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REFINEMENT OF THE CRYSTAL STRUCTURE OF CRYOLITE

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ABSTRACT

Three-dimensional counter-diffractometer data and a full-matrix least-squares method have been used to refine the crystal structure of cryolite, Na_3AlF_6, from Ivigtut, Greenland. The space group is $P2_1/n$ with cell dimensions $a = 5.4024(2)$, $b = 5.5959(2)$, $c = 7.7564(3)$Å, $\beta = 90.278(1)°$. The final conventional R-factor for 726 observed reflections is 3.3%.

The structure of cryolite consists of isolated regular AlF_6 octahedra linked by two crystallographically distinct Na atoms, one of which occupies a fairly regular octahedron and the other occupies an extremely distorted cubic antiprism. Although of monoclinic symmetry, cryolite is pseudo-cubic with a super-cell multiplicity of 2. From this super-cell, the cells of all the homotypic alkali-metal hexafluorides may be derived, and a structure is proposed for the tetragonal polymorphs of K_3AlF_6, Rb_3AlF_6 and Cs_3AlF_6. The complex polymorphism of these compounds may be related to the co-ordination requirements of the large alkali-metal cations.

RÉSUMÉ

Les données d'un contre-diffractomètre à trois dimensions et une méthode des moindres carrés à matrice entière ont été utilisés pour raffiner la structure cristalline de la cryolite, Na_3AlF_6, d'Ivigtut, Groënland. Le groupe spatial est $P2_1/n$ avec les dimensions de maille $a = 5.4024(2)$, $b = 5.5959(2)$, $c = 7.7564(3)$Å, $\beta = 90.278(1)°$. Le facteur conventionnel final R, pour les 726 réflexions observées, est de 3.3%.

La structure de la cryolite consiste d'octaèdres AlF_6 isolés et réguliers liés par deux atomes cristallographiquement distincts de Na, un qui occupe un octaèdre assez régulier et l'autre qui occupe un anti-prisme cubique très distortionné. Bien que de symétrie monoclinique, la cryolite est pseudo-cubique avec une multiplicité super-maille de 2. De cette super-maille, les mailles de toutes les hexafluorures métalliques homotypiques alkalines peuvent être dérivées et une structure est proposée pour les polymorphes quaternaires de K_3AlF_6, de Rb_3AlF_6, et de Cs_3AlF_6. Le polymorphisme complexe de ces composés peut être relié aux conditions de coordination des grandes cations métalliques alkalines.

(Traduit par le journal)

INTRODUCTION

Cryolite is the principal mineral of the aluminium fluoride group, and the only one to be of any commercial importance. The mineral is associated typically with late-stage pegmatitic activity in granitic terrains, occurring together with fluorite, topaz and the rarer aluminium fluorides listed in Table 1. The limited chemical data available seem to indicate that little or no solid solution can occur in any of these phases. This would suggest that the structure exerts an extreme control on the chemistry of these minerals, and contrasts with the situation extant in the common silicates where a wide variety of continuous chemical variations often exist for a given structure type. All of the structures listed in Table 1 are characterized by an array of AlF_6 octahedra that do not share any element, but are linked together by the large alkali-metal cations. In this respect, these minerals provide an excellent opportunity to examine the crystal-chemical effects of large-cation-anion interactions. Although these effects are often of crucial importance in determining phase stabilities in the silicates, they tend to be obscured by the bonding effects of the smaller di- and tri-valent cations and by polymerization of the silicate tetrahedra. In addition, the fact that structural variation in the aluminium fluorides is discrete rather than continuous imposes

