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<td>Author(s)</td>
<td>Maheswar Repaka, Durga Venkata; Chen, X.; Ramanujan, Raju Vijayaraghavan; Mahendiran, R.</td>
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Citation: AIP Advances 5, 097116 (2015); doi: 10.1063/1.4930592
View online: http://dx.doi.org/10.1063/1.4930592
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Magnetic field dependence of electrical resistivity and thermopower in Ni$_{50}$Mn$_{37}$Sn$_{13}$ ribbons

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(Received 15 July 2015; accepted 27 August 2015; published online 4 September 2015)

We report magnetization, magnetoresistance (MR) and magnetothermopower (MTEP) of melt spun Ni$_{50}$Mn$_{37}$Sn$_{13}$ ribbons which exhibit an austenite to martensite phase transition at a temperature ($T_M$) $\approx$ 294 K. Upon cooling from 400 K, dc-resistivity and thermopower show abrupt changes at $T_M$, indicating a change in the electronic density of states. The thermopower is negative from 400 K down to 10 K. Application of a magnetic field of $\mu_0H = 5$ T decreases $T_M$ by 5 K and induces large negative MR (-23%) but positive MTEP (9%) near $T_M$. While the MR is appreciable from $T_M$ down to 10 K, MTEP is significant only below 60 K (MR = -2.5% and MTEP = +300% at 10 K). The magnetic field dependence of resistivity and thermopower show either reversible or irreversible behavior near $T_M$, depending on whether the sample is zero-field cooled or field-cooled, which indicates that the electronic band structure near $T_M$ is magnetic history dependent.

I. INTRODUCTION

The half Heusler alloys Ni$_{50}$Mn$_{50-x}$Z$_x$ (Z = Sn, In and Sb), which combine magnetism and shape memory effect, are smart functional materials; they exhibit large values of magnetic field induced strain, inverse magnetocaloric effect, and magnetoresistance at the austenite-martensite phase transition temperature. The austenite ($A$) and martensite ($M$) states refer to the high temperature, high crystallographic symmetry (normally cubic) phase and low temperature, low symmetry (monoclinic/orthorhombic/tetragonal/modulated) phase, respectively. The $A$-$M$ transition is a first order diffusion less phase transition and it spontaneously occurs at $T = T_M$ upon cooling. This transition is driven by interfacial strain between these two phases, rather than by thermodynamic fluctuations, and it occurs over a temperature range. $T_M$ increases with an increase in the number of valence electrons per atom ratio ($e/a$); $T_M$ can be tuned by varying the Ni/Mn or Mn/Z ratio. The austenite phase becomes ferromagnetic below $T = T_C$ ($A$) and the $A$-$M$ transition is often accompanied by an abrupt decrease of magnetization at $T_M$. In Ni$_{52-x}$Mn$_{1-x}$Ga, $T_C$ decreases, while $T_M$ increases, with increasing Ni content, for $x = 0.19$ both the structural and magnetic phase transition coincide. Neutron diffraction studies on Ni$_{50}$Mn$_{50}$Sn$_{14}$ revealed that the high temperature austenite cubic phase ($L_2_1$) transformed into a low temperature orthorhombic four layered (4O) structure. Large field induced irreversible transitions of magnetization in Ni-Mn-Sn alloys near and below $T_M$ have been reported.

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While much of the focus in recent years is on the attractive magnetocaloric properties/magnetization of magnetic Heusler alloys, there are few combined studies of thermopower and electrical resistivity. Thermopower or Seebeck coefficient ($\alpha = \Delta V/\Delta T$) is the measure of electrical voltage difference ($\Delta V$) that is developed in response to a temperature difference ($\Delta T$) between the two ends of a sample. Thermopower is sensitive to the asymmetry in the density of states around the Fermi level and thus can be used to monitor changes in the electronic band structure across the $A$-$M$ phase transition. In the non-magnetic shape memory alloy Ti$_{50}$Ni$_{50}$, the thermopower is positive in sign and shows an abrupt increase (decrease) during the $A$-$M$ (reverse) phase transition. On the other hand, thermopower in ferromagnetic Ni$_{24}$Mn$_{1-x}$Ga is negative and shows a dip at the martensite and premartensite transition temperatures for $x = 0.13-0.19$. It was reported that density of states (DOS) changes at the $A$-$M$ transition in Ni-Mn-Ga alloys. However, the negative thermopower in Ni$_{30}$Mn$_{30}$In$_{16}$ and Mn$_{2}$NiGa shows an abrupt decrease in magnitude at the $A$-$M$ transition during cooling, and the anomaly at $T_M$ is very weak in Ni$_{50}$Mn$_{30}$Sn$_{14}$.

