

function of electrolytic gating to better understand this process.

### 1.3 Black phosphorus

Phosphorus has four main allotropes and many more modification subsets of each one[82]. The most popular of these allotropes are red, white, and black. Red and white phosphorus are highly flammable while black phosphorus is the most stable of the allotropes[83–89]. Black phosphorus (BP) was first discovered by P. W. Bridgman[83] in 1914 in an attempt to convert white phosphorus to red phosphorus using high hydrostatic pressure. It packs into orthorhombic structure with space group  $Cmca$  at room temperature and ambient pressure[88]. The orthorhombic structure of BP is shown in Fig1.11. Each phosphorus atom is bonded with two in-plane and one out-of-plane neighboring atoms. The two in-plane atoms are at  $99^\circ$  from one another and the out-of-plane atom is at an average angle of  $120^\circ$ . Due to this anisotropic atomic structure, the effective masses of carriers in BP along arm chair (ac) are lightest and that along the layer stacking (z) are lighter than that along the zigzag (zz)[90]. This induces strong in plane anisotropy in its electronic, optical and phonon properties[91, 92].

BP is a direct band gap semiconductor with the band gap of  $\sim 0.3eV$ . This gap arises from the out-of-plane  $p_z$  like orbitals of phosphorus and hence can be strongly modulated by pressure or c-axis strain. The effect of pressure was studied on crystal structure and electronic properties in the early work[93–99]. It has anisotropic compressibility due to asymmetric crystal structure: lattice parameters  $a$  and  $c$  decrease more in comparison with the lattice parameter  $b$  with increasing pressure. At room temperature, the ambient pressure orthorhombic structure transforms to the rhombohedral structure at 4.7 GPa and then to the simple cubic structure (sc) at 11 GPa[99]. These transition pressures are slightly higher[100] if the sample is cooled to liquid helium temperature first and then pressure is increased (Fig.1.12). Furthermore, the sc phase transforms to a simple hexagonal (sh) phase at 137 GPa via an intermediate phase[101]. Recently, Akahama et al. [102] investigated the crystal structure of phosphorus up to 280 GPa at room temperature using x-ray-diffraction and found that the sh phase goes to a new structural phase transition at 262 GPa (Fig.1.13). This

