

# Temperature dependent neutron powder diffraction study of the Laves phase compound $\text{TbCo}_2$

Z.W. Ouyang<sup>a</sup>, F.W. Wang<sup>a</sup>, Q. Hang<sup>b</sup>, W.F. Liu<sup>a</sup>, G.Y. Liu<sup>a</sup>,  
J.W. Lynn<sup>b</sup>, J.K. Liang<sup>a,c</sup>, G.H. Rao<sup>a,\*</sup>

<sup>a</sup> Institute of Physics and Center for Condensed Matter Physics, Chinese Academy of Sciences,  
P.O. Box 603, Beijing 100080, People's Republic of China

<sup>b</sup> NIST Center for Neutron Research, National Institute of Standards and Technology,  
Gaithersburg, MA 20899, USA

<sup>c</sup> International Center for Materials Physics, Academia Sinica, Shenyang 110015,  
People's Republic of China

Received 30 July 2004; received in revised form 17 August 2004; accepted 18 August 2004

## Abstract

The structure, magnetization and magnetostriction of Laves phase compound  $\text{TbCo}_2$  are investigated by temperature dependent high resolution neutron powder diffraction. The compound crystallizes in the cubic Laves phase C15 structure above its Curie temperature  $T_C$  and exhibits a rhombohedral distortion (space group  $R\bar{3}m$ ) below  $T_C$ . By an appropriate extrapolation of the temperature factor of Co atom above  $T_C$ , the Rietveld refinement of the neutron powder diffraction data of the rhombohedral structure converges satisfactorily and reveals that the moments of Co1(3b) and Co2(9e) are almost equal. Tb moment follows well the Brillouin function. The total magnetic moment of  $\text{TbCo}_2$  is about  $5.8\mu_B/\text{f.u.}$ , the anisotropic magnetostriction constant  $\lambda_{111}$  is about  $4.6 \times 10^{-3}$  and the volume magnetostriction  $\omega_s$  is about  $8.7 \times 10^{-3}$  at 14 K.

© 2004 Elsevier B.V. All rights reserved.

PACS: 75.25.+z; 61.12.-q; 75.80.+q

Keywords: Magnetic structure; Neutron powder diffraction; Laves phase; Rhombohedral distortion

## 1. Introduction

For more than 20 years the cubic Laves phase compounds  $\text{RCO}_2$  (R = rare earth) have been one of particularly interesting subjects in solid state physics. The main reason for this is that  $\text{RCO}_2$  exhibits a metamagnetic transition due to the instability of Co moment [1–5]. X-ray diffraction analysis revealed that  $\text{TbCo}_2$  undergoes a rhombohedral distortion around the magnetic ordering temperature [6]. The spontaneous anisotropic magnetostriction constant  $\lambda_{111}$  and volume magnetostriction constant  $\omega_s$  of  $\text{TbCo}_2$  reach  $4.5 \times 10^{-3}$  and  $6.8 \times 10^{-3}$  at 4.2 K, respectively [7]. Neutron powder diffraction (NPD)

study of some  $\text{RCO}_2$  compounds was performed by Hendy and Lee [8]. However, limited information of crystal and magnetic structures was given in these investigations. Magnetic ordering will cause a reduction of the symmetry of the cubic structure. A structural distortion occurs below  $T_C \approx 240$  K, leading to two different Co atoms in  $\text{TbCo}_2$  [6,7]. It is likely that the two different Co atoms will have different magnetic moments, whereas Hendy and Lee simply considered that all the Co atoms have the same magnetic moment at low temperature. To clear this paradox, a neutron diffraction experiment is necessary. In this paper, we re-investigate the crystal and the magnetic structures of  $\text{TbCo}_2$  by means of temperature dependent neutron powder diffraction. Detailed information of crystal and magnetic structures as well as the spontaneous magnetostriction of the compounds is reported in this paper.

\* Corresponding author. Tel.: +86 1082649085; fax: +86 1082649531.  
E-mail address: ghrhao@aphy.iphy.ac.cn (G.H. Rao).

