Effects of the Mn/Co ratio on the magnetic transition and magnetocaloric properties of $Mn_{1+x}Co_{1-x}Ge$ alloys*

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We have investigated the magnetic transition and magnetocaloric effects of $Mn_{1+x}Co_{1-x}Ge$ alloys by tuning the ratio of Mn/Co. With increasing Mn content, a series of first-order magnetostructural transitions from ferromagnetic to paramagnetic states with large changes of magnetization are observed at room temperature. Further increasing the content of Mn ($x = 0.11$) gives rise to a single second-order magnetic transition. Interestingly, large low-field magnetic entropy changes with almost zero magnetic hysteresis are observed in these alloys. The effects of Mn/Co ratio on magnetic transition and magnetocaloric effects are discussed in this paper.

Keywords: Mn/Co ratio, magnetic transition, magnetocaloric properties, magnetic hysteresis losses

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1. Introduction

Magnetic refrigeration, which is based on the magnetocaloric effect (MCE), has been regarded as a possible alternative to current vapour-cycle refrigeration due to its environmental friendliness and high efficiency.[1−5] In order to achieve large MCE, much attention has been paid to materials with a first-order magnetic phase transition (FOMT).[1−6] However, the reversibility in FOMT materials is far from being guaranteed in the vicinity of the phase transition temperature, where the maximum MCE is obtained.[2,6] It is well known that the efficiency of the magnetic refrigeration cycle depends on not only the size of the MCE but also the reversibility between magnetizing and demagnetizing processes.[6] Therefore, the magnetic material with large MCE and small magnetic hysteresis is greatly desired for magnetic refrigeration.

Stoichiometric MnCoGe alloy undergoes a structural transition from low-temperature orthorhombic TiNiSi-type structure (space group $Pnma$) to high-temperature hexagonal Ni_2In-type structure (space group $P6_3/mmc$) on heating at the structural transition temperature (T_t) $\sim$ 650 K.[6−9] Both structures of the MnCoGe alloy are ferromagnetic while their Curie temperatures (345 K and 275 K, for TiNiSi- and Ni_2In-type, respectively) are all lower than T_t.[7−11] As a result, the structural transition of MnCoGe alloy occurs between two paramagnetic (PM) phases, which is difficult to identify from the thermomagnetic curves owing to the small magnetization change (ΔM) around T_t. It is reported that the magnetic phase transition with large ΔM often accompanies many interesting physical properties, such as MCE,[8,9] magnetoresistance,[12] and magnetic field-induced strain.[13] Therefore, much effort has been devoted to reduce T_t of MnCoGe-based alloys, in which a magnetostructural transition between ferromagnetic (FM) and PM states can be observed.[6,8,9,14−17]

Up to now, most of the methods used to decrease T_t in MnCoGe-based alloys are as follows: (i) doping interstitial atoms,[9] (ii) substituting Mn or Ge with other elements,[6,8] (iii) introducing transition metal-vacancies,[15−17] and (iv) applying hydrostatic pressure.[14] It has been reported that tuning the Ni/Mn ratio is an effective way to adjust the martensitic transition temperature in NiMn-based ferromagnetic shape memory alloys,[18,19] since this structural transition temperature is related to the valence electron concentration e/a.[18−21] Here, the number of valence electrons is calculated as the sum of s, d, and p electrons. With this in mind, the method of changing

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Mn/Co ratio of MnCoGe alloy is proposed in this paper. The experimental results show that T_t decreases with decreasing e/a. As a result, an FM/PM magnetostructural transition with large ΔM is observed in $Mn_{1+x}Co_{1-x}Ge$ alloys, resulting in large low-field MCEs near room temperature (RT). It is worthwhile noting that almost a zero magnetic hysteresis is simultaneously observed in these alloys, which is of great importance to the application in magnetic refrigeration.

