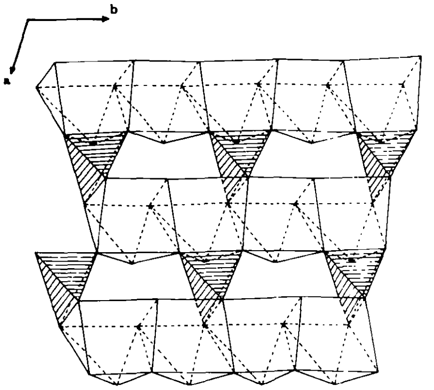

Fig. 3. Enchaînement des polyèdres de coordination de l'europium (7-prismatiques) et du germanium (tétraédriques).

Eu—S contenue dans le plan équatorial est nettement supérieure aux distances séparant l'atome central des six sommets du prisme (Carré *et al.*, 1973).

Les polyèdres 7-prismatiques accolés par leurs bases triangulaires forment des rangées parallèles à la direction [010]. Ces rangées, liées les unes aux autres tous les deux polyèdres par l'intermédiaire de tétraèdres GeS_4, constituent des couches parallèles en plan (001) (Fig. 3). Enfin, ces couches, qui se déduisent naturellement les unes des autres par une opération de symétrie autour d'un axe binaire hélicoïdal, sont empilées, de telle sorte que les arêtes des faces rectangulaires des polyèdres soient communes à deux couches successives. Par ailleurs, ces couches sont étroitement imbriquées dans la mesure où l'atome de soufre, situé dans le plan équatorial d'un polyèdre 7-prismatique, est partagé avec un polyèdre de la couche précédente.

Nous remercions M le Professeur R. Chevalier qui a bien voulu nous apporter son aimable collaboration pour les mesures expérimentales des intensités diffractées.

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Absolute Atomic Arrangement of Ferroelectric Lithium Trihydrogendiselenite

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Abstract. $LiH_3(SeO_3)_2$, monoclinic, Pn, a = 6·2554 (3), b = 7·8823 (5), c = 5·4339 (5) Å, β = 105·325 (5)°, V = 258·404 Å^3, Z = 2, d_x = 3·391 Mg m^{-3}, $\mu_{\rm obs}$ = 0·571 mm^{-1}. The absolute atomic arrangement of a single-domain crystal of $^6LiH_3(SeO_3)_2$ has been determined from the anomalous scattering of ^6Li for neutrons. The structure has been refined to R_w = 0·0313 for the correct configuration. The sense of the spontaneous polarization has been related to the absolute atomic arrangement.

Introduction. $LiH_3(SeO_3)_2$ (henceforth LHS) is ferroelectric at room temperature and remains so up to its melting point of 383 K. The X-ray crystal structure of LHS was first reported by Vedam, Okaya & Pepinsky (1960), and was further refined, based on these data, by Mohana Rao & Viswamitra (1971). In the latter study the Li^+ ion was approximately located and a hydrogen-bond system was proposed. These results were in conflict with those reported in a preliminary neutron diffraction study by Van den Hende & Boutin (1963) and NMR studies by Gavrilova-Podol'skaya (1966) and Soda & Chiba (1969). Accurate positions for all atoms, including Li and H, were finally reported in a

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neutron diffraction study by Tellgren & Liminga (1972) which also confirmed the proposals made by Mohana Rao & Viswamitra (1971) concerning the positions of H and Li.

The present study has been undertaken to relate the absolute atomic arrangement to the sense of the spontaneous polarization, $\mathbf{P}_s$. This type of result may provide insight into the relation between atomic arrangement and the origin of the polarization. The absolute atomic arrangement was determined in a single-domain crystal of $^6LiH_3(SeO_3)_2$ from the anomalous scattering of ^6Li for neutrons. Successful use of this isotope as an anomalous neutron scatterer for absolute atomic arrangement determination has been reported earlier (Johnson, Gabe, Taylor & Rose, 1965). In the present study the sense of $\mathbf{P}_s$ was determined on the same crystal as used for the neutron diffraction experiment. The absolute atomic arrangement for LHS was not determined in the previous X-ray study (Vedam *et al.*, 1960) and was not possible in the neutron diffraction study (Tellgren & Liminga, 1972) as there was no anomalous scatterer for neutrons in the crystal.

