# Behavior of the elastic properties near an intermediate phase transition in $Ni_2MnGa$

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(Received 16 July 1996)

An ultrasonic pulse echo technique was employed to measure the single-crystal elastic constants and their temperature dependence in the vicinity of an intermediate phase transition at 265 K in a $Ni_2MnGa$ single crystal. The measured elastic constants at 300 K (in units of $10^{11}$ dyn/cm$^2$) are as follows: $C_{44}=10.3$, $C'=0.445$, and $C_L=25.0$, where $C'=1/2(C_{11}-C_{12})$ and $C_L=1/2(C_{11}+C_{12}+2C_{44})$. The present ultrasonic results differ from a earlier ultrasonic study and provide the first direct determination of the elastic constant $C'$. All three elastic constants soften as the premartensitic transformation temperature is approached, and the ultrasonic attenuation also increases dramatically as the intermediate phase transition is approached. The behavior of the elastic constants and the ultrasonic attenuation is consistent with inelastic neutron-scattering results and confirms the existence of the intermediate phase. The ultrasonic results are compared with the neutron data, with earlier ultrasonic results in $Ni_2MnGa$, and with studies of the martensitic phase transition in NiAl alloys. [S0163-1829(96)04646-2]

## INTRODUCTION

The behavior of the elastic properties in the vicinity of a structural transformation in a solid provides much insight into the nature of the transition. A number of metals and alloys undergo martensitic phase transformations, a diffusionless, displacive, first-order transformation. For NiAl alloys,[1,2] it is well established that the elastic constant $C'$, associated with the slow transverse acoustic ($TA_2$) branch, plays an important role in the occurrence of the transformation. In the NiAl system, ultrasonic studies[3,4] show not only that $C'$ is small, but that it softens as the temperature is lowered. Neutron-scattering studies show that phonon anomalies exist in the $TA_2$ branch; these studies also provide valuable information about the relationship between the phonon anomalies and the transformation in this system.

Recent x-ray[5] and neutron studies[6–8] in $Ni_2MnGa$ show that similar phonon anomalies exist in the $TA_2$ branch. The intermetallic compound $Ni_2MnGa$ is the only ferromagnetic Heusler alloy which undergoes a martensitic transformation. At room temperature, $Ni_2MnGa$ has a fcc $L2_1$ Heusler structure; upon cooling, it undergoes a martensitic transformation to a modulated crystal structure with approximate tetragonal symmetry. The martensitic transformation temperature $T_M$ varies with the composition of the alloy, and values of $T_M$ between 175 and 293 K have been reported.[9] $Ni_2MnGa$, like NiAl, is a shape memory alloy and in many respects, the martensitic transformation is quite similar to the transformation in the NiAl alloy system. For both alloy systems, phonon anomalies occur in the $TA_2$ phonon dispersion in the parent cubic phase. Softening is observed in the $TA_2$ branch at a wave vector $\zeta_0 \approx 0.33$ in $Ni_2MnGa$, approximately the same value as in the $Ni_{62.5}Al_{37.5}$ system when the size of the unit cell is taken into account. While the softening is much more pronounced for $Ni_2MnGa$, it is incomplete for both systems. In $Ni_2MnGa$, the phonon softening results in a premartensitic intermediate transformation at a temperature $T_I = 265$. K. The intermediate phase is approximately fcc, but a new [220] modulation, corresponding to a wave vector $\zeta \approx 0.33$ occurs. This modulation is different from the five-layer modulation in the martensitic phase which occurs at a lower temperature. Despite the large number of studies of the martensitic phase transformation in $Ni_2MnGa$, the only evidence of the existence of an intermediate phase transformation at $T > T_M$ was obtained by magnetoelastic measurements.[10] The neutron studies have now provided not only strong evidence of this intermediate state, but also much information about the structure of this premartensitic state.

