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EXPERIMENTAL STUDY OF THE VIBRATIONAL SPECTRUM AND STRUCTURE VARIATIONS IN NH_4Cl UNDER HIGH PRESSURE

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INTRODUCTION

Ammonium halides NH_4A, where A=Cl, Br or I, are rather simple, convenient and interesting objects for neutron scattering experiments. The strong influence of pressure on phase transitions in these systems has already been established by different methods, including neutron scattering[1,2]. Under pressure the NaCl type cubic structure converts first into a CsCl type cubic structure with disordered and then with ordered ammonium ion arrangements, space group P43m, with the single parameter of a hydrogen atom centered at the threefold position (*u u u*).

Vibration frequencies of NH_4Cl have also been thoroughly studied. Together with intramolecular (175-400 meV range) and lattice vibrations (0-20 meV range), there is the libration mode (~42 meV) which is non-active in optical spectra and corresponds to the rotation of the NH_4^+ ion as a whole. In[3] it was established that most part of the intramolecular frequencies decrease with pressure. As follows from the optical data[4] a phase transition of unknown nature takes place for ammonium halides at high pressure, and the question arose about their stability if the density is high. It seems that molecular ions are less stable than natural molecules. The NH_4^+ ion is formed from ammonia with an attached proton. Obviously, at high compression, the proton would no longer remain localized near the ammonia. Recently, several studies of the atomic dynamics in these compounds by means of neutron inelastic scattering were performed under high pressure. For instance, NH_4Cl has been investigated[5] at the IBR-2 pulsed reactor under pressures up to 10 kbar. The pressure of 25 kbar in the study of NH_4Br has been achieved[6] at the pulsed source ISIS. Therefore, it is interesting to investigate the frequencies and structural parameters behavior of ammonium halides under pressure higher than before[5,6] using sapphire anvils technique.

EXPERIMENTAL TECHNIQUE

The neutron scattering experiments were performed at the IBR-2 pulsed reactor with the DN-12 spectrometer[7]. The sample was placed between sapphire anvils, which were used to create the pressure. The sample volume was 2.5 mm^3. A ring-shaped detector (16 independent ^3He-counters) 800 mm in diameter was used to gather the scattered neutrons. The scattering angle was 90°; the diameter of the incident neutron beam was 2 mm.

For analysis of the neutron energy transfer, Be filters (a 120 mm thick Be layer, without cooling) were placed between the sample position and each counter. Inelastic scattering experiments were carried out under pressure of 0, 10, 16, 27 and 40 kbar at room temperature. Additionally, neutron diffraction patterns were measured at 0 and 25 kbar. Exposure time for the maximum pressure was ~50 hours for the inelastic and ~10 hours for the elastic scattering measurements. The background was measured with the high-pressure cell but without the sample.

RESULTS

The inelastic neutron scattering spectra were converted into generalized vibrational density of states G(E) (Figure 1). After spectra processing the positions and widths of three low-frequency modes were obtained: libration, transverse optical and longitudinal acoustic. The mode identification was carried out with zero-pressure measurements according to[/8/]. One can see from Figure 2 that with increasing pressure the values of the observed lattice and libration frequencies increase also, though with a different slope ($d\omega_{LA}/dP$ and $d\omega_{TO}/dP \approx 0.17$ meV/kbar; $d\omega_{Libr}/dP \approx 0.056$ meV/kbar). The libration mode behavior reveals a fracture near 10 kbar which is apparently connected with the ordering of the NH_4^+ ion orientation[/5/]. Below 10 kbar $d\omega_{Libr}/dP \approx 0.29$ meV/kbar, while above 10 kbar it is only ≈ 0.056 meV/kbar. At the same time the width of the libration line decreases and, in spite of bad resolution, the change in the width can be clearly seen.

To study the structure parameter variations with pressure the deuterated analog, ND_4Cl, was investigated. The neutron diffraction patterns of ND_4Cl at 0 and 25 kbar are shown in Figure 3. One can observe the sharp change in the set and intensity of the lines with pressure. After Rietveld refinement of the diffraction spectra at 0 and 25 kbar a definite result was obtained: position parameter *u* increases with pressure from 0.154 to 0.168 at 25 kbar while the unit cell volume decreases, with just the same slope as in[/9/]. The agreement of the calculated intensities to experimental ones may be considered as satisfactory, taking into account a low statistical precision. For zero pressure the *u* value agrees well with[/10/].

