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## Tetragonal Ferroelastic/Antiferroelectric Chromium–Chlorine Boracite, $\text{Cr}_3\text{B}_7\text{O}_{13}\text{Cl}$ , from X-ray Diffraction on a Single-Domain Crystal at 230 K

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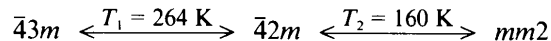
### Abstract

$\text{Cr}_3\text{B}_7\text{O}_{13}\text{Cl}$ ,  $M_r = 475.12$ , tetragonal,  $P\bar{4}2_1c$  (114),  $a = 12.1410$  (3),  $c = 12.1606$  (4) Å,  $V = 1792.52$  (9) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 3.521$  mg mm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 3.393$  mm<sup>-1</sup>,  $F(000) = 1824$ ,  $T = 230$  K,  $R = 0.029$ ,  $wR = 0.024$  for 1991 unique reflections. The structure contains five symmetry-independent Cr sites, four with sixfold (4O + 2Cl) and one with fivefold (4O + 1Cl) coordination.

### Introduction

$\text{Cr}_3\text{B}_7\text{O}_{13}\text{Cl}$  (hereafter Cr-Cl) belongs to the class of fully ferroelectric/fully ferroelastic [nomenclature of Aizu (1970)]  $M_3\text{B}_7\text{O}_{13}X$  boracites, where  $M$  denotes a divalent metal ion and  $X$  a halogen ion. The optic, dielectric and pyroelectric properties of Cr-Cl have been studied by various authors (Nesterova, Pisarev & Andreeva, 1974; Bochkov & Drozhdin, 1975; Schmid & Tippmann, 1978). At room temperature Cr-Cl has cubic symmetry and space group  $F\bar{4}3c$

(Nelmes & Thornley, 1974). Upon decreasing the temperature it undergoes two structural phase transitions, one at  $T_1 = 264$  K to a tetragonal ferroelastic/antiferroelectric modification of symmetry  $\bar{4}2m$ , and another at  $T_2 = 160$  K to an orthorhombic fully ferroelectric/fully ferroelastic modification of symmetry  $mm2$  (Ye, Rivera & Schmid, 1990, 1991a):



Structural data for the two low-temperature modifications are not yet available. Here we report the single-crystal data of the tetragonal modification. It is the first tetragonal boracite structure to be characterized.

### Experimental

Crystals were grown by the chemical vapour transport method (Schmid, 1965; Schmid & Tippmann, 1979). A rectangular parallelepiped single-crystal platelet delimited by cubic (100), (010) and (001) faces (dimensions 0.212 × 0.550 × 0.025 mm) was