## 2. Experimental procedures

Polycrystalline sample of  $\text{TbCo}_2$  was prepared by arc melting the constituent elements with a purity of 99.9% in an atmosphere of high-purity argon. The sample was arc-melted 4–5 times with the button being turned over. The weight loss during arc-melting was less than 0.1 wt.%. The ingots were annealed at 800 °C under vacuum for 14 days. X-ray powder diffraction analysis showed that the compound has a cubic Laves phase C15 structure at room temperature. All the neutron diffraction experiments were performed at the NIST Center for Neutron Research (NCNR). The magnetic order parameter was determined on the BT-7 spectrometer with a wavelength of 2.4649 Å. NPD data for refinement of the magnetic structure were collected on the high-resolution, 32-counter BT-1 diffractometer. A Cu (3 1 1) monochromator was used to produce a monochromatic neutron beam of wavelength 1.5402(1) Å. Collimators with horizontal divergence of 15, 20, and 7 min of arc were used before and after the monochromator and after the sample, respectively. Data were collected in the  $2\theta$  range of 10–160° with a step of 0.05°. The program Fullprof [9,10] was used for the Rietveld refinement of the crystal and magnetic structures of the compound, using the following values of the scattering amplitudes:  $b(\text{Tb}) = 0.738$  and  $b(\text{Co}) = 0.249$  ( $\times 10^{-12}$  cm).

## 3. Results and discussion

Typical NPD patterns at different temperatures are presented in Fig. 1, in which the open circles stand for the observed intensities and the solid lines are the calculated patterns. The calculated patterns agree well with the experimental ones. The pattern above  $T_C$  is contributed exclusively by the nuclear structure. In Fig. 2 is shown the temperature dependence of intensity of the (1 1 1) peak referred to the cubic structure measured on the BT-7 diffractometer when warming and cooling the sample. An evident hysteresis is seen on the curves in the vicinity of Curie temperature. Details of the refinement of the magnetic and crystal structures are described as follows.

Because of the overlap of the magnetic reflections with the nuclear Bragg reflections, the nuclear structure was first refined by using the NPD data in high angle region where the contribution from the magnetic ordering is negligible. The data in the range of  $2\theta = 100$ –160° were used at this stage for the refinement of nuclear structure. The structural and profile parameters obtained from the refinement were used to derive the profile generated by the nuclear structure. A careful analysis reveals that  $\text{TbCo}_2$  has a cubic Laves phase structure with space group  $Fd\bar{3}m$  at room temperature. With decreasing temperature,  $\text{TbCo}_2$  exhibits a rhombohedral distortion (space group  $R\bar{3}m$ ) when the temperature is below  $T_C \approx 240$  K. This result is in good agreement with that revealed by X-ray powder diffraction [6]. Table 1 gives the structural information of  $\text{TbCo}_2$ , where the lengths of Co–Co bonds are

