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Ab initio calculations and experimental study of the electronic properties of $CdGa_2S_4$ single crystals by spectral ellipsometry

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Received September 23, 2021
Revised September 23, 2021
Accepted November 6, 2021

The electronic properties of $CdGa_2S_4$ single crystals have been studied experimentally using spectral ellipsometry and theoretically from first principles using density functional theory (DFT). Using ellipsometric studies in the energy range of 0.7−6.5 eV, the imaginary and real parts of the dielectric function along and perpendicular to the optical axis, the dispersion of the refractive, extinction, and absorption coefficients are determined. The width of the direct band gap is estimated. The band structure, the origin of the energy states, the optical functions, and the partial densities of states (PDOS) projected onto the atoms are determined by *ab initio* calculations. The theoretically calculated results are compared with the experimental data of the present work obtained by the method of spectral ellipsometry and with the experimental results available in the literature.

Keywords: spectral ellipsometry, ellipsometric angles, dielectric function, refractive index, extinction coefficient, Brillouin zone, band structure.

DOI: 10.21883/PSS.2022.03.53190.211

1. Introduction

Single crystals of $CdGa_2S_4$ belong to the group of compounds $A^{II}B_2^{III}C_4^{VI}$ (A — Zn, Cd; B — In, Ga; C — S, Se, Te), attracting the attention of researchers in connection with the possibility of their use in semiconductor instrumentation [1]. These compounds are characterized by birefringence, significant values of the coefficient of nonlinear susceptibility, and bright photoluminescence [2]. Owing to their large band gap (2−4.0 eV) and high photosensitivity, they are the basis for the development of ultraviolet radiation detectors used in medicine, biology, space physics, and other fields. Crystals of the $A^{II}B_2^{III}C_4^{VI}$ group, and $CdGa_2S_4$, in particular, are promising materials for creating tunable narrow-band optical filters due to the presence of the so-called „isotropic point", at which the dispersion curves of the ordinary and extraordinary refractive indices intersect [3]. Recently, $CdGa_2S_4$ and $CdGa_2Se_4$ crystals have been positioned as materials for solar batteries [4].

The band gap of $CdGa_2S_4$ has been experimentally studied in papers [5–7]. In [5] the band gap E_g of $CdGa_2S_4$ single crystals, determined from studies of absorption spectra, turned out to be 3.5 eV at 300 K, and in [6,7] the band gap of $CdGa_2S_4$, also determined from studies of absorption spectra at 300 K, is defined as 3.43 and 3.15 eV, respectively.

For the first time, the band gap was theoretically calculated by the pseudopotential method [8], and a value of 3.43 eV was obtained for the direct band gap. Further theoretical calculations of the electronic band structure were made *ab initio*. In the paper [9], the results of calculations in the local density approximation (LDA) are presented, and the corrected value of the direct band gap at the Γ point is obtained — 3.3 eV. Based on *ab initio* calculations of the electronic and optical properties of $CdGa_2S_4$ by the DFT method, the papers [10,11] present the values of the direct band gap at the point Γ — 2.118 and 2.2 eV, respectively. There are the calculated real parts of static dielectric constants in the work [10] $\varepsilon_1(0)_\perp = 4.292$, $\varepsilon_1(0)_\parallel = 4.229$, and the refractive indices are $n(0)_\perp = 2.072$ and $n(0)_\parallel = 2.056$. Some different values of the calculated real parts of the static dielectric constants are presented in [11]: $\varepsilon_1(0)_\perp = 7.32$, $\varepsilon_1(0)_\parallel = 5.35$, and the refractive indices $n(0)_\perp = 2.70$ and $n(0)_\parallel = 2.31$.

Thus, despite the large amount of experimental data on $CdGa_2S_4$ crystals, there is a scatter in the literature in the values of the main optical parameters (band gap, dielectric constants, refractive indices, and etc.), which requires additional research. This article presents the results of an experimental and theoretical study of the electronic band structure and optical properties of $CdGa_2S_4$ single crystals. For experimental studies, the spectral ellipsometry method was used, which is one of the

accurate methods for determining the optical characteristics of crystals.

2. Experiment

Samples for measurements were synthesized from the initial components Cd, Ga, and S, taken in a stoichiometric ratio in graphitized quartz ampoules. The growth of single crystals was carried out by the method of gas transport reactions, crystalline iodine was used as a transporter.

