

Effect of Strong Correlations on the Spin-polarized Electronic Energy Bands of the CdMnTe Solid Solution

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The influence of strong d -electron correlations on the values of the parameters of the electron energy bands in the solid solution $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ($x = 0.25$) was studied. At the first stage, the spin-resolved electronic energy bands were obtained in the GGA approach. At the second stage, strong correlations were taken into account for the Mn d -electrons by means of the hybrid exchange-correlation function PBE0, and at the third stage, correlations of the Mn and Cd d -electrons were included simultaneously. It was revealed that the material is a semiconductor for both spin channels. Found that for spin-up electrons, after taking into account the strong correlations of the Mn $3d$ -electrons, the top of the valence band was shifted by -0.10 eV, and the bottom of the conduction band has increased by 0.02 eV, which resulted in an increase in the band gap, E_g , by 0.12 eV. Strong correlations of the Cd $4d$ -electrons add to an increase in E_g a value of 0.03 eV. The total increase in E_g for spin-up electrons is equal to 0.15 eV. For the spin-down electrons, the inclusion of strong $3d$ -electron correlations of Mn led to an increase in the top of the valence band by 0.12 eV, and the bottom of the conduction band has increased by 0.54 eV, resulting in an increase in the band gap by 0.42 eV. Strong correlations of the Cd $4d$ -electrons add to an increase in E_g a value of 0.02 eV. The total increase in E_g for spin-down states equals 0.44 eV. It was found that for spin-up electrons, the value of E_g of solid solution, without taking into account strong correlations of d -electrons, is 1.32 eV, and the inclusion of $3d$ -electron correlations of Mn leads to the E_g value of 1.44 eV. And the additional inclusion of $4d$ -electron correlations of Cd gives the E_g value of 1.47 eV. It was found that for spin-down electrons, the value of E_g of a solid solution, without taking into account the strong correlations of d -electrons, is 1.69 eV, and the inclusion of $3d$ -electron correlations of Mn leads to the E_g value of 2.11 eV. And the accounting of $4d$ -electron correlations of Cd has caused only a slight increase in the E_g to 2.13 eV.

Keywords: Solid solution, Strong correlation, Electronic energy bands, Spintronics.

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1. INTRODUCTION

Solid solutions of the $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ system, which are obtained in the quasi-binary CdTe–MnTe section via the controlled substitution of Mn for Cd, represent a quite broad class of dilute magnetic semiconductors (DMSs) [1-3]. The main specific feature of DMSs consists in the fact that, apart from pure semiconductor properties, they also exhibit giant magneto-optical effects and magnetic polarons, which is caused by the high magnetic moments of the atoms with unfilled $3d$ shells in their compositions [3-5]. As a result, DMSs exhibit a strong exchange interaction between their magnetic atoms and between the magnetic atoms and electrons. This exchange interaction can be used in the spintronics which is promising for discovering a new way of data storage media in the chip-producing industries [6]. Spintronics is a branch of science and technology which employs both the charge and the spin of the electron. This, in turn, requires the materials which exhibit both ferromagnetic and semi-conductor properties in order to combine the permanent magnetic storage and the conventional electronics of semiconductors in one device [7]. Namely these properties are characteristic of CdMnTe solid solution.

In this article we present the results of investigation of the electronic structure of zinc blende solid solution $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ($x = 0.25$) that was carried out within the GGA [8] and PBE0 [9] approaches. All the calculations have been done by means of ABINIT code [10, 11]. It

should be noticed that the self-consistent wave functions and crystalline potential obtained on the basis of ABINIT code can be used to calculate the electrical properties of spintronics devices. This can be done in future by using the method proposed in [12, 13]. This method is based on the short-range scattering models for electron interaction with a various types of crystal defects and demonstrates much better qualitative and quantitative agreement with experiment compared with commonly used long-range scattering models.

