Journal of Alloys and Compounds 509 (2011) 1796–1799

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Large magnetocaloric effect in $TbCo_3B_2$ compound

Lingwei Li[a,b,*], Dexuan Huo[a], Hiroto Igawa[b], Katsuhiko Nishimura[b]

[a] Institute of Materials Physics, Hangzhou Dianzi University, Hangzhou 310018, China
[b] Graduate School of Science and Engineering, University of Toyama, Toyama 930-8555, Japan

ARTICLE INFO

Article history:
Received 25 June 2010
Received in revised form 7 October 2010
Accepted 10 October 2010
Available online 21 October 2010

PACS:
75.30.Sg
75.30.Kz

Keywords:
$TbCo_3B_2$ compound
Magnetocaloric effect
Magnetic transition

ABSTRACT

A single-phased $TbCo_3B_2$ compound has been prepared by an arc-melting method. The magnetic properties and magnetocaloric effect (MCE) have been studied by the magnetization and heat capacity measurements. A large reversible magnetocaloric effect has been observed accompanied by a second-order phase transition at around Tb–Tb sublattice ordering temperature. The values of maximum magnetic entropy change ($-\Delta S_M^{max}$) reach 4.9 and 10.3 J kg^{-1} K^{-1} for the field change of 2 and 7 T with no obvious hysteresis loss around 30 K, respectively. The corresponding maximum adiabatic temperature changes (ΔT_{ad}^{max}) are evaluated to be 4.0 and 8.6 K. The magnetic transition and the origin of large MCE in $TbCo_3B_2$ were discussed.

1. Introduction

Recently, the magnetocaloric effect (MCE) in various magnetic materials has been extensively studied experimentally and theoretically, not only because of their great potential for magnetic refrigeration applications but also for further understanding the fundamental physical properties of the materials [1–11]. The MCE is a magnetothermodynamic phenomenon, it manifests as an isothermal magnetic entropy change (ΔS_M) or an adiabatic temperature change (ΔT_{ad}) when the magnetic material is exposed to a varying magnetic field. Magnetic refrigeration based on the MCE is advantageous being an environment friendly and energy efficient refrigeration mechanism, which is expected to be an important future cooling technology [1–4]. A large value of MCE is considered to be the most important requirement of the application, and therefore it is desirable to find new materials with large MCE especially at low magnetic fields and with a wide temperature range. Some rare-earth based compounds with a ferromagnetic (FM) or an antiferromagnetic (AFM) phase transition have been found to possess not only large magnetic entropy change but also a small hysteresis loss.

The ternary intermetallic compounds of the RCo_3B_2 where R is a rare earth or yttrium have attracted some attentions due to their interesting physical properties [12–15]. The RCo_3B_2 compounds are paramagnetic at room temperature and undergo a Co–Co sublattice magnetic order transition at ~160 (20) K. In addition, a second R–R sublattice magnetic order transition was also observed at 54, 47, 28 and 22 K for R = Gd, Sm, Tb and Dy, respectively [12–15]. Very recently, a giant/large reversible MCE in ternary R–Co–B intermetallic compounds RCo_2B_2 (R = Gd, Pr and Nd) [16–18] was reported, respectively. To search new material displaying large MCE and further understand the physical properties of RCo_3B_2 system, in this paper, the magnetic properties and MCE in $TbCo_3B_2$ were systematically studied.

2. Experimental

The polycrystalline $TbCo_3B_2$ was synthesised by an arc melting method using a tungsten electrode under an argon atmosphere. Stoichiometric amounts of high purity Tb, Co and B were melted more than six times for homogeneity on a water-cooled copper hearth. The total weight loss of the sample in this step was less than 0.5%. Then the samples were finally annealed at 1073 K for one week in evacuated quartz tubes. The sample was proved to be single phase with the $CeCo_3B_2$-type hexagonal crystal structure belonging to the *P6/mmm* space group by X-ray diffraction (XRD) using Rigaku RINT 2250 diffractometer. The lattice parameters a and c were evaluated to be 5.047 and 3.003 Å, respectively, from XRD data using Rietveld refinement method. The magnetization measurements were done using a superconducting quantum interference device magnetometer (Quantum Design, MPMS-7) in the temperature range 2–300 K, with DC magnetic fields from 0 to 7 T. The specific heat measurements were carried out by the adiabatic heat relaxation method in the temperature range from 2 to

* Corresponding author at: Graduate School of Science and Engineering, University of Toyama, Toyama 930-8555, Japan. Tel.: +81 76 445 6804; fax: +81 76 445 6703.
E-mail address: wei0396@hotmail.com (L. Li).

