

REFINEMENT OF THE CRYSTAL STRUCTURE
OF CRYOLITHIONITE, $\{\text{Na}_3\}[\text{Al}_2](\text{Li}_3)\text{F}_{12}$

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ABSTRACT

The crystal structure of cryolithionite, originally solved by Menzer, has been refined by least squares treatment of single-crystal data. Cryolithionite has the garnet structure with lattice constant $12.122 \pm 0.002 \text{ \AA}$. The ionic distribution as originally given by Menzer, namely $\{\text{Na}_3\}[\text{Al}_2](\text{Li}_3)\text{F}_{12}$, is confirmed. Cryolithionite is the only known garnet in which the tetrahedral cation-anion ($\text{Li}^+ - \text{F}^-$) distance, $1.846 \pm 0.003 \text{ \AA}$, is longer than the octahedral cation-anion ($\text{Al}^{3+} - \text{F}^-$) distance, $1.807 \pm 0.003 \text{ \AA}$. The $\text{Na}^+ - \text{F}^-$ distances are 2.351 ± 0.003 and $2.544 \pm 0.003 \text{ \AA}$.

INTRODUCTION

The structure of cryolithionite, $\{\text{Na}_3\}[\text{Al}_2](\text{Li}_3)\text{F}_{12}$, was solved by Menzer (1927, 1930) about 40 years ago. He showed that it has the garnet structure with the ionic distribution indicated by the formula as written (*e.g.*, Geller, 1967). In all garnet structures thus far refined (*e.g.*, Geller, 1967), it has been found that the largest cation-anion (heretofore, always oxygen) distance is that of the *c*-site cation, the smallest, that of the *d*-site cation.

In the NaCl-type LiF, in which the Li^+ ion is surrounded by a regular octahedron of F^- ions, the $\text{Li}^+ - \text{F}^-$ distance is 2.01 \AA , whereas the average octahedral $\text{Al}^{3+} - \text{F}^-$ distance in AlF_3 is only 1.80 \AA (Ketelaar, 1933). In the oxides, the octahedral $\text{Li}^+ - \text{O}^{2-}$ distance is also substantially larger than the $\text{Al}^{3+} - \text{O}^{2-}$ distance. For example, in synthetic lithiophilite, LiMnPO_4 (Geller and Durand, 1960), the average $\text{Li}^+ - \text{O}^{2-}$ distance is 2.17 \AA , while in $\text{Y}_3\text{Al}_2\text{Al}_3\text{O}_{12}$ (yttrium aluminum garnet) and in several rare-earth aluminum garnets (Euler and Bruce, 1965), the octahedral $\text{Al}^{3+} - \text{O}^{2-}$ distance is 1.94 \AA . One might be tempted to infer from the above that the cation distribution in cryolithionite might not be as given by the above formula, but that a substantial amount of the Li^+ could be in octahedral sites, the maximum possible being as represented by the formula $\{\text{Na}_3\}[\text{Li}_2](\text{LiAl}_2)\text{F}_{12}$. On the other hand, if one accepts the distribution to be that given by $\{\text{Na}_3\}[\text{Al}_2](\text{Li}_3)\text{F}_{12}$, some rather interesting interionic distances should be anticipated.

The results of the refinement of the structure of cryolithionite confirm the distribution originally proposed by Menzer (1927, 1930) and show that cryolithionite is the only garnet structure thus far refined in which the tetrahedral cation-anion distance is longer than the octahedral cation-anion distance.

CRYSTAL DATA

The specimen of cryolithionite was obtained from the Smithsonian Institution (Catalog Number 106833) and was part of a larger specimen found originally in Ivigtut, Greenland. The pieces received showed only conchoidal fracture (*i.e.*, no faces) and were optically isotropic.

Crystals of $\{\text{Na}_3\}[\text{Al}_2](\text{Li}_3)\text{F}_{12}$ are cubic, $a = 12.122 \pm 0.002 \text{ \AA}$ (Menzer reported 12.121 \AA for his specimen also from Ivigtut, Greenland), most probable space group $Ia\bar{3}d-O_h^{10}$. The unit cell with volume 1781.2 \AA^3 contains eight formula units with formula weight 371.73. The calculated density at 25°C is 2.771 g/cm^3 , exactly equal to the density measured by flotation. The linear absorption coefficient for $\text{MoK}\alpha$ radiation is 7.17 cm^{-1} .

