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Reference

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TWINNING AND SECTOR GROWTH IN NICKEL BORACITES GROWN BY TRANSPORT REACTIONS

Hans Schmid*

Abstract

The space groups of the \( \alpha \)- and \( \beta \)-phases of Ni-Cl- and Ni-Br-boracite were determined to be \( \text{C}_{\text{2}} \) and \( \text{T}_{\text{d}} \), respectively, in accord with the mineral boracite. The absolute orientations of the \( \alpha \)- and \( \beta \)-phase unit cells were determined and correlated to their respective etching behavior. Ferroelectric domains of the \( \beta \)-phase were studied in detail on Ni-Cl- and Ni-Br-boracite under static conditions. It was found possible to distinguish all six possible domain orientations and to indicate their positive and negative dipole ends by polarization optical means only, provided relevant morphological characteristics are noted before cutting the slabs. Ferroelectric domains of \( 180^\circ \) and \( 90^\circ \) were observed, the latter occurring in head-head (tail-tail) or head-tail configurations. "Interpenetrating" tetrahedra growth twins of the \( \alpha \)-phase can be explained by twinning along \( \{100\} \).

The growth sectors of Ni-I-boracite, their fields of strain, deviations from cubic symmetry, and twinning were studied optically. The results allowed interpretation of ferromagnetoelectric domains and behavior in the \( \beta \)-phase below \( 60^\circ \)K and explained the origin of mimetic twinning in other boracites. The directions of the spontaneous polarization and magnetization of nickel-iodine boracite were determined by means of electric- and magnetic-field-induced domain switchings, Faraday effect, birefringence, and the symmetry of the magnetoelectric effect. The deduced most probable magnetic point group is \( \text{m''m'} \).

1. Introduction

Evidence for ferroelectricity in boracites was found in Mg\(_{3}\)B\(_{7}\)O\(_{13}\)Cl \([1]\), Ni\(_{3}\)B\(_{7}\)O\(_{13}\)Cl \([2]\), Ni\(_{3}\)B\(_{7}\)O\(_{13}\)Br \([3]\), and Ni\(_{3}\)B\(_{7}\)O\(_{13}\)I \([4]\). The latter compound displays mutually interacting ferroelectricity and ferromagnetism \([4]\). The twinning behavior of ferroelectric domains in boracites is therefore of particular interest. In this paper we describe ferroelectric twinning under static conditions in Ni-Cl- and Ni-Br-boracite, growth anomalies and their influence on twinning, and the observation of ferroelectric/ferromagnetic domains in Ni\(_{3}\)B\(_{7}\)O\(_{13}\)I.

All known boracites have a piezoelectric cubic high-temperature phase (\( \alpha \)) and a pyroelectric low-temperature phase (\( \beta \)), the transition temperatures varying between \( 60^\circ \) and \( 800^\circ \)K according to composition \([5]\). Ito et al. \([6]\) determined the crystal structure of the \( \alpha \)- and \( \beta \)-phases of the mineral boracite Mg\(_{3}\)B\(_{7}\)O\(_{13}\)Cl; the space groups accepted were \( \text{T}_{d} \) and \( \text{C}_{\text{2v}} \), respectively.

Twinning in natural boracite has been studied repeatedly \([7-13]\). All these papers contain a host of observation material that can be applied mutatis mutandis to other boracites. However, many of the indications

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were found of little or no value for the unequivocal diagnosis of ferroelectric twinning configurations, particularly because the importance of the determination of the orientation of the indicatrix and dipole directions of the \( \beta \)-phase in respect to the invariant \( \alpha \)-phase skeleton was not recognized. A new study therefore became necessary. Before proceeding to the proper description of twinning we shall describe some relevant structural aspects of boracite and a few experiments that we found necessary to clarify the relation between the \( \beta \)- and \( \alpha \)-phases.

2. Some Aspects of Crystal Structure

2.1. Verification of the Space Groups of \( \alpha \)- and \( \beta \)-Phases

According to symmetry considerations by Sonin and Zheludev [14] and Ascher [15] (based on different reasoning), the phase transition \( T^5_2 \rightarrow C^5_{2y} \) should not be of the ferroelectric type. Because no or not convincing hysteresis loops were observed for some time in boracites, it was conjectured that the \( \beta \)-phase might be antiferroelectric [14]. This possibility can now definitely be discarded for the Ni-Cl-, Ni-Br-, and Ni-I-boracite where we have obtained evidence for ferroelectricity. We were also able to show [3, 4] on single crystals of Ni-Cl-, Ni-Br-, and Ni-I-boracite that the absence of hysteresis loops found by previous authors [14, 16] was due to the application of too low electric fields. This also explains the narrow hysteresis loop found by Le Corre [1] on Mg-Cl-boracite.

Because ferroelectricity was indeed observed, there remained the possibility that the space groups \( T^5_2 \) and \( C^5_{2y} \) were not adequate. Therefore we tried to verify these symmetries. We made Weissenberg (Cu \( K\alpha \)) photographs of the \( \alpha \)-phase of Ni-1-, Cu-Br-, Cr-Br-, and Cr-I-boracite at 20°C, and of the \( \alpha \)-phase of Ni-Br- and Ni-Cl-boracite at 200° and 450°C, respectively. The reflexes were limited by \( h+k, k+l, l+h=2n \), and \( hkl \) with \( l=2n \) only. This is exactly the case for \( T^5_2 \). Less probable is \( T^3_3 \), which cannot be excluded on the basis of positive experimental criteria. According to Ascher's selection rules for transitions without change of unit cell [15, 17], only the transitions \( T^5_2 \rightarrow C^5_{2y} \) and \( T^3_3 \rightarrow C^5_{2y} \) are possible for the ferroelectric type. To check the space groups of the \( \beta \)-phase, we made Weissenberg photographs of carefully prepared untwinned \( \beta \)-phase single domain samples of Ni-Cl- and Ni-Br-boracite (rotation round the \( a \)- and polar c-axis). The reflexes were limited by: a) 0kl with \( l=2n \) only, b) h0l with \( h=2n \) only, c) 00l with \( l=2n \) only, d) h00 with \( h=2n \) only. These rules are most adequate for \( C^5_{2y} \). It derived the extinction rules for the \( \beta \)-phase from twinned crystals of Mg-Cl-boracite and could not fully exclude \( C^5_{2y} \) and \( C^5_{2y} \) from \( C^5_{2y} \) (rules a and b are violated in twinned crystals). We observed that the rule 0kl with \( k+l=2n \) only is not satisfied, thereby excluding \( C^5_{2y} \). We could not discard \( C^5_{2y} \) on the basis of positive experimental criteria; however, observance of rules a, b, and c, which are not required by \( C^5_{2y} \), lets \( C^5_{2y} \) appear as the only reasonable space group. The extinction rules exclude \( C^5_{2y} \) and \( C^5_{2y} \) from \( C^5_{2y} \).

