Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Magnetism and Magnetic Materials 290–291 (2005) 706–708
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Magnetocaloric effect of $Co(S_{1-x}Se_x)_2$

H. Wada*, K. Tanaka, A. Tajiri

Department of Materials Science and Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

Available online 15 December 2004

Abstract

The magnetic entropy change, ΔS_M, was measured for $Co(S_{1-x}Se_x)_2$ with $0 \leqslant x \leqslant 0.103$, which is a system showing the itinerant electron metamagnetism (IEM). It was found that the peak value of $-\Delta S_M$ shows a maximum at around $x = 0.08$. The origin of this behavior is discussed in terms of the Clausius–Clapeyron relation.

PACS: 75.30.Sg; 75.30.Kz; 75.10.Lp

Keywords: Magnetocaloric effect; Magnetic entropy; Itinerant electrons-metamagnetism

The discovery of the giant magnetocaloric effect in $MnAs_{1-x}Sb_x$ [1], $MnFeP_{0.45}As_{0.55}$ [2] and $La(Fe_{1-x}Si_x)_{13}$ [3] and their hydrides [4] has demonstrated that the 3d transition-metal based compounds are more attractive as magnetic refrigerant materials. These compounds exhibit a first-order magnetic transition at their Curie temperatures, T_C, which is responsible for giant magnetocaloric effects. Above T_C, a transition from a paramagnetic state to a ferromagnetic state is induced by a magnetic field, which is the so-called itinerant electron metamagnetism (IEM). In this paper, we report the magnetocaloric effect of $Co(S_{1-x}Se_x)_2$, which is a typical system showing the IEM.

The Pyrite compound CoS_2 is a ferromagnet with $T_C = 122$ K. With the substitution of S by Se, the Curie temperature is rapidly decreased and the ferromagnetic to paramagnetic transition becomes of first order for $x \geqslant 0.05$ [5]. For $x \geqslant 0.12$, ferromagnetism disappears and the compounds become enhanced Pauli paramagnets in which the magnetic susceptibility shows a maximum in its temperature dependence. The IEM behavior is observed above T_C for $0.05 \leqslant x < 0.12$ and in the ground state for $0.12 \leqslant x \leqslant 0.20$ [5,6]. These results are well described by the spin fluctuation theory of IEM developed by Yamada [6,7]. We have studied the magnetic entropy change of ferromagnetic $Co(S_{1-x}Se_x)_2$ with $0 \leqslant x \leqslant 0.103$.

The samples were prepared by a direct reaction of the constituent elements in a vacuum at elevated temperature. Powders of Co (3 N), S (6 N) and Se (5 N) weighted in a required proportion were sealed in an evacuated quartz tube. The tube was heated at 400 °C for 7 days for a preliminary reaction. After this treatment, the resultant products were pulverized, mixed, sealed again and heated at 700 °C for 3 days. This procedure was repeated twice. Samples were checked by X-ray diffraction and were confirmed to be of a single phase with the Pyrite structure. The magnetic measurements were performed using a commercial SQUID magnetometer. The isothermal magnetic entropy change, ΔS_M, was evaluated from the temperature dependence of magnetization in various magnetic fields by using the

*Corresponding author. Present address: Department of Physics, Kyushu University, Higashi-ku, Fukuoka 812-8581, Japan. Tel.: +81 92 642 2549; fax: +81 92 642 2553.

E-mail address: wada6scp@mbox.nc.kyushu-u.ac.jp (H. Wada).

0304-8853/$ - see front matter © 2004 Published by Elsevier B.V.
doi:10.1016/j.jmmm.2004.11.343

