Low temperature magnetoelectric effects on Co3B7O13I

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Abstract

A linear and a quadratic magnetoelectric effect have been detected in cobalt-iodine boracite (Co3B7O13I). Second order $\alpha_{32}$ (linear effect) and third order $\beta_{311}$ and $\beta_{322}$ (quadratic effect) magnetoelectric coefficients have been measured vs. temp. from 4 K to 70 K. The coefficients obtained at 4 K are given.

Reference


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LOW TEMPERATURE MAGNETOELECTRIC EFFECTS ON \(\text{Co}_3\text{B}_7\text{I}_{13}\).

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Abstract A linear and a quadratic magnetoelectric effect have been detected in cobalt-iodine boracite (Co, B, 0, I). Second order \(\alpha_{32}\) (linear effect) and third order \(\beta_{311}\) and \(\beta_{322}\) (quadratic effect) magnetoelectric coefficients have been measured versus temperature from 4 K to 70 K. The values of the coefficients obtained at 1.4 K are: \(\alpha_{32} = 4.17 \times 10^{-1}\) s.m, \(\beta_{311} = -3.0 \times 10^{-18}\) s.A, \(\beta_{322} = -1.79 \times 10^{-17}\) s.A and \(\beta_{333} = -1.7 \times 10^{-19}\) s.A.

INTRODUCTION

Below 200 K, cobalt-iodine boracite \(\text{Co}_3\text{B}_7\text{I}_{13}\) (Co-I boracite) has orthorhombic symmetry mm21, 1,2, and undergoes a weak ferromagnetic transition 3 at 37.5 K. The magnetoelectric effect in Co-I boracite has been discovered by Baturov et al 3,4. However, because the conductivity of the sample, these authors were unable to create a ferroelectric single domain by poling the crystal, even in a field of 40 KV/cm, and their measurements, which have been performed on a polycrystalline state single crystal, have not permitted to determine the contributions of the independent magnetoelectric coefficients. In our work, a ferroelectric single domain of a (001) orth cut platelet has been used, and the second and third order magnetoelectric coefficients \(\alpha_{32}, \beta_{311}, \beta_{322}\) and \(\beta_{333}\) measured as a function of temperature (1/\([100]_\text{orth}\), 2/\([010]_\text{orth}\) //spontaneous magnetization \(M_s\) and 3/\([001]_\text{orth}\) //spontaneous polarization \(P_s\)).

EXPERIMENTAL

A single crystal of Co-I boracite was grown by chemical vapour transport 5. The final dimensions of the prepared sample were approximately 1.6 x 0.7 x 0.15 mm 3. For optical control under a
polarising microscope, semi transparent gold electrodes were evaporated onto the principal (001)_{orth} faces. Quasistatic and dynamical methods$^6$ were used to detect the electric charges induced on the (001)_{orth} faces by an applied magnetic field. Prior to the magnetoelectric measurements, the sample has been poled and cooled down through the ferroelectric transition in an electric field of 20 KV/cm. On the basis of optical observations, measurements of birefringence$^7$ and spontaneous polarization versus temperature (Fig.1), it has been assumed that the crystal presented a ferroelastic/ferroelectric single domain state. The value of the spontaneous polarization measured on our sample, was about fifteen times and fifty times higher than that reported by Smutny et al$^8$ and Drozhdin et al$^9$, respectively. The high value of spontaneous polarization, and the optically controlled single domain state, prove the good quality of our crystal.

FIGURE 1 Spontaneous polarization $P_s$ versus temperature. Inset shows detail of $P_s$ near the weak ferromagnetic transition at 37.5 K.
RESULTS AND DISCUSSION

Onto the (001)$_{\text{orth}}$ faces, perpendicular to the polar direction of the crystal, induced electric charges were detected versus applied magnetic field rotating in a (001)$_{\text{orth}}$ plane (Fig. 2). At constant temperature,

\[
Q[C] = 3.06 \times 10^{-11} \text{C}
\]

\[
T = 4.14 \text{K}
\]

\[
\theta = -40^\circ
\]

\[
Q[C] = 1.7 \times 10^{-11} \text{C}
\]

\[
T = 4.14 \text{K}
\]

\[
\theta = +40^\circ
\]

\[
H[\text{KOe}]
\]

\[
H[\text{KOe}]
\]

(a) \hspace{1cm} (b)

**FIGURE 2** Induced electric charges $Q$ versus applied magnetic field $H$. Electric charges are detected on the (001)$_{\text{orth}}$ faces.

