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Calculation of the Stability and Reconstruction of the Crystal Surface within DFT-Calculations

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The thin films' surface is not perfect, so its properties and properties of the massive part of the film will differ significantly. Since a regularity in the formation of surface irregularities is observed, then the possibilities of computer modeling can be used to study such structures. To reproduce the surface of crystals with a NaCl structure, one can apply the same approaches in modeling properties as for metal oxides. The fundamental difference from the previous studies is in considering the structure in the direction (111), since such assumptions allows to use a smaller simulation cell for computer calculations, which greatly speed them up. Approbation of the technique of repositioning the surface of lead sulfide thin films has been carried out.

Keywords: lead sulfide, DFT, methods of computer quantum chemistry, reorganization of the thin films' surface.

Article acted received 02.08.2018; accepted for publication 15.09.2018.

Introduction

The study of surface states is one of the important tasks of modern material science. There are a number of reasons for this. First, the surface is a certain limit, the study of which combines the methods inherent in the physics of a condensed state and a deep knowledge of the chemical processes that take place on the interfaces between solids and the gas phase (air). Correct consideration of chemical reactions is necessary to describe a whole spectrum of surface phenomena. For example, research of the materials' properties for renewable energy industry applications is very important today. These are, for example, thin-film elements for photovoltaic energy converters, thin-film thermocouples, infrared sensors, or energy-accumulation materials that function due to the properties of a developed surface.

Experimental studies performed, for example, in [1-3] indicate the basic principles that are the basis for studying surface phenomena. In particular, these studies allowed to compare large amounts of experimental data with calculated surface parameters obtained using DFT [4-8].

Crystal surface modeling requires taking into account not only the crystalline structure of the material, but also the deformations associated with the finiteness of the crystals' boundaries. For simulation of planes use

the finite-sized slab technique. Widespread technique for locking dangling bonds is using hydrogen atoms on the boundaries of planes [9]. In [10], [11] were described the method of 'frozen' nuclei using the wave functions of valence electrons.

The surface energy of Lead Sulfide for different surfaces (001), (010) and (100) are calculated. Special attention is paid to the surface (111). Performing calculations within density functional theory (DFT) applied different levels of difficulty, namely the local density approximation (LDA), generalized gradient approximation (GGA) and Perdew, Burke, Ernzerhof (PBE), Heyd, Scuseria, Ernzerhof (HSE06) hybrid functionals.

I. Elements of theory

The density functional theory framework allows to calculate not only the properties of ideal crystals, but also to explore the surface layers of solids. Thus, the authors [10], [11] used several models. In the octopolar model, three atoms of the surface are pulled out of the plane, and the atom nearest to them, which is located below the surface plane. In this way, pyramidal structures directly on the surface are obtained. The spinel model differs from the octopolar only by the fact that the atoms are "pulled out" in such a way that the highest atom of the "pyramid" is located directly over one of the

atoms of the near-surface layer. The "Alpha" model takes place in the case of removing the highest atom of the octopolar model. Such a model describes the non-stoichiometric composition of the crystals in a better way.

Since all shells of the crystal lattice atoms are charged, then, when calculating the Madelung constant, there is a need to hold over the neutral shells, that is, the shells of the Bravais lattice, followed by the attachment of a neutral molecule. This leads to the formation of two identical, oppositely charged crystal lattice shifted relative to each other in the main vector b .

The "molecular" Coulomb energy of a certain ion i according to [12] is defined as:

$$E_{mol}^{full} = -q^2/b + q^2 \sum_{j \neq i} \sum_{j'} (1/r_{ij} - 1/r_{ij'}) = E_{mm} + \sum_{r_s} E_{mm}(r_s), \quad (1)$$

where the first term is responsible for the molecular interaction inside, and the second is the outside of the ion i with the molecules in the lattice radii $r_{ij} \equiv r_s$.

The method of direct summation includes octoporous molecules and intermolecular contributions:

$$E_{mm} = (q^2/a)[-6 + 3\sqrt{2} - 2\sqrt{3}] \approx -2,91206(q^2/a). \quad (2)$$

Calculated by this method, the internal energy has the same value as obtained by the Evjen's method [13], [14] if it is eliminated by ambiguities caused by the assignment of small charges to the ions at different sections of the crystallographic unit cells [12]. Therefore, although it turns out that a direct dipolar sum reproduces the Evjen's method (if an octopolar molecule is chosen) in calculations [12], it avoids some of the ambiguities of molecule, whose property is especially important in describing defects.

PbS is binary semiconductor with a crystal lattice type NaCl. The direct estimation of the Madelung energy for such crystals containing octoporous molecules is not complicated and has been described by Lacman's [15]. This "octopolar approximation" is based on the assumption that the interaction between the formed octopolar molecules decreases in proportion to r^{-7} . However, consideration of this model is not limited such an interaction between the formed octupoles. On the other hand, this approximation follows from a more fundamental convergence behavior, avoiding surface-dipole problems in general [16].

