

Effect of flexural phonons on the hole states in single-layer black phosphorus

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(Received 31 October 2016; published 23 January 2017)

Flexural thermal fluctuations in crystalline membranes affect the band structure of the carriers, which leads to an exponential density-of-states (DOS) tail beyond the unperturbed band edge. We present a theoretical description of this tail for a particular case of holes in single-layer black phosphorus, a material which exhibits an extremely anisotropic quasi-one-dimensional dispersion ($m_y/m_x \gg 1$) and, as a result, an enhanced Van Hove singularity at the valence band top. The material parameters are determined by *ab initio* calculations and then are used for quantitative estimation of the effect of two-phonon (flexural) processes have on the charge carrier DOS. It is shown that unlike the isotropic case, the physics is determined by the phonons with wave vectors of the order of q^* , where q^* determines the crossover between harmonic and anharmonic behavior of the flexural phonons. The spectral density of the holes in single-layer black phosphorus at finite temperatures is calculated.

DOI: [10.1103/PhysRevB.95.041406](https://doi.org/10.1103/PhysRevB.95.041406)

Few-layer black phosphorus attracts a lot of attention now as a prospective two-dimensional (2D) semiconducting material with a tunable energy gap [1–5]. Being, as other 2D materials, an atomic-thick crystalline membrane, it is affected by thermal flexural fluctuations which results in anomalous structural and mechanical properties at finite temperatures [6–14]. It was suggested [15] that these thermal fluctuations can essentially influence on the states of charge carriers in 2D semiconductors and even lead to an autolocalization, that is, formation of a self-trapped state (flexuron). That general consideration assumed an isotropic electronic spectrum whereas black phosphorus is highly anisotropic, with dramatically different effective masses, $m_y/m_x \gg 1$. Especially, in the hole-doped case the situation is quite peculiar, with a formation of Van Hove singularity near the top of the valence band, which is essentially enhanced by mass anisotropy [16]. One can expect that the holes in single-layer black phosphorus (also called phosphorene) are quasi-one-dimensional quasiparticles and thus are strong candidates for a pronounced effect of localization due to interaction with bosonic modes.

In general, deformation of the lattice in 2D materials results in distortion of the carrier dispersion. For different types of deformations this effect can be accounted for by different phonon modes interacting with fermionic charge carriers. The interaction parameters then can be determined either from experiment or from different theoretical approaches. In 2D materials like graphene or black phosphorus, it is a well-justified approach to separate in-plane from out-of-plane, or flexural phonon modes for not too small wave vectors [12]. On the other hand, for smaller wave vectors, these modes begin to interact, which results in changing of the functional form of the correlation function dependence on the wave vector [9–12]. This will be discussed in more detail below, in particular for the anisotropic case.

In what follows, we calculate the spectral function and the density of hole states (DOS) in black phosphorus renormalized due to the interaction with flexural phonons. To this end, we use the diagrammatic approach and calculate the hole self-energy using the Ward identity as a low momentum transfer

approximation for the vertex. This seems to be the minimal model that allows one to get an exponential DOS tail and is thus a more suitable approach than, e.g., the self-consistent Born approximation. This approximation was earlier suggested in a context of magnetic semiconductors near the critical point [17]. Its relation to the path-integral approach used in Ref. [15] is discussed in Ref. [18].

The fermionic Hamiltonian is given by

$$\hat{H}_e = \sum_{\mathbf{p}} \epsilon_{\mathbf{p}} c_{\mathbf{p}}^{\dagger} c_{\mathbf{p}} + \int d\mathbf{r} V^{\text{eff}}(\mathbf{r}) c_{\mathbf{r}}^{\dagger} c_{\mathbf{r}}. \quad (1)$$

Here, $c_{\mathbf{p},\mathbf{r}}^{\dagger}$, $c_{\mathbf{p},\mathbf{r}}$ are the creation and annihilation operators of the fermions with momentum \mathbf{p} (at point \mathbf{r}), $\epsilon_{\mathbf{p}}$ is the dispersion of the fermions, and $V^{\text{eff}}(\mathbf{r})$ is the effective potential acting on them due to lattice distortion. For flexural deformations in systems with symmetry plane (or gliding plane as in case of black phosphorus), the effective potential is quadratic in gradients of the lattice atoms shift $h(\mathbf{r})$ in the direction, perpendicular to the sample plane (x, y) [15,19]:

$$\begin{aligned} V^{\text{eff}}(\mathbf{r}) &= g_x \left(\frac{\partial h}{\partial x} \right)^2 + g_y \left(\frac{\partial h}{\partial y} \right)^2 \\ &= \sum_{\mathbf{q}_1, \mathbf{q}_2} h_{\mathbf{q}_1} h_{\mathbf{q}_2} (g_x q_{1x} q_{2x} + g_y q_{1y} q_{2y}) e^{i\mathbf{r}(\mathbf{q}_1 + \mathbf{q}_2)}. \end{aligned} \quad (2)$$

The mixed xy term is suppressed for the orthorhombic symmetry and we disregard it in our consideration. $h_{\mathbf{q}}$ is the Fourier transform of the flexural lattice displacement field.

