RAMAN SPECTRA AND THE DYNAMIC STRUCTURE
OF THE HIGH PRESSURE PHASE OF NH_4Br (V) AND ND_4Br (V)*

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Similar Raman spectra are observed at high pressures for phases II and V of ND_4Br and NH_4Br. Deuteration lowers the II–V phase transition from 20 to 9 kbar at 296 K. ND_4Br V and NH_4Br V are interpreted as mixed phases, and their spectra as the superposition of the spectra of two other phases, III (antiparallel arrangement of the 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 NH_4Br. Four of these phases (II–V) are basically formed from the CsCl-like units with the NH_4^+ ions having a different orientational arrangement in each phase [1,2]. NH_4Br II is considered to be disordered, the NH_4^+ ions occupying the two possible orientations in a random fashion. In the tetragonal phase III, the 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 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 NH_4^+ ions show parallel ordering along each principal axis in the lowest temperature phase (IV) which has T_d^1 space group symmetry. NH_4Br 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 NH_4Br V and ND_4Br 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 NH_4Br II, IV and V will be described in detail elsewhere [2].

NH_4Br IV (ND_4Br IV) has the simplest Raman spectrum of these phases, with the following representation for the fundamental mode:

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

ν_1 to ν_4 are internal vibrations of the NH_4^+ ion, while ν_5 and ν_6 are lattice phonons. All modes except the libration (ν_6) are Raman active. The Raman active fundamental modes of NH_4Br IV are also observed in NH_4Br II and V; therefore, the same designation will be employed for these modes in the three phases. The two molecular units in NH_4Br III (ND_4Br 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 NH_4^+ and ($3E_g + 1A_{1g} + 1B_{2g}$) for the lattice phonons [3–5]. In NH_4Br III, the librational motion is designated as $\nu_6'\,(E_g)$, while the translational motion of the NH_4^+ and 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 NH_4Br II as a consequence of the breakdown in the k-conservation rule;

however, many aspects of the Raman spectrum of NH_4Br 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° scattering geometry and capable of 45 kbar was employed in this work. The NH_4Br 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 ND_4Cl [6]. The powdered sample was compacted and placed in the high pressure cavity of the Raman cell. The results on ND_4Br are compared to both the single crystal and powdered NH_4Br data.

3. Results and discussion

The stability range of the phases in NH_4Br can be placed with the previously reported phase diagram [2]. Phase II extends from 235 to 411 K at 1 bar. Under isothermal compression, NH_4Br II becomes unstable and the II–V phase boundary is crossed, for example, at 11 and 20 kbar at 260 and 296 K, respectively. NH_4Br 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. NH_4Br V which is bordered by phase II at low pressures and by NH_4Br 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 ND_4Br covers a limited temperature–pressure range of phase II, III and IV; no observation of ND_4Br V has

previously been reported [7,8].

The Raman spectra of phase V is related to both NH_4Br II and to NH_4Br 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 NH_4Br 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. NH_4Br IV has the simplest spectrum. If one approaches NH_4Br 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 cm^{-1} at 20 kbar) on the low energy side of ν_5 (TO) and the disappearance of an extremely weak mode (90 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
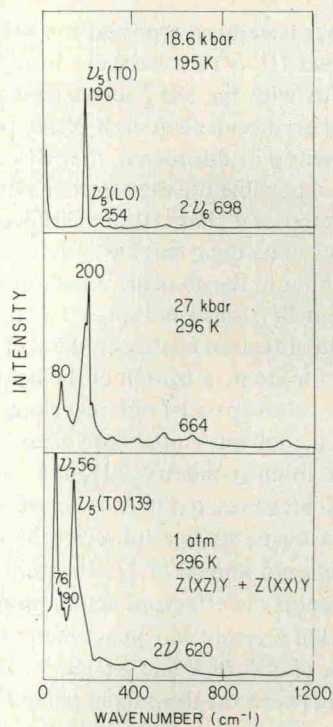

