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Communications

High Pressure Raman Study of Ammonium Fluoride

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High pressure studies of ammonium halide have been done extensively by many authors since those have shown pressure-induced phase transitions.^{1,2} At atmospheric pressure and room temperature, the crystal structures of ammonium chloride, bromide, and iodide are cubic, but that of ammonium fluoride is hexagonal, so called a wurtzite-like structure, due to a strong hydrogen bonding of N-H...F.³ A series of pressure-induced phase transitions of ammonium fluoride at room temperature was observed. From volume change and compressibility measurement at high pressure, three phases were known to exist.⁴ The first phase transition from phase I (wurtzite-like structure) to phase II (unknown structure, but maybe NaCl-like structure) was occurred at around 0.4 GPa pressure. The second phase transitions from phase II to phase II (maybe CsCl-like structure) was observed at 1.15 GPa. However the structures of phase II and phase III are still controversial due to lack of direct structural information. Recently other high pressure phase transitions at 1.5 GPa and 14.3 GPa were reported from high pressure Raman study of ammonium fluoride.⁵ In present work, the Raman spectra of the external (lattice) mode of ammonium fluoride were investigated at room temperature for pressures up to 16 GPa. The observed phase transitions will be discussed in comparison with previous reports and the shift of the external modes with increasing pressure will be analysed by the Born-Huang lattice dynamic theory.

NH₄F samples were obtained from Aldrich Chemical Co. (99.99+ %). The high pressures of specimen were produced by using a diamond anvil cell (DAC).⁶ The powder sample

of ammonium fluoride was placed in a 0.3 mm hole in stainless steel gasket of average thickness 0.3 mm, and the gasket was then compressed between two diamond anvils. Because ammonium fluoride is hygroscopic, all procedures to load samples in DAC were done under dry nitrogen atmosphere. The pressures inside gasket hole were determined by means of the shifts of the R_1 and R_2 luminescence lines of a ruby chip placed in the hole and the pressures are accurate within $\pm 5\%$.⁷ On the pressure range studied, the high pressure sample without any pressure transmitting medium could be regarded as at least quasihydrostatic because the ruby fluorescence R_1 - R_2 separation remained constant at 29 cm^{-1} . The Raman spectra were excited by an Ar⁺-laser (488.0 or 514.5 nm) and the scattered light was detected using a back-scattering geometry and analysed in a Jobin-Yvon U-1000 1.0 m double monochromator and a PM tube with a photon counting system.

At room temperature and atmospheric pressure, the Raman spectrum of NH₄F showed a sharp peak at 238 cm^{-1} and a very weak broad band between 2850 and 3150 cm^{-1} . The sharp peak has been assigned previously as a coalesced peak of optical translational (OT) modes A_1 and E_1 from space group (C_{6v}) analysis for the external vibration.³ The weak broad band might be from internal vibration of ammonium ion, but could not be measured due to low intensity at high pressures. Therefore only the OT mode was observed with increasing pressure, Raman spectra of the OT mode at various high pressures are shown in Figure 1. Also the pressure dependence of the frequency are illustrated in Figure 2. The Raman frequencies remain almost constant with increasing pressure up to 0.4 GPa pressure. With increasing pressure further, the peak was suddenly disappeared. This should be a phase transition from phase I to phase II, which was observed previously. We can infer with disappearing the peak that a change of space symmetry group should be undergone through this transition. As the pressure was increased more, the reappearance of Raman peak was observed above 1.2 GPa. This should correspond the phase transition from phase II to phase III. There should be another change of space symmetry group through this phase transition. The frequency of the peak at 1.2 GPa pressure was measured at 231 cm^{-1} , which is slightly lower than the frequency in phase I. Upon increasing pressure further up to 16 GPa,

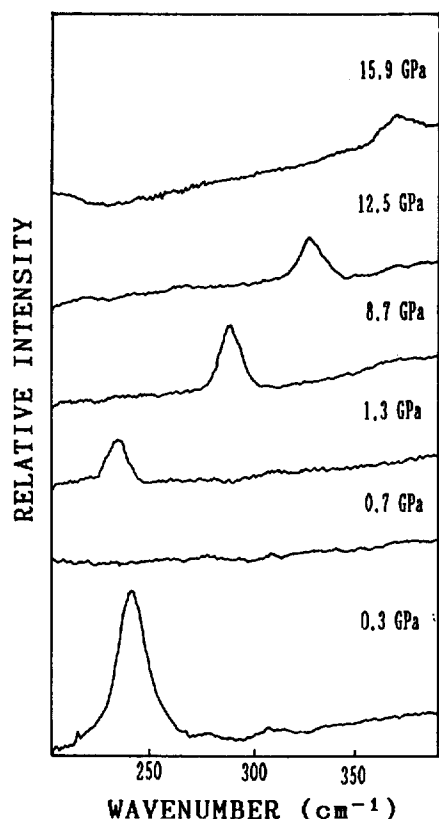


Figure 1. Raman spectra of the optical translational mode of ammonium fluoride at various pressures and room temperature.

