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The Crystal Structure of $Nb_{12}O_{29}$(o-rh)

ROLF NORIN

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden

The crystal structure of $Nb_{12}O_{29}$(o-rh) has been studied using single-crystal X-ray methods. The unit cell has the dimensions:

$$a = (28.90 \pm 0.02)\ \text{Å}$$
$$b = (3.835 \pm 0.002)\ \text{Å}$$
$$c = (20.72 \pm 0.02)\ \text{Å}$$
$$V = 2296\ \text{Å}^3$$

and contains 4 units of $Nb_{12}O_{29}$. The structure proposed has the symmetry *Amma* and may be described in terms of regular NbO_6-octahedra, which share edges and corners to form an infinite three-dimensional framework.

A monoclinic modification of $Nb_{12}O_{29}$ has been identified from its powder pattern.

The present study has been carried out in continuation of previous work in the field of the structural chemistry of niobium oxides conducted by members of this research group [1–3]. A phase analysis of this metal oxide system [2] performed within this research programme has demonstrated the existence of a few previously unknown phases at high contents of oxygen. The present structure investigation is concerned with an oxide obtained from the "phase" reported to form at the approximate composition $NbO_{2.40}$[2]. Actually all the samples of this composition hitherto prepared have invariably been found to contain two different phases which, however, both ideally have the composition $Nb_{12}O_{29}$ ($NbO_{2.42}$).

In the course of the present study it was found that the phase investigated is isostructural with the mixed titanium niobium oxide phase $Ti_2Nb_{10}O_{29}$ (o-rh) recently reported by Wadsley [4]. The powder pattern of the phase coexisting with the former indicates that it is isostructural with the monoclinic modification of $Ti_2Nb_{10}O_{29}$(mon).

EXPERIMENTAL

The crystals used in this study were prepared in two different ways. In the first preparation an appropriate mixture of Nb_2O_5 (purity 99.9 %) and NbO_2 (prepared by reducing Nb_2O_5 in a stream of hydrogen) was pressed into small tablets and melted in an electric arc furnace in an argon atmosphere. The powdered sample was then tempered 14 days in evacuated silica tubes at 1100°C. In the second preparation the oxide mixture was not melted but tempered in the same way for 60 days. The Guinier powder patterns of the two preparations were identical, but in the first case the crystals were bigger and better suited for single crystal work. The crystals of the samples $NbO_{2.40}$ were black and formed aggregates which were easy to cleave into small rods.

To determine the oxygen content weighed samples were heated in a stream of oxygen at 700°C to constant weight, forming Nb_2O_5. No deviation was found from the synthesis compositions of the samples.

Table 1. Powder photograph of the sample $NbO_{2.40}$ containing $Nb_{12}O_{29}$(o-rh) and $Nb_{12}O_{29}$(mon). Cu$K\alpha$ radiation. $\lambda_{CuK\alpha} = 1.5418$ Å.

		$Nb_{12}O_{29}$(o-rh)			$Nb_{12}O_{29}$(mon)		
I obs	$\sin^2\Theta \times 10^5$ obs	$h\,k\,l$	$\sin^2\Theta \times 10^5$ calc	$p\,F^2$ calc	$h\,k\,l$	$\sin^2\Theta \times 10^5$ calc	$p\,F^2$ calc
w	286	2 0 0	285	1	1 0 0	285	1 *
vw	603				1 0 $\bar{2}$	601	2
vw	625	1 0 2	625	3			
vvw	652				0 0 2	652	1
w	1143	4 0 0	1139	4	2 0 0	1141	1 *
st	2221	0 0 4	2214	18	1 0 $\bar{4}$	2221	26 *
vvw	2281	1 0 4	2285	5			
m	2566	6 0 0	2563	17	3 0 0	2567	5 *
vst	4185	0 1 1	4177	51			
vst	4205				0 1 1	4205	19
m	4251	1 1 1	4248	77			
w	4319				1 1 $\bar{1}$	4322	6
vvst	4563	8 0 0	4557	127	4 0 0	4563	27 *
vvw	4662				1 1 1	4658	5
vvw	4819	3 1 1	4818	12			
vst	4993	0 0 6	4982	63	2 0 $\bar{6}$	4993	2 *
m	5063	1 0 6	5063	34			
st	5289	0 1 3	5285	31	1 1 $\bar{3}$	5290	7 *
vvw	5678				2 1 1	5682	5
vvw	6378				5 0 $\bar{4}$	6378	10
vvw	6760	8 0 4	6771	7			
vw	7119	10 0 0	7120	11	5 0 0	7130	2 *
vw	7271				3 1 1	7276	11
vvst	7575	1 1 5	7570	123	1 1 $\bar{5}$	7562 }	36 *
					2 1 $\bar{5}$	7578 }	15 *
vw	7668	7 1 1	7666	73			
vw	8090				4 1 $\bar{1}$	8096	31
w	8137	3 1 5	8140	17	3 1 $\bar{5}$	8164	26 *
vvw	8472	7 0 6	8471	31			
vvw	8740	8 1 1	8734	40			
vvw	8892				6 0 $\bar{2}$	8903	1
vvw	8915	1 0 8	8929	10			
vw	9039				2 0 6	9025	5
w	9269	5 1 5	9282	17	1 1 5	9242	22 *
vvw	9426				4 1 1	9440	6
vw	9535	8 0 6	9539	34			

* Overlap.

The density of the crystals was determined from the apparent loss of weight in benzene. It was found to be (4.62 ± 0.02) g cm^{-3}.

UNIT CELL AND SPACE GROUP

A rod-shaped crystal about 0.3 mm in length and 0.05 mm in diameter was split from a larger one. It was rotated around the rod axis and rotation and Weissenberg photographs ($h0l - h2l$) were taken with CuK radiation. With another crystal, roughly cubic in shape and with an edge of about 0.2 mm, rotation and Weissenberg photographs ($0kl$) were taken. It was concluded that the crystals have orthorhombic symmetry and that the dimensions of the unit cell are about 28.9 Å, 3.84 Å and 20.7 Å. The reflexions were recorded photographically with the multiple film technique and the relative intensities were estimated visually by comparison with an intensity scale, obtained by photographing a suitable reflexion with different exposure times. Lorentz and polarisation factors according to Lu[5] were applied to the observed intensities. The effect of temperature factor was found to be negligible when calculated by the ordinary procedure. Probably it cancels out with the specimen absorbtion.

