

## RAMAN INVESTIGATION OF HIGH-PRESSURE "DISORDER-ORDER" PHASE TRANSITIONS IN $\text{NH}_4\text{Br}$ AND $\text{NH}_4\text{Cl}$ \*

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$\text{NH}_4\text{Br}$  II-V and  $\text{NH}_4\text{Br}$  V-IV phase transitions and the associated Raman spectra are reported. The spectrum of  $\text{NH}_4\text{Br}$  V and the changes accompanying the  $\text{NH}_4\text{Br}$  V-IV transition are shown to be similar to the spectrum of "disordered"  $\text{NH}_4\text{Cl}$  "II" and to the changes at "disorder-order"  $\text{NH}_4\text{Cl}$  "II"-IV transition.

### 1. Introduction

$\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$  are two of the more extensively studied ammonium halides. Although they have several similar solid phases, the reported "disorder-order" phase transitions of the two systems are surprisingly different [1-4]. Only one "cooperative disorder-order" phase transition ("II"-IV) has been reported for  $\text{NH}_4\text{Cl}$ , while at least four such transitions between several ordered and disordered phases have been reported for  $\text{NH}_4\text{Br}$ . At atmospheric pressure, for example, three solid phases of  $\text{NH}_4\text{Br}$  ( $\text{NH}_4\text{Br}$  II, III, and IV) are known which have CsCl-like basic structural units;  $\text{NH}_4\text{Br}$  II is "disordered", while  $\text{NH}_4\text{Br}$  III ( $D_{4h}^7$ ) and  $\text{NH}_4\text{Br}$  IV ( $T_d^1$ ) are ordered. A high-pressure phase ( $\text{NH}_4\text{Br}$  V) also has been reported [5], and the phase boundaries between  $\text{NH}_4\text{Br}$  V and  $\text{NH}_4\text{Br}$  II, III and IV have been determined to 7 kbar; but no detailed spectroscopic or structural evidence has been given about  $\text{NH}_4\text{Br}$  V or about the associated high-pressure phase transitions [6] which would establish the structural relationship between  $\text{NH}_4\text{Br}$  V and other phases of the ammonium halides.

This paper reports the results of studies by Raman spectroscopy of the nature of the  $\text{NH}_4\text{Br}$  II-V and  $\text{NH}_4\text{Br}$  V-IV phase transitions and on the character

of the structure of  $\text{NH}_4\text{Br}$  V in relation to other ammonium halide phases. The spectroscopic evidence about  $\text{NH}_4\text{Br}$  described herein, when compared with similar results about the "disorder-order" transformation of  $\text{NH}_4\text{Cl}$  at high pressures, suggests that the similarities between  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{Cl}$  are much closer than previously supposed. The Raman spectrum of  $\text{NH}_4\text{Br}$  V and the changes of the Raman spectrum of  $\text{NH}_4\text{Br}$  which accompany the  $\text{NH}_4\text{Br}$  V-IV transition are remarkably similar to the spectrum of "disordered"  $\text{NH}_4\text{Cl}$  "II" and to the changes at the "cooperative disorder-order"  $\text{NH}_4\text{Cl}$  "II"-IV transition. This correspondence between  $\text{NH}_4\text{Br}$  V and "disordered"  $\text{NH}_4\text{Cl}$  "II" implies that there is a difference between the degrees of order of  $\text{NH}_4\text{Cl}$  "II" and  $\text{NH}_4\text{Br}$  II such that the chloride is more ordered. These results also raise questions as to whether a high-temperature phase of  $\text{NH}_4\text{Cl}$  exists which corresponds more closely to  $\text{NH}_4\text{Br}$  II than does  $\text{NH}_4\text{Cl}$  "II"; and preliminary results are reported which indicate a subtle change of the Raman spectra of  $\text{NH}_4\text{Cl}$  occurs at about 8 kbar and 355°K which may correspond to the  $\text{NH}_4\text{Br}$  II-V transition.

