INVESTIGATION OF TEMPERATURE DEPENDENT CHARACTERISTICS OF COMPOUND $TbCo_2$ USING NEUTRON POWDER DIFFRACTION TECHNIQUE

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Abstract

The structure, magnetization and magnetostriction of Laves phase compound $TbCo_2$ were 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 R3m) 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 Co_1 (3b) and Co_2 (9e) are almost equal. The moment follows well the Brillouin function. The total magnetic moment of $TbCo_2$ was found to be 5.8μ_B/ f.u; the anisotropic magnetostriction constant λ_{III} is about 4.6 x 10^{-3} and the volume magnetostriction ω_s is about 8.7 x 10^{-3} at 14K.

Keywords: *Magnetic structure; neutron powder diffraction; laves phase; rhombohedral distortion.*

Introduction

For more than 20 years the cubic Laves phase compounds RCo_2 (R = rare earth) have been one of particularly interesting subjects in solid state physics. The main reason for this is that RCo_2 exhibits a metamagnetic transition due to the instability of Co moment. X –ray diffraction analysis revealed that $TbCo_2$ undergoes a rhombohedral distortion around the magnetic ordering temperature. The spontaneous anisotropic magnetostriction constant λ_{III} and volume magnetostriction constant ω_s of $TbCo_2$ reach 4.5 x 10^{-3} and 6.8 x 10^{-3} at 4.2K, respectively. Neutron powder diffraction (NPD) study of some RCo_2 compounds was performed by Hendy and Lee (1978). 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 Tc ≈ 240K, leading to two different co atoms in $TbCo_2$. It is likely that the two different Co atoms will have different magnetic moments, whereas Hendy and Lee (1978) 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 $TbCo_2$ 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.

Experimental Procedures

Polycrystalline sample of $TbCo_2$ 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 Physics laboratory of the ABU Zaria, Nigeria. The magnetic order parameter was determined on the BT-7 spectrometer with a wavelength of 2.4649A. NPD data for refinement of the magnetic structure were collected on the high-resolution, 32-counter BT-1 diffractometer. A Cu (311) 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 2θ range of 10-160° with a step of 0.05°. The program fullprof of Rietveld (1967) was used for the rietveld refinement of the crystal and magnetic structures of the compound, using the following values of the scattering amplitudes: b(Tb) =0.738 and b(Co) = 0.249 ($x10^{-12}$cm).

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 (111) peak referred to the cubic structure measured on the BT-7 diffractometer when warming and cooling the sample. An evident hystersis 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 2θ = 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 $TbCo_2$ has a cubic Laves phase structure with space group Fd3m at room temperature. With decreasing temperature, $TbCo_2$ exhibits a rhombohedral distortion (space group R3m) when the temperature is below Tc ≈240K. This result is in good agreement with that revealed by X –ray powder diffraction of khmelevskyi and Mohn (2000). Table 1 gives the structural information of $TbCo_2$, where the lengths of Co-Co bonds are also derived.

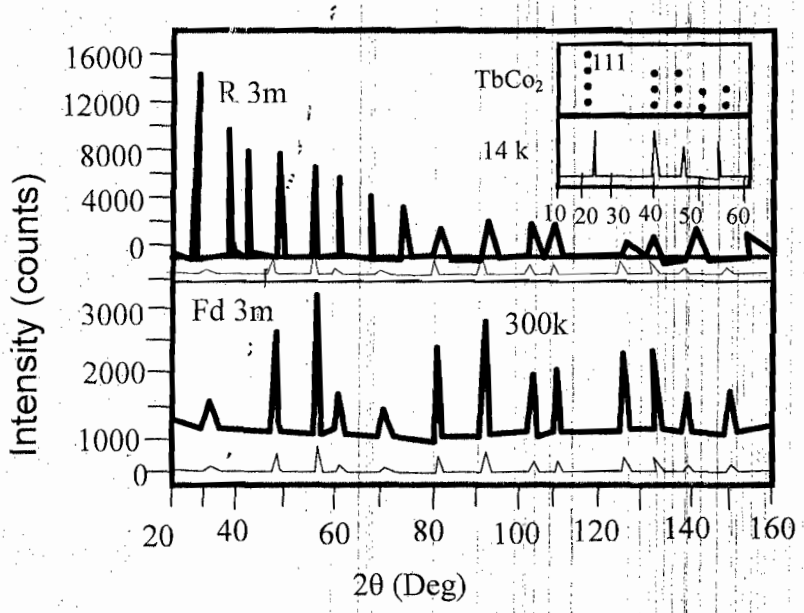

Fig.1: Typical NPD patterns of $TbCo_2$ at 14 and 300K.

