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SPONTANEOUS BIREFRINGENCE AND SPONTANEOUS FARADAY EFFECT IN COBALT BROMINE BORACITE $Co_3B_7O_{13}Br$

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Abstract Measurements of the spontaneous birefringence of the ferroelectric phase (4K to $T_{C(f.e.)}$ = 466K), of its dispersion in the visible (300K) and of the spontaneous Faraday rotation in the ferromagnetic phase (4K to $T_{C(f.m.)}$ =16K) are reported. The rotation amounts to 3450 deg.cm^{-1} at 4K and λ = 643nm along an optic axis.

INTRODUCTION

Cobalt bromine boracite (abbreviated CoBr) undergoes an improper phase transition at $T_{C(f.e.)} \cong$ 466K from a cubic ($\bar{4}3m1'$) to an orthorhombic ferroelectric/ferroelastic phase (mm21') [1], which becomes ferromagnetic at low temperature [2]. This work intended to determine the magnetic point symmetry and to measure the spontaneous Faraday rotation of the ferromagnetic phase on single domains. To date only little magnetic data on CoBr - obtained from powders - have been available : spontaneous magnetisation $\bar{M}_s$(4.2K) = 9.5 emu.g^{-1} (= 0.0482 T), coercive field H_c(4.2K) = 0.3 T, and effective magnetic moments corresponding to high spin Co^{2+} ns [2].

SPONTANEOUS BIREFRINGENCE

Orthoscopic observation on (100)** and (110) platelets (thickness t = 30-80μm) and conoscopic studies on (100)-cuts (t = 170μm) confirmed earlier studies that the optical indicatrix of CoBr resembles that of NiBr [1] with $n_\beta // \vec{P}_s //$ [001] and the acute bisectrix parallel to $n_\gamma //$ [110], where n_α, n_β, n_γ are the principal refractive indices and $\vec{P}_s$ the spontaneous polarisation. The ferroelectric domain structure is similar to that of other orthorhombic boracites [3]. The ferromagnetic domains have been evinced at $T < T_{C(f.m.)}$ = 16K owing to high and strongly dispersive Faraday rotation, even along highly birefringent directions whereas

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** pseudo cubic indices are used throughout this paper

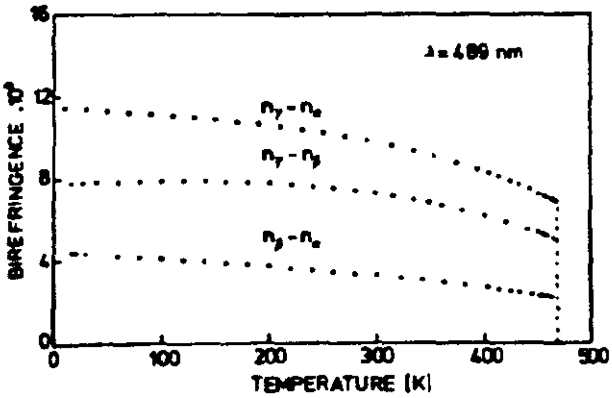
in NiCl [4] and NiBr [4] magnetic domains are seen along and close to the optic axes only. For the measurement of the Faraday rotation it is advantageous to direct the light beam along an optic axis. With a view to finding the orientation of the optical axes by means of Mallard's approximation [4] the three principal birefringences of CoBr have been measured from 16K to 466K (Fig. 1), yielding the optic axial angle 2V $\sim$ 71° at 16K. There exist two strong absorption bands centred at $\sim$ 17500 cm^{-1} and $\sim$ 22000 cm^{-1} connected with the ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ transition of high spin Co^{2+} [5] which causes strong "anomalous" dispersion of the birefringence (Fig. 2) and hence also of the optic axial angle 2V. In addition it causes the crystal to act as a filter for red and blue at t $\gtrsim$150µm. Owing to i) the necessity to use very thin platelets (30-80µm) due to absorption and ii) because of extreme sensitivity to slight misorientation due to the strong anisotropic dispersion (Fig. 2), the measurements of birefringence were delicate.

