Magnetic field-induced martensitic transformation and large magnetoresistance in NiCoMnSb alloys

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Magnetic field-induced martensitic transformation was realized in $Ni_{50-x}Co_xMn_{39}Sb_{11}$ alloys. The partial substitution of Co for Ni has turned the antiferromagnetically aligned Mn moments in the starting material $Ni_{50}Mn_{39}Sb_{11}$ into a ferromagnetic ordering, raising the magnetization at room temperature from 8 emu/g for NiMnSb to ~110 emu/g for $Ni_{41}Co_9Mn_{39}Sb_{11}$. In the same quaternary sample, a magnetization difference up to 80 emu/g was measured across the martensitic transformation, and the transformation temperature (T_0=259 K) could be lowered by 35 K under a field of 10 T. Also a magnetoresistance over 70% was observed through this field-induced transformation. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2748095]

Off-stoichiometric Heusler alloys $Ni_{50}Mn_{50-y}X_y$ (X =In, Sn) and the related intermetallic compounds having Co partially replacing Ni have attracted considerable attention in recent years because of their potential technological applications.[1–4] In some particular composition ranges, these alloys undergo a martensitic transformation from the ferromagnetic parent phase to an antiferromagneticlike martensite phase, exhibiting strong change in both the magnetization and the electrical resistance. In 2006, Kainuma *et al.* reported the magnetic field-induced shape recovery through reversed phase transformation in NiCoMnIn alloys[1] and later observed a giant magnetocaloric effect and large magnetoresistance[5–9] in these alloys. Another intriguing member of this intermetallic family is the NiMnSb system. For those NiMnSb alloys free from martensitic transformation, earlier studies have disclosed their magnetic and thermal properties in great detail.[10–14] However, research on the martensitic transformation in the NiMnSb alloys is still in its early stages; only the composition dependence of the phase transformation temperature and the Curie temperature has been investigated.[15] Magnetic properties of the NiMnSb alloys in the presence of a martensitic transformation and the effect of magnetic field on the transformation have not been reported. In this letter, we report the observation of a magnetic field-induced martensitic transformation and the measurement of a large magnetoresistance in $Ni_{41}Co_9Mn_{39}Sb_{11}$. The field-induced reduction of the transformation temperature in this alloy is 3.5 K/T, and a magentoresistance over 70% can be obtained with field of 1–10 T. The underlying mechanism of these effects will be briefly discussed.

Crystalline $Ni_{50-x}Co_xMn_{50-y}Sb_y$ alloys (x=0–9 and y =11–13) were prepared by arc melting of high-purity metals under argon atmosphere. The samples were remelt a few times and annealed at 1173 K for 3 days to ensure homogeneity. X-ray diffraction was employed to characterize the crystal structures for both the parent and martensite phases, and ac magnetic susceptibility measurements were performed to determine the martensitic transformation temperature T_M and the Curie temperature T_C. The magnetization and electrical resistance for the samples were measured in a physical properties measurement system (Quantum Design) equipped with a magnetic field up to 13.0 T in the temperature range from 5 to 300 K. The latent heat upon transformation was determined by the differential scanning calorimetry (DSC).

For all the samples $Ni_{50-x}Co_xMn_{50-y}Sb_y$ with x=0–9 and y=11–13, the x-ray diffraction patterns (not shown) point to a pure $B2$ structure for parent phase and the ac susceptibility measurements reveal a well-defined thermoelastic martensitic transformation. The partial substitution of Co for Ni in the given composition range leads to a lowered martensitic transformation temperature and an increased Curie temperature. The increasing content of Sb in the given range also lowers the martensitic transformation temperature. Based on the above observations, the specimen $Ni_{41}Co_9Mn_{39}Sb_{11}$ was chosen for a detailed study to highlight the effect of Co substitution on the magnetic and electrical properties of the NiMnSb alloys. Its Curie temperature T_C, martensitic transformation temperature T_M, and the reverse transformation temperature T_A are 361, 258, and 260 K, respectively. For comparison, the Co-free alloy $Ni_{50}Mn_{37}Sb_{13}$ with T_C=330 K, T_M=278 K, and T_A=272 K has also been investigated in parallel. Both samples demonstrate the same $B2$ structure in their high temperature phases, with a lattice constant of 5.9757 Å for $Ni_{41}Co_9Mn_{39}Sb_{11}$ and of 5.9788 Å for $Ni_{50}Mn_{37}Sb_{13}$. Upon cooling, both samples undergo a martensitic transformation from the bcc structure to a complicated 14M monoclinic martensite structure. This is quite similar to the observations in the NiMnIn alloys.[16]

