

With these assumptions three-dimensional electron-density calculations were made using signs, for all but the (400) and (111) reflections, obtained from the spherically disordered model. The (400) reflection was put into the calculation as zero since its observed structure amplitude is small and its sign unknown. The sign of the (111) reflection was taken positive in one calculation and negative in the other. The Fourier expression was evaluated over the asymmetric unit at intervals of 1/40 of the unit-cell edge. For both (111) sign choices the choline ion appeared more extended in the body diagonal direction than in any other. A distortion of the spherical choline model in this way would decrease the contribution of the choline to the (111) structure factor and hence the sign of this reflection would be the same as that of the chloride contribution, negative. Electron-density maps of the $y=0$ and $x=y$ sections with the sign of $F(111)$ negative are shown in Fig. 1. Calculations with the chloride ion contribution subtracted out show little change in the contours around the choline ion, and hence the observed asymmetry of this ion cannot be attributed to diffraction effects from the much heavier chloride ion.

That the choline ions tend to lie along the body diagonals is not surprising since this is the direction in which most room exists, 16.4 Å between the two neighboring chloride ions. It is not possible to say whether the

disorder is static or whether the choline ion is a hindered rotator in an octahedral potential field. No prominent diffuse scattering has been observed in the high temperature phase.

The able assistance of Mr Edward McGandy, Boston University, with the IBM-650 calculations of the electron density is greatly appreciated.

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Acta Cryst. (1961). **14**, 80

A neutron diffraction study of orthorhombic PbO.* MORTIMER I. KAY,† *Brookhaven National Laboratory, Upton, New York, U.S.A. and Crystal Research Laboratory, Department of Physics, The Pennsylvania State University, University Park, Pa., U.S.A.*

(Received 21 September 1959 and in revised form 18 December 1959)

The structure of tetragonal (red) PbO (Moore & Pauling, 1941) is comprised of layers of oxygen sandwiched between layers of lead, the lead being at the apex of a PbO₄ pyramid with a square O₄ base. The Pb-O-Pb layers repeat in c .

Byström (1943) attempted to determine the structure of orthorhombic (yellow) PbO. He placed the Pb atoms quite well, but could only surmise the oxygen coordinates. He reported the space group to be either $Pbma$ or $Pb2a$, $N=4$. The leads or oxygens by themselves must be in the centrosymmetric $Pbma$; however, unless both atoms have the same y coordinates, the space group must be the non-centrosymmetric $Pb2a$. It was this that Byström felt contained his most 'logical' structure.

Since tetragonal PbO shows an interesting chemical bonding scheme, and since the oxygen in the yellow (orthorhombic) phase could not be found by means of X-ray data, a neutron powder diffraction pattern of the latter was taken.

The unit-cell edges used were those determined at the

National Bureau of Standards (Swanson & Fuyat, 1953). They are

$$a = 5.489, b = 4.775, c = 5.891 \text{ \AA}.$$

Simultaneous equations utilizing the $h0l$ data readily established the x and z coordinates, which would be the same in either space group. The y parameter for Pb was taken as 0.25. The remaining O coordinate (y) was then found from hkl data to be equal or very close to the 0.25 assigned to Pb. $Pbma$ was thus accepted as the probable space group. The positions are: $x, \frac{1}{4}, z$; $\bar{x}, \frac{3}{4}, \bar{z}$; $\frac{1}{2} + x, \frac{1}{4}, \bar{z}$; $\frac{1}{2} - x, \frac{3}{4}, z$.

Final refinement was carried out on the x and z coordinates using Busing & Levy's (1958) least-squares program with the measurable single reflections. A few preliminary rounds of refinement showed that the structure factors included did not go far enough out in reciprocal space to give meaningful temperature factors. Therefore, B was assumed to be 0.8 Å² for lead and 1.2 Å² for oxygen, on the basis of similar structures. The final $R' = \Sigma |F_o^2 - F_c^2| / \Sigma F_o^2$ for the included reflections was 0.04. When all intensities were included, $\Sigma |I_o - I_c| / \Sigma I_o$ rose to 0.071. Refinement was thus considered satisfactory. The observed and calculated intensities are given in Table 1. The final parameters are given in Table 2, together with Byström's results.

It is seen from Fig. 1 that the Pb-O-Pb layers are

* Work completed under the auspices of the U.S. Atomic Energy Commission, and under Contract No. AF 18(603-35) with the Directorate of Solid State Sciences, Air Force Office of Scientific Research, ARDC.

