Elastic constants of Ni-Mn-Ga magnetic shape memory alloys

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We have measured the adiabatic second order elastic constants of two Ni-Mn-Ga magnetic shape memory crystals with different martensitic transition temperatures, using ultrasonic methods. The temperature dependence of the elastic constants has been followed across the ferromagnetic transition and down to the martensitic transition temperature. Within experimental errors no noticeable change in any of the elastic constants has been observed at the Curie point. The temperature dependence of the shear elastic constant C' has been found to be very different for the two alloys. Such a different behavior is in agreement with recent theoretical predictions for systems undergoing multi-stage structural transitions.

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I. INTRODUCTION

The martensitic transition is a diffusionless solid-solid phase transition with a predominant shear distortion of the lattice. In spite of the transition being first order, many of the solids undergoing martensitic transitions exhibit anomalous behavior (termed precursor phenomena in the literature) at temperatures well above the transition. These precursor phenomena are a consequence of weak restoring forces along specific directions, evidenced by low values of the corresponding elastic constants and phonon energies.[1] Hence, a good knowledge of the vibrational behavior close to the transition temperature is of crucial importance for the understanding of the martentisic transition.

In this paper we present the results of the measurement of the elastic behavior of Ni-Mn-Ga. This alloy is ferromagnetic, with a Curie temperature slightly dependent on composition, and undergoes a transition from an ordered (Heusler) cubic structure towards a martensitic phase at a temperature which is strongly dependent upon composition. It has been shown that the stability of the magnetic and structural phases in these Heusler compounds is mainly controlled by the average valence electrons per atom (e/a).[2–4] For low e/a values, the martensitic phase is tetragonal (with a very small monoclinic distortion) with a five-layer modulation; at high e/a, the structure is tetragonal nonmodulated, and an orthorhombic structure with a seven-layer modulation has also been reported at intermediate e/a.[5]

In recent years this alloy system has received extensive investigation due to the fact that the shape-memory effect associated with the martensitic transition can be influenced by applied magnetic fields.[6] The pretransitional effects of this alloy system have also been found to be very peculiar. For the stoichiometric compound Ni_2MnGa, the transverse TA_2 branch has a pronounced dip at $q=1/3$. On cooling, the frequency of this anomalous phonon decreases down to a certain temperature T_I (above the martensitic transition temperature) below which it increases again.[7,8] Such a change in behavior at T_I is due to the development of a micromodulated phase,[9] which occurs via a weakly first order phase transition.[10] The micromodulated (or intermediate) phase has a cubic symmetry with a three-fold modulation of the (110) planes.[11] It is also worth mentioning that neutron powder diffraction experiments[12] have suggested that an orthorhombic supercell could be more appropriate to describe the intermediate phase. It has been shown that magnetoelastic coupling is responsible for the occurrence of such a phase transition.[10,13] Recent calculations of the Fermi surface in the ferromagnetic phase suggest that Fermi Surface Nesting is a dominant driving force for the phonon softening in the ferromagnetic phase.[14] Ultrasonic measurements of the elastic constants for compositions close to the stoichiometric one have revealed pronounced softening of the shear constants at the premartensitic transiton.[15–17]

The phase transition to this micromodulated phase has been investigated by using different experimental techniques. Results show that this transition only occurs at low values of the electron concentration ($e/a \leqslant 7.7$).[18] In this range of compositions, the martensitic transition is well below the Curie point. Recently, inelastic neutron scattering experiments have been carried out in off-stoichiometric samples with the martensitic and ferromagnetic transitions very close each other.[8,19] Results have evidenced a phonon behavior different from that of the samples exhibiting a premartensitic transition. For high e/a, there is a dip on the TA_2 branch centered at $q=1/4$. There is pronounced temperature softening of these anomalous phonons, which is enhanced below the Curie point. The distinct feature is that this softening continues down to the martensitic transition temperature, without any upturn associated with an intermediate phase, as occurs for low e/a samples. It is our purpose in this paper to extend the

study of the elastic constants in Ni-Mn-Ga, to those alloys with high e/a.

