

AN INVESTIGATION OF THE CRYSTAL STRUCTURE
OF THOMSENOLITE $\text{NaCaAlF}_6 \cdot \text{H}_2\text{O}$

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CHAPTER I

THE ALUMINOFLUORIDE MINERALS

The natural aluminofluorides comprise twelve rare minerals, the commonest of which is cryolite, Na_3AlF_6 . Except for fluellite with composition $\text{AlF}_3 \cdot \text{H}_2\text{O}$, these minerals are aluminofluorides of Na, Ca, Li, and Sr, sometimes with Mg and OH substituting for Al and F respectively; several members contain H_2O . The twelve aluminofluoride minerals are set forth in Table I, p. 3. In addition to these natural aluminofluorides, some that do not occur in nature are also known.

Structural Classification. The crystal structures of about half a dozen natural and an equal number of synthetic aluminofluorides have been determined. In all of them there has been found a common structural unit, the AlF_6 octahedron--six F ions arranged in octahedral coordination around one Al. These octahedra pervade each structure, and Brosset (1942) has suggested that they apparently play the same role in the aluminofluorides as do the SiO_4 tetrahedra in the silicates. Thus, the AlF_6 octahedra may exist in a given structure as separate units, chains, sheets, or 3-dimensional frameworks, and the Al:F ratio in the chemical formula varies accordingly. Since no one had previously suggested a classification of the aluminofluorides based on the AlF_6 structural unit, R. B. Ferguson did so in April, 1948 in a private communication to Dr. Clifford Frondel of Harvard University. This was

sent to Dr. Frondel as a possible aid in his compilation of Volume II of the Seventh Edition of Dana's System of Mineralogy; this volume is to include the aluminofluorides. This communication came into the hands of Dr. Adolph Pabst of the University of California (Berkeley), at that time a guest in Dr. Frondel's laboratory, and Dr. Pabst used it as the basis for a complete summary, including the structural classification, of the aluminofluoride minerals (Pabst, 1950). Table I lists the aluminofluoride minerals as classified originally by Ferguson and including some of Pabst's modifications.

Occurrence. All the aluminofluoride minerals are rare and occur in only a few isolated deposits throughout the world. The most important locality is Ivigtut, Greenland, where cryolite is abundant and most of the other aluminofluorides including thomsenolite occur in small amount. Thomsenolite has also been described from Pike's Peak, Colorado; Yellowstone Park, Wyoming; Aragon, Spain; and the Ilmen Mountains in Russia. The thomsenolite crystals used for the present investigation are from Ivigtut.

Physical Description of Thomsenolite. For reasons which are given later, the aluminofluoride chosen for the present structural study was thomsenolite, one of the dimorphs of $\text{NaCaAlF}_6 \cdot \text{H}_2\text{O}$; the other is pachnolite. Thomsenolite occurs as an alteration product of cryolite as well-developed, colorless, white, or light amber crystals of monoclinic symmetry in vugs in the cryolite, and as massive white, gray,

TABLE I

THE ALUMINOFLUORIDE MINERALS AND THEIR STRUCTURAL CLASSIFICATION

Mineral	Composition	Formula Type	Structure Type
Cryolite	Na_3AlF_6		
Cryolithionite	$\text{Na}_3\text{Li}_3\text{Al}_2\text{F}_{12}$		
Elpasolite	K_2NaAlF_6	$(\text{AlF}_6)^{3-}$	Separate octahedra
Thomsenolite [*]	$\text{NaCaAlF}_6 \cdot \text{H}_2\text{O}$		
Pachnolite [*]	$\text{NaCaAlF}_6 \cdot \text{H}_2\text{O}$		
Gearsutite [*]	$\text{CaAl}(\text{F},\text{OH})_5 \cdot \text{H}_2\text{O}$	$(\text{AlF}_5)^{2-}$	Chains
Chiolite	$\text{Na}_5\text{Al}_3\text{F}_{14}$	$(\text{Al}_3\text{F}_{14})^{5-}$	Interrupted sheets
Prosopite [*]	$\text{CaAl}_2(\text{F},\text{OH})_8$	$(\text{AlF}_4)^-$	Sheets
Weberite	$\text{Na}_2\text{MgAlF}_7$	$(\text{MgAlF}_7)^{2-}$	Interrupted framework
Ralstonite	$\text{Na}_x(\text{Mg}_x\text{Al}_{2-x})(\text{F},\text{OH})_6 \cdot \text{H}_2\text{O}^{x-}$	$(\text{MgAlF}_6)^- \dagger$	Pyrochlore framework
Fluellite [*]	$\text{AlF}_3 \cdot \text{H}_2\text{O}$	AlF_3	Complete frameworks
Jarlite	Disproven as $\text{NaSr}_3\text{Al}_3\text{F}_{16}$; still unknown	Unknown	

^{*}Structures not published; classified according to the structure type which seems most likely from the Al:F ratio.

[†]This formula type results if $x = 1$ and all anions are F in the ralstonite formula; in the mineral $x \sim 3/8$.

or bluish coatings on the cryolite. The crystals are frequently coated with a brownish stain of iron oxide. In size they may be up to 4 - 5 mm. in thickness and 8 - 10 mm. in length. They are typically columnar with elongated $m(110)$, prominent $p(111)$, and usually with $c(001)$. Thomsenolite has a perfect (001) cleavage with a pearly lustre, a fair (110) cleavage, and a nearly square cross section ($\alpha = 90^\circ 21\frac{1}{2}'$). Its hardness is 2 and its specific gravity 3.0.

CHAPTER II

EXPERIMENTAL WORK

X-Ray Photographs and Unit Cell Data. Since thomsenolite is monoclinic with a comparatively large unit cell, an X-ray powder photograph is not sufficiently definitive for a structure determination, and single-crystal photographs must be taken. The prismatic habit and the perfect basal cleavage of the crystals make it easy to cleave off tabular fragments suitable for single-crystal X-ray photographs. Three cleavage fragments of this kind, all about 0.25 mm. or less in cross section, were obtained from the same crystal of thomsenolite and mounted for rotation about $a[100]$, $b[010]$, and $c[001]$. Rotation, zero-, first-, and second-layer Weissenberg photographs were taken about each of the three axes using Cu radiation, unfiltered for the rotation photographs and filtered through Ni foil for the Weissenbergs.

From these twelve photographs, values of the cell dimensions in Ångström units were obtained. These differ a small amount from those published by Ferguson (1946):

	<u>a</u>	<u>b</u>	<u>c</u>	β
Ferguson (1946):	5.58	5.51	16.13 A	$96^{\circ}27'$
Ferguson and Clark (this paper):	5.59	5.56	16.15 A	$96^{\circ}27'$

The cell dimensions are believed to be accurate within $\frac{1}{2}\%$, and the angle within $15'$. The second values of the cell dimensions were used for all

calculations in this investigation. As stated in Ferguson (1946), the cell dimensions combine with the specific gravity of ~ 3.0 to give the cell content of $4[\text{NaCaAlF}_6 \cdot \text{H}_2\text{O}]$, i.e. $Z = 4$.

The systematically missing reflections from the Weissenberg photographs agreed with those of Ferguson (1946) and confirmed the unique space-group as $P2_1/c (= C_{2h}^5)$.

Intensity Measurements. In order to measure the relative intensities of the spots on the Weissenberg photographs, an intensity scale consisting of a series of spots of known relative intensities was made in the following manner. A small cleavage rhomb of Iceland Spar about $\frac{1}{4}$ mm. in cross section (the same size as the thomsenolite crystals photographed) was mounted for rotation about a cleavage edge, and then adjusted on the X-ray goniometer so as to oscillate through about 5° on either side of the angle necessary to give the strong 200 (or $20\bar{2}2$) reflection of calcite. Since $d(200)$ of calcite is 3.029 kX, the glancing angle θ is $14^\circ 42'$ for CuK_α radiation. This crystal was oscillated in the X-ray beam for variable, controlled periods, to give a row of spots of known relative intensities on one film. In this way the intensity scale was made on which are 12 spots $\frac{1}{2}$ cm. apart whose relative intensities are 1, 2, 3, 4, 6, 8, 12, 16, 20, 24, 28, 32. By superimposing this scalar film on any one of the Weissenberg photographs of thomsenolite, and translating the scale until there is substantial

visual agreement between the intensity of a spot on it and one on the Weissenberg, a good objective value for the intensity of the latter may be read off. Thus a set of relative intensity values was compiled for all spots on each of the Weissenberg photographs of thomsenolite.

Since no attempt had been made, however, to standardize the photographic conditions, including exposure, of the different Weissenberg photographs, intensity relationships had to be established between these different photographs in order that all intensities could be reduced to the same standard. Because certain reflections appear on two or more Weissenbergs, such reflections can be used to work out an intensity factor which relates all spots on both films. Thus, the 001 reflections appear on both the zero layer-line Weissenberg about a and that about b, and the intensities of these reflections from both films will relate the intensities of all spots on both. By working out such factors between pairs of photographs with some reflections in common, a large set of intensities all related to the same standard was obtained. These intensities appear in Table II with the spacings calculated from the adopted cell dimensions.

$$a = 5.59, \quad b = 5.56, \quad c = 16.15 \text{ \AA}, \quad \beta = 96^{\circ}27'$$

using the formula

$$\frac{1}{d^2} = \frac{h^2}{a^2 \sin^2 \beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2 \sin^2 \beta} - \frac{2hl \cos \beta}{ac \sin^2 \beta}$$

which relates the spacing d to the monoclinic cell dimensions.

TABLE II
 THOMSENOLITE: RELATIVE INTENSITIES FROM WEISSENBERG PHOTOGRAPHS AND
 CALCULATED SPACINGS

hkl	I	d(A)	hkl	I	d(A)	hkl	I	d(A)
002	2	8.024	0.2.10	0	1.390	$\bar{2}04$	4	2.414
004	16	4.012	0.2.11	$\frac{1}{2}$	1.292	$\bar{2}06$	3	2.045
006	0	2.675	0.2.12	$\frac{1}{2}$	1.205	$\bar{2}08$	$7\frac{1}{2}$	1.721
008	42	2.006	0.2.13	1	1.128	$\bar{3}02$	3	1.850
0.0.10	3	1.605	0.2.14	$<\frac{1}{2}$	1.060	$\bar{3}04$	$2\frac{1}{2}$	1.758
0.0.12	1	1.337	031	1	1.841	$\bar{3}06$	1	1.609
0.0.14	$<\frac{1}{2}$	1.146	032	0	1.806	$\bar{4}02$	$3\frac{1}{2}$	1.395
0.0.16	0	1.003	033	0	1.751	404	0	1.361
0.0.18	$<\frac{1}{2}$	0.892	034	$<\frac{1}{2}$	1.682	406	1	1.293
0.0.20	$<\frac{1}{2}$	0.802	035	1	1.605	111	2	3.749
020	$4\frac{1}{2}$	2.780	036	0	1.523	112	5	3.423
040	$1\frac{1}{2}$	1.390	037	$<\frac{1}{2}$	1.441	113	$3\frac{1}{2}$	3.053
060	$2\frac{1}{2}$	0.927	038	$<\frac{1}{2}$	1.361	114	5	2.702
100	0	5.555	039	$\frac{1}{2}$	1.285	115	$<\frac{1}{2}$	2.394
200	21	2.777	041	$3\frac{1}{2}$	1.385	116	$2\frac{1}{2}$	2.134
300	$\frac{1}{2}$	1.852	042	0	1.370	121	$3\frac{1}{2}$	2.438
400	3	1.389	043	1	1.345	122	$<\frac{1}{2}$	2.342
110	16	3.930	044	$<\frac{1}{2}$	1.313	123	$\frac{1}{2}$	2.212

