

RAMAN SPECTRUM OF AMMONIUM CHLORIDE AT HIGH PRESSURES *

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Received 5 May 1969

Raman spectra of single crystals of ammonium chloride have been studied to 40 kbar at room temperature. Effects of pressure on the frequencies of the Reststrahlen, librational, and internal modes are described, and the origins of these shifts are discussed.

1. INTRODUCTION

Room temperature, Raman spectra of single crystals of ammonium chloride have been studied to 40 kbar. This halide is an interesting candidate for such an investigation owing to the presence in its Raman spectrum of lines associated with many lattice and internal vibrational normal modes [1], to its large compressibility [2, 3], and to phenomena associated with an order-disorder transition that occurs at about 10 kbar at room temperature [4]. A few of the salient features of these spectra will be outlined in this communication including the effects of pressure on the Reststrahlen frequency (ν_5), the librational binary overtone frequency (ν_6), and the frequencies of internal modes of the ammonium ion ($\nu_1 - \nu_4$) [5].

2. EXPERIMENTAL

The technique for Raman spectroscopy of crystals under high pressures used in this work has been described elsewhere [6]. Recent calibration studies in this laboratory confirm that the pressure of the sample is about 20% less than the "pressure" calculated from the applied load and the area of the piston that has been used in our earlier work. The revised pressure scale, that will be reported elsewhere [7], is used in this work; it is probably accurate within ± 2 kbar

* The support provided by Contract AT(11-1)34, Project 88 with the U.S. Atomic Energy Commission is gratefully acknowledged.

‡ Contribution No. 2351.

from 5 to 40 kbar. Single crystals of NH_4Cl were grown from saturated aqueous solution of recrystallized NH_4Cl containing urea.

3. RESTSTRAHLEN FREQUENCY

In fig. 1, the Reststrahlen frequency, representing the vibration of the NH_4^+ sublattice against the Cl^- sublattice, is plotted as a function of pressure. The plot can be roughly divided into two regions; this division is typical of the shifts of almost all of the vibrational modes of NH_4Cl . In the disordered phase below 10 kbar, the shift can be fitted to a straight line of slope ($\Delta\nu_5/\Delta P$) of $+2.65 \text{ cm}^{-1}\text{kbar}^{-1}$. This slope is of similar magnitude to those of the transverse optic modes of alkali halides [8], and it is among the largest known for lattice or internal vibrations, being two to twenty times larger than those of the in-

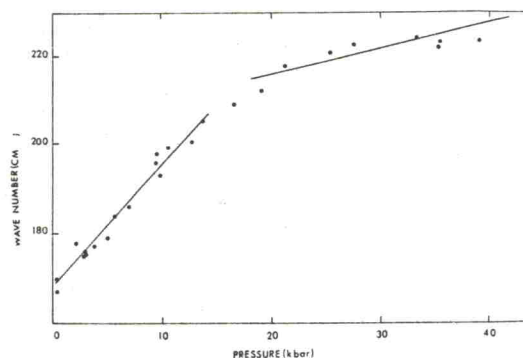


Fig. 1. A plot of ν_5 versus pressure. The slopes of the solid lines are $+2.65$ and $+0.61 \text{ cm}^{-1}\text{kbar}^{-1}$.