Magnetoelastic effects and magnetic anisotropy in Ni_2MnGa polycrystals

F. Albertini[a)]
Istituto MASPEC del CNR, Parco Area delle Scienze, 43010 Fontanini, Parma, Italy

L. Morellon, P. A. Algarabel, and M. R. Ibarra
Departamento de Fisica de la Materia Condensada–ICMA, Universidad de Zaragoza–CSIC, 50009 Zaragoza, Spain

L. Pareti
Istituto MASPEC del CNR, Parco Area delle Scienze, 43010 Fontanini, Parma, Italy

Z. Arnold
Institute of Physics AS CR, Cukrovarnická 10, 162 53 Praha 6, Czech Republic

G. Calestani
Dipartimento di Chimica, Università di Parma, Parco Area delle Scienze, 43100 Parma, Italy

(Received 19 July 2000; accepted for publication 2 January 2001)

Linear thermal expansion and magnetostriction measurements under a magnetic field up to 20 kOe, applied parallel and perpendicular to the measuring direction and in the temperature range of 10–300 K, have been performed on a Ni_2MnGa polycrystal. The effects of zero-field cooling and field cooling on both the self-strain ($H=0$) and the magnetic-field-induced strain (MFIS) have been studied. We have found that the MFIS strongly depends on whether a magnetic field was applied during the cooling process. The applied magnetic field facilitates the growth of specific orientation variants along the field direction as the sample is cooled down through martensitic transformation. However, the application of a field in the martensitic phase induces a negligible motion of twin boundaries. On this basis, the singular point detection technique performed on polycrystalline specimens results in being the easiest and most direct way by which to determine the anisotropy field in this class of materials. The temperature behavior of the anisotropy constant and field has been determined for Ni_2MnGa. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1350630]

INTRODUCTION

Ferromagnetic martensites are an emerging class of active materials due to their possibility to obtain strains up to few percent by the application of a magnetic field along specific crystallographic directions, and to control the martensitic transformation with magnetic field, temperature, and stress.[1,2] A great deal of interest has been recently attracted by NiMnGa Heusler alloys. Ullakko *et al.*[3] first reported a magnetic-field-induced extensional strain (0.2%) in an unstressed Ni_2MnGa off-stoichiometry single crystal at 8 kOe. Later, a 4.3% extensional strain was observed for stress biased samples.[4] More recently, Murray *et al.*[5] have reported a shear strain of 5.7% at an applied field of 4 kOe at room temperature.

Ni_2MnGa undergoes a martensitic transformation upon cooling from cubic $L2_1$ to a complex tetragonal structure.[1,6] In the martensitic phase, the strain associated with the transformation (6.5% along the *c* axis) is accommodated by the formation of twin variants in configurations that minimize the elastic energy. The observed large magnetic-field-induced strain (MFIS) in the martensitic phase is a consequence of twin boundaries displacements in order to increase the volume fraction of variants with the easy magnetization direction oriented parallel to the direction of the applied field.[3,7] This can occur if the magnetocrystalline anisotropy energy is strong enough to make the boundaries motion rather than the magnetization rotation energetically more favorable.[8]

The occurrence of boundary motion significantly changes the shape of the magnetization curve, which can reach saturation at a field lower than the anisotropy one. For this reason, the determination of the anisotropy field is not trivial. The above effect was predicted in a simple two-dimensional model[8] and was observed by comparing the magnetization curve of a multivariant specimen with that of a single-variant single crystal specimen.[4] The same authors derived the anisotropy constant for an off-stoichiometry composition from magnetization measurements of single crystals after field and stress-cooling processes in order to obtain a single variant state. *In situ* microscopic observations of the sample were required to check its single-variant state.

Large MFIS in single crystals has also been observed for the application of a magnetic field during a cooling procedure across the transition. Also in this case, the magnetocrystalline anisotropy plays an important role: preferred nucleation of variants with the easy magnetization direction parallel to the applied field has been observed.[9,10] The extension of the above results to polycrystalline specimens would markedly increase the application capabilities of this class of materials. A complete anisotropic and magnetoelastic study of polycrystalline materials is still lacking.

a)Electronic mail: franca@maspec.bo.cnr.it

In the present work thermal expansion, parallel and perpendicular magnetostriction measurements in a magnetic field up to 20 kOe in the temperature range of 10–300 K have been performed on Ni_2MnGa polycrystals. Particular attention has been paid to the effect of field cooling (FC) and zero-field cooling (ZFC) on both self-strain and MFIS. The singular point detection (SPD) technique[11] has been utilized to measure the temperature dependence of the anisotropy field. We will discuss how SPD measurements on polycrystals can represent the simplest and most direct way by which to measure the magnetic anisotropy in this class of materials.

