

AB INITIO SIMULATION OF TWO-DIMENSIONAL MoS₂ WITH VACANCY CLUSTERS USING GRID TECHNOLOGIES

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Abstract. This paper contains the information about the investigation of two-dimensional MoS₂ structure with vacancy clusters within the framework of basic Grid computing approaches. Simulation results of electron density and band diagram are presented. All the calculations were performed using Vienna *Ab initio* Simulation Package (VASP) with the multiprocessor computer complex (supercomputer) SKIF K1000.

1. Introduction

The trend of modern technology is the development of new functional low-dimensional structures, linear dimensions of which are limited in one or more crystallographic directions to a certain critical value below which the physicochemical properties of the structure changes substantially in comparison to three-dimensional counterparts. Calculation and optimization of the electronic properties of such nanosystems is only possible by using first principles (*ab initio*) methods and tools, implemented on the basis of high-performance cluster computing systems. The use of latter in its turn can be significantly improved through Grid technologies. Two-dimensional materials are attractive for the application in nanoelectronic devices because of their extraordinary properties manifestation at the near atomic scales. The object of our interest is transition metal dichalcogenides (TMD) group of materials that exhibit a variety of interesting properties and offer issues for low-dimensional structures applications [1-4]. Molybdenum disulfide (MoS₂), the main representative the transition metals dichalcogenides (TMD) group, is one of such materials. The results of experimental and theoretical studies show [4-11], the MoS₂ compound is a perspective material for nanoelectronics and solar energetics, in particular, for creating a broad class of sensors, transistors, diodes and solar cells. MoS₂ monolayer could also complement graphene in applications that require thin transparent semiconductors, such as optoelectronics and energy harvesting. Interesting direction in materials research is the creation of internal and external elastic deformations in the structure, which can lead to the appearance of new unexpected properties.

In this paper the electronic properties of MoS₂ two-dimensional (2D) structure with vacancy clusters obtained with the help of *ab initio* simulation are presented.

2. Grid computing for simulation of nanostructured materials from the first principles

Grid technology is one of the modern trends of information technology; it is designed to extend the capabilities of supercomputers, both within a single region (e.g., the national grid network of the Republic of Belarus), and on a more global level (BalticGrid, EuroGrid, WorldGrid) by combining and distributing computing resources located in different organizations, countries and continents. This technology is especially effective for physical

properties calculations of nanostructured materials with the first-principles (*ab initio*) methods in molecular dynamics and quantum chemistry that requires colossal computing resources.

The installation of the licensed software package VASP to the server multiprocessing computer system SKIF Joint Institute of Informatics Problems of the National Academy of Sciences of Belarus was a major contribution to the national grid network [12]. The Vienna *Ab initio* Simulation Package (VASP) is a computer program for performing *ab initio* quantum-mechanical molecular dynamics (MD) simulations. The approach implemented in VASP is based on a local-density approximation and an exact evaluation of the instantaneous electronic ground state. The interaction between ions and electrons is described using either the ultra-soft Vanderbilt pseudopotentials (US-PP) or the projector augmented wave method (PAW), or the generalised gradient approximation (GGA). Forces and stresses can be calculated with VASP and are used to allow relax the atoms into their instantaneous ground state.

The main purpose of VASP methods is to solve the many-body Schrödinger equation, either within density functional theory (DFT), solving the Kohn-Sham equations, or within the Hartree-Fock (HF) approximation, solving the Roothaan equations. Furthermore, hybrid functionals that mix the Hartree-Fock approach with density functional theory are implemented and Green's functions methods (GW quasiparticles, and ACFDT-RPA), many-body perturbation theory are also available in VASP [13, 14].

Thus, one of the problems to be solved during the creation of a prototype Grid system modeling from first principles of nanostructured materials is the creation of conditions for efficient adaptation (gridification) of this software package.

3. Simulation details

Interatomic interactions in the MoS₂ crystal are determined by the crystallographic parameters and the type of a chemical bond. Natural MoS₂ (α -MoS₂) has a hexagonal structure (trigonal prism) layer type and is similar in form to graphene. The bulk MoS₂ unit cell was represented as a hexagonal crystallographic structure of P63/mmc space group (No 194). The cell has 4 rectangular faces with sides equaled to 3.16 Å and 12.72 Å, parallel to <001> crystallographic axis, and intersecting <010> and <100> axes at different distances. The bottom part of the MoS₂ cell is a rhombus with an angle, equal to 120° [6, 7].