The Ni$_{50}$Mn$_{50-x}$Sn$_x$ alloys have been studied by different research groups because of the significance for the magnetocaloric effect and magneto resistance, but simultaneous measurements of resistivity and thermopower and the impact of external magnetic field on these properties were not reported so far. In the present work, we studied the influence of external magnetic field on the electrical resistivity and thermopower in Ni$_{50}$Mn$_{30}$Sn$_{13}$ ribbons.

II. EXPERIMENTAL DETAILS

Polycrystalline ingots of Ni$_{50}$Mn$_{37}$Sn$_{13}$ were prepared by an arc melter (MAM1, Edmund Buehler) from the constituent elements, Ni (99.5%, Alfa Aesar), Mn (99.95%, Sigma Aldrich) and Sn (99.8%, Sigma Aldrich) in an inert Ar atmosphere. These ingots were used to make the ribbons by melt-spinner (HIT 6, Edmund Buehler) at 60 rpm wheel speed in Ar atmosphere. Magnetic measurements were performed by a vibrating sample magnetometer (VSM) probe in Physical Property Measurement System (PPMS, Quantum Design USA). Four probe dc-electrical resistivity and thermopower were simultaneously measured using a home-made set-up, integrated with the PPMS. The PPMS sample puck was used as a thermal stage to stabilize the base temperature. The sample was mounted between two copper blocks. Two sapphire sheets were used to electrically insulate the sample from the copper blocks. Two chip resistors attached to these copper blocks were used as heat sources. We measured the thermopower in differential mode by alternating the temperature gradient across the sample in both directions to eliminate the spurious and off-set voltages. Differential scanning calorimetry, DSC (TA instruments, TA DSC Q10) was used to detect the martensitic transition.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the temperature dependence of magnetization ($M(T)$) of Ni$_{50}$Mn$_{37}$Sn$_{13}$ while cooling (field cooled cooling mode or FCC) and warming (field cooled warming mode or FCW) under magnetic fields of $\mu_0H = 0.1$ and 5 T. Upon cooling, the austenite ($A$) phase undergoes

![Figure 1](https://example.com/figure1.png)

**FIG. 1.** (a) Temperature dependence of magnetization, $M(T)$ of Ni$_{50}$Mn$_{37}$Sn$_{13}$ for $\mu_0H = 0.01$ and 5 T while cooling (FCC) and warming (FCW) modes (b) Field dependence of magnetization, $M(H)$ at 10 K. The inset of fig. 1(b) shows the differential scanning calorimetry (DSC) curves of Ni$_{50}$Mn$_{37}$Sn$_{13}$ while cooling and warming.
a paramagnetic (PM) to ferromagnetic (FM) transition at $T_C(A) = 299$ K followed by an abrupt decrease in magnetization at $T = T_M = 294$ K due to the austenite to martensite ($A$-$M$) structural transition under $\mu_0H = 0.1$ T. As temperature decreases further, the sample undergoes another ferromagnetic transition in the martensitic phase at $T_C(M) = 231$ K. The $M(T)$ curve shows a large thermal hysteresis ($\Delta T = 8$ K) between FCC and FCW curves at $T_M$ which implies that the $A$-$M$ transition is first-order in nature. On the other hand, no thermal hysteresis is observed for the ferromagnetic transitions at $T_C(A)$ and $T_C(M)$ because they are second order.

The abrupt decrease of $M(T)$ around $T_M$ while cooling is attributed to development of antiferromagnetic (AF) correlations between Mn ions and it is promoted by the shortening of Mn-Mn distance in the $M$-phase.29 As Sn concentration decreases in Ni$_{50}$Mn$_{34+y}$Sn$_{13-y}$, additional Mn atoms become nearest neighbors for Mn atoms along the [110] direction, which promotes AF exchange through non-collinear spin structures.30 The presence of AF exchange interaction below $T_M$ has been confirmed by a polarized neutron diffraction study on Ni$_{50}$Mn$_{17}$Sn$_{13}$. Application of the external magnetic field of $\mu_0H = 5$ T causes an increase in Curie temperature of $A$-phase from $T_C(A) = 299$ K to 313 K but a decrease in the $M$-phase transition from $T_M = 294$ K to 288 K ($\Delta T_M = 6$ K). The shifts of $T_M$ to lower temperatures indicate that the magnetic field stabilizes the high temperature austenite phase.