The extinction laws of \( T^5_2 \) might equally well account for space group \( T^2 \). The ferroelectric transition \( T^2 \rightarrow C^2_3 \) should be allowed [17]. However, \( C^2_3 \) is inconsistent with the observed \( \beta \)-phase extinction laws, and Laue back-reflection diagrams - made on \{100\} growth sectors of \( \alpha \)-Ni-Br- (200°C), \( \alpha \)-Ni-I- (20°C), and \( \alpha \)-Cu-Br- (20°C) boracite - gave no evidence for Laue symmetry \( m3 \), and thereby \( T^2 \). Therefore we have to admit that \( T^5_2 \) and \( C^5_{2y} \) are correct and apply also to the ferroelectric nickel boracites. Now \( C^5_{2y} \) is a maximal
2.2 Determination of the Absolute Orientation of the \( \alpha \)- and \( \beta \)-Phase Unit Cells

In the following we consider the space groups \( \text{C}_{\text{IV}} \) and \( \text{T}_d \) as adequate for Mg–Cl–, Ni–Cl–, and Ni–Br–boracite. It is a property of the symmetry \( \text{T}_d \) that the cube space diagonals are polar. This becomes manifest in the different growth speeds, sizes, and etching properties of opposite \{111\} faces (Fig. 1, Table 1). An ordinary X-ray structure determination, such as Ito’s, cannot provide an answer to the question what kind of \( \text{T}_d \) cube corners, or \{111\} faces, etch better. But without having to have recourse to anomalous dispersion of X-rays, in the case of boracites a way is open via an experimental determination of the dipole direction of the \( \beta \)-phase because Ito indicates how the \( \alpha \)- and \( \beta \)-phases are correlated with each other. In Fig. 2, we have represented the unit cell of \( \alpha \)-boracite with the Cl\(^-\) and Mg\(^{++}\) ions only. The boron-oxygen skeleton that remains invariant during the phase transition, and is responsible for the polar [111] directions, is not shown, but the movements of the Mg\(^{++}\) and Cl\(^-\) ions at the phase transition are indicated. All Mg\(^{++}\) ions move along [100]\(_{\text{Cub}}\), and Cl\(^-\) ions along [111]\(_{\text{Cub}}\). We can distinguish two mutually perpendicular sublattices in which Mg\(^{++}\) ions perform antiparallel (antiferroelectric) movements, while in a third one, perpendicular to the former, the movements of the Mg\(^{++}\) ions are parallel, and therefore their center of gravity is displaced from the center of the cube (downwards in Fig. 2). However, the center of gravity of the negative Cl\(^-\) ions is displaced in the opposite direction. Therefore it appears reasonable that the direction of the electric dipole is given (from bottom to top in Fig. 2). The corresponding orthorhombic unit cell and its relation to the cubic one are shown in Fig. 3.

We have adopted Ito’s transformation matrix from cubic to orthorhombic (direct) axes \( \frac{1}{2} \frac{1}{2} 0 / \frac{1}{2} \frac{1}{2} 0 / 001 \), but only after verification by X-ray rotation photographs round the cubic [100] and [110] directions of a care-

Fig. 1. a) Frequent aspect of a gas-phase-grown boracite; b) representation of its sector
growth; c) \{100\} growth pyramid with (i) sharp and (i’) broad beam of cross of strain; d) \{110\} growth pyramid, Q.O.A. = quasi optical axis; e) \{111\} growth pyramid with sub-
sectors \( \text{A}' \), \( \text{A}'' \), \( \text{A}''' \). Items b) to e) refer only to NIB.

...
fully prepared single domain of Ni-Cl- and Ni-Br-\-boracite. We found that the orthorhombic unit cell had the same size and orientation as that in Mg-Cl-boracite: \(a_{\text{cub}} \approx b_{\text{cub}} \approx a_{\text{cub}}(\sqrt{2}/2), c_{\text{cub}} \approx a_{\text{cub}}\). Doubling of the \(a\) and \(b\) parameters, as reported in reference [18] for Mg-Cl-boracite, can be shown to occur apparently only when the sample is twinned by the law: twinning axis = [111]_{\text{cub}}.

Because we know the direction of the electric dipole relative to the atomic coordinates in the \(\alpha\)- and \(\beta\)-phases of Mg-Cl-boracite (Figs. 2 and 3), the problem of the absolute determination of the orientation of the unit cells is reduced to an experimental determination of the dipole direction and its correlation to the macroscopic properties of the A, B corner skeleton of the \(\alpha\)-phase. For the following experiments we postulate that the Cl-(Br) and Ni ions displace in the same directions as do the Cl and Mg ions according to Ito et al.

2.2.1. Determination of the Dipole Direction. We have determined the direction of the dipole moment by qualitative pyroelectric measurements with an electronic voltmeter (Keithley 610 A) on single domain slabs (~4 x 4 x 0.1 mm) of Ni-Cl-, Ni-Br-, and Ni-I-boracite, following the convention [19] that the electrode on the positive dipole end becomes positive during cooling. This convention is applicable to the \(\beta\)-phase because the spontaneous polarization \(P_s\) increases with falling temperature, as can be judged from the temperature dependence of the birefringence \(\Delta n\) (see Appendix). The Ni-Cl- and Ni-Br-boracite samples were as-grown [5], the Ni-I-boracite sample was obtained by poling. By many checks we always reconfirmed that a \(\beta\)-phase domain with one of the six possible orientations always has the same configuration, formed by its electric dipole direction, the orientation of the optic indicatrix, and the position of the A, B corners, as shown in Fig. 4. In other words, when the polarization (arrow) enters on a \(\{100\}_{\text{cub}}\) face, then the vibration direction of \(n_y\) lies parallel to the \([110]\) line connecting those B corners that lie on the polarization entrance side of the slab. For domain studies, this rule should be kept in mind because its application generally allows the complete

*For lattice parameters of boracites, see Ref. 5.
elucidation of a domain configuration with the polarizing microscope only. Determination of the A, B faces or corners necessary for this purpose is usually easy (see Table 1).

2.2.2. Correlation between Optic Indicatrix and Orthorhombic Axes. Because the orthorhombic a and b parameters are practically identically long, we had to determine their directions by means of a Weissenberg first layer photograph (all 0kl extinguished, h0l with h = 2n only, for rotation round the polar axis) and correlate them to the crystal's position and indicatrix that we identified by the polarizing microscope. The results are: n_y lies parallel to the b axis and n_α parallel to the a axis (Figs. 3 and 4).

