The Crystal Structure of Mercury(II)oxide Studied by X-Ray and Neutron Diffraction Methods

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The crystal structure of mercury(II)oxide has been investigated by X-ray and neutron diffraction methods. The symmetry has been found to be *Pnma* (No. 62) and the unit cell twice the one reported by previous authors. The positions of the mercury and oxygen atoms have been determined. The structure is built up of infinite, planar zig-zag chains $-O-Hg-O-$ running parallel to the *a*-axis and lying in the *ac* plane. Within the chains the $Hg-O$ distance is 2.03 ± 0.10 Å and the angles $O-Hg-O$ and $Hg-O-Hg$ $179° \pm 3°$ and $109° \pm 1°$, respectively.

In connection with studies of the crystal chemistry of mercury in various mercury oxide halides [1], knowledge of the mercury-oxygen distance was of fundamental importance for the discussion of the spatial arrangement of the atoms. No exact value of this distance could be obtained from the literature and it was thus found appropriate to undertake a detailed investigation of the crystal structure of mercury(II)oxide.

A previous study of this substance carried out in 1927 by Zachariasen [2] by means of X-ray powder photographs indicated an orthorhombic structure with the unit cell dimensions $a = 3.303$ Å, $b = 3.520$ Å, $c = 5.515$ Å.

The following positions of the mercury atoms were given:

Space group *Pmmn*, No. 59 *, 2 Hg in 2(a): $0, 0, z; \frac{1}{2}, \frac{1}{2}, \bar{z}; z \sim \frac{1}{4}$ or space group *Pmn2₁*, No. 31*, 2 Hg in 2(a): $0, y, z; \frac{1}{2}, \bar{y}, \frac{1}{2}+z; y \sim \frac{1}{4} z = \frac{1}{4}$

Three possible arrangements for the oxygen atoms were discussed but it was not possible to decide between them. The mercury-oxygen distances were 2.15 Å for two of the alternative structures and 2.41 Å for the third.

The considerable difference in scattering power for X-rays between mercury and oxygen makes it almost a hopeless enterprise to locate the latter atoms in mercury(II)oxide. On the other hand the relative scattering power

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* Notations rearranged to conform with *International Tables for X-ray Crystallography*, Birmingham 1952.

of the two elements for neutrons is much more favourable. The author was thus very happy in having the privilege of performing a neutron diffraction study at the *Joint Establishment for Nuclear Energy Research*, Kjeller, Norway, in addition to the X-ray investigation performed at the University of Stockholm.

X-RAY DIFFRACTION STUDIES

For the X-ray studies, three samples of various origins were used, *viz.* commercial mercury(II)oxide (Baker's Analysed), a sample obtained by carefully heating mercury(II)nitrate in air and naturally occurring montroydite from Terlingua, Texas. All the samples gave identical powder photographs. Tiny rods and thin plates were observed in the samples of the synthetic materials while the natural substance showed only rods. The registering of single crystal reflexions was accompanied by considerable difficulties, due to the extreme delicacy of the crystals. The very slight mechanical stress applied when mounting the crystals often gave rise to serious damage noticeable by the occurrence of multiple spots or even powder lines in the Weissenberg photographs. In some cases, however, it was possible to register the diffraction patterns of obvious single crystals and all calculations were based on data obtained in this way.

CELL DIMENSIONS AND SPACE-GROUP

The powder photographs were taken in a Guinier focussing camera of 80 mm diameter using monochromatic Cu-$K\alpha_1$ radiation and potassium chloride ($a = 6.2930$ Å[3]) added as an internal standard. The powder pattern is given in Table 1. Normally exposed photographs (30 minutes) were found to be in fair agreement with that given by Zachariasen but, in amply exposed ones (3 hours), several extra lines were found which were also observed in single crystal photographs (see below). The unit cell was thus found to have the dimensions $a = 6.612_1$ Å, $b = 5.520_1$ Å, $c = 3.521_3$ Å, corresponding to a doubling of the a axis of the orthorhombic cell reported by Zachariasen.

The observed density of 11.3 indicates a cell content of 4 formula units of HgO per unit cell. The calculated density is 11.2.

Cu-K radiation was used for the single crystal photographs. Rotation diagrams were taken around all the three axes and also Weissenberg photographs registering the reflexions $h0l$—$h3l$, $0kl$—$3kl$, $hk0$—$hk3$. Weak interspacing layer lines in the rotation photograph around [100] showed the a axis to be twice that reported by Zachariasen. This was confirmed by the powder patterns (see above) and by the Weissenberg photographs. The layer line $1kl$ showed no less than 4×18 reflexions.

The Laue symmetry *mmm* was confirmed. The following spectra were systematically missing: $0kl$ with $k+l =$ odd and $hk0$ with $h =$ odd, which is characteristic of the space groups No. 33, $Pn2_1a$ * and No. 62, *Pnma*.

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* Orientation analogous to that of No. 62 but different from that given in the *International Tables*.