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.

The temperature dependence of the lattice constant and the unit cell volume of $TbCo_2$ 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 substracting the contribution of nuclear structure from the observed intensities. Example of this procedure is illustrated in the inset of Fig. 1 for 14K. The calculated profile in the upper part (solid line) does not include the magnetic contribution and therefore the difference.

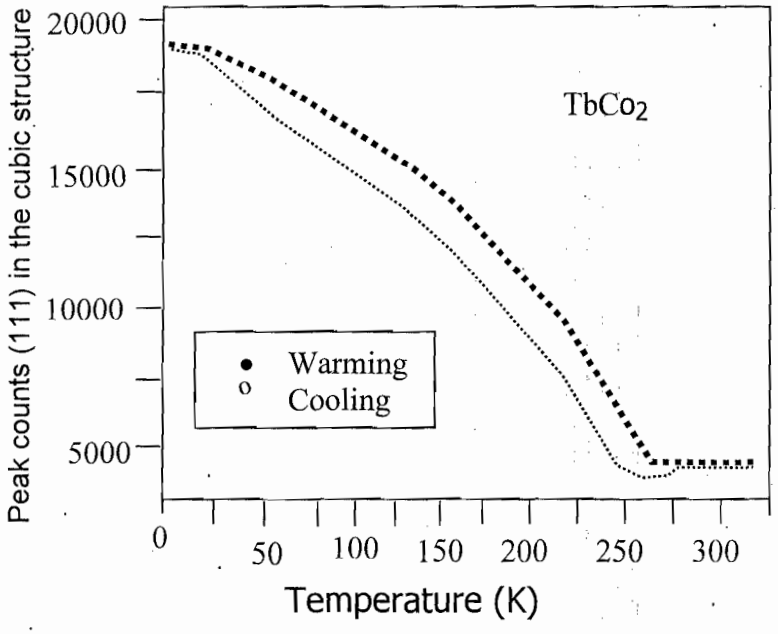

Fig. 2: The temperature dependence of the NPD counts of (111) peak in the cubic structure measured with the BT-7 diffractometer.

Table 1: Structural parameters and atomic moments of $TbCo_2$ at selected temperatures

Parameters	14k	50k	100k	150k	200k	300k
a (Å)	5.0824(6)	5.0832(2)	5.0864(4)	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)	
p ($Å^3$)	46.73(2)	46.74(1)	46.77(1)	46.79(1)	46.79(1)	46.85(1)
Tbz	0.1264(1)	0.1268(2)	0.1264(3)	0.1258(0)	0.1241(9)	
M_z (μ_β)	8.30(5)	8.17(9)	7.46(9)	6.33(9)	4.54(10)	
Co1 M_z (μ_β)	1.30(4)	1.11(6)	1.23(7)	1.08(8)	0.76(10)	
Co2 M_z (μ_β)	1.19(3)	1.23(4)	1.12(5)	1.10(6)	0.94(9)	
d_{Co-Co}(ave)(Å)	2.5470(2)	2.5472(1)	2.5478(2)	2.5481(1)	2.5481(1)	2.5491(1)
$d_{Co1-Co2}$(Å)	2.5530(1)	2.5525(1)	2.5521(2)	2.5510(1)	2.5501(3)	
$d_{Co2-Co2}$(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
X^2	1.86	1.31	1.34	1.21	1.55	1.40

When $T < T_C \approx 240k$, the compound has a rhombodedral structure (space group R3m) with atomic sites: Tb(6c) (0.0,z). Col (3b) (0,0,0.5) and Co_2(9e) (0,5,0,0). When $T > T_C$, the compound has a cubic structure (space group Fd3m) 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. dco1 – Co2 is the lengths of Co_1 - Co_2 bonds. dco2 – Co2 is the lengths of Co_2 –Co_2 bonds in one tetrahedron and dco (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.