X-ray diffraction studies were carried out on a Bruker D8 Advance instrument. $CdGa_2S_4$ crystallizes in a tetragonal structure with space group $\overline{I}4$. The samples had the shape of a rectangular parallelepiped with dimensions of approximately $8 \times 3 \times 3$ mm. The tetragonal axis was directed along the largest dimension. The unit cell parameters determined from X-ray diffraction data [12] and the optimized equilibrium values of these parameters from theoretical calculations are given in Table 1.

The Raman spectra of $CdGa_2S_4$ were measured on a Nanofinder 30 confocal Raman microspectrometer (Tokyo Instr., Japan). An Nd:YAG laser with an output wavelength at the second harmonic $\lambda = 532$ nm and a maximum power of 10 mW was used as an excitation source. The spectral resolution when using a diffraction grating 1800 lines/mm was no worse than 0.5 cm^{-1}. The scattered radiation detector was a cooled (thermoelectrically up to $-100°C$) CCD-camera (1024×128 pixels) operating in the photon counting mode. Raman spectra were measured in backscattering geometry.

The characterization of $CdGa_2S_4$ samples by X-ray diffraction and Raman scattering testifies to the high quality of the samples and is described in detail in a previous work [15].

To study the optical characteristics of $CdGa_2S_4$ crystals, we carried out spectral ellipsometric studies based on determining the change in the polarization state of light as a result of its interaction with the crystal surface upon reflection. The measurements were carried out on an optical range ellipsometer M-2000 DI (J.A. Woollam Co, Inc.). The spectral dependence of the ellipsometric parameters Δ and Ψ was recorded in the photon energy range of 0.7–6.5 eV with a step of 50 meV at angles of incidence in the range of 60°–75° in step 5°.

Table 1. Structural parameters of $CdGa_2S_4$

a, Å	c, Å	c/a	Literature
5.56	10.00	1.799	[13]
5.536	10.16	1.835	[14]
5.644	10.347	1.833	[10]
5.55	10.19	1.834	given work (experiment)
5.4272	9.9297	1.8296	given work (theory)

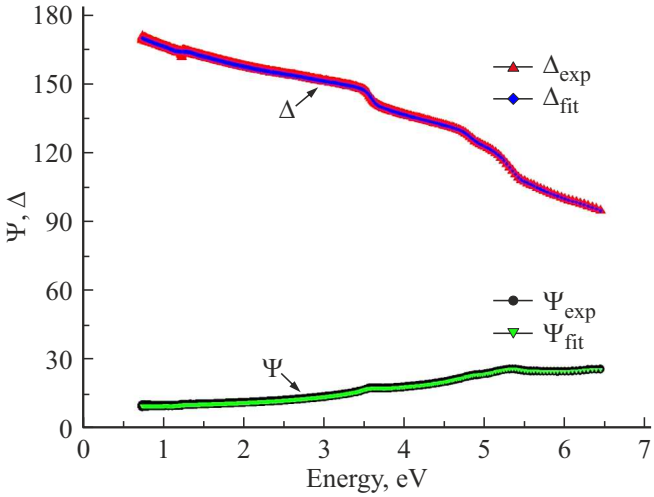

Figure 1. Experimental and calculated data of ellipsometric parameters Ψ and Δ for $CdGa_2S_4$ in the energy range 0.7–6.5 eV.

The basic equation of ellipsometry, which relates the ellipsometric parameters Δ, Ψ and the complex-valued Fresnel reflection coefficients r_p and r_s, for p- and s-components of elliptically polarized light, is written in the form [16,17]:

$$\mathrm{tg}(\Psi)\exp(\mathrm{i}\Delta) = \frac{r_p}{r_s}. \quad (1)$$

Experimental and calculated data of the ellipsometric parameters Ψ and Δ for $CdGa_2S_4$ in the energy range 0.7–6.5 eV are shown in Fig. 1.

The values of optical characteristics calculated from ellipsometric measurements (real and imaginary parts of the dielectric function, extinction and absorption coefficients, and refractive index) will be given below together with the data of theoretical calculations *ab initio*.

3. Calculation method

Ab initio calculations of electronic and optical properties were carried out on the basis of DFT [18] using the method of full potential linearized augmented plane waves (FP-LAPW) [19], implemented in the program code Wien2k [20]. The exchange-correlation interaction was described in the generalized gradient approximation (GGA) [21]. The radii of the muffin-tin (MT) spheres were chosen to be 2.5 a.u. for Cd, 2 a.u. for Ga and S. The expansions of the potential and charge density inside MT spheres were made with $l_{max} = 10$. In the expansion of the basis functions, $R_{MT}K_{max} = 7$ was used, which determines the number of basis functions, where R_{MT} is the smallest of all radii of atomic sphere, and K_{max} is the maximum wave vector of a plane wave. For self-consistent calculations, 186 k-points in the irreducible part of the Brillouin zone (BZ) were used, which corresponds to 1500 k-points in BZ. Self-consistent calculations

continued until the convergence of the total energy was reached 10^{-4} Ry.

