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Evolution of magnetostructural transition and magnetocaloric effect with AI doping in $MnCoGe_{1-x}AI_x$ compounds

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Abstract

The effect of Al doping in MnCoGe_{1-x}Al_x compounds has been investigated. The substitution of Al for Ge enhances Mn–Mn covalent bonding by shortening the distance of nearest Mn atom layers, and thus stabilizes the hexagonal structure. As a result, first-order magnetostructural transition between ferromagnetic martensite and paramagnetic austenite takes place for the optimized compositions (x = 0.01, 0.02). Accompanied with the magnetostructural transition, large magnetocaloric effect (MCE) is observed. More doping of Al(x = 0.03, 0.04) leads to the separation of magnetic and structural transitions and remarkable reduction of MCE.

Keywords: magnetocaloric effect, magnetostructural transition, $MnCoGe_{1-x}Al_x$ compounds

(Some figures may appear in colour only in the online journal)

1. Introduction

An increasing attention has been attracted to magnetic refrigeration technology based on magnetocaloric effect (MCE) because of its high efficiency and environmental friendliness. In the past years, many experimental and theoretical studies have been conducted to investigate the refrigerants undergoing first-order magnetostructural or magnetoelastic transition [1-10]. Here, 'magnetostructural' phase transition refers to the system where crystal symmetry changes along with magnetic transitions, while 'magnetoelastic' phase transition refers to the one where only lattice parameters and volume changes [10]. These transitions are accompanied by an abrupt change in crystal lattice, resulting in large MCE. Some materials, such as $Gd_5Si_{4-x}Ge_x$ [1], MnFeP_{1-x}As_x [2], LaFe_{13-x}Si_x-based alloys [3, 4], MnAs [5], and NiMn-based Heusler alloys and ribbons [6–9] has been discovered to exhibit large or giant MCE.

MnCoGe alloy, as a member of MnMX family, has attracted particular interest since the first report of

field-induced martensitic transformation in Mn_{1.07}Co_{0.92}Ge [11]. The stoichiometric MnCoGe alloy undergoes martensitic structural transition from Ni₂In-type hexagonal structure (space group P6₃/mmc) to TiNiSi-type orthorhombic structure (space group Pnma) at the structural transition temperature $T_{\rm stru} \sim 420 \,{\rm K}$ [12]. It is noteworthy that the distance between the dominant magnetic Mn atoms in the orthorhombic martensitic structure is longer than that in the hexagonal austenitic structure, which leads to a narrower 3d bandwidth and a larger exchange splitting between majority and minority bands in orthorhombic structure [13]. Therefore, the Curie temperature T_c and the saturation magnetic moment M_s in the orthorhombic structure ($T_c^M = 355$ K and $M_s = 4.13 \mu_B$) are higher than those in the hexagonal structure ($T_c^A = 275 \text{ K}$ and $M_{\rm s} = 2.76\mu_{\rm B}$) [13, 14]. Due to the big difference between the $T_{\rm c}$ and $T_{\rm stru}$, the magnetic and structural transition cannot overlap in the stoichiometric MnCoGe. In 2004, Koyama and his colleagues found that the $T_{\rm stru}$ can be tuned to 210 K in Mn_{1.07}Co_{0.92}Ge system [11], and the following ab initio calculation revealed that the Co vacancies can induce the transition from hexagonal to orthorhombic

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structure because of the change of the structural symmetry and modification of the coupling distance between Mn-Mn atoms [13]. This theoretical result agrees fairly well with the experimental one of $MnCo_{1-x}Ge$ and provides a credible understanding of microscopic mechanism for structural transition and corresponding magnetic moment alterations. Subsequently, studies on Mn-vacancy MnCoGe systems showed that Co atoms can fill in Mn vacancies, resulting in the appearance of Co vacancies again. Thus, the $T_{\rm stru}$ also can be tuned to lower temperature, and a martensitic transition temperature window as wide as about 100 K was observed [15]. The so-called 'transition temperature window' usually refers to the temperature span from T_c^A to T_c^M where the coupling of magnetic and structural transition takes place [15]. Here, the T_c^A and T_c^M represent the intrinsic Curie temperature of hexagonal austenite and orthorhombic martensite, respectively. Moreover, large MCE (ΔS_m = $26 \,\mathrm{J\,kg^{-1}\,K^{-1}}$ (289 K) for $\Delta B = 5 \,\mathrm{T}$) stemming from the PM/FM-type martensitic transition with hysteresis was obtained in Mn_{1-x} CoGe alloys (x = 0.035) [16]. Apart from Mn- or Co-vacancy employed to decrease $T_{\rm stru}$, introducing interstitial atoms [16] or physical hydrostatic pressure [10] in MnCoGe system can also effectively tune Tstru, even leading to a magnetostructural coupling and a giant MCE. In addition, the alloying method or atom substitution can also tune T_{stru} , even in MnNiGe systems [17, 18]. However, there is limited discussion in the literature on the correlation between magnetostructural transition and detailed structure information.