TABLE 1. MINERALS OF THE ALUMINIUM FLUORIDE GROUP

cryolite	Na_3AlF_6	$P2_1/n$	This study
cryolithionite	$Na_3Al_2Li_3F_{12}$	$Ia3d$	Geller (1971)
chiolite	$Na_5Al_3F_{14}$	$P4/mnc$	Brosset (1938)
weberite	Na_2MgAlF_7	$I2mm$	Byström (1944)
elpasoite	K_2NaAlF_6	$Pa3$	Frondel (1948)
jarlite	$NaSrAlF_6$	$C2/m, C2, Cm$	Ferguson (1947, 1949)
prosopite	$CaAl_2(F,OH)_8$	$C2/c$	Ferguson (1949)
pachnolite	$NaCaAlF_6.H_2O$	$C2/c$	Ferguson (1946)
thomsenolite	$NaCaAlF_6.H_2O$	$P2_1/c$	Cocco *et al.* (1967)
gearksutite	$CaAl(F,OH)_5.H_2O$	Monocl.	Ferguson (1949)
ralstonite	$Na_{2-8}(Al,Mg)_{16}$ $(F,OH)_{48}.7H_2O$	$Fd3m$	Pabst (1939)

much more rigid boundary conditions on cation-anion interactions.

The crystal structure of cryolite is of particular interest as it is the type structure for a large number of hexafluoride compounds (Wyckoff 1965), many of which are of commercial interest. The structure was originally solved by Náray-Szabó & Sasvári (1938) who confirmed the monoclinic symmetry established by earlier morphological studies (Krenner 1883; Böggild 1912; Hintze 1915).

EXPERIMENTAL

The crystals used in this study were from the Ivigtut cryolite deposit in southwest Greenland. Single-crystal precession photographs exhibited monoclinic symmetry, with systematic absences *h*0*l*, $h+l = 2n+1$ and 0*k*0, $k = 2n+1$. This is compatible with the space group $P2_1/n$ as found by Náray-Szabó & Sasvári (1938) and not with $P2_1/m$ as reported by Steward & Rooksby (1953) and Holm (1965). Cell dimensions were determined by least-squares refinement of 15 reflections aligned automatically on a 4-circle diffractometer. The values obtained here (Table 2) correspond closely with those reported by Menzer (1928) and not those of Náray-Szabó & Sasvári (1938).

An irregular equidimensional crystal of 0.15mm was used to collect the intensity data. The crystal was mounted on a Syntex P$\bar{1}$ automatic diffractometer operating in the θ-2θ scan mode with variable rates from 2.0-24.0°/min. depending on the peak count through an angle of 2° and the α_1-α_2 separation. Graphite monochromatized Mo*K*α radiation (λ = 0.71069Å) was used, and background counts were made at the beginning and end of each scan. Two standard reflections were monitored every 50 reflections, and no significant change was noted during data collection. A total of 823 reflections was measured out to a 2θ value of 65°. The data were corrected for Lorentz, polarization and background effects, but no absorption corrections were done as preliminary calculations showed them to be negligible for this crystal. A reflection was considered to be observed if its magnitude was greater than three standard deviations based on counting statistics. Application of this procedure resulted in 726 observed reflections.

REFINEMENT

The atomic coordinates of Náray-Szabó & Sasvári (1938) were used as initial parameters for the least-squares program RFINE (Finger 1969). Scattering factors for neutral atoms were taken from Cromer & Mann (1968) and ano-

TABLE 2. UNIT-CELL DIMENSIONS OF CRYOLITE

a(Å)	b(Å)	c(Å)	β(°)	
5.46	5.61	7.80	90.2	Naray-Szabo & Sasvari (1938)
5.39(1)	5.59(1)	7.76(1)	90.2	Menzer (1928)
5.4024(2)	5.5959(2)	7.7564(3)	90.278(1)	This study

TABLE 4. ATOMIC POSITIONS AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS FOR CRYOLITE.

	x	y	z	$B_{equiv.}$
Al	0	0	0	0.67(1)Å^2
Na(1)	0	0	1/2	1.07(2)
Na(2)	0.5133(2)	-0.0519(2)	0.2474(1)	1.55(2)
F(1)	0.1026(2)	0.0455(2)	0.2194(2)	1.31(2)
F(2)	-0.2732(2)	0.1737(2)	0.0462(2)	1.34(2)
F(3)	0.1634(2)	0.2690(2)	-0.0630(2)	1.39(2)

