Giant room-temperature magnetocaloric effect in $Mn_{1-x}Cr_xAs$

N. K. Sun,[1,2,a] W. B. Cui,[1] D. Li,[1] D. Y. Geng,[1] F. Yang,[1] and Z. D. Zhang[1]
[1]*Shenyang National Laboratory for Materials Science, Institute of Metal Research and International Centre for Materials Physics, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, People's Republic of China*
[2]*School of Science, Shenyang Ligong University, Shenyang 110168, People's Republic of China*

(Received 2 January 2008; accepted 31 January 2008; published online 21 February 2008)

A giant magnetocaloric effect was observed at room temperature in $Mn_{1-x}Cr_xAs$ compounds with $x=0.006$ and 0.01. The Cr dopant reduces (or even eliminates) the large thermal hysteresis of MnAs, while it lowers the first-order transition temperature from 313 K for MnAs to 265 K for $Mn_{0.99}Cr_{0.01}As$. Near the Curie temperature, a magnetic field induces a first-order phase transition from a ferromagnetic hexagonal phase to a paramagnetic orthorhombic phase, leading to a maximum value of ΔS_M of 20.2 J/kg K at 267 K for a 5 T field change for $Mn_{0.99}Cr_{0.01}As$. The study on the $Mn_{1-x}Cr_xAs$ system may open an important field in searching proper materials for room-temperature magnetic refrigeration. © *2008 American Institute of Physics*.
[DOI: 10.1063/1.2884524]

Currently, there is a great deal of interest in utilizing the magnetocaloric effect (MCE) as an alternate technology for refrigeration, replacing the common gas-compression/expansion technology, due to higher efficiency and environmental concerns.[1–3] In particular, much attention has been paid to room-temperature magnetic refrigeration.[4–11] For this purpose, it is of great importance to explore the compounds which exhibit large entropy changes near room temperature. As well known, in materials showing a conventional MCE, the magnetic transitions are of second-order type and, usually, a first-order magnetic transition occurs in giant-MCE (GMCE) materials.[4,5] Although the magnetic-entropy change (ΔS_M) of these GMCE materials is larger than that of Gd metal, the magnetic hysteresis being the characteristic of a first-order transition is very large, which makes the magnetic refrigeration less efficient. Consequently, from the aspect of industrial applicability, how to reduce or even eliminate the magnetic hysteresis is a challenging topic. MnAs exhibits a colossal MCE with Fe/Cu doping or under a high pressure.[12–14] However, the thermal hysteresis is too large (10–30 K) to allow any practical use of these materials. Here, we report a large MCE at room temperature in $Mn_{1-x}Cr_xAs$ compounds. The thermal hysteresis is reduced (or even eliminated) by a small amount doping of Cr, while a large room-temperature MCE is retained.

MnAs is a commercially available material, which has been intensively explored both theoretically and experimentally since the beginning of past century. Interest in this compound came up again because of its MCE (Refs. 6 and 12–14) and colossal magnetoresistancelike effect.[15] MnAs exhibits a first-order phase transition from a ferromagnetic (FM) high-spin phase to a paramagnetic (PM) low-spin one at $T_C=313$ K, which is accompanied by a structural transition from a hexagonal NiAs-type to an orthorhombic MnP-type structure.[15] Crystal structure and magnetic properties of $Mn_{1-x}Cr_xAs$ solid solutions have been investigated systematically in the whole composition range.[16] For $x>0.5$, the $Mn_{1-x}Cr_xAs$ compounds are antiferromagnetic with MnP-type structure; near $x=0.4$, the compounds are ferromagnetic in low temperatures, and there is a phase transition from ferromagnetism to antiferromagnetism with increasing temperatures; for $0.05<x<0.3$, the compounds show a metamagnetic behavior. The ferromagnetic mode of MnAs with NiAs-type structure is kept for a slight doping ($x<0.05$) with Cr.

Polycrystalline $Mn_{1-x}Cr_xAs$ compounds with $x=0.006$ and 0.01 were synthesized by a method we developed to avoid the volatilization of As and long reaction-sintering treatments. Powders of Mn, Cr, and As of purity larger than 99.9% were mixed according to the nominal compositions. The mixtures of 10 g were sealed in hardened-steel vials with steel balls of 12 mm diameter in a high-purity-argon-filled glovebox. Mechanical alloying of the mixtures was carried out for 5 h using a high-energy ball-mill machine. The mechanically alloyed powders were then annealed at 500 °C for 2 h in a vacuum furnace connected directly to a closed glovebox. X-ray diffraction was carried out to verify that the samples yielded diffraction peak characteristic of a single phase material with NiAs-type hexagonal structure. The magnetic properties were measured using a superconducting quantum interference device magnetometer at applied magnetic fields up to 5 T at temperatures from 200 to 350 K. The change of the magnetic entropy was calculated from the *M-B* plots at various temperatures close to the phase transitions, with a temperature step of 2 K.

