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## The role of orientational disorder in the pressure-induced amorphization of lithium potassium sulphate

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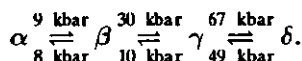
**Abstract.** Raman scattering investigations of lithium potassium sulphate at high pressures have revealed that the sulphate tetrahedra are orientationally disordered in the high-pressure phases. In order to understand the nature of the disorder, the temperature dependence of the relative intensities of Raman lines associated with the sulphate internal modes are investigated. The results suggest a frozen-in static disorder rather than dynamic equilibrium between the occupancies of different orientations. The behaviour of the Raman linewidths up to a pressure of 250 kbar indicates successively broader distributions of the sulphate orientations. A mechanism of amorphization involving disorder in cation sublattices induced by the orientational disorder of sulphate is proposed.

### 1. Introduction

There are a number of ways of obtaining a material in the amorphous state, such as rapid cooling of the melt, vapour deposition on a cold substrate and ion implantation. Mishima *et al* [1] found, for the first time, that crystalline ice turned amorphous at 77 K when pressurized to 10 kbar. This generated considerable interest in the new possibility of obtaining an amorphous state at high pressures and in understanding the underlying mechanism. Subsequently a variety of systems with widely different bonding natures have been found to exhibit the phenomenon of pressure-induced amorphization (PIA). Crystals with covalent bonding such as  $\text{SiO}_2$  [2] and  $\text{AlPO}_4$  [3], molecular crystals such as  $\text{C}_2(\text{CN})_4$  [4],  $\text{SnI}_4$  [5], and resorcinol [6], ionic crystals such as  $\text{LiKSO}_4$  [7, 8],  $\text{Ca}(\text{OH})_2$  [9] and  $\text{Fe}_2\text{SiO}_4$  [10], and a number of other complex systems such as  $\text{CaAlSi}_2\text{O}_8$  and  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  [11] with bondings intermediate to those mentioned above constitute the ever-growing list of systems which exhibit PIA. Disappearance of the diffraction peaks in powder x-ray diffraction [5, 7] and associated broadening or disappearance of Raman lines [4, 5] or infrared absorption bands [9] have been used to identify the amorphization transition pressure. In many cases, PIA is found to be reversible with a large hysteresis. Although this phenomenon is not very well understood, it is believed that the system becomes trapped in a metastable amorphous state while transforming from a low-pressure crystalline phase  $C_1$  to a high-pressure crystalline phase  $C_2$  if the kinetics of transition are slow [1, 2]. Although a number of systems which have shown PIA have tetrahedral units (e.g.  $\text{SnI}_4$  and  $\text{LiKSO}_4$ ) or have corner-linked tetrahedra (e.g.  $\text{H}_2\text{O}$  and  $\text{SiO}_2$ ), the mechanisms of this transition are expected to be different in different systems because of their different bonding natures. For example, in quartz, the breaking of Si-O bonds due to

bending of Si–O–Si angles beyond their energetic limit has been proposed to be the cause of PIA [12]. Recent molecular dynamics simulations suggest an accompanying mechanical instability [13]. Dimerization is found to be associated with PIA in  $\text{SnI}_4$  [5]. Recent Raman scattering investigations suggest that the amorphization in  $\text{LiKSO}_4$  may be strongly influenced by the orientational disorder of sulphate ions [14].

There have been a number of investigations of temperature-induced [15–22] and pressure-induced [7, 8, 14, 22, 23] phase transitions in  $\text{LiKSO}_4$  using a variety of techniques such as Raman spectroscopy [8, 14–17, 23], x-ray and neutron diffraction [7, 18, 19, 21], EPR [20] and dielectric loss [22]. The phase at ambient pressure and temperature belongs to  $C_6^2$  and has two formula units per unit cell. Raman scattering measurements up to 100 kbar have revealed transitions to phases  $\beta$ ,  $\gamma$  and  $\delta$  occurring at 9 kbar, 30 kbar and 67 kbar, respectively [23]:



The hysteresis seen in the transition pressures suggests that the transitions could be first order in nature. Although this system has been investigated subsequently up to 150 kbar using energy-dispersive x-ray diffraction [7], the structures of the high-pressure phases  $\beta$ ,  $\gamma$  and  $\delta$  are still unknown. From the gradual decrease in the Bragg diffraction intensities in the  $\delta$ -phase and their complete disappearance at 130 kbar, it is speculated [7] that the system becomes amorphous. Raman results suggest that the high-pressure phases are orientationally disordered, as is evident from the splitting of the sulphate non-degenerate  $\nu_1$  internal mode [8, 23].

