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High-temperature phase transitions in $LiKSO_4$

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The high-temperature sequence of phase transitions in $LiKSO_4$ has been investigated by means of infrared reflectivity, Brillouin scattering, and electrical measurements. Results show the strong correlation between the lithium-ion mobility and the reorientational motion of the sulfate groups. The sulfate-ion orientational order-disorder phase transition, which occurs at 435 °C, is triggered by the instability of the librational modes. The lowering of symmetry and the increase of the number of formulas per unit cell above this phase transition are explained by the existence of an orthorhombic spatial modulation of the disorder probability along two different directions in the basal plane, between 435 and 670 °C. This model reconciles two explanations for the structure of this intermediate phase which seemed to be incompatible: an incommensurate phase and an orthorhombic structure. The frustration mechanism of "three-member gear" type is proposed to be the cause for the incommensurate modulation.

I. INTRODUCTION

Lithium potassium sulfate is the object of great interest today, due to the complexity and richness of its sequence of phase transitions, an unusual case for an inorganic crystal with such a simple chemical formula: a set of ten phase transitions has been proposed between 20 and 100 K, including, for example, ferroelastic,[1,2] incommensurate[3,4] and superionic phases.[5] However, there is an important controversy concerning symmetries, phase-transition temperatures, and even the existence of some of these phases, in particular for those below room temperature. Some authors have observed a mixture of different structures at low temperatures.[6] It seems clear today that the sequence of phase transitions of $LiKSO_4$ is strongly dependent on crystal-growth conditions, on the thermal cycle, and on the presence of twinnings and defects in the as-grown crystal.

The structure of $LiKSO_4$ at room temperature has a hexagonal symmetry, belonging to the space group C_6^6 (stuffed trydimite type). The lattice parameters of the unit cell, which contains two molecular formulas ($Z=2$) are $a=5.147$ Å and $c=8.633$ Å.[7] In this structure, the lithium ion is surrounded by tetrahedrally coordinated oxygens, each one belonging to a different sulfate group: conversely, each sulfate group is associated with four lithium ions.

Lithium potassium sulfate undergoes at least two phase transitions above room temperature: at about 435 and 670 °C. The structures of the high-temperature phases are not yet well established. A structure of hexagonal symmetry, isomorphic with that of α-K_2SO_4 [space group D_{6h}^4 ($P4/nnc$)] has been proposed for the highest temperature phase ($T > 670$ °C).[3]

The structure of the intermediate phase ($435 < T < 670$ °C) is more controversial: some authors proposed an orthorhombic symmetry[8] while others suggested a modulated structure, commensurate between 435 and 470 °C (space group C_6^6 with $Z=8$) and incommensurate in the temperature range 470–670 °C. Drozdrowski *et al.*[9] have observed anomalies at 60 °C in some elastic constants of $LiKSO_4$, measured by Brillouin scattering, and proposed a new phase transition. However, no anomaly has been observed in a recent Brillouin study of $LiKSO_4$ in the vicinity of 60 °C.[10] The possible existence of such a phase transition is another controversial and interesting aspect of the sequence of phase transitions of $LiKSO_4$.

In order to understand the mechanisms of the high-temperature phase transitions and to obtain some insight into the structure of these phases, we have studied single crystals of $LiKSO_4$ from room temperature up to the melting point (~ 720 °C) using three experimental techniques: infrared (ir) reflectivity, Brillouin scattering, and electrical conductivity measurements. Main results and their interpretation are presented here.

II. EXPERIMENTAL

$LiKSO_4$ single crystals have been obtained by seed growth from aqueous solution by slow evaporation at 40 °C. The structure of the crystals has been confirmed by powder x-ray analysis.

The ir reflection spectra have been performed with a Bruker IFS 113C spectrometer adapted to work between 10 and 1200 K. The available frequency domain is 20–4000 cm^{-1}. The Brillouin spectrometer is a pressure-scanned triple-passage-plane Fabry-Pérot interferometer (effective finesse 70, resolving power 760 000) which is frequency-controlled by a Michelson interferometer. The light source is an Ar-ion laser emitting at $\lambda_0 = 514.5$ nm. Complex-impedance spectroscopy was used to determine the dc electrical conductivity. This ac technique is very interesting in the study of ionic conductors because it allows the elevation of the specific contribution of the electrodes to the total impedance of the sample due to polarization phenomena. The experimental setup used in this study permits the measurement of very high resistances, up to 10^9 Ω. Evaporation of gold and silver was used to obtain the metal electrodes. The latter gives smaller electrode impedance but the former was preferred for working at high temperature to avoid diffusion of silver ions into the crystal.

III. RESULTS

A. ir reflection

The ir reflection spectra have been fitted by using the factorized form of the dielectric function

$$\epsilon(\omega)=\epsilon_\infty \prod_j \frac{\Omega_{j\mathrm{LO}}^2-\omega^2+i\gamma_{j\mathrm{LO}}\omega}{\Omega_{j\mathrm{TO}}^2-\omega^2+i\gamma_{j\mathrm{TO}}\omega} \tag{1}$$

in which each mode TO or LO is described by its frequency Ω_j and its damping γ_j.