More accurate values for the unit cell dimensions were calculated from a powder photograph, taken with Cu$K\alpha$ radiation in a Guinier focusing camera. KCl was used as an internal standard (see Table 1). In addition to the lines due to $Nb_{12}O_{29}$ (o-rh), the photograph contained many extra ones that will be discussed later in this paper. The following cell dimensions were obtained:

$$a = (28.90 \pm 0.02) \text{ Å}$$
$$b = (3.835 \pm 0.002) \text{ Å}$$
$$c = (20.72 \pm 0.02) \text{ Å}$$
$$V = 2296 \text{ Å}^3.$$

The value found for the density of the heterogeneous sample suggests that there are 4 formula units in the unit cell. The reflexions systematically absent are:

$$hkl \text{ with } k + l = \text{odd}$$
$$hk0 \text{ with } h = \text{odd}$$

This is characteristic of the three space groups No. 63 *Amma*, No. 40 *Am*2*a* and No. 36 $A2_1ma$.*

At first only the space group of highest symmetry (*Amma*) was considered. Since it was possible to find a plausible structure assuming this space group, the low symmetry ones (*Am*2*a* and $A2_1ma$) were not taken into account. In space group No. 63 *Amma* the following point positions are possible:

* To facilitate a comparison with related substances, the space groups have been given in orientations differing from those given in the *International Tables for X-ray Crystallography* [6].

$(0,0,0;\ 0,\frac{1}{2},\frac{1}{2})\ +$

4(*a*): $0,0,0;\ \frac{1}{2},0,0.$

4(*b*): $0,0,\frac{1}{2};\ \frac{1}{2},0,\frac{1}{2}.$

4(*c*): $\pm\ (\frac{1}{4},0,z).$

8(*d*): $0,\frac{1}{4},\frac{1}{4};\ 0,\frac{1}{4},\frac{3}{4};\ \frac{1}{2},\frac{1}{4},\frac{1}{4};\ \frac{1}{2},\frac{1}{4},\frac{3}{4}.$

8(*e*): $\pm\ (0,y,0);\ \pm\ (\frac{1}{2},y,0).$

8(*f*): $\pm\ (x,0,z);\ \pm\ (\frac{1}{2}-x,0,z).$

8(*g*): $\pm\ (\frac{1}{4},y,z);\ \pm\ (\frac{1}{4},\bar{y},z).$

16(*h*): $\pm\ (x,y,z);\ \pm\ (\bar{x},y,\bar{z});\ \pm\ (\frac{1}{2}-x,y,z);\ \pm\ (\frac{1}{2}+x,y,\bar{z},).$

POSITIONS OF THE ATOMS

The fact that the values of $[F(h0l)]^2$ were found to be identical with those of $[F(h2l)]^2$ (with due regard for observational errors) indicated that all the atoms of the structure are situated in, or very close to, two planes normal to the y axis and at a distance of $b/2$ Å apart.

In order to find the niobium positions, the Patterson projection $P(upw)$ and the Harker sections $P(u0w)$ and $P(u\frac{1}{2}w)$ were calculated from the $|F|^2$ values of the layer lines $h0l$ and $h1l$.* The strongest maxima in $P(upw)$ (Fig. 1) are arranged in rows parallell to the axes, and situated close to the corners of square nets with an edge length of about 3.8 Å, which is also the length of the b axis. This is in conformity with the distribution of a considerable number of the niobium atoms in approximately the same way as the metal atoms of a structure of the ReO_3-type. There are also peaks corresponding to vectors with a length of $(n \times 3.8 + 2.9)$ Å where $n = 0, 1, 2, 3$. The Harker sections (Fig. 2 *a* & *c*) indicate that the atoms giving rise to these vectors are situated in planes $b/2$ Å apart. Furthermore, $a = 28.9$ Å $\approx$ $\approx (6 \times 3.8 + 2 \times 2.9)$ Å and $c = 20.7$ Å $\approx (4 \times 3.8 + 2 \times 2.9)$ Å.

All this leads to the suggestion that the structure is built up of sheets of NbO_6-octahedra sharing corners, the sheets being normal to the y axis and extending four octahedra in the x direction and three in the z direction (Fig. 3*a*). The unit cell contains four such sheets, two in each of the planes $b/2$ Å apart, the sheets being joined by octahedra edge sharing.

Three different possible arrangements result, and it is a matter of trial and error to find out which of these is the right one. An idealized picture of the structure thus arrived at is given in Fig. 3 *b*. It is built up of niobium atoms in 8(*f*) positions and oxygen atoms in 4(*c*) and 8(*f*) positions of space group *Amma*. From the Patterson projection $P(upw)$ x and z parameters of the niobium positions could be determined. As the scattering factors for the metal atoms are dominant, the signs of the F-values could with few exceptions be determined from the contributions of these atoms only. In this way the electron density projection $\varrho(xpz)$ was calculated * (Fig. 4). In addition to the high metal atom peaks there are much lower ones midway

* The electronic computer BESK was used to calculate [7,8] the Patterson and electron density projections and the Harker sections using the atomic scattering factors given by Vand, Eiland and Pepinsky [10].

