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Band parameters of phosphorene

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Abstract. Phosphorene is a two-dimensional nanomaterial with a direct band-gap at the Brillouin zone center. In this paper, we present a recently derived effective-mass theory of the band structure in the presence of strain and electric field, based upon group theory. Band parameters for this theory are computed using a first-principles theory based upon the generalized-gradient approximation to the density-functional theory. These parameters and Hamiltonian will be useful for modeling physical properties of phosphorene.

1. Introduction

Two-dimensional nanomaterials are expected to revolutionize material science and the next generation devices. The first example was graphene [1] but there are now a few candidates beyond graphene, particularly MoS₂ [2], silicene [3] and phosphorene [4]. Phosphorene is the latest promising candidate for both electronics and photonics due to the presence of a band gap (~ 2 eV) and relatively high electron mobility.

For applications, such as in nanoelectronics, it is necessary to have a band structure model that is efficient in order to simulate the electrical properties. A widely-used band-structure model is the $k \cdot p$ model [5], often giving energy bands analytically in the vicinity of extrema in terms of meaningful parameters such as effective masses and optical matrix elements. For phosphorene, a few $k \cdot p$ models have recently appeared [6, 7, 8]. In our recent paper, we presented a model in the presence of external fields. Our present goal is to evaluate the parameters of the model.

2. Theory

2.1. Structure

Phosphorene can be viewed as a single layer of black phosphorus. They have the same in-plane translational symmetry and the nonsymmorphic space group is base-centered orthorhombic [7] (Fig. 1).

2.2. Effective Hamiltonian

The effective Hamiltonian for phosphorene in the presence of strain and an external electric field has recently been derived [8]:

$$\mathcal{H} = \mathcal{H}_i + \mathcal{H}_e, \quad (1)$$

$$\mathcal{H}_e = \mathcal{H}^e + \mathcal{H}^E, \quad (2)$$



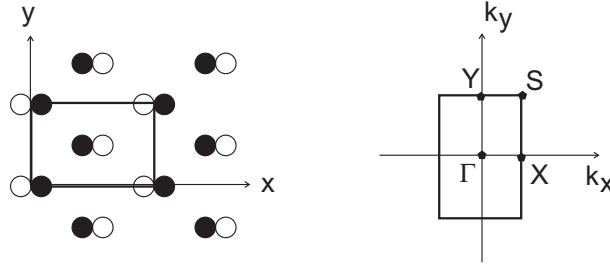


Figure 1. Real (left) and reciprocal (right) space drawings of phosphorene. The two atoms (solid and open circles) are at different vertical heights.

$$\mathcal{H}_i = a_1 k_x^2 + a_2 k_y^2 + \sum_{i \leq j} a_{ij} k_i^2 k_j^2 + \dots, \quad (3)$$

$$\begin{aligned} \mathcal{H}^\epsilon &= (e_1 + e_2 k_x^2 + e_3 k_y^2) \epsilon_{xx} + (e_5 + e_6 k_x^2 + e_7 k_y^2) \epsilon_{yy} \\ &+ (e_9 + e_{10} k_x^2 + e_{11} k_y^2) \epsilon_{zz} + \dots, \end{aligned} \quad (4)$$

$$\begin{aligned} \mathcal{H}^E &= (c_4 + c_5 k_x^2 + c_6 k_y^2) E_x^2 + (c_8 + c_9 k_x^2 + c_{10} k_y^2) E_y^2 \\ &+ (c_{12} + c_{13} k_x^2 + c_{14} k_y^2) E_z^2 + \dots, \end{aligned} \quad (5)$$

where \mathbf{k} is the two-dimensional wave vector, ϵ_{ij} is the strain tensor, and \mathbf{E} is a homogeneous, external electric field. The above result is obtained in the absence of spin-orbit interaction.

2.3. Intrinsic band structure

It is known from group theory [8] that all the bands are nondegenerate; thus, the Hamiltonians give the electronic energies directly. Thus, from Eq. (3), the intrinsic band structure near the Brillouin zone center is given by

$$E_n(\mathbf{k}) = a_1 k_x^2 + a_2 k_y^2 + \sum_{i \leq j} a_{ij} k_i^2 k_j^2, \quad (6)$$

for band n . It can be seen that only terms in even powers of k_i are allowed. Thus, the linear dispersion present in graphene and silicene is not present in the band structure of phosphorene in the neighborhood of the Brillouin zone center. a_1 and a_2 are band parameters related to the effective masses. We would expect an anisotropy in the effective masses due to the orthorhombic symmetry of the crystal lattice.

