Havinga, E. E., Boswijk, K. H. & Wiebenga, E. H. (1954). *Acta Cryst.* **7**, 487.

Inorganic Synth. (1939). **1**, 165.

Mooney, R. C. L. (1937). *Z. Kristallogr.* **98**, 324.

Mooney, R. C. L. (1938). *Z. Kristallogr.* **98**, 377.

Mooney, R. C. L. (1939). *Z. Kristallogr.* **100**, 519.

Pauling, L. (1945). *The Nature of the Chemical Bond.* Ithaca: Cornell University Press.

Tasman, H. A. & Boswijk, K. H. (1955). *Acta Cryst.* **8**, 59, 857.

Weidner, R. T. (1947). *Phys. Rev.* **72**, 1268.

Acta Cryst. (1956). **9**, 277

The Structure of Mercuric Oxide

By W. L. Roth

General Electric Research Laboratory, Schenectady, N.Y., U.S.A.

(*Received* 1 *September* 1955)

The atomic arrangement of mercuric oxide has been determined by neutron and X-ray diffraction methods. The structure is based on zigzag chains of mercury oxide, and the chains in turn are packed to form planar layers. The Hg–O distance within a chain is $2{\cdot}01_5$ Å and the Hg–O–Hg angle is 109·8°.

Introduction

The structures of many heavy metal oxides are not known because it is difficult by X-ray diffraction techniques to locate the positions of light oxygens relative to heavy metal atoms. During the course of a separate investigation, the neutron diffraction pattern of mercuric oxide was required. These data, in conjunction with X-ray data, have led to a solution of the mercuric oxide arrangement.

Mercuric oxide may be prepared as powders which are either yellow or red, and many early investigations were concerned with the question of polymorphism. Careful X-ray work has shown that both materials give identical X-ray powder diffraction patterns (Levi, 1924; Zachariasen, 1927). Zachariasen showed that mercuric oxide crystallized in an orthorhombic unit cell

$$(a_0 = 3{\cdot}296,\ b_0 = 3{\cdot}513,\ c_0 = 5{\cdot}504 \text{ kX.})$$

containing 2 HgO. The mercury atoms are at the origin and body center of the cell, but it was not possible to locate the positions of the oxygen atoms.

A comparison of the coherent scattering amplitudes of mercury and oxygen for neutrons and X-rays shows that neutron diffraction should be more suited for the structure determination:

	Neutron	X-ray
Hg	1·31	80
O	0·58	8

However, since mercuric oxide is orthorhombic and the powder diffraction pattern is quite complex, only the first four diffraction peaks could be resolved with the relatively limited resolution available to the neutron spectrometer. The four neutron diffraction peaks were sufficient to solve the structure in an approximate sense. Once the appropriate structure was known, it was possible to refine the parameters by utilizing the greater resolving power of the X-ray spectrometer.

Neutron diffraction

Neutron diffraction patterns were obtained with the General Electric Company neutron spectrometer located at the Brookhaven National Laboratory. The data were taken by transmission through a flat powder sample of red mercuric oxide contained between spectrographic glass plates. Individual points were measured at angular increments of 08′, and each point was counted for a monitored time interval of 16 min. Integrated intensities were obtained by measuring with a planimeter the areas under peaks on an intensity versus angle plot.

The integrated intensity is given by the expression:

$$P_{hkl} = K(N^2h\varrho'/\varrho) \exp\,[-\mu h \sec\theta]\,\operatorname{cosec}^2\theta \times \exp\,[-2B\,(\sin\theta/\lambda)^2]\,J_{hkl}F^2_{hkl}\,, \quad (1)$$

where K is an instrumental constant which depends upon the incident neutron flux, neutron wavelength and counter slit dimensions, N = number of unit cells per cm.³ of sample, h = thickness of sample, ϱ' = apparent density of powder, ϱ = crystal density, μ = effective linear absorption coefficient, $\exp\,[-2B\,(\sin\theta/\lambda)^2]$ = correction for temperature motion, J_{hkl} = multiplicity and F_{hkl} = structure factor for the plane (hkl). The data were placed on an absolute scale by determining that $K = 0{\cdot}3211 \times 10^{-24}$ from a standard sample of nickel. The absorption coefficient was measured by transmission when $\theta = 0$. The experimental constants are given in Table 1.

