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Temperature dependence of magnetic anisotropy in Ni–Mn–Ga alloys exhibiting giant field-induced strain

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Temperature dependence of structure and magnetic anisotropy of single crystalline $Ni_{48.8}Mn_{28.6}Ga_{22.6}$ alloy exhibiting giant field-induced strain or magnetic shape memory (MSM) effect was studied in the temperature range 80–420 K. Upon cooling the alloy transforms from cubic austenite at 307 K to the martensite which exhibits five-layered (modulated) tetragonal structure ($5M$) with $a=0.595$ nm and $c=0.559$ nm. Reverse transformation occurs at 317 K. An additional intermartensitic transition takes place at about 95 K. The basic mechanism of the MSM effect was corroborated by direct simultaneous measurements of strain and magnetization as a function of magnetic field. The magnetic anisotropy of the martensite exhibiting the giant strain was determined from the magnetization curves measured by a vibrating sample magnetometer at different temperatures. The anisotropy of the single variant $5M$ martensite is uniaxial with easy axis along the tetragonal c axis. The first magnetic anisotropy constant is $K_{u1}=2.0\times10^5$ J/m^3 at 283 K and increase to $K_{u1}=2.65\times10^5$ J/m^3 at 130 K. Above room temperature the anisotropy steeply decreases. The second anisotropy constant is negligible and less than 4% of the first anisotropy constant. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1453944]

I. INTRODUCTION

Magnetic shape memory (MSM) materials are a new class of active material exhibiting large magnetic-field-induced strain.[1] Up to 6% extensional (linear) strain was observed in off-stoichiometric Ni_2MnGa at room temperature in magnetic fields lower than 1 T.[2–4] The material showing the giant field-induced strain (MSM effect) possesses a twinned tetragonal martensitic lattice. The mechanism of the MSM effect is the lattice rearrangement (martensitic twin variant redistribution) produced by twin boundary motion driven by magnetic field.[2,5–8] In a moderate magnetic field the martensitic variant rearrangement, i.e., the MSM effect, is energetically favorable compared with simple magnetization rotation if the magnetic anisotropy of the variant is large and the twinning stress, i.e., stress needed to move twin boundary, is low.

In this article we report a study of the temperature dependence of the magnetic anisotropy in off-stoichiometry Ni_2MnGa single variant martensite. Moreover, by simultaneous measurement of giant field-induced strain and magnetization as a function of the magnetic field we corroborate the basic mechanism of the MSM effect.

II. EXPERIMENTAL PROCEDURES

Various {100} oriented single crystalline samples were cut from the ingot produced by AdaptaMat OY, Finland. The samples with composition $Ni_{48.8}Mn_{28.6}Ga_{22.6}$ for the magnetization measurements were approximately cube shaped with $a=4$ mm with {100} cube faces and a disk with diameter 10 mm and thickness 2 mm with one of ⟨100⟩ directions perpendicular to the disk plane.

A 5 mm×5 mm×10 mm prism with average composition $Ni_{48.9}Mn_{27.7}Ga_{23.4}$ was used for simultaneous measurements of magnetization and magnetic field-induced strain (MSM effect). The composition of the samples was determined by energy dispersive spectroscopy with precision of about 0.5 at. %. Low field ac susceptibility at 488 Hz was measured in the temperature range 80–420 K to determine the transition temperatures. For structural studies at room temperature, a Philips X'pert diffractometer was used. The magnetization curves at different temperatures were measured by a vibrating sample magnetometer up to 1.5 T. The quasistatic MSM effect and field dependence of magnetization were measured simultaneously by a contactless dilatometer using laser vibrometer equipped with displacement sensor coupled with an in-house made vibrating coil magnetometer. The device was built inside 12 in. electromagnet with a maximum field of 1.15 T.

III. RESULTS AND DISCUSSION

Figure 1 shows the magnetic susceptibility as a function of temperature during heating and cooling. The susceptibility curve shows several large abrupt changes and minor, slow gradual changes. The Curie temperature of austenite is about $T_C=373$ K in agreement with previous measurements on slightly different compositions.[2,3,9,10] It shows that the T_C is insensitive to small changes of the Mn/Ga ratio. The sharp decrease of the susceptibility indicates the onset of the martensite transition, as the magnetic anisotropy of martensite is much higher than the anisotropy of the cubic austenitic phase. The austenite-to-martensite transformation takes place

