

Electronic Energy Spectra of ZnX (X = O, S, Se, Te) Crystals Obtained by Combining the Green's Function and the Hybrid Functional

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We have found that the energies of the Zn semicore 3d electrons in crystals ZnX (X = O, S, Se, Te), in the wurtzite phase, are localized in narrow intervals within the valence band. It was found that the widths of these intervals at Γ point of the first Brillouin zone are equal to 1.24, 0.68, 0.50 and 0.40 eV for ZnO, ZnS, ZnSe and ZnTe crystals, respectively. It was found that the wave functions of the Zn 3d electrons strongly overlap with the states of the valence and the conduction bands. Consequently, the widely used exchange-correlation energy functionals, constructed in the LDA and GGA-PBE approaches, are inappropriate for systems with narrow band of highly correlated 3d electrons. That is why we performed calculations based on the hybrid exchange-correlation energy functional, HSE06, and the obtained eigenenergies and eigenfunctions were used in the construction of the Green's function. Consequently, the basis of this study is based on the two modern concepts of electronic theory of crystals, namely the hybrid exchange-correlation functional and quasiparticle approach. The values of the bandgap, E_g , obtained here in the GGA-PBE approximation, are well-matched to the results found by other authors. The values of E_g , calculated using the combination of Green's function methods and the hybrid functional for the exchange-correlation energy, HSE06, are equal to 2.34, 3.28, 2.35 and 2.13 eV for ZnO, ZnS, ZnSe and ZnTe crystals, respectively, if the mixing factor in the functional is 0.25, that it is the standard. We calculated the electron energy spectra for ZnO, ZnS, ZnSe and ZnTe crystals, with mixing factors, different from the standard ones, namely of 0.40, 0.375, 0.35 and 0.325. The corresponding band gaps have been acquired the values of 3.29, 3.83, 2.81 and 3.43 eV, which are very well matched with the experiment.

Keywords: A₂B₆, Wurtzite phase, Strong correlation, HSE06, GW, Electronic energy bands.

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1. INTRODUCTION

Wide-band-gap semiconductor zinc compounds have a potential for a variety of applications in production of electronic devices. In particular, ZnO is very resistive to high-energy radiation making it a very suitable candidate for space applications [1]. It can be used as a substrate for epitaxial growth of high-quality GaN films [2], and it is also a promising candidate for spintronics applications [3]. Also ZnO nanomaterials have attracted tremendous interest in the fields of photocatalysis, sensors, solar cells, and supercapacitors [4]. Zinc sulfide finds application in production of solar cells, liquid crystal displays, light-emitting diodes and sensors transmission windows [5, 6]. Also the ZnS nanostructures find a wide application in photoluminescence, photocatalysis, light-emitting diodes, field-effect transistors, sensors, and dye-sensitized solar cells [7]. In turn, zinc telluride finds use as an integral part of *p-n* homo-junction diodes [8], green/ultraviolet photodetectors [9], and CdTe based multi-layer graded bandgap solar cells. A material such as ZnSe is one of the most important optoelectronic materials that are used for manufacturing of indicator devices and medical lasers [10].

The search for the realistic theoretical approaches for the electronic structure description in ZnX crystals for today is not completed. The reason for this is that LDA (GGA) approaches do not properly account the strong correlations of the Zn 3d electrons.

We were convinced that the realistic band gaps, wave functions, and crystal potentials, obtained with the hybrid functional PBE0 of the exchange-correlation energy,

allowed us to obtain the kinetic coefficients in the CdTe [11] and ZnSe [12] materials, that show a very good comparison with the experiment.

The electron energy spectrum of ZnX crystals was studied earlier by other authors in the framework of various theoretical approaches, namely, generalized gradient approximation (GGA-PBE) [13], a new hybrid functional ACBNO, and the self-interaction-relaxation correction (SIRC-LDA) [14]. It turned out that the values of the band gaps are underestimated, that is, the comparison with the experiment is not satisfactory. For example, the calculated values of the band gap in the ZnO crystal are found in a wide interval from 0.75 to 3.40 eV. For ZnS crystal, this interval extends from 2.20 to 3.6 eV. The values found for the ZnSe crystal are also scattered in a fairly large range of values from 1.27 to 2.46 eV. The width of the band gap of the ZnTe crystal calculated in different approximations is also characterized by a sufficiently large interval of values from 1.17 to 2.22 eV.