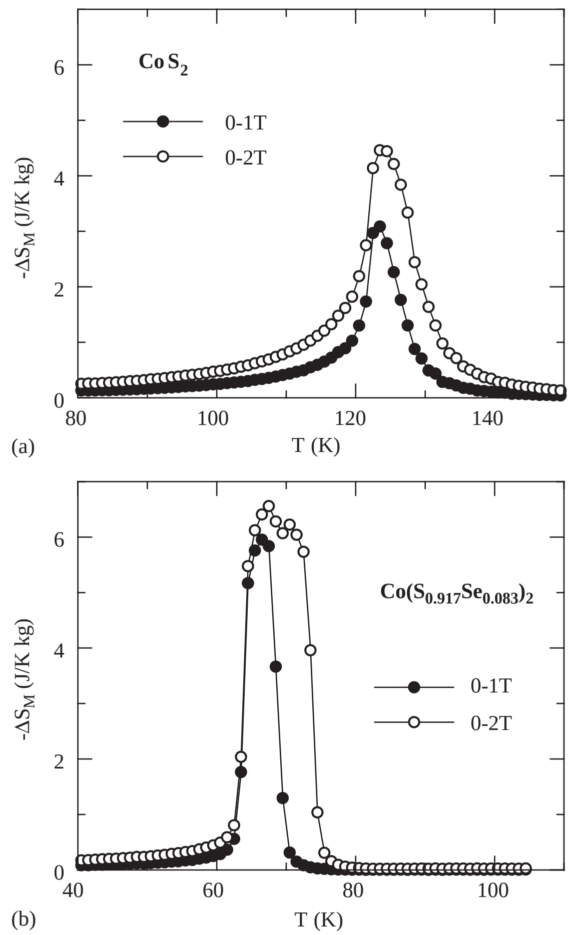

Fig. 1. Temperature dependence of magnetic entropy change, ΔS_M, of CoS_2 (a) and that of $Co(S_{0.917}Se_{0.083})_2$ (b).

Maxwell relation,

$$\Delta S_M = \int_0^H \left(\frac{dM}{dT}\right)_H dH. \tag{1}$$

We observed a first-order magnetic transition for the compounds with $0.032 \leqslant x \leqslant 0.103$. The T_C decreases down to 28 K with increasing x up to 0.103. In the ferromagnetic state, the magnetization is saturated above 0.2 T. Figs. 1(a) and (b) show the temperature dependence of ΔS_M of CoS_2 and $Co(S_{0.917}Se_{0.083})_2$, respectively. For CoS_2, the ΔS_M–T curves are rather symmetric with respect to T. Both the peak height and the peak width of $-\Delta S_M$ depend on a magnetic field. These are the characteristics of systems showing a second-order magnetic transition. In contrast, the $-\Delta S_M$ of $x = 0.083$ is abruptly increased at T_C. The peak height is a little sensitive to a magnetic field, while the peak width increases with increasing field. These features are often observed in systems showing a first-order magnetic transition.

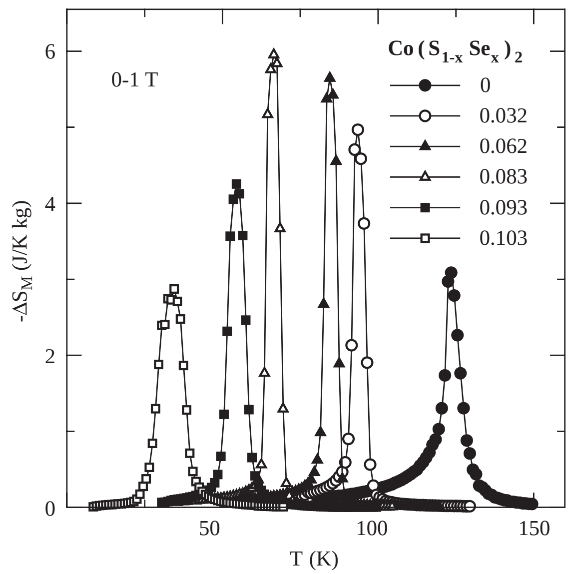

Fig. 2. Temperature dependence of ΔS_M of $Co(S_{1-x}Se_x)_2$ in a field change of 1 T.

The ΔS_M–T curves of $Co(S_{1-x}Se_x)_2$ in a field change of 1 T are depicted in Fig. 2. The peak height of $-\Delta S_M$ strongly depends on x. With increasing x, the peak height increases, reaches a maximum at around $x = 0.083$. Further increase in x reduces the peak value of $-\Delta S_M$. Recently, Yamada and Goto discussed the magnetocaloric effect in terms of the spin fluctuation theory of IEM [8]. They calculated the temperature dependence of ΔS_M by changing the parameter, ac/b^2, where a, b and c are the Landau expansion coefficients when the free energy is expanded in powers of M^2. It has been clarified from previous experimental results that ac/b^2 is increased with increasing x in the present system [6]. They have shown that the peak value of $-\Delta S_M$ has a maximum at a certain value of ac/b^2. Our observations in Fig. 2 are in agreement with their calculated results. The origin of a maximum of $-\Delta S_M$ can be understood from the Clausius–Clapeyron relation

$$\Delta S_M = -\left(\frac{\partial H_C}{\partial T}\right)|\Delta M|, \tag{2}$$

where H_C is the critical field from a paramagnetic state to a ferromagnetic state above T_C and ΔM is the change in the magnetization between two magnetic states. According to the calculated results by Yamada and Goto, both $|\Delta M|$ and $\partial H_C/\partial T$ are dependent on ac/b^2 and their product shows a maximum at a certain value of ac/b^2 [8]. To check these points, we estimated $|\Delta M|$ and $\partial H_C/\partial T$ of $Co(S_{1-x}Se_x)_2$ from the magnetization data, which are illustrated in Fig. 3 as a function of T_C.

