phase for ALn_2S_4 (A = Sr, Ba and Pb and Ln = lanthanide) with large radius of A, but for $CaLn_2S_4$ (Ln = Ho → Lu, Y), with smaller radius of A at low temperature, the Yb_3S_4 structure type with seven coordination of Ca is formed (Flahaut, 1968; Rodier & Tien, 1977).

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A Neutron Diffraction Study of the Ferroelectric State of Deuterated Lithium Trihydrogenselenite, $LiD_3(SeO_3)_2$

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Abstract. $LiD_3(SeO_3)_2$, monoclinic, Pn, a = 6·2473 (4), b = 7·9030 (7), c = 5·4471 (3) Å, β = 104·995 (5)°, V = 259·78 (3) Å^3, Z = 2, d_x = 3·412 Mg m^{-3}, μ_{obs} = 0·0691 (1) mm^{-1}, λ = 1·210 Å. Large single crystals were grown by the slow evaporation at room temperature of a solution made up from Li_2CO_3 and SeO_2 in D_2O (0·02% H_2O). The data were collected with a voltage of 540 V mm^{-1} applied in the **c*** direction. The crystal structure is built up of Li^+ and $DSeO_3^-$ ions and of D_2SeO_3 molecules. The isotope effect in the hydrogen bonds shows the general trend as expected for hydrogen bonds in the range 2·5–2·6 Å, *i.e.* a lengthening of the O···O distances and a shortening of the O—D distances. [The final R values were $R(F^2)$ = 0·034, $R_w(F^2)$ = 0·044, and $R(F)$ = 0·021 for 818 unique reflexions.]

Introduction. Ferroelectric $LiH_3(SeO_3)_2$ (henceforth LHS or LDS for the deuterated compound) has been the subject of several diffraction studies. Two complete neutron diffraction studies have been published (Tellgren & Liminga, 1972; Chomnilpan, Liminga & Tellgren, 1979). An as-grown crystal, *i.e.* most probably multidomain, was used in the first case. The crystal was prepared from chemicals containing a naturally occurring mixture of Li isotopes (about 92% ^7Li and 8% ^6Li). The anomalous-dispersion effects for neutrons, originating from ^6Li, were thus negligible, and although the crystal was multidomain, the results were not affected (Chomnilpan *et al.*, 1979). The latter study was made using a single-domain crystal of $^6LiH_3(SeO_3)$. The absolute atomic arrangement was determined using the anomalous-scattering contribution from ^6Li for neutrons.

The structure of LHS consists of H_2SeO_3 molecules and $HSeO_3^-$ ions, hydrogen bonded to ring-formed dimers. A third hydrogen bond, originating from the $HSeO_3^-$ ion, interlinks the dimers to form chains (Fig. 1 and figures in Tellgren & Liminga, 1972). In the two previous studies mentioned above, it was observed that one of the H atoms, H(2), had a rather elongated 'thermal' ellipsoid along the bond direction. The O—H distance, about 1·14 Å, was also much larger than expected for a 2·52 Å O···O hydrogen bond. No anomalous features were observed for the rest of the atoms.

This effect having been observed in two independent studies, based on a multi- and a single-domain crystal, respectively, there are reasons to believe that it is genuine. The most probable explanation is that the 'anomalous' H atom is situated in a shallow skew potential well. Information about the potential well in a

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hydrogen bond may be obtained when H is replaced by D. It was therefore decided to collect a three-dimensional neutron-diffraction data set from a deuterated crystal. In order to avoid introduction of systematic errors in the data due to the multidomain character of the crystal, measures were taken to maintain a single-domain crystal during the entire data collection (see further below). The diffraction symmetry and systematic absences confirmed the monoclinic space group *Pn* found earlier for the protonated compound (Vedam, Okaya & Pepinsky, 1960).

The unit-cell dimensions were determined from a powder photograph recorded in a Guinier–Hägg XDC-700 focusing camera with Cr $K\alpha_1$ radiation ($\lambda = 2{\cdot}28975$ Å) and with CoP_3 as an internal standard ($a = 7{\cdot}7073$ Å at 298 K). Observed θ values from 38 reflexions provided the parameters and standard deviations given in the *Abstract*. On deuteration the volume of the unit cell increases by about 0·5%; the a axis and β angle both decrease (0·13 and 0·31%, respectively) whereas the b and c axes both increase about 0·25%.

