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ELECTRICAL AND OPTICAL MEASUREMENTS ON NICKEL IODINE BORACITE

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Abstract - Measurements of resistivity, spontaneous polarization, pyroelectric coefficient, piezoelectricity, dielectric constant, spontaneous Faraday rotation, spontaneous birefringence and rotation of the optical indicatrix with temperature are reported. Between 4K and 61.5K a single ferroelectric/ferromagnetic/ferroelastic phase, consistent with Shubnikov point symmetry m', exists.

Although a great number of experimental and theoretical work[1,2] followed the announcement of simultaneous ferroelectricity and ferromagnetism in NiI boracite[3], ($Ni_3B_7O_{13}I$), abbreviated NiI, no clear-cut answer to the question of the nature of the phases of this composition has been given so far. Therefore some clarifying measurements with accent on simultaneous visual control of the state of the crystal appeared timely.

EXPERIMENTAL

Optical Cryostat - The tail of a Raman dewar (Oxford Instr. CF204) has been transformed and adapted for polarized light microscopy (4-300K) and served for optical and electrical measurements under visual control.

Samples - Half a dozen crystals, from different batches of synthesis[4], have been studied. Optically homogeneous regions with weak parasitic birefringence were cut out of the crystals in the form of bars or platelets (Fig.8 of Ref.5), the largest face being parallel to $(001)_{cub}$ and the greatest extension parallel to $\langle 110 \rangle_{cub}$. After polishing and deposition of semi-transparent electrodes (Au on Cr), gold wires (d.40μm) were fixed by silver/epoxy at the centre of the large faces. Measurements on two samples with different dimensions are described in this paper : Crystal a : ℓ_a = 1.86mm, w_a = 0.660mm (S_a = 1.118mm^2) and t_a = 0.118mm; crystal b : ℓ_b = 2.15mm, w_b = 0.394mm and t_b = 0.239mm.

Resistivity - Resistivity is a good indication of crystal quality. Therefore its measurement was always performed first (Electrometer Keithley 417 for DC data). Indeed, the resistance of crystals with similar geometry scattered at 295K between $10^5\Omega$ and $10^8\Omega$. For crystal a, $R_{DC}(295K) = 3.31\times10^8\Omega$ at 4.5Volts DC, i.e. $\rho(295K) \cong 3.44\cdot10^6\Omega$.m, measured without guard ring. From 295K to 188K there is a linear dependence of ℓog R vs. 1/T, and the activation energy $E_a \simeq 0.60$ eV ($R = R_o \exp(E_a/kT)$).

Spontaneous polarization P_s versus temperature (Fig. 1) has been obtained by measuring the surface charge density (Electrometer Keithley 616) on upheat after poling the crystal (a) by cooling in an electric field from T = 62K to T = 4K. At 4.5K $P_s = 0.076[\mu C/cm^2]$, in good agreement with measurements on $(110)_{cub}$ cuts[6].

Pyroelectric coefficient (Fig. 2) has been obtained from the temperature derivative of

P_s (T), p = dP_s/dT and by the method of Byer and Roundy[7].

Piezoelectric measurements on NiI are described elsewhere[8] in detail and have been realized by the "admittance circle" and "motional capacitance" methods. Typical values of piezoelectric coefficient of NiI (crystal a) are e.g. $|d_{14}(295K)| \cong 11.8$pm/V and $|d_{14}(61.5K)| \cong 19.6$pm/V. In the system of pseudo-orthorhombic axes $|d_{31}| \cong |d_{32}|$ with e.g. $|d_{31}(61.5K)| \cong 9.81$pm/V and $|d_{31}(4.2K)| \cong 11.7$pm/V. One of the important results of these studies is the observation of the frequency dependence of the temperature of the internal loss peaks ($1/Q_m$) at 18K(2MHz, fundamental) → 20K(6MHz, 3nd overtone) and 142K (2MHz) → 152K(6MHz), suggesting the absence of phase transition at these temperatures.