EXPERIMENTAL

A Buerger-Supper-Pace-Picker automatic diffractometer was used to collect the intensity data, obtained with $\text{MoK}\alpha$ radiation and balanced Zr and Y filters from a spherical crystal of 0.18 mm radius. The spherical shape was attained with a Bond (1951) sphere grinder, and the crystal was aligned along a unit cell axis. Only independent reflections were measured in the range $2\theta \leq 55^\circ$. The continuous scan mode was used: scan rate $2.00^\circ/\text{min}$., scan interval 2.0° or more. Background counts at the beginning and end of the scan interval were taken at $1/6$ the scan time of each reflection. The absorption was essentially constant and therefore no absorption correction was made. Lorentz-polarization-Tunell factors were applied to the intensities. A total of 176 independent structure amplitudes was obtained, of which nine were below threshold.

The lattice constant was obtained from measurements of an X-ray powder diffraction photograph taken with $\text{CuK}\alpha$ radiation.

REFINEMENT OF THE STRUCTURE

In the completely ordered structure, the cations Na^+ , Al^{3+} and Li^+ are in the special positions $24c$, $16a$, and $24d$, respectively of space group $Ia\bar{3}d$. The fluoride ions are in the general positions $96h$. There are thus 3 positional and 13 thermal parameters and a scale factor to be refined. The Cromer-Waber (1965) scattering factors were used for all ions. The real parts of the anomalous dispersion corrections (Cromer, 1965) were small but were applied to the scattering factors of Na^+ and Al^{3+} ; imaginary parts were neglected.

The least squares calculations were carried out with the Busing-Martin-Levy (1962) program. Observed structure amplitudes with values between 14.7 and 185 were assigned $\sigma = 0.05|F_0|$; when $|F_0| \leq 14.7$, $\sigma = 0.74$; $|F_0| > 185$, *i.e.*, reflections 400, 800, 840, 611, 642, and 444, were assigned very low weights, because of extinction. Nine structure amplitudes of reflections too weak to be observed were also given very low weights. Excluding the six largest structure amplitudes, the conventional $R = \Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.031$. Calculated and observed structure am-

TABLE 1. OBSERVED AND CALCULATED STRUCTURE AMPLITUDES

$\lambda = 0$		$\lambda = 1$		$\lambda = 1$		$\lambda = 2$		$\lambda = 2$		$\lambda = 3$		$\lambda = 5$			
h	k	$ F_o $	$ F_c $	h	k	$ F_o $	$ F_c $	h	k	$ F_o $	$ F_c $	h	k	$ F_o $	$ F_c $
2	2	182	193	5	4	5	4	11	10	27	29	12	6	76	81
4	0	249	298	6	1	208	227	12	9	46	46	13	5	18	19
4	2	143	141	5	3	30	28	15	2	34	33	11	9	31	31
4	4	94	92	7	2	10	7	13	8	< 6	1	12	8	32	32
6	2	171	177	6	5	92	90	15	4	6	2	14	4	150	159
6	4	183	191	7	4	56	55	14	7	10	10	13	7	21	20
8	0	284	338	8	3	31	29					14	6	11	9
8	2	56	57	9	2	38	37					15	3	43	43
6	6	93	92	7	6	40	40	3	3	107	108	11	11	< 6	5
8	4	207	222	8	5	66	66	4	2	17	14	12	10	109	118
8	6	15	16	9	4	94	95	5	3	127	128				
10	2	60	58	10	1	32	31	5	5	154	161				
10	4	116	116	10	3	22	21	6	4	185	201	5	4	52	51
8	8	163	166	8	7	21	21	7	3	54	53	6	3	18	17
10	6	< 5	0	9	6	94	93	8	2	139	145	6	5	22	22
12	0	39	41	11	2	34	34	7	5	29	28	7	4	62	59
12	2	52	51	10	5	75	77	8	4	64	65	7	6	12	11
12	4	44	42	11	4	12	11	9	3	63	62	8	5	108	113
10	8	28	30	10	7	13	12	7	7	51	51	9	4	16	16
12	6	57	56	9	8	60	59	8	6	60	61	10	3	< 4	1
14	2	70	71	12	3	61	61	9	5	33	33	8	7	63	64
10	10	108	111	11	6	33	33	10	4	134	138	9	6	49	48
12	8	67	67	12	5	7	6	11	3	13	12	10	5	71	73
14	4	55	55	13	2	12	10	9	7	15	15	11	4	5	5
14	6	30	27	10	9	8	7	10	6	31	32	10	7	15	15
12	10	31	31	11	8	25	23	11	5	< 5	2	9	8	27	28
				12	7	19	18	12	2	107	111	11	6	85	87
				13	4	6	2	12	4	14	12	12	5	29	27
2	1	31	42	14	1	42	43	9	9	33	33	10	9	10	9
3	2	28	26	14	3	21	22	10	8	31	33	13	4	39	40
4	3	122	122	13	6	25	25	11	7	27	27	11	8	< 5	6
5	2	156	161	14	5	8	7	13	3	38	38	12	7	23	21