In the present work, we report an investigation of the behaviour of the sulphate  $\nu_1$  internal mode as a function of pressure at ambient temperature and at elevated temperatures up to 374 K. The temperature dependence of the Raman modes is analysed to obtain further information on the nature of the orientational disorder. The dependence of the Raman linewidths on pressure is discussed in the context of the smearing of orientational potential wells. A mechanism of gradual amorphization driven by orientational disorder is proposed.

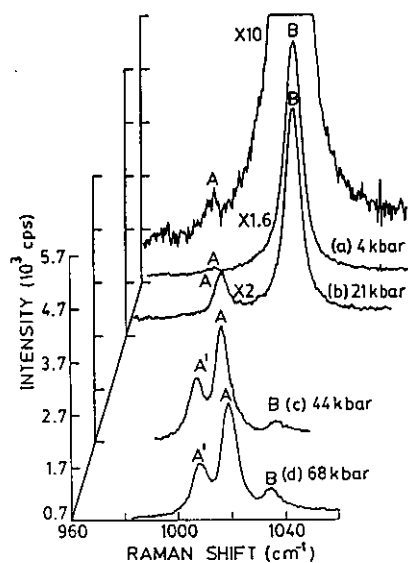
## 2. Experimental details

Raman spectra of unoriented single-crystal pieces of  $\text{LiKSO}_4$  at a high pressure were recorded in the back-scattering geometry in a gasketed diamond anvil cell (DAC). Other details of DAC loading have been described elsewhere [8]. The single crystal used in this work was kindly supplied by Dr M L Bansal, now deceased, of Bhabha Atomic Research Centre. A methanol–ethanol mixture (methanol:ethanol = 4:1) was used as the pressure-transmitting medium. In order to avoid dissolution of the sample in the pressure-transmitting medium, an extra dry methanol–ethanol mixture with a total water content of less than 0.07% was used [8]. The pressure in the DAC was estimated by the ruby fluorescence technique. The ruby chip used in the present investigations was amorphous ruby. The Raman spectra were excited using the 488 nm line of an argon ion laser. The scattered light was analysed using a Spex double monochromator and detected using a cooled PMT and photon-counting unit. The scanning of the spectra and data acquisition were done using a home-built microprocessor-based acquisition–control system. Data were transferred from the microprocessor system to a PC after each scan was over, for further processing.

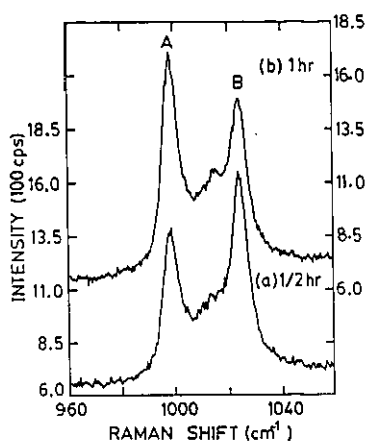
### 3. Results and discussion

The Raman spectra of  $\text{LiKSO}_4$  in various regions of the sulphate internal modes have been reported earlier [8, 23]. The frequencies of all the internal modes increase with increasing pressure. The internal modes of sulphate ions are found to split across phase transitions. Splitting of the degenerate  $\nu_3$  and  $\nu_4$  modes across the  $\beta \rightarrow \gamma$  and  $\gamma \rightarrow \delta$  transitions can be assigned to the lowering of symmetry. The non-degenerate  $\nu_1$  mode of symmetry A also split into two components across the  $\beta \rightarrow \gamma$  transition and into three components across the  $\gamma \rightarrow \delta$  transition. As the intensities of the  $\nu_2$ ,  $\nu_3$  and  $\nu_4$  modes are much weaker than that of the  $\nu_1$  (symmetric stretching), the pressure dependences of the Raman modes, lineshapes and intensities of the  $\nu_1$  modes are investigated in maximum detail. Figure 1 shows the Raman spectra of  $\text{LiKSO}_4$  at different pressures in the  $\nu_1$  region of the sulphate internal mode. Splitting of the non-degenerate  $\nu_1$  mode can arise owing either to correlation effects or to non-equivalent orientations of sulphate ions. Correlation splitting of a non-degenerate mode can arise because of cell doubling–tripling across the phase transition, e.g.  $\text{LiNaSO}_4$  has six formula units per unit cell leading to three Raman lines in the  $\nu_1$  region [24] in contrast with  $\text{LiKSO}_4$  which has only two formula units per unit cell. However, the observed variation in relative intensities of different components as a function of pressure within each phase [8] strongly supports orientational disorder rather than a correlation splitting of the  $\nu_1$  mode. Guided by the variation in relative intensities of different components within the  $\beta$ -phase, Melo *et al* [23] have assigned it to an incommensurate phase and the subsequent transition to a lock-in phase. However, a similar variation in the relative intensities of different components has been seen in all the phases [8]. Hence it is appropriate to assign this variation to the orientational disorder rather than to an incommensurate and lock-in phase type of transition. The intensity  $I$  of various split components can hence be considered to be proportional to the occupancy  $p$  of different orientations.