II. EXPERIMENTAL DETAILS

The single crystals used in the present study were cut from the larger single crystals used in previous neutron-diffraction experiments[8] at the High Flux Isotope Reactor (HFIR) at Oak-Ridge National Laboratory (ORNL). The compositions of the crystals are $Ni_{52.0}Mn_{23.0}Ga_{25.0}$ (sample 2, $e/a=7.56$), and $Ni_{50.5}Mn_{29.5}Ga_{20.0}$ (sample 3, $e/a=7.71$). From our earlier study, the transition temperatures of the crystals are $T_c=359$ K and $M_s=227$ K for sample 2 and $T_c=365$ K and $M_s=345$ K for sample 3. From the original rods, parallepipedical specimens with dimensions $8.30\times10.35\times10.55$ mm^3 (sample 2) and $9.30\times9.80\times11.30$ mm^3 (sample 3) with faces parallel to the (110), $(1\bar{1}0)$ and (001) planes, respectively, of the high temperature cubic phase were cut. X-cut and Y-cut quartz ultrasonic transducers were used to generate and detect the ultrasonic waves, and the velocities of the these waves were determined by the pulse-echo technique. The transducers were acoustically coupled to the sample by means of Dow Corning Resin 276-V9, in the temperature range 210–330 K and by Crystalbond509 (Aremco Products, Inc.) in the temperature range 320–390 K. The temperature was measured by a Pt-100 resistor mounted in close proximity to the sample.

III. EXPERIMENTAL RESULTS

We have measured the velocity of the longitudinal and shear ultrasonic waves propagating along the [001] direction at room temperature for sample 2 and at 350 K for sample 3. Along the $[1\bar{1}0]$ direction, we have also measured the velocity of longitudinal and [001] polarized shear waves at the same temperatures. It was not possible to obtain direct measurements of the velocity of the [110] polarized shear waves because no reliable echoes were detected for these waves. From the measured velocities we have obtained the following values of the adiabatic second-order elastic constants: $C_{11}=157\pm1$ GPa; $C_L=252\pm1$ GPa and $C_{44}=107\pm2$ GPa for sample 2 and $C_{11}=149\pm1$GPa; $C_L=241\pm1$ GPa and $C_{44}=110\pm1$ GPa for sample 3. These values correspond to an average over four independent runs, and the estimated error is the maximum deviation from the mean value.

The temperature dependence of the relative change in three independent ultrasonic velocities are shown in Fig. 1 for sample 2 and in Fig. 2 for sample 3. Data correspond to cooling and heating runs and are obtained as an average over four independent runs. The hysteretic behavior observed for sample 3 is due to the martensitic transition undergone by this sample. For sample 2, the surface relief associated with the appearance of the martensitic domains breaks the acoustic coupling (which is brittle at low temperatures) between the sample and transducer, causing the ultrasonic echoes to disapear below ~225 K.

It is well known that large crystals (as those under investigation here) grown by the Bridgman method are likely to be inhomogeneous in composition.[20] Since the martensitic and premartensitic transition temperatures are sensitive to the actual composition of the sample, it is desirable to perform a proper characterization of these phase transitions on exactly the same specimens used for elastic constants measurements. We have performed differential scanning calorimetric measurements on the same samples used for ultrasonic studies over the temperature range covering the structural transitions. The transition temperatures for the martensitic, ferromagnetic and intermediate phases (only observed in sample