TABLE 5. ANISOTROPIC TEMPERATURE FACTORS FOR CRYOLITE.*

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al	558(23)	521(23)	286(11)	0	2(12)	0
Na(1)	919(35)	855(35)	448(17)	0	-25(19)	0
Na(2)	1234(29)	1114(29)	758(15)	-175(24)	2(16)	15(17)
F(1)	1306(41)	1275(43)	339(17)	36(33)	-162(20)	-77(21)
F(2)	935(38)	1091(39)	647(20)	438(31)	177(21)	83(23)
F(3)	1139(40)	847(38)	737(22)	-335(32)	-63(23)	239(23)

* All values X10^5

TABLE 6. SELECTED INTERATOMIC DISTANCES AND ANGLES FOR CRYOLITE

Al-F(1)	x 2	1.806(1)Å	Na(2)-F(1)	x 1	2.294(2)Å
Al-F(2)	x 2	1.805(1)	Na(2)-F(1)e	x 1	2.353(2)
Al-F(3)	x 2	1.813(1)	Na(2)-F(2)a	x 1	2.703(2)
Al-F		1.808	Na(2)-F(2)b	x 1	2.319(2)
			Na(2)-F(2)f	x 1	2.621(2)
Na(1)-F(1)	x 2	2.263(1)	Na(2)-F(3)d	x 1	2.816(2)
Na(1)-F(2)	x 2	2.227(1)	Na(2)-F(3)c	x 1	2.569(2)
Na(1)-F(3)	x 2	2.282(1)	Na(2)-F(3)g	x 1	2.305(2)
⟨Na(1)-F⟩^{VI}		2.257	⟨Na(2)-F⟩^{VIII}		2.498
F(1)-F(2)	x 2	2.533(2)	F(1)-Al-F(2)		89.12(6)°
F(1)-F(2)a	x 2	2.572(2)	F(1)-Al-F(2)a		90.88(6)
F(1)-F(3)d	x 2	2.545(2)	F(1)-Al-F(3)d		89.38(6)
F(1)-F(3)a	x 2	2.573(2)	F(1)-Al-F(3)a		90.62(6)
F(2)-F(3)	x 2	2.566(2)	F(2)-Al-F(3)		90.34(6)
F(2)-F(3)a	x 2	2.550(2)	F(2)-Al-F(3)a		89.66(6)
⟨F-F⟩		2.557	⟨F-Al-F⟩		90.00
F(1)-F(2)h	x 2	3.291(2)	F(1)-Na(1)-F(2)h		94.29(5)
F(1)-F(2)g	x 2	3.054(2)	F(1)-Na(1)-F(2)g		85.71(5)
F(1)-F(3)d	x 2	3.326(2)	F(1)-Na(1)-F(3)d		94.06(5)
F(1)-F(3)i	x 2	3.098(2)	F(1)-Na(1)-F(3)i		85.94(5)
F(2)-F(3)j	x 2	3.200(2)	F(2)-Na(1)-F(3)j		90.41(5)
F(2)-F(3)k	x 2	3.177(2)	F(2)-Na(1)-F(3)k		89.59(5)
⟨F-F⟩		3.191	⟨F-Na(1)-F⟩		90.00
F(1) -F(2)		2.572(2)Å	F(1) -Na(2)-F(2)		61.32(5)°
F(1) -F(2)b		3.694(2)	F(1) -Na(2)-F(2)b		106.92(6)
F(1)e-F(2)		3.054(1)	F(1)e-Na(2)-F(2)		73.95(5)
F(1)e-F(2)f		2.533(2)	F(1)e-Na(2)-F(2)f		68.94(5)
F(1) -F(3)d		3.326(1)	F(1) -Na(2)-F(3)d		80.50(5)
F(1) -F(3)g		3.613(2)	F(1) -Na(2)-F(3)g		103.55(6)
F(1)e-F(3)d		2.566(1)	F(1)e-Na(2)-F(3)d		58.17(5)
F(1)e-F(3)c		3.098(1)	F(1)e-Na(2)-F(3)c		77.88(5)
F(2) -F(2)b		3.206(1)	F(2) -Na(2)-F(2)b		78.96(6)
F(2) -F(3)c		3.200(2)	F(2) -Na(2)-F(3)c		74.71(5)
F(2)f-F(3)d		2.545(1)	F(2)f-Na(2)-F(3)d		56.17(4)
F(2)b-F(3)c		2.550(2)	F(2)b-Na(2)-F(3)c		62.67(5)
F(2)d-F(3)g		3.177(2)	F(2)d-Na(2)-F(3)g		80.03(5)
F(2)b-F(3)g	x 2	3.069(2)	F(2)b-Na(2)-F(3)g	x 2	83.18(6)
F(3)d-F(3)g		3.282(2)	F(3)d-Na(2)-F(3)g		79.02(6)
⟨F-F⟩		3.035	⟨0-F-0⟩		76.32