2. CALCULATION

The electronic structure calculations have been carried out using the PAW [14] method, in which the electron wave function with its full nodal structure $|\psi_n(\mathbf{r})\rangle$ is represented in terms of the smooth nodeless function $|\tilde{\psi}_n(\mathbf{r})\rangle$ as

$$|\psi_n(\mathbf{r})\rangle = \tau |\tilde{\psi}_n(\mathbf{r})\rangle, \quad (1)$$

where τ is the transformation operator,

$$\tau = 1 + \sum_a \sum_i \left(\left| \phi_i^a \right\rangle - \left| \tilde{\phi}_i^a \right\rangle \right) \left\langle \tilde{p}_i^a \right| \quad (2)$$

and $|\phi_i^a(\mathbf{r})\rangle$ is the all-electron basis function, $|\tilde{\phi}_i^a(\mathbf{r})\rangle$ is the pseudopotential basis function, and $|\tilde{p}_i^a(\mathbf{r})\rangle$ is

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the projector function, which was calculated using the AtomPAW code [15]. The subscript i denotes the quantum numbers, and the superscript a represents the atomic augmentation sphere index.

Substituting (1), (2) to the Kohn-Sham equation

$$H|\psi_{\alpha\mathbf{k}}\rangle = |\psi_{\alpha\mathbf{k}}\rangle \varepsilon_{\alpha\mathbf{k}}, \quad (3)$$

we obtain the system of linear equations

$$\tau^+ H \tau |\tilde{\psi}_{\alpha\mathbf{k}}\rangle = \tau^+ \tau |\tilde{\psi}_{\alpha\mathbf{k}}\rangle \varepsilon_{\alpha\mathbf{k}}, \quad (4)$$

where α is the band number, \mathbf{k} denotes the vector in the first Brillouin zone, and τ^+ defines the Hermitian conjugate of τ . The exchange-correlation potential was calculated in the form of PBE0 [9], according to which the exchange-correlation energy is written as

$$E_{xc}^{PBE0}[\rho] = E_{xc}^{PBE}[\rho] + \beta(E_x^{HF}[\psi_s] - E_x^{PBE}[\rho_s]), \quad (5)$$

where E_{xc}^{PBE} corresponds to the PBE exchange-correlation functional [8], and ψ_s , ρ_s represent the wave function and the electron density of the selected electrons, respectively [10]. The latter are the Mn 3d-electrons and Cd 4d-electrons. The mixing coefficient value $\beta=0$ corresponds to the usual exchange-correlation functional PBE without strong correlations. In order to take into account the strong correlations in formula (5), the authors recommend the value $\beta=0.25$.

The crystal symmetry is described by the space group P-43m (number 215) Bravais lattice is cP (primitive cubic).

We have generated the PAW functions for the following valence basis states: $\{4s^2 4p^6 4d^{10} 5s^2 5p^0\}$ for Cd, $\{3s^2 3p^6 3d^5 4s^2 4p^0\}$ for Mn and $\{5s^2 5p^4\}$ for Te. The PAW functions have been evaluated by means of the AtomPAW code [14, 15]. The inclusion in the basis of 4s and 4p states of the Cd atom and of 3s and 3p states of the Mn atom slows down the calculation, but increases the precision and eliminates the problem of ghost states which can appear among solutions of the secular equation constructed on a minimal set of functions [16]. The radii of the augmentation spheres are 2.2, 2.1 and 2.4 a.u. for Cd, Mn and Te, respectively.

3. RESULTS AND DISCUSSION

Let us consider the results obtained in the GGA and PBE0 approaches. In the GGA approach, the strong correlations of 4d (Cd) and 3d (Mn) electrons are not taken into account, whereas in the PBE0 approach they are included in the calculation scheme.

First, we consider the electronic energy band spectrum of a solid solution obtained using the hybrid exchange-correlation functional PBE0. Fig. 1a-b shows energy bands with the spin-up (1a) and spin-down (1b), respectively. We can see that for both values of the spin moment we have a material with a direct optical and fundamental band gap at the point Γ of the first Brillouin zone. In addition, we note that the Fermi level is inside the band gap.

