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Magnetocaloric effect in $ErCo_2$ compound*

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The $ErCo_2$ compound is prepared by arc-melting and its entropy changes are calculated using Maxwell relation. Its entropy change reaches 38 J/(kg·K) and its refrigerant capacity achieves 291 J/kg at 0–5 T. The mean field approximation is used to calculate the magnetic entropy of $ErCo_2$ compound. Results estimated by using the Maxwell relation deviate from mean field approximation calculations in ferrimagnetic state; however, the data obtained by the two ways are consistent in the vicinity of phase transition or at higher temperatures. This indicates that entropy changes are mainly derived from magnetic degree of freedom, and the lattice has almost no contribution to the entropy change in the vicinity of phase transition but its influence is obvious in the ferrimagnetic state below T_C.

Keywords: magnetocaloric effect, mean field approximation, metamagnetic transition
PACC: 7530S, 0500, 7530K

1. Introduction

Recently, the magnetocaloric effect (MCE) appearing in the vicinity of first-order phase transition has attracted considerable attention.[1−25] MCE means isothermal entropy change or adiabatic temperature change through magnetizing or demagnetizing magnetic solids. Large entropy changes are observed in $Gd_5Si_2Ge_2$,[1] $LaFe_{13-x}M_x$ (M = Si, Al),[2−9] MnFePAs,[10] $MnAs_{1-x}Sb_x$,[11] $Mn_{1-x}Fe_xAs$,[12] and NiMnX (X = Ga, Sn) Heusler alloy[13−15] etc. However, new progresses show that these large entropy changes may be composed of the magnetic, lattice, and electronic contributions. In other words, the results calculated by using the Maxwell relation are not magnetic entropy change, but total entropy change.[20,21] The entropy change of MnAs compound under a static pressure or its Fe-doped compound under ambient pressure [12] shows that the results calculated using Maxwell relation are far larger than the utmost value of magnetic entropy change, and this outcome can be ascribed to the contributions of lattice entropy changes. In contrast, the results of MnAs compound under ambient pressure show rather good consistency between total entropy changes (calculated by using the Maxwell relation) and magnetic entropy changes (calculated by mean field approximation (MFA)). Furthermore, the total entropy change of $LaFe_{13-x}Si_x$ compound achieved by magnetic measurement and heat capacity are lower than half of magnetic entropy changes (calculated by MFA).[22] This is attributed to the lattice entropy changes which counteract most of the magnetic entropy changes.[23] Further researches show that the Maxwell relation may give spurious results because of coexistence of paramagnetic and ferromagnetic phases.[24] It is indicated that the problem of magnetocaloric effect in the vicinity of first-order phase transition is complex and needs further experimental and theoretical research. Unfortunately, this kind of work is deficient.

Laves phase $ErCo_2$ compound is of a C15 structure and is a good candidate for studying the above problem. It is a ferrimagnet with first-order phase transition from ferrimagnetic state to paramagnetic state. The moment of heavy rare earth Er atom is antiparallel with that of Co atom. The moments of Co atoms can be induced by the molecular field from Er atoms, and the first-order phase transition is related to the metamagnetic state of 3d band.[25] The $ErCo_2$ compound shows a large MCE due to the itinerant electron metamagnetic transition.[16−19] Heat capacity measurements indicate that the magnetic entropy change may be derived mainly from the contribution of Er atoms.[16] The MFA applied to $ErCo_2$ compound is reasonable because the moment of rare earth atoms is localized. By comparing the experimental results

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with the theoretical calculation, the MCE of $ErCo_2$ compound can be explained.

2. Experimental details

Stoichiometric $ErCo_2$ sample with the normal composition was prepared by arc-melting in an ultrapure argon gas atmosphere with a 5% excess of erbium over the stoichiometric composition. The purity of the raw materials is 99.9% for erbium, and 99.87% for cobalt. The product was sealed in a quartz tube of high vacuum, and a post-annealing at 1073 K for 7 days was carried out for homogenization. Single-phase specimens with the Laves phase C15 structure were confirmed by x-ray powder diffraction measurement. Magnetization measurement was performed using a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design, Inc). The temperature dependence of magnetization from 20 to 50 K was measured with increasing temperature through zero-field-cooling. The isothermal magnetization from 0 to 5 T was measured between 20 and 42 K with increasing field.