prepared by polishing with 0.25  $\mu\text{m}$  diamond paste and mounted on a quartz fibre with silicone glue. Preliminary observations under a polarized light microscope in conjunction with an optical He-flow cryostat revealed domains typical of the tetragonal ( $160 < T < 264$  K) and orthorhombic ( $T < 160$  K) modifications. Thereafter the crystal was mounted on a CAD-4 automatic four-circle diffractometer equipped with a liquid-nitrogen cooling device (model FR 537, Enraf-Nonius, Delft) and a polarizing microscope. After cycling the crystal several times through the orthorhombic  $\leftrightarrow$  tetragonal phase transition (between 160 and 180 K), a tetragonal ferroelastic single domain was stabilized at 230 K. It should be noted that cycling through the cubic  $\leftrightarrow$  tetragonal transition does not usually lead to a tetragonal ferroelastic single-domain crystal. On the other hand, the presence of antiphase domains cannot be excluded. The tetragonal cell parameters at 230 K were determined by the least-squares analysis of 25 reflections with  $27 < \theta < 29^\circ$ . A full sphere of 10 637 reflections was collected at 230 K for  $(\sin\theta/\lambda)_{\text{max}} = 0.7027 \text{ \AA}^{-1}$  and  $-11 \leq h \leq 12$ ,  $-16 \leq k \leq 16$ ,  $-16 \leq l \leq 16$ , in the  $\theta$ - $2\theta$  scan mode by using monochromatic Mo  $K\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). During data collection the crystal remained single domain as controlled regularly through a polarizing microscope mounted on the diffractometer. The standard reflections 400 and 044 did not vary by more than 1.3 and 2.2%, respectively. After averaging equivalent reflections, 2597 unique reflections were obtained ( $R_{\text{int}} = 0.021$ ). The observed systematic absences of the reflections  $hhl$  ( $l = 2n + 1$ ),  $h00$  ( $h = 2n + 1$ ),  $00l$  ( $l = 2n + 1$ ) and theoretical considerations (Tolédano, Schmid, Clin & Rivera, 1985) led to the unique space group  $P\bar{4}2_1c$  (*International Tables for X-ray Crystallography*, 1983, Vol. A). The positions of the heavy atoms were obtained using the *MULTAN87* program (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987) and the other atom positions were obtained from electron density maps. The structure was refined with the *XTAL2.6* program system (Hall & Stewart, 1989) by minimizing the function  $\sum w_i(|F_o|_i + |F_c|_i)^2$  with  $w_i = 1/\sigma^2(|F_{\text{rel}}|)$ . Anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). An absorption correction was made with maximum and minimum transmission factors of 0.8150 and 0.4405 respectively; the absolute structure parameter (Flack, 1983) was refined in a first step but showed no significant variation from 0; 184 variables, including 69 positional parameters, 106 anisotropic (Cr, Cl, O) and 7 isotropic (B) atomic displacement parameters for 27 independent atoms, secondary-extinction correction parameter [Gaussian distribution of mosaic  $G = 0.82$  (3)], one scale factor (0.50875); final  $R = 0.029$ ,  $wR = 0.024$  and  $S = 2.321$ ,

Table 1. Atomic parameters for  $\text{Cr}_3\text{B}_7\text{O}_{13}\text{Cl}$  at 298 K ( $F\bar{4}3c$ ) and at 230 K ( $P\bar{4}2_1c$ ) (e.s.d.'s in parentheses)

The origin in the tetragonal structure is shifted by (0.25 0.25 0) from that in the cubic structure.  $W$  denotes Wyckoff symmetry positions of atoms.  $U_{\text{eq}}$  denotes equivalent isotropic displacement parameters where  $U_{\text{eq}} = \frac{1}{3}(\sum_i U_{ii})$ .

	$W$	$x$	$y$	$z$	$U_{\text{eq}}(\text{\AA}^2 \times 100)$
<i>F<math>\bar{4}3c</math></i>					
Cr <sub>r</sub>	24(c)	0.25	0.25	0	0.97 (2)
Cl	8(b)	0.25	0.25	0.25	1.70 (2)
O(1)	8(a)	0	0	0	0.73 (4)
O(2)	96(h)	0.01960 (6)	0.09689 (6)	0.18015 (6)	0.49 (3)
B(1)	24(d)	0.25	0	0	0.46 (4)
B(2)	32(e)	0.0802 (1)	0.0802 (1)	0.0802 (1)	0.87 (3)
<i>P<math>\bar{4}2_1c</math></i>					
Cr(1)	8(e)	0.24357 (6)	0.00235 (6)	0.25540 (6)	0.61 (5)
Cr(2)	8(e)	0.49561 (6)	0.25599 (5)	0.25641 (6)	0.58 (5)
Cr(3)	4(d)	0	0.5	0.02399 (5)	0.57 (5)
Cr(4)	2(b)	0	0	0.5	0.58 (8)
Cr(5)	2(a)	0	0	0	0.55 (8)
Cl(1)	4(d)	0	0.5	0.24456 (7)	1.3 (1)
Cl(2)	4(c)	0	0	0.2480 (2)	1.2 (1)
O(1)	8(e)	0.2586 (3)	0.2417 (3)	0.0093 (3)	0.3 (1)
O(2)	8(e)	0.0676 (2)	0.6521 (2)	0.0225 (2)	0.4 (1)
O(3)	8(e)	0.0724 (2)	0.2318 (2)	0.0927 (2)	0.3 (1)
O(4)	8(e)	0.0735 (2)	0.1548 (2)	0.5174 (2)	0.4 (1)
O(5)	8(e)	0.1463 (2)	0.2745 (2)	0.3166 (2)	0.3 (1)
O(6)	8(e)	0.1559 (2)	0.0688 (2)	0.0208 (2)	0.4 (1)
O(7)	8(e)	0.2258 (2)	0.4336 (2)	0.3981 (2)	0.3 (1)
O(8)	8(e)	0.2275 (2)	0.1535 (2)	0.1850 (2)	0.3 (1)
O(9)	8(e)	0.2674 (2)	0.0701 (2)	0.4081 (2)	0.4 (1)
O(10)	8(e)	0.2689 (2)	0.3468 (2)	0.1798 (2)	0.3 (1)
O(11)	8(e)	0.3412 (2)	0.2340 (2)	0.3253 (2)	0.3 (1)
O(12)	8(e)	0.4335 (2)	0.2725 (2)	0.1012 (2)	0.4 (1)
O(13)	8(e)	0.5671 (2)	0.1503 (2)	0.0218 (2)	0.4 (1)
B(1)	8(e)	0.0001 (3)	0.2511 (4)	0.0000 (5)	0.5 (1)
B(2)	8(e)	0.0009 (3)	0.2486 (4)	0.4953 (4)	0.4 (1)
B(3)	8(e)	0.1508 (4)	0.3483 (4)	0.4028 (2)	0.65 (6)
B(4)	8(e)	0.1746 (4)	0.1708 (4)	0.0787 (3)	0.36 (8)
B(5)	8(e)	0.2480 (4)	0.2515 (4)	0.2517 (5)	0.51 (6)
B(6)	8(e)	0.3268 (4)	0.1726 (4)	0.4266 (2)	0.35 (5)
B(7)	8(e)	0.3283 (4)	0.3258 (4)	0.0791 (3)	0.40 (8)

