Magnetic and magnetoelastic properties of Ni-Mn-Ga – Do they need a revision?

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Abstract. The magnetic anisotropy, magnetostriction and behaviour of elastic constants in magnetic field are important for fundamental understanding of martensitic transformation and magnetic shape memory effects. Here we present the measurement of the properties of cubic austenite and tetragonal martensite as a function of temperature and compare it with previously published results. In austenite, while the magnetostriction broadly agrees with published data, measured anisotropy was about ten times smaller. Using single variant tetragonal martensite the magnetic anisotropy constants were revisited. The magnetic anisotropy of modulated (10M and 14M) and tetragonal martensites can be related using tetragonal distortion within the concept of adaptive phase consisting of nanotwinned tetragonal building blocks. The elastic constants measured by pulse echo methods vary only slightly with magnetic field with apparent exception of shear constant c', which is field dependent. However, due to very low value of c', the pulse echo method is not suitable and other method as resonant ultrasound spectroscopy has to be used.

Introduction

Ni-Mn-Ga alloys are key materials exhibiting magnetic shape memory effects [1-3]. Thus precise knowledge of the magnetic anisotropy, magnetostriction [4-6] and behavior of elastic constants [7-10] in magnetic field is vital for fundamental understanding of martensitic transformation in these materials and resulting magnetic shape memory effects. However, there are only few reports about these properties in cubic high temperature parent phase – austenite and some of them are controversial.

Ni-Mn-Ga austenite transforms to the lower symmetry phase called martensite. To accommodate large lattice deformation during transformation, the martensite is twinned. Depending on composition the martensite can be modulated 10M (called also 5M) and 14M (called 7M) or non-modulated martensite [11-13]. These modulated phases transform at lower temperature to non-modulated (NM) tetragonal martensite phase. The non-modulated phase is thermodynamically stable [14,15]. The modulated phases exhibit high mobility of twin boundaries. Large field-induced deformation due to twin boundary motion in magnetic field called magnetically induced reorientation (MIR) or magnetic shape memory (MSM) effect is observed in modulated 10M and 14M martensites [1-3, 11].

To explain the sequence of martensitic and intermartensitic transformations and existence of the modulated phases the concept of adaptive phase was developed [16, 17]. The concept asserts that the
modulated phases are not thermodynamic phases in strict sense but they are adaptive phases to accommodate large difference between cubic austenite and tetragonal martensite during martensitic transformation. For Ni-Mn-Ga phases it was shown that modulated phases can be built from the unit cells of non-modulated tetragonal phase. The modulated phase consists of tetragonal building blocks which are twinned on the scale of five and two atomic layers in the case of 14M martensite and three and two layers in the case of 10M. As the matching is not perfect a large amount of stacking faults are introduced. These nano-twinned layers are then eliminated by coarsening resulting in macroscopic variant of NM martensite. This transition occurs at certain temperatures as intermartensitic transformations. The adaptive concept allows us to determine some properties of the modulated phases from the knowledge of the properties of non-modulated phase. On the other hand the agreement between calculated and measured values can be taken as a test of validity of the adaptive concept.

In the martensite the magnetic anisotropy strongly increased compared to cubic austenite. The usual magnetostriction is masked by much larger magnetic shape memory effect and thus it is very difficult to determine it unambiguously. The precise values of magnetic anisotropy constants of different phases can be determined only from single crystal. However, usually after martensitic transformation the single crystal is in twinned state with domains or variants with different crystal orientation connected by twin planes. Therefore the utmost care should be taken to prepare a single crystal with only single variant of martensite. Here we compare some previous measurements of modulated and non-modulated phases of single variant martensite and discuss the agreement with the adaptive concept.

During martensitic transformation large deformation is involved and thus the knowledge of elastic constant is crucial for understanding the transformation. Additionally as the transformation appears in ferromagnetic state magnetic and magnetoelastic properties and the effect of magnetic field on elastic constant can be important. However, there is a controversy of the elastic constants of austenite and particularly about their dependence on magnetic field and temperature. Here we re-measure magnetic properties of austenite, determine whole set of elastic constant of cubic austenite and compared them with previous measurements.

### Experimental

Magnetic and elastic properties of austenite were measured using single crystals cut from same ingot with composition close to stoichiometric Ni$_2$MnGa. The samples were in the shape of discs of 13.5 mm diameter and thickness of 4.3 mm with two different nominal orientations 100 and 110 in axis of the discs. Precise orientation of the samples was determined by Laue and single crystal X-ray diffraction. It shows that there is a deviation from perfect orientation of about 2 deg for 100 and 9 deg for 110 orientation. The transformation temperature from austenite to martensite was about 221 K and Curie point at 385K.

