In Prague 29th of November, 2018

Dear Editor,

Please find enclosed our manuscript “Magnetic coercivity control by heat treatment in Heusler Ni-Mn-Ga(-B) single crystals” by authors L. Straka, L. Fekete, M. Rameš, E. Belas, and O. Heczko, which we would like to publish in Acta Materialia.

The manuscript presents new findings on the effect of thermal treatment and increased antiphase boundaries density on the magnetic coercivity of Ni-Mn-Ga magnetic shape memory alloys. In addition, broad and complete experiment proved without doubt that the coercivity enlargement is due to high density of APB not boron doping. This is necessary correction and expansion of our previously published paper in Scripta Materialia [Straka, L., et al. "Mechanically induced demagnetization and remanent magnetization rotation in Ni–Mn–Ga (–B) magnetic shape memory alloy." Scripta Materialia 87 (2014): 25-28., later supported theoretically in Peng, Qi, et al., Scripta Materialia 127 (2017): 49-53.].

Enlarged magnetic coercivity enables novel functionality in magnetic shape memory (MSM) alloys such as mechanically induced demagnetization or remanent magnetization rotation. Thus understanding how it can be achieved is an important new challenge in the MSM field. Controlling density of thermal antiphase boundaries (APBs) provides a method how to increase the coercivity without deteriorating other properties critical for the functionality, especially the ability of twin microstructure to reorient and to show magnetic shape memory functionality.

The report is not limited only to the study of the relation between the thermal treatment and coercivity but more broadly it shows the method how the antiphase boundaries can be visualized using magnetic force microscopy and especially how novel functionality can be enabled in MSM alloys. Thus we expect significant impact of the results and hope that the manuscript can be published in the journal. We believe that the manuscript fits perfectly the journal's aims and scope such as in-depth understanding of the relationship between the processing, the structure and the properties of inorganic materials ... with emphasis to functional behavior.

The manuscript is our original work and has not been submitted anywhere else.

Language editing of the manuscript has been done by a native speaker.

All authors are aware of the manuscript submission and agree on it.

All funding agencies are properly acknowledged in the manuscript.

Thank you for considering our manuscript,
Yours faithfully,

Ladislav Straka
On behalf of all authors
Magnetic coercivity control by heat treatment in Heusler Ni-Mn-Ga(-B) single crystals

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\textbf{Abstract}

The combination of enlarged magnetic coercivity and magnetic shape memory (MSM) functionality is essential for novel magnetomechanical effects in MSM alloys. We found that increasing the density of thermal antiphase boundaries (APBs) provides a method to increase the magnetic coercivity without deteriorating the MSM functionality. APB density was controlled by different heat treatments in Ni-Mn-Ga(-B) MSM single crystals with five-layered modulated martensite structure. Slow cooling ~1 K/min of Ni-Mn-Ga through the B2'–L2\textsubscript{1} transition resulted in a low density (<1/micrometer) of APBs observed by magnetic force microscopy and low coercivity <2 mT. Water quenching resulted in fine magnetic and APB patterns and enlarged the coercivity to 24 mT at room temperature, and this further increased with decreasing temperature up to 41 mT at 10 K. The analysis of magnetization approach to saturation indicated the antiferromagnetic character of APBs on which the magnetic domain walls were pinned. Despite the one to two order increase of coercivity, the twinning stress remained low, between 0.7 to 1.4 MPa, and about 6\% MSM effect was observed. The best ratio between coercivity and twinning stress (17 mT / 0.7 MPa) was obtained for the sample quenched in air. Contrary to previous reports, 100 ppm B doping of Ni-Mn-Ga had no or weak effect on the magnetic coercivity. Instead, the major effect originated from the high density of antiphase boundaries.

\textit{Keywords:} Magnetic shape memory alloys; Antiphase boundary; Magnetic properties; Coercivity; MSM functionality

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Preprint submitted to Elsevier December 11, 2018
1. Introduction

The $X_2YZ$ Heusler alloys are promising modern magnetic materials which show a plethora of multifunctional properties such as magneto-optical, magnetocaloric, magneto-resistive or magnetostructural characteristics [1, 2, 3, 4]. Ni$_2$MnGa Heusler system is yet distinct among the Heuslers for its extraordinarily strong magneto-structural characteristics manifested experimentally as the so-called magnetic shape memory (MSM) effect or magnetically induced reorientation of martensite (MIR) [5, 6]. There are only few other systems exhibiting the MSM effect or MIR such as Fe$_3$Pt or Fe-Pd [7, 8]. Among Heuslers, there are many materials exhibiting magneto-structural characteristics but have only very small or no MIR, such as Ni–Fe–Ga or Co–Ni–Al [9]. Magnetic shape memory alloys or MSMAs can be defined as multiferroic materials with interacting ferromagnetic and ferroelastic microstructure and consequent magnetostructural characteristics, which may or may not exhibit MIR.

The MIR is macroscopically manifested as giant magnetic field-induced strain or MFIS. The successful development of Ni-Mn-Ga alloys can be seen in increases in achieved maximum MFIS. Starting in 1996 with 0.2% MFIS at liquid nitrogen temperature [10], and reaching 6% MFIS at room temperature around year 2000 [11, 12] and 10% MFIS in 2002 [13], the so-far maximum of 12% MFIS has been obtained by Sozinov et al. [14] in Ni-Mn-Ga alloyed by Co and Cu in 2012. Nonetheless, not only large MFIS but also other effects related to MIR are relevant such as magnetically assisted superelasticity [15, 16, 17, 18] or strain-induced change of magnetization [19, 20, 21]. The spectrum of magnetomechanical effects observed makes the material promising for applications such as magnetic sensors, low power magnetic actuators [22], magnetic dumpers, energy harvesting devices [23], micro-actuators [24] and even magnetomechanical memories [25]. A microfluidic pump is a distinct interesting example of innovative practical use of MSM material exhibiting localized MIR [26, 27].

