

The Crystal Structure of $\text{Na}_{2-x}\text{V}_6\text{O}_{15}$

By A. D. WADSLEY

Division of Industrial Chemistry, Commonwealth Scientific and Industrial Research Organization, Melbourne, Australia

(Received 8 March 1955 and in revised form 13 June 1955)

The structure of $\text{Na}_{2-x}\text{V}_6\text{O}_{15}$ has been determined by Patterson and electron-density projections. The compound crystallizes in the monoclinic system, space group $A2/m$, and the unit cell, which contains two formula units, has the dimensions $a = 10.08$, $b = 3.61$, $c = 15.44$ Å, $\beta = 109.6^\circ$. The structure consists of zigzag double strings of VO_6 octahedra forming sheets by joining corners. Adjacent sheets are joined by additional chains of doubled VO_5 trigonal bipyramids, giving rise to unidirectional tunnels. Each tunnel in projection contains two interstitial sites which are never more than half filled with sodium ions. Each sodium is coordinated to seven oxygens, six at the corners of a trigonal prism and a seventh through the centre of a prism face. It is considered that in any one tunnel the polyhedra grouped around the sodiums are linked by sharing edges in a staggered string, but that these strings are disordered throughout the structure. A discussion of compounds in which V^{5+} is known to have 4, 5 or 6 oxygen ligands indicates that the coordination number increases with the complexity of grouping, and is consequently dependent upon environment. Comparison of oxides with molecular tunnels affords some generalities on variable chemical composition in compounds of this type.

Introduction

Variability of composition in inorganic compounds may be due to several causes. The commonest is mixed-crystal formation, the substitution for one ion by another of similar size or by the absence of some of the ions themselves, accompanied by a necessary valency adjustment (Hägg, 1935). Alternatively, a compound may consist of a framework with interstitial sites which, in Buerger's nomenclature (1954) can be 'stuffed' with other ions. To these, a third class can be added. A host, crystallizing in the presence of ions incapable of substitution, may form a new phase embodying tubes or tunnels which afford the foreign ions a normal environment and will not necessarily require integral numbers in a unit formula.

In a study of the system V_2O_5 - NaVO_3 , Flood & Sörum (1943) found two phases of indeterminate composition, the first of which, β - $\text{Na}_x\text{V}_2\text{O}_5$, having the limits of composition $0.15 \leq x \leq 0.31$, is the subject of this paper. The second, γ - $\text{Na}_x\text{V}_2\text{O}_5$, with x approximately equal to 0.8, had a narrower composition range and was more difficult to isolate. The unit-cell dimensions indicated substantial differences in structure from the two end members.

These compounds appeared to fulfil the conditions appropriate to the third class. Na^+ and V^{5+} differ considerably in size, and mixed-crystal formation was unlikely. V_2O_5 does not contain interstitial sites large enough to accommodate sodium ions. Finally, pentavalent vanadium in many of its compounds whose structures are known forms infinite linear strings of closely coordinated polyhedra, believed necessary as building blocks of a structure possessing the con-

tinuous rows of vacant interstitial sites defining a tunnel structure.

Experimental

Crystals with the upper limit of composition $\text{Na}_{0.33}\text{V}_2\text{O}_5$ were prepared by fusing together the appropriate amounts of NaVO_3 and V_2O_5 in a platinum crucible and allowing to cool overnight in a furnace. Irregular growths due to spitting, which accompanies the loss of oxygen at the freezing point (Prandtl, 1905), contained well formed greenish-black needles. The crystallographic data given for these in Table 1 agree closely

Table 1. *Crystallographic data*

System	Monoclinic
$a = 10.08$, $b = 3.61$, $c = 15.44$ Å; $\beta = 109.6^\circ$	
General spectra absent only for $k+l \neq 2n$	
Space group	Am , $A2$ or $A2/m$
Density (obs.)	3.55 g.cm.^{-3}
Density (calc.)*	3.57 g.cm.^{-3}

* For $\text{Na}_2\text{V}_{12}\text{O}_{30}$.

with those published by Flood & Sörum (1943) for their β phase.

A crystal of nearly cylindrical section of height approximately equal to diameter was used to obtain the intensities which were recorded by means of the multiple-film technique on a Weissenberg camera. Very long exposures enabled 273 $h0l$ and 45 $0kl$ visible reflexions to be indexed, the intensities of which were measured by a film strip prepared by timed exposures of a representative spot. Filtered molybdenum radiation was used, and no corrections for absorption were

made. The intensities, corrected by the Lorentz and polarization factors, were subsequently placed on an absolute scale by direct comparison with structure factors calculated for half the unit-cell contents. Scattering curves for Na and O (Viervoll & Ögrim, 1949) and for V (Qurashi, 1954) were modified by an isotropic temperature factor, $B = 0.4 \text{ \AA}^2$, which was found experimentally.

Structure determination

A plot of the intensity distribution for each zone, $h0l$ and $0kl$, favoured the centrosymmetrical curve in each case, and the space group was therefore assumed to be $A2/m$.

