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Effect of Temperature on Interatomic Distances in Pyroelectric α-$LiIO_3$

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Abstract

The crystal structure of α-$LiIO_3$ (space group $P6_3$) has been refined from neutron and X-ray diffraction data at different temperatures between room temperature and 525 K. The Li atom is well located even at temperatures close to the α → γ phase transition and its thermal parameters do not exhibit any anomalous behaviour. The thermal expansion is analysed in terms of IO_3-group rotations and expansion of LiO_6 octahedra; the role of the iodine lone pair in the packing of iodate structures is discussed. The spontaneous polarization is calculated on the basis of a simple point-charge model and the calculated pyroelectric coefficient P_3 is found to be in fair agreement with the experimental value.

Introduction

Although the room-temperature (RT) structure of α-$LiIO_3$ has been extensively studied by X-ray (Rosenzweig & Morosin, 1966; de Boer, van Bolhuis, Olthof-Hazekamp & Vos, 1966) and neutron diffraction (Emiraliev, Kocharov, Yamzin & Lyubimtsev, 1976), little is known about its modifications at higher temperatures. Among the pecularities which are not yet understood are the structural mechanism of the Li^+ conduction and the differences in the sequence of phase transitions between single crystals and powders: indeed, single crystals usually transform directly from α- to β-$LiIO_3$ whereas powdered samples transform from α- to β-$LiIO_3$ through an intermediate, orthorhombic γ-$LiIO_3$ whose structure is still unknown.

As part of an extensive program of research on the structures and physical properties of the three phases of lithium iodate, we report in this paper a structural investigation of α-$LiIO_3$ at four different temperatures (RT, 373, 475 and 525 K). Consequently, the thermal expansion, the lone pair and the pyroelectric coefficient are also discussed.

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Experimental

The α-$LiIO_3$ single crystal used for neutron diffraction (size 2 × 2 × 6 mm) was grown by slow evaporation of an aqueous solution of $^7LiIO_3$ at pH = 6 and $T = 318$ K. The crystals used for the X-ray diffraction experiment were grown in a similar way from a natural lithium iodate solution (size 0·2 × 0·2 × 0·45 mm); powders were prepared from these crystals. All crystals show the characteristic morphology previously described by Rosenzweig & Morosin (1966).

The powder diffraction patterns were recorded on the D1A high-resolution diffractometer of the ILL with $\lambda = 1{\cdot}3885$ (3) and 1·9066 (3) Å, the wavelength being calibrated with a Ni powder standard ($a = 3{\cdot}5238$ Å). The powdered sample was inserted in a cylindrical vanadium container (∅ = 15 mm). The heating device was a conventional furnace with a vanadium heater working under low helium pressure. The temperature was measured with a Ni–Cr thermocouple in contact with the sample holder. Data were collected from $2\theta =$ 10° to 160° in steps of 0·05°. Measurement times were about 15 s (1·91 Å) and 30 s (1·39 Å) per step. The data of the 10 counters were summed using a conventional ILL Program (Hewat, 1978). The *RIETVELD* program (Rietveld, 1969) as modified by Hewat (1973) was used for the profile-fitting structure refinement. The thermal parameters were corrected for absorption ($\mu R = 0{\cdot}42$) according to Hewat (1979) (correction to be divided by 2) ($\mu = 0{\cdot}55$ cm^{-1}).

Single-crystal neutron experiments were performed at room temperature, 373 and 475 K on the D9 four-circle diffractometer located on the hot source of the ILL. Data were collected with a wavelength of 0·5499 (3) Å. The crystal was mounted in a small aluminium furnace (kindly provided by Dr G. Heger, KFZ, Karlsruhe) which allows the temperature to vary in the range RT to 523 K. Totals of 526 (RT), 465 (373 K) and 700 (475 K) reflections with $0 < h, k, l \leq 10$ were measured by ω scans to $\sin\theta/\lambda = 1{\cdot}17$ Å^{-1}. The raw data were reduced to F^2 values by the method of Lehmann & Larsen (1979); no attempt was made to correct for absorption ($\mu = 0{\cdot}057$ cm^{-1}). The data were then averaged so that the final refinements in space group $P6_3$ (C_6^6) are based on about 400 independent reflections with $F/\sigma(F) > 3$. The scattering lengths used for the refinement of neutron data were taken from Koester & Rauch (1981): $b(\mathrm{Li}) = -2{\cdot}03$, $b(^7\mathrm{Li}) = -2{\cdot}197$, $b(\mathrm{I}) = 5{\cdot}28$ and $b(\mathrm{O}) = 5{\cdot}805$ fm.