4. Electronic structure and optical functions

The band structure and projected onto atoms partial densities of states (PDOS) are shown in Figs. 2 and 3, respectively. The band structure of $CdGa_2S_4$ (Fig. 2) has a number of characteristic features: the valence band conventionally consists of five subbands. The lowest subband, in fact, these are dispersionless states of about -14 eV, which owe their origin mainly to the *d*-states of the Ga1 and Ga2 atoms, the contribution of which is not quite equivalent — the contribution of *d*-states. There are more than 3 fold more of Ga1 atoms, with some contribution from *s*-states of chalcogen S atoms. The second subband is a group of valence bands between energies -13 and -11 eV, which originate from *s*-states of chalcogen S atoms and *d*-states of Ga1 and Ga2 atoms (Fig. 3). As follows from the PDOS (Fig. 3), almost dispersionless states near -7 eV owe their origin to the *d*-states of Cd atoms. An analysis of the partial density of states shows that the group of valence bands in the energy range approximately from -6.5 to -4.5 eV comes from *s*-states of Ga1 and Ga2, as well as *p*-states of chalcogen S atoms.

And finally, the uppermost group of valence bands can be assigned to *p*-states of chalcogen S atoms with a small contribution of *p*- and *d*-states of Cd and *p*-states of Ga1 and Ga2.

The top of the valence band and the absolute minimum of the conduction band are located at the point Γ and, so $CdGa_2S_4$ is a direct-gap semiconductor with a band gap of ~ 2.2 eV. This value is close to the values 2.118 eV [10] and 2.2 eV [11] calculated earlier *ab initio*, but is significantly lower than the experimentally determined 3.3–3.5 eV. It is well known that DFT underestimates the band gaps, including those in these crystals. The paper [9] reviews data on band gaps in compounds of defective chalcopyrites of the $A^{II}B_2^{III}C_4^{VI}$ group (*A* — Zn, Cd, Hg; *B* — Al, In, Ga; *C* — S, Se, Te) and there is a significant discrepancy between the values theoretically calculated *ab initio* by the LDA method and experimentally determined. It is noted that the reason is that the local exchange-correlation potential v_{xc} is replaced by a non-local self-energy operator Σ_{xc}, and the empirical band gap correction outside the local density approximation gives good agreement between theoretically calculated and experimentally determined data.

It is also seen from the partial density of states that the bottom of the conduction band consists mainly of *s*-states of Ga1 and Ga2 atoms with some addition of *p*-states of S atoms.

Comparison of the calculated band structure with experimental studies of optical properties allows us to verify

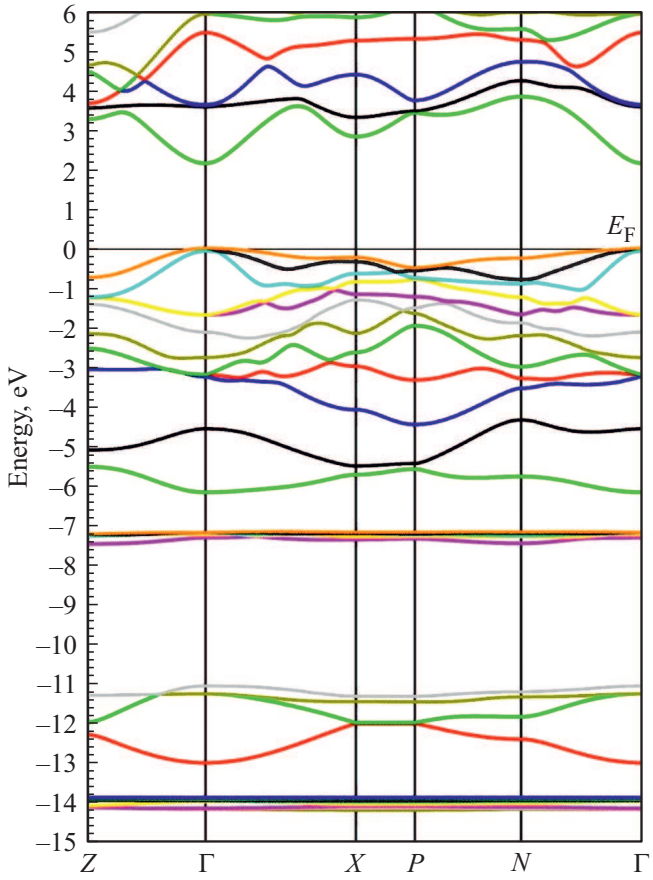

Figure 2. Band structure of $CdGa_2S_4$.