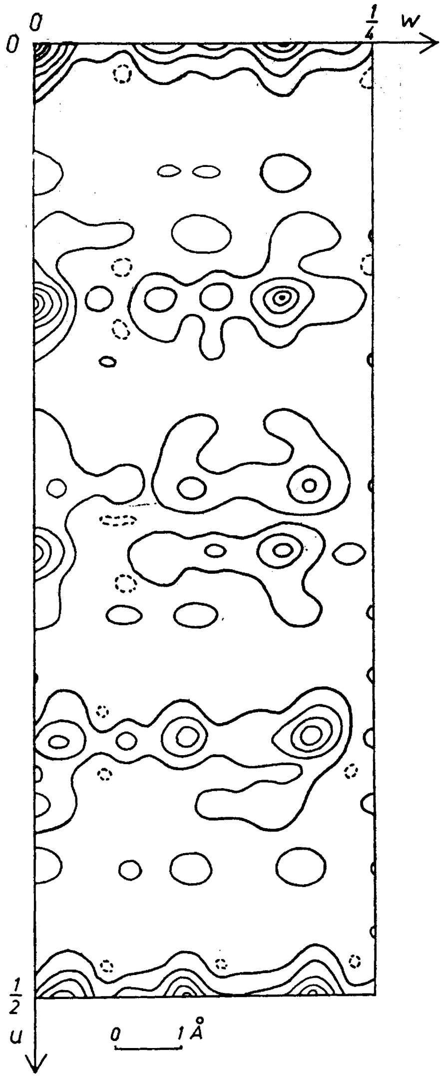


Fig. 1. The Patterson function $P(upw)$. Dashed lines indicate negative values.

between those niobium peaks that are 3.8 Å apart, indicating the positions of the oxygen atoms linking the octahedra together by corners. Some other maxima are supposed to be due to termination effects, typical of structures of this kind [9]. In order to trace the positions of the oxygen atoms situated above and below the niobium atoms, an electron density projection $\varrho(xpz)$ with the metal atoms subtracted was calculated (Fig. 5). The oxygen atom positions obtained in this way are certainly rather approximate. However, they are in good accordance with reasonable geometrical requirements for the structure, giving fully plausible interatomic distances and coordination.

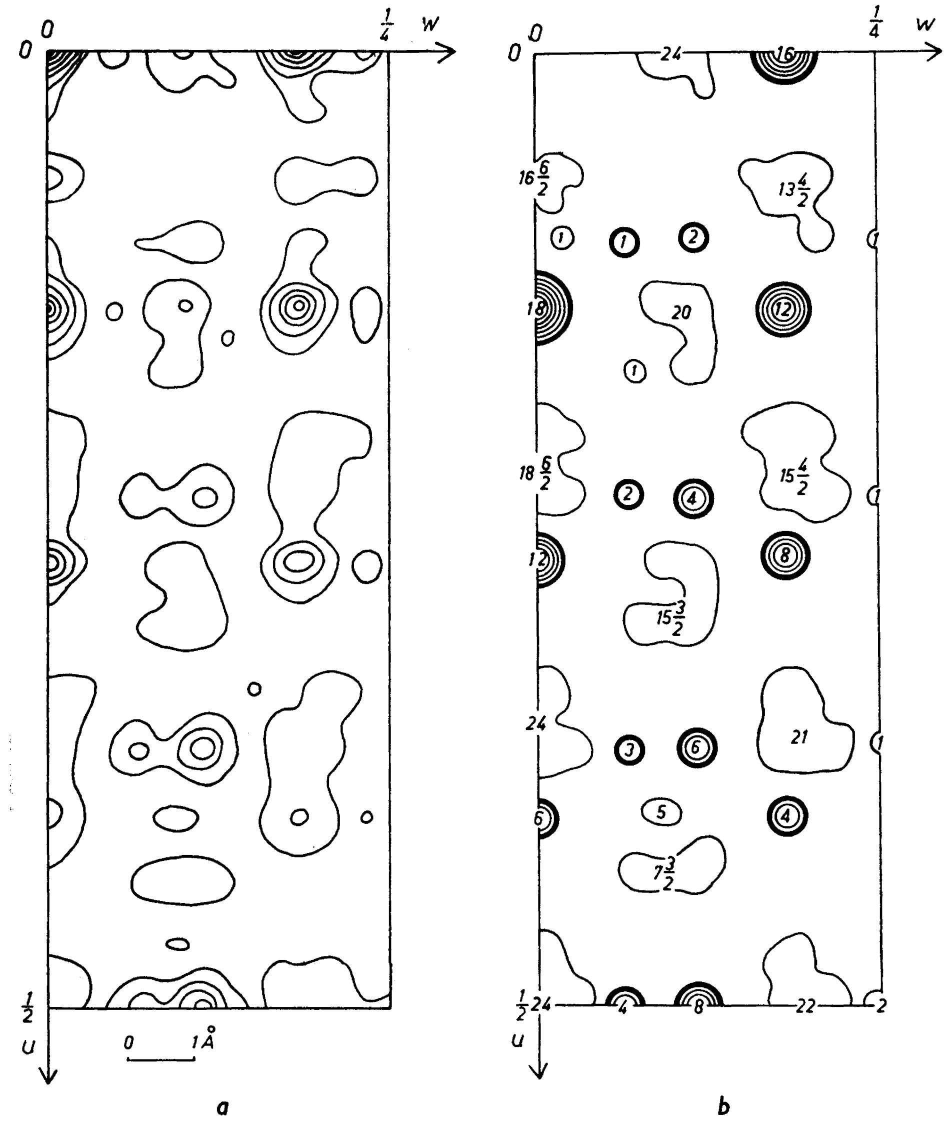
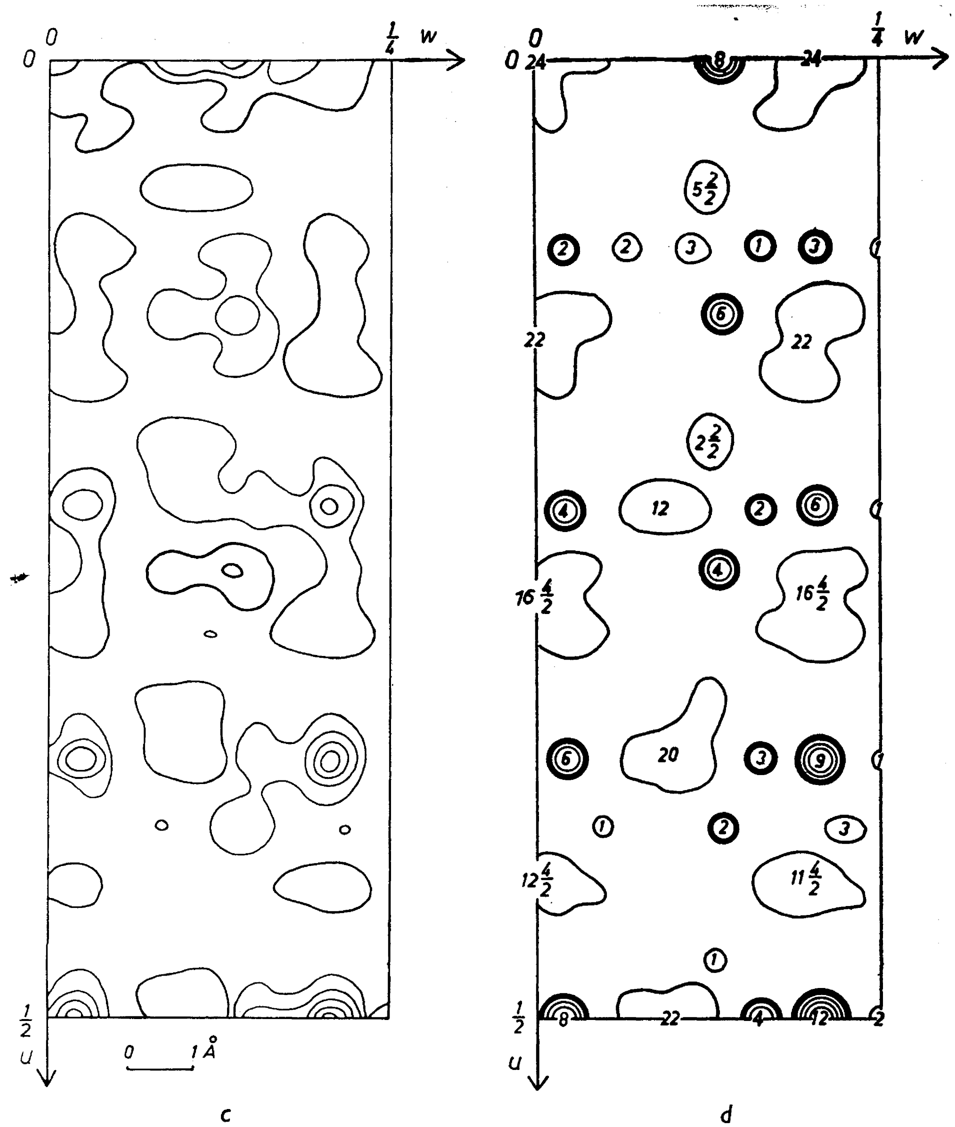