Correlators of the h field are found from the elasticity theory equations for membranes. For isotropic membranes the well-known result is [9–12,15]

$$\langle h_{\mathbf{q}} h_{-\mathbf{q}} \rangle = \begin{cases} \frac{T}{\kappa q^4} & \text{for } q > q^*, \\ \frac{T}{\kappa q^{4-\eta} q^{\eta}} & \text{for } q < q^*. \end{cases} \quad (3)$$

Here, $\langle \dots \rangle$ denotes Gibbs averaging, T is the temperature, κ is the material constant, determining the flexural rigidity of the membrane, η is the critical exponent ($\eta \approx 0.82$ in the self-consistent screening approximation [9] and $\eta \approx 0.85$ in Monte Carlo simulations for graphene [12]) and q^* is the characteristic wave vector, such that for $q < q^*$ the interplay between flexural and in-plane deformations becomes crucial

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and softens the flexural modes. Neglecting this effect would lead to unphysical low wave-vector divergence in $\langle(V^{\text{eff}})^2\rangle$. In the isotropic case q^* is given by

$$q^* = \sqrt{\frac{3TY}{16\pi\kappa^2}}, \quad (4)$$

where Y is the Young modulus [6].

Before we proceed, note that averaging of V^{eff} yields a constant that just shifts the whole fermionic band and has no nontrivial effects. To account for those we have to calculate the second cumulant of the bosonic field $\mathcal{K}_2(\mathbf{q}) = \langle(V^{\text{eff}})^2\rangle_{\mathbf{q}} - \langle(V^{\text{eff}})\rangle_{\mathbf{q}}^2$. Then, neglecting higher cumulants, we can write for the fermionic self-energy

$$\Sigma(E, \mathbf{p}) = \int \frac{d^2q}{(2\pi)^2} \gamma(\mathbf{p} - \mathbf{q}, \mathbf{p}, \mathbf{q}, E) \mathcal{K}_2(\mathbf{q}) G(E, \mathbf{p} - \mathbf{q}), \quad (5)$$

where G is the fermion's Green's function, γ is the three-leg vertex, and E is the energy of the fermion (cf. Refs. [17,18]). The approximation $\gamma = 1$ corresponds to the self-consistent Born approximation which is supposed to be enough for positive energies (that is, within the band). To take into account also the fluctuation DOS tail, vertex corrections should be taken into account. At this stage, we argue that for energies far enough from the band edge only small momentum transfers play a role [17,18], so that we neglect momentum dependence of the vertex and of the self-energy and use the Ward identity for the vertex:

$$\gamma(\mathbf{p}, \mathbf{p}, 0, E) = 1 - \frac{\partial \Sigma}{\partial E}, \quad (6)$$

ending up with the following closed differential equation for the self-energy:

$$\Sigma(E) = \left(1 - \frac{\partial \Sigma}{\partial E}\right) \int \frac{d^2q}{(2\pi)^2} \frac{\mathcal{K}_2(\mathbf{q})}{E - \epsilon_{\mathbf{q}} - \Sigma(E)}. \quad (7)$$

Now we go on to estimate $\mathcal{K}_2(\mathbf{q})$ for the anisotropic case, which is a question of its own significance. For $q > q^*$, it has been done recently in Ref. [20], so here we do the calculations for small wave vectors.

