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Crystal Chemistry of Non-stoichiometric Pentavalent Vanadium Oxides: Crystal Structure of $Li_{1+x}V_3O_8$

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$Li_{1+x}V_3O_8$ crystallizes in the monoclinic system, space group $P2_1/m$, with the unit-cell dimensions $a = 6{\cdot}68$, $b = 3{\cdot}60$, $c = 12{\cdot}03$ Å, $\beta = 107° 50'$. The structure is formed by VO_6 octahedra and VO_5 distorted trigonal bipyramids grouped as sheets by sharing edges and corners. The sheets are held together by Li ions in octahedral interlayer sites, and it is presumed that more are located in additional tetrahedral positions which, however, cannot be directly deduced. The relationships in configuration to V_2O_5, V_6O_{13}, $Na_{2-x}V_6O_{15}$ and $NaVO_3$ are briefly discussed in terms of a system of variable oxygen content.

1. Introduction

Much recent crystallographic work has been devoted to the study of non-stoichiometric oxides, and a recent survey (Wadsley, 1955*a*) showed that chemical variability was reflected in the structure in a variety of ways. Changes of composition for annealed phases may often occur in steps. The stepwise principle, commonest when the anions are defective, is shown by the homologous series of shear structures $(Mo, W)_nO_{3n-1}$ formed by changes of polyhedral grouping (Magnéli, 1953), by the ordered resolution of lattice vacancies as in the oxides $Ce_{32}O_{64-n}$ (Bevan, 1955), and in the uranium oxides $(U_4O_9)_nO$ where additional oxygens find interstitial positions in the crystal lattice (Perio, 1953). So far as is known, ordered oxygen defects in ternary oxides are limited to the hexagonal spinel-like phases $Ba(Fe_{2n}O_{3n+m})$ in which Ba^{++} or an ion of similar size substitutes for oxygen (Went, Rathenau, Gorter & Oosterhout, 1952) and possibly to $BaNiO_{2+\delta}$ (Lander, 1951).

Several phases of intermediate composition are found in each of the binary systems V_2O_5–RVO_3 (R = Na, Li, Ag) (Flood & Sörum, 1943; Flood, Krog & Sörum, 1946*a*, *b*), TiO_2–$BaTiO_3$ (Statton, 1951; Rase & Roy, 1955) and Nb_2O_5–$KNbO_3$ (Reisman & Holtzberg, 1955) (Table 1). Compounds in any one group cannot always be rationalized in terms of the classical 'oxide-type' formulae (e.g. $AO_x.BO_y$), which in any case have little meaning in structural inorganic chemistry. The crystal structures of the end members in any one group are dissimilar, and the passage from one end to the other involves the gain of oxygen as well as metal by the system as a whole in a series of discrete steps.

Not only are these intermediate compounds of considerable intrinsic interest, but some have potentially useful properties. We have examined the crystal structures of the two non-stoichiometric vanadium oxides which, like the better known tungsten 'bronzes' are chemically inert semiconductors. The first of these, $\beta Na_{2-x}V_6O_{16}$ was reported earlier (Wadsley, 1955*b*). In this paper the structure determination of γ $Li_{1+x}V_3O_8$ is described, and the two compounds are discussed in terms of the system V_2O_5–RVO_3.

2. Experimental

It was initially intended to examine the γNa phase, but although readily prepared from a melt of $NaVO_3$ and V_2O_5 of the appropriate proportions it formed fibrous crystals unsuited to accurate measurements. The γLi crystals on the other hand were fairly robust bluish-black needles giving good diffraction patterns. Flood *et al.* (1943, 1946*b*) showed that these two compounds were not isomorphous, but the cell dimensions were of the same order of magnitude (Table 6). The

Table 1. *Intermediate ternary oxides in binary phase systems of* V, Ti, *and* Nb *oxides*

Fractional formulae (approximate)			Whole-number formulae (approximate)		
	$NbO_{2\cdot5}$	TiO_2		Nb_6O_{15}	Ti_8O_{16}
$VO_{2\cdot5}$	$K_{0\cdot14}NbO_{2\cdot5}$	†Ba_wTiO_2	V_6O_{15}	$K_{0\cdot8}Nb_6O_{15}$	$Ba\ Ti_8O_{16}$
*β-phase $R_xVO_{2\cdot5}$	$K_{0\cdot33}NbO_{2\cdot67}$	$Ba_{0\cdot25}TiO_{2\cdot25}$	$R\ V_6O_{15}$	$K_2Nb_6O_{16}$	$Ba_2Ti_8O_{18}$
*γ-phase $R_yVO_{2\cdot67}$	$K_{0\cdot67}NbO_{2\cdot83}$	$Ba_{0\cdot33}TiO_{2\cdot33}$	$R_2V_6O_{16}$	$K_4Nb_6O_{17}$	$Ba_{2\cdot67}Ti_8O_{19}$
R_zVO_3	$KNbO_3$	$Ba_{0\cdot5}\ TiO_{2\cdot5}$	$R_6V_6O_{18}$	$K_6Nb_6O_{18}$	$Ba_4Ti_8O_{20}$
		$BaTiO_3$			$Ba_8Ti_8O_{24}$

* R = Na, Li, Ag. $0{\cdot}08 \le x \le 0{\cdot}17$; $y = 0{\cdot}33$ (Na, Ag); $0{\cdot}33 \le y \le 0{\cdot}50$ (Li only); $0{\cdot}9 \le z \le 1$ (Na only).
† $0 < w \le 0{\cdot}17$ (Dryden & Wadsley, 1957).

principal structural features were therefore most probably alike. The differences between them could possibly be related to the fact that only the γLi compound had an extended composition range; further comments on this will be made in § 5.

