First-principles calculations of the electronic, optical and elastic properties of CdIn$_2$S$_4$ thiospinel at ambient and elevated pressure

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Abstract
CdIn$_2$S$_4$ thiospinel was studied by means of first-principles calculations in both generalized gradient and local density approximations (GGA and LDA). One of the main results of this paper is that the controversy regarding the character of the CdIn$_2$S$_4$ band gap previously encountered in the literature was clearly resolved in favor of the indirect gap. The calculated density of states was compared with the experimental XPS spectrum; very good agreement was demonstrated. The structural, electronic, optical and elastic properties were calculated in the pressure range of 0 to 10 GPa, below the pressure of phase transition for this compound. The estimated pressure coefficient of the band gap of 0.071/0.063 eV GPa$^{-1}$ (GGA/LDA) is in excellent agreement with the experimental data of 0.076 or 0.069 eV GPa$^{-1}$ found in the literature. The calculated pressure dependence of the unit cell volume follows the experimental results very closely. The dependence of the interionic distances, lattice parameter and all elastic constants on pressure was calculated. Refined estimations of the Debye temperature for CdIn$_2$S$_4$ are given as 280 K (LDA) and 252 K (GGA). The elastic anisotropy of CdIn$_2$S$_4$ was visualized by plotting the three-dimensional dependence of the Young’s modulus on a direction in the crystal lattice; it was established that the lowest Young’s moduli are realized if the external stress is applied along the crystallographic axes.

Keywords: spinel, first principles calculations, electronic structure, optical properties, elastic properties
1. Introduction

Crystals with a spinel structure form a very large group of compounds with very diverse properties. They can be often encountered in nature, occurring as pure or mixed minerals all over the globe, forming a very important part of the Earth’s mantle and, as such, providing scientists with information about the geological evolution of minerals and their behavior under extreme conditions, such as extremely high pressure and/or temperature. Besides this, spinels are also significant from the point of view of technological applications. Many representatives of this group of compounds are typical semiconductors with a rather narrow band gap (this is true especially for spinels containing halogen atoms), whereas oxygen-based spinels possess wider band gaps, which opens the possibility of easy and efficient doping with rare earth and transition metal ions. For example, MgAl₂O₄:Co²⁺, ZnGa₂O₄:Co²⁺ and MgAl₂O₄:Ni²⁺ spinels were shown to be promising materials for solid state lasers [1, 2]. Spinel-based transparent ceramics were also designed recently for high-energy laser systems [3]. Highly efficient luminescent materials based on spinel compounds have been also reported [4–6]; the application of spinels in diagnostics as fluorescence markers has been noted [7]. It should also be mentioned that rare-earth-ion-doped spinels possess electrical conductivity, magnetic and semiconducting properties that can be potentially used in spintronics [8]. These examples (even being grouped into this very short list, which is not exhaustive and is far from complete, as reviewing the properties of all spinels is not the aim of the present paper) show the undoubtedly great potential and importance of this group of materials.

We shall focus our attention on one member of the thiospinel (here thio refers to sulfur) subgroup of a much larger spinel group, namely cadmoindite (cadmium indium sulfide), with the chemical formula CdIn₂S₄. It is a chalcogenide semiconductor that belongs to the AB₂X₄ family of ternary compounds (A and B are metals in the II and III oxidation states, respectively (II: Cd, Mg, Mn, Zn; III: Al, Ga, In) or in the II and IV oxidation states (IV: Si, Ge, Sn), and X usually stands for oxygen or a chalcogen [9–12]).

The thiospinel subfamily forms an interesting group of materials for optoelectronic applications, which stem from their nonlinear optical properties. Their crystal structure is characterized by a partial degree of cation inversion, which leads to a high concentration of antisite defects. The concentration of these defects can be adjusted by varying the external pressure, which makes thiospinels the materials of choice for defect engineering applications [13]. Furthermore, indium thiospinels have been recently proposed as ideal materials for photovoltaic cells operating with an intermediate band. The unusual physical properties of thiospinels are of interest because they present a new type of the metal-insulator transition [14, 15] and a pressure-induced superconductor-insulator transition [16].

