Electronic and magnetic properties of doped 2D MoS_2/Ph systems

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Abstract

Doping of heterostructure made from two-dimensional crystals of molybdenum disulfide and phosphorene was theoretically modelled in order to reveal impurities modifying the electronic band structure of the system and having impact on its magnetic properties. Variants of substitution of one of the molybdenum atoms by Cr, Fe, Mn atoms, and one of the sulfur atoms by C, N, P ones in the MoS_2 layer were simulated; doping of the phosphorene layer with C, N, S atoms was considered as well. The effect of impurities on electronic and magnetic properties of the structure is determined.

Keywords: dichalcogenide, phosphorene, monolayer, heterostructure, magnetic ordering.

Introduction

Nowadays the fabrication of semiconductor devices may need a various types of band-gap engineering, and one of such ways is the creation of heterostructures employing different effects in order to manipulate the properties of origin materials. Such engineering implies combination of several materials in one structure, substitution or adsorption of different atoms, strains, etc. [1]. Stacking of two-dimensional (2D) crystals in van der Waals heterostructures opens the way to novel applications in electronics and optoelectronics. One of a trending 2D crystal is the monolayer black phosphorus, named phosphorene (Ph), and the first-principle study of strained heterobilayers constructed of phosphorene on $MoSe_2$ and WSe_2 was already presented [2]. In our work, we intend to investigate the impact of impurities on properties of MoS_2/Ph heterostructure, which is combined of two direct-gap semiconductors [3], and discover the possibilities of introducing magnetic ordering to the system.

In theoretical works it is already claimed that chemical absorption of H, B, C, N, O, and F atoms on the surface of 2D MoS_2 substrate may induce magnetic moments in the range of 1.0–2.0 μB per 4×4 supercell [4]. Mn dopants substituting Mo sites also lead to ferromagnetic coupling via a double-exchange mechanism, demonstrating the potential for a new generation of devices made from 2D semiconductors [5]. Calculations of the effect of phosphorene doping with various 3*d* elements to introduce a stable magnetic order were presented elsewhere [6], though investigations of heterostructures combined from doped layers of chalcogenides and phosphorene are still lacking. Thus, our goal is to analyze the possibility of appearance of magnetic moment in MoS_2/Ph heterostructure depending on the positions of impurity atoms and the location of vacancy defects.

Computational details

All the calculations were made within Density Functional Theory approximation with the help of Vienna ab initio simulation package (VASP) [7, 8] using the Projector Augmented Plane-Wave (PAW) method [9, 10]. Van der Waals forces were considered by means of correction of J. Klimeš [11] as optB86b-vdW optimized exchange functional. Model of MoS_2/Ph system was prepared by stacking of MoS_2 and phosphorene layers with preliminary optimized geometry as described in [12,

13, 14] (Figure 1). The atomic positions were relaxed until the forces acting on atoms became smaller than 0.01 eV/Å. Energy cutoff of 380 eV and the 17×2×1 grid for Γ-centered mesh of k-points were used. For the band structure representation, 20 k-points were chosen for each segment along the high-symmetry directions of the orthorhombic Brillouin zone. 4*p*-electronic states of molybdenum were considered as valence states.

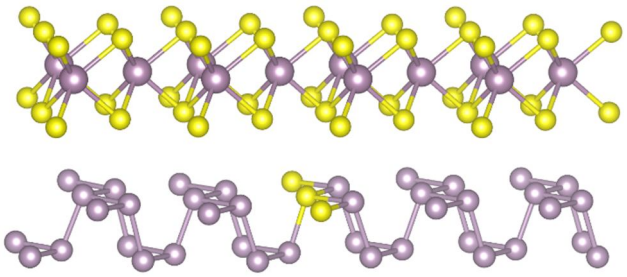

Figure 1. Crystal structure of the MoS2/Ph heterostructure with an S atom in the phosphorene (lower) layer

Results and discussion

For all configurations considered, the analysis of the total energy of the systems was performed in order to assess its stability. Substitutions were made in the MoS_2/phosphorene heterostructure as follows: in the MoS_2 layer one molybdenum atom was replaced by a chromium, iron, or manganese atom; one sulfur atom was replaced by atom of carbon, nitrogen, or phosphorus. At the same time the cases were considered with a sulfur atom adjacent to the phosphorene layer (S_1) or located closer to the vacuum layer (S_2). In the phosphorene layer one of the phosphorus atoms was replaced by carbon, nitrogen, or sulfur atom. Impurity concentrations in these cases were 0.125; 0.0625 and 0.05, respectively. It was established that all considered structures remain stable upon substitution. Then, the effect of impurities on band gap and magnetic properties of the MoS_2/Ph heterostructure was evaluated.

Analysis of spin-polarized densities of states (DOS) (Figure 2) for doped layers in ferromagnetic (FM) state reveals that non-zero spin polarization appears only when sulphur atoms are replaced by carbon ones, or molybdenum atom is replaced by manganese atom. Partial magnetic moments in the first case are 0.9 μ_B/atom (S_1 position) and 0.8 μ_B/atom (S_2 position), and 1 μ_B/atom, respectively. In the latter case the heterostructure obtains half-metallic properties with the band gap of 0.4 eV in spin-up channel and zero gap in spin-down channel. When one Mo atom is replaced by Cr and Fe ones the band gap of the structure decreases up to 0.1 eV. Structure with one P atom replaced by N atom stays semiconductor, whereas in all other cases there are states at the Fermi level.

