

Ab Initio Calculations of Optical Constants of GaSe and InSe Layered Crystals

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Abstract—The dielectric functions, refractive indices, and extinction coefficients of GaSe and InSe layered crystals have been calculated within the density functional theory. The calculations have been performed for the values of theoretical structural parameters optimized using the exchange-correlation functional, which allows one to take into account the dispersion interactions. It has been found that optical functions are characterized by the most pronounced polarization anisotropy in the range of photon energies of ~4–7 eV. The frequency dependences for InSe compound in the range up to 4 eV demonstrate the more pronounced anisotropy as compared to GaSe. The results obtained for GaSe crystal agree better with the experimental data as compared to the previous calculations.

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1. INTRODUCTION

Compounds GaSe and InSe possess the clearly pronounced anisotropic characteristics being of interest from the viewpoint of their application in the field of nonlinear optics and optoelectronics, particularly, to generate monochromatic [1] and broadband [2–4] terahertz radiation and develop the sources for systems of near-field IR nanoscopy [5, 6], photodetectors, and detectors of ionizing radiations. Due to the layered structure, mechanical stresses arising as a consequence of the lattice mismatch rapidly relax in these compounds, which makes them the promising materials to apply the van der Waals epitaxy [7].

Theoretical investigations into the electronic and mechanical properties of InSe and GaSe crystals were performed with the necessary completeness in [8–11] and earlier studies with the use of both pseudopotential approximation and full-potential methods. To date, there are the calculated data on the elastic constants and parameters of electronic spectra for single crystals of InSe, GaSe, and a number of $\text{Ga}_{1-x}\text{In}_x\text{Se}$ solid solutions including the obtained estimations of the position of the local charge neutrality level in GaSe [8]. However, despite the primary importance of the knowledge of optical constants for applying III–VI crystals, their theoretical evaluations were absent up to date. There is only one published work in the literature [12] devoted to the first-principles calculation of dispersion dependences of gallium selenide optical constants. The theoretical investigations into the optical characteristics of indium selenide apparently were not performed previously. At the same time, the computational approaches and new exchange-correlation

functionals proposed in recent years [13–15] allow us to describe the electronic properties of crystals with van der Waals bonds more accurately. In this study, we calculated the optical constants in the fundamental absorption and optical transparency regions of InSe and GaSe compounds using the methods of the density functional theory (DFT).

2. COMPUTATIONAL PROCEDURE

Almost all previously published theoretical investigations of structural characteristics of III–VI compounds were performed in terms of the local density approximation (LDA) or generalized gradient approximation (GGA). These approximations give the quite satisfactory results when calculating lattice parameters and binding energies of semiconductors, for example, of III–V family, which crystallize in the sphalerite and wurtzite structures. However, LDA and GGA are unable to describe the van der Waals interaction playing an important role in layered compounds and molecular crystals, which leads to the errors in corresponding quantum-chemical calculations for InSe and GaSe.

In order to obtain more accurate results, we use the recently developed method for the account of van der Waals interactions within the electron density functional theory (vdW-DF) [13, 14], in which the expression for the exchange-correlation energy is written as

$$E_{xc} = E_x^{GGA} + E_c^{LDA} + E_c^{nl}. \quad (1)$$

Summands in the right side of (1) are, correspondingly, the exchange energy in the GGA approximation, LDA correlation energy, and a nonlocal correction for the correlation energy:

$$E_c^{nl} = \iint d\mathbf{r}d\mathbf{r}'n(\mathbf{r})\varphi(\mathbf{r}, \mathbf{r}')n(\mathbf{r}'), \quad (2)$$

where $\varphi(\mathbf{r}, \mathbf{r}')$ is a certain function, which depends on the difference of coordinates $\mathbf{r} - \mathbf{r}'$, electron density $n(\mathbf{r})$, and its gradient; and determines the dispersion energy of interacting fragments of the many-electron system. The authors of [13] proposed the expression for $\varphi(\mathbf{r}, \mathbf{r}')$, which is suitable for systems of arbitrary geometry and provides the required asymptotic behavior of $O(-1/|\mathbf{r} - \mathbf{r}'|^6)$ at large values of $|\mathbf{r} - \mathbf{r}'|$.

