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Temperature dependence of the low-frequency vibrational modes in $LiNaSO_4$ and $LiKSO_4$

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The Raman spectra of the external modes in $LiNaSO_4$ and $LiKSO_4$ are measured from 12 to 1000 K. Each crystal has at least one phase transition in this interval. As the temperature increases, one low-frequency mode in each crystal decreases markedly in frequency as the bandwidth rapidly broadens. The relative contributions of overdamping and soft-mode behavior to the observed temperature dependence are calculated. The temperature dependence of the bandwidths are analyzed in terms of current theories. Finally, differences in the dynamics of the constituent ions in the high-temperature phases of the two crystals are discussed.

INTRODUCTION

A large number of crystals in which fast-ionic conductivity is observed exhibit this behavior only after a transition into a phase. Since the structure and dynamics of this fast-ion conducting phase (or superionic phase) determine the mechanism and magnitude of the ionic conductivity, one is interested in studying not only the motion of the mobile ion but also the nature of the supporting lattice of the fast-ion phase. The fast-ion phase of a small number of crystals is a plastic phase in which the anomalously high conductivity of the mobile ion may be enhanced by the dynamical motion of the supporting lattice.[1] Examples of this are lithium sulfate Li_2SO_4 and lithium sodium sulfate $LiNaSO_4$. In these systems it is useful to study the motion of the lattice as the phase transition is approached, since this provides information about the nature of the lattice motion after the transition into the plastic phase. One of the most sensitive probes for the study of phase transitions is Raman scattering from vibrational modes involved in the phase transition (e.g., soft modes) at various temperatures up to the transition temperature.[2] Therefore this technique was used as part of a comparative spectroscopic study of fast-ion conductivity in a series of selected sulfate crystals.

In a previous study the motion of lithium ion was studied using temperature-dependent Raman scattering from crystals of $LiNaSO_4$ and $LiKSO_4$ in which modes primarily due to the motion of the lithium ion had been unambiguously identified utilizing crystals isotopically enriched with ^6Li.[3] Lithium sodium sulfate $LiNaSO_4$ is hexagonal at room temperature, crystallizing in a hexamolecular unit cell in space group $P31c$ (C_{3v}^4).[4] At 518 °C there is a transition into a body-centered cubic phase[5] that exhibits high ionic conductivity.[6] At room temperature lithium potassium sulfate $LiKSO_4$ crystallizes in a bimolecular unit cell in space group $P6_3$ (C_6^6).[7] It undergoes a transition at 436 °C into an orthorhombic phase.[8] No phase of $LiKSO_4$ is reported to have unusually high ionic conductivity.

To complement the earlier comparative study and to provide additional insight into the nature of the fast-ion conducting plastic phase, the comparative study was extended to consider the temperature dependence of the additional external modes in $LiNaSO_4$ and $LiKSO_4$ and was expanded to include sodium potassium sulfate $NaK_3(SO_4)_2$. The latter crystal forms a unimolecular unit cell at room temperature in space group $P\bar{3}m1$ (D_{3d}^3).[9] It undergoes a transition into a hexagonal phase in space group $P6_3mc$ (C_{6v}^4) at 440 °C.[10]

EXPERIMENTAL

Single crystals of $LiKSO_4$ and $LiNaSO_4$ were grown by slow evaporation from aqueous solution as previously described.[3] Sodium potassium sulfate was prepared in a similar manner.

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-line laser for excitation at 600 mW. Raman spectra at temperatures below 25 °C were measured using an Air Products Displex model CSA-202E closed-cycle refrigeration system equipped with a DMX-1E vacuum shroud for Raman spectroscopy. The temperature could be controlled to 0.1 °C. A high-temperature cell modified after a design described by Quist[11] was used to measure Raman spectra at temperatures above room temperature. The temperature in this cell could be controlled within 1 °C.

TEMPERATURE DEPENDENCE OF THE EXTERNAL MODES IN $LiNaSO_4$

As expected, all of the external modes of $LiNaSO_4$ decrease in frequency and broaden as the temperature is increased. These data are shown in Fig. 1. Many of them merge with other external modes or become too weak in intensity to observe. It is important to note that no external modes are observable above the phase transition temperature, an observation that will be shown to have important structural implications. The lowest-frequency external mode is observed to be most temperature sensitive, and representative spectra are shown in Fig. 2. This mode is of A_1 symmetry with a room-temperature frequency of 63 cm^{-1}. As the temperature is increased it eventually disappears at about 100 °C into the broad "wing" that emerges from the excitation line. Figure 3 shows spectra above and below the phase transition. In the spectrum above the phase transition (upper curve) a large scattering intensity is observed in the wing of the laser line. This behavior is quite similar to that observed in a Raman study of AgI by Burns *et al.*[12]: In that study they postulated that the disorder in the high-temperature fast-ion phase of AgI completely breaks down the selection rule. This observation in $LiNaSO_4$ is compatible with the picture of a high-temperature plastic phase characterized by significant disorder.