Magnetic anisotropy of martensite was measured on various rectangular prismatic samples with approximate 100 orientation of the sides. The shape of the samples is not ideal but this shape is necessary to prepare samples in single variant state by mechanical compression or tension. We used the samples having NM martensite at room temperature. Magnetic anisotropy was determined from the magnetization curves.

Magnetization curves were measured by vibrating sample magnetometer (VSM) with electromagnet up to 2 T field. The same space of the electromagnet was used to measure magnetostriction and elastic properties as a function of the field. Magnetostriction was measured by semiconductor strain gages using four-wire resistivity of Keithley 2001 multimeter. The measurement of strain of the disc with 110 orientation in saturation field provides both anisotropy constants $\lambda_{100}$ and $\lambda_{111}$.

The elastic constants were measured by pulse echo method using piezoelectric transducers. Details are described in ref. [10, 27]. By measuring phase velocity of the sound wave with different polarizations along [100] and [110] directions, we can determine all independent elastic constants of cubic material from the following equations. Errors in determination elastic constant are mainly due to
imprecise planparalelity of the sample sides and the deviation of wave vector from precise crystal orientation.

For the wave propagation direction [100] measured velocity $v_L$ of longitudinal wave and $v_T$ of transversal wave gives elastic constants

$$c_{11} = \rho v_L^2, \quad c_{44} = \rho v_T^2.$$  

In the direction [110] by measuring velocity $v_L$ of longitudinal wave we get elastic constant

$$c_L = \rho v_L^2 = (c_{11} + c_{12} + 2c_{44})/2.$$

In this case for transversal wave we must distinguish between two polarization modes along [100] and [110] (so called slow mode) and we get two elastic constants

$$c_{44} = \rho v_{T1}^2 \quad \text{and} \quad c' = \rho v_{T2}^2 = (c_{11} - c_{12})/2,$$

respectively. It is known that $c'$ is very difficult to determine in shape memory alloys by pulse echo method due to very low velocity of the wave. Density $\rho$ of Ni-Mn-Ga is 8.1 g/cm$^3$. From above equations we can also calculate $c' = c_{11} + c_{44} - c_L$, using directly measured constants $c_{11}$, $c_{44}$, and $c_L$.

**Results and Discussion**

**Martensite**

Magnetization curves of non-modulated martensite single crystal measured along principal axis [100] are in Fig. 1. The samples were prepared by compression and tensile stress along one of the axis. It was expected that this would result in single variant state of the martensite. The NM martensite has tetragonal structure with $c > a = b$ and $c/a \cong 1.2$, where a, b, and c are lattice parameters. Thus by compression a single variant sample cannot be created as there is ambiguous selection rule for variant orientation. The selection of long c axis along stress works only for the tensile stress. Thus observed difference of the magnetization curves of differently prepared samples can be ascribed to the fact that only by tensile stress the true single variant martensite can be formed. Both curves, however, indicates that NM martensite has easy plane anisotropy with hard axis along long c-axis. Small deviation of the easy curves can be due to the presence of residual variants with different orientation.

![Figure 1](image.png)

*Figure 1.* Magnetization curves of NM martensite measured along [100] directions at room temperature. Steep curves (black and red) are measured along a and b axis, tilted curve (green) along c-axis.
The curvature of the compression curve suggests that there are both anisotropy constants, $K_1$ and $K_2$. This was wrongly attributed before [19, 20]. Using sample prepared by tensile stress, $K_2$ became negligible. Small kink observed on hard axis curve in Fig. 2 is due to residual variants or variants re-created during preparation of the sample for measurement. Using correction for these residual twin variants one obtained a linear curve with $K_2 = 0$. The anisotropy constant $K_1$ is higher than that determined before. The absolute value of the anisotropy increases with decreasing temperature, from $2.6 \times 10^5$ J/m$^3$ at room temperature up to $5 \times 10^5$ J/m$^3$ at 10 K, which is about 1.5 times higher than for 10M martensite with c/a=0.94.

