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Phase transitions in $LiKSO_4$ below room temperature

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Results of Raman spectroscopy and dielectric measurements in $LiKSO_4$ single crystals are presented. A comprehensive discussion of these results, together with those of previous works using the same as well as different techniques, leads to a better understanding of the mechanisms responsible for the several phase transitions which occur at temperatures from 10 to 300 K.

I. INTRODUCTION

The sequence of phase transitions displayed by $LiKSO_4$ (LKS) below room temperature has been extensively studied in recent years but a definite picture is still lacking. A list that includes most of the recent experimental work on the different phases of LKS is given in Ref. 1. At room temperature LKS has hexagonal symmetry belonging to the $P6_3$ space group. At least three phase transitions are observed by different techniques down to 10 K but the reported transition temperatures and suggested phase structures are not consistent. The picture is complicated by strong temperature-hysteresis effects and domain formation. It is agreed that reorientation of the sulfate-ion tetrahedra is related to some of these transformations. Bansal *et al.*[2] used Raman spectroscopy to show that the reorientation of the $SO_4{}^{2-}$ ions about an axis parallel to the basal (xy) plane is the driving vector for a transition occurring at 201 K when cooling and at 242 K when heating the LKS crystal. They advocate, based on their Raman spectra, that below the transition the crystal structure is in a phase belonging to the $P31c$ space group. This is in variance with the interpretation of x-ray observations by Tomaszewski and Lucaszewicz[3] where a $P6_3mc$ space group is suggested instead. These authors have also observed another phase transition at 190 K. According to them, below this temperature the crystal would be orthorhombic, probably belonging to the $Cmc2_1$ space group. A sequence of phase transitions that includes two intermediary incommensurate phases was first proposed by Fonseca *et al.*[4] although no satellite lines were seen in the x-ray study of Tomaszewski and Lucaszewicz. The possibility of an intermediary incommensurate phase for LKS was considered by the phonon-dispersion studies of Chaplot *et al.*[5] and discussed by Mendes-Filho *et al.*[6] Neutron-diffraction studies by Balagurov *et al.*[7] favor a monoclinic structure for LKS below 190 K. Recent EPR measurements by Murthy and Bhat[8] also suggest that at 135 K, LKS belongs to a Cc space group, rather than a $Cmc2_1$ space group. At still lower temperatures a new phase transition was observed by Raman scattering and other techniques.[6] No structural studies of LKS are known below 160 K. The scheme for the observed phase transitions of LKS below room temperature is given here. A "?" means ambiguity in the interpretation of different authors or a structure not known at all. An incommensurate phase is not included since it is discarded by most investigators. Transition temperatures are those measured in the present work, both for heating (up) and cooling (down) cycles:

$$\mathrm{I}(P6_3) \underset{210\ \mathrm{K}}{\overset{253\ \mathrm{K}}{\leftrightarrows}} \mathrm{II}(P3_1c \text{ or } P6_3mc) \underset{172\ \mathrm{K}}{\overset{190\ \mathrm{K}}{\leftrightarrows}} \mathrm{III}(Cmc2_1 \text{ or } Cc?) \underset{20\ \mathrm{K}}{\overset{30\ \mathrm{K}}{\leftrightarrows}} \mathrm{IV}(?)\ .$$

In this paper we report a study of LKS and its phase transitions below room temperature. Raman-scattering and dielectric techniques were used. In Sec. II the experimental arrangements are described. In Sec. III a short description of the crystal structure and lattice modes of LKS at room temperature is given; this is necessary for a comparison with the results in different phases of the crystal. The experimental results are presented in Sec. IV and a comprehensive discussion of these results as related to the behavior of LKS through its phase transitions is given in Sec. V. Finally, a summary to the main results and conclusions is presented.

II. EXPERIMENTAL TECHNIQUES

The experiments were performed on monocrystalline samples grown at controlled temperature (30 °C) from aqueous solutions of $Li_2SO_4 \cdot H_2O$ and K_2SO_4 in stoichiometric proportions. The quality of the samples was checked under a microscope using polarized light propagating along the c direction. Nontwinned platelets of excellent optical quality were then obtained. The samples were neither annealed nor submitted to any thermal treatments before the measurements.

