



Abnormal e/a -dependence of T_M and large inverse magnetocaloric effect in $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ alloys

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ABSTRACT

The influence of Cu substitution for Ni on magnetic properties and magnetic entropy change has been investigated in the $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ alloys with $x=0, 1$ and 2 . With increasing Cu content from $x=0$ to 2 , a decreasing dependence of the martensitic transformation temperature (T_M) on the number of valence electrons per atom (e/a) is observed, which cannot be explained by the size factor or the number of valence electrons per atom. An inverse magnetocaloric effect was observed in the vicinity of the first order martensitic transition. The maximum value of $-\Delta S_M^{\text{max}}$ in the nominal $\text{Ni}_{48}\text{Cu}_1\text{Mn}_{39}\text{Sb}_{12}$ alloy is $9.38 \text{ J kg}^{-1} \text{ K}^{-1}$ at 291 K for a magnetic field change from 0 to 5 T , with the refrigerant capacity of 25.9 J kg^{-1} . The large ΔS_M indicate that nominal $\text{Ni}_{48}\text{Cu}_1\text{Mn}_{39}\text{Sb}_{12}$ alloy may be a promising candidate for magnetic refrigeration at room temperatures.

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1. Introduction

Increasing attention has been attracted by magnetocaloric cooling technology due to the recent discoveries of magnetocaloric materials near room temperature [1–3]. These materials often exhibit a large magnetocaloric effect (MCE), the temperature and entropy changes that result from a change in applied magnetic field. Commonly, the most noticeable MCE occurs at temperatures near magnetic transitions [4]. Several systems undergoing a first-order transition, such as Gd–Si–Ge [1], Fe–Mn–P–As [2], La–Fe–Si [5], and Ni–Mn–Ga [6,7], have demonstrated large MCE.

Among the materials, Ni–Mn–X ferromagnetic shape memory alloys (FSMAs) with X=Ga, Sn, In and Sb are receiving increasing attention [7–9]. As is well known, FSMAs undergo a first-order structural transition from a parent austenitic phase to a martensitic one on cooling, which may cause an abrupt change of magnetization, and a giant MCE. According to Khan et al. [10], a maximum positive magnetic entropy change of 19 J/kg K for a magnetic field change $\Delta B=0\text{--}5 \text{ T}$ was observed at 297 K in $\text{Ni}_{50}\text{Mn}_{37+x}\text{Sb}_{13-x}$ with $x=1$. Du et al. [11] reported a maximum value of 9.1 J/kg K in $\text{Ni}_{50}\text{Mn}_{50-x}\text{Sb}_x$ with $x=13$ at 287 K for a magnetic field change of $0\text{--}5 \text{ T}$. Ren et al. [12] reported the resistivity increases, while the

Curie temperature decreases, with increasing Cu concentration in $\text{Cu}_x\text{Ni}_{1-x}\text{MnSb}$ alloys.

On the other hand, it was reported that the number of valence electrons per atom (e/a) can influence the martensitic transformation temperature of Ni–Mn–X. Suppose the number of valence electrons for Ni ($3d^8 4s^2$), Mn ($3d^5 4s^2$), X ($4s^2 4p^m$) atoms as 10 , 7 and n , respectively, the calculated e/a is as follows [13,14]:

$$e/a = \frac{10 \times (\text{Ni}_{\text{at.}\%}) + 7 \times (\text{Mn}_{\text{at.}\%}) + n \times (\text{X}_{\text{at.}\%})}{\text{Ni}_{\text{at.}\%} + \text{Mn}_{\text{at.}\%} + \text{Y}_{\text{at.}\%}}$$

The e/a -dependence of T_M was found to increase monotonously in many NiMn-based FSMAs [15]. That is, when the Fermi surface reaches the Brillouin zone boundary, martensitic structural transition occurs due to structural instabilities [16]. Therefore, the change in e/a as well as the Brillouin zone boundary becomes the driving forces for the occurrence of the martensitic structural transformation. Some reported the monotonously increasing e/a -dependence of T_M . However, an opposite/abnormal dependence of T_M on e/a is also observed in $\text{Ni}_{2-x}\text{Cu}_x\text{MnGa}$ [17] and $\text{Ni}_{50}\text{Mn}_{35-x}\text{Cu}_x\text{Sn}_{15}$ alloys [18].

