Magnetic phase transition and magnetocaloric effect in $Mn_{1-x}Zn_xCoGe$ alloys*

Shen Cheng-Juan(沈程娟), Liu Qiang(刘 强), Gong Yuan-Yuan(龚元元), Wang Dun-Hui(王敦辉)†, and Du You-Wei(都有为)

National Laboratory of Solid State Microstructures and Jiangsu Key Laboratory for Nanotechnology, Nanjing University, Nanjing 210093, *China*

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The magnetic phase transition and magnetocaloric effect are studied in a series of $Mn_{1-x}Zn_xCoGe$ ($x = 0.01$, 0.02, 0.04, and 0.08) alloys. By introducing a small quantity of Zn element, the structural transformation temperature of the MnCoGe alloy is greatly reduced and a first-order magnetostructural transition is observed. Further increasing the Zn concentration results in a second-order ferromagnetic transition. Large room-temperature magnetocaloric effects with small magnetic hysteresis are obtained in alloys with $x = 0.01$ and 0.02, which suggests their potential application in magnetic refrigeration.

Keywords: magnetocaloric effect, magnetostructural transition

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1. Introduction

The magnetocaloric effect (MCE), which is an intrinsic property of a magnetic material, has drawn increasing attention owing to its promising application in magnetic refrigeration.[1] Compared with the traditional vapor-cycle refrigerators, the magnetic refrigerator has many potential advantages, such as high efficiency, low noise, and environmental safety.[2,3] Due to these advantages, the MCE has been extensively studied in many systems, especially in magnetic alloys undergoing a magnetostructural transition.[4–8] In the first order magnetic transition (FOMT) system, a large MCE is usually obtained since it has different crystal structures on either side of the magnetic transition and exhibits a large magnetization difference around the transition temperature.[6–8] For example, the Ni–Mn based ferromagnetic shape memory alloys, which experience a magnetostructural transformation between an austenitic phase and a martensitic phase, are reported to possess large magnetic entropy changes (ΔS_m) since they show sudden changes of magnetization in the vicinity of the martensitic transformation.[9–11] Owing to the nature of the FOMT, the magnetostructural transition in these alloys is often accompanied with a large thermal hysteresis, which would reduce the efficiency of magnetic refrigeration.[12] Therefore, magnetic refrigerants with small hysteresis, as well as large low-field MCE, are extremely desirable for practical applications.

Based on recent reports, MnCoGe is regarded as a magnetic alloy with martensitic transformation.[13] It has an orthorhombic TiNiSi-type structure at a low temperature and transfers to a hexagonal Ni_2In-type structure at the structural transition temperature T_t (~ 650 K) with increasing temperature.[14–16] The Curie temperatures T_C for the orthorhombic and the hexagonal structures are 345 K and 275 K, respectively.[17] Since the ferromagnetic transition temperatures of the two phases are lower than T_t by 305 K and 375 K, respectively, the structural transformation of the MnCoGe alloy occurs between two paramagnetic states. Due to the little magnetization difference around the phase transition, it is difficult to drive the magnetostructural transformation in the MnCoGe alloy by an external magnetic field.[14] If T_t can be reduced to the temperature window between T_C's of the aforementioned two phases, then a magnetostructural transformation with an abrupt change of magnetization is likely to be observed between the ferromagnetic TiNiSi-type and the paramagnetic Ni_2In-type structures.[6,7,13] Therefore, many efforts have been devoted to decrease the T_t of the MnCoGe alloy by inducing vacancies,[13,16] substituting Mn with other elements, or doping interstitial atoms.[4,5,18–21] Up to now, the most used substitution elements are 3d transition metals, such as V, Cr, Fe, and Cu.[4,18–20] To our best knowledge, there are few reports about the Zn-substituted MnCoGe alloys. In this paper, we use the transition metal Zn to substitute Mn and prepare a series of $Mn_{1-x}Zn_xCoGe$ ($x = 0.01$, 0.02, 0.04, and 0.08) alloys to investigate their magnetic phase transition and MCE.