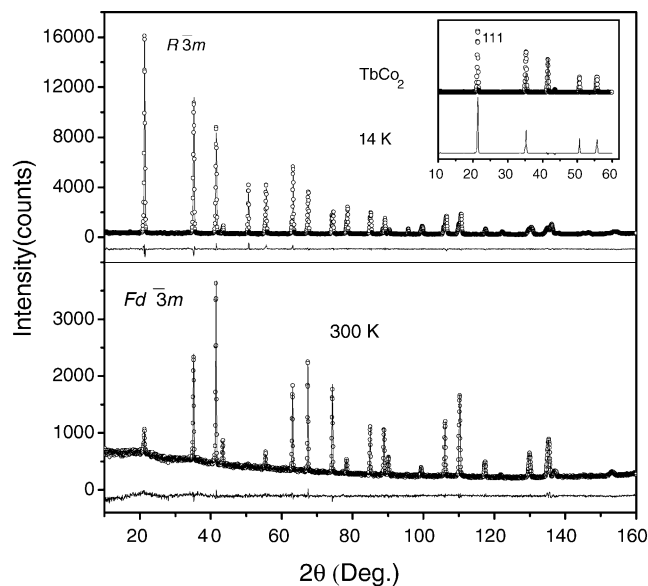


Fig. 1. Typical NPD patterns of  $\text{TbCo}_2$  at 14 and 300 K. The open circles stand for the observed intensities, the solid lines are the calculated profiles. At the bottom is shown the difference between the experimental and the calculated intensities. In the inset is shown the calculated pattern without the magnetic contribution in the low Bragg angle range. The difference at the bottom represents the contribution of the magnetic structure to the diffraction peaks. The index of the reflections refers to the cubic structure.

also derived. The temperature dependence of the lattice constant and the unit cell volume of  $\text{TbCo}_2$  are shown in Fig. 3. It exhibits a second-order structural transition in the vicinity of  $T_C$ .

As the second step, the intensities of the magnetic reflections were determined by subtracting the contribution of nuclear structure from the observed intensities. Example of this procedure is illustrated in the inset of Fig. 1 for 14 K. The calculated profile in the upper part (solid line) does not include the magnetic contribution and therefore the difference

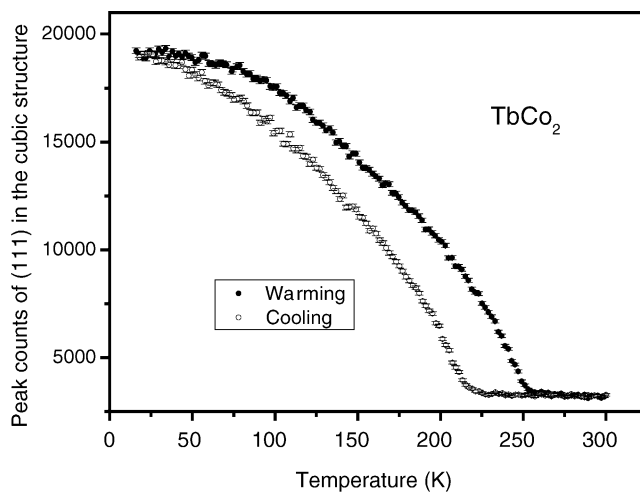


Fig. 2. The temperature dependence of the NPD counts of (1 1 1) peak in the cubic structure measured on the BT-7 diffractometer. The errors bars are also shown.

Table 1  
Structural parameters and atomic moments of TbCo<sub>2</sub> at selected temperatures

Parameters	14 K	50 K	100 K	150 K	200 K	300 K
$a$ (Å)	5.0824(6)	5.0832(2)	5.0864(2)	5.0900(2)	5.0932(3)	7.2099(1)
$c$ (Å)	12.5351(5)	12.5344(6)	12.5266(6)	12.5140(7)	12.4981(9)	
$V$ (Å <sup>3</sup> )	46.73(2)	46.74(1)	46.77(1)	46.79(1)	46.79(1)	46.85(1)
Tb $z$	0.1264(1)	0.1268(2)	0.1264(3)	0.1258(0)	0.1241(9)	
$M_z$ ( $\mu_B$ )	8.30(5)	8.17(9)	7.46(9)	6.33(9)	4.54(10)	
Co1 $M_z$ ( $\mu_B$ )	1.30(4)	1.11(6)	1.23(7)	1.08(8)	0.76(10)	
Co2 $M_z$ ( $\mu_B$ )	1.19(3)	1.23(4)	1.12(5)	1.10(6)	0.94(9)	
$d_{\text{Co-Co(ave.)}}$ (Å)	2.5470(2)	2.5472(1)	2.5478(2)	2.5481(1)	2.5481(1)	2.5491(1)
$d_{\text{Co1-Co2}}$ (Å)	2.5530(1)	2.5525(1)	2.5521(2)	2.5510(1)	2.5501(3)	
$d_{\text{Co2-Co2}}$ (Å)	2.5410(2)	2.5421(3)	2.5429(3)	2.5448(2)	2.5471(1)	
$R_p$ (%)	4.84	6.79	7.08	6.59	7.31	4.24
$R_{wp}$ (%)	6.36	9.15	9.46	8.61	9.87	5.88
$\chi^2$	1.86	1.31	1.34	1.21	1.55	1.40

