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Reorientational motion in superionic sulfates: A Raman linewidth study

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Raman spectra of two superionic conducting crystals, fcc Li_2SO_4 and bcc $LiAgSO_4$, have been recorded in the frequency range 300—1400 cm^{-1} across the entire temperature range of stability of each compound. Comparison of polarized and depolarized spectral bandwidths for the symmetric A_1 sulfate internal mode permits a component due to the sulfate-ion reorientation to be separated, which confirms the plastic behavior of the superionic phases of the two crystals. In the case of Li_2SO_4, the reorientation time derived corresponds well with the value 2 ps recently reported on the basis of computer-simulation studies. Our measurements are precise enough to yield the temperature dependence of the reorientation time in each type of crystal. The Arrhenius activation energies are significantly different: 0.40 and 0.72 eV for fcc Li_2SO_4 and bcc $LiAgSO_4$, respectively. These values are sufficiently close to the contrasting activation energies for cation diffusion, 0.34 and 0.52 eV, respectively, to support the "paddle-wheel" migration postulate for this type of plastic crystal.

INTRODUCTION

Li_2SO_4 and $LiAgSO_4$ belong to a group of materials which undergo a first-order phase transition from a normal ionic conducting phase into a highly conducting phase (fcc Li_2SO_4 and bcc $LiAgSO_4$). The conductivity[1] ($\simeq 1\ \Omega^{-1}\,cm^{-1}$) in the high-temperature fast-ion conducting phase is for both materials close to that of α-AgI,[2] which is often regarded as the archetypal superionic conductor or solid electrolyte. Below the phase transition at 848 K, Li_2SO_4 is monoclinic, and above, it is fcc ($a = 7.07$ Å at 883 K)[3] up to its melting point at 1133 K. The ionic conductivity is ascribable to the cations only, while the sulfate ions form a translationally fixed lattice. It is a striking fact that not only Li^+ but several other monovalent and divalent ionic species are mobile in the fcc lattice, even large ionic species such as Ag and Rb ions.[4] The variety of mobile ionic species in this phase is unparalleled in other solid electrolyte systems. The cations occupy mainly the position $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ while the other available site $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ is only occupied for a short time.[5,6] The activation energy for Li^+ diffusion in the fcc lattice is notably high (0.34 eV) compared to other solid electrolytes (0.10 eV for α-AgI).[7] For $LiAgSO_4$ the phase of high ionic conductivity is in the temperature range 728—848 K with nearly equal diffusion coefficients ($\simeq 1\times10^{-5}\ cm^2\,s^{-1}$)[8] for Li^+ and Ag^+. The sulfate ions form a rigid bcc lattice in which Ag^+ occupy octahedral sites $(0,\frac{1}{2},\frac{1}{2})$ and Li^+ mainly occupy tetrahedral sites $(\frac{1}{4},0,\frac{1}{2})$.[5] The activation energy for cation diffusion in bcc $LiAgSO_4$ (0.52 eV for both Li^+ and Ag^+)[7] is even higher than that found in fcc Li_2SO_4 and both phases are characterized by a high degree of oxygen disorder.[5] This, together with a high latent heat (214 $kJ\,kg^{-1}$ for fcc Li_2SO_4 and 155 $kJ\,kg^{-1}$ for bcc $LiAgSO_4$)[9] compared to the heat of fusion[9] ($\simeq 70\ kJ\,kg^{-1}$) for both materials, suggests a premelting process with rapid rotational reordering of the sulfate groups.[5] In view of the broad variety of possible mobile ionic species in sulfate-based solid electrolytes, it has been proposed that the rotations of the sulfate ions enhance the cation diffusion and thus explain the high conductivity.[3] There is, however, so far no experimental evidence for any reorientational motions of the sulfate ions in the high conducting phase of these materials, even though previous Brillouin scattering studies in this laboratory report plastic behavior and low transverse sound velocities attributed to possible rotational-translational coupling.[10,11] Simulation studies suggest that the structure could be described as a mixture of C_{3v} and D_{2d} configurations[12] and indicate an orientational disorder with a characteristic time of 2 ps.[13] Also, softening of vibrational Raman modes has been observed in some sulfate systems below the phase transition, which gives evidence for the onset of the sulfate rotational motion as the phase transition is approached.[14,15] The purpose of the present work is to use Raman scattering to investigate the dynamics of the sulfate ions in the superionic phase of Li_2SO_4 and $LiAgSO_4$ by studying vibrational line shapes, which have been shown to be sensitive to molecular reorientations.[16,17] These systems were chosen not only to get insight in the proposed rotational mechanism but also to investigate a suggested relation between such a mechanism and the cation diffusion, with the high but different activation energies for the cations of the two systems in mind.