Recently it has been suggested that with enlarged magnetic coercivity the spectrum of interesting phenomena broadens to include mechanically-induced demagnetization (MID) and mechanically-induced remanent magnetization rotation [28, 29]. The additional effects and functionality presents a new paradigm of the interaction of magnetization with (very low) external stress and expands the application potential of MSMAs. Consequently the understanding and control of magnetic coercivity becomes of significant interest and presents a new challenge for the MSM field. Naturally it is desirable to understand the phenomena first in Ni-Mn-Ga, the most studied and so far still the most promising MSM material.
The magnetic coercivity in Ni-Mn-Ga has been sometimes reported but typically not in relation to additional functionality. For example coercivity of up to 30 mT was measured by Kök and Aydogdu [30] in Ni-Mn-Ga. Cai [31] and Zhang et al. [32] demonstrated coercivity of 120 mT in aged alloys, which was ascribed to domain wall pinning at Mn-rich γ-phase precipitates. In our previous work we ascribed an enlarged coercivity of 27 mT to boron doping [28, 33]. Mathur et al. [34] obtained coercivity of 37 mT in Ni-Mn-Ga-B-Al alloy.

It is well known and seen also in the above reports that various lattice defects and precipitates pin magnetic domain walls and thus increase the coercivity [35, 36, 37]. However these defects can simultaneously pin the martensite twin boundaries, suppressing the structure reorientation or MIR [38]. Precipitates especially, as rigid defects, cannot accommodate the large pseudoplastic strain associated with the rearrangement of ferroelastic domains. Thus they are not suitable for coercivity control in MSM alloys to achieve the novel functionality. To obtain the additional functionality, one faces the contradictory requirements to pin magnetic domain walls but not to pin martensite twin boundaries.

Antiphase boundaries (APBs) are defects in structure order which can, due to their modified magnetic properties, pin the magnetic domain walls [39, 40, 41, 42, 43, 44, 45]. Importantly, as the defect occurs only in atomic order and not in crystal structure, i.e. the lattice geometry or coherence, one can expect that APBs will be only weak obstacles for martensite twin boundary motion. Thus controlling the antiphase boundaries by thermal treatment is a promising method how to simultaneously increase the magnetic coercivity but keep the MSM properties and MIR, allowing for the desired novel functionality of the material.

Venkateswaran et al. [41, 42] observed decreased density of APBs using Lorentz microscopy in well annealed polycrystalline Ni-Mn-Ga foils in comparison to quenched samples of the same material. The decreased APB density was related to decreased magnetic coercivity (from 2.1 mT to 0.4 mT [41] or 15 mT to 5.5 mT [42]) and APBs were identified as the primary pinning sites for magnetic domain walls (see also [44]). Thus, in thin foils, the coercivity can be varied by controlling the density of APBs. Seiner et al. [46] demonstrated that the increased density of APBs in bulk material results in the change of elastic properties. However, there is no study of the relation between APB density and coercivity in Ni-Mn-Ga single crystals. Likewise, there is no report on the influence of APBs upon twin boundary mobility or material functionality. It is important to note that MIR with simultaneous large output force and large MFIS occurs only in single crystals, in spite of the efforts to achieve the same robust effect in
polycrystals, films or foams [47].

The observation of APBs is additionally complicated by the fact that the conventional TEM method cannot be used because of the large extinction coefficient of Mn and Ga [41, 42]. However, we recently found a new method using magnetic force microscopy and particularly oriented single crystals, which enables observation of the APBs directly in bulk [48].

In this work, we study the effect of different heat treatments on the density of thermal antiphase boundaries and the resulting magnetic coercivity and twin boundary mobility in Ni-Mn-Ga(-B) MSM single crystals. We observe the APBs and magnetic microstructure using magnetic force microscopy and compare these observations with magnetization loops and measurements of stress-strain curves and MIR. We demonstrate that heat treatment with a moderate cooling rate can increase the magnetic coercivity by two orders without degrading significantly the twin boundary mobility or ordinary MSM functionality of the material. Finally we compare the non-doped and B-doped material and demonstrate that B-doping is not important for magnetic coercivity increase.

2. Experimental

The {100}-cut single crystals of size 0.9×2.4×20 mm³ were obtained from Adaptamat Ltd. Nominal compositions were Ni₅₀Mn₂₈Ga₂₂ (non-doped alloy) and Ni₅₀Mn₂₈Ga₂₂B₁₀₀ppm (B-doped alloy). The crystals were initially electropolished by Lectropol-5 instrument by Struers and investigated using MFM. Then they were cut to parts of size about 0.9×2.4×6 mm³ which were characterized by magnetometry and then underwent different heat treatments followed again by grinding, electropolishing, MFM observations, and magnetometry. Three samples made of the non-doped alloy were labeled S1, S2, and S3, and one sample of the B-doped alloy was labeled S4.

The structural and magnetic transformation temperatures were determined by DC susceptibility measurement using the vibrating sample magnetometer (VSM) mode in a Physical Property Measurement System (PPMS) by Quantum Design. The temperature rate was 4 K/min and the dependencies and respective transformation temperatures were corrected for the rate.

