An examination of equivalent atomic temperature factors (Table 1) shows that all atoms, and in particular O atoms, are affected by a much larger overall thermal motion in the α' than in the β phase. To investigate the effects of thermal anisotropy, the r.m.s. displacements along the principal directions of vibration have been reported in Table 5. All O atoms in α' have a very anisotropic vibration, and the principal direction with largest displacement is normal to the (100) mirror plane for all atoms lying on it. Two different interpretations are possible for this vibrational behaviour in the orthorhombic structure: (i) the SiO_4 tetrahedra are dynamically disordered and 'jump' between two different orientation states of the monoclinic phase, related by the twinning plane (100); (ii) some microdomains of the β phase, in its two possible orientations, are contained in the α' modification. A refinement of the α' structure according to a split-atom model for O(1) and O(2) was tried, but gave no satisfactory results: this probably means that either the dynamic disorder is only partial, or the amount of monoclinic microdomains present in the α' phase is small. Such phenomena of dynamic disorder or permanency of low-symmetry domains in the high-symmetry phase very often seem to be associated with displacive phase transitions between structures related by point group/subgroup symmetry relations; a typical example is the case of the $\alpha \rightleftharpoons \beta$ quartz transformation (Liebau & Böhm, 1982).

Table 5. *R.m.s. displacements along the principal directions of vibration*

	β Form	α' Form		β Form	α' Form
Sr(1)	0·12 Å	0·14 Å	O(1)	0·13 Å	0·32 Å
	0·11	0·09		0·11	0·09
	0·08	0·08		0·05	0·08
Sr(2)	0·11	0·14	O(2)	0·11	0·34
	0·09	0·09		0·09	0·09
	0·08	0·05		0·01	0·05
Si	0·08	0·10	O(3)	0·11	0·29
	0·04	0·08		0·10	0·11
	0·01	0·05		0·02	0·07
			O(4)	0·12	
				0·09	
				0·05	

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Structure of Pyroelectric Lithium Potassium Sulphate, $LiKSO_4$

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Abstract. $M_r = 142 \cdot 10$, hexagonal, $P6_3$, $a = 5 \cdot 1452$ (2), $c = 8 \cdot 6343$ (6) Å, $V = 197 \cdot 952$ (1) $Å^3$, $Z = 2$, $D_x = 2 \cdot 384$ Mg m^{-3}, $T = 298$ K, $\lambda(\text{Mo } K\alpha) = 0 \cdot 71069$ Å, refinement with all 1575 independent measured X-ray intensities with $\sin\theta/\lambda \leq 1 \cdot 12$ $Å^{-1}$ gave $R_w(F^2) = 0 \cdot 035$. The structure was derived from a lamellar twin crystal formed by alternating layers of laevo- and dextrorotatory-type crystals with opposite polarity along the optic axis. The inclusion of third-order cumulants in the refinements demonstrates highly anharmonic thermal motion of the O atoms.

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Introduction. Lately great attention has been paid to the physical properties of and phase transitions in materials with the general formula $M'M''BX_4$ (M' = Li; M'' = Na,K,Rb,Cs,NH_4,N_2H_5; BX_4 = BeF_4,SO_4,SeO_4). Recent studies have been reported of the crystal structures of the following sulphates in this family: $LiRbSO_4$ (Kruglik, Misyul' & Simonov, 1979; Tanisaki, Mashiyama, Hasebe, Shiroishi & Sawada, 1980), $LiCsSO_4$ (Kruglik, Simonov, Zhelezin & Belov, 1979), and $LiNH_4SO_4$ (Dollase, 1969; Kruglik, Simonov & Aleksandrov, 1978; Itoh, Ishikura & Nakamura, 1981). Several studies of the properties of $LiKSO_4$ have recently appeared in the literature, but the structural information about this material is still limited. This paper reports a detailed crystallographic investigation of the room-temperature phase of $LiKSO_4$.