Functionals constructed according to formula (1) were called the van der Waals density functionals; they are currently actively used when studying adsorption processes and energy characteristics of molecular and crystalline systems. It should be noted that vdW-DF method is an important theoretical development since the description of the dispersion interaction is included immediately into the expression for DFT total energy in this approach, and correlations for all distance ranges are taken into account in one formula.

Since different GGA variants are proposed in literature, the selection of expression for the first term in (1) is ambiguous. In this study, to calculate the structural parameters of InSe and GaSe compounds, we used the vdW-DF2(C09_x) functional including exchange term C09_x proposed by Cooper [15] with the purpose to correct the systematic overestimation of interatomic distances in calculations with the revPBE functional, which was considered in the initial study by Dion et al. [13]. The structure was optimized in the Quantum ESPRESSO package [16] using the projector-augmented wave (PAW) method to take into account the electron–ion interaction, which provides high accuracy of calculations of the total energy and interatomic forces. Calculation parameters (the plane wave cut-off energy and the density of k -point mesh for the integration over the Brillouin zone) were selected so that to provide a sufficiently high convergence level.

The calculations of the frequency dependence of the imaginary part of dielectric function $\varepsilon_2(\omega)$ have been performed for the optimized structures using a fine grid $30 \times 30 \times 7$ according to the expression

$$\varepsilon_2(\omega) = \frac{4\pi^2 e^2}{m^2 \omega^2} \sum_{v, c} \int_{\text{BZ}} \frac{2d\mathbf{k}}{(2\pi)^3} |\mathbf{u} \mathbf{p}_{vc}(\mathbf{k})|^2 \times \delta(E_c(\mathbf{k}) - E_v(\mathbf{k}) - \hbar\omega), \quad (3)$$

where $E_c(\mathbf{k}) - E_v(\mathbf{k})$ is the magnitude of the direct band-to-band transition in point \mathbf{k} , $\mathbf{p}_{vc}(\mathbf{k})$ is the matrix element of the momentum operator, and \mathbf{u} is the polarization vector of the electromagnetic wave. In

order to compensate the underestimation of the band gap E_g in DFT calculations, conduction bands were shifted upward in energy to fit the experimental value of E_g (2.01 and 1.26 eV at room temperature for GaSe and InSe, respectively). Real part $\varepsilon_1(\omega)$ was obtained using the Kramers–Kronig transformation. To calculate optical functions, we employed the SIESTA package [17], which implements the computation method in the localized basis with the use of norm-conserving pseudopotentials.

3. RESULTS AND DISCUSSION

3.1. Crystal Structure of GaSe and InSe

Layered crystals of the III–VI family demonstrate the diversity of crystalline modifications caused by the possibility of different arrangement of the layers relative to each other. All layers have the identical internal structure, are characterized by hexagonal symmetry, and consist of four parallel atomic planes composed in sequence VI–III–III–VI, i.e., two internal planes of Group III atoms are sandwiched between the planes of group VI atoms. A strong covalent bond in VI–III–III–VI layers and weak interlayer van der Waals bond with a small ionic-covalent contribution lead to strong anisotropy of GaSe, InSe, and GaS properties—optical characteristics, conductivity, thermal conductivity, etc., which substantially differ in directions along the c -axis (perpendicular to the layer plane) and along the layers.

The most common crystallographic polymorphs of III–VI compounds are polytypes ε , β , γ , and δ described in publications (corresponding space groups $P\bar{6}m2$, $P6_3/mmc$, $R3m$, and $P6_3mc$) [18]. Polytypes ε , β , and δ possess the hexagonal lattice with the number of atoms in the unit cell from eight (ε , β) to 16 (δ), while the γ -phase is characterized by a rhombohedral lattice (four atoms in the unit cell). The GaSe single crystals grown by the Bridgman method usually have the structure of the ε -polytype with a small impurity of the γ -phase. Stable modifications of InSe are γ -phase and β -phase. In this study, we performed calculations for ε -GaSe and β -InSe, which are combined by a common type of the Bravais lattice with the same number of atoms in the unit cell. The corresponding unit cells are presented in Fig. 1.

