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Incommensurate phase in lead monoxide α-PbO below 208 K

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We report a low-temperature x-ray investigation of lead monoxide α-PbO. Our results reveal for the first time the existence of a modulation below $T_I = 208$ K which breaks the tetragonal symmetry and leads to an average orthorhombic structure. The direction of the modulation vector was determined thanks to very precise powder-diffraction measurements, despite the very low orthorhombic distortion. This incommensurate ferroelastic phase possesses a modulation vector $\mathbf{k} = \delta \mathbf{b}^*$ which remains constant ($\delta = 0.370$) from T_I down to 5 K. The absence of a lock-in transition as well as an abnormally low critical exponent $\beta = 0.24$ shows the great similarity of this incommensurate phase with that of $BaMnF_4$.

I. INTRODUCTION

Lead monoxide PbO presents an unusual sequence of phases: the high-temperature phase (or β phase) possesses a lower symmetry than the low-temperature phase (or α phase). Above 765 K the thermodynamically stable β phase crystallizes in the orthorhombic system with the space group *Pbma* ($Z = 4$).[1] Below 765 K the stable phase is the tetragonal α phase with the space group $P4/nmm$ ($Z = 2$).[2] However, the $\alpha \rightarrow \beta$ polymorphic transformation observed at 765 K is not reversible and the β phase is metastable below 765 K down to 5 K. In this range of metastability the $\beta \rightarrow \alpha$ transformation can be induced by a small shear stress or by water.[3,4] This result agrees with the fact that the α and β structures are characterized by similar packing of lead atoms (distorted fcc); they differ mainly by the positions of the oxygen atoms. Another important feature is the following: both structures are characterized by layers (orthogonal to the **c** axis) and the interlayer spaces are occupied by the electronic lone pairs of the Pb^{2+} ions (Fig. 1).[5]

We have recently seen evidence for a second-order ferroelastic transition for the α phase.[6] It transforms at about 200 K into an orthorhombic phase (called the α' phase) with the cell vectors $\mathbf{a} = \mathbf{a}_T + \mathbf{b}_T$, $\mathbf{b} = \mathbf{a}_T - \mathbf{b}_T$, $\mathbf{c} = \mathbf{c}_T$, where $\mathbf{a}_T$, $\mathbf{b}_T$, and $\mathbf{c}_T$ are the cell vectors of the tetragonal phase. The temperature dependence of their modulus (with $|a| > |b|$) is shown in Fig. 2. The associate spontaneous strain is very small: e_{12}^s is equal to 0.70×10^{-4} and 4.37×10^{-4}, respectively, at 180 and 5 K. Structural refinements from neutron-diffraction data on powder samples are in favor of the space group *Cmma* with $Z = 4$. The $\alpha \rightarrow \alpha'$ transition is characterized by very small atomic displacements.[2] So this new orthorhombic α' phase is very similar to the tetragonal α phase and quite different from the well-known orthorhombic β phase.

Furthermore, weak extra lines were disclosed on the diffraction diagram at 5 K and could not be indexed with a simple superstructure. At room temperature these weak lines are absent; however, important diffuse scattering intensity is seen in the background (see Fig. 3). As

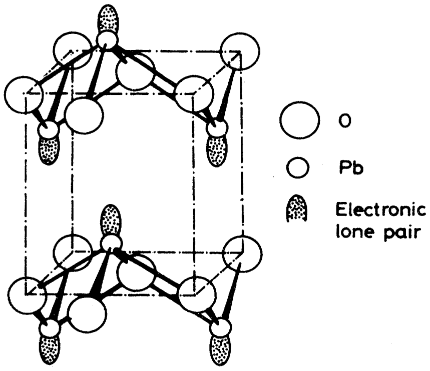

FIG. 1. Crystalline structure of the tetragonal α-PbO (electronic lone pairs are represented by means of dashed lobes).

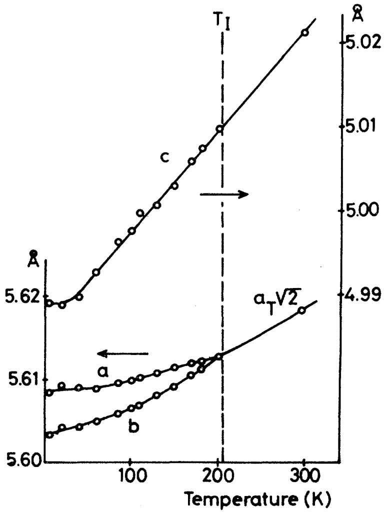

FIG. 2. Cell parameters of α-PbO vs temperature (orthorhombic *Cmma* cell).