It was unlikely that two vanadium atoms would overlap in projection on (010) since the b axis had a length of only 3.6 \AA . The twelve vanadium atoms in the unit cell were therefore probably in the general positions $4(i)$ listed in the *International Tables* (1952, p. 95). The Patterson function $P(u, w)$ sharpened by the method of Lipson & Cochran (1953, p. 172) is illustrated in Fig. 1. The symmetrical unit of six vanadium atoms will give fifteen peaks in Patterson space consisting of six double and three single vectors. The former are marked *A, B, C, D, E* and *F* in Fig. 1, and it will be seen that there are seven peaks of intermediate size, only three of which are due to V-V vectors. The selection of these was made with the method of Clastre & Gay (1950) by making two identical maps on transparent material and transferring the origin of one to a known or postulated single interaction on the other, keeping the axial directions parallel. The coincident peaks then represented a reduced set of points which, after several trials, ap-

peared to correspond to two sets of three related by a symmetry centre.

Attempts to position the oxygens and sodium by further application of this image-seeking method were unsuccessful. The coordination of oxygen around vanadium is known to be variable, and it was therefore necessary to locate oxygens without assumption. To do this, electron-density projections were calculated with phases fixed at first by the vanadium atoms alone. Despite false maxima due to some sign errors, several additional peaks appeared at positions affording distances to the metal atoms consistent with values published for V-O bonds. Seven of these were in fourfold sites and an eighth in a twofold position at the origin. The sodium could not be reliably identified with any of the detail. Inclusion of oxygen in the calculation of structure amplitudes failed to reduce the reliability factor below 0.30, and the signs of some ten reflexions of appreciable magnitude were left in doubt.

In projection an oxygen partly overlapped each vanadium, so that the correct parameters of each were difficult to deduce even from an $F_o - F_c$ synthesis. Since, however, the scattering power of oxygen diminishes more rapidly than does that of vanadium, the outermost reflexions are more sensitive to parameter changes in the metal atoms. A Fourier projection was made with data for which $2 \sin \theta \geq 0.8$. By this means the oxygens were so reduced in strength as to be barely visible, and the V atoms had shifted by appreciable amounts. The new parameters then permitted the structure to be refined by conventional iterative procedures, the final electron-density projection being illustrated by Fig. 2. An additional peak in a fourfold site is attributed to sodium. Since there are only two of these atoms in the unit cell, the four sites related by symmetry can be only half occupied.

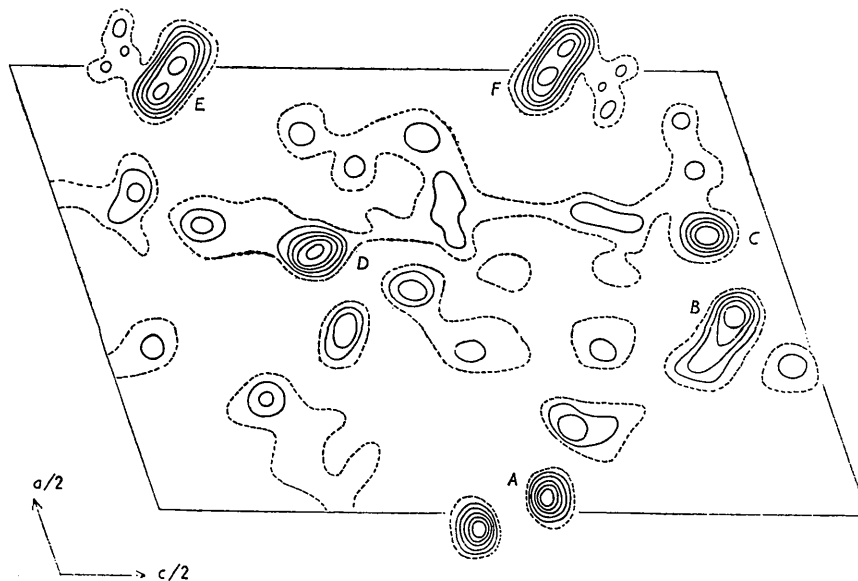


Fig. 1. Projection of the Patterson function $P(u, w)$. Zero contour dotted, and positive regions only are shown. The origin peak is omitted. The heavier peaks, *A, B, C, D, E* and *F* are those due to known V-V interactions.

