

Refinement of the Crystal Structure of Some Rare Earth Vanadates RVO_4 (R = Dy, Tb, Ho, Yb)

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The positional parameters of oxygen atoms in the tetragonal rare earth vanadates have been refined on the basis of neutron diffraction powder patterns. The values obtained for $DyVO_4$, $TbVO_4$, $HoVO_4$ and $YbVO_4$ are compared with theoretical predictions of Baglio and Sovers.

Introduction

The vanadates of the rare earth ions RVO_4 , with R a rare earth, crystallize in the tetragonal space group $I4_1/amd$ and are isomorphous with zircon $ZrSiO_4$ (1). The atoms occupy the following positions

rare earth ions	$4a$ (000)
vanadium	$4b$ ($00\frac{1}{2}$)
oxygen	$16h$ ($0xz$)

The structures of $ErVO_4$ (2) and $DyVO_4$ (3) were recently refined by neutron diffraction powder data. Baglio and Sovers (4) reported a single

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crystal X-ray refinement of $NdVO_4$ and calculated theoretical parameters for the other members of the series.

Considerable interest is actually concentrated on the luminescent and magnetic properties of these compounds. Specific heat measurements of Cooke et al. (5) suggested a crystallographic phase transition at 14 K for $DyVO_4$ which was contested by Will and Schäfer (3) on the basis of their neutron diffraction powder measurements. Low temperature X-ray diffraction on a powder sample by Sayetat et al. (6) showed, however, clearly a change from tetragonal to orthorhombic symmetry.

This result was confirmed by Forsyth and

TABLE I
CRYSTALLOGRAPHIC PARAMETERS OF RARE EARTH VANADATES (WITH STANDARD DEVIATIONS)

	Temp. [K] of data collection	Unit cell parameters at room temperature (12)		Oxygen positional parameters		Thermal parameters		
		<i>a</i>	<i>c</i>	<i>x</i>	<i>z</i>	<i>B_R</i>	<i>B_V</i>	<i>B_O</i>
		Å	Å					
$TbVO_4$	4.2	7.1772	6.3289	0.185(1)	0.326(1)	0.35	0.47	0.72
$DyVO_4$	77	7.1434	6.3130	0.185(2)	0.324(2)	0.10	0.49	0.58
$HoVO_4$	4.2	7.1214	6.2926	0.186(1)	0.328(1)	0.22	0.48	0.65
$YbVO_4$	4.2	7.0435	6.2470	0.188(1)	0.328(1)	0.20	0.52	0.68
$ErVO_4$ (2)	77	7.0975	6.2723	0.186(1)	0.324(2)	0.27	0.54	0.64
$DyVO_4$ (3)	4.2	7.1434	6.3130	0.185(2)	0.321(2)	0.2	0.2	0.2
$NdVO_4$ (4)	300	7.3290	6.4356	0.1801(6)	0.3284(9)	<i>anis. refinem.</i>		

TABLE II
MAIN BOND DISTANCES AND ANGLES (WITH STANDARD DEVIATIONS)

R	Nd (4)	Tb	Dy	Dy (3)	Ho	Er (2)	Yb
R—O(1) ^a	2.398(4)	2.31(1)	2.28(2)	2.29	2.29(1)	2.27(1)	2.25(1)
R—O(4) ^d	2.492(5)	2.45(1)	2.44(2)	2.41	2.45(1)	2.44(1)	2.44(2)
V—O(1)	1.721(5)	1.72(1)	1.72(2)	1.73	1.71(1)	1.72(1)	1.71(1)
O(1)—O(2) ^b	2.640(6)	2.66(2)	2.64(3)	2.64	2.65(3)	2.66(2)	2.65(3)
O(1)—O(3) ^c	2.811(8)	2.89(2)	2.90(3)	2.92	2.86(3)	2.89(2)	2.85(3)
O(1)—V—O(2)	100.2(2)	100.7(9)	99.5(1.4)	100.7	101.5(9)	100.8(8)	101.9(9)
O(1)—V—O(3)	114.3(2)	114.0(6)	114.5(9)	114.9	113.6(5)	114.0(4)	113.5(5)

^a O(1)—Oxz; ^b O(2)—O \bar{x} z; ^c O(3)—xO \bar{z} ; ^d O(4)—x $\frac{1}{4}$ +z.