EXPERIMENT

Polycrystalline samples of nominal composition Ni_2MnGa were prepared in a standard arc melting furnace starting from pure elements (better than 99.99% purity and remelted three times in order to obtain good homogeneity. X-ray powder diffraction and thermomagnetic analysis (TMA), which consists of the measurement of the thermal variation of the initial ac susceptibility, were performed to check the quality of the sample. Magnetization measurements were performed in a superconducting quantum interference device (SQUID) magnetometer in the temperature range of 10–300 K. The singular point detection technique, with high pulsed magnetic fields up to 300 kOe, was used to measure the temperature dependence of the anisotropy field H_A. Thermal expansion and magnetostriction measurements were carried out using the strain-gauge technique in steady magnetic fields of up to 20 kOe. The magnetic field was applied parallel and perpendicular to the measuring direction.

RESULTS AND DISCUSSION

The samples obtained were single phase, with the expected Heusler structure at room temperature and lattice parameter $a=5.818(1)$ Å. The low temperature phase, below the martensitic transformation, has been reported to have a tetragonal structure, with the a and c parameters being larger ($+1.4\%$) and shorter (-6.5%), respectively, than the original cubic one.[12]

The determined Curie temperature, $T_C=377$ K, is in good agreement with the data of Vasil'ev *et al.*[13] for stoichiometric Ni_2MnGa. In Fig. 1, we display isothermal magnetization curves measured at increasing values of temperature. It is worth noting that the magnetization curves change shape when changing temperature from $T=230$ to 240 K, due to the transformation from the harder tetragonal to the softer cubic phase. The transformation temperature was determined from linear thermal expansion measurements and resulted in $T_M=235$ K upon heating. This first-order transformation is reversible and presents a thermal hysteresis of about 18 K.

The linear thermal expansion (LTE) of Ni_2MnGa measured upon heating after different cooling procedures is shown in Fig. 2. Curve 1 represents the spontaneous ($H=0$) LTE after the sample was zero-field cooled. The change in $\Delta 1/1$ associated with the martensitic transformation is about -0.1% and is only a small fraction of the change that can be estimated from the reported variation in the lattice parameters ($\Delta V/V=3\Delta 1/1=4\%$).[12] The application of a magnetic field when cooling the sample through T_M has a dramatic effect on the thermal expansion, as observed in curves 2 and 3 (FC at 15 kOe, field applied parallel to the measuring direction). In this case, the change in $\Delta 1/1$ is three times larger, $\Delta 1/1 \approx -0.3\%$. Furthermore, no significant difference is seen by heating the sample in either $H=0$ (curve 3) or in a field of 15 kOe along the measuring direction (curve 2). In the case in which the magnetic field is applied perpendicular to the measuring direction (curve 4), an opposite effect in the LTE is observed with a positive change in $\Delta 1/1 \approx +0.1\%$ at the martensitic transformation. In this case (like in the measurement described by curve 2) the field upon heating is applied in the same direction as the field upon cooling.

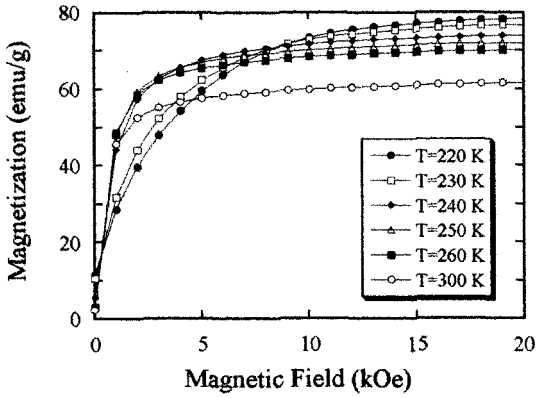

FIG. 1. Isothermal magnetization measurements (in decreasing fields) at selected increased values of temperature.