the correctness of our band structure. The eigenvalues and eigenvectors obtained from band structure calculations were used to determine the real and imaginary parts of the dielectric function, the extinction and absorption coefficients, and the refractive index. The optical functions of $CdGa_2S_4$ calculated *ab initio* and experimentally measured by spectral ellipsometry are shown in Figs. 4, 5 and 6. Note that only direct transitions that conserve momentum are included in our calculations for optical properties. Indirect transitions involving phonons have a very weak effect on the absorption edge, since $CdGa_2S_4$ is a direct-gap semiconductor.

Calculated *ab initio* in the spectral region 0–15 eV and experimentally measured in the photon energy region 0.7–6.5 eV, the real and imaginary parts of the dielectric function $CdGa_2S_4$ for different polarizations of the incident light (along and perpendicular to the tetragonal axis *c*) are shown in Fig. 4.

The main peaks of the calculated real and imaginary parts are located around 3.4 and 5.5 eV, respectively. Using the known values of the real $\mathrm{Re}\varepsilon(\varepsilon_r)$ and imaginary $\mathrm{Im}\varepsilon(\varepsilon_i)$ parts of the dielectric function ε for $CdGa_2S_4$ crystals, we calculated the refractive indices *n* and extinction

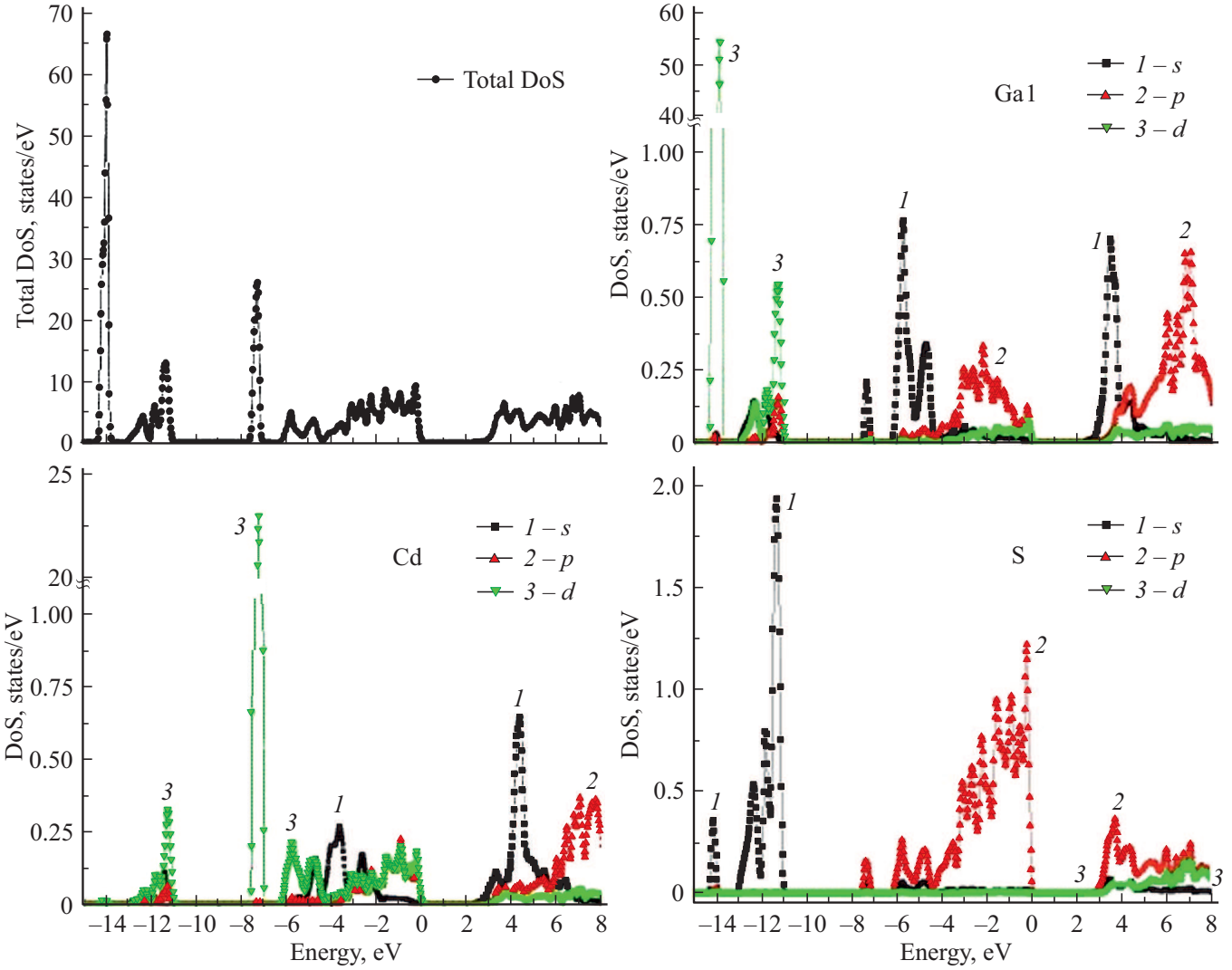

Figure 3. Total (DoS) and partial densities of states (PDOS) of Cd, Ga, and S atoms. The Fermi level corresponds to zero energy.

coefficient k, respectively, using formulas (2) and (3):

$$n = \sqrt{\frac{\varepsilon_r + \sqrt{\varepsilon_r^2 + \varepsilon_i^2}}{2}}, \qquad (2)$$