The oscillator strength of the j mode is given by the relation

$$\Delta\epsilon_j=\epsilon_\infty \Omega_{j\mathrm{TO}}^{-2}\frac{\prod_k \Omega_{k\mathrm{LO}}^2-\Omega_{j\mathrm{TO}}^2}{\prod_{k\,(\neq j)} \Omega_{k\mathrm{TO}}^2-\Omega_{j\mathrm{TO}}^2} \tag{2}$$

deduced by comparing the classical and factorized forms of the dielectric function.

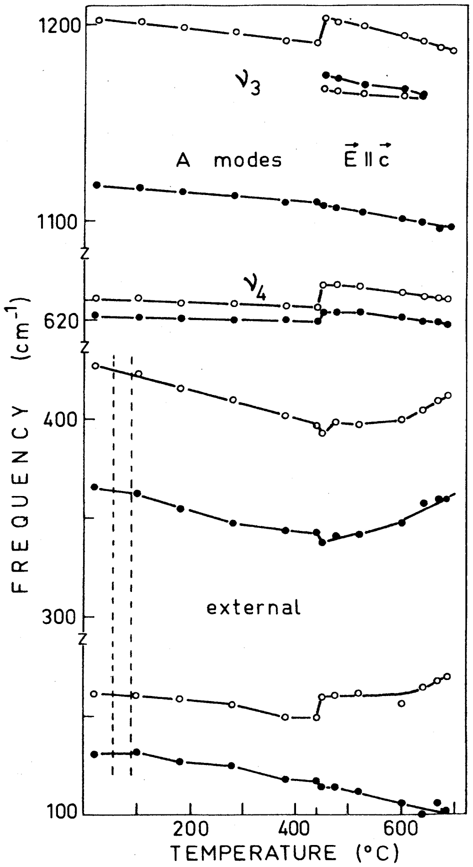

FIG. 1. Temperature dependence of the TO (solid circles) and LO (open circles) A-symmetry lattice mode frequencies of $LiKSO_4$. Solid curves are guides to the eye.

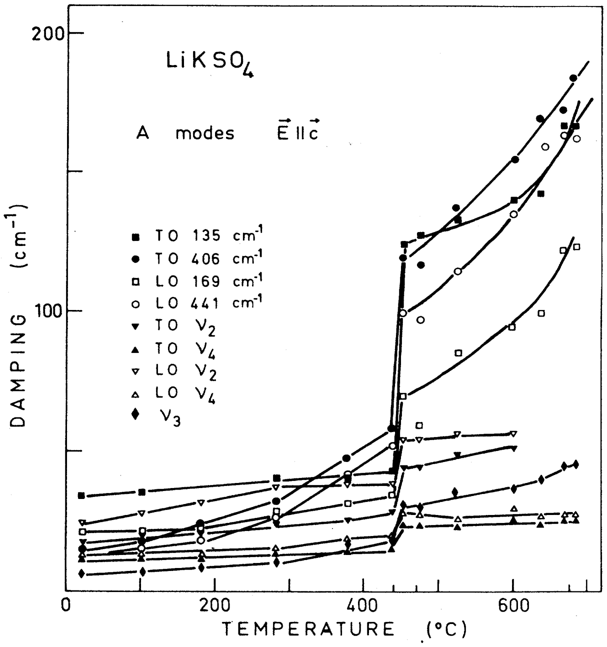

FIG. 2. Temperature dependence of the A-symmetry lattice mode dampings of $LiKSO_4$. Solid curves are guides to the eye.

Figure 1 shows the temperature dependence of the A-mode frequencies. One observes a slight decrease of frequencies when the phase transition at 453 °C is approached from below. The external modes are the most affected, but there is properly no significant softening.

The temperature dependence of the vibrational-mode dampings presents a marked behavior. Figure 2 evidences the broadening of the phonon response when temperature is increased and an important discontinuous increase of damping at $T=435$ °C, typical of order-disorder phase transitions. It should be noted that the mode associated with the oxygen-lithium stretching (that with frequency at about 400 cm^{-1}) is the most affected.

Figure 3 shows the evolution with temperature of the sum $\epsilon_\infty+\sum_j \Delta\epsilon_j$. If one compares this curve with the temperature dependence of the dielectric constant at 100 KHz (Ref. 11), agreement is found below the phase transition at $T=435$ °C. Above this phase transition there is a disagreement by a factor of 3 (parallel to the hexagonal c axis), or 2 (perpendicular to the c axis), revealing the existence of a low-frequency dispersion mechanism associated with the disorder above the phase transition. We have introduced a relaxational mode to simulate the ir reflection spectra above $T=435$ °C. We have found a relaxation time of about 0.25 ps, which should be compared with the time of reorientation of the sulfate ions, 0.5 ps, calculated by Chaplot and Rao.[12]

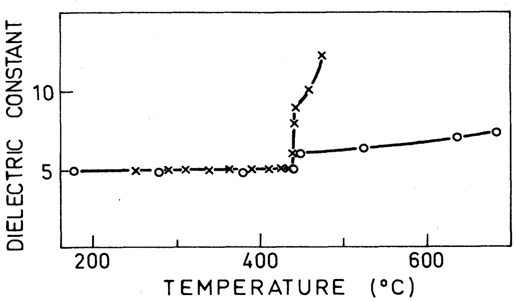

FIG. 3. Temperature dependence of the sum $\epsilon_\infty + \sum_j \Delta\epsilon_j$ of the modes polarized perpendicular to the c axis (×) and the dielectric constant (Ref. 11) $\epsilon_\perp$ at 100 kHz (○) of LiKSO$_4$. The noncoincidence of these curves above 435 °C reveals the existence of a low-frequency dispersion mechanism associated with the disorder above the phase transition.

