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Effect of substitution of In for Co on magnetostructural coupling and magnetocaloric effect in $MnCo_{1-x}In_xGe$ compounds

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Effect of replacement of Co by In with larger atomic radius but fewer valence numbers on magnetostructural coupling and magnetocaloric effect is studied in $MnCo_{1-x}In_xGe$ compounds. The substitution of Co by a small amount of In (1.5%–2%) can shift martensitic transformation T_{stru} to lower temperature and make it overlap with Curie temperature T_C. As a result, magnetostructural coupling is created and large entropy change (ΔS) takes place. Further increasing In content to $x = 0.03$ leads to decoupling, but the martensitic transition ($T_{stru} \sim 249$ K) is still close to the magnetic transition ($T_c^A \sim 269$ K). As a result, two close ΔS peaks appear. Mechanism related to different large entropy change in the coupled and decoupled samples are discussed. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4863255]

An increasing attention has been attracted to magnetic refrigeration technique, based on magnetocaloric effect (MCE), due to its superiority over the gas refrigeration on energy saving and environmental concerns. The materials with first-order magnetic phase transition, such as $Gd_5(Si,Ge)_4$,[1] $La(Fe,Si)_{13}$,[2,3] $MnFeP_{1-x}As_x$,[4] MnAs,[5] and NiMn-based Heusler alloys,[6–9] have been discovered to exhibit great magnetocaloric effect (GMCE). Usually, "magnetoelastic" phase transition refers to the system where only lattice parameters and volume changes, while "magnetostructural" phase transition refers to the one where crystal symmetry also changes. Systems $La(Fe,Si)_{13}$[2,3] and $MnFeP_{1-x}As_x$[4] belong to magnetoelastic phase transition while $Gd_5(Si,Ge)_4$[1] and NiMn-based Heusler alloys,[6–9] belong to magnetostructural phase transition. The discontinuous characteristics during the transitions lead to high entropy change, ΔS_M.

To realize magnetoelastic or magnetostructural coupling is an effective way to achieve large MCE. One knows that magnetic and crystallographic phase transitions are sensitive to both chemical and physical pressures. It has been reported that introducing physical hydrostatic pressure[10] in MnCoGe-based system can effectively tune martensitic transformation temperature, leading to a magnetostructural coupling and a giant MCE. On the other hand, introducing atomic substitutions with different radius and valence electron number, the so-called chemical pressure, can also affect magnetic interactions and crystallographic stability. For the optimized cases, the separate magnetic and crystallographic phase transitions can be tuned to coincide with each other, and magnetoelastic or magnetostructural couplings can be created.

The stoichiometric MnCoGe alloy shows ferromagnetic properties with Curie temperature $T_c \sim 345$ K and undergoes martensitic structural transition from Ni_2In-type hexagonal structure (space group $P6_3/mmc$) to TiNiSi-type orthorhombic structure (space group Pnma) at a higher temperature $T_{stru} \sim 420$ K.[11] Due to different crystal symmetry, the hexagonal and orthorhombic states show quite different ferromagnetic properties. The T_c and magnetic saturation moments M_s in the orthorhombic structure ($T_c^M = 345$ K and $M_s = 4.13\ \mu_B$) are higher than those in the hexagonal structure ($T_c^A = 283$ K and $M_s = 2.76\ \mu_B$)[12,13] noting the Mn–Mn distance in the latter is shorter than that in the former. For the MnCoGe-based materials, magnetic moment is mainly confined on Mn and Co atoms. Detailed investigations revealed that introducing chemical pressure in different ways, such as introducing atomic doping with different radius and valence electron number on magnetic positions (Mn, Co) or nonmagnetic positions(Ge), will produce different results. Moreover, the effect of hydrostatic pressure on coupled and uncoupled MnCoGe-based system is also not the same. For coupled systems, hydrostatic pressure as a clean way can push the magnetostructural transition temperature to lower temperature,[10] but shift T_c to higher temperature for the uncoupled second-order ferromagnetic systems.[14]

The present work aims to investigate the substitution of In for Co in $MnCo_{1-x}In_xGe$ systems. In atom (2.00 Å) has a larger radius than Co (1.67 Å). Our investigations indicate that a little replacement of In for Co ($x = 0.015$, 0.02) can tune martensitic structural transition T_{stru} and make it coincide with T_C, thus a magnetostructural coupling appears, and a large MCE takes place. More In concentration leads to decoupling of T_{stru} and T_c.

