## STRUCTURAL TRANSITION FROM SIMPLE CUBIC TO SIMPLE HEXAGONAL IN PHOSPHORUS AT 137 GPa

The phosphorus (P) of the group-Vb elements exhibits a unique sequence of structural phase transitions under pressure. At 4.5 GPa, black P which is the most stable form A17 structure (Cmca: P-I) at ambient conditions, undergoes a transition to the A7 phase ($R\bar{3}m$: P-II). At 10 GPa, it transforms further to the simple cubic (*sc*) phase ($Pm\bar{3}m$: P-III), which is metallic. The *sc* structure, a Bravais lattice with only one atom in the unit cell, is rare in all elements. The high-pressure stability of the *sc* phase has attracted special interest because it has the lowest packing fraction of atoms (0.524) and predicted Peierls' lattice instability. Because of the relatively low Z number of phosphorus, the X-ray diffraction studies had been limited to 83 GPa up to now. In this study, an angle dispersive X-ray diffraction technique has been applied to the study of the pressure-induced structural transition of phosphorus at the beamline **BL10XU**. The obtained powder diffraction patterns revealed that the *sc* phase transforms to the simple hexagonal (*sh*) phase (P6/mmm: P-V) at 137 GPa via an intermediate phase (unknown: P-IV). The instability of the *sc* phase was confirmed at 107 GPa. The typical powder patterns are shown in Figure 1. The *sh* structure is also as rare as the *sc* structure in the monoatomic system. The *sh* lattice can be easily derived from the *sc* lattice by a monoclinic distortion along the [110] direction (Figure 2). The volume reduction of the transition is estimated to be 7.6 % of the atomic volume of the *sc* phase ($-\Delta V = 0.74$ $^3$) at 103 GPa. The estimation is done from the atomic volume versus pressure relation shown in Figure 3. The relatively large reduction comes from an increase in the coordination number from 6 to 8. Therefore, the structure of the P-IV phase may be found in the process of this distortion. The simplest and fundamental transition from the *sc* to *sh* structure is the first observation in the monoatomic system.

Iwasaki & Kikegawa [1] have proposed a transition to the (disordered-)bcc structure for the post-*sc* phase based on an analogy to the other group Vb elements (As, Sb and Bi), and another theoretical study has predicted the *sc*-*bcc* phase transition at 135 GPa [2]. However, phosphorus exhibited a different sequence of the structures from the one they proposed. Intense interest has thus been shown in the mechanism of the *sc*-*sh* transition. The fact that the *sh* structure has a lower packing fraction of the atoms (0.605) than any of the *bcc* (0.680), *fcc* and/or *hcp* (0.740) structures strongly suggests a survival of covalent bond in the cohesion of the metallic phase of phosphorus.

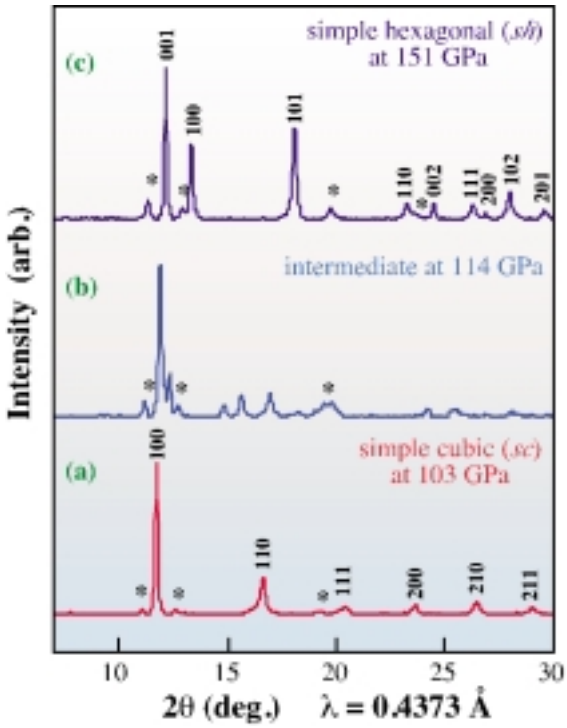


*Fig. 1: Typical powder diffraction patterns of the high-pressure phases of phosphorus at RT; **(a)** simple cubic (sc) phase at 103 GPa, **(b)** intermediate phase (P-IV) at 114 GPa, and **(c)** simple hexagonal (sh) phase at 151 GPa. They were obtained with an X-ray beam of λ=0.4373 Å. Miller indexes in **(a)** and **(c)** are appropriately assigned to the reflections from the sc (a=2.1374±0.0008 Å) and sh (a=2.1750±0.0004 Å, c=2.0628±0.0005 Å) phases, respectively. Since the P-IV phase exists in a narrow pressure region, it must be an intermediate phase between the sc and sh phases. The structure is unknown. Asterisk (*) represents reflection from an Re gasket. Courtesy of the Amer. Phys. Soc. [#].*

