Resistivity and thermopower of $Ni_{2.19}Mn_{0.81}Ga$

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In this paper, we report results of the first studies on the thermoelectric power (TEP) of the magnetic heusler alloy $Ni_{2.19}Mn_{0.81}Ga$. We explain the observed temperature dependence of the TEP in terms of the crystal field splitting and compare the observed behavior to that of the stoichiometric system Ni_2MnGa. The resistivity as a function of temperature of the two systems serves to define the structural transition temperature T_M, which is the transition from the high-temperature austenitic phase to the low-temperature martensitic phase. The occurrence of the magnetic (Curie-Weiss) and martensitic transitions at almost the same temperature in $Ni_{2.19}Mn_{0.81}Ga$ has been explained from TEP to be due to changes in the density of states at the Fermi level.

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Ni_2MnGa is one of the shape memory effect compounds which is currently exciting and has gained considerable interest since it is ferromagnetic. The origin of the shape memory effect in Ni_2MnGa is in the martensitic transition which takes place on cooling through 220 K from the cubic $L2_1$ Heusler structure to a tetragonal phase. If the material is plastically deformed in the low-temperature martensitic phase and the external load removed, it regains its original shape when heated above the transition temperature. Based on early neutron diffraction data the transformation has been described as a simple contraction along the {100} direction of the cubic cell without any change in atomic positions.[1] This phase transition is remarkable in that, inspite of the large deformation, it is reversible and a single crystal can be cycled through it many times without breaking. In recovering their shape the alloys can produce a displacement or a force, or a combination of the two, as a function of temperature. Because of these novel and remarkable properties shape memory alloys find themselves in a large number of applications in the fields of engineering and medicine.[2] Since Ni_2MnGa orders ferromagnetically below 375 K, the possibility of producing giant field-induced strains, which are an order of magnitude larger than those observed in rare-earth transition-metal alloys, has stimulated a large number of investigations.[3]

Recently it has been found that in Ni-Mn-Ga systems huge strains can be induced by application of a magnetic field.[4–7] These compounds undergo a martensitic transformation between a low-temperature tetragonal phase which is magnetically hard and a high-temperature cubic phase (magnetically soft).[1,8] This difference in the anisotropy strongly modifies the field dependence of the magnetization in the two phases, with the saturation magnetization value being slightly lower in the cubic austenite.[9,10] Some recent works have evidenced the occurrence of significant isothermal variations of the magnetic entropy in NiMnGa compounds [up to $|\Delta S_m| = 18$ J/(kg K) for $H = 5$ T] in correspondence with the martensitic transformation. In these cases, the martensitic transition temperatures T_M are lower than the Curie temperature T_C and, as a consequence, the martensitic transformation takes place between two ferromagnetic phases.[9–11] For a composition for which $T_C \sim T_M$ the occurrence of a large magnetocaloric effect has been demonstrated recently.[12]

Studies of $Ni_{2+x}Mn_{1-x}Ga$ alloys have emerged with a phase diagram which indicate that partial substitution of Mn for Ni results in the increase in the structural phase transition temperature T_M (martensitic transition) and the decrease in the Curie temperature T_C up to their coincidence at $x \approx 0.19$ (Refs. 13 and 14). Theoretical analysis demonstrating the importance of the conduction electron density in stabilizing the Heusler structure was noted a while ago and the suggestion that the structure is stabilized because the Fermi surface touches the Brillouin zone boundary was made by Ref. 15. The aim of the present work is to investigate the transport properties of the polycrystalline $Ni_{2.19}Mn_{0.81}Ga$ alloy and compare it with the stoichiometric Ni_2MnGa alloy in order to understand the effect of excess Ni on the density of states (DOS) at the Fermi level. For this purpose we have studied the temperature-dependent resistivity and thermoelectric power (TEP) which is sensitive to changes in the DOS at the Fermi level of the two alloys.