$MnCo_{1-x}In_xGe$ ($x = 0.015$, 0.02, 0.03, and 0.04) alloys were prepared by repeatedly arc-melting appropriate amounts of starting materials in high-purity argon atmosphere (99.996%) with a base pressure of 10^{-4} Pa. The commercial purities of Mn, Co, In, and Ge are 99.9 wt%, 99.9 wt%, 99.99 wt%, and 99.999 wt%, respectively. The obtained ingots were each wrapped with Mo foil and subsequently homogenized in a sealed quartz tube with a high vacuum of 10^{-4} Pa at 875 K for 6 days, then cooled down to room temperature in

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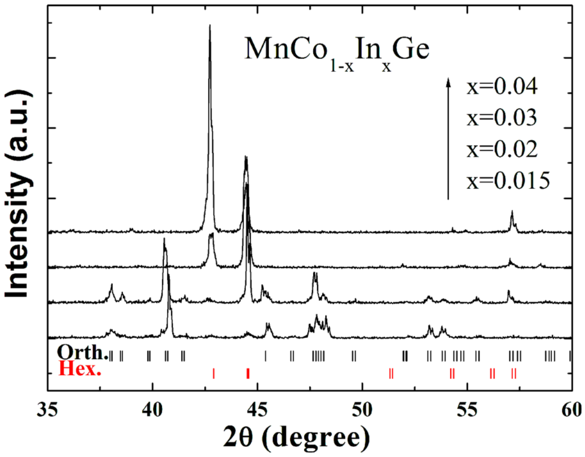

FIG. 1. The powder XRD patterns of MnCo$_{1-x}$In$_x$Ge ($x = 0.015$, 0.02, 0.03, and 0.04) measured at room temperature. The vertical black and red bars represent the Bragg reflection positions of orthorhombic and hexagonal structure, respectively.

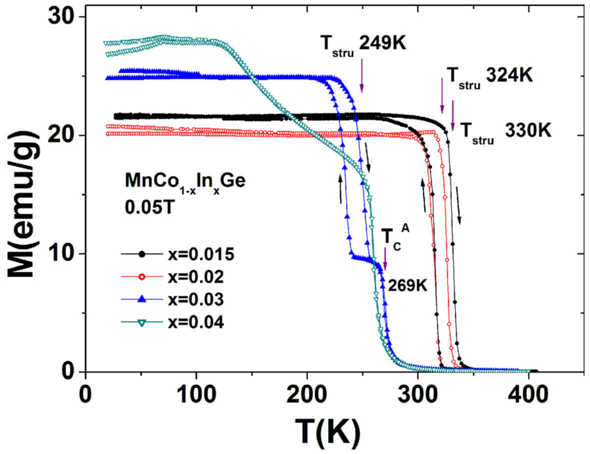

FIG. 2. The M-T curves measured under a magnetic field of 500 Oe for MnCo$_{1-x}$In$_x$Ge ($x = 0.015$, 0.02, 0.03, and 0.04). Black arrows indicate the cooling/warming paths.

oven. Samples for measurements were cut from the central parts of each ingot. All magnetic measurements were performed using a superconducting quantum interference device (SQUID-VSM).

X-ray diffraction (XRD) analysis was carried out using Cu Kα radiation to identify crystal structure. Fig. 1 shows the XRD patterns collected at room temperature. For samples MnCo$_{1-x}$In$_x$Ge ($x = 0.015$, 0.02), the patterns can be indexed as mixture of martensitic TiNiSi-type orthorhombic and austensic Ni$_2$In-type hexagonal structure. The fractions of orthorhombic and hexagonal phase are 90.1% and 9.9 wt. %, 66.7% and 33.3% for $x = 0.015$, 0.02, respectively. The coexistence of two phases and high ratio of martensitic phase indicate the martensitic temperature $T_{\rm stru}$ is close to but higher than room temperature for the two samples. Moreover, the higher hexagonal ratio in $x = 0.02$ indicates its $T_{\rm stru}$ should be lower than sample $x = 0.015$. For samples with more In content, $x = 0.03$, 0.04, almost single hexagonal phase (above 97 wt. %) was identified, indicating their $T_{\rm stru}$ should locate below room temperature. The gradual increase of the hexagonal austenite fraction with In concentration indicates that the substitution of In for Co atoms has the effect of maintaining Ni$_2$In-type austenite and then lowering the $T_{\rm stru}$.

