Magnetoelastic behavior of the Heusler Ni_2MnGa alloy

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In this work the effect of the interplay between magnetic and structural degrees of freedom in the structural transitions undergone by Ni_2MnGa alloy is investigated. Elastic constant and magnetic susceptibility measurements in a magnetic field are presented. A simple phenomenological model is proposed to account for the experimental observations. © *1998 American Institute of Physics.* [S0021-8979(98)25911-1]

I. INTRODUCTION

The Ni_2MnGa alloy is the only known ferromagnetic material exhibiting a martensitic transition from a high temperature Heusler structure towards a close-packed phase.[1,2] Associated with this phase transition, this material exhibits shape memory properties.[3] These properties are related to the ability of the system to reverse large deformations in the martensitic phase by heating the alloy up to the high temperature phase. The interest of ferromagnetic compounds compared with other shape memory alloys is the possibility of magnetic field control of the shape memory properties. The potentiality of the Ni_2MnGa alloy for such a purpose has been recently proved by Ullakko and co-workers.[4] They have shown that the application of a magnetic field provokes a tendency of the martensitic variants to be aligned with the field. As a consequence, the field modifies the induced transformation strain.

More fundamental is the fact that, in this material, the martensitic transition is preceded by the appearance of a micromodulated structure which is accompanied by the condensation of a $q=0.33$ TA_2 phonon.[5] Recently, we have shown[6,7] that this premartensitic structure develops via a weakly first order transition. Since such a premartensitic transition is not observed in other nonferromagnetic materials, it seems reasonable to believe that it is a consequence of a magnetoelastic interaction.

In this paper we show the existence of magnetoelastic effects in this material, from elastic constant and magnetic susceptibility measurements in an applied magnetic field. The relevance that the magnetoelastic interplay between structural and magnetic degrees of freedom has on the premartensitic transition is finally discussed in the framework of a Landau model.

II. EXPERIMENTAL RESULTS

A single crystal grown by the Bridgman method with composition very close to stoichiometric Ni_2MnGa was investigated. From the original rod two samples were cut using a low-speed diamond saw. The smaller sample ($3.1\times1.0\times1.4$ mm^3) was used in ac susceptibility measurements. The larger one ($6.75\times4.8\times11.45$ mm^3), which had its faces parallel to the (110), (1$\bar{1}$0), and (001) planes, was used in ultrasonic measurements.

Magnetic susceptibility measurements were conducted on an ac susceptometer. The elastic constants were obtained from ultrasonic measurements (pulsed-echo technique). In these ultrasonic measurements, a magnetic field up to 1 T was applied.

The Ni_2MnGa sample investigated displays a bcc structure with an $L2_1$ atomic order (space group $Fm3m$) at high temperature. It orders ferromagnetically below $T_c=381$ K, and it transforms martensitically to a modulated tetragonal structure at $T_M=175$ K. The premartensitic transition occurs at $T_I=230$ K.

Clear evidence of the existence of a magnetoelastic interaction is the dependence of the elastic properties on the magnetic structure of the solid. To show this for Ni_2MnGa, we have measured its elastic constants under different magnetic fields, at room temperature. Prior to each measurement, the sample was subjected to a thermal treatment to ensure that the measured dependence of each elastic constant corresponded to the first magnetization process. A typical example of the behavior found is presented in Fig. 1, which shows the evolution of the three independent elastic constants as functions of a magnetic field applied along the

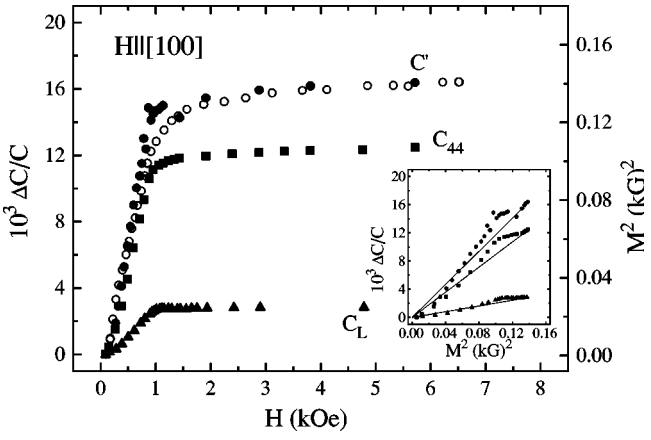

FIG. 1. Relative changes of the elastic constants (solid symbols) as functions of a magnetic field applied along the [100] direction. Open symbols correspond to the square of the magnetization extracted from Ref. 4. The inset shows the relative changes of the elastic constants as functions of the square of the magnetization.

