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The influence of atomic order on the magnetic and structural properties of the ferromagnetic shape memory compound Ni_2MnGa

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Abstract

The effect of atomic order on the martensitic phase transition and magnetic properties of stoichiometric Ni_2MnGa has been investigated in a sample quenched from 1000 °C. Magnetization, resistivity and x-ray diffraction measurements indicate that the structural phase transition occurs at ∼103 K, substantially lower than the value reported for samples quenched from 800 °C and ordered in the Heusler $L2_1$ structure. A small reduction in the ferromagnetic moment was also observed, although the Curie temperature remained largely unaffected. The electronic Sommerfeld coefficient obtained from heat capacity measurements is enhanced but smaller than that observed for the 800 °C quenched sample. The results are consistent with band structure calculations and the electronic changes brought about by atomic disorder.

1. Introduction

Ni_2MnGa is the only known ferromagnetic material exhibiting a martensitic transition from a high-temperature Heusler structure to a related orthorhombic form [1, 2]. Associated with this phase transition the material exhibits shape memory properties enabling the unstressed systems to reverse large deformations ∼0.2% in the martensitic phase by heating into the cubic parent phase. The possibility of controlling the phase transition by the application of a magnetic field has led to the material becoming one of the most actively researched shape memory alloys [3]. Detailed measurements show that for stoichiometric Ni_2MnGa the phase transition occurs at $T_m \sim 200$ K and the Curie temperature at 365 K. Despite the intense activity on this system many results have been reported ostensibly for Ni_2MnGa but on samples with phase transitions that differ by as much as 80 K [4]. Diffraction measurements have shown that the enhanced transition temperatures T_m reported for some samples are associated with departures from stoichiometry. Magnetization and resistivity measurements on the $Ni_{2+x}Mn_{1-x}Ga$ system with $x < 0.2$ show that T_m increases with x, becoming equal at $x = 0.19$ to the Curie temperature which has decreased to 325 K [5, 6]. Band structure calculations [7] suggest that the phase transition is driven by a redistribution of electrons associated with a high density of states

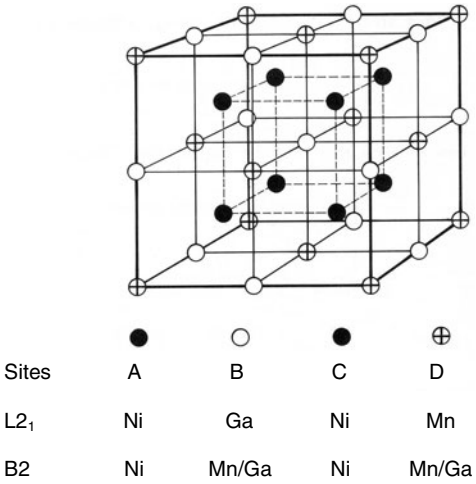

Figure 1. The Heusler structure [1] comprising four interpenetrating fcc sublattices A, B, C and D, showing the atomic arrangement for $L2_1$ and B2 order.

at the Fermi level. The mechanism, known as the band Jahn–Teller effect, was originally proposed to account for the structural transformation observed in the A15 compounds [8]. Experimental support, directly showing a change of symmetry in the electron distribution on going through the phase transition, has been provided by polarized neutron diffraction [9]. If the phase transition is indeed driven by a redistribution of electrons between orbitals then a change in the atomic order should significantly affect the electronic structure and hence the phase transition T_m. Stoichiometric Ni_2MnGa is reported to melt at 1382 K [10] and on cooling undergoes a B2 $\rightarrow$ $L2_1$ phase transition at 1071 K [11]. The two structures are shown in figure 1, where it can be seen that B2 order occurs as a result of disorder between the Mn and Ga atoms. To date the majority of experiments have been carried out on specimens heat treated and quenched from 800 °C which is well within the $L2_1$ region. Reported here are the results of an investigation of the magnetic, transport and structural properties obtained using a stoichiometric sample of Ni_2MnGa annealed and quenched from 1000 °C. The results of similar measurements on paramagnetic Ni_2TiGa are also presented.