TABLE II (Continued)

hkl	I	d(A)	hkl	I	d(A)	hkl	I	d(A)
120	3	2.486	045	$< \frac{1}{2}$	1.276	124	$3\frac{1}{2}$	2.067
130	2	1.758	046	0	1.233	125	$< \frac{1}{2}$	1.919
140	$1\frac{1}{2}$	1.348	047	1	1.189	221	6	1.932
150	$< \frac{1}{2}$	1.090	048	0	1.143	222	$1\frac{1}{2}$	1.874
210	1	2.485	049	1	1.096	223	$2\frac{1}{2}$	1.799
220	17	1.965	102	2	4.452	224	$\frac{1}{2}$	1.712
230	$< \frac{1}{2}$	1.542	104	3	3.092	225	$\frac{1}{2}$	1.619
240	1	1.243	106	5	2.311	226	$\frac{1}{2}$	1.527
310	$1\frac{1}{2}$	1.757	108	5	1.822	$\bar{1}11$	4	3.889
320	$< \frac{1}{2}$	1.541	202	3	2.538	$\bar{1}12$	1	3.645
011	1	5.254	204	16	2.226	$\bar{1}13$	5	3.294
012	$< \frac{1}{2}$	4.570	206	6	1.827	$\bar{1}14$	17	2.926
013	1	3.855	302	$1\frac{1}{2}$	1.761	$\bar{1}15$	1	2.589
014	3	3.252	304	$\frac{1}{2}$	1.614	$\bar{1}16$	$< \frac{1}{2}$	2.298
015	1	2.780	306	0	1.448	$\bar{1}21$	$1\frac{1}{2}$	2.476
016	0	2.410	308	$\frac{1}{2}$	1.290	$\bar{1}22$	1	2.409
017	1	2.119	3.0.10	6	1.150	$\bar{1}23$	10	2.299
018	7	1.887	402	$2\frac{1}{2}$	1.343	$\bar{1}24$	3	2.162
019	1	1.698	404	0	1.269	$\bar{1}25$	12	2.015
0.1.10	1	1.542	406	$\frac{1}{2}$	1.179	$\bar{1}26$	$< \frac{1}{2}$	1.868

TABLE II (Continued)

hkl	I	d(A)	hkl	I	d(A)	hkl	I	d(A)
0.1.11	1	1.411	502	$1\frac{1}{2}$	1.084	$\bar{2}11$	4	2.494
0.1.12	2	1.300	602	1	0.908	$\bar{2}12$	3	2.444
021	$5\frac{1}{2}$	2.739	$\bar{1}02$	0	4.828	$\bar{2}13$	$1\frac{1}{2}$	2.345
022	0	2.627	$\bar{1}04$	3	3.441	$\bar{2}14$	1	2.214
023	$<\frac{1}{2}$	2.467	$\bar{1}06$	0	2.523	$\bar{2}15$	1	2.068
024	$4\frac{1}{2}$	2.285	$\bar{1}08$	21	1.958	$\bar{2}16$	4	1.919
025	10	2.101	$\bar{1}0.10$	0	1.590	$\bar{2}21$	20	1.969
026	2	1.927	$\bar{1}0.12$	7	1.335	$\bar{2}22$	4	1.944
027	3	1.769	$\bar{1}0.14$	0	1.148	$\bar{2}23$	$<\frac{1}{2}$	1.894
028	$<\frac{1}{2}$	1.626	$\bar{1}0.16$	6	1.007	$\bar{2}24$	2	1.823
029	1	1.501	$\bar{2}02$	0	2.721	$\bar{2}25$	$1\frac{1}{2}$	1.738

Intensity Calculations. Once a reasonable structure of the crystal has been postulated, a set of intensities must be calculated from the proposed parameters (which define the atomic positions) and compared with the observed intensities. It is only when there is substantial agreement between the relative intensities calculated for a proposed structure and those observed for a large number of reflections that the proposed structure may be considered the correct one.

Each spot on a single-crystal X-ray diffraction photograph may be regarded as the "reflection" of the X-ray beam by one set of parallel lattice planes. The intensity of each reflection is determined by several factors: the diffracting powers of the atoms, the relative positions of the atoms in space (the "structure factor"), the Bragg or glancing angle at which reflection occurs, the number of crystallographically equivalent planes contributing towards the total intensity of the spot (the "multiplicity"), the amplitude of thermal vibration of each atom (allowed for by a temperature factor), and the absorption of the X-rays by the specimen. For zero-layer Weissenberg reflections the above mentioned factors are so related that the following equation holds:

$$I \propto F^2 p \left(\frac{1 + \cos^2 2\theta}{\sin 2\theta} \right) T A$$

where I = intensity of reflection,

F = the structure factor,

p = the multiplicity,

θ = the glancing angle,

T = the temperature factor, and

A = the absorption factor.

The multiplicity p is the number of equivalent lattice planes contributing to any one reflection and it usually differs for different types of planes in powder and rotation photographs. The nature of Weissenberg photographs, however, is such that any spot on the film results from the reflection from one set of lattice planes only. Thus the multiplicity need not be considered (or it is always unity) when Weissenberg photographs are used.

The expression $\frac{1 + \cos^2 2\theta}{\sin 2\theta}$, known as the angle factor, takes account of i) the increasing polarization of the X-rays with increasing glancing angle, the intensity of any reflection being reduced by this effect to the fraction $\frac{1 + \cos^2 2\theta}{2}$; and ii) the relative time any crystal plane spends within the narrow angular range over which reflection occurs. This latter angle factor, known as the Lorentz factor, is proportional to $\frac{1}{\sin 2\theta}$. In the ITDCS (1935), p. 567, is a table giving values of the above angular expression for different values of θ .

The structure factor F takes account of i) the diffracting power and ii) the position of each atom or ion. The diffracting power f is determined by the number of electrons surrounding the nucleus, i.e. by

the atomic number of the element, and it varies with the interplanar spacing in such a way that f is a function of $\frac{1}{2}d$ ($= \sin\theta/\lambda$). A table of the diffracting powers of all atoms for a range of values of $\sin\theta/\lambda$ is given in the ITDCS (1935), p. 571. It is convenient to plot graphs of f against $\sin\theta/\lambda$ for all atoms or ions present in a structure under investigation in order to be able to read off accurate values of f for any value of $\sin\theta/\lambda$. Such graphs were drawn up during this investigation for Na^+ , Ca^{2+} , Al^{3+} , F^- , and O^{2-} (in place of H_2O). These are reproduced in Figure 1, p. 14.

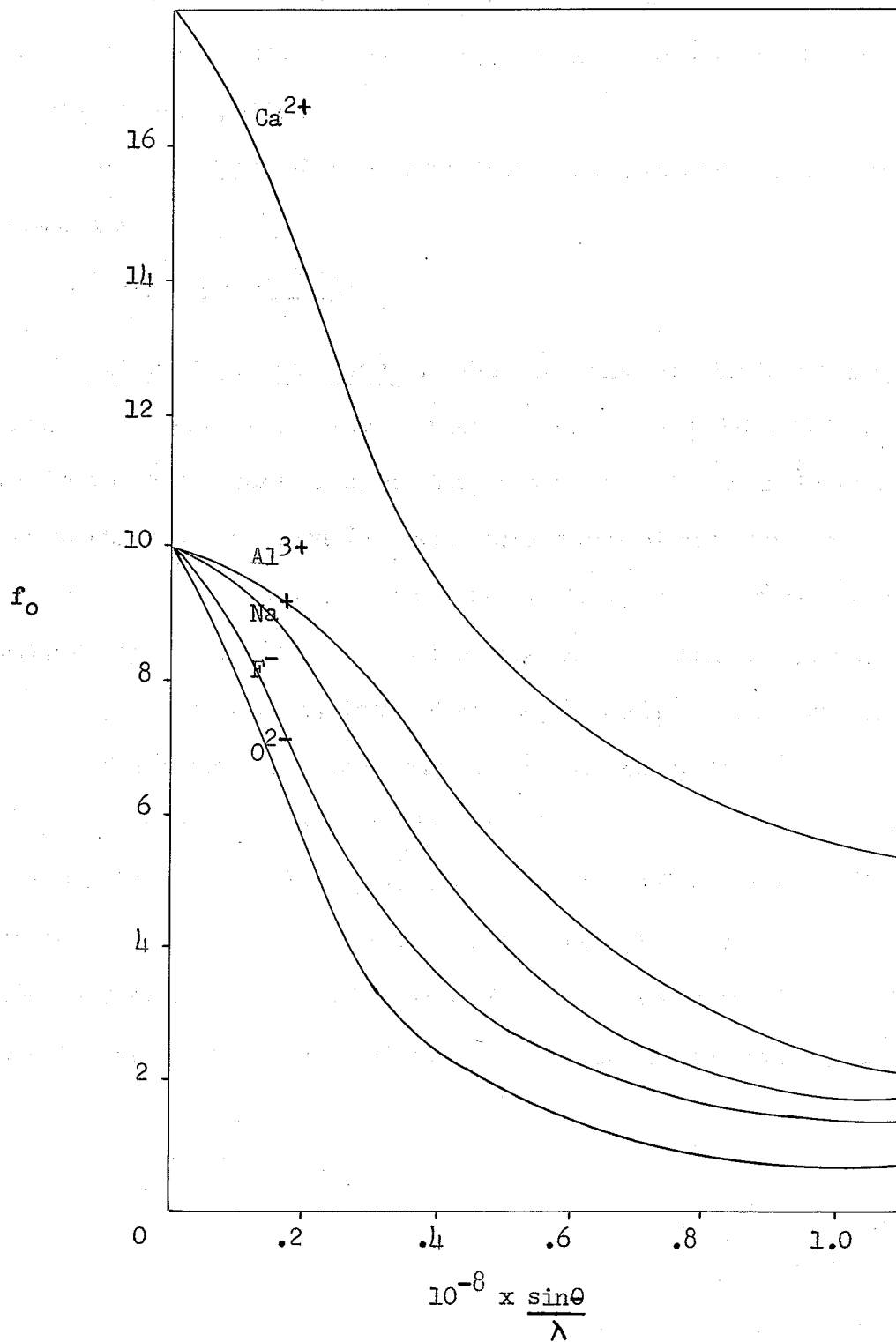
Regarding the position of each atom, the ITDCS (1935) gives the structure factor for each space group; this is an expression for the contribution to the structure amplitude of all structurally equivalent atoms in the general position. This expression includes the diffracting power f of the atom whose contribution is being calculated. In the case of the space group $\text{P}2_1/\text{c}$, the intensity contribution to the plane hkl of four structurally equivalent atoms of diffracting power f and in a general position with parameters $x y z$ is, for the origin at a symmetry centre,

$$4f \cos 2\pi \left(hx + lz + \frac{k+1}{4} \right) \cos 2\pi \left(ky - \frac{k+1}{4} \right).$$

The total structure amplitude for any plane hkl is of course the sum of the structure amplitudes of all atoms, that is

$$F_{hkl} = \sum 4f \cos 2\pi \left(hx + lz + \frac{k+1}{4} \right) \cos 2\pi \left(ky - \frac{k+1}{4} \right).$$

FIGURE 1

GRAPH OF DIFFRACTING POWERS (f_o)

The temperature and the absorption are difficult to correct for, and their respective factors, T and A, tend to cancel each other. For these reasons and because neither effect is considered serious in the case of thomsenolite which has a moderate melting point (probably about 400° C) and is weakly absorbing, both factors were neglected in the present investigation.