Single-crystal X-ray measurements were performed at 525 K with an automatic four-circle diffractometer (Philips PW 1100) using monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). The sample was heated by a temperature-controlled nitrogen gas flow device. The temperature calibration was made using the transition temperature of $NaNO_3$ ($T = 549$ K) and gives an accuracy certainly better than ±3 K (mainly due to thermal gradient). Data ($0 < h, k \leq 9$, $0 < l \leq 8$) were collected by the ω–2θ scan method up to $\sin\theta/\lambda = 0{\cdot}96$ Å^{-1}. Reflections are scanned with a speed of 0·03 s^{-1}; a fixed scan width of 2° was used. A total of 1081 reflections were collected and corrected for Lorentz–polarization. An attenuation filter was used for the most intense reflections. The data were subsequently corrected for absorption ($\mu = 115$ cm^{-1}) using a local version of the grid method (Coppens, Leiserowitz & Rabinovich, 1965). After symmetry-equivalent reflections were averaged, 318 independent reflections were judged to be observed by the criterion $F > 6\sigma(F)$. The scattering factors and anomalous-dispersion corrections for all atoms (Li^+, I, O^-) were taken from *International Tables for X-ray Crystallography* (1974).

All structure refinements were performed with the computer program *SHELX* (Sheldrick, 1976). Anisotropic thermal parameters were used except for Li which was not located accurately enough by X-rays at that temperature. In the final refinement cycles, the weighting scheme was $w = 12/[\sigma^2(F) + 0{\cdot}000135F^2]$.

Crystal data and structure refinements

Table 1 gives the results of structure refinements at different temperatures and wavelengths under the conditions defined in *Experimental.*[*] The results of Rosenzweig & Morosin (1966), de Boer *et al.* (1966), and Emiraliev *et al.* (1976) are also reported. The α-$LiIO_3$ space group is $P6_3$, with two formula units in the cell. All relative atomic positions are given in the same system of coordinates, *i.e.* Li in $[0,0,z(\mathrm{Li})]$, I in $(\frac{2}{3},\frac{1}{3},0)$, O in (x,y,z). Such a configuration corresponds to an L-type crystal where the $z > 0$ axis is chosen along the $-\mathbf{c}$ direction of the absolute configuration (Li, 1981). Standard deviations are given in parentheses and refer to the last digit. The equivalent isotropic thermal parameters are reported in Table 1 as $B_{\mathrm{eq}} = 8\pi^2(2U_{11} + U_{33})/3$ for Li and I, and $B_{\mathrm{eq}} = 8\pi^2[4(U_{11} + U_{22} - U_{12})/3 + U_{33}]/3$ for O. The results of different authors are in good agreement at room temperature.

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[*] Lists of observed and calculated structure factors at room temperature, 373, 475 and 525 K for a single crystal and those for powder at room temperature have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38426 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. α-$LiIO_3$ *cell parameters, relative atomic positions* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å^2) *calculated from refined anisotropic thermal parameters*