In our previous work, the nominal $\text{Ni}_{49}\text{Mn}_{39}\text{Sb}_{12}$ alloy displays $\Delta S_M=6.15 \text{ J kg}^{-1} \text{ K}^{-1}$ for a magnetic field change of $0\text{--}1 \text{ T}$ at 279 K [19], and large reversible magnetic entropy change of $\Delta S_M=5.21 \text{ J kg}^{-1} \text{ K}^{-1}$ is observed at 347 K [20]. Also, Refs [21,22] reveal that in the Cu-substituted $\text{Ni}_{2.15}\text{Mn}_{0.85}\text{Ga}$ and $\text{Ni}_{43}\text{Mn}_{46}\text{Sn}_{11}$, the higher T_M temperature and large MCE are obtained with increasing Cu content. Therefore, in the present paper, we employed Cu to substitute Ni of $\text{Ni}_{49}\text{Mn}_{39}\text{Sb}_{12}$, aiming to

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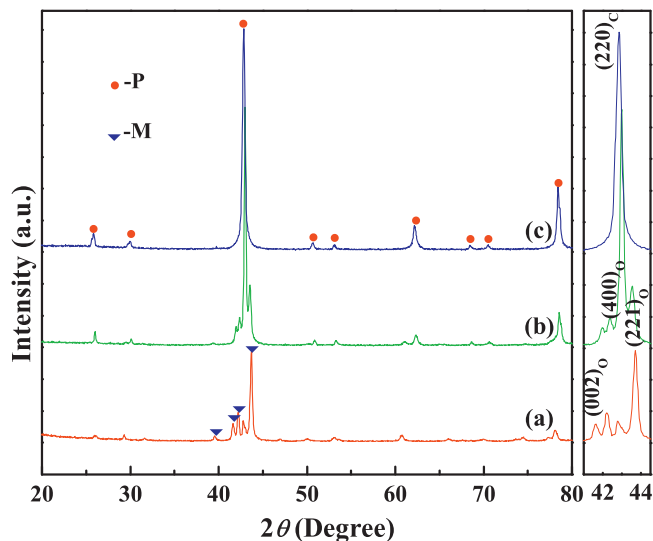


Fig. 1. XRD patterns of the $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ with (a) $x=0$; (b) $x=1$; (c) $x=2$ alloys at room temperature, and the suffices C and O are for cubic and orthorhombic phases, respectively.

improve the ΔS_M values by the means of the e/a dependence of T_M . Large magnetic entropy change of $\Delta S_M = 9.38 \text{ J kg}^{-1} \text{ K}^{-1}$ at 291 K for a magnetic field change of 0–5 T, as well as abnormal dependence of T_M on e/a , in $\text{Ni}_{48}\text{Cu}_1\text{Mn}_{39}\text{Sb}_{12}$ was observed.

2. Experimental

Polycrystalline $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ ($x=0, 1, 2$) alloys were prepared by arc-melting the appropriate amounts of Ni, Cu, Mn, and Sb with purity of 4 N in argon atmosphere. The ingots were sealed in a silica tube and annealed at 1123 K for 50 h, then quenched in water. X-ray diffraction (XRD) was carried out at room temperature with Cu $K\alpha$ radiation in a BD2008 diffractometer. The phase concentration was analysed by using a scanning electron microprobe (SSX550) and energy dispersive X-ray (EDX). The magnetic properties were measured in Lake Shore's 7400 series vibrating sample magnetometer (VSM) in magnetic fields up to 5 T.

3. Results and discussion

Fig. 1 represents the XRD patterns of the $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ alloys with $x=0, 1, 2$ obtained at room temperature. The pattern of $\text{Ni}_{47}\text{Cu}_2\text{Mn}_{39}\text{Sb}_{12}$ displays peaks characteristic of the Heusler $L2_1$ structure (parent phase) at room temperature. However, for $\text{Ni}_{48}\text{Cu}_1\text{Mn}_{39}\text{Sb}_{12}$, some weak peaks of the martensite phase appear besides those for the $L2_1$ structure, while for $\text{Ni}_{49}\text{Mn}_{39}\text{Sb}_{12}$, the XRD peaks for the martensite phase become obvious, also shown as (a) in **Fig. 1**. With increase of Cu substitution for Ni, the martensitic transformation temperatures become lower, and even below room temperature. The EDX microanalysis reveal that the average elemental chemical composition of $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ with $x=0, 1, 2$ is determined as $\text{Ni}_{49.2}\text{Mn}_{39.5}\text{Sb}_{11.3}$, $\text{Ni}_{48.3}\text{Cu}_{1.1}\text{Mn}_{39.4}\text{Sb}_{11.2}$ and $\text{Ni}_{47.2}\text{Cu}_{2.0}\text{Mn}_{39.6}\text{Sb}_{11.2}$, respectively. Sutou et al. [23] suggested that the martensite structure possesses an orthorhombic four-layered structure indicated as 4O(22) in NiMnSb alloy. A martensitic transformation of $L2_1$ structure into an orthorhombic four-layered (4O) structure [23] is present in the Ni–Mn–Sn Heusler system. Recent results of neutron diffraction measurements by Brown et al. suggest that the space group of the 4O structure is $Pm\bar{m}a$ [24]. Therefore, we can index $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ alloys with $x=0$ assuming an orthorhombic 4O structure in the region

