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LETTER TO THE EDITOR

Soft modes in Ni_2MnGa single crystals

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Abstract. We report on measurements of the thermal diffuse x-ray intensity from a single crystal of Ni_2MnGa in the temperature range 180 to 250 K. The martensitic phase transition is clearly to be seen. It is accompanied by a strong soft-mode behaviour in the transverse acoustic phonon branch with q along the [110] direction and polarization along $[1\bar{1}0]$ in the high-temperature phase. A peak splitting and a super-structure characterize the low-temperature martensitic phase.

The intermetallic compound Ni_2MnGa shows a structural phase transformation of martensitic type [1]. Recently, a modulated structure has been observed in the martensitic phase, produced by cooling through the transition [2]. This structure consists of a shifting of planes along the (110) $[1\bar{1}0]$ system with a periodicity of five atomic layers. Further structural transformations can be induced by applied stresses [3].

Taking into account the ability of the martensitic phase to change the sequence of the (110) atomic layers it is also interesting to investigate the high-temperature phase structure. Since this phase transition is nearly of second order, the existence of a soft-mode behaviour can be anticipated in the high-temperature phase. The soft-mode concept has proven to be important in describing the phase transitions in materials such as $BaTiO_3$ or $SiTiO_3$ [4]. Soft modes have been observed also in an NiAl compound [5] by means of inelastic neutron scattering. The latter transition is also weakly of first order. Thermal diffuse x-ray scattering is capable of revealing soft-mode behaviour, especially if its temperature dependence is recorded. Here, we report the results of such an x-ray study, performed on the high-temperature phase of Ni_2MnGa.

The compound Ni_2MnGa was melted in an induction melting furnace in an argon atmosphere. Since the martensitic start temperature M_s can change essentially with composition, we deduce from $M_s \simeq 170$ to 180 K the following atomic concentrations: Ni: 50%, Mn: 25% and Ga: 25%. Single crystals were grown by the Bridgman technique without using seed crystals. These crystals were oriented by Laue photographs and cut by a diamond saw. The flat surface coincided with the (100) plane. The specimens with a rectangular cross-section had dimensions $1.5 \times 10 \times 12$ mm^3. The thermal diffuse x-ray intensity was determined using a two-circle goniometer equipped with a low-temperature closed-cycle refrigerator. The angular position of the sample and of the detector with respect to the primary beam was controlled by a computer. Cu Kα radiation monochromatized by a curved monochromator was applied in focusing geometry. Data were taken along certain lines in reciprocal space selecting proper scattering planes, such as (100) and (110). The absolute temperature of the sample could be reported with an accuracy of about 1.5 K.

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A previous study [2], done at room temperature, has shown that the martensitic structure can be described by a different stacking of (110) planes. A long-period martensitic structure was found. An acoustic examination of the high-temperature phase [6] has revealed that the $[\eta\eta 0]$-transverse acoustic mode—displacements are along the $[1\bar{1}0]$ direction—exhibits an anomaly for $T \geqslant M_s$ in the limit $\eta \to 0$. Such a behaviour corresponds to a decrease of the elastic constant $c' = (c_{11} - c_{12})/2$ when approaching the transition. The thermal diffuse one-phonon intensity $I(\kappa)$ can be described in the high-temperature limit by the expression:

$$I(\kappa) = B(\kappa \cdot e(q))^2 k_B T / \omega^2(q) \tag{1}$$

where κ denotes the diffraction vector, q the phonon vector involved, $e(q)$ the polarization vector of the mode considered, $\omega(q)$ is the angular frequency of this mode, B is a constant coefficient and k_B the Boltzmann constant. A soft mode is characterized by a decreasing $\omega(q)$ and hence produces a temperature-dependent maximum in $I(\kappa)$. The vectors κ and q are related by $q = \kappa - \tau$, where τ is the reciprocal lattice vector closest to κ. The scattering geometry should be selected in accordance with the polarization factor $(\kappa \cdot e(q))$. In particular, a soft mode with $q \parallel [110]$ and $e \parallel [1\bar{1}0]$ will be visible, when the scattering plane is a (100) plane and the intensity is scanned along a [110] direction. This goal is achieved best when the surface of the samples is parallel to the (100) planes and the goniometer axis coincides with a [100] direction. The intensity distributions of such a measurement for several temperatures are shown in figure 1 between the reflections [200] and [310]. At 250 K two weak maxima can be observed around the [200] reflection. They are indicated by arrows. Their positions are characterized by $q_p = \pm 0.17\tau$, where τ is the distance between the two reflections [200] and [310] along the direction (110) in reciprocal space. This quantity is given by $\tau = 2\pi\sqrt{2}/a$, where a denotes the cubic lattice constant.

