Studies on Vanadium Oxides

II. The Crystal Structure of Vanadium Dioxide

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The crystal structure of VO_2 has been investigated by X-ray methods. It has been found to belong to the space-group $P2_1/c$. The unit cell dimensions and the parameters of the metal and oxygen atoms are given. The structure is shown to be of a deformed rutile type with the metal atoms within the strings of VO_6 octahedra occurring in doublets as in the MoO_2 structure type. The interatomic distances and angles in the VO_6 octahedra are compared with those in the TiO_6 octahedra (rutile).

In a recent report [1] on a phase analysis of the vanadium-oxygen system carried out at this Institute it was stated that the crystal structure of the dioxide is not of the simple rutile type proposed by Goldschmidt [2] but constitutes a monoclinic deformation of this structure type. The unit cell dimensions obtained from powder photographs in a Guinier focussing camera using $CrK\alpha$ radiation and sodium chloride, added as an internal standard ($a_{NaCl}= 5.640$ Å), were thus found to be

$$a = 5.743 \text{ Å}, \ b = 4.517 \text{ Å}, \ c = 5.375 \text{ Å}, \ \beta = 122.61°$$

The observed density of 4.65 corresponds to a cell content of 4 formula units of VO_2 (calculated density 4.67).

The dimensions of the rutile type cell reported by Goldschmidt [2] were:

$$a_r = 4.54 \text{ Å}, \ c_r = 2.88 \text{ Å}$$

Evidently the following relations exist between the monoclinic cell and the rutile type subcell:

$$a = 2c_r, \ b = a_r, \ c = a_r - c_r$$

Crystals grown by heating vanadium trioxide-vanadium pentoxide mixtures of the gross composition $VO_{2.00}$ in evacuated sealed silica tubes at 900° C for about a week were used for the single crystal X-ray investigations. The blue-black crystals showed prismatic form elongated along the a direction.

MoK radiation was used throughout for the single crystal photographs. Weissenberg diagrams were registered with the prism axis as rotation axis (layer lines $h = 0$—6). The intensity scales of these photographs were correlated by means of precession photographs of the layer lines $h0l$, $h1l$ and $h2l$ taken with a Buerger camera.

The intensities of the reflections were estimated using a calibration scale of reflections of known relative intensities. The structure factor values were derived using the curves of Lu [3] for the Weissenberg photographs and those of Waser [4] and of Burbank *et al.*[5,6] for the precession diagrams.

All reflections $h0l$ with l odd were found to be absent while reflections $0k0$ were only observed for k even. This is characteristic of the space-group $P2_1/c$ (No. 14), the symmetry of which thus is very likely to be that of vanadium dioxide.

The crystal structure of the isomorphous dioxides of molybdenum and wolfram are known to be of deformed rutile type [7]. Their unit cell dimensions are similar to those of vanadium dioxide and show the same relation to the basic rutile-type subcell as does the latter. This observation suggested the possibility of structural similarities between vanadium dioxide and the MoO_2-type. However, due to the lower symmetry [$P2_1$ (No. 4)] observed for the latter the structure problem for vanadium dioxide was attacked without postulating the existence of such a structural relation.

DETERMINATION OF THE STRUCTURE

The space-group $P2_1/c$ contains a general point position 4(e): x, y, z; $\bar{x}$, $\bar{y}$, $\bar{z}$; $\bar{x}$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; $x,\frac{1}{2}-y,\frac{1}{2}+z$ and four sets of twofold point-positions corresponding to the symmetry centers of the cell. The occurrence of the glide plane and the twofold screw axis in this space-group suggested that the Harker sections $P(0v\frac{1}{2})$ and $P(u\frac{1}{2}w)$ should be investigated. The former was found to contain only one major maximum $(v=\frac{1}{2})$ which shows that all the metal atoms are situated close to the planes $y = 0$ and $y = \frac{1}{2}$. The latter section shows a heavy maximum in $u = 0$, $w=\frac{1}{2}$ and peaks of about half the height of the maximum in $u = 0.48$, $w = 0.55$ and $u = 0.52$, $w = 0.45$ and in addition a few maxima of considerably lower magnitude. This observation excludes the possibility of the vanadium atoms occupying specialized point positions. An arrangement of four vanadium atoms in 4(e) with y close to 0 (and $\frac{1}{2}$), however, requires the following maxima in the section $P(u\frac{1}{2}w)$:

(1) $u = 2x$, $w = 2z + \frac{1}{2}$ (weight $= 1$)
(2) $u = -2x$, $w = -(2z + \frac{1}{2})$ (weight $= 1$)
(3) $u = 0$, $w = \frac{1}{2}$ (weight $= 2$)