B. The appearance of an extra mode above 435 °C

A ν_3 internal mode polarized along the c axis appears in the spectra *above* the phase transition at $T=435$ °C. This appearance reveals unusual behavior: a phase transition towards a structure with *lower symmetry at higher temperature.* The oscillator strength of this extra mode (Fig. 4) decreases with increasing temperature and it vanishes at $T=670$ °C, confirming the high-temperature phase transition and the hexagonal structure above this phase transition.

C. Effective charges

The splitting of the TO and LO frequencies is a measure of the Coulombic field associated with the effective charges carried by the ions. Therefore, from the knowledge of the TO and LO frequencies of all polar modes, one can calculate the effective charges (Ze) by using the relation[13]

$$\sum_j (\Omega_{j\mathrm{LO}}^2 - \Omega_{j\mathrm{TO}}^2)_\alpha = \frac{1}{\epsilon_v V} \sum_k \frac{(Ze)_{k\alpha}^2}{m_k} , \qquad (3)$$

where m_k is the mass of the k ion, V the volume of the unit cell occupied by the k ions, ϵ_v the vacuum permittivity, and α an index which denotes a direction of polarization. In the case of LiKSO$_4$ we have at least four unknowns (namely, the mean effective charge of each ion) and two equations [Eq. (3) and the electrical neutrality]. Nevertheless, for semimolecular crystals like LiKSO$_4$, when the internal and external modes of SO$_4$ are decoupled enough, one can consider, as a first step, the molecular entities as nonpolar and calculate the molecular effective charges by summing the left-hand side of Eq. (3) over the external modes only. This leaves us with three equations and four unknowns. An approximate effective charge attributed to the potassium ion, namely $(Ze)_\mathrm{K}=0.9e$, permits us to calculate Z_Li, Z_S, Z_O, and Z_{SO_4}. This approximation is supported by the facts that (i) the contribution of potassium to Eq. (3) is small because of large mass in the denominator, and (ii) potassium, being less mobile than lithium, is expected to play a minor role at the phase transition. In the evolution of the effective charges (Fig. 5), we must pay attention to the discontinuous jump which manifests at $T=435$ °C, particularly important for the case of the lithium ion.

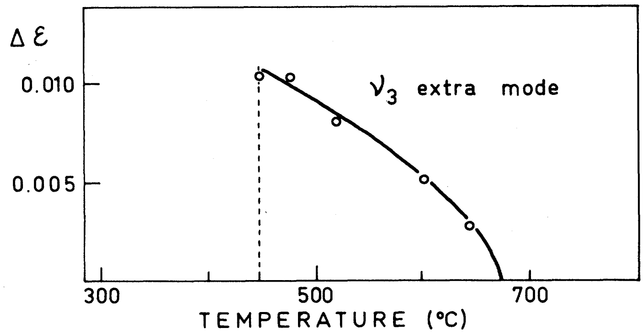

FIG. 4. Temperature dependence of the LiKSO$_4$ ν_3 extramode oscillator strength. The existence of this mode between 435 and 670 °C reveals the lowering of symmetry in this intermediate phase with respect to the room- and higher-temperature phases.

D. Electrical conductivity

The temperature dependence of the electrical conductivity of LiKSO$_4$ (perpendicular to c) is shown in Fig. 6. One observes a discontinuous increase—by a factor of 20—of the conductivity at $T=435$ °C. The high-temperature phase transition at $T=670$ °C manifests itself also by an increase of the electrical conductivity, which amounts to values typical of superionic materials, namely $10^{-2}\ \Omega^{-1}\mathrm{cm}^{-1}$. As can be seen in Fig. 6, the curve $\ln\sigma T$ versus $1/T$ does not follow the classical Arrhenius behavior, namely a straight line, when the phase transitions are approached from below, but its slope in-

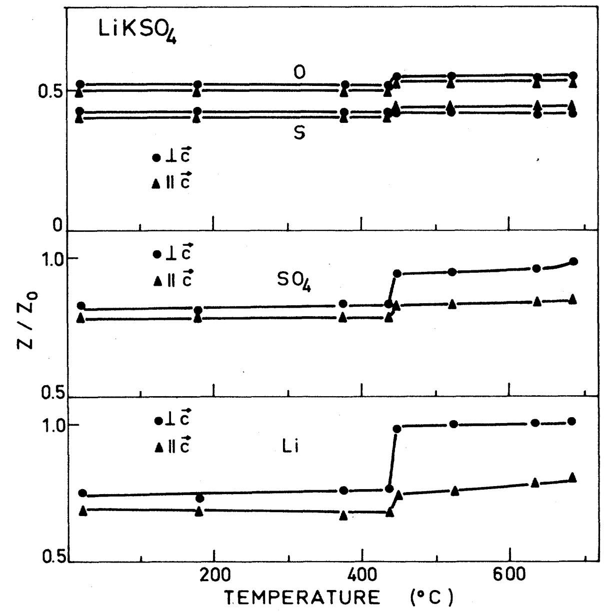

FIG. 5. Temperature dependence of the relative effective charges of LiKSO$_4$.

