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Cooperative Jahn–Teller induced phase transition of TbVO_4 : single crystal structure analyses of the tetragonal high temperature phase and the twinned orthorhombic phase below 33 K*

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Abstract. The rare earth vanadate TbVO_4 , undergoes a crystallographic phase transition below 33 K induced by a cooperative Jahn–Teller effect. Twinning of the crystal occurs upon this transition from the tetragonal high temperature phase to the orthorhombic low temperature phase resulting in a domain structure. Single crystal x-ray analyses of the tetragonal and the twinned orthorhombic phase verify a reduction in the site symmetry of the Tb ion from D_{2d} ($\bar{4}m2$ -dodecahedral) for the high temperature phase to D_2 (222-distorted dodecahedral) for the low temperature phase. Concomitantly, the space group symmetry is lowered from D_{4h}^{19} ($I4_1/amd$) to D_{2h}^{24} ($Fddd$). The twinned orthorhombic phase is described as domains related to each other by a 180° rotation about the orthorhombic [110] axis.

1. Introduction

The unexpected discovery of a cooperative Jahn–Teller distortion in a series of rare-earth salts has led to extensive investigations of their structural phase transitions at low temperatures (Bleaney 1988). Further interest in this class of compounds lies in their magnetic properties (Bowden 1998).

Lanthanide zircons with the general formula LaXO_4 ($X = \text{V, As, P}$) crystallize at room temperature in the tetragonal space group D_{4h}^{19} ($I4_1/amd$) with two metal ions on D_{2d} sites related by an inversion centre. The tetragonal crystal field creates low lying degenerate or almost degenerate electronic states that split or increase their separation upon lowering the symmetry. The phase transition is initiated by coupling of the degenerate or almost degenerate levels of these electronic states with a singly degenerate lattice mode, resulting in lowering of the symmetry at the metal site (Gehring and Gehring 1975).

Jahn–Teller induced phase transitions were observed for TbPO_4 and LaXO_4 ($\text{La} = \text{Tb, Dy, Tm}$; $X = \text{V, As}$) (DyVO_4 : Cooke *et al* 1970; TbAsO_4 : Klein *et al* 1971; TmVO_4 : Cooke *et al* 1972; TmAsO_4 : Mangum *et al* 1971, TbPO_4 : Nägele *et al* 1980; DyAsO_4 : Kahle *et al* 1971) and initiated a series of extensive investigations on this phenomenon beginning in the early 1970s (e.g. DyVO_4 : Cooke *et al* 1971, Sayetat *et al* 1971, Elliott *et al* 1971, Gehring *et al* 1972, Becker and Laugsch 1971, TbAsO_4 : Wüchner and Laugsch 1973, Wüchner *et al* 1972, Berkhahn *et al* 1973, TbVO_4 : Ergun *et al* 1976, Harley *et al* 1980, Gehring *et al* 1976,

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TmAsO₄: Becker *et al* 1972, Colwell and Mangum 1972, TbPO₄: Mensinger *et al* 1993, Müller *et al* 1993, Anderer *et al* 1993).

Optical absorption measurements of Gehring *et al* (1971) and Raman studies of Elliott *et al* (1972) and Harley *et al* (1971) determined the phase change for TbVO₄ to be of second order. A domain structure in the low temperature phase was described and the crystal symmetry for the low temperature phase was concluded to be D_{2h}^{24} (*Fddd*) with a point symmetry for the metal ion of D_2 (222). These results were in contradiction to powder x-ray diffraction measurement on TbVO₄, which suggested the space group to be D_2^7 (*F222*) (Sayetat 1972). Extensive research of Sandercock *et al* (1972) on Brillouin scattering, ultrasonic and theoretical studies of acoustic anomalies of TbVO₄ later confirmed the original choice of D_{2h}^{24} (*Fddd*). Specific heat measurements (Wells and Worswick 1972) confirmed the phase transition temperature to be 33.0(1) K, and x-ray studies on single crystals and powder (Will *et al* 1972) showed the temperature dependence of the unit cell parameters at low temperatures; however the crystal symmetry could not be unambiguously determined. Recent efforts on the properties of TbVO₄ were directed towards thermal expansion anomalies (Kazei *et al* 1998) and compressibility (Chen *et al* 1992) along with thermodynamic (Sirota *et al* 1990) and magnetic properties (Bleaney *et al* 1997).

