First principles study on superconductivity of distorted bcc phase in phosphorus

A Nakanishi, T Ishikawa and K Shimizu
Center for Science and Technology under Extreme Conditions, Graduate School of Engineering Science, Osaka University, Japan

E-mail: nakanishi@hpr.stec.es.osaka-u.ac.jp

Abstract. We investigated structural stability and superconductivity of phosphorus under high-pressure using first-principles calculations. We found the structural transition from the simple hexagonal (sh) structure into the experimentally observed cI16 structure via the body-centered cubic (bcc) structure in pressure range of 262-286 GPa. The superconducting transition temperature $T_c$ is largely increased from 0.5 K to 12 K by the transition from sh into bcc, which is the highest $T_c$ in phosphorus. The $T_c$ value is decreased to 6 K by the transition into the cI16 phase. The change of $T_c$ is related to that of the density of states at the Fermi level.

1. Introduction
Phosphorus takes an orthorhombic $Cmca$ (A17) (P-I) at ambient condition [1,2], and it transforms to a rhombohedral $R3m$ (A7) (P-II) at 4.5 GPa and then to a simple cubic (sc) structure (P-III) at 10 GPa [3]. In the sc phase, the superconductivity is experimentally observed. The superconducting quantum interference device with vibrating coil clarified that the superconducting transition temperature $T_c$ takes a maximum value of 9.5 K at 32 GPa and then gradually decreases to 4.3 K with increase of pressure to 100 GPa [4]. The sc structure takes the structural phase transition to the simple hexagonal (sh) structure (P-V) via an intermediated phase (P-IV) in the pressure range from 107 to 137 GPa [5]. The structure of the P-IV phase was theoretically predicted to be a modulated structure [6], and then it was experimentally identified to be an incommensurately modulated (mod) structure of an orthorhombic $Cmmm(00\gamma)s00$ with $\gamma = 0.267$ [7].

Phosphorus takes a further phase transition (P-VI) at 262 GPa. Sugimoto et al. experimentally identified the P-VI phase as a distorted bcc structure (cI16) using a synchrotron radiation x-ray powder diffraction measurements [8]. However, first-principles calculations predict that the sh structure first transforms into the bcc structure and then into an orthorhombic modulated superlattice of bcc (IM7), which is different from the experimentally observed structure [9]. Furthermore, the IM7 structure is predicted to transform into the hexagonal close-packed (hcp) structure at 346 GPa.

The experimental observations and first-principles calculations ensure the emergence of a distorted bcc phase in high pressure region, whereas the consistent results have not been obtained. In the present study, we carefully compared the enthalpies among the candidate structures in phosphorus and determined the sequence of the pressure-induced structural phase transitions using first-principles calculations based on density functional theory. Then, we calculated the superconducting $T_c$ on the basis of the sequence to clarify the superconductivity of phosphorus in pressure region above 100 GPa, which has not been experimentally investigated.
2. Computational details

We used the exchange-correlation energy functional of Perdew-Burke-Ernzerhof [10] for the generalized gradient approximation, and the Vanderbilt ultrasoft pseudopotential [11]. We performed the calculations using the code package, Quantum ESPRESSO [12]. For the mod phase, we used the approximated structure with commensurate periodicity of $\gamma = 0.250$. The structural parameters for sc, mod, sh, bcc, cI16, IM7, and hcp at each pressure were obtained by the constant-pressure variable-cell structural optimization based on the Parrinello-Rahman method [13]. The $k$-space integration over the Brillouin zone was performed by a $16 \times 16 \times 16$ grid for sc, sh, bcc, and hcp, a $16 \times 16 \times 4$ grid for mod, a $24 \times 24 \times 12$ grid for IM7, and an $8 \times 8 \times 8$ grid for cI16 in the Monkhorst-Pack grid [14]. The cut-off kinetic energy for wave functions was set at 30 Ry. These $k$-point grids and cut-off energies are enough to achieve convergence within 0.1 mRy/atom in the total energy.