Equivalent Positions: a = $\bar{x}$, $\bar{y}$, $\bar{z}$; b = 1+x, y, z; c = 1-x, $\bar{y}$, $\bar{z}$;
d = 1/2-x, y-1/2, 1/2-z; e = 1/2-x, y+1/2, 1/2-z; f = 1/2-x, y-1/2, 1/2-z;
g = 1/2+x, 1/2-y, 1/2+z; h = -1/2-x, y-1/2, 1/2-z; i = x-1/2, 1/2-y, 1/2+z;
j = x-1, y, z; k = $\bar{x}$, 1-y, $\bar{z}$.

malous dispersion corrections from Cromer (1965). From an initial R-factor (Finger 1969) of 68%, the refinement converged rapidly to an R-factor of 6.2% with isotropic temperature factors. At this stage, the temperature factors were converted to anisotropic of the form

$$\exp\left[-\sum_{i=j}^{3}\sum_{j=1}^{3} h_i h_j \beta_{ij}\right]$$

and a correction was made for isotropic extinction (Zachariasen 1968) with the extinction coefficient included as a variable in the refinement. Full-matrix refinement of all variables resulted in convergence at R-factors of 3.3% (observed) and 3.8% (all data), and R_w factors (unit weights) of 3.5% (observed) and 3.8% (all data). Final observed and calculated structure factors are listed in Table 3*, atomic positions and equivalent isotropic temperature factors in Table 4, and anisotropic temperature factor coefficients in Table 5. Interatomic distances and angles were calculated using the program ERRORS (L. W. Finger, personal communication) and are given in Table 6. The magnitudes and orientations of the principal axes of the thermal ellipsoids were calculated with ERRORS.

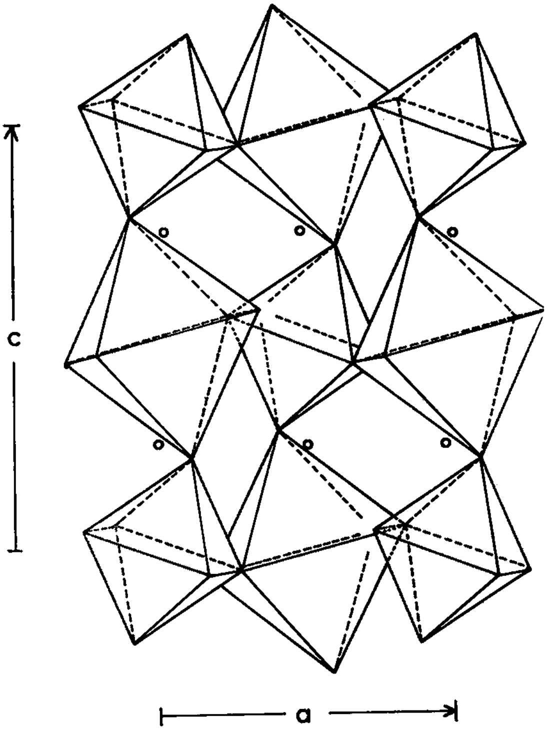

FIG. 1. b-axis projection of part of the crystal structure of cryolite. The smaller octahedra correspond to $^{\mathrm{IV}}(\mathrm{AlF_6})^{3-}$ and the larger to $^{\mathrm{VI}}(\mathrm{NaF_6})^{5-}$; the small circles show the Na(2) sites.

