

# A STRUCTURAL CLASSIFICATION OF FLUOALUMINATES\*

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## INTRODUCTION

During 1948, while a guest in the laboratory of Professor Frondel, I had the opportunity to look into the classification of certain mineral fluorides to be described in the second volume of the *System of Mineralogy*. Although nearly a dozen structures of fluoaluminates and related compounds had been determined, there existed no unified summary of these structures, much less a comprehensive statement of their common features. Since it appeared that these structures must be based on  $AlF_6$  octahedra which might be discrete units or joined in chains, sheets, frameworks, and other groupings, much as silicate structures are based on linked  $SiO_4$  tetrahedra, it appeared worthwhile to attempt a complete summary of the  $AlF_6$  structures and to compare and contrast the results with the general features of silicate structures.

TABLE 1. FLUOALUMINATES OF KNOWN STRUCTURE

Formula	Mineral Name	Structure Type	Investigators	Year
$Na_3AlF_6$	Cryolite	$J2_6$	Náray-Szabó & Sasvari	1938
$K_2NaAlF_6$	Elpasolite		Menzer	1928
$Li_3Na_3Al_2F_{12}$	Cryolithionite	$S1_4$ (Garnet)	Menzer	1930
$Tl_2AlF_5$		*	Brosset	1942
$Na_5Al_3F_{14}$	Chiolite	$K7_5$	Brosset	1938
$TlAlF_4$		$H0_8$	Brosset	1937
$Na_2MgAlF_7$	Weberite		Bystrom	1945
$Na_x(Al_{2-x}, Mg_x)(F,OH)_6 \cdot H_2O$	Ralstonite	$E8_1$ (pyrochlore)	Pabst	1939
$AlF_3$		$D0_{14}$	Ketelaar	1933
$KMgF_3$		$E2_1$ (perovskite)	van Arkel	1925

\* Earlier description of this structure by Brosset in 1937 was designated Type  $K3_3$  in Strukturbericht.

Search of the literature led to ten structure types, determined between 1925 and 1945, for which examples are given in Table 1. For several of these other representatives are also known. The compounds are listed in order of decreasing ratio of F to Al. One compound is included which

\* Address of the retiring President of the Crystallographic Society of America delivered at the annual meeting of the Society at the University of Michigan, April 7, 1949.

contains no Al. The reason for this will appear shortly. Compounds on which structural data are meager or confused have been omitted. Complete structure determinations have been published for all those listed except  $K_2NaAlF_6$ , elpasolite. Menzer (1928) published only an extended abstract on this but the powder pattern of natural material for this cubic substance published by Frondel (1948) supports the space group and the main features, at any rate, of the structure proposed by Menzer. The structure type designations in the table are those of the Strukturbericht. For three substances the structure type is also designated by a mineral name since the structures are known to many by these names. The fluorides listed are not the compounds on the basis of which these types were established.

#### DESCRIPTION OF STRUCTURES

Diagrams for most of the structures listed have been published in the Strukturbericht and elsewhere but they are drawn on various projections and with differing conventions so that they are not suitable for comparison.

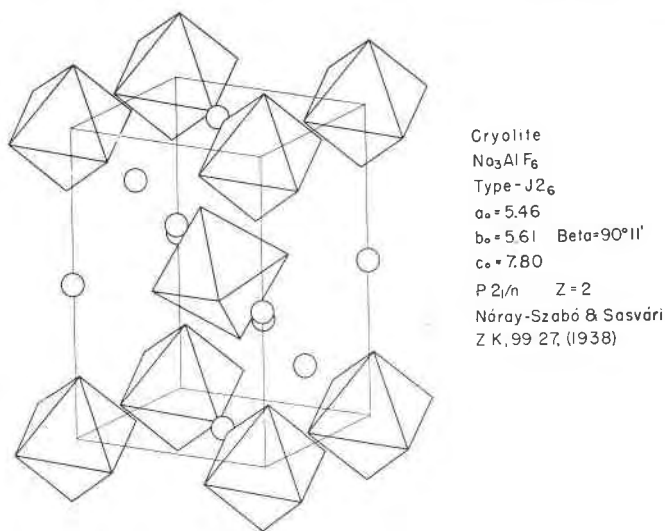


FIG. 1

son. New drawings have been prepared for each of these structures using exactly the same conventions, scale and projection for all. The projection is a 30–15 degree clinographic. Identity of scale has been maintained in the reproductions. In the originals the scale was 4 centimeters per angström unit.

The structure of cryolite was earlier unsuccessfully investigated by

Menzer. Though monoclinic the structure is pseudocubic as may be seen from the cell dimensions or from Fig. 1. Above its transition point at about  $570^\circ$  cryolite is isometric. The 110 plane of monoclinic cryolite corresponds to the face of a pseudocube very similar to the unit cube of elpasolite.