2. Experimental details

The appropriate amounts of spectrographically pure constituent elements were repeatedly melted in an argon arc furnace to produce homogeneous ingots of Ni_2MnGa and Ni_2TiGa. The weight losses after melting were less than 0.05% in both cases, indicating a high degree of stoichiometry. Specimens suitable for magnetometry, resistivity and heat capacity measurements were spark eroded from the ingot, with the remainder being crushed to a particle size of less than 250 μm. The powder and the solid pieces were sealed in quartz tubes under a reduced argon atmosphere and annealed for 48 h at 1000 and 800 °C, for the Ni_2MnGa and Ni_2TiGa samples respectively, prior to a rapid quench into ice water. Subsequent room temperature x-ray powder diffraction measurements were analysed using the profile refinement technique [12]. The Ni_2MnGa and Ni_2TiGa samples quenched from 800 °C were found to be ordered in the $L2_1$ structure (figure 1) with lattice parameters of 5.837 and 5.885 Å respectively. As expected, the sample quenched from 1000 °C had a considerable amount of preferential

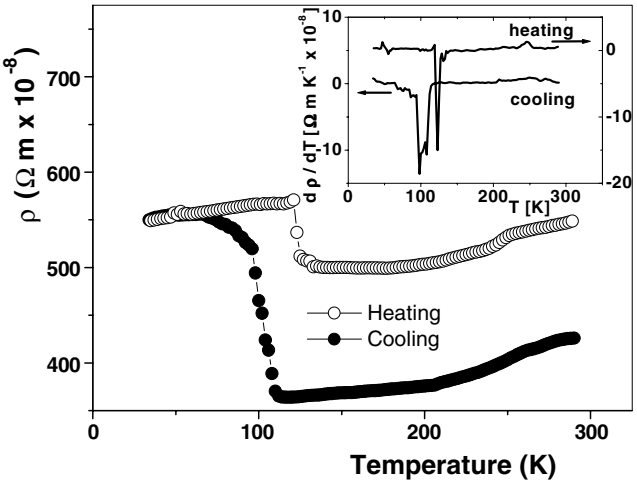

Figure 2. The resistivity of the Ni_2MnGa sample quenched from 1000 °C measured both whilst heating and cooling. The inset shows the derivative of the resistivity obtained in the cooling and heating sequence. The general form of the resistivity is similar to that reported by Khovailo *et al* [5] who identified the anomalies with the onset of the premartensitic phase T_p and the phase transition T_m.

disorder between the Mn and Ga atoms (B and D sites). This disorder does not involve the Ni atom (A and C) sites and only the intensities of the odd superlattice peaks are affected. Their intensities are reduced by a factor $(1–2\alpha)^2$ where α is the occupation parameter defined as the number of Ga or Mn atoms not on their correct sites. Thus when $\alpha = 0.5$ complete disorder exists between the Ga and Mn atoms and the structure reduces to the singly ordered B2, CsCl type. A structural refinement was carried out using FullProf [12]. The value of α obtained for the sample quenched from 1000 °C corresponds to $\alpha \sim 0.42 \pm 0.17$, i.e. approximately 40% of the Mn and Ga atoms interchange sites. The α parameter for the 800 °C quenched sample was refined to $\alpha \sim 0.07 \pm 0.10$. The large error bar arises due to weak contrast for the x-ray investigation.

Resistivity measurements were carried out using the four-terminal technique with the sample in thermal contact with the second stage of a closed-cycle refrigerator. The results obtained on cooling from room temperature to 19 K and then warming again to room temperature are shown in figure 2. From this figure it may be seen that there is a strong discontinuity at low temperatures with a 20 K hysteresis suggesting that the structural phase transition has been suppressed by almost 100 K compared with the value for the 800 °C quenched sample. Confirmation of a structural phase transition was made using low-temperature x-ray diffraction [13] which showed a splitting of the (400) reflection at 80 K. This is consistent with the observation in figure 2 that the resistivity does not go back to its original high-temperature value on reheating. The structural phase transition changes the magnetic domain pattern due to the presence of an easy axis of magnetization in the low-temperature phase. On reheating the magnetic domain structure is not changed back to its previous pattern. In order to retrieve the original resistivity value, annealing at a temperature above the ferromagnetic transition is required. This, however, has not been done for the resistivity measurements reported in figure 2. Differentiating the resistivity data with respect to temperature gives 103 and 123 K for the phase transition T_m, whilst cooling and heating respectively. Furthermore the transition occurred over a temperature range of 4 K whilst heating and 14 K on cooling. Above and below the transition the thermal variation of the