In the last few years, there has been increasing interest in understanding the behavior of materials under compression based on calculations or measurements, as this provides an insight into the nature of solid state theories and determines the values of fundamental parameters [17]. This applies especially to the compounds from the spinel family as well as to the thiospinel subfamily [9, 18, 19].

Cadmium indium sulfide is currently used for optoelectronic applications as a photoconductor [19]. This compound is also considered to be a promising candidate for intermediate-band (IB) formation, because its band gap lies in the region of optimum gaps for the implementation of an IB material [20]. Also, CdIn₂S₄ and a similar compound of MgIn₂S₄ attract more and more attention because they are visible-light-driven (VLD) photosensitive
semiconductors that can be used in solar cells [21–23], hydrogen evolution [24] and the degradation of organic dyes such as MB (Methylene Blue) [25], indicating that they may represent new VLD photocatalysts for bacterial inactivation [26].

CdIn$_2$S$_4$ has been known for a long time, being the subject of many experimental [22, 26–28] and theoretical works [18, 19, 29–32]. Several reports on its optical properties, e.g. photoluminescence, absorption, reflectivity and Raman scattering, can be found in the literature [27, 33–38]. Its electronic properties have been also studied [33, 39–42]. Furthermore, the elastic, electronic and optical properties of the MgIn$_2$S$_4$ and CdIn$_2$S$_4$ spinels have been investigated by Semari et al [19]. More recently Bouhemadou et al [18] have considered the influence of pressure on the thermodynamic properties of MgIn$_2$S$_4$ and CdIn$_2$S$_4$ compounds.

At the same time, although CdIn$_2$S$_4$ has been studied by several experimental and theoretical groups, still there exists some controversy regarding its physical properties such as band gap character (direct or indirect), pressure coefficients of the band gap value and Debye temperature. These so-far-ambiguously defined properties will be mentioned below in the main body of the article.

Therefore, the main goal of this paper is to clarify those questionable issues and gain more information on how some macroscopic parameters are affected by applied hydrostatic pressure, with subsequent comparison of the obtained results with the corresponding experimental and theoretical data available in the literature. With this aim, we have carried out density functional calculations in order to model the pressure effects on the structural, elastic and thermodynamic properties of CdIn$_2$S$_4$.

The presented results are structured as follows: the details of the crystal structure and calculating settings are all given in the next section. Then the electronic and optical properties (including a comparison with the experimental XPS spectra) are presented, followed by the pressure-affected changes of the physical properties of CdIn$_2$S$_4$. The paper is concluded with a summary of the most important results.

2. Crystal structure and details of calculations

As a typical member of the spinel group, cadmium indium sulfide CdIn$_2$S$_4$ crystallizes in the $Fd\bar{d}$ – $\bar{3}m$S cubic space group, no. 227. In this structure, the A and B atoms occupy the tetra- and octahedral sites, respectively [43]. Each X anion is bonded to three B cations located at the octahedral sites and with only one A cation located at each tetrahedral site [9]. In other words, each In cation is surrounded by six S anions and each Cd cation is surrounded by four S anions. Figure 1 shows one unit cell of CdIn$_2$S$_4$, with the explicitly indicated coordination of cadmium, indium and sulfur ions.