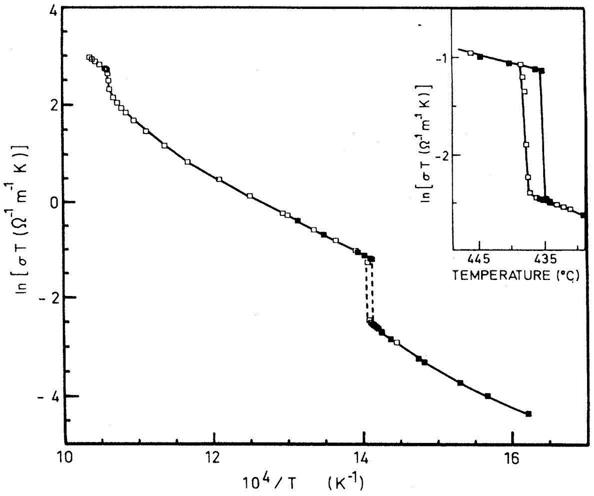

FIG. 6. Temperature dependence of the electrical conductivity of $LiKSO_4$ measured perpendicular to the c axis by heating (open circles) and by cooling (solid squares). An hysteresis of 3 °C is observed at the phase transition at $T = 435\,°C$ (inset).

creases with temperature. Derivating the Arrhenius relation with respect to $1/T$ one obtains

$$-k_B\frac{d[\ln(\sigma T)]}{d(1/T)}=E_a-T\frac{d(E_a)}{dT} . \tag{4}$$

It must be noted that the activation energy E_a is no longer given by the slope of $\ln(\sigma T)$ versus $1/T$ when E_a depends on temperature; an increase in the slope of the experimental curve can correspond to a decrease in the activation energy. This seems to be the case when the phase transitions of $LiKSO_4$ are approached from below. Using Eq. (4), the decrease in the activation energy just below the first phase transition was calculated as being about 0.05 eV. This value must be compared with k_BT at 435 °C, i.e., 0.06 eV.

E. Brillouin scattering

Figure 7 shows the temperature dependence of ρV^2 (ρ, density; V, velocity) of longitudinal-acoustic waves propagating along two different directions in the basal plane: [110] and [100]. These values correspond to the elastic constant c_{11} in the hexagonal phases ($T < 435\,°C$ and $T > 670\,°C$). The observation of two Brillouin lines in the intermediate phase ($435 < T < 670\,°C$) reveals the existence of crystallographic domains in this temperature range. Besides, the comparison of the Brillouin shifts for the longitudinal waves propagating along [110] and [100] directions confirms the symmetries of the hexagonal phases (since it coincides) and proves that the symmetry of the intermediate phase is lower than hexagonal since the isotropy of the velocity in the basal plane is canceled.

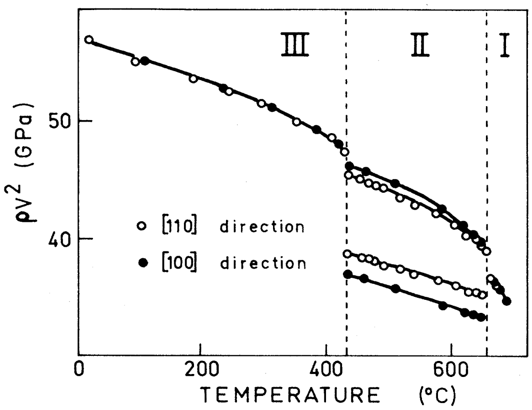

FIG. 7. Temperature dependence of ρV^2 for longitudinal-acoustic waves propagating along the [110] direction (open circles) and the [100] direction (solid circles) in $LiKSO_4$. These values correspond to c_{11} elastic constant in the hexagonal phases ($T < 435\,°C$ and $T > 670\,°C$).

IV. DISCUSSION

A. The mechanisms of high-temperature phase transitions

Figure 8 shows the structure of $LiKSO_4$ at room temperature projected (a) into the basal plane and (b) perpendicular to it.

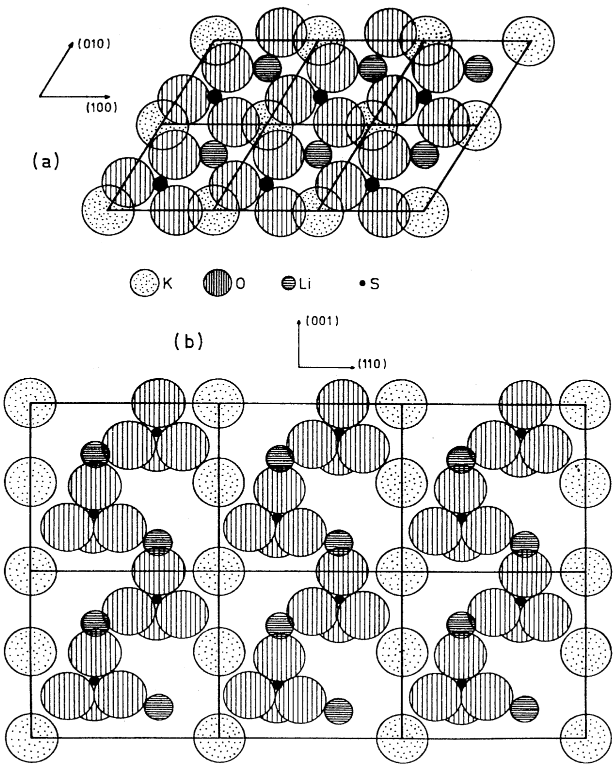

FIG. 8. Structure of $LiKSO_4$ at room temperature projected (a) into the basal plane and (b) perpendicular to it. The radii of the circles that represent the ions are proportional to the ionic radii.