3. Results and discussions

According to thermodynamics, the internal energy is a function of physical quantities such as magnetization M, volume V and total entropy S when the magneto–elastic coupling exists. Then the Maxwell relations are written as

$$\left(\frac{\partial V}{\partial H}\right)_{P,T} = -\left(\frac{\partial M}{\partial P}\right)_{H,T}, \quad (1)$$

$$\left(\frac{\partial V}{\partial T}\right)_{P,H} = -\left(\frac{\partial S}{\partial P}\right)_{T,H}, \quad (2)$$

$$\left(\frac{\partial M}{\partial T}\right)_{H,P} = \left(\frac{\partial S}{\partial H}\right)_{T,P}, \quad (3)$$

where P is pressure, H is magnetic field and T is temperature. According to Eqs.(1)–(3), it is easy to draw a conclusion that the entropy change calculated by Maxwell relation is not magnetic entropy change, but total entropy change. Based on Eq.(3) and under constant pressure, the total entropy change under applied field is written as

$$S(H_2,T) - S(H_1,T) = \int_{H_1}^{H_2} \left(\frac{\partial M(H,T)}{\partial T}\right)_H \mathrm{d}H. \quad (4)$$

Figure 1 shows the temperature dependence of magnetizations under different applied fields, and the inset shows the result under 0.02 T. Curie temperature, $T_C = 30$ K, increases with applied field linearly at 2 K/T. The above results are consistent with previous reports.[16–19]

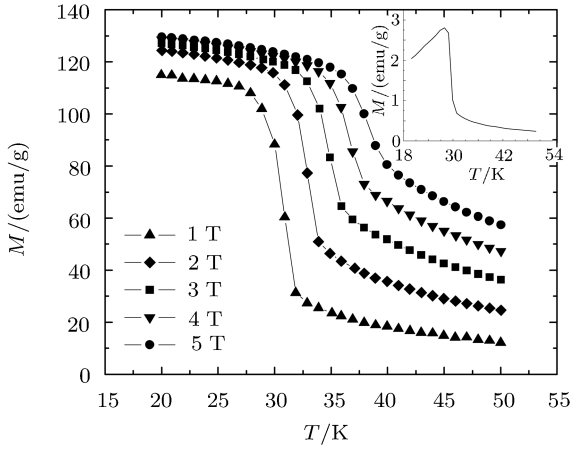


Fig.1. The temperature dependence of magnetization from 20 to 50 K, measured on temperature increase under different magnetic fields. The inset shows the result under 0.02 T.

Isothermal magnetizations measured with increasing applied field are shown in Fig.2 in which the temperature changes from 20 to 42 K. Figure 2 shows that $ErCo_2$ can go back to ferrimagnetic state from paramagnetic state when the applied field is larger than the critical field, and the critical field is driven up by the temperature increase. These two phenomena are both the characteristics of metamagnetic transition, in which the Curie temperature is driven by the increase of applied field or the critical field is driven by the increase of temperature.

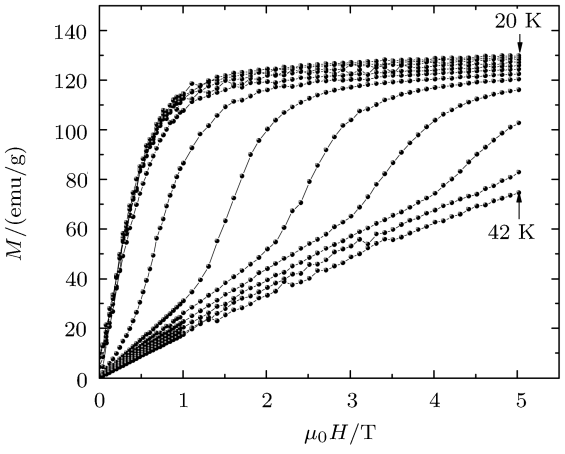


Fig.2. The isothermal magnetization curves versus applied field. The temperature changes from 20 to 42 K.

Theoretical studies[26,27] show that the negative slope and inflexion in the Arrot plot are the signs of

the metamagnetic transition. The metamagnetic transition of $ErCo_2$ is verified by the Arrot plot (shown in Fig.3) where the curves show 'S' shape and the inflexions appear above T_C. It is imaginable that the metamagnetic transition can result in a large MCE. Total entropy changes are calculated by Eq.(4) and shown in Fig.4.

