AB-INITIO SIMULATION OF VANADIUM OXIDE ELECTRONIC PROPERTIES

V. Koleshko[1], *A. Gulay*[1], *V. Gulay*[1],
I. Bobachenok[1], *O. Kozlova*[2], *V. Nelayev*[1]
[1]*Belarusian National Technical University, Minsk, Belarus*
[2]*Belarusian State Universities of Informatics and Radioelectronics, Minsk, Belarus*

Abstract – The modeling of the electronic properties of vanadium oxides with the effect of the Mott—Hubbard was conducted. Software package VASP was used as the simulation tool, in particular,r method of augmented plane wave (PAW-method). Calculated electron densities and the band structures of vanadium compounds of homologous series V_nO_{n+1} and V_nO_{n-1} are presented.

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The crucial feature of some transition compounds is a jump of conductivity with increasing temperature or pressure, which can reach many orders of magnitude (the effect of Mott-Hubbard). Mott-Hubbard insulators are crystals with dielectric properties, the manifestation of which connected with the strong electron-electron interaction, but not with the influence of the periodic field of the lattice crystal (as in usual insulators or semiconductors). This state realizing in the case when the energy U of the electron-electron (Coulomb) interaction is greater than the average kinetic energy of the electrons. In that case, a measure became the width of the allowed band W. A simple band diagram of a solid state is suitable, when U < W, and, if U > W, the energy band may be partially filled with electrons, as in metals, but electrons located on adjacent atoms inhibit to the movement of electrons required to charge transfer. Due to the manifestation of the repulsion forces they localize each electron in its atom that actually turns into a dielectric material.

Typical representatives of materials with the "metal-insulator" transition are homologous series of vanadium oxides V_nO_{n+1} and V_nO_{n-1}. A software package VASP (Vienna *Ab-Initio* Simulation Package) was used as a simulation environment of its electronic properties, which implements *ab-initio* approach to quantum-mechanical calculations in molecular dynamics (MD). *Ab-initio* method uses pseudopotentials system with sets of basic elements of plane waves. This approach, implemented in the VASP, based on the local density approximation (a free energy as a variable value) and accurate estimation of instantaneous electronic ground state in each of MD-step and also using of effective diagonalization of the matrix schemes and effective Puley mixing.

The interaction between ions and electrons in the software package is described by Vanderbilt ultrasoft pseudopotential (US-PP), or a method augmented plane wave (PAW). Both methods allow for a significant reduction of required number of plane waves in the transition metal atoms. Besides, VASP relatively simple calculates strength values, which are used for relaxation of atoms into ground state. VASP also allows to trace the displacement of the individual particles in the system and evaluate their self-diffusion coefficients, to calculate the average change time of the nearest neighboring particles, and to identify a range of other physical properties. Particularly attractive in the study of active sensor materials is the ability of using VASP to calculate the dependences of these characteristics on the temperature and the external and internal elastic deformations.

The main methodology used in VASP involves the solution of the Schrodinger equation for the electron-nuclear subsystem of the modeled structure and evaluation of the final full energy of the system, forces and other parameters and values. The method used in this paper is the PAW-method, which allows properly calculating the lattice constants, adequately estimating spin-polarization and physical properties of the materials. The problem of modeling atomic structures and electronic properties of rare-earth compounds in a general form involves finding optimal calculation algorithms in the VASP software package, estimating input parameters of the modeled system for attaining the required precision and selecting a methodology for adequate determination of properties of the sensory materials in question.

The idea of the used algorithm is that the calculations start from a relatively small number of atoms in the modeled crystallite, afterwards based on these results the structure is translated to the required size. Although before that a number of tests are run, for example the optimal number of points that determine the degree of fragmentation of the reciprocal space is calculated, the minimum energy of the modeled system is evaluated as well. The number of points determines the precision of the determined atomic coordinates in the lattice: for dielectric materials ten points per unit cell are enough.

A cubic lattice structure of the F_{m3m} (No. 225) space group was used to represent a primitive cell of VO (Fig. 1). The following procedures were used for modeling vanadium oxides: creating input files with the simulation task; relaxation of vanadium oxide lattice structure; analysis of the compounds lattice unit cell; determination of electronic properties of vanadium oxide. The static self-consistent potential of the crystallographic structure of the compound was calculated after the relaxation procedure. The results were obtained in the form of DOS and zone diagram structure at the k-points of the Brillouin zone: L–Γ–M–W–X–L (Figs. 2, 3).

