Table 2. Content of carbonyl compounds in tall oil and tall oil distillation products.

Product	Acid value	% Resin acids	% Unsaponifiables	% Carbonyl compounds	
				In unsaponifiables	In product
Crude tall oil	148	34.5	11.5	9.9	1.1
Tall oil distillate	177	10.6	9.9	22	2.2
Tall oil fatty acids	195	2.0	2.8	23.5	0.6

methyl dehydroabietate, 1.54; methyl abietate, 1.74.

The relative retention times for the aldehydes are given in Table 1 and those of the acetates are (acetyl pimarinol, 1.00): acetyl palustrinol, 1.12; acetyl isopimarinol, 1.26; acetyl dehydroabietinol, 1.53; acetyl abietinol, 1.74.

Norin and Westfelt [4] have given retention data for the mentioned type of compounds on a column consisting of 1 % E 301 on Gaschrom P operating at 150°C.

Isolation of carbonyl compounds. The unsaponifiable fractions from the various sources were isolated by saponification with 2 N alcoholic KOH followed by extraction with petroleum ether in a continuous extractor. From the unsaponifiable fractions the carbonyl compounds were isolated with Girard's Reagent T according to a method described by Sandermann and Weissmann.[5]

Oxidation of aldehydes. The oxidation of aldehydes to the corresponding carboxylic acids was carried out with chromic acid in acetic acid according to the method described in Ref. 6. The acids thus obtained were methylated with ethereal diazomethane.

Reduction of aldehydes. The reduction of aldehydes to the corresponding alcohols was carried out using sodium borohydride in aqueous methanol according to the standard procedure. The alcohols thus formed were acetylated in the usual way (refluxing with acetic anhydride).

Reduction of resin acid methyl esters. For comparison, resin acids of known composition were methylated (ethereal diazomethane) and the esters reduced with lithium aluminium hydride in ether solution according to the usual procedure.

1. Erdtman, H. and Westfelt, L. *Acta Chem. Scand.* **17** (1963) 1826.
2. Sandermann, W. and Weissmann, G. *Paperi Puu* **12** (1962) 639.
3. Brooks, T. W., Fisher, G. S. and Joye, N. M. *Anal. Chem.* **37** (1965) 1063.
4. Norin, T. and Westfelt, L. *Acta Chem. Scand.* **17** (1963) 1828.
5. Sandermann, W. and Weissmann, G. *Z. anal. Chem.* **189** (1962) 137.
6. Harris, G. C. and Sanderson, T. F. *J. Am. Chem. Soc.* **70** (1948) 3870.

Received March 30, 1966.

Phase Transitions and Structure of Lithium Cryolite

JAN LÜTZOW HOLM*

Institute of Inorganic Chemistry, The Technical University of Norway, Trondheim, Norway

In a recent publication [1] it was shown that the sodium, potassium, rubidium and cesium compounds of the cryolite family, M_3AlF_6, all are polymorphic. The sodium compound Na_3AlF_6 changes from a monoclinic to a cubic symmetry at 560°C while the other compounds K_3AlF_6, Rb_3AlF_6, and Cs_3AlF_6 change from a tetragonal to a cubic symmetry at 327°C, 357°C, and 287°C, respectively. In their high-temperature forms they all belong to the space group $Fm3m-O_h{}^5$.

A preliminary examination of the lithium compound will here be reported.

* Present address: Institute for the Study of Metals, University of Chicago, Chicago, Illinois 60637, U.S.A.
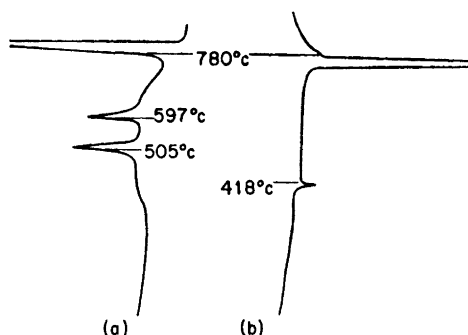
Fig. 1. DTA diagrams for Li_3AlF_6 (a) heating curve, (b) cooling curve from above melting point.

