Acta Cryst. (1961). **14**, 1304

On the crystal structure of tetragonal (red) PbO.

By JANUSZ LECIEJEWICZ, *Institute for Nuclear Research, Warszawa, Poland*

(*Received* 3 *July* 1961)

The crystal structure of tetragonal modification of lead monoxide has been studied by several workers. Dickinson & Friauf (1924) have found the tetragonal unit cell to contain two Pb atoms at $\frac{1}{4}, \frac{1}{4}, z$ and $\frac{3}{4}, \frac{3}{4}, \bar{z}$, and two oxygen atoms at $\frac{3}{4}, \frac{1}{4}, 0$ and $\frac{1}{4}, \frac{3}{4}, 0$, the space group D_{4h}^7–$P4/nmm$ being assigned as the most probable. An interesting coordination arrangement was discovered: each Pb atom was bound to four oxygen atoms forming a square pyramid with a lead atom at the apex. Each oxygen atom was surrounded tetrahedrally by four lead atoms. The Pb–O distance was found to be 2·30 Å. Subsequently Levi & Natta (1926) placed the O atoms in $\frac{1}{4}, \frac{1}{4}, v$, and $\frac{3}{4}, \frac{3}{4}, \bar{v}$ sites with $v = 0{\cdot}76$, Pb atoms occupying $\frac{1}{4}, \frac{1}{4}, z$ and $\frac{3}{4}, \frac{3}{4}, \bar{z}$ sites with $z = 0{\cdot}26$. This arrangement was a distorted NaCl structure with every lead atom surrounded by six oxygens at distances 2·5–2·8 Å. Dickinson & Friauf's (1924) conclusions were supported later by Moore & Pauling (1941) using powder data and by Bystrøm (1945) using a single-crystal. The results of the X-ray investigations are summarized in Table 1.

Table 1. *Summary of X-ray results for red* PbO

z_{Pb}	a (Å)	c (Å)	References
0·24	3·99	5·01	Dickinson & Friauf (1924)
0·26	3·96	5·02	Levi & Natta (1926)
0·233	3·947	4·988	Moore & Pauling (1941)
0·2385	3·964	5·008	Bystrøm (1945)

Space group: D_{4h}^7–$P4/nmm$

2 Pb in	(2*c*)	$\frac{1}{4}, \frac{1}{4}, z_{Pb}$	$\frac{3}{4}, \frac{3}{4}, \bar{z}_{Pb}$
2 O in	(2*a*)	$\frac{3}{4}, \frac{1}{4}, 0$	$\frac{1}{4}, \frac{3}{4}, 0$

Only Levi & Natta placed O in 2(*c*): $\frac{1}{4}, \frac{1}{4}, v$; $\frac{3}{4}, \frac{3}{4}, \bar{v}$. $v = 0{\cdot}76$.

However, there is another possibility of placing the oxygen atoms in space group $P4/nmm$: i.e. in (2*b*) at $\frac{3}{4}, \frac{1}{4}, \frac{1}{2}$ and $\frac{1}{4}, \frac{3}{4}, \frac{1}{2}$. For these positions the form of the coordination pyramid would be retained, the Pb–O distances being enlarged by approximately 3%. The intensity of some reflections would be altered, but these changes could not be detected using X-rays. Neutron-diffraction provides much better possibilities for the determination of oxygen atoms positions since the neutron scattering amplitudes for lead and oxygen are, in units of 10^{-12} cm., $b_{Pb} = 0{\cdot}960 \pm 0{\cdot}005$ and $b_O = 0{\cdot}58 \pm 0{\cdot}02$ (Hughes & Schwartz, 1958).

Red lead monoxide X-ray and chemically controlled was used. The lattice constants were determined as:

$$a = 3{\cdot}96 \pm 0{\cdot}01,\ c = 5{\cdot}01 \pm 0{\cdot}01 \text{ Å},\ c/a = 1{\cdot}27\ .$$

Powder neutron measurements up to $2\theta = 50°$ were made using 1·36 Å neutrons reflected from an Al monochromator. The neutron source was the Swierk reactor EWA operating at 2 mW. power. Second-order radiation contamination was found to be about 5%. Integrated intensities were obtained by measuring areas under peaks on the neutron diffraction pattern. Observed jF^2 values were derived after correction for Lorentz and scale factors, the influence of temperature factor being neglected. A comparison between observed jF^2 values and those calculated for alternative oxygen positions is given in Table 2.

Table 2. *Neutron diffraction data for tetragonal (red)* PbO

hkl	$jF^2{}_o$	$jF^2{}_c$*	$jF^2{}_c$†	$jF^2{}_c$‡
001	3·2	3·47	2·01	0·00
101	29	29·30	29·30	4·60
110	2·6	2·30	2·30	37·94
002	0·8	1·08	1·08	18·90
111	8	8·08	13·87	0·00
102	1·0	0·78	0·78	1·18
200	42	40·45	40·45	37·94
112, 201	73	88·53 (74·66, 13·87)	82·72 (74·66, 8·06)	74·71 (74·71, 0·00)
003, 121	59	59·57 (0·96, 58·61)	63·90 (5·29, 58·61)	9·24 (0·04, 9·20)

* O atoms placed in (2*a*): $\frac{3}{4}, \frac{1}{4}, 0$; $\frac{1}{4}, \frac{3}{4}, 0$. $z_{Pb} = 0{\cdot}237 \pm 0{\cdot}002$.

† O atoms placed in (2*b*): $\frac{3}{4}, \frac{1}{4}, \frac{1}{2}$; $\frac{1}{4}, \frac{3}{4}, \frac{1}{2}$. $z_{Pb} = 0{\cdot}237 \pm 0{\cdot}002$.

‡ O atoms placed in (2*c*): $\frac{1}{4}, \frac{1}{4}, v$; $\frac{3}{4}, \frac{3}{4}, \bar{v}$; with $v = 0{\cdot}76$. $z_{Pb} = 0{\cdot}26$.

The discrepancy factor is 0·092 for atomic sites, as proposed by Dickinson & Friauf (1924) and 0·11 for O placed in 2(*b*). For the former structure a systematic variation of the lead-atom parameter z_{Pb} gives the best agreement between observed and calculated intensities for $z_{Pb} = 0{\cdot}237 \pm 0{\cdot}002$. From the last column of Table 2 it becomes apparent, that the neutron diffraction data disagree with jF^2 values calculated for Levi & Natta's structure. A better agreement between jF^2 values, in particular for well resolved peaks, as compared to the structure model with O atoms in 2(*b*) shows, that the structure of tetragonal PbO as proposed by Dickinson & Friauf (1924) is supported also by a neutron diffraction study.

The technical assistance of Miss Barbara Rutkowska is gratefully acknowledged.

References

BYSTRØM, A. (1945). *Ark. Kemi Min. Geol.* A, **20**, No. 11, 1–31.

DICKINSON, R. G. & FRIAUF, I. B. (1924). *J. Amer. Chem. Soc.* **46**, 2457.

HUGHES, D. J. & SCHWARTZ, R. B. (1958). *Neutron Cross Sections*, 2nd Ed. Upton, New York: Brookhaven National Laboratory.

LEVI, G. R. & NATTA, E. G. (1926). *Nuovo Cim.* **3**, 114.

MOORE, W. J. & PAULING, L. (1941). *J. Amer. Chem. Soc.* **63**, 1392.