FERRETTI, A., ROGERS, D. B. & GOODENOUGH, J. B. (1965). *J. Phys. Chem. Solids,* **26**, 2007-2011.

GOODENOUGH, J. B. (1965). *Bull. Soc. Chim. Fr.* **4**, 1200-1201.

MAGNÉLI, A. (1953). *Acta Chem. Scand.* **7**, 315-324.

SATO, M., GRIER, B. H, SHIRANE, G. & FUJISHITA, J. (1982). *Phys. Rev. B,* **25**, 501-503.

SIENKO, M. J. (1963). *Adv. Chem.* **39**, 224-245.

SKOKAN, M. R., MOULTON, W. G. & MORRIS, R. C. (1979). *Phys. Rev. B,* **20**, 3670-3677.

STANLEY, R., MORRIS, R. C. & MOULTON, W. G. (1978). *Solid State Commun.* **27**, 1277-1280.

STANLEY, R. K., MORRIS, R. C. & MOULTON, W. G. (1979). *Phys. Rev. B,* **20**, 1903-1914.

Crystal Structure of KLiSO$_4$ as a Function of Temperature

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Abstract

A crystal structure investigation focused on the thermal motion of O and Li and based on single-crystal X-ray diffraction data (Mo $K\alpha$) has been carried out at 293, 398 and 568 K in space group $P6_3$ with the assumption of complete atomic order. Anharmonic temperature factors based on the Gram-Charlier expansion have been refined up to the third order for O and Li with about 600 observed F_o values ($R_w = 0.017-0.024$). Probability densities (O, Li) and one-particle potentials have been calculated from the coefficients of the temperature factors. These allow the following conclusions: both oxygens show large and strongly anharmonic thermal motion as well as static disorder; the oxygens on the threefold axes [O(1)] vibrate mainly perpendicular to c with a pronounced threefold symmetry; O(2) atoms exhibit their main vibrations parallel to c. The thermal vibrations can be explained by coupled rotational vibrations of the oxygens around the S atoms. The Li atoms develop a strong anharmonic thermal motion above 400 K with a pronounced threefold symmetry.

Introduction

KLiSO$_4$ undergoes several phase transitions; those at approximately 180, 700 and 950 K may be considered as main transitions.

The phase transition at 180 K has been investigated by Raman scattering (Bansal, Deb, Roy & Sahni, 1980), pyro- and dielectric studies (Breczewski, Krajewski & Mróz, 1981; Madhu & Narayanan, 1981), piezoelectric studies (Mróz, Krajewski, Breczewski, Chomka & Sematowicz, 1982), X-ray diffraction (Tomaszewski & Lukaszewicz, 1982) and NMR studies (Meng-Quingan & Cao-Quijuan, 1982). An orthorhombic structure model has been proposed for the low-temperature phase ($\leq$180 K) by Tomaszewski & Lukaszewicz (1982).

An intermediate phase has been reported in a temperature range of about 250-180 K. Further conclusions on this phase are contradictory. Bansal, Deb, Roy & Sahni (1980) propose from Raman-scattering data a trigonal structure caused by cooperative reorientation of the tetrahedra. For the same phase Tomaszewski & Lukaszewicz (1982) assume a hexagonal structure to explain their X-ray diffraction data. Holuj & Drozdowski (1981) found hints in an EDR study that this phase may have an incommensurate structure.

The phase transition at 700 K was found by several experimental techniques, including double reflection (Blittersdorf, 1929), differential thermal analysis (Lepeshkov, Bodaleva & Kotova, 1961), measurements of thermal-expansion coefficients, DC resistivity, pyroelectric current and dielectric constants (Ando, 1962), X-ray diffraction study (Prasad, Venudhar, Iyengar & Rao, 1978; Fischmeister & Rönnquist, 1960), and Raman scattering (Bansal, Deb, Roy & Sahni, 1981).

The phase transition at 950 K was detected by differential thermal analysis (Lepeshkov *et al.*, 1961). The phases stable up to 946 K and stable above 946 K are reported to show orthorhombic and hexagonal symmetry, respectively (Schroeder, 1975).