In the simple approximation that vibration (v) and reorientational (R) motions are uncorrelated and that dipole-dipole coupling and collision-induced effects can be neglected, the reorientational relaxation time τ can be determined for a totally symmetric Raman vibration of low depolarization ratio from the half-widths of the isotropic and anisotropic spectrum:

$$\Gamma_{\rm iso}=\Gamma_v\ , \tag{1}$$

$$\Gamma_{\rm aniso}=\Gamma_v+\Gamma_R\ , \tag{2}$$

$$\tau^{-1}=2\pi c\Gamma_R=2\pi c(\Gamma_{\text{aniso}}-\Gamma_{\text{iso}})\ , \qquad (3)$$

where c is the speed of light and Γ is the half-width in cm^{-1}. The width of the isotropic component is only due to vibrational relaxation and is observed in the polarized spectrum. The anisotropic broadening of the depolarized spectrum involves both vibrational and orientational relaxation and in order to obtain the orientational width the intrinsic broadening must be removed from the observed depolarized spectrum. When the half-width of the anisotropic spectrum is greater than that of the isotropic spectrum the difference can be ascribed to reorientational relaxation and used to measure the reorientation time. It should, however, be noted that Raman scattering refers to a correlation time associated with the decay of a second-order spherical harmonic[18] and therefore, τ in Eq. (3) is the time it takes a molecule to turn through 41°.

EXPERIMENT

The Raman spectra for fcc Li_2SO_4 and bcc $LiAgSO_4$ were excited by an Ar^+ laser (Spectra Physics model 165-00) operating at 488.0 and 514.5 nm, respectively, with a typical output of 600 mW. The beam was focused into the sample cell which was mounted in a furnace designed for 90° scattering geometry. The furnace is described in detail elsewhere.[10] The polarization of the incident beam was controlled by a half-wave plate and the polarization of the scattered light was analyzed by rotating a polarizing prism. A Spex double monochromator (model 1403) with 1800-lines/mm holographic gratings was used in series with a third monochromator to resolve the Raman spectra. The slits were set to give a measured resolution of 2 cm^{-1}. The detector system includes a cooled photomultiplier (RCA model 31034-76) connected to a lock-in amplifier (PAR model 126) essential to extract the signal from thermal noise since the samples were investigated at high temperatures. Spectra were obtained in the ranges 913—1100 K for Li_2SO_4 and 742—822 K for $LiAgSO_4$; the temperature was controlled by a thermostat to within 1 K with a temperature stability better than 0.2 K. The sample cell was made of cylindrical quartz tubing (inside diameter 3 mm) with an optical flat window fused to the bottom of the tube. The samples, which were unoriented single crystals, were grown by the Bridgman method from the melt of suprapure Li_2SO_4 and Ag_2SO_4.[10] The salts were dried for 24 h in a vacuum oven before sample preparation. The crystals were approximately 5 mm long and perfectly transparent, the Li_2SO_4 crystals being uncolored whereas the $LiAgSO_4$ crystals were pale yellow.

