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VARIATION OF THE RAMAN FREQUENCY OF A SOFT MODE WITH THE PRESSURE (20 ^{O}C) FOR THE PHASE TRANSITIONS IN NH_4F

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ABSTRACT

The Raman frequency of a soft mode (238 cm^{-1}) is analyzed as a function of pressure at 20 ^{o}C for NH_4F using the experimental data from the literature. This analysis is performed for the pressure dependence of the Raman frequency shifts $(1/\nu)(\partial\nu/\partial P)_T$ of the soft mode close to the I - III, III - V and V – VI transitions in NH_4F. The frequency shifts increase as the pressure increases toward the phase transitions at T = 20 ^{o}C (293 K) in this ammonium structure. From the frequency shifts of the soft mode studied, the pressure dependence of the isothermal compressibility is predicted through the mode Grüneisen parameter. Our calculated isothermal compressibility can be compared with the experimental measurements.

Keywords: Raman frequency. Soft mode. Phase Transitions. NH_4F

1. INTRODUCTION

Phase transitions in molecular crystals under the temperature, pressure and concentration can be investigated spectroscopically. Experimental measurements of the spectroscopic parameters (frequency, intensity and bandwith) can be performed using various spectroscopic techniques such as Raman, infrared, NMR (nuclear magnetic resonance) etc. close to the phase transitions in molecular crystals. Phase diagrams of those crystalline systems which exhibit phase transitions, can also be obtained spectroscopically. Using various theoretical models, the observed spectra can be interpreted and the phase transitions in molecular crystals can be explained. This then provides to identify the molecular crystals for their technological applications.

In this study, we give as an example one of those molecular crystals, namely, ammonium fluoride (NH_4F) within the ammonium halide structures. All the ammonium halides have the NaCl structure. Experimentally, at room temperature and atmospheric pressure, only NH_4I crystallizes in this structure while NH_4F has the ZnO (wurtzite) structure and, NH_4Cl and NH_4Br occur in the CsCl structure [1]. The CsCl phases have the tetragonal NH_4^+ ions orientated randomly between the two equivalent positions in the unit cell, whereas in the ferroordered phase (below T_C) the NH_4^+ ions are parallel to each other [2]. In the ZnO (wurtzite) structure of NH_4F, hydrogens in the NH_4^+ ion are taken to be oriented towards the four nearest anions with no orientational disorder, which occurs at 0 kbar and 300 K with the nearest neighbour distance of 2.707 Å (experimental) and 2.685 Å calculated using the distributed charge model [1]. Experimentally, it was found that ZnO (wurtzite) structure transforms into the CsCl structure in NH_4F at 13.1 kbar at 100 ^{o}C [3, 4]. Its T – P phase diagram was obtained some years ago [4].

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Ammonium fluoride (NH_4F) exhibits various phases (I, II, III, IV, V and VI) as obtained experimentally in the temperature - pressure (T-P) phase diagram up to 200 kbar [5], as we have also calculated [6] previously using the mean field theory.

In NH_4F, I-II phase transition occurs at 3.6 kbar at room temperature, which was obtained by the measurements of compressibility [3]. As the pressure increases to 11.5 kbar at 25 ^oC, II-III transition occurs in NH_4F, which was also obtained in earlier experiments [7]. It was shown that at 100 K and 1 bar, there were three possible phases at low temperatures [8]. From the measurements of the Raman spectra at 20 ^oC up to 20 kbar, two new phases of V and VI have been observed at 15 and 143 kbar, respectively [5].

The crystal structure of phase I was determined as a wurtzite – like structure, II an unknown one and III a distorted CsCl – like structure [9, 10], as also pointed out previously [5]. In recent years, the structures of the phases of NH_4F have been identified according to a different type of ordering of the ammonium halides [11]. Phase I with the space group $P6_3mc$ transforms into phase II which has a complicated rhombohedral structure containing 24 molecules in a hexagonal unit cell with the space group R3c [11]. At P=1.15 GPa, transition occurs from phase II to an ordered cubic phase III [11] in NH_4F. It has been pointed out that the structure of phase II has stronger hydrogen bonds N-H-F than the I and III phases of NH_4F [12].

Experimental studies have been conducted for NH4F. From the resistivity measurements, the transition from high-resistance state to low-resistance state has been obtained in ammonium halides, in particular, at 42 GPa for NH_4F [13]. Also, high pressure induced phase transition dynamics in ammonium halides (at about 40 GPa in NH_4F) has been investigated experimentally [14].