Lattice constants a , c , and interlayer distance d_{inter} of ε -GaSe compound optimized using the vdW-DF2(C09_x) functional have the following values: $a = 3.761 \text{ \AA}$, $c = 15.943 \text{ \AA}$, and $d_{\text{inter}} = 3.189 \text{ \AA}$. These results excellently agree with the experimental data [19], according to which, $a = 3.743 \text{ \AA}$, $c = 15.919 \text{ \AA}$, and $d_{\text{inter}} = 3.184 \text{ \AA}$. We can easily see that theoretical values of c and d_{inter} are in the error limits of 0.16% as compared to the experiment, while the standard LDA approximation demonstrates deviations larger by an order of magnitude [10, 11]. The magnitude of con-

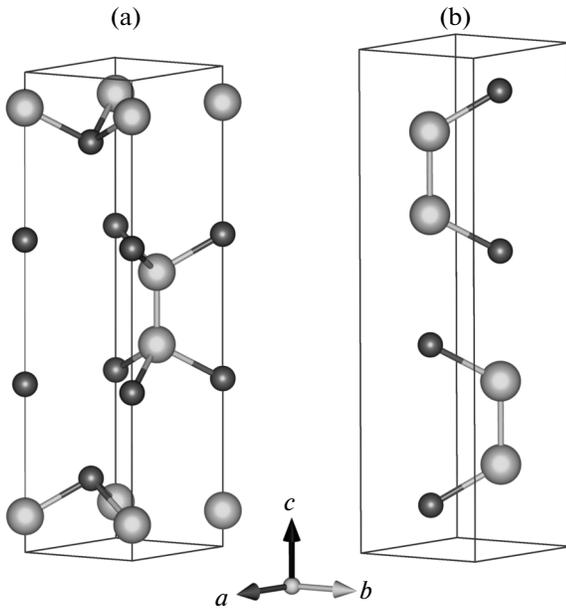


Fig. 1. Unit cells of (a) ϵ -GaSe crystals and (b) β -InSe crystals. Metal atoms are depicted by larger balls.

stant a is affected by interactions of Group III and VI atoms inside the layers, which have the covalent-ionic nature; therefore, the magnitude of a is reproduced well in terms of the LDA (for example, according to the LDA calculations using PAW potentials [10], $a(\text{GaSe}) = 3.715 \text{ \AA}$). However, the use of the van der

Waals functional allows to improve the correspondence with the experiment in this case as well.

According to our calculations for β -InSe phase, $a = 4.022 \text{ \AA}$, $c = 16.828 \text{ \AA}$, and $d_{\text{inter}} = 3.051 \text{ \AA}$. Due to the larger radius of indium atoms, lattice constants rise; however, the interlayer distance decreases by 0.14 \AA , which points to the higher interaction energy of the layers. In the case of indium selenide, the experimental data in literature are mainly presented for the γ -phase. Based on the data for GaSe compound, here we also expect high accuracy of the obtained theoretical results. This can be indirectly judged based on the closeness of our values for a and d_{inter} to the results of corresponding measurements for γ -InSe ($a = 4.002 \text{ \AA}$, $d_{\text{inter}} = 3.035 \text{ \AA}$ [20]) accounting for the closeness of these parameters in different polytypes.