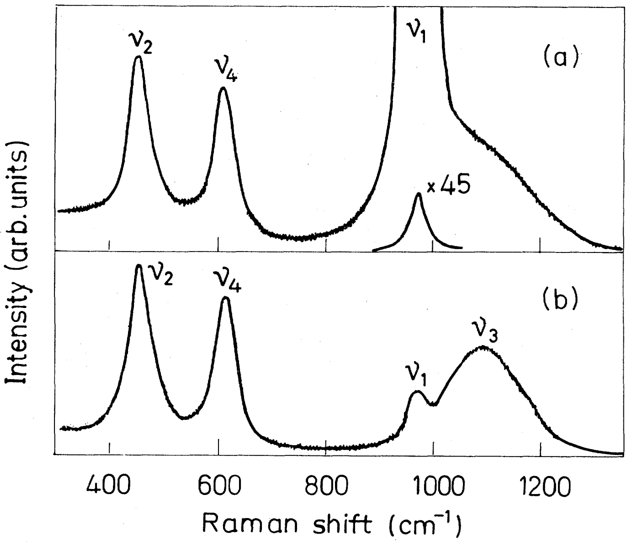

FIG. 1. Raman spectra of bcc $LiAgSO_4$ at 742 K, (a) polarized (isotropic) and (b) depolarized (anisotropic) spectrum.

EXPERIMENTAL RESULTS AND DISCUSSION

Internal optic modes

Raman spectra were obtained over the entire temperature range of fcc Li_2SO_4 and bcc $LiAgSO_4$ and a few spectra of the melts were also recorded. Typical polarized and depolarized spectra of bcc $LiAgSO_4$ are shown in Fig. 1. No external modes were observable in the spectra, in accordance with the model that the high-conducting solid phases of these systems are plastic phases with reorienting sulfate ions; the spectra look very similar to those of the melts, which is a general finding for superionic materials.[19] The observed mode frequencies of the ν_1, ν_2, ν_3, and ν_4 sulfate-ion intramolecular modes are given in Table I. The tabulated frequencies are mean values of the crystalline phases, since no temperature dependence was found for the Raman shifts within the experimental accuracy. Furthermore, the mode frequencies of the solid phases agree with those of the melts. In Table I the present data are compared with the reported values from melts of pure Li_2SO_4 and mixtures of Li_2SO_4 and K_2SO_4;[20] the tabulated frequency range give the range for the band maxima for melts of composition from pure Li_2SO_4 to 40 mol % Li_2SO_4—60 mol % K_2SO_4. As can be seen in Table I, ν_1 and ν_4 decrease with increasing size of the alkali-metal cation. This is probably also true for the ν_2 band though the effect is much smaller in magnitude. The present results give the same trend for the ν_3 band in contrast with the observations of Child *et al.*[20] for the molten Li_2SO_4-K_2SO_4 systems. It should, however, be noted that Child *et al.* reported a splitting of the ν_3 band with a definite indication of two maxima, which have not been observed in the present case although the band is very broad. For crystalline Li_2SO_4, $LiNaSO_4$, and $LiKSO_4$ at room temperature there is a remarkable similarity in frequency,[15] whereas results for crystalline Na_2SO_4 (Ref. 21) and K_2SO_4 (Ref. 22) give a cation trend ($\nu_1=994$ and 984 cm,[1] respectively). The same observations have also been reported for the nitrates, where the decrease in peak frequency has been explained by decreased values of the product $P\alpha$ where P is the cation polarizing power and α the cation polarizability.[23,24]

The widths of the internal modes were determined for $LiAgSO_4$ over the whole superionic temperature range together with an observation of the melt close to the melting temperature. Both the polarized and the depolarized spec-

TABLE I. SO_4 bands in fcc Li_2SO_4, bcc $LiAgSO_4$, and in Li_2SO_4-K_2SO_4 melts.

	fcc Li_2SO_4 present results	bcc $LiAgSO_4$ present results	Li_2SO_4-K_2SO_4 melts reported values[a]
$\nu_1(A_1)$ (cm^{-1})	993	970	990—973
$\nu_2(E)$ (cm^{-1})	455	453	456—451
$\nu_3(T_2)$ (cm^{-1})	1107	1097	~1100, ~1170
$\nu_4(T_2)$ (cm^{-1})	629	614	629—621

[a] Reference 20.

