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Orientational phase transition in $LiKSO_4$

M. L. Bansal and A. P. Roy
Nuclear Physics Division, Bhabha Atomic Research Centre,
Trombay, Bombay 400085, India

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Raman scattering results on low-lying external modes in $LiKSO_4$ across the phase transition $C_6^6 \rightarrow C_{3v}^4$ ($T_c = 201$ K) are presented. Based on these data and the lattice-dynamical calculations of Chaplot, Rao, and Roy it is shown that reorientation of $SO_4{}^{2-}$ ions at the phase transition is likely to take place about an axis normal to the c axis.

I. INTRODUCTION

A new phase transition ($T_c \simeq 201$ K, while cooling) in $LiKSO_4$ has been reported earlier.[1] The space-group change accompanying this transition is shown to be $C_6^6 \rightarrow C_{3v}^4$. This has been established on the basis of Raman intensity redistribution of the lithium translational mode and sulfate internal vibration modes across T_c. It has been further argued that the phase transition is associated with cooperative reorientation of SO_4 tetrahedra. In the present paper, we provide additional evidence of the 201-K phase transition, based on the behavior of low-frequency external modes, across T_c. These results, in conjunction with the lattice dynamical work of Chaplot, Rao, and Roy,[2] throw some light on the way reorientation of SO_4 may occur at T_c. From EPR measurements, Holuz and Drozdowski[3] and Fonseca, Ribeiro, Gazzinelli, and Chaves[4] have suggested the presence of an incommensurate phase below 226 K. However, they do not find any evidence of C_{3v}^4 structure below 201 K. We also comment on this aspect in the paper.

II. RESULTS

The experimental details are the same as given in an earlier paper.[1] Figure 1 shows $Y(XZ)X$ spectra at three different temperatures for $LiKSO_4$. Figure 2 gives the corresponding spectra for $Y(XY)X$ configuration. The modes appearing in these configurations are labeled as E_1 and E_2, respectively, in the C_6^6 phase. In Fig. 1 (above T_c), a low-frequency mode at 40 cm^{-1}, having a width of approximately 40 cm^{-1}, is seen, which is labeled as E_1(TO). The LO counterpart appears at 44 cm^{-1} in the $Y(ZY)X$ configuration—its frequency variation is shown in the inset of Fig. 1. The linewidths and frequencies of E_1(TO) and E_1(LO) remain practically unchanged right down to T_c. Below 201 K, the spectra in these configurations, viz., $Y(XZ)X$ and $Y(ZY)X$ (Fig. 1), show a sudden qualitative change. The mode at 40 cm^{-1} is no longer there. Instead two modes appear at 64 and 135 cm^{-1}. No additional modes are expected below T_c if the structure is C_{3v}^4. Therefore the 135 cm^{-1} mode may be just the missing lattice mode of C_6^6 phase (seen at 135 cm^{-1} in the ir spectra by Hiraishi, Taniguchi, and Takahashi[5]). Similarly in E_2 spectra (Fig. 2), though there is no qualitative change, the lowest E_2 mode of 52 cm^{-1} jumps to about 61 cm^{-1} below T_c. These facts clearly indicate that at 201 K, a phase transition does occur in $LiKSO_4$ while cooling, as reported earlier.[1] In the heating cycle the transition takes place at ~242 K.

III. ANALYSIS

As mentioned in the introduction, $C_6^6 \rightleftharpoons C_{3v}^4$ phase transition is associated with reorientation of one of the sulfate ions in the unit cell.[1] This can be brought about either by rotation of 60° about the c axis along which one of the S–O bonds points, or by a rotation of 108° about an appropriate axis passing through sulfur and normal to the c axis (Fig. 3). In this connection it is instructive to examine torsional oscillations, i.e., small-angle rotation or libration of SO_4 ions about these two orthogonal axes.