The hybrid functional PBE0 allows to correct significantly the values of band gaps in crystals, especially for materials containing transition *d* or *f* elements. This approach combines the LDA (GGA), with the Hartree-Fock exact exchange for *d* or *f* electrons, in the exchange-correlation energy functional, as implemented within the ABINIT code [15].

Here we use a combination of two theoretical approaches, namely, the Green's function, built on base of eigenstates, found with the hybrid functional HSE06 [16] of the exchange-correlation energy, (HSE-GF) [15].

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2. CALCULATION

The electronic structure calculations have been carried out by means of the ABINIT code [15] using the norm-conserving pseudopotential (NCP) method [17]. These NCP have been generated on the base of the exchange-correlation energy functional within the GGA. They were used as the basis for the first stage of our calculations of the electron energy spectra of ZnX crystals within the GGA-PBE.

The second stage of the calculations was performed using a more perfect exchange-correlation energy functional proposed by Heyd, Scuseria, and Ernzerhof (HSE) [16]. In this approach, the screened Coulomb potential is used, which can be splitted into the short-range (SR) and long-range (LR) components. The corresponding partitioning of the Coulomb potential is

$$1/u = \text{erfc}(\omega u) / u + \text{erf}(\omega u) / u, \quad u = |\mathbf{r} - \mathbf{r}'|, \quad (1)$$

where u is the distance between electrons in a crystal. For example, the exact long-range contribution to the exchange energy is

$$E_x^{LR} = -\frac{1}{2} \sum_{k,l}^{OCC} \int d\mathbf{r} \int d\mathbf{r}' \phi_k(\mathbf{r}) \phi_k^*(\mathbf{r}') \frac{\text{erf}(\omega u)}{u} \phi_l^*(\mathbf{r}) \phi_l(\mathbf{r}'), \quad (2)$$

where $\phi_k(\mathbf{r})$ is the wave function of the occupied electron in the state k .

The general formula of the exchange-correlation energy functional, defined in the HSE approach, is as follows:

$$E_{xc}^{HSE}(\omega) = \alpha E_x^{SR}(\omega) + (1 - \alpha) E_x^{PBE,SR}(\omega) + E_x^{PBE,LR}(\omega) + E_c^{PBE}, \quad (3)$$

where SR, LR denote the short- and long-range parts of the exchange energy. Only the first term in formula (3) is determined on the basis of an exact expression of type (2), in which a function $\text{erf}(\omega u)$ needs to be replaced by $\text{erfc}(\omega u)$ one. The mixing factor lies in the range of 0.0 to 1.0. The adjustable screening parameter $\omega = 0.11$ corresponds to the HSE06 approximation. For $\omega \rightarrow 0$, the second long-range term in Eq. (1) vanishes and the first one is equivalent to the full Coulomb operator.

As can be seen from Eq. (3), the HSE functional includes three PBE terms. The functional of the HSE enables to calculate the electron energy spectra of crystals in an acceptable amount of time. This became possible only after the replacement of the exact long-range contribution to the exchange energy E_x^{LR} [16] by the third term in equation (3).

The *third stage* of the calculations was performed within the Green's function (GF) formalism. The GF was built on the eigenstates, found on the HSE level [16].

3. RESULTS AND DISCUSSION

Here we present the results of the investigation of the electronic structure for ZnX crystals. All the calculations have been done by means of ABINIT code [15]. In this paper, we present the results of calculating the electron energy band spectrum performed in the follow-

ing three approaches. In the first approach, the GGA-PBE exchange-correlation potential is used, in which the exact Hartree-Fock term is absent, that is, the mixing factor $\alpha = 0$. The corresponding results are shown in Fig. 1a, Fig. 2a, Fig. 3a, and Fig. 4a.

The second approach combines the HSE06 hybrid functional of the exchange-correlation energy and the GF method, in the GW approximation, as implemented within the ABINIT code [15]. First, we present results obtained with default value of the mixing factor $\alpha = 0.25$. These results are shown in Fig. 1b, Fig. 2b, Fig. 3b, and Fig. 4b. Second, we did some more calculations with higher values of the parameter α . These results are presented in Fig. 1c, Fig. 2c, Fig. 3c, Fig. 4c.

The energy parameters listed in Table 1-Table 4 mean a band gap E_g , the $E_{\text{val}}-E_{3d}$ energy differences, higher (max) and lower (min), respectively, and the width of the 3d band dE_{3d} in the ZnX crystals (in eV).

3.1 Band Energies in the Wurtzite Crystal ZnO

Fig. 1a shows the energy bands obtained for ZnO crystal with the GGA exchange-correlation functional.

