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The Structure of Fluoborite

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The crystal structure of fluoborite, $3Mg(OH, F).BO_3$, has been analysed using the Weissenberg–Buerger method (Mo$K\alpha$, $\lambda = 0{\cdot}710$ A.). The unit cell has the dimensions: $a = 9{\cdot}06 \pm 0{\cdot}02$, $c = 3{\cdot}06 \pm 0{\cdot}01$ A., with two molecules per cell. The space group has been assumed to be C^2_{6h}–$C6_3/m$. The structure is composed of linked octahedra of oxygen atoms and OH (or F) groups around magnesium, boron atoms being in the middle of oxygen triangles.

Fluoborite is a rather rare boron-bearing mineral. The result of our recent study of three of its kindred minerals, warwickite, ludwigite and pinakiolite, between which a strikingly close structural relationship has been found (Takéuchi, Watanabé & Ito, 1950), has led us to inquire if the crystal structure of fluoborite may not be worked out on similar lines.

Material

The specimen used in the investigation came from Tallgruvan, Sweden, and was kindly placed at our disposal by Dr Takéo Watanabé, who had obtained a slender prismatic crystal about 1·5 mm. in length and 0·3 mm. in width by separating it from the matrix of dolomite, ludwigite and magnetite. A chemical composition of the mineral may be expressed by the formula $3Mg(OH, F).BO_3$, with OH:F = 12:5 (Geijer, 1926).

Unit cell and space group

The hexagonal unit cell has the dimensions,

$$(\mathrm{Mo}\ K\alpha,\ \lambda=0{\cdot}710\ \mathrm{A.})$$

$$a=9{\cdot}06\pm0{\cdot}02,\quad c=3{\cdot}06\pm0{\cdot}01\ \mathrm{A.},$$

giving $c/a = 0{\cdot}337$ in agreement with the value given by Aminoff (Geijer, 1926). The a dimension was determined from Weissenberg and the c dimension from rotation photographs, using Mo $K\alpha$ radiation ($\lambda = 0{\cdot}710$ A.) in both cases. There are two molecules of $3Mg(OH, F).BO_3$ in the cell. The Laue symmetry being C_{6h}, deduced from the Weissenberg photographs, the space group is either C^6_6 or C^2_{6h}, since there is no observed rule governing the absent reflexions excepting the (00*l) spectra which occur only when l is even. We could not, however, decide between these groups before we started the analysis owing to the lack of morphological or other evidence.

Analysis

The zero-level and 2nd-level Weissenberg–Buerger photographs about the c axis are virtually identical. We may conclude, considering the structure amplitudes for C^6_6 and C^2_{6h}, that this can take place only when all the atoms in the cell are at $z=\frac{1}{4}$ or $\frac{3}{4}$, regardless of the choice of C^2_{6h} or C^6_6 as the space group of fluoborite. Atoms placed in such positions will automatically give rise to the reflexion planes, which go through these points and are parallel to (00*1). We prefer, therefore, C^2_{6h}–$C6_3/m$ to C^6_6–$C6_3$ as the space group. The possibility of C^6_6 should not be entirely set aside because we are basing our argument on the intensity and not on the absence of reflexions.

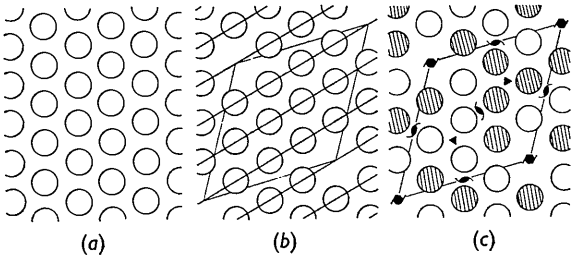

Fig. 1. The way in which the scheme underlying the structure of fluoborite is derived from the hexagonal close-packed layer of oxygen atoms. (*a*) The hexagonal close-packed layer. (*b*) The unit cell of fluoborite placed on to the layer so as to make (13*0) reflexion strong. An oxygen atom is subtracted to give twelve (instead of thirteen) oxygen atoms per cell. The traces of (13*0) are shown as a system of parallel full lines. (Projection on (00*1).) (*c*) The height of oxygen atoms in the layer readjusted to conform to the requirements of the space group assumed. Open circles represent oxygen atoms at $\frac{3}{4}$ and shaded circles those at $\frac{1}{4}$ of the c length. (Projection on (00*1).)

In view of the dimensions of the cell, we began the analysis by trying to place in it a hexagonal close-packed layer of oxygen atoms (Fig. 1(*a*)). The very strong (13*0) reflexion suggests immediately that the unit cell should be so related to the arrangement that the *c* direction is at right angles to the extension of the layer and in other respects as illustrated in Fig. 1(*b*). There are, however, only twelve O and OH (or F) in the unit cell, against thirteen oxygen atoms in this ideal cell, but by subtracting one oxygen atom and by subjecting the rest to the operation of the space group we obtain an arrangement of oxygen atoms on which may be based the structure of fluoborite (Fig. 1(*c*)). The final parameters (Table 1) have been determined by trial and error. The visually estimated intensities are compared in Table 3 with the *F* values calculated from these parameters.