When  $T < T_C \approx 240$  K, the compound has a rhombohedral structure (space group  $R\bar{3}m$ ) with atomic sites: Tb(6c) (0,0, $z$ ), Co1(3b) (0,0,0.5) and Co2(9e) (0.5,0,0). When  $T > T_C$ , the compound has a cubic structure (space group  $Fd\bar{3}m$ ) with atomic sites: Tb(8a) (0.125,0.125,0.125), Co(16d) (0.5,0.5,0.5).  $V$  is the volume per chemical formula.  $d_{\text{Co1-Co2}}$  is the lengths of Co1–Co2 bonds,  $d_{\text{Co2-Co2}}$  is the lengths of Co2–Co2 bonds in one tetrahedron and  $d_{\text{Co(ave.)}}$  is the average bond length (see Fig. 7). The magnetic moments of Tb and Co are set along  $c$  direction in the rhombohedral structure, i.e.,  $M_x = M_y = 0$ .

curve at the bottom shows the magnetic reflections. It can be seen that the contribution due to the magnetic ordering is very large compared with that of the nuclear structure. From the difference curve it is in principle possible to determine the orientation of the magnetic moments. Since the character of the unit cell distortion is determined by the orientation of the easy axis of magnetization in  $R\text{Co}_2$ , the rhombohedral distortion of the cubic unit cell indicates that the magnetic moment has a preferential orientation along  $\langle 111 \rangle$  of the cubic structure.

In the present model of magnetic structure for the refinement, it is assumed that the moments of the magnetic atoms in the compound have a collinear alignment. The initial moments are set to be along the  $c$  axis of the rhombohedral structure, corresponding to the direction  $\langle 111 \rangle$  in the cubic structure. The magnetic moments of Co1(3b) and Co2(9e) in TbCo<sub>2</sub> are initially set to have different values. For the sake of simplicity, Co1(3b) and Co2(9e) are set to have identical isotropic temperature factor. It was found that the temper-

ature factor  $B$  and the magnetic moment showed a strong correlation in the refinement.  $B_{\text{Co}}$  of TbCo<sub>2</sub> is successfully determined for the cubic phase (paramagnetic), whereas it varies irregularly with temperature in the low temperature region due to the small Co moment. Therefore, in our model, the value of  $B_{\text{Co}}$  at low temperature is estimated by extrapolating that in cubic structure. Then  $B_{\text{Tb}}$  can be derived and shows an almost linear variation with temperature, as illustrated in Fig. 4. The magnetic moments at different temperatures are thus derived from the refinement. The magnetic moments of Tb and Co at some selected temperatures are listed in Table 1. The refinement of the magnetic structure reveals that the Tb moment and Co moment couple antiferromagnetically, in accordance with the general rule for the heavy rare earth  $R\text{Co}_2$  compounds. The magnetic moment as a function of temperature is shown in Fig. 5. The solid lines are Brillouin function normalized to the magnetic moments at 14 K and to the ordering temperature ( $T_C \approx 240$  K) with  $J = 6$  and  $1/2$  for Tb and Co, respectively. The Tb moment

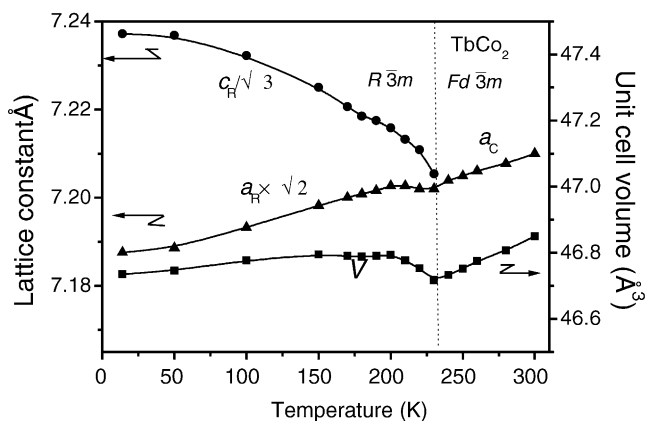


Fig. 3. The temperature dependence of the lattice constant and the unit cell volume of TbCo<sub>2</sub>.

