

Structure of Lithium Tetrafluoroindate

BY P. GRAVEREAU, J. P. CHAMINADE, T. GAUSDANG, J. GRANNEC, M. POUCHARD AND P. HAGENMULLER

Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, 351 cours de la Libération, 33405 Talence CEDEX, France

(Received 1 August 1991; accepted 10 October 1991)

Abstract. LiInF_4 , $M_r = 197.75$, orthorhombic, $Pbcn$, $a = 4.752$ (1), $b = 11.721$ (4), $c = 4.971$ (1) Å, $V = 276.9$ (2) Å³, $Z = 4$, $D_m = 4.67$, $D_x = 4.74$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 8.35$ mm⁻¹, $F(000) = 352$, $T = 298$ K, $R = 0.0144$ for 568 independent reflections with $I > 3\sigma(I)$. The three-dimensional network consists of $(\text{InF}_4)_n^{4-}$ layers formed by InF_6 corner-sharing octahedra perpendicular to the b axis and connected by Li^+ ions forming $(\text{LiF}_4)_n^{3-}$ chains running along the c direction. The chains are built up by LiF_6 octahedra sharing common edges. This structure appears to be a new structure type within the AMF_4 compounds.

Introduction. Attention has recently been paid to transparent crystals containing a large amount of ¹¹⁵In for the detection of low-energy solar neutrinos according to Raghavan's reaction (Raghavan, 1976; Gonzalez-Mestres & Perret-Gallix, 1988, 1989). An initial investigation was devoted to crystal growth of Tb^{3+} -doped InBO_3 (Chaminade, Garcia, Pouchard, Fouassier, Jacquier, Perret-Gallix & Gonzalez-Mestres, 1990). Research into other indium-rich lattices led us to investigate the so far largely neglected fluorine chemistry of this element. One of us has prepared a great number of fluorides in the systems $MF-\text{InF}_3$ ($M = \text{Li, Na, K}$) (Grannec, Champarnaud & Portier, 1970) and $MF_2-\text{InF}_3$ ($M = \text{Ca, Sr, Ba}$) (Grannec & Ravez, 1970). Of these compounds, LiInF_4 appeared to be a possible candidate for neutrino detection as it contained 58% In.

A preliminary study revealed a reversible phase transition and an incongruent melting point, *i.e.* phenomena which did not favour the preparation of large-size crystals of LiInF_4 . Despite these drawbacks small single crystals have been obtained and it seemed worthwhile to investigate their structural features. The present work is devoted to the crystal structure determination of LiInF_4 .

Experimental. LiInF_4 was prepared by solid-state reaction from stoichiometric mixtures of InF_3 and LiF . The starting fluorides were mixed in a dry glove box and introduced into gold tubes before outgassing at 423 K and filling with dry argon. After sealing

and reaction at 853 K for 15 h, single crystals were obtained by heating to 943 K followed by slow cooling to 473 K (3 K h⁻¹). The D_m value was obtained by hydrostatic pressure measurements.

Translucent colourless single crystal with a parallelepipedic shape: $\{101\}$ ($120 \times 120 \mu\text{m}$) and $\{010\}$ ($70 \mu\text{m}$) crystal-form planes. Orthorhombic symmetry determined with Laue, Weissenberg and precession photographs. Cell parameters refined with 18 reflections ($6 < \theta < 28^\circ$) from an X-ray powder diffraction pattern (graphite-monochromated $\text{Cu } K\alpha$ radiation and NaCl as internal standard). Data collection with an Enraf-Nonius CAD-4 diffractometer; graphite-monochromated Mo $K\alpha$ radiation, ω scan; 6742 reflections; $(\sin \theta)/\lambda < 0.90$ Å⁻¹, $-8 \leq h \leq 8$, $-21 \leq k \leq 21$, $-8 \leq l \leq 8$; scan width $(1.20 + 0.35 \tan \theta)^\circ$; counter slit width $(2.00 + 2.00 \tan \theta)$ mm. Three standard reflections remeasured every 6 h with no systematic variation observed and with $\sigma(I)/\langle I \rangle < 0.04$. Data corrected for Lorentz-polarization effects and for absorption using *SHELX76* (Sheldrick, 1976), crystal shape and size, and incident- and diffraction-beam direction cosines ($0.431 < T < 0.577$). Equivalent reflections for which $I/\sigma(I) > 3$ were averaged to give 568 unique reflections ($R_{\text{int}} = 0.025$). Systematic absences $k = 2n + 1$ for $0kl$, $l = 2n + 1$ for $h0l$ and $h + k = 2n + 1$ for $hk0$ consistent with space group $Pbcn$. 13 inconsistencies, but for the seven strongest ones [$4 < I/\sigma(I) < 11$] ψ scans showed that they are due to Renninger double reflections. Atomic scattering for Li^+ , In^{3+} and F^- and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Structure solved by heavy-atom methods with *SHELX76* on an IBM 3090-400 computer of the Computing Center of Montpellier. In-atom sites found by Patterson-function deconvolution ($R = 0.17$), and F and Li atoms located with several difference Fourier syntheses. Calculations (on F) with individual isotropic thermal parameters, a weighting scheme $w = 1/\sigma^2(F_o)$ and an empirical isotropic extinction parameter x [$F_c = F(1 - 10^{-4}x^2/\sin \theta)$] converged to $R = 0.028$, $wR = 0.043$. The structure refined to $R = 0.014$ and $wR = 0.031$ with