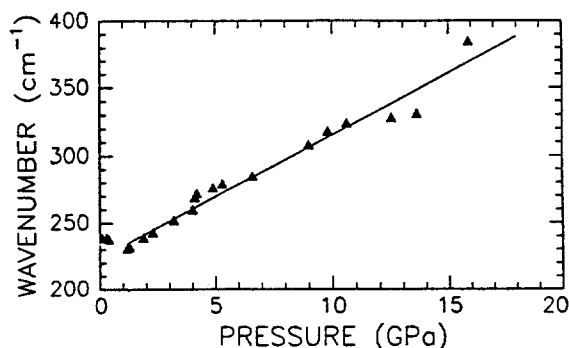


Figure 2. Pressure dependence of the OT modes. The solid line shows linear fit to the data in phase III.

the Raman peak shifts to higher frequency with an approximate linear relation of frequencies *vs.* pressures. Any significant change of Raman mode shift at 1.5 GPa pressure was not observed. We observed an indication of softening in Raman peak at around 14 GPa. However above 14 GPa pressure, Raman intensity was still observed although it was very weak. Therefore the phase III seems to be maintained up to 16 GPa pressure.

The crystal structure of phase I has been known to be wurtzite-like structure from X-ray diffraction data,⁸ but direct structural information of phase II and phase III is not available although phase II and phase III were inferred to be a NaCl-like structure and a CsCl structure, respectively.⁴ Based on the present experimental results, the phase II may be a NaCl-like structure since the space symmetry group

Table 1. Gruneisen Parameter for the Optical Translational Mode of Ammonium Fluoride

	γ
Experimental	2.78 ^a
Born-Huang model with rigid ions	3.34 ^b
Born-Huang model with polarizable ions	2.92 ^c

^a $\nu_0 = 228 \text{ cm}^{-1}$ and $\beta = 1.4 \times 10^{-6} \text{ bar}^{-1}$ were used, ^b $\alpha_+ = \alpha_- = 0$ were used, ^c $\alpha_+ = 1.62 \times 10^{-24} \text{ cm}$ and $\alpha_- = 0.664 \times 10^{-24} \text{ cm}$ were used.

of the NaCl structure does not give rise a strong Raman active OT mode.⁹ However more direct evidence would be required to confirm the structure. The phase III might be a CsCl-like structure since there exists a Raman active lattice mode according to the space symmetry group analysis of the CsCl structure¹⁰ and an external Raman mode was observed in the present experiment. The pressure dependence of the OT mode in the CsCl structure could be estimated from Born-Huang lattice dynamic theory in ionic crystal.¹¹ In terms of the isothermal compressibility β , the pressure dependence of the OT mode may be written as $(\partial\nu/\partial P)_T = \gamma\nu_0$, where γ is the Gruneisen parameter, given by¹²

$$\gamma = -d(\ln \omega)/d(\ln V) \quad (1)$$

where ω is the phonon frequency and V is the volume of the crystal. The Gruneisen parameter is expected to be a constant within the limits of quasi-harmonic oscillator model. The experimental value from the present work is given in Table 1. For an ionic solid with polarizable ions, the frequency of the OT mode may be written as

$$\omega^2 = \frac{f}{\mu} - \frac{e^2/\mu}{3\epsilon_0 V_p - (\alpha_+ + \alpha_-)} \quad (2)$$

where f is the nearest-neighbor force constant, μ is the reduced mass per Bravais unit cell of volume, $V_p = xr_0^3$, where r_0 is the nearest-neighbor distance and x is a constant depending on unit cell structure (2.83 in CsCl structure), ϵ_0 is electric permittivity of free space, and α_+ and α_- are the ionic polarizabilities ($\alpha_+(\text{NH}_4^+) = 1.62 \times 10^{-24} \text{ cm}$, $\alpha_-(\text{F}^-) = 0.644 \times 10^{-24} \text{ cm}$).¹³ The volume dependence of the force constant may be evaluated using the Born-Mayer potential given by

$$U = -A/r + \phi \quad (\phi = Mb \exp(-r/\rho)) \quad (3)$$

where $A = \alpha e^2/4\pi\epsilon_0$, α is the Madelung constant (1.7627 in CsCl structure), M is the coordination number, b and ρ and potential parameters, which are independent of the volume and can be determined from the equilibrium distance ($r_0 = 2.83 \text{ \AA}$) and the compressibility data ($\beta = 1.4 \times 10^{-6} \text{ bar}^{-1}$).⁴ According to the Born-Huang theory, the force constant is given to be

$$f = 1/3\{\phi''(r) + (2/r)\phi'(r)\} \quad (4)$$

Therefore using the Eq. (1), (2), (4), the Gruneisen parameter may be written as

$$\gamma = \frac{r}{6} \frac{\frac{1}{3}[\phi'''(r) + \frac{2\phi''(r)}{r} - \frac{2\phi'(r)}{r^2}] + \frac{9e^2\epsilon_0 r^2}{[3\epsilon_0 x r^3 - (\alpha_+ + \alpha_-)]^2}}{\frac{1}{3}[\phi''(r) + \frac{2}{r}\phi'(r)] - \frac{e^2}{3\epsilon_0 x r^3 - (\alpha_+ + \alpha_-)}} \quad (5)$$