Table 1. Powder photograph of HgO. CuKa₁ radiation. $a(KCl) = 6.2930\ \AA$. *Time of exposure 3 hours.*

hkl	$10^4 \times \sin^2\Theta$ obs	$10^4 \times \sin^2\Theta$ calc	I_{obs}	I_{calc} *
200	544	543	vw	14
101	615	614	vw	11
011	673	673	vst	1700
210	737	737	vst	1500
020	778	779	vst	1100
111	807	809	vvw	5
201	1021	1021	vst	1800
211	1215	1216	w	59
220	1320	1322	vw	23
121	1393	1393	vw	13
301	1704	1700	vvw	6
221	1798	1800	vst	3000
311	—	1895	—	0.2
002	1914	1914	st	1300
102	2047	2050	vvw	10
400	2170	2171	st	1400
031	2231	2231	st	660
112	—	2244	—	0.1
230	2295	2295	st	1100
410 131	2363	2366 2366	w	90 1
202	—	2457	—	22
321	—	2479	—	10
401 212	2651	2650 2651	vst	700 2500
022	2692	2693	st	1100
231	2772	2774	vw	42
122	—	2829	—	15
411	2846	2844	vst	2100
420	2951	2950	st	1200
040	3116	3115	m	630
302	—	3135	—	7
222	3230	3236	vw	39
312	—	3330	—	0.1
421	3246	3428	w	130
331	—	3452	—	0.0
240	—	3658	—	16
141	—	3729	—	6
132	—	3802	—	0.4
501	—	3871	—	2
430	3919	3923	w	69
511	—	4066	—	1
402	4085	4085	m	900
241	4138	4137	vst	1800
232	4208	4209	vst	2000
412	4277	4280	w	110
431	4402	4402	vst	1700
103	—	4442	—	4
013	4501	4501	m	600

* $I_{calc} = 6.25 \cdot 10^{-3}(pF^2)_{calc}$.

The intensities of the reflexions, which were visually estimated, were considerably influenced by the high absorption in the crystal. Unfortunately, a source of harder radiation than Cu-K radiation was not available at that time. Attempts to cut or grind the crystals to a cylindrical form were not successful due to the extreme delicacy of the material (*cf.* above). However, the absorption was minimized by using as small crystals as possible.
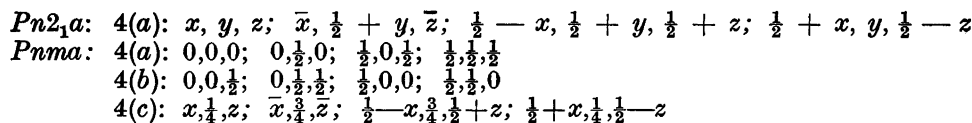
POSITIONS OF THE MERCURY ATOMS

The projections $P(pvw)$, $P(uvp)$ and $P(upw)$ of the Patterson function were calculated on the basis of F^2 values derived in the usual way. The maps thus obtained were of a rather simple appearance, indicating the existence of the heavy maxima listed in Table 2.

Table 2. Observed maxima in the Patterson functions.

u	v	w	Relative weight obs.	Relative weight calc.
$\frac{1}{2}$	0	0	2.0	2
$\frac{1}{4}$	$\frac{1}{2}$	$\frac{1}{4}$	2.0	2

In the space-groups $Pn2_1a$ and $Pnma$, the following positions are possible for the four mercury atoms:

$Pn2_1a$: $4(a)$: x, y, z; $\bar{x}, \frac{1}{2}+y, \bar{z}$; $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$; $\frac{1}{2}+x, y, \frac{1}{2}-z$

$Pnma$: $4(a)$: $0,0,0$; $0,\frac{1}{2},0$; $\frac{1}{2},0,\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$

　　　　　$4(b)$: $0,0,\frac{1}{2}$; $0,\frac{1}{2},\frac{1}{2}$; $\frac{1}{2},0,0$; $\frac{1}{2},\frac{1}{2},0$

　　　　　$4(c)$: $x,\frac{1}{4},z$; $\bar{x},\frac{3}{4},\bar{z}$; $\frac{1}{2}-x,\frac{3}{4},\frac{1}{2}+z$; $\frac{1}{2}+x,\frac{1}{4},\frac{1}{2}-z$
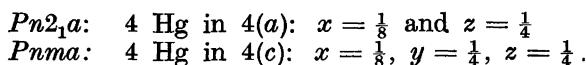
All the maxima of Table 2 are undoubtedly due to mercury-mercury interactions. This excludes the possibility that the positions $4(a)$ and $4(b)$ in $Pnma$ are the sites of the metal atoms.

If the mercury atoms occupy the point positions $4(a)$ in $Pn2_1a$ or $4(c)$ in $Pnma$, the following set of interatomic vectors will occur in the Patterson function in addition to the trivial peak at the origin (Table 3).