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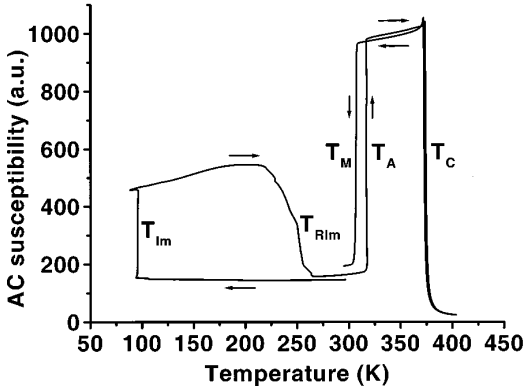

FIG. 1. Low field ac susceptibility as a function of temperature of NiMnGa indicating Curie point, T_C, martensitic transformation above room temperature, T_M and T_A, and low temperature intermartensitic transformation, T_{Im} and $T_{R\,\mathrm{Im}}$. The arrows indicate the direction of the heating/cooling. The heating rate was about 7 K/min.

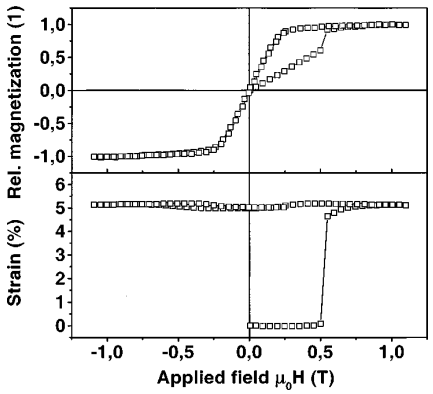

FIG. 2. Magnetization and strain as a function of applied magnetic field measured simultaneously. The sample was pressed beforehand in the direction perpendicular to applied field to create single variant state.

at about $T_M = 307$ K and the reverse transformation from martensite back to austenite at $T_A = 317$ K. The room temperature martensite structure abruptly transforms at low temperature to yet another martensitic phase at $T_{\mathrm{Im}} = 95$ K. Some minor changes of susceptibility already occur at 110 K. The large difference in temperatures between principal austenite-to-martensite and intermartensitic transitions is advantegous for the existence of the MSM effect. It also allows to determine the magnetic anisotropy of martensite in a broad range. During heating the reverse transformation occurs gradually between 220 and 270 K. The observed intermartensitic transformation exhibits a large thermal hysteresis of more than 100 K.

The high temperature austenitic phase is a cubic Heusler phase $L_2 1$ with lattice constant $a = 0.584$ nm. At room temperature the martensite exhibits the five-layered (modulated) tetragonal structure $(5M)$ with $a = 0.595$ nm and $c = 0.559$ nm known to exist in Ni_2MnGa martensite.[11] It seems that the modulated structure is an essential condition for the MSM effect. This modulated structure might be the reason for the extremely low twinning stress which in turn implies the existence of the MSM effect. The nonmodulated tetragonal structure with c/a ratio larger than unity has a much larger twinning stress.[12] The difference between the a and c lattice constants, i.e., tetragonal lattice distortion, gives the maximum theoretical obtainable strain $(a/c - 1) = 6.4\%$. After intermartensitic transformation the low temperature phase is probably a nonmodulated tetragonal phase with c/a ratio greater than unity, analogous to a very similar system studied previously[10] and also suggested by *ab initio* computation of tetragonal variants in the NiMnGa system.[13] This kind of martensite does not show any MSM effect.

Figure 2 shows the field dependence of strain and magnetization measured in a single variant prism at room temperature. A small load of 0.2 MPa was used to fix the sample. Before measurement the sample was pressed at about 3 MPa to obtain a detwinned sample (single variant state) and well defined single c axis in the direction of the stress. The single variant state of the sample was confirmed by optical microscopy. The magnetic field was then applied perpendicularly to the c axis (stress axis) which is also the easy magnetization axis as known from previous studies.[2,8] The orientation of the easy axis was also confirmed by magnetic domain structure observation. In the low field the magnetization increases linearly with increasing field and no measurable strain occurs (Fig. 2). This suggests that the magnetization rotates off the easy axis without structural changes. After further increase of the field, at about $\mu_0 H = 0.5$ T, a simultaneous jump in the magnetization and strain takes place. It signifies that the rotational process is replaced by structural rearrangement due to martensitic twin boundary motion, which is easier and energetically favorable. The single variant martensitic state with magnetic easy axis perpendicular to field, changes to the nearly single variant state with the easy axis (tetragonal c axis) along the field direction. This mechanism leads to a simultaneous increase of the magnetization and increase of the dimension of the sample perpendicular to the field as the lattice constant a is larger than c. This also results in large transitional hysteresis of the magnetization curve in the first quadrant. After the jump the sample quickly reaches magnetic saturation and a maximum strain of 5.2%. The magnitude of the strain suggests that the transition to the second martensitic variant is not complete and the sample contains small volume fractions of other, residual variants with different orientations. The presence of the residual variants is also reflected in the imperfect squareness of the magnetization curve. The return path of magnetization and following magnetization cycles are squarelike and with very small hysteresis typical for materials with predominant easy axis along the field direction. The shearing of the magnetization curve in Fig. 2 is caused by the demagnetization field. During the following magnetization cycles a small reversible field induced strain appears due to the small stress overimposed on the sample.