2.2.3. Correlation of the Etching Behavior of the α- and β-Phases to Their Structures. Slabs of Ni–Cl-, Ni–Br-, and Ni–I-boracite – cut parallel to {110}_cub and {111}_cub – were etched with boiling concentrated hydrochloric acid. We made use of the fact that polishing scratches (from 0.3 μ diamond paste) produce a large number of etch figures. The results are:

α-Phase (Ni–I-boracite) (see Fig. 5)

a) On the {111} A faces, large triangles develop, whereas they are absent or very small on the B faces. The sides of the triangles are parallel to those [110]_cub directions which are parallel to the edges between the {111} and {100} planes. The B faces become dull and the A faces remain brilliant after etching.

b) On the cubic {100} faces, rhomb-like etch figures develop, the long diagonal of which points to the neighboring B faces. On opposite surfaces, the rhombs are rotated by 90° against one another (Fig. 5).

β-Phase (Ni–Cl- and Ni–Br-boracite)

a) On antiparallel domains with their polar axes perpendicular to a {100}_cub-cut platelet, the size of the rhombs – uniform in the α-phase – is modulated by the polar character, while their form and orientation is the same as in the α-phase and independent of the dipole end at the surface. The positive dipole ends etch more rapidly (large rhombs) than the negative ends (Fig. 5a).

b) Analogous results to the preceding item are obtained on the {111} faces (Fig. 6b). The A faces, which are etched more rapidly than the B faces, give better contrast in size of the triangles for opposite dipole ends.

From Sections 2.2.1 to 2.2.3 and reference [6] we can now deduce that the A corners are those of the unit cell of Ito's setting on which a tetrahedron (with four borons at its corners and an oxygen in its center) points with one of its corners into the unit cell, while on the B corners a tetrahedron is placed with one of its corners pointing out of the cell along {111}_cub.
3. Twinning in the β-Phase

3.1. Determination of the Polarization Direction of Ferroelectric Domains with the Polarizing Microscope

In practical work, crystal sections parallel to the pseudocubic \{100\}, \{110\}, and \{111\} planes are of interest. We have therefore represented in Table 2 how the six possible ferroelectric domains (with the polarization along one of the cubic [100] directions) present themselves in the three cuts under the microscope. The indicated orientations of indicatrix, conoscopic figures, and polarization direction are in strict correspondence to the crystal orientation shown in the right-hand column of Table 2 and to that of Figs. 2, 3, and 4. The conoscopic figures provide a means for determining the polarization direction, because their form, or orientation, is different for all six domain orientations. Rinne [11], who described some conoscopic figures and extinction directions of twinned natural boracite, did not notice this possibility because he used the normal instead of the 45° position; the latter one is unequivocal and to be preferred for the case where the optic axes come out very close to the pseudocubic [100] directions as in Ni- and Mg-boracites (Table 2 and Fig. 4). For cases where the conoscopic method is not applicable, the orthoscopic method is equally valuable.

On \{100\}_{cub} cut platelets, the antiparallel up and down domains, and 90° domains in the plane are easily distinguishable by any kind of retardation plate. The polarization direction of domains in the plane of the platelet is somewhat more difficult to determine, but slight tilting of the slab towards the microscope axis (creating differences in birefringence) or application of the twinning laws (see further on) can help (Tables 2, 3, 4).

---

Fig. 5. Schematic etch figures on the unfolded surface of a NIB crystal; they do not "feel" the subsectors.

Fig. 6. Etch pattern on the + and − dipole ends of antiparallel domains of Ni-Cl-boracite. a) Cut parallel to \{001\}_{o.r.}, etching: 20 min boiling concentrated hydrochloric acid; b) cut parallel to \{111\}_{cubA}, etching as under a).
Fig. 7. Domain pattern of a \{100\}_cub-cut Ni-Cl-boracite. Crossed polaroids \{100\}_cub, Red-I plate, platelet slightly tilted towards microscope axis round indicated [100] direction. All six domain orientations A to F occur. Legend (refers to Table 4): R$_1$ = O/R/a, R$_2$ = O/R/b, S$_1$ = O/S/a, S$_2$ = O/S/b, T$_1$ = O/T/a, T$_2$ = O/T/b.

\{111\}_cub-cuts allow a particularly straightforward determination of the polarization directions, because all six domains distinguish themselves, antiparallel domains in birefringence, 90° domains in extinction direction (and birefringence) (Tables 2 and 4).

In \{110\}_cub-cuts, antiparallel domains in the plane of the slab differ in birefringence and the $n'_y$/$n'_x$ orientation. 90° domains with the polarization at 45° to the platelet can be distinguished by a retardation plate, but antiparallel ones at 45° to the surface have the same birefringence and $n'_y$/$h'_x$ orientation. In this case, tilting of the crystal or application of the twinning laws again will help (Tables 2, 3, 4).
TABLE 2. Chart for the Determination of the Polarization Directions of β-Phase Twins on \{100\}, \{110\}, and \{111\}_cub-Cuts. Generally Applicable to Boracites. For Details of Birefringence, see Appendix to Table 2.

<table>
<thead>
<tr>
<th>ORIENTATION OF DOMAIN:</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>section of indicatrix</td>
<td>$n_x$</td>
<td>$n_y$</td>
<td>$n_x'$</td>
<td>$n_y'$</td>
<td>$n_x'$</td>
<td>$n_y'$</td>
</tr>
<tr>
<td>$\Delta n$ (for Ni-CI-B, measured at 20°C)</td>
<td>0.022</td>
<td>0.022</td>
<td>0.0017</td>
<td>0.0017</td>
<td>0.0017</td>
<td>0.0017</td>
</tr>
<tr>
<td>conoscopy figure (45°-position)</td>
<td>-</td>
<td>-</td>
<td>$A + 120^\circ$</td>
<td>$B + 120^\circ$</td>
<td>$A + 240^\circ$</td>
<td>$B + 240^\circ$</td>
</tr>
<tr>
<td>direction of polarization</td>
<td>down</td>
<td>up</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

For \alteration{100}_cub-Cut:

<table>
<thead>
<tr>
<th>ORIENTATION OF PLATELET</th>
</tr>
</thead>
<tbody>
<tr>
<td>[001]_cub on top</td>
</tr>
</tbody>
</table>

For \alteration{110}_cub-Cut:

<table>
<thead>
<tr>
<th>ORIENTATION OF PLATELET</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110) _cub on top</td>
</tr>
</tbody>
</table>

