

## Crystal Structure of $\text{Li}_3\text{ThF}_7$ Solved by X-Ray and Neutron Diffraction

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The crystal structure of  $\text{Li}_3\text{ThF}_7$  has been determined using both X-ray ( $T = 300$  K) and neutron ( $T = 5$  K) powder diffraction data, together with a X-ray single-crystal study ( $R = 0.039$ ,  $R_w = 0.042$ ).  $\text{Li}_3\text{ThF}_7$  is orthorhombic [space group  $Ccca$  (No. 68)],  $a = 8.7885(3)$ ,  $b = 8.7686(3)$ , and  $c = 12.958(1)$  at  $T = 300$  K (X-ray powder data). In this compound,  $\text{Li}^+$  octahedra build up double layers with a defect NaCl arrangement. Two double layers are connected by vertices.  $\text{Th}^{4+}$  are inserted between these double layers and are ninefold coordinated. © 1989 Academic Press, Inc.

### Introduction

$\text{Li}_3\text{ThF}_7$  was first isolated by Thoma and co-workers (1). Its pattern was tentatively indexed in a tetragonal cell (2) (space group  $P4/nmm$  or  $P4/n$ ) with parameters listed in Table I. Further, a complete single-crystal structure determination, carried out by Cousson and co-workers (3) using space group  $P4/ncc$ , was the subject of controversy. Indeed, from the anomalous Li-Li distances and valence bond analysis (4),

Pauling immediately claimed that the lithium positions proposed by Cousson "are certainly wrong" (5); Pauling thought that the space group was doubtful and that "the lithium atoms perhaps occupy a larger number of equivalent positions with some randomness." He did not succeed however in finding a satisfactory solution.

The lack of accurate structural data forbids any interpretation of the  $\text{Li}^+$  conduction properties of  $\text{Li}_3\text{ThF}_7$  above 500 K (6). We have therefore undertaken a full determination of its crystal structure. The joint use of powder neutron diffraction at 5 K and powder and single-crystal X-ray dif-

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TABLE I  
CELL PARAMETERS AND SPACE GROUPS PROPOSED FOR  $\text{Li}_3\text{ThF}_7$

<i>a</i>	<i>b</i>	<i>c</i>	Space group	Technique	Refs.
6.206(6)	6.206(6)	6.470(2)	<i>P4/nmm</i> or <i>P4/n</i>	Debye–Scherrer film	(2)
6.206(2)	6.206(2)	12.940(5)	<i>P4/ncc</i>	X-ray single crystal	(3)
8.7885(3)	8.7686(3)	12.958(1)	<i>Ccca</i>	X-ray powder diffraction ( <i>T</i> = 300 K) <sup>a</sup>	This work
8.7590(2)	8.7280(2)	12.8956(3)	<i>Ccca</i>	Neutron diffraction ( <i>T</i> = 5 K)	This work
8.7885(1)	8.7685(1)	12.958(2)	<i>Ccca</i>	X-ray single crystal ( <i>T</i> = 300 K) <sup>b</sup>	This work

<sup>a</sup> W as internal standard.

<sup>b</sup> Calibrated with a Ge sphere.

fraction at 300 K was necessary to determine the true symmetry and the  $\text{Li}^+$  positions of  $\text{Li}_3\text{ThF}_7$ .

### Experimental and Data Analysis

Single crystals were grown using the flux method described by Cousson *et al.* (7), or by a long heating (1 month) of the mixture 3  $\text{LiF}$  + 1  $\text{ThF}_4$  at 550°C. Powder samples, prepared in the same way, were always contaminated by small amounts of  $\text{LiTh}_2\text{F}_9$ .

In order to locate the lithium ions, a neutron diffraction pattern of  $\text{Li}_3\text{ThF}_7$  was first recorded at 5 K on the D1A diffractometer of Institut Laue-Langevin (Grenoble) using a wavelength of 1.9107 Å. The sample (15 g) was contained in a cylindrical vanadium can (diameter 15 mm) held in a vanadium-tailed liquid helium cryostat.

Attempts to refine the structure in the *P4/ncc* space group with Cousson's positions failed. Indeed, the observed and calculated patterns were in very good agreement within the range  $6^\circ < 2\theta < 86^\circ$ , but they did not coincide for upper  $2\theta$  values (Fig. 1): some peaks exhibited a splitting at these large angles and could not be indexed in *P4/*

*ncc* or in any other tetragonal space group (Fig. 2a).

