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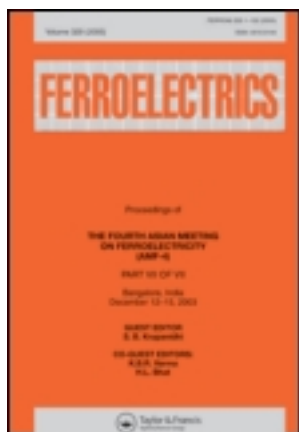
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MAGNETOELECTRIC EFFECT IN Co–Cl BORACITE

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The ferromagnetoelectric boracite $\text{Co}_3\text{B}_7\text{O}_{13}\text{Cl}$ has been investigated on (111) cubic cut single crystal platelets in its low temperature monoclinic ferroelectric/ferroelastic/weakly ferromagnetic phase. These platelets were electroded and poled by a thermal process or by the application of a high enough electric field to get a “ferroelectric/ferroelastic nearly single domain” with polarization along the $\langle 111 \rangle_{\text{cub}}$ direction perpendicular to the platelets. Magnetoelectric measurements were performed on these platelets in the temperature range 1.5–40 K and up to an applied magnetic field of 10 kOe. The induced polarization, at a dc magnetic field of 0.5 kOe, which is proportional to the coefficient of the linear magnetoelectric effect, shows an anomaly at about 11.3 K. With further increase in temperature, a sharp change at nearly 12 K corresponding to the Néel temperature was observed. The coefficient α_{32} of the linear magnetoelectric effect, measured quasi-statically at 4.2 K, is about 13 ps/m ($\sim 3.9 \times 10^{-3}$ in Gaussian units). The ferromagnetic domain switching with the angular variation of magnetic field is consistent with the monoclinic Shubnikov point group m . The coercive field as a function of temperature measured magnetoelectrically shows an exponential behaviour.

Keywords: Co–Cl boracite; magnetoelectric effect; weak ferromagnetism; magnetic transition; coercive field; domains

1. INTRODUCTION

Boracites with general formula $\text{M}_3\text{B}_7\text{O}_{13}\text{X}$ (M = divalent metals like Mn, Fe, Co, Ni, etc. and X = Cl, Br or I) are one of the classes of materials known for their interesting ferroelectric, ferroelastic, weakly ferromagnetic and magnetoelectric (ME) properties^[1, 2]. These boracites exhibit several successive phase transitions when the temperature is lowered from their high

temperature non-ferroelectric cubic phase. In the case of $\text{Co}_3\text{B}_7\text{O}_{13}\text{Cl}$ (hereafter Co–Cl), there are four phase transitions,

$$\bar{4}3m1' \xrightarrow{\sim 623\text{ K}} mm21' \xrightarrow{\sim 538\text{ K}} m1' \xrightarrow{\sim 468\text{ K}} 3m1' \xrightarrow{\sim 12\text{ K}} m.$$

The first three are structural transitions leading to fully ferroelectric/ferroelastic phases. The transition at about 12 K from trigonal to monoclinic (Shubnikov point group m) is a magnetic transition due to essentially antiferromagnetic ordering. Thus, the coexistence of ferroelectricity, ferroelasticity and weak ferromagnetism is found in this low temperature phase.

First observations of the ME_H effect (i.e., the polarization induced due to applied magnetic field) on electrically poled Co–Cl boracite were reported by Schmid^[3] in 1973. Later, the studies on the ME_E effect (i.e., the magnetization induced due to applied electric field) reported on the Co–Cl boracite at 4.2 K by Baturov *et al.*^[4] show an anomaly at about 11 K which is just below the magnetic phase transition temperature. Clin *et al.*^[5] found a “Schottky type” specific heat anomaly just below the magnetic phase transition temperature. On the other hand, the measurements like spontaneous Faraday rotation, spontaneous polarization and dielectric constant as a function of temperature did not reveal any such anomaly^[6].

In this article, the results obtained from the ME measurements performed on Co–Cl boracite in its low temperature monoclinic phase are presented.