For \alteration{111}_cub-Cut:

<table>
<thead>
<tr>
<th>ORIENTATION OF PLATELET</th>
</tr>
</thead>
<tbody>
<tr>
<td>(III) A</td>
</tr>
</tbody>
</table>

HANS SCHMID
APPENDIX TO TABLE 2
A) Refractive Indices of Some Boracites at 20°C
(If not otherwise specified, determination in this work by the immersion technique)

<table>
<thead>
<tr>
<th></th>
<th>Mg-Cl [2]</th>
<th>Cr-Cl</th>
<th>Cr-Br</th>
<th>Mn-Cl [22]</th>
<th>Ni-Cl</th>
<th>Ni-Br</th>
<th>Ni-I</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_\alpha$</td>
<td>1.658</td>
<td></td>
<td></td>
<td>1.732</td>
<td>1.769</td>
<td>1.794</td>
<td>n = 1.914*</td>
</tr>
<tr>
<td>$n_\beta$</td>
<td>1.662</td>
<td>$n = 1.780$</td>
<td>$n = 1.800$</td>
<td>1.737</td>
<td>1.780</td>
<td>1.795</td>
<td></td>
</tr>
<tr>
<td>$n_\gamma$</td>
<td>1.668</td>
<td></td>
<td></td>
<td>1.744</td>
<td>1.791</td>
<td>1.803</td>
<td></td>
</tr>
</tbody>
</table>

*By the refined Duc de Chaulnes' method [33]. Variations of $n$ from sample to sample up to 0.002 are common in the $\beta$-phase and probably due to a strain induced piezo-optic effect.

B) Birefringence Versus Temperature of Ni-Cl- and Ni-Br-Boracite
(Figs. A1, A2)
TABLE 3. Summary of Twinning Laws Observed on Ni–Cl– and Ni–Br–Boracite (Indices refer to Fig. 3)

<table>
<thead>
<tr>
<th>Type of domain</th>
<th>Twinning operation</th>
<th>Twinning plane</th>
<th>Composition plane</th>
</tr>
</thead>
<tbody>
<tr>
<td>180°-domains</td>
<td>180° rotation round [110]</td>
<td>None</td>
<td>a) {110}<em>{o.r.}/{010}</em>{cub} {110}<em>{o.r.}/{100}</em>{cub}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b) {101}<em>{o.r.}/{011}</em>{cub}</td>
</tr>
<tr>
<td>90° head–head</td>
<td>120° rotation round one of</td>
<td>{112}<em>{o.r.}/{011}</em>{cub}</td>
<td></td>
</tr>
<tr>
<td>(tail–tail) domains</td>
<td>the [111]_cub directions</td>
<td></td>
<td>a) {112}<em>{o.r.}/{011}</em>{cub}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b) {102}<em>{o.r.}/{012}</em>{cub}</td>
</tr>
<tr>
<td>90° head–tail</td>
<td>Cubic phase: twinning phase</td>
<td>{110}<em>{o.r.}/{010}</em>{cub}</td>
<td></td>
</tr>
<tr>
<td>domains</td>
<td>is {100}_{cub}</td>
<td></td>
<td>a) {132}<em>{o.r.}/{112}</em>{cub} {132}_{o.r.}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>b) {011}<em>{o.r.}/{111}</em>{cub} {011}_{o.r.}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>or {101}<em>{o.r.}/{111}</em>{cub} {101}_{o.r.}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>{110}<em>{o.r.}/{010}</em>{cub}</td>
</tr>
<tr>
<td>α-phase growth twins</td>
<td></td>
<td></td>
<td>others not observed</td>
</tr>
<tr>
<td>tetrahedra</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2. Twinning "Laws"

The aspect of a boracite domain pattern is usually much more bewildering than that of a BaTiO₃ crystal. This comes from the fact that the ferroelectric phase is optically biaxial and that the spontaneous distortions from cubic to orthorhombic are small, leading to twin interfaces with considerable deviations from rational indices, and which are often heavily curved. Nonetheless, some important "laws" can be distinguished. They are summarized in Table 3. In Table 4 we have shown schematically how the most important ones appear on cubic \{100\}, \{110\}, and \{111\} cuts.

3.2.1. 180° Domains. Antiparallel domains have the composition plane \{110\}_{o.r.}. Deviations of several degrees from the ideal \{110\} plane are common. The optic indicatrix of one domain is rotated by 90° (round the polar axis) with respect to that of the antiparallel partner. Examples of 180° domains are shown in Table 4/R and Figs. 6 to 10. Multiple twinning according to this law leads to the lamellar structure observed in many boracites.

3.2.2. 90° Domains. For twins with the polar axes at 90° to each other, we observed head–head (tail–tail) and head–tail configurations. For both cases, the twinning operation is a 120° rotation round one of the cubic [111] directions, and the twinning plane is \{112\}_{o.r.}/\{011\}_{cub} (indices according to Fig. 3). The composition planes are different for the two cases.

3.2.2.1. 90° Head–Head (Tail–Tail) Domains. These domains were found with the composition planes \{112\}_{o.r.} and \{102\}_{o.r.}, \{112\} appearing very frequently. Deviations from the ideal plane of up to several degrees are frequent. By conoscopic studies we were able to show that only head–head or tail–tail configurations but never head–tail contact occurs at the \{112\} composition planes. While one would expect a head–tail interface from electrostatic reasons, this case is ruled out sterically. Although not yet observed experimentally,
TABLE 4. Schematic Representation of the Most Frequent Twinning Laws Experimentally Observed on Ni-Cl- and Ni-Br-Boracite. Applicable Also to Other Boracites

<table>
<thead>
<tr>
<th>Composition Plane</th>
<th>180°- Domains</th>
<th>Head-Head (Tail-Tail) Domains</th>
<th>Head-Tail Domains</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110) ABC</td>
<td>R</td>
<td>S</td>
<td>T</td>
</tr>
<tr>
<td>(100)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b)</td>
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Note: The diagram shows schematic representations of crystallographic domains and orientations for different composition planes.
Fig. 8. Domain pattern of a \(\{100\}_{\text{cub}}\)-cut Ni–Cl-boracite. \(U = \{102\}_{\text{o.r.}}\) as composition plane, other symbols as in Fig. 7. Upper surface is natural.

There must exist a small shear distortion of the cubic lattice in the \(ab\) plane of the orthorhombic cell and consequently a rhomb-like section of the unit cell along \(\{112\}_{\text{o.r.}}\). For the symmetric head–head configuration, the long and short diagonals of the rhombs meet the long and short diagonals of their partners, respectively, while for a head–tail relation it can be shown easily that the long diagonals would meet short ones and vice versa, an unfavorable case which we have never observed.

