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Low temperature rhombohedral distortion in $TbCo_2$

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A strong rhombohedral distortion takes place in the $TbCo_2$ Laves compound below its magnetic ordering temperature. The analysis of the low-temperature powder diffraction spectra enabled the determination of a giant magnetostriction coefficient, λ_{111}, of the order of 3×10^{-3} at 80 K.

1. Introduction

The rare-earth iron Laves phase compounds display a variety of interesting magnetoeleastic properties. Particularly noteworthy is the giant magnetostriction which has been observed in $TbFe_2$ [1, 2]. In this compound the easy axis of magnetization is parallel to the [1 1 1] direction and λ_{111}, the magnetostriction coefficient, is positive. Dwight and Kimball [3] reported that in the magnetically ordered state the allegedly cubic $TbFe_2$ compound actually displays a pronounced rhombohedral distortion. Similar rhombohedral distortions were observed by Barbara *et al.* [4] in the RFe_2 compounds, R = Sm, Tm which, like $TbFe_2$, have at room temperature an [1 1 1] easy axis of magnetization. Cullen and Clark [5] have recently shown that in RFe_2 Laves compounds having spontaneous axis of magnetization parallel to the [1 1 1] direction, an internal rhombohedral distortion takes place. This distortion is coupled to the external strain and leads to the giant observed magnetostriction. Contrary to the above, the R = Dy, Ho Laves compounds possess easy axes of magnetization parallel to the [1 0 0] direction. Cullen and Clark showed that there was no corresponding structural distortion associated with this direction and, therefore, the latter compounds maintained their cubic symmetry.

The single rare-earth ion magnetic anisotropy gives a fully consistent account of the bulk magnetic and magnetoelastic properties of the RFe_2 Laves phases. The relatively high magnetic ordering temperatures (> 600 K) are ascribed to the strong Fe–Fe exchange interactions. The isostructural RCo_2 compounds have much lower ordering temperatures, attributed to the weaker R–Co interactions which are the dominant ones in these compounds. Nevertheless, the magnetic anisotropy and the magnetoelastic properties are still determined by the single rare-earth ion anisotropy as shown, for instance, by Mössbauer effect measurements [6]. The objective of the present work was to study possible structural distortions in the magnetically ordered RCo_2 compounds. In this paper we report the presence of a strong rhombohedral distortion in the $TbCo_2$ Laves phase.

2. Experimental details and procedures

The Laves compound $TbCo_2$ was prepared by arc-melting 99.9% pure Tb and 99.99% Co lumps under a gettered argon atmosphere. $TbCo_2$ melts non-congruently at $\simeq 1180^\circ$ C [7], lengthy anneals are, therefore, necessary to ensure single-phase homogeneous samples. The arc-melted buttons were wrapped in thin Ta foils and annealed for 1 week at 1100° C in evacuated quartz capsules. This anneal yielded a practically single-phase sample as shown by metallographic and electron microprobe

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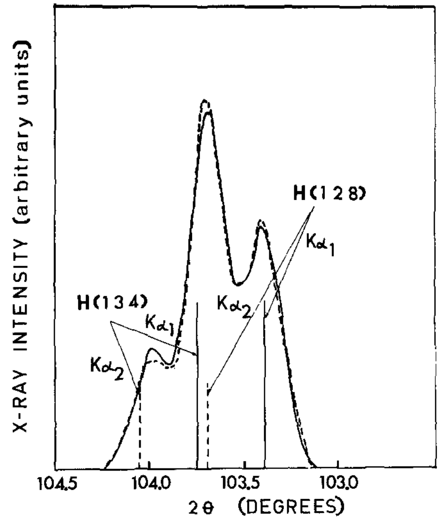

Figure 1 Diffraction profile of the cubic (6 2 0) reflection taken at 120 K. At this temperature the reflection splits into the two (1 2 8) and (1 3 4) reflections (the Miller indices correspond to the hexagonal representation of the unit cell). Each such reflection in itself is a doublet due to the $K\alpha_1$ and $K\alpha_2$ splitting. The dashed curve represents the experimental profile and the full curve, the least-squares computer-fitted profile.

analysis. At room temperature, the measured lattice parameter of $TbCo_2$ was 7.208 ± 0.002 Å, in good agreement with results reported in the literature.

