

RAMAN INVESTIGATION OF HIGH-PRESSURE "DISORDER-ORDER" PHASE TRANSITIONS IN NH_4Br AND NH_4Cl *

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NH_4Br II-V and NH_4Br V-IV phase transitions and the associated Raman spectra are reported. The spectrum of NH_4Br V and the changes accompanying the NH_4Br V-IV transition are shown to be similar to the spectrum of "disordered" NH_4Cl "II" and to the changes at "disorder-order" NH_4Cl "II"-IV transition.

1. Introduction

NH_4Cl and NH_4Br are two of the more extensively studied ammonium halides. Although they have several similar solid phases, the reported "disorder-order" phase transitions of the two systems are surprisingly different [1-4]. Only one "cooperative disorder-order" phase transition ("II"-IV) has been reported for NH_4Cl , while at least four such transitions between several ordered and disordered phases have been reported for NH_4Br . At atmospheric pressure, for example, three solid phases of NH_4Br (NH_4Br II, III, and IV) are known which have CsCl-like basic structural units; NH_4Br II is "disordered", while NH_4Br III (D_{4h}^7) and NH_4Br IV (T_d^1) are ordered. A high-pressure phase (NH_4Br V) also has been reported [5], and the phase boundaries between NH_4Br V and NH_4Br II, III and IV have been determined to 7 kbar; but no detailed spectroscopic or structural evidence has been given about NH_4Br V or about the associated high-pressure phase transitions [6] which would establish the structural relationship between NH_4Br V and other phases of the ammonium halides.

This paper reports the results of studies by Raman spectroscopy of the nature of the NH_4Br II-V and NH_4Br V-IV phase transitions and on the character

of the structure of NH_4Br V in relation to other ammonium halide phases. The spectroscopic evidence about NH_4Br described herein, when compared with similar results about the "disorder-order" transformation of NH_4Cl at high pressures, suggests that the similarities between NH_4Br and NH_4Cl are much closer than previously supposed. The Raman spectrum of NH_4Br V and the changes of the Raman spectrum of NH_4Br which accompany the NH_4Br V-IV transition are remarkably similar to the spectrum of "disordered" NH_4Cl "II" and to the changes at the "cooperative disorder-order" NH_4Cl "II"-IV transition. This correspondence between NH_4Br V and "disordered" NH_4Cl "II" implies that there is a difference between the degrees of order of NH_4Cl "II" and NH_4Br II such that the chloride is more ordered. These results also raise questions as to whether a high-temperature phase of NH_4Cl exists which corresponds more closely to NH_4Br II than does NH_4Cl "II"; and preliminary results are reported which indicate a subtle change of the Raman spectra of NH_4Cl occurs at about 8 kbar and 355°K which may correspond to the NH_4Br II-V transition.

2. Experimental

The variable-temperature, high-pressure optical cell and its calibration have been described previously [7].

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One unfortunate limitation of the cell is that polarization studies are not possible due to the highly-strained state of the windows. NH_4Cl crystals were grown by vapor deposition which avoids formation of an eutetic ($\text{NH}_4\text{Cl} : \text{H}_2\text{O}$ at 257.8°K) [8,9]. Solution-grown crystals of NH_4Br were used since none were grown successfully from the vapor phase. These bromide crystals were carefully dried for a long time under vacuum.

3. Results

3.1. The spectra and identification of NH_4Br V

This discussion of the spectral characteristics of NH_4Br phases proceeds from the "disordered" NH_4Br II, which is stable at atmospheric pressure and temperatures near 300°K , to NH_4Br V and NH_4Br IV, which can be produced by isothermal compression of NH_4Br II at, e.g., 265°K . These NH_4Br results will be compared with spectral characteristics of the NH_4Cl phases; especial attention will be paid to differences between the numbers and intensities of the Raman-active modes of the various phases and to changes of the anharmonicities of the modes that accompany the phase transformations*. Although spectra of the internal† and lattice modes change with pressure and with temperature, the largest changes occur for the low-frequency modes; and only these changes are discussed here.

An interesting feature of "disordered" NH_4Br II is

* Except that the "cooperative order-disorder" phase transition of NH_4Cl is sharp – with a significant volume discontinuity and distinct change of the frequency of $\nu_5(\text{TO})$, for example – at 1 atm (242.6°K) and is very gradual at higher pressures (e.g., 10 kbar, 300°K) (preliminary results are given in ref. [10], see also ref. [11]), the spectral characteristics associated with the transition are essentially identical at all pressures and temperatures studied. The comparison between NH_4Br and NH_4Cl is more clear for the isothermal pathway that is adopted for this presentation than for other paths.

† For both NH_4Cl and NH_4Br , the intensity of the LO component of the bending vibration of the NH_4^+ ion, $\nu_4(\text{F}_2)$, increases as the crystal orders and becomes piezoelectric. The subsidiary peak, ν'_4 , on the high-frequency side of ν_4 disappears at the NH_4Cl "II"–IV and NH_4Br V–IV transitions respectively [12].

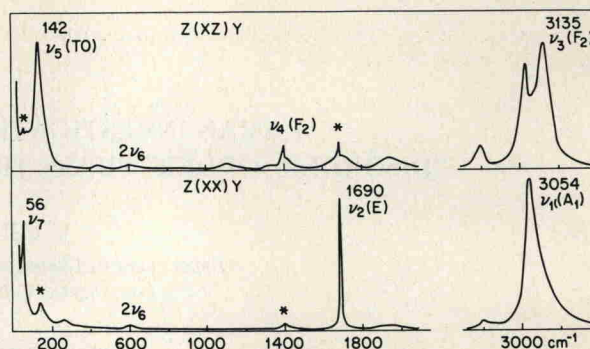


Fig. 1. Polarization spectra for "disordered" NH_4Br II (1 atm, 296°K) in two scattering geometry. The directions of incident and scattered light are given outside the parentheses while the corresponding polarization are placed inside. The asterisks indicate the spillover of scattering from peaks active in other scattering geometry.

the well defined polarization of the spectra for both the internal and lattice modes; see fig. 1. This result is rather surprising; however, it is consistent with the depolarization factors measured by Couture and Mathieu in 1948 [13] and with recent polarization spectra for several low-frequency modes [14]. The observed Raman tensors for the fundamental modes of NH_4Br are those expected for the ordered structure (T_d^1) [15]. The tensor elements for modes which become Raman inactive at the NH_4Br V–IV transition were also evaluated from the polarization spectra and are given in table 1.

Many features of the NH_4Br II polarization spectra are similar to features of the spectra of "disordered" NH_4Cl "II"; however, these phases differ significantly with respect to the number of Raman-active lattice modes and to the temperature and pressure dependences of the intensities of certain modes. For both phases, no unusual splittings of internal modes are resolved; and fairly large volume-dependent anharmonicities, as indicated by mode γ_i 's ($= \delta \ln \nu / \delta \ln V$) are observed. Nevertheless, as the low-frequency spectra of NH_4Br II and NH_4Cl "II" in fig. 2 indicate, the bromide lacks a peak which corresponds to the strong peak on the low-energy side of $\nu_5(\text{TO})$ of the NH_4Cl "II" spectrum. Also, there is no band in the NH_4Cl "II" spectrum which corresponds to the weak band in the NH_4Br II spectrum with off-diagonal components near 78 cm^{-1} at 1 atm and 296°K . (This 78 cm^{-1} band disappears, and a strong band appears on the