	Rosenzweig & Morosin	de Boer *et al.*	Emiraliev *et al.*			This work		
Method*	X	X	NP	NP	N	N	N	X
T (K)	RT	RT	RT	RT	RT	373	475	525
λ (Å)	0·7107	0·70926	1·24	1·3885	0·5499	0·5499	0·5499	0·7107
a (Å)	5·4815 (3)	5·478 (3)	5·48	5·4851 (1)	5·477 (3)	5·489 (3)	5·507 (2)	5·516 (3)
c (Å)	5·1709 (4)	5·170 (2)	5·17	5·1752 (1)	5·170 (2)	5·193 (2)	5·219 (2)	5·236 (2)
z (Li)	8907 (123)	9110 (50)	9270 (67)	9244 (14)	9231 (10)	9195 (15)	9202 (12)	9034 (90)
x (O)	3440 (20)	3425 (8)	3437 (13)	3431 (2)	3418 (1)	3422 (2)	3425 (2)	3428 (8)
y (O)	2504 (21)	2485 (8)	2470 (13)	2477 (2)	2471 (2)	2462 (3)	2449 (2)	2413 (13)
z (O)	1698 (20)	1652 (25)	1618 (23)	1623 (14)	1617 (3)	1601 (4)	1587 (3)	1588 (14)
B_{eq}(Li)	2·†	1·†	1·27 (43)	1·59 (15)	1·18 (7)	1·80 (10)	2·31 (10)	2·90 (5)
B_{eq}(I)	0·84 (2)	0·5	0·49 (24)	0·58 (5)	0·43 (2)	0·89 (3)	1·19 (2)	1·13 (3)
B_{eq}(O)	1·29 (28)	1·02	1·11 (21)	1·25 (5)	0·96 (4)	1·54 (5)	2·01 (5)	1·71 (5)

[*] X: X-ray, single-crystal; N: neutron, single-crystal; NP: neutron, powder.

† Fixed isotropic thermal parameter.

Table 2. *Experimental conditions for the measurement of thermal expansion of* α-LiIO$_3$ (*see Fig.* 1)

Sample	Instrument	Wavelength (Å)	Symbol in Fig. 1
Powder 1	Neutron D1A	1·3885	○
Powder 2	Neutron D1A	1·9066	□
Powder 3	Neutron D1A	1·9066	×
Powder 4	Neutron D1B	2·524	+
Crystal 1	Neutron D9	0·5499	■
Crystal 2	X-ray PW1100	0·7107	△
Crystal 3	X-ray PW1100	0·7107	⊙
Crystal 4	X-ray PW1100	0·7107	▲
Crystal 5	X-ray PW1100	0·7107	▽

Thermal expansion

Cell parameters of α-LiIO$_3$ have been measured at various temperatures on different samples (powders, single crystals) and with different diffractometers and wavelengths (X-rays and neutrons). The experimental conditions are summarized in Table 2. Variations of a, c and c/a *versus* temperature are plotted in Fig. 1. For each measurement, the unit-cell constants were obtained by least-squares refinement; these cell parameters were subsequently fitted to the polynomials:

$$a(T) = 5{\cdot}4771\ (11) + 1{\cdot}54\ (7) \times 10^{-4}\,T \quad (T\ \text{in K})$$

$$c(T) = 5{\cdot}1642\ (10) + 2{\cdot}81\ (3) \times 10^{-4}\,T.$$

These polynomials fit the observations to better than two standard deviations. The thermal-expansion coefficients calculated as

$$\alpha_a(T) = \frac{1}{a(T)}\left(\frac{\mathrm{d}a}{\mathrm{d}T}\right)_T$$

are, at 273 K: α_a = 2·81 (13) × 10^{-5} and α_c = 5·44 (5) × 10^{-5} K^{-1}, in fair agreement with previous measurements (Haussühl, 1970; Thierry, Coquet & Crettez, 1976). Most of these data have been obtained from diffraction experiments aimed at the study of the α ⇌ γ phase transition; in this respect it is worth mentioning that this transition, which usually occurs at about 493 K in powdered samples, has never been observed for needle-shaped crystals even at temperatures as high as 533 K; such crystals transform directly into the β phase through a destructive transition.

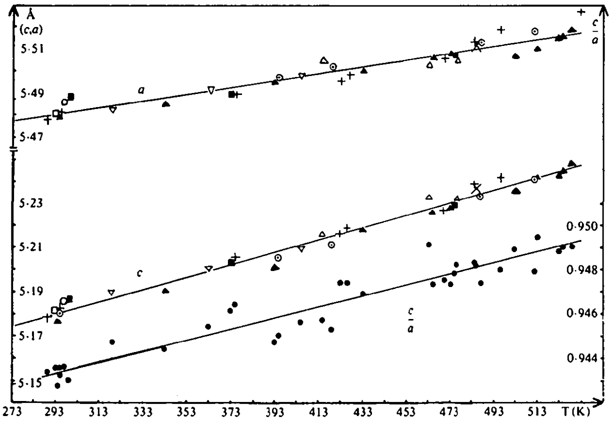

Fig. 1. α-LiIO$_3$ cell constants *versus* temperature. See Table 2 for explanation of different signs. The solid lines are least-squares fits to the data.