Polycrystalline $Ni_{2+x}Mn_{1-x}Ga$ ($x = 0, 0.19$) ingots were prepared by the conventional arc-melting method in argon atmosphere. The starting materials with 99.99% purity were taken in the stoichiometric ratio and were remelted 4–5 times to attain good compositional homogeneity. Since the weight loss during melting was approximately $\leqslant 0.5\%$, the composition of the ingots was assumed to be nominal. X-ray diffraction (XRD) powder pattern recorded in the range $20° \leqslant 2\theta \leqslant 100°$ confirmed that the samples were homogeneous and of single phase with no detectable impurity and the patterns are presented in Fig. 1. The Ni_2MnGa has a cubic $L2_1$ structure at room temperature with lattice parameter $a = 5.824$ Å. As the martensitic transition temperature for $Ni_{2.19}Mn_{0.18}Ga$ is ~ 320 K, the XRD pattern represents a structure with lower symmetry. This pattern can be indexed to a body-centered-tetragonal structure (I_4/mmm) (Ref. 16) or to a face-centered-orthorhombic structure ($Fmmm$) with $a = b$ (Ref. 1). It may be noted here that the tetragonal and orthorhombic structural models are related to each other by a simple transformation matrix.[17] In the orthorhombic structural model only the lattice parameters change from that of a cubic high-temperature phase but the relative atom coordinates remain unchanged. The lattice parameters obtained from the orthorhombic model were $a = 5.416$ Å and $c = 6.523$ Å.

Electrical resistivity was measured using the standard

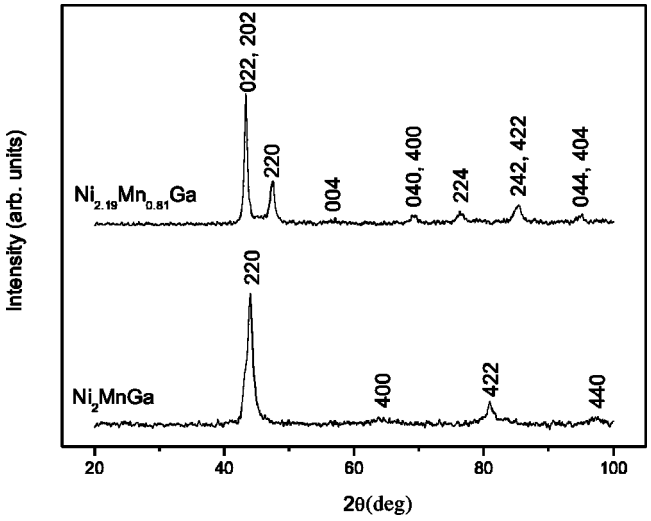

FIG. 1. X-ray diffraction patterns of Ni_2MnGa and $Ni_{2.19}Mn_{0.81}Ga$.

four-probe technique. The samples were first cooled to 80 K and the resistance was measured upon warming up to 350 K followed by subsequent cooling back to 80 K. The thermopower measurements were carried out using the differential method where the voltage difference ΔV due to the temperature difference ΔT across the sample was measured in the temperature range 100–400 K in the warming and cooling cycles similar to that of resistivity measurements. The sample was kept between two highly polished copper plates, electrically insulated from the rest of the sample holder. Two heater coils, one on the bottom and the other on the top copper plate, served to raise the overall temperature of the sample and to maintain a temperature gradient across the length of the sample, respectively. The overall temperature of the sample was measured by a platinum resistance thermometer (PT-100) while the gradient was monitored by a copper-Constantan thermocouple operating in the differential mode. To measure the thermopower S at a particular temperature—say, T—the temperature difference across the sample is first adjusted to nearly 0 K ($\sim 1\ \mu$V) by passing current through the two heater coils. The top copper plate of the sample holder is then heated, resulting in a thermo emf V_s across the sample. The voltages V_s and that developed across the thermocouple V_{th} are measured for different temperature gradients between the two plates. A graph of V_s versus V_{th} is plotted and its slope ($\Delta V_s/\Delta V_{th}$) is measured. Knowing the slope and the thermopower, S_{th} of the thermocouple at T, the thermopower S is obtained.