tra were analyzed. In Table II the observed widths (half-widths at half maximum) of the depolarized spectra are given, where the values of the bcc structure correspond to readings 25 K below the upper limit of the superionic temperature range and the values of the melt correspond to observations slightly above the melting temperature. No abrupt changes in the widths were observable between the solid and the molten phase. For fcc Li_2SO_4 only the symmetric mode (ν_1) was investigated in detail to determine reorientational properties of the sulfate ions (see below) since the widths of the internal vibrational mode frequencies have already been reported from Raman studies of the melt,[20] and they are given in Table II for comparisons. No cation effect was found in accordance with the observations of Child *et al.*[20] We assume that the reported value for the ν_1 width is determined from the polarized spectra, and in Table II the present values from the polarized spectra are given in the parantheses. The widths of the depolarized spectra are, within the experimental accuracy, the same as the widths observed in the polarized spectra for the ν_2 and ν_4 modes with a small increased broadening with increasing temperature of less than 2 cm^{-1} over the entire superionic temperature range (see Fig. 2). The ν_3 band could only be properly analyzed in the depolarized spectra due to the fact that overlapping occurs between ν_3 and the much stronger ν_1 mode in the polarized spectra (see Fig. 1). For the ν_1 mode the widths in the polarized spectra were considerably smaller than the depolarized widths and a definite temperature dependence was found. The broadening of the ν_1 mode is discussed in detail below.

Vibrational and orientational broadening of the symmetric mode

In the anisotropic spectrum the symmetric internal sulfate mode ν_1 partly overlaps the ν_3 mode [see Fig. 1(b)]. The ν_3 mode was therefore subtracted from the spectra by assuming a symmetric shape and using its profile from the high-frequency side. The remaining ν_1 mode was then fitted to a Lorentzian, see Fig. 3, where the low-frequency side of the peak has been used to minimize the overlap effects as well as contributions from hot bands. The discrepancy between the observed anisotropic component and the Lorentzian curve at higher frequencies is probably due to the existence of a very broad component attributed to collision-induced processes, which is reported to become significant for liquids beyond about 20 cm^{-1} from the peak value.[17] The band shape of the isotropic ν_1 mode [Fig. 1(a)] was also found to be approximately Lorentzian as can be seen in Fig. 3. In Figs. 4 and 5 the measured half-widths of the isotropic and the anisotropic component of the symmetric mode in fcc Li_2SO_4 and bcc $LiAgSO_4$ are shown for different temperatures. Without any further analysis it is obvious that the anisotropic widths are considerably broader than the isotropic widths which thus confirms a rotational motion of the sulfate ions over the entire temperature range in the systems, i.e., the superionic conducting phase can be characterized as a plastic phase for both Li_2SO_4 and $LiAgSO_4$. Since both the anisotropic and isotropic components can be fitted to Lorentzians and since the ν_1 mode has a low depolarization ratio, Eq. (3) can be used to obtain the reorientational time, and no instrumental corrections are needed.[18] The reorientational relaxation times obtained for the present systems are given in Tables III and IV. The mechanism of reorientation can be classified by comparing the reorientational relaxation time τ with the free-rotor time $\tau_{FR}(41°)$,[18] where τ refers to Eq. (3) and $\tau_{FR}(41°)$ is the time for a free rotor to travel 41°. The latter can be obtained from the relation

$$\tau_{FR}(41^\circ)=(41^\circ/360^\circ)2\pi(I/kT)^{1/2}\,, \tag{4}$$

where I is the moment of inertia for rotation. Litovitz *et al.*[18] in their study of liquids and plastic crystals con-

TABLE II. Bandwidths of SO_4 bands in bcc $LiAgSO_4$, molten $LiAgSO_4$ and in Li_2SO_4-K_2SO_4 melts.

	bcc $LiAgSO_4$ present results	Molten $LiAgSO_4$ present results	Li_2SO_4-K_2SO_4 melts reported values[a]
Γ_{ν_1} (cm^{-1})	26 (p: 19)[b]	28 (p: 20)[b]	~18
Γ_{ν_2} (cm^{-1})	29	28	~28
Γ_{ν_3} (cm^{-1})	85	88	~75
Γ_{ν_4} (cm^{-1})	24	24	~25

[a] See Ref. 20.
[b] p stands for polarized.

