Structure of Lithium Potassium Sulphate, LiKSO₄: A Neutron Diffraction Study

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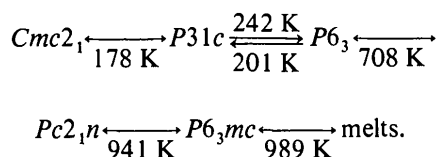*Neutron Physics Division, Bhabha Atomic Research Centre, Trombay, Bombay* 400 085, *India*

Abstract. $M_r = 142.07$, hexagonal, $P6_3$ (or monoclinic, $P2_1$), $a = 5.146$ (1), $c = 8.636$ (2) Å, $V = 198.05$ (8) Å³, $Z = 2$, $D_m = 2.33$, $D_x = 2.382$ (1) g cm⁻³, λ(neutron) = 1.036 Å, $\mu_c = 0.44$ cm⁻¹, $T = 302$ K. Refinement with 278 observed ($>\sigma$) reflections with $\sin\theta/\lambda \le 0.65$ Å⁻¹ gave $R(F) = 0.0358$. The study has revealed merohedral twinning of the crystal by rotation around the [110] axis, and large thermal motion for the apical sulphate oxygen. Attempts to refine the structure by displacing this oxygen off the threefold axis in $P6_3$ resulted in excessively high distortion (~9°) in the bond angles of the SO_4^{2-} ion. An alternative refinement in space group $P2_1$ gives a somewhat better R value than in $P6_3$ (ordered).

Introduction. Lithium potassium sulphate is a member of the family of crystals with the general formula $M^IM^{II}BX_4$ (where M^I = Li, Na; M^{II} = Na, K, Rb, Cs, NH₄, N₂H₅; BX_4 = BeF₄, SO₄, SiO₄). In the classification of Buerger (1954), LiKSO₄ is a 'stuffed derivative' of the tridymite-type of silica structure. The structure is exactly isotypic with the kalsilite form of KAlSiO₄.

The title compound is known to exhibit the following phase transitions:

$$Cmc2_1 \xrightleftharpoons[178\ K]{} P31c \underset{201\ K}{\overset{242\ K}{\rightleftharpoons}} P6_3 \xrightleftharpoons[708\ K]{}$$

$$Pc2_1n \xrightleftharpoons[941\ K]{} P6_3mc \xrightleftharpoons[989\ K]{} melts.$$

The existence of the phase transition at 198 K has been reported recently by Breczewski, Krajewski & Mróz (1981), from pyroelectric and dielectric properties, and by Bansal, Deb, Roy & Sahni (1980) using laser-Raman scattering. Bansal *et al.* have attributed the phase transition to a reorientation of one of the SO_4^{2-} tetrahedra in the unit cell.

Extensitve studies on the physical and thermal properties of the substance have been reported. Some of these properties show anomalous behaviour indicating the phase transitions. These include thermal expansion (Sharma, 1979; Ranga Prasad, Venudhar, Iyengar & Krishna Rao, 1978; Ando, 1962), pyroelectric and dielectric properties (Madhu & Narayanan, 1981;

Ando, 1962), *etc.* A weak anomaly at 253 K has been observed by Holuj & Drozdowski (1981), Breczewski *et al.* (1981) and Sharma (1979), and the possibility of a new phase has been suggested.

The preliminary structural data on LiKSO₄ based on X-ray powder diffraction date back to 1925 (A. J. Bradley), with the approximate positions of all the atoms in the structure (except lithium) having been determined. A later structural study by Chung & Hahn (1973), using single-crystal X-ray diffractometer data, revealed a possible splitting of the anions around the threefold axis, but the details of the structure have not been published.

This study was carried out to determine the precise structure of LiKSO₄ at room temperature. Preliminary accounts have been presented elsewhere (Bhakay-Tamhane, Sequeira & Chidambaram, 1981, 1982a) and a brief summary has been reported (Bhakay-Tamhane, Sequeira & Chidambaram, 1982b). After completing this manuscript, we were informed of the recent paper by Karppinen, Lundgren & Liminga (1983) describing the results of their X-ray study.

