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Magnetic properties and magnetocaloric effect in $TbCo_{2-x}Fe_x$ compounds*

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Magnetic properties and magnetocaloric effect in $TbCo_{2-x}Fe_x$ compounds are studied by DC magnetic measurement. With increasing content of Fe, the entropy changes decrease slightly, though the Curie temperature is tuned from 231 K ($x = 0$) to 303 K ($x = 0.1$). Magnetic entropies of $TbCo_2$ compound are calculated by using mean field approximation (MFA). Results estimated by using Maxwell relation are consistent with that of MFA calculation. It is shown that the entropy changes are mainly derived from the magnetic entropy changes. The lattice has almost no contribution to the entropy change in the vicinity of phase transition.

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

1. Introduction

Currently, researches on magnetocaloric effect (MCE) are in the spotlight because of important impact on the magnetic refrigerant technique.[1−15] There is some degree of resemblance between the magnetic refrigerant technique and the traditional compressing gas refrigerant technique. But compared with the traditional compressing gas refrigerant technique, the magnetic refrigeration technique is friendly to environment and energy-efficient. The realization of magnetic refrigerant technique relies on the excellent magnetic refrigerant materials. Large MCE is the most important yardstick of quality to magnetic refrigerant material. MCE in the vicinity of phase transition attracts much attention. Giant MCE has been observed in some first-order phase transition materials, such as $Gd_5Si_2Ge_2$, [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. Large MCEs also are observed in some rare earth metals, alloys and compounds with second-order phase transition.[16−19] Second-order phase transition materials do not show hysteresis effect and are thermally stable; therefore, they are given much research attention. This paper is mainly concerned with the $TbCo_{2-x}Fe_x$ compounds.

Laves phase of $TbCo_2$ compound is of a C15 structure at room temperature. The moments of Co atoms can be induced by the molecular field from Tb atoms. Moreover, the moment of heavy rare earth Tb atom is antiparallel to that of Co atom. A second-order phase transition takes place from ferrimagnetic state to paramagnetic state. During a magnetic phase transition, its structure undergoes a transformation from the rhombohedral structure (ferrimagnetic state, space group $R\bar{3}m$) to cubic structure (paramagnetic state, space group $Fd\bar{3}m$).[20] Duc *et al*[17,18] and Gomes *et al*[19] have reported the MCE in $TbCo_2$ compound, and the results show that the magnitude of MCE in $TbCo_2$ compound is comparable to that of Gd, indicating that $TbCo_2$ comes to the foreground near room temperature. However, magnetic phase transition couples with a structural phase transition; this indicates that there exists a strong magneto-elastic coupling. The influence of magneto-elastic coupling on the MCE in the vicinity of phase transition has not been clarified, though it is important in understanding the mechanism of MCE.

The aim of this paper is to investigate the magnetic properties and MCE of $TbCo_{2-x}Fe_x$ compounds. By comparing the experimental results with the theoretical calculations, the influence of lattice entropy change on the MCE can be revealed clearly.

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2. Experimental details

Stoichiometric $TbCo_{2-x}Fe_x$ (x = 0, 0.05, 0.1) samples with the normal compositions were prepared by arc-melting in an ultra-pure argon gas atmosphere with a 5% excess of terbium over the stoichiometric composition. The purity of the raw materials is 99.9% for terbium and iron, and 99.87% for cobalt. The products were sealed in a quartz tube of high vacuum, and a post-annealing at 1273 K for 7 days was carried out for homogenization. Single-phase specimens with the Laves C15 structure were confirmed by x-ray powder diffraction study at room temperature. Magnetization measurement was carried out using a commercial superconducting quantum interference device (SQUID) magnetometer and a physical property measurement system (PPMS) from Quantum Design, Inc. The temperature dependence of magnetization was measured with increasing temperature through zero-field-cooling. Variation of isothermal magnetization from 0 to 5 T was measured under an increasing field.

3. Results and discussions

Figure 1 shows the temperature dependence of magnetizations for $TbCo_{2-x}Fe_x$ (x = 0, 0.05, 0.1) compounds at 1 mT DC magnetic field. A small doping content of Fe can improve T_C dramatically. The T_C can be adjusted form 231 to 303 K just by 5% doping of Fe, T_C increases linearly with the increase of Fe content (inset in Fig.1). With the increase in the content of Fe, the interaction between the 3d transition metal atoms is enhanced, which results in the increase of T_C. Magnetizations carried out at 4.2 K are shown in Fig.2.

