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Temperature dependence of the Raman-active lithium modes in $LiKSO_4$ and $LiNaSO_4$

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External optic vibrational modes originating primarily in the motion of lithium ions are unambiguously identified by Raman scattering from isotopically enriched $^6LiKSO_4$ and compared with similar modes found in $LiNaSO_4$. These modes in both $LiKSO_4$ and $LiNaSO_4$ appear to be overdamped, broadening with increasing temperature and essentially vanishing at temperatures far below the reported phase-transition temperature. An anomalous maximum in the bandwidths of these modes is observed and discussed.

INTRODUCTION

One of the major problems in the study of fast-ion-conducting materials is to understand in some detail the dynamical behavior of the mobile ion species. Of particular interest is the effect of the potential-energy environment of the crystal on the motion of the mobile ion. A temperature-dependent vibrational spectroscopic study can provide information about not only the potential-energy environment of the mobile ion but also information concerning dynamical processes in the crystal which are coupled to the ionic motion and affect the behavior of the ion.

Certain sulfate crystals offer an excellent opportunity to carry out a comparative study of the temperature-dependent vibrational dynamics in a series of related crystals. A high-temperature transition into a fast-ion-conducting phase is observed in several sulfate salts such as Li_2SO_4,[1] $LiAgSO_4$,[2] and $LiNaSO_4$.[3] However, many sulfate crystals exhibit high-temperature phases which are not fast-ion conducting, e.g., K_2SO_4,[4] $LiKSO_4$, and $NaKSO_4$.[5]

Among the sulfates mentioned above, the binary-cation sulfates $LiNaSO_4$ and $LiKSO_4$ are especially interesting because both have hexagonal unit cells with lithium ions present as one of the cations, yet only the high-temperature phase of $LiNaSO_4$ is a fast-ion-conducting phase. The room-temperature structure of $LiNaSO_4$ belongs to space group $P31c$ (C_{3v}^4) with six molecules per unit cell.[6] It undergoes a structural phase transition into a body-centered-cubic phase[4,7] with a specific conductivity of 1.008 $\Omega^{-1}\,\mathrm{cm}^{-1}$ at 563 °C.[3] Lithium potassium sulfate crystallizes in a $P6_3$ (C_6^6) space group with two molecules per unit cell.[8] A phase transition occurring at approximately 436 °C has been observed by measurement of the dielectric constant, dc resistivity, and pyroelectric current,[9] by x-ray measurements of the thermal expansion of the unit cell,[10] by thermal analysis,[4,11] and by heat-capacity measurements.[12] The high-temperature phase is reported to be orthorhombic.[4]

As part of an extensive comparative spectroscopic study of a series of sulfate crystals, the Raman-active vibrational modes of $LiKSO_4$ and $LiNaSO_4$ were measured at various temperatures. In an earlier study[13] vibrational-mode assignments were made for $LiNaSO_4$ at room temperature based on both Raman and infrared spectra. External modes due predominantly to lithium-ion motion were identified from isotopic shifts in enriched $^6LiNaSO_4$ crystals. It was observed in that study that the lithium ions were relatively decoupled from the rest of the external modes. Therefore, the spectra of an enriched $^6LiKSO_4$ crystal were also measured in an attempt to identify similar modes. The temperature dependence of the bandwidth of these modes in both $LiKSO_4$ and $LiNaSO_4$ is particularly interesting and is the focus of this paper.

EXPERIMENTAL

Single crystals of $LiKSO_4$ were grown by slow evaporation from an aqueous solution at 32 °C containing equimolar proportions of $Li_2SO_4{\cdot}H_2O$ and K_2SO_4. The optic axis (c axis) was identified with a polarizing microscope. Single crystals of $^6LiKSO_4$ were grown using $^6Li_2SO_4{\cdot}H_2O$ which had been prepared by a technique described earlier.[13]

Raman spectra were recorded on a Spex Ramalog-5 spectrometer with a 2-cm^{-1} spectral bandpass using the 488.0-nm line of an argon-ion laser for excitation at 600 mw. The Raman spectra at temperatures below 25 °C were obtained by using an Air Products Displex model CSA-202E closed-cycle refrigeration system equipped with a DMX-1E vacuum shroud. Temperatures could be controlled to ±0.1 °C. Raman spectra at temperatures greater than 25 °C were recorded with the crystal in a high-temperature cell similar to that described by Quist,[14] but modified for compatibility with the optics of the Spex Raman system. With this apparatus temperature could be controlled to within 1 °C.