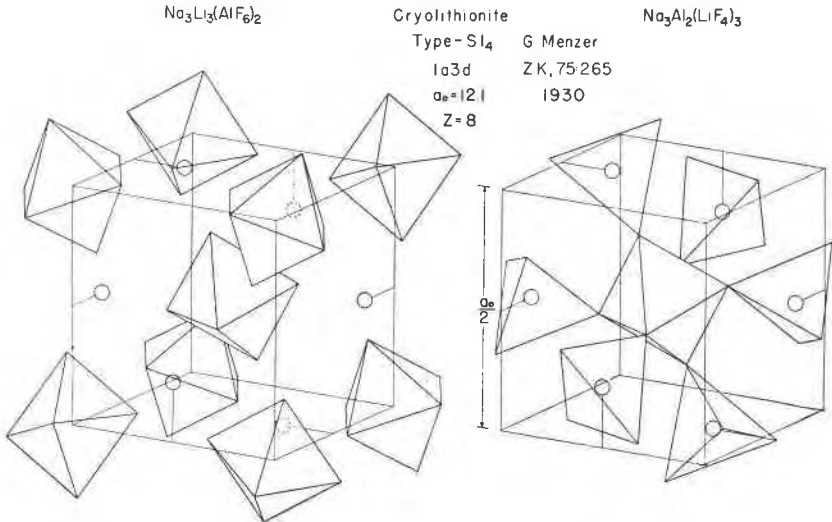


FIG. 2

For cryolithionite, which has the garnet structure, it is only necessary to draw small cubes having one eighth the volume of the unit cube to picture the structure. Two such small cubes are shown in Fig. 2. The faces of these cubes are  $a$  glide planes. In the left cube  $\text{AlF}_6$  octahedra are shown and such units are bracketed in the formula written above. If we wish to group cryolithionite with the materials here considered the structure should be looked at in this way and the formula written in this manner. There is, however, an alternative way of looking at this structure which may be preferable. The small circles in the diagram represent lithiums. They are situated in each of the small cube faces. The sodiums are not shown. Each of the lithiums is at the center of a tetrahedron of fluorines and in the right hand drawing the six tetrahedra about the lithiums in each of the small cube faces are indicated. The octahedra have been omitted here except for the one in the center which has been left to show the manner in which tetrahedra and octahedra are tied together. Each fluorine is at the corner of a tetrahedron and also at the corner of an octahedron. If the formula of cryolithionite is written as at the right it resembles the formula of garnet, for instance grossularite

as ordinarily written with Na taking the place of Ca and  $\text{LiF}_4$  taking the place of  $\text{SiO}_4$ . If garnet is considered an orthosilicate then cryolithionite having precisely the same structural arrangement, should be described by the formula at the right and we may exclude it from a classification of structures based on  $\text{AlF}_6$  groups. This is no loss since we have other examples of structures with discrete  $\text{AlF}_6$  groups.

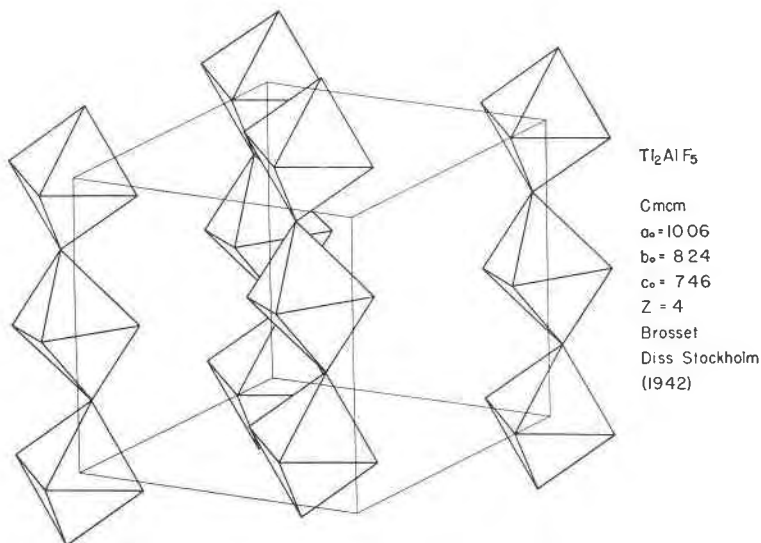


FIG. 3

If  $\text{AlF}_6$  octahedra are linked into chains by the corners the ratio of F to Al becomes 5 and hence a chain structure might have been expected for  $\text{Tl}_2\text{AlF}_5$ . In Fig. 3, showing this structure, the light lines indicate the unit cell edges. With a base-centered lattice there is a slightly kinked chain parallel to the  $c$  axis through the center of the cell and at each corner. In the drawing the chain at the nearer corner is omitted. The thalliums which lie in  $xyz$  positions near  $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ , etc., are not shown. The structure here pictured corresponds to that described by Brosset in his dissertation in 1942. At the same time he reported on the structure of  $\text{K}_2\text{AlF}_5 \cdot \text{H}_2\text{O}$  to which he assigned the same structure with  $\text{H}_2\text{O}$  going into positions  $0\frac{1}{2}\frac{1}{4}$ , etc. An earlier examination of  $\text{Tl}_2\text{AlF}_5$  had led Brosset in 1937 to assign this material to a cell of the same dimensions but to space group  $C222_1$  and to propose for it a slightly different structure, which, however, also involved slightly kinked  $\text{AlF}_6$  chains. That structure, now superseded by the one here pictured, was taken into the *Strukturbericht* as type  $K3_3$ .

