

## First-principles simulations of the electronic density of states for superionic $\text{Ag}_2\text{CdI}_4$ crystals

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### ABSTRACT

Energy band dispersion calculations have been performed for  $\text{Ag}_2\text{CdI}_4$  superionic within a framework of local density approximation (Perdew–Zunger parameterization) exploiting the first-principles CASTEP computer code. The *ab-initio* electronic structure simulations were performed for both ( $I\bar{4}$  and  $I\bar{4}2m$ ) types of  $\varepsilon$ - $\text{Ag}_2\text{CdI}_4$  crystalline structures. Principal optical functions as well as the density of electronic states in the spectral range of inter-band optical transitions (2.5 eV–20 eV) were determined. Theoretically calculated absorption coefficients derived from the obtained band structure are compared with appropriate experimental data.

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### 1. Introduction

Over the past few decades an enhanced interest takes place to the studies of silver-containing fast ionic conductors [1–3]. These crystals are first of all of interest due to phenomena of the reversible transformation of luminescence centers structure as well as mobile silver ions concentration changes within the local irradiated region of the crystals.

A lot of efforts, both computational and experimental were put to shed light on the mentioned above and related phenomena. Experimental reports confirm, in particular, new effects of irradiation on the ionic conductivity and activation energy of mobile  $\text{Ag}^+$  cations migration in  $\text{RbAg}_4\text{I}_5$  superionic crystals [2]. Further photostimulated recovery of the ionic conductivity was also observed which is explained by the excitation of centers in complexes generated by previous irradiation of superionic crystals.

Reversible changes in the ionic conductivity due to incident light energy are caused by the reversible change in the structure of electron centers induced by the elastic strain around these defects. In order to study the effect of elastic deformation on the process of ionic transport and on the activation energy for the diffusion of mobile silver cations an information about principle electronic bands of valence states is required.

The first-principle calculations allow not only to have an insight into the origin of electronic bands but are also helpful for the understanding of the relationship between microscopic structure and ionic conductivity mechanisms.

This work completes our thorough investigation of  $\text{Ag}_2\text{CdI}_4$  solid electrolyte. In addition to previous results of electrical [4], optical and thermal properties [5] of this model compound and following recent report on its microstructure studied by SEM, impedance spectroscopy and fractal dimension analysis [6] as well as  $\text{Ag}_2\text{CdI}_4$  infrared spectra and phonon density of states calculation [7] herewith we focus on the band energy structure calculations of the  $\text{Ag}_2\text{CdI}_4$  single crystals and determination of partial densities of states in the valence band.

### 2. Crystal structure

$\text{Ag}_2\text{CdI}_4$  superionic compound is a representative of the  $A_2BI_4$  group, where  $A = \text{Ag}, \text{Cu}$ ;  $B = \text{Hg}, \text{Cd}, \text{Pb}, \text{Zn}$ . The investigations of  $\text{AgI}-\text{CdI}_2$  system [8] show, that in the phase diagram of  $\text{AgI}-\text{CdI}_2$  only single narrow area of  $\text{Ag}_2\text{CdI}_4$  phase exists at ~67 mol% of  $\text{AgI}$ . Moreover, the peritectical crystallisation of  $\text{Ag}_2\text{CdI}_4$  complicates the synthesis of bulk samples.

At room temperature and atmospheric pressure the  $\text{Ag}_2\text{CdI}_4$  crystalline structure is either tetragonal ( $\varepsilon$ -phase,  $a \sim 6.35 \text{ \AA}$ ,  $c \sim 12.70 \text{ \AA}$  [8,9]) or hexagonal ( $\beta$ -phase,  $a \sim 4.578 \text{ \AA}$ ,  $c \sim 7.529 \text{ \AA}$ , [10]).

During the long-term (several months) annealing at temperatures below ~370 K tetragonal  $\varepsilon$ - $\text{Ag}_2\text{CdI}_4$  is formed, whereas hexagonal  $\beta$ - $\text{Ag}_2\text{CdI}_4$  (with  $\beta$ - $\text{AgI}$  phase inclusion) is observed at higher

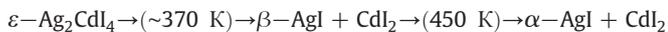
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temperatures [9]. From the analysis of  $\text{Ag}_2\text{CdI}_4$  ionic conductivity studies data two sequences of the phase transition were discovered:

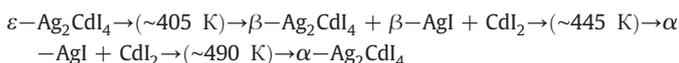


[9] or



[8].

