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Anomalies related to the TA_2-phonon-mode condensation in the Heusler Ni_2MnGa alloy

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We present specific-heat, elastic constants, and magnetic susceptibility measurements in a ferromagnetic Ni_2MnGa Heusler alloy, in a temperature range where partial condensation of the $[110]TA_2$ phonon at $q=0.33$, accompanied by the development of a micromodulated structure has been reported to occur. All these quantities have been found to exhibit anomalous behavior at the temperature of condensation. From the results presented, it can be concluded that the appearance of the micromodulated structure takes place via a phase transition which is very weakly first order. It is found that at the transition point there is a significant reduction of the dynamical stability of the lattice not just for the transverse phonon at $q=0.33$, but also for any shear long wavelength distortion. It is particularly remarkable the large softening of C' (around 60%) at the transition point. Finally, it is also shown that the intermediate transition is related to a magnetoelastic interaction. [S0163-1829(97)13917-0]

There is experimental evidence of a number of precursor phenomena when bcc solids approach a martensitic transformation. These precursors have been observed by many different experimental techniques such as x-ray, electron, and neutron scattering, and ultrasonic measurements among others. Some of these phenomena, such as the observation of an intermediate tweed structure[1] are not common to all systems transforming martensitically but others, which are intimately related to the transformation mechanism, have been reported to occur in all materials investigated so far. This is the case of the anomalous dynamical response of the lattice to some specific displacements; all bcc martensitic materials exhibit a low $TA_2[110]$ ($[110]$ propagation, $[1\bar{1}0]$ polarization) phonon branch which is accompanied by a low value of the elastic constant $C'[=(C_{11}-C_{12})/2]$.[2,3] Both the elastic constant and the phonon branch soften on approaching the transition. Usually, a more or less pronounced minimum of frequency (ω) is also observed on the phonon branch. It has been argued that this anomaly occurs at a wave number (q) that corresponds to the periodicity of the close-packed planes of the martensitic phase.[4] Although this seems to be the case in a number of materials, this is still an open issue since there are other materials in which there is not such a correspondence.[2,5] Even so, the low value in the phonon modes ω results in a higher entropy of the bcc structure in comparison with that of the martensitic (close-packed) one. This excess of entropy drives, on cooling, the martensitic transition.[6–8]

Examples of solids undergoing martensitic transformations are alkali metals, noble-metal-based alloys and a number of Ni-based alloys. Among them, the intermetallic Ni-Mn-Ga alloy close to the stoichiometric Ni_2MnGa composition has the interesting feature of being the only ferromagnetic Heusler alloy that undergoes a martensitic transformation. Precursor phenomena have been recently reported for this alloy system. Inelastic neutron-scattering experiments have evidenced a well-defined dip in the TA_2 phonon branch close to $q=0.33$.[9,10] The existence of these soft phonon modes gives rise to diffuse x-ray[11] and electron[9,12] scattering at temperatures far above the martensitic transformation temperature (M_s). When the sample is cooled down, this dip becomes more pronounced, but the softening is always incomplete and below a given temperature still above M_s the frequency of the soft modes starts to increase again.[9] The prototype alloy system where similar softening effects have been observed is Ni-Al;[13] however, the amount of softening measured in Ni_2MnGa is larger and in Ni-Al there is not an increase of the frequency below a given temperature. Also, recent measurements by some of the present authors[14] have shown that, at the temperature of phonon condensation, the thermal expansion and elastic modulus versus temperature curves exhibit a minimum, which is accompanied by an increase in the internal friction.

On the other hand, low-temperature electron microscopy[14,15] has evidenced the existence of a micromodulated structure that can be explained as the result of the freezing of thermal vibrations of the soft TA_2 mode which become the static displacements in this intermediate phase. The cubic symmetry remains unchanged but the system exhibits a micromodulated domain structure.

All these experimental evidences suggest that the appearance of the micromodulated structure is a true phase transition. Indeed, the observation of a Bragg-like peak around $q=0.35$, with a small thermal hysteresis, led Zheludev and Shapiro[10] to claim the existence of a first-order structural phase transition. Nevertheless, no latent heat has been detected using microcalorimetric devices.[14] In this paper we present measurements of the specific heat (dynamical and isothermal) in a Ni_2MnGa single crystal on a temperature range where the crystal goes from the bcc to the micromodulated (intermediate) structure. In addition, we report measurements of elastic constants and magnetic susceptibility as a function of temperature. Anomalous behavior of all these quantities has been found at the temperature of condensation of the soft phonons.