Single crystals of $LiNaSO_4$ were grown by slow evaporation from an aqueous solution as described previously.[13] The optic axis (c axis) was identified with a polarizing microscope in order to properly orient the crystals used in these studies.

Cracking of the $LiKSO_4$ crystals was a problem at higher temperatures. This problem was solved by heating crystals in an oven to a temperature slightly above the phase transition at 436 °C, holding them there for a day, and then slowly cooling them back to room temperature. Pieces of these crystals were then cut, polished, and used for high-temperature studies. The room-temperature spectrum of these annealed crystals was checked against crystals that had not been heated. Only slight changes in the frequencies were noticed in a few of the samples; in these cases the shifts were from 1 to 2 wave numbers. No detectable water was incorporated into the crystals during growth.

VIBRATIONAL-MODE ASSIGNMENTS IN $LiKSO_4$

The irreducible representations of the Raman-active external optic modes are $\Gamma_{\text{ext}}=3A+3E_1+4E_2$. Hiraishi, Taniguchi, and Takahashi[15] observed all of the A and E_2 modes but found only one of the expected three E_1 modes. In this study all of the modes reported in Ref. 15 were observed as well as one additional E_1 mode at 43 cm^{-1}. These frequencies agree well with Hiraishi *et al.* and are listed in Table I. In an earlier Raman study of $LiKSO_4$, Mathieu, Couture, and Poulet[16] were primarily concerned with variations in intensity and frequency as a function of crystal orientation. In that study, modes at 443 and 402 cm^{-1} were incorrectly identified as internal optic modes originating in the intramolecular motions of the sulfate ions. These modes are in fact external modes primarily due to the motion of lithium ions as the data from isotopically enriched crystals clearly shows. Rao *et al.*[17] studied the ν_1, ν_3, and ν_4 internal optic modes in $LiKSO_4$. Wu and Frech[18] also studied the internal optic modes, calculating molecular parameters from observed LO-TO splittings using a molecular dipole model.

TABLE I. External-mode frequencies (in cm^{-1}) of isotopically substituted $LiKSO_4$ with calculated frequency ratios.

Symmetry of mode	Frequency (cm^{-1}) $^7LiKSO_4$	$^6LiKSO_4$	$\nu(^6Li)/\nu(^7Li)$
A	128	128	
	202	202	
	370	395	1.07
E_1	43	43	
	410	429	1.05
	445(LO)	449	1.01
E_2	53	53	
	103	103	
	130	130	
	404	421	1.04

LITHIUM MODES IN ISOTOPICALLY SUBSTITUTED CRYSTALS

Hiraishi *et al.*[15] postulated that the modes around 400 cm^{-1} in $LiKSO_4$ were due to lithium-ion motion. Modes in this same frequency region were also observed in a previous study of $LiNaSO_4$.[13] In that work the modes were identified as originating in the lithium-ion motion through the observed isotopic shifts in a $^6LiNaSO_4$ crystal. Therefore crystals of $^6LiKSO_4$ were grown and Raman spectra of the modes in the 400-cm^{-1} region were compared with similar spectra of naturally abundant $LiKSO_4$.

