

## The Crystal Structure of Aluminum Niobium Oxide (AlNbO<sub>4</sub>)

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The crystal structure of aluminum niobium oxide has been determined by two-dimensional X-ray methods. The oxide crystallizes in the monoclinic system, space group  $C2/m$ , with a cell content of 4 AlNbO<sub>4</sub>, and the unit cell dimensions,  $a = 12.13 \text{ \AA}$ ,  $b = 3.726 \text{ \AA}$ ,  $c = 6.46 \text{ \AA}$ ,  $\beta = 107.2^\circ$

The structure may be described as built up of distorted oxygen-octahedra sharing edges and corners, and linked together to give an infinite three-dimensional network. Both the aluminum and niobium atoms are located in octahedral positions.

In the course of an X-ray study of the system Nb-O performed at this institute an unknown oxide was observed. It was found by heating niobium pentoxide in a corundum crucible to about 1400°C.

From oscillation and Weissenberg diagrams the dimensions of the unit cell were found to differ markedly from all known modifications of niobium pentoxide. A spectroscopic analysis was therefore made on the sample. The result showed a content of approximately 45 mole % Al<sub>2</sub>O<sub>3</sub> in the sample. Consequently the niobium pentoxide must have reacted with the crucible.

The mixed oxide grew as thin colorless platelets on top of the melt, mainly along the edge of the crucible. It is reasonable to believe this to be a 1:1 compound; the deviation from 50 mole % may be accounted for by the bulk of the oxide not having reacted with the crucible, and consequently the difficulty to pick out a pure sample to perform the analysis on.

Previously AlNbO<sub>4</sub> has been synthesized in connection with an X-ray investigation on ABO<sub>4</sub> compounds of rutile structure<sup>1</sup>. AlNbO<sub>4</sub>, however, did not have the rutile type structure, and is only mentioned as probably being monoclinic with  $b = 3.72 \text{ \AA}$ . In a recent X-ray investigation<sup>2</sup> of the system niobium pentoxide-aluminum oxide this mixed oxide was found to be the only new phase in the system.

### EXPERIMENTAL

A platelet of approximate dimensions (0.02 × 0.2 × 1) mm<sup>3</sup> was used in this investigation, which was carried out at room temperature. It turned out that the longest edge of the plate was parallel to the direction of the  $b$ -axis, whereas the  $c$ -direction was perpendicular to the plate.

Oscillation and zero-, first- and second-layer Weissenberg diagrams were taken rotating about the longest edge of the crystal and using  $\text{CuK}\alpha$  radiation. The intensity data consisted of integrated Weissenberg (Wiebenga) diagrams about the same edge using Zr-filtered Mo-radiation ( $\lambda_{\text{Mo}} = 0.7107 \text{ \AA}$ ). The intensities were recorded photo-metrically except the very weakest ones which were estimated visually. The number of reflections recorded was 287 (theoretically 449). The intensities were corrected for Lorentz and polarization effects. No absorption corrections were applied although systematic variation in the background blackening of the films indicated an absorption effect. This, however, will be discussed later. The linear absorption coefficient for  $\text{MoK}\alpha$  radiation is  $47.3 \text{ cm}^{-1}$ .

## RESULTS

From oscillation- and Weissenberg-diagrams using  $\text{CuK}\alpha$  radiation the unit cell dimensions were found to be:

$$a = 12.13 \text{ \AA}, b = 3.726 \text{ \AA}, c = 6.46 \text{ \AA}, \beta = 107.2^\circ$$

These figures are believed to be accurate to within 0.5 %.

With four formula units  $\text{AlNbO}_4$  in the cell a density of  $4.38 \text{ g/cm}^3$  is derived, whereas the calculated density based on the specific volumes of  $\text{Al}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  is  $4.32 \text{ g/cm}^3$ . Due to experimental difficulties a pycnometric density determination was not undertaken.

Systematic absences were, in  $hkl$ ;  $h + k = 2n + 1$ . This gives three possible space groups:  $C2/m$  (No. 12),  $Cm$  (No. 8),  $C2$  (No. 5)

The intensity distribution in the  $h2l$  Weissenberg diagram very closely resembled that of the  $h0l$  film, strongly indicating that all the atoms comprising the structure were situated in, or very close to two planes normal to the  $y$ -axis and  $b/2$  apart, making  $C2/m$  or  $Cm$  the most probable space group. In both space groups the atoms would be in special positions, the space group  $Cm$  requiring two  $\text{AlNbO}_4$  in the asymmetric unit.