(a) The magnetic field is applied in the [\(\bar{0}10\)]$_{\text{orth}}$ direction, linear and quadratic magnetoelectric effect appeared.

(b) The magnetic field is applied in the [100]$_{\text{orth}}$ direction, a pure quadratic magnetoelectric effect is detected.

and at a determined value of the magnetic field, the experimental points of the induced polarization can be fitted by an expected function, the variable of which is the angle $\theta$, formed between the field direction and the reference axis (Fig. 3). For the m'm2' symmetry and our choice of axes, the expected function is:

\[
P_3 = \alpha_3 H_2 + \beta_{331} H_1^2 + \beta_{332} H_2^2 + \beta_{333} H_3^2,
\]

which is reduced to

\[
P_3 = \alpha_3 H_2 + \beta_{331} H_1 + \beta_{332} H_2\]

when the magnetic field rotates in a (001)$_{\text{orth}}$ plane. For different temperature values in the ferromagnetic phase, the results are well consistent with the magnetic symmetry m'm2' (Fig. 3). The second order magnetoelectric coefficient $\alpha_3$ was determined by fitting the induced polarization as a function of magnetic field, at different temperatures (Fig. 4 (a)). These results, obtained for the first time on Co-I boracite
are rather similar to those obtained on Co-Br boracite\(^6\). Dynamical measurements of \(\alpha_{32}\) by detecting continuously versus temperature the electric charges induced by an a.c magnetic field, with magnitude and frequency of about 10 Oe and 160 Hz, respectively, yield the same curve (Fig.4 (b)). The third order magnetoelectric coefficients \(\beta_{311}\) and \(\beta_{322}\) as a function of temperature, have been extracted from the quasistatic measurements (Fig.5 (a), (b)). The coefficient \(\beta_{333}\) has been calculated at 4 K by fitting the experimental points of induced polarization, when the magnetic field rotates around \([100]\)\text{orth}\ direction (Fig.6). At 4 K, the calculated value of \(\beta_{333}\) is \(-1.7 \times 10^{-19} \text{ s.A}^{-1}\).

**FIGURE 3** Induced polarization versus applied magnetic field angle \(\theta\). The experimental points are fitted by the expression: 
\[ P_3 = \alpha_{32} H_2 + \beta_{311} H_1 + \beta_{322} H_2 (1 \text{ // } [100] \text{ orth}, 2 \text{ // } [010] \text{ orth } \text{ // } H_1, 3 \text{ // } [001] \text{ orth } \text{ // } P_3).\]

The selected value of the magnetic field is 70 Koe. H rotated around \([001]\)\text{orth}\ direction. (a), (b) and (c), the measurements are obtained at 4.74 K, 18.97 K and 31.94 K, respectively.
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\[ \frac{dI}{dt} = \frac{5}{mn} \]

\[ \alpha_{32} \]

FIGURE 4 Quasistatic (a) and dynamical (b) measurements of the second order magnetoelectric coefficient \( \alpha_{32} \) versus temperature.

\[ \beta_{311} \]

\[ \beta_{322} \]

FIGURE 5 Quasistatic measurements of the third order magnetoelectric coefficients \( \beta_{311} \) (a) and \( \beta_{322} \) (b), versus temperature.
FIGURE 6  Induced polarization $P$ versus applied magnetic field angle $\theta$. The magnetic field is rotated around [100] direction with a selected value of 10 KOe. The measurements are obtained at 4.01 K, and the experimental points are fitted by the expression:

$$P_3 = \alpha_3 H_2 + \beta_3 H_2^2 + \gamma_3 H_2^3.$$  

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