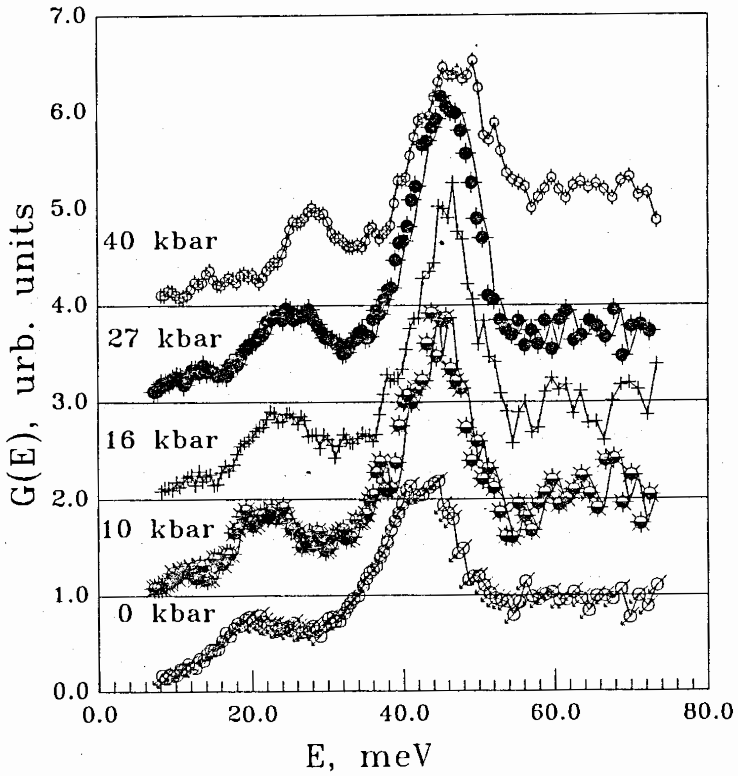

Figure 1 *Pressure dependence of the generalized vibrational density of states G(E) for NH_4Cl.*

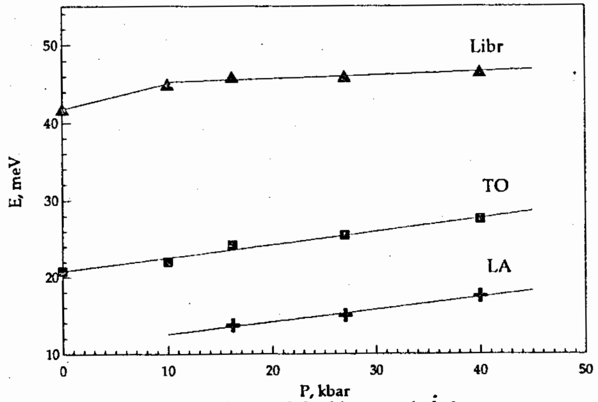

Figure 2 *Pressure dependence of the libration (Libr), transverse optical (TO) and longitudinal acoustic (LA) peak positions for NH_4Cl.*

DISCUSSION

Contrary to the intramolecular vibrations, all the low-frequency vibrations obviously increase with pressure. The difference between the increasing rates of the lattice and libration frequencies indicates the possibility of frequency crossing. The point of intersection obtained by linear extrapolation is about 230 kbar. The increase of structural parameter *u* means that a reduction in the D-Cl bond length takes place with pressure (from 2.300 to 2.175 at 25 kbar) while the length of N-D bond remains nearly the same (1.038 A at ambient pressure, 1.052 Å at 25 kbar). It is evident that as parameter *u* reaches the value of 0.25, either a collapse of molecular ND_4^+ ion or a change in its form or orientation towards the anion should be observed, because as u=0.25 the length of the N-D bond will be equal to the length of the D-Cl bond. The linear extrapolation of *u* to 0.25 gives a pressure value about 130 kbar for this transition. So, we may assume that the phase transition of unknown nature in ammonium halides[/6/] is connected with the existence of a dynamics and structural critical point. It is also possible that the transition pressure is determined by the anion polarization ability and decreases with its growth (P =100 ±10 kbar for NH_4Cl, P =80 ±10 kbar for NH_4Br and P =54 ±4 kbar for NH_4I).