Twinning on \(\{112\}_{\text{o.r.}}\) is frequently observed at higher temperatures, where the conductivity is already sufficient to allow compensation of the electrostatic charges. It also occurs in the mimetic growth twins (twelve-pyramid system [8, 11] and six-pyramid system [10], Figs. 12 and 13) observed on natural Mg–Cl-boracites. Because these crystals have probably been formed below the transformation temperature of 265°C in aqueous solution, the charge compensation at the \(\{112\}_{\text{o.r.}}\) interface could easily be accomplished during growth. Since we have now shown that twinning along \(\{112\}_{\text{o.r.}}\) is always symmetric, the results of the work on pyroelectrically delineated domain boundaries on natural Mg-8% Cl, by Mack [20], become fully plausible and are in accord with the twelve- and six-pyramid crystals. Examples of \(\{112\}_{\text{o.r.}}\) twinning are given in Table 4/S and Figs. 7 to 10.
Fig. 9. Domain pattern of a \{111\}_{\text{cub}}-\text{cut Ni-Cl-boracite}. A face on top, close to natural surface. Crossed polaroids nearly parallel to extinctions of domains A. Legend for the composition planes (refers to Table 4): \( S = Q/S, T_1 = Q/T/a, T_2 = Q/T/b \).

Fig. 10. Domain pattern of a \{110\}_{\text{cub}}-\text{cut Ni-Cl-boracite}. Crossed polaroids parallel to upper \{100\} edge, Red-1 plate. Legend (refers to Table 4): \( R_1 = P/R/c, R_2 = P/R/b, S_1 = P/S/a, T_1 = P/T/a, T_2 = P/T/c \).
Fig. 11. "132\text{o.r.}", twinning: a) rhombs based on "132\text{o.r.}
planes, produced with a pin on a \{001\}_\text{o.r.} cut platelet. Interior of rhomb has the orientation of the surroundings, Ni-Br-boracite; b) repeated
\{110\}_\text{o.r.} and "\{132\}_\text{o.r.}", twinning on Ni-Cl-boracite; c) schematic explanation of b).
Fig. 12. Idealized schematic mimetic twin of Mg₃B₁₇O₁₃Cl of the Stassfurt type.

Fig. 13. Idealized schematic mimetic twin of Mg₃B₁₇O₁₃Cl of the Lüneburg type.

In some rare cases, head—head relations were found with the composition plane approximately parallel to {102}₀.₀/{112}₁₁cub.

3.2.2. 90° Head—Tail Domains. If for some reason a boracite crystal forms head—tail domains, the sterically unfavorable {112} plane is avoided in different ways. Most frequently, an interface with irrational indices is observed, coming near to the indices {132}₀.₀/{121}₁₁cub.

In Table 4/T this twinning is shown in terms of {132}₀.₀, for reasons of simplicity. In reality the composition plane is often tilted 3 to 6° around the [110]₁₁cub trace which this twinning produces on one of the cube faces (Table 4/T/N and Fig. 14). The tilt can best be seen on a {111}₁₁cub—cut, where {132} would appear as a sharp line (Table 4/T/Qa), while in reality narrow, steep bands with interference fringes are visible, very often in the form of spikes (Fig. 9). Owing to the tilt, the planes approach {101}₀.₀/{111}₁₁cub (Fig. 14, No. 3).

Examples for “{132}” twinning are shown in Figs. 7 to 10. Examination of a large number of crystals showed that only the set of {132} (and adjacent planes) occurs; the set {312} has never been observed. This behavior is compatible with the orthorhombic symmetry, but would also be consistent with monoclinic symmetry. We used this rule for the elucidation of domain configurations. The rule becomes particularly well manifested by the pressure induced twinning figures on {001}₀.₀—cuts (Fig. 11). The rhombs are due to repeated “{132}” twinning. The long diagonal of a rhomb is always parallel to n₁, never to n₂.

Beside the frequent “{132}”₀.₀ twinning, sometimes {101}₀.₀ twinning and twinning on intermediate planes between these two extremes has been observed for head—tail combinations.

4. Twinning in the High—Temperature Phase

"Interpenetrating" Tetrahedra

For natural Mg—Cl-boracite and chambersite (Mn—Cl-boracite), "interpenetrating" tetrahedra were reported [21, 22]. We observed this kind of growth twinning on Ni—Cl-boracite. These crystals formed at 900°C,
Fig. 15. Domain pattern of a \(\{100\}_{\text{cub}}\)-cut "interpenetrating" tetrahedra growth twin of Ni-Cl-boracite. Sectors 1 and 3, and 2 and 4 respectively, have the same orientation. U-cubic \(\{100\}\) composition and twinning plane.

Fig. 16. "Interpenetrating" tetrahedra. a) Frequent aspect of Ni-Cl-boracite; b) aspect of individual sector; c) \(\{100\}_{\text{cub}}\) twinning and composition plane.

i.e., in the cubic phase [5]. A thin section, cut parallel to \(\{100\}_{\text{cub}}\) (Fig. 15), enabled us to determine the following composition. The two "interpenetrating" tetrahedra are in reality an assembly of eight individuals; neighboring ones are related by the law, twinning plane = composition plane = \(\{100\}_{\text{cub}}\), (Fig. 16). The \{111\} A faces of the individual sectors never show growth centers as ordinary boracite crystals do, thus indicating that the growth starts from the reentrant grooves formed by these faces.

Because this kind of twinning involves the boron oxygen skeleton – which is not responsible for the ferroelectricity – no movement of the composition plane by electric fields is possible.
5. Nickel—Iodine Boracite (NIB)

Nickel—iodine boracite deserves particular attention for two reasons. First, it is to our knowledge the first substance in which mutually interacting ferromagnetism and ferroelectricity have been evidenced by domain switchings [4]. Second, the crystals produced by growth from the vapor phase display a sector structure, the study of which has become elucidative a) for the understanding of the highly symmetric "mimetic" twinning (Figs. 12, 13) that occurs in most natural and some gas-phase-grown boracites, and b) for the visual diagnosis of ferroelectric—ferromagnetic domains in NIB itself.

5.1. Sector Structure of NIB

One would expect NIB to become cubic above the ferroelectric phase transition at 64°K. In reality considerable birefringence persists up to the decomposition point. To establish the origin of the birefringence, we have cut platelets parallel to the natural \{100\}, \{110\}, and \{111\} faces and investigated by use of polarized light.