$$k = \frac{\varepsilon_i}{\sqrt{2\left(\varepsilon_r + \sqrt{\varepsilon_r^2 + \varepsilon_i^2}\right)}}, \qquad (3)$$

Figure 5 shows the data obtained experimentally (curves *1*) and calculated from the first principles (curves *2*) of refractive indices n (Fig. 5, *a* and *b*) and extinction coefficients k (Fig. 5, *c* and *d*) along ($\parallel$) and perpendicular ($\perp$) to the tetragonal axis c in a wide energy range.

Note that the measured refractive indices in the case of $E \perp c$ and $E \parallel c$ $n_\perp$ and $n_\parallel$ (curves *1*, Fig. 5, *a* and *b*), as well as theoretically calculated ones (curves *2*, Fig. 5, *a* and *b*), show the same dependences $n \perp (E)$ and $n \parallel (E)$, do not show significant anisotropy and reach a maximum of about 3.5 eV. The theoretical values of the static refractive indices $n_\perp(0)$ and $n_\parallel(0)$ (the value of the refractive index at zero energy) are ~ 2.5. Measured extinction coefficients in the case of $E \perp c$ and $E \parallel c$ — $k_\perp$ and $k_\parallel$ (curves *1*), Fig. 5, *c* and *d*), as well as theoretically calculated ones (curves *2*, Fig. 5, *c* and *d*), show the same dependences $k_\perp(E)$ and $k_\parallel(E)$ numerically coincide up to the energy 5 eV; in this case, the positions of singularities on the dependences $k(E)$ coincide at energies 3.6 and 4.8 eV. We also note that no significant anisotropy of the extinction coefficients $k_\perp(E)$ and $k_\parallel(E)$ is observed either. Table 2 lists some optical parameters of $CdGa_2S_4$.

To calculate the absorption coefficient α, we used the relation:

$$\alpha = 4\pi k/\lambda. \qquad (4)$$

Here, k is the extinction coefficient, and λ is the wavelength.