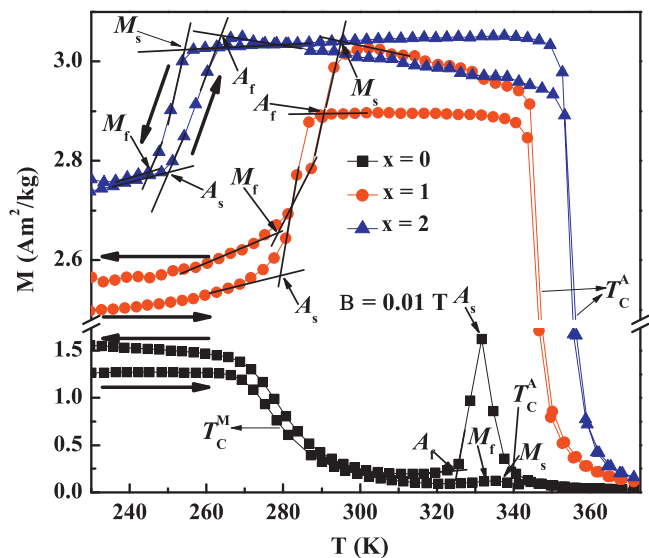


Fig. 2. Magnetization curves as a function of temperature of $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ with $x=0, 1, 2$ alloys on heating and cooling measured in a magnetic field of 0.01 T on heating.

$41^\circ < 2\theta < 44.5^\circ$ (see the right panel of **Fig. 1**). Our previous results reveal that [19,20], XRD pattern of the nominal $\text{Ni}_{49}\text{Mn}_{39}\text{Sb}_{12}$ alloy displays a $L2_1$ -type structure, which is different from our present investigation. However, as mentioned above, the average elemental chemical composition of the present $\text{Ni}_{49}\text{Mn}_{39}\text{Sb}_{12}$ alloy is determined as $\text{Ni}_{49.2}\text{Mn}_{39.5}\text{Sb}_{11.3}$, with less Sb composition than that of previous nominal $\text{Ni}_{49}\text{Mn}_{39}\text{Sb}_{12}$ alloy (or $\text{Ni}_{51.6}\text{Mn}_{36.7}\text{Sb}_{11.7}$). According to Khan et al. [9], less Sb composition in Ni–Mn–Sb alloy means a higher martensitic temperature, which is basically correspondent with our observation.

In the unit cell of the $L2_1$ Heusler alloys structure with a space group of $Fm\bar{3}m$, the austenitic phase is based on a cubic structure with four interpenetrating Fcc lattices Ni, Mn, Ni, Sb. By interchange of atoms the structure easily becomes atomic disorder, which can often influence first-order phase transition [23]. That is, the martensitic transition temperature, T_M , is extremely sensitive to the composition in these alloys [24].

Magnetization as a function of temperature of $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ with $x=0, 1, 2$ alloys on heating and cooling measured in a magnetic field of 0.01 T are plotted in **Fig. 2**. The alloys were initially cooled in the absence of field and data were collected on warming from 220 to some temperature, followed by cooling back to 220 K while recording the data. The characteristic temperatures of structure transition, i.e. A_s , A_f , M_s and M_f , determined from M - T curves, where both the M_f and A_s denote the martensitic transition finishing temperature and reverse martensitic starting transition temperature, respectively. For Cu-free alloy ($x=0$), with the increasing temperature, magnetization remains almost constant until a gradual decreases occurs in the range of 270–300 K. Negligible thermal hysteresis appears. This magnetization transition temperature is defined as the Curie temperature (T_C^M) of martensite phase (about 280 K), which has been reported in many Refs [9,25–27]. With the further increasing temperature, an antiferromagnetic-type transition was observed in both heating and cooling magnetization curves in the range of 320–350 K. According to Khan et al. [9,10], this transition should be ascribed to martensitic transformation, with a transition temperature of T_M (the temperature corresponding to the maximum on the curves of the $dM_{ZFC}/dT-T$), followed by a decrease of magnetization at the Curie temperature of the austenite (T_C^A). It should be noted that temperature hysteresis occurs between heating and cooling pro-

cess at around T_C^A . We conjecture that this temperature hysteresis is associated with the continuous transitions, i.e. structural and para- to ferromagnetic ones, as observed for $\text{Ni}_{50}\text{Mn}_{35}\text{In}_{15}$ alloy in Fig. 2 of Ref. [26]. $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ with $x=1, 2$ both share the similar temperature dependences of magnetization. That is, on heating, a gradual increase of magnetization is first observed in the martensite state. Then, a jump in the magnetization occurs between A_s and A_f . This reverse martensitic transition from a low-temperature martensitic phase to a high-temperature austenitic phase can be seen in Refs. [28–30]. The magnetization in the ferromagnetic austenitic phase remains almost constant, until a transition from ferro- to paramagnetism occurs at T_C^A . On cooling, a martensitic transition from a high-temperature austenitic phase to a low-temperature martensitic phase occurs between M_s and M_f .