All presented calculations were performed using the CASTEP module [44] of the Materials Studio software. The initial structural data needed for the optimization of the crystal structure were taken from reference [12]. To ensure consistency and a better compatibility of the obtained results and subsequent conclusions, two independent computational runs were made, using both the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof functional [45] and the local density approximation (LDA) with the Ceperley–Alder–Perdew–Zunger (CA–PZ) functional [46, 47]. Since no defects have been considered, the calculations were performed for a primitive cell.
The plane-wave basis energy cutoff was chosen to be 350 eV. The Monkhorst–Pack scheme $k$-points grid sampling was set at $9 \times 9 \times 9$ for the Brillouin zone. The convergence parameters were set as follows: total energy tolerance $-5 \times 10^{-6}$ eV atom$^{-1}$, maximum force tolerance 0.01 eV nm$^{-1}$, maximum stress 0.02 GPa and maximum displacement $5 \times 10^{-4}$ Å. The electronic configurations were 4d$^{10}$5s$^2$ for Cd, 4d$^{10}$5s$^2$5p$^1$ for In and 3s$^2$3p$^4$ for S. The effect of hydrostatic pressure on the structural parameters of CdIn$_2$S$_4$ at zero temperature has been investigated in the pressure range up to 10 GPa with a step of 2 GPa. A complete optimization of the structural parameters was performed at each pressure.

3. Results of calculations: structural, electronic and optical properties at the ambient pressure

The structural parameters of CdIn$_2$S$_4$, along with the band gap values, are summarized in table 1, which offers a comparison of our calculated data with other corresponding results found in the literature. The agreement between the lattice constants calculated in the present work and those from experiments at ambient pressure is very good; the calculated results are also consistent with those reported in references [9, 18, 19]. It can be noted that the GGA-obtained lattice constant is greater than the LDA-obtained one, which is a common observation for this type of calculation. The calculated fractional ionic positions (including that of the S anion) are also very close to the experimental results.

The calculated band gap is underestimated if compared to the experimental results, by about 1.2–1.4 eV. This is a usual underestimation, which can be handled later on (when calculating the optical properties) in a standard way by introducing the scissor operator producing a rigid upward shift of the conduction band.

Figure 2 presents the calculated band structure of CdIn$_2$S$_4$, whereas the Brillouin zone for a primitive cell of CdIn$_2$S$_4$, indicating a path for the shown band structure, is depicted in figure 3.

The valence band is about 5 eV wide, whereas the conduction band width is about 6 eV. It should be pointed out that in the literature there is still some controversy regarding the character
Figure 2. The calculated band structure of CdIn$_2$S$_4$ (a), and an enlarged view of the band gap region (b).

Table 1. Summary of the structural and electronic properties of CdIn$_2$S$_4$.

|                                | LDA          | GGA          | Experiment | Calculated (other works) |
|--------------------------------|--------------|--------------|------------|--------------------------|
| Lattice constant, Å            | 10.78673     | 11.06467     | 10.853$^a$, 10.797$^b$, 10.8378$^c$, 10.7863$^e$, 11.107$^f$ |
| Unit cell volume, Å$^3$         | 1255.074     | 1354.613     | 1278.349$^a$, 1258.977$^b$, 1272.985$^c$ | 1254.924$^e$, 1370.220$^f$ |
| Cd–S distance, Å               | 2.5044       | 2.5814       | 2.54$^b$  |                          |
| In–S distance, Å               | 2.6028       | 2.6632       | 2.59$^b$  |                          |
| Band gap, eV                   | 1.212        | 1.047        | 2.35$^c$, 2.45$^d$, 2.02$^g$, 2.2$^h$ | 1.92$^f$, 1.12$^f$ |

Fractional ionic positions

|       | LDA          | GGA          | Experiment$^b$ |
|-------|--------------|--------------|----------------|
| x     | y     | z     | x     | y     | z     | x     | y     | z     |
| Cd    | 0     | 0     | 0   | 0     | 0     | 0     | 0     | 0     | 0     |
| In    | 0.625 | 0.625 | 0.625 | 0.625 | 0.625 | 0.625 | 0.625 | 0.625 | 0.625 |
| S     | 0.384 | 0.384 | 0.384 | 0.385 | 0.385 | 0.385 | 0.386 | 0.386 | 0.386 |