2. Experiments and characterizations

Polycrystalline ingots with the nominal compositions of $Mn_{1-x}Zn_xCoGe$ ($x = 0.01$, 0.02, 0.04, and 0.08) were synthesized by the arc-melting method. Before casting, the raw materials of Mn were pre-cleaned in a diluted hydrochloric acid and arc-melted for several times. To reduce the volatilization of the Mn and Zn elements in the $Mn_{1-x}Zn_xCoGe$ alloys, the

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†Corresponding author. E-mail: wangdh@nju.edu.cn

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melting time and the melting current should be carefully controlled. Then, the resulted ingots were annealed in some vacuated quartz tubes at 1073 K for 10 h and quenched in water. The structure of the $Mn_{1-x}Zn_xCoGe$ alloys was identified by X-ray diffraction (XRD) analysis at room temperature with Cu $K\alpha$ radiation. The magnetic measurements were performed using a multifunctional vibrating sample magnetometer (Versalab, Quantum Design).

3. Results and discussion

Figure 1 shows the XRD patterns for the $Mn_{1-x}Zn_xCoGe$ alloys at room temperature. It is known that the stoichiometric MnCoGe alloy undergoes a magnetostructural transition from an orthorhombic TiNiSi-type structure to a hexagonal Ni_2In-type structure at 650 K with increasing temperature. As shown in Fig. 1, both the XRD peaks of the orthorhombic and the hexagonal structures can be observed in the alloys with $x = 0.01$ and 0.02, which indicates the coexistence of the TiNiSi-type and the Ni_2In-type phases. In the cases of $x = 0.04$ and 0.08, only the hexagonal structure can be observed at room temperature, suggesting that T_t can be reduced in the $Mn_{1-x}Zn_xCoGe$ alloys by substituting Zn for Mn. Moreover, with the increase of the Zn content, the peaks of the hexagonal structure slightly shift to the higher angles, demonstrating the decrease of the lattice parameters in the $Mn_{1-x}Zn_xCoGe$ alloys with the substitution of Zn.

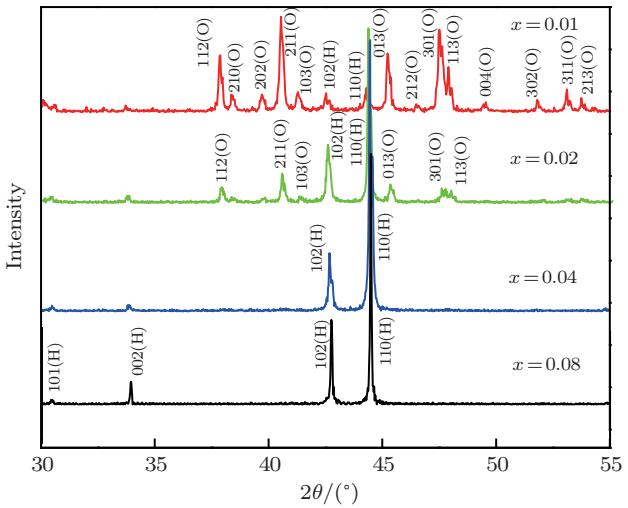


Fig. 1. (color online) The XRD patterns for the $Mn_{1-x}Zn_xCoGe$ alloys at room temperature.

The variation of magnetization as a function of temperature ($M(T)$) for the $Mn_{1-x}Zn_xCoGe$ alloys under an external magnetic field of 1 kOe is shown in Fig. 2. With increasing temperature, the magnetic transitions from a ferromagnetic TiNiSi phase to a paramagnetic Ni_2In phase with a large magnetization difference are observed around 320 K and 300 K for the samples with $x = 0.01$ and 0.02, respectively. It is worth noting that these magnetostructural transformation temperatures are only around room temperature, which is meaningful for practical applications of magnetic refrigeration. As shown in Fig. 2, thermal hystereses of about 12 K and 9 K are clearly observed for the alloys of $x = 0.01$ and 0.02, respectively, indicating that the magnetostructural transformation is of the first-order type.[22] However, for the case of $x = 0.04$, as the temperature increases the sample first undergoes a martensitic transformation from the ferromagnetic TiNiSi phase to the ferromagnetic Ni_2In phase and then experiences a ferromagnetic transition of the Ni_2In phase.[17] The case of $x = 0.08$ also shows a magnetic transition from a ferromagnetic phase to a paramagnetic phase but the thermal hysteresis disappears, which suggests the existence of a reversible second-order magnetic transition (SOMT).[17,20] It is worth noting that the results of the magnetic measurement are consistent with those of the XRD patterns.

