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The Crystal Structure of the High Temperature form of Niobium Pentoxide

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High temperature Nb_2O_5 is monoclinic, space group $P2$, with fourteen formula units in the cell:

$$a=21\cdot16,\ b=3\cdot822,\ c=19\cdot35\ \text{Å};\ \beta=119°\ 50'\ .$$

Twenty-seven of the Nb atoms are in octahedral coordination and one is tetrahedral. The structure contains ReO_3-type blocks of two different sizes. At one level these are three octahedra wide and five long, and are joined, by sharing edges on both sides, into slabs running right through the structure in two directions. The second kind of block, three octahedra by four, cements these together by additional edge sharing, and leaves tetrahedral holes partly, but systematically, filled with niobium atoms. This form of Nb_2O_5 is the member $n=9$ of a possible series of structural homologues $Nb_{3n+1}O_{8n-2}$.

Introduction

It is becoming increasingly clear that oxide and chalcogenide systems contain a wealth of problems equally interesting to the crystallographer and to the chemist, physicist or ceramist concerned with their properties. Their crystal structures can be straightforward and related to well-known kinds; but often the atomic arrangement is far from simple, and if such is the case it may be easier to describe by taking it to pieces, as it were, in order to identify fragments of different kinds joined by regular discontinuities of one sort or another (Wadsley, 1963), in much the same way as a polypeptide or protein is referred to a sequence of amino-acid residues.

We are currently exploring the crystal chemistry of pentavalent niobium and its binary and ternary oxides which constitute a considerable gap in the literature. Niobium pentoxide itself occurs in several different modifications, the number and indeed the identity of its forms at the present being uncertain, and each appears to have a structure of some complexity. There is general agreement about the high temperature form obtained from a slowly cooled melt, or by heating the other varieties to 900 °C or more. We now wish to report its structure, using methods which recognize fragments of the ReO_3 type within it, and to speculate briefly upon the likely existence of related structures.

Experimental

A crystal of dimensions $0\cdot03\times0\cdot03\times0\cdot05$ mm was selected from a melt of high purity niobium pentoxide (New Metals and Chemicals) annealed for a further 72 hours at 1000 °C. The lattice parameters, given in Table 1 with the rest of the crystallographic constants, were derived from a Guinier film internally calibrated with potassium chloride, and are in good agreement with previous estimations summarized by Roth (1959). The $h0l$, $h1l$ and $h2l$ levels were recorded by the integrating Weissenberg technique, each with four films simultaneously exposed to filtered copper radiation. Less than half of the possible reflexions were strong enough to be recorded. Measurements of intensity were made by visual comparison with a calibrated film strip and reduced to structure factors with the Elliott 803 computer programmed in Autocode for Lorentz–polarization corrections. Specimen absorption was neglected. Fourier summations and structure factors were computed on SILLIAC at the University of Sydney, and we would like to acknowledge the generous assistance of Dr J. G. Sime who wrote special sub-routines to lighten the task of plotting out the very large Fourier maps. Scattering

Table 1. *Crystallographic data for* Nb_2O_5

System: Monoclinic
Unit-cell dimensions:

$$a=21\cdot16,\ b=3\cdot822,\ c=19\cdot35\ \text{Å};\ \beta=119°\ 50'$$

Systematic absent reflexions: None
Possible space groups: $P2$ (No. 3), Pm (No. 6), $P2/m$ (No. 10)
D_m*: $4\cdot55$ g.cm^{-3}
D_x (for $Z=14$): $4\cdot55$ g.cm^{-3}
$\mu=502$ cm^{-1}

* Holtzberg, Reisman, Berry & Berkenblit (1957).

curves for Nb^{5+} were derived from the tables of Thomas & Umeda (1957) corrected for dispersion, together with Suzuki's (1960) curve for doubly ionized oxygen. Towards the end of the analysis it became clear that several of the more intense reflexions were severely affected by extinction. As the main objective was to determine the positions of the large number of atoms in the unit cell and to examine the principles upon which the structure is based, a high degree of refinement, requiring reliable corrections for extinction and perhaps for double Bragg scattering as well, was considered to be unnecessary.

Structure determination

One may assume with some confidence that the axis of symmetry of length 3·8 Å corresponds to the length of an NbO_6 octahedral body diagonal. The ideal octahedron, projected down this axis, appears as a square of oxygens with the metal, in this case niobium, together with an overlying oxygen atom, present at the centre. Octahedra are commonly joined in oxide structures by having edges and corners in common (Fig. 1), and two-dimensional methods are usually sufficient to work them out, as overlap is restricted to the metals and one oxygen for each. The initial problem was to find the positions of the twenty-eight metal atoms by interpreting the Patterson projection, $P(u, w)$. There will be only fourteen to find if they occupy twofold positions of the space groups $P2$ or $P2/m$ as both are centrosymmetric in projection on to (010). Owing to the short b axis there was little likelihood that the fourfold positions of $P2/m$, $\pm(x, y, z)$, $(x, \bar{y}, z)$ would be used.

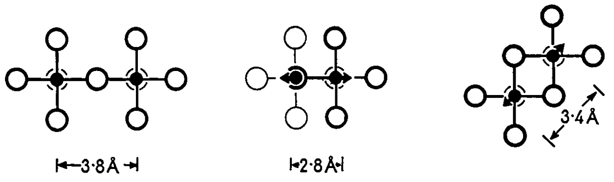


Fig. 1. Ways of joining two octahedra: (a) By a corner, one oxygen in common. (b) By an edge at different levels, two common oxygen atoms. (c) By an edge at the same level, two common oxygen atoms. Arrows attached to the metals (small black circles) indicate direction of distortion, with the distances (projected down a body diagonal) between them.

The first requirement for a trial structure of metal atoms was to position seventy oxygen atoms around them in the unit cell, either in the unique positions of Pm, or single and twofold in $P2$ or $P2/m$. Initially it can be assumed that oxygen atoms are in 'ideal', or undistorted, positions, the number of them being more important at the preliminary stages than their real parameters. If all the octahedra are joined by corners only, the formula must be BO_3, and a reduction in the number of oxygen atoms can be achieved by omitting them entirely from the structure — an unlikely event — or preferably by joining octahedra by their edges (two bridging oxygen atoms) at the same or at different levels along the b axis (Fig. 1). When joined by corners, the distances between metals can be expected to be about 3·8 Å, but 3·4 Å or 2·8 Å in projection when joined by an edge (Wadsley, 1961). A trial arrangement of metals containing these distances should therefore lead to the ideal positions for oxygen. The application of this 'formula criterion' requires a virtual solution of the whole structure, and the model eventually selected for refinement contained fewer errors in the ideal positions for oxygen than of niobium.

A second important criterion arose from the presence of a sub-cell. Although the films gave little or no evidence of it, the Patterson projection $P(u, w)$ (Fig. 2) which was prepared without sharpening, contained parallel ridges of strong vectors at right angles to each other, the vector peaks themselves being unusually sharp and well rounded, and with an abundance of 3·8 and 2·8 Å separations. The majority of the niobium atoms evidently form a grid more or less orthogonal, with two of the octahedral diagonals aligned parallel to the sub-cell axes and the third extending upwards along b.

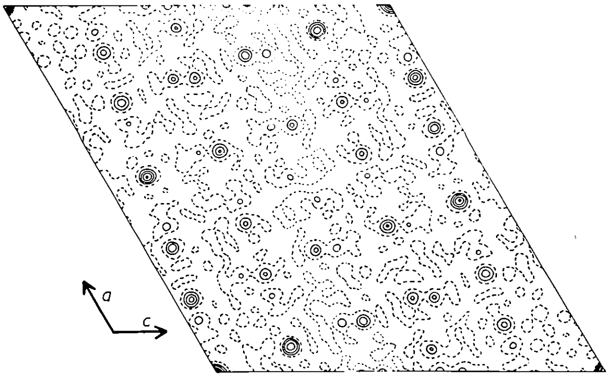


Fig. 2. Patterson projection $P(u, w)$, zero contour dotted.

When the origin of a tracing of the Patterson function on a transparent sheet is transferred to one of the vectors on an identical underlying one, keeping the axial directions parallel, the coincident peaks comprise a reduced vector set containing the atomic positions but not the origin of the unit cell. In a structure of the present kind where there are many heavy atoms separated by only two or three different distances, and therefore many coincident interactions between them, the reduced set will almost certainly not be the fundamental one, and the method must be continued as before but with two maps of the reduced set. We decided instead to use the restrictive tests already outlined. A single superposition eliminates some of the vectors, and if the coincident peaks are plotted on squared paper and called metal atoms, and the octahedra are sketched in to give the correct orientation based on the sub-cell, then the numbers of atoms of both kinds must agree with the experimentally determined contents of the unit cell, $Nb_{28}O_{70}$, if the model is to receive any further consideration.

Several models were tried and rejected, but each nevertheless contained an identical feature, three octahedra at one level sharing corners and alternating with three at a level $y/2$ below, joined with edges in common and extending along one direction of the sub-cell (Fig. 3). This grouping has already been noted in the pseudobinary oxides $TiNb_2O_7$ and $Ti_2Nb_{10}O_{29}$, where it was convenient to call it an *S* unit (Wadsley, 1961). In niobium pentoxide it evidently cannot continue indefinitely as a two-dimensional sheet, but will be interrupted at regular intervals as in $NaNb_{13}O_{33}$ (Andersson, 1963). The breadth of these finite units of three in the other sub-cell direction also emerged from the image-seeking technique. At one level, arbitrarily taken to be $y=0$, the octahedra are five deep, while at the other level, $y=\frac{1}{2}$, they are four. Viewed separately these 3×5 and 3×4 groups, of infinite extension in the third direction (out of the plane of the paper), are slabs of the ReO_3-type structure.