The physical properties of KLiSO$_4$ reported in the above-mentioned papers deal with the two phases stable below and above 190 K. The low-temperature phase has been shown to be ferroelastic (Mróz *et al.*,

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1982). At the phase transition an anomalous change of the pyroelectric and dielectric properties was observed, which vary in a non-linear way with temperature in both phases (Delfino, Loiacono, Smith, Shaulov, Tsuo & Bell, 1980; Breczewski *et al.*, 1981; Mróz *et al.*, 1982). Madhu & Narayanan (1981) reported KLiSO₄ to be an improper ferroelectric. An unusual overdamping and broadening of several vibrational modes (Teeters & Frech, 1981, 1982) and a frequency increase of a longitudinal optic mode (Bansal *et al.*, 1981) was found in the room-temperature phase.

The phase stable up to 700 K can be considered as a 'stuffed derivative of tridymite' which is one of the polymorphic SiO₂ crystal structures (Nowacki, 1942; Buerger, 1954). This phase belongs to a structure family with the general formula $M'M''AX_4$ ($M' = $ Li; $M'' = $ K, Rb, Cs, NH₄, N₂H₅; $AX_4 = $ SO₄, BeF₄). These compounds form framework structures built up of six-membered rings of vertex-connected MX_4 and AX_4 tetrahedra. Different arrangements of the tetrahedra in these rings lead to different space groups for ideal crystal structures. The actual structure may deviate from the ideal arrangement by slight distortions (Hahn, Lohre & Chung, 1969, 1970; Chung & Hahn, 1972a, b; Hahn & Chung, 1973).

The crystal structure of KLiSO₄ was determined by Bradley (1925). Crystal structure refinements at room temperature have been carried out by Karppinen, Lundgren & Liminga (1983) and Bhakay-Tamhane, Sequeira & Chidambaram (1985) for a twinned crystal and by Chung & Hahn (1985) for twinned and untwinned crystals. KLiSO₄ crystallizes in space group $P6_3$. The SO₄ and LiO₄ tetrahedra form an ordered three-dimensional framework structure characterized by six-membered rings of three LiO₄ and three SO₄ tetrahedra. The apices of the three LiO₄ tetrahedra point in the opposite direction to those of the three SO₄ tetrahedra (Fig. 1). The K atoms occupy positions on the hexagonal c axis. They are coordinated by nine oxygens (Fig. 1). The oxygens O(1), which form the vertices of the tetrahedra, play a special role in the crystal structure investigations

of this compound. In the ideal structure model these oxygens occupy a twofold position on the threefold axes. However, these oxygens exhibit an unusually high temperature factor. Furthermore, large residual densities with a pronounced threefold symmetry were observed in difference Fourier maps. These densities were treated by a threefold O(1) split position with an occupation probability of $\frac{1}{3}$ by Bhakay-Tamhane, Sequiera & Chidambaram (1985) and Chung & Hahn (1985). Contrary to this model Karppinen, Lundgren & Liminga (1983) expanded the temperature-factor formalism to a third-rank tensor (γ tensor). Both structure models work comparably well in treating the residual O(1) densities. A behaviour similar to that of O(1) was found for F(1) in KLiBeF₄, but RbLiBeF₄ has been described with an ordered twofold F(1) position with a reasonable F(2) temperature factor (Chung & Hahn, 1985). KLiSO₄ exhibits 'twinning by merohedry'. This type of twinning has been studied by Donnay & Donnay (1974), Catti & Ferraris (1976), Klapper & Hahn (1979), Hahn (1981) and Rees (1982). The influence of the twinning of LiKSO₄ on a crystal structure investigation has been studied by Chung & Hahn (1985). The formation of twin domains and twin boundaries in KLiSO₄ has been investigated with X-ray topography by Klapper, Hahn & Chung (1985).

The Raman studies (Teeters & Frech, 1981, 1982) and the unusual pronounced threefold symmetry of the O(1) atoms (Karppinen *et al.*, 1983; Bhakay-Tamhane *et al.*, 1985; Chung & Hahn, 1985) stimulated this structure investigation of KLiSO₄ as a function of temperature to answer the following questions: (1) does a state of O(1) disorder exist which is correctly described by split atoms or do the O(1) atoms show strong anharmonic temperature motion, not correctly described by the standard harmonic temperature-factor formalism (anisotropic temperature factors)?; (2) do the Li atoms exhibit a tendency to disorder with increasing temperature?