Neutron studies show that a temperature-dependent peak in the elastic diffuse scattering begins to develop at the same wave vector $\zeta_0$ as $T \to T_I$. Below $T_I$, this peak develops into a Bragg peak representative of an intermediate state between the high-temperature Heusler structure and the low-temperature martensitic structure. The neutron results suggest that the intermediate state is driven by a soft mode, and the occurrence of a martensitic transformation at lower temperatures is consistent with anharmonic coupling of the modulated strains to homogeneous lattice distortions.[8,11]

The velocity associated with the elastic constant $C'$, obtained from the phonon dispersion data for the $TA_2$ branch, is low, as it is in NiAl. In contrast, the value of $C'$, obtained previously by an electromagnetic generation of ultrasound technique,[12] is surprisingly much larger than the neutron results. The present study was undertaken to resolve this discrepancy and to confirm the existence of the intermediate phase. Since ultrasonic velocity and attenuation measurements are very sensitive to anharmonic effects and defects, they can provide additional important information about the nature of this premartensitic transformation.

## EXPERIMENT

The single crystal used in the present study was cut from the large single crystal used in previous neutron-diffraction experiments at the Brookhaven National Laboratory. The sample had rectangular faces with dimensions $3.00 \times 7.05 \times 7.96$ mm$^3$. The large rectangular face was ori-

 

TABLE I. The ultrasonic velocities for longitudinal and two shear modes at 300 K obtained in the present study, neutron-scattering studies, and from electromagnetic generation of ultrasound (EMG).

| Study | $V_L$ | $V_{44}$ $10^5$ cm/s | $V'$ |
|---|---|---|---|
| Present | 5.54 | 3.56 | 0.740 |
| Neutron[a] | 5.23 | 3.94 | 0.772 |
| EMG[b] | 5.46 | 3.36 | 2.77 |

[a]Reference 6.
[b]Reference 12.

ented perpendicular to a [110] direction. The appropriate quartz transducers were mounted on this face to generate longitudinal or shear waves. The absolute values of the three independent elastic constants ($C_L$, $C_{44}$, and $C'$) and their temperature derivatives were determined by an ultrasonic pulse echo technique employing a magnesium buffer rod. The temperature dependence of the velocities associated with the three independent elastic constants was measured between 300 and 250 K. A thermistor was mounted in close proximity to the sample so that the temperature was known to at least 0.007 K in each run. A Fisher Scientific® temperature bath comprized of antifreeze and water was used for the longitudinal and fast shear runs, while a thermoelectric cell and analog temperature controller were used for the slow shear runs. For studies near room temperature, a salol bond was used between the magnesium buffer rod and the $Ni_2MnGa$ crystal. For studies below 285 K, a Dow Corning® V-9 resin or Nonaq stopcock grease was used between the transducer and buffer rod or sample.

## RESULTS AND DISCUSSION

The measured velocities, for propagation in the [110] direction, associated with the three independent elastic constants $C_L = 1/2(C_{11}+C_{12}+2C_{44})$, $C_{44}$ and $C' = 1/2(C_{11} - C_{12})$ are shown in Table I. The velocities determined by an earlier ultrasonic study and the velocities obtained from the inelastic neutron-scattering experiments are also shown. All velocities are at 300 K.

The absolute velocities measured by a buffer technique are known to 0.25% for $C_{44}$ and $C_L$ and 1% for $C'$. Since velocities from the phonon dispersion curves typically have an accuracy between 4 and 10 %, the neutron results are in agreement with the more accurate ultrasonic measurements. The velocities in the earlier ultrasonic study were obtained by an electromagnetic generation technique (EMG), which is an excellent technique for studying the velocity near a structural phase transformation because no bonds are required between the transducer and sample. This technique was, in fact, used in our laboratory to study the martensitic transformation in Li (Ref. 13) and Na (Ref. 14). However, for electromagnetic generation of ultrasound to occur, the ultrasonic wavelength must be much greater than the skin depth. Since the velocity associated with $C'$ is very low in $Ni_2MnGa$, this requirement is not met. This would account for the large discrepancy between the present value for the slow shear velocity and the value of a shear velocity which they erroneously associate with the $C'$ mode, obtained by the EMG technique. The present experiment therefore provides a direct determination of the velocity associated with the elastic constant $C'$ by an ultrasonic technique. The values for the longitudinal and fast shear velocities are in better agreement with the EMG study, but the small difference cannot be accounted for by experimental uncertainty. Some of the difference may be associated with the temperature dependence of the velocity, which is different in the two studies near room temperature. The temperature derivatives of the velocity in the vicinity of 300 K are shown in Table II. In the present study, the longitudinal and fast shear velocities have very small, but negative, values. In contrast, even above 300 K, the temperature derivatives are very large and positive for the EMG study. It is not clear why the temperature dependence is different in the two studies, but it may be associated with the nonstoichiometric character of the crystal used in the EMG study. In addition, since $Ni_2MnGa$ is ferromagnetic, magnetoelastic effects and motion of domain boundaries may also affect the EMG results. It should also be noted that a transformation in the present study occurs near 265 K, while the EMG study lists $T_M$ as between 270 and 280 K. Since the velocity changes more rapidly in the vicinity of the transformation, this may also account for the different values of the velocities obtained in the two studies. For the $C_{44}$ and $C_L$ modes, the agreement is, however, reasonable. For $C'$, the temperature derivative obtained in the present study, near room temperature, is positive and large. As mentioned above, the values of the slow shear velocity and its temperature dependence were not measured in the EMG study.