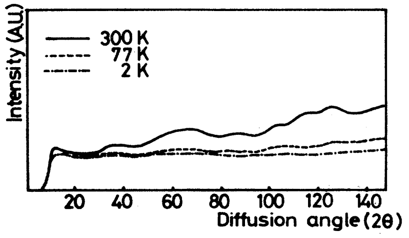

FIG. 3. Diffuse background of neutron diffraction powder above (300 K) and below (77 and 2 K) the ferroelastic transition temperature.

the temperature is lowered, the disappearance of the diffuse intensity seems correlated with the appearance of the ferroelastic phase.

In this paper we present an x-ray study on both single crystals and powder samples which shows that the α' phase is incommensurate. The temperature dependence of the misfit parameter δ and of the intensity of the satellite reflections were also investigated.

II. EXPERIMENTAL

Single crystals were synthesized by a hydrothermal process at 645 K.[7] Thin sheetlike crystals, normal to the c axis, were selected (typical size: $0.5\times0.5\times0.03$ mm^3). Well-crystallized powder samples were obtained by thermal decomposition of tetragonal lead dioxide β-PbO$_2$ (Merck for analysis) in air at 845 K for 2 h.[8]

X-ray experiments on single crystals were performed using a Buerger precession camera (radiation Mo $K\alpha$; 1.2 kW). Cooling was achieved using an Enraf-Nonius low-temperature device. The thermal stability was ±2 K and the absolute temperature was estimated to be within ±10 K. Experiments were performed at room temperature and at 120 K. At 120 K, typical exposure times for the main Bragg reflections $hk0$ and $hk1$ were 5 h. For a full rotation with a precession angle of 25°, the weak additional reflections are detected after 20 h of exposure, but time as long as 120 h is necessary for a good observation.

More accurate observations were performed on powder samples using a very precise prototype x-ray diffractometer whose angular accuracy is 10^{-3} Θ.[9] The Cu $K\alpha$ monochromatic radiation (graphite-bent crystal) of a Rigaku rotating anode (18 kW) was used. The sample was cooled in a He cryostat; the thermal stability was 0.1 K and the absolute temperature was estimated to within 1 K.

III. RESULTS

A. X-ray precession pattern

At room temperature, the precession photographs of the ($hk0$) and ($hk1$) planes are consistent with the space group of the tetragonal phase $P4/nmm$: only the $hk0$ reflections with $h+k=2n$ are observed (Fig. 4).

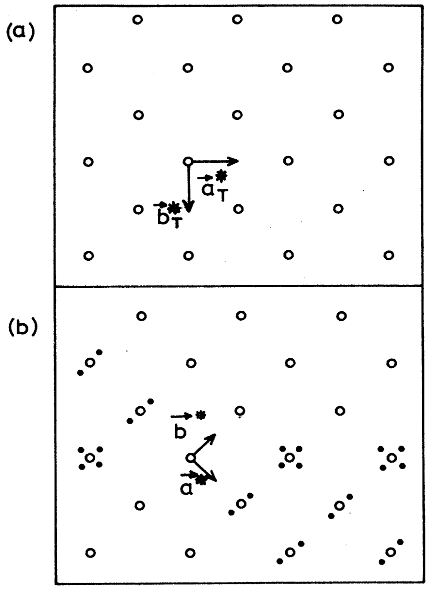

FIG. 4. Schematic representation of the hkl reciprocal plane as observed by precession photographs at (a) room temperature and (b) 120 K: Basic spots are represented by open circles and satellites by solid circles.

At 120 K, the orthorhombic distortion is too small to be seen by this method. In addition to the basic orthorhombic reflections, spots of very small intensity appear in the [100] and [010] directions of the orthorhombic reciprocal lattice. They are located at $[h\pm\delta,k,0]$ and $[h,k\pm\delta',0]$ with $\delta=\delta'=0.37\pm0.01$. The location of these extra reflections is not associated with a simple multiplication of the unit cell and reveals the existence of an incommensurate modulation.

