extent, and may well account for the similarity in the c_0 parameter.

The Pb ion apparently plays an important role in maintaining strong linkages between NbO_6 octahedra in the (001) planes. Removal of more than a small amount of Pb from the lattice seems to result in a breakdown of these linkages, and of the co-operative ionic displacements associated with ferroelectricity.

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The Crystal Structure of Nolanite

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Nolanite is hexagonal, probably $P6_3mc$, with $a = 5{\cdot}85$, $c = 9{\cdot}29$ Å, and formula approximately $Fe^{+2}_{2\cdot5}V^{+3}_{1\cdot5}V^{+4}_{6}O_{16}$. The structure, which was refined by *c*- and *a*-axis projections, consists of a close-packed hexagonal (*ABAC*) framework of 16 oxygen anions, with metal ions in some of the interstices. The tetravalent vanadium ions occupy a 6-fold position of octahedral coordination, while the iron and trivalent vanadium ions are distributed among two 2-fold positions (on the 3-fold axes), one of octahedral and one of tetrahedral coordination. Results obtained with different radiations suggest that trivalent vanadium has a strong, but not exclusive, preference for tetrahedral coordination.

Introduction

The recently-named iron–vanadium mineral Nolanite has been discussed by Barnes & Qurashi (1952) and by Robinson, Evans, Schaller & Fahey (1957). Their crystallographic conclusions may be summarized as follows:

Nolanite is hexagonal, $P\bar{6}2c$, $P6_3mc$, or $P6_3/mmc$

$$a = 5{\cdot}854\pm0{\cdot}005,\quad c = 9{\cdot}295\pm0{\cdot}010\ \text{Å}\ .$$

The structure suggested by the unit cell is a framework of 16 close-packed oxygen anions, with cations in some of the interstices.

Two chemical analyses are quoted, one for a reasonably large sample of impure massive material, and the other for 25 mg. of hand-picked crystalline material. Assuming 16 anions per unit cell, the chemical formulae suggested by these analyses are, respectively

$$Fe^{+2}_{2\cdot8}V^{+3}_{1\cdot5}V^{+4}_{5\cdot5}O_{16\cdot0}\quad\text{(analysis 1)}$$

and

$$Fe^{+2}_{2\cdot5}V^{+3}_{1\cdot7}V^{+4}_{5\cdot5}O_{16\cdot0}\quad\text{(analysis 3)}\ .$$

Because of recognized uncertainties in the analyses, no definite chemical formula was given.

It is suggested on crystal chemical grounds that there are 10 cations in the unit cell. Moreover, it is expected that iron may substitute for vanadium on one or more crystallographic sites, so that the Fe:V and V^{3+}:V^{4+} ratios need not be rational.

Assumptions for the present paper

In what follows, the chemical formula is assumed, for convenience, to be

$$(Fe, V)_4V_6O_{16}$$

where (Fe, V) is a composite ion such that $(Fe,V)_4 = 2{\cdot}5\ Fe^{2+}+1{\cdot}5\ V^{3+}$ and V is tetravalent vanadium. This formula was obtained, somewhat arbitrarily, by averaging the two given in the preceding section, and rounding out the quantities to integral values. It will be shown that the assumption of this formula leads to a plausible structure which is consistent with the X-ray data. Nevertheless, it must be emphasized that the formula can be only approximately true, and that minor departures from it would not be detected by the methods employed.

Experimental details

The material available for X-ray examination consisted of irregular platelets normal to *c*. Satisfactory crystals were scarce, but two were finally selected for the collection of intensity data. One of these, approximately $0{\cdot}09 \times 0{\cdot}09 \times 0{\cdot}015$ mm., was used for recording $(h0.l)$ reflexions on Weissenberg photographs, with rotation about the *a* axis. Absorption corrections were applied following the method of Howells (1950), and assuming the crystal to be a prism of cross-section $0{\cdot}09 \times 0{\cdot}015$ mm. The absorption coefficients used were 97 cm.^{-1} for molybdenum, and 327 cm.^{-1} for chromium. For the latter radiation, some of the corrections were found to be large, and critically dependent on the angles between the plane of the platelet and the incident and emergent beams. The reflexions involved were omitted from the structure analysis.