Despite these efforts, the complete crystal structure of a low temperature phase of these compounds has not been determined until now. However, short reports on x-ray diffraction experiments on single crystals of DyVO₄ by Forsyth and Sampson (1971) and TbVO₄ (Will *et al* 1972) provide unit cell information on the low temperature phases.

The present paper describes the solution of the crystal structure of the low temperature phase of TbVO₄ based on x-ray diffraction study on a twinned crystal below 33 K and compares it to the room temperature phase.

2. Experiment

2.1. X-ray diffraction measurement of high temperature phase

A clear brownish crystal of approximate dimensions 0.28 mm × 0.21 mm × 0.19 mm was glued to the tip of a diamond cleaved 0.1 mm diameter thin wall glass capillary of approximately 4 mm in length using epoxy resin. Preliminary examination and data collection were performed at room temperature on a Siemens SMART Platform diffractometer. The diffractometer was equipped with a 1k CCD detector located 4.96 cm from the crystal and a graphite monochromated Mo K α radiation source. 0.3° ω -scans were carried out at three different ϕ -settings and a detector position of -30° in 2θ , corresponding to a nominal hemisphere of data, with the frame time set at 20 seconds. Coverage of unique data was 96% complete to a resolution of at least 0.75 Å. The final unit cell was obtained from the *xyz* centroids of 1108 reflections after integration using the *SAINT* software package (Siemens 1996). The intensity data were corrected for decay and absorption using *SADABS* (Sheldrick 1996). The structure was refined using *SHELXL-97* (Sheldrick 1997). The final full matrix least squares refinement with anisotropic displacement parameters converged to $R_1 = 2.37\%$ (F , 114 observed unique data) and $wR_2 = 5.64\%$ (F^2 , all data).

2.2. X-ray diffraction measurement of low temperature phase

A transparent brownish TbVO₄ crystal of dimensions 0.08 mm × 0.10 mm × 0.18 mm was epoxied to a thin wall glass capillary of 2 mm length. The crystal was mounted on the same Siemens SMART Platform diffractometer. In this data collection, the diffractometer was

equipped with the APD open flow helium cryostat (Hardie *et al* 1998). The crystal temperature was estimated to be 22 K based on the determined unit cell of the low temperature phase.

The CCD detector was set 5.55 cm from the crystal. The data collection nominally covered over a hemisphere of reciprocal space by a combination of three runs of exposures, each set having a different ϕ -setting for the crystal. Each 10 seconds exposure covered 0.3° in ω . Coverage of the unique data set is over 97% complete to a resolution of 0.77 Å.

Out of this data set, a subset of ~200 reflections was selected in order to determine the orientation matrices of the two twin components and the lattice parameters. Using the beta-test twin software from R A Sparks (TWINDX; Sparks 1997), two out of several orientation matrices were identified as the reduced settings of the two twin components and transformed into the orthorhombic unit cells. Based on these matrices, integer numbers (*hkl*) could be assigned to all but five reflections. Further improvement of the orientation matrices was achieved by identifying and removing the reflections that originated from both twin components simultaneously (TWUTIL, TWINDX; Sparks 1997). The resulting unit cell dimensions for the two components are in agreement within 0.02 Å.

Reflection intensities were obtained by integrating the 1371 frames twice (Siemens 1996), once with each of the orthorhombic orientation matrices describing the two orientations of the twin domains. The program TWHKL (Sparks 1997) identified 2683 single, 1720 fully and 928 partially overlapped reflections in the resulting two files and prepared a twin resolved intensity data file containing only the fully separated and the fully overlapped reflections. This file was used in the further calculations with *SHELXTL* (Sheldrick 1990, 1997) together with lattice parameters which were averaged over the two twin components.

Table 1. Summary of crystallographic data for TbVO₄.

