

## RAMAN SPECTRA AND THE DYNAMIC STRUCTURE OF THE HIGH PRESSURE PHASE OF $\text{NH}_4\text{Br}$ (V) AND $\text{ND}_4\text{Br}$ (V)\*

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Similar Raman spectra are observed at high pressures for phases II and V of  $\text{ND}_4\text{Br}$  and  $\text{NH}_4\text{Br}$ . Deuteration lowers the II-V phase transition from 20 to 9 kbar at 296 K.  $\text{ND}_4\text{Br}$  V and  $\text{NH}_4\text{Br}$  V are interpreted as mixed phases, and their spectra as the superposition of the spectra of two other phases, III (antiparallel arrangement of the  $\text{NH}_4^+$  ions) and IV (parallel arrangement). The phonons which become Raman inactive at the V-IV phase transition are assigned to clusters or domains of phase V which have antiparallel arrangement.

### 1. Introduction

Five phases have been reported for  $\text{NH}_4\text{Br}$ . Four of these phases (II-V) are basically formed from the CsCl-like units with the  $\text{NH}_4^+$  ions having a different orientational arrangement in each phase [1,2].  $\text{NH}_4\text{Br}$  II is considered to be disordered, the  $\text{NH}_4^+$  ions occupying the two possible orientations in a random fashion. In the tetragonal phase III, the  $\text{NH}_4^+$  ions are ordered parallel along the *c* axis but ordered antiparallel to each neighbor in the *ab* plane. In addition, the neighboring rows of  $\text{Br}^-$  ions are displaced along the *c* axis in an opposite direction relative to the *ab* plane to compensate for the polarization of the halogen ion. The  $\text{NH}_4^+$  ions show parallel ordering along each principal axis in the lowest temperature phase (IV) which has  $T_d^1$  space group symmetry.  $\text{NH}_4\text{Br}$  V, which only exists at high pressures, has been observed in both Raman and acoustic studies, however, the structure of this phase is not known [1,2]. The purpose of this paper is to report the effects of deuteration on the II-V transition pressure and an assignment of the lattice phonons of  $\text{NH}_4\text{Br}$  V and  $\text{ND}_4\text{Br}$  V. The spectral differences between the disordered phase II and the

high pressure phase V are also pointed out. Extensive Raman data which establish the pressure-temperature phase boundaries, polarization characteristics, temperature (195-407 K) and pressure effects (1 bar-42 kbar) in the stability range of  $\text{NH}_4\text{Br}$  II, IV and V will be described in detail elsewhere [2].

$\text{NH}_4\text{Br}$  IV ( $\text{ND}_4\text{Br}$  IV) has the simplest Raman spectrum of these phases, with the following representation for the fundamental mode:

$$\nu_1 (A_1) + \nu_2 (E) + \nu_3 (F_2) + \nu_4 (F_2) + \nu_5 (F_2) + \nu_6 (F_1).$$

$\nu_1$  to  $\nu_4$  are internal vibrations of the  $\text{NH}_4^+$  ion, while  $\nu_5$  and  $\nu_6$  are lattice phonons. All modes except the libration ( $\nu_6$ ) are Raman active. The Raman active fundamental modes of  $\text{NH}_4\text{Br}$  IV are also observed in  $\text{NH}_4\text{Br}$  II and V; therefore, the same designation will be employed for these modes in the three phases. The two molecular units in  $\text{NH}_4\text{Br}$  III ( $\text{ND}_4\text{Br}$  III) give rise to 36 vibrational degrees of freedom, the representation for the Raman active modes being:  $(2A_{1g} + 1B_{1g} + 2B_{2g} + 2E_g)$  for the internal modes of the  $\text{NH}_4^+$  and  $(3E_g + 1A_{1g} + 1B_{2g})$  for the lattice phonons [3-5]. In  $\text{NH}_4\text{Br}$  III, the librational motion is designated as  $\nu'_6 (E_g)$ , while the translational motion of the  $\text{NH}_4^+$  and  $\text{Br}^-$  ions are  $\nu'_5 (E_g)$  and  $\nu''_5 (B_{2g})$ . One usually expects to observe excitations throughout the Brillouin zone in a disordered crystal such as  $\text{NH}_4\text{Br}$  II as a consequence of the breakdown in the *k*-conservation rule;

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however, many aspects of the Raman spectrum of  $\text{NH}_4\text{Br}$  II such as the origin of the Raman peaks and their polarization characteristics are still not completely understood.