A second crystal, of mean 'diameter' 0·2 mm. and 0·023 mm. thick, was used for recording $(hk.0)$ and a few of the more intense $(hk.l)$ reflexions. The latter were recorded on levels normal to *c*, for values of l up to 8. For this crystal the *c* axis was always used as the rotation or precession axis, with the result that, for any photograph, the angles between the plane of the platelet and the incident and emergent beams were constant. In order to reduce absorption errors, the recording techniques were so devised that these angles were never less than 10°; for this purpose it was necessary to record some of the upper levels (corresponding to low values of l) on general-inclination Weissenberg photographs. Absorption corrections were deemed to be unnecessary for data recorded with this crystal.

A summary of the recording techniques and the radiations used to obtain three classes of reflexion is given in Table 1. The more intense reflexions in the $(hk.0)$ and $(h0.l)$ zones were recorded by integrating techniques, and photometered. The others were recorded without integration, and estimated visually.

Table 1. *Summary of recording techniques*

Radiation	$(hk.0)$*	$(h0.l)$*	$(hk.l)$
Mo	*A*, *B*	*C*	*D*, *E*
Cu	*A*		
Co	*A*, *B*		
Fe	*A*		
Cr	*A*, *B*	*C*	
Number of reflexions observed, and number theoretically observable for group (molybdenum only)	36, 74	121, 318	39, 890 (Excluding $(hk.0)$ and $(h0.l)$)

* More intense reflexions integrated:

A Precession photograph.
B Anti-equi-inclination Weissenberg.
C Normal-beam Weissenberg.
D Equi-inclination Weissenberg.
E General-inclination Weissenberg.

The intensity data for the $(hk.0)$ zone are believed to be the most accurate. The data for the $(h0.l)$ zone, because of absorption errors perhaps not precisely corrected, are probably somewhat less reliable. The few general $(hk.l)$ data depend entirely on visual estimates, and are also probably in error because of difficulties in correlating the different levels; they are probably the least reliable of all the intensity data.

Determination of the structure

The main features of the structure were established with the aid of the molybdenum data alone, and data obtained with other radiations were used to investigate certain secondary characteristics.

For a structure based on a close-packed hexagonal framework of 16 anions, all interionic vectors should terminate on or near the lines (in vector space) $(00.z)$, $(\frac{1}{2}0.z)$, $(\frac{1}{3}\frac{\bar{1}}{3}.z)$, $(\frac{1}{6}\frac{\bar{1}}{6}.z)$. A three-dimensional Patterson synthesis, rapidly computed for these lines only, suggested a plausible structure (in the non-centrosymmetrical space group $P6_3mc$) which was subsequently refined.

The close-packing of the anions in this structure is double-hexagonal (*ABAC*). The 10 cations occupy one 6-fold position of octahedral coordination, and two 2-fold positions (on the 3-fold axes), one of octahedral and one of tetrahedral coordination.

Refinement of the structure

The structure was refined with the aid of *c*- and *a*-axis projections. In order to minimize errors due to the omission of the many unobserved reflexions, the atomic positions were estimated at each stage of refinement by comparison of F_o and F_c syntheses. Much of the refinement was achieved by computing these syntheses for a few lines only.

The atomic scattering-factor curves used in the structure-factor calculations are those listed for neutral atoms in the *Internationale Tabellen* (1935). The curves for iron and vanadium are modified, for each of the several radiations used, by the addition of $\Delta f'$, the real part of the dispersion correction. The values of $\Delta f'$ for molybdenum, copper, and chromium radiation were taken from the table published by Dauben & Templeton (1955). Values for iron and cobalt radiation were obtained by interpolation of this table. A temperature factor $B = 0{\cdot}58$ Å^2 was estimated during the refinement of the *c*-axis projection; this value was used for all subsequent structure-factor calculations.

It was initially assumed that the 6 vanadium ions (V^{4+}) occupied the 6-fold position, and that the 4 composite (Fe, V) ions occupied the two 2-fold sites. This seems a reasonable assumption; that it is not inconsistent with the X-ray data is shown by the agreement in Table 2 between the observed and the