This could be due to a phase transition at low temperature. In order to check the validity of such a hypothesis, an X-ray powder diffraction pattern was then recorded at room temperature on a Siemens D501 diffractometer with back-monochromatized  $\text{CuK}\alpha$ . The sample was passed through a 63- $\mu\text{m}$  sieve, and the method of filling the sample holder described in (8) was used in

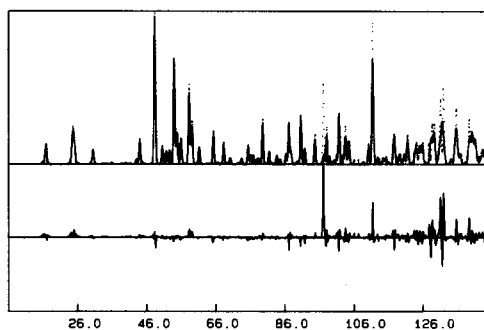


FIG. 1. Observed and calculated neutron diffraction pattern with Cousson's positions. The difference pattern, at the same scale, shows the problem at  $2\theta$  up to  $86^\circ$ .

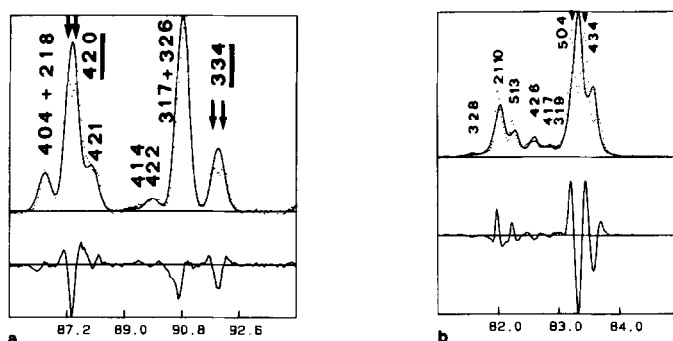


FIG. 2. (a) Splitting of some peaks [(4 2 0) and (3 3 4) reflections] at high angle in the neutron pattern ( $T = 5$  K). (b) Characteristic splitting in the X-ray diffraction pattern. Note the difference between observed and calculated pattern.

order to avoid possible preferential orientation. At  $2\theta > 83^\circ$ , the splitting, previously observed with the neutrons, also occurs with X-rays (Fig. 2b), and rules out any phase transition between room temperature and 5 K. The splitting of some peaks at high angles may be due, for instance, to an orthorhombic symmetry with a very small difference between the  $a$  and  $b$  parameters in the Cousson's cell. With this hypothesis, it is however impossible to generate two  $hkl$  for the (3 3 4) reflection. To justify its splitting, it was necessary to use parameters oriented at  $45^\circ$  from those of Cousson; this leads to a doubling of the volume of the cell (Table I). In this new orthorhombic cell, the conditions limiting possible reflections are then consistent with the space group  $Ccca$  (No. 68).

In order to verify these data, a colorless single crystal was selected by optical examination. Data, collected on an AED2 Siemens-Stoe four-circle diffractometer, confirm the powder results using high-angle reflections. Some experimental data and characteristics of the measurement are summarized in Table II. The intensities were corrected from Lorentz-polarization effects and absorption (Gaussian method). Ionic scattering factors and anomalous dispersion parameters were taken from "In-

ternational Tables for X-Ray Crystallography" (9). In the space group  $Ccca$ , application of the fast automatic centrosymmetric direct-method facilities of the

TABLE II  
CONDITIONS OF INTENSITY DATA COLLECTION  
AND REFINEMENT

Symmetry: Orthorhombic
Systematic extinctions:
$hkl: h + k = 2n$
$0kl: l = 2n$ ( $k = 2n$ )
$h0l: l = 2n$ ( $h = 2n$ )
$hk0: h = 2n$ ( $k = 2n$ )
$h00: h = 2n$
$0k0: k = 2n$
$00l: l = 2n$
Space group: No. $Ccca$
Crystal size: $0.038 \times 0.144 \times 0.152$ mm
Radiation: $MoK\alpha$ ( $\lambda = 0.71069$ Å)
Scan mode: $\omega$ - $2\theta$ with profile fitting data collection
Step scan range: $1.0045 + 0.0028 \text{ tg}(\theta)$
Detector aperture: 3 mm
$\theta_{\max}$ : $45^\circ$
Lattice constants refined from 34 reflections (see Table I)
Range of measurement: $-16 < h < 16$
$0 < k < 16$
$0 < l < 24$
Standard reflections: 3 (measured every 4500 sec)
1 -3 2
3 -1 2
3 -1 -4
Intensity variation max: 3%
Reflections measured: 4217 (without standards)
Reflections rejected: $[\sigma(I)/I > 0.33]$ : 1096
independent reflections: 1922
$R_{\text{int}} = 4.70$
Absorption coefficient: $309.1 \text{ cm}^{-1}$
Transmission factors: $A_{\max} = 0.320$ ; $A_{\min} = 0.056$
$F$ magnitudes used in least-squares refinement