The intensity data were collected using the neutron diffraction facilities at the Swedish R2 reactor in Studsvik. The experimental arrangement is described briefly elsewhere (Tellgren, Ramanujam & Liminga, 1974). The crystal used for the data collection was cut from a larger crystal, and was an approximate cube with a volume of 28·6 mm^3.

The six cube faces were $\pm(010)$, $\pm(001)$ and approximately $\pm(50\bar{1})$. Aluminum electrodes were applied on the $\pm(001)$ faces and the crystal was poled and mounted for data collection as described in a previous paper (Chomnilpan *et al.*, 1979). A voltage of 1500 V, corresponding to about 540 V mm^{-1}, was applied during the entire data collection to maintain the single-domain character of the crystal. Intensities were measured in an ω–2θ scan mode for reflexions comprising two octants of reciprocal space (hkl, $\bar{h}kl$) with $\sin\theta/\lambda < 0{\cdot}693$ Å^{-1}. After reversing the external field a second complete data set was collected from the crystal with reversed polarity. As a check on experimental stability, three standard reflexions were measured at regular intervals. No significant changes were observed. A total of 1599 reflexions were measured. The equivalent reflexions in the two data sets were compared using a δm normal-probability plot (Abrahams & Keve, 1971). Before this the variances of the intensities were estimated using the procedure of McCandlish, Stout & Andrews (1975) including contributions from counting statistics and fluctuations observed in the standards (instability constant $P = 0{\cdot}0059$). The plot was linear with a y intercept of $-0{\cdot}02$ and slope 1·15, indicating a slight underestimation of the variances but otherwise no systematic differences between the two data sets. The common reflexions were averaged giving 818 unique reflexions. The consistency index $R = \sum |I_{obs} - I_{av}|/\sum I_{obs}$ was 0·009. The intensities were corrected for Lorentz and absorption effects. The linear absorption coefficient was determined experimentally to be 0·0691 (1) mm^{-1}. The transmission factors varied between 0·804 and 0·850.

The structure was refined by minimizing $\sum w(F^2_{obs} - F^2_{calc})^2$ with the full-matrix least-squares program *UPALS* (Lundgren, 1980). The reflexions were assigned weights $w = 1/\sigma^2(F^2)$. The 11 reflexions with $F^2_{obs} < 1\sigma(F^2)$ were given zero weight in the refinement. The total number of parameters refined was 113, including 34 positional and 72 thermal parameters, one scale factor and six anisotropic extinction factors. The extinction model used was the type 1 formalism by Becker & Coppens (1974*a*,*b*; 1975) with a Lorentzian distribution of the mosaic blocks according to Thornley & Nelmes (1974). About 65% of the reflexions had an extinction correction factor $>1{\cdot}17$ multiplying F^2_{obs}. The scattering amplitudes used were taken from the compilation by Bacon (1972) except for Li where a

Table 1. *Atomic coordinates* ($\times 10^4$) *in* $LiD_3(SeO_3)_2$

	x	y	z
Li	39 (8)	2433 (7)	4778 (10)
Se(1)	2330*	3946 (1)	880*
Se(2)	7713 (2)	1008 (1)	9157 (2)
O(1)	1960 (3)	2299 (2)	−1343 (3)
O(2)	8014 (3)	2737 (2)	11036 (3)
O(3)	3029 (3)	2912 (2)	3600 (4)
O(4)	7160 (3)	2012 (2)	6144 (4)
O(5)	4796 (3)	4781 (2)	530 (4)
O(6)	5229 (3)	248 (2)	9189 (3)
D(1)	3286 (3)	1484 (2)	−980 (3)
D(2)	6116 (3)	3876 (2)	722 (3)
D(3)	5581 (3)	2275 (2)	5332 (3)

* Fixed to define the origin.

Table 2. *Selected bond distances and hydrogen-bonding data*

Selected bond distances (Å) in $LiD_3(SeO_3)_2$

Li—O(2)	2·116 (5)	Se(1)—O(3)	1·649 (2)
—O(1)	2·143 (5)	—O(5)	1·731 (2)
—O(4)	2·146 (5)	—O(1)	1·752 (2)
—O(6)	2·151 (6)		
—O(3)	2·160 (5)	Se(2)—O(6)	1·669 (2)
—O(5)	2·252 (6)	—O(2)	1·688 (2)
		—O(4)	1·775 (2)

A comparison of hydrogen-bond distances (Å) and angles (°) in $LiD_3(SeO_3)_2$ (upper line) and $LiH_3(SeO_3)_2$ (lower line)