This work aims to investigate the substitution of main-group element Al for Ge in MnCoGe_{1-x}Al_x system where earlier studies have shown that the magnetic moments are only related with Mn and Co atoms [19]. Replacing Ge by Al atoms with different radius and valence electron number can be expected to affect local environment, Mn–Mn distance, and hence exchange interaction and transition temperatures. We experimentally found that the Al substitution can shorten Mn–Mn distance of hexagonal phase, thereby strengthening the covalent bonding and stabilizing the hexagonal phase. As a result, T_{stru} decreases and overlaps with T_c^M , and a transition temperature window as wide as 80 K was observed. The concurrent magnetic and structural transitions lead to a large MCE.

2. Experiments

MnCoGe_{1-x}Al_x alloys with x = 0.01, 0.02, 0.03 and 0.04 were prepared by arc-melting constituent metals with purity better than 99.9 wt% under argon atmosphere. The ingots were annealed at 875 °C for 6 days and then cooled to room temperature in oven naturally. The room-temperature powder x-ray diffraction (XRD) was measured by Rigaku XRD D/max 2400 diffractometer with Cu-K α radiation. The XRD measurements at different temperatures were performed on Buker non-ambient D8 advance diffractometer with Cu-K α radiation. Rietveld refinement was carried out to calculate lattice parameters, phase fraction, and Mn–Mn distance. Magnetic measurements were performed



Figure 1. (*a*) The powder XRD patterns of the MnCoGe_{1-x}Al_x (x = 0.01, 0.02, 0.03, and 0.04) measured at room temperature ($\sim 300 \text{ K}$), (*b*) the XRD patterns of MnCoGe_{1-x}Al_x (x = 0.01) measured at 300, 325, 400, and 425 K. The Miller indices *hkl* denotes the Ni₂In-type hexagonal (red) and TiNiSi-type orthorhombic (black) structures, (*c*) typically, a refining pattern including experimental and calculated results, and their difference is presented for sample x = 0.03.

using a superconducting quantum interference device (MPMS SQUID VSM, Quantum Design TM, USA). During magnetic measurements, we chose needle-like samples with slenderness ratio better than 4:1 (corresponding demagnetization factor smaller than 0.08) to minimize demagnetization effect. Similar mass, around \sim 3 mg, was chosen for all samples to eliminate possible extrinsic factors that may affect hysteresis behaviours. The field step in field-dependent magnetization measurements (*M*–*H* curves) is 500 Oe for all samples.

3. Results and discussion

To identify structure, we performed XRD measurements at room temperature (~293 K) for MnCoGe_{1-x}Al_x (x = 0.01, 0.02, 0.03 and 0.04), as seen in figure 1(*a*). The pattern of x = 0.01 can be indexed as TiNiSi-type orthorhombic structure, mixed with a small amount of hexagonal phase (2.4 ± 0.2 wt%). For the sample x = 0.02, the ratio of hexagonal phase increases and a mixed ratio of orthorhombic (86.0 ± 0.2 wt%) and hexagonal (14.0 ± 0.11 wt%) phase was found. The other two samples (x = 0.03 and 0.04) are almost single hexagonal phase with Ni₂In-type structure (x = 0.03: 97.4 ± 0.03 wt%, x = 0.04: 97.3 ± 0.02 wt%), indicating



Figure 2. The M-T curves measured under a magnetic field of 500 Oe for MnCoGe_{1-x}Al_x (x = 0.01, 0.02, 0.03, and 0.04). The solid and open symbols correspond to zero-field cooling (ZFC) and field cooling (FC) modes, respectively. Arrows indicate the cooling/warming paths. Inset is the dM/dT plot on heating (ZFC mode) for sample x = 0.01.