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

| Study | $\frac{d(\ln V_L)}{dT}$ | $\frac{d(\ln V_{44})}{dT}$ $10^{-4}$ K$^{-1}$ | $\frac{d(\ln V')}{dT}$ |
|---|---|---|---|
| Present | −0.567 | −1.26 | 23.2 |
| EMG[a] | 17.2 | 27.7 | 14.6 |

[a]Reference 12.

The single-crystal elastic constants, calculated from the velocities shown in Table I, are listed in Table III. A density of 8.13 g/cm$^3$ was used in the calculation. The values of $C_{11}$ and $C_{12}$ were obtained from the directly measured values of $C_L$, $C_{44}$, and $C'$ using the relations $C_{11} = C_L + C' - C_{44}$ and $C_{12} = C_L - C' - C_{44}$. Values of $C_{11}$, $C_{44}$, and $C_{12}$, listed in the EMG study are also shown. The values of $C_{11}$ and $C_{12}$ in the EMG study are in error because the elastic

TABLE III. Single-crystal elastic constants at 300 K obtained from the velocities shown in Table I and the density $\rho = 8.13$ g/cm$^3$.

| Study | $C_L$ | $C_{44}$ | $C'$ $10^{12}$ dyn/cm$^2$ | $C_{11}$ | $C_{12}$ |
|---|---|---|---|---|---|
| Present | 2.50 | 1.03 | 0.045 | 1.52 | 1.43 |
| EMG[a] | 2.42 | 0.92 | 0.63 | 2.13 | 0.87 |

[a]Reference 12.

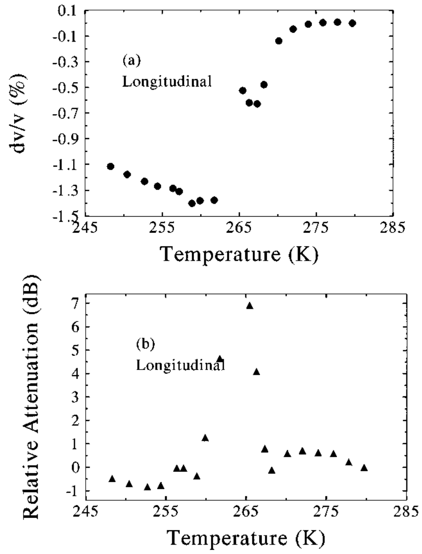


FIG. 1. Temperature dependence of the relative velocity, $V_L$ (a) and the relative attenuation (b) associated with the elastic constant $C_L$.

constant $C'$ is incorrect by a factor of 16.

