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New compounds of boron nitride with atoms in the $sp+sp^2$ hybridized state formed on the basis of the BN-L_{4-8} layer

Dmitry S. Ryashentsev, Anna K. Kudryavtseva

Chelyabinsk State University, https://www.csu.ru/

Chelyabinsk 454001, Russian Federation

E-mail: ryashentsev_dmitry@mail.ru, tsipyshevaanna@yandex.ru

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Abstract: **The density functional theory (DFT) method was used to determine the crystal structures and electronic properties of new layered polymorphic varieties of boron nitride with a graphyne-like structure. The structures of new graphyne-like monolayers consist of boron and nitrogen atoms in the sp- and sp^2-hybridized state and were model-built from a layer of graphene-like boron nitride BN-L_{4-8} by partial replacement of atoms in the three-coordinated (sp^2-hybridized) state by atoms in the two-coordinated state (sp-hybridized). As a result of theoretical analysis, the possibility of the existence of seven $sp+sp^2$ new structures of boron nitride was established: one α-type, three β-types and three γ-types, differing in the proportion of atoms in the sp-hybridized state and their spatial arrangement. However, two of the three structural varieties with a minimum content of atoms in the sp-hybridized state (γ-type) turned out to be unstable and, in the process of geometric optimization, were transformed into structures of graphene-like layers of boron nitride. The structure of the BN-L_{4-8}-γ2 layer passed into the structure of the original graphene-like layer BN-L_{4-8}, while the structure of the BN-L_{4-8}-γ3 layer passed into the structure of the graphene-like layer BN-L_{4-6-8}, where there are no atoms in the sp-hybridized state. The sublimation energies of the new polymorphic varieties range from 16.23 eV/(BN) to 16.70 eV/(BN). The band gap varies from 3.777 eV to 3.878 eV.**

Keywords: **polymorphism, boron nitride, crystal structure, ab initio calculations, electronic properties**

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1. INTRODUCTION

Boron nitride compounds are isoelectronic and isostructural analogues of carbon compounds, and their crystal structure can be similar to that of graphite and diamond [1–2]. Theoretically predicted hybrid carbon materials, consisting of atoms with different hybridization of electron orbitals. The most interesting are

sp+sp^2 carbon materials, consisting of carbon atoms in two- and three-coordinated states, which were called graphynes [3–6]. Boron and nitrogen atoms in BN, as well as carbon atoms in carbon materials, can be in various sp, sp^2, or sp^3 hybridized states [7–9]. Therefore, the existence of hybrid sp+sp^2 compounds of boron nitride, similar to graphyne compounds, consisting of carbon atoms is theoretically possible [10–11]. The structure of BN-graphyne compounds can theoretically be built from three main polymorphic varieties of graphene-like boron nitride: BN-L_6; BN-$L_{4\text{-}8}$ and BN-$L_{4\text{-}6\text{-}12}$ [12,13], by partial replacement of atoms in the three-coordinate state with atoms in the two-coordinate state. Earlier, in [14,15], the structure and electronic properties of a number of new polymorphic varieties of boron nitride with a graphyne-like layer structure, formed on the basis of hexagonal boron nitride BN-L_6, were theoretically studied. Polymorphic varieties of such hybrid compounds differ in the ratio of atoms in different hybridized states, the degree of deformation of their structure, and the value of the band gap, as a result of which their properties may differ. In this article, the structure and electronic properties of new polymorphic layered varieties of boron nitride with a graphyne-like structure, modeled from a BN-$L_{4\text{-}8}$ graphene-like layer, are theoretically studied.