$^6LiH_3(SeO_3)_2$ was prepared from an aqueous solution of $^6Li_2CO_3$ (Oak Ridge National Laboratory, Tennessee) and H_2SeO_3 in a stoichiometric ratio. Large single crystals were grown by slow evaporation at room temperature. Mass spectral analyses showed that the crystals contained 94% ^6Li. A crystal with a volume of 13 mm^3, cut from a larger piece, was selected for the experiments. The crystal had ten boundary planes: the predominant three pairs of parallel faces $(\pm1,0,0)$, $(0,\pm1,0)$ and $(0,0,\pm1)$ with separations of 3·1, 2·5 and 1·8 mm, respectively, and the four minor faces (011), $(01\bar{1})$, (101) and $(10\bar{1})$.

The ferroelectric axis is almost perpendicular to the (001) plane (Berlincourt, Cook & Rander, 1963). Silver-paste electrodes were applied on the (001) and $(00\bar{1})$ faces of the crystal prepared earlier. The crystal showed a small pyroelectric signal, detected with an operational amplifier circuit (Abrahams, 1975). After a first application of an electric field of 1200 V (corresponding to about 0·6 kV/mm) at room temperature for about 1 min, a large pyroelectric signal was observed. This signal was not increased by prolonged application of the field or increase of the field to about 0·8 kV/mm. Similar experiments with other crystals showed that reversal of the sign of an external field of about 0·5 kV/mm was enough to reverse the sign of the pyroelectric signal, and its magnitude was approximately the same in both directions. It was therefore assumed that the crystal prepared above was fully poled and hence single domain.

The silver-paste electrodes were removed with acetone, and the crystal was mounted on an Al pin for the neutron diffraction experiment. The intensities were collected at 295 K on a PDP-8-controlled Hilger & Watts four-circle diffractometer at the R2 reactor at Studsvik, Sweden. The neutron beam had a mean wavelength of 1·210 Å after passing through a double-crystal monochromator (Stedman, Almqvist, Raunio & Nilsson, 1969). The flux at the sample was $1{\cdot}26 \times 10^4$ neutrons mm^{-2} s^{-1}. A complete quadrant of data, together with some Friedel-related pairs, was collected out to $\sin\theta/\lambda = 0{\cdot}69$ Å^{-1} with an $\omega/2\theta$ scan mode. 902 reflexions resulted, of which 792 were independent and the rest Friedel-related. Three standard reflexions, measured at regular intervals, showed only the variations expected from counting statistics. Background corrections were made with the profile-analysis method (Lehmann & Larsen, 1974), and the intensities were corrected for Lorentz and absorption effects. The linear absorption coefficient was measured experimentally to be 0·571 mm^{-1}. The transmission factors were in the range 0·27–0·44.

The known orientation of the crystal used in the neutron diffraction experiment was preserved, and silver-paste electrodes were applied again and the pyroelectric signal was detected as described earlier. A 20% decrease was observed in the signal, indicating either partial depoling or a difference in the electrodes in comparison with the previous measurement. The sense of the pyroelectric coefficient p_3 was determined; the (001) face developed a positive charge on heating. As $\mathbf{P}_s$ decreases with increasing temperature (Berlincourt *et al.*, 1963; Samara, 1968), this result indicates that $\mathbf{P}_s$ is antiparallel to $\mathbf{c}^*$. As was described earlier, the ferroelectric axis lies very nearly along $\mathbf{c}^*$.