The heat treatment was made according to programme shown in Fig. 1. As the homogenization treatment was made previously (1273 K for 48 hours) by the producer, the additional heat treatment in Ar-filled quartz ampules was only short. Samples were kept at 1273 K for 15 minutes to remove the L2₁ order and all possible defects, and then held for 60 minutes at 1073 K
Figure 1: Different heat treatments applied on samples S1–S4.

Figure 2: Magnetizing directions and resulting orientations of easy magnetization c-axis and of magnetization in samples for MFM observations.
to establish B2’ order. Sample S3 was then quenched in water (in quartz ampule), sample S2 was quenched in air (in quartz ampule), and samples S1 and S4 were slowly cooled in the furnace (~1 K/min). In additional round of measurements, sample S4 was quenched in water. The B2’→L2₁ transition temperature was estimated to be 1053 K by comparison with compositions in previous reports [49, 50]. The aim was to obtain different densities of APBs by crossing the B2’→L2₁ transition at different temperature rates. Even in rapidly quenched samples, the L2₁ order is established and dominates [49]. However, faster cooling rates gives shorter time for growth of antiphase domains, resulting in their smaller size and a higher density of thermal APBs [46, 41, 42, 51]. After heat treatment, the samples were ground with P4000 paper and electropolished for 10–20 s at 253 K and 12 V by in-house made electropolishing set-up with 75% ethanol–25% HNO₃ electrolyte.

Sample preparation for MFM observations is illustrated in Fig. 2. At first the samples were magnetized by the field of 1.4 T either in plane or out of plane. Owing to MIR, the in-plane magnetizing resulted in easy magnetization c-axis lying in plane. Similarly, the out-of-plane magnetizing in 1.4 T field resulted in easy magnetization c-axis pointing out of plane. The former orientation provides contrast from APBs and magnetic domains, while the latter orientation provides contrast mainly from magnetic domains [48]. The MFM measurements were performed using a Bruker Dimension Icon ambient AFM microscope with tips MESP-LC and MESP-HR (with magnetic CoCr coating). The image resolution was 512 × 512 points. The magnetic contrast was evaluated from the shift of the resonant frequency of the magnetic tip which followed the topography 30 nm above the surface for the in-plane measurements and 100 nm above the surface for the out-of-plane measurements.

The coercive field or coercivity Hₖ was determined as the field where magnetization loop crosses the abscissa, or more precisely as the double distance between the crossings at positive and negative field. Magnetization loops were measured along the magnetically easy direction [001], for which the magnetizing process occurs by the motion of magnetic domain walls. No coercivity is expected for other principal directions where the magnetization process occurs by magnetization rotation [42, 33]. Magnetization loops up to 9 T field were measured using the VSM option in a Quantum Design PPMS. The field sweep rate was 10 mT/s for intermediate field and when approaching saturation and 1 mT/s for measurements near zero field. Even this lowest possible sweep rate resulted in an apparent hysteresis of about 1 mT. Although corrections were made for this effect, we considered all values of sample coercivity below 1 mT.
as only informative. No corrections for demagnetization were made in the presented curves. As
the measurements were performed along the long sample axis, the demagnetization was small
and not important for the discussion presented here.

Uniaxial compressive testing was performed using in-house built instrument based on a mi-
crometer screw mechanism. The piezoelectric force sensor had 15 N range which allowed high
precision of force and stress measurement. Loading curves were measured on mechanically
extended samples. The α-axis was along the compressive stress prior to experiment and the
loading (mechanically-induced reorientation) resulted in c-axis along the stress. Only one or
two twin boundaries propagated through the sample during the measurement. Twinning stress
was determined as the average level of the twinning plateau on the stress-strain curves.

The MIR was tested by measurement of magnetization loops. Samples were first out-of-
plane magnetized (Fig. 2), which resulted in the easy magnetization c-axis pointing out of plane.
Then the samples were attached to the VSM holder by a teflon tape and the measurement was
performed with field along [100] direction coinciding with the long geometrical axis of the
sample.

3. Results and discussion

3.1. Non-doped Ni-Mn-Ga

3.1.1. MFM observations and magnetization loops in as-received Ni-Mn-Ga samples

MFM micrographs for the in-plane and the out-of-plane magnetized sample and their com-
parison are shown in Fig. 3. The curved contrast for in-plane magnetizing in Fig. 3a corresponds
to the APBs [48]. Owing to the chemical disorder and consequently depressed ferromagnetism
within APBs [41, 43], the antiphase boundary can be modeled qualitatively as a thin planar
nonmagnetic defect within the ferromagnetic matrix. The interaction of a nonmagnetic planar
defect or APB with the locally uniform magnetization generates free magnetic poles on the
APB edges resulting in bipolar out-of-plane field component. This is seen by the MFM probe as
bipolar, i.e. darker on one side and lighter on other side, “APB contrast”. Only APBs oriented
perpendicular to in-plane magnetization generate the contrast. For full APB mapping, two per-
pendicular in-plane magnetizings must be performed (not shown). Magnetic domain walls are
not seen in Fig. 3a owing to the large magnification but were also observed (not shown). From
Fig. 3a we can conclude that the linear density of APBs is of the order of 1/μm.