Experimental. Neutron data recorded using the TDC-312 computer-controlled four-circle diffractometer (Sequeira *et al.*, 1978) at the CIRUS reactor, Trombay. Crystal 0.44 × 0.27 × 0.21 cm, weight 56.8 mg, cut from a large solution-grown single crystal and mounted with its b axis along the φ axis of the diffractometer. θ–2θ step-scanning mode, 215 reflections ($+h$, $+k$, $+l$) up to $\sin\theta/\lambda = 0.65$ Å⁻¹ recorded. Cell parameters from the peak positions of 51 strong reflections.* Systematic absences consistent with space group $P6_3$.

Preliminary examination of the intensities indicated the possible existence of secondary extinction in the crystal. Hence 85 $\bar{h}kl$ data within $\sin\theta/\lambda = 0.40$ Å⁻¹ were collected additionally. Intensities of equivalent reflections were not averaged. Those of nine reflections which were observed negative were retained as negative. The data were reduced to structure factors using *DATRED* (Rajagopal, Srikanta & Sequeira, 1973, unpublished), which includes the absorption-correction program *ORABS* (Wehe, Busing & Levy, 1962). Absorption factors varied between 0.88 and 0.92.

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* Cell parameters in $P2_1$ refinement: $a = 5.146$ (2), $b = 5.144$ (2), $c = 8.635$ (2) Å, $\gamma = 119.98$ (1)°.

The atomic parameters (x,y,z) reported by Bradley (1925) were used as the starting parameters and the initial structure with isotropic temperature factors and extinction was refined on F^2 using the full-matrix least-squares program *TRXFLS* [Rajagopal & Sequeira, 1977, unpublished – a modified version of *ORFLS* (Busing, Martin & Levy, 1962)] based on 215 independent hkl reflections. Since the space group is hexagonal polar with $|F(hkl)| \neq |F(khl)|$, there existed an ambiguity in the choice of a and b axes. Therefore, refinement of the structure with the atomic parameters changed to (y,x,z) was also carried out. The structure, even in this left-handed system of axes, hereafter model *B*, refined to a local minimum, though the residual $R(F) = 0.195$ was much higher than $R(F) = 0.139$ for the starting model, *A*. Model *A*, refined further using anisotropic temperature factors and isotropic extinction (Zachariasen, 1968), gave $R(F) = 0.0682$. This reduced to 0.0653 on introduction of anisotropic extinction (type II) which is rather high in comparison with our earlier experience with data from the same diffractometer [typically, $R(F) \sim 0.03$]; the mutual agreement factor for the intensities of standard reflections, repeated after every 20 reflections, was also better than 3.0%. In view of this, refinement using various models with different types of disorder for the SO_4^{2-} group was attempted. This included partial disorder between models *A* and *B* and also disorder between two SO_4^{2-} positions staggered by 60° rotation about the threefold symmetry axis, neither of which converged satisfactorily. In another disordered model which incorporated splitting of O(1) as proposed by Chung & Hahn (1973), the O(1) atom did not converge to a unique position.

At this stage, twinning in the crystal was suspected.* Accordingly, a refinement incorporating twinning around the [110] axis was attempted by averaging intensities (rather than structure factors) from the two models *A* and *B*. The F_c^2 for the twin model was defined as

$$F_c^2 = (1-f) F_c^2(A) + f F_c^2(B).$$

This refinement involving the variation of only one additional parameter (f), defining the proportion of the two twin domains, was carried out with a minor alteration of the least-squares program *TRXFLS* and resulted in a dramatic fall in the R value to 0.0312. Addition of the $\bar{h}kl$ data at this stage increased R to 0.0358. All further refinements were continued with the enhanced data set. The relative fractions of the two twin domains refined to 0.790:0.210 (6).

