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THE CRYSTAL STRUCTURE OF FLUELLITE, $Al_2PO_4F_2(OH)\cdot 7H_2O$

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ABSTRACT

The crystal structure of the mineral fluellite has been determined with the use of three-dimensional *x*-ray photographic data. The composition, previously reported as that of an aluminum hydroxy-fluoride monohydrate, was found to be $Al_2PO_4F_2(OH)\cdot 7H_2O$. The presence of phosphorus in the structure was confirmed by electron microprobe analysis. The space group is *Fddd* with unit cell dimensions $a=8.546$, $b=11.222$ and $c=21.158$ Å, and Z=8. The phase problem was solved by the interpretation of a multiple minimum Patterson function and of its convolution with the original Patterson synthesis. The final R-factor for 468 observed reflections is 0.12. The structure is that of infinite chains of corner-sharing $[AlF_2\cdot O_4\cdot H_{3.5}]$ octahedra linked through $[PO_4]$ tetrahedra, forming channels which contain water molecules. The water molecules and hydroxyl ions are hydrogen-bonded in a way which permits proton configurational alternatives. Of the four oxygen atoms in the aluminum octahedra, two are shared with the $[PO_4]$ tetrahedra and the other two are statistically one quarter that of a hydroxyl ion and three quarters that of a water molecule.

INTRODUCTION

The mineral fluellite has been described from only a limited number of localities, chiefly in southern England and Germany, where it occurs in small quantities in granitic regions as minute dipyramidal crystals lining cavities or veins. It was originally named and described in 1824 by Lévy, who observed it on quartz associated with fluorite, wavellite, arsenopyrite and torberite. No quantitative chemical tests were attempted on the small amounts of material available, and Lévy only reported the presence of aluminum and fluorine. No further chemical data were presented until 1882 when Groth recorded the following percentage composition; F 56.25, Al 27.62, Na 0.58, H_2O by difference 15.5, and proposed the formula $AlF_3\cdot H_2O$. In 1920, Laubmann and Steinmetz described a mineral, kreuzbergite, from the Oberpfalz, Bavaria, occurring with phosphosiderite and strengite. It was described as an aluminum phosphate chiefly on the basis of crystal morphology and its association with other hydrated aluminum phosphates. Several further reports of kreuzbergite followed, and Larsen and Berman (1934) noted the similarity of this mineral with fluellite. In 1940, Scholz and Strunz carried out qualitative chemical tests on kreuzbergite and concluded that is was the same as fluellite. They obtained only 1 to 2 per cent of phosphorus by precipitation as the ammonium phosphomolybdate. *X*-ray powder data confirmed

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the structural similarity of the two minerals and small compositional discrepancies were attributed to variation in the (OH) and F ionic ratio. The name kreuzbergite was then discredited and a composition of $Al(F_x \cdot OH_{1-x})_3 \cdot H_2O$, where $x < 1.0$, was accepted for fluellite. Scholz and Strunz postulated that fluellite is a secondary product formed when pyrite breaks down with acid solutions attacking fluoro-phosphates (*e.g.* apatite and triplite) and alumino silicates.The only additional data was that of Palache, *et al.* (1951) who report a personal communication from C. W. Wolfe on the cell dimensions and space group.

The present crystal structure determination was undertaken in the belief that the mineral was a hydrate of aluminum fluoride, since several such hydrates have been described, but the literature is somewhat contradictory (*cf.* Simons, 1950) and the monohydrate is unknown as a laboratory product. We found that fluellite is a hydrated aluminum fluoro-phosphate and believe that both minerals described as kreuzbergite and fluellite are in fact one species, with minor compositional variations. The difficulty in obtaining sufficient quantities of fluellite for detailed chemical analysis was presumably the principal factor causing the confusion in composition.

CRYSTAL DATA

The specimens of fluellite[1] that were selected for structure determination were small (<0.15 mm), colorless, dipyramidal crystals lining the surface of a somewhat altered granitic rock. Only the {111} form was observed. The crystals have orthorhombic symmetry with $a = 8.546 \pm 0.008$, $b = 11.222 \pm 0.005$, and $c = 21.158 \pm 0.005$ Å, and $V = 2029$ Å^3. The measured density was $D_m = 2.18$ g. cm^{-3}, in agreement with the calculated value of $D_x = 2.16$ g. cm^{-3}, with the molecular formula, $Al_2PO_4F_2(OH) \cdot 7H_2O$ and $Z = 8$. The space group is uniquely determined as *Fddd* from systematic absences, (hkl) with $h+k,\ k+l,\ l+h \neq 2n$; $(0kl)$ with $k+l \neq 4n$; $(h0l)$ with $k+l \neq 4n$; $(hk0)$ with $h+k \neq 4n$; and $(h00)$, $0k0)$, $(00l)$ with $h \neq 4n$, $k \neq 4n$ and $l \neq 4n$ respectively. The refractive indices are $\alpha = 1.478$; $\beta = 1.490$; $\gamma = 1.510$, with $\alpha = a$, $\gamma = c$.

