

18. RAMAN SCATTERING INVESTIGATION OF THE COOPERATIVE ORDER-DISORDER PHASE TRANSITION IN AMMONIUM CHLORIDE AND AMMONIUM BROMIDE

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INTRODUCTION

Extensive studies on NH_4Cl show a strong volume dependence of the temperature for the cooperative order-disorder transition.¹ This suggests a relationship between volume and the ordering process of the NH_4^+ ion. Thus a knowledge of the volume and temperature dependence of the vibrational spectra would be most useful for a better understanding of this transition.

This chapter reports the most recent results on the volume and temperature dependence of the libration and translational motion of the NH_4^+ ion and changes of Raman activity due to the ordering process. The existence of the direct cooperative phase transition in NH_4Br also is reported.

EXPERIMENTAL

At low temperatures, both NH_4Cl and NH_4Br have ordered cubic phases in which the NH_4^+ ions have parallel orientations. The fundamental modes and their representations are

$$\nu_1(A_1) + \nu_2(E) + \nu_3(F_2) + \nu_4(F_2)$$

[internal modes of the NH_4^+ ion] and

$$\nu_5(F_2) + \nu_6(F_1)$$

[lattice modes]. Only the lattice modes are of immediate interest. These are the translational motion of the NH_4^+ against the Cl sublattice, ν_5 , and the librational motion about the four-fold axes of the cube, ν_6 . In the ordered phase, the librational mode is the only Raman-inactive fundamental, and it must be observed as a two-phonon process. However, in the disordered phase, NH_4Cl shows a complex spectrum with all fundamentals being Raman active.

Figure 1 shows the polarization spectra of the lattice modes for several scattering geometries of the disordered phase of NH_4Cl (296 K, 1 atm). The internal modes also are