

Fig. 4. Mean molecular dimensions.

than the other four. The overall mean C–C length is 1.382 Å, which agrees well with that found in many other compounds. The C(1)–N bond deviates by 8° from linearity, presumably in order to relieve the close approach between N' and C(6) while maintaining the whole molecule as nearly planar as possible.

The equation of the plane of the mean half-molecule, referred to standard orthogonal axes, is

$$0.2540X - 0.7236Y + 0.6418Z = 0.0549$$

while those of the two constituent pairs, rotated from the mean through $\pm 5.0^\circ$ are

$$0.1973X - 0.7223Y + 0.6628Z = 0.0656$$

$$0.3089X - 0.7241Y + 0.6166Z = 0.0602$$

The mean deviation of the atoms from these two planes respectively is 0.007 Å, and the perpendicular separation of the two centrosymmetric halves is 0.125 Å.

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Neutron Diffraction Investigation of WO_3 *

BY B. O. LOOPSTRA AND P. BOLDRINI

Reactor Centrum Nederland, Petten (NH), The Netherlands

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The structure of the room-temperature modification of stoichiometric WO_3 was determined by a neutron-diffraction powder investigation. The space group is $P2_1/n$ and the cell constants are $a = 7.297$, $b = 7.539$, $c = 7.688$ Å, $\beta = 90.91^\circ$. W–O bonds form zigzag chains in three directions with W–O–W angles of 158° and O–W–O angles of 166° . In the x direction the bonds are of equal length, while in the y and z directions they are alternately long and short.

Introduction

The room-temperature modification of polycrystalline WO_3 has been extensively investigated by X-ray methods. Recent unit-cell data show that it is monoclinic,

pseudocubic, with space group $P2_1/a$ and cell dimensions: $a = 7.306(1)$, $b = 7.541(1)$, $c = 3.845(1)$ Å and $\beta = 90.85(5)^\circ$ (Westman & Magnéli, 1958). Tungsten coordinates have been determined from the X-ray powder intensities (Andersson, 1953), but the oxygen atoms were placed on the basis of packing considerations, resulting in a deformed ReO_3 -type structure.

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Although the substance has a strong tendency to twin, Tanisaki (1960) obtained single crystals of sufficient size for an X-ray analysis. He found that the c axis had to be doubled with an accompanying change in space group to $P2_1/n$. In addition to tungsten, the oxygen positions were derived from zero-layer Weissenberg intensities and from qualitative data for higher layers. However, a considerable margin of doubt is left regarding the uniqueness of the results (see *e.g.* Wyckoff, 1964). This made it worth while to try to obtain more reliable information about the WO_3 structure. The neutron-diffraction technique is very suitable for this purpose, the neutron scattering lengths being 0.466 and 0.577×10^{-12} cm for tungsten and oxygen, respectively. As no single crystals were available, the investigation has been performed with polycrystalline material.

Experimental

Commercial tungsten trioxide (Riedel-de-Haën) was recrystallized by heating in oxygen at 900°C for several hours, followed by slow cooling. The oxygen content of the sample, determined by reduction with hydrogen, was found to correspond to $WO_{2.985}$. This is well within the homogeneous range of the phase $WO_{3.0}$ which at room-temperature extends down to $WO_{2.96}$ (Ackermann & Rauh, 1963; Kellet & Rogers, 1963).

Even small amounts of impurities can affect the stability of the WO_3 phase (Westman & Magnéli, 1958; Crowder & Sienko, 1965). Therefore, a spectrographic analysis was undertaken, giving the following results: Mo, 0.004%; Fe, 0.001%; U, not detectable (<0.1%); Cr, Mn, Ni, V, not detectable (<0.001%); Ti, not detectable (<0.0001%). These amounts are within the permissible limits.

