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Pressure dependence of magnetic entropy change and magnetic transition in $MnAs_{1-x}Sb_x$

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The pressure dependence of magnetic entropy change, ΔS, of $MnAs_{1-x}Sb_x$ has been examined. The peak values of ΔS of MnAs and $MnAs_{0.93}Sb_{0.07}$ are slightly increased with increasing pressure below the critical pressure for disappearance of the NiAs-type structure. It has been revealed that $MnAs_{0.93}Sb_{0.07}$ undergoes a first-order magnetic transition with and without a structural transformation depending on pressure. The entropy change associated with the structural transformation, ΔS_{st}, is found to be at most 10% of ΔS in this compound. The origin of small ΔS_{st} in this system is discussed. The peak value of ΔS of $Mn_{1.03}As_{0.7}Sb_{0.3}$ is gradually decreased with increasing pressure above 2.47 kbar, which is due to broadening of the magnetic transition under high pressure.

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The magnetocaloric effect (MCE) of a magnetic material is defined as the isothermal magnetic entropy change or as the adiabatic temperature change in the presence of a magnetic field. In the last decade, materials with large MCEs have been attracting considerable interest for their potential application as working materials in magnetic refrigeration. Recently, several materials, such as $Gd_5Si_2Ge_2$, $MnFeP_{0.45}As_{0.55}$, and $La(Fe_{1-x}Si_x)_{13}$ and its hydrides, which undergo a first-order magnetic transition (FOMT), have been found to exhibit giant MCEs near room temperature.[1–4] The details of the MCE of these compounds have been summarized in recent reviews.[5,6]

$MnAs_{1-x}Sb_x$ is a member of giant MCE materials.[7,8] MnAs has the hexagonal NiAs-type structure below a Curie temperature, $T_C=317$ K and above $T_t=398$ K. Between T_C and T_t, the compound has the orthorhombic MnP-type structure. The ferromagnetic (FM) to paramagnetic (PM) transition at T_C is first-order accompanied by large thermal hysteresis of ~ 6 K, while that at T_t is second order. The isothermal magnetic entropy change, ΔS, of MnAs in a field change of 5 T is 35 J/K kg at T_C, which is one of the largest values near room temperature. The substitution of Sb for As stabilizes the NiAs-type structure. Although the structural transformation is suppressed, a FOMT is observed for $0 \leq x \leq 0.30$. The Curie temperature decreases from 317 to 220 K with increasing the Sb content from 0 to 30%, while the ΔS has almost the same high value in this concentration range. Furthermore, the width of thermal hysteresis is reduced to less than 1 K by the Sb substitution. These results indicate that $MnAs_{1-x}Sb_x$ is a possible candidate for magnetic refrigerant materials near room temperature.

In 2004, Gama *et al.*[9] studied the MCE of MnAs under hydrostatic pressure. They reported strong enhancement of ΔS by pressure with a maximum value of 267 J/K kg at $p=2.23$ kbar. Surprisingly, this ΔS value is far above the total magnetic entropy, $R\log(2S+1)=103$ J/K kg, where R is the gas constant and S is the spin quantum number, if we adopt $S=2$ for MnAs. Subsequently, they reported that $Mn_{1-x}Fe_xAs$ with $0.003 \leq x \leq 0.0125$ and $Mn_{1-x}Cu_xAs$ with $0.006 \leq x \leq 0.02$ also show the "colossal" ΔS at ambient pressure.[10,11] However, the origin of the colossal MCE is still unclear. von Ranke *et al.*[12] proposed a model, in which the lattice entropy change makes a significant contribution to ΔS due to strong magnetoelastic coupling. However, they had to assume anomalously large and negative values for the Grüneisen parameter of approximately −10, which are one order of magnitude larger than those of ordinary metals and compounds. Moreover, the reason why the colossal MCE appears in a narrow pressure range or in a specific composition range has not been clarified. Quite recently, Plaza and Campoy pointed out that the abrupt change in the exchange constant at T_C is a possible origin of the giant or colossal MCE in the FOMT system with the structural transformation.[13]

Keeping these results in mind, we reexamined the pressure dependence of ΔS of MnAs. Another purpose of the present study is to investigate the magnetic and structural transitions of $MnAs_{1-x}Sb_x$ under high pressure. Early studies have reported that pressure stabilizes the MnP-type structure in MnAs and $MnAs_{0.9}Sb_{0.1}$.[14,15] The magnetic ground state of MnAs with the MnP-type structure is antiferromagnetic (AF). Thus, MnAs undergoes a first-order NiAs-type (FM) $\rightarrow$ MnP-type (PM) transition at $p=0$ kbar, while a second-order AF to PM transition within the MnP-type structure takes place at $p>3$ kbar. On the other hand, we have recently revealed that $MnAs_{0.9}Sb_{0.1}$ undergoes a first-order FM to PM transition within the NiAs-type structure at ambient pressure.[16] A question arises as to where the MnP-type structure emerges in the T-p phase diagram. As described later, the magnetization measurements give fruitful information on the pressure-induced structural and magnetic transitions.