2. MATERIALS AND METHODS

As the initial structures for modeling the graphyne-like layers of boron nitride, we took the graphyne layers described in [5,6]. A number of new structural varieties of graphyne-like boron nitride can be obtained by considering the gradual transformation of the structure of graphene-like boron nitride BN-$L_{4\text{-}8}$, in which all atoms are in the state of sp^2 hybridization to graphyne-like (sp+sp^2), where the number of atoms in the sp-hybridized state maximum. Depending on the structure, the graphyne-like layers can be divided into three groups (α, β and γ), differing in the proportion of atoms in the sp-hybridized state. To construct an α-graphyne-like layer, it is necessary to replace all three bonds of a three-coordinated atom with two-coordinate ones, for a β-graphyne-like layer, two of the three bonds must be replaced, and to construct a γ-graphyne-like layer, one bond must be replaced. The analysis of graphyne-like boron nitride compounds showed that it is possible to build seven sp+sp^2 new boron nitride structures: one α-type, three β-types, and three γ-types, differing in the proportion of atoms in the sp-hybridized state and their spatial arrangement. Model construction was performed using the Quantum ESPRESSO software package [16]. The density functional theory method [17] in the generalized gradient approximation [18] was used to calculate the structures of three-dimensional crystals consisting of stacks of graphyne-like layers, the distance between which was 10 Å to exclude the influence of neighboring layers in the stacks. The calculations were carried out for k-point grids: 12×12×12, the cutoff energy on the basis of plane waves was 70 Rydbergs at a temperature of 0.01 K. The lengths of the elementary translation vectors (a, b), the lengths of interatomic bonds (Å) were determined as structural parameters and the angles between them (°). To determine the number of structural positions, the value of the ring Wells parameter (Rng) was determined; to determine the stability of the structures, the deformation parameter (Def) and sublimation energy (E_{sub}) were calculated. From the plots of the band structure and densities of electronic states, the numerical values of the band gap were determined.

3. RESULTS AND DISCUSSION

The density functional theory (DFT) method in the generalized gradient approximation (GGA) was used to perform geometric optimization

