Rev. Adv. Mater. Tech. vol. 3 no 4 (2021) 19–23
DOI: 10.17586/2687-0568-2021-3-4-19-23

Lattice Design for Non-Carbon Two-Dimensional Allotropic Modifications

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Received: December 22, 2021

Abstract. In this article, an approach to lattice design for two two-dimensional allotropic materials is proposed. The approach is based on the use of crystal lattices of disclinated graphene known as pseudo-graphenes. The approach is demonstrated on pseudo-graphenes G5-7v1 and G5-6-7v2 and target crystals originated from molybdenum disulfide and phosphorene. Geometry optimization done by density functional theory calculations display that the designed lattices for new materials are structurally stable, which means that they could be synthesized and that the new approach could successfully be used to produce lattice designs for novel two-dimensional allotropic materials.

1. INTRODUCTION

Carbon is able to form many allotropes — solids from the same element, but different in structure. Depending on their crystal structure, these allotropes can exhibit different behavior of electrons on the outer electron shell responsible for the interaction between carbon atoms [1]. Graphene is a two-dimensional carbon crystal with a hexagonal lattice. It has unusual electronic properties [2], high thermal conductivity [3] and a unique set of mechanical characteristics [4]. Its successful synthesis [5] attracted much attention and marked an active growth of interest in the study of two-dimensional crystals.

In addition to graphene, the family of two-dimensional crystals includes such representatives as molybdenum disulfide (MoS_2) and phosphorene. Both of these materials have interesting properties [6] and are promising candidates for use in optics [7], electronics [8] and other fields [9].

The physical and mechanical properties of two-dimensional materials can be controlled by external influences: mechanical, electrical, magnetic and/or by changing the local crystalline perfection of the crystal lattice [10–12]. Crystal lattice defects, in turn, change the mechanical properties (which is similar to the effects observed in ordinary three-dimensional crystals [10]), while at the same time contributing to a change in the electrical [11] and thermal conductivity of these crystals [12]. Nowadays, it is well established that any structural defect in graphene can be considered as a disclination or group of disclinations [13,14]. While there exist a plenty of studies regarding the influence of periodic disclination ensembles on graphene (new materials called pseudo-graphenes [14,15] are modelled and their characteristics are predicted [16]) there is a point of study where much less investigation is made. That is, the research on periodic defect influence on crystal parameters of single-layer two-dimensional non-carbon materials [17] such as, for example, molybdenum disulfide [18] or phosphorene [19].

In most cases, the density functional theory [16] is used to perform ab-initio calculation of two-dimensional crystals and pseudo-graphenes. This method is based on the fact that the most important properties of a system of interacting particles can be expressed using

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the electron density functional. We perform our calculations in Quantum Espresso [20] software package. In addition, various types of functionals are used for calculations. We, for instance, use Perdew-Burke-Ernzerhof one [21].

Our global research efforts pursue modeling of various characteristics of new non-carbon two-dimensional materials with periodic distributions of defects. In this article we propose a new approach to lattice design for these materials. The approach is based on the use of crystal lattices of disclinated graphene known as pseudo-graphenes. As the example for this article, lattices of crystals G5-7v1 and G5-6-7v2 will be used to model new materials originated from MoS_2 and phosphorene.

2. BACKGROUND

Fig. 1 and Fig. 2 demonstrate the initial lattice structures for pseudo-graphene crystals G5-7v1 and G5-6-7v2, respectively (for details see Ref. [15]). They are two low-energy pseudo-graphenes with energies of 0.37 and 0.28 eV/atom, respectively. Their crystal lattice is formed by embedding negative (7-member rings) and positive (5-member rings) wedge disclinations with a strength of $\omega = \pm 60°$ into the graphene lattice. The G5-6-7v2 crystal has lattice parameters equal to $a = 8.22$ Å and $b = 6.48$ Å, in which stresses from disclinations lead predominantly to distortion of defect-free hexagonal rings. The G5-7v1 crystal has lattice parameters equal to $a = 7.38$ Å and $b = 5.81$ Å, in which defect-free graphene rings are completely absent. These atomic configurations will serve as a basis for future lattice designs on new materials.

