Phase transitions in boracite $Co_3B_7O_{13}I$

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An intermediate phase (α) has been observed in boracite $Co_3B_7O_{13}I$ between the paraelectric (T_d^5) and the ferroelectric (C_{2v}^5) phases. Coexistence of two phases is observed in the region of the transition $\alpha \leftrightarrow C_{2v}^5$ and is a consequence of the internal stresses produced in the course of twinning of the crystal.

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It is regarded as reliably established that spontaneous polarization in boracite is the result of the phase transition $T_d^5 \rightarrow C_{2v}^5$.[1,2] Three singularities distinguish this transition: first C_{2v}^5 is not the highest polar subgroup of the paraelectric phase; second, the dielectric constant has a behavior unusual for classical ferroelectrics; third, anisotropy of the physical properties is observed far above the transition temperature.[3] Whereas the first two singularities have found a theoretical explanation[4] the anisotropy of the crystal in the cubic phase still remains unexplained.[5]

The ferroelectric transition in $Co_3B_7O_{13}I$ (CoIB) was first reported in[6]. More detailed measurements were performed by Smutny *et al.*[7,8] We have carried out an x-ray diffraction investigation of the character of this transition. The measurements were performed on powder obtained by crushing single crystals, and also a needle-shaped single crystal ($0.1 \times 0.1 \times 0.7$ mm) in the form of an {110} growth pyramid. The [110] direction coincided with the needle axis.

Figure 1 has shown the temperature dependence of the shape of the reflection 12 4 0 (Co $K\alpha$, powder). The increase of the half-width in the low-temperature phase (curve 1) compared with the high-temperature phase (curve 5) is due to splitting caused by lowering the symmetry of the unit cell. A characteristic feature of the transition is the presence of a two-phase region in a broad temperature interval. Measurement of the intensity at the maxima $K\alpha_1$ for the low temperature phase and $K\alpha_2$ for the high-temperature phase makes it possible to obtain the temperature dependences of the concentrations of these phases (Fig. 2). The abrupt jumps of $c(T)$ indicate that the observed two-phase region is not the consequence of the difference between the properties of the individual crystallite or of the temperature gradient within the sample.

The phase-transition mechanism becomes understandable after measurements are made on the single crystal. The intensity distribution near the reciprocal-lattice sites 14 0 0, 10 10 0 and 888 attest to the fact that the high-temperature phase (α) is not cubic. Figure 3 shows the rocking curves for the reflection 14 0 0. The splitting observed at 219 K is due to twinning as a result of the phase transition that occurs between 317 and 327 K. When the temperature is decreased, the initial cubic cell is continuously deformed, and this increases the angles between the twins. Measurements of the lattice constants at 219 K have shown that $a \neq b \neq c$, but their difference

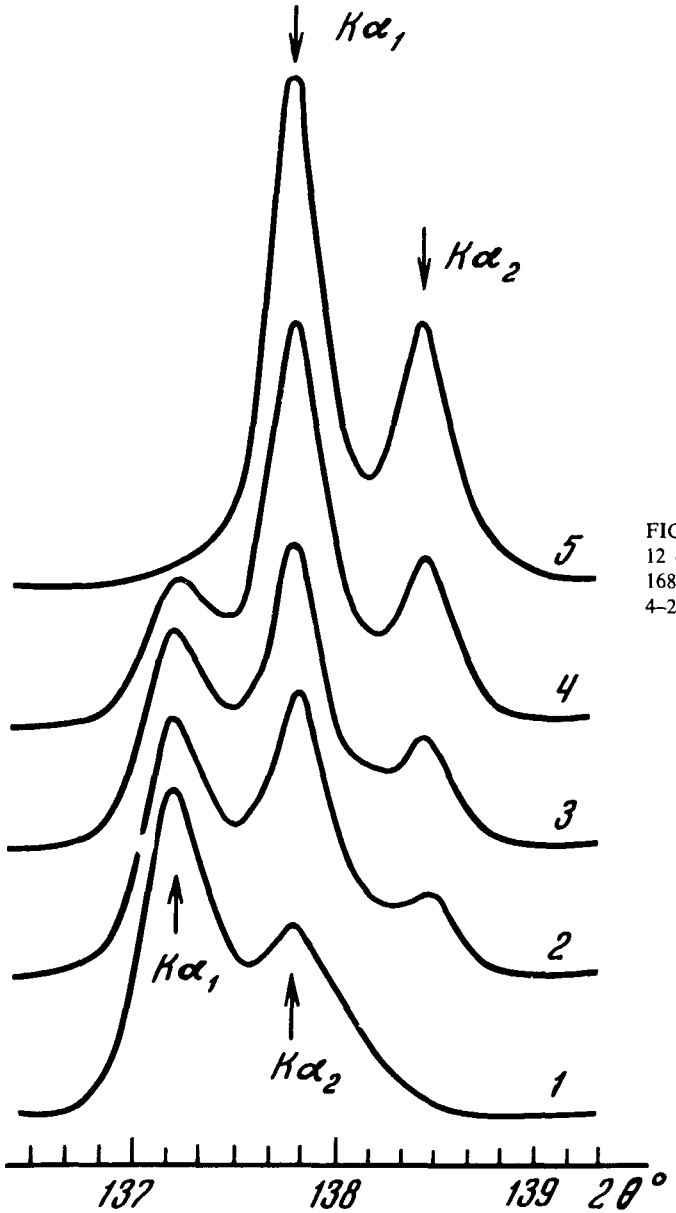

FIG. 1. Shape of the reflection 12 4 0 at the temperatures: 1–168.5 K; 2–192.5 K; 3–196.5 K; 4–201 K; 5–216 K.