TABLE III  
REFINED ATOMIC COORDINATES AND THERMAL PARAMETERS OF Li<sub>3</sub>ThF<sub>7</sub> (SINGLE-CRYSTAL DATA)

Atom	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>	B <sub>eq</sub> (Å <sup>2</sup> )
Th	$\frac{1}{4}$	0	0.1889(0)	69(1)	75(1)	59(1)	0	0	7(1)	0.54(1)
F1	$\frac{1}{4}$	0	0.3718(4)	183(22)	140(20)	117(15)	0	0	42(20)	1.2(2)
F2	0.0632(4)	0.0995(5)	0.5772(2)	134(15)	173(16)	147(12)	29(13)	-8(11)	-7(13)	1.2(1)
F3	0.1496(5)	0.3125(4)	0.4212(3)	171(15)	137(16)	182(13)	64(13)	42(13)	20(13)	1.3(1)
F4	0	0.4364(6)	$\frac{1}{4}$	85(19)	165(24)	218(22)	0	-60(17)	0	1.2(2)
F5	0.3153(6)	$\frac{1}{4}$	$\frac{1}{4}$	142(22)	166(24)	222(22)	-36(21)	0	0	1.4(2)
Li1	0.354(2)	0.186(2)	0.431(1)	262(37)	K = $\frac{2}{3}$					2.1(3)
Li2	0.067(2)	0.099(2)	0.419(1)	250(33)	K = $\frac{2}{3}$					2.0(3)

Note. Standard deviations are given in parentheses and refer to the last digit.  $U_{ij}$  are multiplied by 10<sup>4</sup>. The  $U_{ij}$  relate to the expression:  $T = \exp[-2\pi^2(h^2a^*U_{11} + \dots + 2kh^*c^*U_{23})]$ .

SHELX76 program (10) gave the position of thorium atom. After a least-squares refinement and a Fourier difference, the five fluorine sites appear. With anisotropic thermal parameters for thorium and F<sup>-</sup>, the  $R$  values are respectively  $R = 4.80(\%)$  and  $R_w = 5.57(\%)$ . Addition of the two lithium sites further determined from neutron data (see below) led to  $R = 3.93(\%)$  and  $R_w = 4.23(\%)$ . Final atomic coordinates and thermal parameters are listed in Table III. Some characteristic distances are given in Table V.

Starting from the X-ray-refined positions

of Th<sup>4+</sup> and F<sup>-</sup> (single crystal), the 5 K neutron diffraction pattern was then analyzed by the classical Rietveld method (11) as modified by Hewat (12). Nuclear scattering lengths were taken from Koester and Rauch (13). The conventional reliability factors were  $R_1 = 19.89(\%)$ ,  $R_p = 22.98(\%)$ , and  $R_{wp} = 26.09(\%)$ . A Fourier difference map showed two strong negative peaks corresponding to two lithium sites. Refinement (Table IV) of their coordinates and occupancy factor [0.75(3)] led to a very significant drop of the  $R$  values:  $R_1 = 7.30(\%)$ ,  $R_p = 11.52(\%)$ ,  $R_{wp} = 13.46(\%)$ ,  $R_{exp} =$

TABLE IV  
REFINED ATOMIC COORDINATES AND THERMAL PARAMETERS OF Li<sub>3</sub>ThF<sub>7</sub> FROM THE 5 K NEUTRON DIFFRACTION DATA

Atom	x	y	z	B <sub>eq</sub> (Å <sup>2</sup> )	
Th	$\frac{1}{4}$	0	0.1892(1)	0.31(3)	
F1	$\frac{1}{4}$	0	0.3742(3)	1.65(7)	
F2	0.0610(4)	0.0973(4)	0.5796(4)	1.35(8)	
F3	0.1476(4)	0.3106(4)	0.4224(4)	1.25(7)	
F4	0	0.4341(5)	$\frac{1}{4}$	1.14(9)	
F5	0.3152(5)	$\frac{1}{4}$	$\frac{1}{4}$	1.12(9)	
Li1	0.338(1)	0.179(1)	0.423(1)	1.2(1)	K = $\frac{2}{3}$ (3)
Li2	0.056(1)	0.103(1)	0.431(1)	1.2(1)	K = $\frac{2}{3}$ (3)

Note. Standard deviations are given in parentheses and refer to the last digit.

