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ELECTRONIC PROPERTIES OF SOLID

Theoretical Study of the Influence of Vacancies on the Electronic Structure of a Hexagonal Boron Nitride Monolayer

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Abstract—The influence of boron and nitrogen vacancies and divacancies on the electronic structure of a hexagonal boron nitride *h*-BN monolayer is studied. In the presence of vacancies in the structure, the introduced states appear in the forbidden band. The position of an introduced state with respect to the upper occupied level and the lower vacant level depends on deformation. Calculations show that, depending on the defect type and the magnitude of the applied deformation, the introduced state can be both localized and not localized on atoms surrounding the defect. When the state is localized in the system, the inhomogeneous distribution of the spin density is observed, resulting in the appearance of the magnetic moment in the system.

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1. INRODUCTION

The studies of hexagonal boron nitride *h*-BN have attracted recent interest in connection with applications of this material in nonferrous metallurgy and the semiconductor industry. The chemical inertness and anti-adhesion properties with respect to metal and alloys are the main advantages of *h*-BN.

The geometrical structure of *h*-BN is similar to that of graphite and represents graphite-like networks with boron and nitrogen atoms alternating along the *z* axis [1]. The cell parameters of both compounds are similar; however, the distance between networks in the *h*-BN structure is smaller than that in graphite. As a result, the lubricating properties of the former are better [2, 3]. Hexagonal boron nitride in the pressed state has semiconductor properties and can emit luminescence in the presence of impurities [4]. Like carbon, the *h*-BN structure can form monolayers, which are similar to graphene. Such materials were produced experimentally [5, 6]. Their electronic structure was calculated in [7, 8].

It is known from the literature that the energy gap in *h*-BN varies from 3 to 7.5 eV [4, 9, 10]. However, this fact has not been explained experimentally. We can assume that such a spread in the energy gap is caused by defects, which are always present in certain amounts in a crystal. The presence of defects changes the structure stability. The authors of [6] prepared *h*-BN films containing from two to five layers and found that the rigidity of these films depended on the concentration of vacancies. Because the presence of vacancies suggests the existence of broken bonds, this can lead not only to a change in the material strength but also to the appearance of the magnetic moment in it and a change in its electron structure. Such structures are prepared on a substrate. The interaction of the material with a substrate produces stresses in the material, which cause changes in its properties. The simultaneous influence of vacancies and deformations on the properties of *h*-BN has so far not been studied. In this paper, we investigated the influence of vacancies on the electronic structure and magnetic properties of a *h*-BN monolayer and the action of stresses in the system on the structure containing vacancies.

2. OBJECTS AND EXPERIMENTAL METHODS

Calculations were performed using the density functional theory (DFT) [11] with gradient corrections [the Perde–Burke–Ernzerhof (PBE) functional] and VASP (Vienna ab initio simulation package) [12–14]. The Vanderbilt ultrasoft pseudopotential [15] was used in calculations.

An *h*-BN monolayer was simulated in the form of a supercell containing $5 \times 3 \times 1$ rectangular cells. This supercell is shown in Fig. 1. It contained five and three translation vectors of a rectangular cell along the *a* axis and *b* axis, respectively. Thus, the supercell size in a plane was 12.3×11.2 Å. Such parameters were chosen to exclude the interaction of simulated defects located in different supercells. Because the program employed for calculations assumes the use of periodic condi-

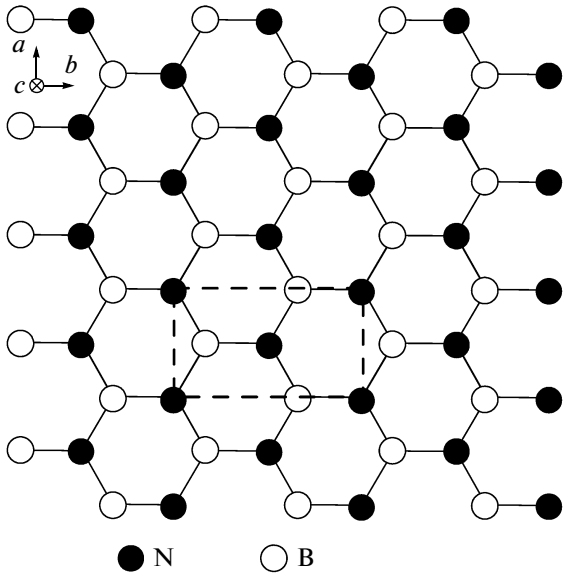

Fig. 1. Supercell of an *h*-BN monolayer; the dashed line shows a rectangular cell.