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 RCo_2, the rhombohedral distortion of the cubic unit cell indicates that the magnetic moment has a preferential orientation along (111) 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 (111) in the cubic structure. The magnetic moments of Co1 3b) and Co2 (9e) in $TbCo_2$ 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 temperature factor *B* and the magnetic moment showed a strong correlation in the refinement. Bc_o of $TbCo_2$ 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_{CO} at low temperature is estimated by extrapolating that in cubic structure. Then B_{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 Rco2 compounds. The magnetic moment as a function of temperature is show in Fig. 5. The solid lines are Brillouin function normalized to the magnetic moments at 14K and to the ordering temperature ($T_C \approx$ 240K) with J=6 and ½ for Tb and Co, respectively. The Tb moment

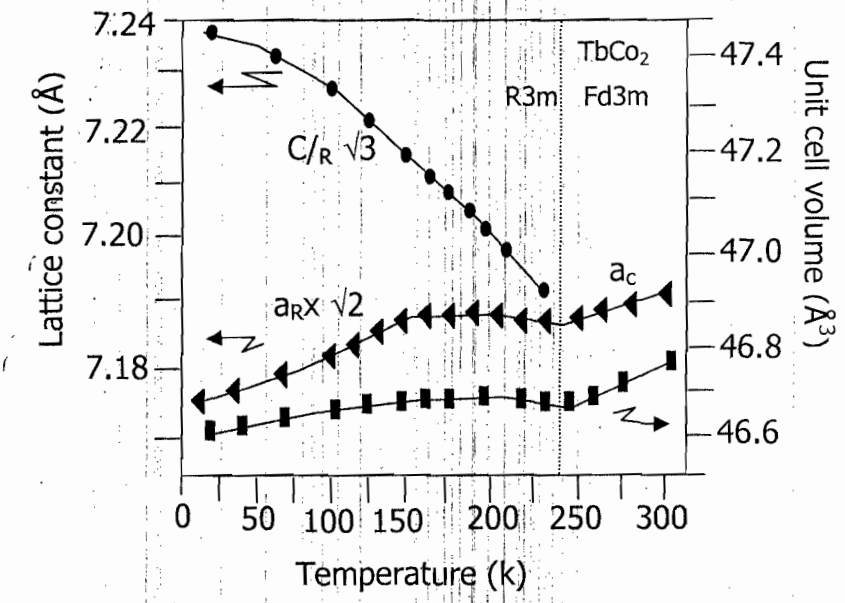

Fig. 3. The temperature dependence of the lattice constant and the unit cell volume of $TbCo_2$

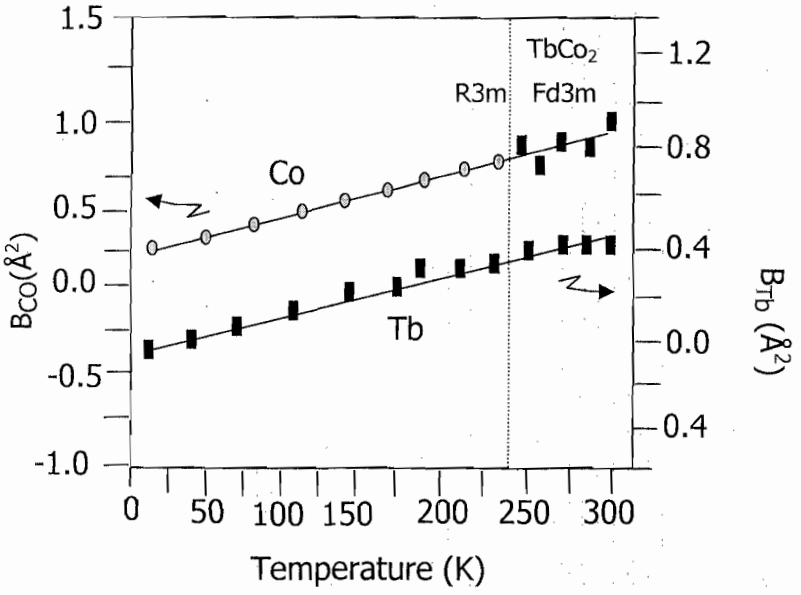

Fig. 4. The temperature dependence of the temperature factor of $TbCo_2$.