The structure found for chiolite (Fig. 4) by Brosset (1938) involves sheets of linked octahedra. These octahedra are of two kinds, those with four corners shared and those with two corners shared. The latter are twice as numerous as the former. As the drawing shows this linkage results in sheets with large holes, so large, in fact, that they might accommodate another octahedron to make an unbroken sheet. Dr. R. B.

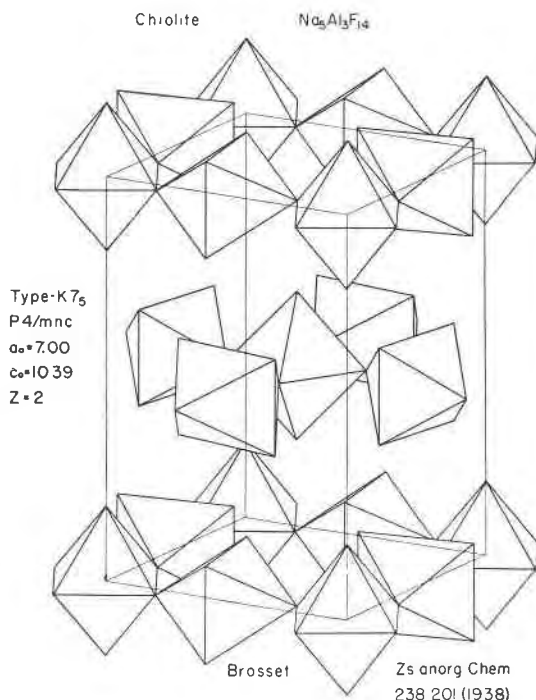


FIG. 4

Ferguson, in a communication to Professor Frondel, has referred to the chiolite sheets as "interrupted sheets." This term may be appropriate but it must be understood that the continuity of the sheets would cease only at a crystal boundary or imperfection, the word "interrupted" referring merely to the aforementioned "holes."

A much simpler sheet structure (Fig. 5) was found in  $\text{TlAlF}_4$ , also studied by Brosset (1937). The light lines in the picture again indicate the edges of the tetragonal cell. There is an octahedron at the center of each cell linked to octahedra in adjoining cells making a sheet of composition  $\text{AlF}_4$ . Thalliums, not indicated in the diagram, are at cell corners

and are situated between sheets that parallel the base. A segment of the next sheet above is shown in the picture at the correct height. The following year Brosset (1938) showed that  $\text{KAlF}_4$ ,  $\text{RbAlF}_4$  and  $\text{NH}_4\text{AlF}_4$  are all isostructural with  $\text{TlAlF}_4$ .

In his paper on the thallium aluminum fluorides in 1937 Brosset pointed out that the structures of these compounds might be considered to belong to a series extended from cryolite involving discrete  $\text{AlF}_6$  octahedra

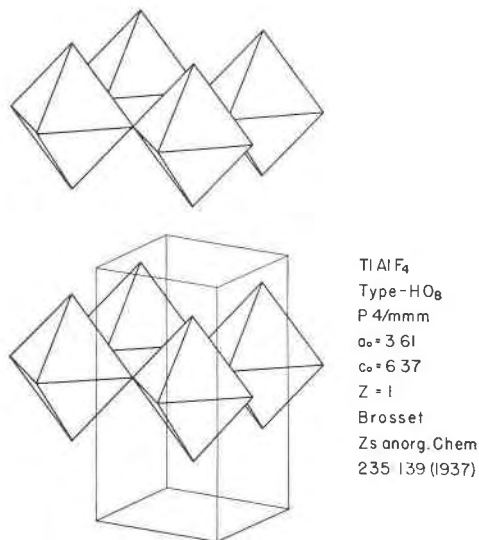


FIG. 5

through chains and sheets to the network structure of  $\text{AlF}_3$ , and said that "the  $\text{AlF}_6$  octahedron has the same sort of role in the structure of the alkalialuminumfluorides as the  $\text{SiO}_4$  tetrahedron in the varieties of silica and the silicates." The following year, in his paper on chiolite, Brosset showed diagrammatically the relations of the three aluminofluoride structures that he had investigated. Fig. 6 shows these three structures in somewhat simplified fashion and oriented in such a manner as to show the dimensional relations. The scale of Fig. 6 and Fig. 7 is one half that used for the diagrams of single structures and the projection is 20-10 clinographic. For  $\text{TlAlF}_4$  the volume outlined by the light lines is 8 unit cells, for the other two it is one cell each. Starting at the bottom with a chain structure we may think of the interrupted sheet structure as arising from it by cross linking with the turning of alternate octahedra. At the top the "holes" in the interrupted sheet are filled in and all octahedra are again in common orientation.