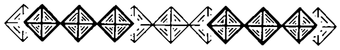
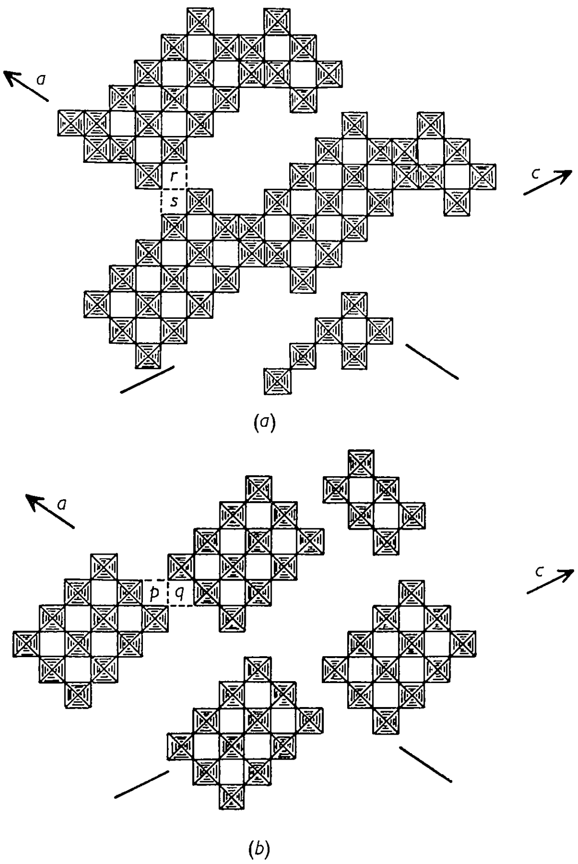


Fig. 3. Characteristic feature of Nb_2O_5, three octahedra (heavier outline) sharing edges with three at a level $y=\frac{1}{2}$ above and below (lighter outline); an *S* unit, found in related phases (Wadsley, 1961; Andersson, 1963).

Closer examination of the reduced vector set seemed to indicate that the 3×5 groups were staggered and joined together at the same level by sharing edges (Fig. 4(*a*)), the terminal atoms being 3·4 Å apart. These groups run right throughout the structure and the 3×4 units will then fit into the open spaces between them. The formula for this model, however, is $Nb_{27}O_{70}$. An extra metal atom could be present in one of two positions *p* or *q*, each of which can be visualized as an additional octahedron linking the 3×4 blocks together (Fig. 4(*b*)), the overlying oxygen being supplied in the complete structure from the 3×5 blocks above (and below). But with this procedure, which could be neither confirmed nor dismissed by image seeking, the model would lose its centre of inversion. The two alternative positions for this twenty-eighth niobium atom are identical but with different senses in the now polar model.

Three cycles of iterative Fourier syntheses projected on to (010) with all ninety-eight atoms in the single positions 1(*a*) or 1(*b*) for the space group *Pm* showed the structure to be substantially correct, but considerable uncertainty centred around this one metal atom which appeared to move in between the neighbouring 3×5 blocks. These provide another two alternative octahedral positions *r* and *s* of the same kind (Fig. 4(*a*)). However, a careful analysis of the positions of the metal and oxygen atoms appearing in the electron-density projections showed, within limits of error, that a centre of symmetry did indeed exist if this one dubious atom alone were ignored. A re-location of the unit cell relating both kinds of ReO_3-type block across the centre of symmetry could lead to the correct formula *only if a metal atom in projection were present at the origin of it.* One additional metal, together with its overlying oxygen atom and one more oxygen atom as well, must also occupy unique positions; all of this was not in conflict with the electron-density projections. The metal at the origin has *tetrahedral* coordination, not octahedral like the remaining twenty-seven. Its distances to neighbouring metals in projection were 3·4 Å, and it alone of the metals was out of line with the sub-cell.



(*a*)

(*b*)

Fig. 4. ReO_3-type blocks present in Nb_2O_5. (*a*) Blocks $3\times5\times\infty$, joined with common edges. (*b*) Isolated blocks $3\times4\times\infty$. The dashed squares *p*, *q*, *r* and *s* are the four additional octahedral sites discussed in the text.

This revised model refined with F_o Fourier syntheses to a reliability index of 18%. Some of the oxygen atoms can be identified with small peaks (Fig. 5), but the map as a whole contains much false detail arising from series termination. The centres of the metal peaks, their heights and curvatures, were estimated by the Gaussian ellipsoid approximation (Dawson, 1961); the contributions of these atoms to the structure factors were subtracted from the scaled observed data and processed in an $F_o - F_{\mathrm{Nb}}$ synthesis. Several of the strong reflexions, obviously affected by extinction, were omitted.

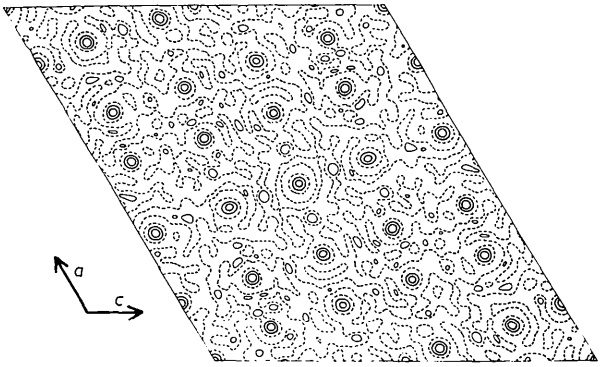


Fig. 5. F_o electron-density projection on to (010), arbitrary scale. Heavier contours are the metals, and the lighter the oxygen atoms and series termination effects at half of this scale; zero contour dotted.

Thirty-five of the oxygen atoms of the asymmetric unit are recognizable in Fig. 6, and only one of the thirty-six, O(20) lying directly over Nb(15), is poorly defined. A final $F_o - F_c$ synthesis gave additional small shifts as well as removing some minor ambiguities. At this stage the reliability index was 11·8%, and the structure was refined no further.

The crystal providing the data was evidently not ideally imperfect. Extinction, which reduces the intensity of the strong reflexions appearing at low angles, is likely to be accompanied by double Bragg scattering reinforcing the weaker ones, as Willis (1963) showed in a recent neutron diffraction examination of UO_2 and ThO_2. Perhaps for these reasons as well

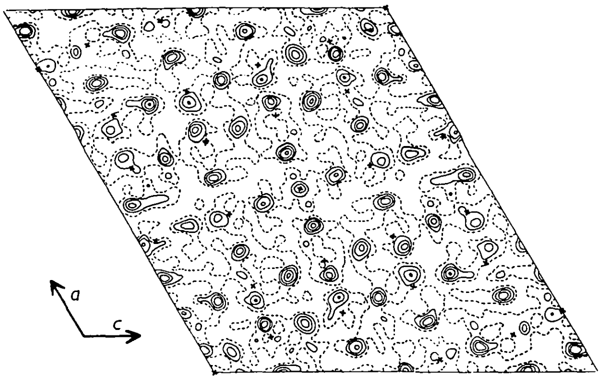


Fig. 6. $F_o - F_{\mathrm{Nb}}$ electron-density projection on to (010) showing the oxygen atoms. Contours at equal arbitrary intervals, zero contour dotted. Metals indicated by black crosses.

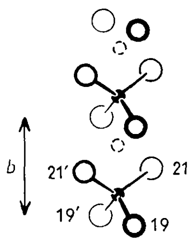


Fig. 7. Tetrahedral environment provided by O(19) and O(21), Nb(1) black circle, alternative position dotted.

Table 2. *Fractional atomic parameters*

Space group *P*2 (No. 3); unique axis *b*

Atom	Point position	*x*	σ(*x*)	*y*	*z*	σ(*z*)
Nb(1)	1(*a*)	0		0·25	0	
Nb(2)	1(*d*)	½		0	½	
Nb(3)	2(*e*)	0·1623	0·0005	0	0·0000	0·0005
Nb(4)	2(*e*)	0·2354	0·0005	0	0·2310	0·0005
Nb(5)	2(*e*)	0·3017	0·0005	0	0·4544	0·0005
Nb(6)	2(*e*)	0·3609	0·0005	0	0·0447	0·0005
Nb(7)	2(*e*)	0·4331	0·0005	0	0·2776	0·0005
Nb(8)	2(*e*)	0·5635	0·0005	0	0·0936	0·0005
Nb(9)	2(*e*)	0·6303	0·0005	0	0·3239	0·0005
Nb(10)	2(*e*)	0·0938	0·0005	0·5	0·2007	0·0005
Nb(11)	2(*e*)	0·1598	0·0005	0·5	0·4245	0·0005
Nb(12)	2(*e*)	0·7028	0·0005	0·5	0·1237	0·0005
Nb(13)	2(*e*)	0·7701	0·0005	0·5	0·3513	0·0005
Nb(14)	2(*e*)	0·8990	0·0005	0·5	0·1635	0·0005
Nb(15)	2(*e*)	0·9650	0·0005	0·5	0·3891	0·0005
O(1)	1(*b*)	0		0·5	½	
O(2)	1(*d*)	½		0·5	½	
O(3)	2(*e*)	0·131	0·004	0	0·204	0·004
O(4)	2(*e*)	0·200	0·004	0	0·443	0·004
O(5)	2(*e*)	0·194	0·002	0	0·114	0·002
O(6)	2(*e*)	0·261	0·002	0	0·341	0·002
O(7)	2(*e*)	0·260	0·002	0	0·014	0·002
O(8)	2(*e*)	0·330	0·002	0	0·249	0·002
O(9)	2(*e*)	0·398	0·002	0	0·480	0·002
O(10)	2(*e*)	0·407	0·002	0	0·155	0·002
O(11)	2(*e*)	0·461	0·002	0	0·384	0·002
O(12)	2(*e*)	0·460	0·002	0	0·037	0·002
O(13)	2(*e*)	0·535	0·002	0	0·295	0·002
O(14)	2(*e*)	0·590	0·002	0	0·198	0·002
O(15)	2(*e*)	0·663	0·002	0	0·428	0·002
O(16)	2(*e*)	0·657	0·004	0	0·096	0·004
O(17)	2(*e*)	0·743	0·004	0	0·340	0·004
O(18)	2(*e*)	0·883	0·004	0	0·128	0·004
O(19)	2(*e*)	0·944	0·002	0	0·028	0·002
O(20)	2(*e*)	0·965	0·004	0	0·389	0·004
O(21)	2(*e*)	0·056	0·002	0·5	0·075	0·002
O(22)	2(*e*)	0·068	0·002	0·5	0·406	0·002
O(23)	2(*e*)	0·135	0·002	0·5	0·311	0·002
O(24)	2(*e*)	0·194	0·004	0·5	0·215	0·004
O(25)	2(*e*)	0·266	0·004	0·5	0·447	0·004
O(26)	2(*e*)	0·355	0·004	0·5	0·010	0·004
O(27)	2(*e*)	0·426	0·004	0·5	0·241	0·004
O(28)	2(*e*)	0·594	0·004	0·5	0·091	0·004
O(29)	2(*e*)	0·658	0·004	0·5	0·312	0·004
O(30)	2(*e*)	0·732	0·002	0·5	0·231	0·002
O(31)	2(*e*)	0·799	0·002	0·5	0·455	0·002
O(32)	2(*e*)	0·793	0·002	0·5	0·130	0·002
O(33)	2(*e*)	0·862	0·002	0·5	0·365	0·002
O(34)	2(*e*)	0·845	0·004	0·5	0·029	0·004
O(35)	2(*e*)	0·933	0·002	0·5	0·265	0·002
O(36)	2(*e*)	0·000	0·002	0·5	0·176	0·002