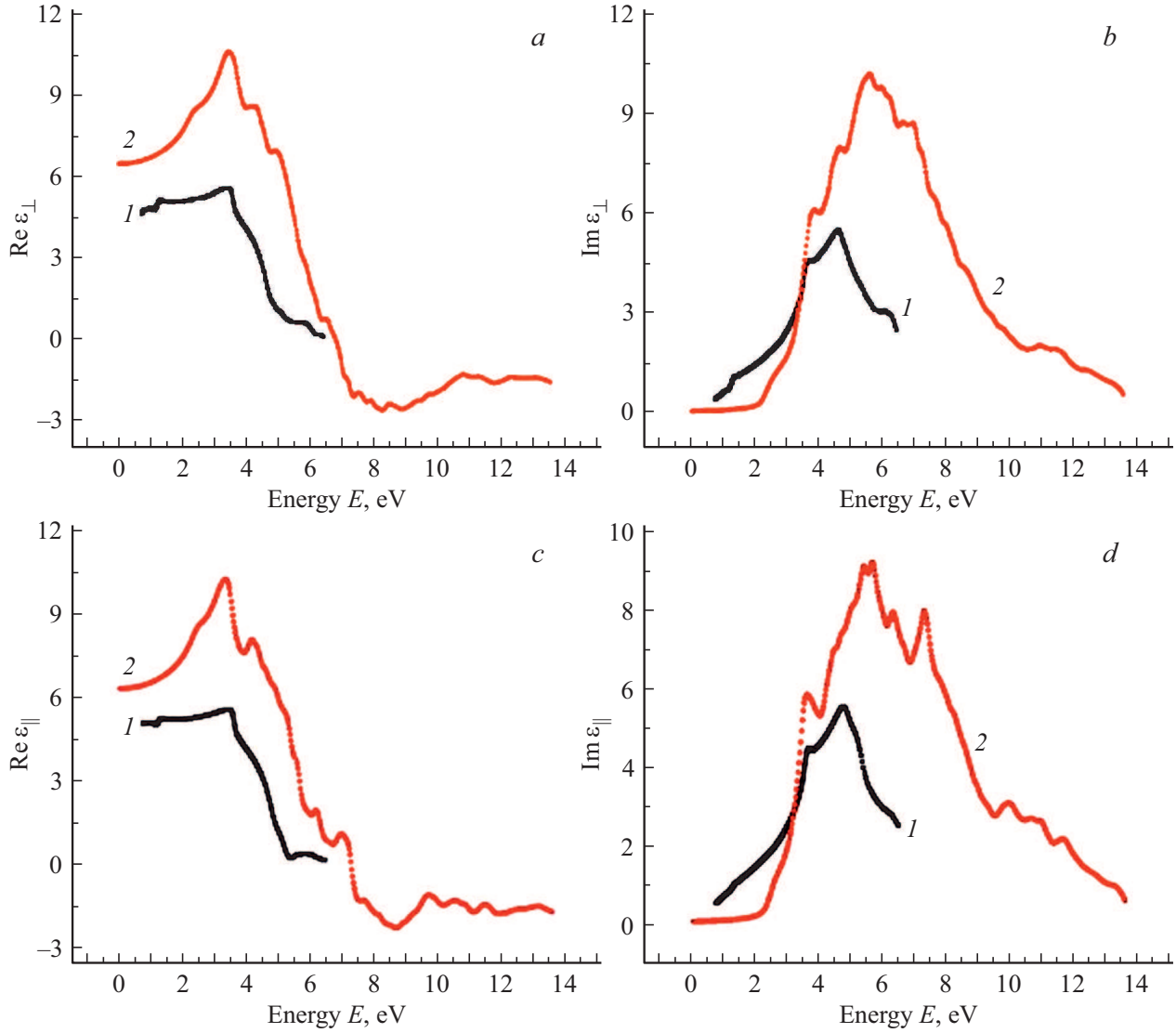

Figure 4. Real and imaginary parts of the dielectric function $CdGa_2S_4$ (*1* — experiment, *2* – theory; ∥ — along the tetragonal axis *c*, ⊥ — perpendicular to the tetragonal axis *c*).

Table 2. Some optical parameters of $CdGa_2S_4$

$\varepsilon_1(0)_\perp$	$\varepsilon_1(0)_\parallel$	$n(0)_\perp$	$n(0)_\parallel$	Literature
4.292	4.229	2.072	2.056	[10]
7.32	5.35	2.70	2.31	[11]
6.473	6.307	2.544	2.511	given work (theory)

Figure 6 shows the experimentally measured (curves *1*) and *ab initio* calculated (curves *2*) values of the absorption coefficient α (Fig. 6, *a* and *b*) calculated from (4).

High absorption coefficient α ($10^4-10^5\,cm^{-1}$), its sharp increase in the energy range of 1.5–4 eV indicate the direct allowed nature of the band gap. For a direct-gap transition, the dependence of the absorption coefficient on the photon energy is as follows:

$$\alpha\hbar\nu \sim (E_g - \hbar\nu)^{1/2}. \quad (5)$$

Extrapolation from relation (5) allowed us to estimate the widths of the direct band gap of $CdGa_2S_4$ single crystals along ($E \parallel c$) and perpendicular ($E \perp c$) to the tetragonal axis (Fig. 6, *c* and *d*). It turned out to be equal to 3.27 eV (for $E \parallel c$) and 3.31 eV (for $E \perp c$), respectively, which agrees with experimental data from measurements of absorption spectra [5–7].

