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ELECTRONIC PROPERTIES OF TERNARY COMPOUNDS WITH VACANCY CLUSTERS: *AB INITIO* SIMULATION

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Abstract. Electronic and magnetic properties of ternary crystal $TlMeX_2$ compound ($TlGaS_2$ as an example) with alone vacancy or their clusters were studied by means of first-principle (ab initio) approximation. It was shown that presence of S-vacancy clusters narrows the band gap of $TlGaS_2$ crystal significantly while Tl - vacancy clusters increase it slightly. Restructuring $TlGaS_2$ crystal due to vacancy or vacancy clusters presence leads to manifestation of ferromagnetic properties of the compound with the spin polarization value approx. 22 % when the number of vacancies in the cluster increases up to extremely high values. Revealed phenomena may be used in the censoring applications.

1. Introduction

Semiconductor $TlGaS_2$ belongs to $TlMeX_2$-type chalcogenide compounds (where Me is Ga or In, and X is S or Se) which have flaky ($TlGaS_2$, $TlGaSe_2$, $TlInS_2$) or chain ($TlInSe_2$, $TlInTe_2$, $TlGaTe_2$) structures [1]. These compounds are crystallized in a monoclinic ($TlGaS_2$, $TlGaSe_2$, $TlInS_2$) or tetragonal ($TlInSe_2$) cells [2-4]. $TlGaS_2$ has a monoclinic structure $C2/c(C^6_{2h})$ (Fig. 1) with the cell parameters a=b=10.40 Å (b=10.77 Å [2]), c=15.17 Å [5]. Indirect band gap for $TlGaS_2$ is varied in the range of 2.38–2.46 eV [6, 7] and its conductivity is about $10 \cdot 10^{-8}$ $(\Omega\text{-cm})^{-1}$ at the room temperature [8, 9]. A high photosensitivity in the visible range, high double refraction and its wide transparency range of 0.5−14 μm make these wide band gap crystals useful for optoelectronic applications [10].

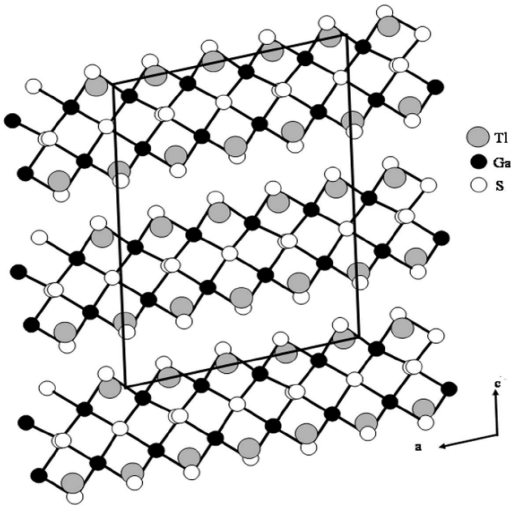

Fig. 1. Crystal structure of $TlGaS_2$ [11].

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$TlMeX_2$ compounds has attracted much attention to its structural [12, 13], electrical [14], photoconductive [15], and optical properties [16-18], caused by extraordinary electronic properties. So, $TlGaS_2$ is expected to have a potential application for optoelectronic devices and nonlinear optics [19]. Moreover, thermally stimulated current [20], thermal expansion [21], electron paramagnetic resonance [22], heat capacity [23] and Raman scattering [24] features have also represents additional interest. Indicated fundamental properties of $TlGaS_2$ compound can be used in switching and memory elements of electronic devices [25].

Indicated electronic and associated magnetic properties of $TlMeX_2$ compounds, in particular $TlGaS_2$, determine their use as materials structural elements of sensory devices and for spintronics, and can be "forced" in certain conditions. As shown in [26], such "useful" conditions include an elastic deformation of a uniaxial tension and compression. Thus, the spin anisotropy in the compounds of $TlMeX_2$ depends linearly on the magnitude of the external uniaxial elastic deformation (increases with stretching and decreases under compression) along the <100>- and <010>- crystallographic directions.

