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Magnetic properties and magnetocaloric effect of $(Mn_{1-x}Ni_x)_3Sn_2$ (x=0–0.5) compounds

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The effects of Ni substitution on the magnetic properties and magnetocaloric effect (MCE) of $(Mn_{1-x}Ni_x)_3Sn_2$ compounds (x=0–0.5) have been investigated by x-ray diffraction and magnetization measurements. It was found that Ni substitution decreases the crystal cell volume and the magnetic transition temperatures compared with pure Mn_3Sn_2. The MCE for all samples has been calculated from the magnetization data in terms of the isothermal magnetic entropy change ΔS_M. The maximum values of ΔS_M^{max} at the magnetic phase transition temperatures resulting from a change in magnetic field of ΔH=5 T were found to be 28.2 mJ/cm^3 K for Mn_3Sn_2 ($T_{C1}\sim$257 K), increasing to 31.2 mJ/cm^3 K for $(Mn_{0.9}Ni_{0.1})_3Sn_2$ ($T_C\sim$167 K). © *2009 American Institute of Physics*. [DOI: 10.1063/1.3062953]

I. INTRODUCTION

Magnetic cooling technology based on the magnetocaloric effect (MCE) has become increasingly important in recent years since it is expected to provide a mechanism for environmentally friendly and energy-efficient refrigeration. The giant MCE is generally considered to be associated with a first-order magnetic transition (FOMT) as the large difference in magnetization between the two adjacent magnetic phases offers an intense, sharp MCE response, in contrast to the less intense but broader peak produced by second-order magnetic transitions (SOMTs).[1] However, the refrigerant capacity (*RC*) (the amount of heat which can be transferred in one thermodynamic cycle,[1–4] which also takes into account the width and shape of the ΔS_M versus T curves, where ΔS_M is the isothermal magnetic entropy change), is a more relevant parameter when evaluating the technological interest of a refrigerant material.

Despite their lower atomic moments, Mn-based intermetallic compounds are now a particular object of research because they are often magnetically ordered near, or above room temperature, and are comparatively cheap. Mn-based compounds often present multiple magnetic phase transitions, thereby resulting in a broad peak in the ΔS_M versus T curves and an increase in the *RC* value.[4] In this work, in order to understand the influence of introducing small amounts of transition elements on the MCE behavior in the Mn_3Sn_2 system, we have investigated the magnetic properties and entropy changes around the magnetic phase transitions by partly replacing Mn with Ni in $(Mn_{1-x}Ni_x)_3Sn_2$ for Ni contents of x=0.01–0.5.

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II. EXPERIMENTAL

Ingots of about 2 g were prepared by arc melting pure metals (x=0.0, 0.01, 0.05, 0.1, 0.2, 0.3, and 0.5) under argon atmosphere in a water cooled Cu crucible. The ingots were then sealed under argon atmosphere in quartz tubes and annealed at 1073 K for 1 week before being quenched into ice water. The x-ray diffraction (XRD) (Cu $K\alpha$) measurements on all seven samples were conducted at room temperature with Rietveld refinement analysis applied to determine the crystal structures and lattice parameters. Magnetic measurements were performed using a conventional physical properties measurement system (PPMS-9, Quantum Design| and a superconducting quantum interference device) over the temperature range 5–340 K and under applied magnetic fields of $\mu_0 H$=0–5 T. Except when otherwise stated, the thermomagnetic curves were recorded upon heating after zero-field cooling (ZFC) or field cooling (FC). The magnetic entropy change, ΔS_M, was evaluated from magnetization isotherms for temperatures between 5 and 320 K, with field steps of 0.2 T and temperature increments of 2 and 5 K.

III. RESULTS AND DISCUSSION

Figure 1(a) shows room temperature XRD patterns of all of the $(Mn_{1-x}Ni_x)_3Sn_2$ samples (x=0.00 to 0.5). Rietveld refinements of the x-ray data [Fig. 1(a), analyzed using FULLPROF software] confirm that all samples are isotopic with the Ni_3Sn_2 type of structure (*Pnma*) and that the lattice parameters decrease as expected [Fig. 1(b)] due to substitution of Mn (ionic radius 0.08 nm) with the smaller Ni atoms (ionic radius 0.069 nm), leading to a change in unit cell volume with Ni concentration of $dV/dx\approx-23.8$ Å^3. As an example, compared with Mn_3Sn_2 (where a=7.596 Å,

