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Authors
Ueki, Tatzuo
Zalkin, Allan
Templeton, David. H.

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University of California

Ernest O. Lawrence Radiation Laboratory

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Tatzuo Ueki, Allan Zalkin, and David H. Templeton

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The Crystal Structure of Osmium Tetroxide

By Tatzuo Ueki, Allan Zalkin and David H. Templeton

Lawrence Radiation Laboratory and Department of Chemistry,

University of California, Berkeley, California, U. S. A.

Crystals of OsO_4 are monoclinic, space group $C2/c$, with 4 molecules in the cell with dimensions

$$a = 9.379,\ b = 4.515,\ c = 8.632\ \text{Å};\quad \beta = 116.6^\circ.$$

By least-squares refinement of three-dimensional X-ray diffraction data the molecules are tetrahedral with Os—O = 1.74 Å (uncorrected for thermal motion). The molecular arrangement is approximately cubic closest packing. The intermolecular O—O distances exceed 2.98 Å and are consistent with weak intermolecular forces indicated by the high vapor pressure and low melting point.

Introduction

The crystal structure of oxmium tetroxide was investigated previously by X-ray photographic methods (Zalkin & Templeton, 1953), but oxygen positions were not determined from the intensity data. The complete structure has now been established with intensity data from the direct counting technique.

The new study shows that the old unit cell must be doubled and that the wrong space group had been chosen.

Experimental

Crystals of OsO_4 were grown in sealed glass capillaries by sublimation at room temperature. Raw crystals were obtained from A. D. Mackay, Inc. Rotation, oscillation and Weissenberg photographs were taken using Cu radiation with Ni filter. A crystal with dimensions 0.19 × 0.063 × 0.092 mm was mounted in a goniostat on a General Electric XRD-5 apparatus equipped with a scintillation counter and pulse height discriminator. Accurate cell dimensions were determined using the goniostat and Mo$K\alpha_1$ radiation (λ = 0.70926 Å). Intensities were measured for each independent reflection with $\sin\theta/\lambda$ less than 0.71 ($2\theta < 60^\circ$) with 10 seconds counting time for each reflection. A total of 479 independent reflections were measured exclusive of space group extinctions. The linear absorption coefficient is estimated to be $\mu = 394$ cm^{-1} for Mo$K\alpha$ radiation, and the absorption effect is appreciable. Absorption corrections were made after partial refinement of the structure, as described later. No correction was made for extinction.

Calculations were made with an IBM-7090 computer using our version of the Gantzel-Sparks-Trueblood full matrix least squares program (unpublished). The function minimized was

$$\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2.$$

The atomic scattering factors for neutral O and Os were taken from Ibers (1962).

Crystal Data

The crystals are colorless, with a low melting point (about 40°) and high

vapor pressure (Ogawa, 1931). They are monoclinic, with

$$\underline{a} = 9.379 \pm 0.005 \text{ Å } (9.39 \text{ Å}),$$

$$\underline{b} = 4.515 \pm 0.002 \text{ Å } (4.52 \text{ Å}),$$

$$\underline{c} = 8.632 \pm 0.003 \text{ Å } (8.66 \text{ Å}),$$

$$\beta = 116.6^\circ \pm 0.05^\circ \ (116.7^\circ),$$

$$\underline{V} = 330.7 \text{ Å}^3.$$

The values in parentheses are from Zalkin & Templeton (1953), changed to the new setting. With $\underline{Z} = 4$ the calculated density is 5.10 g cm^{-3}, compared with 4.95 observed by Krauss & Schrader (1928). The systematic absences:

($\underline{hk\ell}$) absent if $\underline{h} + \underline{k} \neq 2\underline{n}$; ($\underline{h}0\underline{\ell}$) absent if $\underline{h} \neq 2n$ or if $\underline{\ell} \neq 2\underline{n}$ are characteristic of space groups $\underline{C}c$ and $\underline{C}2/\underline{c}$. The centrosymmetric group, $\underline{C}2/\underline{c}$, was chosen, and later it was confirmed by the successful result of the structure determination. Reflections are strong if $\underline{h} + \underline{k} = 2\underline{n}$ and $\underline{h} + \underline{\ell} = 2\underline{n}$; otherwise they are weak or absent. If these weak reflections were all absent, the lattice would be face-centered, and a smaller $\underline{C}$-centered cell could be chosen. In the previous study (Zalkin & Templeton, 1953) these weak reflections escaped notice, and the lattice was described on the smaller cell.