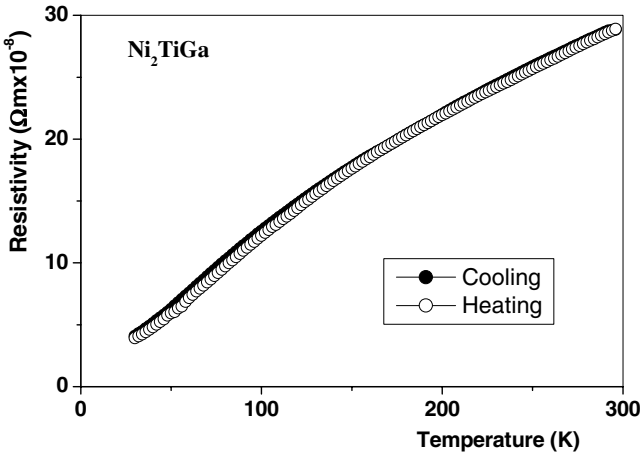

Figure 3. The thermal variation of the resistivity of Ni_2TiGa (800 °C quenched sample) obtained whilst heating and cooling between 20 and 300 K.

resistivity is rather small, as may be seen from the inset to figure 2. Closer examination of the thermal variation of the resistivity observed whilst heating shows a small change in slope at approximately 250 K. Although the change is not so obvious in the cooling data it is similar to that reported for Ni_2MnGa quenched from 800 °C [5]. Neutron single-crystal diffraction [2] and triple-axis [14] measurements indicate that a premartensitic phase is formed above the phase transformation between 260 and 200 K associated with the incomplete softening of the TA_2 phonon branch at $q = (\frac{1}{3}\frac{1}{3}0)$. Thus the anomaly at $T_p \sim 250$ K may be identified with the onset of the premartensitic phase. In contrast, similar measurements on Ni_2TiGa and shown in figure 3 indicate that the resistivity increases smoothly as the temperature was raised with no apparent anomalies. The variation is consistent with metallic behaviour.

Magnetization measurements were made using a SQUID magnetometer in accurately controlled fields up to 5.5 T and at temperatures between 2 and 350 K. Demagnetizing corrections were applied to the values of the externally applied field. Initially the magnetization was determined in a field of 0.1 T whilst heating and cooling over the temperature range 5–350 K. These results which are shown in figure 4 indicate a transition to a magnetically hard state at low temperatures consistent with the resistivity results and suggesting a structural phase transition, as observed for the 800 °C quenched sample [1]. However, the magnetic transition is not as abrupt as that observed for the 800 °C sample, with the transition in 0.1 T taking place over a temperature range of ∼100 K. The extended temperature range probably arises from local fluctuations associated with the disorder of the Mn atoms. The lowering of crystal symmetry gives rise to magnetic anisotropy which can be represented by an effective anisotropy constant $K_{eff} = \frac{1}{2}\int_0^{M_s} B\,\mathrm{d}M$. At 5 K in the transformed phase K_{eff} is determined to be 17 J kg^{-1} reducing to 12 J kg^{-1} on warming to 300 K. The small change again may reflect effects of atomic disorder. This is confirmed by the similarity of the hysteresis curves measured at both temperatures and shown as inserts to figures 5 and 6. A slightly larger anisotropy constant, $K_{eff} = 23$ J kg^{-1}, characterizes the martensitic phase of a nominal Ni_2MnGa specimen but with $T_m = 273$ K [15]. A phenomenological model for the magnetization process has been proposed based on twin and phase boundary motion characterized by the relative strengths of the anisotropy and Zeeman energies [15]. The value of the anisotropy energies in Ni_2MnGa is smaller than the 64 J kg^{-1} which characterizes the hard basal plane magnetization direction in α cobalt. Consequently the structural phase transition in Ni_2MnGa can be influenced