CONCLUSIONS

In the present paper the structural (up to 25 kbar) and vibrational (up to 40 kbar) changes in NH_4Cl under high pressure were studied. The results obtained demonstrate the good prospects for using the sapphire anvils technique for inelastic neutron scattering under high pressure. At the moment P=40 kbar is the highest pressure obtained in an inelastic scattering experiment. We hope that in studies of hydrogen contain systems a higher values of pressure can be achieved at DN-12 spectrometer. In particular, these values are high enough to study the behavior of some halides in the vicinity of the above mentioned phase transition point. So, our experiments will be continued.

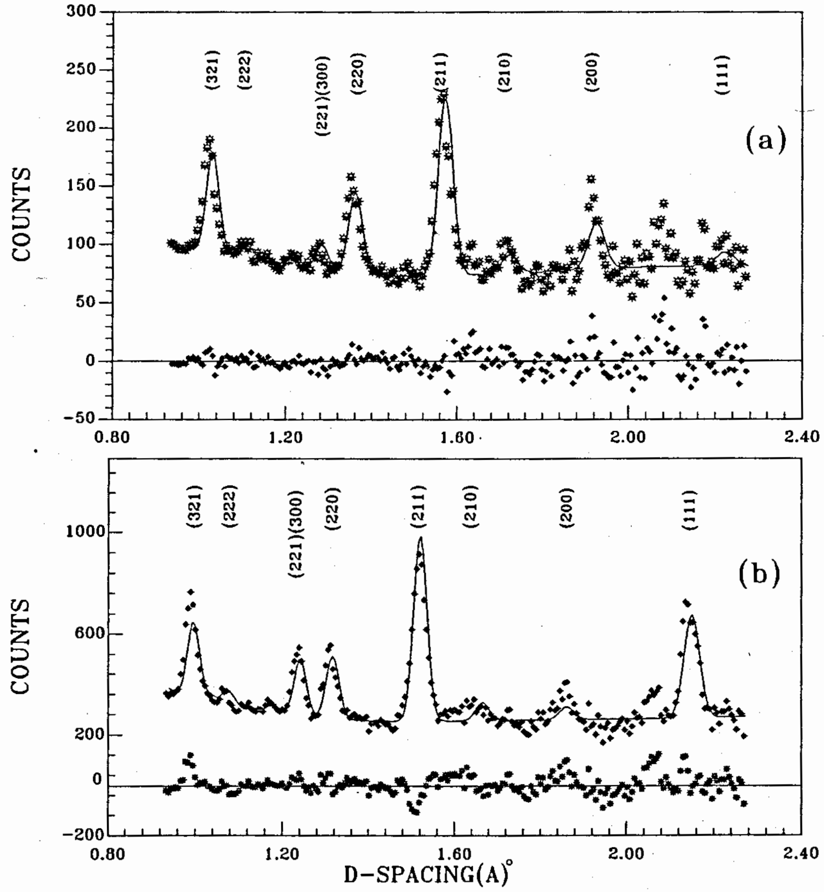

Figure 3 *Diffraction patterns of ND_4Cl at 0 (a) and 25 (b) kbar.*

Acknowledgments

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Экспериментальное исследование вибрационного спектра и структурных изменений в NH_4Cl при высоком давлении

Приведено описание техники сапфировых наковален в приложении к изучению спектра колебаний содержащих водород материалов методом неупругого рассеяния нейтронов. Эксперименты проведены на спектрометре по времени пролета ДН-12 на импульсном реакторе ИБР-2. Изменения под давлением структуры и характерных частот колебаний атомов (либрационных и решеточных мод) NH_4Cl прослежены до $P = 40$ кбар. Полученные результаты свидетельствуют о нестабильности структуры иона NH_4^+ при воздействии внешнего давления.

Работа выполнена в Лаборатории нейтронной физики им.И.М.Франка ОИЯИ.

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Experimental Study of the Vibrational Spectrum and Structure Variations in NH_4Cl under High Pressure

In this paper an application of the sapphire anvils technique to the study of the vibrational spectra of hydrogen contain systems by inelastic neutron scattering under high pressure is described. The experiments were performed with a time-of-flight spectrometer DN-12 at the IBR-2 pulsed reactor in Dubna. The structural changes and pressure dependence of the libration and lattice modes in NH_4Cl were studied up to 40 kbar. The results give some evidence of the NH_4^+ ion instability.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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