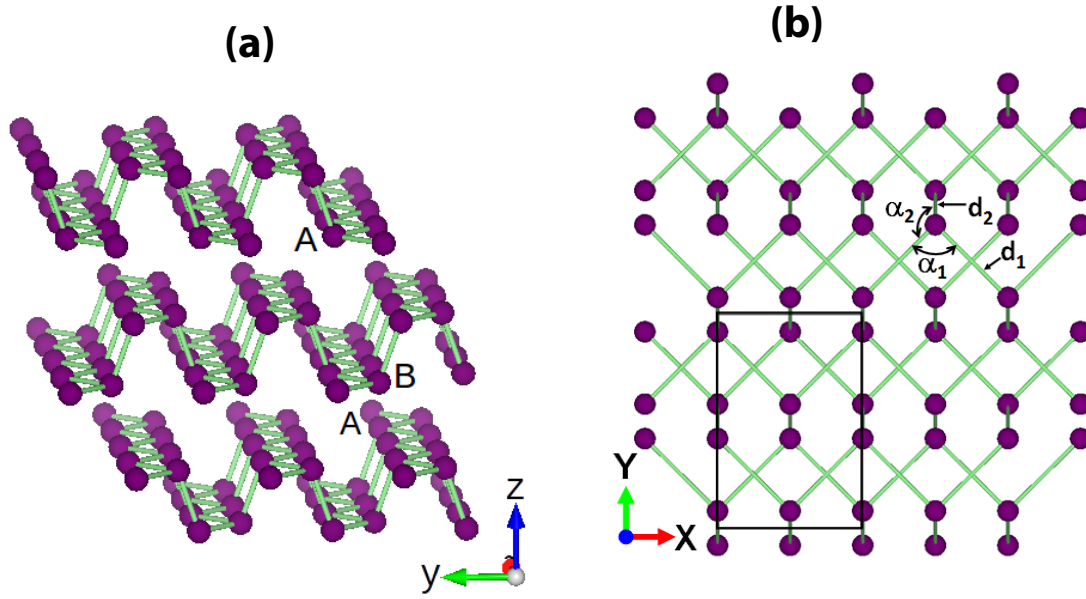


FIGURE 1.11: Crystal structure of BP in orthorhombic phase (a) side view (b) top view.

new structure is proposed to be the bcc structure. The sc phase shows superconductivity at 4.7 K[103, 104]. The superconducting temperature is slightly pressure dependent and increases with increasing pressure. The superconducting state remains for several hour even when pressure is removed. BP shows superconductivity with high transition temperature (10K) if it is cooled to 4K first and then pressure is applied, showing that high pressure can be used to tune the material characteristic significantly. The electrical conductivity of BP is also very sensitive to pressure[105–107]. Two anomalies have been reported at 1.7 and 4.2 GPa, the latter coinciding with the structural phase transition from orthorhombic to rhombohedral structure. The earlier report[108] showed that the band gap decreased linearly with pressure coefficient of  $\sim 0.17$  eV/GPa and the band gap closes at  $\sim 1.5$  GPa. Recent magneto-resistance studies[109] have termed this transition as electronic topological transition (ETT) monitoring the transformation from semiconductor to 3D Dirac semimetal due to band crossing near the z-point in the Brillouin zone with linear dispersion. Interestingly, a colossal magneto-resistance of  $\sim 80,000$  is seen at 2 GPa at a field of 9T, similar to 2D  $\text{WTe}_2$ , making BP as an elemental semimetal. The role of lattice in pressure-induced electronic topological transition has been seen by softening of an acoustic phonon mode at 1.54 GPa in

an earlier inelastic neutron scattering[110], where anomalous compressibility and softening of longitudinal ultrasonic wave propagating along c-axis further point out the role of electron-phonon interaction in pressure-induced transition. High pressure Raman spectroscopy, a novel probe of lattice distortion under pressure, has been done up to 13 GPa, displaying changes in the pressure coefficients of Raman frequencies at the structural transition at 4.7 GPa and 10.5 GPa[99]. We have revisited the high pressure Raman studies to see the Raman signatures of electronic topological transition at  $\sim 1.5$  GPa; and to extend the pressure range to 24 GPa.

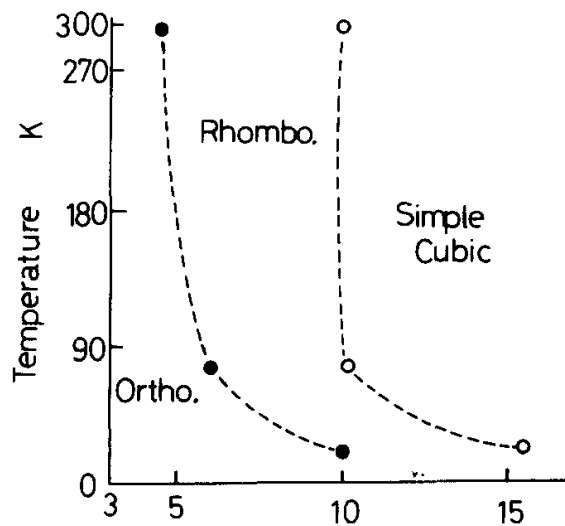


FIGURE 1.12: P-T phase diagram of BP at low temperature and high pressure[100]

At the beginning of 2014, BP was reintroduced from the prospective of layered thin film materials. Out-of-plane interactions between each layer are weak van der Waals interactions (exfoliation energy is about -151 meV/atom) while the in-plane bonding is much stronger and is governed by atomic orbital hybridization. Similar to graphite, the layered structure of BP can be exfoliated to its single and few atomic layers by micromechanical exfoliation techniques. The monolayer of BP is called phosphorene. Due to the anisotropic bonding between the phosphorus atoms, phosphorene does not form atomically flat sheets like graphene.

