On the birefringence dispersion of TbVO$_4$

## LETTER TO THE EDITOR

# On the birefringence dispersion of TbVO$_4$

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**Abstract.** The birefringence in Jahn–Teller-distorted TbVO$_4$ shows an anomalous behaviour. Via different excitation mechanisms it drops to zero and even changes sign in the visible part of the spectrum. The linear parts of the Tb$^{3+}$ and vanadate contributions are separated in a two-oscillator model with different excitation energies.

At low temperatures ($T_D \simeq 33$ K) TbVO$_4$ exhibits a structural phase transition from tetragonal (I4$_1$/$a$md) [1] to orthorhombic (Fddd) symmetry [2, 3] caused by the cooperative Jahn–Teller effect [4]. The order parameter of the phase transition is proportional to the macroscopic distortion $e$.

The phase transition has been extensively studied both experimentally and theoretically. The results are reviewed by Gehring and Gehring [5]. TbVO$_4$ is a nearly ideal mean-field substance, as confirmed, e.g., by specific heat [6] and elastic constant measurements [7]. A theoretical mean-field description for TbVO$_4$, involving the four lowest crystal-field states of the Tb$^{3+}$ ground term, was successfully employed by Elliott and co-workers [4].

In an appropriate experimental set-up (light parallel to the tetragonal $c$ axis) birefringence in the same way shows mean-field behaviour, as demonstrated by measurements at $\lambda = 455$ nm [8], thus confirming the proportionality between birefringence and the order parameter. At longer wavelengths, however, the birefringence and order parameter are by no means proportional [9]. The reason for this behaviour is that the total birefringence is the sum of different contributions which may have different signs. The linear parts of these contributions may also have different dispersions and thus cancel at some wavelength $\lambda_0$. In the vicinity of $\lambda_0$, contributions to the birefringence are visible that are functions of higher powers of the order parameter. According to Becker and Gehring [10], the driving mechanisms for the birefringence are classified into excitations of the Tb$^{3+}$ ions (4f$^8 \rightarrow$ 4f$^7$5d transitions) and excitations of the vanadate complex caused by charge transfer. Excitations of optical phonons are neglected. The aim of this Letter is to separate these two contributions and thus to establish the relative magnitudes of the higher-order parts of the birefringence.

The experimental set-up, using a modulation technique, is the same as has been described earlier [11, 12]. The light of a Xe high-pressure lamp was monochromatised for $450 \leqslant \lambda \leqslant 650$ nm by a 0.25 m Ebert monochromator (half-width of the light $\Delta\lambda =$

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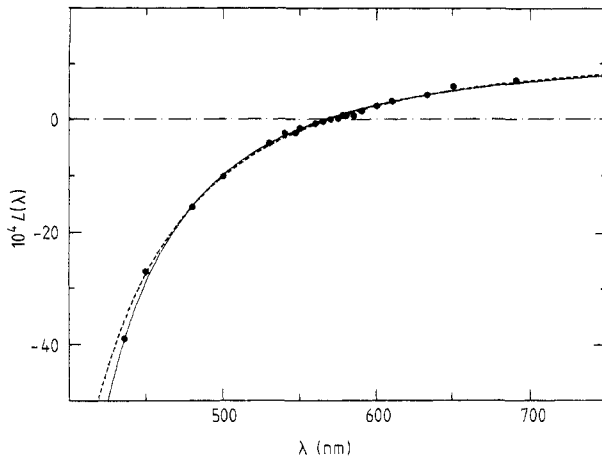
**Figure 1.** The linear coefficient $L(\lambda)$ of $TbVO_4$. Full circles: from a decomposition of the measured birefringence according to equation (1). Full curve: calculation I according to equation (7); broken curve: calculation II according to equation (7). The fitting parameters are listed in table 1.

2.4 nm). Additionally a Hg high-pressure lamp with interference filters ($\lambda = 436, 578, 691$ nm), a green He–Ne laser ($\lambda = 543.5$ nm) and a red He–Ne laser ($\lambda = 632.8$ nm) were used.

The temperature-dependent birefringence $\delta n(\lambda)$ was fitted to the mean-field distortion $e$ using the *ansatz* [9]

$$\delta n(\lambda) = L(\lambda)\, e/e_0 + K(\lambda)(e/e_0)^3 \tag{1}$$

with $e_0 = 0.0232$ the maximum distortion resulting from the mean-field calculation. A quadratic term is forbidden by symmetry, so the cubic term is the next one in the expansion of the birefringence.

$L(\lambda)$ and $K(\lambda)$ are fitting parameters, both corresponding to the sum of the $Tb^{3+}$ and vanadate contributions to the birefringence. Details of the measurements and the fitted birefringence curves are given elsewhere [9]. While the parameter $K$ is nearly independent of $\lambda$ (within fitting accuracy) ($K \approx 0.7 \times 10^{-4}$), the parameter for the linear part, $L$, strongly depends on $\lambda$ (figure 1).

