Pressure-induced metallization and reentrant insulativity in elemental crystal of phosphorus: a prediction by ab initio calculations

Quan Zhuang1,2, Xilian Jin1,4, Kuo Bao1 and Tian Cui1,3,4

1 College of Physics, State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, People’s Republic of China
2 Inner Mongolia Key Laboratory of Carbon Nanomaterials, Nano Innovation Institute (NII), College of Chemistry and Materials Science, Inner Mongolia University for Nationalities, Tongliao 028000, People’s Republic of China
3 School of Physical Science and Technology, Ningbo University, Ningbo 315211, People’s Republic of China
4 Authors to whom any correspondence should be addressed. E-mail: jinxilian@jlu.edu.cn and cuitian@jlu.edu.cn

Keywords: high pressure, reentrant insulativity, elemental phosphorus

Abstract
Elemental materials made up from just one type of element is more unpredictable than people usually think at pressures. For examples, alkali metals are reported to transform into insulator firstly and then reenter into metallic state with pressures. Here, we have deeply investigated the structures and electronic properties of elemental phosphorus under high pressure. The phase sequence of phosphorus is improved, and two new close-packed structures are proposed to be stable beyond 350 GPa. Strikingly, for the insulate phosphorus at ambient pressure, the feature of pressure-induced metallization and subsequently reentrant insulativity with pressures is deduced, which is opposite to the evolutionary electronic structures in alkali metals upon compression. Furthermore, the electronic density of states at Fermi level is disclosed to dominate the variation trend of electron–phonon coupling strength and superconducting critical temperature.

1. Introduction
Many elemental materials are usually discovered in simple crystal lattice, e.g. cubic or hexagonal lattice at ambient pressure. Alkali metals and group 5, 6 elements, as we know, can crystallize into body-centered cubic lattice under room pressure. Some alkali-earth metals take close-packed structures, for examples, Ca, Sr, Ba, and Be, Mg can crystallize into face-centered cubic and hexagonal lattice, respectively. Except alkali-earth metals, some elemental materials (e.g. Al, Sc, and group 4, 10, 11 elements) also stack to close-packed structures [1]. However, elemental materials cannot always keep the simple crystal lattice up to high-pressure environment, and transform into various complex structures companied with significant changes of their physical and chemical properties. Under high pressure, the incommensurate modulation structures have been observed in many elements, Rb, Ba, Sr, Sc, P, As, Sb, and Bi [2–8]. Certain elements have found to become superconducting at sufficient pressure, i.e. 29 K at 216 GPa for Ca, 8.2 K at 74.2 GPa for Sc, 17 K at 89 GPa for Y, though they are not superconducting at ambient pressure even down to mK temperatures [9–14]. Besides, some metallic solid even exhibited the strikingly pressure-induced antimetallization, i.e. Li and Na will transform into insulating states at 80 GPa and 120 GPa, respectively [15–17].

For the familiar element in the group 15, phosphorus is an indispensable ingredient for life together with carbon, hydrogen, nitrogen, oxygen, and sulfur [18, 19]. And it is essential to explore whether extra-terrestrial life exists on other planets, in which the pressure may reach up to hundreds of gigapascal (GPa) and even terapascal (TPa) [20, 21]. As we discoursed above, such extreme pressures can trigger abundant structural phase transitions and significant changes of physicochemical properties in materials. Recent investigations on phosphorus have focused on the pressures below 300 GPa. Structurally, phosphorus adopts the orthorhombic


