# A Note on the Polymorphy and Structure of $Li_3AlF_6$

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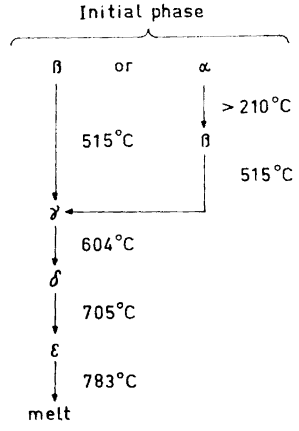
The polymorphy of $Li_3AlF_6$ has been studied independently by Holm [1] and by Garton and Wanklyn.[2]

Holm [1] reported three polymorphic forms of $Li_3AlF_6$ with phase transitions at 505°C and 597°C. The transition points were found by differential thermal analysis (DTA). He found the high-temperature form to be cubic, with $a = 12.03$ Å, and suggested that the space group should be the same as for the mineral cryolithionite, $Na_3Li_3Al_2F_{12}$. His preliminary studies of the low-temperature modification, the $\beta$-form, indicated an orthorhombic unit cell with $a = 8.39$ Å, $b = 11.92$ Å, $c = 7.82$ Å, and 8 formula units in the cell. The density was measured at 25°C, and was found to be 2.75 g/cm [3].

Garton and Wanklyn [2] reported five polymorphic forms of $Li_3AlF_6$ between room temperature and its melting point.




Here too, the transition points were found by DTA. According to Greene, Gross and Hayman,[3] Garton and Wanklyn later have found by X-ray studies that the transition points should be 475°C and 575°C rather than 515°C and 604°C. The α-form could only be obtained by rapid cooling from above 475°C. Garton and Wanklyn [2] found, by examining the powder diagrams, the α-form to be hexagonal, with $a = 9.70$ Å, $c = 12.32$ Å. The $\beta$-form was also hexagonal, with $a = 13.71$ Å, $c = 12.32$ Å, and the $\gamma$-form cubic with $a = 14.2$ Å (at 596°C) space group $P2_13$ or $P4_232$. However, Burns, Tennissen and Brunton [4] have made single-crystal studies of $Li_3AlF_6$ at room temperature. They found an orthorhombic unit cell with $a = 9.510$ Å, $b = 8.2995$ Å, $c = 4.8762$ Å, space group $Pna2_1$, and with 4 formula units in the unit cell. Their X-ray powder pattern agreed with that reported for α-$Li_3AlF_6$ by Garton and Wanklyn,[2] whose observed intensities also agreed with those calculated from the orthorhombic structure. Burns, Tennissen and Brunton [4] pointed out that Garton and Wanklyn's interpretation of the α-modification was not correct. They did not refer to the work by Holm,[1] they pointed out however, that the cubic cell assigned by Garton and Wanklyn [2] to the γ-$Li_3AlF_6$ modification did not have the proper dimensions indicative of the cryolite structure.

Because of these rather contradictory results, it was decided to reexamine the polymorphy of $Li_3AlF_6$ by DTA and high-temperature X-ray diffraction studies.

*Experimental.* Lithium cryolite was made by fusing $AlF_3$ and LiF in molar proportion 1:3. The aluminium fluoride was prepared by vacuum sublimation of technical grade $AlF_3$ (Riedel de Haën AG, Germany). The lithium fluoride (Fisher Certified Reagent, Fisher, USA) was dried in a vacuum furnace at 400°C, and then melted before use. Clear crystals were selected from the samples. The X-ray experiments were carried out in a metal ribbon furnace similar to the type described by Smith.[5] The heating element was a flat strip made from platinum/10 % rhodium. The temperature was recorded with a Pt/Pt 10 % Rh thermocouple and was constant within ±1°C with time. Calibration at the transition point of $Na_3AlF_6$ ($\alpha \rightarrow \beta$) at 560C°, showed the temperature recording to be correct within ±5°C.