Lithium cryolite was made by fusing aluminum fluoride and lithium fluoride in molar proportion 1:3. The aluminum fluoride was prepared by vacuum sublimation of anhydrous AlF_3 (A. D. Mackay Inc. USA). The lithium fluoride (LiF, Fisher Certified Reagent, Fisher, USA) was carefully dried in a vacuum furnace at 400—500°C before use. The lithium cryolite was examined by differential thermal analysis (DTA) and X-ray diffraction. The technique and equipment was the same as reported earlier.[1]

The DTA diagrams are given in Fig. 1. The diagram taken by heating (Fig. 1a) contains three endothermic peaks, one at 505 ± 5°C, a second at 597 ± 5°C, and a third at 780°C. The last temperature is the melting temperature for lithium cryolite. By cooling from above the melting temperature only one small peak could be observed between 400 and 430°C depending on the cooling rate (Fig. 1b). However, when the cooling was started below the melting point and after equilibration both peaks appeared in the diagram at somewhat lower temperatures than those found by heating.

This indicates that the transformation mechanism for Li_3AlF_6 is different from the other members of the cryolite family. In the sodium, potassium, rubidium, and cesium compounds, the transformation is associated with a change in the nearest neighbour distances $M(1)-F$ and $M(2)-F$ in $M_2(2)M(1)AlF_6$ (1. order transformation).[2]

A study of the high-temperature modification of Li_3AlF_6 above 597°C by X-ray diffraction analysis indicates a cubic structure with a cell constant 12.03 ± 0.05

Table 1. X-Ray data for the cubic high-temperature modification of Li_3AlF_6 at 625°C (Space group $O_h^{10}-Ia3d$).

Int.	$\sin^2 \theta_{obs}$ $\times 10^4$	hkl		$\sin^2 \theta_{calc}$ $\times 10^4$
vs	328	(220)		328
vs	492	(222)		492
m	818	(420)		820
m	982	(422)		984
vs	1228	(521)		1230
s	1968	(444)		1968
m	2296	(642)		2296
m	2539	(732)	(651)	2542
m	2788	(820)	(644)	2788
m	2950	(822)	(660)	2952
w	3198	(752)		3198
m	3280	(840)		3280

vs = very strong; s = strong; m = medium; w = weak

Å at 625 ± 10°C (Table 1). The unit cell contains 16 molecules of Li_3AlF_6. Thus, the structure of the high-temperature modification of Li_3AlF_6 is not the same as for the other alkali cryolites, but seems instead to be related to the structure of the mineral cryolithionite, $Na_3Li_3Al_2F_{12}$. According to Menzer[3] this compound has the same structure as the garnets, and should therefore be written $Na_3Al_2(LiF_4)_3$. Cryolithionite has a cell constant $a_0 = 12.097$ Å at room temperature. The space group is O_h^{10} and the number of molecules in the unit cell is 8. It is therefore fair to assume that the high-temperature modification of Li_3AlF_6 has the garnet structure as well. While it has been common to compare cryolithionite and grossularite, the lithium cryolite should be compared with pyrope

$Na_3Al_2(LiF_4)_3$	$Li_3Al_2(LiF_4)_3$
$Ca_3Al_3(SiO_4)_3$	$Mg_3Al_2(SiO_4)_3$
Grossularite	Pyrope
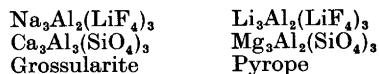
According to this formula half of the Li^+ ions are in 8-coordination while the other half are 4-coordinated. Thus, the high-temperature structure of Li_3AlF_6 is retained at room temperature by cryolithionite. Phase studies in the system $Na_3AlF_6-Li_3AlF_6$ carried out by the author supports this view. Preliminary studies indicate that there exist large regions of solid solutions on both sides of the system (may be continuous).

