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Fe_3BO_6, a borate isostructural with the mineral norbergite.

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In the course of an investigation of compounds of $FeBO_3$, with various transition element dopings (Bernal, Struck & White, 1963), we found a new borate phase in single-crystal form.

Table 1. *Observed and calculated lattice spacings for* Fe_3BO_6 (Fe *Kα radiation*)

hkl	d_{obs}	d_{calc}	I_{obs}
101	4·06	4·09	*vw*
111	3·69	3·69	*m*
121	2·96	2·95	*s*
301	2·68	2·68	*vw*
311	2·56	2·56	*m*
400	2·52	2·51	*vw*
230	2·48	2·48	*w*
410	2·41	2·41	*vvw*
131	2·37	2·34	*vw*
321	2·24	2·27	*vw*
002	2·24	2·24	*vvw*
401	2·19	2·19	*vw*
420	2·17	2·17	*w*
141	1·894	1·892	*w*
222	1·842	1·843	*vvw*
521	1·685	1·685	*vw*
341	1·671	1·670	*vw*
402		1·670	
232	1·660	1·660	*m*
421	1·641	1·640	*vvw*
151	1·576	1·577	*vw*
620	1·558	1·560	*vvw*
332		1·557	
422		1·555	
042	1·543	1·545	*vw*
611		1·543	
531		1·542	
432	1·441	1·441	*w*
351		1·441	
060	1·424	1·424	*vvw*
541	1·392	1·391	*vvw*
260	1·369	1·370	*vvw*

This particular compound was prepared by forming a slurry from equal molar amounts of Na_3BO_3 and Fe_2O_3 and then drying at 200 °C. The dried powder was ground and then melted in a platinum crucible and maintained at 1200 °C in air for 18 hours. The material was then heated with boiling water to leach out the excess Na_3BO_3. The remaining residue was treated with hydrochloric acid to remove any unreacted Fe_2O_3. Black crystal plates, several millimeters on edge, were found among the $FeBO_3$ crystals. These were separated from the green $FeBO_3$, and chemical analysis was consistent with the formula Fe_3BO_6, (Fe calc. 61·1 %, found 60·0 %; B calc. 3·9 %, found 4·6 %).

X-ray measurements showed that the crystals are orthorhombic with $a = 10{\cdot}05 \pm 0{\cdot}01$, $b = 8{\cdot}55 \pm 0{\cdot}01$, $c = 4{\cdot}47 \pm 0{\cdot}005$ Å. The large face of the plate is (010). The reflections $0kl$ with $k+l$ odd and $hk0$ with h odd are systematically absent. Hence the space group is limited to *Pnma* or $Pn2_1a$. Details of the X-ray powder pattern are given in Table 1.

The $hk0$ and $h0l$ reflections were recorded on Weissenberg photographs with zirconium-filtered Mo *Kα* radiation and the intensities estimated visually. The crystals used were about 0·1 mm square in cross section and absorption corrections were not made. Patterson projections showed the iron atom positions quite clearly and favored the higher symmetry space group. The positions of the lighter atoms were found from projection electron density maps com-

Table 2. *Coordinates of the atoms in* Fe_3BO_6

	x	*y*	*z*
Fe(1)	0·127	0·064	−0·018
Fe(2)	0·412	0·250	−0·028
O(1)	0·288	0·115	0·269
O(2)	0·467	0·081	−0·260
O(3)	0·085	0·150	0·259
O(4)	0·220	0·250	−0·269
B	0·220	0·250	0·406

Table 3. *Calculated and observed values of the structure factors* (× 0·25) *for* Fe_3BO_6 (Mo *Kα radiation*)

