

## Refinement of the Structure of Orthorhombic PbO (Massicot) by Rietveld Analysis of Neutron Powder Diffraction Data

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(Received 25 January 1985; accepted 25 March 1985)

**Abstract.**  $M_r = 223.19$ , orthorhombic,  $Pbcm$ ,  $a = 5.8931$  (1),  $b = 5.4904$  (1),  $c = 4.7528$  (1) Å,  $V = 153.78$  (1) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 9.640$  g cm<sup>-3</sup>,  $\lambda = 1.893$  Å,  $\mu = 0.210$  cm<sup>-1</sup>,  $F(000) = 608$  fm<sup>2</sup>,  $T = 295$  K,  $R_{wp} = 0.0846$  for 2623 step intensities,  $R_B = 0.0182$  for 98 reflections. The structure consists of sheets 2.71 Å thick, separated by 3.19 Å in the [100] direction, and corrugated parallel to [001]. The Pb atoms are located on the surface of these layers, differing little from their positions in metallic Pb, but square-pyramidally bonded to four O atoms in the interior of the layers. The O atoms are in distorted tetrahedral coordination by Pb. The sheets are bonded together solely by van der Waals interactions between lone-pair orbitals on Pb atoms separated by 3.977 (2) and 4.206 (1) Å across the interlayer gap. The puckered geometry of the sheets is stabilized by similar lone-pair interactions between Pb atoms separated by 3.728 (2) Å across the corrugations.

**Introduction.** Lead monoxide occurs in two polymorphic forms: a red, tetragonal modification (litharge) stable at room temperature, and a yellow, orthorhombic variety (massicot) which is stable above about 760 K (Söderquist & Dickens, 1967). These oxides are of considerable interest because they exhibit photoactivity over a wide range of electromagnetic radiation wavelengths (Heyne, Beekmans & de Beer, 1972) and are extensively used in the manufacture of paints, ceramics, silicate glasses, and porous, pasted electrodes in lead-acid batteries (Greninger, Kollonitsch & Kline, 1975; Perkins, 1977). Our interest lies primarily in battery applications, where the ratio between the two phases in the commercial battery oxide formulations is claimed to influence the final charge/discharge performance of the battery by altering the reactivity, surface area, composition and morphology of the component phases during the processes of plate 'curing' and 'formation'. In addition, both polymorphs have been identified as undesirable corrosion products on the lead-alloy grids used to support the battery paste materials (Bullock, Trischan & Burrow, 1983).

Structure determinations of massicot by Kay (1961) and Leciejewicz (1961a), using integrated intensity

neutron powder diffraction data, have resolved the ambiguities remaining from the X-ray analysis of Byström (1943), but the relatively low precision of these studies has left some doubt about the detailed geometry of the structure. A new refinement of the massicot structure is desirable since recent neutron and X-ray diffraction analyses of the dioxides of lead (Hill, 1982; Jorgensen, Varma, Rotella, Cook & Yao, 1982; Santoro, D'Antonio & Caulder, 1983; Hill & Madsen, 1984; Hill, Jessel & Madsen, 1984) have indicated that small changes in structure and Pb:O stoichiometry may play an important role in determining the electrochemical activity of lead oxides in a battery environment.

**Experimental.** The material used for the structural studies was a bright yellow 50 g sample of Merck 'pro analyse' PbO (batch number 0093820), determined to be phase-pure orthorhombic PbO by X-ray powder diffraction analysis. Neutron diffraction data were collected at 295 K on the high-resolution, fixed-wavelength diffractometer (HRPD) attached to the Australian Atomic Energy Commission research reactor HIFAR at Lucas Heights, New South Wales. This instrument has been described in detail by Howard, Ball, Davis & Elcombe (1983). The sample was contained in a 16 × 50 mm spinning vanadium can and data recorded under monitor control at intervals of 0.05° between 17.0 and 148.1° 2 $\theta$ . The linear attenuation coefficient was determined by measuring the intensity of the straight-through beam with and without a sample in the can.\*

Least-squares structure refinements were performed with an extensively modified version of the Rietveld analysis program *DBW3.2* (Wiles & Young, 1981). The more important modifications to this program include the incorporation of a Voigt peak-shape function (Suortti, Ahtee & Unonius, 1979; David &

\* The list of step-scan diffraction data and coefficients of the anisotropic thermal vibration ellipsoids have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42144 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Matthewman, 1984; Hill & Howard, 1985),\* a sum of five Voigtians peak-asymmetry correction (Howard, personal communication: the sum of three Gaussians case is described in Howard, 1982), a correction for sample absorption in the neutron beam (Hewat, 1979), the inclusion of intensity contributed by peaks lying just beyond the end of the pattern, and improvements to the method of extraction of 'observed' integrated peak intensities for the calculation of Fourier coefficients and Bragg agreement index. The scattering lengths used for Pb and O were 94.003 and 58.03 fm<sup>2</sup>, respectively.