Assuming the symmetry to be the higher one ( $C2/m$ ), it was possible to find an atomic arrangement compatible with the appearance of the Patterson function and giving calculated  $F$ -values in acceptable conformity with the observed ones.  $C2/m$  has eight-fold general positions, but as there are only four niobium and four aluminum atoms in the unit cell, these will have to occupy special positions. On the basis of the corrected  $(F(h0l))^2$  values a Patterson map was computed. The choice of point positions was restricted by: (1) The absence of a maximum at  $u = 0$ ,  $w = 1/2$  in the Patterson map  $P(u, w)$ . (2) The length of the  $b$ -axis being only  $3.7 \text{ \AA}$ . From (1) and (2) it can be concluded that four metal or four oxygen atoms can not occupy 2-fold positions. (3) The requirement that at least the heavy atoms are situated in mirror planes. This excludes the 4-fold positions on the rotation axes. Thus the special position  $m$  of  $C2/m$  is the only possible one. If all the atoms are situated in mirror planes, a complete structure determination can be done based on the (010) projection, as the  $y$ -coordinates for the atoms will be either 0 or  $1/2$ .

From the Patterson projection  $P(u, w)$ , Fig. 1, the niobium atom was located. The coordinates for the aluminum atom might also have been determined, but as the Nb-Al peaks were rather irregular it was decided to carry

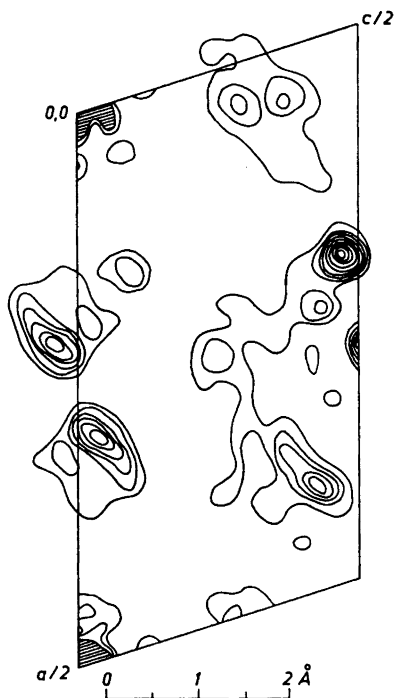


Fig. 1. Patterson projection along the  $b$ -axis.

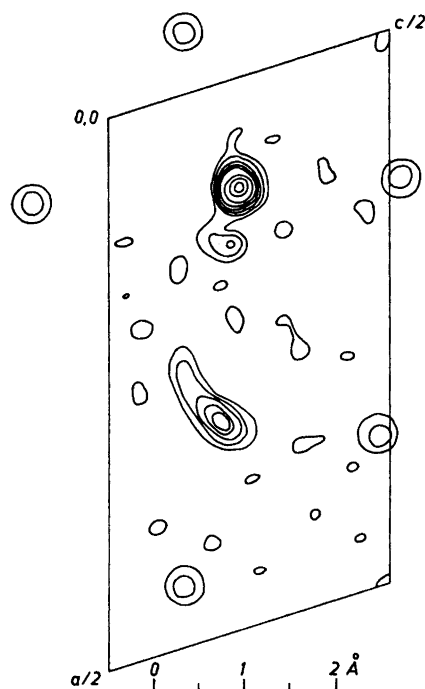


Fig. 2. Electron density projection along the  $b$ -axis. Contour lines at 5, 10, 15, 20, 25, 50, 75, 100  $\text{el}/\text{\AA}^2$ .

out a Fourier synthesis based on the strongest reflections. The structure factors were given the signs calculated from the positions of the Nb-atoms. From this Fourier map the aluminum atom could be located. In addition there were several peaks indicating possible positions for the four oxygen atoms. The oxygens were placed in the most probable sites, and a theoretical vector map was drawn including all possible interatomic distances within the unit cell. This drawing showed a close resemblance to the original Patterson projection, and this was taken as a good support for the proposed structure. Structure factors were calculated on the basis of all atoms in the unit cell, and a new Fourier summation was made including all observed reflections. The result is shown in Fig. 2.

### Refinements

The structure was refined by the method of least squares and by difference syntheses. As the intensity data were thought to suffer from absorption it was tried to make least squares refinement first on the complete set of data, and secondly by excluding about half of the data suffering most from absorption.

In this calculation the analytical approximation to the scattering factors for the neutral atoms computed by Forsyth and Wells<sup>3</sup> was employed. The omission of the mentioned reflections did not seem to have a marked influence on the results. The parameters for the Nb and Al atoms differed by less than 0.0001 Å in the two cases. Further refinement was carried out varying the parameters for all the atoms. This brought the discrepancy factor down to 0.16. Least squares refinement gave a value of the parameter  $B$  in the temperature-correction very close to zero.

At last a total difference synthesis, based on structure factors calculated from the parameters after least squares refinements, and using  $B = 0$  was computed. In this calculation the scattering factors for the ions were used. The scattering factor for the Nb ion was taken from Thomas and Umeda<sup>4</sup>, for the Al ion from Veenendaal *et al.*<sup>5</sup> and for the O ion from James and Brindley<sup>6</sup>. From this Fourier difference map the parameters were corrected in the usual manner. The final coordinates for the atoms together with calculated standard deviation according to Cruickshank<sup>7</sup> are found in Table 1.