2. EXPERIMENTAL TECHNIQUES

2.1. Sample Preparation and Ferroelectric Poling

The $\text{Co}_3\text{B}_7\text{O}_{13}\text{Cl}$ boracite single crystals were grown by gas phase transport^[7]. Two thin platelets with a thickness of 30 μm were cut parallel to a cubic (111) plane and thinned by polishing. The area of the platelets is 1.85 mm^2 and 2.81 mm^2 for platelet #1 and #2, respectively. Thin transparent gold electrodes were deposited on both (111)_{cub} faces by thermal evaporation using a thin film coating unit. The platelets were heated to the temperature of 150°C during the deposition of the gold films to get a better adherence of these films. Gold wires of 40 μm diameter were attached to these electrodes using electrically conductive two-component silver epoxy. For the platelet #1, a single domain was obtained accidentally, when heating the platelet to a temperature of about 150°C during the deposition of the gold film electrodes. This probably happened due to the

removal of strains produced while polishing the crystal. The platelet #2 was poled by the application of an electric field of about 550 kV/cm to get a nearly ferroelectric/ferroelastic single domain. During this process the platelet was immersed in silicon oil which was maintained at an elevated temperature of about 250°C. The changes in domain states during the poling process were monitored simultaneously using polarized light microscope.

2.2. ME_H Measurements

Magnetoelectric measurements were carried out on these platelets in the temperature range 1.5–40 K and up to an applied magnetic field of 10 kOe. These measurements were performed using both dynamic and quasi-static techniques^[8]. In the case of the measurements using the dynamic technique, the frequency of the ac field used was 163 Hz. An ac amplitude of 230 mV_{pp} was applied providing a magnetic field of 13 Oe_{rms}. A Hewlett-Packard 3325 A synthesizer was used for generating the aforesaid ac signal and a power amplifier for amplification. The amplified signal was fed to a pair of modulating coils, in the Helmholtz geometry, kept between the pole pieces of a dc electromagnet. A Stanford SR530 Lock-in-amplifier was used to detect the induced ac signal at the same frequency as that of the modulated field. The dc magnetic field was applied along a $\langle 110 \rangle_{\text{cub}}$ direction lying in the $(111)_{\text{cub}}$ plane of the poled platelet to obtain a ferromagnetic single domain. The quasi-static measurements were performed by sweeping the magnetic field at a constant rate of about 4 kOe/min. A Keithley 642 Electrometer was used to measure the induced charges due to the ME_H effect. The coercive field was also measured magnetoelectrically using the quasi-static method in the forward and reverse directions of the magnetic field. A Janis 8DT liquid helium cryostat and a LakeShore DRC 91C low temperature controller were used to perform the experiments at low temperatures. The sample temperature was measured independently using a calibrated LakeShore carbon-glass resistor.

3. PHENOMENOLOGICAL CONSIDERATIONS OF THE ME EFFECT

The general expression, in SI units, for the density of stored free enthalpy which includes the linear and bilinear magnetoelectric effects is given by,

$$-g(\mathbf{E}, \mathbf{H}; T) = \cdots + \alpha_{ij} E_i H_j + \frac{1}{2} \beta_{ijk} E_i H_j H_k + \cdots \quad (1)$$

where α_{ij} and β_{ijk} are linear and bilinear ME coefficients, respectively and \mathbf{E} and \mathbf{H} represent electric and magnetic field vectors, respectively. By differentiating $-g$ with respect to T , E_i and H_j , one obtains the density of entropy, the polarization and the magnetization respectively (for e.g. ref. [3]). The definitions of these terms are described in the article by Rivera^[8]. Thus, the functional form for the magnetic field induced polarization could be described as

$$P_i = -\frac{\partial g}{\partial E_i} = \cdots + \alpha_{ij}H_j + \frac{1}{2}\beta_{ijk}H_jH_k + \cdots \quad (2)$$

where the first and second terms represent the linear and bilinear ME effect. The permissible non-zero components of the tensors α_{ij} and β_{ijk} could be derived from the magnetic point group. The 58 magnetic point groups permitting the linear magnetoelectric effect^[9] (corrected tables are given by Rivera^[8]) and the coefficient β_{ijk} of the bilinear effect^[10] which has the same form as the piezoelectric one^[11, 12] are well known.

For the weakly ferromagnetic phase of Co-Cl, the monoclinic Shubnikov point group m was postulated^[3]. Thus, the components of the total polarization for this symmetry are given by

$$P_1 = \alpha_{12}H_2 + \frac{1}{2}[\beta_{111}H_1^2 + \beta_{122}H_2^2 + \beta_{133}H_3^2 + \beta_{113}H_1H_3] \quad (3)$$

$$P_2 = \alpha_{21}H_1 + \alpha_{23}H_3 + \frac{1}{2}[\beta_{223}H_2H_3 + \beta_{212}H_1H_2] \quad (4)$$

$$P_3 = \alpha_{32}H_2 + \frac{1}{2}[\beta_{311}H_1^2 + \beta_{322}H_2^2 + \beta_{333}H_3^2 + \beta_{313}H_1H_3] \quad (5)$$