Figure 1(b) shows the field dependence of magnetization, $M(H)$ of Ni$_{50}$Mn$_{37}$Sn$_{11}$ at $T = 10$ K. The $M(H)$ shows soft magnetic behavior with saturation magnetization of $M_S = 35$ emu/g and coercivity of $H_C = 0.05$ T. The inset of Fig. 1(b) shows the DSC results of Ni$_{50}$Mn$_{37}$Sn$_{11}$ alloy. The DSC curves show exothermic and endothermic peaks while cooling and heating at $T_M = 291$ K and 306 K, respectively. These peaks are the characteristic transition temperatures for the austenite to martensitic and martensitic to austenite structural transitions, respectively.

Figure 2(a) shows the temperature dependence of dc-electrical resistivity, $\rho(T)$ of Ni$_{50}$Mn$_{37}$Sn$_{11}$ under $\mu_0H = 0$ T for cooling and warming cycle. $\rho(T)$ shows metallic behavior (i.e., $\partial \rho / \partial T$ is positive) for $T > T_M$. The resistivity rises abruptly at $T_M = 292$ K. Below $T_M$, the resistivity increases with decreasing temperature. It again shows a metallic behavior below $T \sim 150$ K. $\rho(T)$ exhibits noticeable thermal hysteresis between cooling and warming cycle at $T_M$ as a consequence of the first-order structural phase transition.

Figure 2(b) shows the temperature dependence of thermopower, $\alpha(T)$ while cooling and warming under $\mu_0H = 0$ T. The negative sign of the thermopower throughout the measured temperature range indicates that electrons are majority charge carriers. $\alpha(T)$ is weakly temperature dependent above $T_C(A)$ and undergoes an abrupt jump at $T_M$. The magnitude of $\alpha(T)$, decreases linearly with decreasing temperature below $T_M$ until it shows a slope change at $T = 60$ K. The value of thermopower tends towards zero at 10K, as expected for the diffusive contribution of electrons to thermopower in normal metals. Such a change in slope was also found in nonmagnetic Ni$_{50}$Ti$_{50}$ alloy and was attributed to phonon drag contribution that was broadened by disorder. However, this feature was not observed in the ferromagnetic shape memory alloy Ni$_{50}$Mn$_{34}$In$_{16}$. Upon heating from 10 K, $\alpha(T)$ exhibits hysteresis at $T_M$ as is the case with the resistivity, due to the first-order structural phase transition.

Figure 3(a) and 3(b) compare the temperature dependence of resistivity and thermopower under $\mu_0H = 0$ T (black) and 5 T (red) while cooling. The value of $\rho$ just below and above $T_C(A)$

![Fig. 2. Temperature dependence of (a) resistivity $\rho(T)$ and (b) thermopower $\alpha(T)$ under $\mu_0H = 0$ T while cooling and warming.](image-url)
decreases in the presence of the external magnetic field. The resistivity jump shifts to lower temperature ($T_M = 288$ K under 5 T). While the insulating state is not destroyed by the magnetic field, the value of $\rho$ decreases all the way from $T_M$ down to 10 K. Under the magnetic field, the abrupt decrease of thermopower at $T_M$ also shifts to lower temperatures. Interestingly, $|\alpha(T)|$ increases just below the ferromagnetic transition in the A phase and is virtually field independent from $T_M$ down to $\sim 60$ K, unlike the resistivity. We show the behavior of $\alpha(T)$ below 80 K in the inset of fig. 3(b) in expanded scale. It is clear that the applied magnetic field enhances the magnitude of thermopower below $T \sim 60$ K.

Figure 4(a) and 4(b) show the calculated magnetoresistance (MR($\%) = \left[ \frac{\rho(H) - \rho(0)}{\rho(0)} \right] \times 100)$ and magnetothermopower (MTEP($\%) = \left[ \frac{\alpha(H) - \alpha(0)}{\alpha(0)} \right] \times 100)$, respectively for field change of $\Delta H = 5$ T. The MR shows a dip at $T_M$, where it reaches a value of $-23$ %. This value is smaller than the value of $-36$% observed at $T_M (= 200$ K) in the $x = 0.4$ composition of Ni$_2$Mn$_{1.5}$Sn$_{1-x}$.