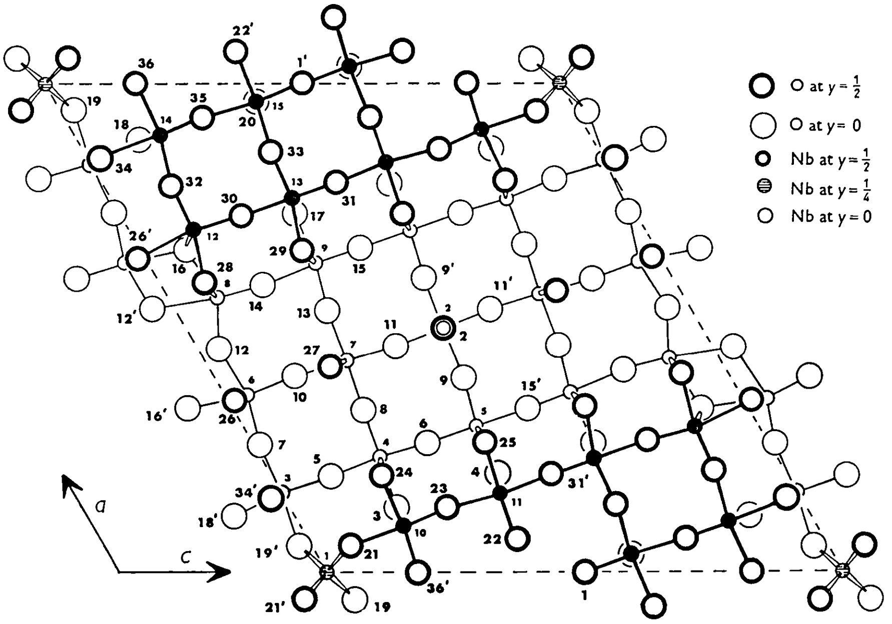


Fig. 8. Drawing of atoms in Nb_2O_5 projected on (010). Smaller numbers are metal, larger oxygen.

Table 3. *Octahedral niobium. Interatomic distances*

Octahedral metal	Bonded* oxygen atoms	Nb–O distances (Å) (same order as in column 2)	Average	O–O distances (Å) Max.	Min.	Average
Nb(2)	2 (2); 9(2), 11(2)	1·91(2); 1·99(2), 1·97(2)	1·96	2·83	2·74	2·77
Nb(3)	34′(2); 7, 5, 19′ 18′	1·92(2); 1·98, 1·96, 2·16, 2·17	2·02	3·11	2·54	2·84
Nb(4)	24 (2); 3, 5 8, 6	2·06(2); 2·06, 1·98, 1·84, 1·92	1·98	3·23	2·28	2·76
Nb(5)	25 (2); 4, 6 9, 15′	2·03(2); 2·04, 1·92, 1·85, 2·01	1·98	3·17	2·34	2·78
Nb(6)	26 (2); 12, 10, 7, 16′	2·01(2); 2·19, 1·85, 1·92, 2·14	2·02	3·39	2·53	2·89
Nb(7)	27 (2); 10, 13, 11, 8	2·02(2); 2·16, 2·00, 1·84, 1·98	2·00	3·13	2·44	2·80
Nb(8)	28 (2); 16, 14, 12, 12′	2·02(2); 1·95, 1·82, 1·89, 2·31	2·00	3·12	2·31	2·78
Nb(9)	29 (2); 17, 15, 13, 14	2·04(2); 2·24, 1·77, 1·81, 2·14	2·01	3·11	2·49	2·81
Nb(10)	3 (2); 24, 23, 36′, 21	2·06(2); 2·00, 1·85, 1·80, 2·14	1·99	3·19	2·28	2·78
Nb(11)	4 (2); 25, 31′, 22, 23	2·04(2); 2·07, 2·04, 1·80, 2·00	2·01	3·17	2·34	2·79
Nb(12)	16 (2); 32, 30, 28, 26′	2·09(2); 1·85, 1·84, 2·02, 2·24	2·03	3·25	2·31	2·81
Nb(13)	17 (2); 33, 31, 29, 30	1·98(2); 1·82, 1·79, 2·11, 2·06	1·96	3·00	2·49	2·75
Nb(14)	18 (2); 36, 35, 32, 34	2·00(2); 2·02, 1·73, 2·00, 2·26	2·00	3·00	2·54	2·80
Nb(15)	20 (2); 22′, 1′, 33, 35	1·91(2); 2·03, 1·89, 2·00, 2·14	1·98	2·97	2·69	2·80

* Given by numbers only (Table 2 and Fig. 8). The first, followed by (2) and a semicolon are the two oxygen atoms lying over and under the metal. The distances between these oxygen atoms and metal atoms throughout the table have e.s.d.'s of ±0·08 Å. The remaining metal–oxygen distances are ±0·05 Å.

as the possibility of absorption, no meaningful overall thermal parameter was obtainable on a Wilson plot of $|F_o|$ and $|F_c|$. Were these optical effects to be measured and then removed from the experimental data, a most necessary task for further refinement and an almost impossibly laborious one for a unit cell of this size, the individual temperature factors, except perhaps for some of the oxygen atoms, would still be small for a compound with a melting point about 1500 °C.

There are two tetrahedral positions at the origin (Fig. 7). If the space group is $P2/m$, Nb(1) must be distributed equally over $2(i)$, $\pm(0, y, 0)$ with y approximately $\frac{1}{4}$, while the atoms in twofold positions will be in $2(m)$ or $2(n)$ with $y=0$ or $\frac{1}{2}$. The alternative $P2$ has the provision for only one tetrahedral site, $1(a)$, $(0, y, 0)$ with y approximately $\frac{1}{4}$ (or $\frac{3}{4}$), but in this space group the twofold positions include y as an additional variable, which we can nevertheless expect

Table 4. *Tetrahedral interatomic distances and angles*

Nb(1)–O(19)	1·68±0·05 Å
Nb(1)–O(21)	1·65±0·05
O(19)–O(19′)	2·76±0·10
O(21)–O(21′)	2·69±0·10
O(19′)–O(21)	2·69±0·07
O(19)–O(21)	2·74±0·07
O(19′)–Nb(1)–O(19)	110·4°
O(21)–Nb(1)–O(21′)	109·1
O(19′)–Nb(1)–O(21)	107·7
O(19)–Nb(1)–O(21)	109·5