Table 1. *Co-ordinates of atoms in fluoborite*

Atoms	*x*/*a*	*y*/*b*	*z*/*c*	No. of atoms per cell
OH, (F)	0·310	0·218	0·25	6
O	0·537	0·156	0·75	6
Mg	0·381	0·038	0·25	6
B	$\frac{2}{3}$	$\frac{1}{3}$	0·75	2

The structure described

The structure is illustrated in Fig. 2 projected on (00*1). The structure may be considered to be made up of linked octahedral groups of oxygen atoms and OH groups (or F atoms) around magnesium atoms. An octahedral group, $MgO_3(OH, F)_3$, is linked to a similar group sharing an O–OH edge. This linking is continued indefinitely, forming a string stretched parallel to the *c* direction. Six parallel strings are combined into a bundle with every two of them holding OH groups at the octahedral corners in common, leaving an open space in the form of a channel, also parallel to *c*, throughout the structure. Such a bundle of strings or pipe is laterally joined to similar ones sharing O–O edges (Fig. 3), reinforced by boron atoms, which are each in the middle of a regular triangle of oxygen atoms.

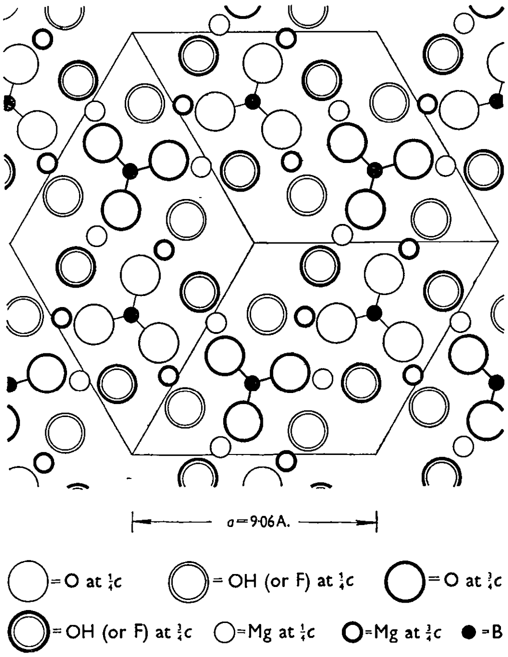

Fig. 2. The structure of fluoborite projected on (00*1).

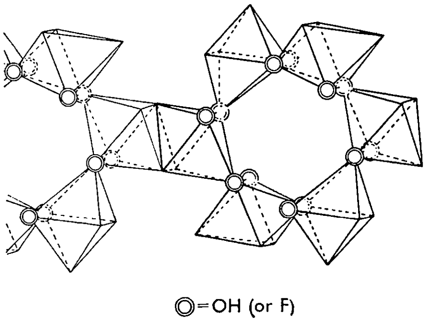

Fig. 3. A bundle of $MgO_2(OH)_2$ strings from the structure of fluoborite (as seen from the direction of the strings). The bundle is joined to the neighbouring similar ones sharing O–O edges. Double circles represent OH molecules (or F atoms) at the corners of octahedra of oxygen atoms (not shown). The positions of atoms are displaced from the actual positions to show the polyhedral linkage.

From the point of view of the oxygen arrangement the structure is very similar to that of warwickite, the unit cell containing two hexagonally close-packed and two quadratically packed strips of oxygen (or F or OH) atoms which lie parallel with ($\bar{4}$1*0) and are stretched along the *c* direction. Owing, however, to the vacancies of oxygen positions as compared with warwickite, there is between these two structures no such simple relationship as found previously (Takéuchi, *et al.* 1950). The interatomic distances calculated are listed in Table 2.

Table 2. *Interatomic distances in fluoborite*

Atom	Neighbour	Distance (A.)
Mg (octahedron)	OH(F)	2·03
	OH(F)*	2·35
	OH(F)′*	
	O	1·99
	O′	
	O′*	2·33
B (triangle)	O	1·50
	O″	
	O‴	
O	O″	2·45
O″	O‴	
O‴	O	
OH(F)	OH(F)′	3·06

Dashes denote equivalent atoms and asterisks atoms in the neighbouring cell.

In conclusion the writer wishes to express his sincere thanks to Prof. Ito, upon whose suggestion the present work was carried out, for his interest and guidance throughout the work.