Fig. 2. a and *c*, the Harker sections $P(u0w)$ and $P(u\frac{1}{2}w)$, respectively; *b* and *d* show areas containing the terminal points of the corresponding calculated Nb—Nb vectors as heavy circles, and irregular areas in which the Nb—O vectors end. The numbers of vec-

REFINEMENT OF THE STRUCTURE

To refine the parameters of the structure, a least squares program [11] on the computer FACIT EDB was used. The refinement was started with the set of atomic positions derived as mentioned above. The atomic scattering



tors that terminate in the areas are given as integers for multiplicity eight and as half integers for multiplicity four.

factors used for niobium were derived from those given for Nb(0) to Nb(IV) by Thomas and Umeda [12], and for oxygen those given by Suzuki [13]. For each atom, the coordinates and the "isotropic temperature factor" were refined together with the scale factor for each layer. Of the observed 169 structure

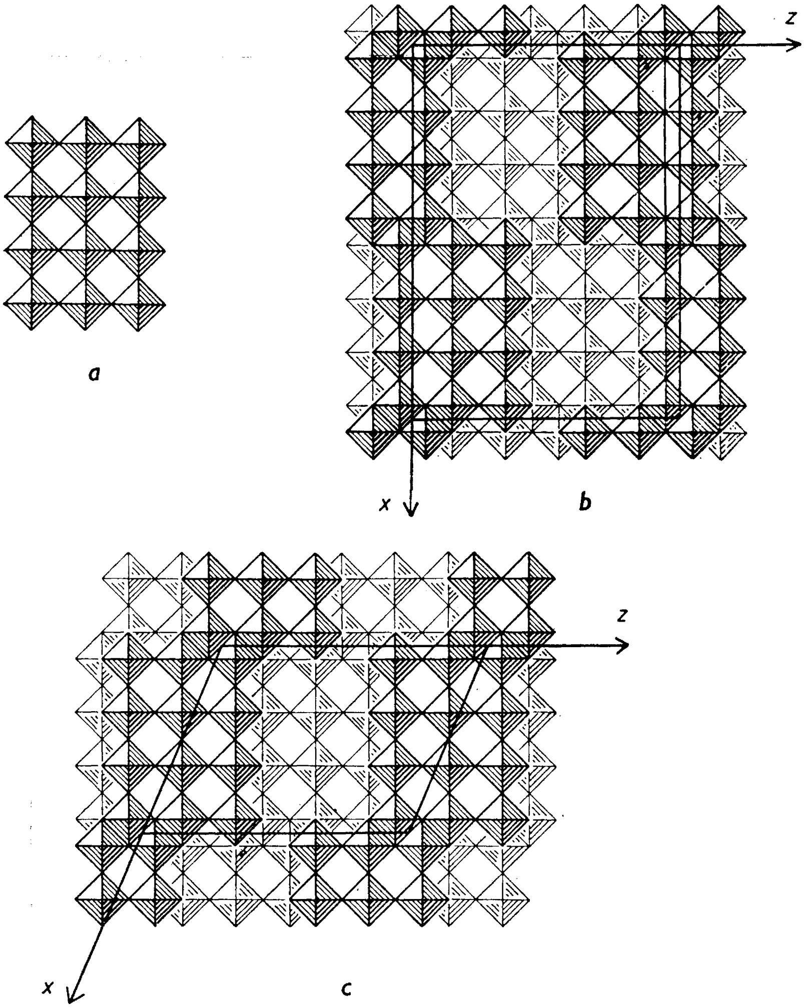


Fig. 3. a. Sheet of twelve NbO_6-octahedra with a lattice of ReO_3-type; *b* and *c*. Idealized structures of orthorhombic and monoclinic $Nb_{12}O_{29}$, respectively, with one unit cell indicated.