Results. Each of the three kinds of growth faces was found to grow by a particular mechanism of its own and left a "keel water" of physically and probably chemically slightly differering growth pyramids behind themselves (Fig. 1b,c). In the interior of the pyramids, further growth anomalies such as layer structures, twins, and fields of strain owing to growth centers, were observed.

\{100\} and \{111\} A and B pyramids grow by means of at least one growth center (Fig. 1). We observed the centers in steeply reflected light or in transmission (Figs. 17a,b). On the growth facet they were generally surrounded by growth steps, the height of which decreased towards the center. Therefore, it has not been possible so far to decide whether a spiral mechanism was responsible for growth. At low degrees of supersaturation, the step height on the entire facet was under the resolution of the light microscope, and "vicinal faces" (irrational low index faces) appeared (Figs. 18, 19).
TABLE 5. Birefringence in NIB Growth Sectors (compare also Figs. 1 and 20)

| Orientation of quasioptic axis | Birefringence in sections  
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<tr>
<td></td>
<td>( \parallel ) to quasi-optic axis</td>
</tr>
<tr>
<td>{100} growth pyramid</td>
<td>( \perp ) to {100} pyramid basis</td>
</tr>
<tr>
<td>{110} growth pyramid</td>
<td>( \parallel ) to cut-off cube edge</td>
</tr>
<tr>
<td>{111} growth pyramid sub-sector</td>
<td>Identical to the adjacent {110} sector</td>
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</table>

Fig. 18. \{100\} "vicinal" faces on NIB. The pyramidal character is exaggerated by the illumination.

Fig. 19. \{111\} "vicinal" faces on NIB.

By cutting thin slabs perpendicular to the growth facets we observed two kinds of layer structure parallel to the facets. First, there were thick layers (C\(_1\) and C\(_2\) in Fig. 24b) that were associated with the operating period of a particular growth center (sometimes comprising an entire pyramid). Second, we found layers (1 to 100 \( \mu \) thick) that formed within the operating period of a particular center (Fig. 24). Both kinds of layer were observable with crossed polarizers (45° position), owing to differences of birefringe (sometimes associated with differences in color) of the order of \( 0.0001 \) in the layers.

5.1.1. \{100\} Growth Pyramids. From the trace of the growth center in the pyramid, there spreads a field of strain (Fig. 17b) that has a twofold symmetry axis (the fourfold inversion axis of \( T_d \) is lost). When the crossed polarizers are parallel to [110], a dark cross, with its narrow beam linking \{111\} A faces, and its broad beam linking \{111\} B faces, can be seen (Figs. 5, 18). At greater distance from the growth center, a \{100\} pyramid cut parallel to its basis has extinction approximately parallel to the cube edges (Fig. 20, D"), but the birefringence is extremely small (\( \sim 0.0001 \)), and we can speak of a quasi-optic axis (optically positive) perpendicular to these sector faces. Cuts perpendicular to the growth faces have parallel extinction
Fig. 20. a) Schematic \{100\}_cub-cut according to Fig. 1 of a NIB-crystal with sector structure. The growth pyramids are idealized, with their apex in the center of the crystal; b) \{100\}_cub-cut of NIB, close to 20a but without A'.

(Fig. 20, D') and the maximum birefringence (~0.0001), which is still very small (Table 5). \{100\} pyramids show the lowest birefringence of all sectors (Table 5) and are therefore most adequate for physical experiments.

5.1.2. \{110\} Growth Pyramids. \{110\} growth facets are generally small and never show growth centers of the kind seen on \{100\} and \{111\} faces. The growth on the \{110\} facets proceeds by some other sort of dislocation (Fig. 21). The interior of these sectors is very homogeneous, although strongly birefringent (Table 5). The indicatrix is quasi-monoaxial positive, the quasi-optical axis lying parallel to the cut-off cube edges (Figs. 1d, 20C'). The extinction directions of the extremely weak birefringence (Table 5) perpendicular to the quasi-optic axis is shown in Fig. 20, C'.

5.1.3. \{111\} Growth Pyramids. From the trace of all \{111\} A and B growth centers (Figs. 1, 22, 23), three twin-like subsectors (Figs. 1e, 23) spread out. These twins are joined by \{110\}_cub-twinning planes. Their traces on the \{111\} surface invariably point from the center to the adjacent \{100\} faces (Figs. 1a, 5). The extinction directions of the three subsectors (viewed on a \{111\}-cut slab) are given in Fig. 24. They are sharp where a single growth center is responsible for the formation of the whole thickness of the slab as in Fig. 23. The optical indicatrix of a subsector is quasi-monoaxial positive and has the same orientation as that of the neighboring \{110\} sector (Figs. 1, 20A',A''A''''). Birefringence is given in Table 5.

When more than one growth center occurred in a \{111\} pyramid, we distinguished different cases. Either two or more centers were operating simultaneously (Figs. 23 and 24a). Thus, in the most simple case the regions A'' + A', A'' + A'', and A'' + A' (Fig. 24) were found, in which an intimate mutual overgrowth leads to undulating extinction and heavy strain. In other cases, cuts perpendicular to the \{111\} growth face indicated that a particular layer was associated with a particular center (Fig. 24b); the equivalent of superposed birefringent plates is thus obtained. Both kinds of overgrowth can be described by a twinning law: twinning opera-
Fig. 21. Surface of \(\{110\}_\text{cub} \) NIB growth face in steeply reflected light.

Fig. 22. Two \(\{111\}\) growth centers with growth steps of NIB in steeply reflected light.

The sector structure, strain fields owing to growth centers, and the twinning in the \(\{111\}\) sectors are particularly observable in NIB. However, the phenomenology is the same for other boracites under certain growth conditions. On Ni–Cl- and Ni–Br-boracite crystals we were able to show that the strain field of the \(\{100\}\) growth center and the \(\alpha\)-phase growth twins in the \(\{111\}\) sectors are re-
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Fig. 23. The same \{111\} growth centers as in Fig. 22 in transmission; crossed polaroids in a position for maximum contrast of twins.