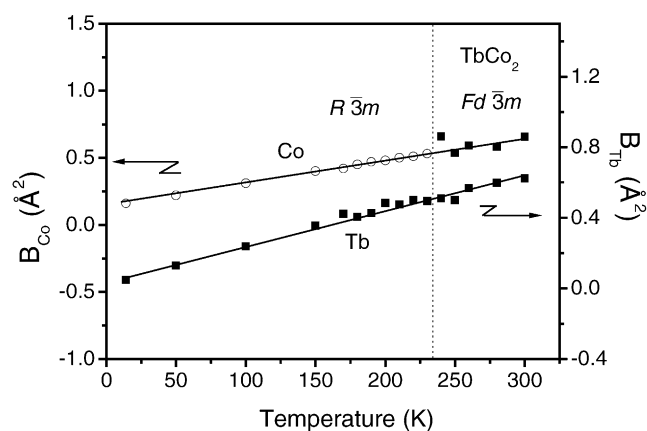


Fig. 4. The temperature dependence of the temperature factor of TbCo<sub>2</sub>.

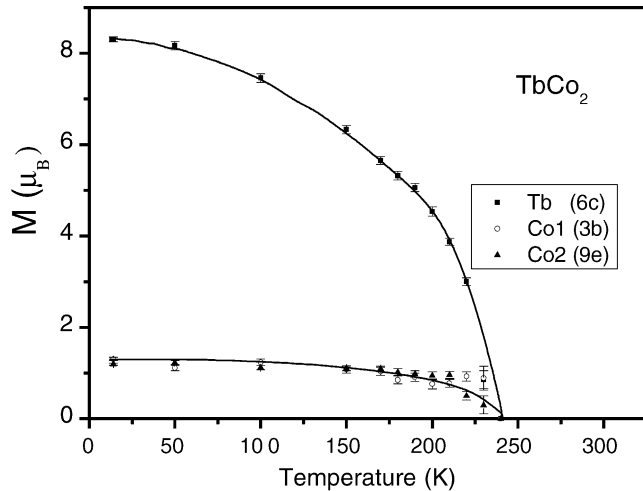


Fig. 5. The temperature dependence of magnetic moments of Tb and Co in TbCo<sub>2</sub>. The solid lines are Brillouin functions normalized to the magnetic moments at 14 K and to the ordering temperature ( $T_C \approx 240$  K) with  $J = 6$  and  $1/2$  for Tb and Co, respectively.

follows well the Brillouin function for  $J = 6$ . The moments of Co1(3b) and Co2(9e) are almost equal. The Co moment also follows the Brillouin function for  $J = 1/2$ , except around  $T_C$ , indicating the predominant contribution of the itinerant electron spin of Co atom. Both the Tb and the Co moments are a little larger than the report of Hendy and Lee [8]. However, the total magnetic moment of the compound is derived to be  $5.8\mu_B/\text{f.u.}$  at 14 K, in good accordance with the result of Hendy and Lee [8].