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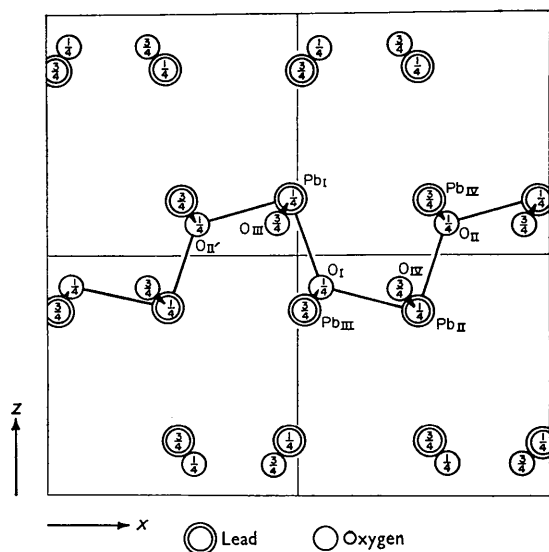


Fig. 1. Projection of PbO on y plane, four cells. Fractions show y coordinates.

Table 1. Comparison of calculated and observed intensities

Indices	I_c	I_o	Indices	I_c	I_o	
001	283	312	220	272	266	
101	123	123	113	} 690	} 583	
111	408	399	221			
002	259	271	301			
200	328	326	122			
102	46	40	311	277	289	
201	31	32	203	42	46	
020	} 444	} 466	302	} 407	} 404	
210			222			
112			42			62
211			136			177
021	} 136	} 177	023	} 120	} 116	
121			004			
202			131			
003			312			
103	} 334	} 339	123			
022						
212			217	195		

Table 2. Atomic coordinates for PbO, in units of cell edges, with standard deviations and temperature factors, compared with the results of Byström (1943)

Lead atoms

M. Kay		A. Byström	
x	-0.0208	$\sigma(x)$	0.0027
y	0.2500		-0.014
z	0.2309	$\sigma(z)$	0.0020
B	$0.8 \times 10^{-16} \text{ cm.}^2$		0.231

Oxygen atoms

x	0.0886	$\sigma(x)$	0.0025	-0.150
y	0.2500			0.358
z	-0.1309	$\sigma(z)$	0.0034	-0.111
B	$1.2 \times 10^{-16} \text{ cm.}^2$			

more or less retained (stacked in the z direction) in the yellow phase. The oxygen layers, however, pucker to give distorted PbO_4 'pyramids'.

Table 3 gives the bond distances and angles, compared with those in the tetragonal phase. Two of the Pb-O bonds shorten by about 0.08 Å to 2.21 and 2.22 Å, and the remaining two are about 2.49 Å. The Pb-O lengths in the x direction are roughly the sum of the covalent radii and those in the y direction approximately the sum of the ionic radii.

Table 3. Bond distances and angles in orthorhombic PbO compared with tetragonal PbO

Bond	Distances	
	r Orthorhombic	$\sigma(r)$
$\text{Pb}_I\text{-O}_I$	2.214 Å	0.023 Å
$\text{Pb}_I\text{-O}_{I'}$	2.223	0.015
$2(\text{Pb}_I\text{-O}_{III})$	2.487	0.006
	r Tetragonal	
	2.30 Å	
	2.30	
	2.30	

For numbering system see Fig. 1.

Angles

Bond	Orthorhombic	Tetragonal
$\text{O}_I\text{-Pb}_I\text{-O}_{I'}$	90.4°	118°
$\text{O}_{III}\text{-Pb}_I\text{-O}_{III}^*$	147.5	118
$\text{O}_I\text{-Pb}_I\text{-O}_{III}$	79.8	75
$\text{O}_{II}\text{-Pb}_I\text{-O}_{III}$	79.0	75
$\text{Pb}_I\text{-O}_I\text{-Pb}_{II}$	120.9	105
$\text{Pb}_{III}\text{-O}_I\text{-Pb}_{III}$	147.5	105
$\text{Pb}_I\text{-O}_I\text{-Pb}_{III}$	100.9	118
$\text{Pb}_{II}\text{-O}_I\text{-Pb}_{III}$	94.7	118

Standard deviations for all angles are *ca.* 1°.

* O_{III} is at $y=0.75$; O'_{III} is at $y=-0.25$, as are Pb_{III} and Pb'_{III} .

The forces between Pb-O-Pb layers in z should be quite weak. Byström (1943) does indeed point out that the crystals develop in flat c plates. The shortest Pb-Pb distance is 3.47 Å within a sheet and 3.63 between Pb layers.

The oxygens, as can be seen from Fig. 1, are surrounded by an exceedingly distorted tetrahedron of leads. The close oxygen approaches are: $\text{O}_I\text{-O}_{II}$, $\text{O}_{II'}=3.15$; $2(\text{O}_I\text{-O}_{III})=3.00$; $2(\text{O}_I\text{-O}_{IV})=2.97$ Å.

The writer is grateful to Prof. R. Pepinsky and Dr B. C. Frazer for helpful discussions.

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