The sample used in this work was a single crystal grown by the Bridgman method with composition close to the stoichiometric Ni_2MnGa. From the original rod two samples were cut using a low-speed diamond saw. The larger sample, used for elastic constants measurements was oriented by x-ray scattering and it was cut as a parallelepiped ($6.75 \times 4.8 \times 11.45$ mm^3) with faces parallel to the (110), (110), and (001) planes. The smaller one, used in magnetic and specific-heat measurements, was also a parallelepiped ($3.1 \times 1.0 \times 1.4$ mm^3) with a face parallel to the (001) plane. The martensitic transition temperature and Curie temperature were measured calorimetrically and were found to be $M_s = 175$ K and $T_c = 381$ K, respectively.

Specific-heat (Cp) measurements were carried out in the temperature range from 500 to 200 K using a modulated differential scanning calorimeter from TA Instruments.[16] The elastic constants were obtained from the measurement of the velocity of ultrasonic waves in the temperature range from 300 to 200 K, using the phase sensitive technique (MATEC MBS-800).[17] X-cut and Y-cut quartz ultrasonic transducers were used to generate and detect the ultrasonic waves. Finally, the magnetic susceptibility was measured in the temperature range from 300 to 200 K by means of an ac susceptometer (LakeShore).

In Fig. 1 we present a typical example of the measured specific heat as a function of temperature. It corresponds to a cooling rate of 1 K/min with a superimposed temperature modulation of 0.3 K and a period of 30 s. The large λ-type peak at 381 K corresponds to the Curie point. A clearly observable anomaly is also present at the temperature where the micromodulated phase is expected to develop. In addition, isothermal measurements (same amplitude and period) have also been performed in a restricted temperature range covering the spread of the small peak. Results are shown in the inset of Fig. 1. It is remarkable that the maximum of the isothermal and dynamic measurements coincide at the same temperature. The existence of an anomaly in the specific-heat curve is the definitive proof that the micromodulated phase develops through a real phase transition. The fact that, within the experimental uncertainties, Cp measurements performed on heating, cooling, and isothermically exhibit the peak at the same temperature, together with the reported absence of measurable latent heat,[14] suggests that the transition is second order or very weakly first order (with an hysteresis and latent heat smaller than the detection limit). Some thermal hysteresis has been previously observed in the measurement of different quantities.[10,14] Nevertheless, it must be taken into account that in all those experiments the sample was subjected to mechanical stresses, which could result in a modification of the characteristics of the phase transition.

As already mentioned, inelastic neutron-scattering experiments have revealed an anomaly of a transverse phonon on approaching the phase transition. In this work we have searched for the possibility of an instability at the center of the Brillouin zone. Although neutron measurements do not seem to show any anomalous behavior in this region,[9] ultrasonic methods are a much more sensitive tool to investigate the behavior of the solid at long wavelengths. We have measured the velocity of ultrasonic waves propagated along the [001] and [110] directions by the pulse echo method and using the phase sensitive technique. From the obtained values we have determined the following elastic constants at room temperature: $C_{11} = 136 \pm 3$ GPa, $C_{44} = 102 \pm 3$ GPa, and $C_L [= (C_{11} + C_{12} + 2C_{44})/2] = 222 \pm 9$ GPa. The velocity of shear waves propagating in the [110] direction with [110] polarization was affected by strong attenuation and this compelled us to make use of two transducers, coupled on opposite faces of the sample that enabled us to work in the through transmission method. The corresponding elastic constant $C' [= (C_{11} - C_{12})/2]$ found is 22 ± 2 GPa. C_L and C_{44} have similar values to those recently reported by Worgull *et al.*[18] By contrast, we have found a larger value for C'; such a difference is likely to be due to small differences in the composition of the two samples[19] (it is worth recalling that for martensitic alloys this elastic constant is the more sensitive to the alloy composition). Also, the slopes of the phonon dispersion curves computed using the values of the elastic constants given above are in reasonable agreement with those measured by neutron scattering.[15] An example of the evolution of the elastic constants with temperature is shown in Fig. 2. A noticeable decrease of the two shear elastic constants C_{44} and C' occurs at the phase transition. It is specially remarkable for C', for which the amount of softening at the transition point is around 60%. Although the