3.2. Optical Properties

Dispersion dependences of the real and imaginary parts of permittivity $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ as well as the refractive indices $n(\omega)$ and extinction coefficients $k(\omega)$ of ϵ -GaSe and β -InSe crystals obtained in our calculations are presented in Figs. 2 and 3. The results are presented for two polarizations of the optical radiation relative to the hexagonal axis (corresponds to ordinary $\mathbf{E} \perp \mathbf{c}$ and extraordinary $\mathbf{E} \parallel \mathbf{c}$ waves in the crystal). It is seen from Figs. 2 and 3 that optical functions of compounds under study possess the strongest dependence on the direction of vector \mathbf{E} of the electromagnetic wave in the range of $\sim 4\text{--}7 \text{ eV}$. The InSe compound demonstrates the more pronounced polar-

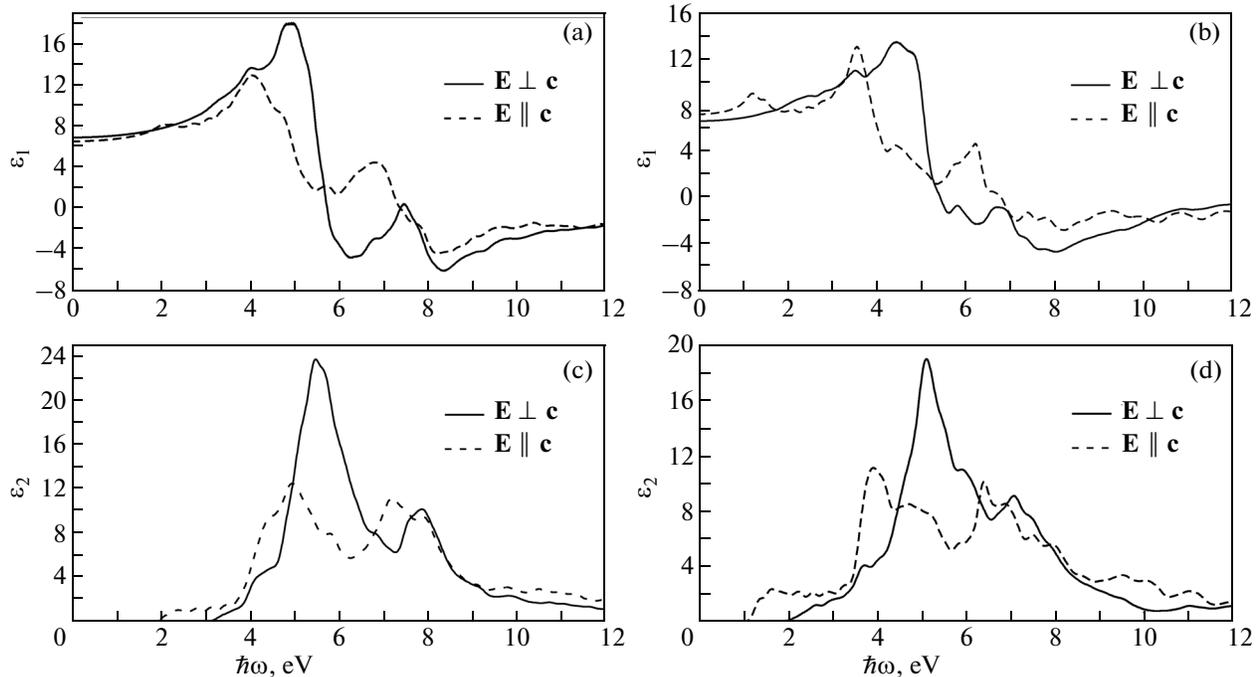


Fig. 2. Real ϵ_1 and imaginary ϵ_2 components of permittivity of (a, c) ϵ -GaSe and (b, d) β -InSe crystals.

