# Tuning Martensitic Phase Transition by Non-Magnetic Atom Vacancy in MnCoGe Alloys and Related Giant Magnetocaloric Effect *

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*The effects of non-magnetic atom vacancy on structural, martensitic phase transitions and the corresponding magnetocaloric effect in $MnCoGe_{1-x}$ alloys are investigated using x-ray diffraction and magnetic measurements. The introduction of non-magnetic atom vacancy leads to the decrease of the martensitic transition temperature and realizes a temperature window where magnetic and martensitic phase transitions can be tuned together. Moreover, the giant magnetocaloric effect accompanied with the coupled magnetic-structural transition is obtained. It is observed that the peak values of magnetic entropy change of $MnCoGe_{0.97}$ are about $-13.9$, $-35.1$ and $-47.4\,J{\cdot}kg^{-1}K^{-1}$ for $\Delta H = 2$, 5, 7 T, respectively.*

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The magnetic refrigeration is considered as one of the most promising technologies due to its high efficiency and environmentally friendly refrigerants. The materials with 'large' or 'giant' magnetocaloric effect (MCE) can be used as refrigerants in magnetic refrigeration systems.[1–4] Therefore, the interest in researching for valuable magnetocaloric materials has been considerably enhanced. It is well known that the giant MCE in magnetocaloric materials is related to the so-called first-order magnetic transition (FOMT) due to the high entropy change appearing near the transition. Some materials, such as $La(FeSi)_{13}$, undergoing the FOMT, can maintain the same crystal structure but different lattice parameters,[5] which is called the first-order 'magnetoelastic' transition (FOMET) conventionally.[6,7] In contrast, crystal symmetry changes when materials such as $Gd_5Si_2Ge_2$[8], MnAs[9] undergo the FOMST. Then the materials, presenting either the FOMET or the FOMST, can be potential candidates as magnetic refrigerants.

MnCoGe alloy is a 3*d* metal-based ferromagnet and undergoes the martensitic transition from the austenite phase with $Ni_2In$-type hexagonal structure to the martensite phase with the TiNiSi-type orthorhombic structure at 420 K.[10] Both the phases are collinear ferromagnet. The theoretical calculation shows that the martensite structure has a larger Mn–Mn distance than the austenite structure, leading to narrower 3*d* bandwidth in the former. This result can explain the facts that the Curie temperature $T_c$ and the saturation magnetic moment $M_s$ in the martensite phase (355 K, $4.13\mu_B$) are higher than those in austenite phase (275 K, $2.76\mu_B$).[11–13] One can find that the magnetic and structural transitions do not take place at the same time for the stoichiometric MnCoGe alloy. However, the FOMST would occur if magnetic and martensitic structural transitions can be tuned together. The theoretical calculations for the MnCoGe alloy reveal that the Co-vacancy can lead to the change of crystal symmetry and modify the coupling distance between Mn atoms in the Co-poor system.[11] For the Mn-vacancy case,[14] the Co atom tends to fill the Mn vacancy, which may make Co vacancy appear again. It is also experimentally proved that Mn vacancy can decrease the martensitic transition temperature ($T_M$), then magnetic and martensitic structural transitions can overlap.[14] However, there is limited discussion and studies on relations between the non-magnetic-atom vacancy and transition, even MCE.

In this Letter, we introduce non-magnetic-atom vacancy (Ge vacancy) in MnCoGe alloys. It is expected that Ge vacancy can affect the valence electron number, local environment of atoms and hence the transition temperature, thereby further investigating giant MCE involving with the concurrent of magnetic and structural transitions.

Samples of $MnCoGe_{1-x}$ ($x$ = 0, 0.01, 0.03, 0.04, 0.045 and 0.05) were prepared by arc melting stoichiometric amounts of the pure elements under argon atmosphere (Mn∼3N, Co∼3N and Ge∼5N). To obtain the homogeneous phase, the polycrystalline ingots were annealed at 1148 K for 144 h and cooled down to the room temperature in the oven naturally. The structure of alloys was determined by powder x-ray diffraction (XRD) measured using a Rigaku XRD D/max 2400 diffractometer with Cu-$K\alpha$ radiation.