Conca (P-I) structure at ambient environment [22, 23], then transforms into the semimetallic R-3m phase (P-II) at 4.5 GPa and to the simple cubic Pm-3m phase (P-III) at 10 GPa [24]. According to the experiment data obtained by Akahama et al, Pm-3m is the stable form of phosphorus up to 107 GPa, then it transforms into the simple hexagonal P6/mmm phase (P-V) at 132 GPa via an incommensurate modulation phase, Cmcm(000),00 (P-IV) [5, 25–27]. With increasing pressure, P6/mmm undergoes a structural transition to the body-centered cubic Im-3m structure (P-VI) at 262 GPa [28]. Mikhailushkin et al further proposed that Im-3m transforms into a hexagonal close-packed (HCP) structure via an intermediate phase, nevertheless, the HCP structure has not been expounded [29]. Recently, Sugimoto et al claimed a superlattice structure with the space group I-43d to be the candidate for P-VI. The maximum pressure of x-ray diffraction experiment for phosphorus reaches up to 340 GPa in the current experiments [30]. However, physical properties study for I-43d is absent in the paper. Aside from the unusually abundant structural phase transitions, the superconductivity has also been investigated experimentally and theoretically at the pressures lower than 150 GPa [31–40]. And the anomalous pressure-dependent superconductivity has been deeply investigated [35, 37–39].

In this paper, we have extensively explored the candidate structures for phosphorus at extreme pressures of terapascal. Two close-packed structures of P63/mmc and Fm-3m are predicted at higher pressures. New phase sequence of phosphorus is proposed by investigating the structure stability of all proposal phases. Electronic structures, phonon dispersions, and superconductive behaviors of the structures including the I-43d phase are deeply investigated. The tendency of pressure-induced reentrant insulating property in phosphorus has been disclosed, and the electronic density of states at Fermi level is demonstrated to be the main contributor to the variation in electron–phonon coupling (EPC) strength and Tc.

2. Computational methods

We utilize the ELocR code to probe the structures of phosphorus under high pressures [41, 42]. The structural relaxation is performed with the Vienna ab initio simulation package within density-functional theory using the Perdew–Burke–Ernzerh of generalized gradient approximation [43–45]. The 'hard' PAW pseudopotential is adopted and the 3s3p 2 electrons are treated as valence electrons. A plane-wave cutoff of 1000 eV and appropriate Monkhorst–Pack k-meshes are employed with the resolution of 2π × 0.025 Å−1 for Brillouin zone (BZ) sampling to ensure that all the enthalpy calculations are well converged to less than 1 meV per atom. The property of electronic structures is rechecked by CASTEP [46]. The phonon and electron–phonon calculations are carried out by QUANTUM-ESPRESSO code [47]. Ultrasoft pseudopotentials with an energy cutoff of 60 Ry and Brillouin zone (BZ) sampling grid of spacing 2π × 0.025 Å−1 are adopted to ensure the convergence of the energy less than 10−8 Ry. For the electron–phonon interaction matrix element, the q-point meshes of 6 × 3 × 5 for P63/mmc, 8 × 8 × 8 for Im-3m, 4 × 4 × 4 for I-43d, 6 × 6 × 3 for P63/mmc, and 6 × 6 × 6 for Fm-3m in the first BZ are chosen, respectively. Moreover, the reliabilities of pseudopotentials are tested by the comparison of Birch–Murnaghan equation of states (see figure S1 in supplementary material is available online at stacks.iop.org/NJP/22/033011/mmedia), and the reliabilities of computational methods are checked by comparing the x-ray diffraction patterns and enthalpy difference curves in lower pressure range (0–260 GPa) with previous works (see figures S2 and S3 in supplementary material).

3. Phase sequence of phosphorus under pressure

We explore the high-pressure structures of phosphorus by the ELocR structure searching method in conjunction with first principle calculations. At 350 GPa, the HCP structure P63/mmc with two P atoms in the 2d Wyckoff positions is obtained, and its conventional structure with 2 × 2 × 1 is shown in figure 1(a). The distance between the two P atoms in the primitive cell is 2.104 Å. At 1.5 TPa, a face centered close-packed Fm-3m structure is found to be the stable phase of phosphorus (figure 1(b)). There are twelve nearest-neighbor atoms around each other with a distance of 1.783 Å.

