Domain model for the magnetic shape-memory effect in non-modulated tetragonal Ni-Mn-Ga

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Abstract. We employ a general phenomenological domain theory for ferromagnetic shape memory (FSM) materials to model equilibrium domain states in martensites with tetragonal twin variants having axes ratios $c/a > 1$ and easy-plane magnetic anisotropy. The model is evaluated for realistic material parameters of non-modulated (NM) Ni$_2$MnGa alloys. Phase diagrams under competing external stresses and magnetic fields are presented that show regions of fully magnetized single-variant states and various multiphase regions. The theoretical elastic stresses that block single-variant states are found to be much smaller in NM than in the 5M structure of Ni$_2$MnGa alloys.

1. Introduction

The magnetic shape-memory effect relies on the rearrangement of crystallographic twin variants in ferromagnetic martensitic microstructures [1]. It has been argued that modulated structures, as the 5M or 7M structure in the archetypical Ni-Mn-Ga FSM alloys, can be construed as adaptive martensite [2] and that these nano-twinned microstructures are crucial for the FSM effect to reach large field-driven strains up to 10%. However, experiments on single crystals of Ni-Mn-Ga Heusler alloys in the non-modulated (NM) state with tetragonal axis ratio $c/a = 1.18$ find sizeable field-driven strains up to 0.1% [3]. As these alloys own uniaxial magnetic anisotropy of the easy-plane type, their magnetic behavior and the FSM effects are different, as compared to the pseudo-tetragonal easy-axis behavior in the modulated Ni-Mn-Ga structures.

Based on a phenomenological domain model, we here report theoretical phase-diagrams depending on applied magnetic fields and stresses. These diagrams can be used to distinguish the FSM behavior in NM Ni-Mn-Ga from the behavior of the usual modulated easy-axis alloys. The model was presented previously [4] and was worked out for easy-axis systems and for the easy-plane case with relevant tetragonal anisotropy, yielding four-fold magnetic domains in each variants. It has been applied to calculate twin-variant and domain-state phase diagrams for modulated Ni-Mn-Ga with pseudo-tetragonal structure and axis ratio $c/a < 1$ and for Fe-Pd [5].

2. Domain model

The total energy $E_t$ of the twinned ferromagnetic structure is composed of an elastic part $E_{el}$ and a magnetic energy $E_m$:

$$E_t = E_{el}(\hat{u}) + E_m(M)$$

depending on strain tensor $\hat{u}$ and magnetization $M$. The domain state model for thermodynamic equilibrium states in such a ferromagnetic twinned microstructure assumes that the material can
be decomposed into homogeneous twin variants with uniform strain and matching boundary conditions at twin boundaries. These crystallographic domains may be further subdivided into different magnetic domains. For details, see Ref. [5]. The magnetic properties are described within a simplified micromagnetic approach appropriate for bulk systems. Thus, the magnetic energy contribution from one twin variant labelled \( l \) is given by

\[
E^l_m = -\mu_0 M_s \mathbf{m} \cdot \mathbf{H}^{(ext)} - \frac{1}{2} \mu_0 M_s \mathbf{m} \cdot \mathbf{H}^{(demag)} + w^l_0(\mathbf{m})
\] (2)

with the external magnetic field \( \mathbf{H}^{(ext)} \), the demagnetization field \( \mathbf{H}^{(demag)} \), the intrinsic magnetic anisotropy energy \( w^l_0(\mathbf{m}) \). Here, \( \mu_0 \) is the magnetic vacuum permeability, \( M_s \) is the saturation magnetization, and \( \mathbf{m} = \mathbf{M}/M_s \). For martensites with tetragonal crystal structure the three twin variants can be labelled \( l = x, y, z \) by the orientation of the unique axis. The magnetic anisotropy of variant \( z \) is

\[
w^z_0(\mathbf{m}) = B_1 (\mathbf{m} \cdot \mathbf{\hat{z}})^2 + B_2 (\mathbf{m} \cdot \mathbf{\hat{z}})^4 + B_3 (\mathbf{m} \cdot \mathbf{\hat{x}})^2 (\mathbf{m} \cdot \mathbf{\hat{y}})^2.
\] (3)