X—D···Y	X—D	D···Y	X···Y	X—D···Y
O(1)—D(1)···O(6)	1·027 (2)	1·542 (2)	2·564 (2)	172·6 (2)
	1·040 (6)	1·517 (6)	2·552 (3)	173·3 (4)
O(5)—D(2)···O(2)	1·076 (2)	1·463 (3)	2·538 (2)	176·2 (2)
	1·141 (7)	1·378 (7)	2·518 (3)	176·6 (5)
O(4)—D(3)···O(3)	0·993 (2)	1·705 (2)	2·690 (2)	170·8 (2)
	1·003 (4)	1·649 (4)	2·646 (4)	172·3 (4)

value of −1·94 fm was used (*International Tables for X-ray Crystallography*, 1974). The occupation factors for the three D atoms were also allowed to vary. The refined values [0·97 (1), 0·98 (1), 0·96 (1)] are slightly lower than 1·0 thus indicating that a small percentage of H remains at these sites. The final R values were $R(F^2) = 0{\cdot}034$, $R_w(F^2) = 0{\cdot}044$, and $R(F) = 0{\cdot}021$. The standard deviation of an observation of unit weight was 0·73. The final positional parameters are given in Table 1,* bond distances and angles in Table 2.

Discussion. The main features of the LDS structure are illustrated in Fig. 1. The D_2SeO_3 molecules and $DSeO_3^-$ ions are hydrogen bonded to ring-formed dimers, interconnected to form chains by means of a third hydrogen bond originating from the $DSeO_3^-$ ion. The hydrogen-bonded chains are interlinked *via* Li—O bonds, each Li^+ ion having an octahedral coordination of six O atoms belonging to four different chains (Table 2).

A detailed comparison of the atomic position parameters in LHS (Tellgren & Liminga, 1972) and the present study is not possible, as the unit cell changed significantly on deuteration. A comparison of the thermal parameters and r.m.s. components in the two studies indicates systematic differences. The r.m.s. components in LHS are all (except for two values) larger than the corresponding values in LDS (Table 3). This systematic difference may be caused by the different extinction models used in the two studies. An isotropic model was used in LHS, whereas an anisotropic model was assumed in the present study. The largest difference for the non-H atoms is about six times the e.s.d. Systematic differences are expected for the H and D atoms; the observed differences are, however, of the same magnitude as for the other atoms.

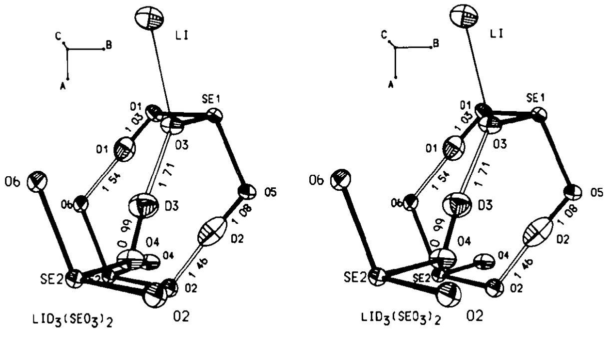

Fig. 1. A stereoscopic illustration of the hydrogen-bonded D_2SeO_3 molecules and $DSeO_3^-$ ions.

Table 3. *R.m.s. amplitudes* R_i (×10^3, Å) *of thermal vibration along the principal-ellipsoid axes in* $LiD_3(SeO_3)_2$ (*upper line*) *and* $LiH_3(SeO_3)_2$ (*lower line*)

	R_1	R_2	R_3
Li	126 (7)	132 (7)	168 (6)
	131 (8)	149 (7)	171 (6)
Se(1)	89 (2)	105 (2)	111 (2)
	96 (3)	109 (2)	126 (3)
Se(2)	90 (2)	99 (2)	117 (2)
	92 (3)	113 (2)	120 (2)
O(1)	101 (3)	114 (3)	144 (3)
	107 (4)	137 (3)	155 (3)
O(2)	101 (3)	114 (3)	144 (2)
	111 (4)	126 (4)	155 (3)
O(3)	101 (3)	118 (3)	150 (2)
	107 (4)	123 (3)	168 (3)
O(4)	106 (3)	110 (3)	181 (2)
	115 (3)	122 (3)	178 (3)
O(5)	96 (3)	116 (3)	161 (3)
	110 (4)	144 (4)	159 (3)
O(6)	104 (3)	111 (3)	146 (2)
	107 (4)	138 (4)	150 (3)
D(1)	139 (2)	163 (2)	171 (2)
H(1)	153 (5)	173 (5)	194 (5)
D(2)	139 (2)	157 (2)	235 (2)
H(2)	149 (6)	173 (5)	271 (7)
D(3)	131 (3)	156 (2)	185 (2)
H(3)	141 (5)	168 (5)	202 (5)

