ESRF	**Experiment title:** Structure solution and refinement of high pressure phases with short H-bonds	**Experiment number:** HC131
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Report:

Introduction

Systems with short hydrogen bonds are of considerable interest for our understanding of hydrogen bonding in general. Questions of fundamental importance are e.g.:

1) What governs the transition from the common double minimum H-potential into a (symmetric) single minimum. It is not simply the O...O distance as may be seen from some of the frequently displayed O...O vs. O-H plots. Rather it is a more complicated (sterical) interaction involving other atoms in the neighbourhood of a H-bond.
2) Is the proton transfer in a short double minimum H-bond governed by tunneling processes? Although repeatedly evoked in the past, serious doubts have been expressed more recently, yet tunneling may be important at least at low temperatures and for very short H-bonds.

We have started a series of X-ray and neutron diffraction as well as Raman-scattering experiments on members of the KDP (KH_2PO_4)- family in search of short symmetric H-bonds. Several high pressure phases exist, for some of which we only know their existence. The poor quality of conventional high pressure X-ray data prevent the indexing and structure solution of these phases. This is true in particular for the phase V (stable above 4 GPa) and VI (stable above 10.5 Gpa) of KDP. Phase VI may be structurally related to phase V and may even be its symmetrically H-bonded equivalent. The structure solution and subsequent X-ray Rietveld-refinement of these phases was the purpose of this proposal. It

needed the high brilliance of a dedicated synchrotron source, a very good angular resolution and good spatial averaging of the powder rings. Due to the limited beam time only KDP (and not its deuterated analogue KD_2PO_4) were investigated.

Experimental

KDP phase V was formed by heating a KDP sample up to 220 °C at 5 GPa in the home laboratory (as the transition at ambient temperature is too slow). Three different DACs were used in the experiment. Pressure dependent data were taken in the range from 5.6 GPa to 18 GPa to assist the indexing procedure and to provide in the refinement stage structural compressibility data. Optimal use of the beam time was assured by cyclic use of different pressure cells with off-beam periods used for loading, pressure increase and calibration. The cells were rocked during the exposure by typicaIly ±3° to avoid diamond Bragg reflections. The image plate data were analysed using FIT2D; a typical powder pattern is shown in Fig. 1.

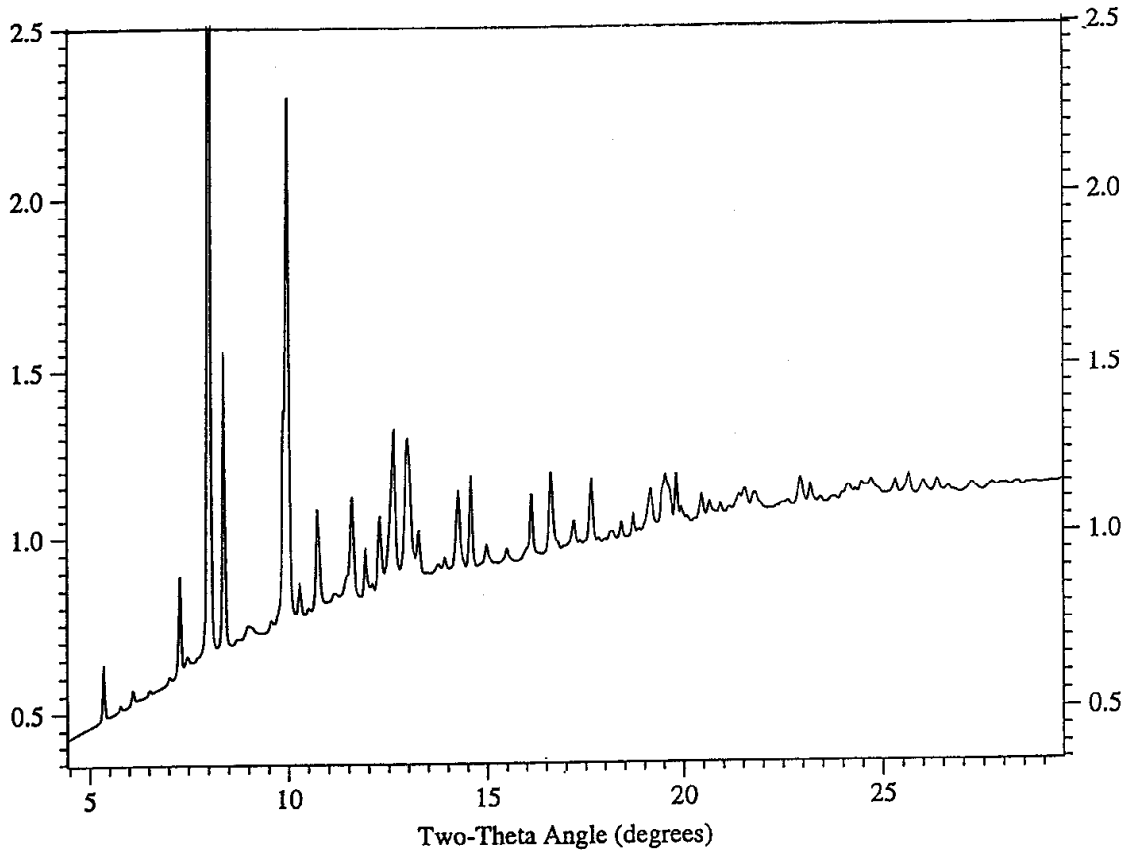

Fig.1 KDP phase V at 5.6 GPa 30 min exposure

The indexing of the 23 pressure dependent data sets (of seemingly isostructural material) turned out to be extremely difficult. All indexing programs on the market were tried with very little success initially. Later efforts gave a solution with an orthorhombic cell, lattice constants of 9.36, 6.65 and 5.20 Å and a unit cell volume of 323.8 $Å^3$ (this volume is not far from the cell volume of KDP phase II). This solution explains the strong and medium strong reflections, but does not explain all weak ones. A structural model could not be worked out so far; further work is in progress however.