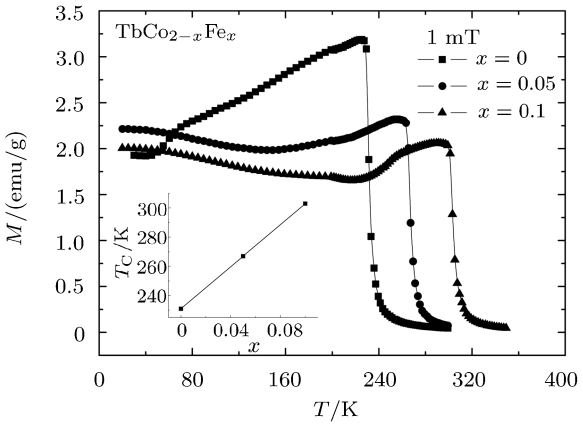


Fig.1. Temperature dependence of magnetization of the $TbCo_{2-x}Fe_x$ (x = 0, 0.05, 0.1) compounds at 1 mT applied field. The inset shows that the T_C increases linearly with increasing Fe content.

The inset in Fig.2 shows the content dependence of saturated magnetization per formula unit. These results show that M_s of polycrystalline $TbCo_2$ sample is 5.34 μ_B/f.u at 4.2 K, which is smaller than the results along easy magnetization direction.[21] As for $TbCo_2$ compound, a value for M_s of 6.83 μ_B/f.u at 4.2 K has been found along easy magnetization direction, and this value for the spontaneous moment is accounted for by Tb and Co moments (8.93 μ_B and 1.12 μ_B, respectively).[21] With increasing content of Fe, the saturated magnetization decreases.

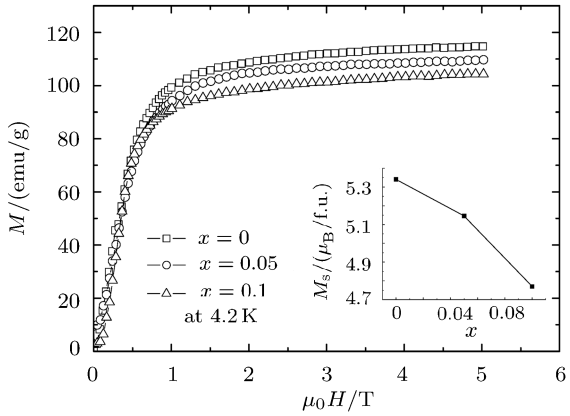


Fig.2. Variation of magnetization of the $TbCo_{2-x}Fe_x$ (x = 0, 0.05, 0.1) compounds with increasing applied fields at 4.2 K. The inset shows the dependence of saturated magnetization on x.

Shimizu[22] and Yamada[23] have proposed a phenomenological model to discuss the feature of phase transition. The free energy F can be expanded in powers of order parameter, in which the magnetic part of the free energy ΔF at a finite temperature for a system with magnetic moment is written as

$$\Delta F(M) = \frac{1}{2}A(t)M^2 + \frac{1}{4}B(T)M^4 + \frac{1}{6}C(T)M^6; \quad (1)$$

and the magnetic equation of state is written as:

$$H = \frac{\mathrm{d}\Delta F}{\mathrm{d}M} = A(T)M + B(T)M^3 + C(T)M^5. \quad (2)$$

The condition for the appearance of the metamagnetic transition is given by

$$A(T) > 0, \quad B(\mathrm{T}) < 0, \quad C(T) > 0;$$
$$\frac{3}{16} < \frac{A(T)C(T)}{B(T)} < \frac{9}{20}. \quad (3)$$

It is well known that the negative slope or s-shape curves with inflexions, sign of metamagnetic transition, will appear in the Arrot plot when the conditions (3) are satisfied. Figure 3 shows the isothermal magnetization of $TbCo_{2-x}Fe_x$ (x = 0, 0.05) measured

under increasing field. The step of temperature increase is 2 K. The Arrot plots of $x = 0$, 0.05 samples are shown in Fig.4, which shows the feature of the second-order phase transition.