Assuming that phosphorus shows the phonon-mediated superconductivity under high-pressure condition, we estimated $T_c$ by the use of the Allen-Dynes formula [15]. We set effective screened Coulomb repulsion constant $\mu^*$ at 0.1. In the calculation of the phonon frequency, we employed the linear response method in which the first order corrections are calculated by means of the density functional perturbation theory [16,17]. The electron-phonon matrix element was calculated using a $32 \times 32 \times 32$ grid for sc, sh, bcc, cI16, and hcp and a $32 \times 32 \times 8$ grid for mod. These grids ensure the convergence of the $k$-point sampling with Gaussian width of 20 mRy, which approximates the zero-width limits with respect to double-delta functions of the line width. To obtain the electron-phonon coupling constant $\lambda$ and the logarithmic-averaged phonon frequency $\omega_{\text{hop}}$, we used an $8 \times 8 \times 8$ $\mathbf{q}$-point grid for sc, sh, bcc, and hcp, an $8 \times 8 \times 2$ $\mathbf{q}$-point grid for mod, and a $4 \times 4 \times 4$ $\mathbf{q}$-point grid for cI16.

![Graph](image)

**Figure 1.** Enthalpies comparison in phosphorus. The relative enthalpies with respect to sh are plotted.

3. Results

3.1. Sequence of the structural phase transitions

First we investigated stable regions for the sc, mod, sh, bcc, cI16, IM7, and hcp phases. Figure 1 shows the comparison of the enthalpies among these seven phases in the pressure range from 50 to 350 GPa. The zero-point energies were not included in the calculations. The results indicate that the mod phase emerges in pressure range from 120 to 136 GPa, which shows a slight discrepancy with the experimentally observed one, 107-137 GPa, owing to the commensurate approximation. In our calculations, first sh transforms into bcc at 262 GPa and then into the experimentally observed cI16 at 286 GPa. The earlier-predicted IM7 has no stable pressure region up to at least 350 GPa. Sugimoto et al. reported that the sh and cI16 phases coexist over a wide pressure region of 262-322 GPa at room temperature [8]. Therefore, the predicted bcc phase could be experimentally obtained by careful
investigation on the pressure region at low temperatures. By further compression, the hcp structure emerges as the most stable structure above 336 GPa.

![Graph](image)

**Figure 2.** Changes of superconducting transition temperature $T_c$ (open circle) and normalized density of states at the Fermi level $N(E_F)$ (open triangle) through the sequence of the structural phase transitions: sc → mod → sh → bcc → cI16 → hcp. Experimentally observed $T_c$ values (solid circle) for sc [4] are also plotted together.

3.2. *Superconducting properties*

On the Basis of the sequence of the structural transitions shown above, we investigated the superconductivity of phosphorus under high-pressure. Figure 2 shows calculated $T_c$ values as a function of pressure with the experimentally observed $T_c$ data [4]. We eliminated the data at pressures where the phonon modes have imaginary frequency, i.e. the data at 10 GPa in sc and at 270 and 280 GPa in bcc. In 30-100 GPa, the calculated $T_c$ values are in good agreement with the experimental values, which ensures the reliability of the results in pressure region above 100 GPa.

According to Figure 2, our calculations predict that $T_c$ decreases from 6 to 3 K by the transformation from sc to mod, increases to 7 K by the transformation to sh, and gradually decreases to almost 0 K with further pressurization. However, $T_c$ is largely enhanced to 12 K through the phase transition from sh to bcc at 260 GPa. This value exceeds that observed in the sc phase and sets a record for the highest $T_c$ in phosphorus. The superconducting $T_c$ decreases to 6 K through the phase transition to cI16, and again increases to 8 K by the transition to the hcp phase.