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All the magnetic measurements were performed on a superconducting quantum interference device (Quantum Design$^{TM}$, SQUID VSM).

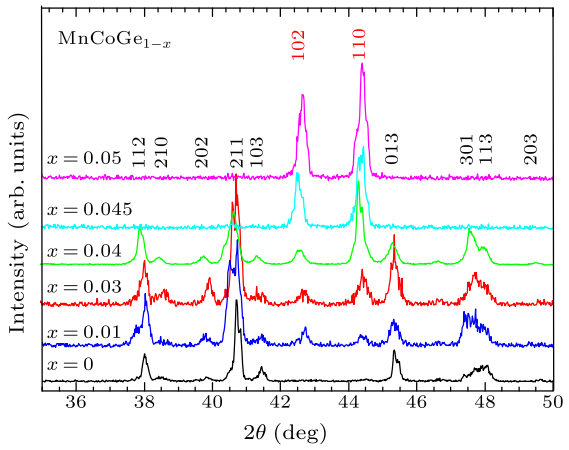


**Fig. 1.** The powder XRD patterns of MnCoGe$_{1-x}$ ($x = 0$, 0.01, 0.03, 0.04, 0.045 and 0.05) measured at room temperature. The miller indices *hkl* denote the $Ni_2In$-type hexagonal (red) and TiNiSi-type orthorhombic (black).

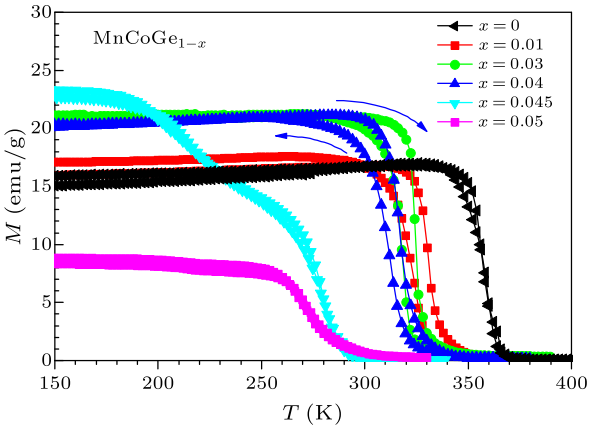


**Fig. 2.** The $M$–$T$ curves measured under the magnetic field of 500 Oe for MnCoGe$_{1-x}$ ($x = 0$, 0.01, 0.03, 0.04, 0.045 and 0.05). The arrows indicate the warming/cooling paths.

Figure 1 shows the powder XRD patterns of MnCoGe$_{1-x}$ ($x = 0$, 0.01, 0.03, 0.04, 0.045 and 0.05) measured at room temperature (~295 K). The stoichiometric MnCoGe can be indexed as the orthorhombic structure, which means that stoichiometric MnCoGe is completely in the martensite phase at room temperature. This result is consistent with the fact that $T_M$ of MnCoGe is 420 K. A small amount of hexagonal structure gradually appears when introducing Ge vacancy. For the sample of $x = 0.01$, one can find the mixture between orthorhombic and hexagonal structures, indicating that the MnCoGe$_{0.99}$ alloy is a two-phase mixture at room temperature. As mentioned above, the austenite phase with the hexagonal structure cannot exist in the stoichiometric MnCoGe due to the fact that room temperature is lower than $T_M$. The co-existence of austenite and martensite phases at room temperature proves that $T_M$ may shift to lower temperature due to Ge vacancy. With introducing more Ge-vacancy, the characteristic peaks of the hexagonal structure become more prominent. The MnCoGe$_{1-x}$ alloys show nearly single hexagonal structure at room temperature when the content of Ge vacancy is adequate ($x = 0.045$ and 0.05), which indicates that the tuned $T_M$ may be lower than room temperature.