Using concept of adaptive phase for modulated martensites, 10M and 14M, we can calculate expected anisotropy constants in these phases from the knowledge of the anisotropy of non-modulated phase. Fig. 2 shows the comparison of calculated values from above described measurement and directly measured values taken from ref [22] for 14M martensite. The 14M martensite is considered as built from five and two layers of tetragonal unit cell connected by twinning. Thus we can calculate expected value just taking the proper fraction 5/7 and 2/7. The agreement between calculated and measured values is quite good in whole temperature range where 14M phase exists. The difference can be ascribed to different composition of compared martensites and to interaction between nanoscale twin variants of tetragonal martensite, which should lead to a decrease of high value constant and an increase of low value constant in 14M as observed.

![Figure 2. Calculated magnetic anisotropy constants for 14M martensite and comparison to measured ones (in color) marked in figure as 7M.](image)

Similar comparison can be made for 10M and NM martensite. In this case 10M contains three and two layers of tetragonal martensite. The agreement cannot be expected to be very good as the tetragonal martensite as building block of this modulated phase should have a different c/a ratio (i.e. smaller) [17,18] than used here. The comparison is summarized in the table showing calculated and measured values for 10M [19]. The agreement is suspiciously good, which can be just accident.

| Temperature (K) | $K_{NM}$ (J/m$^3$) | $-3/5K_{NM}$ (J/m$^3$) | $K_{10M}$ (J/m$^3$) |
|-----------------|---------------------|------------------------|----------------------|
| 10              | $-5 \times 10^7$    | $3 \times 10^7$        | $3 \times 10^7$      |
| 300             | $-2.6 \times 10^5$  | $1.56 \times 10^5$     | $1.65 \times 10^5$   |

Table 1. Calculated and measured values of magnetic anisotropy constant in 10M martensite
One may also speculate about a second constant considering the arrangement of nano-twins in analogy with 14M case. The second constant should be given as $-2/5K_{NM}$. However, this was not observed. Reason for that can be that the difference between $a$ and $b$ are very small and it might not be possible to prepare unique single orientation i.e., $a$ or $b$ in large volume. Result is that the different orientations of modulation are mixed together and only some average is measured. In this case one can expect the constant close to $2.5/5K_{NM}$.

The calculation shows that we can predict anisotropy properties of modulated phases from non-modulated phase with reasonable precision. Viewing it from the other side, the presented calculation can be taken as another supporting evidence for the adaptive concept of modulated martensite. Suggested method can be also used for estimation of other properties of modulated phases which are not accessible in this phase due to MSM effect.

Austenite

Magnetic properties
Magnetization curves of the discs were measured in different directions. The curves were very similar. As example the magnetization curve measured in plane of the disc is shown in Fig. 3. The magnetization curve has very low hysteresis, less than 0.002 T and it is saturating fast. The magnetic anisotropy was evaluated as difference between the curves measured in [100], [110], [111] directions in the disc plane with 110 orientation (Fig. 3b). The difference between the curves are very small but it is clear that [100] direction is easy axis in agreement with Tickle and James [4]. However, the calculation of area between curves gives anisotropy $K_1 \equiv 3 \cdot 10^2$ J/m$^3$, which is of one order magnitude smaller then their measurement, $K_1 = 2.7 \cdot 10^3$ J/m$^3$. Some of the difference might be ascribed to the composition difference and closeness of martensitic transformation in latter case, but in general the anisotropy is smaller than previously thought.

![Magnetization curves](image1.png)

**Figure 3.** a) Measured magnetization curve up to 0.5 T of austenite disc at room temperature. Saturation induction $J_s = 0.67$ T. b) Detail of magnetization curves measured at different directions as marked in the disc with 110 orientation. The curves are corrected for demagnetization to enhance the visibility of the difference.
The easy axis of magnetization of cubic austenite is along [100] directions. Magnetic domains are therefore separated by 90 deg domain walls. From the magnetic anisotropy constant one can determine domain wall width by minimization of exchange and anisotropy energies [28]

\[ \delta_{dw90\text{deg}} = \frac{\pi}{2\sqrt{A/K}}. \]

Using approximate exchange constant \( A \approx 1 \times 10^{-11} \text{ J/m} \) the domain width is \( \delta_{dw90\text{deg}} = 280 \text{ nm} \). This very broad domain wall can explain very low hysteresis as in the single crystal the walls are not pinned or potential pinning sites are much smaller than the wall thickness.

Direct observation of magnetic domain is apparently difficult due to broad wall and in the bulk no observation has been published, yet. However, the observation in thin foil by TEM [29] shows quite random magnetic domain structure with large number of vortices. As authors pointed out, this most likely correlates with the low magnetocrystalline anisotropy of the austenitic phase. They also reported that magnetic domain walls are pinned on antiphase boundaries in the foil but apparently this pinning cannot be very strong in the bulk as measured magnetic hysteresis is negligible (Fig. 3).

