Teze disertace

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Magnetically Induced Reorientation

New physical effect providing giant magnetic-field-induced strain

Komise pro obhajoby doktorských disertací v oboru

Fyzika kondenzovaných systémů

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Acknowledgment: The results presented in this dissertation are outcomes of research I have done or led in various research sites (Helsinki University of Technology now Aalto University, Helsinki, Finland, IFW Dresden, Germany and finally in FZU-Institute of Physics CAS from 2008) for the last 25 years. I would like to thank especially to the former head of the research group and my supervisor Kari Ullakko at HUT, who introduced me to the field of magnetic shape memory. During the course of my research, I worked and collaborated with many colleagues, PhD and Master students and skilful technicians. I cannot list all here individually but I hope that all are well appreciated in the paper published, either as authors or in acknowledgement.

I experimentally measured and independently evaluated magnetic and (magneto-)elastic behaviour of magnetic shape memory materials mainly till 2006. Since then I led small group of students and postdoc. Although continuing and loving laboratory work till now, the main part of experimental labour is now on my younger colleagues. Currently, I mostly manage and lead the research, collect all the results and interpret them, and writing papers, and securing funding.

My work could not be imagined without international cooperation and discussions. I benefited from a fruitful collaboration with various research groups particularly with Kari Ullakko, A. Sozinov, and S.P. Hannula int Helsinki University of Technology, Finland, Petr Švec, from SAS in Slovakia, Peter Mullner in Boise University USA, and Sebastian Fahler from IFW Dresden now in HZDR, Germany.

Introduction

Magnetically Induced Reorientation (MIR) the term we coined together with S. Fähler in 2008 [1, 2] is one of the effects from the family summarily called magnetic shape memory phenomena or **MSM** in short. The most visible characteristic of these effects is giant magnetic-field induced deformation which can reach up to 12%. The MSM phenomena are of multiferroic nature combining ferroelasticity and ferromagnetism. The MIR name was suggested to separate it clearly from the others MSM effects involving the martensitic structural transformation.

Magnetic shape memory (MSM) is the name directly derived from the analogy with the more common and longer known shape memory phenomena. It describes a material which remembers its shape, i.e. the material deformed at lower temperature returns to original shape upon heating. The easiness of the deformation in low symmetry phase is provided by the occurrence of ferroelastic domains or twins separated by twin boundaries. These domains and their interfaces formed upon martensitic transformation during cooling. When heating, the deformed twinned phase transforms back to high symmetry, usually cubic phase with no twinning, and the material thus reverts to the original shape.

The transformation from high to lower symmetry phase is diffusionless and displacive. To obtain shape memory effect the transformation has to be also reversible or thermoelastic with low thermal hysteresis, i.e. none or only minor plastic deformation occurs. Instead of plastic deformation the material upon transformation accommodates the shape by twinning. The twinning occurs to conserve the original shape of the high temperature phase.

Such twinned crystal of low symmetry phase can be then relatively easily deformed by moving twin boundaries which results in the redistribution of ferroelastic domains or lattice reorientation and macroscopic deformation. The deformation is pseudoelastic, i.e. it is reversible and ideally no plastic deformation occurs. The twinning stress or the stress needed to move twin boundary in shape memory materials is usually of order tens up to hundreds of MPa and only exceptionally of few MPa. If such materials with extremely low twinning stress is also ferromagnetic having high magnetic anisotropy, the ferroelastic domains can be also manipulated by magnetic field resulting in giant magnetically induced strain (MFIS) reflecting lattice reorientation. This effect was discovered by Kari Ullakko and reported in 1996 when at MIT [3]. It was only slowly and half-heartedly accepted. In 1999 we reported 6% deformation in $Ni_{50}Mn_{28}Ga_{22}$ in magnetic field less than 1 T [4]. Invariably, it is also called magnetic shape memory effect but magnetically induced reorientation (MIR) describes better what is going on.

Later on, in 2006 R. Kainuma at al. [5] reported magnetically induced martensitic transformation in $Ni_{45}Co_5Mn_{36.7}In_{13.3}$ single crystal in large field of several Teslas. This results in large deformation due to difference of parent and transforming phases and it can be considered as direct analogue to shape memory effect, in this case induced by field instead of temperature. The driving force for the transformation is the difference of magnetization in two phases. To distinct it from previously observed MIR we have suggested new name magnetically induced martensite/austenite (MIM/MIA) depending which phase has higher magnetization and thus it is preferential in magnetic field [1]. It seems that only after the discovery of MIM also previously reported MIR was fully accepted [6]. By observation of these MIM/MIA effects was the starting point for a new field of magnetocalorics using structural transformation. All described effects are schematically summarized in Fig. 1 [7].

Although discovered and firstly correctly described for Ni-Mn-Ga in 1996, the MIR was not entirely new effect. A large deformation in magnetic field was reported for Dy and Tb crystals in large field of several tens of Teslas and low temperature already in the sixties of last century. The twinning was observed and deformation ascribed to twinning but it was not further investigated and remains as magnetic curiosity in some textbooks [8].

Several different materials have been later reported exhibiting MIR, however, most of them exhibit just deformation of fraction of percent or at low temperature as Fe-Pt and Fe-Pd or Co-Ni-Al and several other Heusler alloys [9]. Even more, in many reports it is not clear if the observed deformation is really caused by twining and thus it is MIR. For time being the most investigated and most promising with largest observed deformation to date are materials based on Ni_2MnGa Heusler alloy and further we will focus only on this compound.

In order to shift the transformation up above room temperature, excess Mn is added and most of work was done on materials close to formula $Ni_{50}Mn_{28}Ga_{22}$ keeping the Ni contents constant at 50%. Here we exclude any materials with other modifications of the compositions or alloyed by other elements.

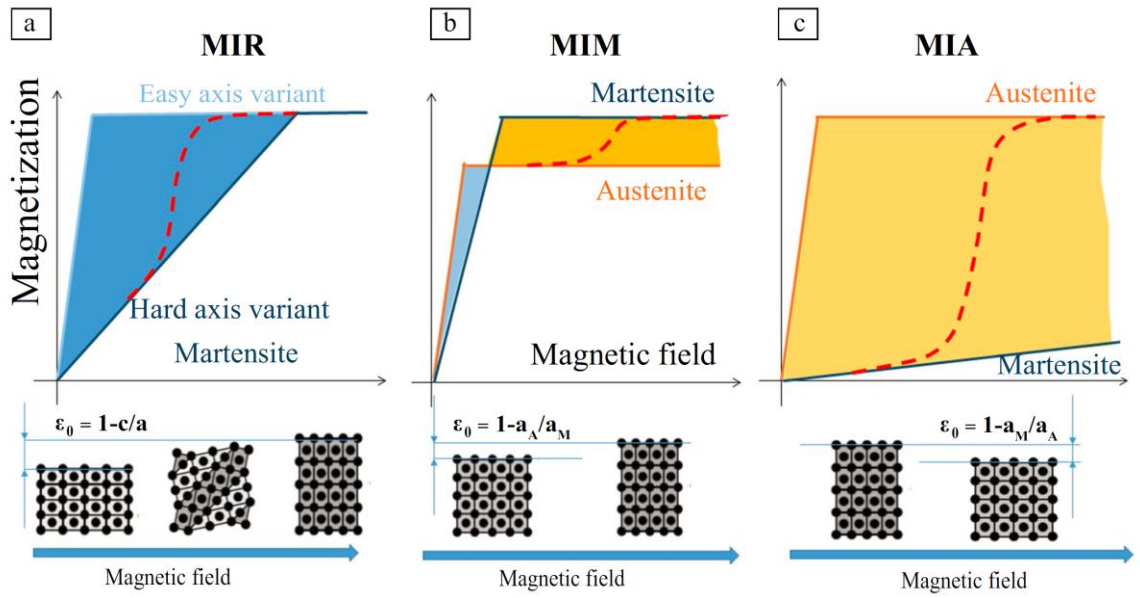

Fig. 1. *Schematics of MSM phenomena based on magnetic energy which is available for the magnetically induced reorientation (MIR) (a) and magnetically induced transformations to austenite/martensite (MIM/MIA) (b,c). Red broken line marks magnetization changes related to the effects which also correspond to the macroscopic strain. For MIR the energy is given by the difference between the magnetization curves for two differently oriented martensite variants and thus ultimately it is limited. In contrast the energy for MIM/MIA, given by filled area between magnetization curves, is limited only by the strength of available magnetic field. The strain is due to lattice reorientation or phase transformation as sketched. The maximum strain is given by the difference of lattice constants as marked, i.e., for MIR the difference between lattice constants of tetragonal martensite, for MIM/MIA by the difference between cubic and tetragonal lattice constants [7].*

But before we will start with the subject of my thesis, I would like to make small explanatory personal note. I was lucky to be in the right place at right time. In Finland I met the inventor of the effect, Kari Ullakko, who search for somebody who understand the magnetism. I joined the small group pursuing on many fronts the investigation of the effect discovered just few years ago. My research focus was on magnetic properties, crucial for the effect in the group with expertise of shape memory (non-magnetic) alloys. Although the group was headed by Kari Ullakko, discoverer of the effect we were not able or were perhaps not clever enough to publish our first ground-breaking discovery (as I can see it with hindsight now) in high ranking magazine.

In the same time, we had or hosted one doctoral student from MIT on visit in Helsinki. And we blindly showed him all what we knew about the effects and how to get the effect and so on. This knowledge given was somehow well used. The MIT group then published paper in APL [10] in the same time as our initial paper. Perhaps not surprisingly, our publication of the new effect was somehow difficult to push through, being from HUT not at least from MIT. It is hard to push a publication of the effect so unbelievable claiming that relatively small field (less 1T) was able to manipulate crystal structure and cause huge magnetic-field-induced deformation. In that time the giant magnetostriction intensively studied in Terfenol was considered as record deformation of 0.2% strain [7] and thus the new effect was hard to be believed. In that time Kari Ullakko pushed for the invited lecture on main magnetic conferences in US but he was rejected. Consequently, it was only me who travel to US as contributed author and the paper was published in proceeding [4].

Our leader Kari Ullakko was anyway interested mostly in applications and pushed hard for that. He felt, perhaps correctly, that we had enough phenomenological understanding of it and we should strive for some great and resolved applications. It, however, turns out to be tall order, indeed even now after twenty years of research we are not so much closer as the effect does not yield easily. But anyway, we investigated the new effect with all effort and interest but in contrast to well-equipped laboratories on rather modest means and premises. The large boost of the research was the *ICOMAT (International Conference of Martensitic transformation)* which we organized in Helsinki in 2002.

