Electron-doped phosphorene: A potential monolayer superconductor

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Abstract – We predict by first-principles calculations that the electron-doped phosphorene is a potential BCS-like superconductor. The stretching modes at the Brillouin-zone center are remarkably softened by the electron-doping, which results in the strong electron-phonon coupling. The superconductivity can be introduced by a doped electron density \( n_{2D} \) above \( 3 \times 10^{14} \text{ cm}^{-2} \), and may exist over the liquid-helium temperature when \( n_{2D} > 2.6 \times 10^{14} \text{ cm}^{-2} \). The superconductivity can be significantly tuned and enhanced by applying tensile strain. The maximum critical temperature of electron-doped phosphorene is predicted to be higher than 10 K. The superconductivity of phosphorene will significantly broaden the applications of this novel material.

The two-dimensional (2D) monolayer superconductor bears consequences for both applications and fundamental science. It can be used as the component of nanoscale superconducting devices, such as nano-superconducting quantum interference devices and nano-superconducting transistors [1–5], with the goal of achieving single-spin sensitivity for measuring and controlling. Moreover, the high-\( T_c \) superconductors with the quasi-2D layered structures, such as MgB\(_2\) [6], cuprate superconductors [7,8], and iron-based superconductors [9], can be seen as the assembly of multiple monolayers. Geim et al. [10] proposed to construct the high-\( T_c \)-superconductor-like van der Waals heterostructures using the monolayer superconductors, which may be helpful for the exploration of new high-\( T_c \) superconductors. A graphene-like monolayer superconductor seems to be the natural choice of such applications. It is suggested that the carrier-doped graphene [11–13] and graphane [14] may exhibit superconductivity with notable \( T_c \). However, the experimental evidences are still lacking. Using the liquid-gate method, one can introduce the superconductivity into the few-layer semiconductor MoS\(_2\) [15], which may be driven by the electron-phonon coupling [16].

But the thickness of such material is still far from one layer. More monolayer superconductor candidates still need to be found.

Here we show a potential monolayer superconductor: electron-doped phosphorene. Based on the density functional theory (DFT) calculations, we found that the electron doping can make the stretching modes at the zone center significantly softened, leading to a strong electron-phonon coupling. The superconductivity starts showing up when the carrier density \( n_{2D} \) is \( 1.3 \times 10^{14} \text{ cm}^{-2} \). When \( n_{2D} > 2.6 \times 10^{14} \text{ cm}^{-2} \), the \( T_c \) exceeds the liquid-helium temperature. Moreover, the application of tensile strain can significantly tune and enhance the superconductivity. The maximum \( T_c \) is predicted to be higher than 10 K. Our prediction can be readily verified by the liquid-gate method [15,17–19], or the adsorption of the alkali/alkaline-earth metal atoms.

Figure 1 shows the structures of bulk black phosphorus (black-P) and monolayer black-P (which is called phosphorene). Phosphorene can be obtained by exfoliating the black-P [20,21], the most stable allotropic form of phosphorus and the only layered structure of an elemental solid besides graphitic carbon [22]. The phosphorus atoms are covalently bonded, forming a special puckered 2D structure [23–25]. Both bulk black-P and phosphorene

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than 10 Å was introduced to the previous PBE calculation [34]. It might be due to the overestimation of lattice constant in (b). The Vanderbilt-Marzari Fermi smearing method with a smearing parameter of $\sigma = 0.02$ Ry was used for the calculations of the total energy and electron charge density. Phonon spectra and electron-phonon coupling constants were calculated using density functional perturbation theory [40] with an $8 \times 8 \times 1$ mesh of $k$-points. The double Fermi-surface averages of electron-phonon matrix elements were calculated using the tetrahedron method on grids of $160 \times 120 \times 1$ $k$-points. To simulate the monolayer, a vacuum layer more than 10 Å was introduced\(^1\). Electron-doping was simulated by adding electrons into the system, together with a compensating uniform positive background [16]. For each doping concentration, we relaxed the atomic positions with the fixed in-plane lattice constants of the optimized lattice structure of the undoped phosphorene.