Table 2. *Observed and calculated structure amplitudes for* (*hk*.0) *zone, molybdenum radiation*

hk.l	F_o	F_c	*hk.l*	F_o	F_c
10·0	19·9	−24·2	15·0	7·4	− 7·8
20·0	66·5	−65·3	17·0	15·5	15·5
30·0	29·8	31·0	1,10,0	9·3	9·3
40·0	46·3	−48·1	23·0	8·2	−12·6
50·0	12·4	−11·6	24·0	36·5	−40·0
60·0	95·5	98·7	25·0	15·9	16·6
80·0	24·2	−24·4	26·0	25·6	−28·7
10,0,0	17·8	−17·2	27·0	7·8	− 6·7
12,0,0	29·4	27·8	28·0	48·0	50·6
11·0	42·1	42·7	2,10,0	14·8	−14·2
22·0	188·2	175·2	2,12,0	11·3	− 9·6
33·0	22·6	23·4	34·0	12·2	− 8·8
44·0	81·4	80·9	36·0	13·3	12·8
55·0	16·6	13·7	39·0	11·5	9·6
66·0	40·4	39·5	46·0	22·2	−21·7
12·0	19·3	−16·6	48·0	16·2	−15·5
13·0	10·6	−12·4	4,10,0	24·2	24·7
14·0	24·1	24·6	68·0	12·6	−11·6

ultimate calculated values of $F_{(hk.0)}$. The agreement residual ($R = \Sigma|F_o - F_c|/\Sigma|F_o|$) is 5·9% for this zone. Values of $F_{(hk.0)}$ corresponding to unobserved reflexions were calculated, but are not tabulated because none of them exceeds the estimated minimum observable value.

The agreement, although good, does not establish the proposed structure beyond doubt. The difference in the effective scattering powers of the vanadium and of the composite (Fe,V) ions is, for molybdenum, only about 2 electrons, and the agreement residual is not very sensitive to changes in their distribution. Stronger evidence is provided by the corresponding agreement (in Table 3, column *b*) for chromium radiation. The difference in effective scattering power of the two cations is approximately doubled, and it is found that any significant change in their distribution causes a rapid worsening of agreement. Data for some other radiations are given in adjacent columns of Table 3. It is perhaps well to point out that the variations in the observed values of $F_{(hk.0)}$ are real, and do not result from errors in scaling. This fact is illustrated in the final column of Table 3 in which observed and calculated values of the ratio

$$F_{(hk.0)}(\text{cobalt}) : F_{(hk.0)}(\text{chromium})$$

are compared. These two radiations were chosen as extreme examples; for cobalt the difference in effective scattering powers of the cations is very small, and for chromium it is a maximum.

The agreement throughout Table 3 is good. It is therefore surprising to find that for all radiations the calculated value of $|F_{(10\cdot0)}|$ exceeds the observed value by about 4·8, or more than 25%. However, for this reflexion, $\sin\theta/\lambda = 0\cdot099$, and the effect of ionization must be considered. Now, $|F_{(10\cdot0)}|$ can be calculated, with an error of less than 2%, as

$$2f_{(\text{2-fold cation})} - f_{(\text{6-fold cation})}\,.$$

The sense and magnitude of the discrepancy suggest that the 2-fold cations (that is, (Fe,V)) are much more strongly ionized than the others. No reasonable assumptions for the ionization of the anions have any

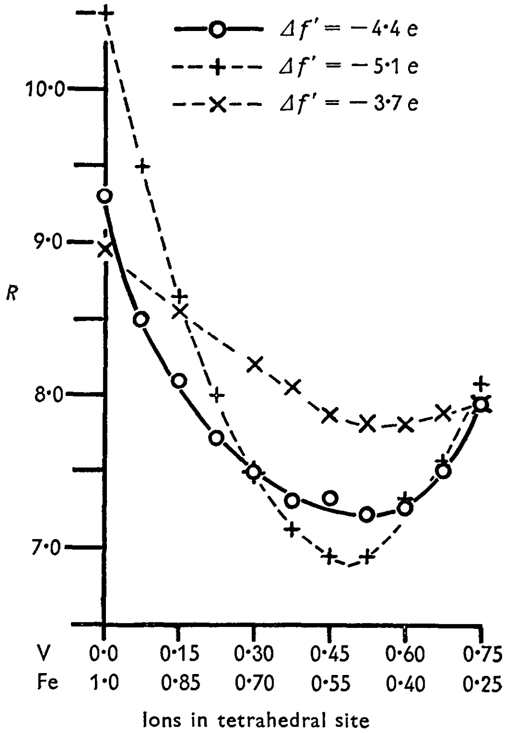

Fig. 1. Curves of agreement residual ((*h*0.*l*) reflexions) against structure type, assuming different values of $\Delta f'$ for vanadium, with Cr radiation.