Submitted thesis brings brief but hopefully enough comprehensive summary of my contribution to the magnetically induced reorientation (MIR) effect spanning two decades of my (and my students and colleagues) research. In separate subchapters dealing with the particular topics I will mostly follow the historical perspectives in the order as our papers were published. Apart of few summarizing reviews the work published was always group work in which I took the leading or decisive part. During these years I published more than 200 papers, majority dealing with magnetic shape memory. The thesis however, is based on only limited selection highlighting what I considered as breakthrough or important seminal papers pushing the field forward and in which I was the first author and in later papers the last one as a group leader. Due to my training as magnetician the main stress will be on magnetic measurements of various physical properties and behaviour in magnetic field.

In the first part we start with the description of the magnetically induced reorientation (MIR) effect and stress the difference from the other MSM effects. We looked on martensitic transformation and existing or known low symmetry martensitic phases. In the end of the first part, we will focus on magnetic properties of Ni-Mn-Ga and other properties of different martensites which may be important for the effect understanding. The second part is devoted to

high mobility of twin boundaries in the martensite phases, particularly in 10M martensite. The third part describes shortly newly discovered observation methods which deepen our understanding and underline the new potential functionalities.

Since the submitted text should describe my contribution to the field, the reference list is heavily biased towards my work and only a few other papers are listed for context. The full picture can be obtained by referring to the original literature cited in the articles. Additionally, since the work is based on published work, the quality of the images varies depending on the graphic availability and skills of the presenter at the time.

I. Phenomenology of magnetically induced reorientation

Already our first paper published about magnetically induced reorientation (MIR) effect [4] contained many basic features which were then studied further following years and the research is still far from completed. The paper was submitted in February 2000 but extended abstract was submitted already in October 1999 for Intermag2000 conference. As the paper was published in the conference proceeding, it was not widely available and the initial impact of the paper was limited, although the most of phenomenology the effect was already included in the paper, based on previous Ullakko's papers reporting the discovery [3].

The paper reported about five percent deformation induced in the magnetic field below 1 T for the first time. The effect was amazing in contrast to the giant magnetostriction about 0.2% in Terfenol, and till now no other materials exhibit such large magnetic field induced strain. This is perhaps the most interesting and eye-catching feature but for the future physical research and understanding the effect, the importance lies elsewhere.

Strain induced by magnetic field

It was understood from the beginning that the material should be in low symmetry, low temperature phase called martensite [3]. Parent phase is cubic austenite, ordered phase $L2_1$, which transform to martensite with lower crystal symmetry. The available single crystal exhibited martensitic transformation, about 35°C with thermal hysteresis of about 10 deg. At room temperature the material was thus in martensite and we could easily measure the strain induced by magnetic field. As the deformation was large compared to the magnetostriction, usual method to measure the deformation of metals, i.e. the strain gages usually failed. Indeed, the deformation was observable by naked eye. In addition, as the deformation was pseudoelastic, it stayed constant after magnetic field was removed and thus it can be measured later, out of the device. To obtain deformation as a function of the field, the deformation was then measured in situ by laser interferometer with sample located in homogenous magnetic field and subjected to mechanical stress provided by piston driven by compressed air. One of the first example in shown in Fig. 2

The dependence of the field induced strain on external load indicated that the magnitude of the effect decreased with increasing mechanical load and magnetic field needed for the effect increased with increasing load too. It is caused by limited magnetic energy available for the reorientation working against external mechanical load.

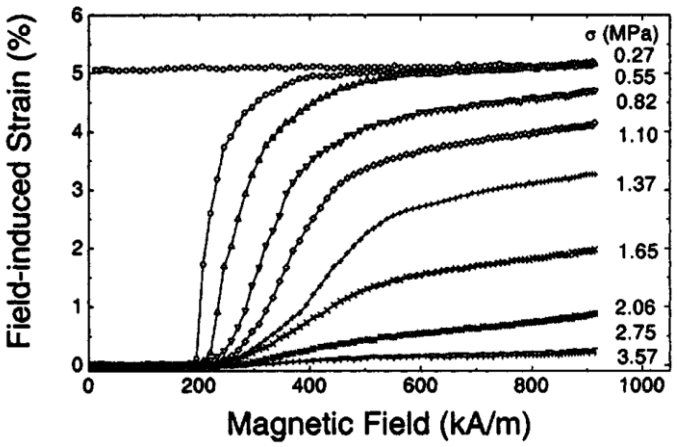

Fig. 2. *Magnetic field induced strain due to structural reorientation under various load as marked [IEEE2000]. The small load (close to zero stress) had to be applied in order to keep the sample in place. The experiment demonstrated the decrease of the magnitude of the effect and increase of the field needed for reorientation with increasing load [4].*

Magnetization curve – signature of MIR

The most important feature, as we can see now with hindsight, was to report the specific shape of magnetization loop, which characterize the effect (Fig. 3). Our proper understanding and interpretation of the shape of magnetization curve and its relation to the magnetically induced strain, i.e. MIR, provides new tool to characterize the effect apart of direct measurement of stress-strain curve. As the magnetic measurement is much easier and any commercial magnetometer can be used it was main and decisive step in MIR research.

However, to measure a magnetization curve in our laboratory I had to build a new device, vibrating sample magnetometer. Although it is standard piece of equipment no such device was available in our laboratory not even on HUT campus. The construction of the VSM was actually the first task when I started in Ullakko's group in Helsinki University of Technology in July 1999. In HUT nobody was interested in magnetic materials. It also somehow demonstrated how the laboratory was underequipped for magnetic and magnetoelastic measurements and research.

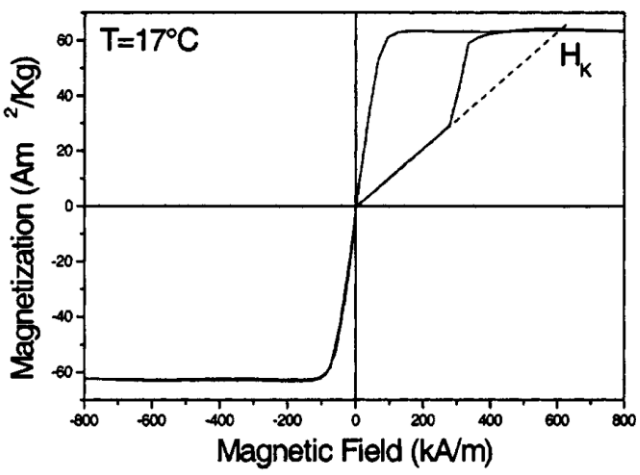

Fig. 3. *Magnetization curve of the single crystal exhibiting magnetically induced reorientation. The sharp jump in the first quadrant indicates the structure reorientation from variant with hard axis to easy axis along the field. As the sample is stress-free the orientation stayed after removing the field and loop exhibited square-like loop. Slight tilt is caused by demagnetization [4].*

After successfully constructing relatively primitive VSM instrument, the measurement of magnetization loop has become the main and relatively simple tool to investigate the effect, not only in our laboratory but everywhere. Despite the fact that we have reasonable interpretations it took several years to be accepted [6].

Relation between strain and magnetization

Although we were quite sure in the interpretation of the observed jump in magnetization loop as originating from the structure reorientation and thus resulting in large magnetically induced strain, we needed to prove the relation between magnetically induced strain and magnetization directly. The first such measurement was published in 2002 [11]. We also showed the measurement for other martensite called now 14M, previously labelled 7M [12]. An example of the measurement is in Fig. 4. Later using neutron diffraction, we directly proved the twin reorientation by structural studies in magnetic field [13].

To prove the relation directly we build with my new PhD student L. Straka the device which measured simultaneously the strain and magnetization as a function of applied magnetic field, thus providing all data when measuring quasistatic MIR (MSM) effect. The strain was measured by a contactless dilatometer using laser vibrometer equipped with displacement sensor. This was coupled with an in-house made vibrating coil magnetometer measuring magnetization changes. Whole device was built inside large 12 inches electromagnet with a maximum field of 1.15 T. The 12 inches diameter of the poles brought large advantage as it allows to fit whole device to homogenous field without need for too much miniaturization.

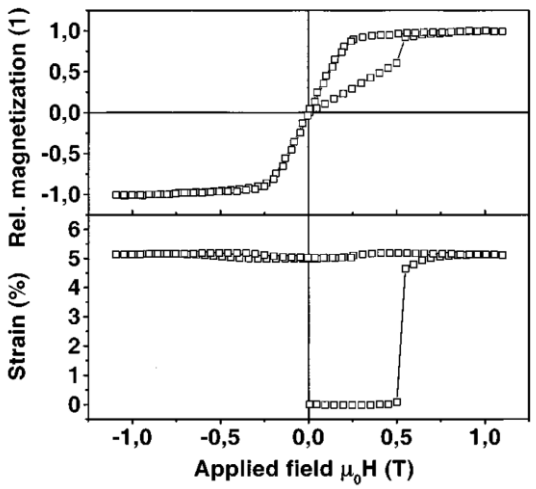

Fig. 4. *Example of simultaneous measurement of magnetization curve and magnetically induced strain demonstrating that jump in magnetization curve corresponds to fast increase of the strain given by the reorientation of the lattice or martensite variant orientation. [12]*

The measurement on single crystal martensitic sample having faces along {100} planes of austenite is shown in Fig. 4 and explained schematically on Fig. 5. It demonstrated that initial process of magnetization occurs by magnetization rotation out of easy plane toward magnetic field in the variant with magnetization perpendicular to the field. This does not provide any strain apart of magnetostriction which is minuscule and not to be detectable on this scale [14]. The rotation of magnetization increases the energy of the variant in the field. If the difference exceeds the energy needed for the nucleation and twin boundary motion, the effect takes place. At first the nucleation of the twin with different orientation occurs followed by twin boundary motion,

i.e. the structural orientation change from a-axis to c-axis (easy magnetization axis) along the field. We can be also said, that the variants favourable oriented in magnetic field grows on the expenses of other twin variants. This results in large strain $\varepsilon = 1\text{-}c/a$ where c and a are lattice constants of martensite and sharp increase of magnetization in the first quadrant. The increase is caused by the fact that due to reorientation the easy magnetization axis of the sample is along the field and thus it can be easily magnetized to saturation. Usually after the nucleation of twins and the formation of twin boundaries the process of twin boundary motion and thus the reorientation is fast and in the pseudo-static measurement of VSM it occurs in one step (Fig. 4).