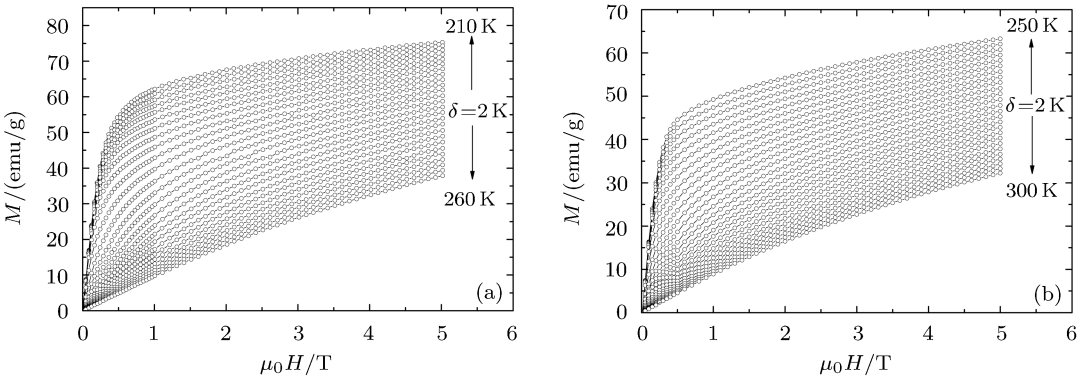


Fig.3. Isothermal magnetization of the $TbCo_{2-x}Fe_x$ ($x = 0$, 0.05) compounds versus applied field; (a) isothermal magnetization of $x = 0$ sample from 210 to 260 K with 2 K/step, (b) isothermal magnetization of $x = 0.05$ sample from 250 to 300 K with 2 K/step.

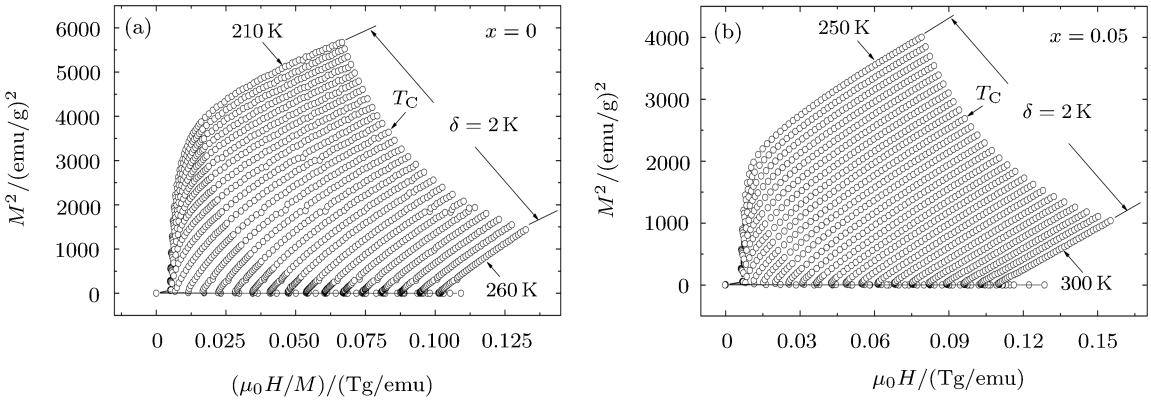


Fig.4. Arrot plots of the $TbCo_2$ compound from 210 to 260 K with 2 K/step (a) and the $TbCo_{1.95}Fe_{0.05}$ compound from 250 to 300 K with 2 K/step (b).

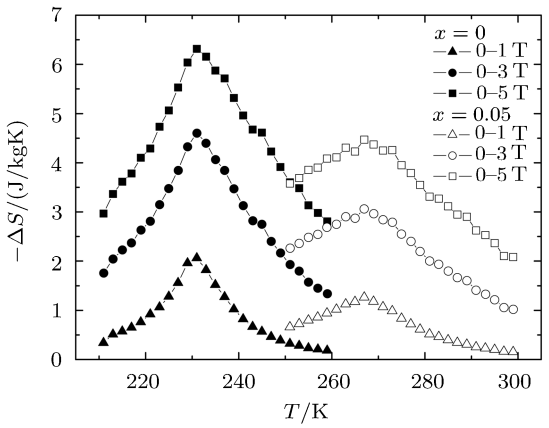


Fig.5. Temperature dependence of total entropy changes of the $TbCo_{2-x}Fe_x$ ($x = 0$, 0.05) compounds under different applied fields, $x = 0$ sample (solid symbols) and $x = 0.05$ sample (empty symbols).