Table 3. *Comparison of observed and calculated structure amplitudes for* (*hk*.0) *zone, with different radiations*

	a		*b*		*c*		*d*		*e*		*f*	
	Mo		Cr		Co		Cu		Fe		$F_{Co} : F_{Cr}$	
	$\Delta f' = +0\cdot3$ (V) $= +0\cdot4$ (Fe)		$\Delta f' = -4\cdot4$ (V) $= -1\cdot6$ (Fe)		$\Delta f' = -0\cdot4$ (V) $= -3\cdot6$ (Fe)		$\Delta f' = 0$ (V) $= -1\cdot1$ (Fe)		$\Delta f' = -0\cdot9$ (V) $= -2\cdot1$ (Fe)			
hk.l	F_o	F_c	F_o	F_c	F_o	F_c	F_o	F_c	F_o	F_c	Obs.	Calc.
10·0	19·9	−24·2	18·4	−23·1	15·3	−19·6	17·6	−22·5	16·2	−21·6	0·83	0·85
20·0	66·5	−65·3	44·4	−45·9	54·8	−58·2	62·0	−62·6	58·9	−58·2	1·23	1·27
30·0	29·8	31·0	28·8	28·7	23·6	22·1	26·6	27·6			0·82	0·77
40·0	46·3	−48·1	30·6	−29·8	41·0	−41·3					1·34	1·39
11·0	42·1	42·7	39·3	40·1	34·0	33·3	38·8	39·0	37·3	37·2	0·86	0·83
22·0	188·2	175·2	140·2	137·6	159·1	161·0					1·13	1·17
12·0	19·3	−16·6					16·6	−14·8				

Table 4. *Observed and calculated structure amplitudes for* ($h0.l$) *zone, chromium radiation*

$h0.l$	F_o	F_c	$h0.l$	F_o	F_c
00·2	49·6	37·2	20·2	62·0	53·9
(00·2)	—	(43·5)	20·3	53·2	48·7
00·4	36·5	34·8	20·4	48·2	47·0
00·6	52·5	60·6	20·5	95·5	97·9
10·1	10·2	10·3	20·6	28·6	29·6
10·2	42·2	41·8	20·7	17·1	11·4
10·3	60·0	60·3	30·2	50·0	52·2
10·4	10·2	5·9	40·1	30·6	33·0
10·5	24·6	28·1	40·2	28·0	26·2
10·7	35·7	37·0	40·3	24·2	27·2
20·1	52·3	55·3			

appreciable effect on the calculated value of $F_{(10\cdot0)}$.

In the c-axis projection, the two non-equivalent (Fe,V) ions overlap completely, and there is no possibility of distinguishing between them. In the a-axis projection, however, they are well resolved, and it is possible, at least in principle, to discover their individual compositions.

At a late stage in the refinement of this non-centrosymmetrical projection two extreme structures were proposed. In the first, the 2-fold tetrahedral site was assumed to be occupied exclusively by iron; in the second, the 2-fold octahedral site was assumed to be so occupied. In each structure, of course, the formula was satisfied by assuming the unspecified 2-fold site to be occupied by 0·75 V and 0·25 Fe. Structure factors corresponding to the ($h0.l$) data obtained with chromium radiation (for which the difference in the effective scattering powers of iron and vanadium is a maximum) were calculated for the extreme and for various intermediate structures. The agreement residual was calculated for each structure. ($F_{(00\cdot2)}$ was not considered, because its value might have been affected by ionization.) A curve of agreement residual against structure type (Fig. 1) shows that the best agreement is obtained for an intermediate structure in which the tetrahedral site is occupied by 0·53 V and 0·47 Fe. The 2-fold octahedral site in this structure is occupied by 0·22 V and 0·78 Fe.

Values of $\Delta f'$ are stated to be uncertain in the neighbourhood of an absorption edge, and it is therefore of interest to investigate the effect of variations in $\Delta f'$ for vanadium, with chromium radiation. Values of $-5\cdot1$ and $-3\cdot7$ electrons (instead of the initially assumed value of $-4\cdot4$ electrons) were therefore used in additional structure-factor calculations. The larger

Table 5. *Observed and calculated structure amplitudes for* ($h0.l$) *zone, molybdenum radiation*

