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On the Crystal Structure of $W_2O_3(PO_4)_2$

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$W_2O_3(PO_4)_2$ possesses a monoclinic unit cell which contains four formula units and has the dimensions

$$\begin{aligned} a &= (\ 7.83 \pm 0.01)\ \text{Å} \\ b &= (12.48 \pm 0.02)\ \text{Å} \\ c &= (\ 7.76 \pm 0.01)\ \text{Å} \\ \beta &= (91.9\ \ \pm 0.1)^\circ \\ V &= 758\ \text{Å}^3 \end{aligned}$$

A structure is proposed with the symmetry No. 11, $P2_1/m$. The positions of the wolfram and phosphorus atoms in the unit cell were determined from the Patterson and Fourier electron density functions. The parameters of the oxygen atoms were deduced from geometrical considerations, using interatomic distances from previoulsy determined structures. The arrangement arrived at may be considered as an idealized structure that should be slightly distorted in order to give an explanation of the very weak reflexions with k = odd.

In $W_2O_3(PO_4)_2$, there are WO_6 octahedra joined by PO_4 tetrahedra giving a three-dimensional arrangement, the groups being joined in such a way that, firstly, every WO_6 octahedron is linked to four PO_4 tetrahedra and one WO_6 octahedron and, secondly, every PO_4 tetrahedron is linked to four WO_6 octahedra.

During the course of crystal structure studies at this Institute on phosphorus-oxygen compounds of molybdenum and wolfram, reports have been published on the structures of the phases WOP_2O_7[1] and $Mo(OH)_3PO_4$[2]. According to Schulz [3], the WO_3-P_2O_5 system contains, in addition to the former compounds, a phase of the composition 2 $WO_3 \cdot P_2O_5$ which is insoluble in water, acids and dilute ammonia and slowly soluble in hot dilute sodium hydroxide. In solutions of 2 $WO_3 \cdot P_2O_5$, only orthophosphate ion could be proved — diphosphate or polyphosphate ions were not found.

This article will describe investigations on the structure of 2 $WO_3 . P_2O_5$.

PREPARATION OF THE CRYSTALS

A viscous, colourless solution of WO_3 (10 g) in concentrated (14.5 M) H_3PO_4 (25 ml) was prepared at about 220°C. The solution was heated at about 475°C for several hours, after which crystals satisfactory for X-ray work were obtained (the method according to Schulz [3]). After cooling, the crystals were washed with hot water and dried in air. Under the microscope, they were seen to be colourless rods.

Analysis. A sample was fused with sodium potassium carbonate in a platinum crucible and the cake was dissolved in boiling water. From an ammoniacal solution, the *phosphorus* was precipitated (according to Kolthoff and Sandell [4]) with a magnesium solution. The precipitate was filtered off, washed with water, dissolved in hot 1 M HNO_3 and from this solution the phosphorus was finally precipitated with ammonium molybdate and weighed as $(NH_4)_3PO_4 \cdot 12\ MoO_3$. The amount of *wolfram* in the filtrate — made neutral — was determined gravimetrically by precipitation with mercury(I)nitrate according to Cumming and Kay [5] and weighing, after ignition, as WO_3. The methods of analysis were tested carefully on samples with known compositions and the errors were found to be very low.

The *density* of the crystals was determined from the apparent loss of weight in benzene.

	Calculated for $2\ WO_3 \cdot P_2O_5$	Found	
% WO_3	75.56	76.3	76.5
% P_2O_5	23.44	23.3	23.5
Density	5.30	5.02 ± 0.01	

The density is calculated for 4 formula units per cell.

UNIT CELL AND SPACE GROUP

From rotation and Weissenberg photographs (*hk*0—*hk*4; *h*0*l*—*h*6*l*, 0*kl*—4*kl*), taken with Cu*K* radiation, of small crystals of different shapes (one needle about 0.1 mm in length and about 0.04 mm in diameter rotated around the needle axis, [010], and one cube-like body with an edge of only about 0.06 mm rotated around [100] and [001]), it was concluded that the crystals are monoclinic and that the dimensions of the unit cell are about 7.7_7 Å, 12.5_3 Å, 7.8_3 Å and that the monoclinic angle is about 91°.

The reflections were recorded photographically using the multiple film technique and the relative intensities were estimated visually by comparison with an intensity scale obtained by photographing a reflection with different exposure times. The F^2 values were then calculated using the nomograms given by Lu[6]. No correction was applied for the absorption.

More accurate values for the unit cell dimensions were calculated from a powder photograph taken with strictly monochromatized Cu$K\alpha_1$ radiation in a focusing camera of Guinier type. KCl was used as an internal standard (see Table 1, p. 671).

$$a = (\ 7.83 \pm 0.01)\ \text{Å} \qquad \beta = (91.9 \pm 0.1)^\circ$$
$$b = (12.48 \pm 0.02)\ \text{Å} \qquad V = 758\ \text{Å}^3$$
$$c = (\ 7.76 \pm 0.01)\ \text{Å}$$

The value (5.02) found for the density gives 3.8 ≈ 4 formula units in the unit cell.

The reflections with k = odd are very weak but the only ones systematically absent are

$$0k0 \text{ with } k = \text{odd}$$

This is characteristic of the space groups No. 4 $P2_1$ and No. 11 $P2_1/m$. The absence of the piezo-electric effect is consistent with the latter space group and the investigation was started by examining whether the structure was consistent with this space-group with the higher symmetry.

In No. 11 $P2_1/m$, the following point positions are possible

$2(a)$:000; $0\frac{1}{2}0$; $2(b)$: $\frac{1}{2}00$; $\frac{1}{2}\frac{1}{2}0$; $2(c)$: $00\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$;
$2(d)$: $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; $2(e)$: $\pm(x\frac{1}{4}z)$;
$4(f)$: $\pm(xyz)$; $\pm(x,\frac{1}{2}-y,z)$

POSITIONS OF THE WOLFRAM AND PHOSPHORUS (P_1) ATOMS

Patterson projections. In order to find the eight wolfram positions, the three Patterson projections $P(uvp)$, $P(pvw)$ and $P(upw)$ were calculated (Figs. 1 and 2).

The eight wolfram atoms in the unit cell must occupy either two fourfold positions ($2 \times 4(f)$) or combinations of the twofold positions and the fourfold position or four of the twofold positions. Now, if the wolfram atoms occupy any twofold position $2(a)-(e)$, we will get this as a special case of the general point position $4(f)$. Therefore, we will start the examination assuming that the eight wolfram atoms occupy point positions $4(f)$.

In the point position $4(f)$, the interatomic vectors are:

$\pm[2x$	$2y$	$2z]$	weight	1
$\pm[2x$	$1/2$	$2z]$	»	2
$\pm[0$	$2y-1/2$	$0]$	»	2

By comparing this table with $P(uvp)$ in Fig. 1, we see that at $u = 0$ there is (besides the origin maximum) only one high maximum at $v = 1/2$, and thus we find that the y-coordinates will be ≈ 0 or $1/4$. Now, in $P(uvp)$ there are also pronounced peaks at $v = 1/4$ (A and B in Fig. 1). These maxima certainly correspond to W—W vectors and the position at $v = 1/4$ will exclude the possibility that all of the wolfram atoms have the same y coordinate. Thus we conclude that the y-coordinates of the wolfram atoms are 0 and 1/4, which will give

$4\ W_1$ in $4(f)$ with $x = x_1 \quad y \approx 0 \quad z = z_1$
$2\ W_2$ in $2(e)$ » $x = x_2 \quad y = 1/4 \quad z = z_2$

The W—W distances would then be

$\pm[0$	$\frac{1}{2}$	$0]$	weight	2
$\pm[2x_1$	$1/4 \pm 1/4$	$2z_1]$	»	2
$\pm[2x_2$	$\frac{1}{2}$	$2z_2]$	»	1
$\pm[x_1 \pm x_2$	$\pm 1/4$	$z_1 \pm z_2]$	»	2

Now in $P(uvp)$ and $P(pvw)$ (Fig. 1), we see that all peaks at $v = 0$ are nearly identical with the maxima at $v = 1/2$. This is not in agreement with the