Experimental

Crystals of LiKSO₄ were grown by slow evaporation at 405 K from an aqueous solution containing equimolar proportions of Li₂SO₄, H₂O and K₂SO₄. Spheres of approximate diameter 200 μm were ground in a sphere mill. A sphere of diameter 190 μm was used for the data collection [automatic Philips PW 1100 diffractometer, Mo $K\alpha$ radiation, graphite monochromator, $\sin \theta/\lambda \le 1\cdot08\text{Å}^{-1}$, scan speed $0\cdot72°$ min^{-1}, scan width $1\cdot5°$; ω scan for $\theta \le 45°$, otherwise $\theta/2\theta$ scan; step-scan (60 steps); $h, k \le 0, l \le 0 +$ Friedel reflections; background determination by the algorithm of Lehmann & Larsen (1974); observed reflections with $I > 3\sigma(I)$, $\sigma^2(I) = (\sigma_c)^2(I) + (0\cdot01I)^2$, σ_c calculated from counting statistics alone; total of about 2600 reflections; for
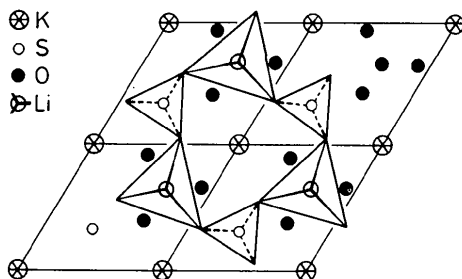

Fig. 1. Projection of the structure of LiKSO₄ on the (0001) plane. The oxygens are represented either by black dots or by the apices of the corners of the tetrahedra.

number of averaged reflections and unobserved reflections see Table 1; absorption correction for spheres (*International Tables for X-ray Crystallography*, 1967), $\mu/\rho = 25\cdot54$ cm² g⁻¹ for Mo $K\alpha$ radiation; lattice constants determined from 24 centred single-crystal reflections by least-squares refinement of the orientation matrix: at 293 K: $a = 5\cdot147$ (3), $c = 8\cdot633$ (4), at 398 K: $a = 5\cdot160$ (3), $c = 8\cdot634$ (4), at 568 K: $a = 5\cdot190$ (3), $c = 8\cdot637$ (4) Å. The crystals were heated with an airblower with a relative and absolute accuracy of ±2 and ±4 K, respectively. Investigation temperatures were 293, 398, 568 K.

The data reduction was carried out with the program system *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983). The averaging of the intensities was carried out including negative net intensities of single intensity measurements. Standard deviations of the averaged intensities were calculated from the $\sigma^2(I)$ values and from the deviations of the single measurements from the mean. The larger σ value was taken as the standard deviation of the mean. The twin ratio K was calculated with equation (10) of Chung & Hahn (1985) with their suggested reflection intensities. The K values may range from 0 for a single crystal to 1 for a balanced twin. We found from our data that $K = -0\cdot020$ (14). The extinction factors were taken into account for this calculation. We concluded that we had used a single-crystal for the data collection.

Scattering curves for Li, K, S were taken from *International Tables for X-ray Crystallography* (1974), and for $O^{1/2-}$ by interpolation between O and O^- from the oxygen scattering curves of Schwarz & Schulz (1978).

Structure refinements

The structure refinements were carried out with anharmonic temperature factors up to third order based on the Gram–Charlier expansion. The coefficients of these anharmonic temperature factors were used for the calculations of probability density functions. The theoretical background for this method of structure investigation has been discussed by Zucker & Schulz (1982a) and its application was illustrated by structure investigations of the ionic conductors Li₃N (Zucker & Schulz, 1982b) and β-PbF₂ (Schulz, Perenthaler & Zucker, 1982). The refinement technique has been described by Schulz *et al.* (1982).

The final refinements included the following parameters: one scale factor, two extinction parameters (Becker & Coppens, 1974a, b), all variable positional parameters (six parameters) and 32 thermal parameters. K and S were refined with second-order (anisotropic) temperature factors only. O(1) occupied the atomic position 2(b) ($\frac{1}{3}, \frac{2}{3}, z$) on the threefold axes in all refinements. Occupation probabilities were not

Table 1. *Atomic parameters, numbers of reflections and R values*

The Wyckoff notation of the atomic position is in square brackets after the atomic designation. B_{eq} was calculated from the volume of the vibrational ellipsoid.

