ESRF	**Experiment title:** Search for Incommensurate Structures in Phosphorus above 100GPa	**Experiment number**: HS-2817
Beamline: ID09	**Date of experiment**: from: 27/10/2005 to: 30/10/2005	**Date of report**: 25/02/07
Shifts: 9	**Local contact(s)**: M. Hanfland	*Received at ESRF:*

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Report: While the electronic structure of the elements at ambient conditions is well known and understood, the relative movement of electron levels under pressure can result in electronic structures that are completely different to those found at ambient pressure. This can lead to structural transitions from high-symmetry close-packed structures to complex, open-packed structures. Recently, we have reported an entirely new complex structure type at high pressure. This structure, first observed in the group-II element barium, comprises a body-centred tetragonal (bct) 'host' structure that has channels along the *c* axis [1]. Contained within these channels are chains of atoms from one or more 'guest' structures that are incommensurate with the host along *c*. Since its discovery in Ba, we have found the same structure type to be stable in Sr, and in the group V elements Bi, Sb, As and Sc [2,3]. While the host structure is the same in each element, a number of different guest structures are observed: face-centred tetragonal, face-centred monoclinic, body-centred tetragonal and body-centred monoclinic. The observation of incommensurate host-guest structures in all of the heavier group-V elements begs the question as to whether the same structure also exists in the lighter member of this group – that is, in phosphorus. A previous diffraction study of phosphorus has reported a transition to a complex “intermediate” phase (P-IV) of unknown structure at 107GPa, which in turn transforms to a primitive hexagonal phase (P-V) at 137GPa [4]. **In this proposal we asked for 3 days of beamtime on ID09 to determine the crystal structure of P-IV above 107GPa, and to follow its pressure dependence up to ~140GPa.**

The sample of black phosphorous was provided by Dr U. Schwarz of the Max-Planck-Institut fuer Chemische Physik fester Stoffe in Dresden and was loaded with H_2 as a pressure medium. Diffraction data were collected in small pressure increments up to 115GPa, where the transition from primitive cubic P-III to the intermediate P-IV phase was observed. This phase was observed to be stable up to 131GPa, where the sample began to transform to the primitive-hexagonal P-V phase. A single-phase diffraction profile from P-IV at 124GPa is shown in Fig. 1.

The diffraction profiles from P-IV are very different to those obtained from the host-guest structures of the heavier group-V elements, suggesting that P-IV does not have a composite structure. Attempts at indexing the profiles from P-IV were unsuccessful. However, in 2006, Japanese researchers proposed a structural model for P-IV which although incommensurate, is different to those incommensurate structures observed in other elements. A fit of this proposed structure to the diffraction data from P-IV at 124GPa is shown in Fig. 2, and is extremely good, especially considering the effects of preferred orientation and texture that existed in the diffraction profiles. A full account of this study, including a detailed study of both the incommensurate wavevector q and the amplitude of the incommensurate modulation as a function of pressure, is currently being prepared from Physical Review.

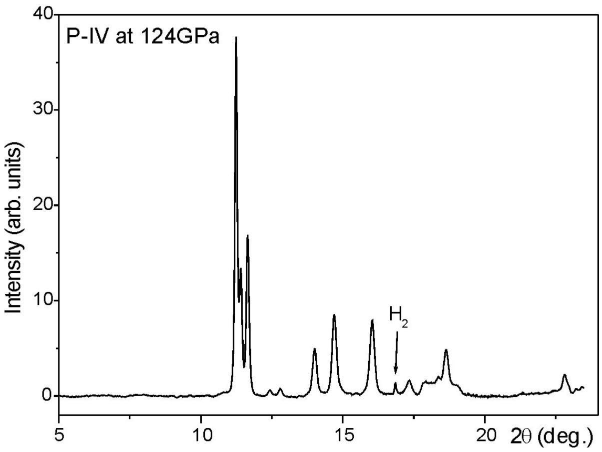

Fig 1: Diffraction profile from phase-IV of phosphorous at 124GPa. A diffraction peak from the H_2 pressure medium is indicated.

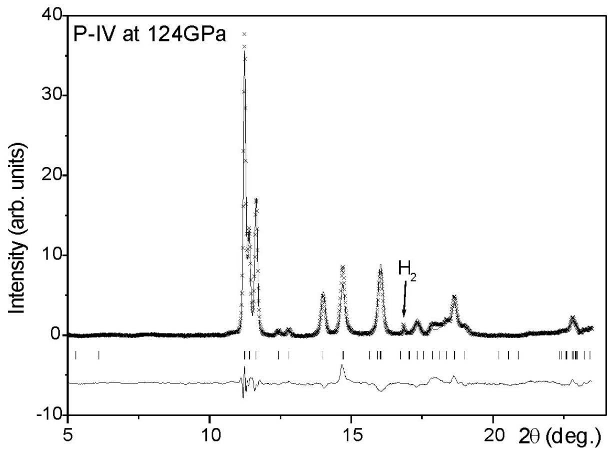

Fig 2: Rietveld refinement of P-IV at 124GPa using the incommensurate structure proposed by Akahama *et al.*

References:

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