As mentioned in Section 1, the characteristic temperatures in Ni–Mn–X are related to e/a . Here, the calculated valence electron includes Ni ($3d^84s^2$), Cu ($3d^{10}4s^1$), Mn ($3d^5, 4s^2$), Sb ($5s^2, 5p^3$). These data listed in Table 1 shows that, with the increasing e/a value, all martensitic/austenitic characteristic temperatures decrease, while T_C^A increase slightly. This relation is opposite to the accepted monotonously increasing e/a -dependence of T_M [31]. The simple rule between e/a and T_M does not fit the present system. In $\text{Ni}_{2-x}\text{Cu}_x\text{MnGa}$ alloys [17], an opposite dependence is also observed. In $\text{Ni}_{43}\text{Mn}_{46-x}\text{Cu}_x\text{Sn}_{11}$ alloys [22], the characteristic temperatures of the alloys increase with increasing values of e/a , while in $\text{Ni}_{50}\text{Mn}_{35-x}\text{Cu}_x\text{Sn}_{15}$ alloys, an first increasing and then decreasing dependence of T_M on e/a is observed [18]. Here, a brief exploration on the mechanism of the dependence of T_M on e/a was proposed. First, the electron configuration of Cu is commonly regarded as $3d^{10}4s^1$ [17,18]. However, due to the filled shell of $3d$, some researcher chose only $4s^1$ electron [32] as the valence electron of Cu. If so, our calculation without the presence of $3d$ electron shell should agree with the accepted rule. Second, some reports indicated [33] that in $\text{Mn}_{48}\text{Co}_x\text{Ni}_{32-x}\text{Ga}_{20}$ alloys, the replacement of Co would break the crystallographic symmetry, which causes an aligned ferromagnetic order. In the $\text{Ni}_{50}\text{Mn}_{35-x}\text{Cu}_x\text{Sn}_{15}$ [18] alloys, due to the Ni atom larger than Cu but smaller than Mn, the addition of Cu may substitute Ni partially and some of the Ni atoms have to occupy Mn positions. As a result, Cu-substitute may indirectly reduce the antiferromagnetism between Mn atoms and therefore, boost the ferromagnetism, which can be observed in the present work. Third, it is assumed that both e/a [34] and size factor [35] can influence the transformation temperatures T_M . Jin et al.'s report [34] indicates that the T_M increases with increasing e/a , i.e., $T_M = 702.5 (e/a) - 5067 \text{ K}$, in NiMnGa alloys. However, the present system shows a contrary finding. In the $\text{Ni}_2\text{MnGa}_x\text{In}_{1-x}$ system [35], the decrease of the unit-cell volumes, i.e. the effect of size factor, results in the increase of T_M when the small Ga atom substitutes for the large In atom. The atomic radius for Ni, Mn, Cu, and Sb is 0.162, 0.179, 0.157 and 0.153 nm, respectively. A similar decrease of the unit-cell volumes can be observed as the smaller Cu atom replaces Ni. Based on the above theory, the Cu-substitute will increase the transformation temperatures. Unfortunately, we obtain contrary results. Therefore, the mechanism of the effect of Cu-substitute on T_M is very complex, which cannot be explained by the size factor or e/a . The Cu-substitute NiMn-based Heusler alloys might exhibit unusual e/a -dependence of T_M , like our observation and $\text{Ni}_{2-x}\text{Cu}_x\text{MnGa}$ [17], $\text{Ni}_{50}\text{Mn}_{35-x}\text{Cu}_x\text{Sn}_{15}$ alloys [18], and $\text{Ni}_{48.7}\text{Mn}_{30.1-x}\text{Fe}_x\text{Ga}_{21.2}$ [36].