Raman spectra were recorded on a Spex monochromator using the 4800-Å line of an argon-ion laser for excitation. The sample was placed into an Air Products closed-cycle refrigeration system where the temperature could be maintained constant to ±0.5 K with a Thermac 600 controller. The lowest temperature attained with this system was 15 K. Geometries for the spectra listed in the text and figures follow the usual Porto notation, $A(BC)D$.

For the dielectric measurements the samples were prepared as wafers less than 0.05 cm thick with areas of about 0.5 cm^2. They were transformed into capacitors of less than 10 pF by painting their surfaces with a conductive paint. The samples were held in a Model 8DT Janis Research liquid-helium cryostat and the temperature was controlled to 0.1 K by a model DRC80C Lake Shore controller. The dielectric constant and dielectric loss were measured with a model 1620 AP General Radio capacitance measuring assembly.

It should be remarked that both the Raman spectra and the dielectric measurements were taken at fixed temperatures. Usually one or two runs through the transitions were done before data were taken. For some points near the transitions the sample was kept at a fixed and controlled temperature for a long time (up to 8 h) while measurements were done in a repeated way, ensuring that no variation of the results with time was going on. Results so obtained, both for the Raman and dielectric measurements, were completely reproducible for the same or for different samples.

III. CRYSTAL STRUCTURE AND LATTICE VIBRATIONS OF LKS AT ROOM TEMPERATURE

At room temperature the space group of LKS is $P6_3$ with two molecules in the hexagonal unit cell, as shown in Fig. 1(a). In order to classify the observed Raman modes we use the irreducible multiplier representations of the group of the wave vector $\mathbf{q}$ along the hexagonal c direction. The 42 degrees of freedom can be divided among the irreducible representations as follows:

$$\Gamma = 7A + 7B + 7E_1 + 7E_2 .$$

These modes can then be classified as the following. Acoustic modes, $A + E_1$; optical translational modes, $2A + 3B + 2E_1 + 3E_2$; optical librational modes, $A + B + E_1 + E_2$; internal (SO$_4$) modes, $3A + 3B + 3E_1 + 3E_2$.

Li$^+$ and K$^+$ ions rest in C_3 symmetry sites. The fundamental modes of the SO$_4{}^{2-}$ ion are given in the usual sequence: ν_1 (981 cm^{-1}, symmetrical stretching), ν_2 (451 cm^{-1}, symmetrical bending), ν_3 (1104 cm^{-1}, antisymmetrical stretching), and ν_4 (613 cm^{-1}, antisymmetrical bending).

The Raman and infrared spectra of LKS at room temperatures were studied by Hiraichi *et al.*[9] Our Raman results are in good agreement with theirs so we shall adopt their assignment, denoting each Raman line by its symmetry type at phase I. Modes of A, E_1, and E_2 representations of the C_6 unit cell group are Raman active while B modes are silent. Modes belonging to A and E_1 representations are polar and should exhibit LO-TO splittings. The geometry of our experiments allows the observation of the A (TO) modes separately and the E_1(TO) + E_1(LO) modes simultaneously.

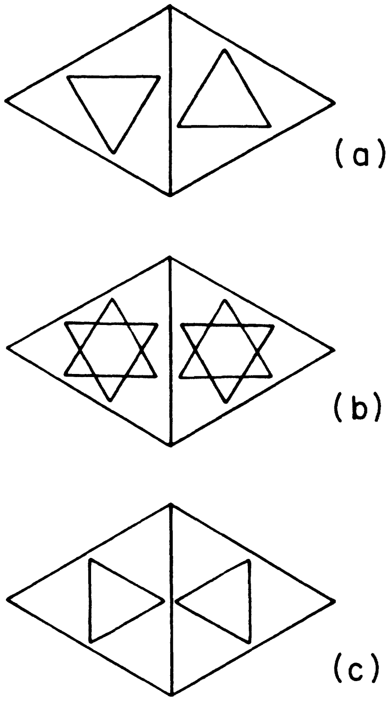

FIG. 1. Relative orientations of the sulfate-ion tetrahedra in three phases of LiKSO$_4$ below room temperature. (a) phase I, (b) phase II, (c) phase III.

IV. RESULTS

A. Raman spectroscopy

The Raman spectra shown in this paper are divided in three geometries corresponding to the three Raman-active representations of the room-temperature hexagonal phase: A (ZZ), E_1 (XZ), and E_2 (XY). Spectra taken in the YZ geometry are identical to those corresponding to the XZ geometry. Axis Z is taken parallel to the crystallographic axis c and axis X is parallel to axis a (or axis b) in the hexagonal phase. Since the structure of LKS at the low-temperature phases is not known with certainty, the C_6^6 space group representations are used, even when referring to the other phases.

