established by methods of X-ray phase analysis and infrared spectroscopy. The maximum saturation magnetization was found for the composition $Mn_{0.3}Fe_{2.7}O_4$ (M_s = 68 A·m^2·kg^{-1} at 300 K and M_s = 85 A·m^2·kg^{-1} at 5 K), which is associated with a change in the cationic distribution over tetrahedral and octahedral voids. The materials obtained were stabilized in the form of colloidal solutions using a number of polyelectrolytes. It was found that poly(diallyldimethylammonium chloride) – PDDA had the best stabilizing effect due to its structural features. A method for controlling the magnetic properties of magnetite by partial replacement of iron ions in the magnetite structure with manganese is proposed. Changing the magnitude of the magnetization and coercive force is possible by changing the degree of substitution. Relatively high values of specific magnetization, as well as uniformity of magnetic particles in size, can be of practical interest, for the manufacture of contrast agents in MRI diagnostics.

Key words: nanoparticles; saturation magnetization; contrast agents; MRI diagnostics.

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STRUCTURE AND ELECTRONIC PROPERTIES OF $MoS_{1.5}Se_{0.5}$ ALLOY FROM FIRST-PRINCIPALS CALCULATIONS

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The effects of relative positions of Se atoms in a real monolayer alloy $MoS_{1.5}Se_{0.5}$ have been studied. It is demonstrated that the distribution of Se atoms between top and bottom chalcogen planes is most energetically favorable. For a more probable distribution of Se atoms $MoS_{1.5}Se_{0.5}$ monolayer alloy is a direct semiconductor with the fundamental band gap equal 2.35 eV. We have also evaluated the optical band gap of alloy at 77 K (1.86 eV) and room temperature (1.80 eV), which is in good agreement with the experimentally measured band gap of 1.79 eV.

Key words: transition metal dichalcogenides; alloy; DFT.

INTRODUCTION

Semiconducting transition metal dichalcogenides (TMDs) represent a class of layered materials with a nonzero band gap, which exploration started decades ago and continues until present [1, 2]. Transition metal dichalcogenides have attracted much attention owing to their rich physics and promising applications in electronic and optoelectronic devices [2]. TMD monolayers such as MoS_2, $MoSe_2$, WS_2, WSe_2 are direct band gap semiconductors (with optical band gap of 1–2 eV) [3]. The crystal-phase engineering of TMDs is criti-

cally important to form new structures phase-based TMD, showing tunable physicochemical properties.

In this report we present the theoretical analysis of the energy of formation of monolayer $MoS_{2(1-x)}Se_{2x}$ alloy (x = 0.25) and the microscopic structural stability (different alloy configurations with variation of positions of substituting atoms of Se). Our study is based on the recently proposed GVJ-2e method, developed within DFT framework for accurate band gap calculation [4, 5, 6, 7].

RESULTS

$MoS_{2(1-x)}Se_{2x}$ alloy represents 2D monolayer alloy. It is built from MoS_2 monolayer, when some of S atomsare substituted with Se atoms. We considered $MoS_{2(1-x)}Se_{2x}$ alloy with substitution rate of S equal to 25% (x=0.25).

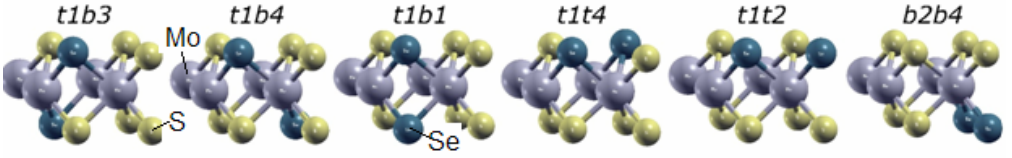

Figure 1. – $MoS_{1.5}Se_{0.5}$ monolayer alloy with different Se atoms positions

Thus two Se atoms substituted two S atoms in MoS_2supercell containing 12 atoms. There are several possible atomic positions for the Se atoms. Such configurations include the distribution of Se atoms between top and bottom chalcogen planes (t1b3, t1b4, 'stacking' t1b1) and occupation of a single chalcogen plane by Se atoms (t1t2, t1t4, b2b4). Fig. 1 demonstrates all configurations t1b1, t1b3, t1b4, t1t2, t1t4, b2b4 of MoS_2 monolayer with two S atoms substituted with Se which corresponds to $MoS_{1.5}Se_{0.5}$ alloy. We analyzed the formation energy of $MoS_{1.5}Se_{0.5}$supercell with different positions of Seatoms to study the real structure of alloy. The formation energy ($E_{\text{formation}}$) of the particular configuration of alloy is calculated according to