The Raman spectra of NH_4F were obtained for different lattice modes at 1 bar at various temperatures for the phases I and II [15]. In particular, peaks at 84 cm^{-1}, 125 cm^{-1}, two strong peaks at 244 cm^{-1} and 252 cm^{-1} with a broad band at 250 – 250 cm^{-1} were obtained at 1 bar and -170 ^oC in phase I of NH_4F [15]. The Raman spectra of phases I and II of NH_4F were also obtained, in particular, a strong peak at 238 cm^{-1} and at 243 cm^{-1} [16]. The order-disorder transition in ammonium fluoride at high pressures and room temperature has also been studied experimentally and the Raman frequencies of the 238 cm^{-1} mode have been measured as a function of pressure up to 200 kbar [5].

From the change of the Raman frequency of 238 cm^{-1} with the pressure, it has been found that the phase transition from I to II occurs at 3.6 ± 0.5 kbar and the sample becomes transparent in NH_4F [5]. At 25 ^oC and 11.5 kbar, transparency of the sample sharply increases and the main Raman peak disappears, which indicate the existence of phase III in NH_4F, as pointed out previously from the Raman measurements [5]. As the pressure increases to 15 kbar, the transparency of the sample suddenly decreases with the Raman peak shifted to 235 cm^{-1}, which also indicates the existence of phase V in NH_4F and finally at very high pressure of 143 kbar the Raman active optic mode (238 cm^{-1}) softens giving rise to a new phase VI, as observed experimentally [5]. Behaviour of this optic mode (TO) and also the vibrational mode (L) has been observed in relation to the ammonium ion accompanying orientational phase transitions at pressures up to 4.7 GPa in NH_4F by inelastic incoherent neutron scattering [12].

In order to investigate the order – disorder phase transitions in NH_4F including all the phases in the T-P phase diagram at room temperature (293 K) and at the pressures up to 200 kbar, we analyze the pressure dependence of the lattice mode (238 cm^{-1}) in this molecular crystal using the experimental data [5].

2. ANALYSIS AND RESULTS

We analyze the pressure dependence of the Raman frequency according to a quadratic equation

$$\nu_T(P) = a_0 + a_1 P + a_2 P^2 \tag{1}$$

where a_0, a_1 and a_2 are constants. The pressure - induced frequency shift $(1/\nu)(\partial\nu/\partial P)_T$, can be obtained from Eq. (1) as

$$\frac{1}{\nu}\left(\frac{\partial\nu}{\partial P}\right)_T = \frac{a_1 + 2a_2P}{a_0 + a_1P + a_2P^2} \tag{2}$$

Here we obtained the pressure dependence of the frequency shifts $(1/\nu)(\partial\nu/\partial P)_T$ for the lattice mode (238 cm^{-1}) at T = 293 K according to Eq. (2). This analysis was done for the transitions of the I – III and V - VI in NH_4F using the experimental data [5] which was obtained ν against P for T = 293 K. By fitting Eq.(1) to the ν vs. P data [5], the coefficients a_0, a_1 and a_2 for both transitions (I - III and V – VI) were determined. Using the values of a_0, a_1 and a_2 (Table 1), the pressure dependence of the $(1/\nu)(\partial\nu/\partial P)_T$ was obtained (Eq. 2). Figures 1 and 2 give $(1/\nu)(\partial\nu/\partial P)_T$ versus P for the transition I – III (through the solid phase II) and V – VI, respectively, at T = 293 K for NH_4F.

Table 1. Values of the coefficients according to Eq. (1) using the observed Raman frequencies [5] of the soft mode (238 cm^{-1}) for the transitions within the pressure intervals indicated (T = 293 K) in NH_4F. Transition pressures are also given

NH_4F	**Transition**	**P_c (kbar)**	**a_0 (cm^{-1})**	**a_1 (cm^{-1}/kbar)**	**$a_2 \times 10^{-2}$ (cm^{-1}/kbar^2)**	**Pressure Interval (kbar)**
Eq. (1)	I – II, II – III, III - V	3.6, 11.5, 15	238.85	1.003	3.08	0 < P < 11.5
	V - VI	143	217.20	1.176	-0.13	15 P < 143