Table 3. Expected maxima in the Patterson functions.

u	v	w	Relative weight
$\pm 2x$	$\frac{1}{2}$	$\pm 2z$	1
$\pm (2x \pm \frac{1}{2})$	$\frac{1}{2}$	$\frac{1}{2}$	2
$\frac{1}{2}$	0	$\pm (2z \pm \frac{1}{2})$	2

A comparison of this set of vectors with the Patterson function derived from experimental data immediately gives the following approximate parameter values:

$Pn2_1a$: 4 Hg in $4(a)$: $x = \frac{1}{8}$ and $z = \frac{1}{4}$

$Pnma$: 4 Hg in $4(c)$: $x = \frac{1}{8}$, $y = \frac{1}{4}$, $z = \frac{1}{4}$.

The y parameter for the former space-group may be arbitrarily chosen equal to $\frac{1}{4}$ — the two possibilities will thus become identical, making possible the use of the second space group with its higher symmetry.

The approximate arrangement of the metal atoms thus derived is actually bodycentered with the symmetry identical with that proposed by Zacharia-sen [2]. However, it does not account for several reflexions observed in the Weissenberg diagrams, e. g. hkl with $h = 2n + 1$ and $h0l$ with $\frac{h}{2} + l = 2m + 1$ (n, m are integers). The F^2 values of these reflexions are too high to be ascribed only to the influence of the oxygen atoms. The parameters of the mercury atoms must thus be somewhat different from the values given above. By trial methods it was found that a slight shift of the metal atoms to the position (I) with $x = 0.115$ and $z = 0.245$ (or, which is equivalent, (II) with $x = 0.115$ and $z = 0.255$) was enough to give a better agreement between observed and calculated X-ray intensities (cf. Table 4). The former alternative (I) was arbitrarily chosen as giving the sites of the mercury atoms.

NEUTRON DIFFRACTION STUDIES

A comparison of the coherent scattering amplitudes of the mercury and oxygen atoms for neutrons and for X-rays shows the great advantage in investigating mercury(II)oxide by neutron diffraction.

Scattering amplitude (10⁻¹² cm) [4]

	Neutron	X-ray ($\Theta = 0°$)
Hg	1.31	22.5
O	0.58	2.25

While the amplitude values for neutrons are independent of the scattering angle, those for X-rays decrease with Θ — relatively more so for oxygen than for mercury.

Due to the relatively low neutron flux of the pile, which was run at an effect of 200—250 kW, it was necessary to use a large single crystal. A beautiful crystal of montroydite (1.5 × 1.5 × 14 mm) from Terlingua in Texas was kindly lent by Drs. W. F. Foshag and G. Switzer, Smithsonian Institution, U.S. National Museum, Washington, D. C. The absorption of the radiation in the crystal was neglected for the wavelength of 1.01 Å applied. X-Ray photographs confirmed that this specimen is a single crystal.

The crystal was mounted in a thinwalled glass capillary tube to prevent mechanical injury and oriented on the spectrometer table with rotation around the longest edge (the a direction). With the strongest reflexion 020 as a starting point, the diffraction peaks of the reflexions $0kl$ were measured at counter intervals of 0.5° scattering angle. The monitor counter serving as a measure of the incident monochromatic beam intensity was set at 40 000 counts for the weaker reflexions and 20 000 for the stronger ones. The ap-

Table 4 a.

Calculated structure factor values and observed intensities $h0l$, $h1l$ and $h2l$ from Weissenberg photographs of HgO. CuK radiation.

I. $I = 6.25 \cdot 10^{-3} \, (f_{Hg} \cdot A_{Hg})^2$, II. $I = 6.25 \cdot 10^{-3} \, (f_{Hg} \cdot A_{Hg} + f_O \cdot A_O)^2$

The reflexions $h0l$

The dotted line indicates the range of heaviest absorption.

$h \longrightarrow$

l		0	1	2	3	4	5	6	7	8
0	I			8		312		30		127
	II			7		354		28		138
	obs			—		vw		—		m
1	I		0.3	417	0.1	19	0.2	181	0.0	37
	II		3	453	2	18	0.5	190	0.4	35
	obs		—	w	—	—	—	w	—	m
2	I	350	0.5	5	0.7	230	0.2	25		
	II	328	2	6	2	218	1	26		
	obs	vst	vw	vvw	vvw	m	—	w		
3	I		1	217	0.5	12	1	137		
	II		1	196	0.5	13	1	125		
	obs		vw	st	vvw	m	vvw	st		
4	I	171	1	3	2					
	II	162	0.5	3	1					
	obs	st	vvw	w	vw					

The reflexions $h1l$

$h \longrightarrow$

l		0	1	2	3	4	5	6	7	8
0	I			452		20		187		37
	II			375		23		171		41
	obs			m		vvw		w		vw
1	I	472	0.2	7	0.2	279	0.1	28	0.1	122
	II	429	0.6	7	0.0	262	0.2	29	0.0	116
	obs	vst	—	—	—	w	—	vvw	—	m
2	I		0.7	298	0.3	15	0.6	158	0.1	
	II		0.0	316	0.0	14	0.1	164	0.0	
	obs		—	st	—	vvw	—	w	—	
3	I	160	0.8	3	1	120	0.3	15		
	II	141	0.8	3	1	108	0.3	16		
	obs	vst	—	vvw	vvw	st	—	w		
4	I		2	160						
	II		3	168						
	obs		vw	vst						