The effect of spin anisotropy is also appeared in the internal deformation of crystal $TlMeX_2$ compounds caused by introduction of point defects (vacancies and interstitials) and their complexes. The investigation of magnetic properties of graphene with vacancy cluster in *ab initio* approximation showed [27] that spin polarization took place with a monotonic increase of the magnetic moment in the system "graphene + vacancy cluster" .

Therefore, it is reasonably to suppose that the spin anisotropy can occur also in the layered $TlGaS_2$ compound. However, no experimental and theoretical data are available about electronic properties of the $TlGaS_2$ crystal with the point defects and their clusters.

2. Methodology

Simulations of $TlGaS_2$ electronic properties were carried out with the use of the program package VASP (Vienna *Ab initio* Simulation Package) [28, 29]. VASP is intended for atomic-molecular and electron-nuclear systems simulation by quantum mechanics and molecular dynamics methodologies based on the density functional theory, which does not require any input experimental data. Vanderbilt-type ultra-soft pseudopotentials were used for Tl, Ga and S. A mesh of 40 *k*-points was used for Brillouin-zone auto generated grid in the basic part centered at Γ point. Tests on density of *k*-points mesh showed that this sampling is enough for achievement of adequate results.

The initial conditions for simulation of the investigated $TlGaS_2$ structure were taken from experimental data [11]. Simulations were performed using the multi-processor cluster, supercomputer SKIF-K1000 in the same way as in [30].

The interaction between the ions and electrons in the simulated system is described by the augmented plane wave's method. In the frame of the program package VASP it is possible to calculate the forces and stresses, which are used to relax atoms into their ground state. The electron-electron exchange and correlation interactions are described by the density functional exchange-correlation functional of Ceperley-Alder [27].

First iteration calculations were carried out at the fixed volume with relaxation of the atomic positions only. At the next iteration procedure, simulations were performed with relaxation of atomic positions of the modeling crystallite. This procedure was repeating in the iterative process in order to obtain a set of total energy of the system as a function of the volume of the modeling crystallite. Relaxation of the simulated structure was carried out until inter-atom interaction forces do not exceed 0.05 eV/Å. Energy optimization was performed in such manner and the electronic structure was calculated using the optimized lattice parameters and coordinates of atoms.

3. Results and discussion

The simplest point defect in the simulated crystal is a vacancy. Three types of simulations have been performed for the $TlGaS_2$ crystal with vacancy and its clusters: with Tl-, Ga- and S-vacancies and its clusters. Modeling crystallite consisting of 512 atoms was used to simulate the system with the lowest vacancy concentration. Such dimension of the modeling crystallite enables to study alone vacancy (or its clusters) influence on electronic properties of the simulated structure. In order to simulate the system with specified vacancy concentration (in other words, the system "$TlGaS_2$ crystal + vacancy cluster with specified number of vacancies in the cluster") the modeling crystalline was formed from superposition of unit cells with variable volume. Such superimposed crystalline contained only one vacancy inside, 2×1×1, 2×2×1, and 2×2×2 unit cells being used as base systems. Therefore, modeling crystallites consisting of two, four, and eight such unit cells corresponds to systems "$TlGaS_2$ crystal with vacancy concentrations 25 %, 12.5 %, 6.25 %, and 3.125 %", respectively; i.e. to values x equal approximately to 0.25, 0.13, 0.06, and 0.03 in the investigated stoichiometric compositions $Tl_{(1-x)}GaS_2$,$TlGa_{(1-x)}S_2$ and $TlGaS_{(2-x)}$.

In Table 1 the electronic zone characteristics of $TlGaS_2$ vs. stoichiometry of the compound are presented. Here E_g and E_{spin} are the band gap and spin polarization energy of the investigated compounds respectively. The spin polarization energy [31] is given by the following expression (1), where $DOS(E_{f(spin-up)})$, $DOS(E_{f(spin-down)})$ – density of states at the Fermi level for spin-up and spin-down, respectively; E_{spin} - spin polarization value, in percentage:

$$E_{spin} = \frac{DOS(E_{f(spin-up)}) - DOS(E_{f(spin-down)})}{DOS(E_{f(spin-up)}) + DOS(E_{f(spin-down)})} \cdot 100\% .$$

Calculated density of states (DOS) dependencies for various spin directions (spin up/spin down) in $Tl_{0.25}GaS_2$ crystal are shown in Fig. 2. From the figure it follows that Tl-vacancies almost do not influence on the electronic properties of the ternary compound. Increasing of the cluster size with Tl-vacancies leads to small increasing of the band gap of the $TlGaS_2$ compound. However, the same changes in the size of Ga and S vacancies lead to the destabilization of the structure (decreasing of structural stability, the saturation of the conduction band) and to the band gap decrease.

