ELECTRONIC PROPERTIES OF QUASI-TWO-DIMENSIONAL MOLYBDENUM DISULFIDE WITH Fe, Co, AND Ni IMPURITIES

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Abstract. Possibility of molybdenum disulfide (MoS_2) manifest magnetic properties under Fe, Co, and Ni impurities condition is shown. Density of electron state and band diagram of quasi-two-dimensional structure of MoS_2 with Fe, Co, and Ni impurity clusters are presented. Calculations were carried out using VASP (Vienna *Ab initio* Simulation Package).

1. Introduction

In variety of new materials, materials with a nanoscale structure hold a special place. Two-dimensional materials have attached a great attention due to its outstanding physical phenomena occurred at the nanolevel. There is a big interest in transition-metal dichalcogenides, due to its layered structure; they have extremely anisotropic properties, and therefore an intercalation processes easy to conduct. Reduced dimensionality can sometimes lead to magnetic behavior in systems, which are not magnetic in a bulk.

Recent studies have demonstrated the important role of nanostructures in various fields of science and technology. Spin-dependent properties of nanostructures represent a particular interest for fundamental investigations as well as for practical applications. Transition metal dichalcogenide (TMD) group opens up new opportunities for advance material science: due to its chemical composition and quasi-nanometer dimension, TMDs exhibit a variety of interesting properties and offer issues for low-dimensional structures applications [1-3]. High-inert surface and low defect concentration in this type of structures allow using it in micro- and nanoelectronics where the high mobility of charge carriers gives a significant impact on output parameters of a device. Mono- or few-layered TMD are going to replace graphene in such fields as catalysis, energy storage, sensing, and microelectronic devices [1, 3, 4]. Tunable electronic structure and wide range of functional properties vary depending on transition metal and its *d*-electron count [3].

Molybdenum disulfide is a "layered" transition-metal-dichalcogenide semiconductor with an indirect band gap that has attracted considerable interest in connection with its distinctive electronic, catalytic and optical properties [4-6]. The layered structure of MoS_2 is formed by S–Mo–S sandwiches (Fig. 1) bonded together by weak Van-der-Waals forces (hexagonal unit cell parameters: $a = 3.12$ Å; $b = 3.12$ Å $c = 11.98$ Å). The two-dimensional unit MoS_2 cell has one Mo atom and two S atoms. Each of the Mo atoms is coordinated to six S atoms in a triangular prismatic form [7]. However, taking into consideration that Mo layer doesn't lie in one plane with S layer, it would be more correctly to conclude quasi-two-dimensional structure of MoS_2. Because of the weak van der Waals interactions between the sheets of sulfide atoms, MoS_2 has a low coefficient of friction, resulting in their lubricating properties. Another important property of MoS_2 is the possibility of doping it with different fragments (ions, molecules, atoms) in the van der Waals hollow between the layers.

The ability to form intercalation compounds is a key feature of any layered systems in terms of their chemical properties. It is possible to obtain high-quality single crystals (by methods of high-temperature synthesis in the gas transport agents) due to the relatively high chemical stability; so the intercalation compounds with transition metals are the best studied from a structural point of view. MoS_2 can be mechanically exfoliated using scotch tape to create 2D MoS_2 samples, similarly to graphene. The papers [4, 5] confirm the previous assumptions that molybdenum electronics can overcome the physical limitations imposed on the silicon technology in respect to such characteristics as miniaturization, power consumption, and mechanical flexibility. Thus, MoS_2 has a number of unique properties, which allow its potential application in transistors, flexible displays, and optics [4-9].
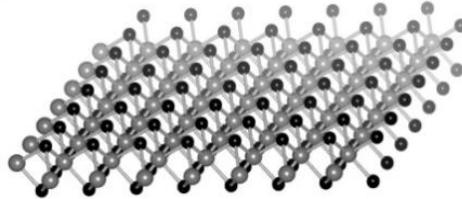

Fig. 1. Crystallographic structure of quasi-two-dimensional MoS_2.

A rather interesting problem is the investigation of nanostructured materials with impurities of magnetic metallic fragments, due to which manifestation of significant magnetic properties became possible as it was with the ternary compound $TlMeX_2$ [9] and binary nanostructures of ZnO [10, 11] and SnO_2 [12].

Nowadays a very important further step in electronic properties prediction is development of modern methods of materials simulation. Thus, further progress in understanding of physical phenomena at nanoscale level may be realized by use of *ab initio* simulations taking into account difficulties of experimental investigations of nanoobjects.