The calculations were performed using periodic conditions, therefore 4 × 4 supercell of MoS₂, corresponding to 12.64 × 12.64 Å, was used to exclude the effect of vacancies on each other. In order to remove the interaction between MoS₂ plates, vacuum gap of 10 Å was inserted between them [7]. The sampling for Brillouin zone integrations is performed using the Gamma Scheme with a regular 4 × 4 × 1 k-point grid.

Crystallographic structure of perfect two-dimensional MoS₂ is shown in Fig. 1.

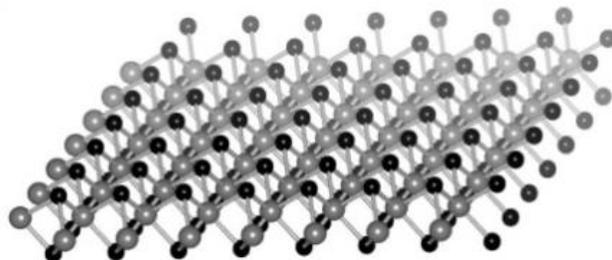


Fig. 1. Crystallographic structure of two-dimensional MoS₂.

Simulation was carried out by the means of the *ab initio* molecular dynamics approaches realized in the program package VASP (Vienna *Ab initio* Simulation Program). The interaction between the ions and electrons in the simulated system is described by

the Plane Augmented Waves (PAW) method. GGA-PBE pseudopotentials were applied for description of the interaction between the atomic cores and electrons. The Perdew-Burke-Ernzerhof algorithm of the generalized gradient approximation (GGA) was used for the exchange-correlation potential.

4. Simulation results and discussion

The investigation MoS₂ two-dimensional structure with sulfur (S) and molybdenum (Mo) vacancy clusters was conducted. The cluster size has been increased from 1 to 4 vacancies. Every possible combination of vacancy structures was checked. The calculation results of densities of electron states (DOS) and energy bands are presented in Figs. 3 and 4, respectively. For comparison, here DOS and energy band diagram for perfect two-dimensional MoS₂ structure is also presented (Fig 2).

Analysis of the DOS and energy band calculations of the studied structures shows the appearance of additional energy levels in the band gap, which can be used as trap levels in laser technology. However, it's worth noting a slight change of the band gap value from 1.71 eV (perfect two-dimensional structure) to 1.64 eV with increasing S-vacancy cluster. By contrast, the Mo-vacancy cluster increase causes a sharp narrowing of the band gap to 0.11 eV and increasing of the magnetic moment value from 0.0008 μ B (perfect two-dimensional structure) to 1.89 μ B. One of the studied structures, two-dimensional MoS₂ with four Mo-vacancy cluster (Fig. 5) showed significantly different magnetic moment value equal to 4,4 μ B. The electron density and spin density distribution of this structure is shown in Fig. 6.

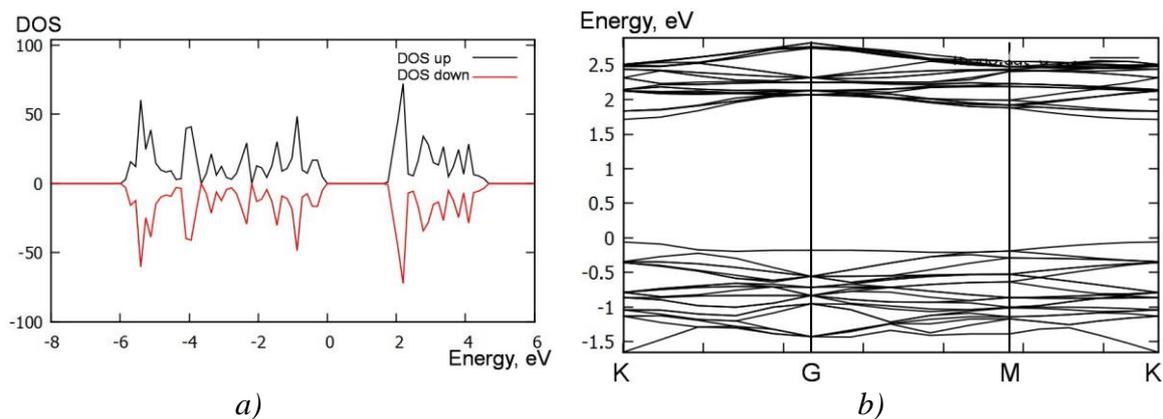


Fig. 2. DOS (a) and energy bands (b) of perfect two-dimensional MoS₂ structure.