Wilson statistics<sup>8</sup> was used to determine the value of the parameter  $B$  in the temperature correction. A value of  $B = 0.208 \text{ \AA}^2$  was found and this value was applied in calculating a new set of structure factors. At the very end the strongest reflections for low  $2\theta$  values were corrected for secondary extinction<sup>9</sup>. The final Fourier map is shown in Fig. 3. The discrepancy factor including all reflections was calculated to 0.12. (For the unobserved reflections calculated greater than the minimum observable value, the difference between the calculated and half the minimum value were included.) A comparison between observed and calculated structure factors is given in Table 4. It should be pointed out that there might be some deviation from coplanarity of the lighter atoms, as this would not have much influence on the reflections  $h2l$  as compared to  $h0l$ . In that case the correct space group would be  $C2$ . However, the symmetry of the (010) projection for  $C2$  would be equal to the (010) projection for  $C2/m$ .

#### DISCUSSION OF THE STRUCTURE

The structure of  $\text{AlNbO}_4$  is illustrated in Fig. 4. Each metal atom is coordinated to six nearest oxygens forming an octahedral grouping.

The structure may be described as built up of chains of octahedra in the  $c$ -direction. The structural unit is actually 4 octahedra sharing edges and linked

Table 1. Final positional parameters as fractions of the cell edges and their standard deviations. All the atoms occupy point positions 4 ( $i$ ) of space group  $C2/m$ ,  $(0,0,0; \frac{1}{2}, \frac{1}{2}, 0) + x0z, \bar{x}0\bar{z}$ .

Atom	$x$	$z$	$\sigma(x)$	$\sigma(z)$
Nb	0.1030	0.2354	0.0004	0.0008
Al	0.3071	0.1986	0.001	0.002
$O_2'$	0.364	0.484	0.002	0.004
$O_3''$	0.443	0.149	0.002	0.004
$O_4$	0.274	0.149	0.002	0.004
$O_1$	0.130	0.203	0.002	0.004

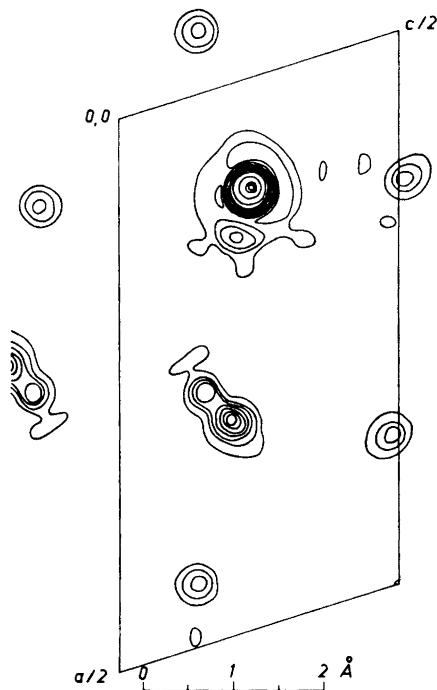


Fig. 3. Final electron density projection along the  $b$ -axis. Contour lines at 5, 10, ----- 35, 50, 75, 100, 125  $\text{el}/\text{\AA}^2$ .

to the next unit by sharing two corners. These chains are coupled together by sharing edges with adjacent octahedra displaced  $b/2$  in the  $y$ -direction. This bonding gives an infinite three-dimensional network of oxygen atoms, having the metal atoms in the octahedral holes. Distances calculated on the assumption that all the atoms are situated in planes normal to the  $y$ -axis and  $b/2$  apart, are given in Table 2. The atoms are numbered according to Fig. 4.

The niobium-oxygen distances vary between 1.74 Å and 2.38 Å, the distance  $\text{Nb}-\text{O}_2$  to the shared corner being the shortest one. This is to be expected as the metal atoms on each side of a shared edge tend to be as far apart as

Table 2. Interatomic distances.

$\text{Nb}-\text{O}_1$	1.91 Å	$\text{Al}-\text{O}_4$	1.89 Å	<i>O-O distances between shared corners</i>	
$\text{Nb}-\text{O}_2$	1.74 »	$\text{Al}-\text{O}_3'$	1.77 »	(1) <i>In the niobium octahedron</i>	
$\text{Nb}-\text{O}_3$	1.85 »	$\text{Al}-\text{O}_3''$	1.77 »	$\text{O}_1-\text{O}_3'$	2.87 Å
$\text{Nb}-\text{O}_4$	2.30 »	$\text{Al}-\text{O}_4'$	2.17 »	$\text{O}_1-\text{O}_3$	2.87 »
$\text{Nb}-\text{O}_3'$	2.38 »	$\text{Al}-\text{O}_1$	2.05 »	$\text{O}_1-\text{O}_2$	2.73 »
<i>O-O distances (shared edge)</i>				$\text{O}_2-\text{O}_3$	2.79 »
$\text{O}_4-\text{O}_3'$	2.77 Å			$\text{O}_2-\text{O}_4$	3.28 »
$\text{O}_3-\text{O}_3'$	2.67 »			(2) <i>In the aluminium octahedron</i>	
$\text{O}_1-\text{O}_4$	2.65 »			$\text{O}_3''-\text{O}_4$	2.77 Å
$\text{O}_4-\text{O}_4'$	2.62 »			$\text{O}_2'-\text{O}_4$	2.82 »
				$\text{O}_2'-\text{O}_3''$	2.62 »
				$\text{O}_4'-\text{O}_1$	2.85 »
				$\text{O}_1-\text{O}_2'$	2.88 »
					2.79 Å