To clarify the origin of the $T_c$ change through the structural phase transitions, we investigated the change of the density of states at the Fermi level $N(E_F)$ (open triangle in Figure 2). Since the unit cell of the mod, cI16, and hcp structures contain two or more atoms, $N(E_F)$ was normalized to the unit per atom. Above 120 GPa, $T_c$ and normalized $N(E_F)$ have similar pressure dependency. This means that the $T_c$ change is mainly involved by the $N(E_F)$ change. In the mod phase, the electronic states escape from the Fermi level by the formation of the modulated structure and pseudogap is formed, which causes the decrease of the normalized $N(E_F)$. The details have been discussed by Marquès et al.[18], Ishikawa et al. [19], and Nakamishi et al. [20]. The reason for the decrease of $N(E_F)$ in the mod phase is also applied to the case of the cI16 phase. The cI16 structure is formed by the distortion of bcc, which causes the creation of the pseudogap at the Fermi level. As the results, the $N(E_F)$ value of the cI16 phase is lower than those of the bcc and hcp phases.

4. **Conclusion**

In this study, we investigated the sequence of the pressure-induced structural phase transitions of phosphorus by comparing the enthalpies among the seven candidate structures. We found that the sh structure transforms to the bcc structure at 262 GPa and then to the experimentally observed cI16 structure at 286 GPa. The earlier predicted IM7 structure has no stable region for pressure.
On the basis of the sequence of the structural phase transitions, we examined the pressure dependence of the superconducting transition temperature $T_c$. Our calculations predict that $T_c$ largely increases from almost 0 K to 12 K by the structural transition from sh to bcc at 260 GPa, which sets a record for the highest $T_c$ in phosphorus. The superconducting $T_c$ was found to decrease by the transformation from bcc to cI16 and increase again by the transformation to hcp. The decrease of $T_c$ in the cI16 phase is closely related to the decrease of DOS at the Fermi level $N(E_F)$, which is caused by the creation of the pseudogap at the Fermi level owing to the distortion from bcc.

References
[1] Hultgren R, Gingrich N S and Warren B E 1935 J. Chem. Phys. 3 351.
[2] Brown A and Rundqvist S 1965 Acta Crystallogr. 19 684.
[3] Kikegawa T and Iwasaki H 1983 Acta Crystallogr. Sect. B 39 158.
[4] Karuzawa M, Ishizuka M and Endo S 2002 J. Phys.: Condens. Matter 14 10759.
[5] Ishikawa T, Nagara H, Kusakabe K and Suzuki N 2006 Phys. Rev. Lett. 96 095502.
[6] Fujihisa H, Akahama Y, Kawamura H, Ohishi Y, Gotoh Y, Yamasaki H, Sakishima M, Takeya S and Honda K 2007 Phys. Rev. Lett. 98 175501.
[7] Sugimoto T, Akahama Y, Fujihisa H, Ozawa Y, Fukui H, Hirao N and Ohishi Y 2012 Phys. Rev. B 86 024109.
[8] Mikhaylushkin A S, Simak S I, Johansson B and Häussermann U 2007 Phys. Rev. B 76 092103.
[9] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865.
[10] Vanderbilt D 1990 Phys. Rev. B 41 7892.
[11] Giannozzi P et al. 2009 J. Phys.: Condens. Matter 21 395502.
[12] Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188.
[13] Allen P B and Dynes R C 1975 Phys. Rev. B 12 905.
[14] Savrasov S Y 1996 Phys. Rev. B 54 16470.
[15] Baroni S, de Gironcoli S, Corso A D and Giannozzi P 2001 Rev. Mod. Phys. 73 515.
[16] Marquès M, Ackland G J, Lundegaard L F, Falconi S, Hejny C, McMahon M I, Contreras-García J and Hanfland M 2008 Phys. Rev. B 78 054120.
[17] Ishikawa T, Nagara H, Mukose K, Kusakabe K, Miyagi H, and Suzuki N 2008 High Pressure Res. 28 459.
[18] Nakamishi A, Ishikawa T, Nagara H, Shimizu K and Katayama-Yoshida H 2012 High Pressure Res. 32 3.