2. Experimental

Ingots of polycrystalline $Mn_{1+x}Co_{1-x}Ge$ (x = 0.02, 0.04, 0.055, 0.07, 0.09, and 0.11) alloys were prepared by arc-melting appropriate amounts of starting materials with stoichiometric proportions under a high-purity Ar atmosphere in a water cooled copper crucible and then remelted up to several times to ensure homogeneity. In order to reduce the volatilization of the Mn element, the melting current and melting time were carefully controlled during the preparation of the $Mn_{1+x}Co_{1-x}Ge$ alloys. After that, the as-cast ingots were annealed in vacuated quartz tubes at 850 °C for 120 h and then quenched into cool water. The magnetic measurements were carried out using a vibrating sample magnetometer (VSM, Lakeshore 7407).

3. Results and discussions

The temperature dependence of the magnetization $M(T)$ of $Mn_{1+x}Co_{1-x}Ge$ alloys is measured in a field of 1 kOe (1 Oe = 79.5775 A/m). For clarity, only some typical $M(T)$ curves are shown in Fig. 1. On heating, for the samples with x = 0.02 and 0.055, a series of sharp FM/PM transitions with an abrupt drop of magnetization occur at transition temperatures $\sim$ 338 K and 314 K, respectively. It is worthwhile pointing out that these transition temperatures are around RT, which is important to practical applications. The existence of thermal hysteresis ΔT_{hys} between the cooling and heating processes clearly evidences the first-order nature of these transitions.[6,8,9,16,17] It should be noted that an alloy with x = 0.09 exhibits an incomplete martensitic transformation, evidenced by the existence of ΔT_{hys} ($\sim$ 3 K), as shown in the inset of Fig. 1. In this case, the structural transformation occurs around 274 K, slightly below the Curie temperature of this sample, implying that martensitic transformation would occur between two FM states with an increase in x.[15,17] In the case of x = 0.11, the disappearance of ΔT_{hys} indicates that a reversible second-order FM/PM transition of Ni_2In-type structure occurs.[6] However, the Curie temperature of the samples with x = 0.09 and 0.11 presents a weak Mn/Co ratio dependence, which is consistent with the earlier reports on some other MnCoGe based alloys.[6,17]

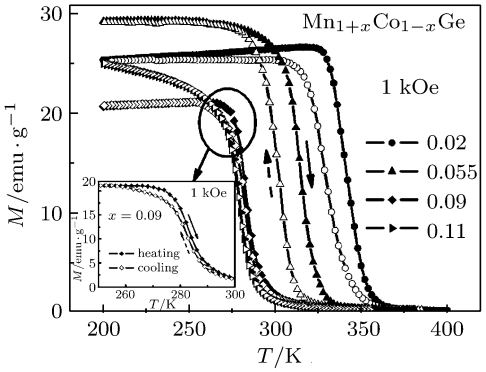


Fig. 1. Temperature dependence of the magnetization for $Mn_{1+x}Co_{1-x}Ge$ (x = 0.02, 0.055, 0.09, and 0.11) alloys on heating (solid symbols) and cooling (open symbols) under a field of 1 kOe. The inset indicates the enlarged view of thermomagnetic properties for the sample with x = 0.09.

Based on the above results, the Mn/Co ratio dependence of T_t for $Mn_{1+x}Co_{1-x}Ge$ alloys is shown in Fig. 2. It can be seen that T_t decreases with increasing content of Mn, implying that the high-temperature Ni_2In-type structure has been stabilized, relative to the low-temperature TiNiSi-type structure, with the substitution of Mn for Co in $Mn_{1+x}Co_{1-x}Ge$ alloys.[6,8,9,11,15,17] In MnCoGe alloy, the main difference between the hexagonal and orthorhombic structures is the closer Mn–Mn distance in the former and much closer Co–Co spacing in the latter case.[11,15,22] Actually, the TiNiSi-type structure can be regarded as an orthorhombic distortion of the Ni_2In-type structure from the crystallographic point of view.[9] The substitution of Mn for Co atoms would modify the Mn–Mn and Co–Co distance due to the different ionic radius between these two elements, which would impact the relative stability between the TiNiSi-type and Ni_2In-type structures in $Mn_{1+x}Co_{1-x}Ge$ alloys and then result in a decrease in T_t.[6,8,9,11,15,17] In addition, the valence electron concentration e/a is proposed for examining the change in T_t with Mn content in $Mn_{1+x}Co_{1-x}Ge$ alloys. As shown in Fig. 2, T_t increases with the increase in e/a, exhibiting an