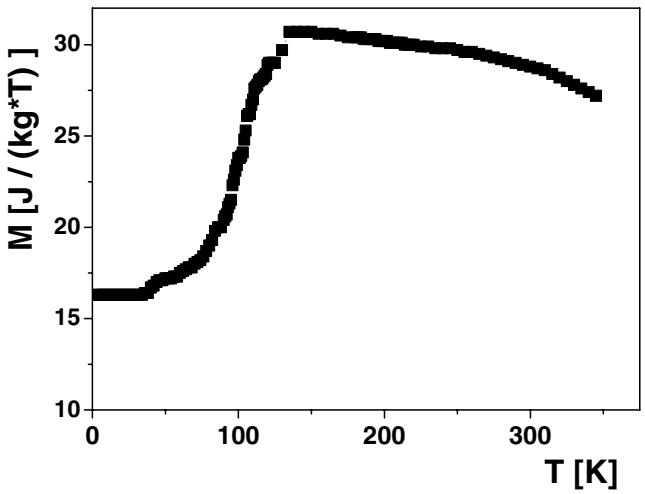

Figure 4. The magnetization of the Ni_2MnGa sample quenched from 1000 °C measured in a field of 0.1 T whilst cooling.

by moderate fields $\leqslant 1$ T. Extrapolation of the low-field and high-field linear portions of the magnetic isotherms shown in figures 5 and 6 gives a critical field of 0.4 T. Single-crystal neutron diffraction measurements as a function of applied field showed that a similar field was required to switch the crystallographic domains [16]. The magnetization varied linearly in high fields but did not saturate in fields up to 5.5 T. The high-field susceptibility $\chi_{hf} = \frac{\partial M}{\partial B}$ was determined to be 0.39 J T^{-2} kg^{-1} at all temperatures up to 300 K. Extrapolation of the linear high field portions of the magnetic isotherms enabled the spontaneous magnetization to be determined and hence the ground state moment as 3.63 μ_B/manganese atom. This value is 13% smaller than that reported for the 800 °C quenched sample [1]. Although the maximum experimental temperature was 350 K, comparison of the thermal variation of the spontaneous magnetization for the two samples indicates that the sample quenched from 1000 °C has a slightly higher (by $\sim$10 K) Curie temperature. Magnetization measurements on Ni_2TiGa and subsequent analysis based on Arrott plots (M^2 versus B/M) showed the absence of cooperative behaviour indicating that the compound was weakly paramagnetic with $\chi(0) = 0.017$ J T^{-2} kg^{-1}. At 5 K the moment induced in a field of 5.5 T was 0.007 μ_B which reduced to 0.006 μ_B at 300 K.

The specific heat C_p, of Ni_2MnGa, measured between 5 and 200 K using an adiabatic calorimeter [17], is shown in figure 7. In contrast to the sample quenched from 800 °C there is no apparent anomaly in the specific heat associated with the phase transition [9]. This is consistent with the magnetization measurements which indicate that the phase transition in the 1000 °C quenched sample is spread out over a wide temperature range of approximately 100 K. The low-temperature portion of the data was analysed assuming electronic, lattice and spin wave contributions

$$C_p = \gamma T + \beta T^3 + \delta T^{3/2}.$$

The term linear in T gives the electronic Sommerfeld coefficient γ, the second term β is attributed to lattice vibrations and the final term δ arises from spin waves. The spin wave stiffness constant D for an 800 °C quenched sample has been determined from neutron scattering measurements as 108 meV Å^2 [18]. Since quenching from 1000 °C only increases the Curie temperature by 3% at most the spin wave stiffness constant can be considered

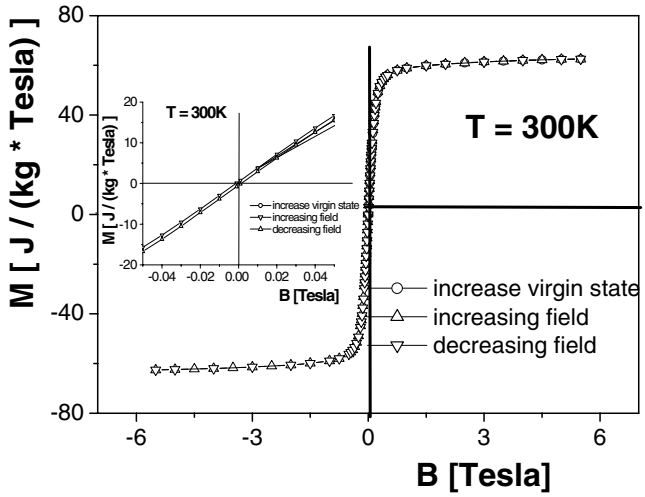

Figure 5. The magnetization of Ni_2MnGa quenched from 1000 °C measured at 300 K. The isotherm was measured starting from a zero field state up to 5.5 T and then in decreasing field down to −5.5 T before returning to zero field. The low-field hysteresis is shown as an inset.

