

The Effect of Compressive and Tensile Strains on the Electron Structure of Phosphorene

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Received May 13, 2021; revised May 13, 2021; accepted May 13, 2021

Abstract—A new promising semiconductor material (phosphorene) is studied using theoretical simulation. The possibilities of changing the magnitude and nature of interband transitions under the action of compressive and tensile stresses on the phosphorene crystal lattice are determined. It is found that phosphorene can be both direct-gap and indirect-gap semiconductors, depending on the magnitude and direction of stress action. Phosphorene can be used in new generation nanoelectronic devices with controlled movement of charge carriers.

Keywords: phosphorene, monolayer, band structure, band gap, deformation, stresses

DOI: 10.1134/S1063783421100188

INTRODUCTION

The discovery of the possibilities for graphene [1] has caused a surge of interest in materials consisting of monoatomic layers interconnected by means of van der Waals forces. The unique properties of two-dimensional materials such as binary transition metal chalcogenides and materials of one type of atoms, for example, phosphorene, make it possible to design new type of nanoelectronic devices on their basis [2, 3]. Such compounds have structural stability and high mobility of charge carriers at room temperature and can be used to create field-effect transistors [4]. There are papers on the successful creation of structures from individual layers of refractory metal dichalcogenides [5, 6] and studies of their optical absorption and photoconductivity spectra [7]. Samples of low-power field-effect transistors, logic circuits, phototransistors [4, 8, 9] are made on the basis of MoS₂, one of the most stable and best studied layered dichalcogenides [2]. A study of the strains of the crystal lattice of MoS₂ showed that biaxial stress leads to a decrease in its band gap, and the MoS₂ monolayer, which is a direct-gap semiconductor, transforms into an indirect-gap semiconductor already at 2% deformation [10].

A new promising semiconductor material for optoelectronics and nanoelectronics is phosphorene (a two-dimensional modification of black phosphorus). The experimental production of phosphorene by separating black phosphorus into layers of monoatomic thickness has increased the attention to this material

[3, 11–13]. Unlike graphene, the atoms in phosphorene do not lie in the same plane, but form a curved structure [11]. Phosphorene is a direct-gap semiconductor with a band gap of about 2 eV [12]. There is information about the manufacture of field-effect transistor based on phosphorene [3]. The authors of [13] proposed to use phosphorene in medicine as a carrier agent for a targeted drug delivery system (chlorambucil) in the treatment of oncological diseases.

The development of new devices based on layered materials requires a detailed study of their properties and the conditions for changing their physical characteristics under various influencing factors. The influence of impurities, vacancies, and ways of different arrangement of dichalcogenide layers on their properties is studied in [14–16]. Another possibility of modifying properties is the strain of the crystal lattice of the material due to the compressive or tensile stresses, as a result of which magnetic properties can appear in non-magnetic materials, and the nature of direct and indirect transitions also changes [10, 17–23]. The number of publications describing the possibility of engineering the band gap of two-dimensional materials using applied stresses is increasing. Such stresses can be produced by bending or tension of the substrate, on which the material layer is located, or by the inhomogeneities in the material [24]. The described engineering is used to design a new class of straintronic devices based on two-dimensional crystals, in which the electrical and optical parameters of the devices are controlled by

applying controlled levels of uniaxial and biaxial stresses [24]. The possibility of increasing the Seebeck coefficient and the electrical conductivity of phosphorene due to the application of uniaxial stresses has been theoretically confirmed. This fact indicates that this material is promising for thermoelectric applications [25, 26]. However, the effect of strain of the phosphorene crystal lattice on its physical properties has not been studied.

This work presents the results of theoretical simulation of the effect of compressive and tensile stresses in the crystal lattice of phosphorene on the change in its band gap and the nature of interband transitions. These data are necessary to determine the possibilities of targeted modification of the properties of two-dimensional materials.

EXPERIMENTAL

Phosphorene has an orthorhombic crystal lattice (space group is $Cmca$) [27]; the arrangement of phosphorus atoms in it is shown in Fig. 1. Here Z denotes a parameter, the value of which was varied to realize the effect of compressive or tensile stress.