2.4. Strained band structure

At the Γ point, the band energies are

$$E_n(\epsilon) = E_n + e_1 \epsilon_{xx} + e_5 \epsilon_{yy} + e_9 \epsilon_{zz}, \quad (7)$$

where E_n are the band edges in the absence of strain. The e_i 's are deformation potentials for a given band. Since the lattice is two-dimensional, a perpendicular strain from continuum elasticity theory is not defined (nor can it be described within the first-principles software since the latter uses an artificial superperiodic in the z direction). It can be defined as an internal deformation potential of the basis atoms inside the unit cell as some are outside the lattice plane. However, since it is not described by continuum elasticity theory, we will neglect in this work.

For a finite wave vector, the energies are

$$E_n(\epsilon) = E_n(\epsilon) + (a_1 + e_2\epsilon_{xx} + e_6\epsilon_{yy} + e_{10}\epsilon_{zz})k_x^2 + (a_2 + e_3\epsilon_{xx} + e_7\epsilon_{yy} + e_{11}\epsilon_{zz})k_y^2. \quad (8)$$

2.5. Electric field

Our prediction, from Eq. (5), is that the band gap changes quadratically with an externally-applied perpendicular electric field. This is in contrast to silicene where the dependence is linear, whereas there is no gap opening for graphene. At $k = 0$, the band gap as a function of a perpendicular field is

$$\Delta E_\Gamma(E_z) = E_\Gamma(0) + cE_z^2. \quad (9)$$

3. Results

Our density-functional theory (DFT)-based calculations were conducted using the projector augmented-wave method [9] and the PBE-GGA exchange-correlation functional [10] as implemented in the VASP code [11, 12, 13]. The wave functions were expanded using a plane-wave basis set with an energy cutoff of 1200 eV. Atomic positions were fully relaxed and k-point sampling was achieved by using a $9 \times 9 \times 1$ special-points grid until residual forces were lower than 5 meV/Å. The interlayer separation in the z direction was chosen large (~ 30 Å) to minimize fictitious interactions. The optimized lattice constants obtained were 3.300 and 4.624 Å.

3.1. Intrinsic band parameters

The valence band structure near the Γ point is shown in Fig. 2. The gap is almost direct at the Γ point and the GGA value is about 0.912 eV; Tran *et al.* [14] have shown that a GW correction increases the gap to 2.0 eV. The strong anisotropy in the band structure is evident. We did a fit

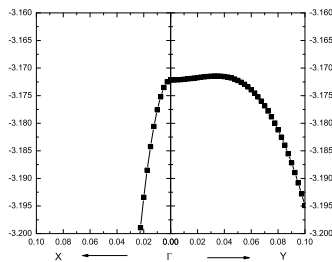


Figure 2. Highest valence band of phosphorene near the Γ point.

to our DFT calculations to obtain the intrinsic band parameters of the $k \cdot p$ theory (Table 1).

Table 1. Band parameters a_i (in units of $1/m_0$) and effective masses (in units of m_0) of the highest valence and lowest conduction bands of phosphorene at the Γ point. The effective mass of the VB along ΓY is very sensitive to the computation [8].

	a_1	$m^*(\Gamma Y)$	a_2	$m^*(\Gamma X)$
CB	0.808	1.24	5.804	0.173
		1.246 [15], 1.16 [16]		0.146 [15], 0.22 [16]
VB	0.106	7.20	-6.263	-0.160
		3.24 [16]		-0.19 [16]

3.2. Strain deformation potentials

We present here our results for the strain deformation potentials. Neglecting the e_9 deformation potential, we see that there are six deformation potentials for each band: e_1, e_2, e_3, e_5, e_6 and e_7 . In order to compute the deformation potentials, strain is applied in one direction (e.g., x direction) while restricting the atomic displacements in the perpendicular direction (i.e., ϵ_{yy}) to be zero. Values obtained by fitting to our DFT calculations are given in Table 2 for the highest valence band and lowest conduction band. The anisotropy is again clear. Additionally, one of

Table 2. Strain deformation potentials (e_1 and e_5 in units of eV, all others in units of $1/m_0$) of the highest valence and lowest conduction bands of phosphorene.

	e_1	e_2	e_3	e_5	e_6	e_7
CB	5.801	-0.678	-27.241	1.584	-0.710	-1.497
VB	0.502	-6.286	28.850	-2.745	-0.435	6.291

the deformation potentials has the opposite sign which can lead to band crossing effects.

3.3. Electric Field

It is fairly straightforward to compute the band structure change in the presence of a perpendicular electric field E_z . Hence, this is the only electric deformation potential to be presented here. Using DFT and Eq. (9), for an electric field between 0 and 0.5 V/\AA , we find that $c = -0.41 e\text{\AA}^2/\text{V}$.

4. Conclusion

The fundamental band parameters needed to simulate the electronic properties of phosphorene under the influence of an external in-plane strain and an external perpendicular electric field have been obtained by comparing a $k \cdot p$ theory to the band structures computed using a density-functional theory. Qualitative results are that the properties of phosphorene are expected to be highly anisotropic in the plane, and that the electric field dependence of the energy gap is quadratic rather than the linear behaviour shown by silicene.

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