Table 1. Atomic parameters and equivalent isotropic temperature factors (\AA^2) with e.s.d.'s in parentheses
$$B_{\text{eq}} = (8\pi^2/3) \sum_{i=1}^3 \sum_{j=1}^3 a_i^* a_j^* U_{ij} a_i a_j$$

	Site	Position	symmetry	x	y	z	B_{eq}
Li	4(c)	.2	0	0.0561 (7)	$\frac{1}{4}$	$\frac{1}{4}$	1.14 (11)†
In	4(c)	.2	0	0.33113 (2)	$\frac{1}{4}$	$\frac{1}{4}$	0.490 (5)
F(1)	8(d)	1	0.2620 (3)	0.4423 (2)	0.4308 (4)	0.96 (5)	
F(2)	8(d)	1	0.2272 (4)	0.1928 (2)	0.4199 (4)	0.88 (5)	

† B_{iso} .Table 2. Selected distances (\AA) and angles ($^\circ$) in LiInF_4 with e.s.d.'s in parentheses

Li—F(1 ^u)	2 × 1.949 (7)	In—F(1)	2 × 2.014 (2)
Li—F(1 ^h)	2 × 1.966 (7)	In—F(2)	2 × 2.123 (2)
Li—F(2)	2 × 2.109 (7)	In—F(2')	2 × 2.110 (2)
F(1 ^h)—Li—F(1 ^h)	88.2 (3)	F(1)—In—F(1')	99.4 (1)
F(1 ^h)—Li—F(1 ^u)	178.9 (3)	F(1)—In—F(2)	90.1 (1)
F(1 ^h)—Li—F(1 ^u)	92.6 (3)	F(1)—In—F(2')	93.1 (1)
F(1 ^h)—Li—F(2)	91.2 (3)	F(1)—In—F(2 ^h)	96.8 (1)
F(1 ^h)—Li—F(2')	87.9 (3)	F(1)—In—F(2')	170.4 (1)
F(1 ^u)—Li—F(1 ^h)	94.6 (3)	F(2)—In—F(2')	84.0 (1)
F(1 ^u)—Li—F(2)	173.2 (3)	F(2)—In—F(2 ^h)	84.4 (1)
F(1 ^u)—Li—F(2')	92.2 (3)	F(2)—In—F(2')	80.4 (1)
F(2)—Li—F(2')	81.1 (3)	F(2)—In—F(2 ^h)	164.7 (1)

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $x - \frac{1}{2}, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$; (iv) $\frac{1}{2} - x, y - \frac{1}{2}, z$; (v) $-x, y, \frac{1}{2} - z$.

anisotropic thermal factors for In and F atoms; 27 parameters refined; $S = 1.348$; extinction parameter $x = 0.0027$ (6); max. shift/e.s.d. in last cycle < 0.02 ; residual electron density between 1.9 (near In atoms) and $-1.2 e \text{\AA}^{-3}$. The final atomic parameters are given in Table 1. Selected bond lengths and angles are listed in Table 2.*