Neutron diffraction data were collected on the powder diffractometer at the Petten HFR, using a cylindrical vanadium container of 0.2 mm wall thickness and 20 mm diameter. Monochromatic radiation with a wavelength of 1.104 Å was obtained from a copper (200) plane. In order to make sure that the modification investigated was the room-temperature form, neutron diffraction diagrams were obtained with the sample at 100°C, room-temperature and 0°C. Soller slits of 10' were inserted between the reactor and the monochromator, and in front of the BF_3 detector. Apart from slight shifts in the line positions, no significant change in the diagrams was found. As there was considerable overlap between neighbouring reflexions in the above diagrams, the final room-temperature data were collected with Soller slits of 5½' and 5' angular divergence between the reactor and the monochromator, and in front of the detector respectively. Thus, the minimum value of the width at half maximum of a reflexion peak was 8.6' in 2θ . In the range of observation up to $\sin \theta/\lambda = 0.334$, 42 peaks were observed, containing 78 reflexions. Another 50 reflexions in this range were not observed (Table 3). As the absorption varies only very little with $\sin \theta$, it was not corrected

for. F^2 values were derived from the intensities by multiplication by $\sin \theta \sin 2\theta$ (Bacon, 1962); they were then brought to an absolute scale by comparison with the calculated values. Unit-cell constants were determined from X-ray counter diffractometer data obtained with Cu $K\alpha$ radiation. Sodium chloride ($a_0 = 5.6396(9)$ Å) was used as an internal standard. Cell parameters were fitted by a least-squares calculation. The results are:

$$a = 7.297(4), b = 7.539(3), c = 7.688(3) \text{ \AA}, \beta = 90.91(6)^\circ.$$

For $Z = 8$, this gives a calculated density of 7.27 g.cm⁻³, as compared with 7.21 g.cm⁻³ observed pycnometrically at 22°C.

Determination of the structure

Initial tungsten parameters

From the X-ray powder data a c axis of 3.845 Å is derived. On the other hand, the neutron powder data as given in Table 3 can only be indexed with a c axis of 7.69 Å and the space group $P2_1/n$; some reflexions with $l = \text{odd}$ are in fact quite strong. It follows that the doubling has to be ascribed primarily to the oxygen atoms. Initial tungsten parameters can therefore be obtained by interpreting the X-ray data which belong to a unit cell with axes a , b , and $c' = c/2$, having the space group $P2_1/a$.

In the full cell two possibilities for the idealized tungsten positions can be derived from the data of Tanisaki (1960).

		x/a	y/b	z/c
(I)	W(1)	$\frac{1}{4}$	0	$\frac{1}{4}$
	W(2)	$\frac{3}{4}$	0	$\frac{3}{4}$
(II)	W(1)	$\frac{1}{4}$	0	0
	W(2)	$\frac{3}{4}$	0	$\frac{1}{2}$

In the halved cell these two models are identical, and moreover there is only one tungsten atom in the asymmetric unit. Therefore, the parameters of this atom can be derived from the X-ray data without ambiguity. They were determined by Tanisaki from trial and error calculations, leading to $x/a = 0.250$, $y/b = 0.030$ and $z/c' = 0.066$. Using the observed structure factors for the layers $h0l$, $hk0$ and $0kl$ given by Tanisaki, an attempt was made to refine these parameters by a least-squares calculation on an Electrologica X1 computer. To remove the ambiguity due to the oxygen atoms as much as possible, they were introduced at fixed positions halfway between the initial tungsten positions. Reflexions with $l = \text{odd}$ were neglected. The function to be refined was $R = \sum w(F_o^2 - F_c^2)^2$, in which the weight w was taken as 1 for the observed and 0.1 for the unobserved reflexions. The final coordinates following from the calculations were: $x/a = 0.250$, $y/b = 0.031$, $z/c' = 0.067$.

To extend these results to the full cell, a choice must be made between model II, in which two out of six oxygen atoms occupy centres of symmetry, and model

I, in which this is not so. The neutron data, which are much more sensitive to this difference than the X-ray data, give a good fit only when model I is selected.