The magnetic domain maze pattern is seen for the out-of-plane magnetized sample, Fig. 3b.
Figure 3: Example MFM observations for as-received Ni-Mn-Ga samples S1–S3 with 10M martensite structure: a) APB contrast for in-plane magnetizing (as in Fig. 2a) b) magnetic domain maze pattern for out-of-plane magnetizing (as in Fig. 2b), and c) comparison of (a) and (b) with edge-detected APB contrast overlaid over magnetic domain pattern. Yellow rectangles point to selected similar features in the patterns indicating domain wall pinning on APBs.
Such pattern is typical for a material with uniaxial magnetocrystalline anisotropy and corresponds in character and scale to previous reports on Ni-Mn-Ga [52]. The comparison between the magnetic domains and APB contrast is shown in Fig. 3c. Virtually all APBs are decorated by magnetic domain walls, indicating the pinning of magnetic domain walls on APBs. Two selected cases are marked in the figure by yellow rectangles.

The magnetization loops of as-received samples S1–S3 are given in Fig. 4. All curves are nearly identical, which is expected for samples cut from the neighboring location of the same single crystal. The slight differences in initial slope were caused by slightly different sample lengths. For all samples the magnetic coercivity was very small, ≈0.1 mT. Thus in spite of the pinning on APBs clearly observed in Fig. 3, the overall pinning effect of low density APBs was relatively weak.

3.1.2. Effect of heat treatment on transformation temperatures in Ni-Mn-Ga

Martensite and magnetic transformation temperatures of heat treated samples are listed in Table 1. While slowly cooled sample S1 showed martensite transformation at 310 K, the quenched samples S2 and S3 exhibited an eight kelvins lower transformation temperature of 302 K. Similarly, the Curie temperature was two and four kelvins lower in air quenched and water quenched samples S2 and S3, respectively, in comparison with the Curie temperature of 377 K in slowly cooled sample S1.

The decrease of transformation temperatures in rapidly quenched samples was observed and discussed before by Chernenko et al. [53] It was ascribed to the quenched-in short range chemical disorder. It was additionally suggested that the quenching also modifies the relative stability of martensite owing to the internal stresses developed due to the high density of grain boundaries and dislocations present. Analogous to previous work, we can ascribe the decrease of transformation temperatures to the quenched-in disorder and internal stress. In Refs. [54, 55, 56], a Hopkinson peak was observed near the Curie temperature in polycrystalline Ni-Mn-Ga ribbons, which is a typical indication of internal stress. We observe a large peak for sample S3, a small peak for sample S2 and nearly no peak for sample S1, Fig. 5. This indicates stress evolution with quenching and significant internal stress for sample S3.

According to Buchelnikov et al. [57] the chemical disorder causes hardening of soft TA$_2$ mode phonon with wavevector [0.33,0.33,0]. This phonon mode is related to the initial modulations of austenite at the onset of martensite transformation [46, 58, 59]. Thus the shifts of martensite transformation temperatures might in part be caused by this phonon hardening effect.
Figure 4: Magnetization loops of as-received Ni-Mn-Ga samples S1–S3 with 10M martensite structure measured along easy magnetization axis. Curves were not corrected for demagnetization; the slight differences in initial slope are caused by slightly differing sample lengths.

Figure 5: DC magnetic susceptibility (applied field 10 mT) near Curie temperature and Hopkinson peak observed for Ni-Mn-Ga samples S1–S3 after heat treatment.

| Sample                  | $T_M$  | $T_A$  | $T_C$  | $H_C(10\,\text{K})$ | $H_C(293\,\text{K})$ | $H_C(340\,\text{K})$ |
|-------------------------|--------|--------|--------|---------------------|---------------------|---------------------|
| S1 slow cooling         | 310    | 320    | 377    | 1.3                 | 1.7                 | 2.0                 |
| S2 air quenched         | 302    | 311    | 375    | 24                  | 17                  | $\approx 0.4$       |
| S3 water quenched       | 302    | 312    | 373    | 41                  | 24                  | $\approx 0.1$       |
| S4 as received          | 315    | 325    | 371    | 42 (100 K)          | 22.0                | 3.0                 |
| S4 slow cooling         | 320    | 328    | 375    | 1.8 (120 K)         | 1.5                 | 3.0                 |
| S4 water quenched       | 316    | 324    | 369    | 41 (120 K)          | 29                  | $\approx 0.0$       |

Table 1: Transformation temperatures and coercivity determined from magnetic measurements: martensite transformation temperature $T_M \approx M_S \approx M_F$, reverse martensite transformation temperature $T_A \approx A_S \approx A_F$, Curie temperature $T_C$, and $H_C(T)$ coercivity at temperature $T$. 
3.1.3. MFM observations on heat treated Ni-Mn-Ga samples

Example MFM observations for in-plane and out-of-plane magnetized samples with different heat treatments are shown in Fig. 6.

The slowly cooled sample S1 exhibited similar in-plane and out-of plane contrasts as as-received samples, Fig. 6a–c. The APBs were clearly seen and had linear density of \(\approx 1/\mu\text{m}\), about the same as in as-received samples. The maze magnetic domains were also of similar scale. Based on this agreement and measurements of coercivity shown below we can infer that the original heat treatment on as-received samples must have been slow cooling.