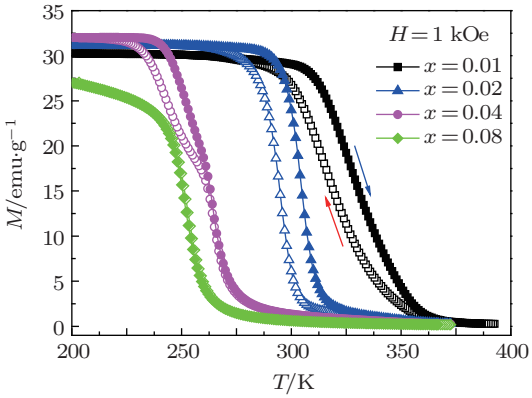


Fig. 2. (color online) The magnetization as a function of temperature for the $Mn_{1-x}Zn_xCoGe$ ($x = 0.01$, 0.02, 0.04, and 0.08) alloys on heating (solid symbols) and cooling (open symbols) with a magnetic field of 1 kOe.

According to the aforementioned experimental results, it is obvious that T_t of the MnCoGe alloy can be effectively reduced by the introduction of Zn atoms. It has been reported that the T_t of the CoMnGe alloy is very sensitive to chemical pressure.[23] For the $Mn_{1-x}Zn_xCoGe$ alloys, the introduction of Zn atoms would produce a chemical pressure since it has a different atomic radius from Mn.[18,20,23] This internal pressure would modify the lattice stability between the TiNiSi-type and the Ni_2In-type structures, giving rise to a reduction of T_t. On the other hand, the magnetic interaction of the MnCoGe alloy is related to the atomic distance between the Mn atoms.[16,17] The lattice distortion caused by the substitution of Zn would change the Mn–Mn atomic distance, resulting in the shift of T_C of the MnCoGe alloy. As shown in Fig. 2, the T_C of the $Mn_{0.92}Zn_{0.08}CoGe$ alloy changes from 275 K to 251 K with the introduction of Zn element.

Figure 3 shows the magnetic field dependences of magnetization ($M(H)$) of $Mn_{0.99}Zn_{0.01}CoGe$ and $Mn_{0.92}Zn_{0.08}CoGe$ alloys with a maximum magnetic field of 10 kOe. A series

of typical ferromagnetic and paramagnetic $M(H)$ curves are observed in these two alloys with the increase of temperature. A magnetic hysteresis is observed in the magnetizing and demagnetizing process for the $Mn_{0.99}Zn_{0.01}CoGe$ alloy, indicating its FOMT nature, which is consistent with the result of the thermomagnetic measurement. It is worth noting that the magnetic hysteresis in the $Mn_{0.99}Zn_{0.01}CoGe$ alloy around the transition temperature is very small. By taking advantage of this feature, the cooling efficiency can be remarkably enhanced in the magnetic refrigeration. As we know, the critical field for inducing the magnetostructural transition of the MnCoGe alloy is high, so there is no obvious metamagnetic behavior observed in the $Mn_{0.99}Zn_{0.01}CoGe$ alloy under the applied magnetic field of 10 kOe,[17] which would be the origin of the small magnetic hysteresis. For the $Mn_{0.92}Zn_{0.08}CoGe$ alloy, the magnetization curve shows no magnetic hysteresis, which is a typical character of SOMT.