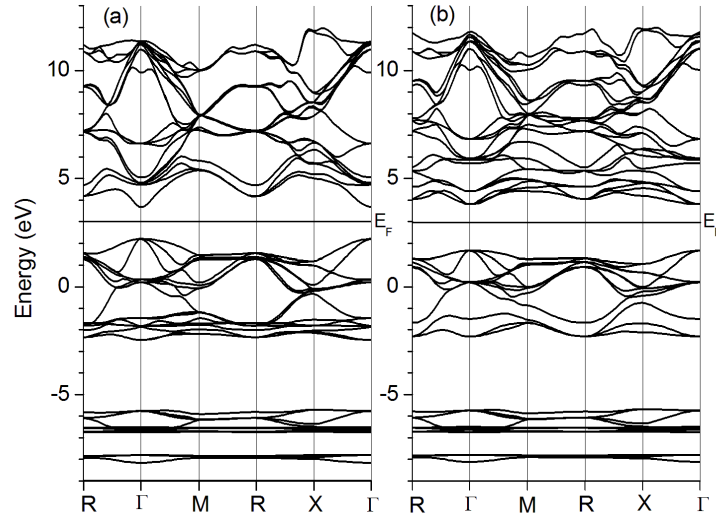


Fig. 1 – The band structure of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ($x=0.25$) with the spin-up (a) and spin-down (b), in the zinc-blende phase, calculated using hybrid functional PBE0, plotted along various symmetry directions

The densities of electronic states obtained without taking into account the strong correlations of the Mn-3d and Cd-4d states, i.e. in the GGA approximation, are presented in Fig. 2a-d. We will concentrate our attention on the states of the upper part of the valence band and the lower part of the conduction band. The parameters of the electronic energy bands in the considered $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ($x=0.25$) solid solution, obtained within the GGA, are as follows. The examined material is the direct band semiconductor for

both spin orientations. The minimum optical and fundamental gaps are equal to 1.32 eV for spin-up and 1.69 eV for spin-down, and both are attributed to the $\Gamma - \Gamma$ transition. The upper part of the valence band consists of the hybridized d-states of Mn-d, Te-p and Cd-s states, covering the energy range from -5.0 to -0.5 eV for electrons with spin up, and the range from -5.0 to -1.0 eV for electrons with spin down. The strong asymmetry of the curves in Fig. 2a-d indicates a ferromagnetic ordering in the crystal. The

lower part of the conduction band consists of the Mn- d and Te- p states.

Let us draw attention to the quantitative and qualitative changes in the electronic properties obtained by considering strong correlations of the $3d$ -states of Mn. The corresponding densities of states are shown in Fig. 3a-d. Comparing the curves depicted in Figs. 2c and 3c, we note that taking into account the strong correlations of the Mn d -electrons has led to the displacement of the main peaks of the corresponding densities of states. In particular, the maximum of the density of states with spin up dropped by about 1.5 eV in the valence band. Conversely, the peak of states with spin down shifted in the conduction band of about 0.5 eV up. Taking into account the strong correlations of the Mn d -electrons has led to an increase in the direct band gap of 0.12 eV for spin up and of 0.42 eV for spin down. The minimum optical and fundamental gaps are equal to 1.44 eV for spin-up and 2.11 eV for spin-down, and both are attributed to the $\Gamma - \Gamma$ transition.

Finally, we consider the results of calculating the electronic structure of the material $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$

($x = 0.25$) obtained with the inclusion of strong correlations of the Mn and Cd d -electrons depicted in Fig. 3a-d. As can be seen from Figs. 2c, 3c and 4c, the main peaks of the PDOS of Cd d -states were dropped by about 0.5 eV in the valence band. The influence of the inclusion of strong correlations of the Cd d -electrons on the parameters of the electron energy spectrum, as shown in Figs. 2, 3 and 4, was insignificant. In fact, the direct band gap for electrons with spin up is 1.47 eV, i.e. it has increased only by 0.03 eV. The band gap for electrons with spin down is 2.13 eV and it has increased only by 0.02 eV due to the inclusion of strong correlations of the Cd d -electrons. This contrasts very much with the results obtained with taking into account the strong correlations of the Cd d -electrons in a pure CdO crystal, as well as in CdO doped with transition elements [17].

In the case of the PBE0 approach, i.e. with strong correlations, the minimum optical and fundamental gaps are equal to 1.47 eV for spin-up, and 2.13 eV for spin-down. Table 1 summarizes the quantitative parameters of the electron energy band spectrum of a solid solution CdMnTe.