Fig. 1. Raman spectra of the lattice phonons of NH_4Br II (296 K and 1 bar), V (296 K and 27 kbar) and IV (195 K and 18.6 kbar). The spectrum at 1 bar was taken with the crystal outside the high pressure cell.
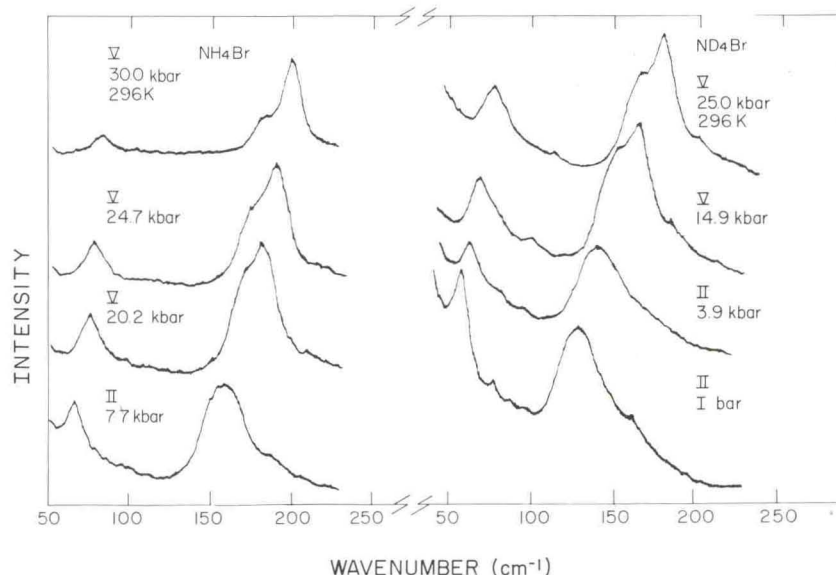
Fig. 2. The spectral changes in the strong, low wavenumber phonons of compressed NH_4Br and ND_4Br powder. The II–V phase transition is observed at 20 kbar and 9 ± 2 kbar at 296 K in NH_4Br and ND_4Br, respectively. The spectrum of ND_4Br II at 1 bar is taken with the sample outside the high pressure cavity.
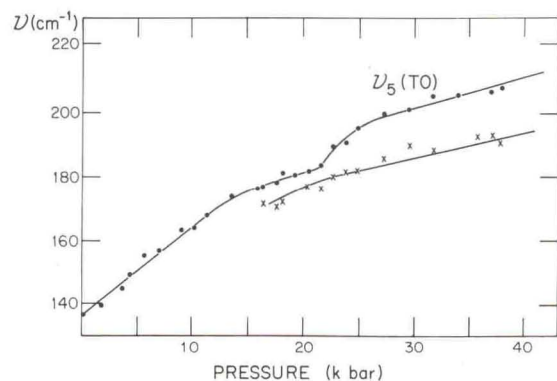

Fig. 3. Plot of wavenumber versus pressure for ν_5 (TO) and the low energy shoulder ν_5'' (B_{2g}) appearing in NH_4Br V.