The temperature dependence of the magnetization of the $Mn_{1-x}Cr_xAs$ compounds was measured during both warming and cooling processes in a field of 0.01 T (for $x=0.01$) or 0.02 T (for $x=0.006$) from 200 to 350 K (as shown in Fig. 1). The Curie temperature T_C was defined as the temperature corresponding to a minimum in the temperature dependence of the first order derivative of the magnetization (dM/dT) (as shown in the inset of Fig. 1). It can be clearly seen that with increasing temperature, the magnetization drops abruptly at Curie temperature T_C of 265 K (or 290 K) for $Mn_{0.99}Cr_{0.01}As$ (or $Mn_{0.994}Cr_{0.006}As$). The magnetic phase transition temperatures are roughly in agreement with the previous work.[16] As reported earlier,[16,17] in analogy with MnAs, this transition is accompanied by a structural transi-

[a]Electronic mail: nksun@imr.ac.cn.

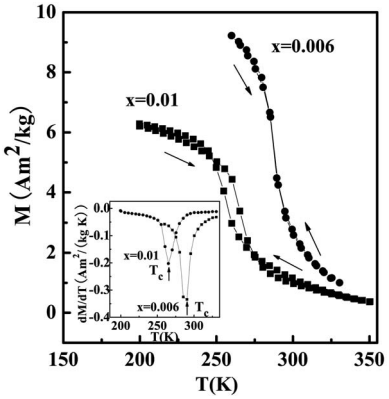

FIG. 1. Temperature dependence of the magnetization of $Mn_{0.994}Cr_{0.006}As$ (at 0.02 T) and $Mn_{0.99}Cr_{0.01}As$ (at 0.01 T). The arrows indicate the warming and cooling processes. The inset shows the first derivative of the magnetization (dM/dT) as a function of temperature.

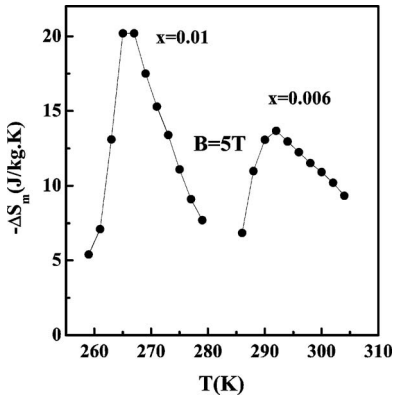

FIG. 3. Magnetic-entropy changes of $Mn_{0.994}Cr_{0.006}As$ and $Mn_{0.99}Cr_{0.01}As$ for an external field change of 5 T.

tion from a hexagonal NiAs-type to an orthorhombic MnP-type structure, indicating that it is of the first order. However, in contrast with MnAs, $Mn_{1-x}Fe_xAs$ or $Mn_{1-x}Cu_xAs$, the present $Mn_{1-x}Cr_xAs$ compounds exhibit a smooth variation of the temperature dependence of the magnetization. As a result, instead of showing a large thermal hysteresis (10–30 K) in MnAs, the warming and cooling magnetization curves for $Mn_{0.994}Cr_{0.006}As$ almost overlap, meaning that the thermal hysteresis has been eliminated. From Fig. 1, the thermal hysteresis of $Mn_{0.99}Cr_{0.01}As$ is reduced to about 5 K. Such reduction/elimination is somehow similar to the large reduction of hysteresis losses by the iron addition in $Gd_5Ge_2Si_2$.[18]

Mira *et al.*[15] observed directly a field-induced structural transition from the orthorhombic $B31$ phase to the hexagonal $B8_1$ phase in MnAs. To explore the influence of the external field on the structural transition and the possible GMCE in $Mn_{1-x}Cr_xAs$, the M (B) curves are shown in Figs. 2(a) and 2(b). For $Mn_{0.99}Cr_{0.01}As$, from 260 to 266 K, the magnetization rises abruptly at a rather low field and shows a rapid tendency to saturate, suggesting that the compound is in the FM state with hexagonal NiAs-type structure. In sharp contrast, from 268 to 280 K, after an initially linear increase at low fields, revealing that the compound is in the PM state with an orthorhombic MnP-type structure at zero field, the magnetization increases abruptly at a certain critical field. This abrupt increase of the magnetization indicates a field-induced PM-FM transition, accompanied by a structural transition. An abrupt increase in magnetization is traditionally taken as evidencing a first-order magnetic phase transition. $Mn_{0.994}Cr_{0.006}As$ exhibits similar magnetic behavior near the Curie temperature where a magnetic field can induce a first-order metamagnetic/structural transition.