FERROMAGNETIC DOMAINS

On cooling ferroelectric domains with $\Delta n_s = n_\beta - n_\alpha$ ((110-cut) in zero magnetic field through $T_{C(f.m.)}$ = 16K, ferromagnetic stripe domains - sometimes elongated "bubbles" - form with vivid contrast, e.g. red/green, if viewed with nearly crossed polars. At crossed polars the domain wall traces appear dark (Fig. 3a). They are essentially directed along $\sim$ [001]// n_β. By rotating a field $\vec{H}$ = 0.022T around n_α, n_β and n_γ, the stripe pattern was found to be stable for $\vec{H} \perp n_\gamma$ only, suggesting $\vec{M}_s$ to lie along n_γ. Just below T_c saturation was achieved with $\vec{H}$ = 0.022T// n_γ. After field removal the energetically more favourable stripe pattern reappeared. Rapid cooling from T = 16K (or above) in $\vec{H}$ = 0.022T// n_γ leads to the pattern of figure 3b, with the traces of the walls aligned along $\sim$ [112]. On field removal this pattern relaxes to the one of figure 3a. Explanation of this phenomenon requires further study of the parameters of the material , such as magnetocrystalline energy, coercive field, etc. The black areas of figure 3a represent ferroelectric domains with $\Delta n_s = n_\gamma - n_\beta$ and $\vec{M}_s$ // [110] // n_γ in extinction position (No Faraday effect !).

FARADAY ROTATION

The measurement of the rotation angle, $\Theta_{o.a.}$, for light propagating along an optic axis was realised by means of a (100) platelet (t = 170µm) on a domain with $\vec{P}_s$(// n_β) within (100). In that case the optic axis lies close to the vertical. After preorientation - based on 2V derived from Δn-data, see above - the accurate orientation of the incidence angle (α) in the n_γ/n_α - plane for light (λ = 643nm) propagation along the optic axis, was realised by using the Faraday effect itself as a detector i.e. by searching the maximal rotation



.IGURE 1 Spontaneous birefringences versus temperature.

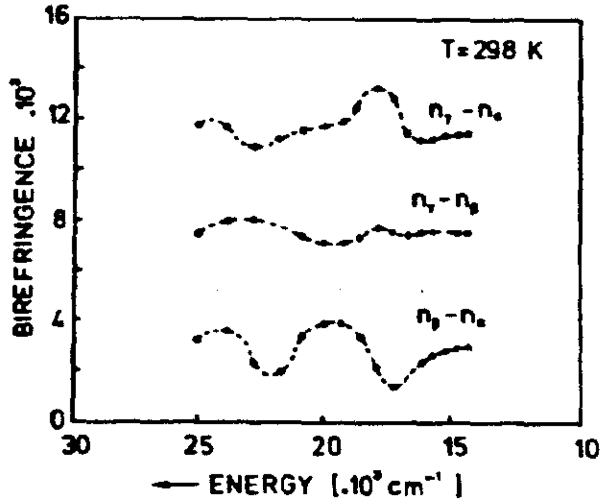


FIGURE 2 Dispersion of spontaneous birefringences in the visible.

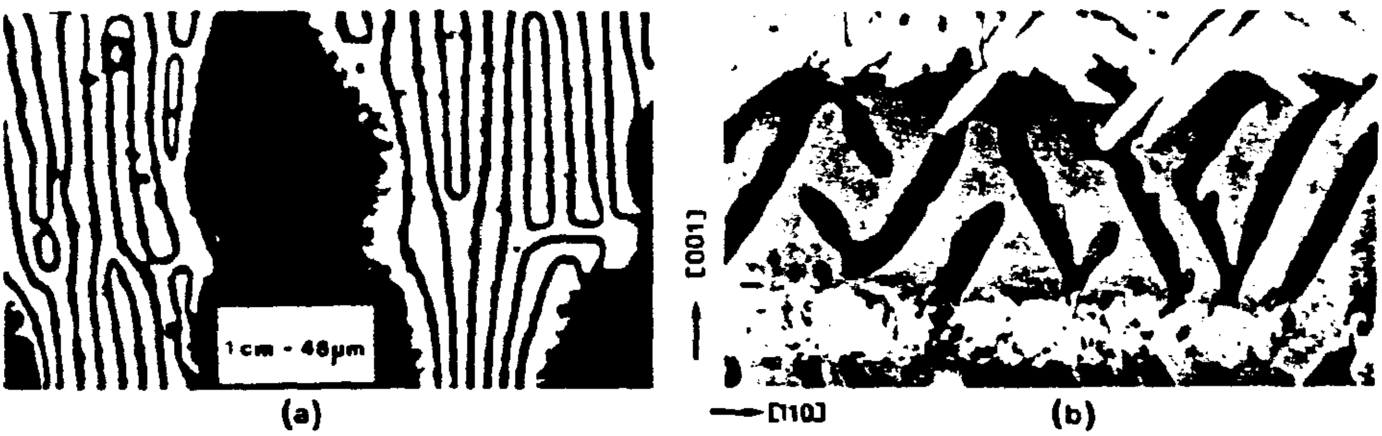


FIGURE 3 Ferromagnetic domains, n_β/n_α-cut, (a) stripe domains T = 8 K, polars crossed, (b) walls along ∿ [112]at T = 4.5 K after quenching from T = 16 K, polars decrossed.