DISCUSSION

The crystal structure of cryolite is made up of isolated $\mathrm{AlF_6}$ octahedra linked by [6] - and [8] - coordinated Na atoms (Fig. 1). The Al octahedron is extremely regular with both bond lengths and angles differing little from the mean values. Na(1) also shows a fairly regular octahedral coordination by F, and these octahedra share corners with the Al octahedra. Na(2) is coordinated by eight fluorines arranged in a highly distorted cubic antiprism (Fig. 2). The wide range of bond lengths exhibited by the Na(2) atom results from the bond-strength requirements of the fluorine anions. This may be seen by inspection of Table 7, which shows the bond-strength (Brown & Shannon 1973) table for cryolite calculated from the curves of Brown (personal communication). F(1) is [4]-coordinate while F(2) and F(3) are [5]-coordinate, necessitating the contraction of some of the metal-F(1) bonds to satisfy the F(1) bond-strength requirements. Although the eight-fold coordination of Na by F may be unusual (Cocco *et al.* 1967), it is fairly characteristic of the aluminium fluorides as it is present in cryolite (this study), cryolithionite (Geller 1971) and thomsenolite (Cocco *et al.* 1967). This coordination is not altogether unexpected as cryolite becomes cubic at high temperatures, with the Na(2) site [12]-coordinate; thus in the derivative monoclinic structure, the Na(2) site will exhibit the maximum coordination consonant with the anion bond-strength requirements.

Although cryolite exhibits the lowest symmetry of the homotypic aluminium hexafluorides $M_3^+\mathrm{AlF_6}$ (Table 8), it is pseudo-cubic (Donnay 1952) with a super-lattice of multiplicity 2. As $\beta \approx 90°$, the transformation $\bar{1}10/110/001$ produces a face-centred cubic array with $a_{\mathrm{cubic}} \approx 7.76\text{Å}$ and a space-group symmetry of $Fm3m$. This corresponds to the high-temperature form of cryolite investigated by Steward & Rooksby (1953); the following atomic positions are proposed for this structure:

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*Table 3 may be obtained from: Depository of Unpublished Data, National Science Library, National Research Council of Canada, Ottawa, Ontario.

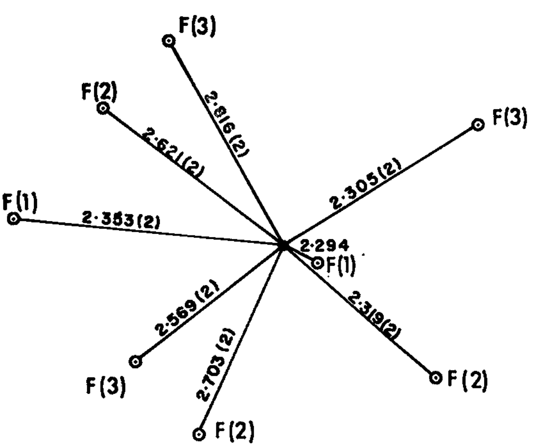
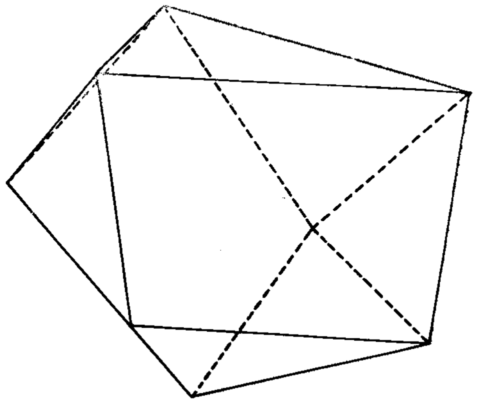


FIG. 2. Details of the coordination of Na(2).



