2·49 (2·49 = 2·35 − 0·6 log n) corresponds to $n = 0·58$, a value near 0·5 as expected for bonds between Si atoms from the above electronic balance.

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Structure and Absolute Chirality of $Rb_4LiH_3(SO_4)_4$ at 293 K

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Abstract. Lithium tetrarubidium trihydrogentetrasulfate, $Rb_4LiH_3(SO_4)_4$, $M_r = 736·1$, tetragonal, $P4_1$, $a = 7·615$ (2), $c = 29·458$ (5) Å, $V = 1708·2$ (6) Å^3, $Z = 4$, $D_x = 2·86$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 11·63$ mm^{-1}, $F(000) = 1384$, $T = 293$ K, $R = 0·042$, 4966 unique reflections. Crystals optically laevorotatory at 293 K belong to the enantiomorphic space group $P4_1$, rotatory power $\rho = -0·28°$ mm^{-1} at $\lambda = 6330$ Å. The structure consists of tetrahedral sulfate groups arranged together with Rb atoms on layers stacked perpendicularly to the tetragonal axis.

Introduction. The title compound belongs to a new family of crystals with general formula $M_4LiH_3(XO_4)_4$ (M = K, Rb and X = S, Se), which exhibit phase transitions between 100 and 140 K.

For $Rb_4LiH_3(SO_4)_4$ crystals, the pyroelectric, dielectric, elastic and thermal properties in the temperature range 100 to 400 K have been reported (Wolejko, Piskunowicz, Breczewski & Krajewski, 1988; Wolejko, Pakulski & Tylczynski, 1988), confirming the existence of a ferroelastic phase transition at 132 K. From the behaviour of the measured physical properties, these authors have suggested that the transition is of second-order type and have assigned the symmetry change 4*mm*–*mm*2.

Mróz, Kiefte & Clouter (1988) have also reported experimental results on the behaviour of the velocity of phonons [101] and [011] through the transition, and have assigned the same sequence of point symmetry groups as above. On the basis of dielectric and heat capacity measurements, Hempel, Maack & Sorge (1989), have confirmed the second-order nature of the phase transition. However, the results obtained for the elastic-stiffness coefficients are not compatible with the previously mentioned point-group scheme. Consequently, these authors have proposed a 4–2 sequence for the point-group symmetry in this material.

On the other hand, a similar ferroelastic phase transition has also been found at 100 K in the analogous compound $Rb_4LiH_3(SeO_4)_4$ (Pietraszko & Lukaszewicz, 1988). It has been reported that the space group is $P4_1$ (or $P4_3$) at 293 K, and therefore (Aizu, 1972) the point-group sequence should be 4–2 in this case.

With the aim of clarifying the contradictory results published for the (Rb,S) compound, we have undertaken a crystallographic study. X-ray anomalous scattering together with optical-activity measurements have allowed us to determine the structure and absolute chirality of the material in the paraelastic phase. We will also present some preliminary results about the low-temperature phase.

Experimental. Crystals were grown isothermally at 310 K from an acid aqueous solution (pH < 1) of stoichiometric initial salts by using the dynamic method. Large colourless crystals, with a mor-

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phology of a tetragonal bipyramid were obtained, typically about 50 mm long and 30 mm across and of good optical quality. The chemical composition was determined by atomic spectroscopy (Li^+,Rb^+) and chemical analysis $(SO_4)^{2-}$.

Rotatory power measurements along the *c* axis were performed on two polished plates about 5 mm thick, cut from opposite pyramids of one of the grown crystals. The samples were set between two calcite Glan–Thompson prisms driven by continuous motors, which allow the polarizers to be placed with a resolution of approximately 10^{-4}°. An He—Ne laser was employed as a light source and a photomultiplier tube was used to detect the light transmitted through the whole set. At several places along the optical path, scattered light was blocked by means of diaphragms. Several rotatory-power data were taken for each crystal by scanning the spot position over the sample area. The final values were the average of the individual runs. The rotatory power was found to be −0·28 (3) and 0·30 (3)° mm^{-1} for the samples obtained from each pyramid (the sign convention is the same as that used in Glazer & Stadnicka, 1986).