$^a$Reference [34].
$^b$Reference [12].
$^c$Reference [13] (Direct band gap was reported).
$^d$Reference [49] (Direct band gap was reported).
$^e$Reference [18].
$^f$Reference [19].
$^g$Reference [26].
$^h$Reference [40].
of the band gap. Some authors state that the CdIn$_2$S$_4$ is a direct band gap material [9, 13, 49], whereas others suggest an indirect character of the band gap in this spinel [19, 21, 40]. As is evidenced by figure 2(b), our calculated band structure places CdIn$_2$S$_4$ into the group of indirect band gap compounds, because the maximum of the valence band and the minimum of the conduction band are realized at different points of the Brillouin zone (K and G, respectively), in agreement with reference [19]. However, the difference between the energies of the top of the valence band at the K and G points is very small and is equal to only about 0.07 eV, which may affect the results and final conclusions of the experimental studies of the fundamental absorption of CdIn$_2$S$_4$.

The dispersion of the electronic states (figure 2(a)) shows a low mobility of the holes in the conduction band and a higher mobility of the electrons in the conduction band, especially in the vicinity of the Brillouin zone center G.

The composition of the electronic bands can be analyzed using the element-resolved density of states (DOS) diagrams (figure 4). The conduction band is mainly composed of the Cd and In 5s, 5p states, with an admixture of the S 3p states. It should be emphasized that the 5s states form the bottom of the conduction band, whereas the 5p states of In and the 3p states of S (due to the hybridization effects) tend to be located at the top of the conduction band. The S 3p states dominate in the upper part of the valence band; a minor contribution of the In and Cd 5s, 5p states to the valence band (especially its lower part, where the In 5s states are sharply peaked) can be also traced down. The completely filled Cd 4d states produce a narrow band at around −7.5 eV; the In 3d states are somewhat lower in energy at about −12 eV. Finally, the S 3s states are located somewhat deeper, stretching from −14 eV to −10 eV.

Figure 3. The Brillouin zone for a primitive cell of CdIn$_2$S$_4$ and a path from the band structure diagram. The coordinates of the special points of the Brillouin zone are (in terms of the reciprocal lattice unit vectors: W(0.5, 0.25, 0.75), L(0.5, 0.5, 0.5), G(0, 0, 0), X(0.5, 0, 0.5), K(0.375, 0.375, 0.750).
A reliable check of the calculated electronic band structure and DOS diagrams comes from experimental x-ray photoelectron spectroscopy (XPS). The experimental XPS spectra of CdIn$_2$S$_4$ were reported in references [50, 51]. They are compared with the sum of the partial density of states (PDOS) in figure 5.

The energy scales of the XPS spectra are shifted, as is done usually, to reach the best agreement with the relative features of the DOS distributions, which, in their turn, are drawn in respect to the valence band top. The sum of the PDOS was calculated by adding the contributions of individual chemical elements (Cd, In, S), each of which was multiplied by the number of atoms of a particular element in the chemical formula (1 for Cd, 2 for In, 4 for S). The spectra were normalized by the intensity of the most prominent feature in the considered spectral region.

The highest energy peak in the experimental XPS spectrum is located at about 17 eV; it is well reproduced by the In 4d states’ distribution; the Cd 4d states, which are located higher in energy, are in charge of the 10 eV peak in the XPS spectrum (figure 5(a)). The width of the low-energy part of the XPS spectrum (figure 5(b)) is very close to the width of the calculated...
valence band. The contribution of the sulfur 3p states determines the overall structure of this range of the experimental spectrum: the most intensive contribution (at about 2 eV) comes from the S 3p states located closer to the top of the valence band; other well-seen experimental features at about 2.5 and 5 eV follow the peculiar behavior of the 3p states distribution closer to the bottom of the valence band.