EXPERIMENTAL

The unit cell dimensions were determined by diffractometer methods, and the intensity data were recorded photographically with equi-inclination Weissenberg techniques using CuKα radiation. The intensities were eye-estimated, by comparison with a calibrated scale, from multiple-film photographs for layers zero to eight about the b-axis and zero to fifteen

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[1] From Cornwall, England. Specimen (Catalogue No. C1028) on loan from Smithsonian Institution, Washington, D. C.

about the *c*-axis. The 855 measured reflections were assigned values from 1 to 20,000 and the conversion of intensities to structural amplitudes was carried out with a series of IBM 7070 programs (McMullan, 1964) with least squares correlation of the equivalent reflections occurring along both the *b* and *c*-axes. Due to the space group extinctions, only reflection of the type *ggg* and *uuu* are present, so that it was impossible to obtain direct correlation between these two sets of data without information from an oblique axis. However, because "even" and "odd" layers were recorded alternately along both the *b* and *c* axes, a scale factor of one could be assumed between these sets of data without giving rise to errors significant enough to hinder the solution to the phase determination. This scale factor was subsequently redetermined more precisely in the refinement stage of the structure determination. The number of observed independent reflections was 468, representing approximately 83 per cent of the limiting sphere for CuKα radiation. An additional 72 reflections were recorded as unobserved and given intensity values of one half the lowest observable intensity. Approximately 75 per cent of the unobserved reflections were in the sin θ range of 0.7 to 1.0. The Wilson statistical method was used to place the observed structure factors on an absolute basis and to obtain approximate isotropic temperature factors. No correction was made for absorption since the value of μ.r was about 1.0. The crystal density was determined by flotation methods in a mixture of bromoform and alcohol.

THE STRUCTURE DETERMINATION

Initially it was assumed that the molecular formula was approximately $AlF_3 \cdot H_2O$ (with $Z=24$ or 32), although it was evident that this exact stoichiometry was incompatible with the cell dimensions, density and space group requirements. The presence of phosphorus in the structure was not suspected until the bond distances and electron density distributions indicated that not all the cations could possibly be aluminum. The true composition of the mineral was therefore unknown until after the solution of the phase problem, when it was revealed in the process of the refinement calculations.

An examination of the Harker sections of a three-dimensional Patterson synthesis suggested two alternatives for a pair of independent atoms: these were the combinations of the equivalent positions of 8(a) and 16(c) or of 8(b) and 16(c). Assuming that the atoms were aluminums, combination (1) was selected on the basis of a better agreement between observed and calculated structure factors, but further interpretation by inspection of the Patterson function was not possible. Difference Fourier synthesis based on this partial structure revealed two lighter atoms, (4) and (5), in the 16(g) and 32(h) positions. The former corresponded to a tetrahedral arrangement about the aluminum atoms at the eight-fold (8a) position. The inclusion of these atoms resulted in little improvement in the disagreement index R, which was discouraging and further interpretation of the Fourier synthesis was not possible.

The solution of the Patterson function was then approached more systematically using the method of multiple superposition of the vector shifted function to calculate a minimum function (Buerger, 1951). Vector shifts corresponding to the aluminum sites originally located were made and a three-dimensional multiple minimum function (MMF) was calculated, using the programs of Corfield (1965a) for the IBM 1620. This function definitely confirmed the position of the two sets of lighter atoms obtained previously, *i.e.* (4) and (5). Further vector shifts involving these two atoms revealed a fifth set of atoms, (3) in the 32(h) positions. The combinations of the positions (3), (4) and (5) now completed octahedral and tetrahedral arrangements of anions about the heavier (supposedly aluminum) atoms. Despite the fact that five out of six of the symmetry independent atoms, (excluding hydrogens), had been located, the R-factor was still high at 0.46 and further vector shifts failed to reveal additional atomic positions. The original Patterson function was then convoluted with the MMF using the IBM 1620 program of Corfield (1965b), which computes the value $\Sigma_{r}'\rho(r-r')\cdot\sigma(r')$ at various values of r' over the unit cell, where $\rho(r)$ and $\sigma(r)$ represent the two three-dimensional periodic functions (*viz.* the Patterson and MMF). The peaks for the two heavier atoms and the three lighter atoms were considerably sharpened and a new peak (6) appeared above the background. Structure factor calculations with aluminum for the heavier atoms and oxygen or fluorine for the lighter atoms reduced the R value to 0.35. The difference Fourier syntheses then indicated that all the atomic sites had probably been located. The formula unit at this stage was thought to be either $Al_3F_{10}\cdot(H)\cdot 4H_2O$ or $Al_3F_8O_2\cdot(3H)\cdot 4H_2O$, so as to approximate as closely as possible a hydrated aluminum fluoride, with the appropriate number of hydrogen atoms necessary to achieve neutrality at undetermined positions.