The cell dimensions used were those reported by Tellgren & Liminga (1972). As the first step a difference synthesis was calculated, based on the positional parameters for Li, Se and O reported in the previous paper, estimated isotropic thermal parameters and a least-squares-refined scale factor. The H-atom positions derived from these maps agreed with those reported earlier (Tellgren & Liminga, 1972). The structure was refined with the full-matrix least-squares program *UPALS*, minimizing $\sum w(|F_o| - |F_c|)^2$. Each reflexion was assigned a weight $w = 1/\sigma^2(F)$, where $\sigma^2(F) = \sigma^2_{\text{count}}/4F^2 + K^2$; K was empirically chosen as $0{\cdot}02F$ for $F \geq 1{\cdot}0$ on an absolute scale, and $0{\cdot}02(2{\cdot}0 - F)$ for the rest. Reflexions with $|F| < 3\sigma(F)$ were deleted from the refinement, which was based on 848 observations. The 108 parameters refined were one scale factor, one isotropic extinction parameter, and positional and anisotropic thermal parameters for the 12 independent atoms. The shifts in the final cycle were all $<0{\cdot}1\sigma$. The positional and thermal parameters were all in good agreement with those reported earlier (Tellgren & Liminga, 1972; see below).

The agreement factors were: $R = (\sum ||F_o| - |F_c||)/\sum |F_o| = 0{\cdot}0265$, and $R_w = [(\sum w||F_o| - |F_c||)^2/\sum w|F_o|^2]^{1/2} = 0{\cdot}0322$. The standard deviation of an observation of unit weight $S = [\sum w(|F_o| -$

$|F_c|)^2/(m-n)]^{1/2}$ = 1·37, where m is the total number of observations and n the number of parameters varied.

The anomalous scattering of ^{6}Li leads to violations of Friedel's law, making it possible in principle to determine the absolute configuration of LHS. The relation of the atomic coordinates, obtained in the refinement described above, to the Miller indices of the structure factors was tested by replacing all xyz coordinates by $\frac{1}{2}-x, y, \frac{1}{2}-z$ and then further refining as above. The resulting R = 0·0262, R_w = 0·0313 and S = 1·33. The one-dimensional hypothesis that the absolute configuration corresponds to xyz may be tested by comparing the experimental Hamilton (1965) ratio $R_w(xyz)/R_w(\frac{1}{2}-x, y, \frac{1}{2}-z)$ = 1·029 with the predicted ratio $R_{1,740,0\cdot005}$ = 1·006. Since $R_{\text{exp}} > R_{\text{pred}}$, and $R_{\text{exp}}^{-1} \gg R_{\text{pred}}^{-1}$ (Abrahams, 1974), the hypothesis may be rejected at the significance level; *i.e.* the coordinates in Table 1 corresponding to $\frac{1}{2}-x, y, \frac{1}{2}-z$ together with the Miller indices of the structure factors* represent the correct absolute atomic arrangement. Hence the previously published coordinates have to be transformed to $\frac{1}{2}-x, y, \frac{1}{2}-z$, *i.e.* the structure as depicted earlier (Tellgren & Liminga, 1972) is rotated around **b** by 180°, and the origin translated by $(\frac{1}{2},0,\frac{1}{2})$.

No systematic features could be found in a difference synthesis based on the final parameters. The final fit between F_o and F_c was further examined by the $\delta R = (F_o - F_c)/\sigma(F_o)$ normal probability plot (Abrahams & Keve, 1971). The plot was essentially linear with slope 1·23 and intercept 0·08, indicating that the δR are random-normally distributed with some underestimation of $\sigma(F)$.

The coherent scattering amplitudes used were (all × 10^{-11} mm): b_{Se} = 0·800, b_{O} = 0·580, b_{H} = −0·374, and b_{Li} = 0·155 + 0·024i (Bacon, 1972). The value for Li corresponds to a mixture of 94% ^{6}Li and the rest ^{7}Li. The final value of the isotropic extinction coefficient g (Coppens & Hamilton, 1970) was 0·51 (2), with a maximum correction of 25% in F(004). Some interatomic distances and angles based on the cell dimensions from Tellgren & Liminga (1972) and the parameters in Table 1 are listed in Table 2. All calculations were made on IBM 1800 and IBM 370/155 computers with programs described by Lundgren (1976).