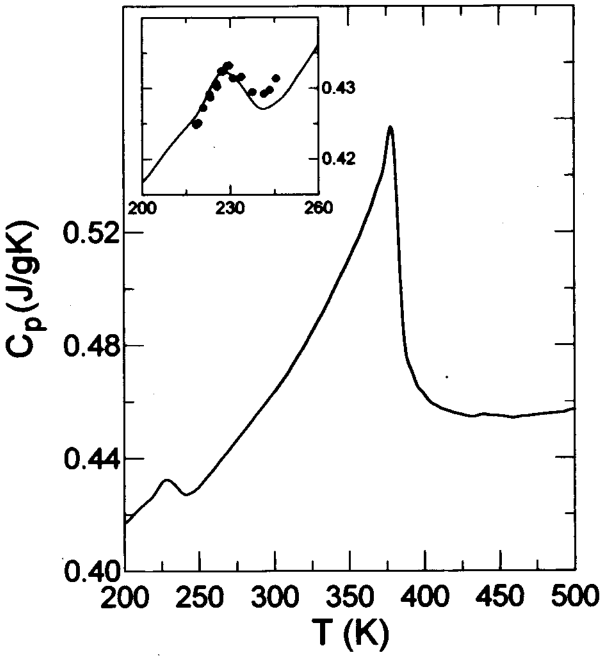

FIG. 1. Specific heat as a function of temperature showing the λ peak at the Curie point and the small peak at the temperature of the transition towards the intermediate phase. An enlarged view (continuous line) is shown in the inset, where points correspond to isothermal measurements.

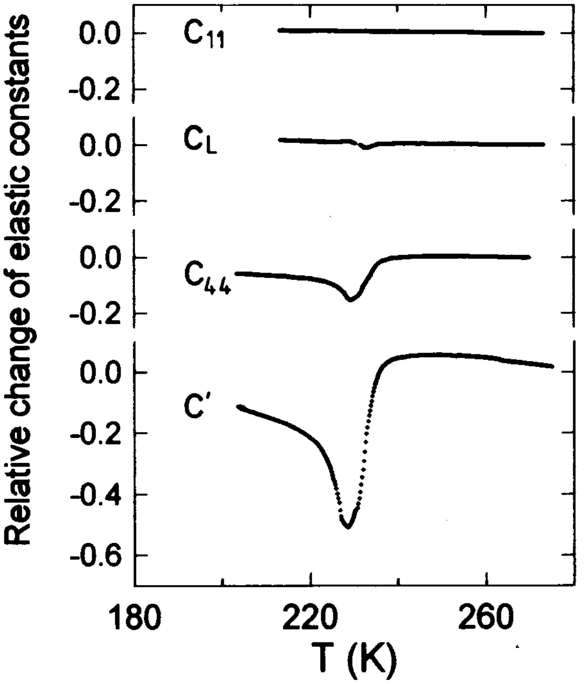

FIG. 2. Relative changes of the elastic constants as a function of temperature. C_{11}, C_L, and C_{44} have been obtained by the pulse-echo method. C' has been obtained by the through transmission method.

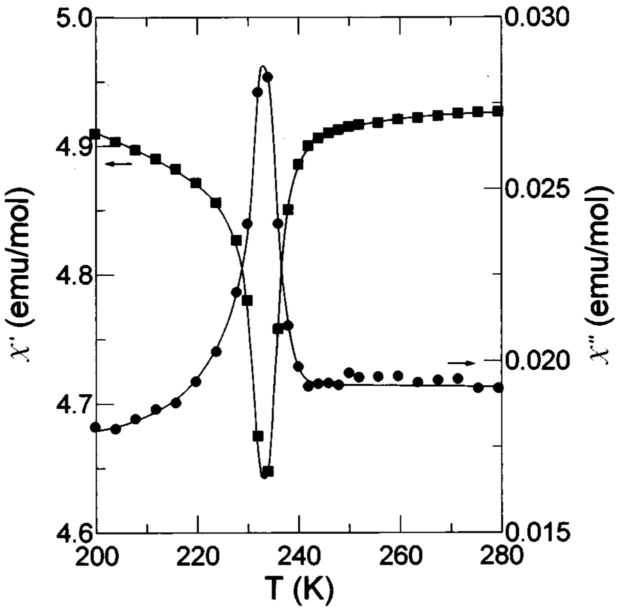

FIG. 3. Real (squares) and imaginary (circles) parts of the ac magnetic susceptibility as a function of temperature. Lines are guides to the eyes. Data have been obtained with a 10 Oe field at 66 Hz, applied along the [001] direction.