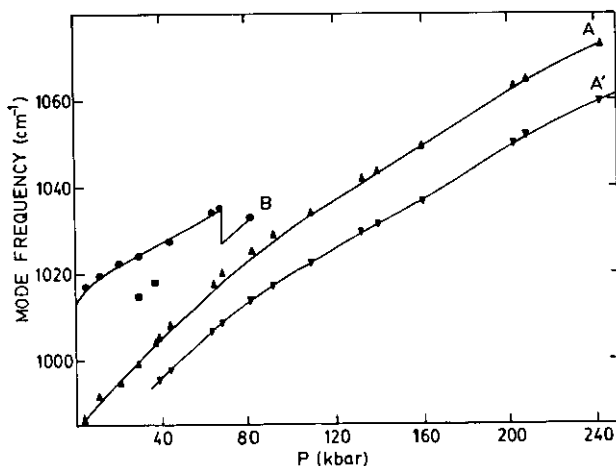
One can see from figure 1 that, in the  $\alpha$ -phase at 4 kbar, component B (of orientation B) at  $1014 \text{ cm}^{-1}$  has the maximum intensity; however, there is a small intensity at  $986 \text{ cm}^{-1}$  corresponding to component A (of orientation A). In other crystal pieces, component A was found to be as much as 4% of the main peak. This implies that even in the  $\alpha$ -phase ( $C_6^2$ ) at ambient pressure there is a fraction of sulphate ions which have orientations different from those of the rest of the sulphate ions. Note that in the  $\beta$ -phase the intensity of component A relative to that of component B increases, implying that an increasing number of sulphate ions change their orientation from orientation B to orientation A. Across the  $\beta \rightarrow \gamma$  transition, there is a gradual reversal of the relative intensities of components A and B. Eventually in the  $\gamma$ -phase, component A becomes strongest. From the time evolution of the relative intensities of components A and B close to transition pressure (shown in figure 2) it appears that the sulphate ions slowly reorient themselves in orientation A from orientation B. Another peak also appears, say peak A', at a frequency lower than that of component A. Figure 3 shows the dependence of mode frequencies on pressure up to 250 kbar. Across the  $\gamma \rightarrow \delta$  transition, component B exhibits a decrease in frequency consistent with the previously reported results [8]. This decrease in frequency can also be viewed as if sulphate ions in orientation B reorient themselves into another orientation whose frequency lies in between orientation A and orientation B. Such a mode (orientation) has indeed been detected at a few pressures in the  $\beta$ -phase, as seen in figure 2.



**Figure 1.** Raman spectrum of  $\text{LiKSO}_4$  at different pressures in the  $\nu_1$  region of the sulphate internal mode in the  $\alpha$ -phase (curve (a)), the  $\beta$ -phase (curve (b)), the  $\gamma$ -phase (curve (c)) and the  $\delta$ -phase (curve (d)). Curves (a) and (b) are expanded by factors of 1.6 and 2, respectively. Curve (a) is also shown after an expansion of ten times as the uppermost curve. Note the small peak in position A in the  $\alpha$ -phase which is not permitted by factor group analysis.

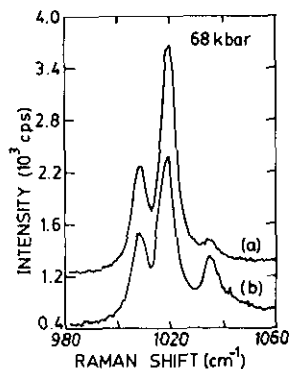


**Figure 2.** Time evolution of the relative intensities of the components A and B at the  $\beta \rightarrow \gamma$  phase transition pressure, 29 kbar.