Even in the twinned model, oxygen O(1) on the threefold axis showed large thermal motion normal to the S—O(1) bond. A refinement with disorder (splitting)

of O(1) in $P6_3$ led to a significant improvement in $R(F)$ (0.0338). This refinement, however, results in a considerable distortion ($\sim 9°$) of the bond angles in the SO_4^{2-} tetrahedron with O(1) displaced from the threefold axis by ~ 0.27 Å. Further, the O(1) position could converge to three distinct sets of positions, depending on the starting coordinates. Attempts to refine the structure incorporating the tilting of the SO_4^{2-} ion as a whole so as to correspond to one of the three disordered O(1) positions resulted in a considerably worsened agreement, thereby ruling out possible orientational disorder of sulphate ions.

The structure was also refined in the lower-symmetry space group $P2_1$ varying only the O(1) parameters and freezing the parameters of other atoms at the values obtained in the $P6_3$ refinement. The final residual was 0.0342. However, the refinement did not result in any significant reduction in the thermal motion of O(1). O(1) in this space group $(P2_1)$ converged to a position very close to that obtained in $P6_3$ [O(1) atom ordered].* The distortion of the SO_4^{2-} tetrahedron in this space group is practically negligible.

In general, the O atoms have large anharmonic thermal motion which could perhaps be accounted for by using higher-order cumulants as in the X-ray study (Karppinen et al., 1983). However, since our twinned model has already refined to $R(F) = 0.0342$, we do not expect as significant an improvement with inclusion of cumulants as was observed in the X-ray study.

All the twin-model refinements were carried out using type II anisotropic extinction (Coppens & Hamilton, 1970) which gave marginally lower R values compared with type I. The final extinction parameters $(\times 10^6 \, \text{mm}^{-2})$ in the $P2_1$ refinement were:

$$W_{11} = 9.8 \, (1.3) \qquad W_{12} = -0.9 \, (7)$$
$$W_{22} = 4.8 \, (7) \qquad W_{13} = 0.2 \, (7)$$
$$W_{33} = 1.3 \, (5) \qquad W_{23} = 1.7 \, (4)$$

where W defines the anisotropic particle size $r(N) = |\tilde{N}WN|^{1/2}$ in the direction of unit vector $\hat{N}$, normal to the incident beam in the scattering plane, having components (N_1, N_2, N_3) in the φ-axis system. The weighting scheme, $w = [0.035 + (0.035F_o^2)]^{-2}$ based on error analysis was used in all the final stages of refinement.

The parameters resulting from the $P6_3$(ordered), $P6_3$ (disordered) and $P2_1$ refinements are given in Table 1. Irrespective of the number of parameters varied in the least-square cycle and the space groups used, the twin fraction converges to ~ 0.206 within 2σ. The constrained $P6_3$ (disordered) and $P2_1$ refinements have only 19 variable parameters (one scale factor + one twin fraction + nine O(1)-atom parameters + six extinction parameters + the scattering amplitudes b_S and

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* It would be pertinent to note here that the crystal used for data collection did not have any re-entrant angles and did not show any twinning when examined under a polarized microscope. Thus twinning was not suspected initially.

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* When the atoms O(2), S, Li, K were also floated, the resulting changes in their parameters were insignificant.

Table 1. *Atomic parameters* ($\times 10^4$) *and the average r.m.s. component of thermal displacement along the principal axes, U_{eq}* ($\times 10^3$), *in* LiKSO$_4$ (*see 'Note added in proof'*)