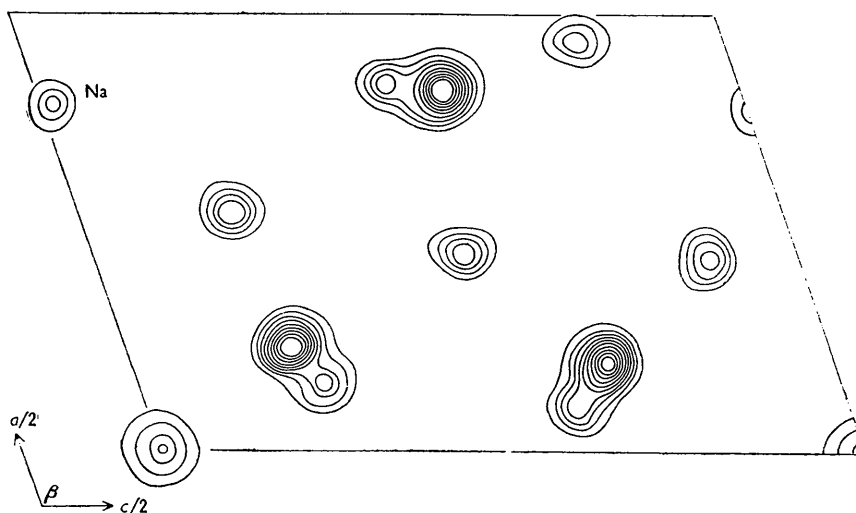
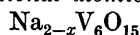


Fig. 2. Electron density projected on (010). The first four contours are at intervals of 2 electrons, and the remainder at 4 electrons. The zero contour is omitted.

The parameters of the atoms listed in Table 2 were derived from Fig. 2 with the exception of O_2 , O_3 and O_7 . These were obtained from a difference syn-

are therefore assumed to be in error by a maximum of $\pm 0.05 \text{ \AA}$.

Table 2. Fractional atomic parameters for



Space group $A2/m (0, 0, 0; 0, \frac{1}{2}, \frac{1}{2})+$

Atom	No. of equivalent atoms	x/a	y/b	z/c
V_1	4 in 4(<i>i</i>)	0.103	0	0.339
V_2	4 in 4(<i>i</i>)	0.119	0	0.117
V_3	4 in 4(<i>i</i>)	0.411	0	0.289
Na	4-2 <i>x</i> in 4(<i>i</i>)	0.394	0	0.007
O_1	2 in 2(<i>a</i>)	0	0	0
O_2	4 in 4(<i>i</i>)	0.053	0	0.811
O_3	4 in 4(<i>i</i>)	0.078	0	0.633
O_4	4 in 4(<i>i</i>)	0.219	0	0.436
O_5	4 in 4(<i>i</i>)	0.225	0	0.264
O_6	4 in 4(<i>i</i>)	0.271	0	0.108
O_7	4 in 4(<i>i</i>)	0.419	0	0.750
O_8	4 in 4(<i>i</i>)	0.467	0	0.396

thesis in which the calculated metal atom contributions were subtracted from the observed data. If the space group is $A2/m$, all atoms in the positions 4(*i*) or 2(*a*) lie on planes parallel to (010) and $\frac{1}{2}b$ apart. The good agreement between observed and calculated structure amplitudes suggests that this is substantially correct. The reliability index for $h0l$ and $0kl$ is 0.17 and 0.13 respectively (Table 3).

The structure discussed below is based upon the space group $A2/m$. As only 45 visible $0kl$ reflexions were found despite long exposures, it is possible that some of the oxygens may have very small y parameters if in the positions 4(*c*) ($x, y, z; \bar{x}, y, \bar{z}$) of the space group $A2$. These would be difficult to deduce except by the extensive use of three-dimensional data; their effect on the structure itself is of minor importance save in the accuracy of interatomic distances. These

Description

The coordination of vanadium is of two kinds. V_1 and V_2 are each linked to six oxygens disposed at the corners of distorted octahedra. The metal atoms are displaced from the centres so that the bonds vary in length from 2.33 \AA to 1.57 \AA . The distances between oxygen atoms vary from 2.55 \AA for a shared edge to 2.84 \AA for an unshared edge with one of 3.14 \AA , having in all a mean of 2.70 \AA . Whilst V_3 has five bonds to oxygen similar in length with those of V_1 and V_2 , the sixth is 2.68 \AA , some 0.35 \AA longer than the comparable bonds in the octahedra. For this reason, it is considered that V_3 is in fivefold coordination, being displaced from the centre of a distorted trigonal bipyramid polyhedron of oxygens. This figure has been demonstrated for V_2O_5 (Byström, Wilhelmi & Brotzen, 1950) and also for $KVO_3 \cdot H_2O$ (Christ, Clark & Evans, 1954).

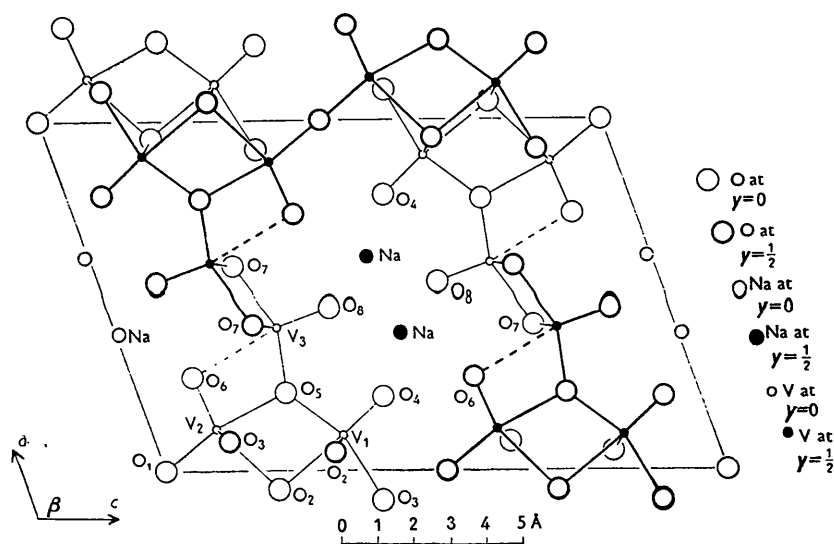
The octahedra are associated in pairs with a shared edge which unite with similar pairs above and below by further edge sharing to form a zigzag ribbon extending along y . The ribbons are joined by sharing corners (the atoms O_1) to form a puckered layer, the median of which forms the plane (100).