	293 K	398 K	568 K
K [2(a)]			
z	0	0	0
B_{eq}(Å²)	1·8	2·3	3·2
Li [2(b)]			
z	0·815 (1)	0·822 (2)	0·818 (2)
B_{eq}(Å²)	1·4	2·0	2·6
S [2(b)]			
z	0·20626 (8)	0·20683 (9)	0·2081 (2)
B_{eq}(Å²)	1·0	1·3	1·6
O(1) [2(b)]			
z	0·0367 (7)	0·0398 (9)	0·0462 (7)
B_{eq}	3·6	4·5	6·1
O(2) [6(c)]			
x	0·3474 (4)	0·3494 (5)	0·3547 (8)
y	0·9399 (4)	0·9395 (5)	0·9367 (8)
z	0·2634 (5)	0·2638 (6)	0·2667 (7)
B_{eq}(Å²)	2·5	3·2	4·4
Observed reflections	630	631	607
Unobserved reflections	29	33	57
R (observed)	0·027	0·030	0·034
R_w (observed)	0·023	0·024	0·017
R (all)	0·030	0·033	0·038
R_w (all)	0·025	0·026	0·018

refined. Only observed reflections were used. Final parameters and R values are listed in Table 1.*

The extinction-correction parameter y ($F_{cor} = F_o/y$) was a maximum for the 300 reflection. $Y_{max} = 0\cdot10, 0\cdot14, 0\cdot26$ for the lowest, medium and highest temperature, respectively. The highest correlation coefficients of $|0\cdot9|$ were observed between scale-factor and extinction-correction parameters. All other correlation coefficients were $\le|0\cdot8|$.

The structure refinements were carried out with the program system *PROMETHEUS* (Zucker, Perenthaler, Kuhs, Bachmann & Schulz, 1983).

Anharmonic thermal vibrations

As reported in *Introduction*, the density of the O(1) atoms shows a pronounced threefold symmetry perpendicular to the c axis. This density distribution was successfully described by two different structure models: (1) split atomic positions with an occupation probability of $\frac{1}{3}$ and harmonic (anisotropic) temperature factors (Bhakay-Tamhane, Sequeira & Chidambaram, 1985; Chung & Hahn, 1985); (2) completely occupied twofold atomic positions on the threefold axes and an anharmonic temperature factor formalism with a third-rank tensor (γ tensor) (Karpinnen *et al.*, 1983).

Karppinen *et al.* (1983) conclude from their structure refinement with the γ tensor that the O(1) atoms undergo anharmonic thermal vibrations with threefold symmetry. However, this is an overinterpretation of their results. Both structure models allow only a description of an observed density, but they do not allow a conclusion to be made on the nature of its dynamic or static disorder. Such conclusions may be drawn from structure investigations as a function of temperature.

A very simple (however, only approximate) way to distinguish between static and dynamical disorder lies in an extrapolation of the mean-square displacements $\overline{u^2}$ of the anisotropic temperature factors to $T = 0$ K. Such an extrapolation is displayed in Fig. 2 for all atoms. It shows the $\overline{u^2}$ values along the main axes of the thermal vibrational ellipsoids. The following can be read from Fig. 2:

(1) All $\overline{u^2}$ follow straight lines.

(2) Li, K, S have isotropic $\overline{u^2}$ values. But this holds only in the frame of the harmonic approximation (see below).

(3) Both oxygens exhibit a strongly anisotropic thermal motion. The directions of the largest thermal vibrational components of O(1) and O(2) are perpendicular and parallel to the c axis, respectively.

____(4) All extrapolations of the straight lines cut the $\overline{u^2}$ axes at positive $\overline{u_o^2}$ values. The two largest $\overline{u^2}$ values extrapolate to $u_o^2 = 0{\cdot}01$ Å^2; all other straight lines cut at $u_o^2 = 0{\cdot}005$ Å^2. The latter value is typical for the zero-point vibrations and compares well with similar studies (Zucker & Schulz, 1982*b*). However, $u_o^2 = 0{\cdot}01$ Å^2 of the two largest oxygen components points to a weak static disorder. This means that the refined oxygen positions represent only point-of-gravity positions. The split distance s, *i.e.* the distance between the 'true' atomic positions to the refined point-of-gravity position on the threefold axes, can be estimated from $\overline{u_o^2} = 0{\cdot}01$ Å^2 to be $s \simeq 0{\cdot}1$ Å (Schulz, 1972). But the $\overline{u^2}$ are dominated by thermal vibrations. This follows from the pronounced temperature dependence of all $\overline{u^2}$ values in Fig. 2.