Discussion

The anisotropic thermal parameters obtained in the structure refinements are given in Table 3. It is worth noting that the anisotropy of the Li thermal parameters does not increase drastically as a function of temperature as might be expected from the strong increase of the ionic conductivity along the **c** direction (Remoissenet, Garandet & Arend, 1975). This is actually in agreement with the powder NMR data (Durand-Le Floch, 1982) which unambiguously show:

– the presence of a single kind of Li atom with axial symmetry;

– no change of the electric-field gradient at the Li site between RT and 473 K;

– no motional narrowing of the ^{7}Li NMR line in the same temperature range.

The thermal motion of I is almost isotropic, that of the O atom is slightly anisotropic. As expected the shortest axis of the ellipsoid (Fig. 2) lies along the direction of the shortest bond (r.m.s. displacement 0·081 Å along I—O at RT) whereas the longest axis (0·129 Å at RT) is perpendicular to the I—O—Li plane.

The coordination environment of the Li atoms is a slightly elongated octahedron. Each LiO$_6$ octahedron shares two opposite faces with two neighbouring octahedra and the resulting arrangement is an infinite string of LiO$_6$ octahedra extending along the **c** direction

Table 3. α-LiIO$_3$: *anisotropic thermal parameters* (×10^4 Å^2) *and R factors*

Symmetry restrictions are $U_{11} = U_{22} = 2U_{12}$ and $U_{13} = U_{23} = 0$ for I and Li atoms. R factors quoted in this table refer to the positional parameters given in Table 1.

Method*	*NP*	*N*	*N*	*N*	*X*
T (K)	RT	RT	373	475	525
λ (Å)	1·3885	0·5499	0·5499	0·5499	0·7107
U_{11} (Li)	236 (15)	155 (6)	223 (10)	309 (10)	367 (68)†
U_{33} (Li)	135 (26)	140 (13)	237 (21)	260 (17)	
U_{11} (I)	102 (5)	58 (2)	118 (3)	157 (2)	151 (1)
U_{33} (I)	19 (7)	49 (3)	102 (4)	140 (3)	132 (2)
U_{11} (O)	124 (4)	79 (2)	146 (3)	192 (3)	140 (12)
U_{22} (O)	160 (4)	146 (3)	234 (4)	295 (4)	305 (20)
U_{33} (O)	152 (5)	132 (3)	204 (4)	259 (3)	219 (19)
U_{12} (O)	40 (4)	50 (2)	90 (3)	108 (3)	67 (12)
U_{13} (O)	35 (7)	23 (2)	33 (3)	38 (3)	75 (17)
U_{23} (O)	26 (5)	−7 (2)	−9 (4)	−12 (3)	−34 (22)
R (%)	4·80	5·36	6·58	5·13	2·64

* X: X-ray, single-crystal; N: neutron, single-crystal; NP: neutron, powder.

† Isotropic thermal parameter.

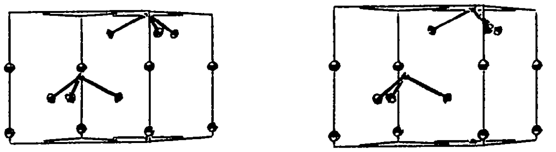

Fig. 2. Stereoscopic drawing (*ORTEP*, Johnson, 1965) of an α-$LiIO_3$ unit cell.

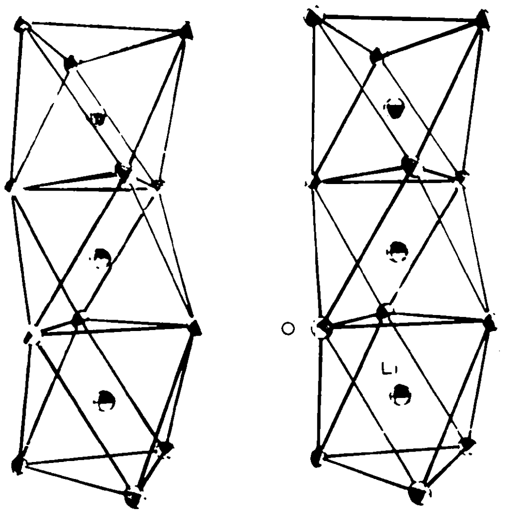

Fig. 3. Stereoscopic drawing (*ORTEP*) of the Li environment in α-$LiIO_3$.

