transient, highly reactive species [41] were in our Department developed for their utilization in high-power COILs (=Chemical Oxygen Iodine Lasers). During last years, an original device of the spray singlet oxygen generator with a centrifugal separation of the gas/liquid reaction mixture (CentSpraySOG) [42] was designed, constructed and experimentally tested for COIL driving. Singlet delta oxygen was generated by the most efficient chemical reaction between alkaline solution of hydrogen peroxide in the spray form and gaseous chlorine introduced by a special two-phase nozzle in the rotating separator. The generator can operate at much higher partial pressure of produced singlet oxygen and nearly atmospheric total pressure, which is one of the advantages of the CentSpraySOG in comparison with other types of generators used in the COIL systems.

5. Theory and computer simulations of laser interactions and plasmas

The theory group of the Department splits into two parts according to the subject of the research. The first group (TG-I) studies the interaction of intense radiation with isolated atoms and molecules while the second group (TG-II) investigates solids and plasmas exposed to short and ultra-short pulses provided by high-power photon sources.

5.1 The theory of laser interaction with atoms

In the last five years the theory group I (TG-I) has focused on the theoretical study of the laser-matter interaction in the XUV range. TG-I has developed a new methodology for quantum dynamical simulations of isolated atomic and molecular systems, which is built upon approaches borrowed from physics (complex scaling transformations), quantum dynamics (the (t,t')-method for calculations of Floquet states), and quantum chemistry (the use of Gaussian basis sets for molecules and the construction of the wavefunction based on linear combination of Slater determinants). In 2009-2011, TG-I has worked on an explanation of numerical errors that typically arise in complex scaling calculations of multidimensional systems such as many-dimensional electronic wavefunctions [43]. The obtained understanding of the numerical background of the complex scaling applications helped us to propose solid Gaussian basis sets suitable for the use of complex scaling in 2013 [44]. Further an original quantum dynamical approach was developed for efficient simulations of atoms in electromagnetic pulses containing from hundreds to millions and more optical cycles [45]. The approach has been tested for different XUV pulses between 20 to 60 nm and GW to PW/cm^2. In 2013 the TG-I joint our affords with the group of N. Moiseyev in the Israel Institute of Technology (Technion) in order to apply the new

methodology in the prediction of the “time-asymmetric phenomenon”, which had until then been demonstrated only in model systems. The phenomenon for the laser excitation of the helium atom, showing that some additional conditions need to be fulfilled in order to see the effect [46,47], has been predicted. The current numerical methodology has been deliberately based on such approaches that allow for its straightforward generalization for larger atoms and molecules, which TG-I would like to accomplish in the following years.

5.2 The theory of laser plasmas

Interest of TG-II is focused on hot dense plasmas and warm dense matter. The key results obtained by TG-II members during last years are summarized in refs [48]. The papers deal with the phase space evolution of the electron gas for the case of Raman scattering from the laser plasma. The Raman scattering if one of the key non-linear processes interfering with an efficient absorption of laser energy a nearly collisionless plasmas. Easier models concentrated mainly on the energy transfer between the wave modes and treated the electron dynamics just within a hydrodynamic approach. Solving the Maxwell-Vlasov model at least in 1D is, however, is giving a much more complete picture of what the electron gas is actually doing during the interaction, including particle trapping, development of the trapped particle instability, electron acceleration etc. Moreover, the Fourier-Hermite transform method used for the solution involves no numerical entropy growth as some of the grid dependent methods and readily allows a direct physical interpretation of the underlying phenomena.

6. References

1. S. M. Vinko, O. Ciricosta, B.-I. Cho, K. Engelhorn, H.-K. Chung, C. Brown, T. Burian, J. Chalupsky, R. Falcone, C. Graves, V. Hajkova, A. Higginbotham, L. Juha, J. Krzywinski, H. J. Lee, M. Messerschmidt, C. Murphy, Y. Ping, A. Scherz, W. Schlotter, S. Toleikis, J. J. Turner, L. Vysin, T. Wang, B. Wu, U. Zastrau, D. Zhu, R. W. Lee, P. A. Heimann, B. Nagler, J. S. Wark: Nature **482**, 59 (2012).
2. O. Ciricosta, S. M. Vinko, H.-K. Chung, B.-I. Cho, C. R. D. Brown, T. Burian, J. Chalupský, K. Engelhorn, R.W. Falcone, C. Graves, V. Hájková, A. Higginbotham, L. Juha, J. Krzywinski, H. J. Lee, M. Messerschmidt,C. D. Murphy, Y. Ping, D. S. Rackstraw, A. Scherz, W. Schlotter, S. Toleikis, J. J. Turner, L. Vyšín, T. Wang, B. Wu, U. Zastrau, D. Zhu, R.W. Lee, P. Heimann, B. Nagler, J. S. Wark: Phys. Rev. Lett. **109**, 065002 (2012).
3. D. Umstadter: Extreme X rays probe extreme matter, Physics **5**, 88 (2012); available only at: http://physics.aps.org/articles/v5/88
4. B. I. Cho, K. Engelhorn, S. M. Vinko, H.-K. Chung, O. Ciricosta, D. S. Rackstraw, R.W. Falcone, C. R. D. Brown, T. Burian, J. Chalupský, C. Graves, V. Hájková, A. Higginbotham, L. Juha, J. Krzywinski, H. J. Lee, M. Messersmidt, C. Murphy, Y. Ping, N. Rohringer, A. Scherz, W. Schlotter, S. Toleikis, J. J. Turner, L. Vyšín, T. Wang, B. Wu, U. Zastrau, D. Zhu, R.W. Lee, B. Nagler, J. S. Wark, P. A. Heimann: Phys. Rev. Lett. **109**, 245003 (2012).
5. J. Chalupský, J. Krzywinski, L. Juha, V. Hájková, J. Cihelka, T. Burian, L. Vyšín, J. Gaudin, A. Gleeson, M. Jurek, A. R. Khorsand, D. Klinger, H. Wabnitz, R. Sobierajski, M. Störmer, K. Tiedtke, S. Toleikis: Opt. Express **18**, 27836 (2010).
6. J. Chalupský, T. Burian, V. Hájková, L. Juha, T. Polcar, J. Gaudin, M. Nagasono, R. Sobierajski, M. Yabashi, J. Krzywinski: Opt. Express **21**, 26363 (2013).
7. J. Chalupský, L. Juha, J. Kuba, J. Cihelka, V. Hájková, S. Koptyaev, J. Krása, A. Velyhan, M. Bergh, C. Caleman, J. Hajdu, R. M. Bionta, H. Chapman, S. P. Hau-Riege, R. A. London, M. Jurek, J. Krzywinski, R. Nietubyc, J. B. Pelka, R. Sobierajski, J. Meyer-ter-Vehn, A. Krenz-Tronnier, K. Sokolowski-Tinten, N. Stojanovic, K. Tiedtke, S. Toleikis, T. Tschentscher, H. Wabnitz, U. Zastrau: Opt. Express **15**, 6036 (2007).
8. *Damage to VUV, EUV, and X-ray Optics IV* (Eds L. Juha, S. Bajt and R. London) and *EUV and X-ray Optics: Synergy between Laboratory and Space III* (Eds R. Hudec and L. Pína), Proc. SPIE **8777**, 1-364 (2013).
9. J. Gaudin, N. Medvedev, J. Chalupský, T. Burian, S. Dastjani-Farahani, V. Hájková, M. Harmand, H. O. Jeschke, L. Juha, M. Jurek, J. Krzywinski, R. A. Loch, S. Moeller, M. Nagasono, C. Ozkan, K. Saksl, H. Sinn, R. Sobierajski, P. Sovák, S. Toleikis, K. Tiedtke, M. Toufarova, T. Tschentscher, V. Vorlíček, L. Vyšín, H. Wabnitz, B. Ziaja: Phys. Rev. B **88**, 060101 (2013).
10. J. Gaudin, C. Ozkan, J. Chalupský, S. Bajt, T. Burian, L. Vyšín, N. Coppola, S. Dastjani Farahani, H. N. Chapman, G. Galasso, V. Hájková, M. Harmand, L. Juha, M. Jurek, R. A. Loch, S. Möller, M. Nagasono, M. Störmer, H. Sinn, K. Saksl, R. Sobierajski, J. Schulz, P. Sovak, S. Toleikis, K. Tiedtke, T. Tschentscher, J. Krzywinski: Opt. Lett. **37**, 3033 (2012).

11. U. Zastrau, S. M. Vinko, J. S. Wark, R. R. Fäustlin, N. Medvedev, S. Toleikis, T. Tschentscher, T. Burian, J. Chalupsky, L. Juha, C. Fortmann, S. H. Glenzer, R. W. Lee, A. J. Nelson, T. W. J. Dzelzainis, D. Riley, B. Nagler, E. Galtier, F. B. Rosmej, E. Förster: Laser Part. Beams **30**, 45 (2012).
12. O. Renner, R. Liska, F. B. Rosmej: Laser and Particle Beams **27**, 725 (2009).
13. O. Renner, E. Krousky, R. Liska, M. Smid, O. Larroche, E. Dalimier, F. B. Rosmej: J. Phys. – Conf. Ser. **244**, 022024 (2010).
14. O. Renner, T. Pisarczyk, T. Chodukowski, Z. Kalinowska, E. Krousky, P. Pisarczyk, M. Smid, J. Ullschmied, E. Dalimier: Phys. Plasmas **18**, 093503 (2011).
15. O. Renner, M. Smid, T. Burian, L. Juha, J. Krasa, E. Krousky, I. Matulkova, J. Skala, A. Velyhan, R. Liska: High Energy Density Physics **9**, 568 (2013).
16. O. Larroche, R. Liska, O. Renner, E. Dalimier: EPJ Web of Conferences **59**, 05017 (2013).
17. M. Šmíd, O. Renner, R. Liska: J. Quant. Spectr. Rad. Transfer **125**, 38 (2013).
18. O. Renner, E. Dalimier, R. Liska, E. Oks, M. Smid: J. Phys. – Conf. Ser. **397**, 012017 (2012).
19. O. Renner, E. Krousky, M. Smid, R. Liska, P. Vachal, F Y. Khattak, E. Dalimier, E. Oks: EPJ Web of Conferences **59**, 14005 (2013).
20. E. Oks, E. Dalimier, A. Faenov, O. Renner: J. Phys. – Conf. Ser. **548**, 012030 (2014).
21. F. P. Boody, R. Höpfl, H. Hora, and J. C. Kelly, Laser Part. Beams **14**, 443 (1996).
22. J. Wołowski, J. Badaiak, A. Czarnecka, P. Parys, M. Pisarek, M. Rosiński, R. Turan, and S. Yerci, Laser Part. Beams **25**, 65 (2007).
23. M. Roth, D. Jung, K. Falk, N. Guler, O. Deppert, M. Devlin, A. Favalli, J. Fernandez, D. Gautier, M. Geissel, R. Haight, C. E. Hamilton, B. M. Hegelich, R. P. Johnson, F. Merrill, G. Schaumann, K. Schoenberg, M. Schollmeier, T. Shimada, T. Taddeucci, J. L. Tybo, F. Wagner, S. A. Wender, C. H. Wilde, and G. A. Wurden: Phys. Rev. Lett. **110**, 044802 (2013).
24. V. Malka, S. Fritzler, E. Lefebvre, E. d'Humières, R. Ferrand, G. Grillon, C. Albaret, S. Meyroneinc, J-P. Chambaret, A. Antonetti, D. Hulin: Med. Phys. **31**, 1587 (2004).
25. S. V. Bulanov, V. S. Khoroshkov: Plasma Phys. Rep. **28**, 453 (2002).
26. J. Krása: Appl. Surf. Sci. **272**, 46 (2013).
27. A. Picciotto, D. Margarone, A. Velyhan, P. Bellutti, J. Krasa, A. Szydlowsky, G. Bertuccio, Y. Shi, A. Mangione, J. Prokupek, A. Malinowska, E. Krousky, J. Ullschmied, L. Laska, M. Kucharik, G. Korn: Phys. Rev. X **4**, 031030 (2014).
28. J. Krása, P. Parys, L. Velerdy, A. Velyhan, L. Ryć, D. Delle Side, V. Nassisi: Laser Part. Beams. **32**, 15 (2014).
29. J. Krása, D. Klír, A. Velyhan, D. Margarone, E. Krouský, K. Jungwirth, J. Skála, M. Pfeifer, J. Kravárik, P. Kubeš, K. Řezáč, J. Ullschmied: Laser Part. Beams **31**, 395 (2013).
30. J. Krása, D. Klír, A. Velyhan, E. Krouský, M. Pfeifer, K. Řezáč, J. Cikhardt, K. Turek, J. Ullschmied, K. Jungwirth: High Power Laser Science and Engineering, 2, e19, 2014, doi:10.1017/hpl.2014.25.
31. R. F. Benjamin, G. H. McCall, A. W. Ehler: Phys. Rev. Lett. **42**, 890 (1979).
32. J. Cikhardt, J. Krása, M. De Marco, M. Pfeifer, A. Velyhan, E. Krouský, B. Cikhardtová, D. Klír, K. Řezáč, J. Ullschmied, J. Skála, P. Kubeš, J. Kravárik: Rev. Sci. Instrum. **85**, 103507 (2014).
33. M. Kopecký, J. Kub, F. Máca, J. Mašek, O. Pacherová, A. W. Rushforth, B. L. Gallagher, R. P. Campion, V. Novák, T. Jungwirth: Phys. Rev. B **83**, 235324-1 (2011).
34. M. Kopecký, J. Fábry, J. Kub: J. Appl. Cryst. **45**, 393 (2012).
35. D. Babánková, S. Civiš, L. Juha: Prog. Quant. Electron. **30**, 75 (2006) and references cited therein.
36. L. Juha, S. Civiš: Laser-plasma chemistry: Chemical reactions initiated by laser-produced plasmas, In: *Lasers in Chemistry* (Ed. M. Lackner), Vol. 2, Wiley-VCH, Weinheim 2008, p. 899-921.
37. M. Ferus, S. Civiš, A. Mládek, J. Šponer, L. Juha, J. E. Šponerová: J. Am. Chem. Soc. **134**, 20788 (2012).
38. M. Ferus, D. Nesvorný, J. Šponer, P. Kubelík, R. Michalčíková, V. Shetivska, J. E. Šponerová, S. Civiš: Proc. Natl. Acad. Sci. USA **112**, 657 (2015).
39. V. Jirásek, M. Čenský, O. Špalek, J. Kodymová: Chem. Eng. Technol. **36**, 1755 (2013).
40. V. Jirásek, J. Hrubý, O. Špalek, M. Čenský, J. Kodymová: Appl. Phys. B **100**, 779 (2010).
41. V. Jirasek, J. Schmiedberger, M. Čenský, J. Kodymová: J. Phys. D **44**, 1 (2011).
42. J. Hrubý, O. Špalek, J. Kodymová, V. Jirásek, M. Čenský: Czech Patent Nr. 301755 (2010).
43. P. R. Kapralova-Zdanska: J. Chem. Phys. **134**, 204101 (2011).
44. P. R. Kapralova-Zdanska, J. Smydke: J. Chem, Phys. **138**, 024105 (2013).
45. P. R. Kapralova-Zdanska, J. Smydke, S. Civis: J. Chem. Phys. **139**, 104314 (2013).
46. P. R. Kapralova-Zdanska, N. Moiseyev: J. Chem. Phys. **141**, 014307 (2014).
47. P. R. Kapralova-Zdanska, N. Moiseyev: Time-asymmetric rapid passage in bound to resonance transitions, to be submitted.
48. M. Mašek, K. Rohlena: Eur. Phys. J. **56**, 79 (2010); **69**, 109 (2015).

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Laser Development and Applications

Team overview

The research team **Laser Development and Applications (LDA)** is exclusively composed of researchers from the **Department of Diode-pumped Lasers.** The core of LDA team originates from the former SOFIA laboratory, part of the former Department of Nonlinear Optics, which was abolished in 2011. A new Department of Diode-pumped Lasers was established in 2011 with the key mission to implement the **HiLASE project** (**www.hilase.cz**). The team is led by Tomáš Mocek, being supported by 3 research group leaders Akira Endo, Antonio Lucianetti, and Danijela Rostohar.

Tomáš Mocek (born 1970) provides leadership and scientific supervision of 36 researchers working in the field of high-average power, diode-pumped solid-state laser development and applications in the framework of HiLASE project co-financed by the European Regional Development Fund. He obtained his PhD in 2000 at KAIST in South Korea. He is employed at the Institute of Physics since 1994. He worked as Marie Curie Fellow at the Ecole Polytechnique/ENSTA in France (2002-2004). His research activity is documented by 102 papers in international peer-reviewed journals with impact factor which acquired 1482 citations, and by H-index of 20 (ResearcherID: G-5344-2014). He was Principal Investigator of standard research projects on Development and applications of ultrafast coherent X-ray beamlines (GAČR, 2007-2009, 244k EUR) and on Development of high repetition rate X-ray lasers for applications (AVČR, 2009-2011, 150k EUR).

Akira Endo (born 1949) is a leader of the thin-disk laser development program at HiLASE. He obtained his PhD in 1981 at the Tokyo Institute of Technology in Japan. His main expertise is high power lasers and EUV radiation sources. He worked as Guest Professor at the University of Jena in Germany (2009-2010), Visiting Scientist at Forschungszentrum Dresden Rosendorf (2010) and Scientific Advisor at Waseda university and Gigaphoton company in Tokyo.

Antonio Lucianetti (born 1965) is a leader of the cryogenically cooled multi-slab laser development program at HiLASE. He obtained his PhD in 1999 at the University of Bern in Switzerland. He worked as Senior Researcher in the field of high power lasers at the Lawrence Livermore National Laboratory in USA (2004-2006), University of Florida & California Institute of Technology (2007–2009) and at Ecole Polytechnique in France (2009-2011).

Danijela Rostohar (born 1970) is a leader of the laser application program at HiLASE. She obtained her PhD degree in 2003 at the University of Stockholm in Sweden. She worked as Senior Researcher at ANKA synchrotron facility in Karlsruhe (2004-2006), Laser Process Engineer in Ysolar company in China (2010-2011), and Research Group Leader at the National Centre for Laser Applications, University of Galway in Ireland (2011-2012).

Genesis of the team

SOFIA laboratory was a test facility for the laser system PALS (Prague Asterix Laser System) and its major task was getting know-how on the OPCPA technique (Optical Parametric Chirped Pulse Amplification). This technique shows gradually increasing importance for short pulse laser systems and high peak power lasers. The SOFIA system was a hybrid laser where the oscillator beam was generated in a solid-state optical parametric oscillator tuned to 1315 nm and then amplified in two gaseous iodine amplifiers. A combination of a gaseous and solid-state lasers made the system quite unique worldwide. A pump beam from the gaseous amplifiers was successfully used for pumping of non-collinear optical parametric amplifiers (KDP, LBO) and boosting the pulse peak power up to terawatt level. The project was particularly important for considerations of possible upgrade of the iodine PALS laser system to the

petawatt level. Key know-how obtained in CPA systems and parametric amplifiers was fully transferred to the HiLASE project.

Department of Diode-pumped Lasers operates a brand **new R&D Centre HiLASE** which deals with the **technological development of high average power pulsed lasers.** HiLASE's *"next generation"* technology is based on diode pumped, solid state laser (DPSSL) architecture that incorporates highly efficient laser emitting diodes to generate the intense light pulses for driving the laser amplifiers. This DPSSL technology brings unique combination of high average power, high pulse repetition rate and high efficiency. The main applications of our lasers include laser induced damage threshold (LIDT) measurements of optical materials, laser shock peening (LSP), development of compact extreme ultraviolet (EUV) sources for lithography, mid-infrared generation, and laser micromachining. Activities of HiLASE are being developed in close collaboration with industrial users, universities and other research institutions worldwide. There are 3 research groups established within the HiLASE Centre: (1) Development of pulsed kW class thin-disk diode pumped solid state laser systems with energy up to J level for industrial and scientific applications, (2) Development of a 100 J / 10 Hz class multi-slab laser system and validation of computer codes to demonstrate scalability up to kJ level, and (3) Development of future industrial applications and technologies.

Scientific activity

SOFIA (2010-2011)

To date, the cutting-edge technique for producing intense laser pulses beyond terawatt level is the OPCPA method (Optical Parametric Chirped Pulse Amplification). This method is used for power increasing of laser pulses, if no further amplification in the laser media is possible, due to some nonlinear effects appearing under strong radiation. Shortening of the pulse is principally limited by its spectral bandwidth: the broader is the bandwidth, the shorter pulse can be produced. Some laser media, unfortunately, support only narrow spectral bandwidth of the amplified laser pulse so that no short pulse (ps-fs) can be produced. However, the OPCPA technique enables to transfer the energy of a strong long laser pulse (pump) to a weak and short pulse (signal) of another laser. The transfer takes place in crystals possessing high non-linear optical activity. To get efficient transfer of the energy, the arrival of both laser pulses into the nonlinear crystal must be well synchronized and both pulses must be of similar duration. For the first time in the world, we used this sophisticated physical method for the amplification of an ultra-short pulse of a Ti:sapphire laser by the energy transfer from a pulse of a gas photodissociation iodine laser. This type of laser is extremely narrow-band and thus the pulses cannot be optically compressed to femtosecond region. On the contrary, its beam can be very energetic and, therefore, ideal for OPCPA pumping. We constructed a two-stage parametric amplifier based on two nonlinear crystals LBO and KDP. The signal beam was produced by a Ti:sapphire laser, its wavelength was 800 nanometers (nm), pulse duration 12.5 femtoseconds (fs) and energy 1 nanojoule (nJ). The pump beam was the third harmonic (438 nm) of the fundamental wavelength (1315 nm) of the iodine single shot laser. In the two-stage crystal amplifier the signal beam was amplified 2×10^8 times (Fig. 1). It was for the first time ever when a Ti:sapphire laser beam was amplified on its strongest wave line of 800 nm in a KDP crystal. Using a small iodine laser we succeeded in amplifying the weak ultra-short pulse at 800 nm wavelength to terawatt level. The pulse duration after the optical compression was 27 femtoseconds (Fig. 2). The suitability of the gaseous iodine photodissociation laser as a pump laser in the OPCPA technique was thus proved experimentally. As a consequence the upgrade of the kilojoule single shot terawatt (TW) laser PALS to a petawatt level was assessed as technically feasible and several high quality journal papers were published. Based on the results attained with the SOFIA laser system, a detailed design of two ultra-high power laser beams, 130 TW and 1.4 PW, using a chain of the OPCPA amplifiers was elaborated.

Besides the OPCPA research we also focused on ultrashort laser pulse diagnostics. A new, highly simplified technique for ultrashort pulse measurement and retrieval was developed. The technique, which is analogous of tomographic ultrashort pulse measurement, was called Dispersoscopy. A patent for the dispersoscopy was granted in February 2014. The dispersoscopy is based on controlled spectral phase modulation of a measured pulse by a dispersive delay unit only and its detection by a temporally integrating spot detector. Such a detector can be a nonlinear crystal (time gating) followed by a photodiode or directly a multi-photon absorbing photodetector. An optimizing algorithm enabling phase retrieval from one-dimensional experimental trace and independently measuring pulse frequency

spectrum was also proposed and claimed in the patent. The dispersoscope has a great potential to be modified for many spectral regions and ranges of pulse lengths.

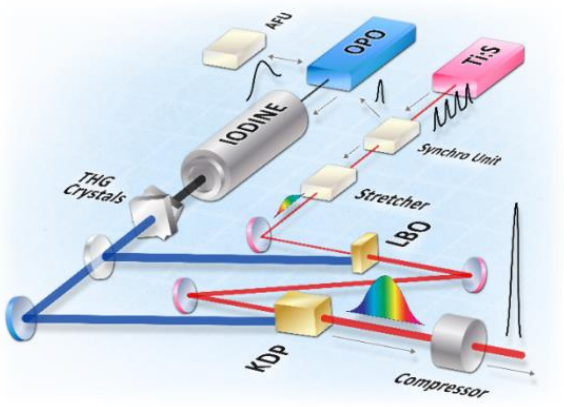


Fig. 1. Schematic of the single shot OPCPA SOFIA facility.

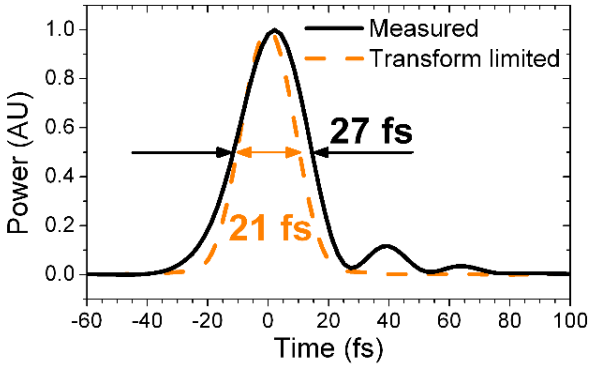


Fig. 2. Temporal evolution of the amplified 800 nm terawatt pulse after compression.

HiLASE (2011-2014)

The HiLASE R&D Centre is in the implementation phase from 01/09/2011 to 31/08/2015. Within the HiLASE project, about 30 mil. EUR from structural and national funds have been invested in order to **develop advanced *"next generation"* lasers** and build up from scratch a new facility in Dolní Břežany in the Central Bohemia Region. At the moment of its full commissioning at the end of 2015, HiLASE will be an important facility of the Institute of Physics with an **ambitious mission to become an excellent science and technology asset for the region and for Europe.** This new generation laser technology is based on highly efficient laser diode pumped solid state laser amplifiers designed with several different concepts. One amplifier concept is based on **thin-disk** architecture with a thin (≈ 200 μm) laser active medium directly bonded to a heat sink which makes cooling highly efficient while other one uses a cryogenically-cooled **multi-slab** architecture. In both cases, DPSSL technology brings a unique combination of high peak power, high average power, high pulse repetition rate and high efficiency. In the operational phase, HiLASE will provide DPSSL systems with **kW average power**, pulse energy ranging from mJ up to 100 J, with 1 ps to 10 ns time scale, and repetition rates from 10 Hz to 100 kHz. Most of the lasers will offer photons at the nominal wavelength of 1030 nm. However, our laser systems are also planned to be used as a pump source for frequency conversion to mid-infrared (MIR, 2-4 μm), higher harmonic frequencies (2nd to 5th) in VIS-DUV, and EUV generation (13.5 nm).

Research Programme 1: Development of picosecond kW class thin-disk diode pumped solid state laser systems with pulse energy up to 1J and high repetition rate (kHz to MHz) for industrial and scientific applications

Current status: Three standalone laser systems (Fig. 3) based on thin-disk technology with different application-motivated output parameters are being commissioned. All beamlines are Yb:YAG based with 1030 nm wavelength and adopt the chirped pulse amplification (CPA) technique. They differ in parameters such as pulse energy and repetition rate which match requirements of prospective applications. Development of **Beamline A** is realized by a subcontractor, a company Dausinger &

Giesen from Stuttgart, Germany, with planned delivery in May 2015. Development of **Beamline B** is done fully **in-house** by the HiLASE team. A regenerative amplifier, which will deliver a 1 kHz pulse train with 100 mJ pulse energy, is in the final phase of testing. The amplifier delivers routinely pulses with energy up to 45 mJ in a fundamental spatial mode with beam quality parameter M^2<1.15. A compressibility of the pulse to several ps has been demonstrated. A second stage, power amplifier, is currently undergoing final testing and optimization of key components; booster amplifier is under development. **Beamline C** (also fully **in-house** developed) provides routinely a train of 0.85 mJ pulse after pulse compression with 100 kHz repetition rate in fundamental spatial mode (M^2=1.2). Compression of pulses to 2 ps (FWHM) by using of a novel concept of small size Chirped Volume Bragg Gratings (CVBG) has been demonstrated. This allowed to build a very compact system with dimensions 90x120 cm^2. The output from Beamline C has been already used for parametric light conversion to 1.9 and 2.2 μm, and also to second and fourth harmonics generation in UV region. The 0.5 kW upgrade is now being built like a new standalone system, i.e. two different systems will be available. More than 500 W of output power in a fundamental spatial mode in CW output has been recently demonstrated. In collaboration with our engineering support we also managed to develop several high-tech products for commercialization such as 100 kHz Pockels cell, thin-disk laser head for 5 kW pumping, new bonding method for thin-disk. We also published important results explaining the importance and benefits of so-called Zero Phonon Line pumping (direct pumping to upper laser level).

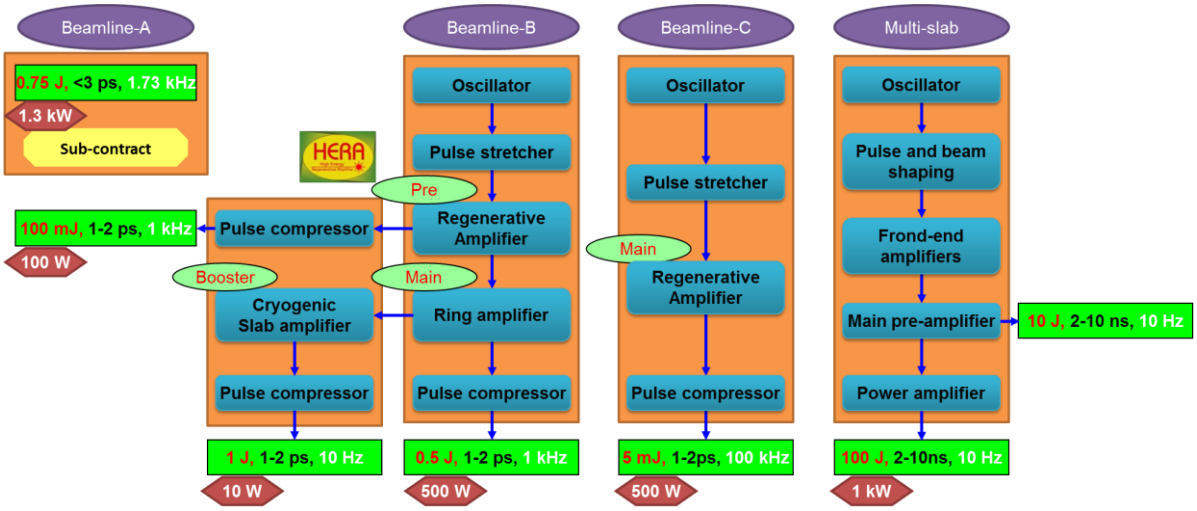


Fig. 3. Schematic presentation of HiLASE laser systems.

Research Programme 2: Development of a 100 J/10 Hz multi-slab laser system and validation of computer codes to demonstrate scalability to 1 kJ level

Current status: We are equipped with an apparatus for precise measurement of spectroscopic characteristics of optical materials at cryogenic temperatures down to 4 K, a compact station for characterization of semiconductor laser diode stacks, and an experimental setup for investigation of laser beam wavefront deformation in heated optical materials and its correction. These in-house developed devices, along with home-made 3D codes for simulation of the energy storage, ASE, heating, internal stress and depolarization in the active laser areas, were crucial for the physical design of the 100 J / 10 Hz laser system.

Fig. 4. Completed HiLASE Centre (left) and thin-disk laser laboratory therein (right).

Research Programme 3: Development of future scientific and industrial applications of lasers developed in programme 1 & 2, and development of key technologies for high repetition-rate amplifiers in partnership with industry

Current status: For selected applications we are currently using a nanosecond fiber laser with an average power of 20 W (10 kHz-1 MHz, 3 ns, 0.2 mJ) with a possibility of burst mode operation (several pulses in one repetition period). The beam can be focused to a spot of 50 μm in diameter. We have realized various experiments in the field of engraving and cutting materials, and also in research of the interactions of laser radiation with materials. Part of this infrastructure is also a set for measurements of laser-induced damage threshold (LIDT). The station consists of a XYZ computer-controlled micrometer translation stage and damage detection based on monitoring of light scattering from the sample surface. A high-speed camera (up to 31,000 frames per second) with continuous data storage options is used to monitor the samples under exposure by laser pulses. In parallel with the development of laser systems, HiLASE also develops several experimental stations where different laser-mater interaction processes can be investigated. Due to the unprecedented parameters of HiLASE lasers and high industrial demand for testing of new optical components with a high damage threshold, the LIDT measurement station was designed according to strict ISO standards. The main demand from industry related to laser processing is to develop high quality, reliable and low cost ways of material processing. After commissioning, it will be possible to investigate and develop processes related to an efficient processing (hardening, drilling, cutting, welding, pattering, structuring etc.) of novel materials used for example in aircraft engines and turbines, solar industry, car industry, electronics, etc. Industry applications also include plastic and polymer processing. New breakthrough results are expected in the field of waveguides in silicon for production of new integrated photonics devices. Scientific applications that will benefit from HiLASE mid-IR sources include high-order harmonic generation, dielectric laser acceleration, and frequency-combs. Sources of secondary photons in the EUV and mid-IR region are especially interesting for emerging applications in Life Sciences due to the novelty in generation of these wavelengths with high fluxes. EUV sources are of high importance for development of new generation EUV lithography.

The research agenda of HiLASE consists of two major phases. **Phase 1 (Implementation)** has been under way since 01/09/2011 and continues until 31/08/2015. After that, in **Phase 2 (Operational)**, HiLASE Centre will be used by scientific and industrial users for various laser experiments and testing of new technologies and materials. Both phases, implementation and operational, are regarded as unique with respect to the **breakthrough laser parameters and applications of these novel lasers, all under one roof**. Since the start of the implementation phase of the HiLASE R&D Centre in 2011, our research team has generated articles in high-profile impacted journals such as Optics Letters, Applied Physics Letters, Nature Materials, etc. Figure 5 demonstrates our scientific leadership (1st author) and quality of our publications (IF).

