



REGULAR ARTICLE

Electronic and Magnetic Properties of the Solid Solution Cr: ZnSeTe
with the Cationic Vacancy

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The focus of this study is the structural, electronic, and magnetic characteristics of the ZnSeTe solid solution with chromium impurity. The structure of this solid solution was determined in two steps. At the first stage the internal coordinates of atoms are optimized, and at the second one the lattice parameter relaxation, including re-optimization of internal coordinates, were done. Further, after the introduction of Cr substitution impurity, electronic energy spectra and densities of electronic states were calculated. Significant changes in parameters of the electronic structure and magnetic properties caused by cationic vacancy were revealed. It was found that the doped solid solution of Cr:ZnSeTe is a semiconductor for both electron spin polarizations. The study of the supercell with a cationic vacancy revealed significant differences in the parameters of electronic energy bands as well as magnetic properties, compared with those in crystal with no defects.

Keywords: ZnSeTe solid solution, Cr impurity, Cationic vacancy, Electronic energy bands, DOS, Magnetic moment.

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1. INTRODUCTION

The mechanical properties of ZnSeTe solid solutions, which are important for applications in semiconductor devices, were studied in detail in the work [1]. For zinc selenide semiconductor crystals, the parameters of the mechanical strength and cracking resistance are especially important in their operation in optical devices of IR lasers and ionizing-radiation detectors operating over a wide range of temperatures. The cracking resistance or the brittleness of materials also substantially affects the conditions of mechanical treatment of crystals and the yield of good scintillation products.

Zinc semiconducting chalcogenides thin films have been extensively studied recently due to their technologically important applications in optoelectronic devices, solar cells, IR detectors and lasers. Ternary ZnSeTe thin films have been successfully used in light emitting devices, full-color display elements, scintillating material in radiation detectors, solar cells and semiconducting lasers [2].

Zinc-selenide-based ternary alloys, such as ZnSe_{1-x}Te_x, have attracted attention in thin film technology during the past several years because of their potential applications for advanced opto-electronic devices. However, the vapor growth of bulk ZnSe_{1-x}Te_x crystals has not been studied extensively and was reported more than three decades ago. Recently, the mass flux of ZnSeTe by physical vapor transport (PVT) was measured using an in situ dynamic technique and a one-dimensional diffusion limited analysis of the mass transport rate for the system was performed. The PVT growth of ZnSe_{1-x}Te_x crystals from source materials for

$x = 0.10, 0.20$ and 0.30 with well-defined stoichiometries under horizontal and vertical stabilized configurations has been reported [3].

ZnSe_{1-x}Te_x films with different tellurium (Te) contents were deposited by using an electron beam (EB) evaporation technique onto glass substrates for applications to optoelectronic devices. The structural and the optical properties of the ZnSe_{1-x}Te_x films were studied. The host material ZnSe_{1-x}Te_x were prepared by using the physical vapor deposition method of the electron beam evaporation technique (PVD: EBE) under a pressure of 1×10^{-5} mbar. The X-ray diffractogram indicated that these alloy films had cubic structure with a strong preferential orientation of the crystallites along the (111) direction. The optical properties showed that the band gap (E_g) values varied from 2.73 to 2.41 eV as the tellurium content varied from 0.2 to 0.8 [4].

The ZnX compounds (X = S, Se or Te) with impurities of transition 3d elements are currently well studied experimentally. In particular, works [5, 6] study the characterization of energy transfer, in iron-chromium co-doped ZnSe middle-infrared laser crystals. The room temperature kinetics of the Fe:Cr:ZnSe sample under excitation of chromium ion at 1560 nm shows that energy transfer in Fe-Cr- centers could be as fast as 290 ns.

Peculiarities of the impact of transition 3d elements impurities on the electronic structure of wide-gap cubic crystals were studied in theoretical works [7-9].

ZnSeTe solid solutions are also well-studied materials [10]. However, there is very little information in scientific periodicals about ZnSeTe [11] solid solutions with impurities of transition 3d elements.

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2. CALCULATION

2.1 The Structure Optimization

The electronic structure of ZnSeTe solid solutions doped with Cr atoms was calculated using the ABINIT complex of programs [12] in two stages.

At the first stage, structural optimization was done, which also consisted of two steps. The first step was to optimize the lattice parameter, and the second was to find the precise coordinates of the atoms in the supercell. In order to save space, we present the optimization results for the $\text{Zn}_4\text{Se}_3\text{Te}_1$ supercell, which contains eight atoms. The corresponding results are shown in Table 1.

