

# An infrared spectroscopy study of the phase transition in solid ammonia

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## Abstract

The infrared spectra of solid ammonia at different phases and the existence of a metastable phase have been in controversy for the last fifty years. In order to address this problem, we studied the infrared spectra of solid ammonia in an ultrahigh vacuum chamber at distinct temperatures. Having prepared amorphous ammonia at 10 K, we observed a transition from the amorphous phase to the cubic crystalline phase at 57 K; successive re-cooling from 85 K back to 10 K confirms the presence of crystalline ammonia. No metastable phase has been detected.

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## 1. Introduction

The ammonia molecule (NH<sub>3</sub>) has three nitrogen–hydrogen (N–H) bonds and one lone electron pair. This structure makes ammonia an important hydrogen bonding molecule. The strength of the hydrogen bonds between two ammonia molecules is about 13 kJ mol<sup>-1</sup>, slightly lower than that between water molecules of 21 kJ mol<sup>-1</sup> [1]. An investigation of the transition from isolated, single ammonia molecules via ammonia clusters to ammonia in the condensed phases is valuable for understanding the characters of hydrogen bonds and intermolecular forces. In addition, ammonia is not only a precursor to prebiotic molecules, but also an important chemical constituent found in our Solar System [2]. Ammonia has been detected in the atmospheres of the outer planets Jupiter [3], Saturn [3], Uranus [4], and Neptune [5]. Solid ammonia was identified on the surfaces of their icy satellites such as Miranda and Enceladus [6,7]. Recently, the existence of ammonia hydrates on Kuiper Belt Objects (KBOs) has also been reported [8].

It is believed that solid ammonia has three phases: a cubic crystalline phase, a low temperature amorphous

phase, and an intermediate temperature metastable phase [9]. However, there is a strong controversy on the infrared (IR) spectra of the cubic phase and a possible metastable phase. A comprehensive review of this topic can be found in Ferraro et al. [9]. Briefly, the debate started about 50 years ago and involved papers by Reding and Hornig [10] and Staats and Morgan [11]. Staats and Morgan suggested that the spectra of cubic crystalline ammonia recorded by Reding and Hornig are better attributed to a metastable phase. Since then, various research groups have reproduced Reding and Hornig's results [2,9,12–15]. These studies confirmed that the cubic ammonia phase assigned by Reding and Hornig is correct. Staats and Morgan's spectra were suggested to be contaminated by water which in turn changed the infrared spectrum significantly [16]. Therefore, the debate has been solved partially. However, the exact temperature of the transition from the amorphous structure to the cubic crystalline phase is still unknown. No reproducible spectrum of a potentially metastable ammonia phase can be found in the literature [17–21]. Based on the previous experience about water contamination [16], to minimize the impurities might be very crucial for addressing this problem. Thus, it is necessary to conduct the experiments in ultrahigh vacuum chambers.

To solve this controversy on the existence/non-existence of a metastable phase and to provide reliable data on the

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transition from amorphous ammonia to the crystalline phase, we conducted a systematic study of the phase transition of solid ammonia under ultrahigh vacuum conditions. Our investigations identified a phase transition from the amorphous to the cubic phase at 57 K; no metastable phase was detected.