We also report here that the calculated values of the refractive index in the limit of infinite wavelengths are 2.25 (GGA) and 2.33 (LDA), which are in good agreement with the experimental result of 2.55 [33] and other calculated values of 2.4 [19] and 2.625, 2.893 [29].

Figure 6 exhibits a cross-section of the electron density difference in the plane, whose normal is along the \((-\frac{\sqrt{2}}{2}, 0, \frac{\sqrt{2}}{2})\) direction in the crystal lattice. As follows from figure 6, the Cd–S bond is more covalent than the In–S one, because the electron density distribution around In ions is more spherical and does not exhibit any directional dependence like the one for Cd. Such a conclusion is also confirmed by the PDOS diagrams (figure 4), which show the presence of the p electron density (transferred from the sulfur ions) on the cadmium ions.

4. Results of calculations: elastic and thermodynamic properties

The optimized crystal structure of the studied cadmoindite was used as an initial structure to calculate components of the elastic constants tensor; all calculating settings were kept the same as for the geometry optimization. Since CdIn$_2$S$_4$ is a cubic crystal, only three non-zero elastic constants, $C_{11}$, $C_{12}$, and $C_{44}$, are needed to describe completely the response of such a material to external stresses. The bulk modulus $B$ for a cubic crystal can be calculated as $B = (C_{11} + 2C_{12})/3$. The values of $C_{ij}$ and $B$, calculated at ambient pressure, are all collected in table 2. As a common observation, it can be noted that the LDA-calculated elastic constants are greater than their GGA counterparts. The stability criteria for a cubic crystal \( \left( \frac{1}{3}(C_{11} + 2C_{12}) > 0, C_{44} > 0, \frac{1}{2}(C_{11} - C_{12}) > 0 \right) \) [52] are all fulfilled, thus meaning that the cubic phase of CdIn$_2$S$_4$ is stable.

Very few experimental data on the CdIn$_2$S$_4$ elastic constants and bulk modulus exist in the literature. In particular, the $C_{ij}$ values reported here can be compared only to other theoretical estimations and only one experimental study (table 2). The calculated values of the bulk modulus at zero pressure (especially calculated by LDA) are in good agreement with the experimental result from reference [13].
Agreement between our and other calculated values of $C_{ij}$ is good. We also note that the experimental value of $C_{12}$ reported in reference [53] seems to be considerably underestimated.

In spite of the cubic crystal structure of CdIn$_2$S$_4$, its elastic properties exhibit certain anisotropy, which can be analyzed by plotting the three-dimensional dependence of the Young's modulus on the direction in the crystal lattice described by the following equation [54]:

$$E(\vec{n}) = \frac{1}{S_{11} - \beta(S_{11} - S_{12} - S_{14})},$$

(1)

where $\beta = 2S_{11} - 2S_{12} - S_{14}$.

The $S_{ij}$ entries in equation (1) are the elastic compliance constants, which form the matrix inverse to the matrix of the elastic constants $C_{ij}$, and $n_1$, $n_2$, $n_3$ are the direction cosines specifying the direction in the crystal lattice. In the case of a perfect elastically isotropic medium, equation (1) would describe a sphere. But in the case of CdIn$_2$S$_4$ such a surface deviates from the spherical shape, as is evidenced by figure 7. It turns out to have the shape of a cube with depressions at the center of each face, which indicates that the smallest Young's moduli are realized if the stress is applied along the crystallographic axes, whereas the (111) direction in the crystal lattice is characterized by the greatest Young's moduli values.