Nilsson *et al.* postulated that the fast-ion conducting phase in Li_2SO_4, a well-known fast-ion conductor, is a plastic phase characterized by rotational disorder of the sulfate ions.[1] Polishchuk and Bogdanova[13] suggested that the high-temperature phase of $LiNaSO_4$ could also be a plastic phase. They reported values for the heat of transition and heat of fusion for $LiNaSO_4$ of 5380 and 760 cal mol^{-1}, respectively, indicating a plastic phase since plastic phases are associated with large volume changes at the transition together with a larger heat of transi-

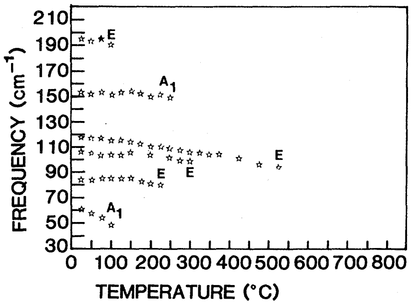

FIG. 1. Temperature dependence of the external-mode frequencies in $LiNaSO_4$ from room temperature to 550 °C.

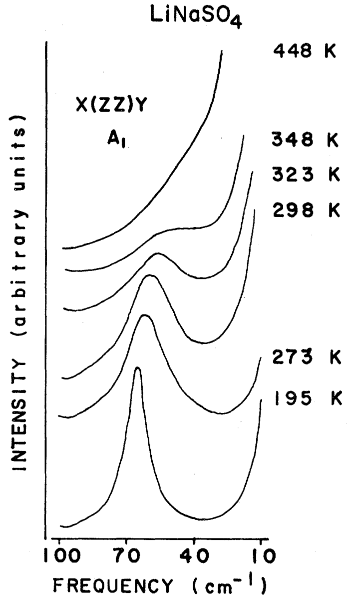

FIG. 2. Raman spectra of the low-frequency A_1 mode in $LiNaSO_4$ at various temperatures. The spectra are offset along the ordinate for visual clarity. Full scale intensity is 5000 counts/sec.

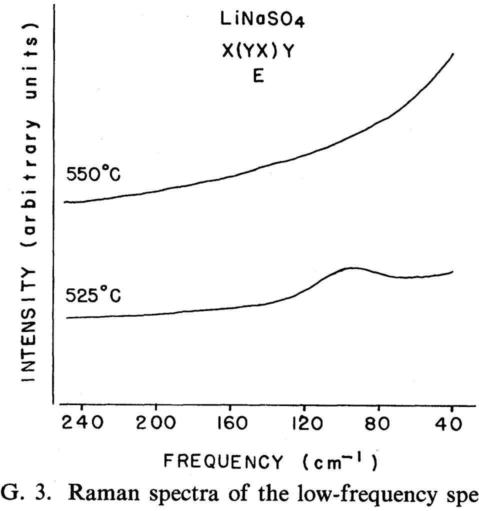

FIG. 3. Raman spectra of the low-frequency spectral region in $LiNaSO_4$ above and below the phase transition showing the increased intensity in the wing of the laser line. Full scale intensity is 5000 counts/sec.

tion than the heat of fusion. Jansson and Sjoblom[14] reported a value of 2.70 $\mathrm{cm}^3\,\mathrm{equivalent}^{-1}$ for the change in volume at the phase transition. This value can be compared to a value of 1.16 $\mathrm{cm}^3\,\mathrm{equivalent}^{-1}$ for Li_2SO_4 with its plastic phase and 0.06 $\mathrm{cm}^3\,\mathrm{equivalent}^{-1}$ in $LiKSO_4$,[14] which does not have a plastic phase.