3. APPROACH TO MODELLING

To perform the lattice design for disclinated MoS_2 and phosphorene, data on new materials must be prepared. This includes coordinates of atoms for a new crystal lattice. Defect-free MoS_2 and phosphorene share the same crystal lattices as graphene — hexagonal one. This means that we can transfer the defective structure of pseudo-graphenes to the hexagonal lattice of other materials (the before-mentioned MoS_2 and phosphorene). It was decided to pick crystal lattice coordinates of two pseudo-graphene crystals — G5-7v1 and G5-6-7v2 to form new lattice designs for crystals based on MoS_2 and phosphorene.

For coordinate data to be adapted to a new crystal type, several steps are to be made. The first thing we should do is to pick coordinates of atoms that represent the crystal unit cell. A unit cell is enough for the

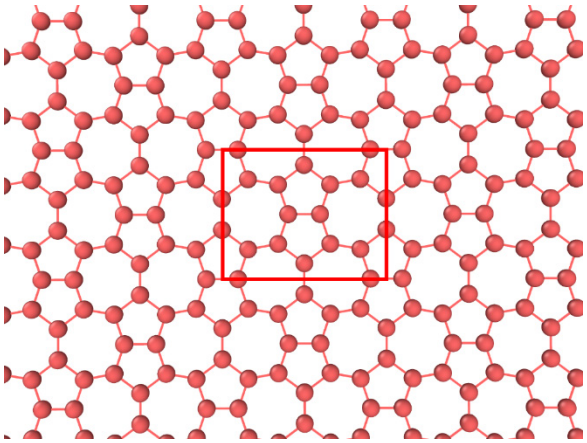

Fig. 1. Lattice structure for pseudo-graphene crystal G5-7v1. Rectangle area displays lattice basis.

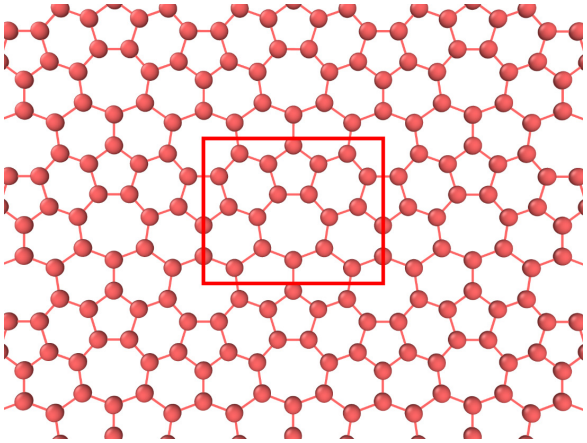

Fig. 2. Lattice structure for pseudo-graphene crystal G5-6-7v2. Rectangle area displays lattice basis.

method, as we will translate it to form a new crystal structure for non-carbon crystals. For every atom in the selected unit cell, we should decide on required transformations. As this is a computer experiment, we decided to introduce three per-atomic transformations:

– Element assignment. As the original unit cell is processed as an array of coordinates, we can assign a corresponding element to each coordinate. This is required if we need to adapt lattice to materials composed of several atom types.

– Coordinate shift. For a selected atom in the cell, we can perform coordinate shift by three axes, if required. In this study, we only perform a Z axis shift for several atoms in the original lattice. This is done to reproduce "multilayer" structure of phosphorene, molybdenum disulfide and other similar crystals.

– Atomic replication. For a selected atom in the cell, we can create a "clone" and perform the same number of transformations. This, as well, is used to recreate specifics of target crystal structure.