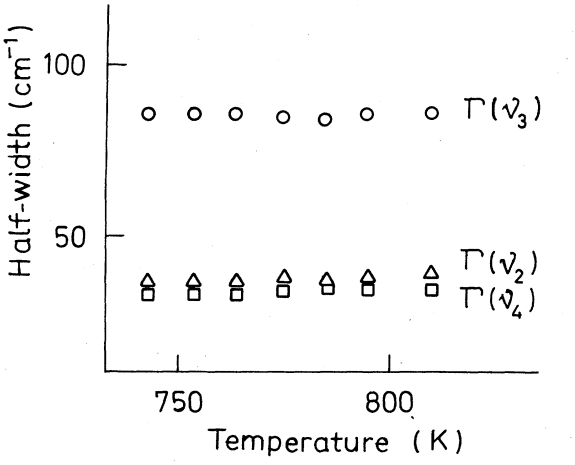

FIG. 2. Bandwidth (half-width at half maximum) vs temperature for the anisotropic components of the internal modes in bcc $LiAgSO_4$.

sidered two possible limiting models for molecular reorientation: free diffusion and jump diffusion. For free-diffusion systems the mechanism for the reorientation in the liquids is collision-limited free diffusion, while for jump-diffusion systems the reorientation is structure limited. For free-diffusion liquids an average value of $\tau/\tau_{\mathrm{FR}}(41^\circ)\cong 4$ was found while for structure-limited liquids considerably larger values were reported. For the present systems the calculated values for $\tau/\tau_{\mathrm{FR}}(41^\circ)$ are given in Tables III and IV. The data are further evidence that the sulfate ions are free to reorient and that fcc Li_2SO_4 and bcc $LiAgSO_4$ can be classified as free-diffussion systems like the plastic crystals.[18] For the present case the reorientation is not only collision limited but also limited by changing electrical forces of the surrounding lattice for different rotation angles. The values of the reorientation time obtained are in close agreement with the reported characteristic time of $\simeq$2 ps found from molecular-dynamics computer simulations of the fcc phase of Li_2SO_4.[13]

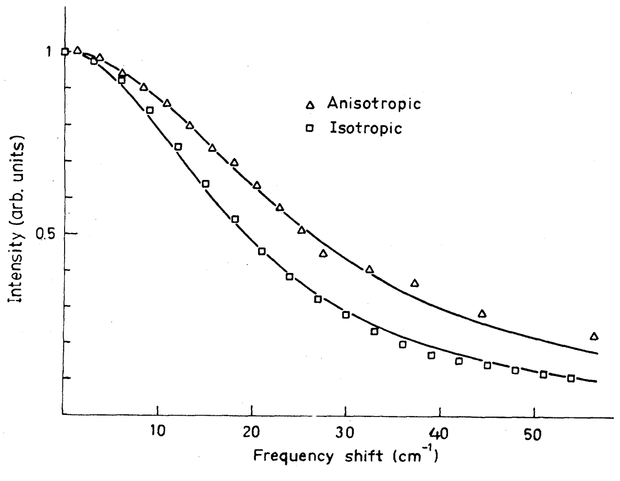

FIG. 3. Lorentzian fits to the anisotropic (△) and isotropic (□) components of the symmetric internal mode ν_1 in bcc LiAg-SO_4 at 822 K. Zero frequency of the graph corresponds to 970 cm^{-1}.

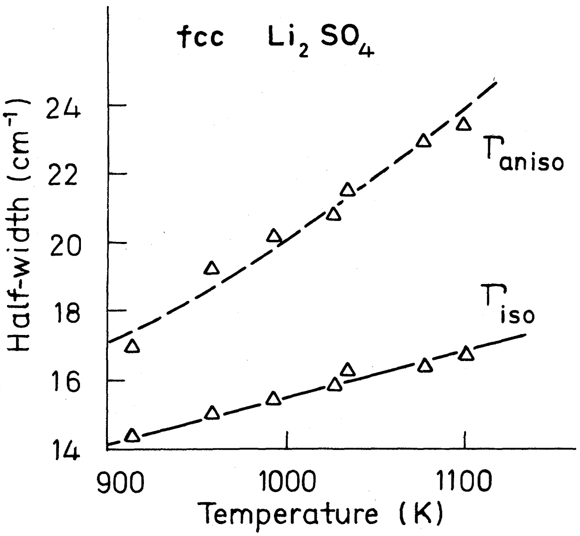

FIG. 4. Bandwidth vs temperature for the anisotropic and isotropic components of the symmetric internal mode ν_1 in fcc Li_2SO_4. Solid line represents a linear fit and dashed line is an exponential fit using Eqs. (2), (5), and (7).