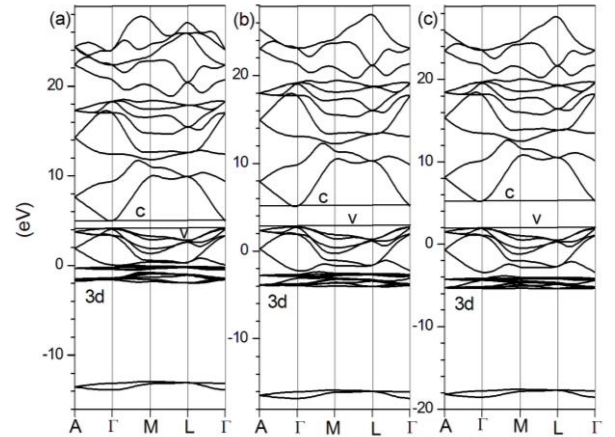


Fig. 1 – The band structure of the ZnO crystal

The top of the valence (bottom of the conduction) band, $\varepsilon_v(\varepsilon_c)$, is denoted with $v(c)$, respectively. As seen, ZnO crystal has a direct optical and fundamental band gap at the point Γ of the first Brillouin zone. The band gap $\varepsilon_g = 0.87$ eV and it is much underestimated compared to the experimental value of 3.2-3.4 eV.

Now let us consider the results shown in Fig. 1b, which were found from the HSE-GF approach with default mixing factor $\alpha = 0.25$. The band gap $\varepsilon_g = 2.34$ eV and it is still narrower than experimental one. We found that the value $\alpha = 0.40$ ensures the band gap of 3.29 eV, which compares very well with experimental values listed in Table 1.

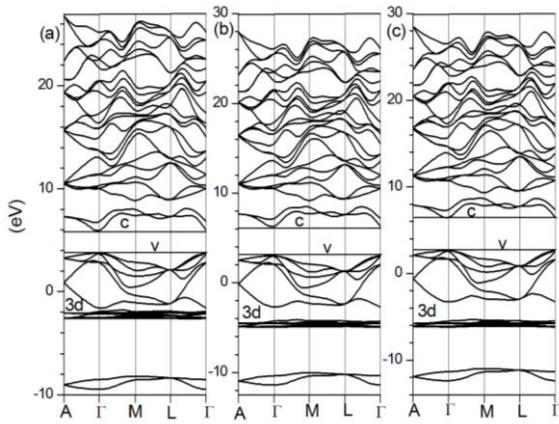
As can be seen from Fig. 1 and Table 1, the greater value of the mixing coefficient α corresponds to the lower energy of the 3d Zn states in the valence band. An increase in the coefficient α means an increase in the fraction of the precise screened Hartree-Fock's exchange potential in the functional of the exchange-correlation energy. From Table 1 it follows that an increase in the parameter α leads to a noticeable narrowing of the interval $\Delta\varepsilon_{3d}$ at the Γ point of the first Brillouin zone.

Table 1 – Parameters of the electron energy spectrum (in eV) in the ZnO crystal

	$E_g(\alpha)$	$E_{3d\max}$	$E_{3d\min}$	dE_{3d}
PBE	0.87 (0.0)	4.36	5.72	1.36
HSE GW	2.34 (0.25)	5.46	6.70	1.24
HSE GW	3.29 (0.40)	6.15	7.33	1.18

3.2 Band Energies in the Wurtzite Crystal ZnS

Fig. 2 shows that the crystal has a direct band gap at the Γ point in the first Brillouin zone. The dispersion curves have been obtained with the values of the mixing parameter 0.0, 0.25, and 0.375. The corresponding band gaps values are equal to 2.22, 3.28, and 3.83 eV, respectively. The last calculated value of the band gap agrees very well with the measured one. Fig. 2 and data represented in Table 2 also show the decrease in the Zn 3d levels, in the valence band, with the increase of the parameter α . However, the interval of localization of 3d states in the ZnS crystal is more than twice as low as in the crystalline ZnO. The interval $\Delta\varepsilon_{3d}$ at the Γ point of the first Brillouin zone practically does not depend on the mixing parameter α , as it does, on the contrary, in the ZnO crystal.