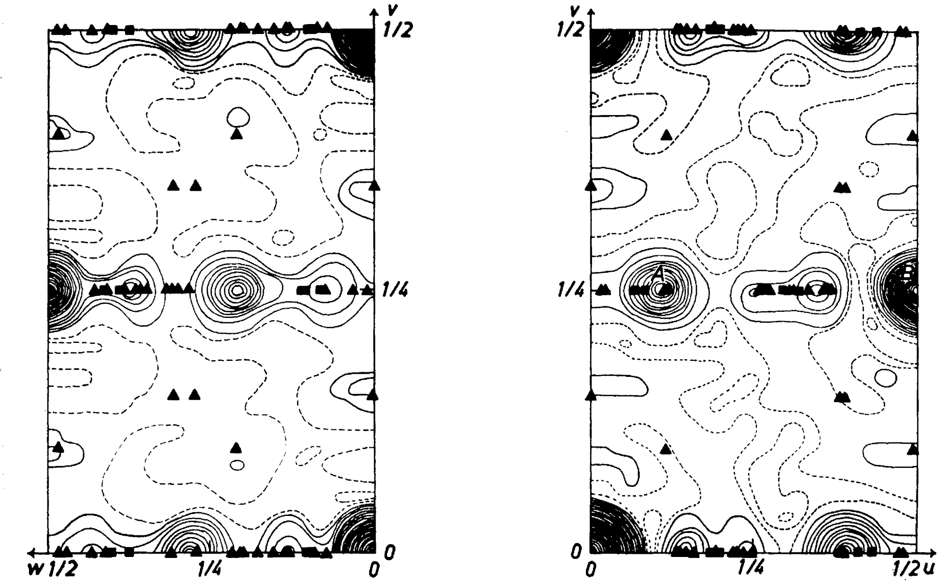

Fig. 1. The Patterson projections $P(uvp)$ and $P(pvw)$. The W—P (■) and W—O (▲) vectors have been indicated for the final structure. Dashed lines indicate negative values.

table above. The only way to explain this is that the remaining two wolfram atoms (W_3) are situated in the point position $2(e)$ with $x \approx -x_2$ and $z \approx -z_2$. Thus we have

$$2\ W_3 \text{ in } 2(e) \text{ with } x \approx -x_2 \quad y = 1/4 \quad z \approx -z_2$$

The W—W distances would then be:

$\pm[0$	$\frac{1}{2}$	$0]$	weight 4
$\pm[2x_1$	$1/4 \pm 1/4$	$2z_1]$	» 2
$\pm[2x_2$	$1/4 \pm 1/4$	$2z_2]$	» 2
$\pm[x_1 \pm x_2$	$\pm 1/4$	$z_1 \pm z_2]$	» 4

The Patterson projection on the *uw* plane should therefore show (besides the origin maximum) the following maxima

I	$\pm[2x_1\ ,$	$2z_1]$	weight 4
II	$\pm[2x_2\ ,$	$2z_2]$	» 4
III	$\pm[x_1 + x_2,$	$z_1 + z_2]$	» 8
IV	$\pm[x_1 - x_2,$	$z_1 - z_2]$	» 8

There are two high peaks in $P(upw)$ at $u = 0.39_0$, $w = 0.27_4$ (C in Fig. 2) and at $u = 0.61_4$, $w = 0.31_2$ (D in Fig. 2) and, in addition, two peaks at

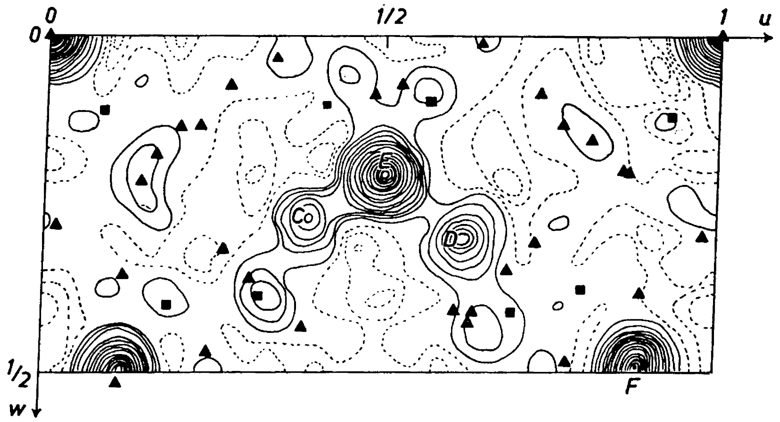

Fig. 2. The Patterson projection $P(upw)$. The positions of the vectors for the final structure have been marked as in Fig. 1. For the largest maxima (00) and (10), only every second contour has been marked. Dashed lines indicate negative values.

$u = 0.49_7$, $w = 0.20_7$ (E in Fig. 2) and at $u = 0.88_8$, $w = 0.48_1$ (F in Fig. 2) whose heights are about double those of the former. (All maxima have been located by the interpolation table given by Booth [7]). These maxima certainly correspond to the W—W wectors I—IV so the peak C must correspond to the vector I or II (and D to II or I) and the peak E to the vector III or IV (and F to IV or III). By calculating the vectors I—IV for all possible combinations of x_1, x_2, z_1 and z_2, the following two alternatives were found for the arrangement of the wolfram atoms (it is sufficient to consider the range $0 \leq x \leq \frac{1}{2}$, $0 \leq z \leq 1$):

Alt. a:	4 W_1	in	4(*f*)	with	$x \approx 0.19_5$	$y \approx 0$	$z \approx 0.13_7$
	2 W_2	»	2(*e*)	»	$x \approx 0.31_0$	$y = 1/4$	$z \approx 0.65_3$
	2 W_3	»	2(*e*)	»	$x \approx 0.69_0$	$y = 1/4$	$z \approx 0.34_7$
Alt. b:	4 W_1	»	4(*f*)	»	$x \approx 0.31_0$	$y \approx 0$	$z \approx 0.65_3$
	2 W_2	»	2(*e*)	»	$x \approx 0.19_5$	$y = 1/4$	$z \approx 0.13_7$
	2 W_3	»	2(*e*)	»	$x \approx 0.80_5$	$y = 1/4$	$z \approx 0.86_3$

These two sets of wolfram parameters will give identical W—W vectors and the values obtained checked well with the Patterson projections $P(uvp)$ and $P(pvw)$ in Fig. 1. The positions and heights of the maxima in these projections were found to be in good agreement with the claculated W—W-distances. The parameters obtained from $P(upw)$ should, however, be more accurate since, in the calculation of this projection, more F^2 values were used and since less overlapping occurs in this projection.

Thus, from the Patterson projections we get two alternatives for the arrangement of the wolfram atoms and, at this state of the investigation, it was not possible to rule out one of them.

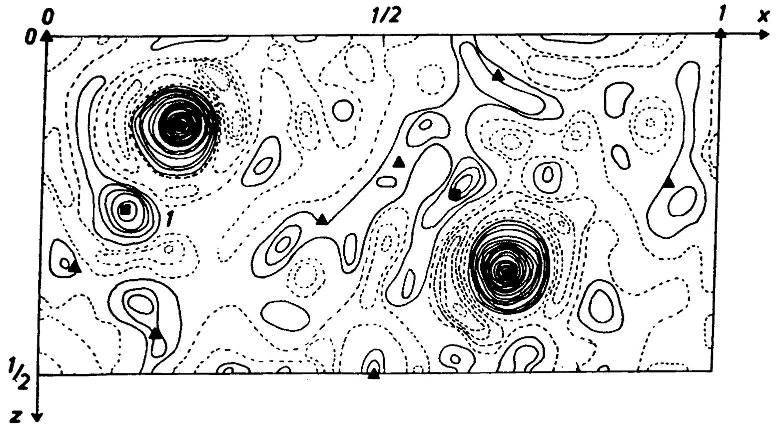

Fig. 3. Electron density projected on the xz plane. The final positions of the phosphorus (■) and oxygen atoms (▲) have been marked. In the wolfram peaks, only every second contour has been marked. Dashed lines indicate negative values.

However, in the Patterson projections there are, in addition to peaks corresponding to the W—W vectors, several lower maxima which perhaps could be ascribed to the W—P distances. In the unit cell, there are eight phosphorus atoms situated in 4(f) and/or 2(a)—(e) and consequently the corresponding possible W—P distances were calculated. From the positions of the lower maxima, situated at $v = 0$, 1/4 and ½ in Fig. 1, 2(a)—(d) can at once be ruled out as possible point positions if the peaks are real and correspond to W—P vectors. Thus the phosphorus atoms must occupy 2(e) and/or 4(f). It should now be possible to obtain possible alternatives for the parameters of the phosphorus atoms but it would be preferable to determine their sites from a map giving electron density since such a map gives maxima that are sharper and less in number than those of the corresponding vector map.

Electron density projection. For a compound of this type, the electron density projections can easily be calculated since the signs of all the F_{hkl} values can be determined from the contributions given by the wolfram atoms because of their dominant scattering factors. In this case, the projection $\varrho(xpz)$ should be favourable for calculation since the two alternatives for the wolfram arrangement will give equal F_{h0l} values. In this way, $\varrho(xpz)$ was calculated and the result is given in Fig. 3. We see that the wolfram atoms are clearly indicated at $x = 0.195$, $z = 0.137$ and at $x = 0.690$, $z = 0.347$.

