

## THE SPIN-POLARIZED ELECTRONIC AND MAGNETIC PROPERTIES OF ZINC SELENIDE HEAVY DOPED WITH CHROMIUM

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**Abstract.** At the first stage, the structure of the ZnSe crystal doped with chromium atoms (ZnCrSe) has been found by optimization procedure. At the second stage, the electronic properties of this material have been evaluated within the two approaches. The exchange-correlation functionals used here are based on the generalized gradient approximation (GGA) and the hybrid functional PBE0. The GGA approach provides the metallic state for electrons with the spin up, and for opposite spin orientation the material ZnCrSe behaves as semiconductor, with the band gap of 2.48 eV. The hybrid functional approach also gives a gapless state for a spin up electron states, and for a spin down it provides the forbidden gap value of 2.39 eV. The magnetic moment of the unit cell, found with the two functionals, is the same and equals to  $4 \mu_B$  (Bohr magnetons). So, the calculations with the two exchange-correlation functionals provide the prediction of half-metallic properties of the ZnCrSe material, which is an interesting candidate for spintronic applications.

**Key words:** doped semiconductor, half-metal, strong correlations, spintronics.

### 1. Introduction

Doping of semiconductors II–VI with transition metals aims to find materials that can be used in optoelectronics and spintronics. Recently, studies of crystal ZnTe doped with Cr, Mn, and Ti atoms have been performed [1]. In a work [2] the optical properties of the material CdMnTe were studied, and a work [3] was devoted to the study of the influence of taking into account the strong correlations of 3d electrons on the parameters of the electronic energy spectrum of this material.

### 2. Calculation

The calculations have been done within the projector augmented waves (PAW) approach [4]. This method reveals the features of the pseudopotential and the all-electron method of augmented plane waves. The all-electron  $y_n$  function is derived from pseudo-wave  $|y_n^0\rangle$  one by means of transformation  $t$ , namely:

$$|y_n(\mathbf{r})\rangle = t |y_n^0(\mathbf{r})\rangle, \quad (1)$$

where operator

$$t = 1 + \hat{a} \hat{a} \left( |f_i^a\rangle - |f_i^{0a}\rangle \right) \langle y_i^a | \quad (2)$$

is built on the atomic  $|f_i^a(\mathbf{r})\rangle$ , pseudoatomic  $|f_i^{0a}(\mathbf{r})\rangle$  and projector  $\langle y_i^a |$  functions. The equations (1) and (2) define the basis states PAW. The energy band spectrum  $\epsilon_n$  of the crystal is evaluated from the following system of equations,

$$t^+ H t |y_n^0\rangle = t^+ t |y_n^0\rangle \epsilon_n, \quad (3)$$

where the spectra of the effective Hamiltonian  $t^+ H t$  and initial one  $H$  are identical. The exchange-correlation energy functional was taken in the hybrid form [5], named as the PBE0.

$$E_{xc}^{PBE0}[\mathbf{r}] = E_{xc}^{PBE}[\mathbf{r}] + \alpha (E_x^{HF}[\mathbf{Y}_{3d}] - E_x^{PBE}[\mathbf{r}_{3d}]). \quad (4)$$

This form combines the usual PBE approach [6] and Hartree-Fock exchange energy (HF). The parameter  $\alpha$  is a mixing coefficient. If  $\alpha = 0$ , the PBE0 approximation becomes a usual functional of PBE. The recommended value of mixing parameter is  $\alpha = 0.25$  [5]. Both values of the  $\alpha$  are used here. The hybrid functional PBE0 used with mixing parameter  $\alpha \neq 0$  causes removing the self-interaction error (SIE), which is very important for transition metal compounds [3, 7].

The supercell of the material is built on base of the sphalerite structure. The unit cell contains 3 Zn atoms, 1 Cr atom and 4 Se atoms. The parameters of a unit cell were optimized by the Broyden-Fletcher-Goldfarb-Shanno [8] (BFGS) scheme of the search of stable structure geometry.

The calculations have been done by means of the ABINIT code [9].

### 3. Results and discussion

The spin-polarized electronic energy bands, obtained without the SIE, are given in Fig. 1. The Fermi level defines the origin on the energy axis. As can be seen from Fig. 1 the Fermi level crosses the the dispersion curves in the upper part

of the valence band. So, the electrons with the spin up move in a considered material as in a metal.