The Structure Refinement

Full matrix least squares refinements of the structure were carried out on the IBM 7090 using a modification by Shiono (1965) of the program by Busing *et al.* (1962). Four cycles of refinement on the positional parameters and a scale factor reduced R to 0.20, and a further four cycles on the positional parameters with isotropic temperature factors and a different scale factor for the *ggg* and *uuu* reflections lowered R to 0.15. The temperature factor for the aluminum atoms in the 8(a) positions then became negative. Interatomic distance calculations showed that these atoms had four neighbors at 1.55 Å, which was too short for Al-F or Al-O distances. Difference Fourier syntheses also suggested that there were more electrons at these sites than those assumed for aluminum. Alternate cations were therefore either silica or phosphorus, either of which could be tetrahedrally coordinated to the four surrounding oxygen or fluorine atoms. An electron microprobe analysis of the specimen for aluminum, silicon and phosphorus showed that Si was entirely absent and Al and P were estimated at 17 and 10 weight per cent respectively. These values agreed reasonably well with the theoretical 16.4 per cent Al, by occupying the (16c) sites, and 9.4 per cent P, by occupying the (8a) sites in the structure.

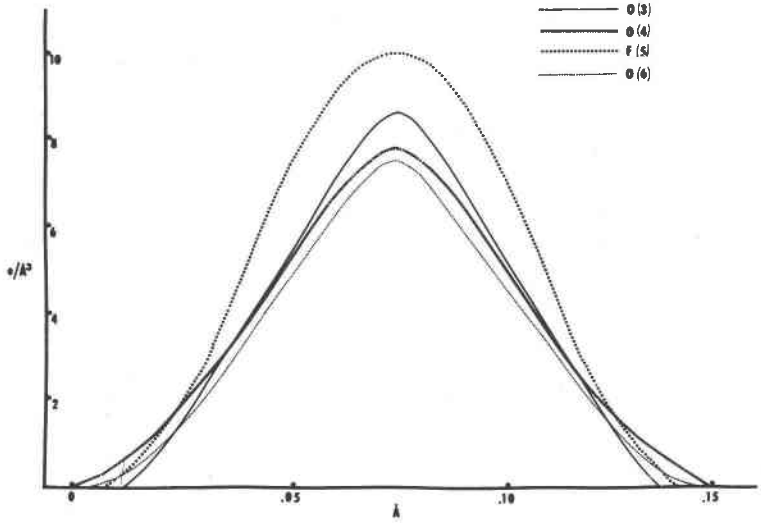

FIG. 1. Electron density distribution of anions in fluellite. The distribution for fluorine, F(5), is significantly different from that of the oxygens.

With the introduction of phosphorus into the tetrahedral sites, there was a further improvement in the structure factor agreement and the P-O or P-F distances of the surrounded tetrahedron were 1.52 Å. Since the $[PF_4]^-$ ion is a very unlikely mineral ion (Wells, 1962, p. 643), it was assumed that a phosphate group was present. The electron density distribution at the anion sites was then carefully examined in the three-dimensional Fourier syntheses. A very similar distribution was observed for atoms (3), (4) and (6), but atom (5) had a significantly sharper, and greater electron density, as shown in Fig. 1. On this basis atoms (3), (4) and (6) were identified as oxygens and (5) as the fluoride ion. These assignments resulted in an improved electron density on the difference synthesis as well as more appropriate temperature factors for the cations and the fluoride ion. A sensible formula and hydrogen-bonding scheme could then be postulated for the structure consistent with the composition of $Al_2PO_4F_2(OH)\cdot 7H_2O$. One hydrogen atom was located directly on a final difference Fourier synthesis in a 32(h) position between O(4) and O(6) and this corresponded to four of the fifteen hydrogens in the formula unit given above.

For the terminal cycles of least squares refinement, a correction for anomalous dispersion for the Al and P atoms was included. Although small, the fact that these atoms are in special positions appears to enhance the importance of this correction, which significantly improved the electron density distributions and prevented some of the anisotropic temperature factors from becoming negative. The atomic parameters and their standard deviations are listed in Table 1. The corresponding observed and calculated structure factors are listed in Table 2.[1] Only the hydrogen atom H(7) on O(6), which was directly observed, is included in these calculations. Eight reflections having a high observed structure factor and poor agreement with calculated values are marked**; they were omitted from the final cycles of refinement. The final *R*-factor was 0.12 for the observed reflections and 0.13 per cent including the unobserved values.