If the phase transition in $LiNaSO_4$ is associated with rotational motion of the sulfate ion as is the case in several sulfate crystals,[15] one might expect a mode that is primarily due to sulfate-ion librational (hindered rotational) motion to be the most affected by temperature. A symmetry-based vibrational analysis for the external modes[16] shows that the librational motion of the sulfate ion about the c axis is of A_1 symmetry. One must not forget that the A_1 external modes will be a mixture of the various motions of appropriate symmetry, but it is possible that one mode is due primarily to sulfate librational motion.

A simple relationship for the frequency of such a librational mode is

$$\bar{\nu}=\frac{1}{2\pi c}\left[\frac{K}{I_{\mathrm{rot}}}\right]^{1/2}, \tag{1}$$

where I_{rot} is the moment of inertia for rotation and K is the force constant. If this describes vibration in a periodic potential of the form

$$V(\alpha)=\tfrac{1}{2}V_0(1-\cos n\alpha)\,, \tag{2}$$

where α is the angular coordinate describing the rotation and n is the periodicity, then V_0 may be viewed as a potential barrier which would have to be overcome for rotation into the next potential energy minimum. Identifying

$$K=\left[\frac{d^2V}{d\alpha^2}\right]_0=\frac{n^2V_0}{2}, \tag{3}$$

one then has

$$\bar{\nu}=\frac{1}{2\pi c}\left[\frac{V_0n^2}{2I_{\mathrm{rot}}}\right]^{1/2}. \tag{4}$$

Using the A_1-mode frequency value of 63 cm^{-1} and $n=3$, and calculating I_{rot} by the use of crystallographic data,[4] one obtains a value of 0.3 eV for V_0. Takahashi *et al.*[17] estimated that the potential energy barrier to rotation should be not less than 0.3 eV in alkali-metal–sulfate crystals. This estimate and the value calculated here are certainly compatible with the suggestion that the A_1 mode at 63 cm^{-1} contains a large contribution from sulfate rotational motion.

The rapidly decreasing frequency of this mode with increasing temperature is also of interest since it appears to behave as a soft mode, that is, a mode whose frequency goes towards zero as the temperature approaches the phase-transition temperature. A structural phase transition is often characterized by a soft mode.

Although the 63-cm^{-1} A_1 mode could be a soft mode associated with some structural order parameter in the crystal, overdamping of this mode could also cause the decreasing frequency with increasing temperature. The intensity of a Raman mode can be written

$$I_{\mathrm{Ram}}(\omega,T)=\frac{A[n(\omega,T)+1]\omega\Gamma(T)}{[\omega_0(T)^2-\omega^2]^2+\omega^2\Gamma(T)^2}, \tag{5}$$

where A is a constant, ω_0 is the harmonic frequency, $\Gamma(T)$ is the damping constant, and $n(\omega,T)$ is the Bose-Einstein factor $[\exp(\hbar\omega/kT)-1]^{-1}$. With increasing temperature the vibrational amplitudes increase and anharmonic effects become more important. This results in an increasing damping constant that affects the frequency of the observed maximum of the Raman intensity.

To determine if a mode softens or is overdamped, the reduced Raman intensity was calculated from the Raman spectrum according to

$$I_{\mathrm{red}}=\frac{\omega}{n(\omega,T)+1}I_{\mathrm{Ram}}(\omega,T)\,. \tag{6}$$

As Habbal, Zvirgzds, and Scott[18] explained, I_{red} is a maximum at the frequency ω_0 regardless of the size of the damping constant Γ.

The A_1 mode was resolved from the laser excitation wing at each temperature by subtracting the

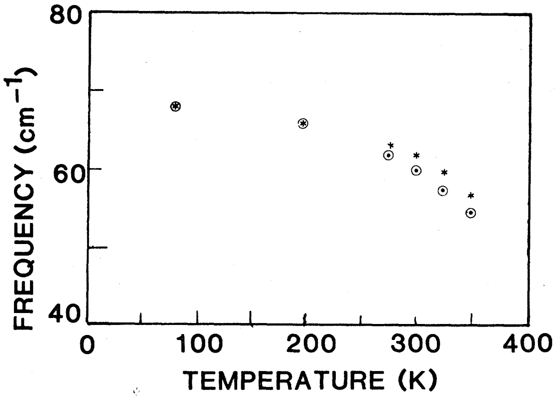

FIG. 4. Temperature dependence of the low-frequency A_1-mode band maximum in $LiNaSO_4$. The circled points are the maxima in the observed Raman intensities, while the asterisks denote frequency maxima of I_{red} calculated according to Eq. (6).