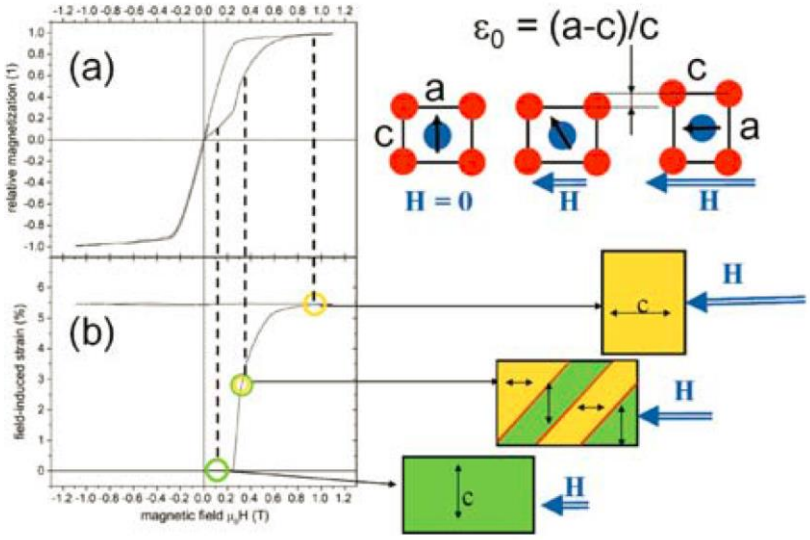

Fig. 5. *Magnetically induced reorientation (MIR) in a Ni2MnGa single crystal. (**a**) Magnetization loop. Initially, the c-axis of the unit cell is oriented perpendicular to the magnetic field $\mu_o H$. Magnetic moment is marked by arrows inside unit cells. Magnetization rotation occurs in low fields only. Due to twin boundary motion, reorientation of the unit cell takes place and the c-axis changes to the field direction. The difference between the lattice constants gives the maximum strain ε_0. (**b**) Simultaneously measured magnetically induced strain. The redistribution of twin variants with increasing magnetic field and the resulting shape changes are sketched* [1].

Existential Conditions for MIR

In already extensively quoted initial paper [4] following the interpretation of the magnetization curve we also published the existential condition for the MIR effect (in that time called MSM effect). From the energy model [15] the magnetically induced reorientation takes place if the difference of magnetic energy (Zeeman energy) between differently oriented ferroelastic variants ΔE_{mag} is larger than the work needed for twin boundary motion,

$$\Delta E_{mag} \geq \sigma_{tw} \cdot \varepsilon_0 \qquad (1)$$

where σ_{tw} is twinning stress and $\varepsilon_0 = 1\text{-}c/a$ is the strain given by the difference between lattice constants, a and c, of the 5M (now called 10M) martensite considering pseudotetragonal approximation, i.e. a=b > c. In this approximation we have three ferroelastic variants with different orientations of easy magnetization axis, approximately perpendicular to each other. It can be also said in analogue to magnetic domain wall motion that the variant favourable oriented to external field grows on the expenses of other variants. From this simple energy model and considering the maximum energy in magnetic field of the variant which is equal to magnetic anisotropy energy K_u, the existential condition for MIR effect can be written as

$$K_u > \sigma_{tw} \cdot \varepsilon_0 \quad (2)$$

i.e. the anisotropy energy must be larger than the work needed to move twin boundary in order to exceed the twinning stress. It appears that this simple energy equation for a tetragonal structure satisfying the requirement of both anisotropy and low twinning stress leads to an explanation for the stress limit of MIR phenomenon without further assumption.

Magnetic anisotropy of 10M martensite

In this first initial paper, we were also able to determine the magnitude of magnetocrystalline anisotropy of the 5M (now marked 10M) martensite by measuring magnetization loops in different crystal directions assuming (pseudo)tetragonal structure. We supposed, in agreement with previous reports [16], that the anisotropy is uniaxial with easy axis along crystallographic c-axis which is short axis of tetragonal structure. The tetragonal structure of martensite was some kind of approximation and it took many other years to evaluate the structure and in fact it is not properly solved till now.

Comparing the loops measured in easy and hard direction of single martensitic twin variant and extrapolating the initial slope of magnetization measured in hard magnetization direction, we obtained the anisotropy field H_a in T. Using saturation magnetization M_s in Am^2/kg we the magnitude of magnetocrystalline anisotropy is given

$$K_u = ½ \rho M_s \cdot H_a \quad (3)$$

where ρ is the density of the material. Such evaluation has had become the basic method to determine the magnetocrystalline anisotropy of various single crystals and the majority of our samples. Here we exploited to our great advantage the existence of MIR, so the easy and hard variant could be formed in the same sample in the same directions, thus we can assume the same demagnetization factor. Due to large deformation (of 6%) the demagnetization factor can slightly change but this change is smaller than measuring precision. The demagnetization factor can be also approximate by measuring the austenite which is magnetically soft with negligible anisotropy, which was also often done.

In this method it is however quite important to use properly prepared sample containing only one crystal orientation, i.e. single twin variant. It can be obtained by compression of the sample which results in mechanically induced reorientation and formation of single variant with short c-axis along the stress. If the reorientation is possible and complete, the single variant can be prepared also by magnetizing in high field above 1T. The applied stress, in contrast to magnetic field, is not limited and thus even materials with unmovable twin boundary could be prepared in single variant state. The way how to prepare single variant, however, is sometimes misunderstood as it is not method for the usual magnetic material and it took some time to be accepted by the community. Later we also showed that the anisotropy could be determined more simple way without need to prepare single variant. Since the variants are macroscopic and magnetically interfere only very weakly, the magnetization loops belonging to different variants are easily recognizable and the anisotropy can be easily determined with reasonable precision. The near independence of the variants was also supported by the observation of magnetic domains as shown later.

Knowing the magnitude of the anisotropy $K_u = 1.7 \times 10^5$ J/m^3 and the mechanism of reorientation already suggested by Ullakko in his original papers, provides the path to the evaluation of simple phenomenological model for the effect suggested in [15]. From the value of magnetocrystalline anisotropy we estimated blocking stress, about 2.8 MPa and demonstrated its agreement with

the experiment [4]. This was direct confirmation of the validity of the model. From the other side, we have also demonstrated that the external work done by material is limited and determined by magnetocrystalline anisotropy. The temperature dependence of magnetic anisotropy was published soon after [17].

Magnetic domains

As the martensite exhibits large magnetic anisotropy one can expect well-ordered magnetic domain structure. The question was thus how the twinning and twins with different crystal orientations and thus different easy magnetization directions, interfere with it. The magnetic domains of martensite were observed for the first time in our group in cooperation with FZU in Prague [18]. We used a method based on Lorenz contrast of second type in SEM developed in FZU. Observed domain pattern was in agreement with uniaxial character of magnetic anisotropy. We observed band domains in the sample sides when magnetization was in plane. The expected labyrinth pattern for the magnetization out of plane could not be observed by this method. Using traditional Bitter method revealed that twin boundary is also 90 deg magnetic domain wall. The sharp changes of domains pattern upon twin variants indicate nearly independent magnetic behaviour of the variants with different crystal orientations. This further supports the assumption that the measured magnetization curved can be considered in good approximation as the superposition of the magnetization curves of individual variants. Later on, the Bitter pattern method was abandoned and most of the observation was done using magnetoptical indicator (MOIF) and polarized optical microscopy [19] which helps to visualized expected labyrinth pattern. The magnetic domain structures occurring on different sides of twinned sample, i.e. for different magnetization axis orientations were summarized in [1].

Direct observation of magnetic domains by Kerr microscopy failed and thought impossible as Kerr rotation for Ni-Mn-Ga was considered to be zero [20]. However, after many years we measured the Kerr spectrum again showing that Kerr rotation fluctuates around zero having the maximum, albeit weak, in violet end of spectrum [21]. This produced more focused experiments and magnetic domains were observed by Kerr method in particular arrangement as described later in third part. We failed to observe the magnetic domains of austenite and the domains have not

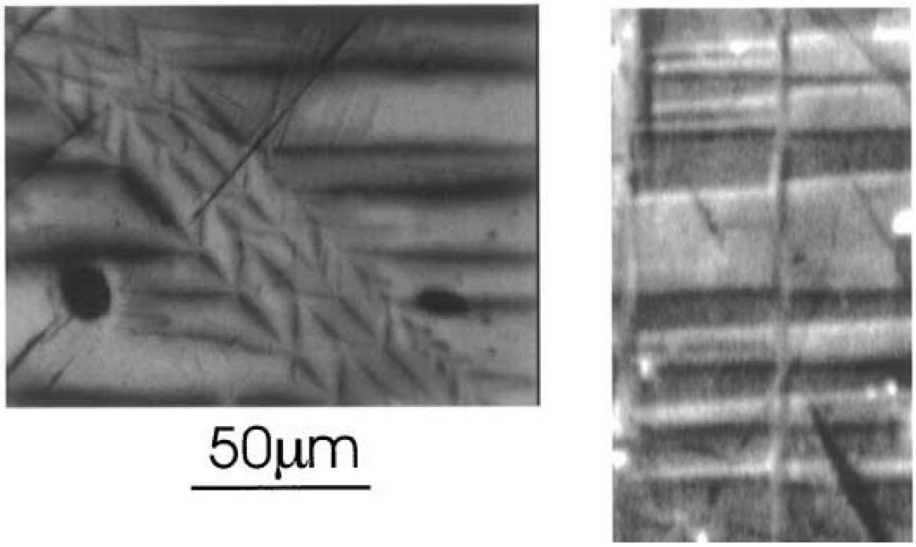

Fig. 6. *Magnetic domains with two variants with the magnetization in plane horizontally and vertically oriented easy axis (twin bands running diagonally over the figure) forming staircase pattern (Bitter method) (a), and magnetic domains of nearly single variant with magnetization*

along horizontal line (b). the vertical weak line is residual variant with magnetization perpendicular to the field (SEM - Type II Lorenz contrast) [18].

been observed up to now presumably due to very low anisotropy of austenite producing very large domains and wide domains walls with small contrast. Although we used quite traditional method it brough important new results and understanding for MIR. The demonstration that the differently oriented twin variants are not affected too much by each other and their behaviour can be treated separately brings important point for the modelling the effect and for the interpretation of the magnetization curve of the material.

It should be noted that later we published several papers about magnetic domains observed by SEM which were only partially correct, e.g. [22]. Misled by the assumption of pseudotetragonal lattice, we considered band and staircase features observed on the sample surface as some kind of magnetic domains. Only with deeper understanding of twinning hierarchy later it has become clear that the observed features are not domains but different twins. Published observations should be reconsidered.

Transformation sequence and different martensite phases

The temperature of martensitic transformation has been determined by the measurement of AC susceptibility and/or the measurement of DC magnetization in low field, usually 0.01 T (also often called susceptibility). These measurements also allowed to determine ferromagnetic Curie temperature, i.e. disappearance of ferromagnetic order. The AC susceptibility and DC measurement of low field magnetization became the standard method for evaluating transformation temperatures in MSM field. The martensitic transformation is expressed in the thermomagnetic curve as the sharp decrease of magnetization upon transformation to low symmetry phase. The decrease occurs due to sharp increase of magnetocrystalline anisotropy of low temperature phase – martensite, even though the saturation magnetization increases upon transformation to martensite.

One of the first measurements is shown in Fig. [7] It is also accompanied by measurement of saturation magnetization at 1 T indicating increase of saturation magnetization upon MT. These measurements also indicate presence of intermartensitic transformations, however in that time the nature of low temperature martensitic phases was not clear. Now the established transformation sequence is 10M-14M-NM martensite.

