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Reference

DOI: 10.1051/jphyscol:19888383

Available at:
http://archive-ouverte.unige.ch/unige:33099

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LINEAR AND QUADRATIC MAGNETOELECTRIC (ME) EFFECTS IN COPPER CHLORINE BORACITE

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Abstract. - The magnetoelectric effect, on a (001) orthorhombic cut Cu-Cl boracite crystal (Cu$_3$B$_7$O$_{13}$Cl) shows linear and second order components. At 4 K, with $P_{\text{induced}} = \alpha_{33} H_3 + (\beta_{311} H_1^2 + \beta_{322} H_2^2 + \beta_{333} H_3^2) / 2$, one obtains: $\alpha_{33} = 1.2 \times 10^{-13}$ [C/m], $\beta_{311} \approx 0$, $\beta_{322} = 3.6 \times 10^{-19}$ [C/A] and $\beta_{333} = -1.2 \times 10^{-19}$ [C/A], the signs being understood relative to one another. These results, together with the observation of ME butterfly loops, corroborate magnetic point group m'm'2, as deduced from magnetic torque measurements (M. Haida et al., 1975).

1. Introduction

The Cu-Cl boracite transforms at about 365 K from a cubic (43m1') to an orthorhombic (mm21') paramagnetic ferroelectric/ferroelastic phase and becomes a weak ferromagnet at about 8.4 K [1, 2]. Measurements of magnetic torque and dynamic ME effect at 4.2 K have shown [2] that the spontaneous magnetization $M_s$ lies parallel to the spontaneous polarization $P_s$ [001] suggesting the magnetic point group to be m'm'2, in contrast to several other ferroelectric/ferromagnetic orthorhombic boracites which are characterized by the magnetic point group m'm'2'. Measurements of magnetic field induced charges (MEH), consistent with the notation of reference [4], are found to be of comparable order of magnitude so that both have to be taken account of, in contrast to reference [2] in which only the linear effect was inferred.

The ME terms of the density of stored free enthalpy of a crystal, $g(T, E, H)$, at zero mechanical stress (with $T$ the temperature, $E$ the electric field and $H$ the magnetic field intensity) is given by

$$-g = \alpha_{ik} E_i H_k + (\alpha_{ijk} H_j E_k + \beta_{ijk} E_i H_j H_k) / 2$$

with the notation of reference [4].

The total magnetic field induced polarization (at $E = 0$) is obtained by

$$P_i = -\partial g / \partial E_i = \alpha_{ik} H_k + (\beta_{ijk} H_j H_k) / 2$$

where $\alpha_{ik}$ and $\beta_{ijk}$ are the coefficients of the linear and second order magnetoelectric effect, respectively. Using a coordinate system with axes 1, 2 and 3 the only non-vanishing coefficients of the linear ME effect for point group m'm'2' are $\alpha_{23}$ and $\alpha_{32}$ with 1.m', 2 || M$_s$ and 3 || P$_s$, whereas for point group m'm'2 with P$_s$ and M$_s$ colinear along axis 3, the only allowed linear coefficients are $\alpha_{11}$, $\alpha_{22}$ and $\alpha_{33}$ (diagonal tensor) [5].

The tensor $\beta_{ijk}$ of the second order ME effect has the same form [6] as that of the piezoelectric tensor $d_{ijk}$ [7]. The three point groups m'm'2', m'm'2 and mm21' have the same set of non-vanishing coefficients, i.e. $\beta_{311}$, $\beta_{322}$, $\beta_{333}$, $\beta_{223}$ and $\beta_{113}$. When numerical data of $\beta_{ijk}$ are given, care is recommended with a view to take correctly account of the factor 1/2 in the various definitions. Since the boracite platelets used had P$_s$ perpendicular to the platelet, the relevant equations are

$$P_3 = \alpha_{33} H_1 + (\beta_{311} H_1^2 + \beta_{322} H_2^2 + \beta_{333} H_3^2) / 2$$

with $i = 2$ for m'm'2' and $i = 3$ for m'm'2, where $P_3$ is the polarization induced by the applied magnetic field and, for guidance, let us underline that for boracites it is two to four orders of magnitude smaller (for a field of e.g. 5 kOe) than the spontaneous polarization $P_s$ which is oriented along the same axis 3. One obtains the coefficients $\alpha_{32}$ or $\alpha_{33}$ and the $\beta_{3ij}$'s by measuring the induced charges $Q (P_3 = Q(S)$, where $S$ is the surface of the platelet) with an electrometer, e.g. Keithley 642 LNFP.

It is the advantage of the MEH effect that no calibration is needed in contrast to the less convenient inverse effect, i.e. the electric field induced magnetoelectric effect (ME$_E$).

2. Sample preparation and experiments

The single crystals of Cu-Cl boracite were prepared by gas phase transport [8]. The measured sample was a (001)$_{\text{ortho}}$ single domain platelet (area 5.37 mm$^2$, thickness 80 [m]), electroded with semi-transparent gold on chromium and with P$_s$ perpendicular to the surface. The single domain state was optically checked by means of a polarizing microscope (refractive index $n_\beta < n_\alpha < n_\gamma$).

