

Pressure-induced phase transitions in LiNH_4SO_4

V. Lemos and R. Centoducatte*

Instituto de Física, Universidade Estadual de Campinas (UNICAMP), 13081 Campinas, São Paulo, Brazil

F. E. A. Melo, J. Mendes Filho, J. E. Moreira, and A. R. M. Martins

Departamento de Física, Universidade Federal do Ceará, 60 000 Fortaleza, Ceará, Brazil

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Raman spectra of LiNH_4SO_4 in the frequency range from 600 to 1200 cm^{-1} were measured from atmospheric pressure up to a pressure of 82 kbar. Two distinct phases are identified in the ranges below 13 kbar (β phase) and above 35 kbar (δ phase). In the range between 13 and 35 kbar the spectrum changes qualitatively in a continuous manner, both as a function of time for fixed pressure and as a function of pressure when the latter is rapidly changed. The results suggest a dynamical reorientation of the SO_4^{2-} ions taking place in this pressure interval.

I. INTRODUCTION

Lithium ammonium sulfate, LiNH_4SO_4 (LAS), crystallizes by evaporation in two rhombic modifications α and β .¹ In the β modification the crystal is pseudo-hexagonal and has space group $C_{2v}^9-Pna2_1$ at room temperature.² This material is a member of a class of $AA'BX_4$ -type compounds with crystallographic structures that are currently being considered as slight distortions of the prototype α - K_2SO_4 structure.³ Several members of this class undergo ferroelectric and ferroelastic phase transitions which are triggered by rotation or reorientation of radicals.⁴⁻⁶ An identification of 25 theoretically predicted phases has been recently proposed for this family of materials, taking into consideration only the possible orientations of the BX_4 groups.³ Within this model, first-order phase transitions are predicted for LAS involving rotations of these groups around the pseudo-hexagonal axis. Two such transitions are reported in LAS occurring, at atmospheric pressure, at 186.5 and 10.5 °C respectively.⁷ Measurements of second-harmonic generation suggest that these transitions are related to deformations or reorientation of the $\text{SO}_4(\text{NH}_4)$ tetrahedra.⁸ So far, only one phase transition has been reported as a function of pressure,^{7,9} occurring at 8 kbar (room temperature) and probably corresponding to a structural change given by $Pna2_1-P2_1$. Raman-scattering measurements in KLiSO_4 indicate that these reorientations of SO_4 tetrahedra are slow processes, giving rise to spectral configurations that are forbidden in the initial and final phases and that persist for periods of time of the order of several minutes.⁶

In the present work we report a study of the room-temperature Raman spectra of LAS as a function of pressure in the range $1 \text{ bar} \leq P \leq 82 \text{ kbar}$. The evolution of the spectrum was studied as pressure was rapidly varied and also as a function of time at constant pressure. In the first type of experiment we observed two discontinuous changes in our spectra, taking place at 13 and 35 kbar, respectively. For pressures below 13 kbar or above 35 kbar the spectrum remains qualitatively the same, showing linear frequency shifts induced by pressure. The spectra, in these pressure ranges, also remain unaltered as a func-

tion of time when pressure is kept constant. However, in the pressure range between 13 and 35 kbar the Raman spectrum undergoes qualitative changes in a continuous manner as pressure increases. A similar observation was reported by Melo, Lemos, Cerdeira, and Filho¹⁰ in KLiSO_4 . In contrast to this previous report, however, our spectra are seen to evolve qualitatively as a function of time, at constant pressure, in the interval $13 \text{ kbar} \leq P \leq 35 \text{ kbar}$. This suggests that we are observing a dynamical process in which the SO_4 tetrahedra reorient themselves with very long time constants.