The samples of MnAs, $MnAs_{0.93}Sb_{0.07}$, and $Mn_{1.03}As_{0.7}Sb_{0.3}$ were prepared by solid-vapor reaction. Here, Mn is slightly enriched for $x=0.3$ to obtain a single phase of the NiAs-type structure.[8] Powder of Mn (3 N), As (6 N), and Sb (5 N) weighed in a required proportion were sealed in an evacuated quartz tube, which was heated at 600 °C for 7 days. The products were pulverized, mixed, and subjected to further heat treatments. The samples were annealed at 1000 °C, then quenched into iced water and finally annealed at 600–800 °C for 4 days. The magnetization (M) under pressure was measured by using either a commercial superconducting quantum interference device (SQUID) magnetometer or our extraction-type magnetometer combined with a clamp cell made of a Cu-Ti alloy up to 7 kbar. Fluorinert 70/77 was used as the pressure transmitting medium. Pressure was determined by comparing the observed T_C with the one from the T-p phase diagram. The T-p phase diagram of MnAs was already established by early studies.[14,15] For $MnAs_{1-x}Sb_x$, we measured the temperature dependence of magnetization of the mixture of MnAs and the Sb substituted compound under pressure. From the observed T_C's, we constructed the T-p phase diagram for each Sb composition. The magnetic entropy change, ΔS, was estimated from the Maxwell relation,

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

For $x=0$ and 0.07, the M-T curves were measured in the heating process after the samples were cooled down far below T_C in zero field. The isothermal magnetization curves were measured below and above T_C for $x=0.03$. Since the hysteresis is quite small, we used the M-H curves with increasing magnetic field to calculate ΔS.

Figures 1(a) and 1(b) show the temperature dependence of magnetization of MnAs and $MnAs_{0.93}Sb_{0.07}$ in a magnetic field of 1 T under various pressures, respectively. As pressure is increased from 0 to 2.09 kbar, the T_C of MnAs is decreased nearly linearly, while the ferromagnetic moment remains in a high value more than 100 emu/g. Further increase in pressure suddenly reduces the ferromagnetic moment. This is because MnAs is transformed from the NiAs-type structure to the MnP-type structure over the whole temperature range studied. The critical pressure for disappearance of the NiAs-type structure, p_C, is in the vicinity of 2.5 kbar. We observed an antiferromagnetic peak in the susceptibility (χ) vs temperature curve of MnAs at 230 K under a pressure of 3.0 kbar. In the case of $MnAs_{0.93}Sb_{0.07}$, the high ferromagnetic moment is retained up to 5.93 kbar. These results indicate that the substitution of 7% Sb for As increases p_C up to about 6 kbar. We notice a significant difference in the magnetization of $MnAs_{0.93}Sb_{0.07}$ just above T_C between the M-T curves below 3 kbar and those above 3 kbar. The M-T curves show tails in the paramagnetic region below 3 kbar. On the other hand, the M just above T_C at $p=3.37$ kbar and 5.93 kbar is quite small. This behavior is similar to MnAs. It has been reported that the paramagnetic χ of MnAs is weakly temperature dependent in the MnP-type phase, while it shows the Curie-Weiss behavior in the NiAs-type phase.[17] The χ^{-1}-T curve of $MnAs_{0.93}Sb_{0.07}$ at $p=0$ kbar was found to follow the Curie-Weiss law with the paramagnetic effective magnetic moment, μ_{eff}, of $4.0\mu_B/\text{Mn}$ and the Weiss temperature, Θ, of 284 K. These values are close to those of MnAs with the NiAs-type structure above T_t at $p=0$ kbar: $\mu_{\text{eff}}=4.45\mu_B/\text{Mn}$ and $\Theta=288$ K.[17] At $p=2.27$ kbar, we obtained $\mu_{\text{eff}}=4.0\mu_B/\text{Mn}$ and $\Theta=267$ K. On the other hand, the χ does not show the Curie-Weiss behavior above 3 kbar. These results strongly suggest that the FOMT of $MnAs_{0.93}Sb_{0.07}$ above 3 kbar is accompanied by the structural transformation from the NiAs-type structure to the MnP-type structure. This is also supported by thermal hysteresis. Previously, Zavadskiĭ and Todris examined the pressure dependence of the M-T curves of $MnAs_{0.88}Sb_{0.12}$.[18] They reported that the magnetic transition has no thermal hysteresis at ambient pressure, while large thermal hysteresis of $\sim$10 K associated with the magnetic transition is observed above 4 kbar. From these results, we conclude that the FOMT within the NiAs-type structure takes place in $MnAs_{0.93}Sb_{0.07}$ below 2.27 kbar, while the compound undergoes the first-order NiAs-type (FM)→MnP-type (PM) transition at $3.37\ \text{kbar} \leq p \leq 5.93$ kbar. Above 7 kbar, the ferromagnetic NiAs-type structure is replaced by the paramagnetic (or antiferromagnetic) MnP-type structure.