Series of Raman spectra taken while increasing or decreasing the temperature of the sample are similar. Only the temperature of the phase transitions are different because of the hysteresis. The Raman spectra shown in this paper were taken while increasing the temperature.

Figures 2(a)–2(c) show a series of complete Raman spectra for the A (ZZ), E_2 (XY), and E_1 (XZ) representations, respectively. Some peaks in the room-temperature spectra are labeled to facilitate the identification of the internal sulfate-ion Raman modes. This is in part the assignment proposed by Hiraishi *et al.* and supported by the phonon dispersion studies of Chaplot *et al.* Peaks marked with an asterisk are leaks from very strong

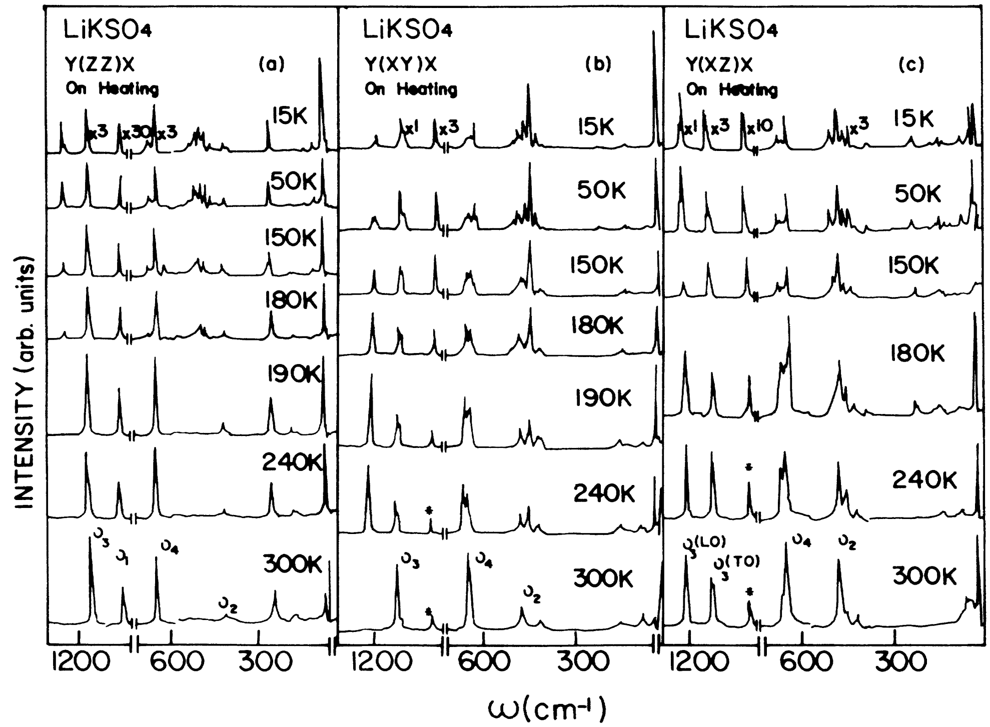

FIG. 2. Raman spectra of LiKSO$_4$ at different temperatures, taken while heating the crystal, for three scattering geometries. (a) $Y(ZZ)X$, (b) $Y(XZ)X$, (c) $Y(XY)X$.

modes belonging to another representation.

Some modifications occurring in the low-frequency regions of the spectra are important to understand the mechanism of the phase transitions of LKS. These modifications are more easily seen in the detailed Raman spectra of Fig. 3. These spectra were taken in the temperature range from 165 to 285 K where subtle changes in the region of external modes are taking place.