Isothermal magnetization curves of $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ with $x=0, 1$, and 2 in a magnetic field up to 5 T are shown in Fig. 3(a–c), respectively. The measurement of $M-H$ was carried out in a series of temperatures arranged in a continuous heating sequence [31]. From Fig. 3(a), a gradual decrease of magnetization was observed

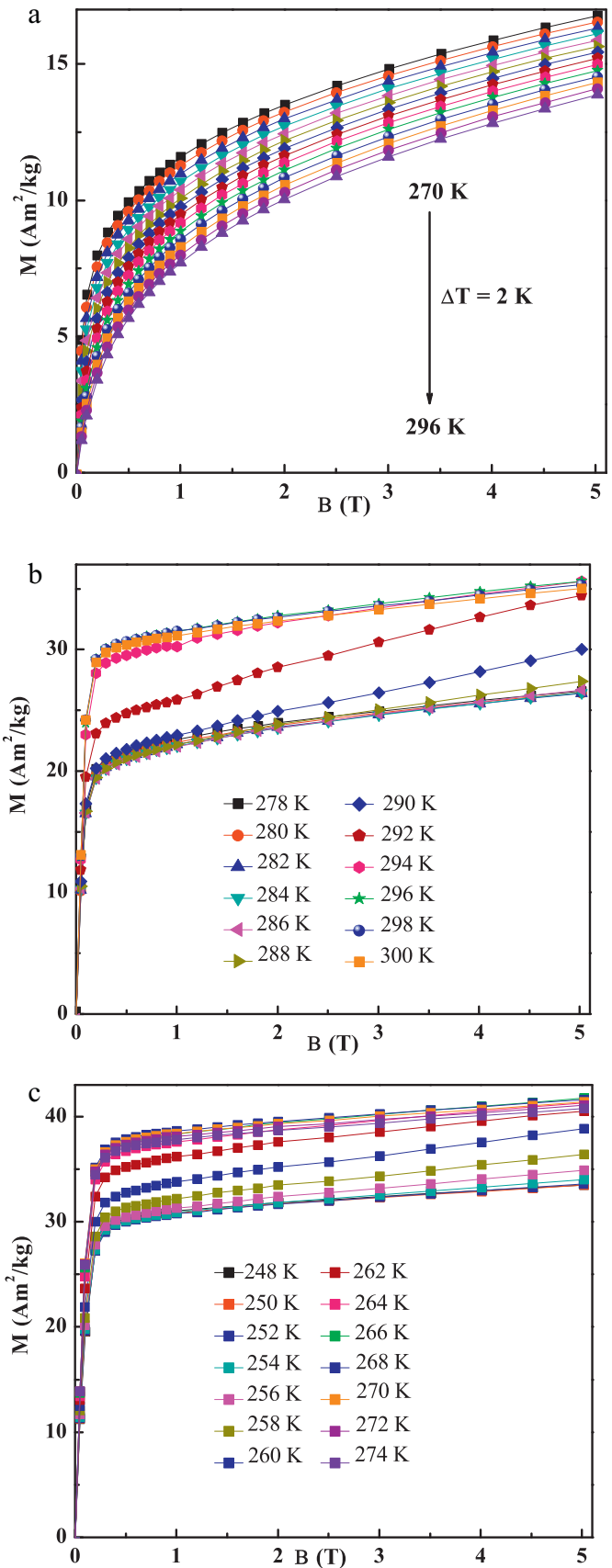


Fig. 3. Isothermal magnetization curves of $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ with (a) $x=0$ from 270 to 296 K; (b) $x=1$ from 278 to 300 K; and (c) $x=2$ from 248 to 274 K in a magnetic field up to 5 T.

Table 1
Starting temperature and finishing temperature, of the structural transition, Curie temperature, electrons per atom (e/a), and maximum magnetic entropy changes ΔS_M , the refrigeration capacity RC, of the $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ alloys with $x = 0, 1, \text{ and } 2$, for magnetic field changes 0–5 T.

x	M_s (K)	M_f (K)	A_s (K)	A_f (K)	T_c^A (K)	e/a	ΔS_M^{\max} (5T) ($\text{J kg}^{-1} \text{K}^{-1}$)	RC (J kg^{-1})
0	340	328	323	330	334	8.23	−0.48	5.65
1	296	248	256	295	347	8.24	9.38 (291 K)	25.9
2	257	244	248	266	356	8.25	5.48 (261 K)	30.1

in the range of 270–296 K, basically correspondent with $x = 0$ shown in Fig. 2, which indicates a second-order transition. For the nominal $\text{Ni}_{48}\text{CuMn}_{39}\text{Sb}_{12}$ and $\text{Ni}_{47}\text{Cu}_2\text{Mn}_{39}\text{Sb}_{12}$ alloys (see Fig. 3(b and c), respectively), the magnetization at temperatures above M_s is higher than that below it, which indicates an inverse MCE. The magnetization increases rapidly within a narrow temperature range. The structural transition from the martensite to the austenite phase at the same temperature, as shown in Fig. 2, should be the origin of this rapid increase of magnetization. This is ascribed to different ferromagnetic exchange interactions in the two phases, leading to a large magnetization difference ΔM between two phases, as observed in various systems [28–30].