the $T_{\rm stru}$ of these two samples are below room temperature. A typical refining pattern including the experimental data, the calculated one, and their difference is presented in figure 1(c). These results illustrate that the fraction of hexagonal austenite increases as the Al-doping level increases at room temperature. In other words, the substitution of Al for Ge tends to maintain Ni₂In-type austenite and lower the $T_{\rm stru}$. To get more details, we carried out Rietveld refinements to examine the change of atomic distance with altering Al content. Our refinements on hexagonal structure reveal that the distance of Mn-Mn atoms changes from 2.6706 (± 0.0062) to 2.6520 (± 0.0003)Å for x = 0.02 to 0.04, consistent with the shortage of c axis from $5.3412 (\pm 0.0062)$ to $5.3041 (\pm 0.0003)$ Å. This fact evidences that the covalent bonding between the nearest Mn-Mn atoms is strengthened upon the substitution of Al for Ge. As a result, the hexagonal phase is stabilized and $T_{\rm stru}$ shifts to a lower temperature.

In order to determine transition temperature and the nature of transition, temperature dependent magnetization (M-T)curve) was measured under a low field of 500 Oe using zero-field cooling (ZFC) and field cooling (FC) modes [20] (see figure 2). For the sample of x = 0.01, a sharp magnetic transition between ferromagnetic (FM) and paramagnetic (PM) phase was observed, and the FM ordering temperature, $T_{\rm c}$, locates at ~352 K. Here, the transition temperature is defined as the one at which the largest slope occurs on heating (ZFC mode), and the T_c here represents general meaning of Curie temperature, i.e. the transition temperature between FM and PM phases. As a typical display, dM/dT plot on heating (ZFC mode) for sample x = 0.01 has been given in the inset of figure 2. The peak position is the T_c . Along with the FM-PM transition, a temperature hysteresis about 3 K was observed, which evidences first-order nature of the transition involving the coupling of magnetic and structural transition. Here, the $T_{\rm stru}$ equals $T_{\rm c}^{\rm M} \sim 352 \, {\rm K}$. Due to the overlap of magnetic and structural transitions, a large MCE can be expected. Similarly, for the case of x = 0.02, a transition



Figure 3. The variation of T_{stru} , T_c of martensitic phase (T_c^M) , and T_c of hexagonal phase (T_c^A) with Al content and e/a ratio for MnCoGe_{1-x}Al_x. The orth-M and hex-A denote orthorthombic martensite and hexagonal austenite, respectively. The T_{stru} , and T_c^M for the case of x = 0 is obtained from [12, 22]. The black square, red circle, and blue triangle represent the T_{stru} , T_c^M and T_c^A , respectively.

between FM and PM state takes place at 324 K in ZFC mode. A larger thermal hysteresis about 18 K was observed, signifying the occurrence of strengthened first-order magnetic-structural transition and the possibility of larger MCE. However, as Al content is increased to x = 0.03, magnetic and structural transitions become separated, and the martensitic structural transition (T_{stru}) occurs between FM orthorhombic martensite and FM hexagonal austenite (figure 2). The concurrent thermal hysteresis is about 10 K, meanwhile the T_{stru} and Curie temperature T_c^A of austenitic phase locate at 174 and 269 K, respectively. The maximal hysteresis gap in sample x = 0.02indicates that the energy barrier in between the PM hexagonal and the FM orthorhombic phases is higher and harder to be overcome by thermal activation than the other two samples. On continuously increasing Al content to x = 0.04, the martensitic structural transition nearly disappears, meanwhile T_c^A (270 K) remains. Thus, the 'transition temperature window' [15, 17], as wide as about 80 K (from $T_c^A \sim 270$ K to $T_c^M \sim 350$ K), can be observed (see figure 3). Figure 3 summarizes the structural transition temperature $T_{\rm stru}$ as functions of Al content and valence-electron concentration e/a ratio. One can clearly find that T_{stru} decreases monotonically with increasing Al substitution (deceasing e/a).

