

Table 1. Modes which become Raman inactive upon 'cooperative disorder-order' transition in NH_4Cl and NH_4Br .

NH_4Cl (cm^{-1}) ^a	NH_4Br (cm^{-1}) ^a
96 (ν_7) [Z(XX)Y]	56 (ν_7) [Z(XX)Y]
119 ^b [Z(YZ)Y, Z(XZ)Y]	80 [Z(YZ)Y, Z(XZ)Y]
144 ^b [Z(YZ)Y, Z(XZ)Y]	141 ^b [Z(YZ)Y, Z(XZ)Y] (low energy shoulder appearing on this peak in phase V)
198 ^b [Z(YZ)Y, Z(XZ)Y]	180 ^b [Z(YZ)Y, Z(XZ)Y] (found at low T in phase V weak, broad, unresolved)
310 ^c [Z(XX)Y]	
350 (ν_6) [Z(XX)Y, Z(XZ)Y, Z(XZ)Y]	

^a Frequencies are given at 1 atm and 296 K. [] Indicate scattering geometry in which the mode is Raman active.

^b Modes fitted to an uncoupled damped harmonic oscillator.

^c Frequency has a large uncertainty.

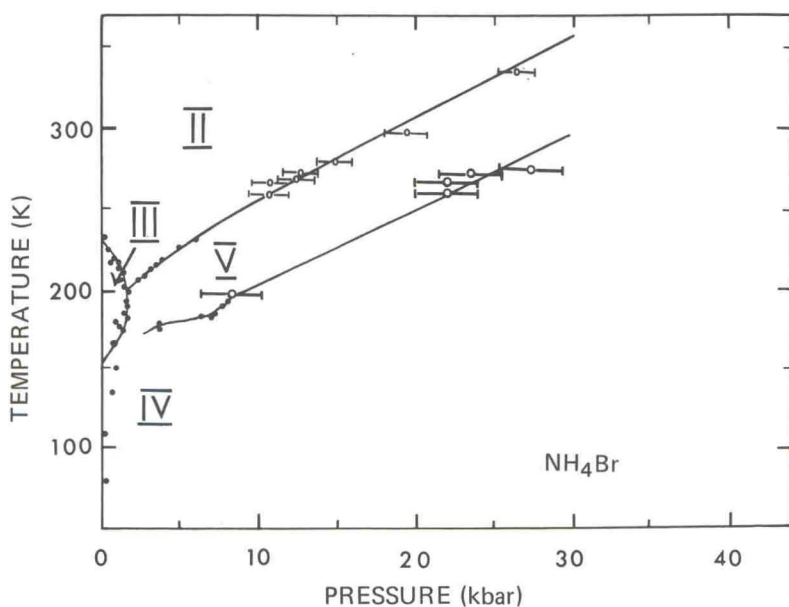


Fig. 4. Phase diagram for NH_4Br . Open circles with error bars represent data obtained in the present study; solid circles represent the literature values (ref. 4).

are 1.30 and 0.29 for the disordered and the ordered phase respectively. The magnitude of γ_i for the disordered phase indicates that there is a fair amount of anharmonicity associated with the librational mode. This anharmonicity probably arises from repulsive interactions between hydrogens on adjacent NH_4^+ ions. The large frequency increase in ν_6 as the transition temperature is approached isobarically from room temperature cannot

be accounted for with the room temperature Grüneisen constant. That is the self-energy or explicitly temperature dependent shift is larger than the volume shift.

The phase diagram⁴ for NH_4Br is shown in Fig. 4. Both II–V and V–IV transitions are disorder-order transitions with slopes of 5.0 ± 0.8 and 5 ± 1 K/kbar respectively. Experimental evidence for identifying V–IV transition as the cooperative disorder-order phase transition consists in the fact that at this transition, the Raman spectrum shows the same characteristic changes as at the disorder-order transition in NH_4Cl . This is true in the change of the number of Raman active peaks (Table 1), intensity increase of $\nu_5(\text{TO})$ and decrease of the Grüneisen constants upon ordering. The II–V transition is accompanied by a decrease of the Grüneisen constants, with typical changes being: 3.2 to 0.75 (ν_7); 0.72 to 0.46 ($2\nu_6$); and 0.036 to 0.003 ($\nu_2(E)$). These decreases of the γ 's suggest that there must be some type of ordering which leads to a decrease in anharmonicity. This is especially true for the librational overtone ($2\nu_6$) where the orientation-dependent part of the force constant between the NH_4^+ ions would be expected to decrease upon ordering.

The interesting implication of the studies on NH_4Br is that both NH_4Br V and NH_4Cl II are ordered. Also, the possible existence of another high temperature phase in NH_4Cl is suggested; and this aspect is now being explored.

The present Raman data give no indication of a disorder-order transition mechanism involving a soft or other low-energy mode. However, the experimental data indicate the presence of volume- and temperature-dependent anharmonicity associated with the librational mode in the disordered state. There are also modes coupled to the translation motion of the NH_4^+ ion in the disordered phase, but their role in the phase transition is not known.

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