wing contribution as fit to a power function. The intensity data for the A_1 mode were then converted to reduced Raman intensities using Eq. (6). From these the frequencies of the band maximum were obtained at each temperature and compared with the frequency of the uncorrected Raman band maximum in Fig. 4. If the mode was overdamped instead of softening, the reduced Raman frequency would not be expected to decrease. Figure 4 shows that both mechanisms are important, although at higher temperatures the Raman frequency decreases faster with increasing temperature than does the reduced Raman frequency, indicating that overdamping becomes more important at higher temperatures. Since the reduced Raman band maximum decreases in frequency one must assume that this mode is also softening and that it can probably be associated with a structural parameter in the crystal.

If rotational motion of the sulfate ion is involved in the A_1 mode at 63 cm^{-1}, it is possible to estimate the contribution that this motion makes to the bandwidth. Rakov[19] has derived an expression for the bandwidth in terms of vibrational and orientational contributions, which is

$$\Gamma=\Gamma_{\text{vib}}+B\exp\left[\frac{-E_a}{RT}\right]. \tag{7}$$

The second term on the right-hand side represents the orientational contribution to bandwidth while Γ_{vib} is the constant vibrational bandwidth contribution. The E_a corresponds to an activation energy. The computer-resolved A_1 modes were corrected for the thermal population of vibrational levels using the Bose-Einstein factor and are shown in Fig. 5. Temperature-dependent bandwidth data from these corrected modes were fitted to Eq. (7) and are shown in Fig. 6. The activation energy for the orientational contribution is found to be 0.09±0.01 eV, which is relatively low. This indicates that the orientational contribution to the bandwidth becomes quite important as the temperature increases.

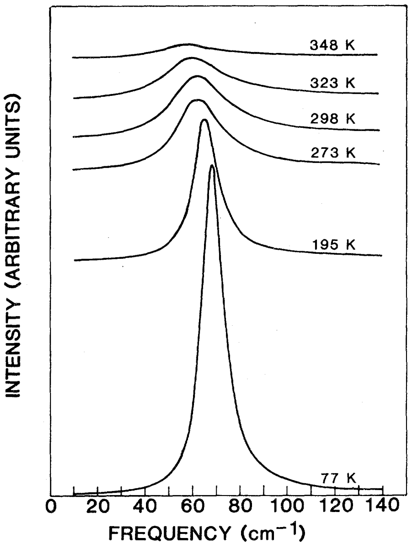

FIG. 5. Raman spectra of the low-frequency A_1 mode in LiNaSO_4 at various temperatures corrected for thermal population effects by dividing the observed scattering intensity by $n(\omega,T)+1$, where $n(\omega,T)$ is the Bose-Einstein factor.

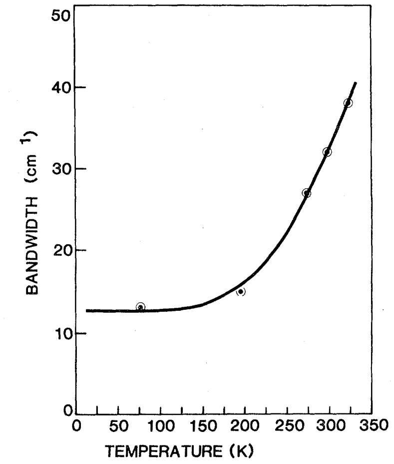

FIG. 6. Orientational contribution to the bandwidth of the low-frequency A_1 mode in LiNaSO_4. The solid line is the best fit to Eq. (7).

TEMPERATURE DEPENDENCE OF THE EXTERNAL MODES OF LITHIUM POTASSIUM SULFATE

The external modes of LiKSO_4 also broaden and decrease in frequency as the temperature increases. The E_1 mode at 103 cm^{-1} (room-temperature frequency) merges with the mode of the same symmetry at 130 cm^{-1} (room-temperature frequency) at approximately 300 °C, although the rest of the external modes are observable up to the phase transition at 436 °C. The temperature dependence of these modes is shown in Fig. 7. The two lowest frequency E_1 and E_2 modes at 43 and 53 cm^{-1} change only a few wave numbers with increasing temperature, merging to a frequency of 47 cm^{-1} at 450 °C. At temperatures above the phase transition only one external mode is observable at 163 cm^{-1} (frequency at 500 °C) in an $X(ZZ)Y$ experiment.