II. EXPERIMENTAL DETAILS

Single crystals of LiNH_4SO_4 were obtained from evaporation at about 30 °C from an aqueous solution prepared from equimolar amounts of reagent grade $(\text{NH}_4)_2\text{SO}_4$ and $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ dissolved in distilled water. The crystals thus prepared belong to the β modification¹ and always form twinned pseudo-hexagonal plates. Untwined regions were selected as samples from an unprepared crystal by using a polarizing microscope. They were oriented using x rays and a thin slice with (001) face was cut. After cutting, the crystals were polished on metcloth polishing cloth with successively finer grade diamond pastes, to obtain the $\sim 150 \mu\text{m}$ plates used in our experiments. Unpolarized spectra were obtained from backscattering configuration using about 500 mW of power of the 5145 Å line of an argon-ion laser as exciting radiation. 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, one of the anvils made of sapphire.¹¹ A 4:1 mixture of methanol and ethanol was used as the pressure-transmitting fluid. The measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

The Raman and infrared spectra of LAS were studied by Acharya and Narayanan.¹² Their assignments for the lattice vibrations are based on the free modes of the

NH_4^+ and SO_4^{2-} ions. In the free state either of the ions has tetrahedral symmetry having two triply degenerate modes $\nu_3(T)$ and $\nu_4(T)$, a doubly degenerate mode $\nu_2(E)$, and the totally symmetric nondegenerate mode $\nu_1(A)$. According to their classification the lowest-frequency region ($\omega < 420 \text{ cm}^{-1}$) corresponds to lattice oscillations, rotational modes of NH_4^+ and Li-O stretching modes. The internal modes of SO_4^{2-} observed by Raman scattering were a ν_2 bending at about 470 cm^{-1} , two ν_4 bending modes at 630 cm^{-1} and 642 cm^{-1} , one ν_1 stretching mode at 1012 cm^{-1} , and six ν_3 stretching modes in the region between 1080 and 1200 cm^{-1} . The highest-frequency region ($\omega > 1200 \text{ cm}^{-1}$) corresponds to internal modes of NH_4^+ , and N-H stretching modes. Although a complete identification of the 129 optic modes predicted by group theory has not yet been reported, for the purposes of the present study we adopt the following assignments for the SO_4^{2-} internal modes: the frequency region between 620 and 650 cm^{-1} contains bending modes while that around 1012 cm^{-1} corresponds to stretching modes, in accordance with the description given above. These regions of the Raman spectrum of LAS were studied as a function of pressure in two different

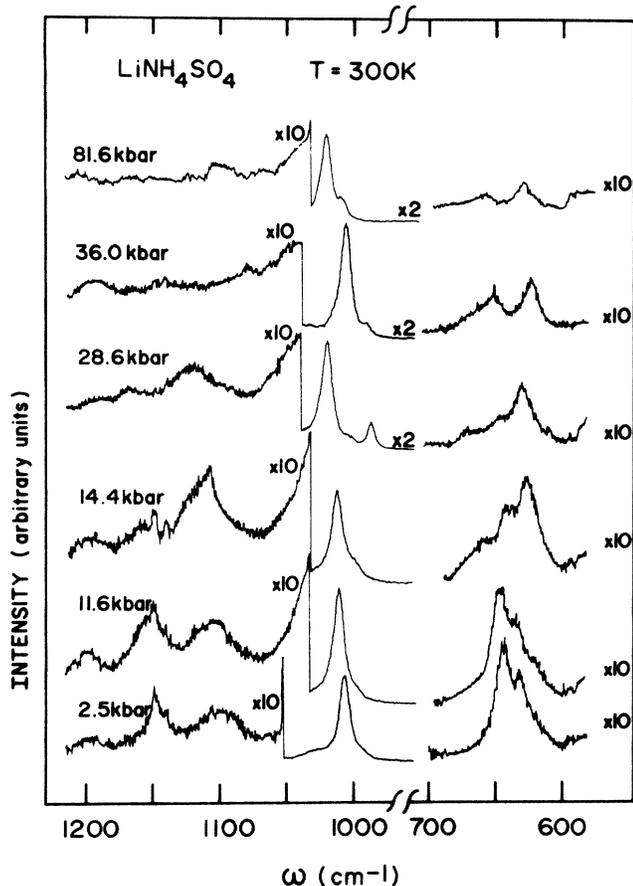


FIG. 1. Raman spectra of LiNH_4SO_4 for different pressure values, taken sequentially as pressure is increased at a fast rate. Two spectra for each of the three phases (β , γ , and δ) are shown defining the pressure range in which the phase is found to exist.

ways: (i) increasing pressure rapidly and (ii) at constant pressure, taking successive spectra at different times during periods of up to 24 h. The results of the first type of experiments are illustrated in Figs. 1 and 2, while the time evolution of the Raman spectrum at constant pressure is shown in Fig. 3.