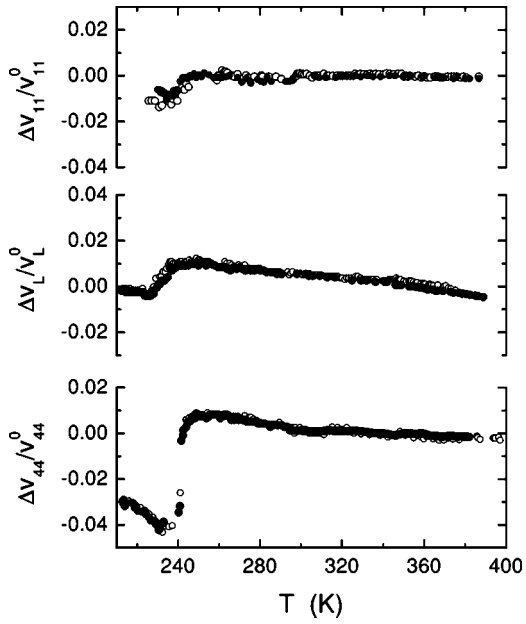

FIG. 1. Temperature dependence of the relative change in the velocity of ultrasonic waves for sample 2 during cooling (solid symbols) and heating (open symbols) runs.

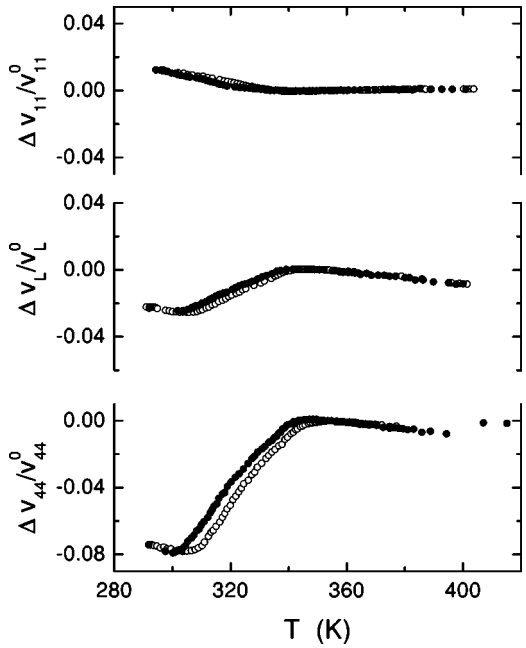

FIG. 2. Temperature dependence of the relative change in the velocity of ultrasonic waves for sample 3 during cooling (solid symbols) and heating (open symbols) runs.

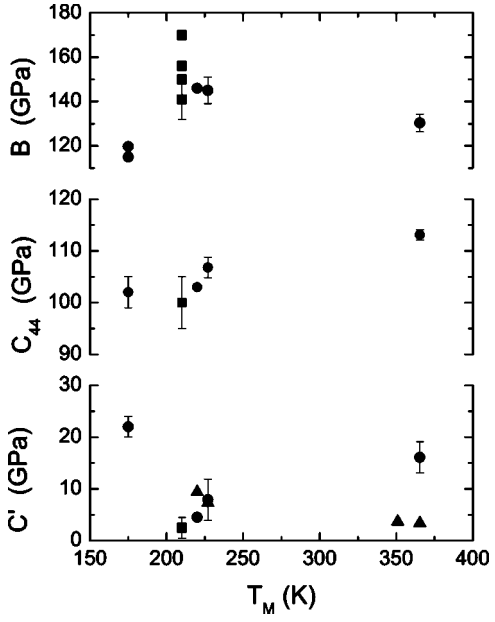

FIG. 3. Elastic moduli as a function of the martensitic transition temperature for different Ni-Mn-Ga alloys: data are from ultrasonic measurements (●), inelastic neutron diffraction (▲) and *ab-initio* calculations (■). For the theoretical calculations on the stoichiometric composition we have assumed $T_M=210$ K. Data are taken from Refs. 7, 9, 15–17, 19, and 21–23.