Fig. 2 displays temperature dependent magnetization (M-T curve) measured under a low field of 500 Oe using zero-field cooling (ZFC) and field cooling (FC) modes.[15] For samples $x = 0.015$, 0.02, sharp magnetic transition between ferromagnetic (FM) and paramagnetic (PM) phase with pronounced hysteresis can be observed. The FM ordering temperature, T_c, locates at ~330 K, ~324 K while the hysteresis gap is ~19 K, ~10 K for $x = 0.015$, 0.02, respectively. The pronounced hysteresis behavior evidences the first-order nature of transition involving magnetostructural coupling ($T_{stru} = T_c$), thus a large MCE can be expected. Here, the transition temperature is defined as the one at which the largest slope occurs on heating (ZFC mode). Further increasing In content to $x = 0.03$ leads to decoupling of T_{stru} and T_C, but surprisingly the martensitic transition ($T_{stru} \sim 249$ K) with hysteresis about 15 K is close to T_c^A of austenitic phase (~269 K), indicating that the magnetostructural coupling is just decoupling. Continuously increasing In content to $x = 0.04$, T_{stru} is nearly missing, and the T_c^A of austenitic phase slightly shifts to lower temperature (~260 K). For all samples, the $T_{\rm stru}$ shows monotonous drop with increasing In substitution, consistent with the observations from XRD measurements discussed above.

Generally, unit cell volume increases by 3%–4% along martensitic transformation from paramagnetic hexagonal to ferromagnetic orthorhombic phases for MnMX family. This fact prompts us to think that the introduction of smaller atoms will stabilize hexagonal phases and shift T_{stru} to lower temperature. For example, the replacement of Mn by smaller atoms Cr in Mn$_{1-x}$Cr$_x$CoGe (Ref. 10) or Co by V in MnCo$_{1-x}$V$_x$Ge (Ref. 16) can make a lower T_{stru} and create magnetostructural coupling. However, the change of local environments due to smaller atoms is not the sole role to affect T_{stru}. Valence electron concentration e/a ratio also plays an important role, and the reduction of e/a usually make T_{stru} decrease.[17] We notice the valence electron number of In atom ($5s^25p^1$) is fewer than that of Co ($3d^74s^2$), thus the monotonous decrease of T_{stru} with increasing the substitution of In for Co in present MnCo$_{1-x}$In$_x$Ge should be competition result of the change of e/a and local environments.

Through magnetic measurements, we investigated magnetic entropy change for samples $x = 0.015$, 0.02 with magnetostructural coupling, and also for the just decoupled sample $x = 0.03$ with close T_{stru} and T_c. Figs. 3(a)–3(c) display magnetization isotherms (M-H) up to 5T in field increasing and decreasing processes. The temperature/field step/rate is the same for the 3 samples. Temperature step, ~2 K, was chosen for the temperature regions near T_{stru} or/and T_c and field step is always 500 Oe. Unlike the pronounced temperature hysteresis behaviors around T_{stru}, no obvious magnetic hysteresis appears within 5T field for the three samples. This fact indicates that magnetic field may be not an effective way to trigger the magnetostructural transition, and the energy barrier during the first-order transition can be easily overcome by temperature than by field-induced spin-lattice coupling.