## 2. Experimental

The experiments were carried out in an ultrahigh vacuum chamber [22]. Briefly, a two-stage closed-cycle helium refrigerator coupled with a rotary platform is attached to the main chamber and holds a polished polycrystalline silver mirror serving as a substrate for the ice condensation. With the combination of the closed-cycle helium refrigerator and a programmable temperature controller, the temperature of the silver mirror can be regulated precisely to  $\pm 0.3$  K between 10 K and 350 K. The infrared spectra of the samples can be measured by a Fourier transform infrared spectrometer (Nicolet 6700 FTIR) within the absorption–reflection–absorption method. The near infrared mode of the spectrometer covers 10,000–2000  $\text{cm}^{-1}$ ; the middle infrared range comprises 6000–400  $\text{cm}^{-1}$ . Besides measuring the infrared spectra in the solid phase, we also utilized a quadrupole mass spectrometer (Balzer QMG 420) to monitor the ammonia molecules released to in the gas phase. Ammonia ices were prepared by condensing anhydrous ammonia (99.99%; Matheson Gas Products, Inc.) onto the silver mirror at 10 K. The gas lines and the gas reservoir were baked and pumped down to  $2 \times 10^{-7}$  Torr for several hours to eliminate possible contamination from water molecules and air. The background pressure in the main chamber, in which the sample was deposited, was  $7 \times 10^{-11}$  Torr. During the condensation, the capillary array was located 4 cm from the silver mirror; the pressure of the ammonia in the main chamber was maintained at  $2.4 \times 10^{-8}$  Torr for 40 min. The thickness of the ammonia ices formed on the silver mirror was estimated to be about 190 nm based on the integrated infrared absorption coefficient of the 3  $\mu\text{m}$  band ( $A_{\text{ref}}(3000\text{--}3700 \text{ cm}^{-1}) = 1.03 \times 10^6 \text{ cm}^{-2}$ ) [2] and a modified Lambert-Beers relationship [22]. The relative variations of the thickness in our experiments were less than 5% from day to day.

## 3. Results

We first determined the sublimation temperature of solid ammonia in the vacuum before investigating the phase transition of solid ammonia. This goal was accomplished by preparing amorphous ammonia at 10 K and warming it up at a rate of  $0.5 \text{ K min}^{-1}$ . Fig. 1 shows a typical profile of the ion counts of ammonia ( $\text{NH}_3^+$ ,  $m/z = 17$ ) during the warming up. The ammonia signal in the gas phase started to increase at about 80 K. It reached the maximum at 108 K and dropped abruptly at 110 K. This indicates that the sublimation started at about 80 K and was completed at about 110 K under our experimental condi-

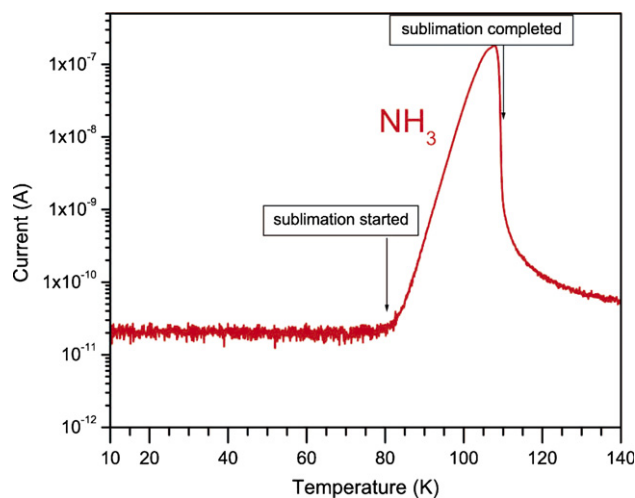


Fig. 1. The ion current of ammonia ( $m/z = 17$ ) monitored via the quadrupole mass spectrometer in the gas phase versus the temperature of the solid ammonia sample.

tions. In Fig. 2, we plotted the corresponding decay of the ammonia absorptions in the infrared spectra from 100 K to 110 K. At 110 K, no ammonia was left on the substrate.

In order to investigate the phase transition(s) in solid ammonia, we monitored the evolution of the infrared absorption spectra at different temperatures in 1 K intervals between 10 K and 84 K (Fig. 3). The absorption features are almost invariant in the temperature range from 10 K to 56 K. Significant changes of the infrared spectra are evident from 57 K on. Between 58 K and 84 K, the absorption features look identical. We would like to stress that the spectra between 58 K and 84 K are very diverse from the spectra recorded between 10 K and 56 K. This suggests that the phase of solid ammonia does not change in the temperature interval from 58 K to 84 K. However,

