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Ultrasonic study of the two-step martensitic phase transformation in Ni_2MnGa

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The temperature dependence of the ultrasonic attenuation and velocity was measured in a Ni_2MnGa single crystal in the temperature range from above a weakly first-order intermediate phase transition at $T_I \sim 265$ K down to the martensitic phase-transformation temperature, $T_M \sim 220$ K. The martensitic phase transformation occurs as a two-step process. The behavior of the velocity and attenuation in this premartensitic phase, $T_I > T > T_M$, is consistent with neutron-scattering data and shows that the premartensitic phase is a more ordered modulated phase than the parent phase. While precursor effects are observed above T_I, the martensitic phase transformation occurs abruptly. These results are compared with neutron-scattering results, transmission electron microscopy, and previous ultrasonic studies in Ni_2MnGa and martensitic phase transformations in other metals. [S0163-1829(98)07005-2]

INTRODUCTION

Since Ni_2MnGa is the only ferromagnetic Heusler alloy known to undergo a martensitic phase transformation and exhibit the shape memory effect, it has been the subject of a number of investigations in recent years. The most interesting feature of this transformation is that the alloy not only undergoes a martensitic phase transformation at $T_M \sim 220$ K, but prior to this it undergoes a weakly first-order transformation to a premartensitic structural phase at $T_I \sim 265$ K.

Neutron studies were the first to report that the martensitic phase transformation in Ni_2MnGa is a two-step process.[1] These studies established the existence of a weakly first-order structural phase transition at $T_I \sim 265$ K, and the existence of a premartensitic phase for $T_I > T > T_M$ before the martensitic phase transformation occurs at $T_M \sim 220$ K. A phonon anomaly exists in the slow transverse acoustic branch (TA_2) well above T_I. The soft mode in the TA_2 branch occurs at the wave vector $\zeta_0 = 0.33$. The premartensitic phase is approximately fcc with a modulation corresponding to the wave vector $\frac{1}{3}$ [1 1 0], at which the phonon anomaly is observed. Upon further cooling to $T_M \sim 220$ K, the martensitic transformation occurs and the structure is approximately tetragonal.[1] The behavior of the phonon anomaly above T_I and the ultrasonic velocity and attenuation above T_I are very similar to the behavior observed in NiAl above the martensitic phase transformation in that alloy.[2,3] The phonon softening in Ni_2MnGa, however, is more pronounced than in NiAl, but it is also incomplete. Elastic scattering was also observed and includes strain diffuse streaking, plus the development of a temperature-dependent diffuse peak (satellite) at the same wave vector $\zeta_0 = 0.33$, as T_I is approached. Conventional transmission electron microscopy at room temperature shows a pretransformation microstructure of the single crystal to be comprised of ultrafine scale local distortions (i.e., the ''tweed'' strain image contrast) that are the signature of a dense array of tiny, randomly oriented strain embryos of the new phase to be formed.[1,2] Using high-resolution techniques it was confirmed that these strain embryos have a modulated structure inversely related to ζ_0 as was the case in NiAl.[1,2]

Below T_I, the elastic streaking disappears, the diffuse peak develops into a well-defined Bragg satellite and becomes fully developed at approximately 240 K. In addition, below $T_I \sim 265$ K, the soft-mode phonon frequency increases as the martensitic phase transformation is approached, and the intensity of the $\frac{1}{3}$ [1 1 0] elastic satellite increases as T_M is approached and then decreases at T_M.[4] These data are consistent with the existence of a premartensitic phase involving a transverse modulation of the parent cubic structure with a simple periodicity of $\frac{1}{3}$ [1 1 0] related to ζ_0. A previous ultrasonic study conducted at our laboratory as well as a more recent ultrasonic study, have confirmed the existence of this intermediate phase transformation and the existence of a premartensitic phase below T_I.[5,6]