High-temperature X-ray studies indicate that cryolithionite is stable to about 660—680°C. Above this temperature an increasing disorder of the Na^+ and the Li^+ ions causes cryolithionite to become a part of the solid solution series (Na, $Li)_3AlF_6$ where the Na^+ and Li^+ ions are completely disordered. The mixed crystal of this composition melts at about 720°C. Note that the artificially formed cryolithionite probably contains some excess Li_3AlF_6 so that the formula should be written $Na_{3-x}Li_{3+x}Al_2(LiF_4)_3$. Preliminary studies indicate that x may be as large as 3/8.

Also lithium cryolite seems to undergo a similar order-disorder transition at temperatures above 700°C. This is indicated by a rapid change in the intensities of most of the cryolithionite reflections and the appearance of new reflections as the temperature is increased. By rapid cooling some of the disorder can be retained causing the observed lowering in the phase transition temperature as shown on Fig. 1b.

A preliminary study of the low-temperature modification of Li_3AlF_6 indicates that the compound has an orthorhombic structure with 8 units of Li AlF$_6$ in a cell of dimensions $a = 8.39$ Å, $b = 11.92$ Å, $c = 7.82$ Å. The calculated density is 2.748 g/cm^3 as compared with the measured density 2.75 g/cm^3. While the other alkali cryolites all have structures which are super structures of the perovskite structure (Wells [4]), $NaNa_{0.5}Al_{0.5}F_3 - CaTiO_3$, the present X-ray work indicates that lithium cryolite may have its structural analogues in the pyroxen group (ortho- and proto-enstatite), $Li_{0.5}Al_{0.5}LiF_3 - Mg_{0.5}Mg_{0.5}SiO_3$. According to this formula one third of the Li^+ ions should be in 6-coordination while the other two thirds should be in 4-coordinated positions. If this assumption holds, the transformation to the cubic garnet structure should be associated with the following changes in coordination-number for the Li^+ ions: One fourth of the Li^+ ions in 4-coordination plus all the Li^+ ions in 6-coordination should increase its coordination number to 8, while the rest remain in 4-coordination.

1. Holm, J. L. *Acta Chem. Scand.* **19** (1965) 261.
2. Steward, E. G. and Rooksby, H. P. *Acta Cryst.* **6** (1953) 49.
3. Menzer, G. *Z. Krist.* **75** (1930) 265.
4. Wells, A. F. *Structural Inorganic Chemistry,* 3rd Ed., Oxford 1962, p. 369.

Least Squares Refinement of the Molecular Structure of 1,2-Dithiolane-4-carboxylic Acid

OLAV FOSS, ASBJØRN HORDVIK and JORUNN SLETTEN

Chemical Institute, University of Bergen, Bergen, Norway

The crystal and molecular structure of 1,2-dithiolane-4-carboxylic acid, from two-dimensional $F_o - F_c$ refinement of two zones, was reported by Foss and Tjomsland [1] in 1958. The found $S-S$ bond length and CSS/SSC dihedral angle were 2.096 ± 0.009 Å and 26.6 ± 1°, respectively.

One of us (A.H.) has recently shown that the sulphur-sulphur bond length in disulphides appears to vary with the dihedral angle, and that 2.10 Å probably is a better value than the generally accepted 2.08 Å for the length of a pure sulphur-sulphur single bond in a *cis* planar disulphide group.[2] Because the sulphur-sulphur bond length in 1,2-dithiolane-4-carboxylic acid played an important role in the considerations which led to that conclusion, a confirmation of the bond length, as found by the two-dimensional difference refinement, was sought. A least squares refinement of the structure has been undertaken with this view.

The crystals of 1,2-dithiolane-4-carboxylic acid are triclinic, with [1] $a = 5.34$ Å, $b = 5.85$ Å, $c = 10.75$ Å, $\alpha = 93\frac{1}{2}°$, $\beta = 89\frac{1}{2}°$, $\gamma = 109\frac{1}{2}°$, and $Z = 2$. The space group is $C_i^1 - P\bar{1}$. In addition to the $0kl$ and $h0l$ reflections, on which the difference refinement [1] was based, the least squares refinement comprises the reflec-