	293 K	22 K
Lattice type	Tetragonal	Orthorhombic
Space group	<i>I</i> 4 ₁ / <i>amd</i>	<i>Fddd</i>
Radiation	Mo K α	Mo K α
Wavelength (Å)	0.710 73	0.710 73
<i>a</i> -axis (Å)	7.1841(3)	10.239(2)
<i>b</i> -axis (Å)	7.1841(3)	10.029(2)
<i>c</i> -axis (Å)	6.3310(4)	6.3154(13)
<i>V</i> (Å ³)	326.75(3)	648.6(2)
<i>Z</i>	4	8
<i>D_x</i>	5.567	5.609
μ (mm ⁻¹)	24.15	24.34
<i>F</i> (000)	480	960
θ (range)	4.29–28.06	4.30–28.49
Extinction	0.023(2)	0.0011(4)
<i>R_{int}</i>	0.0467	N/A
<i>R</i> ₁ (<i>F</i> , > 2 σ (<i>I</i>))	0.0237	0.0782
<i>R_w</i> (<i>F</i> ² , all)	0.0564	0.2031
Reflections measured	2232	5331 total 928 rejected, overlapped 2683 singles 1720 mults
Unique reflections	117	836, sym. equiv. not merged
Reflections > 2 σ (<i>I</i>)	114	798
Parameters	12	9

The space group—based on systematic absences—was determined to be $Fddd$ (D_{2h}^{24}). Placing Tb and V on the appropriate positions as derived from the known tetragonal high temperature phase solved the structure and least-squares refinements followed by difference Fourier syntheses revealed the O position. All atoms were refined with isotropic atomic displacement factors. In addition, a scale parameter was included in the refinement describing the ratio of the two twin components. Attempts to refine the structure with anisotropic atomic displacement factors were unsuccessful. This is most likely caused by the high absorption of the crystal ($\mu = 24.34 \text{ mm}^{-1}$), which was not corrected for. The structure is refined to $R_1 = 7.82\%$ (F , 798 observed unmerged data) and $wR_2 = 20.31\%$ (F^2 , all data) with a 0.54:0.46 ratio of the twin components. Further details of the crystal structure refinements for both measurements are reported in table 1.

3. Results and discussion

The single crystal x-ray diffraction study of the tetragonal crystal structure of the high temperature phase of TbVO_4 ($I4_1/amd$, zircon structure) as derived from the room temperature x-ray diffraction measurement shows alternating VO_4 tetrahedra and TbO_8 triangulated dodecahedra connected over common edges and extending along the c -axis. These results are of no surprise and agree with the Rietveld analysis from powder neutron diffraction data (Chakoumakos *et al* 1994) and the single crystal x-ray analysis on the isotypes SmVO_4 , EuVO_4 , GdVO_4 , DyVO_4 (Mullica *et al* 1996), CeVO_4 (Range *et al* 1990) and NdVO_4 (Baglio and Sovers 1971). Final refined fractional coordinates are given in table 2. Table 3 shows a comparison of selected geometric parameters of the high and the low temperature phases.

Table 2. Fractional coordinates of high^a and low^b temperature phase of TbVO_4 .

	$T = 293 \text{ K}$				$T = 22 \text{ K}$			
	x	y	z	$U_{eq} (\text{\AA}^2)$	x	y	z	$U_{iso} (\text{\AA}^2)$
Tb	0.0	0.75	0.125	0.0036(4)	0.125	0.125	−0.375	0.0014(4)
V	0.0	0.25	0.375	0.0039(7)	0.125	0.125	0.125	0.0028(9)
O	0.0	0.4333(5)	0.2016(7)	0.0070(8)	0.2162(5)	0.0319(5)	−0.0494(9)	0.0045(10)

^a Origin at $2/m$.

^b Origin at T.

The phase transition below 33 K results from coupling of the low lying electronic states of the Tb ions with a B_{2g} phonon causing a distortion of the tetragonal ab -plane along the $[110]$ and $[1\bar{1}0]$ axes. Concomitantly, the I centred tetragonal crystal lattice is converted into an orthorhombic F centred lattice where the orthorhombic a - and b -axes are the $[110]$ and $[1\bar{1}0]$ diagonals of the tetragonal unit cell, and the tetragonal and orthorhombic c -axes coincide. During this displacive transformation from higher to lower symmetry, two alternative orientations of the orthorhombic setting are produced resulting in a domain structure (figure 1(a)). Concomitant reduction of the angle between two neighbouring domains brings the lattice points at the twin interface into register (figure 1(b)). This mechanism is in agreement with the observed smooth change in lattice parameters over the temperature range of 20–33 K (Will *et al* 1972). The relationship between the two twin components may then be described by a 180° rotation about the orthorhombic $[110]$ axis in direct space. The x-ray diffraction pattern of this twinned orthorhombic phase shows imperfect overlap of some reflections, typical for a ‘non-merohedral’ twin of type TLQS, $n = 1$ (Donnay and Donnay 1974).