The analysis of the anharmonic thermal vibrations has been carried out by calculation of the probability density function (p.d.f) from the refined coefficients of the anharmonic temperature factors. The p.d.f. allows the calculation of the probability Δp of finding atomic centres displaced by Δr from their average position into a volume element ΔV. The p.d.f. $p/V(\Delta r)$ is the Fourier transform of the temperature factor. It can be displayed in the form of density contours around the atomic position (average position). Theoretical background, mathematical details, and a detailed example are described by Zucker & Schulz (1982*a, b*).

The p.d.f. of O(1) perpendicular to c shows a very pronounced threefold symmetry and a clear tendency to spread with increasing temperature (Fig. 3). The direction of the lowest thermal vibrations deviates by only a few degrees from the direction of the O(1)–K bond. It reflects the resistance against bond shortening towards the K atoms. The probability densities of Fig. 3 can be transformed into a one-particle potential of the oxygens. Fig. 4 shows this potential for all three temperatures along the [120] direction, *i.e.* along the K–O bond. Only the significant parts of these three potentials are shown. The significance levels are calculated from Boltzmann statistics. These energy levels are chosen so that 99% of the atoms have energies below this level. It follows that these significance levels increase with increasing temperature.
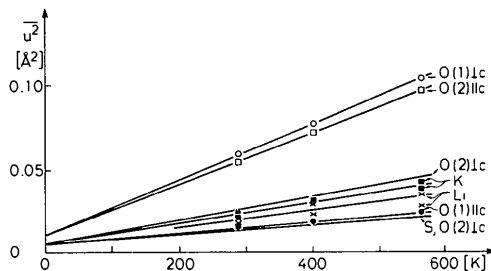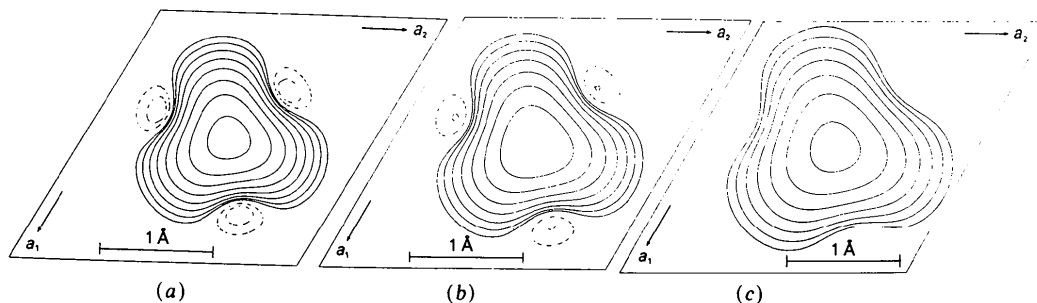

Fig. 2. Mean-square displacements $\overline{u^2}$ as a function of temperature. The $\overline{u^2}$ values along the main axes of the thermal vibrational ellipsoids are drawn. Two straight lines have been drawn without data points to avoid overlapping. The ellipsoids of Li, K, S and O(1) have the form of a rotational ellipsoid with the rotation axes parallel to c. The main thermal axes of O(2) form the following angles with a_1, a_2 and c: approximately parallel to c (80, 108, 18°), approximately perpendicular to c, larger value (20, 100, 94°), smaller value (108, 21, 73°).

Fig. 3. Probability density O(1) perpendicular to c as a function of temperature [O(1) at ($\frac{1}{3}$, $\frac{2}{3}$, 0·04)]. Density lines at 1, 2, 4, 8, ... eÅ^{-3}. Investigation temperatures: (*a*) 293 K, (*b*) 398 K, (*c*) 568 K.