The dielectric constant was measured with the "3 point technique", using a Booton 75C bridge(70mV$_{RMS}$) at 100kHz and a Boonton 72BD bridge (15mV$_{RMS}$) at 1MHz. The choice of f≧100kHz is justified by the fact that certain crystals showed relaxation phenomena at 500Hz<f<50kHz and T = 295K, describable by a Cole-Cole formalism of the dielectric constant (e.g. $1-\alpha \cong 0.90$). In Fig. 3 the dielectric constant ($\varepsilon^* = \varepsilon' - j\varepsilon''$) at 100kHz versus temperature is given for NiI sample a. The insets show the detail at the phase transition of 61.5K for 100kHz and 1MHz. The down-jump of ε on upheat at 61.5K is analogous to that observed on MnI[9,10] and CuCl[11]. Previous measurements on NiI were described, e.g., in Ref. 3 and 12.

Faraday rotation - All of the half a dozen crystals studied showed strong Faraday rotation at T<61.5K after poling with an electric field along $\langle 001 \rangle_{cub}$ and for light propagating along that same direction. A conventional method - using a polarizer, an analyser and a microphotometer - was applied for measurement at λ = 546nm. Figure 4 gives the temperature dependence of the apparent Faraday rotation θ_A along the poled $\langle 001 \rangle_{cub}$ direction. At 4.2K, $\theta_A \cong 700$ deg/cm (crystal NiI a). The rotation disappears at T=61.5K. The observation of this strong Faraday component along $\langle 001 \rangle_{cub}$ is in disagreement with the initially postulated Shubnikov point group m'm2' [3]. By apparent Faraday rotation we mean the angle between the initially linearly polarized wave and the plane of the major axis of the elliptically polarized wave leaving the crystal. (Fig. 5).

By observing the same sample along $\langle 110 \rangle_{cub}$, i.e. perpendicularly to the applied electric field a Faraday component is observed for one polarity and absence thereof and sharp extinction of birefringence for the reverse polarity. The extinction directions of that section of indicatrix were found to rotate with temperature, leading to the conclusion that the symmetry of NiI below 61.5K is consistent with the monoclinic Shubnikov point group m'. Evidence for a symmetry lower than m'm2' was also obtained from magnetoelectric measurements[13] and neutron diffraction work.[14]

Birefringence and rotation of index ellipsoid - In Fig. 6 the spontaneous birefringence and the rotation of the extinction directions (in a $(110)_{cub}$ plane) versus temperature are represented for a ferroelectric single domain of sample b. Since $w_b < w_a$, crystal b was preferable for measurement of Δn. At T=5K $\Delta n \cong 0.0023$ (λ=546nm) and the extinction direction γ' forms an angle of 28° with the applied electric field of -12.4kV/cm. This angle tends to zero at 61.5K. For the reverse polarity magnetic domains are observed but the birefringence has not been measured. On crystal NiI (sample a) two mutually symmetric domains with $\gamma' \simeq +30°$ and $\gamma' \simeq -30°$, resp. have been observed simultaneously at 4.5K. These angles also tended to γ'=0 at 61.5K.

CONCLUSIONS

1. The continuity of P_s,p,ε,Δn,γ' and Faraday rotation as well as the frequency

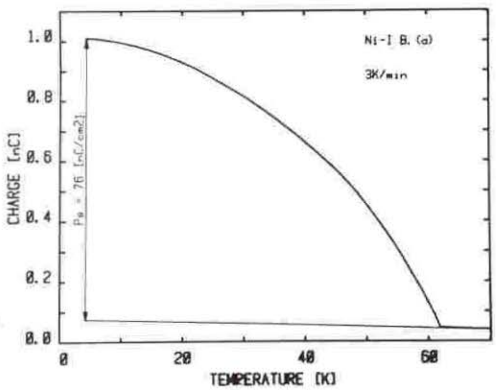

FIGURE 1. Spontaneous polarisation P_S vs.T Sample a.