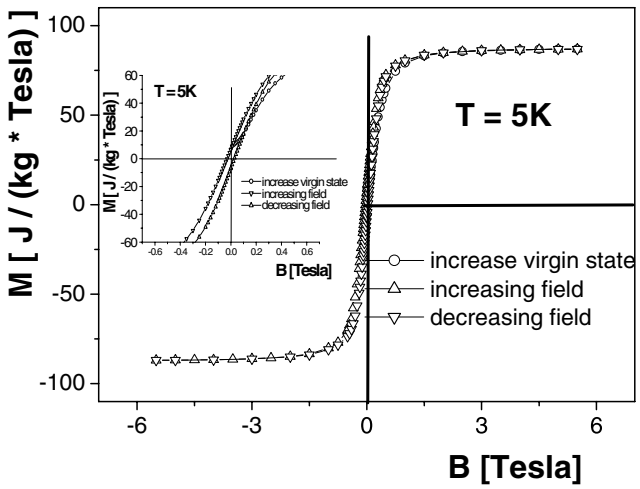

Figure 6. The magnetization of Ni_2MnGa quenched from 1000 °C measured at 5 K. The isotherm was measured starting from a zero field state up to 5.5 T and then in decreasing field down to −5.5 T before returning to zero field. The low-field hysteresis is shown as an inset.

unchanged. Thus the spin wave contribution to the measured specific heat can be determined using

$$\delta = 39.43\left(\frac{M}{\rho}\right)D^{-\frac{3}{2}}$$

where M is the atomic mass in grams and ρ is the mass density g cm^{-3}. On subtraction of the spin wave component from the observed specific heat the coefficients γ and β were then obtained by linear regression, the results of which are given in table 1. For Ni_2TiGa, which is paramagnetic, only the Sommerfeld and lattice contributions were considered. These are also

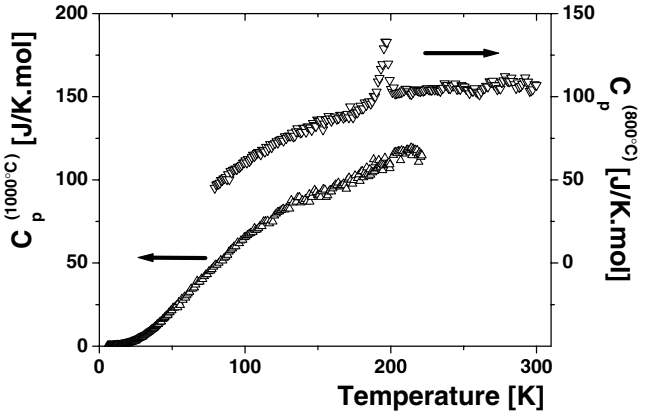

Figure 7. The specific heat of Ni_2MnGa quenched from 1000 °C and from 800 °C [9].

Table 1. A summary of the specific heat results obtained on samples of Ni_2MnGa quenched from 1000 and 800 °C and on a sample of Ni_2TiGa also quenched from 800 °C.