Besides the very high wolfram maxima in the calculated electron density projection, there is a lower peak in $\varrho\ (xpz)$ at $x = 0.12$, $z = 0.26$ (1 in Fig. 3). If this lower peak is a real maximum, and not a false one due to diffraction effects or inadequate intensity data, it is possible that two overlapping phosphorus atoms could give a peak of this height. As mentioned above, the point positions 2(e) and 4(f) were possible for the arrangement of the phosphorus atoms. If four phosphorus atoms are situated in 4(f), two phosphorus maxima overlap in the xz projection of the electron density. Since the projection $\varrho(xpz)$ really shows one rather distinct maximum (1 in Fig. 3), which could be ascribed to overlapping phosphorus atoms, we may conclude that this peak, if real, gives the position of four phosphorus atoms (4 P_1) in 4(f). Now all $W-P_1$ distances were calculated and the lower maxima in the Patterson projections were compared with the $W-P_1$ vectors. From Fig. 1, we see that most of the lower peaks outside $v = \pm 1/4$ are situated in or close to the planes $v = 0$ and ½. From this we immediately obtain $y_{P_1} \approx 0$ and thus we may conclude

$$4\ P_1 \text{ in } 4(f) \text{ with } x \approx 0.12 \qquad y \approx 0 \qquad z \approx 0.26$$

For the arrangement of the wolfram atoms we have already found two possible sets of parameters (see p. 661) and consequently we obtain two alternatives for the W—P vectors

$$\left.\begin{aligned} u &= \pm\ (0.195 \pm 0.12) \\ w &= \pm\ (0.137 \pm 0.26) \end{aligned}\right\} \qquad \begin{aligned} v &= 0 \text{ and } 1/2 \text{ if alt. a} \\ &= 1/4 \text{ and } 3/4 \text{ if alt. b} \end{aligned}$$

$$\left.\begin{aligned} u &= \pm\ (0.310 \pm 0.12) \\ w &= \pm\ (0.653 \pm 0.26) \end{aligned}\right\} \qquad \begin{aligned} v &= 1/4 \text{ and } 3/4 \text{ if alt. a} \\ &= 0 \text{ and } 1/2 \text{ if alt. b} \end{aligned}$$

Thus it should be possible, from the positions of the maxima corresponding to the vectors above, to decide which alternative for the wolfram coordinates is the correct one. The vectors were therefore compared with $P(uvp)$ and $P(pvw)$ in Fig. 1 and it was found that the two alternatives seemed to be about equally plausible, even if the agreement might be a little better for b than for a.

Three-dimensional Patterson calculations. By introducing three dimensional Patterson calculations, it should, however, be possible to decide which of the two sets gives the correct wolfram position in the unit cell. Therefore $P(u0w)$ and $P(u1/4w)$ were calculated using all reflexions (975) obtained with CuK radiation. In order to obtain more reflexions and in this way reduce the cutting-off effects, trials were also made with MoK radiation but it was found that these experiments gave no additional information. However, the data obtained with CuK radiation should be sufficient, even if it would have been advantageous to get reflexions with higher h and l values than nine which was the highest index in these directions obtained with CuK radiation. The results are given in Fig. 4 ($P(u0w)$) and Fig. 5 ($P(u1/4w)$).

In $P(u0w)$ there are, besides the maxima due to W—W vectors, two maxima at $w = 0.19_2$, $w = 0.41_0$ (1 in Fig. 4) and at $u = 0.56_1$, $w = 0.09_2$ (2 in Fig. 4). In $P(u1/4w)$ there are also, besides the high "wolfram" peaks, two maxima at $u = 0.32_3$, $w = 0.38_5$ (3 in Fig. 5) and at $u = 0.92_9$, $w = 0.11_9$ (4 in Fig. 5). All these maxima certainly correspond to the $W-P_1$ wectors given above since the positions and heights of the peaks are in good agreement with calculated data and, moreover, from the position of the peaks 1 and 2 at $v = 0$ (and 3 and 4 at $v = 1/4$) we obtain immediately that the alternative b will give the correct position of the wolfram atoms. Thus we may conclude (the values are weighted means of the parameters found in the calculated functions):

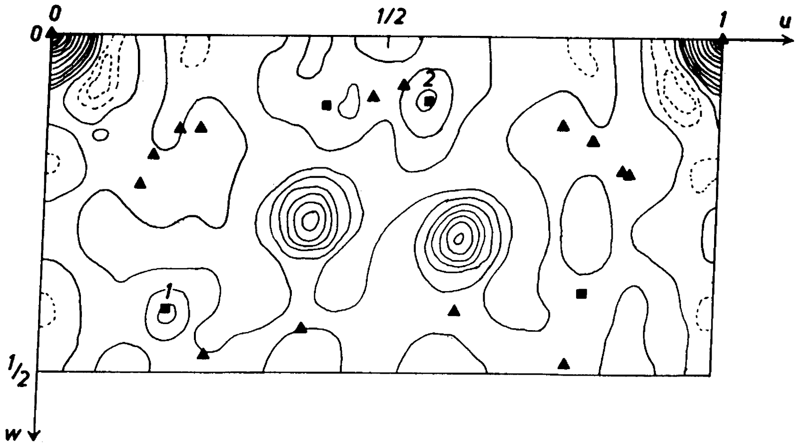

Fig. 4. The Patterson function $P(u0w)$. The positions of the vectors for the final structure have been marked as in Fig. 1. For the maxima at (00) and (10), only every second contour has been marked. Dashed lines indicate negative values.

4 W_1	in $P2_1/m$	4(*f*)	with	$x = 0.310$	$y = 0$	$z = 0.653$
2 W_2	» »	2(*e*)	»	$x = 0.195$	$y = 1/4$	$z = 0.137$
2 W_3	» »	2(*e*)	»	$x = 0.805$	$y = 1/4$	$z = 0.863$
4 P_1	» »	4(*f*)	»	$x = 0.12$	$y = 0$	$z = 0.25$

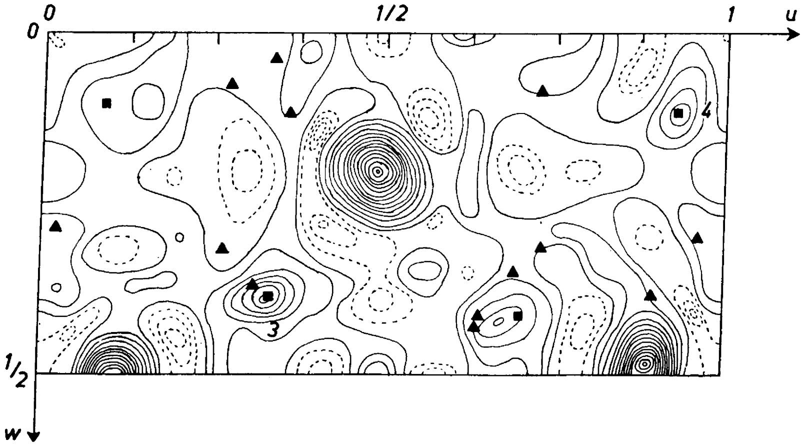

Fig. 5. The Patterson function $P(u1/4w)$. The positions of the vectors for the final structure have been marked as in Fig. 1. For the two largest maxima, only every second contour has been marked. Dashed lines indicate negative values.

Using these parameters, W—P_1 distances were calculated and these vectors have been indicated in Figs. 1 and 2. The agreement between observed and calculated data is quite good thus indicating that the coordinate values are reasonably correct.

The remaining maxima in the Patterson functions and electron density projection may correspond to W—P and W—O vectors or phosphorus and oxygen atom positions but, at this stage of the investigation, they were not considered since these peaks are about the same height as the false maxima.

POSITIONS OF THE OXYGEN ATOMS

General remarks. The light oxygen atoms do not make any appreciable contribution to the intensities of the reflections and their positions had thus to be found from considerations of the interatomic distances. The following assumptions were made:

1. The W—O distance was assumed to be not less than that found[8–10] in WO_3 and related compounds, *i.e.* 1.8_5 Å.

2. Each phosphorus atom was assumed to be surrounded by four oxygen atoms giving a tetrahedron with the bond lengths within the limits: P—O = $1.4_5 - 1.6_5$ Å and O—O = $2.4_8 - 2.6_8$ Å (these distances are limits for those published[11–13]).

3. The distance between two oxygen atoms not belonging to the same PO_4-group was assumed to be not less than 2.6_0 Å.

With these assumptions, the space free for oxygen atoms will be deduced as follows.

There are two symmetry planes in the unit cell at $y = \pm 1/4$. If an oxygen atom is not situated exactly in a symmetry plane, it must be at a distance of at least 1.3_0 Å (1.2_4 Å if belonging to the same PO_4-group) from it. Accordingly, the y coordinates of the atoms should be either $y = 1/4$ and $y = 3/4$ or within the limits $-0.14_5 \leq y \leq 0.14_5$, $0.35_5 \leq y \leq 0.64_5$ Moreover there are eight symmetry centres per unit cell (the point positions $2(a)-(d)$). If an oxygen does not coincide with a symmetry centre, it must be situated outside a sphere of radius 1.3_0 Å around it. For the same reason, spheres of radii 2.6_0 Å around each oxygen atom which has been located and of radii 1.8_5 Å around each wolfram atom enclose domains forbidden for the centres of other oxygen atoms.