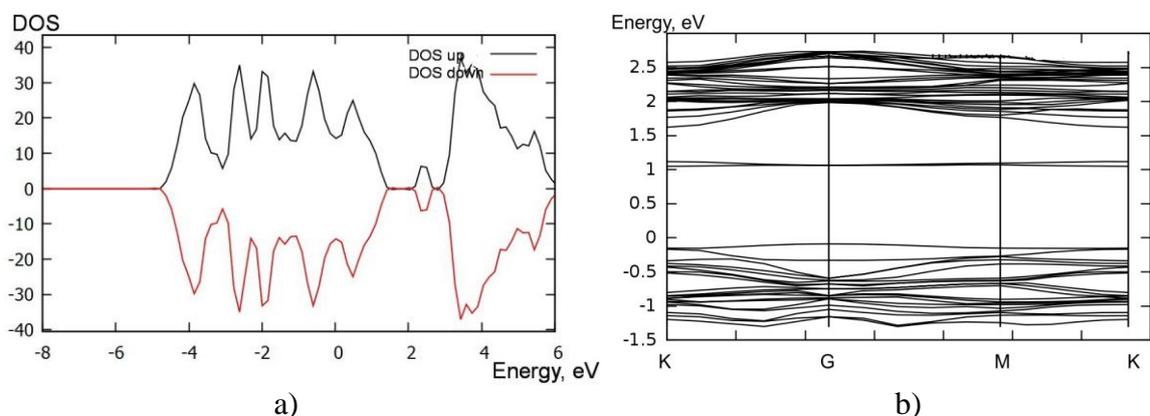


Fig. 3. DOS (a) and energy bands (b) of two-dimensional MoS₂ structure with two S-vacancy clusters.

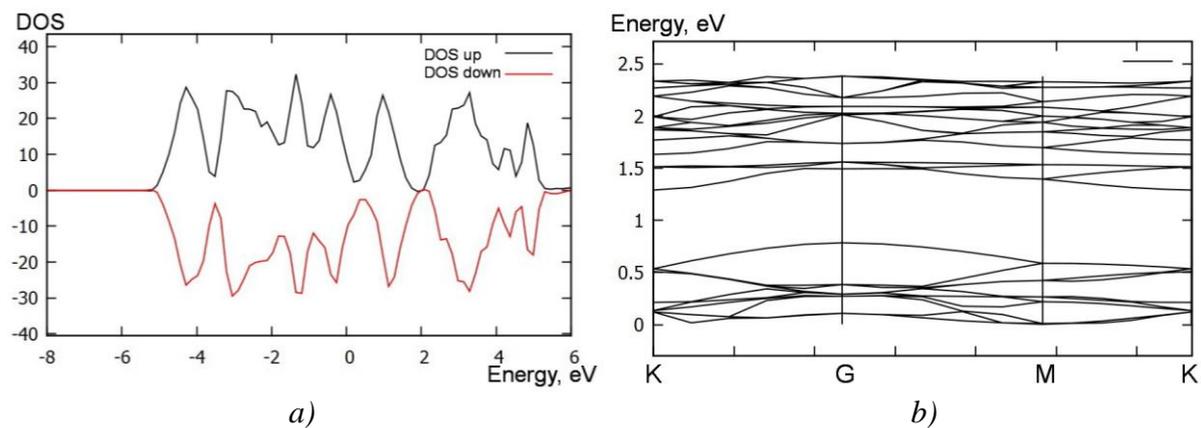


Fig. 4. DOS (a) and energy bands (b) of two-dimensional MoS₂ structure with three Mo-vacancy clusters