One should examine these series of spectra taking into account the phase-transition scheme already given. It is observed that some modifications in the spectra are abrupt in the transition region but others are taking place

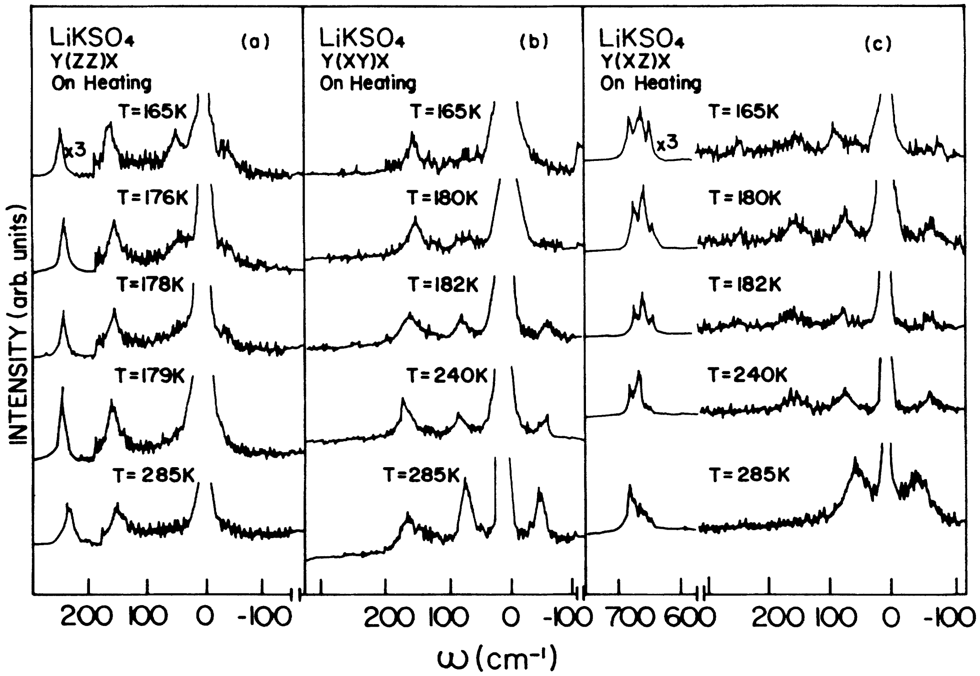

FIG. 3. Raman spectra of LiKSO$_4$ at a range of low- and intermediary-frequency modes, taken while heating the crystal, for the same geometries as in Fig. 1.

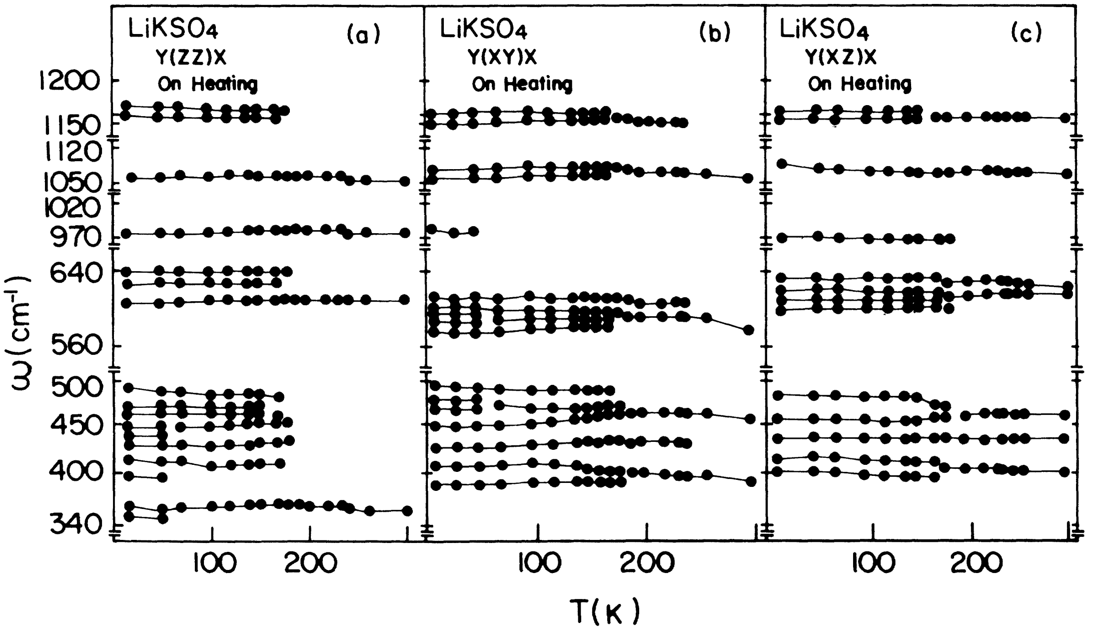

FIG. 4. Raman frequencies vs temperature for internal modes of sulfate ions. Values were taken while heating the crystal and scattering geometries are the same as in Fig. 1. Solid lines are drawn only to guide the eye.

through an extended temperature range. The relevant modifications are discussed in the next section.