Though the linear ME effect vanishes in the paramagnetic region, i.e., above the Néel temperature, the persistence of the bilinear effect is allowed by the Shubnikov point group $3\ m1'$ with a different set of bilinear coefficients. Those components of the total polarization, in this case, are

$$P_1 = \frac{1}{2}[\beta_{111}(H_1^2 - H_2^2) + \beta_{113}H_1H_3] \quad (6)$$

$$P_2 = \frac{1}{2}[\beta_{113}H_2H_3 - 2\beta_{111}H_1H_2] \quad (7)$$

$$P_3 = \frac{1}{2}[\beta_{322}(H_1^2 + H_2^2) + \beta_{333}H_3^2] \quad (8)$$

Hence, to evaluate the possible coefficients from the experimental investigations, it is necessary to obtain platelets with a ferroelectric single domain state whose polarization has the required orientation. It is also necessary to select a proper coordinate system.

3.1. Reason for Perparing (111)_{cub} Cut Platelet

In the case of trigonal boracites such as Co–Cl, characterized by the Aizu species ^[13] $\bar{4}3m1'F3m1'$, one cannot obtain 180° reversal of the spontaneous polarization due to symmetry reasons^[14]. However, a reorientation of the spontaneous polarization to one of the other three possible $\langle 111 \rangle_{\text{cub}}$ directions can be performed. Hence, it is possible to obtain the ferroelectric single domain state in electroded (111)_{cub} and (110)_{cub} cut platelets for one of the two possible electric field polarities. In this article, the results obtained on (111)_{cub} platelets in the ferroelectric single domain state, whose polarization direction is perpendicular to the platelet, are presented.

3.2. Selection of Coordinate System

The coordinate system has been chosen (for Shubnikov point group m), with axis 1 $\parallel \langle 112 \rangle_{\text{cub}} \parallel m$, axis 2 $\parallel \langle \bar{1}10 \rangle_{\text{cub}} \perp m$, axis 3 $\parallel \langle 111 \rangle_{\text{cub}} \parallel \mathbf{P}_s$. Experiments were performed by keeping $H_{\text{dc}} \parallel H_{\text{ac}} \parallel$ axis 2 and therefore, in this case, $H_1 = H_3 = 0 \neq H_2$. The magnetic field induced polarization P_3 was measured along axis 3. By incorporating these conditions in relations (5) and (8), we obtain,

$$P_3 = \alpha_{32} H_2 + \frac{1}{2} \beta_{322} H_2^2 \quad (\text{weakly ferromagnetic state}) \quad (9)$$

$$P_3 = \frac{1}{2} \beta_{322} H_2^2 \quad (\text{paramagnetic state}) \quad (10)$$

It should be noticed that the bilinear coefficient β_{322} is the same for both the weakly ferromagnetic and the paramagnetic states.

4. RESULTS AND DISCUSSION

4.1. ME_H Data

The results of magnetoelectric measurements performed on platelets #1 and #2 using the dynamic as well as the quasi-static methods, are presented here.

Figure 1 shows the temperature variation of the magnetic field induced polarization for the platelet #1 with $H_{dc} \parallel H_{ac} \parallel \langle \bar{1}10 \rangle_{\text{cub}}$, i.e., along axis 2, measured by the dynamic technique. The data were taken while heating the sample which was previously cooled under a dc magnetic field of 1 kOe also along axis 2, in order to obtain a ferromagnetic single domain. It can be seen from the figure that the induced polarization measured at a dc magnetic field of 0.5 kOe shows an anomaly (indicated by arrow) at about 11.3 K. This indicates that the temperature variation of α_{32} exhibits such an anomaly, since the induced polarization is proportional to the linear magnetoelectric coefficient α_{32} . Baturov *et al.* [4] have also reported a similar anomaly from