Positions of the oxygen atoms around the phosphorus atoms (P_1). The four phosphorus atoms, the positions of which have been found above, are surrounded by four wolfram atoms at the distances: P_1—W_2; W_2—2 P_1 = 3.2_9 Å; P_1—W_3, W_3—2 P_1 = 3.2_9 Å; P_1—2 W_1, W_1—2 P_1 = 3.4_2 Å, 3.4_7 Å. The angles, W—P—W, between the phosphorus and the four neighbouring wolfram atoms are 104°, 101°, 100° and 143°. Now it seems very probable that the four oxygen atoms around the phosphorus atom P_1 will be strongly attracted by the wolfram atoms and, with the assumptions made above and from the calculated angles and W—P_1 distances, we see that it is possible for all oxygen atoms belonging to the same PO_4 tetrahedron to be in contact with four different wolfram atoms. Assuming this, which seems to be very probable, the following coordinates are obtained

4 O_1	in	$P2_1/m$	4(*f*)	with	$x = 0.20$	$y = 0.10_0$	$z = 0.14$
4 O_2	»	»	»	»	$x = 0.20$	$y = 0.90_0$	$z = 0.14$
4 O_3	»	»	»	»	$x = 0.17$	$y = 0$	$z = 0.44$
4 O_4	»	»	»	»	$x = 0.93$	$y = 0$	$z = 0.22$

Positions of the oxygen atoms O_5 and O_6. In this structure, the wolfram atoms are situated in pairs, W_1-W_1 and W_2-W_3, with the distances 3.8_7 Å or 3.6_6 Å. Now, in several oxygen compounds of wolfram, a similar value, about 3.75 Å, has been found [8,9,14] for the distances between wolfram atoms joined by oxygen atoms. It seems therefore very probable that the wolfram atoms mentioned above are also joined in the same way; *i.e.* by oxygen atoms. Assuming this, the parameters of the oxygen atoms O_5 and O_6 would be

2 O_5	in	$P2_1/m$	2(*d*)	with	$x = 1/2$	$y = 0$	$z = 1/2$
2 O_6	»	»	2(*e*)	»	$x = 0$	$y = 1/4$	$z = 0$

Positions of the oxygen atoms O_7-O_{14}. For the remaining 24 oxygen atoms in the unit cell we note, as before for the oxygen atoms O_1-O_6, that they must be strongly attracted by the wolfram atoms and, consequently, should be situated as close to them as possible. Now we have found contacts W—3 O and if all of the remaining 24 oxygen atoms are in contact with wolfram, we obtain the coordination W—6 O. A higher coordination number is excluded since spatial reasons will prevent the latter O atoms being in contact with more than one W atom. Now, in most of the oxygen compounds of wolfram the same coordination number has been reported [9,14,15] and thus, it seems very reasonable that the coordination W—6 O also occurs in $2WO_3 \cdot P_2O_5$. We must therefore investigate the possibility that all of the remaining oxygen atoms in the unit cell are in contact with wolfram. Now, the wolfram atoms W_2 and W_3 are situated in the symmetry planes ($y = \pm 1/4$) and each of them is in contact with three oxygen atoms (O_1, O_2 and O_6). Two of these oxygen atoms (O_1 and O_2) are situated outside the symmetry planes and, with the assumptions made above (see p. 665), we get immediately that the only possibility for obtaining the coordination W_2-6 O and W_3-6 O is with 12 oxygen atoms in the point position 2(*e*). Reasonable interatomic distances were only obtained assuming:

2 O_7	in	$P2_1/m$	2(*e*)	with	$x = 0.05$	$y = 1/4$	$z = 0.34$
2 O_8	»	»	»	»	$x = 0.95$	$y = 1/4$	$z = 0.66$
2 O_9	»	»	»	»	$x = 0.42$	$y = 1/4$	$z = 0.27$
2 O_{10}	»	»	»	»	$x = 0.58$	$y = 1/4$	$z = 0.73$
2 O_{11}	»	»	»	»	$x = 0.67$	$y = 1/4$	$z = 0.06$
2 O_{12}	»	»	»	»	$x = 0.33$	$y = 1/4$	$z = 0.94$

From the positions given above for the oxygen atoms O_3, O_4 and O_5 — which atoms are in contact with the wolfram atoms W_1 and situated in the same planes ($y = 0$ and $1/2$) — we obtain at once that the only possibility for obtaining the coordination W_1-6 O is if the remaining twelve oxygen atoms are situated in the point position 4(*f*). It is now easy to calculate the coordinates of those atoms so that reasonable O—O and W—O distances are obtained. Thus we get

4 O_{13} in $P2_1/m$ 4(*f*) with $x = 0.47$ $y = 0$ $z = 0.83$
4 O_{14} » » » » $x = 0.31$ $y = 0.15_0$ $z = 0.65$
4 O_{15} » » » » $x = 0.31$ $y = 0.85_0$ $z = 0.65$

POSITIONS OF PHOSPHORUS ATOMS P_2 AND P_3

Now when the positions of all oxygen atoms have been determined, the parameters of the four remaining phosphorus atoms should be obtainable. It was assumed above that the coordination figure around the phosphorus atoms is a tetrahedron. Thus it should be possible using the known oxygen positions to find the remaining phosphorus positions so that each of these atoms will be surrounded by four oxygen atoms in a tetrahedral arrangement and with the P—O distances within the limits assumed above (p. 665).

Since a PO_4-group has not a centre of symmetry as would be required in 2(*a*)—(*d*), the four phosphorus atoms must occupy the positions 4(*f*) or 2 × 2(*e*). Now, in the Patterson projections in Fig. 1, we see that most of the maxima are situated at $v = 0$, 1/4 and ½ and from this we conclude that, if the phosphorus atoms are situated in 4(*f*), the y-coordinate ≈ 0. Otherwise, we would have pronounced peaks due to W—P vectors outside these planes. As a matter of fact, the low maxima situated outside the planes ($v = 0$, 1/4 and ½) were found to correspond to W—O vectors (see p. 670). However, at $y = 0$ through the unit cell, there are only two tetrahedral interstices of the kind described above *viz.* those coinciding with the positions of the phosphorus atoms P_1. Thus the remaining four phosphorus atoms must be situated in the symmetry planes ($y = \pm 1/4$), *i.e.* in the position 2(*e*). The x and z coordinates of these phosphorus atoms — situated with $y = 1/4$ — are easy to determine since there are also in this section through the unit cell only two possible phosphorus positions. Thus we obtain

2 P_2 in $P2_1/m$ 2(*e*) with $x = 0.61$ $y = 1/4$ $z = 0.26$
2 P_3 » » » » $x = 0.39$ $y = 1/4$ $z = 0.74$

REFINEMENT OF THE PARAMETERS

The parameters found above will only give an idealized structure since the weak reflections with odd k remain unexplained. The appearance of these reflections could be explained by assuming a distortion of the structure in such a way that some or all of the atoms are displaced from the positions given above. A refinement of the structure was therefore started.

In order to eliminate the diffraction effects as much as possible and get more reliable x and z coordinates for the phosphorus atoms, the wolfram atoms were subtracted from the Fourier image in Fig. 3. The structure factors were then corrected by an exponential factor, $e^{-0.28 \sin^2 \Theta}$, obtained in the

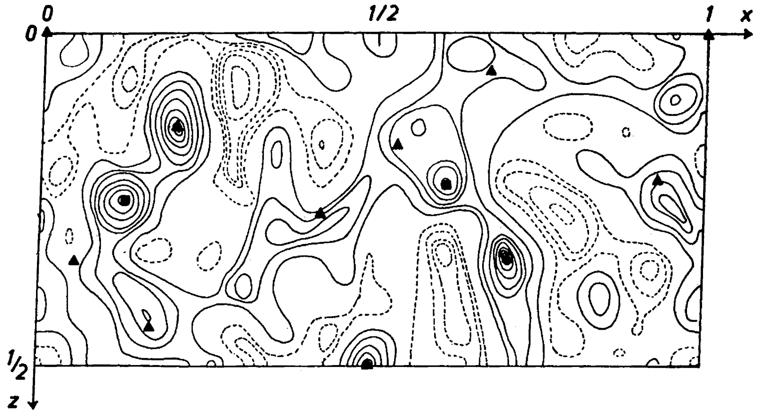

Fig. 6. Electron density projected on the xz plane with the wolfram atoms subtracted. The final positions of the phosphorus and oxygen atoms have been indicated as in Fig. 3. Dashed lines indicate negative values.