The magnitude of MR decreases from 2.67% at 248 K to 2.18% at 10 K. On the other hand, the MTEP is positive, increases below 350 K and achieves a peak, value of 9 % around $T_M$. Then it decreases to almost zero value at $\sim 250$ K. While the MTEP is nearly zero at temperatures between 250 K and 60 K, it shows a rapid increase below 30 K and reaches 300% at 10 K.

To demonstrate that the MR and MTEP observed in the temperature sweep are not artifacts, we did field sweep measurements at selected temperatures. Fig. 5(a) shows $\rho(H)/\rho(0)$ as a function of the magnetic field at $T = 10, 25, 50, 100, 150$ and 200 K. The ratio $\rho(H)/\rho(0)$ decreases linearly with increasing $H$ at all temperatures. The field dependence of resistivity ratio $\rho(H)/\rho(0)$ close to and above the high temperature ferromagnetic transition in the austenite phase can be seen in fig. 5(c).

The thermopower ratio $\alpha(H)/\alpha(0)$ in fig. 5(b) also increases linearly with magnetic field at 10 K and reaches a value of $\sim 3$ at 5 T. A linear dependence of $\alpha(H)/\alpha(0)$ on $H$ is also seen at 50 K. The thermopower ratio is negligible at 100 K, 150 K and 200 K. On the high temperature side (fig. 5(d)), the ratio $\alpha(H)/\alpha(0)$ is small. $\alpha(H)/\alpha(0) = 1.026$ at 320 K and quickly decreases for $T > 320$ K. Since the changes are small, the data is much noisy above 320 K.
Now let us focus on the transport properties close to the structural phase transition. Figure 6(a), 6(b) and 6(c) show $M(H)$, $\rho(H)$ and $\alpha(H)$ at 290 K, just below $T_M = 294$ K. These measurements were done after cooling the sample from 350 K to 290 K in zero magnetic field, i.e., in the zero field cooled mode (ZFC). $M(H)$ increases rapidly at low fields like a typical soft ferromagnet but it does not saturate even at the highest field of 5 T. In fig. 6(b), $\rho(H)$ decreases linearly with increasing field. The variation in resistivity with applied field is monotonic and negligible hysteresis is observed in the field cycle (0 → 5 → -5 → 5 T). Similarly, $\alpha(H)$ in Fig. 6(c) also shows very small variation with $H$, the change being less than 0.2 $\mu$V/K between 0 T and 5 T, with negligible hysteresis during field cycling (0 → 5 → -5 → 5 T). Since the change in the value of the thermopower...
with magnetic field is small, it is dominated by noise. At $T = 290 < T_M$ ($\mu_0H = 0$ T), the sample is mostly in the martensitic phase after zero field cooling and hence it is in the high resistance state.

Figure 6(d), 6(e) and 6(f) show $M(H)$, $\rho(H)$ and $\alpha(H)$ isotherms at 290 K, obtained after cooling the sample in $\mu_0H = 5$ T from 350 K to 290 K, i.e. in the field cooled mode (FCC). The field cooling has shifted $T_M$ to 288 K and hence a fraction of the sample is in the ferromagnetic austenite phase at $T = 290$ K at 5 T. The $M(H)$ curve traced from 5 T to 0 T lies above the curves obtained in subsequent field sweeps of $0 \rightarrow -5$ T (path 1) and $-5 \rightarrow 0$ T $→ +5$ T (path 2). The $M(H)$ curve traced in path 2 in the FCC mode is similar to the path 2 curve traced in the ZFC mode in fig. 6(a). Thus, the initial branch (5 T $→ 0$ T) of $M$-$H$ is irreversible after field cooling.