In this study of thomsenolite then, the intensity relationship was simplified to

$$I \propto F^2 \frac{(1 + \cos^2 2\theta)}{\sin 2\theta}.$$

Structure Amplitude Charts. The structure amplitude of any reflection from one of the three principal zones, hk0, h0l, 0kl, depends upon only two parameters of each atom, and thus it is possible to draw up charts which can be used for ready evaluation of the structure amplitude of particular planes in a given zone. These charts were suggested by Bragg & Lipson (1936) and are also described in Bunn (1945, pp. 264 - 271). In the present case, that of space-group P2₁/c, the structure amplitude of all atoms in, for example, the h0l zone, is

$$4f \cos 2\pi \left(hx + \frac{1}{4} \right) \cos 2\pi \left(lz + \frac{1}{4} \right),$$

and for particular h0l planes, i.e. for specific values of h and l, this expression may be evaluated for variable values of x and z and the results plotted to form a chart. Such charts which are like those illustrated in Bunn (1945, figures 168, 169) were drawn, during the investigation

of thomsenolite, for all the simpler combinations of permissible indices in each of the three principal zones. About 15 charts were made and, because of the interchangeability of indices, these 15 charts enabled the reading off of the structure factors for about 35 different lattice planes. These valuable charts were of great assistance in evaluating the structure amplitudes of these 35 planes in thomsenolite.

Heating Experiment on the Dehydration of Thomsenolite. In his textbook Structural Inorganic Chemistry, Wells (1945, p. 364) briefly summarizes the different effects of dehydration on different hydrated compounds:

"We see therefore that there are different effects on dehydration, from the complete breakdown of the crystal in the case of a salt hydrate through the intermediate examples such as clay minerals and certain proteins, where removal of water merely brings the structural units closer together with continuous changes in one or more of the cell dimensions, to the 'framework' crystal which may be reversibly hydrated without appreciable alteration of the structure of the anhydrous crystal."

Although the authors strongly suspected that thomsenolite was simply a salt hydrate, the heating experiment was carried out to check this idea, to determine the dehydration temperature and, if possible, to identify the dehydration product(s).

Two samples of cleavage fragments of thomsenolite, one weighing about $1/3$ gm., the other about $2/3$ gm., were independently heated in a controlled electric furnace equipped with a mercury thermometer and a simple apparatus for condensing and catching any water vapour given

off. The two samples were heated in stages and were held at the final stage until the residues were of constant weight. The experiment resulted in the following observations and conclusions:

- (1) Clear crystals of thomsenolite are apparently little affected by temperatures below about 300°C.
- (2) At that temperature, 300°C, the crystals were heated to a constant weight in about 9 hours with an accompanying breakdown of the structure.
- (3) The loss in weight after 9 hours' heating at 300°C was 8.04% although the water collected constituted only 6.34% of the original sample. Part of this difference is likely due to experimental error in the water determination. The theoretical water content of thomsenolite is 8.11%. The condensate gave an acid reaction with litmus and, although it gave a negative reaction for F with CaCl_2 solution, it did etch the glass tubing indicating that some F was present in the water.
- (4) The previously clear colourless cleavage fragments became, at 300°C, milky and cryptocrystalline. Attempts to take single-crystal X-ray pictures of some of the fragments failed but a powder picture was taken and the observed data for it appear in Table III. A microscopic examination of the fragments confirmed their cryptocrystalline character, and yielded the refractive index $n \sim 1.354$.
- (5) The X-ray powder picture referred to in (4) is different from that of any known aluminofluoride mineral or combination of minerals, and the refractive index 1.354 does not agree with any known aluminofluoride.

Thus it is concluded that the disintegration product of thomsenolite heated to 300°C for 9 hours is no existing aluminofluoride. The evidence in (3) suggests that the residue may have the composition NaCaAlF_6 but this is by no means convincing. The residue was not analysed chemically.

The principal contribution of the heating experiment to the immediate problem was to prove that the water forms an essential feature of the structure, i.e. thomsenolite is a true salt hydrate and does not "hydro-structurally" resemble either the clay minerals or the zeolites.

TABLE III

OBSERVED X-RAY POWDER DATA OF RESIDUE OF THOMSENOLITE HEATED TO 300°C
FOR 9 HOURS

I	θ (Cu)	d	I	θ (Cu)	d
2	9.95°	4.45 A	3	23.85°	1.901 A
4	10.6	4.18	4	24.6	1.847
$\frac{1}{2}$	11.45	3.87	3	25.2	1.805
10	12.1	3.67	$\frac{1}{2}$	26.15	1.744
9	13.2	3.37	$\frac{1}{2}$	26.95	1.696
$\frac{1}{2}$	15.25	2.92	1	27.55	1.662
5	16.05	2.78	1	28.6	1.606
$\frac{1}{2}$	17.95	2.49	2	30.0	1.537
$\frac{1}{2}$	18.95	2.37	1	31.2	1.484
1	19.6	2.29	$\frac{1}{2}$	33.25	1.402
$\frac{1}{2}$	20.8	2.16	$\frac{1}{2}$	34.25	1.366
1	21.6	2.09	$\frac{1}{2}$	36.3	1.299
1	22.15	2.04	$\frac{1}{2}$	38.2	1.243
4	23.2	1.951	$\frac{1}{2}$	44.2	1.103

CHAPTER III

CONSIDERATIONS IN POSTULATING A STRUCTURE OF THOMSENOLITE

There are several reasons why the authors elected to investigate the structure of thomsenolite rather than that of one of the other aluminofluorides whose structures are also unknown: thomsenolite shows good crystals suitable for single-crystal work; it has a unique space-group; and perhaps of most importance thomsenolite is closely related to cryolite.

Similarity of Thomsenolite to Cryolite. Thomsenolite which is an alteration product of cryolite, whose structure is known, resembles it in at least four respects: chemical formula, morphology, cell dimensions, and space-group. The formula of cryolite is Na_3AlF_6 , and of thomsenolite $\text{NaCaAlF}_6 \cdot \text{H}_2\text{O}$. If two Na^+ ions of cryolite are replaced by one Ca^{2+} and one H_2O , the formula of thomsenolite is obtained. Morphologically both minerals are monoclinic but pseudocubic through the development of forms (001) and (110). Parallel to these planes cryolite has poor cleavage (or partings) and thomsenolite one perfect cleavage (001) and one poor cleavage (110). The cell dimensions and space-groups of the two minerals are closely related:

Cryolite
(Náray-Szabó & Sasvári, 1938)

a = 5.46 A

Thomsenolite
(this paper)

b = 5.56 A

<u>Cryolite</u>	<u>Thomsenolite</u>
$b = 5.61 \text{ \AA}$	$a = 5.59 \text{ \AA}$
$c = 7.80$	$\frac{1}{2}c = 8.08$
$\beta = 90^{\circ}11'$	$\beta = 96^{\circ}27'$
Sp. gr. $P2_1/n$	Sp. gr. $P2_1/c$
$Z = 2$	$Z = 4.$

These similarities suggested strongly to the authors that the crystal structure of thomsenolite must be related in some fairly simple way to that of cryolite.

Ionic Size and Coordination. The effective ionic radii of all the commoner ions have, through numerous structure determinations, been well established, and lists of such radii are available in several works. One such list of ionic radii proposed by Pauling appears in Wells (1945, p. 93) where the following values in Ångström units are given for the ions in thomsenolite:

$\text{Na}^+ 0.95$	$\text{Ca}^{2+} 0.99$
$\text{Al}^{3+} 0.50$	$\text{F}^- 1.36$

These values were assumed during this investigation of the structure of thomsenolite. The water molecules present a special problem which is described below.

The significance of the ionic radii is, of course, that sufficient space must be allotted each ion in any structure proposed.

Furthermore, in ionic crystals such as thomsenolite, the relative size

of adjacent anions and cations usually determines the coordination of the larger anions (F^- in thomsenolite) around the smaller metallic cations (Na^+ , Ca^{2+} , and Al^{3+} in thomsenolite). The usual coordination numbers of the common anions (O^{2-} , OH^- , F^-) around the common cations (including the three in thomsenolite) have, like ionic radii, been well established by numerous structure determinations. Thus, in thomsenolite we would expect all the three metallic cations Na^+ , Ca^{2+} , and Al^{3+} to be octahedrally coordinated by F^- . Since Al^{3+} has the highest charge and the smallest size of the three cations, its octahedral coordination may be expected to be the most regular and the best-defined. In fact, as mentioned in Chapter I, the octahedral coordination of F^- around Al^{3+} is so persistent in the aluminofluorides that the AlF_6 octahedra may be regarded as structural units suitable for both describing and classifying those structures. Experience has shown that the octahedral coordination of F^- around Ca^{2+} is not as regular as in the case of Al^{3+} and this was kept in mind when proposing a structure for thomsenolite.

Possible Arrangements of the AlF_6 Octahedra. To determine the possible octahedral arrangements for thomsenolite, it is helpful to look briefly at the structure of cryolite which is described and illustrated in the original paper by Náráy-Szabó & Sasvári (1938), and in the Strukturbericht (1938). The unit cell of cryolite has the centre of one AlF_6 octahedral group (i.e. one Al ion) at each corner and another at the body centre; the octahedra are just slightly distorted.

The orientation of each corner octahedron is such that its a_3 axis is roughly vertical, and its a_1 and a_2 axes are roughly at 45° to the a and b axes of the cell, i.e. the horizontal edges of each octahedron are roughly parallel to the horizontal axes of the crystal. The departure from true parallelism of these quasi-parallel directions may be conveniently expressed in terms of the downward tilt of the equatorial plane of an AlF_6 octahedron, a tilt which may be either positive or negative along a and/or b .

In cryolite, then, at each corner of the cell is one AlF_6 octahedron, and it is tilted down slightly in both the positive a and the positive b directions; at the body-centre is the only other octahedron, tilting the same amounts along positive a , but along negative b since, as the space-group symmetry $P2_1/n$ demands, this body-centred octahedron is related to the corner octahedra by an n -glide across (010) and by a 2_1 screw around $[010]$. The relationship of the a and b cell dimensions to the size and orientation of the four AlF_6 octahedra at the lower cell corners is such that there is just space for one Na at the base-centre of the cell. The other Na ions which are not of immediate concern are approximately in the vertical edges and faces of the cell.