We performed the temperature dependence of magnetization measurements for MnCoGe$_{1-x}$ ($x = 0$, 0.01, 0.03, 0.04, 0.045 and 0.05) to investigate the influence of Ge vacancy on magnetic and martensitic structural transitions. The $M$–$T$ curves were measured under a 500 Oe field by zero-field cooling (ZFC) and field cooling (FC) modes (seen in Fig. 2). Here we define that the maximum value of $dM/dT$ of the $M$–$T$ curves is the transition temperature for convenience. For the sample of $x = 0$, it can been seen that the transition temperature is 356 K, which is similar with the Curie temperature ($T_c$) of the martensite phase (355 K) reported before. This transition is the second-order magnetic transition (SOMT) without thermal hysteresis obviously. In other words, stoichiometric MnCoGe presents the transition between paramagnetic (PM) martensite and ferromagnetic (FM) martensite phases at 356 K. For the sample of $x = 0.01$, the transition temperatures are 330 K and 322 K in ZFC and FC modes, respectively. As is known, the SOMT does not show thermal hysteresis behavior which is one of the differences between the FOMT and the SOMT. For the MnCoGe-based alloy, the nature of martensite structure transition is of first order. Thus the thermal hysteresis of about 8 K is the evidence of the FOMT which is the transition between the PM austenite phase and the FM martensite phase. With further introducing Ge vacancy, the transition temperature tends to decrease but maintains the thermal hysteresis behavior for the sample of $x = 0.03$ and 0.04. It is noteworthy that there are two transitions without thermal hysteresis behavior for the sample of $x = 0.045$. The transition temperatures are 220 K and 280 K, respectively. The transition at 280 K is the SOMT between PM and FM austenite phases. The transition at 220 K can hardly be recognized as the FOMT due to the slight thermal hysteresis behavior although $T_M$ probably is tuned to this temperature range by adequate Ge vacancy, which needs further investigation. The sample shows clearly the SOMT between the PM and FM austenite phases at 276 K when $x = 0.05$. It is noteworthy that there is a difference of the Curie temperature between MnCoGe$_{0.955}$ and MnCoGe$_{0.95}$. For the MnCoGe system, the Co atom is strongly related to electronic states at the Fermi level, which is in-

fluenced by ferromagnetic exchange according to the spin-fluctuation theory.[14,15] The Ge-vacancy introducing does not have impact on the Co content but may have influence on distance of Co atoms, causing the variation of ferromagnetic exchange and the Curie temperature. Therefore, the difference of hexagonal lattice constant between $MnCoGe_{0.955}$ ($a = 4.0842$ Å) and $MnCoGe_{0.95}$ ($a = 4.0807$ Å) may be responsible for the different Curie temperatures of the two samples. From the above discussion, it comes to the conclusion that $T_M$ can be manipulated by controlling the Ge-vacancy amount.

The mechanism of tuning $T_M$ is related to some factors. In this case, it can be found that the variation of $T_M$ with Ge-vacancy content and valence-electron concentration $e/a$ ratio. Apparently, the $e/a$ ratio decreases monotonically with increasing the amount of Ge vacancy. Thus in the Ge-vacancy case, we suggest that the valence-electron concentration ($e/a$ ratio) may be responsible for the decrease of $T_M$. Furthermore, the effects on the structure due to appearance of Ge vacancy should be considered. It is necessary to mention that in the crystal structure of MnCoGe, the Co and Ge atoms form covalent bonding, which originates from orbital hybridization and plays an important role in maintaining crystal stabilization.[14,15] The Ge vacancy appears in the Co–Ge atom chain, which can lead to weakening of the austenite phase and hence lower $T_M$. Therefore, the magnetic and martensite structural transitions can be tuned together in the system with proper Ge-vacancy content due to the fact that $T_M$ is sensitive to the amount of Ge vacancy while the Curie temperature is not. It is found that the 'temperature window' of about 76 K is defined as the area between the Curie temperatures of martensite and austenite phases[16–18] (280–356 K in this Ge-vacancy case). This means that the expected FOMST which is necessary to the large MCE could happen in this temperature area.