The MFM micrographs of in-plane magnetized quenched samples S2 and S3 exhibited different features than sample S1, Fig. 6d, g. The curved APB pattern was not directly seen, presumably due to increased APB density and relatively low resolution of the MFM owing to the relatively large magnetic tip. However, there was a clear and dense pattern of dipole-like contrast (DLC, marked in the figure by red rectangles). This contrast was occasionally seen also in slowly-cooled samples (as marked by red rectangles in Fig. 6a). It was bipolar and depended on the magnetization direction in the same way as the observed APB contrast. Thus it originated from some kind of point-like defect interacting with in-plane magnetization in similar manner as APBs. We suggest that this defect might come either from some special arrangement within APB boundary (e.g. cluster of Mn) or from the geometry of antiphase boundaries such as crossing or sharp edge. With this assumption we can link the increasing density of dipole-like contrast (or finer patterns) with the increasing density of APBs when comparing air-quenched and water-quenched samples.

The magnetic domain patterns for out-of-plane magnetizations corresponded well to the in-plane observations. There was intermediate density of magnetic domain walls for air-quenched sample, Fig. 6 e, f and a much larger density of magnetic domain walls and smallest domains for water-quenched sample, Fig. 6 h, i. This indicates larger pinning of magnetic domain walls on a denser net of APBs.

3.1.4. Magnetization loops of heat treated Ni-Mn-Ga samples

Magnetization loops of heat-treated samples are shown in Fig. 7. Air quenched and water quenched samples S2 and S3 exhibited an increased magnetic coercivity of 24 mT and 41 mT, respectively, at 10 K, Fig. 7a, and 17 mT and 24 mT at 293 K, Fig. 7b. Slowly cooled sample S1 had much lower coercivity, less than 2 mT. All samples exhibited less than 2 mT coercivity in austenite at 340 K. The coercivities for selected temperatures are given in Table 1.
Figure 6: MFM observations for in-plane and out-of-plane magnetizing for different heat treatments of Ni-Mn-Ga samples: a–c) S1, slowly cooled, d–f) S2, quenched in air, g–i) S3, quenched in water. Antiphase boundaries (APBs) and dipole-like contrast (DLC) are marked by arrows and red rectangles.
Figure 7: Magnetization loops of heat-treated Ni-Mn-Ga samples S1–S3 for a) martensite at 10 K, b) martensite at 293 K, c) austenite at 340 K. Curves were not corrected for demagnetization.
Figure 8: Detailed magnetization loops of heat-treated Ni-Mn-Ga samples S2 (a, b) and S3 (c,d) at different temperatures. Additional fine features or nonlinearities on the loops for S3 are indicated by arrows. Curves were not corrected for demagnetization.
Figure 9: Approach to saturation at 10 K in heat-treated Ni-Mn-Ga samples S1–S3 (red line) and corresponding fits according to Eq. 1 (dashed blue line).
Detailed magnetization loops are shown in Fig. 8. There is an immediately apparent difference between air quenched and water quenched samples. The former showed uniform magnetization loops at all temperatures while the latter exhibited additional nonlinearities on the magnetization curves which developed with changing temperature. This is a strong indication of internal stress but might be partly caused by a proximity effect of APBs [60]. The internal stress can also induce residual martensite variants as observed e.g. in thin films. The volume fraction of residual variants decreases in magnetic field but they reappear due to internal stress when the field is removed. This result in nonlinearities and increased magnetic hysteresis both in first and third quadrant of the magnetization loop [61].

The approach to magnetic saturation at 10 K for all three different thermal treatments is shown in Fig. 9. The approach was much slower in air and water quenched samples S2 and S3 than in slowly cooled sample S1. The slower approach to saturation can be ascribed to the greater density of antiphase boundaries in the quenched samples.

In order to reveal more about the pinning mechanism we performed fitting of the approach-to-saturation magnetization curves following previous work by Umetsu et al. [51]. The approach to saturation was supposed to have the form of

\[ M(H) = M_S \left( 1 - \frac{a_{1/2}}{H^{1/2}} - \frac{a_1}{H} \right) + cH, \tag{1} \]

where \( c \) is high field magnetic susceptibility and \( a_{1/2} \) and \( a_1 \) are coefficients ascribed in Ref. [51] to antiferromagnetic clusters acting against magnetization and to the existence of nonmagnetic pinning defects, respectively. Similarly as the previous work we assumed the same \( c \) for all fitted curves. The fit was made only for field higher than 0.5 T and the shape demagnetization effects were neglected.

The best fits obtained and related coefficients are shown in Fig. 9 and Table 2. It is apparent that Eq. 1 describes well the observed dependencies. The \( a_{1/2} \) coefficient was dominant and significantly affected by the thermal treatment while \( a_1 \) coefficient was nearly zero for all three dependencies. More specifically, the \( a_{1/2} \) was close to zero for slowly cooled sample S1, 15 (A/m)^{1/2} for air quenched sample S2, and about double of that, 35 (A/m)^{1/2} for water quenched sample S3. The coefficient did not change significantly with increasing temperature.

The dominant \( a_{1/2} \) coefficient suggests antiferromagnetic pinning of magnetic domain walls, or, in other words, antiferromagnetic character of antiphase boundaries [51]. The increase of the \( a_{1/2} \) coefficient correlates with the increasing APBs density obtained by higher quenching.
rate. Together with MFM observations in Fig. 6 it supports the idea that the dipole like contrast (DLC) originates from antiferromagnetic order such as clusters of Mn and agrees with the notion that the antiphase boundaries are at least partly antiferromagnetic and that pinning occurs primarily on the antiferromagnetic parts of the antiphase boundaries. The topic certainly deserves deeper future investigations but these are out of the scope of this article.