dicular to it. The radius of the circles that represent the ions are proportional to the ionic radius. We observe that the structure is very compact in the basal plane (the lithium ions are tightly closed into a tetrahedral cage of oxygen) if compared with the perpendicular direction. This is to be correlated with the considerable difference between the sulfate-ion librational frequencies around axes parallel to the c axis ($\sim 200\ \text{cm}^{-1}$) and into the basal plane ($\sim 50\ \text{cm}^{-1}$).[14,15] Librations around axes parallel to c are submitted to restoring forces more important due to stronger chemical bonds in the basal plane with respect to the other direction. The ternary symmetry of the density probability of the oxygen ions, observed by Schulz *et al.*,[7] suggests that highly anharmonic librations take place around three equivalent axes in the basal plane of the hexagonal structure. The increase of the thermal amplitude of the sulfate-ion librations with temperature is evidenced by the broadening of the phonon response at high temperature; the phase transition at $T = 435\,^{\circ}\text{C}$ is preceded by the divergence of the external mode damping, principally those associated with the lithium-ion vibrations. It must be noted that those modes vanish in the Raman spectra far below the phase transition.[14–16] The increase of anharmonicity reflects coupling of the sulfate orientational disorder with the cation vibrations.

The structure of $LiKSO_4$ at room temperature presents a hollow cage just above the lithium site [Fig. 8(b)]. This position is forbidden to the lithium ions because they are closed into a tetrahedral cage formed by oxygen, each one belonging to a different sulfate group. However, a rotation of a sulfate group around an axis in the basal plane permits a lithium ion to reach this position. To minimize the energy in this new local configuration associated with the displacement, the other three sulfate groups linked to this particular lithium ion will rotate and, consequently, provoke the displacement of the other lithium ions out of their sites, and so on. The lithium-ion mobility is, therefore, coupled with the rotation movements of the sulfate groups by a "gear" mechanism.

The temperature dependence of the electrical conductivity of $LiKSO_4$ (Fig. 6) shows that the onset of this mechanism takes place below the phase transition. The decrease of the activation energy of about 0.05 eV described earlier reflects the beginning of the reorientational motion of the lithium ions. However, the compacted structure of the room-temperature phase makes the reorientation of the sulfate groups difficult. When the thermal amplitude of the librations is large enough to give rise to reorientations of the sulfate ions, it is energetically more interesting for the system to adopt a new configuration which accommodates these motions. The instability of the librational modes triggers a phase transition toward a structure which accommodates the reorientational motion of the sulfate groups and the lithium-ion mobility. The jump in the effective charges of $LiKSO_4$ at $T = 435\,^{\circ}\text{C}$ (Fig. 5) reflects the increase of ionicity due to the rearrangement of the structure. In the sulfate-ion orientationally disordered state, the lithium ions will be partially relaxed from the constraint of the oxygen tetrahedral coordination. This is to be related with the argumentation, especially important, of the lithium effective charge at $T = 435\,^{\circ}\text{C}$.

Figure 9 illustrates the remarkable similarity in the evolution of the electrical conductivity, the elastic constant c_{33}, and the lithium-mode damping. The broadening of the low-frequency vibration response is behavior typical of ionic conductors. The fluctuations of the force constants due to the motions of the mobile ions imply a local mode-frequency distribution and, therefore, the broadening of the phonon response. The dynamical disorder of the ionic conductors provokes important effects on the elastic constants. In these compounds, the phase transition is, in general, accompanied by the softening of one or more elastic constants. Fluorine-type crystals such as CaF_2, SrF_2, BaF_2, PbF_2, and $SrCl_2$ show a continuous but important decrease of the c_{11} elastic constant[17–19] in accordance with the evolution of the electrical conductivity which increases continuously to superionic values. On the other hand, in the superionic phase transition of AgI, in which the electrical conductivity presents a discontinuous jump, one observes an abrupt downward jump in the evolution of the frequency of a longitudinal-acoustic mode.[20]

Following Huberman and Martin's model for the collective excitations in the ionic conductors,[21] the longitudinal-acoustic phonons couple with intersite hopping of the mobile ions. In the case of $LiKSO_4$, the c_{33} elastic constant presents a marked behavior when the crystal is heated and its evolution is similar to that of the

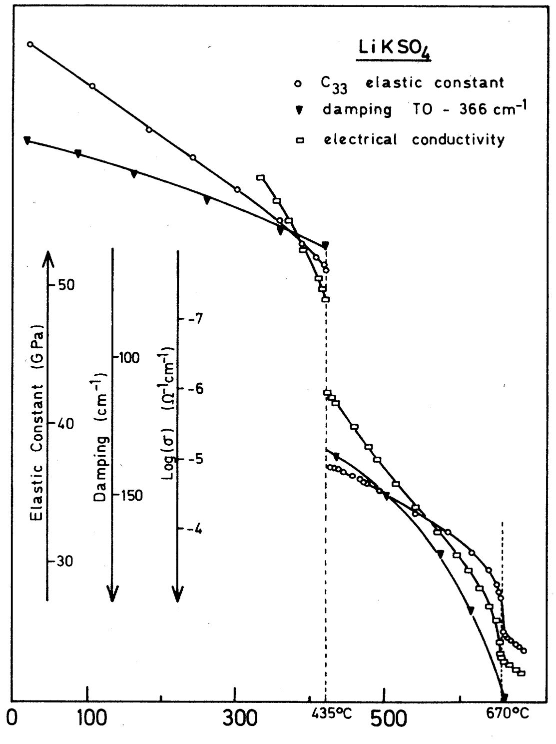

FIG. 9. Temperature dependence of the c_{33} elastic constant (open circles), the "lithium-mode" damping (solid triangles), and the electrical conductivity (open squares) of $LiKSO_4$.