The focus of the present ultrasonic investigation is to study the entire two-step martensitic phase transformation from above T_I down to T_M. Ultrasonic velocity and attenuation measurements at two ultrasonic frequencies are reported. These new measurements, together with previous neutron, transmission electron microscopy (TEM), x-ray, specific heat, magnetic susceptibility, and ultrasonic studies, now provide a complete and consistent description of the two-step martensitic phase transformation in Ni_2MnGa.[1,4–9]

EXPERIMENTAL PROCEDURE

The Ni_2MnGa single crystal used in the present study is the same one used in an earlier ultrasonic study, and it was cut from the same boule used in the neutron-diffraction studies at Brookhaven National Laboratory.[1] The dimensions of the crystal are $7.96 \times 7.05 \times 3.00\ \mathrm{mm}^3$, with the large face oriented perpendicular to the [1 1 0] direction.

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A Mg buffer rod was employed to directly measure the three independent elastic constants (C_L, C_{44}, and C'). A pulse-echo technique was used to directly measure C_L, C_{44}, and their temperature dependences, while C' was measured in the transmission mode using a technique in which the buffer time was measured using a pulse-echo method and its temperature dependence was subtracted out of the transmitted signal. The value of C' obtained using this method at room temperature agreed with previous results.[5] The elastic constant C_{11} was not directly measured due to the small size of the (1 0 0) faces that made them unsuitable for ultrasonic measurements.

The appropriate quartz transducers were bonded to the large face of the crystal using Nonaq stopcock grease for longitudinal waves and Dow-Corning© V-9 resin for the shear waves due to its ability to better couple shear waves near room temperature.

The temperature control system was comprised of an FTS© Systems FC-100 immersion cooler in a bath of Dow-Corning© Syltherm™ XLT silicone oil that was circulated using a magnetic stirrer far from the crystal so that it had no effect on the measurements. The sample temperature was monitored using a Lake Shore© Cryotonics DT-471 silicon diode in close proximity to the sample and the temperature was known to 0.1 K.

The ultrasonic system was composed of a Matec© 310 gated amplifier and a Matec© 625 broadband receiver for the longitudinal and fast shear waves, while a Panametrics© 5055-PR pulse generator-receiver was used for the slow shear. In all cases the amplitude and time were measured using a LeCroy© 9310A digital oscilloscope. The times were measured using a zero crossover method and were known to at least 0.0025 μs.

RESULTS AND DISCUSSION

The temperature dependence of the velocity associated with the longitudinal and fast shear modes at two ultrasonic frequencies is shown in Figs. 1 and 2, respectively, for the temperature range from 280 K down to T_M. The surface relief present at the martensitic phase transformation prevented data to be taken below T_M with conventional quartz transducers. Of particular interest, is the behavior of the velocities near the phase transformations at T_I and T_M in this two-step martensitic transformation. While large precursor effects exist above the intermediate phase transition, no precursor effects are present near the martensitic phase transformation. In addition, for both modes the velocity increases linearly in the premartensitic phase as T_M is approached.

The temperature dependence of the velocity associated with the elastic constant C' is shown in Fig. 3(a) from 295 K down to T_M. As the sample is cooled, large precursor effects are present and a rapid decrease in the velocity occurs approximately 15° above the intermediate phase transformation at T_I. The velocity in the premartensitic phase, $T_I > T > T_M$, increases dramatically as the temperature is lowered and exhibits no anomalous behavior near T_M. It should be noted that the velocity in the premartensitic phase at 225 K is actually higher than in the parent phase at 290 K. The behavior of the velocity in the vicinity of T_I is the same as previously reported in our earlier study and is similar to the behavior more recently reported by Mañosa *et al.*[5,6] However, it should be noted that the transformation temperatures in the crystal used by Mañosa *et al.* are different, $T_I \sim 275$ K and $T_M \sim 175$ K and no ultrasonic measurements were taken within 20 K of the martensitic phase transformation in their study. The difference in the transformation temperatures implies that the stoichiometry is different in the two crystals.