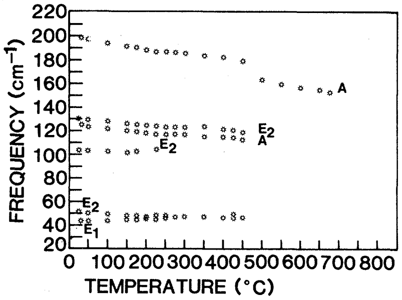

FIG. 7. Temperature dependence of the external mode frequencies in $LiKSO_4$ from room temperature to 700 °C.

The bandwidth of the A mode at 202 cm^{-1} increases to a greater extent than any other external mode in $LiKSO_4$. Temperature-dependent spectra for this mode are shown in Fig. 8. Hiraishi, Taniguchi, and Takahashi[20] assign this mode as a sulfate librational mode based on infrared reflection and Raman intensities. The frequency of 202 cm^{-1} along with I_{rot} calculated by using appropriate crystallographic data[7] was used in Eq. (4) to calculate a potential barrier for rotation. The value obtained was 3.0 eV, which is much higher than that calculated for the low-frequency mode in $LiNaSO_4$. Recalling that Takahashi *et al.*[17] postulated that the potential barrier for rotation should be approximately 0.3 eV in alkali-metal sulfates suggests that the high value calculated here for the A mode of $LiKSO_4$ could mean that other kinds of ionic motion such as translational motion of the potassium ion and the sulfate ion contribute significantly to this mode. Takahashi *et al.* assigned the highest-frequency external mode as resulting from metal-sulfate relative (translational) motion in an infrared study of several sulfate crystals. In the mixed cation sulfate $LiKSO_4$ there are two vibrational modes primarily involving lithium-ion motion that have already been identified in the spectral region of roughly 400 cm^{-1} (Ref. 3) and are the highest-frequency external modes. The external mode of next highest frequency in $LiKSO_4$ is the A mode at 202 cm^{-1}, suggesting a significant contribution from potassium-ion translational motion.

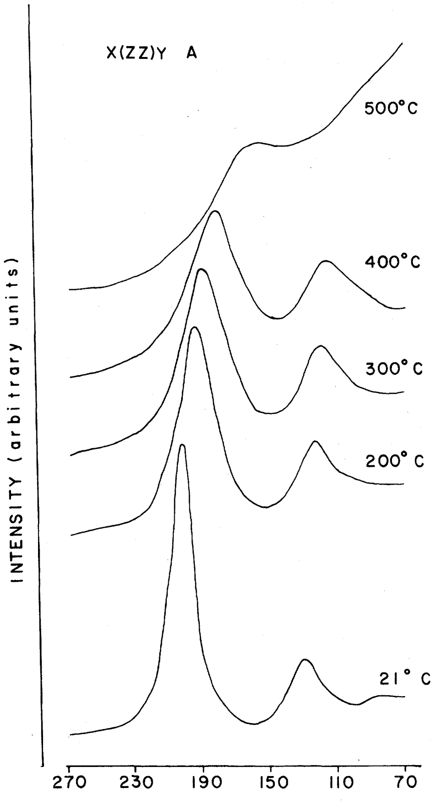

FIG. 8. Raman spectra of the A mode at 202 cm^{-1} (room-temperature frequency) in $LiKSO_4$ at various temperatures. The spectra are offset along the ordinate for visual clarity. Full scale intensity is 5000 counts/sec.

Reduced Raman curves were calculated for a computer-resolved band of the 202-cm^{-1} mode at various temperatures as was done in the case of the A_1 mode in $LiNaSO_4$. The Raman frequencies and the reduced Raman frequencies are plotted versus temperature in Fig. 9. The frequency of the reduced Raman intensity maximum is seen to decrease almost as much as the Raman frequency as the temperature is increased. Therefore this mode seems to soften in a similar manner as the low-frequency A_1 mode at 63 cm^{-1} in $LiNaSO_4$, strongly suggesting that the mode is associated with a structural change occurring in the unit cell.