electrical conductivity: a discontinuous jump at $T = 435\,^{\circ}\mathrm{C}$ and a smooth variation at $T = 670\,^{\circ}\mathrm{C}$. This is explained by the fact that the lithium-ion jumps between the two equivalent sites in the disordered phase are found to be parallel to the c axis. The decrease of c_{33} elastic constant is, therefore, correlated with the increase of disorder.

B. The structure of LiKSO$_4$ at high temperature

1. The highest temperature phase

The results of the Brillouin and infrared studies of LiKSO$_4$ have confirmed the hexagonal symmetry of the structure above $T = 670\,^{\circ}\mathrm{C}$. The very high values observed for the electrical conductivity in this phase imply a structure disordered enough. The D_{6h}^{4} space group is compatible with our experimental results. We must remember that the symmetry elements of the D_{6h}^{4} group, absent in the C_{6}^{6} group, are due to the orientational disorder of the sulfate groups and, moreover, that in this structure two equivalent positions are available for each lithium ion, a necessary condition for a good ionic conductivity.

2. The intermediate phase

The Brillouin study for LiKSO$_4$ has evidenced the existence of a structure with symmetry lower than hexagonal and the presence of domains which conserves the c axis in common. Krajewski *et al.*[2] have also observed three types of ferroelastic domains in this intermediate phase which led them to propose an orthorhombic symmetry. In the infrared study, the lowering of symmetry at $T = 435\,^{\circ}\mathrm{C}$ manifests itself by the appearance of one ν_3 extra mode polarized along the c axis. This is surprising considering that one would expect extra modes polarized perpendicular to the c axis due to the lifting of the hexagonal degeneracy in the basal plane. But the only extra mode being polarized parallel to c reveals that the two sulfate groups of a unit cell, which were equivalents in the room-temperature phase, are no longer equivalents above $T = 435\,^{\circ}\mathrm{C}$. Consequently, the hexagonal symmetry axis, which was responsible for bringing one sulfate in the position occupied formerly by the other (followed by a translation of $c/2$), disappears at $T = 435\,^{\circ}\mathrm{C}$, yielding a superstructure (more than two formulas per unit cell) with symmetry lower than hexagonal.

If the existence of a ν_3 extra mode reflects the nonequivalence of the sulfate groups, its disappearance at $T = 670\,^{\circ}\mathrm{C}$ is the signature of the high-temperature phase transition. Therefore, above $670\,^{\circ}\mathrm{C}$, the sulfate groups become equivalent again and orientationally disordered. This analysis must be confronted with the behavior of the electrical conductivity near the high-temperature phase transition; the increase of the conductivity at $T = 670\,^{\circ}\mathrm{C}$ reveals that the intermediate phase is somewhat less disordered than the high-temperature phase. One can deduce the following scheme for the high-temperature phase transition of LiKSO$_4$:

$$\text{order}\ \overset{T=435\,^{\circ}\mathrm{C}}{\text{———}}\ \text{partial disorder}\ \overset{T=670\,^{\circ}\mathrm{C}}{\text{———}}\ \text{total disorder}\ .$$

Results suggest that a fraction of the sulfate groups is well oriented while the other ones are orientationally disordered in the intermediate phase. The intensity of the ν_3 extra mode, i.e., its oscillator strength $\Delta\epsilon$, is a parameter that measures the remaining degree of order. Figure 10 shows the evolution of $\Delta\epsilon$ versus $670\,^{\circ}\mathrm{C} - T$ on a log-log scale. Results fit a law $\Delta\epsilon \propto (670\,^{\circ}\mathrm{C} - T)^{x}$, where the exponent x was found to be equal to 0.5 ± 0.05.

3. Triple-k modulation

The observation of x-ray satellite lines by Li (Ref. 3) in the intermediate phase of LiKSO$_4$ have been interpreted as due to a triple-**k** modulation of the type

$$P(x,y) = A_1\cos(\mathbf{k}_1\cdot\mathbf{r}) + A_2\cos(\mathbf{k}_2\cdot\mathbf{r}) + A_3\cos(\mathbf{k}_3\cdot\mathbf{r})\ , \qquad (5)$$

where $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$ are wave vectors along three equivalent axes a_1, a_2, and a_3 in the basal plane of the hexagonal structure. In accordance with this model, the bases of the sulfate tetrahedra located at (x_0, y_0) tilt at an angle proportional to $P(x_0, y_0)$; the probability of orientational disorder is also modulated according to Eq. (5). This modulation would be incommensurate between 670 and $470\,^{\circ}\mathrm{C}$ and commensurate in the temperature range $435-470\,^{\circ}\mathrm{C}$, corresponding to a superstructure of hexagonal symmetry belonging to the same space group of the room-temperature phase (C_{6}^{6}) but with eight formulas per unit cell. Three tetrahedra over four would be orientationally disordered in this commensurate phase. A picture of the triple-**k** modulation as well as the positions of its maxima and minima are showed in Fig. 11. It should be noted that the type of modulation proposed by Li (Ref. 3) has a hexagonal symmetry (hence, the incommensurate structure also has a hexagonal symmetry) and that the amplitude of the minima of $P(x,y)$ is smaller than that of the maxima. In other words, this modulation favors one sense for the orientation of the sulfate tetrahedra with respect to the other.

