[CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Crystal Structure of Pb_3O_4

BY S. T. GROSS

Crystal structure investigations have been reported for PbO_2,[1] PbO(r)[2] and PbO(y).[3] The structures for the first two compounds are well established. Few structural data have been available for the other oxides of lead. The preparation of single crystals of Pb_2O_3 and Pb_3O_4 by Clark, Schieltz and Quirke[4] made possible a study of these structures, and perhaps will eventually show how the transition from one form to another is effected. Dimensions and likely space group assignments have been published for these compounds.[5] Investigations of this type are of interest both because of the variation in chemical composition (without change in X-ray diffraction effects) and also because of the commercial importance of such phenomena in the field of the lead–acid accumulator.

The individual crystals of Pb_3O_4 are transparent red needles about 4 mm. long, show parallel extinction, and have a perfect cleavage parallel to the axis of the needle. Powder diffraction patterns and chemical analysis confirm the identity of the material. Optical and X-ray examination prove the crystals to be tetragonal, the cleavage corresponding to the 110 plane.

Laue patterns of the single crystals show distorted and split interferences (indicating considerable strain and fragmentation within the crystal), but serve to require a Laue symmetry $4/mmm$. This limits the possible point groups to $4/mm$, 42, $4mm$ or $\bar{4}2m$. No pyroelectric effects could be detected, and such face development as could be observed in a large number of individual crystals failed to require any symmetry lower than $4/mmm(D_{4h})$.

Rotation patterns with rotation about the c-axis were used to calculate c_0, equatorial interferences and goniometer patterns served to establish the value for a_0 (Table I).[6] The best values are

$$a_0 = 8.86 \pm 0.03\ \text{Å}.$$
$$c_0 = 6.66 \pm 0.02\ \text{Å}.$$

If four Pb_3O_4 units are considered included in one unit cell, the calculated density is 8.66, which agrees satisfactorily with the value of 9.1 given in the literature. (The literature density value corresponds to the powdered material and was probably contaminated with the dense yellow PbO.)

TABLE I

UNIT CELL DIMENSIONS

Sample-film distance 5 cm., rotation pattern, CuK_α.

Layer line separations. No. of layer line	Measurement, cm.	sin 2ϕ	c_0
1	2.53	0.2306	6.678
2	5.23	.4634	6.646

Equatorial layer line measurements of $hh0$ interferences:

h	k	l^a	Measurement, cm.	sin Θ	a_0
1	1	0	2.5	0.1248	8.71
2	2	0	5.0	.2474	8.79
3	3	0	7.56	.3692	8.83
4	4	0	10.26	.4907	8.86
5	5	0	13.23	.6134	8.86
6	6	0	16.54	.7359	8.86

$$a_0 = 8.86 \pm 0.1\ \text{Å}.$$
$$a_0\ (\text{goniometer}) = 8.87\ \text{Å}.$$

[a] The low values of the inner interferences are probably the result of the dimensions of the crystal under examination, since Pb_3O_4 is quite opaque to copper radiation.

One extinction is observed, $h0l$ interferences are absent when h is odd. In addition the hhl reflections are extremely weak when l is odd (only two such interferences can be observed, and these are both extremely faint). Examination of the X-ray patterns (and subsequent examination of the intensity data) indicate that the correct space group is probably P$\bar{4}$b2, although the structure very closely approximates special positions in the holohedral space group P4/mbc (assuming that the hhl reflections are entirely absent when l is odd). For this reason the analysis was based on the assumption of the higher symmetry.