ordinary way for the determination of temperature factors. From Fig. 6, which shows this new electron density projection, we see the phosphorus atoms P_1 at $x = 0.11_8$, $z = 0.25_4$ and $P_2 + P_3$ at $x = 0.60_6$, $z = 0.23_7$. The four overlapping oxygen atoms are also clearly indicated at $x = 0.20$, $z = 0.15$ (O_1 and O_2) and at $x = 0.70$, $z = 0.34$ (O_{14} and O_{15}). The positions of these peaks are in good agreement with the corresponding parameters given above except for the z-parameter of the phosphorus atoms P_2 and P_3 which should be changed from 0.26 to 0.23 according to this new electron density projection. The positions of the oxygen atoms, belonging to the tetrahedra around P_2 P_3, consequently had to be shifted a little in order to get reasonable P—O distances. It is remarkable that most of the remaining maxima — although rather diffuse and about the same heigh as the false maxima — were found to coincide fairly well with oxygen positions. However, by means of this calculation, it was not possible to obtain any deviations which could explain the double b axis even if the maximum formed by the overlapping atoms P_2 and P_3 is a little elongated, indicating perhaps that x_{P_2} and z_{P_2} not are exactly equal to $\bar{x}_{P_3}$ or $\bar{z}_{P_3}$ as assumed above. An attempt to solve the structure by trial and error methods assuming a displacement of these phosphorus atoms and of the surrounding oxygen atoms was however, without success.

It was thought that three-dimensional Patterson calculations would perhaps solve the problem. Such calculations were therefore performed, firstly, in order to discover any deviation from the space group considered and, secondly, to investigate displacements like those proposed above for P_2 and P_3 or distortions produced when some of the atoms are not situated exactly in the planes $y = 0$ or $1/4$ ($\frac{1}{2}$ or $3/4$) as obtained — except in the case of the oxygen atoms O_1, O_2, O_{14} and O_{15} — in the structure investigation given above. However, all these attempts to perform a complete structure determination were in vain. Neither was it possible to solve the structure by calculating the generalized

Patterson functions using the observed values of $|F_{h1l}|^2$, $|F_{h3l}|^2$ or $|F_{h5l}|^2$. This was probably due to the poor experimental intensity material from the weak zones, *h*1*l*, *h*3*l* and *h*5*l*, obtained with Cu*K* radiation (as to Mo*K* radiation *cf.* p. 663).

Finally, attempts to solve the structure by trial and error methods assuming that the weak reflections were due to the displacement of the wolfram and some of the oxygen atoms were also without success.

FINAL STRUCTURE PROPOSITION

Thus, in spite of all the attempts to make a complete structure determination, we must restrict our conclusions to the following idealized structure for 2 $WO_3.P_2O_5$.

Space group No. 11 $P2_1/m$. Four formula units per unit cell. Atomic positions:

	x	*y*	*z*
4 W_1 in 4(*f*)	0.310 ± 0.003	0	0.653 ± 0.003
2 W_2 in 2(*e*)	0.195 ± 0.003	1/4	0.137 ± 0.003
2 W_3 in 2(*e*)	0.805 ± 0.003	1/4	0.863 ± 0.003
4 P_1 in 4(*f*)	0.12	0	0.25
2 P_2 in 2(*e*)	0.61	1/4	0.24
2 P_3 in 2(*e*)	0.39	1/4	0.76
4 O_1 in 4(*f*)	0.20	0.10_0	0.14
4 O_2 in 4(*f*)	0.20	0.90_0	0.14
4 O_3 in 4(*f*)	0.17	0	0.44
4 O_4 in 4(*f*)	0.93	0	0.22
2 O_5 in 2(*d*)	½	0	½
2 O_6 in 2(*e*)	0	1/4	0
2 O_7 in 2(*e*)	0.05	1/4	0.34
2 O_8 in 2(*e*)	0.95	1/4	0.66
2 O_9 in 2(*e*)	0.42	1/4	0.27
2 O_{10} in 2(*e*)	0.58	1/4	0.73
2 O_{11} in 2(*e*)	0.67	1/4	0.06
2 O_{12} in 2(*e*)	0.33	1/4	0.94
4 O_{13} in 4(*f*)	0.47	0	0.83
4 O_{14} in 4(*f*)	0.31	0.15_0	0.65
4 O_{15} in 4(*f*)	0.31	0.85_0	0.65

The accuracy of the parameters for the phosphorus and the oxygen atoms is estimated to be about ± 0.02. Using these parameters, all the structure factors *hk*0—*hk*4, 0*kl*—4*kl* and *h*0*l*—*h*6*l* were calculated, multiplied by the factor $e^{-0.28 \sin^2 \Theta}$ (*cf.* above) and compared with the observed ones. Some of the results are shown in Table 2 where the values for *hk*0, *h*0*l*, *h*2*l* and 0*kl* for even values of *k* have been listed. All the *observed* structure factors with odd *k* from *hk*0, 0*kl* and *h*1*l* have been listed in Table 3. As is seen from Table 2, there is quite a good agreement between the observed and calculated data. The reliability index according to Booth (see Ref.[5], p. 101) was found to be 0.18 for *hk*0, 0.16 for *h*0*l* and 0.17 for 0*kl* (absent reflections not included) and 0.22, 0.21 and 0.22 for the same reflections calculated without the phosphorus and oxygen atoms. This shows that the structure should be essentially correct as regards the heavy atoms and also indicates that the proposed coordinates for the phosphorus and the oxygen atoms will give a better agreement between observed and calculated intensities than that obtained when the phosphorus and oxygen atoms are omitted from the calculations. The coordinates were also checked against the Patterson functions and the electron density projections. The positions of all W—P and W—O vectors have been indicated in Figs. 1, 2, 4 and 5 and the positions of the phosphorus and oxygen atoms have also been market in Figs. 3 and 6. From the figures, we see that the agreement between calculated maxima and observed peaks is fairly good, which also seems to indicate the coordinate values to be plausible.

In the structure determination described above, we have assumed that the structure is consistent with the space group $P2_1/m$ having the higher symmetry and, since nothing was found against this, the asumption may be correct. Nevertheless, it is of course possible that all or some of the atoms are arranged according to the low-symmetry space group $P2_1$ and this has also in part been considered since all calculations made for the structure determination are independent of the space group assumption. However, it does not seem possible to get any essential difference for the atom arrangement even if the space

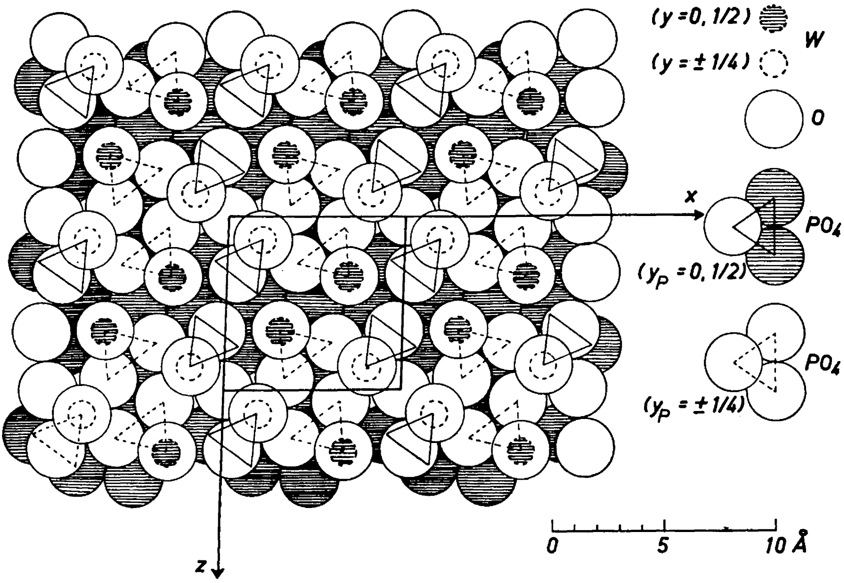

Fig. 7. Projection on the *xz* plane of the structure of $W_2O_3(PO_4)_2$.

group $P2_1$ is considered. This will perhaps increase the errors in the parameters since all of the coordinates are therefore obtained from overlapping peaks.

DESCRIPTION OF THE STRUCTURE

The structure of $2WO_3.P_2O_5$ may be described as built up of WO_6-octahedra and PO_4-tetrahedra. Every wolfram atom is in contact with four PO_4-groups and every PO_4-group with four wolfram atoms. Every wolfram atom is also in contact with one oxygen atom (O_{7-8}; O_{13}), which is bound only to this wolfram atom, and one oxygen atom (O_{5-6}) that is shared by two wolfram atoms. In this way, the crystals are built up of plane W_2O_3-groups parallel to the *xz* plane and joined by PO_4-tetrahedra so that every tetrahedron links together four W_2O_3-groups giving a threedimensional arrangement. The building principle might be expressed by the formula $W_2O_3(PO_4)_2$ and the compound should then be written according to this rather than $2WO_3 \cdot P_2O_5$. A further discussion of the structure will be given later on in a separate article.

