Evidence for the magnetoelectric effect in nickel-bromine boracite, Ni$_3$B$_7$O$_{13}$Br

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Abstract

A ferromagnetic/ferroelectric/ferroelastic phase, consistent with Point Group m'm2' and TC(f.m.) = 17 K, was identified by measurements of the magnetoelectric coeff. $\alpha_{32}$, peak value at TC (7 ps/m), and the ferromagnetic coercive field, Hc, vs. temp. A magnetoelectric effect persists above 17 K up to $\sim$30 K, indicating a phase of still unknown nature. The dielectric const. $\varepsilon_{33}$ is insensitive to magnetic ordering, but a striking anomaly of spontaneous polarization, Ps, occurs in the magnetic ordering range and is attributed to a spontaneous magnetoelectric interaction. Further, Ps is (290 nC/cm$^2$) at TC(f.e.).

Reference


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EVIDENCE FOR THE MAGNETOELECTRIC EFFECT IN NICKEL-BROMINE BORACITE, \( \text{Ni}_3\text{B}_7\text{O}_{13}\text{Br} \)

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Abstract A ferromagnetic/ferroelectric/ferroelastic phase, consistent with point group \( m'm2' \) and \( T_C(\text{f.m.}) = 17 \text{K} \), has been identified by measurements of the magnetoelectric coefficient \( a_{12} \), peak value at \( T_C(7 \text{ ps/m}) \), and the ferromagnetic coercive field, \( H_C \), versus temperature. A magnetoelectric effect persists above 17K up to \( \sim 30 \text{K} \) indicating a phase of still unknown nature. The dielectric constant \( \varepsilon_{33} \) is insensitive to magnetic ordering, but a striking anomaly of spontaneous polarization, \( P_s \), occurs in the magnetic ordering range and is attributed to a spontaneous magneto-electric interaction. Furthermore, \( P_s \) has its maximum value \( (290 \text{ nC/cm}^2) \) at \( T_C(\text{f.e.}) \).

INTRODUCTION
The 3d-metal boracites \( \text{M}_3\text{B}_7\text{O}_{13}\text{X} \), abbreviated \( \text{MX} \), with \( \text{M} = \text{Fe, Co, Ni, Cu} \) and \( \text{X} = \text{Cl, Br, I} \), have weakly ferromagnetic/ferroelectric/ferroelastic phases 1,2,3,4 except for \( \text{CuI} \), for which no data are as yet available. This paper reports magnetoelectric and dielectric data on \( \text{NiBr} \) which - on the basis of Faraday effect and domain switching properties - was believed to have Shubnikov point group \( m'm2' \) at low temperature 4.

SAMPLE PREPARATION
For the measurement of \( a_{12}(T) \), \( H_C(T) \), \( \varepsilon_{33}(T) \) and \( P_s(T) \), the same ferroelectric single domain sample, prepared at room temperature from an unpoled virgin crystal, was used: (100)\( _{c} \)-platelet, thickness \( t = 84 \mu \text{m} \), surface \( S = 1.795 \text{mm}^2 \), with \( P_s \perp \) surface, hence orthorhombic indicatrix principal section \( n_y/n_\alpha \) in the plane of the platelet, electroded with transparent gold.

MAGNETOELECTRIC MEASUREMENTS (ME)_H

Linear magnetoelectric coefficient : \( a_{12} \). In this paper the same coordinate system as that described in detail for the magnetoelectric measurements of \( \text{NiCl} \) 5 is adopted, because the same correlation between the orientations of \( P_s \), \( M_s \) and the optical indicatrix
was deduced for NiBr as found for NiCl: \[ P_3 = \alpha_{32} H_2 \]
\[ (P_3//P_s//n, H_2//M_s//n_Y) \]. For the supposed point group \( m'm2' \) of NiBr, two coefficients of the linear magnetoelectric effect, labelled \( \alpha_{32} \) and \( \alpha_{23} \) in the adopted system, are allowed. So far it was only possible to isolate a single domain sample (see above) permitting the measurement of \( \alpha_{32} \). The measurement technique adopted was similar to that described earlier. A He-flow cryostat served for cooling the sample down to 1.5K, a Varian 12" magnet allowed to increase/decrease the magnetic field linearly in time. An electrometer (Keithley 642) served for charge measurements. The results are given in figure 1. The temperature dependence of \( \alpha_{32} \) is characterised by a sign reversal at about 9K and a peak value of 7 ps/m, reached at \( \sim 16.5K \). Above that temperature the magnetoelectric signal drops sharply to about 36% of the peak value and decreases smoothly to reach zero at about 30K. The peak of \( \alpha_{32} \) of NiBr resembles the peak of \( \alpha_{32} \) of NiCl at 9K, the temperature at which \( \sim \) 6 and the Faraday effect of NiCl disappear. 