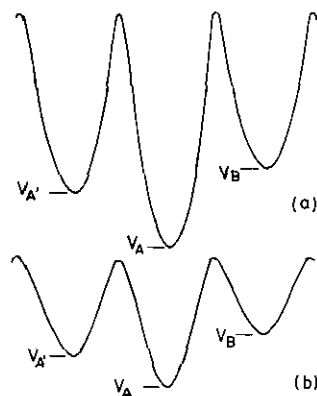


**Figure 3.** Pressure dependence of the  $\nu_1$  internal modes as a function of pressure. The labels A', A and B correspond to the frequencies of  $\text{SO}_4$  in the orientations A', A and B. The full squares represent the position of a broad peak between components A and B observed only at some pressures as seen in figure 2. The lines drawn through the points are guides to the eye.

In the present investigations, some of the single-crystal pieces exhibited, instead of component  $A'$ , a component  $C$  at a frequency higher than that of component  $B$  in the  $\gamma$ - and  $\delta$ -phases similar to that reported earlier. The frequency of the component  $A'$  and its pressure dependence matches those of the 'new mode' observed between 50 and 30 kbar during the pressure-reducing cycle in the previous investigation [8]. Thus, some of the single-crystal pieces exhibited components  $A'$ ,  $A$  and  $B$  while others exhibited components  $A$ ,  $B$  and  $C$  in the  $\gamma$ - and  $\delta$ -phases, component  $A$  being the strongest in the former and component  $B$  in the latter. This difference in behaviour can be understood if one visualizes the sulphate ions as disordered in more than three distinct orientations in the high-pressure phases and the relative occupancies of different orientations are different in different runs perhaps depending on parameters such as the rate of change in pressure, the degree of quasi-hydrostaticity and the extent of twinning in the crystal [25]. Different regions of the sample, when selectively probed by a focused laser beam of diameter less than  $25 \mu\text{m}$ , exhibited different relative occupancies of different orientations as seen from figure 4. This suggests that the orientational disorder is also inhomogeneous across the sample of size  $100 \mu\text{m}$ . From the investigations carried out so far on  $LiKSO_4$ , there appears to be a certain degree of diversity between different pressure runs as far as the relative populations of different orientations are concerned; however, an increase in pressure leading to the reorientation of sulphate ions to newer orientations, which have successively lower frequencies, emerges as a clear trend. This suggests the softening of force constants and consequently an instability.



**Figure 4.** Raman spectra of different regions of the sample in the  $\nu_1$  region of  $SO_4$  in the  $\delta$ -phase: curve (a), close to the edge; curve (b), at the centre of the sample. Curve (b) is vertically displaced for clarity.



**Figure 5.** Schematic diagram of the potential wells for the sulphate ions in the orientation space in high-pressure phases: (a) for  $P < 100$  kbar, potential wells are well defined; (b) close to amorphization, the wells become smeared.

The potential wells corresponding to different orientations in the orientational space can be schematically shown as in figure 5. A variation in the relative occupancies of different orientations within each phase can arise if the potential minima corresponding to different orientations are affected by the change in pressure. If the sulphate ions occupying different potential wells are in thermal equilibrium with each other (dynamic disorder) [26], relative vertical shifts of the potential minima  $V_{A'}$ ,  $V_A$  and  $V_B$  due to a change in pressure can change the equilibrium relative

occupancy of each orientation. In thermal equilibrium, the probability  $p_A$  that the sulphate ion occupies the potential well  $V_A$  (corresponding to orientation A) is proportional to  $\exp(-V_A/k_B T)$ , where  $k_B$  is the Boltzmann constant and  $T$  is the temperature. Likewise the occupancies of other potential wells can also be expressed in a similar manner. If the system exhibits dynamic disorder, one would also expect  $V_A < V_{A'} < V_B$ , guided by the relative intensities of the components at ambient temperature, as schematically shown in figure 5. A change in temperature would result in a change in relative intensities. Using the principle of detailed balance, it is straightforward to show [26] that the relative occupancies  $p_{A'}/p_A$  can be given as

$$\ln(p_{A'}/p_A) = -(V_{A'} - V_A)/k_B T.$$

One can obtain the difference between the potential minima from the negative slope of the Arrhenius plot of  $\ln(I_{A'}/I_A)$  versus  $1/T$ .

