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Structure of the Fully Ferroelectric/Fully Ferroelastic Orthorhombic Room-Temperature Phase of Iron Iodine Boracite, $\text{Fe}_3\text{B}_7\text{O}_{13}\text{I}$

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Abstract. $\text{Fe}_3\text{B}_7\text{O}_{13}\text{I}$, $M_r = 578.13$, orthorhombic, $Pca2_1$, $a = 8.6540(3)$, $b = 8.6481(3)$, $c = 12.2336(5)$ Å, $V = 915.57(6)$ Å³, $Z = 4$, $D_x = 4.19$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 8.31$ mm⁻¹, $F(000) = 1080$, $T = 298$ K, $R = 0.03$ for 1936 reflections from an optically controlled single-domain crystal. The metal surroundings of the three Fe atoms are analyzed in detail; two of three metal sites (Fe2, Fe3) have similar chemical environments and equal displacement parameters. The averaged difference between the two Fe—I distances is compared with those of other non-cubic boracites. It decreases linearly as the ionic radius of the halogen increases, except for boracites containing Cr and Cu atoms with degenerate electronic states (showing Jahn–Teller effect).

Introduction. Iron–iodine boracite (Fe–I) undergoes an improper phase transition at 348 K from a cubic paramagnetic/paraelectric high-temperature phase ($F43c$) to an orthorhombic paramagnetic/ferroelectric low-temperature phase ($Pca2_1$). The compound undergoes first-order (f) and second-order (s) phase transitions with associated magnetic point-group symmetry changes of $mm\ 21' \xrightarrow{203\text{ K}(f)} m\ 1' \xrightarrow{180\text{ K}(f)} 3m\ 1' \xrightarrow{30\text{ K}(s)} m$ (Ye, Janner, Rivera & Schmid, 1992). No structural data for the non-cubic iodine boracites are known at present. In order to analyze their magnetic properties, accurate X-ray structural data are required.

Experimental. Twinned crystals of Fe–I were prepared by chemical transport reactions (Schmid, 1965). For the determination of accurate lattice constants and atomic positional parameters, single-domain crystals are required. Such a crystal was prepared in a similar way as described elsewhere (Kubel, Mao & Schmid, 1992) from a polished 0.045 mm thick (100)_{cub} plate by mechanical compression using a pair of tweezers, and a polarizing light microscope for simultaneous control of the domain state. The single-domain crystal to be studied was then broken out; residual 90° domains near

the corners were nearly all broken off. Less than 5% of such domains were still present in the crystal. Crystal dimensions were approximately $0.232 \times 0.220 \times 0.045$ mm. Space group $Pca2_1$ was confirmed by analysis of systematically absent reflections. This analysis allowed correlation of the directions of the main axes of the optical indicatrix with the lattice; n_γ is the refractive index for light polarized along b . Lattice parameters were determined from 25 reflections over $\theta = 23.7$ – 24.7° .

Data were collected on a CAD-4 diffractometer using θ – 2θ scans to $\theta_{\text{max}} = 30^\circ$ and for $h - 12 \rightarrow 12$, $k - 12 \rightarrow 12$, $l - 17 \rightarrow 17$. Of 9905 reflections measured, 2636 were independent with 1956 having $I > 3\sigma(I)$. Two standard reflections, measured every 60 min, showed <3% variation; correction applied. Absorption was corrected by Gaussian integration; R_{int} lowered from 0.100 to 0.043 after the absorption correction ($T_{\text{min}} = 1.44$, $T_{\text{max}} = 3.55$). Atomic scattering factors and f' , f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B).