The values of γ calculated from the Born-Huang theory for the phase III of ammonium fluoride with rigid ions and polarizable ions are summarized in Table 1. The calculated value of γ with rigid ions is 20% larger than the measured value. But the value of γ calculated with polarizable ions is deviated from the measured value with only 5%, which is in experimental error. This result provides a strong evidence that the phase III would be a CsCl-like structure. However, in order to determine the structures of the high pressure phases of ammonium fluoride conclusively, high pressure X-ray or neutron scattering studies would be required.

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A New Quantitative Analysis of Phosphates by ^{31}P -NMR Spectroscopy¹

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A quantitative analysis of phosphates is generally well established by conventional wet chemistry for a long time because of their important role in all areas of chemistry.² The ASTM D 515,³ which measures the total orthophosphate of sample by oxidation or hydrolysis, is very sensitive method, but it has many interferences and no selectivity. These drawbacks could be overcome by the several useful method such

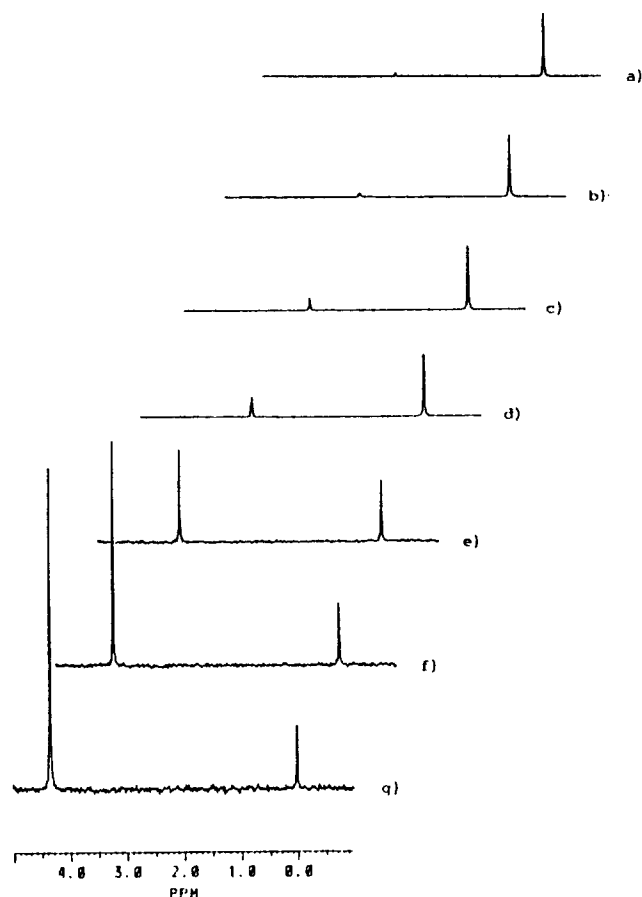


Figure 1. ^{31}P -NMR spectra of trisodium orthophosphate at various concentrations with 500 ppm phosphoric acid as an external standard. The concentrations (a-g) are 10, 20, 50, 100, 250, 500, and 1000 ppm as phosphorus.

as anion-exchange chromatography,⁴ paper chromatography,⁵ and TLC.⁶ However, all of these mentioned are time-consuming and inconvenient methods.

NMR is generally much less sensitive than other analytical methods. However, rapid growth during the last decade in NMR technique, most notably in the increasing use of a high-field spectrometer with further hardware developments, reduced the absolute detection thresholds drastically and made the NMR technique a viable alternative and a preferred technique in all areas of chemistry. With these advantages, the use of ^{31}P nucleus, which has 100% natural abundance, relatively high sensitivity, and wide chemical shift range in NMR, has become more and more popular in chemistry.⁷

In this communication, we now report what appears to be the new preferred alternative method for the quantitative analysis of phosphates. The phosphates studied were trisodium orthophosphate, tetrasodium pyrophosphate, and pentasodium tripolyphosphate in $\text{H}_2\text{O}/\text{D}_2\text{O}$ (50%, v/v). The representative ^{31}P -NMR spectra of orthophosphate obtained on a Bruker AM-300 spectrometer at 121 MHz are shown in the Figure 1. The upfield singlet is the peak of the 500 ppm phosphoric acid which is contained at 3 mm tube (inside radius 1.75 mm)⁸ and placed co-axially in a 5 mm NMR tube containing various concentrations of phosphates. The spectra were accumulated by using 17.8° pulse width and