factors, 165 were included in the minimizing of the residuals $S = \sum_{hkl} w(|F_o|) - |F_c|)^2$. For the weight w, the function:

$$w = \frac{1}{a + |F_o| + c|F_o|^2}$$

given by Cruickshank[14] was used with $a = 2|F_o|_{min}$ and $c = 2/|F_o|_{max}$. During fifteen cycles of refinement the discrepancy factor R fell from 16.3 % to 11.6 %. At this stage, the average coordinate shift for the niobium atoms

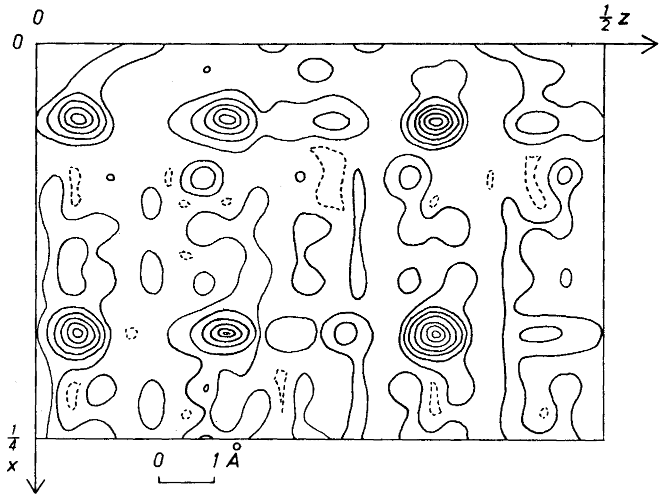


Fig. 4. Electron density projection on the xz plane. Dashed lines indicate negative values.

was 0.1σ and for the oxygen atoms 0.2σ. It was concluded, that the rather limited number of data did not merit further refinement of the structure. $(|F_o| - |F_c|)$ syntheses were calculated [15, 16] in the neighbourhood of each atomic position. No maximum or minimum with an absolute value greater than $\frac{1}{3}$ of the lowest oxygen maximum was found. In Table 2 the final atomic parameters and their estimated errors 2σ are listed together with the values of the "temperature factor". (Since no absorbtion correction was applied,

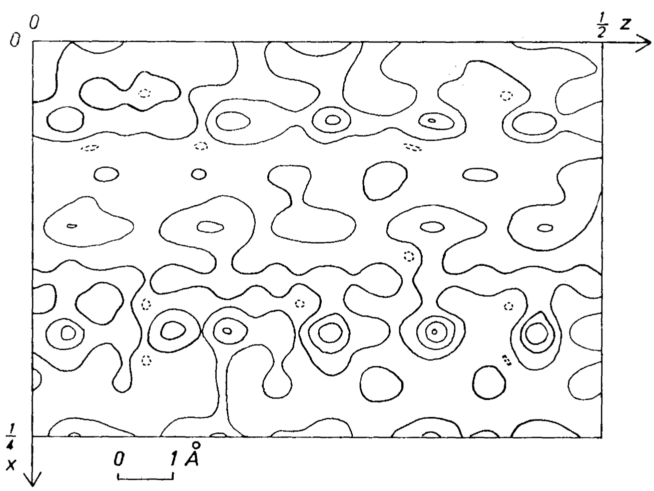


Fig. 5. Electron density projection on the xz plane with the niobium atoms subtracted. Dashed lines indicate negative values.

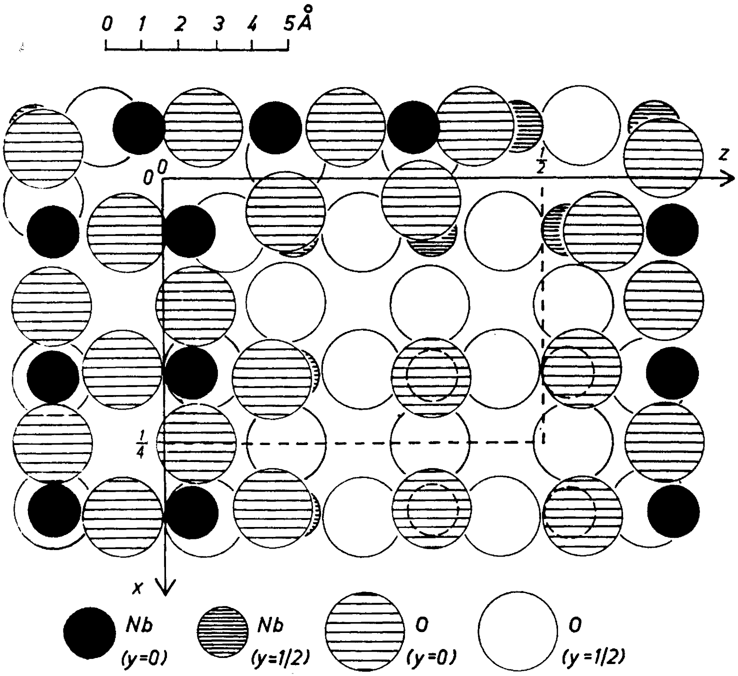


Fig. 6. Projection on the xz plane of the structure of $Nb_{12}O_{29}$(o-rh). Dashed circles indicate the positions of niobium atoms at $y = \frac{1}{2}$ completely overlapped by oxygen atoms at $y = 0$.