The total energy for different phases, the structures presented by predecessors and the two close-packed structures we proposed have been calculated. It is worth mentioning that the incommensurate phase is replaced by the Ima2 structure proposed by Rajeev Ahuja, owing to the nearly isenthalpic feature of them [48]. The enthalpy difference curves, which are relative to Im-3m as a function of pressure, are presented in figure 2(a) and figure S4. Afterwards, we obtain a new phase sequence of phosphorus in 150 GPa ~2 TPa as plotted in figures 2(d) and (e). Below 220 GPa, P63/mmm is the stable form of phosphorus, and in the pressure range of 220–250 GPa, Im-3m structure is adopted. With pressurization, Im-3m transforms into P63/mmc at about 325 GPa via the superlattice structure I-43d. Ultimately, P63/mmc transforms into Fm-3m, as displayed in figure 2(a) insert. The phase sequences given by previous studies are shown as figures 2(b) and (c). They regarded
Im-3m or I-43d as the most competitive structure of phosphorus above 262 GPa, respectively. As for our work, at about 250 GPa, Im-3m transforms to the I-43d structure then attains P63/mmc at about 325 GPa. Lacking of......
the total energy calculation of \textit{I-43d} is the main reason of the difference of phase sequence between this work and previous studies. The stabilities of two close-packed structures we proposed in this work and \textit{I-43d} given by Sugimoto \textit{et al} are evaluated by calculating the elastic constants and phonon dispersion curves. The calculated elastic constants of matrix $C_{ij}$ meet the Born–Huang stability criteria (table 1), indicating the mechanical stabilities of the phases $49$–$51$. Meanwhile, the phonon dispersion curves along several high symmetry directions in the first Brillouin zone have been calculated, as shown in figure 3. Apparently, all the structures with no imaginary frequencies in the whole Brillouin zone demonstrate their dynamical stabilities. The analyzes of elastic constants and phonon structures reveal the same stable pressure ranges with the thermodynamically stable pressure ranges.

4. Pressure-induced metallization and reentrant insulativity

Elemental materials may exhibit peculiar properties under high pressure, e.g. the alkali metals are reported to possess unexpected electronic behavior at high pressures $52$–$54$. Here, we predict the tendency of pressure-induced reentrant insulativity character of phosphorus, while it is opposite to the reentrant metallicity of lithium and sodium at high pressures. Lithium (Li) and sodium (Na), the familiar alkali metals, are known to possess simple electronic structures at ambient pressure that are well explained by a nearly free-electron model. With the increasing pressure, the metal-insulator transition appears, at about 80 GPa for lithium and 200 GPa for sodium, respectively $17$, $52$. With further compression, both of them revert to metal. Semiconducting lithium is affirmed to revert to ‘poor metal’ above 120 GPa $53$ and sodium is reported to reenter into metal at a surprisingly high pressure of 15.5 TPa $54$. While as for phosphorus, which own the insulate state at ambient pressure, might undergo the pressure-induced insulator-metal-insulator transition and is further substantiated by the electronic density of states, three-dimensional Fermi surface and the electron localization function.

Figures 4(a) and (b) present the calculated electronic projected density of states of \textit{P6$_3$/mmc} and \textit{Fm-3m} at different pressures. Comparing with the semiconducting phase at 1 atm, as expected, the pressure-induced metallization happens and phosphorus shows the nearly free-electron metallic feature. The pressure dependency of density of states at the Fermi level ($N(E_F)$) is plotted in figure 5(d). Obviously, above 150 GPa, $N(E_F)$ first rises and reaches a maximum value of 0.29 electrons/eV/atom at about 250 GPa, then declines to 0.11 electrons/eV/atom at 2 TPa. Three-dimensional Fermi surfaces of HCP phase are calculated to verify the downward of $N(E_F)$ in the corresponding pressure range. As shown in figures 4(c) and (d), there are four electronic bands across the Fermi surface at selected pressures. From 350 GPa to 1 TPa, the variation trend of the two bands identified by pink and navy blue surrounded by yellow color shrinks is consistent with the decreasing of $N(E_F)$. Furthermore, $N(E_F)$ descends with increasing pressure and should vanish near 4 TPa by the extrapolation of $N(E_F)$ in figure 5(d), which indicates that phosphorus would reenter into insulate state by higher pressure. The variation of metallicity can be interpreted by the calculated electronic localization function shown in figure 6. It is noteworthy that the localized electrons vary obviously with pressure. At ambient pressure
(figure 6(a)), the electrons are localized between two P atoms. As pressure is up to 250 GPa (figure 6(b)), green area appears in the interstitial region which symbolizes the pressure-induced metallization. Upon compression, the localized electrons first decrease and almost vanish at about 650 GPa, and then keep ascending when up to 2 TPa, which implies the tendency of pressure induced antimetallization above 650 GPa (see figures 6(b)–(d)). The similar metal-insulator transition in Li and Na is reported as originating from the localization of valance electrons in the voids of crystal [17, 52].
5. Effect of electronic properties on superconductivity