In Ref. [5], magnetic phase diagrams have been analysed for modulated Ni-Mn-Ga with easy-axis anisotropy, \( B_1 < 0 \) and \( B_2, B_3 \equiv 0 \), and for easy-plane anisotropy with \( B_1 > 0, B_1 > -B_2 \) and strong 4-fold anisotropy \( B_3 \neq 0 \). Both systems have been modelled as pseudo-tetragonal crystals with axis ratio \( c/a < 1 \). In non-modulated (NM) Ni-Mn-Ga with the tetragonal structure \( c/a > 1 \) and easy plane anisotropy, the four-fold anisotropy is expected to be weak, and we set \( B_3 = 0 \). As saturation of twins is achieved already in very small magnetic fields, we assume full saturation of the twin variants. This means that the model neglects magnetic domain structures within the single twins. Owing to the easy-plane character of its uniaxial anisotropy, the domain structure in NM is different from domain structures in easy-axes systems: the easy magnetization directions of two differently oriented twins intersect in a certain joint easy axis [6]. This is the reason why the magnetic anisotropy of modulated adaptive martensites, that are composed by NM variants with easy-plane anisotropy, acquires an effective easy-axis character [2]. Magnetic domains may encompass two different twins, if the magnetization oriented along this common easy direction, and twin boundaries are not necessarily associated with a magnetic domain wall. This type of domain structure has been observed in experiments on NM Ni\textsubscript{2}MnGa[7].

The microstructure of a bulk sample is described by the volume fractions \( \xi_l \) of the three variants, \( l = x, y, z \) and \( \sum_l \xi_l = 1 \), see Fig. 1. To solve the magnetostatic problem, the phase-theory approximation [8],[9] is used, as discussed in Ref. [5].

For the evaluation of phase diagrams, we have employed different sets of elastic constants and magnetic materials constants. Only one complete set of elastic constants from experiments has been reported for a Ni-Mn-Ga alloy with the pseudo-tetragonal 5M structure [10]. For
stoichiometric NM Ni\textsubscript{2}MnGa, theoretical values of the constants from density functional theory calculations (DFT) have been presented by Özdemir Kart et al. \cite{11}. These constants are listed in Table 1 in our notation of \cite{5}. Magnetic anisotropies for NM Ni-Mn-Ga have been reported earlier \cite{12}, but very recently a new measurement has been performed \cite{13}. Corresponding magnetic constants and the deviatoric strain from Refs. \cite{13} and \cite{12} along with the demagnetization tensor components \( N \) are listed in Table 2. Our calculations have first been done using the earlier experimental data for elastic constants Table 1 (A) and magnetic anisotropy model Table 2 (I), as representative for the Ni-Mn-Ga system generally. This is model AI in an obvious notation. In order to quantify the dependence of the phase diagrams on the different materials constants, we have compared them also with the corresponding model BII, which may provide a better description of NM Ni-Mn-Ga. While there are quantitative differences, the qualitative behavior is identical for the two models.

### Table 1.
Elastic constants (in GPa) in Voigt notation and in our notation from Ref. \cite{5}. (A) experimental data for 5M pseudo-tetragonal structure from Ref. \cite{10} and (B) theoretical calculations for non-modulated Ni\textsubscript{2}MnGa from Ref. \cite{11}.

| Material & method       | \( c_{11} \) | \( c_{12} \) | \( c_{13} \) | \( c_{22} \) | \( c_{23} \) | \( c_{33} \) | \( c_{44} \) | \( c_{55} \) | \( c_{66} \) |
|------------------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| (A) Ni\textsubscript{0.5}Mn\textsubscript{0.28}Ga\textsubscript{0.216} 5M experiment | 179         | 163         | 161.4       | 39.54       | 47.51       | 45.0        |
| (B) Ni\textsubscript{2}MnGa NM by DFT                  | 249         | 193         | 141         | 71          | 101         | 56          |

### Table 2. Magnetic constants, deviatoric strain \( e_0 \) and demagnetization tensor used in the calculations. Experimental magnetic anisotropy constants for NM Ni-Mn-Ga are (I) from Ref. \cite{12} and (II) new experiments, Ref. \cite{13}.

|                | \( B_1 \)        | \( B_2 \)        |
|----------------|------------------|------------------|
| (I)            | \(-0.24+0.06\) MJ/m\(^3\) | \(0.06\) MJ/m\(^3\) |
| (II)           | \(-0.26\) MJ/m\(^3\)          |                  |
| \( M_s \)      | 0.422 MJ/(Tm\(^3\))          |                  |
| \( e_0 \)      | -0.21             |                  |
| \( N_x \)      | 0.2               |                  |
| \( N_y \)      | 0.2               |                  |
| \( N_z \)      | 0.4               |                  |