### 2. Experimental

The variable-temperature, high-pressure optical cell and its calibration have been described previously [7].

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One unfortunate limitation of the cell is that polarization studies are not possible due to the highly-strained state of the windows.  $\text{NH}_4\text{Cl}$  crystals were grown by vapor deposition which avoids formation of an eutectic ( $\text{NH}_4\text{Cl} : \text{H}_2\text{O}$  at  $257.8^\circ\text{K}$ ) [8,9]. Solution-grown crystals of  $\text{NH}_4\text{Br}$  were used since none were grown successfully from the vapor phase. These bromide crystals were carefully dried for a long time under vacuum.

### 3. Results

#### 3.1. The spectra and identification of $\text{NH}_4\text{Br}$ V

This discussion of the spectral characteristics of  $\text{NH}_4\text{Br}$  phases proceeds from the "disordered"  $\text{NH}_4\text{Br}$  II, which is stable at atmospheric pressure and temperatures near  $300^\circ\text{K}$ , to  $\text{NH}_4\text{Br}$  V and  $\text{NH}_4\text{Br}$  IV, which can be produced by isothermal compression of  $\text{NH}_4\text{Br}$  II at, e.g.,  $265^\circ\text{K}$ . These  $\text{NH}_4\text{Br}$  results will be compared with spectral characteristics of the  $\text{NH}_4\text{Cl}$  phases; especial attention will be paid to differences between the numbers and intensities of the Raman-active modes of the various phases and to changes of the anharmonicities of the modes that accompany the phase transformations\*. Although spectra of the internal† and lattice modes change with pressure and with temperature, the largest changes occur for the low-frequency modes; and only these changes are discussed here.

An interesting feature of "disordered"  $\text{NH}_4\text{Br}$  II is

\* Except that the "cooperative order-disorder" phase transition of  $\text{NH}_4\text{Cl}$  is sharp – with a significant volume discontinuity and distinct change of the frequency of  $\nu_5(\text{TO})$ , for example – at 1 atm ( $242.6^\circ\text{K}$ ) and is very gradual at higher pressures (e.g., 10 kbar,  $300^\circ\text{K}$ ) (preliminary results are given in ref. [10], see also ref. [11]), the spectral characteristics associated with the transition are essentially identical at all pressures and temperatures studied. The comparison between  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{Cl}$  is more clear for the isothermal pathway that is adopted for this presentation than for other paths.

† For both  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{Br}$ , the intensity of the LO component of the bending vibration of the  $\text{NH}_4^+$  ion,  $\nu_4(\text{F}_2)$ , increases as the crystal orders and becomes piezoelectric. The subsidiary peak,  $\nu'_4$ , on the high-frequency side of  $\nu_4$  disappears at the  $\text{NH}_4\text{Cl}$  "II"-IV and  $\text{NH}_4\text{Br}$  V-IV transitions respectively [12].

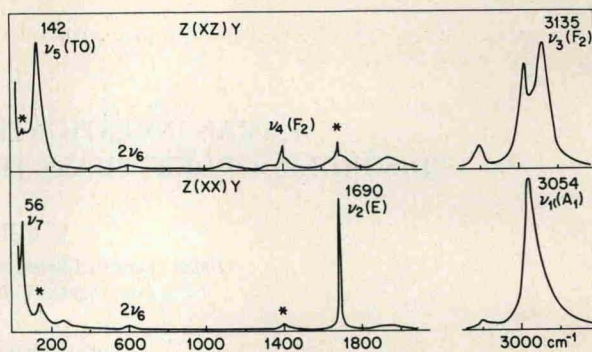


Fig. 1. Polarization spectra for "disordered"  $\text{NH}_4\text{Br}$  II (1 atm,  $296^\circ\text{K}$ ) in two scattering geometry. The directions of incident and scattered light are given outside the parentheses while the corresponding polarization are placed inside. The asterisks indicate the spillover of scattering from peaks active in other scattering geometry.