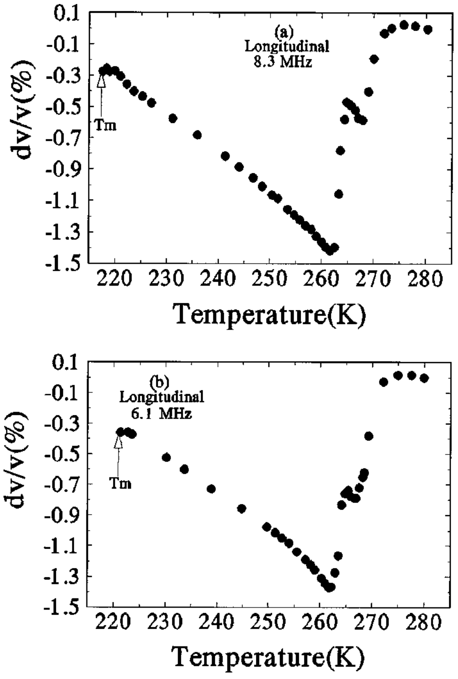

FIG. 1. Temperature dependence of the velocity V_L associated with the elastic constant C_L, at the ultrasonic frequencies (a) 8.3 MHz and (b) 6.1 MHz.

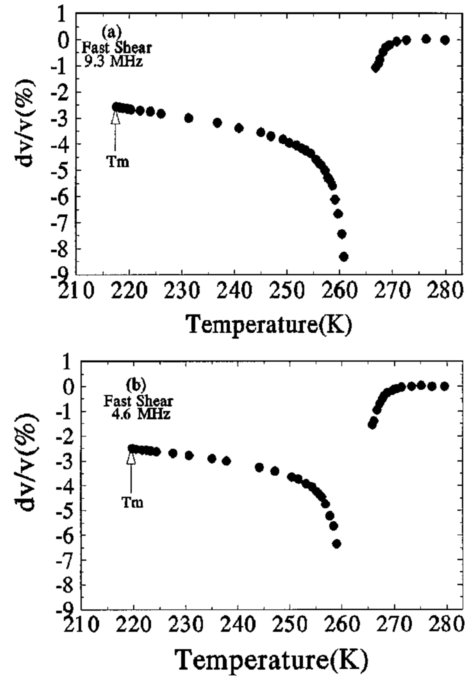

FIG. 2. Temperature dependence of the velocity V_{44}, associated with the elastic constant C_{44}, at the ultrasonic frequencies (a) 9.3 MHz and (b) 4.6 MHz.

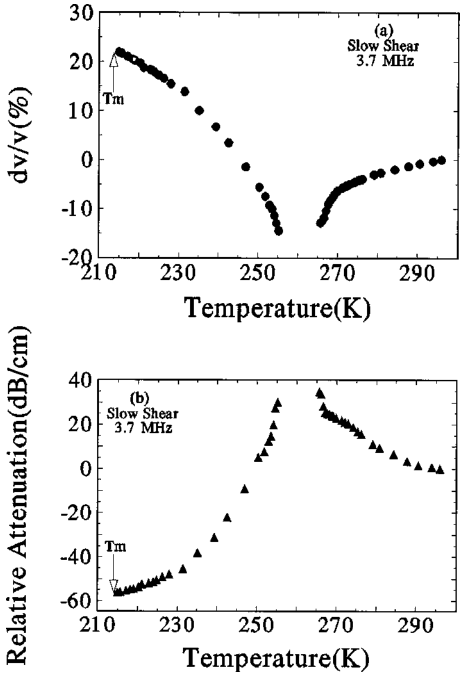

FIG. 3. Temperature dependences of (a) the velocity V', associated with the elastic constant C', and (b) the relative attenuation.