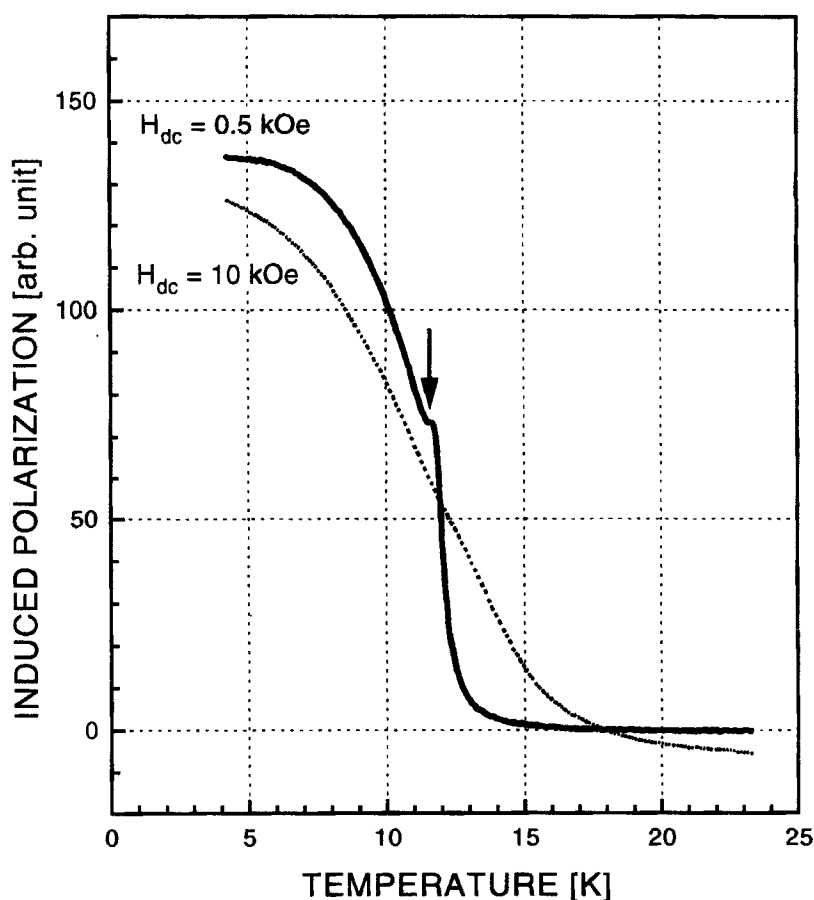


FIGURE 1 Temperature dependence of the induced polarization measured by the dynamic technique. The arrow indicates the anomaly observed just below T_N .

ME_E effect measurements on ferroelectric polydomain single crystal platelets. However, a corresponding anomaly was not observed in other measurements like the temperature variation of spontaneous Faraday rotation, spontaneous polarization and dielectric constant reported by Mendoza *et al.*^[6]. On the other hand, Clin *et al.*^[5] have reported a “Schottky type” specific heat anomaly, in the form of a shoulder, at about 9 K which is just below the Néel temperature. They found such an anomaly in the case of Co₃B₇O₁₃Br (Co-Br) as well. Their earlier magnetoelectric measurements^[15] on Co-Br showed an abrupt change in the magnetoelectric signal, in the same temperature range at which the specific heat anomaly was observed. Recent magnetization measurements on Co-Br using a vibrating sample magnetometer, carried out by Senthil Kumar *et al.*, have also shown an anomaly in the same temperature range. Neutron diffraction results on Co-Br also indicated two different magnetic structures, below and above the temperatures at which the anomaly was observed^[17]. All these results suggest that the magnetoelectric anomaly and the specific heat anomaly observed in the Co-Cl boracite may also have the same origin. Probably these anomalies are the manifestation of a change in the magnetic structure which is yet to be resolved.

With further increase in temperature, a sharp change at nearly 12 K corresponding to the Néel temperature (T_N) is observed in the measurements performed at 0.5 kOe. Above T_N , the induced polarization becomes almost zero. However, it is noteworthy that a sharp specific heat peak^[5] measured at zero magnetic field coincides exactly at the temperature where the above anomaly of the linear ME effect at 0.5 kOe has been observed. On the contrary, the data of the ME effect taken at a field of 10 kOe falls smoothly near the transition temperature without showing any anomaly. The cause for this smooth change is the effect of high magnetic field. Moreover, the induced polarization does not become zero, rather it becomes negative, above T_N indicating the presence of a bilinear effect.

Quasi-static measurements were performed in order to obtain the magnetoelectric coefficients α_{32} and β_{322} . The induced charge as a function of the applied magnetic field is shown in Figure 2. In this case also, the dc magnetic field is applied along axis 2, i.e., parallel to the $\langle \bar{1}10 \rangle_{\text{cub}}$ direction. From these data, the coefficients of the linear (α_{32}) and the bilinear (β_{322}) ME effect were evaluated by fitting the data available at each temperature, in the magnetic field range 0 to 10 kOe, to quadratic functions using the expressions (9) and (10). From these fits at each temperature, the coefficients α_{32} and β_{322} were evaluated and they are plotted in Figure 3. The α_{32} falls smoothly near the transition temperature which is similar to the one