Recently, Balli et al. [37] and Caron [38] both reported the over-estimated entropy change in $\text{Mn}_{0.99}\text{Fe}_{0.01}\text{As}$ and $\text{Mn}_{0.99}\text{Cu}_{0.01}\text{As}$, respectively, due to the coexistence of both ferro- and paramagnetic phases at temperatures close to T_c . However, the martensitic and austenite phases of the present Cu-substituted $\text{Ni}_{49}\text{Mn}_{39}\text{Sb}_{12}$ alloys show ferromagnetic ordering but with different exchange correlation, which should be different from the reports of Balli et al. [37] and Caron [38]. Based on the magnetic field dependence of magnetization measurements with continuous heating [31,39], Magnetic entropy changes, ΔS_M , as a function of temperature and magnetic field in the FSMAs was calculated by

$$\Delta S_M(T_{av}, B) = \int_0^B \left(\frac{\partial M}{\partial T} \right)_B dB \approx \frac{1}{\Delta T} \int_0^B [M(T_{i+1}, B) - M(T_i, B)] dB \quad (1)$$

Here, $T_{av} = ((T_{i+1} + T_i)/2)$ denotes the average temperature between T_{i+1} and T_i . ΔT is the temperature difference between two magnetic isotherms involved.

Fig. 4 shows the temperature dependences of ΔS_M , calculated by using Eq. (1) from different M – B curves of $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ alloys (recorded in the field-increasing process) for a $\Delta B = 0$ –5 T. The sign of ΔS_M is positive, indicating an inverse MCE, i.e., the sample cools when a magnetic field is applied adiabatically. Maxima can be observed near T_M . All calculated results are listed in Table 1. For a magnetic field change of $\Delta B = 0$ –5 T, the values of ΔS_M^{\max} are 9.38 (291 K) and 5.48 (261 K) $\text{J kg}^{-1} \text{K}^{-1}$ for $x = 1$ and 2, respectively. This value of $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ with $x = 1$ is lower than that of the nominal $\text{Ni}_{49}\text{Mn}_{39}\text{Sb}_{12}$ alloys (21.9 $\text{J kg}^{-1} \text{K}^{-1}$ at 279 K) from Ref. [19] but with a higher working temperature. This value is remarkably high, comparable to that of $\text{Ni}_{54}\text{Fe}_{19}\text{Ga}_{27}$ [40], $\text{Ni}_{50}\text{Mn}_{12}\text{Sb}_{13}$ [26], and Gd, in which the absolute value $|\Delta S_M|$ for $\Delta B = 0$ –5 T is 4.4 $\text{J kg}^{-1} \text{K}^{-1}$ at 300 K, 9.1 $\text{J kg}^{-1} \text{K}^{-1}$ at 287 K, and 9.8 $\text{J kg}^{-1} \text{K}^{-1}$ at 283 K. Khan et al. [10] have reported a maximum positive magnetic entropy change of 19 $\text{J kg}^{-1} \text{K}^{-1}$ at 297 K for a magnetic field change $\Delta B = 0$ –5 T in $\text{Ni}_{50}\text{Mn}_{37+x}\text{Sb}_{13-x}$ alloys with $x = 1$. Du et al. [11] have reported a maximum value of 9.1 $\text{J kg}^{-1} \text{K}^{-1}$ for $\text{Ni}_{50}\text{Mn}_{50-x}\text{Sb}_x$ with $x = 13$ at 287 K for a magnetic field change $\Delta B = 0$ –5 T. We also have reported a large reversible magnetic entropy change of $\Delta S_M = 5.21 \text{ J kg}^{-1} \text{K}^{-1}$ at 347 K in the nominal

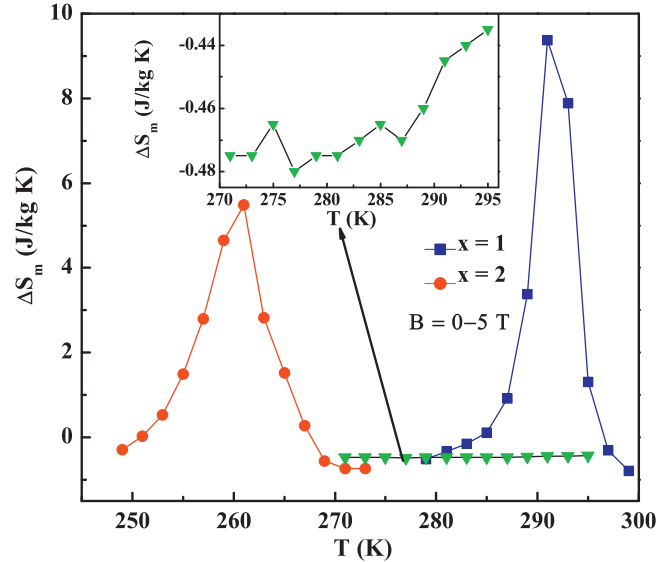


Fig. 4. Temperature dependence of ΔS_M of $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ with $x = 0, 1, 2$ alloys for a magnetic field change $\Delta B = 0$ –5 T. Inset: the same dependence of ΔS_M of $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ with $x = 0$ in a larger scale.