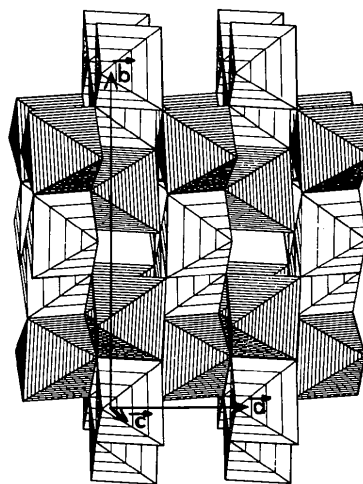
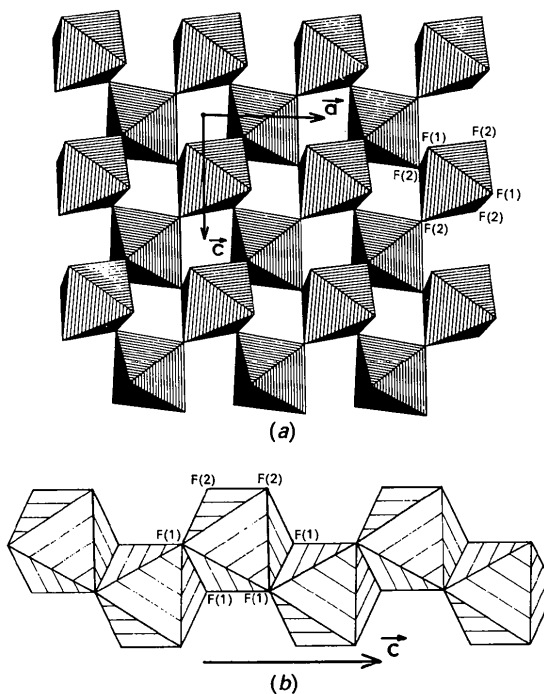
Discussion. The drawings were made using the *STRUPLO* program (Fischer, 1985). The lattice consists of a three-dimensional framework made up of InF_6 and LiF_6 octahedra (Fig. 1). It can be described as $(\text{InF}_4)_n^{n-}$ layers of tilted InF_6 octahedra perpendicular to the b axis, each octahedron sharing four corners with four surrounding octahedra in the sheets. The two free fluorine corners occupy *cis* positions on each InF_6 octahedron. The corresponding edge is located on the opposite edge for the four surrounding octahedra, leading to tilting of the $(\text{InF}_4)_n^{n-}$ layer (Fig. 2a).

Such layers are associated by Li^+ ions forming chains of LiF_6 octahedra running along the c direction. Each chain of formula $(\text{LiF}_4)_n^{3n-}$ is formed by

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54739 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU0320]

LiF_6 octahedra with a common F(1)—F(1) edge (Fig. 2b). $(\text{InF}_4)_n^{n-}$ layers and $(\text{LiF}_4)_n^{3n-}$ chains are connected by the common F(2)—F(2) edge and common F(1) corners.

This description allows the two fluorine atoms F(1) and F(2) to be distinguished: the cationic environment of F(1) comprises one In^{3+} and two Li^+ ions, whereas F(2) is linked to one Li^+ and two In^{3+} .

Fig. 1. Perspective view of LiInF_4 showing both the In octahedra (heavily hatched) and the Li octahedra (lightly hatched).Fig. 2. (a) (101) projection of the $(\text{InF}_4)_n^{n-}$ layers. (b) $(\text{LiF}_4)_n^{3n-}$ chain running along the c axis.

As shown in Table 2, the In—F distances vary from 2.014 to 2.123 Å with $\langle \text{In—F} \rangle = 2.082$ Å. In contrast, a wider range of bond lengths is observed for the LiF_6 octahedra owing to weaker bonds (the Li—F distances are between 1.949 and 2.109 Å, $\langle \text{Li—F} \rangle = 2.008$ Å). Nevertheless, the angular dispersion is larger in the InF_6 ($\Delta = 19^\circ$) than in the LiF_6 octahedra ($\Delta = 13.5^\circ$).

This framework is a new structural type in the AMF_4 family (Babel & Tressaud, 1985). A recent report has pointed out a relationship between the LiCoF_4 - and NaCoF_4 -type structures (Lacorre, Pannetier, Averdunk, Hoppe & Ferey, 1989). Similarities have been found either with the rutile-type structure or with perovskite-type layers, thus leading to two possible descriptions for LiCoF_4 : (a) a dirutile-type structure consisting of an alternation of edge-sharing $(\text{CoF}_6)^{3-}$ and $(\text{LiF}_6)^{5-}$ octahedra along the [101] direction of the monoclinic cell; or (b) $(\text{CoF}_4)_n^-$ perovskite-type sheets of tilted corner-sharing octahedra, between which Li^+ ions are inserted. For LiInF_4 : (a) the $(\text{InF}_4)_n^-$ layers can be idealized as

rutile-type sheets with free edges alternatively up and down ($a_{\text{R}} = a$, $b_{\text{R}} = c$); and (b) the $(\text{LiF}_4)_n^{3-}$ chains represent a zigzag staking of LiF_6 octahedra similar to that found in the α - PbO_2 -type structure.

