Order of magnetic transition and large magnetocaloric effect in Er_3Co*

Shen Jun(沈 俊)[a)b)†], Zhao Jin-Liang(赵金良)[b)], Hu Feng-Xia(胡凤霞)[b)],
Wu Jian-Feng(吴剑峰)[a)], Sun Ji-Rong(孙继荣)[b)], and Shen Bao-Gen(沈保根)[b)]

[a)] *Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing* 100190 *China*
[b)] *State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing* 100190, *China*

(Received 3 January 2010)

We have studied the magnetic and magnetocaloric properties of the Er_3Co compound, which undergoes ferromagnetic ordering below the Curie temperature $T_C = 13$ K. It is found by fitting the isothermal magnetization curves that the Landau model is appropriate to describe the Er_3Co compound. The giant magnetocaloric effect (MCE) without hysteresis loss around T_C is found to result from the second-order ferromagnetic-to-paramagnetic transition. The maximal value of magnetic entropy change is 24.5 J/kg·K with a refrigerant capacity (RC) value of 476 J/kg for a field change of 0–5 T. Large reversible MEC and RC indicate the potentiality of Er_3Co as a candidate magnetic refrigerant at low temperatures.

Keywords: Er_3Co compound, magnetocaloric effect, magnetic transition

PACC: 7530S, 7550C

1. Introduction

In recent years, the giant magnetocaloric effect (MCE) around transition temperatures has been observed in many materials that experience a first-order phase transition.[1−10] These materials usually have a large magnetic entropy change (ΔS_M) and a high adiabatic temperature change, but magnetic hysteresis loss also happens inevitably. The slow kinetic inherence in first-order magnetic transition can greatly reduce the actual refrigerant capacity (RC) of the materials. Therefore, it is necessary to acquire efficient magnetic materials with a large reversible MCE and a high RC. Recently, much attention has been paid to the rare-earth(R)-based intermetallic compounds with a low-temperature phase transition for the purposes of magnetic refrigerant application.[11−17] R_3T (T=Co and Ni) have the highest R content among the binary 3d–4f compounds and crystallize in the orthorhombic Fe_3C-type crystal structure (space group $Pnma$). Although these compounds have identical crystallographic structures, they exhibit interesting magnetic properties, such as complex magnetic structures and natures of different magnetic transitions, which will induce good magnetocaloric properties. Recently, Tripathy *et al.*[14] reported the MCEs of Gd_3T (T=Co and Ni). The maximal ΔS_M values of Gd_3Co and Gd_3Ni are observed to be 11 and 5 J/Kg·K for a field change of 0–5 T, respectively. A large ΔS_M of 18 J/Kg·K for a field change of 0–5 T has been observed in Tb_3Co, which results from an FM to PM transition.[15]

The neutron diffraction investigation on single crystal Er_3Co has revealed that the compound posesses a non-collinear magnetic structure, in which there is strong ferromagnetic (FM) ordering along the b-axis and antiferromagnetic (AFM) ordering along the a and c-axes at low temperatures.[18] Polycrystalline Er_3Co orders ferromagnetically below the Curie temperature T_C, but undergoes a non-collinear spin structure caused by the magnetocrystalline anisotropy.[19] Such a complex magnetic structure for Er_3Co will bring interesting physical properties. In the present paper, we study the order of magnetic transition and the MCEs of the Er_3Co compound. It is found that the Landau model is appro-

*Project supported by the National Basic Research Program of China (Grant No. 2006CB601101), the National Natural Science Foundation of China (Grant No. 50731007) and the Knowledge Innovation Project of the Chinese Academy of Sciences.
†Corresponding author. E-mail: sj@g203.iphy.ac.cn
© 2010 Chinese Physical Society and IOP Publishing Ltd

priate to describe the Er_3Co compound. Giant reversible MCE and considerable RC without hysteresis loss around T_C for Er_3Co are obtained.

2. Experimental details

A polycrystalline Er_3Co sample was prepared by arc melting appropriate quantities of raw materials of Er (99.9% in purity) and Co (99.9%) in an atmosphere of high-purity argon. The sample was turned over and remelted several times to ensure its homogeneity. Ingots obtained by arc melting were wrapped by molybdenum foil, sealed in a quartz tube of high vacuum, annealed at 923 K for 7 days and then quenched to room temperature. Powder x-ray diffraction (XRD) measurements were performed using Cu $K\alpha$ radiation to identify the phase structure and the crystal lattice parameters. Magnetizations were measured as functions of temperature and magnetic field by using a superconducting quantum interference device (SQUID) magnetometer. By using the Maxwell relation $\Delta S_M = \int_0^H (\partial M/\partial T)_H \mathrm{d}H$, the ΔS_M was calculated based on the isothermal magnetization data. The sweep rate of the field was quite slow to ensure that the M–H curves could be recorded in an isothermal process.