The external-mode frequencies of $^6LiKSO_4$ and $^7LiKSO_4$ are listed in Table I. From the observed shifts, one can assume that the A mode at 370 cm^{-1}, the E_1 modes at 410 and 445 cm^{-1} (longitudinal-optic mode), and the E_2 mode at 404 cm^{-1} are primarily due to lithium-ion motion since the data suggest significant vibrational decoupling of these modes from the other external optic modes. Assuming pure Li^+ translational motion and the harmonic approximation, the expected isotopic frequency ratio is $\nu(^6Li)/\nu(^7Li)=1.08$. The calculated values of the frequency ratios are listed in Table I and indeed indicate that these modes are relatively decoupled from the other external modes. This is exactly the same conclusion drawn in the earlier study of $LiNaSO_4$. These modes in both $LiKSO_4$ and $LiNaSO_4$ will subsequently be referred to as lithium modes, however, it should be clearly understood that they contain some contribution from other ionic motion.

TEMPERATURE DEPENDENCE OF THE LITHIUM MODES IN $LiKSO_4$

Temperature-dependent polarized Raman spectra were measured for the lithium modes from 12 to 775 K and are shown in Fig. 1. The increasing intensity in the high-frequency wing is due to the ν_2 intramolecular mode of the sulfate ion. The bands generally broaden and decrease in intensity with increasing temperature, although anomalous behavior is observed in the bandwidths and discussed in detail below. The bands were fit to a Lorentzian curve by a nonlinear least-squares program using a standard Marquardt strategy and corrected for the thermal population by dividing the intensities by $[n(\omega,T)+1]$ where $n(\omega,T)$ is the usual Bose factor. The effect of the ν_2 intramolecular mode was accounted for by simultaneously fitting this to a Lorentzian using the same procedure. The resulting bandwidth data are shown in Fig. 2. The average scatter in each data point is estimated to be less than 10% of the bandwidth as determined from multiple runs of the same data point at various temperatures. Data for the E_1 lithium mode could not be obtained due to the weak scattering intensity.

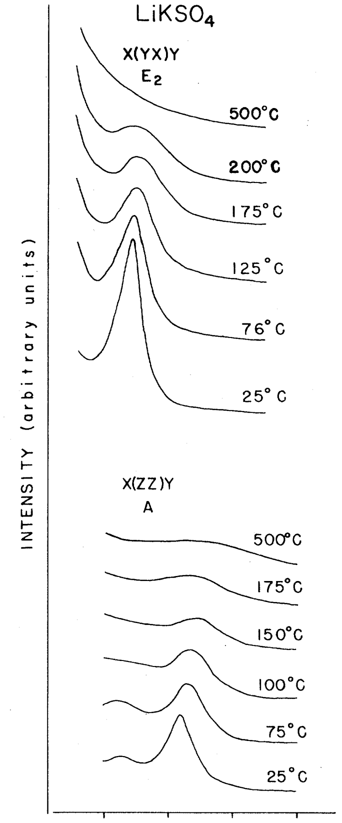

FIG. 1. Temperature-dependent Raman scattering from the A and E_2 lithium modes in $LiKSO_4$. Full scale intensity is 5000 counts/sec.

The bandwidth of both the A and E_2 modes exhibits rather unusual behavior. In Fig. 2 the bandwidth of the E_2 lithium mode increases from 12 to about 475 K and then begins to decrease as the band "sharpens up" over a relatively narrow temperature range. At approximately 600 K the bandwidth again begins to increase. The bandwidth of the A mode increases from 12 to 270 K and then begins to decrease. Reliable data could not be obtained above 500 K due to the weak scattering intensity. It should be pointed out that the maxima in the bandwidth curves occur at different temperatures for the lithium A and E_2 modes when measured in the same crystal. The maximum of the E_2 mode is roughly at 475 K while the maximum of the A mode occurs at approximately 370 K. The frequencies of these modes decrease with temperature with no unusual changes apparent in the data, particularly in the temperature region of the anomalous bandwidth behavior.