the well defined polarization of the spectra for both the internal and lattice modes; see fig. 1. This result is rather surprising; however, it is consistent with the depolarization factors measured by Couture and Mathieu in 1948 [13] and with recent polarization spectra for several low-frequency modes [14]. The observed Raman tensors for the fundamental modes of  $\text{NH}_4\text{Br}$  are those expected for the ordered structure ( $T_d^1$ ) [15]. The tensor elements for modes which become Raman inactive at the  $\text{NH}_4\text{Br}$  V-IV transition were also evaluated from the polarization spectra and are given in table 1.

Many features of the  $\text{NH}_4\text{Br}$  II polarization spectra are similar to features of the spectra of "disordered"  $\text{NH}_4\text{Cl}$  "II"; however, these phases differ significantly with respect to the number of Raman-active lattice modes and to the temperature and pressure dependences of the intensities of certain modes. For both phases, no unusual splittings of internal modes are resolved; and fairly large volume-dependent anharmonicities, as indicated by mode  $\gamma_i$ 's ( $= \delta \ln \nu / \delta \ln V$ ) are observed. Nevertheless, as the low-frequency spectra of  $\text{NH}_4\text{Br}$  II and  $\text{NH}_4\text{Cl}$  "II" in fig. 2 indicate, the bromide lacks a peak which corresponds to the strong peak on the low-energy side of  $\nu_5(\text{TO})$  of the  $\text{NH}_4\text{Cl}$  "II" spectrum. Also, there is no band in the  $\text{NH}_4\text{Cl}$  "II" spectrum which corresponds to the weak band in the  $\text{NH}_4\text{Br}$  II spectrum with off-diagonal components near  $78 \text{ cm}^{-1}$  at 1 atm and  $296^\circ\text{K}$ . (This  $78 \text{ cm}^{-1}$  band disappears, and a strong band appears on the



Table 1  
Wavenumbers and polarization characteristics of modes which become Raman inactive upon "disorder-order" phase transitions  
NH<sub>4</sub>Cl "II"-IV and NH<sub>4</sub>Br V-IV

NH <sub>4</sub> Cl (cm <sup>-1</sup> ) a)	NH <sub>4</sub> Br (cm <sup>-1</sup> ) a)	Assignment, intensity
95 ( $\alpha_{xx}$ )	56 ( $\alpha_{xx}$ )	$\nu_7$ , strong
119 b) ( $\alpha_{x3}$ )	90 ( $\alpha_{x3}$ )	weak
144 b) ( $\alpha_{x3}$ )	(in NH <sub>4</sub> Br V as a low energy shoulder: e.g., 176 cm <sup>-1</sup> at 296°K and 20 kbar)	strong
198 b) ( $\alpha_{x3}$ )	180 b) ( $\alpha_{x3}$ )	strong
350 ( $\alpha_{xx}$ , $\alpha_{x3}$ )	(in NH <sub>4</sub> Br V at low temperature, e.g., 340 cm <sup>-1</sup> at 195°K and 5.2 kbar)	$\nu_6$ , weak
<u>1440</u> c) ( $\alpha_{x3}$ )	<u>1470</u> ( $\alpha_{x3}$ )	$\nu_4$ , weak
d)		

a) Wavenumbers are given for 1 atm and 296°K.

b) Mode fitted to an uncoupled damped oscillator.

c) Underlined wavenumbers have large uncertainties ( $> \pm 10$  cm<sup>-1</sup>).

d) Another mode ( $\approx 310$  cm<sup>-1</sup>,  $\alpha_{xx}$ ) in NH<sub>4</sub>Cl which disappears around the transition point (1 atm) was not included in the table since its relation to the transition was not clear.