The measured velocities associated with the three independent elastic constants C_L, C_{44}, and C' in the intermediate phase at 225 K are shown in Table I along with those of the parent phase at 300 K from our previous ultrasonic study, which were also obtained with a buffer technique.[5] The logarithmic temperature derivatives associated with these velocities are shown in Table II. The most interesting features in these tables are associated with the elastic constant C'. At 225 K, V' is 17% larger than at 300 K, and its logarithmic temperature derivative is negative and almost three times the magnitude of the corresponding value at 300 K. Table III shows the values of the three independent elastic constants C_L, C_{44}, and C', as well as values for C_{11} and C_{12} at 225 K and 300 K. While C_L and C_{44} are slightly lower at 225 K, there is a marked increase in C' in the premartensitic phase. The values of the elastic constants at room temperature reported recently by Mañosa *et al.* are also shown in Table III.[6] While the values of C_L and C_{44} are in excellent agreement with our values at 300 K, their value of C' is a factor of 5 larger than the value obtained in our laboratory. This large discrepancy is most likely due to differences in the stoichiometry of the crystals. Stoichiometry also plays a large role in the Ni_xAl_{1-x} alloy system, which is structurally similar to Ni_2MnGa. Both the premartensitc transformation in Ni_2MnGa and the martensitic transformation in NiAl are driven by soft modes in the TA_2 branch. In NiAl the elastic constant C' changes by nearly an order of magnitude as the nickel concentration is increased from stoichiometric, 50 at. % nickel, to 63 at. %, while C_L and C_{44} are independent of nickel concentration.[3] In fact, studies have been proposed to quantify these effects.[4] It should be noted that the velocities obtained from the neutron data are in excellent agreement with our ultrasonic velocities, a correlation that was expected since our crystal came from the same boule.[1]

TABLE I. The ultrasonic velocities associated with the three independent elastic constants in the parent phase at 300 K and in the premartensitic phase at 225 K

	V_L	V_{44} 10^5 cm/sec	V'
300 K[a]	5.54	3.56	0.740
225 K	5.52	3.47	0.895

[a]Reference 5.

TABLE II. Logarithmic temperature derivatives of the ultrasonic velocities near 300 K and near 225 K.

	$\frac{d(\ln V_L)}{dT}$	$\frac{d(\ln V_{44})}{dT}$ 10^{-4} K^{-1}	$\frac{d(\ln V')}{dT}$
300 K[a]	−0.567	−1.26	23.2
225 K	−2.67	−3.05	−61.4

[a]Reference 5.

The temperature dependence of the relative attenuation for the slow shear mode is shown in Fig. 3(b) and those of the longitudinal and fast shear modes at two different ultrasonic frequencies are shown in Figs. 4 and 5, respectively. For all modes in the region near but above T_I, the increase in attenuation is accompanied by a decrease in the velocity as shown in Figs. 1, 2, and 3(a). Similarly, in the region below T_I, the decrease in attenuation is accompanied by a corresponding increase in velocity. In the premartensitic phase, the attenuation for the longitudinal and fast shear modes is comparable or less than that of the parent state, while the attenuation for the slow shear mode drops markedly in the premartensitic phase and continues to decrease until T_M is reached. Since attenuation measurements are very sensitive probes to lattice defects, this decrease in attenuation suggests that the premartensitic phase is a more ordered state than the parent state. These data are consistent with the neutron results, which show that the $\frac{1}{3}$ [1 1 0] peak increases dramatically as the T_M is approached.[4] Conventional transmission electron microscopy and diffraction during cooling of the same specimen studied in the earlier work of Zheludev *et al.* was recently carried out.[1,10] The single-crystal structure was observed to transform below T_I into coarse domains of 0.5 to 1 μm size, where each domain is a different orientation variant of the new phase, and the fine scale tweed strain contrast is no longer present. Furthermore, as with elastic neutron scattering, electron diffraction showed only sharp

TABLE III. Single-crystal elastic constants obtained from the velocities in Table I and the density $\rho = 8.13$ g/cm^3.

	C_L	C_{44}	C' 10^{12} dynes/cm^2	C_{11}	C_{12}
300 K[a]	2.50	1.03	0.045	1.52	1.43
293 K[b]	2.22	1.02	0.22	1.36	0.92
225 K	2.48	0.98	0.065	1.56	1.43

[a]Reference 5.
[b]Reference 6.