Moreover, the full-precession photograph can be indexed with a monoincommensurate modulation $1q$. Indeed, the numerical coincidence for δ and δ' when the orthorhombic symmetry does not impose it, as well as the absence of satellite spots at positions $\delta\mathbf{a}^*\pm\delta'\mathbf{b}^*$, is in favor of a single modulation along one basic orthorhombic reciprocal vector ($\mathbf{a}^*$ or $\mathbf{b}^*$). Then the extra satellite spots can be explained by the simultaneous presence of the two ferroelastic orientations $1q$ in the crystal. The sensitivity of the relative intensity to thermal cycling, for the two sets of satellites, confirms the $1q$ hypothesis.

Finally the existence of a $1q$ modulation breaks the tetragonal symmetry and leads to an average orthorhombic symmetry and therefore connects the appearance of the ferroelasticity and of the incommensurability.

B. X-ray powder diffractometry

Full diffraction diagrams were recorded in the temperature range 295–5 K. At room temperature, the diagrams have been indexed with the tetragonal cell. Upon cooling, satellites appear at $T_I=208\pm1$ K. Below T_I, their intensity increases down to 5 K. At this tempera-

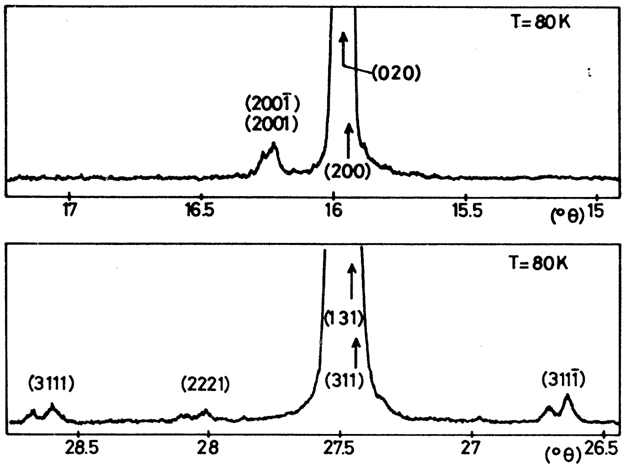

FIG. 5. Part of x-ray powder-diffraction diagram showing Bragg and satellite peaks (Cu $K\alpha_1+K\alpha_2$ radiation, graphite monochromator).

ture, the diagram displays about 30 satellite peaks with a typical intensity of a few per cent of the Bragg peaks intensity. In the whole temperature range T_1-5 K the full diagrams have been indexed using the three basic vectors of the orthorhombic cell and a fourth vector **k** (Fig. 5). Each peak corresponds to a reciprocal vector G with four Miller indices $hklm$: $G=h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*+m\mathbf{k}$ with $m=\pm1$ (no higher-order satellites were detected). The vector **k** can be *a priori* equal to $\delta\mathbf{a}^*$ or $\delta\mathbf{b}^*$.

But contrary to the precession results, the measurements on powder samples show clearly that the direction of the modulation is parallel to the $\mathbf{b}^*$ axis: $\mathbf{k}=\delta\mathbf{b}^*$. Indeed, taking the modulation vector **k** along $\mathbf{a}^*$ gives a systematic mismatch for the δ value whether calculated with $hkl\bar{1}$ satellites or $hkl1$ satellites. For example, at 5 K we obtain $\delta_-=0.384(2)$ for the $131\bar{1}$ satellite and $\delta_+=0.364(2)$ for the 1311 satellite. Taking k along $\mathbf{b}^*$, the mismatch disappears, $\delta_+=0.371(2)$, and $\delta_-=0.369(2)$, respectively (Fig. 6). Using 2001, $311\bar{1}$, and 3111 satellites the thermal evolution of the misfit parameter δ was recorded. An important point to notice is the constant value of δ in the whole temperature range T_I-5 K: $\delta=0.370\pm0.003$ (let us notice that the closest rational ratio to this value is $7/19=0.3684\ldots$). The choice of the modulation direction was only possible thanks to the very precise accuracy of the diffractometry; indeed, the difference between the theoretical angular positions of the satellites for $\mathbf{k}=\delta\mathbf{a}^*$ and $\mathbf{k}=\delta\mathbf{b}^*$ is less than $20.10^{-3°}\,\theta$.