Structural and differential scanning calorimetric studies of  $\text{Ag}_2\text{CdI}_4$  compounds show the existence of a more complicated transition route at elevating temperatures [10,11]:



Different authors report the superionic transition temperature within 385–410 K [5,11]. Furthermore,  $\beta\text{-Ag}_2\text{CdI}_4$  may be considered as a metastable phase formed upon cooling (on non-equilibrium crystallisation conditions).

The  $\text{Ag}_2\text{CdI}_4$  X-ray diffraction studies [12] suppose the reflection conditions for eight different space groups for  $\varepsilon\text{-Ag}_2\text{CdI}_4$ . Among them,  $I\bar{4}$  and  $I\bar{4}2m$  are considered to be the most probable crystalline structure adopted by  $\beta\text{-Ag}_2\text{HgI}_4$  and  $\beta\text{-Cu}_2\text{HgI}_4$ , respectively [13].

The crystalline structures of  $I\bar{4}$  and  $I\bar{4}2m$  of  $\varepsilon\text{-Ag}_2\text{CdI}_4$  with point groups  $I\bar{4}$  and  $I\bar{4}2m$  are presented in Fig. 1. Both comprise a slightly disordered *ccp* anion sublattice, with  $\text{Ag}^+$  and  $\text{Cd}^{2+}$  placed within tetrahedral cavities. In such a way, both can be considered as a pair of zincblende unit cell along [001] direction. Vacant cation sites in  $I\bar{4}2m$  structure are occupied by  $\text{Ag}^+$  in  $I\bar{4}$  structure and contrariwise.

### 3. Calculation method

Band energy dispersion calculations have been performed within a framework of local density approximation (LDA) (Perdew–Zunger

parameterization) for the exchange and correlation effects with application of the first principles CASTEP (Cambridge Serial Total Energy Package) code [14].

The ultrasoft pseudopotentials were used. They require a quite low energy cutoff and guarantee good transferability, that is, the same potential correctly reproduces the valence electron scattering by the ionic core in different chemical environments.

Specific energy cutoff values defined by these settings depend on the convergence properties of the pseudopotentials used for the current model. Each pseudopotential file was provided with CASTEP code containing three suggested cutoff energies corresponding to the COARSE, MEDIUM and FINE settings. These values were determined from convergence tests for isolated atoms and diatomic molecules, and they roughly correspond to the total energy convergence of 2, 0.3 and 0.1 eV/atom, respectively.

The default electronic minimization scheme in CASTEP is the density mixing one with the conjugate gradient (CG) method for eigenvalues minimization.

Calculation of the total energy and charge density using density functional theory requires several integrals in reciprocal space (over the Brillouin zone). We have approximated these integrals by numerical summation over a finite number of *k* points.

We have used a special *k*-point approach to select an optimal set of IBZ points such that the greatest possible accuracy is achieved from the number of points used. The primary method of Chadi–Cohen special-point generation implemented in the CASTEP module is the Monkhorst–Pack scheme, which produces a uniform mesh of *k* points in reciprocal space. Its main benefits consist in a possibility to reproduce more precisely band energy dispersions at low wave function vectors.

The kinetic energy cut-off for plane waves was about 340 eV. The total energy convergence was equal to 0.1 eV/atom (FINE settings).

Structural data from [12] and [7] were used. No additional structure optimization has been performed.