Figure 1 displays the temperature dependence of magnetization for $Ni_{41}Co_9Mn_{39}Sb_{11}$ measured under different magnetic fields in contrast to that measured in $Ni_{50}Mn_{37}Sb_{13}$ at 5.0 T. The abrupt change in magnetization marks the martensitic and the reverse martensitic transformations. It can be seen that in $Ni_{41}Co_9Mn_{39}Sb_{11}$, the transformation tempera-

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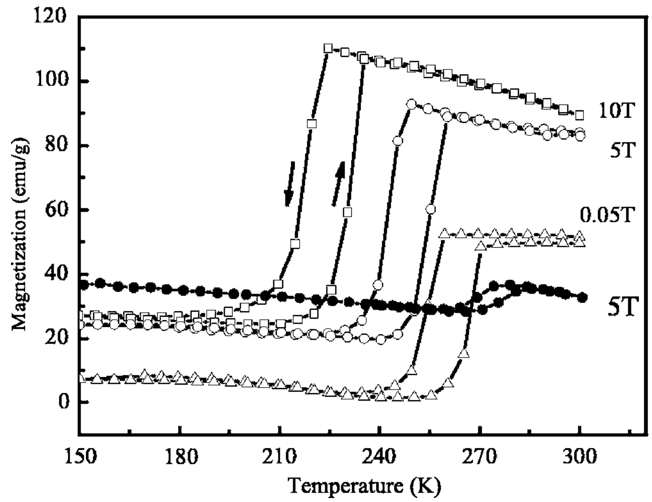

FIG. 1. Temperature dependence of magnetization measured in $Ni_{41}Co_9Mn_{39}Sb_{11}$ (open symbols) under different magnetic fields. The data for $Ni_{50}Mn_{37}Sb_{13}$ at 5 T (solid symbol) were plotted for comparison. The arrows indicate the direction of temperature regulation.

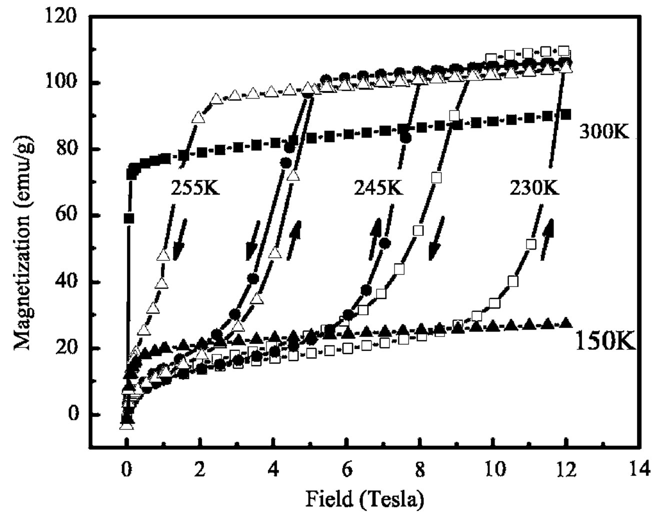

FIG. 2. Magnetization curves of $Ni_{41}Co_9Mn_{39}Sb_{11}$ at various temperatures. The arrows indicate the direction of field variation.

ture has been depressed by the magnetic field; however, this phenomenon is absent in the NiMnSb alloys. By applying a field of 10 T, the shift in T_M and T_A for $Ni_{41}Co_9Mn_{39}Sb_{11}$ amounts to 35 K. Moreover, the magnetization difference ΔM across the transformation was significantly enhanced at a field over 5 T, which measures up to $\sim$80 emu/g. For comparison, the ΔM for $Ni_{50}Mn_{37}Sb_{13}$ at 5 T is only 8 emu/g.

