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ANOMALOUS TEMPERATURE DEPENDENCE OF A LO MODE IN LiKSO_4

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Abstract.— Raman scattering measurements for LiKSO_4 over the temperature range 200 K to 725 K are reported. The results corroborate the occurrence of a phase transition at 700 K and also exhibit two unusual lattice dynamical features viz an inverted LO-TO splitting and an increase in the frequency of a normal mode with rise in temperature. A phenomenological explanation for these features is given.

1. **Introduction.**— We had recently¹ established a subtle first order low temperature phase transition in LiKSO_4 ($C_6^6 \rightarrow C_{3V}^4$) (at 201 K) using Raman scattering measurements and we have extended our measurements to high temperature region since additional phase transition ($\sim 700\text{K}$) had been proposed for this crystal in the literature².

In extending our measurements upto 725K while we have found evidence that a phase transition does occur around 700K, in addition, we have found two interesting features of vibrational modes in the temperature range between the transition points (crystal symmetry C_6^6). These features are: (i) the LO frequency of a ν_2 mode of SO_4 appears below its TO counterpart and (ii) the frequency of this LO mode increases with the rise in temperature. Since these are somewhat unusual features we propose to discuss these in greater detail here and except for a brief mention, omit the discussion of the changes pertaining to high temperature phase transition.

In section 2 we describe experimental details and present the spectra. Discussion of the results and a possible explanation for the LO-TO frequency inversion and anomalous temperature dependence of the $E_1(\text{LO})\nu_2$ mode are given in section 3.

2. **Experimental details.**— Polarized Raman Spectra were recorded using a home made 40 mW He-Cd laser and a grating double monochromator³ with spectral bandpass of 3.5cm^{-1} .

For high temperature studies, we used a cell, wherein the sample is mounted mechanically and its three faces are in contact with copper to ensure uniformity of temperature. The temperature was

Fig. 1 Raman spectra at different temperatures for two orientations.

Fig. 2 Frequency variation of modes of Fig. 1 with temperature.

Fig. 3 Dependence of LO frequencies on S_1 & S_2 . Input TO frequencies are also shown.

monitored using a copper constant thermocouple and a proportional temperature controller was used to maintain it constant within $\pm 0.5^\circ\text{C}$. The reported temperature values refer to the temperature of the copper block; the sample temperature is somewhat lower (by $\sim 10\text{K}$ at 600K).

3. Results and Discussion— Fig. 1 shows the temperature dependence (210K – 675K) of $\text{Y}(\text{ZY})\text{X}$ and $\text{Y}(\text{XZ})\text{X}$ spectra over the frequency range 400 cm^{-1} – 520 cm^{-1} . ν_{tr} and ν_2 label modes involving predominantly Li translation and SO_4 internal vibration respectively. Further as is often the case with Li salts, the ionic conductivity increases considerably with the rise in temperature. So the former mode can be expected to broaden more rapidly with increasing temperature. The assignment of LO modes in Fig. 1 is based on this premise and is different from earlier assignments. Fig. 2 shows plot of frequencies versus temperature. Note that for the ν_2 mode LO–TO splitting is inverted. The behaviour can be understood using a picture of two nearby oscillators where one of them carried a much larger dipole moment. An approximate expression for the dielectric function, valid in this frequency range is

$$\epsilon(\nu) = \text{Const} + \frac{S_1 \nu_{tr}^2(\tau_0)}{\nu_{tr}^2(\tau_0) - \nu^2} + \frac{S_2 \nu_2^2(\tau_0)}{\nu_2^2(\tau_0) - \nu^2} \quad (1)$$

The LO frequencies obtained from the zeros of eqn. (1) for a given set of TO frequencies and oscillator

strengths S_1 and S_2 are given in Table 1. Hiraishi et al⁴ give values of S_1 and S_2 from an analysis of their room temperature IR reflection spectra. The values chosen by us at 210K are close to theirs.

The most notable feature about temperature variation of various modes (Figs. 1&2) is that both $\nu_{tr}(LO)$ and $\nu_2(LO)$ converge towards $\nu_2(TO)$ as temperature is increased; the former decreases by 17cm^{-1} whereas the latter increases by 6cm^{-1} over the temperature interval 210K-420K. This behaviour can be quantitatively reproduced using eq.(1) assuming a decrease in the value of S_2 from 0.065 to 0.015 (Table 1). In eqn(1), the damping has been neglected and to that extent choice of the initial values of S_1 and S_2 is somewhat uncertain. A glance at Fig.3 clearly shows that for predicting the observed relative shifts of $\nu_2(LO)$ and $\nu_{tr}(LO)$, S_2 has to decrease with increasing temperature, irrespective of the uncertainty in the initial choice of S_1 and S_2 . Variation of S_1 keeping S_2 fixed leads to simultaneous increase or decrease of both $\nu_2(LO)$ and $\nu_{tr}(LO)$, whereas experimentally $\nu_2(LO)$ increases and $\nu_{tr}(LO)$ decreases with increasing temperature. At still higher temperature ($> 420\text{K}$) Li modes can not be traced experimentally but $\nu_2(LO)$ moves progressively closer to $\nu_2(TO)$. Since the ν_2 mode is IR inactive in the free ion state, this continuous decrease in the oscillator strength implies that the SO_4 distortion (from tetrahedral shape) diminishes with increasing temperature. Across 700K changes in the Raman spectra occur over the entire frequency range. Further, the widths of most of the modes change abruptly across the transition point. However, as the widths of the peaks are rather large (FWHM even as much as 40cm^{-1}) detailed examination of the transition by Raman scattering alone, seems unfeasible and other techniques may be necessary for elucidation of the transition.

Table 1: Observed and calculated LO frequencies (in cm^{-1})

<u>T(K)</u>	<u>obs(TO)</u>	<u>obs(LO)</u>	<u>cal(LO)</u>	
210	408	440	441	$S_1 = 0.50$
	466	480	480	$S_2 = 0.065$
420	408	446	446	$S_1 = 0.50$
	462	463	466	$S_2 = 0.015$

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