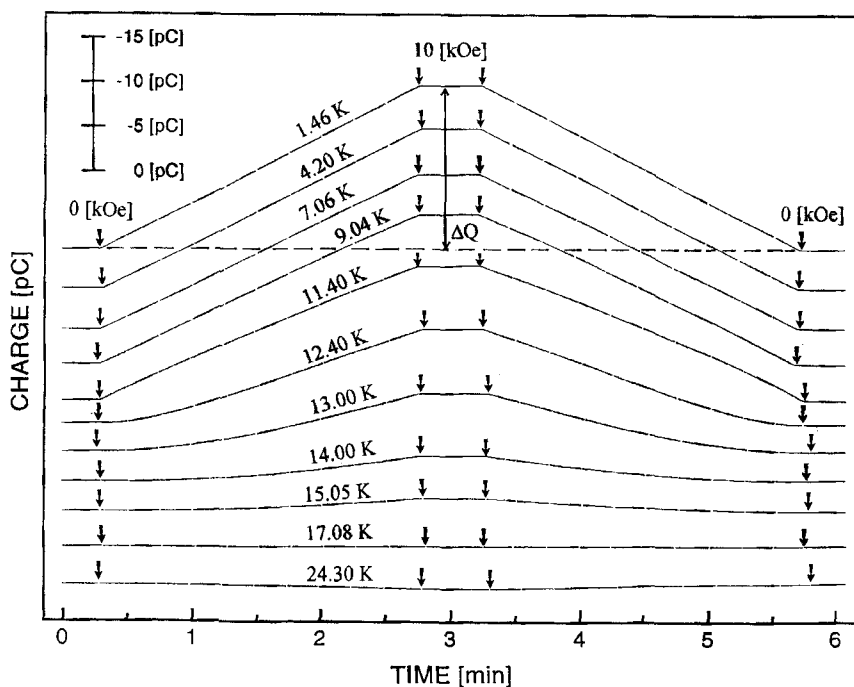


FIGURE 2 Induced polarization as a function of applied magnetic field measured quasistatically at various temperatures. The x-axis represents the time which is proportional to the magnetic field swept at a constant rate. The magnetic field was increased from zero to 10 kOe and then decreased to zero again.

measured by the dynamic technique. The anomaly as observed in the dynamic technique could not be detected since the data are more scattered in the quasi-static measurements. The bilinear coefficient shows a sharp change just below T_N with a change of sign. In the paramagnetic region, a non-vanishing bilinear effect similar to the one observed by the dynamic technique, was noticed. It should also be noted that, due to the effect of relatively high magnetic field, the T_N measured using quasi-static measurements is higher than that of the one obtained from the dynamic method (at 0.5 kOe).

The values of capacitance measured at room temperature using a HP4192A LF Impedance analyser (1 V_{rms}) at 100 kHz and at 1 MHz on both platelets, showed lower values than that reported by Mendoza *et al.*^[6] The capacitance value for the platelet #1 is 3.55 pF (38% lower) and for the platelet #2 is 6.22 pF (28% lower). This could be due to the improper contact area of the electrodes. Hence, the absolute values of the coefficients