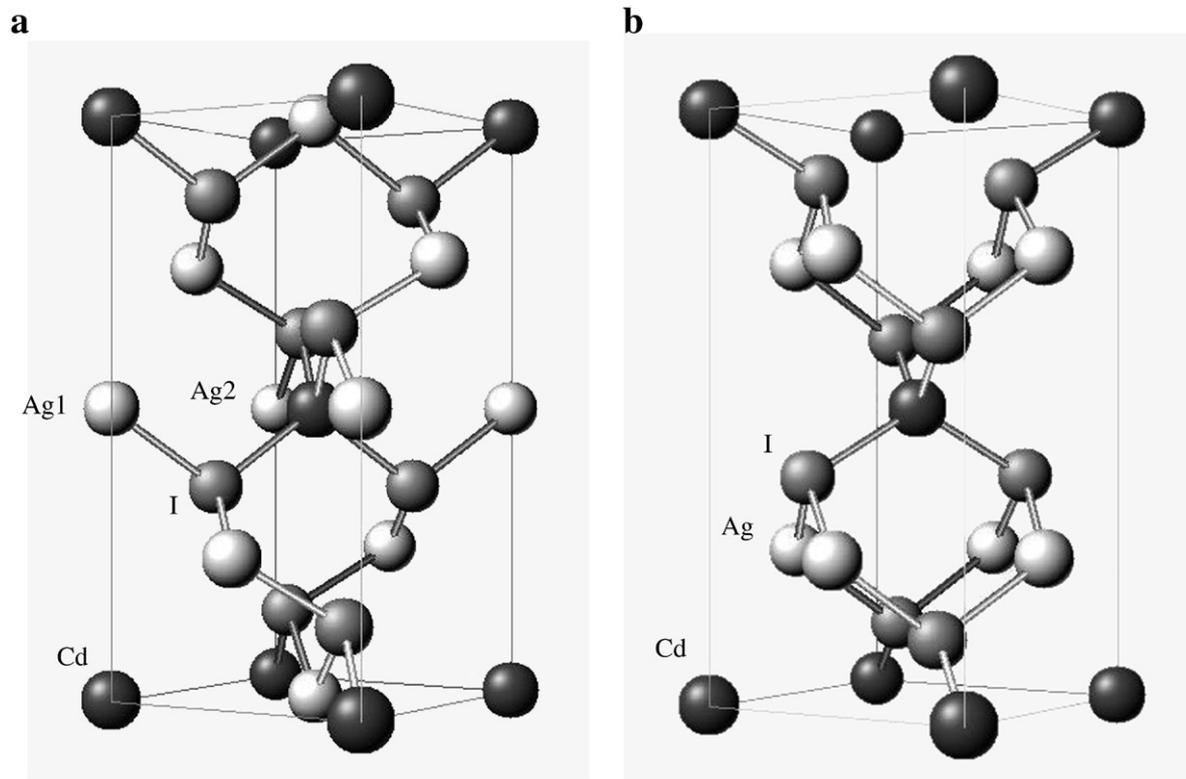
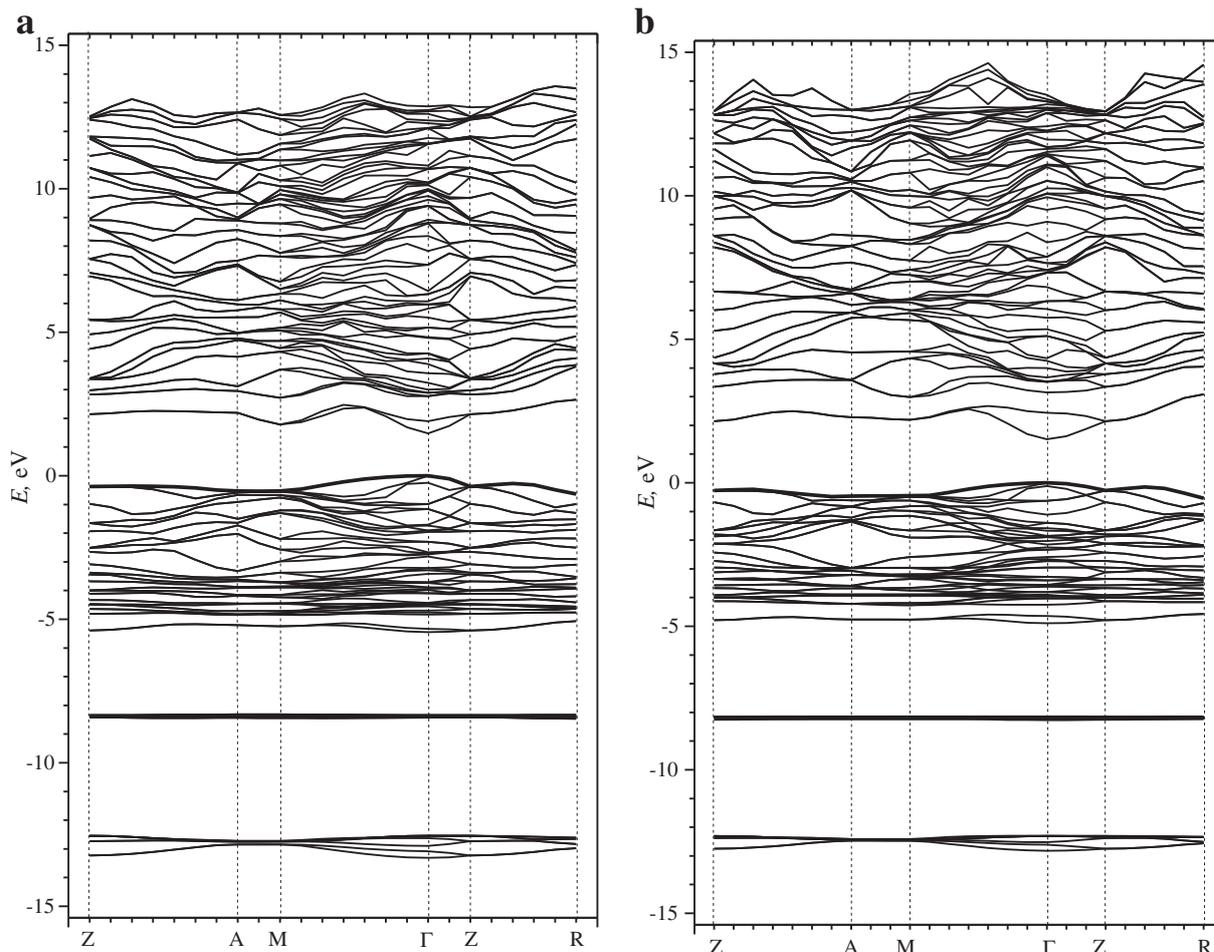