To help the reader in following the numerous changes in the spectra where the transitions are taking place, these changes are schematically shown in the diagrams of Fig. 4 for the frequency range going from 350 to 1200 cm^{-1}. The continuous lines seen in these diagrams are drawn only to guide the eye.

B. Dielectric constant and dielectric loss

The large hysteresis in the phase transitions is clearly observed in the dielectric-constant and dielectric-loss diagrams of Fig. 5. The effects of the transitions on these curves taken against temperature are seen as abrupt discontinuities at the transition points. In the cooling process the dielectric constant decreases gradually and shows an abrupt increase at around 201 K. After a small decrease another transition is observed as a sharp discontinuity at 172 K. This is followed by a large temperature region extending down to below 100 K where the dielectric-constant curve shows a slow and continuous decrease. In the heating curve the transitions are observed as discontinuities at 190 and 253 K.

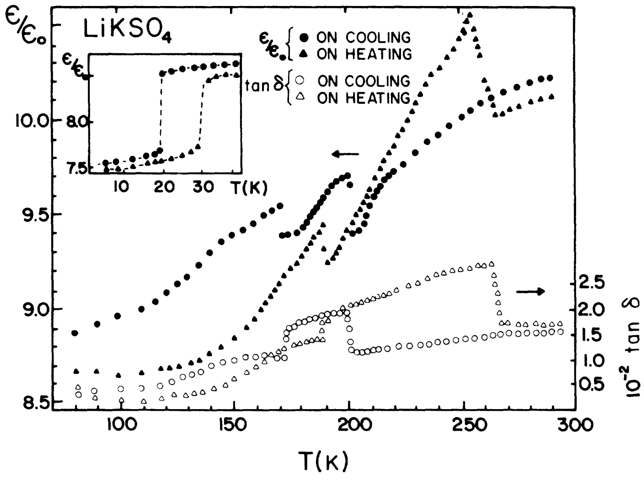

FIG. 5. Temperature dependence of the dielectric constant and dielectric loss of $\mathrm{LiKSO_4}$ for heating and cooling cycles in the range from 100 to 300 K. An inset shows the temperature dependence of the dielectric constant from 4 to 40 K.

In the dielectric-loss ($\tan\delta$) curve, while cooling the sample, there is a sharp increase at the first transition (201 K), then a slow decrease down to 172 K where the other transition is seen as an abrupt decrease in the curve. A slow decrease of $\tan\delta$ is then observed down to 100 K. For a heating process the transition temperatures show the same hysteresis observed in the dielectric-constant results. An inset in Fig. 5 shows the dielectric-constant curves in the region of the transition from phase III to phase IV for both heating and cooling processes. The transition is seen as a discontinuity at 20 K (30 K) in the cooling (heating) curve.

V. DISCUSSION

Raman and electrical results show the existence of four distinct phases of LKS in the range from room temperature to 15 K. Phase transitions occur at 201, 172, and 20 K when cooling the crystal (253, 190, and 30 K, respectively, for the heating process). Below the transition at 190 K there is a region that goes down to around 120 K where the crystal structure seems to be adjusting itself to a lower symmetry. This is reflected in the gradual modification of the Raman spectra in all representations and in the slow decreasing of the dielectric-constant curve in this range.

In what follows, each phase transition is discussed separately. Phase-transition temperatures will be referred to as those found while heating the sample.

A. Phase I (room-temperature phase)

As shown in the preceding section, room-temperature Raman spectra in all three Raman-active representations are in good concordance with the proposed hexagonal space group $P6_3$.

From the group-theoretical analysis, six Raman-active modes are predicted to the A_1 (ZZ) representation (TO modes) in this phase. These six (ν_1, ν_3, ν_4, ν_{lib}, and two ν_{ext}) modes are clearly seen in Fig. 2(a) in the spectrum taken at 300 K. Only one ν_1 Raman band belonging to the A_1 representation is expected since the two SO$_4$ molecules are in equivalent C_3 symmetry sites.

