Phonon softening in Ni$_2$MnGa with high martensitic transition temperature

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Abstract. Phonon softening in the Heusler alloy Ni_2MnGa crystal was investigated by neutron spectroscopy for a crystal where the martensitic phase transformation temperature is close to the Curie temperature. The main result is a softening of the TA_2-phonon branch ($\xi \, \xi \, 0$) of the cubic phase in a broad range between $\xi = 0.1$ and 0.4 when the temperature approaches the phase transformation. The behaviour of the present sample is compared with results for samples with lower transition temperature.

1. Introduction

Ni_2MnGa is a ferromagnetic Heusler alloy which shows a martensitic phase transition. Depending on composition this transition may occur in the ferromagnetic or in the paramagnetic phase. This is due to a strong composition dependence of the martensitic transition temperature T_M whereas the Curie temperature T_C shows only much smaller variations [1]. The common feature of these alloys is the cubic $L2_1$ structure in the parent (austenitic) phase. The thermally induced martensitic transformation of these alloys, however, shows significant differences. With respect to their transformation properties the alloys can be divided into three groups. Group 1 alloys transform from the parent cubic to a tetragonal ($c/a \approx 0.94$) structure which is preceded by a pre-martensitic cubic phase with a six layer modulation in the [1 1 0] direction. Group 1 alloys have typically a T_M below 250 K. Group 2 alloys transform near ambient temperature to the same martensitic structure, but in contrast to group 1 alloys, no pre-martensitic phase is observed. The T_M of group 3 samples is close to or above T_C ($\approx$360 K) and the martensitic phase of these alloys is orthorhombic (or monoclinic with a deviation of angle γ less than 0.5° from 90°). In group 2 alloys this orthorhombic (or monoclinic) phase can be induced as an inter-martensitic transformation by uniaxial stress [2–4]. Up to now, only phonons in group 1 and 2 alloys have been investigated by neutron spectroscopy [5, 6]. The $TA_2 - [\xi \, \xi \, 0]$-phonon branch of the cubic parent phase of these samples shows a strong softening near $\xi = 1/3$ when the temperature approaches the transition to the pre-martensitic or martensitic phase, respectively.

Different experiments proved that the magneto-elastic interaction strongly influences the properties of Ni_2MnGa. It has been shown that the magneto-elastic interaction is not only one of the driving forces for the formation of the pre-martensitic phase in a group 1 alloy [7] but it also strongly influences the softening of the TA_2-phonon branch in a crystals without pre-martensitic phase (group 2 alloy) [6]. This is in line with the results of a recent theoretical
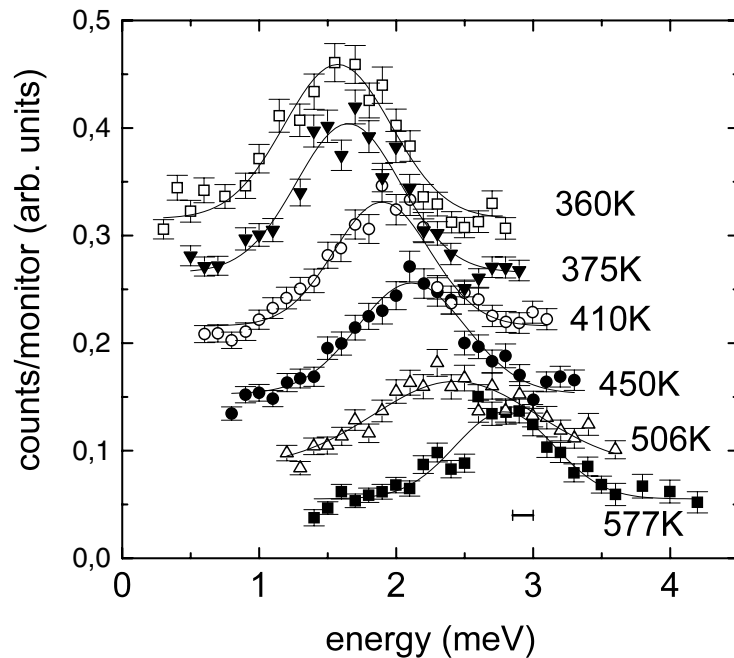
Figure 1. Phonon spectra at $Q = (1.67\,2.33\,0)$ measured at different temperatures. Each spectrum is vertically shifted by 0.05 against the previous higher temperature one.

investigation which demonstrates that these magneto-elastic interactions are important for both the pre-martensitic as well as for the martensitic transformation [8]. For a better understanding of the martensitic transformations and the influence of the magneto-elastic interactions more experimental data about the phonon softening in Ni$_2$MnGa with different compositions and phase transition behaviours seem to be necessary. Therefore, we extended our studies and investigated a single crystal of a group 3 alloy with a transition temperature very close to the Curie temperature.