The existence of an incommensurate modulation is supported by a LiKSO$_4$ lattice-dynamics calculation of Chaplot *et al.*,[22] who have predicted the existence of an E_1-symmetry incommensurate softening which involves

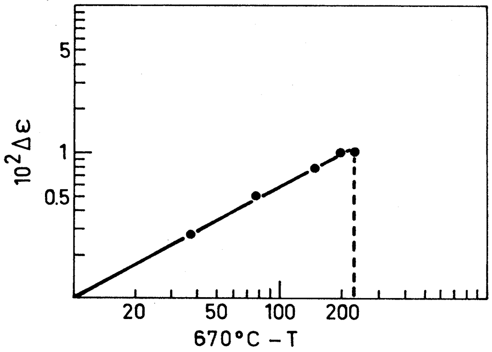

FIG. 10. Temperature dependence of the ν_3 extra-mode oscillator strength of LiKSO$_4$ vs $670\,^{\circ}\mathrm{C} - T$ on a log-log scale. Results fit a law $\Delta\epsilon\alpha(670\,^{\circ}\mathrm{C} - T)^{x}$, with the exponent x equal to 0.5 ± 0.05.

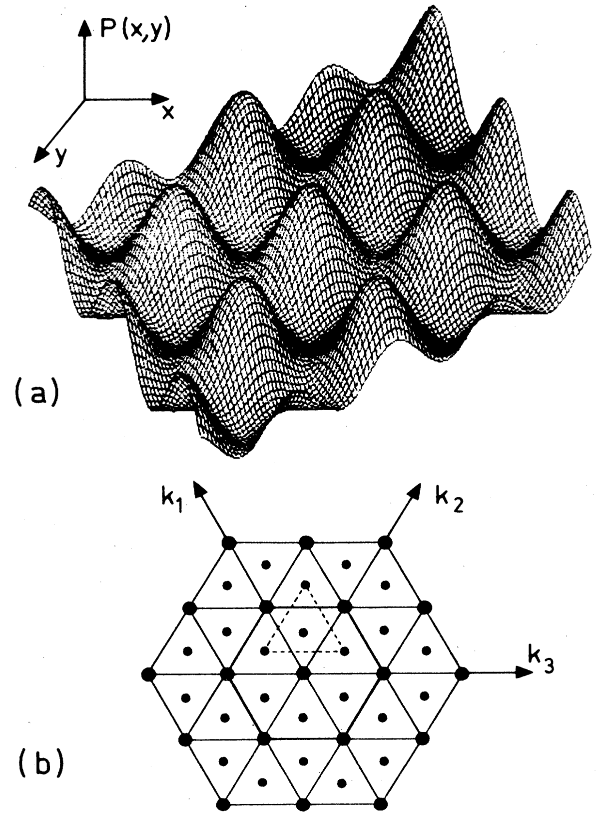

FIG. 11. (a) Triple-**k** modulation described by Eq. (5) (modulation along the three equivalent directions of the hexagonal structure in the basal plane). (b) Position of the absolute minima (small circles) and absolute maxima (large circles) of this modulation.

librations of the sulfate groups around axes in the basal plane. Besides, experimental evidence of the lock-in phase transition (commensurate-incommensurate) has been obtained in a recent Raman study[4] of LiKSO$_4$ (Zhang *et al.*); the ν_3 internal modes seem to disappear from their Raman spectra at $T=470\,^{\circ}\mathrm{C}$. However, a triple-**k** modulation model which explains a part of our results (partial disorder, appearance of extra modes) is definitively incompatible with the Brillouin results, namely the symmetry lower than hexagonal for the whole intermediate phase (435–670 °C) and the presence of crystallographic domains.

4. Double-k modulation

The x-ray satellite lines observed by Li (Ref. 3) can also be explained by a double-**k** modulation of the type

$$P(x,y)=A_1\cos(\mathbf{k}_1\cdot\mathbf{r})+A_2\cos(\mathbf{k}_2\cdot\mathbf{r})\ , \qquad (6)$$

where the sum on the right-hand side of this relation is done over two of the three equivalent directions in the basal plane of the hexagonal structure.

Figure 12 shows a picture of this double-**k** modulation and the positions of its maxima and minima. Firstly, we observed that a periodic modulation is also observed along the third direction that is not present in the sum of Eq. (6). The maxima and minima of this modulation form hexagonal lattices displaced of half-wavelength along the third direction, yielding an orthorhombic symmetry. Therefore, the commensurate structure also has an orthorhombic symmetry in agreement with the results of Chung and Hahn.[8] The three possible types of combinations of two equivalent directions in Eq. (6) give rise to three types of orthorhombic domains observed experimentally. Finally, since the maxima and minima of this double-**k** modulation have the same amplitude, there is no direction favored for the orientation of the tetrahedra, as would be expected in a nonpolar structure.

