Band structure calculation of GaSe-based nanostructures using empirical pseudopotential method

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Abstract. In this paper we present the results of band structure computer simulation of GaSe-based nanostructures using the empirical pseudopotential method. Calculations were performed using a specially developed software that allows performing simulations using cluster computing. Application of this method significantly reduces the demands on computing resources compared to traditional approaches based on ab-initio techniques and provides receiving the adequate comparable results. The use of cluster computing allows to obtain information for structures that require an explicit account of a significant number of atoms, such as quantum dots and quantum pillars.

1. Introduction

Layered semiconductors AIIIBVI groups (e.g., gallium selenide GaSe, gallium sulfide GaS, etc.) are widely used as nonlinear elements in laser technology. In this list, the crystalline GaSe is especially allocated because it is used as a second harmonic generator in CO2 laser [1,2]. Despite this, the applicability of this material, due to a limited spectral operation range, is not so wide, as it may be expected. In recent years, due to the significant advances in the study of another layered material - graphene, the interest to such material grows back. This is one of the reasons for a new direction of work on the synthesis, a comprehensive study and practical application of nanostructured materials based on GaSe. The layer structure similar to graphite, makes it relatively easy to tear the individual layers for obtaining the samples consisting of one or few layers. Recently several new works dedicated to this subject have been published [3,4,5]. Nevertheless this area is still insufficiently investigated.

This work aims to study the band structure of nanomaterials based on gallium selenide using the method of empirical pseudopotential. The main idea is to demonstrate the size effects observed in this area for further experimental work on the fine tuning of optical properties and broaden the application range of GaSe in laser technology.
2. Computation methods

Computer modeling was carried out using the method of empirical pseudopotential, which belongs to a group of techniques in which the effective potential in the one-electron Schrödinger equation in part is parameterized so that the obtained values of the energy and electron wave functions of electron states reproduced the experimental data.

The method is the solution of the pseudo wave Schrödinger equation:

\[
\left[-\frac{1}{2}\Delta + V_{ps}(\vec{r})\right] \varphi_{ps,j}(\vec{r}) = \epsilon_j \varphi_{ps,j}(\vec{r}),
\]

where \(V_{ps}(\vec{r})\) – pseudopotential of crystal, \(\varphi_{ps,j}(\vec{r})\) – one-electron pseudo wave functions, \(\epsilon_j\) – electron eigenvalue energies.

Pseudo wave function is represented as an expansion in plane waves:

\[
\varphi_{ps}(\vec{r},\vec{k}) = \sum_{\nu} C_{\nu} e^{i(\vec{k} + \vec{G}_\nu) \cdot \vec{r}},
\]

where \(\vec{k}\) – electron wave vector, \(M\) – plane wave number, \(C_{\nu}\) – coefficients of expansion, \(\vec{G}_\nu\) - reciprocal lattice vectors. By substituting (2) at (1) and multiplying scalar on \(e^{i(\vec{k} + \vec{G}_\nu) \cdot \vec{r}}\) we obtain secular equation:

\[
\det \left\{ \left[ (\vec{k} + \vec{G}_\nu)^2 - \epsilon(\vec{k}) \right] \delta_{m,n} + V_{ps}^{m,n} \right\} = 0,
\]

where \(V_{ps}^{m,n}\) - the matrix element of the pseudopotential operator.

\[
V_{ps}^{m,n} \equiv V_{ps}(\vec{G}_m - \vec{G}_n) \equiv \frac{1}{\Omega} \int e^{-i\vec{q}\cdot\vec{r}} V_{ps}(\vec{r}) d\vec{r},
\]

where \(\Omega\) – crystal volume, \(\vec{q} = \vec{G}_m - \vec{G}_n\). Crystal pseudopotential is represented as a superposition of atomic pseudopotentials and represented as:

\[
V_{ps}^{m,n} = \frac{1}{N} \sum_{i=1}^{N} \exp(-i\vec{q}\cdot\vec{r}) FF_i(\vec{q})
\]

where \(N\) – amount of atoms in crystal basis, \(FF_i(\vec{q})\) - form factor of i-th atom:

\[
FF_i(\vec{q}) = \frac{c_i^4 (|\vec{q}|^2 - c_i^2)}{\exp(c_i^4 (|\vec{q}|^2 - c_i^4)) + 1}\cdot \lambda,
\]

where \(c_i\) – empirical coefficients of pseudopotential for the i-th atom, \(\lambda\) – normalization factor.

Thus, substituting (6), (5) and (4) in the secular equation (3) and solving it, it is possible to obtain electronic dispersion curves for investigated material.