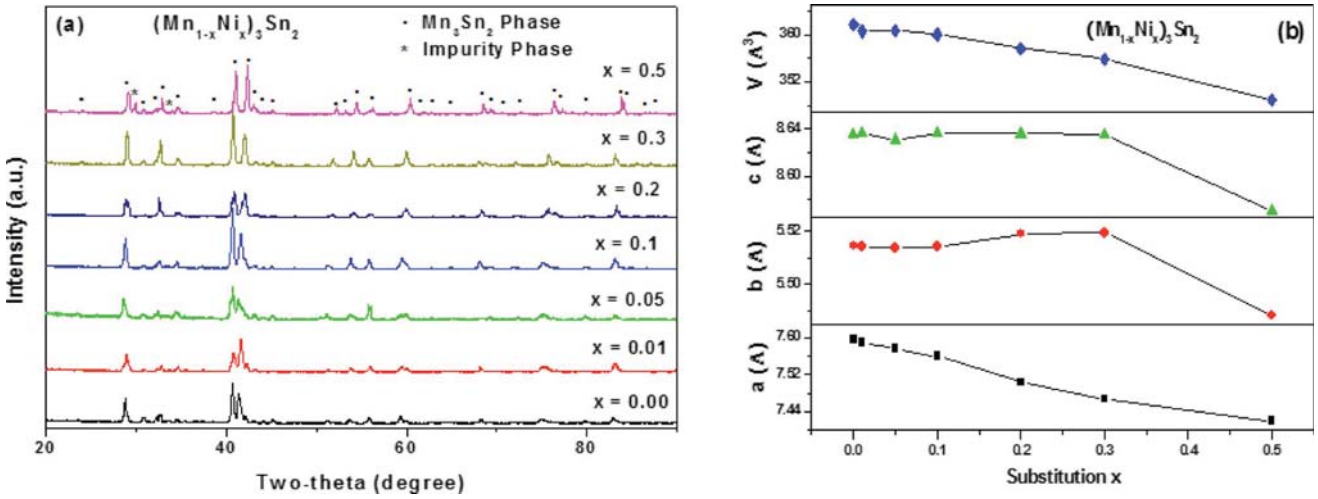

FIG. 1. (Color online) (a) Room temperature XRD patterns of the seven $(Mn_{1-x}Ni_x)_3Sn_2$ samples (x=0.01–0.5); except x=0.5 sample shows very low content impurity phase, all other samples show single phase with slightly peaks shifting due to lattice parameters changing. (b) the lattice parameters and unit cell volume of $(Mn_{1-x}Ni_x)_3Sn_2$ as a function of Ni concentration (x=0.01–0.5).

b=5.514 Å, c=8.635 Å, and V=361.7 Å^3), the unit cell volume for $(Mn_{0.7}Ni_{0.3})_3Sn_2$ has contracted by about 0.46% with a=7.560 Å, b=5.514 Å, c=8.637 Å, and V=360.0 Å^3.

Figure 2(a) shows the temperature dependence of the magnetization in a field of 100 Oe for selected samples (x=0, 0.05, 0.1, 0.2, and 0.5) after FC in a field of 100 Oe. It can be seen clearly that four anomalies exist in the M-T curves for the x=0 (Mn_3Sn_2) sample indicating four possible magnetic transitions of transition temperatures marked by arrows. With increasing Ni content the number of anomalies in M-T curves decrease: three for x=0.1, two for x=0.2, and one for x=0.5. Moreover, it can be seen that the magnetic phase transition temperature T_{c1} of Mn_3Sn_2 decreases with increasing Ni substitution x. It is interesting to note that the M-T curve for x=0.2 in Fig. 2(a) exhibits significantly different behavior from that of the other samples and that a sharp decrease in magnetization is detected below T_2 =82 K; this behavior indicates a change in magnetic state from ferromagnetism at higher temperature to antiferromagnetic (AFM) or ferrimagnetism at lower temperature. For x=0.5, the M-T reflects the typical character of ferromagnetism. We plan to carry out neutron diffraction studies to clarify the possible occurrence of antiferromagnetic Mn interactions for the $(Mn_{0.8}Ni_{0.2})_3Sn_2$ sample and to establish the magnetic structures for the system as a whole.

