Extremely Large Magnetic Entropy Change of MnAs$_{1-x}$Sb$_x$

near Room Temperature

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Magnetization of MnAs$_{1-x}$Sb$_x$ was measured as functions of temperature and magnetic field for 0 ≤ x ≤ 0.4. The entropy change caused by a magnetic field, $\Delta S_{mag}$, was estimated on the basis of the Maxwell relation. The $\Delta S_{mag}$ for 0 ≤ x ≤ 0.3 in a field change of 5 T reaches 25–30 J/K kg, which exceeds that of other materials by a factor of 2–4. The substitution of Sb for As can tune the Curie temperature between 230 K and 315 K without any significant reduction of $\Delta S_{mag}$. The large $\Delta S_{mag}$ originates in a paramagnetic to ferromagnetic transition induced by a magnetic field. These results indicate that MnAs$_{1-x}$Sb$_x$ is a promising material for a working substance in magnetic refrigeration near room temperature.

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1. Introduction

Magnetocaloric effect (MCE) refers to the isothermal entropy change or the adiabatic temperature change caused by the application or removal of a magnetic field. Magnetic materials showing a large MCE have attracted much attention for their potential application as a working substance in magnetic refrigeration. Compared with gas refrigeration, the magnetic refrigeration has a number of advantages such as high energy efficiency and environmental safety. Recently, Pecharsky and Gschneidner Jr. found that Gd$_5$Si$_2$Ge$_2$ exhibits an extraordinarily large MCE near room temperature. This compound undergoes a first-order magnetic transition (FOMT) between ferromagnetic and paramagnetic states at 276 K. The discovery of a large MCE of Gd$_5$Si$_2$Ge$_2$ has a significant impact on the utilization of FOMT materials in magnetic refrigeration. Subsequently, the MCE of various materials undergoing a FOMT has been examined. Although some materials have a large MCE comparable to Gd$_5$Si$_2$Ge$_2$, no studies have reported a material superior to Gd$_5$Si$_2$Ge$_2$ in the MCE.

We have independently pointed out the possibility of a large MCE of a FOMT system between ferromagnetic and paramagnetic states in the study of ErCo$_2$. Quite recently, we reported that MnAs shows a giant MCE, which undergoes a first-order ferromagnetic to paramagnetic transition at 318 K. The magnetic entropy change caused by a magnetic field of 5 T is as large as 30 J/K kg at a maximum value, which exceeds that of Gd$_5$Si$_2$Ge$_2$ by a factor of 2. The adiabatic temperature change reaches 13 K in a field change of 5 T. However, the FOMT of MnAs is accompanied by a large thermal hysteresis, which is unfavorable to practical use. Furthermore, it is desirable to tune the Curie temperature in the subroom temperature range (~250–300 K). It has been reported that the FOMT of MnAs is suppressed by the substitution of Sb for As. In this paper, we present the results of the entropy change by magnetic field of MnAs$_{1-x}$Sb$_x$.

2. Experiments

The MnAs$_{1-x}$Sb$_x$ samples with 0 ≤ x ≤ 0.4 were prepared by solid-vapor reaction. Powders of Mn and As were sealed in evacuated quartz tubes and sintered at 800°C for 7 days. The reaction products were crushed and subjected again to the same heat treatment. The X-ray diffraction patterns indicated that the samples were almost of a single phase with the NiAs-type structure. The lattice parameters a and c increases with increasing x, being in agreement with the previous reports. Magnetic entropy change, $\Delta S_{mag}$, was evaluated by using the relation,

$$\Delta S_{mag} = \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH. \quad (1)$$

The magnetization, $M$, vs. temperature curves were measured in a commercial SQUID at a constant field from 0 to 5 T.

3. Results

MnAs is a ferromagnet with saturation magnetization of 3.4 $\mu_B$/Mn. A first-order ferromagnetic to paramagnetic transition takes place at $T_C$ = 318 K. This transition is accompanied by a structural transformation from a hexagonal NiAs-type to an orthorhombic MnP-type structure. Figure 1(a) shows the $M$-$T$ curves of MnAs near $T_C$ in various magnetic fields. Data were collected in the heating process. The $M$-$T$ curves exhibit discontinuities at $T_C$ in any of the magnetic fields studied, indicating that a sharp FOMT is retained in high magnetic fields. The Curie temperature increases remarkably with increasing $\mu_0 H$ with a slope of 3.4 K/T.