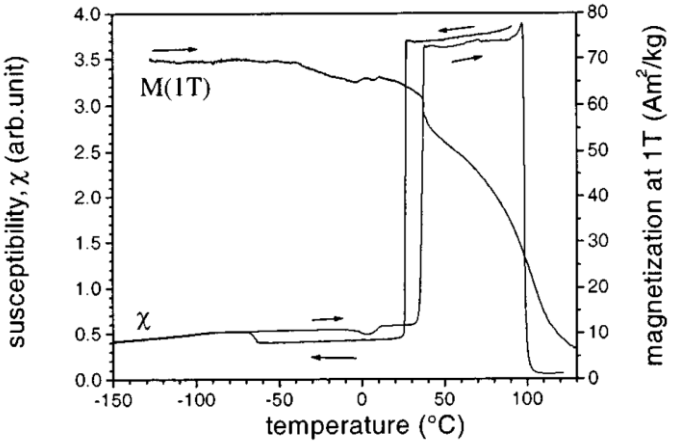

Fig. 7. *Variation of low field AC susceptibility and magnetization (at 1T) with temperature. The arrows indicate the direction of temperature change. The erroneous fluctuation in saturation magnetization below zero temperature is partly due to freezing, not by transition to different phases [23].*

Soon we understood that 5M phase was not only martensite which occurred in off-stoichiometric Ni-Mn-Ga. Thanks to Outokumpu prepared alloys of various off-stoichiometry we were able to discover and characterize three different phases of Ni-Mn-Ga martensites particularly their magnetic properties and evaluate their feasibility for the MIR effect.

All three phases of martensite occurred in off-stoichometric Ni-Mn-Ga alloys with Mn excess at room temperature. Also, the successive occurrence of the phases takes place during cooling by so-called intermartensitic transformation as shown in Fig. 7. We magnetically characterized the phases in that time called 5M, 7M and non-modulated NM phase [12]. The 5M and 7M phases were considered tetragonal and orthorhombic and modulated with periodicity referred by number. Later structural refinement showed that the phases were monoclinic [24]. Moreover, the modulated phases were later relabelled to 10M and 14M to reflect chemical ordering properly, i.e. only after 10 or 14 layers the plane with the same occupancy is repeated. Non-modulated phase (NM) is tetragonal phase without modulation. While the martensitic transformation can be widely varied depending on slight changes of the composition the Curie temperature is barely changing, staying about 100°C.

From magnetic point of view the modulated phases can be considered tetragonal or orthorhombic with easy magnetization axis along short crystallographic c-axis as demonstrated in Fig. 8. Due to orthorhombicity of 7M phase there are two different hard axis, a and b of different strength reflecting different size of the unit cell. Non-modulated phase is purely tetragonal with long c-axis. The c-axis is hard magnetization axis forming easy magnetization plane in the a-a plane. Initially the NM phase we could not structurally identified but from magnetization curve wrongly considered to be magnetically soft. Later we understand that this phase is non-modulated martensite with easy plane [12] in contrast to uniaxial anisotropy of 5M and 7M. Particular arrangement of twin variants with easy plane produced the structure which seems to exhibit low magnetocrystalline anisotropy. This kind of errors was common in the early days of the research.

Despite the fact that the magnetic structures are relatively simple and can be considered as reflecting simple approximation of phases the underlining crystal structure is more complicated and become the subject of intensive research in following years. Precise knowledge of the structure of the phases is very important as it may be a key for the understanding of the extremely high mobility of twin boundaries in modulated phases. However, up to now there is no definitive answer to that question.

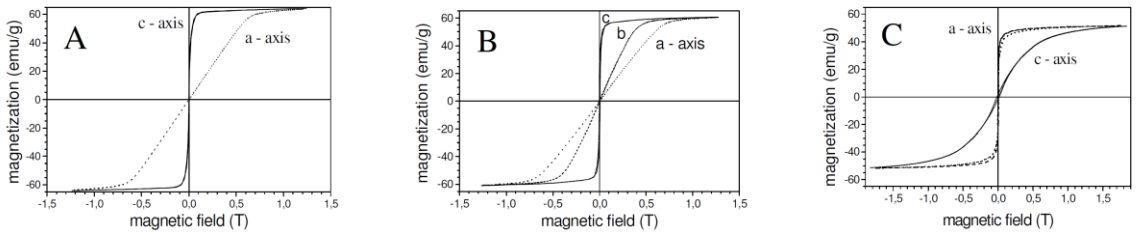

Fig. 8. *Magnetization loops for all martensitic phases observed in Ni-Mn-Ga in single variant state as indicated. A) 10M martensite measured along easy (c-axis) and hard (a-axis) direction, magnetically pseudotetragonal phase. B) 14M phase indicating two hard axes with different strength and one easy axis (c-axis) magnetically orthorhombic phase. C) Non-modulated martensite with short (a-axis) being easy plane axis and hard direction along c-axis (long tetragonal axis)* [12]. *As understood later the curved loop in hard direction is caused by presence of other variants, i.e. non-ideal single variant [26].*

Although some temperature observation was done before [17] the precise determination of the magnetocrystalline anisotropy and its temperature dependence of all know phases of martensite were another cornerstone in the field [25]. Knowing the magnetic anisotropy and its temperature dependence provided the first step in evaluation of effect feasibility in various phases, Eqs. 1 – 3, and the means to estimate the temperature dependence of the effect.

Temperature dependences of MIR

Having applications in mind we focused on temperature dependence of the effect in 5M martensite exhibiting 6% deformation in the field [23]. For that we have to build cryogenic system to our custom-build magnetometers. Despite the primitive condition we were able to evaluate the temperature dependence of magnetic properties and MIR in broad range of martensite and demonstrate its disappearance due to limited magnetic energy by magnetocrystalline anisotropy and increasing twinning stress in low temperature. We showed that the switching field for the effect increases approximately linearly with decreasing temperature and when the field needed to move twin boundary exceeds the anisotropy field no MIR occurred. By measuring magnetization curve down to low temperature, we observed not only blocking temperature, below which the MIR ceased to exist, but also intermartensitic transformation and different martensite phases.

Crucial detailed measurement and interpretation of temperature dependence of MIR was published later in the experiment in which we measured temperature dependence of twinning stress directly [27]. Knowing the anisotropy and twinning stress we could set and properly interpret the limit of MIR effect. The high temperature limit is determined by martensitic transformation, the low temperature limit by sharp increase of twinning stress with decreasing temperature which exceeds available magnetic energy. This is summarized in Fig. 10.

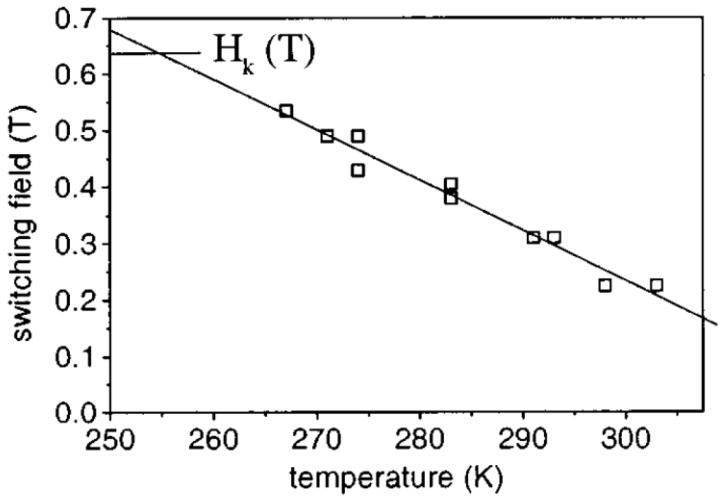

Fig. 9. *Temperature limit of MIR due to increasing switching field needed for the reorientation (nucleation and twin boundary motion) [23].*

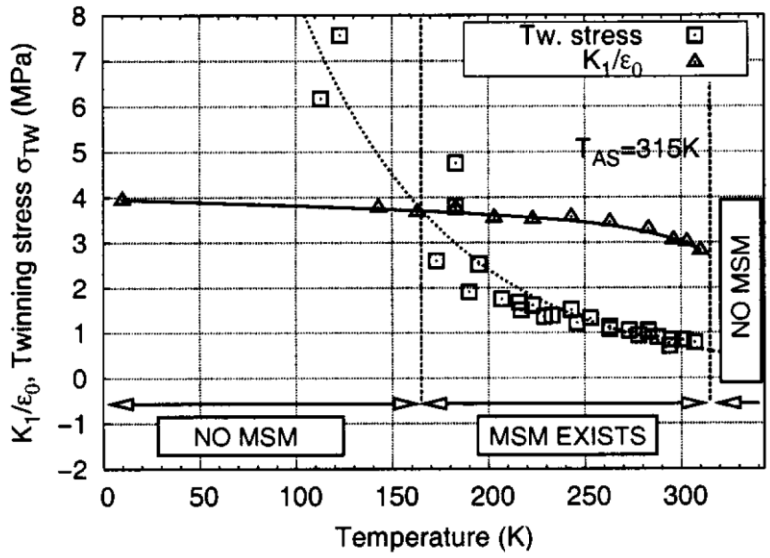

Fig. 10. *Direct determination of the limits of MIR. Lower limit is due to increasing energy needed for the reorientation and upper limit by martensitic transformation [27].*

Reversibility of the effect

Observed structure reorientation effect under magnetic field or mechanical force is in general one way effect. Since the reorientation occurs by twin boundary motion there is no force to reverse the reorientation. To obtain reversible effect two differently oriented forces are necessary. It may be magnetic field applied in two perpendicular directions (or by rotation of magnetic field) or as it is usually done and suitable for mechanical actuator, magnetic field working against mechanical force applied perpendicularly to the field. The field induced deformation against external load provides useful work. Based on simple phenomenology, the mechanical load in the form of external stress ε_{ext} can be included to Eq. 2 and expanded equation is

$$K_u/\varepsilon_0 \geq \sigma_{tw} + \sigma_{ext} \qquad (4)$$

The inclusion of external load provides even more strict condition for the existence of the effect. It is even more strict for fully reversible effect [28]. The reversible behaviour of the field induced strain and magnetization is shown in Fig. 11. The magnetic anisotropy must be very high and twin boundaries very highly mobile. If the conditions are not fully satisfied the partial reversibility can occur. The validity of the approach we demonstrated in several papers.

The reversibility immediately raises a question about repeatability and fatigue. As no transformation is involved it was demonstrated that the elements can withstand millions of cycles in rotating magnetic field provided by rotating permanent magnets [29] and more than hundred millions cycles if subjected to mechanical force.