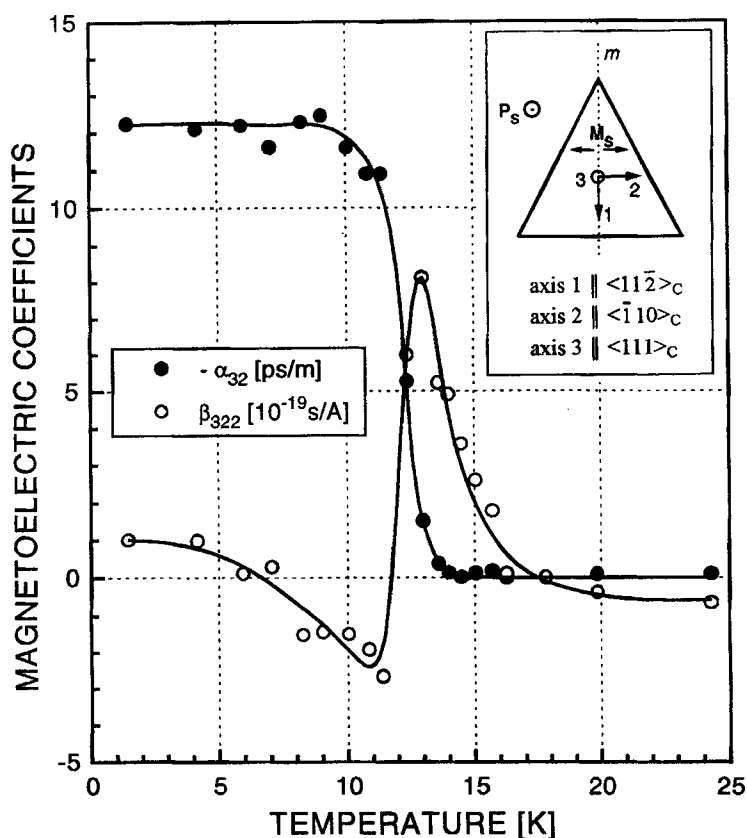


FIGURE 3 Variation of the magnetoelectric coefficients α_{32} and β_{322} with temperature. The open and closed circles are the experimental data and the lines drawn are guide-to-eyes.

α_{32} and β_{322} could be higher than the one reported here. Nevertheless, all other results and arguments put forward in this article hold good.

All the measurements described above performed on the platelet #2 yielded the same kind of results. However, their domain switching phenomena observed in the angular variation studies showed peculiar behaviour which will be discussed later.

4.2. Magnetic Domain Switching

The Figure 4(A) shows the angular variation of the induced polarization (for platelet #1) at 4.18 K. Here, θ is the angle between the applied magnetic field direction and the axis 2. The magnetic field is rotated in the plane of the

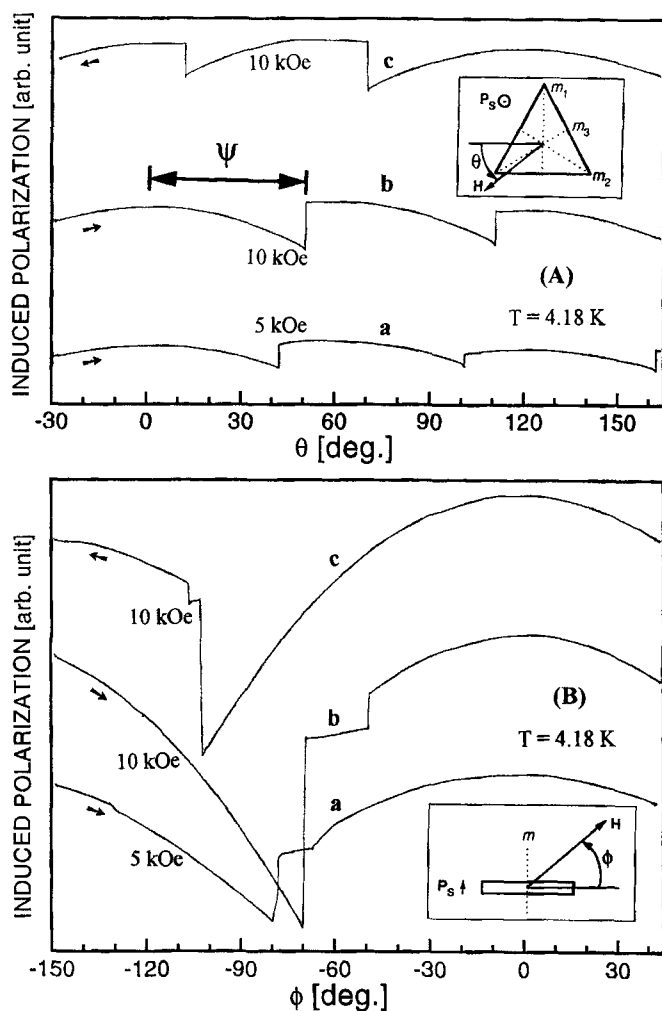


FIGURE 4 Angular variation of the magnetoelectric signal, at 4.18 K, at an applied magnetic field of 5 and 10 kOe, in platelet #1, with the magnetic field rotated (A) in the plane of the platelet and (B) perpendicular to the plane of the platelet. The geometry of the mirror planes corresponding to the Shubnikov point group m are given in the inset.