Figure 2 shows the conduction bands and the corresponding Fermi sheets of three typical doping concentrations. The effect of doping obviously enlarges the Fermi surface. For the low doping concentrations, electrons occupy the states near the conduction band minimum at the $\Gamma$-point, forming an oval Fermi sheet around the zone center, as shown in figs. 2(a) and (b). When the doping concentration is up to $x = 0.3$ electrons/cell, the second-lowest conduction band starts crossing the Fermi level ($E_F$) at the place near $Y$-point, and new sheets start to show up, as shown in figs. 2(c) and (d). These sheets expand with increasing the doping concentration. When the doping concentration is above $x = 0.7$ electrons/cell, the $\Gamma$ valley of the second-lowest conduction band is occupied. The valley becomes the energy minimum of such band, and forms a circle-like Fermi sheet around the zone center (figs. 2(e) and (f)). Such relative shift in energy of the conduction band valleys with doping was also found in the electron-doped monolayer MoS$_2$ [16].

The calculated phonon dispersions of the pristine and electron-doped phosphorene are presented in fig. 3. For the pristine phosphorene, our calculation is in good agreement with the previous result reported by Zhu and Tománek [22]. Compared with the zone center modes of phosphorene recently measured and bulk black phosphorus previously reported [20,41–44], our calculated zone center modes seem to have slightly smaller frequencies. It might be due to the overestimation of lattice constant for PBE [34]. However, our calculation is still enough to discuss the variation trends of the properties upon doping. In fig. 3, one can notice that the highest four optical branches are slightly softened while other five optical

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\(^1\)For the low doping concentration of $x = 0.1$ electrons/cell, the smaller $\sigma = 0.005$ Ry and the denser $64 \times 48 \times 1$ mesh of $k$-points were used. For the vacuum layer, we tested different values of the thickness. It turns out that a vacuum layer more than 10 Å can lead to the converged lattice parameters ($a = 3.32$ Å and $b = 4.64$ Å) and band structure (the band gap is $\sim 0.9$ eV) in good agreement with the previous PBE calculation [34].
branches are softened significantly upon doping. A remarkable softening can be found at the high-frequency optical zone center $A^{1}_{4}$ mode associated with the out-plane stretching (fig. 3(e)). The region of the reciprocal space where the softening is observed matches the diameter $2k_{F}$ of the Kohn sheets around $\Gamma$, which is a typical signature of the Kohn effect [45]. Such softening generally exists in some superconductors such as MgB$_2$ [46,47], hole-doped diamond [48,49], hole-doped graphane [14], etc. When the doping concentration is above $x = 0.7$ electrons/cell, the $A^{1}_{4}$ mode is further softened. This is due to a new Kohn anomaly caused by the new $\Gamma$ centered circular Fermi sheets from the second-lowest conduction band (see figs. 2(e) and (f)). Another prominent softening happens in the low-frequency optical mode $B^{1}_{3g}$ at the zone center, which is related to the in-plane stretching (fig. 3(f)). For the pristine phosphorene, the $B^{1}_{3g}$ mode has the highest energy among the low-frequency optical modes at the zone center. With the electron doping, the $B^{1}_{3g}$ mode significantly softens, and gradually becomes frequency minimum of the optical modes at $\Gamma$. Besides the two remarkable softenings at the zone center, some other anomalies, such as the anomaly at $q \approx \frac{\pi}{4} Y$ (figs. 3(c) and (d)), have been found in the low-frequency optical branches. These anomalies start to show up for $x = 0.3$ electrons/cell, when the new Fermi sheets are introduced into the system. It indicates such anomalies might be due to the nesting between the Fermi sheets. When $x \geq 1.2$ electrons/cell, frequencies of $B^{1}_{3g}$ and its adjacent modes become negative, indicating the appearance of the lattice instability induced by doping. Such instability suggests the electron-doping limit of phosphorene should be smaller than 1.2 electrons/cell.

Figure 4 plots the Eliashberg spectral function:

$$\alpha^{2}F(\omega) = \frac{1}{N(E_F)} \sum_{k, q, \nu, n, m} \delta(\epsilon^{n}_{k}) \delta(\epsilon^{m}_{k+q}) | g^{\nu,n,m}_{k,k+q}|^{2} \times \delta(\omega - \omega^{\nu}_{k}),$$

(1)

where $N(E_F)$ is the density of states at $E_F$, $\omega^{\nu}_{k}$ is the phonon frequency, $\epsilon^{n}_{k}$ is the electronic energy, and $g^{\nu,n,m}_{k,k+q}$ is the electron-phonon coupling matrix element. The total electron-phonon coupling strength is then

$$\lambda = 2 \int_{0}^{\infty} \frac{\alpha^{2}F(\omega)}{\omega} d\omega = \sum_{\nu, q} \lambda_{\nu q},$$

(2)