The trigonal bipyramids are associated in pairs to form a double chain by each having an edge in common with each V_3 neighbour, and, like the ribbons of octahedra, are elongated along y (Fig. 4(a)). The chains of 5-coordinated vanadium bridge adjacent layers of 6-coordinated vanadium by corner sharing (the atoms O_5). The plane of the chains is nearly parallel to (001) so that the structure as a whole forms an open framework or tunnel, the sides of which are the extended strings of closely coordinated polyhedra.

Table 3. Observed and calculated structure factors

The non-observed reflexions are omitted except when at variance with F_c .

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
100	21	26	104	21	26	208	23	21	20012	12	11	9020	12	8	013	32	38
200	29	32	204	8	7	708	28	23	21012	13	9	5020	9	9	015	27	29
300	27	23	304	56	80	808	36	36	12014	19	18	1020	13	14	017	25	24
400	36	43	404	35	26	1108	12	9	10014	9	12	1020	11	10	019	25	24
500	10	7	504	57	71	1208	29	27	8014	13	20	2020	7	10	0111	16	16
600	50	52	604	9	8	1508	18	19	7014	10	14	3020	9	9	0113	22	29
700	12	12	704	23	26	1608	11	11	6014	16	21	4020	8	9	0117	21	23
800	15	15	804	11	8	1708	10	9	5014	17	13	7020	13	10	0119	16	14
900	21	18	904	32	31	1808	13	10	4014	6	7	8020	15	14	0121	12	9
1000	27	26	1004	5	9	1908	12	11	3014	24	20	13020	19	15	020	84	104
1100	9	11	1104	13	13	17010	10	8	2014	23	28	15020	13	11	022	30	24
1300	14	14	1204	22	22	15010	19	20	1014	29	25	19020	18	16	024	18	15
1400	13	7	1304	19	20	12010	10	10	2014	19	24	8022	10	14	028	18	17
1600	12	9	1604	15	15	11010	17	15	3014	10	5	6022	10	9	0210	13	12
1700	13	15	2004	10	9	9010	13	14	4014	10	14	4022	13	15	0218	21	23
1902	13	12	2204	11	10	8010	17	16	5014	33	30	2022	9	9	0222	15	24
1702	12	12	2006	16	14	7010	24	25	6014	12	14	0022	17	20	0224	13	12
1502	10	10	1406	19	21	6010	14	14	7014	21	18	2022	9	12	033	21	20
1302	19	20	1106	14	12	5010	16	16	8014	11	14	3022	14	15	035	25	22
1202	12	12	1006	21	24	4010	22	19	9014	8	8	4022	13	13	037	15	16
1102	10	11	906	7	7	3010	8	8	11014	22	21	5022	9	8	039	20	17
1002	13	8	806	10	12	2010	27	24	8016	13	13	6022	11	15	0311	13	13
902	15	12	706	31	25	1010	27	31	7016	7	8	7022	14	18	0313	22	25
602	41	36	606	8	8	0010	13	14	2016	10	7	8022	25	23	0317	18	20
502	10	9	506	10	8	2010	38	49	1016	11	13	10022	14	13	0319	12	13
402	6	4	406	23	21	3010	23	23	2016	11	10	13022	27	27	040	65	62
302	20	19	306	33	33	4010	25	20	3016	8	7	15022	9	8	042	20	18
202	24	31	206	25	25	5010	< 5	5	4016	15	13	19022	15	13	044	11	11
102	13	11	106	43	63	6010	20	17	5016	6	5	4024	16	16	048	12	12
002	25	46	006	< 4	4	7010	8	3	6016	15	15	0024	10	9	048	17	19
102	12	10	106	12	13	8010	17	13	7016	21	19	2024	11	10	053	13	14
202	17	12	206	16	11	9010	9	9	8016	11	7	4024	12	13	055	19	17
302	32	34	306	22	12	12010	12	10	11016	11	7	7024	9	11	057	12	11
402	31	24	406	19	18	13010	12	8	12016	13	12	8024	10	9	059	14	13
502	17	15	506	34	23	15012	10	8	14016	23	25	12024	11	10	0513	18	19
702	8	9	706	23	18	10012	8	8	15016	17	14	18024	13	11	060	49	45
802	17	17	806	13	8	9012	11	8	16016	16	12	1026	17	15	062	15	12
902	14	12	906	13	10	7012	< 8	8	9018	15	15	1026	8	11	080	38	32
1002	7	8	1006	8	7	6012	8	9	8018	< 9	10	5026	10	12	0100	18	21
1102	11	11	1106	9	10	4012	13	10	7018	14	17	8026	15	14			
1202	8	6	1206	12	8	2012	7	10	5018	7	6	9026	15	12			
1402	7	6	1406	7	7	1012	9	10	4018	10	7	12026	23	21			
1602	16	15	1506	7	9	0012	< 5	7	3018	26	31	13026	12	8			
2202	13	12	1208	13	13	1012	28	27	0018	24	21	16026	12	12			
1404	16	17	1108	8	11	2012	7	7	1018	13	16	18026	13	16			
1104	16	18	908	12	13	5012	12	11	3018	14	19	5028	13	10			
1004	8	8	608	17	19	7012	34	36	4018	16	15	1028	18	17			
804	21	21	508	19	21	9012	7	5	5018	15	15	3028	8	8			
704	29	24	408	18	14	10012	20	18	6018	21	20	5028	12	9			
604	8	7	308	8	7	11012	25	27	7018	8	10	10028	10	9			
504	40	48	208	35	38	12012	11	7	8018	17	22	4030	15	15			
404	11	11	108	6	9	13012	< 8	10	10018	22	20	7030	10	12			
304	22	17	008	22	24	15012	17	12	11018	9	12	8030	10	8			
204	9	6	208	33	41	16012	8	8	14018	22	20	11030	13	11			
104	40	30	308	8	7	17012	18	15	16018	10	8	17030	14	10			
004	20	23	408	44	43	19012	10	11	18018	14	13	2032	14	17			