hkl	F_c	F_o	hkl	F_c	F_o	hkl	F_c	F_o	hkl	F_c	F_c	hkl	F_c	F_o	hkl	F_c	F_o	hkl	F_c	F_o	hkl	F_c	F_o
020	0	< 3	480	30	30	840	- 6	9	12,1,0	12	11	16,2,0	24	24	20,6,0	12	15	26,5,0	- 3	< 5	603	-19	19
040	30	33	490	8	7	850	- 6	9	12,2,0	-39	37	16,3,0	- 8	9	20,7,0	6	8	26,6,0	3	< 4	703	43	48
060	-101	102	4,10,0	29	30	860	-19	17	12,3,0	0	< 6	16,4,0	- 9	9	20,8,0	11	10	26,7,0	- 6	6	803	26	29
080	8	< 7	4,11,0	-19	17	870	10	7	12,4,0	21	19	16,5,0	- 1	< 7	20,9,0	- 6	< 7	002	55	58	903	16	12
0,10,0	-39	39	4,12,0	- 7	8	880	-36	33	12,5,0	14	16	16,6,0	2	< 7	20,10,0	8	9	004	79	86	10,0,3	14	<11
0,12,0	22	23	4,13,0	9	8	890	-11	9	12,6,0	12	12	16,7,0	- 7	< 8	20,11,0	4	< 6	006	12	12	11,0,3	-33	34
0,14,0	1	< 8	4,14,0	-11	11	8,10,0	-12	9	12,7,0	- 5	< 7	16,8,0	-26	27	20,12,0	- 3	< 6	101	25	27	12,0,3	3	<13
0,16,0	28	25	4,15,0	- 3	< 8	8,11,0	2	< 7	12,8,0	31	32	16,9,0	6	< 8	20,13,0	- 7	9	201	2	< 5	13,0,3	-18	16
0,18,0	- 2	< 7	4,16,0	-19	18	8,12,0	- 1	< 7	12,9,0	2	< 7	16,10,0	- 2	< 8	20,14,0	- 6	8	301	-52	56	14,0,3	8	<14
9,20,0	3	< 6	4,17,0	8	7	8,13,0	- 2	< 8	12,10,0	1	< 7	16,11,0	1	< 7	20,15,0	2	< 4	401	-49	53	104	22	24
0,22,0	-14	10	4,18,0	- 7	< 7	8,14,0	17	16	12,11,0	-10	9	16,12,0	- 7	< 7	20,16,0	- 7	8	501	-14	12	204	7	< 9
200	4	< 3	4,19,0	- 6	< 6	8,15,0	6	< 8	12,12,0	6	< 8	16,13,0	5	< 7	22,0,0	10	13	601	- 1	< 8	304	26	27
210	1	< 3	4,20,0	- 2	< 6	8,16,0	11	10	12,13,0	2	< 8	16,14,0	15	16	22,1,0	2	< 7	701	65	68	404	-37	45
220	- 2	< 3	4,21,0	3	< 5	8,17,0	- 3	< 7	12,14,0	-17	15	16,15,0	- 3	< 6	22,2,0	- 4	< 7	801	-14	16	504	- 6	<10
230	-75	78	4,22,0	9	6	8,18,0	- 8	< 7	12,15,0	- 2	< 7	16,16,0	4	< 6	22,3,0	8	8	901	18	18	604	-13	11
240	15	19	600	-35	35	8,19,0	0	< 6	12,16,0	- 7	< 7	16,17,0	1	< 5	22,4,0	7	8	10,0,1	10	13	704	-16	16
250	-38	41	610	28	27	8,20,0	- 3	< 6	12,17,0	5	< 6	16,18,0	9	8	22,5,0	9	10	11,0,1	-43	44	804	21	19
260	-10	11	620	47	46	8,21,0	- 5	< 5	12,18,0	-11	10	18,0,0	-12	14	22,6,0	- 8	9	12,0,1	- 8	<12	904	3	<12
270	-35	37	630	88	83	10,0,0	14	11	12,19,0	- 1	< 5	18,1,0	-13	14	22,7,0	6	< 7	13,0,1	-26	20	10,0,4	6	<12
280	- 4	< 6	640	-35	36	10,1,0	-24	24	12,20,0	6	6	18,2,0	2	< 7	22,8,0	2	< 6	14,0,1	- 6	<13	11,0,4	5	<13
290	25	28	650	32	33	10,2,0	-23	24	14,0,0	12	14	18,3,0	-16	16	22,9,0	- 4	< 6	15,0,1	24	23	12,0,4	-18	15
2,10,0	- 1	< 7	660	23	24	10,3.0	- 9	8	14,1,0	18	17	18,4,0	- 6	9	22,10,0	- 7	8	102	25	29	13,0,4	- 2	<14
2,11,0	19	17	670	11	8	10,4,0	13	14	14,2,0	- 4	< 6	18,5,0	-17	18	22,11,0	- 8	8	202	15	16	105	13	11
2,12,0	10	8	680	-28	28	10,5,0	-42	38	14,3,0	14	13	18,6,0	11	11	22,12,0	5	< 5	302	17	19	205	4	<11
2,13,0	27	26	690	-25	25	10,6,0	- 9	6	14,4,0	3	< 6	18,7,0	1	< 8	22,13,0	- 8	7	402	-97	87	305	-20	19
2,14,0	1	< 8	6,10,0	17	13	10,7,0	- 3	< 7	14,5,0	29	29	18,8,0	0	< 8	24,0,0	16	19	502	- 6	< 8	405	-23	23
2,15,0	- 1	< 8	6,11,0	-17	15	10,8,0	20	20	14,6,0	- 6	8	18,9,0	4	< 7	24,1,0	0	< 6	602	-14	13	505	- 3	<12
2,16,0	0	< 8	6,12,0	-13	10	10,9,0	- 2	< 7	14,7,0	0	< 7	18,10,0	8	9	24,2,0	2	< 6	702	-14	16	605	-13	13
2,17,0	- 2	< 8	6,13,0	-20	17	10,10,0	- 7	< 7	14,8,0	4	< 7	18,11,0	13	12	24,3,0	- 6	8	802	41	42	705	22	23
2,18,0	- 5	< 7	6,14,0	14	11	10,11,0	28	25	14,9,0	- 2	< 7	18,12,0	- 6	9	24,4,0	3	< 6	902	- 2	<10	805	4	<13
2,19,0	-15	13	6,15,0	- 1	< 8	10,12,0	5	< 8	14,10,0	- 4	< 8	18,13,0	6	< 6	24,5,0	- 1	< 6	10,0,2	-11	<11	905	13	13
2,20,0	1	< 6	6,16,0	- 8	< 8	10,13,0	9	10	14,11,0	-22	24	18,14,0	1	< 6	24,6,0	-11	13	11,0,2	4	<11	10,0,5	21	22
2,21,0	- 5	< 5	6,17,0	5	< 7	10,14,0	-11	10	14,12,0	2	< 8	18,15,0	5	< 6	24,7,0	- 3	< 5	12,0,2	- 7	<12	11,0,5	-24	26
2,22,0	0	< 4	6,18,0	7	< 7	10,15,0	10	< 8	14,13,0	- 6	< 7	18,16,0	- 5	6	24,8,0	- 4	< 5	13,0,2	- 3	<12	106	19	21
400	-67	60	6,19,0	14	12	10,16,0	5	< 7	14,14,0	- 3	< 7	18,17,0	- 6	6	24,9,0	4	< 5	14,0,2	4	<13	206	4	<12
410	32	31	6,20,0	- 6	< 5	10,17,0	-10	10	14,15,0	- 7	< 7	20,0,0	-17	19	24,10,0	- 8	8	15,0,2	3	<14	306	22	24
420	-26	31	6,21,1	3	< 5	10,18,0	- 4	< 7	14,16,0	5	< 7	20,1,0	- 5	< 7	26,0,0	- 4	< 5	103	14	13	406	-30	30
430	-24	23	800	36	37	10,19,0	- 5	< 6	14,17,0	9	11	20,2,0	- 8	7	26,1,0	- 1	< 5	203	8	11	506	- 9	<13
440	-25	28	810	-13	15	10,20,0	4	< 6	14,18,0	2	< 5	20,3,0	11	12	26,2,0	- 1	< 5	303	-36	40	606	- 2	<14
450	35	40	820	41	42	10,21,0	-10	9	16,0,0	1	< 7	20,4,0	- 1	< 7	26,3,0	-12	14	403	15	16	706	-17	16
460	38	43	830	7	5	12,0,0	-26	26	16,1,0	4	< 7	20,5,0	- 5	< 7	26,4,0	0	< 5	503	-13	10	806	-13	14
470	-14	14																					