considering 1991 unique reflections with  $F_{\text{rel}} > 3\sigma(F_{\text{rel}})$ ; the maximum shift/e.s.d. in the last cycle was 0.00112; maximum (minimum) residual electron density 1.2 ( $-2.5$ )  $\text{e \AA}^{-3}$ .\*

The data collection for the cubic modification was carried out at room temperature on the same crystal before the low-temperature experiment;  $(\sin\theta/\lambda)_{\text{max}} = 0.8243 \text{ \AA}^{-1}$ ,  $0 \leq h \leq 20$ ,  $0 \leq k \leq 20$ ,  $0 \leq l \leq 20$  and antireflections, 3064 reflections collected (467 unique,  $R_{\text{int}} = 0.048$ ); cell parameters refined from 24 reflections with  $32 < \theta < 33^\circ$ ,  $T = 298$  K; 20 atomic parameters refined from 467 contributing unique reflections gave  $R = 0.020$  and  $wR = 0.018$  ( $S = 1.380$ ); residual electron density 1.1 ( $-0.6$ )  $\text{e \AA}^{-3}$ .

The atomic parameters of the tetragonal and cubic modifications are listed in Table 1. They are partially standardized by using the *STRUCTURE TIDY* program (Gelato & Parthé, 1987). Those of the cubic modification are included because of their higher

\* Lists of structure factors, form factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54146 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) in tetragonal Cr<sub>3</sub>B<sub>7</sub>O<sub>13</sub>Cl at 230 K and comparison with those of cubic Cr<sub>3</sub>B<sub>7</sub>O<sub>13</sub>Cl at room temperature (*e.s.d.*'s in parentheses)