Raman measurements at 300 K in the $Y(XZ)Y$ geometry, shown in Fig. 2(c), give $E_1(\text{TO})+E_1(\text{LO})$ modes. One mode of low frequency, at 40 cm^{-1}, was not seen in the Raman spectra of Hiraishi *et al.* but it is reported in the work of Bansal *et al.* This mode is probably due to librations of the sulfate ion, according to lattice dynamical studies of Chaplot *et al.* Seven Raman-active (ν_2, ν_3, ν_4, ν_{lib}, and three ν_{ext}) modes are predicted to the E_2 (XY) representation of the $P6_3$ space group. At least six modes are visible in the spectrum taken at 300 K, shown in Fig. 2(b).

B. Phase II ($190 < T < 253$ K)

Raman measurements done by Bansal *et al.* were interpreted as evidence that around 245 K there is a first-order transition that takes LKS from a $P31c$ to the room-temperature $P6_6$ space group. This is reflected by a complete similarity in the Raman spectra taken at XZ and XY geometries below the transition point. These geometries correspond to the E_1 and E_2 representations of the original ($P6_3$) room-temperature symmetry. Indeed, this similarity is observed in the Raman spectra taken at 240 K, shown in Figs. 2(b) and 2(c) and 3(b) and 3(c). This can be understood as a combination of the two representations (E_1 and E_2) into a common E representation of the factor group C_{3v}. According to Bansal *et al.* the symmetry C_{3v} is reached through the reorientation of one of the two sulfate tetrahedra in the unit cell. This reorientation would be around an axis parallel to the XY plane, with one of the tetrahedra flipping by an angle of 108°. Taking into account the C_{3v} local symmetry and since there is no evidence of cell doubling, the ν_1 modes related to the two SO$_4$ ions will be accommodated into two unidimensional representations, at most. Also, only two ν_3 (and two ν_4) modes are expected for each geometry corresponding to the bidimensional representation. These results are indeed obtained in phase II.

X-ray results from Tomaszewski and Lucaszewicz, however, indicate the formation of a mirror plane without the disappearance of the hexagonal axis. This would lead to a $P6_3mc$ space group below the transition. As this interpretation is in contradiction to Raman results, one looks for a model that can accommodate both Raman and x-ray observations. Of course, it is unlikely that only one of the two sulfate ions reorients itself leading to a unit cell like the one proposed by Bansal *et al.* If the reorientation takes place with any of the two sulfate tetrahedra, after the transition there are two equally populated types of unit cell. Both types would have C_{3v} local symmetry. The arrangement of Fig. 1(b) is only schematic and one has to notice that the domain structure is characterized by planar walls parallel to the c axis. An x-ray experiment would then indicate the presence of an (average) mirror plane containing the hexagonal axis, as observed by Tomaszewski and Lucaszewicz.

Such a model conciliates interpretations of Raman and x-ray experiments. The transition is driven by the libration of the sulfate ion around an axis parallel to the XY plane. This is a mode belonging to the E_1 representation, probably the large and weak Raman line seen around 40 cm^{-1}. This line disappears at the transition, as seen in Fig. 3(c).

The random distribution of the two types of unit cell along the crystal can be thought of as equivalent to an average symmetry belonging to the $P6_3mc$ space group. However, both orientations would belong, separately, to a C_{3v} factor group. This would result in a smearing of the original E_1 and E_2 Raman spectra into a common type of spectrum, belonging to the E representation of the C_{3v} local group, as seen in the spectra of XZ and XY geometries taken at 240 K (Fig. 3). It should be noted that the Raman spectra taken at the A (ZZ) geometry do not change in going through the transition at 253 K. This can be tested with the strong E_1 mode at 1200 cm^{-1} that is completely absent from the A_1 spectrum, Fig. 2(a). A 90° turning of the polarizer at the incident beam from an XZ to a ZZ geometry flattens out the strong line at 1200 cm^{-1}. This is a clear indication that all changes are occurring only in the basal XY plane, in accordance with the observations of domain walls parallel to the original c axis.[10]

The spatial disorder proposed above can also explain the EPR observations of Fonseca *et al.*[4] Their EPR curves taken at 177 K show twelve lines; each of the three lines present in the room-temperature spectra splits into four new lines. This can be understood through the observation of the average C_{6v} unit cell by allowing a small displacement of the bases of the sulfate tetrahedra, creating 12 magnetically distinct orientations of the sulfate ion, Fonseca *et al.* estimate this displacement as less than 6°. Such displacement would also prevent any possible mirror plane perpendicular to the original a axis that would lead to an orthorhombic structure in this phase.