Table 5. *Comparison of observed and calculated intensities*

hkl	F_o	$\lvert F_c \rvert$
0 0 1	**	58
0 0 2	66	75
0 0 3	66	63
0 0 4	39	36
0 0 5	108	124
0 0 6	80	73
0 0 7	67	61
0 0 8	60	71
0 0 9	176	190
0 0 10	87	78
0 0 11	<53	46
0 0 12	<57	39
0 0 13	<60	6
0 0 14	<62	35
0 0 15	<64	14
0 0 16	<63	5
0 0 17	<61	11
0 0 18	169	177
0 0 19	<52	13
0 0 20	<44	72
0 0 21	68	73
1 0 0	<13	15
1 0 1	<18	28
1 0 2	22	43
1 0 3	53	67
1 0 4	108	130
1 0 5	<34	12
1 0 6	<37	7
1 0 7	<41	15
1 0 8	<45	2
1 0 9	48	46
1 0 10	<52	37
1 0 11	<55	36
1 0 12	73	59
1 0 13	208	207
1 0 14	<63	24
1 0 15	64	95
1 0 16	88	89
1 0 17	120	114
1 0 18	<55	29
1 0 19	69	82
1 0 20	57	58
1 0 21	<25	18
$\bar{1}$ 0 1	<13	9
$\bar{1}$ 0 2	53	41
$\bar{1}$ 0 3	115	127
$\bar{1}$ 0 4	206	326*
$\bar{1}$ 0 5	470	904*
$\bar{1}$ 0 6	163	167
$\bar{1}$ 0 7	128	145
$\bar{1}$ 0 8	100	85
$\bar{1}$ 0 9	<45	36
$\bar{1}$ 0 10	108	100
$\bar{1}$ 0 11	73	63
$\bar{1}$ 0 12	<55	23
$\bar{1}$ 0 13	<59	16
$\bar{1}$ 0 14	123	99
$\bar{1}$ 0 15	109	84
$\bar{1}$ 0 16	64	63
$\bar{1}$ 0 17	62	45
$\bar{1}$ 0 18	<59	20
$\bar{1}$ 0 19	<54	26
$\bar{1}$ 0 20	<48	0
$\bar{1}$ 0 21	<39	45
$\bar{1}$ 0 22	<23	47
2 0 0	74	74
2 0 1	<22	22
2 0 2	<25	4
2 0 3	<29	5
2 0 4	32	35
2 0 5	36	41
2 0 6	39	48
2 0 7	60	61
2 0 8	272	274
2 0 9	<50	37
2 0 10	<53	50
2 0 11	<56	27
2 0 12	<60	46
2 0 13	<62	25
2 0 14	<64	23
2 0 15	<64	18
2 0 16	86	69
2 0 17	377	372
2 0 18	104	119
2 0 19	45	40
2 0 20	34	43
$\bar{2}$ 0 1	94	121
$\bar{2}$ 0 2	<19	26
$\bar{2}$ 0 3	<22	7
$\bar{2}$ 0 4	<26	7
$\bar{2}$ 0 5	100	89
$\bar{2}$ 0 6	57	65
$\bar{2}$ 0 7	109	115
$\bar{2}$ 0 8	204	251
$\bar{2}$ 0 9	534	793*
$\bar{2}$ 0 10	410	545*
$\bar{2}$ 0 11	142	107
$\bar{2}$ 0 12	108	100
$\bar{2}$ 0 13	100	67
$\bar{2}$ 0 14	85	104
$\bar{2}$ 0 15	<62	43
$\bar{2}$ 0 16	<64	22
$\bar{2}$ 0 17	<63	6
$\bar{2}$ 0 18	60	39
$\bar{2}$ 0 19	<57	26
$\bar{2}$ 0 20	<51	38
$\bar{2}$ 0 21	43	43
$\bar{2}$ 0 22	55	44
3 0 0	<23	9
3 0 1	<25	32
3 0 2	57	60
3 0 3	132	158
3 0 4	119	137
3 0 5	38	38
3 0 6	42	61
3 0 7	55	40
3 0 8	109	100
3 0 9	52	58
3 0 10	96	84
3 0 11	144	128
3 0 12	296	260
3 0 13	263	261
3 0 14	64	47
3 0 15	<62	42
3 0 16	59	60
3 0 17	122	128
3 0 18	<48	17
3 0 19	<39	2
3 0 20	<8	18
$\bar{3}$ 0 1	<21	7
$\bar{3}$ 0 2	<22	8
$\bar{3}$ 0 3	<24	12
$\bar{3}$ 0 4	<26	28
$\bar{3}$ 0 5	78	72
$\bar{3}$ 0 6	32	40
$\bar{3}$ 0 7	<36	23
$\bar{3}$ 0 8	<39	19
$\bar{3}$ 0 9	<42	30
$\bar{3}$ 0 10	102	100
$\bar{3}$ 0 11	<50	9
$\bar{3}$ 0 12	<53	27
$\bar{3}$ 0 13	126	126
$\bar{3}$ 0 14	462	575
$\bar{3}$ 0 15	183	197
$\bar{3}$ 0 16	<64	10
$\bar{3}$ 0 17	<64	52
$\bar{3}$ 0 18	87	87
$\bar{3}$ 0 19	117	116
$\bar{3}$ 0 20	<53	0
$\bar{3}$ 0 21	<46	10
4 0 0	60	57
4 0 1	<29	43
4 0 2	55	39
4 0 3	83	73
4 0 4	<60	48
4 0 5	76	79
4 0 6	139	121
4 0 7	279	279
4 0 8	448	511
4 0 9	109	81
4 0 10	<57	42
4 0 11	<60	33
4 0 12	109	112
4 0 13	64	54
4 0 14	<63	9
4 0 15	<61	27
4 0 16	57	67
4 0 17	125	103
4 0 18	62	56
4 0 19	<32	18
$\bar{4}$ 0 1	221	351*
$\bar{4}$ 0 2	78	100
$\bar{4}$ 0 3	<25	55
$\bar{4}$ 0 4	<28	60
$\bar{4}$ 0 5	<30	41
$\bar{4}$ 0 6	<32	13
$\bar{4}$ 0 7	<36	31
$\bar{4}$ 0 8	<39	13
$\bar{4}$ 0 9	<42	8
$\bar{4}$ 0 10	101	104
$\bar{4}$ 0 11	<45	25
$\bar{4}$ 0 12	52	60
$\bar{4}$ 0 13	55	63
$\bar{4}$ 0 14	131	114
$\bar{4}$ 0 15	<61	31
$\bar{4}$ 0 16	63	75
$\bar{4}$ 0 17	100	91
$\bar{4}$ 0 18	93	86
$\bar{4}$ 0 19	464	538
$\bar{4}$ 0 20	<54	50
$\bar{4}$ 0 21	<49	22
$\bar{4}$ 0 22	<41	34
$\bar{4}$ 0 23	92	114
5 0 0	31	49
5 0 1	<32	29
5 0 2	<35	9
5 0 3	44	55
5 0 4	<41	25
5 0 5	<44	33
5 0 6	46	33
5 0 7	50	60
5 0 8	93	86
5 0 9	<57	35
5 0 10	<60	13
5 0 11	<61	30
5 0 12	216	172
5 0 13	<64	49
5 0 14	<61	5
5 0 15	<59	3
5 0 16	120	114
5 0 17	<47	35
5 0 18	<38	19
$\bar{5}$ 0 1	<28	39
$\bar{5}$ 0 2	<28	39
$\bar{5}$ 0 3	<28	49
$\bar{5}$ 0 4	<29	41
$\bar{5}$ 0 5	<32	50
$\bar{5}$ 0 6	183	166
$\bar{5}$ 0 7	36	36
$\bar{5}$ 0 8	39	33
$\bar{5}$ 0 9	42	74
$\bar{5}$ 0 10	64	78
$\bar{5}$ 0 11	<49	23
$\bar{5}$ 0 12	52	57
$\bar{5}$ 0 13	55	59
$\bar{5}$ 0 14	58	69
$\bar{5}$ 0 15	<60	1
$\bar{5}$ 0 16	<62	21
$\bar{5}$ 0 17	<64	52
$\bar{5}$ 0 18	126	96
$\bar{5}$ 0 19	187	189
$\bar{5}$ 0 20	<57	10
$\bar{5}$ 0 21	88	103
$\bar{5}$ 0 22	128	153
6 0 0	47	38
6 0 1	<36	24
6 0 2	<38	2
6 0 3	91	99
6 0 4	44	55
6 0 5	46	50
6 0 6	70	79
6 0 7	270	273
6 0 8	<56	16
6 0 9	<59	3
6 0 10	<60	23
6 0 11	<63	57
6 0 12	90	80
6 0 13	<63	18
6 0 14	<60	3
6 0 15	<55	1
6 0 16	384	413
6 0 17	<42	10
6 0 18	42	50
$\bar{6}$ 0 1	144	138
$\bar{6}$ 0 2	481	830*
$\bar{6}$ 0 3	139	157
$\bar{6}$ 0 4	119	138
$\bar{6}$ 0 5	92	82
$\bar{6}$ 0 6	77	65
$\bar{6}$ 0 7	104	122
$\bar{6}$ 0 8	78	81
$\bar{6}$ 0 9	103	108
$\bar{6}$ 0 10	180	188
$\bar{6}$ 0 11	136	125
$\bar{6}$ 0 12	<52	19
$\bar{6}$ 0 13	<54	12
$\bar{6}$ 0 14	<58	47
$\bar{6}$ 0 15	85	80
$\bar{6}$ 0 16	<62	31
$\bar{6}$ 0 17	64	60
$\bar{6}$ 0 18	78	63
$\bar{6}$ 0 19	87	96
$\bar{6}$ 0 20	<58	28
$\bar{6}$ 0 21	<52	0
$\bar{6}$ 0 22	<45	24
$\bar{6}$ 0 23	<36	54
7 0 0	74	61
7 0 1	79	76
7 0 2	172	155
7 0 3	87	75
7 0 4	<46	16
7 0 5	<49	31
7 0 6	<52	1
7 0 7	124	122
7 0 8	59	68
7 0 9	61	65
7 0 10	118	128
7 0 11	417	413
7 0 12	63	73
7 0 13	<61	42
7 0 14	<57	55
7 0 15	<52	16
7 0 16	63	67
7 0 17	49	75
$\bar{7}$ 0 1	43	56
$\bar{7}$ 0 2	<34	25
$\bar{7}$ 0 3	<33	7
$\bar{7}$ 0 4	<85	74
$\bar{7}$ 0 5	85	74
$\bar{7}$ 0 6	230	239
$\bar{7}$ 0 7	352	442
$\bar{7}$ 0 8	153	124
$\bar{7}$ 0 9	135	137
$\bar{7}$ 0 10	109	113
$\bar{7}$ 0 11	48	28
$\bar{7}$ 0 12	114	98
$\bar{7}$ 0 13	94	93
$\bar{7}$ 0 14	114	94
$\bar{7}$ 0 15	158	136
$\bar{7}$ 0 16	<62	46
$\bar{7}$ 0 17	<64	31
$\bar{7}$ 0 18	<64	10
$\bar{7}$ 0 19	<61	26
$\bar{7}$ 0 20	83	69
$\bar{7}$ 0 21	<54	15
$\bar{7}$ 0 22	<48	26
$\bar{7}$ 0 23	<39	0
$\bar{7}$ 0 24	<24	28
8 0 0	<40	1
8 0 1	<42	3
8 0 2	88	91
8 0 3	47	67
8 0 4	86	90
8 0 5	148	155
8 0 6	422	485
8 0 7	266	297
8 0 8	60	37
8 0 9	<62	11
8 0 10	<64	18
8 0 11	<64	36
8 0 12	<61	31
8 0 13	<59	29
8 0 14	53	37
8 0 15	181	183
8 0 16	114	131
8 0 17	21	29
$\bar{8}$ 0 1	54	38
$\bar{8}$ 0 2	205	182
$\bar{8}$ 0 3	165	168
$\bar{8}$ 0 4	73	55
$\bar{8}$ 0 5	<37	24
$\bar{8}$ 0 6	<38	39
$\bar{8}$ 0 7	<39	34
$\bar{8}$ 0 8	<41	9
$\bar{8}$ 0 9	<43	26
$\bar{8}$ 0 10	122	114
$\bar{8}$ 0 11	378	541
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$\bar{8}$ 0 13	77	40
$\bar{8}$ 0 14	81	87
$\bar{8}$ 0 15	85	76
$\bar{8}$ 0 16	<61	33
$\bar{8}$ 0 17	90	52
$\bar{8}$ 0 18	<64	44
$\bar{8}$ 0 19	76	50
$\bar{8}$ 0 20	168	166
$\bar{8}$ 0 21	<55	8
$\bar{8}$ 0 22	<49	22
$\bar{8}$ 0 23	<41	3
$\bar{8}$ 0 24	<29	3
9 0 0	75	79
9 0 1	203	197
9 0 2	395	513
9 0 3	132	105
9 0 4	74	70
9 0 5	78	80
9 0 6	58	34
9 0 7	74	49
9 0 8	108	85
9 0 9	90	75
9 0 10	168	148
9 0 11	191	170
9 0 12	<59	12
9 0 13	<54	2
9 0 14	<49	3
9 0 15	91	88
9 0 16	<28	32
$\bar{9}$ 0 1	59	40
$\bar{9}$ 0 2	<41	23
$\bar{9}$ 0 3	<39	11
$\bar{9}$ 0 4	<39	11
$\bar{9}$ 0 5	<39	21
$\bar{9}$ 0 6	<40	10
$\bar{9}$ 0 7	170	148
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$\bar{9}$ 0 9	<45	34
$\bar{9}$ 0 10	47	47
$\bar{9}$ 0 11	99	97
$\bar{9}$ 0 12	<53	43
$\bar{9}$ 0 13	<54	22
$\bar{9}$ 0 14	<58	16
$\bar{9}$ 0 15	60	71
$\bar{9}$ 0 16	356	415
$\bar{9}$ 0 17	64	84
$\bar{9}$ 0 18	<64	36
$\bar{9}$ 0 19	<62	0
$\bar{9}$ 0 20	<60	49
$\bar{9}$ 0 21	68	67
$\bar{9}$ 0 22	<50	20
$\bar{9}$ 0 23	<42	8
$\bar{9}$ 0 24	<32	19
10 0 0	46	61
10 0 1	<49	20
10 0 2	<51	36
10 0 3	65	88
10 0 4	68	61
10 0 5	101	108
10 0 6	291	295
10 0 7	<62	8
10 0 8	<64	4
10 0 9	<64	18
10 0 10	62	57
10 0 11	<60	66
10 0 12	<55	1
10 0 13	<50	15
10 0 14	<42	16
10 0 15	102	86
$\overline{10}$ 0 1	<45	1
$\overline{10}$ 0 2	<43	2
$\overline{10}$ 0 3	570	814*
$\overline{10}$ 0 4	<42	30
$\overline{10}$ 0 5	<42	4