The magnetization curves at room temperature measured in the plane of the single variant disk and along hard and easy magnetization directions are shown on the inset of Fig. 3. The magnetization curves have negligible hysteresis

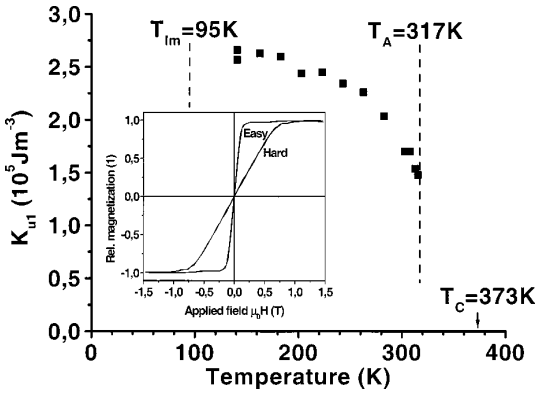

FIG. 3. Magnetic anisotropy constant, K_{u1}, of the martensite as a function of temperature. The Curie, T_C, martensitic, T_A, and intermartensitic, T_{Im}, temperatures are indicated in the figure. The inset shows an example of the magnetization curves measured in easy and hard directions at room temperature. From the hard-direction magnetization curve the K_{u1} was determined.

and the curve measured in the hard direction is linear nearly to saturation. This confirms that the magnetization process is governed by magnetic rotation and the anisotropy of the single variant martensite is uniaxial with easy axis in the direction of the tetragonal distortion.[2,8] The saturation magnetization of the martensite at room temperature is $M = 68\ \mathrm{Am^2/kg}$. The single variant state in the cube-shaped sample was established by application of a compressive stress of about 10 MPa prior to measurements. The magnetization curves of the cube were used for magnetic anisotropy determination. The curves were corrected for demagnetization. The measurement was limited by the temperature range in which the particular martensite exists. The magnetization curve measured along the hard direction of the single crystal has a singularity or knee at the saturation field which is equal to the anisotropy field H_A. The anisotropy field is given by $H_A=(2K_{u1}+4K_{u2})/M_s$, where K_{u1} and K_{u2} are anisotropy constants of the first and second order, respectively, and M_s saturation of the single crystal.[14]

The first magnetization constant, K_{u1}, as a function of temperature, is shown in Fig. 3. The anisotropy steeply decreases above room temperature, which is probably due to the proximity of the Curie temperature. At low temperature the anisotropy saturated and by extrapolation the first anisotropy constant at zero temperature is about $2.8\times10^5\ \mathrm{J/m^3}$. The determined magnitude of the anisotropy constant is comparable to the anisotropy constant $K_u=2.45\times10^5\ \mathrm{J/m^3}$ of $Ni_{51.3}Mn_{24}Ga_{24.7}$ measured at 256 K, (Ref. 8) and it agrees well with our previous measurements for a similar material at room temperature ($K_u=1.7\times10^5\ \mathrm{J/m^3}$).[2,3] According to Murray *et al.*[4] the anisotropy of $Ni_{49.8}Mn_{28.5}Ga_{21.7}$ at room temperature is $K_u=1.5\times10^5\ \mathrm{J/m^3}$. The determined value is also in accord with numerical calculation of the magnetic anisotropy energy of Ni_2MnGa.[15]

Further analysis of the magnetization curves according to Ziljistra[14] indicates that the second anisotropy constant is negligible and less than 4% of the first anisotropy constant. This is also supported by the numerical calculation of angular dependence of the calculated magnetic anisotropy energy. It somehow differs from the measurement of Chu *et al.*[16] who indicate that the second anisotropy constant is about 1/4 of the first anisotropy constant $K_{u1}=2.0\times10^5\ \mathrm{J/m^3}$ in stoichiometric Ni_2MnGa measured at 170 K. The difference can be explained by the fact that the sample used in Chu's measurement was not in a single variant state and might also contain some retained (residual) austenite due to which some spurious terms may arise. Additionally their sample had a different composition and the analyzed martensite could have a different structure than the $5M$ martensite measured here.

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