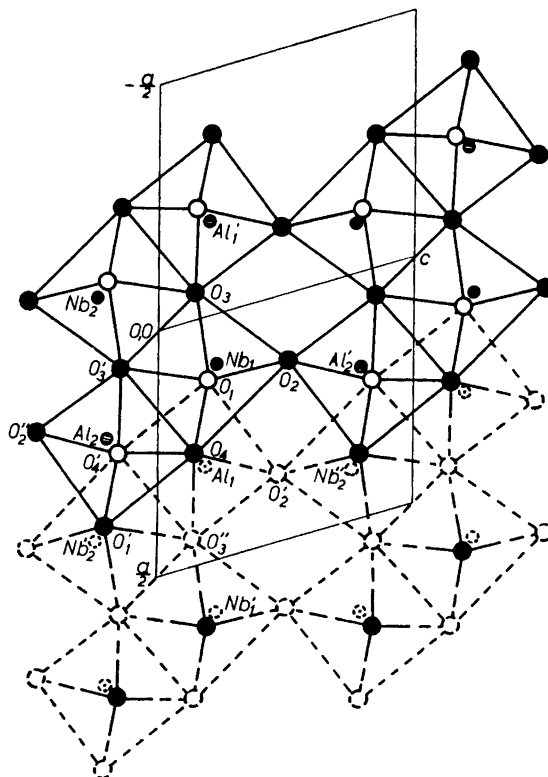


Fig. 4. The structure of AlNbO<sub>4</sub>. Filled circles indicate atoms situated at  $y = 0$ . Open circles indicate atoms situated at  $y = \pm 1/2$ .

possible because of repulsion between equally charged ions. Consequently one could expect Nb-O<sub>2</sub> and Nb-O<sub>3</sub> to be shorter than the other bonds and further Nb-O<sub>2</sub> to be the shortest one. This is exactly what is found. The mean niobium oxygen distance is calculated to 2.07 Å.

The aluminum oxygen distances vary between 1.77 Å and 2.17 Å, the mean value being 1.94 Å. The two shortest distances in this octahedron are, naturally enough, Al-O<sub>2</sub> and Al-O<sub>3</sub>.

The oxygen-oxygen distances in the two octahedra vary from 2.73 Å to 3.28 Å in the niobium octahedron and from 2.62 Å to 2.88 Å in the aluminum octahedron. The O-O distances in the two octahedra are not likely to be equal, as the central ion in the two differ in size. The O-O distances in the niobium octahedron have a mean value of 2.91 Å, whereas the O-O distances in the aluminum octahedron have a mean value of 2.79 Å. The overall mean value is 2.85 Å.

From the calculated distances the metal and oxygen radii were determined to:

$$\text{Nb}^{5+} = 0.65 \text{ \AA}, \text{Al}^{3+} = 0.52 \text{ \AA}, \text{O}^{2-} = 1.42 \text{ \AA}$$

Table 3. Metal-metal distances.

<i>Over shared edge</i>			
$2 \times \text{Nb}_1\text{-Al}_1$	3.16 Å	$2 \times \text{Al}_1\text{-Al}_2$	3.14 Å
$\text{Nb}_1\text{-Al}_2$	3.30 »	$2 \times \text{Al}_1\text{-Nb}_1$	3.16 »
$\text{Nb}_1\text{-Nb}_2$	3.32 »	$\text{Al}_1\text{-Nb}_2'$	3.30 »
<i>Over shared corner</i>			
$\text{Nb}_1\text{-Al}_1'$	3.56 Å	$\text{Al}_1\text{-Nb}_2''$	3.50 Å
$\text{Nb}_1\text{-Al}_2'$	3.50 »	$\text{Al}_1\text{-Nb}_1'$	3.56 »

in fair agreement with the ones reported by Wadsley<sup>10</sup> for (Ti, Nb) and  $\text{O}^{2-}$ , namely 0.61 Å and 1.38 Å and Paulings values of 0.70 Å, 0.50 Å and 1.40 Å for  $\text{Nb}^{5+}$ ,  $\text{Al}^{3+}$ ,  $\text{O}^{2-}$ , respectively<sup>11</sup>. Formal valencies may be assigned to the Nb and Al atoms by considering how the adjacent oxygen atoms are held in common by their metal atom neighbours. In this way, valencies of 4 1/6 can be calculated for the Nb atoms and 3 5/6 for the Al atoms.