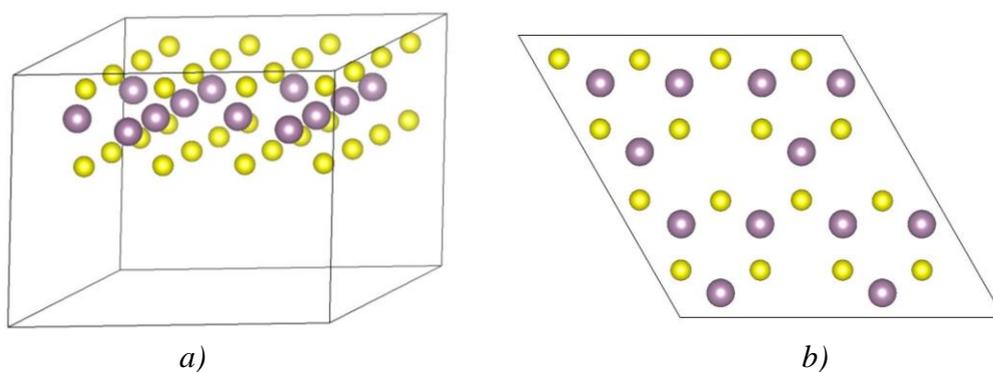


Fig. 5. Two-dimensional MoS₂ structure with four Mo-vacancy clusters: (a) side view; (b) view from above.

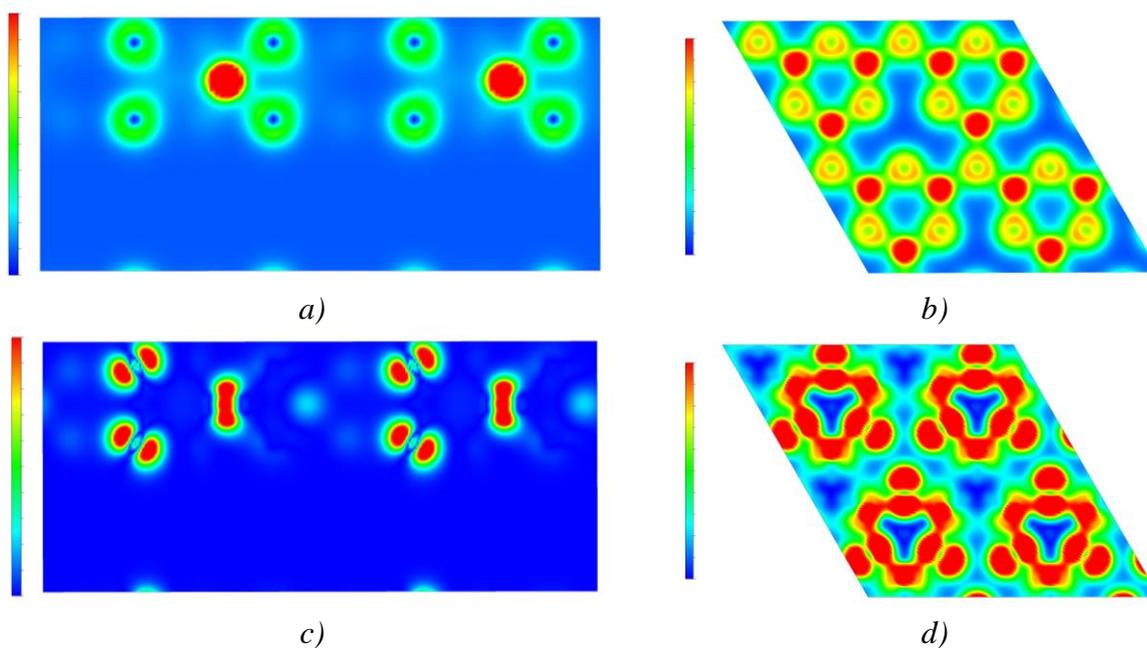


Fig. 6. Electron density (a, b) and spin density (c, d) distribution of two-dimensional MoS₂ structure with four Mo-vacancy clusters.

It is evident that the electronic and spin density distribution is concentrated near the molybdenum atoms which has the highest impact on electronic and magnetic properties of this structure. We note that, despite the above-mentioned changes in the electronic characteristics with the growth of vacancy clusters, majority of MoS₂ structures still maintains direct band transition, which is clearly seen from the band diagram figures. A significant manifestation of the magnetic properties in these structures and presence of direct-gap transition suggests the possibility of using two-dimensional MoS₂ as a structural element for sensors and spintronic devices. However, it remains an unsolved problem of sharp band gap decrease that requires further research in this area.

5. Conclusions

Thus, electronic properties of two-dimensional molybdenum disulfide with a different number and type of vacancies in the cluster was investigated using the density functional theory of VASP software package implemented on the basis of Grid computing systems. A significant effect on the electronic and magnetic properties of MoS₂ from the size and type of vacancy cluster was shown. Further research in this area will help to examine in detail and explain Mo-vacancies effect on the characteristics of investigated semiconductor.

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