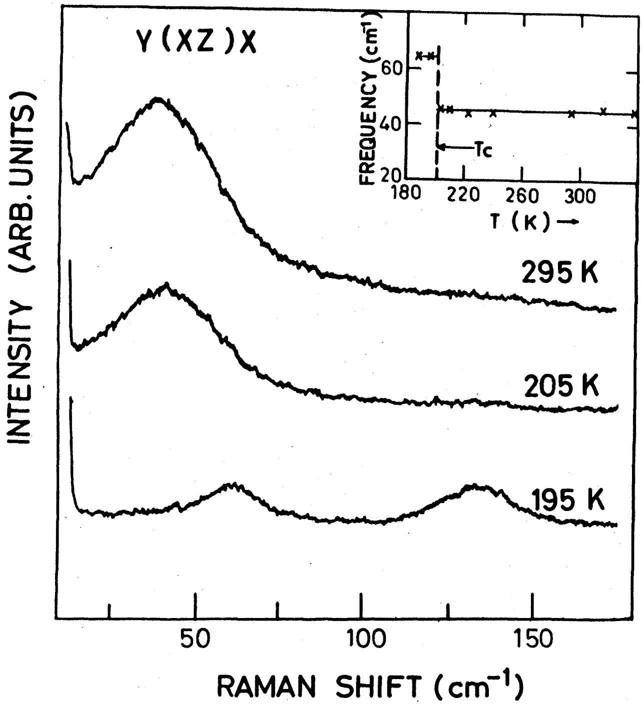

FIG. 1. Raman spectra (0–180 cm^{-1}) above and below the phase transition ($T_c = 201$ K) for the $Y(XZ)X$ scattering geometry. Similar patterns are obtained in the $Y(ZY)X$ scattering geometry. The inset shows frequency variation of the low-lying mode in the latter geometry.

From a detailed knowledge of eigenvectors of various

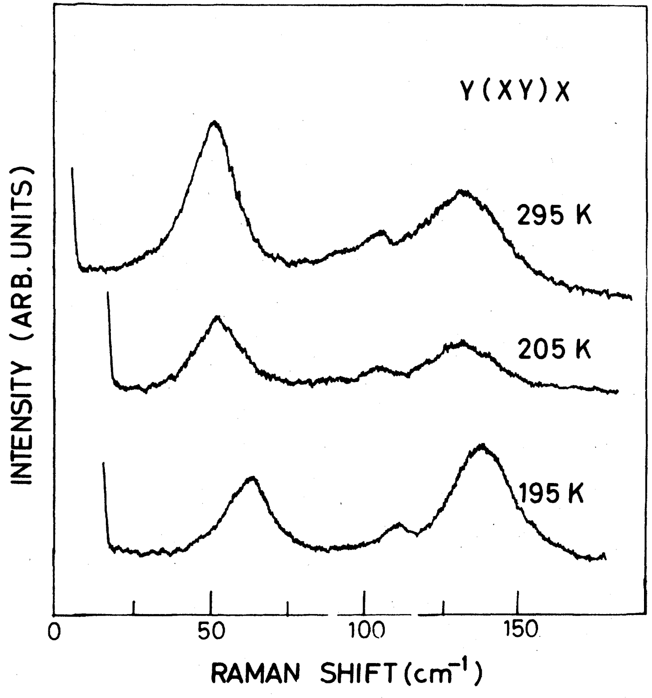

FIG. 2. Raman spectra (0–180 cm^{-1}) above and below the phase transition in $Y(XY)X$ scattering geometry.