intimate correlation with valence electrons. This relationship has been reported in NiMn-based ferromagnetic shape memory alloys and some MnCoGe-based ones,[17,18−21] suggesting that the e/a dependence of the structural transition temperature is a universal character for the transition element-based intermetallic alloys.[17,18−21] Therefore, tuning e/a may be considered as a meaningful method to tune the phase transition in MnCoGe-based alloys.

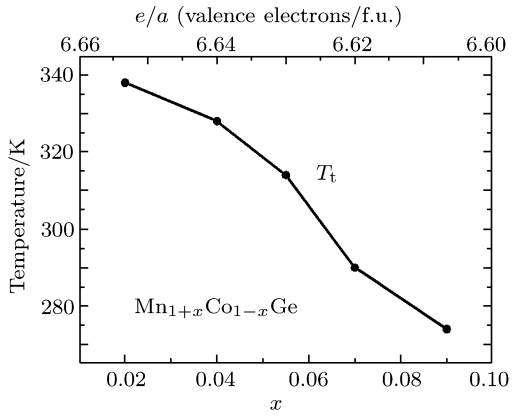


Fig. 2. The Mn/Co ratio and valence-electron concentration (e/a) dependencies of structural transition temperature in $Mn_{1+x}Co_{1-x}Ge$ alloys.

Figure 3 shows the isothermal magnetization curves M (H) for $Mn_{1.02}Co_{0.98}Ge$ alloy for the field up to 12 kOe. Among them, several typical magnetizing and demagnetizing M (H) curves are plotted.

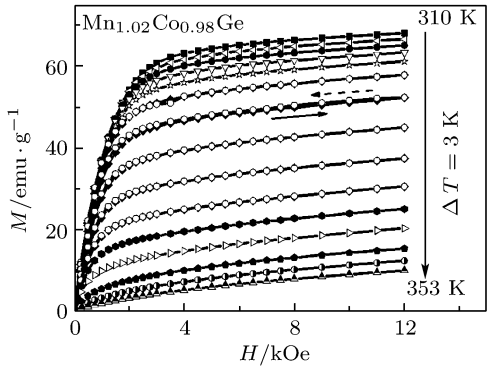


Fig. 3. The isothermal magnetization curves for $Mn_{1.02}Co_{0.98}Ge$ alloy under a field up to 12 kOe. Among them, several typical magnetizing (solid diamonds) and demagnetizing (open circles) curves are plotted.

No obvious metamagnetic behaviour can be observed up to 12 kOe in this alloy, even around magnetostructural transition temperature. It is reported that the magnetic field does not affect the structural phase transition in $Mn_{1.07}Co_{0.92}Ge$ alloy markedly with an applied field of up to 50 kOe.[15] Accordingly, in the case of $Mn_{1.02}Co_{0.98}Ge$ alloy, the magnetic field-induced metamagnetic transition would be suppressed due to the relatively low field. As a result, almost zero magnetic hysteresis is observed between the field-up and field-down processes around the transition temperature of this alloy, which is meaningful for the magnetic refrigeration.