Fig. 1. The views of  $\varepsilon\text{-Ag}_2\text{CdI}_4$  crystal structure for the space groups  $I\bar{4}$  (a) and  $I\bar{4}2m$  (b).



**Fig. 2.** Band energy dispersion  $E(k)$  for  $\epsilon$ - $\text{Ag}_2\text{CdI}_4$  for the space groups  $I\bar{4}$  (a) and  $I\bar{4}2m$  (b): Z-[0 0 1/2], A-[1/2 1/2 1/2], M-[1/2 1/2 0],  $\Gamma$ -[0 0 0], R-[0 1/2 1/2].  $[k_x, k_y, k_z]$  are the electron wave vector components in the first Brillouin zone. The highest occupied state is marked by thick line.

#### 4. Results and discussion

Previous  $\text{Ag}_2\text{CdI}_4$  band energy structure investigation and a comparison with optical spectra were carried out in [15]. Band energy structure calculations in [15] were limited to very primitive band approximation scheme based on semi-empirical Huckel method.

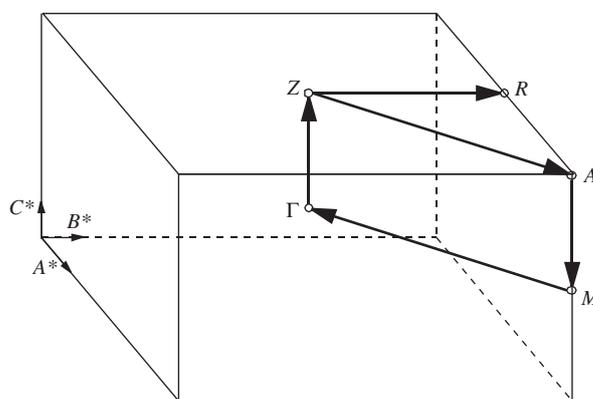
This work deals with *ab-initio* band energy structure simulation for both ( $I\bar{4}$  and  $I\bar{4}2m$ ) types of  $\epsilon$ - $\text{Ag}_2\text{CdI}_4$  crystalline structure and the determination of the principal optical functions as well as density of states in the spectral range of inter-band optical transitions, e.g. 2.5 eV–20 eV.

It is necessary to emphasize, that there are principal differences with respect to the previously calculated band energy features obtained in [15] and the band energy parameters presented here. They may be explained by the very row approximation of semi-empirical Huckel methods with respect to the first principles ones, as well as by difference between tight binding bases with respect to plane-wave approximations.

Fig. 2 shows  $k$  dispersions of energy curves along the IBZ directions marked by arrows in Fig. 3. The qualitative analysis of obtained results allows for supposing that there are no principle differences between  $I\bar{4}$  and  $I\bar{4}2m$  types of  $\epsilon$ - $\text{Ag}_2\text{CdI}_4$ . One can see that the maximal dispersion of the bands is observed in the M- $\Gamma$ -Z directions of the IBZ. It is important that the top of the valence band and the bottom of the conduction band are situated at the  $\Gamma$ -point of the IBZ. Therefore, we have the direct energy gap of 1.48 eV and 1.51 eV for  $I\bar{4}$  and  $I\bar{4}2m$  types, respectively. These values are lower than the fundamental

absorption edge at 3.28 eV in stoichiometric  $\text{Ag}_2\text{CdI}_4$  thin films [16]. Such disagreement, however, is not surprising, as it is well known, that calculations using a local density approximation considerably underestimate bandgaps in most of semiconductors and insulators [17].