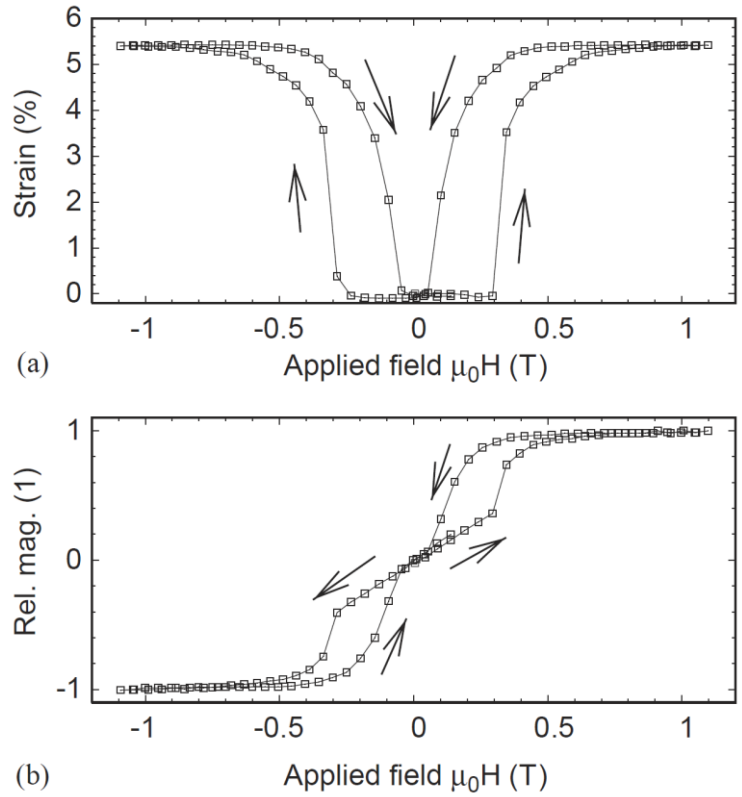

Fig. 11. *Simultaneous measurement of (a) strain and (b) magnetization of sample S2 in quasistatic magnetic field under constant 1MPa compressive stress. The reversible strain occurring due to the MSME is 5.6%. The same reversible strain is observed in the following cycles (not shown) [28].*

Apart of direct MIR we can also consider reverse situation when magnetic field is constant and large enough to saturate the active elements and mechanical force is variable. This provides magnetically driven spring and the effect was called magnetically induced superelasticity in analogy with shape memory superelasticity, in which, however, the transformation is involved in contrast with our effect in which only twin boundary motion and reorientation occurs. The demonstration of the effect and model of the behaviour was published in [30].

Mechanism of the effect - Concluding summary

The mechanism and basic phenomenology of bulk MIR effect was summarized in the invited paper for JEMS conference [6] in 2005. In the same time the magnetic properties of bulk Ni-Mn-Ga crystals, both austenite and all martensite were fairly well known and crystal structures of all martensite occurring in Ni-Mn-Ga compounds were described in some precision although the discussion about character of modulation phases continues till now. It can be said that till 2005 we laid basic groundwork for the phenomenological understanding or at least description of the effect (MIR in that time called MSM). The new mechanism, unknown in solid material, was tentatively and hesitatingly accepted. All available knowledge including other forms of materials as thin films, ribbons and thin wires I summarized in the review published in the book [1]. In that time, it seemed that there were not much more to discover and explain about this new effect. Of course, the temperature limit of the effect and very low twinning stress providing extreme mobility of twin boundary in magnetic field remains vexing questions both from basic physical understanding and applications.

II. Two types of highly mobile twin boundary

New stage of the MIR research starts with realization and discovery of two different kinds of highly mobile twin boundaries [31,32] acting in reorientation in 10M martensite. Precluding fact was to recognize and consider the monoclinicity of 10M pseudotetragonal structure which was known for some time [24] but not considered. It was known from shape memory research that the monoclinic structure provides rich spectrum of the possible twinning and types of twin boundaries [33].

All started with the observation that a/c twin boundary in bulk single crystal can exhibit very low twinning stress down to 0.1 MPa, again made in Helsinki. In that time I was back in Prague, since 2008, and intensively cooperate with HUT. Important step was methodologic finding how to prepare single twin boundary which sweeps whole sample. Soon become apparent that there are two different twin boundaries with sharply different twinning stress. Optical microscopy showed relatively complex twinning structure but the character of observed domains was puzzling. One reason for the puzzle was the usual (but misleading) consideration of 10M phase as tetragonal or pseudotetragonal, i.e. only one twinning system was available. The second reason was experimental - how to identify the structural domains of relatively small size.

The necessary condition for the proper classification of the boundaries was an acceptance of the crystal structure of 10M martensite. It was classified as monoclinic structure with modulation although the deviation from the average tetragonal structure was small, i.e. the difference between a and b lattice constant was less than 0.5 % and monoclinic angle deviates no more than 0.5 deg from 90 deg. Despite these small differences the consequences are profound. From the elastic continuum theory follows that the transformation from cubic (austenite) to monoclinic structure (10M martensite) result in several different twinning systems and different twin boundaries [33]. Importantly in this system, there are two different kinds of a-c twin boundaries, called Type I and II.

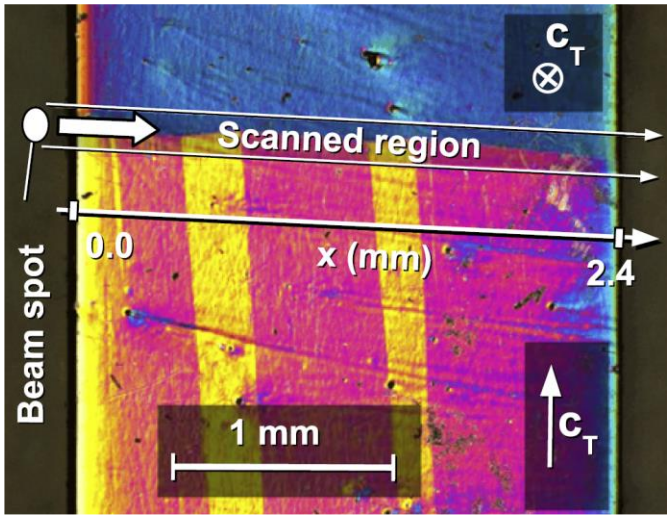

Fig. 12. *Detail of the highly mobile twinned interface (oriented horizontally) observed by optical microscopy using Nomarski (DIC) contrast. The boundary separates two ferroelastic variant with different orientation of c-axis. The direction of c-axis is marked in both variants. XRD scans using capillary microdiffraction were performed along the interface in the region marked. The approximate size of the X-ray beam spot is marked on the left, x-axis used in mapping is marked along the interface [31].*

Using dedicated XRD microbeam experiment together with theoretical calculation thanks to our colleague Hanuš Seiner, we were able to identify the twins along the macroscopic a-c twin boundaries and demonstrated the crystal orientation in each domain [31]. Fig. 12 show the optical observation of twinning structure and summarizes the experimental investigation. Thanks to join effort and broad cooperation whole twinned structure was then identified and twin hierarchy evaluated. The schematics of twinning hierarchy for both macroscopic Type I and II twin boundary is shown in Fig.13 [34].

In general, the various twinning occurs on different scales and the optical microscopy observation reveals a-c twins and also monoclinic or modulation twins. Although a-b twinning could be interfered from the X-ray diffraction it was not observable by optical microscopy due to low contrast and small size. We have succeeded the direct observation of a-b twins using SEM later as described below.

After this seminal paper we continued to investigate other features on MIR focusing on the reorientation provided by single twin boundaries. We were able to separated pure twin types of Type I and II and their twinning stresses. Invariably we found that at room temperature the twining stress in various samples are about 1 MPa for Type I twin boundary and about 0.1 MPa for Type II. However sometimes the twinning stress was somehow between these values even for the single boundary. We showed that this can be ascribed to, firstly unexpected, the combination of both twin boundary types, i.e. Type I and II in single moving twin boundary [35] as shown in Fig. 14.

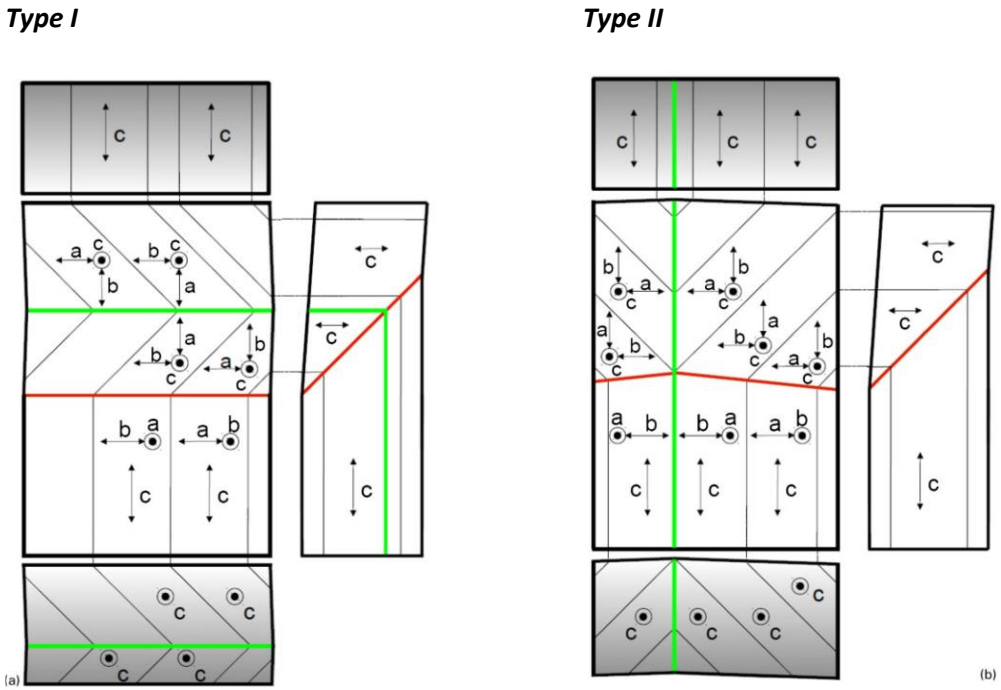

Fig. 13. *Full hierarchy of the twinning in bulk single crystal. The orientation of lattice in individual twin variants is marked. Also, macroscopic deformation due to twinning is apparent. Red and thick are macrotwin boundary of Type I and II, green modulation or monoclinic twinning and black thin line marked the ab twin boundary. The width of a/b laminate twin boundary is grossly exaggerated to be visible. Note different orientation of monoclinic twin boundary for macrotwin boundary of Type I and II [34*].