For the calculation of the dispersion of $L$, we follow the theoretical treatment of the birefringence given in its general form by Becker and Gehring [10] and formulated for the $Tb^{3+}$ and vanadate contributions elsewhere [9]. The vanadate ion is assumed to have a singlet ground state. Its contribution to the birefringence mainly arises from the splitting of excited doublets. On contracting all excitation energies to one intermediate energy, i.e. going to a single-oscillator model, the linear part of the vanadate contribution to the birefringence is found to be

$$L_V(\lambda) = (1/2\bar{n}(\lambda))b_V\, \lambda_V^2\lambda^2(\lambda^2 + \lambda_V^2)/(\lambda^2 - \lambda_V^2)^2 \tag{2}$$

where $\lambda_V$ is the wavelength corresponding to the mean absorption energy of the vanadate excitation by charge transfer, $\bar{n}(\lambda)$ is a mean refractive index and $b_V$ is a parameter. For the cubic part, the leading term in perturbation theory is proportional to

$$\lambda_V^4\lambda^4(\lambda^4 + 6\lambda^2\lambda_V^2 + \lambda_V^4)/(\lambda^2 - \lambda_V^2)^4. \tag{3}$$

The ground state of the $Tb^{3+}$ ion consists of two singlets and one doublet. Thus the linear

**Table 1.** Fitting parameters for the dispersion $L(\lambda)$ of the linear part of the birefringence according to equation (7).

| | $\bar{n}$ | $\lambda_V$ (nm) | $\lambda_{Tb}$ (nm) | $b_V$ (nm$^{-2}$) | $a_{Tb}$ (nm$^{-1}$) | $b_{Tb}$ (nm$^{-2}$) |
|---|---|---|---|---|---|---|
| Calculation I | 2.0 | 320 | 300 | $-4.58 \times 10^{-4}$ | $3.22 \times 10^{-1}$ | 0 |
| Calculation II | 2.0 | 280 | 220 | $-1.80 \times 10^{-3}$ | 0 | $3.97 \times 10^{-3}$ |

part of the $Tb^{3+}$ contribution includes both linear and quadratic terms in $1/(\lambda^2 - \lambda_{Tb}^2)$, leading to

$$L_{Tb}(\lambda) = \frac{1}{2\bar{n}(\lambda)} \left( a_{Tb} \frac{\lambda_{Tb}\lambda^2}{\lambda^2 - \lambda_{Tb}^2} + b_{Tb} \frac{\lambda_{Tb}^2 \lambda^2 (\lambda^2 + \lambda_{Tb}^2)}{(\lambda^2 - \lambda_{Tb}^2)^2} \right). \tag{4}$$

For the cubic part, there are terms proportional to

$$\lambda_{Tb}^3 \lambda^4 (\lambda^2 + 3\lambda_{Tb}^2)/(\lambda^2 - \lambda_{Tb}^2)^3 \tag{5}$$

and

$$\lambda_{Tb}^4 \lambda^4 (\lambda^4 + 6\lambda^2 \lambda_{Tb}^2 + \lambda_{Tb}^4)/(\lambda^2 - \lambda_{Tb}^2)^4. \tag{6}$$

The total linear part is the sum of equations (2) and (4):

$$L(\lambda) = L_V(\lambda) + L_{Tb}(\lambda). \tag{7}$$

Even if the dispersion of the mean refractive index were known, this equation would still contain five parameters ($\lambda_V$, $\lambda_{Tb}$, $b_V$, $a_{Tb}$ and $b_{Tb}$). Since the number of measuring points is finite, an attempt to determine the individual contributions looks promising only if some of the parameters can be fixed. Reliable values of the absorption wavelengths do not seem to be known. We therefore used firstly published values for the absorption edges, $\lambda_V = 320$ nm [13] and $\lambda_{Tb} = 300$ nm [14], and secondly some smaller values that correspond to the middle of the absorption bands—in particular, $\lambda_{Tb} = 220$ nm from an early publication on aqueous solutions of $Tb^{3+}$ salts [15]. For a further simplification we tried putting either $b_{Tb} = 0$ or $a_{Tb} = 0$. For the mean refractive index $\bar{n}(\lambda)$ we used the rough approximation that it is independent of the wavelength and used the value $\bar{n}(633 \text{ nm}) = 2.0$ [16].

