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Magnetoelectric and Magneto-Optical Measurements on Nickel-Bromine Boracite $Ni_3B_7O_{13}Br$

J.-P. RIVERA, F.-J. SCHAEFER*,
W. KLEEMANN* and H. SCHMID

Département de Chimie minérale, analytique et appliquée Université de Genève, CH-1211 Genève 4, Switzerland
**Laboratorium für Angewandte Physik, Universität Duisburg,*
D-4100 Duisburg 1, Federal Republic of Germany

Various anomalies of Faraday rotation, magnetoelectric coefficient $\alpha_{23}(T)$, $\alpha_{32}(T)$, coercive field and birefringence of three principal cuts as well as new direct observations of magnetic domains of NiBr boracite single crystals complete the knowledge of phase transition in the following way:

$(\bar{4}3m1')$-398 K-(mm21')-29 K-(m'm2')-21 K-(1)

§1. Introduction

NiBr boracite is a member of the 3d-transition metal boracite family $M_3B_7O_{13}X$, abbreviated MX, with M=Fe, Co, Ni, Cu and X=Cl, Br, I, which are known to be weakly ferromagnetic/ferroelectric/ferroelastic[1] (except CuI).

NiBr boracite is cubic $(F\bar{4}3c)$[2] above $T_c=125$ C and orthorhombic $(Pca2_1)$ below that temperature.[2,3] At low temperature NiBr becomes a weak ferromagnet with a spontaneous magnetization of 2.15 emu/g, measured on powder at 4.2 K.[4] The birefringence (at 546 nm) of the three principal cuts of the orthorhombic phase has been measured from T_c to 20 C[2] and to 5 K[5] as well as an apparent Faraday rotation perpendicular to a cubic platelet $(n_\gamma, -n_\beta)$.[5]

In the present work, anomalies of the spontaneous birefringence in the ferromagnetic phases of NiBr are presented as well as the linear magnetoelectric coefficient $\alpha_{23}(T)$, coercive field and apparent spontaneous Faraday rotation at 480 nm. Magnetic domains have been observed on the three orthorhombic principal cuts (at $T<21$ K).

§2. Sample Preparation

For the measurement of spontaneous birefringence on the three orthorhombic indicatrix principal sections, platelets cut perpendicularly to the three orthorhombic axes have been prepared from vapour phase grown crystals[6]: I$(n_\gamma-n_\beta)$, II$(n_\beta-n_\alpha)$, III$(n_\gamma-n_\alpha)$ (Fig. 1). The orthorhombic cell has its axes 1 and 2 turned by 45 deg. around the spontaneous polarization $\boldsymbol{P}_s$ (axis 3) relative to the cubic axes. The thickness of these crystals is 62, 60 and 58 $[\beta m]$, respectively. For the Faraday rotation a pseudo-(100) cubic cut was prepared with $\boldsymbol{P}_s$ within the plane of the platelet, in such a way as to have an optic axis emerging close to the plate normal[2] (crystal IV, thickness=130 $[\mu m]$). The measurement of the magnetoelectric coefficient $\alpha_{23}(T)$, for m'm2', would require the same cut as that of crystal II. However because of lack of such a specimen a (100) cubic cut of type IV with $\boldsymbol{P}_s$ in the plane of the platelet has been used. In this case the induced polarization has to be multiplied by $\sqrt{2}$. For this experiment two small single domain platelets have been aligned in order to increase the effective area (crystal V, total area: 1.15 mm^2).