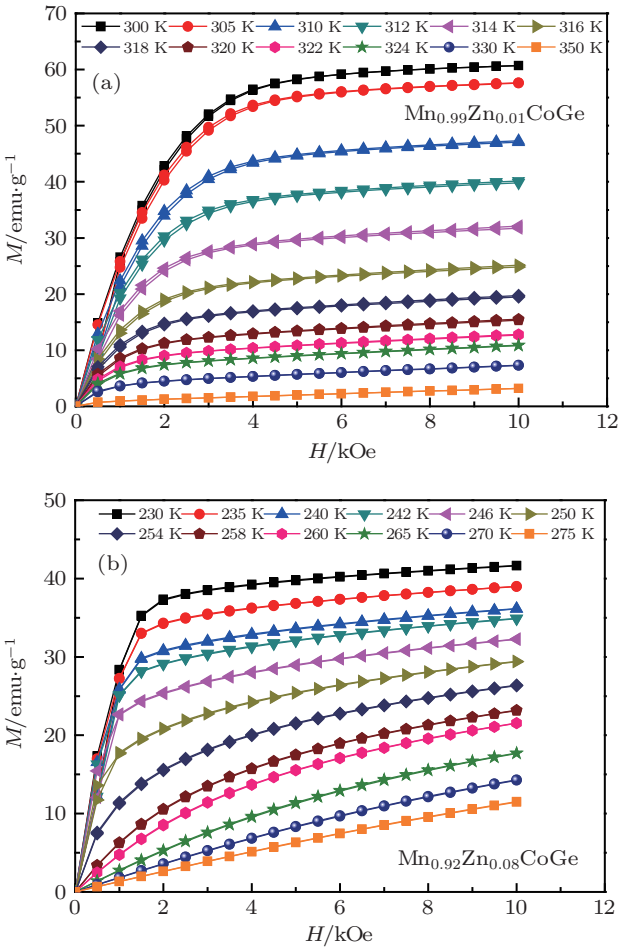


Fig. 3. (color online) The isothermal magnetization curves for (a) $Mn_{0.99}Zn_{0.01}CoGe$ and (b) $Mn_{0.92}Zn_{0.08}CoGe$ alloys with the maximum magnetic field of 10 kOe.

Although $Mn_{0.99}Zn_{0.01}CoGe$ and $Mn_{0.92}Zn_{0.08}CoGe$ alloys undergo FOMT and SOMT, respectively, it is difficult to judge the phase transition order only from the $M(H)$ curves shown in Fig. 3. It is known that the Arrott plot, which is obtained by plotting M^2 as a function of H/M, provides a valid method to distinguish the phase transition order.[24] In order to further investigate the order of the magnetic transition in the $Mn_{1-x}Zn_xCoGe$ alloys, the corresponding Arrott curves for $x = 0.01$ and 0.08 are plotted in Figs. 4(a) and 4(b), respectively. It is reported that a negative slope or an S-shaped curve would be observed in the Arrott curve if the material undergoes FOMT.[10,20,22] As shown in Fig. 4(a), a negative slope is observed in the Arrott plot of the $Mn_{0.99}Zn_{0.01}CoGe$ alloy, indicating the nature of FOMT. In the case of the $Mn_{0.92}Zn_{0.08}CoGe$ alloy, the SOMT can be confirmed by the absence of negative slope or S-shaped curve in the Arrott plot.

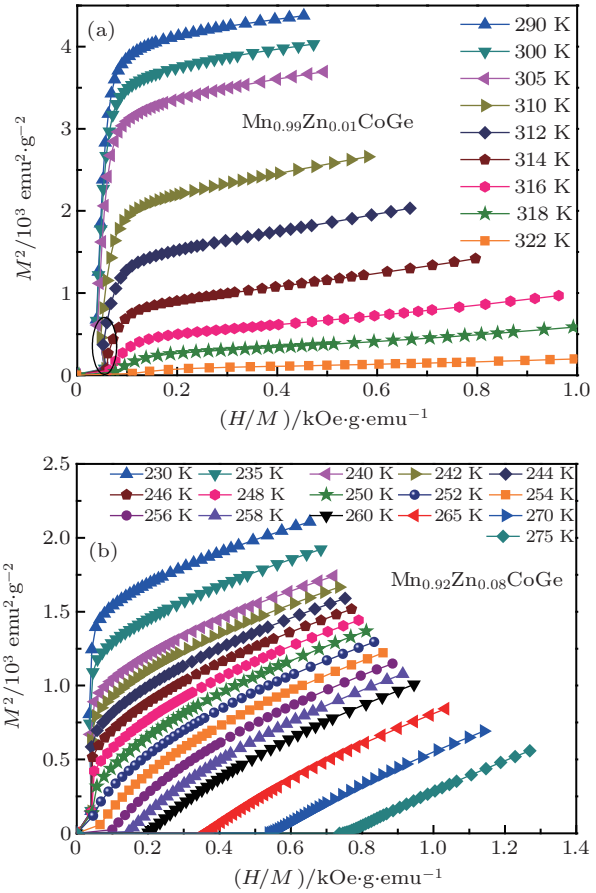


Fig. 4. (color online) Arrott plots for (a) $Mn_{0.99}Zn_{0.01}CoGe$ and (b) $Mn_{0.92}Zn_{0.08}CoGe$ alloys. The ellipse shows the negative slope area in the Arrott curves.