$\overline{10}$ 0 6	<43	39
$\overline{10}$ 0 7	62	59
$\overline{10}$ 0 8	<45	2
$\overline{10}$ 0 9	66	47
$\overline{10}$ 0 10	48	42
$\overline{10}$ 0 11	<50	23
$\overline{10}$ 0 12	219	217
$\overline{10}$ 0 13	<55	14
$\overline{10}$ 0 14	<58	34
$\overline{10}$ 0 15	<60	57
$\overline{10}$ 0 16	139	141
$\overline{10}$ 0 17	<64	13
$\overline{10}$ 0 18	64	79
$\overline{10}$ 0 19	108	106
$\overline{10}$ 0 20	104	104
$\overline{10}$ 0 21	369	373
$\overline{10}$ 0 22	<51	17
$\overline{10}$ 0 23	76	61
$\overline{10}$ 0 24	<34	17
11 0 0	71	60
11 0 1	341	370
11 0 2	<54	21
11 0 3	<57	18
11 0 4	<59	21
11 0 5	<60	5
11 0 6	88	76
11 0 7	<64	15
11 0 8	<64	26
11 0 9	<62	39
11 0 10	134	108
11 0 11	<56	4
11 0 12	<51	44
11 0 13	44	48
11 0 14	99	123
$\overline{11}$ 0 1	84	65
$\overline{11}$ 0 2	66	52
$\overline{11}$ 0 3	92	80
$\overline{11}$ 0 4	120	103
$\overline{11}$ 0 5	111	106
$\overline{11}$ 0 6	163	160
$\overline{11}$ 0 7	207	247
$\overline{11}$ 0 8	337	446
$\overline{11}$ 0 9	<49	9
$\overline{11}$ 0 10	<50	25
$\overline{11}$ 0 11	<52	45
$\overline{11}$ 0 12	132	125
$\overline{11}$ 0 13	<56	2
$\overline{11}$ 0 14	<59	47
$\overline{11}$ 0 15	74	72
$\overline{11}$ 0 16	88	85
$\overline{11}$ 0 17	110	88
$\overline{11}$ 0 18	<64	10
$\overline{11}$ 0 19	<62	13
$\overline{11}$ 0 20	<60	25
$\overline{11}$ 0 21	160	176
$\overline{11}$ 0 22	<52	9
$\overline{11}$ 0 23	78	92
$\overline{11}$ 0 24	151	169
12 0 0	53	52
12 0 1	87	85
12 0 2	<57	27
12 0 3	59	50
12 0 4	61	66
12 0 5	147	136
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12 0 8	<62	15
12 0 9	<60	49
12 0 10	113	111
12 0 11	<52	15
12 0 12	55	67
12 0 13	116	112
$\overline{12}$ 0 1	52	42
$\overline{12}$ 0 2	<50	10
$\overline{12}$ 0 3	139	134
$\overline{12}$ 0 4	348	414
$\overline{12}$ 0 5	167	158
$\overline{12}$ 0 6	136	159
$\overline{12}$ 0 7	109	98
$\overline{12}$ 0 8	130	124
$\overline{12}$ 0 9	133	156
$\overline{12}$ 0 10	137	143
$\overline{12}$ 0 11	214	226
$\overline{12}$ 0 12	380	520
$\overline{12}$ 0 13	243	267
$\overline{12}$ 0 14	<59	10
$\overline{12}$ 0 15	<61	36
$\overline{12}$ 0 16	<63	10
$\overline{12}$ 0 17	110	132
$\overline{12}$ 0 18	<64	11
$\overline{12}$ 0 19	62	63
$\overline{12}$ 0 20	74	90
$\overline{12}$ 0 21	160	155
$\overline{12}$ 0 22	<52	27
$\overline{12}$ 0 23	<45	12
$\overline{12}$ 0 24	<36	32
$\overline{12}$ 0 25	<14	21
13 0 0	113	87
13 0 1	100	61
13 0 2	<60	10
13 0 3	62	60
13 0 4	<62	51
13 0 5	156	163
13 0 6	90	82
13 0 7	140	122
13 0 8	186	162
13 0 9	310	285
13 0 10	226	198
13 0 11	<45	13
13 0 12	<38	10
13 0 13	<23	26
$\overline{13}$ 0 1	55	55
$\overline{13}$ 0 2	76	70
$\overline{13}$ 0 3	64	69
$\overline{13}$ 0 4	<52	54
$\overline{13}$ 0 5	<51	44
$\overline{13}$ 0 6	<51	51
$\overline{13}$ 0 7	<52	16
$\overline{13}$ 0 8	200	212
$\overline{13}$ 0 9	219	229
$\overline{13}$ 0 10	107	92
$\overline{13}$ 0 11	95	85
$\overline{13}$ 0 12	57	70
$\overline{13}$ 0 13	83	68
$\overline{13}$ 0 14	85	52
$\overline{13}$ 0 15	62	69
$\overline{13}$ 0 16	141	130
$\overline{13}$ 0 17	325	393
$\overline{13}$ 0 18	64	99
$\overline{13}$ 0 19	<62	38
$\overline{13}$ 0 20	<60	32
$\overline{13}$ 0 21	<88	36
$\overline{13}$ 0 22	115	126
$\overline{13}$ 0 23	<45	13
$\overline{13}$ 0 24	<36	32
14 0 0	142	127
14 0 1	60	63
14 0 2	116	114
14 0 3	148	123
14 0 4	270	260
14 0 5	394	401
14 0 6	62	47
14 0 7	<60	10
14 0 8	<57	22
14 0 9	73	90
14 0 10	<43	10
14 0 11	<38	19
14 0 12	<25	1
$\overline{14}$ 0 1	81	70
$\overline{14}$ 0 2	<56	50
$\overline{14}$ 0 3	<55	10
$\overline{14}$ 0 4	122	92
$\overline{14}$ 0 5	108	82
$\overline{14}$ 0 6	<54	39
$\overline{14}$ 0 7	<54	33
$\overline{14}$ 0 8	<54	42
$\overline{14}$ 0 9	<55	4
$\overline{14}$ 0 10	<56	32
$\overline{14}$ 0 11	57	58
$\overline{14}$ 0 12	<59	8
$\overline{14}$ 0 13	253	301
$\overline{14}$ 0 14	106	84
$\overline{14}$ 0 15	<62	9
$\overline{14}$ 0 16	<64	17
$\overline{14}$ 0 17	<64	0
$\overline{14}$ 0 18	<64	8
$\overline{14}$ 0 19	<61	20
$\overline{14}$ 0 20	<59	34
$\overline{14}$ 0 21	<56	33
$\overline{14}$ 0 22	366	377
$\overline{14}$ 0 23	<45	22
$\overline{14}$ 0 24	36	49
$\overline{14}$ 0 25	<19	25
15 0 0	404	452
15 0 1	<62	13
15 0 2	<64	11
15 0 3	<64	17
15 0 4	<64	51
15 0 5	<61	37
15 0 6	<60	32
15 0 7	<56	21
15 0 8	73	63
15 0 9	<45	30
15 0 10	<39	19
15 0 11	<26	10
$\overline{15}$ 0 1	<60	35
$\overline{15}$ 0 2	<59	10
$\overline{15}$ 0 3	<59	28
$\overline{15}$ 0 4	<58	21
$\overline{15}$ 0 5	<57	16
$\overline{15}$ 0 6	<57	23
$\overline{15}$ 0 7	<57	54
$\overline{15}$ 0 8	<57	31
$\overline{15}$ 0 9	121	97
$\overline{15}$ 0 10	<58	23
$\overline{15}$ 0 11	<59	2
$\overline{15}$ 0 12	<60	6
$\overline{15}$ 0 13	<61	52
$\overline{15}$ 0 14	<61	28
$\overline{15}$ 0 15	<63	2
$\overline{15}$ 0 16	<64	46
$\overline{15}$ 0 17	<64	15
$\overline{15}$ 0 18	252	265
$\overline{15}$ 0 19	<61	3
$\overline{15}$ 0 20	<59	39
$\overline{15}$ 0 21	<55	51
$\overline{15}$ 0 22	<50	46
$\overline{15}$ 0 23	<44	23
$\overline{15}$ 0 24	36	64
16 0 0	<64	16
16 0 1	<64	25
16 0 2	<64	6
16 0 3	<63	22
16 0 4	<61	57
16 0 5	<59	8
16 0 6	<55	8
16 0 7	<51	11
16 0 8	<40	22
16 0 9	<38	34
16 0 10	<26	11
$\overline{16}$ 0 1	<62	48
$\overline{16}$ 0 2	<61	6
$\overline{16}$ 0 3	106	88
$\overline{16}$ 0 4	159	136
$\overline{16}$ 0 5	524	574
$\overline{16}$ 0 6	59	50
$\overline{16}$ 0 7	59	63
$\overline{16}$ 0 8	<59	8
$\overline{16}$ 0 9	<59	37
$\overline{16}$ 0 10	<60	21
$\overline{16}$ 0 11	<60	38
$\overline{16}$ 0 12	<61	58
$\overline{16}$ 0 13	<61	44
$\overline{16}$ 0 14	141	115
$\overline{16}$ 0 15	<64	2
$\overline{16}$ 0 16	<64	11
$\overline{16}$ 0 17	<64	10
$\overline{16}$ 0 18	88	83
$\overline{16}$ 0 19	<60	26
$\overline{16}$ 0 20	<58	7
$\overline{16}$ 0 21	76	69
$\overline{16}$ 0 22	120	105
$\overline{16}$ 0 23	207	197
$\overline{16}$ 0 24	<35	4
17 0 0	<64	20
17 0 1	<64	44
17 0 2	<62	26
17 0 3	<60	33
17 0 4	<58	27
17 0 5	<54	3
17 0 6	<50	11
17 0 7	<45	8
17 0 8	<37	39
17 0 9	<24	9
$\overline{17}$ 0 1	142	139
$\overline{17}$ 0 2	<64	49
$\overline{17}$ 0 3	<62	40
$\overline{17}$ 0 4	<62	28
$\overline{17}$ 0 5	62	53
$\overline{17}$ 0 6	84	75
$\overline{17}$ 0 7	86	72
$\overline{17}$ 0 8	183	160
$\overline{17}$ 0 9	280	265
$\overline{17}$ 0 10	306	316
$\overline{17}$ 0 11	<61	35
$\overline{17}$ 0 12	88	64
$\overline{17}$ 0 13	<63	22
$\overline{17}$ 0 14	78	93
$\overline{17}$ 0 15	<64	17
$\overline{17}$ 0 16	<64	0
$\overline{17}$ 0 17	<63	45
$\overline{17}$ 0 18	87	81
$\overline{17}$ 0 19	<59	40
$\overline{17}$ 0 20	<57	3
$\overline{17}$ 0 21	<53	2
$\overline{17}$ 0 22	<48	10
$\overline{17}$ 0 23	109	113
$\overline{17}$ 0 24	<33	17
18 0 0	<62	7
18 0 1	<61	28
18 0 2	<59	26
18 0 3	<57	21
18 0 4	65	69
18 0 5	<49	21
18 0 6	<43	5
18 0 7	<36	29
18 0 8	**	108
$\overline{18}$ 0 1	<64	39
$\overline{18}$ 0 2	90	65
$\overline{18}$ 0 3	63	55
$\overline{18}$ 0 4	<64	51
$\overline{18}$ 0 5	<64	2
$\overline{18}$ 0 6	118	109
$\overline{18}$ 0 7	77	77
$\overline{18}$ 0 8	88	84
$\overline{18}$ 0 9	<62	42
$\overline{18}$ 0 10	109	87
$\overline{18}$ 0 11	109	88
$\overline{18}$ 0 12	90	76
$\overline{18}$ 0 13	201	178
$\overline{18}$ 0 14	417	479
$\overline{18}$ 0 15	190	184
$\overline{18}$ 0 16	<63	13
$\overline{18}$ 0 17	<61	57
$\overline{18}$ 0 18	<60	42
$\overline{18}$ 0 19	100	108
$\overline{18}$ 0 20	<55	23
$\overline{18}$ 0 21	<51	11
$\overline{18}$ 0 22	46	50
$\overline{18}$ 0 23	125	105
$\overline{18}$ 0 24	<30	8
19 0 0	95	76
19 0 1	92	83
19 0 2	110	102
19 0 3	163	140
19 0 4	94	68
19 0 5	151	140
19 0 6	150	150
$\overline{19}$ 0 1	107	95
$\overline{19}$ 0 2	<62	33
$\overline{19}$ 0 3	<64	37
$\overline{19}$ 0 4	<64	45
$\overline{19}$ 0 5	<64	40