Of particular interest in the present ultrasonic study is the behavior of the elastic properties in the vicinity of the premartensitic transformation. The temperature dependence of the longitudinal and fast shear velocities from 285 to 265 K are shown in Figs. 1(a) and 2(a), respectively. For both modes, the velocity begins to decrease with temperature in a dramatic way below approximately 270 K. This behavior is more consistent with results obtained in the EMG study. Figure 3(a) shows the temperature dependence of the velocity associated with the elastic constant $C'$. For this mode, the velocity decreases very rapidly with temperature from 300 to 282 K. A much more dramatic decrease then occurs below

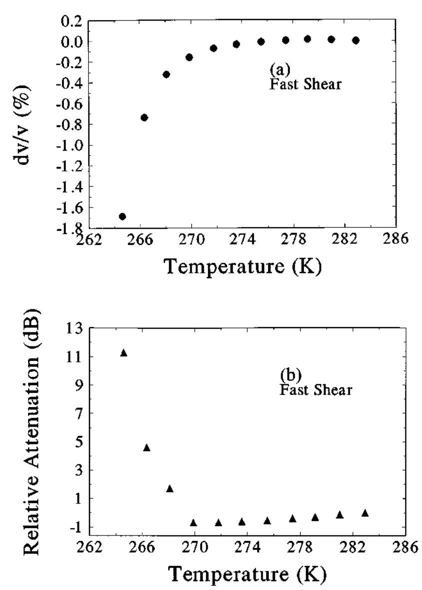


FIG. 2. Temperature dependence of the relative velocity, $V_{44}$ (a) and the relative attenuation (b) associated with the elastic constant $C_{44}$.

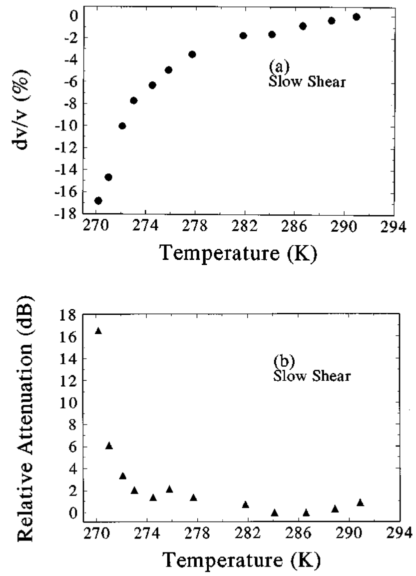


FIG. 3. Temperature dependence of the relative velocity, $V'$ (a) and the relative attenuation (b) associated with the elastic constant $C'$.

280 K, rather than 270 K, as is the case for the other modes. Both ultrasonic studies, therefore, show that the velocity decreases dramatically as the intermediate phase transformation is approached. This decrease in the velocity for all three modes above the transformation temperature is clearly the signature of an incipient structural instability.

Ultrasonic attenuation measurements provide additional information about the transformation. Figures 1(b) and 2(b) also show the temperature dependence of the attenuation for the longitudinal and fast shear modes, respectively, for an ultrasonic frequency of 10 MHz. For temperatures below 270 K, a large increase in the attenuation occurs along with a more rapid decrease in velocity as $T_I$ is approached. Figure 3(b) also shows, for an ultrasonic frequency of 5 MHz, the temperature dependence of the attenuation associated with the elastic constant $C'$. For this mode, large changes in attenuation together with more rapid decreases in the velocity are observed for temperatures as high as 282 K. Below 270 K, the attenuation is so large that no echoes are observed for the $C'$ mode. Ultrasonic attenuation and velocity measurements associated with the $C'$ mode clearly are very sensitive probes of the structural instability, which is not surprising since this mode is anomalously low. Pretransformation effects in the slow shear velocity and attenuation are clearly observed 20 K above the actual transformation. It is interesting to compare the behavior of the ultrasonic attenuation with the neutron-scattering results. As mentioned earlier, neutron-scattering studies show the formation of a Bragg-like peak at the location of the soft mode in the Brillouin zone. The onset of this peak is observed near 270 K. Below $T_I$, the intensity of this peak increases two orders of magnitude to about 250 K as the temperature decreases. While no $C'$ echoes were observed below $T_I$, the temperature dependence of the velocity and attenuation was studied below $T_I$ for the $C_{44}$ mode. These results are shown in Figs. 4(a) and 4(b). As the temperature is lowered, the echoes disappear at approximately 265 K. Upon further cooling, to approxi-

