Polarization-optical domain study of the ferromagnetic/ferroelectric/ferroelastic phase of cobalt-iodine boracite (Co3B7O13I)

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**Abstract**

Measurements of the spontaneous birefringence between 200 K to 10 K are reported. The symmetry of the ferromagnetic phases below 38 K is determined and consistent with Shubnikov point group m'1m'. A possible mechanism associated with the 28 K magnetic transition is proposed.

**Reference**


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Polarization-Optical Domain Study of the
Ferromagnetic/Ferroelectric/Ferroelastic Phase of Co$_3$B$_7$O$_{13}$I

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§1. Introduction

Cobalt-iodine boracite Co$_3$B$_7$O$_{13}$I (Co-I boracite) undergoes three successive phase transitions, an improper ferroelectric/ferroelastic first order one$^8$ at about 200 K, followed by two ferromagnetic transitions at 38 K and 28 K revealed by spontaneous magnetization$^6$ and magnetoelectric$^5$ measurements. The 200 K transition has been studied relatively well by means of several techniques, as optical studies of ferroelectric domains,$^3$ X-ray$^5$ and neutron$^9$ diffraction, spontaneous polarization$^5$ and specific heat$^9$ measurements, that allowed to clarify in particular the order and symmetry of the phases on both sides of the transition point, and to associate it with the symmetry change F43c1$' ightarrow$Pca21$'2$ with a twofold increase of the high temperature primitive cell. The aim of the present work is the determination of the symmetry of the ferromagnetic phases which remained unknown so far. Therefore we have made inquires into the optical properties of the magnetic phases by means of magnetic domain studies and measurements of spontaneous birefringence on the three Shubnikov principal sections below 200 K. This work replies partly to proposals expressed in a previous paper,$^{11}$ in which properties and possible symmetry changes associated with magnetic transitions in boracites are outlined in the framework of the Landau theory of phase transitions. Let us give a summary of the main results: 1) The order parameter of the magnetic transitions is an antiferromagnetic ordering of the spins in each sublattice. 2) This antiferromagnetic ordering leads to a latent antiferromagnetism$^{12}$ in Ni-I boracite, which should be recognised macroscopically by a $(T_c - T)^{1/2}$ variation law, near the transition point, for the spontaneous magnetization, and to weak ferromagnetism$^{13,14}$ for the trigonal and orthorhombic boracites, the spontaneous magnetization behaving as $(T_c - T)^{1/2}$. 3) Symmetry groups predicted below an orthorhombic paramagnetic phase Pca21$'$ and suitable to depict a ferromagnetic phase, are: Pca2j, Pca2j and Pca2j. 2.

In several compounds (Co-Br),$^{13}$ Ni-Cl,$^{16,17}$ Ni-Br$^{16,18}$ and Cu-Br) magnetic domain studies show a m'm$_2'$ point group, whereas for Cu-Cl$^{19}$ boracite, magnetic torque and magnetoelectric measurements indicate that both ferromagnetic moment and spontaneous polarization are parallel to the [001] axis, indicating a m'm$_2'$ point group. For Co-I boracite, neutron diffraction studies$^{20}$ have been performed in a polycrystalline sample and failed to identify reliably the type of magnetic ordering. This has incited us to attempt optical observations on single crystals.

§2. Sample Preparation

Single crystals of Co-I boracite were grown by chemical vapour transport.$^{20}$ All used samples originated from the same batch of synthesis. The typical dimensions of samples after polishing were 2x1x0.1 mm$^3$. For measuring principal birefringences, (100)$_{ab}$ and (110)$_{ab}$-cut platelets were used, and semi-transparent gold on chromium electrodes were evaporated onto the principal (100)$_{ab}$ faces.

§3. Spontaneous Birefringence Measurements and Investigation of the Shubnikov Point Groups of Ferromagnetic Phases.