Oxygen parameters

Oxygen positions are most easily discussed in terms of shifts from the idealized structure, obtained by putting the tungsten atoms at general positions $\frac{1}{4}, 0, \frac{1}{4}$ and $\frac{1}{4}, 0, \frac{3}{4}$ of space group $P2_1/n$ and the oxygen atoms halfway between. The oxygen sites referred to below are the ones closest to the final positions given in Table 2. Following Tanisaki, oxygen atoms can be grouped according to the main direction of the W–O bonds into three pairs called O_x, O_y, O_z , subdivided again into $O_{x1}, O_{x2}, etc.$ Δ_i is the absolute magnitude and s_i the sign of the shift of an oxygen atom O_{jk} from its ideal position ($i, j = x, y, z; k = 1, 2$). To a first approximation it was assumed that $\Delta_i(O_{j1}) = \Delta_i(O_{j2}) = \Delta_i(O_j)$. The signs of the shifts were considered to be independent.

Owing to the fact that the tungsten atoms deviate appreciably from the ideal positions in the y and z directions, the signs $s_y(O_{y1}) = s_y(O_{y2}) = s_z(O_{z1}) = +$ and $s_z(O_{z2}) = -$ can be derived directly as long as a W–O distance of less than 1.7 Å is considered unacceptable. For the other signs it was found that even with initial rough estimates of the Δ_i values, some reflexions could only be explained by certain combinations of signs. All results were consistent with the following relations:

$$\begin{aligned} s_y(O_{x1}) &= -s_y(O_{x2}) = s_x(O_{y1}) = s_z(O_{y1}) = \\ &= -s_x(O_{y2}) = -s_z(O_{y2}) = s_y(O_{z1}) = -s_y(O_{z2}), \end{aligned}$$

derived from the 131 reflexion; $s_z(O_{x1}) = s_z(O_{x2}) = -s_x(O_{z1}) = -s_x(O_{z2})$, derived from the 10 $\bar{3}$ and the 103 reflexions.

From Table 3 it is seen that the 131 reflexion is observed together with 13 $\bar{1}$ and the 10 $\bar{3}$ together with 013. The profile of the 131 peak shows that 13 $\bar{1}$ is less than 10% of 131, while the 013 reflexion can be neglected because all $0kl$ reflexions with k and l odd are observed to be zero or very weak. This is sufficiently accurate to lead to the above sign relations.

The two relations given above, together with $s_y(O_{y1}) = s_y(O_{y2}) = s_z(O_{z1}) = +$, and $s_z(O_{z2}) = -$, contain the signs of all coordinates except $s_x(O_{x1})$ and $s_x(O_{x2})$. Combining then the plus and minus values of $s_x(O_{x1})$, $s_x(O_{x2})$, $s_y(O_{x1})$ and $s_z(O_{x1})$, 16 different sign combinations are obtained. Only 8 of these are independent, the other 8 being related to them by interchanging W(1)

and W(2). As the tungsten atoms are indistinguishable at this stage, the two models of a pair are equivalent. A complete set of models was obtained by dropping the minus value for $s_y(O_{x1})$. The remaining models were refined step by step, each step consisting of a few least-squares cycles in which the function $\sum_i [w_i(\sum_r JF_o^2 -$

$\sum_r JF_c^2)]$ was minimized. Here \sum_i is the sum over all

peaks that can be measured separately in the diagram, w_i the weight of such a peak, taken as $w_i = 1/(N_p + N_b)$ where N_p is the integrated peak plus background intensity and N_b the background intensity, \sum_r the sum over

all reflexions that together form one peak and J the multiplicity of each reflexion. The agreement factor is defined as $\frac{\sum_i (\sum_r JF_o^2 - \sum_r JF_c^2)}{\sum_i \sum_r JF_o^2}$ (Rietveld, 1966).