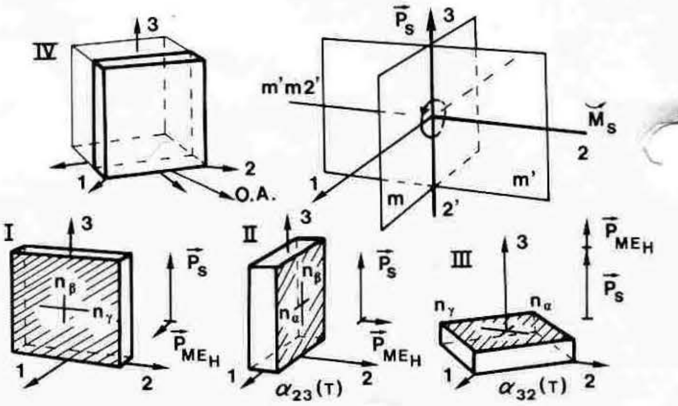

Fig. 1. Orientation of crystallographics axes and optical indicatrix for the NiBr boracite platelets used. Symmetry elements for m'm2' point group are indicated.

§3. Measurements

3.1 The linear magnetoelectric effect $(P_i=\alpha_{ij}H_j)$ is allowed for certain Shubnikov point groups.[7] Based on a strong evidence[5,8] the magnetically ordered phase of NiBr boracite belongs to Shubnikov point group m'm2' below 29 K (Fig. 1; see also Fig. 1 in Ref. 9). In order to complete the earlier measurements of the magnetoelectric coefficient $\alpha_{32}(T)$[8] by $\alpha_{23}(T)$, this latter one has been measured (Fig. 2a). Because of the appearence of a second magnetic transition at $T=21$ K (see below) the $\alpha_{23}(T)$ and the $\alpha_{32}(T)$ coefficients are in fact pseudo-orthorhombic coefficients below that temperature. The temperature is measured here with a calibrated carbon glass resistor close to the sample. So the last transition on cooling NiBr boracite occurs in fact at 21 K instead of 17 K.[8] The magnetic coercive field obtained in the same experiment is shown in Fig. 2b.

3.2 The Faraday rotation versus temperature of NiBr, is presented in Fig. 3, at 480 nm. This rotation, measured along an optic axis (by tilting the crystal round n_β) is more than 20 times the value determined at 546 nm and vertical incidence on a (100) cubic cut.[5] In this latter case the effective rotation was reduced due to non-zero birefringence.[14-16]

3.3 Spontaneous birefringence. Let us recall that the spontaneous polarization versus temperature curve showed two anomalous kinks at 29 K and 21 K respectively

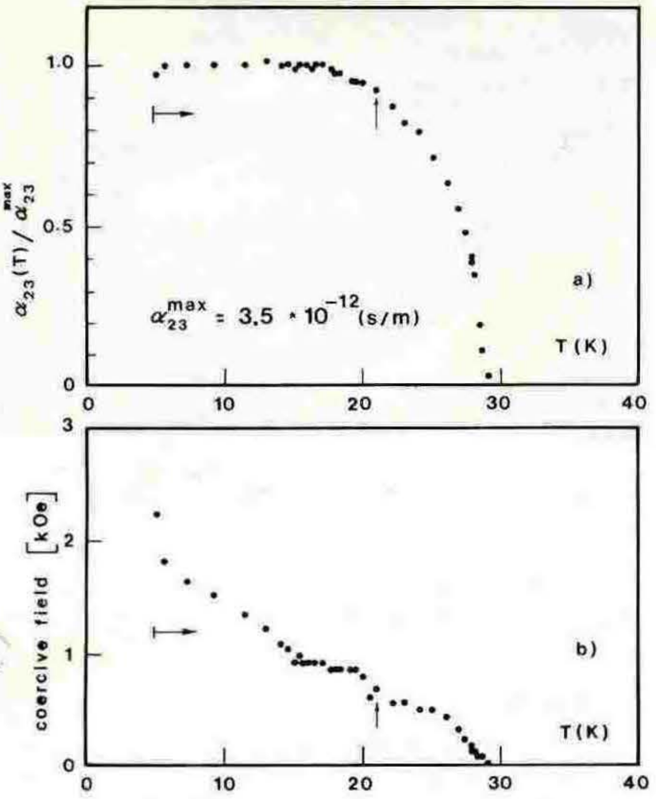

Fig. 2. Magnetoelectric (ME_H) coefficient $\alpha_{23}(T)$ (a), and coercive field vs temperature (b). The vertical arrows indicate the lower magnetic transition.