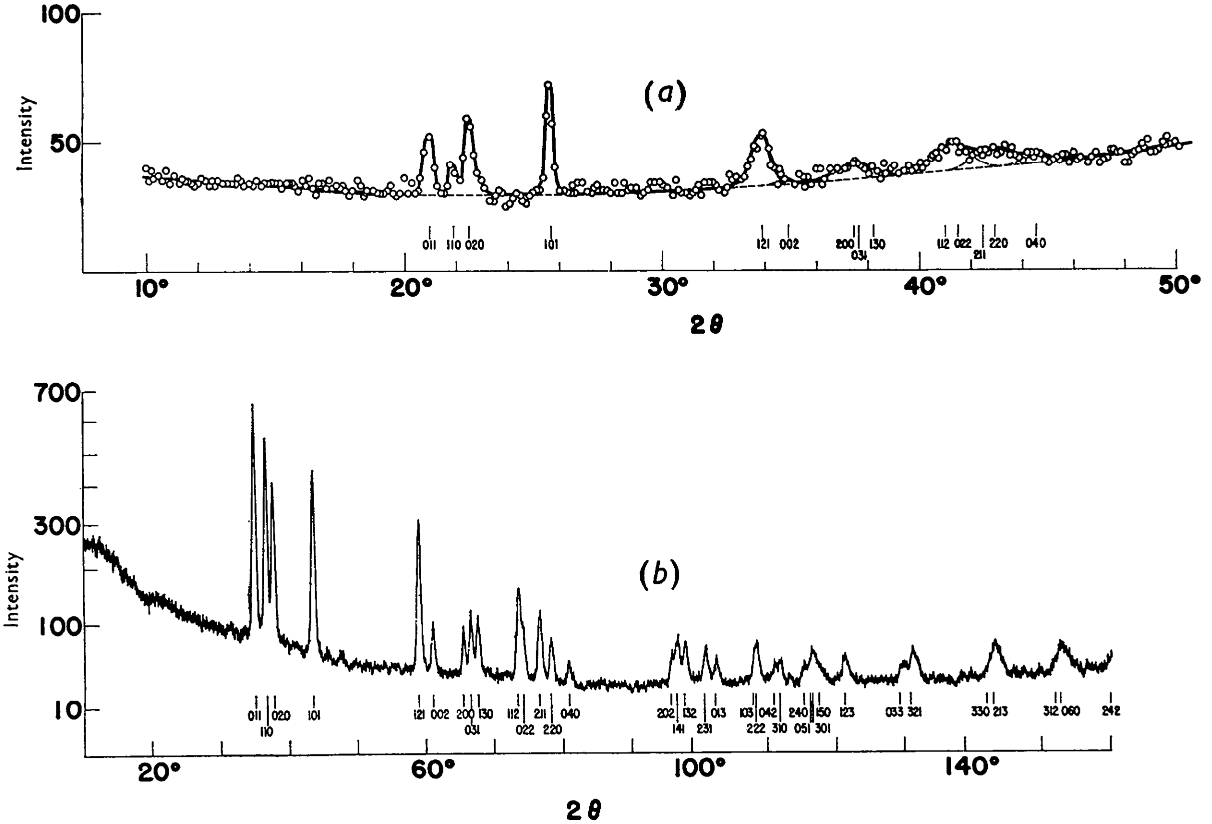


Fig. 1. (*a*) Neutron diffraction pattern of HgO. (*b*) X-ray diffraction pattern of HgO. $\lambda = 1{\cdot}790$ Å.