*Results and discussion.* The heating curves from DTA showed transformations at 510°C and 597°C. By cooling from above the melting point, only one peak was observed, between 430°C and 350°C. The shape of this peak indicates strong supercooling. When the sample was equilibrated below the melting point and then cooled, both peaks appeared, at somewhat lower

*Table 1.* $\beta$-$Li_3AlF_6$ (at 20°C). Orthorhombic, $a = 11.78 \pm 0.03$ Å, $b = 8.43 \pm 0.02$ Å, $c = 7.77 \pm 0.02$ Å.

| *hkl* | Int. | $\sin^2\theta_{obs.} \times 10^4$ | $\sin^2\theta_{calc.} \times 10^4$ | $d_{calc.}$ |
|---|---|---|---|---|
| 020 | s | 340 | 335 | 4.215 |
| 211 | vs | 352 | 353 | 4.101 |
| 120 | vw | 375 | 377 | 3.969 |
| 002 | s | 390 | 394 | 3.885 |
| 301 | vvw | 491 | 484 | 3.505 |
| 311 | vw | 585 | 567 | 3.236 |
| 221 | | | 604 | 3.136 |
| 400 | m | 674 | 685 | 2.945 |
| 022 | m | 728 | 728 | 2.857 |
| 222 | vw | 912 | 900 | 2.570 |
| 230 | | | 924 | 2.536 |
| 203 | m | 1049 | 1057 | 2.371 |
| 500 | m | 1068 | 1071 | 2.356 |
| 402 | | | 1079 | 2.347 |
| 510 | m | 1153 | 1154 | 2.269 |
| 331 | s | 1238 | 1237 | 2.192 |
| 232 | s | 1315 | 1318 | 2.124 |
| 313 | m | 1363 | 1355 | 2.094 |
| 133 | m | 1683 | 1681 | 1.880 |
| 233 | m | 1809 | 1810 | 1.812 |

vs=very strong, s=strong, m=medium, w=weak, vw=very weak, vvw=very, very weak.

*Table 2.* $\gamma$-$Li_3AlF_6$ (at 520°C). Tetragonal, $a = 11.81 \pm 0.02$ Å, $c = 8.74 \pm 0.02$ Å.

| *hkl* | Int. | $\sin^2\theta_{obs.} \times 10^4$ | $\sin^2\theta_{calc.} \times 10^4$ |
|---|---|---|---|
| 002 | s | 311 | 311 |
| 220 | vs | 335 | 341 |
| 102 | s | 360 | 354 |
| 202 | vw | 485 | 482 |
| 212 | w | 523 | 524 |
| 222 | s | 650 | 652 |
| 312 | m | 738 | 737 |
| 411 | vvw | 810 | 802 |
| 213 | w | 904 | 913 |
| 421 | w | 932 | 930 |
| 402 | m | 1001 | 993 |
| 223 | m | 1040 (LiF) | 1041 |
| 332 | vw | 1079 | 1078 |
| 510 | m | 1099 | 1107 |
| 004 | m | 1245 | 1245 |
| 440 | w | 1351 | 1363 |
| 204 | vw | 1403 (LiF) | 1416 |
| 333 | vvw | 1489 | 1467 |
| 314 | w | 1667 | 1671 |
| 442 | | | 1674 |
| 602 | m | 1853 | 1844 |

*Table 3.* $\delta$-$Li_3AlF_6$ (at 620°C). Cubic, $a = 11.98 \pm 0.01$ Å, space group $Im3m$.

| *hkl* | Int. | $\sin^2\theta_{obs.} \times 10^4$ | $\sin^2\theta_{calc.} \times 10^4$ |
|---|---|---|---|
| 220 | vs | 335 | 331 |
| 222 | m | 498 | 497 |
| 321 | vw | 589 | 580 |
| 411, 330 | vw | 751 | 745 |
| 420 | m | 829 | 828 |
| 332 | w | 910 | 911 |
| 422 | w | 996 | 994 |
| 521 | s | 1239 | 1242 |
| 440 | vw | 1323 | 1325 |
| 530, 433 | m | 1400 (LiF) | 1408 |
| 600, 442 | w | 1494 | 1491 |
| 444 | w | 1982 | 1988 |
| 642 | w | 2302 | 2319 |
| 820, 644 | w | 2804 | 2816 |
| 822, 660 | w | 2970 | 2981 |

temperature (535°C and 450°C) than those found by heating.

