Co Doping Enhanced Giant Magnetocaloric Effect in Mn_{1-x}**Co**_x**As**

Films Epitaxied on GaAs (001)

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1. Introduction

Magnetic refrigeration, acting as a promising alternative to the well-established compression-evaporation cycle for room-temperature applications, is attracting more and more attention for its lower energy consumption, less noise generation and environment-protection. During the past decade much progress has been made in searching materials that exhibit large magnetocaloric effect (MCE). However, the main obstacle for this technology is still the need of high magnetic fields to obtain large enough temperature variations. Although Fe or Cu doped MnAs show colossal MCE around room temperature [1], the large thermal hysteresis severely hindered their practical application. While for MnAs films epitaxied on GaAs (001) or GaAs (111) B, although the entropy change does not fall in the colossal magnetocaloric effect range, the thermal hysteresis is small. An interesting question is what about the magnetocaloric effect of transition metal doped MnAs epitaxied on GaAs. In this letter, we will present some experimental results for Co doped MnAs films on GaAs (001).

2. Materials and methods

All the samples were grown on semi-insulating GaAs (001) substrates by molecular-beam epitaxy (MBE) using a V80 MARKI system. The growth process was monitored *in situ* by reflection high-energy electron diffraction (RHEED) at 11 keV and the substrate temperature *Ts* was measured by a W–Re thermal couple. A 100 nm undoped GaAs buffer layer was first grown to smoothen the surface at *Ts* =560 °C. Then the substrate temperature was lowered to 260°C for the growth of Co doped MnAs films. The nominal Co concentration for samples A, B, C and D are 0%, 0.24%, 0.5% and 1% respectively. The Mn_{1-x}Co_xAs film mass was obtained after the thickness determined by scan-

scanning electron microscope, assuming a density of 6.3 g/cm³ for MnAs.

The temperature dependence of the magnetization of series of Mn_{1-x}Co_xAs compounds was measured during both warming and cooling process in a field of 0.02 Tesla from 5 to 400 K (as shown in Fig. 1). For all the Co doped MnAs films studied here, the saturation magnetization enhances drastically comparing with the pure MnAs film at low temperature, which is with inverse trend from that of Fe or Cu doped MnAs [1,2]. Clearly as the concentration of Co increases the transition temperature shifts to lower temperature. Similar feature can be observed in the minimum of first order derivative of the magnetization (dM/dT) (not shown here). The warming and cooling magnetization curves almost overlap for MnAs and Mn_{0.9975}Co_{0.0025}As the meaning that thermal hysteresis is small.



Fig. 1. Temperature dependence of the remnant magnetization M_r for samples A–D. The inset is an enlargement of the M_r -T curve from 260 K to 330 K. It is clear that as the concentration of Co increases the transition temperature shifts to lower temperature.

Magnetic field dependence of magnetization was monitored in a step of 0.2 Tesla from 0 to 4 Tesla in the temperature range of 270 K -334 K with increasing both magnetic field and temperature. The value of the isothermal entropy change Δ SM (T, B) is given by the following expression associated with the Maxwell relationship:

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

This equation predicts a significant MCE when the magnetization variation with temperature is maximum, which occurs at the magneto-structural transition temperature of $Mn_{1-x}Co_xAs$. Figure 2 shows the entropy changes as a function of temperature and magnetic field intervals for both MnAs films and $Mn_{1-x}Co_xAs$. For MnAs films on GaAs (001) the MCE curve shows a maximum with the value of 11 J/Kg K. Substitution of Mn atoms by a few percent of Co (0.25%) results in an enhanced MCE with a maximum entropy change of about 25 J/Kg K. Further increasing the concentration of Co atoms results in a reduced MCE accompanied by a slightly drop in M_s (saturation magnetization).



Fig. 2. The giant magnetocaloric effect for $Mn_{1-x}Co_xAs$ as a function of temperature and Co content for a magnetic field variation of 1 Tesla (circles), 2 Tesla (up triangles), 3 Tesla (diamonds) and 4 Tesla (pentacles), respectively. The measurements were carried out with increasing temperature and magnetic field.

4. Conclusions

In summary, we have investigated the MCE of Co doped MnAs films grown on GaAs (001). It comes out that the saturation magnetization shows a sudden increase with small amount of Co doping. Comparing with pure MnAs films, $Mn_{1-x}Co_xAs$ compounds exhibit enhanced MCE around room temperature with transition temperature tunable by varying Co content, which may find applications in construction of layered magnetic regenerator refrigerators with drastically enhanced refrigerating power. The small thermal hysteresis makes $Mn_{1-x}Co_xAs$ materials more attractive comparing with other magnetic refrigeration materials. Our experimental result may find applications in the microelectronic circuitry as well as spintronic devices.

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References

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 (2006) 802.

[2] 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** (2007) 242507.