The crystal structure of $LiKSO_4$ was determined by Bradley (1925). It crystallizes in the hexagonal system and is classified by Chung & Hahn (1972) as a 'proper derivative' of the tridymite structure. $LiKSO_4$ undergoes several phase transitions: the three major ones occur at 178, 695 and 946 K, respectively (Fischmeister & Rönnqvist, 1960; Schroeder, 1975; Prasad, Venudhar, Iyengar & Rao, 1978; Sharma, 1979; Teeters & Frech, 1981). The dielectric and pyroelectric properties not only show large anomalies at these temperatures, but also exhibit nonlinear, temperature-dependent anomalies in the range 200–300 K (Breczewski, Krajewski & Mróz, 1981). Recently, a transition at 201 K on cooling and at 242 K on heating has been reported based on Raman studies (Bansal, Deb, Roy & Sahni, 1980). Attempts to switch the polarization have not been successful, indicating that $LiKSO_4$ is not ferroelectric (Ando, 1962; Delfino, Loiacono, Smith, Shaulov, Tsuo & Bell, 1980).

Experimental. $LiKSO_4$ was crystallized from a saturated aqueous solution at 298 K, with a Li/K molar ratio of 2/1 to prevent crystallization of K_2SO_4; $LiKSO_4$ grows as hexagonal prisms and plates. A microscopic study under polarized light of a plate cut along the crystallographic c axis revealed the existence of two distinct lamellar layers alternating along the optic axis. In a plate cut perpendicular to the c axis twin segments separated by a 60° rotation could be observed under the microscope. Adjacent segments represent electrical twins, as the pyroelectric coefficient, detected as described by Abrahams (1975), showed opposite signs for such segments.

Cell dimensions determined from a powder photograph recorded with a Guinier–Hägg XDC-700 focussing camera, Cu $K\alpha_1$ radiation ($\lambda = 1{\cdot}540598$ Å), Si ($a = 5{\cdot}431065$ Å at 298 K) as internal standard; least-squares refinement of the observed θ values of 32 reflexions provided the cell parameters which are in good agreement with previously reported measurements (Fischmeister & Rönnquist, 1960; Prasad *et al.*, 1978); space-group symmetry confirmed from Weissenberg and precession photographs; systematically absent reflexions together with the polar properties indicated space group $P6_3$ as assumed by Bradley (1925); in an X-ray oscillation photograph (±10°) exposed for 15 h extra reflexions with low θ values were discovered implying a doubling of the a axis; no indication of a doubling of the c axis could be found; the origin of this superstructure is presently not known; the crystal used for data collection was ground to a sphere of radius 0·15 mm ($\mu R = 0{\cdot}257$), intensities of 6283 reflexions up to $\sin\theta/\lambda = 1{\cdot}12$ Å^{-1} collected, PDP 8/a-controlled Enraf–Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, $\omega/2\theta$ scan mode, five standard reflexions measured at regular intervals, maximum time spent on a reflexion 240s, raw intensities corrected for background by a profile-analysis method (Lehmann & Larsen, 1974), intensities of the five standard reflexions decreased less than 2% on average during the data collection, a scaling function derived from the five standard reflexions was used to correct the measured intensities; a contribution for the instability in the measurement and for uncertainty in the scaling function (McCandlish, Stout & Andrews, 1975) was added to the estimated standard deviations, based on counting statistics, of the intensities; corrections for Lorentz, polarization and absorption effects applied; after exclusion of the standard reflexions and space-group extinctions averaging of the intensities of equivalent reflexions within the $\{hk.l\}$ and $\{hk.\bar{l}\}$ subsets gave 1575 independent intensities for the refinement; $R_{\rm int} = \sum|I_o - \bar{I}_o|/\sum I_o = 0{\cdot}016$; atomic scattering factors for Li^+, K^+, S^0 and O^0 and corrections for anomalous scattering from *International Tables for X-ray Crystallography* (1974); $F(000) = 140$.

A structure model was derived from a Patterson synthesis and successive Fourier syntheses; this model was refined with the full-matrix least-squares program *UPALS*; the function minimized was $\sum w(F_o^2 - k^2F_c^2)^2$, where $w^{-1} = \sigma^2(F_o^2)$; a refinement including a scale factor, positional and anisotropic thermal parameters for all atoms and an isotropic extinction coefficient converged at an unsatisfactorily high R value, $R_w = [\sum w(F_o^2 - k^2F_c^2)^2/\sum wF_o^4]^{1/2} = 0{\cdot}136$. A Fourier residual map showed large remaining peaks (Fig. 1*a*). It was concluded that these peaks originate from twinning. Crystals of $LiKSO_4$ occur as two distinct types: one is laevo- and the other dextrorotatory. A lamellar twin may be formed by layers of the two types alternating along the optic c axis without distortion of the lattice (Bradley, 1925). This type of twinning means that reflexions $hk.l$ and $kh.l$ from the two twin orientations are superimposed. Designating $F_o'^2$ and F_o^2 as observed squared structure factor amplitudes for the twinned and untwinned structures, respectively, the observed twin structure factor is