One common feature throughout the structure is the shortening of the edge shared by two octahedra. This shortening can also be accounted for by repulsion between equally charged ions, in fact this is considered a characteristic feature of ionic structures<sup>12</sup>. This shortening of one edge will give rise to an elongation in the opposite one, which is found to be present in all instances as seen in Table 2. (Shared edges:  $\text{O}_3\text{-O}_3'$ ,  $\text{O}_4\text{-O}_3'$ ,  $\text{O}_1\text{-O}_4$ ,  $\text{O}_4\text{-O}_4'$ , opposite edges:  $\text{O}_2\text{-O}_4$ ,  $\text{O}_2\text{-O}_3$ ,  $\text{O}_2''\text{-O}_1'$ ,  $\text{O}_1\text{-O}_3$ ,  $\text{O}_3''\text{-O}_4$ ,  $\text{O}_2'\text{-O}_4$ .)

There are rather few data with which to compare the interatomic distances obtained in the present investigation. Frevel and Rinn<sup>13</sup> found distances of 1.95 Å and 2.76 Å between metal and anion and anion-anion respectively in  $\text{NbO}_2\text{F}$ . Vousden<sup>14</sup> found 2.00 Å and 2.82 Å in  $\text{KNbO}_3$  and 1.95 Å and 2.76 Å for  $\text{NiNbO}_3$ . Wadsley<sup>10</sup> reports Me-O distances varying from 1.64 Å to 2.34 Å and O-O distances from 2.52 Å to 3.14 Å in  $\text{TiNb}_2\text{O}_7$ .

Each niobium atom is surrounded by six metal atoms forming a very distorted octahedral arrangement. The distances from Nb to its nearest metal neighbours are shown in Table 3. In the same table are given the distances to the seven metal atoms surrounding an aluminum atom.

As one can see there is a marked difference in the metal-metal distances for the two kinds of octahedral coupling. The mean niobium-aluminum distance over a shared edge is 3.21 Å whereas the distance over a shared corner of the oxygen octahedron is pronounced longer, the mean value being 3.53 Å.

In an ideal arrangement of octahedral ions one would expect the metal-metal distance over a shared edge to be 0.71 times the metal-metal distance over a shared corner. However, in a real structure these distances tend to equal out as the figures for  $\text{AlNbO}_4$  show, where the distance is only shortened by a factor of 0.90.

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Table 4. Observed and calculated structure factors. (Reflections marked \* are corrected for secondary extinction).