The *xz* projection of the structure is shown in Fig. 7.

Table 1. Powder photograph of $2WO_3 \cdot P_2O_5$. CuK_{α_1}-radiation. Reflections systematically absent in space group $P2_1/m$ have been omitted. KCl (a = 6.2930 Å) has been used as an internal standard.

h k l	$10^4\sin^2\Theta$ calc	$10^4\sin^2\Theta$ obs	$p\,F^2$ calc	I obs
1 0 0	97	96	< 1	v v w
0 0 1	99	—	< 1	—
1 1 0	135	—	0	—
0 1 1	137	—	0	—
0 2 0	152	—	0	—
1 0 $\bar{1}$	189	190	12	v w
1 0 1	202	203	10	v v w
1 1 $\bar{1}$	227	228	0	v v w
1 1 1	240	—	0	—
1 2 0	249	250	218	v v st
0 2 1	251		242	
1 2 $\bar{1}$	341	342	196	v v st
1 2 1	354	355	192	st
2 0 0	388	385	114	m
0 0 2	394	396	52	w
2 1 0	426	426	0	v v w
0 1 2	432	—	0	—
1 3 0	440	—	0	—
0 3 1	442	—	0	—
2 0 $\bar{1}$	473	476	147	v v st
1 0 $\bar{2}$	478		172	
2 0 1	499	498	110	st
1 0 2	504	505	213	m
2 1 $\bar{1}$	511	—	0	—
1 1 $\bar{2}$	516	—	0	—
2 1 1	537	540	0	v v w
1 3 $\bar{1}$	539		0	
2 2 0	540		< 1	
1 1 2	542	—	0	—
1 3 1	545	—	0	—
0 2 2	547	550	5	v v w
0 4 0	610	607	372	v v st
2 2 $\bar{1}$	626	625	92	m
1 2 $\bar{2}$	631	—	3	—
2 2 1	652	655	122	m
1 2 2	657		4	
1 4 0	706	697	< 1	v v w
0 4 1	708	—	< 1	—
2 3 0	731	733	0	v w
0 3 2	737	—	0	—
2 0 $\bar{2}$	756	—	3	—
2 1 $\bar{2}$	794	—	0	—
1 4 $\bar{1}$	799	799	11	v v w
2 0 2	808	—	2	—
1 4 1	812	813	8	v v w
2 3 $\bar{1}$	816	—	0	—
1 3 $\bar{2}$	821	—	0	—
2 3 1	842	—	0	—
2 1 2	846	—	0	—
1 3 2	847	847	0	v v w
3 0 0	872	—	> 1	—
0 0 3	877	—	> 1	—
2 2 $\bar{2}$	908	910	212	st
3 1 0	910	—	0	—
0 1 3	925	—	0	—
3 0 $\bar{1}$	951	953	42	w

Table 2. Comparison between calculated and observed structure factors from Weissenberg photographs of $W_2O_3(PO_4)_2$. Cu*K*-radiation.

h k l	*F* calc	/*F*/ obs	*h k l*	*F* calc	/*F*/ obs	*h k l*	*F* calc	/*F*/ obs	*h k l*	*F* cals	/*F*/ obs
3 0 9	16	—	7 0 5	15	—	9 0 $\bar{3}$	21	26	0 2 9	20	33
2 0 9	26	28	6 0 5	−89	72				1 2 $\bar{9}$	42	51
1 0 9	11	9	5 0 5	−22	18	9 0 2	−69	79	2 2 $\bar{9}$	−16	—
0 0 9	31	24	4 0 5	78	70	8 0 2	4	—	3 2 $\bar{9}$	−8	9
1 0 $\bar{9}$	−19	21	3 0 5	16	—	7 0 2	59	67	4 2 $\bar{9}$	−11	11
2 0 $\bar{9}$	−67	66	2 0 5	−35	50	6 0 2	8	—			
3 0 $\bar{9}$	27	26	1 0 5	3	—	5 0 2	−18	8	5 2 8	−48	52
4 0 $\bar{9}$	53	47	0 0 5	−23	24	4 0 2	11	9	4 2 8	55	46
			1 0 $\bar{5}$	−5	7	3 0 2	−85	95	3 2 8	23	18
5 0 8	9	—	2 0 $\bar{5}$	80	73	2 0 2	13	29	2 2 8	−14	15
4 0 8	18	15	3 0 $\bar{5}$	12	—	1 0 2	146	118	1 2 8	7	18
3 0 8	−45	50	4 0 $\bar{5}$	−86	73	0 0 2	−72	58	0 2 8	−28	18
2 0 8	−41	34	5 0 $\bar{5}$	−1	—	1 0 $\bar{2}$	−131	102	1 2 $\bar{8}$	−20	15
1 0 8	70	71	6 0 $\bar{5}$	71	64	2 0 $\bar{2}$	17	10	2 2 $\bar{8}$	50	58
0 0 8	48	45	7 0 $\bar{5}$	1	—	3 0 $\bar{2}$	65	71	3 2 $\bar{8}$	36	33
1 0 $\bar{8}$	−53	54				4 0 $\bar{2}$	18	21	4 2 $\bar{8}$	−69	63
2 0 $\bar{8}$	−11	12	8 0 4	2	—	5 0 $\bar{2}$	36	35	5 2 $\bar{8}$	−30	26
3 0 $\bar{8}$	3	—	9 0 4	23	13	6 0 $\bar{2}$	−4	—			
4 0 $\bar{8}$	−14	13	8 0 4	69	65	7 0 $\bar{2}$	−68	72	6 2 7	−12	—
5 0 $\bar{8}$	38	30	7 0 4	−19	30	8 0 $\bar{2}$	25	26	5 2 7	3	—
6 0 $\bar{8}$	17	—	6 0 4	−35	37	9 0 $\bar{2}$	67	55	4 2 7	−39	33
			5 0 4	14	—				3 2 7	−7	—
6 0 7	12	15	4 0 4	−44	51	9 0 1	4	14	2 2 7	71	69
5 0 7	79	69	3 0 4	41	37	8 0 1	−15	38	1 2 7	−15	18
4 0 7	0	6	2 0 4	101	100	7 0 1	−40	58	0 2 7	−77	79
3 0 7	−63	63	1 0 4	−64	67	6 0 1	55	62	1 2 $\bar{7}$	11	15
2 0 7	−5	—	0 0 4	−90	96	5 0 1	73	77	2 2 $\bar{7}$	37	45
1 0 7	0	—	1 0 $\bar{4}$	57	57	4 0 1	−97	111	3 2 $\bar{7}$	10	—
0 0 7	−1	9	2 0 $\bar{4}$	64	78	3 0 1	−71	72	4 2 $\bar{7}$	13	—
1 0 $\bar{7}$	59	60	3 0 $\bar{4}$	−31	26	2 0 1	105	104	5 2 $\bar{7}$	−7	—
2 0 $\bar{7}$	−6	—	4 0 $\bar{4}$	−9	—	1 0 1	32	26	6 2 $\bar{7}$	−54	47
3 0 $\bar{7}$	−89	79	5 0 $\bar{4}$	−31	35	0 0 1	8	6	7 2 $\bar{7}$	5	—
4 0 $\bar{7}$	15	11	6 0 $\bar{4}$	−60	55	1 0 $\bar{1}$	35	26			
5 0 $\bar{7}$	67	59	7 0 $\bar{4}$	50	40	2 0 $\bar{1}$	−119	90	7 2 6	26	37
6 0 $\bar{7}$	−18	18	8 0 $\bar{4}$	68	64	3 0 $\bar{1}$	−65	60	6 2 6	54	55
7 0 $\bar{7}$	−12	12	9 0 $\bar{4}$	40	38	4 0 $\bar{1}$	112	107	5 2 6	−45	43
						5 0 $\bar{1}$	61	90	4 2 6	−59	56
7 0 6	−38	33	9 0 3	−2	12	6 0 $\bar{1}$	−60	81	3 2 6	45	48
6 0 6	17	8	8 0 3	−12	18	7 0 $\bar{1}$	−25	38	2 2 6	19	24
5 0 6	−5	—	7 0 3	54	67	8 0 $\bar{1}$	15	32	1 2 6	−28	21
4 0 6	42	33	6 0 3	55	59	9 0 $\bar{1}$	−1	—	0 2 6	22	24
3 0 6	45	57	5 0 3	−85	100				1 2 $\bar{6}$	−68	56
2 0 6	−50	59	4 0 3	−55	52	9 0 0	8	—	2 2 $\bar{6}$	−44	47
1 0 6	−82	89	3 0 3	107	113	8 0 0	−75	77	3 2 $\bar{6}$	67	68
0 0 6	56	52	2 0 3	28	30	7 0 0	−9	—	4 2 $\bar{6}$	61	56
1 0 $\bar{6}$	67	50	1 0 3	−19	35	6 0 0	58	63	5 2 $\bar{6}$	−51	46
2 0 $\bar{6}$	−34	45	0 0 3	6	—	5 0 0	2	—	6 2 $\bar{6}$	−32	28
3 0 $\bar{6}$	−7	—	1 0 $\bar{3}$	−55	47	4 0 0	4	—	7 2 $\bar{6}$	15	18
4 0 $\bar{6}$	7	—	2 0 $\bar{3}$	−39	38	3 0 0	2	—	8 2 $\bar{6}$	−3	—
5 0 $\bar{6}$	−32	19	3 0 $\bar{3}$	128	121	2 0 0	−107	103			
6 0 $\bar{6}$	53	40	4 0 $\bar{3}$	42	42	1 0 0	−4	17	8 2 5	−21	10
7 0 $\bar{6}$	40	34	5 0 $\bar{3}$	−93	77				7 2 5	42	37
8 0 $\bar{6}$	−53	37	6 0 $\bar{3}$	−36	36	3 2 9	56	56	6 2 5	3	—
			7 0 $\bar{3}$	41	47	2 2 9	−24	26	5 2 5	−10	—
8 0 5	30	26	8 0 $\bar{3}$	−5	—	1 2 9	−58	61	4 2 5	6	—