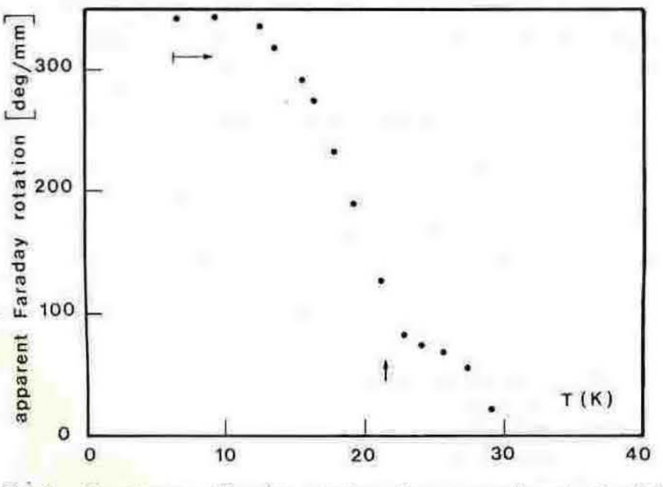

Fig. 3. Spontaneous Faraday rotation along an optic axis (λ=480 nm) vs temperature, showing two magnetic phase transitions. The vertical arrow in the figure indicate the lower magnetic transition.

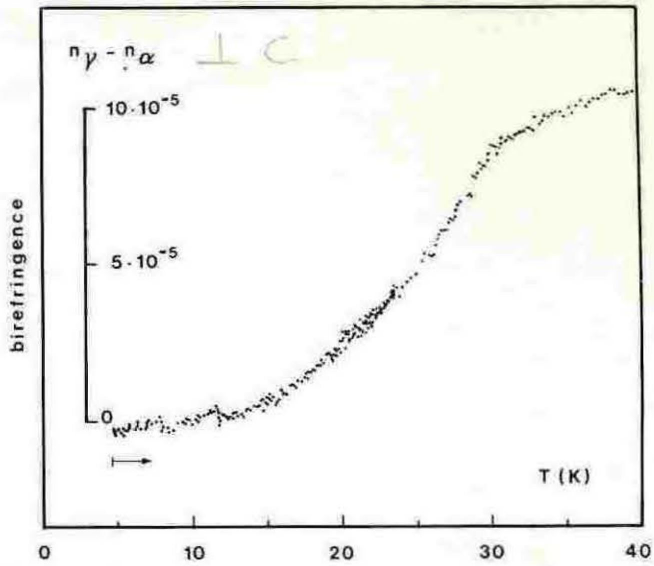

Fig. 4. Detail of spontaneous birefringence ($n_\gamma - n_\alpha$) vs temperature at λ=589 nm. Only the upper magnetic transition is clearly visible.