0925-8388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2010.10.043

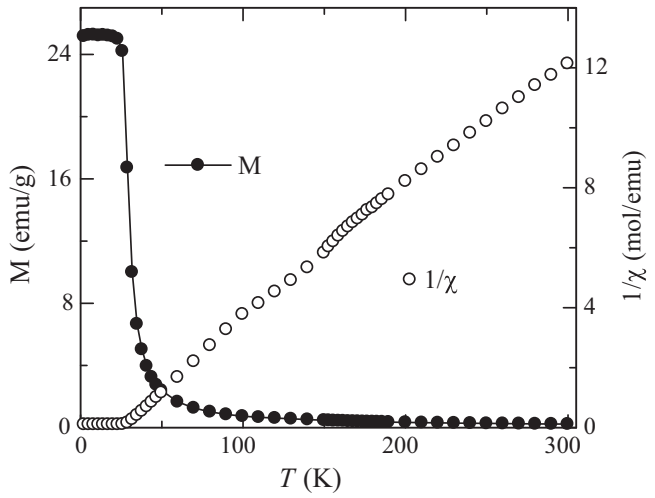

Fig. 1. Temperature dependence of magnetization (M) and inverse susceptibility ($1/\chi$) for $TbCo_3B_2$ in an external magnetic field $H = 0.1$ T.

300 K using a physical property measurement system (PPMS-9) from Quantum Design.

3. Results and discussion

The temperature dependence of magnetization (M) and the reciprocal susceptibility ($1/\chi$) for $TbCo_3B_2$ in an external magnetic field $H = 0.1$ T are shown in Fig. 1. A sharp transition around 30 K and the anomaly change around 170 K were observed. The reciprocal susceptibility shows Curie–Weiss behaviour above 200 K. Dubman et al. [14] studied the magnetic ordering of $TbCo_3B_2$ by means of neutron diffraction method, and they concluded that the magnetic ordering transition of the Tb sublattice (~30 K) accompanied by the rotation of the magnetic moment towards the basal plane, the anomaly (~170 K) was due to the Co–Co sublattice magnetic ordering transition. The temperature dependence of zero field specific heat results for $TbCo_3B_2$ is shown in Fig. 2, a clear λ-shape indicating a magnetic transition around 28 K which is a typical character of second order phase transition, and no obvious change can be observed around 170 K. These behaviours were consistent with the magnetic measurements and previous reported results [14,15].

A set of magnetic isothermals on increasing and decreasing field were measured for $TbCo_3B_2$ with the temperature range from 4 to

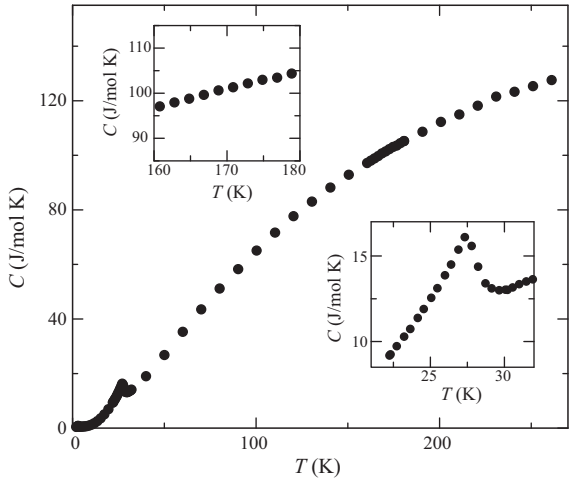

Fig. 2. Temperature dependence of zero field specific heat (C) for $TbCo_3B_2$. Inset show the $C(T)$ curves for $TbCo_3B_2$ around 28 K and 170 K, respectively.