Table 1. *Experimental constants*

	HgO	Ni
a_0 (Å)	3·311	3·524
b_0 (Å)	5·526	—
c_0 (Å)	3·526	—
h (cm.)	0·317	1·29
ϱ' (g.cm.$^{-3}$)	4·447	5·735
ϱ (g.cm.$^{-3}$)	11·14	8·903
$e^{-\mu h}$	0·353	0·227
λ (Å)	1·011	—

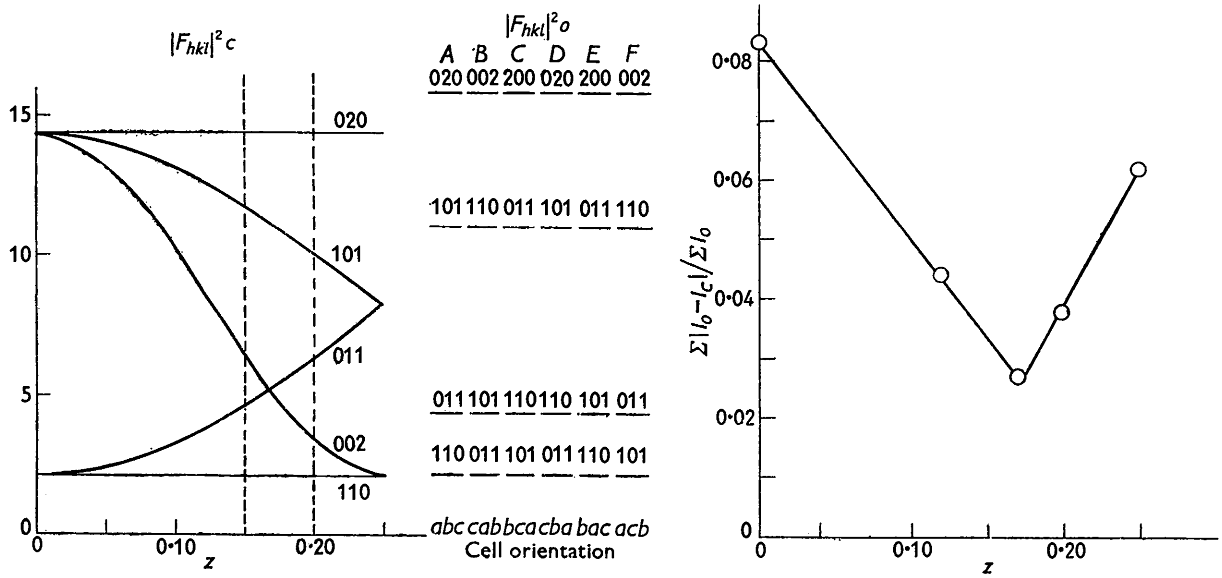
The neutron diffraction pattern of mercuric oxide is given in Fig. 1(*a*). All peaks may be indexed on an orthorhombic cell which agrees with that found by X-rays. Of the fourteen peaks observed, only the first four are clearly resolved. Despite the use of fairly long counting times, the statistical precision is relatively low. This results despite the large coherent cross section of mercury (21·5 barns) because the total cross section is dominated by capture processes in the thermal range ($\sigma_{\text{capture}} = 350$ barns).

For neutron diffraction (in agreement with X-rays) only those reflections for which $h+k+l = 2n$ are observed. From the volume of the unit cell and the crystal density, there are 2 HgO per cell. The probable space groups are D_{2h}^{13}–*Pmmm*, C_{2v}^{10}–*Pnn*, C_{2v}^{20}–*Imm* and C_{2v}^{7}–*Pmn*. Each of these space groups has one adjustable parameter for atoms in twofold positions, except for *Pmn* which has two parameters. Since the oxygen contribution is appreciable in the neutron case, the body-centered criterion is significant, and structures based on *Pmn* can be only slightly distorted from structures based on *Imm*. Considering first the one-parameter arrangements, there are four possible structures:

	Mercury	Oxygen
I	$0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$0, 0, z;\ \frac{1}{2}, \frac{1}{2}, \bar{z}$
II	$0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$0, \frac{1}{2}, z;\ \frac{1}{2}, 0, \bar{z}$
III	$0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$0, 0, z;\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}+z$
IV	$0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$0, \frac{1}{2}, z;\ \frac{1}{2}, 0, \frac{1}{2}+z$

Since the choice of axes is arbitrary, various orientations of the unit cell with respect to the variable parameter must be considered.