Figure 1(b) displays the magnetization curves of MnAs near $T_C$ of which the data were converted from $M$-$T$ curves in various fields. A sharp metamagnetic transition was observed above 320 K. This is a field-induced paramagnetic to ferromagnetic transition. The transition field increases as the temperature is raised. The magnetic entropy change of MnAs is depicted in Fig. 2 as a function of temperature. Note that the vertical scale of Fig. 2 is negative. The $\Delta S_{mag}$ of MnAs shows a precipitous rise at 315 K irrespective of magnetic

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Fig. 1 (a) Magnetization vs. temperature curves of MnAs in the heating process. (b) Magnetization curves of MnAs near $T_C$. The data were converted from $M$-$T$ curves in various magnetic fields.

Fig. 2 Magnetic entropy change caused by a magnetic field, $\Delta S_{\text{mag}}$, of MnAs as a function of temperature. The thick line represents the $\Delta S_{\text{mag}}$-$T$ curve of Gd$_5$Si$_2$Ge$_2$ in a field change of 5 T. The peak height of $\Delta S_{\text{mag}}$ is not strongly dependent on $\Delta H$, while the peak width increases linearly with increasing $\Delta H$. These are characteristics of FOMT systems. Spikes were observed at 317 K. These spikes are probably artifacts due to the procedure to evaluate $\Delta S_{\text{mag}}$, in which the integral of eq. (1) was approximated by the summation with a finite field interval. In Fig. 2, $\Delta S_{\text{mag}}$ of Gd$_5$Si$_2$Ge$_2$ in a magnetic field change of 0–5 T was also plotted for comparison. This compound is known as a material with a giant field change, $\Delta H$. The peak height of $\Delta S_{\text{mag}}$ is not strongly dependent on $\Delta H$, while the peak width increases linearly with increasing $\Delta H$. These are characteristics of FOMT systems. Spikes were observed at 317 K. These spikes are probably artifacts due to the procedure to evaluate $\Delta S_{\text{mag}}$, in which the integral of eq. (1) was approximated by the summation with a finite field interval. In Fig. 2, $\Delta S_{\text{mag}}$ of Gd$_5$Si$_2$Ge$_2$ in a magnetic field change of 0–5 T was also plotted for comparison. This compound is known as a material with a giant $\Delta S_{\text{mag}}$ near room temperature.

MCE. The $\Delta S_{\text{mag}}$ of MnAs is about twice as large as that of Gd$_5$Si$_2$Ge$_2$. These results indicate that MnAs shows an extremely large $\Delta S_{\text{mag}}$ near room temperature.