The crystals used in this investigation were formed by slowly cooling a melt of Li_2CO_3 and V_2O_5 in the molar ratio 1:2. The lattice constants, measured from rotation and Weissenberg photographs and listed in Table 2, agree with those of Flood *et al.* (1946*b*) after interchanging their *a* and *c*, and making their β obtuse to conform with convention. Intensity data for the *h0l*, *h1l* and *h2l* terms were recorded by multiple-film Weissenberg patterns using Mo/Zr radiation. Numerical values of the diffraction spots were obtained by comparison with a film strip calibrated by timed exposures of a representative reflexion. The intensities were corrected for Lorentz and polarization factors and subsequently placed on an absolute scale by comparison with structure factors calculated for half the unit cell contents, the asymmetrical unit. The scattering curves prepared by Qurashi (1954) for vanadium, and for lithium and oxygen by Viervoll & Ögrim (1949) were modified by an isotropic temperature factor $B = 0{\cdot}6$ Å^2 obtained experimentally for both *h0l* and *h1l* terms.

Table 2. *Crystallographic data*

System: monoclinic
Unit-cell dimensions:
$a = 6{\cdot}68 \pm 0{\cdot}02$, $b = 3{\cdot}60 \pm 0{\cdot}01$,
$c = 12{\cdot}03 \pm 0{\cdot}02$ Å, $\beta = 107° 50'$
Absent spectra: $0k0 \neq 2n$
Space group: $P2_1$ or $P2_1/m$
Density (obs.): $3{\cdot}45 \pm 0{\cdot}05$ g.cm.$^{-3}$
Density (calc.*): $3{\cdot}49$ g.cm.$^{-3}$

* For $Li_3V_6O_{16}$.

3. Derivation of structure

Close visual inspection of the *h0l* and *h2l* intensities revealed that they were virtually identical in distribution, suggesting that all atoms were situated on or very near the levels $y = \pm\frac{1}{4}b$. In view of the shortness of the *y* axis, the space-group ambiguity then became one of deciding between the twofold positions 2(*e*) $(x, \frac{1}{4}, z;\ \bar{x}, \frac{3}{4}, \bar{z})$ of the centrosymmetric $P2_1/m$ and 2(*a*) $(x, y, z;\ \bar{x}, \frac{1}{2}+y, \bar{z})$ of $P2_1$ where $y \simeq \frac{1}{4}b$. This was deferred until after solution and refinement of the *h0l* projection, which is centred in both space groups.

The Patterson function $P(u, 0, w)$ shown in Fig. 1 was computed from F_o^2 terms sharpened and modified by the method of Lipson & Cochran (1953, p. 172). Solution of the map for the positions of the vanadiums requires two sets of three atoms related by a symmetry centre which will produce fifteen V–V vector peaks some of which must be expected to overlap. These will be much stronger than the V–O and O–O vectors unless many arbitrarily coincide.

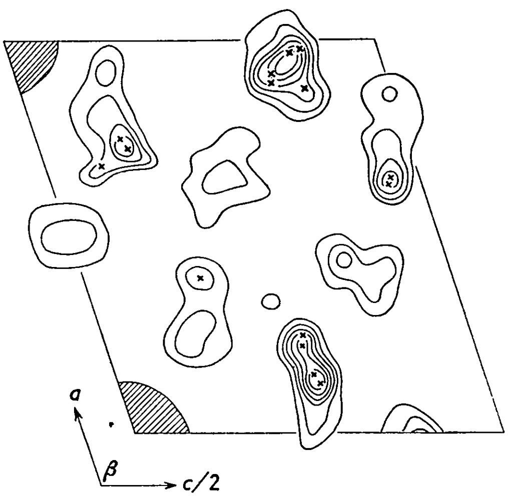

Fig. 1. Projection of the Patterson function $P(u, w)$ of which only the positive contours are drawn. The origin peak is hatched. Crosses are the vectors of points representing the vanadium atoms in the model which was subsequently refined.

By simple trial-and-error procedures a set of points was found which gave the vectors indicated by crosses in Fig. 1. Assuming this model to correspond with the positions of vanadium, oxygen could then be placed in octahedral or near-octahedral groups around them, giving a structure which was not at variance with the remaining detail in the map.

Atomic parameters were refined by successive structure-factor calculations and electron-density projections using the *h0l* terms, until there were no further changes of sign. A small persistent peak of about 4 e.Å^{-2} appearing in a twofold position at all stages of refinement probably represented a lithium atom (Fig. 2). An $F_o - F_{O+V}$ projection was next prepared, from which small corrections to the oxygen and

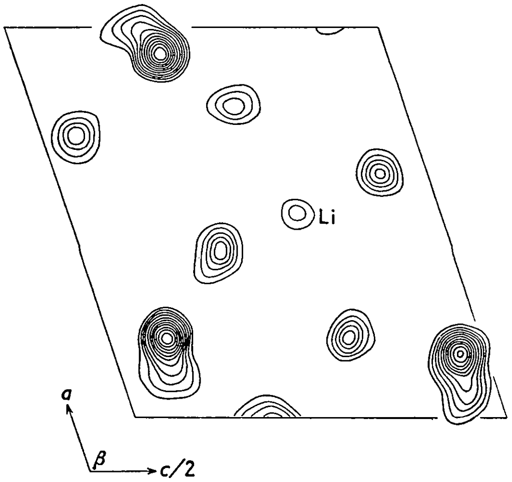

Fig. 2. Projection of the electron density $\varrho(x, z)$. The first four contours are at intervals of 2 e.Å^{-2}, the remainder at 4 e.Å^{-2}. The zero contour is omitted.

vanadium parameters were derived by Cochran's method (1951). The discrepancy factor for $h0l$ in the final set of structure factors was 0·14 without lithium and 0·12 with the lithium, given the parameters found in the $F_o - F_c$ synthesis, confirming its position.

In an attempt to resolve the space-group ambiguity already referred to, the atomic parameters x and z for each atom were combined with the constant $y = \frac{1}{4}b$ required by $P2_1/m$ in a set of hll structure-factor calculations. A discrepancy factor of 0·12 was obtained. The excellence of this agreement, whilst not unexpected in view of the close visual similarity of the $h0l$ and $h2l$ intensities mentioned earlier, does indicate that the structure, for the purposes of this investigation at any rate, can be adequately described in terms of $P2_1/m$. Any degradation to the lower space group $P2_1$, if present at all, will be of such a small order as to affect bond lengths by only a few per cent, but the structural features discussed here will remain unaltered.