The structure factors for each of the four arrangements were computed and it was possible from the intensities of the first four peaks to eliminate all structures based on I, II or III for all values of the parameter z and for any orientation of the unit cell. Values of F_{hkl}^2 as a function of z were computed for Model IV and the results were compared with F_o^2 calculated from the observed intensities and equation (1). The results are shown in Fig. 2(*a*) for the various possible orientations of the orthorhombic cell. It is apparent that IV(*A*) with $0{\cdot}15 < z < 0{\cdot}20$ is satis-



(a) (b)

Fig. 2. HgO parameter (a) from neutron diffraction, (b) from X-ray diffraction.

factory, but that a precise value for z requires higher index data. Using the value $z = 0{\cdot}17$, intensities computed with equation (1) are compared with the observed values in Table 2.

Table 2. *Mercuric oxide neutron intensities*

C_{2v}^{20}–Imm; Hg (0, 0, 0; ½, ½, ½); O (0, ½, 0·17; ½, 0, 0·67)

hkl	I_c	I_o
011	20·9	17·3
110	7·7	7·8
020	24·5	27·2
101	29·3	29·0
121 002	29·0	28·8

X-ray diffraction

The approximate structure deduced from the neutron data was refined by X-ray methods. An X-ray powder pattern, using filtered Co $K\alpha$ radiation, was obtained with a General Electric XRD-3 spectrometer (Fig. 1(b)). The red HgO used in the neutron diffraction investigation consisted of thin flat plates parallel to (010) and it was not possible to produce reproducible random powder samples for precision X-ray analysis. (This was not a serious problem in the neutron case since random sampling was assured by transmission through the 3 mm.-thick powdered specimen.) Since tests showed that yellow HgO could be packed with negligible preferred orientation, and earlier work (Zachariasen, 1927) had established the identity of the red and yellow powders, the X-ray data were obtained from yellow mercuric oxide. The powder specimen was larger than the X-ray beam and of depth sufficient to absorb all the incident beam, thus simplifying absorption corrections. The pattern was scanned at 0·2°/min. and the chart pattern was replotted on a true intensity scale obtained from calibration curves. Integrated intensities on an arbitrary scale were obtained by measuring with a planimeter the areas of peaks above background.

For the X-ray case we have

$$I_{hkl} = k\left(\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}\right)\exp\left[-2B(\sin\theta/\lambda)^2\right]J_{hkl}F^2_{hkl}\,. \quad (2)$$

The effect of small shifts of the oxygen coordinates on the calculated intensities is quite small, so the following technique was used to refine the structure. The quantities F^2_{hkl} were computed for all observed hkl for values of the parameter $z = 0$, 0·12, 0·17, 0·20 and 0·25, using the atomic structure factors for mercury and oxygen which are tabulated in the *Internationale Tabellen* (1935). For each value of z, the observed intensities and F_c^2 were fitted to equation (2) by a least-squares calculation. From the least-squares values of k and B, I_{hkl} was computed and the results were compared with I_o. The deviation from the true structure was taken as

$$\Delta = \Sigma|I_o - I_c| \div \Sigma I_o\,.$$

The variation of Δ with z is shown in Fig. 2(b), and the minimum deviation corresponds to $z = 0{\cdot}170$. The calculated and observed X-ray intensities for $z = 0{\cdot}170$ are given in Table 3. The excellent agreement, reflected by the reliability index

$$\Sigma|I_o - I_c| \div \Sigma I_o = 2{\cdot}7\,\%\,,$$

shows that the assumption of a single-parameter space group was justified. If the true symmetry were Pmn instead of Imm, the effect would be to produce a slight shift of the oxygen atoms in the y direction.

Table 3. *Mercuric oxide X-ray intensities*

C_{2v}^{20}–*Imm*; $z = 0{\cdot}170$; $B = 1{\cdot}22 \times 10^{-16}$ cm.$^{-2}$

hkl	I_c	I_o
011	425	424
110	346	353
020	221	236
101	272	275
121	209	206
002	40	39
200	39	39
031	62	56
130	54	54
112 022	144	149
211	79	79
220	44	45
040	20	19
202 141	73	78
132	50	51
231	42	42
013	24	26
103 222	58	63
042 310	38	36
240 051 301 150	82	81
123	38	42
033	25	26
321	49	48
330 213	90	90
312 060	99	93

Discussion of the structure

A drawing of the crystal structure of mercuric oxide is shown in Fig. 3. The structure is based on infinite zigzag chains –Hg–O–Hg–O–Hg parallel to the *a* axis of the orthorhombic cell. The chains pack to form planar layers parallel to the *b* face of the crystal.