The difference in anisotropic and isotropic bandwidths discussed above shows a marked temperature dependence which is of great interest in connection with the interpretation of the conductivity of these materials. As can be seen in Figs. 4 and 5 the orientational contributions are most affected by temperature and become quite important as the temperature increases. The temperature dependence of the vibrational contributions is, however, significant and may not be neglected for the sulfate systems.

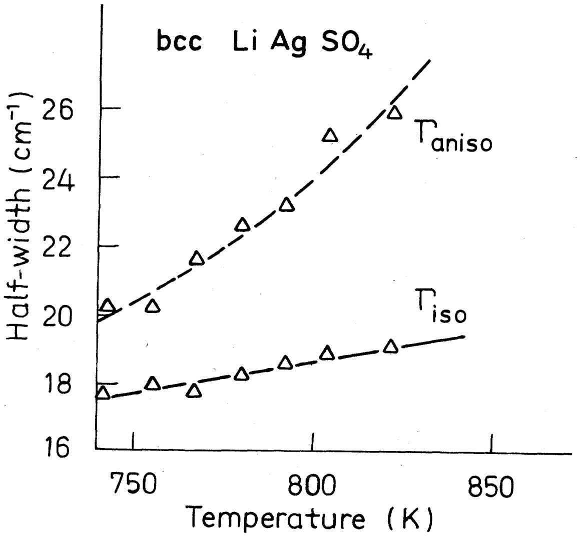

FIG. 5. Bandwidth vs temperature for the anisotropic and isotropic components of the symmetric internal mode ν_1 in bcc $LiAgSO_4$. Solid line represents a linear fit and dashed line is an exponential fit using Eqs. (2), (5), and (7).

TABLE III. Reorientational time for the sulfate ion in fcc Li_2SO_4.

T (K)	Γ_R (cm^{-1})	τ (ps)	$\tau/\tau_{FR}(41°)$
913	2.7	2.0	6.3
958	4.2	1.3	4.2
993	4.8	1.1	3.8
1027	4.9	1.1	3.7
1034	5.3	1.0	3.5
1077	6.5	0.8	2.9
1100	6.7	0.8	2.8

Neglect of temperature-dependent vibrational widths can lead to significant errors in the interpretation of both Raman and infrared data.[18] For fcc Li_2SO_4 the vibrational broadening in the superionic temperature range (848—1133 K) is given by

$$\Gamma_{iso}=\Gamma_v=13.6+0.0129(T-848)\ cm^{-1}\ , \tag{5}$$

which is a linear fit to the measured widths with a correlation of 0.93 and represented by a solid line in Fig. 4. For bcc $LiAgSO_4$ (728—848 K) the corresponding fit was found to be

$$\Gamma_{iso}=\Gamma_v=17.3+0.0195(T-728)\ cm^{-1}\ , \tag{6}$$

with a correlation of 0.91. The orientational linewidths ($\Gamma_R=\Gamma_{aniso}-\Gamma_{iso}$) change by less than one decade in the present study and the temperature can be described by a simple Arrhenius expression, i.e.,