DESCRIPTION OF THE STRUCTURE

Framework. The fluellite structure consists of octahedrally and tetrahedrally coordinated cations in a rather open framework arrangement, within which there are distinct channels containing hydrogen-bonded water molecules. The aluminum atoms are situated at centers of symmetry and are bonded octahedrally to two centro-symmetric pairs of oxygen atoms, and one pair of fluoride ions, O(3), O(3)′, O(4), O(4)′ and F(5), F(5)′. These octahedra are connected by corner-sharing at the fluorides to form infinite chains along the [110] and $[1\bar{1}0]$ directions. The chains with aluminum atoms at $z=0$ and $\frac{1}{2}$ extend along [110] and alternate with those at $z=\frac{1}{4}$ and $\frac{3}{4}$ which are in the $[1\bar{1}0]$ direction. The equatorial planes of the octahedra which contain O(3), O(3)′ and F(5), F(5)′ are nearly perpendicular to the c-axis, with a small tilt so that the atoms O(4), O(4)′ at the apices alternately approach and withdraw from each

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[1] Table 2 has been deposited as Document No. 9117 with the American Documentation Institute, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. Copies may be secured by citing document number, and remitting $2.50 for photoprints or $1.75 for 35 mm microfilm. Advance payment is required.

TABLE 1. ATOMIC PARAMETERS FOR FLUELLITE

Estimated standard deviations in parentheses refer to the last decimal position reported.
The temperature factor expression consistent with the B-values is:

$$\exp\left[-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3} B_{ij}h_ih_ja_i^*a_j^*\right]$$

Atom	Equivalent Set $(Fddd)$[1]	Fractional Coordinates			Anisotropic Temperature Coefficients (Å^2)					
		x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Al (1)	16 (c)	0	0	0	0.06 (13)	0.38 (14)	0.47 (13)	−0.07 (7)	0.02 (6)	−0.10 (7)
P (2)	8 (a)	0.125	0.125	0.125	0.23 (14)	0.52 (15)	0.56 (15)	0	0	0
O (3)	32 (h)	0.1812 (5)	0.9071 (4)	0.0033 (2)	1.00 (22)	0.94 (21)	1.20 (23)	0.46 (15)	−0.09 (14)	−0.17 (16)
O (4)	32 (h)	0.0220 (5)	0.0457 (4)	0.0834 (2)	0.51 (18)	1.01 (22)	0.67 (20)	−0.05 (14)	−0.07 (13)	0.34 (15)
F (5)	16 (g)	0.125	0.125	0.2767 (3)	0.07 (26)	0.93 (26)	0.73 (25)	0.67 (18)	0	0
O (6)	32 (h)	0.2415 (7)	0.9986 (6)	0.8414 (3)	1.09 (23)	2.18 (28)	1.81 (23)	−0.54 (18)	0.22 (16)	0.16 (18)
H (7)	32 (h)	0.166 (19)	0.993 (13)	0.874 (7)	1.8	1.8	1.8	—	—	—

The following parameters are for hydrogen atoms not observed and not included in structure factor calculations. Parameters inferred, for configuration shown in Fig. 5(a), using O-H = 1.0 Å along line of O · · · O centers, except for the "free" hydrogen (see text).

Atom	Set	Fractional Coordinates			Occupancy	Hydrogen Bond
		x	y	z		
H (8)	32 (h)	0.28	0.06	0.25	0.81	O (6)-H · · · O (3)′
H (9)	32 (h)	0.29	0.10	0.78	0.75	O (6) · · · H-O (3)′
H (10)	32 (h)	0.22	0.94	0.81	0.25	O (6)-H · · · O (3)″
H (11)	32 (h)	0.21	0.90	0.78	0.75	O (6) · · · H-O (3)″
H (12)	32 (h)	0.34	0.96	0.14	0.50	O (6) · H · · H-O (6)′
H (13)	32 (h)	0.28	0.96	0	0.25	(non-bonding)

[1] Origin at $\bar{1}$.

other along the direction of the chain, as illustrated in Fig. 2. The chains of octahedra at adjacent levels are linked through a tetrahedral arrangement of oxygens O(4), O(4)'', O(4)''', O(4)$'^{\mathrm{v}}$ about a central phosphorus atom (see Table 3). The shorter distances between the apices of adjacent octahedra which result from the tilt of the O_4-O_4 axes form the edges of the tetrahedra.