Table 3. Selected distances (Å) and angles (°) of high and low temperature phase of TbVO₄.

	293 K	22 K
Terbium coordination ^a		
Tb–A	2.452(4)(4×)	2.444(6)(4×)
Tb–B	2.326(4)(4×)	2.312(5)(4×)
M_A/M_B	1.054	1.057
a	2.634(7)	2.642(9)
b	3.360(5)	3.289(10)
		3.389(10)
m	2.727(8)	2.703(12)
g	3.068(1)	3.075(2)
		3.043(2)
θ_A	32.50(9)	32.7(1)
θ_B	77.95(11)	78.1(2)
δ	33.5(1)(4×)	34.3(2)(2×)
		31.9(2)(2×)
τ	0	1.6(6)
O–Tb–O		
12, 34	64.99(18) (2×)	65.4(2) (2×)
17, 28, 35, 46	69.54(17) (4×)	69.2(2) (4×)
15, 16, 25, 26, 37, 38, 47, 48	79.87(9) (8×)	79.49(14) (4×)
		80.50(14) (4×)
57, 58, 67, 68	92.49(4) (4×)	94.2(3) (2×)
		90.7(3) (2×)
18, 27, 36, 45	134.53(11) (4×)	134.62(13) (4×)
13, 14, 23, 24	135.35(11) (4×)	135.1(2) (4×)
56,78	155.9(2) (2×)	156.2(3) (2×)
Vanadium coordination		
V–O	1.714(4) (4×)	1.720(5) (4×)
O–V–O	100.4(3) (2×)	100.4(4) (2×)
O–V–O	114.20(15) (4×)	114.2(4) (4×)

^a Nomenclature for edges and angles for a dodecahedron (figure 2) is taken from Hoard and Silverton (1963) and Drew (1977).

Assignment of the collected intensities to two independent orientations—as described in the experimental part—and comparison of the two resulting orientation matrices (TWR0T, Sparks 1997) indicate that the two twin components are indeed related by a 180° rotation about the orthorhombic [110] axis in direct space. Thus figure 1(b) shows two domains of the twinned structure with the orthorhombic crystal face (110) as the coherent twin boundary. It should be mentioned here that the domain structure of TbVO₄ and other rare earth vanadates/arsenates is often described as a lattice consisting of domains rotated by 90° to each other (see e.g. Becker *et al* 1972, Harley *et al* 1971, Bleaney *et al* 1997). In the present case, a 90° rotation about the crystallographic c -axis [001] results in a similar lattice (see figure 1(a)); however, the unit cell faces at the twin interface would not exactly match. In addition, the rotation required to transform one set of reciprocal lattice points into the other calculates here as 88.8° ($2 \arctan b_0/a_0$) and is only 90.0° for $b = a$.

An interesting experiment using Bragg-regime diffraction of light originated by the twin interface (Reza and Taylor 1991) not only showed the periodic reoccurrence of this interface[†], it also determined the size of the domains to be of the order of 4.1 μm.

[†] Reza and Taylor refer to the tetragonal {100} domain walls, which coincide with the orthorhombic {110} faces.