3. Results and discussion

The x-ray powder diffraction pattern confirmed the single-phase nature of the Er_3Co compound, crystallizing in the orthorhombic Fe_3C-type structure (space group $Pnma$). The lattice parameters a, b, and c were determined to be 6.930(8), 9.227(8), and 6.205(2) Å (1 Å=0.1 nm), respectively, by using the Rietveld refinement method. Figure 1(a) shows the temperature dependences of zero-field-cooling (ZFC) and field-cooling (FC) magnetization (M) in a 0.05-T field for Er_3Co. It can be seen from Fig. 1(a) that Er_3Co undergoes a magnetic transition from FM to PM states, and its Curie temperature T_C is determined to be 13 K, which is in good agreement with the value reported by Saito *et al.*[19] In addition, it is also observed that there is no hysteresis in ZFC and FC curves above T_C. Below T_C, the difference between the ZFC and FC curves may be related to the domain-wall pinning effect. Figure 1(b) shows the reciprocal magnetic susceptibility χ^{-1} versus temperature for Er_3Co in a field of 1 T. The magnetic susceptibility of the Er_3Co compound exhibits Curie–Weiss behaviour in the paramagnetic region. Calculation results show that the effective paramagnetic moment (μ_{eff}) and the paramagnetic Curie temperature (θ_P) equal 10.1 μ_B/Er^{3+} and 27 K, respectively. The μ_{eff} value is slightly higher than the free ion moment of Er^{3+} (9.59 μ_B).

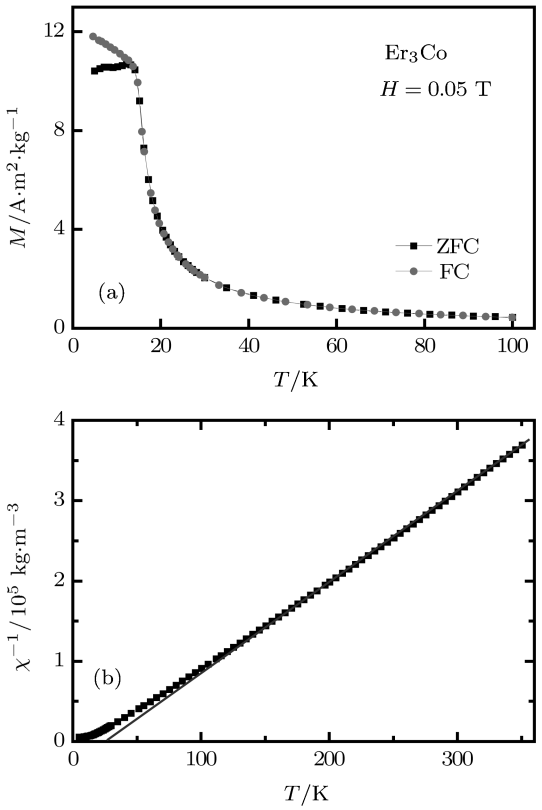


Fig. 1. Temperature dependences of magnetization for Er_3Co under a magnetic field of 0.05 T (a) and the reciprocal magnetic susceptibility χ_m^{-1} versus temperature in a field of 1 T (b).

The order of the phase transition of magnetic material can be determined by the temperature dependence of magnetic free energy based on the Inoue–Shimizu model.[20] The phenomenological description can be given by the Landau expansion of the magnetic free energy up to the sixth power of the total magnetization M as follows:

$$F(M,T) = (1/2)c_1(T)M^2 + (1/4)c_2(T)M^4 + (1/6)c_3(T)M^6 + \cdots - HM. \quad (1)$$

The Landau coefficients $c_1(T)$, $c_2(T)$ and $c_3(T)$ are available through the equation of state linking M and H as indicated below,

$$H = c_1(T)M + c_2(T)M^3 + c_3(T)M^5, \quad (2)$$

and they can be determined by fitting the magnetization isothermal data around T_C using expression (2). The magnetization isothermal data around T_C for Er_3Co at different temperatures together with the fitted curves are shown in Fig. 2. It is found

that the fitted M–H curves according to the Landau model are in good agreement with the experimental one. This result indicates that the Landau model is appropriate to describe the Er_3Co compound. Figure 3 shows the temperature dependences of Landau coefficients $c_1(T)$, $c_2(T)$ and $c_3(T)$ for Er_3Co derived from the fitting results.