The temperature dependences of resistivity measured upon warming and cooling in Ni_2MnGa and $Ni_{2.19}Mn_{0.81}Ga$ are presented in Fig. 2. A large hysteresis is observed upon thermal cycling in both the compositions as evident from Fig. 2 and the inset therein. This could be due to the variation in the percentage conversion from a five-layered modulation (5M) to seven-layered modulation (7M) termed as the intermartensitic transition occurring at low temperatures.[23] In such a transition, the sample undergoes a transformation from the 5M state to the 7M state upon cooling. This transformation depends on the warming-cooling rate and in

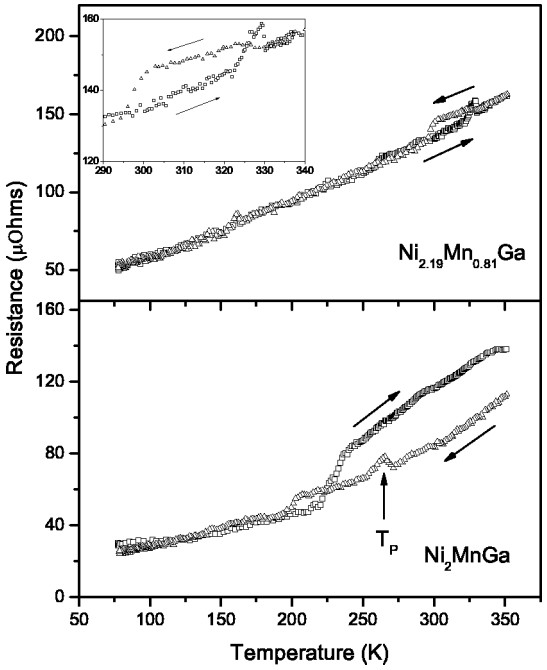

FIG. 2. Plots of resistance versus temperature for Ni_2MnGa and $Ni_{2.19}Mn_{0.81}Ga$.

a given experimental condition a complete conversion may not be achieved. Upon subsequent heating, the reverse transformation—i.e., 7M→5M—is absent and this leads to different behavior of transport properties upon warming and cooling.

On warming, Ni_2MnGa exhibits a jumplike feature at around 210 K which is associated with a transition from the martensitic to the austinitic phase for this alloy. Cooling from the high-temperature austinitic phase results in a well-defined peak at around 265 K which marks the premartensitic transition (T_p) in agreement with Khovailo *et al.*[18] As reported in the literature the ferromagnetic transition for this alloy takes place at $T_C \sim 380$ K which is beyond the studied temperature range and hence we do not observe any such signature in the resistance measurement for this alloy. In $Ni_{2.19}Mn_{0.81}Ga$, the structural transition T_M (320 K) and the ferromagnetic transition T_C (322 K) occur at almost the same temperatures. Moreover, these transitions being very broad, the premartensitic transition as observed in Ni_2MnGa is not revealed in this alloy. Also, theoretical as well as experimental studies of Ni-Mn-Ga indicate that the premartensitic transformation is observed only in the alloys with $T_M < 260$ K (Ref. 19–22). Thus absence of the anomaly assigned as T_P in the $Ni_{2.19}Mn_{0.81}Ga$ alloy is expected due to its high martensitic transition temperature.

The thermopower is very sensitive to the energy dependence of the carrier mobility near the Fermi level which in turn depends on the crystal structure concerned. Hence, the TEP of $Ni_{2.19}Mn_{0.81}Ga$ alloy would be expected to exhibit interesting behavior in the vicinity of the austenitic-to-martensitic phase transition given that the two different crystal structures are involved along with the ferromagnetic transition occurring at the same temperature. Figure 3 shows the temperature dependences of the TEP for the two alloys in the

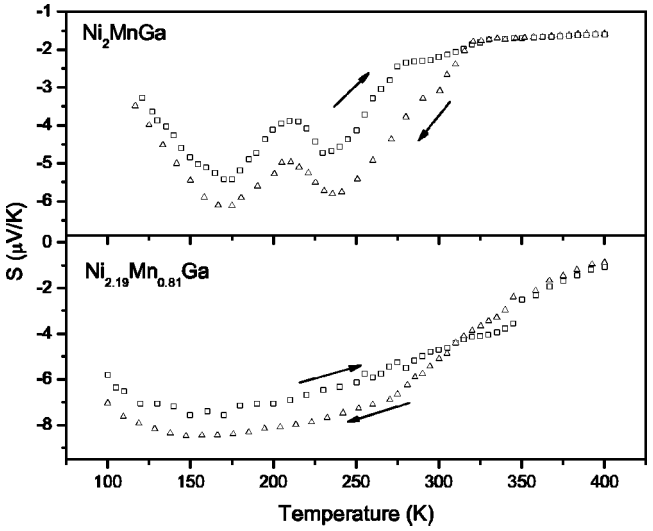

FIG. 3. Thermoelectric power as a function of temperature for Ni_2MnGa and $Ni_{2.19}Mn_{0.81}Ga$.