$$\Gamma_R=Ae^{-E/kT}\ , \tag{7}$$

where A is an arbitrary constant and E is the activation energy necessary for reorientations. In Figs. 6 and 7 the present bandwidth data are analyzed in this manner. For fcc Li_2SO_4 the slope corresponds to an activation energy of 0.40 eV with a correlation of 0.94. Frech *et al.*[15] have reported a value of 0.28 eV from an analysis of bandwidth data of the 92-cm^{-1} librational mode of the sulfate ion in the monoclinic phase of Li_2SO_4 in a temperature interval 723—858 K, i.e., just below the phase transition. A difference in the activation energies is to be expected since the reorientations in the monoclinic phase are limited by different potential barriers than in the fcc phase. In their analysis three different models were proposed to explain the large observed increase in the bandwidth with increasing temperature of the 92-cm^{-1} mode: (1) anharmonic vibrations of additional higher order, (2) a constant vibrational part and a temperature-dependent orientational contribution (Rakov's method[25]) and (3) a combination of anharmonic vibrations and a beginning orientational disordering of the sulfate ions. The second model mentioned resulted in the reported activation energy of 0.28 eV. A temperature-independent vibrational component is, however, not in accordance with the present study of the symmetric internal mode. In the interpretation of the third model it is suggested that near the phase transition the temperature orientational broadening might be the dominant mechanism for the 16-cm^{-1} broad librational mode reported by them, which seems rather improbable to us since in the present study the orientational contribution was measured to be only 3 cm^{-1} just above the transition temperature for the observed 17-cm^{-1} broad internal mode. A much broader rotational width would correspond to an unreasonably short rotational time. For in-

TABLE IV. Reorientational time for the sulfate ion in bcc $LiAgSO_4$.

T (K)	Γ_R (cm^{-1})	τ (ps)	$\tau/\tau_{FR}(41°)$
742	2.5	2.2	6.2
755	2.3	2.3	6.7
767	3.9	1.4	4.0
780	4.4	1.2	3.5
792	4.5	1.2	3.5
804	6.3	0.8	2.5
822	6.9	0.8	2.3

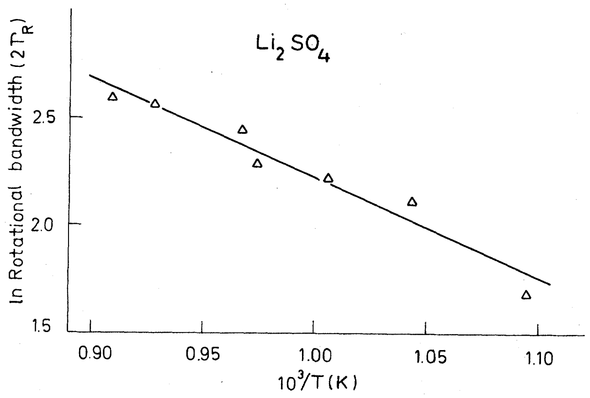

FIG. 6. Arrhenius plot of the reorientational broadening ($2\Gamma_R$) of ν_1 in fcc Li_2SO_4, where Γ_R is in units of cm^{-1}.

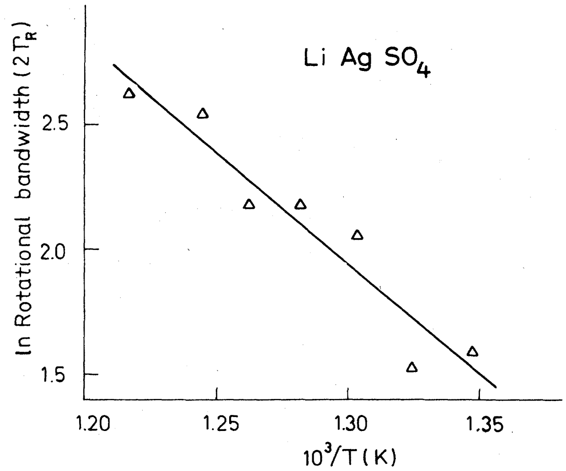

FIG. 7. Arrhenius plot of the reorientational broadening ($2\Gamma_R$) of ν_1 in bcc $LiAgSO_4$, where Γ_R is in units of cm^{-1}.

stance we observed a 7-cm^{-1} rotational width in the high-temperature limit of the superionic phase which corresponds to a low value of the reorientation time compared to the free-rotor time ($\tau/\tau_{\mathrm{FR}} \cong 3$). One would hardly expect rotational times in the monoclinic phase to be shorter than the extreme values of the superionic plastic phase. This is not in conflict with the proposed idea of an onset of disorder of the sulfate ions below the transition temperature, which also has been observed by Frech *et al.* in other sulfate systems.[14] The transition is characterized by a remarkable latent heat, about 3 times that of melting, and one might therefore expect a drastic increase of disorder at the transition.