The special positions for P4/mbc[7] are

4: (a) $000;\ 00\tfrac{1}{2};\ \tfrac{1}{2}\tfrac{1}{2}0;\ \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}$
(b) $00\tfrac{1}{4};\ 00\tfrac{3}{4};\ \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{4};\ \tfrac{1}{2}\tfrac{1}{2}\tfrac{3}{4}$
(c) $0\tfrac{1}{2}0;\ 0\tfrac{1}{2}\tfrac{1}{2};\ \tfrac{1}{2}00;\ \tfrac{1}{2}0\tfrac{1}{2}$
(d) $0\tfrac{1}{2}\tfrac{1}{4};\ 0\tfrac{1}{2}\tfrac{3}{4};\ \tfrac{1}{2}0\tfrac{1}{4};\ \tfrac{1}{2}0\tfrac{3}{4}$

8: (e) $00z;\ 00\bar{z};\ 0,\ 0,\ \tfrac{1}{2}+z;\ 0,\ 0,\ \tfrac{1}{2}-z;$
$\tfrac{1}{2}\tfrac{1}{2}z;\ \tfrac{1}{2}\tfrac{1}{2}\bar{z};\ \tfrac{1}{2},\ \tfrac{1}{2},\ \tfrac{1}{2}+z;\ \tfrac{1}{2},\ \tfrac{1}{2},\ \tfrac{1}{2}-z$
(f) $0\tfrac{1}{2}z;\ 0\tfrac{1}{2}\bar{z};\ 0,\ \tfrac{1}{2},\ \tfrac{1}{2}+z;\ 0,\ \tfrac{1}{2},\ \tfrac{1}{2}-z;$
$\tfrac{1}{2}0z;\ \tfrac{1}{2}0\bar{z};\ \tfrac{1}{2},\ 0,\ \tfrac{1}{2}+z;\ \tfrac{1}{2},\ 0,\ \tfrac{1}{2}-z$

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(1) Bragg, "Atomic Structure of Minerals." Cornell University Press, 1937, p. 103.

(2) Dickinson and Friauf, THIS JOURNAL, **46**, 2457 (1924); G. R. Levi, *Nuovo Cimento*, **1**, 335 (1924).

(3) F. Halla and F. Pawlek, *Z. physik. Chem.*, **128**, 49 (1927).

(4) G. L. Clark, N. C. Schieltz and T. T. Quirke, THIS JOURNAL, **59**, 2305 (1937).

(5) S. T. Gross, *ibid.*, **63**, 1168 (1941).

(6) DeJong and Bouman, *Physica*, **5**, 220 (1938).

(7) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Gebrüder Borntraeger, Berlin, 1935.

(g) $x, \frac{1}{2}+x, \frac{1}{4}; \bar{x}, \frac{1}{2}-x, \frac{1}{4}; \frac{1}{2}+x, \bar{x}, \frac{1}{4}; \frac{1}{2}-x, x, \frac{1}{4};$
$x, \frac{1}{2}+x, \frac{3}{4}; \bar{x}, \frac{1}{2}-x, \frac{3}{4}; \frac{1}{2}+x, \bar{x}, \frac{3}{4}; \frac{1}{2}-x, x, \frac{3}{4}$
(h) $xy0; \bar{x}\bar{y}0; \frac{1}{2}+x, \frac{1}{2}-y, 0; \frac{1}{2}-x, \frac{1}{2}+y, 0;$
$\bar{y}x\frac{1}{2}; y\bar{x}\frac{1}{2}; \frac{1}{2}+y, \frac{1}{2}+x, \frac{1}{2}; \frac{1}{2}-y, \frac{1}{2}-x, \frac{1}{2}$

Assuming P4/mbc correct, there must be four plumbic ions in a, b, c or d and eight plumbous ions in e, f, g or h. For interferences *hkl* where *l* is odd, a, b, c, d, f and g all require zero contribution to the intensity. Since each layer line observed on the rotation patterns is quite intense and therefore could not be due to oxygen ions alone, the plumbous ions must occupy *h*. The 440 interference is one of the more intense reflections on the patterns, but the 442 interference is not evident. This requires that the plumbic ions occupy either b or d.