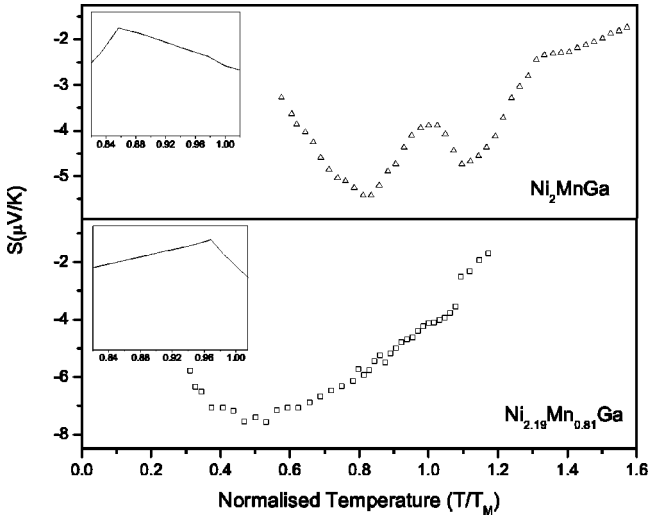

FIG. 4. Thermoelectric power as a function of normalized temperature for Ni_2MnGa and $Ni_{2.19}Mn_{0.81}Ga$.

temperature range 100–400 K. The striking feature is the broad hump obtained in the vicinity of T_M for Ni_2MnGa due to the austinitic-to-martensitic transition. Such a feature is absent for $Ni_{2.19}Mn_{0.81}Ga$. As the fact that the T_C for Ni_2MnGa and $Ni_{2.19}Mn_{0.81}Ga$ is ~380 K and ~322K, respectively, there is a contribution from the magnetic scattering to the TEP in the austinitic phase which is clearly evident from the steep fall of S with the decrease in temperature in this region. As the temperature is further decreased $|S|$ shows a strong negative dip in TEP and finally resumes the normal metallic behavior of $S \rightarrow 0$ as $T \rightarrow 0$. Such a behavior is typical of the Heusler alloys representing the fact that they are a good approximation towards local-moment ferromagnetic systems.[24] The negative dip occurs at $T \sim 0.4T_C$ and a weak temperature dependence of TEP around the Curie temperature is also seen as observed for other Heusler alloys.[24]

The warming data for the TEP are lower in magnitude in comparision with the subsequent cooling results. This as mentioned above can be explained to be due to the 5M $\rightarrow$7M intermartensitic transition occurring due to thermal cycling of the alloys during measurements.

To explain the observed anomalies in S, we consider two scattering contributions to TEP: the magnetic scattering of the thermal current as both the alloys are magnetically ordered at lower temperatures and the structural (martensitic) transition scattering. Thus the total TEP can be written as

$$S = S_m + S_s,$$

where

$$S_m = \alpha \times T^{3/2},$$

is the magnetic contribution, and

$$S_s = -\frac{1}{e\sigma T}\int (\epsilon - \mu)\frac{\partial f_0}{\partial \epsilon}\sigma(\epsilon)d\epsilon,$$

where f_0 is the Fermi-Dirac distribution function, μ is the chemical potential, and

$$\sigma = \int \sigma(\epsilon)\frac{\partial f_0}{\partial \epsilon}d\epsilon,$$

which is the simple semiclassical result for thermal diffusion in metallic systems.

Owing to the fact that there is not much change in the atom positions in the transition from cubic to tetragonal structure, a safe assumption that any change in the TEP is a direct manifestation of the changes in the density of states (DOS) can be made.