h k l	*F* calc	*/F/* obs
3 2 5	−14	13
2 2 5	−54	46
1 2 5	121	119
0 2 5	21	18
1 2 $\bar{5}$	−100	99
2 2 $\bar{5}$	−9	—
3 2 $\bar{5}$	9	25
4 2 $\bar{5}$	−2	—
5 2 $\bar{5}$	47	51
6 2 $\bar{5}$	2	—
7 2 $\bar{5}$	−69	44
8 2 $\bar{5}$	−9	—
8 2 4	−19	11
7 2 4	−51	63
6 2 4	28	38
5 2 4	66	69
4 2 4	−34	38
3 2 4	−85	79
2 2 4	20	21
1 2 4	36	32
0 2 4	12	21
1 2 $\bar{4}$	78	77
2 2 $\bar{4}$	−42	33
3 2 $\bar{4}$	−97	94
4 2 $\bar{4}$	47	43
5 2 $\bar{4}$	41	45
6 2 $\bar{4}$	−26	49
7 2 $\bar{4}$	−31	33
8 2 $\bar{4}$	10	18
9 2 $\bar{4}$	−13	—
9 2 3	30	37
8 2 3	−57	61
7 2 3	−12	—
6 2 3	31	42
5 2 3	13	—
4 2 3	20	32
3 2 3	24	24
2 2 3	−111	94
1 2 3	−54	35
0 2 3	92	77
1 2 $\bar{3}$	48	35
2 2 $\bar{3}$	−88	80
3 2 $\bar{3}$	−4	11
4 2 $\bar{3}$	−12	—
5 2 $\bar{3}$	−15	13
6 2 $\bar{3}$	53	56
7 2 $\bar{3}$	10	—
8 2 $\bar{3}$	−67	76
9 2 $\bar{3}$	−11	18
9 2 2	−14	12
8 2 2	26	32
7 2 2	−11	21
6 2 2	−80	78
5 2 2	38	39
4 2 2	115	116
3 2 2	−19	21
2 2 2	−89	68
1 2 2	−17	21
0 2 $\bar{2}$	−15	25
1 2 $\bar{2}$	−12	9
2 2 $\bar{2}$	103	96
3 2 $\bar{2}$	−36	33
4 2 $\bar{2}$	−119	102
5 2 $\bar{2}$	51	54
6 2 $\bar{2}$	59	73
7 2 $\bar{2}$	−14	30
8 2 $\bar{2}$	−14	13
9 2 $\bar{2}$	−18	11
9 2 1	51	61
8 2 1	53	57
7 2 1	−64	61
6 2 1	−46	52
5 2 1	−8	26
4 2 1	−15	37
3 2 1	49	60
2 2 1	78	74
1 2 1	−98	92
0 2 1	−110	59
1 2 $\bar{1}$	99	77
2 2 $\bar{1}$	68	45
3 2 $\bar{1}$	44	54
4 2 $\bar{1}$	1	10
5 2 $\bar{1}$	−5	—
6 2 $\bar{1}$	−39	39
7 2 $\bar{1}$	75	77
8 2 $\bar{1}$	35	45
9 2 $\bar{1}$	−64	66
9 2 0	12	—
8 2 0	1	—
7 2 0	49	61
6 2 0	12	—
5 2 0	−126	117
4 2 0	−4	18
3 2 0	81	73
2 2 0	3	9
1 2 0	−33	33
0 2 0	0	—
0 4 0	193	136
1 4 0	−2	7
2 4 0	−64	56
3 4 0	0	—
4 4 0	−3	9
5 4 0	4	—
6 4 0	45	51
7 4 0	−6	—
8 4 0	−61	76
9 4 0	5	21
0 6 0	0	—
1 6 0	−35	39
2 6 0	3	—
3 6 0	81	85
4 6 0	−6	—
5 6 0	−117	92
6 6 0	12	—
7 6 0	48	68
8 6 0	−1	—
9 6 0	10	—
0 8 0	155	136
1 8 0	−2	—
2 8 0	−67	70
3 8 0	1	—
4 8 0	1	—
5 8 0	2	—
6 8 0	44	51
7 8 0	−6	—
8 8 0	−61	67
0 10 0	0	—
1 10 0	−18	26
2 10 0	1	—
3 10 0	49	58
4 10 0	−3	—
5 10 0	−79	76
6 10 0	7	—
7 10 0	32	52
0 12 0	112	111
1 12 0	−1	—
2 12 0	−53	67
3 12 0	1	—
4 12 0	1	—
5 12 0	1	—
6 12 0	36	40
0 14 0	0	—
1 14 0	−20	30
2 14 0	1	—
3 14 0	51	54
4 14 0	−4	—
0 16 0	74	50
1 16 0	−1	—
0 4 1	6	12
0 6 1	−90	82
0 8 1	5	—
0 10 1	−52	47
0 12 1	3	—
0 14 1	−48	53
0 16 1	3	14
0 4 2	−50	40
0 6 2	−12	24
0 8 2	−42	38
0 10 2	−8	—
0 12 2	−31	37
0 14 2	−7	—
0 4 3	4	9
0 6 3	89	92
0 8 3	4	—
0 10 3	55	66
0 12 3	3	—
0 14 3	56	61
0 4 4	−56	61
0 6 4	11	23
0 8 4	−60	61
0 10 4	7	18
0 12 4	−49	62
0 14 4	6	15
0 4 5	−18	24
0 6 5	18	—
0 8 5	−17	28
0 10 5	12	—
0 12 5	−14	24
0 14 5	11	—
0 4 6	39	39
0 6 6	19	21
0 8 6	41	38
0 10 6	14	26
0 12 5	34	33
0 4 7	−1	—
0 6 7	−73	74
0 8 7	−1	—
0 10 7	−50	52
0 4 8	39	42
0 6 8	−24	21
0 8 8	38	42
0 4 9	27	21
0 6 9	19	25

The distances between neighbouring atoms in $W_2O_3(PO_4)_2$ will be (in Å):

$W_1 - O_3 \quad ; \quad O_3 - W_1 = 1.9_3$
$W_1 - O_4 \quad ; \quad O_4 - W_1 = 2.1_6$
$W_1 - O_5 \quad ; \quad O_5 - 2\ W_1 = 1.9_3$
$W_1 - O_{13} \quad ; \quad O_{13} - W_1 = 1.8_5$
$W_1 - O_{14} \quad ; \quad O_{14} - W_1 = 1.8_7$
$W_1 - O_{15} \quad ; \quad O_{15} - W_1 = 1.8_7$
$W_2 - 2_1O = W_3 - 2\ O_2 \quad ; \quad O_1 - W_2 \quad ; \quad O_2 - W_3 = 1.8_7$
$W_2 - O_6 = W_3 - O_6 \quad ; \quad O_6 - W_2 \quad ; \quad O_6 - W_3 = 1.8_3$
$W_2 - O_7 = W_3 - O_8 \quad ; \quad O_7 - W_2 \quad ; \quad O_8 - W_3 = 1.9_5$
$W_2 - O_9 = W_3 - O_{10} \quad ; \quad O_9 - W_2 \quad ; \quad O_{10} - W_3 = 2.0_1$
$W_2 - O_{12} = W_3 - O_{11} \quad ; \quad O_{12} - W_2 \quad ; \quad O_{11} - W_3 = 1.9_1$