An incommensurate structure in this range of temperature, from 226 to 180 K, was proposed by Fonseca *et al.* Raman experiments alone are not enough to give support or to discard such a possibility, but no satellite lines were found in the x-ray[3] and neutron-diffraction[7] studies. An analysis of the transition at 253 K, using the theoretical argumentation of Heine and McConnel,[11] indicates that it is unlikely that this transition leads to an incommensurate phase. There are not two symmetrically different modes at the center or at the boundary of the Brillouin zone going to the same symmetry at a point nearby, as required by that model. The group of the room-temperature phase has a too-low symmetry. If two modes are to interact leading to an incommensurate phase, this can only be explained by some energy consideration and not induced by symmetry.

Some authors[7] suggest that below the transition there is a coexistence of the two phases, $P6_3$ and $P3_1c$. It is also said that the transition is very sluggish, taking some hours to be completed.[10] This behavior was not observed in the present work. Raman spectra taken a few degrees below the transition temperature do not change appreciably with time even when the temperature is maintained constant for many hours. The same is true for the dielectric measurements. It is possible, as suggested by Cach *et al.*,[10] that the quality of the sample or its thermal treatment will affect the results.

Dielectric constant and dielectric observations indicate that the transition at 253 K is first order, with a large temperature hysteresis. Below the transition both properties show a strong temperature dependence, as shown in Fig. 5. It is clear that the spatially disordered structure proposed here can lead to an intricate domain formation. Motion of the domain walls as the temperature is varied would be responsible for this behavior.

C. Phase III ($30 < T < 190$ K)

The phase transition at 190 K was first studied by Tomaszewski and Lucaszewicz[3] using x-ray diffraction. These authors proposed that at 190 K the crystal would go from a $P6_3mc$ symmetry to an orthorhombic structure, possibly belonging to the $Cmc2_1$ space group. They also related the transition to a freezing of the top oxygen in the sulfate-ion tetrahedra. This transition is known to be ferroelastic. A Landau-type model was applied to the study of the transition by Zeks *et al.*[12]

Raman and dielectric measurements indicate that the transition at 190 K is also first order (see Fig. 5). However, both Raman and dielectric results show that below the transition there follows a large temperature region, extending down to around 120 K, where continuous changes are taking place. The most prominent changes are as follows: (a) splitting of the ν_2 (bending) mode at 460 cm^{-1} in the (original) XZ geometry; (b) splitting of ν_4 (stretching) mode at 640 cm^{-1} in the XZ and YZ geometries; (c) disappearing of the 60 cm^{-1} external mode in the YZ geometry; (d) emergence of a new mode in the low-frequency region of the ZZ spectrum that starts around 179 K and gradually increases in intensity and frequency, being around 42 cm^{-1} at 150 K [see Fig. 3(a)]; (e) emergence of the ν_3 (LO) internal stretching mode at 1210 cm^{-1} in the ZZ spectrum.

These Raman results are difficult to conciliate with a $Cmc2_1$ space group as proposed by Tomaszewski and Lucaszewicz. A correlation between local and global symmetries considering the group of phase III as $Cmc2_1$ places the sulfate ions in sites of C_3 local symmetry. No mixing of the ZZ and XZ (or YZ) modes would then be allowed. The extensive splitting of pratically all internal modes of the original XZ and YZ representations are a clear indication that the sulfate ions that were occupying sites of C_3 symmetry in phase II turn to sites of C_1 local symmetry. In such a case the cell group goes to a lower symmetry, possibly C_2 or C_s.

At temperatures higher than 190 K it is known[3] that the oxygen ion on the top of the sulfate tetrahedra is rapidly hopping among three different positions around the C_3 axis through the sulfur atom. Tomaszewski and Lucaszewicz suggest that a freezing of the oxygen ion would create a mirror plane perpendicular to the original a axis. A different model that does not need to assume a freezing of the oxygen ion and is more compatible with the Raman results is now proposed. At some temperature above the transition point the sulfate ions start librating strongly around an axis parallel to the original c axis. Such libration would be a mode belonging to the B_1 representation of the (average) $P6_3mc$ space group. This mode, that is neither Raman nor infrared active, would drive the transition at 190 K leading (approximately) to an arrangement as shown in Fig. 1(c).

