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Structural resolution of the incommensurate phase of α-PbO from x-ray- and neutron-powder-diffraction data

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The modulated structure of the incommensurate phase of α-PbO was determined from x-ray- and neutron-powder-diffraction data. The four-dimensional structural refinement has led to the superspace group $P(C2mb)$:$(\bar{1}\bar{1}1)$. It has shown that even if the average atomic positions remain almost equivalent to those of the centrosymmetric tetragonal structure of PbO, the atomic modulated displacements only agree with a noncentrosymmetric space group. It has allowed us to give a first interpretation of the incommensurate behavior, which seems to point out a competition between α and β phases.

Lead monoxide (PbO) crystallizes below 765 K in the tetragonal α phase ($a=3.9704$ Å; $c=5.022$ Å) with the space group $P4/nmm(Z=2)$ (Ref. 1) (Fig. 1). A second-order transition at 208 K, transforms this phase into an orthorhombic phase (α' phase).[2] Both phases are similar and the associated spontaneous strain is very small ($e_{12}^s=4.37\times10^{-4}$ at 2 K). The lattice basic vectors of the orthorhombic phase are defined from those of the tetragonal phase ($\mathbf{a}_T,\mathbf{b}_T,\mathbf{c}_T$) by the relations: $\mathbf{a}=\mathbf{a}_T+\mathbf{b}_T$, $\mathbf{b}=\mathbf{a}_T-\mathbf{b}_T$, $\mathbf{c}=\mathbf{c}_T$, with $|\mathbf{a}|>|\mathbf{b}|$. The structure was refined, from neutron-powder-diffraction data, in the space group $Cmma$ ($Z=4$).[3] Regardless of the orthorhombic deviation, the refined atomic positions remain equivalent to the positions in the tetragonal phase and do not allow us to explain the structural transition. The various diffraction experiments have also evidenced weak extra lines in the x-ray and neutron patterns, recently interpreted as satellite reflections of an incommensurate phase.[4] It has been shown by very accurate measurements of the satellite reflection positions that the modulation wave vector is along the **b** direction. Its modulus remains constant when the temperature decreases ($\delta=-0.370$). No lock-in transition has been observed down to 2 K.

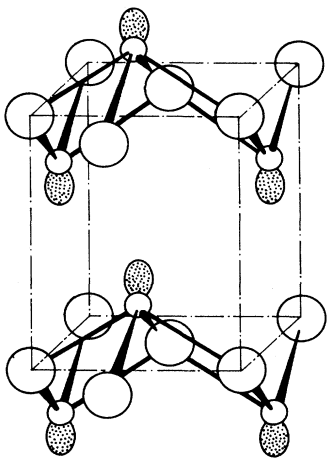

FIG. 1. Cell representation of the tetragonal α-PbO corresponding approximately to the average structure of the α' phase. Big circles represent the oxygen atoms and the small ones the lead atoms. The electron lone pairs of the Pb^{2+} ions are schematized by lobes.

In order to explain the incommensurate behavior, structural investigations of the α' phase were realized from both x-ray- and neutron-powder-diffraction studies. The use of powder samples was imposed by the difficulties to obtain single crystals adapted for diffraction techniques; the platelet crystals are too thin for neutron diffraction and too anisotropic to make satisfactory absorption corrections of x-ray-diffraction data. Moreover, it seems evident that the modulated positions of oxygen atoms cannot be refined from only x-ray data. The association of both kinds of diffraction techniques has allowed us to give a description of the modulated structure, despite the weak number of observed Bragg and satellite reflections. Furthermore, the experiments on powder samples allow us to ignore the existence of ferroelastic domains in the refinements and do not increase the number of refinement parameters.

X-ray-diffraction analysis was performed at 80 K on a very precise diffractometer (θ angular accuracy: 10^{-3} deg, Cu $K\alpha$ monochromated radiation). 38 Bragg reflections and 21 satellite reflections were indexed, corresponding, respectively, to 22 and 14 independent intensities (Table I).

Neutron-diffraction data, recorded at 2 K with the radiation $\lambda=1.909$ Å on D1A at the Laue Langevin Institute (to solve the average structure), were again analyzed, taking into account the satellite intensities. 52 Bragg reflections and 19 satellite reflections were indexed, corresponding, respectively, to 27 and 13 independent intensities (Table I).