$\text{Ni}_{49}\text{Mn}_{39}\text{Sb}_{12}$ alloy [19]. All the large magnetic entropy change was attributed to the first-order transition from a low-temperature weak-magnetic martensitic phase to a high-temperature ferromagnetic austenitic phase. On the other hand, the refrigeration capacity (RC) of alloys can be calculated by integrating the $\Delta S_M(T)$ curve over the full width at half maximum, which yields a value of about 25.9 and 53.2 J kg^{-1} , for the magnetic field change of 0–5 T, in $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ alloys with $x = 1$ and 2, respectively. Besides, the T_M in $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ can be easily tuned by changing the ratio of Cu substitution for Ni. All these information suggests that this alloy is a promising candidate for application of magnetocaloric materials at room temperature.

4. Conclusions

The magnetocaloric effect related to the first-order martensitic to austenitic transitions in the $\text{Ni}_{49-x}\text{Cu}_x\text{Mn}_{39}\text{Sb}_{12}$ alloys with $x = 0, 1$ and 2 has been studied. With the increasing Cu content, a decreasing dependence of T_M on e/a is observed, which cannot be explained by the size factor or the number of valence electrons per atom. An inverse magnetocaloric effect was observed in the vicinity of the martensitic transition, i.e. from a low-temperature martensitic phase to a high-temperature austenitic one. The maximum value of ΔS_M^{\max} in nominal $\text{Ni}_{48}\text{Cu}_1\text{Mn}_{39}\text{Sb}_{12}$ alloy is 9.38 $\text{J kg}^{-1} \text{K}^{-1}$ at 291 K for $\Delta B = 0$ –5 T, with the refrigerant capacity of 25.9 J kg^{-1} . The large ΔS_M indicate that nominal $\text{Ni}_{48}\text{Cu}_1\text{Mn}_{39}\text{Sb}_{12}$ alloy may be a promising candidate for magnetic refrigeration at room temperatures.