The powder patterns from our X-ray experiments, and our interpretation of them, are given in Tables 1—3. The standard deviations of the lattice parameters were found by a least squares treatment. We have adopted the designations for the various modifications introduced by Garton and Wanklyn [2] in their work. The powder diagrams for the $\beta$ and the $\gamma$ modification obtained by us are in general agreement with those reported by Garton and Wanklyn.[2] The $\alpha$ modification was never found by us in samples made by fusing and cooling at a normal rate. In two samples quenched from 647°C and 790°C, respectively, we found both the $\alpha$ and the $\beta$ modification present. However, samples with an excess of LiF or $AlF_3$ (17 % and 36 % by mole of LiF, respectively), quenched from 645°C, consisted of pure $\alpha$-$Li_3AlF_6$ in addition to LiF or $AlF_3$. Cooling from 550°C in the camera itself, also at a high cooling rate, gave $\beta$-$Li_3AlF_6$ only.

The DTA peak found by Garton and Wanklyn [2] at 705°C is not caused by a transition in $Li_3AlF_6$, but is the eutectic point in the system LiF-$AlF_3$, as reported by several authors. Due to evaporation, the composition of $Li_3AlF_6$ will not be the stoichiometric one at high temperatures but have a slight excess of LiF. By addition of small amounts of $AlF_3$ to our lithium cryolite, we obtained a composition, cor-

*Table 4.* $Li_3AlF_6$ modifications.

| Modification | Stability range (°C) | Structure | Lattice parameters at temperature $t$ | | | | Number of formula units in unit cell | Calculated (g/cm³) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| | | | $t$(°C) | $a$(Å) | $b$(Å) | $c$(Å) | | | |
| $\alpha$ | metastable | orthorhombic | Room temp. | 9.510 | 8.2295 | 4.8762 | 4 | 2.815 | 4 |
| $\beta$ | <510 | orthorhombic | 20 | 11.78 | 8.43 | 7.77 | 8 | 2.79 | This work |
| $\gamma$ | 510–597 | tetragonal | 520 | 11.81 | | 8.74 | 12 | 2.64 | » » |
| $\delta$ | >597 | cubic | 620 | 11.98 | | | 16 | 2.50 | » » |

responding to stoichiometric $Li_3AlF_6$, where no peak could be observed at 705°C.

The conclusions of our investigation are given in Table 4. The orthorhombic $\beta$-$Li_3AlF_6$ is transformed at 510°C to the tetragonal $\gamma$-$Li_3AlF_6$, which transforms at 597°C to the cubic $\delta$-$Li_3AlF_6$. We found $\delta$-$Li_3AlF_6$ to be stable at least up to 700°C.

$$\underset{\text{orthorhombic}}{\beta\text{-}Li_3AlF_6} \xrightarrow{510°C} \underset{\text{tetragonal}}{\gamma\text{-}Li_3AlF_6} \xrightarrow{597°C} \underset{\text{cubic}}{\delta\text{-}Li_3AlF_6}$$

The transformation from the $\gamma$ to the $\beta$-form on cooling seems to be of higher order, passing through an activated intermediate form, which is $\alpha$-$Li_3AlF_6$. On rapid cooling (quenching), this metastable modification remains, and is gradually transformed to the stable $\beta$-$Li_3AlF_6$ upon renewed heating. This shows that $\beta$-$Li_3AiF_6$ is the stable modification at room temperature.

The high-temperature modification of $Li_3AlF_6$, although cubic is not the same as for the other cryolites, but is related to the structure of cryolithionite, $Na_3Li_3Al_2F_{12}$, which is cubic with the cell constant $a = 12.097$ Å.[6] The space group of cryolithionite is, according to Menzer,[6] $Ia3d$, while that of $\delta$-$Li_3AlF_6$ found by us is $Im3m$. New phase examinations of the system $Na_3AlF_6$–$Li_3AlF_6$ which have been carried out,[8] show that with small additions of $Na_3AlF_6$ (less than 5 % by mole at 650°C), the space group of $\delta$-$LiAiF_6$ is changed from $Im3m$ to $Ia3d$, thus becoming identical with that of cryolithionite.