plitudes are compared in Table 1. Final values of parameters and their estimated standard errors are given in Table 2.

INTERIONIC DISTANCES AND ANGLES

Interionic distances and angles, computed (Busing, Martin and Levy, 1964) from the final parameters (Table 2) are given in Table 3. The order

TABLE 2. FINAL PARAMETERS^a

	F ⁻	Na ⁺	Li ⁺	Al ³⁺
x	-0.02888 (10)	$\frac{1}{4}$	$\frac{3}{8}$	0
y	.04268 (9)	0	0	0
z	.13989 (8)	$\frac{1}{4}$	$\frac{1}{4}$	0
$\beta_{11} \times 10^5$	187 (11)	114 (12)	87 (37)	72 (9)
β_{22}	201 (10)	252 (11)	189 (30)	= β_{11}
β_{33}	114 (10)	= β_{22}	= β_{22}	= β_{11}
β_{12}	9 (6)	0	0	8 (3)
β_{13}	28 (5)	0	0	= β_{12}
β_{23}	-10 (5)	32 (8)	0	= β_{12}

^a (Estimated standard errors are in parentheses.)

TABLE 3. INTERATOMIC DISTANCES AND ANGLES

LiF ₄ tetrahedron	Li-F	(4) 1.846 (1)Å ^a
	F-F	(2) 2.863 (2)Å, (4) 3.087 (2)Å
	∠ F-Li-F	(2) 101.71 (07)°, (4) 113.48 (4)°
AlF ₆ octahedron	Al-F	(6) 1.807 (1)Å
	F-F	(6) 2.515 (2)Å, (6) 2.596 (2)Å
	∠ F-Al-F	(6) 88.20 (6)°, (6) 91.80 (6)°
NaF ₈ dodecahedron (distorted cube)	Na-F	(4) 2.351 (1)Å, (4) 2.544 (1)Å
	F-F ^b	(2) 2.863 (2)Å, (4) 2.515 (2)Å (4) 3.108 (2)Å, (2) 3.080 (3)Å (4) 3.605 (1)Å, (1) 3.906 (3)Å (1) 4.605 (3)Å
	∠ F-Na-F	(4) 61.69 (6)°, (2) 78.72 (4)° (4) 75.01 (6)°, (2) 74.52 (6)°
	Na-Al	(4) 3.388Å
	Na-Li	(2) 3.031Å, (4) 3.712Å
	Al-Li	(6) 3.388Å
	∠ Al-F-Li	(6) 136.10 (7)°
	∠ Al-F-Na	(6) 100.93(5)°, (6) 108.42 (6)°
	∠ Li-F-Na	(4) 91.64 (4)°, (4) 114.56 (6)°
	∠ Na-F-Na	(8) 98.54 (4)°

^a (Frequency of occurrence) distance or angle (estimated standard error).