Reducing of energy through octopolar reconstruction, which is accompanied by a decrease of surface tensions, may be sufficiently significant for certain surfaces [12]. The obvious advantage of this model is that such a structure is in a thermodynamically equilibrium state. There is no need to introduce impurities for its stabilization.

Regarding the physical cause of these reconstructions, it is stated in [12] that, unlike Lacman's assumption, the convergence of the sum over octopuses does not collapse when the octopuses are broken into neutral fragments. Instead, the gap, as a rule, leads to the formation of superficial charges or dipoles and the associated increase in energy. Based on this analysis it can be expected that the surfaces of all ionic crystals with

the dipolar base molecule will be reconstructed in such a way as to eliminate or at least minimize the surface-dipole problem.

The complete harmonization of such approaches with the Ewald's method for the case of free surfaces [17] opens the prospect of determining the Coulomb energy not only for ideal crystals at zero temperature but for finite temperatures too.

The essential advantage of this approach is that it is possible to investigate substantially larger systems and to obtain data on the structure and properties of defects in ionic materials.

The comparison of the results [12] with the values, obtained by the Ewald's method, for the case of free surfaces [17] is explained by the fact that the direct dipolar estimation of the Coulomb energy is not limited to nonperfect crystals at zero temperature, predicting that the expansion to the finite temperatures and most likely the liquid, it will be possible to implement.

The computational efficiency compared to the Ewald's method will allow us to create a surface reconstruction based on the convergence behavior and to obtain new information on the basic structure and properties of defects in ionic materials.

II. The method of calculation and results analysis

Previously, for calculating the thermodynamic properties of massive PbS crystals, the structure was studied using a model of a quasi-molecular cluster [18]. Such approaches were accompanied by the need to construct four clusters (at 8, 27, 56 and 64 atoms) (Fig. 1), which greatly complicates the calculation and increases its duration. However, the results with acceptable accuracy describe the investigated values and allow us to speak about their reliability.

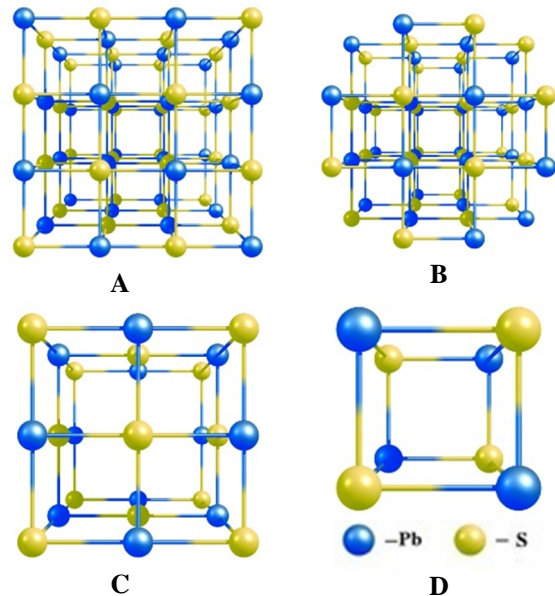


Fig. 1. Cluster model A ($Pb_{32}S_{32}$), B ($Pb_{28}S_{28}$), C ($Pb_{14}S_{13}$) and D (Pb_4S_4) for PbS in cubic phase.

The study of surface effects requires the use of new approaches to modeling structures. Such attempts have

already been made by the authors [7], [8], [11], [19] and proved themselves, since the obtained results are well consistent with each other and are reproducible and applicable to all investigated structures such as NaCl. The above studies were carried out in the plane (111) (Fig. 2), since this approach allows using a smaller simulation cell.

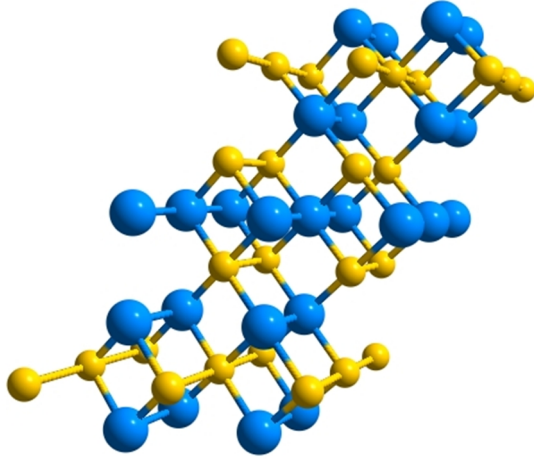


Fig. 2. Structure of PbS, constructed in the framework of the octopolar approximation in the direction (111) for the calculation of the surface energy.

