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PIEZOELECTRIC AND DIELECTRIC RELAXATION IN NICKEL IODINE BORACITE AT LOW TEMPERATURE

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Abstract With a view to elucidating the anomaly of various physical properties found near 120K, the complex dielectric constant has been measured versus temperature (4K – 300K) and frequency (10kHz – 1MHz) and is compared to previous piezoelectric studies. Substantial shifts in temperature of the ε"-peak and 1/Ωpeak with frequency indicate a Debye type relaxation mechanism due to defects and exclude new phase transitions as previously claimed in literature. A similar, but weaker anomaly occurs near 15K. Relaxation times and activation energies are given.

INTRODUCTION
Nickel iodine boracite (Ni$_3$B$_7$O$_{13}$I = NiI) has been the object of controversies concerning the number of existing phase transitions, the symmetry of phases and the simultaneity of the onset of spontaneous polarization, P$_s$, and spontaneous magnetization, M$_s$. However, this simultaneous onset of P$_s$ and M$_s$ is now rather well established for T = 61.5K, though first evidence for it was already obtained in 1966. During those first experiments a strong anomaly of dielectric constant ε' and magnetic susceptibility had been noted at approximately 120K. Although anomalies of the cubic lattice parameter have been reported for about 120K, no deviation from the cubic structure (F43c) has been detected, neither by X-rays, nor by neutron diffraction. An isomorphous phase transition was therefore proposed to occur at about 120K. Finally, also Raman effect and piezoelectric experiments clearly showed anomalies in that temperature range. Our piezoelectric measurements at the fundamental frequency and third overtone (of a length extensional mode) showed, however, that the anomaly shifted in temperature for a change of measuring frequency, thus suggesting an explanation in terms of defects rather than by an isomorphous transition. That is why more systematic measurements of dielectric constant (ε* = ε' – iε") versus temperature and frequency have been undertaken in this work. So far only a study of ε* versus frequency at 20°C, and of ε' and ε" vs. temperature at a fixed frequency has been reported for NiI.
EXPERIMENTS

For both the piezoelectric and dielectric experiments the same sample, cut out from a (100) growth pyramid of a vapour transport grown crystal, was used and had the following dimensions: \( l = 1.86\text{mm} \parallel [110]_c \), \( w = 0.66\text{mm} \parallel [110]_c \) and \( t = 0.118\text{mm} \perp [001]_c \). Gold wires (D. 40 \text{\mu}m) were attached to the centre of the electroded (semitransparent Au on Cr) (100) \(-\) faces. An Impedance Meter (HP 4815A), linked via a synthesizer and two digital voltmeters to a desktop computer, was used for the piezoelectric measurements by the techniques of admittance circle and motional capacitance. An LCR Meter (HP 4275A) directly connected to a computer served for dielectric measurements.

RESULTS

Figure 1a shows the piezoelectric series resonance frequencies of the fundamental mode and of the third overtone mode of the same crystal, (note that the sound velocity is \( V = 2.1 f_c \)). In Figure 1b, the internal mechanical losses \( (1/Q_m) \) are given also for the fundamental frequency and the third overtone. The absorption peak is clearly displaced in temperature. Figures 1c and 1d show the dielectric constant \( \varepsilon' \) and \( \varepsilon'' \), vs. temperature for some frequencies. Also here, the absorption peak is clearly displaced in temperature. Smaller absorption peaks \( (1/Q_m \) and \( \varepsilon'' \) ) are also observed between 10K and 20K.

DISCUSSION

By plotting \( \log \omega \) versus \( 1/T_p \), where \( \omega = 2\pi f \) (\( f \) = measuring frequency) and \( T_p \) the temperature of the peak of \( 1/Q_m \) or \( \varepsilon'' \) (\( \varepsilon'' = \frac{\pi}{2} \), since \( \varepsilon' = \text{const.} \)), a straight line is obtained (Fig. 2). In first approximation such a relationship can be explained by a Debye type relaxation mechanism, both for \( 1/Q_m \) and \( \varepsilon'' \). Then it follows that \( \ln \omega = -\ln \tau_0 - E/(kT_p) \), where \( \tau_0 \) is a relaxation time, \( E \) an activation energy and \( k \) Boltzmann's constant. Whereas the peak centred at 95K for \( f = 10\text{kHz} \), shifting to 152K for \( f = 6\text{MHz} \), can be attributed to a relaxation mechanism with \( E = 0.14 \text{eV}(1130 \text{cm}^{-1}) \) and \( \tau_0 = 7.8 \times 10^{-13} \text{s} \), the peak moving from 10K to 20K is characterized by \( E = 0.0092 \text{eV}(74 \text{cm}^{-1}) \) and \( \tau_0 = 1.9 \times 10^{-12} \text{s} \). Figure 3 shows a Cole-Cole plot for 128K. Figure 4 reveals, also for 128K, that the width of the peak is larger than 1.144 decade at half height. Both figures indicate a mechanism different from a true Debye-type relaxation with a single relaxation time. There is no doubt that the origin of these relaxations are defects (O\(_1\) - vacancies, impurities, . . .), and not phase transitions near 10K and 120K as previously claimed in the literature. No anomaly of \( P_s \), birefringence and Faraday rotation is observed near 10K; the only phase transition
FIGURE 1 Piezoelectric resonance frequencies of the fundamental and third overtone of a bar vs. T (a), internal mechanical loss (b), ε′ (c) and ε″ (d) for some frequencies. In (b) and (d) the shift of the absorption peaks for different frequencies are clearly evidenced.

FIGURE 2 log ω vs. 1/TP of the absorption peaks of 1/Qm and ε″.

FIGURE 3 Cole-Cole plot at 128K. A true Debye type relaxation would be a circle on the ε′-axis.

FIGURE 4 ε″ vs. log f at 128K. A mechanism with a single relaxation time would have a width, at half maximum, of 1.144 decade.
of NiI is that found at 61.5K \(^1\),\(^{12}\). It is noteworthy that NiBr shows no anomaly of whatsoever down to 4K \(^{15}\). This difference in behaviour between NiBr and NiI seems to be related to the frequent observation that iodine boracites tend to show strong "parasitic" birefringence and deep coloration in certain growth sectors \(^{16}\) — indicating a strong defect concentration — whereas in Br- and Cl-boracites such anomalies are usually weaker or hardly perceptible.

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