Bandwidth data as a function of temperature were collected from two other crystals as a check of the reproducibility of these observations. The band-

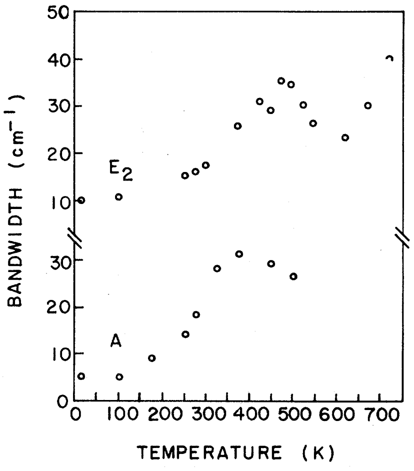

FIG. 2. Bandwidth (full width at half maximum) vs temperature for the lithium modes of $LiKSO_4$. Maximum in the E_2 mode occurs at approximately 475 K and maximum in the A mode occurs at approximately 370 K.

widths in all three crystals were almost identical at temperatures below 275 K. Data for the E_2 mode above this temperature are shown in Fig. 3. Curve *a* shows the same E_2 bandwidth data as shown in Fig. 2 while curves (b) and (c) are from different crystals of $LiKSO_4$. Bandwidth-versus-temperature data for crystals (b) and (c) could not be obtained above 600 K due to the weak intensity of the lithium modes at these temperatures. The maximum of curve (a) occurs at approximately 475 K, while curves (b) and (c) exhibit maxima at 400 and 375 K, respectively. The presence of a maximum seems to be reproducible although the temperature at which the maximum occurs apparently depends on the sample.

TEMPERATURE DEPENDENCE OF THE LITHIUM MODES IN $LiNaSO_4$

Temperature-dependent polarized Raman spectra were measured for the lithium modes for 75 K to temperatures above the phase transition at 791 K (518 °C). Representative spectra of the two A_1 lithium modes are shown in Fig. 4. Both the mode at 314 cm^{-1} and the mode at 404 cm^{-1} (room-temperature frequencies) decrease in frequency and increase in bandwidth as the temperature increases.

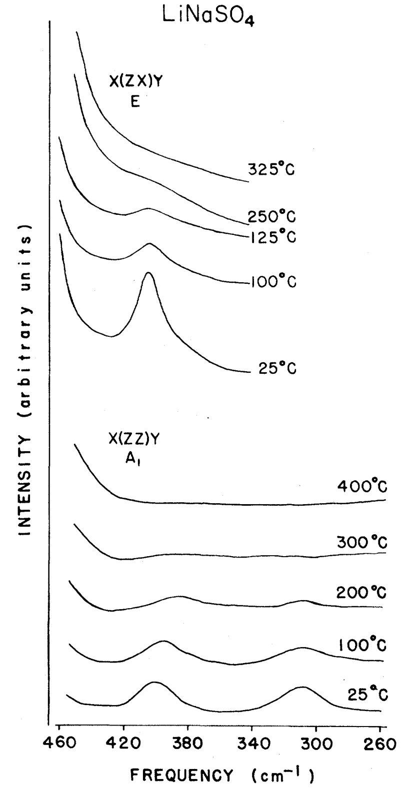

FIG. 4. Temperature-dependent Raman scattering from the A_1 and E lithium modes in $LiNaSO_4$. Full scale intensity is 5000 counts/sec.

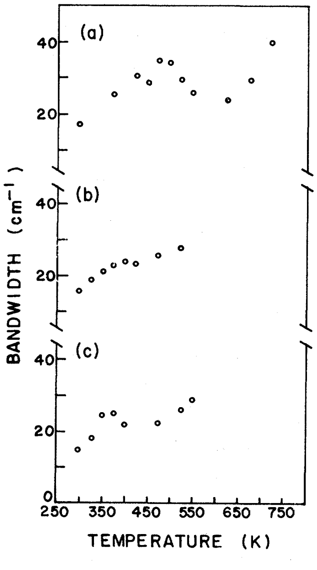

FIG. 3. Temperature-dependent bandwidth data (full width at half maximum) for the E_2 lithium mode in three different crystals of $LiKSO_4$. In (a) the maximum occurs at 475 K, in (b) at 400 K, and in (c) at 375 K.