3.1.5. Temperature dependence of magnetic coercivity in heat treated Ni-Mn-Ga samples

![Graphs showing temperature dependence of magnetic properties](image)

Figure 10: Relative saturation magnetization (a) and magnetic coercivity (b) as a function of temperature in Ni-Mn-Ga samples S1–S3: Red squares – S1 slowly cooled. Green circles – S2 air quenched. Blue triangles – S3 water quenched. $c \cdot M_S^2$ dependencies are marked in (b) by dashed line for S2 and S3.

The relative saturation magnetization as a function of temperature $M_S(T)/M_S(10 \text{ K})$ is given in Fig. 10a. As the long samples were not suitable for determining absolute magnetization values, we provide only informative magnitude of absolute saturation magnetization of $\approx 90 \text{ Am}^2/\text{K}$ at 10 K for all three samples S1–S3. All heat treated samples showed the same temperature dependence of $M_S$ except for a slight misfit at 310 K, which might be caused by partial transformation to austenite.
All samples displayed low coercivity in austenite, Fig. 10b, which is explained by the very low magnetocrystalline anisotropy of austenite. Since the austenite phase is not relevant for MIR, we will not discuss it further.

Magnetic coercivity of martensite as a function of temperature is shown in Fig. 10b. There were distinct differences between the samples. Slowly cooled sample S1 exhibited very small and about constant coercivity over the entire temperature range. Air quenched sample S2 exhibited some increase of coercivity with decreasing temperature, which saturated at low temperatures. Water quenched sample S3 exhibited the similar increase of coercivity as S2 but moreover there was an additional gradual increase at low temperatures. This increase at low temperatures might have the same origin as the extra features on the magnetization loops, Fig. 8c, d – quenched-in internal stress which increased with lowering temperature due to a change in lattice constants.

Alternatively the anomalous increase of coercivity at low temperature can be related to the thermal activation of magnetic domain walls. This becomes important when the area of the domain wall segment involved in the elementary thermally activated process becomes small. Thermal activation then causes a linear decrease of coercivity with temperature [62, 63, 64].

When disregarding sample S1 with small coercivity and the low temperature region for S3, the dependencies $H_C(T)$ scale well to $M_S^2(T)$, i.e. $H_C(T) \sim M_S^2(T)$, Fig. 10b. Considering further that anisotropy constant

$$K_1(T) \sim M_S^2(T)$$

(2)

in 10M Ni-Mn-Ga martensite [65], it is then obvious that the coercivity is directly proportional to anisotropy field $H_C(T) \sim K_1(T)/M_S(T) \sim H_A(T)$, or shortly $H_C \sim H_A$.

According to micromagnetic model by Paul [66, 67] the coercivity field $H_C$ resulting from planar defects such as APBs can be expressed as

$$H_C = \frac{K_1}{M_S} h_C = \frac{1}{2} H_A h_C,$$

(3)

where $h_C$ is the reduced coercive field being a function of magnetic parameters of the matrix and the planar defect and its width. Upon initial analysis, the observed dependencies follow the theory, however, $h_C$ is also temperature dependent in a nontrivial way. Alternative theories on planar defect coercivity [35, 64] predict $H_C(T) \sim M_S(T)^{7/2}$ when using Eq. 2, i.e. much higher exponent than we observe.
3.1.6. Twin boundary mobility and MIR in Ni-Mn-Ga

The compressive stress-strain curves are shown in Fig. 11. Only one or two twin boundaries propagated through the sample during the tests. Thus the level of detwinning plateau reflected the mobility (twinning stress) of the individual twin boundary. Based on the comparison with previous works, the twin boundaries in question were of type 1 for all measurements as the twinning stress was relatively high [68, 69, 70].

From the measurement it can be seen that the twinning stress was slightly influenced by the thermal treatment. For slow cooling and air quench the position of twinning plateau or twinning stress was on average about 0.7 MPa. The twinning stress was larger, 1.4 MPa, for water quenched sample. That may again indicate the presence of internal stress in the sample hindering twin boundary motion. Importantly, twinning stress was low enough (<3 MPa) for all three treatments to allow for MIR and other related magnetomechanical effects and functionality.

The MIR was tested by measurement of magnetization loops along [100] direction, Fig. 11b. The MIR was clearly seen for all specimens as an abrupt jump on magnetization loops and associated large hysteresis in the first quadrant [12]. The relative position of magnetization jumps corresponded to twinning stress measurements as the switching field was largest for water quenched sample. Nearly 6% MIR in all specimens was confirmed additionally by the measurement of elongation prior and after magnetizing by 1.4 T field.

3.1.7. Summary for Ni-Mn-Ga

The thermal treatment had profound effect on the microstructure as well as on the coercivity in martensite. Slow cooling resulted in small coercivity and low density of APBs. Quenching resulted in fine magnetic microstructure observed for in-plane magnetization indicating a high density of APBs. This high density of APBs resulted in fine magnetic domains for out-of-plane magnetization and enlarged coercivity, which further increased with decreasing temperature. Air quenching increased the coercivity but not the twinning stress. Water quenching increased both coercivity and twinning stress. However, MIR was observed for all these three treatments.