Table 1. $TlGaS_2$ electronic characteristics *vs.* its stoichiometric composition.

$TlGaS_2$ stoichiometric composition	x	E_g, eV	E_{spin}, %
$TlGaS_2$	0	2.163	0
$Tl_{(1-x)}GaS_2$	0.03	2.17	0.05
	0.06	2.17	1.92
	0.13	2.17	8.48
	0.25	2.18	-22.00
$TlGa_{(1-x)}S_2$	0.03	2.13	-0.01
	0.06	2.13	-0.80
	0.13	2.13	-3.19
	0.25	2.13	11.30
$TlGaS_{(2-x)}$	0.00	1.67	0.00
	0.01	1.65	0.00
	0.03	1.62	-0.00
	0.06	1.59	-0.01
	0.13	1.55	-0.05

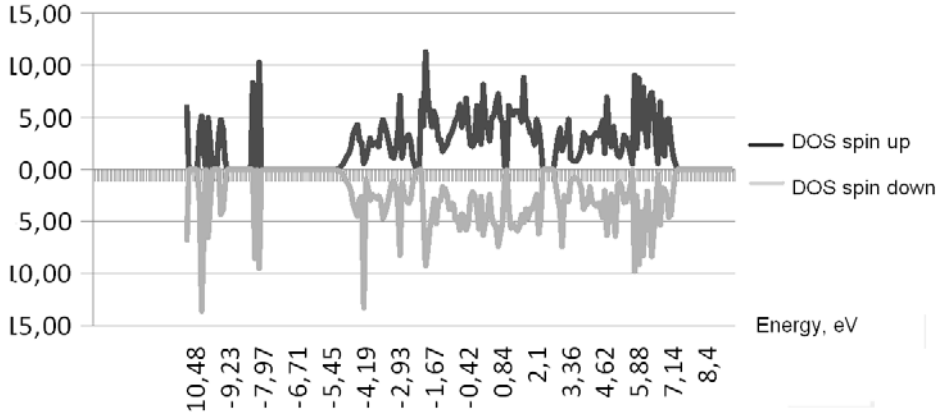

Fig. 2. Density of States (DOS) of charge carriers (electrons) dependencies for various spin directions (spin up/spin down) in $Tl_{0.25}GaS_2$ crystal.

A large defect-free crystal $Tl_{0.25}GaS_2$ (see the 4-th line for $Tl_{(1-x)}GaS_2$ and $TlGa_{(1-x)}S_2$ in Table 1), by our opinion, can be grown if the intrinsic point defect supersaturation in the crystal prior to the onset of nucleation is very low and radially uniform. Such manner can be achieved when the crystal is grown in a relatively radially uniform temperature field near the critical condition, when an acceptable balance between the total vacancy flux (convection and vacancy diffusion) and the self-interstitial flux (convection and diffusion of self-interstitials) is achieved. The concentration of the intrinsic point defects is very sensitive to the relative shifts of their equilibrium concentrations and their diffusion coefficient under the temperature changing. On the other hand, the creation of energy disbalance in the structure can lead to vacancy cluster appearance. The same calculations were performed for $TlGaS_2$ crystallite with clusters from 2, 10, 18 and 24 vacancies. Schematic presentation of the simulated structures is shown in Fig. 3 (thick lines the indicate vacancy clusters).