In order to determine the nature of disorder in the  $\delta$ -phase, i.e. whether it is dynamic or static, the temperature dependence of relative intensities was investigated after reaching 92 kbar in the temperature range 298–374 K. The pressure remained constant within  $\pm 1.5$  kbar during the heating cycle. In order to find out the changes in the pressure in the DAC due to heating, the temperature dependence of ruby fluorescence outside the DAC was investigated separately and the temperature coefficient of the ruby shift was determined. The value of  $-0.15 \text{ cm}^{-1} \text{ K}^{-1}$  obtained in the present work agrees well with that reported recently [27]. The temperature coefficient obtained at ambient pressure was assured to be the same as that at high pressures. Such an assumption has been found to be reasonable at low temperatures [28]. Figure 6 shows the relative intensity  $I_{A'}/I_A$  as a function of temperature. Note that the data points represent a weak positive slope rather than a negative slope, i.e. the intensity of component A' decreases as the temperature increases whereas in dynamic equilibrium the intensity of component A' is expected to increase as a function of  $T$ . Thus, this opposite behaviour means that the population of sulphate ions in a potential well is not in dynamic equilibrium with those of other wells. This suggests that the disorder is a static frozen-in disorder as the barrier to reorient may be too large to be overcome by thermal energy. At the moment it is not possible to make further comment on the exact nature of the different orientations in the high-pressure phases because of the lack of detailed x-ray diffraction data in these phases.

Having discussed the nature of the orientational disorder, one can now address the role that orientational disorder may play in amorphization. The linewidths of Raman and infrared bands associated with atomic vibrations in the amorphous state are expected to be much larger than those of the corresponding phonons in their crystalline counterparts. Across the amorphization transition, the internal modes of molecular ions are expected to broaden as the orientations, bond lengths and bond angles now have distributions instead of being unique, whereas the external modes are expected to disappear as the amorphous state has no periodicity. The disappearance of lattice modes has been recently used to identify the amorphization in  $\text{LiCsSO}_4$  [29]. Amorphization has also been found to be associated with the disappearance of Raman lines in  $\text{C}_2(\text{CN})_4$  [4] and  $\text{SnI}_4$  [5], the broadening of the infrared absorption band of OH in  $\text{Ca}(\text{OH})_2$  [9] and the broadening of the Raman line associated with the OH internal mode in ice by a factor of about 5 [30]. Preliminary investigations in  $\text{LiKSO}_4$  have also indicated broadening of all the components of the sulphate internal modes

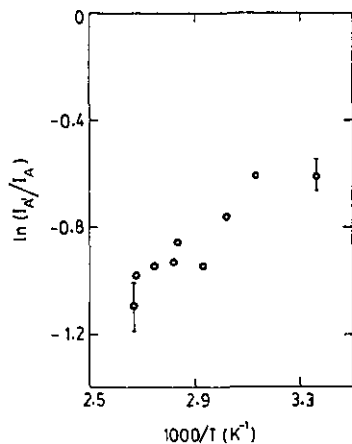


Figure 6. Temperature dependence of the intensity ratio of the components  $A'$  and  $A$  in the  $\delta$ -phase.

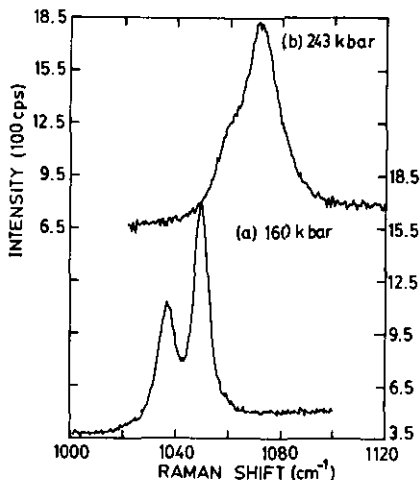


Figure 7. Raman spectra of  $\text{LiKSO}_4$  in the  $\nu_1$  region of  $\text{SO}_4$  at 160 kbar (curve (a)) and 243 kbar (curve (b)). Note the excessive broadening of lines at the high pressure.