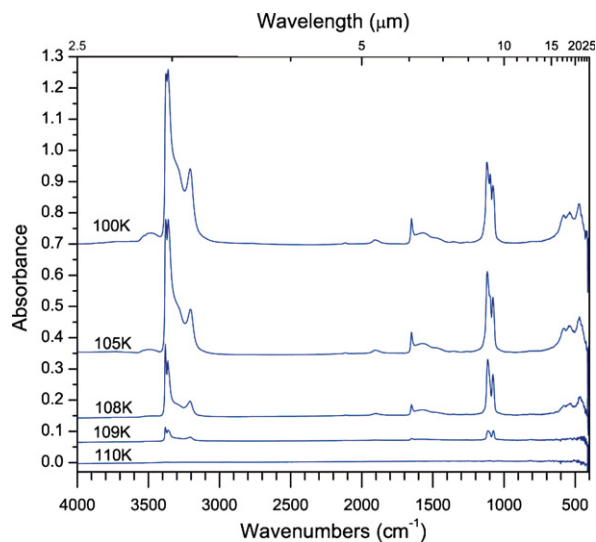


Fig. 2. Infrared spectra of ammonia at various temperatures in the sublimation range of the sample.

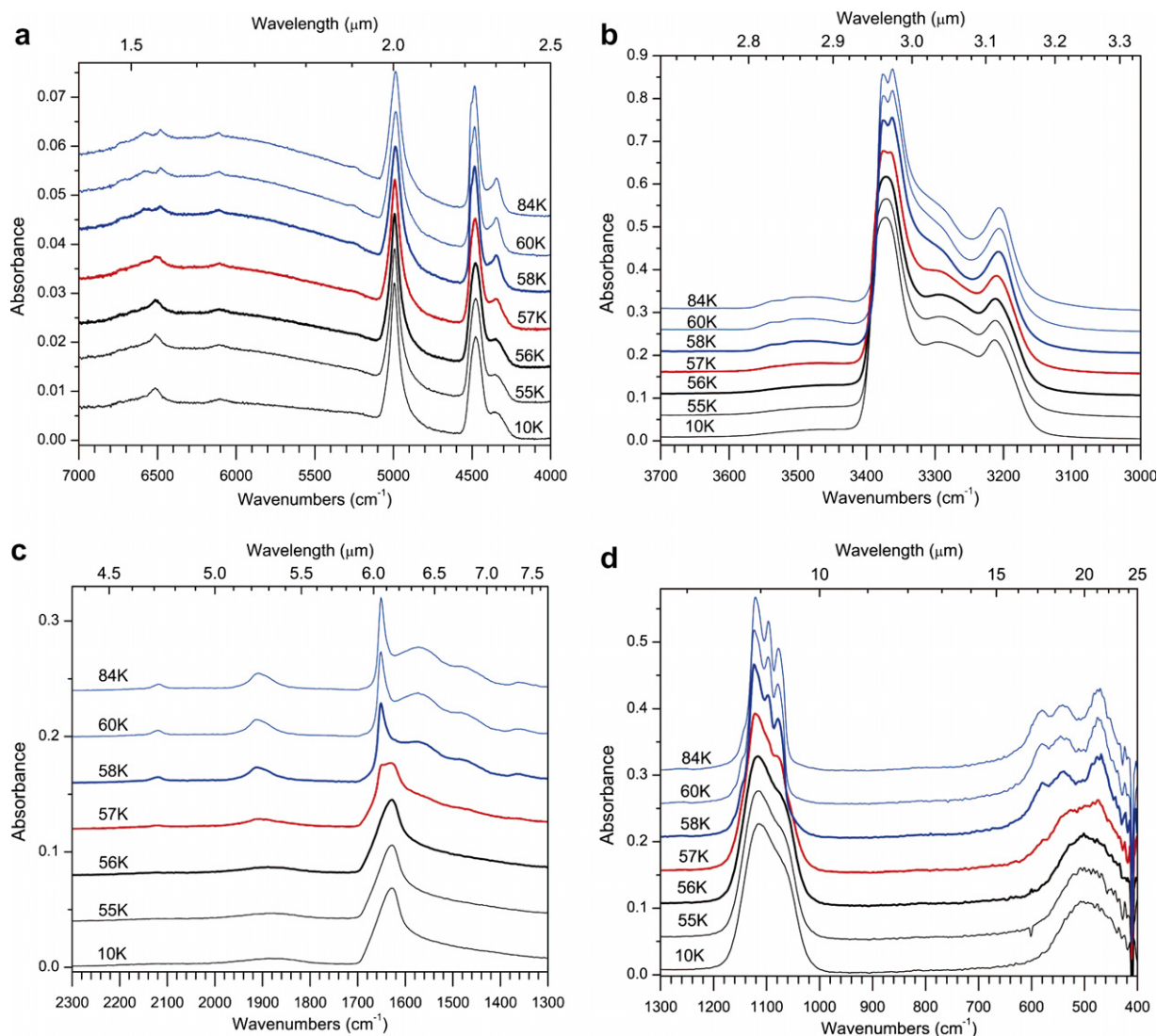


Fig. 3. Infrared spectra of ammonia at different temperatures during the warm up phase of amorphous ammonia. The amorphous-cubic phase transition happens at about 57 K. The spectra are offset for clarity.

can this phase be attributed to a metastable or the cubic crystalline phase? In order to answer that question, we kept solid ammonia at 84 K for 3 h. According to previous studies, solid ammonia undergoes a transition to the cubic crystalline phase at a temperature above 80 K [21]. We re-cooled the sample to 10 K at  $1 \text{ K min}^{-1}$ ; hereafter, we warmed it up back to 84 K. Again, no significant change has been found during the cooling and warming cycle from 84 K to 10 K and back from 10 K to 84 K. We also warmed up the solid ammonia sample to 100 K. The spectrum at 100 K is almost the same as those recorded at 84 K and 58 K – except that the intensity dropped slightly due to the sublimation at elevated temperatures. These data suggest that solid ammonia is reaching the cubic crystalline phase when it was heated from 10 K to 58 K for the first time.

Also, the spectra between 58 K and 84 K show a pronounced fine structure compared to the spectra recorded in the amorphous phase. The absorption features in the

