

intensities and numbers of lattice modes differ between phases. The ordered phase has the simplest spectrum. In the polarization spectra of "disordered" NH_4Br 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" NH_4Cl "II" and NH_4Br II, the fundamental modes have Raman tensors expected for the ordered state. Many modes (table 1) in NH_4Br II, NH_4Br V and NH_4Cl "II" spectra have intensities comparable to the fundamentals but are only active in the "disordered" phase. The low-frequency modes at 95 cm^{-1} in NH_4Cl and 56 cm^{-1} in NH_4Br are believed to be "zone-edge" transverse acoustic modes [14, 21, 22]. The experimental dispersion curves for NH_4Cl at 78°K [23, 24] and the calculated one for NH_4Br [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 NH_4Br and NH_4Cl . The results on the polarization characteristics, implied order of NH_4Cl "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 NH_4Br II, which may be only correlated reorientations. The estimated reorientation rate (10^{11} sec^{-1} at 300°K) of the 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 NH_4Br and NH_4Cl [28–30]. Diffuse neutron peaks have been found in NH_4Br II at position which become superstructure reflection in NH_4Br III. Correlated displacements of the Br^- ions in NH_4Br II have also been detected in the diffuse X-ray studies. Both the large thermal factors for Br^- and Cl^- ion in neutron diffraction study of the "disordered" phase [1–3] and the occurrence of correlated displacement of the Br^- ion suggest doubling of CsCl-like structure with antiparallel orientations of the adjacent NH_4^+ ions in

NH_4Br II, NH_4Br V and NH_4Cl "II". In such a case, zone-edge modes can become allowed zone center modes [31]. The difference between NH_4Br II and V (NH_4Cl "II") might involve the arrangement of the doubled cell, with the arrangement of NH_4Br V involving a smaller amount of H–H repulsion between adjacent NH_4^+ ions.

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