With this very large magnetization difference realized in NiCoMnSb, we thus expect it to manifest a field-induced martensitic transformation. According to the Clausius-Clapeyron equation, $dT/dH = -\Delta M/\Delta S$, where ΔM and ΔS denote the differences in magnetization and in entropy across the transformation, it is the quotient of $\Delta M/\Delta S$ that signifies the magnitude of the magnetic field required to induce the transformation. The entropy change ΔS across the martensitic transformation under zero field by the DSC measurements for $Ni_{41}Co_9Mn_{39}Sb_{11}$ was determined to be 24.5 J/K kg, which is about twice the value of 12.1 J/K kg for $Ni_{50}Mn_{37}Sb_{13}$. This suggests that the field-induced transformation in $Ni_{41}Co_9Mn_{39}Sb_{11}$ has been facilitated due to the large ΔM value across the transformation or, to be more precise, to the dramatically increased magnetization in the parent phase.

The effect of Co substitution for Ni in NiMnSb to enhance the field-induced martensitic transformation can be assessed from three aspects. First, it increases T_C of the alloy so that the martensitic transformation therein would then occur at a temperature farther from T_C. On the other hand, each Co atom at the site of Ni contributes a magnetic moment of $\sim 1.0\mu_B$, whereas the Ni atoms in this system should each have a magnetic moment less than $0.31\mu_B$, based on *ab initio* calculation and magnetization measurement at nearly 0 K. The last, and also the most important, consequence of Co substitution is that it turns the magnetic moments of Mn atoms into a ferromagnetic ordering instead of the previous antiferromagnetic one. To this point, a brief explanation seems appropriate.

In some Ni_2Mn-based Heusler alloys, such as Ni_2MnGa, Ni_2MnIn, and Ni_2MnSn,[17] the magnetic moment per Mn atom is as large as $\sim 4.0\mu_B$, which explains the ferromagnetism of these alloys. In their off-stoichiometric variants as specified in $Ni_{50}Mn_{50-y}X_y$ (X=Ga, Sn, and In and y is less than 25), the "extra" Mn atoms couple with the neighboring Mn atoms antiferromagnetically in NiMnGa (Ref. 18) and NiMnSn (Refs. 19 and 20) but ferromagnetically in NiMnIn.[16] In the Ni_2MnSb alloy, the Mn atoms even suffer a considerable reduction in magnetic moment, being only $3.27\mu_B$/at.[17] This explains why in $Ni_{50}Mn_{37}Sb_{13}$ both the magnetization of the partially antiferromagnetic parent phase and the ΔM across the martensitic transformation are so low (see Fig. 1). Due to the partial substitution of Co for Ni, the ferromagnetic parent phase of the alloy $Ni_{41}Co_9Mn_{39}Sb_{11}$ acquires a magnetization as high as 100 emu/g, which is comparable with that in NiMnIn.[3] As mentioned above, the Co substituent has only a negligible effect on the lattice constant, thus the ferromagnetic ordering in $Ni_{41}Co_9Mn_{39}Sb_{11}$ might originate from the altered electronic structure due to the presence of the Co 3d electrons. Further data and analysis are needed to gain a clear picture.

The magnetization curves of $Ni_{41}Co_9Mn_{39}Sb_{11}$ at various temperatures are plotted in Fig. 2. At temperatures between 230 and 255 K, which are below T_M, the curves show a metamagnetic transition from the martensitic phase of low magnetization to the parent phase of high magnetization triggered by field and ΔM of 80 emu/g is read which is in agreement with the thermomagnetization measurement (cf. Fig. 1). The data measured at 150 K for the martensite phase (at 300 K for the parent phase) reveal a typical ferrimagneticlike (ferromagnetic) behavior.