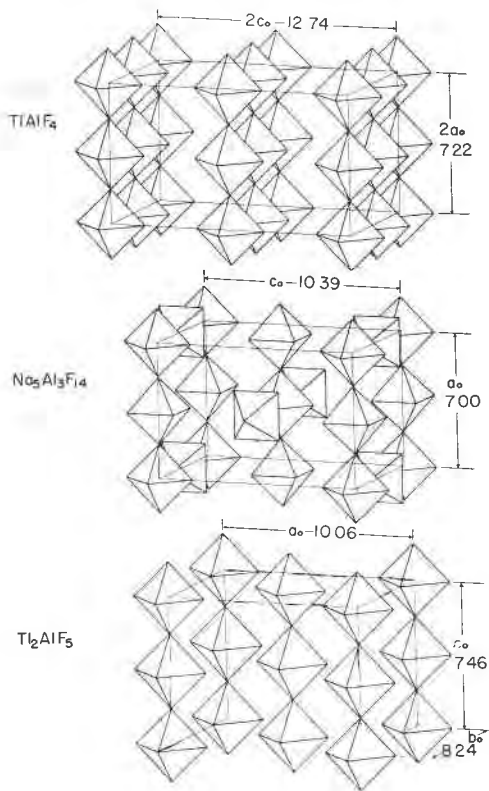


FIG. 6

Groupings not found in aluminofluorides

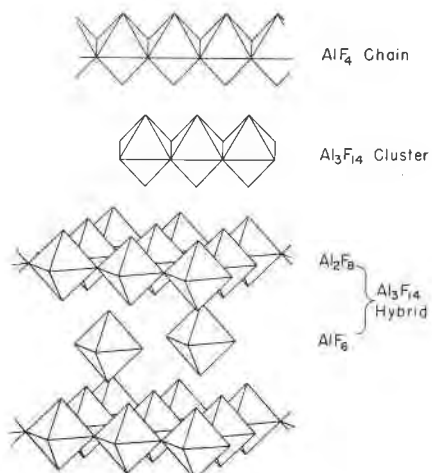


FIG. 7

In passing it is worthwhile to consider other linkages (Fig. 7) that might account for the fluorine-aluminum ratios in the structures just considered. The F/Al ratio would be 4 if octahedra were linked into endless chains by sharing of edges. No *x*-ray evidence has been found for such a situation. The ratio  $\text{Al}_3\text{F}_{14}$  would be accounted for by at least 2 other groupings besides the interrupted sheet structure. One such would be clusters of three octahedra sharing edges and making up the composition  $\text{Al}_3\text{F}_{14}$ . Another would be a hybrid structure of  $\text{AlF}_4$  sheets, we can also call them  $\text{Al}_2\text{O}_8$  sheets, associated with discrete  $\text{AlF}_6$  octahedra. Brosset eliminated both of these possibilities for chiolite by intensity considerations.

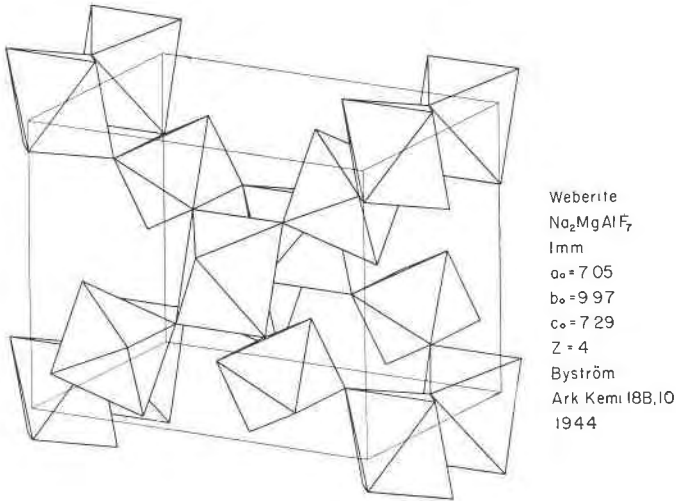


FIG. 8

In Fig. 8 the orientation chosen for weberite by Byström (1945) has been modified. He had taken the symmetry axis in the class  $2mm$  as the *b* axis. By interchanging his *b* and *c* axes weberite is put in the conventional orientation for this class. The drawing shows that the structure may be looked upon as a framework of linked octahedra and that these octahedra are of two types. Half of the octahedra have one edge parallel to *b*. These share all corners, 4 with octahedra of the same kind and 2 with octahedra of the other kind. The other octahedra have one edge parallel to *a*. They each share four corners with octahedra of the first kind and have two unshared corners. Such a structure might be called an "interrupted framework" since we can go from any octahedron in the structure to any other by a path lying entirely along octahedra but there are octahedral corners at which we cannot continue to another



octahedron. Byström assigns the magnesiums to the centers of octahedra sharing all corners and the aluminums to those having free corners, but points out that there is no basis in intensity considerations for checking on the distribution because of the similarity of the scattering power of  $Mg^{+2}$  and  $Al^{+3}$  and that both ions may be statistically distributed over the two positions. Byström further points out that this can be checked by a little simple arithmetic and Pauling's rules. He seems to feel that these favor statistical distribution but are not conclusive. The same author has shown (1945) that  $Ca_2Sb_2O_7$  has a structure similar to webberite and here, of course, the centers of the octahedra are all occupied by like ions.