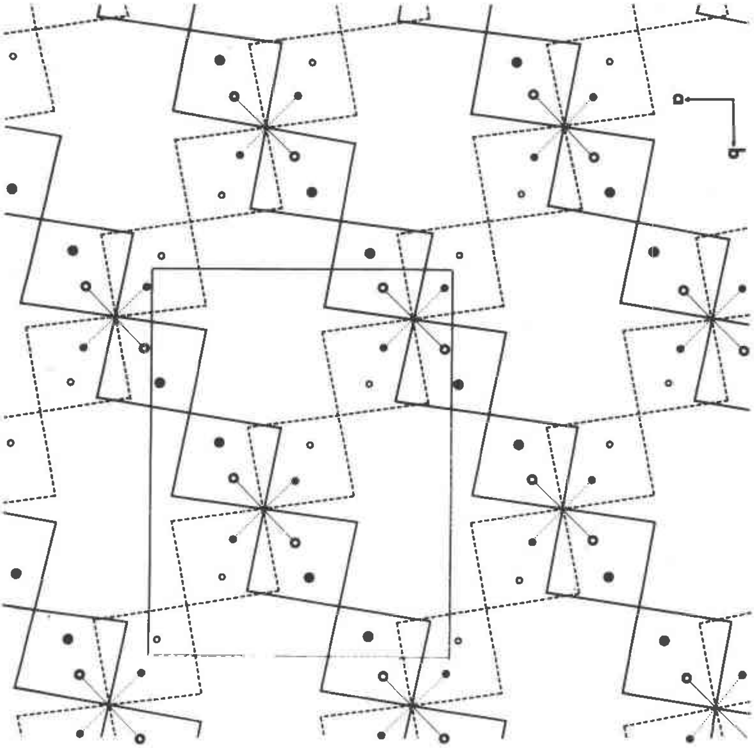

FIG. 2. Projection of the anionic framework on to (001). The equatorial planes at $z=0$ and $z=\frac{1}{4}$ and the oxygen atoms at the apices of the octahedra are shown. Edges of phosphorus tetrahedra (thin lines) linking octahedral chains are indicated. A unit cell is outlined. Broken lines: Octahedra at $z=0$ and lower edge of tetrahedra; Solid lines: Octahedra at $z=\frac{1}{4}$ and upper edge of tetrahedra; Open circles: Oxygens at base of octahedra; Solid circles: Oxygens at top of octahedra.

The octahedra and tetrahedra of the structure are regular within 3σ as shown by the interatomic distances and angles given in Table 3. The mean Al-O, Al-F distance is 1.855 Å, and it is interesting to note that there is no distinction between the oxygens and the fluoride ions with respect to these bond lengths.

TABLE 3. INTERATOMIC DISTANCES AND ANGLES IN FLUELLITE

Estimated standard deviations in parentheses refer to the last decimal position reported.

Octahedra

Al-O(3)	1.868(5) Å
Al-O(4)	1.847(5)
Al-F(5)	1.851(5)
O(3)-Al-O(4)	92.0(2)°
O(3)-Al-F(5)	92.5(2)
O(4)-Al-F(5)	88.7(2)

Channels

O(6)-O(6)$'$	2.688(8) Å
O(6)-O(3)$'$	2.660(8)
O(6)-O(3)$''$	2.708(8)
O(6)-O(4)$'$	2.802(8)
O(6)-O(3)$'''$	3.410(9)
O(6)-O(3)$'^{\mathrm{v}}$	3.591(9)
O(4)-O(6)-O(6)$'$	110.8(3)°
O(3)$'$-O(6)-O(6)$'$	100.5(3)
O(3)$''$-O(6)-O(6)$'$	124.6(3)
O(3)$'$-O(6)-O(4)	135.7(3)
O(3)$''$-O(6)-O(4)	98.8(3)
O(3)$'$-O(6)-O(3)$''$	87.7(3)

Tetrahedra

P-O(4)	1.530(3) Å
O(4)-P-O(4)$''$	109.8(2)°
O(4)-P-O(4)$'''$	108.9(2)
O(4)-P-O(4)$'^{\mathrm{v}}$	109.8(2)

Hydrogens

O(4)-H(7)	1.80(16) Å
O(6)-H(7)	1.11(16)
O(4)-H(7)-O(6)	147.0(12.0)°

Symmetry relations:

(3)	x, y, z	(4)	x, y, z	(6)	x, y, z
(3)$'$	$\frac{1}{2}-x, \frac{1}{4}+y, \frac{3}{4}+z$	(4)$'$	$\bar{x}, \bar{y}, \bar{z}$	(6)$'$	$\frac{3}{4}-x, y, \frac{3}{4}-z$
(3)$''$	$x, \frac{3}{4}-y, \frac{3}{4}-z$	(4)$''$	$x, \frac{1}{4}-y, \frac{1}{4}-z$	(6)$''$	$\frac{3}{4}-x, \frac{1}{4}-y, \frac{1}{2}+z$
(3)$'''$	$\frac{3}{4}+x, -y, \frac{3}{4}+z$	(4)$'''$	$\frac{1}{4}-x, y, \frac{1}{4}-z$	(6)$'''$	$\frac{1}{4}+x, \frac{3}{4}+y, \frac{1}{2}-z$
(3)$'^{\mathrm{v}}$	$\frac{3}{4}-x, y, \frac{3}{4}-z$	(4)$'^{\mathrm{v}}$	$\frac{1}{4}-x, \frac{1}{4}-y, z$		

Channels. The framework of corner-linked [AlO_4F_2] octahedra and [PO_4] tetrahedra form channels in the [110] and [1$\bar{1}$0] directions which contain the water molecules (or hydroxyl ions) corresponding to the O(6) atoms in 32-fold (h) positions. These oxygens occur in pairs, linked by one of the shorter hydrogen bonds in the structure of 2.688 Å, in the upper and lower regions of these channels, as shown in Fig. 3. Their hydrogen-bond coordination is that of a distorted tetrahedron (Table 3). The O(6)-O(6) bonds lie in the (010) plane, being nearly perpendicular to the *c*-axis and directed towards the *a*-axis, as shown in Fig. 4. The remaining three bonds from O(6) are to the framework structure, one to the O(4) and two to the O(3). Each O(3) atom is thereby involved in hydrogen bonding to both pairs of channel oxygens through the lower oxygen in the upper region and the upper oxygen in the lower region. There are four channel oxygens per formula unit, and they participate in all fourteen hydrogen bonds, either with each other or to the anionic framework. These fourteen distances are between 2.688 and 2.802 Å, as shown in Table 3. Since fifteen protons are required to produce an electrically neutral structure, there is presumably one "free" hydrogen present which is not involved in hydrogen-bonding. The shortest F-O distances are those which form the edges of the AlO_4F_2 octahedra which are 2.57, 2.59, 2.65 and 2.69 Å. These are normal non-bonding distances and there is no evidence that the fluoride ions are involved as acceptors in the hydrogen bonding in the structure.

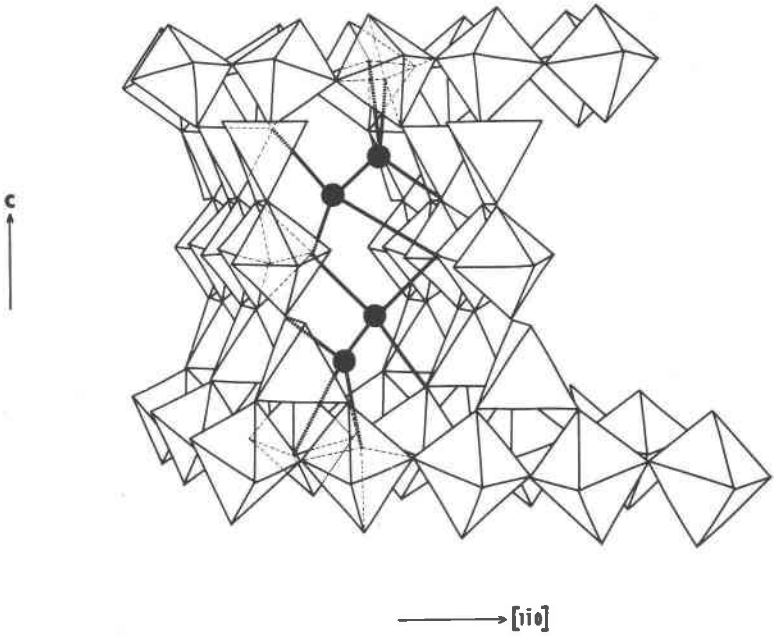

FIG. 3. [110] view of framework polyhedra and channel oxygen pairs. The bonding of the O(6) atoms in indicated.