The above described approach allows simulation of a wide range of materials, including various nanostructures, with the method of supercell [6]. At the same time, the usage of this approach for calculation of nanomaterial parameters, especially those, requiring an explicit consideration of significant numbers of atoms (quantum dots, disks, pillars, and layered materials such as gallium selenide) encounters significant problems in the large Hamiltonian matrices requiring huge amounts of computer memory. This problem is a major difficulty in the simulation of quantum dots and quantum pillars of gallium selenide and other layered semiconductors. To solve the problem the computer algorithm parallel computation was implemented where eigenvectors and eigenvalues of the Hamiltonian matrix were obtained by filling and diagonalizing matrix in a part using a large number of cluster supercomputer nodes [7]. Implement of this approach on computational center K100 which located in the M.V. Keldysh IPM made it possible to take into account up to 10^7 atoms in the system.

The next problem of the method applicability is a significant dependence of adequacy of the obtained results on the used pseudopotential parameters. In case of crystalline GaS, the pseudopotential parameters providing a good coincidence with the experimental data have been
published [8,9]. However, the research carried out for the nanostructures based on these materials have shown that the quality of electron dispersion relations is not sufficient for the practical applicability of the results. The work for optimization of the pseudopotential parameters for Ga and Se was needed.

The problem was solved by developing an algorithm of pseudopotential parameters $C^k_i$ variation for performing the minimization of deviation function of electronic dispersion dependences for a bulk crystal and for a single layer of GaSe, obtained by the empirical pseudopotential method, and the reference data published in the literature [10]. A gradientless method of finding a local minimum has been used for optimization [11]. The obtained pseudopotential parameters are provided in Table 1.

Table 1. A comparison of parameters of atomic pseudopotentials presented in the literature and obtained by optimization.

| Atom | Source          | C1  | C2  | C3  | C4  |
|------|----------------|-----|-----|-----|-----|
| Ga   | Schlüter [9]   | 0.21| 2.75| 0.6 | 3.0 |
|      | Optimization   | 0.545| 2.870| 1.867| 0.255|
| Se   | Schlüter [9]   | 0.27| 3.45| 0.42| 1.86|
|      | Optimization   | 0.332| 2.305| 1.655| 2.553|

The optimization results listed above have been used for calculations of band structure of nanomaterials based on GaSe. In the simulation, the number of plane waves of M used for the expansion of electronic wave vector was selected based on the cut-off energy of 14 Ry. The expansion involved the plane waves with energy lower than the cut-off energy.

3. Results and discussions

The main objective of this work was the modeling of band structure of different types of nanomaterials, based on layered semiconductor GaSe. Figure 1 shows the electronic dispersion relations for the bulk crystal of GaSe, calculated by the method based on density functional theory (Fig. 1) [12] and the empirical pseudopotential described above, using the pseudopotential parameters listed in Table 1 (Fig. 2).

From obtained dependence it can be seen that the width of the direct band gap for bulk β-GaSe, calculated by method based on the electron density functional theory, and obtained in this work are significantly different. The bandgap in Figure 1 is 0.8 eV, while in figure 2 it is 1.8 eV. At the same time, the experimental data published in literature demonstrate a band gap of 2.1 eV [13]. Thus, a method based on the electron density functional theory, significantly lowers the bandgap (by more than 1 eV). This prevents the use of this method for predicting the optical properties of the material. At the same time, the method used in this work shows the band gap value which is much closer to the experimental values.

The next step of the work was modeling various types of nanostructured materials based on gallium selenide. Figure 3 shows the band structure of one- and two-layered GaSe, calculated by the method of empirical pseudopotential.

From the obtained dependence it can be seen that the width of the indirect band gap for a single layer of gallium selenide is 2.11 eV. This value is in a good agreement with published data [12]. Also, a ring-shape dependence of the dispersion in valence band on k-vector can be seen from Figures. This is completely similar to data shown in [14].

Thus, a good agreement between results obtained with the abovementioned method, the published experimental and theoretical data, have been obtained. Thus, a promising possibility of this approach to simulate different nanostructures with the explicit account of a considerable number of atoms along with much less requirements for computational resources than the widely used methods (including those based on electron density functional theory and GW-approximation) and the possibility of performing calculations on cluster supercomputers have been demonstrated.
Figure 1. The band structure of $\beta$-GaSe, calculated by the electron density functional method [12].

Figure 2. The electronic structure of $\beta$-GaSe, calculated by the method of empirical pseudopotential.

Figure 3. The band structure of a single-layer (right) and a double layer (left) of gallium selenide, calculated by the method of empirical pseudopotential.

4. Conclusions
In the work the numerical simulation of the band structure of different types of nanostructures based on layered gallium selenide has been performed. The calculation was performed using the method of empirical pseudopotential. The parameters of gallium and selenium atomic pseudopotentials have been optimized in this paper for the best reproduction of published experimental data. The results showed a good agreement with the experimental data for a variety of structures, along with the significantly lower requirements for computing resources than the widely used ab-initio methods, and made this method more prospective for such structures modeling.
During the work a computer program implementing this approach has been developed allowing using both personal computers and clusters with the distributed memory supercomputers. This significantly extends the application range of the method (allows one to explicitly take into account the significant number of atoms). Because the program is developed in a general way, one can use it for a wide range of different materials.

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