This immediately gives the approximate arrangement of the vanadium atoms

4 V in 4(e): $x \approx 0.24$, $y \approx 0$, $z \approx 0.025$.

After deriving the signs of the structure factors $F(h0l)$ from these vanadium positions the projection parallel to the b axis of the electron density function was calculated. It was found to show high peaks very close to the positions
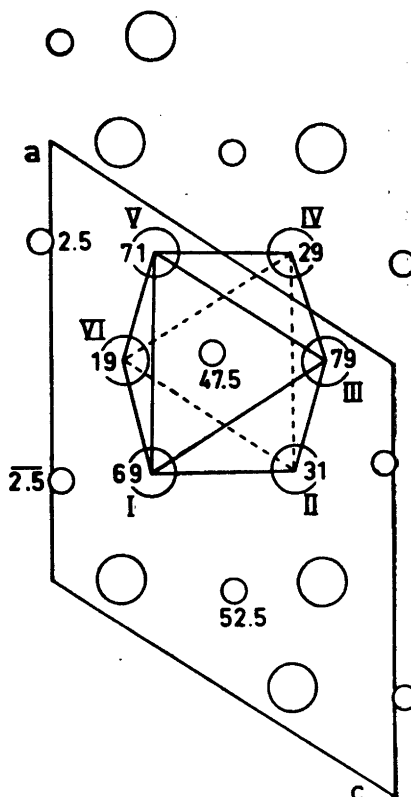
Fig. 1. VO₂. Projection of the structure on (010). The large circles denote O atoms and the small circles V atoms. The arabic numerals give the levels of the atoms in per cent of b. One VO₆ octahedron is marked out and its O atoms are denoted with roman numerals (cf. Table 2).

assumed for the vanadium atoms and minor maxima, the heights and arrangement of which suggested that they corresponded to the oxygen atoms. The oxygen atoms were found to have no influence on the signs of the structure factors $F(h0l)$.

Atoms situated in the planes $y = 0$ and $y = \frac{1}{2}$ do not contribute to the intensities of reflections $0kl$ with $k + l =$ odd. As several reflections of this type were found with too high intensities to be accounted for by mere influence of the oxygen atoms, it was concluded that the y parameter of vanadium was slightly different from zero. The signs of the structure factors $F(hkl)$ were thus calculated from a y_V value of —0.02 obtained by a rough trial and error estimation. The values of the y parameters of vanadium and oxygen were then finally obtained from the bounded projection $\varrho_{12}(y,z) = \int\limits_{x_1}^{x_2} \varrho(x, y, z)a \, dx$

evaluated between the planes $x_1 = 0$ and $x_2 = \frac{1}{2}$.

In this way the following structure was arrived at:

Space-group: $P2_1/c$ (No. 14)

Unit cell content: 4 VO₂

Table 1. *VO₂. Comparison between observed and calculated |F| values for reflections 0kl, 3kl and 4kl. Weissenberg photographs with MoK radiation.*