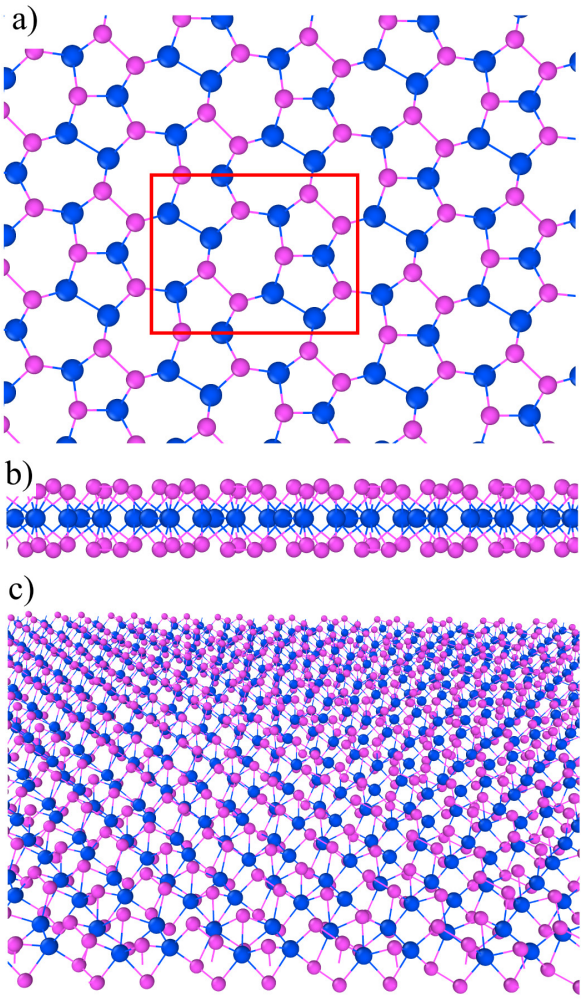

Fig. 3. Lattice structure for MoS_2 allotrope based on the lattice of pseudo-graphene crystal G5-7v1. a) Plane view, rectangle area displays lattice basis; b) side view; c) 3D view. S atoms – pink, Mo atoms – blue.

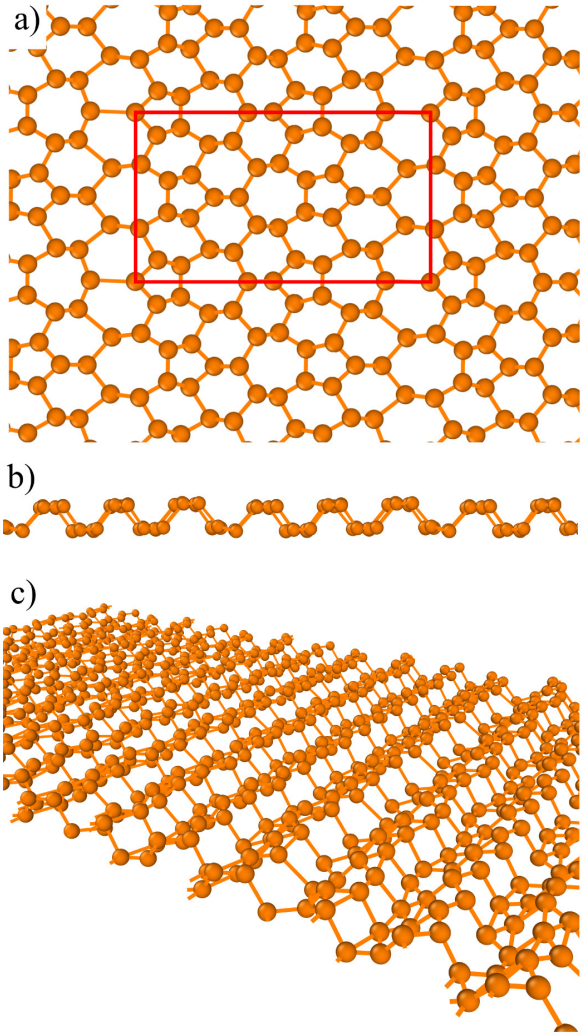

Fig. 4. Lattice structure for phosphorene allotrope based on lattice of pseudo-graphene crystal G5-6-7v2. a) Plane view, rectangle area displays lattice basis; b) side view indicating two-layer phosphorene structure; c) 3D view.