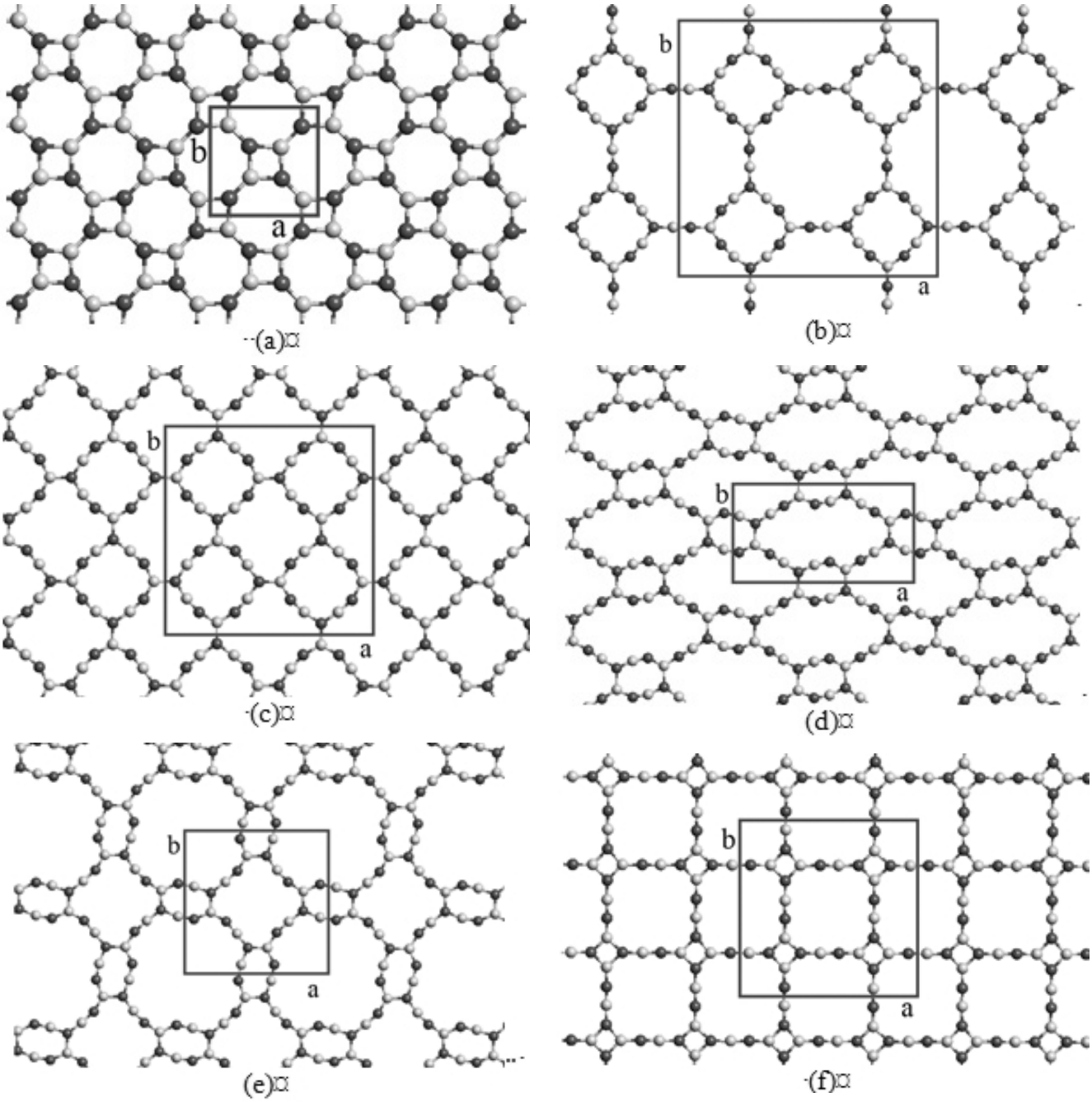

Fig. 1. *Geometrically optimized layer structures and unit cells of polymorphic varieties of boron nitride as a result of DFT-GGA calculations: (a) BN-L_{4-8}; (b) BN-L_{4-8}-a1; (c) BN-L_{4-8}-β1; (d) BN-L_{4-8}-β2; (e) BN-L_{4-8}-β3; (f) BN-L_{4-8}-γ1.*

of seven model-built layers of boron nitride with a grahyne-like structure. As a result of the performed calculations, the geometrically optimized structures of five new graphyne-like layers of boron nitride were determined. Monolayers with the smallest number of atoms in the sp-hybridized state BN-L_{4-8}-γ2 and BN-L_{4-8}-γ3 turned out to be unstable; in the process of geometric optimization, their structure was transformed into graphene-like compounds of boron nitride BN-L_{4-6-8} and BN-L_{4-8}, their structure was not considered further. The remaining five layers: BN-L_{4-8}-α1, BN-L_{4-8}-β1, BN-L_{4-8}-β2, BN-L_{4-8}-β3 and BN-L_{4-8}-γ1 have a stable structure, and their images are shown in **Fig. 1**. This figure shows images of a layer of graphene-like boron nitride BN-L_{4-8}, on the basis of which polymorphic varieties of graphyne-like

Table 1

Properties and structural parameters of polymorphic varieties of boron nitride with a graphyne-like structure

Laier	BN-L_6	BN-L_{4-8}	BN-L_{4-8}-α1	BN-L_{4-8}-β1	BN-L_{4-8}-β2	BN-L_{4-8}-β3	BN-L_{4-8}-γ1
Crystal system	Hex	Tetr	Tetr	Tetr	Rhomb	Tetr	Tetr
a, Å	2.512	4.942	19.689	14.307	14.868	11.096	12.286
b, Å					6.996		
c, Å	10.000	10.000	10.000	10.000	10.000	10.000	10.000
β, °	120	90	90	90	90	90	90
Rng_I	63	4182	242121	122161	20281	24116181	16241
Rng_{II}	-	-	242	161121	202	24181	162
N, atom	2	8	64	48	24	24	32
ρ, g/sm^2	0.754	0.675	0.3402	0.4832	0.4754	0.4017	0.4368
Def, °	0.325	50.55	14.04	22.73	39.79	27.62	60.00
E_{total}, eV/(el.c.)	-353.43	-1410.64	-11248.80	-8443.13	-4220.88	-4220.39	-5631.84
E_{total}, eV/(BN)	-353.43	-352.66	-351.52	-351.80	-351.74	-351.70	-351.99
E_{sub}, eV/(BN)	18.14	17.36	16.23	16.51	16.45	16.41	16.70
Δ, eV	4.686	3.894	3.878	3.877	3.853	3.868	3.777