puted on the basis of the iron atom phase contributions. Refinement was carried out by difference electron density calculations. Final coordinates are given in Table 2 where Fe(2), O(3), O(4) and B are in the 4(*c*) positions of the space group *Pnma* while Fe(1), O(1) and O(2) are in the 8(*d*) positions. A final *R* value of 0·086 was obtained for 187 observed reflections using isotropic temperature factors with $B=0{\cdot}52$ Å^2 for the iron atoms and $B=0{\cdot}90$ Å^2 for the lighter atoms. The calculated and observed values of the structure factors are given in Table 3.

The structure is an unusual one for boron compounds, as it contains the tetrahedral BO_4^{5-} anion. However, the crystals are isostructural with the mineral norbergite, $Mg_2SiO_4Mg(OH,F)_2$ (Taylor & West, 1929). Since for Fe_3BO_6 the conditions of preparation preclude the existence of divalent iron and hence of hydroxyl groups, both crystallographically independent iron atoms are octahedrally coordinated by six oxygen atoms, whereas in norbergite the octahedra coordinating the magnesium atoms contain both oxygen atoms and hydroxyl groups (or fluorine atoms). The accuracy of the coordinates and bond distances is limited by the almost exact overlap of O(1) and O(4) and the poor resolution of O(2) and O(3) in the *h*0*l* projection. The mean distances are 1·47 Å for the B–O bonds and 2·04 Å for the Fe–O bonds.

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The importance of the imaginary part of the scattering factor of bonded carbon.