The energy bands are more flat for the Z-A and Z-R directions. In general, the dispersion for the conduction band is higher with respect to the valence band. One can see substantial splitting of the bands in the M- $\Gamma$  directions of the IBZ as well as large energy distances



**Fig. 3.** The first Brillouin zone of  $\text{Ag}_2\text{CdI}_4$  crystal for the spatial groups  $I\bar{4}$  and  $I\bar{4}2m$ , special points, and paths Z, A, M,  $\Gamma$ , Z, and R.

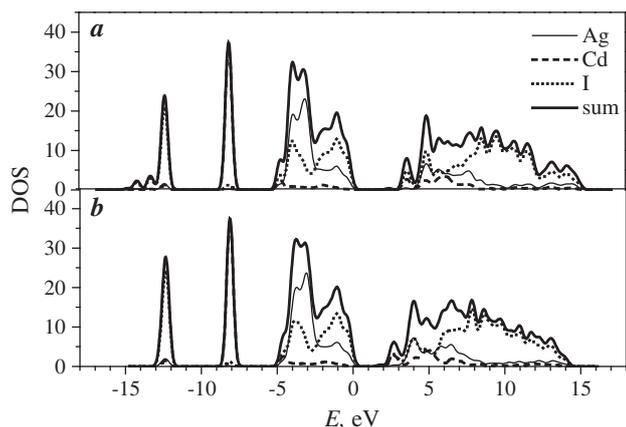


Fig. 4. Total density of electron states of  $\epsilon$ - $\text{Ag}_2\text{CdI}_4$  for the space groups  $I\bar{4}$  (a) and  $I\bar{4}2m$  (b) and its projections onto Ag, Cd, and I atoms. The energy  $E = 0$  eV corresponds to the top of the valence band (Fig. 2).

between the sub-bands corresponding to the top of VB and the localized core like bands.

Total density of electronic states (DOS) is presented in Fig. 4. Partial DOS clarifying contribution of particular orbitals are shown in Figs. 5 and 6.

Obtained densities of electronic states in the valence band may be grouped into three principal sub-bands. The electron density spectra the lower region ( $-12, -15$  eV) correspond to core-like dispersionless  $s$ -states of iodine. The middle sub-band, (very narrow sub-band at

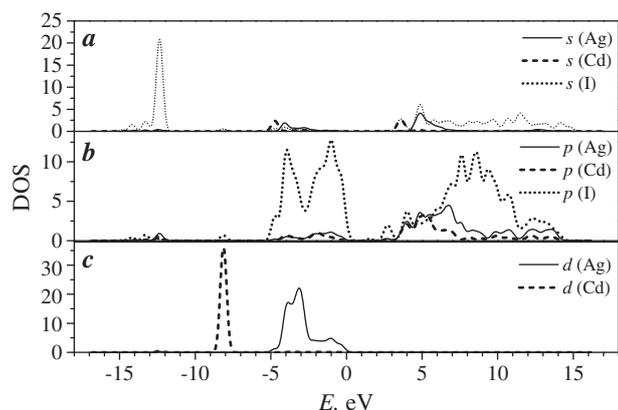


Fig. 5. Partial densities of electron states of  $\epsilon$ - $\text{Ag}_2\text{CdI}_4$  for the space group  $I\bar{4}$  projected onto  $s$ - (a),  $p$ - (b) and  $d$ - (c) states.

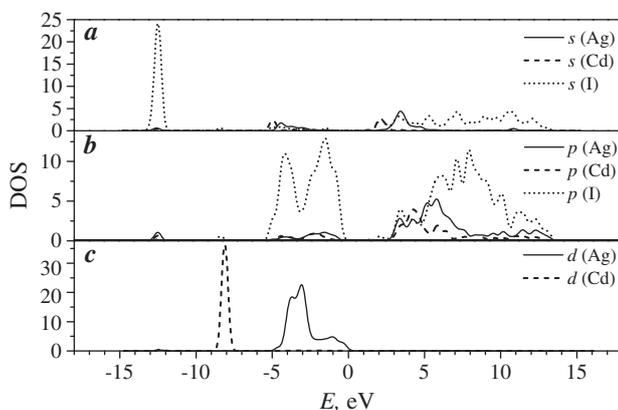


Fig. 6. Partial densities of electron states of  $\epsilon$ - $\text{Ag}_2\text{CdI}_4$  for the space group  $I\bar{4}2m$  projected onto  $s$ - (a),  $p$ - (b) and  $d$ - (c) states.