3.2. Doped alloy Ni-Mn-Ga-B

The light boron doping was indicated to be the main cause of enlarged coercivity in previous reports [28, 33]. To further understand the properties of the previously studied B-doped alloy and for comparison with non-doped alloys, we studied the effects of thermal treatment also in a B-doped Ni-Mn-Ga sample. Based on the comparison we come to the conclusion that thermal
Table 2: Fitting coefficients according to Eq. 1 for approach to saturation at 10 K.

| Sample                  | $a_1$       | $a_{1/2}$  | $c$       |
|-------------------------|-------------|------------|-----------|
| S1 slow cooling         | $2 \times 10^{-2}$ | 0          | $6 \times 10^{-11}$ |
| S2 air quenched         | $2 \times 10^{-2}$ | 15         | $6 \times 10^{-11}$ |
| S3 water quenched       | $2 \times 10^{-2}$ | 35         | $6 \times 10^{-11}$ |

Figure 11: a) Compressive stress-strain tests on Ni-Mn-Ga samples S1–S3 performed at room temperature. b) Measurement of magnetization loops along [100] in order to detect the MIR. The occurrence of MIR is marked by arrows.
treatment is actually the main cause of the increased coercivity, not the boron doping.

3.2.1. Effect of heat treatment on transformation temperatures in Ni-Mn-Ga-B

The martensite and magnetic transformation temperatures of heat treated Ni-Mn-Ga-B sample S4 are listed in Table 1. The transformation temperatures were several kelvins higher for the slowly cooled sample than for the as-received (or water quenched) sample S4. This indicates, analogous to the above discussion on non-doped samples, that as-received sample underwent some kind of quenching or fast cooling treatment at the producer. The producer indicated “heat treatment at 1093 K and quenching in air”. This is different from the as-received non-doped Ni-Mn-Ga samples, which apparently underwent heat treatment with slow cooling.

3.2.2. MFM observations and magnetization curves of as received Ni-Mn-Ga-B samples

MFM observations of in-plane and out-of-plane magnetized Ni-Mn-Ga-B sample S4 are shown in Fig. 12. There was a dense pattern with dipole-like contrast on the as-received sample similar to that observed in water quenched sample S3, Fig. 12a. The magnetic domain pattern for out-of-plane magnetizing was correspondingly dense, Fig. 12b, c. Thus, as the MFM observations of as-received sample S4 were qualitatively the same as for sample S3, the samples could be expected to show also comparable magnetic hysteresis. This was confirmed by the magnetization loop measurements in Fig. 13a, which shows that the hysteresis was 22 mT at room temperature. The loop exhibited similar fine features as the water quenched sample S3, Fig. 8 c, d.

The similarity of magnetic microstructure and coercivity between the water-quenched Ni-Mn-Ga and the as-received sample S4 motivated the additional heat treatment experiments with slow cooling and water quenching of sample S4 (Fig. 1).

MFM micrographs of slowly cooled sample S4 are shown in Fig. 12d, e, f. The curved pattern of APB contrast with low density of APBs was clearly observed for in-plane magnetization, Fig. 12d. The APB pattern was very similar to that for slowly cooled sample S1, Fig. 6a–c. The magnetic domain contrast for out-of-plane magnetization was also correspondingly coarse, suggesting the same low coercivity as in S1. This was directly confirmed by the measurement of magnetization loops, Fig. 13a. The coercivity was less than 2 mT in slowly cooled Ni-Mn-Ga-B sample in martensite state (Table 1).

There were close similarities between the behaviors of Ni-Mn-Ga-B and Ni-Mn-Ga alloys. Quenched samples S2 and S3 of Ni-Mn-Ga exhibited enlarged coercivity ≈20 mT, compara-
Figure 12: MFM observations of B-doped Ni-Mn-Ga for in-plane and out-of-plane magnetizing: a–c) S4 as received, d–f) S4 after slow cooling in furnace. Antiphase boundaries (APBs) and dipole-like contrast (DLC) are marked by arrows and red rectangles.
Figure 13: Magnetization loops (not corrected for demagnetization) for B-doped Ni-Mn-Ga: a) S4 as-received and S4 after slow cooling in furnace. b) S4 after additional quenching in water. Small artifacts around ±0.1 T are caused by change of field sweep rate.
ble to the ≈20 mT coercivity of (quenched) as-received Ni-Mn-Ga-B (S4). Likewise, when
the Ni-Mn-Ga-B sample S4 underwent heat treatment with slow cooling, its coercivity dropped
significantly to a few mT as found also for slowly cooled Ni-Mn-Ga sample S1. Correspond-
ing magnetic microstructure observations were nearly identical in Ni-Mn-Ga and Ni-Mn-Ga-B
alloys (compare Figs. 6 and 12).

The above observations implied strongly that B-doping actually played no role in magnetic
coefficency and that all effects could be ascribed to heat treatment instead. To confirm the idea,
we performed additional water quenching using previously slowly-cooled sample S4. After this
final water quenching, sample S4 exhibited similar features as the water quenched Ni-Mn-Ga
sample supporting our hypothesis.

The MFM observation for sample S4 quenched in water were nearly identical to those for
water quenched sample S3, Fig. 12g, h, i. The room temperature magnetization loop for S4
quenched in water is displayed in Fig. 13b. The coercivity was 29 mT, comparable to water
quenched non-doped sample S3 (see also Table 1). The curve showed significant nonlinearity,
which may be ascribed to internal stress and complex magnetization processes in the sample.
Similarly as discussed above for sample S3, the nonlinearity can reflect the presence of magnet-
ically hard residual martensite variants, reduced by the field during magnetization but restored
by the internal stress when the field is removed.
3.2.3. Temperature dependence of magnetic coercivity in Ni-Mn-Ga-B

![Graph](image)

**Figure 14:** Relative saturation magnetization (a) and magnetic coercivity (b) as a function of temperature in B-doped Ni-Mn-Ga: Blue triangles – S4 as received. Red squares – S4 after slow cooling in furnace. Green circles – S4 after additional quenching in water.