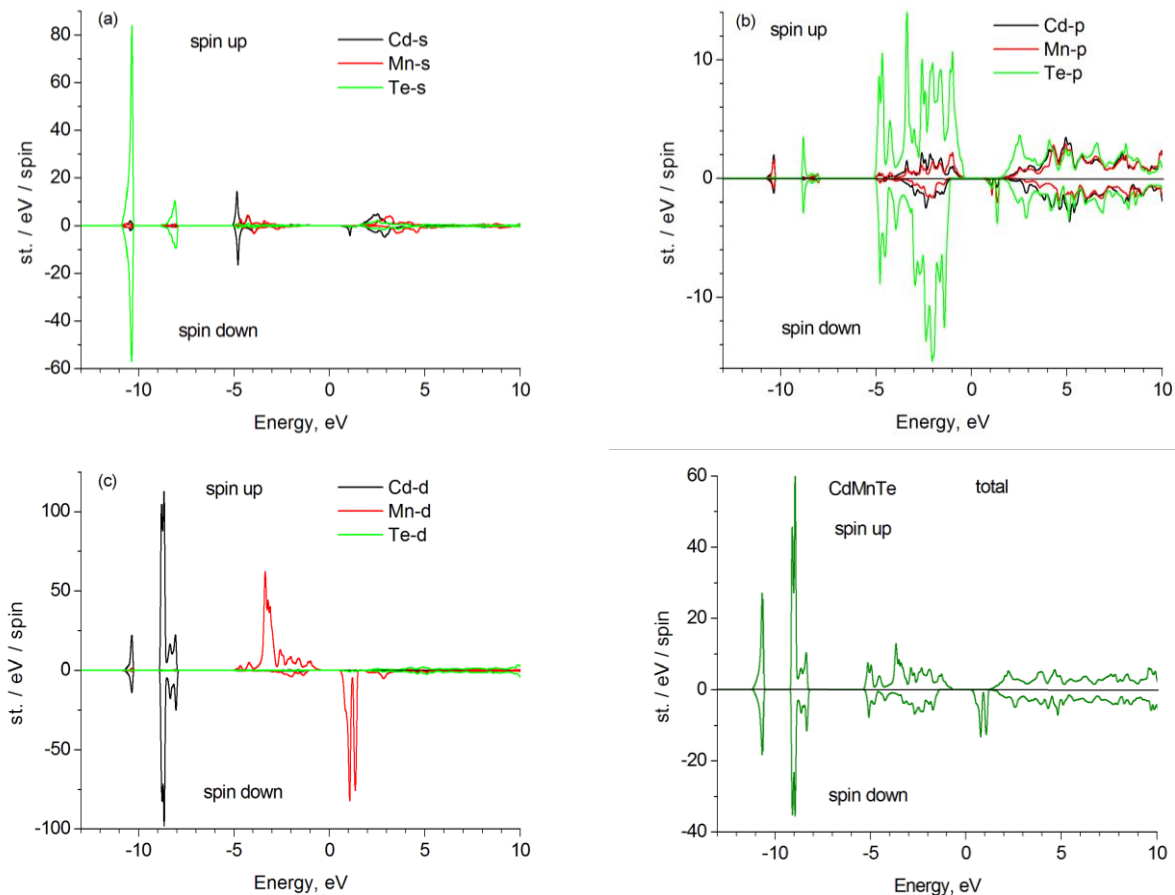


Fig. 2 – Partial and total density of states in the zinc-blende solid solution $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ($x = 0.25$) obtained within the spin-polarized GGA approach without the strong correlation of d electrons