Sample	γ (mJ K^{-2} mol^{-1})	β (mJ K^{-4} mol^{-1})	Θ_D (K)
800 °C	21.7 ± 0.9	0.241 ± 0.005	318 ± 7
1000 °C	16.1 ± 0.8	0.200 ± 0.005	339 ± 8
Ni_2TiGa	11.5 ± 0.6	0.292 ± 0.005	299 ± 5

given in table 1. The Debye approximation is valid for temperatures below $\sim\Theta_D/12$ where Θ_D is the Debye temperature given by

$$\Theta_D = \sqrt[3]{\frac{234\,R}{\beta}}.$$

The values obtained for the Sommerfeld coefficients are all significantly larger than those expected for normal metals, suggesting a large density of states at the Fermi level. The Sommerfeld coefficient is related to the density of states at the Fermi level $N(E_F)$ through $\gamma = \frac{2\pi^2}{3}k_B^2 N(E_F)(1 + \lambda_{ep} + \lambda_{sf})$ where λ_{ep} and λ_{sf} are possible electron–phonon and spin fluctuation enhancements. Results for isostructural compounds, including the 800 °C quenched sample, in which the magnetic moment is confined to the Mn atoms, indicate that Ni_2MnGa is close to the local moment limit and therefore the effects of spin fluctuations may be considered negligible. The experimental values obtained for γ and β are similar to those found for the isostructural non-magnetic compound Ni_2TiGa which is close to a ferromagnetic instability [19]. The analysis of the specific heat assumes that the three components are independent. However, large strains of nearly 0.2% can be induced in the transformed phase by a magnetic field of 0.8 T applied along the (001) direction [20]. Evidence of a magneto-elastic interaction in the cubic parent phase has been demonstrated by the field dependence of the elastic constants [21]. Thus there exists a coupling of the lattice and magnetic degrees of freedom which must be included in any description of the shape memory effect in these systems. However the precise form of this interaction is unknown. For non interacting electrons the Sommerfeld coefficient $\gamma(0)$ is proportional to the bare electronic density of states and therefore $n(\varepsilon_F) = 0.212\gamma$, which yields 4.6 states/atom eV. This result is consistent with the band structure calculations of Fujii *et al* [7]. The calculations which were undertaken using both the linear muffin tin orbital (LMTO) and Korringa, Kohn and Rostoker (KKR)

methods and for cubic and tetragonal forms of Ni_2MnGa yield a peak in the density of states at the Fermi level. The peak is predicted to come primarily from the manganese d bands which give rise to 10.3 states/atom eV. On the basis of these calculations it was argued that it is the redistribution of electrons around the Fermi level which drives the structural phase transition [7]. The reduction in symmetry, brought about by the phase transition is able to lift the degeneracy of electronic bands at the Fermi level causing the peak in the density of states to split. Combined with the energy required for creating the lattice distortion the resulting shift in the energy of bands and the resulting repopulation of these bands lowers the free energy of the whole system making such a transformation energetically favourable. A polarized neutron diffraction measurement of the unpaired spin distribution in the related shape memory compound Ni_2MnGa has revealed a change in symmetry at the phase transition [9]. The redistribution of magnetization found in the experiment supported the band Jahn–Teller mechanism, in that the $xz \pm yz$ and $3z^2 - r^2$ components of the subbands were populated at the expense of the xy and $x^2 - y^2$ components.

From table 1 it may be seen that for the 1000 °C sample the Sommerfeld coefficient is lower and hence the associated density of states which is entirely consistent with the sample having a significantly lower phase transition T_m. Quenching the sample from 1000 °C increases the degree of B2 disorder in which the Mn and Ga atoms interchange sites. The broad transition indicated by the low-field magnetization measurements suggests that the B2 disorder may not be entirely random. However the increased number of nearest-neighbour Mn atoms augments the overlap of the e_g d functions and hence the associated band width. The increased band width lowers the density of states and within the band Jahn–Teller model the transition temperature T_m.

3. Summary

The structural phase transition in Ni_2MnGa, essential for shape memory behaviour, has been found to depend on heat treatment and hence the degree of atomic order in the specimen. For stoichiometric specimens ordered in the $L2_1$ structure the phase transition occurs at 200 K but when atomically disordered into the B2 structure the phase transition is suppressed to 100 K. Although the change in atomic order significantly affects the phase transition it only has a minimal influence on the magnetic properties. Analysis of the low-temperature specific heat indicates an enhanced Sommerfeld coefficient, a feature observed in other shape memory alloys [22]. The amount of enhancement depends on the degree of atomic order being a maximum for the sample with the $L2_1$ structure which has the highest transition temperature T_m. The results lend further support to band structure calculations which predict a peak in the density of d states at the Fermi energy and a possible band Jahn–Teller mechanism for the phase transition.

Acknowledgments

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