Table 1. *Atomic coordinates* (× 10^5) *in* ^{6}LiH$_3$(SeO$_3$)$_2$

	x	y	z
Se(1)	26700*	39508 (16)	41200
Se(2)	73288 (17)	10069 (15)	58909 (19)
O(1)	30689 (35)	22793 (22)	63312 (35)
O(2)	70152 (34)	27426 (21)	39822 (35)
O(3)	19762 (36)	29062 (23)	13821 (36)
O(4)	78973 (37)	20126 (23)	88927 (35)
O(5)	1903 (35)	47579 (24)	44549 (34)
O(6)	97983 (32)	2481 (22)	58330 (33)
Li	49063 (115)	24952 (110)	2039 (114)
H(1)	17090 (70)	14571 (44)	59946 (59)
H(2)	87977 (83)	38014 (53)	42774 (66)
H(3)	94842 (50)	23056 (35)	97213 (55)

* The x and z coordinates of Se(1) were fixed to define the origin. The values used were those given in the neutron study by Tellgren & Liminga (1972) transformed as described in the text.

Table 2. *Interatomic distances* (Å) *and angles* (°) *in* ^{6}LiH$_3$(SeO$_3$)$_2$

Ionic bonds

Li—O(1)	2·121 (6)	Li—O(4)	2·204 (7)
Li—O(2)	2·136 (6)	Li—O(5)	2·219 (5)
Li—O(3)	2·120 (7)	Li—O(6)	2·193 (4)

Angles

O(1)—Li—O(2)	174·86 (36)	O(2)—Li—O(4)	87·99 (22)
O(1)—Li—O(3)	91·53 (22)	O(2)—Li—O(5)	91·61 (19)
O(1)—Li—O(6)	92·55 (19)	O(3)—Li—O(6)	92·23 (24)
O(1)—Li—O(4)	87·09 (25)	O(3)—Li—O(4)	178·27 (26)
O(1)—Li—O(5)	86·85 (20)	O(3)—Li—O(5)	91·36 (21)
O(2) Li—O(3)	93·41 (26)	O(4)—Li—O(6)	86·79 (20)
O(2)—Li—O(6)	88·68 (20)	O(4)—Li—O(5)	89·61 (23)
		O(5)—Li—O(6)	176·37 (35)

Covalent bonds

O—Se—O	O—Se	Se—O	O—Se—O
O(1)—Se(1)—O(3)	1·756 (3)	1·655 (3)	101·41 (12)
O(3)—Se(1)—O(5)	1·655 (3)	1·730 (4)	104·37 (16)
O(5)—Se(1)—O(1)	1·730 (4)	1·756 (3)	99·97 (15)
O(2)—Se(2)—O(4)	1·697 (3)	1·763 (3)	99·51 (12)
O(4)—Se(2)—O(6)	1·763 (3)	1·665 (3)	102·58 (15)
O(6)—Se(2)—O(2)	1·665 (3)	1·697 (3)	103·66 (16)

Hydrogen bonds

O—H···O	O—H	H···O	O···O
O(1)—H(1)···O(6)	1·046 (6)	1·513 (6)	2·555 (3)
O(5)—H(2)···O(2)	1·137 (7)	1·368 (8)	2·503 (4)
O(4)—H(3)···O(3)	1·003 (6)	1·651 (5)	2·648 (4)

Se—OH···O—Se	∠Se—O—H	∠O—H···O	∠H···O—Se
Se(1)—O(1)—H(1)···O(6)—Se(2)	112·53 (27)	173·50 (46)	119·70 (22)
Se(1)—O(5)—H(2)···O(2)—Se(2)	115·82 (38)	175·78 (57)	117·48 (27)
Se(2)—O(4)—H(3)···O(3)—Se(1)	116·92 (30)	172·49 (51)	128·28 (27)

Discussion. In LHS, pairs of crystallographically independent atoms are related by a pseudo-screw axis. Application of an electric field causes atoms to move by Δ according to the relation $x_1y_1z_1 = (1-x_2, \frac{1}{2}-y_2, 1-z_2) - \Delta$. The structure is reversed, but there are no changes in the directions of the real or reciprocal axes. The only observable change in diffraction intensities would be a reversal of the small Friedel (or Bijvoet) differences, assuming the radiation used shows anomalous-dispersion effects. In the previous neutron diffraction study (Tellgren & Liminga, 1972), an as-grown crystal was used, and it was most probably multi-domain. The crystal was prepared from chemicals containing a naturally occurring mixture of Li isotopes, *i.e.* about 92% ^{7}Li and 8% ^{6}Li. The anomalous-dispersion effects for neutrons, originating from ^{6}Li, were thus negligible, and although the crystal