List of our publications - **http://www.hilase.cz/en/research-programs/publications/**

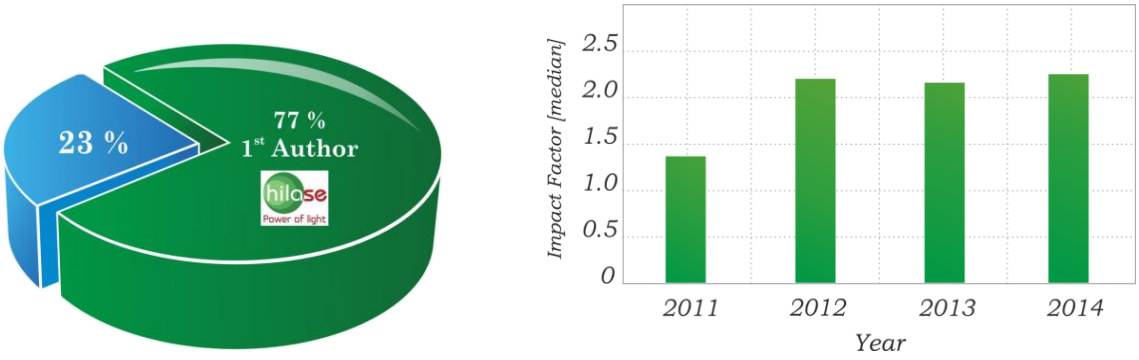


Fig. 5. Authorship of the publications by HiLASE team (left) and evolution of the Impact Factor (right).

Research collaborations (covered by MoU):

1) Laboratoire d'Optique Appliquée, ENSTA-ParisTech, Palaiseau, France
Collaborative Program for Applications of High Energy, Diode-Pumped Lasers in Laser Induced Damage Studies

2) Institute of Optics and Quantum Electronics, Jena, Germany
Collaborative Program for High Power, Diode-Pumped Laser Science and Technology

3) Faculty of Engineering, Graduate School of Engineering, Utsunomiya University, Japan
Collaborative Program for Applications of Laser Driven Plasma X-ray Source Studies

4) Waseda Research Institute for Science and Engineering, Waseda University, Japan
Collaborative Program for Applications of High Energy, Diode-Pumped Lasers in Soft X-ray Source Studies

5) Italian National Research Council, Institute of Photonics and Nanotechnology, Padova, Italy
Collaborative Program on Adaptive Optics Technology for High Average Power

6) Laser-Laboratorium Göttingen e.V., Germany
Collaborative Program on EUV light source and applications

7) Ferdinand-Braun-Institut, Leibniz-Institut fuer Hoechstfrequenztechnik, Berlin, Germany
Collaborative Program on Laser-Diode Technology for High Average Power, Diode-Pumped Solid State Lasers

8) Institute of Thermophysics, Russian Academy of Sciences, Novosibirisk, Russia
Collaborative Program on Material Processing with Average Power, Diode-Pumped Solid State anf Fiber Lasers

9) Centro Láser de la Universidad Politécnica de Madrid, Madrid, Spain
Collaborative Program on Development of Laser Shock Processing

10) University of Parma, Information Engineering Department, Italy
Collaborative Program on Fiber Development for High Average Power, Diode-Pumped Solid State anf Fiber Lasers

11) Japan Atomic Energy Agency, Kansai, Japan
Cooperation in Research, Development and Applications of High Power Laser Systems

12) Frontier Research Institute for Interdisciplinary Sciences, Tohoku University, Sendai, Japan
Joint Research Agreement on Development of Extremely High Power Solid State Lasers

Commercialization of research results

HiLASE Centre started to realize contract research in 2013 and so far the revenues largely exceed our expectations. **In 2014, HiLASE generated about 50% of the total annual income from contract research of the whole Institute of Physics.** Another important achievement is a recently awarded patent entitled "Device for single-shot measurement of M^2 laser beam quality" (Fig. 6).

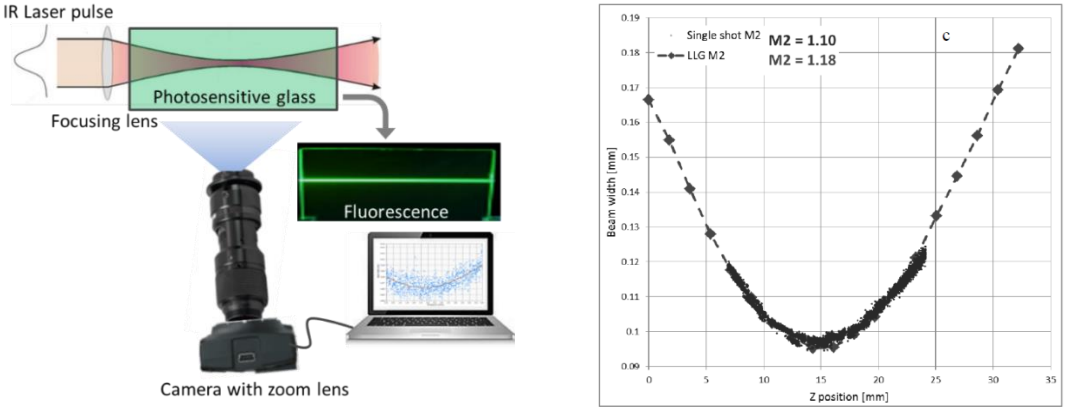


Fig. 6. Principle of the patented Single-Shot M^2 measurement device (left) and a single shot measured caustic of a laser beam (right, dots) in comparison with conventionaly measured data (dashed line).

Major results of Research Programme 1

Beamline B

- Operation of 45 mJ/1 kHz picosecond amplifier with fundamental spatial mode of high quality (M^2) which is now available for application experiments
- Novel concept of quasi-continuous wave pumping of high power thin-disk based lasers
- Prototype of a new thin-disk laser head for laser pumping up to 5 kW
- Development of a new bonding technology of laser active media to a high thermal conductivity heat sink for efficient laser cooling
- Successful development of compact fiber oscillator, pulse picker, and fiber preamplifiers
- Method for in-situ thin-disk deformation measurement

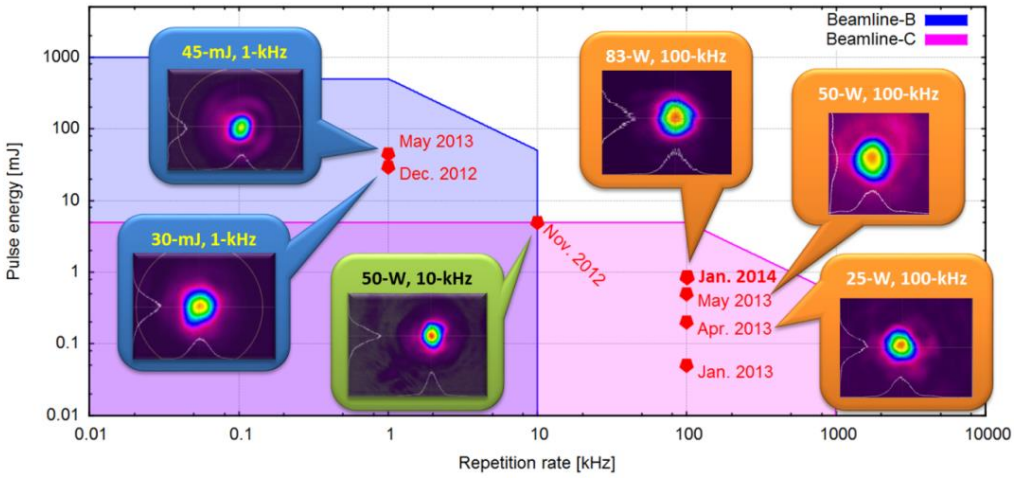


Fig. 7. Stable generation of picosecond pulse train from thin disk beamlines.

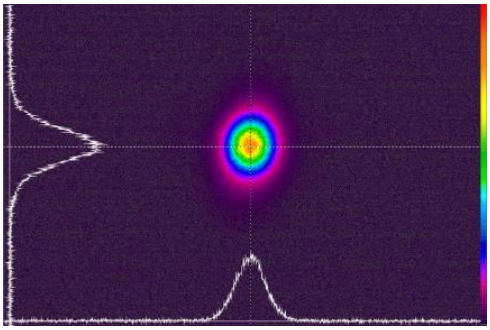


Fig. 8. Beam quality of Beamline B (45 mJ at 1 kHz, 20 % O-O eff., compressed to 2.7 ps).

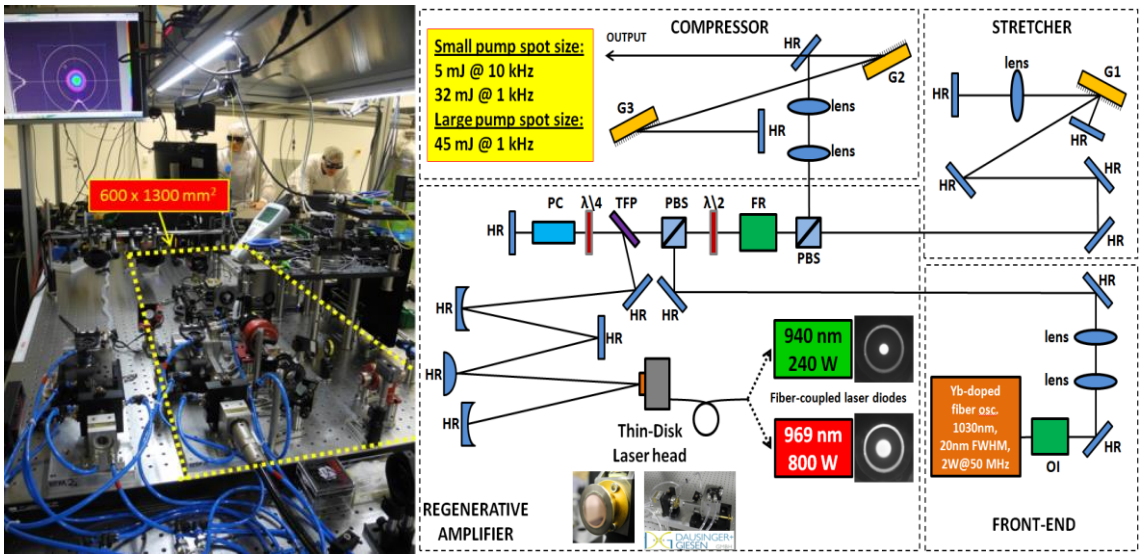


Fig. 9. Reliable and compact high energy thin disk amplifier (45 mJ/1 kHz).

Beamline C

- Zero phonon line pumping (969 nm) demonstrated
- Compact thin-disk Yb:YAG regenerative amplifier (100 kHz, >90 W output, 30% O-O eficiency, fundamental spatial mode, 2 ps) developed
- BBO home-made Pockels cells developed
- Tiny CVBG compressor demonstrated (up to 90% efficiency)
- Ring cavity for the Beamline C upgrade designed and tested
- Demonstration of > 500 W CW output in fundamental spatial mode
- Generation of second and fourth harmonic from the Beamline C demonstrated
- Wavelength conversion to 2 μm radiation demonstrated
- High power Yb:YAG KLM and SESAM mode-locked oscillator under development
- High power femtosecond Yb:YGAG reg. amplifier under development

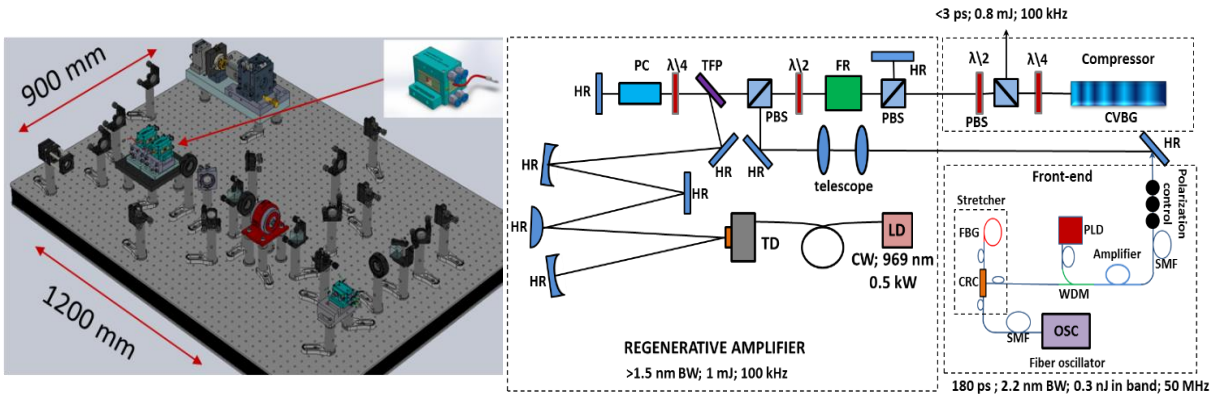


Fig. 10. Optical setup of a compact 100 W high repetition rate regenerative amplifier.

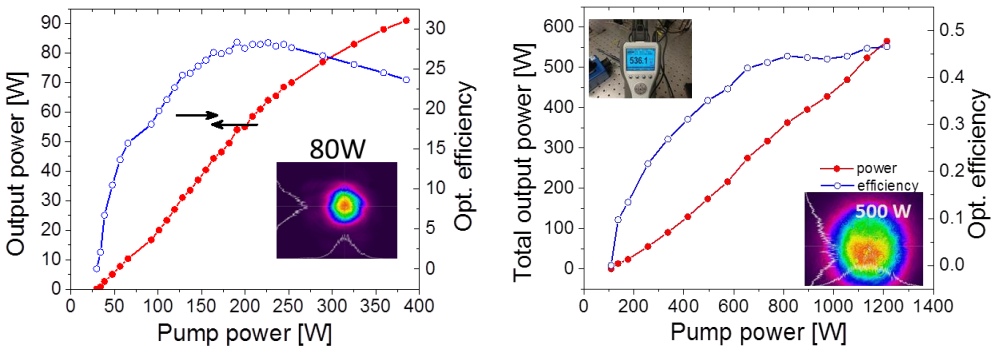


Fig. 11. Output power, extraction efficiency, and near field beam profile Beamline C (left). CW output power and optical efficiency from a fundamental mode operating ring cavity (right).

Major results of Research Programme 2

- 10 J / 10 Hz cryo cooled multislab system in operation in collaboration with RAL-STFC
- Development of 100 J / 10 Hz upgrade in collaboration with RAL-STFC
- Advanced numerical laser model (ASE, thermomechanical modelling, wavefront deformation, depolarization losses, gain calculation, fluid dynamics) developed and benchmarked
- Modeling of TGG Faraday rotators
- Modeling of Ti:sapphire crystal for J-Karen PW laser system at JAEA
- Station for diode stack characterization developed
- Successful high-resolution (15 pm) spectroscopic measurements of variety of materials at different temperatures (Yb:YAG, Yb:LuAG, Yb:CaF2, Yb:YGAG, etc.)
- Q-switched nanosecond cryo laser for LIDT measurements demonstrated
- Method for wavefront correction of the multislab laser
- Development of a new photocontrolled deformable mirror

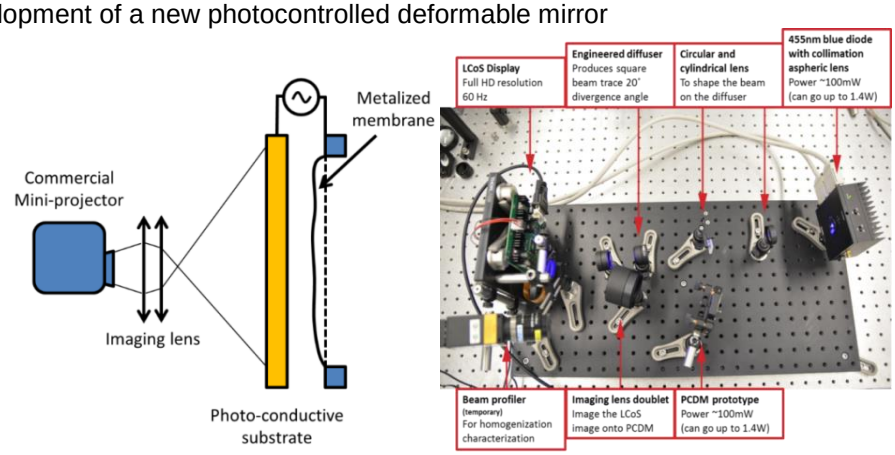


Fig. 12. Novel Photo-Controlled Deformable Mirror

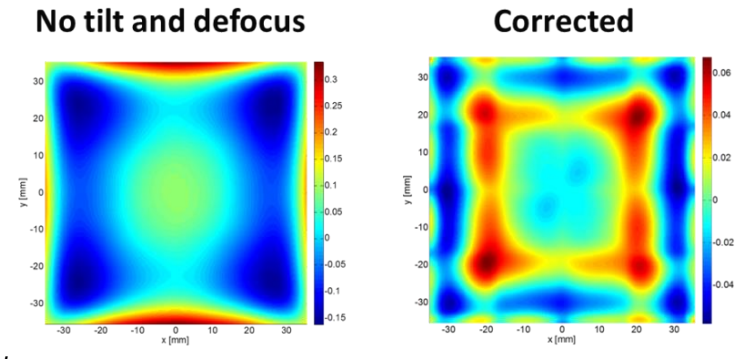


Fig. 13. Realistic modelling of wavefront correction: OPD before (left) and after (right) correction.

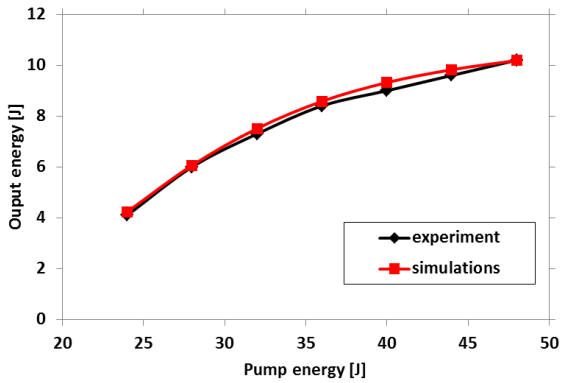
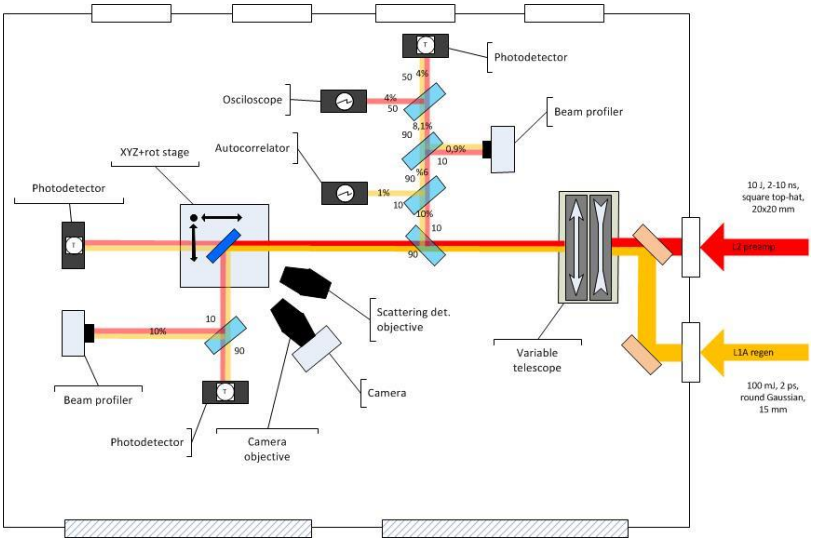


Fig. 14. Benchmarking of ASE numerical model and experiment.

Major results of Research Programme 3

- Laser-induced damage threshold station (ISO 21245 standard)
- Numerical modelling of damage threshold mechanism
- Laser shock peening (LSP) station under development (processing optics, beam delivery)
- State-of the art theoretical and numerical studies of laser-material interactions, surface nanostructuring, and semiconductor bandgap modification
- Research of laser induced periodic surface structures (LIPSS)



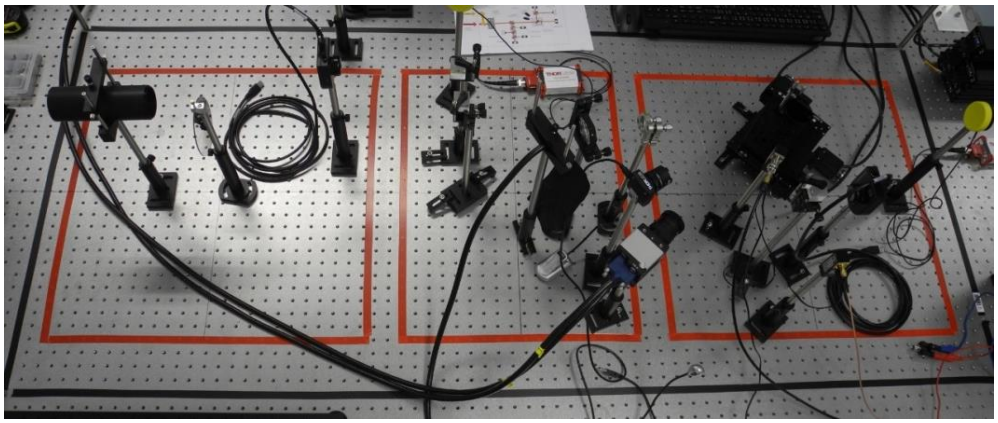


Fig. 15. LIDT experimental station (design concept, optical setup).

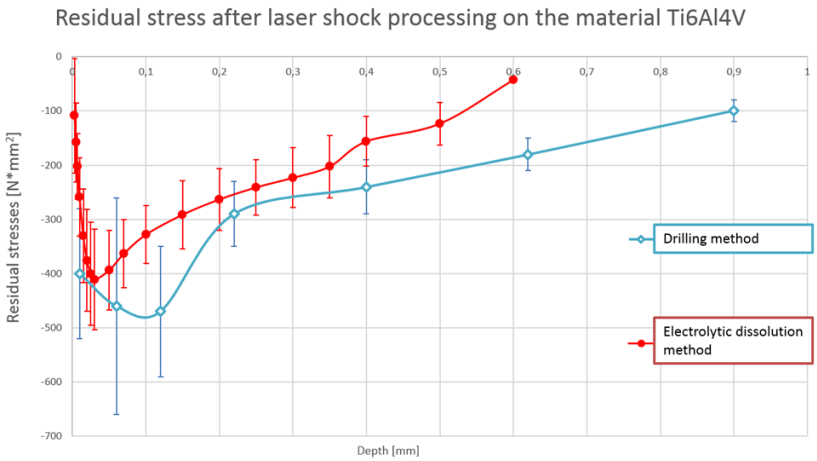


Fig. 16. Characterization of the LSP processing (measurement of residual stress after treatment).

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	ELI Beamlines

The main task of the team 16 – composed of three research departments of the Division 9 of the Institute of Physics CAS is the development and construction of the new international laser center ELI Beamlines. ELI Beamlines is conceived as a research user center for scientific and technological investigations in different fields. ELI Beamlines will combine four high power and high intensity lasers sources (primary sources) with enhanced repetition rates and will provide to users synchronized short pulse primary sources, fs-laser driven secondary sources of X-rays and particles as well as different experimental platforms including end-stations for sophisticated pump-probe experiments with fs-time resolution.

The backbone of the facility will be the newly (currently under construction) developed diode pumped solid state lasers (DPSSL) which allow a considerable enhanced repetition rate (10 Hz and higher) of the lasers even in the PW range. A new cooling technology will allow generating lasers pulses at the 10 PW level, a never achieved before peak power, with a shot rate of 1 shot per minute. It is worth noting that all lasers sources are leading edge technology developments which will ensure a highly competitive research facility for the next years of operation of the facility. The details about the laser sources are given in the subsection RP1 of this report.

New concepts of high power laser driven X-ray generation in combination with particle acceleration will allow providing to users for the first time synchronized, short pulse high intensity beams of lasers, continuously tunable X-rays and particles (electrons and ions) in a very broad energy range (eV- MeV).

The research team consists of highly specialized groups of scientists and engineers to prepare and build the experimental capabilities of the facility. To efficiently organize the work the following Research Programs (RP, or in some cases these are called RA - research activities) are pursued:

RP1: Lasers generating rep-rate ultrashort pulses & multi-petawatt peak powers
RP2: X-ray sources driven by rep-rate ultrashort laser pulses
RP3: Particle acceleration by lasers
RP4: Applications in molecular, biomedical and material science
RP5: Laser plasma and high-energy-density physics
RP6: High-field physics and theory

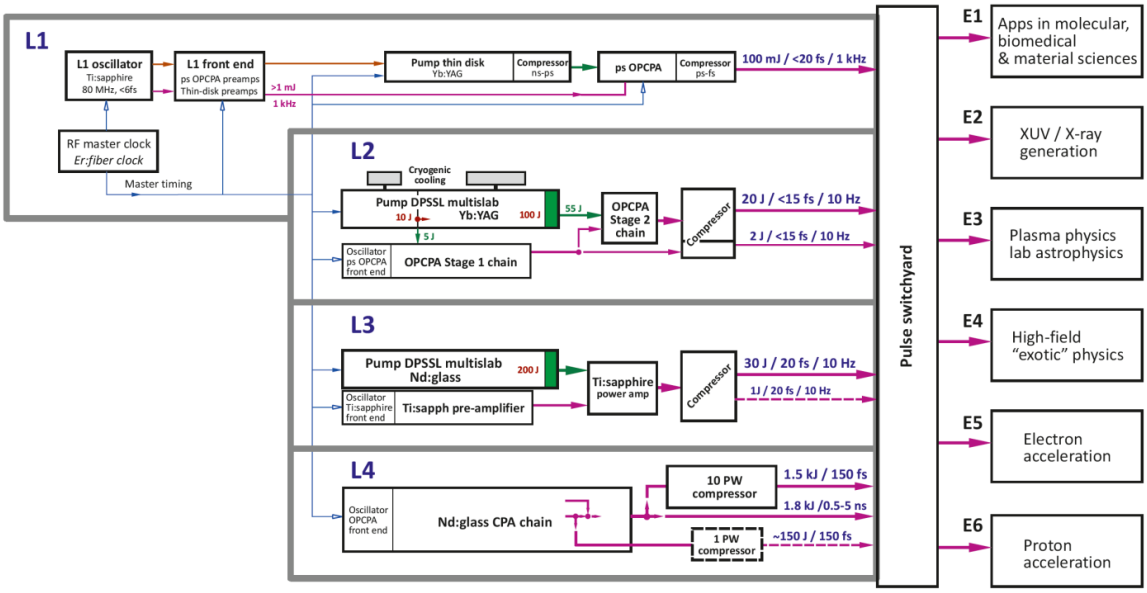
Moreover, as a service group for RP1-RP5 there exists also a **Radiation protection and dosimetry team**. The radiation protection at the PW level reached at ELI Beamlnes will be world unique, and therefore the research results and research plans of this team are presented below separately.

The reader should in a sense look at the RPs as separate science groups. Due to the size of the grant (278 Mio €) an overall number of over 250 people have been hired for Division 9 to efficiently design, construct and build the whole new infrastructure. This includes a large building complex and its complete technical infrastructure. More details about ELI research activities and their scientific foundations can be found in the ELI White Book, available here: http://www.eli-beams.eu/media/documents/.

The work during last years was concentrated on developing the general and detailed facility layout, conceptual and detailed designs of laser and secondary sources beamlines as well as the concept and

detailed design of end-stations. The performed scientific activities are strongly connected with the user facility development and its practical realization. This included education and training of students and performing of experiments and testing of components with partner institutions inside the Czech Republic and abroad for proof of new concepts and the practical preparation of integration and implementation of highly complex experimental systems. This work has resulted in a large number of publications in impacted journals. Besides this, considerable effort has been spent by the group on preparing tenders for large pieces of equipment.

In the following text we present the basic scientific results of the ELI Beamlines team. While these results illustrate high scientific quality of the ELI team, it is necessary to be aware that an enormous work and many important results, which are not captured in this report, were achieved in the area of construction of the first world class scientific user facility based on high intensity lasers and their applications.

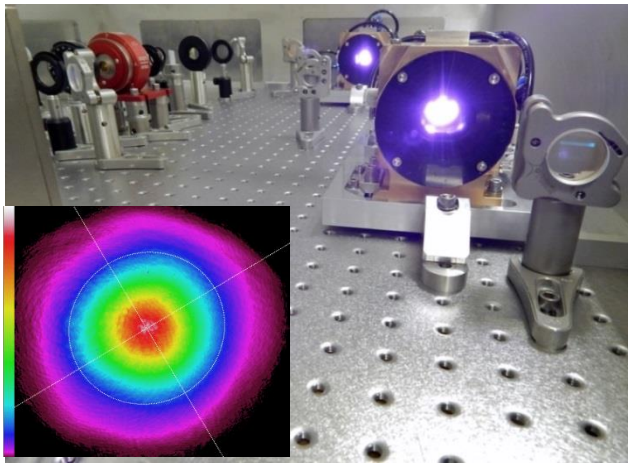


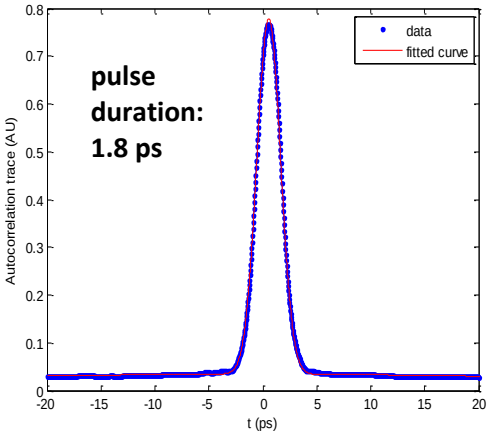
Master scheme of the ELI-Beamlines laser systems and their routing to the thematic experimental areas

RP1: Research activities on development of new lasers generating repetition-rate ultrashort pulses and multi-petawatt peak powers

The team of Department 91 develops lasers systems and/or subsystems for the four high power laser systems of the ELI-Beamlines project. The facility will make available for users high-brightness multi-TW ultrashort laser pulses at kHz repetition rate, PW 10 Hz repetition rate laser pulses, and kilojoule nanosecond laser pulses for generation of 10 PW peak power. These systems will allow meeting requirements of international user community for cutting-edge laser resources for programmatic research in generation and applications of high-intensity X-ray sources, in particle acceleration, and in dense-plasma and high-field frontier physics. The ELI-Beamlines high repetition rate lasers being now developed will extensively employ the emerging technology of diode-pumped solid state lasers (DPSSL), to pump OPCPA (Optical Parametric Chirped Pulse Amplification) and Ti:sapphire short-pulse amplifiers. ELI-Beamlines will specifically use ps OPCPA driven by thin-disk laser units with kHz repetition rate, PW-class ns OPCPA using cryogenic Yb:YAG laser as a driver, PW Ti:sapphire running at 10 Hz and pumped by gas-cooled Nd:glass DPSSL system, and mixed Nd:glass CPA technology with liquid cooled kJ amplifiers generating 10-PW pulses and operating at shot rate of 1 per minute. Amongst major technology development partners and /or laser technology suppliers of ELI-Beamlines are industry and national laboratories, most notably STFC Rutherford Appleton Laboratory (UK), Lawrence Livermore National Laboratory (USA), Max-Planck Institute for Quantum Optics (MPQ), Trumpf Scientific Lasers GmbH (Germany), and National Energetics-EKSPLA (USA/Lithuania).

An example of the systems developed by Dept. 91 is the thin-disk diode-pumped regenerative amplifier for the L1 chain. The laser will be used as a picosecond pump of the OPCPA nonlinear amplification chain to generate pulses with duration of 20 fs or shorter.

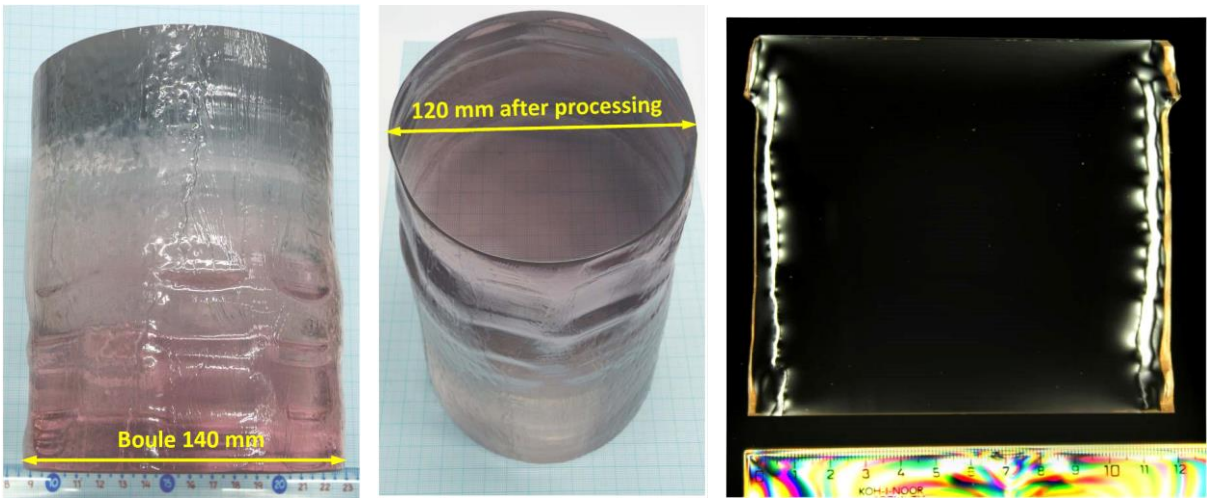




Thin-disk pump laser for the L1 beamline, developed by the FZU / ELI-Beamlines team. The laser generates 120 mJ of energy at 1 kHz, in approximately 1.8 ps pulses.