Figure 4 represents the TEP data with the temperature axis normalized with respect to the matensitic temperatures of the respective alloys. The TEP data in the $0.86 \leqslant T/T_M \leqslant 1.02$ range show an inflection point at normalized temperatures of ~0.86 and ~0.94 (see inset) for Ni_2MnGa and $Ni_{2.19}Mn_{0.81}Ga$, respectively. If a model for the DOS near the Fermi level is assumed consisting of a peak near the Fermi level, the TEP of both alloys can be accounted for by this peak shifiting closer to the Fermi level in $Ni_{2.19}Mn_{0.81}Ga$. The shift of the inflection point from 0.86 to 0.94 can then be associated with the shift of the peak in the DOS towards the Fermi level as the Ni content is increased in going from Ni_2MnGa to $Ni_{2.19}Mn_{0.81}Ga$.

Increasing Ni doping for Mn results in doping electrons in the DOS at the Fermi level. This considerably alters the band structure as is evident from the change in magnitude of the thermopower in proceeding from the martensitic to the austenitic phase. The decrease in the magnetic ordering temperature coupled with the increase in the martensitic transition temperature can also be understood from here. The 3*d* band in Ni is nearly full whereas that in Mn is half filled. Hence replacement of Mn by Ni results in reduction of magnetic moment and the magnetic transition temperature. Similarly, a change in the position of the peak in the DOS at the Fermi level, which is associated with the Ni 3*d* band results in a phase instability and therefore a phase transition from the cubic austentic phase to the tetragonal martensitic phase. Such peaks in the electronic DOS are known to lead to a

structural phase transition.[25] These changes are probably a result of a redistribution of 3*d* electrons among the 3*d* orbitals whose degeneracy is further broken by the lowered symmetry from cubic to tetragonal. Substitution of Ni for Mn results in a transfer of electrons from the nearly full 3*d* band of nickel to the more than half filled 3*d* band of manganese. It is the splitting of energy subbands which are degenerate in the cubic phase which enables the electrons to redistribute themselves so as to lower the free energy. This is the well-known band Jahn-Teller mechanism. In the band model there is an increase in the width of the energy bands because, when the crystal deforms, there is a change in the degree of overlap of the associated orbitals. Unlike in the case of stoichiometric Ni_2MnGa, where the c/a ratio of the tetragonal phase is <1, for $Ni_{2.19}Mn_{0.81}Ga$, the c/a ratio is >1. This will lead to a redistribution of electrons in the crystal-field-split 3*d* band of this alloy. A redistribution of magnetization is found for stoichiometric Ni_2MnGa in the neutron scattering experiment as a function of temperature when it undergoes a transition from the high-temperature austinitic to low-temperature martensitic phase.[26]

The band structure of Ni_2MnGa has been in Ref. 27. The composition of bands that are active at the Fermi surface could be identified. With this identification the Fermi level lies just above a peak in the DOS of the minority-spin Ni e_g band and at a position in the Mn band there is an almost equal DOS of majority- and minority-spin t_{2g} states. For a martensitic transition to occur an important feature required is that the peak in the DOS should have some asymmetry, whereby it has more weighting towards lower energies, and that the Fermi level is situated very close to the peak. Such a DOS can explain the observed thermopower very well, especially in the martensitic phase, and has been used to explain thermopower data of shape memory NiTi alloys.[28] In the present study, the thermopower can be explained by assuming a similar model of the DOS. A shift in the position of the peak in the DOS is observed towards the Fermi level with increasing Ni concentration. The assumed model, on integration, yields the same variation as the TEP observed experimentally in the present study.

In conclusion, we have studied the resistivity and investigated the variation in thermopower for the magnetic heusler alloys Ni_2MnGa and $Ni_{2.19}Mn_{0.81}Ga$. The experimental results indicate that the TEP for $Ni_{2.19}Mn_{0.81}Ga$, though different from that for Ni_2MnGa, the general trend in the variation of TEP is that of a typical Heusler alloy with local-moment ferromagnetism. With the assumed model, the peak in the DOS just below the Fermi level is seen to shift towards higher energy in the region of the martensitic transition with increasing Ni content. All the anomalies observed in the TEP have been explained to be due to crystal field splitting and the associated changes in the density of states near the Fermi level.

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