The reflexions h2l

l		0	1	2	3	4	5	6	7	8
0	I			7		272		28		121
	II			6		306		25		132
	obs			vvw		st		vw		st
1	I		0.2	350	0.1	17	0.2	167	0.0	
	II		2	376	1	16	0.5	175	0.4	
	obs		vvw	vst	—	vw	—	m	—	
2	I	300	0.5	5	0.6	209	0.1	24		
	II	283	2	5	2	199	1	25		
	obs	vst	vw	w	vvw	st	vvw	w		
3	I		1	200	0.5	11	1			
	II		1	182	0.5	12	1			
	obs		vw	vst	vvw	w	vvw			
4	I	163	1	3						
	II	155	1	3						
	obs	vst	vvw	w						

Table 4 b

Calculated structure factor values and observed intensities 1kl from a Weissenberg photograph of HgO. CuK radiation.

I. $I = 0.625 \ (f_{Hg} \cdot A_{Hg})^2$ II. $I = 0.625 \ (f_{Hg} \cdot A_{Hg} + f_O \cdot A_O)^2$

l		0	1	2	3	4	5	6
1	I	24	18	20	13	13	8	9
	II	269	58	166	14	73	2	35
	obs	st	m	m	—	—	—	—
2	I	53	66	46	51	33	37	25
	II	239	2	187	5	108	6	75
	obs	st	—	st	—	m	w	m
3	I	106	80	97	67	80	55	
	II	110	77	99	65	82	54	
	obs	m	m	m	m	m	m	
4	I	127	162	121	147			
	II	36	255	55	229			
	obs	m	st	m	st			

pearance of the curves obtained by plotting the intensities against the angles is given in Fig. 1. The observed intensities obtained by measuring the areas under the peaks with a planimeter and corrected for the Lorentz factor are given in Table 5. Because of the mechanical arrangement of the
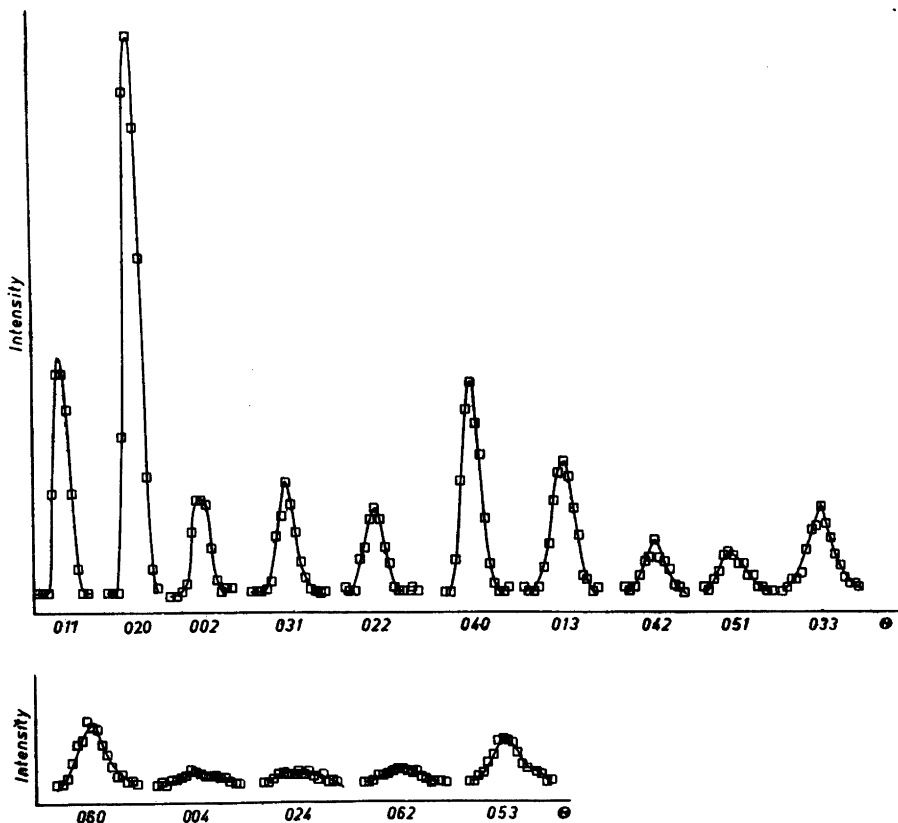
Fig. 1. Neutron reflexions 0kl from the single crystal investigation. Counts for angular intervals of 0.5°.

apparatus it was only possible to measure the intensities of the reflexions of the 0kl layer line.

Neutron diffraction powder diagrams were also taken using both a cylindrical and a flat container for the sample.