$h0.l$	F_o	F_c	$h0.l$	F_o	F_c	$h0.l$	F_o	F_c	$h0.l$	F_o	F_c
00·2	79·0	55·5	20·8	13·5	14·1	40·10	44·1	41·9	70·3	19·8	22·7
(00·2)	—	(62·2)	20·9	45·8	38·4	40·11	30·6	31·8	70·5	12·1	12·0
00·4	59·6	51·7	20·10	55·6	52·4	40·12	22·6	20·2	70·7	28·6	26·9
00·6	92·0	88·5	20·11	34·3	38·4	40·13	35·1	33·9	70·8	13·5	11·7
00·8	87·6	85·4	20·12	25·4	24·4	40·15	31·9	29·3	70·9	< 10	10·3
00·10	74·0	74·3	20·13	40·9	39·5	40·17	15·8	16·8	70·13	< 12	14·8
00·12	25·2	23·3	20·15	40·0	33·9	40·18	15·3	18·3	70·15	< 12	14·7
00·14	44·7	32·1	20·16	< 10	11·5	40·21	< 10	10·6			
00·16	36·5	30·4	20·17	19·8	19·1	40·23	17·0	15·4	80·0	24·2	24·4
00·18	36·6	27·4	20·18	15·5	20·7				80·1	21·8	25·5
00·20	21·6	21·1	20·19	10·9	9·6	50·0	12·4	11·6	80·3	12·8	18·3
00·22	21·1	19·4	20·21	< 11	12·9	50·2	17·4	24·8	80·4	13·2	17·9
00·24	12·9	8·0	20·23	20·4	17·0	50·3	42·6	46·8	80·5	46·0	45·9
						50·4	< 5	5·1	80·6	9·7	13·0
10·0	19·9	24·2	30·0	29·8	31·0	50·5	17·9	23·4	80·7	< 10	10·8
10·1	17·7	15·6	30·1	14·5	8·1	50·7	28·7	27·1	80·9	15·3	15·9
10·2	57·6	51·6	30·2	69·2	70·1	50·8	13·4	16·4	80·10	19·2	22·1
10·3	76·5	75·1	30·4	14·1	11·4	50·10	8·9	10·9	80·11	16·5	18·2
10·4	14·0	8·0	30·5	< 5	5·8	50·11	13·7	11·4	80·13	18·2	20·7
10·5	34·0	32·5	30·6	9·1	12·0	50·12	< 10	10·3	80·15	18·4	18·3
10·6	< 5	6·6	30·7	4·9	4·4	50·13	10·9	12·7			
10·7	54·8	51·5	30·8	36·1	42·9	50·15	11·2	13·4	90·2	22·2	21·7
10·8	27·0	25·3	30·10	30·6	28·4				90·8	15·6	16·5
10·9	11·8	15·1	30·12	30·1	26·6	60·0	95·5	98·7	90·10	< 12	12·1
10·10	14·2	16·5	30·14	< 9	12·2	60·2	19·1	19·4	90·12	< 12	12·2
10·11	10·8	10·9	30·16	< 9	9·2	60·4	30·8	32·7			
10·12	11·4	14·5	30·20	15·7	14·8	60·6	40·4	43·1	10,0·0	17·8	17·2
10·13	22·2	22·0				60·8	41·5	42·1	10,0·1	15·2	17·5
10·15	20·9	21·3	40·0	46·3	48·1	60·10	48·0	44·7	10,0·3	< 11	11·8
10·17	10·0	10·9	40·1	51·0	56·3	60·12	15·8	14·4	10,0·5	17·4	30·7
			40·2	28·1	30·0	60·14	19·5	19·6	10,0·11	< 11	11·9
20·0	66·5	65·3	40·3	35·8	40·3	60·16	19·6	20·6	10,0·13	< 11	14·6
20·1	75·7	78·7	40·4	39·8	42·7	60·18	25·2	20·5	10,0·15	15·1	13·7
20·2	65·4	57·2	40·5	87·9	95·2	60·20	15·1	14·9			
20·3	64·5	62·2	40·6	25·2	26·8	60·22	13·7	13·4	11,0·3	15·6	15·4
20·4	63·5	61·8	40·7	22·4	23·7						
20·5	131·8	128·6	40·8	10·2	12·7	70·1	< 8	8·1	12,0·0	29·4	27·8
20·6	38·3	36·0	40·9	32·8	31·5	70·2	21·0	16·7	12,0·10	16·2	16·8
20·7	33·2	28·6									

value was obtained from Hön'l's equation for the *K* electrons only (James, 1948), while the smaller was chosen arbitrarily. Curves corresponding to these values are also shown in Fig. 1. It appears that the position of the minimum is only slightly altered by the use of the extreme values for $\Delta f'$. However, for the lower value, the minimum is very shallow, and its actual position is therefore indefinite. This curve could hardly be said to imply more than a strong preference of the vanadium for the tetrahedral site.