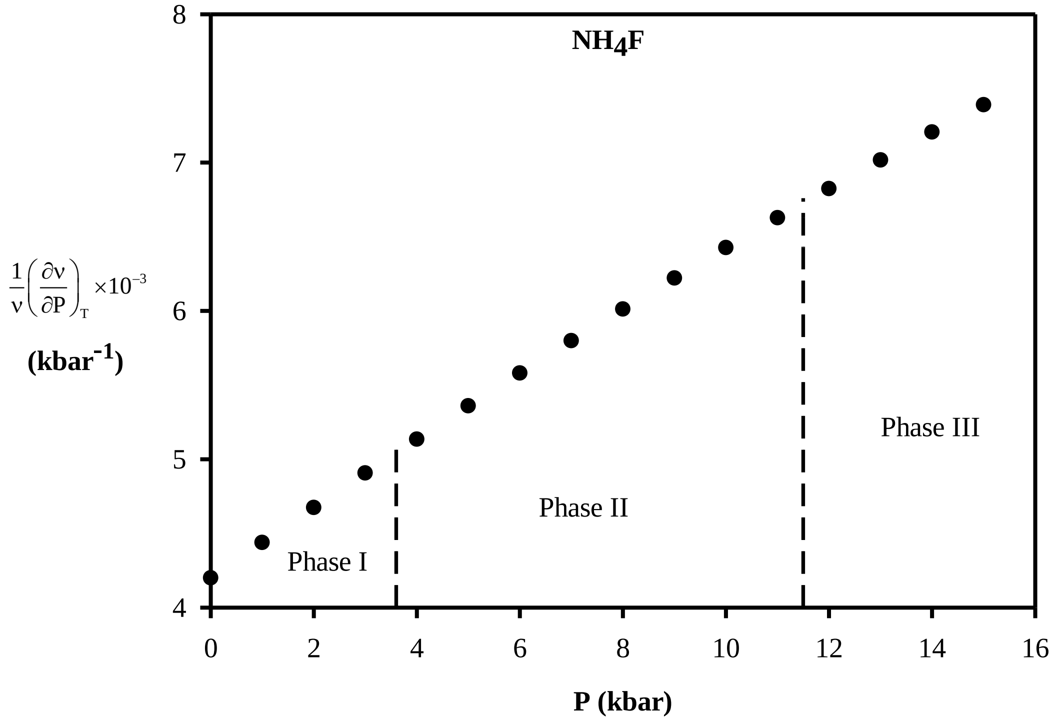

Figure 1. The Raman frequency shifts $(1/\nu)(\partial\nu/\partial P)_T$ of the soft mode (238 cm^{-1}) as a function of pressure (T = 293 K) according to Eq. (2) using the experimental data [5] for the phases I, II and III in NH_4F.