does not exceed 0.001 Å. The parameter of the "almost cubic" cell is $a=12.125(1)$ Å [$a_c=12.1360(5)$ Å at 327 K]. To determine the symmetry of the intermediate phase, which may turn out to be quite peculiar,[9] calls for additional precision measurements. In the region of the transition $\alpha \longleftrightarrow C_{2v}^5$ we measured the area under the rocking curve corresponding to the α phase. The plot of $c_\alpha^{(T)}$ constructed from the results of these measurements duplicates qualitatively Fig. 2. The difference lies in the fact that

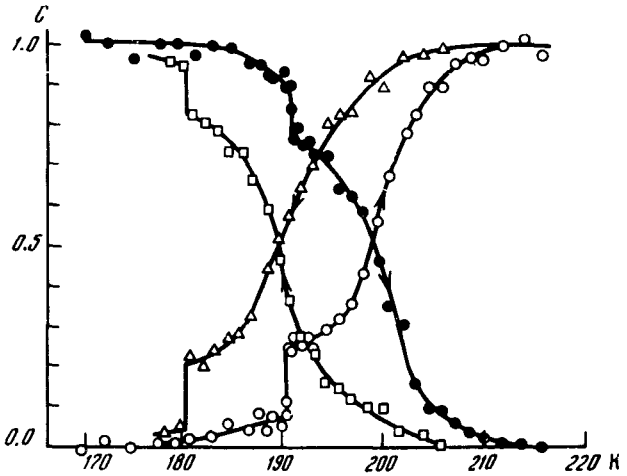

FIG. 2. Temperature dependences of the concentrations of the $\alpha(\Delta,\circ)$ and $C_{2v}^5(\square,\bullet)$ phases.

in the two-phase region there are additional jumps of $c_\alpha^{(T)}$, which are accompanied by a twin realignment that is distinctly revealed by the change of the shape of the rocking curve. The parameters of the orthorhombic cell at 178 K are $a_0=8.6020(3)$ Å, $b_0=8.5757(3)$ Å, $c_0=12.1545(5)$ Å. Thus, in the transition into C_{2c}^5 the volume of the pseudocubic cell ($a=c_0\approx\sqrt{2a_0}$) increases by 0.6%.

The investigations suggest the following mechanism of the $\alpha\rightarrow C_{2v}^5$ phase transition. In the α phase, as a result of twinning, an inhomogeneous stressed state is produced and leads to a difference between the local Curie temperature (T_C) in the individual twins, in accordance with the Clayperon-Clausius equation

$$\frac{dT_C}{dp} = T_C \frac{\Delta V}{\Delta Q}, \tag{1}$$

where ΔV is the difference between the volumes of the α and C_{2v}^5 phases and ΔQ is the heat of the transition. In a single crystal with a small number of twins it is possible to

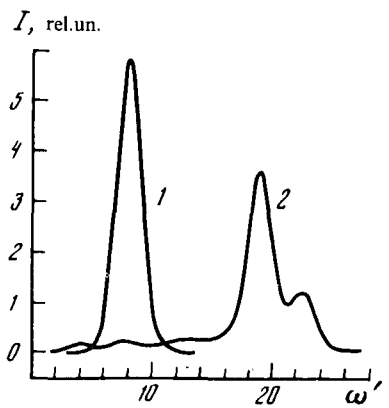

FIG. 3. Rocking curves of the reflection 14 0 0: 1–327 K, 2–219 K.

distinguish between transitions corresponding to the individual twins [jumps on the $c_\alpha(T)$ plots], with T_C lower the larger the pressure in the given twin. The onset of regions of the new phase will be accompanied by a redistribution of the pressures and by a restructuring of the twins. The large number of the different twins in a polycrystalline sample leads to a smoothing of the $c(T)$ dependence. It can be readily assumed, however, that there exists a maximum value of the pressure reached in the system, which corresponds to residues of the high-temperature phase compressed from all sides by the low-temperature phase. All these regions should undergo a transition at the same temperature [the $c(T)$ jump on Fig. 2]. This character of the phase transition is not unique to CoIB. In principle, two phases should always be present whenever the transition is between two phases, each of which contains twins. What is in question is only the width of the interval, which is determined by the parameters that enter in Eq. (1).

It can be assumed that an intermediate α phase exists also in other boracites and causes anisotropy of their properties.

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