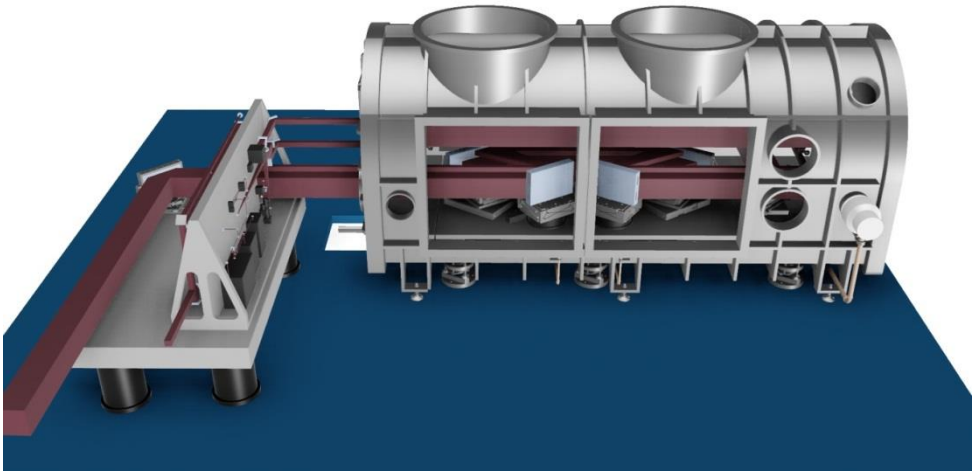
Assembling the ps vacuum compressor for the L1 laser of ELI-Beamlines, designed by the Dept 91 research and technical team, in cooperation with the engineering support by Dept. 93.

An important auxiliary activity of Dept. 91 is improvement, in cooperation with industry, of techniques of growing large crystals. A novel technology of growing of large doped YAG crystals has been developed since 2011, which allows producing highly homogeneous crystals without the central inhomogeneity, which is characteristic e.g. for the Czochralski technique. In 2014, a joint patent application FZU-Crytur for this technique was filed.



Yb: YAG laser monocrystals (Yb doping 2%) with a diameter of 14 cm, grown by novel technology developed in FZU in cooperation with Crytur Ltd. company. It is the largest YAG monocrystal of this type in the world. The image on right shows a 10x10 cm slab vertically cut from the monocrystal in crossed polarizers demonstrating its excellent optical quality (note image of the plastic ruler in the crossed polarizers).

Amongst other examples of development by Department 91 are subsystems for the L3 repetition-rate PW laser, where FZU designs, develops and builds the PW pulse compressor, femtosecond laser pulse diagnostics, and short-pulse beamline control systems and timing. The figure below shows the designed pulse compressor; the compressor constitutes a highly complex optical, optomechanical, electronic and vacuum system, with total length exceeding 5 m.



PW pulse compressor with the femtosecond diagnostics unit (left in the image) for the L3 laser system of ELi-Beamlines, designed by Dept. 91 team.

Example of advanced laser diagnostic instrumentation, developed by FZU to characterize the PW pulses with duration <30 fs, is shown below. The unit has a dynamic range of >100 dB (measurement of temporal pulse contrast >1:10^{10}) and allows measurements in the time interval up to 200 ps before arrival of the high-power pulse.

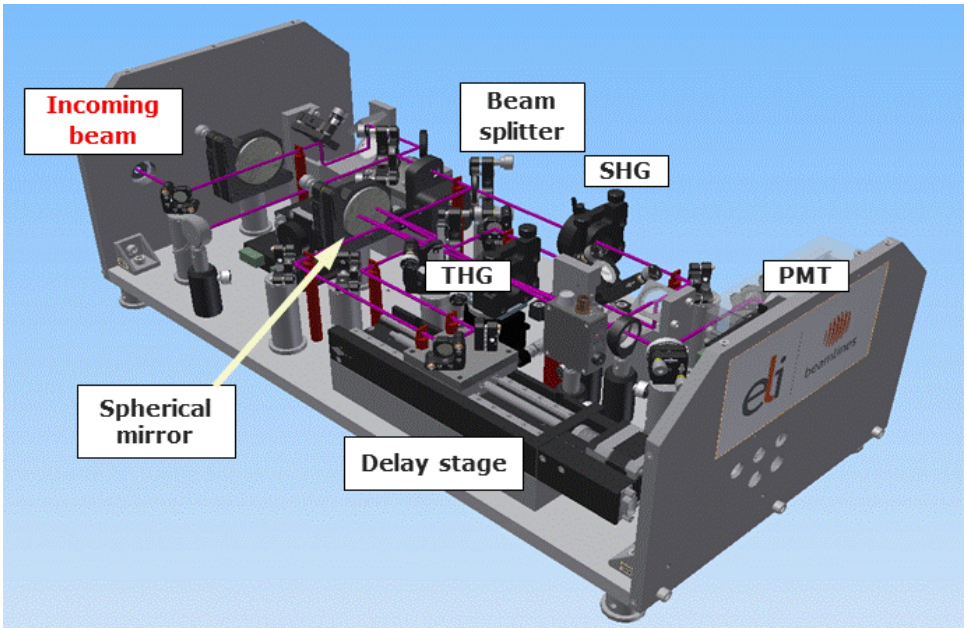


Figure (left): Scanning third-order autocorrelator for measuring temporal contrast of femtosecond laser pulses generated by the L3 system, developed by Dept. 91.

Publications of RP1: See the complete list of references at the webpage:
http://pc048b.fzu.cz/~prouza/ELI_publications.pdf

Research activities of RP2: X-ray sources

One of the main goals of RP2 is to produce ultrashort X-ray beamlines, both coherent as well as incoherent, paving the way towards imaging nature with atomic resolution both in space and time with university-lab sized devices. The laser-based sources have, in contrast to large-scale facilities such as third-generation synchrotrons or X-ray Free-Electron-Lasers (XFELs), the great perspective of having only university-lab size and can, thus, offer a much broader accessibility as only few large-scale facilities exist world-wide. Another added value besides reduction in size and costs is the intrinsic synchronization between the (optical) driver laser and the generated X-ray pulses as well as the spectrum of different X-ray sources each delivering its specific feature from single attosecond spikes to coherent X-ray bursts with peak brilliances competitive with large-scale facilities. An additional important feature will be the combination of perfectly synchronized sources of short pulse coherent optical radiation, UV, XUV and X-ray radiation (coherent and incoherent) and short pulse high energy particle beams including electrons, protons and ions. The available wavelength range of short pulses will be extended in the future to the gamma range well above 100 keV.

Investigation of laser driven coherent soft x-ray beams :

Soft-x-ray lasers (SXRL) and High order harmonics (XRL) have been proven to be tools of great interest for practical applications. The main activities of the group on x-ray lasers included source developments [1-2] and applications in dense plasma diagnostics [3-6], warm-dense matter generation [7], fusion relevant plasmas studies [8], investigations related to astrophysics in laboratory [7], [9], and holographic microscopy [10].

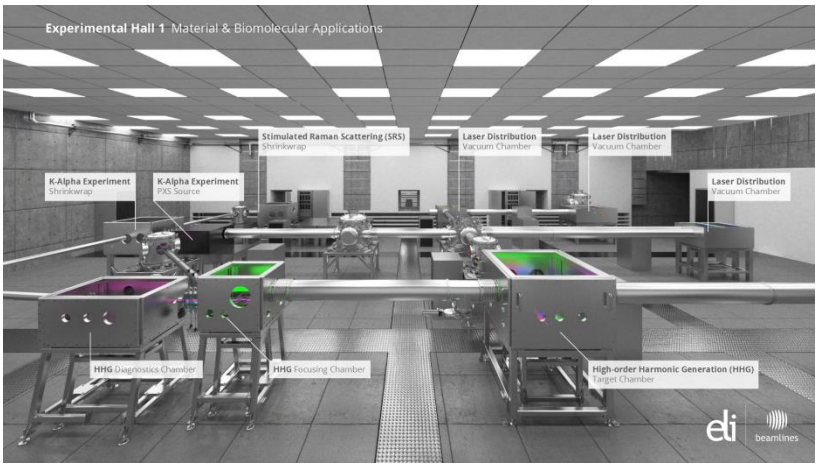


Figure (left): View of the implementation of the X-ray beamlines in the E1 experimental hall

Recently, the research got oriented towards high-repetition rate sources of XUV radiation as high-order harmonic generation with quasi-phase matching to enhance the conversion efficiency [11] and the design of dedicated HHG beamline that will be constructed in the E1 hall of the ELI Beamlines facility. The goal parameters should be achieved at different stages of the kHz laser development. Actual design includes a two-color driving (ω and 2ω) to improve the conversion efficiency. This technique generates even and odd harmonics and the conversion efficiency can be significantly increased up to 10^{-3}. Few μJ of coherent EUVs are thus expected per shot at kHz repetition rate. Moreover, we can take advantage of the high energy of the laser driver and of the large size of the room to set extra-long focal length geometry. A shorter focusing will be available to generate reasonable EUV photon fluxes at lower laser energies or to generate shorter wavelength radiation. The main HHG beamline parts have been tendered and biding is expected in May 2015. It will be manufactured and tested before the installation in the new building at a different place.

Furthermore harder x/ray sources and new concepts of short few fs-long soft x/ray beamlines will be built for users, this will include:

1. **kHz repetition rate X-ray plasma source,** few 10^{th} of keV using a laser driven plasma as the emitter
2. **Betatron and LUX beamlines**, using laser accelerated electrons who are wiggling in a channel or in an external magnetic field as emmitters soft x/ray range and keV range
3. **Compton source,** colliding short pulse lasers with laser driven electrons, 100 keV to MeV range

Publications of RP2: See the complete list of references at the webpage:
http://pc048b.fzu.cz/~prouza/ELI_publications.pdf

Research activities of RP3: Particle acceleration by lasers

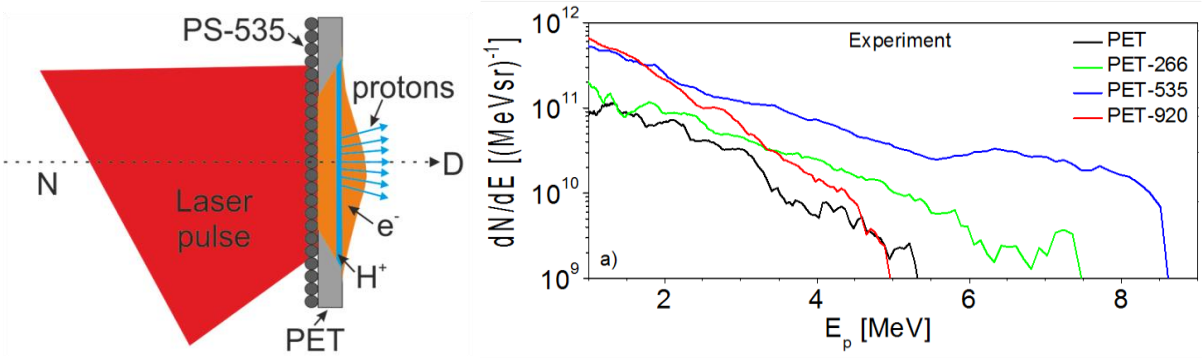
Our main research results during the evaluated period are well-illustrated by two following publications in journals with high impact factor and by the one patent awarded within the evaluated period:
Phys. Rev. Lett. **109** (2012) 234801

1. Laser-Driven Proton Acceleration Enhancement by Nanostructured Foils

D. Margarone, O. Klimo, I. J. Kim, J. Prokupek, J. Limpouch, T. M. Jeong, T. Mocek, J. Psikal, H. T. Kim, J. Proska, K. H Nam, L. Stolcova, I.W. Choi, S. K. Lee, J. H. Sung, T. J. Yu, and G. Korn

Laser driven ion acceleration is a very promising approach which might drastically reduce the typical size and cost of standard acceleration systems. Nevertheless the laser accelerated beams have to be improved in terms of energy, current, divergence, shot-to-shot stability, etc. In a recent experimental campaign our team has greatly improved both the maximum energy (about 60%) and number (approximately 5 times) of the proton source by using a high intensity laser and advanced nanostructured targets.
This is the first theoretical and experimental proof of such enhanced TNSA (Target Normal Sheath Acceleration) regime. Using a special technique sub-micron spheres with diameters close to the wavelength (or slightly smaller) are placed on the front side of a thin target. This leads to an increase of

laser light absorption and connected with this an enhancement of the hot electron population and temperature, thus leading to a more efficient acceleration (higher energy and number of accelerated protons).
This result was achieved in cooperation with the scientific teams working at the PW-class APRI-GIST laser facility in South Korea and at the Czech Technical University in Prague. The projection of such a result towards higher laser intensities seems to be very promising for the application of laser accelerated particle beams in various societal fields, e.g. the design of new hadron therapy Centres for cancer treatment



Left: TNSA mechanism with the target geometry used in the experiment (side view). The laser beam is absorbed at the nanospheres-vacuum interface with an incidence angle of 22.5 degrees. The hot electrons (generated at the target front side) propagate forward and accelerate protons at the rear side. Right: proton energy distributions for different irradiated targets.

2. Phys. Rev. X 4 (2014) 031030

Boron-Proton Nuclear-Fusion Enhancement Induced in Boron-Doped Silicon Targets by Low-Contrast Pulsed Laser

D Margarone, A Picciotto, A Velyhan, J Krasa, M Kucharik, A Mangione, A Szydlowsky, A Malinowska, G Bertuccio, Y Shi, M Crivellari, J Ullschmied, P Bellutti, and G Korn

Currently laser-induced nuclear fusion reactions are being investigated for their potential use as alternative energy sources for the society. The most commonly investigated laser fusion reactions are the DD and DT because they have a high cross section at relatively low temperatures [. Nevertheless different nuclear reactions have been theoretically and experimentally studied [2-5]. Nuclear fusion involving boron has garnered interest since the 1930s being investigated by Oliphant and Rutherford because of the ability to produce copious numbers of alpha particles, which can in turn be used for generating fusion energy without production of neutrons.

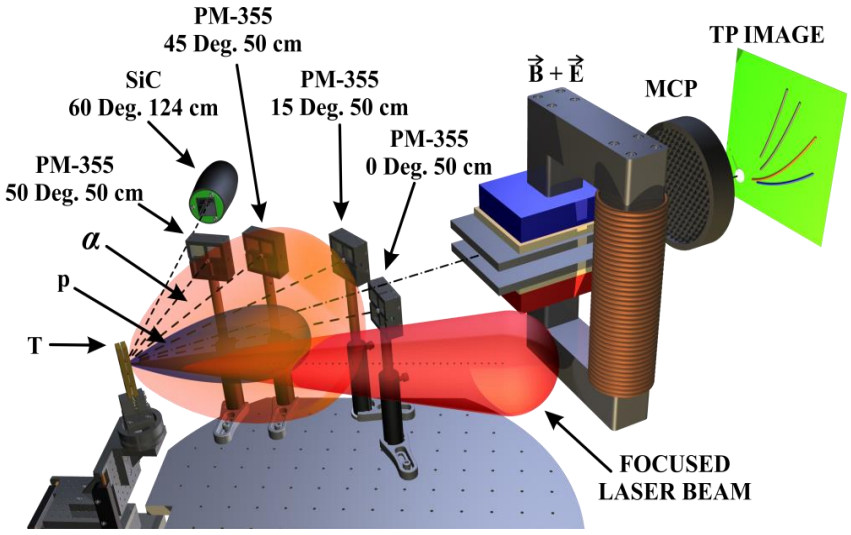


Figure (left): *Experimental setup*

Our papers show a clear enhancement of the 11B(p,α)2α fusion reaction yield by using modest laser intensities and advanced multi-layer targets. A fusion rate of ~10^9 alpha particles per steradian per pulse was achieved by using boron–hydrogen enriched silicon targets. This result is ascribable to the high proton yield generated by the long (nanosecond) laser pulse, which presented an optimal energy spectrum with a plateau around the maximum of the nuclear reaction cross section.

A similar scheme could be attractive for the generation of high directionality, high current ion beams with very compact systems to be used 'in-situ' in laser plasma experiments as a diagnostic tool, e.g. to investigate the so-called 'warm dense matter,' or to determine the ion stopping power in plasmas, which is also of interest for the ignition and burn of an inertial confinement fusion capsule. Furthermore, the potential restrictions coming from the ionizing radiation protection protocols can be drastically reduced thanks to the aneutronic nature of such fusion reaction.

The advantage of our proposed experimental method lies in the use of a moderate laser power (2 TW) and intensity (3×10^{16} Wcm^{-2}) that could enable future possibilities to use compact laser systems and simple irradiation geometries. Our approach does not require special laser techniques for compressing the pulse such as the chirped pulse amplification method; thus, a less sophisticated and cheaper system is sufficient.

Furthermore, preliminary hydrodynamic simulations suggest that the relevant physical mechanisms which enable such high yield fusion reactions can occur with lower laser energy. Thus, in principle, this scheme can be realized using small and cost-effective laser systems (tens of joules, nanosecond-class and high repetition rate), for instance based on newly established diode-pumped laser technology, which might pave the way for more advanced technological applications.

***Patent:* a patent entitled "Method of enhancing nuclear fusion reaction using temporally shaped intense laser pulses and advanced targets" was filed in 2013**

Authors: D. Margarone, A. Picciotto, G. Korn, P. Bellutti

Significance of the work: using temporally shaped (or low contrast) high intensity laser pulses and "ad hoc" prepared targets a method for enhancing the output of laser induced nuclear fusion reaction is proposed. The method reduces the necessary laser intensity and peak-power for efficient fusion in various nuclear reactions, for instance the B^{11}(p,α)2α which allows producing three alpha particles with kinetic energy convertible into useful energy without any neutron production, as demonstrated by us in a recent experiment. Thus, this method can have high societal impact since it paves the way towards potential nuclear reactors based on "ultra-clean" fusion playing an important role in the field of new generation energy sources.

Publications of RP3: See the complete list of references at the webpage:
http://pc048b.fzu.cz/~prouza/ELI_publications.pdf

RP4 ELI Beamlines, Applications in Molecular, Biomedical and Materials sciences

Due to the fact that the group ist just building up the experimental capabilities within ELI Beamlines research has been performed with partner institutions or other world leading centers in photon based sciences. This research is concentrated on different aspects of future Beamlines implementations including the training of new team members. Recently, members of the ELI Beamlines Research Activity 4 (RA4) for Application in Molecular, Biomedical and Materials (MBM) sciences have performed research in the applied fields of materials and nano-science, structure and dynamics in solids and characterization of high intensity laser-matter interactions. RA4 is maintaining a strong presence at leading international light sources such as 3rd generation synchrotrons and X-ray Free Electron Lasers. The pursued research activities are well represented by the scientific work published by RA4/IoP employees. The research conducted by present and past members of the ELI Beamlines RA4 group has resulted in the following publications with relevance to IoP and/or ELI Beamlines:

The past activities in RA4 have been focused on the detailed definition of the research areas and capabilities to be realized in the commissioning and early users operation phase of the ELI Beamlines facility. The following areas and capabilities have been identified and the development and procurement of the required instrumentation has been initiated:
1: Coherent Diffractive Imaging (CDI) and Atomic, Molecular and Optical (AMO) Science: Performed in a multi-purpose vacuum chamber at either the HHG source or the LUX beamline. Sample delivery techniques will cover gas, cluster, aerosol and liquid jet sources as well as solid targets. Detectors will be available for imaging, as well as for photon, ion and electron spectroscopy.
2: Soft X-ray Materials Science: This research will be supported by a unique ellipsometer for time-resolved magneto-optical ellipsometry in the VUV range (10 to 40 eV). The instrument will have a sample holder with a closed cycle cryostat and a +/- 1.5 T magnetic field that is switchable with the 1 kHz rep rate of the L1 laser.
3: Hard X-ray science, diffraction, spectroscopy and imaging: Implemented at a modular experimental area served either by the laser driven plasma X-ray source or the Betatron source. Detectors will include a high read out rate Mpixel detector capable of reading out at the 1 kHz rep. rate of the L1 laser.
4: Optical Spectroscopy and pump beams: This work package will serve all X-ray beamlines for applied sciences with pump beams for advanced pump-probe experiments. Pump beams will be generated from the THz range up to 180 nm (also to a pulse duration as short as 5 fs) covering delays from fs to ms. The area for the generation of pump beams will also be capable of advanced spectroscopy studies in the IR to UV range, most notably the development of Stimulated Raman Spectroscopy for applications in molecular dynamics and pulse radiolysis.

Publications of RP4: See the complete list of references at the webpage:
http://pc048b.fzu.cz/~prouza/ELI_publications.pdf

Research activities of RP5: Plasma Physics

Plasma amplification experiments

The first successful proof-of-principle experiment for ion-wave based plasma amplification was carried out in 2010 using the ELFIE laser system of the LULI laboratory [1]. Subsequent experimental campaigns optimized the set-up, the interaction conditions and the geometry. In the latest experiment a head-on collision between pump and seed was performed. Absolute amplification and large energy transfers were obtained [2]. Plasma amplification provides a longterm perspective to overcome present limitations to increase the focused intensity of light pulses (see Fig. 1). Plasma amplification as well as plasma focusing is part of the growing field of plasma optics which can cope with very high energy densities and responds to present technological and scientific needs of high-field science.

X-ray spectroscopy of laser-matter interaction

The plasma produced by the interaction of sub-ns long laser pulses was studied in wide experimental collaborations as a possible medium for achieving the inertial confinement fusion [3]. The x-ray spectroscopy provided information about the plasma parameters and thus the interaction phenomena like shock wave generation and laser ablation were studied in well defined environments. In another experiment, the generation of collimated plasma jets and their consequent collision with secondary targets was studied, providing information about the plasma-solid interaction [4]. The acceleration of electrons via laser irradiation of solid targets and their propagation in plasmas was diagnosed via the

collisionaly induced Kα radiation, both with sub-ns and fs lasers [5]. Concerning the studies of atomic physics, the charge-exchange process was experimentally observed, and the atomic processes accompanying isochoric heating of material irradiated by the high-intensity x-ray free electron laser radiation were studied via the radiation driven K-shell emission. X-ray imaging can be used in an efficient way to image hot electrons (see Fig. 2).

Neutron generation with the PALS laser system

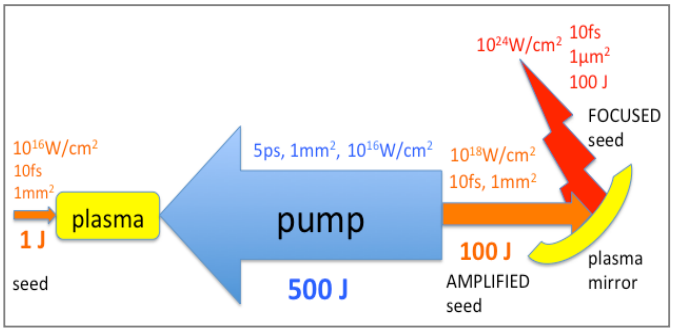
Plasmas produced at the PALS facility are sources of a very high number of fast ions. This fact allowed us to produce a high yield of alpha particles of ~10^9 per steradian per shot from a well-defined layer of boron dopants in a hydrogen-enriched silicon target irradiated with an intensity of 3×10^{16} Wcm^{-2} triggering the fusion reaction $^{11}B + p \rightarrow 3\alpha + 8.7$ MeV. Moreover, deuterons accelerated by the PALS facility are capable of initiating the $^{7}Li(d,n)^{8}Be$ reaction in a secondary LiF (catcher) target as well as the $D(d,n)^{3}He$, and $^{12}C(d,n)^{13}N$ reactions in the primary target.

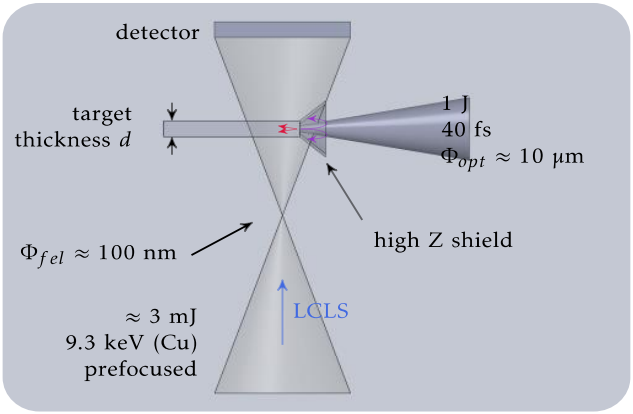
The observed yield of neutrons from the D+D $\rightarrow$ ^{3}He (0.82 MeV) + n (2.45 MeV) nuclear reaction was of 2×10^8 neutrons per laser shot for the average laser energy of 550 J. Figure 3 shows a spread in the neutron yield dependence on the energy delivered on deuterated targets with the use of various fs-, ps- and sub-ns lasers. The spread can be limited by a baseline which was estimated to be $Y_{BL} = 2000\times E^{1.65}$. Deuterons with energy up to ~2.5 MeV accelerated from the front surface of a massive CD_2 target in the backward direction with respect to the laser beam impacted a thick natural LiF slab, as Fig. 4 shows. Neutrons produced through the fusion reaction $^{7}Li(d,n)^{8}Be$ had a mean energy ~13.5 MeV. Only minority of them reached up to ~16-MeV energy. The neutron yield obtained under these non-optimised reaction conditions reached a value up to 5×10^7 neutrons per shot [6,7].

Equation of state under warm dense matter conditions

A new approach to equation of state experiments based on a laser-driven shock and release technique combined with spatially resolved x-ray Thomson scattering, radiography, velocity interferometry, and optical pyrometry to obtain independent measurements of pressure, density, and temperature for carbon at warm dense matter conditions. The uniqueness of this approach relies on using a laser to create very high initial pressures to enable a very deep release when the shock moves into a low-density pressure standard. This results in material at near normal solid density and temperatures around 10 eV. The spatially resolved Thomson scattering measurements facilitate a temperature determination of the released material by isolating the scattering signal from a specific region in the target. Our results are consistent with quantum molecular dynamics calculations for carbon at these conditions and are compared to several equation of state models [8].

Publications of RP5: See the complete list of references [1-8] at the webpage:
http://pc048b.fzu.cz/~prouza/ELI_publications.pdf





Left - Fig. 1: A possible future scenario of creating very intense light pulses. / Right - Fig. 2: X-ray imaging of hot electron propagation and filamentation in solids.

Research activities of R6: Theory, Simulation & Computing

Tight focusing analysis and subsequent electron dynamics

How to focus a multi-petawatt laser pulse to very high intensities is a major issue for all the forthcoming 10PW installations such as ELI-Beamlines. Small focal length parabolas can not be used easily due to potential damage and debris production. A possible solution is to perform tight focusing with a combination of an off-axis parabola in conjunction with an ellipsoidal plasma mirror [1]. This will allow to attain intensities in the focal spot above 10^{23} W/cm^2. However, for these extreme conditions the standard paraxial approach breaks down and a direct integral approach to Maxwell's equations has to be used. In the focal spot a longitudinal electric field develops. This strongly affects the motion of electrons as it is exposed to the ponderomotive forces in longitudinal and transverse direction as well as the longitudinal field. At these high intensities the radiation-reaction force needs to be taken into account. Such a setup will eventually allow to study extreme relativistic and quantum effects of electron motion.

Shock-ignition approach to inertial confinement fusion

The shock-ignition (SI) approach to inertial confinement fusion (ICF) attempts to overcome certain deficiencies of the standard direct or indirect drive. However, as it operates at a much higher intensity than is normally employed in ICF, parametric instabilities play a major role. Laser-plasma interaction for SI is still little studied and the issue of laser energy absorption and preheat are still of major concern. Large-scale, multi-dimensional kinetic simulations on long time scales provide answers to these open questions [2,3,4].

Theoretical and simulation analysis of plasma amplification

The quest for ever higher focused laser intensities is limited by the damage threshold of solid-state based optical materials and the size of gratings that can be easily manufactured. A new approach for creating short and intense laser pulses is based on the collision of a relatively long pump pulse of low intensity with a short seed pulse inside a plasma. The two transverse modes are coupled by a longitudinal plasma mode (in the present case an ion-acoustic mode in the strong-coupling regime) which allows the energy transfer from the ump to the seed. As the duration of the final pulse is given by the seed, the energy transfer implies a considerable increase in intensity [5,6,7,8].

Laboratory astrophysics

The upcoming petawatt laser installations such as ELI will allow to study certain astrophysical phenomena in the lab based on the principle of limited similarity which uses dimensionless parameters to bridge the difference in scale between laser and astrophysical plasmas. In particular soliton creation, magnetic reconnection [9], collisionless shocks and plasma instabilities are ubiquitous phenomena in the universe and can be partially recreated by the interaction of plasmas with powerful lasers.

Radiation-reaction and pair creation at ultra-high intensities

Acceleration of electrons in ultra-intense laser pulses with intensity above 10^{22} W/cm^2 results in significant emission of energetic photons and radiation damping of electron kinetic energy. The influence of the radiation reaction force on laser interaction with solid foil targets has been studied in PIC simulation and different approaches to the radiation reaction force (continuous slowing down and discrete Monte Carlo) have been studied in [10]. It is shown that for the solid foil targets, the radiation emission strongly depends on the recirculation of high-energy electrons, which in turn depends on the target material and efficiency of ion acceleration. The interaction of emitted photons with the laser field may result in effective generation of electron-positron pairs by means of the Breit-Wheeler process. The influence of laser pulse polarization on gamma-ray generation during interaction of two colliding and tightly focused laser pulses with a low-density target composed of electrons has also been studied. It is shown that in the case of circularly polarized and tightly focused laser beams, electrons are not following circular trajectories at the magnetic node of the standing wave established in the focus, which leads to lowering the radiation emission efficiency (see Fig. 1).

Computing infrastructure

The aforementioned topics rely heavily on a computing infrastructure based on parallel machines. The recent acquisition of the high-performance cluster ECLIPSE (**E**xtreme **C**oherent **L**ight **I**nteraction-**P**lasma **S**imulations of the **E**xtreme) provides a platform for the very CPU-demanding simulation work which is required to understand high-intensity laser-matter interaction and to provide predictive modeling of future experiments. ECLIPSE in its present configuration has about 1400 cores and 1 Peta-byte of storage.

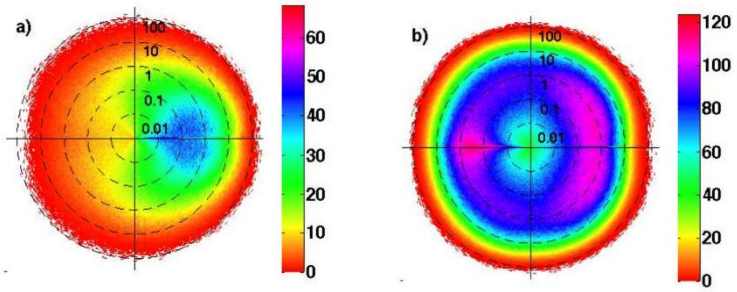


Fig. 1: The angular energy distribution of emitted radiation in the simulation with proton (panel a) and the heavier ion - $10 \times m_p$ (panel b) targets calculated by the PIC code EPOCH. The numbers at each circles correspond to the respective photon energy in MeV and the color scale gives the radiation energy emitted in the respective direction and the energy range (arb. units).

Publications of RP6: For the complete list of references [1 - 10] check the webpage:
http://pc048b.fzu.cz/~prouza/ELI_publications.pdf

Radiation protection and dosimetry

Radiation protection and dosimetry topics specific to the fields generated by laser driven accelerators have been studied since 2010. In 2013, the Monte Carlo group has been established in order to provide support for experimental and technical groups. Up to now, its activities have been mostly devoted to safety issues. It has produced simulations to evaluate radiation and activation levels and to optimize the design of devices like beam dumps and spectrometers and has participated in the definition of tender requirements. In collaboration with HZDR, a long term project aiming at the creation of an activation database for different materials, primaries, energies, and cooling time has started. In collaboration with HZDR and SLAC the group has started important for the future user facility action experimental work on the characterization of the source term for particles generated in laser-target interactions.
Our representative is a member of EURADOS e.V. (European Radiation Dosimetry Group), in particular we have participated in the activities of working group 11, focused on High energy radiation fields and working group 6 dedicated to Computational dosimetry. Recently, our interest lay primarily in the effort to characterize response of dosimeters in pulsed fields. This is of major importance for the safe exploitation of ELI Beamlines experimental area. We participate in common EURADOS experiments and collaborate in experiments run by other ELI experimental groups. Besides, we have been cooperating with the Institute of nuclear physics (INP ASCR) and the National Personal Dosimetry Service Ltd. (CSOD, Prague).

Also the publications of the radiation protection and dosimetry team are available at the webpage: http://pc048b.fzu.cz/~prouza/ELI_publications.pdf

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Experimental particle physics

Two institute's organizational units are involved in experimental particle physics: *Department of Experimental Particle Physics* and *Department of Detector Development and Data Processing*. The report covers the work of both departments and it was written by Alexander Kupčo (the head of the Department of Experimental Particle Physics).

The team consists of 40 scientists, from whom 11 are Ph.D. students and four post-docs or assistants. The research activities are focused on particle physics experiments realized in collaboration with major European and world laboratories, in particular CERN in Geneva, Switzerland and FNAL in Batavia, USA. Main aim of this basic experimental research is to obtain new facts about the nature of our world at the most extreme conditions achievable in the earth laboratories.

We are engaged in the analysis of experimental data as well as in the preparation of experiments and construction of experimental devices. We participate also in research programs developing new types of detectors and experimental techniques. Our activities in individual projects are described below.

Institute of Physics is also operating regional computing center which provides services for Czech particle physics community. This important contribution runs across many experiments and is described in a separate paragraph.

ATLAS Experiment

The ATLAS experiment at CERN represents the major activity of our group of experimental particle physics. Institute of Physics is one of the founding members of the ATLAS Collaboration. In the past, we contributed significantly to the design and construction of the ATLAS inner tracker pixel detector and hadronic calorimeter Tilecal.

The last five years have been exciting, as the experiment collected until the end of 2012 almost 29 fb^{-1} of proton-proton collision data at center of mass energies 7 and 8 TeV. Using this unique dataset, the ATLAS Collaboration, together with the CMS experiment, discovered in 2012 a new particle, a candidate for long sought Higgs boson [1]. More data confirmed that the properties of the newly observed particle with mass of 125 GeV are in agreement with predictions of the Standard Model of particle physics for Higgs boson. Thanks to this discovery, the Nobel Prize in Physics 2013 was awarded to F. Englert and P. Higgs "*for the theoretical discovery of a mechanism*

that contributes to our understanding of the origin of mass of subatomic particles, and which recently was confirmed through the discovery of the predicted fundamental particle, by the ATLAS and CMS experiments at CERN's Large Hadron Collider " (citation from the Nobelprize.org). The ATLAS and CMS experiments obtained for their discovery the prestigious "High Energy and Particle Physics Prize" from European Physics Society. Both detectors, the inner tracker and the calorimeter, played crucial role in the discovery. Researchers from Institute of Physics thus have their share on this fundamental result.

