

Phase Diagrams of NH_4I and NH_4Br by Raman
Spectroscopy under High Pressure

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We report on the Raman spectra of the three CsCl-type phases of NH_4Br and NH_4I which differ in the orientations of the NH_4 -tetrahedra. The two possible orientations are randomly occupied in phase II (O_h -symmetry). The tetrahedra are all oriented parallel to each other in phase IV (T_d -symmetry). In the tetragonal phase III neighbouring tetrahedra are parallel oriented along the tetragonal axis and antiparallel in the planes perpendicular to this axis (D_{4h} -symmetry). The Raman spectra of the three phases differ drastically. In phase II all modes are more or less Raman active by disorder. The D_{4h} -symmetry of phase III bisects the B.Z. Only M-point modes and the libration (ν_6) can be observed in this phase. In the T_d -symmetry of phase IV the $\text{TO}(\Gamma)$ -mode is strongly active but the intensity of the other bands is weak ($\text{LO}(\Gamma)$ and $\text{TA}(\text{M})$). The $\text{TA}(\text{M})$ band is due to the residual disorder. The libration ν_6 is forbidden by symmetry but the second harmonic $2 \cdot \nu_6$ is allowed. In the phase diagram for NH_4I derived from these measurements the triple point is found at lower pressure than in the diagrams of Zlunitsyn¹⁾ and of Stevenson²⁾.

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Special attention was given to the possible occurrence of a fifth phase in NH_4Br as reported by Garland and Young³⁾ and more recently by Ebisuzaki⁴⁾ and by Wang and Wright⁵⁾. We calculated the Raman spectra of phase IV and of the two suggested structures of phase V³⁾ using a method published recently⁶⁾. Comparison of the calculated spectra with our measurements and with those published previously⁴⁾⁵⁾ shows that in the P,T-range where phase V was expected, actually only phase IV was observed.

The Raman scattering experiment was performed in a high pressure He-cell kept in a temperature regulated cryostat. Near the triple point in NH_4I a hysteresis between $3^\circ - 4^\circ \text{K}$ and 100 - 200 bar was found.

References:

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Fig. 1

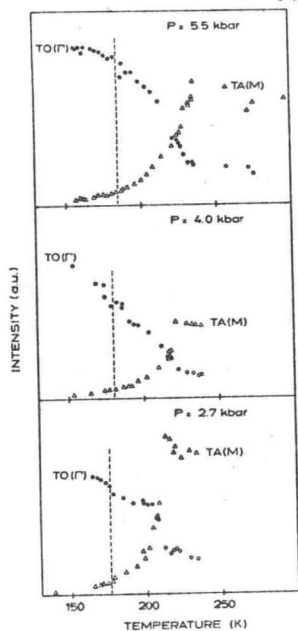
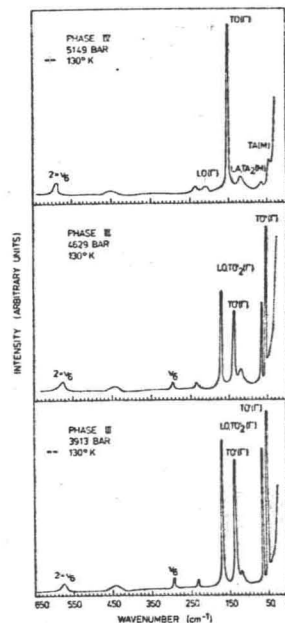


Fig. 2

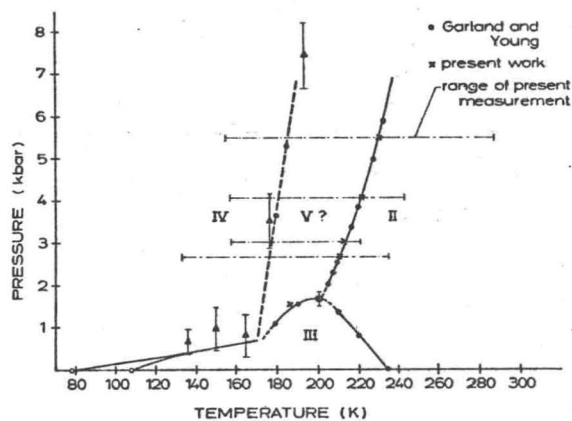


Fig. 3

Fig. 1 Raman spectra of NH_4I at 3 different pressures.

Fig. 2 The change of scattering intensities of two modes in NH_4Br . The dashed vertical line shows the expected $\text{IV} \rightleftharpoons \text{V}$ phase transition which was not observed.

Fig. 3 Phase diagram of NH_4Br with present data (x) and range of measurement (—).