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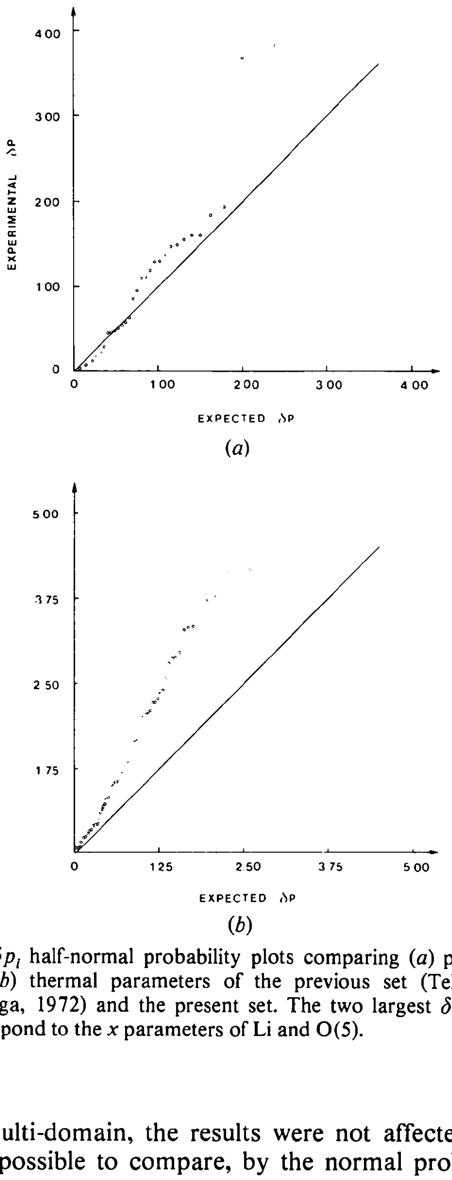
* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34665 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.



(a)

(b)

Fig. 1. δp_i half-normal probability plots comparing (*a*) positional and (*b*) thermal parameters of the previous set (Tellgren & Liminga, 1972) and the present set. The two largest δp_i in (*a*) correspond to the *x* parameters of Li and O(5).

was multi-domain, the results were not affected. It is hence possible to compare, by the normal probability plot method (Abrahams & Keve, 1971), the coordinates and temperature factors from the present study with those from Tellgren & Liminga (1972), after changing the signs of the *x* and *z* coordinates in the latter case, and translating ($\frac{1}{2}$,0,$\frac{1}{2}$) (see above). The comparison was made with half-normal $\delta p_i = |\Delta_i|/\sigma_i$ plots (Abrahams & Keve, 1971), where $\Delta_i = [p_i(2) - p_i(1)]$ and $\sigma_i = [\sigma_i^2(1) + \sigma_i^2(2)]^{1/2}$, and (1) is the previous set (Tellgren & Liminga, 1972), (2) the present set (Fig. 1). The solid line represents an ideal normal distribution of δp_i. The comparison of the positional parameters in Fig. 1(*a*) may indicate the presence of some systematic error, and an underestimation of the pooled σ_i by about 1·5. The δp_i for the thermal parameters (Fig. 1*b*) are approximately random-normally distributed, but with pooled standard deviations underestimated by a factor of 1·9. The standard deviations should be corrected by these factors in order to make a more realistic estimation of σ_i (Abrahams & Keve, 1971). If this correction is performed, all δp_i for the positional parameters are <2·5, and for the thermal parameters <2·2.

The relationship of the spontaneous polarization, $\mathbf{P}_s$, to the absolute atomic arrangement and the origin of $\mathbf{P}_s$ will be discussed elsewhere (Chomnilpan, Liminga & Tellgren, 1979).

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