## 2. Experimental

A high pressure optical cell designed for  $90^\circ$  scattering geometry and capable of 45 kbar was employed in this work. The  $\text{NH}_4\text{Br}$  crystal ( $2 \times 2 \times 3$  mm) was placed in a high pressure cavity so that the (100) face was normal to the incident laser beam. Raman spectra were excited at 5145 and 4880 Å (1.5–1.8 W) and detected with a Spex monochromator in conjunction with a photon counting system. The temperature was altered by circulating a refrigerant through the casing of the cell and by immersing the cell in a cold temperature bath. Detailed description of the high pressure Raman experimental method can be found in a previous publication [2].

The deuterated ammonium bromide powder used in the phase transition study was prepared in a manner similar to that previously reported for  $\text{ND}_4\text{Cl}$  [6]. The powdered sample was compacted and placed in the high pressure cavity of the Raman cell. The results on  $\text{ND}_4\text{Br}$  are compared to both the single crystal and powdered  $\text{NH}_4\text{Br}$  data.

## 3. Results and discussion

The stability range of the phases in  $\text{NH}_4\text{Br}$  can be placed with the previously reported phase diagram [2]. Phase II extends from 235 to 411 K at 1 bar. Under isothermal compression,  $\text{NH}_4\text{Br}$  II becomes unstable and the II–V phase boundary is crossed, for example, at 11 and 20 kbar at 260 and 296 K, respectively.  $\text{NH}_4\text{Br}$  IV, which exists at lowest temperatures ( $< 102$  K at 1 bar) or at highest pressures of all the CsCl-like phases, is observed for example at pressures higher than 8 and 22 kbar at 195 and 260 K, respectively.  $\text{NH}_4\text{Br}$  V which is bordered by phase II at low pressures and by  $\text{NH}_4\text{Br}$  IV at high pressures has been detected in Raman studies from 195 K ( $< 8$  kbar) to 335 K ( $> 23$  kbar). The available phase diagram for  $\text{ND}_4\text{Br}$  covers a limited temperature–pressure range of phase II, III and IV; no observation of  $\text{ND}_4\text{Br}$  V has

previously been reported [7,8].

The Raman spectra of phase V is related to both  $\text{NH}_4\text{Br}$  II and to  $\text{NH}_4\text{Br}$  IV, the combination bands and the fundamental modes of the  $T_d^1$  space group being Raman active in all three phases. The spectra for the lattice phonons of  $\text{NH}_4\text{Br}$  II, IV and V are shown in figs. 1 and 2. There are differences in the relative intensities, wavenumbers, Grüneisen constants, and number of the lattice modes in the different phases.  $\text{NH}_4\text{Br}$  IV has the simplest spectrum. If one approaches  $\text{NH}_4\text{Br}$  V from low pressures at 296 K (Figs. 2–4), the changes in the Raman activity accompanying the transition from phase II to V occur around 20 kbar with the appearance of a strong characteristic shoulder ( $182\text{ cm}^{-1}$  at 20 kbar) on the low energy side of  $\nu_5$  (TO) and the disappearance of an extremely weak mode ( $90\text{ cm}^{-1}$  at 1 bar). Figs. 1, 2 and 4 indicate that the low energy shoulder appears intense at 296 K. The anharmonicity of the crystal potential affecting the observed wavenumber shifts (fig. 3) of the

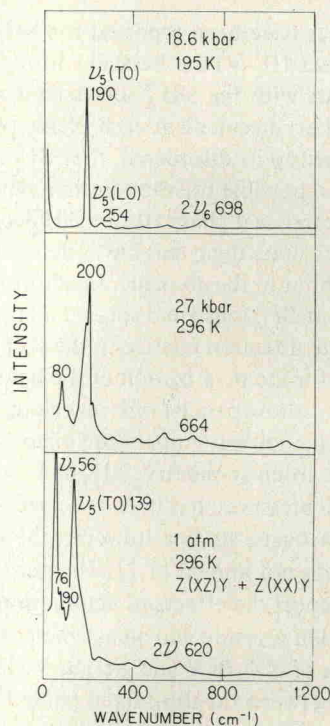


Fig. 1. Raman spectra of the lattice phonons of  $\text{NH}_4\text{Br}$  II (296 K and 1 bar), V (296 K and 27 kbar) and IV (195 K and 18.6 kbar). The spectrum at 1 bar was taken with the crystal outside the high pressure cell.