Microdensitometer curves were made for the equatorial layer line of several rotation patterns, and the relative intensities of a series of *hh*0 interferences measured. Values obtained are listed in Table II, calculated as relative structure factors with the usual formula

$$I = \text{Const.}\,\frac{(1+\cos^2 2\Theta)}{\sin 2\Theta}\,F^2$$

where the structure factor F was considered equal to Af_{Pb}. This assumption is justified since the scattering of the oxygen is negligible, and that due to plumbous and plumbic lead will be practically identical to the atomic scattering factor for lead. Values for f_{Pb} (atomic) were taken from the table by Pauling and Sherman.[8]

TABLE II

CALCULATED AND OBSERVED SCATTERING FACTORS FOR *hh*0 INTERFERENCES

Assumed position for plumbous ion $x = 0.165$, $y = 0.14$.

h k l	sin Θ	Intensity	$F/f_{\mathrm{Pb}}(x\mathrm{C})$	F/f_{Pb}(calcd.)
1 1 0	0.124	0.174	10	1.40
2 2 0	.245	.776	34	4.72
3 3 0	.366	.175	25	3.04
4 4 0	.482	1.07	79	8.02
5 5 0	.606	0.328	58	5.12
6 6 0	.734	.519	83	8.32

The inequalities evident in the table (except for the somewhat questionable 440–660) limit the x and y values for the plumbous ions to the region 0.16–0.18 and 0.125–0.15. In this region the best agreement of F/f_{Pb} was found at the position $x = 0.165$, $y = 0.14$. In the absence of absorption and extinction corrections the agreement is satisfactory.

Table III compares visually estimated intensities with intensities calculated in the manner of the above table. No measured sin Θ values are included since the data were obtained by means of a goniometer somewhat similar to that described

TABLE III

CALCULATED AND ESTIMATED INTENSITY VALUES

k k l	$I_{\text{calcd.}}$	$I_{\text{est.}}$	*h k l*	$I_{\text{calcd.}}$	$I_{\text{est.}}$
2 0 0	0.51	0	7 2 0	0.37	5
4 0 0	0.34	1	8 2 0	.19	3
6 0 0	4.0	3	4 3 0	.14	1
8 0 0	0.62	3	5 3 0	.79	7
2 1 0	0.11	0	6 3 0	.00	0
3 1 0	10.3	5	7 3 0	2.5	20
4 1 0	0.15	0	8 3 0	0.06	?
5 1 0	.69	?	5 4 0	.12	0
6 1 0	.28	0	6 4 0	.02	0
7 1 0	.01	0	7 4 0	.06	1–2
8 1 0	.00	0	8 4 0	.35	1
3 2 0	.28	3	6 5 0	.19	2
4 2 0	2.9	18	7 5 0	.18	2
5 2 0	0.00	0	8 5 0	.02	0
6 2 0	.18	2	7 6 0	.18	0
2 0 1	7.5	18	6 2 1	.00	0
4 0 1	0.21	0	7 2 1	.20	3
6 0 1	.12	1	8 2 1	.07	2
8 0 1	.49	5	4 3 1	.15	2–3
2 1 1	.15	0	5 3 1	.31	5
3 1 1	.08	0	6 3 1	.00	0
4 1 1	1.22	8	7 3 1	.10	2
5 1 1	0.16	0	8 3 1	.07	3
6 1 1	.34	3	5 4 1	.66	20
7 1 1	.01	0	6 4 1	.16	5
8 1 1	.58	15	7 4 1	.01	2
3 2 1	.34	3	8 4 1	.22	2
4 2 1	.13	1	6 5 1	.26	10
5 2 1	2.2	25	7 5 1	.14	3
2 0 2	6.0	2	3 2 2	.19	0
4 0 2	6.4	2	4 2 2	.18	0
6 0 2	0.13	0	5 2 2	.00	0
8 0 2	0.14	0	6 2 2	.99	1–2
10 0 2	2.8	5	7 2 2	.30	0
2 1 2	0.06	0	8 2 2	.55	2
3 1 2	.01	0	9 2 2	.24	½
4 1 2	.11	0	4 3 2	.11	0
5 1 2	.91	0	5 3 2	.45	1
6 1 2	.23	0	6 3 2	.00	0
7 1 2	1.3	2	7 3 2	.08	0
8 1 2	0.00	0	8 3 2	.06	0
9 1 2	.04	0	9 3 2	1.5	5
10 1 2	.61	2	5 4 2	0.10	0
6 4 2	1.95	7	9 6 2	0.00	0
7 4 2	0.06	0	8 7 2	0.10	1
8 4 2	.35	2	1 1 2	7.1	3
9 4 2	.31	½	2 2 2	1.1	3
6 5 2	.17	½	3 3 2	7.3	20
7 5 2	.55	5	4 4 2	0.00	0
8 5 2	.03	0	5 5 2	.21	1
9 5 2	.92	4	6 6 2	.00	0
7 6 2	.19	1	7 7 2	1.3	7
8 6 2	.12	1			