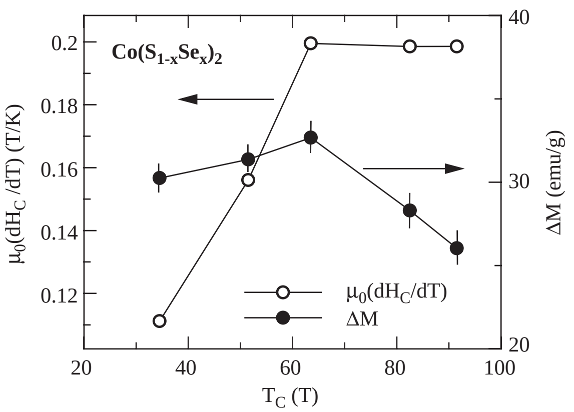

Fig. 3. Estimated values of $|\Delta M|$ and $\partial H_C/\partial T$ of $Co(S_{1-x}Se_x)_2$ as a function of the Curie temperature.

It is seen that $|\Delta M|$ increases with decreasing T_C, while $\partial H_C/\partial T$ decreases on lowering T_C below 60 K.

These results are explained as follows. In $Co(S_{1-x}Se_x)_2$, the ferromagnetic moment is about $0.85\,\mu_B$ per Co irrespective of x. Therefore, it is natural that $|\Delta M|$ increases, as T_C is lowered, because the magnetic transition is of first order. On the other hand, early experimental results have revealed that temperature dependence of H_C of $Co(S_{1-x}Se_x)_2$ with $0.10 \leqslant x \leqslant 0.20$ is expressed as [6],

$$H_C(x,T) = H_0(x) + \alpha T^2, \tag{3}$$

where H_0 and α are constants and α is independent of x. The T^2 dependence of H_C is also obtained from the spin fluctuation theory of IEM in a low-temperature approximation [6,7]. From Eq. (3), we have, $\partial H_C/\partial T = 2\alpha T$. This means that $\partial H_C/\partial T$ becomes smaller, as T_C is lower. Actually, $\partial H_C/\partial T$ varies with T_C in a linear fashion below 60 K, as shown in Fig. 2. From these results, we can conclude that the T_C dependence of $|\Delta M|$ and that of $\partial H_C/\partial T$ shown in Fig. 3 are intrinsic for itinerant electron metamagnets with low T_C. Using the values of $|\Delta M|$ and $\partial H_C/\partial T$ in Fig. 3, we have $-\Delta S_M = 6.5 \pm 0.2$ J/K kg at $T_C = 63.5$ K from Eq. (2), which is close to a maximum of $-\Delta S_M$ in Fig. 2, 5.94 J/K kg. These results have demonstrated that the temperature dependence of ΔS_M of $Co(S_{1-x}Se_x)_2$ is well understood by the Clausius–Clapeyron relation.

In conclusion, we studied the magnetic entropy change of $Co(S_{1-x}Se_x)_2$ with $0 \leqslant x \leqslant 0.103$, which is a typical system showing the IEM. The peak value of $-\Delta S_M$ in a field change of 0–1 T shows a maximum at around $x = 0.08$. The maximum in $-\Delta S_M$ originates from the T_C dependence of $|\Delta M|$ and $\partial H_C/\partial T$ in the present system. The spin fluctuation theory of IEM accounts for these results.

The authors are indebted to Prof. H. Yamada for useful discussion. This work was supported by a Grant-in-Aid for Scientific Research (No. 15360334) from Ministry of Education, Culture, Sports, Science and Technology of Japan, by The Iwatani Naoji Foundation and by JFE 21st Century Foundation.

References

[1] H. Wada, Y. Tanabe, Appl. Phys. Lett. 79 (2001) 3302.
[2] O. Tegus, E. Brück, K.H.J. Buschow, F.R. de Boer, Nature 415 (2002) 150.
[3] F.X. Hu, B.G. Shen, J.R. Sun, Z.H. Cheng, G.H. Rao, X.X. Zhang, Appl. Phys. Lett. 78 (2001) 3675.
[4] A. Fujita, S. Fujieda, K. Fukamichi, Y. Yamazaki, Y. Iijima, Mater. Trans. 43 (2002) 1202.
[5] K. Adachi, M. Matsui, M. Kawai, J. Phys. Soc. Japan 46 (1979) 1474.
[6] T. Goto, Y. Shindo, H. Takahashi, S. Ogawa, Phys. Rev. B 56 (1997) 14019.
[7] H. Yamada, Phys. Rev. B 47 (1993) 11211.
[8] H. Yamada, T. Goto, Phys. Rev. B 68 (2003) 184417.