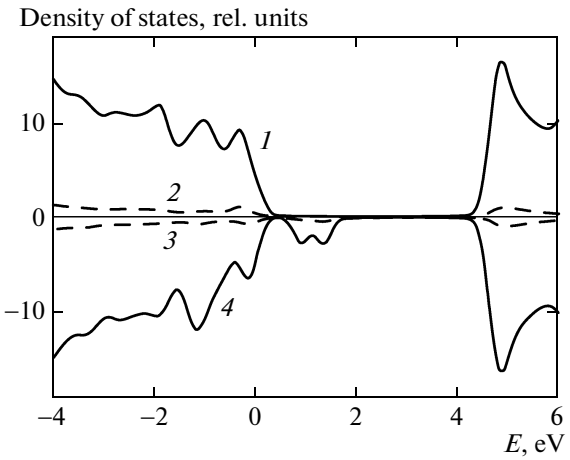

Fig. 2. Total and partial densities of states for the *h*-BN structure with a boron defect without deformations. Here and in other figures, $E = 0$ eV corresponds to the Fermi level. (*1*, *4*) The total spin density of states with the spin directed downward and upward, respectively; (*2*, *3*) the partial spin density of states of nitrogen atoms surrounding the defect with the spin directed upward and downward, respectively

tions, a vacuum gap (15 Å) was introduced to separate the monolayer along the *c* direction. The vacuum gap width was selected assuming that the *h*-BN layers located in neighboring supercells will not affect each other at this distance. The reciprocal space in the first Brillouin zone was automatically divided with geometry optimization into a network according to the Monkhorst–Pack scheme [16], the number of *k*-points along each of the directions being $2 \times 2 \times 1$. The number of *k*-points used in calculations of the density of states was $6 \times 6 \times 1$.

The properties of the electronic structure were studied by calculating the band picture and the density of states. The inhomogeneous distribution of the spin density was found by calculating the density of states for the subsystem of electrons with different directions of the spin moment (spin density of states). We constructed the spin density of states containing contributions from all atoms in the structure (from here on, the total spin densities of states) and from individual atoms of most interest, on which unpaired electrons are localized (the partial spin density of states).

We also analyzed the spatial distributions of the electron and spin densities using the Bader program [17–19] for processing the data obtained with VASP.

The influence of deformations was studied by calculating structures with the translation vector increased and decreased along one of the axes by 2 and 4%, respectively.

3. CALCULATION RESULTS

First, we calculated the electronic structure of an *h*-BN monolayer without defects and deformations. The calculation results showed that the *h*-BN monolayer is an indirect-gap dielectric with a band gap of 4.94 V, which is consistent with the band gaps in the range from 4.8 to 5.5 eV calculated in [5, 7, 8].

Then, we studied the electronic structure of the *h*-BN monolayer with a boron vacancy, a nitrogen vacancy, and a boron–nitrogen divacancy located in adjacent sites. Vacancies in the atomic *h*-BN structure change the electronic structure of the compound. In the case of a boron defect, an internal state (an introduced level) partially occupied by electrons appears in the forbidden band (i.e., electrons are located at broken nitrogen bonds surrounding the defect). In the case of a nitrogen defect, a state formed by the vacant orbitals of the boron atom is observed. If the plate contains a divacancy, two partially occupied introduced levels are observed.

Studying the behavior of the density of states upon uniaxial deformation showed that the introduced level shifted upon compression to the vacant lower level or the occupied upper level. In the case of a boron defect, the introduced level approaches the occupied upper level during compression and approaches the vacant lower level upon extension.

In the case of a nitrogen defect, the introduced level approaches the vacant lower level during compression and approaches the occupied upper level upon extension.

In the case of a divacancy, two introduced states are observed. Both these states approach the occupied upper level during compression. During extension, the state related to the vacant boron orbitals (nitrogen vacancies) shifts slightly toward the occupied upper level while the state related to the occupied electronic

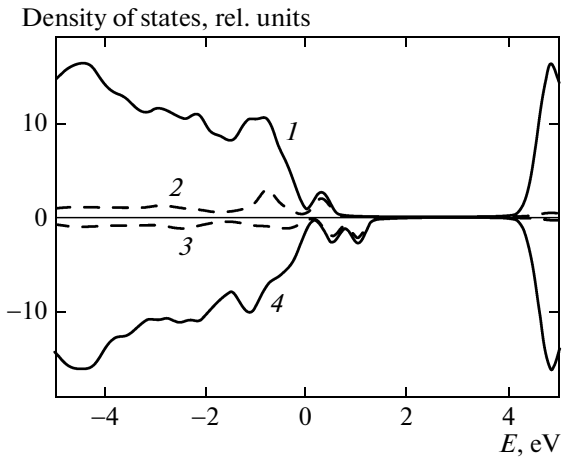

Fig. 3. Same as in Fig. 2, but upon compression by 2%.

