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Neutron-diffraction study of orthorhombic lead monoxide.

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The structure of orthorhombic modification of PbO was studied recently by Kay (1960) using a powder neutron diffraction method. A similar investigation has been carried out independently in this Institute and a brief account is presented here.

Neutron powder diffraction diagrams were taken on the universal double-crystal spectrometer designed by O'Connor & Bońkowski (1959), using 1·41 Å neutrons reflected from an Al monochromator. The second-order radiation in the monochromatic beam was measured to be 5% in this case. The neutron source was the Swierk reactor 'EWA' running at 1800 kW. The data were recorded automatically by an apparatus described by O'Connor & Blinowski (1957). Counts were taken for periods of 18 min. at intervals 04·26′ scattering angle. The statistical counting error was about 2·5%. Measurements were made up to $2\theta = 37°$, since well resolved peaks appeared only in this region. Intergrated intensities were obtained by measuring the areas under peaks. The estimated accuracy of measurement of the integrated intensities was 5% for the stronger peaks. In comparing the measured intensities with their calculated values, relative intensities were calculated using one of the peaks as reference. No temperature factor was taken into account since only low-angle reflexions were used.

The diffraction pattern of PbO was indexed on a primitive orthorhombic cell with following dimensions:

$$a = 5{\cdot}876,\ b = 5{\cdot}476,\ c = 4{\cdot}743\ \text{Å}\ .$$

By the trial-and-error method the best agreement between observed and calculated $j|F|^2$ values was obtained for Pb atoms placed in positions given by Byström (1943) and oxygen atoms with the coordinates:

$$x = 0{\cdot}082,\ y = 0{\cdot}132,\ z = 0{\cdot}750,$$

as compared with

$$x = 0{\cdot}150,\ y = -0{\cdot}111,\ z = 0{\cdot}358$$

found by Byström (1943). Space group $Pca2_1$ was adopted by Byström on grounds of systematic absences and spatial considerations. However, the parameter $z = 0{\cdot}750$ indicates that the oxygen atoms should be in centrosymmetrical positions. For this reason the adoption of space group *Pbcm*, as done by Kay (1960) seems to be more logical. The lead and oxygen atom parameters are then:

	x	*y*	*z*
Pb	0·231	−0·014	0·25
O	−0·132	0·082	0·25

Lead-atom parameters are taken from Byström's work (1943). A summary of observed and calculated values for PbO is given in Table 1.

For this set the minimum *R* factor defined as

$$R = \Sigma[j|F_o|^2 - j|F|_c^2]/\Sigma j|F_o|^2$$

was 0·07, compared with 0·28 found for Byström's model.

Table 1. *Neutron diffraction data for* PbO

hkl	$j\|F\|_o^2$	$j\|F\|_c^2$
100	8	8·6
110	10	5·2
111	50	42·4
200	31	31·0
020	50	50·0
210	10	8·8
120	5	6·2
002 }	81	81·1 { 75·0
021 }		{ 6·1

In the model of the proposed structure each Pb atom is bounded to oxygen atoms at a distance of 2·21 ± 0·02 Å lying on the same level and thus forming a zigzag chain. The next two oxygen atoms are situated below and above in neighbouring chains at a distance of 2·49 ± 0·02 Å. The principal bond angles are:

O–Pb–O	146 ± 1°

for oxygen atoms belonging to neighbouring chains above and below Pb atom, and

O–Pb–O	89 ± 1°
Pb–O–Pb	124 ± 1°

for Pb and O atoms in the same chain.

The structure may be described as composed of zig-zag chains running along the *b* axis at a height 0·25 and 0·75. The chains are packed to form a layer lying in the *bc* plane.

The distance from a lead atom to an adjacent oxygen atom should be 2·28 Å for an ionic bond with coordination number 2 or about 2·00 Å for a planar *s–p* covalent bond (Wells, 1950). As the shortest Pb–O distance actually found within the chain is 2·21 Å it can be assumed that this bond is covalent with quite a strongly polarized character. The interchain bonding is weaker, since the atomic distances are larger. The two nearest Pb atoms belonging to neighbouring layers are separated by a distance of 3·51 ± 0·02 Å. This indicates very weak interlayer bonding, most probably of the van der Waals type.

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