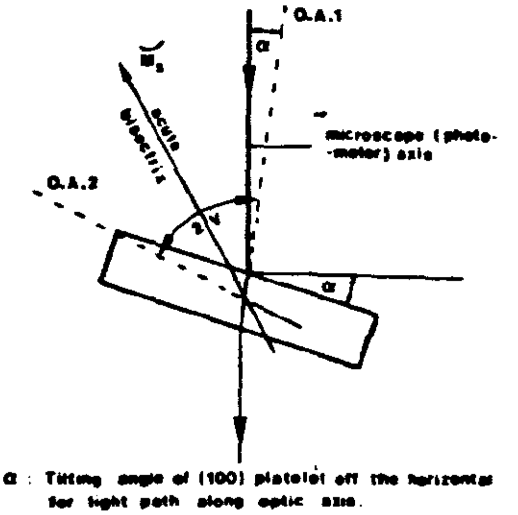


FIGURE 4 Experimental arrangement for the measurement of the Faraday rotation along an optic axis.

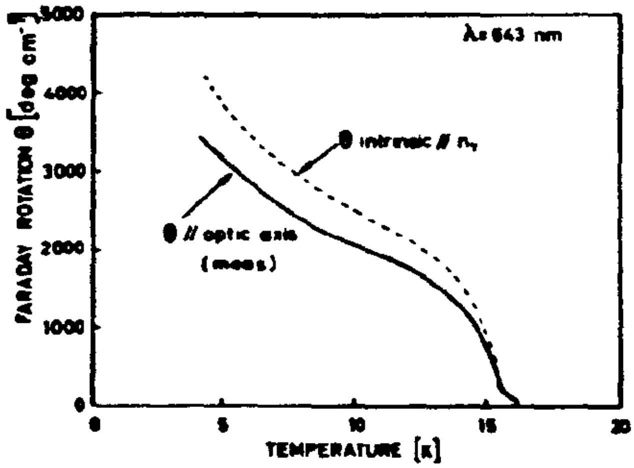


FIGURE 5 Spontaneous Faraday rotation versus temperature.

angle below $T_{C(f.m.)}$ as a function of the angle or rotation of the crystal around n_β. Small misalignments decrease the effective rotation due to birefringent phase retardation. This represents a direct method for determining 2V in a ferromagnetic phase (Fig. 4). The ferroelectric single domain, used for the measurement of $\Theta_{o.a.}$, has been magnetically poled by cooling through $T_{C(f.m.)}$ in a field $H = 0.045T$ parallel to n_γ. To determine the extinction angle, a polariser, analyser and microphotometer were employed. Figure 5 shows the measured Faraday rotation, $\Theta_{o.a.}$, along an optic axis, and the intrinsic, calculated one, Θ_i, along $n_\gamma // \vec{M}_s$ at $\lambda = 643$nm. These rotations are related by $\Theta_i = \Theta_{o.a.}/\cos V$. Half the acute optic axial angle was found to be 35.8°. The temperature dependence of Θ_i is unusual (Fig. 5) and does not seem to follow that of $\vec{M}_s$ as in NiCl [4].

CONCLUSIONS

Spontaneous birefringence versus temperature and the immobility of the ferroelectric domain pattern between 4 and 466K ($T_{C(f.e.)}$) show that the phase transition $\bar{4}3m1' \rightarrow mm21'$ at 466K is the only structural one of CoBr. Below $T_{C(f.m.)} = 16K$ a ferromagnetic phase - most probably with Aizu species $\bar{4}3m1Fm'm2'$ - is evinced with a spontaneous Faraday rotation along an optic axis of ~ 3450 deg.cm^{-1} at 4K and $\lambda = 643$nm. More detailed work is necessary to describe and to explain the optical and magneto-optical properties of CoBr, e.g. the potential reciprocal rotatory power - neglected in the present study - will have to be separated from birefringence and Faraday rotation.

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