In RCo<sub>2</sub>, the existence of structure distortion would cause a large anisotropic magnetostriction along the direction of magnetization. Within first approximation the magnetostriction of a cubic crystal in any direction given by the direction cosines  $\beta_i$  can be expressed by

$$\lambda = \left(\frac{3}{2}\right) \lambda_{100} \left( \sum_i \alpha_i^2 \beta_i^2 - \frac{1}{9} \right) + 3\lambda_{111} \sum_{i<j} \alpha_i \alpha_j \beta_i \beta_j \quad (1)$$

where  $\alpha_i$  represent the direction cosines of the magnetization. From Eq. (1), one can easily obtain the following expressions:

$$\lambda_{111} = \Delta\alpha \quad (2)$$

where  $\Delta\alpha$  is a deviation of the angle between neighboring edges of the distorted cube from  $\pi/2$  [11]. The obtained anisotropic magnetostriction constant  $\lambda_{111}$  at 14 K is about  $4.6 \times 10^{-3}$ , in good agreement with the result of Levitin and Markosyan [11]. The temperature dependence of  $\lambda_{111}$  is shown in Fig. 6.

The RCo<sub>2</sub> compounds have a large spontaneous volume magnetostriction due to the magnetic ordering of the itinerant electron system. The thermal expansion measurement serves as a useful tool to study the  $d$ -electron magnetism in the RCo<sub>2</sub> compounds. The difference between the unit cell volume at a given temperature  $V_m$  and the “paramagnetic” unit cell vol-

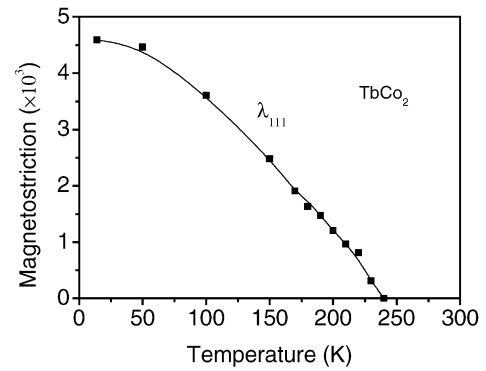


Fig. 6. The temperature dependence of the anisotropic magnetostriction constant of TbCo<sub>2</sub>.

ume  $V_p$ , gives the spontaneous volume magnetostriction

$$\omega_s(T) = \frac{V_m(T) - V_p(T)}{V_p(T)} \quad (3)$$

where  $V_p$  is obtained by extrapolation from the paramagnetic temperature region. In the first approximation, Eq. (3) is related to the  $d$ -electron magnetic moment  $M_{Co}$  by  $\omega_s = kCM_{Co}^2$ , where  $k$  is the isotropic compressibility and  $C$  is the volume magnetostriction coupling constant [11]. The obtained  $\omega_s$  at 14 K is about  $8.7 \times 10^{-3}$ , which is larger than  $6.8 \times 10^{-3}$  at 4.2 K [7]. Taking  $M_{Co} \approx 1.2\mu_B$ , the value of  $kC$  is estimated to be  $6.0 \times 10^{-3} \mu_B^{-2}$ .

Finally we calculate the distortion of the Co tetrahedron. A schematic representation of a cubic unit cell of TbCo<sub>2</sub> is shown in Fig. 7, where four Co tetrahedrons are embedded in the diamond structure consisting of Tb atoms. Co1(3b) occupies the top of the tetrahedron and the Co2(9e) occupies the plane perpendicular to  $\langle 111 \rangle$ . The Co–Co bond lengths are calculated and given in Table 1, where  $d_{Co}(\text{ave.})$  is the aver-