The field dependence of resistivity also shows irreversible behavior. When the field is reduced from 5 to 0 T (path 1), $\rho(H)$ in fig. 6(e) increases smoothly between 5 T and 2 T, and then increases rapidly. When the field is decreased from 0 T to -5 T, resistivity shows a small decrease and no obvious hysteresis. $\rho(H)$ shows a gradual decrease when the field is increased in the positive direction (0 T $→ +5$ T, path 2). Thus, resistivity does not recover to the initial value at 5 T $→ 0$ T. The thermopower (fig. 6(f)) also shows irreversible behavior. The thermopower starts from $\sim -6$ $\mu$V/K at 5 T and decreases to $\sim -7.5$ $\mu$V/K at -5 T, the thermopower traces a different path (-5 T $→ +5$ T, path 2) and shows little changes in negative values. These experimental results show that the irreversibility in magnetization directly affects the resistivity and thermopower.

The abrupt jump of resistivity at the onset of martensitic transition was also found in Ni$_{30}$Mn$_{75}$Sn$_{15}$ thin film, bulk Ni$_2$Mn$_{1-x}$Sn$_{1-x}$ (x = 0.40, 0.44) and Ni$_2$Mn$_{1-x}$Ga (x = 0.24). The abrupt increase of $\rho(T)$ at $T_M$ is either due to antiferromagnetic exchange between Mn ions on Sn sites and Mn ions in the Mn sub lattice or due to changes in the band structure caused by band Jahn-Teller distortion or a combination of both mechanisms. It is to be highlighted that the resistivity in nonmagnetic shape memory alloy Ni$_{30}$Ti$_{70}$ also shows abrupt increase at the martensitic transition, driven by Fermi surface nesting rather than by antiferromagnetic interactions. Hard X-ray photoelectron spectroscopy revealed a change in valence band structure across $T_M$ in Mn$_2$NiGa. Hence, the abrupt increase in the magnitude of the thermopower at $T_M$ accompanied by the abrupt increase of the resistivity is most likely to be a consequence of changes in band structure in the vicinity of the Fermi level. The change in the density of the states affects the magnitude of the thermopower since the diffuse component of the thermopower in Mott’s model is proportional to the energy derivative of the density of states at the Fermi level, $a = \frac{e^2 k_F^2}{\pi ^2} T \left( \frac{1}{N(E)} \frac{\partial N(E)}{\partial E} \right)_{E=E_F}$, where $N(E)$ is the DOS.

The applied magnetic field shifts the structural phase transition to lower temperatures. Hence, the anomalies in the resistivity and thermopower also shift to lower temperatures. The large negative MR at $T_M$ is due to the field-induced structural transition. While the occurrence of negative MR just above and below $T_M$ ($\sim 5$ T) in the austenite phase can be due to the suppression of $s$-$d$ scattering by the external magnetic field, the existence of MR from $T = T_M$ to 10 K well within the ferromagnetic state indicates that the martensitic phase is not a homogeneous ferromagnet because of the presence of antiferromagnetic interactions between the Mn atoms present on the Sn sublattice and those on the Mn sublattice. The value of $M$ at 10 K and at 5 T is 36.44 emu/g which is only slightly higher than its peak value (33.94 emu/g) at $T_M$. The 5 T field is insufficient to break the antiferromagnetic interaction in the martensitic phase. Hence, the magnetoresistance does not saturate at 5 T.

IV. CONCLUSION

In summary, we have reported the temperature and field dependent magnetization, electrical resistivity and thermopower of the magnetic shape memory alloy Ni$_{30}$Mn$_{75}$Sn$_{15}$. The electrical resistivity and thermopower show abrupt changes at $T_M$. An applied magnetic field of 5 T leads to -23% magnetoresistance (MR) and + 9 % magnetothermopower (MTEP) around the martensitic phase transition. The MR and MTEP at $T_M$ are consequences of the field-induced structural phase transition. It is shown that field dependence of the resistivity and thermopower at 290 K can either show irreversible or reversible behavior, depending on whether the sample is zero-field cooled or field-cooled. At 10 K, the magnetoresistance is only -2.4%, whereas the magnetothermopower is...
very large (∼ +300%). The apparently very large magnetothermopower below 60 K is due to small values of the thermopower in zero field.

ACKNOWLEDGEMENT

R. Mahendiran acknowledges the Ministry of Education, Singapore for supporting this work through the grant R144-000-332-112.

This Research is conducted by NTU-HUJ-BGU Nanomaterials for Energy and Water Management Programme under the Campus for Research Excellence and Technological Enterprise (CREATE), that is supported by the National Research Foundation, Prime Minister’s Office, Singapore.