Figure 1a shows the induced charge as a function of time for $H || P_s || n_\beta$ || 3, uncorrected for the drift. Figure 1b represents the induced charge versus time for $H$ perpendicular to $P_s$ and parallel to the crys-
tallographic b-axis (n_3). Note the reversible jump at
H > 10 [kOe], probably due to spin reorientations.
This phenomenon will be treated in a forthcoming pap­
er. After correction for the drift, the curves can be
fitted with a polynomial of the form
\[ y_i = a x_i + b x_i^2 \]
where \( x_i \) are 1, ..., 10 [kOe] and \( y_i \) the corresponding
induced charges.

Let \( \mathbf{X} = (x_i, x_i^2) \) be a rectangular matrix and \( \mathbf{C} = (a, b, y_i) \) a 2-vector and a N-vector, respectively,
one has \( \mathbf{Y} = \mathbf{X} \cdot \mathbf{C} \) giving \( \mathbf{C} = (\mathbf{X}^\top \mathbf{X})^{-1} \mathbf{X}^\top \mathbf{Y} \), where
\( \mathbf{X}^\top \) is the transposed matrix of \( \mathbf{X} \) and \( \cdots \)^{-1} an inverse
matrix. Thus one obtain the linear and second order
magnetoelectric coefficients.

In the case of figure 1a (H || P_\text{a}) \( a \neq 0 \), i.e. \( \alpha_{33} \) is
not zero, consistent with the symmetry m'm'H deduced
earlier from magnetic torque measurements, whereas
in the case of figure 1b, \( a \approx 0 \), i.e. \( \alpha_{33} \approx 0 \).

As a final result we obtain at 4 K (remembering that: 1 [A/m] (\rightarrow) \( 4\pi \times 10^{-3} \) [Oe])
\[
\begin{align*}
\alpha_{33} &= 1.2 \times 10^{-13} \text{[s/m]} , \quad \beta_{311} \approx 0 \\
\beta_{322} &= 3.6 \times 10^{-10} \text{[s/A]} , \quad \beta_{333} = -1.2 \times 10^{-19} \text{[s/A]}
\end{align*}
\]
The accuracy is of the order of 5% to 10%. The
given signs are to be understood relative to one an­
other, but have not yet been correlated with the sense
of the spontaneous polarization.

3. Discussion

First, we note that \( \alpha_{33} \) is very small, i.e. about
30 times smaller than \( \alpha_{32} \) of Ni-Cl boracite [4], even
about 70 times smaller than \( \alpha_{32} \) of Co-Br boracite [9]
but 20 times larger than was found in reference [2] for
Cu-Cl boracite (also from a Geneva synthesis): \( \alpha_{33} \)
(Ref [2]) = \( 2 \times 10^{-19} \) [cgs], at 4.2 K, or else by dividing
by the speed of light (\( c = 3 \times 10^8 \text{[m/s]} \)), one obtains:
\( \alpha_{33} \) (Ref [2]) = \( 6.8 \times 10^{-15} \) [s/m].

Second, the method used in reference [2] is a dy­
namic one which may hide the real nature of the ME
effect if a quadratic effect is superposed on the linear
one, in particular when the dynamic a.c. ME experi­
ment is not run as a function of \( H_0 \) or not com­ple­
mented by quasi-steady measurements.

Let be \( \mathbf{P}_{\text{induced}} = \alpha H + \beta H^2 / 2 \), with \( H = H_0 +
h \sin (\omega t) \), one obtains:
\[
\mathbf{P}_{\text{induced}} = \mathbf{P}_0 + \mathbf{P}_\omega \sin (\omega t) + \mathbf{P}_2 \omega \cos (2\omega t)
\]
where \( \mathbf{P}_\omega = (\alpha + \beta H_0) \mathbf{h} \) and \( \mathbf{P}_{2\omega} = -\beta h^2 / 4 \). One can see that \( \alpha \) is increased or reduced by \( \beta H_0 \), depending
on the relative signs of \( \alpha \) and \( \beta \). Using our values
for \( \alpha_{33} \), \( \beta_{333} \) and the value \( H_0 = 6.8 \) [kOe] given on
figure 2 of reference [2], the two experiments are more
consistent.

Third, the observation of MEH “butterfly loops” on
our Cu-Cl boracite sample – demonstrated e.g. also
for Ni-Cl boracite [4] –, also confirms that \( M_a \parallel \mathbf{P}_s \).

Fourth, the measurement of the charges as a func­tion
of \( H \) and temperature (for \( H \parallel \mathbf{P}_s \)) has been un­
tertaken but was difficult because of the smallness of
the MEH signal compared with the pyroelectric one
due to \( \mathbf{P}_s \) perpendicular to the electrodes and the insuffi­
cient temperature stability of the sample. Never­
theless the MEH signal seems to disappear at about
8.5 K.

Fifth, at 4 K and at a field of about 8 [kOe] and
above – depending on the magnetic field direction – a
new magnetic field induced phase transition has been
detected by means of the ME effect. For example,
with \( H \parallel \mathbf{P}_s \), the linear effect disappears abruptly at a
critical field and the quadratic one changes sign. More
detailed experiments at higher fields are planned in
order to clarify this point for Cu-Cl boracite crystals.

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