Because of the near-equivalence of the a and b dimensions in thomsenolite with the b and a dimensions in cryolite, it was assumed that the arrangement of the four octahedra at the basal corners of the unit cell is approximately the same in both crystals. The ion at the

base-centre which is Na in cryolite may be either Na or Ca in thomsenolite since these two ions have practically the same radii. In anticipation of what is to follow it may be said that because the space-group of thomsenolite includes a c-glide plane, the authors envisaged for thomsenolite a unit cell resembling two unit cells of cryolite, one stacked upon the other; two such upper and lower halves of the thomsenolite cell would be related to each other by the c-glide plane.

Starting with the assumption that the four lower corners of the unit cell of thomsenolite are occupied by AlF_6 octahedra as in cryolite, and assuming for the moment a small tilt along positive b only, the next step is to note the various ways in which the space-group symmetry elements ($2_1/c$) can reproduce these octahedra. Considering first the possible positions of the 2_1 screw axes and their effects, it can be shown that for an origin at the centre of a basal octahedron (i.e. at an Al ion), only the six following positions of the screw axis are reasonable:

- | | | |
|--------------------|----------------|----------------------|
| (i) 0 y 0 | (ii) $1/4$ y 0 | (iii) 0 y $1/8$ |
| (iv) $1/4$ y $1/8$ | (v) 0 y $1/4$ | (vi) $1/4$ y $1/4$. |

If a screw axis were in position (i), 0 y 0, it would reproduce another octahedron at the middle of the b edge ($0 \frac{1}{2}$ 0) where there is not sufficient space for it. Consequently this position for a screw axis is impossible. Similar reasoning rules out positions (ii), (v), and (vi)

as well as (i), all of which need not be considered further. The only two possible positions are (iii) and (iv). If a screw axis is in position (iii), $0 y \frac{1}{8}$, it would reproduce an octahedron at $0 \frac{1}{2} \frac{1}{4}$, the centre of the lower half of the A face of the cell (Figure 2a). It is because there is space there for an octahedron that position (iii) is one of the possibilities. If a screw axis is in position (iv), $\frac{1}{4} y \frac{1}{8}$, it would reproduce an octahedron at $\frac{1}{2} \frac{1}{2} \frac{1}{4}$, the body-centre of the lower half-cell (Figure 2b). Again, it is because there is sufficient space for this octahedron that position (iv) is another (the other) possibility.

Considering now the possible positions of the c-glide plane and their effects, again it may be shown that there is a limited number of reasonable positions, only two in this case, $x 0 z$ and $x \frac{1}{4} z$. Of the two of these, only the first will combine with the two possible screw axis positions to give spatially permissible arrangements of the octahedra. The existence of the c-glide plane at $x 0 z$ simply repeats the upper half of the unit cell as the mirror image of the lower. For this reason, only the lower halves of the unit cells are shown in Figure 2.

To summarize this section, if one assumes for thomsenolite four AlF_6 octahedra at the four lower corners of the cell as in cryolite, space and symmetry considerations reduce to two the number of possible positions of the two space-group symmetry elements 2_1 and c , and hence

only two arrangements of the octahedra are likewise possible. With the origin at the centre of one of the basal octahedra, the two possible symmetry positions are:

(1) 2_1 in $0\ y\ 1/8$; c in $x\ 0\ z$ (Figure 2a)

(2) 2_1 in $\frac{1}{4}\ y\ 1/8$; c in $x\ 0\ z$ (Figure 2b).

As Figure 2 shows, the second of these combinations rather than the first gives rise to an arrangement of the octahedra which resembles that of cryolite, and this is the principal reason the authors chose the second arrangement for more detailed analysis.

Choice of Origins in Proposed Structures. In the previous section, the origin was arbitrarily located, for convenience, at the centre of one of the basal octahedra, and the screw axes and glide planes have been located relative to this origin. However, by convention (as in the ITDCS (1935) and for convenience in calculating structure amplitudes as explained in Chapter II, the origin is chosen at a centre of symmetry if the space-group has one, as has $P2_1/c$. The positions of the symmetry centres are of course determined by the positions in space of the other symmetry elements and are fixed in relation to them. For the two possible arrangements of the octahedra arrived at for thomsenolite in the last section, the authors' origins at an octahedral centre are not symmetry centres in the space-group. Transformations from the authors' origins to the conventional are as follows:

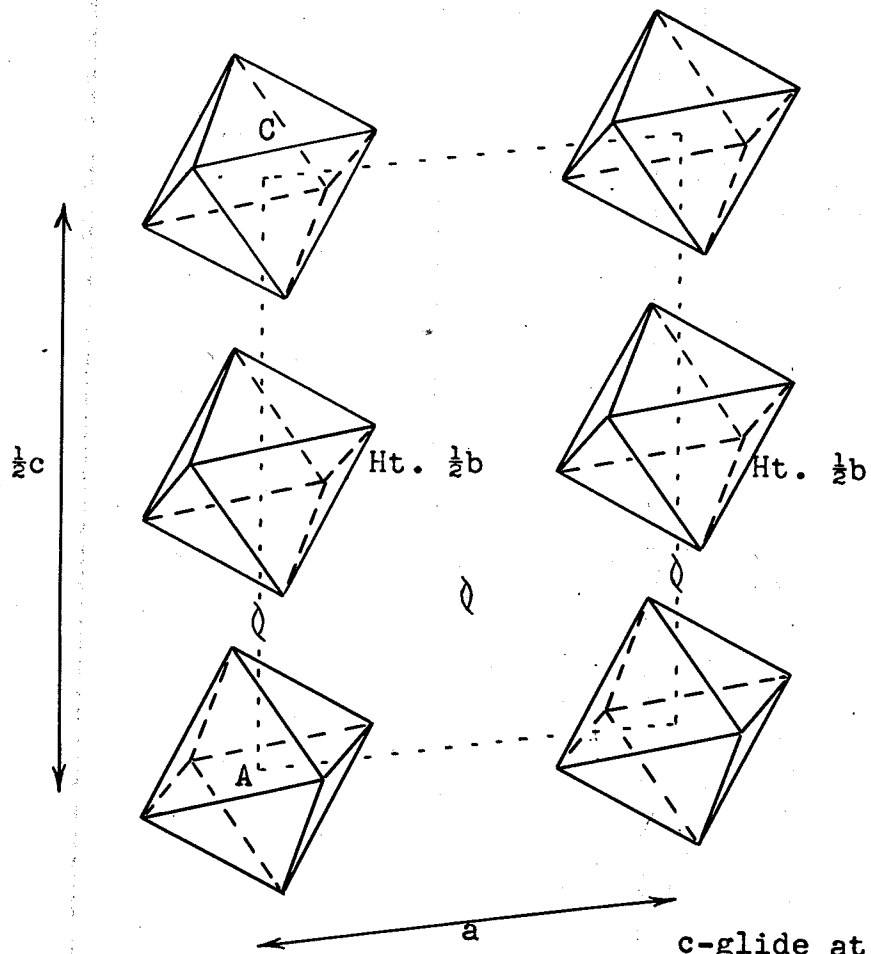
Position (iii) (1st octahedral arrangement): $x, y + \frac{1}{4}, z + 1/8$

Position (iv) (2nd octahedral arrangement): $x + \frac{1}{4}, y + \frac{1}{4}, z + 1/8$.

FIGURE 2
 THE TWO POSSIBLE ARRANGEMENTS OF THE AlF_6 OCTAHEDRA IN THE THOMSENCLITE
 LOWER HALF-CELL -- PROJECTED ON (010)

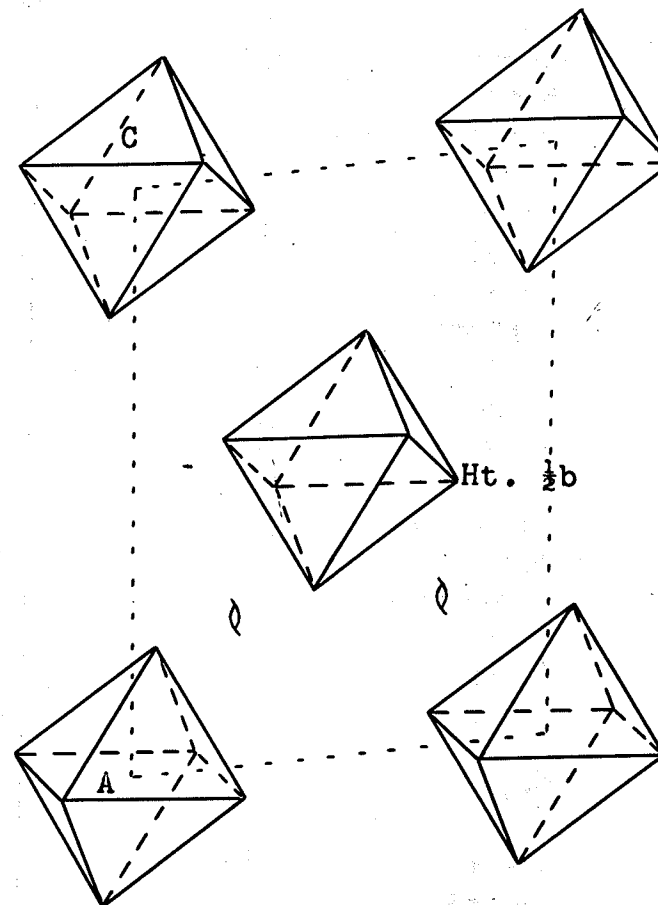
First Octahedral Arrangement

Figure 2a



Second Octahedral Arrangement

Figure 2b



c-glide at Ht. 0b and $\frac{1}{2}b$

Coordination and Size of Water Molecules. In the discussion of ionic size and coordination on p. 21, it was pointed out that the water molecules present a special problem. The role of water in the structures of salt hydrates is discussed by Wells (1945) on pages 364 to 381, and another subject which seems pertinent to the present problem, the hydrogen bond, is discussed in the same text on pages 249-266. The relevant conclusions from these discussions are first, that in many crystalline hydrates the H_2O molecule behaves as if there were a tetrahedral distribution of two positive and two negative charges, and thus the molecule is attached on the one side to two anions and on the other to two univalent cations or to one divalent cation. The second conclusion is that in salt hydrates where the anion is strongly electronegative (as is F^-), H bonds are usually formed between each water molecule and its two adjacent anions. These H bonds are characterized by abnormally short interatomic distances. In the later structures which were proposed for thomsenolite, structural features which incorporated these ideas were assumed. The only neighbouring cations possible for the water molecules in thomsenolite are Na^+ and Ca^{2+} . No reasonable structure could be found which would permit two Na^+ ions to be in contact with one H_2O and so the equally reasonable situation was assumed in which one Ca^{2+} is in contact with each H_2O . Projections of the proposed structures and cork ball models of them showed that the whole structure is too close-packed to permit only two

F^- ions to closely approach each H_2O , and for this reason in the proposed structures each H_2O has several F^- neighbours (as well as one Ca^{2+}).

The lengths of the H bonds between various electronegative ions have been established by previous structure determinations, but this is not the case with the presumed O-H-F bond in thomsenolite since this aspect of a hydrated aluminofluoride crystal has not previously been studied. The following interatomic distances through H bonds are averages taken from the values summarized in Wells (1945, p. 252):

<u>bond</u>	<u>length</u>
F-H-F	2.29 A
O-H-O	2.67 A

The arithmetic mean of these two averages is probably reasonably close to the O-H-F bond length, and so approximately the following bond length was assumed in this present work:

O-H-F	2.48 A
-------	--------

For an assumed F^- radius of 1.36 A, this means the assumed effective radius of H_2O through H is 1.12 A. The effective radius of H_2O not through H has been established as about 1.38 A.