Hydrogen Bonding. With the reasonable assumption that the mineral is a tertiary orthophosphate, O(4) will be a hydrogen-bond acceptor only and the four O(4) · · · H(7)—O(6) bonds per formula unit will have a single proton location closer to O(6) than O(4). This corresponds to the longest O · · · · O hydrogen bond separation of 2.802 Å. There are then two possible sets of hydrogen atom configurations, depending upon whether the hydroxyl ions are associated with the framework octahedra or the channel oxygens. The proton configuration corresponding to the formula $\{Al_2PO_4F_2 \cdot 3H_2O \cdot OH\}4H_2O$, with the framework enclosed in the brackets, is shown in Fig. 5(a). All the other ten hydrogen bonds can

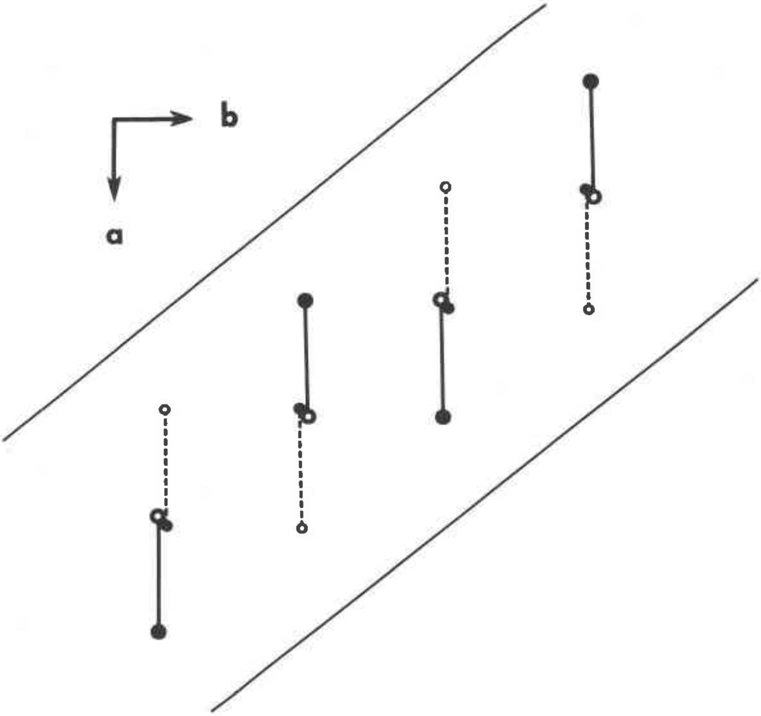

FIG. 4. Projection on to (001) of oxygen pairs in the upper and lower regions of a $[1\bar{1}0]$ channel (outlined). Adjacent oxygens, O(6), at $z=0.07$ (small solid circle) and at $z=0.25$ (large open circle) share O(3) oxygens of the framework. Oxygens at $z=0$ (small open circle) and at $z=0.32$ (large solid circle) share O(3) oxygens with O(6) atoms in [110] channels. Broken line: Hydrogen bond between lower oxygen pair; Solid line: Hydrogen bond between upper oxygen pair.

then have a double potential minimum with a synchronized distribution of the hydrogen atoms. The non-bonding hydrogen atom H(13), would be attached to one fourth of the O(3) framework oxygens in a statistical random arrangement, being also synchronized locally with the donor/acceptor distribution of the hydrogen bonds. There are reasonable positions for this atom in the directions of O(6)'' or O(6)''' at 3.5 Å away, as shown in Fig. 6a which illustrates the O(3) environment. The angles between the O(3)-H(13) bond and the O(3) · · · · O(6) hydrogen-bond directions for the coordinates given in Table 1 and shown in Fig. 6a are 99° and 103°.

The alternative configuration, $\{Al_2PO_4F_2\cdot 4H_2O\}3H_2O\cdot OH$, in which the hydroxyl ions are located in the channels, permits the double minimum proton position for the O(6) · · · · O(6) hydrogen bonds only, as shown in Fig. 5b. This would therefore be a configuration of less residual entropy. The non-bonding hydrogen atom for this configuration is then located on one of the four O(6) atoms. A possible position is along the O(6) · · · · O(3)″ direction, such that the O(6)-H bond would be at angles of about 65° to three of the four hydrogen bonds from O(6). This is stereochemically less acceptable than that for the configuration 5a, as shown in Fig. 6b. The observation that the only hydrogen atom directly located on the Fourier difference synthesis was that on O(6), which forms the donor bond to the phosphate O(4), suggests that this is the only site with unit weight for the hydrogen atoms and thus also favors the configuration 5a with only water molecules in the channels and the maximum number of double minimum hydrogen bonds.