The intensity of these two maxima increases during cooling, demonstrated in figure 1(b), which was taken at 200 K. The first sign of the low-temperature phase appears at this temperature, indicated by a new peak (double arrow in figure 1(b)). On further cooling the volume of the new phase grows, as can be seen by inspection of figure 1(c). This situation corresponds to a temperature of 180 K, lying in the two-phase region of this first-order transition.

On a more expanded intensity scale, more details can be seen. We observe a main maximum at $q = 0$ which is the 200 reflection of the high-temperature phase. Two neighbours to the right and left are two reflections from the low-temperature phase indicating the splitting of the 200 reflection into two peaks.

The observation of the strong temperature dependence of the two maxima at $\pm 0.17\tau$ is the key result of this paper. Since the x-ray experiment always shows the sum of elastic and inelastic intensities, the temperature dependence is a strong argument for an inelastic origin of these two peaks. This intensity depends on the factor $(\kappa \cdot e(q))$. From the scattering geometry we deduce that those peaks are caused by a phonon with $q \parallel [110]$ and $e \parallel [1\bar{1}0]$ and with $q = (1/6)\tau_{110}$. At the moment, we have no explanation for the further pair of peaks at $\pm 0.23\tau$.

The appearance of these new maxima corresponds to a novel periodicity in the lattice with period $\lambda = 6d_{110}$, where d_{110} describes the distance between the (110) planes. This new periodicity is of dynamic origin above the transition and yields a super-structure of the low-temperature phase below the transition. In addition a splitting of the [200] reflection occurs to $+0.077\tau$ and -0.038τ.

In summary, this result demonstrates the existence of a soft-mode behaviour in the high-temperature phase of the Heusler alloy Ni_2MnGa. A significant decrease in the