A small piece of the laevorotatory crystal used to measure the optical rotatory power was ground to a sphere of radius 0·23 mm and used to collect intensities with a four-circle CAD-4 diffractometer (graphite-monochromated Mo $K\alpha$ radiation). A total of 6347 measured reflections with $2\theta_{max} = 60°$, [*hkl* range: $-10 < h < 10$, $0 < k < 10$ ($|k| < |h|$), $0 < l < 41$ and Friedel pairs]. θ–2θ scan mode [$\Delta\omega = (0{\cdot}65 + 0{\cdot}35\tan\theta)°$] with variable speed; three standard reflections measured every 7200 s without significant variation; absorption correction factors for a spherical crystal (max./min. = 33·8/18·3); 3062 independent reflections with $I > 3\sigma(I)$. Unit-cell parameters refined the tetragonal constraints from diffractometer angles of 16 centred reflections ($34° < 2\theta < 40°$).

The structure was solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The refinement based on $|F|$ was performed with *XRAY*72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972), using full-matrix least squares, anisotropic atomic displacement parameters for Rb, S, O and isotropic for Li. Scattering factors for Rb, S, O and Li from Cromer & Mann (1968) and anomalous scattering for Rb, S and O from Cromer & Liberman (1970). The refinement process, with 227 variables, included at the final stages the extinction and the enantiomorph-polarity (Flack, 1983) parameters. A final difference electron-density map showed peaks of height up to 0·7 e $Å^{-3}$, but attempts to refine H atoms failed. For the $P4_1$ space group the refinement converged for an enantiomorph-polarity parameter $x = 0{\cdot}13$ (1), with the final agreement factors $R = 0{\cdot}042$, $wR = 0{\cdot}054$ [$w = 1/\sigma^2(F_o)$], $S = 1{\cdot}20$ and $(\text{shift/e.s.d.})_{max} = 0{\cdot}45$. The value of *x* clearly indicates that the sample is an inversion (enantiomorphic) twin consisting of 87% of the laevorotatory crystal in space group $P4_1$ and 13% of dextrorotatory crystal in the space group $P4_3$.

The diffraction patterns corresponding to the (*hk*0), (*hk*1) and (*h*0*l*) levels of the reciprocal lattice of the low-temperature phase were obtained at 100 K with a precession camera. The only change observed was a splitting in the diffraction spots except for (00*l*). The systematic extinctions detected were (00*l*) $l = 2n + 1$.

Discussion. The optical-activity results indicate that the bipyramidal samples were not constituted by a single crystal, but were formed by juxtaposition to two enantiomorphic twins which gave rise to an enhancement of the symmetry of the crystal habit. In fact, the tetragonal bipyramidal shape for a single crystal is not compatible with the point group 4.

As pointed out by Glazer & Stadnicka (1989), in order to give a full meaning to the term 'absoute structure', it is necesary to relate the atomic coordinates with one physical tensorial property of the material which allows one enantiomorph to be distinguished from the other. In our case, such a property is the optical activity and the structural data refer to the laevorotatory crystal.

The fractional coordinates and equivalent isotropic atomic displacement parameters are given in Table 1.* A (100) projection of the structure is shown in Fig. 1. The structure consists of tetrahedral sulfate groups arranged together with Rb atoms on layers stacked perpendicularly to the tetragonal axis. The four symmetry-independent Rb atoms and SO_4 groups are distributed on two consecutive layers as shown in Fig. 2. Li atoms are intercalated every two independent layers and are surrounded by tetrahedra of O atoms with an average Li—O distance of 1·92 Å. The Rb atoms have an environment of eight oxygens at distances ranging from 2·8 to 3·12 Å. The relevant bond lengths and angles are listed in Table 2.