In the process of modeling, a translational cell with a size of 1×1 in the xy plane corresponding to a primitive cell was used. In the z direction, a vacuum layer with a thickness of 15 \AA was added to exclude the interaction between the layers during translation. When modeling deformation in phosphorene, two parameters (Z parameter corresponds to the distance between atoms of 2 and 3 and Y parameter corresponds to the distance between atoms of 1 and 2) were controlled by changing the projection parameter Δy with a step of 0.01 \AA .

The atomic positions in the crystal lattice were optimized in the context of the density functional theory using the PAW-PBE approximation [28] implemented in the VASP program code [29]. The cutoff energy given by the ENCUT parameter was 340 eV . Integration over the Brillouin zone was performed by the method of linear tetrahedra over a grid of $12 \times 12 \times 1$ points centered at the Γ point. The change in atomic positions stopped when the forces acting on the atoms reached a value of 1 meV \AA^{-1} .

RESULTS AND DISCUSSION

First, we calculated the values of the lattice constants a and b , at which the total energy of the system is minimum, which corresponds to an unstressed crystal lattice. For this, parameters a and b were changed sequentially with a step of 0.01 \AA . The optimized lattice parameters of phosphorene are $a = 3.30 \text{ \AA}$ and $b = 4.62 \text{ \AA}$; the minimum values are $Z = 2.26 \text{ \AA}$ and $Y = 2.22 \text{ \AA}$. Then, in order to model the effect of stress in the lattice at the optimized values of a and b , the parameters Z and Y were changed in the range selected

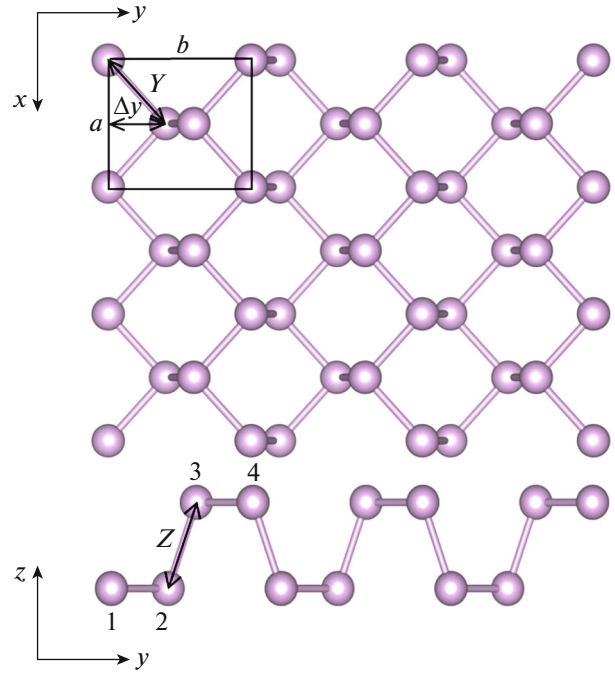


Fig. 1. 1×1 cell of phosphorene. The solid line shows the unit cell without taking into account the vacuum.

for each particular case with a step of 0.01 \AA . We considered two types of impacts (only the parameter Z is varied in the range from 2.20 to 2.32 \AA ; both parameter Z (in the same range of values) and Y (from 2.17 to 2.28 \AA) varied simultaneously).

According to calculations, the band gap of phosphorene with an undeformed crystal lattice is 0.89 eV (Fig. 2a); the material is a direct-gap semiconductor with the first direct transition at Γ point. The band gap and structural parameters of the material are in good agreement with the results of other theoretical calculations for phosphorene ($E_g = 0.9 \text{ eV}$ [30], $a = 3.30 \text{ \AA}$, and $b = 4.624 \text{ \AA}$ [31]). The distance between phosphorus atoms in the plane of the layer (between atoms of 1 and 2, 3 and 4) is 2.22 \AA ; the distance between phosphorus atoms in the direction perpendicular to the layer (between atoms of 2 and 3, Fig. 1) is 2.26 \AA .