The origin of T_{stru} shift is related to many factors [15–18]. Apart from the impact of the altering of covalent bonding and local environments on T_{stru} , as discussed above, the change of valence-electron concentration e/a ratio with the substitution of Al for Ge may also play an important role [18]. It can be seen, from figure 3, that the T_{stru} decreases while both of T_c^M and T_c^A remain almost unchanged with lowering e/a for MnCoGe_{1-x}Al_x. Similar dependences of the transition temperatures T_{stru} , T_c^A or T_c^M on e/a ratio have also been observed in many other systems, such as the Al-doping MnNiGe [18] and vacancy-doping Mn_{1-x}CoGe compounds [15]. In the scenario of spin fluctuation theory,



Figure 4. Magnetization isotherms of $MnCoGe_{1-x}Al_x$ for (*a*) x = 0.01, (*c*) x = 0.02, and (*e*) x = 0.03 at representative temperatures. Arrows indicate the paths of field change. Magnetic entropy change ΔS as a function of temperature in the fields up to 5 T for samples (*b*) x = 0.01, (*d*) x = 0.02, and (*f*) x = 0.03. Insets of (*b*) and (*d*) display ΔS_m curves under different fields below 1 T for the corresponding samples.

the weak e/a dependence of T_c^A or T_c^M signifies weak change of ferromagnetic exchange, which is due to little alteration of electronic states at Fermi level [15, 21]. Therefore, the high sensitivity of T_{stru} and insensitivity of T_c^A or T_c^M to Al content leads to the overlap of magnetic and structural transitions.

In order to obtain details of structural transition and the concurrant change of lattice along with magnetic transition, we chose typical sample MnCoGe_{0.99}Al_{0.01} with magnetostructural transition and performed XRD measurements at various temperatures around $T_{\rm stru}$, i.e. 300, 325, 400, 425 K. The patterns are shown in figure 1(b). At temperatures away from $T_{\rm stru} \sim 352\,{\rm K}$, the coexistence of martensitic and austenitic phase still exists. For example, at room temperature \sim 300 K (below $T_{\rm stru} \sim$ 352 K), about $2.4 \text{ wt\%}(\pm 0.2 \text{ wt\%})$ hexagonal austenitic phase is found. However, when the temperature goes above 400 K (far above $T_{\rm stru} \sim 352$ K), the sample displays almost single austenitic phase, implying a complete transformation from orthorhombic martensitic to hexagonal austenitic phase. This fact verifies the occurrence of martensitic structural transition along with magnetic transition (compared to figure 2). The coexistence of two phases at temperatures away from $T_{\rm stru}$ indicates that the structural transition may have broader temperature area than that of magnetic transition. Similar behaviour was also reported in other MnCoGe-based alloys. For example, residual hexagonal phase was observed at temperatures far below $T_{\rm stru}$ for MnCoGeB_{0.02} ($T_{\text{stru}} = 287 \text{ K}$) [16]. There is 11.3 vol% hexagonal phase found at 100 K with the main phase being orthorhombic phase. Trung et al attributed this observation to the inhomogeneous B atom distribution in lattice. They believed that structural phase transition does not occur at relatively boron-rich region. Similarly, inhomogeneous Al atom distribution might also appear in the lattice because the Al-doping level is only x = 0.01 in MnCoGe_{1-x}Al_x, possibly leading to the appearance of residual hexagonal structure at temperatures away from T_{stru} . However, the exact reason is not clear and further detailed investigation is still required. According to the unit-cell volume relationship ($V_{\text{ortho}} = 2V_{\text{hex}}$) of the two structures [22], we determined that the unit- cell volume increases by 3.3% $((V_{ortho} - 2V_{hex})/2V_{hex})$ due to large lattice distortion upon martensitic transformation from hexagonal to orthorhombic structure for sample x = 0.01. The significant volume expansion along with magnetic transition predicts large MCE will take place.

The concurrent magnetic and structural transitions are necessary to achieve large MCE in present systems. To evidence this point, we measured isothermal magnetization/demagnetization (M-H) curves and calculated magnetic entropy change for the samples of x = 0.01, 0.02 and 0.03. Figures 4(a), (c), and (e) display the M-H curves for the samples of x = 0.01, 0.02, and