Table 2. Fractional atomic parameters, their estimated errors 2σ and "temperature factors" for $Nb_{12}O_{29}$(o-rh). Space group No. 63 *Amma*.

Atom	Point position	$x \pm 2\sigma$	y	$z \pm 2\sigma$	B
Nb_1	8 *f*	0.049 ± 0.001	0	0.033 ± 0.002	+0.36
Nb_2	8 *f*	0.049 ± 0.002	0	0.670 ± 0.002	+0.57
Nb_3	8 *f*	0.049 ± 0.001	0	0.852 ± 0.003	0
Nb_4	8 *f*	0.184 ± 0.002	0	0.034 ± 0.002	+0.52
Nb_5	8 *f*	0.185 ± 0.002	0	0.669 ± 0.002	+0.62
Nb_6	8 *f*	0.187 ± 0.001	0	0.852 ± 0.002	+0.16
O_1	4 *c*	1/4	0	0.04 ± 0.01	−1.8
O_2	4 *c*	1/4	0	0.66 ± 0.02	+2.4
O_3	4 *c*	1/4	0	0.85 ± 0.02	+1.3
O_4	8 *f*	0.05 ± 0.01	0	0.58 ± 0.01	−2.3
O_5	8 *f*	0.03 ± 0.01	0	0.16 ± 0.01	−0.2
O_6	8 *f*	0.05 ± 0.01	0	0.76 ± 0.01	−2.1
O_7	8 *f*	0.02 ± 0.01	0	0.34 ± 0.02	+2.2
O_8	8 *f*	0.05 ± 0.01	0	0.95 ± 0.01	−1.4
O_9	8 *f*	0.12 ± 0.01	0	0.04 ± 0.01	0
O_{10}	8 *f*	0.11 ± 0.01	0	0.66 ± 0.01	+0.4
O_{11}	8 *f*	0.12 ± 0.01	0	0.85 ± 0.02	+2.1
O_{12}	8 *f*	0.18 ± 0.01	0	0.55 ± 0.01	−1.9
O_{13}	8 *f*	0.19 ± 0.01	0	0.14 ± 0.01	−1.1
O_{14}	8 *f*	0.18 ± 0.01	0	0.76 ± 0.01	−1.5
O_{15}	8 *f*	0.19 ± 0.01	0	0.35 ± 0.01	−1.0
O_{16}	8 *f*	0.18 ± 0.01	0	0.94 ± 0.01	−1.2

Table 3. Interatomic distances and their standard deviations for $Nb_{12}O_{29}$(o-rh).

Atom	Number and kind of neighbouring atom.	Distance in Å	Atom	Number and kind of neighbouring atom.	Distance in Å
Nb_1	Nb_1	3.15 ± 0.03	O_3	2 × O_{16}	2.8 ± 0.2
	Nb_2	3.43 ± 0.03		4 × O_{15}	2.6 ± 0.1
	Nb_3	3.70 ± 0.02		2 × O_{14}	2.8 ± 0.2
	2 × O_4	2.15 ± 0.03	O_4	2 × O_5	2.6 ± 0.1
	O_5	2.7 ± 0.2		O_{10}	2.4 ± 0.1
	O_9	2.1 ± 0.1		2 × O_9	2.9 ± 0.1
	O_8 (1)	1.7 ± 0.1		2 × O_8 (1)	3.2 ± 0.1
	O_8 (2)	2.9 ± 0.1		O_4	4.4 ± 0.1
Nb_2	Nb_3	3.45 ± 0.02		2 × O_8 (2)	3.6 ± 0.1
	2 × O_5	2.01 ± 0.04		O_7	2.6 ± 0.2
	O_6	1.9 ± 0.1	O_5	2 × O_6 (1)	2.9 ± 0.1
	O_{10}	1.8 ± 0.1		2 × O_{10}	3.0 ± 0.1
	O_4	1.87 ± 0.07		O_9	3.6 ± 0.2
	O_7	2.0 ± 0.2		O_8	3.2 ± 0.1
Nb_3	2 × O_7	2.11 ± 0.08		2 × O_7	2.4 ± 0.1
	O_8	2.0 ± 0.1		O_6 (2)	2.8 ± 0.2
	O_1	2.1 ± 0.1	O_6	2 × O_7 (1)	2.7 ± 0.1
	O_6	1.9 ± 0.1		O_{11}	2.8 ± 0.2
	O_5-	2.3 ± 0.1		O_{10}	2.7 ± 0.2
Nb_4	Nb_5	3.39 ± 0.02		O_7 (2)	2.9 ± 0.2
	2 × O_{12}	1.95 ± 0.02		2 × O_6	3.5 ± 0.1
	O_{13}	2.20 ± 0.08	O_7	2 × O_8	3.2 ± 0.1
	O_1	1.91 ± 0.04		2 × O_{11}	3.5 ± 0.1
	O_{16}	2.0 ± 0.1	O_8	O_9	2.7 ± 0.2
	O_9	1.9 ± 0.1		O_{11}	2.9 ± 0.2
Nb_5	2 × O_{13}	2.01 ± 0.03		O_8	3.5 ± 0.2
	O_{14}	1.89 ± 0.08	O_9	2 × O_{10}	3.2 ± 0.1
	O_2	1.89 ± 0.04		O_{13}	2.9 ± 0.2
	O_{12}	2.5 ± 0.1		2 × O_{12}	2.6 ± 0.1
	O_{10}	2.2 ± 0.1		O_{16}	2.7 ± 0.2
Nb_6	2 × O_{15}	1.92 ± 0.02	O_{10}	O_{14}	2.9 ± 0.2
	O_{16}	1.8 ± 0.1		2 × O_{13}	3.0 ± 0.1
	O_3	1.82 ± 0.03		O_{12}	3.0 ± 0.2
	O_{14}	1.92 ± 0.09	O_{11}	O_{16}	2.5 ± 0.2
	O_{11}	1.9 ± 0.1		2 × O_{15}	2.8 ± 0.1
O_1	2 × O_2	3.1 ± 0.2		O_{14}	2.5 ± 0.2
	2 × O_{13}	2.7 ± 0.1	O_{12}	2 × O_{13}	2.7 ± 0.1
	4 × O_{12}	2.8 ± 0.1		2 × O_{16}	3.0 ± 0.1
	2 × O_{16}	2.9 ± 0.1	O_{13}	2 × O_{14}	3.2 ± 0.1
O_2	2 × O_{14}	2.9 ± 0.2	O_{14}	2 × O_{15}	2.7 ± 0.1
	4 × O_{13}	2.6 ± 0.1	O_{15}	2 × O_{16}	2.7 ± 0.1
	2 × O_{12}	3.0 ± 0.2			