The same ratio of negative to positive ions, 7 to 2, is also characteristic of the so-called pyrochlore structure which is represented by a large

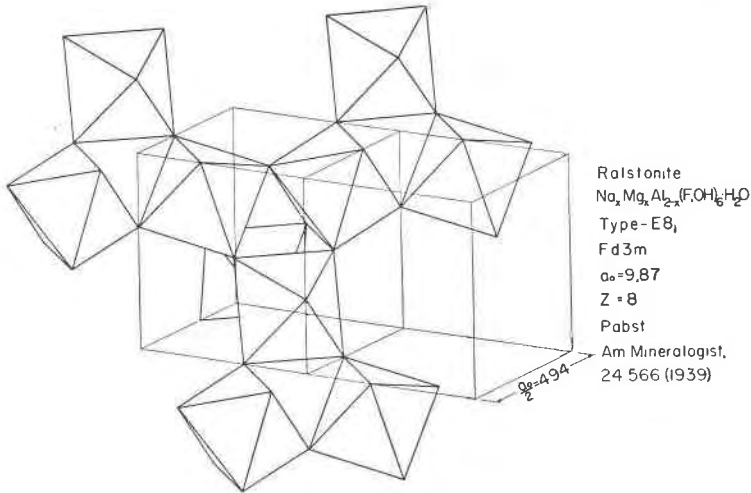


FIG. 9

number of minerals. An example is microlite, ideally  $Ca_2Ta_2O_7$ . The structure is cubic. Oxygen octahedra are linked at all corners to make a continuous framework of composition  $TaO_3$  or  $Ta_2O_6$ . The extra oxygen is not involved in the linked octahedra. It has been found (Pabst, 1939) that the rare mineral ralstonite is essentially a fluoride with pyrochlore structure. The composition of ralstonite had previously been represented by a formula which seems inappropriate to me. Considered as a fluoride pyrochlore the composition may be expressed by the formula shown in Fig. 9. The octahedral corners are occupied by F or OH, the centers by Al or Mg. The drawing shows two small cubes of one eighth the volume

of the unit cube. Their faces are  $d$  glide planes. Alternate small cubes contain the octahedral centers, in the drawing the one on the left. There are only as many sodium ions as there are Mg's substituting for Al's, this being required to preserve neutrality. The sodiums are in the small cube at right and so on. In the mineral the value of  $x$  is about  $\frac{3}{8}$ , the extra-octahedral metal positions being only partly occupied. The extra-octahedral anion positions are largely filled up with water in ralstonite. Among oxygen compounds with pyrochlore structure a few are known in which the extra anion positions are entirely unoccupied.

The possible composition range of ralstonite is unknown but it may be that some of the unnamed and unanalyzed cubic minerals from Ivigtut

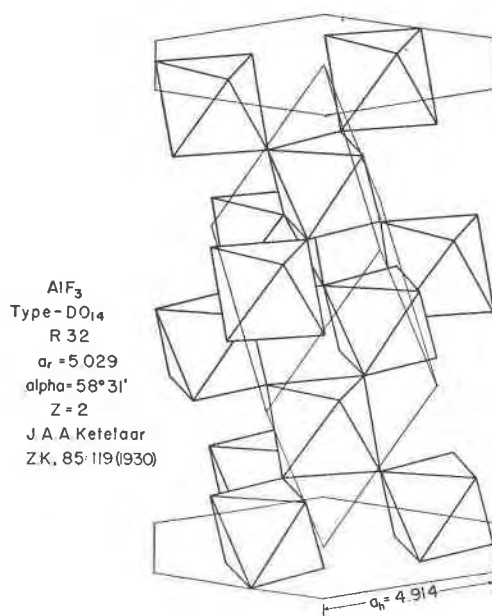


FIG. 10

having slightly different refractive indices and densities are but variants of ralstonite.

In the case of weberite there remained some doubt as to whether Mg and Al are distributed statistically over equivalent positions. In ralstonite there can hardly be any doubt on this point. It may be looked upon as an  $\text{AlF}_3$  framework structure that has received a negative charge by substitution of Mg for Al at octahedral centers, this charge being satisfied by the Na ions.

The framework structure of pure  $\text{AlF}_3$  (Fig. 10) was investigated by Ketelaar (1933). There are also varied hydrated forms of this fluoride including the mineral fluellite, whose structures remain undetermined.  $\text{AlF}_3$  is rhombohedral. Each cell contains two  $\text{AlF}_6$  octahedra. These are in two orientations and each is linked at all corners to octahedra of the other orientation with centers in adjacent rhombohedral cells. To picture this linkage it is necessary to draw much more than the volume

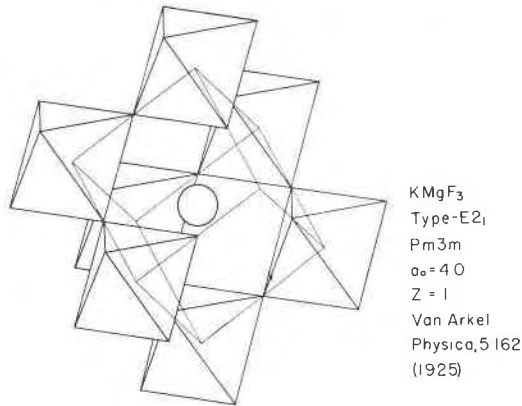


FIG. 11

of one cell. The outline of the unit rhombohedron is shown lightly in the diagram. Above and below are shown hexagonal rings whose edges are the  $a_h$  of the hexagonal cell and which are separated by the distance  $c_h$ .