Determination of the Structure

The osmium atoms must conform closely to a face-centered structure to explain the strong reflections. In space group $\underline{C}2/\underline{c}$ this is possible with special positions 4(c), 4(d), and 4(e). Since we expected OsO_4 to be tetrahedral, the sets (c) and (d), at centers of inversion, were discarded, and the set 4(e):

$$(0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, 0) + (0, \underline{y}, \tfrac{1}{4})$$

was chosen with y approximately 0.25.

This structure for the oxmium atoms explains the largest peaks in the Patterson function. On the basis of smaller peaks in the Patterson function and expected molecular dimensions, two sets of oxygen atoms were placed in general positions 8(f):

$$(0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, 0) \pm (x, y, z;\ x, -y, \tfrac{1}{2} + z)$$

with coordinates (0.12, 0.05, 0.19) and (0.12, 0.45, 0.43). This trial structure was refined by least squares with unit weight assigned to each of the 479 reflections. With isotropic temperature factors of the form $\exp(-B\,\lambda^{-2}\sin^2\theta)$ and no correction for absorption, the discrepancy index $R = \sum||F_o|-|F_c||/\sum|F_o|$ was reduced to 0.170.

At this stage the discrepancies between the observed and calculated structure factors were fairly large; therefore some of the intensities were remeasured. Another series of least square refinement reduced R to 0.165. Inspection of the structure factors then revealed a systematic discrepancy which we attribute to absorption errors. In general, $|F_o|$ exceeded $|F_c|$ for negative ℓ, and $|F_o|$ was less than $|F_c|$ for positive ℓ. The intensities were measured with phi less than or more than 33° for these two classes of reflections, respectively. Measurements of (020) and (040) as a function of phi (the spindle axis of the goniostat) in the full circular range showed that their intensities varied in a manner that could be approximated by a sinusoidal curve. The ratios of observed to calculated intensities for strong reflections, when arranged as a function of phi, tend to follow a similar variation (Fig. 1). While the absorption effect cannot be a function simply of phi, it obviously has a strong correlation with this variable. The intensities were corrected with the empirical relation:

$$|F_o|^2(\text{corrected}) = |F_o|^2\,[1 + 0.45\cos(2\phi + 64^\circ)]^{-1}.$$

After this correction, refinement reduced R to 0.107.

With an anisotropic temperature factor of the form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}\ell^2 - 2\beta_{13}h\ell)$ for the osmium atom, R was reduced to 0.082. The final series of refinement was carried out with similar anisotropic temperature factors (except that all three cross terms are included) for the oxygen atoms. The final R = 0.082 was no better, the sum of squares of residuals decreased only slightly, and the deviations from isotropy of the oxygen atoms hardly exceed the standard deviations. No coordinate changed as much as 0.001. The final parameters are listed in Tables 1 and 2, and the observed and calculated structures in Table 3.

Discussion

Bond lengths and angles are listed in Table 4 with standard deviations. The deviations from tetrahedral symmetry of the molecule are not experimentally significant. This result is in accord with the interpretation of Raman and infrared spectra by Woodward & Roberts (1956) and Dodd (1959). The average Os—O bond distance is 1.74 ± 0.02 Å, uncorrected for thermal motion. The r.m.s. interatomic distance is larger because of thermal motion by an amount which is estimated as 0.02 Å (with the assumption that oxygen rides on osmium), but the magnitude of this correction is doubtful because of the low precision of the thermal parameters. An early electron-diffraction study (Brockway, 1936) gave 1.66 Å for the Os—O distance, but this result is likely to be in error because of failure of the Born approximation (Glauber & Schomaker, 1953). A check on our result is given by the consistency of the isoelectronic sequence WO_4^{-2}, ReO_4^{-}, OsO_4, with bond distances W—O = 1.79 Å (Zalkin & Templeton, 1964; Kay, Frazer & Almodovar,

1964) and Re—O = 1.77 Å (Morrow, 1960).