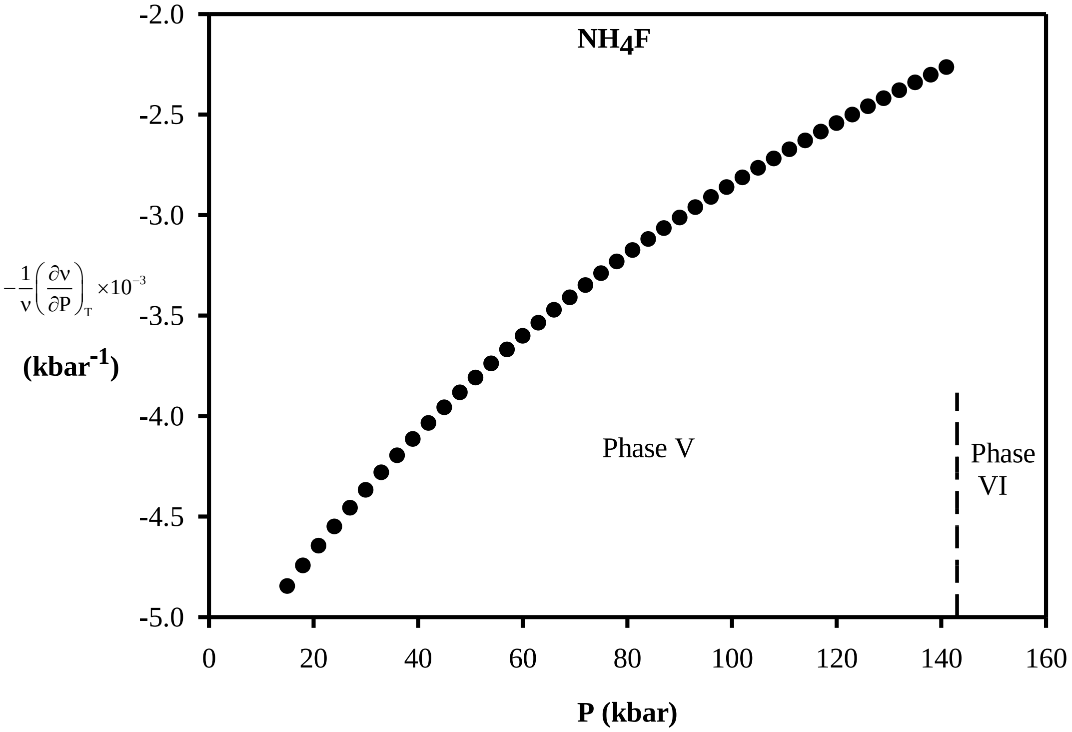

Figure 2. The Raman frequency shifts (1/ν)(∂ν/∂P)$_T$ of the soft mode (238 cm^{-1}) as a function of pressure (T = 293 K) according to Eq. (2) using the experimental data [5] for the phases V and VI in NH_4F.

3. DISCUSSION

As shown in Figures.1 and 2, the frequency shifts (1/ν)(∂ν/∂P)$_T$ increase with increasing pressure as expected, when one approaches toward the I – III transition (around 11.5 kbar) and the V-VI transition (around 143 kbar) at T = 20 °C in NH_4F. So, this Raman mode (238 cm^{-1}) is associated with those transitions in this ammonium halide, as obtained spectroscopically. In terms of the values of the slope dν/dP using Eq. (1) with the coefficients a_0, a_1 and a_2 (Table 1) due to the translational optic mode (238 cm^{-1}), we determined transitions between the phases in NH_4F according to

$$d\nu/dP = a_1 + 2a_2P \tag{3}$$

as given in Table 2. The slope value increases from dν/dP = 1 cm^{-1}/kbar in phase I at P = 0 to 1.2 cm^{-1}/kbar at the critical pressure (P_c = 3.6 kbar) for the transition I-II. This increase in the slope as dν/dP = 1.7 cm^{-1}/kbar appearing at P_c = 11.5, indicates the transition from phase II to phase III and also for the III-V transition which occurs at P_c = 15 kbar with the slope value of dν/dP = 2.1 cm^{-1}/kbar (Table 2). Finally, at high pressures up to 143 kbar, the slope suddenly decreases down to dν/dP = 0.8 cm^{-1}/kbar, which is an indication of a new phase transition from phase V to VI in NH_4F, as pointed out previously [5]. The Raman peak of the TO mode (238 cm^{-1}) shifts to the blue region in phase V with a nearly – linear relation of the frequency shift with pressure roughly dν/dP = 1 cm^{-1}/kbar and the intensity of this soft mode decreases with increasing pressure from 15 kbar to 143 kbar, as also pointed out in an earlier study [5]. This sudden decrease in the frequency shift (dν/dP = 0.8 cm^{-1}/kbar) as we also obtained here in our analysis, is associated with the Raman peak of this mode disappearing at 143 kbar [5] above which phase VI takes place.

Table 2. Values of the slope dν/dP of the soft mode (TO) using the observed Raman frequencies [5] at the critical pressures for the transitions indicated according to Eq. (3) in NH_4F (see Table 1)

Transition	P_c (kbar)	dν/dP (cm^{-1}/kbar)
I – II	3.6	1.2
II - III	11.5	1.7
III - V	15	2.1
V - VI	143	0.8

Since the Raman TO mode (238 cm^{-1}) is associated with the phase transitions in NH_4F, as stated above, this leads to predict the pressure dependence of the isothermal compressibility defined as

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{4}$$

close to the transitions studied in NH_4F.

By defining the isothermal mode Grüneisen parameter γ_T as

$$\gamma_T = -\frac{1}{\nu}\left(\frac{\partial \nu}{\partial P}\right)_T / \kappa_T \tag{5}$$

the pressure dependence of the isothermal compressibility κ_T can be predicted. By determining the isothermal mode Grüneisen parameter γ_T as positive for the 238 cm^{-1} mode, which measures the anharmonicity in the NH_4F crystal, it is expected that the isothermal compressibility κ_T decreases as the pressure increases.