$$F_o'^2(hkl) = (1-p)F_o^2(hkl) + pF_o^2(khl).$$

A preliminary value of the twin parameter, p, was estimated from the expression

$$p = \tfrac{1}{2} - \tfrac{1}{2}\,\frac{F_o'^2(hkl) - F_o'^2(khl)}{F_o^2(hkl) - F_o^2(khl)}.$$

A least-squares refinement of the same parameters as in the previous refinement and including also the twin parameter converged at $R_w = 0{\cdot}0531$. The total number of refined parameters was 23. The value of the twin parameter was $p = 0{\cdot}242\,(2)$. Fourier residual maps calculated for an untwinned crystal,

$$F_o^2(hkl) = \frac{1-p}{1-2p}\,F_o'^2(hkl) - \frac{p}{1-2p}\,F_o'^2(khl),$$

are shown in Figs. 1(*b*) and 2(*a*). Some remaining residues are still observed in these maps indicating either disorder of the sulphate ion or large anharmonic motion of the O atoms.

A disordered model was tried in a series of refinements allowing the sulphate group to be randomly distributed among three possible orientations. The parameters varied for the sulphate ion were: the z coordinate of S, the S—O(1) and S—O(2) bond lengths, the O(1)—S—O(2) angle, anisotropic thermal parameters for all atoms and the three angles describing the orientation of the ion. The threefold symmetry about the S—O(1) bond was retained. The positions converged to positions very near to the ordered model. Residual maps were for all practical purposes identical to residual maps for the ordered model. R_w was 0·051.

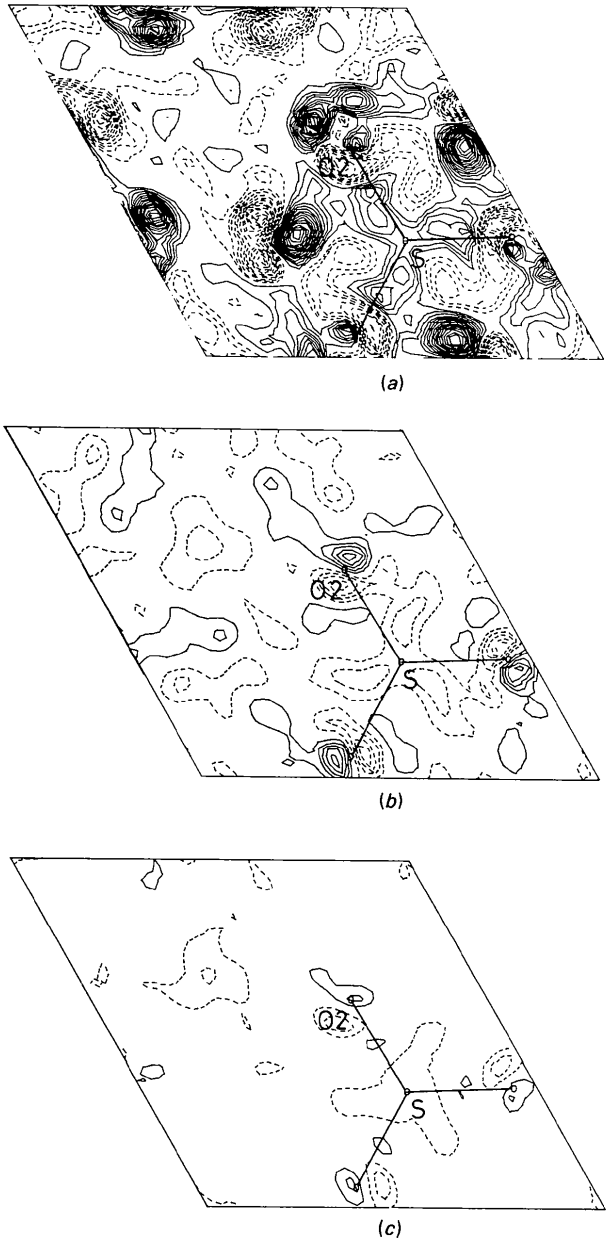

Fig. 1. Residual maps in a plane parallel to the *ab* plane through the O(2) atoms. The S atom, projected on the plane, is located 0·48 Å below the plane. Contour level at 0·1 e Å^{-3}. (*a*) Untwinned model. (*b*) Twin model. (*c*) Twin model and γ tensors on O(1) and O(2).