Below room temperature, the diffraction spectra were obtained using a low-temperature attachment (Air Products and Chemicals) in conjunction with a Philips diffractometer. Diffraction spectra of the powdered specimen were taken at a series of temperatures, stabilized within 1 K, in the 80 to 300 K range. The low-temperature attachment was calibrated using high-purity silicon powder.

Visual inspection of the diffraction patterns obtained below the magnetic ordering temperature of $TbCo_2$, $T_C = 240$ K, showed the presence of a strong structural distortion. Most diffraction peaks of the f c c structure of $TbCo_2$ broaden or split into two or more peaks (Fig. 1). The distortion was ascribed to the transformation – similar to that taking place in $TbFe_2$ – from the initial C-15 cubic structure into a rhombohedral structure. The diffraction pattern of the rhombohedral structure was interpreted using a computer program which generated line positions and intensities. It used as input the general positions of the corresponding space group – $R\bar{3}m$, in the present case – the special positions of the atoms in the structure type and approximate lattice parameters. The intensities of the individual reflections were computed according to $p|F|^2LP$ where p is the multiplicity, F, the structure factor and LP, the combined Lorentz–polarization factor. The diffraction profiles of the peaks listed in Table I were used as experimental data for least-square fitting to computer-generated diffraction profiles. In the course of this analysis, four free parameters were used, namely a_H and c_H, the lattice constants of the rhombohedral unit cell in the hexagonal representation, a normalization factor and Γ, the width of the diffraction line for which a Gaussian profile was assumed.

TABLE I Calculated intensities of the reflections of the rhombohedral unit cell of $TbCo_2$ used for the determination of the lattice parameters and the magnetostriction coefficient

Original C-15 cubic structure	Rhombohedral structure in its hexagonal representation. Space group $R\bar{3}m$	
Indices *hkl*	Indices *hkl*	Intensities
4 4 0	2 0 8	22.8
	2 2 0	22.7
6 2 0	1 2 8	11.6
	1 3 4	11.5
5 3 3	0 1 11	5.8
	1 3 5	11.5
	0 4 1	5.8
6 4 2	1 1 11	8.9
	3 1 8	8.9
	3 2 4	8.9
	4 1 0	8.9

3. Discussion

The temperature dependence of the lattice parameters of the hexagonal unit cell of $TbCo_2$ is plotted in Fig. 2. The lattice parameters at each

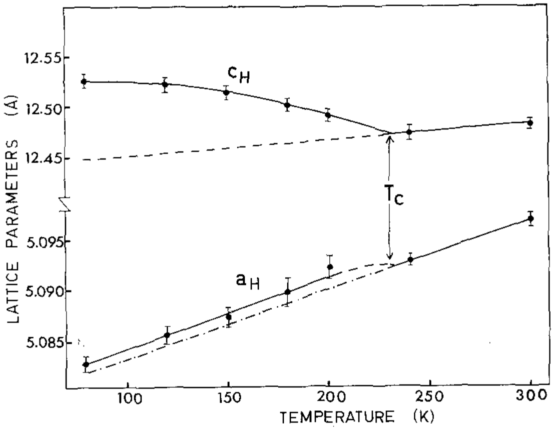

Figure 2 Temperature dependence of the lattice parameters of the hexagonal unit cell of $TbCo_2$.

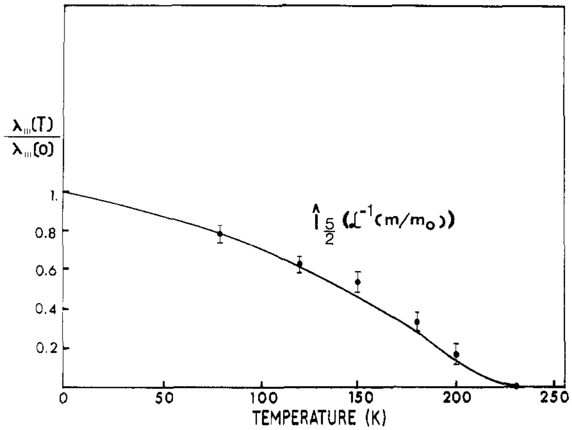

Figure 3 Temperature dependence of the normalized magnetostriction coefficient. The value measured at the lowest temperature (80 K) was plotted to fit the Callen–Callen expression (Equation 1).