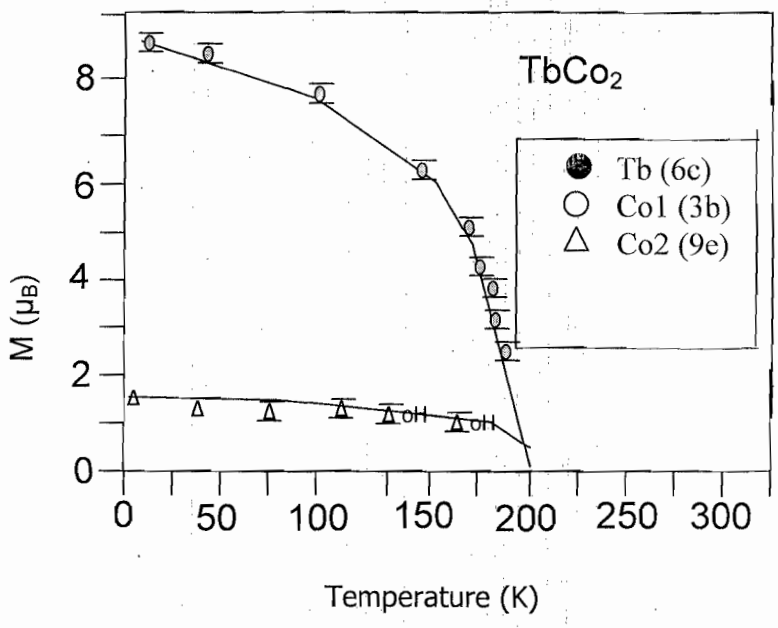

Fig. 5. The temperature dependence of magnetic moments of Tb and Co in $TbCo_2$. The solid lines are Brillouin functions normalized

to the magnetic moments at 14K and to the ordering temperature (Tc ≈240K) with J =6 and ½ 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 = ½, 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 (1978).

However, the total magnetic moment of the compound is derived to be 5.8μB/f.u. at 14K, in good accordance with the result of Hendy and Lee (1978).
In RCo_2, the existence of structure distortion would cause a larger anisotropic magnetostriction along the direction of magnetization. Within first approximation the magnetostriction of a cubic crystal in any direction given by the direction cosines β_i can be expressed by

$$\lambda = (^3/_2)\,\lambda_{100}\,(\sum_i \alpha^2_i\,\beta_i^2 - {}^1/_9) + 3\lambda_{111} \sum_{i<j} \alpha_i\,\alpha_j\,\beta_i\,\beta_j \qquad (1)$$

where α_i represent the direction cosines of the magnetization.

From Eqn. (1), one can easily obtain the following expressions:

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

where $\Delta\alpha$ is a deviation of the angle between neighboring edges of the distorted cube from $\pi/2$. The obtained anisotropic magnetosriction constant λ_{111} at 14K is about 4.6×10^{-3}, in good agreement with he result of Levitin and Markosyan (1990). The temperature dependence of λ_{111} is shown in Fig. 6.

The RCo_2 compounds have a large spontaneous volume magnetostiction 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_2 compounds. The difference between the unit cell volume at a given temperature V_m and the "paramagnetic" unit cell volume V_p, gives the spontaneous volume magnetostriction

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

where v_p is obtained by extrapolation from the paramagnetic temperature region.

