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### Reference

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## TENTATIVE MODEL FOR THE INCOMMENSURATE AND FERROELECTRIC PHASES IN $\text{Pb}_2\text{CoWO}_6$

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Abstract The sequence of cubic, incommensurate and ferroelectric phases found in  $\text{Pb}_2\text{CoWO}_6$  is described in the framework of the Landau theory. The model, which involves two different order-parameters, accounts for the first-order character of the transitions, the reentrant behaviour of the incommensurate phase and its coexistence with the ferroelectric phase.

### INTRODUCTION

In order to clarify the controversial data previously reported in  $\text{Pb}_2\text{CoWO}_6$  (PCW), large single crystals of this composition were synthesized, and a comprehensive set of experiments were recently undertaken, which include polarized light microscopy, electric poling, birefringence measurements, and neutron scattering. These experiments confirmed the sequence of phase transitions which is schematized in Fig. 1, namely: 1) a strongly first-order transition at  $T_I = 298$  K from the high-temperature paraelectric phase, with the elpasolite-like structure (space-group  $O_h$ ), to an incommensurate (INC) phase (II). The temperature dependence of the satellite peak intensities which appear at  $T_I$ , show a reentrant behaviour, i.e. a sharp increase at 285 K and a saturation around 240 K, followed by a continuous decrease with decreasing temperature. The satellites survive the transition to phase III and can be observed down to about 100 K.

2) At 235 K another first-order transition to a ferroelectric phase (III) takes place, characterized by the onset of a superstructure corresponding to a different wave-vector. In this phase one can observe a non-standard dependence on temperature, for the spontaneous polarization and hysteresis loops.

The aim of this paper is to present a tentative model which accounts for the preceding experimental results. A more detailed model will be published elsewhere.

## SYMMETRY ANALYSIS

According to the X-ray<sup>3</sup> and elastic and inelastic neutron diffraction data obtained for PCW<sup>5,7</sup>, at  $T_I=298$  K the satellite peaks appear on the S-line of the fcc Brillouin-zone, which correspond to the wave-vector  $k_1=(k_x, k_x, 2\pi/a)$  (see for example the tables by Zak *et al.*). By reducing the temperature the peaks show characteristic displacements revealing that the wave-vector remains on the S-line with a positioning parameter  $\delta$  varying from  $0.171\text{\AA}^{-1}$  at 285 K to  $0.202\text{\AA}^{-1}$  at 220 K. As the symmetry group of  $k_1$  is  $C_{2v}^{xy}$ , the star of  $k_1$  has twelve arms, and consequently the order-parameter associated with the paraelectric I-INC II transition possesses twelve components.

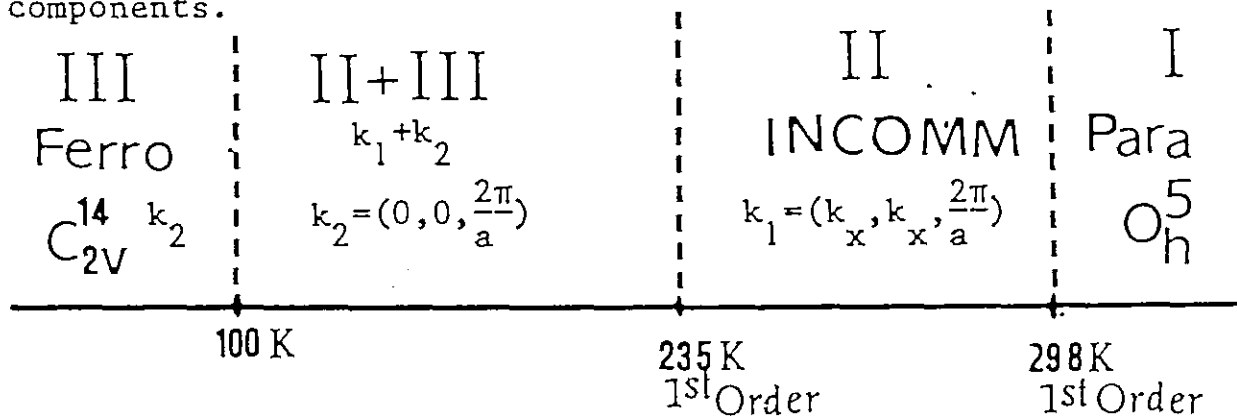


FIGURE 1 Sequence of transitions observed in  $\text{Pb}_2\text{CoWO}_6$

At  $T_I=235$  K the new satellite peaks, which reveal the onset of phase<sup>III</sup>, correspond to the wave-vector  $k_2=(0,0,2\pi/a)$  (the  $k_{10}$  point of the fcc Brillouin-zone, i.e.  $k_{10}$  in the Kovalev notation) and are associated with a doubling of the cell parameters in the x and y directions. Their position remains fixed as the temperature is lowered, by contrast to the satellites related to  $k_1$  with which they coexist down to about 100 K. The star of  $k_2$  has three arms, as the symmetry group of  $k_2$  is  $D_{4h}$ . A symmetry analysis of the irreducible representations (IR's) constructed from the ten small representations of  $k_2$  shows that only the six-dimensional IR labelled  $\tau_{10}$  in Kovalev's tables may lead to ferroelectric low-symmetry phases. Actually the polar character of phase III is attested by the whole set of dielectric measurements<sup>5,6</sup>. More precisely, the domain pattern below 235 K is only compatible with an orthorhombic point-group  $C_{2v}$ , having an axis parallel to  $[110]$ . These data designate unambiguously the space-group  $C_{2v}^{14}(xy)$ , with a four-fold multiplication of the cubic primitive cell, as the symmetry of phase III. The stabilization of this group, following our analysis, requires to take into account sixth-degree invariants of the six-dimensional order-parameter in the thermodynamic potential associated with  $\tau_{10}(k_2)$ . The corresponding equilibrium conditions for this phase are:

$$\eta_1 = \eta_2 \neq 0, \quad \eta_3 = \eta_6 \neq 0, \quad \eta_4 = \eta_5 = 0 \quad (1)$$

From the preceding symmetry considerations, we are now able to propose a phenomenological model for the sequence of phases in PCW.