It is clear that the validity of the proposed iron–vanadium distribution depends on both the accuracy of the experimental data and the approximate correctness of Dauben & Templeton's value of $\Delta f'$. In support of the latter it can be shown that the agreement between observed and calculated values of $F_{(hk.0)}$ (Table 3, column *b*) is appreciably worsened if either of the extreme values of $\Delta f'$ for vanadium is assumed. It seems likely that the true value of $\Delta f'$ is within the limits investigated, and that the apparent distribution of iron and vanadium among the 2-fold sites merits tentative consideration.

Structure factors were calculated for the intermediate structure, and are compared with the observed data in Tables 4, 5, and 6. For molybdenum radiation, values of $F_{(h0.l)}$ corresponding to unobserved reflexions were calculated, but are tabulated only when they exceed the estimated minimum observable value for the reflexion. The agreement residual for the (*h*0.*l*) data (molybdenum) is 9·5% if the unobserved reflexions in the table are ignored, and 12·2% if they are assumed to have half their minimum observable value. Values of $F_{(hk.l)}$ corresponding to unobserved reflexions were not calculated. The agreement residual for the (*hk.l*) data (excluding (*hk*.0) and (*h*0.*l*)), is 11·0%.

Table 6. *Observed and calculated structure amplitudes for (hk.l) reflexions, molybdenum radiation*

hk.l	F_o	F_c	*hk.l*	F_o	F_c
11·2	94·0	89·4	21·3	76·2	66·2
11·4	16·5	14·6	21·5	32·7	30·7
11·6	10·0	13·9	21·7	43·5	40·8
11·8	38·4	47·5	31·3	48·4	50·0
21·2	40·0	37·3	31·5	25·0	24·2
31·2	34·1	31·1	31·7	41·7	40·2
41·2	50·7	53·1	51·3	34·5	38·7
41·8	32·2	34·4	51·7	26·8	27·3
22·2	40·9	31·8	61·7	31·3	26·7
22·4	46·6	43·7	32·3	35·1	40·2
22·6	61·6	66·5	32·5	19·2	19·8
22·8	49·2	63·8	32·7	38·4	39·5
32·2	32·0	27·8	42·1	38·2	45·5
42·4	46·6	32·7	42·3	26·1	31·0
42·6	19·6	21·5	42·5	76·4	75·9
52·2	33·6	38·2	62·5	59·2	53·0
33·2	41·1	48·2	43·3	32·2	37·3
44·4	25·7	27·4	43·7	23·5	22·6
44·6	29·6	36·1	64·5	44·8	39·6
44·8	32·6	35·8			

The differences between the observed and calculated values of $|F_{(00\cdot 2)}|$ are rather large, for both molybdenum and chromium. Unfortunately the observed values are probably not very accurate; for molybdenum the reflexion was partly obscured by low-angle scatter, and for chromium the absorption correction was large and therefore probably unreliable. However, $\sin\theta/\lambda = 0\cdot108$ for this reflexion, and it may be that ionization of the 2-fold cations contributes to the discrepancies. The structure factors were recalculated with the scattering factors of each of the 2-fold cations reduced by 2·4 electrons; that is, by the amount required to remove the discrepancy in $F_{(10\cdot 0)}$. ($F_{(00\cdot 2)}$, like $F_{(10\cdot 0)}$ is virtually unaffected by reasonable assumptions for the ionization of the neighbouring anions.) The values obtained are given in parentheses in their appropriate tables. The agreement is improved, but in spite of the obviously excessive adjustment of scattering factors, the differences remain fairly large. It is therefore probably unsafe to speculate, on the basis of this reflexion, on the state of ionization of the 2-fold cations.

The final F_o syntheses for the *c*- and *a*-axis projections are shown in Fig. 2; the atomic positions, obtained from these and the corresponding F_c syntheses, are given in Table 7.