2. Experiment

The present Ni$_2$MnGa single crystal was grown by the Bridgman technique with a composition of 52.9 at.% Ni, 26.6 at.% Mn and 20.5 at.% Ga. The transition temperatures (when cooling) were determined by neutron scattering, magnetic susceptibility and specific heat measurements to be $T_M = (351 \pm 2)$ K and $T_C = (360 \pm 1)$ K. The martensitic transition temperatures of the samples investigated in previous neutron scattering studies were 284 K [6] and 212 K [5]. The transition temperature for the reverse process was about 6 K above T_M which is well in range with the previous crystals where a temperature difference of 6 K [6] and 16 K [5] was found.

The lattice constant of the cubic parent phase was determined to be 5.824 Å. Since the present sample is a group 3 alloy, in contrast to the previous investigated samples, the martensitic phase was found to be orthorhombic with $a = 6.136(2)$ Å, $b = 5.80(3)$ Å and $c = 5.521(2)$ Å (and probably a small monoclinic distortion of $\leqslant 0.3°$). This is the same phase which was also found in crystals with $T_M = 333$ K [4] and 370 K [9]. The details of the phase transition of the present crystal and its precursors will be published elsewhere.
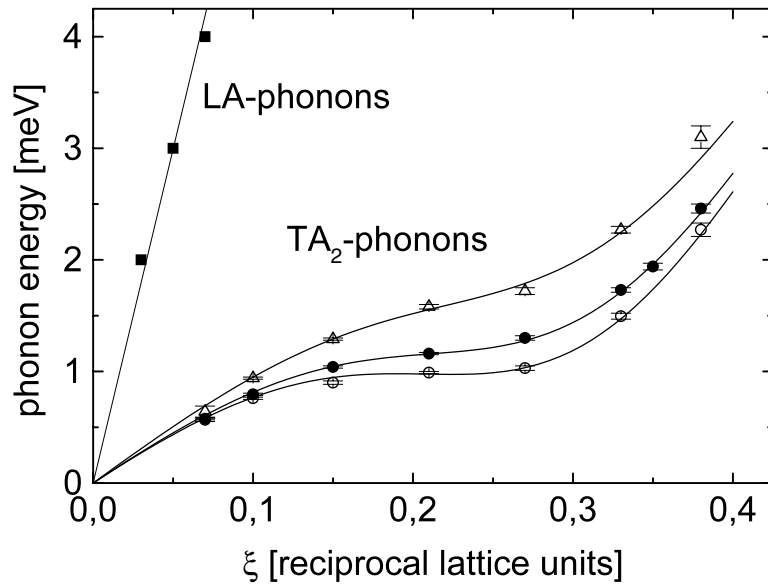
Figure 2. Low energy part of the $(\xi\,\xi\,0)$ acoustic phonon branches. The three TA_2 data sets represent measurements at 477 K (open triangles), 381 K (closed circles) and 354 K (open circles).

The neutron scattering experiments were performed at the triple-axis spectrometer for cold neutrons V2 (FLEX) at the Hahn–Meitner-Institut in Berlin with a constant final wavevector of 1.8 Å^{-1}. The obtained (incoherent) energy resolution was 0.15 meV.

3. Results and discussion

Figure 1 shows neutron spectra of the soft phonon measured at $(2 - \xi\,2 + \xi\,0)$ with $\xi = 0.33$ for five temperatures. The linewidths of these phonons are much broader than the resolution of the instrument which is indicated by the horizontal bar. In figure 2 the low energy parts of the longitudinal $[\xi\,\xi\,0]$- and TA_2-phonon branches are shown. The TA_2 branch shows a softening in a very broad region between $\xi = 0.1$ and $\xi = 0.4$. Therefore a precise determination of the soft mode wavevector is not possible. A central peak, which also would allow us to determine the soft phonon wavevector, could not been measured since (i) the softening of the phonon might be not strong enough to cause a detectable central peak and (ii) a precursor of the $(2\,0\,2)$ Bragg reflection of the martensitic phase grew at $\xi = 0.21$ when the temperature approached T_M. The shape of the dispersion curve in figure 2, however, indicates a soft mode wavevector between $\xi = 0.2$ and 0.25, although the absolute softening is strongest at $\xi \approx 0.3$. In a comparison of the softening behaviour of the TA_2 dispersion curves for the three crystals investigated up to now, it turns out that the crystal with the lowest T_M (and a chemical composition which is closest to the stoichiometric one) [5] has the smallest softening region ($\Delta\xi$ about 0.17) and the present one the largest ($\Delta\xi$ about 0.26). This might be an indication that the cubic to orthorhombic transformation is caused by a phonon instability at a ξ value between 0.2 and 0.25 whereas the cubic to tetragonal transformation is caused by the instability at $\xi = 0.33$. A wavevector of $\xi = 0.2$ would correspond to the position of the $(2\,0\,2)$ reflection of the orthorhombic phase whereas $\xi = 1/3$ corresponds to the position of the modulation peak in the tetragonal phase and of its pre-martensitic phase. A pre-martensitic phase occurs only
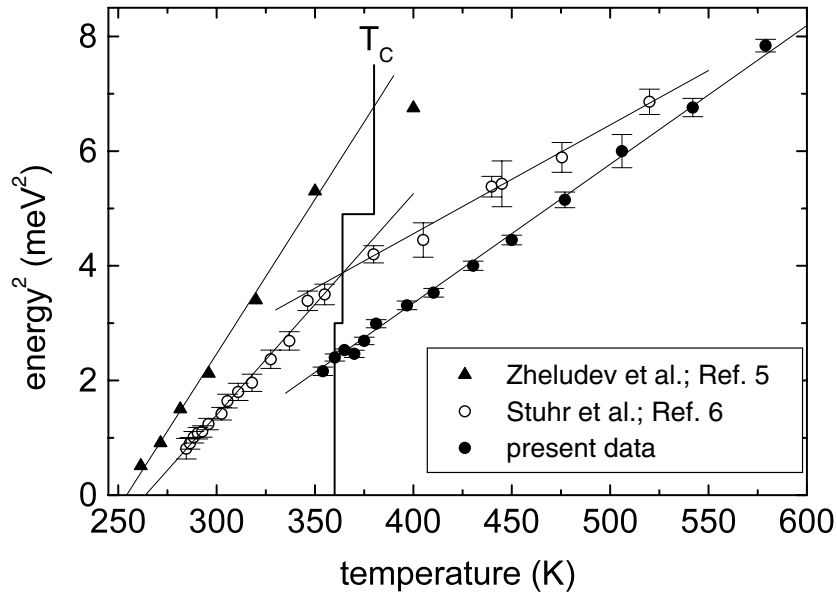
Figure 3. Temperature dependence of the squared excitation energy of the TA_2 phonon at $\xi = 0.33$. The solid circles represent data of the present study, open circles those of [6] and triangles are data taken from [5]. The thin solid lines are separate fits to data points in the ferro- and paramagnetic phases. The different Curie temperatures for the three samples are indicated by the thick solid line.