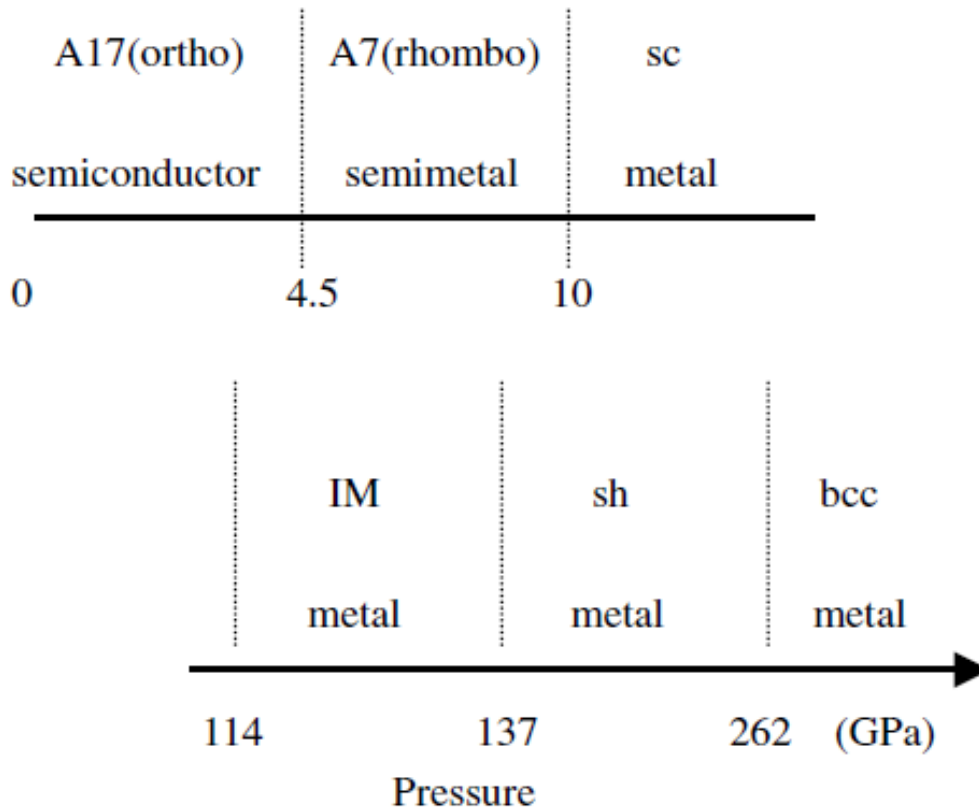


FIGURE 1.13: Phase diagram of BP at high pressure [102].

Instead it forms a puckered honeycomb structure which gives phosphorene very unique properties not found in other members of the 2D materials family. Unlike gapless graphene, mono or few layer black phosphorus is a direct band gap material with gap ranging from 0.3 eV in bulk to 2 eV in monolayer, covering a wide range of electromagnetic spectrum[91, 111–116]. This is again distinctive from transition metal dichalcogenides (TMD) which exhibit a direct band gap of  $\sim 1$  to 2 eV only in their monolayer form. The narrow band gap of BP (in few layer form) bridges the gap between the zero gap graphene and large band gap TMDs, thus making BP a suitable candidate for near and mid infrared optics[117]. For possible applications in electronic devices, mono or few layers black phosphorus offers a good possibility with mobility of  $\sim 1000$   $\text{cm}^2/\text{V}\cdot\text{sec}$  at room temperature and On-Off ratio of  $\sim 10^5$  with excellent current saturation characteristics (Fig.1.14)[118].