low-energy side of  $\nu_5$ (TO) at the NH<sub>4</sub>Br II-V transition. Thus, NH<sub>4</sub>Br V and NH<sub>4</sub>Cl "II" have the same number of corresponding lattice modes.) Furthermore,  $\nu_5$ (TO) and its high-energy shoulder in NH<sub>4</sub>Br II are not so sensitive to alteration of pressure or temperature as the corresponding bands of NH<sub>4</sub>Cl "II", whereas the pressure dependences of  $\nu_5$ (TO) and the two associated bands of the NH<sub>4</sub>Br V spectra are similar to the corresponding bands of NH<sub>4</sub>Cl "II". The very noticeable spectral characteristics of the NH<sub>4</sub>Br V-IV transition - the large intensity increase of  $\nu_5$ (TO) and large decrease in the number of Raman-active modes - are essentially identical to changes of the spectrum of the chloride at the NH<sub>4</sub>Cl "II"-IV transition (table 1). Thus, several striking similarities between the spectra of NH<sub>4</sub>Cl "II" and NH<sub>4</sub>Br V suggest that these phases - not NH<sub>4</sub>Cl "II" and NH<sub>4</sub>Br II - have similar structures.

### 3.2. Frequency shifts and NH<sub>4</sub>Br phase diagram

The frequencies of the majority of the vibrational modes of the ammonium halides increase as interatomic distances decrease. However, the magnitudes of the frequency shifts depend upon the particular mode and

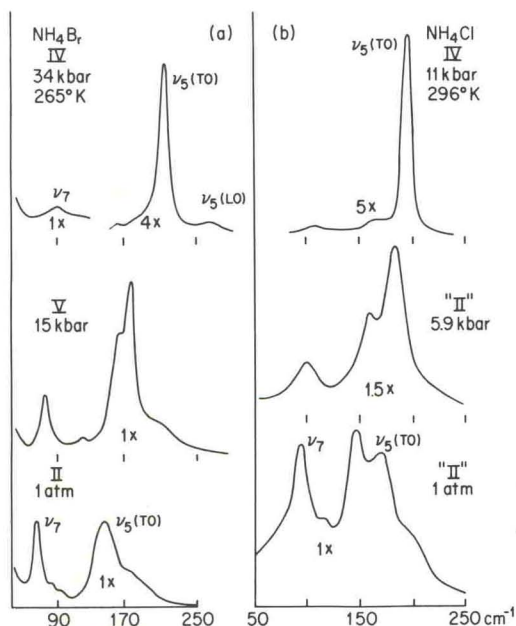


Fig. 2. (a) Low frequency Raman spectra ( $\alpha_{xx} + \alpha_{xy}$ ) of NH<sub>4</sub>Br II, V and IV. The pressure for the NH<sub>4</sub>Br II-IV phase transitions respectively at 265°K are 11 and 22 kbar. (b) Some spectral changes accompanying the high pressure "disorder-order" phase transition in NH<sub>4</sub>Cl at 296°K. The transition occurs between 9-10 kbar pressure in NH<sub>4</sub>Cl at this temperature. The similarities between the upper two spectra of NH<sub>4</sub>Cl and NH<sub>4</sub>Br should be observed.



are measures of the volume-dependent anharmonicities of the modes. These anharmonicities depend upon the phase of the halide; and, thus, relatively abrupt changes of the slopes of frequency–pressure isotherms accompany the phase transitions. The transition pressures for the  $\text{NH}_4\text{Br}$  II–V and  $\text{NH}_4\text{Br}$  V–IV boundaries in fig. 3 (open circles with error bars) were established from such slope-discontinuities of frequency–pressure isotherms. These transition points show smaller scatter than those obtained from the disappearance or appearance of Raman peaks. The linear slope for the  $\text{NH}_4\text{Br}$  II–V transition at high pressures is  $5.0 \pm 0.8^\circ\text{K kbar}^{-1}$ ; similar slope is noted for the  $\text{NH}_4\text{Br}$  V–IV phase boundary.