However, it is important to note that the onset of the dramatic spectral changes in these modes occurs between 25 and 100 °C. The modes are virtually unobservable by 300 °C, well below the phase transition temperature at 518 °C. The E lithium mode at 406 cm^{-1} exhibits similar behavior which is also illustrated in Fig. 4. Again the onset of band broadening somewhat above room temperature is followed by a virtual disappearance of the mode by 300 °C. The high-frequency wing is due to the E component of the ν_2 intramolecular sulfate mode at 476 cm^{-1}.

The frequencies of the lithium modes are shown as a function of temperature in Fig. 5. As expected the frequencies all decrease as the temperature is increased. However, there seems to be a small anomaly associated with the the lower-frequency A mode where the frequency appears to go through a maximum at about 375 K. It is not clear from the data if similar behavior occurs in the other two modes. The temperature dependence of the bandwidths of these modes is given in Fig. 6. In both of the A_1 modes anomalous behavior is observed similar to that seen in the lithium modes of $LiKSO_4$. The

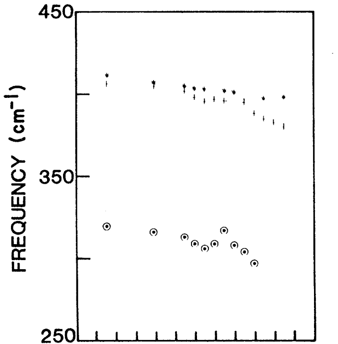

FIG. 5. Normal-mode frequencies of the A_1 and E lithium modes in $LiNaSO_4$ as a function of temperature. Asterisks refer to the E mode, the circles designate the lower-frequency A mode, and the plusses indicate the higher-frequency A mode.

bandwidths increase with increasing temperature until about 300 K where the bandwidths begin to decrease. At about 330 K the bandwidth of the lower-frequency A_1 mode again begins to increase while the bandwidth of the higher-frequency mode does not appear to increase again until 375 K. With the exception of a very-low-frequency mode, these are the only modes in $LiNaSO_4$ exhibiting a striking bandwidth broadening in a temperature region well below the phase transition temperature of 791 K. Furthermore, only the lithium modes exhibit the anomalies in bandwidth and frequency in the temperature region around 300 K. However, the bandwidth anomalies are smaller than those observed in $LiKSO_4$.

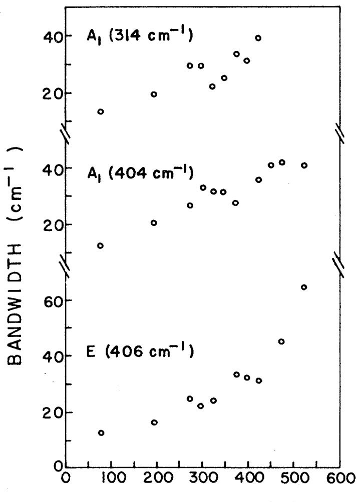

FIG. 6. Normal-mode bandwidths of the A_1 and E lithium modes in $LiNaSO_4$ as a function of temperature. Error in the bandwidth is about ±10%.

DISCUSSION

Since all of the lithium modes in both $LiKSO_4$ and $LiNaSO_4$ dramatically increase in bandwidth with increasing temperature, one might postulate that the lithium ions undergo a thermally activated transition into a disordered state. A model suggested by Andrade and Porto[19,20] describes the linewidth of a phonon associated with a Brownian sublattice as

$$\Gamma = a + bT + c\frac{\tau_c}{1+\omega^2\tau_c^2} , \qquad (1)$$

where a, b, and c are constants and the correlation time τ_c is given by

$$\tau_c = \tau_0 \exp(\Delta U/kT) . \qquad (2)$$

The activation energy ΔU calculated from the two lithium modes in $LiKSO_4$ was obtained from a least-squares fit of bandwidth-versus-temperature data, taking into account the measured temperature dependence of ω in Eq. (1). It would seem from Fig. 2 that there are two distinct regions in the bandwidth data. Therefore, the portion of the E_2 lithium mode bandwidth curve from 12 K to the maximum at 475 K was used, resulting in an activation energy of 0.04 eV. Next, the best curve was drawn through the bandwidth data over the entire temperature range of 12 to 725 K, ignoring the maximum by treating it as superimposed on the underlying "true" bandwidth curve (see Fig. 7). The activation energy found was 0.9 eV. Finally the portion of the bandwidth data for the A lithium mode from 12 to 370 K was used, resulting in an activation energy of 0.03 eV.