Our group is contributing to the effort of the ATLAS Collaboration in several areas: operation, maintenance, and upgrades of the inner tracker [2] and Tilecal [3], R&D for future high luminosity upgrade of those two detectors, physics analyzes of the data, and computing. Those activities were closely related to the LHC schedule. The collider was operating until the beginning of 2013. Then it underwent a long, two years maintenance shutdown. As of the beginning of April 2015, the machine is back in operation.

Inner Tracker

During the two years LHC shutdown, the ATLAS detector underwent significant maintenance and upgrade as well. In particular, Institute of Physics contributed to the upgrade of inner tracker pixel detector. Our researchers and engineers contributed to two projects: nSQP (new Service Quarter Panel) and Insertable B-Layer (IBL).

The aim of nSQP project was a design and construction of new service panels for pixel detectors. New panels provide two times faster data transfer rates which would be important in upcoming years as LHC will be providing more intense beams. The panels provide important services to the pixel sensors: high and low power supply, electronic shielding and grounding, cooling, and safety monitoring of the beam with new Pixel Diamond Beam Monitors. New panels have been installed in years 2013-2014. Three our engineers and technicians contributed significantly to the nSQP project, namely to the assembly of the panels, development of new technologies of thin wall tube bending and welding, and cabling.

Insertable B-Layer is new layer of pixel detectors placed very close to the interaction point in front of existing pixel detector. This additional fourth layer of pixel detectors will improve significantly the reconstruction of the tracks near the interaction point. In particular, it will improve the performance of the detection of displaced vertices coming from the decays of the b-quark mesons. The researcher from Institute of Physics contributed to: the development and testing of new semiconductor sensors that were used in IBL, development of new software for collection and analysis of the data from the pixel detector, and to the IBL assembly and integration with existing pixel detector.

We also contributed to the upgrade of pixel detector control system. The new system required complete rebuild of cabling. In addition, new low and high voltage power supplies have been installed. Our engineer, P. Šícho, was responsible for coordination of these activities. He is also serving as a member of Pixel Office, the main management group of the whole pixel detector.

Our inner tracker group is also involved in R&D activities concerning semiconductor sensors with large radiation hardness for future high luminosity upgrade. We contributed to various tests of irradiated sensors [4-5].

Hadronic calorimeter Tilecal

Our next contribution in the two year shutdown went into the maintenance of hadronic calorimeter Tilecal. S. Němeček was responsible for replacement of low voltage power supplies. He is also the member of main Tilecal management group. The team is also involved in the design, and radiation hardness testing of new power supplies for future upgrades.

Atlas Forward Physics – AFP

AFP is proposal for new detectors to be installed about 210m from the ATLAS interaction point. These detectors are designed to measure momenta of forward protons from diffractive processes. Institute of Physics was one of the key institutions in ATLAS actively pushing the AFP project through the approval procedure. Our researchers were involved in various aspects of the preparation: from basic scientific concept, to the formulation of physics program [6], detector design, mechanical construction of the first prototypes, including cooling, and to the management of the project. A. Kupčo was physics coordinator of the project, P. Šícho technical coordinator, and M. Taševský is a member of the main AFP management team. He was responsible for the selection of silicon detectors. The project was approved by the ATLAS Collaboration in the beginning of year 2015.

Physics Analyzes

With the first LHC data, the focus of our group turned from detector construction to the physics analysis of the collected data. In total, our scientists and PhD students are co-athors of more than 300 original papers produced by the ATLAS Collaboration. Our researchers are primary authors of several ATLAS papers on QCD and diffraction physics, physics of bottom and top quarks, and pair production of intermediate vector bosons. Four PhD. theses were defended on physics analyzes during years 2010-2014.

We have been active from the very beginning, our physicists contributed already to the first ATLAS paper on LHC data, the measurement of charged-particle multiplicities at center of mass energy of 900 GeV [7]. The strong position and the expertise of our group are also recognized by the collaboration. Our young postdoc, O. Kepka, was convening the activities of the whole ATLAS Soft QCD Group. In the same physics domain of strong interactions (described by Quantum Chromodynamics – QCD), we have contributed directly to few more results on properties of minimum bias proton-proton collisions [8], to the measurement of production rate of events with large rapidity gap sizes [9-10], and to the double parton scattering measurement [11-12]. The team is working on several new analyses: jet+gap, production of jets with high transverse momenta, and charged particles multiplicities at 13 TeV.

The second major focus of our team is physics of top quark. Here we contributed directly to the measurement of top quark pair charge asymmetry [13] and to the

measurement of top quark charge [14]. From the b-quark results, we made significant contribution to the measurement of the properties of $B_S \rightarrow J/\psi+\phi$ channel [15]. The last physics group is focusing on measuring properties of intermediate vector bosons. In particular, we made direct contributions to the measurement of WW pair production [16-17]. Similar analysis performed on larger data sample at 8 TeV is being in the final collaboration review.

More details about our physics results, together with physics motivation, are given in the separate document with the list of selected papers.

Fermilab experiments

DØ Experiment

The Institute of Physics started, together with Charles University in Prague and Czech Technical University in Prague, the collaboration with the DØ experiment in 1997 during a long shutdown of collider TEVATRON in Fermilab. From 2001 to 2011 (so called Run2 period), the experiment was collecting and analysing the results of proton-antiproton collisions at centre of mass energy of 1.96 TeV.

We joined the Run2 upgrade effort, detector commissioning and data analysis. The run finished in 2011, but physics analysis continues. The DØ authors from our institute are A. Kupčo and M. Lokajíček. In total, we are co-authors of 159 DØ papers during 2010-14. Further, computing specialists and technical staff contributed to our activities.

Our major hardware contribution for the DØ experiment is providing large scale computing resources for data processing and Monte Carlo simulations of the detector. This started already in 2001, when we were producing the necessary detector simulations on personal computers in Prague. This had given the base for today's WLCG (Worldwide LHC Computing Grid) Tier2 centre, located in FZU, for the LHC experiments. The simulations for DØ and other non-LHC experiments continue. We delivered up to the second highest amount of outside simulations capacities to DØ. In particular, we were providing more than 15% of the DØ computing resources in years 2010-2015. This was an appreciated contribution to the DØ collaboration. Besides computing, we have fulfilled other service tasks like shifts during accelerator run.

Long term scientific interest of A. Kupčo is physics of jets with high transverse momentum. He substantially contributed to several DØ papers on this subject. For example, he was one of the three main authors of paper [18]. Kupčo was also heavily involved in jet energy calibration – a major systematic uncertainty for many DØ measurements, not only for dedicated jet studies. He was leading the DØ Jet Energy Scale Group as the convener for 2 years. During this time, the final correction was derived for the first $1fb^{-1}$ of Run2 data. The results, together with the method, were summarized in paper [19]. Thanks to the unprecedented precision of the jet energy callibration, the above mentioned jet measurement was the most precise one at that time. The results were in good agreement with theoretical predictions based on quantum chromodynamics, implying that quarks and gluons behave as point-like particles without further structure even at TeV scales. The data brought also new information on proton composition, especially on the gluon content at high fractional

momentum of proton. A. Kupco also served as Editorial Board member for jet physics and top mass measurement.

NOvA experiment

The Institute of Physics joined the NOvA experiment together with Charles University in Prague and Czech Technical University in Prague in 2011. Our group consists of 2 physicists (M. Lokajíček and J. Zálešák), electronic engineers, computer specialists and technicians.

The NOvA experiment studies neutrino beam oscillations, their mass ordering and neutrino antineutrino oscillation symmetry. Muon neutrinos are produced at Fermilab proton accelerator in collisions of protons with carbon target. Created muons decay into muon neutrinos that enter the near detector on Fermilab territory and continue through the earth to 800 km distant far detector at Ash River on Canadian border in Minnesota. Due to neutrino oscillation they can change to electron neutrinos. The NOvA detectors are optimized to provide efficient electron neutrino identification using a technology which can be scaled to very large masses. The NOvA detectors are constructed from liquid scintillator contained inside extruded PVC modules and read out with the help of optical fibre by silicon APDs (Avalanche Photo Diode). The far detector has a total mass of 15 kilotons and is 15.7 meters wide, 15.7 meters high, and 78 meters long. The near side detector is a smaller 300 tons copy of the far detector. Its purpose is to measure the neutrino fluxes prior to the oscillation.

The detector construction has been successfully finished in summer 2014 and NOvA experiment records data since then. The accelerator power is step by step upgraded from initial 300 kW to target 700 kW to reach desired precision in coming 6 years of data collection.

Our technicians and physicists contributed to the detector construction both in Fermilab and in our institute. We have designed and produced two dark boxes in our laboratories that have been used for quick checks of all APDs before mounting on both near and far detectors. Our engineers and physicist have long term experience with APDs from parallel experiments and one colleague (J. Zalesak) obtained FNAL International Fellowship to help solving NOvA APD problems and to work on data acquisition system. He is “NOvA run coordinator”, i.e. person responsible for 24/7 detectors run and data recording, from 2014. In parallel, our engineers and technicians have been building a setup in our institute for the long term APDs tests and for the study of their temperature dependence. Another our contribution is the usage of institute computing centre capacities for NOvA simulations. Prague serves as Open Science Grid (OSG) site and can run several thousands of concurrent NOvA simulation tasks.

DESY – H1 experiment

The H1 experiment at HERA collider at DESY stopped the data taking in 2007. In the period 2010-2014, data from ep collisions at the centre-of-mass energy 319 GeV has been still analysed. In total, 33 papers were published in leading journals with 2 - 4 co-authors from our Institute. The main highlights belong to the most accurate measurements of the momentum distribution of u, d, s, quarks and gluon in the proton

in the deep inelastic scattering [1]. These so-called parton distribution functions are used nowadays in most cross section calculation of the scattering on protons. Especially they are indispensable for calculation of processes at the LHC. With HERA collider closed the structure functions cannot be significantly improved in the foreseeable future. The measurement of the neutral and charged current cross sections over an extended interval of Q^2 namely 60 GeV^2 < Q^2 < 50000 GeV^2, where Q^2 is the four momentum transfer squared between electron and proton (inversely proportional to the space resolution in the proton) illustrated the unified behaviour of the electromagnetic and the weak interactions and serve as the text book example of unification of the interactions. The investigation of jet properties led to one of the most accurate determinations of the coupling constant of strong interactions α_S [2]. The study of diffractive processes provided an essential input for the understanding of quantum chromodynamics at high parton densities. Various exotic processes were searched for signs of physics beyond the Standard model. The ep collisions provided a unique opportunity to search for new particles coupling directly to a lepton and a quark – so called leptoquarks. Nevertheless, no signs of new physics were observed.

During the H1 detector construction, the physicists from the Institute contributed to LAr calorimetry (jet detection and large angle electron scattering) and Spacal calorimeter (forward electron scattering) and to the monitoring and calibration of these detectors during data taking. The physics interests were predominantly oriented to data from these detectors – deep inelastic scattering, proton structure functions and jet production at low Q^2. In 2010-2014, the physicists contributed by their expertise during the process of preparation of publications in the field of their physics interests [20-22].

Research & Development

Development of detectors represents an important activity of our Department. In years 2010-2014, we were participating in the following programs

- radiation hard pixel detectors for ATLAS;
- low-voltage supplies for the ATLAS SCT;
- voltage supplies for the photomultipliers of the TileCal calorimeter;
- silicon pad detectors for the electromagnetic ECal calorimeter of the CALICE project;
- pixel detectors for the MediPix project.

These activities were carried on in close collaboration with international projects AIDA, RD50, EUDET, CALICE, and MediPix. We have contributed to many results obtained within those programs, in particular, in the field of testing radiation hardness of newly developed sensors or in the area of development front-end electronics for those detectors. Few examples have been given in the ATLAS detector chapter [4,5].

Calice

The R&D project aims at the significant improvement in the energy resolution of jets using the imaging calorimetry. We participate in the CALICE collaboration in two directions: the compact electromagnetic SiW calorimeter [23] and the hadron

scintillator tile calorimeter HCAL with silicon photomultiplier (SiPM) readout [24]. During 2010, the four year test beam campaign of the calorimeter prototypes was finished. The campaign exploited the particle beams at DESY, CERN and Fermilab. The results from the tests are continuously published.

The second generation of calorimeter prototypes is now under construction. This research is supported by the EU grants AIDA (2011-2015) and AIDA-2020 (2015-2019). Our group primarily collaborates with Ecole Polytechnique (J.-C. Brient), with DESY HCAL group (F. Sefkow) and University of Bergen (G. Eigen). Our contribution in the SiW calorimetry was the design and the following production of sensors. Half of the calorimeter prototype sensors (150 pieces of 36 large size 1 cm2 pad sensors) were produced by Czech industry. The sensors were tested in our institute. The calorimeter assembly was carried on by French groups. We participated in calorimeter beam tests and data analysis. For the HCAL, we designed the LED calibration and monitoring system. The system enabled to keep the gain of SiPMs constant by off-line corrections to data due to the SiPM gain dependence on temperature, bias voltage and SiPM saturation.
The R&D project was mainly oriented to the energy range of future linear colliders but several spinouts have found applications both in the particle physics as well outside. E.g., SiPMs first massively used in the CALICE tile calorimeter prototype (8 500 pieces) are now foreseen in calorimeter upgrades of the CMS and COMPASS experiments. SiPMs found their way also in the proton computed tomography and positron emission tomography.

Computing

Modern HEP experiments produce large quantities of data and their processing is more and more challenging and requires novel approaches. LHC collaborations adopted model of distributed data processing based on the grid middleware. We built one of the participating centers and operate it for ATLAS and ALICE experiments. Because the underlying grid technology and also computing models of experiments continuously develop, we must adapt to frequent changes and implement many requirements coming from WLCG and from experiments. The main achievement is that we managed to meet required availability and reliability of our Tier-2 center and fully cover pledges to WLCG [25].

We have significantly contributed to the central ATLAS monitoring and operations tasks. We have covered many types of computing shifts including senior and expert level, and coordinated shifts organization. We have reported about these tasks on many international conferences and workshops (for example [26]).

Our pioneering role was in deployment of IPv6 protocol in a grid site. We tested IPv6 only configuration on a small testbed and later dual stack deployment. Later we applied tested procedure in the production environment where applicable (worker nodes and DPM servers). We presented our results on several international conferences and workshops (for example [27]).

We used our experience with grid computing from LHC experiments to apply this emerging technology in the field of astroparticle physics. We changed the computing

model of Pierre Auger Observatory to use distributed resources connected by the grid middleware. We had to create a framework for job processing and tools for basic data management [28]. In the years 2011 to 2013, the Auger group became the biggest user of the computing grid resources if we exclude 4 LHC projects [29]. There were more than 300 projects registered in the EGI grid.

References

[1] ATLAS Collaboration, "*Observation of a new particle in the search for the Standard Model Higgs boson with the ATLAS detector at the LHC*", PLB 716 (2012) 1-12

[2] ATLAS Collaboration, "*Operation and performance of the ATLAS semiconductor tracker*", Journal of Instrumentation 9 (2014), 1-80

[3] Abdallah, J., et al., "*Mechanical construction and installation of the ATLAS tile calorimeter*", Journal of Instrumentation 8 (2013) 1-26

[4] Hara, K, et al., "*Testing of bulk radiation damage of n-in-p silicon sensors for very high radiation environments*", NIM A636 (2011), 83-89

[5] Affolder, A., et al., "*Silicon detectors for the sLHC*", NIM A658 (2011) 11-16

[6] Tasevsky, M., "*Review of central exclusive production of the Higgs boson beyond the Standard Model*", Internation Journal of Modern Physics, A29

[7] ATLAS Collaboration, "*Charged-particle multiplicities in pp interactions at sqrt(s) = 900 GeV measured with the ATLAS detector at the LHC*", PLB 688 (2010), 21-42

[8] ATLAS Collaboration, "*Charged-particle multiplicities in pp interactions measured with the ATLAS detector at the LHC",* New Journal of Physics 13 (2011), 1-69

[9] ATLAS Collaboration, „*Rapidity gap cross sections measured with the ATLAS detector in pp collisions at sqrt{s} = 7 TeV",* EPJ C72 (2012), 1-20

[10] Ruzicka, P., *„Diffraction processes at the ATLAS experiment"*, PhD Thesis, Czech Technical University in Prague, 2012

[11] ATLAS Collaboration, „*Measurement of hard double-parton interactions in W(→lv)+ 2 jet events at √s =7 TeV with the ATLAS detector*", New Journal of Physics 15 (March 2013) 1-39

[12] M. Myska, PhD thesis, Czech Technical University in Prague, 2013

[13] ATLAS Collaboration, „*Measurement of the top quark pair production charge asymmetry in proton-proton collisions at √s = 7 TeV using the ATLAS detector*", JHEP 2014/2, 1-38

[14] ATLAS Collaboration, „*Measurement of the top quark charge in pp collisions at √s = 7 TeV with the ATLAS detector*", JHEP 2013/11, 1-42

[15] ATLAS Collaboration, "*Flavour tagged time dependent angular analysis of the Bs→J/ψϕ decay and extraction of ΔΓ and the weak phase ϕs in ATLAS*", PRD 90 (2014) 052007

[16] ATLAS Collaboration, "*Measurement of W.sup.+./sup.W.sup.-./sup. production in pp collisions at √s = 7 TeV with the ATLAS detector and limits on anomalous WWZ and WWγ couplings*", PRD 87 (2013) 112001

[17] Zeman M., *"WW production in the ATLAS experiment at the LHC."*, PhD Thesis, Czech Technical University in Prague and Universite Paris-Sud XI, 2014

[18] DØ Collaboration, *"Measurement of the inclusive jet cross section in pp¯ collisions at √s=1.96 TeV."* , Phys.Rev. D85 (2012) 052006

[19] DØ Collaboration, *"Jet energy scale determination in the D0 experiment"*, NIM A763 (2014), 442-475

[20] H1 and ZEUS Collaborations, *"Combined measurement and QCD analysis of the inclusive e(+/-)p scattering cross sections at HERA"* , JHEP 01 (2010) 109

[21] H1 Collaboration, "*Jet production in ep collisions at low Q2 and determination of* α_S", EPJ C67 (2010), 1-24
[22] H1 Collaboration, "*Measurement of the inclusive ep scattering cross section at high inelasticity y and of the structure function FL*", EPJ C71 (2011) 1-50
[23] CALICE Collaboration, "*Performance of the first prototype of the CALICE scintillator strip electromagnetic calorimeter*", NIM A763 (2014) 278-289
[24] CALICE Collaboration, "*Construction and commissioning of the CALICE analog hadron calorimeter prototype*", Journal if Instrumentation 5 (2010) P05004
[25] EGI accounting portal, Tier2 accounting reports: http://accounting.egi.eu/reptier2.php
[26] ATLAS Distributed Computing Monitoring tools after full 2 years of LHC data taking. J. Schovancova, J. Phys.Conf.Ser. 396 (2012) 032095
[27] Enabling IPv6 at FZU - WLCG Tier2 in Prague - T. Kouba et al., J.Phys.Conf.Ser. 513 (2014) 062027
[28] Simulation and reconstruction of cosmic ray showers for the Pierre Auger Observatory on the EGEE grid, J. Chudoba et al., J.Phys.Conf.Ser. 219 (2010) 072033
[29] EGI accounting portal, http://accounting.egi.eu

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Particle Physics Theory and Phenomenology

The *Particle Physics Theory and Phenomenology research team* is formed by the members of Department of Particle Theory and Phenomenology headed now by Dr. Martin Schnabl. The team is composed mostly of postdocs who are chosen in open international competitions thanks to the continuing support from the national funding agency. There are currently two graduate students and a number of master and bachelor students (not shown in the above table). The team also includes several soon-to-retire or already retired faculty members with miniscule appointments.

Our team focuses on a range of topics from purely theoretical and formal subjects within string theory, to the phenomenological aspects of real-world hadrons - strongly interacting particles. On the theoretical side a dominant subject of interest is string theory, conformal field theory, higher spin theory and quantum gravity, which are often interrelated. On the phenomenological side the research is mostly concerned with issues of direct experimental relevance. In fact, all four phenomenology researchers are members in one of the major international high-energy particle physics collaborations at CERN (Atlas, Alice, Totem). In the rest of this section we describe our activities in the three main domains: string field theory, quantum gravity and particle phenomenology

String Field Theory

One of the major research lines of the theory and phenomenology department since 2009 when Dr. Schnabl joined our institute is the study of string field theory. String field theory is a particular approach to string theory, a highly mathematical theory which aims to unite purely on principles of mathematical beauty and consistency the four fundamental forces in quantum realm. Vibrating modes of a given string correspond to a spectrum of elementary particles, which in a proper quantum theory must give rise to quantum fields. The string field theory is a theory of such fields.
Quantum field theory is one of the most useful and universal tools in contemporary theoretical physics, not only limited to high energy physics. In general it becomes indispensable when we study collective phenomena (e.g. phase transitions) in a system with lots of degrees of freedom. Another example is the celebrated Higgs mechanism, which explains why in the standard model of elementary particle physics initially massless particles obtain mass.
Open string field theory is in many respects very much like the gauge theory of the standard model. The analog of the Higgs field is called for historical reasons the tachyon field. While in the standard model, the Higgs field condenses uniformly to a single value and its fluctuation behave as the recently discovered Higgs particle, in string field theory the tachyon field tends to condense in a much wider variety of ways. Often the field condenses everywhere, except in the neighborhood of some hypersurface, which were identified by Ashoke Sen to be objects called Dirichlet membranes, or D-branes for short, introduced by Polchinski.

For strings freely roaming through a flat Minkowski space these D-branes can be easily described as loci on which the string coordinate takes assumed value – a Dirichlet boundary condition. In more general situations the D-branes can be identified with the possible consistent (i.e. conformal) boundary conditions in the two-dimensional conformal field theory (CFT) on the string worldsheet.

The theory of conformal boundary conditions in two dimensions is not only important in string theory, it has very diverse applications in other branches in science: from study of quantum impurities in one-dimensional system of condensed matter to highly abstract concepts in pure mathematics. The string field theory presents a radically new approach to this problem and promises new results, if not the complete solution. Kudrna, Maccaferri and Schnabl [1] in 2012 showed how the solutions to string field theory equations can be turned into a proper boundary state, object very familiar to everyone dealing with two-dimensional CFT's, an object encoding a great deal of information about the boundary condition. What is now difficult in practice is to construct these solutions explicitly.

Simplest solutions can be found easily numerically, as was realized already a while ago. In 2005 however, it was realized by Schnabl that a solution describing spatially homogenous tachyon condensation can be found analytically [2]. In 2009 with Erler they found a conceptually much simpler expression which then enabled lots of subsequent progress [3]. Schnabl and Murata then in 2011 discovered a very simple general formula for the energy and the boundary state for this and other solutions, which raised the possibility for the existence of multiple D-brane solutions [4,5]. While most of these developments took place in the simplified bosonic string theory, Erler in 2013 succeeded in solving the analogous problem for the more realistic superstring theory [6].

Inhomogenous, or background dependent solutions are much harder to find. In 2014 Kudrna, Rapčák and Schnabl presented a systematic approach how to search numerically for such solutions [7]. They demonstrated it in the context of the critical Ising model, where they were able to find most of the fundamental boundary conditions. Incidentally, later that year Erler and Maccaferri took a major step towards analytic description of these, and we may very likely witness rapid development in this area in the near future [8].

Besides these formal and interdisciplinary aspects of string field theory, there are important physical applications which we plan to address in the near future. To name just two: the physics of intersecting D-branes in string theory is tantalizingly close to the physics of standard model, including the Higgs mechanism. Could the Higgs field be the stretched string tachyon? Another intriguing possibility to relate the string field theory to real world is via the physics of the early universe inflationary period.

Quantum gravity

The 20th century saw the emergence of two of the most successful theories in physics: Einstein's general relativity theory describing the gravitational force, and quantum mechanics, describing the peculiar behavior of particles on the smallest scales. Under closer scrutiny, these theories turn out to be incompatible: general relativity seems to have insurmountable problems when viewed as a quantum theory of particles. The aim of quantum gravity is to reconcile general relativity with quantum mechanics. In string theory, which is widely believed to be a consistent quantum gravity theory, the conundrum is resolved by replacing particles as the smallest constituents of matter with tiny vibrating strings. An important insight which came out of string theory, but which may be more generally valid, is the concept of holography: quantum gravity

can be reformulated as a quantum mechanical theory without gravity which lives on a `holographic screen', a surface of one lower dimension.
The research in our group aims to use tools from string theory and holography to address open questions in quantum gravity. In the period 2010-2014 we have focused on three main problems.

Are time machines unphysical?

After having thrown a bombshell in the field of axiomatic mathematics with his incompleteness theorems, Kurt Gödel presented his friend Albert Einstein in 1949, on the occasion of his 70th birthday, with a poisoned gift. He demonstrated the mathematical possibility of time machines: solutions to Einstein's equations of general relativity representing universes where observers can travel back in time to an earlier point in their history. In the jargon we say that such a universe contains closed timelike curves. The effect on Einstein was so profound that he reportedly started to doubt his own theory. Besides sparking the imagination of science fiction writers, time machines present the physicist with seemingly unresolvable puzzles such as the grandfather paradox, where one would travel back in time to murder one's grandfather. Basically, a time machine destroys the relation between cause and effect which allows us to formulate physical laws. Therefore, time machines are widely believed to be unphysical, leading Hawking to formulate his famous chronology protection conjecture in order to `make the universe safe for historians'. To this day, it remains a conjecture which has not yet been proven from first principles, perhaps because such a proof requires a complete theory of quantum gravity such as string theory.
Our interest in the chronology protection conjecture was sparked after we discovered that Gödel's universe also arises as a so-called `BPS solution' in certain theories of gravity, implying that it is more stable and well-behaved than we originally thought [9]. We decided to study chronology protection using ideas from holography and asked the following question: suppose the universe contains a time machine, do we see any unphysical behavior in the quantum mechanical theory on the holographic screen? In the cases we have studied, which include the Gödel universe, it turns out that indeed a basic principle of quantum mechanics is violated which goes under the name of unitarity. Our investigations hence suggest that quantum mechanical unitarity forbids the construction of time machines in general [10-13].

The internal structure of black holes

Einstein's theory of general relativity was long known to predict the existence of black holes, the end products of gravitational collapse from which not even light can escape. Initially, it was unclear if these objects actually exist in nature, since an observer falling into a black hole will eventually hit a singularity where space and time cease to exist. Nevertheless astronomers have since then indirectly observed several candidate black holes.
Naively, black holes seem to be rather simple objects which are completely determined by three parameters: mass, angular momentum and charge. However, it was argued by Bekenstein and Hawking in the 1970s that black holes behave like thermodynamic systems possessing a temperature and an entropy, suggesting instead that a black hole can be in any of a gigantic number of microscopic configurations which are indistinguishable for the outside observer. It is expected that a quantum theory of gravity should give a description of these so-called microstates and explain the origin of the black hole temperature and entropy. One of the main successes of string theory is that it passes this test, as was shown by Strominger and Vafa who gave a microscopic accounting of the entropy of certain black holes. Again, the concept of

holography was crucial, as the microstates were identified and counted in the quantum mechanical theory living on a holographic screen.
This exciting result immediately raised the question if we can identify the microstates also in the gravity theory, not just on the holographic screen, and study their geometry and physical properties. As stressed by Mathur, the standard ideas of holography suggest that this should be possible and that the gravity theory should contain smooth solutions which correspond to the microstates. In Mathur's picture the naive singular black hole geometry has to be replaced by a smooth microstate geometry with some internal structure, a so-called `fuzzball'.
The program of constructing these microstate geometries has so far succeeded only for the simplest `small' black holes, where our theoretical description is however not completely reliable. For the `large' black holes, where we do have a reliable description, the microstate geometries have not yet been found although several suggestions have been made on how to construct them. In our work, we have focused on one of these suggestions which we find promising: the black hole deconstruction proposal of Denef et. al. The main technical hurdle was that the proposed solutions live in a branch of the theory which is not much studied, requiring us to develop new techniques to construct them. After much hard work however we were able to construct the simplest microstate geometries, albeit so far not analytically but only in a perturbative expansion [14].

Holography for higher spin gravity

The last topic we have studied is perhaps a little more abstract but nevertheless very exciting for us, as it part of a field which saw major progress in the last few years. The idea is to construct holographic quantum gravity theories where the quantum mechanical theory on the holographic screen is as simple as possible. In such theories, we get the most mileage out of holography as it is easy to do computations in the theory on the holographic screen. Such theories then seem the ideal setup to address the thorniest questions in quantum gravity such as the black hole information paradox, the nature of the cosmological big bang singularity and so on.
It turns out that the simplest holographic theories do not only describe gravity but also contain exotic massless `higher spin' particles which have not been observed in nature. Theories containing these hypothetical particles were constructed only fairly recently by Vasiliev. They are not only of academic interest since string theory resembles a higher spin theory at high energies or temperatures such as occurred in the early universe; therefore the higher spin theories may be relevant to describe early universe physics.
Our interest in this subject was sparked in 2011 when Gaberdiel and Gopakumar proposed a very concrete example of a simple holographic theory. They proposed that three dimensional higher spin gravity theories are holographically described by the well-studied `minimal model conformal field theories' in two spacetime dimensions, and since then their proposal has passed many impressive tests. Our research has focused on resolving a puzzle in the Gaberdiel-Gopakumar proposal: the holographic minimal model theory contains excitations (the so-called `light states') which don't seem to be present in the higher spin theory. We were able to show that, at least in some region of parameter space, these excitations do appear in the higher spin theory as previously unknown smooth classical solution [15]. These solutions resemble conical geometries, where the singular point at the tip of the cone is smoothened out by the higher spin fields. Since then we have accumulated further evidence that these conical solutions have the correct charges and symmetry properties to be identified with the minimal model excitations [16,17].

Phenomenology

Our group activities in phenomenology fall in several relatively narrow areas. This is quite understandable as the scientists concerned are primarily involved in experimental data analysis within large collaborations and/or coordination and development of new detectors. Závada who is mostly involved with coordinating the ALICE experiment studying ultra-relativistic heavy ion interactions has also been working on three dimensional covariant parton models trying to understand the properties of quarks and gluons within a nucleon. Kundrát and Lokajíček are participating at the TOTEM experiment and their theoretical studies concern studies of elastic scattering of protons which are needed to interpret properly the experimental results. Kepka, a member of ATLAS collaboration, has studied theoretically anomalous couplings of gauge bosons and feasibility of their experimental detection. Fischer has studied issues pertaining to Borel summability of QCD perturbation theory. Let us now describe these areas in more detail.

The three-dimensional quark-gluon structure of the nucleon

The theoretical study and the experimental exploration of the internal structure of protons and neutrons (nucleons) have recently entered a new phase. Over the past 40 years an understanding of nucleons in terms of elementary constituents (partons, i.e. quarks and gluons) has gradually and successfully emerged. Much has been learned about the nucleon in terms of its "one-dimensional" parton structure, relevant when partons are assumed to move co-linearly with their parent nucleon, and encoded in the so-called parton distribution functions (PDFs). In the last few years theoretical breakthroughs have extended this simple picture, leading to new concepts, like the "Generalized Parton Distributions" (GPDs) and the "Transverse Momentum Dependent parton distributions" (TMDs). These concepts help to address long-standing questions concerning the motion of quarks and gluons inside the nucleon, their orbital motion, their spin and their spatial distribution. The study of these questions in the framework of the covariant parton model, developed in our department, is a contribution to this extensive program [18].

Interaction of ultra-relativistic ions in the LHC experiment ALICE

Study of heavy ion collisions at ultra high energies represents a hot issue in the contemporary nuclear and particle physics. A fundamental motivation for this study is to verify the prediction of the current theory of the strong interaction (called Quantum Chromo-Dynamics), which implies that at very high temperatures and very high densities of the nuclear matter, quarks and gluons should no longer be confined inside composite particles. Instead they should exist freely in a new state of matter known as quark-gluon plasma (QGP). We believe that entire Universe was in this state for the short moment just after the Big Bang. The similar conditions are created in the volume of colliding nuclei in the experiment ALICE at LHC. Our Institute participates in this project and at present carries out the following tasks:

1. Our group participates in completion, maintenance and operation of the PHOS spectrometer, which is an important component of the ALICE.

2. Monte-Carlo simulations and analysis of some processes in the ALICE experiment are performed on the PC farm GOLIAS.

Experiment TOTEM

Experiment TOTEM at the LHC at CERN has been devoted mainly to the detection of proton-proton collisions in which one or both protons may survive the corresponding collision. Particle detectors inside special movable devices called the Roman pots are used to detect these diffractive protons very close to the proton beam. The Roman pots have been produced by the company Vacuum Praha.

Dedicated LHC magnet settings (beam optics) enabled measurement of collisions where no new particles are produced and the two colliding protons just slightly change direction (elastic scattering) at very low scattering angles which provided data to study two fundamental interactions: the long-ranged Coulomb and short-ranged strong interaction. TOTEM experiment measured proton-proton elastic scattering at the energy of 7 and 8 TeV [19,20]. It has been found that corresponding distribution of elastic scattering angles has similar structure as at lower energies (so called dip-bump structure corresponds to lower momentum transfers at higher energies). The analysis of elastic scattering data have given the following values of integrated elastic cross section: for the energy of 7 TeV the value of (25.4 ± 1.1) mb, for 8 TeV the value of (27.1 ± 1.4) mb. Assuming the validity of the optical theorem the value of total cross section has been established to (98.6 ± 2.2) mb at the energy of 7 TeV and to (101.7 ± 2.90) mb at the energy of 8 TeV.
The values of the mentioned hadronic cross section (or some other interesting proton characteristics) depend also on the model of elastic collisions. The description of Coulomb-hadronic interference based on eikonal model and optical theorem proposed earlier by the scientists of our institute has been used, too. It enables to describe the elastic hadronic scattering as more peripheral than the inelastic one.
It has been also shown that none of the contemporary models of elastic hadronic collisions has reproduced reliably and satisfactorily the elastic scattering data [21]. Yet another model of elastic proton-proton collisions is being developed by the scientists of our institute which would be able to describe the whole process taking into account also more reliable dependence of the collisions on impact parameter and which would allow determining some further proton characteristics.