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The theoretical evaluation of scattering factors for atoms in the bonded state is assuming increasing importance with the improvement in the accuracy of X-ray structure analyses. In particular, experimental evidence has been obtained for the distribution of σ-bonding electrons along the carbon–carbon bonds of the benzene ring (*e.g.* Rietveld & Maslen, 1965). A considerable amount of effort has been expended on the calculation of aspherical scattering curves (*e.g.* McWeeny, 1951, 1952, 1953, 1954; Freeman, 1959; Dawson 1961, 1964*a*, *b*). Most of this work refers to atoms in the ground or prepared valence state, which latter is spherically symmetric in the case of carbon (McWeeny, 1951) and is therefore not a sufficiently good approximation to account for the experimental observations. The only treatment of bonded carbon is that of McWeeny (1954) who derived aspherical scattering factors for the carbon atom in the diamond and graphite structures. Carbon in benzene would be expected to have a scattering factor similar to the latter to an approximation one order beyond that of spherically symmetric atoms. However, examination of the values given for the graphite scattering factor in Table 1 of McWeeny (1954) shows that, within the plane of the molecule, it is isotropic to within 0·02e. This extremely small variation is clearly not sufficient to account for the comparatively prominent σ-bond features which have been observed experimentally. Further examination of McWeeny's calculations shows that an imaginary contribution to the scattering factor has been ignored as insignificant. The present paper derives values for the imaginary contributions to the carbon scattering factor in diamond and in graphite and shows how it is related to the asymmetry arising from the σ-bonding. The practical application of complex scattering curves with particular reference to the structure of *p*-diphenylbenzene is discussed.

Diamond

The effective scattering factor for carbon in the diamond structure is given, using McWeeny's (1954) equation (5), by

$$f_0^e = f_{0c} + q_0{}^\sigma \sum_{n=1}^{4} f_0(\varrho_0{}^{\sigma n}) + \tfrac{1}{2}\, q_{01}{}^\sigma \sum_{n=1}^{4} f_0(\varrho_{0_n}{}^{\sigma n})$$

where the first two terms are isotropic and the last, which is the relevant anisotropic term, may be expanded as,

$$\tfrac{1}{2} q_{01}^0 \sum_{n=1}^{4} f(\varrho_{0n}{}^{\sigma n}) \exp\,(2\pi i\, X\, R\, \hat{\mathrm{S}}\,.\,\hat{\mathbf{r}}_n)\,.$$

It follows from the above expression that the imaginary part of the scattering factor is antisymmetric with respect to $\hat{\mathrm{S}}$ and reaches a maximum in a direction parallel to one of the bonds [the direction $\hat{\mathrm{S}}_4$ as defined by McWeeny (1954)] where it is equal to,

$$\tfrac{1}{2}\, q_{01}{}^\sigma\, [\sin\,(2\pi\, X\, R)\, f_0'' - 3 \sin\,(2\pi\, X\, R/3)]\, f_0{}^\psi]$$

where ψ is the tetrahedral angle corresponding to $\cos\psi = -\frac{1}{3}$. (The minus sign is missing in McWeeny's paper but his results, which depend only on $\cos\,(2\pi\, X\, R \cos\psi)$ are correct.) In a direction perpendicular to the plane containing two bonds (McWeeny's $\hat{\mathrm{S}}_3$) and in a direction bisecting the angle between two bonds (McWeeny's $\hat{\mathrm{S}}_1$ and $\hat{\mathrm{S}}_2$), the imaginary component falls to zero. Thus the anomaly whereby the scattering factors along $\hat{\mathrm{S}}_3$ and $\hat{\mathrm{S}}_4$ were almost identical is removed. The variations of the real and imaginary parts with X are illustrated in Fig. 1 and tabulated in Table 1.

Graphite

The effective scattering factor for graphite is given by McWeeny (1954) equation (7) as,

$$\begin{aligned} f_0^e = f_{0c} &+ q_0{}^\sigma f_{0v} + (q_0{}^\pi - q_0{}^\sigma)\, f_0(\varrho_0{}^\pi) \\ &+ \tfrac{1}{2}\, q_{01}{}^\sigma \sum_{n=1}^{3} f(\varrho_{0n}{}^{\sigma n}) \exp\,(2\pi i\, X\, R\, \hat{\mathrm{S}}\,.\,\hat{\mathbf{r}}_n) \\ &+ \tfrac{1}{2}\, q_{01}{}^\pi \sum_{n=1}^{3} f(\varrho_{0n}{}^{\pi \dot{a}}) \exp\,(2\pi i\, X\, R\, \hat{\mathrm{S}}\,.\,\hat{\mathbf{r}}_n) \end{aligned}$$