The background was defined by a four-parameter polynomial in  $2\theta^n$ , where  $n$  has values between 0 and 3, and was refined simultaneously with the unit cell, zero point, scale, peak width/shape/asymmetry, and crystal structural parameters. The calculated peak intensity was distributed over 4.0 peak full-widths at half-maximum on either side of the peak centre. The function minimized in the least-squares procedure was  $w_i(Y_{io} - Y_{ic})^2$ , where  $Y_{io}$  and  $Y_{ic}$  are the observed and calculated intensities at each step  $i$  in the pattern, and  $w_i = 1/Y_{io}$ . Convergence was assumed to have been achieved when the parameter shifts in the final cycle of refinement were less than 20% of their associated e.s.d.'s.

Starting values for the coordinates of the single Pb and O atoms at  $(x, y, \frac{1}{4})$  in space group  $Pbcm$  were obtained from Leciejewicz (1961a). A full-matrix, anisotropic thermal parameter refinement (14 profile and 13 structural parameters) converged at the conventional Rietveld agreement indices (Young, Prince & Sparks, 1982) given in the *Abstract* together with  $R_p = 0.0630$ , and goodness of fit = 1.436. The maximum level of residual nuclear density was less than

\* The width of the Gaussian component of the Voigt function was coded to vary in accordance with the usual function  $(U \tan^2 \theta + V \tan \theta + W)^{1/2}$  (Caglioti, Paoletti & Ricci, 1958), while the width of the Lorentzian component was varied with  $\sec \theta$  in order to describe particle-size effects.

10% of that of an O atom and the Pb:O ratio was 1.008 (6). The Lorentzian component of the Voigt function varies between 15 and 44% of the convoluted peak shape across the pattern, and has a width consistent with a mean crystallite size of about 2100 Å; the Gaussian component width is instrumental in origin. A summary of the refined structural parameters is given in Table 1, and the corresponding observed, calculated and difference neutron powder diffraction profiles are presented in Fig. 1.

**Discussion.** The present refinement confirms the structure obtained for massicot by Kay (1961) and Leciejewicz (1961a), but has resulted in changes in bond lengths and angles of up to 0.026 Å and 3.0°, respectively, and has produced an overall reduction in the parameter e.s.d.'s by an order of magnitude.

The crystal structure of both monoxide polymorphs may be visualized as a face-centred cubic array of Pb atoms (as in Pb metal), swelled and distorted by the introduction of double layers of O atoms between every second layer of Pb atoms. However, whereas the Pb and O atom layers in litharge are flat (Moore & Pauling, 1941; Leciejewicz, 1961b), the (100) sheets in massicot are steeply corrugated in the [001] direction (Fig. 2), producing significant increases in both their thickness (2.71 relative to 2.37 Å) and separation (3.19 relative to 2.64 Å). In spite of this expansion perpendicular to the layers the lateral contraction resulting from the corrugation of the sheets is so

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters

	$x$	$y$	$z$	$B_{eq}(\text{Å}^2)^\dagger$
Pb	0.2297 (2)*	-0.0116 (3)	0.25	1.07 (3)
O	-0.1347 (3)	0.0917 (3)	0.25	1.14 (5)

\* Parenthesized figures here and elsewhere in the tables represent the e.s.d. in terms of the least-significant figure to the left.

†  $B_{eq}$  is defined as  $8\pi^2$  (mean-square radial displacement)/3.