Table 3. *Fractional atomic parameters for* $Li_{1+x}V_3O_8$

All atoms in positions $2(e)$ $(x, \frac{1}{4}, z; \bar{x}, \frac{3}{4}, \bar{z})$ for space group $P2_1/m$

Atom	x/a	y/b	z/c
Li	0·494	$\frac{1}{4}$	0·690
V_1	$0{\cdot}839_2$	$\frac{1}{4}$	$0{\cdot}536_0$
V_2	$0{\cdot}204_2$	$\frac{1}{4}$	$0{\cdot}077_8$
V_3	$0{\cdot}069_4$	$\frac{1}{4}$	$0{\cdot}802_2$
O_1	0·075	$\frac{1}{4}$	0·458
O_2	0·879	$\frac{1}{4}$	0·928
O_3	0·796	$\frac{1}{4}$	0·675
O_4	0·422	$\frac{1}{4}$	0·188
O_5	0·616	$\frac{1}{4}$	0·438
O_6	0·286	$\frac{1}{4}$	0·956
O_7	0·225	$\frac{1}{4}$	0·725
O_8	0·992	$\frac{1}{4}$	0·175

The atomic parameters are given in Table 3, the list of observed and calculated structure factors in Table 4, and the interatomic distances in Table 5. The standard errors for the V–O and O–O distances are ±0·03 and ±0·04 Å respectively. Since the lithium atom was not included in the F_c values used for the $F_o - F_c$ synthesis, the accuracy of its position is not high. The Li–O distances may therefore be in error by perhaps ±0·06 Å.

4. Description

The structure of $Li_{1+x}V_3O_8$ is illustrated by Fig. 3, in which it can be seen that the vanadium coordination is of two kinds. V_2 and V_3 are each bonded to six oxygens at the corners of a distorted octahedron. Two octahedra have an edge in common in the same reflexion plane, and are joined by further edge sharing to other double units of the same kind above and below to form a zigzag ribbon extending along y (Fig. 4(a)).

The metals are displaced from the octahedral centres so as to oppose one another, and the V–O bonds as a consequence vary from 1·59 Å to 2·36 Å in length. Disturbances of this kind are doubtless due to mutual repulsion usually present in closely bonded structures formed by metal ions of high valency. Additional polyhedra of a similar kind having edges or corners in common will also contribute to this effect, so that, even amongst closely related structures, differences in bond length cannot be directly compared as they will depend upon the way in which the units are grouped together.

V_1 has only five near oxygen neighbours grouped at the corners of a distorted trigonal bipyramid, a polyhedron formed by discarding one of the four oxygens

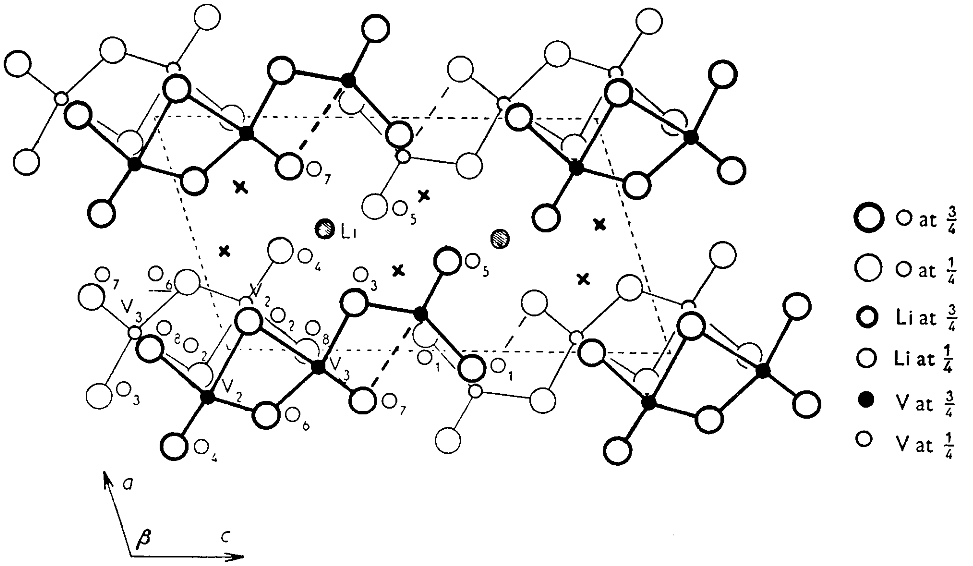

Fig. 3. Structure of $\gamma Li_{1+x}V_3O_8$ projected on to (010); the unit cell is dotted. No bonds to lithium are drawn. The dashed lines represent the long bonds from V_1 to O_7 which alter the grouping from octahedral to trigonal bipyramidal (see Fig. 4(b)). The crosses are the tetrahedral sites into some of which excess lithium could fit.

Table 4. *Observed and calculated structure factors h0l and h1l*

hkℓ	F_o	F_c
001	7.9	10.4
002	20.6	20.7
003	44.8	-48.7
004	17.5	17.1
005	7.7	-9.9
006	<5.5	-2.2
007	25.7	26.7
008	54.8	-48.6
009	<5.7	-4.2
00,10	<6.1	3.7
00,11	28.5	29.5
00,12	<7.2	-4.9
00,13	7.3	7.3
00,14	<7.7	-7.0
00,15	22.0	22.7
00,16	<8.9	2.6
00,17	<8.9	-0.3
00,18	13.0	-15.4
10,18	19.8	-19.9
10,17	<9.0	-3.5
10,16	13.7	-13.4
10,15	<8.3	10.9
10,14	11.1	-14.8
10,13	<7.5	-3.1
10,12	8.7	10.7
10,11	23.3	22.2
10,10	22.0	23.3
109	<6.0	3.3
108	15.4	12.9
107	26.8	-27.7
106	20.8	23.0
105	14.0	-13.0
104	5.7	-5.6
103	71.4	-77.6
102	<3.2	-2.4
101	5.1	-3.0
10$\underline{0}$	52.9	69.4
10$\underline{1}$	11.9	16.3
10$\underline{2}$	6.6	8.7
10$\underline{3}$	12.3	13.3
10$\underline{4}$	25.9	25.8
10$\underline{5}$	18.6	20.6
10$\underline{6}$	13.3	-15.4
10$\underline{7}$	10.8	-10.0
10$\underline{8}$	58.3	-50.8
10$\underline{9}$	<5.6	-0.5
10,$\underline{10}$	16.5	-16.5
10,$\underline{11}$	6.4	6.7
10,$\underline{12}$	23.5	-23.8
10,$\underline{13}$	14.3	14.1
10,$\underline{14}$	9.3	6.7
10,$\underline{15}$	23.3	21.6
10,16	11.8	10.4
20,14	14.3	-14.4
20,13	13.6	-15.6
20,12	7.5	8.4
20,11	11.2	11.3
20,10	18.4	21.4