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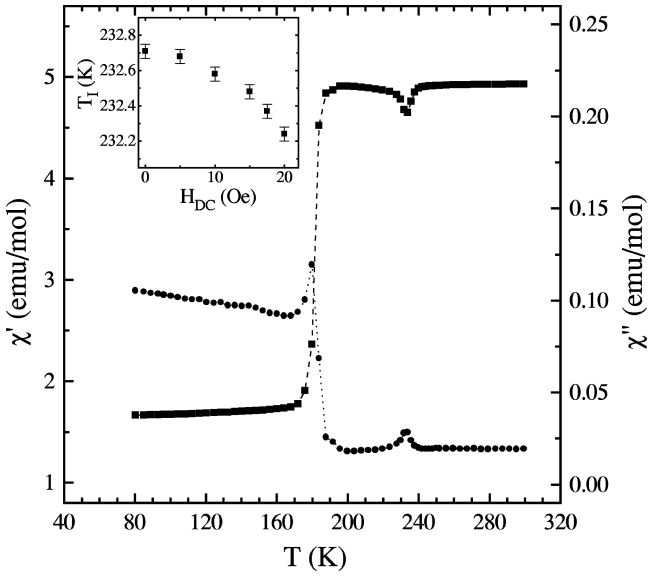

FIG. 2. Real (χ', squares) and imaginary (χ'', circles) parts of the magnetic susceptibility as functions of temperature measured for $H_{dc}=10$ Oe and $f=66$ Hz. The inset shows the dependence of the temperature of the intermediate transition with a magnetic field applied along the [100] direction.

[100] direction. As the magnetic field is increased, all the elastic constants slightly increase up to a saturation value. Similar behavior is obtained with the magnetic field applied along the [110] direction: the same saturation values are obtained (within experimental error) but at a larger value of the magnetic field. In order to prove that the measured change in the elastic constants is due to a change in the value of the magnetization, and is not due to rotation of the equilibrium magnetization, we have plotted the square of the magnetization (M) measured by Ullakko and co-workers in a similar sample.[4] A good correlation exists between the change in the elastic constants and that of M. In the inset we have plotted the relative change of the elastic constants as functions of M^2. It is interesting to note that, within the experimental errors, the same linear behavior is observed for low and high values of M^2. At intermediate values, the data points deviate from this linear behavior. Such a deviation can be ascribed to the fact that ultrasonic and magnetic measurements have been conducted on different specimens and also to minor misalignments of the magnetic field in both sets of measurements which can result in slightly different values for the saturation field.

The interplay between the magnetic and structural degrees of freedom is also apparent in the change of the magnetic properties of the alloy as it goes through the structural phase transitions. This behavior is illustrated in Fig. 2, which shows an example of the evolution of the real (χ') and imaginary (χ'') parts of the magnetic susceptibility as functions of temperature. χ' has a significant change at around 175 K associated with the martensitic transition, and it displays a small anomaly at around 230 K. Such an anomaly is located at the temperature where a peak in the specific heat curve has been measured,[6] and it is related to the condensation of the $q=0.33$ TA_2 phonon. At the temperatures of the structural transitions, χ'' increases; this is an indication of a dissipative effect which, in each case, is due to the motion of domain boundaries.[6] This phenomenon is in agreement with a measured increase in the internal friction at these phase transitions.[8] Another manifestation of the magnetoelastic interplay is a dependence of the temperature of the premartensitic transition upon the magnetic field. In particular, for a first order phase transition the Clausius–Clapeyron law must hold. We have explored such a possibility by applying a low dc magnetic field along the [100] direction during the measurement of the ac susceptibility. We have found that T_I decreases with increasing magnetic field as shown in the inset of Fig. 2. These low magnetic fields do not modify the martensitic transition temperature and do not affect the characteristics of this transition. Fields in the range of several kOe are needed to induce significant changes in the characteristics of the martensitic transition.