* Affected by extinction. ** Unobservable.

Table 5 (*cont.*)

hkl	F_o	$\lvert F_c\rvert$
$\overline{19}$ 0 6	<64	46
$\overline{19}$ 0 7	<64	36
$\overline{19}$ 0 8	<64	34
$\overline{19}$ 0 9	<64	33
$\overline{19}$ 0 10	<64	62
$\overline{19}$ 0 11	90	61
$\overline{19}$ 0 12	<64	44
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$\overline{14}$ 1 18	325	366
$\overline{14}$ 1 19	64	70
$\overline{14}$ 1 20	61	76
$\overline{14}$ 1 21	<56	43
$\overline{14}$ 1 22	80	96
$\overline{14}$ 1 23	42	32
15 1 0	68	68
15 1 1	<67	42
15 1 2	116	94
15 1 3	142	128
15 1 4	402	362
15 1 5	202	186
15 1 6	83	60
15 1 7	<57	20
15 1 8	<51	29
15 1 9	108	112
$\overline{15}$ 1 1	<63	50
$\overline{15}$ 1 2	<62	39
$\overline{15}$ 1 3	62	70
$\overline{15}$ 1 4	108	141
$\overline{15}$ 1 5	116	134
$\overline{15}$ 1 6	<62	42
$\overline{15}$ 1 7	<62	45
$\overline{15}$ 1 8	<62	30
$\overline{15}$ 1 9	<62	26
$\overline{15}$ 1 10	<63	29
$\overline{15}$ 1 11	<64	48
$\overline{15}$ 1 12	65	61
$\overline{15}$ 1 13	123	150
$\overline{15}$ 1 14	<67	41
$\overline{15}$ 1 15	<63	22
$\overline{15}$ 1 16	<63	27
$\overline{15}$ 1 17	<67	24
$\overline{15}$ 1 18	132	132
$\overline{15}$ 1 19	<63	25
$\overline{15}$ 1 20	60	40
$\overline{15}$ 1 21	162	150
$\overline{15}$ 1 22	420	484
$\overline{15}$ 1 23	156	138
16 1 0	364	290
16 1 1	<61	42
16 1 2	<66	30
16 1 3	<65	21
16 1 4	90	98
16 1 5	<60	27
16 1 6	<56	28
16 1 7	<50	28
16 1 8	98	81
16 1 9	96	86
$\overline{16}$ 1 1	254	210
$\overline{16}$ 1 2	122	96
$\overline{16}$ 1 3	114	80
$\overline{16}$ 1 4	66	70
$\overline{16}$ 1 5	64	62
$\overline{16}$ 1 6	64	46
$\overline{16}$ 1 7	64	64
$\overline{16}$ 1 8	79	100
$\overline{16}$ 1 9	92	130
$\overline{16}$ 1 10	<64	50
$\overline{16}$ 1 11	<65	26
1 12	<66	30
1 13	<67	24
$\overline{16}$ 1 14	<67	40
$\overline{16}$ 1 15	<67	22
$\overline{16}$ 1 16	<67	21
$\overline{16}$ 1 17	<66	21
$\overline{16}$ 1 18	66	74
$\overline{16}$ 1 19	<62	20
$\overline{16}$ 1 20	<59	24
$\overline{16}$ 1 21	<54	42
$\overline{16}$ 1 22	84	86
$\overline{16}$ 1 23	78	102
17 1 0	<63	32
17 1 1	<66	21
17 1 2	<64	28
17 1 3	76	80
17 1 4	198	152
17 1 5	<54	27
17 1 6	<48	18
17 1 7	<42	21
17 1 8	82	118
$\overline{17}$ 1 1	<67	48
$\overline{17}$ 1 2	<67	22
$\overline{17}$ 1 3	<67	38
$\overline{17}$ 1 4	<67	29
$\overline{17}$ 1 5	496	446
$\overline{17}$ 1 6	124	106
$\overline{17}$ 1 7	<66	33
$\overline{17}$ 1 8	<66	51
$\overline{17}$ 1 9	<66	35
$\overline{17}$ 1 10	<66	28
$\overline{17}$ 1 11	<67	41
$\overline{17}$ 1 12	<67	25
$\overline{17}$ 1 13	66	56
$\overline{17}$ 1 14	172	216
$\overline{17}$ 1 15	<67	22
$\overline{17}$ 1 16	<66	22
$\overline{17}$ 1 17	<65	26
$\overline{17}$ 1 18	<63	34
$\overline{17}$ 1 19	<61	24
$\overline{17}$ 1 20	<57	35