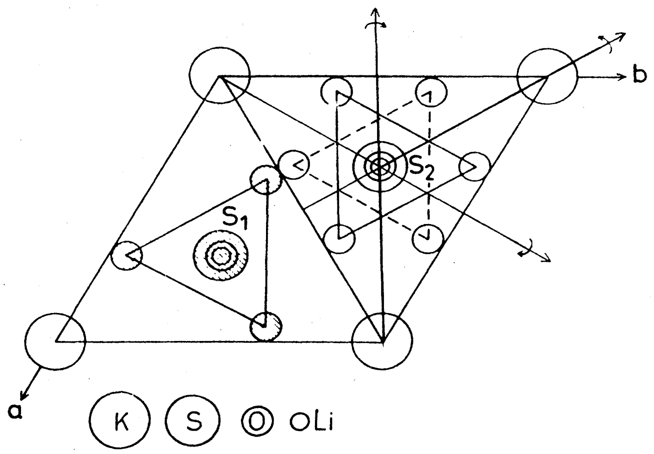

FIG. 3. The projection of sulfate ions S_1 and S_2 in the basal plane is schematically indicated by equilateral triangles. The two ions are displaced by $c/2$ along the symmetry axis. The orientation of S_2 as shown by solid line corresponds to C_6^6 phase, and that depicted by dashed line refers to C_{3v}^4 phase. S_2 can be taken from one orientation to the other either by 60° rotation about c axis along which one of the S–O bonds is directed, or by a rotation of 108° about one of the three equivalent axes passing through sulfur and normal to the c axis. These sense of rotation is indicated by arrows.

external modes in $LiKSO_4$ available from the lattice dynamics calculations by Chaplot *et al.*,[2] one can assign the 202-cm^{-1} A mode in the C_6^6 phase[5] to libration of SO_4 ions about the c axis and the 40-cm^{-1} E_1 mode to librations about an axis normal to it. This immediately shows that for tumbling motion out of the basal plane, the ion experiences a much shallower potential well. The experimentally observed large linewidth (~ 40 cm^{-1}) can be attributed to this feature of the potential. Further, in going to the C_{3v}^4 phase, this particular mode alone is strongly affected.

An explanation of the above behavior is provided by the work of Chaplot *et al.*[2] It is seen from Fig. 2 of their paper that the upper rotational branch (A symmetry) at ~ 200 cm^{-1} corresponding to libration about the c axis is fairly flat throughout the Brillouin zone and undergoes little change across T_c.[6] On the other hand, the other low-lying rotational branch corresponding to libration of SO_4 about an axis normal to the c axis (labeled as E_1 branch in the C_6^6 phase) couples with an acoustic branch of the same symmetry. After anticrossing of these two branches the symmetry vector corresponding to the lower branch becomes predominantly rotational in character. Near the zone boundary the mode frequency is less than 10 cm^{-1} indicating that the barrier to cooperative tumbling of SO_4 ion about an axis perpendicular to the c axis can be very low. On transition to the C_{3v}^4 phase this branch shows a marked change. From the discussions given above, we therefore infer that the axis of reorientation is likely to lie in a plane normal to the c axis (Fig. 3).

X-ray- and neutron-diffraction results[7,8] indicate that the oxygen atom in the S–O bond pointing along the c axis has unusually large thermal motion perpendicular to the bond. This corroborates the above conjecture that the easy axis of reorientation is normal to the c axis.

IV. DISCUSSION

The optical activity along the c axis was measured at room temperature for a number of crystals grown under identical conditions. It was found to vary between 6 and 3 deg/mm at 4416 Å for different crystals and even for different regions within the same crystal. This clearly shows that the crystals are twinned. In an earlier paper[9] we have listed various types of twins that can exist in this crystal. Twins of type A and D give the same sense of optical rotation and is opposite to that given by the type B and C (related through a horizontal mirror plane to D and A, respectively). Therefore, optical activity can be used to distinguish between the twins A and C, which cannot be distinguished by other techniques like Raman, neutron, or x-ray diffraction. In the absence of an absolute maximum value of optical activity it is not possible to deduce a quantitative value for the ratio of twins in a given crystal. However, variation of optical activity clearly indicates that the twins related by a horizontal mirror plane occur in different proportions in different specimens. Below $T_c = 201$ K, the optical activity goes to zero as expected[1] provided one allows sufficient time after the crystal has been cooled. It is perhaps the size and percentage of twin domains which influence evolution of the C_{3v}^4 phase below T_c.