Holm [1] gave a tentative explanation of the mechanism of the transformation from the low-temperature to the high-temperature modification of $Li_3AlF_6$. He suggested that in the low-temperature form one third of the $Li^+$ ions should be in 6-coordinated and two thirds in 4-coordinated positions, while in the high-temperature form one half should be in 4-coordination and the other half in 8-coordination.

The investigation of $\alpha$-$Li_3AlF_6$ by Burns, Tennissen and Brunton [4] does indeed show that the $Li^+$ ions are in a very distorted 6-coordination, which for two thirds of them is close to 4-coordination. The interatomic distances in $\alpha$-$Li_3AlF_6$ should be compared to those found by Menzer [6] in cryolithionite.

| $\alpha$-$Li_3AlF_6$ (Burns *et al.*[4]) | | $Na_3Li_3Al_2F_{12}$ (Menzer [6]) | |
|---|---|---|---|
| Li–F | 1.88–2.43 Å | Li–F | 1.80 Å |
| | | Na–F | 2.40 Å |
| | | | 2.58 Å |
| Al–F | 1.81 ± 0.02 Å | Al–F | 1.81 Å |

This shows the similarity between the lithium cryolite and the cryolithionite (garnet) structure.

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# The Constitution of Diterpenoids from *Solidago elongata* Nutt[1]

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From an ethyl acetate extract of roots of *Solidago elongata* Nutt.[2] we have isolated several oily diterpenoids (see Table 1) by careful column and thin layer chromatography. Polar fractions from the columns, after methylation with diazomethane, have yielded three diterpenoid methyl esters, one of which is identical with an authentic sample of methyl kolavenate (*1*).[3] The close relationship of the other two esters to methyl kolavenate was indicated by their NMR spectra. Indeed, the only major differences are that the new compounds have the resonance of both quaternary methyl groups shifted to lower field and each shows evidence of additional oxygenation. Thus, one ester (*2*) has resonances attributable to a secondary acetate while, in the other (*3*), resonances arising from a secondary angelate are clearly visible (see Fig. 1). The location of these oxygen functions at C-6 in the methyl kolavenate skeleton was demonstrated as follows.

Major peaks in the mass spectra of compounds in this series result from cleavage of either the C-9,C-11 or the C-11,C-12 bonds. Thus, cleavage of the C-9,C-11 bond in methyl kolavenate (*1*) produces a peak at *m/e* 191, while cleavage of the C-11,C-12 bond with transfer of a hydrogen and subsequent loss of a methyl radical gives a peak at *m/e* 189. In the mass spectra of the acetate (*2*), angelate (*3*) and the derived alcohol (*4*), these peaks are two units

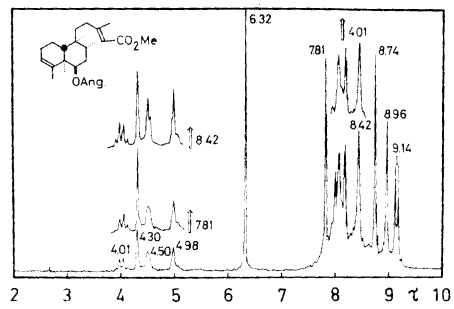


*Fig. 1.* NMR single and double resonance spectra at 100 Mc/s of methyl 6-angeloyloxykolavenate (*3*).

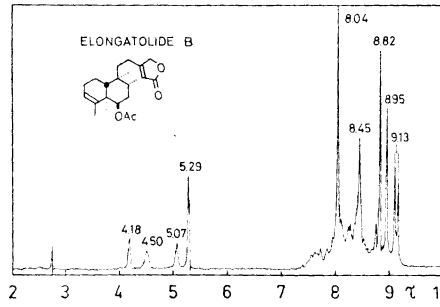


*Fig. 2.* NMR spectrum at 100 Mc/s of elongatolide B (*11*).

lower because of loss of ROH, while the corresponding ketone (*5*), m.p. 75—77°, gives a peak at *m/e* 205. These data exclude the possibility of the oxygen function being in the side chain.