We calculated the pressure dependence of the isothermal compressibility κ_T using the observed Raman frequencies [5] of the translational optic (TO) mode (238 cm^{-1}) at T = 293 K according to Eq. (4) by means of the Grüneisen parameter $\gamma = 5.2 \pm 0.2$ ($\nu_{TO} = 27.2 \pm 0.9$ meV at P = 1.9 GPa in Phase III) [12] for NH_4F. By keeping the mode Grüneisen parameter as constant for all the phases of NH_4F, the isothermal compressibility κ_T was computed for the phases I, II, III, V and VI up to 143 kbar, as plotted in Figure 3. In this figure, vertical lines represent the phase boundaries in NH_4F. Our calculated values can be examined by the measurements of the κ_T as a function of pressure for the I – II and V - VI phase transitions in NH_4F.

4. CONCLUSIONS

The Raman frequencies of the translational optic (TO) mode (238 cm^{-1}) were analyzed at various pressures (T = 293 K) for the phases of I, II, III, V and VI in NH_4F using the observed data from the literature. From the frequency shifts of this soft mode, using its mode Grüneisen parameter, the pressure dependence of the isothermal compressibility was predicted for the phases studied in this ammonium halide (NH_4F). Our predicted values of the isothermal compressibility can be compared with the experimental measurements at various pressures (T = 293 K) for the phases indicated of NH_4F. Also, the pressure dependence of the thermal expansion and the specific heat can be predicted at room temperature (T = 293 K) from the Raman frequency shifts of the TO mode (238 cm^{-1}) for the phases of I, II, III, V and VI of NH_4F.

In general, the thermodynamic quantities such as the heat capacity, thermal expansion and the isothermal compressibility can be predicted from the spectroscopic parameters (frequency shifts, intensity and bandwith) at various temperatures and pressures close to phase transitions in molecular crystals as we exemplified for ammonium fluoride in this study.

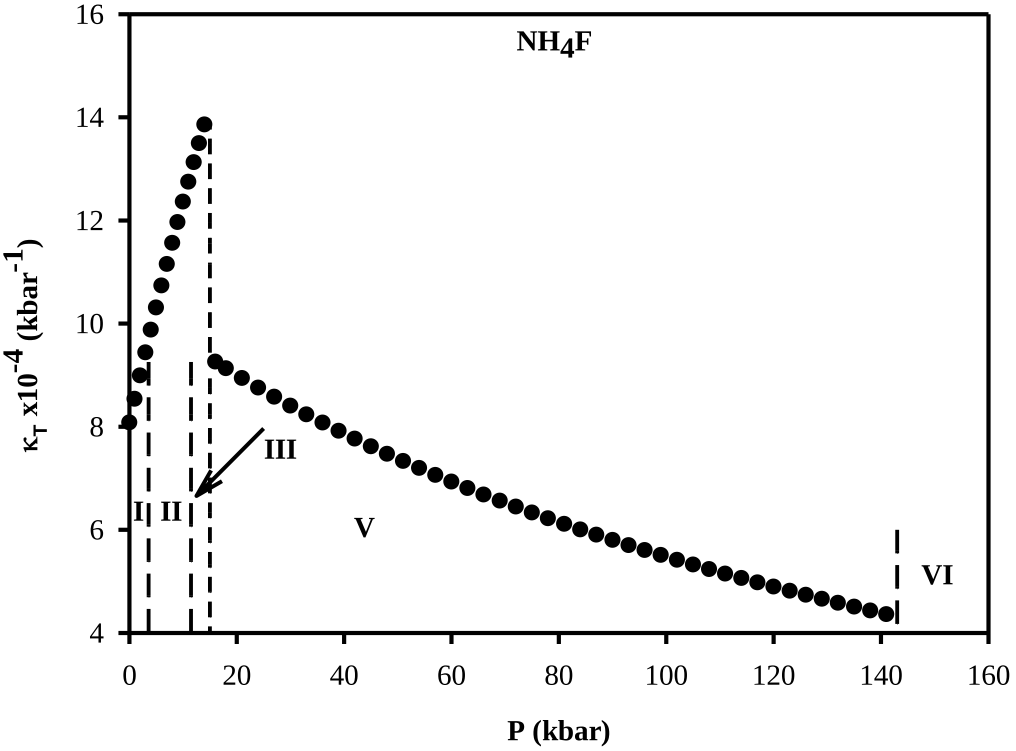

Figure 3. Pressure dependence of the isothermal compressibility κ_T calculated from the observed Raman frequencies of the TO mode [5] according to Eq. (5) for the phases indicated in NH_4F.

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