A monoincommensurate displacive phase is interpreted as a distortion of the basic structure and the symmetry of the distortion can be adequately described by a four-dimensional symmetry space group.[5,6] The atomic positions are characterized by the modulated displacements (**u**) from the average positions (**r**). The three components of these displacements, along the three crystallographic directions, can be approximated in this case, by a harmon-

TABLE I. Observed and calculated structure factors for x-ray and neutron refinements. Lines linked together could not be separated and are one independent datum. The symbol * indicates double lines due to the orthorhombic distortion of the tetragonal structure.

h	k	l	m		F_{ox}	F_{cx}	F_{on}	F_{cn}
Principal reflections								
0	0	1	0		370	286	125	130
1	1	1	0		1382	1430	175	188
2	0	0	0	*	1220	1282	68	75
0	0	2	0		1163	1237	70	73
2	0	1	0	*			96	98
1	1	2	0		214	220	35	31
2	2	0	0		1340	1359	295	291
2	0	2	0	*	1319	1312	281	290
2	2	1	0				118	123
3	1	1	0	*	1183	1178	174	177
0	0	3	0		180	223	67	66
2	2	2	0		1016	1058	72	69
1	1	3	0		1107	1107	181	173
3	1	2	0	*	177	189	32	28
2	0	3	0	*			149	148
4	0	0	0	*	1221	1143	289	275
4	0	1	0	*			128	116
2	2	3	0		1040	1022	65	66
4	2	0	0	*	996	959	74	69
0	0	4	0		998	1020	281	272
4	0	2	0	*	915	934	66	68
4	2	1	0	*			88	90
3	1	3	0	*	1002	968	163	167
1	1	4	0		355	332	60	52
3	3	2	0		178	166		
2	0	4	0	*	888	862	66	61
4	2	2	0	*	982	975	255	259
5	1	1	0	*	949	908	158	158
4	0	3	0	*			60	69
2	2	4	0				256	257
3	3	3	0		793	865	149	154
3	1	4	0	*	292	300		
5	1	2	0	*			22	29
4	2	3	0	*			127	132
0	0	5	0				148	163
4	4	0	0				252	245

h	k	l	m	F_{ox}	F_{cx}	F_{on}	F_{cn}
Satellite reflections							
2	0	0	−1	176	133		
2	0	0	1	176	133		
2	2	0	−1	157	172	60	47
2	0	2	−1	109	125		
2	0	2	1	109	125		
2	2	0	1	218	193	62	56
3	1	1	−1	239	183	33	44
0	2	2	1			33	39
3	1	1	1	235	186	46	41
1	1	3	−1			36	26
2	2	2	1	154	148	32	26
4	0	0	−1	187	223		
4	0	0	1	187	223		
3	3	1	−1	184	211		
2	4	0	−1	236	210		
4	2	0	−1	241	217	47	39
3	1	3	−1	145	156	32	34
1	1	4	−1			39	40
4	2	0	1			47	41
2	4	2	−1	200	217		
3	1	3	1	159	146	33	46
1	1	4	1	194	196		
2	4	0	1	251	224		
1	5	1	−1			69	62
1	3	3	1			38	42
5	1	1	−1	201	233	66	61
4	2	2	1	193	209	77	75
2	2	4	−1			56	50
2	2	4	1			47	40
4	2	3	−1			46	34

ic function of the atomic location along the modulation direction:

$$\mathbf{u}_i(\mathbf{r}) = A_{0i} + S_i \sin(2\pi \mathbf{q}\cdot\mathbf{r}) + C_i \cos(2\pi \mathbf{q}\cdot\mathbf{r}), \quad i = 1, 2, 3,$$

where $\mathbf{q}$ is the modulation wave vector.

The Fourier amplitudes A_{0i}, S_i, and C_i are the refinement parameters; the symmetry of the atomic positions constrains the related modulated displacements and imposes phase relations between their components.

All the refinements of the modulated structure were performed using the REMOS program.[7]

A first refinement was realized in the supposed space group of the basic structure *Cmma*. For both x-ray and neutron data, it has given a correct description of the average structure ($R_B = 0.04$ for Bragg reflections), but pointed out a great disagreement with the description of the modulated atomic displacements ($R_S = 0.90$ for the satellite reflections). This disagreement essentially results from the presence of the mirror plane perpendicular to **a**, which forbids displacements in the **a** direction and tends to decrease the intensity of the satellites with a high-h index. A correct description of the modulation in agreement with the observation of this kind of satellites needs to suppress this symmetry operation.

Then two hypotheses subsist: (i) an orthorhombic hypothesis, with the noncentrosymmetric average space group *C2mb*; or (ii) a monoclinic hypothesis, with the centrosymmetric average space group *P2/b* (unique axis

TABLE II. Positional parameters ($\times 10^4$) and B_{is} thermal parameters (Å^2) refined respectively at 2 and 80 K from neutron- and x-ray-diffraction data.

	r	A_0	S	C	B_{is}
		Neutron-diffraction data			
Pbx	2500	0[a]	0	234(12)	
y	2500	0	242(16)	0	0.20
z	−2367	−8(6)	0	−186(24)	
Ox	0	79(35)	0	133(28)	
y	0	0	118(46)	0	0.55
z	0	0	77(40)	0	
		x-ray-diffraction data			
Pbx	2500	0[a]	0	156(9)	
y	2500	0	153(16)	0	0.25
z	−2367	3(6)	0	−147(26)	

[a]Not refined to fix the origin.

c). The refinements were performed in both hypotheses. In the second case, the modulated displacements of Pb atoms, obtained independently from x-ray and neutron data, were not similar. So the second hypothesis was rejected; only the orthorhombic model will be detailed.