(Fig. 3). The Li^+ ion is slightly off-centred along the same direction which leads to two Li—O distances (Table 4) but the average distance (2·12 Å at RT) is exactly that expected from the ionic radii (Shannon, 1976).

Each I atom is strongly bonded to three O atoms at a distance d_1 = 1·803 (1) Å to form a regular trigonal pyramid (Fig. 4) with O—O distance a_1 = 2·767 (1) Å ($\mathscr{C}$ configuration according to Brown, 1974). This pyramid is rigid and its shape and dimensions are almost temperature independent. The only effect of a temperature change is a rotation of the IO_3^- pyramid around its threefold axis resulting in a variation of the angle θ_1 between the projection of the Li—O and I—O bonds on the xy plane (see Fig. 5 and Table 5). The I atom is also linked to three other O atoms at a distance d_2 = 2·908 (1) Å at room temperature; the triangle formed by these three O atoms does not rotate as a function of temperature but the distance d_2 has a rather large temperature dependence (Table 5).

The thermal expansion can be well accounted for by a combination of (1) the rotation of the rigid IO_3^- group which contributes to nearly half of the α_a value and (2) the homothetic expansion of the LiO_6 which contributes to the other half of α_a and accounts for the total expansion along **c** (see Fig. 4 and numerical values in Table 4). In this connection, it is worth mentioning that the thermal expansion of the Li—O distance [α(Li—O) = 3·6 × 10^{-5} K^{-1}] is almost twice the value

Table 4. *Interatomic distances* (Å), *angles* (°), *and related thermal coefficients for the* LiO_6 *octahedron in* α-$LiIO_3$

	Short			Long	
T (K)	d_1(Li—O)	φ_1(O—Li—O)	a_1(O—O) = a_2	d_2(Li—O)	φ_2(O—Li—O)
RT	2·081 (3)	88·4 (2)	2·902 (1)	2·153 (3)	84·8 (2)
373	2·093 (5)	88·0 (4)	2·908 (2)	2·152 (4)	85·0 (4)
475	1·094 (4)	88·2 (3)	2·916 (2)	2·167 (5)	84·6 (3)
$\alpha = \frac{1}{l}\frac{dl}{dT}$	3·6 × 10^{-5}	$\frac{d\varphi_1}{dT} \sim 0$	2·75 × 10^{-5}	3·7 × 10^{-5}	$\frac{d\varphi_2}{dT} \sim 0$

Table 5. *Interatomic distances* (Å), *angles* (°) *of position in the cell* (*see Fig.* 5) *and related thermal coefficients for the* IO_6 *group in* α-$LiIO_3$

	Short			Long		
T (K)	d_1(I—O)	a_1(O—O)	θ_1	d_2(I—O)	a_2(O—O)	θ_2
RT	1·803 (1)	2·767 (1)	15·16 (5)	2·908 (1)	4·024 (1)	89·00 (5)
373	1·801 (1)	2·767 (2)	14·96 (5)	2·926 (2)	4·042 (2)	88·96 (5)
475	1·801 (1)	2·769 (1)	14·70 (5)	2·947 (1)	4·068 (1)	88·92 (5)
$\alpha = \frac{1}{l}\frac{dl}{dT}$	~0	~0	$\frac{d\theta_1}{dT} = -4·6 \times 10^{-5}$	7·7 × 10^{-5}	6·2 × 10^{-5}	$\frac{d\theta_2}{dT} \sim 0$

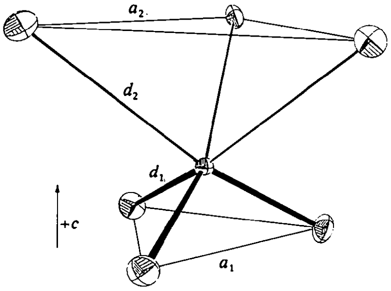

Fig. 4. Perspective drawing (*ORTEP*) of the IO$_6$ octahedron.