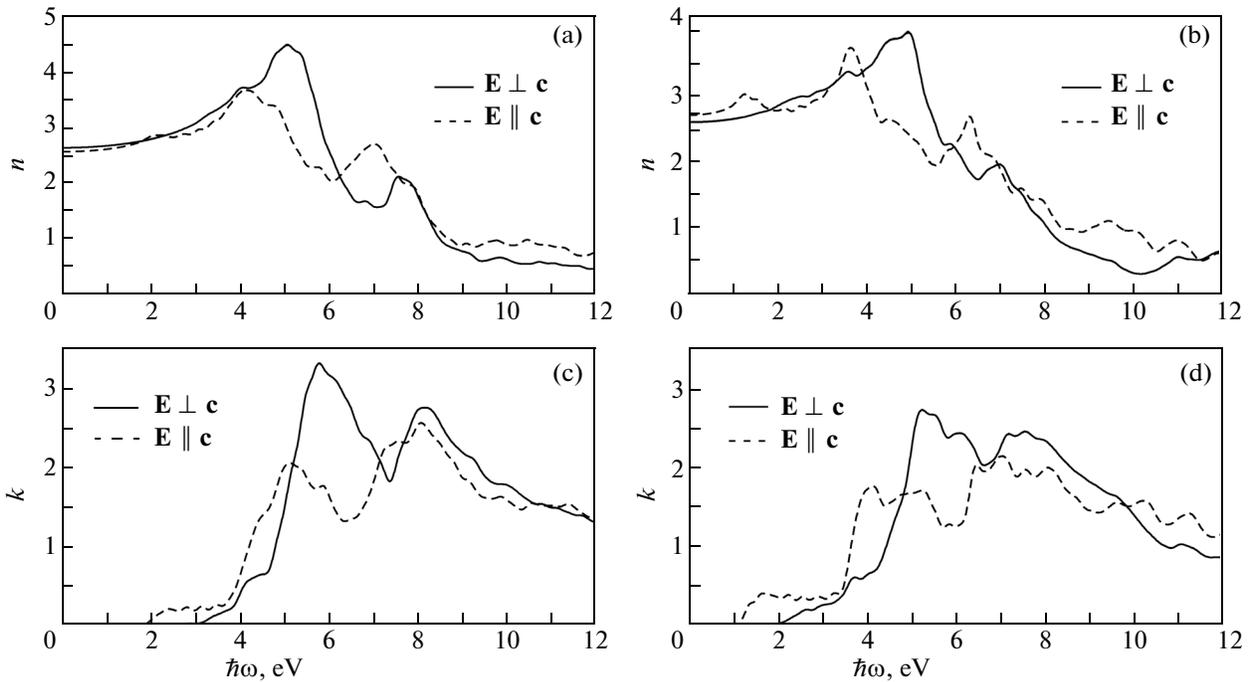


Fig. 3. Refractive indices n and extinction coefficients k of (a, c) ε -GaSe and (b, d) β -InSe crystals.

ization anisotropy as compared to the GaSe compound in the range to 4 eV. Based on numerous electronic structure calculations [8–11], the features in the range of 4–7 eV can be attributed to interband transitions between the levels of the upper valence band formed by the hybridization of p_x, p_y -states of Se with p -states of metal and lower levels of the conduction band.

Unfortunately, there is no theoretical data on the optical properties of InSe crystal in the literature, with which we could compare our calculations. Only one article [12] is published for GaSe, the results of which are qualitatively close to our results. At the same time, there is a number of quantitative distinctions. For example, according to our calculations, the absorbance gets the substantially larger values in the range of photon energies of 6–10 eV. The authors of [12] also obtained clearly underestimated and almost equal to zero birefringence in the transparency region of the GaSe crystal (~ 0.001 in a long-wavelength limit). According to the most verified data [21], the refractive index of gallium selenide at a wavelength of $1.24 \mu\text{m}$ is 2.778 for the ordinary wave and 2.441 for the extraordinary wave. Our values are 2.708 and 2.646, respectively, and determine birefringence $\Delta n = n_e - n_o = -0.062$, which is the more acceptable result as compared to [12] and, according to the experiment, characterizes the GaSe crystal as a negative single-axis crystal.

Optical and dielectric properties of GaSe crystals were investigated experimentally in recent studies [22, 23]. The most informative results were obtained in