Figure 5 shows the isothermal ΔS_m for the $Mn_{1-x}Zn_xCoGe$ alloys under 10 kOe. These ΔS_m values are calculated by the Maxwell relation

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

Although it is still controversial to use Eq. (1) to calculate ΔS_m in a FOMT system,[25–27] the result is reliable for the $Mn_{1-x}Zn_xCoGe$ alloys because there is a small magnetic hysteresis and no obvious metamagnetic behavior in the $M(H)$ curves, which are clearly shown in Fig. 3. It is obvious that large low-field MCEs are obtained in the alloys with $x = 0.01$,

0.02, and 0.04 since they exhibit abrupt changes of magnetization around the phase transition region. The peak values of ΔS_m reach up to -3.17 J·kg^{-1}·K^{-1}, -3.52 J·kg^{-1}·K^{-1}, and -4.30 J·kg^{-1}·K^{-1} for $x = 0.01$, 0.02, and 0.04, respectively, which are comparable to those of some familiar magnetic alloys with FOMT.[4,5,13,22,28,29] For $x = 0.08$, ΔS_m decreases remarkably since it undergoes a SOMT. It is worth noting that, for the alloys with $x = 0.01$ and 0.02, the magnetic refrigeration temperatures range from 300 K to 315 K, which are the ideal temperatures for room temperature magnetic refrigeration. Therefore, by introducing Zn element into the MnCoGe alloy, a large low-field MCE with a small magnetic hysteresis can be obtained around room temperature in the $Mn_{1-x}Zn_xCoGe$ ($x = 0.01$ and 0.02) alloys.

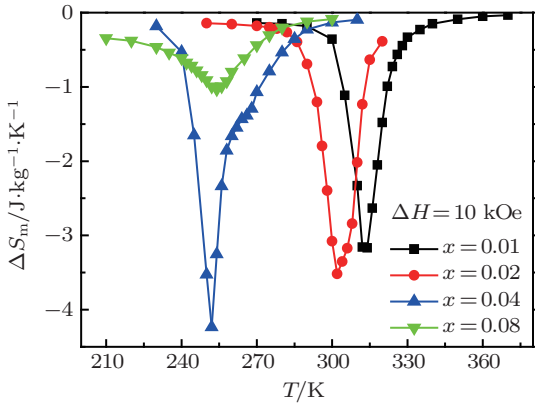


Fig. 5. (color online) The temperature dependence of ΔS_m for the $Mn_{1-x}Zn_xCoGe$ alloys with a field change of 10 kOe.

4. Conclusion

We prepared a series of $Mn_{1-x}Zn_xCoGe$ ($x = 0.01$, 0.02, 0.04, and 0.08) alloys from low-cost transition metals to study their magnetic phase transition and MCE. The substitution of Zn for Mn results in a decrease of T_t of the MnCoGe alloy and various transition behaviors in the $Mn_{1-x}Zn_xCoGe$ alloys. For $Mn_{0.99}Zn_{0.01}CoGe$ and $Mn_{0.98}Zn_{0.02}CoGe$ alloys, large MCEs are observed around room temperature in a low magnetic field of 10 kOe. Furthermore, the magnetic hysteresis of these two alloys are very small, which is desirable for magnetic refrigeration. All of these excellent characteristics indicate that the $Mn_{1-x}Zn_xCoGe$ ($x = 0.01$ and 0.02) alloys have promising applications in room temperature magnetic refrigeration.