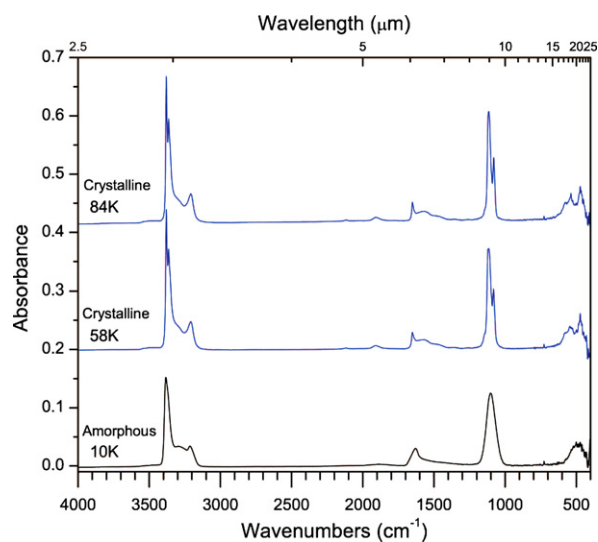


Fig. 4. Mid-infrared spectra of a 40 nm thick solid ammonia film at 10 K (amorphous), 58 K (cubic crystalline), and 84 K (cubic crystalline).

cubic phase are sharper than those of the amorphous phase except the 2.0  $\mu\text{m}$  feature is slightly sharper in the amorphous phase. These features are similar to the differences between crystalline and amorphous water ice [23,24]. For example, the 3  $\mu\text{m}$  and 1.5  $\mu\text{m}$  bands of crystalline water ice have well-established fine structures compared to amorphous water ice. We observed similar changes in the 3  $\mu\text{m}$  and 1.5  $\mu\text{m}$  bands of solid ammonia. The phase transition at 57 K is reproducible for distinct sample thicknesses. We have confirmed this by preparing thinner films of a few tens of nanometers. In Fig. 4, we present the spectra recorded at an ice thickness of 40 nm. The spectra of 40 nm sample taken at 58 K and 84 K (Fig. 4) are very similar to the spectrum recorded at 108 K in Fig. 2, indicating the thickness of the 190 nm decreased to approximately 40 nm at 108 K. In Fig. 2, the variations of the spectra between 100 K and 110 K are due to the change of sample thickness during the sublimation. To present the spectra