Surface energy g determines the state of equilibrium between the surface and the external environment and is determined by the dependence [1]:

$$g(T, p) = \frac{G(T, p, \{n_x\}) - \sum_i n_x \mu_x(T, p_x)}{A}, \quad (3)$$

where G is Gibbs free energy of the solid phase of investigated surface, A is the surface area of the two-dimensional elementary cell, n_x – number of x particles in solids, μ_x and p_x – chemical potentials and pressure of certain parts of the mixture in the gas phase, respectively. For simplicity, the authors [10] assumed the following approximations: vibration of the zero point, oscillatory contributions to entropy; the Gibbs free energy are approximated by the total energy calculated in the framework of the density functional theory. Thus, finding the most stable surface will require unlimited minimization of surface energy, which is almost impossible to accomplish. Therefore, the calculation of surface energy, as a function of the chemical potential of one of the components was made. In this case, the model with a lower free energy of the surface than the value of the chemical potential of the component can be considered a thermodynamically stable phase.

The superficial energy of nonstoichiometric crystals depends on the chemical potentials of the elements in compound. With notions of thermodynamic equilibrium [12]: $m_{Pb} + m_S = E_{PbS}^{(bulk)}$, where $E_{PbS}^{(bulk)}$ – this is the value for one formula unit of which there are four in the elementary cell. Both potentials are separated by the energy of the corresponding chemical elements in a stable allotrope (volumetric structure for a plumbum and

a trigonal α -model for tellurium). Consequently, the chemical potential of tellurium should obey the following conditions: $E_{PbS}^{(bulk)} - E_{Te}^{(bulk)} < m_{Pb} < E_{Pb}^{(bulk)}$.

Taking into account the previous expressions, the surface energy γ can be defined as a function of the chemical potential in the following way:

$$g = \frac{1}{2A} \left[E^{(slab)} - N_S E^{(bulk)} - (N_{Pb} - N_S) m_{Pb} \right] \quad (4)$$

The N_{Pb} and N_S – is the number of corresponding atoms in the model, and A is the surface area of the top and bottom of the model. This equation can describe a phase diagram of a surface at zero temperature. In the study [12] of the model in any direction (001), (010) or (100) the number of atoms N_{Pb} and N_S is the same, and hence the third term will be zero. On the phase diagram, such surfaces are depicted by a straight horizontal line.

Changing of the crystal's properties in the near-surface zone is primarily due to the displacement of the boundary atoms. The magnitude of this bias can be estimated by the ratio proposed Satta and de Gironcoli [3]:

$$\Delta z_i = \frac{z_i^S - z_i^{Pb}}{d_0}, \quad (5)$$

z_i – position of the atom, located on the i^{th} layer (deducing layers relative to the surface, that is, the surface layer will be the first and followed by all the others in ascending order) along [001], d_0 – the distance between the A and B atoms in the optimized structure.

Conclusions

The thin films' surface is not ideal, so its properties will differ significantly from the properties of the massive part of the film. The surface of the films is a significant correction to the determination of their physical and chemical properties, and for thin films it is decisive in comparison with the contribution of the film material volume. Since the regularity in the formation of surface irregularities is seen, then the computer simulations should be used to study such structures. The methods of LDA and GGA are capable of describing the properties of the surface layer of lead telluride thin films. The prospect of such studies is to model and rearrange the surface of films based on binary semiconductors.

A key characteristic of the octopolar model that treats the crystal in the direction (111) is that the surface layer of the atoms consists only of atoms of the same type, in contrast to the structures which consider the directions along the axes. The incomplete surfaces of such crystals consist of an equal number of lead and sulfur atoms. The requirement of symmetry and electroneutrality forces to determine the place of the discontinuity of the slab at the level of atoms of the same variety.

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Розрахунок стабільності і перебудова поверхні кристалів в рамках DFT-обчислень

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Поверхня плівок не є ідеальною, отже її властивості будуть суттєво відрізнятися від властивостей масивної частини плівки. Оскільки проглядається закономірність у формуванні нерівностей поверхні, то до вивчення таких структур можна використати можливості комп'ютерного моделювання. Для відтворення поверхні кристалів зі структурою NaCl можна застосувати ті ж підходи в моделюванні властивостей, що і для оксидів металів. Принципова відмінність від попередніх досліджень полягає в тому, що розглядають структуру в напрямку (111), оскільки такі припущення дозволяють використовувати меншу симуляційну комірку для комп'ютерних розрахунків, що значно прискорює їх. Здійснено апробацію методики перебудови поверхні тонких плівок плумбум сульфід.

Ключові слова: плумбум сульфід, DFT, методи комп'ютерної квантової хімії, перебудова поверхні тонких плівок.