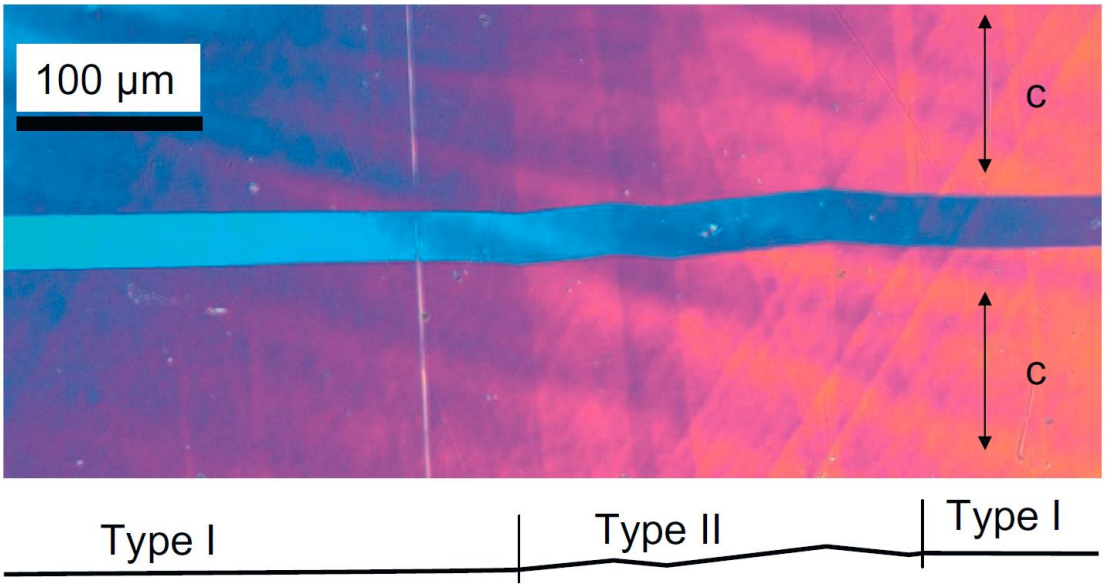

Fig. 14. *Optical micrograph showing an example of the weakly incompatible two parallel macrotwin interfaces identified as the combination of Type I and Type II macrotwin boundaries. The figure demonstrates the different angles between segments of different twin boundaries (marked in the figure): about 6degs between Type I and Type II boundaries, and about 12 degs between two segments of Type II boundary. The weak contrast of nearly vertical bands is due to modulation twinning in the variant with the c-axis in plane. Shown part of the sample contained two differently oriented variants with the variant of c-axis perpendicular to the plane located in the narrow middle band [35].*

It seems that Type II can exhibit even smaller twinning stress in itself, and measured twining stress correspond to some hindering on surface or on bulk imperfections [36]. The tentative model of very low twinning stress was suggested [35] and it is described later. In any case, the twinning stress of Type I is about ten times larger and the dependencies seems to be generally valid which was tested in large assembly of single crystals.

Temperature dependence

In parallel with the investigation of the structure of highly mobile twin boundary the temperature dependence of twinning stress was investigated. In contrast what is usually done in shape memory field, we used the proxy by measuring the magnetic response, i.e. we evaluated the magnetic field needed for reorientation (switching field) as it could be directly determined from the measured magnetization curves as explained before [1] and later in [37]. The method is robust as we have demonstrated previously by direct measurement of strain and magnetization (Fig. 5). The measurement of switching field has also advantage that it not depends how well the sample fixed and particularly it can be measured down to lowest temperature. On the other hand, it is somehow difficult to determine precisely the magnitude of the twinning stress as the parameters in eq. 1 and 2 are not known precisely enough. However, for the relative changes such method is very suitable and easy to implement and it is broadly used.

By studying behaviour of single boundary, we confirmed the previous results that the twinning stress increased sharply with decreasing temperature in one type of twin boundary (Fig. 15). We were able to show that this is typical character of Type I twin boundary which exhibit about 1 MPa twinning stress at room temperature. The twining stress further decreases when approaching martensitic transformation.

The behaviour of Type II is, however, very surprising. We found that temperature dependence of twinning stress of Type II twin boundary was relatively flat and thus sharply different from Type I. The twining stress increases very slowly with temperature thus the MIR was observed down to lowest experiment available temperature 1.7 K [38]. Moreover, due to sharply different temperature dependence of twinning stress of type I and II twin boundary, the twinning stress is similar for both types of boundary in the vicinity of MT. This was confirmed by direct measurement of twinning stress at room temperature and close to MT.

Mixed boundaries consisting from the segments of Type II and Type I boundaries exhibit then twinning stress between pure twin boundaries with intermediate temperature dependence. This is double surprising as there is no reason why Type II should not be blocked. It suggests that the boundary behaves as continuous object and while Type II boundary moves freely it drags Type I twin boundary with higher stress along.

High mobility close to absolute zero seems to clear one mystery observed in the epitaxial films deposited on various substrates exhibiting 14M structure. These films exhibit the magnetization curve which suggest the existence of MIR and thus mobile twin boundary down to 10K [39]. These films we investigated when I was in Germany in 2006-8. It turns out that the twin boundary in 14M are also of Type II and thus they can exhibit flat temperature dependence and thus MIR down to 10 K. The existence of MIR in the thin films has been, however, recently disputed and the observed bump on the curve ascribed to the particular domain structure and purely magnetization process [40]. In contrast, no such behaviour was found in the epitaxial films with 10M structure prepared on NaCl [41]. These films do not exhibit the MIR or jump in magnetization curve in sharp contrast to bulk material. This can be ascribed to complex twin structure established during deposition.

The attempts to explain the extremely mobility in MSM alloys are hindered by several problems. Not only the microstructure of the twin boundary is not known and the mechanism of the twin boundary motion is disputed. Moreover, even crystal structure of modulated phase is not settled. We believed that the extreme high mobility is connected with peculiarities of modulated structure and extreme shear elastic softness in Ni-Mn-Ga as stated in recent review [42].

To explain the extremely high mobility in Type II twin boundary and particularly the flat temperature dependence we proposed a simple model based on irrational indexes of Type II twin boundary, i.e the slight deviation of twinning plane from (101) plane. From the model follows that the twinning stress of Type II boundary should be close to zero as the atoms are not in proper Pierls energy minima [35]. This would also explain the weak temperature dependence of twining stress. However, in connection with this model the question arises why such high mobility would not occur in other shape memory alloys with Type II twin boundary [43]. There is it clear that detail structure of twin boundary plays important role in the mobility at least we demonstrated these in the CuNiAl shape memory alloys [44] as non-magnetic analogue to Ni_2MnGa. From the perspective of elastic continuum, the different compatibility of the hierarchical twinning may be a key to the different mobility between Type I and II twin boundary [45].

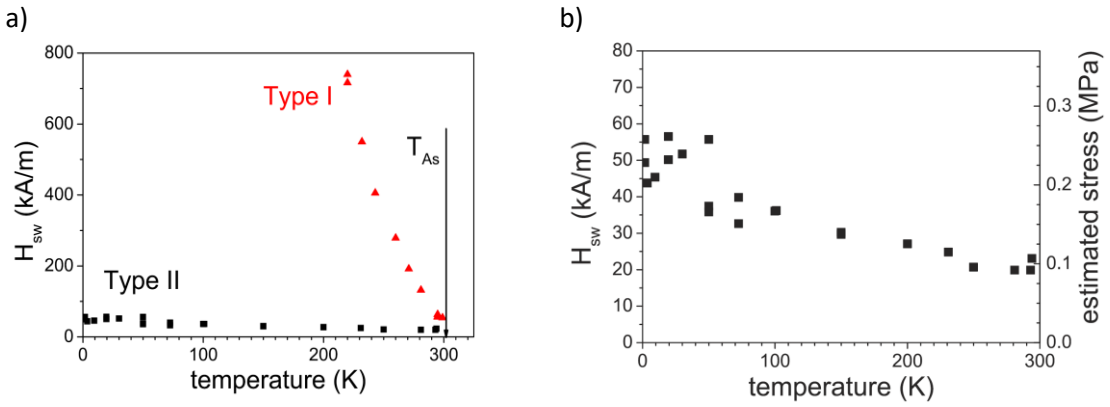

Fig. 15. *a) Temperature dependences of switching field, Hsw, for both types of twin boundaries, Type I and II as marked in the figure. Transformation temperature to austenite, TAs, is shown. b) Detail of temperature dependence for Type II [38].*

Moreover, although the temperature dependence of twinning stress is observed to be flat for Type II it is valid only in material without intermartensitic transformation. In the vicinity of intermartensitic transformation the twinning stress of Type II boundary sharply increases as shown in Fig. 16 and MIR ceased to exist [37, 46].

In summary, it is now well established that there are two types of twin boundary providing structural reorientation (MIR) in magnetic field. These twin boundaries exhibit sharply different twinning stress but both extremely low in contrast to usual shape memory alloy. Even more puzzling is that the boundaries exhibit different temperature dependence of twinning stress. It is not solved till now and remains the most pressing problem for future. It does not help that the structure of 10M martensite is not settled and discussion about modulation versus nanotwinning continue unabated [47]. To date knowledge were summarized in the reviews [34,37] with the stress to the connection of twin mobility and twin hierarchy.

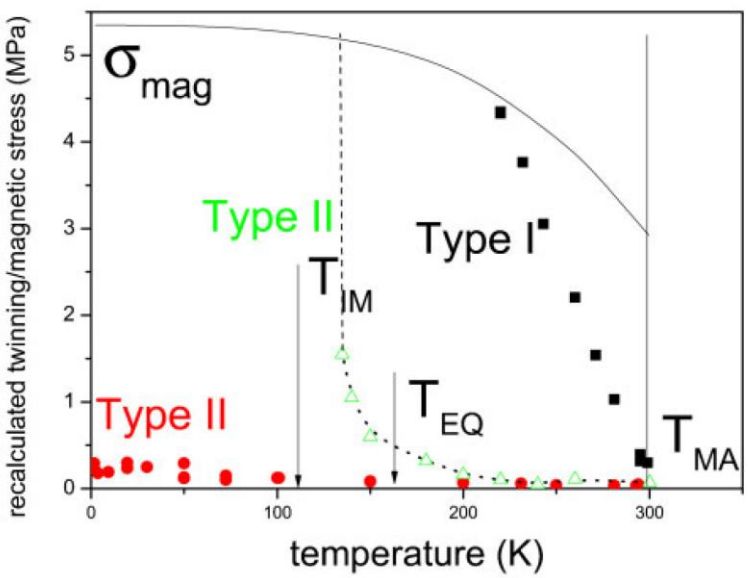

Fig. 16. *Effect of intermartensitic transformation and temperature dependence of magnetic stress (recalculated from magnetic energy) [37].*

III. Towards better understanding

Few notes on martensitic transformation

Although MIR effect is underlined by martensitic transformation, there is not much research about conditions for the existence of martensitic transformation in Heusler alloys particularly focused on the effect. Not that changes upon transformation were not investigated. On the contrary, the magnetically induced martensitic transformation was only effect reported in Nature by group from Sendai, Japan in 2005 [5]. They showed that MT can be induced in the high magnetic field with resulting large linear changes originated from the difference of lattice constants of high temperature cubic phase – austenite and induced martensite. Following publication [48] demonstrated that not only strain but large force or work output can be obtained. The effect is direct analogue to the shape memory effect and strictly MSM effect should be referred to this. We studied the field induced transformation in free standing epitaxial thin films [41] and also suggest the new name MIA/MIM to distinguish the effect from the now classical MIR [1].