These results suggest that the applied magnetic field facilitates the growth of specific orientation variants along the field direction as the sample is cooled down through the martensitic transition. This preferential orientation takes place to minimize the Zeeman energy, favoring the growth of variants with the easy magnetization direction (EMD) parallel to the applied magnetic field. As the EMD in the

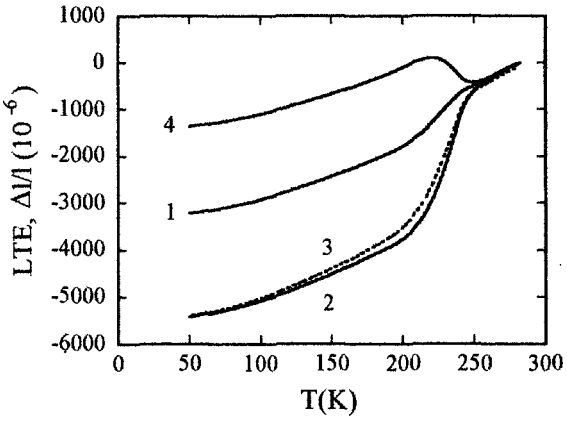

FIG. 2. Linear thermal expansion of Ni_2MnGa measured up on heating after different cooling procedures: LTE at $H=0$ after ZFC (1), parallel LTE at $H=15$ kOe after FC (15 kOe, parallel) (2), LTE at $H=0$ after FC (15 kOe, parallel) (3), perpendicular LTE at $H=15$ kOe after FC (15 kOe, perpendicular) (4).

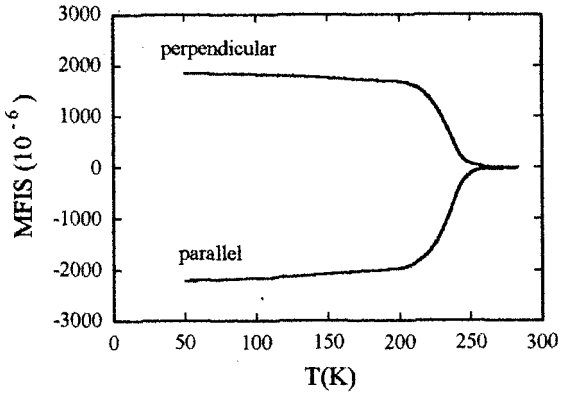

FIG. 3. Matnetic-field-induced strain parallel and perpendicular to the applied magnetic field of Ni_2MnGa obtained upon heating after FC in $H=15$ kOe.

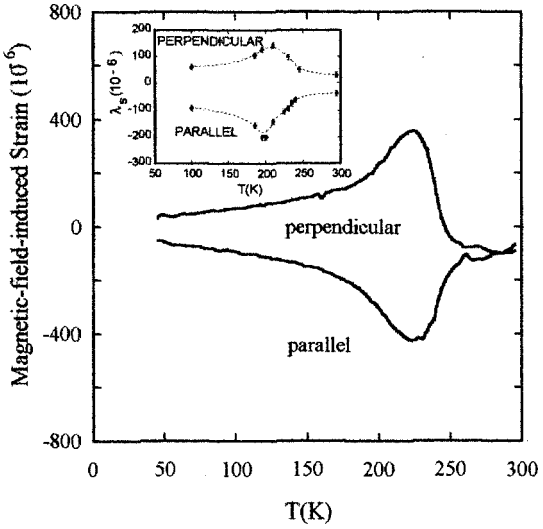

FIG. 4. Magnetic-field-induced strain parallel and perpendicular to the applied magnetic field of Ni_2MnGa obtained upon heating after ZFC. A magnetic field of 15 kOe was applied at 50 K. Inset: Saturation magnetostriction values from isothermal experiments are displayed for comparison.

tetragonal-martensitic phase corresponds to the [001] direction (*c* axis),[4] one expects preferential orientation of the *c* axis (shorter than the cubic *a* axis) parallel to the applied magnetic field and a preferential orientation of the *a(=b)* axis (larger than the cubic one) perpendicular to the applied magnetic field. This mechanism can explain the pronounced negative and positive LTE at the martensitic transformation when measured parallel (curves 2 and 3) and perpendicular (curve 4), respectively, to the applied magnetic field.