Table 2. *Interatomic distances* (Å)

Uncorrected: distances without correction of thermal motion. Corrected: distances corrected for the harmonic part of the temperature factor. S-O: riding thermal motion; K-O, Li-O: independent thermal motion. Thermal corrections have been carried out with the program *ORFFE* (Busing *et al.*, 1977).

	No. of bonds	293 K Uncorrected	293 K Corrected	398 K Uncorrected	398 K Corrected	568 K Uncorrected	568 K Corrected
K-O(1)	3	2·988 (2)	3·009 (2)	2·999 (2)	3·024 (2)	3·023 (2)	3·057 (2)
-O(2)	3	2·832 (4)	2·851 (4)	2·841 (4)	2·865 (4)	2·857 (5)	2·891 (6)
-O(2)	3	3·003 (4)	3·021 (4)	3·016 (4)	3·040 (4)	3·067 (6)	3·094 (6)
Mean		2·941 (3)	2·960 (3)	2·952 (3)	2·976 (4)	2·982 (5)	3·014 (5)
Li-O(1)	1	1·91 (1)	1·96 (1)	1·88 (2)	1·93 (2)	1·97 (1)	2·04 (1)
-O(2)	3	1·916 (2)	1·946 (3)	1·933 (5)	1·973 (5)	1·929 (5)	1·982 (5)
Mean		1·915 (5)	1·950 (6)	1·920 (11)	1·962 (11)	1·939 (7)	1·997 (7)
S-O(1)	1	1·464 (6)	1·497 (6)	1·442 (8)	1·484 (8)	1·398 (6)	1·458 (7)
-O(2)	3	1·458 (2)	1·477 (3)	1·454 (2)	1·478 (3)	1·441 (3)	1·478 (5)
Mean		1·460 (3)	1·482 (4)	1·451 (4)	1·480 (5)	1·430 (4)	1·473 (6)

The potentials in Fig. 4 have the typical form of a pair potential: They are steep towards the K atom and stretched in the opposite direction. The stretched parts become steeper with increasing temperature. This is caused by an unresolved static disorder wrongly described by the anharmonic temperature factors (Bachmann & Schulz, 1984). This result agrees with the conclusions drawn from the temperature
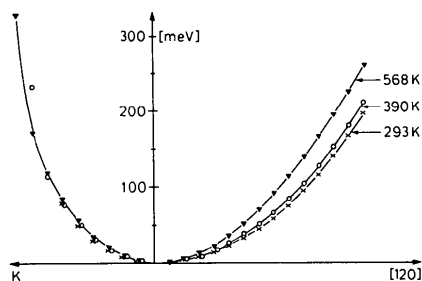

Fig. 4. One-particle potential of the O(1) atom along the [120] direction. Only the significant parts of the potentials are drawn. The zero point of the potential is the O(1) position at ($\frac{1}{3}$, $\frac{2}{3}$, 0·04).
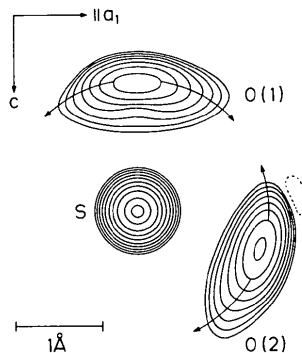

Fig. 5. Probability densities of O(1), O(2) and S in (010) plane at 568 K. Atomic positions: O(1) ($\frac{1}{3}$, $\frac{2}{3}$, 0·04), O(2) (0·35, 0·94, 0·27), S ($\frac{1}{3}$, $\frac{2}{3}$, 0·21). The p.d.f. of S has been calculated with the coefficients of the anisotropic temperature factor only. Lines as in Fig. 3.

dependence of the $\overline{u^2}$ values in Fig. 2. It follows that the potential minimum of the O(1) atoms does not lie on the threefold axes, but is displaced about 0·1 Å from it. This causes a threefold split position, but the potential barrier between these split positions is so low that they are not resolved at room temperature.

Therefore, more than 50% of the O(1) atoms must have energies at room temperature which are higher than this potential barrier. This allows a rough estimate of 0·03 eV (1 eV = 1·60 × 10⁻¹⁹ J) for this potential barrier. Similar considerations hold for the pronounced thermal vibrations of the O(2) atoms parallel to the *c* axis. This can be concluded from the similarities between the largest thermal vibrational amplitudes of O(1) and O(2) as displayed in Fig. 2.