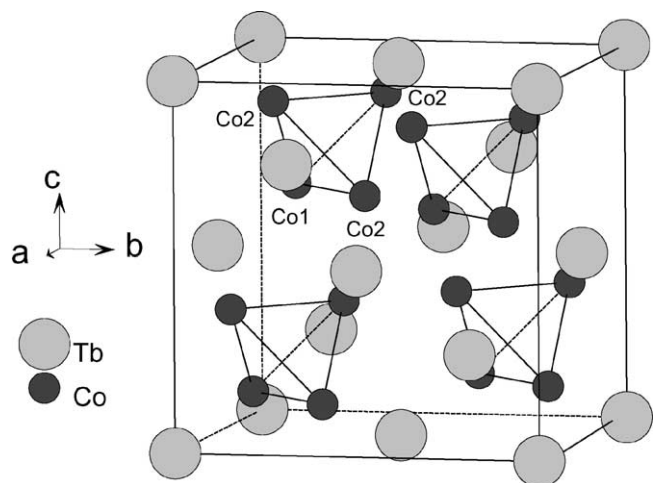


Fig. 7. Schematic representation of the structure of cubic Laves phase (space group  $Fd\bar{3}m$ ), in which four Co tetrahedrons are embedded in the diamond structure consisting of Tb atoms. In the cubic structure, the lengths of all Co–Co bonds are equal. When  $T < T_C$ , the tetrahedron is distorted, leading to a reduction of  $d_{Co2-Co2}$  and an increase of  $d_{Co1-Co2}$ .

age bond length. In the cubic structure, all the Co–Co bond lengths in the tetrahedron are equal. When  $T < T_C$ , the value of  $d_{\text{Co2–Co2}}$  is smaller and  $d_{\text{Co1–Co2}}$  is larger than  $d_{\text{Co}}(\text{ave.})$ . Therefore, the tetrahedrons of Co atoms elongate along the  $\langle 111 \rangle$  direction of the cubic structure. The variation of the bond length agrees with the fact that  $\text{TbCo}_2$  has a positive anisotropic magnetostriction along the easy magnetization direction  $\langle 111 \rangle$ .

#### 4. Conclusions

In present investigation, the crystal structure, magnetization and anisotropic magnetostriction of  $\text{TbCo}_2$  are investigated by temperature dependent high resolution neutron powder diffraction. It is revealed that the compound retains the cubic Laves phase C15 structure above Curie temperature  $T_C$ . As temperature decreases,  $\text{TbCo}_2$  exhibits a rhombohedral distortion below  $T_C$ . The temperature dependence of the unit cell volume, the magnetic moment and the anisotropic magnetostriction constant  $\lambda_{111}$  are derived. It is revealed that the moments of Co1(3b) and Co2(9e) are almost equal. The Tb moment follows very well the Brillouin function for  $J = 6$ . The obtained magnetic moment of  $\text{TbCo}_2$  is about  $5.8 \mu_B/\text{f.u.}$ , the anisotropic magnetostriction constant  $\lambda_{111}$  is about  $4.6 \times$

$10^{-3}$  and the volume magnetostriction  $\omega_s$  is about  $8.7 \times 10^{-3}$  at 14 K.

#### Acknowledgements

National Nature Science Foundation of China and State Key Project of Fundamental Research support the work.

#### References

- [1] M.I. Batashevich, H.A. Katori, T. Goto, H. Wada, T. Maeda, T. Mori, M. Shiga, *Physica B* 229 (1997) 315.
- [2] T. Goto, H.A. Katori, T. Sakakibara, H. Mitamura, K. Fukamichi, K. Murata, *J. Appl. Phys.* 76 (1994) 6682.
- [3] T. Goto, K. Fukamichi, H. Yamada, *Physica B* 300 (2001) 167.
- [4] S. Khmelevskiy, P. Mohn, *J. Phys.: Condens. Matter* 12 (2000) 9453.
- [5] E. Gratz, A.S. Markosyan, *J. Phys.: Condens. Matter* 13 (2001) 385.
- [6] N. Yoshimoto, J. Sakurai, Y. Komura, *J. Magn. Magn. Mater.* 31–34 (1983) 137.
- [7] D. Gignoux, F. Givord, R. Perrier de la Bathie, F. Sayetat, *J. Phys. F: Metal Phys.* 9 (1979) 763.
- [8] P. Hendy, E.W. Lee, *Phys. Stat. Sol. (a)* 50 (1978) 101.
- [9] H.M. Rietveld, *Acta Crystallogr.* 229 (1967) 151.
- [10] J.L. Rodríguez-Carvajal, *Physica B* 192 (1993) 55.
- [11] R.Z. Levitin, A.S. Markosyan, *J. Magn. Magn. Mater.* 84 (1990) 247.