Starting values for the refinements were taken from the earlier work on Co–Br boracite (Kubel, Mao & Schmid, 1992). Refinements (based on F) were performed with the program *Xtal* (Hall & Stewart, 1990) by minimizing the function $\sum w_i(|F_o|_i - |F_c|_i/k_i)^2$ with $w_i = 1/\sigma_i^2(F_o)_i$.^{*} The absolute sense of the polar axis was determined by refinement of the absolute structure factor (Flack, 1983). Refinement converged at $R = 0.03$, $wR = 0.026$, $S = 2.57$ for 118 parameters refined and 1936 observed reflections. $(\Delta/\sigma)_{\text{max}} = 0.04$; $(\Delta\rho)_{\text{min}} = -1.6$, $(\Delta\rho)_{\text{max}} = 1.7$ e Å⁻³. Atomic positions are listed in Table 1 together with displacement factors. In the final stage, 20 reflections at low angle were rejected as they were presumed to be affected by strong extinction, which

^{*} Lists of structure factors and anisotropic temperature factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55717 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH0017]

is found in this type of compound (Thornley & Nelmes, 1974). An extinction correction [0.182 (4)] was applied according to Becker & Coppens (1974). Including all reflections increased the weighted residual from $wR = 2.6$ to 3.5%.

Discussion. The lattice constants found for this crystal [$a = 8.6540$ (3), $b = 8.6481$ (3) and $c = 12.2336$ (5) Å] are smaller (by about 0.005 Å) than those obtained at 303 K by Kobayashi, Mizutani, Schmid & Schachner (1970) from high precision measurements [$a = 8.65879$ (4), $b = 8.65191$ (4) and $c = 12.24034$ (5) Å] – because low-angle measurements were used and absorption was not taken into account. The lattice-constants sequence $b < a < c$ and the proportions between the lattice constants are, however, similar. Of the three lengths a , b , c and $d = [c^2 + (a + b)^2/2]^{1/2}/2$, b is the shortest in Fe-I [$d = 8.6508$ (4) Å]; it is one half of the length of the pseudo-cubic face diagonal $[110]_{\text{cub}}$. This means that squeezing a crystal plate of Fe-I along a pseudocubic $[110]$ direction may lead, under favourable conditions, to a single domain with the b axis along the squeezing direction.

As found for other orthorhombic boracites, the boron-oxygen network is broken up at the position of B₄, which has a particular environment. B₄ is surrounded by three O atoms with short B₄–O distances of 1.371 (7) (B₄–O₃), 1.386 (7) (B₄–O₂) and 1.395 (8) Å (B₄–O₁₁) and is shifted by 0.323 (8) Å from the plane in the direction of O₁; perpendicular to this triangle lies one O atom with a long B–O distance of 2.216 (6) Å (B₄–O₁) and the halogen with an even longer distance of 3.308 (5) Å (B₄–I). The I–B₄–O₁ arrangement is nearly linear with an angle of 179.1 (3)°. The B₄–halogen interaction may play a role in the phase transition of the boracites.

The other B atoms are slightly tetrahedrally distorted with maximum and minimum distances $d_{\text{min}}/d_{\text{max}}$ of 1.43/1.52 (B₁), 1.45/1.50 (B₂), 1.44/1.52 (B₃), 1.44/1.60 (B₅), 1.43/1.56 (B₆) and 1.44/1.60 Å for (B₇) ($\sigma_{\text{B-O}} = 0.01$ Å).

In the orthorhombic phase of iron chlorine, bromine and iodine boracites, two different sites of Fe have been detected by means of Mössbauer studies. (Schmid & Trooster, 1967; Trooster, 1969). Two quadrupole splittings have been observed indicating two different types of Fe²⁺ sites with an occupation ratio of 2:1 (Schmid & Trooster, 1967). The compound under study also shows two distinct types of metal atom. The first type is represented by atoms Fe₂ and Fe₃ and the second type by atom Fe₁. The two types can mainly be distinguished by their anisotropic displacement factors. Those of Fe₂ and Fe₃ are identical within 3 σ (Table 1), whereas those of Fe₁ are different from Fe₂ and Fe₃, but similar to

Table 1. *Atomic positional and isotropic (Å²) and anisotropic (Å²) displacement parameters*