Fig. 24. Intergrowth (a) and superposition (b) of \{111\}-subsectors. Schematic.

responsible for the spontaneously assumed ferroelectric domain configurations in the \(B\)-phase, as schematized in Fig. 12, provided that heavier strains of some other origin are not introduced during cooling. Hereby, the highly symmetric mimetic twinning (12-pyramid system) in natural boracites also finds its explanation.

ii) The principal birefringence in the growth sectors indicates some deviation from cubic symmetry to quasi-tetragonal. It remains an open question whether we are dealing with polytypes (different kinds of stacking order) or structures with small deviations from stoichiometry.

iii) The increase of birefringence from \{100\} over the \{111\} to the \{110\} sectors runs parallel with an increase in absorption, growth velocity and electric conductivity.

iv) The observation of simultaneously and successively operating \{100\} and \{111\} growth centers on NIB stands in close analogy to the observations of Kasatkin [23, 24] on \(\text{NaBrO}_3\) crystals. He found that a particular growth center belongs to particular limits of supersaturation. At a critical concentration an active center loses its activity and another center takes over, which in turn is also bound by upper and lower limits of supersaturation. NIB is one of the few boracites that we were unable to grow at the saturation pressure on the dihalide because the iodine partial pressure of \(\text{NiI}_2\) is extremely high at 900°C. As a consequence, the supersaturation changed during growth, and the sequence of growth layers is plausible. On other boracites, which had been grown at the saturation pressure of the dihalide, we found no evidence for a similar layer structure (e.g., \(\text{NiCl}_2\) and \(\text{NiBr}_2\)-boracite).

v) The growth layers in NIB were found to be responsible for repeated antiparallel ferroelectric domains below 60°K (Fig. 26a).

5.2 Ferroelectric–Ferromagnetic Domains in \(\text{Ni-I-Boracite (NIB)}\)

As reported briefly elsewhere [4], ferromagnetoelectricity in NIB below 64°K was evidenced by a spontaneous Faraday effect and electric/magnetic domain switchings. In the following we shall describe the experiments that led us to consider \(m'm2'\) as the most probable magnetic point group.
of the visual observation of these effects for cubic materials, and those with the optic axis parallel to the magnetization direction, is given in references [25] and [26]. However, NIB is essentially optically biaxial below 60°K, and the direction of magnetization is not parallel to the optic axes. Therefore, in most crystal sections we had a superposition of Faraday rotation with crystallographic, magnetic, and parasitic birefringence. The effect of birefringence on optical rotation has been studied repeatedly in the past by different methods [27, 28, 29, 30]. The phenomenology for magnetic rotation is in a first approximation the same. The noteworthy points for our purposes are the following:

a) When birefringence and rotation are present simultaneously, then it depends on the ratio between the phase difference produced by the rotation alone and the phase difference produced by the birefringence alone, whether the effects of one or the other property are more or less covered. At high birefringence, a small rotation is not detectable, and vice versa.

b) When polarized light enters such a crystal, then elliptically polarized light leaves the crystal, in the general case, also when the plane of polarization of the arriving light is parallel to an axis of birefringence (azimuth 0° and 90°).

c) For the azimuths 0° and 90°, there is also the maximum effective rotation, i.e., the angle between the polarization plane of the arriving light and the plane of the large axis of the ellipse of the leaving beam is maximum. This was important for the observation of magnetic domains in the \{110\} and \{111\} sectors with high parasitic birefringence.

*Close below 60°K, the maximum parasitic birefringence of \{110\} and \{111\} sectors was higher than the natural birefringence of the B-phase.
d) From a measurement of ellipticity and effective rotation, it is in principle possible to separate the birefringence from the rotation [30].

e) Because the maximum effective rotation at azimuth $0^\circ$ or $90^\circ$ is accompanied by maximal dispersion of rotation, this setup is invaluable for quantitative measurement and visual observation as well.

From what precedes it is plausible that precise visual determination of the Curie temperature of a weak ferromagnet like NIB is not possible by means of the Faraday effect when birefringence is present.

Even in the $\{100\}$ growth sectors of NIB that have very low birefringence ($\sim 0.0005$), we detected the onset of color dispersion only at $60^\circ K$ (with nearly crossed polaroids and simultaneous frequent switching of the magnetic field), while susceptibility and magneto-electric effect [4] indicated $62^\circ$ to $64^\circ K$.

5.2.3. Determination of the Directions of Spontaneous Polarization and Magnetization. The study of numerous platelets under electric and magnetic fields showed that the spontaneous polarization lies parallel to one of the cubic edges [100], as is the case for the other boracites, while the magnetization is perpendicular to the polarization, in a $[110]$ or $[110]$ direction. The relevant decisive experiments are described in the following paragraph. They were made between $40^\circ$ and $60^\circ K$, using electric switching fields of up to $20$ kV/cm and magnetic ones of up to $7.6$ kOe. Magnetic coercive fields are given in reference [4]. Crystal dimensions ranged between 4 and $9$ mm$^2$ surface, and 50 to $150 \mu$ thickness.
Experiment 1: Platelets were cut from \{100\} sectors perpendicular to the quasi-optic axis (see Figs. 1, 20). They were equipped with transparent electrodes. When poled perpendicular to the platelet, no color dispersion due to the Faraday effect was visible, but the green-yellow color that is characteristic of nonferromagnetic NIB above 60°K appeared. The extinction directions and n_α/n_γ axes lay at 45° to the cube edges and were detected with a Red-I retardation plate. The 90° rotation of the n_γ/n_α directions in the plane of the platelet was readily observed when the polarization direction was inverted. This is in accord with other boracites (see Table 4/O/R/a). The absence of a Faraday effect in this orientation showed that the magnetization lay in the plane perpendicular to the polarization. Slight tilting of the platelet towards the microscope axis let red or green shades appear, owing to a small component of magnetization becoming in line with the direction of propagation of light.

Experiment 2: \{110\}_cub-cut platelets were equipped with electrodes on the narrow \{001\} and \{001\} facets (Fig. 25), and the polarization was therefore switched in the plane of the platelet. When the electric dipole (+→-) was directed from the \{001\} face with A corners to the \{001\} face with B corners, there was no Faraday effect, the platelet appearing green-yellow in 45° position of the crossed polaroids. With a Red-I retardation plate, n_α and n_γ were found to be in the plane of the platelet (Table 4, P/R/a). When the polarization direction was reversed, an arbitrary distribution of bright green and red antiparallel ferromagnetic domains was obtained. The application of a magnetic field bias enhanced the formation of a single domain. In spite of the superposed Faraday rotation it was fortunately possible, with a Red-I retardation plate, to indicate the axes of the δ-phase birefringence. n_β and n_γ now lay in the plane of the platelet (Table 4, P/R/a).

These two experiments showed that the polarization direction and the orientation of the optical indicatrix are the same as in the other Ni-boracites. The direction of magnetization was found to be parallel to n_α and consequently to the a-axis. Assuming the crystallographic symmetry to be mm2, the magnetic point group must be m'm2', because it is the only point group derivable from mm2 that admits polarization and magnetization perpendicular to each other. Because to each of the six polarization directions there belong two stable states of the magnetization, twelve distinguishable P_z/M_q configurations are possible in a crystal.