It is very probable that the O(1) and O(2) atoms undergo coupled thermal vibrations in the form of a rotation around the S atoms. This conclusion can be drawn from Fig. 5. This type of thermal motion minimizes the repulsion between the O atoms and keeps the S-O bonds constant.

The Li atoms behave in a nearly isotropic manner up to about 400 K. At 568 K a pronounced anharmonic thermal vibration in the plane perpendicular to the *c* axes has been developed (Fig. 6). The directions of the smallest thermal vibrations nearly
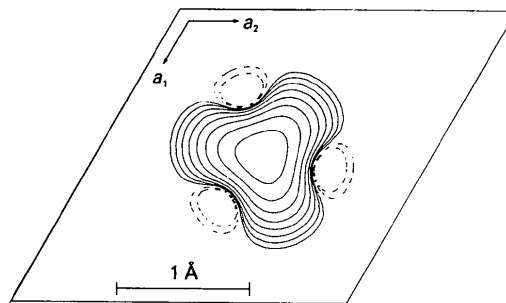

Fig. 6. Probability densities of Li perpendicular to c at 568 K. Li at ($\frac{2}{3}$, $\frac{1}{3}$, 0·31). Lines as in Fig. 3.

coincide with the Li-O(2) bonds. Therefore, the thermal motion of Li above 400 K can be simply described by a resistance against bond shortening and a much less hindered vibration towards the tetrahedral faces.

Interatomic distances and harmonic (anisotropic) thermal vibration

The K-O and Li-O distances as a function of temperature behave as expected; they increase with increasing temperature without correction for thermal vibration (Table 2). However, the S-O distances decrease with increasing temperature (Table 2). Such behaviour has been frequently observed in structural units with strong covalent bonds, for example for $(Si, Al)O_4$ tetrahedra in framework silicates. The whole unit shows large thermal vibrations perpendicular to the bonds. In such cases the interatomic distances are apparently shortened with increasing temperature. As discussed in the previous section the SO_4 tetrahedra have to be considered as such a structural unit. Therefore, the S-O distances must be corrected for thermal vibrations. Unfortunately, no such program exists which takes into account anharmonic thermal vibrations. They can be corrected only in an approximate way by taking the harmonic part of the temperature factor. We have carried out this correction with the program ORFFE (Busing, Martin, Levy, Brown, Johnson & Thiessen, 1977) assuming riding motion for the S-O distances and independent thermal motion for Li-O and K-O (Table 2). The corrected S-O(2) distances are now independent of temperature [1·478 (4) Å]. But the S-O(1) still decreases, only the decrease has become smaller. This shows that the harmonic correction is not sufficient. An extrapolation of the S-O(1) distances to $T = 0$ K results in 1·535 Å and probably gives the best approximation of the correct S-O(1) distance.

References

ANDO, R. (1962). J. Phys. Soc. Jpn, **17**, 937-940.
BACHMANN, R. & SCHULZ, H. (1984). Acta Cryst. A**40**, 668-675.
BANSAL, M. L., DEB, S. K., ROY, A. P. & SAHNI, V. C. (1980). Solid State Commun. **36**, 1047-1050.
BANSAL, M. L., DEB, S. K., ROY, A. P. & SAHNI, V. C. (1981). J. Phys. (Paris) Colloq. C6, **42**, 902-904.
BECKER, P. J. & COPPENS, P. (1974a). Acta Cryst. A**30**, 129-147.
BECKER, P. J. & COPPENS, P. (1974b). Acta Cryst. A**30**, 148-153.
BHAKAY-TAMHANE, S., SEQUEIRA, A. & CHIDAMBARAM, R. (1985). Acta Cryst. C**40**, 1648-1651.
BLITTERSDORF, H. (1929). Z. Kristallogr. **71**, 141-167.
BRADLEY, A. J. (1925). Philos. Mag. **49**, 1225-1237.