hkℓ	F_o	F_o
209	12.7	-10.2
208	16.6	14.3
207	<5.7	-3.2
206	47.9	48.4
205	<4.9	0.5
204	17.4	-16.3
203	76.2	-80.2
202	11.8	-15.9
201	<3.6	1.1
20$\underline{0}$	14.7	-17.9
20$\underline{1}$	10.6	-9.2
20$\underline{2}$	56.9	-57.8
20$\underline{3}$	30.0	31.8
20$\underline{4}$	20.6	18.2
20$\underline{5}$	84.6	84.6
20$\underline{6}$	9.1	-9.4
20$\underline{7}$	18.0	15.9
20$\underline{8}$	28.9	-22.0
20$\underline{9}$	21.7	17.3
20,$\underline{10}$	<6.0	3.4
20,$\underline{11}$	13.5	-12.6
20,$\underline{12}$	26.9	-25.6
20,$\underline{13}$	15.9	-14.1
20,$\underline{14}$	9.2	12.0
20,$\underline{15}$	<7.9	-1.5
20,16	16.5	13.2
30,13	20.2	-20.0
30,12	<7.9	2.4
30,11	<7.4	9.1
30,10	<7.1	5.0
309	24.0	22.5
308	6.4	-5.5
307	11.4	10.7
306	24.8	22.2
305	22.8	20.8
304	8.9	-11.6
303	<6.0	-2.5
302	9.2	-9.4
301	22.2	26.3
30$\underline{0}$	26.8	-28.4
30$\underline{1}$	4.1	-7.9
30$\underline{2}$	34.0	36.4
30$\underline{3}$	<4.3	-2.4
30$\underline{4}$	<4.3	0.3
30$\underline{5}$	51.6	46.4
30$\underline{6}$	<4.7	-0.5
30$\underline{7}$	12.6	6.7
30$\underline{8}$	21.6	20.4
30$\underline{9}$	22.1	22.4
30,$\underline{10}$	7.5	7.4
30,$\underline{11}$	9.1	13.8
30,$\underline{12}$	11.7	-4.2
30,$\underline{13}$	29.7	-22.4
30,$\underline{14}$	<7.9	2.7
30,$\underline{15}$	16.7	-19.9
30,$\underline{16}$	<8.2	-0.7
30,$\underline{17}$	14.9	-14.4
30,18	12.7	11.3

hkℓ	F_o	F_o
40,10	11.3	-9.4
409	22.4	-24.0
408	16.3	-17.8
407	17.0	19.0
406	12.7	10.5
405	<6.1	5.6
404	14.1	-14.4
403	26.5	-26.2
402	8.3	8.2
401	42.3	45.8
40$\underline{0}$	6.2	-3.3
40$\underline{1}$	14.3	-12.1
40$\underline{2}$	40.2	-36.3
40$\underline{3}$	<4.9	1.7
40$\underline{4}$	<4.9	4.0
40$\underline{5}$	15.2	-18.7
40$\underline{6}$	18.3	-15.4
40$\underline{7}$	27.3	-27.1
40$\underline{8}$	30.0	28.3
40$\underline{9}$	10.5	7.6
40,$\underline{10}$	24.3	21.6
40,$\underline{11}$	14.0	-13.8
40,$\underline{12}$	13.0	10.9
40,$\underline{13}$	7.3	-5.2
40,$\underline{14}$	16.1	9.6
40,$\underline{15}$	<7.9	-4.1
40,$\underline{16}$	13.1	-14.2
40,17	12.2	-12.8
50,12	10.8	10.6
50,11	15.9	17.8
50,10	13.0	-11.7
509	<7.9	1.2
508	14.1	-11.5
507	10.3	11.9
506	7.0	-6.8
505	6.7	-7.3
504	18.7	-15.8
503	<6.2	-0.3
502	10.5	11.5
501	16.0	12.1
50$\underline{0}$	16.7	17.2
50$\underline{1}$	13.7	-13.9
50$\underline{2}$	<5.6	2.4
50$\underline{3}$	<5.6	2.1
50$\underline{4}$	9.7	10.3
50$\underline{5}$	26.2	-25.8
50$\underline{6}$	10.8	-10.6
50$\underline{7}$	20.7	-20.6
50$\underline{8}$	<6.2	3.6
50$\underline{9}$	6.4	-4.0
50,$\underline{10}$	9.4	9.6
50,$\underline{11}$	<6.9	-4.3
50,$\underline{12}$	13.4	15.2
50,$\underline{13}$	16.7	10.6
50,14	15.6	13.9
607	7.9	8.1
606	<7.6	-1.6
605	15.6	-17.3

