

Table 1
Wavenumbers and polarization characteristics of modes which become Raman inactive upon "disorder-order" phase transitions
NH₄Cl "II"-IV and NH₄Br V-IV

NH ₄ Cl (cm ⁻¹) a)	NH ₄ Br (cm ⁻¹) a)	Assignment, intensity
95 (α_{xx})	56 (α_{xx})	ν_7 , strong
119 b) (α_{x3})	90 (α_{x3})	weak
144 b) (α_{x3})	(in NH ₄ Br V as a low energy shoulder: e.g., 176 cm ⁻¹ at 296°K and 20 kbar)	strong
198 b) (α_{x3})	180 b) (α_{x3})	strong
350 (α_{xx} , α_{x3})	(in NH ₄ Br V at low temperature, e.g., 340 cm ⁻¹ at 195°K and 5.2 kbar)	ν_6 , weak
<u>1440</u> c) (α_{x3})	<u>1470</u> (α_{x3})	ν_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⁻¹).

d) Another mode (≈ 310 cm⁻¹, α_{xx}) in NH₄Cl 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 ν_5 (TO) at the NH₄Br II-V transition. Thus, NH₄Br V and NH₄Cl "II" have the same number of corresponding lattice modes.) Furthermore, ν_5 (TO) and its high-energy shoulder in NH₄Br II are not so sensitive to alteration of pressure or temperature as the corresponding bands of NH₄Cl "II", whereas the pressure dependences of ν_5 (TO) and the two associated bands of the NH₄Br V spectra are similar to the corresponding bands of NH₄Cl "II". The very noticeable spectral characteristics of the NH₄Br V-IV transition - the large intensity increase of ν_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 NH₄Cl "II"-IV transition (table 1). Thus, several striking similarities between the spectra of NH₄Cl "II" and NH₄Br V suggest that these phases - not NH₄Cl "II" and NH₄Br II - have similar structures.

3.2. Frequency shifts and NH₄Br 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

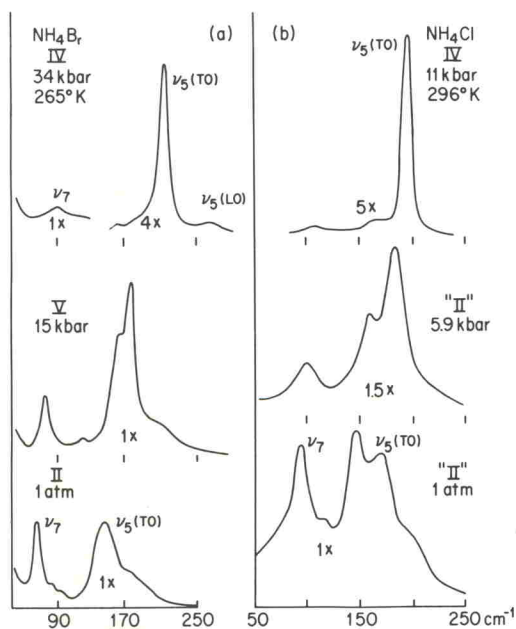


Fig. 2. (a) Low frequency Raman spectra ($\alpha_{xx} + \alpha_{xy}$) of NH₄Br II, V and IV. The pressure for the NH₄Br II-IV phase transitions respectively at 265°K are 11 and 22 kbar. (b) Some spectral changes accompanying the high pressure "disorder-order" phase transition in NH₄Cl at 296°K. The transition occurs between 9-10 kbar pressure in NH₄Cl at this temperature. The similarities between the upper two spectra of NH₄Cl and NH₄Br 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 NH_4Br II–V and NH_4Br 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 NH_4Br II–V transition at high pressures is $5.0 \pm 0.8^\circ\text{K kbar}^{-1}$; similar slope is noted for the NH_4Br V–IV phase boundary.

Additional information on the physical nature of NH_4Br II and V can be inferred by examination of the frequency shifts themselves. These shifts are most conveniently represented by mode Grüneisen constants, γ_i 's. Typical values for NH_4Br II and V at 296°K are: 3.3 and 0.75 (γ_7); 3.2 and 1.2 ($\gamma_5(\text{TO})$); and 0.75 and 0.46 (γ_6) from overtone, respectively. The magnitude of γ_6 for the librational mode in NH_4Br 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 NH_4^+ ions, in which case the decrease in γ_6 at the NH_4Br II–V boundary suggests an ordering process. However, the relative change in γ_6 here is not so large as at the NH_4Cl “II”–IV transition where the corresponding γ_6 's (from fundamental and overtone) are 1.3 and 0.29. That the NH_4Br 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 NH_4Br V is believed to be cubic and different from the ordered structure of NH_4Br IV [5].

The assignment and relationship between phases in NH_4Br and NH_4Cl can best be considered in terms of the generalized NH_4X phase diagram [18] in fig. 4. NH_4Cl “II” is relabeled as NH_4Cl V for reasons cited above. It is reasonable that NH_4Cl “II” with smaller lattice constant should have the same structure as the high-pressure phase of NH_4Br V. This relabeling suggests the possible existence of another NH_4Cl phase at high temperatures. Bridgman's observation of a

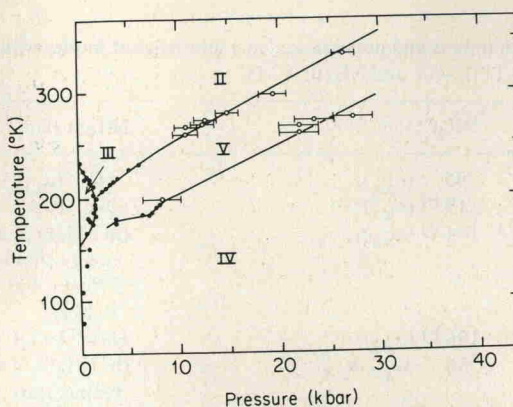


Fig. 3. Phase diagram for NH_4Br . Open circles with error bars represent literature values [5, 16–18].

weak transition at 348°K and 5 kbar supports the existence of such a phase [19]. Preliminary Raman studies of NH_4Cl also indicate a subtle change around 355°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 NH_4Br II, V and IV are closely related. The fundamental and many other peaks remaining basically the same throughout the three phases; however, the in-

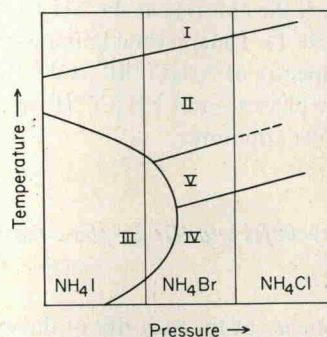


Fig. 4. Generalized phase diagram for NH_4Cl , NH_4Br and NH_4I . The suggested II–V phase boundary for NH_4Cl is indicated by the dotted line (---).