References

- BABEL, D. & TRESSAUD, A. (1985). *Inorganic Fluorides*, edited by P. HAGENMULLER, pp. 77–203. New York: Academic Press.
- CHAMINADE, J. P., GARCIA, A., POUCHARD, M., FOUASSIER, C., JACQUIER, B., PERRET-GALLIX, D. & GONZALEZ-MESTRES, L. (1990). *J. Cryst. Growth*, **99**, 799–804.
- FISCHER, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.
- GONZALEZ-MESTRES, L. & PERRET-GALLIX, D. (1988). *Ann. Phys.* **3**, 181–186.
- GONZALEZ-MESTRES, L. & PERRET-GALLIX, D. (1989). In *Neutrons 88*, Boston. Singapore: World Scientific.
- GRANNEC, J., CHAMPARNAUD, J. C. & PORTIER, J. (1970). *Bull. Soc. Chim. Fr.* **11**, 3862–3864.
- GRANNEC, J. & RAVEZ, J. (1970). *C. R. Acad. Sci.* **270**, 2059–2061.
- LACORRE, P., PANNETIER, J., AVERDUNK, F., HOPPE, R. & FERREY, G. (1989). *J. Solid State Chem.* **79**, 1–11.
- RAGHAVAN, R. S. (1976). *Phys. Rev. Lett.* **37**, 259–262.
- SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1992). **C48**, 771–773

Structure of Europium Zirconium Selenide, EuZrSe_3

BY ARTHUR MAR AND JAMES A. IBERS*

Department of Chemistry and Science and Technology Center for Superconductivity, Northwestern University, Evanston, IL 60208-3113, USA

(Received 12 July 1991; accepted 2 October 1991)

Abstract. EuZrSe_3 , $M_r = 480.07$, orthorhombic, $Pnma$, $a = 8.849$ (2), $b = 3.937$ (1), $c = 14.348$ (5) Å, $V = 499.9$ (2) Å³, $Z = 4$, $D_x = 6.38$ g cm⁻³, $\lambda(\text{Mo } K\alpha_1) = 0.7093$ Å, $\mu = 359.6$ cm⁻¹, $F(000) = 805$ (including anomalous dispersion), $T = 294$ K, $R(F^2) = 0.096$ for 973 averaged reflections (including those having $F_o^2 < 0$) and $R(F) = 0.037$ for 593 reflections having $F_o^2 > 3\sigma(F_o^2)$. The structure of EuZrSe_3 consists of columns of double edge-sharing Zr octahedra. These columns are linked together by Eu bicapped trigonal prisms.

Introduction. The phase Ln_2MQ_5 (Ln = rare earth; $M = \text{Zr, Hf}$; $Q = \text{S, Se}$) exists for most rare earths with the exception of Eu (Cherkasova & Serebrennikov, 1977; Donohue & Jeitschko, 1974; Jeitschko & Donohue, 1975; Kohno & Serebrennikov, 1977). By virtue of the high stability of its divalent state, Eu

forms the phases EuZrS_3 and EuHfS_3 , which adopt a distorted perovskite structure of the GdFeO_3 type (Kazarbina, Maksimov & Serebrennikov, 1981; Lelieveld & IJdo, 1980; Serebrennikov, Senova & Cherkasova, 1979). As part of a general program to elucidate new ternary chalcogenides, we report here the structure of a new ternary selenide, EuZrSe_3 . EuZrSe_3 belongs to the NH_4CdCl_3 structure type (Muller & Roy, 1974), a class of compounds ABX_3 that are differentiated primarily by the coordination number of the large A cation, which can vary from CN3 to CN9. In this respect, the intermediate coordination of Eu (CN8) represents a bridge between the two extremes exhibited by this structure type. This relationship is discussed in more detail below.

Experimental. The compound EuZrSe_3 resulted from a reaction of elemental powders ground together in an atomic ratio of $\text{Eu:Zr:Se} = 1:2:5$ (Eu, 26 mg,

* To whom correspondence should be addressed.