The electronic band structures of phosphorene with parameters corresponding to the unstressed lattice in comparison with the spectra of phosphorene under the action of compressive and tensile stresses are shown in Fig. 2. It is obvious that the application of stresses changes the structural symmetry and leads to a shift in the band extrema from high symmetry points: a decrease in the Z parameter relative to its equilibrium value leads to a shift in the minimum of the conduction band from the Γ point in the $\Gamma-X$ direction (Γ' point), the semiconductor becomes indirect-gap semiconductor. In addition, a region of flat bands appears in the valence band in the vicinity of the Γ point with increasing Z parameter (Fig. 2b), which should

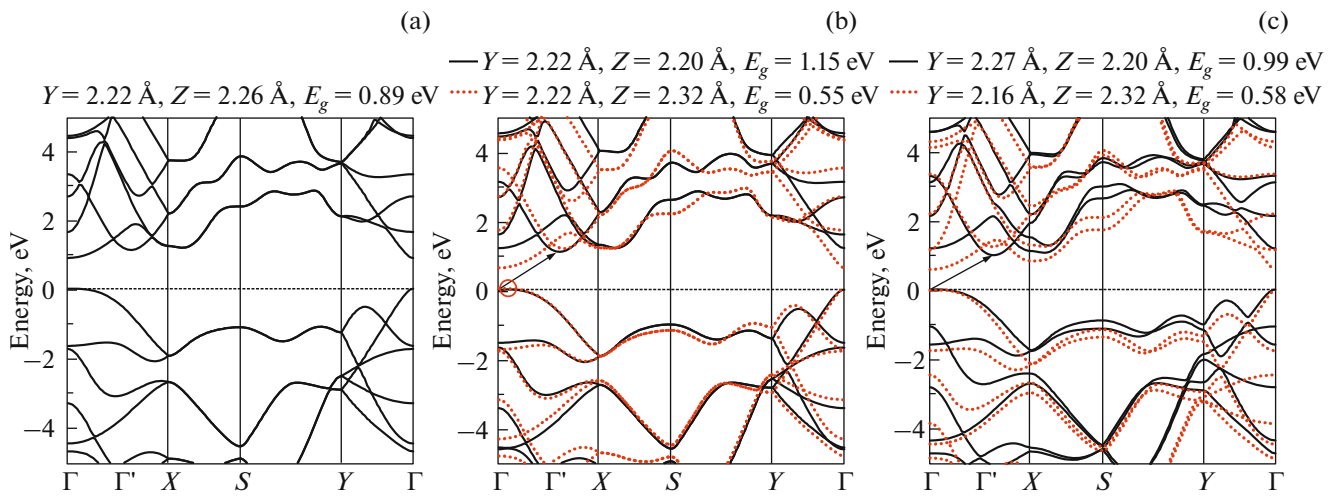


Fig. 2. The electronic band structure of phosphorene with an undeformed crystal lattice (a) under the effect of compressive ($Z = 2.20 \text{ \AA}$) and tensile ($Z = 2.32 \text{ \AA}$) stresses (along the Z direction) (b) and under the effect of stresses that change distances along Z and Y directions (c). Zero on the energy scale corresponds to the position of the maximum of the valence band.