hkl	|F| obs.	|F| calc.	hkl	|F| obs.	|F| calc.	hkl	|F| obs.	|F| calc.
0,0,2	67	63	3,1,4	—	7	3,6,0	—	1
0,0,4	102	108	$\bar{3}$,1,4	—	11	$\bar{3}$,6,1	48	58
0,0,6	54	51	$\bar{3}$,1,5	83	83	$\bar{3}$,6,2	—	31
0,1,1	156	191	$\bar{3}$,1,6	—	10	$\bar{3}$,6,3	38	44
0,1,2	49	40	$\bar{3}$,1,7	64	75	4,0,0	74	72
0,1,3	98	95	$\bar{3}$,1,8	—	0	4,0,2	99	109
0,1,4	54	49	3,2,0	—	19	$\bar{4}$,0,2	142 *	173
0,1,5	73	75	3,2,1	34	38	4,0,4	68	63
0,1,6	—	20	$\bar{3}$,2,1	36	31	$\bar{4}$,0,4	40	35
0,2,0	68	67	3,2,2	—	20	$\bar{4}$,0,6	46	47
0,2,1	47	45	$\bar{3}$,2,2	59	56	$\bar{4}$,0,8	—	14
0,2,2	166	168	3,2,3	—	24	4,1,0	—	27
0,2,3	40	37	$\bar{3}$,2,3	33	36	4,1,1	87	92
0,2,4	64	65	3,2,4	—	25	$\bar{4}$,1,1	103	115
0,2,5	—	15	$\bar{3}$,2,4	71	70	4,1,2	33	33
0,2,6	45	40	$\bar{3}$,2,5	—	14	$\bar{4}$,1,2	—	14
0,3,1	100	95	$\bar{3}$,2,6	72	75	4,1,3	81	85
0,3,2	40	34	$\bar{3}$,2,7	—	11	$\bar{4}$,1,3	93	98
0,3,3	106	110	$\bar{3}$,2,8	55	65	4,1,4	—	23
0,3,4	—	5	3,3,0	46	42	$\bar{4}$,1,4	—	15
0,3,5	—	26	3,3,1	—	3	$\bar{4}$,1,5	46	44
0,3,6	—	43	$\bar{3}$,3,1	36	29	$\bar{4}$,1,6	46	45
0,4,0	110	102	3,3,2	46	46	$\bar{4}$,1,7	—	31
0,4,1	57	51	$\bar{3}$,3,2	47	50	$\bar{4}$,1,8	—	17
0,4,2	68	69	3,3,3	—	27	4,2,0	120	130
0,4,3	—	2	$\bar{3}$,3,3	61	58	4,2,1	—	16
0,4,4	66	58	3,3,4	—	28	$\bar{4}$,2,1	37	40
0,4,5	—	37	$\bar{3}$,3,4	—	34	4,2,2	72	68
0,5,1	79	74	$\bar{3}$,3,5	74	65	$\bar{4}$,2,2	56	52
0,5,2	—	18	$\bar{3}$,3,6	—	13	4,2,3	—	2
0,5,3	—	28	$\bar{3}$,3,7	54	61	$\bar{4}$,2,3	—	6
0,5,4	—	32	3,4,0	—	14	4,2,4	57	56
0,5,5	62	60	3,4,1	44	48	$\bar{4}$,2,4	110	97
0,6,0	65	56	$\bar{3}$,4,1	49	59	$\bar{4}$,2,5	38	39
0,6,1	—	37	3,4,2	—	8	$\bar{4}$,2,6	—	23
0,6,2	—	35	$\bar{3}$,4,2	36	30	$\bar{4}$,2,7	—	21
3,0,0	34	14	3,4,3	48	45	4,3,0	—	3
3,0,2	—	10	$\bar{3}$,4,3	38	42	4,3,1	91	99
$\bar{3}$,0,2	77 *	65	3,4,4	58	59	$\bar{4}$,3,1	77	78
3,0,4	38	42	$\bar{3}$,4,5	—	32	4,3,2	—	12
$\bar{3}$,0,4	95	83	$\bar{3}$,4,6	47	47	$\bar{4}$,3,2	—	22
$\bar{3}$,0,6	85	84	3,5,0	65	68	4,3,3	—	39
$\bar{3}$,0,8	60	65	3,5,1	—	1	$\bar{4}$,3,3	59	60
3,1,0	—	23	$\bar{3}$,5,1	—	17	$\bar{4}$,3,4	48	46
3,1,1	—	4	3,5,2	48	42	$\bar{4}$,3,5	63	67
$\bar{3}$,1,1	45	43	$\bar{3}$,5,2	42	48	$\bar{4}$,3,6	—	16
3,1,2	—	16	3,5,3	—	13	$\bar{4}$,3,7	—	6
$\bar{3}$,1,2	—	16	$\bar{3}$,5,3	38	34	4,4,0	64	59
3,1,3	—	25	$\bar{3}$,5,4	36	40	4,4,1	—	23
$\bar{3}$,1,3	84	73	$\bar{3}$,5,5	48	45	$\bar{4}$,4,1	—	15

* These reflections are obtained from a Buerger camera photograph.

Table 1. *(contd.)*

hkl	$\|F\|$		hkl	$\|F\|$		hkl	$\|F\|$	
	obs.	calc.		obs.	calc.		obs.	calc.
4,4,2	65	62	4,5,0	—	12	$\bar{4}$,5,3	53	61
$\bar{4}$,4,2	79	76	4,5,1	—	31	$\bar{4}$,5,4	—	40
4,4,3	—	17	$\bar{4}$,5,1	65	60	$\bar{4}$,5,5	—	6
$\bar{4}$,4,3	61	58	4,5,2	—	7	$\bar{4}$,6,1	48	46
$\bar{4}$,4,4	—	38	$\bar{4}$,5,2	—	27	$\bar{4}$,6,2	55	45
$\bar{4}$,4,5	—	22	4,5,3	61	65	$\bar{4}$,6,3	—	11
$\bar{4}$,4,6	—	28						

4 V in 4(e): $x,\ y,\ z;\ \bar{x},\ \bar{y},\ \bar{z};\ \bar{x},\ \frac{1}{2}+y,\ \frac{1}{2}-z;\ x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$
$\qquad\qquad\quad x = 0.242,\quad y = 0.975,\quad z = 0.025$

4 O in 4(e): $\quad x = 0.10,\quad y = 0.21,\quad z = 0.20$

4 O in 4(e): $\quad x = 0.39,\quad y = 0.69,\quad z = 0.29.$

The oxygen-oxygen vectors required by this atomic arrangement will give rise to maxima in the Patterson function with v not far from $\frac{1}{2}$ and u and w values close to those of the minor maxima found in the section $P(u\frac{1}{2}w)$.