Al	4*a*	(0, 0, 0)
Na(1)	4*b*	(1/2, 1/2, 1/2)
Na(2)	8*c*	(1/4, 1/4, 1/4; 3/4, 3/4, 3/4)
F	24*e*	$\pm$ (x, 0,0; 0, x, 0; 0, 0, x), $x \approx 0.23$

From this ideal structure, the lower-symmetry aluminium fluorides are derived by rotation of the AlF_6 octahedra from their ideal position given above. For M^+ = Na, K, Rb, and Cs, unit cells are derived from the super-cell by the transformation ½ ½ 0/ -½ ½ 0/ 001. With the exception of cryolite, this results in a tetragonal cell as indicated in Table 8. For this structure, $Z = 2$, imposing limits on the possible space groups if it is assumed that the structure does not depart from an I-centred model. The maximum symmetry possible is $I4/mmm$ with the atoms in the following positions:

Al	2*a*	0, 0, 0
Na(1)	2*b*	0, 0, 1/2
Na(2)	4*d*	0, 1/2, 1/4; 1/2, 0, 1/4
F(1)	4*e*	0, 0, z; 0, 0, $\bar{z}$ $z \approx 0.21$
F(2)	8*h*	$\pm$ (x, x, 0; $\bar{x}$, x, 0) $x \approx 0.29$

The lower symmetries $I\bar{4}2m$, $I\bar{4}m2$, $I4mm$, $I422$, $I4m$, $I4$ and $I\bar{4}$ are also possible with the atoms in the above positions, modified for the change in symmetry. There is evidence that K_3AlF_6 exhibits two non-cubic polymorphs (Holm 1965). According to Holm (1965), both of these are tetragonal; conversely, a twinned monoclinic form is reported (Donnay & Ondick 1973). It is not clear whether three distinct non-cubic phases exist, or whether the symmetry has been incorrectly assigned in one of the above cases. If the onset of cubic symmetry is taken as 327°C, the DTA cooling curves of Holm (1965) suggest that only two phases are present. However, the DTA results of Garton & Wanklyn (1965) on Li_3AlF_6 show that whether or not a transition is observed can be dependent on heating and cooling rates and the maximum temperature attained; this suggests that the results of Holm (1965) do not exclude the possibility of more than two non-cubic polymorphs

TABLE 7. BOND STRENGTH TABLE FOR CRYOLITE

	^{VI}Al	$^{VI}Na(1)$	$^{VIII}Na(2)$	Σ
$^{IV}F(1)$	$.494^{x2}_{\downarrow}$	$.188^{x2}_{\downarrow}$	.177 .159	1.018
$^{V}F(2)$	$.490^{x2}_{\downarrow}$	$.201^{x2}_{\downarrow}$	.088 .169 .100	1.048
$^{V}F(3)$	$.486^{x2}_{\downarrow}$	$.181^{x2}_{\downarrow}$	.073 .109 .173	1.022
Σ	2.940	1.140	1.048	

TABLE 8. ALUMINIUM HEXAFLUORIDES HOMOTYPIC WITH CRYOLITE.

	a(Å)	b(Å)	c(Å)	Symmetry	Ref.*
α-Li_3AlF_6**	9.70		12.32	Hex	1
α-Li_3AlF_6	9.510(1)	8.2295(3)	4.8762(1)	$Pna2_1$	2
β-Li_3AlF_6	13.71		12.32	Hex	1
γ-Li_3AlF_6	14.2			$P2_13/P4_232$	1
Low temp. Li_3AlF_6	8.39	11.92	7.82	Orth	3
High temp. Li_3AlF_6**	12.03(5)			$Ia3d$	3
High temp. Li_2AlF_6	12.03(1)			$Ia3$(?)	4
Low temp. K_3AlF_6	5.95		8.48	Tetrag	5
Intermed. K_3AlF_6	-			Tetrag	5
High temp. K_3AlF_6	8.55			*F.C.C.*	5
Low temp. Rb_3AlF_6	6.19		8.84	Tetrag	5
High temp. Rb_3AlF_6	8.88			*F.C.C.*	5
Low temp. Cs_3AlF_6	6.52		9.17	Tetrag	5
High temp. Cs_3AlF_6	9.42			*F.C.C.*	5