The standard deviations quoted were obtained from Cruickshank's formula (Lipson & Cochran, 1953)

$$\sigma(x_n) = \frac{2\pi\{\sum_q n^2(F_o-F_c)^2\}^{\frac{1}{2}}}{aACn}\,.$$

A further factor of 2 was introduced because all atomic positions were estimated from the non-

Table 7. *Atomic positions*

(Standard deviations are given in parentheses)

Atom	No. of equivalent positions	*x/a* = −*y/b*		*z/c*	
O_1	2	0	—	0·002	(0·002)
O_2	2	$\frac{1}{3}$	—	0·750	(0·002)
O_3	6	0·167	(0·004)	0·248	(0·002)
O_4	6	−0·485	(0·004)	0·000	(0·002)
V	6	0·1667	(0·0008)	0·6370	(0·0005)
$(Fe,V)_1$ (0·78 Fe+0·22 V)	2	$\frac{1}{3}$	—	0·3552	(0·0009)
$(Fe,V)_2$ (0·47 Fe+0·53 V)	2	$\frac{1}{3}$	—	0·9546	(0·0009)

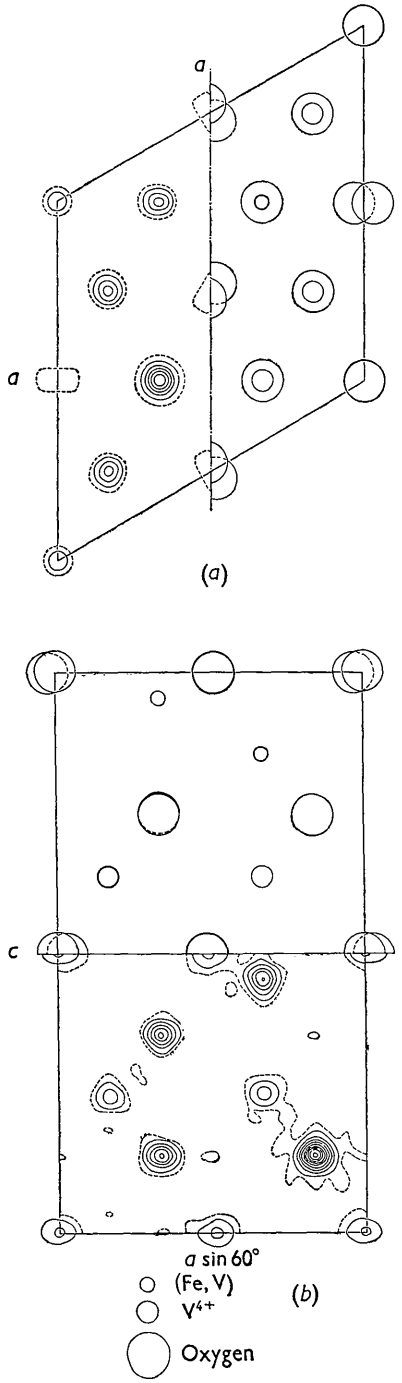

Fig. 2. (*a*) *c*-axis Fourier projection. Solid contours are drawn at intervals of 40 e.Å^{-2}, the lowest being 40 e.Å^{-2}. The dotted contour is at 20 e.Å^{-2}. (*b*) *a*-axis Fourier projection. Solid contours are drawn at intervals of 20 e.Å^{-2}, the lowest being 20 e.Å^{-2}. The dotted contour is at 10 e.Å^{-2}. Heavy circles indicate two completely overlapped atoms of the same type.

centrosymmetrical *a*-axis projection. The central curvatures were calculated by assuming sections through the peaks of the projected electron density to be parabolic in the neighbourhood of the peaks.

Discussion of the structure

It is not at this time possible to write a valid chemical formula for Nolanite. The convenient formula $(Fe,V)_4V_6O_{16}$ assumed initially is crystallographically acceptable and consistent with the X-ray data, but it is clearly in error to some degree since the sum of valency electrons is 1·5. It is not possible to indicate the nature of the error, as any attempt to write a formula demands assumptions which cannot be tested by the X-ray data. The formulation thus remains a problem in chemical analysis, and in the following discussion it must be remembered that the structure described is only approximately correct.

The structure can be described as a system of linked octahedra and tetrahedra (each containing a cation), whose edges terminate in anions. An idealized portion of the system, roughly corresponding to the contents of one unit cell, is shown in Fig. 3. The anions have been numbered for reference. If the oxygen close-packing were perfect, all polyhedron edges would be 2·93 Å long. This is not the case however; moreover, the cations are not in general at the centres of gravity of their respective polyhedra. Departures from an ideal structure seem to be consistent with expected interionic forces. Table 8 gives the more important interionic distances, and their standard deviations. The estimation of the latter was complicated by the high symmetry of the structure.