**Ferromagnetic coercive field, \( H_c \).** Figure 2 shows the ferromagnetic coercive field versus temperature, which has been measured by the "butterfly" loop technique. Figure 3 gives some examples of loop. We note that on crossing the temperature of sign reversal of \( \alpha_{32} \) (\( \sim 9K \)) the loop turns upside down! The remarkable feature of \( H_c \) is that it tends sharply to zero at \( \sim 16.8K \), practically the same temperature at which \( \alpha_{32} \) reaches its maximum. From this coincidence it is concluded that 17K marks the Curie point of a ferromagnetic phase.

**DIELECTRIC MEASUREMENTS**

The dielectric constant \( \varepsilon' \) of the ferroelectric orthorhombic phase of NiBr has been measured at 300kHz and 36Vrms/cm from 1.5 to 440K using an impedance analyzer (HP4192A) (Fig.4). Its value is very small (about \( 7 \) at 1.5K) and no anomaly whatsoever is seen in the temperature range of magnetic ordering (at variance with the case of \( \varepsilon \) for CuBr), nor any anomaly due to defects as found for NiI. The change of spontaneous polarization with temperature has been measured between 1.5 and 400K upon heating, using an electrometer (Keithley 616) in the charge mode (Fig. 5 and Fig. 6). Leaving aside the unusual temperature dependance of \( P_s \), which is not yet understood, a strong anomalous change of \( P_s \) is found below 28K. It is noteworthy that the \( P_s(T) \) curve is marked by kinks at \( \sim 17K \), the temperature of \( T_C(f.m.) \) and at 28K, where \( \alpha_{32} \) tends to zero. The peak values of \( P_s \) and \( p \) (pyroelectric coefficient), 290 nC/cm\(^2\) and \( \sim 5.0 \) nC/(K cm\(^2\)), respectively, are obtained at \( T_C(f.e) \), in agreement with \( P_s(T) \) of MgCl but disagree with previously calculated temperature dependence of \( P_s \) for NiBr.
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FIGURE 1 ME-coefficient $\alpha_{32}$ of NiBr ($H//n_y$) vs.temperature

FIGURE 2 Ferromagnetic coercive field $H_c$ of NiBr vs.temperature deduced from butterfly loops.

FIGURE 3 Some examples of magnetoelectric butterfly loops of NiBr.

FIGURE 4 Dielectric constant $\varepsilon_{33}$ of NiBr vs.temperature

FIGURE 5 Spontaneous polarization $P_s$ of NiBr vs.temperature ($\sim$ 4K/min)

FIGURE 6 Detail of the spontaneous polarization $P_s$ of NiBr vs.temperature in the region of the magnetic phase transitions. Arrows show sens of (ME)$_H$ signal, at $|H|/|H_c|$.
CONCLUSIONS

It is concluded that a ferromagnetic phase exists below $T_C(f.m.) = 17K$, its properties being consistent with Shubnikov group $m'm2'$. Above 17K up to about 30K, another magnetically ordered phase exists. A similar behaviour above $T_C(f.m.)$ (9K) of NiCl was interpreted as an antiferromagnetic phase $mm2\tilde{5}$. Such an interpretation for NiBr would, however, be at variance with the observation of a Faraday effect above 17K 4. There seems little doubt that the strong anomaly of $P_s$ found for NiBr below 28K is caused by a kind of spontaneous magnetoelectric coupling.

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