hkℓ	F_o	F_c
604	20.7	-18.3
603	6.9	-11.1
602	8.2	10.9
601	<6.4	-8.5
60$\underline{0}$	<6.4	-1.9
60$\underline{1}$	14.0	-15.5
60$\underline{2}$	23.3	-22.3
60$\underline{3}$	15.2	16.6
60$\underline{4}$	24.9	25.8
60$\underline{5}$	15.4	-17.0
60$\underline{6}$	<6.4	-0.2
60$\underline{7}$	<6.5	3.2
60$\underline{8}$	<6.7	2.1
60$\underline{9}$	<6.9	-1.1
60,$\underline{10}$	15.7	-14.4
60,$\underline{11}$	14.4	-6.6
60,$\underline{12}$	11.8	-11.1
60,$\underline{13}$	22.7	24.1
60,$\underline{14}$	<8.1	0.5
60,$\underline{15}$	<8.4	2.0
60,$\underline{16}$	<8.7	-8.5
60,17	11.0	10.4
708	12.4	15.1
707	<8.5	2.7
706	14.3	16.3
705	<8.0	-8.3
704	<7.8	4.7
703	10.8	-9.8
702	15.7	13.5
701	12.5	-10.1
70$\underline{0}$	11.2	-14.1
70$\underline{1}$	<7.0	-6.0
70$\underline{2}$	<6.9	3.8
70$\underline{3}$	6.9	9.7
70$\underline{4}$	<6.9	-0.6
70$\underline{5}$	10.9	12.6
70$\underline{6}$	<7.0	-1.5
70$\underline{7}$	17.2	17.3
70$\underline{8}$	<7.1	1.4
70$\underline{9}$	<7.3	2.1
70,$\underline{10}$	20.5	-17.1
70,$\underline{11}$	<7.7	-5.6
70,$\underline{12}$	9.7	-9.1
70,$\underline{13}$	<8.1	2.7
70,$\underline{14}$	11.8	-9.0
70,$\underline{15}$	<8.7	-9.1
70,$\underline{16}$	<8.9	-1.6
70,17	11.3	12.0
804	14.7	12.2
803	8.3	15.4
802	8.3	9.0
801	<7.9	-3.9
80$\underline{0}$	12.3	-17.7
80$\underline{1}$	<7.7	-1.4
80$\underline{2}$	<7.6	-5.0
80$\underline{3}$	<7.5	-0.9
80$\underline{4}$	18.5	-23.4
805	<7.5	0.2

hkℓ	F_o	F_o
80$\underline{6}$	7.6	-9.5
80$\underline{7}$	22.3	20.0
80$\underline{8}$	<7.8	7.9
80$\underline{9}$	9.6	7.2
80,$\underline{10}$	9.8	-11.8
80,$\underline{11}$	<8.2	5.2
80,$\underline{12}$	11.8	12.5
80,$\underline{13}$	<8.6	-1.3
80,$\underline{14}$	<8.8	-5.0
80,15	16.9	-18.1
011	22.7	23.2
012	19.4	-18.1
013	26.1	-26.7
014	6.0	-11.3
015	7.8	6.0
016	<5.7	-2.9
017	26.4	28.1
018	9.4	-5.9
019	14.2	-13.1
01,10	<7.6	-0.9
01,11	25.4	25.4
01,12	<8.5	-0.6
01,13	<9.1	1.1
01,14	21.2	-20.7
01,15	9.9	-8.0
11,14	24.8	-28.5
11,13	<9.4	2.9
11,12	<8.9	-0.2
11,11	8.4	7.7
11,10	18.8	-13.5
119	10.5	7.0
118	<7.0	-3.2
117	34.8	31.0
116	23.6	24.1
115	<5.6	2.8
114	23.2	-23.3
113	12.8	-14.5
112	17.4	19.8
111	26.8	-30.0
11$\underline{0}$	16.4	-18.0
11$\underline{1}$	79.5	-80.6
11$\underline{2}$	13.4	13.5
11$\underline{3}$	<4.0	2.4
11$\underline{4}$	31.0	36.2
11$\underline{5}$	12.3	-13.0
11$\underline{6}$	12.3	9.5
11$\underline{7}$	<6.1	4.0
11$\underline{8}$	22.3	20.1
11$\underline{9}$	27.1	24.9
11,$\underline{10}$	13.0	-11.0
11,$\underline{11}$	18.8	-18.4
11,$\underline{12}$	18.9	-15.5
11,13	14.6	14.2
21,17	25.8	21.9
21,16	<11.1	1.2
21,15	<10.7	10.7
21,14	11.8	-11.9
21,13	<9.7	4.5
21,12	<9.3	-4.5

hkℓ	F_o	F_c
21,11	<8.9	-6.6
21,10	16.7	-14.8
219	20.3	-21.3
218	<7.5	-1.9
217	9.1	-7.5
216	28.2	26.4
215	13.8	-13.8
214	16.3	17.6
213	7.6	6.7
212	37.2	40.5
211	13.9	-14.7
21$\underline{0}$	<4.4	-5.6
21$\underline{1}$	10.2	-15.8
21$\underline{2}$	9.7	-7.7
21$\underline{3}$	<4.5	-1.1
21$\underline{4}$	6.9	-7.3
21$\underline{5}$	10.5	-12.3
21$\underline{6}$	8.1	-7.4
21$\underline{7}$	22.8	21.9
21$\underline{8}$	19.8	17.8
21$\underline{9}$	26.2	26.8
21,$\underline{10}$	12.9	-9.9
21,$\underline{11}$	<7.8	0.5
21,$\underline{12}$	<8.3	-5.5
21,$\underline{13}$	15.2	15.4
21,$\underline{14}$	16.8	-15.8
21,$\underline{15}$	9.7	-10.3
21,16	20.5	-16.9
31,13	11.8	6.6
31,12	9.8	12.3
31,11	9.3	-7.0
31,10	10.2	-10.3
319	23.5	-25.5
318	8.1	9.0
317	15.3	-13.6
316	<7.3	0
315	29.3	-28.4
314	18.7	13.9
313	19.5	20.4
312	49.4	49.7
311	<5.5	4.9
31$\underline{0}$	<5.4	-2.2
31$\underline{1}$	17.7	19.8
31$\underline{2}$	<5.2	2.0
31$\underline{3}$	23.4	22.8
31$\underline{4}$	28.8	-30.0
31$\underline{5}$	24.2	-22.0
31$\underline{6}$	58.4	-58.4
31$\underline{7}$	27.7	21.3
31$\underline{8}$	<6.8	2.1
31$\underline{9}$	9.3	8.9
31,$\underline{10}$	19.0	-18.2
31,$\underline{11}$	<8.0	4.4
31,$\underline{12}$	9.7	13.1
31,$\underline{13}$	21.1	17.7
31,$\underline{14}$	12.0	11.1
31,$\underline{15}$	17.8	-16.4
31,$\underline{16}$	<10.2	-6.9
31,17	10.7	-9.3
41,14	11.2	12.6