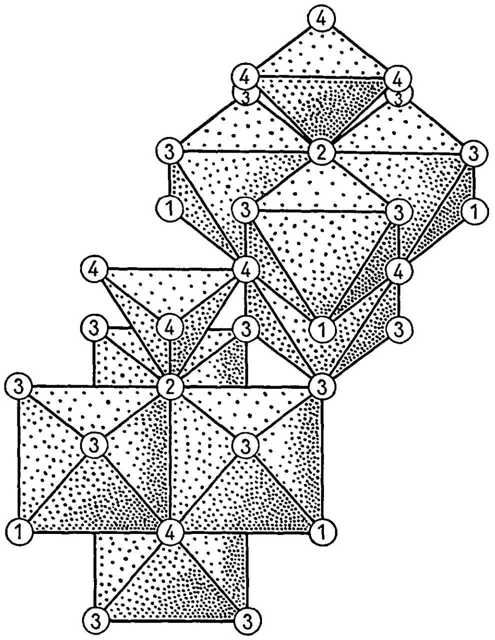

Fig. 3. An idealized portion of the system of linked polyhedra (*c*-axis vertical).

Table 8. *Interionic distances*

(All distances in Å; standard deviations are given in parentheses)

6-fold octahedron		
O–O distances		
2–4	2·82	(0·03)*
3–3	2·93	(0·03)
4–4	2·66	(0·06)*
1–4	2·96	(0·00)
2–3	2·93	(0·00)
1–3	2·82	(0·03)*
V–O distances		
V–1	2·10	(0·01)
V–2	1·99	(0·01)
V–3	1·98	(0·02)
V–4	2·06	(0·02)
2-fold octahedron		
O–O distances		
3–3	2·93	(0·03)
3–4	2·84	(0·03)
4–4	2·66	(0·06)*
$(Fe,V)_1$–O distances		
$(Fe,V)_1$–3	1·96	(0·02)
$(Fe,V)_1$–4	2·04	(0·04)
Tetrahedron		
O–O distances		
2–4	2·96	(0·03)
4–4	3·19	(0·06)
$(Fe,V)_2$–O distances		
$(Fe,V)_2$–2	1·90	(0·02)
$(Fe,V)_2$–4	1·89	(0·04)
Cation–Cation distances		
$(Fe,V)_1$–$(Fe,V)_2$	3·72	(0·01)
	3·51	(0·00)
$(Fe,V)_1$–V	3·12	(0·01)
	3·56	(0·01)
$(Fe,V)_2$–V	3·40	(0·01)
	3·39	(0·01)
V–V	2·93	(0·01)

* Edge shared with adjacent octahedron.

The edges (4–4) forming the base of the tetrahedron are somewhat lengthened, in order to accommodate the (Fe,V) ion, the position of which appears to be fixed by metal–oxygen contacts. The departure of the edge length from the normal value of 2·93 Å is more than 4 times the standard deviation, and is, by the criterion of Cruickshank, significant (Lipson & Cochran, 1953). The other (Fe,V) ion, and the V^{4+} ion are displaced from the centres of gravity of their respective octahedra in such a way as to increase their separation. The edge (4–4) shared by their octahedra is significantly shortened, and it thus appears that there is appreciable repulsion between these cations. The displacement of the V^{4+} ion is not such as to alter either of the V–V distances, and the slight shortening of one of the edges shared by adjacent 6-fold octahedra is probably incidental to the other distortions. If it is accepted that the (Fe,V) ions are strongly ionized, and the V^{4+} ions only weakly so, then the minimum cation–cation distances of the three types which occur are in the order of magnitude of the corresponding charge products.

The structure is very similar to that reported by McCarrol, Katz & Ward (1957) for some ternary oxides of tetravalent molybdenum, with formulae $A_2^{+2}Mo_3^{+4}O_8$. The structure of Nolanite is more regular, however, and there is no evidence of bonding between adjacent tetravalent vanadium ions corresponding to that reported for molybdenum. The tetravalent vanadium ions obey the general rule that ions of higher valency prefer octahedral coordination. The rule is disregarded by trivalent vanadium, however, which shows a strong, but not exclusive, preference for tetrahedral coordination. In this respect Nolanite resembles the inverted spinel $Fe(Mg,Fe)O_4$ (Bijvoet, 1951).

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