As the program did not allow $\Delta_i(O_{j1})$ to be kept equal to $\Delta_i(O_{j2})$, the following procedure was adopted. First, all models with the aforementioned initial Δ_i values were refined through one or two cycles. It was found that the average value of $\Delta_i(O_{j1})$ and $\Delta_i(O_{j2})$ changed by roughly the same amount, independent of the model actually selected. Therefore, the model with the lowest value of the agreement factor was refined through two more cycles. After this, the new average values $\Delta_i(O_j)$ were inserted and for these the sign relations were worked out anew to check whether previous results were still reliable. This was invariably found to be the case. Then a new step was made in the same fashion *etc.* Table 1 gives the initial Δ_i values and those obtained after three refinement steps. During the fourth step the $\Delta_x(O_x)$ values dropped rather suddenly to approximately zero for all models, thereby reducing their number to two, which were identical but for the sign of the group headed by $s_z(O_{x1})$. The positive value of this sign was rejected as it failed to give a vanishing intensity for the unobserved 032 and 034 reflexions, while the other sign also gave better agreement factors and a lower value of the minimum function. After this step the average $\Delta_i(O_j)$ values were no longer used.

Refinement of the structure

All through the refinement of the oxygen atoms so far, the tungsten coordinates were kept fixed at the value derived from the X-ray reflexions with l even. It was now attempted to obtain independent tungsten parameters by a least-squares refinement of the full set of X-ray data of Tanisaki, including the reflexions with

Table 1. Agreement factors and averaged absolute values of oxygen shifts

The agreement factors are obtained for the final signs

	Initial model			After third refinement cycle		
	Δx	Δy	Δz	Δx	Δy	Δz
O_x	0.030	0.040	0.032	0.014	0.034	0.036
O_y	0.047	0.023	0.029	0.041	0.015	0.025
O_z	0.030	0.020	0.020	0.035	0.022	0.011
	$R = 20.2\%$			$R = 12.4\%$		

l odd. In this refinement the oxygen atoms were introduced at positions as derived from the neutron work. A few steps led to

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
W(1)	0.253	0.025	0.285
W(2)	0.242	0.037	0.782

By virtue of the contribution of the oxygen atoms, it was expected that the fit would significantly differ if the shifts of W(1) and W(2) were interchanged

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
W(1)	0.242	0.037	0.282
W(2)	0.253	0.025	0.785

It was found, however, that for both cases the values of the minimum function were equal within one per cent. As a result, the number of models was again increased to two.

Keeping the tungsten parameters fixed, these two models were used for a least-squares refinement on the neutron data. In both cases the convergence was smooth but rather slow, leading to essentially the same

oxygen parameters with $s_x \Delta_x(O_{x1}) \simeq +0.006$ and $s_x \Delta_x(O_{x2}) \simeq -0.006$. It was checked that, starting from different signs for these shifts, refinement led back to the above result, so that the signs may be considered as well established. Finally the two models were refined with both the tungsten and oxygen parameters free. This removed the difference between the models, as both converged to the values for tungsten which are given in Table 2. The refinement was continued until all calculated shifts were smaller than 0.2σ . It was found that convergence could only be reached when relaxation factors no larger than 0.3 were used (Rietveld, 1966).

Results and discussion

Table 2 lists the final parameters and their standard deviations as derived from the neutron data, together with the parameters obtained by Tanisaki. Observed and calculated structure factors are given in Table 3. The *R* index as defined previously is 6.5%, including unobserved reflexions when their calculated value is larger than the estimated observable limit. Isotropic

