

**s6.m2.o3** **Structural and Thermodynamic Properties of Hydrogen-Bonded Solids.** A. Katrusiak, *Department of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznan, Poland*

Keywords: high pressures, hydrogen-bonds, phase transitions.

While hydrogen-bonded crystals belong to the most intensively investigated substances, relatively little is known about their transformations. Meanwhile, usually the transformations of hydrogen bonds can be easily categorized into few types, like H-bond breaking, H-bond formation, H-transfer, H-centering or H-disordering between the donor and acceptor groups. On the other hand, the H-bonds never exist on their own in crystal structures, but along with other cohesion forces. The interplay between H-bonds and other interactions at varying thermodynamic conditions of temperature and pressure will be discussed. It will be shown, that thermodynamic stability and the character of phase transitions can be predicted from structural dimensions and from the type of H-bond transformations. Thus, for example, the H-disordering in the OH- -H bonds in KHPO (KDP) and other KDP-type ferroelectrics is coupled with the displacements of hydrogen-bonded groups, and these displacements shorten the OO distances; consequently the displacements change the volume of crystals and induce a first-order character (i.e. discontinuity) to the phase transitions. High pressures, in turn, reduce the displacements, and the first-order character of the transformations. The structural crystal data can be used for assessing the magnitudes of anomalous thermal expansion at , temperature of the phase transition, the pressure of tricritical point, or other crystal properties of the hydrogen-bonded crystals [A. Katrusiak, *Phys. Rev. B* 48 (1993) 2998; *B51* (1995) 589; *Phys. Rev. Lett.* 77 (1996) 4366; *Pol. J. Chem.* 72 (1998)449; *J. Mol. Struct.* 474 (1999) 125; A. Katrusiak & M. Szafranski, *Phys. Rev. Lett.* 82 (1999) 576].

**s6.m2.o4** **Neutron Diffraction Study of ND<sub>4</sub>I and ND<sub>4</sub>Br Structure at High Pressure and Low Temperature.** D.P. Kozlenko<sup>1</sup>, B.N. Savenko<sup>1</sup>, V.P. Glazkov<sup>2</sup>, V.A. Somenkov<sup>2</sup>, S. Hull<sup>3</sup>, *1 Frank Laboratory of Neutron Physics, JINR, 141980 Dubna Moscow Reg Russia, 2 RRC "Kurchatov Institute" 123182 Moscow Russia, 3 ISIS Facility, RAL, Chilton, Didcot, Oxon OX11 0QX, UK*

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Structural studies of ammonium halides are of great interest due to a number of pressure and temperature induced phase transitions they undergo with respect to relative orientation of ammonium ions [1]. Recently a new high pressure phase V of ammonium halides has been observed in Raman spectra and its structure was unknown for a long time [2]. In this work, structure of ND<sub>4</sub>I and ND<sub>4</sub>Br has been studied at high pressures up to 9 GPa and room temperature with the POLARIS diffractometer and Paris - Edinburgh high pressure cell facility (ISIS, RAL, UK) by means of time-of-flight powder neutron diffraction. Structure of the high pressure phase V was determined and deuterium position parameter as a function of pressure was obtained. Surprisingly, the structure of the phase V was found to bear a strong resemblance to that of ambient pressure, low temperature phase III of ammonium halides - tetragonal structure with antiparallel ordering of ammonium ions, space group *P4/nmm*. To found possible differences between phase III & V structures and study structural changes in ND<sub>4</sub>I at high pressures and low temperatures, ND<sub>4</sub>I was studied at pressures up to 2.5 GPa and temperatures down to 12 K with DN-12 spectrometer (FLNP JINR, Dubna, Russia) and sapphire anvil high pressure cell equipment. Lattice parameters and deuterium positional parameter at different pressures as functions of temperature were obtained. Differences between phases III & V structures and possible mechanisms of the pressure - induced phase transition to the phase V in ND<sub>4</sub>I and ND<sub>4</sub>Br are discussed.

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[2] S.J.Jeon, R.F.Porter, A.L.Ruoff, *J. Raman Spectroscopy*, 19 (1988) 179.