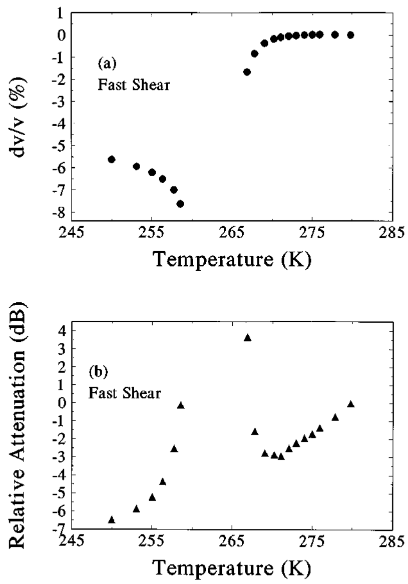


FIG. 4. Temperature dependence of the relative velocity, $V_{44}$ (a) and the relative attenuation (b) associated with the elastic constant $C_{44}$. The gap in the data is due to the high attenuation associated with the transition to the intermediate phase.

mately 259 K, a new series of well-defined shear echoes appear. The echoes continue to grow in amplitude as the temperature is lowered to 250 K. The velocity associated with the fast shear mode, below $T_I$, is lower than in the parent state by 5%. In addition, the velocity now increases, rather than decreasing, as the temperature is lowered. Very little hysteresis is observed in the attenuation and velocity when the temperature is increased. These results suggest that the intermediate state becomes fully developed and ordered below 250 K, a finding which is consistent with the formation of the Bragg peak at $q=(1/31/30)$. Neutron-scattering results suggest that the diffuse peak is defect induced and consistent with the models proposed by Axe *et al.*[15] and Halperin and Varma.[16] The ultrasonic attenuation also manifests the occurrence of this pretransformation behavior, but in a more pronounced way, and is consistent with the formation of defects associated with transformation.

The behavior of the velocity and attenuation for the $C'$ mode, in the vicinity of the intermediate transition, is also very similar to results for $C'$ obtained in NiAl. In both systems, dramatic decreases in the velocity and concurrent increases in attenuation occur prior to the transformation. In $Ni_2MnGa$, however, pretransformation effects in the velocity and the attenuation are observed at temperatures well above the transformation temperature for all modes. In contrast, the longitudinal and fast shear attenuation and velocity in NiAl exhibit no anomalous behavior above $T_M$. That is, for these modes the velocity increases as the temperature is lowered, and changes in the velocity and attenuation only occur very close to $T_M$. It should be emphasized that in $Ni_2MnGa$, the intermediate transformation is a structural transformation and not martensitic, while in NiAl, the transformation is martensitic. Nevertheless, the behavior of the attenuation and velocity is quite similar. The behavior of the attenuation and velocity is very similar to that observed not only in NiAl, but also in In-Tl (Ref. 17) and Ni-Ti.[18] A localized soft mode theory, developed by Clapp,[19] has successfully explained the results in In-Tl and Ni-Ti. Detailed studies of the attenuation and velocity, above and below $T_I$, done as a function of frequency will be performed to see if this model can successfully explain the results in $Ni_2MnGa$. Similar studies of the elastic properties in the vicinity of $T_M$ will also be done for comparative purposes. We also plan to study the behavior of the elastic properties under uniaxial stress to provide additional information about the two-step martensitic phase transition in $Ni_2MnGa$.

## CONCLUSION

The neutron-diffraction and electron transmission experiments show that the intermediate premartensitic phase involves a transverse modulation of the parent phase with a modulation periodicity related to the soft phonon mode in the $TA_2$ branch. The intermediate state forms near 260 K and becomes fully developed by 250 K. The temperature dependence of the ultrasonic attenuation and velocity is entirely consistent with the development of this phase. In addition, the values of the velocity associated with the three independent elastic constants are consistent with the neutron results. The present ultrasonic study provides a direct measurement of the elastic constant $C'$.

The phonon anomalies and the martensitic transformation in NiAl have been extensively studied and many models, including first-principles local-density-functional calculation,[20,21] have been able to reproduce these anomalies. The origin of the phonon anomalies lies in the electron-phonon contributions and Fermi nesting properties of the Fermi surface. Since the phonon anomalies are quite similar in $Ni_2MnGa$, these anomalies are expected to arise from similar interactions.

## ACKNOWLEDGMENTS

The authors are grateful to S. M. Shapiro and L. E. Tanner for providing the crystal and for many valuable discussions. This work was supported by NSF Grant No. DMR 91-123351.

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