Next, we should scale coordinate data according to the difference of lattice parameters between the defect-free graphene crystal and target non-carbon defect-free crystal. As the example for this article, we will operate on graphene to molybdenum disulfide lattice adaptation. In this case, lattice parameter for graphene is 2.46 Å and for MoS_2 it is 3.16 Å. The proportion between the two is 3.16/2.46 = 1.2846, which is the desired scale for X and Y coordinate.

Our last step includes the scaling of a new unit cell and simulation box, which will result in an array of coordinates ready to be used in various calculation packages.

4. RESULTS

As a result of modeling new allotropic modifications of two-dimensional crystals of molybdenum disulfide and phosphorene, we obtained description of crystal lattices (appearance and their atoms coordinates) for each crystal. For this 'raw' data, we have performed crystal lattice geometry optimization.

In Fig. 3 we present the atomic structure for a new two-dimensional disclinated MoS_2 allotrope crystal based on transformed lattice after geometry optimization for pseudo-graphene crystal G5-7v1. Crystal lattice for disclinated MoS_2 has parameters of a = 9.87 Å and b = 7.54 Å.

In Fig. 4 we can observe the lattice for a new two-dimensional phosphorene allotropic modification based on transformed lattice after geometry optimization for G5-6-7v2. It possesses lattice parameters a = 21.55 Å and b = 12.39 Å. It should be noted that the unit cell of phosphorene has twice as many atoms as the unit cell of pseudo-graphene crystal. The choice of such a unit cell is due to the two-level structure of

phosphorene and the need to comply with periodic boundary conditions at the cell boundaries for modeling an infinite crystal.

The results of DFT calculations confirm that both materials have a stable crystal lattice, which in theory confirms the possibility of material synthesis. To conclude our study, we will name these new materials following our classification on materials given in Ref. [13]. Thus, we name the MoS_2 allotrope based on G5-7v1 as [MoS_2]5-7v1 and the phosphorene allotrope based on G5-6-7v2 as [Ph]5-6-7v2.

It is important to mention that our approach to design of crystal lattices with defects using pseudo-graphene lattice data as a basis has proven to be a valid method. This method allows one to model a "family" of two-dimensional materials sharing the same crystal lattice structure at a faster rate, than modelling from zero. As the result of our study shows, it is likely that most material lattices modelled this way are expected to be stable and thus be able to be registered as a new theoretical material.

In the future, it is proposed to conduct the following studies:

– Calculate other characteristics of newly discovered materials using the molecular dynamics method and density functional theory: it is planned to study their band structure, mechanical properties of these crystals and other characteristics.

– Use our approach to design even more non-carbon materials of the same lattice structure family, and have them analyzed; to use other lattice designs in our studies.

5. SUMMARY AND CONCLUSIONS

Using lattice simulation data of already researched pseudo-graphene crystals, lattice designs for MoS_2 and phosphorene were compiled. Based on the obtained data, initial analysis was carried out using the density functional theory. The data obtained as a result of geometry optimization shows that the designed materials are stable thus proving the concept of using a pseudo-graphene crystal lattice data as a base for design of similar two-dimensional materials. It is proposed in the future to apply our lattice modeling method to other crystal lattices as well as to carry out calculations of their physical and mechanical properties.

ACKNOWLEDGEMENTS

Fruitful discussions with Prof. A.E. Romanov and Prof. A.L. Kolesnikova are kindly acknowledged. The work was supported by Russian Science Foundation research project 19-19-00617.

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