The following symmetry operations of the super space group $P(C2mb)$:$(\bar{1}\bar{1}1)$ (De Wolff's notation)[8] generates all the atoms of the cell:

$$\{\sigma_z/(\tfrac{1}{2},0,0),0\},$$

$$\{E/(\tfrac{1}{2},\tfrac{1}{2},0),0\}.$$

Pb and O atoms are, respectively, located in the σ_y and C_{2x} symmetry sites of the basic structure. The special position of the atoms involves the particular form of their modulation, and reduces the number of the parameters. Nine positional parameters were fitted to determine the structure; their values are given in Table II. The parameters of oxygen modulation were only determined from neutron data. We observed a good agreement between modulation parameters of Pb atoms obtained from the two kinds of data. The amplitude of the modulation increases at 2 K, but the form and the phase of the modulation functions remain equivalent. The reliability factors of x-ray ($R_B^x=0.035$, $R_s^x=0.137$) and neutron refinements ($R_B^N=0.040$, $R_s^N=0.143$) show good coherence between both sets of data, given that R^x factors were obtained, fixing the values of the oxygen modulation parameters fitted from neutron data.

The validity of the structural refinements is confirmed by the calculation of the interatomic distances (Table III). They are similar to the observed ones in the orthorhombic modification β-PbO which is stable above 764 K (space group $Pbcn$).[9] In the α phase, the Pb^{2+} ion is at the apex of a regular square pyramid PbO_4. Both symmetry and stacking considerations show that the electron lone pair of the Pb^{2+} ion lies parallel to the fourfold axis of the pyramid.[10] In the α' phase, the four distances are no more equal; as a consequence, the electron lone pair tilts in the opposite direction of the shorter distances.[11] The variation of the modulation phase, or the consideration of all the lone pairs along the b direction, defines a

TABLE III. Comparison of interatomic distances (Å) calculated in the α', α, and β phases. In the α and β phases, the distances are calculated at room temperature, whereas they are calculated at 2 K in the α' phase.

	α' phase (d_{min}–d_{max})	α phase	β phase
Pb-O in	2.18–2.39		
a layer	2.28–2.41	2.30	2.21
	2.27–2.34		2.22
	2.18–2.35		2.49
O-O in	2.80–2.80		2.97
a layer	2.73–2.86	2.80	3.00
			3.15
Pb-Pb in	3.56–3.78		
a layer	3.82–4.02	3.69	3.47
	3.46–3.76		
Pb-Pb between	3.74–3.97	3.85	3.97
layers	3.84–3.84		

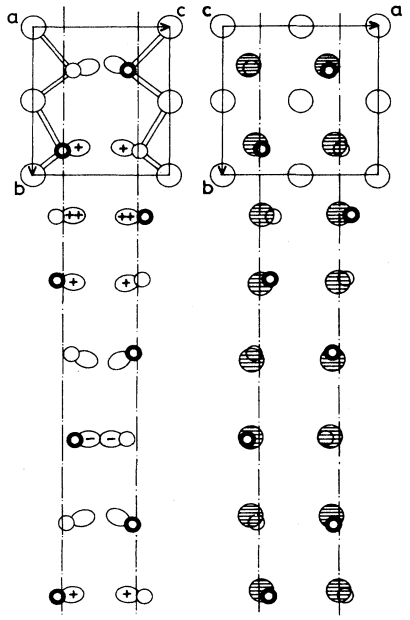

FIG. 2. Description of the modulated Pb and electron lone pair positions, in four consecutive cells, in (a,b) and (b,c) planes. Oxygen atoms are represented in their average positions in the origin cell by big open circles. Electron lone pairs are represented by the dashed circles in the (a,b) plane and by the lobes in the (b,c) plane. The signs in the lobes determine approximately their tilt in the a direction.

precession motion modulated along the b direction (Fig. 2). This tilt of the electron lone pairs from the normal to the layers of the structure is also observed in the β structure. Thus, the incommensurate behavior seems to point out a competition between α and β phases.

Another striking feature is the loss of the inversion center of the structure, which is a consequence of the suppression of the mirror plane perpendicular to **a**. As it can be seen in Table I, it does not significantly modify the average atomic positions and is essentially due to the modulated displacements of Pb and O atoms. As a matter of fact, the transition at 208 K would be principally connected with the realization of an antiferroelectric state, modulated by the displacements of the Pb and O atoms from their average positions.[12] The small shift of the O average position along the **a** direction (given in Table II), certainly involves the existence of a spontaneous polarization, but too weak to be experimentally observed. Therefore, it seems very difficult to confirm the noncentrosymmetric hypothesis by physical measurements (polarization and dielectric-constant experiments).[13]

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