in crystals with low T_M, therefore, with increasing transition temperature the crystals become more and more stable against the cubic pre-martensitic phase. On the other hand group 3 alloys transform at moderate temperatures into the orthorhombic (or monoclinic) phase whereas in group 2 crystals this phase appears only when uniaxial stress is applied. In group 1 alloys this phase could not be induced, even at high uniaxial stress and low temperature simultaneously [10]. Therefore, with increasing T_M the crystals become more and more unstable against the orthorhombic (or monoclinic) phase and the corresponding softening becomes dominating. However, it can also not be excluded that the softening in a broader ξ-range is only an effect of the shortening of the coherency length due to increasing atomic disorder.

In figure 3 the temperature dependence of the phonon softening at $\xi = 0.33$ is shown together with previous results of group 1 and 2 alloys. For better comparison only the softening of the phonon at $\xi = 0.33$ is plotted, despite the fact that the exact wavevector of the soft phonon in the present crystal is not known. The data of Zheludev *et al* [5] shown in figure 3 represent the results of the unmodulated parent phase and the line is a fit to the data which also ignores the single data point in the paramagnetic phase.

Martensitic transformations, which are first order transitions, can be described by a modified Landau theory in which the average displacement of the atoms in the mode which causes the phase transition [11] is the order parameter. A consequence of the assumptions of this theory is that the energy $\hbar\omega$ of this mode can be written as

$$(\hbar\omega)^2 = a(T - T_0) \tag{1}$$

where a is a constant and T_0 is the temperature where the lattice would become dynamically unstable†. The data of all samples presented in figure 3 can, within each magnetic phase, be

† The quantity T_0 corresponds to T_1 in [6]. We replaced T_1 since it is often used to designate the transition temperature to the pre-martensitic phase.

well described by equation (1). For the present sample the best fit is a line with $T_0 = 262$ K and $a = (0.0242 \pm 0.0005)$ meV^2 K^{-1} which is indicated in figure 3 as a solid line. Comparing the three samples, the data indicate that with increasing T_M the slope in the paramagnetic phase increases whereas it shows the opposite behaviour in the ferromagnetic phase. A consequence would be a smaller kink in the slope for the present sample compared to that of the group 2 alloy. This, and the small temperature region between T_C and T_M, may explain that such a kink at T_C is not observable for the present sample. The differences between the slopes in the paramagnetic and the ferromagnetic phases can be assigned to the magneto-elastic interaction [8]. Therefore, the magneto-elastic coupling constant can be expected to be smaller for the samples with higher martensitic transition temperatures. This interpretation is supported by results of a Monte Carlo study of Castán *et al* [8] which predicts that samples with large magneto-elastic coupling constant show an intermediate phase (group 1 alloys) whereas it should be absent for samples with a lower coupling constant.

4. Conclusion

We investigated the temperature dependence of the acoustic phonons in the $(\xi\ \xi\ 0)$-direction in an Ni$_2$MnGa crystal with a martensitic phase transition temperature very close to the Curie temperature. The TA$_2$-phonon branch becomes soft in the range of $0.1 \leqslant \xi \leqslant 0.4$. The temperature of the softening follows the prediction of the Landau theory and is stronger than in the paramagnetic phase of a group 2 sample with lower martensitic transition temperature.

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