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(8) Linus Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

TABLE III (*Concluded*)

h k l	$I_{calcd.}$	$I_{est.}$	*h k l*	$I_{calcd.}$	$I_{est.}$
2 0 3	.05	0	8 2 3	.08	0
4 0 3	.11	0	9 2 3	.40	2
6 0 3	.09	0	4 3 3	.10	2
8 0 3	.48	2	5 3 3	.22	3
2 1 3	2.6	5	6 3 3	.00	1
3 1 3	0.04	0	7 3 3	.09	2
4 1 3	.65	10	8 3 3	.08	2
5 1 3	.11	1	9 3 3	.32	2
6 1 3	.24	7	5 4 3	.51	10
7 1 3	.01	0	6 4 3	.14	2
8 1 3	.55	10	7 4 3	.01	1
9 1 3	.17	½	8 4 3	.25	2
3 2 3	.16	3	9 4 3	.42	8
4 2 3	.07	2	6 5 3	.22	5
5 2 3	1.4	20	7 5 3	.15	1
6 2 3	0.00	0	8 5 3	1.0	12
7 2 3	0.17	3	7 6 3	0.21	3

The crystals are bounded by prism faces (110) so that absorption characteristics will be greatest in the *h*00 planes, and the most intense reflections will be observed for the *hh*0 interferences. The table above has been arranged in such a manner that interferences of like nature are grouped together. Various films were used for l = 0, 1, 2, and 3.

by DeJong and Bouman[6] and there can be no ambiguity of *hkl* data. The calculated intensities were corrected only for polarization and the scattering factor of the lead.

The oxygen ions, with their negligible scattering power, cannot be located by X-ray means alone. Application of the coördination theory may be expected to furnish some information in this respect.

The c_0 dimension of PbO_2, corresponding to the distance between two opposite shared edges of an oxygen octahedron about a plumbic ion, is 3.4 Å.; c_0 for Pb_3O_4 is practically equal to two times this value.

Chains of such shared oxygen octahedra may be arranged up the sides of the Pb_3O_4 unit cell in such a manner that the plumbic lead ions would occupy the positions required by the preceding treatment. Shared oxygen ions on one chain would be in very close proximity to unshared oxygen ions from an adjacent chain. This arrangement would permit plumbous ions to lie very close to three oxygen ions. The various possible positions for such plumbous ions (as the plumbic octahedra chains are rotated) have been graphically determined in Fig. 1, the position determined for the plumbous ion on the basis of intensity data is indicated by a cross. The atomic distances involved were taken from the accepted values for lead dioxide, and from the Dickinson and Friauf structure for red PbO.

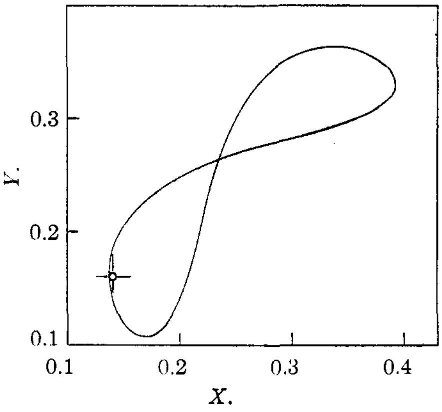

Fig. 1.—Continuous line represents possible positions of the plumbous ions based upon the coördination theory.