The interest in field induced MT has sharply risen later with the onset of research in magnetocaloric or generally caloric (multicaloric) materials. These materials utilize the MT transformation directly. Despite theoretical and computational effort, the temperature, in which MT occurs, cannot be predicted from ab initio calculations although as it lays in the subtle features and changes of electronic structures. Generally accepted conditions for MT is high density of electronic states on Fermi level and wave vector nesting [49]. The high density of states on Fermi level is a simple and rough guide for the prediction of existence MT as is it assumed that MT is conditioned by band Jahn-Teller effect. Still it is difficult to predict with certainty, which Heusler compounds can exhibit the MT.

Usually the discovery of new materials with MT are done by trial and error and there are many new Heusler alloys with improbable combination of elements exhibiting MT. One reason for unsure ab initio prediction is very high sensitivity of MT on minor alloying in Heusler alloys and apparently also on atomic (chemical) ordering which is hard to probe experimentally in sufficient precision. The prediction of MT remains a great challenge for future research. The theoretical calculation and comparison with the experiment, differences and agreement we summarized in the review [42].

Our group also work in this field and as an initial step we investigated the changes of electronic states upon transformation using ARPES [50] and later by magnetooptical spectroscopy (MOKE) [21]. We started with common Ni-Mn-Ga compound with MT close to room temperature. The changes of electronic structures were apparent by ARPES although the direct measurement of electronic structure showed very blurred features and the calculated spectra only broadly remind the measured ones. Using optical probe, we investigate the changes of the magnetooptical spectra in materials with different temperature of martensitic transformation in hope to find the tendency for temperature decrease of MT. The changes in MO spectra were however, not very clear and persuasive indicating that MT indeed depends on very subtle changes [21, 51]. Importantly, but somehow as side result, we showed that Kerr effect in Ni-Mn-Ga has maximum in blue end of spectra which could be and was later utilized in direct magnetic domain observation as described below.

Magnetic domains

Magnetic domains in uniaxial martensite were usually observed using magnetooptical indicator (garnet) film (MOIF) in optical polarizing light microscope. Detailed studies were done; however,

the resolution of the observation was limited by the stay field and domains in the film. We also observed the domains by SEM utilizing Lorenz Type II contrast, the method developed in FZU [18]. We also thought that we observed magnetic domains by direct observation [22]. This report was, however, mistake. Now we know that the alleged domains are twin bands either monoclinic (modulation) twins or a/b twins. Later at FZU we were able to visualize the magnetic domains by magnetic force microscopy (MFM) and comparison with other methods were done [34]. However, all these methods do not allow the dynamical observation. For such observation direct MOKE is a method of choice.

But initial attempts failed, and people resorted back to MOIF. The MOKE failed due to very low magnetooptical activity of Ni-Mn-Ga Heusler alloys which was claimed even to be zero [20]. By measuring the magnetoptical spectra in broad range we showed that in visible range the Kerr rotation can be both positive or negative depending on light used. The maximum Kerr effect occurred in violet end of spectra. And indeed, using narrow spectral blue light and sophisticated picture stabilization we were able, in cooperation with IFW Dresden, to observe magnetic domains by MOKE for the first time and to observe domain dynamics during magnetization [52,53]. We also demonstrated how the domains are skewed by the presence of fine structural twins with different crystal orientation. The domains and the interpretation of their unusual direction is shown in Fig. 17.

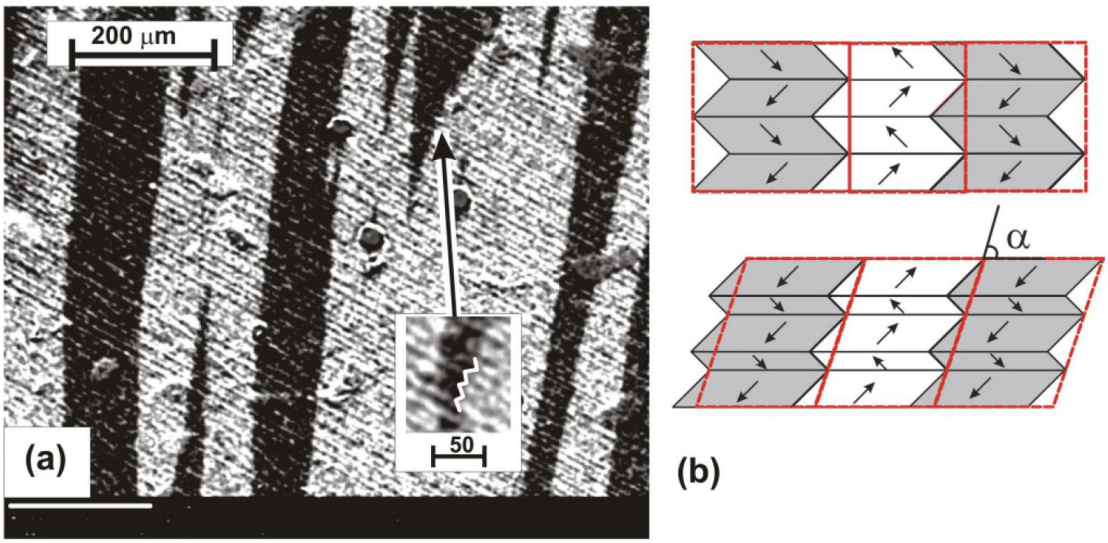

Fig. 17. *Magnetic domains of the twinned sample in the demagnetized state (a) together with sketches of the magnetic domain structure for equal (upper image) and nonequal (lower image) volumes of twins with different orientations (b). This provides the skew of the domains from the expected direction of easy magnetization axis. The inset in (a) shows an enlarged spot where the predicted "stairs" can be seen [52].*

Antiphase boundaries

Last but not least from the new observations was finding how to visualize antiphase boundaries. It started as a puzzle when using AFM/MFM instrument for magnetic domain observation on the polished surface of 10M martensite. During observation we noticed some strange curly lines in magnetic contrast with magnetization in plane. According AFM the surface was flat with no scratches and thus the contrast was indeed magnetic. In contrast to usual magnetic domain wall the line exhibits double contrast. Moreover, the contrast was much weaker than usual contrast of magnetic domain walls. In the presence of magnetization in perpendicular direction to the surface the curly lines were drowned in the domain contrast and not visible. We also found that contrast changed if the magnetization changed the direction. This is demonstrated in Fig. 18 showing two magnetic domains with opposite direction of magnetization. After some speculation excluding magnetic domains walls, we ascribed the observed curly lines to the presence of antiphase boundaries (APB) [54]. The lines are the cuts of the planar APBs by observational surface. The observation was classical case of serendipity. We suggested and developed a model of the arising contrast in MFM and explained the double contrast on these lines which allows to separate APBs from magnetic domain walls [54].

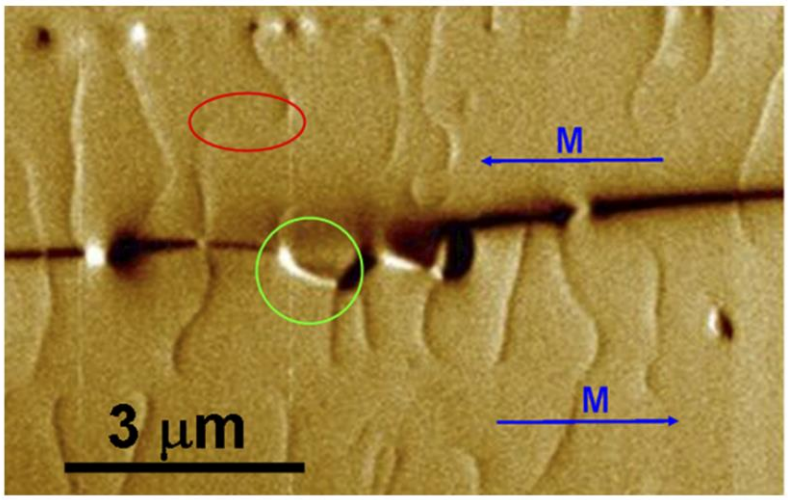

Fig. 18. *Visualization of APBs and magnetic domain wall by MFM. Magnetization directions are marked. Worm-like features are antiphase boundaries and thick mostly dark line is magnetic domain wall. The changing colour of domain wall marks the change of the chirality (an example marked by green circle). The order of dark and light contrast lines depends on the direction of magnetization. The contrast vanishes if the line is approximately parallel to magnetization (an example marked by red ellipse) [57].*

Although the observation of APB by MFM was unexpected, the presence of APBs in ordered compound is no surprise. The APB are known to be presented in $L2_1$ ordered structures and for Ni-Mn-Ga were both theoretically predicted and finally experimentally observed by TEM utilizing magnetic contrast. By traditional TEM the observation of APB in Ni-Mn-Ga is impossible as the constituting elements are close and their chemical arrangement does not provide the contrast due to large scattering length [55] Thus the presence of APB is revealed only by magnetic contrast. This on other hand indicates that the magnetic properties of APB are different from the $L2_1$ bulk.

It may be that APB contains B2 disorder or some other complex atomic arrangement. Indeed, the structure of APB is another puzzling question [56].

Why is the structure of APB important? We found that high level of APB strongly increases the coercivity of the bulk 10M martensite. The coercivity of 10M martensite is usually nearly negligible, which is quite suitable for the MIR albeit surprising as magnetocrystalline anisotropy of the materials is fairly high. Initially, the observed coercivity enhancement was ascribed to the presence of small amount of B atoms, however, it was found wrong and high concentration of APB was a real culprit. It seems that magnetic domain walls are pinned on suitable oriented APB as observation shown Fig. 18 strongly suggested.