Fig. 4. The spectra of NH_4Br V are shown at 296 K and 24.5 kbar, 215 K and 4.4 kbar and 200 K and 4.4 kbar. The spectra of phase V is compared to the combined spectra of NH_4Br III (indicated by the dashed line – – –) and NH_4Br IV (indicated by the dotted line …) shown in the upper figure. ν_5 (TO) and ν_5 (LO) belong to NH_4Br IV, while ν_7'' (A_{1g}), ν_7' (E_g), ν_5'' (B_{2g}) and ν_5' (E_g) are modes arising from NH_4Br III. The Raman active librational mode, ν_6', arising from NH_4Br III and ν_5 (LO) are only observed at low temperatures in NH_4Br V. At 200 K and 4.4 kbar, for example, ν_6 (E_g) and ν_5 (LO) are located at 338 and 235 cm^{-1}, respectively. The approximate positions of the three modes in the band centered on ν_5 (TO) (indicated by the broken line - - -) are shown in the spectrum of NH_4Br V at 296 K and 24.5 kbar.
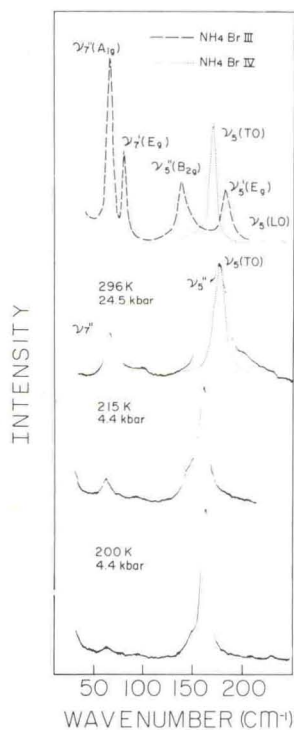

Fig. 4

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phonons are conveniently measured by the Grüneisen constants ($\gamma = -\mathrm{d}\ln\nu/\mathrm{d}\ln V$). For the translational motion (ν_5 (TO)) of the NH_4^+ and Br^- sublattices, a large decrease in the γ (from 3.2 to 1.2) is noted upon going from phase II to V, respectively. The spectrum of phase IV (fig. 1, 195 K and 18.6 kbar) consists only of ν_5 and several weak two-phonon bands [2,9]. The above spectroscopic data of NH_4Br V certainly indicates that this phase is formed from the basic CsCl-like units and that the spectra are different from either NH_4Br II or NH_4Br IV.

Raman spectra of compressed NH_4Br powder show the same spectral changes as the single crystal, the II–V phase transition being observed at 20 kbar and 296 K in both cases. Thus, crystal perfection does not affect to a great extent the spectral changes associated with the transition which encouraged the extension of the phase transition studies to powdered ND_4Br. Fig. 2 shows the stronger lattice modes and their variation with pressure in NH_4Br and ND_4Br. Weaker modes which must be located with much wider spectrometer slits are not shown. The lowest frequency mode of the disordered ND_4Br II at 56 cm^{-1} (1 bar and 296 K) shows no measurable isotope effect when compared with the corresponding mode at 56 cm^{-1} of NH_4Br. This 56 cm^{-1} peak can be assigned as the transverse acoustic mode (TA_2) excited at point M of the zone edge with the aid of the published neutron dispersion relation [10]. The spectra of ND_4Br II also shows a broad band at 100–200 cm^{-1} which consists of the strong ν_5 (TO) and a weaker high energy shoulder. Deuteration lowers the II–V transition pressure, the phase boundary being crossed at 9 ± 2 kbar in ND_4Br rather than at 20 kbar and 296 K as in NH_4Br. Fig. 2 reveals that the same characteristic low energy shoulder appears in both ND_4Br and NH_4Br V.

One of the most interesting features of NH_4Br V is the large intensity change of the lattice phonons with variation in temperature and pressure. This intensity variation is in marked contrast to both phase II and IV where only small changes are noted. Qualitatively, the temperature effect on the intensity of NH_4Br V appears to be stronger than the pressure effect, although the two effects cannot be accurately separated and the transmission of the NaCl windows employed in the high pressure cell varies to a small extent. The relative intensities of the low wavenumber peaks in NH_4Br V are seen in fig. 3 at temperatures