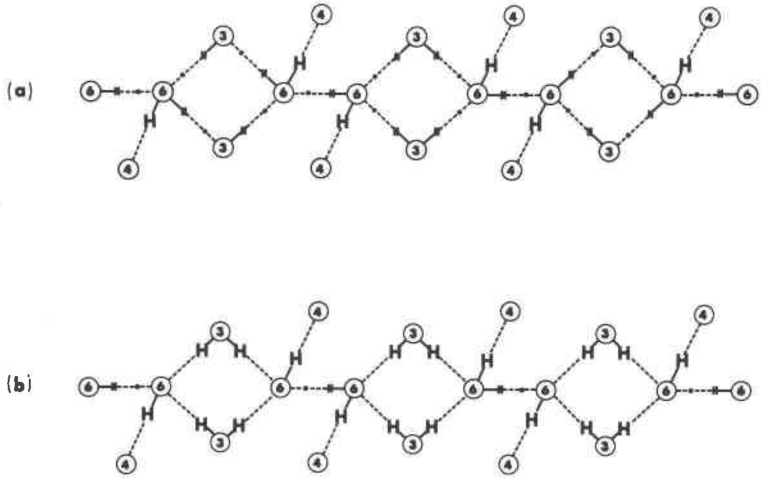

Fig. 5. Schematic diagram for possible hydrogen bonding configuration in fluellite. The non-bonding proton (not shown) is attached to the hydroxyl ions. (a) Hydroxyl ions located on framework O(3) oxygens. Statistically, O(3) atoms are $3H_2O\cdot OH$ and O(6) atoms $4H_2O$ per formula unit. (b) Hydroxyl ions located in channels. Statistically, O(3) atoms are $4H_2O$ and O(6) atoms $3H_2O\cdot OH$ per formula unit. Large H: full proton position; Small H: fractional proton position; Alternative locations for hydrogens along a bond are shown by solid circles.

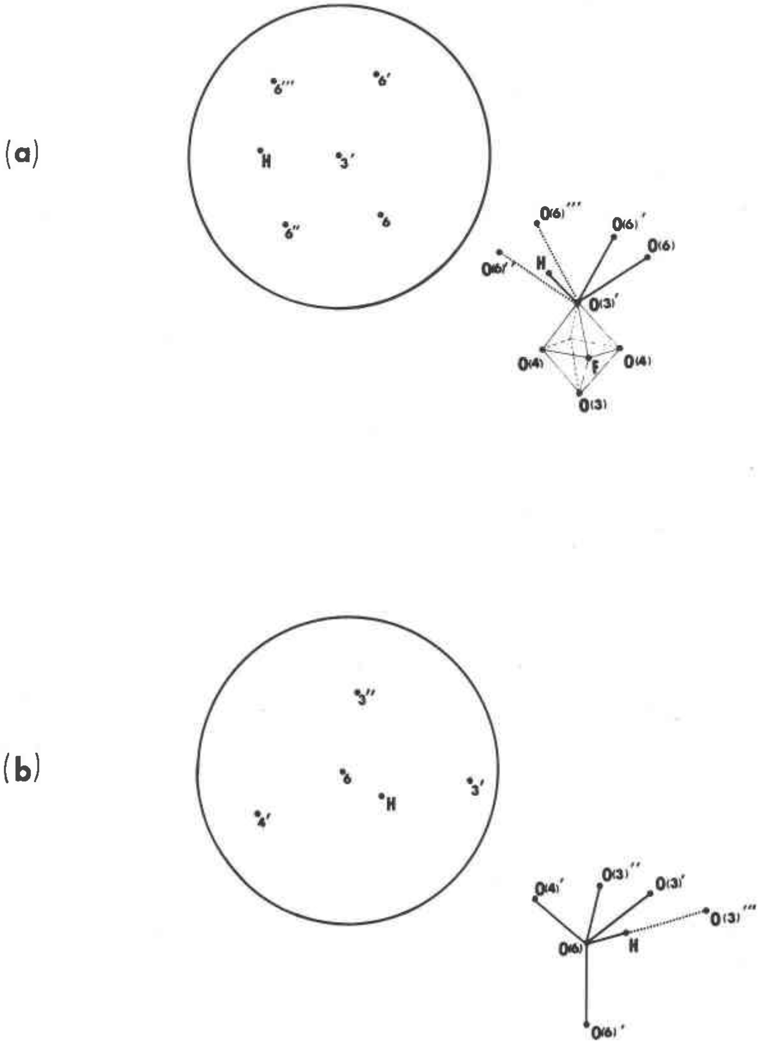

FIG. 6. Stereographic projection showing location of the non-bonding hydrogen in structure. (a) For configuration illustrated in Fig. 5a. An O(3) oxygen is at center of sphere of projection. (b) For configuration in Fig. 5b. The O(6) oxygen is at center of sphere of projection. The environment of the atom at center of the sphere of projection is illustrated adjacent to the stereogram. Solid line: Hydrogen bonding linkages; Broken lines: Van der Waal's contacts.

While it is possible that both sets of configurations represented by 5a and 5b can exist in the structure with a tautomeric exchange such that it is impossible to distinguish whether the $(OH)^-$ ions are on the framework or in the channels, we believe that this is less likely than a structure with only the water molecules in the channels, on the basis of the evidence presently available.

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