This result can be seen more clearly in Fig. 3, where we show the MFIS obtained from the difference between the LTE at an applied magnetic field of 15 kOe and the LTE at zero field. The MFIS obtained from the FC measurements is almost temperature independent below the martensitic transformation and has a value of $\approx\pm 2000$ ppm, depending on the direction of the applied magnetic field, i.e., perpendicular or parallel to the measuring direction. These values are comparable to those obtained in single crystals.[3,14] The temperature behavior observed in the MFIS indicates that he main effect of the magnetic field is produced upon cooling through the martensitic transformation, the effect being negligible in the martensitic phase in which the MFIS is temperature independent.

LTE measurements upon heating under an applied magnetic field of 15 kOe after ZFC were also performed and the MFIS was obtained in the same way as that described previously. The results are shown in Fig. 4. In this case, the magnetic-field-induced strain is almost one order of magnitude smaller than that in the case of the FC process (Fig. 2), and it depends strongly on temperature, showing a maximum in the vicinity of the martensitic transition temperature.

Isothermal magnetostriction measurements with fields up to 20 kOe, applied parallel and perpendicular to the measuring direction, were also performed at selected temperatures in the range of 50–300 K. The temperature dependence of the saturation magnetostriction, which can be directly compared with the MFIS in zero-field-cooled specimens, displays similar behavior (see the inset in Fig. 4).

In this case, at the martensitic transformation during the ZFC procedure, the twin variants grow in a random distribution to minimize the strain energy. However, the subsequent application of a magnetic field in the martensic phase is not effective in producing significant boundary motion, contrary to the case of single crystals, where a high MFIS value was achieved. It is worth noting that in a single crystalline specimen measured by Ullakko *et al.*[3] the two mechanisms (preferential nucleation and twin-boundary motion) had the same relevance and gave rise to a comparable MFIS value.

The SPD technique[1] allows one to determine the anisotropy field by studying the successive derivatives of the magnetization curves in polycrystalline specimens. The required order of derivation depends on the crystal symmetry and on the easy magnetization direction. For uniaxial easy-axis systems, which is the case for Ni_2MnGa, a cusp in the second derivative appears at the saturation field, which is the anisotropy field of the system. The signal is due to the crystallites whose hard axes are oriented in the direction of the applied field. As a consequence, the presence of any texture in the sample does not affect the peak position, only its amplitude.

A poly-twinned martensite, obtained by cooling a cubic single crystal across the transformation, behaves like a polycrystal and the SPD technique could represent an ideal method for anisotropy determination. However, if twin-boundary motion occurs, the anisotropy measurements become more complex. In fact, in that case, saturation could be achieved at a field lower than the anisotropy one as a result of a combination of magnetization rotation and twin-boundary motion,[4,8] and the SPD signal would not give a reliable measurement of the anisotropy.

From the magnetostriction measurements and the MFIS results after ZFC it can be inferred than in polycrystalline Ni_2MnGa a negligible strain related to twin-boundary motion occurs. As a consequence, in the martensitic phase, saturation is substantially achieved by magnetization rotation. Thus, polycrystals are good specimens to use for a simple and direct determination of the magnetocrystalline anisotropy in this class of materials.

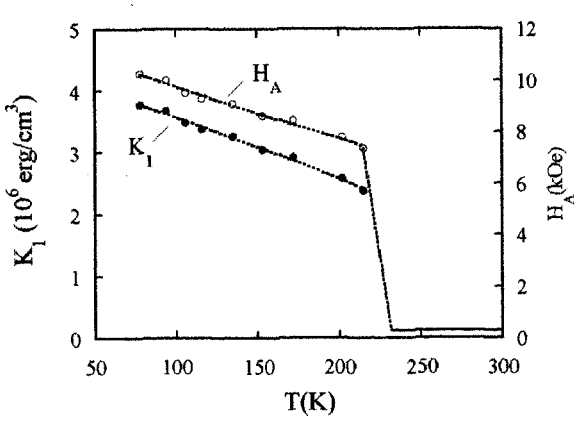

FIG. 5. Temperature behavior of the second order anisotropy constant (K_1) and of the internal anisotropy field (H_A) of polycrystalline Ni_2MnGa in the martensitic phase. The solid line indicates the upper limit for H_A in the austenitic phase.