After the elastic constants are calculated, one can proceed with estimations of the sound velocities in a solid and its Debye temperature $\Theta_D$, related to the maximum phonon energy in the Debye model, using the following equation [55]:

$$\Theta_D = \frac{h}{k} \left[ \frac{3n}{4\pi M} \right]^{1/3} n_m,$$

(2)

where $h$ and $k$ are the Planck and Boltzmann constants, respectively, $N_A$ is the Avogadro number, $\rho$ is the crystal's density, $M$ is the molecular weight, and $n$ denotes the number of atoms per one formula unit. The $v_m$ entry is the mean sound velocity expressed in terms of the longitudinal $v_l$ and transverse $v_t$ sound velocities as [56]

$$v_m = \left[ \frac{1}{3} \left( \frac{2}{v_l^3} + \frac{1}{v_t^3} \right) \right]^{-1/3},$$

(3)

Table 2. Summary of the elastic properties of CdIn$_2$S$_4$.

|                  | Calculated (this work) | Calculated (other works) | Experiment |
|------------------|------------------------|--------------------------|------------|
|                  | GGA        | LDA        |              |            |
| $C_{11}$         | 77.55      | 100.01     | 96$^a$, 102.46$^b$ | 121.5$^c$  |
| $C_{12}$         | 55.51      | 65.73      | 69$^a$, 49.13$^b$ | 24.6$^c$   |
| $C_{13}$         | 34.59      | 38.21      | 38$^a$, 21.46$^b$ | 25.7$^c$   |
| $B$              | 62.86      | 77.15      | 78$^a$, 66.90$^b$ | 78$^d$     |

$^a$ Reference [18].
$^b$ Reference [19].
$^c$ Reference [53].
$^d$ Reference [13].
which, in their turn, are calculated as \[ v_i = \frac{3B \pm 4G}{3p}, \ v_i = \frac{G}{p}, \] with \( B \) being the bulk modulus and \( G = (G_V + G_R)/2 \) being the isotropic shear modulus estimated as the average value of the Voigt’s shear modulus \( G_V \) (an upper limit for \( G \) values) and the Reuss’s shear modulus \( G_R \) (a lower limit for \( G \) values). The \( G_V \) and \( G_R \) values are expressed in terms of the elastic constants \( C_{ij} \):

\[
G_V = \frac{C_{11} - C_{12} + 3C_{44}}{5}, \quad \frac{5}{G_R} = \frac{4}{C_{11} - C_{12}} + \frac{3}{C_{44}}. \tag{4}
\]

Using equations (2)–(4), we estimated the Debye temperature as 280 K (LDA) and 252 K (GGA). There are no experimental estimations of the Debye temperature for CdIn\(_2\)S\(_4\); calculated values of 320 K [18] and 313 K [19] have been reported, which are reasonably close to our results with the deviation presumably caused by the different computational settings employed.

Table 3 summarizes the shear moduli, sound velocities and Debye temperature for CdIn\(_2\)S\(_4\) calculated at ambient pressure. The ambient pressure values are compared to the calculated results from references [18, 19].

As a fundamental parameter, the Debye temperature correlates with many physical properties of solids, such as specific heat, elastic constants and melting temperature. At low temperatures the vibrational excitations arise solely from the acoustic vibrations. Hence, at low temperatures the Debye temperature calculated from the elastic constants is the same as that one determined from the specific heat measurements [58]. It should be noted that the Debye temperature obtained from the elastic constants is always somewhat higher than that obtained from electrical resistivity studies. The discrepancy may be partly ascribed to its temperature dependence [58].
We note that the values of $v_l$ and $v_t$ from the present work and those from references [18, 19] are quite close, although the $v_m$ values differ considerably, which, in turn, causes the discrepancy in the calculated Debye temperature values. Trying to understand this difference, we noticed that most probably it was due to the improper application of equation (3) in references [18, 19]: the interchange of $v_l$ and $v_t$ in equation (3) would yield exactly those data obtained by the authors of those references.

The validity of our estimation of the Debye temperature is indirectly supported by the experimental values of the Debye temperature of 153 K for MnIn$_2$S$_4$ [49], 205 K for CuV$_2$S$_4$ [59] and 230 K for CuRh$_2$S$_4$ [60], which are much closer to our data than to the values of 313 or 320 K from references [18, 19].