<i>h</i>	<i>k</i>	<i>l</i>	$F_o$	$F_c$	<i>h</i>	<i>k</i>	<i>l</i>	$F_o$	$F_c$	<i>h</i>	<i>k</i>	<i>l</i>	$F_o$	$F_c$
0	0	1	15	21	4	0	$\overline{13}$	13	-9	6	0	8	29	-30
0	0	2	88*	-87	4	0	$\overline{12}$	18	-15	6	0	9	<10	-5
0	0	3	75*	-67	4	0	$\overline{11}$	17	17	6	0	10	30	31
0	0	4	49*	53	4	0	$\overline{10}$	18	19	6	0	11	<10	8
0	0	5	36	35	4	0	$\overline{9}$	20	-17	6	0	12	20	-19
0	0	6	20	-21	4	0	$\overline{8}$	36	-40	6	0	13	14	-17
0	0	7	31	-29	4	0	$\overline{7}$	26	19	6	0	14	13	12
0	0	8	23	20	4	0	$\overline{6}$	50*	53	6	0	15	11	11
0	0	9	25	20	4	0	$\overline{5}$	<6	8	6	0	16	<6	0
0	0	10	20	-12	4	0	$\overline{4}$	84*	-82	8	0	$\overline{17}$	<8	7
0	0	11	26	-22	4	0	$\overline{3}$	26	-20	8	0	$\overline{16}$	16	17
0	0	12	<10	6	4	0	$\overline{2}$	56*	59	8	0	$\overline{15}$	<9	-6
0	0	13	18	17	4	0	$\overline{1}$	64*	60	8	0	$\overline{14}$	17	-18
0	0	14	<10	0	4	0	0	68*	-67	8	0	$\overline{13}$	<10	-1
0	0	15	13	-11	4	0	1	33*	-35	8	0	$\overline{12}$	28	25
0	0	16	<9	0	4	0	2	32*	33	8	0	$\overline{11}$	<10	0
0	0	17	<7	6	4	0	3	51*	51	8	0	$\overline{10}$	30	-27
2	0	$\overline{17}$	<7	3	4	0	4	23	-28	8	0	$\overline{9}$	20	-12
2	0	$\overline{16}$	12	-13	4	0	5	32	-37	8	0	$\overline{8}$	34	39
2	0	$\overline{15}$	12	-12	4	0	6	<7	7	8	0	$\overline{7}$	25	18
2	0	$\overline{14}$	14	17	4	0	7	30	33	8	0	$\overline{6}$	27	-34
2	0	$\overline{13}$	10	12	4	0	8	<7	-3	8	0	$\overline{5}$	38	-42
2	0	$\overline{12}$	14	-11	4	0	9	26	-22	8	0	$\overline{4}$	28	36
2	0	$\overline{11}$	18	-20	4	0	10	<8	-2	8	0	$\overline{3}$	36*	40
2	0	$\overline{10}$	21	15	4	0	11	18	17	8	0	$\overline{2}$	<5	-10
2	0	$\overline{9}$	22	23	4	0	12	<10	0	8	0	$\overline{1}$	40*	-48
2	0	$\overline{8}$	11	-11	4	0	13	20	-14	8	0	0	20	18
2	0	$\overline{7}$	27*	-36	4	0	14	<10	0	8	0	1	23	28
2	0	$\overline{6}$	13	9	4	0	15	12	13	8	0	2	<6	-8
2	0	$\overline{5}$	33*	42	4	0	16	<7	4	8	0	3	32	-34
2	0	$\overline{4}$	<2	2	4	0	$\overline{17}$	<9	-9	8	0	4	10	11
2	0	$\overline{3}$	49*	-54	6	0	$\overline{16}$	<10	4	8	0	5	32	31
2	0	$\overline{2}$	6	-5	6	0	$\overline{15}$	14	15	8	0	6	<8	-1
2	0	$\overline{1}$	57*	55	6	0	$\overline{14}$	<10	-9	8	0	7	30	-30
2	0	0	<2	-2	6	0	$\overline{13}$	18	-17	8	0	8	<9	-4
2	0	1	63*	-58	6	0	$\overline{12}$	<10	2	8	0	9	21	23
2	0	2	<4	-9	6	0	$\overline{11}$	25	26	8	0	10	<10	9
2	0	3	61*	67	6	0	$\overline{10}$	<9	3	8	0	11	22	-18
2	0	4	18	19	6	0	$\overline{9}$	21	-22	8	0	12	<10	-10
2	0	5	43*	-46	6	0	$\overline{8}$	10	-9	8	0	13	14	14
2	0	6	38	-38	6	0	$\overline{7}$	13	20	8	0	14	<10	10
2	0	7	30	32	6	0	$\overline{6}$	<7	0	8	0	15	<9	-9
2	0	8	31	32	6	0	$\overline{5}$	18	-26	10	0	$\overline{17}$	16	14
2	0	9	15	-11	6	0	$\overline{4}$	26	11	10	0	$\overline{16}$	<8	5
2	0	10	25	-30	6	0	$\overline{3}$	52*	56	10	0	$\overline{15}$	21	-17
2	0	11	<10	6	6	0	$\overline{2}$	12	4	10	0	$\overline{14}$	10	-6
2	0	12	23	20	6	0	$\overline{1}$	95*	-88	10	0	$\overline{13}$	15	12
2	0	13	<10	2	6	0	0	37*	-39	10	0	$\overline{12}$	<10	8
2	0	14	14	-19	6	0	1	61*	59	10	0	$\overline{11}$	15	-15
2	0	15	<9	0	6	0	2	67*	66	10	0	$\overline{10}$	<9	-4
2	0	16	11	12	6	0	3	30	-33	10	0	$\overline{9}$	20	20
4	0	$\overline{17}$	10	-10	6	0	4	39	-48	10	0	$\overline{8}$	<8	8
4	0	$\overline{16}$	12	-9	6	0	5	<8	8	10	0	$\overline{7}$	35	-32
4	0	$\overline{15}$	12	10	6	0	6	35	42	10	0	$\overline{6}$	22	-20
4	0	$\overline{14}$	13	10	6	0	7	<9	-6	10	0	$\overline{5}$	39	38