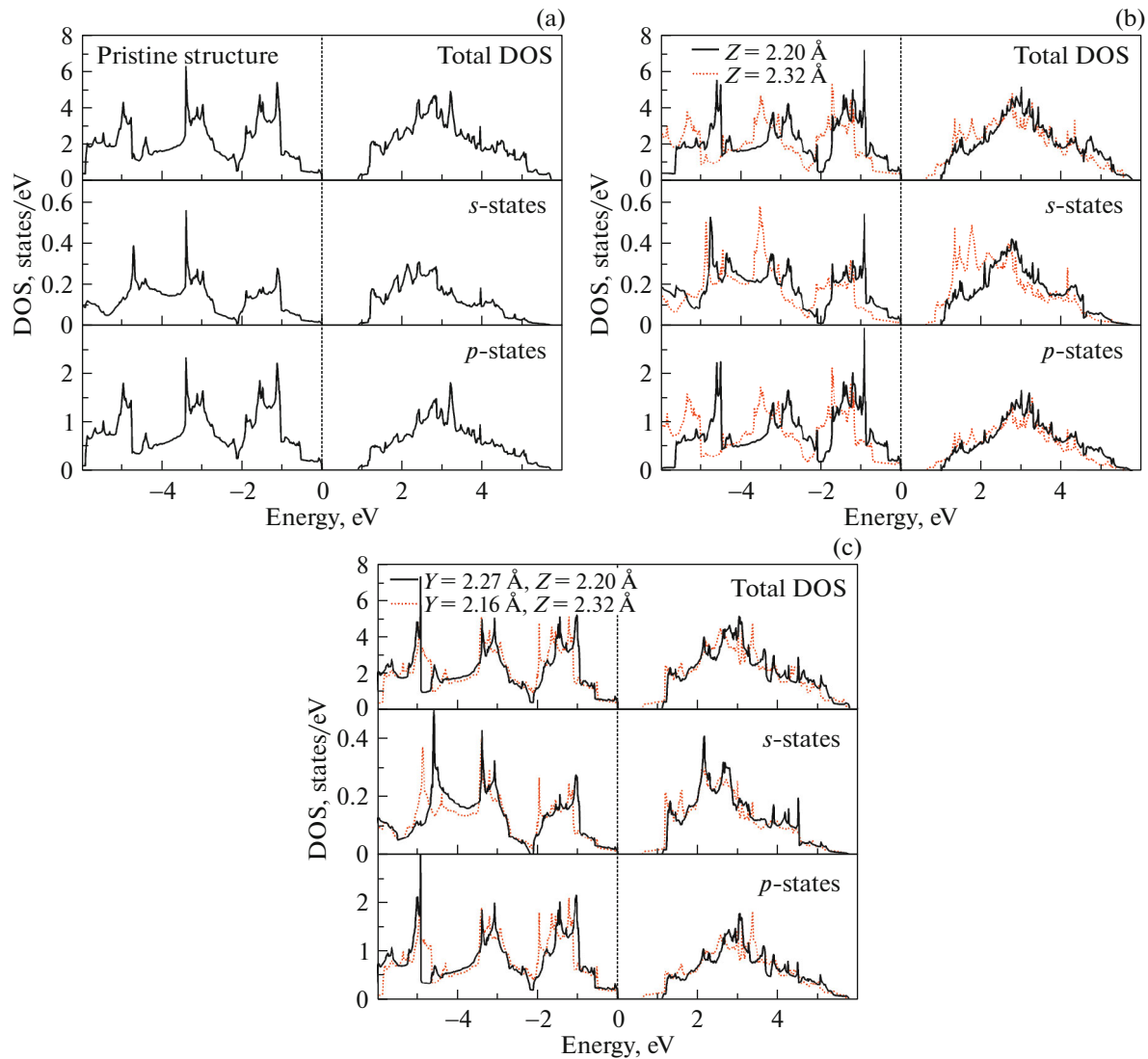


Fig. 3. Total and partial densities of electronic states of phosphorene with an undeformed crystal lattice (a) under the effect of compressive ($Z = 2.20 \text{ \AA}$) and tensile ($Z = 2.32 \text{ \AA}$) stresses (along the Z direction) (b) and under the effect of stresses that change distances along Z and Y directions (c). Zero on the energy scale corresponds to the position of the Fermi level.