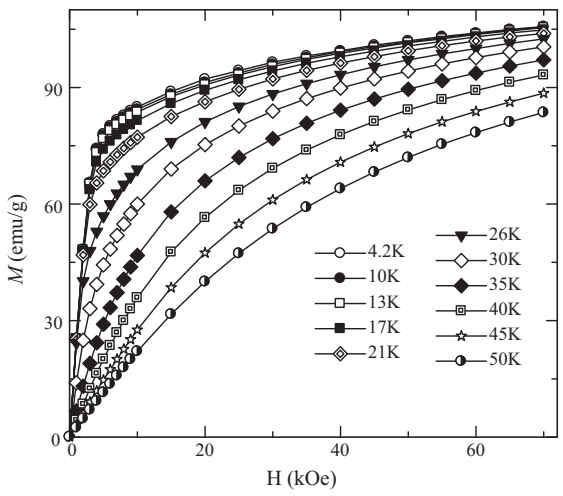

Fig. 3. Magnetic field dependence of the magnetization for $TbCo_3B_2$ at some selected temperatures up to 7 T.

60 K up to 7 T. There is no obvious hysteresis for $T > 10$ K. To ensure the readable of the figure, only several isotherms with increasing field are presented in Fig. 3. For low temperature ones, the magnetization M tends to be saturated at low field. A large reversible MCE is expected around the transition temperature where the magnetization rapidly changes with varying temperature. Based on the Inoue-Shimizu model, which involves a Landau expansion of the magnetic free energy up to sixth power of the total magnetization M, can be used to determine the transition type [19],

$$F(M,T) = \frac{c_1(T)}{2}M^2 + \frac{c_2(T)}{4}M^4 + \frac{c_3(T)}{6}M^6 + \cdots - BM \quad (1)$$

The parameters $c_1(T)$, $c_2(T)$ and $c_3(T)$ represent the Laudau coefficient, and it has been reported that the order of a magnetic transition is related to the sign of the $c_2(T)$. A transition is expected to be the first order when $c_2(T_C)$ is negative, whereas it will be the second order for a positive $c_2(T_C)$. The sign of $c_2(T_C)$ can be determined by means of Arrott plots [20,21]. If the Arrott plot is S-shaped near T_C, $c_2(T_C)$ is negative, otherwise, positive. To further understand the nature of the magnetic transition in $TbCo_3B_2$, the Arrott-plots M^2 vs. H/M at some selected temperatures for $TbCo_3B_2$ are plotted in Fig. 4. Neither the inflection point nor negative slopes

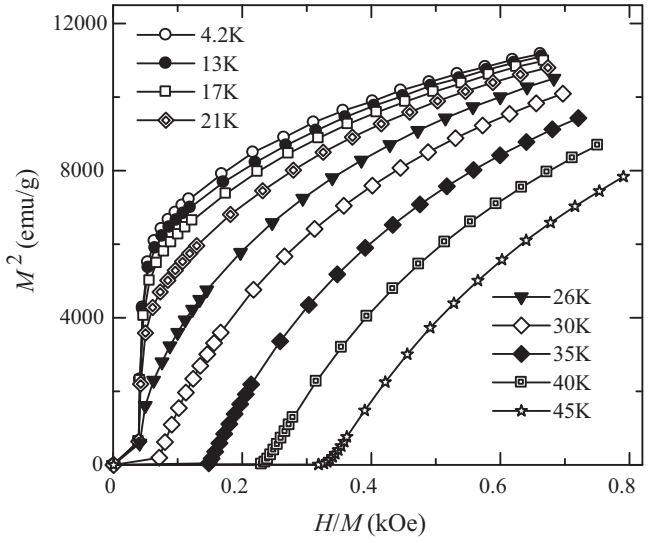

Fig. 4. The Arrot-plot of $TbCo_3B_2$ at some selected temperatures.

is observed. Together with the λ-shape in $C(T)$ (as shown in Fig. 2) the present results confirmed that the $TbCo_3B_2$ compound undergoes a second order magnetic phase transition from paramagnetic to ferromagnetic state.