Fig. 3. Structure of $\text{Na}_{2-x}\text{V}_6\text{O}_{15}$ projected on (010) for one unit cell. No bonds are shown between sodium and its ligands. The broken lines represent the long bonds from V_3 to the sixth oxygen atom.

The sodium atoms lie in two rows in the tunnels. In Fig. 3 each has eight near neighbours, six oxygens forming the corners of a distorted trigonal prism with a seventh through the centre of a rectangular prism face. The eighth is another sodium, so that the figure for the group consists of two 7-coordinated polyhedra with a prism face in common (Fig. 4(b)).

The compound prepared for the present investigation contained the upper limit of sodium found from the phase study of Flood & Sörum (1943), and consequently it seems evident that the sodium sites can never be more than half occupied. If each alternate unit tunnel contains one sodium instead of two, the associated polyhedra may form a staggered string by edge sharing (Fig. 4(c)), and in projection on (010) the sodium atoms appear in a fourfold site. There is no evidence for the doubling of *b*, and the strings, regular for each tunnel, evidently have no periodicity. The sodium atoms may therefore adopt only one of the two possible positions (for example *x*, 0, *z*, or \bar{x} , 0, \bar{z})

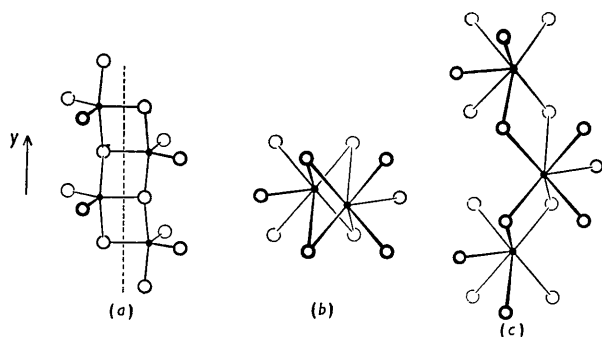


Fig. 4. (a) A double string of 5-coordinated vanadium atoms (small black circles) found for V_3 in the present structure. The broken line shows how this figure provides two 4-coordinated single strings by a hypothetical cleavage.

(b) Coordination of sodium (small black circles) and oxygen (larger circles) from the X-ray data.

(c) Staggered string of 7-coordinated sodium atoms (small black circles) believed present in any one tunnel. The lack of order between strings of this type in different tunnels provides X-ray data consistent with (a).

for any one unit tunnel, and these are distributed at random over the structure as a whole.

Each sodium is now bonded to seven oxygens, the coordination being identical with that reported by Hoard (1939) for $(\text{NbF}_7)^{2-}$. The seventh oxygen bonded through the prism face is the one rejected by V_3 to form a 5- rather than a 6-ligand grouping.

Stereochemistry of pentavalent vanadium

Pentavalent vanadium may be coordinated to four, five, or six oxygen atoms.

Isolated tetrahedra presumably exist only in the orthovanadates, which in BiVO_4 (pucherite), the only compound of this class fully investigated, show considerable distortion (Qurashi & Barnes, 1953).