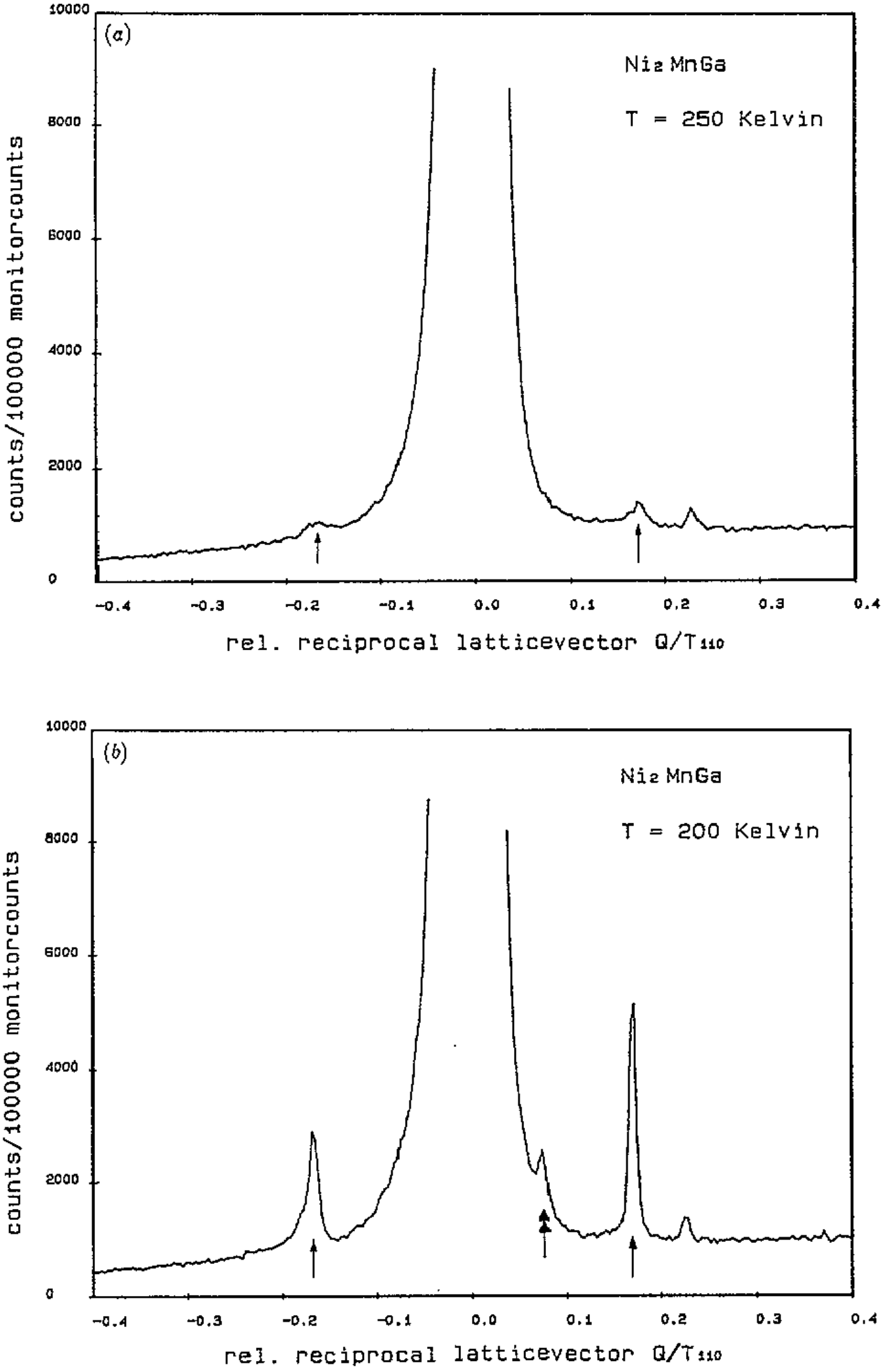

Figure 1. Temperature dependence of the thermal diffuse intensity of Ni_2MnGa in the vicinity of the [200] reciprocal lattice vector. The data correspond to the line from the [200] to [310] reciprocal lattice point with the (100) plane as the scattering plane. (a) High-temperature phase with the 200 Bragg reflection and two additional peaks at $\pm 0.17\tau$ at 250 K; (b) at 200 K those additional peaks have increased in magnitude and a Bragg peak of the new phase appears; and (c) the same situation at 180 K. The needle-like structure to the right of the peak at -0.17τ is an artifact caused by one data point lying extremely high.

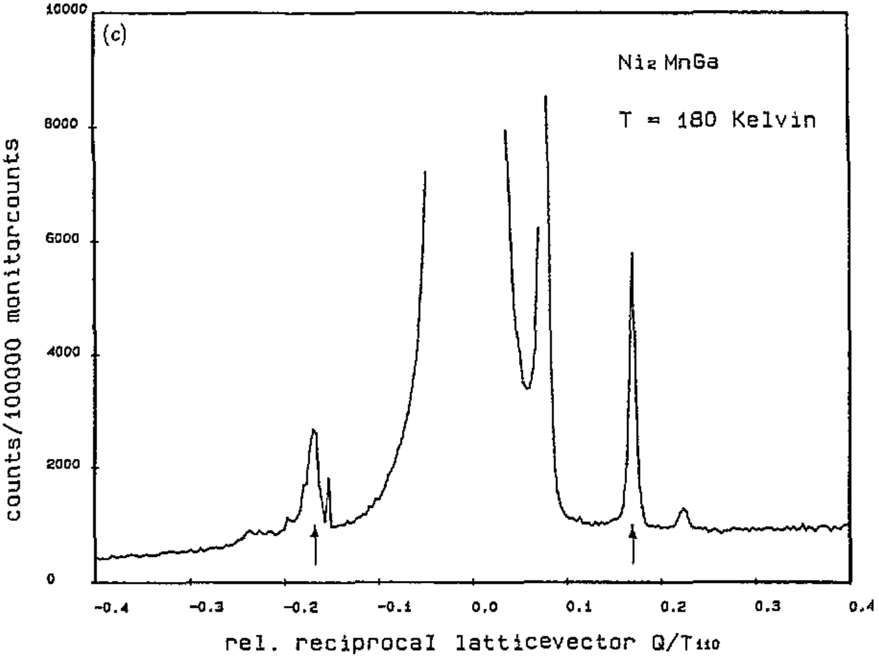

Figure 1. *Continued.*

angular frequency of the TA-phonon with $q = (1/6)\tau_{110}$ is observed when the temperature approaches M_s.

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