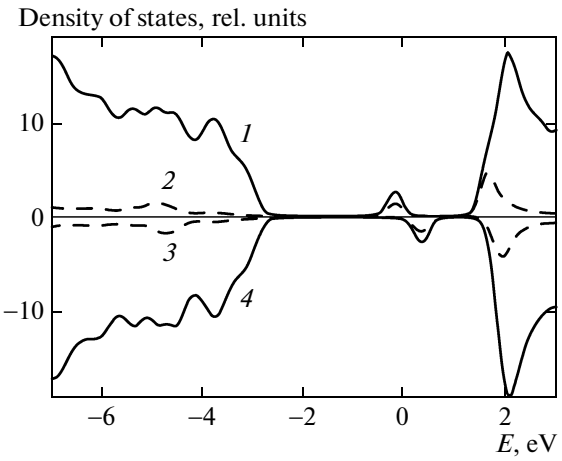

Fig. 4. Same as in Fig. 2, but for the *h*-BN structure with a nitrogen defect.

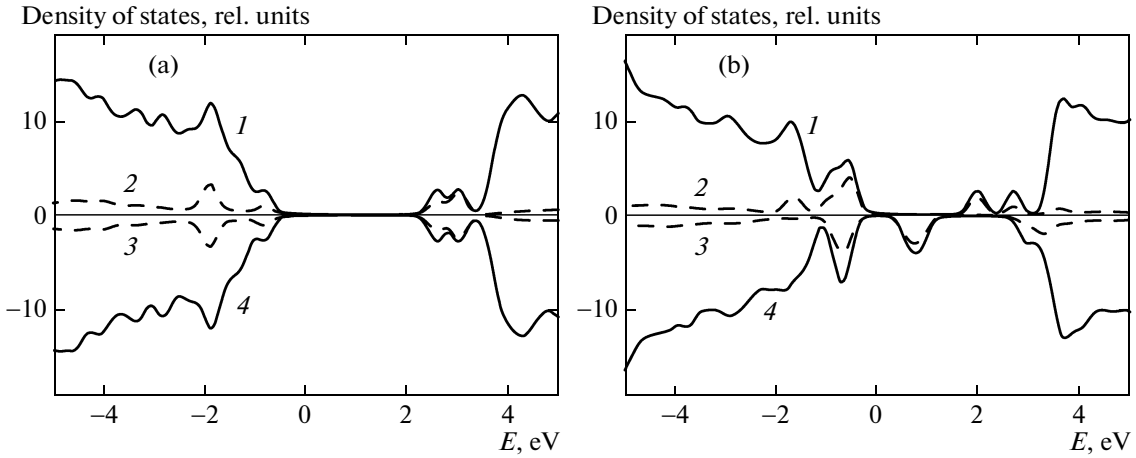

Fig. 5. Total and partial densities of states for the *h*-BN structure with a didefect upon compression by 4% (a) and extension by 4% (b). (*1*, *4*) The total spin density of states with the spin directed downward and upward, respectively; (*2*, *3*) the partial spin density of states of atoms surrounding the didefect with the spin directed upward and downward, respectively

levels approaches the vacant lower level. Thus, the spread in band gaps observed in experiments is caused by defects existing in certain amounts in the material and by the layer deformation.

In the case of a boron defect, the introduced level in a system without compression is delocalized. Figure 2 shows the total and partial spin densities of states for this case. The peaks located in the energy region between 1.3 and 1.8 eV are present only in the total spin densities of states for electrons with spins directed downward, which suggests the presence of spin density in the system and therefore the magnetic moment. However, the partial densities of states of nitrogen atoms surrounding the vacancy make small contributions to these peaks, which means that the spin density is delocalized, i.e., unpaired electrons, existing in the system are uniformly distributed in the structure. A similar situation is observed in the case of a boron vacancy during extension by 4%.