Figure 1 shows the evolution of the Raman spectrum with pressure. The lowest curve, labeled 2.5 kbar, is qualitatively identical to the ambient pressure spectrum characteristic of the β phase of LAS. It remains unchanged as pressure is increased up to $P \sim 12$ kbar (Fig. 1). At about 13 kbar qualitative modifications start to occur in the spectrum. They are readily seen in the bending region of the spectrum (compare curves labeled 11.6 and 14.4 kbar, respectively, on Fig. 1). Beyond 14.4 kbar, the bending region remains essentially unchanged up to about 30 kbar, when a continuous change starts to occur ending in a stable pattern at 35 kbar. On the other hand, the stretching region suffers drastic modifications in this pressure interval. The peak positioned at 1004 cm^{-1} at ambient pressure, the strongest feature of the spectrum, disappears and new peaks appear, positioned at slightly lower frequencies. The pressure at which the 1004 cm^{-1} peak disappears was not reproduced in any one of the several series of measurements performed, but the disappearance always fell in the 13–35 kbar interval. Also, the number of new peaks observed in this region was not reproducible if data from different starting configurations were compared. The lack of reproducibility of the Raman spectrum in the interval $13 \text{ kbar} \lesssim P \lesssim 35 \text{ kbar}$ affects also the relative intensity of the peaks that appear in the stretching region. Some peaks increase and decrease in intensity in an alternating fashion as pressure increases steadily. For $P > 35$ kbar the Raman spectrum remains qualitatively unchanged up to the highest pressure value attained in our experiment (~ 82 kbar), as can be seen when comparing the two uppermost spectra shown in Fig. 1.

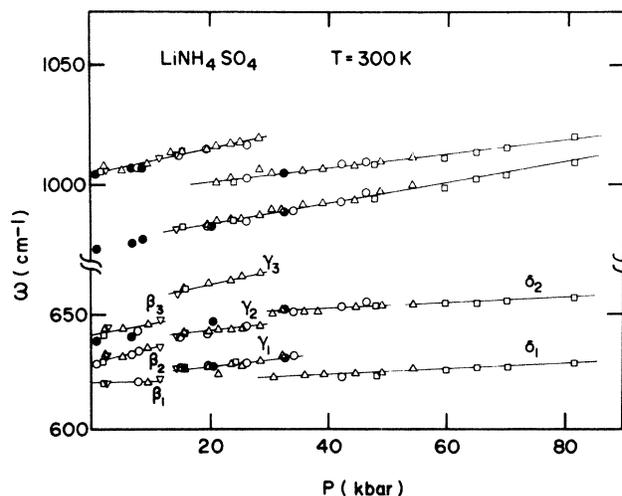


FIG. 2. Raman frequencies vs pressure for internal modes of SO_4^{2-} ions. A different symbol was used for each sample examined; full symbols indicate data taken as pressure was released. Solid lines are least-squares fittings to the data.