hkℓ	F_o	F_c
41,13	<10.7	0.9
41,12	24.7	23.8
41,11	<9.9	-0.2
41,10	15.5	14.7
419	12.9	-10.4
418	19.5	17.5
417	8.3	-6.3
416	15.8	-19.1
415	19.6	-17.9
414	8.4	-12.6
413	<7.0	8.1
412	13.3	-9.9
411	19.5	21.1
41$\underline{0}$	17.4	-16.3
41$\underline{1}$	27.1	29.4
41$\underline{2}$	12.2	13.1
41$\underline{3}$	29.8	32.0
41$\underline{4}$	23.0	-22.1
41$\underline{5}$	8.3	-11.3
41$\underline{6}$	24.7	-22.4
41$\underline{7}$	<6.8	2.5
41$\underline{8}$	<7.2	-5.4
41$\underline{9}$	18.9	-20.9
41,$\underline{10}$	14.2	-14.7
41,$\underline{11}$	<8.2	5.2
41,$\underline{12}$	20.5	20.0
41,$\underline{13}$	13.8	9.5
41,14	22.5	20.8
51,10	10.2	8.3
519	13.9	19.1
518	16.3	14.9
517	<9.1	6.5
516	15.9	-22.7
515	9.7	-6.3
514	13.9	-13.9
513	7.8	7.1
512	30.8	-34.0
511	<7.4	-7.0
51$\underline{0}$	31.3	-34.7
51$\underline{1}$	26.2	21.6
51$\underline{2}$	20.0	22.0
51$\underline{3}$	34.7	35.9
51$\underline{4}$	11.5	-8.8
51$\underline{5}$	<7.1	0.4
51$\underline{6}$	19.5	21.2
51$\underline{7}$	12.1	10.9
51$\underline{8}$	13.9	14.3
51$\underline{9}$	28.9	-30.4
51,$\underline{10}$	13.4	-12.7
51,$\underline{11}$	25.7	-27.0
51,$\underline{12}$	17.9	19.4
51,13	<9.2	-3.8
51,14	9.7	8.7
51,15	15.3	-13.4
61,11	11.2	-8.7
61,10	<10.8	-7.7
619	16.0	19.4
618	<10.1	-2.1
617	16.0	18.6
616	<9.4	-7.5

hkℓ	F_o	F_c
615	15.8	16.6
614	<8.9	-4.6
613	17.6	15.8
612	19.8	-16.0
611	14.9	-19.8
61$\underline{0}$	18.9	-15.6
61$\underline{1}$	<7.8	-5.0
61$\underline{2}$	11.0	15.5
61$\underline{3}$	<7.8	-6.3
61$\underline{4}$	<7.8	6.2
61$\underline{5}$	<7.8	-4.5
61$\underline{6}$	32.0	38.6
61$\underline{7}$	<8.1	9.2
61$\underline{8}$	20.2	16.7
61$\underline{9}$	17.0	-13.9
61,$\underline{10}$	<8.7	-4.3
61,$\underline{11}$	14.7	-17.7
61,$\underline{12}$	<10.7	3.2
61,$\underline{13}$	14.7	-13.9
61,14	16.3	-17.9
715	18.2	17.3
714	13.7	18.9
713	18.9	19.7
712	<9.2	-0.2
711	16.5	-21.6
71$\underline{0}$	<8.9	2.0
71$\underline{1}$	<8.7	-2.1
71$\underline{2}$	<8.6	4.4
71$\underline{3}$	31.3	-35.4
71$\underline{4}$	<8.6	-7.8
71$\underline{5}$	20.4	-21.2
71$\underline{6}$	24.0	25.2
71$\underline{7}$	<8.8	8.6
71$\underline{8}$	15.4	13.5
71$\underline{9}$	9.1	-7.4
71,$\underline{10}$	<9.3	3.4
71,$\underline{11}$	11.0	14.5
71,$\underline{12}$	<9.8	5.3
71,$\underline{13}$	<10.1	4.2
71,14	24.7	-28.8
814	14.9	19.1
813	<10.3	-1.4
812	18.0	10.6
811	<9.9	-12.5
81$\underline{0}$	16.8	16.8
81$\underline{1}$	<9.5	2.1
81$\underline{2}$	<9.5	3.8
81$\underline{3}$	18.8	-22.1
81$\underline{4}$	9.4	-13.0
81$\underline{5}$	12.0	-10.5
81$\underline{6}$	<9.5	-4.6
81$\underline{7}$	<9.5	8.1
81$\underline{8}$	<9.6	-5.2
81$\underline{9}$	<9.7	2.1
81,$\underline{10}$	<9.9	3.6
81,11	24.8	27.5

Table 5. *Interatomic distances*

	No.	Length (Å)		No.	Length (Å)		No.	Length (Å)		No.	Length (Å)
V_1–O_5	1	1·60	V_2–O_4	1	1·64	V_3–O_7	1	1·59	Li–O_7	1	1·99
V_1–O_3	1	1·78	V_2–O_6	1	1·72	V_3–O_6	1	1·96	Li–O_3	1	2·08
V_1–O_1	2	1·88	V_2–O_2	2	1·88	V_3–O_8	2	1·88	Li–O_4	2	2·28
V_1–O_1	1	2·06	V_2–O_2	1	2·36	V_3–O_3	1	1·99	Li–O_5	2	2·33
V_1–O_7*	1	2·86	V_2–O_8	1	2·10	V_3–O_2	1	2·26	O_4–O_5	2	2·89
O_3–O_5	1	2·74	O_6–O_4	1	2·66	O_6–O_7	1	2·68	O_4–O_7	2	2·90
O_5–O_1	1	3·00	O_4–O_8	1	2·83	O_7–O_3	1	2·74	O_5–O_7	2	3·07
O_5–O_1	2	2·74	O_4–O_2	2	2·74	O_8–O_7	2	2·80	O_4–O_3	2	3·10
O_3–O_1	2	2·72	O_2–O_2	2	2·68	O_6–O_8	2	2·71	O_3–O_5	2	3·22
O_1–O_1	2	2·42	O_6–O_2	2	2·71	O_8–O_2	2	2·48	O_5–O_5	1	3·60
O_7–O_3*	1	2·74	O_6–O_2	1	2·64	O_8–O_3	2	2·64	O_4–O_4	1	3·60
O_7–O_1*	2	3·07	O_2–O_8	2	2·48	O_2–O_6	1	2·64			
O_7–O_1*	1	3·05	O_2–O_8	1	2·84	O_2–O_3	1	2·92			