In the case of other deformations (compression by 2 and 4% or extension by 2%), the introduced level is localized at nitrogen atoms surrounding the defect. This is illustrated in Fig. 3, which shows that the peaks of the introduced state are almost completely formed by contributions from nitrogen atoms located near the vacancy. Thus, we can conclude that the magnetic moment of such a system formed by unpaired electrons will be localized only in the defect region.

For an *h*-BN system with a nitrogen defect, the introduced state is localized at the vacant orbitals of boron atoms in all cases (with and without deformation) (Fig. 4).

For an *h*-BN system with a didefect, the introduced level is delocalized in almost all cases. The density of states exhibits partial contributions from nearest

atoms surrounding the defect (Fig. 5a). However, upon extension by 4%, the introduced state is localized at atoms surrounding the didefect (Fig. 5b).

Analysis of the spin density distribution showed that in the case of a structure without vacancies and when introduced states are delocalized, the spin density is uniformly distributed over all atoms contained in a supercell. When the introduced state is localized in the defect region, the spin density is distributed inhomogeneously and the maximum of this inhomogeneous distribution is located at atoms surrounding the defect. This in turn leads to the appearance of the magnetic moment in the system. Thus, the magnetic moment in the undistorted structure appears when there is a nitrogen defect. The magnetic moment can also appear upon the compression of an *h*-BN monolayer with a boron defect by 2 and 4% or its extension by 2% and upon the extension of a monolayer with a didefect by 4%.

4. CONCLUSIONS

The study of the electronic structure of a *h*-BN monolayer with vacancies has shown that the introduced states appear in the forbidden band. The position of the introduced levels with respect to other levels depends on the structure deformation. The deformation magnitude and its type (compression or extension) affect the localization of unpaired electrons and, therefore, the characteristics of the magnetic moment of the system. Thus, we have found that the *h*-BN monolayer containing vacancies can acquire the magnetic moment whose magnitude is determined by the deformation of a plate.

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REFERENCES

1. J. H. Edgar, *Properties of Group III Nitrides* (INSPEC, London, 1994).
2. Y. Kimura, T. Wakabayashi, K. Okada, T. Wada, and H. Nishikawa, Wear **232**, 199 (1999).
3. S. Watanabe, S. Miyake, and M. Murakawa, Surf. Coat. Technol. **49**, 406 (1991).
4. N. Ooi, V. Rajan, J. Gottlieb, Y. Catherine, and J. B. Adams, Modell. Simul. Mater. Sci. Eng. **14**, 515 (2006).
5. K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, Proc. Natl. Acad. Sci. USA **102**, 10 451 (2005).
6. Xingfa Gao, Zhen Zhou, Yuliang Zhao, Shigeru Nagase, S. B. Zhang, and Zhongfang Chen, J. Phys. Chem. C **112**, 12 677 (2008).
7. Li Song, Lijie Ci, Hao Lu, P. B. Sorokin, Chuanhong Jin, Jie Ni, A. G. Kvashnin, D. G. Kvashnin, J. Lou, B. I. Yakobson, and P. M. Ajayan, Nano Lett. **10**, 3209 (2010).
8. A. J. Du Sean, C. Smith, and G. Q. Lu, Chem. Phys. Lett. **447**, 181 (2007).
9. K. Watanabe, T. Taniguchi, and H. Kanda, Nat. Mater. **3**, 404 (2004).
10. V. L. Solozhenko, A. G. Lazarenko, J.-P. Petitet, and A. V. Kanaev, J. Phys. Chem. Solids **62**, 1331 (2001).
11. W. Kohn and L. J. Sham, Phys. Rev. Sect. B **140**, 1133 (1965).
12. G. Kresse and J. Hafner, Phys. Rev. B: Condens. Matter **47**, 558 (1993).
13. G. Kresse and J. Hafner, Phys. Rev. B: Condens. Matter **48**, 13115 (1993).
14. G. Kresse and J. Hafner, Phys. Rev. **49**, 14251 (1994).
15. D. Vanderbilt, Phys. Rev. B: Condens. Matter **41**, 7892 (1990).
16. H. J. Monkhorst and J. D. Pack, Phys. Rev. B: Solid State **13**, 5188 (1976).
17. W. Tang, E. Sanville, and G. Henkelman, J. Phys.: Condens. Matter **21**, 084204 (2009).
18. E. Sanville, S. D. Kenny, R. Smith, and G. Henkelman, J. Comput. Chem. **28**, 899 (2007).
19. G. Henkelman, A. Arnaldsson, and H. Jónsson, Comput. Mater. Sci. **36**, 354 (2006).

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