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Pressure-induced phase transitions in $KLiSO_4$

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The room-temperature Raman spectrum of $KLiSO_4$ was studied as a function of pressure up to ~ 100 kbar. We discuss the evolution of the portion of the spectrum ($\omega > 600$ cm^{-1}) containing the vibrational modes of the $SO_4{}^{2-}$ ions as a function of steadily increasing or steadily decreasing pressure. We identify three distinct phase transitions which show a high degree of hysteresis. In one of the phases (β phase) the Raman spectrum undergoes qualitative changes in a continuous manner as pressure increases. This behavior, which is not shown by any of the other observed phases, may be an indication that the β phase is incommensurate.

Potassium lithium sulfate ($KLiSO_4$) exhibits a rich variety of phase transitions as the temperature is varied (at ambient pressure) in the range 710 K $< T <$ 10 K. In a recent lattice-dynamical calculation, Choudhury, Chaplot, and Rao[1] give a summary of all the experimental studies performed on the different phases of this material. Of particular importance are those transitions occurring below room temperature, where some authors suggest there exists an incommensurate phase associated with rotations of the $SO_4{}^{2-}$ ions.[2] This possibility is reinforced by a calculation of the phonon dispersion relations,[3] which predict, for the room-temperatrue $P6_3$ (C_6^6) phase, the existence of a soft mode involving $SO_4{}^{2-}$ librations at $\mathbf{k} \simeq 0.4\mathbf{c}^*$, where $\mathbf{c}^*$ is the axis in reciprocal space corresponding to the hexagonal c axis. Raman scattering studies have been particularly useful in obtaining information about these phase transitions.[4-7] In particular, the work of Bansal, and coworkers[5,6] shows that the reorientation of the $SO_4{}^{2-}$ ions is responsible for a transition into a $P31_c$ (C_{3v}^4) phase which occurs at 201 K when cooling, and at ~ 242 K when heating. These authors do not rule out the existence of an incommensurate phase, existing in some intermediate temperature range between the C_6^6 (300 K) and C_{3v}^4 (201 K) phase. However, they point to sluggishness of the transition at 201 K, which would make it possible for both phases (C_6^6 and C_{3v}^4) to coexist in wide temperature regions when the cooling (or heating) is performed too rapidly.[6] They quote 35 min as a typical time for completing the phase transition at fixed temperature for the small volumes sampled by the laser beam in a typical Raman experiment. On the other hand, the Raman work of Mendes Filho *et al.*[7] seems to favor the existence of an incommensurate phase, also associated with rotations of $SO_4{}^{2-}$ ions, between the prototype C_6^6 phase (300 K) and the lock-in C_{3v}^4 (201 K) phase.

In spite of the abundance of information regarding the many phases of $KLiSO_4$ at ambient pressure, not much information is available about the behavior of the material under pressure. Fujimoto, Yasuda, and Hibino[8] measured the dielectric constant of the material under hydrostatic pressure covering the range 1 bar $< P <$ 6 kbar and 320 K $> T >$ 150 K. In these pressure and temperature intervals, they identify three distinct phases, which also occur when cooling up to 150 K at ambient pressure. For these transitions they find positive values of dT_c/dP (T_c being the transition temperature and P the pressure), which means that increasing the pressure has effect similar to decreasing the temperature (at constant P) on the stability of a given phase. In particular, they obtain the lowest-temperature phase (probably C_{3v}^4)[9] at room temperature for $P \simeq 5$ kbar. Their study is limited to very low pressures ($P < 6$ kbar) and is not effective in terms of determining the types of atomic motions involved in the transitions. To gain further insight into these matters it would be interesting to study the lattice vibrations of the material over a wider pressure range. In the present work we report a study of the room-temperature Raman spectrum of $KLiSO_4$ as a function of hydrostatic pressure in the interval 1 kbar $< P <$ 100 kbar. We observe three distinct phase transitions, all of which have a large hysteresis. In one of these phases, the β phase, the Raman spectrum undergoes qualitative changes in a continuous manner as the pressure is varied throughout its region of stability (9 kbar $< P <$ 30 kbar). This behavior, and the positive dT_c/dP value,[8] suggests the possibility of associating the β phase with the incommensurate phase provoked by orientational changes in the $SO_4{}^{2-}$ ions, proposed by other authors[2,3] for ambient pressure and temperatures somewhere in the 201 K $< T <$ 300 K range.

