Excitons in bulk black phosphorus evidenced by photoluminescence at low temperature

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Keywords: exciton, black phosphorus, photoluminescence, low temperature, Wannier–Mott

Abstract

Atomic layers of black phosphorus (BP) present unique opto-electronic properties dominated by a direct tunable bandgap in a wide spectral range from visible to mid-infrared (IR). In this work, we investigate the IR photoluminescence (PL) of BP single crystals at very low temperature. Near-band-edge recombinations are observed at 2 K, including dominant excitonic transitions at 0.276 eV and a weaker one at 0.278 eV. The free-exciton binding energy is calculated with an anisotropic Wannier–Mott model and found equal to 9.1 meV. On the contrary, the PL intensity quenching of the 0.276 eV peak at high temperature is found with a much smaller activation energy, attributed to the localization of free excitons on a shallow impurity. This analysis leads us to attribute respectively the 0.276 eV and 0.278 eV PL lines to bound excitons and free excitons in BP. As a result, the value of bulk BP bandgap is refined to 0.287 eV at 2 K.

Since graphene was first isolated by mechanical exfoliation of graphite in 2004 [1], the 2D materials panorama has been considerably broadened. Black phosphorus (BP), a crystal first synthetized by Bridgman a hundred years ago [2], has recently been in the spotlight of the scientific community due to the unique properties of its 2D atomic layers: high carriers mobilities [3–5], in-plane anisotropy [6–9] and highly tunable bandgap [7, 10, 11]. In particular, the bandgap greatly depends on the BP thickness and goes from mid-infrared (IR) energy range in the bulk [12–17] to visible light energy range in the monolayer [4, 5, 10, 18, 19]. One can then observe that BP completes the accessible spectral range between the zero bandgap graphene [20, 21] and semiconducting transition metal dichalcogenides (TMDCs) which exhibit luminescence in the visible range [22, 23]. Furthermore and unlike 2D TMDCs [24, 25], the BP bandgap remains direct whatever the layer number [26, 27] which makes it interesting for optoelectronic applications such as photodetectors [28–31] or light-emitting devices [32–34]. BP exfoliated thinlayers have been intensively investigated by means of different optical measurements [12, 35], electron energy loss spectroscopy [19] and especially through photoluminescence (PL) [4, 5, 36–41]. On the contrary, optical investigations on bulk BP are relatively old and quite sparse [42–47]. In particular, the characteristics of emitted light at low temperatures remains unknown, probably due to the technical difficulties related to the IR spectral region.

Here we report PL spectra at very low temperature of as-synthetized BP crystals. These measurements provide evidence of several contributions from near-band-edge recombinations, which are further investigated by temperature-dependent experiments. The highest energy PL peaks are attributed to the radiative recombination of excitons. An estimate of the binding energy of free excitons and their spatial extension has been done by means of a fully anisotropic Wannier–Mott model. The comparison between experimental and theoretical results is used as a basis for the characterization of observed PL lines.

Bulk BP crystals were purchased from HQ Graphene (99.995% purity) and stored in glove box under argon atmosphere (<0.5 ppm O₂, < 1 ppm H₂O) to prevent its photo-oxidation under ambient conditions.
conditions. For luminescence experiments, PL is performed at 2 K thanks to a helium-bath cryostat at low pressure to reach the superfluid He state. The excitation source is a Nd:YAG (1064 nm) laser focused on the BP crystal with a spot diameter of ~100 μm, well-suited for studying millimeter size BP crystals (see inset of figure 1). The penetration depth of the beam is of the order of 100 nm, defining a probed volume of $8 \times 10^{-10}$ cm$^3$. The PL signal is collected in a Fourier transform infra-red spectrometer (BOMEM DA8, CaF$_2$ beamsplitter, spectral resolution 0.5 meV) equipped with an InSb detector cooled at 80 K. A chopper and a lock-in amplifier are needed to eliminate the undesirable blackbody radiations in the IR spectral range.

Figure 1 shows a low temperature (2 K) PL spectrum of a BP crystal. The intensity of the PL signal is of the same order of magnitude as that of a reference InAs crystal (see supporting information SI1). Note that the PL intensity depends on the polarization of the incident laser with respect to the zigzag and armchair axes of the BP atomic planes, due to the polarization-dependent absorption. This is consistent with both the larger effective mass along the armchair axis, but not as much as in the zigzag direction. An anisotropy of the crystal, we developed and solved a variational effective-mass model which generalizes the works by Baldereschi and Diaz [52] and Schindlmayr [53]. The Hamiltonian of the exciton is written as a sum of a kinetic part which accounts for the band effects (the anisotropic effective mass) and a potential energy accounting for screening effects (anisotropic dielectric function). We further assume that the excitonic wavefunction $\psi_a(r)$ has a 1s shape deformed as an ellipsoid along the three crystallographic axes. Hence, the exciton wavefunction depends on the parameter $a = (a_x, a_y, a_z)$ which quantify the axial deformation.