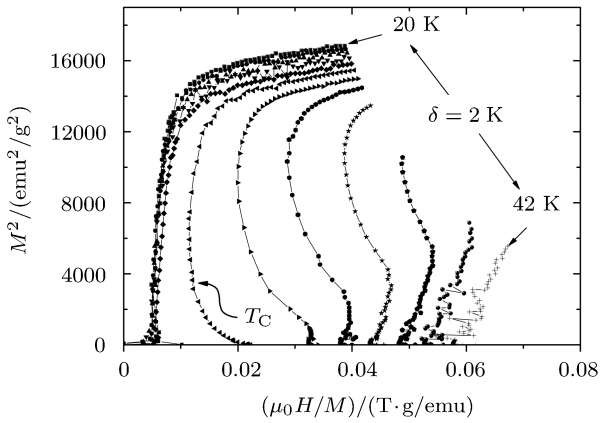


Fig.3. The Arrot plot of $ErCo_2$ compound. The curves show 'S' shape and the inflexions appear above T_C, which indicates the existence of metamagnetic transition.

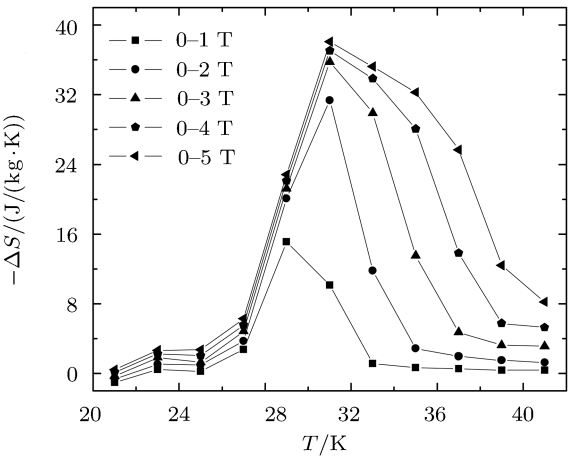


Fig.4. Temperature dependence of total entropy change for different applied fields.

The peak value of entropy change reaches 15 J/(kg·K) at 0–1 T. The larger the magnetic field, the higher and the wider of the entropy changes. The height is near saturation at 0–3 T (0–3 T, 35 J/(kg·K); 0–5 T, 38 J/(kg·K)) but the width gets wider when the magnetic field increases continuously, which is the characteristic of a first-order phase transition. Wada *et al* [18] measured the entropy change of single crystal $ErCo_2$ and the peak value reaches 10.6 J/(mol·K) (37.2 J/(kg·K)) at 0–5 T which is consistent with our polycrystalline result. The excellent refrigerant capacity is no less important to practicality than the large MCE. The refrigerant capacity is expressed as[28,29]

$$q = -\int_{T_1}^{T_2} \Delta S \mathrm{d}T, \tag{5}$$

where T_1 and T_2 are temperature at the cold end and hot end, respectively. In general, T_1 and T_2 can also be the temperatures corresponding to the width of half-maximum of the entropy change peak. The latter expression is adopted and its refrigerant capacity can reach 291 J/kg at 0–5 T, indicating that $ErCo_2$ has an application foreground at low temperatures.

According to the above discussion, $ErCo_2$ compound shows a large total entropy change in the vicinity of first-order phase transition. By comparing the heat capacity of $ErCo_2$ with that of $LuCo_2$, the large entropy change can be ascribed to the Er moment, and the contributions of Co moment are so small that they are negligible.[16] However, the Co sub-lattice has rather strong magnetic order and has an important influence on the metamagnetic transition, so the contribution of Co sub-lattice should not be neglected. Moreover, the lattice parameters show large discontinuous change during the metamagnetic transition.[30] The influence of lattice on the MCE is not clear and needs to be clarified by further study. We use the MFA method to calculate the magnetic entropy. By studying the discrepancy between the total entropy change and the magnetic entropy change, the influence of lattice on the total entropy change can be revealed clearly. The electronic entropy change is often so small that it is negligible.[23] According to MFA, the magnetic entropy is given by