<i>F</i> $\bar{4}3c$		<i>P</i> $\bar{4}2_1c$	$\Delta$	
Cr—2Cl,	3.0329 (1)	Cr(1)—Cl(1)	3.1135 (7)	0.0806
Cr—4O(2),	2.0554 (7)	Cr(1)—Cl(2)	2.9587 (7)	-0.0742
		Cr(1)—O(7)	2.078 (3)	0.023
		Cr(1)—O(8)	2.034 (3)	-0.021
		Cr(1)—O(9)	2.052 (3)	-0.003
		Cr(1)—O(10)	2.052 (3)	-0.003
		Cr(2)—Cl(1)	3.1084 (7)	0.0755
		Cr(2)—Cl(2)	2.9635 (7)	-0.0694
		Cr(2)—O(3)	2.063 (3)	0.008
		Cr(2)—O(5)	2.067 (3)	0.012
		Cr(2)—O(11)	2.071 (3)	0.016
		Cr(2)—O(12)	2.042 (3)	-0.013
		Cr(3)—Cl(1)	2.682 (1)	-0.351
		Cr(3)—Cl(1)	3.398 (1)	0.365
		Cr(3)—O(2)	2.021 (2)	-0.034
		Cr(3)—O(13)	2.074 (2)	0.019
		Cr(4)—2Cl(2)	3.065 (3)	0.032
		Cr(4)—O(4)	2.091 (2)	0.036
		Cr(5)—2Cl(2)	3.016 (3)	-0.017
		Cr(5)—O(6)	2.085 (3)	0.030
Cl—6Cr,	3.0329 (1)	Cl(1)—2Cr(1)	3.1135 (7)	0.0806
		Cl(1)—2Cr(2)	3.1084 (7)	0.0755
		Cl(1)—Cr(3)	3.398 (1)	0.365
		Cl(1)—Cr(3)	2.682 (1)	-0.351
		Cl(2)—2Cr(1)	2.9587 (7)	-0.0742
		Cl(2)—2Cr(2)	2.9635 (7)	-0.0694
		Cl(2)—Cr(4)	3.065 (3)	0.032
		Cl(2)—Cr(5)	3.016 (3)	-0.017
O(1),—4B(2),	1.684 (1)	O(1)—B(4)	1.578 (5)	-0.106
		O(1)—B(6)	1.550 (5)	-0.134
		O(1)—B(7)	1.575 (6)	-0.109
		O(1)—B(3)	2.251 (5)	0.567
		O(2)—Cr(3)	2.021 (2)	-0.034
O(2),—Cr,	2.0554 (7)	O(2)—B(1)	1.459 (5)	-0.009
O(2),—B(1),	1.4684 (7)	O(2)—B(6)	1.445 (5)	-0.012
O(2),—B(2),	1.433 (1)	O(3)—Cr(2)	2.063 (3)	0.008
		O(3)—B(1)	1.448 (6)	-0.020
		O(3)—B(4)	1.455 (5)	0.022
		O(4)—Cr(4)	2.091 (2)	0.036
		O(4)—B(2)	1.466 (5)	-0.002
		O(4)—B(7)	1.448 (5)	0.015
		O(5)—Cr(2)	2.067 (3)	0.012
		O(5)—B(5)	1.492 (6)	0.024
		O(5)—B(3)	1.380 (4)	-0.053
		O(6)—Cr(5)	2.085 (3)	0.030
		O(6)—B(1)	1.449 (5)	-0.019
		O(6)—B(4)	1.442 (5)	0.009
		O(7)—Cr(1)	2.078 (3)	0.023
		O(7)—B(1)	1.505 (6)	0.037
		O(7)—B(3)	1.380 (5)	-0.053
		O(8)—Cr(1)	2.034 (3)	-0.021
		O(8)—B(5)	1.462 (6)	-0.006
		O(8)—B(4)	1.459 (5)	0.026
		O(9)—Cr(1)	2.052 (3)	-0.003
		O(9)—B(2)	1.474 (6)	0.006
		O(9)—B(6)	1.456 (6)	0.023
		O(10)—Cr(1)	2.052 (3)	-0.003
		O(10)—B(5)	1.472 (6)	0.004
		O(10)—B(7)	1.444 (5)	0.011
		O(11)—Cr(2)	2.071 (3)	0.016
		O(11)—B(6)	1.450 (5)	-0.018
		O(11)—B(5)	1.459 (6)	0.026
		O(12)—Cr(2)	2.042 (3)	-0.013
		O(12)—B(2)	1.454 (6)	-0.014
		O(12)—B(7)	1.456 (6)	0.023
		O(13)—Cr(3)	2.074 (2)	0.019
		O(13)—B(2)	1.482 (5)	0.014
		O(13)—B(3)	1.369 (5)	-0.064
B(1),—4O(2),	1.4684 (7)	B(1)—O(2)	1.459 (5)	-0.009
		B(1)—O(3)	1.448 (6)	-0.020
		B(1)—O(6)	1.448 (5)	-0.020
		B(1)—O(7)	1.505 (6)	0.037
		B(2)—O(4)	1.466 (5)	-0.002
		B(2)—O(9)	1.474 (6)	0.006
		B(2)—O(12)	1.454 (6)	-0.014
		B(2)—O(13)	1.482 (5)	0.014
		B(5)—O(5)	1.492 (6)	0.024
		B(5)—O(8)	1.462 (6)	-0.006
		B(5)—O(10)	1.472 (6)	0.004
		B(5)—O(11)	1.459 (6)	-0.009