A more general analysis of the bandwidth data simply recognizes the behavior as an Arrhenius-type and fits the data to

$$\Gamma = a + bT + c \exp\left[-\frac{E_a}{kT} \right] , \qquad (3)$$

where a, b, and c are constants and E_a is an activation energy. In this case the data are fit over the identical temperature intervals for each mode as in the analysis using the Andrade-Porto model. The results are given in Table II and compared with the Andrade-Porto results. The average error in these calculated values is about 40%.

It is also apparent from Fig. 6 that there are two regions in the bandwidth data of $LiNaSO_4$. Howev-

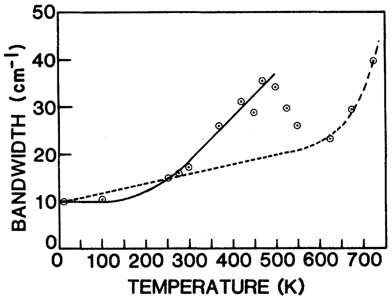

FIG. 7. Curve-fitting procedure for the lithium E_2-mode bandwidth data in $LiKSO_4$. Dashed line is a fit of Eq. (3) over the temperature interval 12 to 725 K. Solid line is a fit of Eq. (3) over the interval 12 to 475 K.

er, in the curve-fitting procedure the maximum was ignored and only the underlying portion was fit to the more general Arrhenius form, Eq. (4). The resulting activation energies are summarized in Table II. The value for the E mode can be compared with that calculated for the E_2 mode in $LiKSO_4$ in the temperature interval 12–725 K, and is found to be lower.

It is tempting to interpret the observed behavior of the lithium ions in $LiNaSO_4$ in terms of the conventional description of a fast-ion conductor, in which the lithium ions at first undergo vibrations with increasing amplitudes as the temperature increases until at sufficiently high temperatures the thermally activated hopping becomes diffusive. However, this is probably not occurring in $LiNaSO_4$ as evidenced by close examination of the data, particularly as one compares the temperature dependence of the bandwidths in $LiNaSO_4$ and $LiKSO_4$ and the activation energies of Table II. It should be apparent that there are at least two distinct thermally activated processes occurring which primarily involve the lithium sublattice. The small anomalous maxima in the frequency and bandwidth data appear to be superimposed onto another process which accounts for the general band broadening in the temperature range from 80 to about 500 K.

The first of these processes has a very low activation energy of a few hundredths of an eV and appears to be slightly sample dependent, at least in the case of $LiKSO_4$. This may be related to the concentration of intrinsic defects, the presence of crystal imperfections, or the existence of grain boundaries, although it is interesting that no other external mode shows the slightest trace of bandwidth anomalies in this or any other temperature region. Another possible explanation is a thermally induced disordering of the lithium-ion sublattice as required by the Andrade-Porto model, although in this case the weak sample dependence is more difficult to explain. In a differential thermal analysis measurement of $LiKSO_4$ by Lepeshkov *et al.*,[11] an exothermic process was reported in the same temperature region as the anomalous bandwidth maxima. However, repeated attempts to observe thermal effects in this region using differential scanning calorimetry have been unsuccessful.

The second type of thermally activated process suggested by the calculated activation energy of 0.4–0.9 eV is consistent with the value expected for the "normal" conductivity of an ionic crystal. The lithium ion is tetrahedrally coordinated with the oxygen atoms of neighboring sulfate ions in the room-temperature structures of $LiKSO_4$ and $LiNaSO_4$. The interaction is so strong in $LiKSO_4$ that an isotopic frequency shift of 6 cm^{-1} is observed in the lowest internal optic mode (ν_2) of the sulfate ion upon enrichment with ^{6}Li. Therefore, the activation energy of roughly 0.5 eV may be associated with the removal of an Li^+ ion from the interior of the oxygen tetrahedron into either a vacant site or an interstitial position.