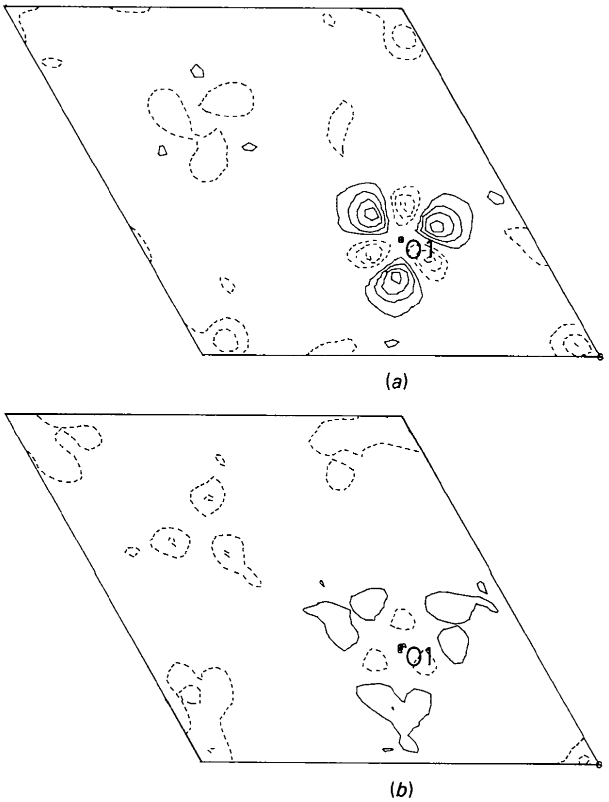

Fig. 2. Residual maps in a plane parallel to the *ab* plane through O(1). Contour intervals at 0·1 e Å^{-3}. (*a*) Twin model. (*b*) Twin model and γ tensors on O(1) and O(2).

The inclusion of third-order cumulants, *i.e.* γ tensors, on O(1) and O(2), to take account of the possible anharmonic thermal motion in the ordered model removed most of the features observed in the earlier residual maps (Figs. 1*c* and 2*b*) and gave $R_w = 0{\cdot}035$. The conventional R value based on F was 0·020. The total number of refined parameters was 37.

The absolute sense of the polar *c* axis of the twinned crystal was related to the measured structure factors through use of Friedel's-law violations caused by anomalous scattering. The $xy\bar{z}$ configuration gave $R_w = 0{\cdot}040$. The case where the twin crystals have opposite polarities gave a slightly lower value, $R_w = 0{\cdot}0348$, as compared to the case where the polarities are the same, $R_w = 0{\cdot}0354$. Parameters from the refinement with opposite polarities are used in the following.

The final value of the twin parameter was $p = 0{\cdot}243\ (2)$ and the value of the isotropic extinction parameter was $g = 4{\cdot}81\ (14) \times 10^3$. The maximum value of the extinction correction factor multiplying F_o^2 was 1·69. Atomic coordinates are given in Table 1.* The extension of the thermal model to include also fourth-order cumulants on the O atoms did not improve the refinement significantly. The programs used for all calculations with a NORD-100 computer have been described by Lundgren (1982).

Discussion. The structure consists of Li^+ and SO_4^{2-} ions lying on threefold axes and K^+ ions on sixfold axes. The Li^+ ion has a tetrahedral coordination with Li—O distances in the range 1·909—1·923 Å (Fig. 3). The K^+ ion is surrounded by nine sulphate O atoms at distances of 2·840—2·989 Å. The arrangement of O ligands may be described as a distorted octahedron with additional O atoms outside three of its edges (Fig. 4). Selected bond distances and angles are given in Table 2.