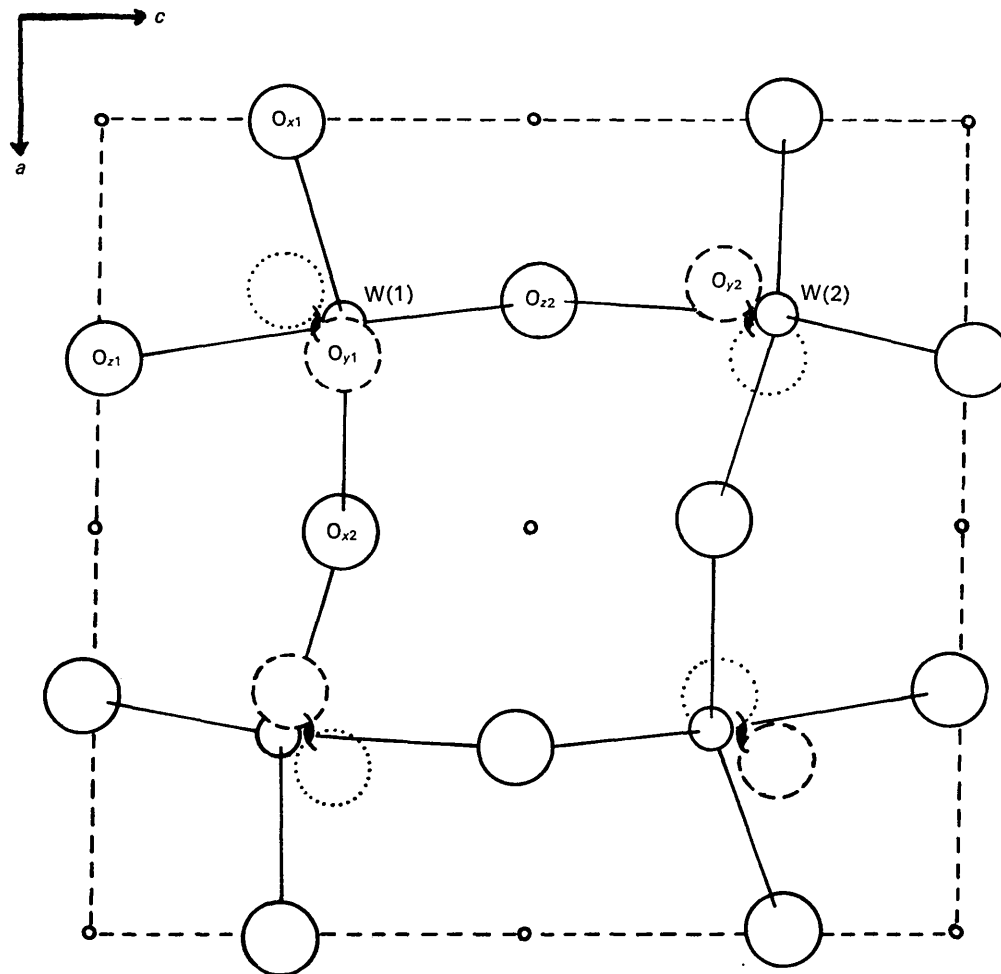


Fig. 1. Projection along the *y* axis of the cell contents between $y/b = +0.30$ and $y/b = -0.30$. Small circles: W; large circles: O. Atoms at $y \simeq \frac{1}{4}$ are dashed, those at $y \simeq -\frac{1}{4}$ dotted.

Table 2. *Coordinates*

	From present investigation			As derived by Tanisaki		
	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
W(1)	0.254 (6)	0.037 (5)	0.282 (5)	0.252	0.026	0.285
W(2)	0.250 (9)	0.023 (6)	0.784 (5)	0.247	0.033	0.781
O _{x1}	0.005 (5)	0.042 (5)	0.211 (4)	0.000	0.025	0.220
O _{x2}	0.993 (6)	0.474 (5)	0.218 (5)	0.000	0.475	0.220
O _{y1}	0.288 (3)	0.262 (6)	0.286 (3)	0.290	0.290	0.265
O _{y2}	0.211 (3)	0.259 (8)	0.730 (3)	0.210	0.290	0.735
O _{z1}	0.292 (6)	0.043 (5)	0.008 (4)	0.280	0.040	0.030
O _{z2}	0.279 (7)	0.487 (6)	0.993 (3)	0.280	0.490	0.970