boron nitride and their structures were built, and elementary cells were identified. In the BN-L_{4-8}-α1, BN-L_{4-8}-β1, BN-L_{4-8}-β3 and BN-L_{4-8}-γ1 layers, the unit cells belong to the tetragonal crystal system, which contain from 24 to 64 atoms (**Table 1**). The lengths of elementary translation vectors ($a = b$) are in the range from 11.096Å, observed for the BN-L_{4-8}-β3 layer, to 19.689Å, for the BN-L_{4-8}-α1 layer. The unit cell of the BN-L_{4-8}-β2 layer belongs to the rhombic crystal system, which contains 24 atoms. The lengths of elementary translation vectors are 14.868Å and 6.996Å.

In layers BN-L_{4-8}-α1, BN-L_{4-8}-β1 and BN-L_{4-8}-γ1 fragments of linear chains turned out to be straight, while in layers BN-L_{4-8}-β2 and BN-L_{4-8}-β3 - they turned out to be curved. Due to the fact that the graphyne-like layers of boron nitride are formed by atoms with different contents of *sp*- and *sp*^{2}-hybridized bonds, the structure of such layers will be characterized by two different structural positions, which are numerically expressed by the value of the Wells ring parameter (Rng). The first structural position is atoms in the *sp*^{2}-hybridized state, characterized by three bond lengths: L_1, L_2, L_3, the values of which are in the range from 1.370Å (BN-L_{4-8}-γ1) to 1.546Å (BN-L_{4-8}-β2). In addition, the first structural position is characterized by the values of three angles between bonds: φ_{1-2}, φ_{1-3} and φ_{2-3}, the values of which vary from 86.27° to 136.86° (BN-L_{4-8}-γ1).

Table 2

Interatomic bond lengths and angles between them in graphyne-like BN layers

Structure	Atom	L_1, Å	L_2, Å	L_3, Å	L_4, Å	φ_{1-2}, °	φ_{1-3}, °	φ_{2-3}, °	φ_{3-4}, °
BN-L_{4-8}	B	1.426	1.416	1.421	-	133.47	136.25	90.28	-
	N	1.410	1.387	1.403	-	135.42	134.58	90.01	-
BN-L_{4-8}-α1	B	1.421	1.435	1.436	1.261	122.15	121.89	115.97	179.52
	N	1.414	1.427	1.427	1.261	124.26	125.15	110.59	179.30
BN-L_{4-8}-β1	B	1.478	1.413	1.412	1.271	119.27	119.40	121.33	171.62
	N	1.478	1.410	1.411	1.271	123.81	124.02	112.18	161.24
BN-L_{4-8}- β2	B	1.397	1.414	1.546	1.279	128.43	113.84	117.73	167.39
	N	1.397	1.407	1.545	1.279	128.33	111.21	120.46	147.48
BN-L_{4-8}- β3	B	1.398	1.421	1.530	1.273	126.32	112.79	120.90	163.38
	N	1.398	1.412	1.530	1.273	127.49	110.41	122.11	175.00
BN-L_{4-8}-γ1	B	1.370	1.499	1.499	1.282	133.14	133.14	93.73	180.00
	N	1.372	1.499	1.499	1.282	136.86	136.86	86.27	180.00

The lengths of interatomic distances and the angles between them are given in **Table 2.** The second structural position is atoms in the *sp*-hybridized state, which is characterized by two bond lengths (L_3 and L_4). The L_3 bond connects the sp^2- and *sp*-hybridized atoms and is common to two structural positions. The interatomic bond L_4 characterizes the distance between atoms in a fragment of a linear chain. It is the shortest and its value ranges from 1.261Å (BN-$L_{4\text{-}8}$-α1) to 1.282Å (BN-$L_{4\text{-}8}$-γ1). Also, the second structural position is characterized by