III. DISCUSSION AND CONCLUSIONS

The results presented above give clear evidence for the existence of magnetoelastic coupling in Ni_2MnGa. In this section we would like to discuss the relevance of this coupling to the features of the premartensitic and martensitic transitions undergone by the studied alloy. We first introduce a Landau model suitable to describe the phase transitions of this system. The primary order parameter is taken to be the amplitude of the $q=0.33$ TA_2 phonon (related to the micromodulation at the premartensitic transition), and we consider two secondary order parameters: ε, a (110)[110] homogeneous shear adequate to describe a cubic to tetragonal change of symmetry, and the magnetization M (considered to be a scalar). We assume the following general form of the Landau free energy:

$$\mathcal{F}(\eta,\varepsilon,M)=F_{str}(\eta,\varepsilon)+F_{mag}(M)+F_{me}(\eta,\varepsilon,M), \quad (1)$$

where F_{str} is a purely structural term, F_{mag} is the magnetic term, and F_{me} is the contribution accounting for the magnetoelastic coupling. The explicit free energy expansion takes into consideration the symmetries of the system and the fact that the two structural transitions take place well below the Curie point, resulting in a breaking of the $\pm M$ invariance in the free energy. For the premartensitic transition, minimization of $\mathcal{F}$ with respect to ε and M [which yields a path $\varepsilon=0$, $M=M(\eta)$], leads to the following effective free energy:[7]

$$\mathcal{F}_{eff}=\frac{1}{2}A\eta^2+\frac{1}{4}B\eta^4+\frac{1}{6}C\eta^6, \quad (2)$$

where A is a linear function of temperature and of the high temperature phase magnetization M_0; B and C are temperature-independent functions of M_0. It is interesting to point out that for large enough magnetoelastic coupling, B can be negative, and in this case the system can show a first order transition before becoming dynamically unstable ($A\rightarrow 0$). Within this picture, the softening of the characteristic phonon is expected to be incomplete at the transition, in accord with experimental observations.[5] From this model the dependence of T_I on an externally applied magnetic field can be obtained. It is given by (Clausius–Clapeyron equation):

$(dT_I/dH) = -\alpha M_0/(1+\alpha|\Delta S|)$, where α is a parameter related to the magnetoelastic coupling and ΔS is the entropy change at the premartensitic transition. From calorimetric measurements $\Delta S = -0.04$ J/K mol has been determined in the absence of magnetic field. The decrease of T_I with H (inset in Fig. 2) appears to be in agreement with the above equation.[9] Even more, the above expression provides a justification for the nonlinear dependence shown in the figure: as the phase transition moves towards lower values, the stability limit of the high temperature phase is approached and the absolute values of ΔS are expected to decrease.

In nonferromagnetic alloys, the martensitic transition has been related to an anharmonic coupling between the TA_2 phonon and the homogeneous strain ε.[10] In our model, this term is supposed to be negligible in comparison with the magnetoelastic coupling term. Nevertheless, it is worth noting that the magnetoelastic interaction indirectly couples η and ε. At the martensitic transition, ε becomes different from zero and a close-packed tetragonal phase is obtained. Such a symmetry change is accompanied by a change in the wave vector of the transverse modulation. In order to account for such a change in the Landau model, an explicit wavevector dependence of the Landau free energy should be considered.

Up to now, the microscopic origin of the magnetoelastic coupling in Ni_2MnGa has not yet been established. Short wavelength anomalies preceding the martensitic transition have also been observed in Ni-Al alloys.[11] They have been related to specific nesting properties of the multiply connected Fermi surfaces.[12] Nevertheless, Ni-Al is not ferromagnetic and no premartensitic transition has been observed in this alloy. In addition, in Ni-Mn-Ga alloys close to stoichiometric Ni_2MnGa but with less Mn content, the premartensitic transition is not observed although a magnetoelastic coupling has been proven to exist.[13] We suggest that this different behavior could be due to the fact that the substitution of Mn by Ni atoms causes an increase in the martensitic transition temperature,[14] and the magnetoelastic coupling is likely to be weaker. These two features imply that the bcc phase transforms to a close-packed one (martensitic transition) at a temperature higher than the temperature at which the intermediate transition would occur (which is essentially controlled by the magnetoelastic coupling), and therefore, the micromodulated phase cannot develop independently of the martensitic transition in alloys with low Mn content.

To conclude, we have experimentally proven the existence of a magnetoelastic coupling in Ni_2MnGa. By means of a simple Landau-type model, it has also been shown that such a coupling leads to a first order phase transition that occurs as a lock-in of a soft phonon in the TA_2 branch. A knowledge of the microscopic origin of such a coupling and its relationship to the martensitic transition is still lacking.

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