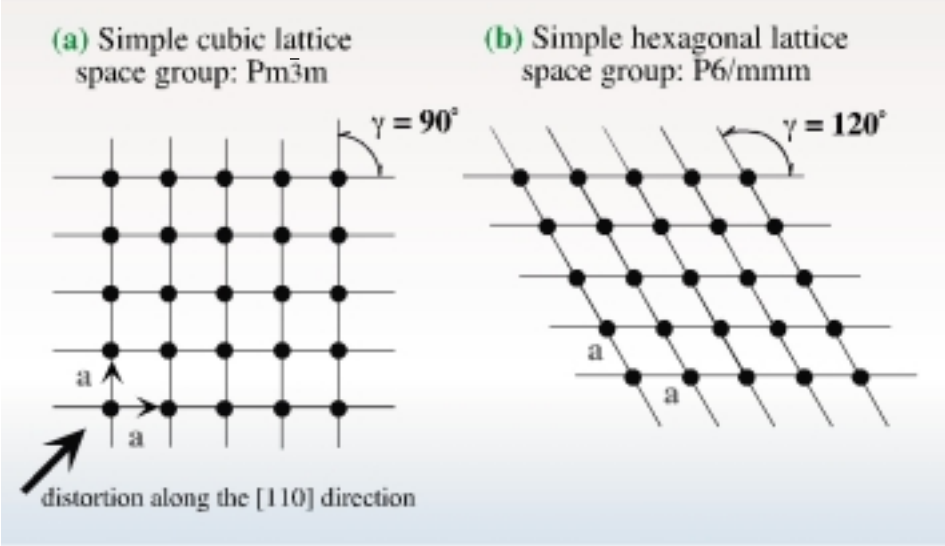


*Fig. 2: Atomic arrangements of the sc lattice (a) and the sh lattice (b) projected onto the (001) plane. The sh lattice can be derived from the sc lattice by a monoclinic distortion along the [110] direction. The transition from the sc to sh structure is completed with a monoclinic angle γ of 120°.* *Courtesy of the Amer. Phys. Soc. [#].*

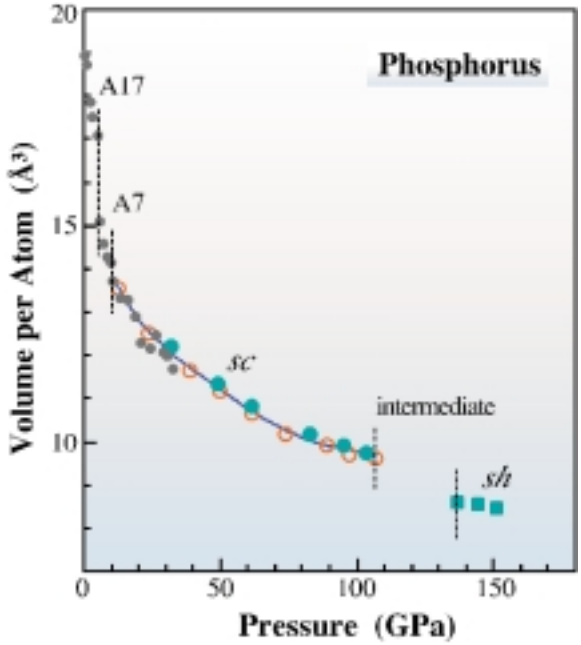


*Fig. 3: Pressure dependence of atomic volume of phosphorus at 300 K. Present data are shown by open circles (for first run), and solid circles and squares (for second run). Small solid circles show previous data by Kikegawa & Iwasaki [3]. Solid line represents the result of a least-squares fitting of the Birch-Murnaghan equation of state to the present data of the sc phase: the bulk modulus ($B_0$)=70.7 GPa, its pressure derivative ($B_0'$)=4.69 and relative atomic volume at atmospheric pressure (V/ V0)=0.815.*
*Courtesy of the Amer. Pys. Soc. [#].*

Further extension of pressure in the multimegabar (>200 GPa) range must lead to a structure with a higher packing fraction of atoms, that is, a free-electron gas state such as the *fcc*-Al.

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**References**

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