Possible Positions of H_2O , Na, and Ca Relative to AlF_6 Octahedra.

It has been pointed out that, of the two possible arrangements of the octahedra, the second is more similar to the cryolite structure than is the first because both the second and the cryolite structures have an

octahedron centred at the body-centre (of the half-cells of thomsenolite). For this reason, and because the 3 Na's in the cryolite formula may be said to have their equivalents in the Na, Ca, and H₂O in the thomsenolite formula, it is useful to consider how a thomsenolite structure might be derived from the cryolite by suitable replacements of Na ions in the latter. For this discussion only the lower half-cell of thomsenolite will be considered, and the assumption will be made, even though it cannot be strictly accurate, that the octahedral arrangement in the lower half-cell of thomsenolite is the same as that in the (full) unit cell of cryolite. All parameters refer to an origin at the centre of a corner octahedron--the conventional origin in cryolite.

Considering now the possible positions for H₂O in the cryolite structure, the base-centre ($\frac{1}{2} \frac{1}{2} 0$) occupied by the smaller Na is virtually ruled out because the space at that site is not large enough to accommodate H₂O. In both the cryolite and the proposed similar thomsenolite cells, the positions halfway along the vertical cell edges, $00\frac{1}{2}$, are structurally equivalent to the base-centre. There is sufficient space however, for the H₂O molecules to occupy the other Na sites in cryolite, approximately $0 \frac{1}{2} \frac{1}{4}$ (in the lower part of the A and B faces), as well as the approximate positions in the corresponding upper parts of these faces, $0 \frac{1}{2} \frac{3}{4}$ (equivalent to $0 \frac{1}{2} \frac{1}{4}$ in cryolite but not in thomsenolite). The only other principal positions in cryolite which are apparently sufficiently large to accommodate H₂O are the A and B

face centres, but these positions are ruled out because they would be repeated by the symmetry at a horizontal cell edge where there is not sufficient space for them. Thus, the only approximate positions large enough to accommodate H₂O in a cryolite-like octahedral arrangement are $0 \frac{1}{2} \frac{1}{4}$ and $0 \frac{1}{2} \frac{3}{4}$ and their structurally equivalent positions, $\frac{1}{2} 0 \frac{1}{4}$ and $\frac{1}{2} 0 \frac{3}{4}$.

By similar reasoning one can reduce to the following and their equivalents all the approximate sites possible for the equal-sized Na and Ca ions in a cryolite-like arrangement: $\frac{1}{2} \frac{1}{2} 0$ (base-centre): $0 \frac{1}{2} \frac{1}{4}$, and $0 \frac{1}{2} \frac{3}{4}$ (the two possible water sites). Space considerations may make $0 \frac{1}{2} 0$ and $\frac{1}{2} 0 0$ (and the equivalent A and B face-centres) possibilities as well, but these are doubtful.

Which of these various possible sites is most likely occupied by which atom was decided upon by the authors on the basis of the larger size of H₂O; on intensity calculations, especially for interchanges of the differently diffracting Na and Ca; and later in the study, on the fact that one Ca and one H₂O are likely in contact.

Chapter Summary. In the previous sections of this chapter, two of the primary considerations in postulating a structure for thomsenolite have been described in detail. These are summarized below and two other considerations are described in brief.

(i) Arrangements of the AlF₆ octahedra. By assuming that regular or nearly regular AlF₆ octahedra exist as separate entities in

the structure, and by considering how the space-group symmetry can reproduce these in a unit cell the size of that of thomsenolite, we reduced to two the number of possible arrangements of these octahedra. (Figures 2a, 2b, p. 27). The second of these is more like cryolite than the first.

(ii) The possible positions of H₂O, Na, and Ca. Because of their relatively large size, the H₂O molecules can only occupy approximately $0 \frac{1}{2} \frac{1}{4}$ or $0 \frac{1}{2} \frac{3}{4}$ (and equivalent sites) in the cryolite-like octahedral arrangement. The smaller Na and Ca (of about equal size) may occupy the two possible water positions or $\frac{1}{2} \frac{1}{2} 0$, or perhaps $0 \frac{1}{2} 0$ or $\frac{1}{2} 0 0$. To provide H₂O with a likely environment, in the later detailed arrangements one Ca was brought in contact with H₂O.

(iii) The downward tilt of the AlF₆ octahedra along a and b. The similarity in cell dimensions of thomsenolite with cryolite suggests that the tilts in thomsenolite are about the same amounts as in cryolite, but the sense of the tilts (down positive or negative a and b) can be established only by intensity calculations. The direction of tilt is important because it determines the manner in which each Ca ion can "leave" its approximate special site to come in contact with H₂O.

(iv) Departure of AlF₆ octahedron from the origin. About the mid-point of the investigation, intensity calculations showed that the AlF₆ octahedron centred at the authors' origin in the above discussions cannot be exactly there but must be slightly removed parallel to

the c axis. The amount of this slight departure of the z parameters of the A1 near the authors' origin and its surrounding F's was another variable of which account had to be taken.

CHAPTER IV

POSTULATED STRUCTURES AND INTENSITY COMPARISONS

Procedure. The method employed in this structure determination, as previously indicated, was that of trial and error. The atoms were moved about independently until the best possible agreement was obtained between the calculated and observed intensities of X-ray reflections from a wide range of planes. The proof of the correctness of the final structure is this agreement.

The transformation of origin from the authors' to the conventional position mentioned in Chapter III has the effect of placing all the atoms in the 4-fold general position, $x y z$. In $P2_1/c$ the other three positions of $x y z$ are $\bar{x} \bar{y} \bar{z}$, $\bar{x} \frac{1}{2} + y \frac{1}{2} - z$, and $x \frac{1}{2} - y \frac{1}{2} + z$. For each proposed structure parameters were determined for each atom, i.e. the position of one atom in each non-equivalent position was expressed by three parameters, $x y z$, which are its coordinates with respect to the unit cell edges, a, b , and c , expressed as fractions of the lengths of these edges. From these parameters F^2 values were calculated in the manner discussed in Chapter II. These calculated F^2 values were then compared to observed F^2 values. The observed F^2 values were arrived at by inserting the observed intensities of Table II, p. 8-10, for "I" in the expression given on p. 15, and extracting F^2 . Such values are directly comparable to the calculated F^2 values.

This present chapter will deal with the different structures which were considered as possible and probable structures for thomsenolite.

In the last chapter two possible symmetry positions were described which led to two arrangements of the octahedra. These arrangements along with the different positions of the Na, Ca, and H₂O will now be discussed in detail.

First Octahedral Arrangement. The first arrangement, resulting from the positions 2_1 in $0 y \frac{1}{8}$ and c in $x 0 z$, will be dealt with initially. As shown in Figure 2a, p. 27, the octahedra occur at the four lower corners of the cell, at the middle of the lower half of the A face, and half way up the vertical cell edges; the upper half of the cell simply repeats the lower in mirror image. The corner octahedra tilt down positive a and down positive b.

Position 1. Various placements of the Na and Ca ions and the H₂O molecules were attempted, the first having the Na ions one-half way along the b edges and one-quarter way up the c edges; the Ca ions in the middle of the B face at height one-quarter and at the base centre; and the H₂O molecules in the middle of the B face at height $\frac{1}{8}$. The parameters, referred to the conventional origin, for this position 1 are:

	<u>x</u>	<u>y</u>	<u>z</u>
4 Na in	0.00	0.25	0.375
4 Ca in	0.50	0.25	0.375

	<u>x</u>	<u>y</u>	<u>z</u>
4 Al in	0.00	0.25	0.125
4 H ₂ O in	0.50	0.25	0.25
4 F _I in	0.060	0.314	0.231
4 F _{II} in	0.161	-0.034	0.139
4 F _{III} in	0.281	0.397	0.096
4 F _{IV} in	-0.060	0.186	0.019
4 F _V in	-0.161	0.534	0.111
4 F _{VI} in	-0.281	0.103	0.154

Table IV gives a comparison of the calculated F^2 values using the above parameters and the observed F^2 . The arbitrarily chosen I scale of table II is such that the observed and calculated F^2 values are approximately comparable when the observed values have been multiplied by 100. Obviously the agreement between the two is poor. For example, the $\bar{1}08$ reflection, which should be very strong, calculates to the low value of 1.04.

Position 2. A second position was examined in which the Ca ions were moved to the middle of the B face at height $3/8$. The new Ca parameters became

$$4 \text{ Ca in } \quad 0.50 \quad 0.25 \quad 0.50.$$

All other parameters remained unchanged. The results of the calculations involving this modification are shown in table V. Once again the agreement between observed and calculated F^2 values is poor. The positions

of the Na and Ca ions were interchanged in an effort to improve the agreement but with little success as the last column of the table indicates.

Position 3. The next step was the interchange of the positions of the Ca ions and the H₂O molecules, with the remainder as in position 1.

The Ca and H₂O parameters became

4 Ca in	0.50	0.25	0.25
4 H ₂ O in	0.50	0.25	0.50.

Table VI lists the calculated F^2 values which again are lacking in good agreement with the observed values. In addition the table shows F^2 values for the interchange of the Na and Ca ions in this last position.

Finally, as no satisfactory agreement could be reached between the observed F^2 values and those calculated for structures based on this first octahedral arrangement and as the arrangement is unlike that in cryolite, the authors decided to abandon it, realizing however, that they have not entirely disproved it as a possibility.

Second Octahedral Arrangement. The second octahedral arrangement originates from the symmetry elements in the following positions: 2_1 in $\frac{1}{4}y$ $1/8z$, c in x 0 z. As was stated previously, more detailed work was done on this arrangement because it closely resembles the octahedral arrangement in the cryolite structure. The symmetry elements are so located that octahedra occur at the four lower corners of the unit cell, at the centre of the lower half cell, and then repeat above in mirror

TABLE IV
OBSERVED AND CALCULATED F^2 'S; ARRANGEMENT I, POSITION I.

hkl	Obs. F^2	Calc. F^2
002	0.19	77.44
100	0	278.22
102	0	61.78
102	0.36	58.83
004	3.19	1666.27
104	0.72	2.10
104	0.82	30.58
200	6.48	836.94
202	0	34.57
202	1.03	30.80
106	0	30.80
106	1.95	26.63
204	7.14	46.10
108	10.14	1.04
108	2.71	256.00

TABLE V
OBSERVED AND CALCULATED F^2 'S; ARRANGEMENT I, POSITION 2.

hkl	Obs. F^2	Calc. F^2	Calc. F^2 (Na and Ca interchanged)
002	0.19	72.25	0.81
100	0	278.22	990.99
$\bar{1}02$	0	78.15	2.53
102	0.36	78.68	2.89
004	3.19	70.56	502.66
$\bar{2}02$	0	74.00	6.35
202	1.03	72.25	7.02
$\bar{1}06$	0	72.25	7.02
106	1.95	71.06	7.84
204	7.14	1108.22	496.84
$\bar{1}08$	10.14	1.04	131.33
108	2.71	256.00	681.21

TABLE VI
OBSERVED AND CALCULATED F^2 'S; ARRANGEMENT I, POSITION 3.

hkl	Obs. F^2	Calc. F^2	Calc. F^2 (Na and Ca interchanged)
002	0.19	72.25	0.81
100	0	278.00	990.99
102	0	78.15	2.53
102	0.36	78.68	2.89
004	3.19	70.56	502.66
202	0	74.48	6.35
202	1.03	72.25	7.02
106	0	72.25	7.02
106	1.95	71.06	7.84
204	7.14	1108.22	496.84
108	10.14	1.04	131.33
108	2.71	256.00	681.21

image to complete the cell (Figure 2b, p. 27).