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Table 3. *Comparison of observed intensities and calculated amplitudes.*

Intensities were estimated visually in Weissenberg and oscillation photographs using Mo $K\alpha$ radiation ($\lambda = 0{\cdot}710$ A.). No correction for the observed intensities was made.

hk^*l	$I_{\text{obs.}}$	$F_{\text{calc.}}$	hk^*l	$I_{\text{obs.}}$	$F_{\text{calc.}}$	hk^*l	$I_{\text{obs.}}$	$F_{\text{calc.}}$	hk^*l	$I_{\text{obs.}}$	$F_{\text{calc.}}$
30*0	*s*–	36·6	50*1	*vw*	13·6	62*0	—	–14·6	27*1	—	2·4
22*0	*w*	–14·6	33*1	*mw*	21·0	44*1	*w*	–17·2	72*1	*w*	22·0
13*0	*s*	40·0	24*1	*vw*	17·8	70*1	*vw*	5·8	37*0	—	–10·8
31*0	—	–14·0	42*1	*mw*	26·0	35*1	—	1·0	73*0	—	– 5·8
30*1	—	3·0	60*0	*vw*–	9·4	53*1	—	3·6	46*0	—	– 2·0
40*0	*m*	27·2	34*0	*w*	–18·8	17*1	—	– 9·0	64*0	—	–12·0
22*1	*s*	47·0	43*0	*m*	–20·4	71*0	—	8·0	81*1	—	0·8
23*0	*s*–	–33·2	15*1	*vw*	14·4	26*1	—	– 4·0	18*1	*vw*	–15·4
32*0	*vw*	–12·0	51*1	—	– 8·0	62*1	*m*	–22·2	55*1	—	– 2·2
13*1	—	0	25*1	—	– 1·0	45*0	—	–10·2	64*1	*vw*	–21·2
31*1	*s*–	–34·0	52*1	—	3·6	54*0	—	8·0	46*1	—	–18·2
14*0	—	– 6·2	60*1	*vw*	13·8	36*0	—	10·0	28*0	—	0·1
41*0	*w*	– 8·2	16*0	*w*	–21·0	63*0	—	– 1·0	82*0	—	– 9·0
40*1	*s*	39·6	61*0	—	– 5·1	17*1	—	0·3	37*1	*vw*	–20·6
50*0	*vw*	5·8	34*1	—	–16·0	71*1	—	– 9·0	73*1	*w*	22·8
23*1	—	8·8	43*1	—	15·2	80*0	—	2·2	90*1	—	0·1
32*1	*ms*	–30·0	25*1	—	– 1·0	27*0	—	– 5·8	28*1	*vw*	–20·6
00*2	*vs*	–87·2	52*1	—	3·6	72*0	—	– 9·4	82*1	—	–13·6
33*0	*m*	21·2	44*0	—	5·2	45*1	*vw*	12·2	19*0	—	6·6
14*1	*vw*	– 5·8	70*0	*w*	–21·0	54*1	—	10·2	91*0	—	10·6
41*1	*s*	–36·8	35*0	—	7·2	36*1	—	– 1·0	19*1	—	– 5·2
24*0	*vw*	8·2	53*0	*w*–	18·0	63*1	—	15·0	91*1	—	– 1·0
42*0	*m*	–25·8	16*1	—	1·6	80*1	—	14·2	00*4	*ms*	50·8
15*0	*mw*–	–25·6	61*1	—	– 7·2	18*0	—	–14·0	10,0,*,1	—	17·4
51*0	*m*	28·6	26*0	*s*	48·4	81*0	—	18·4			

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The Probability Distribution of X-ray Intensities. II. Experimental Investigation and the X-ray Detection of Centres of Symmetry

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The probability distributions of reflected X-ray intensities have been investigated experimentally. The results are in agreement with the theory, and the possibility is demonstrated of distinguishing between centrosymmetric and non-centrosymmetric structures and projections within the limitations of the theory. Details of a convenient distinguishing test are presented and the effects upon it of absorption, extinction and experimental errors in intensities are discussed.

1. Introduction

The probability distribution of reflected X-ray intensities has recently been investigated theoretically by Wilson (1949). He concluded that the structure factors, $F(hkl) = x + iy$, of a crystal are distributed symmetrically in the complex x, y plane according to the Gaussian function

$$ {}_{1}P(x, y)\,dxdy = (\pi\Sigma)^{-1} \exp\{-(x^2+y^2)/\Sigma\}\,dxdy, \tag{1}$$

where

$$\Sigma = \sum_j f_j^2 \tag{2}$$

is the sum of the squares of the scattering powers of the atoms and is identifiable with $\langle I \rangle$, the local average of the calculated intensities (Wilson, 1942).

When the structure possesses a centre of symmetry the structure factors are confined to the real x axis, again with a Gaussian distribution

$$ {}_{\bar{1}}P(x)\,dx = (2\pi\Sigma)^{-\frac{1}{2}} \exp\{-x^2/2\Sigma\}\,dx. \tag{3}$$

The corresponding distribution functions in terms of the intensities ($= |F|^2$) are

$$ {}_{1}P(I)\,dI = \Sigma^{-1} \exp(-I/\Sigma)\,dI \tag{4}$$

and

$$ {}_{\bar{1}}P(I)\,dI = (2\pi\Sigma I)^{-\frac{1}{2}} \exp(-I/2\Sigma)\,dI. \tag{5}$$

The difference led Wilson to suggest as a distinguishing ratio

$$\rho = \langle |F| \rangle^2 / \langle I \rangle, \tag{6}$$

which takes the values $\pi/4 (\doteqdot 0{\cdot}785)$ for (1) and $2/\pi (\doteqdot 0{\cdot}637)$ for $(\bar{1})$.

A consideration of the effects of centring and of symmetry elements other than a centre of symmetry