Measurements of dielectric constant and elastic properties of $LiKSO_4$ in this temperature range have been reported. Breczewski, Krajewski, and Mroz[10] have reported anomaly in dielectric constant at 257 K while heating the crystal (according to Raman measurements[1] transition temperature is 242 K for heating cycle). They do not report any data while cooling.

Mroz *et al.*[11] have found that the elastic constants versus temperature curves show a marked hysteresis of about 50°. Particularly C_{33}' and C_{22} values, while cooling, start decreasing rapidly at around 200 K and, while heating, they start increasing rapidly just below 250 K. These authors have attributed the marked hysteresis to the existence of ferroelastic domains that are formed in this crystal below 190 K. We believe that observations of Breczewski *et al.*[10] and Mroz *et al.*[11] are not inconsistent with Raman work.

We next consider EPR investigations of Holuz and Drozdowski[3] and that of Fonseca *et al.*[4] They report an incommensurate phase between 226 and 181 K. In the absence of any experimental information on the structure of the incommensurate phase, we may assume, following Chaplot *et al.*[2], that it is characterized by softening of the low-lying rotational branch near the zone boundary. Now, in light scattering experiments only the zone-center frequency is observed which is expected to be marginally affected in this incommensurate phase.[2] Hence, it is not surprising that the Raman spectra do not show any observable change across 226 K.

These authors,[3,4] however, do not find any evidence of the phase transition at $T_c = 201$ K. Our experience shows that the transition at $T_c = 201$ K is extremely sluggish;[1] for the sample volume monitored by the laser beam (focal spot ~ 30 μm) it takes typically 35 min for phase transformation to occur when the crystal temperature is maintained just below T_c.[12] If the cooling rate is too fast one directly goes to another phase around 185 K after passing through a supercooled C_6^6 phase.

To summarize, Raman work indicates the presence of a phase transition at 201 K (while cooling) associated with cooperative reorientation of sulfate ions, and the easy axis of reorientation is orthogonal to the *c* axis.

Note added in proof

Subsequent to submission of this paper the following observation has been made which lends direct support to the conclusions drawn in this paper.

The $\nu_1(SO_4)$ mode belongs to the totally symmetric representation in both C_6^6 and C_{3v}^4 phases and its frequency is 1012 cm^{-1}. Therefore, neither phase, below or above $T_c \simeq 200$ K, permits the Raman intensity at 1012 cm^{-1} in the $Y(ZY)X$ configuration (I_{ZY}). However, at the phase transition, when the crystal temperature is held constant at T_c, I_{ZY} starts building up slowly and attains a maximum value of $\simeq 2\%$ of I_{ZZ} over a period of 20 min and then decays slowly to its initial value, the build up and decay of I_{ZY} being symmetric in time.

Only an instability at the transition temperature, which involves angular displacement of SO_4 ions about an axis in the basal plane, can give rise to build up and decay of I_{ZY}. This clearly supports the hypothesis that the transition $C_6^6 \rightarrow C_{3v}^4$ occurs due to the reorientation of SO_4 ions about an axis normal to the *c* axis.

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[6] It may be pointed out here that at zone center, the eigenvector of the mode corresponds to in-phase rotation of sulfate ions in the C_6^6 phase while in the C_{3v}^4 phase the motions are out of phase (see Table III of Ref. 2). Interestingly, however, the frequencies are nearly identical and this is borne out by the Raman experiment.

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[12] An examination of intensities of the Raman lines in ZX and ZY configurations as shown in Ref. 1 indicates that below T_c there exists a residual C_6^6 phase; in other words, the transformation is not complete. Further, some specimens show different transition temperatures, viz., 197 and 253 K for the cooling and heating cycle, respectively.