Numerous positions were tried for the Na, Ca, and H₂O but only the main arrangements will be described here.

Position 1. The first position examined was patterned after the cryolite structure, having one-third of the Na positions filled by the Ca ions, and one-third filled by the water molecules, (Figure 3, p. 42).

Parameters for this arrangement were:

	<u>x</u>	<u>y</u>	<u>z</u>
4 Na in	0.25	0.75	0.50
4 Ca in	0.25	0.25	0.375
4 Al in	0.25	0.25	0.125
4 H ₂ O in	0.25	0.75	0.25
4 F _I in	0.189	0.315	0.232
4 F _{II} in	0.09	-0.04	0.14
4 F _{III} in	-0.03	0.40	0.096
4 F _{IV} in	0.311	0.185	0.018
4 F _V in	0.41	0.54	0.11
4 F _{VI} in	0.53	0.10	0.154

Table VII gives a comparison of the calculated and observed F^2 values.

Particularly bad were the results for the reflections 108 and $\bar{1}08$.

The former should be fairly strong and the latter very strong but both calculate to zero. The discrepancies in these values and others such as those for 104 and $\bar{1}04$ led to the rejection of this arrangement.

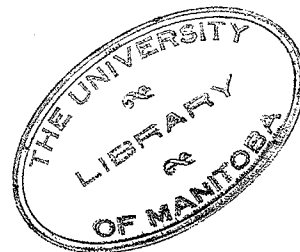
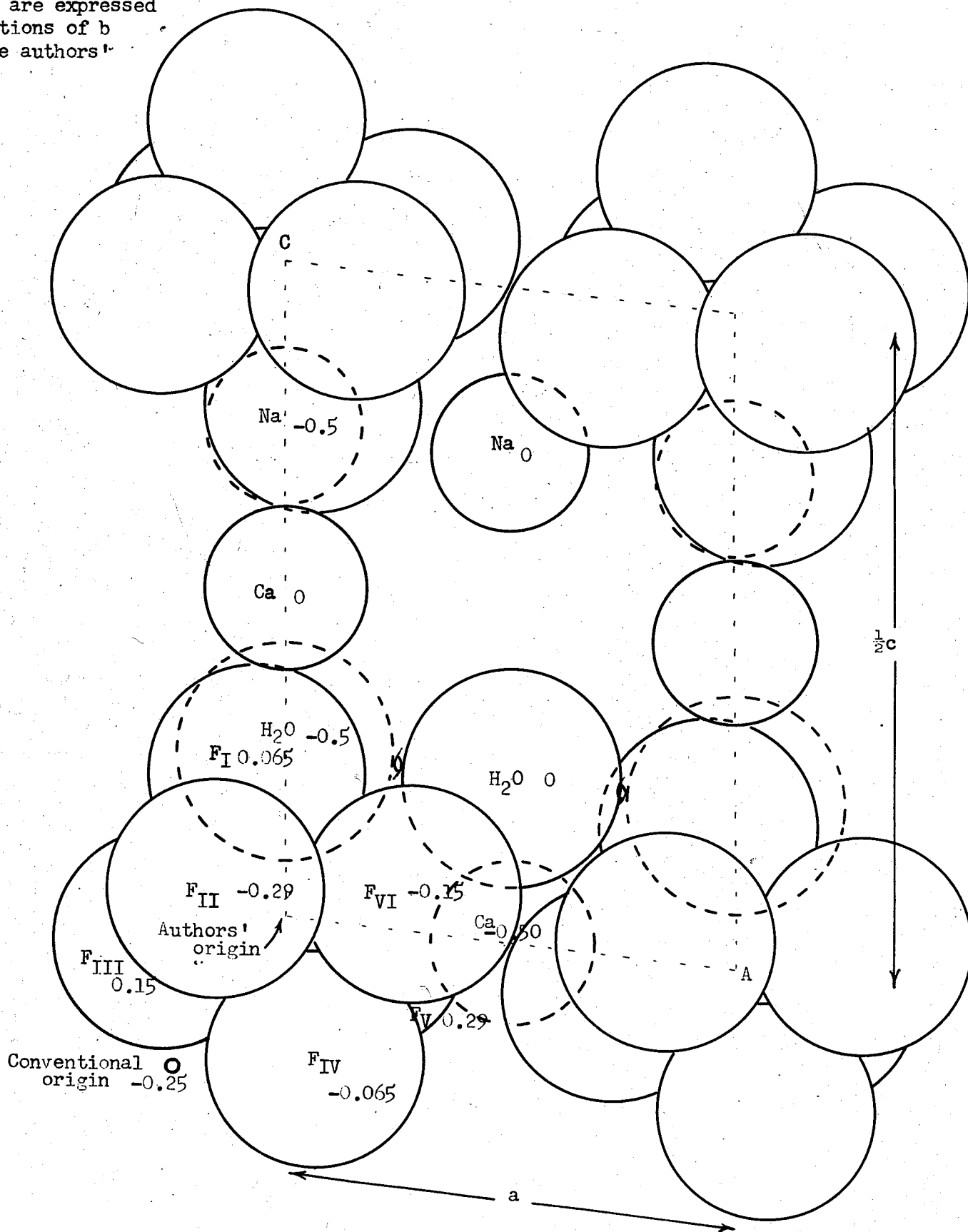


FIGURE 3

POSITION 1, ARRANGEMENT II, STRUCTURE PROJECTED ON (010).

Scale: $1\frac{1}{2}$ cm. - 1 Å.

Heights are expressed as fractions of b from the authors' origin.



Position 2. The origin was raised from .125 below the authors' origin to .100 below it. The effect of this is to raise the screw axis (in order to keep it at height $\frac{1}{4}$ as convention demands) and thus separate the octahedron at the half-cell body centre from the four octahedra at the corners of the base of the cell. The positions of all the ions and molecules remained the same as in position 1. Their parameters became:

	<u>x</u>	<u>y</u>	<u>z</u>
4 Na in	0.25	0.75	0.475
4 Ca in	0.25	0.25	0.35
4 Al in	0.25	0.25	0.10
4 H ₂ O in	0.25	0.75	0.25
4 F _I in	0.189	0.315	0.207
4 F _{II} in	0.09	-0.04	0.115
4 F _{III} in	-0.03	0.40	0.071
4 F _{IV} in	0.311	0.185	-0.007
4 F _V in	0.41	0.54	0.085
4 F _{VI} in	0.53	0.10	0.129

Results are tabulated in table VIII. The 008 reflection, which has the strongest observed intensity, calculates to a fairly low value and minor changes in the parameters failed to increase the value sufficiently to warrant further work on this particular position.

Position 3. Next an attempt was made to provide a probable coordination

for the water molecules. In chapter III it was pointed out that part of the tetrahedrally distributed charge on the water molecule may be satisfied by the attachment, on one side, of a divalent Ca ion.

Accordingly, in the next structure, each Ca ion was brought in contact with a water molecule (Figure 4, p. 45). All other ions were left as in position 1 (Figure 3, p. 42), and the origin was moved back to .125 below the authors' origin. The parameters of the Ca and H₂O for this new position 3 were:

	<u>x</u>	<u>y</u>	<u>z</u>
4 Ca in	0.204	0.25	0.338
4 H ₂ O in	0.202	0.75	0.228

Table IX gives the F^2 values for these new parameters. Variations in the Na, Ca, and H₂O positions failed to improve the agreement for this arrangement.

Position 4. In an effort to rectify the discrepancies in results, the origin was moved upwards again from its previous position, that is, it was moved closer to the authors' original origin. As a result the screw axis and the octahedron at the half-cell body centre were raised. Transformation from the authors' first origin to this new origin is $x + .25$, $y + .25$, $z + .10$. As before the Ca ions and the H₂O molecules were touching. The parameters of the various ions were:

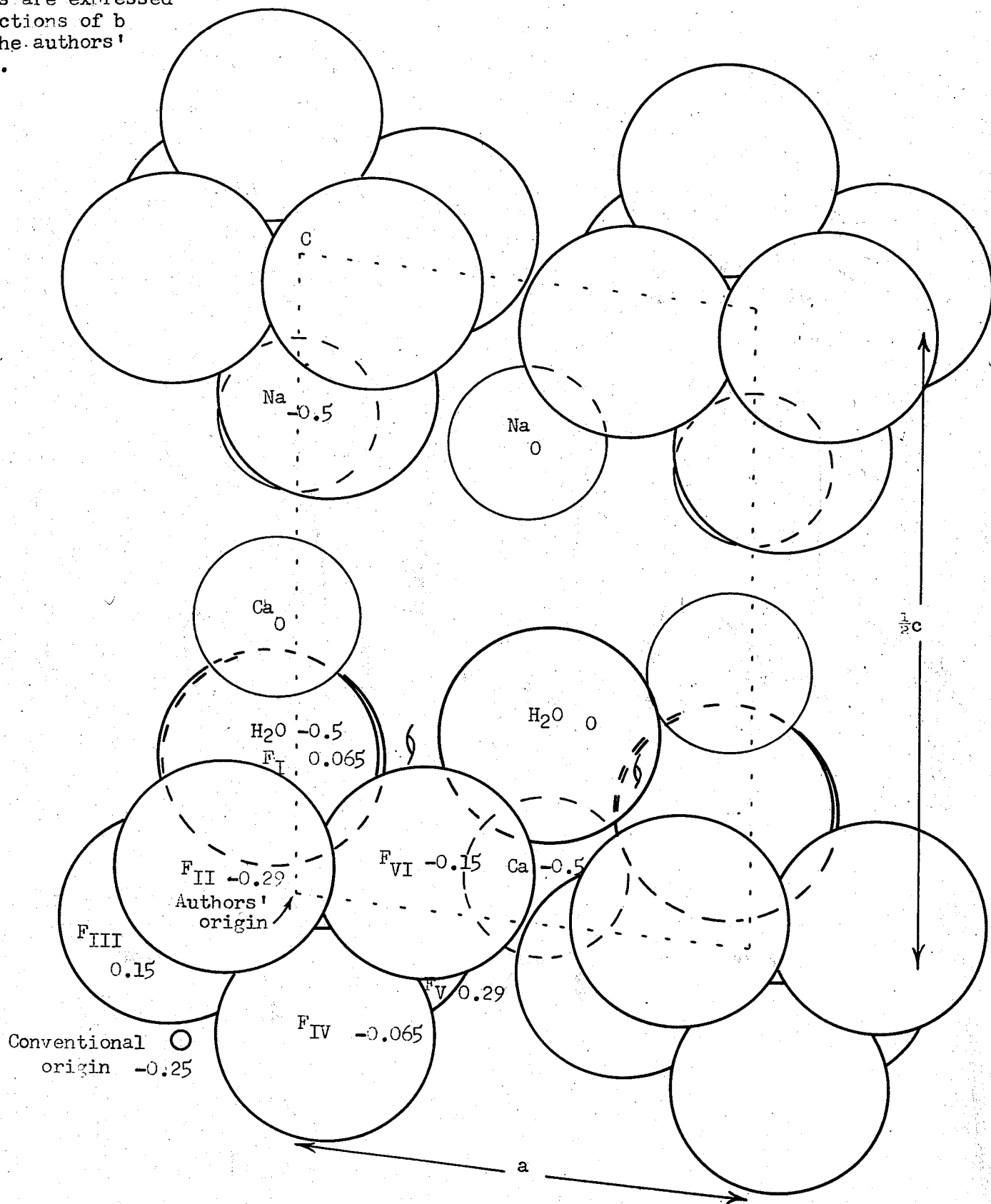
	<u>x</u>	<u>y</u>	<u>z</u>
4 Na in	0.32	0.75	0.53

FIGURE 4

POSITION 3; ARRANGEMENT II, STRUCTURE PROJECTED ON (010).