Positions of the oxygen atoms

On the basis of the neutron reflexions 0kl from the single crystal diagram, the projection P(pvw) of the Patterson function was calculated. As the degree of mosaic character of the crystal was not known, the two extreme possibilities, viz. that the observed intensities are proportional to F^2 or to $|F|$, were considered. The Patterson functions derived from these two assumptions were, however, found to be of a closely similar character. The positions of the maxima were thus exactly the same in both cases and the relative heights were only moder-

Table 5. Calculated and observed neutron intensities 0kl from the single crystal investigation. The observed intensity was considered proportional to F^2.

hkl	$F^2{}_{obs}$	$F^2{}_{calc}$
011	52	63
020	143	171
002	45	48
031	55	48
022	46	42
040	123	142
013	103	108
042	38	28
051	36	28
033	83	83
060	67	70
004	15	20
024	14	17
062	20	14
053	55	47

ately different. The appearance of $P(pvw)$ calculated on the basis of $F^2(0kl)$ is given in Fig. 2. The mercury-mercury vector is superimposed on the origin maximum in this picture. The discussion of the oxygen arrangement is based on the positions of the mercury atoms derived from the X-ray investigation described above. The following sets of projections of the mercury-oxygen vectors correspond to the possible arrangements of the four oxygen atoms in the space-groups $Pn2_1a$ and $Pnma$.

	Mercury-oxygen vectors		Relative weight	
	v	w	obs.	calc.
$Pn2_1a$: 4 O in 4(a):	$\frac{1}{4}-y$	$\pm(0.245-z)$	1	1
	»	$\pm(0.255-z)$	1	1
	$\frac{3}{4}-y$	$\pm(0.245+z)$	1	1
	»	$\pm(0.255+z)$	1	1
$Pnma$: 4 O in 4(a) or 4(b):	$\frac{1}{4}$	$\pm\ 0.255$	—	1
	»	$\pm\ 0.245$	—	1
	$\frac{3}{4}$	$\pm\ 0.255$	—	1
	»	$\pm\ 0.245$	—	1
$Pnma$: 4 O in 4(c):	0	$\pm(0.245-z)$	1	1
	»	$\pm(0.255-z)$	1	1
	$\frac{1}{2}$	$\pm(0.245+z)$	1	1
	»	$\pm(0.255+z)$	1	1

Since the maxima of $P(pvw)$ only occur at $v = 0$ and $\frac{1}{2}$, the y parameter of the oxygen atoms must be $\frac{1}{4}$ which excludes alternatives $Pnma$, 4(a) and 4(b) for the arrangement of the oxygen atoms. It also makes the two alternatives
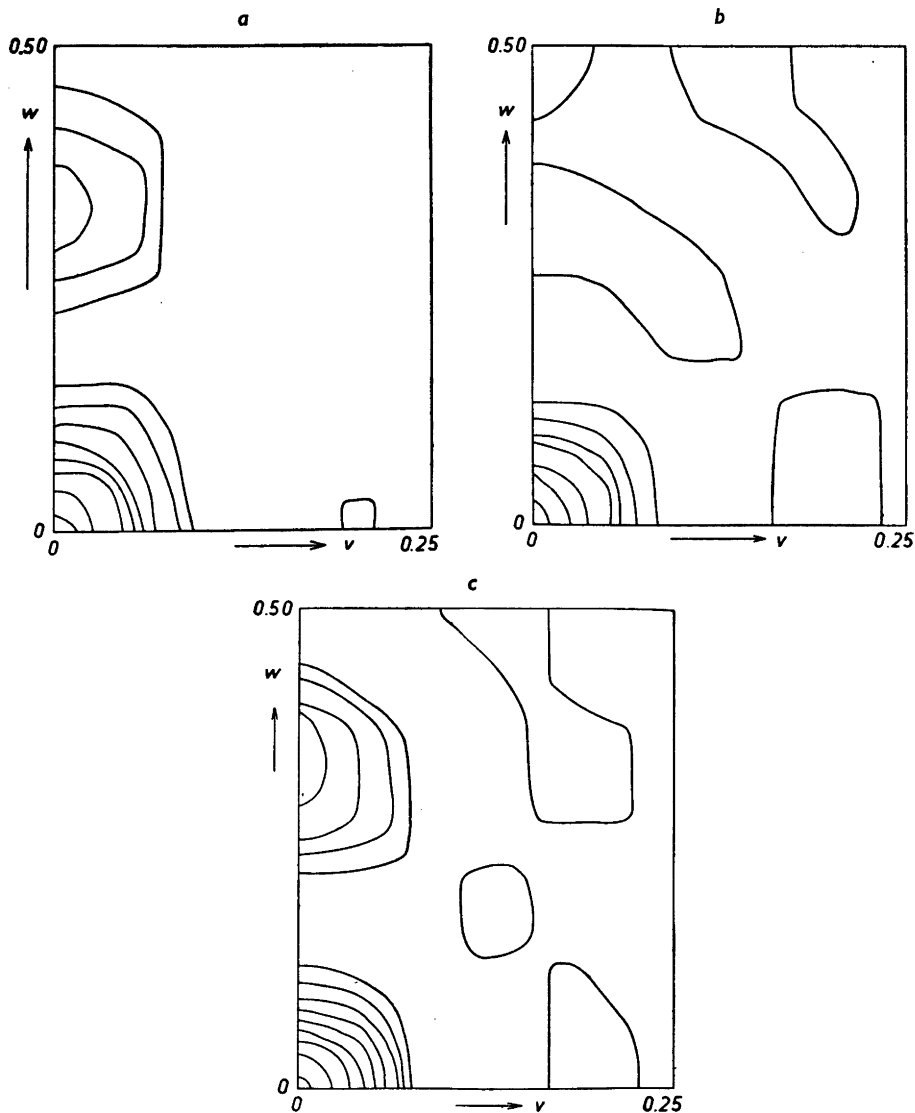
Fig. 2. a) The Patterson function P (pvw) *based on observed neutron intensities* 0kl,
   b) P(pvw) *based on calculated values* $(A_{Hg} \cdot b_{Hg})^2$,
   c) P(pvw) *based on calculated values* $(A_{Hg} \cdot b_{Hg} + A_O \cdot b_O)^2$ *(cf. Ref. 4)*