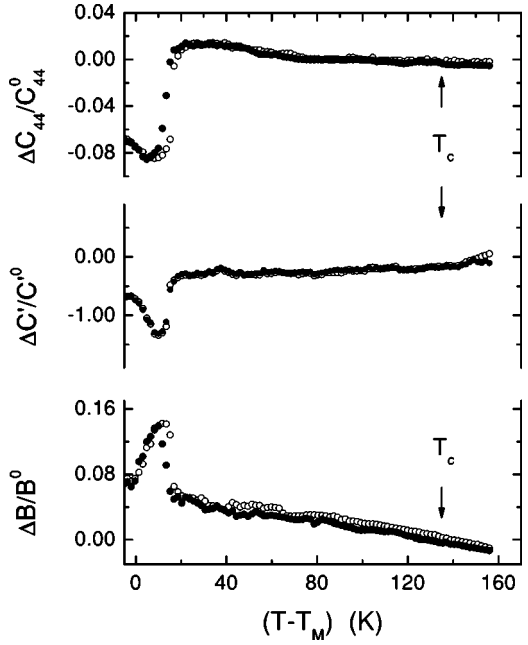

FIG. 4. Temperature dependence of the relative change in the elastic moduli for sample 2 during cooling (solid symbols) and heating (open symbols) runs. T_c indicates the Curie point.

2) are in good agreement with the values reported earlier.[8] The temperature spread of the calorimetric peak associated with the martensitic transition in sample 3 matches the range where hysteresis has been observed in ultrasonic measurements thus confirming the fact that the change in the ultrasonic velocities below ~350 K is due to the occurrence of the martensitic transition. For sample 2, the decrease in the ultrasonic velocities below 250 K is associated with the premartensitic transition.

IV. DISCUSSION

From the measured velocities we have computed the independent elastic constants of the cubic phase. In Fig. 3 we present the computed values at 300 K of $B=(C_{11}+2C_{12})/3$, $C'=(C_{11}-C_{12})/2$ and C_{44}, which are the elastic moduli associated with the symmetry adapted strain tensor components. Present data are compared to ultrasonic values (circles) for other samples, and to the values obtained from the slope of the phonon dispersion curves (triangles) and to the values predicted from *ab initio* calculations (squares). Data are represented as a function of the martensitic transition temperature T_M. It is worth noticing that T_M increases linearly with e/a[4] and therefore, T_M results to be a good parameter to characterize the composition of the different samples. We have selected this parameter instead of e/a because in some cases the exact composition of the sampe is not reported. For those samples which are martensitic at 300 K, the values are obtained from a linear extrapolation of high temperature data, using the corresponding measured temperature dependences. For the theoretical calculations on the stoichiometric composition, we have assumed a transition temperature $T_M=210$ K. The value of the elastic constant C', associated with a shear of the {110} planes along the $\langle 1\bar{1}0\rangle$ direction, is much lower than the remaining elastic moduli. This is a common feature of cubic crystals undergoing martensitic transformations.[1] It is worth stressing that the strong attenuation of the shear waves associated with this mode makes it difficult to perform a very accurate measurement of this elastic constant, and the values are affected from a considerable error. Also the values from neutron diffraction data are affected from error due to the lack of data points at very low wavenumbers. These effects are evidenced by the scatter of the C' values observed in Fig. 3. The elastic constant associated with the fast shear mode (C_{44}) slightly increases with T_M (or e/a), while the bulk modulus (B) seems to present a maximum value at the stoichiometric composition.

The relative change with temperature of the elastic moduli are shown in Figs. 4 and 5. In order to better compare the behavior of the two crystals, results are plotted as a function of the reduced temperature $T-T_M$. For sample 3 we have restricted the plot to the region where the sample is in the cubic phase since the multidomain structure of the martensitic phase does not allow one to associate the velocity of the ultrasonic waves with any specific elastic constant. The onset of the hysteresis is due to the fact that the reverse transition finishes at a temperature higher than T_M.

The salient feature of Figs. 4 and 5 is the different elastic behavior of the two samples. For sample 2, the behavior found for C' and C_{44} conforms to that already observed in samples of close composition which transformed to a premartensitic structure prior to the martensitic transition.[15–17] There is a marked decrease of the shear elastic constants