The possibility of substituting Mg for Al at octahedral centers has been mentioned. Figure 11 shows a structure in which this substitution is carried to the limit.  $\text{KMgF}_3$  has a perovskite structure (van Arkel, 1925). In the drawing the unit cube is placed with a body diagonal vertical to make it appear like a rhombohedron. Potassium, shown by the circle, occupies cube centers, magnesium cube corners with fluorine midway along the edges. The fluorines may be thought of as belonging to octahedra linked at all corners.\*

In the diagram the octahedron centered on the forward cube corner has been omitted.

\* This emphasis on certain geometrical relations in  $\text{KMgF}_3$  is not intended to carry any implication as to the type of bonding involved. A. F. Wells (*J. Chem. Soc. London*, 1962, 1947) has recently stated "In the perovskite structure of  $\text{KMgF}_3$  no discrete complex ions exist; it is to be regarded as an infinite 3-dimensional array of  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{F}^-$  ions."

## SUMMARY AND GENERALIZATIONS

Table 2 shows the distances between fluorine and the ions in six-fold coordination in the substances considered. The range of Al-F distances is from 1.70 to 1.91 and for Mg-F from 1.86 to 2.00, if we consider that the larger octahedra in weberite are exclusively occupied by magnesiums. It will be remembered that this could not be established by intensity considerations. The letter *s* in the table indicates that the distance is to a shared octahedral corner. The data are insufficient to show clearly a consistent difference between these distances and the distances to unshared corners.

The last column of Table 2 shows the near constancy of the distance between the points of two contiguous octahedra in chains and sheets. This distance determines the lattice dimensions of a number of compounds in the same way in which the distance 5.2, twice the edge of a  $\text{SiO}_4$  tetrahedron, determines the dimensions of silicate structures, e.g. the *c* axes of amphiboles and pyroxenes or the *a* axes of micas.

It would require a full tabulation of *F-F* distances to survey the departure of the fluorine octahedra in these structures from the ideal shape but the diagrams show that this departure is slight in most cases.

Seven distinct structure types have been found among the aluminofluorides. They are listed in Table 3. Of structures with separate octahedra there are several variants in addition to the one given as example. These include elpasolite and the so-called potassium cryolite and ammonium cryolite whose structures were not pictured.

For the chain structures there is also at least one more example,  $\text{K}_2\text{AlF}_5 \cdot \text{H}_2\text{O}$ , which is isostructural with  $\text{Tl}_2\text{AlF}_5$ . The simple sheet structure of  $\text{TlAlF}_4$  exists also in the corresponding potassium, rubidium and ammonium compounds. To date the chiolite, weberite and ralstonite structures have not been found among other fluorides but the latter two are represented among oxide compounds.

From this survey it is possible to draw some general conclusions about fluoaluminate structures and to contrast them with the structures of silicates. As suggested by Brosset in 1937 the structures of these compounds are controlled by the linking of octahedra. Seven types have been recognized:—separate octahedra, chains, interrupted sheets, sheets, interrupted frameworks, and two distinctly different types of frameworks. Through this series the ratio of fluorines to six-coordinated cations decreases from 6 to 3 as the number of shared corners per octahedron increases from null to six. This is roughly comparable to the linkage of tetrahedra in silicates and the attendant change in the O/Si ratio. As shown in the diagrams, only corners, not edges, are shared the same as in the linkage of  $\text{SiO}_4$  tetrahedra.

TABLE 2. DISTANCES IN FLUOALUMINATE STRUCTURES

Name	Formula	Distance from center to corner of octahedra	Distance between points of two contiguous octahedra in chains or sheets		
Cryolite	$\text{Na}_3\text{AlF}_6$	2 at 1.79 2 at 1.82 2 at 1.83			
Cryolithionite	$\text{Li}_3\text{Na}_3(\text{AlF}_6)_2$	6 at 1.81			
	$\text{Tl}_2\text{AlF}_5$	2 at 1.81 2 at 1.91 s 2 at 1.91	$c_0$	7.46	
	$\text{K}_2\text{AlF}_5 \cdot \text{H}_2\text{O}$	2 at 1.75* 2 at 1.87 s 2 at 1.88*	$c_0$	7.45	
Chiolite	$\text{Na}_6\text{Al}_3\text{F}_{14}$	2 at 1.92 s 4 at 1.82 s 2 at 1.82 4 at 1.94			
	$\text{TlAlF}_4$	2 at 1.8 s 4 at 1.8	$2a_0$	7.22	
	$\text{KAlF}_4$		$2a_0$	7.10	
	$\text{NH}_4\text{AlF}_4$		$2a_0$	7.18	
	$\text{RbAlF}_4$		$2a_0$	7.24	
	$\text{AlF}_3$	s 3 at 1.70 s 3 at 1.89			
	Weberite	$\text{Na}_2\text{MgAlF}_7$	s 4 at 1.83 2 at 1.84 s 4 at 1.94 s 2 at 1.94		
		$\text{Na}_x(\text{Al}_{2-x}\text{Mg}_x)(\text{F},\text{OH}) \cdot \text{H}_2\text{O}$	s 6 at 1.86		
Ralstonite	$\text{KMgF}_3$	s 6 at 2.00			

\* As given by Brosset (1942). Calculation from his parameters and cell dimensions yields the values 1.65 and 1.90.