The S—O and Li—O distances are comparable to the corresponding values in the structure of $KLiSO_4$ (Karppinen, Lundgren & Liminga, 1983). However, each sulfate group systematically has one of the S—O distances abnormally large, namely S—O(12), S—O(22), S—O(32) and S—O(43). This fact can be

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* Lists of structure factors and anisotropic atomic displacement parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52680 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and equivalent isotropic atomic displacement parameters* (Å^2) *with e.s.d.'s in parentheses*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Rb(1)	0·0645 (2)	0·8853 (2)	0·7180	0·0199 (4)
Rb(2)	0·3652 (2)	0·3840 (2)	0·70491 (5)	0·0216 (4)
Rb(3)	0·5291 (2)	0·9751 (2)	0·08343 (5)	0·0214 (4)
Rb(4)	0·2271 (2)	0·4808 (2)	0·07356 (4)	0·0195 (4)
S(1)	0·4620 (4)	0·1245 (4)	0·20459 (9)	0·0112 (7)
O(11)	0·575 (1)	0·255 (1)	0·2250 (3)	0·020 (3)
O(12)	0·377 (1)	0·209 (1)	0·1618 (3)	0·209 (3)
O(13)	0·319 (1)	0·077 (1)	0·2332 (3)	0·027 (3)
O(14)	0·561 (1)	−0·022 (1)	0·1862 (3)	0·026 (3)
S(2)	0·4107 (3)	0·1222 (4)	0·45631 (9)	0·0124 (8)
O(21)	0·341 (1)	0·253 (1)	0·4867 (3)	0·034 (3)
O(22)	0·256 (1)	0·028 (1)	0·4343 (3)	0·025 (3)
O(23)	0·510 (1)	−0·006 (1)	0·4793 (3)	0·034 (3)
O(24)	0·506 (1)	0·206 (1)	0·4197 (3)	0·046 (3)
S(3)	0·0361 (4)	−0·0053 (4)	0·08669 (8)	0·0118 (8)
O(31)	0·170 (1)	0·108 (1)	0·0664 (3)	0·027 (3)
O(32)	0·130 (1)	−0·154 (1)	0·1088 (3)	0·030 (3)
O(33)	−0·059 (1)	0·087 (1)	0·1221 (3)	0·031 (3)
O(34)	−0·087 (1)	−0·068 (1)	0·0522 (3)	0·023 (3)
S(4)	0·5380 (4)	0·6973 (4)	0·33303 (9)	0·0130 (8)
O(41)	0·393 (1)	0·599 (1)	0·3503 (3)	0·026 (3)
O(42)	0·489 (1)	0·845 (1)	0·3064 (3)	0·028 (3)
O(43)	0·627 (1)	0·774 (1)	0·3766 (3)	0·031 (3)
O(44)	0·668 (1)	0·588 (1)	0·3102 (3)	0·028 (3)
Li	0·279 (2)	0·869 (2)	0·2704 (7)	0·015 (3)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Distances corrected for thermal riding motion are given in square brackets.

S(1)—O(11)	1·445 (9)	[1·460]	S(2)—O(21)	1·44 (1)	[1·46]
S(1)—O(12)	1·555 (9)	[1·565]	S(2)—O(22)	1·522 (9)	[1·537]
S(1)—O(13)	1·422 (9)	[1·436]	S(2)—O(23)	1·41 (1)	[1·43]
S(1)—O(14)	1·45 (1)	[1·46]	S(2)—O(24)	1·45 (1)	[1·47]
S(3)—O(31)	1·46 (1)	[1·48]	S(4)—O(41)	1·432 (9)	[1·440]
S(3)—O(32)	1·49 (1)	[1·50]	S(4)—O(42)	1·421 (9)	[1·437]
S(3)—O(33)	1·455 (9)	[1·467]	S(4)—O(43)	1·564 (9)	[1·586]
S(3)—O(34)	1·461 (9)	[1·478]	S(4)—O(44)	1·46 (1)	[1·48]
Li—O(13$^{\rm i}$)	1·95 (2)		Li—O(34$^{\rm iii}$)	1·89 (2)	
Li—O(21$^{\rm ii}$)	1·89 (2)		Li—O(42)	1·93 (2)	