Scale: $1\frac{1}{2}$ cm. = 1 Å.

Distances are expressed in fractions of b from the authors' origin.



	<u>x</u>	<u>y</u>	<u>z</u>
4 Ca in	0.18	0.25	0.34
4 Al in	0.25	0.25	0.10
4 H ₂ O in	0.20	0.75	0.24

F parameters were the same as in position 2.

Table X compares the F^2 values for this structure. The 008 reflection, which has the strongest observed value of all the planes, calculated to a very low value. Interchange of Na and Ca positions as well as slight changes of position of the metals and the water failed to increase the structure amplitude value of 008 and this arrangement had to be abandoned.

Tilt of the Octahedra. After all the above changes in the positions of the Na, Ca, and H₂O had been examined and calculations had been made using the resulting parameters, attention was focussed on the tilt of the octahedra. Up to this point it had been assumed that the octahedral tilt was the same in thomsenolite as in cryolite. However, it was felt that changes in the tilt should be examined in an effort to arrive at a better proposed structure. The octahedra were tilted, in turn, down positive and negative a and down positive and negative b. Different amounts of tilt were tried in each direction. The final tilt decided upon as the best is described in the next section.

TABLE VII

OBSERVED AND CALCULATED F^2 'S; ARRANGEMENT II, POSITION 1.

hkl	Obs. F^2	Calc. F^2
002	0.19	0.81
100	0	0
011	0.15	1.54
$\bar{1}02$	0	3.80
012	0	1.30
102	0.36	6.25
004	3.19	462.25
110	3.20	370.95
$\bar{1}11$	0.83	15.52
013	0.21	1.30
111	0.44	33.52
$\bar{1}04$	0.72	0
112	1.21	4.45
$\bar{1}13$	1.26	4.04
014	0.77	0
104	0.82	0
113	0.96	43.03
006	0	6.25
008	19.81	2611.21
108	2.71	0
$\bar{1}08$	10.14	0

TABLE VIII
OBSERVED AND CALCULATED F^2 'S; ARRANGEMENT II, POSITION 2.

hkl	Obs. F^2	Calc. F^2
002	0.19	97.6
006	0	17.4
108	2.71	828.0
$\bar{1}08$	10.14	1920.0
104	0.82	16.3
$\bar{1}04$	0.72	37.5
100	0	0
102	0.36	6.45
$\bar{1}02$	0	11.15
004	3.19	207.0
008	19.81	300.0

TABLE IX
OBSERVED AND CALCULATED F^2 'S; ARRANGEMENT II, POSITION 3.

hkl	Obs. F^2	Calc. F^2	hkl	Obs. F^2	Calc. F^2
002	0.19	42.64	006	0	347.08
100	0	52.85	008	19.81	1035.55
011	0.15	1.54	108	2.71	202.78
$\bar{1}02$	0	4.04	$\bar{1}08$	10.14	250.59
012	0	0.62	200	6.48	625.00
102	0.36	124.77	$\bar{2}02$	0	18.66
004	3.19	258.89	202	1.03	55.65
110	3.20	357.97	$\bar{1}06$	0	35.65
$\bar{1}11$	0.83	15.52	$\bar{2}04$	1.47	654.85
013	0.21	1.30	106	1.95	56.25
111	0.44	33.52	204	7.14	107.12
$\bar{1}04$	0.72	58.68	$\bar{2}06$	1.37	153.26
112	1.21	202.49	206	3.24	306.95
$\bar{1}13$	1.26	4.04	$\bar{2}08$	4.39	312.50
014	0.77	251.86	208	0	86.12
104	0.82	88.55			

TABLE X
OBSERVED AND CALCULATED F^2 'S; ARRANGEMENT II, POSITION 4.

hkl	Obs. F^2	Calc. F^2
002	0.19	68.0
006	0	8.8
108	2.71	238.0
$\bar{1}$ 08	10.14	940.0
104	0.82	380.0
$\bar{1}$ 04	0.72	148.0
100	0	30.0
102	0.36	417.0
$\bar{1}$ 02	0	12.0
004	3.19	260.0
008	19.81	90.0
200	6.48	310.0
$\bar{2}$ 02	0	4.4
202	1.03	173.0

The Present Structure. The structure described below is a product of all the different structures examined and is that which to date (May, 1950) gives the best agreement between calculated and observed values.

(i) Parameters and Intensities. All the atoms in the cell are in the 4-fold general positions, xyz. These xyz parameters of each of the ten atoms relative to the conventional origin are:

	<u>x</u>	<u>y</u>	<u>z</u>
4 Na in	0.34	0.75	0.495
4 Ca in	0.19	0.29	0.35
4 Al in	0.25	0.25	0.11
4 H ₂ O in	0.20	0.82	0.23
4 F _I in	0.25	0.315	0.22
4 F _{II} in	0.10	-0.04	0.14
4 F _{III} in	-0.04	0.40	0.10
4 F _{IV} in	0.25	0.185	0.00
4 F _V in	0.40	0.54	0.09
4 F _{VI} in	0.54	0.10	0.12

Table XI gives, for 89 reflections with the simplest indices, the observed F^2 values and the F and F^2 values calculated for the above parameters in the manner described in chapter II. As before, the observed and calculated F^2 values are comparable when the observed values have been multiplied by 100. An x has been placed after those

calculated values that are in very poor agreement with the observed.

(ii) Description of the Structure. Figure 5, p. 53 shows a projection of the structure on (010). The authors' unit cell with origin near one corner Al is more convenient for descriptive purposes than one with the conventional origin, and is shown in dotted lines. The conventional origin is shown at $-.25, -.25, -.11$. The F atoms of only one of the AlF_6 octahedra are shown but all the octahedra in the projected plane of the cell and those at height $\frac{1}{2}b$ at the "half-body-centres" have been outlined. Note that both the upper and lower half-cells are similar to the unit cell of cryolite in that there is one AlF_6 octahedron at each corner and another at the body-centre. The body-centre octahedron in the lower half-cell is, as in cryolite, in glide relationship across (010) and in 2_1 screw relationship around [010] to the octahedron at the origin. Each octahedron centred half-way along a vertical edge in thomsenolite corresponds to one at an upper corner in cryolite, but differs from it in that it is in c-glide relationship to the octahedron at the origin. This results in the doubled c axis of thomsenolite. The corner octahedra tilt a small amount down positive b and enough down negative a to make them vertical in the ac plane.

The Na, Ca, and H_2O occupy very approximately the positions of the three Na ions in cryolite. The chief departure from the cryolite positions results from the bringing together of the Ca and H_2O as shown in Figure 5, p. 53. The Na ion, like its counterpart in the

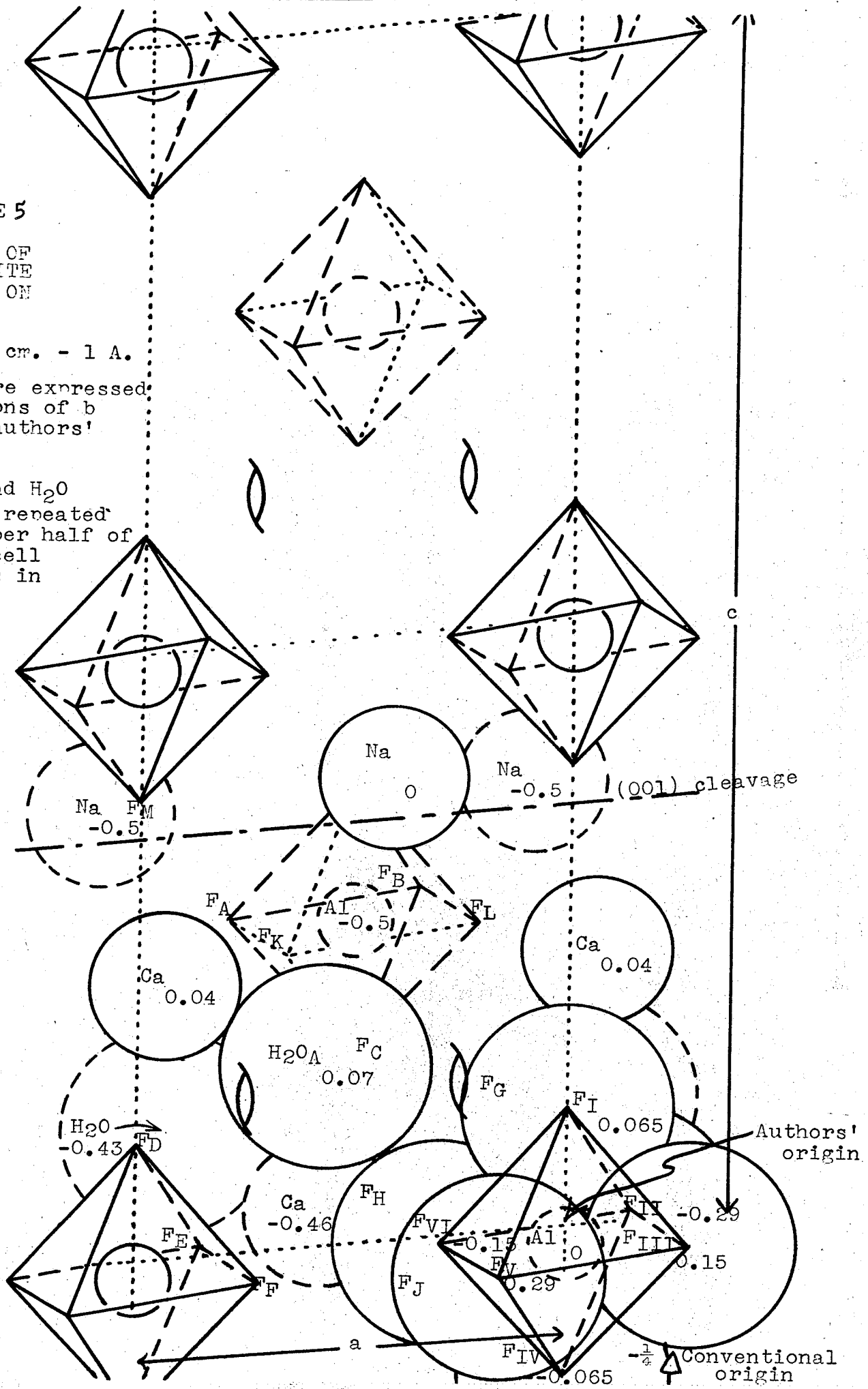
FIGURE 5

STRUCTURE OF THOMSENOLITE PROJECTED ON (010)

Scale: $1\frac{1}{2}$ cm. - 1 A.