As is well-known, the electronic properties play an important role in determining the EPC and superconductivity. Then the effect of electronic properties on EPC $\lambda$ and superconductivity of phosphorus are investigated. The superconducting transition temperature ($T_c$) can be estimated by utilizing the Allen–Dynes-modified McMillan equation [55]:

$$T_c = \frac{\omega_{\text{log}}}{1.2} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right],$$  

(1)

and the formula defined in McMillan’s strong coupling theory is adopted to understand the relations between EPC $\lambda$ and $N(E_F)$ [56]:

$$\lambda = \frac{\eta}{M \langle \omega^2 \rangle} = \frac{N(E_F) \langle I^2 \rangle}{M \langle \omega^2 \rangle},$$  

(2)

where $M$ is the atomic mass, $N(E_F)$ is for a single spin (i.e. one-half of the value shown in figure 3, which is for both spins), $\langle I^2 \rangle$ represents the average over the Fermi surface of the electron–phonon matrix element. $T_c$ as a function of pressure (for two values of $\mu^*$) is presented in figure 5. With the increasing pressure, $T_c$ first declines, then climbs and reaches to a maximum value at about 250 GPa, and then descends to 0 K at about 1 TPa. Above 1 TPa, $T_c$ remains 0 K and this is mainly attributed to the weakly EPC, as shown in figures 5(a) and (b). At 150 GPa, the $T_c$ value ($\mu^* = 0.1$) by our calculation agrees well with the value predicted by Nakanishi et al [36].

The tendency of $T_c$ has been analyzed by the variations in $\lambda$ and $\omega_{\text{log}}$ as a function of pressure and is shown in figure 5. Notably, the variation tendency of $T_c$ is considered to be dominated by EPC $\lambda$ owing to the similarity tendency between EPC $\lambda$ and $N(E_F)$ with pressure. Thus, $N(E_F)$ is the dominant factor for the variation trends of EPC $\lambda$ and $T_c$.

Furthermore, we have plotted the phonon dispersions, Eliashberg spectral function $\alpha^2 F(\omega)$ and EPC $\lambda$ at 350 GPa for P6_3/mmc in figure 7. As shown in figure 7 left, we have projected EPC $\lambda$ on each vibration mode and represent it by the radius sizes of green solid balls. Strikingly, strong EPC exists along the Brillouin zone L–M–H and G–A. EPC $\lambda$ is mainly contributed by these regions. What’s more, the strength of EPC along G–A is stronger than that in other directions. It means that the vibration modes along the different directions through G point make disparate contributions to the EPC.

Figure 6. Calculated electron localization function (ELF) at different pressures. Red isosurfaces of ELF in (b)–(d) corresponding to the value of 0.73. The cyan balls represent P atoms.
6. Conclusion

In summary, we have explored the candidate structures for phosphorus above 150 GPa by utilizing ElocR along with density functional total energy calculations. Two close-packed structures $P6_3/mmc$ and $Fm-3m$ are found to be stable in 350 GPa–1.45 TPa and above 1.45 TPa, respectively. The electronic structures analysis shows the favorable metallicity of both the two close-packed structures. Interestingly, with the pressure increases, $N(E_F)$ first declines, then climbs and reaches a maximum value at about 250 GPa, and then keep descending. More analyzes of $N(E_F)$ implies that phosphorus may transforms into insulate state at about 4 TPa. The tendency of pressure-induced reentrant insulator character of phosphorus is totally different from the reentrant metal feature of lithium and sodium at high pressure. What’s more, the variation tendency of superconducting critical temperature agrees well with the trend of $N(E_F)$, and the $N(E_F)$ is considered to be the main factor which dominates the variations of EPC $\lambda$ and $T_c$ under pressure.