Sampson on single crystal measurements (7) who reported the orthorhombic lattice parameters $a = 7.1405 \text{ \AA}$, $b = 7.1108 \text{ \AA}$, c being unchanged. In this paper we sum up the refinement of four members of the series (DyVO₄, TbVO₄, HoVO₄, YbVO₄).

Crystalline Structure

Neutron powder patterns were recorded at 4.2 and 1.8 K in order to detect a magnetic

structure. Magnetic ordering at 1.8 K was found for DyVO₄ only. This magnetic structure is described elsewhere (3, 6). The liquid helium patterns of HoVO₄ and TbVO₄ were used to refine the crystalline structure parameters. DyVO₄ was refined from a 77 K pattern in order to avoid disturbances from the crystalline distortion. All data were corrected for absorption and the refinement was carried out by least-squares methods based on thirteen resolved intensities with the ORFLS program of Busing, Martin, and Levy

TABLE III
CALCULATED AND OBSERVED INTENSITIES jF^2

	TbVO ₄		HoVO ₄		YbVO ₄		DyVO ₄	
<i>hkl</i>	jF_o^2	jF_c^2	jF_o^2	jF_c^2	jF_o^2	jF_c^2	jF_o^2	jF_c^2
101	52.7	60.4	51.1	50.0	14.1	14.5	75.8	79.8
200	138.6	146.1	112.6	113.0	22.0	24.0	119.0	116.3
211	0.0	4.5	0.9	0.3	2.8	3.1	48.9	36.7
112	5.0	8.9	12.5	15.8	8.5	10.8	72.8	72.5
220	86.2	89.5	59.3	50.7	2.0	1.6	0	0.2
202	622.7	608.1	433.3	427.8	55.9	51.8	142.6	136.1
301	929.1	929.3	682.3	656.0	99.8	101.1	360	387.5
103	755.4	751.0	537.7	533.4	86.8	84.9	320	333.3
321	851.6	898.9	692.2	664.1	109.5	111.8	480	449.6
312	484.9	556.8	457.6	432.1	94.5	95.0	435.7	466.4
400/213	369.7	380.0	286.5	323.3	59.9	67.4	264.5	296.0
411	13.6	8.5	14.9	14.2	10.3	11.0	95.1	75.1
420/303 } 402/004 }	445.3	392.2	262.7	264.7	45.9	45.8	240.0	240.8
332	974.4	877.1	625.1	619.9	117.5	106.2	521.6	471.3
204/323 } 422 }	373.6	436.5	278.9	308.4	41.2	43.6	130.9	176.4
501/431	1143.7	1121.3	819.0	832.5	141.0	139.0	523.0	565.8
413/224	598.3	634.3	495.8	552.2			496.3	480.2
521/314 } 512 }	1109.3	1040.1	670.7	656.0			347.0	288.4
	R = 0.058		R = 0.046		R = 0.043		R = 0.082	