According to thermodynamical theory [22], the isothermal magnetic entropy changes associated with a magnetic field variation is given by

$$\Delta S_M(T, \Delta H) = S_M(T, H) - S_M(T, 0) = \mu_0 \int_0^{H_{max}} \left(\frac{\partial S(H,T)}{\partial H}\right)_T dH \quad (2)$$

From the Maxwell's thermodynamic relation:

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

one can obtain the following expression:

$$\Delta S_M(T, \Delta H) = \mu_0 \int_0^{H_{max}} \left(\frac{\partial M(H,T)}{\partial T}\right)_H dH \quad (4)$$

where S, M, H, and T are the magnetic entropy, magnetization of the material, applied magnetic field, and the temperature of the system, respectively. From the magnetization measurements made at discrete field and temperature intervals, ΔS_M can be approximately calculated by the following expression:

$$\Delta S_M(T, \Delta H) \approx \frac{1}{\delta T}\left[\mu_0 \int_0^{H_{max}} M(T+\delta T, H)dH - \mu_0 \int_0^{H_{max}} M(T,H)dH\right] \quad (5)$$

Based on the method described by Pecharsky and Gschneidner [22], the accuracy of the ΔS_M calculated from the magnetization data for the materials studied here is better than 10%. The ΔS_M was calculated using Eq. (5) in the vicinity of its ordering temperature based on the results of magnetization isotherms. The resulting changes of magnetic entropy $-\Delta S_M$ as a function of temperature for different magnetic field variations up to 7 T are shown in Fig. 5. A large magnetocaloric effect can be observed around 30 K. The maximum values of magnetic entropy change ($-\Delta S_M^{max}$) reach 8.7 and 10.3 J kg^{-1} K^{-1} for a field change of 5 and 7 T, respectively. This large MCE is related to a second order Tb–Tb sublattice magnetic phase transition. Another important parameter for a MCE material is the temperature dependence of adiabatic temperature change ΔT_{ad}, which was also evaluated. Keeping this context in mind, the temperature dependence of ΔT_{ad} (shown in Fig. 6) for various magnetic field changes up to 7 T has been calculated using the $\Delta S_M(T)$ and zero-field specific heat results (Fig. 2). The overall nature of ΔT_{ad} as a function of temperature is remarkably similar to that of $\Delta S_M(T)$. The maximum values of adiabatic temperature change (ΔT_{ad}^{max}) reach 7.3 and 8.6 K for a field change of 5 and 7 T, respectively. The transition temperature (T_M), the order of magnetic transition type, the maximum values of magnetic entropy change $-\Delta S_M^{max}$ and adiabatic temperature change ΔT_{ad}^{max} as well as the relative cooling power [RCP, which is defined as the product of as the product of the maximum magnetic entropy change

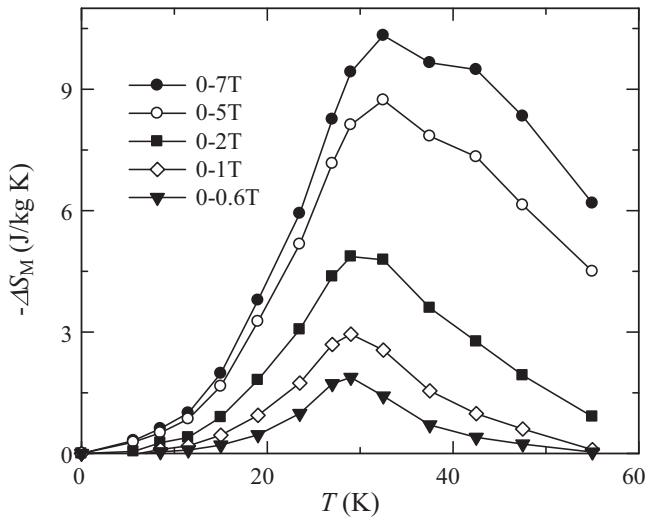

Fig. 5. The magnetic entropy change $-\Delta S_M$ as a function of temperature for various magnetic field changes up to 7 T for $TbCo_3B_2$.