Table 2 (*cont.*)

<i>F</i> $\bar{4}3c$		<i>P</i> $\bar{4}2_1c$	$\Delta$	
B(2),—3O(2),	1.433 (1)	B(3)—O(5)	1.380 (4)	-0.052
B(2),—O(1),	1.684 (1)	B(3)—O(7)	1.380 (5)	-0.053
		B(3)—O(13)	1.370 (5)	-0.063
		B(3)—O(11)	2.251 (5)	0.567
		B(4)—O(3)	1.455 (5)	0.022
		B(4)—O(6)	1.442 (5)	0.009
		B(4)—O(8)	1.459 (5)	0.026
		B(4)—O(1)	1.578 (5)	-0.106
		B(6)—O(2)	1.445 (5)	0.012
		B(6)—O(1)	1.550 (5)	-0.134
		B(6)—O(9)	1.456 (6)	0.023
		B(6)—O(11)	1.450 (5)	0.017
		B(7)—O(4)	1.448 (5)	0.015
		B(7)—O(1)	1.575 (6)	-0.109
		B(7)—O(10)	1.444 (5)	0.011
		B(7)—O(12)	1.456 (6)	0.023

accuracy compared to those reported previously (Nelmes & Thornley, 1974). Bond distances are listed in Table 2.

## Discussion

The tetragonal modification of Cr-Cl derives from the cubic modification as follows. The 24-fold Cr site of symmetry  $\bar{4}$  splits into two eightfold sites of symmetry 1 [Cr(1), Cr(2)], one fourfold site of symmetry 2 [Cr(3)] and two twofold sites of symmetry  $\bar{4}$  [Cr(4), Cr(5)]; the eightfold Cl site of symmetry  $\bar{4}$  splits into two fourfold sites of symmetry 2 [Cl(1), Cl(2)]; the eightfold O site of symmetry  $\bar{4}$  remains unsplit and changes to symmetry 1, whereas the 96-fold O site of symmetry 1 splits into 12 eightfold sites of symmetry 1; the 24-fold B site splits into three eightfold sites [B(1), B(2), B(5)], and the 32-fold B site into four eightfold sites [B(3), B(4), B(6), B(7)], all of symmetry 1. During the phase transition major structural changes occur only in the ligand sphere of the Cr(3) site, and in a particular region of the oxygen-boron network (see last column of Table 2). As shown in Figs. 1 and 2 the metal site in the cubic modification (24 atoms per cell) is sixfold coordinated by four close O ligands (Cr—O = 2.06 Å) and two distant Cl ligands (Cr—Cl = 3.03 Å). In the tetragonal modification one of the metal sites [Cr(3) *i.e.* 4 atoms out of 24 per cell] is displaced parallel to the fourfold axis (see arrows on shaded atoms in Fig. 1) such that it is fivefold coordinated by four close O ligands [Cr—O = 2.02 (2 ×), 2.07 (2 ×) Å] and one close Cl ligand [Cr—Cl(1) = 2.68 Å]. The other four metal sites [Cr(1), Cr(2), Cr(4), Cr(5), *i.e.* 20 atoms out of 24 per cell] are sixfold coordinated by four close O atoms (Cr—O = 2.03–2.09 Å) and two distant Cl atoms [Cr—Cl(2) = 2.96–3.11 Å] similar to the cubic modification. As to the Cl sites, one [Cl(2)] is sixfold coordinated as in the cubic modification and the other [Cl(1)] is fivefold coordinated as in the trigonal (rhombohedral) modification of other boracites. In other words, half of the chlorine-chromium

chains in the tetragonal modification (marked by heavy lines in Fig. 1) are interrupted along the tetragonal axis. Thus, the changes of metal-halogen bonding at the cubic-to-tetragonal phase transition

