From single- to double-first-order magnetic phase transition in magnetocaloric $Mn_{1-x}Cr_xCoGe$ compounds

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Substitution of some Cr for Mn atoms in MnCoGe was employed to control the magnetic and structural transitions in this alloy to coincide, leading to a single first-order magnetostructural transition from the ferromagnetic to the paramagnetic state with a giant magnetocaloric effect observed near room temperature. Further increase in the Cr content in the $Mn_{1-x}Cr_xCoGe$ alloys can induce another first-order magnetoelastic transition from the antiferromagnetic to the ferromagnetic state occurring at lower temperature. The giant magnetocaloric effect as well as the simultaneous tunability of the two magnetic transitions make these materials promising for future cooling applications. © *2010 American Institute of Physics*. [doi:10.1063/1.3399774]

Nowadays, magnetocaloric materials undergoing first-order magnetic transitions (FOMTs) are intensively investigated because of their potential applications at room temperature.[1] In contrast to second-order magnetic transitions, FOMTs fall into two categories: magnetostructural transitions (MSTs) and magnetoelastic transitions (METs). In the former case such as $Gd_5(Si_xGe_{1-x})_4$,[2] $MnAs_{1-x}Sb_x$,[3] and $Ni_{0.50}Mn_{0.50-x}Sn_x$,[4] a different crystal structure is found on either side of the magnetic phase transition. As a common feature, the compounds with a MST often show large thermal and field hysteresis. In the case of METs such as $MnFeP_{1-x}As_x$ (Ref. 5) and $La(Fe_{1-x}Si_x)_{13}$,[6] the same crystal structure is found on both sides of the phase transition. However, a distinct lattice distortion accompanied by a possible change in unit-cell volume is observed near the critical transition point. Usually, the compounds exhibiting a MET reveal small or tunable hysteresis.[7]

Earlier studies on MnCoGe confirmed a martensitic structural transformation from the low-temperature orthorhombic (orth.) TiNiSi-type structure (space group *Pnma*) to the high-temperature hexagonal (hex.) Ni_2In-type structure (space group $P6_3/mmc$).[8,9] On heating, this transformation occurs at the structural transition temperature (T_{str}) ~650 K.[9] In the stable orth. ground state, MnCoGe behaves like a typical ferromagnet with a second-order PM-FM transition occurring at the ordering temperature (T_c) ~345 K, which is far below T_{str}.[10] Recently, we have discovered a giant MCE in the magnetic refrigerants based on MnCoGe.[11] By interstitially adding some boron atoms to MnCoGe, the structural transition at T_{str} and the magnetic transition at T_c can be controlled to coincide, leading to a single first-order magnetostructural transition (FOMST) from the combined two-phase FM region, in which the orth. TiNiSi- and hex. Ni_2In-type structures coexist, to an almost single-phase PM Ni_2In-type structure. In this paper we shall show that, a single FOMST at T_c and a giant MCE can also be attained by substituting some Cr for Mn atoms in MnCoGe. Strikingly, further increase in the Cr content in $Mn_{1-x}Cr_xCoGe$ gives rise to the appearance of a second first-order magnetoelastic FM-AFM transition at a lower transition temperature (T_t).

Polycrystalline $Mn_{1-x}Cr_xCoGe$ (x=0.00,0.04,0.11, 0.18,0.25,0.27) alloys were prepared by arc-melting (see Ref. 11). Shown in Fig. 1(a) are the temperature dependences of the magnetization (*M-T* curves) for x=0.04, 0.11, 0.18, and 0.25. For x=0.04, the *M-T* curve shows a single, sharp PM-FM transition at $T_c \sim 322$ K. The considerable thermal hysteresis (ΔT_{hys}) clearly evidences the first-order nature of this transition, which is attributed to the intimate coupling between the PM-FM transition and the hex.-orth. structural transition.[11] For all temperatures below T_c, the magnetic moments of this sample are well ordered in the FM state. However, the *M-T* curves of x=0.11, 0.18 and 0.25 indicate that the moments of these materials are more likely ordered in the AFM state at low temperatures. With maintaining the first-order PM-FM transition at T_c, another first-order FM-AFM

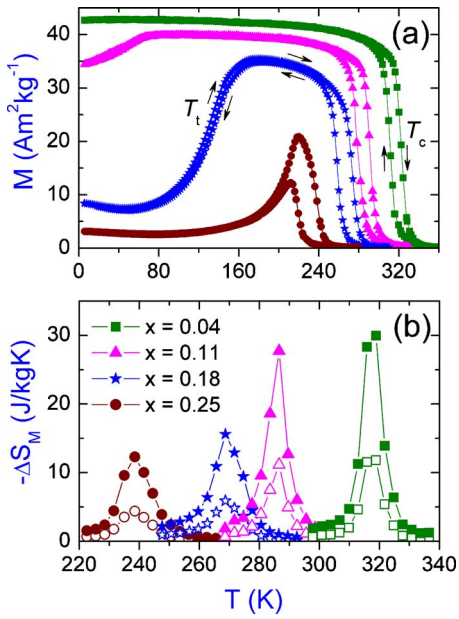

FIG. 1. (Color online) *M-T* curves measured in a magnetic field B=0.1 T of the $Mn_{1-x}Cr_xCoGe$ (x=0.04,0.11,0.18,0.25) alloys (a) and their corresponding ΔS_M at the PM-FM transition under field changes of ΔB =0–2 T (open symbols) and ΔB=0–5 T (closed symbols) (b).