Room temperature magnetostriction was determined from the angular dependence of strain at saturation field. The magnetostriction constants of cubic austenite are \( \lambda_{100} = 120 \text{ ppm} \) and \( \lambda_{111} = 13 \text{ ppm} \). These values broadly agree with the literature for the temperature that is same far from martensite transformation [4, 6] and indicate relatively strong magnetoelastic coupling in this material.

**Elastic properties**

Fig. 4 shows the relative change of the elastic constants in magnetic field. It is apparent that the dependence is weak, below 1% and the constants always increase with increasing magnetic field. Additionally the constants are changing only in low field and then saturated. This is correlated with magnetization change (Fig. 3), i.e., the change of magnetic domain structure affects the value of the constants. Observed small stiffening is due to the disappearance of magnetic domain structure and magnetic saturation.

![Figure 4](image-url)

**Figure 4.** Measured relative change of the elastic constants of cubic austenite in magnetic field at room temperature. The constants were measured up to field of 2 T, for sake of clarity the saturation values are shown only to 1 T. The change of the constant above 0.2 T is within experimental error.
This very weak dependency on magnetic field is in contrast with previous report. It was suggested that constant $c_{44}$ of ferromagnetic austenite is strongly dependent on magnetic field [8]. Our measurement indicated that only constant, which is discernibly field-dependent is $c'$. However, the value of the constant is so low and attenuation so high that reliable dependence cannot be given for this set-up. In fact the relatively strong magnetoelastic coupling as indicated by $\lambda_{1(0)}$ should result in field dependency of elastic constants and particularly $c'$ which is related to shear deformation.

The measured constants at zero field and calculated $c'$ are in Table 2 together with values from literature. Relative error of our pulse echo measurement is apparently even smaller than indicated in table as it can be inferred from the spread of the relative values of the elastic constants in saturation field which is less than 0.1% (Fig. 4). However, much larger error is introduced due to deviation of the crystal orientation from ideal one. Comparing the value of the constant $c_{44}$ measured in both discs with different orientation, we can estimate that the error due to misorientation can easily exceed 10%. This strongly affects the calculated value of $c'$ as it is obtained as difference from three large numbers and its value is only fraction of other constants. In this case the error exceeded easily the value of the constant. Thus better method is needed to determine $c'$. This will be published elsewhere [30].

### Table 2. Elastic constants of cubic austenite at room temperature.

| source  | $c_{11}$ (GPa) | $c_{44}$ (GPa) | $c_{1}$ (GPa) | $c'$ (GPa) | $c'$ (GPa) calculated* |
|---------|---------------|---------------|---------------|------------|------------------------|
| this report | 140 ± 3       | 104 ± 2       | 235 ± 4       | 4 ± 5      | 9 ± 9                  |
| [9]     | 136 ± 3       | 102 ± 3       | 222 ± 9       | 22 ± 9     | 16 ± 15                |
| [7]     | -             | 103           | 250           | 4.4        |                        |

* $c' = (c_{11} - c_{12})/2 = c_{44} + c_{11} - c_{1L}$

Measured values of elastic constants broadly agree with the literature as table indicates, with notable differences of $c'$, which can be ascribed to difficulties of measuring pulse echo for this slow transversal mode. This is also apparent from the quoted error. Measuring this constant by resonance ultrasound spectroscopy (RUS) gives $c' = 3.6 ± 0.03$ GPa. [10] On the other hand Zhao et al. [8] gives very low and field dependent value of constant $c_{44} = 5-10$ GPa, which might be due to cross-effect of $c'$ on the measurement on this constant.

### Conclusion
- Magnetic properties of NM martensite are revisited. It is important to consider microstructure i.e. proper preparation of single crystal single variant.
- Magnetic anisotropy of modulated martensites can be predicted from NM phase using adaptive phase concept.
- Magnetic anisotropy of austenite is even smaller than previously measured
- Elastic constants of austenite are different than in literature and do not depend strongly on magnetic field apart of $c'$.
- For proper determination of the $c'$ the resonance ultrasound spectroscopy in magnetic field is better method, which on the other hand is not suitable for hard elastic constants as in the spectrum most of low lying resonances are given by shear constant $c'$.
- Presented measurements indicate that a revision of the magnetoelastic properties is timely.

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