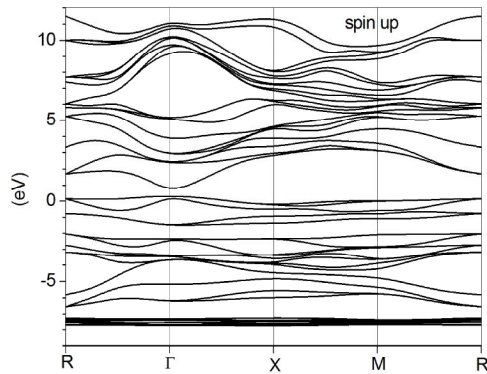


Fig. 1. The electronic energy bands in the ZnCrSe material obtained with a mixing parameter  $a = 0$ .

In contrast to this, the electrons with the spin down, as can be seen from Fig. 2, are characterized by semiconductor energy bands. Here the Fermi level is situated inside the forbidden gap and is slightly shifted towards the conduction band.

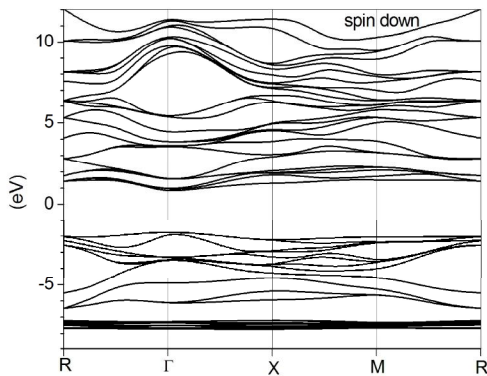


Fig. 2. The electronic energy bands in the ZnCrSe material obtained with a mixing parameter  $a = 0$ .

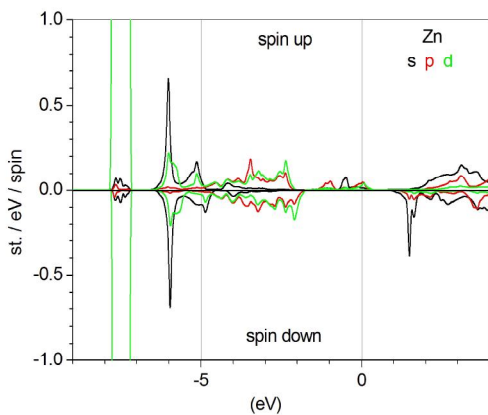


Fig. 3. The partial DOS of Zn in the material ZnCrSe evaluated with a mixing parameter  $a = 0$ .

The partial DOS in Fig. 3 are not symmetric for electrons with opposite spins. The asymmetry is caused by strongly correlated 3d electrons of Cr atom. The Fermi level crosses the p levels of the Zn atom.

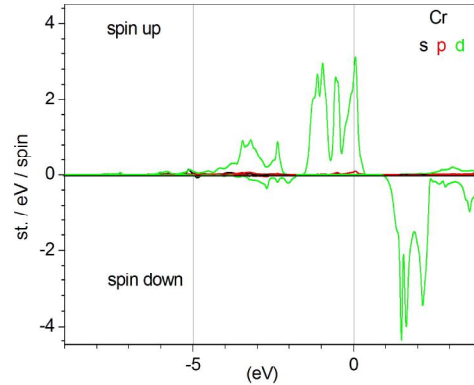


Fig. 4. The partial DOS of Cr in the material ZnCrSe evaluated with a mixing parameter  $a = 0$ .

Fig. 4 shows that the main contributions at the Fermi level make the Cr 3d states.

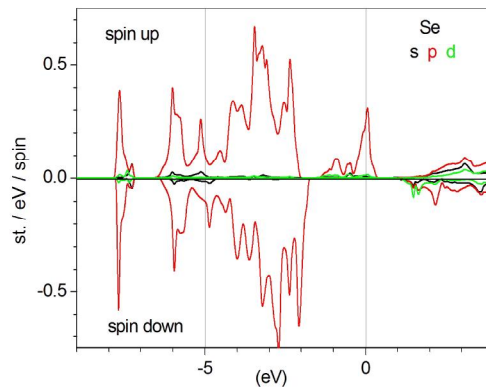


Fig. 5. The partial DOS of Se in the material ZnCrSe evaluated with a mixing parameter  $a = 0$ .