A consistent theory of anisotropic membranes is to our knowledge not yet fully developed, so in this paper we make plausible assumptions for the low- q behavior of the cumulant $\langle h_{\mathbf{q}} h_{-\mathbf{q}} \rangle$ providing their consistence with Eq. (3). Following the reasoning of Ref. [20], we model the anisotropy of the bending rigidity by writing for large q :

$$\langle h_{\mathbf{q}} h_{-\mathbf{q}} \rangle = \frac{T}{(\kappa_x^{1/2} q_x^2 + \kappa_y^{1/2} q_y^2)^2}. \quad (8)$$

$$\mathcal{K}_2(\mathbf{q}) = \frac{T^2 4^{1-\eta}}{2\pi(\kappa_x \kappa_y)^{1/4} (q^*)^{2\eta} q^{2-2\eta}} (\cos(4\alpha)(a_x - a_y)^2 0.062 + \cos(2\alpha)(a_x^2 - a_y^2) 0.54 + (a_x + a_y)^2 1.59 + (a_x - a_y)^2 1.03) - \frac{T^2(3a_x^2 + 2a_x a_y + 3a_y^2)}{16\pi(\kappa_x \kappa_y)^{1/4} (q^*)^2} \frac{\eta}{1-\eta}. \quad (12)$$

Here the numerical factors in the parentheses are results of numerical integration, for which the specific value for $\eta = 0.85$ was used; α is the polar angle of the \mathbf{q}' vector (not the \mathbf{q} vector!).

As a next step, we rescale the x and y components of the wave vector introducing $q'_{x,y} = q_{x,y} \kappa_{x,y}^{1/4}$, and write

$$\langle h_{\mathbf{q}} h_{-\mathbf{q}} \rangle = \begin{cases} \frac{T}{q'^4} & \text{for } q' > q'^* \\ \frac{T}{q'^{4-\eta} q'^{\eta}} & \text{for } q' < q'^* \end{cases} \quad (9)$$

with $q' = (q_x^2 + q_y^2)^{1/2}$, $(q'^*)^2 = 3T(Y_x Y_y)^{1/2} / (16\pi(\kappa_x \kappa_y)^{3/4})$ and $Y_{x,y}$ is the Young moduli in x, y directions. Finally, introducing $a_{x,y} = g_{x,y} \kappa_{x,y}^{-1/2}$, we obtain for $\mathcal{K}_2(\mathbf{q})$:

$$\mathcal{K}_2(\mathbf{q}) = \frac{2}{(\kappa_x \kappa_y)^{1/4}} \int \frac{d^2k'}{(2\pi)^2} \left[a_x \left(k_x'^2 - \frac{q_x'^2}{4} \right) + a_y \left(k_y'^2 - \frac{q_y'^2}{4} \right) \right]^2 \langle h_{\mathbf{k}+\frac{\mathbf{q}}{2}} h_{-\mathbf{k}-\frac{\mathbf{q}}{2}} \rangle \langle h_{\frac{\mathbf{q}}{2}-\mathbf{k}} h_{\mathbf{k}-\frac{\mathbf{q}}{2}} \rangle. \quad (10)$$

To get this expression, we take V^{eff} given by Eq. (2) and calculate the Fourier transform of $\langle V^{\text{eff}}(\mathbf{r}_1) V^{\text{eff}}(\mathbf{r}_2) \rangle$ over $\mathbf{r}_1 - \mathbf{r}_2$, which is done using the Wick's theorem to decouple the average of the product of four $h_{\mathbf{q}}$'s. The latter corresponds to the self-consistent screening approximation [9]. The resulting $\langle hh \rangle$ correlators carry the momenta $\mathbf{k} \pm \mathbf{q}/2$. Finally, the rescaling of the components of \mathbf{q} , \mathbf{k} is made as described above to get \mathbf{q}' and \mathbf{k}' , respectively.

As the conditions $q' < q'^*$, $q > q^*$ are rather crossovers than strict boundaries, we can within the same accuracy split the \mathbf{k}' integral into two parts (1) $k' < q'^*$ and (2) $k' > q'^*$. For the first one, we take the anharmonic expression for the $\langle h_{\mathbf{q}} h_{-\mathbf{q}} \rangle$ correlators, and for the second part we use the harmonic one. Moreover, we limit ourselves to calculating only the leading terms in q'/q'^* , so for $k' > q'^*$ we just neglect the q' dependence to obtain the contribution to \mathcal{K}_2 :

$$\mathcal{K}_2(\mathbf{q}) \leftarrow \frac{2T^2}{(\kappa_x \kappa_y)^{1/4}} \int_{k' > q'^*} \frac{d^2k'}{(2\pi)^2} \frac{(a_x k_x'^2 + a_y k_y'^2)^2}{k'^8} = \frac{T^2(3a_x^2 + 2a_x a_y + 3a_y^2)}{16\pi(\kappa_x \kappa_y)^{1/4} (q^*)^2} \quad (11)$$