the latter values have little physical meaning). The structure of $Nb_{12}O_{29}$ (o-rh) is illustrated in Fig. 6, the interatomic distances and their standard deviations are given in Table 3 and a comparison between calculated and observed structure factors in Table 4.

Table 4. Comparison between calculated and observed structure factors from Weissenberg photographs of $Nb_{12}O_{29}$(o-rh). Cu*K* radiation.

h k l	*F* calc	*F* obs	*h k l*	*F* calc	*F* obs	*h k l*	*F* calc	*F* obs
4 0 0	12	16	22 0 10	−31	25	16 1 11	−26	23
6 0 0	26	36	30 0 10	30	37	22 1 11	−31	32
8 0 0	−80	73	1 0 12	−24	22	23 1 11	−33	27
10 0 0	−22	22	7 0 12	−31	34	29 1 11	−24	25
12 0 0	−28	27	15 0 12	33	36	30 1 11	31	27
14 0 0	−64	61	23 0 12	−22	20	31 1 11	17	19
16 0 0	48	51	0 0 16	−35	39	0 1 13	−11	11
18 0 0	14	20	1 0 16	20	22	0 1 17	−44	50
20 0 0	23	27	7 0 16	24	25	8 1 17	35	35
22 0 0	53	67	8 0 16	23	22	12 1 17	10	—
24 0 0	−10	11	14 0 16	18	16	14 1 17	24	32
26 0 0	−10	—	15 0 16	−25	25	16 1 17	−24	24
30 0 0	−51	63	16 0 16	−15	16	22 1 17	−27	28
34 0 0	−16	16	22 0 16	−17	16	0 1 21	30	37
0 0 4	−23	16	23 0 16	17	16	1 1 21	16	19
1 0 4	−10	11	1 0 22	28	35	7 1 21	18	19
8 0 4	9	11	7 0 22	40	46	8 1 21	−25	23
14 0 4	9	11	15 0 22	−44	45	14 1 21	−16	16
15 0 4	9	—	7 1 1	30	32	15 1 21	−21	19
0 0 6	61	55	8 1 1	−23	23	16 1 21	16	16
1 0 6	−29	25	14 1 1	−18	16	4 2 0	10	12
3 0 6	−11	11	15 1 1	−41	32	6 2 0	20	34
5 0 6	−11	11	16 1 1	17	16	8 2 0	−65	68
6 0 6	11	11	22 1 1	16	19	10 2 0	−18	20
7 0 6	−31	31	23 1 1	26	23	12 2 0	−23	22
8 0 6	−33	40	29 1 1	18	16	14 2 0	−51	59
12 0 6	10	—	30 1 1	−17	16	16 2 0	40	45
14 0 6	−30	27	0 1 3	28	19	20 2 0	20	18
15 0 6	36	34	8 1 3	−15	16	22 2 0	47	53
16 0 6	23	19	14 1 3	−14	16	30 2 0	−47	48
22 0 6	22	22	22 1 3	11	—	0 2 4	−16	14
23 0 6	−22	16	1 1 5	−36	39	1 2 4	− 8	6
27 0 6	−10	—	3 1 5	−12	16	0 2 6	46	49
29 0 6	−16	18	5 1 5	−17	23	1 2 6	−23	20
30 0 6	−21	22	7 1 5	−31	32	3 2 6	− 7	—
31 0 6	13	15	9 1 5	13	19	5 2 6	− 9	9
0 0 8	−10	8	13 1 5	9	10	6 2 6	9	10
1 0 8	−16	16	15 1 5	51	67	7 2 6	−27	23
7 0 8	−13	11	19 1 5	9	—	8 2 6	−29	31
15 0 8	19	19	23 1 5	−32	39	12 2 6	−10	—
23 0 8	9	—	27 1 5	−18	16	14 2 6	−24	24
29 0 8	9	—	29 1 5	−21	25	15 2 6	30	30
0 0 10	−66	59	31 1 5	21	23	16 2 6	19	18
4 0 10	− 7	11	35 1 5	12	12	22 2 6	19	17
6 0 10	−16	19	0 1 7	19	19	23 2 6	−19	17
8 0 10	44	45	0 1 11	−53	57	30 2 6	−17	14
10 0 10	10	11	1 1 11	−36	32	1 2 8	−12	14
12 0 10	12	19	7 1 11	−40	42	7 2 8	−11	11
14 0 10	35	32	8 1 11	41	42	15 2 8	15	13
16 0 10	−27	31	14 1 11	27	23	0 2 10	−52	61
20 0 10	−10	—	15 1 11	50	36	6 2 10	−11	—

Table 4. Continued.

h k l	F calc	F obs	h k l	F calc	F obs	h k l	F calc	F obs
8 2 10	37	41	1 2 12	−20	21	14 2 16	16	14
10 2 10	9	7	7 2 12	−26	34	15 2 16	−21	20
12 2 10	10	11	15 2 12	29	31	16 2 16	−13	13
14 2 10	29	30	0 2 16	−30	37	22 2 16	−15	14
16 2 10	−23	27	1 2 16	17	21	23 2 16	14	14
22 2 10	−29	32	7 2 16	21	21	1 2 22	25	20
30 2 10	28	20	8 2 16	20	17	7 2 22	38	39

DISCUSSION

The analogy between the orthorhombic structure of $Nb_{12}O_{29}$ and the one of $Ti_2Nb_{10}O_{29}$ reported by Wadsley [4] is almost complete, the interatomic distances of the former being at an average somewhat longer. Thus the deviations from the ideal structure of this type derived by Wadsley are the same for both compounds.