Figure 4 shows the temperature dependence of ΔS_m for $Mn_{1+x}Co_{1-x}Ge$ ($x = 0.02$, 0.055, 0.09, and 0.11) alloys under the field change of 12 kOe. These ΔS_m values are estimated from M (H) curves using the Maxwell relation,

$$\Delta S_m(T,H) = \int_0^H \left(\frac{\partial M(T,H)}{\partial T}\right)_H \mathrm{d}H. \quad (1)$$

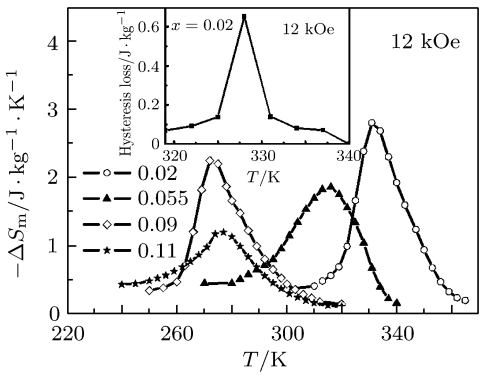


Fig. 4. The temperature dependence of ΔS_m for $Mn_{1+x}Co_{1-x}Ge$ ($x = 0.02$, 0.055, 0.09, and 0.11) alloys under a field change of 12 kOe. The inset shows the hysteresis loss versus temperature curve around the transition temperature for the alloy with $x = 0.02$.

Although it is still controversial to use the Maxwell relation to calculate ΔS_m in FOMT system,[23−25] the result would be credible for the present system since no evident metamagnetic behaviour and magnetic hysteresis are observed in $Mn_{1+x}Co_{1-x}Ge$ alloys.[3] As shown in Fig. 4, large low-field MCEs around RT are observed in the alloys of $x = 0.02$, 0.055, and 0.09, due to the great change in magnetization near T_t. For the alloy of $x = 0.02$, the peak value of ΔS_m reaches up to 2.8 $J \cdot kg^{-1} \cdot K^{-1}$ at $\sim$ 331 K and the field change of 12 kOe. This value is comparable to or even larger than that of some other MnCoGe-based and some NiMn-based alloys, such as, $MnFe_{0.3}Co_{0.7}Ge$ [3 $J \cdot kg^{-1} \cdot K^{-1}$ at $\Delta H = 20$ kOe][10] and $Ni_{50}Mn_{37}Sn_{13}$ [3 $J \cdot kg^{-1} \cdot K^{-1}$ at $\Delta H = 10$ kOe].[26] When $x = 0.11$, the ΔS_m value reduces remarkably due to the second order nature of magnetic transition. In addition, by tuning Mn/Co ratio, large ΔS_m can be obtained in a wide temperature

range around RT, which is beneficial to the magnetic refrigeration.

Another point that deserves attention is the almost negligible hysteresis loss in these alloys, which is advantageous to the improvement of refrigerant efficiency. The inset of Fig. 4 presents the temperature dependence of magnetic hysteresis losses around the transition temperature for the alloy with $x = 0.02$, obtained by calculating the area between the field-increasing and field-decreasing M (H) curves at different temperatures.[27] The refrigerant capacity (RC) and average hysteretic loss of $Mn_{1.02}Co_{0.98}Ge$ alloy are calculated using the method of numerical integration,[27] being 46 $J \cdot kg^{-1}$ and 0.14 $J \cdot kg^{-1}$, respectively. Evidently, the hysteretic loss is very small, only 0.3 percent of the total RC, implying a highly reversible MCE between the magnetizing and demagnetizing processes in this alloy.

4. Conclusions

In conclusion, we have prepared a series of $Mn_{1+x}Co_{1-x}Ge$ alloys and investigated their magnetic and magnetocaloric properties. Various Mn/Co ratios lead to a reduction of T_t, since the substitution of Mn for Co would change the relative stabilities of the orthorhombic and hexagonal phases in $Mn_{1+x}Co_{1-x}Ge$ alloys. Accordingly, sharp FM/PM magnetostructural transition with large ΔM is observed. Large low-field MCE near RT and negligibly small magnetic hysteresis are simultaneously achieved in these alloys, which is very important for the application of magnetic refrigeration. In addition, these alloys are synthesized from low-cost transition metals. All these good properties suggest that $Mn_{1+x}Co_{1-x}Ge$ alloys are attractive candidates for future RT magnetic refrigerants.

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