If at this point the top oxygen ion is still randomly occupying some positions around the axis, the structure would be (in average) an orthorhombic one. However, the emergence of the ν_3 stretching mode in the (original) ZZ Raman spectrum is evidence of mixing with the XZ (and YZ) representations. This is only possible if the local site evolves to a C_1 symmetry below the transition. This evolution is gradual, as shown by the changes that appear in the spectra around 180 K and get more and more prominent as the temperature is lowered.

The silent libration B_1 mode would turn Raman active in the less-symmetric phase, below the transition. This is probably the weak low-frequency mode that appears around 50 cm^{-1} in the XZ spectra at temperatures below 180 K, as seen in Fig. 3(c).

The dielectric constant and dielectric-loss measurements are consistent with a gradual accommodation of the cell structure below the transition. As seen in Fig. 5, after a sudden discontinuity at the transition point, both curves show a marked temperature dependence down to around 120 K, in good concordance with the Raman observations. It is possible that around 120 K, where the modifications of the Raman spectra get completed, the top oxygen ion in the sulfate tetrahedra freezes in a position compatible with the C_1 local symmetry. This is accompanied by rearrangements in the positions of the potassium ions leading to a monoclinic structure, as proposed by some authors.[7,8]

Some comments are in order here on the proposal of Fonseca *et al.* about an incommensurate phase ranging from 175 K to around 90 K. An incommensurate phase is theoretically possible if the direct product of the representations of the two normal modes that form the Lifschitz invariant contains the totally symmetric representation. One of these modes in the average C_{6v} factor group could be the librational B_1 mode described above. The other mode should belong to the same representation, as required by the Lifschitz condition. This could be a deformation mode involving relative displacement of the potassium ions. However, here again the interaction of these modes, although possible, is not required by any symmetry consideration. Also, there is no evidence of any soft mode in the Raman spectra at this range of temperature. It is more plausible that the EPR results obtained by Fonseca *et al.* are related to the extensive disorder in the sulfate ions throughout the temperature range starting below the transition, as described previously. At temperatures below 83 K the EPR spectra of Fonseca *et al.* show the existence of only three magnetically distinct sulfate centers. This suggests that the freezing of the oxygen ion should be in such position that the two sulfate ions in the unit cell are orientationally equivalent. The lowering of the local symmetry required by the Raman results would then be mostly related to displacements of the potassium ions.

D. Phase IV ($T < 30$ K)

The effect of the phase transition at 30 K is easily seen in the dielectric-constant curve against temperature as a sudden discontinuity. There is a thermal hysteresis of about 10 K, as observed by the dielectric measurements. The effect on the Raman spectra in all geometries is less remarkable. Some Raman lines in the region around 500 cm^{-1}, due to bending of the sulfate units, start splitting already near 100 K. The splitting is continuous through the transition and seems to be pratically completed at 15 K, the lowest temperature attained in the Raman experiments. There are no results of x-ray diffraction in this range of temperature. Neutron-diffraction studies of Balagurov *et al.*[7] indicate that phase IV is also ferroelastic, with some modification in the crystal structure.

Until more-precise structure-determination experiments are performed one can only infer, from the Raman spectra, that the phase transition at 30 K is related to a subtle rearrangement of the sulfate ions affecting most the bending modes and thus lowering still more the symmetry of the unit cell.

VI. CONCLUSION

A detailed study of Raman and dielectric results from LiKSO$_4$ monocrystalline samples was presented. Three distinct phase transitions were observed occurring at 253, 190, and 30 K for increasing temperature experiments. By comparing the modifications in the Raman spectra with previously reported x-ray, neutron-diffraction, and EPR results, it was possible to infer some clear understanding of the low-temperature phases. Phase II is a transitional arrangement of the whole crystal structure, while the sulfate-ion tetrahedra, that are in a C_3 symmetry site at phase I, gradually evolve to a lower symmetry. This phase shows a marked spatial disorder in the positioning of the sulfate ions. This complicates the determination of the space group and can only be described as an average trigonal structure. Below the transition to phase III, at 190 K, the sulfate ion settles in a site with C_1 local symmetry leading the LKS crystal to a monoclinic structure at temperatures around and below 120 K. No evidence is observed of incommensurate phases in this range of temperature. A new phase transition at 30 K is clearly observed in the dielectric-constant curve. From the Raman spectra it is seen that this transition is related with low-frequency bending modes of the sulfate ion.

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