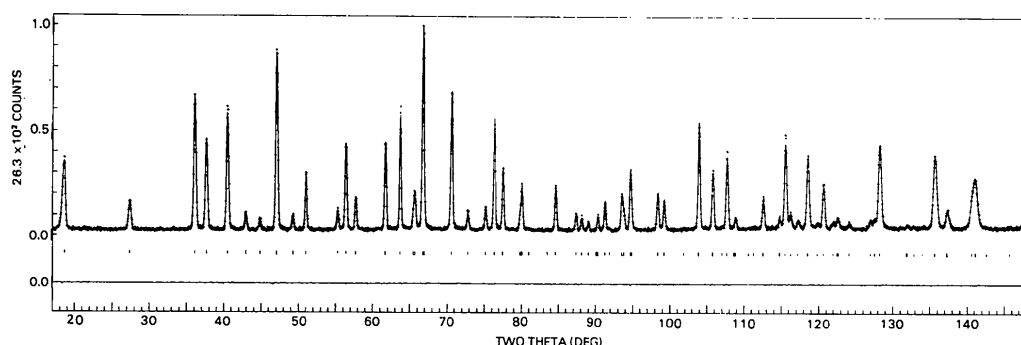


Fig. 1. Observed, calculated and 'difference' neutron powder diffraction profiles for orthorhombic PbO. The observed data are indicated by plus signs and the calculated profile is the continuous line in the same field. The short vertical lines below the profiles represent the positions of all possible Bragg reflections, and the bottom curve is the value of  $\text{sign}(\Delta)w\Delta^2$  at each step, where  $\Delta$  is the difference between the observed and calculated intensity.

pronounced that the density of massicot is still some 3.4% higher than that of litharge, the low-temperature polymorph.

The Pb atom can be described as being either in distorted square-pyramidal coordination, 1.05 Å out of the mean plane of four O atoms at distances of 2.221 (2), 2.249 (2) and  $2 \times 2.481$  (1) Å, or in trigonal-bipyramidal coordination, with one of the equatorial O atoms missing (Fig. 2). The next-nearest O atom is 3.360 (2) Å away, across the trough in the sheet corrugations. Similar 'one-sided' coordination for divalent lead is observed in litharge and a number of other more complex lead salts (Sahl, 1970; Abel, 1973), with the uncoordinated side of the Pb atom generally being considered to be occupied by a lone pair of electrons with predominantly 6s character.

The O atom lies in the interior of the sheets in distorted tetrahedral coordination by Pb atoms (Table 2, Fig. 2). As in the Pb polyhedron, the two short bonds are

Table 2. *Interatomic distances (Å) and angles (°)*

Pb—O	2.221 (2)	O...O	2.944 (2)	76.83 (5) × 2
	2.249 (2)		3.030 (2)	80.04 (4) × 2
	2.481 (1) × 2		3.171 (2)	90.38 (6)
O—Pb	2.221 (2)	Pb...Pb	4.753 (1)	146.65 (8)
			3.536 (2)	96.64 (5) × 2
			3.605 (1)	99.96 (4) × 2
			3.856 (1)	119.21 (8)
			4.753 (1)	146.65 (8)

oriented so as to produce a zigzag subchain of more strongly bonded Pb and O atoms parallel to [010]. Dickens (1965) successfully interpreted this asymmetrical geometry in terms of a covalent bonding model involving the hybridization of *s* and *p* orbitals on O and *p* and *d* orbitals on Pb. The two sets of bonds in massicot can, however, be correlated with the presence of the sheet corrugations: the additional flexibility provided by the warping of the layers allows the set of bonds perpendicular to the corrugation direction to respond to the steric requirements of the Pb atom lone pairs and the sharing of polyhedron edges in a different way to the set of bonds oriented parallel to the corrugations. No such sheet distortions are present in litharge, so the four Pb—O bonds are equal in length with a value which is close to the average in massicot (2.36 Å). In both massicot and litharge the widest bond angles are associated with those polyhedron edges which are not shared.

Each Pb atom is surrounded by an approximately spherical array of twelve Pb atoms at distances ranging from 3.54 to 4.21 Å (the next-nearest is 4.75 Å away), similar to the arrangement in Pb metal. Vectors to six of these Pb atoms (at 3.54 to 3.86 Å) are directed along the surface or towards the interior of the sheets and form the edges of the distorted tetrahedron surrounding O (Table 2). Four of the remaining Pb—Pb vectors are directed towards Pb atoms 3.98 to 4.21 Å away in an adjacent sheet, while the last two bridge the 3.73 Å gap across the sheet corrugations (Fig. 2). All of these Pb—Pb separations are significantly less than twice the value assigned to the van der Waals radius of a Pb atom lone-pair orbital, suggesting that van der Waals interactions between the lone pairs not only provide the primary source of bonding between the sheets (Dickens, 1965), but that they may also represent the major factor contributing to the stabilization of the sheet corrugation relative to the planar configuration in litharge (Söderquist & Dickens, 1967; Adams & Stevens, 1977; Vigouroux, Calvarin & Husson, 1982). Indeed, the lone-pair orbitals appear to pack more efficiently in massicot than in litharge, perhaps thereby accounting for the abnormally low thermal expansion observed perpendicular to the sheets (Garnier, Calvarin & Weigel, 1972; Vigouroux *et al.*, 1982), and for the stabilization of the massicot crystal structure relative to the alternative CsCl and NaCl structure types at high temperatures (Adams & Stevens, 1977). It is, therefore,