$\lambda_{\nu q}$ are visualized as red circles in fig. 3. Acoustic modes near $\Gamma$ contribute a small peak to the $\alpha^{2}F(\omega)$ (fig. 4(a) and (b)). But the predominant contribution is from the softened optical modes. The large contribution of electron-phonon coupling from the $A^{1}_{4}$ mode leads to a sharp peak in $\alpha^{2}F(\omega)$ at high frequency (fig. 4)). Another remarkable
contribution is from the softening of $B_{3g}^1$ mode. Moreover, one can notice that when new Fermi sheets are introduced, the $\lambda_\mathbf{q}$ at some $\mathbf{q}$-vector, such as $\mathbf{q} \approx \frac{1}{2} \Gamma Y$ (see figs. 3(c) and (d)), is largely enhanced. This indicates that the intersheet nesting plays an important role in the electron-phonon coupling as well, similarly to the cases in hole-doped CuAlO$_2$ [50,51] and electron-doped monolayer MoS$_2$ [16]. For the high doping concentration, because of the very low $\omega$ in the denominator of eq. (2), the contributions of $B_{3g}^1$ and its adjacent modes to the electron-phonon coupling become predominant.

We estimated the $T_c$ based on the Allen-Dynes formula [52]

$$T_c = \frac{\omega_{\alpha} \log 1.2}{\lambda} \exp \left( \frac{-1.40(1 + \lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*} \right),$$

where the Coulomb pseudopotential $\mu^*$ is set to a typical value of $\mu^* = 0.1$. The logarithmically averaged characteristic phonon frequency $\omega_{\alpha}$ is defined as

$$\omega_{\alpha} = \exp \left( \frac{2}{\lambda} \int \frac{d\omega}{\omega} \omega^2 F(\omega) \log \omega \right).$$

The calculated total electron-phonon coupling strength $\lambda$ and $T_c$ of the electron-doped phosphorene with different doping concentrations are presented in figs. 5(a) and (b), respectively. For the low doping concentration, the electron-phonon coupling is weak. It gradually increases with increasing doping concentration. When the doping concentration is up to $x = 0.2$ electrons/cell ($1.3 \times 10^{14}$ cm$^{-2}$), the superconductivity starts showing up. The calculated $\lambda = 0.36$ leads to the superconductivity with $T_c \sim 0.5$ K, which already can be detected in routine measurements. When $x > 0.4$ electron/cell ($n_{2D} > 2.6 \times 10^{14}$ cm$^{-2}$), the value of $\lambda$ is above 0.54, generating the superconductivity with $T_c$ above the liquid-helium temperature of 4.2 K. The maximum $T_c$ is predicted to be 11.2 K when $x = 1.1$ electrons/cell. Such value can be comparable to the maximum $T_c$ of high pressure phase of phosphorus [53–55], clearly indicating that the electron-doped phosphorene may be another superconducting phase of phosphorus.

The electron doping can be processed using the liquid-gate method, which is considered as a clean route to achieve superconductivity with $T_c$ in monolayer phosphorene. However, the application of strain is still a useful method to dope electrons into layered materials. How-ever, for the black-phosphorus system, to the best of our knowledge, there are no homogeneous and stable donor intercalated compounds yet [58]. Although the donor-type atoms or molecules can hardly be intercalated inside the interlayers, it is suggested that those can be adsorbed at the surface [29], which implies the chemical doping by adsorption for monolayer will be much easier and more efficient than that for bulk. Alkali atom Cs might be a promising donor-type atom for the adsorption [58]. The bands of the adsorbed atoms in phosphorene may occur at the $E_F$ and have multiple beneficial effects on $\lambda$ [11,59], which may enhance the superconductivity.