TABLE 3. TYPES OF FLUOALUMINATE STRUCTURES

Structure type	Shared octahedral corners	F/W ratio	Example	
			Formula	Name
Separate octahedra	0	6	$\text{Na}_3\text{AlF}_6$	Cryolite
Chains	2	5	$\text{Tl}_2\text{AlF}_5$	
Interrupted sheets	2 & 4	$4\frac{2}{3}$	$\text{Na}_5\text{Al}_2\text{F}_{14}$	Chiolite
Sheets	4	4	$\text{TlAlF}_4$	
Interrupted frameworks	4 & 6	$3\frac{1}{2}$	$\text{Na}_2\text{MgAlF}_7$	Weberite
Frameworks	6	3	$\text{AlF}_3$	
Frameworks (pyrochlore type)*	6	3*		Ralstonite

\* With the possibility of additional anions and an F/W ratio of  $3\frac{1}{2}$ .

In some respects there are notable differences from the silicates. No cases of the sharing of 1, 3 or 5 corners of  $\text{AlF}_6$  octahedra have been found. Even numbers of corners only are shared and a close inspection of structures will show that the diametrically opposite corners are always shared together. In tetrahedra there are, of course, no diametrically opposite corners and known silicate structures involve the sharing of either 0, 1, 2, 3 or 4 corners.

In Table 4 a list of most of the recognized silicate types is arranged alongside a list of the fluoaluminate types for comparison. For instance, silicate structures include finite groups of linked tetrahedra such as  $\text{Si}_2\text{O}_7$  pairs or  $\text{Si}_3\text{O}_9$  and  $\text{Si}_6\text{O}_{18}$  rings. Nothing comparable, such as, say, an  $\text{Al}_2\text{F}_{11}$  pair, has been found among fluoaluminates.

Both the sheet structure with the F/Al ratio 4 and the interrupted sheet structure with the ratio  $4\frac{2}{3}$  have unshared octahedral corners on both sides of the sheets. This is in marked contrast to the most familiar of the silicate sheet structures in which the unshared tetrahedral corners are all on one side though complex silicate sheets like that in the tetragonal gillespite,  $\text{BaFeSi}_4\text{O}_{10}$ , with unshared corners on both sides have been reported.

In the presence of very small cations  $\text{RF}_4$  coordinations may occur together with  $\text{RF}_6$ . Among the fluoaluminates so far studied  $\text{Li}^{+1}$  is the only suitable cation. Of course, tetrahedral groups of F are well known among compounds other than the aluminofluorides, for instance, in  $\text{BeF}_2$  ( $\text{NH}_4$ ) $_2\text{BeF}_4$ , ( $\text{NH}_4$ ) $\text{BF}_4$ , and others.

Mg is six coordinated by F in fluorides and may substitute for Al in random fashion. Such substitution has been found in ralstonite and probably exists in weberite. It also seems not unlikely that homogeneous phases intermediate between  $\text{AlF}_3$  and, say,  $\text{KMgF}_3$  could be obtained

TABLE 4. ANALOGIES BETWEEN STRUCTURES BASED ON  $\text{AlF}_6$  OCTAHEDRA AND  $\text{SiO}_4$  TETRAHEDRA

Type	Fluoaluminates		Silicates	
	Group Formula	Example	Group Formula	Example
Isolated octahedra or tetrahedra	$(\text{AlF}_6)^{-3}$	Cryolite $\text{Na}_3\text{AlF}_6$	$(\text{SiO}_4)^{-4}$	Forsterite $\text{Mg}_2\text{SiO}_4$
Pairs			$(\text{Si}_2\text{O}_7)^{-6}$	Thortveitite $(\text{Sc, Y})_2\text{Si}_2\text{O}_7$
Rings	$(\text{AlF}_5)^{-2}$	$\text{Tl}_2\text{AlF}_6$	$(\text{Si}_3\text{O}_9)^{-6}$	Benitoite $\text{BaTiSi}_3\text{O}_9$
Simple chains			$(\text{SiO}_3)^{-2}$	Enstatite $\text{MgSiO}_3$
Bands			$(\text{Si}_4\text{O}_{11})^{-6}$	Tremolite $(\text{OH})_2\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2$
“Interrupted” sheets	$(\text{Al}_3\text{F}_{14})^{-5}$	Chiolite $\text{Na}_3\text{Al}_3\text{F}_{14}$	$(\text{Si}_2\text{O}_5)^{-2}$	Gillespite* $\text{BaFe}(\text{Si}_2\text{O}_5)_2$
Simple sheets	$(\text{AlF}_4)^{-1}$	$\text{TlAlF}_4$		
“Interrupted” frameworks	$(\text{MgAlF}_7)^{-2}$	Weberite $\text{Na}_2\text{MgAlF}_7$	$\text{SiO}_2$	Quartz $\text{SiO}_2$
Pyrochlore frameworks	$((\text{Mg}_2\text{F}_6)\text{F})^{-5}\dagger$	Ralstonite		
Complete frameworks	$\text{AlF}_3$	$\text{AlF}_3$		

\* This obscure example is used because other sheet silicates all contain anions in addition to those that form part of the linked tetrahedra.