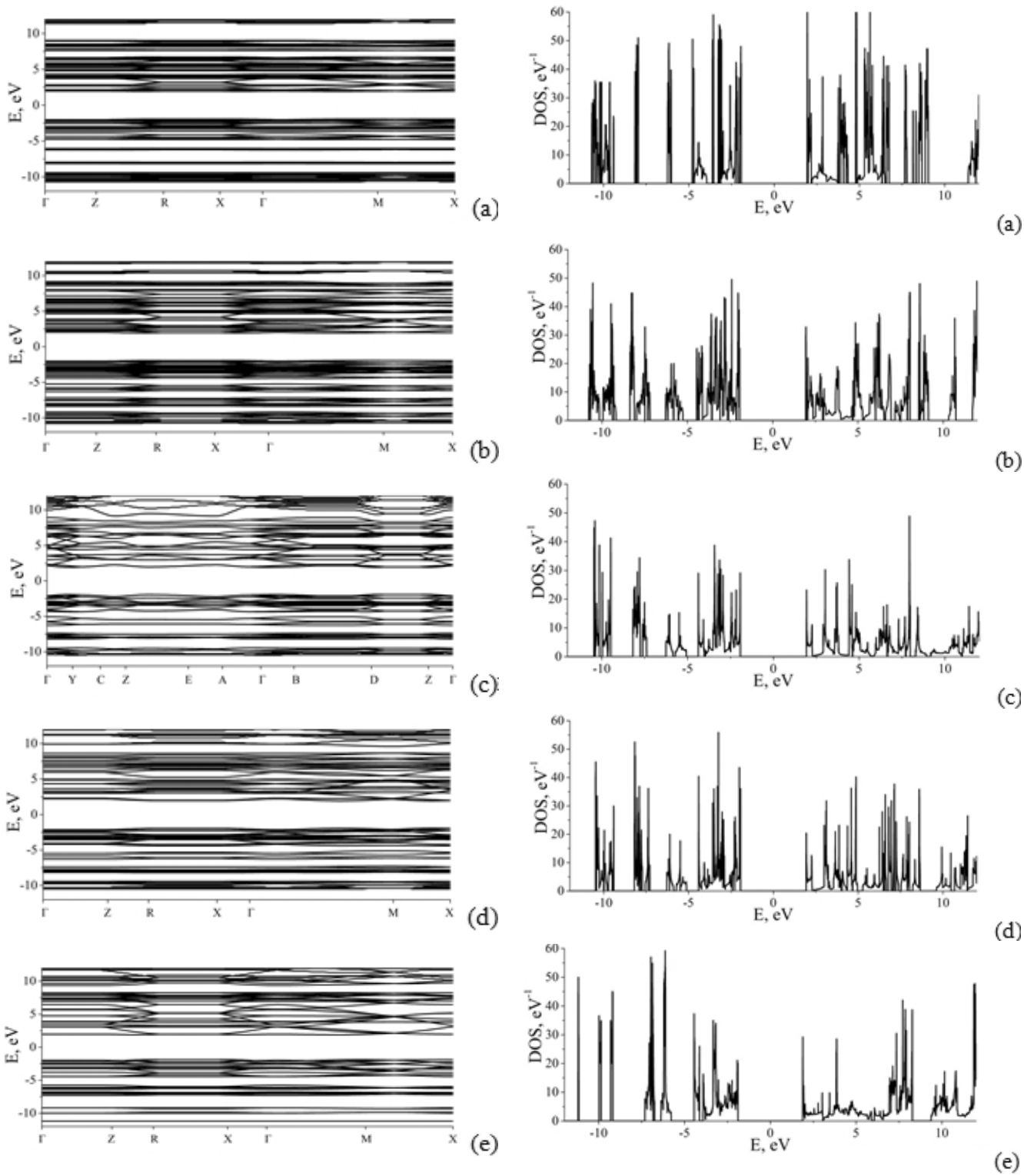

Fig. 2. *The band structure and density of electronic states of new layered BN polymorphs with a graphyne-like structure formed on the basis of the BN-$L_{4\text{-}8}$ layer: (a) BN-$L_{4\text{-}8}$-a1; (b) BN-$L_{4\text{-}8}$-β1; (c) BN-$L_{4\text{-}8}$-β2; (d) BN-$L_{4\text{-}8}$-β3; (e) BN-$L_{4\text{-}8}$-γ1.*

