Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 89, Number 5, October 1980, pp. 449–454.

Infrared spectroscopic study of the rotation of the NH_4^+ ion in ammonium halides*

SOMNATH GANGULY
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

MS received 16 June 1980

Abstract. Infrared correlation functions have been obtained from the analysis of band shapes of the 1400 cm^{-1} bending mode of NH_4Cl, NH_4Br and NH_4I in both the Pm3m and Fm3m phases. The NH_4^+ ion seems to undergo relatively free rotation in the high temperature Fm3m phases of these halides.

Keywords. Ammonium halides ; phase transitions ; infrared correlation functions.

1. Introduction

NH_4Cl, NH_4Br and NH_4I undergo a low temperature λ type transition followed by a transition at a higher temperature when the symmetry changes from CsCl type (Pm3m) to NaCl type (Fm3m) (Rao and Natarajan, 1972). Thermodynamic data on the transitions are shown in table 1. The λ transition has been shown to be of the order-disorder type (Frenkel 1935; Levy and Peterson 1952, 1953a) above the λ transition, the NH_4^+ tetrahedra are randomly distributed between two possible orientations. NH_4^+ ions behave as torsional oscillators, both, above and below the λ transition (Wagner and Hornig 1950). Above the first order Pm3m-Fm3m transition, however, the NH_4^+ ions appear to show relatively free rotation (Leung *et al* 1968). Thus, the NH_4^+ ion in NH_4I rotates freely about the hydrogen bond formed by I^- in the high temperature phase (Plumb and Hornig 1953). Rotation of the NH_4^+ ion has been examined by NMR (Gutowsky *et al* 1954; Woessner and Snowden, 1967) neutron scattering and other techniques (Leung *et al* 1968; Levy and Peterson 1953b; Wagner and Hornig 1950; Krishnan 1948) generally in the low temperature phases. We have investigated the rotation of NH_4^+ ion in these ammonium halides in both the Pm3m and Fm3m phases by the method of infrared correlation functions (Gordon 1965).

* Communication No. 73 from the Solid State and Structural Chemistry Unit.