The temperature dependence of entropy change under different applied field can be calculated by using Maxwell relation

$$\Delta S = \int_0^H \left(\frac{\partial M(H,T)}{\partial T}\right)_H \mathrm{d}H. \qquad (4)$$

The result obtained by using Maxwell relation is the total entropy change. Figure 5 shows the temperature dependence of entropy changes for the samples with $x = 0$, 0.5 under different applied fields. The peak value is 6.3 J/kgK for $x = 0$, and reaches 4.5 J/kgK for $x = 0.05$ at 0−5 T. Results of $TbCo_2$ are consistent with the results of Duc *et al.*[17] It is obvious that the peak value of entropy change decreases slightly due to Fe-doping, though T_C are tuned to room temperature.

Structural transformations during the magnetic phase transition indicate the existence of strong magneto-elastic couplings. Contributions of lattice to the total entropy change in the vicinity of phase tran-

sition are revealed by investigating the discrepancy between the total entropy change and the magnetic entropy change. MFA is used to calculation the magnetic entropy. According to MFA, the magnetic entropy is written as

$$S_{\rm M}(T,H) = Nk_{\rm B}\left[\ln\frac{\sinh\dfrac{2J+1}{2J}x}{\sinh\dfrac{x}{2J}} - xB_J(x)\right], \quad (5)$$

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

$$x = \mu_{\rm s}\left[H + \frac{3Jk_{\rm B}T_{\rm C}\sigma}{(J+1)\mu_{\rm s}}\right] \Big/ k_{\rm B}T. \quad (6)$$

The normalized magnetization is $\sigma = M/N\mu_{\rm S}$ with $\mu_{\rm s} = gJ\mu_{\rm B}$. No more than the moments of rare earth atoms are taken account in the MFA calculation. The peak values are shown in Table 1.

Table 1. Total entropy changes (calculated by using Maxwell relation) and the magnetic entropy changes (calculated by using MFA) of the $TbCo_2$ compound under different applied fields.

ΔH/T	1	2	3	4	5
$\Delta S_{\rm MAR}$/(J/kgK)	2.06	3.52	4.61	5.49	6.32
$\Delta S_{\rm MFA}$/(J/kgK)	1.66	3.38	4.73	5.81	6.74

The consistency between the total entropy changes and the magnetic entropy changes are rather good. Moreover, a relation of $\Delta S_{\rm m}$-$-H^{2/3}$ exists in $TbCo_{2-x}Fe_x$ (x = 0, 0.05) compounds at $T_{\rm C}$, which is shown in Fig.6; the entropy changes increase linearly with $H^{2/3}$. Based on molecular field models, Oesterreicher and Parker[24] have pointed out that the $\Delta S_{\rm m}$-$-H^{2/3}$ relation will be followed during a second-order phase transition. It means that the total entropy changes are mainly derived from the magnetic entropy changes. As for the lattice entropy change, it has almost no contribution to the total entropy change.

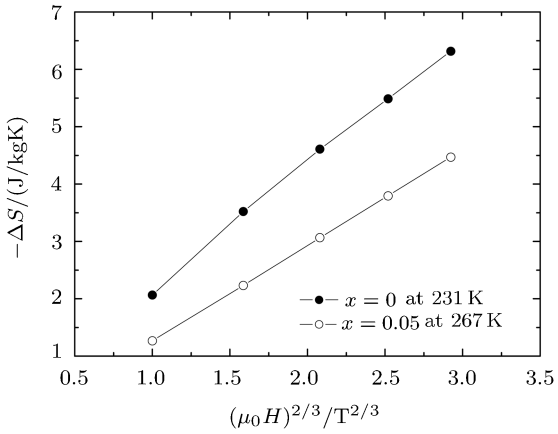


Fig.6. Dependence of entropy changes of the $TbCo_{2-x}Fe_x$ (x = 0, 0.05) compounds on applied field at $T_{\rm C}$, for $x = 0$ sample (solid circle), and $x = 0.05$ sample (empty circle).

