

# The Hidden Tetragonal Phase of Ammonium Fluoride

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Crystalline water (ice) must be one of the most heavily studied materials known. It is of importance simply because of the ubiquity of the water molecule, and ice is also a model system for studies of hydrogen bonding. Additionally, the structural versatility of ice's tetrahedral bonding (there are at least 17 crystalline ice structures) allows it to form a wide variety of inclusion compounds (for example, the gas hydrates) which have potential applications for storage and transport of gases. Ammonium fluoride is an interesting comparator for ice. Like ice it is hydrogen-bonded [1], at ambient pressure it adopts the same network topology [2], and, as we shall see below, at high pressures it may form a double network H-bond structure like ice VII/VIII. Unlike ice it has fully ionic bonding lead and alternating H-bond donor ( $\text{NH}_4^+$ ) and acceptor ( $\text{F}^-$ ) sites.

The phase diagram of ammonium fluoride is shown in figure 1. At ambient pressure it adopts a wurzite-related structure which has heavy atom positions like those of ice Ih. At 295K and 0.35GPa this phase I transforms to rhombohedral phase II which has a complex rhombohedral structure related to that of ice IV. Both of these structures have been determined by neutron diffraction for deuterated ammonium fluoride [2]. At about 1.5GPa and 295K, phase II transforms to phase III. Phase III has a cubic unit cell and a CsCl heavy-atom arrangement [3]. Bellin *et al* have recently published x-ray and Raman studies of the behaviour of phase III. The Raman spectra collected by Bellin *et al* at 295K showed changes in the pressure dependence of the lattice, librational, bending and combination (bending and stretching) modes at 10GPa and of the combination mode at 25GPa [4]. They also observed an anomaly in the equation of state beginning at 22GPa. Additionally, Bellin *et al* also observed a splitting of the lattice and bending modes at low temperatures, beginning at 10GPa and 100K. On this basis they proposed a transition to an ordered tetragonal structure in P-42m (phase III<sub>t</sub> in the phase diagram).

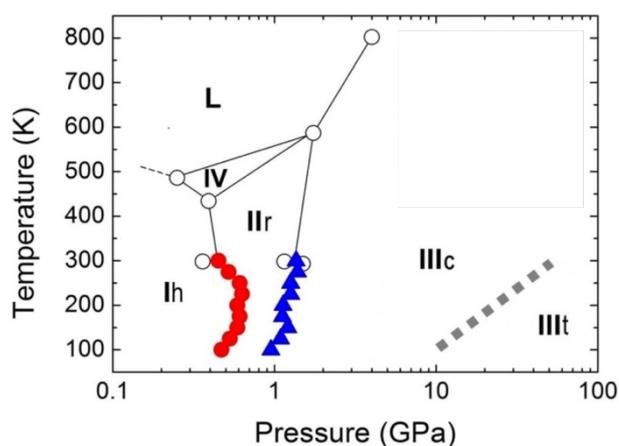


Figure 1. The phase diagram of ammonium fluoride, as measured by Bellin *et al* using x-ray and Raman techniques [4].

In our work, we are aiming to expand the understanding of the phase diagram of ammonium fluoride by using neutron diffraction in a Paris-Edinburgh press. This technique has the benefit of revealing information on the hydrogen positions that is not provided by x-ray scattering. We have measured the neutron diffraction patterns of deuterated ammonium fluoride at pressures ranging between 3 and 12GPa at 295K, and carried out measurements at 12GPa and 120K. These results suggest an additional phase transition to a tetragonal phase at 5.9GPa and room temperature, implying that the low temperature phase III<sub>t</sub> proposed by Bellin *et al* may exist at lower pressures and higher temperatures that first anticipated. Additionally, the measurements at 12GPa and 120K did not show any difference to the 295K results at the same pressure.

Ongoing work is being carried out to confirm these neutron diffraction results using DFT calculations in CASTEP; Raman spectroscopy; and x-ray scattering.

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