Heights are expressed as fractions of b from the authors' origin.

Na, Ca, and H₂O atoms are repeated in the upper half of the unit cell exactly as in the lower.



cryolite structure, is irregularly coordinated by F's. Ca is surrounded by six F's and one H₂O; three of the F's (B, L, and M in the Figure) are farther from Ca than its other F neighbours. Interatomic distances were not calculated for Na and Ca and their neighbours. H₂O is in contact with one Ca, and it has eleven F's as neighbours. These interatomic distances are given below.

Interatomic Distances. In a monoclinic crystal, the distance D between any two atoms with parameters $x_1 y_1 z_1$ and $x_2 y_2 z_2$ is given by the relationship

$$D = \sqrt{(x_1 a \sin \mu - x_2 a \sin \mu)^2 + b^2 (y_1 - y_2)^2 + (z_1 c - x_1 a \cos \mu - z_2 c + x_2 a \cos \mu)^2}$$

In the structure of thomsenolite whose parameters are given above, the interatomic distances were calculated for Al and its six neighbouring F ions, and for H₂O and its twelve closest neighbours which are one Ca and eleven F's. The distances in Ångström units are:

	F _I	F _{II}	F _{III}	F _{IV}	F _V	F _{VI}
Al	1.81	1.90	1.81	1.81	1.86	1.81
	Ca	F _{A(III)}	F _{B(V)}	F _{C(I)}	F _{D(I)}	F _{E(II)}
H ₂ O	2.41	3.99	3.06	2.77	2.73	3.48
	F _{F(III)}	F _{G(I)}	F _{H(VI)}	F _{J(V)}	F _{K(II)}	F _{L(VI)}
H ₂ O	3.03	3.09	2.96	3.68	3.14	3.15

These interatomic distances are discussed in the next chapter.

TABLE XI
OBSERVED F^2 'S AND CALCULATED F 'S AND F^2 'S

hkl	Obs. F^2	Calc. F	Calc. F^2	In very poor agreement
100	0	3.73	13.9	
200	6.48	-26.25	689.1	
300	0.27	- 7.39	54.6	
020	1.39	-26.76	716.1	x
040	1.19	14.94	223.2	
060	2.03	- 7.15	51.1	
002	0.19	4.0	16.0	
004	3.19	-19.93	397.2	
006	0	6.03	36.4	
008	19.81	35.92	1290.2	
102	0.36	-12.71	161.5	x
104	0.82	-11.4	130.0	
106	1.95	- 3.28	10.8	x
108	2.71	23.34	544.8	
202	1.03	12.09	146.2	
204	7.14	-10.11	102.2	x
206	3.24	-15.14	229.2	
302	0.85	18.38	337.8	x
102	0	- 6.19	38.3	
104	0.72	- 5.03	25.3	
106	0	9.27	85.9	x
108	10.14	-28.57	816.2	

TABLE XI (Continued)

hkl	Obs.F ²	Calc.F	Calc.F ²	In very poor agreement
202	0	- 2.21	4.9	
204	1.47	-18.37	337.5	
206	1.37	- 8.77	76.9	
302	1.58	12.57	158.0	
304	1.42	11.86	140.7	
110	3.20	-20.39	415.8	
120	1.07	- 1.22	1.5	x
130	1.14	19.2	368.6	
210	0.35	-13.75	189.1	x
220	8.21	35.69	1273.8	
310	0.85	27.4	750.8	x
011	0.15	3.65	13.3	
012	0	- 1.57	2.46	
013	0.21	- 7.16	51.3	
014	0.77	-13.94	194.3	
015	0.31	7.57	57.3	
016	0	0.21	0.04	
017	0.43	20.07	402.8	x
018	3.57	20.24	409.7	
021	1.73	15.38	236.5	
022	0	0.63	0.4	
023	0	- 6.35	40.3	

TABLE XI (Continued)

hkl	Obs.F ²	Calc.F	Calc.F ²	In very poor agreement
024	1.78	-12.65	160.0	
025	4.42	- 1.07	1.14	x
026	1.00	-15.55	241.8	
027	2.81	- 0.02	0	x
031	0.53	-10.16	103.2	
032	0	- 2.51	6.3	
033	0	0.37	0.14	
111	0.44	2.97	8.82	
112	1.21	11.06	122.3	
113	0.96	0.94	0.88	x
114	1.59	9.21	84.8	
115	0	3.67	13.5	
116	1.05	- 9.15	83.7	
117	0	0.71	0.5	
121	2.00	6.78	46.0	x
122	0	- 0.96	0.92	
123	0.21	13.82	191.0	x
124	1.58	8.82	77.8	
125	0	- 3.32	11.0	
126	0	10.59	112.1	x
221	2.97	-12.83	164.6	

TABLE XI (Continued)

hkl	Obs. F^2	Calc. F	Calc. F^2	In very poor agreement
222	0.78	- 5.43	29.5	
223	1.37	7.60	57.8	
$\bar{1}11$	0.83	- 1.71	2.9	x
$\bar{1}12$	0.22	1.91	3.6	
$\bar{1}13$	1.26	- 5.05	25.5	x
$\bar{1}14$	5.0	-23.14	535.5	
$\bar{1}15$	0.34	2.83	8.0	
$\bar{1}16$	0	3.23	10.4	
$\bar{1}21$	0.54	22.11	488.9	x
$\bar{1}22$	0.38	9.71	94.3	
$\bar{1}23$	3.92	17.95	322.2	
$\bar{1}24$	1.28	1.39	1.9	x
$\bar{1}25$	5.71	- 8.42	70.9	x
$\bar{1}26$	0	0.63	0.4	
$\bar{2}11$	1.41	6.13	37.6	x
$\bar{2}12$	1.09	2.93	8.6	x
$\bar{2}13$	0.57	10.83	117.3	
$\bar{2}14$	0.41	2.61	6.8	
$\bar{2}15$	0.45	- 1.14	1.3	x
$\bar{2}16$	2.00	19.07	363.7	

TABLE XI (Continued)

hkl	Obs. F^2	Calc. F	Calc. F^2	In very poor agreement
221	9.66	- 8.33	69.4	x
222	1.97	7.88	62.1	
223	0	2.13	4.5	
224	1.08	-23.37	546.2	x

CHAPTER V

DISCUSSION AND CONCLUSIONS

Interatomic Distances. The Al-F distances for the final structure are about the same as those in cryolite where they are 1.79 to 1.83 Å, and they are also in good agreement with the value 1.86 Å, given by the accepted ionic radii mentioned in Chapter III. The difference in interatomic distances to F_{II} and F_V from the others is a measure of the slight departure of the AlF_6 octahedra from perfectly regular octahedral coordination.

The interatomic distance H_2O-Ca is 2.41 Å and agrees well with the sum of the corresponding radii, 2.37 Å. The H_2O-F distances do not fully bear out the suggestion put forth earlier that the H_2O molecules form two short O-H-F bonds opposite Ca. The effective radius of water, 1.12 Å, proposed for such a bond would give an O-H-F distance of 2.49 Å, whereas the shortest distance (to F_D) in the structure described here is 2.73 Å. This corresponds to an effective radius of H_2O of 1.37 Å, the normal radius. In view of the discrepancies between many of the calculated and observed F^2 's noted in Table XI, however, it may well be that a refinement of the atomic positions, especially those of H_2O and its neighbouring F's, will show that such short interatomic distances do in fact exist. More work on the structure is also necessary to prove with certainty which two F ions form the presumed H bonds with H_2O .

In the present structure, the shortest H_2O distances are those from H_2O to the F ions labelled F_C and F_D in Figure 5, but the latter is close to Ca and hence is not a likely one to form an H bond. More likely F ions for H bond formation from the point of view of position are F_J and F_L with the latter favoured by the present interatomic distances.

Intensities. From table XI, pp. 55-59 it may be seen that 26 of the 89 calculated F^2 's are in very poor agreement with observed values. Despite this number, it is felt that the much larger percentage which are in good agreement indicated that the general structural scheme is correct and that refinements of the present structure will lead to a fully acceptable one. Although more work was done on the $h0l$ zone than on either of the other two principal zones, the agreement here (6 out of 24 in very poor agreement) is just slightly better than the overall. Of the six $hk0$ reflections, half are poor. Of the three sets of pinakoidal reflections, the $0k0$ are generally in less good agreement than the $h00$ and $00l$. These observations suggest that the y parameters of certain atoms must be changed more than the x and z parameters, but some of the latter undoubtedly require some change as well.

Cleavage. The perfect (001) cleavage of thomsenolite has a possible explanation in the present structure, and the trace of the most likely plane of the cleavage is shown as a chained line in Figure 5.

The AlF_6 octahedra adjoining this plane have no strong electrostatic forces linking them together. The charge of the univalent Na ion is dissipated among nearly a dozen neighbouring F ions at variable distances from it and hence it acts as no strong binding force in this plane. The only other cation (excluding Al) near this plane is Ca. Much of its charge is expended in satisfying the H_2O , and its remaining charge must be distributed among six F's, the furthest removed from the Ca being the one across the proposed cleavage plane. Thus it appears that Ca too provided no strong binding force across this plane. In contrast, the cryolite Na next this Ca position is right on the vertical edge, is of course next no H_2O , and is about equally close to all six neighbouring F's. Thus it provides the force--lacking in thomsenolite--to hold together the AlF_6 octahedra across this plane.

No simple explanation of the poor (110) cleavage of thomsenolite is offered by the present structure.

Conclusions. The results of this investigation have led to the following conclusions:

(1) Of the two possible arrangements in thomsenolite of the AlF_6 octahedra permitted by the space-group symmetry and the size of the cell, the cryolite-like (body-centred) seems much the more probable although the other (the A-face centred) is not entirely ruled out.

The final structure described here is based on the cryolite-like arrangement.

(2) The present structure described in chapter IV, p. 51 is essentially the correct one, and small movements of certain of the atoms from their positions in that structure will describe the true structure accurately. A comparison of calculated F^2 's with observed suggests that certain y parameters require more change than the x and z.

(3) The H_2O is coordinated approximately correctly with one Ca touching it on one side and probably two F's linked by H bonds to it on the other. The H_2O -F interatomic distances in the structure do not establish either the O-H-F bond length or the particular F's which are strongly bonded to H_2O . Further refinements of the atomic positions will be required to clarify these features of the structure. The dehydration experiment proved that the water is, as in any true salt hydrate, an essential part of the structure; it is not interchangeable as is water in the zeolites and the clay minerals.

(4) The present structure offers a reasonable explanation of the perfect (001) cleavage of thomsenolite as described above, but it offers no simple explanation of the poor (110) cleavage.

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