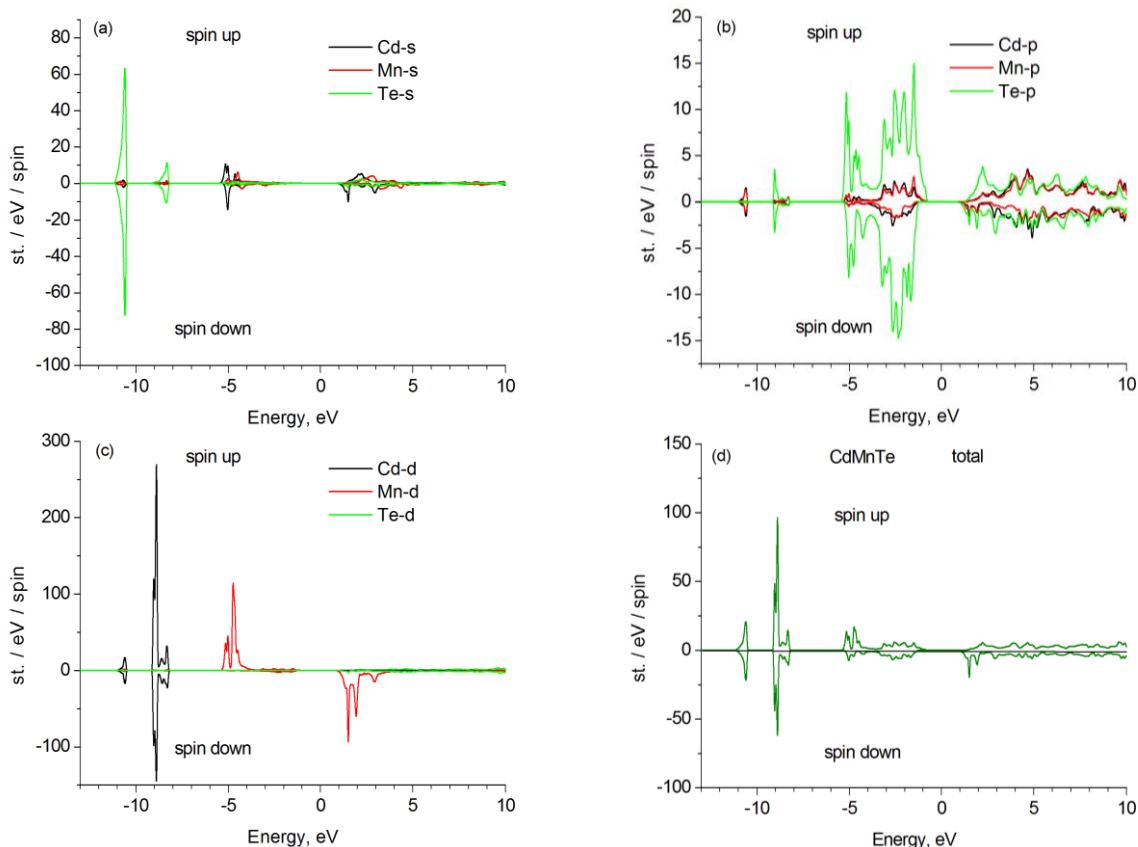


Fig. 3 – Partial and total density of states in the zinc-blende solid solution $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ($x = 0.25$) obtained within the spin-polarized hybrid exchange-correlation functional PBE0 with the strong correlation of the Mn d -electrons