Acknowledgments

This work was supported by the National Key R&D Program of China (No. 2018YFA0305900), the National Natural Science Foundation of China (Nos. 51632002, 51572108, 91745203, 11634004, 11174102, 11774119, 11904187), National Key Research and Development Program of China (2016YFB0201204), Program for Changjiang Scholars and Innovative Research Team in University (No. IRT_15R23), National Found for Fostering Talents of basic Science (No. BS480). Parts of calculations were performed in the High Performance Computing Center (HPCC) of Jilin University.

ORCID iDs

Xilian Jin  https://orcid.org/0000-0003-2505-9685
Tian Cui  https://orcid.org/0000-0002-9664-848X

References

[1] Mcmahon M I and Nelmes R J 2006 Chem. Soc. Rev. 35 943
[2] van Smaalen S and George T F 1987 Phys. Rev. B 35 7839
[3] Kenichi T, Kyoko S, Hiroshi F and Mitsuko O 2003 Nature 423 971
[4] Mcmahon M I, Rekhi S and Nelmes R J 2001 Phys. Rev. Lett. 87 055501
[5] Mcmahon M I, Bovornratanaraks T, Allan D R, Belmonte S A and Nelmes R J 2000 Phys. Rev. B 61 3135
[6] Mcmahon M I, Lunegdaard I F, Hejny C, Falconi S and Nelmes R J 2006 Phys. Rev. B 73 134102
[7] Mcmahon M I, Degtyareva O and Nelmes R J 2000 Phys. Rev. Lett. 85 4896