Anomalous couplings of gauge bosons

Although the gauge principle underpinning today's most successful theory of elementary particles, the so called standard model, is well established theoretically, it is nevertheless of significant interest to confirm it experimentally. We studied various possible anomalous couplings of gauge bosons and how they would show up at the Large Hadron Collider with feasible future upgrades of today's experiments [22]. Forward proton tagging devices, similar to TOTEM described above, can select events in which light is emitted of the scattered protons, allowing precise measurements of various final states produced via two-photon exchanges. It appears that this novel technique may lead to much better constraints of anomalous gauge boson couplings than those obtained with conventional methods [23].

Perturbative expansion in QCD

As is well known, the perturbative treatment of quantum field theories in most cases yields infinite power series which are not only divergent for every value of the coupling constant, but also fail to reproduce the physically expected singularities of correlators. Using the Borel

summation method together with optimal conformal mapping technique pioneered by Fischer one can significantly enlarge the convergence domain and achieve fastest convergence. In this approach one takes advantage of the knowledge of the singularities of the Borel transform of the particular correlator. As a practical application Fischer applied this technique to studies of hadronic decays of the τ-lepton and found a new accurate value of the strong coupling constant α_s at the energy scale given by the τ-lepton mass [24].

[1] Matej Kudrna, Carlo Maccaferri, Martin Schnabl; Boundary State from Ellwood Invariants. [arXiv:1207.4785 [hep-th]], 10.1007/JHEP07(2013)033, JHEP 1307 (2013) 033.

[2] Martin Schnabl; Analytic solution for tachyon condensation in open string field theory. [hep-th/0511286], 10.4310/ATMP.2006.v10.n4.a1, Adv.Theor.Math.Phys. 10 (2006) 433-501. **Cited by 195 records**

[3] Theodore Erler, Martin Schnabl; A Simple Analytic Solution for Tachyon Condensation. [arXiv:0906.0979 [hep-th]], 10.1088/1126-6708/2009/10/066, JHEP 0910 (2009) 066. **Cited by 77 records**

[4] Masaki Murata, Martin Schnabl; Multibrane Solutions in Open String Field Theory. [arXiv:1112.0591 [hep-th]]. 10.1007/JHEP07(2012)063. JHEP 1207 (2012) 063.

[5] Masaki Murata, Martin Schnabl; On Multibrane Solutions in Open String Field Theory. [arXiv:1103.1382 [hep-th]]. 10.1143/PTPS.188.50. Prog.Theor.Phys.Suppl. 188 (2011) 50-55.

[6] Theodore Erler; Analytic solution for tachyon condensation in Berkovits` open superstring field theory. [arXiv:1308.4400 [hep-th]],10.1007/JHEP11(2013)007, JHEP 1311 (2013) 007.

[7] Matej Kudrna, Miroslav Rapcak, Martin Schnabl; Ising model conformal boundary conditions from open string field theory. [arXiv:1401.7980 [hep-th]].

[8] Theodore Erler, Carlo Maccaferri; String Field Theory Solution for Any Open String Background. [arXiv:1406.3021 [hep-th]],10.1007/JHEP10(2014)029, JHEP 1410 (2014) 029.

[9] Thomas S. Levi, Joris Raeymaekers, Dieter Van den Bleeken, Walter Van Herck, Bert Vercnocke; Godel space from wrapped M2-branes. [arXiv:0909.4081 [hep-th]],10.1007/JHEP01(2010)082, JHEP 1001 (2010) 082.

[10] Joris Raeymaekers, Dieter Van den Bleeken, Bert Vercnocke; Relating chronology protection and unitarity through holography. [arXiv:0911.3893 [hep-th]], 10.1007/JHEP04(2010)021. JHEP 1004 (2010) 021.

[11] Joris Raeymaekers, Dieter Van den Bleeken, Bert Vercnocke; Chronology protection and the stringy exclusion principle. [arXiv:1011.5693 [hep-th]],10.1007/JHEP04(2011)037, JHEP 1104 (2011) 037.

[12] Joris Raeymaekers; Chronology protection in stationary three-dimensional spacetimes. [arXiv:1106.5098 [hep-th]], 10.1007/JHEP11(2011)024, JHEP 1111 (2011) 024.

[13] Joris Raeymaekers; Chronology protection in stationary 3D spacetimes. [arXiv:1111.0161 [hep-th]], 10.1088/1742-6596/343/1/012099. J.Phys.Conf.Ser. 343 (2012) 012099.

[14] Joris Raeymaekers, Dieter Van den Bleeken; Unlocking the Axion-Dilaton in 5D Supergravity. [arXiv:1407.5330 [hep-th]], 10.1007/JHEP11(2014)029, JHEP 1411 (2014) 029.

[15] Alejandra Castro, Rajesh Gopakumar, Michael Gutperle, Joris Raeymaekers; Conical Defects in Higher Spin Theories. [arXiv:1111.3381 [hep-th]], 10.1007/JHEP02(2012)096. JHEP 1202 (2012) 096. **Cited by 67 records**

[16] Eric Perlmutter, Tomas Prochazka, Joris Raeymaekers; The semiclassical limit of W_N CFTs and Vasiliev theory. [arXiv:1210.8452 [hep-th]], 10.1007/JHEP05(2013)007, JHEP 1305 (2013) 007.

[17] Andrea Campoleoni, Tomas Prochazka, Joris Raeymaekers; A note on conical solutions in 3D Vasiliev theory. [arXiv:1303.0880 [hep-th]],10.1007/JHEP05(2013)052, JHEP 1305 (2013) 052.

[18] A.V. Efremov, P. Schweitzer, O.V. Teryaev, P. Zavada;The relation between TMDs and PDFs in the covariant parton model approach. [arXiv:1012.5296 [hep-ph]],10.1103/PhysRevD.83.054025, Phys.Rev. D83 (2011) 054025.

[19] Luminosity-independent measurements of total, elastic and inelastic cross-sections at $\sqrt{s} = 7$ TeV. By TOTEM Collaboration (G. Antchev et al.). 10.1209/0295-5075/101/21004, Europhys.Lett. 101 (2013) 21004.

[20] Luminosity-Independent Measurement of the Proton-Proton Total Cross Section at $\sqrt{s}=8$ TeV. By TOTEM Collaboration (G. Antchev et al.), 10.1103/PhysRevLett.111.012001, Phys.Rev.Lett. 111 (2013) 1, 012001.

[21] Jan Kaspar, Vojtech Kundrat, Milos Lokajicek, Jiri Prochazka; Phenomenological models of elastic nucleon scattering and predictions for LHC. ,10.1016/j.nuclphysb.2010.09.020, Nucl.Phys. B843 (2011) 84-106.

[22] E. Chapon, C. Royon, O. Kepka; Anomalous quartic W W gamma gamma, Z Z gamma gamma, and trilinear WW gamma couplings in two-photon processes at high luminosity at the LHC. [arXiv:0912.5161 [hep-ph]], 10.1103/PhysRevD.81.074003, Phys.Rev. D81 (2010) 074003.
Cited by 78 records

[23] S. Fichet, G. von Gersdorff, O. Kepka, B. Lenzi, C. Royon, M. Saimpert; Probing new physics in diphoton production with proton tagging at the Large Hadron Collider. [arXiv:1312.5153 [hep-ph]]. 10.1103/PhysRevD.89.114004, Phys.Rev. D89 (2014) 114004.

[24] Irinel Caprini, Jan Fischer; Expansion functions in perturbative QCD and the determination of $\alpha_s(M_\tau^2)$. [arXiv:1106.5336 [hep-ph]], 10.1103/PhysRevD.84.054019. Phys.Rev. D84 (2011) 054019.

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Optical and biophysical systems

The team is formed by the employees of the department of Optical and Biophysical systems of the Institute of Physics (IoP) (http://www.fzu.cz/en/department/21). The team is headed by Alexandr Dejneka has currently 30 workers including 16 researchers and 5 Ph.D. students. The team is mainly focused on the research and development of optical materials and systems for micro-electronic, optoelectronic and biomedical applications. Four years ago, the new research area of biophysics in the framework of the team was established. The biophysical research line is strongly supported by the team experience in the field of optics and magnetism. The interdisciplinary research is conducted in close cooperation with the Institute of Experimental Medicine (IEM) AS CR in the framework of the Joint Laboratory of Biophysics of IoP and IEM. The research comprised several lines: magnetic targeting of stem cells, magnetic hyperthermia, magnetically driven cellular endocytosis, stem cells networking with micro-magnet arrays, application of atmospheric low-temperature plasma for bacteria deactivation and regenerative medicine. Our Lab experimental facilities make it feasible to design, manufacture, and characterize materials suitable for biomedical applications, diagnostic and therapeutic purposes.

The main experimental technique used in the team for optical study of the materials is spectroscopic ellipsometry. This technique enabled us to investigate the complex refractive index of novel materials in the wide spectral range giving access to other fundamental physical parameters (crystalline structure, polarization, surface roughness etc.). The ellipsometry lab is equipped by the temperature dependent ellipsometry system allowing the study of optical properties of nanostructures, surfaces, and thin films; detection of surface, bulk and interface phase transitions; dynamic of biological films and surfaces, and nondestructive profile calculation of inhomogeneous structures. The optical structures for the research are prepared by pulsed laser deposition technique by the technology group from the team. The next direction of the research is focused on the development of dynamical theory of x-ray diffraction of perfect crystals and the utilization of the results for the design and realization of new x-ray optical elements based on Si and Ge single crystals. In this area we are able to realize novel elements of X-ray monochromator systems and test it at European synchrotron facilities in collaboration with other x-ray optics groups of these facilities.

In the period 2010-2014 the team published 128 papers in journals with impact factor and registred 5 patents. For each research direction, the summaries of achieved results are listed below.

1. Optical Study of Novel Materials

1.1. *Interface and strain effects in epitaxial perovskite structures*

Perovskite-type metal oxides exhibit variety of electronic phases and ferroic orderings that makes these materials multifunctional and enables numerous applications. Conceptually new devices can be created using advanced oxides, in which composition-dependent or epitaxy-controlled nanoscale phenomena lead to creation of novel or improved response functions. One of the fundamental problems here is a detection of the phase states in ultra–thin perovskite epitaxial films (couple of nm thick). The team succeeded in the analysis revealing the phase states of such films using the temperature-dependent ellipsometric studies. For example, in the work [1] we demonstrated the existence of the predicted strain-

induced ferroelectric ordering in quantum paraelectric $KTaO_3$ epitaxial films by combining experimental study and density functional theory calculations. The most important proof of the existence of the ferroelectric state was obtained from ellipsometry experiment. The work was done with the contribution of the University of Oulu (UO), IoP, Ioffe Physical Technical Institute of the RAS (PT) and Aalto University School of Science and Technology (AUS).

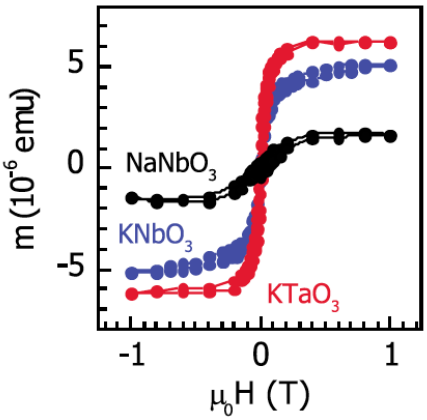


Fig. 1 SQUID measured sample magnetization as a function of external magnetic field determined at room temperature in as-deposited films of $KTaO_3/SrTiO_3$ (red curve), $KNbO_3/SrTiO_3$ (blue curve), and $NaNbO_3/SrTiO_3$ (black curve).

The team designed the optical setup for high temperature measurements and performed the optical experiments. All partners contributed to the data analysis and manuscript preparation. For the team this work established the basement for the optical study of ultra-thin perovskite films and helped us to develop new experimental strategy. The next fundamental problem in study of these perovskite ultra-thin systems is knowledge of electronic energies and excitations. Through combining optical ellipsometric studies, examination of the ferroelectric states, and materials characterization, we intend to explore connections between electronic transitions and ordering behavior that contribute to fundamental understanding of perovskite-type oxides and nanoscale phenomena therein. In this direction we recently found d^0 ferromagnetism at a charge-imbalanced interface between two non-magnetic perovskites. Epitaxial d^0 $SrTiO_3/KTaO_3$, $SrTiO_3/KNbO_3$, and $SrTiO_3/NaNbO_3$ interfaces were observed by transmission electron microscopy and their optical properties were determined from spectroscopic ellipsometry measurements [2]. Magnetic measurements of these samples exhibited the ferromagnetic hysteresis at room temperature (fig.1). Even though the observed phenomenon is mainly important for the basic research, its application potential is also very significant. Use of such interface-induced magnetism allows the development of new materials combining ferroelectric and ferromagnetic ordering (magnetoelectric multiferroics) without any conventional magnetic materials. The work was done with the contribution of the University of Oulu (UO), IoP, and Aalto University (AU). The team prepared the samples by PLD technique and performed magnetic and optical experiments as well as analyzed the obtained results. All partners contributed to the data analysis and manuscript preparation.

The next our achievement in the research of thin films under various strain conditions is the complex optical study of epitaxial $PbSc_{0.5}Nb_{0.5}O_3$ (PSN) films. In particular, it was shown that a biaxial epitaxial compression can favor the relaxor state appearance over ferroelectricity. The absence of the ferroelectric transition and the existence of the low temperature relaxor state are evidenced by a combination of dielectric, polarization, and optical studies of epitaxial PSN films [3]. This finding is beyond existing models of polarization in perovskite structure epitaxial films and beyond the established ability to induce ferroelectricity by an epitaxial strain. Moreover, the dramatic changes in the spectra of the dielectric functions and the absorption coefficient are found under various strain conditions. A frustration of the ferroelectric phase transition is evidenced by thermooptical studies. A complex relationship between strain, polarization, and optical properties is discussed in terms of possible ionic displacements in metrically tetragonal PSN films [4]. In these studies, the major part of the work including sample preparation, characterization and optical study was done by the team.

1.2. *Characterization of phase transitions in martensites by ellipsometry*

Ellipsometric study of a martensitic single crystal NiMnGa was carried out in a wide temperature range and allowed to detect all the critical temperatures of the sample (Fig.2).

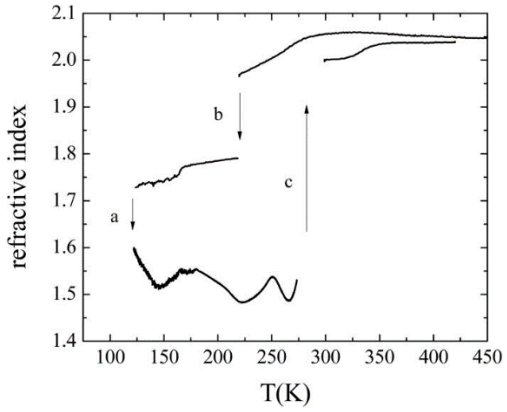


Fig.2. Temperature dependence of the refractive index at wavelength of 620 nm. The points (a), (b), and (c) show the temperatures where cooling/heating was stopped to analyze relaxation. The arrows indicate the isothermal relaxation of the refractive index at temperatures 120 K, 220 K, and 280 K during times t_a = 3 h, t_b = 7 h, and t_c = 15 h, respectively.

The performed optical measurements revealed the earlier onset of premartensitic transition at the sample surface. The giant isothermal creep (relaxation up to 20%) of the refractive index was found below room temperature (fig.2). It was shown that the creep amplitude is temperature dependent. The underlying mechanisms of the observed effects are revealed [5]. This work was done with the contributions of the Public University of Navarra, Pamplona, the University of País Vasco, Bilbao and IoP, Prague. The team designed and carried out the optical experiments, performed modeling and data analysis. All partners contributed to the manuscript preparation.

1.3. *X-ray crystal optics for synchrotron radiation*

The research was focused on elaboration of a dynamical model of x-ray diffraction of perfect crystals and the utilization of the results for the design and realization of new x-ray optical elements based on Si and Ge single crystals (fig. 3). For example, it was recently shown by the team that cut in a certain direction of double crystal X-ray monochromator could change after diffraction the polychromatic and parallel incident beam to spatially spread with wavelength dispersion. This may be utilized for compression of properly chirped X-ray pulses [6]. This work was fully done by the team, but there are other important works realized in a close cooperation with such local and international partners as Czech company Polovodice a.s., Masaryk University in Brno, and Paul Scherrer Institute (Swiss Light Source) [7,8]. The tests of some elements are performed at European synchrotron facilities in collaboration with x-ray optics groups there. In such common works the team was responsible for elaboration of the new method including theory, sample preparation and data evaluation.

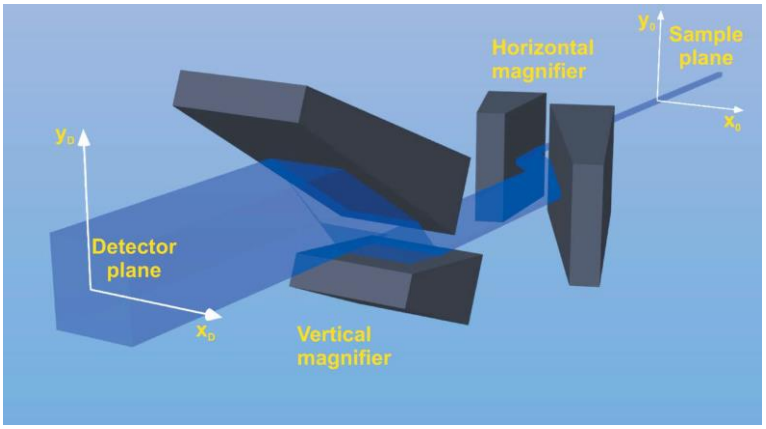


Fig. 3 Experimental setup for testing of the developed magnification system with special arrangement Ge crystals

2. Advanced Physical Methods in Cell Biology

2.1. Nanomechanics of Magnetically Driven Cellular Endocytosis

It has been shown that, driven by externally applied magnetic fields, magnetic nanoparticles (MNPs) offer the unique opportunity to influence cell functions and even the behavior of living organisms. Thus, we studied important features of magnetic nanomaterials, namely direct effects of a magnetic field on the parameters of endocytosis of coated magnetic nanoparticles. The characteristic time and force scales of the cellular uptake machinery were found. The results demonstrate how the cellular uptake rate could be controlled by applied magnetic field, membrane elasticity, and nanoparticle magnetic moment (fig.4). The endocytosis rate was increased in 20 times by the magnetic forces [9]. The characteristic endocytosis time and rate can be controlled by a magnetic field if the magnetic force has the same order of magnitude as the actin force (tens of pN). The possibility of remote control of the cellular endocytosis and/or exocytosis rates by a magnetic field without using various types of inhibitors seems to be a very intriguing direction in nanomedicine. Moreover, patterned micromagnets specially designed to produce multigradient magnetic flux distributions modulated on the nanoscale [10], in combination with magnetically targeted functionalized NPs could guide NPs motion with high precision to cell membrane significantly increasing efficacy of magnetic hyperthermia [11].

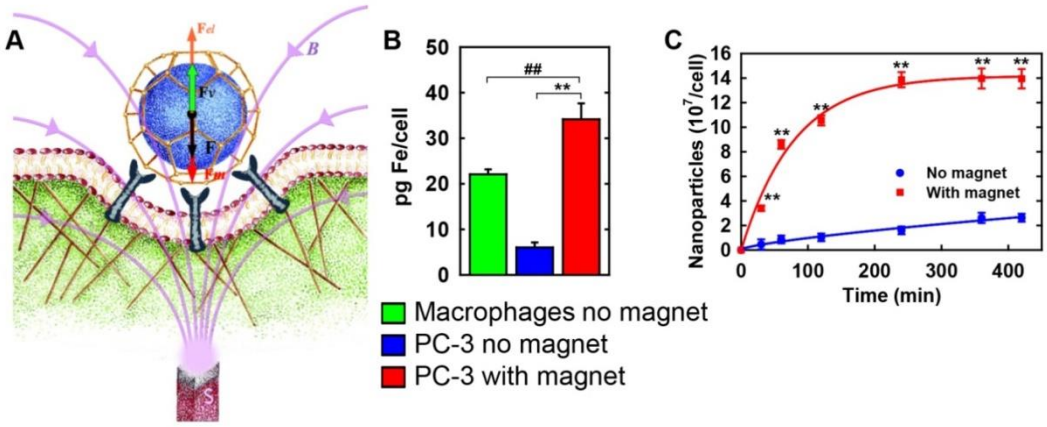


Fig. 4 (A) Scheme of magnetically-controlled endocytosis. (B) Cellular uptake of SPIO NPs by PC-3 cells and human macrophages. Cells were treated with 100 μg/ml of particles for 6 h. Nanoparticle uptake was analyzed by spectroscopic measurement of intracellular iron. (C) Number of internalized SPIO NPs as a function of time with and without magnet.

2.2. Magnetic Control of Living Cell Machinery

The influence of spatially modulated high-gradient magnetic fields on human leukemia cells behavior is second line of research.

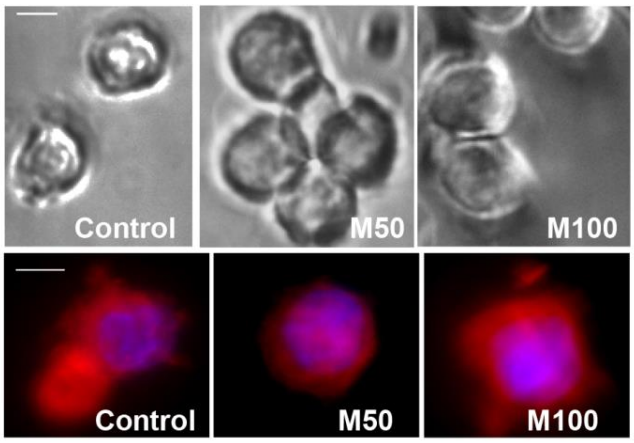


Fig. 5 Changes in cell diameter and cell volume after exposure to a static high-gradient magnetic field (M50 and M100 micro-magnet arrays). Representative images are shown. Alternatively, the cell membranes were stained with CellMask Deep Red (red), nuclei were counterstained with DAPI (blue), and the images were recorded with a fluorescent microscope. Scale bar 10 μm.

We demonstrate that exploiting high-gradient micro-magnet arrays induces swelling and apoptosis of THP-1 cells as well as inhibits cell proliferation in the absence of chemical or biological agents (fig.5). Under a prolonged exposure to a high-gradient magnetic field THP-1 cells were observed to swell up to 90% in volume. Mechanical stress raising due to the magnetic gradient forces exerted on a cell is shown to be responsible for triggering of cell swelling, formation of reactive oxygen species followed by apoptosis [12]. Such a magnetically controlled cell swelling could be also used to manipulate cell-to-cell communication which is affected by the extracellular space volume as well as cell size.

A strategy based on the magnetic control of cell swelling proposed here in conjunction with the relationship between enlarged cell size and gene expression may have fundamental implications in understanding a wide circle of biological processes accompanied by enlarged cell size [12].

Academy of Science of the Czech Republic acknowledged this work, among the best research achievements in the annual report 2014.

2.3. Stem Cell Networking on Micro-Magnet Arrays

To manipulate stem cells by magnetic field submicron-patterned NdFeB films were developed. The micromagnet arrays produce magnetic fields (fig. 6) which affect the cells' life as: causing the cell migration and adherence to a magnetic pillar [13]. The underlying mechanisms which incorporate the both physical and biological factors affecting cells life were suggested. The building up of tunable interconnected stem cell networks is a challenging perspective for tissue engineering and regenerative medicine. The discovered cell patterning has a great application potential. Manipulating the fate and spatial organization of stem cells and the creation of an interconnected cell network with externally applied magnetic fields opens exciting perspectives for tissue engineering and regenerative medicine.

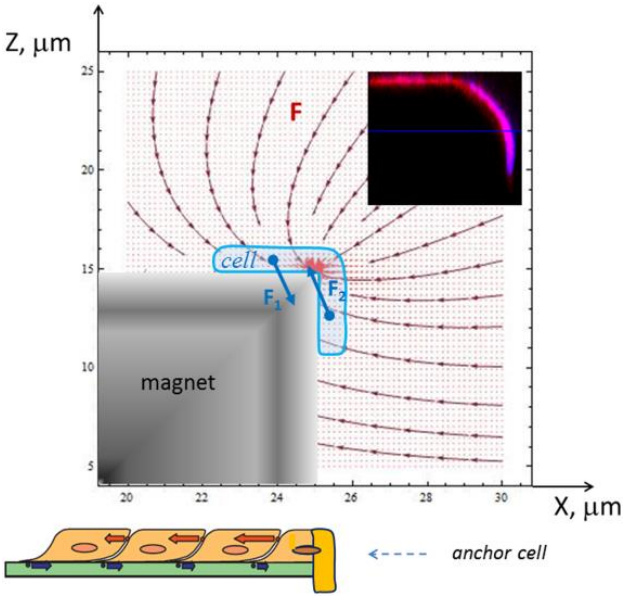


Fig. 6 Magnetic field, forces and cell position on a micro-magnet. Magnetic force distribution and force directions acting on a cell adhered to the edge of a micro-magnet calculated for a magnet of size: 50×50×30 µm. Inset shows a cell in the area near the edge of a micro-magnet.

For example, since cell seeding is the main step in engendering tissue structures in 3D scaffolds, micro-magnet arrays may be used as building blocks for new types of magnetic scaffolds, allowing us to enhance the adhesion, proliferation, and function of magnetic nanoparticle-free cells. Moreover, the magnetic stress arising near micro-magnets may serve as a tool driving stem cell differentiation, in a similar way as cyclic mechanical stress of 10–20 Pa applied to embryonic stem cells induces their differentiation.

2.4. Magnetic Targeting of Mesenchymal Stem Cells

Spinal cord injury (SCI) is a condition that results in significant mortality and morbidity. Treatment of SCI utilizing stem cell transplantation represents a promising therapy. However, current conventional treatments are limited by inefficient delivery strategies of cells into the injured tissue. In this study, we designed a magnetic system and used it to accumulate stem cells labelled with superparamagnetic iron oxide nanoparticles (SPION) at a specific site of a SCI lesion. The loading of stem cells with engineered SPIONs that guarantees sufficient attractive magnetic forces was achieved. Further, the magnetic system allowed rapid guidance of the SPION-labelled cells precisely to the lesion location. Histological analysis of cell distribution throughout the cerebrospinal channel showed a good correlation with the calculated distribution of magnetic forces exerted onto the transplanted cells. The results suggest that focused targeting and fast delivery of stem cells can be achieved using the proposed non-invasive magnetic system (fig.7). With future implementation the proposed targeting and delivery strategy bears advantages for the treatment of disease requiring fast stem cell transplantation.

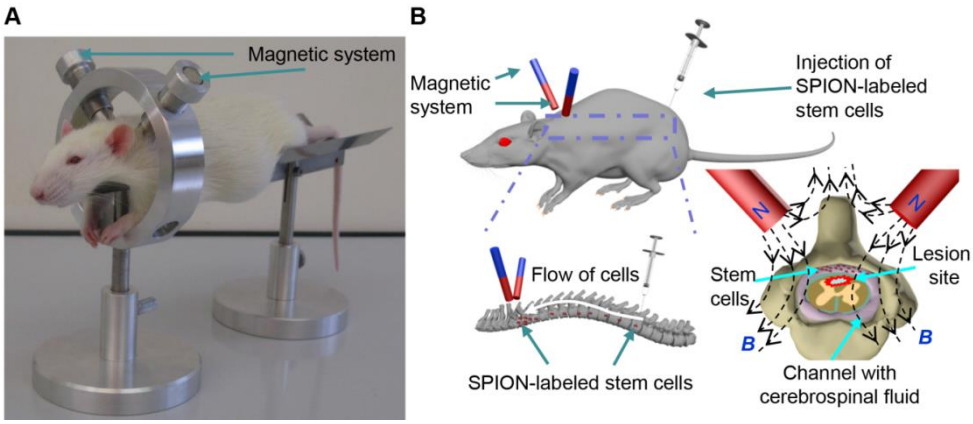


Fig. 7 Magnetic system for MSC targeting into SCI. (A) In vivo application of the non-invasive magnetic system for MSC targeting into SCI of a rat. (B) Schematic representation of the magnetic targeting strategy.

For cell therapy, the number of transplanted cells that reach the injured area is one of the critical parameters. In this study, transplanted cells labelled with superparamagnetic iron oxide nanoparticles (SPIONs) were guided by a magnetic field and successfully targeted near the lesion site in the rat spinal cord injury [14,15]. Such magnetic systems with tuneable geometric parameters may provide an additional level of control needed to enhance the efficiency of stem cell delivery in spinal cord injury.

2.5. Down-regulation of Adipogenesis of Mesenchymal Stem Cells by Oscillating High-Gradient Magnetic Fields and Mechanical Vibration

Nowadays, the focus in medicine on molecular genetics has resulted in a disregard for the physical basis of treatment even though many diseases originate from changes in cellular mechanics. Here, we show that oscillating high-gradient magnetic field (HGMF) and mechanical vibration affect adipogenic differentiation of mesenchymal stem cells by the transmission of mechanical stress to the cell cytoskeleton, resulting in F-actin remodeling and subsequent down-regulation of adipogenic genes [16]. Our results showed that low-frequency oscillating HGMF and mechanical vibration reduced the adipogenic differentiation of MSCs (fig.8). Furthermore, the presented results imply that both oscillating HGMF and mechanical vibration may affect the adipogenic differentiation by the applied mechanical stress channeled along cytoskeletal filaments. Indeed, forces acting on the nucleus might induce changes in its shape, modify higher-order DNA organization (as we detected using "comet assay"), and thereby alter gene transcription. Interestingly, oscillating but not static HGMFs significantly decreased the expression of the adipogenic genes adiponectin, PPARγ, and AP2. Understanding the mechanisms and possibilities of controlled adipogenesis by HGMF may represent promising approaches in the treatment of diseases related to excessive expansion of white adipose tissue, including diabetes, cardiovascular disease, and cancer.

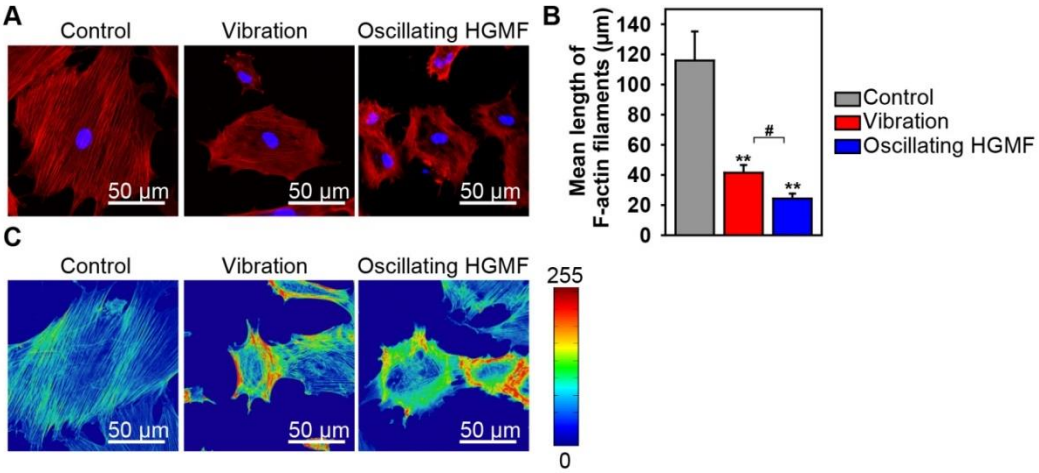


Fig. 8 (A) MSCs were exposed to either mechanical vibrations or an oscillating HGMF for 7 days. After the treatment cells were fixed and stained for F-actin filaments. Nuclei were counterstained with DAPI. (B) ImageJ (NIH) software was used for image processing and fluorescent micrograph quantification. (C) Confocal fluorescence analysis of cytoskeleton organization of the cell treated as in (A). The fluorescence distribution and intensity of F-actin are shown in the reported pseudo-color scale.

2.6. Plasma Medicine

Non-thermal plasma has been recognized as a promising tool across a vast variety of biomedical applications, with the potential to create novel therapeutic methods. However, the understanding of the

molecular mechanisms behind non-thermal plasma cellular effects remains a significant challenge. In this study, we show how two types of different non-thermal plasmas induce cell death in mammalian cell cultures via the formation of multiple intracellular reactive oxygen/nitrogen species [17-19]. Our results showed a discrepancy in the superoxide accumulation and lysosomal activity in response to air and helium plasma, suggesting that triggered signaling cascades might be grossly different between different plasmas. In addition, the effects of ozone, a considerable component of non-thermal plasma, have been simultaneously evaluated and have revealed much faster and higher cytotoxic effects (fig.9). Our findings offer novel insight into plasma-induced cellular responses, and provide a basis for better controlled biomedical applications.

Our study shows that the antibacterial efficacy [19] of air plasma was comparable to ozone [17], whereas helium plasma possessed significantly lower antibacterial effects. Furthermore, ozone exhibits dramatically higher toxic effects on living cells than air or helium plasma. Indeed, the extent of cytotoxicity may grossly differ between fibroblasts and phenotypically distinct tumor cell lines. Moreover, despite having the same cytotoxicity upon air and helium plasma treatment, our findings imply that the triggered signaling cascades may be grossly different. This indicates that these processes depend critically on the chemical composition of the plasma jet. In addition, proteins of the mTOR signaling pathway, which are overexpressed or deregulated in human cancers, represent a target for cancer therapy, and a link between the deregulation of lysosomal activity and mTOR inhibition has been revealed. In light of these facts our data on lysosomal acidification by helium plasma are of great value and bring new perspectives for the development of novel therapeutic strategies of cancer.