[23], where the spectra of pseudodielectric function $\langle \varepsilon \rangle = \langle \varepsilon_1 \rangle + i\langle \varepsilon_2 \rangle$ and complex refractive index $\langle N \rangle = \langle n \rangle + i\langle k \rangle$ in the range up to 6.5 eV were measured at room temperature by optical ellipsometry. There are two pronounced peaks in the region of photon energies of 3.5–3.7 and 4.6–5 eV in the experimental spectra of n and k (for the case $\mathbf{E} \perp \mathbf{c}$) [22, 23]. The direct comparison shows that the shape and intensity of main peaks in theoretical spectra (Figs. 2, 3) are in good agreement with the data [23]. Indeed, peak intensities in spectra of $\langle \varepsilon_1 \rangle$, $\langle \varepsilon_2 \rangle$, $\langle n \rangle$, and $\langle k \rangle$ in experiment [23] constitute 17.7 (at 4.6 eV), 26.0 (5.0 eV), 4.6 (4.7 eV), and 3.5 (5.1 eV), respectively; where the position of maxima over the energy scale is indicated in parentheses. According to our calculations, the heights of fundamental peaks of ε_1 , ε_2 , n , and k for polarization $\mathbf{E} \perp \mathbf{c}$ have values 18.2 (at energy of 5.0 eV), 23.8 (5.5 eV), 4.5 (5.1 eV), and 3.3 (5.8 eV). It is seen from the comparison of the presented magnitudes that the theoretical peaks are shifted by 0.4–0.7 eV into the higher energy region. There are divergences with the results [22] by the magnitude of extrema, but we should take into account that the measurements in [22] were performed for GaSe crystals doped with tellurium.

Among the obtained disagreements, we should note the underestimated peak height in the spectrum of the extinction coefficient in the range of ~ 4 eV as compared to the experiment [23]. This underestimation and observed small deviations of peak positions are probably associated with inaccuracies of the ran-

dom phase approximation (RPA), in terms of which, the dielectric functions were calculated.

There are considerably fewer experimental data for the InSe compound than for the GaSe compound. According to [24], the values of refractive index for the extraordinary wave in InSe crystal in the transparency region are smaller than the refractive indices for the ordinary wave as in the case of GaSe crystal. However, our calculated data contradict these results. It is possible that this is associated with the fact that the measurements [24] were performed for the γ -polytype of InSe or the studied sample, which was grown from the $\text{In}_{1.05}\text{Se}_{0.95}$ nonstoichiometric melt with phosphorus additives, had a more complex structure. In any case, due to the smallness of birefringence in InSe crystal (according to [24], the magnitude of Δn is about -0.03 at $T = 20^\circ\text{C}$), further experimental investigations, which could clarify this question, are desirable.

Despite a number of described disagreements, our calculations reproduce well the important dielectric characteristics of GaSe and InSe. The calculated values of static permittivity $\varepsilon_1^{\parallel} = 6.77$ and $\varepsilon_1^{\perp} = 7.15$ of GaSe crystal are comparable with the results of measurements $\varepsilon_1^{\parallel} = 6.1 \pm 0.3$ [24] and $\varepsilon_1^{\perp} \sim 7.4$ [23] (the last value is obtained by extrapolation). In the case of InSe, the theory predicts $\varepsilon_1^{\parallel} = 7.52$ and $\varepsilon_1^{\perp} = 6.93$. The computed magnitude of $\varepsilon_1^{\parallel}$ is in good agreement with the experimental value of $\varepsilon_1^{\parallel} = 7.6 \pm 0.4$ determined in [24].

4. CONCLUSIONS

Structural characteristics of InSe and GaSe crystals are calculated using new approximations of the density functional theory, which allow to perform the quantitative account of dispersion interactions. It is shown that the inclusion of the nonlocal correction for the correlation energy into the expression for the total energy in terms of DFT allows us to substantially increase the accuracy of calculations of the interlayer distance and, consequently, constant c of studied compounds. Dispersion dependences of the real and imaginary parts of permittivity, as well as the refractive indices and extinction coefficients, are calculated for the optimized structures. Optical functions of InSe compound are calculated for the first time. In the case of GaSe compound, the considerably better correspondence with the experimental data is attained as compared to the previous calculations. According to our results, the spectra of optical functions for GaSe and InSe crystals possess considerable polarization anisotropy being qualitatively close to each other. The heights of fundamental peaks in the spectra of InSe are smaller as compared to the GaSe.

Our results can be used when analyzing the experimental data for GaSe and InSe single crystals and represent the starting point for the theoretical investigation into the optical characteristics of other semiconductors of this group.

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