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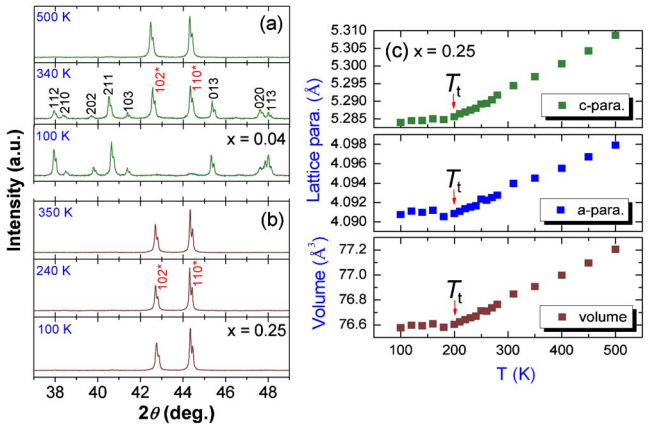

FIG. 2. (Color online) XRD patterns measured in zero-field upon heating at 100, 340, and 500 K for x=0.04 (a) and at 100, 240, and 350 K for x=0.25 (b).In Fig. 2(a), the pattern measured at 340 K confirms the coexistence of the *orth*. phase (*hkl* Miller indices without ∗) and the *hex*. phase (*hkl* Miller indices with ∗) (c) Variation in lattice parameters and volume of the hex. Ni_2In-type unit-cell as a function of temperature for the x=0.25 sample.

transition can thus take place at T_t. Note that the double FOMTs at T_t and T_c as in $Mn_{1-x}Cr_xCoGe$ have not been observed in any other type of martensitic transition materials yet. Strikingly, these two FOMTs are simultaneously tunable. With increasing Cr doping, T_c is significantly lowered, however, T_t is strongly shifted to higher temperatures. Here, the occurrence of small hysteresis at T_t indicates that the FM-AFM transition may have a magnetoelastic character. As can be seen from Fig. 1(a), the substitution of some Cr atoms has a strong influence on the magnetization in both the FM and AFM phases. The total entropy change (ΔS_M) of materials with hysteretic first-order transitions can reliably be calculated from the Maxwell relation.[12,13] Displayed in Fig. 1(b) are the ΔS_M calculated for the PM-FM transition of $Mn_{1-x}Cr_xCoGe$ (with x=0.04,0.11,0.18,0.25). Here all samples exhibit a giant MCE around T_c. For ΔB=0–5 T, large ΔS_M values of −28.5 J kg^{-1} K^{-1} and −27.7 J kg^{-1} K^{-1} are obtained for the sample with x=0.04 and 0.11, respectively. When further increasing the Cr content, the MCE becomes much lower, with ΔS_M values of −15.6 J kg^{-1} K^{-1} and −12.3 J kg^{-1} K^{-1} for x=0.18 and 0.25, respectively.

The structural properties of $Mn_{1-x}Cr_xCoGe$ were investigated by x-ray diffraction (XRD). The volume fraction (vol %) of the orth. and the hex. phase was calculated by Rietveld refinement using the FULLPROF package.[11,14] Figure 2(a) presents XRD patterns for x=0.04 taken below, near and above T_c. At 100 K we observe predominantly the orth. TiNiSi-type structure with a small fraction of the hex. Ni_2In-type. Obviously, the single hex. Ni_2In-type phase above T_c can largely transform to the orth. TiNiSi-type phase below T_c. Indeed, this again verifies the occurrence of a FOMST at T_c. In contrast, the XRD patterns presented in Fig. 2(b) for x=0.25 show almost single phase of the hex. structure from below T_t to above T_c. Only by carefully analyzing the XRD pattern measured below T_c, a small amount of orth. phase (~2.4 vol %) is detected. Although the volume change due to the structural transformation is negligibly small, the FOMST at T_c is still evident for this sample. Apparently, the substitution of Cr for Mn can stabilize the hex. phase relatively to the orth. phase. As shown in Table I, the variation in phase fractions is strongly dependent on the Cr content. Note that when the Cr content is slightly higher than 0.25 at. %, as for x=0.27, refinement of the XRD data shows that all reflections can only be indexed on the basis of a single hex. Ni_2In-type phase. Since the magnetostructural coupling can no longer take place and the AFM arrangement is no longer stable, we only observe the second-order PM-FM transition in this sample.[15] In comparison with $MnCoGeB_x$,[11] the properties of $Mn_{1-x}Cr_xCoGe$ are even more complicated due to the appearance of the FM-AFM transition at T_t. In these materials, the lower limit of T_c is always given by T_t. As the hex. phase fraction below T_c strongly increases with Cr doping, the magnetostructural *decoupling* is only observed for the x=0.27 sample with no structural change.