The temperature dependencies for B-doped Ni-Mn-Ga are summarized in Fig. 14. The saturation magnetization as a function of temperature showed a sudden drop between 90 and 50 K, Fig. 14a. This was caused by intermartensite transformation to seven-layered modulated or non-modulated martensite. The low-temperature (<100 K) phases are not investigated here and are not further discussed.

The magnetic coercivity as a function of temperature is displayed in Fig. 14b. There was a very distinct difference between the as-received and slowly cooled sample with the former showing relatively high coercivity of up to 42 mT at 100 K and the latter <2 mT coercivity throughout the measured temperature range. The water quenched sample S4 showed similar magnitudes and dependencies of coercivity as the as-received sample S4. The coercivity in austenite was only slightly larger, about 3 mT for both as-received as well as slowly cooled sample comparable to non-doped samples. At low temperatures the measurement was limited
by intermartensite transformation but despite this the trends are clearly seen. The coercivity of the as-received and water quenched sample S4 increased with decreasing temperature similarly as in non-doped water quenched sample S3, and scaled similarly well with $M_S^2$. The similar temperature dependence of coercivity in samples S3 and S4 and similar extra features on their magnetization loops indicated the same origin of their coercivity and minor or no role of boron doping.

4. Conclusion

In this work, we proposed and explored heat treatments to control APB density in Heusler Ni-Mn-Ga MSM alloys as a method to enlarge magnetic coercivity without deteriorating MIR or the ability of twin microstructure to reorient. Moreover, we disproved the notion that B-doping is necessary for enlarged coercivity.

In non-doped Ni-Mn-Ga alloy, we found that air and water quenching generate a dense net of antiphase boundaries resulting in fine magnetic domain structure and enlarged coercivity up to 41 mT at 10 K and 24 mT at room temperature. Heat treatment with slow cooling results in a low density of antiphase boundaries (<1/µm) and coercivity less than few mT. Antiphase boundaries of low density were observed by MFM directly while highly dense APBs were seen only indirectly as dipole-like contrast. We suggest that the dipole-like contrast may come from Mn clusters or geometry of antiphase boundaries (crossing or sharp edge). The inverse square-root dependence of the magnetization approach to saturation suggests antiferromagnetic character of the antiphase boundaries.

The mobility of individual martensite twin boundaries is influenced only moderately by the thermal treatment as the twinning stress doubles to 1.4 MPa in water quenched sample in comparison to 0.7 MPa in slowly cooled sample. This increase does not prevent the normal MSM functionality as all heat treated samples showed nearly full 6% MFIS in 1.4 T magnetic field. Considering the benefit of coercivity enlargement against decreased twin boundary mobility, the air quench may be the most suitable treatment to obtain enlarged coercivity. It provides large enough coercivity (17 mT) but simultaneously keeps very high twin boundary mobility (0.7 MPa).

In B-doped Ni-Mn-Ga, we found nearly identical features and behavior in as-received and water quenched samples as in non-doped water quenched samples. Furthermore, after heat treatment with slow cooling, the B-doped alloy showed nearly identical characteristics as the
slowly cooled non-doped alloy. This gives the inevitable conclusion that light (100 ppm) boron doping plays little or no role in the control of magnetic coercivity of Ni-Mn-Ga. This is contrasting our previous reports [28, 33], where the B-doping was thought to be the origin of coercivity increase. Here we conclude, based on the comparison with non-doped alloys, that the primary reason for the enlarged coercivity is actually the heat treatment with quenching or rapid cooling, not boron doping.

In summary, the cause of enlarged coercivity is rapid cooling from above the ordering temperature both in Ni-Mn-Ga as well as in Ni-Mn-Ga-B. Increased coercivity correlates with the increased density of APBs, identifying the APBs as the primary origin of the coercivity increase. However, there seems to be also some effect from quenched-in internal stress, which becomes significant especially at large cooling speeds (water quench) in the thermal treatment. In samples with moderate cooling speeds (air quench), the internal stress seems to be low as indicated by the unchanged high mobility of twin boundaries. Thus, in this case, the ordinary MSM functionality such as the 6% MFIS is possible, maintaining original large efficiency, while the novel functionality such as MID [28, 29] is additionally enabled.

Acknowledgment

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 701867 – FUNMAH. This work was supported by the Czech Science Foundation [grant number 16-00043S] and Czech MEYS project LO1409 and infrastructure project SAFMELT LM2015088. The work was supported by the Ministry of Education, Youth and Sports of the Czech Republic within the program OP VVV “Excellent Research Teams” under Project CZ.02.1.01/0.0/0.0/15_003/0000487-MATFUN. Some magnetic measurements were performed in the Materials Growth and Measurement Laboratory MGML (see: http://mgml.eu). We kindly thank Alexei Sozinov for fruitful discussion on thermal treatment, Ross Colman for help with sample cutting, and Andrew Armstrong for twinning stress measurements.

Declarations of interest: none

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Scripta Mat. 67 (1) (2012) 25–28.
SLOW COOLING – APBs <1/μm, \( H < 2 \) mT

QUENCHING – dense APBs, \( H_c > 20 \) mT

Ni-Mn-Ga(-B) MSM single crystals

MSM functionality did not deteriorated

\( H_c = f(T) \)