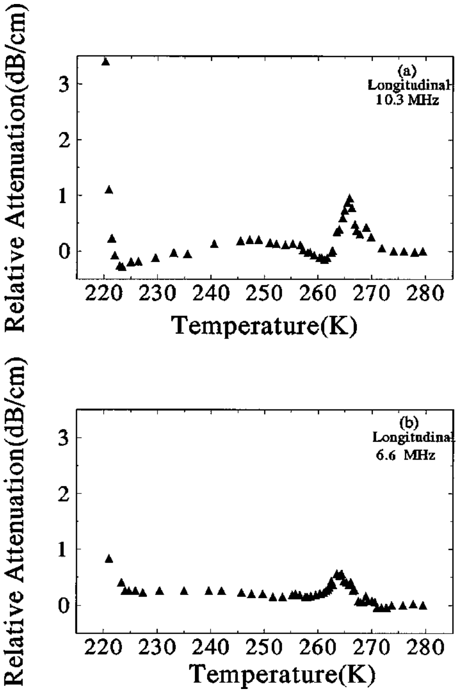

FIG. 4. Temperature depencence of the relative attenuation for the longitudinal mode at the ultrasonic frequencies (a) 10.3 MHz and (b) 6.6 MHz.

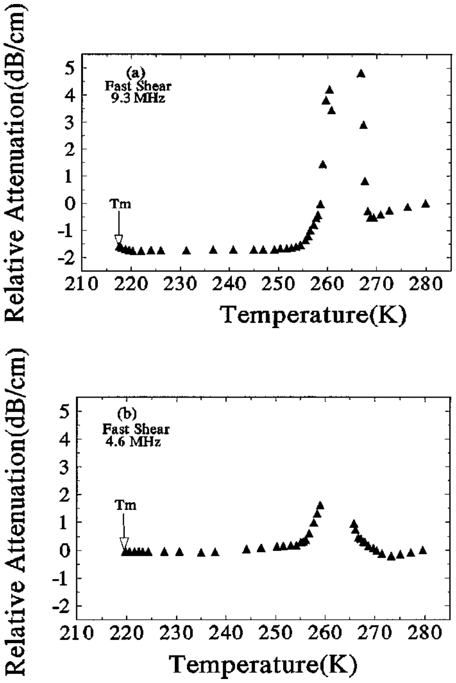

FIG. 5. Temperature dependence of the relative attenuation for the fast shear mode at the ultrasonic frequencies (a) 9.3 MHz and (b) 4.6 MHz.

satellites; the strain diffuse streaking has disappeared. The foregoing are clear indications that the new phase has a uniform, albeit modulated, microstructure without the effects of a dense population of localized strains as was seen prior to transformation.

The intermediate phase transformation at T_I in Ni_2MnGa shows many of the same features as the martensitic phase transformation in NiAl alloys. In both systems inelastic neutron-scattering results show phonon anomalies in the TA_2 branch.[1,2] The large softening in the elastic constant C' is consistent with these data. While the frequency of the soft phonon decreases as the transformation temperature is approached the softening is incomplete for both systems. Elastic diffuse scattering data also show a peak at the same wave vector as the phonon anomaly in the inelastic scattering data. Ultrasonic measurements in NiAl show very small precursor effects in the velocity and attenuation for the longitudinal and fast shear modes except within a few degrees of the transformation temperature.[3] However, large precursor effects are observed in the slow shear mode associated with the TA_2 branch approximately 20 K above the transformation. All of these data suggest that the transformations in both alloy systems are driven by a soft mode. It should be noted that while the intermediate phase transformation in Ni_2MnGa is structural and weakly first order it is not martensitic like that in NiAl.