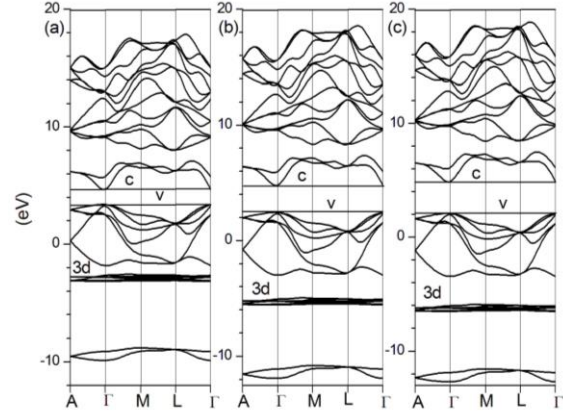
**Fig. 2** – The band structure of the ZnS crystal**Table 2** – Parameters of the electron energy spectrum (in eV) in the ZnS crystal

	$E_g(\alpha)$	$E_{3d\max}$	$E_{3d\min}$	dE_{3d}
PBE	2.22 (0.0)	5.67	6.36	0.69
HSE GW	3.28 (0.25)	7.31	7.99	0.68
HSE GW	3.83 (0.375)	8.14	8.83	0.69

3.3 Band Energies in the Wurtzite ZnSe Crystal

As can be seen from Fig. 3, the crystal has a direct band gap at the Γ point of the first Brillouin zone. The electronic band energies evaluated with the parameter α of 0.0, 0.25, and 0.35, are equal to 1.29, 2.35, and 2.81, respectively. The last value of the band gap agrees very well with the experimental one 2.87 eV.

It is seen from Fig. 3 and also from the data listed in Table 3 that the Zn 3d levels become progressively deeper in the valence band, when the parameter α increases. We also note that the interval of localization of the Zn 3d states at the point Γ is narrower than that in the ZnS crystal by about 0.2 eV.

**Fig. 3** – The band structure of the ZnSe crystal**Table 3** – Parameters of the electron energy spectrum (in eV) in the ZnSe crystal

	$E_g(\alpha)$	$E_{3d\max}$	$E_{3d\min}$	dE_{3d}
PBE	1.29 (0.0)	6.04	6.54	0.50
HSE GW	2.35 (0.25)	7.52	8.02	0.50
HSE GW	2.81 (0.35)	8.12	8.62	0.50

Table 4 – Parameters of the electron energy spectrum (in eV) in the ZnTe crystal

	$E_g(\alpha)$	$E_{3d\max}$	$E_{3d\min}$	dE_{3d}
PBE	1.24 (0.0)	6.51	6.88	0.37
HSE GW	2.13 (0.25)	8.21	8.61	0.40
HSE GW	2.43 (0.325)	8.70	9.11	0.41

Table 5 – The band gap values (in eV) in the ZnX crystals obtained with other theoretical methods and found from experiment

	ZnO	ZnS	ZnSe	ZnTe
PBE [14]	0.85		1.27	1.17
HSE [14]	2.90	3.42, 3.34	2.46	2.22
SIRC [14]	3.40	3.6	–	–
OEPx GW [18]	3.11	3.70	–	–
ACBN0 [14]	2.91	3.31	1.90	1.82
Exper. [14]	3.2, 3.4	3.86, 3.91	2.87	2.38 (zb)

3.4 Band Energies in the Wurtzite Crystal ZnTe

The electronic energy bands of the ZnTe crystal are illustrated in Fig. 4. It is seen that the crystal has a direct band gap at the point Γ in the first Brillouin zone. The electron energies have been evaluated with the parameters α of 0.0, 0.25, and 0.325. The corresponding band gaps are equal to 1.24, 2.13, and 2.43 eV, respectively. As can be seen from Table 4, the last value of the band gap is well compared with the measured one given in Table 5. The results of the calculation show that with the increase of the mixing coefficient α , the Zn 3d levels become deeper with respect to the top of the valence band. The interval of localization of the Zn 3d states, $\Delta\varepsilon_{3d}$, at the Γ point is the smallest compared to that in the previous three materials.

In Table 1-Table 4, parameter α determines the degree of mixing of the screened exact exchange Hartree-Fock interaction and is found in the GGA approximation, which is represented by the first two terms in Eq. (3).

The parameter E_g is the band gap, and $E_{3d\max}$ and $E_{3d\min}$ mean the distances between the top of the va-

lence band and the higher and lower $3d$ levels at the Γ point, respectively. Parameter dE_{3d} denotes a width of $3d$ zone at the Γ point. Table 5 contains the results, obtained by other authors.

The results presented in Table 1-Table 4 indicate the noticeable impact of strong correlations of the Zn $3d$ electrons on the values of the band gaps for all the ZnX crystals. In fact, an increase in the mixing parameter α leads to a noticeable increase in the band gap and also contributes to the deepening of the Zn $3d$ energy levels within the valence band.