It has been reported[5–7] that Mn_3Sn_2 undergoes two successive transitions of ferromagnetic nature at $T_{C1}\approx 262$ K [paramagnetic (PM)-ferromagnetic FM1] and $T_{C2}\approx 227$ K (FM1-FM2). Even though the exact spin configurations of the FM1 and FM2 structures are not yet known, it was suggested that they are likely to correspond to some kind of canted ferromagnetism or ferrimagnetism, with FM2 having a higher magnetization. Our ZFC and FC observations in Fig. 2(a) indicate that Mn_3Sn_2 may exist in more complicated spin configurations since the decrease in the magnetization in the low temperature range (ZFC curves) might be related to the appearance of weak transverse AFM interactions. The small thermal irreversibility is hard to only ascribe to domain wall pinning or freezing.[8] It is also possible that a spin glass state exists in the low field range in this system although further investigations are required to clarify this possibility. Even though the exact spin configurations of Mn_3Sn_2 over the temperature range 5–340 K are not yet

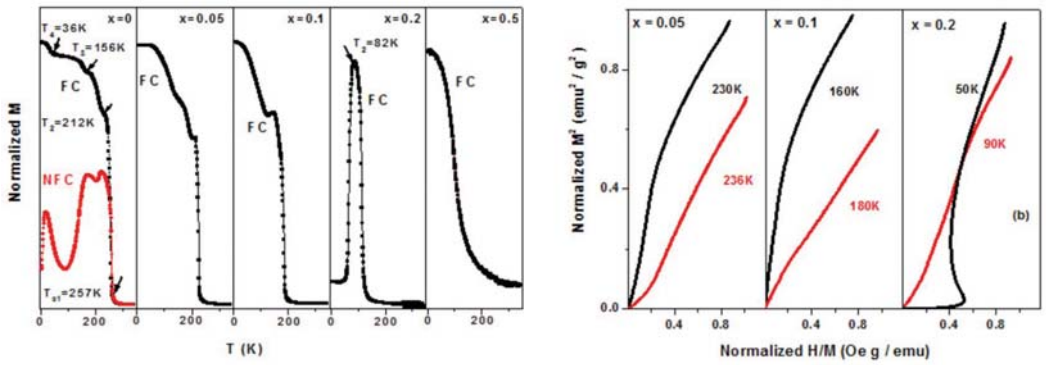

FIG. 2. (Color online) (a) The temperature dependence of the magnetization in a field of 100 Oe for selected samples (x=0, 0.05, 0.1, 0.2, and 0.5) during FC. The zero-field heating (ZFC) curve for Mn_3Sn_2 is also shown. (b) Arrott plots M^2 versus H/M of the $(Mn_{1-x}Ni_x)_3Sn_2$b, x=0.05, 0.1, 0.2 samples around the transition temperature within field range of 0–2T.

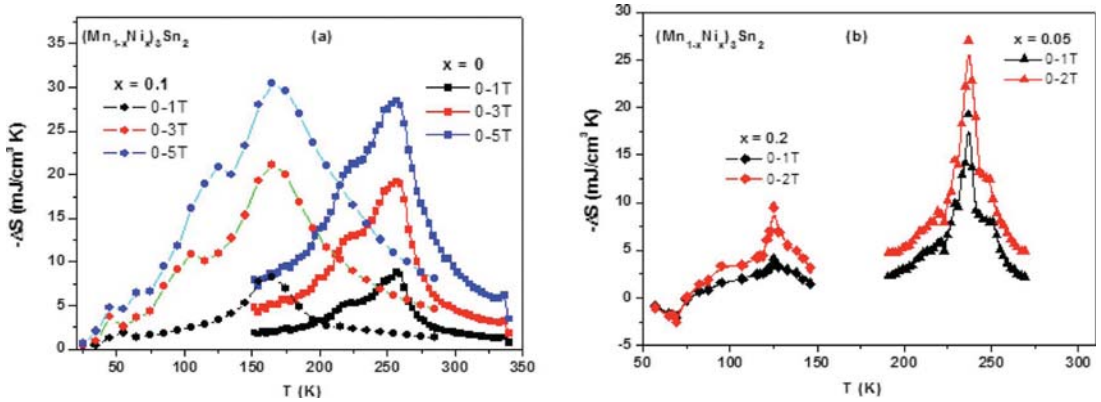

FIG. 3. (Color online) The temperature dependence of the isothermal magnetic entropy change, $-\Delta S_M$, calculated for different magnetic-field changes around the transition temperature range (a) $x=0$ and 0.1 samples in magnetic-field changes (ΔH) up to 5T, (b) $x=0.05$, and 0.2 samples in $\Delta H=1$ T and 2T.