The crystal structure (Fig. 2) can be described approximately as cubic closest packing of oxygen atoms, with osmium in tetrahedral holes. The pseudo-cubic pseudo-cell corresponding to the close packed oxygen structure has axes which are related to the monoclinic axes by the matrix $\frac{1}{2}\ 0\ \frac{1}{4}\ /\ 0\ 1\ 0\ /\ 0\ 0\ \frac{1}{2}$. From a different point of view, the structure can be described less accurately as cubic closest packing of OsO_4 molecules, an arrangement which is common in crystals of spherical or nearly spherical molecules. The axes of the pseudo-cell describing this packing are derived from the monoclinic axes by the matrix $\frac{1}{2}\ 0\ -\frac{1}{2}\ /\ \frac{1}{2}\ 1\ \frac{1}{2}\ /\ \frac{1}{2}\ -1\ \frac{1}{2}$. In this packing each osmium atom has 12 osmium neighbors at distances ranging from 4.52 to 5.20 Å. The intermolecular O—O distances exceed 2.98 Å and are consistent with weak intermolecular forces indicated by the high vapor pressure and low melting point.

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Table 1. Final coordinates and estimated standard deviations

Atom	$\underline{x}$	$\underline{y}$	$\underline{z}$	$\sigma(\underline{x})$	$\sigma(\underline{y})$	$\sigma(\underline{z})$
Os	0	0.2601	1/4	---	0.0004	---
O(1)	0.121	0.038	0.190	0.003	0.007	0.004
O(2)	0.115	0.476	0.425	0.003	0.006	0.003

Table 2. Final thermal parameters and estimated standard deviations[a]

Atom	$\underline{B}_{11}$	$\underline{B}_{22}$	$\underline{B}_{33}$	$\underline{B}_{12}$	$\underline{B}_{13}$	$\underline{B}_{23}$
Os	1.47	1.96	1.84	0	0.54	0
O(1)	4.0	4.2	5.1	0.9	3.1	0.2
O(2)	3.8	3.8	2.9	-0.9	0.4	-1.2

Atom	$\sigma(\underline{B}_{11})$	$\sigma(\underline{B}_{22})$	$\sigma(\underline{B}_{33})$	$\sigma(\underline{B}_{12})$	$\sigma(\underline{B}_{13})$	$\sigma(\underline{B}_{23})$
Os	0.05	0.06	0.06	---	0.04	---
O(1)	1.1	1.3	1.3	1.0	1.1	1.1
O(2)	1.1	1.2	1.0	1.0	0.8	0.9

[a] $4\beta_{\underline{ij}} = \underline{b}_{\underline{i}}\underline{b}_{\underline{j}}\underline{B}_{\underline{ij}}$, where $\underline{b}_{\underline{i}}$ is the length of the $\underline{i}$th reciprocal axis.

Table 3. Observed structure factor magnitudes (FOB) and calculated structure factors (FCA), each multiplied by 10

(table to be reproduced photographically)