The agreement of position predicted by this coördination treatment with that previously determined furnishes strong evidence that the coördination suggested is correct, and also shows that the ionic distances are identical with those found in PbO (red) and PbO_2.

A projection of the unit cell on 001 is shown in Fig. 2a, with a scale projection on 001 of PbO(r) beside it to show the similarity in plumbous ion arrangement in the two cells. Also a projection of PbO_2 has been included to show the similarity of the PbO_4 shared octahedron chain positions. Figure 3 is a cross-section to show how the plumbous ions are arranged between adjacent chains of the shared octahedra. For the proposed Pb_3O_4 structure Pb^{++} has as its nearest neighbors three almost equidistant oxygen ions at an average distance of 2.30 Å., the next nearest oxygen ion is separated by about 3.01 from the lead ion. This may be compared with PbO(r) where each Pb^{++} is adjacent to four oxygen ions at about 2.302 Å., and is separated from four additional oxygen ions by 4.10 Å.

The c glide plane assumed in working with P4/*mbc* as pointed out previously is only a very good approximation. The space group which probably describes the material is $P\bar{4}b2$, with the plumbous ions so arranged that their separation in the c_0 direction will correspond very closely to 0.25. (The physical nature of the Pb_3O_4 crystals available made it impossible to obtain orders of the 001 interference to establish the value accurately.)

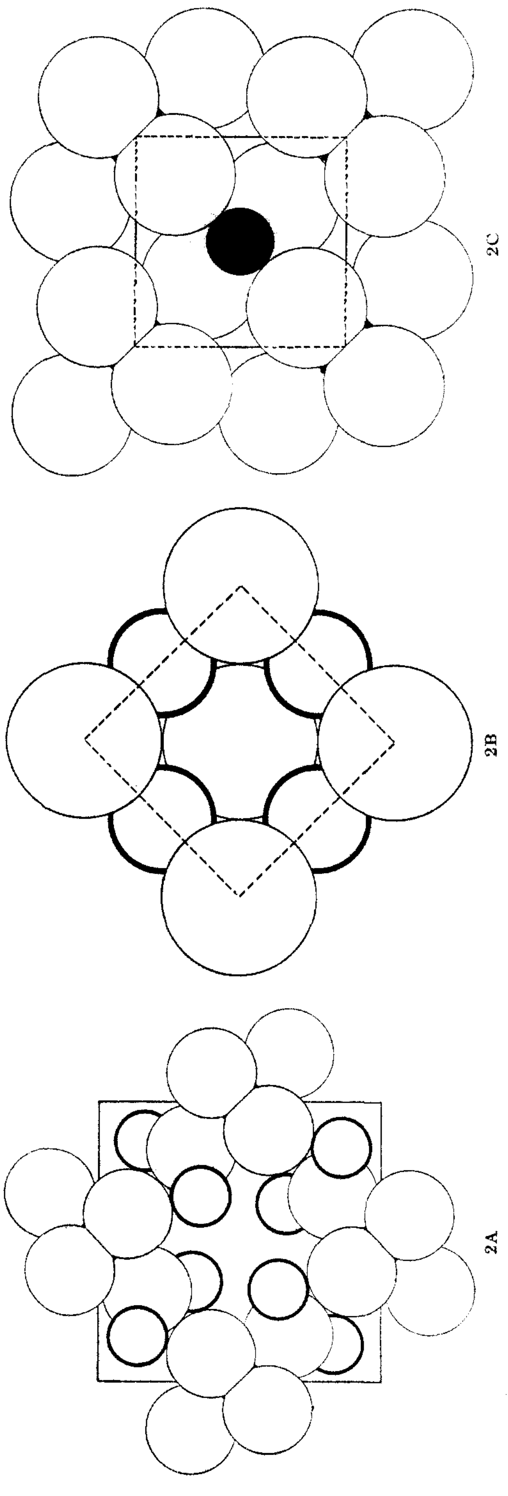

Fig. 2.—Comparison of 001 projections of PbO (red), PbO_2 and Pb_3O_4.