The field-induced martensitic transformation in the NiCoMnSb alloys is correlated with a modification of the electronic structure in the samples; therefore, a large magnetoresistance effect ensues. Figure 3(a) illustrates the temperature dependence of the electrical resistance measured in $Ni_{41}Co_9Mn_{39}Sb_{11}$ under zero field and under a field of 10 T. In both cases, the electrical resistance undergoes an abrupt change upon transformation, resulting from the variation of the density of state in the vicinity of the Fermi level, as confirmed in the NiMnIn and NiMnSn alloys.[7,8] Because the field can remarkably downshift the transformation temperature, a large magnetoresistance is expected in a temperature range over which the applied magnetic field is sufficiently

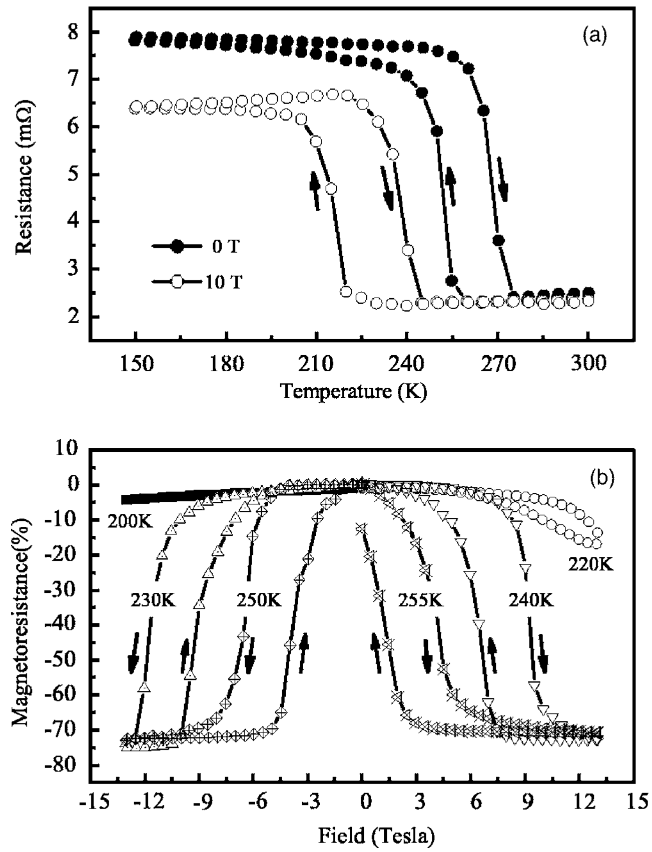

FIG. 3. (a) Temperature dependence of electrical resistance for $Ni_{41}Co_9Mn_{39}Sb_{11}$ at zero field (solid circles) and at 10 T (open circles) and (b) variation of magnetoresistance of the same sample vs field strength at various temperatures.

strong to be able to induce the transformation. In the temperature range from 230 to 250 K, a recoverable magnetoresistance over 70% was achieved with fields within 13.0 T [Fig. 3(b)]. At temperatures slightly below T_A, as demonstrated by the curve for 255 K, a smaller critical magnetic field is needed to reach the same maximum magnetoresistance but at the cost of an incomplete recovery.

In summary, partial substitution of Co for Ni in the $Ni_{50}Mn_{39}Sb_{11}$ alloys facilitates the magnetic field induced reversible martensitic transformation. The characteristic decreased of the transition temperature by a magnetic field dT/dH measures up to 3.5 K/T in $Ni_{41}Co_9Mn_{39}Sb_{11}$. Our preliminary investigation suggests that the substituent Co atoms in NiCoMnSb help align the Mn moments in a ferromagnetic ordering, giving rise to a significantly enhanced magnetization in the parent phase and a large ΔM across the transformation. Upon this field-induced transformation, a magnetoresistance over 70% has been measured. Further efforts will be devoted to highlight the detailed underlying mechanism of field-induced martensitic transformation and to formulate the applications for these alloys.

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