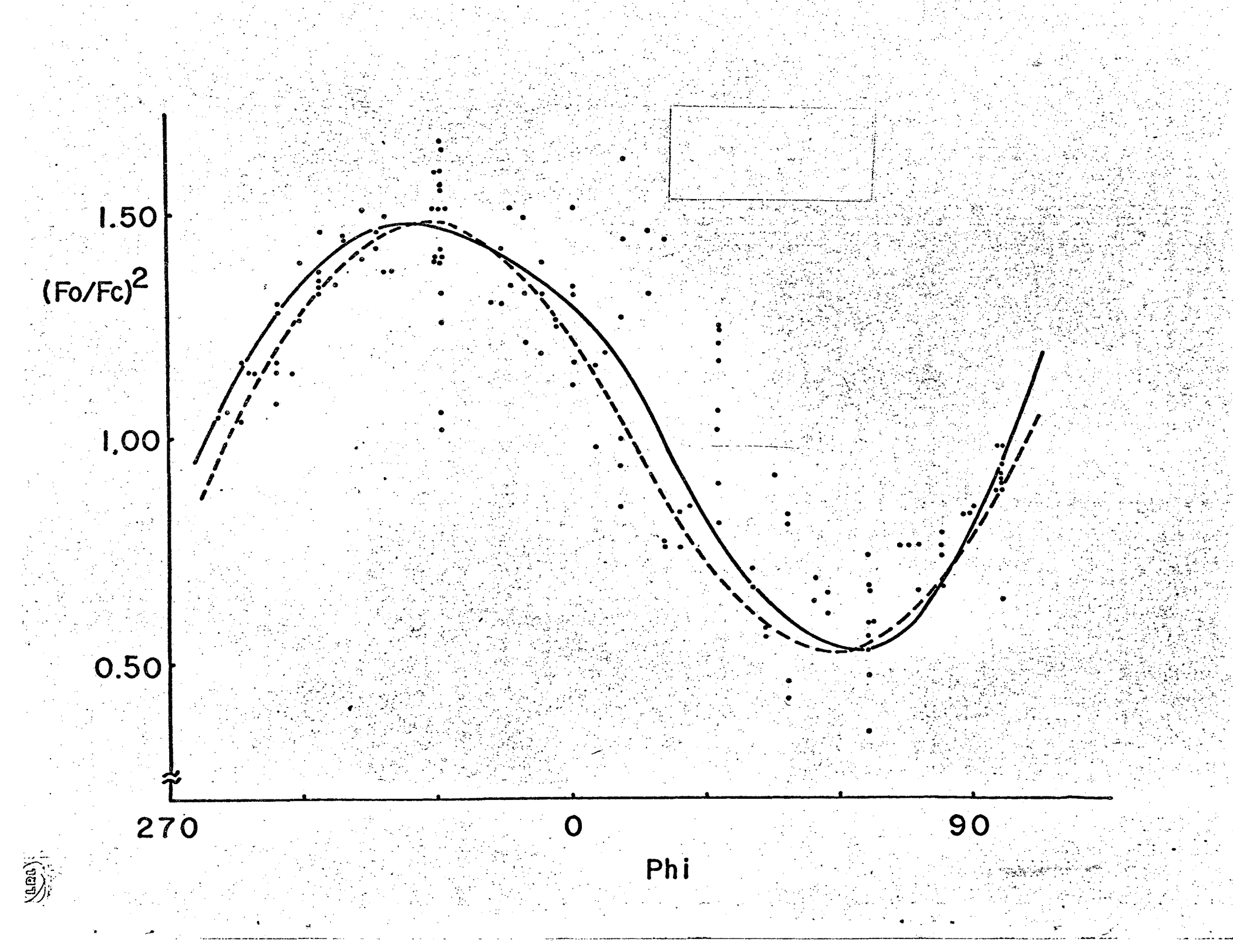
Table 4. Interatomic distances and angles in OsO_4, with standard deviations

Atoms	Distance (Å)	Atoms	Angle (°)
Os—O(1)	1.76 ± 0.03	O(1)—Os—O(1)	110.3 ± 1.9
Os—O(2)	1.71 ± 0.03	O(1)—Os—O(2)	110.5 ± 1.3
O(1)—O(1)	2.89 ± 0.06	O(1)—Os—O(2')	107.6 ± 1.3
O(1)—O(2)	2.85 ± 0.04	O(2)—Os—O(2')	110.4 ± 1.9
O(1)—O(2')	2.80 ± 0.04		
O(2)—O(2')	2.81 ± 0.05		

Figure Captions

Fig. 1. Ratio of observed to calculated intensity as a function of phi. The ~~broken~~ solid curve is the ratio for (020), which can be measured at any phi because chi is 90°. The ~~solid~~ broken curve corresponds to the correction equation.

Fig. 2. Crystal structure of OsO_4. The y coordinates (multiplied by 100) are indicated for some atoms.