The work part named as “Advanced Physical Methods in Cell Biology” was done with contributions of the following organizations: Institute of Experimental Medicine (IEM); Institute of Pharmacology of Natural Products & Clinical Pharmacology (IPNP), Ulm University, Germany; Institute Néel (IN), CNRS/UJF, Grenoble, France; Institute for Clinical and Experimental Medicine (ICEM) AS CR, and Institute of Macromolecular Chemistry (IMC) AS CR.

The team designed and characterized the plasma system, performed mathematical modelling and statistical analysis. The team also proposed the main ideas, designed the experiments, elaborated physical models explaining the discovered effects, and performed modelling and mathematical calculations. The team also designed and characterized the magnetic systems used for targeted magnetic cell delivery, performed mathematical modelling and statistical analysis of data. SEM observation of bacterial cultures affected by plasma treatment was also done by the team.

The IEM performed most of the in vitro experiments. The IEM performed proof-of-concept experiments on stem cells networking and migration, cell cultivation and made conclusions on cell functions. The IPNP cultivated cells and performed the experiments and data analysis. The IPNP also performed proof-of-concept experiments on magnetically assisted endocytosis and THP-1 cell functions, used pharmacological and in vitro knockdown approaches to register cells functionality.

The IN fabricated the micromagnet arrays, characterized them and performed data analysis. The both ICEM and IMC performed atomic force microscopic study of cellular membranes affected by plasma treatment.

This work was acknowledged by the President of the Czech Academy of Sciences at XLVI Meeting of Academy Assembly (http://www.cas.cz/sd/novinky/hlavni-stranka/2015/150423-xlvi-zasedani-akademickeho-snemu-av-cr.html available in Czech language).

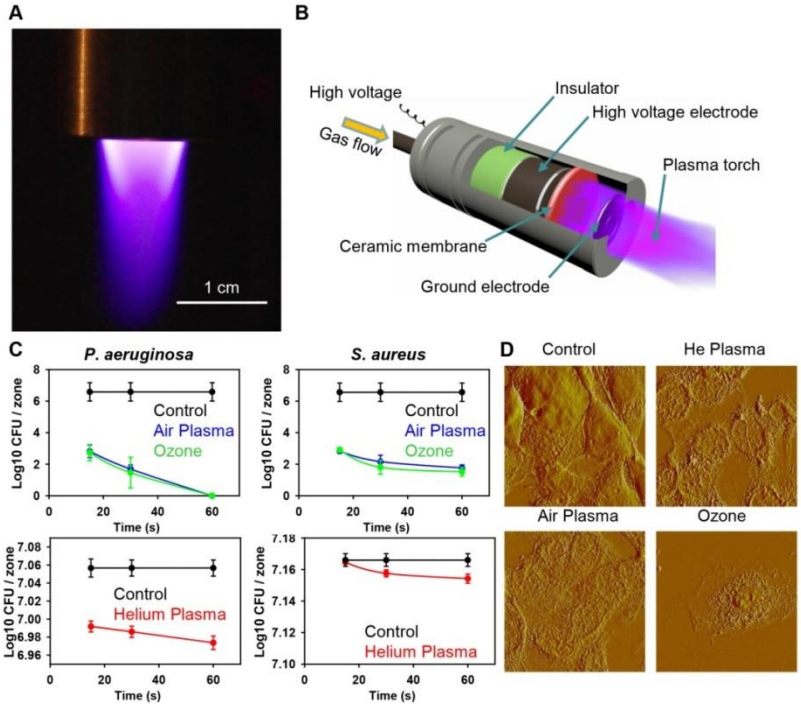


Fig. 9 (A) An image of the plasma torch. (B) Schematic diagram of plasma nozzle. (C) The inactivation (number of colony forming units) of P. aeruginosa and S. aureus after treatment for indicated periods of time with air, helium plasmas or ozone. (D) AFM analysis of cell membrane integrity 4 h after air, helium plasmas or ozone treatment.

References

1. M. Tyunina, J. Narkilahti, M. Plekh, R. Oja, R. M. Nieminen, A. Dejneka, V. Trepakov, Evidence for Strain-Induced Ferroelectric Order in Epitaxial Thin-Film $KTaO_3$. ***Phys. Rev. Lett.*** (2010) 104: 227601.

2. R. Oja, M. Tyunina, L. Yao, T. Pinomaa, T. Kocourek, A. Dejneka, O. Stupakov, M. Jelinek, V. Trepakov, S. van Dijken, R. M. Nieminen d0 Ferromagnetic Interface between Nonmagnetic Perovskites. ***Phys. Rev. Lett.*** (2012) 109: 127207.

3. Tyunina, Marina ; Levoska, J. ; Janolin, P.E. ; Dejneka, Alexandr. Low temperature relaxor state induced by epitaxial compression in $PbSc_{0.5}Nb_{0.5}O_3$ films. ***Phys. Rev. B*** (2013) 87: 2241071.

4. Lynnyk, Anna ; Chvostová, Dagmar ; Pacherová, Oliva ; Kocourek, Tomáš ; Jelínek, Miroslav ; Dejneka, Alexandr ; Tyunina, Marina. Optical properties of epitaxial relaxor ferroelectric $PbSc_{0.5}Nb_{0.5}O_3$ films. ***Appl. Phys. Lett.*** (2013) 103: 132901.

5. A. Dejneka, V. Zablotskii, M. Tyunina, L. Jastrabik, J. I. Pérez-Landazábal, V. Recarte, V. Sánchez-Alarcos, V. A. Chernenko, Ellipsometry applied to phase transitions and relaxation phenomena in Ni_2MnGa ferromagnetic shape memory alloy. ***Appl. Phys. Lett.*** (2012) 101: 141908.

6. J. Hrdý, P. Oberta, Possibility of X-ray pulse compression using an asymmetric or inclined double-crystal monochromator. ***J. Synchrot. Radiat.*** (2013) 20: 550.

7. G.Lovric, P.Oberta, I.Mohacsi, M.Stampanoni, R.Mokso, A robust tool for photon source geometry measurements using the fractional Talbot effect. ***Opt. Express*** (2014) 22: 2745.

8. P.Oberta, P.Mikulík, J.Hrdý, A proof-of-principle experiment of a novel harmonics separation optics for synchrotron facilities. ***J. Synchrot. Radiat.*** (2012) 19: 1012.

9. V. Zablotskii, et al., Nanomechanics of magnetically driven cellular endocytosis. ***Appl. Phys. Lett.*** (2011) 99: 183701.

10. V. Zablotskii et al., High-field gradient permanent micromagnets for targeted drug delivery with magnetic nanoparticles. ***AIP Conf. Proc.*** (2010) 1311: 152.

11. O. Lunov, et al. Thermal destruction on the nanoscale: Cell membrane hyperthermia with functionalized magnetic nanoparticles. ***AIP Conf. Proc.*** (2010) 1311: 288.

12. V: Zablotskii, et al., Modulation of monocytic leukemia cell function and survival by high gradient magnetic fields and mathematical modeling studies. ***Biomaterials*** (2014) 35: 3164.

13. V: Zablotskii, et al., Life on magnets: stem cell networking on micro-magnet arrays. ***PLoS One*** (2013) 8: e70416.

14. V: Vanecek, et al., Highly efficient magnetic targeting of mesenchymal stem cells in spinal cord injury. ***Int. J. Nanomed.*** (2012) 7: 3719.

15. D. Tukmachev, et al., An effective strategy of magnetic stem cell delivery for spinal cord injury therapy. ***Nanoscale*** (2015) 7: 3954.

16. V. Zablotskii, et al., Down-regulation of adipogenesis of mesenchymal stem cells by oscillating high-gradient magnetic fields and mechanical vibration. ***Appl. Phys. Lett.*** (2014) 105: 103702.

17. O. Lunov, et al., Cell death induced by ozone and various non-thermal plasmas: therapeutic perspectives and limitations. ***Sci. Rep.*** (2014) 4: 7129.

18. V. Zablotskii, et al., Multijet atmospheric plasma device for biomedical applications. ***Plasma Medicine*** (2011) 1: 135.

19. O. Lunov, et al., Non-thermal plasma mills bacteria: Scanning electron microscopy observations. ***Appl. Phys. Lett.*** (2015) 106: 053703.

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Physical processes in low temperature plasma

Since 2010 the research team "Physical process in low temperature plasma" from Department of Low-Temperature Plasma (hereafter referred as DLTP) have been focusing on the research dealing with physical processes in low temperature plasma sources. The principal investigator of this team is Mgr. Zdeněk Hubička,Ph.D. who is a senior researcher and head of Department of Low-Temperature Plasma. He works in the field processes in low temperature plasma and deposition of thin films by pulsed plasma systems. Key members of this team are Mgr. Martin Čada Ph.D who is a senior researcher working in the field diagnostics of low temperature pulsed plasma and ing. Štěpán Kment, Ph.D. who is a researcher working in the field of low temperature thin film plasma deposition and photochemical analysis of deposited thin films. Doc. RNDr. Vítězslav Straňák, Ph.D is an associate professor and senior researcher working in the field plasma processes in pulsed PVD and PECVD low temperature plasma systems. The team has recently 14 members, 12 researchers, 1 Ph.D student and 1 electrical engineer.

The plasma processes were investigated in various PVD and PECVD plasma systems used for preparation of different types of functional thin films and coatings. The main focus was oriented on the deposition of semiconducting materials for photocatalytic applications, solar water splitting, and photonic applications. The detailed research of physical processes in these types of plasma is a powerful way to understand the growth mechanism of the materials deposited and to make a significant progress in optimization and tailoring their properties for practical applications. The goal was to prepare the semiconducting materials with a high quality, defined microstructure, crystalline structure, texture, photocatalytic properties and simultaneously to understand their growth mechanism. One of the important physical phenomena studied was the interaction of this technological deposition plasma with the substrate. In order to be able to conduct this research, the plasma processes and parameters were investigated by different advanced plasma diagnostic. The time resolved Lagmuir probe system was regularly used for evaluation of electron and ion concentration, electron energy distribution function, and plasma potential. This sophisticated system optimized for the pulsed or unstable

technological plasma was fully designed and developed at DLTP. Furthermore, the composition of the plasma was in-situ examined by the emission spectroscopy as well as the time resolved laser absorption spectroscopy (LAS). The time resolved LAS system was again predominantly developed at DLTP and partially also with our cooperating partner at University of Greifswald, Germany. Particularly the "know how" of time resolution method and development of processing electronics and software to this instrument were adopted and provided from DLTP and the optical part of the LAS system was realized with a significant help and contribution of University of Greifswald. Application of this unique system for the plasma diagnostics in the pulsed magnetron plasma carried out at DLTP was published in [9]. DLTP together with the partner from University of Greifswald published the work [10], in which the experimental data obtained from time resolved LAS measured in a novel high power impulse magnetron system (HIPIMS) were used to establish a new theoretical model describing physical processes in this modern plasma-assisted deposition system. The experimental part of this study was performed at DLTP and the physical model and the manuscript preparation was done with a significant contribution of coauthors from University of Greifswald.

Another significant characteristics influencing the properties of deposited films is the ion flux on the surface of the substrate. For the measurements of the ion flux a high frequency Sobolewski method was employed. Moreover, the ion velocity distribution function of particular ions were measured by ion mass spectrometer providing the energy resolution in a time resolved mode (EQP 1000, Hiden Analytical, Ltd) or by easier configuration using the time resolved retarding field analyzer (Semion, Impedance, Inc). It was also possible to estimate a heating flux on the substrate by a calorimetric probe in order to get information about a heating mechanism of the substrate surface during the deposition process. The outputs of these diagnostic tools provided information about conditions of thin film growth process.

The ion flux on the substrate was measured at DLTP during the preparation of non-conducting TiO_2 films in a plasmatic technological deposition system equipped with a hollow cathode (plasma jet) operated in a pulsed dc regime. The results of this work was published in the paper [1]. The coauthors from different institutes or universities merely contributed to the discussion of obtained results. The experimental results enabled us to formulate a physical analytical model describing the total ion flux as a function of a pulse duty cycle of the hollow cathode discharge. The novelty and importance of this study lies in the fact that it helps to understand how the pulse dc regime influences the total ion flux on the substrate owing to a decay of plasma during its afterglow. On the basis of this theory a low temperature (< 150 °C) growth of TiO_2 thin films in anatase crystal structure could be reasonable described [1].

The pulse multi-plasma jet hollow cathode reactive sputtering system was used for the low temperature depositions of crystalline TiO_2 anatase and Fe_2O_3 hematite thin films for photoelectrochemical applications. This work was published in [2, 3] and was done at DLTP. The coauthors from different institutes and universities contributed to the discussion of obtained results or provided aditional analysis of deposited films by specialized diagnostic methods. A schematic drawing of this plasmatic system can be seen in Fig 1. Materials of hollow cathodes (Fe, Ti) were reactively sputtered by the high density hollow cathode discharge and carried by the flowing plasma towards the substrate. The photography of this system with two plasma jet channels during TiO_2 anatase deposition with the movable substrate holder can be seen in Fig 2. A big advantage of this system is a very high deposition rate for reactive deposition of oxide films and simultaneously very good semiconductor quality and specific nanostructured morphology of the surface. We have deposited a high quality anatase TiO_2 with relatively high photocurrents at low temperatures of the substrate and simultaneously with the high deposition rate. It was demonstrated the possibility to deposit these photoactive anatase TiO_2 on polymer Kapton foil. Similarly, the hematite Fe_2O_3 semiconducting films were prepared by this system with the aim for solar water splitting applications. Some of above mentioned plasma diagnostic systems were implemented in the deposition process for "in situ" plasma monitoring and the growth process characterization.

The HIPIMS and hybrid HIPIMS with superimposed MF power were developed and applied for the deposition of semiconducting oxide films of TiO_2 and Fe_2O_3 highly suitable for photoelectrochemical applications. Physical processes in the depositing plasma were investigated by aforementioned types of plasma diagnostics. A new type of diagnostic sensor for the measurement of ionization of depositing particles was developed. This sensor employs a QCM with the magnetic electron filter and biased collecting electrode. The schematic picture is depicted in Fig 5. The sensor is suitable in plasma-assisted deposition processes because it has a high sensitivity and is resistant against contamination during the process in comparison with similar well known system equipped with QCM and grid electron filter. The sensor was successfully applied for measurements of ionization of deposition fluxes as it is seen in Fig. 6 showing the results for particles in HIPIMS magnetron and pulsed hollow cathode plasma jet system recorded during the Fe and Fe_2O_3 films deposition. Measurement of ionization of depositing particles with this modified QCM sensor equipped with the magnetic filter in HIPIMS magnetron sputtering system was published in [3,6]. This work was done at the DLTP. The coauthors from different institutes or universities contributed to the discussion of obtained results or prepared manuscript for publication. The hybrid HIPIMS +MF plasma system applied for the

low temperature deposition of TiO_2 rutile thin films on polymer substrate was published in [4]. This study dealt with an investigation of time resolved ion velocity distribution function during the deposition process. This work was done at the DLTP. The HIPIMS magnetron reactive sputtering and pulsed hollow cathode depositions of Fe_2O_3 hematite thin films for water splitting applications were published in [5]. Experimental work of thin films depositions was done at the DLTP. The analysis of the prepared hematite films with respect to the potential PEC applications was carried out in the group of Prof. Patrik Schmuki at University of Erlangen, Germany. Other coauthors from different institutes and universities contributed to the discussion of scientific results and manuscript preparation. Examples of Fe_2O_3 thin films photocurrent for the films deposited by pulsed hollow cathodes and HIPIMS magnetron can be seen in Fig 4. Different surface morphology of typical hollow cathode plasma jet and HIPIMS Fe_2O_3 thin films is evident from Fig 3.

The HIPIMS sputtering system was, furthermore, extended to a dual magnetron mode and in addition to the HIPIMS the MF plasma excitation was added. These plasma sources were analyzed by the time resolved Langmuir probe system, time resolved emission spectroscopy, heating flux and high frequency ion flux probe. Physical processes were investigated in this new plasmatic systems during depositions of metal alloys. Results of this research were published in [7, 8]. These works were done in cooperation with University of Greifswald. The experimental arrangements of these experiments together with HIPIMS and MF plasma excitation and with all probe plasma diagnostic systems were realized at DLTP. These systems were subsequently transported to University of Greifswald and were installed there in dual magnetron deposition chamber.

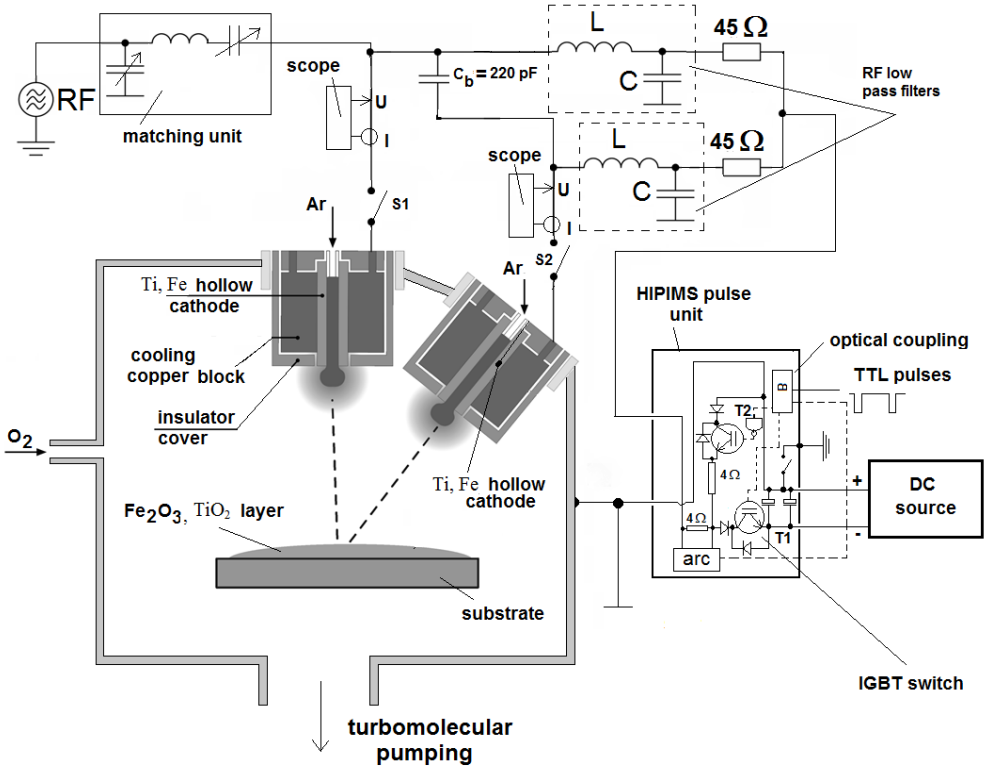


Fig. 1: Dual pulsed hollow cathode plasma jet system for reactive sputtering of oxide semiconductor thin films.

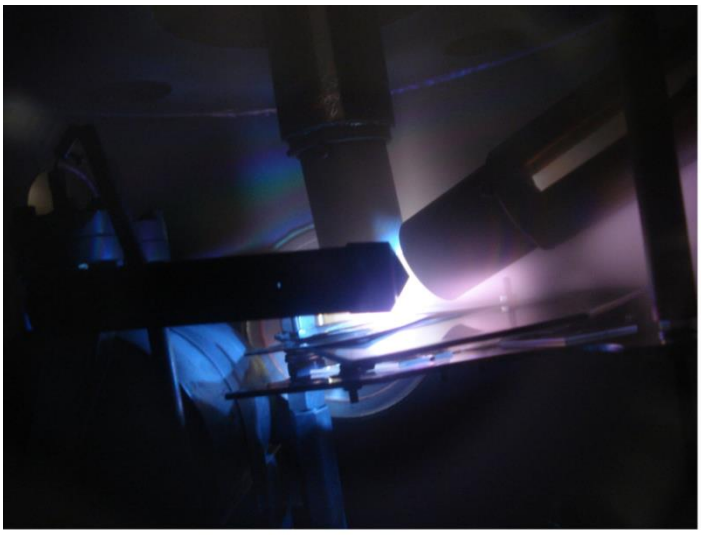


Fig. 2: Photography of pulsed dual hollow plasma jet system.

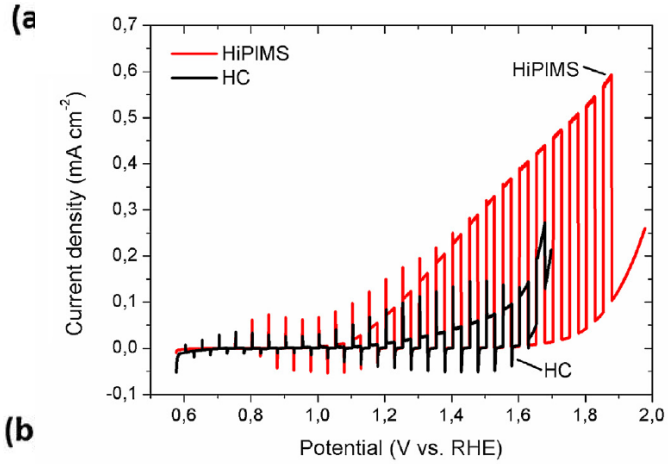


Fig. 4: Photoelectrochemical characteristics of hematite Fe_2O_3 thin films at chopped light illumination with solar intensity AM 1.5 (100 mW/cm^2) deposited by pulsed hollow cathode (HC) and high power pulsed magnetron sputtering (HIPIMS).

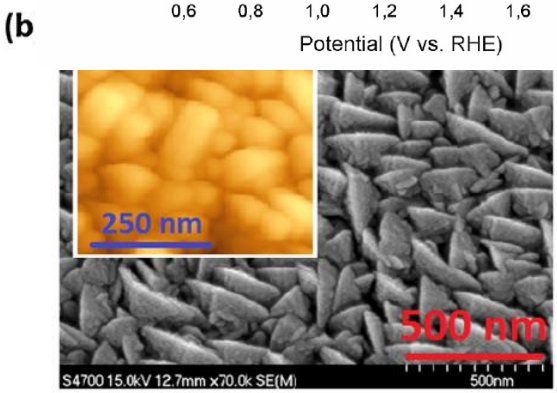


Fig 3 Surface properties of hematite Fe_2O_3 thin films deposited by pulsed hollow cathode (HC) and high power pulsed magnetron sputtering (HIPIMS).

The experimental work was done at the University of Greifswald, however, by researchers from DLTP during their visit. Other coauthors from different institutes and universities contributed to the discussion of scientific results and by diagnostics of deposited thin films. This cooperative research with University of Greifswald continued by development of a hydride HIPIMS + ECWR plasma source working at very low pressure $p \approx 0.05$ Pa. The HIPIMS magnetron plasma excitation was developed at the DLTP and the ECWR plasma source was provided by the University of Greifswald. Plasma processes in this new plasma source were investigated by all the above mentioned plasma diagnostics and TiO_2 anatase textured films were deposited. The results of this research were published in [11, 12, 13]. The experimental work was done at University of Greifswald by researchers from DLTP during their visit. Other coauthors from different institutes and universities contributed to the discussion of scientific results and by diagnostics of deposited thin films. Schematic picture of the HIPIMS+ECWR plasma source is displayed in Fig 7 and an example of measured ion velocity distribution function can be seen in Fig 8.

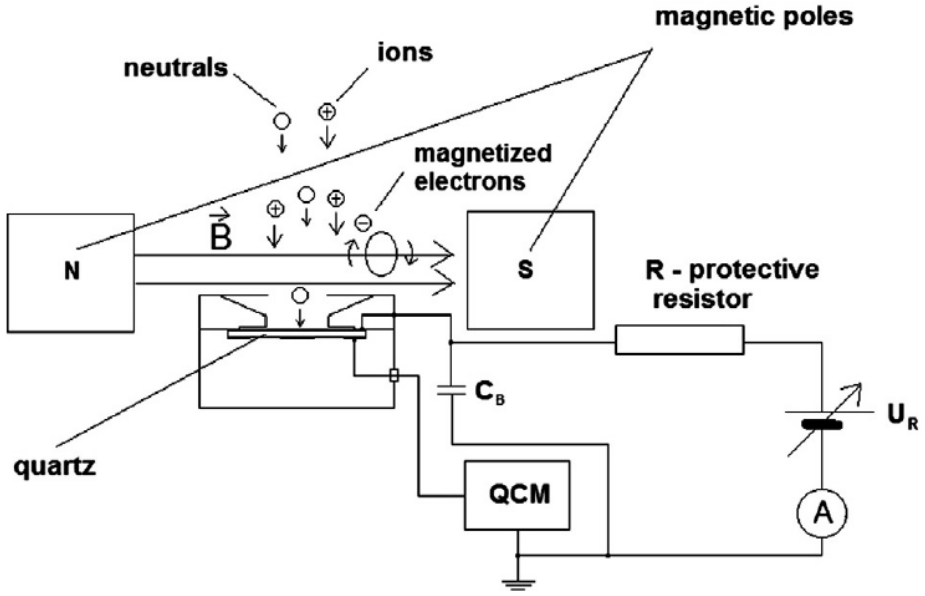


Fig 5 QCM system with magnetic field and biased collecting electrode for the separate measurement of ionized and neutral deposition fluxes.

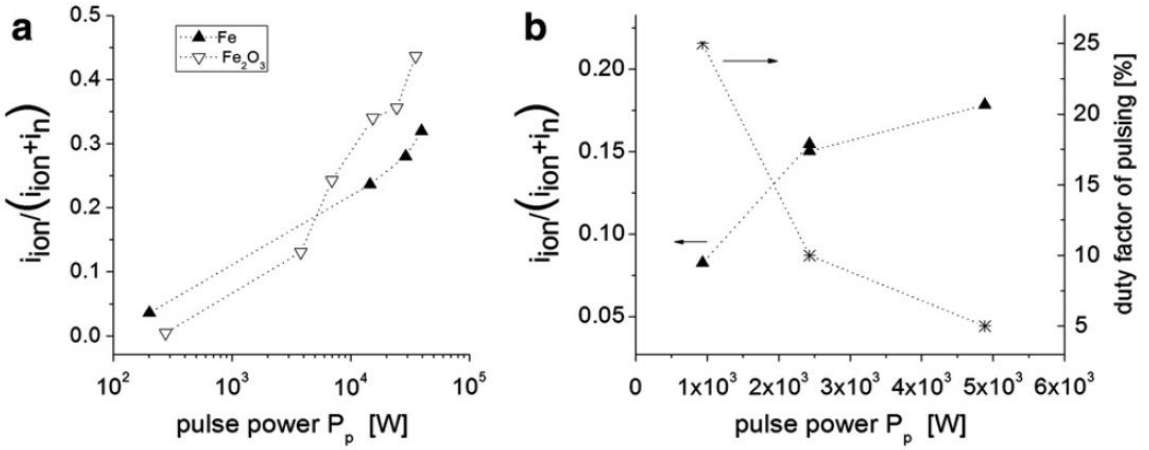


Fig 6 a) The ratio "r" of ionized depositing flux i_{ion} and the total deposition flux $i_T = i_{ion}+i_n$ $r=i_{ion}/(i_{ion}+i_n)$ (i_n is the neutral deposition flux) in dependence on the applied pulse power P_p for the deposition of Fe and Fe_2O_3 by pulse HIPIMS magnetron and b) Left axis- the ratio "r" for the deposition of Fe films by the pulsed hollow cathode single plasma jet system in dependence on applied pulse power P_p; right axis - the duty factor of pulsing in hollow cathode plasma jet in dependence on applied P_p

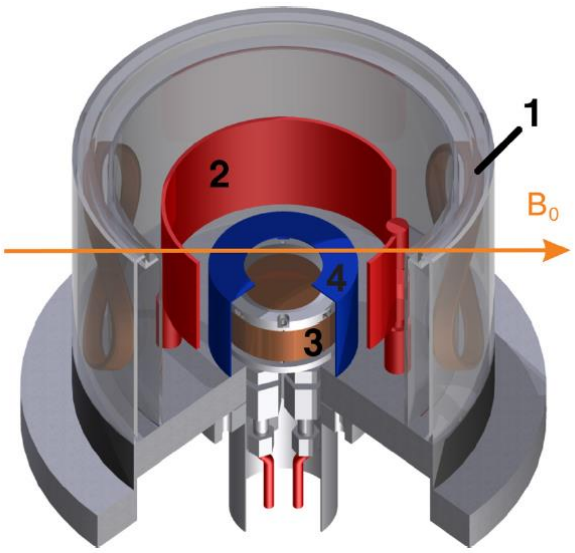


Fig. 7: Scheme of HIPIMS magnetron implemented in ECWR plasma source.

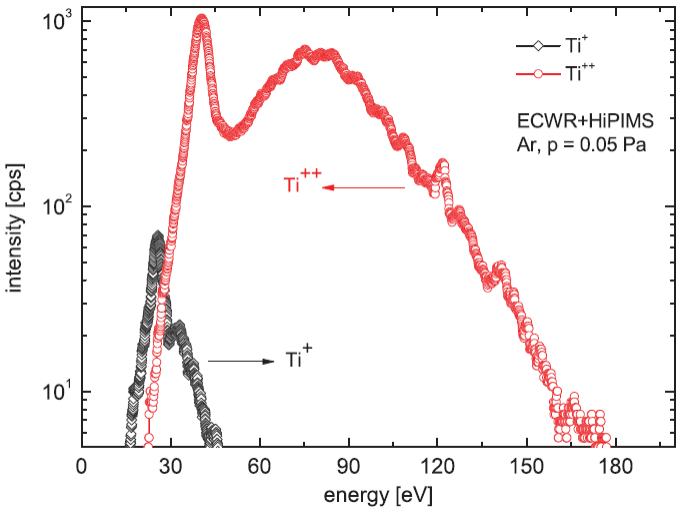


Fig 8 Ion velocity distribution function of Ti^{+} and Ti^{++} in HIPIMS+ECWR plasma measured at p=0.05Pa

Pulsed modulated PECVD system working at atmospheric pressure was developed at DLTP. The emission spectroscopy and plasma impedance probe was employed for the investigation of plasma processes during PECVD deposition of thin films. ZnO:Mn nanocrystalline films with defined optical properties were deposited by this system. Optical-absorption study of these films was done taking special attention to the spectral range of the fundamental absorption edge between 3.1 – 4 eV. Excitonic lines observed in the region 3.40–3.45 eV were found to shift to higher energies with increasing Mn concentration. The optical band-gap energy also increases with *x*, reliably evidencing strong coupling between oxygen holes and localized spins of manganese ions. This research was done under cooperation with Institute of Metal Physics, UD RAS, Yekaterinburg, Russia and Ioffe Institute, RAS, 1 St-Petersburg, Russia. Authors from DLTP (O. Churpita, Z. Hubicka, L. Jastrabik were responsible for development of atmospheric low temperature PECVD deposition source and for all the deposition experiments of nanocrystalline ZnO doped by Mn with defined concentration. Other coauthors from different departments and institutes prepared manuscript for publication and studied properties of deposited films and create proper physical discussion of obtained results.

References:

[1] Ion current to a substrate in the pulsed dc hollow cathode plasma jet deposition system Virostko, P; Hubička, Z ; Čada, M; Tichý, M. Ion current to a substrate in the pulsed dc hollow cathode plasma jet deposition system. **Journal of Physics D-Applied Physics** 43(2010) 124019.

[2] Double hollow cathode plasma jet-low temperature method for the TiO2:N photoresponding films, Kment, Š; Klusoň, P; Hubička, Z; Krýsa, J. ; Čada, M; Gregora, I; Deyneka, A; Remeš, Z; Žabová, H; Jastrabík, L. **Electrochimica acta 55 (**2010) 1548-1556.

[3] Deposition of hematite Fe_2O_3 thin film by DC pulsed magnetron and DC pulsed hollow cathode sputtering systém Hubička, Z; Kment, Š; Olejníček, J; Čada, M; Kubart, T. ; Brunclíková, M; Kšírová, P; Adámek, P; Remeš, Z. **Thin Solid Films** 549 (2013) 184-191.

[4] Investigation of reactive HiPIMS + MF sputtering of TiO_2 crystalline thin films, Olejníček, J; Hubička, Z; Kment, Š; Čada, M; Kšírová, P; Adámek, P; Gregora, I; **Surface and Coatings Technology** 232 (2013) 376-383.

[5] High-power pulsed plasma deposition of hematite photoanode for PEC water splitting Kment, Š. ; Hubička, Z; Krysa, J. ; Olejníček, J; Čada, M; Gregora, I ; Zlámal, M. ; Brunclíková, M; Remeš, Z; Liu, N. ; Wang, L. ; Kirchgeorg, R. ; Lee, Ch.Y. ; Schmuki, P., High-power pulsed plasma deposition of hematite photoanode for PEC water splitting. **Catalysis Today** 2014, roč. 230, jul, 8-14. ISSN 0920-5861.

[6] Investigation of ionized metal flux fraction in HiPIMS discharges with Ti and Ni targets Kubart, T. ; Čada, M; Lundin, D. ; Hubička, Z, Investigation of ionized metal flux fraction in HiPIMS discharges with Ti and Ni targets. **Surface and Coatings Technology** 238 (2014) 152-157.

[7] Time-resolved investigation of dual high power impulse magnetronsputtering with closed magnetic field during deposition of Ti–Cu thin films, Straňák, V; Čada, M; Hubička, Z; Tichý, M. ; Hippler, R. Time-resolved investigation of dual high power impulse magnetronsputtering with closed magnetic field during deposition of Ti–Cu thin films. **Journal of Applied Physics** 108 (2010) 043305.

[8] Effect of mid-frequency discharge assistance on dual-high power impulse magnetron sputtering, V Stranak, S. Drache, R. Bogdanowicz, H. Wulff, A. Herrendorf, Z. Hubicka, M. Cada, M. Tichy, R. Hippler, **Surface & Coatings Technology** 206 (2012) 2801–2809.