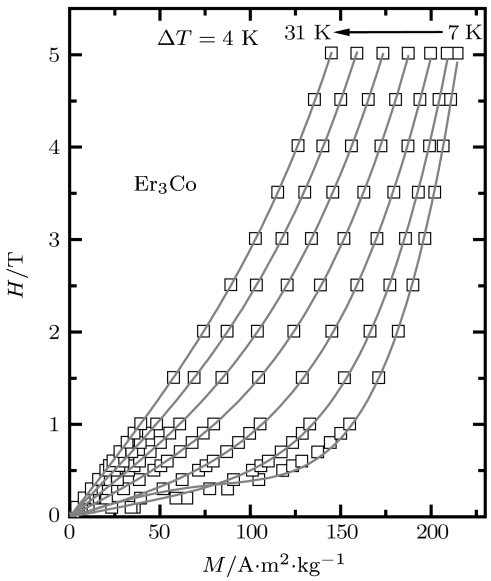


Fig. 2. Magnetization isothermal data around T_C for Er_3Co at different temperatures. The solid lines represent the fits to expression (2).

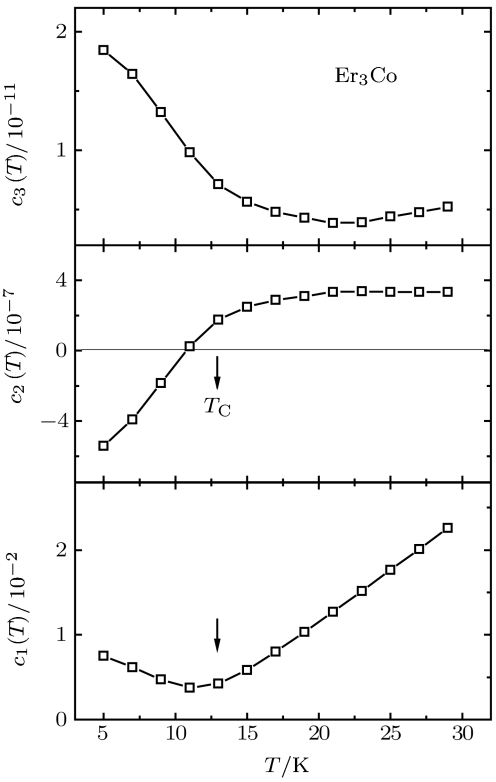


Fig. 3. Temperature dependence of Landau coefficients for Er_3Co. The units for $c_1(T)$, $c_2(T)$ and $c_3(T)$ are $T^2kg=J$, T^4kg^3/J^3 and T^6kg^5/J^5, respectively.

Both the values of $c_1(T)$ and $c_2(T)$ at T_C are found to be positive at T_C. It has been reported that the order of a magnetic transition is related to the sign of the Landau coefficient $c_2(T)$ at T_C, i.e. positive and zero values correspond to a second order transition while the negative value corresponds to a first-order transition.[21,22] This result indicates that the zero external field magnetic transition at T_C for Er_3Co is of second order.

The magnetization isotherms of Er_3Co around T_C are shown in Fig. 4. It is observed that the magnetization curves exhibit typical FM nature below T_C. The isothermal curves obtained well above T_C show strong curvatures at low fields, indicating the existence of short-range ferromagnetic correlations in the paramagnetic state.[23,24] To investigate the reversibility of the magnetic transitions for Er_3Co, we have also measured the M–H curves around T_C in field increasing and decreasing modes. Almost no magnetic hysteresis in each curve is observed, indicating that the magnetization of Er_3Co around T_C is perfectly reversible, which is advantageous for practical applications of the materials.

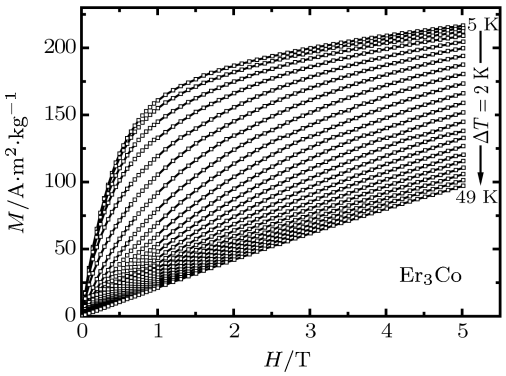


Fig. 4. Isothermal magnetization curves of Er_3Co in a temperature range of 5–49 K.