The temperature dependence of the anisotropy field H_A in the martensitic region for a stoichiometric Ni_2MnGa polycrystal is reported in Fig. 5 together with the deduced values of the anisotropy constant ($K_1 = H_a M_s/2$). The anisotropy field values were corrected for the demagnetizing fields.

Both H_A and K_1 decrease linearly with increasing temperature up to the martensitic transformation where an abrupt decrease takes place. A precise measurement of the anisotropy field in the soft cubic phase is not possible because it is within experimental error (± 300 Oe). Thus, in Fig. 5, only a line representing the upper limit of H_A is reported.

The deduced K_1 values in the martensitic phase are in good agreement with those (2.45×10^6 erg/cm^3) reported by Tickle and James for a single-variant single crystal of composition $Ni_{52.4}Mn_{24}Ga_{24.7}$,[4] and are comparable with the data reported in Refs. 10 and 15 ($K_u = 3\times10^6$ and 1.7×10^6 erg/cm^3, respectively).

We should emphasize that the data reported in the literature usually refer to samples with different nominal or true stoichiometries, as deduced by the spread of the transformation temperature values. It is likely that the anisotropy also varies with composition. Work is in progress in order to determine the composition dependence of the magnetic anisotropy in a series of polycrystalline specimens with modified stoichiometry.

CONCLUSIONS

Preferential growth of twin variants with the *c* axis parallel to the applied field direction has been found for Ni_2MnGa polycrystals. Field cooling of the sample across the transformation temperature gives rise to a MFIS of 0.2%.

On the other hand, no evidence of twin-boundary motion has been found for application of a magnetic field in the martensitic region. Field heating (from the martensitic to the austenitic phase) gives rise to a MFIS contribution that is almost one order of magnitude smaller. Isothermal magnetostriction measurements display similar intensity and temperature behavior.

From the above results, we have determined that the SPD technique used on polycrystalline specimens is a suitable tool for measuring the anisotropy in this class of materials. The temperature dependence of the anisotropy constants and fields of Ni_2MnGa has been determined.

ACKNOWLEDGMENTS

This work was performed within the framework of a CNR/CSIC scientific agreement. The financial support of the Spanish CICYT under Grant No. MAT99-1963-C04 is acknowledged.

[1] R. C. O'Handley, S. J. Murray, M. Marioni, H. Nembach, and S. M. Allen, J. Appl. Phys. **87**, 4712 (2000).
[2] R. D. James and M. Wuttig, Philos. Mag. A **77**, 1273 (1998).
[3] K. Ullakko, J. K. Huang, C. Kanter, and R. C. O'Handley, and V. V. Kokorin, Appl. Phys. Lett. **69**, 1966 (1996).
[4] R. Tickle and R. D. James, J. Magn. Magn. Mater. **195**, 627 (1999).
[5] S. J. Murray, M. A. Marioni, A. M. Kukla, J. Robinson, R. C. O'Handley, and S. M. Allen, J. Appl. Phys. **87**, 5774 (2000).
[6] P. J. Webster, K. R. A. Ziebeck, S. L. Town, and M. S. Peak, Philos. Mag. B **49**, 295 (1984).
[7] H. D. Chopra, C. Hi, and V. V. Kokorin, Phys. Rev. B **61**, R14913 (2000).
[8] R. C. O'Handley, J. Appl. Phys. **83**, 3263 (1998).
[9] Q. Pan and R. D. James, J. Appl. Phys. **87**, 4702 (2000).
[10] S.-Y. Chu, A. Cramb, M. de Graef, D. Laughlin, and M. E. McHenry, J. Appl. Phys. **87**, 5777 (2000).
[11] G. Asti and S. Rinaldi, J. Appl. Phys. **45**, 3600 (1972).
[12] V. V. Martynov and V. V. Kokorin, J. Phys. III **2**, 739 (1992).
[13] A. N. Vasil'ev *et al.*, Phys. Rev. B **59**, 1113 (1999).
[14] G. H. Wu *et al.*, Appl. Phys. Lett. **75**, 2990 (1999).
[15] O. Heczko, A. Sozinov, and K. Ullako, IEEE Trans. Magn. (to be published).