$$E_{\text{formation}} = E_{MoS_{2(1-x)}Se_{2x}} - (1-x)E_{MoS_2} - xE_{MoSe_2} \quad (1)$$

where E is the total energy of the supercell. The *t1b3* and *t1b4* configurations have the lowest formation energy. The *t1b1* configuration (stacking of Se atoms on top of each other) has higher formation energy but still negative. The configurations in which both Se atoms are located at the same plane (*t1t4, t1t2, b2b4)* have positive formation energy. The latter makes them less likely to appear during the synthesis of $MoS_{1.5}Se_{0.5}$ alloy.

We calculate the fundamental band gaps of $MoS_{1.5}Se_{0.5}$ alloy with different positions of Se atoms using GVJ-2e method. Table presents calculated GVJ-2efundamental band gap of $MoS_{1.5}Se_{0.5}$ alloy.

Table

Theoretical fundamental band gap (GVJ-2e) of MoS_2, $MoSe_2$, $MoS_{1.5}Se0.5$ (for each configuration) monolayers. Experimental band gaps - STS measurement. All values are in eV

1L	MoS_2	$MoSe_2$	$MoS_{1.5}Se_{0.5}$						
			t1b3	*t1b4*	*t1b1*	*t1t4*	*t1t2*	*b2b4*	$MoS_{1.5}Se_{0.5}$
GVJ-2e	2.38	2.12	2.37	2.37	2.34	2.33	2.33	2.32	<2.35>
Exp.	2.40 [7]	2.18 [9]	–	–	–	–	–	–	–

The value of the fundamental band gap not only depends on the substitution rate but is also sensitive to relativepositions of Se atoms in MoS_2 matrix. The average value of the fundamental band gap lies between experimental values of 2.40 eV, 2.5 eV for MoS_2, and 2.18 eV for $MoSe_2$ [7, 8, 9] and corresponds to about 30 % shift from experimental band gap of monolayer MoS_2 towards $MoSe_2$.

We provide the calculation of the fundamental band gap, which should be compared with an experimentally obtained band gap via scanning tunneling spectroscopy (STS) measurement. Usually from experiment the optical band gap is available (determined from photoluminescence spectrum (PL)).It was shown previously [10, 11] that the $MoS_{2(1-x)}Se_{2x}$ alloy band gap are mostly in the red part of a visible spectrum (1.65−2.0 eV). PBE calculations [12] give the value of $MoS_{1.5}Se_{0.5}$ band gap 1.63 eV, which differs from the experimentally obtained value of 1.79 eV17 on 0.16 eV (9%). So we also estimate optical band gap ($E_g(PL)$)for $MoS_{1.5}Se_{0.5}$ alloy at low temperature ($E_g(PL)=E_g(QP)-E(exc.\ binding)$). The theoretical exciton binding energy ($E($exc. binding$)$) has been calculated on the basis of BSE (Bethe–Salpeter equation) theory and equals to 0.501 eV and 0.465 eV for MoS_2 and $MoSe_2$ monolayers respectively [13]. The exciton binding energy in alloy $MoS_{1.5}Se_{0.5}$ was obtained by interpolating the exciton binding energy of MoS_2 and $MoSe_2$monolayers and was equal 0.492 eV. Thus for $MoS_{1.5}Se_{0.5}$ alloy configurations optical band gap at low temperature ranges from 1.83 to 1.88 eV. The estimated optical gap at room temperature of 1.80 eV agrees well with experimental value 1.79 eV [14] (deviation of 0.01 eV).

We have analyzed electronic band structure and the projected densities of states of $MoS_{1.5}Se_{0.5}$ alloy in comparison with MoS_2 and $MoSe_2$. The calculation shows that $MoS_{1.5}Se_{0.5}$ monolayer alloy is a direct band gap semiconductor similarly to the monolayers of MoS_2 and $MoSe_2$ (see Fig. 2).