Figure 7. The phonon dispersion (left), Eliashberg spectral function $\alpha^2F(\omega)$ and electron–phonon coupling strength $\lambda$ (right) calculated at 350 GPa for $P6_3/mmc$. Circles in left indicates electron–phonon coupling with the radius proportional to their respective strength.
[8] Degtyareva O, McMahan M I and Nelmes R J 2004 Phys. Rev. B 70 184119
[9] Sakata M, Nakamoto Y, Shimizu K, Matsuoka T and Ohishi Y 2011 Phys. Rev. B 83 220512
[10] Hamlin J J and Schilling J S 2007 Phys. Rev. B 76 012505
[11] Hamlin J J, Tissen V G and Schilling J S 2006 Phys. Rev. B 73 094522
[12] Dunn K J and Bundy F P 1981 Phys. Rev. B 24 1643
[13] Wittig J, Probst C, Schmidt F A and Gschneidner K A 1979 Phys. Rev. Lett. 42 4249
[14] Probst C and Wittig J 1978 Handbook on the Physics and Chemistry of Rare Earths ed K A Gschneidner and L Eyring (Amsterdam: North–Holland) p 749
[15] Matsuoka T and Shimizu K 2009 Nature 458 186
[16] Yao Y, Tse J S and Klug D D 2009 Phys. Rev. Lett. 102 115503
[17] Ma Y, Eremets M, Oganov A R, Xie Y, Trojan I, Medvedev S, Lyakhov A O, Valle M and Prakapenka V 2009 Nature 458 182
[18] Maciá E 2005 Chem. Soc. Rev. 34 691
[19] Koo B C, Lee Y H, Moon D S, Yoon S C and Raymond J C 2013 Science 342 1346
[20] Royal Astronomical Society. ‘Paucity of phosphorus hints at precarious path for extraterrestrial life.’ ScienceDaily, 5 April 2018
[21] Guillot T 1999 Science 286 72
[22] Hühner J, Gingrich N S and Warren B E J 2004 J. Chem. Phys. 3 351
[23] Brown A and Bunsqist S 1965 Acta Cryst. 19 684
[24] Kikegawa T and Iwasaki H 1983 Acta Cryst. B39 158
[25] Akahama Y, Kobayashi M and Kawamura H 1999 Phys. Rev. B 59 8520
[26] McMahan M I, Nelmes R J, Schwarz U and Syassen K 2006 Phys. Rev. B 74 140102
[27] Nelmes R, Allan D, McMahon M and Belmonte S 1999 Phys. Rev. Lett. 83 4081
[28] Akahama Y, Kawamura H, Carlson S, Bihan T L and Häussermann D 2000 Phys. Rev. B 61 3139
[29] Mikhaylushkin A S, Simak S I, Johansson B and Häussermann U 2007 Phys. Rev. B 76 5398
[30] Sugimoto T, Akahama Y, Fujihisa H, Ozawa Y, Fukui H, Hirao N and Ohishi Y 2012 Phys. Rev. B 86 024109
[31] Wittig J and Matthias B 1968 Science 160 994
[32] Kawamura H, Shirotani I and Tachikawa K 1985 Solid State Commun. 54 775
[33] Nagara H, Mukose K, Ishikawa T, Geshi M and Suzuki N 2010 J. Phys.: Conf. Ser. 215 012107
[34] Karuzawa M, Ishituka M and Endo S 2002 J. Phys.: Condens. Matter 14 10759
[35] Chan K T, Malone B D and Cohen M I 2013 Phys. Rev. B 88 1336
[36] Nakashima A, Ishikawa T, Nagara H, Shimizu K and Katayama-Yoshida H 2012 High Press. Res. 32 3
[37] Guo J, Wang H, Von Rohr F, Yi W, Zhou Y, Wang Z, Cai S, Zhang S, Li X and Li Y 2017 Phys. Rev. B 96 224513
[38] Wu X, Jeschke H O, Di Sante D, Von Rohr F O, Cava R J and Thomale R 2018 Phys. Rev. Mater. 2 034802
[39] Li X, Sun J, Shali P, Gao M, MacDonald A H, Uwatoko Y, Xiang T, Goodenough J B, Cheng J and Zhou J 2018 Proc. Natl Acad. Sci. USA 115 9935–40
[40] Flores-Livas J A, Sanna A, Drozdov A P, Boeri L and Goedecker S 2017 Phys. Rev. Mater. 1 024802
[41] Li Y, Jin X, Cui T, Zhuang Q, Lv W, Wu G, Meng X, Bao K, Liu B and Zhou Q 2017 RSC Adv. 7 74724
[42] Zhuang Q et al 2017 Phys. Chem. Chem. Phys. 19 26280
[43] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
[44] Hohenberg P and Kohn W 1964 Phys. Rev. 136 B864
[45] Kohn W and Sham L J 1965 Phys. Rev. 140 A1133
[46] Segall M D, Lindan Philip J D, Pickard C J, Hasnip P J, Clark S J and Payne M C 2002 J. Phys.: Condens. Matter 14 2717–44
[47] Giannozzi P et al 2009 J. Phys.: Condens. Matter 21 395502
[48] Ahuja R 2003 Phys. Status Solidi b 235 282–7
[49] Born M and Huang K 1954 Dynamical Theory of Crystal Lattices (Oxford: Clarendon) pp 104–13
[50] Wang J, Li J, Yip S, Phillpot S and Wolf D 1995 Phys. Rev. B 52 12627
[51] Wu Z J, Zhao E J, Xiang H P, Hao X F, Liu J X and Meng J 2007 Phys. Rev. B 76 054115
[52] Lv J, Wang Y, Zhu L and Ma Y 2011 Phys. Rev. Lett. 106 164
[53] Matsuoka T, Sakata M, Nakamoto Y, Takahama K, Ishimaru M, Ohishi Y, Hidaka N, Ohishi Y and Shimizu K 2014 Phys. Rev. B 89 144403
[54] Li Y, Wang Y, Pickard C J, Needs R J, Wang Y and Ma Y 2015 Phys. Rev. Lett. 114 125501
[55] Allen P B and Dyne R C 1975 Phys. Rev. B 12 905
[56] McMillan W L 1968 Phys. Rev. 167 331