BRECZEWSKI, T., KRAJEWSKI, T. & MRÓZ, B. (1981). Ferroelectrics, **33**, 9-12.
BUERGER, M. J. (1954). Am. Mineral. **45**, 600-614.
BUSING, W. R., MARTIN, K. O., LEVY, H. A., BROWN, G. M., JOHNSON, C. K. & THIESSEN, W. E. (1977). ORFFE. Oak Ridge National Laboratory, Tennessee, USA.
CATTI, M. & FERRARIS, G. (1976). Acta Cryst. A**32**, 163-165.
CHUNG, S. J. & HAHN, TH. (1972a). Acta Cryst. A**28**, S57-S58.
CHUNG, S. J. & HAHN, TH. (1972b). Mater. Res. Bull. **7**, 1209-1218.
CHUNG, S. J. & HAHN, TH. (1985). Acta Cryst. In preparation.
DELFINO, M., LOIACONO, G. M., SMITH, W. A., SHAULOV, A., TSUO, Y. H. & BELL, M. I. (1980). J. Solid State Chem. **31**, 131-134.
DONNAY, G. & DONNAY, J. D. H. (1974). Can. Mineral. **12**, 422-425.
FISCHMEISTER, H. F. & RÖNNQUIST, A. (1960). Ark. Kemi, **15**, 393-396.
HAHN, TH. (1981). Z. Kristallogr. **156**, 114-115.
HAHN, TH. & CHUNG, S. J. (1973). Z. Kristallogr. **137**, 447-449.
HAHN, TH., LOHRE, G. & CHUNG, S. J. (1969). Naturwissenschaften, **56**, 459.
HAHN, TH., LOHRE, G. & CHUNG, S. J. (1970). Z. Kristallogr. **132**, 431.
HOLUJ, F. & DROZDOWSKI, M. (1981). Ferroelectrics, **36**, 379-382.
International Tables for X-ray Crystallography (1967). Vol. II. Birmingham: Kynoch Press.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
KARPPINEN, M., LUNDGREN, J. O. & LIMINGA, R. (1983). Acta Cryst. C**39**, 34-38.
KLAPPER, H. & HAHN, TH. (1979). Z. Kristallogr. **149**, 173-174.
KLAPPER, H., HAHN, TH. & CHUNG, S. J. (1985). Acta Cryst. In preparation.
LEHMANN, S. & LARSEN, F. K. (1974). Acta Cryst. A**30**, 580-584.
LEPESHKOV, I. N., BODALEVA, N. V. & KOTOVA, L. T. (1961). Russ. J. Inorg. Chem. **6**, 864-868.
MADHU, B. R. & NARAYANAN, P. S. (1981). Proc. Nucl. Phys. Solid State Phys. Symp. **24C**, 335-336.
MENG-QUINGAN & CAO-QIJUAN (1982). Wuli Xuebao, **31**, 1405-1411.
MRÓZ, B., KRAJEWSKI, T., BRECZEWSKI, T., CHOMKA, W. & SEMATOWICZ, D. (1982). Ferroelectrics, **42**, 71-74.
NOWACKI, W. (1942). Naturwissenschaften, **30**, 471-472.
PRASAD, T. R., VENUDHAR, Y. C., IYENGAR, L. & RAO, K. V. K. (1978). Pramana, **11**, 81-83.
REES, D. C. (1982). Acta Cryst. A**38**, 201-207.
SCHROEDER, K. (1975). Thesis. Phase Diagrams of some Binary Sulphate Systems, Chalmers Univ. of Technology, Göteborg, Sweden.
SCHULZ, H. (1972). Z. Kristallogr. **136**, 321-349.
SCHULZ, H., PERENTHALER, E. & ZUCKER, U. H. (1982). Acta Cryst. A**38**, 729-733.
SCHWARZ, K. & SCHULZ, H. (1978). Acta Cryst. A**34**, 994-999.
TEETERS, D. & FRECH, R. (1981). Solid State Ionics, **5**, 437-440.
TEETERS, D. & FRECH, R. (1982). Phys. Rev. B, **26**, 4132-4139.
TOMASZEWSKI, P. E. & LUKASZEWICZ, K. (1982). Phys. Status Solidi A, **71**, K53-K55.
ZUCKER, U. H., PERENTHALER, E., KUHS, W. F., BACHMANN, R. & SCHULZ, H. (1983). J. Appl. Cryst. **16**, 358.
ZUCKER, U. H. & SCHULZ, H. (1982a). Acta Cryst. A**38**, 563-568.
ZUCKER, U. H. & SCHULZ, H. (1982b). Acta Cryst. A**38**, 568-576.