Under these approximations, the excitonic ground state is found by minimizing the exciton energy $E(a) = \langle \psi_a | H | \psi_a \rangle$ with respect to the parameter $a$. The value $\hat{a}$ which minimizes $E(a)$ gives an estimate of the exciton extension in the armchair ($x$), zigzag ($y$) and stacking ($z$) directions, and allows to evaluate the binding energy as $E_b = -E(\hat{a})$. Refer to SI4 for additional information about the model.

On the basis of experimental input from literature on the dielectric function [51] and effective masses [50], the fully anisotropic model predicts a free-exciton binding energy equal to 9.1 meV and exciton extensions of 90.9 Å, 39.6 Å and 63.1 Å in the armchair ($x$), zigzag ($y$) and stacking ($z$) directions, respectively. Cuts on the $xy$ and $xz$ planes of the exciton wavefunction squared are reported in figure 2. It clearly illustrates the impact of the crystal anisotropy on the spatial extension of the exciton wavefunction. The average distance between the electron and the hole in the exciton complex appears strongly compressed along the zigzag axis. This is consistent with both the larger effective mass ($\epsilon_{\text{zigzag}} \approx 10\epsilon_{\text{armchair}}$) and the lower dielectric constant ($\epsilon_{\text{zigzag}} = 13$, while $\epsilon_{\text{armchair}} = 16.5$). The extension along $z$ (stacking axis) is also reduced with respect to the extension along the armchair axis, but not as much as in the zigzag direction. An anisotropy at half-maximum of the higher energy peaks is particularly small ($X: 1.7$ meV and $\Gamma X: 2.9$ meV). Moreover, their energy values are fully consistent with the 0.276 eV free-exciton energy extracted from reflectance experiments on bulk BP at 2 K [44, 46].

These two elements allow us to attribute the higher energy peaks $X$ (0.278 eV) and $\Gamma X$ (0.275 eV) to excitons of the bulk BP crystal. To the best of our knowledge, this is the first observation of excitons in bulk BP by PL. The two components $\Gamma X$ and $X$ are less than 3 meV apart and might not be confused with the first two Rydberg series which are 6 meV apart [44].

Morita [44] evaluated the binding energy of free excitons in BP to be 7.9 meV when assuming BP to be an isotropic medium. However, BP is a highly anisotropic crystal with different effective masses [50] and dielectric constants [51], measured and reported along the three crystallographic axes related to the BP unit cell. In order to account for the 3D anisotropy of the crystal, we developed and solved a variational effective-mass model which generalizes the works by Baldereschi and Diaz [52] and Schindlmayr [53]. The Hamiltonian of the exciton is written as a sum of a kinetic part which accounts for the band effects (the anisotropic effective mass) and a potential energy accounting for screening effects (anisotropic dielectric function). We further assume that the excitonic wavefunction $\psi_a(r)$ has a 1s shape deformed as an ellipsoid along the three crystallographic axes. Hence, the exciton wavefunction depends on the parameter $a = (a_x, a_y, a_z)$ which quantify the axial deformation.

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stronger within the plane than out of plane is a singular characteristic for a lamellar material, which points out once more how BP is rather unique among the 2D materials.

Additional simulations done using either an average isotropic dielectric constant or an average isotropic effective mass (see SI4) show that taking into account the anisotropy of the effective mass is crucial, while the anisotropy of the screening has a lower impact on the binding energy and the excitonic radii. This result is in contrast with what is generally observed in thin films, where image charges at the interfaces modify drastically the electron–hole interaction [54]. This indicates that there should be a cross-over thickness at which screening effects starts dominating over band effects. We expect this conclusion to be general, and not only related to BP.

In order to investigate the exciton properties in more details, PL measurements as function of temperature were performed on another part of the crystal studied in figure 1. These spectra are presented in figure 3(a) from 2 K up to 80 K. The measurement at 2 K well reproduces the spectrum shown in figure 1, attesting the reproducibility of the PL spectrum. At high temperature, the \( \Gamma'X \) and \( Y \) PL peaks shift towards higher energies, following the expected behavior of the BP bandgap (see also PL spectra up to 200 K and complementary analysis in SI5). The blue shift of the BP bandgap at high temperature is a well-understood phenomenon [55], though a redshift is more commonly observed in semiconductors [44, 48].