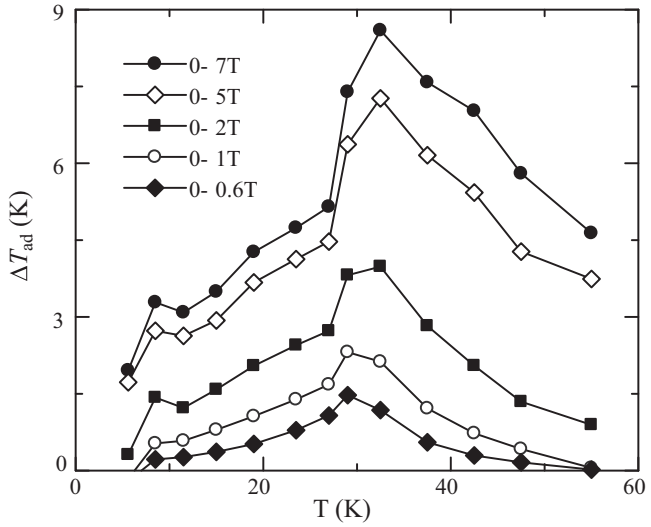

Fig. 6. The adiabatic temperature change ΔT_{ad} as a function of temperature for various magnetic field changes up to 7 T for $TbCo_3B_2$.

Table 1
The transition temperature (T_M), the order of transition type as well as the maximum values of magnetic entropy change $-\Delta S_M^{max}$ and adiabatic temperature change ΔT_{ad}^{max} as well as the relative cooling power (RCP) under 2 and 5 T for $TbCo_3B_2$ and some MCE materials.

Material	T_M (K)	Order of transition	$-\Delta S_M^{max}$ (J kg^{-1} K^{-1})		RCP (J/cm^3)		ΔT_{ad}^{max} (K)		Ref.
			2 T	5 T	2 T	5 T	2 T	5 T	
$TbCo_3B_2$	28	Second	4.9	8.7	0.5	2.5	4.0	7.3	Present
$PrCo_2B_2$	16	Second	4.9	8.1	0.36	1.1	4.3	8.1	[17]
$NdCo_2B_2$	27	Second	4.5	7.1	0.3	0.8	3.3	5.8	[18]
DySb	11	First	–	15.8	–	~1.4	–	–	[23]
$GdCo_2B_2$	25	First	9.3	17.1	1.06	3.8	6.7	15.4	[16]
Ho_5Pd_2	28	First	~7	~18	1.7	6.3	–	–	[19]
$GdPd_2Si$	17	Second	4.5	15	~0.4	~2.3	3.2	8.5	[24]
PrNi	20	Second	2.4	6.1	~0.2	~0.7	0.8	1.7	[25]
$ErCo_2$	35	First	28	33	1.5	3.08	4.2	9.5	[2,5]

ΔS_M^{max} and full width at half maximum δT_{FWHM}] under 2 and 5 T for $TbCo_3B_2$ and some MCE materials with T_M around 25 K are listed in Table 1. Despite the fact that the ΔS_M^{max}, ΔT_{ad}^{max} and RCP values of $TbCo_3B_2$ are smaller than those of which processed the first order magnetic transitions, the present values are comparable with those of which undergoing the second order magnetic transitions. However, compared with some first order magnetic transition materials, the present $TbCo_3B_2$ compound and some second order magnetic transition materials have high reversible MCE which makes them to be competitive materials for active magnetic-refrigeration application.

4. Conclusions

In summary, we have systematically studied the magnetic properties and magnetocaloric effect (MCE) of $TbCo_3B_2$ by determining the magnetization and heat capacity. A sharp transition around 30 K and an anomaly change around 170 K has been observed which was corresponding to the Tb–Tb and the Co–Co sublattice magnetic order transition, respectively. A large reversible MCE has been observed which is related to a second-order Tb–Tb sublattice magnetic phase transition. The present results may give some clue for searching new materials with large MCE.