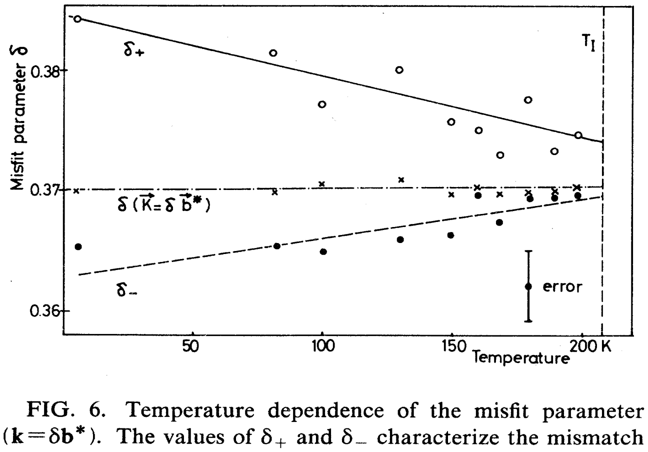

FIG. 6. Temperature dependence of the misfit parameter $(\mathbf{k}=\delta\mathbf{b}^*)$. The values of δ_+ and δ_- characterize the mismatch when the modulation vector is chosen along $\mathbf{a}^*$.

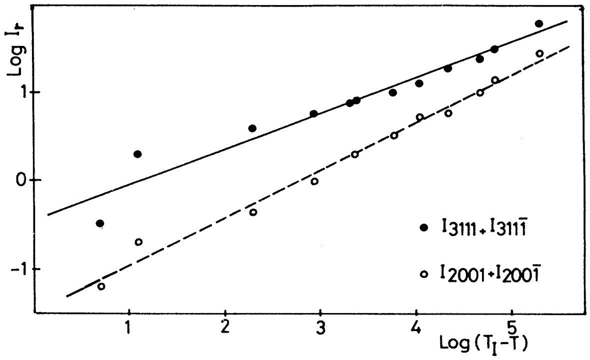

FIG. 7. Integrated intensity as a function of T-T_I in the log-log representation.

The integrated intensity of the satellites can be fitted with the classical law $I_r\sim(T_I-T)^{2\beta}$ with $\beta=0.24\pm0.03$ (Fig. 7). No hysteresis on heating or cooling was detected for both quantities δ and I_r.

IV. DISCUSSION

In summary, lead monoxide α-PbO possesses, below 208 K, an incommensurate ferroelastic phase which is characterized by the following. (i) The existence, at room temperature, of a strong precursor effect in the form of diffuse scattering in the neutron-diffraction diagrams of the tetragonal phase. (ii) A normal-incommensurate second-order phase transition at $T_I=208$ K. (iii) The absence of a lock-in transition down to 2 K. (iv) A modulation vector along the $[110]_T$ reciprocal direction which breaks the tetragonal symmetry and leads to an average orthorhombic symmetry with the space group *Cmma*. (v) A misfit parameter $\delta=0.370$ which remains constant from 208 K down to 2 K. (vi) An abnormally low (for 3*d* systems) critical exponent $\beta=0.24$.

The absence of thermal evolution for the misfit parameter δ as well as the absence of a lock-in transition have already been reported in the ferroelastic incommensurate transitions of $BaMnF_4$, $ThBr_4$, $ThCl_4$, and biphenyl.[10] The challenge in this type of material is to ascertain the physical origin of these phenomena. On the one hand, the Janssen-Tjon model has recently been shown to display solutions which can be incommensurate stable phases at 0 K, leading to a possible intrinsic origin; an application of such a model for biphenyl has been discussed and is suggested for $ThBr_4$.[11] On the other hand, such phenomena, in the case of $BaMnF_4$, could be explained by the pinning of the modulation on defects.[12] This compound possesses, as α-PbO, an abnormally low value for the β exponent (0.23) and indeed it is known that such low values are more likely due to defects than to intrinsic fluctuations (for instance, the vicinity of a tricritical point). A study of several samples of PbO with different defects content could test the possibility of a "defect" origin for the absence of a lock-in phase and for the constancy of the δ value.

The structural nature of the incommensurability in α-PbO cannot be deduced from the neutron-diffraction refinements; the average orthorhombic structure does not show any significant atomic displacements from the tetragonal structure. A structural analysis, actually in progress, on single crystals using the full diffraction diagram (Bragg and satellites) should allow us to test the intrinsic origin by means of the Janssen-Tjon model.

Lastly, it can be mentioned that a phenomenological analysis of the structural transition $P4/nmm \rightarrow Cmma$ reveals that it is induced by an irreducible representation of dimension 1, which obviously satisfies the Lifshitz criterion. In this framework, the existence of an incommensurate phase requires the building of a Lifshitz-like invariant in a similar way as for quartz or $NaNO_2$.

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