The form of the temperature factor is $\exp\{-2\pi^2[U(1,1)h^2a^{*2} + U(2,2)k^2b^{*2} + U(3,3)l^2c^{*2} + 2U(1,2)hka^*b^* + 2U(1,3)hla^*c^* + 2U(2,3)klb^*c^*]\}$.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>		
Fe1	0.75610 (9)	0.2508 (1)	0.2464 (1)	0.0097 (3)		
Fe2	0.50178 (8)	0.51210 (8)	0.5071 (1)	0.0100 (3)		
Fe3	0.00164 (8)	0.01249 (8)	0.5095 (1)	0.0105 (3)		
I	0.75220 (4)	0.25112 (7)	0.50870	0.01082 (7)		
B1	0.5029 (9)	0.500 (1)	0.753 (1)	0.011 (2)		
B2	0.2547 (7)	0.247 (1)	0.506 (1)	0.0125 (8)		
B3	−0.004 (1)	−0.002 (1)	0.254 (1)	0.014 (2)		
B4	0.4408 (6)	0.2504 (9)	0.3518 (5)	0.017 (1)		
B5	0.2438 (6)	0.4023 (9)	0.1770 (7)	0.009 (1)		
B6	0.9066 (5)	0.7506 (8)	0.8321 (5)	0.0083 (8)		
B7	0.7579 (6)	0.9054 (9)	0.6776 (7)	0.011 (2)		
O1	0.2299 (3)	0.2491 (5)	0.2490 (4)	0.0009 (5)		
O2	0.5325 (3)	0.3318 (4)	0.2789 (3)	0.0080 (7)		
O3	0.3749 (4)	0.3267 (4)	0.4383 (3)	0.0081 (7)		
O4	0.9681 (3)	0.1635 (4)	0.2796 (3)	0.0081 (7)		
O5	0.3187 (4)	0.3615 (4)	0.0756 (3)	0.0072 (7)		
O6	0.1622 (4)	0.9739 (4)	0.2350 (4)	0.0075 (7)		
O7	0.1387 (3)	0.1769 (4)	0.4318 (3)	0.0082 (7)		
O8	0.3321 (4)	0.5175 (4)	0.2375 (4)	0.0070 (7)		
O9	0.1726 (4)	0.1266 (4)	0.0709 (3)	0.0086 (7)		
O10	0.9528 (3)	0.5906 (3)	0.8498 (3)	0.0066 (7)		
O11	0.5459 (4)	0.9102 (4)	0.8575 (3)	0.0081 (7)		
O12	0.9139 (4)	0.5423 (4)	0.6590 (3)	0.0069 (6)		
O13	0.5958 (4)	0.9451 (4)	0.6635 (3)	0.0072 (6)		
	<i>U</i> 11	<i>U</i> 22	<i>U</i> 33	<i>U</i> 12	<i>U</i> 13	<i>U</i> 23
Fe1	0.0050 (2)	0.0061 (2)	0.0178 (7)	0.0005 (3)	0.0003 (3)	−0.0002 (6)
Fe2	0.0113 (5)	0.0117 (4)	0.0070 (7)	−0.0053 (3)	0.0003 (4)	0.0013 (5)
Fe3	0.0124 (5)	0.0111 (4)	0.0080 (7)	−0.0060 (3)	0.0001 (4)	0.0026 (5)
I	0.0104 (1)	0.0107 (1)	0.0114 (1)	0.0001 (1)	−0.0002 (2)	−0.0001 (3)

Table 2. *Metal–halogen and metal–oxygen distances (Å)*

Fe1–I	2.9089 (15)	Fe2–I	2.9763 (8)	Fe3–I	2.9865 (8)
I	3.2089 (15)	I	3.1290 (9)	I	3.1462 (9)
O4	2.025 (3)	O12	2.063 (4)	O7	2.082 (4)
O2	2.096 (3)	O10	2.078 (4)	O9	2.070 (4)
O8	2.112 (4)	O5	2.077 (4)	O13	2.085 (4)
O6	2.111 (4)	O3	2.118 (3)	O11	2.100 (4)