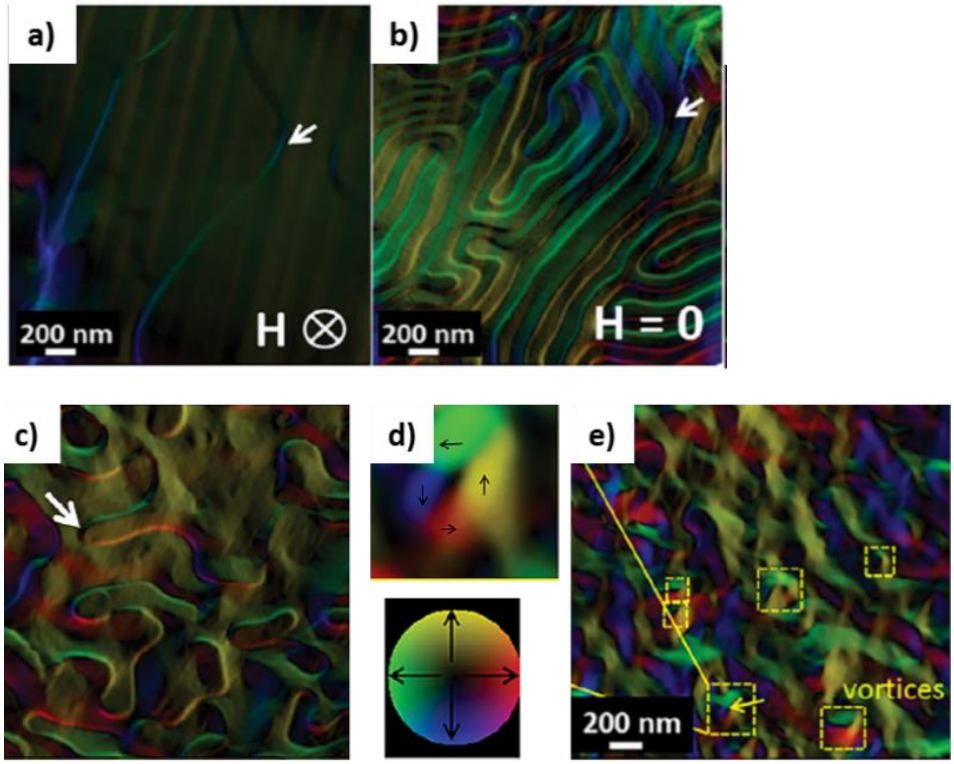

Fig. 19. *Lorenz transmission electron microscopy observation of antiphase boundaries and corresponding magnetic domains. The changes in the concentration of APB and changes of magnetic domain structure with increasing density of APB in (a) annealed, (c) air quenched and (e) water quenched sample. White arrows indicate the same location on the sample and the APB (a) and (b). The corresponding colour maps of the integrated magnetic induction (with field on (b) and off (a). (d) Detail of one magnetic vortex with the direction of induction indicated by black arrows. The colour wheel (d – bottom) indicates the direction of induction - black arrows inside the colour wheel* [56].

The higher amount of APB can be achieved by quenching the material from above ordering temperature at about 800C. The increasing coercivity in combination with MIR can provide new functionality for the material. It may be mechanically induced demagnetization and mechanical rotation of (remanent) magnetization [58]. Supposed increase density of APB was experimentally proved using dedicated experiment and by direct observation of APB density by TEM. Again, as common in this material the usual experimental method in this case TEM method for observation

of APB fails for this material and only magnetic contrast can be observed. Thanks to newly developed method using Lorenz contrast we were able to observed directly the magnetic domains, APB and their mutual interaction and formation of vortices [56], Fig. 19.

The a/b twinning

Although we have had good theoretical and structural knowledge about internal structure of twinned martensite as described in seminal papers published between 2011 and 2014 [31, 35, 45] still the direct method of observation of some of these features were missing. It was clear that optical microscopy lacks the resolution to recognize whole hierarchy of twinned structure. The SEM is then obvious choice. By careful SEM experimentation we were able to identify the structures observed by optical microscopy and additionally we observed some weak regular lines close to macroscopic and mesoscopic twin a/c twin boundaries [59]. After some struggling these were identified as a/b twinning by SEM not observed till then due to low contrast, unprecise alignment (sample tilt) and also due to small scale. After this pioneering work the boom in the observation of a/b laminate occurs and moreover the laminate was confirmed directly by EBSD [60] and even non-conventional twins were observed [61].

The observed contrast in normal SEM backscattered electron image is very weak and visible only in precise alignment of the structure and electron beam. The contrast disappears in few degrees sample tilt. From such observation we concluded that the a/b twin bands contrast can be ascribed to the channelling contrast occurring in backscattered electrons. In fact, at first the observed line features were puzzling. Using EBDS, X-ray microstructural studies and theoretical prediction we were later able to identified the features as missing a/b twinning. It was also some good luck in it as we selected the sample with regular and fairly large a/b twin bands. The new observation [59] also confirms theoretical prediction of twin branching [45]. Fig. 19 shows the a/b twinning and its branching on a/c twin boundary for Type II and no branching at Type I.

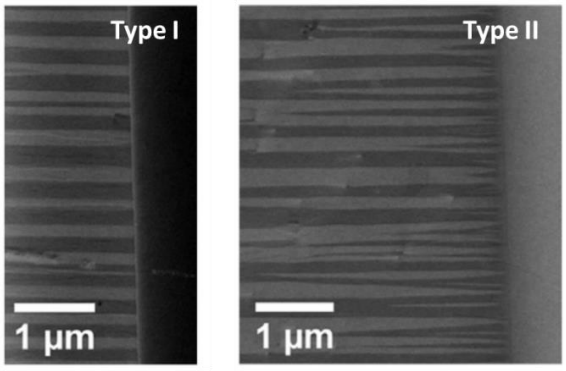

Fig. 20. *Resolved a-b twin laminate in the vicinity of Type II and Type I boundaries showing different terminations of the a-b laminate on these boundaries. The orientation of c-axis is in plane for right variant of the figure and perpendicular in the left variant [*59*].*

Later we were able even to show how the a/b twinning is evolving and getting refined with temperature and proximity of the transformations [62]. Of course, TEM can resolved greater details but TEM is not always useful as mobile twin boundary are not observable as they are wiped out by magnetic field. In general, the TEM observation is made on too small scale while we need observation on mesoscopic features and moreover a thin foil is not good approximant for the bulk. In addition, the foil deformation during sample preparation can wipe out naturally occurring twin microstructure and only some features can be captured. Observed refinement of a/b twinning observed by SEM was later used in the detailed structural studies by X-ray connected with the transition from commensurate to incommensurate modulated structure of 10M martensite [63].

Outlook – work in progress

The summary of newly developed experimental methods concludes the thesis. Apart of the progress in the theoretical approach and ab-initio calculation these experiments open new venue for the research. In the recent reviews for physica status solidi [42] and MRB [7] we have shown that MIR and N-Mn-Ga or Heusler alloys are still exciting topic for full scale research which can bring large application benefits. It may be surprising after so many years of research but truth is that the phenomenon is still quite puzzling and not well understood. The various efforts to capture the properties and performance of Ni–Mn–Ga alloys by first-principles calculations were summarized in the review [42] The review illustrates, how limited the current knowledge is, in terms of both the experimentally observed behaviour and the computational models. It outlines the broad questions arising from the comparison of experiments and models.

There are also several important properties of Ni–Mn–Ga based ferromagnetic Heusler alloys that are out of the scope of our research and thus of this thesis, first of all it is the field of magnetocaloric and its logical extension to (multi-)ferroic cooling in magnetic ferroelastic materials. But although off-stoichiometric Ni–Mn–Ga can be manipulated to exhibit first-order martensitic transformations over a broad temperature range with transformation hysteresis of only a few degrees, it is not suitable for magnetocalorics because the magnetization difference between the phases is relatively small, less than 10%. Other Heusler alloys appear to be much more suitable for magnetocaloric applications, such as off-stoichiometric Ni–Mn–X alloys with excess Mn, where X is In, Sn, or Sb. The study of such alloys motivated by magnetocalorics is a desirable extension for investigations of modulated phases.

Recently also the transport properties of Ni–Mn–Ga were the subject of research interest. For Heusler alloys, the most investigated property is either the spin-transport or spin-polarized current. This fully polarized current can occur in some semimetal Heusler alloys, for example, in Co–Mn-based alloys, as half metallicity is an important parameter for spintronic applications. However, it mainly concerns cubic structures and materials without martensite transformations.

In contrast, martensitic transformation in Ni_2MnGa is characterized by a sharp decrease in conductivity, which could be attributed to the lower electron density at the Fermi level and/or spontaneous twinning of the martensite phase, with the twin boundaries forming obstacles for electron motion. Thus, the changes in transport properties could shed some light on the topics, in particular the characteristics of the ground state; however, there remains a lack of knowledge that prevents such a link. Similarly, the negative magnetoresistance of both austenite and martensite, which sensitively changes with the chemical composition, is most likely related to the effect of doping on the magnetic states, but this understanding is also insufficient. In other words, there are numerous problems that must be treated both experimentally and theoretically for Ni–Mn–Ga systems, and breakthroughs to combine the calculations and experiments can originate from completely unexpected directions [42].

The first-principles models have not yet connected the extensive mosaic of experimental observations. However, they provide clear evidence that the unique behaviour of this material cannot be fully captured in the most basic theoretical treatments, such as in terms of finding the lowest-energy state and analysing its response to external stimuli. An explanation of the physical mechanisms thus remains a challenge for both experimentalists and theorists.

Conclusion

The thesis describes the investigation of physical principles of one of MSM phenomena – magnetically induced reorientation (MIR) and my contribution to this research. The effect was discovered in nineties of last century and I was involved in the research from the onset. The understanding summarized here is mainly phenomenological and experimental and some basic physical questions remain unsolved.

The crucial question remains what makes the Heusler Ni-Mn-Ga alloy so special? Why these materials are so susceptible to twinning deformation or differently said to shear instability essential for MIR? Connected question, which, according to my opinion, cannot be solved independently without having the answer for previous question, is how to increase the temperatures for the effect? This is the most pressing question for any application.

I was lucky to meet Kari Ullakko, discoverer of the effect, in Helsinki. His initial ideas and demands put me firmly on the experimental path in the detail investigation of magnetic shape memory phenomena, first in Helsinki, then in Dresden and finally in Prague. I would like to thank many people with whom I interact and who provide me invaluable advices. It is also partly their work while any mistake I may pursued and even unwittingly mentioned here go after me.

In the course of my research the students whom I lead and advised played important role. The most important was my first student in Finland Ladislav Straka, but I should not forget Outi Soderberg and Yanling Ge on the field of electron microscopy. Alex Soroka was another important member of the team. In Germany it was in particular R. Niemann and other students in Sebastian Fähler group. After return to Prague to FZU, I lead several students I would like to name particularly Marek Vronka on the field of TEM and Petr Veřtát on the studies of physical properties and structure of Ni-Mn-Ga.

Phenomenological understanding of MIR is now quite good also thanks to our work, but physical understanding of the phenomenon is lacking, there are still discussion on fundamental features of the crystal structure of martensite and of course of the structure of highly mobile twin boundaries and generally about microstructure allowing this high mobility. As mentioned above the question why Ni-Mn-Ga exhibit so high shear instability and elastic anisotropy is critical. These problems are also very difficult to solve theoretically as it demands large atomic assembly deeming the computation very expensive and energy demanding.

In my text I could not offer full answer to any feature of MIR I just articulated several features accessible by experiment. What is really missing is to put more flesh on the experimentally obtained bones. It may feel disheartening as even after more than twenty years we were not able to grasp the origin of the effect and obtain full understanding of the relation between crystal structure, twin boundary motion and MIR. However, I am quite optimistic that remaining puzzles can be solved soon and the research to physical fundaments of magnetically induced reorientation can be successfully concluded.

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