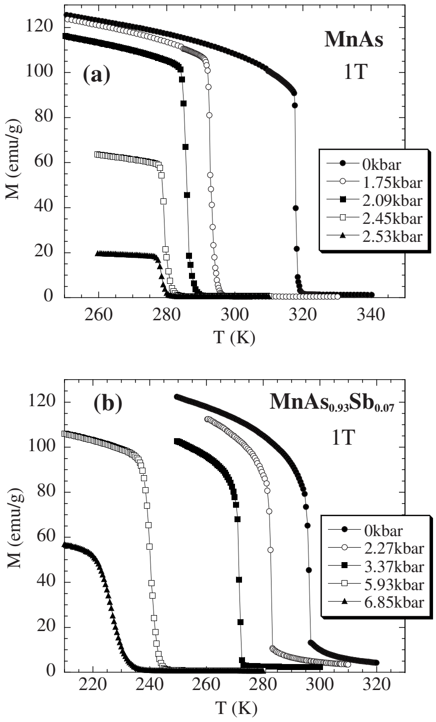

FIG. 1. Temperature dependence of magnetization of (a) MnAs and (b) $MnAs_{0.93}Sb_{0.07}$ in a magnetic field of 1 T under various pressures.

We also measured the M-T curves of $Mn_{1.03}As_{0.7}Sb_{0.3}$ under various pressures. The T_C decreases from 227 to 184 K with increasing pressure from 0 to 5.86 kbar. The high ferromagnetic moment and the Curie-Weiss behavior of χ were observed at $0 \leq p \leq 5.86$ kbar. Our M-T data are in agreement with the previous results by Goto *et al.*,[19] who reported the pressure dependence of magnetization of $MnAs_{0.7}Sb_{0.3}$ up to 12 kbar. These results suggest that $Mn_{1.03}As_{0.7}Sb_{0.3}$ undergoes the NiAs-type (FM)→NiAs-type (PM) transition at any pressures studied.

The temperature dependence of ΔS of MnAs and $MnAs_{0.93}Sb_{0.07}$ was calculated from the M-T curves. Both compounds exhibit the giant MCE in low magnetic fields at ambient pressure. We found that the peak value of ΔS is saturated above 1.4 T. These results allow us to compare the peak value of ΔS in a field change of 2 T at various pressures. The ΔS-T curves of MnAs and $MnAs_{0.93}Sb_{0.07}$ under various pressures are illustrated in Figs. 2(a) and 2(b), respectively. For MnAs, the peak value of ΔS is slightly pressure dependent below p_C and the highest value of 36 J/K kg is observed just below p_C. Above p_C, the ΔS is remarkably reduced due to the loss of ferromagnetism. Similar results were observed for $MnAs_{0.93}Sb_{0.07}$. For both systems, strong enhancement of ΔS was not observed in our study. The ΔS-T curves of $Mn_{1.03}As_{0.7}Sb_{0.3}$ estimated from the M-H curves are shown in Fig. 3. The pressure dependence of ΔS of

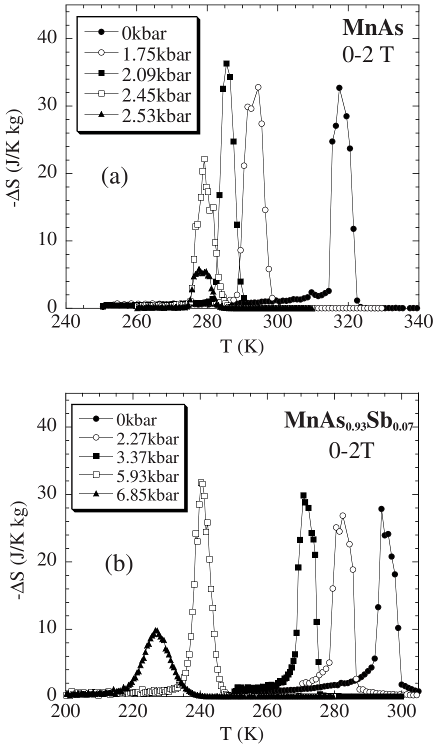

FIG. 2. Temperature dependence of the magnetic entropy change, ΔS, of (a) MnAs and (b) $MnAs_{0.93}Sb_{0.07}$ in a field change of 2 T under various pressures.