The paper presents the results of spin-dependent properties investigation of two-dimensional structure of MoS_2 , the main representative of the transition metals dichalcogenides (TMD) group, with mono- and complexes (clusters) of Fe, Co, and Ni impurities with the first-principles (*ab initio*) simulation methods.

2. Methodology

The research presented in this paper aims to investigate the electronic and magnetic properties of quasi-two-dimensional molybdenum disulfide with impurities of Fe, Co, and Ni, a well-known ferromagnetic metal. These three elements compose the Iron triad, which has very similar chemical and physical characteristics. The Iron triad elements have the ability to create a large magnetic pole due to their unpaired electrons. Moreover, they can quite easily combine with each other in the structures, and create various types of alloys [13]. The study of spin-dependent properties of two-dimensional structure of MoS_2 with Co clusters impurities was carried out by means of the software package VASP (Vienna *Ab initio* Simulation Package) [14, 15]. The interaction between ions and electrons in the simulated system is described by the Plane Augmented Waves (PAW) method. With the use of program package VASP it is possible to calculate the forces and stresses, which are used to relax atoms into their ground state. GGA-PBE pseudopotentials were applied for description of interaction between the atomic cores and electrons.

The calculations were performed using periodic conditions. Super-cell with size of $6 \times 6 \times 1$ hexagonal unit cells of MoS_2 was created in order to exclude the influence of impurities on each other. The hexagonal structure was transformed into the orthorhombic for more adequate reflection of all disturbances occurring during relaxation process. The energy

cutoff of 500 eV for the plane-wave expansion was used. Structure relaxation was carried out until atom interaction forces don't exceed 0.05 eV/Å.

3. Results and conclusion

Interatomic interactions in the MoS_2 crystal are determined by crystallographic parameters and the type of chemical bonds. The simulation was carried out using hexagonal structure MoS_2 of P_{63}/mmc (No194) space group. Modeling crystal consisting of 108 atoms was used for all impurity cluster variations. The cluster size varied from one to four impurities (Fe, Co, and Ni) atoms. All the possible configurations of impurity clusters were studied in order to investigate the influence of Co, Fe, and Ni clusters on the spin-dependent properties of MoS_2. However, the probability of substitution of sulfur atoms with doped ones' is extremely low because of a large difference in atomic radius, whereby impurity atoms only in molybdenum positions were examined.

System disturbance in the case of Fe, Co, and Ni substitution of Mo atom in a supercell was investigated. The corresponding concentration of iron triad metals dopant ranged from 0.92 % to 3.70 at %. Due to the larger atomic radii of Fe, Co, and Ni atoms, Mo and S atoms around the dopants move outward and the displacement is not isotropic. The difference between init and relaxed value of Ni-Mo bond length is the largest and equals to 0.60 Å in comparison with Fe-Mo and Co-Mo bond length which are equal to 0.09 Å and 0.46 Å, respectively. Crystallographic structure of quasi-two-dimensional MoS_2 with two Ni impurities and a charge density of corresponding views are shown in Fig. 2 and Fig. 3, respectively.
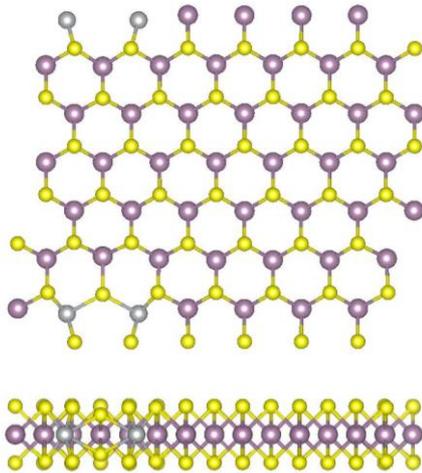

Fig. 2. Crystallographic structure of quasi-two-dimensional MoS_2 with two Ni impurities. Top and side view of the configuration.
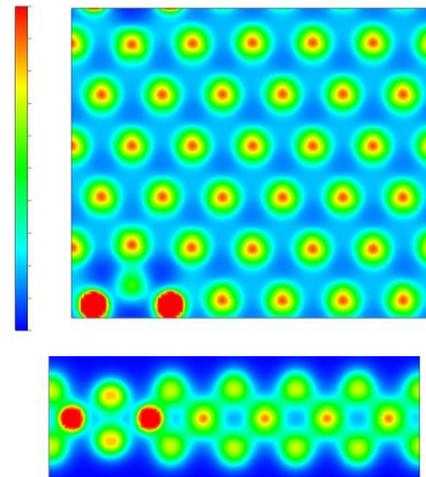
Fig. 3. Charge density of corresponding views. Top and side view of the configuration.