Sörum (1943) derived a trial structure for NaVO_3 based on that of diopside, and Evans & Block (1954) reported that KVO_3 also had this grouping. In both cases, therefore, the metavanadate ion is comprised of tetrahedral groups forming linear strings of the composition $(\text{VO}_3)_n^{2-}$ by corner sharing.

The structure of V_2O_5 is formed by doubled chains of distorted trigonal bipyramids joining corners to form layers which are held together by residual forces (Byström, Wilhelmi & Brotzen, 1950). Similar structural units form isolated ions $(\text{VO}_3)_n^{2-}$ in $\text{KVO}_3 \cdot \text{H}_2\text{O}$ (Christ *et al.*, 1954), and are also present, as we have demonstrated, in $\text{Na}_{2-x}\text{V}_6\text{O}_{15}$ (Fig. 4(a)).

A distorted sixfold grouping was found for the atoms V_1 and V_2 in this structure, and for all the metal atoms in $\text{V}_{12}\text{O}_{26}$ (Aebi, 1948), the octahedra in which are again arranged in double zigzag ribbons grouped together in a rather complex manner.

The bond lengths in Table 4 serve as a basis for comparison between 6- and 5-coordinated vanadium since they are in good agreement with other published values. In each case the figures are substantially identical, with the exception of the distance $V_3\text{-O}_6$ and the attendant oxygen separations. It is undoubtedly true that V_3 can be described in terms of a very dis-

Table 4. *Interatomic distances*

The maximum estimated error is ± 0.05 Å

No.	Length (Å)	No.	Length (Å)	No.	Length (Å)	No.	Length (Å)	
$V_1\text{-O}_4$	1	1.56	$V_2\text{-O}_8$	1	1.58	$V_3\text{-O}_8$	1	1.56
$\{V_1\text{-O}_2$	2	1.89	$V_2\text{-O}_3$	2	1.89	$\{V_3\text{-O}_7$	2	1.91
$\{V_1\text{-O}_2$	1	2.32	$V_2\text{-O}_1$	1	1.80	$\{V_3\text{-O}_7$	1	2.00
$V_1\text{-O}_5$	1	1.95	$V_2\text{-O}_5$	1	2.16	$V_3\text{-O}_5^*$	1	1.78
$V_1\text{-O}_3$	1	2.01	$V_2\text{-O}_2$	1	2.34	$V_3\text{-O}_6^*$	1	2.68
$O_2\text{-O}_3$	2	2.57	$O_3\text{-O}_2$	2	2.55	$O_7\text{-O}_7$	2	2.43
$\{O_2\text{-O}_5$	1	2.65	$O_5\text{-O}_8$	1	2.60	$O_6\text{-O}_5^*$	1	2.60
$\{O_2\text{-O}_5$	2	2.76	$O_2\text{-O}_5$	1	2.65	$O_5\text{-O}_8$	1	2.60
$O_4\text{-O}_5$	1	2.68	$O_1\text{-O}_3$	2	2.65	$O_5\text{-O}_7$	2	2.72
$\{O_2\text{-O}_3$	2	2.71	$O_3\text{-O}_5$	2	2.75	$\{O_7\text{-O}_8$	2	2.80
$\{O_2\text{-O}_3$	1	2.84	$O_3\text{-O}_8$	2	2.77	$\{O_7\text{-O}_8$	1	2.85
$O_2\text{-O}_4$	2	2.76	$O_1\text{-O}_6$	1	2.68	$\{O_6\text{-O}_7^*$	2	2.85
$O_3\text{-O}_4$	1	2.82	$O_1\text{-O}_2$	1	3.14	$\{O_6\text{-O}_7^*$	1	3.16
						$\{Na\text{-O}_8$	2	2.46
						$\{Na\text{-O}_8$	2	2.75
						$Na\text{-O}_4$	2	2.51
						$Na\text{-O}_6$	1	2.29
						$Na\text{-Na}$	1	2.22
						$O_4\text{-O}_8$	2	2.77
						$O_4\text{-O}_6$	2	3.11
						$O_6\text{-O}_8$	2	3.18
						$O_8\text{-O}_4$	2	3.35
						$\{O_8\text{-O}_8$	2	3.05
						$\{O_8\text{-O}_8$	2	3.61
						$O_4\text{-O}_4$	1	3.61

The braces denote symmetry-related pairs.

* These distances are not part of the fivefold coordination of V_3 but are included for comparison.

torted octahedron, and in discussing V_2O_5 Magnéli & Oughton (1951) sought to do this by comparison with MoO_3 , taking into account the limited solid solution of the two components. It is difficult to consider the V_1 and V_2 coordination in $\text{Na}_{2-x}\text{V}_6\text{O}_{15}$ and the structure of $\text{V}_{12}\text{O}_{26}$ (Aebi, 1948) as being anything other than octahedral without introducing needless complexities. On the other hand $\text{KVO}_3 \cdot \text{H}_2\text{O}$ is not readily described in terms of an octahedral arrangement.