The behavior near the martensitic phase transformation in Ni_2MnGa is quite different from that of the intermediate transformation. In the region near T_M there are no precursor effects in the velocity and attenuation to give evidence of lattice instabilities. In contrast to the behavior of the velocity and attenuation near T_I, the velocity and attenuation exhibit no anomalous behavior near T_M. The increase in the longitudinal attenuation a few degrees above T_M is most likely due to the surface relief present when the sample transforms.[9] In the case of the shear modes, the attenuation changes abruptly at the martensitic phase transformation. The most surprising result is the dramatic increase in the slow transverse velocity. These data are consistent with the inelastic neutron-scattering results which report the frequency of the soft phonon in the TA_2 branch increasing from 260 K to as low as 230 K.[4] This would suggest that this soft mode is associated with the premartensitic phase transformation and not the martensitic phase transformation. These results are very similar to the martensitic phase transformations in Na and Li. In these metals, the transformation also occurs abruptly. Ultrasonic velocity and attenuation data show no precursor effects prior to the martensitic phase transformation.[11,12] The diffuse elastic and inelastic neutron-scattering data in these metals also exhibit no anomalous behavior prior to T_M.[13–15]

Vasil'ev *et al.* and Chernenko and Kokorin have reported an ultrasonic study of the martensitic phase transformation in Ni_2MnGa using an electromagnetic generation (EMG) technique.[8,16] These results show softening in the velocities for all three modes as high as 70 K above the reported martensitic phase-transformation temperature. In addition their crystal was nonstoichiometric by a 1% reduction in manganese content through nickel substitution.[16] The martensitic transformation temperature was, however, verified by other methods and occurs at 293 K, although no premartensitic transformation was observed.

While the EMG technique is excellent for studying martensitic transformations because no bonds are needed, Ni_2MnGa is ferromagnetic. Therefore the magnetic fields used in the generation process, approximately 1 T, could result in magnetoelastic and generation effects that could affect the elastic constants and their temperature dependence.[17]

In the present study conventional quartz transducers were used to prevent these effects making this the first ultrasonic study of the martensitic phase transformation without the presence of external magnetic fields. In addition, the condition that the ultrasonic wavelength be much greater than the skin depth is not met for the slow shear mode in Ni_2MnGa. Therefore C' was not directly measured.[5] The more recent results by Mañosa *et al.* also use quartz transducers and report results to within 20 K of the martensitic phase transformation.[6] They report stiffening of the elastic constants in the premartensitic phase as the sample is cooled, which is in excellent agreement with the present study.

Finally, data for the temperature dependencies in the two-step process were taken for different frequencies to test a localized soft-mode theory.[18] This theory has successfully described the behavior of the ultrasonic velocity and attenuation for the martensitic phase transformations in InTl and NiTi. Only the data for the intermediate phase transition were considered since no precursor effects exist near the martensitic phase transition. Data were taken over a relatively narrow frequency range because of the high attenuation in the crystal, therefore detailed comparisons cannot be made. However, the present data do show some interesting results which may be useful in characterizing the transformation. Figure 1 shows no frequency dependence in the fractional velocity change for the longitudinal mode. Due to high attenuation, the fast shear echoes could not be detected at the transition. Figure 2 displays, over the limited temperature range where the echoes could be observed, no frequency dependence in the fractional velocity change. Figures 4 and 5, however, show a definite frequency dependence in the attenuation. The localized theory predicts that dv/v should be proportional to the ultrasonic frequency, yet this frequency dependence is not observed. The attenuation changes, however, clearly show a frequency dependence which, within experimental uncertainty, is consistent with this theory. It should be noted that the intermediate phase transition is very weakly first order and that the localized soft-mode theory may not apply in this case.

SUMMARY

The ultrasonic velocity and attenuation data clearly show that the martensitic phase transformation in Ni_2MnGa is a two-step process. A weakly first-order structural phase transformation occurs at $T_I \sim 265$ K and large precursor effects are observed above T_I. The elastic constants stiffen below T_I and the attenuation decreases dramatically as the temperature is decreased. No precursor effects in the attenuation or velocity occur in the intermediate phase above T_M and the martensitic phase transformation occurs abruptly. All of these results are consistent with neutron-scattering results and TEM studies.

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