References

[1] Pecharsky V K and Gschneidner Jr K A 1999 *J. Magn. Magn. Mater.* **200** 44
[2] Glanz J 1998 *Science* **279** 2045
[3] Gschneidner Jr K A, Pecharsky V K and Tsokol A O 2005 *Rep. Prog. Phys.* **68** 1479
[4] Trung N T, Biharie V, Zhang L, Caron L, Buschow K H J and Brück E 2010 *Appl. Phys. Lett.* **96** 162507
[5] Trung N T, Zhang L, Caron L, Buschow K H J and Brück E 2010 *Appl. Phys. Lett.* **96** 172504
[6] Liu E K, Wang W H, Feng L, Zhu W, Li G J, Chen J L, Zhang H W, Wu G H, Jiang C B, Xu H B and de Boer F 2012 *Nat. Commun.* **3** 873
[7] Liu E K, Zhang H G, Xu G Z, Zhang X M, Ma R S, Wang W H, Chen J L, Zhang H W, Wu G H, Feng L and Zhang X X 2013 *Appl. Phys. Lett.* **102** 122405
[8] Zhang C L, Zhu C, Chen J, Wang T Z and Han Z D 2012 *J. Appl. Phys.* **112** 123911
[9] Wang D H, Han Z D, Xuan H C, Ma S C, Chen S Y, Zhang C L and Du Y W 2013 *Chin. Phys. B* **22** 077506
[10] Chen F H, Gong C W, Guo Y P, Zhang M G and Chai Y S 2014 *Chin. Phys. B* **23** 067501
[11] Krenke T, Duman E, Acet M, Wassermann E F, Moya X, Mañosa L and PlanesA 2005 *Nat. Mater.* **4** 450
[12] Trung N T, Ou Z Q, Gortenmulder T J, Tegus O, Buschow K H J and Brück E 2009 *Appl. Phys. Lett.* **94** 102513
[13] Liu E K, Zhu W, Feng L, Chen J L, Wang W H, Wu G H, Liu H Y, Meng F B, Luo H Z and Li Y X 2010 *Europhys. Lett.* **91** 17003
[14] Koyama K, Sakai M, Kanomata T and Watanabe K 2004 *Jpn. J. Appl. Phys.* **43** 8036
[15] Kanomata T, Ishigaki H, Suzuki T, Yoshida H, Abe S and Kaneko T 1995 *J. Magn. Magn. Mater.* **140** 131
[16] Wang J T, Wang D S, Chen C F, Nashima O, Kanomata T, Mizuseki H and Kawazoe Y 2006 *Appl. Phys. Lett.* **89** 262504
[17] Ma S C, Wang D H, Xuan H C, Shen L J, Cao Q Q and Du Y W 2011 *Chin. Phys. B* **20** 087502
[18] Li G J, Liu E K, Zhang H G, Zhang Y J, Chen J L, Wang W H, Zhang H W, Wu G H and Yu S Y 2013 *J. Magn. Magn. Mater.* **332** 146
[19] SamantaT, DubenkoI, QuetzA, Stadler S and Ali N 2012 *Appl. Phys. Lett.* **101** 242405
[20] Ma S C, Zheng Y X, Xuan H C, Shen L J, Cao Q Q, Wang D H and Du Y W 2012 *J. Magn. Magn. Mater.* **324** 135
[21] Lin S, Tegus O, Brück E, Dagula W, Gortenmulder T J and Buschow K H J 2006 *IEEE. Trans. Magn.* **42** 3776
[22] Zhang C L, Wang D H, Cao Q Q, Ma S C, Xuan H C and Du Y W 2010 *J. Phys. D* **43** 205003
[23] Caron L, Trung N T and Brück E 2011 *Phys. Rev. B* **84** 020414
[24] Arrott A 1957 *Phys. Rev.* **108** 1394
[25] Amaral J S and Amaral V S 2009 *Appl. Phys. Lett.* **94** 042506
[26] Liu G J, Sun J R, Shen J, Gao B, Zhang H W, Hu F X and Shen B G 2007 *Appl. Phys. Lett.* **90** 032507
[27] de Oliveira N A and von Ranke P J 2008 *Phys. Rev. B* **77** 214439
[28] Pecharsky V K and Gschneidner Jr K A 1997 *Phys. Rev. Lett.* **78** 4494
[29] Hu F X, Shen B G, Sun J R, Cheng Z H, Rao G H and Zhang X X 2001 *Appl. Phys. Lett.* **78** 3675