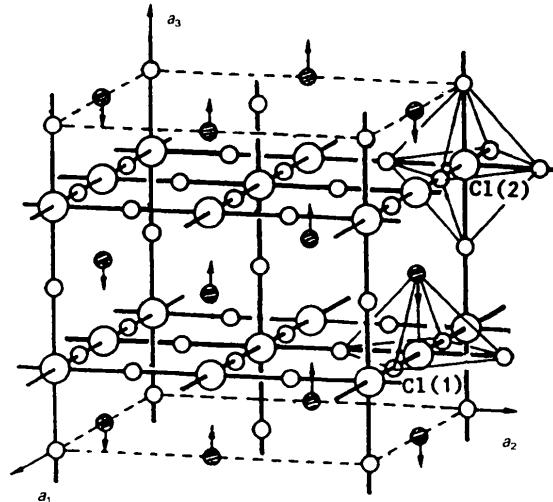


Fig. 1. Schematic illustration of cubic  $\text{Cr}_3\text{B}_7\text{O}_{13}\text{Cl}$ . Large circles: Cl atoms; small open and shaded circles: Cr atoms. Cl(1) and Cl(2) denote halogen sites in the tetragonal modification. Arrows on shaded circles indicate shift directions of Cr(3) towards Cl(1) during the cubic-to-tetragonal phase transition. O and B atoms are omitted.

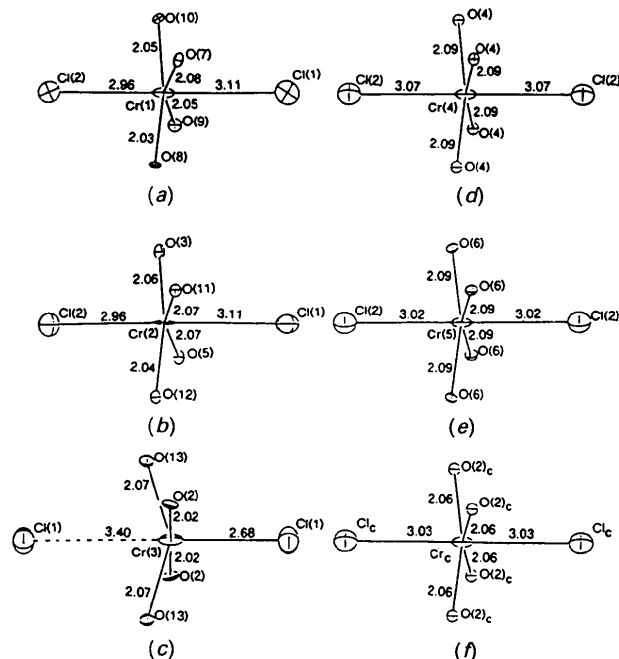


Fig. 2. The coordinations of the five Cr sites in tetragonal  $\text{Cr}_3\text{B}_7\text{O}_{13}\text{Cl}$  boracite at 230 K [(a)–(e)], and comparison with the cubic modification (f). Bond distances are given in Å.

in Cr-Cl differ from those at the cubic-to-trigonal phase transition (Dowty & Clark, 1973; Berset, Yvon, Depmeier, Boutellier & Schmid, 1984) or cubic-to-orthorhombic phase transition (Abrahams, Bernstein & Svensson, 1981) in other boracites. The two latter transitions affect all metal sites and lead to the interruption of all metal-halogen chains.