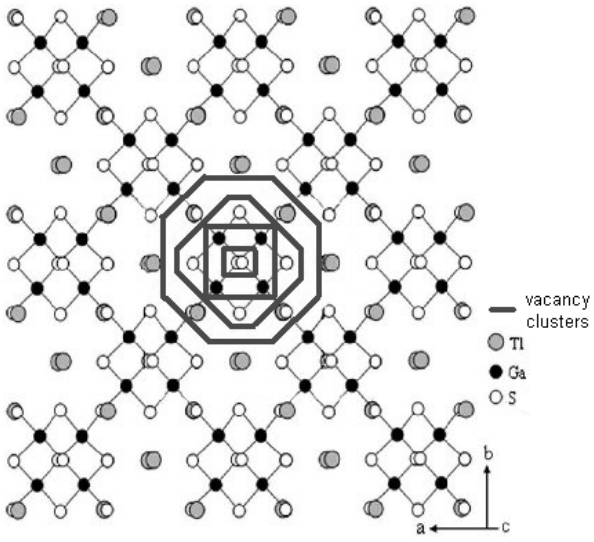

Fig. 3. Crystal structure of $TlGaS_2$ with vacancy clusters.

The calculation results obtained show that the magnetic moment is localized in the defect area, the magnetic moment being proportional to the cluster size (Table 2). Besides, they prove the formation of ferromagnetic state in the region near the vacancy cluster. This is particularly evident for $TlGaS_2$ crystal with the cluster of 24 vacancies (Fig. 4).

Table 2. Band gap energy E_g and spin polarization of $TlGaS_2$ with vacancy clusters.

Number of vacancies in a cluster	E_g, eV	E_{spin}, %
2	2.11	0.00
10	2.05	0.01
18	2.05	0.01
24	1.99	8.96

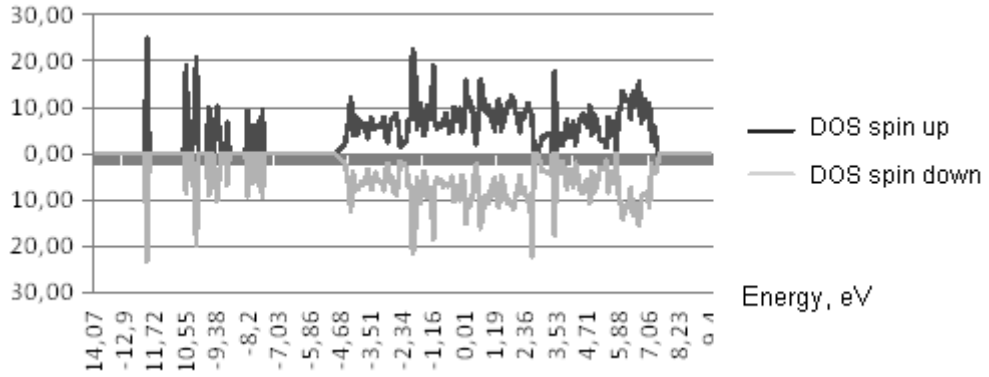

Fig. 4. Density of States (DOS) dependencies for $TlGaS_2$ with 24 vacancy cluster.

The magnetic moments of the investigated complexes "$TlGaS_2$ crystal + vacancy cluster" are concentrated at the edges of the defect region and sharply decrease with distance from the cluster edge. It is found that vacancy clusters form spin-oriented domains (up to approximately 8% and above for the spin polarization in comparison with the investigated free-defect ternary compound) with a small radius of interaction (3.8 Å). Thus, the stability of the spin state and its magnetic moment is expected to be sensitive to the size of vacancy cluster. Therefore, detected magnetic properties of ternary compound $TlGaS_2$ (and other compounds of $TlMeX_2$ type) with vacancy clusters could be considered as important characteristics for spintronics and sensory devices.

4. Conclusions

We have investigated the spin-dependent electronic and magnetic properties of a ternary compound $TlGaS_2$ with vacancy clusters of a various size by *ab initio* simulations with the use VASP program. The main purpose of the work was to find the influence of vacancy number and vacancy cluster configuration on spin polarization of the system. The existence of spin polarization in the system of $TlGaS_2$ with vacancy cluster was confirmed.

It was found that vacancy clusters form spin-oriented domains with a small radius of interaction, appr 3.8 Å. Magnetic moment of the "$TlGaS_2$ crystal + vacancy cluster" complex is located near the vacancy cluster. The stability of the spin state and its magnetic moment is sensitive to the size of vacancy cluster. The results obtained show the possibility to use detected phenomena in structural elements of spintronics and sensory devices.

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