* These distances, included for comparison, are not part of the fivefold coordination of V_1.
The braces group together distances between atoms related by the centres of symmetry.

in the equatorial plane of an octahedron (Fig. 4(*b*)). The long bond in the distorted octahedra of V_2 and V_3 is here lengthened from about 2·3 to 2·86 Å owing to the rearrangement induced by the interstitial lithium atoms. These bipyramids, found also in the structures of V_2O_5 (Byström, Wilhelmi & Brotzen, 1950), $KVO_3.H_2O$ (Christ, Clark & Evans, 1954) and $\beta Na_{2-x}V_6O_{15}$ (Wadsley, 1955*b*) are associated by edge sharing to form zigzag strings extending along the *y* direction of the unit cell.

The two structural units, i.e. the strings of bipyramids and the double octahedral ribbons, are linked together by having corners in common (the atoms O_3). The result is a puckered sheet for which (100) is the medial plane (Figs. 3 and 5(*c*)). The stacking along the *x* axis results in two types of interstitial site being formed between the oxygen atoms of adjacent sheets.

The first of these is a twofold octahedral site formed by six oxygens of which only O_3 is linked to more than one vanadium atom. This is occupied by lithium, the six Li–O bonds having an average length of 2·25 Å. The lower limit of composition found for this phase by Flood *et al.* (1946*b*) corresponds to the formula LiV_3O_8, whence the sites are presumably completely filled. The Li octahedra are joined by sharing edges in the planes parallel to (010) and the linear strings so formed extend along *y*.

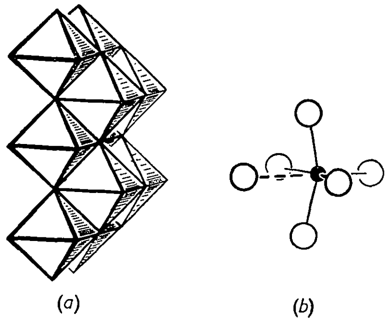

Fig. 4. (*a*) Zigzag ribbon of doubled octahedra (idealized) seen in clinographic projection. (*b*) Distortion of octahedral to bipyramidal configuration due to lengthening of one V–O bond (dashed line). (Drawing not to scale.)

The other kind of site is tetrahedral. There are six of these in every unit cell, marked by crosses in Fig. 3. There is no acceptable evidence, however, in the electron-density or difference projections which proves the presence of scattering matter at these points. The crystals used in this study may have had the lower limit of composition, in which case no tetrahedral lithium could be expected. If they were in fact $Li_{1+x}V_3O_8$, then even at the upper limit only one Li atom is present in each unit cell. In this case the additional atom is randomly distributed in different unit cells amongst the six available sites, and the diffraction data will provide evidence for one-sixth of an atom at any one of them, provided each is given equal weight. Such a small concentration of electron density is quite undetectable by our measurements. The important point, however, is that lithium is capable of both tetrahedral and octahedral coordination in a structure of a similar kind (Hilmer & Dornberger-Schiff, 1956).

5. The sodium and lithium γ phases

In Table 6 the unit-cell dimensions of the sodium and lithium compounds are compared. The principal difference between them is the marked increase in *a*. The silver phase is not included, as Flood *et al.* (1946*a*) state that crystals were difficult to prepare, and we have made no attempt to duplicate their work.

Table 6. *Unit-cell dimensions of* γNa *and* Li *compounds*

	Na*	Li
a	7·38 Å	6·68 Å
b	3·62	3·60
c	12·12	12·03
β	106° 36′	107° 50′

* *a* and *c* interchanged from Flood & Sörum's data (1943); β obtuse.

In view of the considerable variations of interatomic distance which occur in the vanadium oxides, it is clearly impossible to discuss them in terms of the packing together of spherical scattering units each with a

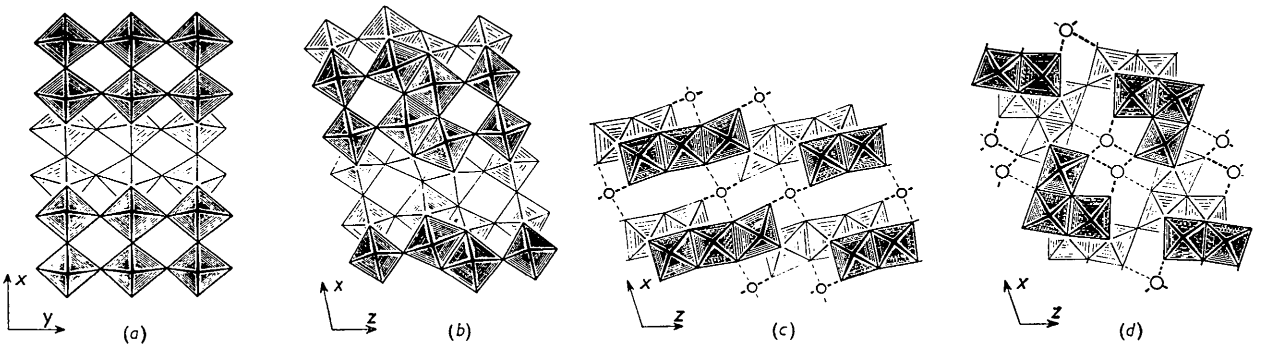

Fig. 5. (a) The structure of V_2O_5 represented as distorted octahedra seen in projection down the corners. (b) V_6O_{13} drawn to the same conditions. (c) Structure of $\gamma Li_{1+x}V_3O_8$ in projection on to (010). The bipyramids are drawn as octahedra and the lithium as circles. (d) $\beta Na_{2-x}V_6O_{15}$. The sodiums are drawn as circles.

definite radius. To a first approximation, however, the average O–O distance will give a value of 1·57 Å for the 'radius' of oxygen in the Li octahedron. The size of the lithium ion by the same token is 0·65 Å. From the published data for $\beta Na_{2-x}V_6O_{15}$ (Wadsley, 1955*b*), in which the sodium has seven oxygen atoms as near neighbours, the 'radii' for Na and O are 0·97 Å and 1·60 Å respectively. The values for the metal ions are in good agreement with Ahrens' recent tabulation (1952).