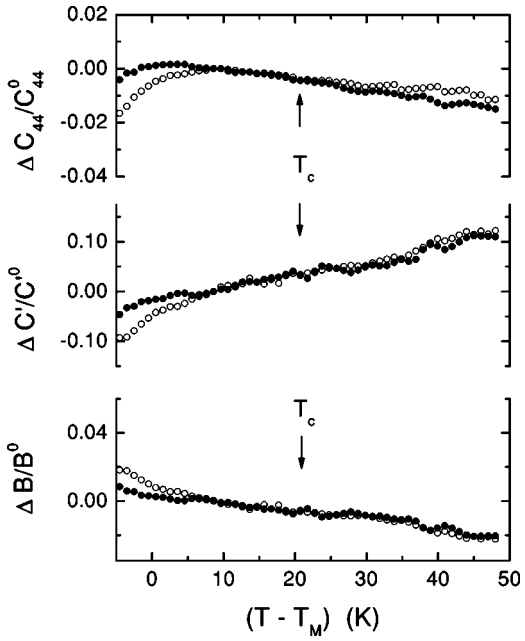

FIG. 5. Temperature dependence of the relative change in the elastic moduli for sample 3 during cooling (solid symbols) and heating (open symbols) runs. T_c indicates the Curie point.

(more pronounced for C') at the premartensitic transition. Interestingly, we have found here that the bulk modulus increases at the premartensitic transition thus indicating a stiffening of the crystal as the volume changes. This is consistent with the fact that cubic symmetry is preserved. The behavior found for sample 3 is very different. Both B and C_{44} monotonically increase as the temperature is decreased. C' exhibits a monotonic temperature softening down to the martensitic transition temperature. In this sense, the behavior found for sample 3 is very similar to that reported for Ni-Al,[24] and indeed it conforms to the general behavior of shape-memory alloys for which C' linearly decreases with temperature down to the martensitic transition temperature.[1] Notice that Ni-Mn-Ga close to stoichiometry which undergo a transition to an intermediate phase at a temperature above the martensitic transition are exceptions to such a general behavior. For those alloys, the elastic constant C' increases on approaching the martensitic transition (see Figs. 4 and 5 and Refs.15–17).

We have also analyzed the behavior of the elastic moduli across the ferromagnetic transition. The temperature of the Curie point obtained in a previous study[8] is indicated as T_c in Figs. 4 and 5. Within the experimental error no significant change in any of the moduli has been observed at the Curie point. Neutron scattering experiments have reported an enhancement of the softening of the anomalous phonon frequencies below the Curie point,[8,19] which reflects an increase in the spin-phonon coupling. The different behavior found for the phonon frequencies and the elastic constants is likely due to the different length scales associated with these two quantities. While the phonon frequencies provide the response of the system at a microscopic scale, the elastic constants provide a macroscopic description. Therefore, in the absence of a magnetic field, the magnetic domain structure below the Curie point results in an almost vanishing magnetization and therefore no significant change in the elastic constants is expected to occur. Actually, ultrasonic experiments under a magnetic field on a sample with composition close to stoichiometry[25] have evidenced an increase in the elastic constants with the square of the magnetization.

Very recently, a unified study of the modulated phases in multi-stage structural transformations has been proposed.[26] The behavior found for the elastic constants in the present study fits nicely within this general framework. In that work, a classification of martensitic materials based on the complexity of their premartensitic behavior is proposed. According to this viewpoint, the two Ni-Mn-Ga crystals studied here belong to different categories. The essential difference arises from the existence of an intermediate modulated phase associated with the condensation of the TA_2 phonon with $q = 1/3$, in those systems with composition close to stoichiometry. The upturn of C' found for sample 2, and in the frequency of the anomalous phonon[8] is characteristic of those materials for which phonon instability occurs prior to the structural transition. Such an upturn reflects the highest stability of the modulated phase with respect to the parent phase. Because magnetism is responsible for the enhancement of the softening of the anomalous phonon at the Curie point, its role is essential in order to understand the behavior of the two different pretransitional behavior in the Ni-Mn-Ga alloy family. To this respect, even if the degree of coupling between magnetic and vibrational degrees of freedom is stronger in nonstoichiometric systems (high e/a), the deviation from stoichiometry stabilizes the martensitic phase and the martensitic transition occurs before the necessary degree of softening which enables the phonon instability to be reached (premartensitic phase).

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