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Giant magnetocaloric effect of $MnAs_{1-x}Sb_x$

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A giant magnetocaloric effect was found in MnAs, 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 the maximum value, which exceeds that of conventional magnetic refrigerant materials by a factor of 2–4. The adiabatic temperature change reaches 13 K in a field change of 5 T. The substitution of 10% Sb for As reduces the thermal hysteresis and lowers the Curie temperature to 280 K, while the giant magnetocaloric properties are retained. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1419048]

A magnetocaloric effect (MCE) means the isothermal entropy change or the adiabatic temperature change by application/removal of a magnetic field. Since magnetic refrigeration is expected to be a future technology because of its energy efficiency and environmental safety, the exploration of new materials with a large MCE is strongly desired. Recently, several systems undergoing a first-order magnetic transition (FOMT) were found to exhibit a large MCE.[1–4] A large entropy change in a FOMT originates from a difference in the degree of magnetic ordering between two adjacent magnetic phases. Thus, the FOMT from a ferromagnetic state to a paramagnetic one is expected to show a large MCE. In this letter, we present the results of the MCE of $MnAs_{1-x}Sb_x$.

MnAs is a ferromagnet with saturation magnetization of $3.4\mu_B$/Mn.[5] A first-order ferromagnetic to paramagnetic transition takes place at $T_C = 318\,K$. This transition is accompanied by a structural transition from hexagonal NiAs type to an orthorhombic MnP-type structure. Kuhrt *et al.* reported the MCE of MnAs.[6] They directly measured the adiabatic temperature change, ΔT_{ad}, and concluded that ΔT_{ad} is at most 0.2 K in a magnetic field change of 0.65 T at T_C. This value is one order of magnitude smaller than that of typical magnetic refrigerant materials, ~2 K/T. In their report, Kuhrt *et al.* corrected data by assuming a temperature gradient inside the sample. However, the reason for the correction was not clear. On the other hand, specific heat measurements of MnAs have revealed that the magnetic entropy jump at T_C is as large as 4.1 J/K mol.[7] This corresponds to 35% of the full magnetic entropy, $R\ln(2S+1) = 11.52$ J/K mol with $S = 3/2$ in the localized moment. Furthermore, T_C increases with an increase in magnetic field at a rate of 3–4 K/T.[8] These results strongly suggest that MnAs has a large MCE, if the large entropy jump is retained at high magnetic fields. With this in mind, we re-examined the MCE of MnAs. The FOMT of MnAs is accompanied by large thermal hysteresis, which is unfavorable for practical use. It has been reported that the substitution of Sb for As makes the transition broad and reduces the thermal hysteresis.[9] Moreover, the Curie temperature can be tuned between 230 and 318 K by varying the Sb concentration.

The samples were prepared by a 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. X-ray diffraction patterns indicated that the samples were almost of single phase with a NiAs-type structure. The magnetic entropy change, ΔS_{mag}, was evaluated using the relation, $\Delta S_{mag} = \int_0^H (\partial M/\partial T)_H dH$. Magnetization, M, versus temperature curves were measured in a commercial superconducting quantum interference device (SQUID) at constant field from 0 to 5 T in field intervals of 0.1 T.

Figures 1(a) and 1(b) show the temperature dependence of the magnetization of MnAs and $MnAs_{0.90}Sb_{0.10}$ at various magnetic fields. For MnAs, the magnetization shows a clear jump at T_C for all of the magnetic fields studied. The Curie temperature increases nearly linearly with an increase in magnetic field with a slope of 3.4 K/T. On the other hand, $MnAs_{0.90}Sb_{0.10}$ exhibits smooth temperature variation of the

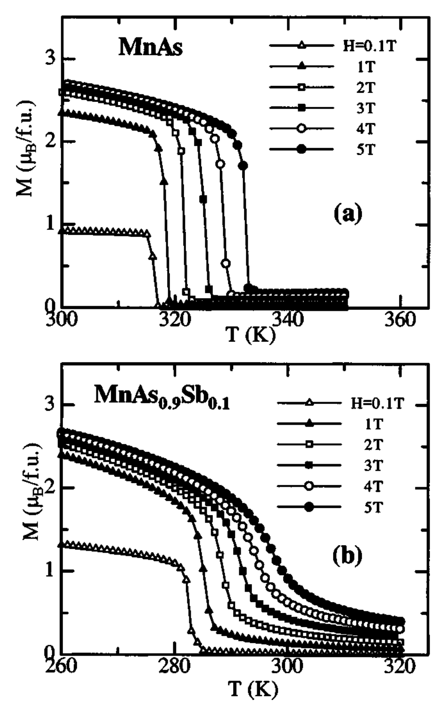

FIG. 1. Magnetization vs temperature curves of MnAs (a) and $MnAs_{0.9}Sb_{0.1}$ (b) at various magnetic fields.

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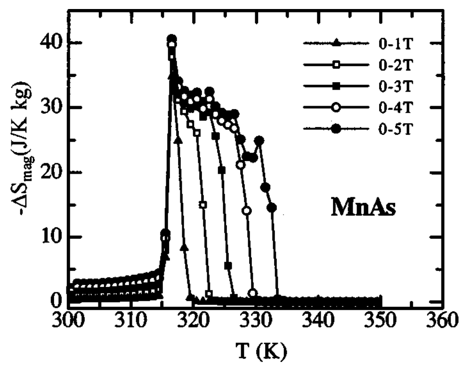

FIG. 2. Change in magnetic entropy caused by a magnetic field, ΔS_{mag}, of MnAs as a function of the temperature.