Table 5 (*cont.*)

hkl	F_o	$\lvert F_c\rvert$
$\overline{17}$ 1 21	<52	24
$\overline{17}$ 1 22	<46	37
$\overline{17}$ 1 23	67	65
18 1 0	<64	28
18 1 1	<62	32
18 1 2	<61	24
18 1 3	<58	64
18 1 4	<52	36
$\overline{18}$ 1 1	230	186
$\overline{18}$ 1 2	<67	21
$\overline{18}$ 1 3	<67	30
$\overline{18}$ 1 4	<67	32
$\overline{18}$ 1 5	<67	28
$\overline{18}$ 1 6	<67	22
$\overline{18}$ 1 7	<67	28
$\overline{18}$ 1 8	<67	37
$\overline{18}$ 1 9	<67	32
$\overline{18}$ 1 10	454	426
$\overline{18}$ 1 11	<67	41
$\overline{18}$ 1 12	67	58
$\overline{18}$ 1 13	<67	56
$\overline{18}$ 1 14	<67	35
$\overline{18}$ 1 15	66	53
$\overline{18}$ 1 16	<65	60
$\overline{18}$ 1 17	64	70
$\overline{18}$ 1 18	<62	20
$\overline{18}$ 1 19	118	122
$\overline{18}$ 1 20	<54	22
$\overline{18}$ 1 21	<50	18
$\overline{18}$ 1 22	<50	21
$\overline{18}$ 1 23	72	64
19 1 0	<61	20
19 1 1	<58	52
19 1 2	88	78
19 1 3	470	464
19 1 4	46	66
$\overline{19}$ 1 1	<63	42
$\overline{19}$ 1 2	<65	38
$\overline{19}$ 1 3	<66	29
$\overline{19}$ 1 4	<67	36
$\overline{19}$ 1 5	94	70
$\overline{19}$ 1 6	242	216
$\overline{19}$ 1 7	<67	22
$\overline{19}$ 1 8	<67	34
$\overline{19}$ 1 9	<67	22
$\overline{19}$ 1 10	<67	29
$\overline{19}$ 1 11	<67	26
$\overline{19}$ 1 12	<67	21
$\overline{19}$ 1 13	94	89
$\overline{19}$ 1 14	210	184
$\overline{19}$ 1 15	354	370
$\overline{19}$ 1 16	102	76
$\overline{19}$ 1 17	108	96
$\overline{19}$ 1 18	60	58
$\overline{19}$ 1 19	<56	36
$\overline{19}$ 1 20	118	92
$\overline{19}$ 1 21	90	70
$\overline{19}$ 1 22	110	104
20 1 0	98	76
20 1 1	<52	30
20 1 2	<48	40
20 1 3	<42	20
20 1 4	<34	18
$\overline{20}$ 1 1	220	208
$\overline{20}$ 1 2	310	308
$\overline{20}$ 1 3	110	108
$\overline{20}$ 1 4	90	84
$\overline{20}$ 1 5	<64	48
$\overline{20}$ 1 6	<66	34
$\overline{20}$ 1 7	<66	22
$\overline{20}$ 1 8	<66	25
$\overline{20}$ 1 9	<66	30
$\overline{20}$ 1 10	162	136
$\overline{20}$ 1 11	124	100
$\overline{20}$ 1 12	<66	29
$\overline{20}$ 1 13	<64	46
$\overline{20}$ 1 14	<64	36
$\overline{20}$ 1 15	64	72
$\overline{20}$ 1 16	<62	22
$\overline{20}$ 1 17	<60	32
$\overline{20}$ 1 18	116	128
$\overline{20}$ 1 19	292	279
$\overline{20}$ 1 20	200	175
$\overline{20}$ 1 21	<44	29
$\overline{20}$ 1 22	64	40
$\overline{20}$ 1 23	<28	33
21 1 0	100	84
21 1 1	84	73
21 1 2	142	117
21 1 3	98	98
$\overline{21}$ 1 1	<52	39
$\overline{21}$ 1 2	<56	38
$\overline{21}$ 1 3	84	74
$\overline{21}$ 1 4	<61	43
$\overline{21}$ 1 5	138	118
$\overline{21}$ 1 6	434	432
$\overline{21}$ 1 7	196	200
$\overline{21}$ 1 8	<64	52
$\overline{21}$ 1 14	<62	41
$\overline{21}$ 1 15	194	191
$\overline{21}$ 1 16	<58	44
$\overline{21}$ 1 17	<56	19
$\overline{21}$ 1 18	<54	38
$\overline{21}$ 1 19	50	50
$\overline{21}$ 1 20	66	80
$\overline{22}$ 1 0	<41	38
$\overline{22}$ 1 1	<46	22
$\overline{22}$ 1 2	166	128
$\overline{22}$ 1 3	74	70
$\overline{22}$ 1 4	<56	44
$\overline{22}$ 1 5	<58	50
$\overline{22}$ 1 6	<58	38
$\overline{22}$ 1 7	<60	35
$\overline{22}$ 1 8	<60	35
$\overline{22}$ 1 9	<61	23
$\overline{22}$ 1 10	61	74
$\overline{22}$ 1 11	402	430
$\overline{22}$ 1 12	<60	26
$\overline{22}$ 1 13	<60	36
$\overline{22}$ 1 14	<58	20
$\overline{22}$ 1 15	<58	32
$\overline{22}$ 1 16	56	56
$\overline{22}$ 1 17	<56	26
$\overline{22}$ 1 18	<50	20
$\overline{22}$ 1 19	<46	18
$\overline{22}$ 1 20	146	142
$\overline{23}$ 1 2	<40	34
$\overline{23}$ 1 3	<45	18
$\overline{23}$ 1 4	<48	18
$\overline{23}$ 1 5	<51	42
$\overline{23}$ 1 6	<53	36
$\overline{23}$ 1 7	212	154
$\overline{23}$ 1 8	<56	23
$\overline{23}$ 1 9	<56	22
$\overline{23}$ 1 10	<56	20
$\overline{23}$ 1 11	<56	30
$\overline{23}$ 1 12	<56	26
$\overline{23}$ 1 13	<56	20
$\overline{23}$ 1 14	78	76
$\overline{23}$ 1 15	93	102
$\overline{23}$ 1 16	400	430
$\overline{23}$ 1 17	49	52
$\overline{23}$ 1 18	56	72
$\overline{23}$ 1 19	<42	18
$\overline{23}$ 1 20	51	50
$\overline{24}$ 1 3	126	91
$\overline{24}$ 1 4	<40	18
$\overline{24}$ 1 5	<42	24
$\overline{24}$ 1 6	<46	30
$\overline{24}$ 1 7	<48	27
$\overline{24}$ 1 8	<49	26
$\overline{24}$ 1 9	<51	32
$\overline{24}$ 1 10	<51	25
$\overline{24}$ 1 11	<51	36
$\overline{24}$ 1 12	218	178
$\overline{24}$ 1 13	50	40
$\overline{24}$ 1 14	48	36
$\overline{24}$ 1 15	48	43
$\overline{24}$ 1 16	56	70
$\overline{24}$ 1 17	74	45
$\overline{24}$ 1 18	68	67
$\overline{24}$ 1 19	132	146
$\overline{25}$ 1 5	<31	17
$\overline{25}$ 1 6	<36	31
$\overline{25}$ 1 7	88	66
$\overline{25}$ 1 8	122	82
$\overline{25}$ 1 9	<43	21
$\overline{25}$ 1 10	<44	23
$\overline{25}$ 1 11	<44	19
$\overline{25}$ 1 12	<44	21
$\overline{25}$ 1 13	<44	38
$\overline{25}$ 1 14	44	44
$\overline{25}$ 1 15	<41	27
$\overline{25}$ 1 16	42	78
$\overline{25}$ 1 17	88	138
$\overline{26}$ 1 8	70	46
$\overline{26}$ 1 9	<31	24
$\overline{26}$ 1 10	34	56
$\overline{26}$ 1 11	<34	24
$\overline{26}$ 1 12	122	92
$\overline{26}$ 1 13	49	40

to be close to 0 and $\frac{1}{2}$ for each atom. Cruickshank, Lynton & Barclay (1962), in an exhaustive analysis of thortveitite, $Sc_2Si_2O_7$, a structure with a similar ambiguity of space group, found that genuine small departures of the atoms from special positions were exceedingly difficult to recognize. This difficulty is almost universal in octahedral oxide structures with an axis of symmetry of length 3·8 Å, and we have simply tried to distinguish between the two alternatives with no attempt to refine y for any atom.

Two sets of hll structure factors left no doubt that Nb_2O_5 is a polar structure, the reliability index for $P2$ being 12·1% and for $P2/m$ 15·8%. Estimations of accuracy in the x and z coordinates were made from the r.m.s. values of slopes parallel to a and c in the final difference synthesis estimated in the regions of the map where atoms did not occur. In view of the uncertainties we have outlined these must necessarily be optimistic, but are included in Table 2 containing the fractional atomic parameters. Interatomic distances are given in Tables 3 and 4, a list of observed and calculated structure factors in Table 5, and the structure is illustrated by a ball-and-spoke drawing in Fig. 8.