[9] Time-resolved tunable diode laser absorption spectroscopy of pulsed plasma, Adámek, P; Olejníček, J; Čada, M; Kment, Š. ; Hubička, Z, **Optics Letters** 38 (2013) 2428-2430.

[10] Time-resolved tunable diode laser absorption spectroscopy of excited argon and ground-state titanium atoms in pulsed magnetron discharges, Sushkov, V. ; Do, H.T. ; Čada, M; Hubička, Z; Hippler, R. , **Plasma Sources Science & Technology** 22 (2013) 015002.

[11] Highly ionized physical vapor deposition plasma source working at very low pressure,

Straňák, V. ; Herrendorf, A.-P. ; Drache, S. ; Čada, M; Hubička, Z; Tichý, M. ; Hippler, R. Highly ionized physical vapor deposition plasma source working at very low pressure. **Applied Physics Letters** 100 (2012) 141604.

[12] Plasma diagnostics of low pressure high power impulse magnetron sputtering assisted by electron cyclotron wave resonance plasma Straňák, V. ; Herrendorf, A.-P. ; Drache, S. ; Čada, M; Hubička, Z; Bogdanowicz, R. ; Tichý, M. ; Hippler, R. **Journal of Applied Physics** 112 (2012) 093305.

[13] Straňák, V. ; Hubička, Z; Čada, M; Drache, S. ; Tichý, M. ; Hippler, R. Investigation of ionized metal flux in enhanced high power impulse magnetron sputtering discharges. **Journal of Applied Physics** 115 (2014) 153301.

[14] Optical evidence of strong coupling between valence-band holes and d-localized spins in ZnO:Mn, Sokolov, V.I. ; Druzhinin, A.V. ; Gruzdev, N.B. ; Dejneka, A; Churpita, O; Hubička, Z; Jastrabík, L; Trepakov, V, **Physical Review. B** 81 (2010) 153104.

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Plasma-based technologies and analyses of functional materials

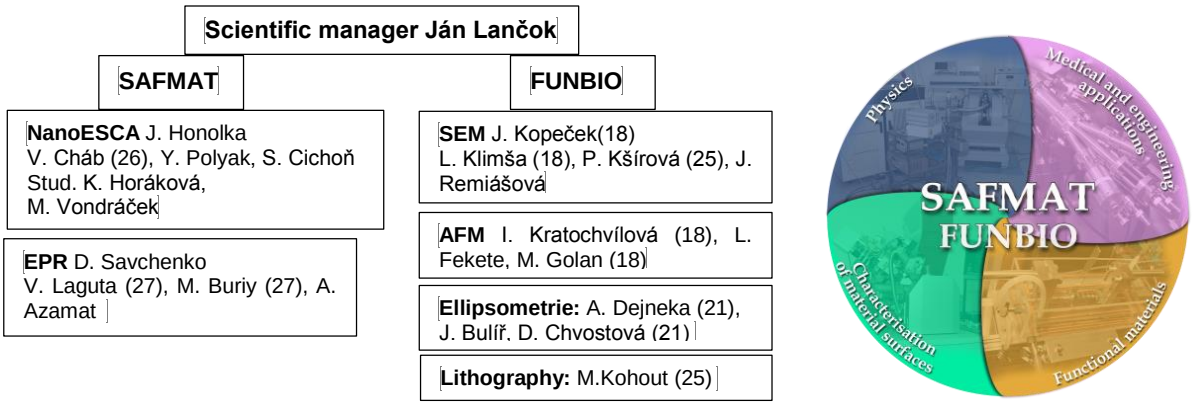
Plasma-based technologies and analyses of functional materials team is based on the Department of Analysis of Functional Materials in Institute of Physics, which was established in 2011 under the leadership of Ján Lančok. The team could be divided into two special parts which are connected by people as well as by research programs:

- **Physical Vapour deposition technologies for thin films and nanostructures fabrication.**

  The laboratories for plasma deposition was started to build in 2006 in frame of project Nanotechnology for society "Self organised magnetic nanostructures". The following small group was established: head Ján Lančok, senior scientists : Jiří Bulíř is an expert for film deposition and in-situ optical properties analyses, Petr Pokorný deals designing of ultrahigh vacuum deposition systems, Jindřich Musil is involved in magnetron sputtering of thin films and nanostructures, Michal Novotný works on plasma characterization by mass and optical emission spectroscopy, junior scientist: Přemysl Fitl, Jan Vlček, Stanislav Cichoň are involved in thin film depositions by magnetron sputtering, evaporation and pulsed laser deposition, 2 PhD and 3 postgraduate students

- **Laboratories for Analyses of Functional Materials.**

These laboratories were financed by Operation Program Prague Competitive (OPPC) through two different strategy projects of Institute of Pysics(IoP): (i) Center for analyses of Functional Materials (SAFMAT) and (ii) Center for Functional Materials for bioaplications (FUNBIO). The projects SAFMAT and FUNBIO, both managed by Ján Lančok, were built in period 2009-2012 and 2013-2014, respectively. Projects include experimental facilities for the newly oriented interdisciplinary research in the field of advanced materials for applications in technique and medicine with high innovation potential. The laboratories are involved currently in the Roadmap for Large Research, Infrastructures in the Czech Republic and belong to the open laboratories for the collaborative research in frame of all IoP. The research focus and personal staff is schematically shown in Fig. bellow. As average we can say, that 30 % of the time is reserved for research in our team.



The number in () denotes the departmnet within Institute of Physics

Physical Vapour deposition technologies

In the field of thin films fabrication by Physical Vapour Depositions techniques we developed and constructed the new technologies for different kind of coatings and nanostructural thin films fabrications. The attention was focused to development hybrid deposition techniques with auxiliary plasma discharges for optical, magnetic and organics films. In our research we don't want to use one deposition technique, for example magnetron sputtering, for fabrication of some specific coatings. The scientific idea in our PVD laboratory is for particular physical and technological problems to find the best methods to fabricate the films and nanostructure with the demand structural and functional (luminescence or magnetic) properties. As an example see the combine systems for fabrication of the nanostructural fluoride thin films for optical applications in Fig. 1.

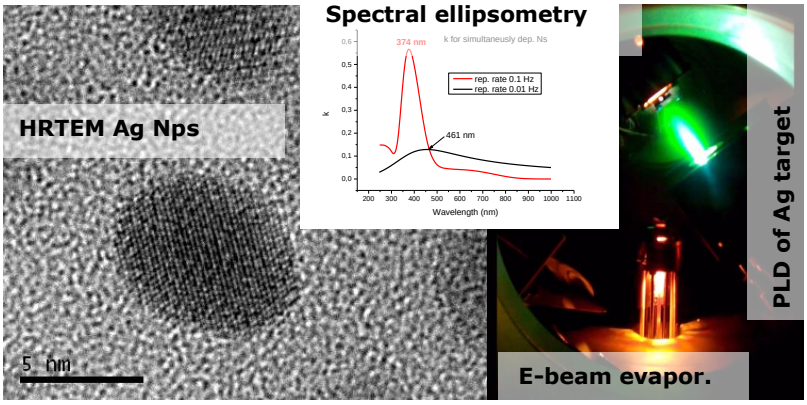


Fig.1 The figure of the deposition system combined e-beam evaporation (for fabrication of fluoride films) and pulsed laser depositon for nanometrically controlled doping by rare earth ions or metals nanoparticles. The sample was characterised by HRTEM and spectral elipsometry.

This method is schematically shown in Fig.2. The attention will be paid also to plasma characterisation and the examination of its influence to the film properties as well as for the application of different techniques suitable (e.g. spectral ellipsometry and reflectometry, real time electrical and transmission measurements) for in situ thin films characterisations.

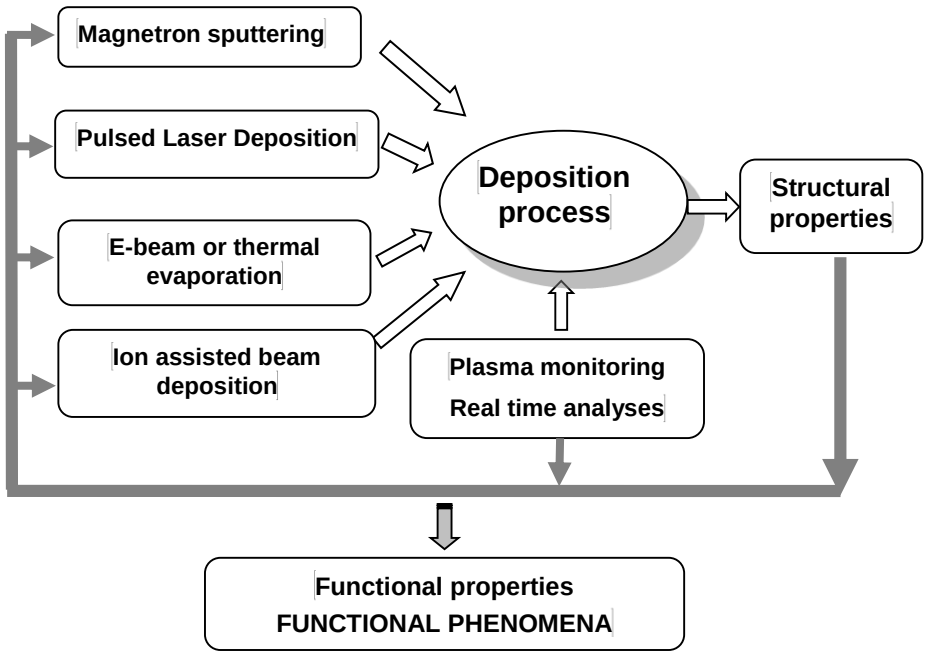


Fig. 2. Scheme of the advanced PVD systems for thin films and nanostructure fabrication

Plasma analyses.

The understanding the properties of plasma during the deposition process performed by magnetron sputtering is the first step to precisely control the deposition processes as well as thin films properties. Due to this we performed in the period 2010-2013 systematically study of the sputtering process of Aluminium and Silver target in different atmosphere. We focused on the plasma composition and energy analyses of the species carried out by ion mass spectroscopy. Our attention was focused on the examination of the negative ions [1,2] and influence of the energy distribution on the gas pressure, power and inert gas [1-3].

The magnetron sputtering deposition was used to fabricate aluminium doped zinc oxide which is very perspective technology and materials for a low cost and large surface area production of transparent conductive oxide for many applications. In this work we presented the detailed study of formation of negative ions during the deposition processes-Fig. 3. This knowledge is very important to understand the growth of thin films and for a correct control of their formation. It was found that intensities of negative ions exhibit maxima in the vicinity of transition between the metallic and transition mode of sputtering.

The research was completely performed in the team of plasma technologies and functional nanomaterials analyses.

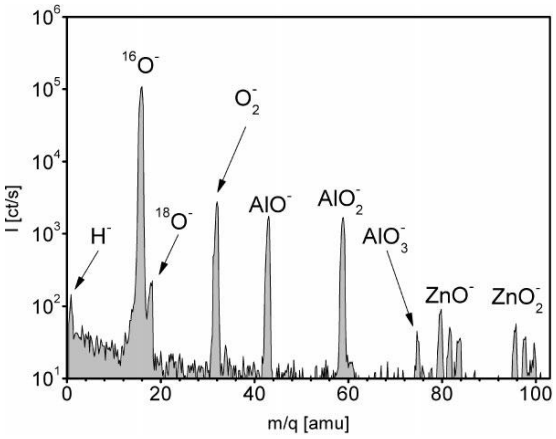


Fig. 3. Mass spectra of O^-, O_2^-, AlO^-, AlO_2^-, AlO_3^-, ZnO^-, and ZnO_2^- negative ions formed in magnetron discharge generated in oxide mode of sputtering

Ultrathin metallic films and Ag plasmons

Detailed study of the initial stage of growth of the thin metallic films was the next logical steps after the detailed examination of the deposition process performed by mass spectroscopy with the purpose to controll the growth mode.

We performed the detailed study by in-situ monitoring of electrical and optical properties of the grown aluminium layer. Simultaneously, the plasma characterization was carried out by means of the mass and optical emission spectroscopy. Optical constants of ultrathin Al film exhibit significant plasmonic behaviour in the UV range and a strong nonlinear character of I–V curves. Results of this study are presented in [4].

The nanostructure of the Ag layer is mainly influenced during the initial stage of the silver nucleation. Therefore, we focused our attention on studying of the initial stage of the nucleation and the layer growth by optical monitoring. The non-continual growth mode of the layer nucleation was clearly distinguished in the monitored data. We proofed, that the the nucleation mode and the resulting nanostructure can be significantly influenced by an ultra-thin silver oxide interlayer [5]. This research was completely done by the team 21 in cooperation with A. Lynnyková from department of optical and biophysical systems.

After the mastering of the deposition technology and in situ thin film monitoring we performed the fabrication of the plasmonic structures. This reasearch was carried out in collaboration with Institute de Optica, CSIC, Madrid Spain (laser patterning experiments) and K. Piksová from Czech Technical University (Scanning Electron Micrographs images of the nano-patterned samples).

Surface plasmon (SP) is the most outstanding property of numerous metals. It is a quasi-particle resulting from quantization of collective oscillation of conduction electrons excited by electromagnetic field of light at the metallic surface. Such possibility offers a great potential in development of new type of photonic devices and their application in sub-wavelength optics, data storage, light generation, microscopy, and bio-photonics. The Ag film is a best candidate for research of novel properties, such as artificial plasmonic response, synthetic magnetism at

terahertz frequencies, and negative refractive index. The strong resonance occurs in metallic nanoparticle (NP), where the oscillating electrons are confined within the nanoparticle's boundary. This phenomenon is denoted as localized surface plasmon resonance (LSPR). The effect is especially enhanced, when the size of the metallic nanoparticle is reduced to a few tens nanometers. The electron oscillations induce an electric field around the NP. This electric field is significantly stronger than that of the incident light one. *LSPR thus allows a possibility for amplification, concentration and manipulation of light at the nanoscale*. Nano-structured materials in form of nano-composite, where the metallic nano-particles are uniformly distributed in a dielectric matrix, represents new type of material with unique optical properties, which are quite different from those of the particular components.

The laser interferometry patterning represents advanced modification of the described method. Our ultrathin silver films were patterned by means of pulsed laser. The laser irradiation is done through phase masks forming parallel fringes-see Fig. 4. They are projected onto the samples by means of two lenses in a telescope configuration leading to a reduction of their period. This configuration can produce a periodic structure consisting of alternate areas containing NPs and continuous metal film with a period down to few micrometers. The resulting structure combines plasmonic and diffractive optical properties [6].

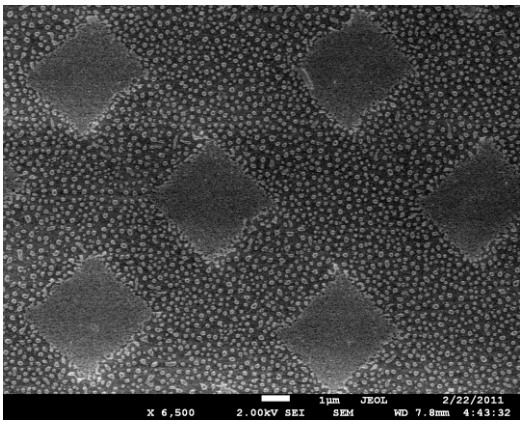


Fig. 4. SEM images of a pattern produced in the 10.8 nm Ag thick film. The square blocks represent the non annealed area surrounded by surface with Ag nanoparticles made by pulsed laser annealing.

Thin films:

After these experiments the fabrication of functional thin films for photovoltaic, chemical sensors, luminescence and materials research in ZnO were carried out.

Phthalocyanines

We have been investigating organic semiconductors based on phthalocyanine compounds for application in chemical gas sensors and photovoltaics. The research led to fabrication of functional chemical gas sensors based on sensitive layers of nanocomposite of organic substance (phthalocyanines, metallocenes) and metallic nanoparticles. Nanocomposite of phthalocyanines with silver nanoparticles were prepared either by means of magnetron sputtering on the top of the organic layer or the organic layer was grown on a substrate covered with metallic nanoparticles. The successful preparation of zinc phthalocyanine thin films using unconventional techniques such as pulsed laser deposition was demonstrated. Substituted - lanthanide phthalocyanines potential in modern optoelectronics and magnetoptics was experimentally and theoretically investigated and evaluated [7,8]. In this field our team performed the deposition experiments, measurements of electronics structures in MSB in Synchrotrone ELETTRA and ellipsometry characterisation. The sensors application and luminescence measurements were performed in collaboration with ILM in Lyon and Institute of Chemical Technology in Prague, respectively.

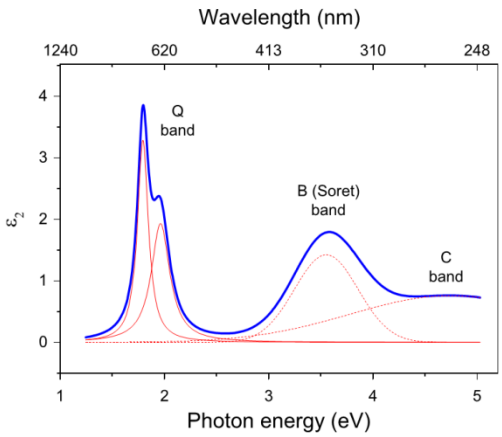


Fig. 5. Imaginary part ε_2 of dielectric function of zinc phthalocyanine thin film prepared by PLD

Fluoride thin films.

Fluoride materials occupy an original and strategic position in modern optics. The fluorides exhibit unique optical features associated with the presence of the rare-earth (RE) ions, which make them excellent candidate for variety of optoelectronics and photonics applications. We performed the deposition of Pr^{3+}-Eu^{2+} doped CaF_2 thin films by means of e-beam evaporation and we analyse the possibility of sensitizing the energy levels of Pr^{3+} ion with Eu^{2+}. This material is promising candidate for the achievement of efficient down-converter systems and could allow strong reduction of thermalization losses in silicon solar cells. The work was performed in cooperation with Institute Lumiere Matiere CNRS in Lyon in frame of bilateral Czech- French project. All deposition experimetns and structural analyses (crystallinity and morphology) were performed in laboratories and by researchers of team.

Zinc oxide

Doped and undoped ZnO films were prepared by pulsed laser deposition. We investigated the role of substrate (fused silica, sapphire, MgO, nanocrystalline diamond (NCD)) on the film growth and its properties [10]. It was found that the films deposited on NCD exhibit remarkably lower concentration of misfit dislocations. Hyrogen-loaded ZnO films were subjected to isochronal annealing in order to determine thermal stability of hydrogen absorbed in the lattice [11,12]. ZnO films doped by selected lanthanides were prepared to analyses energy transfer process between ZnO and lanthanide. Laser annealing of the films was performed that was monitored and controlled by developed insitu system based on optical properties measurement (photoluminescence). Electronic structure of Eu doped ZnO films analyzed by advanced XPS analyses using NanoESCA device confirmed mainly Eu^{3+} ionic state in agreement with photoluminescence results.

SAFMAT Laboratories

The goal of the SAFMAT project center was the development of research and development capabilities, including research infrastructure and human capital in the areas of nanotechnologies. In terms of types of research, the project is focused on:

1) *Analysis of surfaces in extremely clean vacuum conditions using the photoelectron spectroscopy method with the NanoESCA apparatus*
2) *Analysis of volume, study of subsurface centers and defects using paramagnetic (spin) resonance with pulse FT-EPR spectrometer*

The laboratories were open in the beginning of the 2012years and have been used by many teams within Institute of Physics mainly by Thin Films and Nanostructures, Optical Materials, Optical and biophysical systems.

NanoESCA laboratory:

NanoESCA is a new sophisticated analytical instrument designed for imaging and small spot photoemission spectroscopy (XPS) with photoemission electron microscopy (PEEM). Excitation sources range from a high-power monochromatic Al Kα(x-ray) source to UV sources such as He-, Mercury arc- and Deuterium lamps allow to work in three regimes: ●PEEM microscope, ● classical ESCA mode and ●2D imaging ESCA and PEEM modes. PEEM images a surface of a sample with lateral resolution <50 nm and with X-ray source better than 500 nm and energy resolution approx. 0.3 eV. The optical column provides 2D cuts of momentum distribution of photoexcited electrons (ARPES) with energy resolution approx. 0.1 eV and angle of acceptance better than ± 0.1 $Å^{-1}$.

Characterisation of $NaNbO_3$ crystals:

In cooperation with Department of optical and biophysical systems we performed the PEEM analyses of the $NaNbO_3$ (NNO) crystals. These results were presented in [13]

The PEEM analysis reveals regions of strong contrast on the surface of the NNO crystal at room temperature. The bright elongated regions show an inversion contrast at higher kinetic

energies working in the partial yield mode. due to the Ferroelectric (FE) polarization and in the corresponding domains. Our thermo-optical, Raman, and PEEM studies strongly suggest the existence of the FE phase in the NNO crystal at the temperatures up to 830 K
In this research M. Vondráček and J. Honolka performed the PEEM measurement s and interpretation of these results.

Silicene-silicite on Pt surface

This research was done in the collaboration with Department of Thin Films and Nanostructures. An important part of the paper [14] given bellow was done ion the SAFMAT laboratory, namely the mapping of the electronic structure of the clean Pt(111) surface and related changes after Si deposition. Fig 6 shows selected (a), (b) ARUPS **k**-space maps of clean Pt(111) and Si-(√19x√19)-**R**23**.**4°/Pt(111) surfaces at the Fermi level,(c), (d) DFT calculated band maps for the best-fit model and projected to higher Brillouin zones. The changes due to the Si deposition are given in the panel (e) Map of the first two BZ of the (1x1) (red) with the (√19x√19)-**R**23**.**4° (blue) Brillouin zones for one domain. Furthermore we mapped the electronic structure in the **k** -space at the Fermi level using ARUPS. The panel represents the electronic structure of the clean Pt(111)-(1**x**1)with a hexagonally-shaped **s** -like band crossing the Fermi level and weak features spreading from the center of the Brillouin zone (BZ). The band map of the Si (√19x√19)**R**23**.**4°/Pt phase does not change dramatically as shown in the panel b). However, there is a considerable suppression of the overall intensity and a visible change around the center of the BZ. A shape surrounding the point is discernible and intensity also grows on the inside of the main band vertices. In summary, the SRPES data implies a very similar chemical environment for all Si atoms and their strong hybridization with its Pt host. The STM in Fig.2c taken across the √19 and (1x1) shows the negligible height difference, indicating that Si atoms are most likely embedded in the Pt(111) surface. Most of the protrusions in the STM image can be assigned to the regular (1x1) lattice extrapolated from the clean Pt(111), except of the protrusions centered in the Si atom triplets in the used model that gives a value of 52 meV, which is comparable to the experimentally observed energy difference 90 meV of a two-component fit of the photoemission Si-2p doublet in the panel d). The XPS spectra were measured at MSB Czech beamline in synchrotrone ELETTRA in Trieste, Italy. On the operation of this beamline are involved the members of the team (M. Vondráček, J. Lančok)

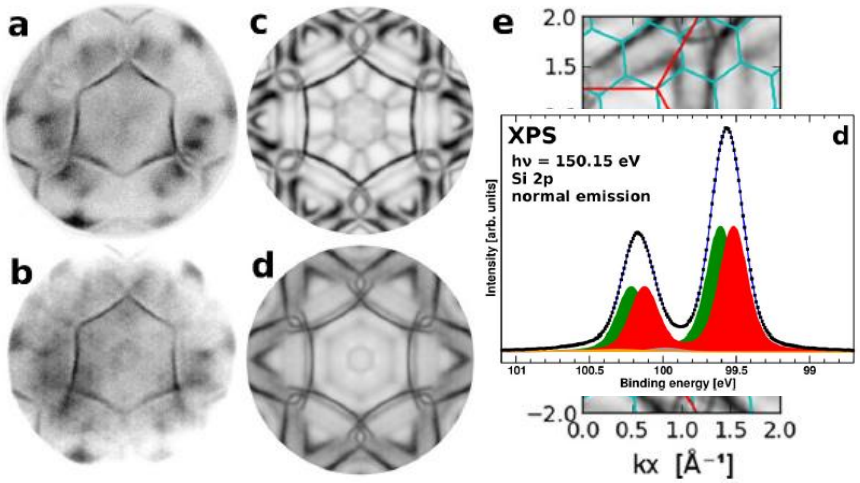


Fig.6. Angle-resolved photoemission **k**-space maps of (a) clean Pt(111) and (b) Si-(√19x√19)**R**23**.**4°/Pt(111) surfaces at the Fermi level. DFT-calculated band maps for the best-fit model at first (c) and higher (d) BZ (e) Map of the first two BZ of the (1x1) (red) with the Si-(√19x√19)**R**23**.**4° (blue) Brillouin zones. Panel (d) shows the photoemission doublet Si-2p fitted with two equivalent components supported the best-fit model.

EPR laboratory is equipped by spectrometer Bruker ELEXSYS E580, which is a top-class scientific device to measure electron paramagnetic (spin) resonance in both modes – classic (CW) and pulsed (FT), in the common X-band (9.4-9.8 GHz) as well as high-frequency Q-band (34 GHz). Flexibility of the system is achieved by modular architecture, which allows operation in CW mode or as a CW/FT system. In both frequency bands the spectrometer contains a system for measurements of ENDOR (electron-nuclear double resonance) and ELDOR (electron-electron double resonance). The Spectrometer operates in the 4 – 300 K temperature range. EPR method allows determining the structure, dynamics and space distribution of paramagnetic particles at atomic level. One can analyse solid state matter, soft materials (e.g. gels), liquids and bio samples. The technique is suitable for investigation of the effect of the structure on functional properties of materials. The typical example of this technique usage is the investigation of structure defects in semiconductors and multifunctional materials (e.g. scintillators, ferroelectric and piezoelectric materials or ferroelectrics), the identification of different gels of adsorbed molecules on surfaces (e.g. implants) etc.

Research in cooperation with Department of Optical materials

Some part of the work in EPR laboratory was carried out by the researcher from Department of Optics. In collaboration, D. Savchenko participated on the EPR measurements in the study of paramagnetic impurities and lattice defects in scintillation and phosphor materials such as Y_2SiO_5, Lu_2SiO_5, $PbWO_4$ [15]. In particular, the processes of hole and electron trapping were studied in Y_2SiO_5 and Lu_2SiO_5 crystals by the advanced pulse EPR technique. It was shown, for the first time, that both holes and electrons are preferably trapped at Si-unbound oxygen sites and their vacancies, respectively, pointing to critical importance of the Si-unbound oxygen in the processes of charge capture in these practically important scintillation crystals widely used for the fast detection of gamma rays in medical applications. The rest results from this laboratory will be presented by team of Optical materials.

Research of our team in cooperation with team Optical and biophysical systems (19)

Fluoride crystals

Lithium fluoride (LiF) play an important role among the alkali halide crystals because it possesses the best physical and optical qualities. The application of LiF in the field of optical data storage and radiation dosimetry have recently attracted renewed attention. The energy levels of the lithium vacancy associated Ni^{2+}-V_{Li} centers in LiF constitute a three-level system and it occurs that this system provide the necessary transitions between the non-Kramers conjugated levels in zero magnetic field. The inversion recovery technique with electron-spin echo (ESE) detection was used in order to study the non-resonant cross-relaxation of Ni^{2+}-V_{Li} with a faster relaxor - the exchange-coupled clusters of Ni^{2+} ions. Analysis of the results has revealed a very high relaxation rate in non-Kramers doublet of LiF: Ni^{2+}. The spectral diffusion process caused by the spin-excitation transfer between spins with non-resonant frequency is observed at low temperature range of 5-15 K [16].

The whole experimental work was performed by D. Azamat with assistance of J. Lančok. The interpretation of the results was done in cooperation with team 19 and with the help of Dr. Andrey G. Badalyan (Ioffe Institute, Russia).

Ferroelectric crystals doped by metals

This work is motivated by the recent observation of current-induced bistable resistance effects on metal-insulator-metal (MIM) structures based on transition metal-doped $SrTiO_3$. This system has become a focus of interest in an attempt to produce nonvolatile memory devices. We obtained a new data on the axial and low-symmetry chromium impurity centers in $SrTiO_3$ crystals. It was shown that the charge compensation of the Cr^{3+}-V_O dominant centers in octahedral environment occurs by the remote defects (such as oxygen vacancies) located at the axial center axis. The electron spin echo technique has been used to measure the spin lattice relaxation time T_1 of the Cr^{3+} impurities in $SrTiO_3$. The results of fitting the temperature

variation of T_1 confirm that the dominant contribution is related to the spin-phonon relaxation time arising from the low-lying local vibrational mode [17]. In cooperation with team 19 the study of Er doped $SrTiO_3$ crystals studied by CW EPR revealed the rhombic symmetry of Er^{3+} impurity centers and it was suggested that Er ions substitute Sr ions in A-sublattice sites [18].

SiC and carbon based materials.

This research is based on the detailed EPR study of the materials carried out by D, Savchenko in cooperation with Institute of Semiconductors Physics in Kiev and Leipzig University.

The EPR measurements of silica-carbon (SiO_2:C) nanocomposites (CS) were performed with the aim to clarify the structural characteristics of the CS and their transformation under chemical treatments. The temperature behavior of the EPR spectra from C-related defect at 200 – 440 K was explained by the presence of the C nanodots at the surface of SiO_2 nanoparticles and the ejection of electrons from the confinement energy levels of C quantum dots when the temperature becomes comparable to the confinement energy [19].

Detailed EPR study was done on amorphous silicon carbonitride (*a*-SiC_xN_y) thin films. It was revealed three EPR signals: one signal is attributed to the carbon-dangling bonds (CDB) and two others are attributed to the interface defects which may appear due to the formation of the oxidized Si on the film surface. From the analysis of temperature dependence of the CDB EPR spectra it was concluded that antiferromagnetic ordering occurs in the CDB spin system [20].

Study of organics molecules and biomaterials

In relation to the project FUNBIO and development of new interdisciplinary research the aateention was focused also to analyses of organic molecules and biomaterials. The EPR spectra are sensitive to minor changes in the arrangement of lipid chains and were used to study lipid peroxidation. In collaboration with J. Heyrovský Institute of Physical Chemistry AS CR and Institute of Biochemistry University of Technology in Graz, we measured the EPR spectra of three differently localised nitroxide bases with spin (doxyl radicals). The studied the membrane bilayers consisting of 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPC) where 5 to 10% of POPC molecules were replaced by 1-palmitoyl-2-glutaryl-sn-glycero-3-phosphocholine (PGPC), with oleoyl residue replaced by truncated carbon chain terminated with a carboxylic acid has been done by CW EPR method in our EPR laboratory. From EPR spectra analysis, we have obtained the order parameter (S) as a function of cholesterol content for three differently located nitroxide-based spin labels (doxyl radicals): 5-, 10-, and 16-doxyl PCs in pure POPC/chol membranes and in membranes with 10% of POPC replaced by PGPC. Changes in the S parameter were attributed to increased order of the central part of the oxidized membrane at higher cholesterol level and vice versa in the inner part of the leaflet and most probably the ordering effect is accompanied with decreased mobility [21]. This research was done in collaboration with Department of Optical and biophysical systems.

FUNBIO

The new important project FUNBIO was successfully built from December 2013 to October 2014 The main meaning of this project under leadership of Ján Lančok was to create a unique biophysical workplace, in which to provide a new space for comprehensive cooperation in the fields of physics, chemistry, biology, and medicine, and which will also serve as an excellence research center for university students. FUNBIO, with its focus, is directly linked to the SAFMAT project, and it is synergistic with it in the field of methods. In frame of this project the 4 following new laboratories were equipped:

1) **Scanning electron microscope (**SEM) Tescan FERA3 with xenon plasma focused ion beam for nanomanipulation and materials' study. The apparatus allows the atomic concentration analysis, the crystal lattice orientation study and observation in nitrogen atmosphere.

2) **AFM for biological application** equipped with Modern atomic force microscope (AFM) Bruker ICON for the organic materials surfaces studies with glove-box for atmosphere and temperature control. The apparatus will be exploited for example in examination of channel opening in the cell membranes interacting with nanocrystals and organomolecules.
3) **Infrared spectral ellipsometer** IR-VASE for nondestructive measurements of optical properties of organic and anorganic coatings. Such experiments allow investigation of optical constants and thickness of coatings as well as their physical properties such as electrical resistivity, concentration of free carriers of charge, phonon structure, etc.
4) **Optical lithography** for microstructured magnetic materials preparation, which will be used in new cancer medicaments development.

Because these laboratories were established only in 2014 we received only few results up to now. Nevertheless some interesting information about this project could be found at: (http://www.fzu.cz/en/funbio-project).