The ΔS_M of Er_3Co was calculated from magnetization isotherms shown in Fig. 4. The temperature dependences of $-\Delta S_M$ for different magnetic field changes are shown in Fig. 5. It is observed from Fig. 5 that both the peak and the width of ΔS_M depend on the applied magnetic field, and increase obviously with increasing field. The temperature dependences of ΔS_M exhibit a λ-shape profile as shown usually in magnetic materials with a second-order magnetic transition. A giant ΔS_M, which results from a second-order FM-to-PM transition, is observed in Er_3Co around T_C. The maximal value of ΔS_M for Er_3Co is found to increase monotonously with applied magnetic field and reaches a value of 24.5 J/kg·K at 16 K for a field change of 0–5 T. It is interesting to note that a large reversible ΔS_M for Er_3Co is as high

as 12.5 J/kg·K for a field change of 0–2 T, which is beneficial to the practical applications because a magnetic field of 2 T can be supplied by a permanent magnet. For comparison, the magnetocaloric properties of several compounds with a similar magnetic transition temperature and our samples are listed in Table 1. It can be seen that the $\Delta S_{\rm M}$ value of Er_3Co is comparable with those of HoCoAl,[11] HoNiAl[24] and $DyNi_2$[25] and it is also much larger than those of $DyNi_5$, $ErNi_5$[26] and DySb.[16]

The values of RC for Er_3Co are calculated by numerically integrating the area under the $\Delta S_{\rm M}$–T curves (Fig. 5), with the temperatures at half maximum of the peak used as the integration limits.[27] Calculations show that the maximal value of RC for Er_3Co is 476 J/kg for a magnetic field change of 0–5 T, which is comparable with or much larger than those for HoCoAl (450 J/kg), HoNiAl (435 J/kg), $DyNi_2$ (349 J/kg), $DyNi_5$ (230 J/kg), $ErNi_5$ (230 J/kg) and DySb (82 J/kg) (see Table 1). In particular, a high value of RC is also obtained to be 163 J/kg for a relatively low field change of 0–2 T. This is attributed to the appreciably large values of $\Delta S_{\rm M}$ obtained at $T_{\rm C}$ for Er_3Co. The present study shows that the large values of RC and no magnetic hystersis for Er_3Co around $T_{\rm C}$ are very useful for magnetic refrigeration applications.

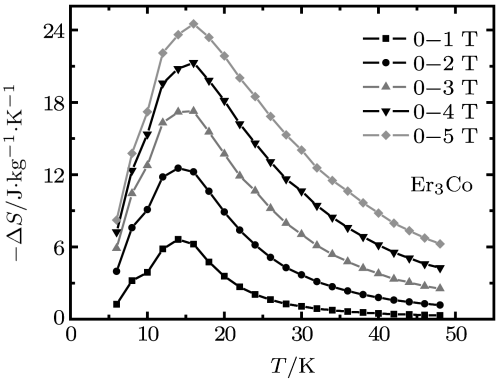


Fig. 5. Temperature dependences of magnetic entropy change $-\Delta S_{\rm M}$ for the Er_3Co compound for different magnetic field changes.

Table 1. Values of Curie temperature $T_{\rm C}$, magnetic entropy change $\Delta S_{\rm M}$ and refrigerant capacity RC at $T_{\rm C}$ for a magnetic field change of 0–5 T for some magnetocaloric materials with a $T_{\rm C} \sim 13$ K.

materials	$T_{\rm C}$ or $T_{\rm N}$/K	$-\Delta S_M$/J·kg^{-1}·K^{-1}	RC/J·kg^{-1}	Refs.
HoCoAl	10	21.5	450[a]	11
HoNiAl	14	23.6	435[a]	24
$DyNi_2$	20	21.3	349[a]	25
$DyNi_5$	11.6	15	230	26
$ErNi_5$	9	15	230	26
DySb	9	15.8	82[a]	16
Er_3Co	13	24.5	476	this work

[a]The RC values are estimated from the temperature dependence of $\Delta S_{\rm M}$ in the literature.