As a large MCE often appears at the magnetic transition, a large magnetic-field-induced ΔS_M is expected in $Mn_{1-x}Cr_xAs$ from the magnetization curves in Figs. 2(a) and 2(b). The value of the isothermal $\Delta S_M(T,B)$ is given by the following expression associated with the Maxwell relationship:

$$\Delta S_M(T,B) = S(T,B) - S(T,0) = \int_0^B \left(\frac{\partial M}{\partial T}\right)_B dB. \quad (1)$$

The sign of ΔS_M is determined by the sign of $\partial M/\partial T$, as shown in formula (1). Figure 3 gives $\Delta S_M(T)$ curves of $Mn_{1-x}Cr_xAs$ compounds for a magnetic field change of 5 T. Here, the sign of ΔS_M is negative. That is, the present compounds show a conventional MCE, cooling by adiabatic demagnetization. The maximum ΔS_M with a field change of 5 T is 20.2 J/kg K at 267 K for $Mn_{0.99}Cr_{0.01}As$ (and 13.7 J/kg K at 292 K for $Mn_{0.994}Cr_{0.006}As$). The ΔS_M exhibits its maximum around the first-order phase-transition temperature, meaning that the field-induced metamagnetic transition is responsible for the giant negative ΔS_M in $Mn_{1-x}Cr_xAs$. The values of ΔS_M exceed those of the conventional room-temperature MCE materials by a factor of 2–3, which are also comparable to those of well-known GMCE materials such as $Gd_5(Ge_{1-x}Si_x)_4$,[4] $MnFeP_{1-x}As_x$,[5] $MnAs_{1-x}Sb_x$,[6] and NiMnGa.[19] Moreover, as stated above, the magnetic hysteresis has been eliminated in $Mn_{0.994}Cr_{0.006}As$. In addition, there are also some other advantages of $Mn_{1-x}Cr_xAs$ as a magnetic refrigerant material. Firstly, the

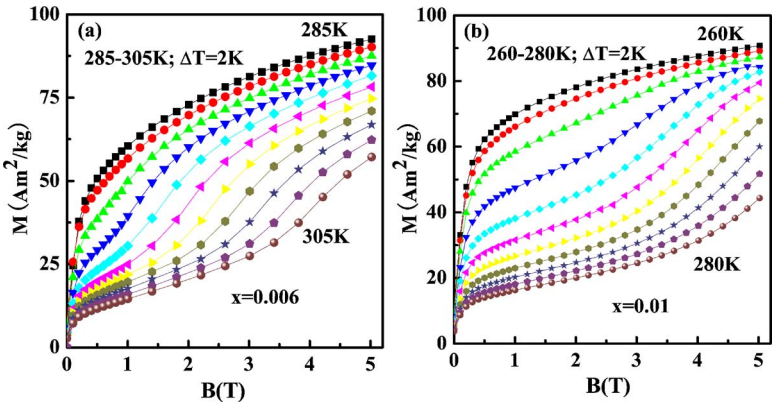

FIG. 2. (Color online) Field dependence of the magnetization of (a) $Mn_{0.994}Cr_{0.006}As$ and (b) $Mn_{0.99}Cr_{0.01}As$ at temperatures indicated.

transition temperature T_C in the $Mn_{1-x}Cr_xAs$ system can be set at any temperature from 313 to 253 K with the Cr concentration being lower than 5 at. %.[16,17] This is practically meaningful, because one can tune the maximum MCE in this temperature range without losing the large MCE. Secondly, unlike $Fe_{0.49}Rh_{0.51}$, cycling of a magnetic field does not induce an irreversible change in the magnetic and magnetocaloric behaviors in the present system. The MCE in $Fe_{0.49}Rh_{0.51}$ is irreversible in alternating magnetic fields (i.e., it disappears after 1 cycle).[4] Finally, the lower cost of the constituent materials, compared with Gd, $Gd_5(Ge_{1-x}Si_x)_4$,[4] and NiMnGa (Ref. 19) alloys, is another advantage of the present system. Consequently, it is believed that the $Mn_{1-x}Cr_xAs$ alloys are suitable candidates for room-temperature magnetic refrigeration.