The integration over $k' < q'^*$ is more involved, as we have to keep the \mathbf{q}' dependence of the integrand, which leads to anisotropic contributions. Here, apart from the leading term $\propto (q'/q'^*)^{2\eta-2}$, we also keep the subleading term $\propto (q'/q'^*)^0$, as for $\eta = 0.85$ they are numerically of the same order of magnitude for not extremely small q' . Evaluating the integral [22] and adding it up with the contribution given by Eq. (11), we arrive at

The case $q' > q^*$ has been considered in Ref. [20]. The result is

$$\begin{aligned} \mathcal{K}_2(\mathbf{q}) = & \frac{T^2}{4\pi(\kappa_x\kappa_y)^{1/4}q'^2} \\ & \times \left(\cos(4\alpha)\frac{(a_x - a_y)^2}{2} + \cos(2\alpha)(a_x^2 - a_y^2) \ln \frac{\gamma q'}{q^*} \right. \\ & \left. + (a_x^2 + a_y^2) \ln \frac{\gamma q'}{q^*} + \frac{(a_x + a_y)^2}{4} \right), \end{aligned} \quad (13)$$

where $\gamma \gtrsim 1$ is some number determined by details of $\langle h_q h_{-q} \rangle$ behavior for $q \sim q^*$.

After obtaining the above expressions for \mathcal{K}_2 , our immediate goal is to evaluate the integral in Eq. (7). As it has been mentioned above, the dispersion of the holes in black phosphorus is quasi-one-dimensional. It has been evaluated using *ab initio* numerical methods in our previous work [20] and can be approximated in atomic units by

$$\epsilon_{\mathbf{q}} = 2.9q_x^2 + 0.05q_y^2 + 13.2q_z^4. \quad (14)$$

In these units, the averaged $q^* \approx 0.015$ for room temperature. Note that if the coefficient at q_y^2 were exactly zero we would have an enhanced Van Hove singularity in the bare density of states $\propto E^{-1/4}$ at the band edge, instead of a step in generic 2D case.

As it will be shown below, the integral in Eq. (7) is determined by $q \sim q^*$. For these values, the first term in the dispersion dominates, so we can take

$$\epsilon_{\mathbf{q}} = \frac{q_x^2}{2m_x}. \quad (15)$$

We perform the same variable change $\mathbf{q} \rightarrow \mathbf{q}'$ and introduce $\epsilon = -E + \Sigma(E) > 0$ to rewrite our equation as

$$\epsilon + E = \frac{\partial \epsilon}{\partial E} \int_0^\infty \int_0^{2\pi} \frac{q' dq' d\alpha}{(2\pi)^2 (\kappa_x \kappa_y)^{1/4}} \frac{\mathcal{K}_2(\mathbf{q})}{\epsilon + \frac{q'^2 \cos^2 \alpha}{2m_x \kappa_x^{1/2}}}, \quad (16)$$

with α being the polar angle of \mathbf{q}' .

Consider first $q' < q^*$. As

$$\int_0^{2\pi} \frac{d\alpha}{1 + a \cos^2 \alpha} = \frac{2\pi}{\sqrt{1+a}} \quad (17)$$

and $\mathcal{K}_2 \propto (q')^{2\eta-2}$ with $\eta = 0.85 > 0.5$, we easily confirm, that for small ϵ the q' integral is determined by the upper limit q^* . Analogously, for $q' > q^*$, the q' integral is determined by the lower limit, as $\mathcal{K}_2 \propto (q')^{-2}$. Note that for conventional 2D-dispersion, this reasoning does not work and the integral acquires its value on $q' \rightarrow 0$ for $\epsilon < (q^*)^2/2m_x$.

Estimation of the integral for $E \ll q^2/2m_x$ allows us to recast Eq. (16) as

$$\epsilon + E = \frac{\partial \epsilon}{\partial E} \frac{(T\beta)^{3/2}}{\epsilon^{1/2}}, \quad (18)$$

where β is a dimensionless constant, depending on material constants. Using the numerical values from the first-principles calculations [20] ($Y_x = 1.31 \text{ eV/\AA}^2$, $Y_y = 5.68 \text{ eV/\AA}^2$, $\kappa_x = 1.29 \text{ eV}$, $\kappa_y = 5.62 \text{ eV}$, $g_x = 2.11 \text{ eV}$, $g_y = 0.89 \text{ eV}$, $m_x = 0.17m_e$, m_e being the free electron mass) it can be estimated