$Pn2_1a$, 4(a) and *Pnma*, 4(c) coincide and evidently shows that the structure of mercury oxide has the symmetry *Pnma* at least as far as can be judged from the present experimental data.
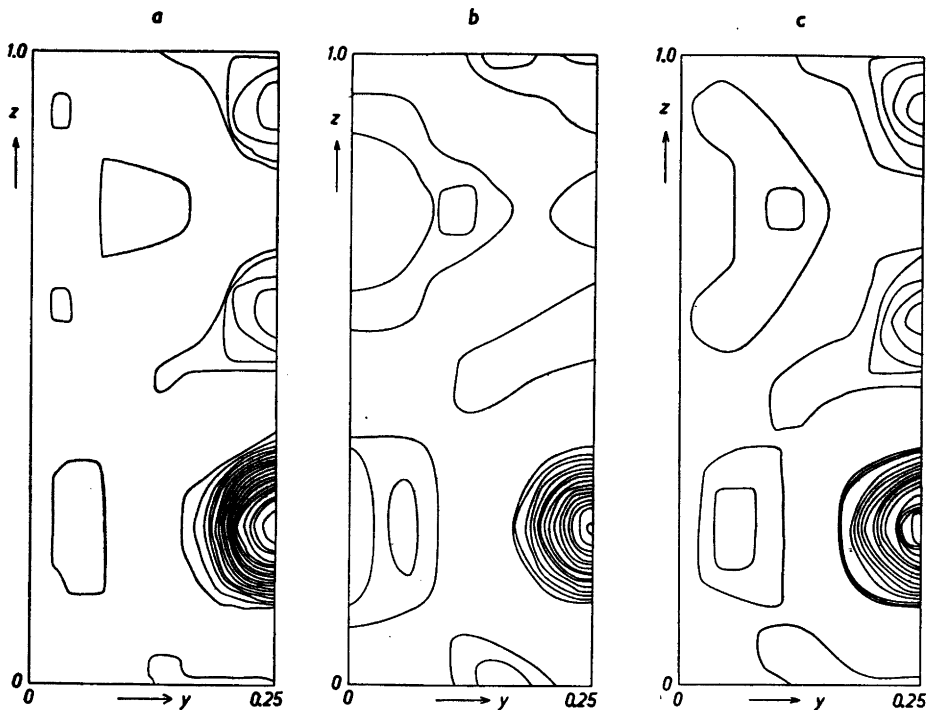
Fig. 3. a) The Fourier projection ϱ(pyz) based on neutron intensities 0kl (the observed
intensity considered proportional to F^2),
b) ϱ(pyz) based on calculated values $A_{Hg} \cdot b_{Hg}$,
c) ϱ(pyz) based on values $A_{Hg} \cdot b_{Hg} + A_O \cdot b_O$.

The mercury-oxygen peaks in $P(pvw)$ at $v = 0$, $w = \frac{1}{3}$ give the following
two alternatives for the arrangement of the oxygen atoms:

$$A: \quad 4 \text{ O in } 4(c): \quad x,y = \tfrac{1}{4}, \ z = 0.58$$
$$B: \quad 4 \text{ O in } 4(c): \quad x,y = \tfrac{1}{4}, \ z = 0.92$$

Due to the slight displacement of the mercury atom positions from
$(x = \tfrac{1}{4}, y = \tfrac{1}{4}, z = \tfrac{1}{4})$ with $|\Delta x| = 0.010$ and $|\Delta z| = 0.005$, these two alter-
natives are not identical. However, the difference between them is not big
enough to affect the signs of the structure factor values $F(0kl)$ for neutron
diffraction. The projection of the electron density function ϱ (pyz) thus deri-
ved, on the assumption that the observed intensity is proportional to F^2,
is represented in Fig. 3. The mercury maximum in this projection (correspond-
ing to two superimposed atoms) appears in $y = 0.250$, $z = 0.250$ and the
oxygen maxima in $y = 0.250$, $z = 0.585$ and $z = 0.915$ respectively. Func-
tions $P(pvw)$ based on F^2 $(0kl)$ values and ϱ (pyz) based on $F(0kl)$ values cal-
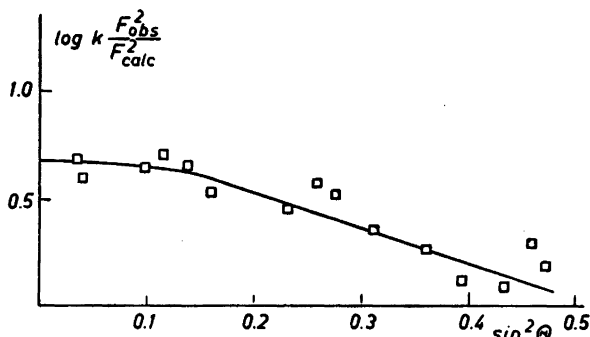culated for the mercury atoms only and also for both the mercury and oxygen