^b These are the *edges* of the dodecahedron. The last three independent F-F distances are the diagonal *edges* of the "twisted cube". There are six other diagonals (not edges of the dodecahedron): (1) 3.906 (3)Å, (1) 4.065 (3)Å, (4) 4.361 (1)Å.

is analogous to that given in Table 3 of the paper by Lind and Geller (1969) on {Mn₃}[Fe₂](Ge₃)O₁₂. Estimated standard errors in Table 3 apply to the last digit of the distance or angle. In the discussion and abstract, *limits* of error are taken as three times the standard errors.

DISCUSSION

Cryolithionite is the only garnet reported to date that does not have oxygen as anion. Thus, this is the first report of precise Na⁺-F⁻, Li⁺-F⁻ and Al³⁺-F⁻ distances in a garnet structure. In all garnet structures refined to date, the tetrahedral cation-oxygen ion distance is substantially shorter than the octahedral cation-oxygen ion distance. In cryolithionite however, the (tetrahedral) Li⁺-F⁻ distance, 1.846 ± 0.003 Å, is longer than the (octahedral) Al³⁺-F⁻ distance, 1.807 ± 0.003 Å.

Very few structures of fluorides which involve the same coordinations of the cryolithionite cations have been refined to comparable precision. In fact, this author could find only one, that of Li₂BeF₄ (Burns and Gordon, 1966), which has tetrahedrally coordinated Li⁺. Average dis-

tances in two nonequivalent tetrahedra are $1.876 \pm 0.002 \text{ \AA}$ and $1.861 \pm 0.002 \text{ \AA}$. These are longer than the Li^+-F^- distance in cryolithionite. Shannon and Prewitt (1969) have shown that anions appear also to have somewhat different effective radii for different coordination. The coordination of an F^- ion is 4 in the garnet and 6 in Li_2BeF_4 . The difference in Li^+-F^- lengths, approximately 0.02 \AA on the average, is in agreement with the difference found by Shannon and Prewitt for the two coordinations.¹ (The Shannon-Prewitt (1969) radii sums, however, are actually all somewhat long; they give 1.84 , 1.90 and 2.47 \AA for $\text{Al}^{3+}-\text{F}^-$, Li^+-F^- and Na^+-F^- respectively, as compared with 1.807 , 1.846 and 2.448^2 \AA in the cryolithionite.)

Cryolithionite is the only known garnet in which the edges of the coordination octahedron are *both* shorter than the shorter of the two edges of the coordination tetrahedron. Cryolithionite and grossularite (Abrahams and Geller, 1958; Prandl, 1966) have the most nearly regular octahedra, but cryolithionite has the most irregular dodecahedron of any of the garnet structures refined thus far (see Table 3).

The low R -value attests to the cation distribution as given by the formula $\{\text{Na}_3\}[\text{Al}_2](\text{Li}_3)\text{F}_{12}$. Remaining individual discrepancies, between $|F_0|$ and $|F_c|$ such as for the (211), are not improved by changing this distribution. The thermal parameter values also support this distribution; one would expect the values for Al^{3+} to be higher³ if there were Li^+ ions in octahedral sites. This distribution is also supported by the interionic distances. It is unlikely that the *average* $\text{Al}^{3+}-\text{F}^-$ distance in an AlF_6 octahedron could be much shorter than 1.807 \AA . Any Li^+ replacement of the Al^{3+} would result in a longer octahedral cation-anion distance; *e.g.*, a 5% replacement would result in a lengthening close to 0.010 \AA .

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¹ In $\{\text{Mn}_3\}[\text{Fe}_2](\text{Ge}_3)\text{O}_{12}$ (Lind and Geller, 1969), the $\text{Ge}^{4+}-\text{O}^{2-}$ distance is longer than the average $\text{Ge}^{4+}-\text{O}^{2-}$ distance in quartz-type GeO_2 . This is also found in a comparison of $\text{Si}^{4+}-\text{O}^{2-}$ distances in garnets and in quartz. In quartz, the O^{2-} coordination is 2, and again observation is in line with the Shannon-Prewitt proposal.

² Average of the two Na^+-F^- distances (see Table 3).

³ Taking coordination into account, the values for Al^{3+} are, if anything, somewhat low in comparison with those for Na^+ .

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