platelet and the arrows marked in this figure indicate whether the rotation is performed in the forward or in the reverse directions. The geometry of the mirror planes corresponding to the symmetry m is shown in the inset. Curves *a* and *b* represent the data obtained at 5 and 10 kOe respectively, in the forward direction of magnetic field rotation and curve *c* represents the data obtained at 10 kOe in the reverse direction of rotation. The magnetic

domain switchings which manifest as sharp jumps in the ME signal, recurring at every 60° , is consistent with the monoclinic symmetry m . The induced polarization as a function of θ at 4.2 K, by neglecting the bilinear effect in relation (9), is given by

$$P_3(\theta) = \alpha_{32}H_{dc}\cos\theta \quad (11)$$

This is obtained after replacing H_2 in the expression (9), by $H_{dc}\cos\theta$. Thus, for a given temperature and magnetic field, the angular variation of polarization is directly proportional to the cosine of the angle θ . Indeed, the cosine variation was observed in the induced polarization, within each magnetic domain state. It should also be noted that the angle ψ , where ψ is the angle between the $\langle 110 \rangle_{\text{cub}}$ direction and the angle at which the switchings occur, is found to increase with increasing magnetic field strength H_{dc} . In principle, one could expect that the product $H_{dc}\cos\psi$ should be equal to the coercive field. Hence, the product $H_{dc}\cos\psi$ is expected to remain the same for any magnetic field strength H_{dc} , at a given temperature. However, the product $H_{dc}\cos\psi$ was found to increase with increasing values of H_{dc} . Probably the applied magnetic field is high enough to break the Shubnikov point symmetry m , slightly, leading to this behavior.

The angular variation of the induced polarization (for platelet #1) at 4.18 K, is shown in Figure 4(B). In this case, the plane of rotation of the magnetic field is perpendicular to the platelet. Here ϕ is the angle between the applied magnetic field direction and the axis 2. The geometry of the mirror planes corresponding to the symmetry m is shown in the inset. Curves *a* and *b* represent the data obtained at 5 and 10 kOe respectively. The induced polarization vs angle of rotation ϕ , in this case as well, satisfies the relation (11).

Similar angular variation experiments were also performed at temperatures higher than 4.2 K. These results showed that the domain switchings tend to become smoother close to the transition temperature T_N and vanish completely above.

In the case of the platelet #2, the angular variation experiments revealed a peculiar phenomenon. Figure 5(A) shows the variation of the induced polarization as a function of θ , where θ is the angle of rotation in the plane of the platelet. Curves *a* and *b* represent the data, at 4.18 K, obtained at 5 and 10 kOe. The domain switchings are rather smooth and exhibit peculiarity, though the values of the coefficients of ME effect deduced from this platelet are the same when compared with platelet #1. Figure 5(B) shows the variation of the induced polarization with ϕ , where the magnetic

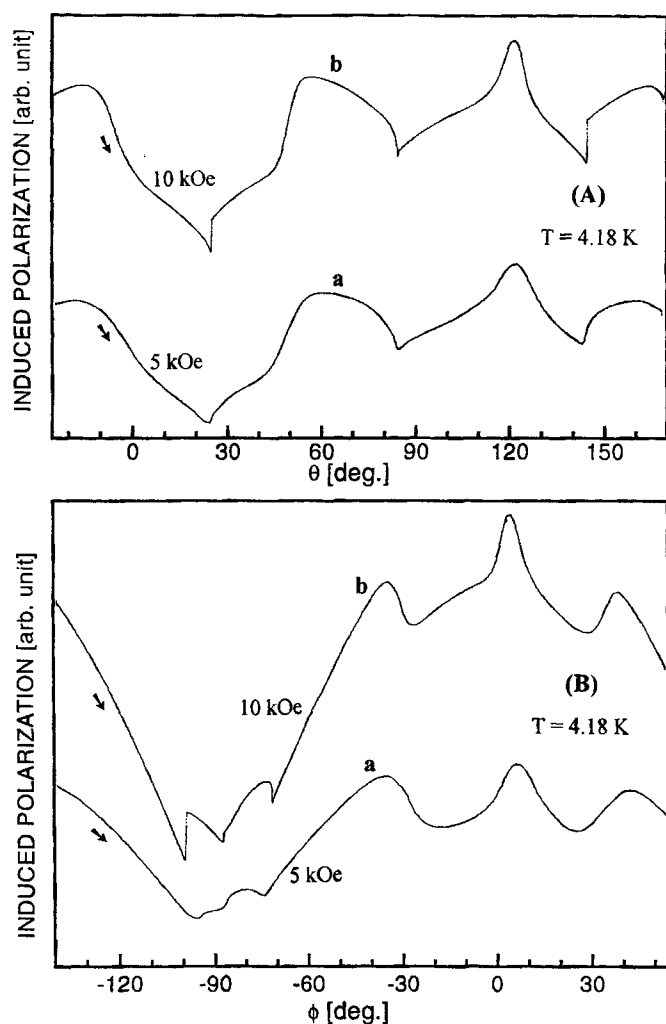


FIGURE 5 Angular variation of the magnetoelectric signal, at 4.18 K, at an applied magnetic field of 5 and 10 kOe, in platelet #1, with the magnetic field rotated (A) in the plane of the platelet and (B) perpendicular to the plane of the platelet.

field is rotated perpendicular to the plane of the platelet. These curves also show the same kind of peculiarity as mentioned earlier. This phenomenon could have arisen due to the persence of high coercivity produced by defects. Unlike the sharp switchings which occur in the platelet #1, from one domain state to another domain state, here the already existing domain state

may annihilate gradually with simultaneous growth of the next domain state, resulting in a smooth transition.