known, on the basis of the FC thermomagnetic curve, as shown in Fig. 2(a), we can identify four transition temperatures $T_{C1}=257$ K, $T_2=212$ K, $T_3=156$ K, and $T_4=36$ K. The absence of thermal hysteresis in the FC and ZFC curves for Mn_3Sn_2 in Fig. 2(a) in the region of T_{C1} suggests that T_{C1} is a SOMT. In order to investigate the Ni substitution effect on magnetic phase transition, we have analyzed the M-H curves of the $(Mn_{1-x}Ni_x)_3Sn_2$ samples using the method of Arrott plots of M^2 versus H/M around the transition temperatures (mainly around T_{c1} and T_2).[9]

Figure 2(b) show the Arrott plots M^2 versus H/M of the $(Mn_{1-x}Ni_x)_3Sn_2$ samples around T_{c1} and T_2 within field range of 2 T for $x=0.05$, $x=0.1$, and $x=0.2$ samples, respectively. It can be seen that the magnetic transition around T_{c1} from PM to FM are all the SOMT, but the transition around T_2 obviously changed to FOMT [the Arrott plot is S-shaped when the temperature lower than 70 K (Ref. 10)] when the substitution content reach $x=0.2$, which confirmed the above analysis of the appearance of weak transverse antiferromagnetic interactions at lower than temperature T_2, and the Ni substitution enhanced the aniferromagntic ordering, such that it reduced the magnetization and changed transition around T_2 from SOMT to FOMT with Ni substitution content increasing. It also explained the appearance of inverse MCEs in $x=0.2$ samples when temperature is lower than 70 K as shown in Fig. 3(b).

The temperature dependence of the isothermal magnetic entropy change, $-\Delta S_M$, calculated for different magnetic-field changes around the transition temperature range are presented in Fig. 3(a) for $x=0$ and 0.1 samples in magnetic-field changes (ΔH) up to 5 T, and (b) for $x=0.05$ and 0.2 samples in $\Delta H=1$ T and 2T. The values of $-\Delta S_M^{\max}$ at 257 K are 8.9, 20.0, and 28.2 mJ/cm^3 K for magnetic-field changes of 0–1, 0–3, and 0–5 T, respectively, for $x=0$ sample. These $-\Delta S_M^{\max}$ values are larger than those reported for Mn_3Sn_2,[5] while the second $-\Delta S_M$ peak located around $T_2 \gg 212$ K is lower than the value reported for Mn_3Sn_2. A third "shoulderlike" feature can also be discerned in the $-\Delta S_M$ versus T curve around $T_2 \gg 156$ K. The values of $-\Delta S_M^{\max}$ at 167 K are 9.2, 21.6, and 31.2 mJ/cm^3 K for ΔH from 0–1, 0–3, and 0–5 T, respectively, for $x=0.1$ sample. It has been observed that the first peak position of $-\Delta S_M^{\max}$ around T_{c1} was in the same position as $M(T)$ curves (at T_{c1}) and has no field dependence for evaluated four samples, and the peak positions around T_2 also have no field dependence for $x=0$ and 0.05 samples, but for the $x=0.1$ and 0.2 samples, it does have strong field dependence, which is normally due to the critical field of the field induced magnetic configuration changes are strong varied with temperature varying.

IV. CONCLUSIONS

In summary, we have investigated the effects of partial replacement of Mn by Ni on the magnetic and MCE properties of $(Mn_{1-x}Ni_x)_3Sn_2$ compounds ($x=0.00$–0.5). It was found that the Ni substitution have significant effects on crystal and magnetic structure, magnetic phase transitions, and magnetiocaloric effect, it decreased the crystal cell volume and the magnetic phase transition temperature, and changed the type of magnetic phase transition from SOMT to FOMT. The maximum value of $\Delta S_M^{\max}$ at magnetic phase transition temperatures was enhanced when the substitution content x is lower than 0.1.

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