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## Trigonal Boracites : A New Type of Ferroelectric and Ferromagnetolectric Material That Allows No 180°-Electric Polarization Reversal

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The Fe-Cl-, Fe-Br-, Fe-I-, Co-Cl- and Zn-Cl-boracites are found to have trigonal space group  $C_{3v}^6$  below 528, 405, ~200, 468 and 472 to 480°K, resp. The trigonal cell corresponds to the primitive trigonal cell for the face-centred cubic parent phase  $T_d^5$  (Fig. 1). Ferroelectricity is evidenced by domain switching. The coercive fields are very high (50 to 800 kV/cm) at room temperature. Due to the high temperature/low temperature phase relationship  $T_d^5/C_{3v}^6$ , the spontaneous polarization is not reversible by 180° but jumps only from *e.g.*  $[\bar{1}\bar{1}\bar{1}]$ , to  $[1\bar{1}\bar{1}]$ ,  $[1\bar{1}\bar{1}]$  or  $[\bar{1}11]$ , etc. (Fig. 2), in accord with crystal structure and group theoretical predictions (E. Ascher: private communica-

tion; K. Aizu: J. Phys. Soc. Japan 23 (1967) 794). Hence we can also expect hysteresis loops that are asymmetric both in polarization and coercive field (Fig. 3). The absolute configuration of the  $C_{3v}^6$ -phase (hence the  $T_d^5$ -phase) has been derived by combining polarization microscopy, switching experiments and Mössbauer effect data (H. Schmid and J. M. Trooster: Solid State Commun. 6 (1965) 447). Two twinning laws are observed:  
 a) head-head (tail-tail) domains with  $\{110\}$  as composition plane,  
 b) head-tail domains with  $\{100\}$  as composition plane (Fig. 4).  
 At the onset of ferromagnetism at low tempera-

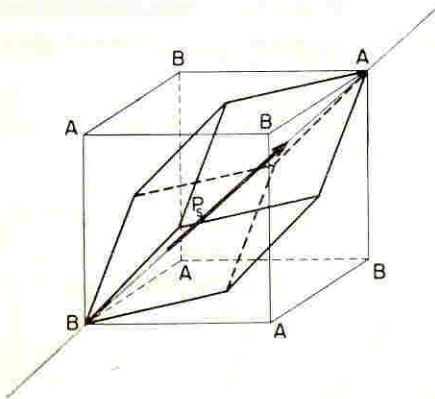


Fig. 1.

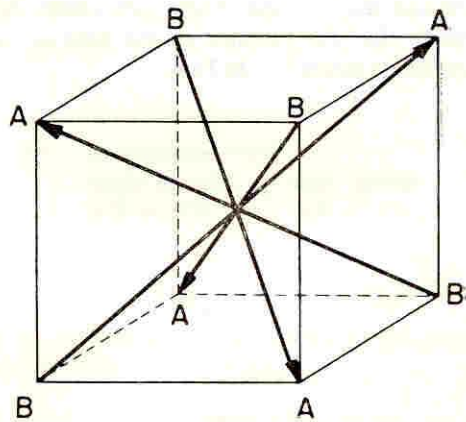


Fig. 2.

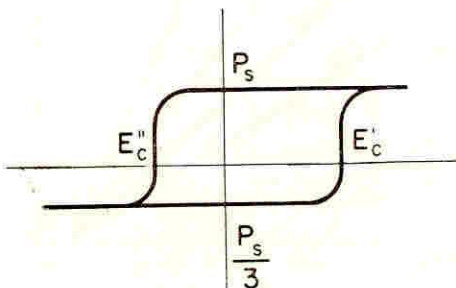


Fig. 3.

ture in Fe-Cl-, Fe-Br-, Fe-I- and Co-Cl-boracite (G. Quézel & H. Schmid: Solid State Commun. 6 (1968) 447), these compounds become ferromagnetolectric (simultaneously ferroelectric and ferromagnetic). The Shubnikov point group of Co-Cl-boracite in this region is  $m_s$  with  $P_s$  along  $\langle 111 \rangle_{\text{cub}}$  and  $M_s$  along  $\langle 110 \rangle_{\text{cub}}$ . The other mentioned boracites are probably isotropic.

Full account to appear in Phys. Status solidi.