Fig. 4. Temperature correction curve. Log k $\dfrac{F^2_{obs}}{F^2_{calc}}$ plotted against $sin^2\Theta$.

atoms in the positions derived above are of reasonable appearance with the heights and positions of the various maxima in accordance with those of the experimentally derived functions (cf. Figs. 2 and 3).

Calculated and observed neutron intensities $0kl$ are given in Table 5. For each reflexion a temperature factor correction was calculated from the curve in Fig. 4. The reliability index

$$R = \frac{\Sigma \, \| F_{obs} | - | F_{calc} \|}{\Sigma \, | F_{obs} |}$$

was calculated to be 6.8 %.

CORRELATION OF X-RAY AND NEUTRON DIFFRACTION DATA

The intensities of the $1kl$ X-ray reflexions were found to be greatly influenced by the oxygen atom positions and allowed a decision to be made between the two alternatives A and B for the oxygen atom arrangement. As a matter of fact, only A was found to be compatible with the arbitrarily chosen position I for the mercury atoms. However, the structure thus obtained was identical with the combination of the mercury arrangement II with the oxygen arrangement B.
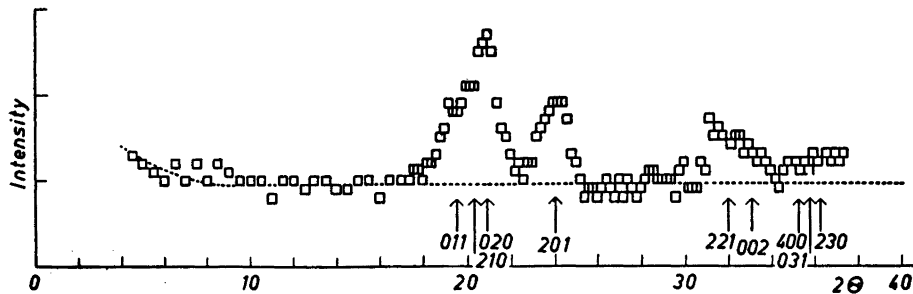
Fig. 5. Neutron diffraction powder diagram of a sample of HgO in a flat container.

Table 6. Observed and calculated neutron intensities of a few reflexions from a powdered sample of HgO.

I. Flat sample.   II. Cylindrical sample.

Calculations according to G. E. Bacon, *Neutron Diffraction*, Oxford 1955.

hkl	I		II	
	F^2_{obs}	F^2_{calc}	F^2_{obs}	F^2_{calc}
011 210	58	{35 {16	114	{75 {34
020	49	50	103	108
201	49	55	118	118

The accuracy of the resolution of the area under the first observed peak into its components, the reflexions 011, 210, and 020 may be rather low. The separate intensities have not been used for any further calculation.

Systematic variation of the x parameter of the oxygen atom position gave the best agreement between observed and calculated structure factor values for adjacent reflexions of comparable absorption when x_0 was equal to 0.36 ± 0.02 (*cf.* Table 4).

The spots in the Weissenberg photograph $3kl$ were highly elongated. It was not possible to estimate their intensities with the accuracy needed for quantitative calculations.

Due to the considerable absorption for several reflexions, the R-index for the X-ray data lacks significance.

The atomic positions thus derived are in accordance with the neutron diffraction powder diagrams. The low resolution of the latter, however, makes these diagrams less reliable than the X-ray data for the determination of the parameter values (*cf.* Fig. 5 and Table 6).
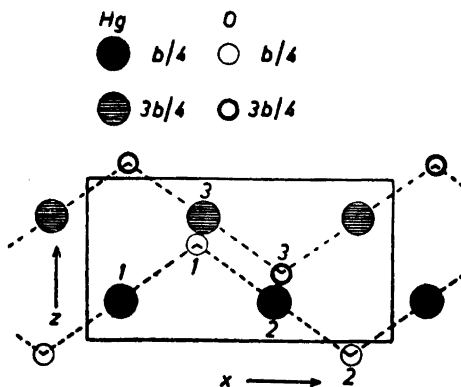

Fig. 6. xz projection of the structure of HgO. The diagram shows the coordination of the atoms. The small circles show the O atoms and the larger ones the Hg atoms. The distances Hg→Hg, Hg→O and O→O are listed in the text. The dotted lines indicate the bonds of one zig-zag chain.