Single crystals of $KLiSO_4$ with good optical quality were grown at room temperature by slow evaporation from aqueous solutions with equal stochiometric concentrations of $Li_2SO_4 \cdot H_2O$ and K_2SO_4. The quality of the samples was checked with a polarizing microscope for light propagating along the c axis. These samples were cut into slices and polished into thin (~ 50 μm) platelets which contained the hexagonal axis. Light scattering measurements were performed in the backscattering configuration, using the 5145-Å line of an argon-ion laser as exciting radiation. Because of the rotatory power of the sapphire window in the pressure cell (which keeps changing as it becomes stressed), incident light was not polarized either along or perpendicular to the c axis. Scattered light was also unpolarized in our experiments. The sample and a ruby chip, for pressure calibration, were placed inside a 300-μm-diameter hole in a Cu-Be gasket. The pressure cell is of the opposed anvil type, with one of the anvils made of sapphire.[10] A 4:1 mixture of methanol and ethanol was used as the pressure-transmitting fluid. The optical arrangement and means of determining the pressure within the gasket are described elsewhere.[10,11] All our measurements were performed at room temperature.

At ambient pressure and temperature the space group of the $KLiSO_4$ structure is C_6^6, with two formula units per unit cell. The Raman and infrared spectra of this phase (which we shall refer to as the α phase from now on) was studied in detail by Hiraishi, Taniguchi, and Takahashi.[12] They classify the modes into vibrations (of which there are four types designated by[12,13] ν_1, ν_2, ν_3, and ν_4) and librations of the $SO_4{}^{2-}$ ion and rigid translation of this and the Li^+ and K^+ ions. Their classification is in good agreement with calculations of the phonon branches for this material.[3] We shall adopt this assignment, denoting each line in the Raman spectrum of the α phase by its symmetry type followed by its room-temperature frequency (in parenthesis) as given in Ref. 12. In our experiments, incident and scattered light propagate perpendicular to the c axis and all polarization combinations in a plane containing that axis are possible. Consequently, modes of A, E_1, and E_2 symmetries are simultaneously allowed. Of these, the A modes must have TO character whereas the E_1 modes can either be TO or LO. We shall limit our discussion to the ν_1, ν_3, and ν_4 vibrational modes of the $SO_4{}^{2-}$ ion because they are the strongest features occurring in the Raman spectrum of the material and are far away from the strong peaks originating in the sapphire window or the strong Rayleigh background, which make difficult observations in the frequency region below 500 cm^{-1}. In Fig. 1(a) we show a typical spectrum of the α phase in this frequency region. The two small peaks appearing around $\omega \sim 1200$ cm^{-1} are attributed to LO modes of A and E_1 symmetry, corresponding to the ν_3 vibration of the $SO_4{}^{2-}$ ion. Of these, the first is forbidden and the second allowed. Since both appear weakly and with slightly shifted frequency, we conclude that they are oblique phonons[14] produced by a slight tilting of the sample within the gasket. It is also permissible to surmise that, fortuitously, our experimental configuration is such that E modes of the LO type contribute only weakly to the features observed in this figure. Hence, the structures in Fig. 1(a) are assigned to the following (in order of increasing frequency): A (623) and E_1 (635)+E_2 (636) (ν_4 vibrations), A (1012) (ν_1 vibration) and the remaining strong peak would correspond to accidentally quasidegenerate modes originating in the ν_3 vibration of the $SO_4{}^{2-}$ ion with A, E_1, and E_2 symmetries ($\omega \simeq 1120$ cm^{-1}).

The spectrum described above remains essentially unchanged as pressure is increased up to $P \simeq 9$ kbar [see Fig. 1(b)], except for a monotonic increase in the frequency of all the spectral features. Beyond this point the spectrum suffers a qualitative change [compare Figs. 1(b) and 1(c)] indicating the onset of a different phase (β phase). The β phase is different from all other observed phases in that the Raman spectrum keeps changing qualitatively throughout the whole pressure interval (9 kbar $< P <$ 30 kbar, for increasing pressure) in which the phase is stable. This can be appreciated by comparing the low-frequency region of the spectra displayed in Figs. 1(a) and 1(d). At $P \simeq 30$ kbar another discontinuous change takes place in the Raman spectrum [Fig. 1(e)], which then remains practically unchanged until pressure reaches $\sim$67 kbar. At this pressure the spectrum changes abruptly again [compare Figs. 1(f) and 1(g)] and from here on it suffers very little change up to $P \sim 100$ kbar [compare Figs. 1(g) and 1(h)]. The distinct phases observed in the pressure intervals 30 kbar $< P <$ 67 kbar and $P >$ 67 kbar are labeled as γ and δ phases, respectively.