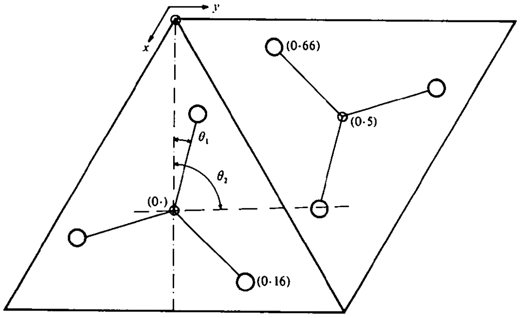

Fig. 5. The *xy*-plane projection of the α-LiIO$_3$ unit cell.

quoted in the literature [α(Li—O) ~ 1·95 × 10^{-5} K^{-1} (Hazen & Prewitt, 1977; Hazen & Finger, 1981)]. However, this large value of the thermal expansion of the Li—O distance can be qualitatively explained by the rather unusual arrangement of the LiO$_6$ octahedra in the structure: indeed, the occurrence of infinite chains of face-sharing octahedra must lead to strong repulsive electrostatic interaction along the **c** direction, from which thermal expansion, larger than the values observed in the more usual corner-sharing structures, occurs.

Lone pair

The crystal chemistry of Sn^{2+}, Sb^{3+}, Te^{4+}, I^{5+} and Xe^{6+} oxides and fluorides has been rationalized by Brown (1974) and Galy, Meunier, Andersson & Åström (1975) who have shown that the existence of lone-pair electrons in the valence shell requires a space comparable to that of an anion. This is clearly shown in Fig. 6 where I and O atoms have been represented by spheres of radius equal to the usual crystal radii of I^{5+} (0·44 Å) and O^{2-} (1·38 Å). In their geometrical approach to the tetrahedral model (three anions + lone pair) Galy *et al.* (1975) assumed a quasi-regular environment of the lone-pair cation, *i.e.* they pictured the volume occupied by the lone-pair electrons as a sphere with the same radius as an O (or F) atom. Analysis of a number of structures of iodates led us to the conclusion that this simplification overestimates the size of the lone pair. This can be seen for instance by comparing the volume per O for some iodate (IO$_3$ + lone pair) and periodate (IO$_4$) structures (Table 6); indeed the volume/anion is about 12% larger in iodates than in periodates (which shows that the lone pair is stereochemically active in iodates) but the average volume per (anion + lone pair) in iodates is 16% smaller than the average anionic volume in periodates. From these average volumes, one can estimate the radius of the I lone pair to be about 1 Å.

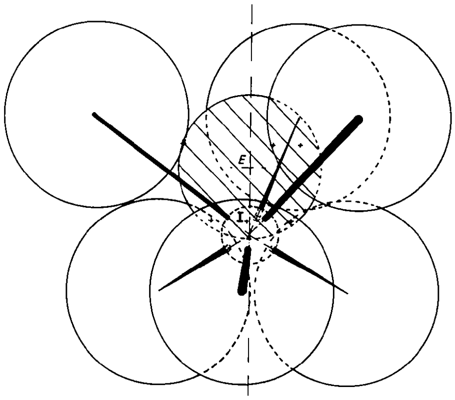

Fig. 6. Projection on a plane parallel to **c** of the IO$_6$ octahedron. Large circle: O, small circle: I, hatched circle: lone pair.

Table 6. *Volume per anion* (*or anion* + *lone pair*) *for some iodate* (IO$_3$ + *lone pair*) *and periodate* (IO$_4$) *structures*

V_1 = volume per anion (oxygen); V_2 = volume per (anion + lone pair).