The temperature factor is of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	$U_{eq}(\text{Å})$
$P6_3$ (ordered) structure										
K	0	0	0	202 (11)	β_{11}	55 (4)	$\tfrac{1}{2}\beta_{11}$	0	0	143 (3)
S	3333	6667	7045 (8)	102 (14)	β_{11}	38 (5)	$\tfrac{1}{2}\beta_{11}$	0	0	108 (5)
Li	3333	6667	3146 (11)	192 (22)	β_{11}	52 (7)	$\tfrac{1}{2}\beta_{11}$	0	0	139 (6)
O(1)	3333	6667	5358 (7)	628 (21)	β_{11}	31 (3)	$\tfrac{1}{2}\beta_{11}$	0	0	214 (3)
O(2)	3446 (4)	4031 (3)	7583 (7)	241 (7)	180 (7)	127 (3)	124 (6)	9 (6)	57 (5)	171 (2)
Twin fraction = 0·210 (6)										
R(F) = 0·0358										
$P6_3$ (disordered) structure*										
O(1)	2828 (42)	6531 (88)	5371 (4)	355 (104)	313 (64)	32 (2)	180 (86)	−49 (16)	−32 (32)	161 (20)
Twin fraction = 0·198 (5)										
R(F) = 0·0338										
$P2_1$† (constrained) structure*										
O(1)	3363 (10)	6697 (13)	5358 (4)	619 (29)	720 (40)	31 (2)	350 (33)	7 (9)	23 (14)	219 (6)
Twin fraction = 0·211 (5)										
R(F) = 0·0342										

* No. of variables = 19. All other atoms fixed at $P6_3$ (ordered) positions.

† 2_1 along c axis.

b_{Li}), while all other parameters are frozen at the $P6_3$ (ordered) values. The scattering amplitudes used in these calculations were $b_{\text{K}} = 3\cdot7$ fm, $b_{\text{O}} = 5\cdot8$ fm. The b values of S and Li, refined in the final cycles, converged to $b_{\text{S}} = 2\cdot98$ (4) fm and $b_{\text{Li}} = -2\cdot09$ (4) fm. Maximum least-squares-shift to error in final refinement = 0·05. Final residual nuclear density = 1·2 fm Å^{-3}.

All calculations were performed on the PRIME-450 computer installation at BARC, Trombay.*

Discussion. The results of this neutron study are in close agreement with the results of the recent X-ray study (Karppinen *et al.*, 1983) regarding the nature of twinning in LiKSO$_4$. It is interesting to note that the value of the twin fraction [0·210 (6)] obtained in this study is surprisingly close to that obtained by the X-ray study (0·242).

Bond distances and angles calculated using *ORFFE* (Busing, Martin & Levy, 1964) for the $P2_1$ twin refinement are shown in Table 2 with those obtained in the $P6_3$(ordered) and $P6_3$(disordered) refinements. The bond distances and angles resulting from the $P6_3$(ordered) refinement are in very good agreement with the corresponding X-ray values.

As stated earlier, the $P2_1$ refinement is marginally better than the $P6_3$(ordered) but there are no significant differences in the cell parameters and the interatomic distances resulting from these two. The ordered space group $P6_3$ cannot, however, be rejected on the basis of the refinements reported in this paper at a significance level better than 1%. Similarly the existence of disorder

Table 2. *Bond distances* (Å) *and bond angles* (°) *in* LiKSO$_4$

	$P2_1$*	$P6_3$ (ordered)	$P6_3$* (disordered)
(i) SO$_4^{2-}$ tetrahedron			
3 × S–O(2)	1·462 (3)	1·462 (3)	1·462 (3)
	1·479 (3)†	1·479 (3)†	
S–O(1)	1·457 (8)	1·457 (9)	1·465 (8)‡
	1·495 (8)†	1·493 (9)†	
O(2)–S–O(2)	110·4 (3)	110·4 (3)	110·4 (3)
O(1)–S–O(2)	108·8 (3)		99·6 (8)
	108·8 (4)	108·5 (3)	110·9 (1·4)
	107·9 (4)		114·6 (1·2)
(ii) LiO$_4$ tetrahedron			
3 × Li–O(2)	1·925 (3)	1·925 (3)	1·925 (3)
Li–O(1)	1·911 (10)	1·911 (11)	1·935 (11)‡
O(2)–Li–O(2)	113·8 (2)	113·8 (3)	113·8 (2)
O(1)–Li–O(2)	104·5 (3)	104·6 (3)	110·8 (7)
	104·3 (3)		103·9 (1·1)
	105·1 (3)		98·9 (8)
(iii) K coordination			
3 × K–O(2)	2·850 (4)	2·850 (4)	2·850 (4)
3 × K–O(2)	2·957 (4)	2·957 (5)	2·957 (5)
3 × K–O(1)	2·974 (4)	2·987 (8)	2·829 (3)
	2·987 (7)		2·936 (3)
	3·000 (7)		3·213 (18)