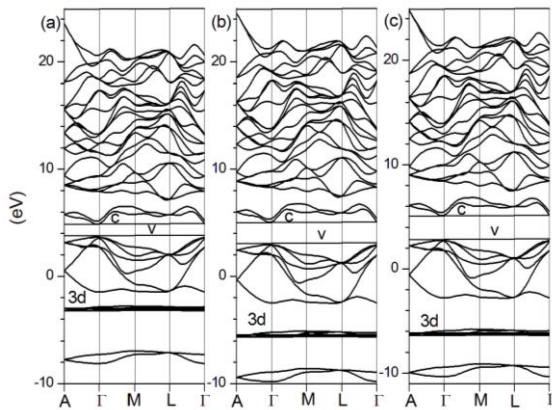


Fig. 4 – The band structure of the ZnTe crystal

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4. CONCLUSIONS

In this work, the electronic energies of the ZnX crystal in a wurtzite phase have been studied. We have found that the Zn $3d$ states are localized in the narrow energy intervals within the valence band. Therefore, they should be treated as the strongly correlated electrons. So, we have applied the combined approach for calculating electronic band energies based on the HSE06 hybrid functional and Green's function. The results obtained here show that E_g found within the GGA is very much underestimated as compared with experiment. The band gaps evaluated here within the HSE-GF approach with mixing coefficient $\alpha = 0.25$ differ from the experimental values by 1.03, 0.58, 0.52, and 0.25 eV for ZnO, ZnS, ZnSe, and ZnTe, respectively.

These differences acquire much smaller values, namely, of 0.11, 0.03, 0.06, and -0.05 eV, respectively, but they have been calculated with other parameters α listed in Table 1-Table 4.

The SIRC and optimized-effective potential (OEPx-GW) [18] approaches yield band gaps for ZnO and ZnS crystals in good agreement with experiment, but their realization is very expensive. The LDA + U scheme is based on the mean-field Hubbard energy U and needs to use three other parameters, which are the system dependent [19, 20]. In summary, we note that the HSE-GF approach used here is a good compromise between the full Green's function approach and other DFT options that have not proved to be reliable in the description of materials with strongly correlated d or f electrons.

**Електронні енергетичні спектри кристалів ZnX (X = O, S, Se, Te),
отримані комбінуванням функції Гріна та гібридного функціонала**

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Нами встановлено, що енергії напівостовних $3d$ електронів Zn у кристалах ZnX (X = O, S, Se, Te) у вюрцитній фазі локалізовані у вузьких інтервалах валентної зони. Знайдено, що величини цих інтервалів в точці Γ першої зони Брилюєна дорівнюють для кристалів ZnO, ZnS, ZnSe та ZnTe 1.24, 0.68, 0.50 та 0.40 eV, відповідно. Виявлено, що хвильові функції $3d$ електронів Zn сильно перекриваються зі станами валентної зони і зони провідності. Отже, широко застосовні функціонали обмінно-кореляційної енергії, побудовані у підходах LDA та GGA-PBE, є неприйнятними для систем з вузькими зонами сильно скорельованих $3d$ електронів. Саме тому ми виконали розрахунки, у яких на основі гібридного функціонала обмінно-кореляційної енергії, HSE06, знайдені власні енергії і власні функції, використані для конструювання функції Гріна. Отже, в основу даного дослідження покладені сучасні дві концепції електронної теорії кристалів, а саме гібридний обмінно-кореляційний функціонал та квазічастинковий підхід. Отримані нами у наближенні GGA-PBE значення ширини забороненої зони E_g добре зіставляються з результатами, знайденими іншими авторами. Значення E_g , обчислені за допомогою комбінування методів функції Гріна та гібридного функціонала обмінно-кореляційної енергії HSE06, дорівнюють 2.34, 3.28, 2.35 та 2.13 eV для кристалів ZnO, ZnS, ZnSe та ZnTe, якщо коефіцієнт змішування у функціоналі є 0.25, тобто стандартним. Ці ж міжзонні щілини набувають значень 3.29, 3.83, 2.81 та 3.43 eV, але отримані вони з коефіцієнтами змішування 0.40, 0.375, 0.35 та 0.325 для кристалів ZnO, ZnS, ZnSe та ZnTe, відповідно. Останні значення ширини забороненої зони дуже добре зіставляються з експериментом.

Ключові слова: A_2B_6 , Структура вюрциту, Сильні кореляції, HSE06, GW, Закон дисперсії.