Iodates: I$^{\mathrm{V}}$			Periodates: I$^{\mathrm{VII}}$	
Compound	V_1 (Å^3)	V_2 (Å^3)	Compound	V_1 (Å^3)
HIO$_3$	21·01	15·76	H$_5$IO$_6$	18·71
HI$_3$O$_8$	20·65	15·02	Li$_5$IO$_6$	17·81
α-LiIO$_3$	22·42	16·81	Li$_2$H$_3$IO$_6$	18·76
CuIO$_3$OH	21·69	17·35	LiIO$_4$.3H$_2$O	19·84
β-Ni(IO$_3$)$_2$	21·59	16·20	MgH$_3$IO$_6$.6H$_2$O	20·22
Co(IO$_3$)$_2$	22·00	16·50	Al(IO$_4$)$_3$.12H$_2$O	19·10
α-Cu(IO$_3$)$_2$	21·68	16·26	YIO$_5$.4H$_2$O	19·87
γ-Cu(IO$_3$)$_2$	21·47	16·10	GdIO$_5$.4H$_2$O	20·18
Mn(IO$_3$)$_2$	22·69	17·02	LuIO$_5$.4H$_2$O	19·54
Al(IO$_3$)$_3$	20·32	15·24		
Cr(IO$_3$)$_3$	20·73	15·54	Average	19·34
Fe(IO$_3$)$_3$	21·39	16·04		
Sc(IO$_3$)$_3$	22·42	16·82		
Y(IO$_3$)$_3$	21·48	16·11		
Gd(IO$_3$)$_3$	22·35	16·76		
α-Lu(IO$_3$)$_3$	21·08	15·81		
β-Lu(IO$_3$)$_3$	22·22	16·67		
Zr(IO$_3$)$_4$	21·82	16·37		
Ce(IO$_3$)$_4$	21·72	17·38		
Ce(IO$_3$)$_4$.H$_2$O	21·77	16·65		
Average	21·63	16·32		

Therefore, in order to describe the structure of iodates, we propose modifying the tetrahedral model of Galy *et al.* (1975) in the following way: the IO$_3$*F* tetrahedron, where E stands for lone pair, is no longer considered as regular and the radius of E is allowed to be smaller than the radius of O. The result is a compressed IO_3E tetrahedron, having only one threefold axis, which can be described by three distances:

a_1 = average O—O distance;

d_1 = average I—O distance;

I—E = iodine—lone-pair distance.

This model is well suited to α-$LiIO_3$ where the IO_3 pyramid has C_3 symmetry but applies as well to other iodate structures (Coquet, 1982). The radius of the lone pair can then be simply evaluated from geometrical considerations, assuming a close packing of the lone pair and its six neighbouring O atoms (Fig. 4). Using our room-temperature structural results (Table 1) one finds for the lone pair a radius of 1·054 Å in fair agreement with the above estimated value. The coordinates of E are calculated as $x, y, z = 0, 0, 0{\cdot}1947$, which gives I—$E$ = 1·007 Å, instead of 1·42 Å in the regular tetrahedron model.

Pyroelectric coefficient

The experimental pyroelectric coefficient P_3 has been found to be positive (Turner, 1976) and equal to about 10^{-5} C m^{-2} K^{-1} (Abrahams, 1978). This value can be well accounted for by a simple point-charge model including the lone pair. On the basis of such a model, the ionic contribution to the polarization P_s may be evaluated as

$$P_s = 4e\Delta z/a^2\sqrt{3}$$

where e is the elementary charge, a the cell parameter of α-$LiIO_3$ and Δz the distance along the c axis between the position of the negative charge of $(IO_3E)^-$ and the nearest layer of Li^+; the negative charge associated with the $(IO_3E)^-$ is taken to be at the centroid of the ionic distribution, every position being weighted by the magnitude of its formal charge (two for O and the lone pair, seven for I). This point-charge model yields a polarization parallel to **c** of about $14{\cdot}2 \times 10^{-2}$ C m^{-2} at room temperature and a pyroelectric coefficient P_3 (estimated from RT and 475 K data) of $0{\cdot}34 \times 10^{-5}$ C m^{-2} K^{-1} in rather fair agreement with the experimental value. It is worth noting that a similar model not including the lone pair gives a negative value $P_3 = -0{\cdot}4 \times 10^{-5}$ C m^{-2} K^{-1}.

In this connection one should mention that the displacement of the Li^+ ions relative to the $(IO_3E)^-$ groups is $0{\cdot}9 \times 10^{-4}$ Å K^{-1} which compares well with the value of $0{\cdot}4 \times 10^{-4}$ Å K^{-1} estimated by Abrahams (1978), assuming zero thermal expansion.

Note added in proof: The authors wish to refer readers to a complementary study by Svensson, Albertsson, Liminga, Kvick & Abrahams [*J. Chem. Phys.* (1983). **78**, 7343–7352].

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