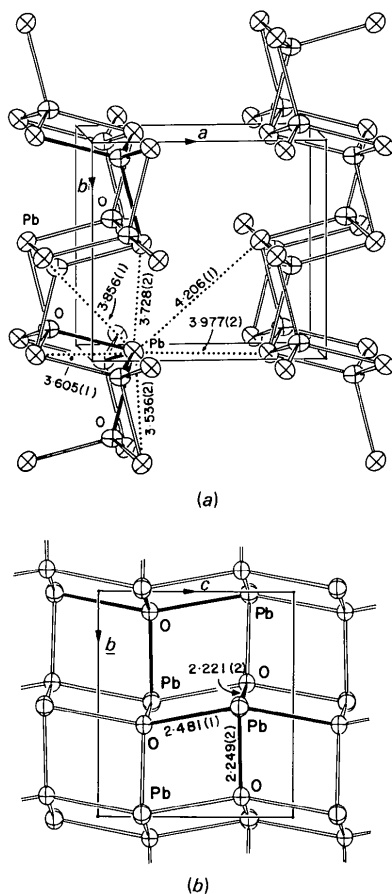


Fig. 2. Diagram of the orthorhombic PbO crystal structure showing (a) the full unit-cell contents viewed approximately down [001], and (b) a single corrugated layer viewed down [100]. Thermal ellipsoids for all atoms represent 50% probability surfaces. One set of Pb—O interactions for each of the Pb and O coordination polyhedra is shown as filled conical bonds. (Distances in Å.)

not surprising that theoretical calculations of Raman and infrared vibrational frequencies can be brought into agreement with observation only by the incorporation of these Pb—Pb interactions (Donaldson, Donoghue & Ross, 1974; Vigouroux *et al.*, 1982).

*Relevance to the lead-acid battery.* The mean distance between the Pb atom and its twelve nearest Pb neighbours is 3.82 Å, only 0.32 Å larger than the corresponding distance in Pb metal. Since litharge and massicot have similar sub-arrays of distorted face-centred-cubic Pb atoms, the two polymorphs can be rather easily interconverted (White, Dachille & Roy, 1961; Hehner & Ritchie, 1974) by a mechanism involving relatively minor movements of the Pb atoms (Söderquist & Dickens, 1967). By a similar argument, either of the two polymorphs would be expected to be formed without difficulty by electrochemical corrosion of the positive-plate Pb-alloy grids in the lead-acid battery since the required O atoms can be intercalated between layers of Pb atoms in the metal with a minimum of structural disruption. Furthermore, as suggested by Anderson & Sterns (1959), the way is then clear for the subsequent formation of the so-called 'intermediate' oxides of lead, with composition  $PbO_x$ , where  $x \approx 1.5$ , by the insertion of further O atoms into the van der Waals gap in the PbO crystal structure. Studies are currently underway to elucidate the mechanism of this corrosion process during battery operation.

The author is grateful to the Australian Associated Smelters Pty Ltd for financial assistance and permission to publish the results.

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*Acta Cryst.* (1985). **C41**, 1284–1286

## Structure of Manganese(II) Iodide Tetrahydrate, $MnI_2 \cdot 4H_2O$

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(Received 21 December 1984; accepted 16 April 1985)

**Abstract.**  $M_r = 380.81$ , monoclinic,  $P2_1/c$ ,  $a = 6.698$  (2),  $b = 7.494$  (3),  $c = 9.308$  (5) Å,

$\beta = 110.21$  (3)°,  $V = 438.5$  (3) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 2.82$  (4),  $D_x = 2.90$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71069$  Å,  $\mu = 84.1$  cm<sup>-1</sup>,  $F(000) = 342$ ,  $T = 291$  K, final  $R = 0.047$ , for 675 unique observed reflections. Unlike

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