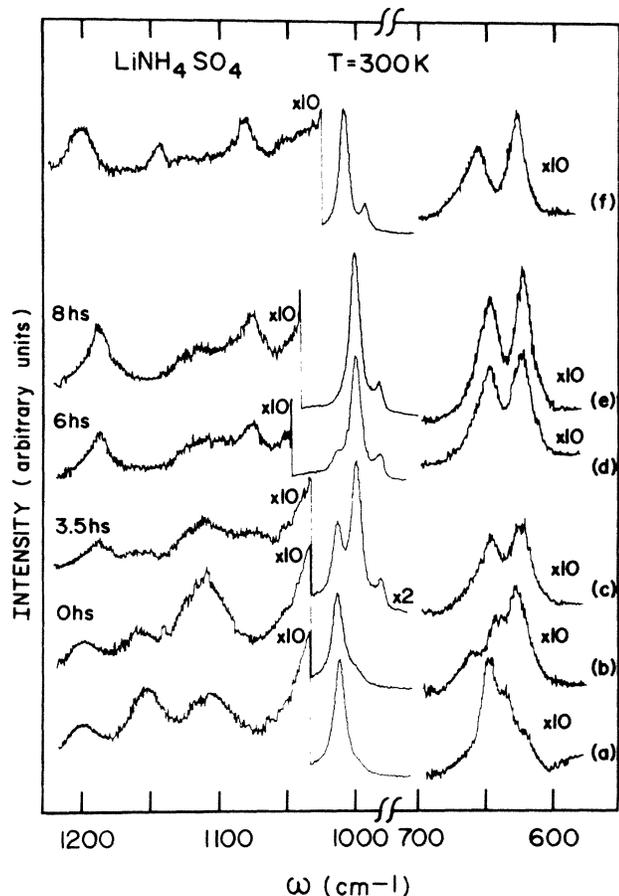


FIG. 3. (a) Raman spectrum of the β phase of LAS at a pressure value just below P_c ($P=12.5$ kbar). (b), (c), (d), (e) Transformations in the Raman spectrum with time, when the pressure is held constant at a value just above P_c ($P=13.5$ kbar). (f) Raman spectrum of the δ phase of LAS at $P=35$ kbar.

All the results are described in Fig. 2, where Raman frequencies are plotted as a function of pressure. A monotonic increase in frequency is observed for all of the modes as pressure is increased from 1 bar to 13 kbar. Between 13 and 35 kbar, several discontinuities occur in the stretching region of the spectrum, the uppermost curve being interrupted and new ones being defined at lower frequencies. No discontinuity is observed outside this interval. The behavior of the stretching modes could be interpreted as a structural transition from the ambient pressure phase (β phase) to a high-pressure phase (δ phase) taking place in a pressure region (13 to 35 kbar) where both phases coexist. However, this interpretation is not consistent with the behavior of the bending modes. The details can be appreciated with the help of Fig. 2. The curves labeled β_i ($i=1,2,3$) in this figure show a monotonic increase in frequency up to $P=13$ kbar. At this pressure, all the curves stop, and new curves labeled γ_i ($i=1,2,3$) in Fig. 2 start. The curves are continuous up to $P=30$ kbar, where γ_3 and γ_2 are interrupted. The γ_1 in-

terruption occurs at $P=35$ kbar. This is the highest pressure discontinuity observed in Fig. 2. From this pressure on, the data define new curves, δ_1 and δ_2 , that are continuous up to $P=82$ kbar.

We shall try to apply to the bending region the mixing-of-phases argument elaborated for the stretching modes behavior. Although we could propose suitable combinations of β_i and δ_i curves resulting in the γ_1 and γ_2 lines, no combination of the former reproduce the γ_3 curve. It would appear more appropriate to attribute the γ_i curves to bending modes of the SO_4^{2-} ion originating in a structural arrangement that is distinct from those of the β or δ phases, rather than attribute them to a mixture of both phases. Hence, the behavior of the bending modes is consistent with the existence of an intermediate phase (γ phase) in which the orientation of the SO_4^{2-} ions evolves continuously during periods of time of the order of several hours. This interpretation is supported by experiments in which we observed the evolution of the Raman spectrum as a function of time at fixed pressure. The spectrum was seen to remain unaltered for periods of up to 24 h for pressures above 35 kbar or below 13 kbar. At pressures contained within the 13–35 kbar interval, however, the spectrum suffers qualitative changes as a function of time at constant pressure.