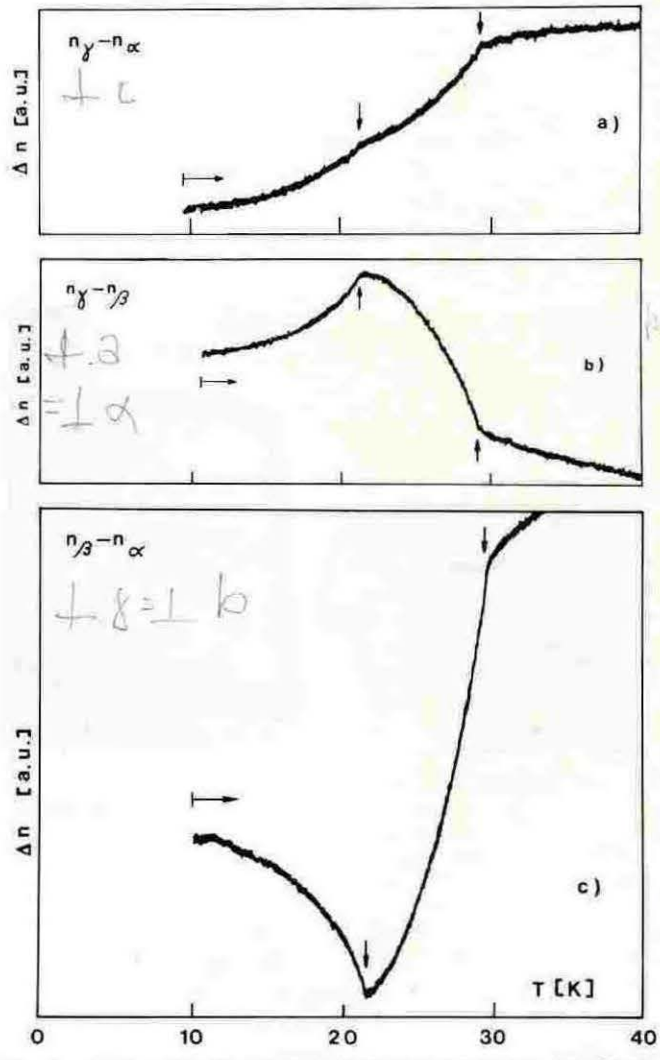

Fig. 5. a), b) and c). Detail of the three principal spontaneous birefringences, all showing the two magnetic phase transitions (λ=480 nm). The vertical arrows in the figure indicate the two magnetic transitions.

whereas no anomaly of ε_{33} (T) (f=300 kHz) was detected.[8] Using a photoelastic modulator, a Babinet-Soleil (B.-S.) compensator[10-12] and a sophisticated automatized experimental set-up (see Fig. 1 of Ref. 13, without the elements 6, 7 and 11) the spontaneous birefringence has been measured (Fig. 4). The first magnetic transition at 29 K, on cooling, is revealed by a clearcut kink, In this latter experiment the B.-S. compensator is set automatically to compensation in order to cancel the in-phase signal detected by a lock-in amplifier at the same frequency the modulator is oscillating. Figures 5a–c show the magnetic anomalies of birefringence for the three principal cuts. Birefringence is given in arbitrary units because here the B.-S. compensator is kept fixed and the in-phase lock-in signal is recorded versus

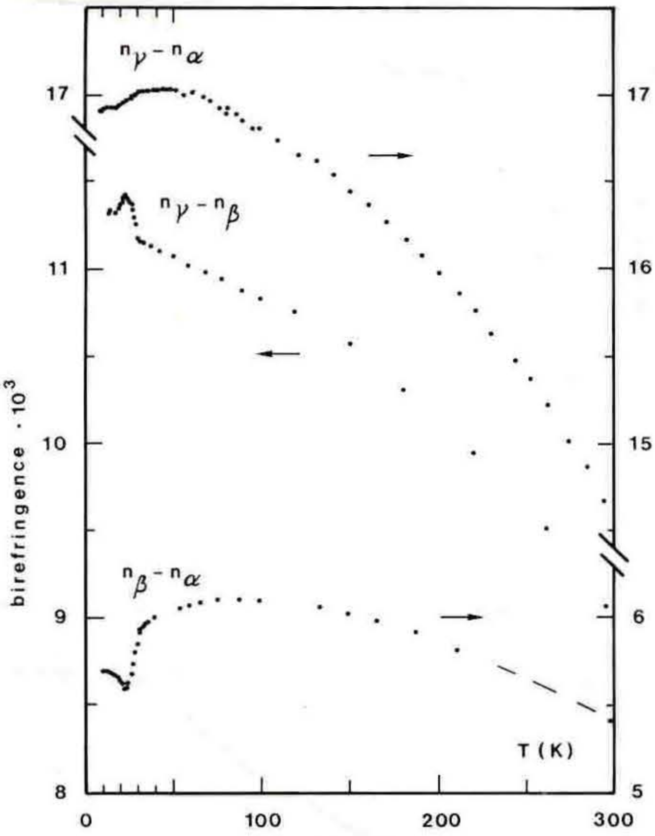

Fig. 6. The three spontaneous birefringences vs temperature with their anomalies at low temperature. Note that each curve has its own scale.