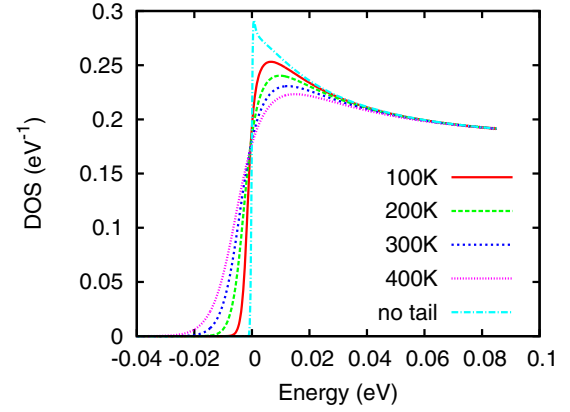


FIG. 1. DOS per unit cell per spin for $T = 100, 200, 300,$ and 400 K . For reference, the DOS corresponding to bare dispersion without the inclusion of the flexuron tail is shown. The Van Hove singularity in the latter manifests the aforementioned quasi-one-dimensionality of the holes in black phosphorus. It is to a large extent smeared by the flexural modes. Zero energy corresponds to the top of the valence band at $T = 0 \text{ K}$.

that $\beta \approx 0.20$ [22]. Introducing

$$\epsilon(E) = \beta T \left[f \left(\frac{E}{T\beta} \right) \right]^2, \quad (19)$$

we arrive at the Riccati equation for the function $f(x)$

$$2f' = f^2 + x. \quad (20)$$

At this point, we note that the inequality $\beta T \ll (q^*)^2/2m_x \kappa^{1/2} \approx 0.65T$ holds reasonably well, what justifies the above calculations.

The last equation can be turned into a linear one by the substitution $f(x) = -2\psi'(x)/\psi(x)$. The corresponding equation reads

$$4\psi''(x) + x\psi(x) = 0, \quad (21)$$

which is the Airy equation. Thus the general solution for $f(x)$ is given by

$$f(x) = 2^{1/3} \frac{\text{Ai}'(-x/4^{1/3}) + z \text{Bi}'(-x/4^{1/3})}{\text{Ai}(-x/4^{1/3}) + z \text{Bi}(-x/4^{1/3})}. \quad (22)$$

Here, Ai and Bi are the Airy functions and z is an arbitrary complex constant, which can be determined by assuring we get correct density of states for $E \rightarrow +\infty$, or in other words $\epsilon(E) \rightarrow -E - i0$ [17]. Using the asymptotic behavior of the Airy functions it can be checked that for $z = -i$, $f^2(x) \approx -x - i/\sqrt{x}$ for large positive x which yields the correct behavior for ϵ .

Now it is straightforward to calculate the DOS:

$$\rho(E) = -\frac{1}{\pi} \int \frac{d^2k}{(2\pi)^2} \Im \frac{1}{-\beta T f^2\left(\frac{E}{\beta T}\right) - \epsilon_{\mathbf{k}}}, \quad (23)$$

with $\epsilon_{\mathbf{k}}$ taken from the *ab initio* GW calculations [21]. The result for different temperature is shown in Fig. 1. The spectral function

$$A(\mathbf{k}, E) = -\frac{1}{\pi} \Im \frac{1}{-\beta T f^2\left(\frac{E}{\beta T}\right) - \epsilon_{\mathbf{k}}} \quad (24)$$

for room temperature is shown in Fig. 2.

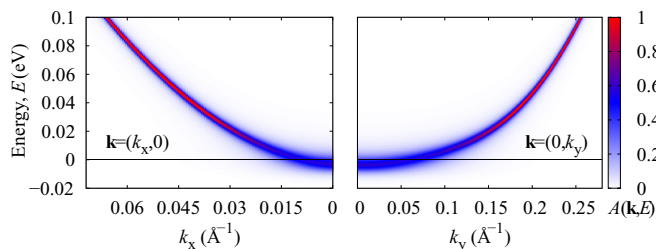


FIG. 2. Spectral function $A(\mathbf{k}, E)$ (shown by color) calculated at $T = 300$ K along Γ - X (left) and Γ - Y (right) directions of the Brillouin zone. Note the different scale for the two plots.

According to the results presented on these figures the effect of flexural phonons on the density of states near the top of the

valence band (the bottom of the band in hole representation) is quite noticeable and can be probed by conventional spectroscopic tools like angle-resolved photoemission or scanning probe microscopy and other tunneling methods. Quasi-one-dimensional character of the charge carrier dispersion makes hole-doped black phosphorus the best candidate to study these effects. Such experiments would be of a great interest, as an electronic probe of complicated physics of fluctuating anisotropic membranes.

The research has received funding from the European Union Horizon 2020 Programme under Grant No. 696656 Graphene Core1, and from the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

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