Giant room-temperature magnetocaloric effect in \(\text{Mn}_{1-x}\text{Cr}_x\text{As}\)

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A giant magnetocaloric effect was observed at room temperature in \(\text{Mn}_{1-x}\text{Cr}_x\text{As}\) compounds with \(x=0.006\) and 0.01. The \(\text{Cr}\) dopant reduces (or even eliminates) the large thermal hysteresis of \(\text{MnAs}\), while it lowers the first-order transition temperature from 313 K for \(\text{MnAs}\) to 265 K for \(\text{Mn}_{0.99}\text{Cr}_{0.01}\text{As}\). 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 \(\Delta S_m\) of 20.2 J/kg K at 267 K for a 5 T field change for \(\text{Mn}_{0.99}\text{Cr}_{0.01}\text{As}\). The study on the \(\text{Mn}_{1-x}\text{Cr}_x\text{As}\) system may open an important field in searching proper materials for room-temperature magnetic refrigeration. © 2008 American Institute of Physics.

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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.\(^3\) In particular, much attention has been paid to room-temperature magnetic refrigeration.\(^4\) 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.\(^5\) Although the magnetic-entropy change \((\Delta S_M)\) of these GMCE materials is larger than that of \(\text{Gd}\) 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. \(\text{MnAs}\) exhibits a colossal MCE with \(\text{Fe}/\text{Cu}\) 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 \(\text{Mn}_{1-x}\text{Cr}_x\text{As}\) compounds. The thermal hysteresis is reduced (or even eliminated) by a small amount doping of \(\text{Cr}\), while a large room-temperature MCE is retained.

\(\text{MnAs}\) 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 magnetoresistance-like effect.\(^15\) \(\text{MnAs}\) 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 \(\text{NiAs}\)-type to an orthorhombic MnP-type structure.\(^15\) Crystal structure and magnetic properties of \(\text{Mn}_{1-x}\text{Cr}_x\text{As}\) solid solutions have been investigated systematically in the whole composition range.\(^16\) For \(x > 0.5\), the \(\text{Mn}_{1-x}\text{Cr}_x\text{As}\) 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 \(\text{MnAs}\) with \(\text{NiAs}\)-type structure is kept for a slight doping \((x < 0.05)\) with \(\text{Cr}\).

Polycrystalline \(\text{Mn}_{1-x}\text{Cr}_x\text{As}\) compounds with \(x=0.006\) and 0.01 were synthesized by a method we developed to avoid the volatilization of \(\text{As}\) and long reaction-sintering treatments. Powders of \(\text{Mn}, \text{Cr}, \text{and As}\) 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 \(\text{NiAs}\)-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 \(\text{Mn}_{1-x}\text{Cr}_x\text{As}\) 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 \(\text{Mn}_{0.99}\text{Cr}_{0.01}\text{As}\) (or \(\text{Mn}_{0.99}\text{Cr}_{0.005}\text{As}\)). The magnetic phase transition temperatures are roughly in agreement with the previous work.\(^16\) As reported earlier,\(^16\) in analogy with \(\text{MnAs}\), this transition is accompanied by a structural transi-
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, $\text{Mn}_{1-x}\text{Fe}_x\text{As}$ or $\text{Mn}_{1-x}\text{Cu}_x\text{As}$, the present $\text{Mn}_{1-x}\text{Cr}_x\text{As}$ 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 $\text{Mn}_{0.994}\text{Cr}_{0.006}\text{As}$ almost overlap, meaning that the thermal hysteresis has been eliminated. From Fig. 1, the thermal hysteresis of $\text{Mn}_{0.99}\text{Cr}_{0.01}\text{As}$ is reduced to about 5 K. Such reduction/elimination is somehow similar to the large reduction of hysteresis losses by the iron addition in GMCE materials such as Gd$_5$Ge$_2$Si$_2$.18

Mira et al.15 observed directly a field-induced structural transition from the orthorhombic B31 phase to the hexagonal $B_8$ phase in MnAs. To explore the influence of the external field on the structural transition and the possible GMCE in $\text{Mn}_{1-x}\text{Cr}_x\text{As}$, the $M$ ($B$) curves are shown in Figs. 2(a) and 2(b). For $\text{Mn}_{0.99}\text{Cr}_{0.01}\text{As}$, 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.

$\text{Mn}_{0.994}\text{Cr}_{0.006}\text{As}$ 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 $\Delta S_M$ is expected in $\text{Mn}_{1-x}\text{Cr}_x\text{As}$ 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:

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

The sign of $\Delta S_M$ is determined by the sign of $\partial M/\partial T$, as shown in formula (1). Figure 3 gives $\Delta S_M(T)$ curves of $\text{Mn}_{1-x}\text{Cr}_x\text{As}$ compounds for a magnetic field change of 5 T. Here, the sign of $\Delta S_M$ is negative. That is, the present compounds show a conventional MCE, cooling by adiabatic demagnetization. The maximum $\Delta S_M$ with a field change of 5 T is 20.2 J/kg K at 267 K for $\text{Mn}_{0.99}\text{Cr}_{0.01}\text{As}$ and 13.7 J/kg K at 292 K for $\text{Mn}_{0.994}\text{Cr}_{0.006}\text{As}$. The $\Delta S_M$ exhibits its maximum around the first-order phase-transition temperature, meaning that the field-induced metamagnetic transition is responsible for the giant negative $\Delta S_M$ in $\text{Mn}_{1-x}\text{Cr}_x\text{As}$. The values of $\Delta S_M$ 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$_x$)$_2$, MnFeP$_{1-x}$As$_x$, MnAs$_{1-x}$Sb$_x$, and NiMnGa.19 Moreover, as stated above, the magnetic hysteresis has been eliminated in $\text{Mn}_{0.994}\text{Cr}_{0.006}\text{As}$. In addition, there are also some other advantages of $\text{Mn}_{1-x}\text{Cr}_x\text{As}$ as a magnetic refrigerant material. Firstly, the...
transition temperature $T_c$ in the Mn$_{1-x}$Cr$_x$As system can be set at any temperature from 313 to 253 K with the Cr concentration being lower than 5 at. %.

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).

Finally, the lower cost of the constituent materials, compared with Gd, Gd$_{5}$Ge$_{23}$Si$_{17}$, and NiMnGa (Ref. 19) alloys, is another advantage of the present system. Consequently, it is believed that the Mn$_{1-x}$Cr$_x$As alloys are suitable candidates for room-temperature magnetic refrigeration.

In conclusion, the Mn$_{1-x}$Cr$_x$As compounds with $x \approx 0.006$ and 0.01 exhibit giant room-temperature MCE with reduced (or even without) hysteretic behavior. A maximum value of $\Delta S_M$ 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 $\Delta S_M$ 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$_x$As system may have significant impact on the realization of room-temperature magnetic refrigeration.

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