References

1. Pokorný, Petr ; Bulíř, Jiří ; Lančok, Ján ; Musil, Jindřich ; Novotný, Michal. Generation of positive and negative oxygen ions in magnetron discharge during reactive sputtering of alumina. Plasma Processes and Polymers 2010, vol. 7, č. 11, s. 910-914.
2. Pokorný, Petr ; Mišina, Martin ; Bulíř, Jiří ; Lančok, Ján ; Fitl, Přemysl ; Musil, Jindřich ; Novotný, Michal. Investigation of the negative ions in Ar/O2 plasma of magnetron sputtering discharge with Al:Zn target by ion mass spectrometry. Plasma Processes and Polymers 2011, vol. 8, č. 5, s. 459-464
3. Pokorný Petr,; Novotný, Michal ; Musil, Jindřich ; Fitl, Přemysl ; Bulíř, Jiří ; Lančok, Mass spectrometric characterizations of ions generated in RF magnetron discharges during sputtering of silver in Ne, Ar, Kr and Xe gases Plasma Processes and Polymers 2013, vol 10, č. 7, s. 593-602.
4. Novotný, Michal ; Bulíř, Jiří ; Lančok, Ján ; Pokorný, Petr ; Bodnár, Michal. In-situ monitoring of the growth of nanostructured aluminum thin film. Journal of Nanophotonics 2011, vol. 5, "051503-1"-"051503-10".
5. Bulíř, Jiří ; Novotný, Michal ; Lynnyková, Anna ; Lančok, Ján. Preparation of nanostructured ultrathin silver layer. Journal of Nanophotonics 2011, vol. 5,"051511-1"-"051511-10"
6. Peláez, R.J. ; Afonso, C.N. ; Bulíř, J.; Novotný, M.; Lančok, J.; Piksová, K. 2D plasmonic and diffractive structures with sharp features by UV laser patterning. Nanotechnology 2013, vol. 24,"095301-1"-"095301-7"
7. Novotný M., Bulíř J., Bensalah-Ledoux, A., Guy S., Fitl P., Vrňata M., Lančok J., Moine B.: Optical properties of zinc phthalocyanine thin films prepared by pulsed laser deposition, Applied Physics A: Materials Science and Processing, 117, (2014), 377-381
8. Fitl P.,Vrňata M., Kopecký D., Vlček J., Škodová J., Bulíř J., Novotný M., Pokorný P.: Laser deposition of sulfonated phthalocyanines for gas sensor, Applied Surface Science 302, 37–41, (2014)
9. Guille, A. ; Pereira, A. ; Bensalah-Ledoux, A. ; Moine, B. ; Novotný, Michal ; Bulíř, Jiří ; Fitl, Přemysl ; Lančok, Ján. Sensitization of Pr^{3+} ions by Eu^{2+} ions in CaF_2 thin films deposited by evaporation. Journal of Applied Physics 2013, vol.114,203509-1
10. Novotný M., Čížek J., Kužel R., Bulíř J., Lančok J., Connolly J., McCarthy E., Krishnamurthy S., Mosnier J-P., Anwand W., Brauer G.: Structural characterization of ZnO thin films grown on various substrates by pulsed laser deposition, *Journal of Physics D: Applied Physics, 45, (2012), 225101*
11. Melikhova O., Čížek J., Lukáč F., Vlček M., Novotný M., Bulíř J., Lančok J., Connolly J., McCarthy E., Krishnamurthy S., Mosnier J-P., Anwand W., Brauer G.: Hydrogen absorption in thin ZnO films prepared by pulsed laser deposition, *Journal of Alloys and Compounds, 580, (2013), S40–S43*
12. Kužel R., Čížek J., Novotný M.: On X-Ray Diffraction Study of Microstructure of ZnO Thin Nanocrystalline Films with Strong Preferred Grain Orientation, *Metallurgical and Materials Transactions A, 44, (2013), 45-57*
13. M. Tyunina, A. Dejneka, D. Rytz, I. Gregora, F. Borodavka, M. Vondráček, and J. Honolka, J. Phys.: Condens. Matter **26**, 125901 (2014)

14. *Švec, Martin ; Hapala, Prokop ; Ondráček, Martin ; Merino, P. ; Blanco-Rey, M. ; Mutombo, Pingo ; Vondráček, Martin ; Polyak, Yaroslav ; Cháb, Vladimír ; Martín Gago, J.A. ; Jelínek, Pavel. Silicene versus two-dimensional ordered silicide: atomic and electronic structure of Si-(√19×√19)R23.4°/Pt(111). Physical Review. B 2014, vol. 89, "201412-1"-"201412-5".*
15. V.V. Laguta, M. Buryi, J. Rosa, D. Savchenko, J. Hybler, M. Nikl, S. Zazubovich, T. Kärner, C.R. Stanek, K.J. McClellan *Electron and hole traps in yttrium orthosilicate single crystals: The critical role of Si-unbound oxygen*/ Physical Review B, Vol. **90**, P. 064104-1-064104-12 (2014).
16. Azamat, Dmitry ; Badalyan, A. G. ; Dejneka, Alexandr ; Jastrabík, Lubomír ; Lančok, Ján. Electron spin-lattice relaxation of low-symmetry Ni^{2+} centers in LiF. Applied Physics Letters 2014, vol. 104, "252902-1"-"252902-4
17. Azamat, Dmitry ; Dejneka, Alexandr ; Lančok, Ján ; Trepakov, Vladimír ; Jastrabík, Lubomír ; Badalyan, A. G. Pulse-electron paramagnetic resonance of Cr^{3+} centers in $SrTiO_3$ Journal of Applied Physics 2013, vol. 113, "174106-1-174106-6“
18. A. Skvortsov, **D. Savchenko**, Z. Potucek, L. Jastrabik, V. Trepakov, A. Dejneka *Optical and EPR characterization of Er^{3+} centers in $SrTiO_3$ single crystals* / **Physica Status Solidi (b)**, Vol. **251**, P. 2270-2273 (2014).
19. Savchenko, Dariia ; Shanina, B.D. ; Kalabukhova, E.N. ; Sitnikov, A.A. ; Lysenko, V.S. ; Tertykh, V.A. Electron paramagnetic resonance study of paramagnetic centers in carbon-fumed silica adsorbent. Journal of Applied Physics 2014, vol.115, "133704-1"-"133704-7"
20. D. Savchenko, V. Kulikovsky, V. Vorlíček, J. Lančok, V. Kiselov, E. Kalabukhova, *Optical and magnetic resonance study of a-SiC_xN_y films obtained by magnetron sputtering*, Physica Status Solidi (b), vol. 251, P. 1178-1185 (2014).
21. M. Štefl, R. Šachl, A. Olzyńska, M. Amaro, D. Savchenko, A. Dejneka, A. Hermetter, L. Cwiklik, J. Humpolíčková, M. Hof *Comprehensive Portrait of Cholesterol Containing Oxidized Membrane*, BBA – Biomembranes, Vol. 1838, P. 1769-1776 (2014).

Research Report of the team in the period 2010–2014

Institute	Institute of Physics of the CAS, v. v. i.

Scientific team	Classical and quantum optics

The team is formed by the employees of the Institute of Physics within the Joint Laboratory of Optics of Palacký University and Institute of Physics AS CR (jointlab.upol.cz, division 38 of the Institute of Physics AS CR). The Joint Laboratory of Optics (established in 1984) is an institute focused on fundamental and applied research in the areas of classical and quantum optics, laser physics and material sciences and it is jointly funded by both founding parties. Some members of the team have only part-time jobs with the Institute of Physics, the other part of their working capacity being covered by Palacky University. In such cases the respective workers affiliate their output alternately to Palacky University and to Institute of Physics. In this report, only results affiliated to Institute of Physics are quoted and remarks related to the Palacky University are noted only where necessary. The portion of the Joint Laboratory of Optics belonging to Palacky University has become a division of the Regional Centre of Advanced Technologies and Materials (www.rcptm.com) since 2010.

The team has currently 35 workers (including 19 research workers, excluding support staff) and is lead by Ondřej Haderka (the main author of this report). As of December 31, 2014, there were 6 Ph.D. students in the team. The results of the team can be divided by main research topics to four topical subgroups that will be treated in detail as follows. The subgroups are not equal in manpower and there is substantial personal overlap among them.

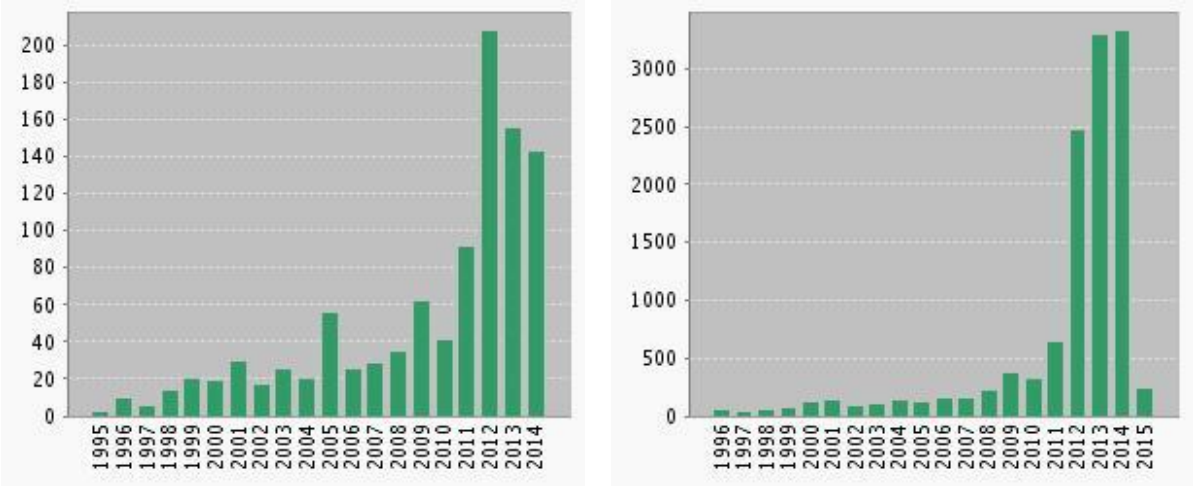


Figure 1: Total number of publications (left) and number of citations (right) of the Joint Laboratory Optics in the period 1995-2014 according to Thomson Reuters Web of Science (to March 13, 2015). The total h-index of the Joint Laboratory of Optics is 45. These graphs include to output of the workplace as a whole, i.e. including its Palacky University part. The large increase in the number of publications in 2011-14 is partly caused by the participation in the CERN-ATLAS Collaboration that is realized mainly in the Palacky University part of the workplace. To document that the output of the workplace has well growing

trend regardless of this effect we show the Web of Science numbers without the large international collaborations in the next Figure.

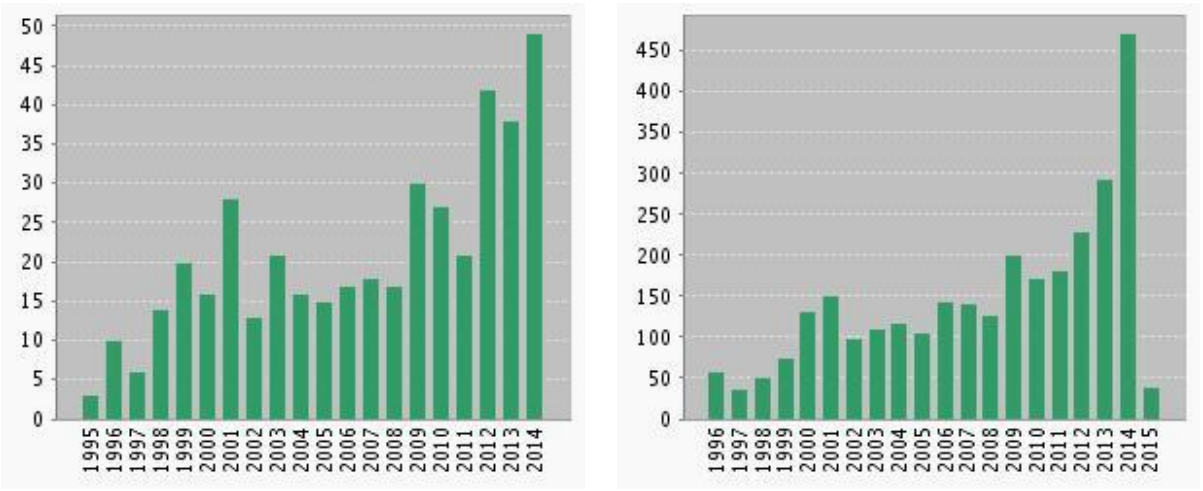


Figure 2: Number of publications (left) and number of citations (right) of the Joint Laboratory Optics in the period 1995-2014 according to Thomson Reuters Web of Science (to March 13, 2015) exluding the output belonging to large international scientific collaborations (CERN-ATLAS, Pierre Auger Observatory). The plots include the output of both the Palacky University and the Institute of Physics parts of the workplace, nevertheless, to large majority of the results workers affiliating to both parts affiliated (h-index 26).

A. Quantum and nonlinear optics

In the area of quantum and nonlinear optics, mainly the topics related to generation, transmission, detection and quantum processing of information are treated, using the fields of photon pairs obtained parametric downconversion as the main tool.

Several proposals of novel sources of photon pairs based on various photonic structures have been published, including randomly poled nonlinear crystals (Opt. Express 2010, 18, 27130), Bragg reflection waveguides (Opt. Express 2011, 19, 3115), ring-fibers (Opt. Express 2014, 22, 23743), or metal-dielectric structures (Phys. Rev. A 2014, 90, 043844). Such sources offer substantial advantages over traditional sources based on bulk nonlinear crystals, usable, e.g., in future metrological and quantum-information schemes. Besides higher compactness and better intensity-to-volume ratio, they may yield paired fields with extremely broad spectra, highly-dimensional entanglement, or pairs entangled in multiple quantities including orbital angular momentum. Some of the proposed sources have been experimentally constructed and tested. In this area works have been done in close cooperation with the Institute of Photonic Sciences, ICFO, Barcelona, Spain.

In the area of quantum information processing, main effort has been exerted on design and construction of elements for manipulation of quantum states based on linear optics. These include controlled phase gate (Phys. Rev. Lett. 2011, 106, 013602), entangling efficiency of quantum gates (Phys. Rev. A 2012, 86, 032321), cloning of quantum bits (Phys. Rev. A 2012, 85, 050307) and cloning-based eavesdropping on quantum channels (Phys. Rev. Lett. 2013, 110, 173601), quantum routing (Phys. Rev. A 2013, 87, 062333) and amplification of quantum bits (Phys. Rev. A 2013, 87, 012327). The effects of the environment on the transmission of quantum states have also been investigated (Phys. Rev. A 2012, 85, 063807). Most of these schemes have been experimentally realized in our laboratories. They may constitute elements of future quantum communication networks.

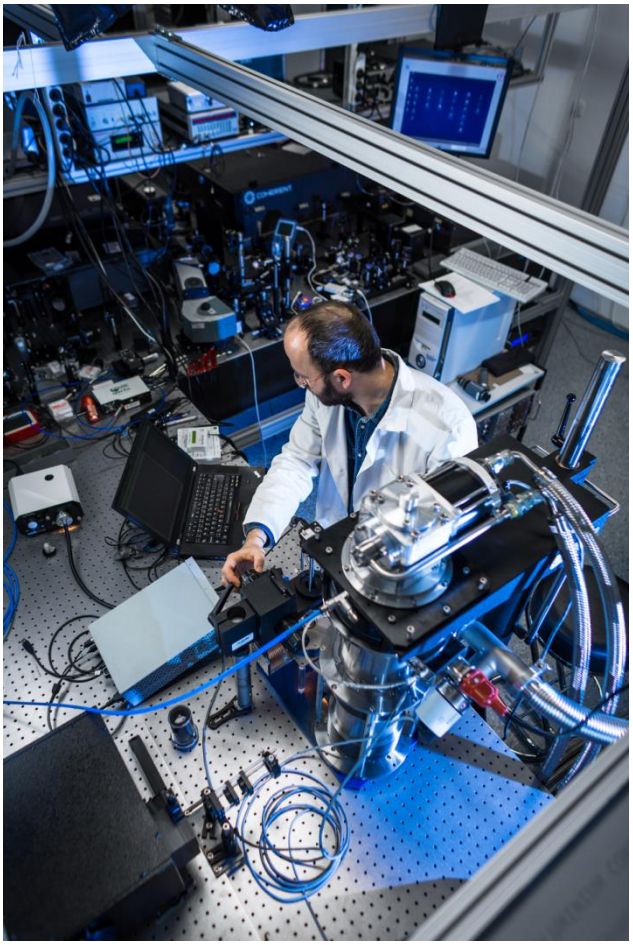


Figure 3: Laboratory of quantum and nonlinear optics.

In the area of detection, approaches employing intensified CCD cameras have been developed to gain a general tool for investigation of photon-number, spatial and spectral correlations in the fields of photons pairs. These were used to investigate in detail the correlations of twin-photons from the process of parametric downconversion both at the single-photon level (Phys. Rev. A 2010, 81, 043827, Phys. Rev. A 2012, 85, 023816) and at the level of strong fields (Opt. Express 2014, 22, 13374). Using the photon-number entanglement, a method for calibration of quantum detection efficiency without the need of any radiation standard has been developed (Opt. Lett. 2012, 37, 2475) and later extended to detectors with analog output (Appl. Phys. Lett. 2014, 104, 041113) and to obtain the whole spectral calibration curve (J. Opt. Soc. Am. B 2014, 31, B1-B7). Efficient preparation of nonclassical states of light

by postselection from photon pairs has also been presented (Opt. Express 2013, 21, 19387, Phys. Rev. A 2013, 88, 062304). Some of these works have been performed in cooperation with University of Insubria, Como, Italy.

In total, 36 publications in journals with impact factor have been published within the subgroup in 2010-2014.

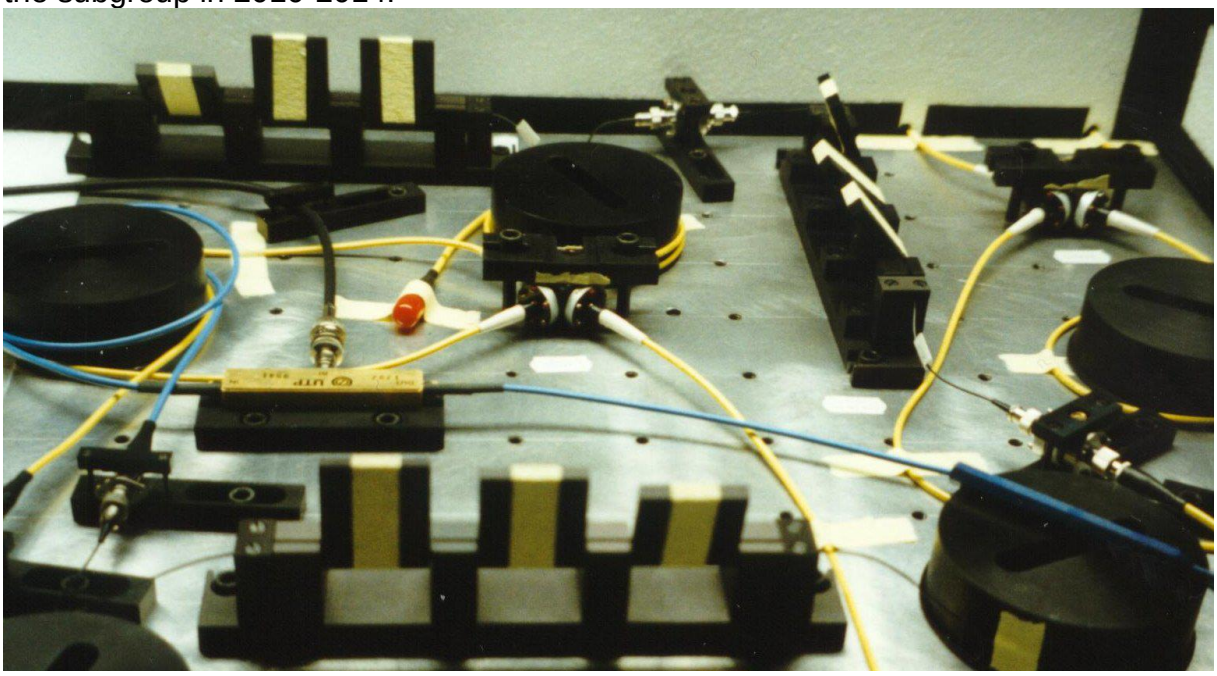


Figure 4: Fiber optical interferometer in the laboratory of quantum and nponlinear optics serves as a basis for many experimental arrangements in teh area of quantum information processing.

B. Applied optics

This subgroup deals for a long time with advanced approaches and applications focused on various areas of applied and technical optics and optoelectronics. The main focus has been on proposals, analyses, designs and production of non-standard optical elements and systems (both imaging and non-imaging), e.g., optical systems of fluorescent detectors determined for cosmic rays research, optical borescopes for visualization and analysis of burning processes in cement, steel and glass furnaces, electric power-station boilers, or as a control and guidance system of primary circle in nuclear power stations and so on. Optical technologies (innovation of classical technologies for processing of hard and very hard materials, especially of glass) – rough and fine grinding, polishing, novel approach to surface glass processing using the subaperture method have been developed and employed. Related development has been performed in the area of optical layers and the methods of their analysis.

Figure 5: L. Nožka examines one of the mirror segments produced for the fluorescence telescope at the Pierre Auger Observatory.

The ability to manufacture ultra-lightweight mirror surfaces of large dimensions is a group specialty employed for instance in the Pierre Auger Observatory (PAO) located in Argentina (see, e.g., Nucl. Instrum. Meth. Phys. Res. Sec. A 2010, 620, 227). The success of PAO resulted in involvement in the international collaboration CTA – Cherenkov Telescope Array – where the subgroup develops measurement systems and methods for quality evaluation of production and service wear of mirror samples, supplied by different potential producers and intended for using in optical telescopes as detectors of cosmic rays (Astropart. Phys. 2013, 43, 3). Since both these projects rely on observation of secondary phenomena in the atmosphere, the fluorescence properties of the atmosphere have been of particular interest (Astropart. Phys. 2013, 42, 90). The need for long-time observation of the cloud-coverage and optical background of the night sky resulted in the design and construction of a specialized autonomous all-sky camera. The cameras have been in the possible locations of CTA observatories (four cameras are already installed in the USA and Argentina, one in Chile, Namibia, Canary Islands and Mexico), and are also included in Pierre Auger Observatory in Argentina as a part of observatory control system.

The subgroup contributes also to other tasks applicable in the industry (e.g., device controlling in real-time color markings of coil springs produced at production line for automotive industry, or research and optimization of optical systems for yarn quality management during its production).

The involvement of the team in Pierre Auger and CTA collaborations resulted in contribution to more than 40 publications in Web-of-Science-registered journals. In these collaborations, the team closely cooperates with the team No. 1 (“Astroparticle physics”). While our team focuses on tasks related to applied optics, optical systems and technologies, team No. 1 concentrates on data processing and astro-particle

physics. Both teams are involved in the daily operation of the Pierre Auger Observatory.

C. Statistical and wave optics

The subgroup members are engaged in the questions concerning wave optics and development and applications of measurement methods based on the principles of wave and statistical optics. The theoretical results are focused on the advancements of complex theory of statistical properties of optical speckle fields, moreover, there was implemented a self-developed numerical model (Sci. World J. 2014, 704368) simulating the generation and propagation of speckle fields for diverse variants of general deformation tensor dealing with object surface (the shift of the object as a solid body, 3D translation, rotation and elastic deformation). Simultaneously, the proposed approach was verified experimentally with a good agreement, including the determination of design methods for actual experimental arrangements or applications, boundary usage conditions, and their accuracy and sensitivity.

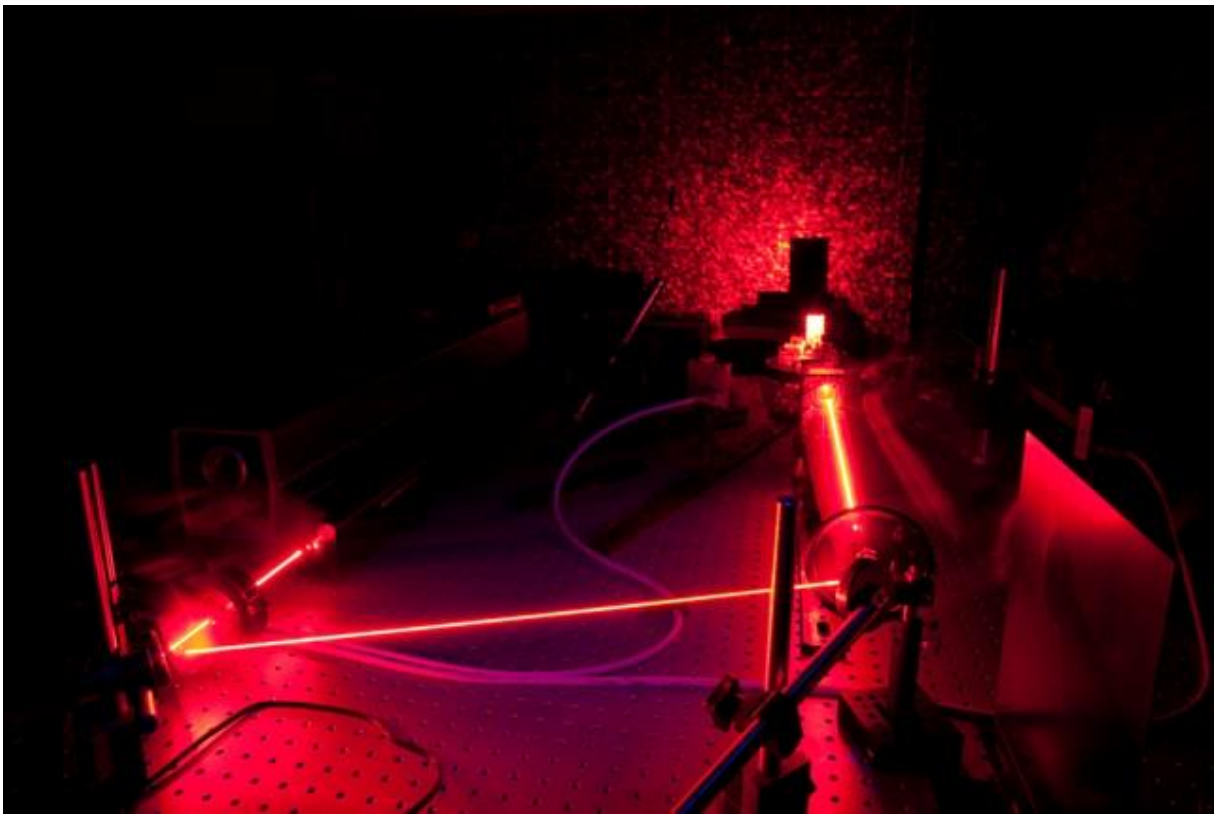


Figure 6: Speckle interferometry setup gor measuremnt of object movement and deformations.

Problems and characteristics of various applications of electronic speckle pattern interferometry (ESPI) methods were studied, for instance an efficient evaluation of high-noise correlograms (Meas. Sci. Rev. 2014, 14, 177). The white-light interferometric methods were also examined, explored and applied as 3D sensors with high information potential.

The subgroup published 5 works in journals with impact factor during 2010-14.

D. Properties of materials and laser technologies

The work done by the subgroup was focused primarily on the experimental analysis of mechanical and tribological properties at small scales using the state of the art equipment and methods. In most cases the work was driven by both the scientific curiosity and the technological interest. Various types of materials were tested including thin films and coatings (ceramics, metals, nanocomposites) (Surf. Coat. Technol. 2011, 205, 3372, Surf. Coat. Technol. 2011, 205, 4052, Surf. Coat. Technol. 2012, 206, 3580), plasma sprayed coatings (Ceramics Int. 2010, 36, 2155), single crystals (Appl. Phys. Lett. 2014, 105, 082906) and other bulks. Depth sensing nanoindentation and scratch tests were performed at room temperature and at elevated temperatures up to 500 °C. It should be noted that this subgroup is the only one in the Czech Republic experienced in the high temperature measurements at nano/micro scale and belongs to a limited number of groups worldwide capable to explore nanomechanical properties at elevated temperatures. In case of thin films and plasma sprayed coatings the mechanical characteristics were correlated with the structure and with the parameters of the deposition process providing a comprehensive description of the studied material. Besides, the temperature stability of the films' structure and mechanical properties was explored. Especially the potential of hard SiCN (Surf. Coat. Technol. 2014, 240, 76) and superhard B4C films were systematically studied. The research works dealing with thin films and coatings were mainly performed under the cooperation with the Institute for Problems of Materials Science, Academy of Sciences of Ukraine. In cooperation with the Virginia Polytechnic Institute and State University, a modified nonisothermal nanoindentation method was developed to directly detect the negative stiffness of ferroelectric material at its Curie point and to quantify the negative stiffness without the need for embedding it into a matrix. The feasibility of this in-situ method was demonstrated on the triglycine sulfate single crystal.

In the area of laser technologies, the overlap welding of thin stainless steel sheets was performed by means of the pulsed Nd:YAG laser system with variable laser parameters, that influence was investigated on the samples cross-sections by laser scanning microscopy. Numerical model of the pulsed welding was created by software SYSWELD with the goal to estimate the amount of the absorbed energy (Metallurg. Mater. Trans. B 2010, 41, 1108; Metallurg. Mater. Trans. B 2014, 45, 1116). The possibility of the on-line monitoring of the welding process was investigated both on our own Nd:YAG pulsed laser system and on industrial continual CO2 laser in LAMBRO 92 a.s. facility. UV – spectrometer or UV – photodiode data were collected and evaluated by the developed software LWM – Laser welding monitor (J. Mater Eng. Perf. 2012, 21, 764). Numerical model of the overlapped laser surface melting was created to demonstrate the influence of delay between the following spot application, spot axis stand-off and the processing speed on the resulting microstructure in the remelted region. Real samples were processed on high power diode laser in MATEX PM Facility in Plzeň and surface modification was evaluated by contact stylus profilometry. Besides these main tasks, laser liquid-assisted scribing of silicon, indirect backside glass marking, and laser interaction with nano-particles were performed. Also the research of propagation and shaping of extremely powerful light beams (in collaboration with ELI project and industrial environment) has been pursued.

The subgroup published 13 papers in journals with impact factor during 2010-2014.

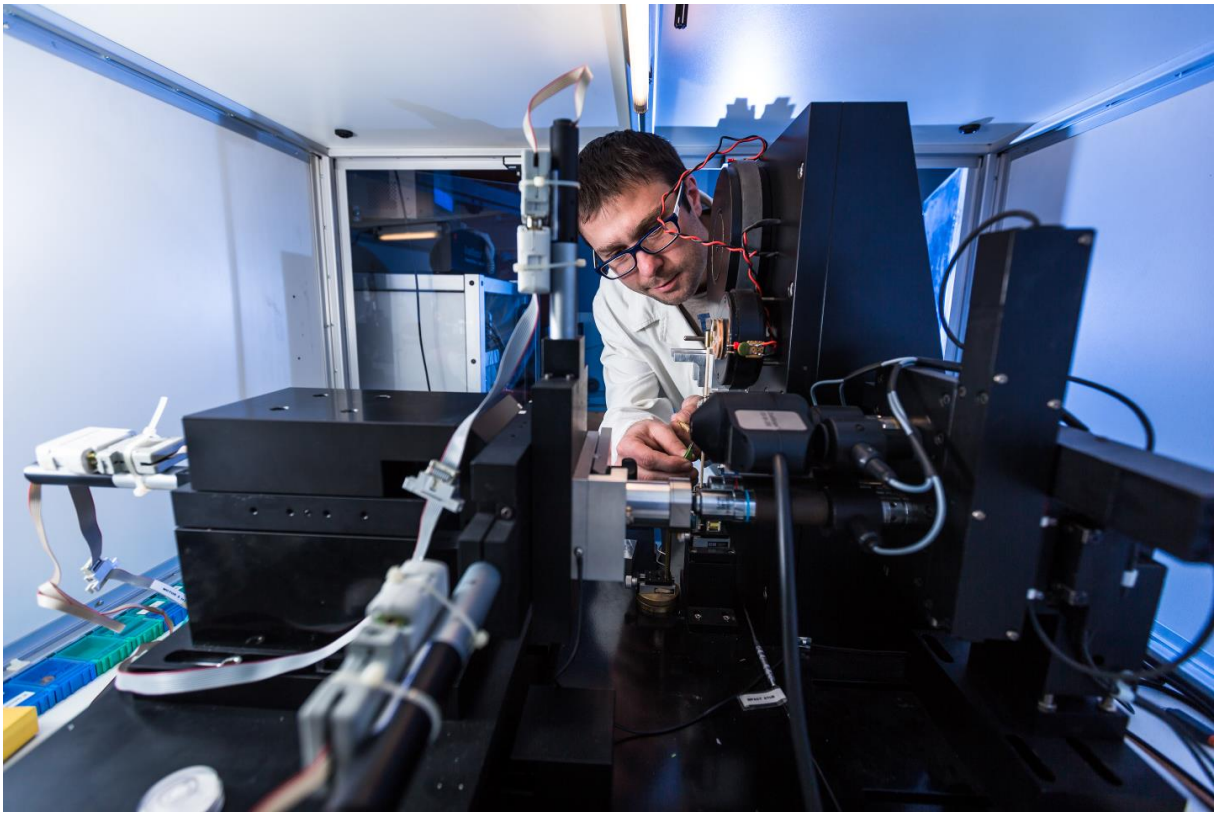


Figure 7: R. Čtvrtlík works with the nanoindentor to investigate mechanical properties of thin layers.

A number of grant projects have been solved in the evaluated period, a short list follows [title, code, provider (period), main (co-)investigator on behalf of the evaluated team]:

- Participation at the Pierre Auger Observatory, INGO LA08016, Ministry of Education, Youth and Sports of the Czech Republic (2008-2012), P. Schovánek.
- Research Centre – Optical structures, detection systems and related technologies for low-photon applications, 1M06002, Ministry of Education, Youth and Sports of the Czech Republic (2006-2011), O. Haderka.
- Generation and characterization of entangled photon pairs in modern nonlinear structures, IAA100100713, Grant Agency of the Academy of Sciences of the Czech Republic (2007-2011), J. Soubusta.
- Nanostructural macroscopic systems – technology of preparation and characterization, KAN301370701, Grant Agency of the Academy of Sciences of the Czech Republic (2007-2011), M. Hrabovský.
- Modern multilayer optical systems, TA01010517, Technological Agency of the Czech Republic (2011-2014), M. Hrabovský.
- Suppression of quantum noise using entanglement of photon pairs, P205/12/0382, Czech Science Foundation (2012-2016), O. Haderka.
- Czech participation at the Pierre Auger Observatory, INGO II LG13007, Ministry of Education, Youth and Sports of the Czech Republic (2013-2015), M. Hrabovský.
- Ensuring the Czech participation in CTA project, EUPRO II LE13012, Ministry of Education, Youth and Sports of the Czech Republic (2013-2015), M. Hrabovský.
- Optical 3D sensors with high information efficiency, Czech Science Foundation (2013-2015), P. Pavlíček.

- Systems of acoustic emission for characterization of mechanical properties and stability of thin layer structures and functional surfaces, TA03010743, Technological Agency of the Czech Republic (2013-2016), M. Hrabovský.