<i>h k l</i>	$F_o$	$F_c$	<i>h k l</i>	$F_o$	$F_c$	<i>h k l</i>	$F_o$	$F_c$
100 $\bar{4}$	34	35	140 $\bar{11}$	20	14	180 $\bar{14}$	15	-15
100 $\bar{3}$	30	-29	140 $\bar{10}$	23	18	180 $\bar{13}$	17	11
100 $\bar{2}$	42	-50	140 $\bar{9}$	21	-17	180 $\bar{12}$	26	25
100 $\bar{1}$	25	24	140 $\bar{8}$	34	-26	180 $\bar{11}$	<10	-4
100 0	37	46	140 $\bar{7}$	17	14	180 $\bar{10}$	35	-33
100 1	< 7	-7	140 $\bar{6}$	40	39	180 $\bar{9}$	< 9	-7
100 2	43	-53	140 $\bar{5}$	< 8	-7	180 $\bar{8}$	34	29
100 3	< 7	2	140 $\bar{4}$	41	-42	180 $\bar{7}$	24	19
100 4	39	41	140 $\bar{3}$	13	-10	180 $\bar{6}$	29	-24
100 5	17	16	140 $\bar{2}$	40	43	180 $\bar{5}$	24	-18
100 6	31	-36	140 $\bar{1}$	21	14	180 $\bar{4}$	18	16
100 7	10	-17	140 0	30	-29	180 $\bar{3}$	29	20
100 8	17	18	140 1	29	-22	180 $\bar{2}$	22	-20
100 9	20	23	140 2	26	27	180 $\bar{1}$	28	-18
100 10	18	-13	140 3	20	16	180 0	14	12
100 11	13	-13	140 4	18	-16	180 1	31	26
100 12	<10	4	140 5	21	-22	180 2	< 9	-9
100 13	13	12	140 6	17	16	180 3	21	-18
100 14	< 8	-6	140 7	18	17	180 4	<10	-1
120 $\bar{17}$	< 7	4	140 8	<10	-6	180 5	21	16
120 $\bar{16}$	18	-16	140 9	17	-19	180 6	<10	-4
120 $\bar{15}$	< 9	-2	140 10	< 9	6	180 7	10	-9
120 $\bar{14}$	23	19	140 11	13	-12	180 8	< 9	3
120 $\bar{13}$	13	13	140 12	< 8	0	180 9	18	16
120 $\bar{12}$	25	-25	140 13	12	-13	180 10	< 8	-5
120 11	26	-21	160 $\bar{17}$	14	-14	180 11	10	-16
120 10	13	15	160 $\bar{16}$	18	14	200 $\bar{16}$	< 7	-5
120 9	37	34	160 $\bar{15}$	15	17	200 $\bar{15}$	13	-15
120 8	< 9	-8	160 $\bar{14}$	<10	-5	200 $\bar{14}$	< 9	-3
120 7	29	-26	160 $\bar{13}$	22	-23	200 $\bar{13}$	16	18
120 6	< 8	-4	160 $\bar{12}$	<10	4	200 $\bar{12}$	<10	2
120 5	22	25	160 $\bar{11}$	15	17	200 $\bar{11}$	15	-14
120 4	< 8	-8	160 $\bar{10}$	<10	2	200 $\bar{10}$	<10	-7
120 3	13	-19	160 $\bar{9}$	22	-21	200 $\bar{9}$	23	20
120 2	< 7	8	160 $\bar{8}$	< 9	3	200 $\bar{8}$	< 9	5
120 $\bar{1}$	32	35	160 $\bar{7}$	23	19	200 $\bar{7}$	21	-19
120 0	11	-10	160 $\bar{6}$	< 9	4	200 $\bar{6}$	17	-13
120 1	33	-34	160 $\bar{5}$	31	-28	200 $\bar{5}$	27	23
120 2	< 8	-5	160 $\bar{4}$	< 8	-3	200 $\bar{4}$	18	17
120 3	28	33	160 $\bar{3}$	23	23	200 $\bar{3}$	17	-18
120 4	< 8	7	160 $\bar{2}$	15	10	200 $\bar{2}$	27	-24
120 5	22	-24	160 $\bar{1}$	25	-26	200 $\bar{1}$	13	14
120 6	<10	-10	160 0	13	-8	200 0	30	23
120 7	21	22	160 1	25	23	200 1	< 9	-8
120 8	15	12	160 2	17	13	200 2	23	-23
120 9	18	-21	160 3	22	-25	200 3	<10	3
120 10	16	-17	160 4	22	-19	200 4	21	22
120 11	12	13	160 5	16	20	200 5	<10	0
120 12	21	22	160 6	21	25	200 6	21	-19
120 13	< 8	-4	160 7	<10	-9	200 7	<10	-7
120 14	15	-18	160 8	18	-25	200 8	17	17
140 $\bar{17}$	12	-12	160 9	<10	1	200 9	< 9	7
140 $\bar{16}$	< 9	-9	160 10	20	19	200 10	< 8	-9
140 $\bar{15}$	14	14	160 11	< 8	5	220 $\bar{16}$	18	-19
140 $\bar{14}$	<10	10	160 12	14	-14	220 $\bar{15}$	< 8	-2
140 $\bar{13}$	10	-12	180 $\bar{16}$	< 7	9	220 $\bar{14}$	20	21
140 $\bar{12}$	15	-14	180 $\bar{15}$	15	-11	220 $\bar{13}$	< 9	8