In order to compare a possible reorientational broadening beginning in the monoclinic phase to the present measured broadening of the superionic phase the following procedure can be used. In the report of the first model of Frech *et al.* mentioned above, the total broadening of the 92-cm^{-1} band was described by the relation

$$\Gamma = a + bT^n , \tag{8}$$

where two different fits (correlations better than 0.98) were reported for two different temperature ranges: $n = 1.53$ for $298 < T < 723$ K and $n = 4.54$ for $723 < T < 858$ K. At about 723 K the orientational contributions were supposed to begin to dominate all other processes. It therefore seems reasonable to assume that $n = 1.53$ will give the relation corresponding to only vibrational broadening, Γ_v, while $n = 4.54$ corresponds to both vibrational and rotational broadening, Γ_{v+R}. Then, by extrapolating Γ_v to the temperature range 723—858 K and subtracting Γ_v from Γ_{v+R} we obtain Γ_R. The results of such calculations—together with the present observed broadening—are shown in Fig. 8. In the calculations we assume that the Γ reported by Frech *et al.* is the full width at half maximum judged from their given spectra. The figure shows that the calculated excess broadening observed in the monoclinic phase joins, within the experimental accuracy, continuously to the present observed broadening of the fcc phase. In view of the above we, therefore, in accordance with Frech *et al.*, support the last-mentioned model, i.e., the broadening can be described as a combination of anharmonic vibrations and a beginning orientational disordering of the sulfate ions, with the addition that the dominant broadening in the monoclinic phase is due to anharmonic vibrations.

For bcc $\mathrm{LiAgSO_4}$ the rotational bandwidth data represented in Fig. 7 yield an activation energy of 0.72 eV with a correlation of 0.93. A paddle-wheel migration model has been proposed for the superionic sulfate systems which suggests that the high mobility of the cations is not only a thermally activated diffusion but that rotations of the sulfate ions play a dominant role in enhancing the diffusion. If there is a coupling between the reorientations of the sulfate ions and the diffusing cations, one would expect the temperature dependence for reorientations and that for cation diffusion to be closely related, i.e., the activation energies would be similar. With this in mind, the remarkably high but different activation energies for cation diffusion in fcc $\mathrm{Li_2SO_4}$ and bcc $\mathrm{LiAgSO_4}$ (0.34 and 0.52 eV, respectively)[7] can be explained by the high but different activation energies found in the present study for sulfate-ion reorientations (0.40 and 0.72 eV, respectively).

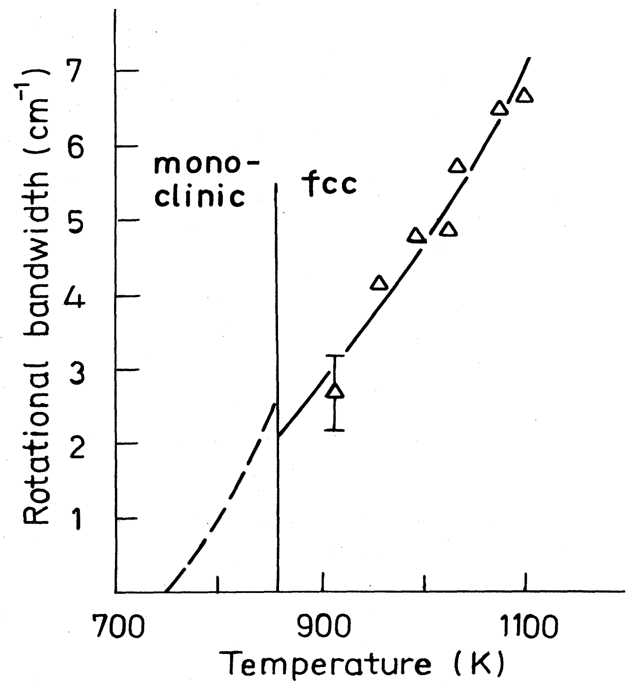

FIG. 8. Reorientational broadening vs temperature in the monoclinic phase (Ref. 15) and the fcc phase of $\mathrm{Li_2SO_4}$.

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