* From constrained (NV = 19) refinements.

† Corrected for thermal motion, oxygen atom assumed to ride on sulphur.

‡ There are three such equivalent distances.

of O(1) in $P6_3$ cannot be rejected at significance levels better than 1%; the excessive distortion in the bond angles of the SO$_4^{2-}$ ion seems to make this kind of disorder less likely.

Figs. 1 and 2, drawn using *ORTEP* (Johnson, 1965), show the LiKSO$_4$ polyhedral linkages in the crystal. The figures are drawn for the $P6_3$ (ordered) model for convenience. Fig. 1 gives the view along the c axis with only one tetrahedral layer being shown. In successive layers, which are almost exactly eclipsed in this view, an

LiO_4 tetrahedron pointing up is replaced by a SO_4^{2-} tetrahedron pointing down *etc*. The K^+ ions have ninefold coordination and fill the large voids in the $(LiSO_4)^-$ network. Fig. 2 gives a view of the unit cell showing the 'double chain' of tetrahedra. The crystal is very loosely packed and shows interesting low-temperature phase transitions. A recent EPR study (Fonseca, Ribeiro, Gazzinelli & Chaves, 1983) has suggested an unusual sequence of incommensurately modulated and commensurately modulated structural phase transitions in $LiKSO_4$. A proper understanding of these phase transitions will not be possible until detailed structures of the low-temperature phases become available.
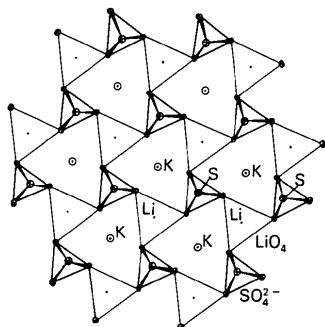
We are grateful to Dr A. P. Roy for helpful discussions and to Shri S. N. Momin for maintenance of the diffractometer.

Note added in proof: The coordinates given in Table 1 have been recast to make them compatible with the X-ray values (Karppinen *et al.*, 1983), as requested by the Editor. They now correspond to the 20% twin fraction *B* described in this paper rather than the 80% fraction *A*.

A quantitative comparison of the neutron and X-ray parameters using a half-normal probability plot shows a straight-line distribution with a slope of about 3, indicating an underestimation of the standard deviations in either or both the studies.

Fig. 1. View along the *c* axis; the thermal ellipsoids include 30% probability density. Only one tetrahedral layer is shown. The arrangement of tetrahedra is trydymite-like with adjacent tetrahedra pointing in opposite directions along the *c* axis. Thus the sequence of '*U*p' (SO_4) and '*D*own' (LiO_4) tetrahedra is *UDUDUD....*

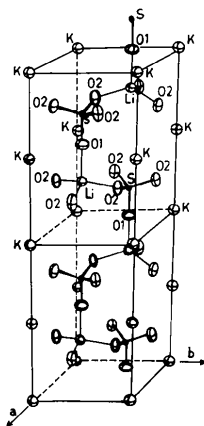
Fig. 2. View of a 'double chain' of tetrahedra in the crystal. The viewing direction is inclined to [210] by 22° off the basal plane. The thermal ellipsoids are drawn to a scale of 50% probability.

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