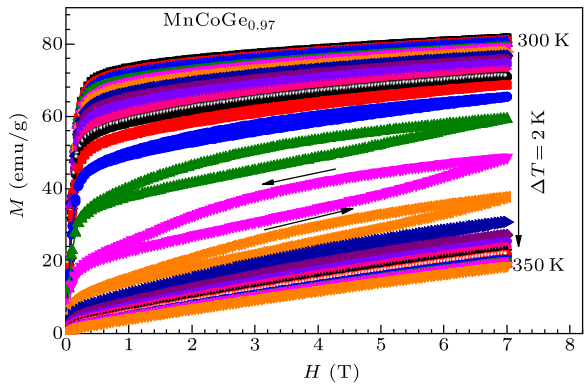


**Fig. 3.** Isothermal magnetization of $MnCoGe_{0.97}$ at representative temperatures. The arrows indicate the paths of field change.

To investigate the MCE from the FOMST of the Ge-vacancy system, the isothermal $M$–$H$ curve of $MnCoGe_{0.97}$ ($T_M \sim 324$ K) is measured around the temperature range of $T_M$ in the field up to 7 T (seen Fig. 3). We can observe obvious magnetic hysteresis behavior near $T_M$. The maximum magnetic hysteresis appears at 328 K, which is 4 K larger than the temperature where the maximum thermal hysteresis appears. Actually, the thermal and magnetic hysteresis sometimes may not happen synchronously for MnCoGe-based alloys. The $Mn_{0.98}V_{0.02}CoGe$,[17] for example, shows no magnetic hysteresis even the magnetic field reaches 12 T but obvious thermal hysteresis is near 298 K. However, the thermal hysteresis behavior can always be observed as long as magnetic hysteresis exists. The hysteresis, either thermal or magnetic ones, is the reflections of the FOMT. Based on the above facts, the temperature seems to drive the transition more easily. Generally speaking, the different external perturbations, such as temperature, magnetic field, electric field, even pressure, triggering transition implicate the different nuclear mechanisms. In this case, it cannot figure out, temperature or magnetic field, which one is more capable to drive transition due to the fact that thermal and magnetic hysteresis may happen synchronously.

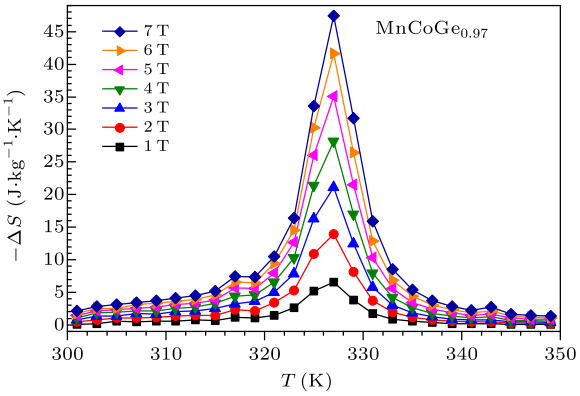


**Fig. 4.** Magnetic entropy change $\Delta S_M$ as a function of temperature in the field up to 7 T for $MnCoGe_{0.97}$.

The MCE can be characterized by isothermal magnetic entropy change $\Delta S_M$ which is calculated by the Maxwell relation ($\Delta S = \int_{H_2}^{H_1} \left(\frac{\partial M}{\partial T}\right) dH$). For the sample of $x = 0.03$, $\Delta S_M$ as a function of temperature in the field up to 7 T is shown in Fig. 4. As seen in Fig. 4, the giant MCE can be observed near room temperature owing to the transition between the PM austenite phase and the FM martensite phase, namely the FOMST. The peak values of $\Delta S_M$ are about $-13.9\,\mathrm{J{\cdot}kg^{-1}K^{-1}}$ for 0–2 T, $-35.1\,\mathrm{J{\cdot}kg^{-1}K^{-1}}$ for 0–5 T and $-47.4\,\mathrm{J{\cdot}kg^{-1}K^{-1}}$ for 0–7 T, respectively. This altitude of MCE is comparable with other MnCoGe-based alloys, even other magnetic refrigerants, such as $Mn_{0.965}CoGe$ ($26\,\mathrm{J{\cdot}kg^{-1}K^{-1}}$ for 0–5 T),[14] $MnCoGe_{0.95}Ga_{0.05}$ ($27.1\,\mathrm{J{\cdot}kg^{-1}K^{-1}}$ for