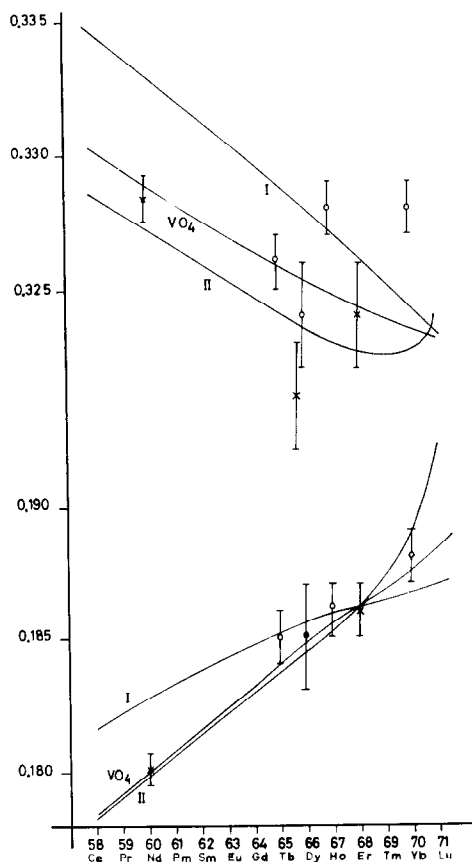


FIG. 1. The oxygen parameters in rare earth vanadates in comparison with calculations of Baglio and Sovers (4). \circ , this work; \times , references (2-4).

(8). The following values of neutron scattering length were taken from a compilation of the International Union of Crystallography (9).

$$\begin{aligned} b(\text{Dy}) &= 1.69, & b(\text{Tb}) &= 0.76, \\ b(\text{Ho}) &= 0.85, & b(\text{Yb}) &= 1.26, \\ b(\text{V}) &= -0.05, & b(\text{O}) &= 0.577 \\ && & \text{(in units of } 10^{-12} \text{ cm).} \end{aligned}$$

The refined x and z parameters are given in Table I together with the temperature factors.

We refined the temperature factors in the following way: First an overall B value was refined. This value was attributed to vanadium and kept constant during the refinement of the temperature factors of the rare earth ions and oxygen. A refinement of the vanadium temperature factor was not attempted because of the small neutron scattering length of this atom. The mean interatomic distances are listed in Table II, the observed and calculated intensities in Table III.

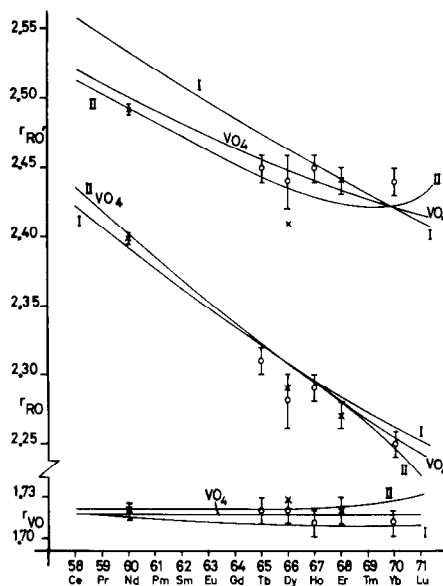


FIG. 2. The rare earth-oxygen and the vanadium-oxygen distances of some rare earth vanadates in comparison with calculations of Baglio and Sovers (4). \circ , this work; \times , references (2-4).

Discussion

In Fig. 1 we compare the x and z parameters with those calculated by Baglio and Sovers (4). Their calculations were based on their own measurements of NdVO_4 and on the refinement of ErVO_4 (2) and consisted of minimizing the crystal energy as a function of the oxygen parameters. The curves called VO_4 were calculated under the assumption of unchanged VO_4 tetrahedron. For details of their models I and II see ref. 4. The x values are quite close to the model calculations while a large discrepancy is observed for the z parameters of HoVO_4 and YbVO_4 . A decision whether model I or model II is more likely to be true is not possible, but the somewhat high x and z parameters of YbVO_4 seem to indicate that the behaviour of the last rare earth ions is better described by model II.

Figure 2 compares the two main rare earth-oxygen and the vanadium-oxygen distances with the model calculations of Baglio and Sovers (4). The shorter rare earth-oxygen distance follows the lanthanide contraction but the longer seems to be independent of the ionic radius of the rare earth for the higher lanthanides (Tb-Yb).

Inspection of Table II shows that the vanadium-oxygen distances in all vanadates as well as the angles within the VO_4 tetrahedron are equal within experimental errors. The observed

distances of 1.71 Å and 1.72 Å are in close agreement with recently published vanadium–oxygen distances in $\text{Ni}_3\text{V}_2\text{O}_8$ (10) and $\text{Ba}_3(\text{VO}_4)_2$ (11). This distance shows clearly a partly covalent character of the vanadium–oxygen bond.

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