The unit cell V_4O_9 was performed using the orthorhombic crystal structure of P_{nma} (No. 62) space group. The Fermi level of compound is 0.57 eV, a direct transition value is 1.05 eV at T *k*-point (in the calculation of the band structure diagram on the following *k*-points of the Brillouin zone: X-D-Z-T-R-S-X). V_2O_5 orthorhombic crystallographic structure of the space group P_{mmn} (No. 59) was used to represent the unit cell. The Fermi level of V_2O_5 is 0.51 eV, indirect transitions was observed at R-Γ and R-Y k-points (traversal path S-D-R-Y-S). VO_2 compound characterized with an indirect transition with value 0.9 eV, wherein the maximum of the valence band is at R k-point, and the minimum of the conduction band is at M k-point (traversal path - Z-L-M-X-R-Z).

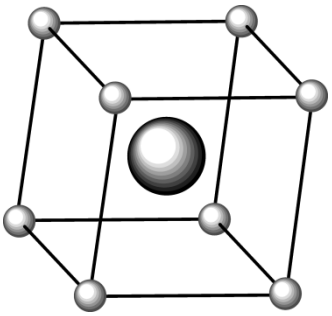

Figure 1 – Primitive unit cell of VO:
● — vanadium, ● — oxygen

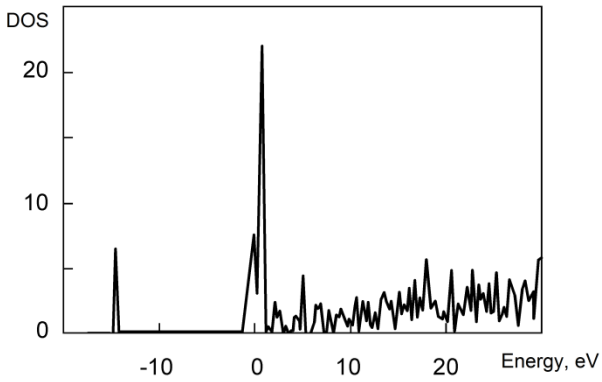

Figure 2 – VO density of states; Fermi level is equal to -2,22 eV and sets at zero point

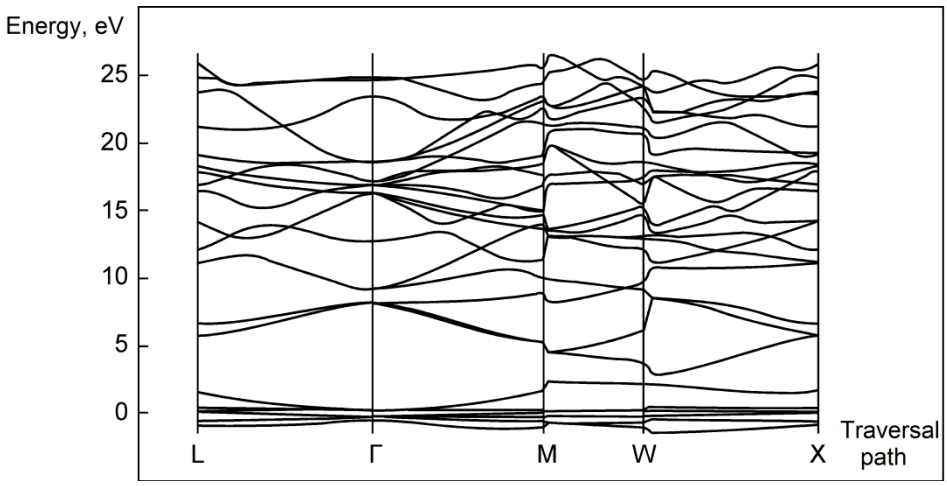

Figure 3 – Zone diagram of VO structure

The analysis of the zone diagram shows that VO has an indirect gap transition with a value of 0.38 eV, wherein the maximum of the valence zone is at the M k-point and the minimum of the conduction zone is at the W *k*-point.