above 100 kbar [8]. Figure 7 shows the Raman spectra, demonstrating the broadening taking place above 150 kbar. Note that the background also increases significantly at high pressures. This is probably due to the scattering from the continuum density of states arising from the amorphous structure. However, some contribution from the glassy methanol-ethanol mixture present in the scattering volume probed by the laser beam is also not ruled out. It may be mentioned that in the previous investigation the Raman intensity was found to decrease above 100 kbar and eventually to submerge in the background which was rather high around 150 kbar [8]. There were also laser plasma lines interfering with the position of Raman lines, making unambiguous identification of the Raman lines difficult. In fact, one does not expect the sulphate internal modes to disappear because  $\text{SO}_4$  tetrahedra, although distorted, would still continue to exist in the amorphous state. In the present work, more careful investigations were carried out. A tunable grating filter was used to filter laser plasma lines. The background intensity in the present investigation was also less by a large factor. Although the intensity of the  $\nu_1$  mode decreased with increasing pressure, it was measurable even at the highest pressure reached in the present set of investigations.

In order to investigate the effect of pressure on the Raman linewidths in  $\text{LiKSO}_4$ , true full widths at half-maximum (FWHMs) of the sulphate  $\nu_1$  internal mode are obtained using a procedure [31] which corrects the measured linewidths for the spectrometer resolution ( $4.1 \text{ cm}^{-1}$ ). Figure 8 shows the behaviour of the true FWHM of the strongest component ( $A$  or  $B$  as the case may be) of the  $\nu_1$  internal mode of sulphate ions in  $\text{LiKSO}_4$  as a function of pressure. Note that the linewidth is typically  $5 \text{ cm}^{-1}$  in the  $\alpha$ - and  $\beta$ -phases and it reduces to  $2 \text{ cm}^{-1}$  in the  $\gamma$ - and  $\delta$ -phases. The large linewidth in the  $\alpha$ -phase may be due to the dynamic orientational disorder of the sulphate ions [32] in the ambient pressure phase  $C_6^6$ , where the oxygen  $\text{O}(1)$  atom occupies three different positions around the threefold axis. However, the average position is on the threefold axis, preserving the hexagonal symmetry. The large



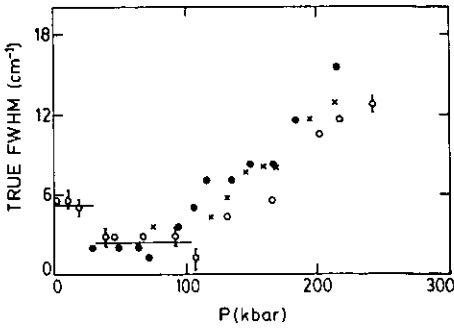


Figure 8. Dependence of the FWHM of the strongest component (A or B as the case may be) on pressure. Different symbols refer to different runs. The lines drawn through the points are guides to the eye.

width of the  $\nu_1$  mode in the  $\beta$ -phase suggests that the dynamic disorder continues to exist even in this phase. The reduction in linewidth across the  $\beta \rightarrow \gamma$  transition is probably associated with the absence of dynamic disorder in the new structure. It may be mentioned that the distinct orientations observed in the high-pressure phases, corresponding to the widely different mode frequencies, are not the same as those corresponding to the  $C_6^I$  structure which exhibits a single broad  $\nu_1$  line.

Note that in the  $\delta$ -phase the width starts to increase rapidly beyond 110 kbar. The increase in the width may also have contributions from the quasi-hydrostatic and inhomogeneous pressure distribution across the sample resulting from freezing of the pressure-transmitting medium. The inhomogeneous pressure distribution leads to broadening of the ruby R lines. As the ruby used in the present investigation is amorphous, the contribution to the broadening and change in the separation of the  $R_1$  and  $R_2$  bands arising because of the anisotropic response of crystalline ruby under uniaxial (non-hydrostatic) stress [33] are avoided. In order to obtain some magnitude of the pressure inhomogeneity within the hole in the gasket, more than one ruby chip was loaded together with the sample. The pressure inhomogeneity was estimated from the position of the  $R_1$  line from different ruby chips and also from the positions of different components of the sulphate  $\nu_1$  mode from the two ends of the sample, as the pressure dependence of the Raman line is known ( $0.3 \text{ cm}^{-1} \text{ kbar}^{-1}$ ). The estimated pressure inhomogeneity was found to be less than 3 kbar across the diameter of the probe beam (about  $25 \mu\text{m}$ ). Such a pressure inhomogeneity cannot account for the increase in the linewidth from  $2 \text{ cm}^{-1}$  at 100 kbar to  $12 \text{ cm}^{-1}$  at 243 kbar. The broadening of an internal mode can arise because of smearing of orientational potential wells which is expected to take place as one approaches amorphization. This is schematically shown in figure 5. It is likely that the amorphization may be a gradual transition, making the identification of the transition pressure difficult from these results as no guideline can be set in terms of the increase in widths.