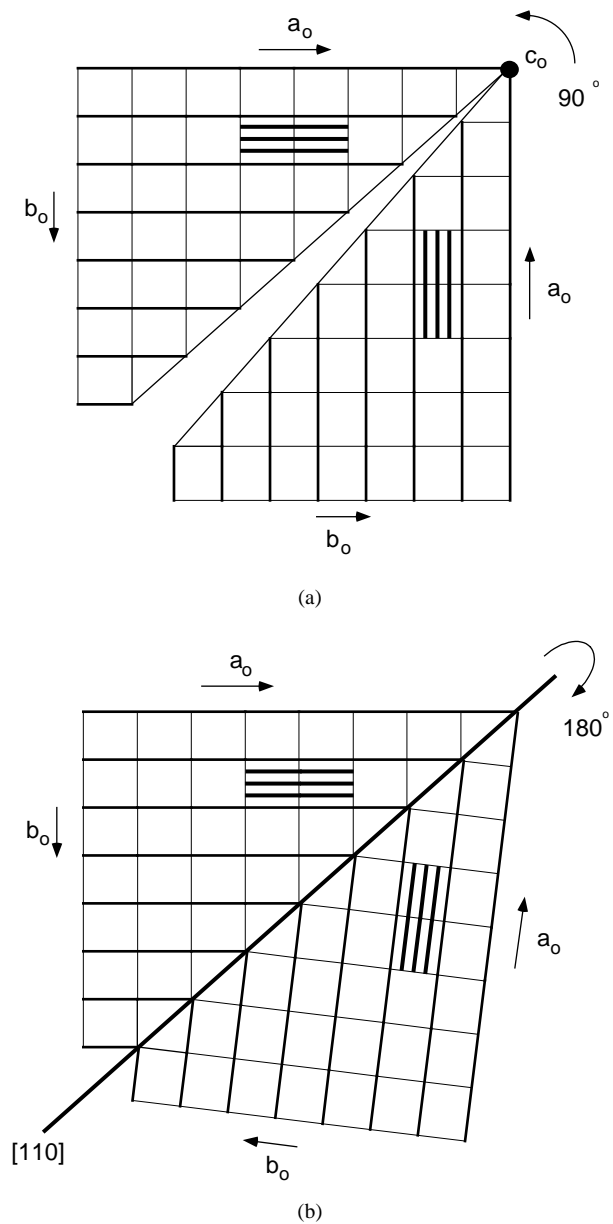


Figure 1. (a) Schematic of alternative orientations of the orthorhombic unit cells and the result of a twin law of a 90° rotation about $[001]$. (b) Schematic of a coherent twin showing the alternative orientations of the orthorhombic unit cells described by a twin law of a 180° rotation about $[110]$.

In both phases the Tb atom is coordinated by eight O atoms to form a triangular dodecahedron (figure 2). Spectroscopic data have shown that the point symmetry of the Tb site is reduced during the phase transition from $D_{2d} (\bar{4}m2)$ to $D_2 (222)$. This is confirmed by the crystallographic results. Using the nomenclature of Hoard and Silverton (1963) and Drew (1977) the dodecahedron may be described as two intersecting tetrahedra (one flattened, the

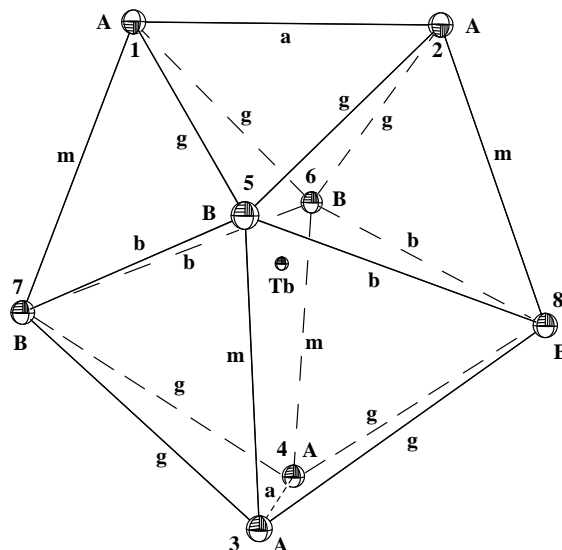


Figure 2. The dodecahedral coordination of terbium showing the nomenclature due to Hoard and Silverton (1963) and Drew (1977).

other one elongated) corresponding to the A and B sites in figure 2, respectively. Alternatively, the polyhedron may be described as two trapezoids lying in mutual perpendicular mirror planes (sites 7128 and 5346, respectively). The lower symmetry of the orthorhombic phase is characterized by loss of mirror symmetry, which is manifested by a twist, τ , of the trapezoids by 1.6° about the a -edge. As seen from table 3, this twist splits both the b and g polyhedral edges into two sets, the b -edges differing by 0.100 \AA and the g -edges by 0.032 \AA . The larger of these differences (b -edge) is reflected in a 3.5° differentiation in the angle subtended at the metal with a concomitant differentiation of 2.4° in the angle (δ) between the faces forming the b -edge of the polyhedron. The vanadate group has $D_{2d} (4m2)$ symmetry in the high temperature phase and $D_2 (222)$ symmetry in the low temperature phase. The coordination polyhedron is an elongated tetrahedron with identical metrical parameters in both phases. Hence, the relative decrease in volume on transforming to the low temperature phase is entirely due to shrinking of the terbium coordination polyhedron.

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