### 3. Results

#### 3.1. Phase diagrams

Phase diagrams have been analysed for bulk single crystals with ellipsoidal shape, having principal axes along the crystallographic directions of the 4 tetragonal variants, see Table 2. If such single crystals show good FSM behavior, the microstructure is expected to consist of macroscopic twins separated by few mobile twin boundaries. Moreover, usually only one twinning system is active, so that only two twin variants exist in a simple lamella structure. Nucleation of the third variant in such a structure creates large elastic stresses, as it is impossible to fulfill simultaneously compatibility conditions at the interfaces of all variants. Thus, nucleation of the third variant is effectively blocked. For the phase diagrams in Figs. 2, such a simple twinned structure is assumed to consist of \( y \) and \( z \) variants, while no \( x \) variant is permitted. The applied magnetic fields along \( z \) axis, left panel Fig. 2, or in the \( x0z \)-plane, right panel always favour the \( y \) variant. Thus, under tensile stresses \( \sigma_{yy} > 0 \) in \( y \) direction a pure \( y \) single-variant state exists. Compressive stresses \( \sigma_{yy} < 0 \) favour the \( z \) variant, but the magnetic field with finite components in \( z \) direction generates thermodynamically stable domain states.
Figure 2. Phase diagram for non-modulated Ni$_2$MnGa alloys. Only the twinning system composed of $x$ and $y$ variants is active, and the nucleation of the $x$-variant is blocked. Left panel: magnetic field in $z$ direction and stresses in $y$ direction $\sigma_{yy}$. Right panel: Magnetic fields in $xz$-plane under strong compressive stresses $\sigma_{yy} = -0.6$ MPa < 0.

Figure 3. Phase diagram for non-modulated Ni$_2$MnGa alloys under applied fields in $xz$-plane under weaker compressive stresses allowing nucleation of the $y$-variant in oblique fields. Left panel: Model AI with $\sigma_{yy} = -0.1$ MPa < 0. Right panel: Model BI with $\sigma_{yy} = -0.25$ MPa < 0.

A rotating field in the $x0z$-plane under compressive stress $\sigma_{yy} < 0$ reveals a FSM behavior with a redistribution between the available $y$ and $z$ variants and a thermodynamically stable twinned structure for fields applied close to (101) directions. For large compressive stresses, the $z$ single-variant state is blocked. Releasing the constraint of a $y$-$z$ twinning system, the fields applied in $x0z$ plane will alternatingly favour $z$ and $x$ variants. In the simplest phase diagram under large compressive stresses $\sigma_{yy} < 0$, the occurrence of $y$ variants is completely suppressed. However, for smaller stresses, the $y$ variant can be nucleated for fields close to the (101) direction, Fig. 3. In a small rotating field, a succession of pure $z$ and $x$ single-variant states, separated by intermediate stable domain states, is found under these conditions. But for larger fields, a succession of pure $z$, $y$ and $x$ single-variant states takes place with intervening mixed states. In increasing fields under fixed angle close to (101) directions, transformations between intermediate states from an $x-z$ twinned structure towards $z-y$ or $y-x$ twinned structures are indicated as ”1st-order lines” in Fig. 3. This domain process is hindered by the provision that the third $y$ variant cannot be nucleated in the $z-x$ twinning structure. However, the 1st order process could take place via another intermediate domain state, where $x-z$ twinned plates co-exist either with $y-x$ or
Figure 4. Blocking stress in dependence on angle of internal field $\phi_0$. Thicker (blue and red) lines for non-modulated tetragonal Ni-Mn-Ga: $\sigma_{yy}$ calculated from Eqs. (4,5) is the equilibrium blocking stress for the $y$-variant in magnetic saturation. The upper lines are for the model with materials parameters AI, the lower with parameters BII. Below the blue lines, only the $x$ variant exists, below the red lines, only the $z$ variant. At the dotted vertical line these two variants coexist. Above the lines, the $y$ variant can be stabilized by a sufficiently strong applied magnetic field in the $x0z$-plane. Thinner (green) line gives the blocking stress for the pseudo-tetragonal 5M martensite with $c/a < 1$, according to Ref. [5]: large compressive stress $\sigma_{xx} < 0$ stabilizes the $z$ variant, large tensile stresses $\sigma_{xx} > 0$ stabilize the $z$-variant. Note the scaling factor $\times 0.1$ for the blocking stress of 5M Ni-Mn-Ga.

3.2. Blocking stress

In Ref. [5], we have defined the blocking stress as the applied stress that enforces, in equilibrium, a single twin variant in its fully saturated state. It can be calculated by comparing the total energies of the different pure states. For the easy axis twins with $c/a > 1$, a sufficiently strong compressive stress $\sigma_{yy} < 0$ stabilizes the $x$ or $z$ and suppresses the $y$-variant. Conversely, an internal field applied in the $x0z$-plane favours the $y$ variant. If the internal field subtends an angle $\phi_0 \in (0, \pi/4)$ with the $\hat{z}$ axis, then the $y$ variant will have lowest magnetic energy, followed by the $x$ variant, and the least favoured variant is $z$. For $\phi_0 = \pi/4$ the $x$ and $z$ variants are equally favourable magnetically and can co-exist. At this point we will have the largest anisotropic magnetic energy that can be used to overcome applied stress. Excluding common terms the total energy can be written in the pure $y$ case as:

$$ E_t|_{\xi_y=1} = -\frac{c_2 e_0^2}{2} + \sigma_{yy} \left( e_0 - \frac{(c_1 + c_3)\sigma_{yy}}{2c_2(c_1 + c_3) - 4c_4^2} \right) - \mu_0 M_s h_0. \quad (4) $$

and for the $x$ and $z$ variants:

$$ E_t|_{\xi_x+\xi_z=1} = \frac{1}{2} \left( \frac{(-c_1 c_2 + c_4^2)\sigma_{yy}^2}{(c_1 - c_3)(c_2(c_1 + c_3) - 2c_4^2)} - c_2 e_0^2 \right) \right) $$

$$ + \sum_{l=x,z} \xi_l \left[ -\mu_0 M_s h_0 (\cos \phi_l \cos \phi_0 + \sin \phi_l \sin \phi_0) + B_1 (m_l \cdot \hat{l})^2 + B_2 (m_l \cdot \hat{l})^4 \right]. \quad (5) $$
where the magnetization vectors of the $l$-variants are written $m_l = (\sin \phi_l, 0, \cos \phi_l)$ and $h_0$ is the magnitude of the internal field. For $\phi_0 \in [0, \pi/4]$ only the pure $x$ variant exists $\xi_x = 1$, and for $\phi_0 \in (\pi/4, \pi/2]$ only the pure $z$ variant. In both cases, the fully saturated states have $\phi_l = \phi_0$. Only at $\phi_0 = \pi/4$ the $x$ and $z$ variant co-exist having the same magnetic energy. From symmetry, one sees that the elastic part of equation (5) also does not depend on the volume fraction of the $x$ and $z$ variants. At the equilibrium blocking stress, the energies (4) and (5) must become equal. The largest stress $|\sigma_{yy}|$ is reached for $\phi = \pi/4$. The dependence of the blocking stress for two different choices of materials constants on $\phi_0$ is plotted in Fig. 4 and compared with blocking stress for 5M easy-axis Ni-Mn-Ga. In the isotropic case the expression of the equilibrium $\sigma_{yy}$ simplifies to

$$\sigma_{yy} = \frac{B_1 \cos^2(\phi)}{\epsilon_0} \tag{6}$$

with a maximum value $B_1/(2\epsilon_0)$.

4. Conclusions
The theoretical model demonstrates important differences in the field- and stress-driven microstructure processes of non-modulated Ni-Mn-Ga. Most importantly, there are certain experimental settings combining stresses and fields as in Fig. 3, would allow to discern whether a FSM derives from an easy-axis or an easy-plane magnetic system. Moreover, the single-variant states in NM Ni-Mn-Ga are blocked by much smaller stresses than in the modulated 5M Ni-Mn-Ga. Therefore, applied stresses will tend to block variants rather than to drive twin boundary motion, unless twinning stresses are comparably small.

Acknowledgments
We acknowledge stimulating discussions with S. Fähler, O. Hečzko, and S. Kaufmann. Supported by DFG SPP1239 (http:www.magneticshape.de) through project RO2238/8.

References
[1] Ullakko K, Huang J K, Kantner C, O’Handley R C and Kokorin V V 1996 Appl. Phys. Lett. 69 1966
[2] Kaufmann S, Rößler U K, Hečzko O, Wuttig M, Buschbeck J, Schultz L and Fähler S 2010 Phys. Rev. Lett. 104 145702
[3] Chernenko V A, Chmielus M and Mülner P 2009 Appl. Phys. Lett. 95 104103
[4] Bogdanov A N, Desimone A, Müller S and Rößler U K 2003 J. Magn. Magn. Mater. 261 204–209
[5] Onisan A T, Bogdanov A N and Rößler U K 2010 Acta Mater. 58 4378
[6] Lvov V A, Gomonaj E V and Chernenko V A 1998 J. Phys.: Condens. Matter 10 4587
[7] Chernenko V A, Lvov V A, Besseghini S and Murakami Y 2006 Scripta Mater. 55 307
[8] Néel L 1944 J. de Physique Radium 5 241
[9] Hubert A and Schäfer R 1998 Magnetic domains (Berlin: Springer)
[10] Dai L, Cullen J and Wuttig M 2004 J. Appl. Phys. 95 6957
[11] Özdemir Kart S, Uludoğan M, Karaman I and Çağın T 2008 phys. stat. sol. (a) 205 1026
[12] Straka L and Hečzko O 2003 J. Appl. Phys. 93 8636
[13] Hečzko O, Straka L, Novak V and Fähler S 2010 J. Appl. Phys. 107 09A914