In each case the vanadium polyhedron is distorted, presumably owing to the Coulombic repulsion of the metal atoms. The similarity in configuration suggests that the bonding orbitals are not extensively regrouped, and it is probable that the five-bonded figure results from hybridization of the d^3sp orbitals, and the octahedron to the d^3sp^2 orbitals. The effect of closer coordination giving a stronger octahedral character to the one implies a rearrangement bringing hitherto unused p orbitals into operation, and with it a diminution in bond length to the sixth ligand atom.

The bonds holding together both units of the double fivefold chain are longest. Two single chains formed by the hypothetical cleavage of one double unit, with some slight rearrangement, become identical with tetrahedral chains of the diopside type (Fig. 4(a)). Conversely, the fusion together of two tetrahedral chains results in the formation of a double fivefold chain without gain or loss of oxygen. At the time of writing, there are no details available either for NaVO_3 or KVO_3 , and consequently the extent of the rearrangement required by this viewpoint is unknown. However, here again the bonding cannot differ substantially, and it is feasible that distorted tetrahedral bonds of the type d^2sp readily evoke an additional d orbital when the grouping is fivefold.

The coordination number of the V^{5+} ion clearly depends upon the environment. With highly electronegative ligands the electrostatic potential energy of the whole crystal lattice presumably competes with different kinds of orbital hybridization possessing small energy differences.

Tunnel structures and variable composition

The structural relations of the organic occlusion compounds was stressed by Schlenk (1951) in a recent review. For example, urea molecules when crystallized in the presence of a straight-chain hydrocarbon, reject their normal grouping and adopt a hydrogen-bonded structure forming linear tunnels of molecular dimensions (Schlenk, 1949). The hydrocarbon is located in the spaces, and, not being chemically bonded to the urea, is not necessarily present in a fixed proportion or in a particular orientation (Smith, 1952). Thiourea, choleic acid, 4-4'-dinitrophenol and dextrin may all form compounds of a similar nature.

Several simple inorganic compounds of this type have been described recently. WO_3 provides inter-

stitial sites which may be occupied by sodium or lithium ions to form the particular tungsten bronze with little change in the framework or host structure. Cs^+ , Rb^+ and K^+ , being larger, are unable to form compounds isomorphous with these and instead cause a reorganization of the framework into a new series of hexagonal symmetry (Magnéli & Blomberg, 1951). The structure then contains a series of tunnels with sites big enough for the larger alkali metal ions (Magnéli, 1952). Hollandite, $\text{Ba}_{2-x}\text{Mn}_8\text{O}_{16}$, and compounds related to it (Byström & Byström, 1950) has tunnels of square cross-section enclosing Ba^{2+} , and psilomelane ($\text{Ba}, \text{H}_2\text{O})_2\text{Mn}_5\text{O}_{10}$ is another closely related structure (Wadsley, 1953). The configuration of $\text{Na}_{2-x}\text{V}_6\text{O}_{15}$ is rather more complex and forces the Na ions into an unusual grouping. All these substances are therefore simple binary oxides which, when crystallized in the presence of ions too large to be substituents, adopt an entirely different structure in which the foreign ions occupy their own set of lattice points. They therefore differ from the derivative structures discussed by Buerger (1947).

Just as the stoichiometrical ratio between the components of the organic compounds is to some extent variable, so these oxides have extended homogeneity ranges. The host structure may be stable by itself once it is formed, and indeed $\text{W}_{18}\text{O}_{49}$ has empty tunnels similar to the hexagonal bronzes (Magnéli, 1949). Ions present in the tunnels upset the charge distribution in the host since, unlike the 'guest' molecules in the organic compounds, they are coordinated to it. Since the host cation is of necessity a transition metal, the electrostatic balance is achieved by the reduction of some of these to a lower valency state and these are distributed between the metal sites, possibly as interchangeable electrons.

Except for the host itself, therefore, no fixed or integral number of ions is required by this type of chemical compound since the net valency of the host cation may vary widely and continuously. The sites which are available to the foreign ions are seldom more than half filled. Having no oxygen atoms between them in the tunnels, the ions are directly opposed to one another and as a result adopt one of two different arrangements. If formed in single rows, they alternate with one or two vacant sites in any one tunnel (hollandite, caesium bronze). If double rows are found, as in psilomelane and in $\text{Na}_{2-x}\text{V}_6\text{O}_{15}$, occupied sites alternate to form zigzag chains of polyhedra sharing edges. The crystallographic data for all of these compounds disclose that the sites are occupied by the foreign ions at random, with no evidence for long-range order resolving vacant and filled positions in larger unit cells. Consequently when half occupied, the straight and zigzag rows are considered to be continuous for any one tunnel (Byström & Byström, 1951; Wadsley, 1953) but disordered in the structure as a whole. With fewer ions present, a random grouping of continuous rows may perhaps give way to a more

disordered sequence in any one tunnel. Crystals of the composition $\text{Na}_{0.5}\text{V}_6\text{O}_{15}$ give no diffuse spectra by which this may be assessed, but single crystals of $\text{Ba}_{2-x}\text{Ti}_8\text{O}_{16}$, which is isomorphous with hollandite, offer additional evidence which is being investigated both by X-ray diffraction and dielectric absorption measurements.