O(11)—S(1)—O(12)	107·6 (5)	O(21)—S(2)—O(22)	107·8 (6)
O(11)—S(1)—O(13)	112·4 (5)	O(21)—S(2)—O(23)	112·2 (6)
O(11)—S(1)—O(14)	112·1 (5)	O(21)—S(2)—O(24)	109·9 (6)
O(12)—S(1)—O(13)	105·4 (5)	O(22)—S(2)—O(23)	107·1 (6)
O(12)—S(1)—O(14)	103·3 (5)	O(22)—S(2)—O(24)	106·1 (5)
O(13)—S(1)—O(14)	115·0 (5)	O(23)—S(2)—O(24)	113·3 (6)
O(31)—S(3)—O(32)	107·1 (6)	O(41)—S(4)—O(42)	114·1 (5)
O(31)—S(3)—O(33)	110·7 (6)	O(41)—S(4)—O(43)	103·8 (5)
O(31)—S(3)—O(34)	110·9 (5)	O(41)—S(4)—O(44)	113·0 (6)
O(32)—S(3)—O(33)	107·1 (5)	O(42)—S(4)—O(43)	105·7 (5)
O(32)—S(3)—O(34)	111·3 (5)	O(42)—S(4)—O(44)	112·1 (5)
O(33)—S(3)—O(34)	109·8 (5)	O(43)—S(4)—O(44)	107·4 (5)
O(13$^{\rm i}$)—Li—O(21$^{\rm ii}$)	114 (1)	O(21$^{\rm ii}$)—Li—O(34$^{\rm iii}$)	109 (1)
O(13$^{\rm i}$)—Li—O(34$^{\rm iii}$)	105·3 (9)	O(21$^{\rm ii}$)—Li—O(42)	107 (1)
O(13$^{\rm i}$)—Li—O(42)	104·8 (9)	O(34$^{\rm iii}$)—Li—O(42)]	117 (1)

Symmetry code: (i) $x,1+y,z$; (ii) $y,1-x,z-\frac{1}{4}$; (iii) $-y,1+x,\frac{1}{4}+z$.

explained by the presence of hydrogen bonds O—H···O′ linking sulfate groups according to the scheme shown in Fig. 1. The distances between the O atoms involved in the hydrogen bonds are given in Table 2.

No attempt was made to relate this crystal structure with the observed optical rotation. Up to now, only in crystals with a rotatory power at least one order of magnitude larger than in the present case has the theoretical treatment which explains the origin of the optical activity been successfully applied

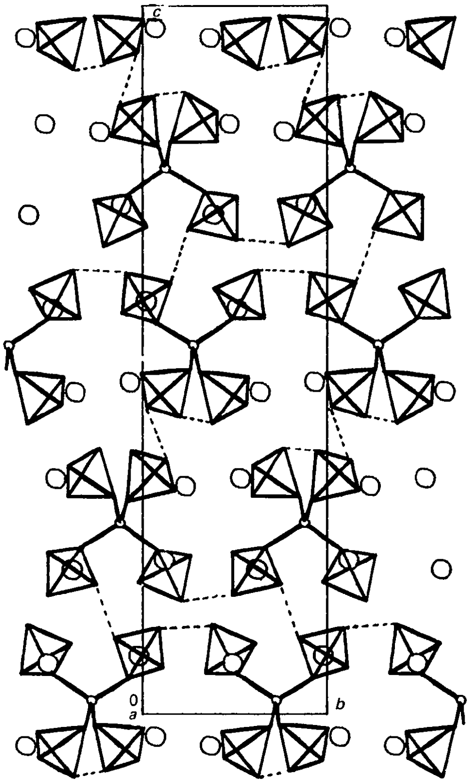

Fig. 1. (100) projection of the structure. Sulfate groups are represented by tetrahedra, Rb atoms by large circles and Li by small circles. The Li—O contacts are denoted by continuous lines and the hydrogen bonds by dashed lines.