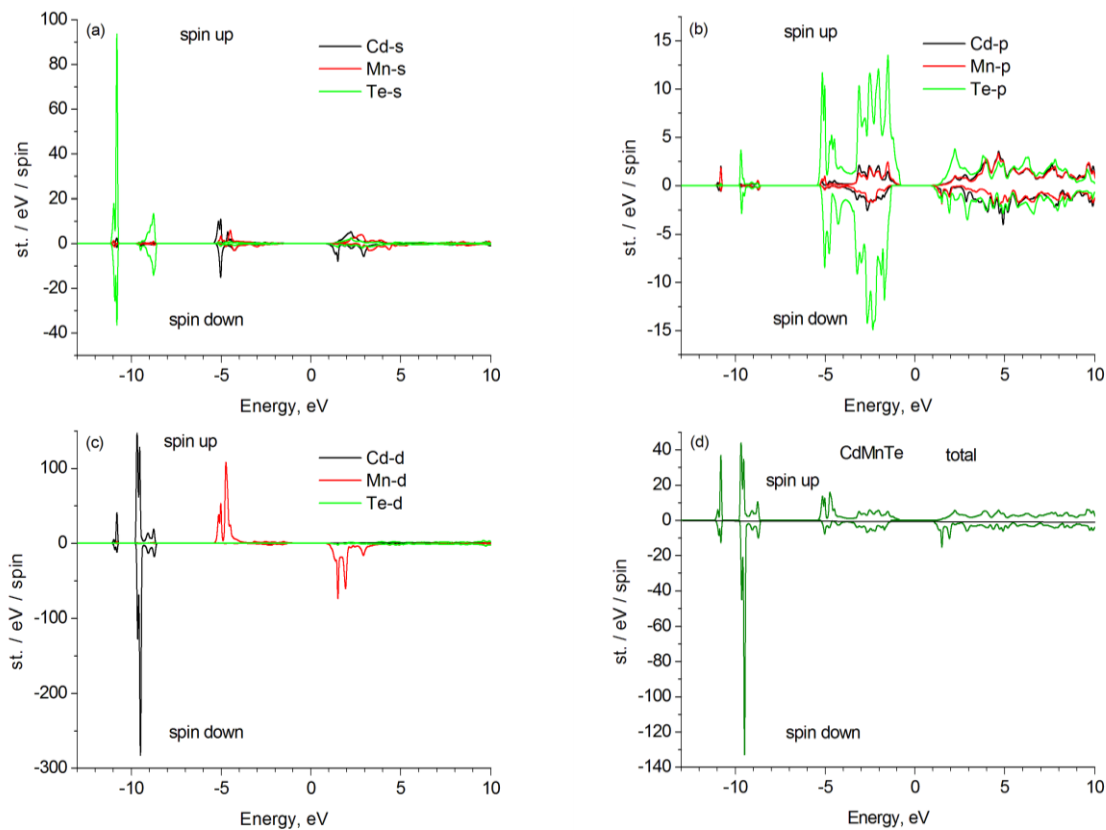


Fig. 4a-d – Partial and total density of states in the zinc-blende solid solution $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ($x = 0.25$) obtained within the spin-polarized hybrid exchange-correlation functional PBE0, with the strong correlation of the Mn and Cd d -electrons

Table 1 – The spin-polarized electronic properties of the solid solution $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ($x = 0.25$) obtained for spin-up (up) and spin-down (dn) states without (GGA) and with (PBE0) the strong correlation of d -electrons

XC	Element	β	ε_c , eV	ε_v , eV	ε_g , eV	ε_F , eV	n	M , μB
GGA, up		0.0	3.64	2.32	1.32	2.67	67.91	4.82
GGA, dn		0.0	3.25	1.56	1.69	2.67	63.09	
PBE0, up	Mn	0.25	3.66	2.22	1.44	2.97	67.98	4.96
PBE0, dn	Mn	0.25	3.79	1.68	2.11	2.97	63.02	
PBE0, up	Mn, Cd	0.25	3.67	2.19	1.47	2.96	67.98	4.96
PBE0, dn	Mn, Cd	0.25	3.79	1.66	2.13	2.96	63.02	

In Table 1, the energy parameters ε_c , ε_v , ε_g denote the bottom of the conduction band, the top of the valence band and the band gap at Γ point of the Brillouin zone, respectively, and ε_F is the Fermi energy. Parameter n denotes the number of electrons in a unit cell with opposite spins, which difference gives the magnetization M . Table 1 shows the parameters of the electron energy spectrum obtained without ($\beta = 0$) and with ($\beta = 0.25$) taking into account the strong correlations of d -electrons. The results evaluated with taking into account the strong correlations of only d -electrons of the Mn atom are present in the third and fourth rows of the Table 1. The last two rows of Table 1 represent the results obtained on the basis of strong correlations of d -electrons of the Mn and Cd atoms.

The results given in Table 1 indicate the weak influence of strong correlations of the Cd d -electrons on the value of the band gap width for both spin orientations. The values of the Fermi energy and the magnetic moment of the elementary cell are also very weakly dependent on strong correlations of the Cd d -electrons.

4. CONCLUSIONS

In this work, the effect of strong correlations of the Mn and Cd d -electrons on the parameters of the electron energy spectrum of a solid solution CdMnTe has been studied. It is established that the Mn $3d$ -electrons are localized in the valence band in the energy range from -4.0 to -1.0 eV, provided that the strong correlations of the $3d$ electrons are neglected. After inclusion of strong correlations of the $3d$ electrons of the Mn atom, this interval increases and extends from -5.0 to -1.0 eV. Simultaneous inclusion of strong correlations of the Mn and Cd d -electrons almost does not cause a change in this interval, although the main peak of the density of states of the Cd $4d$ -electrons shifts down by about 0.7 eV, as can be seen from Figs. 2-c and 3-c. Consequently, we can conclude that there is a small overlap between $3d$ -states of Mn and $4d$ -states of Cd. It is also worth noting that the Cd $4d$ -states reveal a little overlap with the states of the conduction band, since the inclusion of their strong correlations almost does not affect the values of the band gaps and the magnetic moment of the elementary cell, as confirmed by the corresponding data presented in Table 1.