It is of special interest to compare the metal-metal distances for the octahedra, which are joined by sharing edges. This kind of connection of NbO_6-octahedra is also present in the structure of niobium dioxide, recently studied by Marinder [3]. This structure is related to the rutile type, but represents a complicated superstructure of the latter. A main feature of the atomic arrangement of the dioxide is that the niobium atoms are not eqally spaced along the c axis, but form pairs (Nb-Nb distance equal to 2.80 Å) which are at a Nb-Nb distance of 3.10 Å to the adjacent metal atom doublets. The short intermetal distance has been discussed in terms of a metal-metal bond. In $Nb_{12}O_{29}$(o-rh) the niobium-niobium distances of octahedra joined by edges are, however, within the range 3.15—3.70 Å, in close agreement with the metal-metal distances of $Ti_2Nb_{10}O_{29}$(o-rh) (3.21—3.60 Å). This indicates that no metal-metal bonds are present in $Nb_{12}O_{29}$(o-rh).

Most of the niobium-oxygen distances are about 1.9 Å, some, however, are markedly long. There seems to be a tendency toward tetrahedral instead of octahedral configuration of oxygen atoms around some of the niobium atoms (*i.e.* Nb_1).

Wadsley [4] has shown that $TiNb_2O_7$(mon) [17] and $Ti_2Nb_{10}O_{29}$(mon) are members of a homologous series $Me_{3n}O_{8n-3}$ with $n = 3$ and $n = 4$, respectively. For the orthorhombic version of the series only $Ti_2Nb_{10}O_{29}$(o-rh) is known. In the system Nb—O no phase Nb_3O_7 corresponding to $TiNb_2O_7$ was found in samples prepared in the temperature range 1050—1350°C. The existence of a monoclinic modification of $Nb_{12}O_{29}$ is discussed in the next section.

NOTE ON THE CRYSTAL STRUCTURE OF $Nb_{12}O_{29}$(mon)

As mentioned above, the powder patterns of all $NbO_{2.40}$ samples hitherto prepared show a great number of extra lines in addition to the reflexions belonging to the orthorhombic modification of $Nb_{12}O_{29}$. All attempts to separate the two phases have been in vain and it has not been possible to find a single crystal of the extra phase. If, however, we suppose that its structure is isomorphous with that of $Ti_2Nb_{10}O_{29}$(mon) reported by Wadsley [4], it is possible to index its powder pattern. The following data for the unit cell of $Nb_{12}O_{29}$(mon) were thus obtained:

$$a = (15.67 \pm 0.02) \text{ Å}$$
$$b = (3.835 \pm 0.002) \text{ Å}$$
$$c = (20.73 \pm 0.02) \text{ Å}$$
$$\beta = (112.93 \pm 0.02)^\circ$$
$$V = 1153 \text{ Å}^3.$$

With two formula units in the elementary cell the calculated density becomes $d_{calc} = 4.55$ g cm^{-3} (for $Nb_{12}O_{29}$(o-rh) $d_{calc} = 4.54$ g cm^{-3}).

In Table 1 the powder patterns of the $NbO_{2.40}$ sample consisting of both modifications of $Nb_{12}O_{29}$ is given. The intensity values of the monoclinic modification were calculated assuming the atomic coordinates to be the same as those reported by Wadsley for $Ti_2Nb_{10}O_{29}$(mon) [4]. The good agreement between the observed data and those thus calculated indicate that these atomic coordinates are essentially valid also for the niobium oxide. The idealized version of this structure is given in Fig. 3*c*.

Further attempts will be made to find a single crystal of $Nb_{12}O_{29}$(mon) in order to make possible the derivation of its structural details.

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REFERENCES

1. Andersson, G. and Magnéli, A. *Acta Chem. Scand.* **11** (1957) 1065.
2. Norin, R. and Magnéli, A. *Naturwiss.* **47** (1960) 354.
3. Marinder, B.-O. *Arkiv Kemi* **19** (1962) 435.
4. Wadsley, A. D. *Acta. Cryst.* **14** (1961) 664.
5. Lu, C. S. *Rev. Sci. Instr.* **14** (1943) 331.
6. *International Tables for X-ray Crystallography Vol. I,* Birmingham 1952, p. 152.
7. Edstrand, M. *International Union of Crystallography World List of Crystallographic Computer Programs,* 1st Ed., 1962, p. 16 No. 6022.
8. Åsbrink, S., Blomquist, G. and Westman, S. *Arkiv Kemi* **14** (1959) 545.
9. Magnéli, A. *Acta Cryst.* **4** (1951) 447.
10. Vand, V., Eiland, P. F. and Pepinsky, R. *Acta Cryst.* **10** (1957) 303.
11. Åsbrink, S. and Brändén, C.-I. *International Union of Crystallography World List of Crystallographic Computer Programs,* 1st Ed., 1962, p. 16, No. 6023.
12. Thomas, L. H. and Umeda, K. *J. Chem. Phys.* **26** (1957) 293.
13. Suzuki, T. *Acta Cryst.* **13** (1960) 279.
14. Cruickshank, D. W. J. *Computing Methods and the Phase Problems in X-ray Crystal Analysis,* Pergamon Press 1961, p. 45.
15. Liminga, R. and Olovsson, I. *International Union of Crystallography World List of Crystallographic Computer Programs,* 1st Ed., 1962, p. 16, No. 6015.
16. Liminga, R. and Olovsson, I. *International Union of Crystallography World List of Crystallographic Computer Programs,* 1st Ed., 1962, p. 16, No. 6014.
17. Wadsley, A. D. *Acta Cryst.* **14** (1961) 660.

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