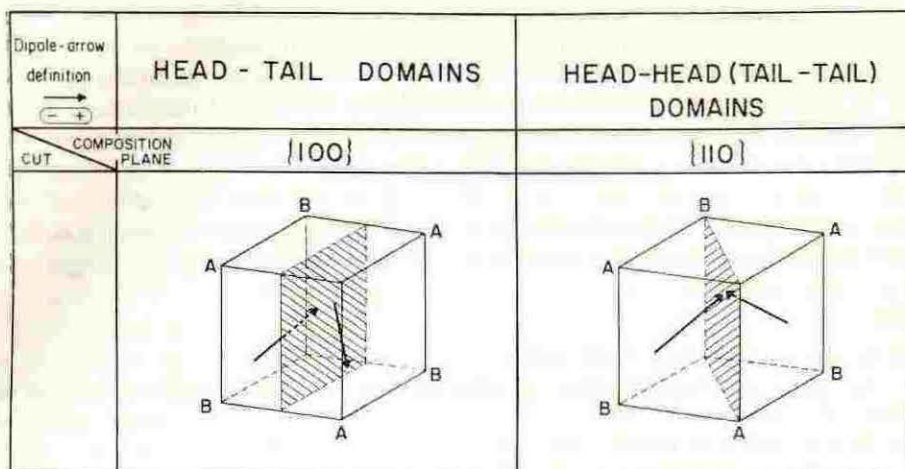


Fig. 4.

## DISCUSSION

H. TAKAHASI: Have you observed the ferroelectric-paraelectric transition? I would like to comment that in case of symmetry  $T_d^5$ , the leading term in the free energy function is of third degree in  $P$ , and in that case the phase change is necessarily of first order.

H. SCHMID: The ferroelectric-paraelectric transition in the boracites is always of the type  $C_{2v}^5 \leftrightarrow T_d^5$  and indeed of first order. All the other known crystallographic polymorphic transitions in the boracites are also of first order. According to magnetoelectric effect measurements the onset of weak ferromagnetism, starting from the  $C_{3v}^6$ -phases, seems to be of second order.

W. KINASE: I think that the head-to-head type domain wall must have very high energy. I wonder why we can give such type domain wall.

W. N. LAWLESS: The head-to-head or tail-to-tail domain wall configuration requires the existence of free charges on the domain wall. Is this reflected in conductivity measurements on these materials?

H. SCHMID: From the symmetry point of view the observed head-to-head walls are allowed. Therefore it seems only necessary to reduce the electrostatic energy in some way or the other. No systematic conductivity measurements are available, however, the following observations are qualitatively plausible: a) during switching experiments on (111) platelets with a specific resistance of  $10^{12} \Omega \text{cm}$  (Co-Cl-boracite) the electrostatically unfavourable head-head (tail-tail) walls are avoided in favour of head-to-tail arrangements, b) head-head configurations appear when the crystals are slowly cooled from above their transition temperatures (*i. e.* from about  $200^\circ \text{C}$ ). At these higher temperatures the (semi)-conductivity is already sufficiently high to allow for space charge dissipation.

J. C. BURFOOT: Even in barium titanates, head-to-head configurations apparently can occur, as I was shown by Prof. V. G. Bhide at NPL Delhi in his topographical study on  $\text{BaTiO}_3$  surface.

L. A. SHUVALOV: 1) In 1963<sup>1)</sup> we have written about the opportunity of the existence of the new type of ferroelectrics which would have nonreversible but reorientable spontaneous polarization  $P_s$ . In 1967<sup>2)</sup> we supposed that boracities would be the first example of such new ferroelectrics. Now Dr. H. Schmid have found that our supposition is realized. 2) The doubts, which are heard in questions, about the existence in boracites of the charged domain walls have no reasons. In 1967<sup>3)</sup> we have found that domain structure in  $\beta$ -phase of  $\text{NaH}_2(\text{SeO}_3)_2$  is such that charged domain walls can appear at the reversal of  $P_s$ . Apparently the

same situation is realized in  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ .<sup>4)</sup> Finally J. Fousek and V. Janovec<sup>5)</sup> have recently shown that with accordance of the symmetry laws of the domain structure many ferroelectrics can have charged domain walls and must have them at the reversal of the spontaneous polarization. 3) There is no any reason for discussion about the order of the phase transitions in boracites. Theory of Landau<sup>6)</sup> shows that all transitions from crystal class  $\bar{4}3m$  (paraelectric phase of boracites) must be transitions of the first order. Then it is clear that transitions between ferroelectric phases with fixed orientations of  $P_s$  ( $mm'2$  and  $3m$ ) must be transitions of the first order too. Transitions of the second order are not forbidden in boracites for transitions between ferroelectric phase with fixed orientation of  $P_s$  and ferroelectric phase with arbitrary orientation of  $P_s$  if best one exists.

#### References

- 1) L. A. Shuvalov: *Kristallografiya* **8** (1963) 617.
- 2) L. A. Shuvalov: Lectures in the Institute of Radiotechnics and Electronics of Czechoslovak Academy Sciences, Prague, 1967.
- 3) L. A. Shuvalov and N. R. Ivanov: *Phys. Status solidi* **22** (1967) 279.
- 4) S. E. Cummins and L. E. Cross: *J. appl. Phys.* **39** (1968) 2268.
- 5) J. Fousek and V. Janovec: *J. appl. Phys.* **40** (1969) 135.
- 6) L. D. Landau and E. M. Lifshitz: *Elektrodinamika sploshnykh sred.* (Gostekhizdat, Moskva, 1957).