The lattice expansion of the γNa phase, reflected in the length *a*, is undoubtedly due to the increase in size of the interstitial alkali metal ion. Whilst the basic framework would be basically unchanged, the distances between sheets of polyhedra must be increased to provide more room for the sodium atom. Some rough calculations have shown that a satisfactory octahedral site can be provided by this means, and any major atomic shifts will be made principally to the atom O_5 which, perhaps significantly, is part of the trigonal bipyramidal group.

The γNa compound has a limited composition range. This may well be due to the reluctance of Na to occupy the tetrahedral positions presumed to be partly filled in $\gamma Li_{1+x}V_3O_8$. The lack of additional ions which would assist in binding together the structural sheets may also result in the enhanced fibrous property.

6. The non-stoichiometric vanadium oxides

Although the system vanadium–oxygen has been surveyed over its entire range (Andersson, 1954), a relatively complete structural picture is available only within the limits VO_2–V_2O_5. In order to facilitate the subsequent discussion, the distorted trigonal bipyramids are regarded as distorted octahedra and are drawn as such in Fig. 5.

Each octahedron of V_6O_{15} (Fig. 5(*a*)) is joined above and below to a similar one by edge sharing to become members or units of a zigzag string perpendicular to the plane of the paper. These link together by corner sharing to form sheets, which are again joined in a three-dimensional lattice by having additional corners common to adjacent sheets. From Fig. 5(*a*) it may be seen that V_6O_{15} is related to WO_3, the heavier and lighter shaded areas representing individual fragments of the WO_3-type structure which are then joined by edges rather than corners. Consequently there are no eightfold interstitial sites in V_2O_5 which would make the β and γ vanadium compounds the exact analogues of the sodium and lithium tungsten bronzes.

If each alternate sheet in V_6O_{15} is replaced by another formed by *doubled* zigzag ribbons and sharing corners (as in Fig. 5(*b*)) the structure of V_6O_{13} is formed (Aebi, 1948). The doubling is due to the 'shearing' of two V_6O_{15}-type sheets, and since these have more edges in common, the net result is the loss of oxygen. This shearing effect is similar to that found in the homologous series $(Mo, W)_nO_{3n-1}$ by Magnéli (1953), and although it is by no means difficult to predict further oxides with plausible structures forming a series $V_{2n}O_{5n-2}$, V_6O_{13} appears to be the only known member (Andersson, 1954).

The γ and β phases are illustrated in Fig. 5(*c*) and (*d*), showing that they are closely related in structure to V_6O_{13}. Each consists of identical double and single zigzag octahedral strings arranged so as to provide room in two different ways for the alkali metals. In the β phase these are arranged in zigzag rows each with seven oxygen neighbours, the rows themselves being disordered throughout the structure (Wadsley, 1955*b*). Tetrahedral and octahedral sites are provided by the γ compound, as we have seen.

In order to provide space for these ions the framework of vanadium polyhedra expands. The closely bonded sheets characteristic of V_2O_5 adopt a tunnel arrangement by a combined process of shear and segregation of structural units. As the concentration of alkali metal increases, this changes to an assemblage of puckered sheets with no oxygen atoms in common. This has its effect in the gain of oxygen by the system as a whole.

The crystal structure of $Na_{6-x}V_6O_{18}(Na_{1-\delta}VO_3)$ has not yet been evaluated in detail (Sörum, 1943); whether it is that of diopside or one closely related to it needs still to be determined. There is little doubt, however, that the coordination of vanadium is tetrahedral, and chains of the formula $(VO_3)_n^{n-}$ are formed by sharing corners. The transition from the γ phase appears to result from the disruption of the closely coordinated sheets into these isolated units which will require additional alkali metal ions, not necessarily in a fixed proportion, to link together in the diopside grouping.

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A Unified Algebraic Approach to the Phase Problem. I. Space Group $P\bar{1}$

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A unified algebraic approach to the phase problem is described, which, under certain limitations, yields explicit formulas for determining the sign of any structure factor. Some of these formulas correspond to those previously derived and throw additional light on them, while others provide a useful addendum to these relations. The unified algebraic approach provides, in general, a basis for deriving phase-determining relations in all the space groups.

1. Introduction

Probability methods utilizing the concept of the joint distribution yield formulas which lead to procedures for phase determination in the centrosymmetric space groups (Hauptman & Karle, 1953 (Monograph I)), and in those non-centrosymmetric space groups (Karle & Hauptman, 1956) which are characterized by having all components of the seminvariant modulus (Hauptman & Karle, 1956) equal to two. For certain structure seminvariants these methods also prove useful in some of the remaining space groups. However we have been unable, by means of the joint probability distribution, to obtain formulas for the remaining structure seminvariants. We have therefore found it necessary to attack the problem from a different point of view which complements the probability approach and throws additional light on the probability formulas already obtained.

The present algebraic approach is based on a formula for the product of an arbitrary number of suitably normalized structure factors. An algebraic approach has been foreshadowed by Hughes (1953) and by Bullough & Cruickshank (1955) in their derivations of certain phase-determining formulas. Our present approach is a unified one in that it can be applied to all the space groups, non-centrosymmetric as well as centrosymmetric. In a forthcoming publication (Karle