Another result from the XRD data obtained on x=0.18 and 0.25 confirms that the relative phase fraction ratio between the orth. and hex. structures does not change at T_t. Hence, a magnetostructural coupling between the FM-AFM transition and the hex.-orth. transition apparently does not occur. A detailed study of the origin of the first-order magnetoelastic FM-AFM transition was carried out on x=0.25. This sample was chosen because it mostly contains the hex. phase. Thus, the errors that might arise from the coexistence of two structures at T_t can be neglected in our analysis. In Fig. 2(c), the variation in lattice parameters and volume of the hex. Ni_2In-type unit-cell for x=0.25 is displayed. Obviously, at ~200 K one can observe a kink, which is very close to T_t of the FM-AFM transition. Like in invar alloys, the lattice parameters and the unit-cell volume of x=0.25 are almost constant below T_t. The increase in these above T_t is consistent with a linear thermal-expansion. Similar to

TABLE I. Variation in magnetic phase transition type, T_t and T_c obtained on heating, ΔT_{hys} at T_c, $\Delta S_{M,max}$ (for ΔB=0–5 T) of the PM-FM transition, and the phase fraction (vol %) of the orth. and hex. structures at 100 K for the $Mn_{1-x}Cr_xCoGe$ alloys.

Samples	Phase transitions	T_t (K)	T_c (K)	ΔT_{hys} (K)	$-\Delta S_{M,max}$ (J kg^{-1} K^{-1})	Phase fraction (vol %)	
						Orth.	Hex.
x=0.00	Second-order PM-FM		345	0	4.8	100.0	0.0
x=0.04	First-order PM-FM	~0	322	10	28.5	96.9	3.1
x=0.11	First-order PM-FM-AFM	43	292	12	27.7	89.4	10.6
x=0.18	First-order PM-FM-AFM	133	274	15	15.6	29.2	70.8
x=0.25	First-order PM-FM-AFM	212	237	20	12.3	2.4	97.6
x=0.27	Second-order PM-FM		190	0	1.8	0.0	100.0

Ni–Mn–In,[12] it is reasonable to assume that, for the sample with $0 < x \leq 0.25$, the smaller distance between the Mn and Co sublattices below T_t favors the AFM state whereas the relatively larger distance above T_t is suitable for the FM arrangement of the magnetic moments.

Because the contribution of electronic entropy change (ΔS_E) is very small, the ΔS_M for a FOMST mainly consists of the spin-entropy change (ΔS_{spin}) plus the lattice-entropy change (ΔS_L).[16] For the martensitic transition in Ni–Mn–In alloys, the contribution of ΔS_L has been estimated at about 50% of ΔS_M.[12] For $Gd_4Si_xGe_{4-x}$, this contribution is found to be lower, varying from 20% to 40%.[17] In $Mn_{1-x}Cr_xCoGe$, the amount of orth. phase below T_c is strongly reduced with increasing the Cr content (see Table I). For $x=0.25$, ΔS_L involving the transformation from the high-symmetry hex. to the low-symmetry orth. structure is negligibly small. The giant MCE found in this compound is attributed to a dominant contribution of the ΔS_{spin} [see Fig. 1(b)]. Actually, the two FOMTs at T_t and T_c imply both a negative and a positive ΔS_M in $Mn_{1-x}Cr_xCoGe$. Although the MCE from the FM-AFM transition is small (for example for $x=0.18$, $\Delta S_M \sim 1.2$ J kg^{-1} K^{-1} for $\Delta B=0-5$ T) in comparison with that from the PM-FM transition, improvement of the MCE magnitude of both these FOMPTs can be utilized to enhance the efficiency of a special type of magnetic refrigerators.[18]

In summary, the substitution of Cr for Mn atoms has been employed to tailor the magnetic and structural transitions in the magnetocaloric $Mn_{1-x}Cr_xCoGe$ compounds. By increasing the Cr content, we can introduce a first-order magnetostructural PM-FM transition at T_c and another first-order magnetoelastic FM-AFM transition at T_t. The occurrence of these double FOMTs in a single material and the possible extraction of the concomitant ΔS_L from the ΔS_M are extremely interesting for further studies on critical phase transitions. The giant MCEs as well as the simultaneous tunability of the two magnetic transitions can make these materials promising for future cooling applications.

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