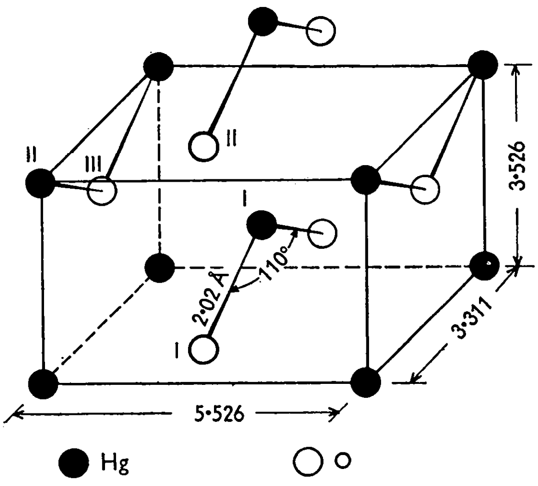


Fig. 3. The structure of mercuric oxide.

Within a chain the interatomic distance is Hg_I–O_I = 2·015 Å and the angle Hg_I–O_I–Hg_I is 109° 46′. The remaining interatomic distances are much greater: $Hg_I \cdots O_{II}$ = 2·87 Å and $Hg_I \cdots O_{III}$ = 2·82 Å. The mercury–oxygen sheets are separated by 2·75 Å.

The extremely short Hg–O distance within a chain and the tetrahedral bond angle suggest that the bonding within a chain is predominantly covalent.* The predicted interatomic distance for covalently bonded mercury and oxygen of $R_{Hg}+R_O$ is $1{\cdot}48+0{\cdot}66 = 2{\cdot}14$ Å. Correcting for the difference in electronegativity by the empirical Schomaker–Stevenson relationship

$$\Delta = -0{\cdot}09|\chi_{Hg}-\chi_O| = -0{\cdot}09|1{\cdot}9-3{\cdot}5| = -0{\cdot}14 \text{ Å},$$

the predicted covalent bond length is 2·00 Å, in reasonable agreement with the observed value 2·015 Å. The tetrahedral O–Hg–O angle may be explained by sp^3 hybridization of electrons promoted from the 5*d* level of mercury. The remaining interchain distances are non-bonded van der Waals interactions. A packing drawing of the chains in a (010) plane is shown in Fig. 4.

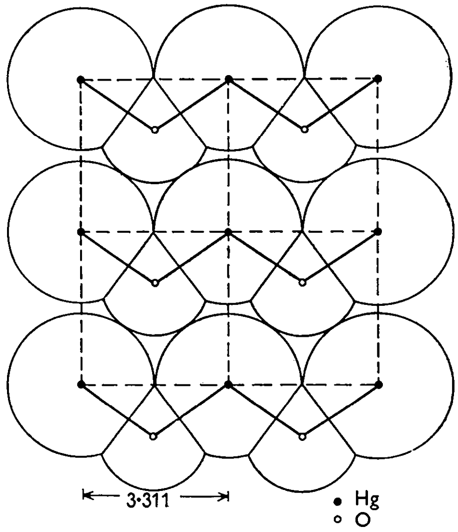


Fig. 4. Packing drawing of mercuric oxide.

The assistance of D. S. Hallgren, who obtained the X-ray data and assisted in many of the computations, is gratefully acknowledged.

References

Internationale Tabellen zur Bestimmung von Kristallstrukturen, (1935). Berlin: Borntraeger.

Levi, G. R. (1924). *Gazz. chim. ital.* **54**, 709.

Zachariasen, W. (1927). *Z. phys. Chem.* **128**, 421.

---

* For ionic bonds the radius sum is $R_{Hg^{2+}}+R_{O^{2-}} = 1{\cdot}10+1{\cdot}40 = 2{\cdot}50$ Å. Correcting for a reduction in coordination from 6 to 2 by the factor $(\frac{2}{6})^{\frac{1}{8}} = 0{\cdot}872$ reduces the calculated Hg^{2+}–O distance to 2·18 Å.