REFERENCES

1. J.K.J. Furduna, *J. Appl. Phys.* **64**, R29 (1988).
2. O. Goede, W. Heimbrod, *phys. stat. sol. b* **146**, 11 (1988).
3. V.F. Agekyan, N.N. Vasil'ev, A.Yu. Serov, N.G. Filosofov, G. Karczewski, *phys. solid state* **44**, 2013 (2002).
4. L.D. Park, S. Yamamura, J. Watanabe, K. Takamura, J. Nakahara, *J. Phys. Soc. Jpn.* **66**, 3289 (1997).
5. V.F. Agekyan, N.N. Vasil'ev, A.Yu. Serov, N.G. Filosofov, G. Karczewski, *phys. solid state* **47**, 2162 (2005).
6. A.M. Pogorily, S.M. Ryabchenko, A.I. Tovstolytkin, *Ukr. J. Phys. Rev.* **6**, 37 (2010).
7. A. Zunger, S. Lany *Physics* **3**, 53 (2010).
8. J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
9. P. Novák, J. Kuneš, L. Chaput, W.E. Pickett, *phys. status solidi b* **243**, 563 (2006).
10. X. Gonze, *Comp. Phys. Comm.* **180**, 2582 (2009).
11. X. Gonze, *Comp. Phys. Comm.* **205**, 106 (2016).
12. O.P. Malyk, S.V. Syrotyuk, *Comp. Mater. Sci.* **139**, 387 (2017).
13. O.P. Malyk, S.V. Syrotyuk, *J. Nano- Electron Phys.* **9**, 06007(6) (2017).
14. N.A.W. Holzwarth, A.R. Tackett, G.E. Matthews, *Comput. Phys. Comm.* **135**, 329 (2001).
15. A.R. Tackett, N.A.W. Holzwarth, G.E. Matthews, *Comput. Phys. Commun.* **135**, 348 (2001).
16. N.A.W. Holzwarth, G.E. Matthews, R.B. Dunning, A.R. Tackett, Y. Zeng, *Phys. Rev. B* **55**, 2005 (1997).
17. S.V. Syrotyuk, V.M. Shved, *Solid State Phenomena* **200**, 123 (2013).

Вплив сильних кореляцій на поляризовані за спіном електронні енергетичні зони твердого розчину CdMnTe

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Досліджено вплив сильних d -електронних кореляцій на значення параметрів енергетичних зон електронів у твердому розчині $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ ($x = 0.25$). На першому етапі у підході GGA отримано поляризовані за спіном електронні енергетичні зони. На другому етапі враховувалися сильні кореляції

для d -електронів Mn за допомогою гібридного обмінно-кореляційного функціонала PBE0, а на третьому етапі одночасно включалися кореляції d -електронів Mn та Cd. Виявлено, що матеріал є напівпровідником для обох спінів. Встановлено, що для електронів зі спіном вгору урахування скорельованих $3d$ -електронів Mn приводить до зсуву стелі валентної зони на $-0,10$ eV, а дно зони провідності підноситься на $0,02$ eV, що спричинює збільшення ширини забороненої зони на $0,12$ eV. Сильні кореляції $4d$ -електронів Cd додають до збільшення E_g значення $0,03$ eV. Сумарне збільшення E_g для спіна вгору дорівнює $0,15$ eV. Для спіна вниз включення сильних $3d$ -електронних кореляцій Mn привело до піднесення вершини валентної зони на $0,12$ eV, а дно зони провідності підвищилося на $0,54$ eV, що привело до збільшення ширини забороненої зони на $0,42$ eV. Сильні кореляції $4d$ -електронів Cd додали до збільшення E_g лише $0,02$ eV. Сумарне збільшення E_g для станів зі спіном вниз дорівнює $0,44$ eV. Встановлено, що для спіна вгору значення E_g твердого розчину без урахування сильних кореляцій d -електронів становить $1,32$ eV, а включення $3d$ -електронних кореляцій Mn приводить до значення E_g $1,44$ eV. Додаткове включення $4d$ -електронних кореляцій Cd дає значення E_g $1,47$ eV. Встановлено, що для спіна вниз значення E_g твердого розчину без сильних кореляцій d -електронів, становить $1,69$ eV, а включення $3d$ -електронних кореляцій Mn приводить до значення E_g $2,11$ eV. Включення $4d$ -електронних кореляцій Cd зумовило лише незначне збільшення значення E_g до $2,13$ eV.

Ключові слова: Твердий розчин, Сильні кореляції, Електронні енергетичні зони, Спінтроніка.