Phase Diagrams of NH_4I and NH_4Br by Raman Spectroscopyunder High Pressure

W. Gebhardt, T. Geisel, H.D. Hochheimer, E. Spanner
University of Regensburg
F.R.Germany

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 TO(Γ)-mode is strongly active but the intensity of the other bands is weak (LO(Γ) and TA(M)). The TA(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 Zlunitsyn[1] and of Stevenson[2].