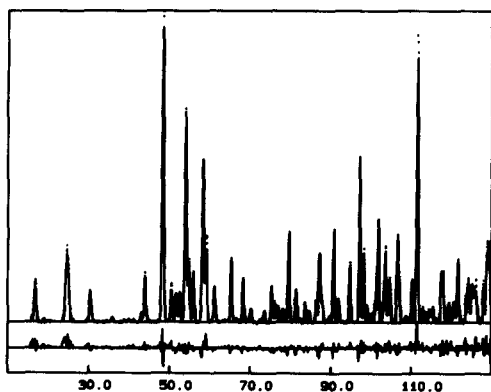


FIG. 3. Observed and calculated neutron diffraction pattern in *Ccca* space group.

1.57(%). These high *R* values have three origins:

- the presence of  $\text{LiTh}_2\text{F}_9$  impurity;
- an important absorption effect;
- a preferential orientation along the  $[0\ 0\ 1]$  direction.

The observed and calculated neutron diffraction patterns are presented in Fig. 3 and characteristic distances in Table V.

The lost of tetragonal symmetry is principally due to the *z* coordinates of lithium atoms (and to a much lower extent to the *x* and *y* coordinates), which deviate significantly (more than 5 e.s.d.) from the real positions related by the  $\bar{4}$  axis in Cousson's cell.

### Description of the Structure

The  $[0\ 0\ 1]$  and  $[0\ 1\ 0]$  projections of the structure are shown in Figs. 4 and 5, respectively.  $\text{Li}^+$ , distributed at random on three-fourths of the corresponding crystallographic sites, are in a distorted octahedral coordination with one distance significantly longer than the others (Table IV). Within the  $(0\ 0\ 1)$  planes, these octahedra share edges and form layers which can be related to a defect NaCl structure (Fig. 4, empty

TABLE V  
INTERATOMIC DISTANCES (Å) IN  $\text{Li}_3\text{ThF}_7$

	Neutron (5 K) [powder]	X-ray (300 K) [single crystal]
<b>Li1 octahedron</b>		
Li1-F1	1.85(1)	2.01(2)
Li1-F2	2.08(1)	1.99(2)
Li1-F2	2.14(1)	2.02(2)
Li1-F3	1.99(2)	1.92(2)
Li1-F3	2.03(1)	2.11(2)
Li1-F5	2.33(2)	2.43(2)
$\langle \text{Li1-F} \rangle$	2.071	2.083
<i>d</i> Shannon = 2.07 [Ref. (14)]		
<b>Li2 octahedron</b>		
Li2-F1	2.05(2)	1.93(2)
Li2-F2	1.92(2)	2.04(2)
Li2-F2	2.03(2)	2.09(2)
Li2-F3	1.94(1)	2.00(2)
Li2-F3	1.99(1)	2.06(2)
Li2-F4	2.40(2)	2.30(2)
$\langle \text{Li2-F} \rangle$	2.056	2.069
<b>Thorium polyhedron</b>		
Th-F1	2.386(4)	2.370(5)
Th-F2	2 × 2.337(4)	2.356(3)
Th-F3	2 × 2.368(6)	2.349(3)
Th-F4	2 × 2.396(1)	2.401(2)
Th-F5	2 × 2.388(2)	2.400(1)
$\langle \text{Th-F} \rangle$	2.374	2.376
<i>d</i> Shannon = 2.40		

Note. Standard deviations are given in parentheses.

octahedra). The vacancy (Fig. 4) is surrounded by four tetrameric units of edge-sharing octahedra, which exhibit a cyclic shear around the vacancy. The same phenomenon was recently observed with cubes instead of octahedra in  $\text{La}_2\text{Pd}_2\text{O}_5$  (15).  $\text{Th}^{4+}$  ions project on the vacancy and adopt the already described ninefold coordination, corresponding to a monocapped tetragonal antiprism. The layers of  $\text{Li}^+$  octahedra, all identical, are connected in two ways. By edge sharing (hatched octahedra of Figs. 4 and 5), they build up double layers very similar to those existing in the rocksalt structure. These double layers are linked