$$S_M(T,H) = Nk_\mathrm{B}\left[\ln\frac{\sinh\dfrac{2J+1}{2J}x}{\sinh\dfrac{x}{2J}} - xB_J(x)\right], \tag{6}$$

where N is the number of magnetic spins, $B_J(x)$ is the Brillouin function with $x = gJ\mu_\mathrm{B}(H+H_m)/k_\mathrm{B}\mathrm{T}$, g is the Landég factor, μ_B is the Bohr magneton, J is the total angular momentum, k_B is the Boltzmann constant, H and H_m are external magnetic field and molecular field respectively. Based on the relation between the molecular field coefficient and the Curie temperature, we can write x as

$$x = \mu_s\left[H + \frac{3Jk_\mathrm{B}T_c\sigma}{(J+1)\mu_s}\right] \Big/ k_\mathrm{B}T. \tag{7}$$

The normalized magnetization is $\sigma = M/N\mu_s$ with $\mu_s = gJ\mu_\mathrm{B}$. The neutron scattering results show

that the moment of Er is $8.9 \pm 0.2\mu_B$, the moment of Co is $-1.0 \pm 0.2\mu_B$, and the total moment is $7.00 \pm 0.2\mu_B/ErCo_2$.[31] The neutron scattering data are used in the calculation. The magnetic entropy under different magnetic fields is calculated using Eq.(6), as shown in Fig.5.

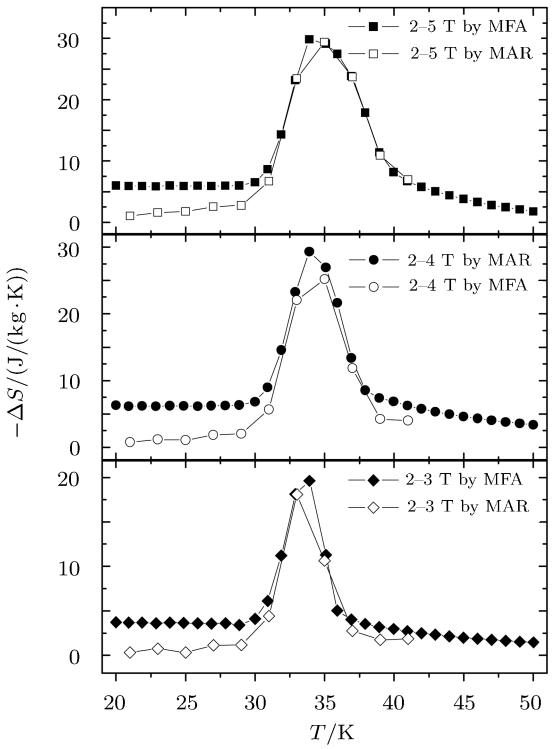


Fig.5. Temperature dependence of total entropy change (calculated by using Maxwell relation, hollow symbols) and magnetic entropy change (calculated by MFA, solid symbols).

For convenience, the data under saturated field (2 T) are used. Obviously, discrepancies exist between total entropy changes and magnetic entropy changes in the ferrimagnetic state. The utmost discrepancy can reach 5 J/(kg·K). It seems that magnetic entropy changes are counteracted by lattice entropy changes, which is responsible for the discrepancies. It may be a clue of strong magneto-elastic coupling. However, the consistency between total entropy changes and magnetic entropy changes is rather good in the vicinity of phase transition or at higher temperatures. The utmost discrepancies of peak values are within 4 J/(kg·K), indicating that magnetic entropy changes are dominant.

4. Conclusion

Entropy changes of polycrystalline $ErCo_2$, based on the data of magnetic measurements, are calculated by using Maxwell relation. The peak value of entropy change is as large as that of the single crystal and reaches 38 J/(kg·K) at 0–5 T. Its refrigerant capacity can reach 291 J/kg at 0–5 T. Magnetic entropies are calculated by MFA method. Results show that the discrepancies between total entropy changes and magnetic entropy changes exist in the ferrimagnetic state. However, the consistency between total entropy changes and magnetic entropy changes is rather good in the vicinity of phase transition or at higher temperatures. This indicates that large total entropy changes in the vicinity of phase transition are mainly caused by magnetic entropy changes, and lattice entropy changes obviously affect total entropy changes in ferrimagnetic state.

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