5. Results of calculations: pressure effects on the structural, optical and elastic properties

For an analysis of the influence of pressure on the properties of CdIn$_2$S$_4$, its crystal structure has been optimized at various hydrostatic pressures in the range from 0 GPa to 10 GPa with a step of 2 GPa. The upper limit of the pressure variation was restricted to 10 GPa, since there is a pressure-induced phase transition at about 10 GPa, as reported in reference [9].

Figure 8 shows how the unit cell volume of CdIn$_2$S$_4$ varies with pressure in comparison with the experimental data from reference [13]. As can be seen from the figure, the LDA-calculated results (empty squares) follow the experimental data very closely, whereas the GGA-data tend to overestimate the experimental unit cell volume by about 5–6%.

Since the GGA-calculated interionic distances are slightly greater than the LDA-calculated ones (table 1), one may expect that the compressibility of the GGA-optimized crystal structure would be greater than the LDA-calculated one. Indeed, the data from figure 8 show that the unit cell volume of CdIn$_2$S$_4$ is reduced by about 12% and 10% in the GGA and LDA calculations, respectively.

Another way to use the data presented in figure 8 is to fit the corresponding data points to the Murnaghan equation of state [61]

$$\frac{V}{V_0} = \left(1 + \frac{P}{B_0} \frac{B'}{B} \right)^{-\frac{1}{n}}$$

Table 3. Calculated values of the shear moduli, density, sound velocities and Debye temperature for CdIn$_2$S$_4$ at ambient pressure. The calculated results from references [18, 19] are given in italic.

|        | $G_V$ (GPa) | $G_R$ (GPa) | $G$ (GPa) | Density (kg m$^{-3}$) | $v_l$ (m s$^{-1}$) | $v_t$ (m s$^{-1}$) | $v_m$ (m s$^{-1}$) | $\theta_D$ (K) |
|--------|-------------|-------------|-----------|-----------------------|-------------------|-------------------|-------------------|----------------|
| LDA    | 29.78       | 25.61       | 27.70     | 4977.78               | 4787              | 2359              | 2648              | 280            |
| GGA    | 25.16       | 18.64       | 21.90     | 4612.00               | 4468              | 2179              | 2448              | 252            |
|        | 25$^a$      | 4978$^a$    | 4730$^a$  | 2240$^a$              | 3030$^a$          | 320$^a$           |                   |                |
|        | 23.41$^b$   | 4560$^b$    | 4640$^b$  | 2270$^b$              | 3050$^b$          | 313$^b$           |                   |                |

$^a$ Reference [18].  
$^b$ Reference [19].
where $V_0$ is the volume at ambient pressure, and $B$ and $B' = dB/dP$ are the bulk modulus and its pressure derivative, respectively. The application of equation (5) to the data from figure 8 yields the following values: $B = 63.8$ GPa, $B' = 4.45$ (GGA, this work); $B = 78.7$ GPa, $B' = 4.51$ (LDA, this work); and $B = 74.6$ GPa, $B' = 1.67$ (experiment, [13]). These values are highly consistent with those from table 2.

Useful information about the response of individual chemical bonds to the applied pressure can be gained by plotting the variation of the lattice constant and interatomic distances versus pressure (figure 9). The lattice constant decreases with the pressure coefficients of $-0.0428$ Å GPa$^{-1}$ (GGA) and $-0.0354$ Å GPa$^{-1}$ (LDA). The Cd–S chemical bond shrinks with the pressure coefficients of $-0.0125$ Å GPa$^{-1}$ (GGA) and $-0.0102$ Å GPa$^{-1}$ (LDA). The In–S chemical bond decreases somewhat more slowly, with the pressure coefficients of $-0.0090$ Å GPa$^{-1}$ (GGA) and $-0.0075$ Å GPa$^{-1}$ (LDA).