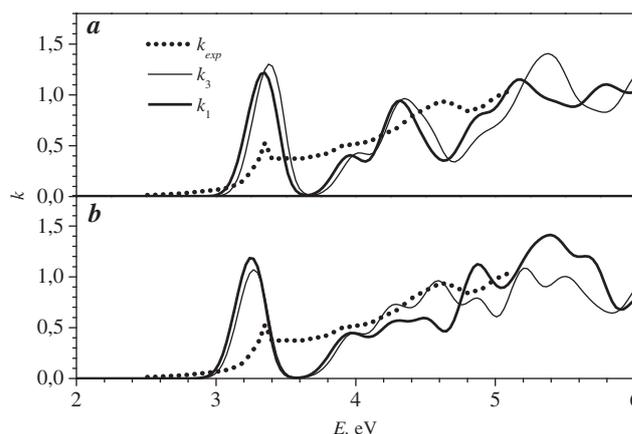


Fig. 7. Photon energy dependencies of the absorption indices of  $\text{Ag}_2\text{CdI}_4$  crystal for the space groups  $I\bar{4}$  (a) and  $I\bar{4}2m$  (b):  $k_1(E)$  and  $k_3(E)$  - calculated data for light polarized along the  $x$  and  $z$ -axes, respectively;  $k_{exp}(E)$  - experimental data [16].

about  $-8$  eV) is formed by localized  $3d$ -states of cadmium. In view of the ionic transfer processes, the most interesting is the first band peaked between  $-5$  eV and the top of valence band. This band is a superposition of at least three sub-bands reflecting principal contribution of the valence bond states. According to Figs. 5 and 6 it is originated from  $5p$  I states with an admixture of  $4d$  Ag states, forming a background of the ground electronic states. Considering the relatively low energies with respect to the Fermi level one can expect that these two states will define the mechanism of the silver ions transfer. Thus, operating by effective distances Ag–I the density of states near these levels can be varied, which in turn will be responsible for the processes of the ionic transfer. The lower conduction band is prevalingly formed by  $5s$  Cd states, which are very close to the  $5p$  Cd states, however the iodine states originated bands give some contribution as well and the thorough study of particular contribution require knowledge of hybridization between these sub-bands, which will be done in a future. The contribution of the  $s$ -states of Ag is substantially less. In this respect, the principal role during the optical inter-band processes will be determined by the charge transfer between prevalingly  $5p$  I valence states and the  $5s$  Cd sub-bands.

In Fig. 7 absorption coefficients ( $k$ ) theoretically calculated from the presented above band structure are compared with those, experimentally derived in [16]. One can see almost the same position of the experimental absorption peak at  $\sim 3.4$  eV and calculated bands in Fig. 7a. In case of  $I\bar{4}2m$  space group (Fig. 7b) the calculated peak is about  $-0.1$  eV shifted with respect to measured absorption maximum. The anisotropy of the spectral maxima is vanishingly small which indicate a low sensitivity of the delocalised band states to the long range anisotropic states. The remaining bands are more pronounced in calculations than in the experiment. This may reflect the effect of the electron-phonon line broadening.

## 5. Conclusions

First-principles calculations of the electronic structure for  $\text{Ag}_2\text{CdI}_4$  superionic crystals were carried out. The estimated direct band gap is  $\sim 1.5$  eV at the  $\Gamma$ -point of the IBZ. It is shown that there are no principal differences between the  $I\bar{4}$  and  $I\bar{4}2m$   $\epsilon$ - $\text{Ag}_2\text{CdI}_4$  isomorphs.

The contribution of particular electronic terms into the total density of electronic states is identified. The valence band is formed by  $s$ -states of iodine,  $3d$ -states of cadmium and the mixture of  $5p$  iodine and  $4d$  silver states. The bottom of the conduction band is formed mostly by  $5s$  cadmium states with noticeable contribution of  $p$ - and  $s$ -iodine states and substantially lower admixtures of silver  $s$ -states. The crucial role of the charge transfer between  $5p$  I and  $5s$  Cd states in the optical interband processes is emphasized.

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