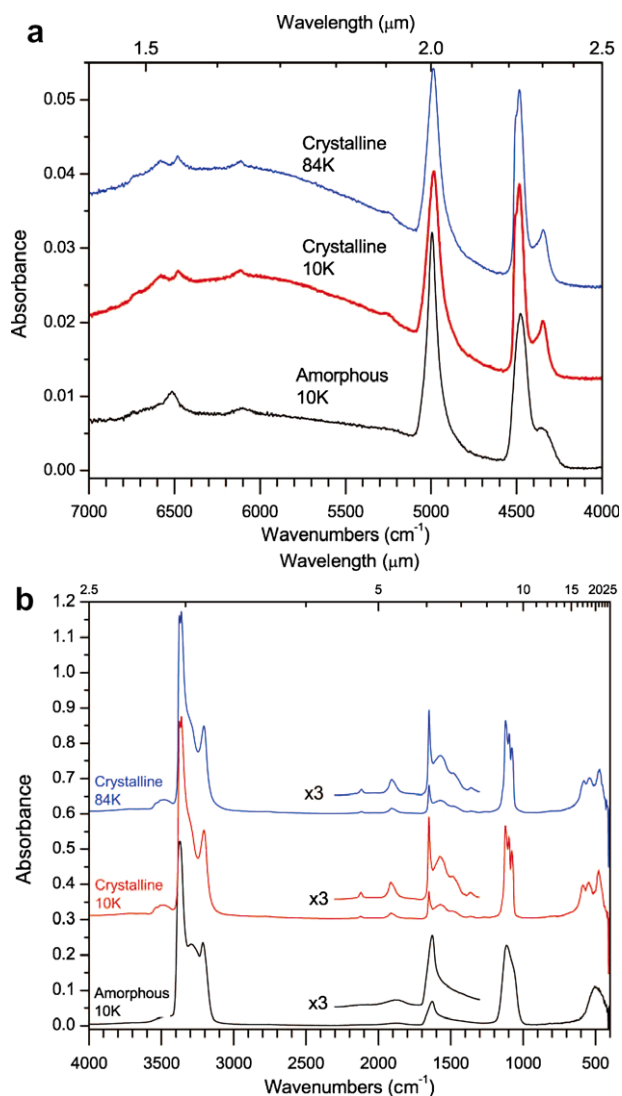


Fig. 5. Near-infrared and middle-infrared absorption spectra of amorphous ammonia and cubic crystalline ammonia at a sample thickness of about 190 nm.

Table 1  
The infrared absorption features of solid ammonia

Tentative assignments	Frequencies ( $\text{cm}^{-1}$ )			
	Amorphous 10 K	Crystalline 10 K	Crystalline 84 K	Gas*
$\nu_L$	500	476 546 586	474 541 581	–
$\nu_2$ (or $2\nu_L$ )	1097	1078 (S) 1097 (S) 1121 (S)	1078 (S) 1097 (S) 1120 (S)	932.5 968.3
$\nu_2 + \nu_L$		1145 (shoulder) 1365 1486 1573	1142 (shoulder) 1359 1483 1571	–
$\nu_4$	1628	1651	1651	1626.1 1627.4
$\nu_4 + \nu_L$	1876	1914	1909	–
$\nu_4 + \nu_L$	2115 (w, b)	2121	2118	
$\nu_1$	3212	3205	3205	3336.2 3337.2
$\nu_1$ or $2\nu_4$	3290	3300	3295	
$\nu_3$	3372 (S)	3361 (S) 3375 (S)	3362 (S) 3376 (S)	3343.6 3343.9
$\nu_1 + \nu_L$	3472	3493 3534 (shoulder)	3483 3531 (shoulder)	
$(\nu_1 + \nu_L)$ or $(\nu_3 + \nu_L)$	3729 (w, b)	3625 (w) 3716 (w)	3625 (w) 3716 (w)	
$\nu_1 + \nu_2$	4345	4347	4345	
$\nu_3 + \nu_2$	4478	4484 4504 (shoulder)	4484 4504 (shoulder)	
$\nu_3 + \nu_4$	4994	4985	4985	
$\nu_3 + \nu_4 + \nu_L$	5235	5247	5240	
$\nu_3 + \nu_2 + \nu_4$	6100	6115	6113	
$2\nu_1$ or $2\nu_3$	6514 6632 6752	6480 6584 6721	6481 6584 6721	

$\nu_1$  – symmetric stretch,  $\nu_2$  – symmetric deformation,  $\nu_3$  – degenerated stretch,  $\nu_4$  – degenerated deformation,  $\nu_L$  – lattice mode, S – strong, w – weak, b – broad.