Conclusion

Theoretical models of doped MoS_2/Ph systems were developed, where molybdenum atoms in MoS_2 layer were replaced by chromium, iron, and manganese atoms, sulfur atoms by carbon, nitrogen, or phosphorus atoms; and phosphorus atoms in the phosphorene layer were replaced by carbon, nitrogen, and sulfur atoms. It was found that all impurities considered have significant effect on the electronic structure of the system: replacing of sulfur atoms by carbon, and molybdenum atoms by manganese ones decreases the band gap of the structure up to the appearance of metallic properties. Replacing of molybdenum atoms by chromium and iron atoms decreased the band gap up to 0.1 eV. Analysis of magnetic moments and spin polarization which appear upon substitution shows possibilities of using heterostructures where sulphur atoms are

replaced by carbon ones, or molybdenum atom is replaced by manganese atom for design of new spintronic devices.

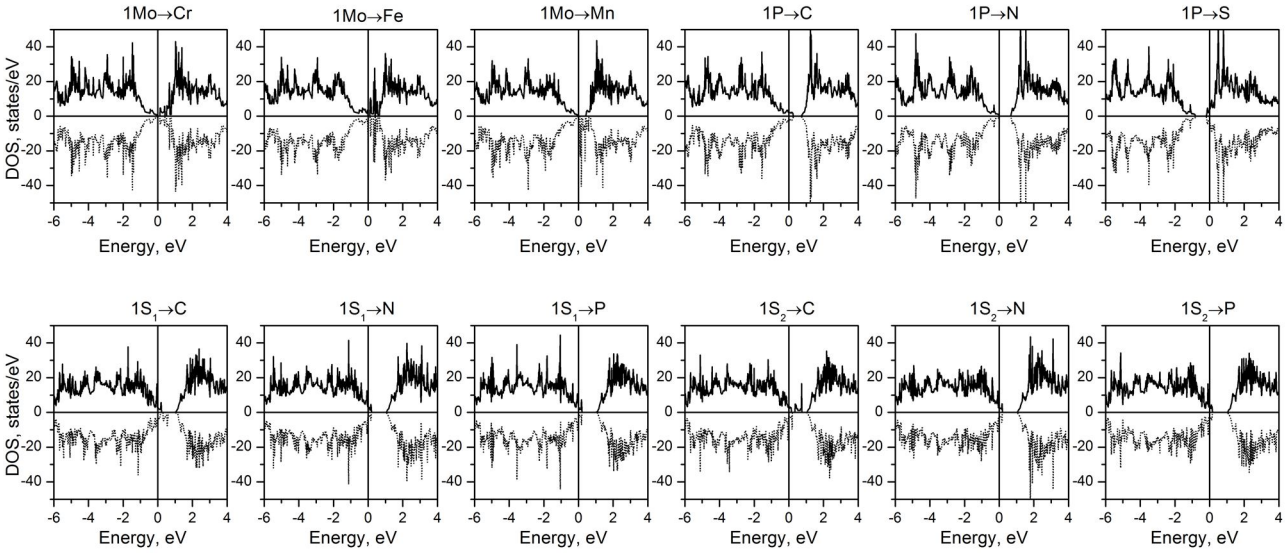

Figure 2. Densities of electronic states of MoS_2/Ph heterostructure upon substitution of Mo, P, and S atoms (FM state)

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References:

[1] A. Chaves [et al.] npj 2D Materials and Applications 29 (2020) 1-21.
[2] D. S. Koda [et al.] J. Phys. Chem. C 121 (2017) 3862−3869
[3] A. V. Krivosheeva [et al.] Lazzari Materials Today: Proceedings 54 (2022) 73–79.
[4] J. He [et al.] Appl. Phys. Lett. 96 (2010) 082504 (1–3).
[5] A. Ramasubramaniam [et al.] Physical Review B 87 (2013) 19520 (1–7).
[6] P. Kumari [et al.] Phys. Chem. Chem. Phys. 22 (2020) 5893-5901.
[7] G. Kresse [et al.] J. Comput. Mater. Sci. 6 (1996) 15–50.
[8] G. Kresse [et al.] Phys. Rev. B 54 (1996) 11169–11186.
[9] P. E. Blöchl, Phys. Rev. B: Condens. Matter Mater. Phys. 50 (1994) 17953−17979.
[10] G. Kresse [et al.] Phys. Rev. B: Condens. Matter Mater. Phys. 59 (1999) 1758−1775.
[11] J. Klimeš [et al.] Phys. Rev. B 83 (2011) 195131 1-13.
[12] A.V. Krivosheeva [et al.] Physics of the Solid State 63 (2021) 1661−1665.
[13] A.V. Krivosheeva [et al.] Int. J. Nanotechnol. 12 (2015) 654–662.
[14] A. V. Krivosheeva [et al.] Proc. IX Int. Sci. Conf. "APSSP" (2021, Minsk, Belarus) 176-180.