The Se atom also is represented at the Fermi level by its p states. So, the Cr and Se atoms are the main contributors of electrons at the Fermi level.

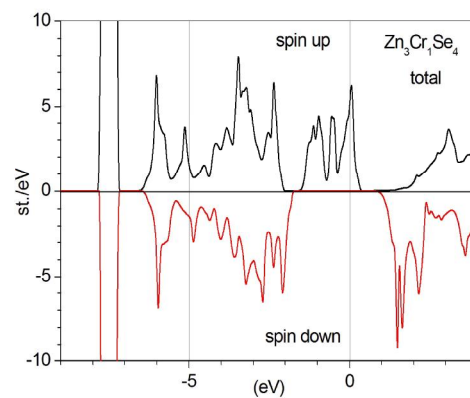


Fig. 6. The total DOS of ZnCrSe material evaluated with a mixing parameter  $a = 0$ .

The Fig. 6 confirm the half-metallicity of the material under study, when the mixing parameter  $a = 0$ , i.e. the strong correlations of 3d electrons are not taken into account.

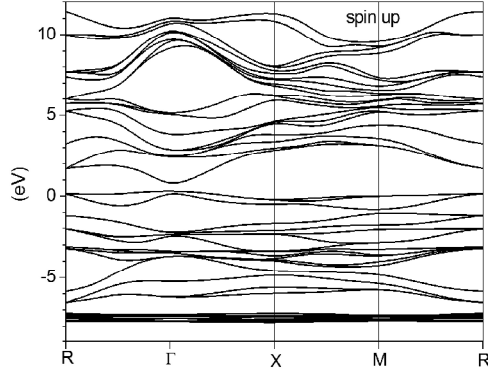


Fig. 7. The electronic energy bands in the ZnCrSe material obtained with a mixing parameter  $a = 0.25$ .

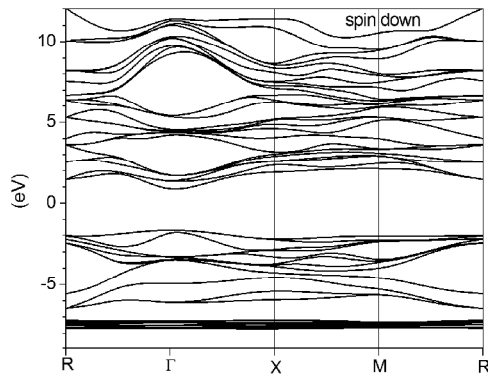


Fig. 8. The electronic energy bands in the ZnCrSe material obtained with a mixing parameter  $a = 0.25$ .

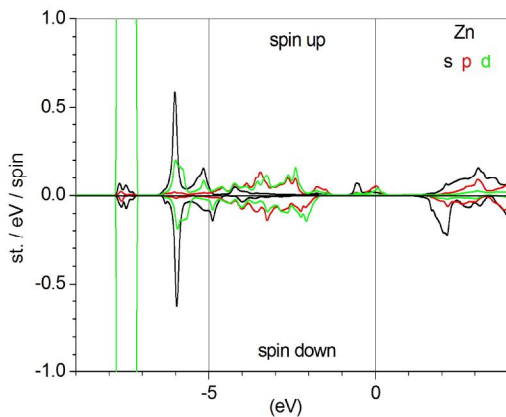


Fig. 9. The partial DOS of Zn in the material ZnCrSe evaluated with a mixing parameter  $a = 0.25$ .

The dispersion curves in Fig. 7 are obtained taking into account the SIE. They show the metallic properties of the material for electrons with spin up. In contrast, the Fermi level in Fig. 8 is located inside the forbidden gap,

confirming the semiconductor nature of the ZnCrSe material for electrons with spin down.

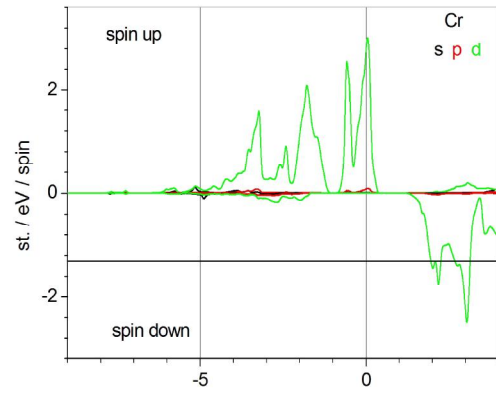


Fig. 10. The partial DOS of Cr in the material ZnCrSe evaluated with a mixing parameter  $a = 0.25$ .