5. Conclusion

We have carried out experimental studies of the optical properties of $CdGa_2S_4$ single crystals along (∥) and

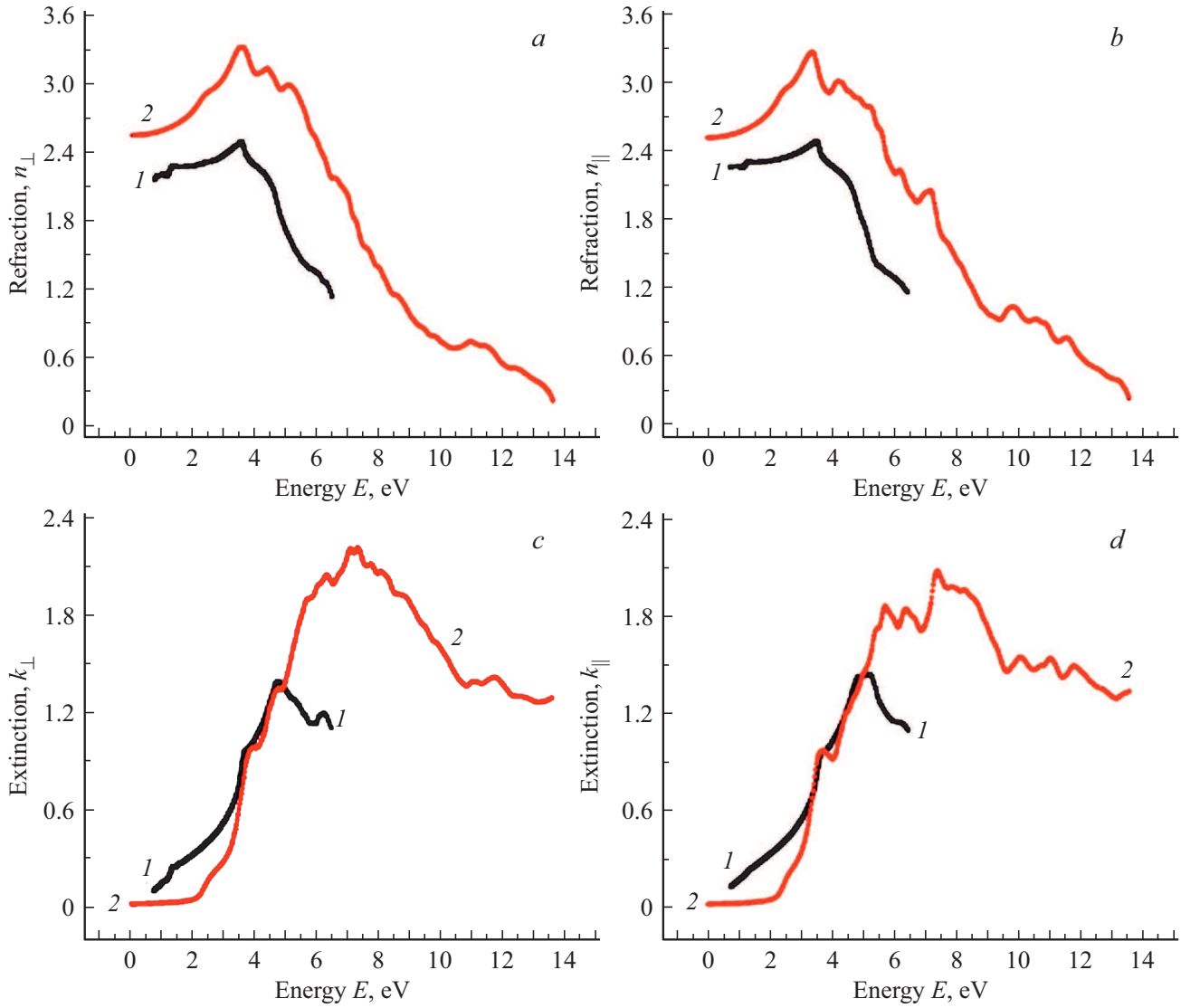

Figure 5. Refractive index n and extinction coefficient k for $CdGa_2S_4$.

perpendicular ($\perp$) to the tetragonal axis c in wide energy range of 0.7–6.5 eV by spectral ellipsometry, the results of which were compared with *ab initio* calculations of the electronic structure and optical functions. From the data of ellipsometric measurements, the real and imaginary parts of the dielectric function, refractive index, extinction and absorption coefficients were determined. The experimental results show that $CdGa_2S_4$ is an allowed direct gap semiconductor with a band gap $\sim 3.3-3.4$ eV.

Using DFT, the electronic band structure of $CdGa_2S_4$ crystals and the partial densities of states (PDOS) projected onto cadmium, gallium, and sulfur atoms are determined. It is shown that the theoretically obtained results agree satisfactorily with the experimentally determined values.