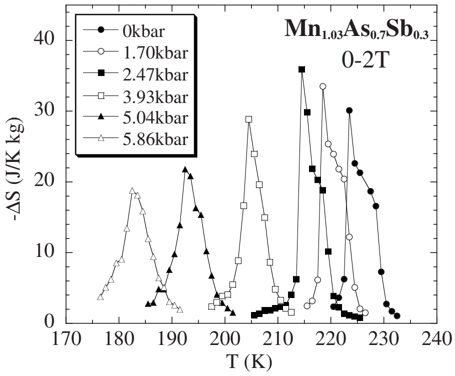

FIG. 3. Temperature dependence of ΔS of $Mn_{1.03}As_{0.7}Sb_{0.3}$ in a field change of 2 T under various pressures.

$Mn_{1.03}As_{0.7}Sb_{0.3}$ is somewhat different from those of MnAs and $MnAs_{0.93}Sb_{0.07}$. With increasing pressure, the peak value of ΔS is increased and shows a maximum, followed by a gradual decrease, although the NiAs-type structure is stable up to the highest pressure.

As pointed out by Gschneidner Jr. *et al.*,[6] we should be careful to apply Eq. (1) to the FOMT system because $(\partial M/\partial T)_H$ is infinite in an ideal FOMT. In real systems, the FOMT takes place over a few Kelvin wide temperature range and $(\partial M/\partial T)_H$ can be measured experimentally. In order to check the ΔS values derived from Eq. (1), we estimated ΔS by using the Clausius-Clapeyron relation given by

$$\Delta S = -\left(\frac{\partial T_C}{\partial H}\right)^{-1} \Delta M, \tag{2}$$

where $(\partial T_C/\partial H)$ is the field dependence of T_C and ΔM is the magnetization jump at T_C. Both quantities can be evaluated from the M-T curves at different fields. The validity of Eq. (2) in the FOMT has been confirmed in $MnAs_{1-x}Sb_x$ at ambient pressure and $Co(S_{1-x}Se_x)_2$.[8,20]

We assumed that the temperature dependence of M in the ferromagnetic region is expressed by a polynomial function of T. By extrapolating the calculated M-T curves to T_C, we obtained ΔM as a difference in magnetization between ferromagnetic and paramagnetic states. The M-T curves were measured in narrow temperature ranges, which make it difficult to estimate ΔM correctly. We plot the ΔS calculated from the Clausius-Clapeyron relation at 2 T for MnAs and $MnAs_{0.93}Sb_{0.07}$ as a function of pressure in Figs. 4(a) and 4(b), respectively, together with the peak values of ΔS from Figs. 2(a) and 2(b). In spite of ambiguity of the estimated ΔM, the agreement between two ΔS's is satisfactory for both compounds. These results strongly support the validity of our estimation of ΔS from the Maxwell relation.

The structural transformation at T_C would cause the lattice entropy change between the two structures, ΔS_{st}, which could contribute to the giant MCE. Thus, the observed ΔS is expressed by the sum of the magnetic entropy change due to pure magnetic origin (derived from magnetic degrees of freedom), ΔS_M, and ΔS_{st}, as[21]