* References: (1) Garton & Wanklyn (1965), (2) Burns *et al.* (1968), (3) Holm (1966), (4) this study, (5) Holm (1965).
** These values are superceded by the following values.

of K_3AlF_6. If two tetragonal polymorphs of this phase exist, presumably the lower-temperature phase will either belong to one of the lower-symmetry space groups listed above, or be primitive.

The situation with respect to Li_3AlF_6 is much more complex. On the basis of a DTA study, Garton & Wanklyn reported the existence of five polymorphs and published cell dimensions for the α, β and γ-phases, with hexagonal cells for the first two polymorphs and a cubic cell for the γ-phase. However, a crystal structure determination on α-Li_3AlF_6 (Burns *et al.* 1968) showed that the α-phase was actually orthorhombic (Table 8). Burns *et al.* (1968) also question the indexing of the β and γ-phase powder patterns. DTA studies by Holm (1966) indicated the existence of only three Li_3AlF_6 polymorphs. He reported that the 'low-temperature' polymorph was orthorhombic, but the cell dimensions differ from those reported by Burns *et al.* (1968) for the α-phase. In addition, *x*-ray diffraction results at 625°C indicated that the 'high-temperature' phase was cubic; Holm (1966) indexed the pattern on a cubic cell of $a = 12.03(5)$Å and reported the space group as $Ia3d$, suggesting that Li_3AlF_6 has the cryolithionite structure at high temperature. However, the reflection (222), listed as very strong in the high-temperature powder pattern, is not compatible with the space group $Ia3d$ as it violates the d-glide criterion of hhl, $2h+l = 4n$. The a-glide criterion of $0kl$, k, $(l) = 2n$ is still obeyed indicating that the most likely space group is $Ia3$. Although this is a sub-group of $Ia3d$, the fact that the (222) reflection is classed as very strong indicates that the structure is not very likely to be a distorted version of the cryolithionite structure. Conversely, the pattern of the high-temperature phase cannot be indexed on a cubic cell of $a \approx 6.95$Å, indicating that the structure does not conform to the cubic cryolite structure. Whilst the observed cell dimensions of $a = 12.03$Å is identical with the body-diagonal of the ideal cubic cryolite structure with $M^+ = $ Li, extreme distortion of the ideal structure would be required to form a cubic cell of this edge-length.

The DTA work by Holm (1966) indicates a transition to the cubic phase at 597°C; the high-temperature *x*-ray pattern of the γ-phase presented by Garton & Wanklyn (1965) was taken at 596°C, exactly at the cubic transition-temperature reported by Holm (1966). Although Garton & Wanklyn indexed the γ-phase as cubic ($a = 14.2$Å), agreement between the observed and calculated peak positions is poor (also see Burns *et al.* 1968). If the pattern was taken at the transition temperature, it is possible that it actually consists of two components, a higher-temperature phase corresponding to the high-temperature phase of Holm (1966), and a lower-temperature phase corresponding to the β-phase of Garton & Wanklyn (1965). Comparison of the three patterns indicates that this could be so, although a few extraneous reflections may correspond to LiF as suggested by Garton & Wanklyn (1965). In view of the confusion still remaining in the polymorphism of Li_3AlF_6, a single-crystal *x*-ray study is planned.

As is apparent from the previous discussion, the degree of complexity in the polymorphism of the $M_3^+AlF_6$ compounds increases as the ionic radius of the alkali cation decreases. As the departure of these phases from cubic symmetry is caused by too small an atom occurring in too large a space, it is not surprising that the cubic transition temperature is a function of cation radius.

ACKNOWLEDGEMENTS

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