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Reference

DOI: 10.1080/00150199008221544

Available at:

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ELECTRON DIFFRACTION STUDY OF THE Pb2CoWO6 PHASES

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Abstract A study by electron microscopy has been started in order to clarify the crystallographic features of Pb2CoWO6. Diffraction patterns have been obtained on monodomains of the incommensurate phase (II). The average monoclinic symmetry has been confirmed and the modulated wave vector determined. For the phase III a new orthorhombic cell is proposed.

INTRODUCTION

Several phase transitions have been reported for the complex perovskite Pb2CoWO6. An incommensurate phase has even been discovered.1 Recently single crystals were synthesized2 and a number of experiments was undertaken. The following phase sequence had been established:3

\[
\text{cubic (I) } \xrightarrow{<T_1> 298 \text{ K}} \text{ monoclinic (II) } \xrightarrow{<T_2> 235 \text{ K}} \text{ orthorhombic (III)}
\]

The two phase transitions are strongly first order. Pb2CoWO6 is one of the singular compounds for which the incommensurate phase sets on at a strongly first order transition.

However the large number of ferroelastic domain states which characterizes the low temperature phases is a serious obstacle for structural studies by X-ray and neutron diffraction. Moreover, the interpretations are complicated because of phase II remaining to some extent metastably captured in phase III. So far only phase I is well known. In this paper we report the first electron diffraction investigation of the structural phases between 300 and 100K.

EXPERIMENTAL

The single crystals were grown from a PbO flux in sealed platinum crucibles.2 The studied platelets were cut perpendicular to the cubic directions [100] and [110], polished mechanically and thinned by ion milling with 5 keV Ar+ ions under 20°.
incidence. The thin foils were coated on one side with an amorphous carbon film of about 20 nm thickness in order to increase the electrical conductivity.

The investigations were carried out with a Philips EM 430ST and a Philips EM 300 electron microscope. A side-entry double-tilt specimen cooling holder (Gatan 636) was used. Liquid N\textsubscript{2} or dry ice (CO\textsubscript{2}) was used as coolant and the temperature was controlled by a small heater in the range [95, 300K] within ±5K. The true specimen temperature at the observed area is not accurately known for the following reasons: local heating of the sample by the electron beam (a few degrees in the thin parts), radiation losses toward the objective lens (289K) and the anticontamination trap (83K), temperature measurement on the cooling rod of the specimen holder.

RESULTS

Before cooling, when the reading of the specimen holder temperature was about 300K, the observed diffraction patterns corresponded to the cubic phase in agreement with the structure determined by neutron diffraction (a=0.801 nm).\textsuperscript{3} For some samples phase II was already observable at that temperature, but the presence of the electron beam, even of strongly reduced intensity, was sufficient to bring on the transition to the cubic phase. This effect shows that these samples were in a state very close below their transition temperature (T\textsubscript{f}). Most of the samples undergo this structural phase transition at about 280K and some even as low as 260K.

In the low temperature phases, the domain structure can easily be observed. However the domain boundaries can easily move under the electron beam in particular in the phase III. This effect is due to the charging up and the heating of the sample. It can be reduced by using a low beam intensity and by coating the sample with a thin carbon film.

a) Phase II

The transition is detected by the arrival on the image of many domains of different crystallographic orientation (Fig.1a) and on the diffraction pattern of well defined reflections of very weak intensity localized close to some of the forbidden cubic reflections. Figure 1b is a diffraction pattern along a [100]\textsubscript{c} zone axis. Four satellite reflections are centered around the (0kl)\textsubscript{c} cubic reflection with k and l odd. Tilting the sample by 4° around the [011]\textsubscript{c} and [0-11]\textsubscript{c} directions shows that the extra spots are not lying in the (100) plane, but are here and there of this plane. In addition, when many domains are present, up to eight spots can be observed (four below and four above this plane). The number and the position of the satellite reflections are in accordance with the X-ray observations.\textsuperscript{1}
FIGURE 1 Observations of phase II along the [100] zone axis. a) bright field image. b) diffraction pattern. Up to four satellite reflections can be observed around the forbidden (0kl) cubic reflections with k and l odd.

FIGURE 2 Selected area diffraction pattern of phase II in a monodomain. Two satellite reflections (one above and one below the plane) are observed (T=245K, $\gamma=0.15$).

FIGURE 3 Reciprocal lattice of phase II. The reflections are indexed in the cubic and the pseudo-orthorhombic cell (dotted lines): $a^*=a^*\quad b^*=b^*+c^*$ (along the 2-fold axis), $c^*=-b^*+c^*$, $\beta^*=90^\circ\quad$ and $q=(1-\alpha)a^*+\gamma c^*$ ($\alpha=1/12,\gamma=1/6$). ○ satellite and ● main reflections.
The advantage of transmission electron microscopy is the possibility to observe the domain structure and to obtain diffraction patterns from areas of 1μm² or less, allowing to distinguish the contribution of each domain to the diffraction pattern. In this manner several diffraction patterns of monodomain regions were obtained and they show unambiguously that only two satellite reflections, one above and one below, originate from the same domain (Fig. 2). Observations along different zone axes of monodomain regions allow to construct the reciprocal lattice as shown in Fig. 3.