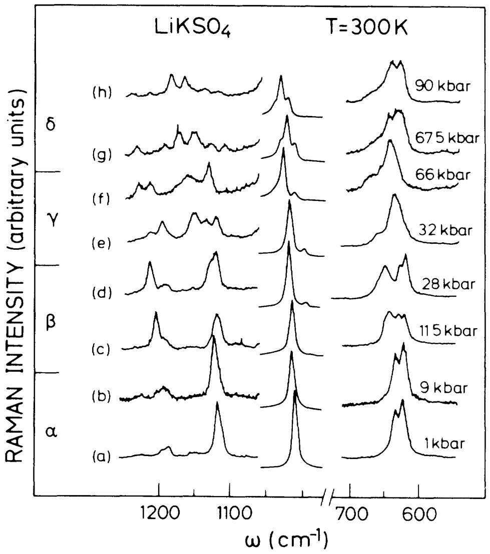

FIG. 1. Unpolarized Raman spectra of $KLiSO_4$ for different pressure values, taken sequentially as pressure increases. Two spectra for each of the four phases (α, β, γ, and δ) are shown at the beginning and at the end of the pressure range in which the phase is found to exist.

The progressive appearance of the different phases as pressure increases is also illustrated in Fig. 2, where the frequencies of the peaks in the Raman spectrum are plotted as a function of increasing pressure.

Abrupt changes in the otherwise monotonic increase in frequency as pressure increases occur at 9, 30, and 67 kbar. Also, at these pressure values new peaks appear which also increase monotonically in frequency up to the next discontinuity. The sequence of phase changes encountered as pressure increases or decreases is shown in the upper part of Fig. 2. Both the onset of each transition and the pressure interval during which each phase is present are very different in the increasing and decreasing pressure experiments, i.e., all transitions show large hysteresis. The most dramatic example of this is the β phase that exists in a pressure interval of $\sim$20 kbar for increasing pressure measurements, while this interval is reduced to about 2 kbar for the descending pressure experiments. It has been reported[6] that the phase transition at 201 K is

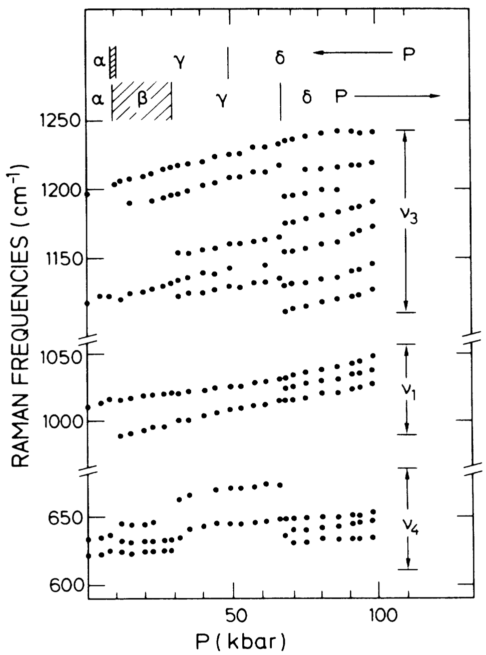

FIG. 2. Peak position vs pressure for the spectral features displayed in Fig. 1. As in this figure, the filled circles represent values obtained for increasing pressure cycles. The onset of each transition is indicated in the top of the figure (as well as the labels given to each phase) both for increasing (bottom) and decreasing (top) pressure cycles. The figure indicates broad frequency regions which are assigned to the ν_3, ν_1, and ν_4 vibrations of the $SO_4{}^{2-}$ ions.

quite sluggish and that complete transformation at fixed temperature was achieved in time intervals of the order of 35 min. Hence, we were careful to raise or lower the pressure slowly, allowing the system to rest at fixed pressure for average intervals of about an hour. In some cases the system was allowed to remain at fixed pressure for a whole day. No changes were observed in the spectra as a function of time at constant pressure. Also, the critical pressures at which each phase transition occurs, both for increasing or decreasing pressure, have been found to be well defined and reproducible for a wide variety of samples examined on different days and subjected to different rates of increasing (decreasing) pressure.