Our observations are illustrated in Fig. 3 where the lowest and uppermost curves, (a) and (f), represent spectra taken at 12.5 and 35 kbar, respectively. The curves labeled (b) to (c) were taken at different times with the pressure constant at 13.5 kbar. It is worthwhile to emphasize that the γ -phase spectrum is completely different from the β -phase spectrum for almost the same pressure value [compare Fig. 3(b) to Fig. 3(a)]. The spectrum continues to evolve as time goes on in such a way that after about 3 h the bending region of the spectrum is qualitatively indistinguishable from that of the δ phase [compare curves labeled (c) to (f) in Fig. 3]. The modifications occurring in the stretching region are not as fast as in the bending region, but are more pronounced. One observes the peak of 1004 cm^{-1} (at ambient pressure) dying down and two new peaks at lower frequencies appearing in the spectra displayed on Figs. 3(c) and 3(d) for 3.5 and 6 h respectively, at the same pressure as before, $P=13.5$ kbar. Over a period of about 8 h the transition is completed and the resulting spectrum is stable and similar to that of the δ phase [compare Figs. 3(e) and 3(f)]. This could indicate that the intermediate γ phase is related to dynamical effects, involving probably deformations or reorientations of the SO_4^{2-} ions induced initially by pressure, and evolving in time until another static arrangement is attained. Since the shape of the spectrum of the γ phase changes with time as well as with pressure, we are able to explain now the lack of reproducibility in the sequential increase of pressure experiments. This peculiar behavior resembles an early observation⁶ of the structural transition in KLiSO_4 due to reorientational effects of sulfate ions at $T_c=201$ K. In both cases great instability of the Raman spectrum was found to occur at the critical value of the parameter driving the transition. Finally, we did not find any evidence for a structural phase transition at 8 kbar as reported before by other authors.⁷

IV. CONCLUSIONS

To summarize, we studied the pressure dependence of the Raman spectrum of LAS in the frequency region of the vibrational modes of SO_4^{2-} ions. We found evidence of a transient phase acting as an intermediate phase for the transition from the original β phase to the high-pressure δ phase of LAS, at $P_c = 13$ kbar on increasing pressure. This phase exists in the pressure interval $13 \text{ kbar} \lesssim P \lesssim 35 \text{ kbar}$. In order to ascertain the nature of this phase, whose atomic arrangement seems to evolve continuously for long periods of time, x-ray diffraction data under pressure would be desirable.

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*Permanent address: Departamento de Física e Química, Universidade Federal do Espírito Santo, 29069 Vitória, Espírito Santo, Brazil.

¹M. G. Wyruboff, *Bull. Soc. Fr. Mineral* **13**, 216 (1980).

²W. A. Dollase, *Acta Crystallogr. B* **25**, 2298 (1969).

³M. Kurzynski and M. Halawa, *Phys. Rev. B* **34**, 4846 (1986).

⁴A. J. Van den Berg and F. Tuinstra, *Acta Crystallogr. B* **34**, 3177 (1978).

⁵H. G. Unruh, *Ferroelectrics* **36**, 359 (1981).

⁶M. L. Bansal and A. P. Roy, *Phys. Rev. B* **30**, 7307 (1984).

⁷T. I. Chekmasova, I. S. Kabanore, and V. I. Yuzvak, *Phys.*

Status Solidi A **44**, K155 (1977).

⁸T. Mitsui, K. Ito, S. Hirotsu, K. Hamano, and S. Savada, *Izv. Akad. Nauk. SSSR, Ser. Fiz.* **41**, 555 (1977).

⁹T. I. Chekmasova and I. P. Aleksandrova, *Phys. Status Solidi A* **49**, K185 (1978).

¹⁰F. E. A. Melo, V. Lemos, F. Cerdeira, and J. Mendes Filho, *Phys. Rev. B* **35**, 3633 (1987).

¹¹R. S. Hawke, K. Syassen, and W. B. Holtzapfel, *Rev. Sci. Instrum.* **45**, 1598 (1974).

¹²P. K. Acharya and P. S. Narayanan, *Indian J. Pure Appl. Phys.* **11**, 514 (1973).