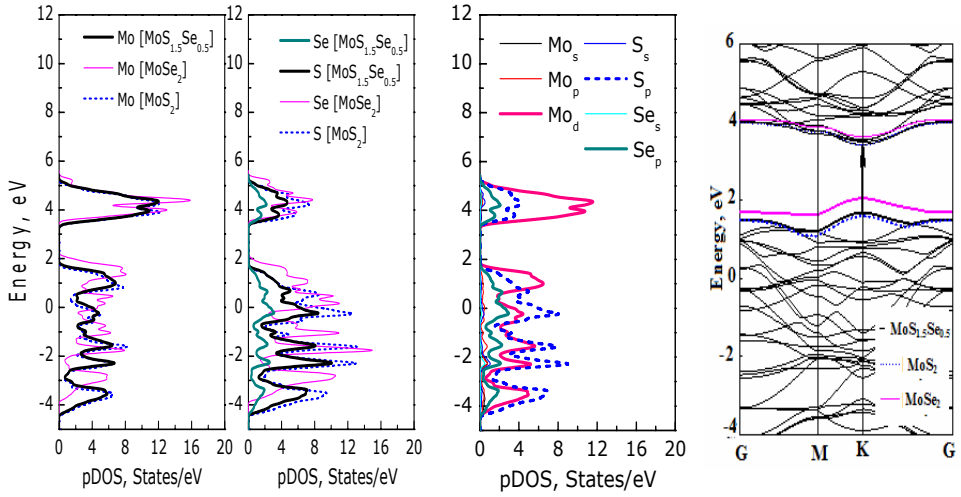

Figure 2. – Band diagram of $MoS_{1.5}Se_{0.5}$ alloy (t1b3) with top v-band and bottom c-band lines of MoS_2 and $MoSe_2$ (LDA PZ)

The presence of Se atoms in MoS_2 matrix affects not only pDOS of sulphur but also pDOS of molybdenum. Presence of Se atoms shifts and changes the shape of Mo pDOS (and the number of states/eV) in the compound comparing to monolayer $MoS_{1.5}Se_{0.5}$ alloy pDOS is dominated by Mo_d, S_p and Se_p states.

We have also analyzed the electron effective mass for the alloy ($0<x<1$). Practically for the whole region of substitution rate the electron effective mass is smaller than the free electron mass. It should be also noted that for the substitution rate in the range $0.6<x_S<0.9$ ($0.1<x_{Se}<0.4$) some peculiarity is observed (electrons become heavier than holes), but more detailed calculations are needed. We have obtained the following effective masses in MoS_2 monolayer:$m_e^*=0.33m_0$ and $m_h^*=0.40m_0$ μ_{exc}^{direct} ($=18m_0$) and in $MoSe_2$ are $m_e^*=0.42m_0$ and $m_h^*=0.49m_0$ μ_{exc}^{direct} ($=23m_0$) from Kohn-Sham band structure calculated using PBE GGA. Also in our calculations for MoS_2 and $MoSe_2$ monolayers both electrons and holes have effective masses smaller than a free electron mass, which agrees well with results obtained with G_0W_0 and HSE [15, 16]. Comparison of the effective masses of electrons (holes) in the alloy with the effective masses of electrons in MoS_2 and $MoSe_2$ monolayers reveals that electrons (holes) become slightly heavier in the alloy.

CONCLUSONS

The first principles calculations of the structure and electronic properties (fundamental and optical band gap) of 2D alloy $MoS_{1.5}Se_{0.5}$ have been presented. Analysis of the formation energies of the $MoS_{1.5}Se_{0.5}$ monolayer alloy with different positions of Se atoms shows that alloy configurations with Se atoms distributed between top and bottom chalcogen planes tend to be more energetically favorable during the synthesis. The calculation shows that $MoS_{1.5}Se_{0.5}$ monolayer alloy is a direct band gap semiconductor with the fundamental band gap equals to 2.35 eV. We have evaluated the exciton binding energy (0.492 eV) and calculated optical band gaps of $MoS_{1.5}Se_{0.5}$ alloy at low (1.86 eV) and room (1.80 eV) temperatures. The estimated optical gap at room temperature of 1.80 eV agrees well with experimental value 1.79 eV (deviation of 0.01 eV). This fact confirms that experimentally observed PL transitions correspond to an optical band gap. This study also confirms the efficiency of the recently proposed GVJ-2e method for band gap calculations for 2D alloys.

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NUMERICAL MODELING OF GEOMETRICAL EFFECTS ON MANIPULATION OF EXCHANGE INTERACTION FOR TWO-ELECTRON STATES IN NANOGATES-DONORS SYSTEM

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Numerical simulation results of exchange coupling in the system of near-surface donor and quantum dot pairs are presented. Exchange energy under the effect of external external electric field has been calculated using Hartree-Fock method. Fourier transform and finite element methods have been used to solve the problem for the Poisson equation. The dependences of exchange energy on external electric field have been obtained. Limits of applicability of electric field for the system control are discussed. The effect of donors position has been investigated.

Key words: qubit; two-electron system; nanogate; quantum dot; modeling.