For x = 0.01, we cannot observe 0.03. respectively. obvious magnetic hysteresis around the martensitic transition temperature, although a thermal hysteresis of 3 K was observed in M-T curves (figure 2). For most of first-order transition systems, the thermal and magnetic hysteresis usually happens synchronously. The different hysteresis behaviours in temperature and field cycles may indicate different nucleation mechanism under different external perturbations. For the sample of x = 0.02, the thermal hysteresis reaches as large as 18 K due to the strengthened nature of first-order transition, which is much larger than that of x = 0.01. As expected, a visible irreversible action, i.e. magnetic hysteresis, is found (figure 4(c)), and the maximal magnetic hysteresis around $T_{\rm stru}$ is about 8.2 J kg⁻¹ at 320 K. For the sample of x = 0.03, no obvious magnetic hysteresis appears around $T_{\rm stru}$ though a considerable thermal hysteresis occurs. This fact indicates that magnetic field may be not an effective way to trigger the martensitic transition between the FM hexagonal and the FM orthorhombic phases, and the energy barrier during the transition can be overcome more easily by thermal activation than by field-induced spin-lattice coupling (noting the different saturation magnetic moments of orthorhombic and hexagonal phases). Generally, hysteresis behaviour is related to many intrinsic and extrinsic factors [23, 24]. Intrinsic ones usually include band structure, impurity and nucleation factors, and strain effect. Extrinsic ones mainly refer to the thermal equilibrium and the situation of heat transfer during measurements, which directly relates to the deviation of temperature detector from sample, field/temperature rate, etc. During our measurements, we adopted the same rampingrate of 5 mT s⁻¹ of magnetic field and 2 K s⁻¹ of temperature, and the sample mass remains similar, around \sim 3 mg. Hence, extrinsic factors involving thermal equilibrium should be negligible [25], and intrinsic factors should play a key role for the observed hysteresis behaviours. For the magnetocaloric systems with first-order magnetostructural or magnetoelastic transitions, thermal activation model was usually considered to investigate dynamic behaviours [26, 27]. The energy barrier in the model, which characterizes the hysteresis gap, closely correlates with the electronic band structure and nucleation factors. For example, the magnetic coupling in Gd₅Si₂Ge₂ system [26] is via itinerant conduction electrons across the (Si,Ge)-(Si,Ge) covalent bonds. As the magnetostructural transformation is triggered by temperature or magnetic field, half of these bonds are broken and reformed, thus the energy barrier is closely connected with the magnetic part of the electronic band structure, and that to forming the (Si,Ge)–(Si,Ge) bonds. For present MnCoGe_{1-x}Al_x system, the detailed information of band structure is unclear, but similarly we believe that the different local environments and electronic band structure caused by different Al-doping level may lead to different energy barrier and hysteresis gaps. For details further investigations are still required.

Based on the M-H measurements, magnetic entropy change, ΔS , was calculated by Maxwell relation, $\Delta S(T, H) = \mu_0 \int_0^H (\partial M/\partial T)_H dH$, and displayed in figures 4(*b*), (*d*) and (*f*) for samples x = 0.01, 0.02, and 0.03, respectively. The ΔS_m of the materials without obvious hysteresis can

be reasonably calculated by Maxwell relation in many cases [15-18, 28-30]. For the samples of x = 0.01, 0.02 with magnetostructural transitions, the magnitude of $\Delta S_{\rm m}$ reaches 29.2 J kg⁻¹ K⁻¹ (357 K), 35.9 J kg⁻¹ K⁻¹ (323 K) under a field change of 0-5 T, respectively. These values are much larger compared to that of traditional material Gd working near room temperature. For the sample x = 0.03, $\Delta S_{\rm m}$ reduces much, and the corresponding magnitude of the two ΔS peaks involving $T_{\rm stru}$ and $T_{\rm c}^{\rm A}$ is only 5.7 (180 K) and 3.5 J kg⁻¹ K⁻¹ (269 K) under 5 T, respectively. Thus, the concurrent magnetic and structural transition, i.e. magnetostructual transition, is essential to get large MCE. It is noteworthy that the working temperature range for MnCoGe_{1-x}Al_x (x = 0.01and 0.02) locates around 320-350 K, which is helpful for magnetic refrigeration applications in this temperature area. Refrigeration at temperatures higher than room temperature is normally required in industry, the aerospace field, scientific research and so on.

4. Conclusions

In conclusion, the substitution of Al for Ge atoms is employed to tune structural transition temperature T_{stru} in MnCoGe_{1-x}Al_x systems. With the increase of Al doping, T_{stru} decreases and overlaps with Curie temperature of martensite T_c^M . As a result, a transition temperature window as wide as 80 K (from 270 to 350 K) is observed. The origin of the reduction of T_{stru} is ascribed to the strengthening of Mn–Mn covalent bonding and the lowering of e/a ratio due to Al doping. For the optimized compositions with x = 0.01and 0.02, large magnetic entropy change ΔS appears. The working temperature region from 320 to 350 K is favourable for magnetic refrigeration applications in this temperature area. More substitution of Al for Ge (x = 0.03, 0.04) leads to the separation of magnetic and structural transitions.

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