Table 3. *Observed and calculated structure factors (bars per unit cell)*

<i>h k l</i>	<i>F_o²</i>	<i>F_c²</i>	<i>F_o²</i>	<i>F_c²</i>	<i>F_o²</i>	<i>F_c²</i>	<i>F_o²</i>	<i>F_c²</i>	<i>F_o²</i>	<i>F_c²</i>	<i>F_o²</i>	<i>F_c²</i>
0 1 1	.0	1.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0
0 1 0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0	.0
1 1 0	.0	.0	30.4	56.7	57.5	33.3	28.1	20.9	33.5	24.1	2.2	4.1
1 1 1	.1	.1	38.2	36.0	36.0	36.0	52.6	52.6	52.6	52.6	52.6	52.6
1 1 2	.1	.1	2.4	.0	.0	.0	.0	.0	.0	.0	.0	.0
1 1 3	.1	.1	153.4	155.0	164.7	164.7	.3	54.3	41.0	3.3	1.0	1.0
1 1 4	.1	.1	25.5	56.1	61.4	61.4	1.2	1.4	3.4	1.2	7.9	7.9
1 1 5	.1	.1	38.2	58.5	73.8	73.8	1.4	2.9	3.9	3.3	7.0	10.5
1 1 6	.1	.1	38.2	260.1	267.0	267.0	1.1	1.3	1.3	3.3	7.0	10.5
1 1 7	.1	.1	194.0	199.0	199.0	199.0	1.6	2.9	3.9	3.3	7.0	10.5
1 1 8	.1	.1	3.0	3.0	3.0	3.0	1.6	1.6	1.6	1.6	1.6	1.6
1 1 9	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 10	.1	.1	5.5	5.5	5.5	5.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 11	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 12	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 13	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 14	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 15	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 16	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 17	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 18	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 19	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 20	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 21	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 22	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 23	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 24	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 25	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 26	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 27	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 28	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 29	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 30	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 31	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 32	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 33	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 34	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 35	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 36	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 37	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 38	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 39	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 40	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 41	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 42	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 43	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 44	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 45	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 46	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 47	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 48	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 49	.1	.1	46.5	52.0	46.5	46.5	1.6	1.6	1.6	1.6	1.6	1.6
1 1 50	.1	.1	4.5	4.5	4.5	4.5	1.6	1.6	1.6	1.6	1.6	1.6

purity and oxygen content of the sample are also well known.

From Table 2 it is seen that Tanisaki's results are in much better agreement with those deduced in the present investigation than could have been expected, particularly so because in his work the shifts of W(1) and W(2) have been interchanged relative to the set of shifts of the oxygen atoms. Part of the reason for the agreement is probably that the *hk0*, *h0l*, and *0kl* single-crystal X-ray data were insensitive to this interchange. As the neutron powder data led to a unique solution, they may be considered as more reliable than the X-ray data, and therefore the tungsten parameters as derived from the neutron work have been given in Table 2. The standard deviations of these parameters are two or three times as large as those derived from the X-ray least-squares calculations, but the positions do agree very well, except in the case of the *x* parameter of W(2) which is found to be 0.242 from the X-ray result. Even in this case the difference is not significant, being less than the standard deviation of the neutron work.

temperature coefficients were taken to be: $B_W = 0.65$ and $B_O = 1.1 \text{ \AA}^2$.

In Fig. 1 the contents of the unit-cell between $y/b = +0.3$ and $y/b = -0.3$ are shown in projection along the 2_1 axis. Very similar deformed oxygen octahedra are obtained around the two tungsten atoms (Table 4). In all directions the W-O bonds form infinite zigzag chains, in which the distances are alternately short and long in the *y* and *z* directions, while in the *x* direction they are of about equal length. Along the zigzag chains the angles are: O-W-O = $166 \pm 5.6^\circ$ and W-O-W = $158 \pm 2.3^\circ$. In the octahedra the O-O distances are $2.70 \pm 0.07 \text{ \AA}$. The deviations quoted for these values are root mean square deviations.

Table 4. *Interatomic distances with standard deviations*

W(1)-O _{x1}	1.89(6) Å	W(2)-O _{x1}	1.92(7) Å
W(1)-O _{x2}	1.91(6)	W(2)-O _{x2}	1.85(8)
W(1)-O _{y1}	1.72(6)	W(2)-O _{y2}	1.85(7)
W(1)-O _{y1}	2.16(6)	W(2)-O _{y2}	2.01(8)
W(1)-O _{z1}	2.13(5)	W(2)-O _{z1}	1.75(5)
W(1)-O _{z2}	1.79(5)	W(2)-O _{z2}	2.15(5)

As is inevitable with powder work, the standard deviations of the atomic parameters are relatively large. On the other hand the powder method is attractive in so far as there is no ambiguity due to twinning, while

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