ranging from 200 to 296 K. At 296 K and 24.5 kbar, the broad band at 150–250 cm^{-1} consists of a strong central peak at 195 cm^{-1} (ν_5 (TO)) and of low and high energy shoulders at 182 (ν_5'') and 218 cm^{-1} (ν_5'), respectively. The other peaks are located at 78 (ν_7'') and 107 (ν_7') cm^{-1} in NH_4Br V at 296 K and 24.5 kbar. At 5.2 kbar and 200 K, the peaks are located at 63 (ν_7''), 80 (ν_7'), 146 (ν_5''), 160 (ν_5 (TO)), 204 (ν_5'), 235 (ν_5 (LO)) and 335 cm^{-1} (ν_6'). Fig. 3 indicates that there are two classes of peaks, those showing a large decrease (ν_7'', ν_7', ν_5'' and ν_5') and a peak (ν_5 (TO)) characterized by some increase of intensity as the temperature is lowered. The intensity change of the ν_5 (TO) peak with decreasing temperature (296–200 K) cannot be accounted for in terms of one phonon excitation process since an 18% decrease would be expected rather than the observed increase. The large relative intensity decrease with decreasing temperature for the other set of peaks does not follow the intensity behavior of either a one or two phonon process (40–50% decrease). The variation of the intensities of the low energy phonons in NH_4Br V suggests a temperature dependent concentration effect with one set of peaks increasing (ν_5) and the other set (ν_7'', ν_7', ν_5'', ν_5', and ν_6') decreasing with decreasing temperature. The latter set of peaks become Raman inactive at the V–IV transition. The Raman peaks of phase V have similar behaviors in both ammonium bromides with correspondence between 77 to 78 (ν_7''), 167 to 182 (ν_5''), and 178 to 195 cm^{-1} (ν_5 (TO)) at 296 K and 24.5 kbar in ND_4Br and NH_4Br, respectively. The strong intensity variation appears to have led to some confusion in Wang and Wright's interpretation of the spectra of NH_4Br V at low temperature and pressures [11]. These pressure and temperature studies — the agreement of the overall characteristics of the low temperature spectra, especially the isolated peak (ν_7), with those reported by Wang and Wright — and the observation of the same features on the compressed powder and single crystal suggest that the features reported here for NH_4Br V spectra are indicative of this phase [2].

There is no question as to the existence of either the II–V or V–IV transition in ammonium bromide since the changes in the acoustical properties and the spectral changes definitely indicate the transition. The question is the nature of phase V. The Raman data described in this paper can be explained if phase V is

interpreted as a mixed phase and its spectrum as the superposition of the spectra of two other phases, III and IV. The spectrum of phase V contains modes $(\nu_5(TO))$ and $(\nu_5(LO))$ that correspond to each fundamental mode of phase IV, and, in addition, five lattice phonons $(\nu_7'', \nu_7', \nu_5'', \nu_5',$ and $\nu_6')$ which correspond to the spectra of phase III. The superimposed spectra of the parallel ordered NH_4Br IV and the antiparallel ordered NH_4Br III are shown in fig. 4. A mixed phase can be expected in a pseudo-spin system as in NH_4Br where a parallel and an antiparallel oriented phase are already present; examples of mixed phases are well known in magnetic systems [12,13].

4. Summary

Raman studies of the high pressure phase V of NH_4Br and ND_4Br are reported. Deuteration lowers the II–V phase transition pressure from 20 to 9 kbar at 296 K, which is certainly welcome since many more experimental techniques are available at lower pressures. The main features of the results for NH_4Br V, namely (1) the anomalous and strongly temperature-dependent intensity of the Raman peaks, and (2) the small volume-dependent anharmonicity, can be interpreted on the basis of a mixed phase. The two dynamic domains or clusters in phase V are identified as the parallel and antiparallel configurations that one observes in NH_4Br IV and III, respectively, while the new low energy shoulder $(\nu_5''(B_{2g}))$ appearing on $\nu_5(TO)$ at the II–V transition represents the translational motion of the NH_4^+ ions in the c direction of the antiparallel configuration. The five lattice modes becoming Raman inactive at the V–IV transition can be assigned to clusters with antiparallel NH_4^+ ions in NH_4Br V. The NH_4^+ ion ordering is an essential feature of the II–V transition although the polarization of the Br^- ion would be a very important factor in stabilizing the clusters with the antiparallel configuration [14].

Acknowledgement

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