Spontaneous principal birefringences have been measured in the temperature range 200 K to 10 K, using a flux cryostat (Oxford instruments special CF204) adapted for observations under a Leitz polarising microscope. Two experimental arrangements have been used: 1) A microscope and tilting compensator. 2) A microscope, photoelectrical modulator, Babinet-Soleil compensator, microphotometer and a Lock-in amplifier detecting the modulator frequency. This latter arrangement, described in ref. 21), gives the better resolution but does not permit to determine easily the absolute values of birefringence. Therefore, these two techniques complement each another. The measuring wavelength selected to give a measurable sensitivity, considering the optical absorption of Co-I boracite,$^{22}$ was $\lambda = 480$ nm. The principal birefringence $n_p - n_p$ (Fig. 1) has been measured on a (110)$_{ab}$-cut, with $n_p||[100]_{ab}$ and $n_p||[110]_{ab}$. Below 38 K down to 10 K a Faraday rotation is visible if the sample is tilted out of the horizontal around $n_p$. At 28 K no new magnetic domains appear, and it has been verified that the spontaneous magnetization $M$, lies in a (110)$_{ab}$ plane. On a (100)$_{ab}$-cut with spontaneous polarization $P$, perpendicular to it (sample having been poled in a field of 25 kV/cm), the smallest principal birefringence $n_p - n_p$ with indicatrix axes parallel to [110]$_{ab}$ directions has been measured (Fig. 1). Below 38 K down to 10 K a Faraday rotation is perceived if the platelet is tilted off the horizontal around $n_p$, whereas absence of Faraday effect is found for rotation around $n_p$. Herewith we have...
verified that $\mathbf{M}_f$ lies in the (100)$_{cub}$ plane with $\mathbf{M}_f \parallel \mathbf{n}_r$. The principal birefringence $n_{\gamma} - n_{\alpha}$ (Fig. 1) has been measured on a (110)$_{cub}$-cut on a domain showing a strong Faraday effect. These different observations are consistent with $n_{\alpha} \parallel P_1 \parallel [100]_{cub}$, $n_{\alpha} \parallel [110]_{cub}$, and Shubnikov point group $m'/m''$ for both ferromagnetic phases. At 38 K the magnetic transition, corresponding to the appearance of spontaneous magnetization along $\mathbf{n}_r$, shows up by a sharp drop in birefringence which reaches a smooth minimum at 28 K (Fig. 2). Moreover, the fact that no modification of the direction of $\mathbf{M}_f$ was detectable means that no symmetry change occurs at and below 28 K. The nature of this second magnetic transition will be discussed in §5.

§4. Ferromagnetic Domains

We have looked for magnetic domain wall motion in-

![Fig. 3. 180° Ferroelectric domain pattern of a (100)$_{cub}$-cut Co-1 boracite. Crossed polars parallel to [100]$_{cub}$ direction. Spontaneous polarization is perpendicular to the plane of the platelet. The optic indicatrix of one domain is rotated by 90° with respect to that of the antiparallel partner.]

![Fig. 4. Ferromagnetic domains at $T=36$ K, (100)$_{cub}$ cut, crossed polars parallel to [110]$_{cub}$ direction. Crystal tilted around index $n_p$. In the temperature range 38 K to 28 K domain walls are oriented along the [110]$_{cub}$ direction.

![Fig. 5. Ferromagnetic domains at $T=20$ K. After applying a weak external magnetic field $< -400$ Gauss, domain walls are oriented along the [100]$_{cub}$ direction.]

Fig. 1. Spontaneous birefringences $\Delta n_i$ of Co$_3$B$_7$O$_{13}$I vs temperature. Measurements have been obtained using a tilting compensator at wavelength $\lambda=480$ nm, by heating sample after cooling to 10 K. The arrows in the figure indicate the onset of magnetic ordering.

Fig. 2. Details of the spontaneous birefringence $\Delta n_i$ of Co$_3$B$_7$O$_{13}$I vs temperature in the region of the magnetic phase transitions. Measurements have been obtained using photoelastic modulator and Babinet-Soleil compensator at wavelength $\lambda=480$ nm.
side a ferroelectric single domain under an applied magnetic field (Fig. 3). In the temperature range 38 K to 10 K in absence of an applied magnetic field, magnetic walls spontaneously align along [110]_{ab} directions (Fig. 4). A magnetic field $< -400 \text{ G}$ does not modify this orientation between 38 K to 28 K. However, below 28 K the magnetic walls turn into [100]_{ab} directions in a field $< -400 \text{ G}$ and remain there, even after removal of the magnetic field (Fig. 5). When the temperature increases, these [100]-walls start to lose their shape (Fig. 6) and finally align again along [110]_{ab} directions (Fig. 4). In the next paragraph we discuss the possible origin of this effect, which should be connected with the 28 K transition.

§5. Discussion and Conclusion

Observations on magnetic wall orientation in both ferromagnetic phases suggest the possibility of existence of head-to-tail magnetic domains below 28 K, and consequently a discontinuity of the magnetization in the direction of the normal to the Bloch wall, i.e., div $M \neq 0$. This suggests a strong temperature dependence of magnetic anisotropy, and must be compared with magnetic and magnetoelectric measurements performed by L. N. Baturov and co-authors, whose results show an increase in magnetic anisotropy below 28 K. Landau theory of phase transitions sheds light on the nature of the 28 K magnetic transition. In fact, this theory predicts two possible types of antiferromagnetic spin arrangement in each cobalt sublattice, which are linear combinations of the two basis functions $L_{1z}$ and $L_{3z}$, suitable to induce a weak ferromagnetic moment along the same direction, hence leading to the same symmetry change mm21' $\rightarrow$ mm'2'. Thus the isosymmetric transition at 28 K should be caused by a simple spin reorientation without any change in the symmetry of the antiferromagnetic ordering. This interpretation will need, however confirmation by neutron diffraction on single crystals. A more detailed theoretical account of the behaviour of birefringence, will be given in a forthcoming paper.

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