Fig. 7. Diagram showing the infinite zig-zag chain $-O-Hg-O-$ *lying in the* ac *plane and running parallel to the* a *axis.*
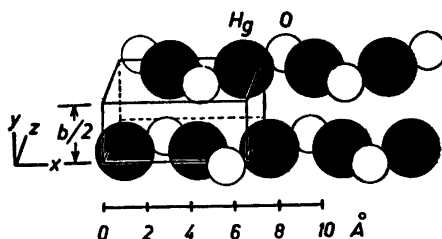
DESCRIPTION OF THE STRUCTURE

The following structure of mercury(II)oxide has thus been arrived at:

Cell content: 4 HgO
Space group: *Pnma*, No. 62
4 Hg in the point position 4(c): $x,\frac{1}{4},z; \bar{x},\frac{3}{4}, \bar{z}; \frac{1}{2}-x, \frac{3}{4}, \frac{1}{2}+z; \frac{1}{2}+x,\frac{1}{4},\frac{1}{2}-z$
$x = 0.115, z = 0.245$
4 O in the point position 4(c): $x = 0.36_5, z = 0.58_5$

The structure is built up of infinite, planar zig-zag chains $-O-Hg-O-$ running parallel to the a axis and lying in the ac plane (*cf.* Figs. 6 and 7).

The distances and angles within the chains are:

$$\begin{array}{ll}
\text{Hg(1)} - \text{O(1)} & 2.03 \pm 0.10 \text{ Å} \\
\text{Hg(2)} - \text{O(1)} & 2.03 \pm 0.10 \text{ Å} \\
\text{Hg(1)} - \text{Hg(2)} & 3.30 \text{ Å} \\
\text{The angle Hg(1)} - \text{O(1)} - \text{Hg(2)} & 109° \pm 1° \\
\text{The angle O(1)} - \text{Hg(2)} - \text{O(2)} & 179° \pm 3°
\end{array}$$

The distances between the chains are:

$$\begin{array}{ll}
\text{Hg(3)} - \text{O(1)} & 2.82 \text{ Å} \\
\text{Hg(2)} - \text{O(3)} & 2.82 \text{ Å} \\
\text{Hg(2)} - \text{Hg(3)} & 3.59 \text{ Å} \\
\text{O(1)} - \text{O(3)} & 3.39 \text{ Å}
\end{array}$$

The distance from a mercury atom to an adjacent oxygen atom should be [5,6]:

for ionic bonds 2.18 Å (coordination number 2)
for covalent sp^3 bonds 2.16 Å
for covalent sp bonds 2.0_1 Å

The Hg—O distances, actually found within the chain, 2.03 Å, and the values of the angles suggest that the bond between Hg and O within the chains is mainly homopolar. Between the chains, the forces are far weaker since the interatomic distances are considerably longer than those within the chains. The chains probably support each other by means of the Hg—O contacts.
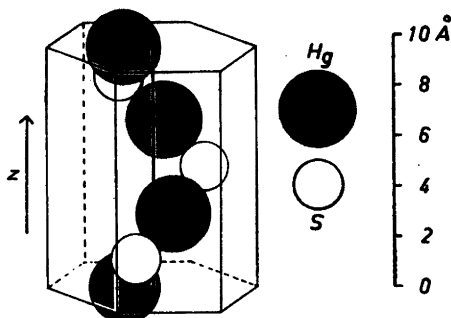
Fig. 8. Diagram showing one spiral chain —S—Hg—S— *of the cinnabar structure. The spiral chain extends indefinitely through the crystal in a vertical direction.*

A comparison between the structures of mercury(II)oxide and the hexagonal modification of mercury(II)sulphide (cinnabar) [7] (*cf.* Figs. 7 and 8) indicates the existence of similar building principles in these two structures. The infinite zig-zag chains —O—Hg—O— of the former correspond to infinite spiral chains —S—Hg—S— running parallel to the c axis of the latter. The angles —X—Hg—X— do not differ much from 180° in either case. The decrease in the angle Hg—X—Hg when going from oxygen (109° ± 1°) to sulphur (105° ± 2°) is in analogy to previously reported structural data.

A recent report by Roth [8] on an X-ray and neutron diffraction study of mercury(II)oxide gives a structure considerably different from that found in the present investigation. The doubling of the a axis and thus also the primitive character of the unit cell were not observed. The oxygen atom arrangement suggested by Roth and leading to a different system of Hg—O chains and to O—Hg—O angles of 105° is likewise inconsistent with the experimental data obtained by the present author.

REFERENCES

1. Aurivillius, K. *Acta Chem. Scand.* 8 (1954) 523.
2. Zachariasen, W. *Z. physik. Chem.* 128 (1927) 421.
3. Hambling, P. G. *Acta Cryst.* 6 (1953) 98.
4. Bacon, G. E. *Neutron Diffraction*, Oxford 1955.
5. Wells, A. F. *Structural Inorganic Chemistry*, Oxford 1950.
6. Pauling, L. *Z. Krist.* 87 (1934) 205.
7. Aurivillius, K. *Acta Chem. Scand.* 4 (1950) 1413.
8. Roth, W. L. *Acta Cryst.* 9 (1956) 277.