TWO ORDER-PARAMETER MODEL FOR THE PHASE DIAGRAM OF  $Pb_2CoWO_6$

In order to work out the qualitative features of the phase diagram of PCW, one can restrict to consider the effective thermodynamic potential associated with the sequence of phases in this compound. It can be written here as:

$$F = \frac{\alpha}{2} \rho^2 + \frac{\beta}{4} \rho^4 + \frac{a}{2} (\eta_1^2 + \eta_3^2) + \frac{b}{4} (\eta_1^4 + \eta_3^4) + \frac{b_1}{2} \eta_1^2 \eta_3^2 + \frac{c}{6} (\eta_1^6 + \eta_3^6) + \delta \rho^2 (\eta_1^2 + \eta_3^2) \quad (2)$$

where  $\rho$  is the order-parameter modulus corresponding to the INC phase, and  $(\eta_1, \eta_3)$  are the non-zero components of the six-dimensional order-parameter associated with the ferroelectric phase. The  $\delta$  term represents the lower degree coupling between the two order-parameters. The minimization of  $F$  with respect to  $\rho$  and  $(\eta_1, \eta_3)$  leads for suitable values of the coefficients in  $F$  (in particular for  $\delta > -2\sqrt{\beta} b_1$ ) to the phase diagram represented in Fig.2. Thus, one can see that for the thermodynamic path indicated in dashed line in Fig.2, one goes from the paraelectric phase ( $\rho=0, \eta_i=0$ ) to the INC phase ( $\rho \neq 0, \eta_i=0$ ) across a line of first-order transitions, then to a region of coexistence of the two phases ( $\rho \neq 0, \eta_i \neq 0$ ) across another line of first-order transitions. The reentrant behaviour observed for the INC phase can be obtained within this picture by assuming that the thermodynamic path corresponds to decreasing values of  $\rho$  when approaching the INC-ferroelectric transition line and within the coexistence region. The continuous vanishing of the INC satellite peaks observed in the vicinity of 100 K may result from the fact that the limit stability region between phases II and III (dotted line in Fig.2) has been reached.

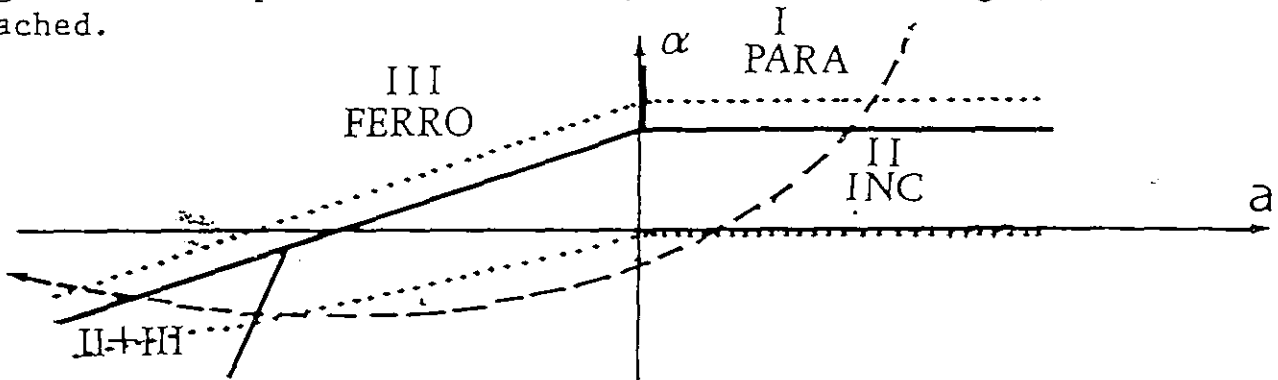


FIGURE 2 Phase diagram corresponding to potential(2) in the  $(\alpha, a)$  plane. Full and dotted lines represent first-order and stability lines respectively. The thermodynamic path suggested for PCW is shown by a dashed line.

DIELECTRIC PROPERTIES IN THE FERROELECTRIC PHASE

The dielectric behaviour of PCW below 235 K is obtained, following the standard procedure by considering the coupling between the six-component order-parameter and the spontaneous polarization. In this respect one finds that the lower degree coupling term can be written:

$$\delta_1^P x (\eta_2 \eta_3 \eta_6 - \eta_1 \eta_4 \eta_5) + \delta_2^P y (\eta_2 \eta_4 \eta_5 - \eta_1 \eta_3 \eta_6) \quad (3)$$

which denotes an unusual faintness index  $l_1 n=3$ . The standard minimization procedure provides the following expressions for the spontaneous polarization components below  $T_{II}$ :

$$P_x = -\chi_0 \delta_1 \eta_1 \eta_3^2, P_y = \chi_0 \delta_2 \eta_1 \eta_3^2, P_z = 0 \quad (4)$$

and a dielectric susceptibility of the form:

$$\chi = \chi_0 \left( 1 + \frac{\chi_0 \delta \eta^2}{\beta - \alpha/\eta^2 - \chi_0 \delta \eta^2} \right) \quad (5)$$

However while the experimental curves obtained for the polarization and dielectric permittivity below 135 K reflect the theoretical temperature dependences given by (4) and (5), between 135 K and 235 K the experimental results are strongly influenced by the INC regime. In particular one has to take into account the domain effects introduced by the coexistence of the INC and ferroelectric phases.

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