those of cubic boracites (Yoshida, Yvon, Kubel & Schmid, 1992). The chemical surrounding of the Fe₂ and Fe₃ atoms differs significantly from that of the Fe₁ atoms. Interatomic distances around the metal atoms are listed in Table 2. Compared to other orthorhombic boracites, the Fe atoms are only slightly shifted from their positions between two I atoms in the high-temperature structure. Differences between the two Fe–I distances are: $\Delta_{\text{Fe1}} = 0.30$ (1), $\Delta_{\text{Fe2}} = 0.15$ (1), $\Delta_{\text{Fe3}} = 0.16$ (1) Å. The averaged difference, together with those of other orthorhombic and rhombohedral boracites, is plotted as a function of the ionic radius of the halogen atom (Shannon, 1976). The result shows a linear relationship (Fig. 1). As the size of the halogen ion increases, the difference between the metal–halogen distances diminishes. As an exception, the boracites with copper and chromium show smaller differences. This may be owing to the degenerated electronic states which favour tetragonal symmetry (Jahn–

Teller effect). It may also explain the absence of phase transitions in chromium bromine and iodine and in copper bromine boracites, where the transition-metal atoms seem to occupy stable positions between the halogen atoms. They find a

favourable symmetry environment needing no Jahn–Teller deformation.

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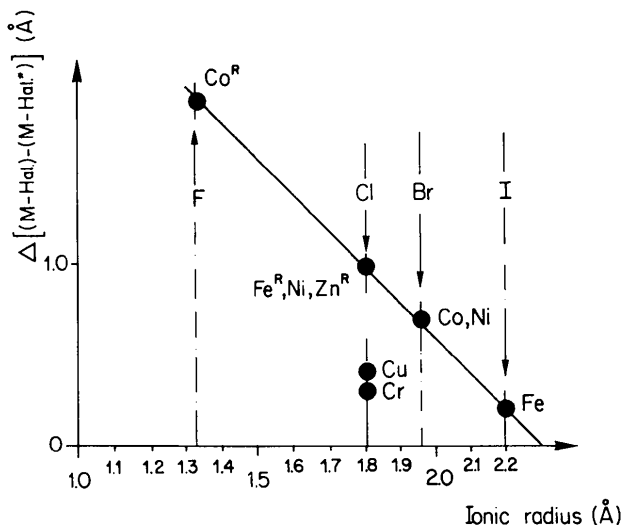


Fig. 1. Difference between the two metal-halogen distances of non-cubic boracites as a function of the halogen ionic radius. Superscript 'R' indicates values from a rhombohedral structure; other structures are orthorhombic. The parameter for Co–F was taken from the work of Berset, Depmeier, Boutellier & Schmid (1985); Zn–Cl from Mao, Mendoza-Alvarez, Depmeier, Kubel, Schmid & Yvon (1991); Ni–Cl and Co–Br from Kubel, Mao & Schmid (1992); Fe–Cl from Dowty & Clark (1973); Cu–Cl from Thornley, Nelmes & Kennedy (1976); Cr–Cl (at 100 K) from Mao, Kubel, Schmid & Yvon (1992); and Ni–Br from Abrahams, Bernstein & Svensson (1981).

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Structure of Ce₁₆Mo₂₁O₅₆ Containing Single Mo Atoms and Isolated Mo₁₀ Clusters

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Abstract. Ce₁₆Mo₂₁O₅₆, $M_r = 5152.63$, monoclinic, $P2_1/c$, $a = 13.450$ (3), $b = 13.398$ (5), $c = 13.357$ (4) Å, $\beta = 99.92$ (1)°, $V = 2371.0$ (1.2) Å³, $Z = 2$, $D_x = 7.217$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 205.97$ cm⁻¹, $F(000) = 4516$, $T = 295$ K, $R = 0.034$ for 5277 observed reflections. The structure

displays MoO₆ octahedra and [Mo₁₀O₁₈]O₈ cluster units sharing O atoms to form the three-dimensional lattice. In the MoO₆ octahedra, the Mo–O distances range between 2.029 (7) and 2.051 (8) Å. The Mo–Mo distances within the two independent Mo₁₀ clusters vary from 2.601 (1) to 2.842 (1) Å and the