Since the strain is proven to be a key method to control the properties of nanoscale material [13,37], we also investigated the strain effects in the electron-doped phosphorene. We found that the strain can significantly tune and enhance the superconductivity. As an example, fig. 6 shows the influence of tensile strain along the armchair direction on electron-doped phosphorene with doping concentration of $x = 0.4$ electrons/cell. The $B_{3g}^1$ mode is largely softened by strain, which strongly enhances the electron phonon coupling and raises $T_c$. When a strain about 8% is applied, the maximum $T_c = 12.2$ K can be obtained. One can notice the strain strongly suppressed $\omega_{\alpha}$, which limits the increase of $T_c$. Moreover, a very large strain can make the $B_{3g}^1$ mode unstable. Therefore, a very high $T_c$ cannot be achieved in electron-doped phosphorene. However, the application of strain is still a useful method to achieve superconductivity with $T_c$ over 10 K for low doping concentration.
In conclusion, we have carried out the first-principles study of phosphorene and found that the phonon-mediated superconductivity can be introduced by a doped electron density above $1.3 \times 10^{14}$ cm$^{-2}$. When $n_{2D} > 2.6 \times 10^{14}$ cm$^{-2}$, the $T_c$ exceeds the liquid-helium temperature. Moreover, the superconductivity can be significantly tuned and enhanced by strain. A maximum $T_c$ over 10 K can be achieved. The electron-phonon coupling is majorly contributed by the softening of the out-plane stretching mode $A_{g}^1$ and the in-plane stretching mode $B_{3g}^1$. Our prediction indicates that phosphorene can be a good platform to realize the nanoscale superconducting devices. Moreover, it can be the “atomic-scale Lego” to construct the van der Waals heterostructure for the attempt of searching for the high-$T_c$ superconductivity.

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REFERENCES

[1] De Franceschi S., Kouwenhoven L., Schönenberger C. and Wernsdorfer W., Nat. Nanotechnol., 5 (2010) 703711.
[2] Hufnert M., May C., Kičin S., Ensslin K., Ihn T., Hilke M., Suter K., de Rooij N. F. and Stauffer U., Phys. Rev. B, 79 (2009) 134530.
[3] Delahaye J., Hassé J., Lindell R., Sillanpää M., Paalanen M., Seppä H. and Hakonen P., Science, 299 (2003) 1045.
[4] Saira O. P., Meschke M., Giazzotto F., Savin A. M., Möttönen M. and Pekola J. P., Phys. Rev. Lett., 99 (2007) 027203.
[5] Romans E. J., Osley E. J., Young L., Warburton P. A. and Li W., Appl. Phys. Lett., 97 (2010) 222506.
[6] Nagamatsu J., Nakagawa N., Muranaka T., Zenitani Y. and Akimitsu J., Nature, 410 (2001) 63.
[7] Bednorz J. G. and Müller K. A., Z. Phys. B: Condens. Matter, 64 (1986) 189.
[8] Wu M. K., Ashburn J. R., Torng C. J., Hor P. H., Meng R. L., Gao L., Huang Z. J., Wang Y. Q. and Chu C. W., Phys. Rev. Lett., 58 (1987) 908.
[9] Kamihara Y., Watanabe T., Hirano M. and Hosono H., J. Am. Chem. Soc, 130 (2008) 2396.
[10] Geim A. K. and Grigorieva I. V., Nature, 499 (2013) 419.
[11] Profeta G., Calandra M. and Mauri F., Nat. Phys., 8 (2012) 131.
[12] Dai J., Li Z., Yang J. and Hou J., Nanoscale, 4 (2012) 3032.
[13] Si C., Liu Z., Duan W. and Liu F., Phys. Rev. Lett., 111 (2013) 196802.
[14] Savini G., Ferrari A. C. and Giustino F., Phys. Rev. Lett., 105 (2010) 037002.
[15] Ye J. T., Zhang Y. J., Akashi R., Bahramy M. S., Arita R. and Iwasa I., Science, 335 (2012) 1193.
[16] Ge Y. and Liu A. Y., Phys. Rev. B, 87 (2013) 241408(R).
[17] Ueno K., Nakamura S., Shimotani H., Ohtomo A., Kimura N., Nojima T., Aoki H., Iwasa Y. and Kawasaki M., Nat. Mater., 7 (2008) 855.
[18] Ye J. T., Inoue S., Kobayashi K., Kasahara Y., Yuan H. T., Shimotani H. and Iwasa Y., Nat. Mater., 9 (2010) 125.
[19] Ueno K., Nakamura S., Shimotani H., Yuan H. T., Kimura N., Nojima T., Aoki H., Iwasa Y. and Kawasaki M., Nat. Nanotechnol., 6 (2011) 408.
[20] Li L., Yu Y., Ye G. J., Ge Q., Ou X., Wu H., Feng D., Chen X. H. and Zhang Y., Nat. Nanotechnol., 9 (2014) 372.
[21] Lu W., Nan H., Hong J., Chen Y., Zhu C., Liang Z., Ma X., Ni Z., Jin C. and Zhang Z., Nano Res., 7 (2014) 853.
[22] Zhu Z. and Tománek D., Phys. Rev. Lett., 112 (2014) 176802.