The MnAs$_{1-x}$Sb$_x$ system forms solid solutions in the whole concentration range of $x$. The substitution of Sb for As stabilizes the NiAs-type structure. No structural transformation was observed for $x \geq 0.1$. The magnetic properties of MnAs$_{1-x}$Sb$_x$ were reported by various groups. Although $T_C$ of MnSb is higher than that of MnAs, $T_C$ first decreases, reaches a minimum value at around $x = 0.3$ and finally increases with increasing the Sb content. We studied the concentration dependence of $T_C$ of MnAs$_{1-x}$Sb$_x$, which was illustrated in Fig. 3. The Curie temperature was determined from the $M$-$T$ curves at $\mu_0 H = 0.01$ T. Our results are in agreement with the previous data reported by Ido et al. Figure 4 shows the $M$-$T$ curves of MnAs$_{1-x}$Sb$_x$ with $0 \leq x \leq 0.10$ in both heating and cooling processes in a magnetic field of 1 T. The magnetic transition of MnAs is accompanied by a large thermal hysteresis with the temperature width of 6.5 K, while the compounds with $x = 0.05$ and 0.10 exhibit no hysteretic behavior in their $M$-$T$ curves. Ido
et al. examined magnetovolume effects of MnAs$_{1-x}$Sb$_x$.\textsuperscript{10) They reported the disappearance of the structural transformation for $x \geq 0.1$. Furthermore, the magnetic transition becomes of second-order for $x \geq 0.1$. These results indicate that the FOMT of MnAs is related with the structural transformation. Thus, the absence of thermal hysteresis is associated with the disappearance of the structural transformation in MnAs$_{1-x}$Sb$_x$. Although the FOMT disappears for $x \geq 0.1$, the magnetic properties of MnAs$_{1-x}$Sb$_x$ with $x \geq 0.1$ are still unusual. The spontaneous magnetization sharply decreases with increasing temperature.\textsuperscript{10) The metamagnetic transition is observed above $T_C$ for $x = 0.3$.\textsuperscript{13} Moreover, the compounds with $x \leq 0.3$ show strong pressure dependences of $T_C$ and $M$.\textsuperscript{8,10,12,14} The $M$-$T$ curves of MnAs$_{1-x}$Sb$_x$ with $x = 0.3$ and 0.4 are displayed in Figs. 5(a) and 5(b). The magnetization of $x = 0.3$ shows a sharp but continuous temperature variation. The $T_C$ of $x = 0.3$ increases with increasing field in a manner similar to that of MnAs. Compared with $x = 0.3$, the magnetization of $x = 0.4$ decreases more gradually with increasing temperature. The magnetization curves of $x = 0.3$ and 0.4 are depicted in Figs. 6(a) and 6(b), respectively. The compound with $x = 0.3$ undergoes a clear metamagnetic transition just above $T_C$, similarly to MnAs. The magnetic moment after the metamagnetic transition is about $2\mu_B$/Mn, which is nearly the same as that of MnAs. The MnAs$_{1-x}$Sb$_x$ compounds with $0.05 \leq x \leq 0.25$ exhibit similar magnetic behavior to $x = 0.3$. The magnetization curves of $x = 0.4$ are still unusual, but the metamagnetic transition is much broader than that of $x = 0.3$. These results suggest that the critical concentration for the onset of metamagnetic transition is at around $x = 0.4$. Therefore, the metamagnetic transition is not associated with the structural transformation. Figures 7(a) and 7(b) show the $\Delta S_{mag}$-$T$ curves of $x = 0.3$ and 0.4. For $x = 0.3$, the peak height of $\Delta S_{mag}$ is little sensitive to $\Delta H$. The peak width increases with increasing $\Delta H$. This is due to the fact that $T_C$ varies in a linear fashion with increasing field. These characteristics are similar to the $\Delta S_{mag}$-$T$ curves of MnAs shown in Fig. 2. On the other hand, the $\Delta S_{mag}$-$T$ curves of $x = 0.4$ are more symmetric than those of $x = 0.3$, especially in high magnetic fields. Both the peak height and the peak width are dependent on $\Delta H$. These are typical behavior of the system undergoing a second-order magnetic transition. The temperature dependence of $\Delta S_{mag}$ of MnAs$_{1-x}$Sb$_x$ with $0 \leq x \leq 0.4$ is depicted in Fig. 8 for $\Delta H = 5$ T. The peak height of $\Delta S_{mag}$ is almost unchanged in $0 \leq x \leq 0.3$, while the Curie temperature is decreased from 315 K to 230 K. For $x = 0.4$, $\Delta S_{mag}$ is considerably reduced. These results indicate that $T_C$ can be tuned in a wide temperature range with retaining the giant $\Delta S_{mag}$ in MnAs$_{1-x}$Sb$_x$.