The results of two of the calculations carried out are shown in figure 1; the values of the parameters used are given in table 1. Both calculations reproduce the experimentally determined dependence of $L(\lambda)$ very well, for the spectral region investigated. The difference seen for the measuring point at $\lambda = 436$ nm is still increasing for shorter wavelengths. A comparison of the two individual contributions $L_V(\lambda)$ and $L_{Tb}(\lambda)$ with values for selected wavelengths published earlier [12]†, however, shows a better agreement for the values used for calculation I (see figure 2). In [12], the sizes of the individual contributions were determined from concentration-dependent measurements on the mixed systems $(Tb_x, Tm_{1-x})VO_4$ and $(Tb_x, Yb_{1-x})VO_4$. It seems, however, improbable that $a_{Tb}$ should vanish, because the contributions to the birefringence result from transitions in the $Tb^{3+}$ ions out of the mixed ground-state singlets to excited doublets as well as from those of the ground-state doublet to excited singlets.

† According to a new understanding [9], the method used in [12] is not absolutely reliable; thus the values given in figure 2 may be uncertain by a factor of up to two.
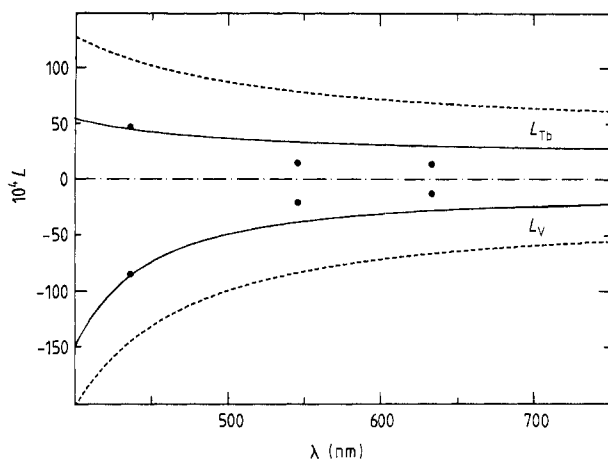
**Figure 2.** The dispersion of the $Tb^{3+}$ and vanadate contributions, $L_{Tb}$ and $L_V$, respectively. Full curves: calculation I; broken curves: calculation II. Full circles: from [12].

It looks likely to be of interest to compare the sizes of the two linear contributions to the sum of the respective cubic parts (which cannot be separated) for the maximum distortion $e_0$. For a medium wavelength $\lambda = 550$ nm calculation I gives: $Q_V = L_V/K = -51.3$; $Q_{Tb} = L_{Tb}/K = 52.2$. The corresponding values for calculation II are: $Q_V = -115.4$; $Q_{Tb} = 112.7$.

Some remarks are necessary concerning the wavelength dependence of the mean refractive index $\bar{n}(\lambda)$. The birefringence and the mean refractive index are composed in similar ways of vanadate and $Tb^{3+}$ contributions. Hence each of these contributions is influenced by the other and, therefore, they are not separable in a simple manner as we are led to believe by equations (2) and (4) for the linear part of the birefringence. Although it was not practicable to separate the vanadate and $Tb^{3+}$ contributions unequivocally, it was nevertheless possible to give a convincing interpretation of the strange wavelength dependence of the birefringence of $TbVO_4$.

# References

[1] Wyckoff R W G 1965 *Crystal Structures* vol 3 (New York: Interscience)
[2] Göbel H and Will W 1972 *Int. J. Magn.* **3** 123–8
[3] Will G, Göbel H, Sampson C F and Forsyth J B 1972 *Phys. Lett.* **38A** 207–8
[4] Elliott R J, Harley R T, Hayes W and Smith S R P 1972 *Proc. R. Soc.* A **328** 217–66
[5] Gehring G A and Gehring K A 1975 *Rep. Prog. Phys.* **38** 1–89
[6] Wells M R and Worswick R D 1972 *Phys. Lett.* **42A** 269–70
[7] Sandercock J R, Palmer S B, Elliott R J, Hayes W, Smith S R P and Young A P 1972 *J. Phys. C: Solid State Phys.* **5** 3126–46
[8] Harley R T and Macfarlane R M 1975 *J. Phys. C: Solid State Phys.* **8** L451–5
[9] Hess G unpublished
[10] Becker P J and Gehring G A 1975 *Solid State Commun.* **16** 795–8
[11] Becker P J, Kahle H G and Keller E 1985 *Phys. Status Solidi* b **130** 191–6
[12] Pilawa B, Hess G, Kahle H G and Kasten A 1988 *Phys. Status Solidi* b **145** 729–39
[13] Gubanov V A, Ellis D E and Fotiev A A 1977 *J. Solid State Chem.* **21** 303–24
[14] Dieke G H 1968 *Spectra and Energy Levels of Rare Earth Ions in Crystals* (New York: Interscience)
[15] Prandtl W and Scheiner K 1934 *Z. Anorg. Allg. Chem.* **220** 107–14
[16] Braun S 1980 *Staatsexamensarbeit* Universität Karlsruhe