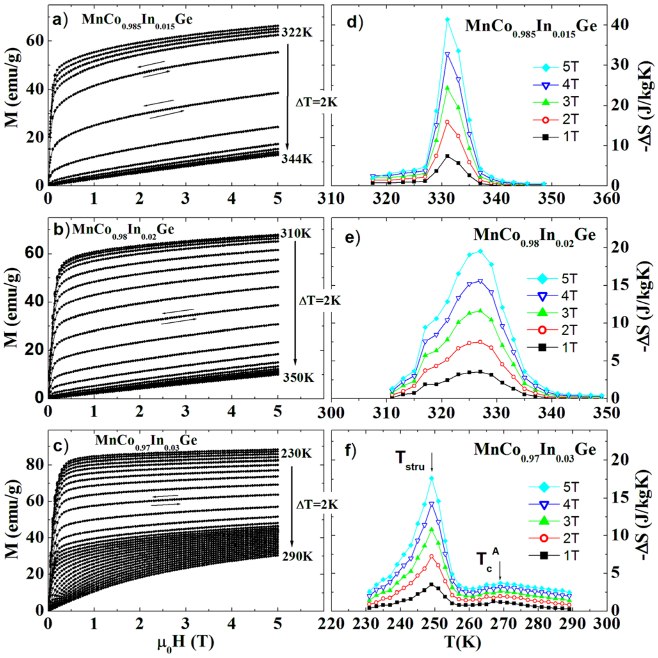

FIG. 3. Magnetization isotherms of $MnCo_{1-x}In_xGe$ for (a) x = 0.015, (b) x = 0.02, and (c) x = 0.03 at representative temperatures. Arrows indicate the paths of field change. Magnetic entropy change ΔS as a function of temperature under different magnetic fields for (d) x = 0.015, (e) x = 0.02, and (f) x = 0.03.

Actually, this is a common feature particularly for the MnCoGe-based alloys,[10,17] also for NiMnSn.[7] A recent study carried out by Caron *et al.*[10] revealed that hydrostatic pressure can tune the MCE effect for similar system $Mn_{0.93}Cr_{0.07}CoGe$ though field-induced metamagnetic behavior is none or very weak. It was suggested that the driving force during the magnetostructural transition is the crystallographic transition, and the magnetic transition occurs cooperatively. Such behavior is different from the most of MCE materials with first-order magnetoelastic or magnetostructural transitions, where both crystallographic change caused by hydrostatic/chemical pressure and magnetic field can drive the transitions. The examples include the well-known materials GdSiGe,[18] MnFePAs,[19] La(Fe,Si)$_{13}$,[20] and also NiMnIn systems.[8,9] For these materials, it is hard to choose which one of the crystallographic or field changes acts the driving force and the other acts cooperatively. For the extremes, such as MnCoGe-based alloys,[10] NiMn-based Heusler alloys (NiMnSn,[7] NiMnGa[6]), where the magnetostructural transition is insensitive to magnetic field, the entropy change usually appears in a narrow and high peak but shifts little upon magnetic field.

Based on the magnetization data shown in Figs. 3(a)–3(c), we calculated entropy change using Maxwell relation $\Delta S(T,H) = \mu_0\int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH$.[1–6,21] The results are shown in Figs. 3(d)–3(f) for the corresponding samples. For the coupled samples x = 0.015, 0.02, the entropy change (ΔS) peaks at the magnetostructural transition temperature, 330 K, 324 K, and the maximal magnitude for a field change of 0–5T reaches 41.4 J/kgK, 19.6 J/kgK, respectively. The different ΔS magnitude might be related to the different strength of spin-lattice coupling in the two coupled samples. We can note that the thermal hysteresis (10 K) of sample x = 0.02 is narrower than that (19 K) of x = 0.015, indicating the energy barrier in between paramagnetic austenitic and ferromagnetic martensitic phases becomes lower and the first-order nature of the transition becomes weaker for sample x = 0.02 compared to x = 0.015. For the just decoupled sample, x = 0.03, the two close transitions at T_{stru} (249 K) and T_C^A (269 K) lead to the appearance of two close ΔS peaks. The maximal ΔS magnitude for a field change of 0–5T is 17.7 J/kgK, 3.7 J/kgK, corresponding to the first-order martensitic transition at T_{stru} and second-order magnetic transition at T_C^A, respectively. The further smaller ΔS magnitude involving T_{stru} in sample x = 0.03 may be related to the decoupling of crystallographic and magnetic transitions.

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