Besides, the \( \Gamma'X \) peak is distinguishable only up to 50 K and vanishes at higher temperatures. Its integrated intensity is analyzed in figure 3(b). The \( \Gamma'X \) PL intensity is fitted with a simple model assuming a thermal activation of a non-radiative processes, \( I(T)/I(0) = (1 + a \exp (-E_a/k_B T))^{-1} \), where \( a \) is the ratio between radiative and non-radiative recombination probabilities and \( E_a \) is the activation energy of non-radiative channels [56–58]. In figure 3(b), \( I(0) \) is assumed as the intensity measured at 2 K and the experimental data are plotted as \( \ln(I(0)/I(T)) - 1 \) as a function of temperature. This plot evidences that a single activation energy is enough to account correctly for the \( \Gamma'X \) thermal quenching. A linear regression gives \( E_a = 1.6 \) meV with a non-radiative parameter \( a = 1.5 \). This activation energy is more than five times lower than the free exciton binding energy (9.1 meV), which rules out free-exciton recombinations as the origin of the \( \Gamma'X \) peak.

It is important to remind now that the purest BP crystals are naturally p-type doped, as demonstrated by the transport studies performed on bulk BP in the 1990s [14, 48]. The nature of the acceptor center responsible for the non-intentional p-type conductivity of BP remains unclear but could be related to the presence of vacancies [59]. Its ionization energy was found to be about 18 meV [48]. Interestingly, the localization energy of free excitons on shallow dopants is known to be typically 10% of the dopant ionization energy according to Haynes rule [60]. The activation energy extracted from the temperature-dependent experiments would rather correspond here to the localization energy of the free exciton \( X \) on a neutral impurity \( \Gamma^0 \), to form a bound exciton complex \( \Gamma^0 + X \rightarrow \Gamma'X \). For that reason, we attribute the \( \Gamma'X \) luminescence to the radiative recombination of the exciton bound to a shallow impurity. The shallow dopant is probably a neutral acceptor in the investigated sample, which deserves to be confirmed by Hall effect measurements. The temperature-dependence of the bound exciton linewidth was further analyzed and a coupling constant with acoustic phonons \( \Gamma_a = 102 \) \( \mu \)eV K\(^{-1} \) was found, with the same order of magnitude than in InP or CdSe (see SI5c).

The results obtained on the activation energy of the bound exciton PL quenching are consistent with the presence of a faint shoulder observed on the high-energy side of \( \Gamma'X \) peak in figure 1. The careful deconvolution presented in figure 1 reveals a peak (the \( X \) peak) located at 2.5 ± 1 meV.
Figure 3. Temperature dependence of bulk BP PL. (a) PL spectra from 2 K up to 80 K. The decrease of I\(^{\circ}\)X intensity at high temperature is modelled with a thermally-activated non-radiative channel (see details in the text). A 1.6 meV activation energy is extracted from the linear fit (red line) in (b).

above the I\(^{\circ}\)X peak, consistent with the order of magnitude of the localization energy extracted from temperature-dependent PL experiments. Though weak, the energy of the X PL signal at 0.278 eV might be associated to the free exciton of BP.

Lastly, we briefly discuss the origin of the lower energy PL contributions, Y and Z, observed respectively at 16 meV and 27 meV lower than the bound exciton I\(^{\circ}\)X. The dominant contribution Y might correspond to a transition from electron to neutral acceptor (eA\(^{0}\)), or donor–acceptor pairs (DAP) recombinations since a 18 meV acceptor was identified in non-intentionally doped BP crystals [14, 48]. The lower PL energy contribution, Z, could come from DAP transitions. Despite experimental evidences consistent with these hypotheses showing that Y and Z peaks vary both in energy and in intensity as function of the excitation power (see SI6 and 7), their complete attributions would deserve further experimental work.

To conclude, our work shows the first PL spectrum of BP crystal at very low temperature and, in contrast to exfoliated layers, the PL spectrum is composed of several peaks between 4.5 \(\mu\)m and 5 \(\mu\)m. The experimental and theoretical results gathered in this work confirm the excitonic nature of the dominant I\(^{\circ}\)X peak, as a bound exciton with a localization energy of 2.5 meV. This result is reinforced by the fact that it is obtained using two strictly independent methods, which are the activation energy of peak I\(^{\circ}\)X quenching and the observation of peak X at this same energy. These experimental results associated with the calculation of the free-exciton binding energy provide a revised and more accurate value of 0.287 \(\pm\) 0.001 eV for the free particle bandgap of bulk BP in the limit of low temperatures. This value deserves to be the bulk reference value for further investigations of thickness dependent properties in thin films and layers.

Acknowledgments

The authors acknowledge funding from the French national research agency (ANR) under the Grant No. ANR-17-CE24-0023-01 (EPOS-BP). This project has also received funding from the European Union’s Horizon 2020 research and innovation program under Grant Nos. 785219 (Graphene Flagship core 2) and 881603 (Graphene Flagship core 3).
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