Acknowledgements

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References

- [1] V.K. Pecharsky, K.A. Gschneidner, *Phys. Rev. Lett.* 78 (1997) 4494.
- [2] O. Tegus, E. Brück, K.H.J. Buschow, F.R. de Boer, *Nature (London)* 415 (2002) 150.
- [3] T. Krenke, E. Duman, M. Acet, E.F. Wassermann, X. Moya, L. Mañosa, A. Planes, *Nat. Mater.* 4 (2005) 450.
- [4] M. Tishin, *Handbook of Magnetic Materials*, Elsevier, Amsterdam, 1999.
- [5] F.X. Hu, B.G. Shen, J.R. Sun, Z.H. Cheng, G.H. Rao, X.X. Zhang, *Appl. Phys. Lett.* 78 (2001) 3675.
- [6] M. Pasquale, C.P. Sasso, L.H. Lewis, L. Giudici, T. Lograsso, D. Schlögl, *Phys. Rev. B* 72 (2005) 094435.
- [7] S. Stadler, M. Khan, J. Mitchell, N. Ali, A.M. Gomes, I. Dubenko, A.Y. Takeuchi, A.P. Guimarães, *Appl. Phys. Lett.* 88 (2006) 192511.
- [8] R. Kainuma, Y. Imano, W. Ito, Y. Sutou, H. Morito, S. Okamoto, O. Kitakami, K. Oikawa, A. Fujita, T. Kanomata, K. Ishida, *Nature* 439 (23) (2006) 957.
- [9] M. Khan, I. Dubenko, S. Stadler, N. Ali, *Appl. Phys. Lett.* 91 (2007) 072510.
- [10] M. Khan, N. Ali, S. Stadler, *J. Appl. Phys.* 101 (2007) 053919.
- [11] J. Du, Q. Zheng, W.J. Ren, W.J. Feng, X.G. Liu, Z.D. Zhang, *J. Phys. D: Appl. Phys.* 40 (2007) 5523.
- [12] S.K. Ren, Y.X. Wang, Y.J. Zhang, G.B. Ji, F.M. Zhang, Y.W. Du, *J. Alloys Compd.* 387 (2005) 32.
- [13] Z.D. Han, D.H. Wang, C.L. Zhang, H.C. Xuan, B.X. Gu, Y.W. Du, *Appl. Phys. Lett.* 90 (2007) 042507.
- [14] A.T. Zayak, W.A. Adeagbo, P. Entel, K.M. Rabed, *Appl. Phys. Lett.* 88 (2006) 111903.
- [15] V.A. Chernenko, E. Cesari, V.V. Kokorin, I.N. Vitenko, *Scr. Metall. Mater.* 33 (1995) 1239.
- [16] P.J. Webster, K.R.A. Ziebeck, S.L. Town, M.S. Peak, *Philos. Mag.* B 49 (1984) 295.
- [17] T. Kanomata, T. Nozawa, D. Kikuchi, H. Nishihara, K. Koyama, K. Watanabe, *Int. J. Appl. Electromagn. Mech.* 21 (2005) 151.
- [18] B. Gao, J. Shen, F.X. Hu, J. Wang, J.R. Sun, B.G. Shen, *Appl. Phys. A* 97 (2009) 443.
- [19] W.J. Feng, J. Du, B. Li, W.J. Hu, Z.D. Zhang, X.H. Li, Y.F. Deng, *J. Phys. D: Appl. Phys.* 42 (2009) 125003.
- [20] W.J. Feng, Q. Zhang, L.Q. Zhang, B. Li, J. Du, Y.F. Deng, Z.D. Zhang, *Solid State Commun.* 150 (2010) 949.
- [21] J.F. Duan, Y. Long, B. Bao, H. Zhang, R.C. Ye, Y.Q. Chang, F.R. Wan, G.H. Wu, *J. Appl. Phys.* 103 (2008) 063911.
- [22] D.H. Wang, C.L. Zhang, H.C. Xuan, Z.D. Han, J.R. Zhang, S.L. Tang, B.X. Gu, Y.W. Du, *J. Appl. Phys.* 102 (2007) 013909.
- [23] Y. Sutou, Y. Imano, N. Koeda, T. Omori, R. Kainuma, K. Ishida, K. Oikawa, *Appl. Phys. Lett.* 85 (2004) 4358.
- [24] P.J. Brown, A.P. Gandy, K. Ishida, R. Kainuma, T. Kanomata, K.U. Neumann, K. Oikawa, B. Oulandiaf, K.R.A. Ziebeck, *J. Phys.: Condens. Matter* 18 (2006) 2249.
- [25] T. Krenke, E. Duman, M. Acet, X. Moya, L. Mañosa, A. Planes, *J. Appl. Phys.* 102 (2007) 033903.
- [26] C. Jing, J. Chen, Z. Li, Y. Qiao, B. Kang, S. Cao, J. Zhang, *J. Alloys Compd.* 475 (2009) 1.
- [27] M. Khan, I. Dubenko, S. Stadler, N. Ali, *J. Appl. Phys.* 102 (2007) 113914.
- [28] K. Koyama, K. Watanabe, T. Kanomata, R. Kainuma, K. Oikawa, K. Ishida, *Appl. Phys. Lett.* 88 (2006) 132505.
- [29] T. Krenke, E. Duman, M. Acet, E.F. Wassermann, *Phys. Rev. B* 75 (2007) 104414.
- [30] S. Chatterjee, S. Giri, S. Majumdar, S.K. De, *Phys. Rev. B* 77 (2008) 012404.
- [31] K.A. Gschneidner, V.K. Pecharsky Jr., A.O. Tsokol, *Rep. Prog. Phys.* 68 (2005) 1479.
- [32] E. Obrado, L. Manosa, A. Planes, *Phys. Rev. B* 56 (1997) 20.
- [33] L. Ma, H.W. Zhang, S.Y. Yu, Z.Y. Zhu, J.L. Chen, G.H. Wu, H.Y. Liu, J.P. Qu, Y.X. Li, *Appl. Phys. Lett.* 92 (2008) 032509.
- [34] X. Jin, M. Marioni, D. Bono, S.M. Allen, R.C. O'handley, T.Y. Hsu, *J. Appl. Phys.* 91 (2002) 8222.
- [35] V.V. Kokorin, I.A. Osipeko, T.V. Shirina, *Phys. Met. Metall.* 67 (1989) 173.
- [36] F. Chen, H.B. Wang, Y.F. Zheng, W. Cai, L.C. Zhao, *J. Mater. Sci.* 40 (2005) 219.
- [37] M. Balli, D. Fruchart, D. Gignoux, R. Zach, *Appl. Phys. Lett.* 95 (2009) 072509.
- [38] L. Caron, Z.Q. Ou, T.T. Nguyen, D.T. Cam Thanh, O. Tegus, E. Brück, *J. Magn. Magn. Mater.* 321 (2009) 3559.
- [39] I. Dincer, E. Yüzüak, Y. Elerman, *J. Alloys Compd.* 506 (2010) 508.
- [40] V. Recarte, J.I. Pérez-Landazábal, C. Gómez-Polo, E. Cesari, J. Dutkiewicz, *Appl. Phys. Lett.* 88 (2006) 132503.