$P_1 - O_1 \quad ; \quad O_1 - P_1 = 1.6_5$
$P_1 - O_2 \quad ; \quad O_2 - P_1 = 1.6_5$
$P_1 - O_3 \quad ; \quad O_3 - P_1 = 1.5_1$
$P_1 - O_4 \quad ; \quad O_4 - P_1 = 1.5_1$
$P_2 - O_9 = P_3 - O_{10} \quad ; \quad O_9 - P_2 \quad ; \quad O_{10} - P_3 = 1.5_1$
$P_2 - O_{11} = P_3 - O_{12} \quad ; \quad O_{11} - P_2 \quad ; \quad O_{12} - P_3 = 1.4_9$
$P_2 - 2\ O_{15} = P_3 - 2\ O_{14} \quad ; \quad O_{15} - P_2 \quad ; \quad O_{14} - P_3 = 1.6_5$
$O_1 - O_2 = 2.5_0$
$O_1 - O_3 = O_2 - O_3 \quad ; \quad O_3 - O_1 \quad ; \quad O_3 - O_2 = 2.6_6$
$O_1 - O_4 = O_2 - O_4 \quad ; \quad O_4 - O_1 \quad ; \quad O_4 - O_2 = 2.5_5$
$O_1 - O_6 = O_2 - O_6 \quad ; \quad O_6 - 2\ O_1 \quad ; \quad O_6 - 2\ O_2 = 2.6_5$
$O_1 - O_7 = O_2 - O_8 \quad ; \quad O_7 - 2\ O_1 \quad ; \quad O_8 - 2\ O_2 = 2.7_2$
$O_1 - O_9 = O_2 - O_{10} \quad ; \quad O_9 - 2\ O_1 \quad ; \quad O_{10} - 2\ O_2 = 2.7_2$
$O_1 - O_{12} = O_2 - O_{11} \quad ; \quad O_{12} - 2\ O_1 \quad ; \quad O_{11} - 2\ O_2 = 2.6_6$
$O_1 - O_{13} = O_2 - O_{14} \quad ; \quad O_{13} - O_1 \quad ; \quad O_{14} - O_2 = 2.8_7$
$O_3 - O_3 = 2.8_5$
$O_3 - 2\ O_4 \quad ; \quad O_4 - 2\ O_3 = 2.5_0 \quad ; \quad 2.7_8$
$O_3 - O_5 \quad ; \quad O_5 - 2\ O_3 = 2.6_1$
$O_3 - O_7 = O_3 - O_8 \quad ; \quad O_7 - 2\ O_3 \quad ; \quad O_8 - 2\ O_3 = 3.3_4$
$O_3 - O_{14} = O_3 - O_{15} \quad ; \quad O_{14} - O_3 \quad ; \quad O_{15} - O_3 = 2.6_9$
$O_4 - O_7 = O_4 - O_8 \quad ; \quad O_7 - 2\ O_4 \quad ; \quad O_8 - 2\ O_4 = 3.3_8$
$O_4 - O_{13} \quad ; \quad O_{13} - O_4 = 3.1_4$
$O_4 - O_{14} = O_4 - O_{15} \quad ; \quad O_{14} - O_4 \quad ; \quad O_{15} - O_4 = 2.8_6$
$O_5 - 2\ O_{13} \quad ; \quad O_{13} - O_5 = 2.5_8$
$O_5 - 2\ O_{14} = O_5 - 2\ O_{15} \quad ; \quad O_{14} - O_5 \quad ; \quad O_{15} - O_5 = 2.6_8$
$O_6 - O_7 = O_6 - O_8 \quad ; \quad O_7 - O_8 \quad ; \quad O_8 - O_6 = 2.6_5$
$O_6 - O_{11} = O_6 - O_{12} \quad ; \quad O_{11} - O_6 \quad ; \quad O_{12} - O_6 = 2.6_4$
$O_7 - O_7 = O_8 - O_8 = 2.6_3$
$O_7 - O_9 = O_8 - O_{10} \quad ; \quad O_9 - O_7 \quad ; \quad O_{10} - O_8 = 2.9_6$
$O_9 - O_{11} = O_{10} - O_{12} \quad ; \quad O_{11} - O_9 \quad ; \quad O_{12} - O_{10} = 2.5_9$
$O_9 - O_{12} = O_{10} - O_{11} \quad ; \quad O_{12} - O_9 \quad ; \quad O_{11} - O_{10} = 2.6_1$
$O_9 - 2\ O_{13} = O_{10} - 2\ O_{13} \quad ; \quad O_{13} - O_9 \quad ; \quad O_{13} - O_{10} = 3.3_4$
$O_9 - 2\ O_{15} = O_{10} - 2\ O_{14} \quad ; \quad O_{15} - O_9 \quad ; \quad O_{14} - O_{10} = 2.5_0$
$O_{11} - O_{12} \quad ; \quad O_{12} - O_{11} = 2.7_9$

$O_{11} - 2\,O_{13} = O_{12} - 2\,O_{13}$; $O_{13} - O_{11}$; $O_{13} - O_{12} = 3.4_3$
$O_{11} - 2\,O_{15} = O_{12} - 2\,O_{14}$; $O_{15} - O_{11}$; $O_{14} - O_{12} = 2.5_7$
$O_{13} - O_{13}$ $= 2.6_6$
$O_{13} - O_{14} = O_{13} - O_{15}$; $O_{14} - O_{13}$; $O_{15} - O_{13} = 2.6_3$
$O_{14} - O_{14} = O_{15} - O_{15}$ $= 2.5_0$

The distances are all within the normal range showing that the lattice is also supported by O—O contacts. However, they may be in error by some tenths of an Ångström unit.

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Table 3. The observed structure factors with k = odd from Weissenberg photographs $hk0$, $0kl$, $h1l$, of $W_2O_3(PO_4)_2$. CuK-radiation.

h k l	|*F*| obs	*h k l*	|*F*| obs	*h k l*	|*F*| obs	*h k l*	|*F*| obs
0 1 $\bar{9}$	7	2 1 4	5	6 1 $\bar{2}$	14	7 5 0	16
2 1 $\bar{9}$	6	1 1 4	7	9 1 $\bar{2}$	9	8 5 0	9
4 1 $\bar{9}$	11	0 1 4	14			9 5 0	7
		1 1 $\bar{4}$	8	9 1 1	5		
4 1 8	7	2 1 $\bar{4}$	6	8 1 1	6	2 7 0	19
0 1 8	8	3 1 $\bar{4}$	12	5 1 1	8		
2 1 $\bar{8}$	11	5 1 $\bar{4}$	13	4 1 1	12		
4 1 $\bar{8}$	6	8 1 $\bar{4}$	7	3 1 1	4	7 9 0	18
				2 1 1	16	8 9 0	20
4 1 7	7	5 1 3	11	1 1 $\bar{1}$	22		
0 1 7	8	4 1 3	5	4 1 $\bar{1}$	14	2 11 0	28
3 1 $\bar{7}$	12	3 1 3	10	7 1 $\bar{1}$	9		
5 1 $\bar{7}$	14	2 1 3	8	9 1 $\bar{1}$	16	2 15 0	18
7 1 $\bar{7}$	6	1 1 3	12				
		0 1 3	11	8 1 0	10	0 3 1	12
2 1 6	12	1 1 $\bar{3}$	9	6 1 0	13	0 3 2	5
1 1 6	13	2 1 $\bar{3}$	15	4 1 0	5	0 3 3	7
3 1 $\bar{6}$	13	5 1 $\bar{3}$	12	2 1 0	22	0 3 4	7
7 1 $\bar{6}$	6	6 1 $\bar{3}$	10			0 3 7	12
		7 1 $\bar{3}$	14	2 3 0	40	0 3 8	6
8 1 5	6	8 1 $\bar{3}$	11	3 3 0	10	0 3 9	6
6 1 5	7			4 3 0	6		
5 1 5	8	9 1 2	9	5 3 0	14		
3 1 5	7	7 1 2	10	6 3 0	17	0 5 1	9
1 1 5	16	6 1 2	12	7 3 0	10	0 5 2	11
3 1 $\bar{5}$	7	5 1 2	6	8 3 0	10	0 5 5	10
4 1 $\bar{5}$	11	4 1 2	6			0 5 7	17
5 1 $\bar{5}$	10	3 1 2	4	1 5 0	5		
6 1 $\bar{5}$	14	1 1 2	5	3 5 0	6	0 7 1	15
7 1 $\bar{5}$	11	0 1 2	8	4 5 0	5		
8 1 $\bar{5}$	5	1 1 $\bar{2}$	19	5 5 0	9	0 13 2	17
		2 1 $\bar{2}$	2				
8 1 4	9	3 1 $\bar{2}$	6	6 5 0	14	0 15 1	12

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