1.50
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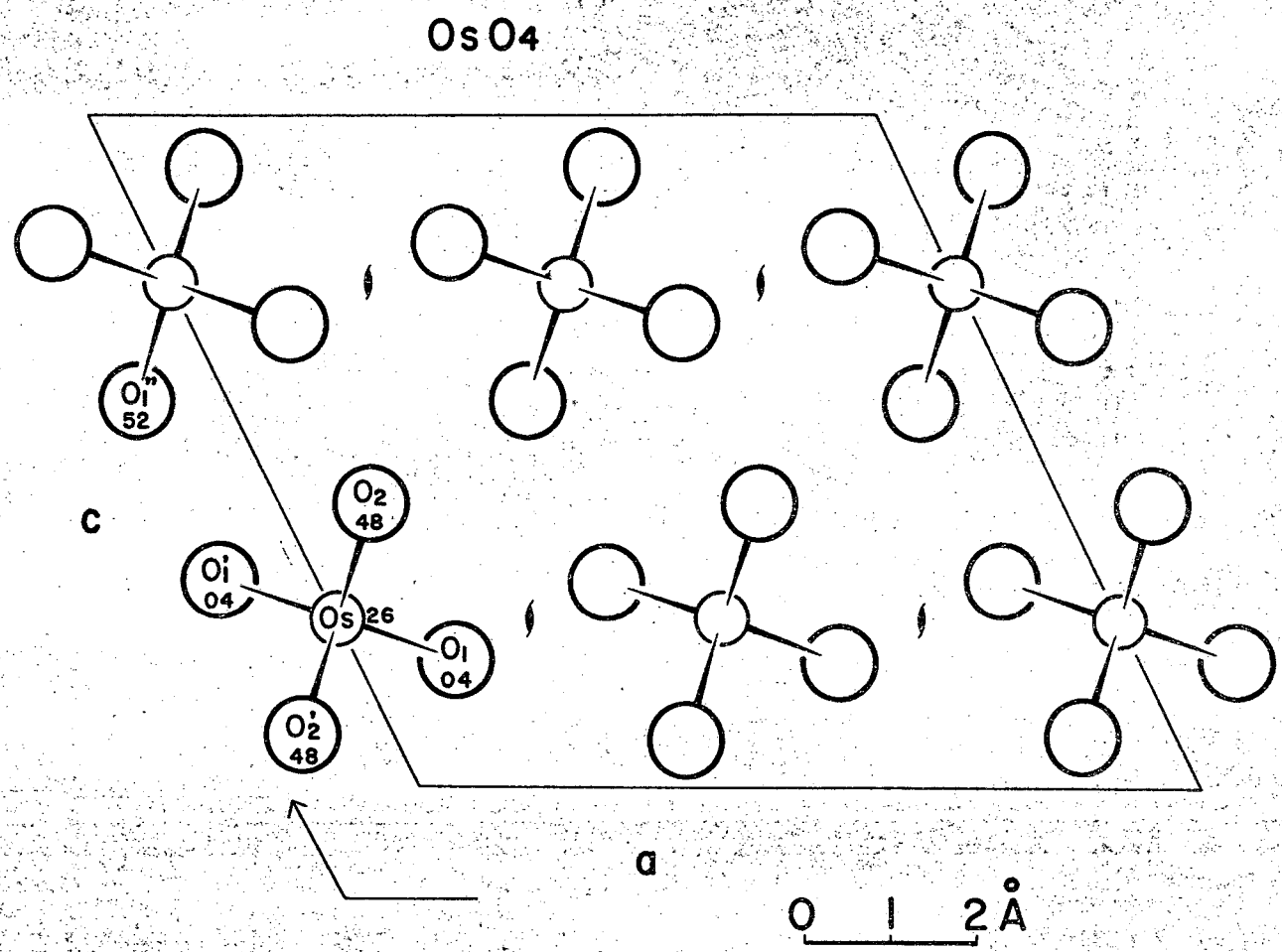
1.00
0.50
270
0
90
Phi



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