\* Ref. [26].

over the full range, we plotted the near-IR and mid-IR spectra of amorphous ammonia and cubic crystalline ammonia of the 190 nm sample in Fig. 5. The assignments of the absorption features have been made by several previous studies [9,10,20,25]. However, to make precise assignments is not an easy task due to the complex of molecule interactions plus the broadening and overlapping of the absorption features in solid phases. Here, we summarize the positions of the absorption features in Table 1. The tentative assignments are also given in the same table.

#### 4. Discussion and summary

The similarities between the hydrogen bonding behavior of  $\text{NH}_3$  versus  $\text{H}_2\text{O}$  make worth comparing the ammonia to the water system. The melting point and boiling point of water are higher than those of ammonia by 78 K and

133 K, respectively. It is also worth mentioning that in our vacuum system and with a heating rate of  $0.5 \text{ K min}^{-1}$ , the sublimation of water ice started at 140 K and was complete at 175 K [27], again the temperatures are higher by 60 K and 65 K compared to solid ammonia. Since the molecular weights of ammonia and water are similar, the difference of their phase transition temperatures is mainly due to their intermolecular interactions. The water molecule has two O–H bonds plus two lone pairs of electrons. Therefore, each water molecule can form four hydrogen bonds in water ice: two through its lone pairs and two via its hydrogen atoms. Ammonia has three nitrogen–hydrogen bonds, but only one lone pair of electrons. In principle, it is possible for one ammonia molecule to form four hydrogen bonds: one through its lone pair and three through its hydrogen atoms. Yet, in solid ammonia, the number of lone pairs is not sufficient for each ammonia molecule to form four hydrogen bonds. On average, one ammonia molecule can only form two hydrogen bonds in solid ammonia. In addition, the hydrogen bonds between ammonia molecules are much weaker compared to water molecules, i.e.  $13 \text{ kJ mol}^{-1}$  versus  $21 \text{ kJ mol}^{-1}$  [1]. It is agreed by most researchers that the amorphous-cubic transition in water ice will happen between 100 K and 150 K [28–30]. It is expected that the amorphous-cubic transition in solid ammonia will be much lower than that. Schmitt et al. [31] found that amorphous water ice converts spontaneously to crystalline ice at a rate that depends exponentially on the

temperature. According to their measurement, the crystalline time for water ice ranges from about 8 days at 125 K to less than 5 min at 150 K. For both water and ammonia, the cubic crystalline phase is more stable than the amorphous phase. Although the amorphous-crystalline transition is energetic favorable, some activation energy is needed to initiate the transition. Schmitt et al. [31] estimated the crystallization activation energy of water ice to be  $44.6 \text{ kJ mol}^{-1}$ . We notice that number is about two times of the hydrogen bond energy between water molecules. Assuming the other parameters of solid ammonia are similar to water ice, we estimate the activation energy of solid ammonia to be  $17 \pm 8 \text{ kJ mol}^{-1}$  based on the transition at 57 K. That is a reasonable agreement since the number of hydrogen bonds in solid ammonia is only half of that in water ice.

In our experiments, no phase transition in solid ammonia has been observed between 58 K and 110 K. The only change in the spectra in the temperature range from 10 K to 110 K was observed at 57 K. The transition at 57 K can be correlated with a change from the amorphous phase to the cubic phase. Further, our experiments do not show the existence of a metastable phase. Based on our results, we suggest that the spectrum of a metastable phase claimed by Holt and coworkers [21] probably arises from the cubic phase. The authors mentioned that their spectra did not change with temperature as soon as the sample was prepared. These are exactly the characteristics of a stable cubic