temperature were deduced from the least-square fitting of the corresponding diffraction spectrum. Above the Curie temperature, at approximately 240 K, the *c/a* ratio of the hexagonal unit cell equals $\sqrt{6}$, corresponding to the f c c unit cell in its hexagonal representation. The bulk expansion coefficient, calculated from the temperature variation of the lattice parameters increases abruptly above the Curie temperature giving rise to a spontaneous volume striction effect in the magnetically ordered state. The magnitude of this effect – 6.8×10^{-3} at 80 K – was estimated by comparing the unit cell volume determined experimentally with that calculated using extrapolated data from the paramagnetic region. The results are in good agreement with those reported by Minakata *et al.* [8] who used dilatometric techniques.

Careful analysis of the diffraction profiles of the rhombohedrally distorted cubic structure allows the straightforward determination of λ_{111}, the magnetostriction coefficient. It can be shown [9] that the splitting of some of the cubic reflections into doublets can be related conveniently to λ_{111}. In particular, for $(h\,h\,h)$ and $(h\,h\,0)$-type cubic reflections, the splitting $\Delta d/d$ equals $4/3\lambda_{111}$ and λ_{111}, respectively. The experimental data thus permitted the determination of λ_{111} at various temperatures in the 80 to 300 K range.

According to the semi-classical model of Callen and Callen [10], the temperature dependence of the normalized magnetostriction can be expressed

$$\lambda_{111}(T)/\lambda_{111}(0) = \hat{I}_{5/2}[\mathscr{L}^{-1}(m/m_0)] \quad (1)$$

where $\hat{I}_{5/2}$ is the hyperbolic reduced Bessel function, $\mathscr{L}^{-1}$, the inverse Langevin function and m/m_0, the reduced magnetization which was estimated from Burzo's [11] data. According to Equation 1 at 80 K, $\lambda_{111}(80)/\lambda_{111}(0) = 0.78$. Using this factor and assuming that up to 80 K, the temperature dependence of λ_{111} follows Equation 1, $\lambda_{111}(0) = 5.2 \times 10^{-3}$. The continuous curve in Fig. 3 represents Equation 1. The experimentally determined values were normalized on the basis of the $T = 80$ K value of λ_{111}. The other points for $T > 80$ lie slightly above the continuous curve. Normalizing the experimental values according to a λ_{111}, determined at a temperature other than 80 K, would have yielded higher values of $\lambda_{111}(0)$ in the range 5.1×10^{-3} to 6.8×10^{-3}. On the other hand, the experimental points in Fig. 3 seem to extrapolate, if one ignores the theoretical curve, to values slightly lower than 5.1×10^{-3}.

It has been established [9] that in the isostructural RFe_2 compounds $\lambda_{111} \gg \lambda_{100}$. Assuming that a similar situation prevails in $TbCo_2$ and since for polycrystalline samples the saturation magnetostriction $\lambda_s = 3/5\lambda_{111}$, we can deduce that $\lambda_s \simeq 3.1 \times 10^{-3}$ at 0 K.

Lee and Pourarian [12] measured the magnetostriction coefficients of several RCo_2 Laves compounds using strain gauge techniques. The results of these bulk, macroscopic measurements were presented in the form of $\lambda_t = \lambda_t(T)$ curves, where $\lambda_t = \lambda_{\|} - \lambda_{\perp}$ and $\lambda_{\|}$, $\lambda_{\perp}$ are the magnetostrictions measured in parallel and perpendicularly to the applied magnetic field, respectively. λ_t represents the volume conserving, anisotropic strain. At $T = 0$ K and a magnetic field of 2.5 *T*, the values obtained by Lee and Pourarian extrapolate to 5.5×10^{-3}. Under the assumption that we are not far from saturation at 2.5 *T*, $\lambda_t \simeq 3/2\lambda_s$ and, therefore, $\lambda_s \simeq 3.6 \times 10^{-3}$, in reasonable accord with the results obtained in the present work.

The giant magnetostriction observed for $TbCo_2$ below its Curie temperature is similar in magnitude to that previously reported for RFe_2 compounds and $TbFe_2$, in particular [1]. Our finding, thus, lends further support to the observation that the single rare-earth ion anisotropy is the predominant factor which determines the magnetoelastic properties of the rare-earth transition metal compounds.

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