Acknowledgements

This work was partially supported by the National Natural Science Foundation of China (Nos. 11004044, 50871036), Japan Society for the Promotion of Science (JSPS) Postdoctoral Fellowships for Foreign Researchers (No. P10060), Major Scientific and Technological Innovation Project for Higher Education of Zhejiang Province (No. ZD2007010), and Innovation Research Team for Spintronic Materials and Devices of Zhejiang Province.

References

[1] A. Kitanovski, P.W. Egolf, Int. J. Refrig. 38 (2010) 449.
[2] K.A. Gschneidner Jr., V.K. Pecharsky, A.O. Tsoko, Rep. Prog. Phys. 68 (2005) 1479.
[3] E. Bruck, J. Phys. D: Appl. Phys. 38 (2005) R381.
[4] V.K. Pecharsky, K.A. Gschneidner Jr., Int. J. Refrig. 29 (2006) 1239.
[5] N.K. Singh, K.G. Suresh, A.K. Nigam, S.K. Malik, A.A. Coelho, S. Gama, J. Magn. Magn. Mater. 317 (2007) 68.
[6] N.K. Sun, S. Ma, Q. Zhang, J. Du, Z.D. Zhang, Appl. Phys. Lett. 91 (2007) 112503.
[7] V.K. Pecharsky, K.A. Gschneidner Jr., Phys. Rev. Lett. 78 (1997) 4494.
[8] A. Fujita, S. Fujieda, Y. Hasegawa, K. Fukamichi, Phys. Rev. B 67 (2003) 104416.
[9] L. Li, K. Nishimura, Appl. Phys. Lett. 95 (2009) 132505.
[10] O. Tegus, E. Bruck, K.H.J. Buschow, F.R. De Boer, Nature (Lond.) 415 (2002) 150.
[11] B.G. Shen, J.R. Sun, F.X. Hu, H.W. Zhang, Z.H. Cheng, Adv. Mater. 21 (2009) 4545.
[12] R. Ballou, E. Burzo, V. Pop, J. Magn. Magn. Mater. 140–144 (1995) 945.
[13] W. Perthold, N.M. Hong, M. Michor, G. Hilscher, H. Ido, H. Asano, J. Magn. Magn. Mater. 157–158 (1996) 649.
[14] M. Dubman, E.N. Caspi, H. Ettedgui, L. Keller, M. Melamud, H. Ahaked, Phys. Rev. B 71 (2005) 024446.
[15] E.J. Wolfson, E.N. Caspi, H. Ettedgui, H. Shaked, M. Avdeev, J. Phys.: Condens. Matter 22 (2010) 026001.
[16] L. Li, K. Nishimura, H. Yamane, Appl. Phys. Lett. 94 (2009) 102509.
[17] L. Li, K. Nishimura, J. Appl. Phys. 106 (2009) 023903.
[18] L. Li, K. Nishimura, J. Phys. D: Appl. Phys. 42 (2009) 145003.
[19] J. Inoue, M. Shimizu, J. Phys. F: Met. Phys. 12 (1982) 1811.
[20] X.B. Liu, Z. Altounian, J. Magn. Magn. Mater. 292 (2005) 83.
[21] N.H. Duc, D.T.K. Anh, P.E. Brommer, Physica B 319 (2002).
[22] V.K. Pecharsky, K.A. Gschneidner Jr., J. Appl. Phys. 86 (1999) 565.
[23] W.J. Hu, J. Du, B. Li, Q. Zhang, Z.D. Zhang, Appl. Phys. Lett. 92 (2008) 192505.
[24] R. Rawat, I. Das, J. Phys.: Condens. Matter 13 (2001) L57.
[25] A.O. Pecharsky, Yu. Mozharivskyj, K.W. Dennis, K.A. Gschneidner Jr., R.W. McCallum, G.J. Miller, V.K. Pecharsky, Phys. Rev. B 68 (2003) 134452.