The changes in the boron-oxygen network concern the breaking of the O(1)–B(3) bond. This bond involves the only O atom not bound to Cr, *i.e.* that which in the cubic modification is tetrahedrally coordinated by boron (B–O = 1.68 Å). As shown in Fig. 3 one of the B ligands in the tetragonal modification is displaced by about 0.7 Å in such a way that O(1) is bound to three B atoms only and B(3) to three O

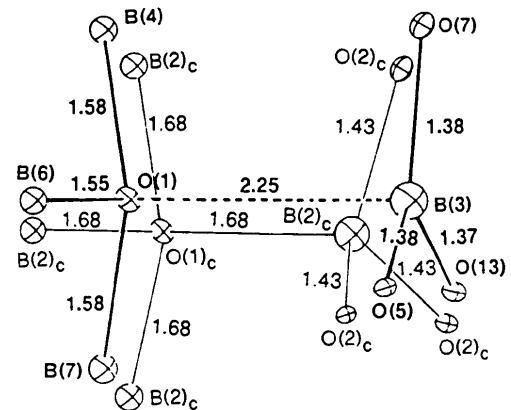


Fig. 3. The breaking of the B–O bond during the phase transition in  $\text{Cr}_3\text{B}_7\text{O}_{13}\text{Cl}$  boracite from the cubic (dotted lines) to the tetragonal (solid lines) modification. Bond distances are given in Å.

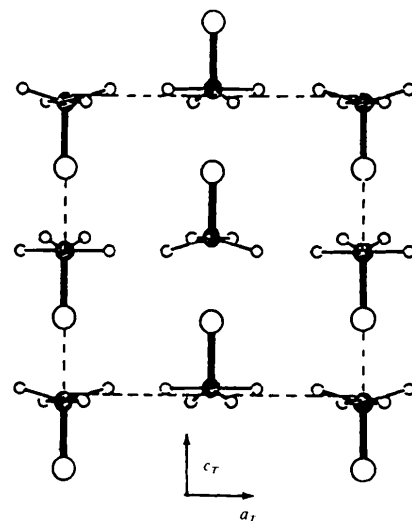


Fig. 4. Antiferroelectric arrangement of polar  $\text{Cr}(3)\text{O}_4\text{Cl}(1)$  groups in tetragonal  $\text{Cr}_3\text{B}_7\text{O}_{13}\text{Cl}$  viewed along [100].

atoms only. The same type of boron–oxygen bond breaking also occurs during the cubic-to-trigonal (rhombohedral) and cubic-to-orthorhombic phase transitions.

The thermal ellipsoids of the tetragonal modification of Cr-Cl are consistent with those in the cubic modification, and also with those in the trigonal and orthorhombic modifications of other boracites. The largest atomic displacements occur with the halogens, and they are nearly isotropic. Those of the metal sites are very anisotropic [Cr(1),  $U_{11}/U_{22} = 4.88$ ; Cr(2),  $U_{22}/U_{11} = 7.41$ ; Cr(3),  $U_{33}/U_{22} = 6.00$ ; Cr(4),  $U_{33}/U_{22} = 4.73$ ; Cr(5),  $U_{33}/U_{22} = 5.59$ ], the largest displacements occurring perpendicular to the strong metal–halogen bonds, *i.e.* parallel to the weak metal–halogen bonds (Fig. 2).

Finally, tetragonal Cr-Cl is the only known example among boracites that has a non-polar structure at low temperature. As shown in Fig. 4 the Cr(3)O<sub>4</sub>Cl groups can be considered as dipoles that are oriented along the tetragonal axis and have opposite signs in neighbouring chains. Such a picture is consistent with the observed antiferroelectric behaviour (Ye, Rivera & Schmid, 1991*b*) and possible occurrence of antiphase domains in the Cr-Cl tetragonal phase (Wondratschek & Jeitschko, 1976).

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## Defect Clustering in the Superionic Conductor Lithium Germanium Vanadate

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### Abstract

The defect structure of Li<sub>3.5</sub>Ge<sub>0.5</sub>V<sub>0.5</sub>O<sub>4</sub> has been determined at 298 and 573 K using high-resolution powder neutron and synchrotron X-ray diffraction

techniques. The compound is one member ( $x = 0.5$ ) of an extensive solid-solution range with the general formula Li<sub>(3+x)</sub>Ge<sub>(x)</sub>V<sub>(1-x)</sub>O<sub>4</sub> and belongs to the family of Li<sup>+</sup>-ion-conducting solids known as the  $\gamma$ -phases. The structure was refined in the ortho-