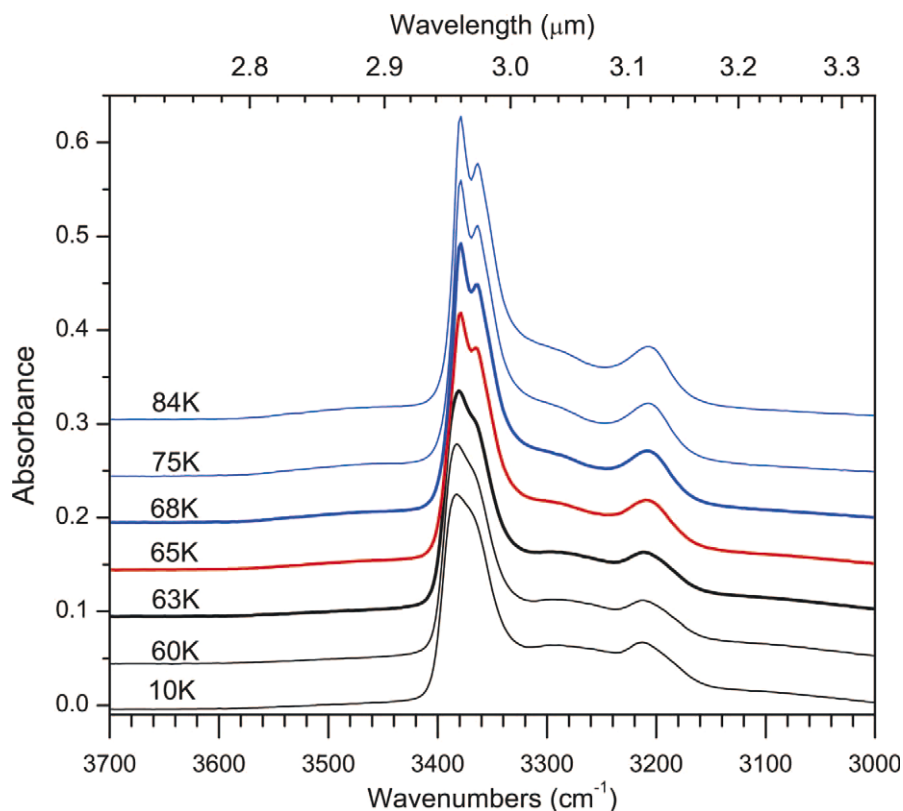


Fig. 6. Infrared spectra of solid ammonia with 1% of water. The change of the spectra at 65 K indicates the amorphous-crystalline transition.

phase as evident from our re-cooling experiment of cubic ammonia from 84 K down to 10 K. The spectra recorded by Holt et al. at 100 K look very similar to the spectrum of the very thin film reported by Reding and Hornig [10]. It had also been discussed by Reding and Hornig that the variation of  $\nu_2$  band in cubic ND<sub>3</sub> ice depended only on the thickness. Our experiments on ammonia agree with this conclusion. We observed three fine structure components of the  $\nu_2$  band in the 190 nm thick cubic phase. In a 40 nm thick sample, only two peaks are visible for the same band (Figs. 2 and 4). The relative intensities of those individual components changed at different thicknesses. The splitting of the 1097 cm<sup>-1</sup> mode in the cubic phase may due to the Fermi resonance between the symmetric deformation ( $\nu_2$ ) and the lattice mode overtone ( $2\nu_L$ ). The  $2\nu_L$  mode is not strong in the thin samples. On the other hand, we notice that most of previous experiments were conducted in vacuum systems with fairly high background pressures of  $>10^{-8}$  Torr. That suggests that the solid ammonia sample could be contaminated by residual water molecules in the vacuum system. The small concentration of water may not bring noticeable change to the infrared spectra because the major absorption band, the 3  $\mu$ m band, of water overlaps with the 3  $\mu$ m band of ammonia. But, it could be sufficient to delay the transition from the amorphous phase to the crystalline phase. Indeed, we found that the temperature of this transition increased to 65 K when we introduced 1% of water into solid ammonia (Fig. 6).

In summary, we conducted an infrared spectroscopy study on the phase transition of solid ammonia at ultrahigh vacuum condition. Significant changes in the infrared spectra were observed at 57 K while warming up the amorphous ammonia from 10 K to higher temperature. These changes correlate with a transition from an amorphous sample to a cubic crystalline phase. The so-called metastable phase previously reported in the literature has not been detected in the present studies.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2007.04.070.

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