$$\Delta S = \Delta S_M + \Delta S_{st}. \tag{3}$$

By comparing the MCE of $Gd_5(Si_{1-x}Ge_x)_4$ with and without FOMT, Pecharsky *et al.*[21] found that ΔS_{st} accounts for about a half of ΔS in low magnetic fields below 2 T. Morellon *et al.* examined the pressure dependence of the MCE of $Tb_5Si_2Ge_2$ and reported that the contribution of ΔS_{st} to ΔS is comparable to that of ΔS_M in a magnetic field of 5 T.[22] In the case of $MnAs_{0.93}Sb_{0.07}$, we observed two kinds of FOMTs: NiAs-type (FM) → MnP-type (PM) and NiAs-type (FM) → NiAs-type (PM) depending on pressure. As shown in Fig. 2(b), the peak value of ΔS at $p=3.37$ kbar is 30.0 J/K kg, which is slightly larger than that at $p=2.27$ kbar, 26.7 J/K kg. The ΔS_{st} is obtained as a difference between two values, which is at most 10% of ΔS in $MnAs_{0.93}Sb_{0.07}$. It should be noted that the ratio of ΔS_{st} to ΔS is expected to be independent of a magnetic field because the peak values of ΔS are saturated in the FOMT system. Our observations are consistent with the calculated results by Zou *et al.*[23] which suggested small ΔS_{st} in MnAs. In a different paper, they discussed ΔS_{st} from a thermodynamical point of view.[24] Assuming nonlinear volume dependence of internal pressure, they concluded that ΔS_{st} makes a negative contribution to ΔS, when the volume expands below T_C. MnAs is just this case and the FOMT is accompanied by a large volume expansion of 2.1% on cooling.[16] Here, we provide an alternative explanation for their conclusion. The volume expansion causes lattice softening below T_C. Therefore, we expect that the Debye temperature in the ferromagnetic state is lower than that in the paramagnetic state. When a ferromagnetic to paramagnetic transition takes place, the Debye temperature is abruptly increased at T_C, which gives a negative ΔS_{st}. Naturally, the Debye model is too simple and the volume change

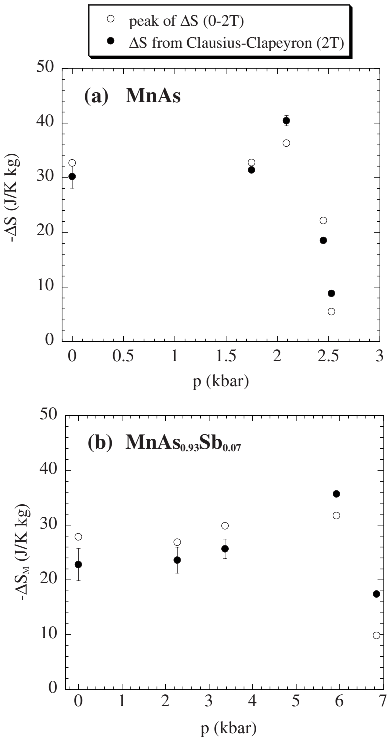

FIG. 4. Pressure dependence of ΔS estimated from the Clausius-Clapeyron relation of (a) MnAs and (b) $MnAs_{0.93}Sb_{0.07}$ in a field of 2 T (closed circles). Open circles represent the peak values of ΔS obtained from Figs. 2(a) and 2(b).

is not isotropic. The anisotropic volume change or the change of crystal symmetry would give a positive contribution of the lattice entropy, but it must be small. When the volume of a paramagnetic state is larger than that of a ferromagnetic state, on the other hand, the Debye temperature is expected to decrease at T_C on heating. This provides a positive contribution of ΔS_{st} to ΔS, as observed in $Gd_5Si_2Ge_2$ and $Tb_5Si_2Ge_2$.

Finally, we comment on the pressure dependence of ΔS of $Mn_{1.03}As_{0.7}Sb_{0.3}$. As shown in Fig. 3, the peak value gradually decreases with pressure above 2.47 kbar, although the NiAs-type (FM) state is retained. This is due to broadening of the magnetic transition under high pressure. We observed a sharp FOMT at ambient pressure, while the magnetization shows smooth temperature variation at $p=5.86$ kbar. Similar results were reported by Goto *et al.*[19] for $MnAs_{0.7}Sb_{0.3}$. In $MnAs_{1-x}Sb_x$, the magnetic transition changes from first order to second order at around $x=0.4$.[25] The $Mn_{1.03}As_{0.7}Sb_{0.3}$ is near the critical concentration for disappearance of the FOMT. The applied pressure destabilizes the FOMT, which reduces the peak value of ΔS in a field change of 2 T.

In conclusion, we studied the pressure dependence of ΔS of $MnAs_{1-x}Sb_x$. The peak values of ΔS of MnAs and $MnAs_{0.93}Sb_{0.07}$ are slightly increased with increasing pressure below the critical pressure for disappearance of the NiAs-type structure. No significant enhancement of ΔS by applied pressure was observed. Magnetization measurements have revealed that $MnAs_{0.93}Sb_{0.07}$ undergoes the first-order NiAs-type (FM) → NiAs-type (PM) transition below 2.27 kbar and the NiAs-type (FM) → MnP-type (PM) transition at $3.37 \text{ kbar} \leq p \leq 5.93$ kbar. The ΔS_{st} is found to be at most 10% of ΔS in this compound. The volume expansion below T_C is responsible for a small contribution of ΔS_{st} to ΔS. The peak value of ΔS of $Mn_{1.03}As_{0.7}Sb_{0.3}$ is gradually decreased with pressure above 2.47 kbar, which is due to broadening of the magnetic transition under high pressure.

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