All switching experiments on \{100\}_cub and \{111\}_cub cuts confirmed the relationship established. We shall mention only a particular domain configuration of antiparallel ferroelectric domains and spikes that occurred frequently spontaneously after cooling as a consequence of the discussed layer structure (5.1.) parallel to the \{100\} growth faces. A \{100\}_cub-cut cross section is shown in Fig. 26. The electric polarization of the \{110\}_o.r., twinned stripes lies in the plane of the platelet. With a magnetic field in the platelet and perpendicular to the domain polarizations, the stripes appear alternately red and green. Application of a magnetic field perpendicular to the platelet makes the slab appear uniformly red or green, although it is then not a ferroelectric-ferromagnetic single domain.
Ferroelectric and magnetic domain switchings did not always work with the same ease. With the stereomicroscope we observed that domains often remained pinned at the surface, probably owing to strains introduced by polishing. While \{100\} sectors switched rather easily, \{110\} and \{111\} sectors did not respond in all cubic directions. Very good ferroelectric single domain were obtained only by cooling from above 64°K in an electric field, using \{100\} sectors.

5.2.4. Confirmation of the \(P_3/M_3\) Configuration by the Magnetoelectric Effect. As reported briefly elsewhere [4], we have measured the magnetic-field-induced magnetoelectric effect in NIB. Denoting the direction of \(P_3\) by \(z\) and that of \(M_3\) by \(y\) (point group \(m'm_2m_2\)), we obtain the following equations for the linear magnetoelectric effects:

\[
P_z = \alpha_{zy} H_y, \quad M_y = \alpha_{zy} E_z, \quad P_y = \alpha_{yz} H_z, \quad M_z = \alpha_{yz} E_y.
\]

We have measured the temperature dependence of \(\alpha\) as defined by the first equation (Fig. 27). The effect as defined by the third equation was too weak to be detectable.

Experimental: Carefully selected slabs with only one growth center were cut from \{100\} growth sectors (Fig. 1c) parallel to the growth face. Silver paint electrodes were applied to the faces. The crystals were cooled from above 64°K in simultaneous magnetic \((H = 7.6\, \text{kOe} \parallel [110]\text{cub})\) and electric \((E = 10\, \text{kV/cm} \parallel [001]\text{cub})\) fields down to 15°K. After this procedure, a quasi-ferroelectric/ferromagnetic single domain was obtained which remained stable without any field up to 50°K, when the polarization direction was chosen in such a way to correspond to the stable state of the growth-induced unidirectional anisotropy perpendicular to the growth face. (This anisotropy is reflected in the displaced ferroelectric hysteresis loop [4].) The magnetoelectric effect was measured by static methods, a) with a Keithley 610A electronic voltmeter [31] or b) a Beckman digital voltmeter and Kistler charge amplifier. To check whether some antiparallel ferroelectric domains were present with \(P_3\) perpendicular to the platelet, the cosine relationship between the magnetoelectric signal along \(z\) and the azimuth of the applied magnetic field was verified. For the planes \(zy\) and \(xy\) we found that the relationship \(P_z = \alpha_{zy} H \cos \theta\) holds when \(\theta\) is understood as the angle between \(M_3\) and the applied magnetic field \(H\). An example for a well-oriented sample is given in Fig. 28. However, no control was possible of whether part of the crystal had some domains in the orientation of one or more of the remaining four polarization directions and thereby may have escaped measurement. Therefore, the constant \(\alpha\) \((3.3 \cdot 10^{-4} \text{ at 15°K})\) may turn out to be somewhat higher for better crystals than indicated in reference [4].

For all magnetic-field-induced charge measurements it was important to stabilize the temperature well. Otherwise the strong pyroelectric effect (Fig. 29) might have disturbed the correct values of \(\alpha\). The pyroelectric effect turned out to give a much more precise indication of temperature stability than the copper—constantan thermocouple. Thus, we regulated the temperature by hand until the electrometer needle came to a standstill.

At temperatures between 45° and 50°K, where the magnetization could be switched easily by the available magnetic fields (up to 7.6 kOe), a butterfly loop of the (ME) response was observed ([4] and Fig. 30a) for a given direction of \(P_3\). When the polarization direction was reversed, the butterfly loop turned upside down and its plane was rotated by 90° round the polarization direction (Fig. 30b) for a fixed experimental setup. In other words, the crystal had to be turned by 90° in order that the butterfly loop, relevant to the opposite direction of polarization, could be measured with an unchanged magnetic field direction. These observations confirm excellently the visual observations of domains and thereby the point group \(m'm_2m_2\).

We observed invariably that the magnetization willingly turns by 90° when the polarization is switched by an electric field. The reverse experiment — the magnetic-field-induced 180° reversal of the polarization, where a magnetic field is applied perpendicular to the magnetization direction — did not work with the same
ease. This experiment was possible only in one crystal after cooling in simultaneous electric and magnetic fields, the directions of which corresponded to the unstable position of the unidirectional growth anisotropy. Below 50°K, this poled domain was frozen in. However, at 50°K and above, the application of a magnetic field perpendicular to $M_S$ produced a 180° reversal of $P_S$ (Fig. 31). Increase in temperature had the same effect: $P_S$ switched back spontaneously. At temperatures just below the phase transition, it was possible to switch $P_S$ easily by the application of a magnetic field of, e.g., 7.6 kOe perpendicular to $M_S$, but because of the above-mentioned unidirectional growth anisotropy for $P_S$, the polarization switched back immediately after removal of the magnetic field. We found that the sign of the signal owing to the magnetic-field-induced 180° reversal of $P_S$, producing charges proportional to $2P_S$, was opposite to that of the magnetoelectric effect. This explains the negative peak of $\alpha$ just below the phase transition (Fig. 27). It is clear that those ferroelectric domains which are pinned unidirectionally to one of the four remaining [100]$_{cub}$ directions may also contribute to the "pseudo-magnetoelectric" signal. For such domains, the magnetic field will produce a 60° rotation of $M_S$ and a 90° rotation of $P_S$. Charges proportional only to $P_S$ will develop. At a 4-keOe bias, i.e., the maximum bias applicable with our experimental setup, the parasitic peak became smaller but did not disappear completely. In dynamic measurements of $\alpha$ with a strong magnetic field bias, the negative peak should disappear completely.

Acknowledgments

The author wishes to thank the Battelle Institute, Geneva Research Center, for support of this paper, Dr. E. Ascher for valuable discussions, H. Rieder for the very able assistance in the low-temperature experiments, and H. Tippmann for the preparation of samples and the measurement of refractive indices.

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