Additional information on the physical nature of  $\text{NH}_4\text{Br}$  II and V can be inferred by examination of the frequency shifts themselves. These shifts are most conveniently represented by mode Grüneisen constants,  $\gamma_i$ 's. Typical values for  $\text{NH}_4\text{Br}$  II and V at  $296^\circ\text{K}$  are: 3.3 and 0.75 ( $\gamma_7$ ); 3.2 and 1.2 ( $\gamma_5(\text{TO})$ ); and 0.75 and 0.46 ( $\gamma_6$ ) from overtone, respectively. The magnitude of  $\gamma_6$  for the librational mode in  $\text{NH}_4\text{Br}$  II and V indicates that this mode is fairly anharmonic. A part of this anharmonicity probably arises from the repulsive interaction between hydrogens on adjacent  $\text{NH}_4^+$  ions, in which case the decrease in  $\gamma_6$  at the  $\text{NH}_4\text{Br}$  II–V boundary suggests an ordering process. However, the relative change in  $\gamma_6$  here is not so large as at the  $\text{NH}_4\text{Cl}$  “II”–IV transition where the corresponding  $\gamma_6$ 's (from fundamental and overtone) are 1.3 and 0.29. That the  $\text{NH}_4\text{Br}$  II–V transition is an ordering process also is supported by the low-temperature elastic-constant measurements which indicate an entropy decrease [5]. The precise value of the entropy change or whether the entropy change is mostly vibrational or configurational is not known. The “average” structure of  $\text{NH}_4\text{Br}$  V is believed to be cubic and different from the ordered structure of  $\text{NH}_4\text{Br}$  IV [5].

The assignment and relationship between phases in  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{Cl}$  can best be considered in terms of the generalized  $\text{NH}_4\text{X}$  phase diagram [18] in fig. 4.  $\text{NH}_4\text{Cl}$  “II” is relabeled as  $\text{NH}_4\text{Cl}$  V for reasons cited above. It is reasonable that  $\text{NH}_4\text{Cl}$  “II” with smaller lattice constant should have the same structure as the high-pressure phase of  $\text{NH}_4\text{Br}$  V. This relabeling suggests the possible existence of another  $\text{NH}_4\text{Cl}$  phase at high temperatures. Bridgman's observation of a

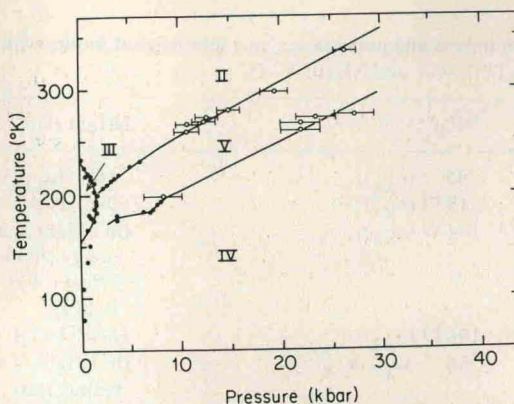


Fig. 3. Phase diagram for  $\text{NH}_4\text{Br}$ . Open circles with error bars represent literature values [5, 16–18].

weak transition at  $348^\circ\text{K}$  and 5 kbar supports the existence of such a phase [19]. Preliminary Raman studies of  $\text{NH}_4\text{Cl}$  also indicate a subtle change around  $355^\circ\text{K}$  and 8 kbar that also may be associated with this transition. The gradual nature and the weakness of the transition is indicated by the very small change in the slope of the frequency–pressure isotherm. Furthermore, in the lower-pressure phase of this transition,  $\nu_5(\text{TO})$  and its low-frequency shoulder can no longer be resolved.