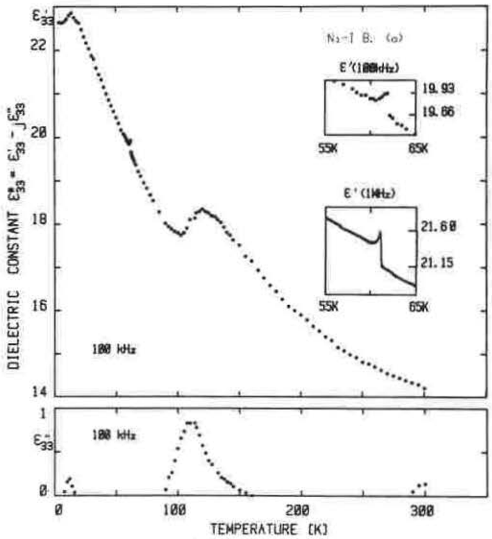

FIGURE 3. Complex dielectric constant ($\varepsilon^*=\varepsilon'-j\varepsilon''$) vs.T, at 100 kHz. Insets show detail at 61.5K, for f=100 kHz and f=1 MHz. Sample a.

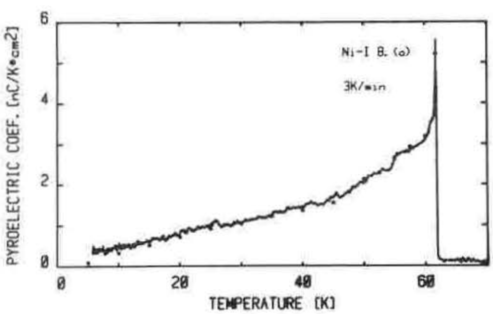

FIGURE 2. Pyroelectric coefficient vs. T, $p = dP_S/dT$ (points calculated from Fig.1), and $p = I/(S\cdot dT/dt)$ where I is the pyroelectric current. Sample a.

FIGURE 5. Typical ferromagnetic domain pattern on NiI B. Sample b, $(001)_{cub}$ face. ℓ_b = 2.15 mm., w_b = 0.39 mm.

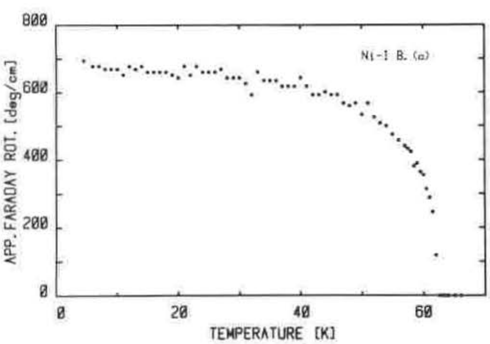

FIGURE 4. Apparent spontaneous Faraday rotation vs. T, light beam perpendicular to $(001)_{cub}$ face. Sample a.

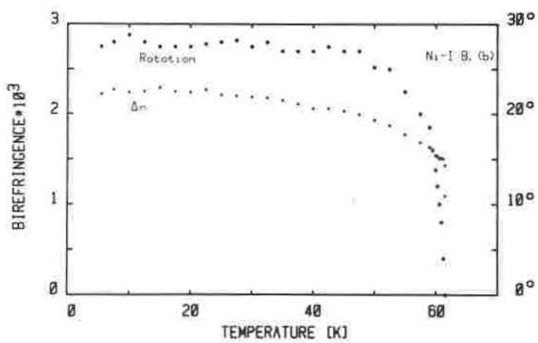

FIGURE 6. Birefringence (Δn) and rotation of extinction angle γ' vs. T, light beam perpendicular to $(110)_{cub}$ face, i.e. // w_b. Sample b.

dependence of the internal loss peaks suggest that no other phase transition down to 4K exists than that observed at 61.5K, in disagreement with other workers.[15-18]

2. The down jump of the dielectric constant of NiI on upheat at the transition at 61.5K is of the type observed in MnI[9,10] and CuCl[11].
3. For the first time the simultaneity of the onset of ferroelectricity and ferromagnetism at the same temperature, i.e. 61.5K, has been unequivocally demonstrated by measuring P_S,ε,Δn,γ' and Faraday rotation on one and the same sample.
4. The presence of a strong Faraday component along $<001>_{cub}$ and the rotation with temperature of the index ellipsoid around a $<110>_{cub}$ direction are in disagreement with the hitherto admitted point group m'm2'.[3] All experimental results of this work are consistent with the monoclinic Shubnikov group m'.

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