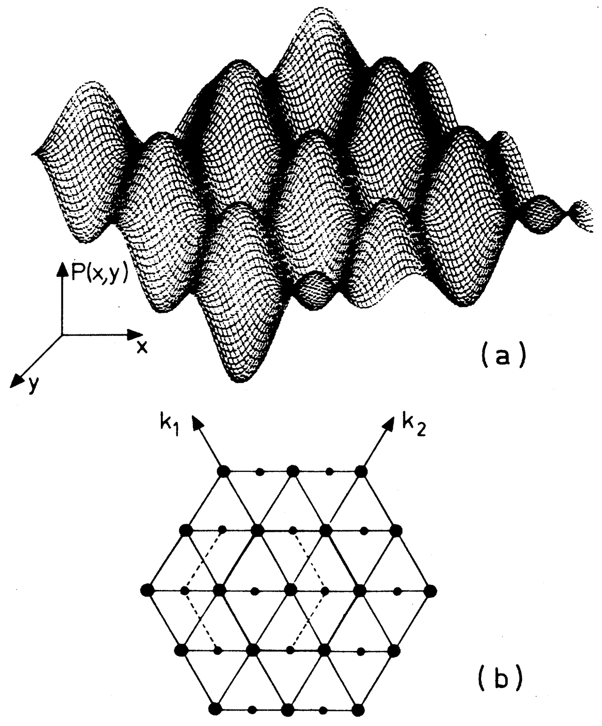

FIG. 12. (a) Double-**k** modulation described by Eq. (6) (modulation along two of the three equivalent directions of the hexagonal structure in the basal plane). (b) Position of the absolute minima (small circles) and absolute maxima (large circles) of this modulation.

A number of compounds that possess a prototype phase of type α-K$_2$SO$_4$ (D_{6h}^4) presents an incommensurate phase at high temperature, as, for example, K$_2$MoO$_4$, K$_2$WO$_4$, and Rb$_2$WO$_4$.[23] It should be emphasized that the double-**k** modulation proposed here to explain the intermediate phase of LiKSO$_4$, can probably also describe the incommensurate phase of this family of compounds. Moreover, a commensurate structure of such orthorhombic modulation ($\chi=0.5$) corresponds to an orthorhombic α-K$_2$SO$_4$-type structure as suggested by Tunistra and van den Berg.[23]

In the incommensurate compounds of K$_2$SeO$_4$ type, the decrease of symmetry in the incommensurate phase manifests itself by the appearance of vibrational extra modes.[24] In the case of LiKSO$_4$, the appearance of an ex-

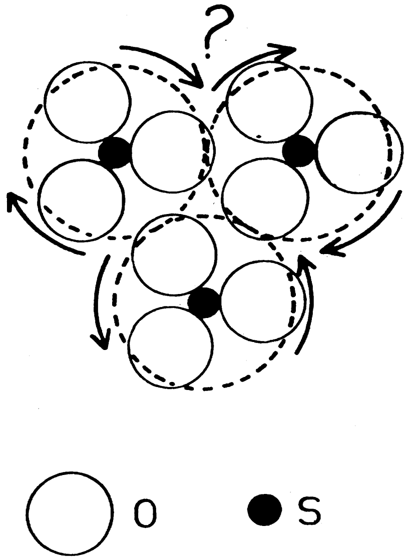

FIG. 13. The rotational dynamics of the sulfate groups in the basal plane is represented by a three-member gear mechanism. A clockwise rotation of one sulfate group around an axis parallel to the *c* axis induces counterclockwise rotation of the two other sulfate groups. The gear mechanism gets stuck in the contact point of these two sulfate groups.

tra mode at $T=435\,^{\circ}\mathrm{C}$ can be the signature of the modulated phase. The oscillator strength of this extra mode, whose evolution is shown in Fig. 10, can therefore be associated with the amplitude of the modulation. As already emphasized, the structure of $\mathrm{LiKSO_4}$ is very closed in the basal plane. Figure 13 illustrates the environment of one lithium ion projected in the basal plane. A clockwise rotation of one sulfate group around an axis parallel to *c* induces counterclockwise rotations of the two other sulfate groups via a gear mechanism. Therefore, the gear mechanism gets stuck in the contact point of these two sulfate groups. The existence of an incommensurate modulation in the basal plane can be explained as the result of the competition between opposite tendencies, or, in other words, as a result of the frustration of this three-member gear mechanism in the basal plane.

V. CONCLUSIONS

We have emphasized the strong correlation between the lithium ionic mobility and the reorientational motions of the sulfate groups. The phase transition to a conducting and orientational disordered phase is triggered by the instability of the librational modes at high temperature. $\mathrm{LiKSO_4}$ becomes an ionic conductor by steps: there is an intermediate phase with intermediate values of the electrical conductivity between the ordered phase of room temperature (of hexagonal symmetry) and the disordered and superionic phase of high temperature (also of hexagonal symmetry). The partial disorder of this intermediate phase leads to a superstructure of symmetry lower than hexagonal. A frustration of a three-member gear mechanism explains the existence of an incommensurate modulation in this intermediate phase. A double-**k** orthorhombic modulation reconciles the two explanations for the structure of the intermediate phase that seemed to be opposites; the incommensurate structure proposed by some authors[3,4] and the orthorhombic symmetry suggested by others.[8]

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