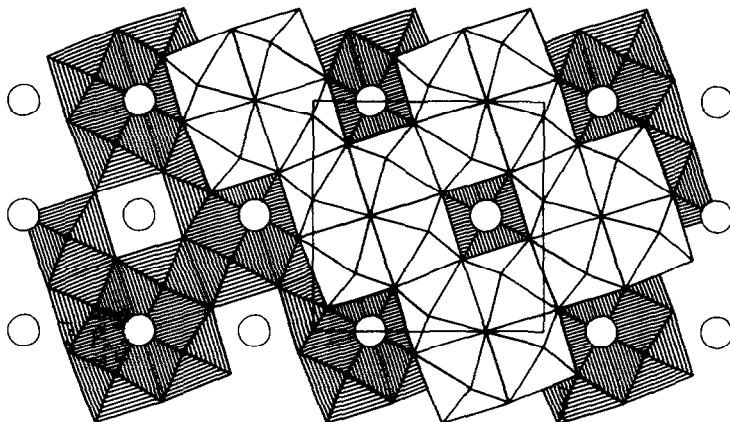


FIG. 4. [0 0 1] view of  $\text{Li}_3\text{ThF}_7$ . White and shaded octahedra correspond respectively to lithium in  $z = 0.57$  and  $z = 0.43$ .

together by corners (Fig. 5) and thorium atoms are inserted between two double layers. This time, a valence bond analysis (16) is in very good agreement with the observed structure (Table VI).

The occupancy factor of  $\frac{3}{4}$  on each  $\text{Li}^+$  site with a random distribution confirms the hypothesis of Pauling (5) and explains the possibility of ionic conduction by  $\text{Li}^+$  at high temperature, already evidenced by  $^7\text{Li}$

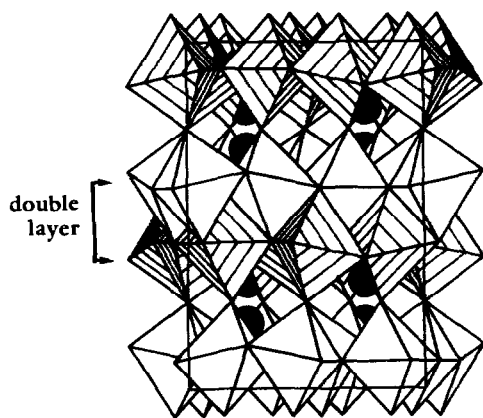


FIG. 5. [0 1 0] view of  $\text{Li}_3\text{ThF}_7$ . The white and shaded octahedra correspond respectively to lithium in  $z = 0.07$ ,  $z = 0.57$  and  $z = 0.43$ ,  $z = 0.93$ .

NMR measurement (6). The problem now is to find the conduction pathways. A neutron thermodiffraction study is planned at Grenoble to determine them.

TABLE VI  
VALENCE BOND ANALYSIS (16) OF  $\text{Li}_3\text{ThF}_7$  USING  
BROWN-SHANNON'S LAW FOR Li AND  
ZACHARIASEN'S LAW FOR Th<sup>b</sup>  
(NEUTRON DATA,  $T = 5$  K)

	Li1	Li2	Th	$\Sigma^c$	$\Sigma_{\text{exp}}$
F1	$[0.24] \times 2$	$[0.16] \times 2$	$[0.43]$	1.03	1
F2	$[0.16]$	$[0.21]$	$[0.49]$	1.00	1
	$[0.14]$	$[0.17]$	$[0.49]$		
F3	$[0.18]$	$[0.20]$	$[0.45]$	1.00	1
	$[0.17]$	$[0.18]$	$[0.45]$		
F4		$[0.09] \times 2$	$[0.42]$	0.97	1
			$[0.42]$		
F5	$[0.10] \times 2$		$[0.43]$	1.00	1
			$[0.43]$		
$\Sigma$	0.99	1.01	4.01		
$\Sigma_{\text{exp}}$	1	1	4		

<sup>a</sup>  $S_{\text{Li}} = (d/1.288)^{-3.9}$  (from (17)).

<sup>b</sup>  $S_{\text{Th}} = \exp\{(2.049-d)/0.40\}$  (18).

<sup>c</sup> The sum corresponds to the bond strength given by Th plus 0.75 times the sum of bond strengths given by all the Li surrounding a given  $\text{F}^-$  (in order to take into account the occupancy factor of 0.75 on Li sites).

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