$h$	$k$	$l$	$F_o$	$F_c$	$h$	$k$	$l$	$F_o$	$F_c$	$h$	$k$	$l$	$F_o$	$F_c$
22 0 $\bar{1}\bar{2}$	14	-17			24 0 $\bar{3}$	<10	2			28 0 $\bar{1}\bar{2}$	11	13		
22 0 $\bar{1}\bar{1}$	13	-14			24 0 $\bar{2}$	28	23			28 0 $\bar{1}\bar{1}$	< 9	- 5		
22 0 $\bar{1}\bar{0}$	17	17			24 0 $\bar{1}$	<10	1			28 0 $\bar{1}\bar{0}$	13	-17		
22 0 $\bar{9}$	13	14			24 0 0	27	-24			28 0 $\bar{9}$	< 9	5		
22 0 $\bar{8}$	10	-13			24 0 1	<10	- 9			28 0 8	17	19		
22 0 $\bar{7}$	22	-22			24 0 2	22	18			28 0 7	< 9	0		
22 0 $\bar{6}$	15	13			24 0 3	18	15			28 0 6	22	-23		
22 0 $\bar{5}$	25	21			24 0 4	17	-11			28 0 5	< 9	- 7		
22 0 $\bar{4}$	<10	- 3			24 0 5	16	-11			28 0 4	20	21		
22 0 $\bar{3}$	27	-24			24 0 6	< 9	3			28 0 3	14	15		
22 0 $\bar{2}$	< 9	1			24 0 7	< 8	8			28 0 2	14	-13		
22 0 $\bar{1}$	18	15			24 0 8	< 7	- 6			28 0 1	14	-17		
22 0 0	<10	4			26 0 $\bar{1}\bar{4}$	10	-12			28 0 0	< 9	6		
22 0 1	21	-15			26 0 $\bar{1}\bar{3}$	10	-13			28 0 1	< 9	11		
22 0 2	<10	3			26 0 $\bar{1}\bar{2}$	< 9	7			28 0 2	< 9	- 2		
22 0 3	<10	10			26 0 $\bar{1}\bar{1}$	13	17			28 0 3	< 8	-10		
22 0 4	<10	0			26 0 $\bar{1}\bar{0}$	<10	- 7			28 0 4	< 8	5		
22 0 5	18	-19			26 0 $\bar{9}$	14	-14			28 0 5	< 7	7		
22 0 6	< 9	0			26 0 $\bar{8}$	<10	2			30 0 $\bar{1}\bar{2}$	< 7	- 4		
22 0 7	17	15			26 0 $\bar{7}$	15	19			30 0 $\bar{1}\bar{1}$	15	-16		
22 0 8	15	9			26 0 $\bar{6}$	<10	- 3			30 0 $\bar{1}\bar{0}$	< 8	2		
22 0 9	14	-14			26 0 $\bar{5}$	15	-16			30 0 $\bar{9}$	12	15		
24 0 $\bar{1}\bar{5}$	< 8	8			26 0 $\bar{4}$	<10	- 5			30 0 $\bar{8}$	< 9	7		
24 0 $\bar{1}\bar{4}$	< 8	2			26 0 $\bar{3}$	20	19			30 0 $\bar{7}$	13	-16		
24 0 $\bar{1}\bar{3}$	14	-18			26 0 $\bar{2}$	<10	3			30 0 $\bar{6}$	< 9	- 5		
24 0 $\bar{1}\bar{2}$	< 9	- 4			26 0 $\bar{1}$	17	-13			30 0 $\bar{5}$	< 9	10		
24 0 $\bar{1}\bar{1}$	16	18			26 0 0	13	- 9			30 0 $\bar{4}$	< 9	9		
24 0 $\bar{1}\bar{0}$	15	17			26 0 1	18	15			30 0 $\bar{3}$	12	-14		
24 0 $\bar{9}$	18	-17			26 0 2	< 9	5			30 0 $\bar{2}$	< 9	- 6		
24 0 $\bar{8}$	18	-20			26 0 3	15	-11			30 0 $\bar{1}$	10	12		
24 0 $\bar{7}$	<10	7			26 0 4	14	-10			30 0 0	15	15		
24 0 $\bar{6}$	22	23			26 0 5	15	12			30 0 1	10	-11		
24 0 $\bar{5}$	<10	- 5			26 0 6	12	10			30 0 2	11	-17		
24 0 $\bar{4}$	25	-20			28 0 $\bar{1}\bar{3}$	< 9	10			30 0 3	< 6	0		

## REFERENCES

1. Brandt, K. *Arkiv Kemi, Mineral. Geol.* **17 A** (1943) No. 15.
2. Goldschmidt, H. J. *Metallurgia* **62**, No. 374 (1960) 241.
3. Forsyth, T. B. and Wells, M. *Acta Cryst.* **12** (1959) 412.
4. Thomas, L. H. and Umeda, K. *J. Chem. Phys.* **26** (1957) 293.
5. Veenendaal, A. L., MacGillavry, D. H., Stam, B., Potters, M. L. and Römgen, M. J. H. *Acta Cryst.* **12** (1959) 242.
6. James, R. W. and Brindley, G. W. *Z. Krist.* **78** (1931) 470.
7. Cruickshank, D. W. T. *Acta Cryst.* **2** (1949) 65.
8. Wilson, A. J. C. *Nature* **150** (1942) 152.
9. Pinnock, P. R., Taylor, C. A. and Lipson, H. *Acta Cryst.* **9** (1956) 175.
10. Wadsley, A. D. *Acta Cryst.* **14** (1961) 660.
11. Pauling, L. *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, N.Y. 1945, p. 346.
12. Wells, A. F. *Structural Inorganic Chemistry*, The University Press, Oxford 1952, p. 93.
13. Frevel, L. K. and Rinn, H. W. *Acta Cryst.* **9** (1956) 626.
14. Vousden, P. *Acta Cryst.* **4** (1951) 373.

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