An alternative explanation invokes dynamic disordering of the lithium ions' potential-energy en-

TABLE II. Calculated activation energies.

Lithium mode		Activation energy E_a (eV) Equation (1)	Equation (3)
	$LiKSO_4$		
A		0.03	0.06
E_2		0.04 (12–475 K)	0.07 (12–475 K)
		0.9 (12–725 K)	0.8 (12–725 K)
	$LiNaSO_4$		
A_1 (404 cm^{-1})			0.2
A_1 (314 cm^{-1})			0.4
E			0.4

vironment through the motion of the oxygen atoms. If the phase transition at 463 °C in $LiKSO_4$ and 518 °C in $LiNaSO_4$ occurs through significant translational and reorientational displacement of the sulfate ions, then the amplitude of the normal vibrational mode consisting primarily of these displacements will be expected to increase with increasing temperature and become more anharmonic. This of course is the usual soft-mode picture of a phase transition, although the mode need not necessarily soften in order for the vibration consisting of the appropriate displacements to significantly increase in amplitude with increasing temperature. Since the tetrahedral coordination of the lithium ions is defined by the oxygen atoms of the sulfate ions, it is the interaction of the lithium ions with the nearest-neighbor oxygen atoms which account for most of the potential energy of the lithium ions. As the temperature and the vibrational amplitude of the oxygen atoms increase with increasing loss of correlation among the sulfate ions within a unit cell, the vibrational motion of the lithium ions reflects the increasing disorder in the potential-energy environment, resulting in decreasing scattering intensity and increasing bandwidth of the lithium modes.

CONCLUSIONS

The spectroscopic observations of isotopically enriched $^6LiKSO_4$ lead to unambiguous identification of an A and an E_2 external optic mode as originating primarily in the motion of lithium ions, analogous to lithium modes previously identified in $LiNaSO_4$. It is these modes whose bandwidths exhibit rather striking temperature-dependent effects, dramatically broadening as the modes decrease in intensity in a temperature region well below the phase transition temperature in each crystal. Two kinds of dynamical behavior can be distinguished. There appears to be a process involving only the lithium-ion sublattice which may involve a local disordering of the lithium ions and would account for the appearance of a maximum in the bandwidth-versus-temperature curve. Such a disordering would be difficult to directly observe by x-ray diffraction techniques because of the inherently weak x-ray scattering intensity of the lithium ions. Scott[21] has pointed out that Raman spectroscopic measurements are much more sensitive to minute displacements of ions within a unit cell than are x-ray determinations. A displacement involving lithium ions represents an extreme case of Scott's contention. The contribution of the postulated local disordering of the lithium ions to the temperature dependence of the bandwidth is superimposed on another thermally activated process which may involve the removal of the lithium ions from their tetrahedral coordination sphere defined by the oxygen atoms of the neighboring sulfate ions. Alternatively the increasing bandwidth and decreasing intensity may reflect the increasing dynamic disorder in the immediate potential-energy environment of the lithium ions due to the increased vibrational amplitude of the oxygen atoms of the sulfate ions which are involved in the phase transition.

A comparison of the behavior of the lithium modes in $LiNaSO_4$ and in $LiKSO_4$ shows that these modes in both crystals exhibit almost identical behavior over about the same temperature interval, although the anomalous bandwidth maxima occur at slightly lower temperatures in $LiNaSO_4$ and the modes seem to decrease in intensity at somewhat lower temperatures. However, the comparison strongly suggests that the rather unusual behavior of these modes is closely related to the tetrahedral coordination of the lithium ions with the nearest-neighbor oxygen atoms of nearby sulfate ions. This comparison further suggests that the unusual behavior of these modes in $LiNaSO_4$ is unrelated to the high mobility of the lithium ion in the fast-ion-conducting phase.

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