The results of density of electron states (DOS) and band diagram calculations for the simulated systems are shown in Figs. 4–7. The systems incorporated perfect MoS_2 quasi-two-dimensional structure and MoS_2 structure with two iron trial metal impurities. The results indicate the presence of additional energetic levels located near to a band gap midpoint. That might be caused by the ripped bonds at the surface of investigated structures. Iron metal triad impurity cluster causes a sharp narrowing of the band gap (in systems with one impurity atom), its smooth increase up to 2.02 eV (in systems with cluster consisting of two and three impurity atoms), and small decrease of band gap value (with cluster consisting of four impurity atoms) (Fig. 7a). Despite the changes in electronic properties, band diagrams

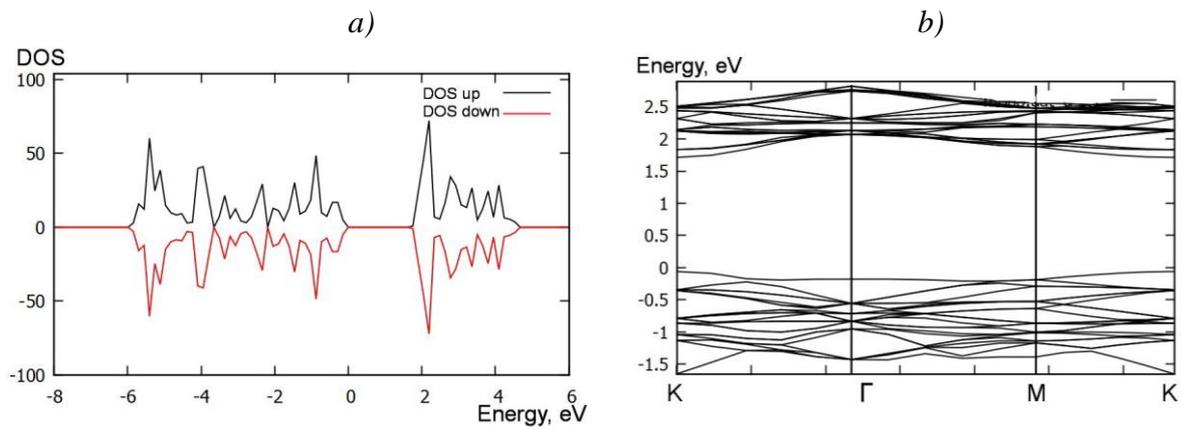confirm that most of the MoS$_2$ structures still retain direct band transition.

a)   *b)*

Fig. 4. DOS (*a*) and energy bands (*b*) of a perfect quasi-two-dimensional MoS$_2$ structure.
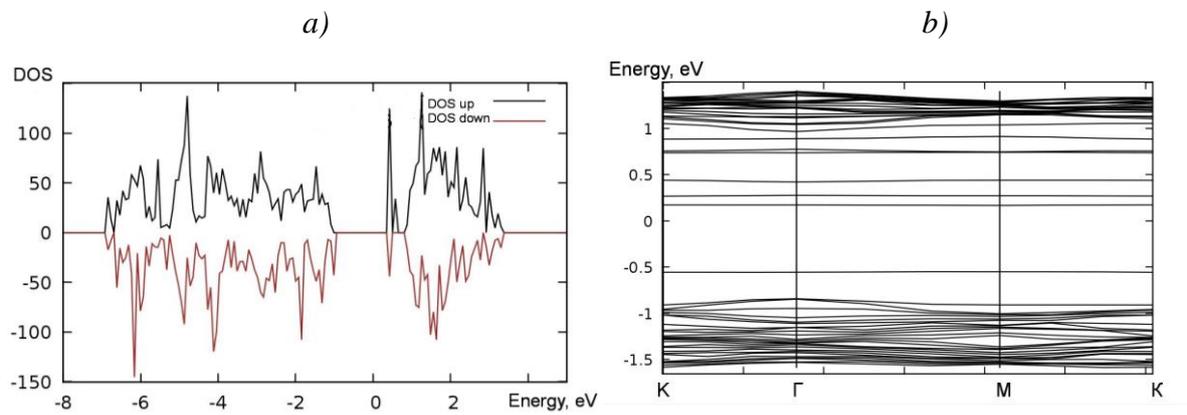
a)   *b)*

Fig. 5. DOS (*a*) and energy bands (*b*) of quasi-two-dimensional MoS$_2$ structure with two Fe-impurity clusters.