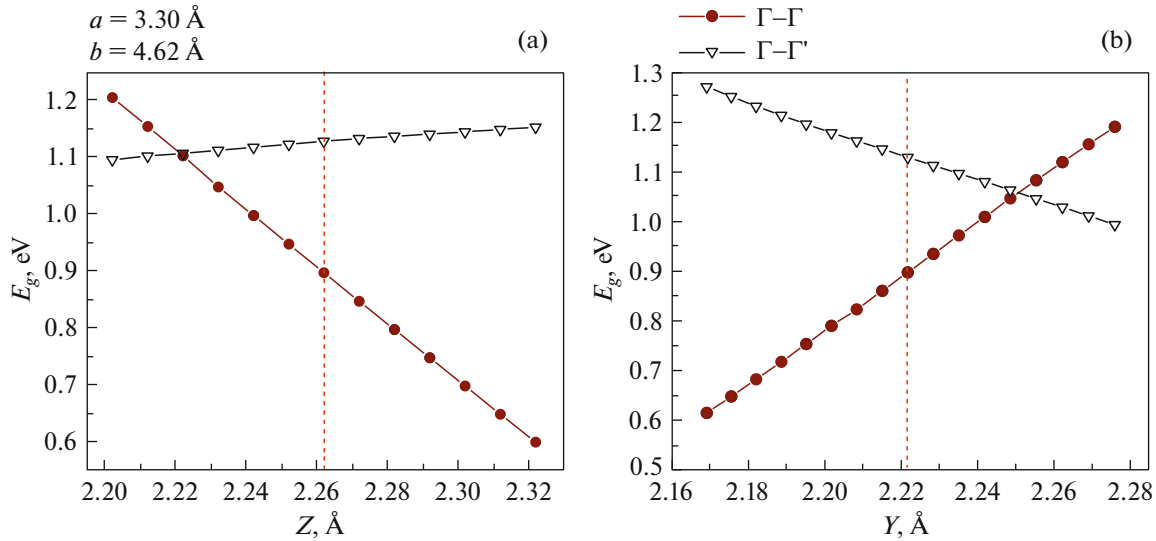


Fig. 4. Changes in the magnitude and nature of electron transitions in phosphorene under the influence of deformation of its crystal lattice (a) when changing the Z parameter and (b) when changing the Z and Y parameters. The dashed line corresponds to the parameters of the unstressed lattice.

lead to an increase in the corresponding components of effective hole masses. This affects the mobility of charge carriers and other physical parameters. The position of the band peaks shifts in a similar way with a simultaneous decrease in the Z parameter and an increase in the Y parameter (Fig. 2c). In its turn, an increase in the Z parameter with a simultaneous change in the Y parameter leads to a decrease in the band gap, the semiconductor remains direct-gap semiconductor.

Figure 3 shows the total and partial densities of electronic states of phosphorene with an undeformed crystal lattice (a) and upon application of compressive and tensile stresses (b, c). The states near the Fermi level are formed due to the hybridization of the s and p states of phosphorus. The impact of stresses predominantly leads to a redistribution of the peaks of the s and p states in the conduction band; the displacement of the peaks leads to a change in the band gap: it decreases for Z tension and increases for Z compression.

The dependences of the change in the band gap of phosphorene on the direction and magnitude of the applied stresses are shown in Fig. 4. They can be extrapolated by linear polynomials such as $E_g(Z) = 12.34 - 5.06Z$ (for $\Gamma-\Gamma$ transition), $E_g(Z) = 0.053 + 0.47Z$ (for $\Gamma-\Gamma'$ transition) (Fig. 4a), $E_g(Y) = -11.16 + 5.43Y$ (for $\Gamma-\Gamma$ transition), and $E_g(Y) = 6.78 - 2.55Y$ (for $\Gamma-\Gamma'$ transition) (Fig. 4b). The data indicate that the direction of movement of charge carriers in the crystal lattice of phosphorene can be controlled by adjusting the magnitude and direction of applied stresses that change the Z and Y parameters due to the displacement of the position of the minima and max-

ima of the bands and the corresponding transformation of a direct-gap semiconductor into an indirect-gap semiconductor. This makes it possible to design new types of electronic devices.

CONCLUSIONS

The influence of deformation of the crystal lattice of phosphorene on the structure of its electronic bands is determined by computer simulation from first principles. It is found that both compressive and tensile stresses arising in semiconductor crystal lattice can lead to the transformation of such a direct-gap semiconductor into an indirect-gap semiconductor and vice versa. The determined conditions for such transitions expand the possibilities of designing new electronic devices based on the materials.

ACKNOWLEDGMENTS

We are grateful to colleagues K. Tokár and J. Brndiar for their help in performing calculations and participation in discussions of the results, as well as to Professor V. E. Borisenko for helpful remarks when writing this article.

FUNDING

This work was supported by an international grant under the scholarship program of the Slovak Academy of Sciences and a state assignment of the Republic of Belarus “Physical Materials Science, New Materials and Technologies” (Fizmattech).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Translated by I. Obrezanova