References

- AEBI, F. (1948). *Helv. chim. Acta*, **31**, 8.
 BUEGER, M. J. (1947). *J. Chem. Phys.* **15**, 1.
 BUEGER, M. J. (1954). *Amer. Min.* **39**, 600.
 BYSTRÖM, A. & BYSTRÖM, A. M. (1950). *Acta Cryst.* **3**, 146.
 BYSTRÖM, A. & BYSTRÖM, A. M. (1951). *Acta Cryst.* **4**, 469.
 BYSTRÖM, A., WILHELMI, K. A. & BROTZEN, O. (1950). *Acta chem. scand.* **4**, 1119.
 CHRIST, C. L., CLARK, J. R. & EVANS, H. T. (1954). *Acta Cryst.* **7**, 801.
 CLASTRE, J. & GAY, R. (1950). *J. Phys. Radium*, **11**, 75.
 EVANS, H. T. & BLOCK, S. (1954). *Amer. Min.* **39**, 327. (Abstract.)
 FLOOD, H. & SÖRUM, H. (1943). *Tidsskr. Kjemii, Bergvesen Met.* **5**, 55.
 HÄGG, G. (1935). *Z. Kristallogr.* **91**, 114.
 HOARD, J. L. (1939). *J. Amer. Chem. Soc.* **61**, 1252.
International Tables for X-ray Crystallography (1952). Birmingham: Kynoch Press.
 LIPSON, H. & COCHRAN, W. (1953). *The Crystalline State*, vol. III, p. 172. London: Bell.
 MAGNÉLI, A. (1949). *Ark. Kemi*, **1**, 223.
 MAGNÉLI, A. (1952). *Nature, Lond.* **169**, 791.
 MAGNÉLI, A. & BLOMBERG, B. (1951). *Acta chem. scand.* **5**, 372.
 MAGNÉLI, A. & OUGHTON, B. M. (1951). *Acta chem. scand.* **5**, 581.
 PRANDTL, W. (1905). *Ber. dtsh. chem. Ges.* **38**, 657.
 QURASHI, M. M. (1954). *Acta Cryst.* **7**, 310.
 QURASHI, M. M. & BARNES, W. H. (1953). *Amer. Min.* **38**, 489.
 SCHLENK, W. (1949). *Liebigs Ann.* **565**, 204.
 SCHLENK, W. (1951). *Fortschr. Chem. Forsch.* **2**, 92.
 SMITH, A. E. (1952). *Acta Cryst.* **5**, 224.
 SÖRUM, H. (1943). *K. norske vidensk. Selsk. Forh.* **16**, 39.
 VIERVOLL, H. & ÖGRIM, O. (1949). *Acta Cryst.* **2**, 277.
 WADSLEY, A. D. (1953). *Acta Cryst.* **6**, 433.

Acta Cryst. (1955). **8**, 701

Polarization Correction for Crystal-Monochromatized X-radiation*

BY LEONID V. AZAROFF

Armour Research Foundation of Illinois Institute of Technology, Technology Center, Chicago 16, Illinois, U.S.A.

(Received 3 January 1955 and in revised form 14 June 1955)

The polarization correction for diffraction of a crystal-monochromatized X-ray beam is derived. Suitable expressions for different experimental methods are also given. The polarization correction is first tabulated in parts so that the appropriate correction for any wavelength and monochromator crystal can be determined. Another table lists selected values of the polarization correction, in a final form, for different wavelength X-radiations reflected from $(10\bar{1}1)$ planes of a quartz monochromator. The maximum correction for Ag $K\alpha$ is a little more than 1%, whereas for Cr $K\alpha$ the maximum correction is 34%.

1. Polarization factor

The use of crystal-monochromatized X-radiation has many advantages over conventional methods using filters. Of greatest importance is the virtual elimination of background scattering due to non-characteristic radiation. Furthermore, it is possible to use a bent-crystal monochromator to obtain integrated intensities photographically, as will be shown in a subsequent communication. The chief objection to the use of crystal monochromators, the intensity decrease in the twice diffracted beam, can be minimized by suitable

choice of monochromator crystal and X-radiation. Thus, single-crystal photographs of inorganic compounds made in the author's laboratory with Ag $K\alpha$ diffracted from $(10\bar{1}1)$ planes of a quartz monochromator have intensities directly comparable with similarly exposed photographs prepared with a conventionally filtered beam.

Whenever crystal-monochromatized X-radiation is used, the beam striking the specimen crystal is partially polarized owing to reflection by the monochromator crystal. The polarization factor for the twice diffracted beam is different, therefore, from the relation, $\frac{1}{2}(1 + \cos^2 2\theta)$, normally used. In order to determine the appropriate polarization factor, consider Fig. 1. The intensity of an unpolarized X-ray beam

* This research was supported by the United States Air Force, through the Office of Scientific Research of the Air Research and Development Command.