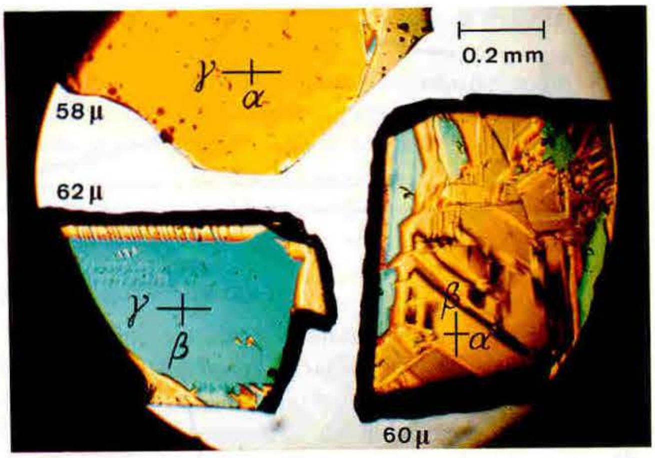

Fig. 7. The three NiBr boracite platelets used for Δn experiments, (T=293 K, polarizers crossed, $\lambda/4$ plate). Below 21 K, the presence of magnetic domains inside the ferroelectric ones is simultaneously observed on all three cuts.

temperature. Again as for P_s and the Faraday rotation we have kinks at 29 K and 21 K. In Fig. 6, the $(n_\gamma - n_\beta)$, $(n_\gamma - n_\alpha)$ and $(n_\beta - n_\alpha)$ birefringence curves are displayed. For these measurements a somewhat less optimized equipment than that used for the measurements shown in Fig. 4 was employed. The values obtained for the three Δn are in good mutual agreement.

3.4 Finally, the direct observation of the magnetic domains on three orthorhombic principal cuts (Figs. 7, 8) indicates: i) for 21 K$<T<$29 K the magnetization lies along n_γ whereas ii) for $T<$21 K it lies close to n_γ but with

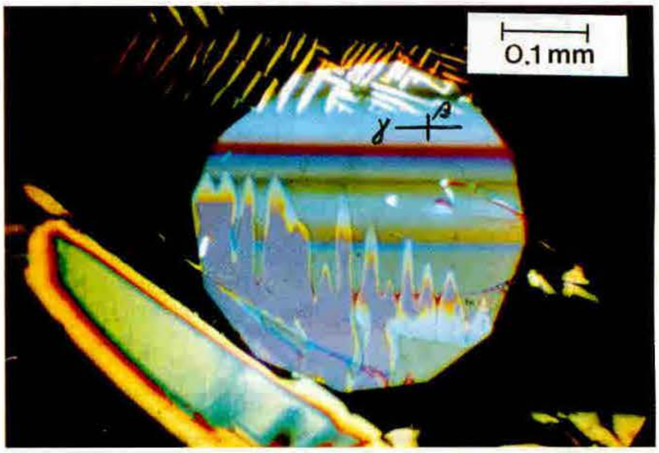

Fig. 8. Crystal I (T=18 K, cut $n_\gamma - n_\beta$) showing the magnetic domains appearing at T=21 K. A small magnetic field (e.g. 400 Oe) can move the magnetic domain walls.

components along all three orthorhombic axes. This observation is compatible only with the lowest Shubnikov point symmetry, i.e. 1.

§4. Conclusions

The different presented experiments show clarly that the weak ferromagnetic phase m′m2′ of NiBr boracite, appearing at 29 K and which was belived to be stable down to 4K[5)] transforms in fact at 21 K into another ferromagnetic phase of triclinic Shubnikov point group 1.

The strong anomalies of spontaneous birefringence in the two ferromagnetic phases could come from the appearence of the order parameter and the magnetostriction; a magnetic precursor effect on the birefringence appears already in the paramagnetic phase.

Acknowledgements

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