The agreement between observed and calculated structure factor values is illustrated in Table 1. The reliability factor $R = \dfrac{\Sigma \|F_{obs}\| - \|F_{calc}\|}{\Sigma |F_{obs}|}$ for all observed reflections was found to be 0.10.

DISCUSSION OF THE STRUCTURE

The structure thus derived corresponds to reasonable interatomic distances throughout (*cf.* Table 2). The vanadium-oxygen distances of 1.76—2.05 Å are comparable with those found in, *e. g.*, paramontroseite (a metastable, naturally occurring form of VO_2) 1.88—2.13 Å [8], in V_6O_{13} 1.85—2.50 Å [9], and in V_2O_5 1.54—2.02 Å [10].

The structure of vanadium dioxide may be described as built up of distorted VO_6 octahedra joined by edges to form strings, which are mutually connected by corners to a three-dimensional network of deformed rutile type. As in the MoO_2 structure type the metal atoms within the strings are grouped pairwise to form doublets. The fundamental analogy between the structures of vanadium dioxide and molybdenum dioxide and the higher symmetry of the former suggest that the vanadium dioxide structure be considered as representing the idealized form of the "MoO_2 structure type", which also comprises the dioxides of wolfram, technetium and rhenium [11].

The metal-metal atom distances within the strings of octahedra are 2.959 Å in titanium dioxide (rutile), 2.65 and 3.12 Å in vanadium dioxide and 2.50 and 3.10 Å in molydebdenum dioxide. The sequence 2.959, 2.65 and 2.50 Å demonstrates the influence of the number of valence electrons of the metal on the formation of metal atom doublets (*cf.* Ref. [11]).

Table 2 gives a survey of the geometry of the MeO_6 octahedra of titanium dioxide (rutile) [12] and vanadium dioxide. The vanadium-oxygen distances are

Table 2. Interatomic distances (Å) and angles in MeO₆ octahedra of VO₂ and TiO₂ (rutile) [12].

Me—O	VO₂	TiO₂	O—O	VO₂	TiO₂	$\wedge$(OMeO)	VO₂	TiO₂
Me—O$_I$	2.03	1.944	O$_I$ —O$_{II}$	2.56	2.520	O$_I$ MeO$_{II}$	79°	80.8°
—O$_{II}$	2.01	1.944	O$_I$ —O$_{III}$	2.76	2.780	O$_I$ MeO$_{III}$	85°	90.0°
—O$_{III}$	2.05	1.988	O$_I$ —O$_V$	2.90	2.959	O$_I$ MeO$_V$	96°	99.2°
—O$_{IV}$	1.86	1.944	O$_I$ —O$_{VI}$	2.73	2.780	O$_I$ MeO$_{VI}$	93°	90.0°
—O$_V$	1.87	1.944	O$_{II}$ —O$_{III}$	2.62	2.780	O$_{II}$ MeO$_{III}$	80°	90.0°
—O$_{VI}$	1.76	1.988	O$_{II}$ —O$_{IV}$	2.84	2.959	O$_{II}$ MeO$_{IV}$	94°	99.2°
			O$_{II}$ —O$_{VI}$	2.74	2.780	O$_{II}$ MeO$_{VI}$	93°	90.0°
			O$_{III}$—O$_{IV}$	2.72	2.780	O$_{III}$MeO$_{IV}$	88°	90.0°
			O$_{III}$—O$_V$	2.71	2.780	O$_{III}$MeO$_V$	87°	90.0°
			O$_{IV}$—O$_V$	2.62	2.520	O$_{IV}$ MeO$_V$	89°	80.8°
			O$_{IV}$—O$_{VI}$	2.66	2.780	O$_{IV}$ MeO$_{VI}$	95°	90.0°
			O$_V$ —O$_{VI}$	2.77	2.780	O$_V$ MeO$_{VI}$	99°	90.0°

probably correct within ±0.05 Å while the oxygen-oxygen distances are likely to be better than ±0.08 Å. The error in the interatomic angles is estimated to a few degrees.

It is evident that the shapes of the oxygen octahedra of titanium dioxide (rutile) and vanadium dioxide differ little in spite of the distortion of the rutile type of the latter structure. Thus the oxygen atoms forming the edge common to the two VO₆ octahedra of a metal atom pair are somewhat forced apart. The corresponding distance in molybdenum dioxide is considerably longer, *viz.* 3.1 Å which is accounted for by the very close molybdenum-molybdenum contact. The conservation of the fairly regular arrangement of the oxygen atoms implies that the metal atom in vanadium dioxide is somewhat removed from the center of gravity and approaching one face of the VO₆ octahedron.

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