Discussion

The ideal or undistorted structure of Nb_2O_5 can be broken up into two groups of octahedra, each being a fragment of the ReO_3 type (Figs. 4(*a*) and 4(*b*)). These are joined up by edge sharing into a three-dimensional structure leaving tetrahedral positions where one niobium atom out of the twenty-eight in the unit cell is situated in an ordered way (Fig. 9).

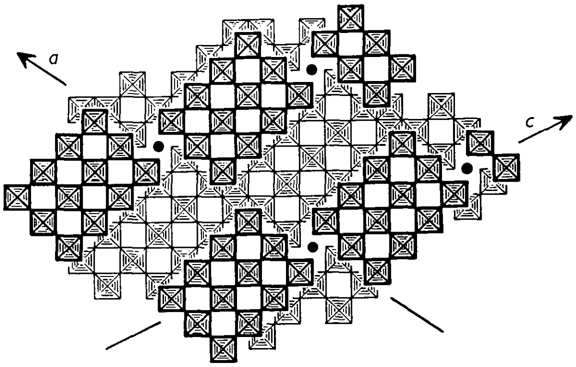

Fig. 9. Nb_2O_5 drawn as idealized octahedra. The lighter form the 3 × 5 blocks of Fig. 4(*a*), the heavier are the 3 × 4 blocks of Fig. 4(*b*). The black circles are the atoms Nb(1) in tetrahedral positions and outline the unit cell in projection.

The metal atoms of octahedra joined by edges are repelled by each other, and the structure is not ideal. Although individual Nb–O bonds vary between 1·73 and 2·26 Å, the average of the six bonds for each metal lies between 1·96 and 2·02 Å, with an average of 1·99 Å for the eighty-four independent determinations. The oxygen–oxygen distances also have a wide range, and two atoms forming a common octahedral edge may be separated by as little as 2·3 Å to ensure Nb–O bonds of reasonable length. In other words if metals repel each other, the overlying oxygen atoms are squashed together. Similar short distances were reported for $TiNb_2O_7$ and $Ti_2Nb_{10}O_{29}$ (Wadsley, 1961), and also in $Mo_{17}O_{47}$ (Kihlborg, 1960) where they are associated with an unusual coordination for molybdenum. In Nb_2O_5 the average O–O distance is 2·80 Å, and this leads to a formal ionic radius of 0·59 Å for Nb^{5+}.

The tetrahedral Nb–O distances, given in Table 4, are very short, and no similar case has been reported. The y parameter of Nb(1) was arbitrarily assigned a value of $\frac{1}{4}$, but two of the bonds would be lengthened and two shortened if this were changed. O(19) and O(21) appear to have been correctly placed, and there is some evidence in the difference synthesis of anisotropic thermal motions of these atoms. There is good reason to believe that tetrahedral coordination is also present in the structures of other niobium oxides, some of which may be easier than the present one to refine in more detail.

Related structures

Polymorphs of Nb_2O_5

Niobium pentoxide crystallizes in several different modifications.* The orthorhombic low-temperature form, identified originally by Brauer (1941), has a sub-cell similar in some ways to α-UO_3 (Holser, 1956; Calvert & Draper, 1962) and not to the present structure. It is likely, however, that one or more varieties directly related to the high-temperature form, and very difficult to distinguish from it, could arise from changes associated with the ions in the tetrahedral positions. Firstly, the structure will become non-polar if these atoms are distributed statistically over the two sites illustrated by Fig. 7 in the space group $P2/m$. Secondly, the tetrahedral niobium could perhaps be shifted to one or more of the octahedral positions, p, q, r and s of Fig. 4(a) and (b). These possibilities could result from quenching below the melting point.

Homologues of Nb_2O_5

Two kinds of solid solution can be recognized in binary and ternary phase systems. The first, arising from the substitution in the solid of an atom by another of similar size and with the same valency and coordination number, is relatively straightforward. On the other hand the number of atoms of one kind or another in the unit cell will change if the compound is partly oxidized or reduced, or if one element is replaced by another of different valency. The unit cell contents of this second kind of solid solution, a non-stoichiometric compound, can be evaluated from the density. To a first approximation the phase may then have an excess of one atom occupying interstitial positions within it, or a deficit where some atoms are assumed to be missing; in both cases structure, as well as composition, is a continuous variable.

Evidence for compounds with complex but invariant formulae, and comprising a family of equilibrium phases within the composition limits of a non-stoichiometric compound, is now accumulating. In any one system, these ordered structural homologues all contain the same kind of 'defect' which may or may not agree with the simpler interpretation of vacancies and interstitials, but they are possibly related to the solid solution by an order–disorder transition at some particular temperature (Wadsley, 1963).

Brauer (1941) proposed that Nb_2O_5 had a range of composition at high temperature extending perhaps to $NbO_{2.40}$, but Norin & Magnéli (1960) more recently prepared and identified the two previously unsuspected compounds $NbO_{2.46}$ and $NbO_{2.40}$. If we assume the first is a structural homologue of Nb_2O_5, its symmetry and unit cell dimensions, as well as those of a hypothetical third phase $NbO_{2.375}$, can be predicted as the members $n=7$ and 5 of a series with the general formula $Nb_{3n+1}O_{8n-2}$ and the space group $P2$.

A structure for $NbO_{2.46}$, or more correctly $Nb_{22}O_{54}$ ($n=7$), can be derived from the pentoxide ($n=9$) by omitting six niobium atoms and sixteen oxygen atoms from the unit cell. These six octahedra are a fragment of an S unit (Fig. 3), and the remainder of the octahedra join up as before with edges in common, while the tetrahedral niobium atoms, in projection, are still at the corners of the unit cell (Fig. 10). The ReO_3-type blocks are again of two sizes, 3 × 4 and 3 × 3, both infinite in extension. $NbO_{2.375}$ (or $Nb_{16}O_{38}$, the member $n=5$) is derived in exactly the same way; two S fragments are missing from Nb_2O_5, and the ReO_3-type blocks are reduced to 3 × 3 and 3 × 2 octahedra.

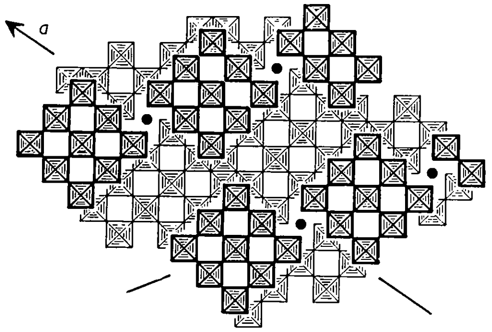

Fig. 10. Possible structure of $Nb_{22}O_{54}$ (*cf.* Fig. 9). ReO_3-type blocks are 3 × 3 and 3 × 4, with one tetrahedral metal at the origin in projection.

Norin & Magnéli's monoclinic unit cell for $Nb_{22}O_{54}$ had the dimensions

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* Roman or Greek letter prefixes to distinguish between them are used in different ways by different authors.

Table 6. *Predicted unit cell dimensions of 'homologues'* $Nb_{3n+1}O_{8n-2}$

System: monoclinic. Space group: *P*2 (or *Pm*)

n in formula $Nb_{3n+1}O_{8n-2}$	Possible compound	*a*	*b*	*c*	β
9	$Nb_{28}O_{70}$ ($=Nb_2O_5$)	21·16 Å	3·822 Å	19·35 Å	119·8°
7	$Nb_{22}O_{54}$ ($=NbO_{2\cdot454}$)	21·2	3·82	15·6	124·5
5	$Nb_{16}O_{38}$ ($=NbO_{2\cdot375}$)	21·2	3·82	12·0	132·2

$$a=18{\cdot}86,\ b=3{\cdot}822,\ c=15{\cdot}75\ \text{Å},\ \beta=102^\circ\ 11'.$$

This can be changed by the axial transform $101/010/00\bar{1}$ to

$$a=21{\cdot}86,\ b=3{\cdot}822,\ c=15{\cdot}75\ \text{Å},\ \beta=122^\circ\ 30',$$

and by comparison with Table 6 it appears that this phase could indeed be a homologue of Nb_2O_5 with a structure closely related to Fig. 10, if not identical with it. As yet there is no evidence that $Nb_{16}O_{38}$ exists. Homologues $Nb_{3n+1}O_{8n-2}$ based upon this principle will arise only when *n* is odd, as significant structural changes are present when *n* is even (Roth & Wadsley, 1964).

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The Crystal Structure of 3,3,4,4-Tetrahydrofurantetrol (An Application of Vector Verification)

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A three-dimensional crystal structure analysis of 3,3,4,4-tetrahydrofurantetrol has determined that this molecule exists in a twisted configuration (44° ring twist), that the space group is $P\bar{4}2_1c$ with eight molecules per unit cell, and that the molecules lie in layers which are held together and interconnected by hydrogen bonds.

The trial model was obtained by a new method called vector verification. The method systematically checks, by applying space group symmetry and other conditions, each point in a three-dimensional grid in electron density space. At each grid point, a series of vectors is computed and compared with the observed Patterson function, and only if the vectors exist in the Patterson map can the grid point be considered as a possibility for an atomic position. The trial model was refined using full matrix least squares to a final model having an agreement index of 0·11.

Introduction

Spectrograms in the ultraviolet, infrared and nuclear magnetic resonance reveal stabilization of the heterocycle, tetrahydro-3,4-furandione, in the dione form with no evidence of enolization. The dione rapidly adds water or alcohol and tends to exist with one or both ketone groups doubly substituted as a tetrol, hydroxydioxane, hydroxydioxolane or hemiketal (Kendall & Hajos, 1960). The subject of this investigation is the tetrol (3,3,4,4-tetrahydrofurantetrol). A small well-formed crystal was carefully selected and, because of instability in contact with air, was sealed in a glass capillary tube.