4. Conclusion

Orders of magnetic transition and magnetocaloric properties of the Er_3Co compound have been studied. It is found that the fitted M–H curves according to the Landau model are in good agreement with the experimental result. This result indicates that the Landau model is appropriate to describe the Er_3Co compound. Our results indicate that Er_3Co possesses a large reversible magnetocaloric effect with a maximal $\Delta S_{\rm M}$ value of 24.5 J/kg·K and an RC value of 476 J/kg at $T_{\rm C} = 13$ K for a field change of 0–5 T. The excellent magnetocaloric properties indicate the applicability of Er_3Co to magnetic refrigeration in the low temperature regime.

References

[1] Pecharsky V K and Gschneidner Jr K A 1997 *Phys. Rev. Lett.* **78** 4494

[2] Giguere A, Foldeaki M, Shcnelle W and Gmelin E 1999 *J. Phys.: Condens. Matter* **11** 6969

[3] Hu F X, Shen B G, Sun J R and Zhang X X 2000 *Chin. Phys.* **9** 550

[4] Hu F X, Shen B G, Sun J R, Chen Z H, Rao G H and Zhang X X 2001 *Appl. Phys. Lett.* **78** 3675

[5] Wada H and Tanabe Y 2001 *Appl. Phys. Lett.* **79** 3302

[6] Tegus O, Brück E, Buschow K H J and de Boer F R 2002 *Nature* (London) **415** 150
[7] Krenke T, Duman E, Acet M, Wassermann E F, Moya X, Mañosa L and Planes A 2005 *Nature Materials* **4** 450
[8] Tishin A M and Spichkin Y I 2003 *The Magnetocaloric Effect and Its Applications* (Bristol: Institute of Physics Publishing)
[9] Gschneidner Jr K A, Pecharsky V K and Tsokol A O 2005 *Rep. Prog. Phys.* **68** 1479
[10] Shen B G, Sun J R, Hu F X, Zhang H W and Chen Z H 2009 *Adv. Mater.* **21** 4545
[11] Zhang X X, Wang F W and Wen G H 2001 *J. Phys.: Condens. Matter* **13** L747
[12] Singh Niraj K, Suresh K G, Nirmala R, Nigam A K and Malik S K 2006 *J. Magn. Magn. Mater.* **302** 302
[13] Shen J, Wang F, Li Y X, Sun J R and Shen B G 2008 *J. Alloys Compd.* **458** L6
[14] Tripathy S K, Suresh K G and Nigam A K 2006 *J. Magn. Magn. Mater.* **306** 24
[15] Li B, Du J, Ren W J, Hu W J, Zhang Q, Li D and Zhang Z D 2008 *Appl. Phys. Lett.* **92** 242504
[16] Hu W J, Du J, Li B, Zhang Q and Zhang Z D 2008 *Appl. Phys. Lett.* **92** 192505
[17] Kumar P, Suresh K G and Nigam A K 2008 *J. Phys.* D: *Appl. Phys.* **41** 105007
[18] Tristan N V, Nikitin S A, Palewski T and Skokov K 2002 *J. Magn. Magn. Mater.* **251** 155
[19] Saito A T, Tutai A, Sahashi M and Hashimoto T 1995 *Jpn. J. Appl. Phys.* **34** L171
[20] Inoue J and Shimizu M 1982 *J. Phys.* F: *Met. Phys.* **12** 1811
[21] Liu X B, Ryan D H and Altounian Z 2004 *J. Magn. Magn. Mater.* **270** 305
[22] Singh N K, Suresh K G, Nigam A K, Malik S K, Coelho A A and Gama S 2007 *J. Magn. Magn. Mater.* **317** 68
[23] Arora P, Tiwari P, Sathe V G and Chattopadhyay M K 2009 *J. Magn. Magn. Mater.* **321** 3278
[24] Singh N K, Suresh K G, Nirmala R, Nigam A K and Malik S K 2007 *J. Appl. Phys.* **101** 093904
[25] von Ranke P J, Pecharsky V K and Gschneidner Jr K A 1998 *Phys. Rev.* B **58** 12110
[26] von Ranke P J, Mota M A, Grangeia D F, Carvalho A Magnus G, Gandra F C G, Coelho A A, Caldas A, de Oliveira N A and Gama S 1998 *Phys. Rev.* B **70** 134428
[27] Gschneidner Jr K A, Pecharsky V K, Pecharsky A O and Zimm C B 1999 *Mater. Sci. Forum* **315** 69