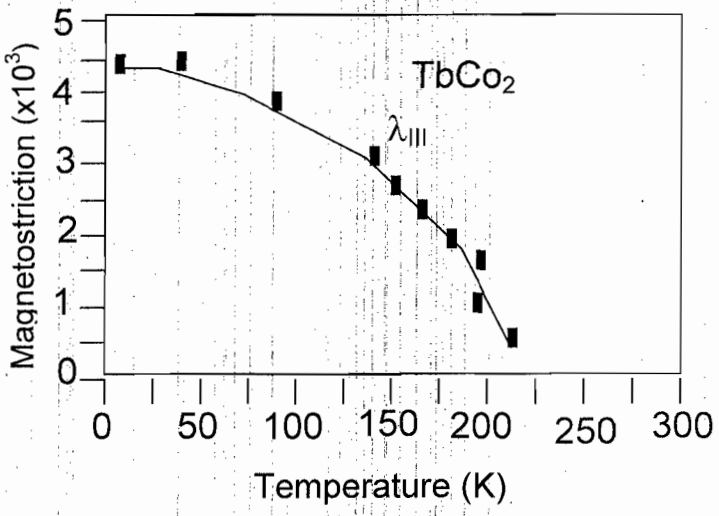

Fig. 6: The temperature dependence of the anisotropic magnetostriction constant of $TbCo_2$.

In the first approximation, Eq. (3) is related to the d-electron magnetic moment M_{Co} by $\omega_s = kCM^2_{Co}$, where k is the isotropic compressibility and C is the volume magnetostriction coupling constant. The obtained ω_s at 14K is about 8.7×10^{-3}, which is larger than 6.8×10^{-3} at 4.2K. Taking Mco = 1.2μB, the value of kC is estimated to be $6.0 \times 10^{-3}\ \mu_\beta^{-2}$.

Finally we calculate the distortion of the Co tetrahedron. A schematic representation of a cubic unit cell of $Tbco_2$ 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 (111). The Co-Co bond lengths are calculated and given in Table 1, where d_{Co} (ave.) is the average bond length.

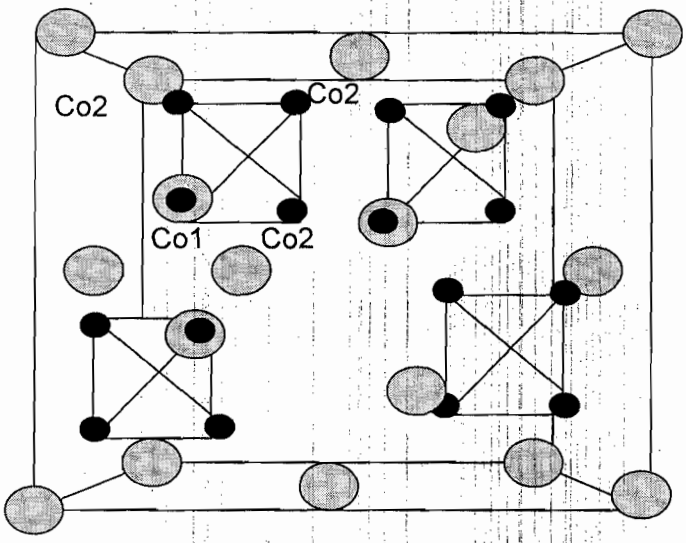

Fig. 7: Schematic representation of the structure of cubic Laves phase (space group Fd3m), in which four Co tetrahedrons are embedded in the diamond structure consisting of Tb atoms.

In the cubic structure, the lengths of all Co-Co bonds are equal. When T < Tc, the tetrahedron is distorted, leading to a reduction of $d_{Co2-Co2}$ and an increase of $d_{Co1-Co2}$.

In the cubic structure, all the Co-Co bond lengths in the tetrahedron are equal. When T < Tc, the value of $d_{Co2-Co2}$ is larger than d_{Co} (ave). Therefore, the tetrahedrons of Co atoms elongate along the (111) direction of the cubic structure. The variation of the bond length agrees with the fact that $TbCo_2$ has a positive anisotropic magnetostriction along the easy magnetization direction (111).

Conclusions

The crystal structure, magnetization and anisotropic magnetostriction of $TbCo_2$ are investigated by temperature dependent high-resolution neutron power diffraction. It is revealed that the compound retains the cubic Laves phase C15 structure above Curie temperature, T_C. As temperature decreases. $TbCo_2$ exhibits a rhombohedral distortion below Tc. The temperature dependence of the unit cell volume, the magnetic moment and the anisotropic magnetostriction constant λ_{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 $TbCo_2$ is about 5.8 μB/f.u., the anisotropic magnetostriction constant λ_{111} is about 4.6 x 10^{-3} and the volume magnetostriction ω_s is about 8.7 x 10^{-3} at 14K.

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