O(2) is the only atom directly affected by the twinning as all other atoms lie on threefold or sixfold axes and are thus invariant to the twinning operation. The only significant changes in atomic parameters on going from the untwinned to the twinned model were therefore observed for O(2). The changes in thermal parameters were up to 7·5σ (0·006 Å²). The position of O(2) shifted 0·010 (3) Å, in a direction to decrease the S—O(2) distance by 0·006 (2) Å. The inclusion of γ tensors on the O atoms introduced further significant shifts for both O atoms, 0·011 (3) and 0·018 (2) Å for

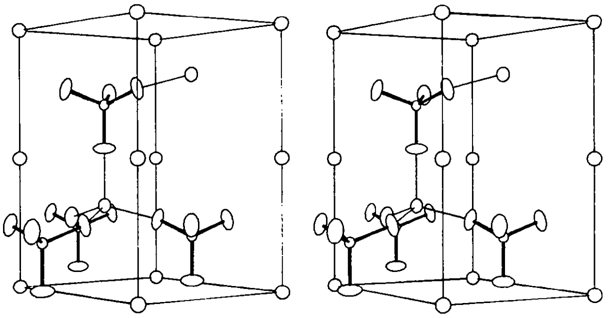

Fig. 3. Stereoscopic *ORTEP* drawing (Johnson, 1976) of $LiKSO_4$ showing the tetrahedral coordination around Li.

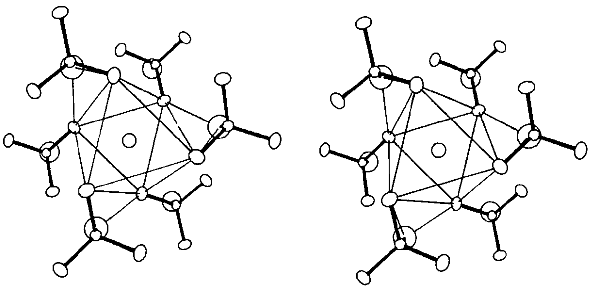

Fig. 4. The environment of K^+ viewed along the *c* axis. This coordination polyhedron may be described as a distorted octahedron with additional O atoms outside three of its edges. The lengths of the octahedron edges are 3·39 Å for edges parallel to the *ab* plane, and 4·74 Å for edges in the **c** direction.

Table 2. *Selected bond distances* (Å) *and angles* (°)

The quantities are calculated from values in Table 1 unless stated otherwise. Distances corrected for thermal riding motion are given in square brackets.

Li–O(1)	1·909 (3)	K–O(1)	2·989 (1) ×3
–O(2)	1·923 (1) ×3	–O(2)	2·840 (1) ×3
O(1)–Li–O(2)	104·68 (8)	–O(2)	2·985 (1) ×3
O(2)–Li–O(2)	113·81 (6)		

		Twin	
	Untwinned	No γ tensors	γ Tensors
S–O(1)	1·456 (5) [1·488]	1·455 (2) [1·488]	1·443 (2) [1·476]
–O(2)	1·467 (2) [1·489] ×3	1·461 (1) [1·480]	1·459 (1) [1·477]
O(1)–S–O(2)	108·81 (13)	108·53 (5)	109·11 (7)
O(2)–S–O(2)	110·12 (13)	110·39 (5)	109·83 (7)

Table 1. *Atomic coordinates* (×10⁵) *and equivalent isotropic thermal parameters*

U_{eq} is the average r.m.s. component of thermal displacement along the principal axes (×10³).

	x	y	z	U_{eq}(Å)
Li	$\frac{1}{3}$	$\frac{2}{3}$	31769 (25)	138 (3)
K	0	0	0	146 (1)
S	$\frac{1}{3}$	$\frac{2}{3}$	70596 (3)	107 (1)
O(1)	$\frac{1}{3}$	$\frac{2}{3}$	53880 (24)	209 (1)
O(2)	34690 (19)	40581 (15)	76126 (20)	172 (1)

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* Lists of structure factors and anisotropic thermal parameters (second- and third-order cumulants) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38186 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

O(1) and O(2), respectively. The shifts in the thermal parameters, U_{ij}, were all insignificant, $<1\cdot4\sigma$ (0·001 Å^2).

The geometry of the sulphate ion thus changes somewhat with the model used. In the final model the two independent S—O distances differ by 0·016 (2) Å, as calculated from the positions of centres of gravity for the electron distribution of the atoms. When correction for thermal riding motion is applied the distances are exactly equal (Table 2). The difference between the O(1)—S—O(2) and O(2)—S—O(2) angles decreases significantly for the γ tensor model; *i.e.* from 1·86 (7)° for the twin model to 0·72 (10)° for the final model.

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