4. Discussion

The present results have demonstrated the extremely large $\Delta S_{mag}$ of MnAs$_{1-x}$Sb$_x$ near room temperature. It is clear that
the large $\Delta S_{\text{mag}}$ is associated with the metamagnetic behavior. The transition from a paramagnetic state to a ferromagnetic state is induced by a magnetic field in $\text{MnAs}_{1-x}\text{Sb}_x$, which causes a giant entropy change. However, the origin of the metamagnetic transition is still unclear. Recently, Goto \textit{et al.} examined the pressure effect on the metamagnetic transition of $\text{MnAs}_{0.7}\text{Sb}_{0.3}$. They found that applying pressure destabilizes the metamagnetic transition, which is in contrast to usual itinerant-electron metamagnets. They also calculated the electronic structure of MnAs as a function of lattice constant, $a$. It was revealed that the magnetic moment varies linearly with increasing $a$ in MnAs. This behavior is different from that of itinerant-electron metamagnets, in which the magnetic moment suddenly appears above a critical lattice parameter. These results suggest that the metamagnetic behavior of MnAs is not understood in a framework of spin fluctuation theory of itinerant-electron metamagnetism. Goto \textit{et al.} pointed out that a large magnetovolume coupling is a possible origin of anomalous magnetic properties of $\text{MnAs}_{1-x}\text{Sb}_x$. To clarify this problem, further investigations on the mechanism of magnetovolume coupling are desired. The adiabatic temperature change, $\Delta T_{ad}$, is another important quantity of the MCE. For MnAs, $\Delta T_{ad}$ was estimated by combining the $\Delta S_{\text{mag}}$ curves and early specific heat data. The $\Delta T_{ad}$ reaches 13 K for $\Delta H = 5$ T. This value is comparable to that of Gd$_5$Si$_2$Ge$_2$, $\Delta T_{ad} = 15$ K. Although $\Delta T_{ad}$ of $\text{MnAs}_{1-x}\text{Sb}_x$ was not estimated yet, we point out that the compound with $x = 0.3$ has a large $\partial T_C/\partial H$ value. Figure 5(a) suggests that $T_C$ increases linearly with increasing field with a slope of 3 K/T. In the FOMT, a large $\partial T_C/\partial H$ is responsible for a large $\Delta T_{ad}$; if a large entropy change at $T_C$ is retained in magnetic field. Although the magnetic transition of $x = 0.3$ is not of first-order, this discussion is applicable to the system in the vicinity of the FOMT. Therefore, we can expect fairly large $\Delta T_{ad}$ values for the Sb substituted compounds. Thermodynamically, $\partial T_C/\partial H$ is expressed as,

$$\frac{\partial T_C}{\partial H} = \frac{\Delta M}{\Delta S},$$

where $\Delta M$ and $\Delta S$ are the magnetization jump and the entropy jump at $T_C$, respectively. Obviously, the large $\Delta S$ is necessary to produce large $\Delta S_{\text{mag}}$, so that we have to request large $\Delta M$ for a large value of $\partial T_C/\partial H$ and hence $\Delta T_{ad}$. As shown in Figs. 1(b) and 6(b), the $\Delta M$ of $\text{MnAs}_{1-x}\text{Sb}_x$ is about $2 \mu_B$/Mn. This large $\Delta M$ value is responsible to large $\partial T_C/\partial H$ in the present system.

The recent progress of an active magnetic regenerator (AMR) has opened the field of room temperature magnetic refrigeration for practical use. Zimm \textit{et al.} presented the proof-of-principle AMR refrigerator, which operates near room temperature. The magnetic field up to 5 T is generated by a superconducting magnet and Gd is used as a working substance. This machine provides 600 W of cooling power in 5 T. In this context, the development of a material with a giant MCE is strongly desired, because it enables us to operate the magnetic refrigerator by using a permanent magnet. The FOMT materials are advantageous to a working substance in the AMR refrigerator, because they exhibit a large MCE in a relatively weak magnetic field. A narrow temperature range of a large MCE in the FOMT system can be overcome by hybridizing the materials with different $T_C$. In this sense, $\text{MnAs}_{1-x}\text{Sb}_x$ is quite promising, because (1) $T_C$ can be tuned between 230 and 315 K without any significant reduction of the MCE, (2) no hysteretic behavior for 0.05 $\leq x \leq 1$ and (3) $\text{MnAs}_{1-x}\text{Sb}_x$ is less costly than any other materials proposed for a working substance so far. We believe the discovery of the giant MCE of $\text{MnAs}_{1-x}\text{Sb}_x$ will have an exciting impact on the realization of magnetic refrigeration using a permanent magnet.
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