4.3. Coercivity

In addition to these measurements, the coercive field as a function of temperature for the 180° reversal of the magnetization vector was also measured magnetoelectrically. Figure 6 shows the temperature variation of

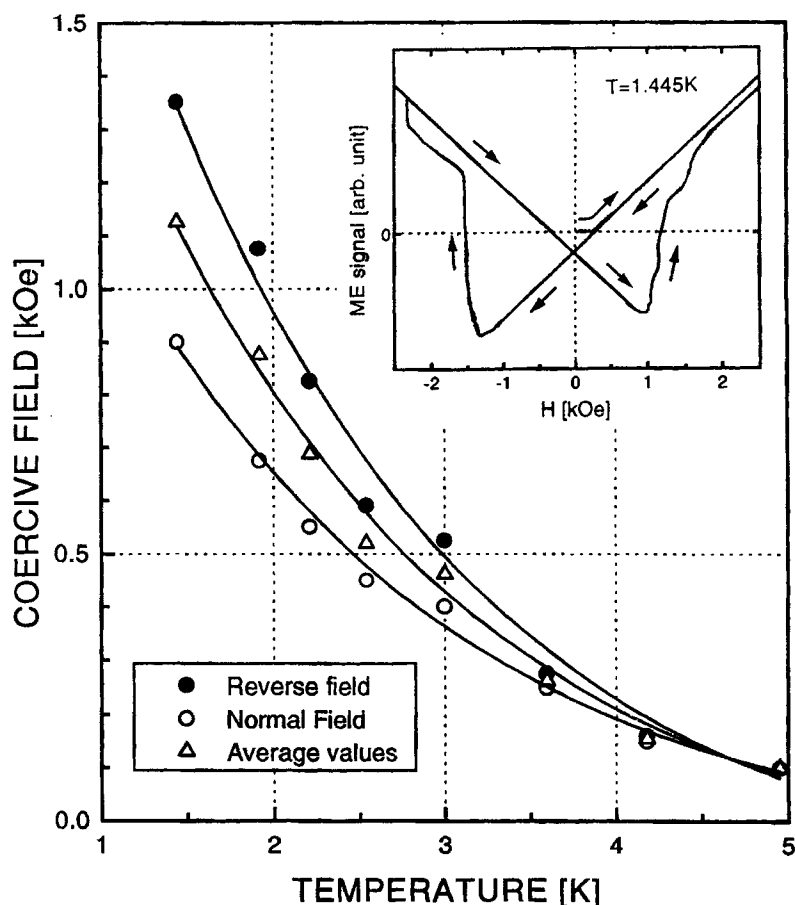


FIGURE 6 Coercive field measured magnetoelectrically as a function of temperature for the platelet #1. The values obtained for the forward and reverse magnetic field directions and the average of these two are plotted. Solid lines show the exponential behaviour. The inset shows the magnetoelectric signal with forward and reverse field directions forming butterfly loops, at 1.445 K.

coercive field for platelet #1 (no attempt was made to measure on platelet #2 due to high coercivity). The inset shows the magnetoelectric signal as a function of the applied magnetic field known as ME effect butterfly loop. The coercive field is not found to be equal for both forward and reverse fields. The bottom curve represents the coercive field when the magnetic field is applied in the forward direction and the top curve in the reverse direction. The central curve is the average of these two coercive fields. The temperature dependence of these coercive fields shows an exponential behaviour.

5. CONCLUSIONS

From the measurements on ferroelectric/ferromagnetic single domain platelets, the linear and bilinear magnetoelectric coefficients, α_{32} and β_{322} , were evaluated. An anomaly observed at about 11.3 K which is just below the Néel temperature has probably been attributed to a change in magnetic structure. The magnetic domain switchings, observed from the angular variation measurements, are consistent with the Shubnikov point group *m*. An exponential decrease in the magnetoelectrically measured coercive field with increasing temperature was observed.

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