The decrease of the interatomic distances induced by pressure can be manifested in the blue shift of the absorption edge. The calculated band gaps, with the corresponding scissor operator 1.303/1.138 eV (GGA/LDA) taken into account, in comparison to the experimental
The band gap value increases linearly with pressure; its pressure coefficient is 0.076 or 0.069 eV GPa$^{-1}$ (as extracted from the experimental data), whereas the GGA/LDA calculated pressure coefficients are 0.071/0.063 eV GPa$^{-1}$, in very good agreement with the experimental results.

An increase of the calculated band gap, as shown in figure 10, also leads to the blue shift of the absorption spectrum (figure 11). What is also worthwhile noting is that the intensities of the calculated absorption bands, which correspond to the band-to-band transitions, increase with pressure, indicating enhanced hybridization effects between the electronic states of Cd and In, on one hand, and S, on the other.

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**Figure 10.** Pressure dependence of the calculated and experimental band gap for CdIn$_2$S$_4$. The experimental data were taken from references [9, 62].

**Figure 11.** Pressure dependence of the calculated absorption spectrum for CdIn$_2$S$_4$. The values of pressure in GPa are given in the figure.

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data [9, 62] are presented in figure 10. The band gap value increases linearly with pressure; its pressure coefficient is 0.076 or 0.069 eV GPa$^{-1}$ (as extracted from the experimental data), whereas the GGA/LDA calculated pressure coefficients are 0.071/0.063 eV GPa$^{-1}$, in very good agreement with the experimental results.

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The elastic constants also increase with pressure (figure 12), except for the $C_{44}$ constant, which does practically not change at all. The linear approximations of all elastic constants as functions of pressure are presented in table 4. It can be noted that the coefficient of linear approximation for the bulk modulus $B$ from table 4 is very close to the $B'$ value obtained after the application of the Murnaghan equation of state.

Another interesting result is that the effective Mulliken charges of all ions differ considerably from the formal charges expected from the chemical formula. They are (in the proton charge units, GGA/LDA values are given): 0.77/0.71 for Cd; 0.74/0.65 for In; and $-0.56/-0.50$ for S. All charges are slightly increased with pressure to reach the following values: 0.78/0.72 for Cd; 0.75/0.66 for In; and $-0.57/-0.51$ for S, which indicates the pressure-induced charge transfer from metal ions to sulfur.

6. Conclusions

In this paper we have reported the results of the first-principles calculations of the structural, electronic, optical and elastic properties of CdIn$_2$S$_4$ thiospinel. After a successfully performed optimization of the crystal lattice, performed by using two approximations—GGA and LDA, the calculations of the electronic properties have shown this compound to possess an indirect band gap, which removes the ambiguous description of this compound previously found in the literature.
We also report refined values of the Debye temperature of 280 K (LDA) and 252 K (GGA), which also correct previous erroneous values reported in earlier publications. The pressure effects on the structure and electronic properties of CdIn₂S₄ were studied in the pressure range up to 10 GPa. The calculated unit cell volumes using the LDA approach and the pressure coefficient of the band gap, calculated here for the first time, excellently follow the experimental data. The values of the elastic constants, bulk modulus and its pressure derivative were all evaluated. The elastic anisotropy of CdIn₂S₄ was assessed by visualizing the three-dimensional surface of the directional dependence of the Young’s modulus. It was demonstrated that the lowest Young’s moduli values (the highest compressibility) of CdIn₂S₄ are realized along the crystallographic axes, whereas the (111) direction is characteristic of the greatest Young’s moduli values.

Both the GGA and LDA approximations employed in the present paper properly describe the physical properties of CdIn₂S₄ (apart from the usual underestimation of the band gap, which is a common feature of the methods of calculations based on the density functional theory). The experimental pressure dependence of the band gap is better reproduced in the GGA, whereas the elastic properties are better described by employing the LDA. Therefore, both approximations should be used to get a more complete picture of the physical properties of CdIn₂S₄ thiospinel.

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