In order to study the effect of non-hydrostaticity and inhomogeneity of pressure on amorphization, in one of the pressure runs a small amount of silicone oil was added to the methanol-ethanol mixture, which led to freezing of the medium at about 25 kbar. Under these conditions, the three components in the  $\delta$ -phase were very broad and the weaker components appeared as unresolved shoulders of the peak. A further increase in pressure up to 120 kbar led to an increase in the linewidth from 9 to  $18 \text{ cm}^{-1}$ . If one considers the increase in the linewidth as a possible signature of amorphization, it appears from the present results that a non-hydrostatic or inhomogeneous pressure can significantly change the amorphization pressure. A similar reduction in the amorphization pressure under a non-hydrostatic stress has been seen in the case of quartz also [2].

Guided by the similarities of the tridamite structure of covalently bonded crystals such as  $\text{SiO}_2$ , which have six-membered rings of  $\text{SiO}_4$  tetrahedra, and  $\text{LiKSO}_4$ , Sankaran *et al* [7] have conjectured that amorphization occurs owing to extreme distortion of the six-membered ring structure formed by the  $\text{SO}_4\text{-LiO}_4$  tetrahedra. It may be pointed out that, although Li has fourfold coordination in the hexagonal phase, it does not form a bound tetrahedral unit with oxygen as sulphur does. This is also evident from the much larger Li-O distance of 1.92 Å compared with the S-O bond length of 1.46 Å. Further, no vibrational modes observed in the Raman spectra can be assigned to the internal mode of the  $\text{LiO}_4$  unit whereas modes assigned to the translation of Li have been identified [16]. Hence it may be inappropriate to invoke a six-membered tetrahedral ring structure to understand the mechanism of amorphization in ionic crystals such as  $\text{LiKSO}_4$  by analogy to that in covalent crystals such as  $\text{SiO}_2$ . Recently, in a molecular dynamics study, Chaplot and Sikka [34] have found an increase in the coordination number of Li from 4 to 6 across amorphization above 100 kbar. Such an increase is similar to that obtained in quartz [13]. However, simulations were carried out on the ambient pressure structure  $\text{C}_6^6$  and neither the orientational disorder nor the structure of the high-pressure phase was taken into account.

It may be pointed out that the energy-dispersive x-ray diffraction results [7] show that the diffraction peak intensities decrease significantly when the pressure is increased from 65 to 84 kbar and completely disappear at around 130 kbar. This suggests that the positional disorder in various sublattices occurs before the actual amorphization takes place. We propose a mechanism for this disorder driven by the orientational disorder of the sulphate ions in the  $\delta$ -phase. As the pressure is increased in the  $\delta$ -phase, in order to achieve more efficient packing, sulphate ions in different orientations begin to tilt and distort in different manners, which leads to a distribution of orientations around each discrete orientation, resulting in the smearing of the potential wells as is evident from the broadening of Raman lines. This causes the cations to be displaced from their ideal sublattice positions which in turn leads to further smearing of potential wells. The disorder in cation sublattices would also lead to the displacement of the sulphur atoms, which represent the anion centres, from the ideal anion sublattice to new equilibrium positions. Thus the orientational disorder becomes coupled to the positional disorder and vice versa. The growth of the coupled orientational and positional disorder continues and eventually leads to amorphization.

It would be of interest to know which other systems in the family of compounds  $\text{ABSO}_4$  exhibit PIA.  $\text{LiCsSO}_4$  has also been reported to show PIA [29]. In this system also, high-pressure phases exhibit splitting of the  $\nu_1$  internal mode of sulphate ions. Both of these compounds have widely different sizes of cations A and B. Such systems are probably better candidates for orientational disorder and hence amorphization.

#### 4. Conclusions

To conclude, the high-pressure phases of  $\text{LiKSO}_4$  are found to have frozen-in (static) orientational disorder of the sulphate ions. The relative occupancies of different orientations depend on pressure. Under the application of pressure the sulphate ions are found to reorient to newer orientations which have successively lower frequencies. This suggests softening of the force constants and consequent instability. The increase in the linewidth of the sulphate internal mode suggests smearing of the orientational

potential wells. Orientational disorder is believed to be the driving mechanism for the PIA in this system.

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