A significant expansion, 0·012–0·044 Å, of the three independent hydrogen-bonded O···O distances is observed in this case on deuteration (Table 2). Positive isotope effects on O—H···O bonds (*i.e.* lengthening) has been reported earlier (Thomas, Tellgren & Olovsson, 1974; Hussain, Schlemper & Fair, 1980, and further references in these papers). Such an effect has also been predicted theoretically for asymmetric hydrogen bonds (Singh & Wood, 1969). The O—H distances are all shortened on deuteration by 0·013, 0·065 and 0·010 Å, respectively. The largest effect is observed for the O—D(2) bond (Fig. 1, Table 2). The changes in the O—H···O angles on deuteration are all small and hardly significant (Table 2).

The O—H distance in the O(5)—H(2)···O(2) bond in LHS (Tellgren & Liminga, 1972) was unusually large, 1·14 Å, for a 2·52 Å hydrogen bond. The O—D distance decreased to 1·08 Å, *i.e.* an increased asymmetry is observed in the D position [a shift towards O(5)] as compared to the H position. This observation is in agreement with results reported in some recent neutron diffraction studies of deuteration effects on short (about 2·4 Å) O···O hydrogen bonds (Takusagawa & Koetzle, 1979; Hussain *et al.*, 1980; Hsu, Schlemper & Fair, 1980). There is a difference, however, as the O···O distances were almost constant in these cases, whereas in the present case the O···O distance increased by 0·020 Å.

As mentioned above the thermal ellipsoid of D(2) is elongated with the largest r.m.s. component (0·235 Å)

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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 36648 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

approximately along the bond direction (Fig. 1). The angle between this component and the O(5)···O(2) direction is 25° [the O(5)—D(2)···O(2) angle is 176°]. For the other two D atoms the largest r.m.s. component (0·171 and 0·185 Å) is in each case closer to a right angle to the O···O bond direction (Fig. 1); the angles are 56 and 102°, respectively. These observations, together with the large isotope effect for D(2), indicate that D(2) is situated in a shallow skew potential well.

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Structure of Thallium Sulfate Tellurate $Te(OH)_6.Tl_2SO_4$

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Abstract. $Te(OH)_6.Tl_2SO_4$ is monoclinic, $P2_1/a$, with $a = 12{\cdot}053$ (5), $b = 7{\cdot}205$ (1), $c = 12{\cdot}354$ (6) Å, $\beta = 110{\cdot}85$ (5)°, $V = 1003$ (1) Å^3, $Z = 4$, $D_x = 4{\cdot}87$ Mg m^{-3}. The structure has been determined using the Patterson method and refined to an R of 0·055 for 1399 independent reflections. The main interest of this structure lies in the presence of two different types of anions in the crystal. A difficulty arose in the structure determination due to the occurrence of two heavy atoms in the crystal.

Introduction. Like the other sulfate tellurate salts of this series (Zilber, Tordjman & Guitel, 1980; Zilber, Durif & Averbuch-Pouchot, 1980, 1981) the title compound was obtained as crystals grown from solution.

A piezoelectric test was inconclusive and a preliminary photographic study by the Weissenberg method showed monoclinic symmetry. Not much effort was invested in the analysis of the photographs since the data collection confirmed the unit cell measured on the film and showed unambiguously the systematic extinctions of the monoclinic space group $P2_1/a$, which are: hkl: no conditions; $h0l$: $h = 2n + 1$; $0k0$: $k = 2n + 1$; $h00$: $h = 2n + 1$. General positions for space group $P2_1/a$: 4(e) (i) x,y,z; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, -z$; (iii) $-x,-y,-z$; (iv) $\frac{1}{2} + x, \frac{1}{2} - y, z$.

The crystal used for the data collection was a small prism of approximate dimensions 0·12 × 0·7 × 0·7 mm. 2316 reflections were recorded on a Philips PW1100 four-circle diffractometer equipped with a graphite monochromator. The radiation used was that of a silver target [λ(Ag $K\alpha$) = 0·5608 Å].

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