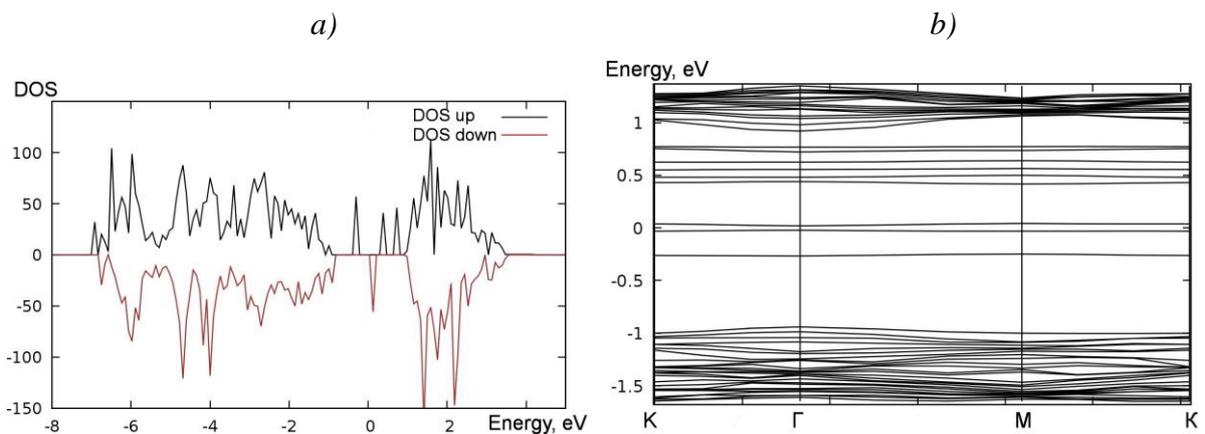*a)*   *b)*

Fig. 6. DOS (*a*) and energy bands (*b*) of quasi-two-dimensional MoS$_2$ structure with two Co-impurity clusters.
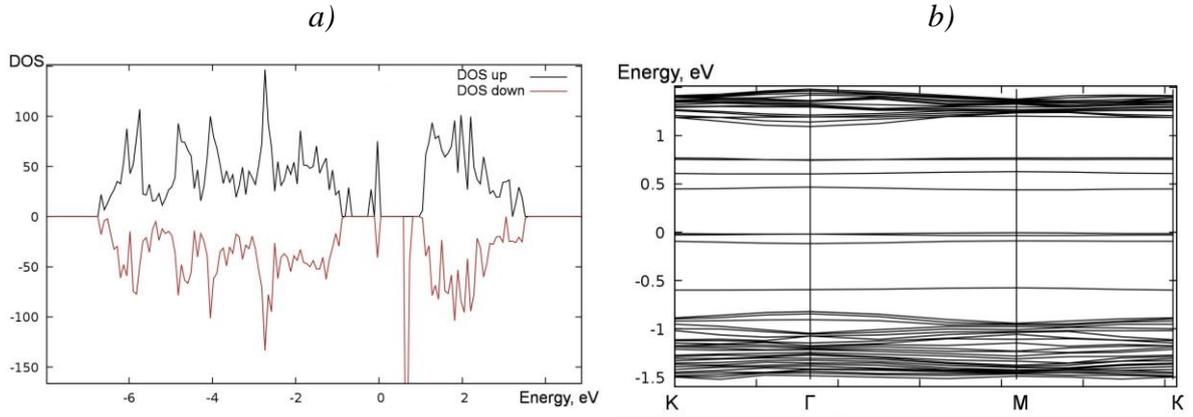
Fig. 7. DOS (*a*) and energy bands (*b*) of quasi-two-dimensional MoS$_2$ structure with two Ni-impurity clusters.

It was found that all investigated structures doped with iron triad metals exhibit magnetic properties. The behavior of magnetic properties depends on a cluster type, and that is why they significantly differ from each other (Fig. 8 *b*). However, the impurity clusters with linear configuration show the most strongly marked magnetic effect with a stable ferromagnetic phase, that's why all the presented data relate to this type of cluster.
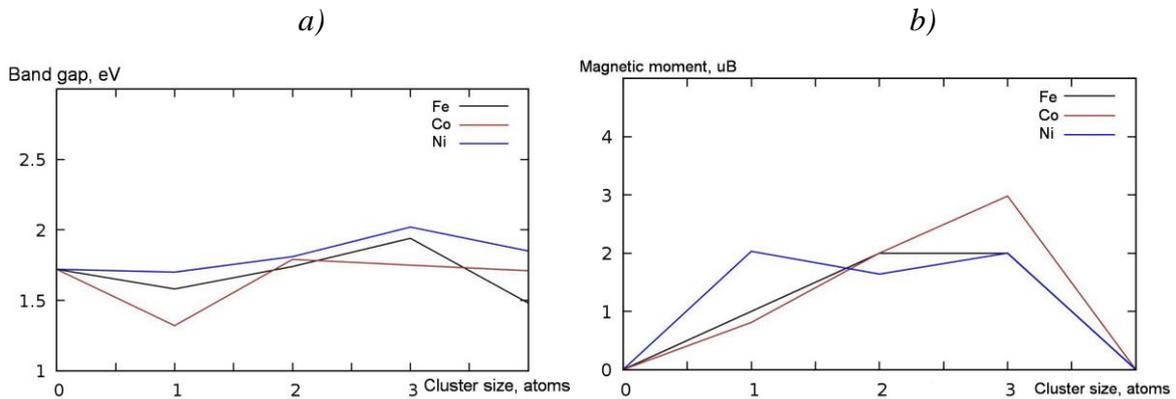