Although we do not have structural information about the high pressure phases, our results suggest that both γ and δ phases have closer packing and the latter probably belongs to a space group of lower symmetry than the ambient pressure α phase. This would explain the appearance of additional lines in the spectra of the γ and δ phases in the frequency region of the ν_3 vibration of the $SO_4{}^{2-}$ ion (Figs. 1 and 2). Bringing the $SO_4{}^{2-}$ ions closer together would remove the accidental degeneracy of the A, E_1, and E_2 modes observed in Fig. 1(a) at $\omega \simeq 1120$ cm^{-1}. Lowering the symmetry would further split the doubly degenerate E_1 and E_2 lines producing even more lines in this region. The appearance of more lines also in the region of the ν_1 vibration [at $\omega \simeq 1012$ cm^{-1} in the α phase, as seen in Fig. 1(a)] suggests that in the δ phase [Fig. 1(g)] both $SO_4{}^{2-}$ ions occupy inequivalent sites. The most interesting result of our experiments, however, is the curious behavior of the β phase. In this phase, the spectrum undergoes qualitative changes in a continuous manner as pressure increases from $P \sim 9$ kbar to $P \sim 30$ kbar. New peaks appear and their relative intensity changes from one pressure value to the next. We emphasize that these changes occur as a function of pressure, and not as a function of time, since no alteration was observed in the spectra of samples which were left at constant pressure (9 kbar $< P <$ 30 kbar) for periods of up to 24 h. This behavior suggests that the β phase is either incommensurate[15] or else a mixture of α and γ phases that coexist during a very large pressure interval. Notice that this coexistence cannot be attributed to sluggishness of the $\alpha \rightleftarrows \delta$ transition. In this case the shape of the spectra in the β region would depend on time rather than on pressure, and the critical pressures at which the transitions to the β and γ phases occur would be fuzzy and depend critically on the rate at which pressure is increased, contrary to our experimental observations. Hence, if both phases coexist they must do so under nearly equilibrium conditions. Also, for the phase mixture hypothesis to be feasible it should be possible to obtain the spectra of the β phase by a judicious combination of the spectra from the α and γ phases, with the spectrum becoming more γ-like as the pressure approached 30 kbar (from below). Comparing Figs. 1(a)–1(e) it is not easy to see how this could be accomplished. This hypothesis would also predict an almost continuous transition in the spectrum as we crossed the 30- kbar transition pressure (where the "mixture" would be 100% γ phase). This is far from being the case as can be seen comparing the spectra of Figs. 1(d) and 1(e), taken very close (in pressure) to each other on both sides of the transition pressure. Hence, although we cannot rule out the possibility that the β phase is merely a mixture of α and γ phases, the explanation based on the sequence

$$\alpha(\text{normal}) \rightarrow \beta(\text{incommensurate}) \rightarrow \gamma(\text{lock-in phase})$$

seems to fit our experimental observations better. This, however, can only be regarded as a tentative conclusion. Other puzzling observations need explanation, such as the extremely narrow range of existence of the β phase for descending pressure experiments (see upper part of Fig. 2). Also, should this β phase be related to the incommensurate phase reported for ambient pressure and low temperatures,[2] we could expect that the $\alpha \rightleftarrows \beta \rightleftarrows \gamma$ transitions be related to the orientation of the $SO_4{}^{2-}$ ions within the unit cell. In this case the modes more affected by the transitions should be those associated with librational motions of the $SO_4{}^{2-}$, i.e., the A (205) and E_1 (44) modes.[3] Unfortunately, we could not observe these modes in our experiment. Efforts are currently being made to study the pressure dependence of these modes with a diamond-anvil cell. We hope this additional information will help to clarify the question raised here.

In summary, we studied the room-temperature Raman spectrum of $KLiSO_4$ in the frequency region corresponding to the vibrational modes of the $SO_4{}^{2-}$ ions, as a function of hydrostatic pressure. We detect three distinct phase transitions which occur at $P = 9$, 30, and 67 kbar for increasing pressure experiments. On experiments where pressure decreases steadily the transition pressures are lower, but each transition still takes place at a well defined pressure (± 1 kbar). Of the four observed phases, the one designated as β phase (9 kbar $< P <$ 30 kbar for increasing pressure) exhibits a peculiar behavior that resembles that of an incommensurate phase.

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