(a) Pb_3O_4: Overlapping large circles represent oxygen ions with $z = {}^1/_2$ (and 0); partly covered large circles oxygen with $z = {}^1/_4$ (and ${}^3/_4$). Overlapping heavy circles are plumbous lead ions with $z = {}^1/_2$, those partly covered with $z = 0$. Only one half of the unit cell is shown.

(b) PbO (red): One oxygen is omitted from the structure to show the position of the lead ions more clearly. Opposite pairs of lead ions at $z = 0.24$ and $z = 0.76$, respectively.

(c) PbO_2: Large light circles oxygen ions; small filled in circles plumbic ions. Overlapping ions have $z = {}^1/_2$, partly covered ions at $z = 0$. The shared oxygen ions at the corners of the cell cover plumbic ions with $z = 0$. Only one half of the unit cell is shown.

The atoms would be arranged as follows

2 plumbic ions in (c) at $0\frac{1}{2}\frac{1}{4}$, $\frac{1}{2}0\frac{3}{4}$
2 plumbic ions in (d) at $0\frac{1}{2}\frac{3}{4}$, $\frac{1}{2}0\frac{1}{4}$
8 plumbous ions in (i) with $x = 0.14$
$y = 0.165$
$z = 0.25$ (approx.)

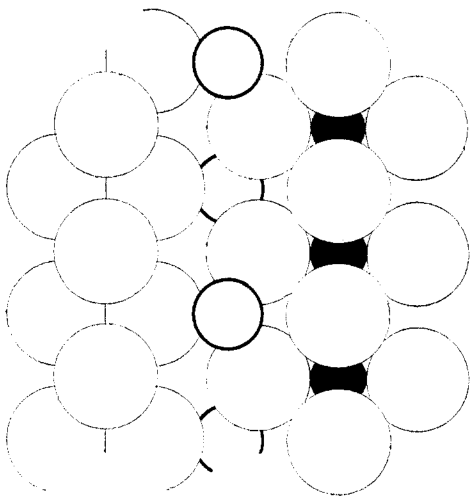

Fig. 3.—Arrangement of the plumbous ions between adjacent chains of the shared octahedra. Large circles oxygen, intermediate circles plumbous lead, small filled-in circles plumbic lead; plane of projection, 110.

4 oxygen ions in (g) with $x = 0.17$
$y = 0.33$
4 oxygen ions in (h) with $x = 0.17$
$y = 0.33$
8 oxygen ions in (i) with $x = 0.40$
$y = 0.10$
$z = 0.25$

Acknowledgment.—The author takes this opportunity to express his appreciation to Professor George L. Clark for his deep interest in this problem and many stimulating discussions helpful to its solution.

Summary

The crystal structure of minium, Pb_3O_4, has been determined. The positions of the lead ions were determined from X-ray intensity values; application of the coördination theory confirmed these positions and placed the oxygen ions. The plumbic ions are associated in chains of coördinated oxygen octahedra with opposite edges shared; practically identical even to the dimensions with those found in lead dioxide. These chains are arranged in a parallel manner, so that shared and unshared oxygen ions from adjacent chains approach closely in such a manner that three oxygen ions are coördinated with each plumbous ion. The plumbous ion arrangement is practically the same as in red PbO, so that the structure can be considered as basically built up from PbO(r) units and PbO_2 units. The space group as based upon the structure is taken as P$\bar{4}$b2.

URBANA, ILLINOIS RECEIVED JANUARY 18, 1943