Fig. 8. Band gap value (a) and magnetic moment (b) dependencies on cluster size.

Electrons, from d-orbital of molybdenum atoms located near to impurity cluster and from d-orbital of metal dopant, make the most significant contribution to magnetic moment of the system (Fig. 9). However, the magnetic moment increases with the size of impurity cluster up to three atoms. But it was also found that there is no magnetic moment in systems with a cluster consisting of four atoms. The same behavior was observed in ZnO nanothin films doped with Fe, Co, and Mn [16-18]. Concentration dependences of magnetization of ZnO doped with Fe, Co, and Mn are nonmonotonic. The addition of first portions of dopant causes an increase of magnetization in one – three orders but further increase of dopant concentration leads to rapid decrease of magnetization. Magnetization dependencies are also different for every dopant metal [16]. One of the reasons of such behavior can be explained by the change of oxidation degree of doping atoms with the increasing of cluster size.

In all the investigated structures magnetic moment is localized near to impurity cluster. That fact suggests the possibility of control of magnetic behavior of MoS$_2$ quasi-two-dimension structure by varying the doping concentration when required in using structural elements for spintronic, micro- and nanoelectronic devices.
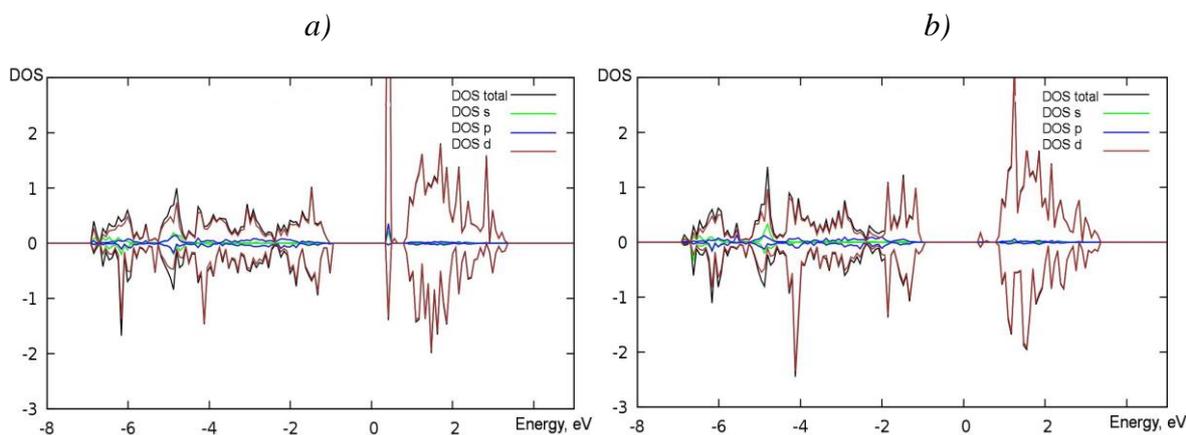
a)   *b)*

Fig. 9. Projected DOS of quasi-two-dimensional MoS$_2$ structure with two Fe-impurity clusters for Mo (*a*) and Fe (*b*) atoms.

4. Conclusions

In the framework of density functional theory using the software package VASP spin-dependent properties of quasi-two-dimensional MoS$_2$ structure with different size of Fe, Co, and Ni impurity clusters were studied. Calculations of density of electron stated and of band diagrams were done for the simulated systems; in particular the dependencies of band gap value and magnetic moment on a cluster size were obtained. A significant effect of iron triad metal impurity cluster on the electronic and magnetic properties of MoS$_2$ was found. Further research in this area will allow studying the effect of impurities on the characteristics of investigated semiconductor in detail.

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