one value of the angle between the bonds L_3 and L_4 ($\varphi_{3\text{-}4}$), the values of which are in the range from 147.48° (BN-$L_{4\text{-}8}$-β2) to 180.00° (BN-$L_{4\text{-}8}$-γ1). Apparently, the differences in the lengths of interatomic bonds are explained by the different electron density in the interatomic space. Thus, the maximum electron density is observed in the L_4 bond.

The minimum layer density is observed for the layer with the maximum number of atoms in the *sp*-hybridized state, BN-$L_{4\text{-}8}$-α1, and is 0.3402 g/cm^2. The maximum layer density is observed for the BN-$L_{4\text{-}8}$-β1 layer and is 0.4832 g/cm^2, which is less than the calculated value for the hexagonal boron nitride (0.754 g/cm^2) and graphene-like BN-$L_{4\text{-}8}$ (0.675 g/cm^2) layer.

To assess the degree of deformation of the layer structure, the values of the deformation parameter were calculated (Table 1), which was determined as the sum of the modules of the angle differences between the bonds and the value of the angle of 120° in an ideal hexagonal structure. A comparative analysis of the numerical values of the deformation parameters of new boron nitride polymorphs with a graphyne-like structure showed that the values of this parameter are minimal for the BN-$L_{4\text{-}8}$-α1 layer and amount to 14.04°, the maximum value of the parameter is observed for the BN-$L_{4\text{-}8}$-γ1 layer (60.00°), which indicates strong deformations due to quadrangular fragments in the layer structure. The sublimation energy (E_{sub}) was calculated as the stability parameter of the structure, which was determined as the difference between the total energy per BN molecular group and the energy of isolated nitrogen and boron atoms. The minimum value of the sublimation energy is observed for the BN-$L_{4\text{-}8}$-α1 layer with the maximum number of atoms in the *sp*-hybridized state and is 16.23 eV/(BN), which indicates the low stability of this layer. The maximum sublimation energy is observed for the BN-$L_{4\text{-}8}$-γ1 polymorph with the minimum number of atoms in the *sp*-hybridized state and is 16.70 eV/(BN), which is lower than the sublimation energy of hexagonal boron nitride (18.14 eV/(BN)), the sublimation energy β-graphyne-like layers take an intermediate value.

The results of calculations of the band structure and densities of electronic states are shown in **Fig. 2.** The band gap (Δ) at the Fermi energy level is in the range from 3.777 eV to 3.878 eV, which indicates that all boron nitride polymorphs with a graphyne-like structure should exhibit semiconductor properties and it may vary depending on the features of the structure.

4. CONCLUSION

In this work, the density functional theory method using the generalized gradient approximation was used to calculate the structures, electronic and energy characteristics of polymorphic varieties of boron nitride with the structures of α-, β-, and γ-graphynes formed on the basis of graphene-like boron nitride BN-$L_{4\text{-}8}$. The highest sublimation energy is observed for the BN-$L_{4\text{-}8}$-γ1 layer and is 16.70 eV/(BN), which indicates that this layer should have a stable structure under normal conditions. In addition, there is a dependence between the values of the sublimation energy of polymorphic varieties and the fraction of atoms in the *sp*-hybridized state. As the fraction of atoms in the *sp*-hybridized state increases, the value of the sublimation energy decreases. The band gap of new polymorphic varieties ranges from 3.777 eV to 3.878 eV; therefore, all considered polymorphic varieties should exhibit semiconductor properties and can find wide practical application in creating heterostructures for nanoelectronic devices [19].

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