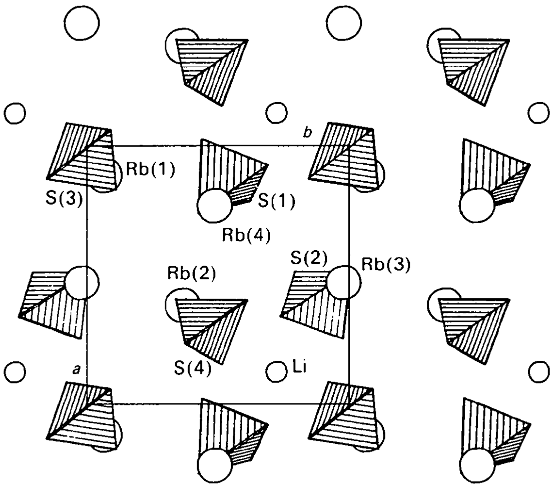

Fig. 2. (001) projection of the two consecutive layers at the bottom of Fig. 1. Labels of sulfate groups refer to the S atoms.

(Devarajan & Glazer, 1986; Stadnicka, Glazer & Koralewski, 1988). We found it difficult even to determine the correct optical activity sign in our crystal by using the simplified model proposed by Glazer & Stadnicka (1986). In order to go on along this line further experimental information such as measurements of the refractive indices would be of great value.

Concerning the low-temperature phase, the precession photographs indicated that the number of molecules Z remained the same in both phases, so the transition is of ferrodistortive type. This fact, together with the splitting of the diffraction spots and the systematic extinctions detected, points to a reduction of the symmetry to a monoclinic group, which must necessarily be $P2_1$ if the transition is to be accounted for within the framework of the Landau theory.

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Refinement of the Structure of Sodium Enneagermanate ($Na_4Ge_9O_{20}$)

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Abstract. $Na_4Ge_9O_{20}$, M_r = 1065·3, tetragonal, $I4_1/a$, a = 15·0263 (9), c = 7·3971 (9) Å, V = 1670·2 Å^3, Z = 4, D_x = 4·236 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 172·9 cm^{-1}, F(000) = 1968, room temperature, 2589 unique reflections, final R = 0·026. Five Ge atoms per formula unit are in tetrahedral coordination with oxygen [Ge(1)—O = 1·742 (2) Å; ⟨Ge(2)—O⟩ = 1·747 (2) Å] and four are in octahedral coordination [⟨Ge(3)—O⟩ = 1·900 (2) Å]. The sodium cation has seven oxygens within the 3·2 Å sphere, with four short bonds in the form of a nearly planar configuration, and its thermal ellipsoid is markedly anisotropic with its major axis almost parallel to the c axis.

Introduction. The structure of tetragonal sodium enneagermanate ($Na_4Ge_9O_{20}$) is of interest as a possible structural model for sodium germanate glasses (*e.g.* Kamiya, Yoko, Miki, Itoh & Sakka, 1987; Weber, 1982) and high-pressure silicate melts (*e.g.* Fleet, Herzberg, Henderson, Crozier, Osborne & Scarfe, 1984). Early confusion about the composition of sodium enneagermanate and its stability relative to that of the tetragermanate $Na_2Ge_4O_9$ was resolved by White, Shaw, Corwin & Pabst (1959) and by Murthy & Aguayo (1964) and Monnaye (1975), respectively. The structures of both of these germanates are based on polymerized GeO_4 tetrahedra (single chains in $Na_4Ge_9O_{20}$ and three-

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