Acknowledgments

The authors consider it their duty to express their gratitude to A.S. Bondyakov (JINR, Russia) and D.A. Kuliyev (Institute of Physics of the National Academy of Sciences of Azerbaijan), as well as to the entire staff of the data center of the Institute of Physics of the National Academy of Sciences of Azerbaijan, for provided resources and technical support for theoretical calculations.

Funding

The work was supported financially by the Foundation for the Development of Science under the President of the Republic of Azerbaijan (grant No. EIF-BGM-3-BRFTF-2+/2017-15/02/1).

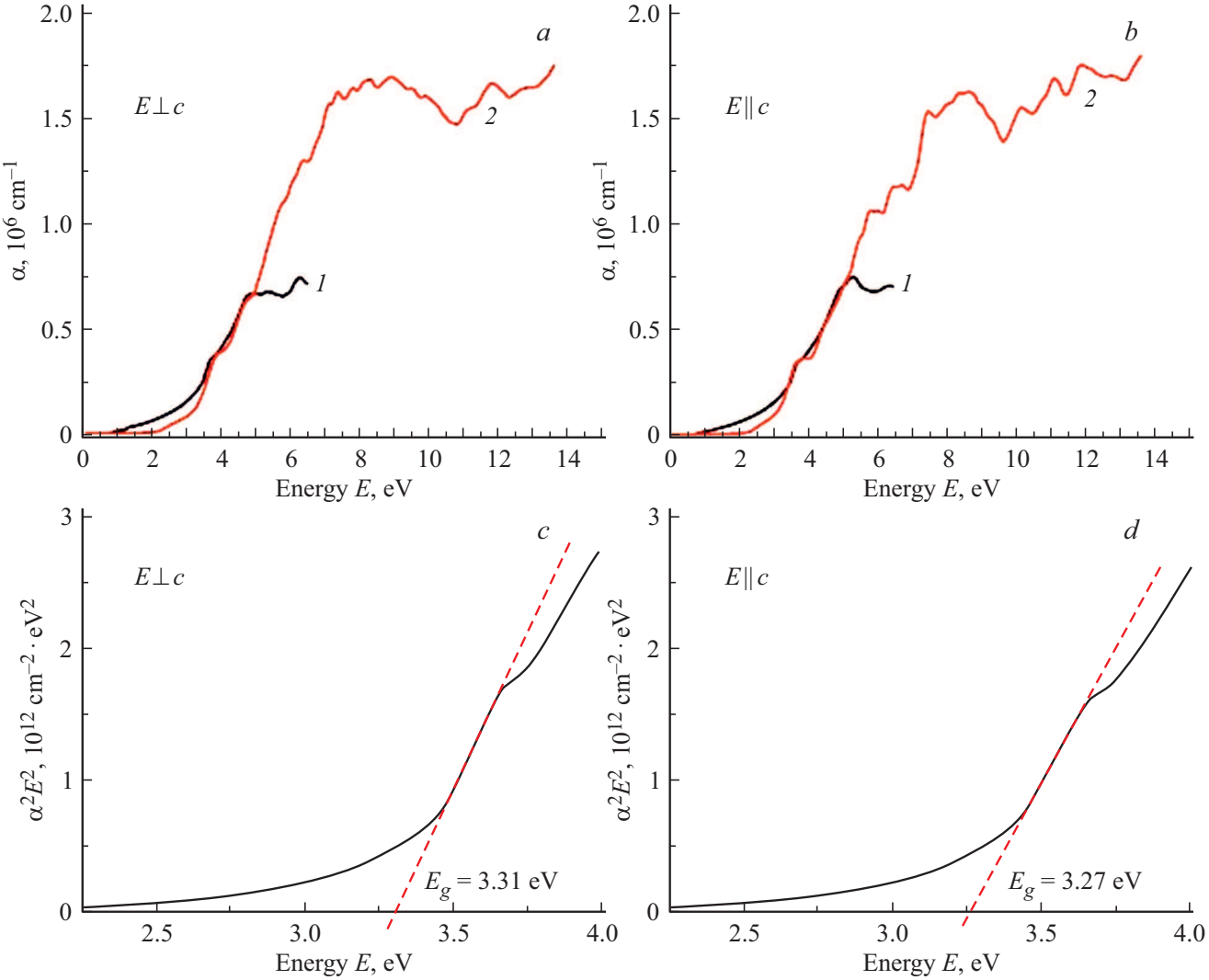

Figure 6. Absorption coefficient α (*a* and *b*) and $\alpha^2E^2(E)$ (*c* and *d*) for $CdGa_2S_4$.

Conflict of interest

The authors declare that they have no conflict of interest.

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