### 3.3. Other observations

The present Raman studies show that the spectra of  $\text{NH}_4\text{Br}$  II, V and IV are closely related. The fundamental and many other peaks remaining basically the same throughout the three phases; however, the in-

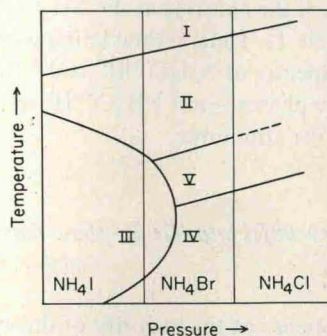


Fig. 4. Generalized phase diagram for  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{I}$ . The suggested II–V phase boundary for  $\text{NH}_4\text{Cl}$  is indicated by the dotted line (---).



tensities and numbers of lattice modes differ between phases. The ordered phase has the simplest spectrum. In the polarization spectra of "disordered"  $\text{NH}_4\text{Br}$  II (300°K and 1 atm), only a few modes are active for all polarizations of the incident light, and the spectrum does not appear to resemble the calculated one-phonon density of states [20]. In the polarization spectra of both "disordered"  $\text{NH}_4\text{Cl}$  "II" and  $\text{NH}_4\text{Br}$  II, the fundamental modes have Raman tensors expected for the ordered state. Many modes (table 1) in  $\text{NH}_4\text{Br}$  II,  $\text{NH}_4\text{Br}$  V and  $\text{NH}_4\text{Cl}$  "II" spectra have intensities comparable to the fundamentals but are only active in the "disordered" phase. The low-frequency modes at  $95\text{ cm}^{-1}$  in  $\text{NH}_4\text{Cl}$  and  $56\text{ cm}^{-1}$  in  $\text{NH}_4\text{Br}$  are believed to be "zone-edge" transverse acoustic modes [14, 21, 22]. The experimental dispersion curves for  $\text{NH}_4\text{Cl}$  at 78°K [23, 24] and the calculated one for  $\text{NH}_4\text{Br}$  [20] suggest that other modes listed in table I are also "zone-edge" modes.

#### 4. Summary

The experimental results described above indicate some of the complexity of the Raman spectra of  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{Cl}$ . The results on the polarization characteristics, implied order of  $\text{NH}_4\text{Cl}$  "II", multiple phase transition, and presence of many strong "zone-edge" modes are difficult to explain in the context of present theoretical understanding of crystals with orientational disorder [21, 22, 25]. The results suggest some order even in  $\text{NH}_4\text{Br}$  II, which may be only correlated reorientations. The estimated reorientation rate ( $10^{11}\text{ sec}^{-1}$  at 300°K) of the  $\text{NH}_4^+$  ion is much longer than the duration of the Raman excitation process [26, 27]. This can give the appearance of order. Recent diffuse neutron and X-ray studies also indicate the existence of spatial correlation in both  $\text{NH}_4\text{Br}$  and  $\text{NH}_4\text{Cl}$  [28–30]. Diffuse neutron peaks have been found in  $\text{NH}_4\text{Br}$  II at position which become superstructure reflection in  $\text{NH}_4\text{Br}$  III. Correlated displacements of the  $\text{Br}^-$  ions in  $\text{NH}_4\text{Br}$  II have also been detected in the diffuse X-ray studies. Both the large thermal factors for  $\text{Br}^-$  and  $\text{Cl}^-$  ion in neutron diffraction study of the "disordered" phase [1–3] and the occurrence of correlated displacement of the  $\text{Br}^-$  ion suggest doubling of CsCl-like structure with antiparallel orientations of the adjacent  $\text{NH}_4^+$  ions in

$\text{NH}_4\text{Br}$  II,  $\text{NH}_4\text{Br}$  V and  $\text{NH}_4\text{Cl}$  "II". In such a case, zone-edge modes can become allowed zone center modes [31]. The difference between  $\text{NH}_4\text{Br}$  II and V ( $\text{NH}_4\text{Cl}$  "II") might involve the arrangement of the doubled cell, with the arrangement of  $\text{NH}_4\text{Br}$  V involving a smaller amount of H–H repulsion between adjacent  $\text{NH}_4^+$  ions.

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