4. Conclusion

Though structural transformation accompanies the magnetic phase transition, the phase transition in the $TbCo_{2-x}Fe_x$ compound is a second-order one. The Arrot plot of $TbCo_{2-x}Fe_x$ compound shows the features of second-order phase transition. The total entropy changes are calculated by Maxwell relation. The peak values of $TbCo_{2-x}Fe_x$ ($x = 0, 0.05$) samples can reach 6.3 J/kgK and 4.5 J/kgK at $0-5$ T, respectively. Compared with the $TbCo_2$ compound, the peak value of total entropy changes in $TbCo_{1.95}Fe_{0.05}$ decreases slightly, though its $T_{\rm C}$ is tuned to 267 K. According to our calculations, the results indicate that the total entropy changes come mainly from magnetic entropy changes and the lattice contributions are so small that they are negligible.

References

[1] Pecharsky V K and Gschneidner K A Jr. 1997 *Phys. Rev. Lett.* **78** 4494;
Pecharsky V K and Gschneidner K A Jr. 1997 *Appl. Phys. Lett.* **70** 3299

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

[3] Hu F X, Shen B G, Sun J R and Zhang X X 2000 *Chin. Phys.* **9** 0550

[4] Hu F X, Shen B G, Sun J R, Wang G J and Cheng Z H 2002 *Physics* **31** 139 (in Chinese)

[5] Wang F, Chen Y F, Wang G J, Sun J R and Shen B G 2004 *Chin. Phys.* **13** 393

[6] Wang F, Chen Y F, Wang G J, Sun J R and Shen B G 2003 *Chin. Phys.* **12** 911

[7] Wang G J, Wang F and Shen B G 2005 *Acta Phys. Sin.* **54** 2868 (in Chinese)

[8] Wang G J, Wang F and Shen B G 2005 *Acta Phys. Sin.* **54** 1410 (in Chinese)

[9] Fujita A, Fujieda S, Hasegawa Y and Fukamichi K 2003 *Phys. Rev.* B **67** 104416
[10] Tegus O, Brück E, Buschow K H J and de Boer F R 2002 *Nature* (London) **415** 150
[11] Wada H and Tanabe Y 2001 *Appl. Phys. Lett.* **79** 3302
[12] Gama S, Coelho A A, de Campos A, Carvalho A M G, Gandra F C G, von Ranke P J and de Oliveira N A 2004 *Phys. Rev. Lett.* **93** 237202
de Campos A, Rocco D L, Carvalho A M G, Caron L, Coelho A A, Gama S, Silva L D, Gandra F C G, Santos A O D, Cardoso L P, von Ranke P J and de Oliveira N A 2006 *Nature Materials* **5** 802
[13] Hu F X, Shen B G, Sun J R and Wu G H 2001 *Phys. Rev.* B **64** 132412
[14] Hu F X, Shen B G and Sun J R 2000 *Appl. Phys. Lett.* **76** 3460
[15] Krenke T, Duman E, Acet M, Wassermann E F, Moya X, Mañosa L and Planes A 2005 *Nature Materials* **4** 450
[16] Tishin A M and Spichkin Y I 2003 *The Magnetocaloric Effect and its Applications* (Bristol: Institute of Physics Publishing) p277
[17] Duc N H, Kim Anh D T and Brommer P E 2002 *Physica* B **319** 1
[18] Duc N H and Kim Anh D T 2002 *J. Magn. Magn. Mater.* **242–245** 873
[19] Gomes A M, Reis M S, Oliveira I S, Guimarães and Takeuchi A Y 2002 *J. Magn. Magn. Mater.* **242–245** 870
[20] Ouyang Z W, Wang F W, Hang Q, Liu W F, Liu G Y, Lynn J W, Liang J K, and Rao G H 2005 *J. Alloys Comp.* **390** 21
[21] Buschow K H J 1993 *Handbook of Magnetic Materials* (Amsterdam: North-Holland) p408
[22] Shimizu M 1982, *J. Phys.* (Paris) **43** 155
[23] Yamada H 1993 *Phys. Rev.* B **47** 11211
[24] Oesterreicher H and Parker T 1983 *J. Appl. Phys.* **55** 4334