The satellite position is only consistent with a monoclinic symmetry having the 2-fold axis along one of the <110> direction. This result confirms the conclusions deduced from the study carried out by light microscopy. Thus the incommensurate phase lattice must be described using an average monoclinic lattice and a diffraction vector given by:

\[ G = h a_m^* + k b_m^* + l c_m^* + mq \]

where \( a_m^* = a_c^* \), \( b_m^* = b_c^* + c_c^* \), \( c_m^* = a_c^* - b_c^* + c_c^* \), \( \beta_m^* \approx 54.7° \) and \( q = (1-\alpha-\gamma)a_m^* + \gamma c_m^* \), the incommensurate wave vector. This symmetry belongs to the four dimensional Bravais class \( \text{P}_4^{2/1}/m \) (\( \text{P}_4^{2/1}/m \)) defined by de Wolff. The relationship between the three phases is better seen by using a non-standard description in a pseudo-orthorhombic I-centered cell (\( h+k+1=2n \)): \( a^* = a_c^* \), \( b^* = b_c^* + c_c^* \), \( c^* = b_c^* - c_c^* \), \( \beta^* \approx 90° \), and \( q = (1-\alpha)a^* + \gamma c^* \). A small variation of the position of the satellites with temperature has been observed (\( \gamma \approx 0.14 \) at 290K and \( \gamma \approx 0.17 \) at 205K, measured on the same area).

b) Phase III

The appearance of phase III has been observed at various temperatures. This could possibly be due to some dispersion in the transition temperature of the different samples or to the presence of ferroelastically induced strains built up during cooling. In several samples both phases II and III were observed simultaneously in a large temperature range. In some samples phase II was still present at 100K in some areas.

The transition to phase III can be followed in diffraction mode and on the TEM image. On the diffraction pattern, the satellite spots disappear and new reflections appear at some of the forbidden cubic positions and at some of the \( \{ h k l \} \) positions. On the [100] oriented sample, domains of thin lamellar shape (Fig.4) are characteristic of phase III. Most often the lamellae have a width of about 100 nm and their walls are oriented close to \( \{ 110 \} \) planes. Some smaller domains delimited by tilted boundaries are also observed. As a consequence, first, the selected area diffraction patterns are always obtained on more than one domain. Second, even in microdiffraction some overlap between adjacent domains may occur along zone axes other than \( [100] \). Figure 5 is a microdiffraction pattern.
FIGURE 4 Lamellar domain pattern of phase III observed along the [100]_c zone axis in bright field (a). The walls are very close to {110}_c planes. b) the diffraction pattern corresponding to (a) (two domain states of [021]_o zone axis rotated by 90° with respect to one another).

FIGURE 5 Microdiffraction pattern along [100]_c on a single domain and corresponding to the [001]_o zone axis.

FIGURE 6 Proposed reciprocal lattice for phase III: a*_c = a_o, b*_c = b_o + c_o, c*_c = (−b_o + c_o)/2. Primitive orthorhombic cell: a_o = a_c, b_o = (b_c + c_c)/2 and c_o = −b_c + c_c.
obtained along [100] on a single domain. Compared with the diagram of the cubic phase, it exhibits three new spots in the [011]$_c$ direction and only one new spot along [0-11]$_c$.

Additional microdiffractions have been obtained along the [210]$_c$ and [110]$_c$ zone axis leading to the reciprocal lattice: $a_0^* = a_c^*$, $b_0^* = b_c^* + c_c^*$ and $c_0^* = (-b_c^* + c_c^*)/2$, $\alpha = \beta = \gamma = 90^\circ$ (Fig.6) within the experimental accuracy and without extinction conditions. Using this lattice, all the selected area diffraction patterns can be indexed by taking the various domain orientations into account.

Considering the information on the point symmetry obtained by polarized light microscopy$^3$, the cell of phase III has to be primitive orthorhombic. This conclusion does not agree with the theoretical prediction$^5$ leading to an A-centered orthorhombic cell with $a_0^* = a_c^*$, $b_0^* = (b_c^* + c_c^*)/2$, $c_0^* = (-b_c^* + c_c^*)/2$.

An electron diffraction study carried out under convergent beam illumination should in principle allow to determine the point and space groups of the low temperature phases. Preliminary experiments have been undertaken, however, the small size of the domains, the mechanical drift of the sample holder at low temperatures, and the small size of the reciprocal lattice cell renders the use of this technique quite difficult. More detailed studies will therefore be required.

ACKNOWLEDGEMENTS

The authors are grateful to D. Laub, B. Garoni and R. Cros for technical assistance, and to the Swiss National Science Foundation for support.

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