† This group formula results if  $x$  is made 2 in the ralstonite formula and the possible anion positions are entirely occupied by F.

in which such random substitution could be shown. The substitution so far has been found only in framework structures and it seems most likely that it is limited to structures in which there is a high measure of linking of octahedra. This is closely analogous to the substitution of Al for Si which is typical in silicate frameworks where many cases of halfway substitution, as in anorthite, are known. In silicate sheets halfway substitution or even beyond also occurs but the most common case is one quarter substitution as in muscovite. In the double chains or bands of amphiboles the substitution is less extensive and in the simple pyroxene chains even more restricted. It may be wholly lacking in orthosilicates though the slight excess of alumina found in some garnets might be accounted for in this way. The experimental hindrances to determination of Mg-Al distribution, referred to earlier, have their counterpart in the similar difficulty in the establishment of Al-Si distributions which has

contributed to the troubles in dealing with the all important feldspars.

Fluorine octahedra centered on a small cation appear in the fluosilicates, which are known in two or more structures, as well as in fluozirconates, fluostannates and so on. In all these there are separate octahedra and they correspond roughly to the fluoaluminate structures in which no octahedral corners are shared. So far as I am aware no chain, sheet or framework structures with ions of higher charge than aluminum at the centers of the fluorine octahedra have been described.

#### CLASSIFICATION OF MINERAL FLUOALUMINATES

A dozen years ago the classification of silicates was considered so well established that Berman undertook a structural classification of all silicate minerals on the basis of composition and properties even in the absence of experimental knowledge of the structures. It might seem that the same could be tried for the fluoaluminates. Among the examples discussed were five minerals, all but elpasolite being from Ivigtut in Greenland. At this locality there are known at least 4 more fluoaluminates and others occur elsewhere. Fitting these into a classification seems too hazardous for two reasons. First, the F/Al ratio alone is no good guide to structure type. For instance, the weberite formula might be explained on the basis of a pyrochlore type of structure and this was, in fact, tried by Byström in working on this mineral. Second, the correlation of structure with properties of fluoaluminates is as yet very uncertain. Most of the pertinent data are given in Table 5. It may be seen

TABLE 5. PROPERTIES AND STRUCTURES OF FLUOALUMINATES

Type	Name	Composition	Symmetry	Optics	Habit	Cleavage
Separate octahedra	Cryolite	$\text{Na}_2\text{AlF}_6$	$P2_1/n$	pos.* $2V = 60^\circ$ B. = 0.01	Pseudotet. equidimen.	poor or absent
Separate octahedra	Cryolithionite	$\text{Li}_2\text{Na}_2\text{Al}_2\text{F}_{12}$	$Ia3d$	Isotropic	{110} {211}†	{110} fair
Chains		$\text{Tl}_2\text{AlF}_6$	$Cmcm$	—	"well developed needles"	—
Interrupted sheets	Chiolite	$\text{Na}_5\text{Al}_3\text{F}_{14}$	$P4/mnc$	neg. uniax. B. = .007	granular massive	{001} perfect
Sheets		$\text{TlAlF}_4$	$P4/mmm$	—	"brittle plates"	—
Interrupted framework	Weberite	$\text{Na}_2\text{MgAlF}_7$	$Imm$ (pseudotet.)	Nc 1.346‡ Na 1.348 Nb 1.350	no crystals	{011} poor {001}‡?
Pyrochlore framework	Ralstonite	$\text{Na}_x(\text{Al}_{2-x}\text{Mg}_x)$ (F, OH) <sub>6</sub> · H <sub>2</sub> O $\text{AlF}_3$	$Fd3m$	Isotropic	Octahedral	{111} imperfect
Framework			$R32$	pos. uniax. B. low	Pseudocubic Rhombohedrons	—

\*  $X = b$ ,  $Z \wedge c = -44^\circ$ .

† The Donnay-Harker rules would require {211} and {110} as dominant forms.

‡ Optical orientation and cleavage from Ferguson (p.c. to Frondel, 4/27/48), but changed to conventional setting.



that some of the materials show properties to be expected from their structures but the data are entirely too fragmentary. This is in part due to the different techniques used by different investigators. For some materials complete structure determinations have been reported without a word about physical properties except the density. For other materials, including some of the minerals referred to a few moments ago, data on crystal habit, cleavage, density and optical properties may be known though no attempt has been made to determine the crystal structure.

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