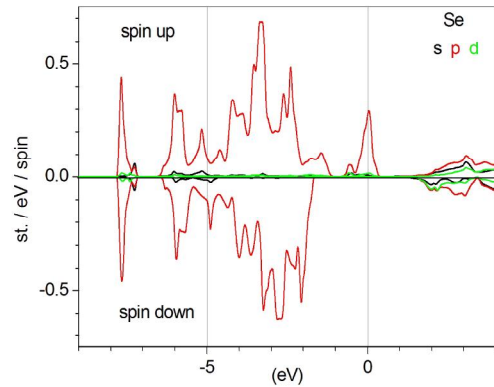


Fig. 11. The partial DOS of Se in the material ZnCrSe evaluated with a mixing parameter  $a = 0.25$ .

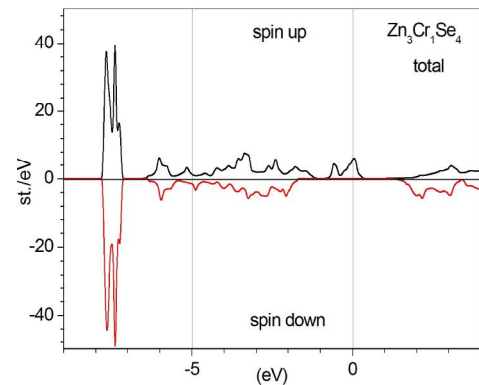


Fig. 12. The total DOS in the material ZnCrSe evaluated with a mixing parameter  $a = 0.25$ .

The Fig. 9 shows that the Zn atoms contribute very little to the electronic DOS at the Fermi level. The main contribution to DOS at Fermi level provide the Cr atom, as can be seen from Fig. 10. The contribution of Se atoms to DOS (Fig. 11) at the Fermi level is quite significant, although smaller compared to Cr atoms.

Summing up, based on the total DOS shown in Fig. 12, we conclude that for electrons with spin up the material ZnCrSe is a metal, and for spin down it exhibits the properties of a semiconductor.

Such compounds are called semi-metals or half-metals. In particular, these are Heusler alloys, whose intensive research has been conducted over the past decade [10, 11].

#### 4. Conclusion

The structural optimization of the material ZnCrSe confirms its mechanical stability. The electronic structure of the compound, obtained by substitution Cr  $\otimes$  Zn, is completely rebuilt, as compared with the crystal ZnSe. In particular, for the spin up the DOS diagrams show the high contribution of the 3d Cr electrons. This would encourage the study of optical properties of this material.

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## СПІН-ПОЛЯРИЗОВАНІ ЕЛЕКТРОННІ ТА МАГНІТНІ ВЛАСТИВОСТІ СЕЛЕНІДУ ЦИНКУ, СИЛЬНО ЛЕГОВАНОГО ХРОМОМ

Степан Сиротюк

На першому етапі методом оптимізації було визначено структуру кристала ZnSe, легованого атомами хрому (ZnCrSe). На другому етапі електронні властивості цього матеріалу були оцінені у межах двох підходів. Обмінно-кореляційні функціонали, введені в розрахунки, ґрунтуються на узагальненому градієнтному наближенні (GGA) та гібридному функціоналі PBE0. Підхід GGA забезпечує металевий стан для електронів зі спіном вгору, а для протилежної орієнтації спіна матеріал ZnCrSe є напівпровідником із шириною забороненої зони 2,48 еВ. Гібридний функціонал PBE0 також приводить до безщільного стану для електронних станів зі спіном вгору, а для спінів униз значення ширини забороненої зони дорівнює 2,39 еВ. Магнітний момент елементарної комірки, знайдений з двома функціоналами, однаковий і дорівнює  $4 \mu_B$  (магнетони Бора). Отже, розрахунки з двома обмінно-кореляційними функціоналами передбачають напівметалеві властивості матеріалу ZnCrSe, що робить його цікавим кандидатом для застосувань у спінтроніці.



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