measured temperature dependences of the elastic constants differ from previously published data obtained in a different sample using a less sensitive technique,[20] they are perfectly consistent with the measurements presented in Ref. 18. It is, however, worth mentioning that in Ref. 18, the relative change in C' is only measured down to ~ 5 K above the transition; the use of a through transmission method has enabled us to measure C' through the transition. The amount of softening found for C' is very similar to that reported for the phonon frequency at $q=0.33$.[9] The larger softening of C' results in an important increase of the elastic anisotropy (C_{44}/C') at the phase transition. On the other hand, the longitudinal elastic constants do not exhibit anomalous behavior: both C_{11} and C_L increase as temperature is reduced (although a small anomaly, reminiscent from those of the shear elastic constants, is still present in C_L). The fact that no elastic constant vanishes at the transition point, together with the incomplete softening of the transverse phonon at $q=0.33$, indicates that the transition is first order rather than continuous. However, since there is no detectable thermal hysteresis and latent heat, the first-order character must be extremely weak. There is also a second interesting feature showing up from Fig. 2: after the intermediate phase transition, upon further cooling (approaching the martensitic phase transition), C' increases. As far as we know, Ni_2MnGa is the first martensitic material exhibiting this behavior. Actually, this finding must be related to the increase in the frequency of the soft phonon mode after the phonon condensation. Both effects are a direct consequence of the phase transition towards the intermediate phase which modifies the intrinsic dynamical response of the bcc structure. Another system showing an intermediate premartensitic structure accompanied by pronounced phonon softening is Ni-Al.[13] The elastic constants of this alloy, however, do not show the aforementioned anomalous behavior.[21] The different behavior in the two alloy systems is due to the existence in Ni_2MnGa of a phase transition towards the intermediate phase. Even though the phononic anomaly reported by Zheludev *et al.*[9] persists above the Curie point, it is still likely that the origin of the significant differences between the two alloy systems originate from magnetoelastic effects due to the ferromagnetic character of the Ni_2MnGa. Indeed, it has already been reported in other ferromagnetic materials that magnetoelastic coupling can result in elastic constants softening on cooling.[22,23] Moreover, within the Landau theory framework, it can be shown[24] that a free energy including a coupling between the vibrational and magnetic order parameters can lead to a weakly first-order phase transition in which the coupling term between the amplitude of the phonon and the magnetization is responsible for the incomplete phonon softening.

With the aim of pursuing the suggested interaction between the structural and magnetic degrees of freedom, we have performed ac magnetic susceptibility measurements on the temperature range of interest. Figure 3 shows the magnetic susceptibility as a function of temperature. The example corresponds to a magnetic field of 10 Oe, oriented along the [001] direction, with a frequency of 66 Hz. The real part of the magnetic susceptibility (χ') exhibits a marked decrease at the same temperature where there is the peak in Cp and the minimum in the shear elastic constants. The imaginary part (χ'') is small in magnitude and also shows a peak at the phase transition. These findings make it clear that the appearance of the micromodulated elastic domains gives rise to a change in the magnetic properties of the alloy, thus evidencing a magnetoelastic interaction. The small peak in χ'' is associated with a dissipative effect, probably due to the motion of domain boundaries. It is suggested that antiphase domains are formed during the intermediate transition which act as additional structural defects (pinning centers) opposing the ferromagnetic domain walls motion. This effect would account for the observed maximum in χ''. This is in agreement with an increase in the internal friction as recently reported.[14]

In conclusion, the present results prove that the appearance of the micromodulated phase occurs via a weakly first-order phase transition. At that point, the lattice exhibits partial dynamical instability for all long wavelength shear distortions, especially for those associated with C'. This instability is a consequence of a magnetoelastic interaction.

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