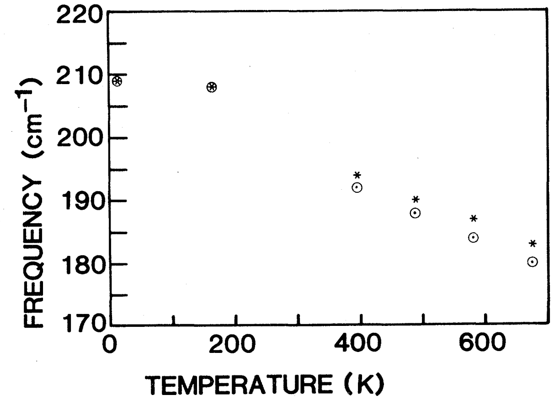

FIG. 9. Temperature dependence of the A-mode (202 cm^{-1}, room-temperature value) band maximum in $LiKSO_4$. The circled points are the maxima in the observed Raman intensities, while the asterisks denote frequency maxima of I_{red} calculated according to Eq. (6).

TEMPERATURE DEPENDENCE OF THE EXTERNAL MODES IN SODIUM POTASSIUM SULFATE

As an additional reference system the Raman spectra of the external modes of sodium potassium sulfate $NaK_3(SO_4)_2$ were measured from room temperature to temperatures somewhat above the phase-transition temperature at 440 °C. The external modes were observed to decrease slowly in frequency as the temperature was increased. An A_{1g} mode at 45 cm^{-1} was the lowest-frequency external mode observed and, like the lowest-frequency external mode in $LiKSO_4$, changed only slightly in frequency with increasing temperature. A broad A_{1g} mode at 104 cm^{-1} (room-temperature value) seemed to decrease in frequency most rapidly with increasing temperature. At 300 °C a broad wing appeared next to the laser line, making many of the external modes unobservable. However, above this temperature additional external modes appeared. The phase diagram given by Eysel[10] for the system Na_2SO_4-K_2SO_4 indicates that the solid solution $NaK_3(SO_4)_2$ can coexist with a phase of K_2SO_4 at temperatures where the disappearance of the peaks occurs. It is possible that at 300 °C the K_2SO_4 phase is first appearing, causing disorder in the system and broadening the wing of the laser line. At the higher temperatures both $NaK_3(SO_4)_2$ and K_2SO_4 exist and contribute external-mode bands. No further analysis was done on the external-mode spectral region due to the possible existence of the K_2SO_4 phase.

CONCLUSIONS

The temperature at which the phase transitions occurred in this study seem to be slightly higher than those previously reported. This is probably due to error associated with determining the temperature of the crystal in the high-temperature cell. It should be mentioned that the transition temperature of $NaK_3(SO_4)_2$ is somewhat dependent on the potassium-ion concentration[10] and that Ando[21] reported a value of 445 °C for the phase transition in $LiKSO_4$, which is closer to the value observed here at 450 °C.

Each of the three sulfate crystals appears to have at least one external mode whose behavior with increasing temperature is unique among the normal modes of that particular crystal. Lithium sodium sulfate has a low-frequency mode at 63 cm^{-1} that appears to soften with temperature and seems to be related to sulfate rotational motion. Lithium potassium sulfate has a relatively high-frequency mode at 202 cm^{-1} that broadens faster than its other external modes and appears to soften, indicating a relationship to a structure parameter. An A_{1g} mode at 104 cm^{-1} in $NaK_3(SO_4)_2$ decreases in frequency at a greater rate than other external modes in this system.

The increase in quasielastic low-frequency scattering intensity after the phase transition in the three sulfate crystals has been seen in other crystals after a phase transition.[12,18] This is generally attributed to disorder in the system and hence the breakdown of the symmetry-based Raman selection rules. It can be postulated that more disorder exists in $LiNaSO_4$ than in $LiKSO_4$ above the phase transition since no external modes are observable in the former crystal.

Both the 202-cm^{-1} mode in $LiKSO_4$ and the 63-cm^{-1} mode in $LiNaSO_4$ are observed to decrease in frequency with increasing temperature. Analysis of the reduced Raman curves indicates that the decrease is in part due to anharmonic effects and in part due to mode softening. The contribution due to mode softening is about the same in both crystals when measured as a percentage of the low-temperature frequency of each mode.

A comparison of the external modes at temperatures above the phase transition is consistent with the view that the high-temperature phase of $LiNaSO_4$ is a plastic phase involving large orientational disorder of the sulfate ions. The failure to observe any external modes in $LiNaSO_4$ at temperatures above the phase transition suggests that the sulfate ions do not remain in fixed, orientationally disordered positions at temperatures above the phase transition. Instead the orientations of the various sulfate ions change on a time scale smaller than that probed by a Raman scattering measurement at these frequencies, i.e., 10^{-13} sec. In this sense the orientational disorder is dynamic rather than structural in origin.

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