0–5 T),[19] $Gd_5Si_2Ge_2$ ($14\,J{\cdot}kg^{-1}K^{-1}$ for 0–2 T),[8] $Ni_{50}Mn_{33.13}In_{13.90}$ ($28.6\,J{\cdot}kg^{-1}K^{-1}$ for 0–5 T),[20] $Mn_{0.96}Zn_{0.04}CoGe$ ($4.3\,J{\cdot}kg^{-1}K^{-1}$ for 0–1 T).[21]

In summary, we have investigated the effect of nonmagnetic atom vacancy (Ge vacancy) on the martensitic transition temperature and the Curie temperature for $MnCoGe_{1-x}$ alloy and resulting magnetocaloric effect. With the introduction of the Ge vacancy, the martensitic transition temperature decreases due to the decrease of the $e/a$ ratio and the vacancy appearing in the Co–Ge bonding, while the Curie temperature almost keeps unchanged. Therefore, the overlapping between martensitic and magnetic transitions can be found. The transition between the PM austenite phase and the FM martensite phase can be realized for $MnCoGe_{1-x}$ ($x = 0.01$, 0.03 and 0.04). Accordingly, the giant MCE about −13.9, −35.1 and $-47.4\,J{\cdot}kg^{-1}K^{-1}$ for 2, 5 and 7 T, respectively, is obtained for the sample of $x = 0.03$. Further introducing Ge vacancy can result in the vanishing of the FOMST.

## References


[1] Franco V, Blázquez J S, Ingale B and Conde A 2012 *Annu. Rev. Mater. Res.* **42** 305
[2] Pecharsky V K, Gschneidner Jr K A, Mudryk Y and Paudyal D 2009 *J. Magn. Magn. Mater.* **321** 3541
[3] Pecharsky V K and Gschneidner Jr K A 1997 *Appl. Phys. Lett.* **70** 3299
[4] Brown G V 1976 *J. Appl. Phys.* **47** 3673
[5] 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
[6] Caron L, Trung N T and Bruck E 2011 *Phys. Rev.* B **84** 020414
[7] Trung N T, Zhang L, Caron L, Buschow K H J and Bruck E 2010 *Appl. Phys. Lett.* **96** 172504
[8] Pecharsky V K and Gschneidner Jr K A 1997 *Phys. Rev. Lett.* **78** 4494
[9] Wada H, Matsuo S and Mitsuda A 2009 *Phys. Rev.* B **79** 092407
[10] Niziol S, Weselucha A, Bazela W and Szytula A 1981 *Solid State Commun.* **39** 1081
[11] Wang J T, Wang D S, Chen C F, Nashima O, Kanomata T, Mizuseki H and Kawazoe Y 2006 *Appl. Phys. Lett.* **89** 262504
[12] Lin S, Tegus O, Bruck E, Dagula W, Gortenmulder T J and Buschow K H J 2006 *IEEE Trans. Magn.* **42** 3776
[13] Hamer J B A, Daou R, Ozcan S, Mathur N D, Fray D J and Sandeman K G 2009 *J. Magn. Magn. Mater.* **321** 3535
[14] 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
[15] Mohn P and Wohlfarth E P 1987 *J. Phys. F: Met. Phys.* **17** 2421
[16] 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 Frank de B 2012 *Nat. Commun.* **3** 873
[17] Ma S C, Zheng Y X, Xuan H C, Shen L J, Cao Q Q, Wang D H, Zhong Z C and Du Y W 2012 *J. Magn. Magn. Mater.* **324** 135
[18] Meng G H, Tegus O, Zhang W G, Song L and Huang J H 2010 *J. Appl. Phys.* **497** 14
[19] Yüzüak E, Durak G, Dincer I and Elerman Y 2012 *J. Alloys Compd.* **541** 256
[20] Zhang X X, Zhang B, Yu S Y, Liu Z H, Xu W J, Liu G D, Chen J L, Cao Z X and Wu G H 2007 *Phys. Rev.* B **76** 132403
[21] Shen C J, Liu Q, Gong Y Y, Wang D H and Du Y W 2014 *Chin. Phys.* B **23** 097502