In conclusion, the $Mn_{1-x}Cr_xAs$ compounds with $x=0.006$ and 0.01 exhibit giant room-temperature MCE with reduced (or even without) hysteretic behavior. A maximum value of ΔS_M of 20.2 J/kg K is observed at 267 K for a 5 T field change for $Mn_{0.99}Cr_{0.01}As$. The large entropy change ΔS_M is ascribed to a field-induced first-order phase transition from a PM orthorhombic phase to a FM hexagonal phase. The discovery of the GMCE in the $Mn_{1-x}Cr_xAs$ system may have significant impact on the realization of room-temperature magnetic refrigeration.

This work has been supported by the National Natural Science Foundation of China under Grant No. 50331030.

[1]E. Warburg, Ann. Phys. **249**, 141 (1881).
[2]C. B. Zimm, A. Jastrab, A. Sternberg, V. K. Pecharsky, K. A. Gschneidner, Jr., M. Osborne, and I. Anderson, Adv. Cryog. Eng. **43**, 1759 (1998).
[3]J. Glanz, Science **279**, 2045 (1998).
[4]V. K. Pecharsky and K. A. Gschneidner, Jr., Phys. Rev. Lett. **78**, 4494 (1997).
[5]O. Tegus, E. Brück, K. H. J. Buschow, and F. R. de Boer, Nature (London) **415**, 150 (2002).
[6]H. Wada and Y. Tanabe, Appl. Phys. Lett. **79**, 3302 (2001).
[7]A. Fujita, S. Fujieda, K. Fukamichi, H. Mitamura, and T. Goto, Phys. Rev. B **65**, 014410 (2001).
[8]S. Yu. Dan'kov, A. M. Tishin, V. K. Pecharsky, and K. A. Gschneidner, Jr., Phys. Rev. B **57**, 3478 (1998).
[9]F. X. Hu, B. G. Shen, J. R. Sun, Z. H. Cheng, G. H. Rao, and X. X. Zhang, Appl. Phys. Lett. **78**, 3675 (2001).
[10]A. Fujita, S. Fujieda, Y. Hasegawa, and K. Fukamichi, Phys. Rev. B **67**, 104416 (2003).
[11]N. K. Sun, S. Ma, Q. Zhang, J. Du, and Z. D. Zhang, Appl. Phys. Lett. **91**, 112503 (2007).
[12]A. de Campos, D. L. Rocco, A. M. G. Carvalho, L. Caron, A. A. Coelho, S. Gama, L. M. da Silva, F. C. G. Gandra, A. O. dos Santos, L. P. Cardoso, P. J. von Ranke, and N. A. de Oliveira, Nat. Mater. **5**, 802 (2006).
[13]D. L. Rocco, A. de Campos, A. M. G. Carvalho, L. Caron, A. A. Coelho, S. Gama, F. C. G. Gandra, A. O. dos Santos, L. M. da Silva, L. P. Cardoso, P. J. von Ranke, and N. A. de Oliveira, Appl. Phys. Lett. **90**, 242507 (2007).
[14]S. Gama, A. A. Coelho, A. de Campos, A. M. G. Carvalho, F. C. G. Gandra, P. J. von Ranke, and N. A. de Oliveira, Phys. Rev. Lett. **93**, 237202 (2004).
[15]J. Mira, F. Rivadulla, J. Rivas, A. Fondado, T. Guidi, R. Caciuffo, F. Carsughi, P. G. Radaelli, and J. B. Goodenough, Phys. Rev. Lett. **90**, 097203 (2003).
[16]N. Kazama and H. Watanabe, J. Phys. Soc. Jpn. **30**, 1319 (1971).
[17]K. Selte, A. Kjekshus, A. F. Andresen, and A. Zieba, J. Phys. Chem. Solids **38**, 719 (1977).
[18]V. Provenzano, A. J. Shapiro, and R. D. Shull, Nature (London) **429**, 853 (2004).
[19]F. X. Hu, B. G. Shen, and J. R. Sun, Appl. Phys. Lett. **76**, 3460 (2000).