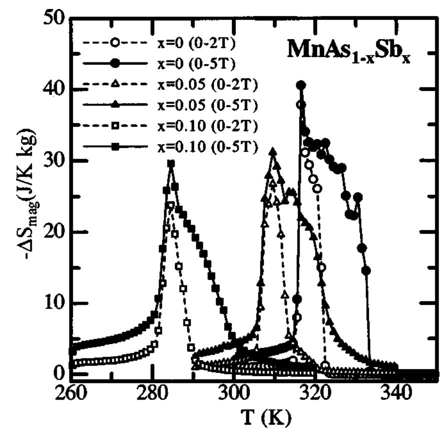

FIG. 4. ΔS_{mag} in field changes of 0–2 and 0–5 T vs the temperature of $MnAs_{1-x}Sb_x$.

magnetization particularly at high fields. However, the T_C of $MnAs_{0.90}Sb_{0.10}$ increases with an increase in the field in a manner similar to that of MnAs. Large thermal hysteresis of about 5 K was observed between the heating and cooling processes for MnAs, while it disappeared for $x \geqslant 0.05$. The change in magnetic entropy of MnAs is displayed in Fig. 2 as a function of the temperature. A large MCE was observed above 315 K. The peak height of ΔS_{mag} is not very sensitive to magnetic field change, ΔH, whereas the peak width increases nearly linearly with increasing ΔH. These are characteristics of systems that undergo a sharp FOMT even at high magnetic fields.[4] Spikes were observed at 317 K in all the $\Delta S_{mag}-T$ curves. These spikes are probably artifacts due to the procedure to evaluate ΔS_{mag}, in which summation with a finite field interval was employed instead of integration. Neglecting the spike, the peak height of ΔS_{mag} is roughly estimated as 32 J/K kg=4.2 J/K mol, which is in agreement with the magnetic entropy jump at T_C in the zero field described earlier. This is about twice as large as the peak value of $Gd_5Si_2Ge_2$, which is known as a material with a huge MCE.[1] It is also much larger than that of pure Gd, 9 J/K kg for $\Delta H = 5$ T.[1] The adiabatic temperature change, ΔT_{ad}, was evaluated using $\Delta S_{mag}-T$ curves and early specific heat data.[10] The results are depicted in Fig. 3 as a function of the temperature. Unlike ΔS_{mag}, both the peak height and the peak width are dependent on the change in magnetic field. The peak value of ΔT_{ad} is as large as 13 K for $\Delta H = 5$ T, which is comparable to that of $Gd_5Si_2Ge_2$, $\Delta T_{ad} = 15$ K.[1] From these results, we conclude that MnAs is a material with a giant MCE near room temperature. Figure 4 shows the temperature dependence of ΔS_{mag} of $MnAs_{1-x}Sb_x$ with $0 \leqslant x \leqslant 0.10$ for $\Delta H = 2$ and 5 T. As shown in Fig. 4, the Curie temperature decreased by 35 K with a 10% substitution of Sb for As, whereas the large MCE is retained up to $x = 0.10$, despite the disappearance of the FOMT. Our preliminary results suggest that T_C is lowered to 230 K for $x = 0.25$ without significant reduction of the MCE properties. These results have demonstrated that T_C can be tuned in a wide temperature range while retaining a giant MCE in $MnAs_{1-x}Sb_x$.

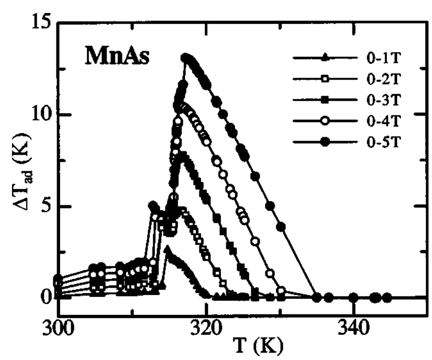

FIG. 3. Temperature dependence of the adiabatic temperature change, ΔT_{ad}, of MnAs.

Finally, we point out some advantages of $MnAs_{1-x}Sb_x$ as a magnetic refrigerant material. First, $MnAs_{1-x}Sb_x$ is less costly than any other magnetic refrigerant material so far proposed, because the conventional materials include some amounts of rare-earth metals. Second, the Sb-substituted compounds exhibit no hysteretic behavior. Furthermore, the Curie temperature varies gently with the Sb concentration, ranging from 318 to 230 K with an increase of x from 0 to 0.25. It is easy to tune the T_C of $MnAs_{1-x}Sb_x$ by changing the Sb concentration. Last, MnAs exhibits metallic behavior. In early studies using single crystals it was reported that its electrical resistivity is $\sim 100\ \mu\Omega$ cm at room temperature,[11] which is of the same order as that of Gd. Although no thermal conductivity has been reported for MnAs, proper thermal conductivity as a refrigerant material is expected, if the thermal conductivity follows Wiedemann–Franz law. These points suggest that $MnAs_{1-x}Sb_x$ is one of the most suitable candidates as a magnetic refrigerant material near room temperature.

The recent development of an active magnetic regenerator (AMR) has opened the field of magnetic refrigeration for practical use.[12] The concept of the AMR is a combination of magnetic refrigerants with a heat regenerating medium. Since AMR materials are required to show a large MCE over a wide temperature range, hybridizing a series of magnetic materials with a large MCE is encouraged. In this context, FOMT systems are advantageous, because they exhibit a large MCE in a relatively weak magnetic field.

In conclusion, we have demonstrated that MnAs exhibits a giant MCE near room temperature, contrary to what was reported previously. The observed values of ΔS_{mag} and ΔT_{ad} are superior or at least comparable to those of the magnetic refrigerant materials thus far proposed when the peak values are compared. The substitution of 10% Sb for As lowers T_C

by 35 K without any significant reduction of the MCE. We believe that the discovery of the giant MCE of $MnAs_{1-x}Sb_x$ will have a significant impact on the realization of magnetic refrigeration.

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