Table 1 – An example of optimizing the structure of a smaller supercell of a $\text{Zn}_4\text{Se}_3\text{Te}_1$ solid solution

Coords	Initial			Optimized		
	x/a	y/b	z/c	x/a	y/b	z/c
Te	0.5	0	0	0.5	0	0
Se	0	0.5	0	0	0.5	0
Se	0	0	0.5	0	0	0.5
Se	0.5	0.5	0.5	0.5	0.5	0.5
Zn	0.75	0.25	0.25	0.7589	0.2589	0.2589
Zn	0.25	0.75	0.25	0.2411	0.7411	0.2589
Zn	0.25	0.25	0.75	0.2411	0.2589	0.7411
Zn	0.75	0.75	0.75	0.7589	0.7411	0.7411

As can be seen from Table 1, the Zn atoms have reduced z-coordinates (z/c) different from the starting ideal values 0.25, 0.25, 0.75, 0.75, respectively. The optimized values of the lattice lengths have acquired the following values: $a = b = c = 11.0628$ a.u., respectively. The starting lattice lengths had the same values $a = b = c = 11.1681$ a.u. For none of the atoms, the condition of fixing the reduced coordinates was not applied. And the lattice angles remained the same as in the ideal starting supercell, i.e. $\alpha = \beta = \gamma = 90$ degrees. The Cartesian forces (0.000011, 0.000011, 0.000011) eV/Å, acting on the Zn atoms, have been reached at the end of a final iteration loop. The corresponding pressure is characterized by a value of 0.0005 GPa. The starting values of the Cartesian forces were equal to (0.018, 0.018, 0.018) eV/Å. The corresponding starting pressure is characterized by the value of 1.4 GPa.

In this work, we performed all calculations for the $\text{Zn}_{31}\text{Cr}_1\text{Se}_{24}\text{Te}_8$ supercell, which consists of 64 atoms. The effect of the cation vacancy was studied on the basis of a 63-atom $\text{Zn}_{30}\text{Cr}_1\text{Se}_{24}\text{Te}_8$ supercell calculation.

2.2 Details of the Calculation Scheme

Electronic structure calculation methods, such as APW, LAPW, and LMTO, are based on the use of MT (spherical-cell, muffin-tin) potentials, i.e., they also involve augmentation of the wave function on the boundary of the augmentation sphere in order to ensure its continuity. The augmentation procedure results in quite complex mathematical calculations, which require significant additional computational costs [13].

These shortcomings have been overcome in the method we use in this study. Calculations of the electronic structure were performed here in the PAW basis

(projector augmented waves) [14].

In the PAW approach, a smooth pseudo-wave function $|\tilde{\psi}_{\alpha\mathbf{k}}\rangle$ is first calculated, from which the true all-electronic wave function $|\psi_{\alpha\mathbf{k}}\rangle$ is obtained. Here α is a band index, and \mathbf{k} is a vector from the first Brillouin zone. The true all-electronic wave function is derived from the smooth pseudo-wave function using the operator τ [14]

$$|\psi_{\alpha\mathbf{k}}\rangle = \tau |\tilde{\psi}_{\alpha\mathbf{k}}\rangle, \quad (2)$$

which is constructed from partial atomic waves φ_i , pseudowaves $\tilde{\varphi}_i$ and projectors \tilde{p}_i , namely [15],

$$\tau = 1 + \sum_i (|\varphi_i\rangle - |\tilde{\varphi}_i\rangle) \langle \tilde{p}_i|. \quad (3)$$

The Schrödinger equation, which is based on the matrix of the Hamiltonian H , after replacing (2), (3) is reduced to the problem of the eigenfunctions and eigenvalues of the matrix of the effective Hamiltonian, with a mutual electronic energy spectrum $\varepsilon_{\alpha\mathbf{k}}$, namely

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

By means of the transformation τ , we obtain from the all-electronic Hamiltonian H an effective Hamiltonian $H_{\text{eff}} = \tilde{H} = \tau^+ H \tau$, the eigenfunction of which is called the pseudo-wave function $\tilde{\psi}_{\alpha\mathbf{k}}$. From the latter, a true all-electronic function $\Psi_{\alpha\mathbf{k}} = \tau \tilde{\psi}_{\alpha\mathbf{k}}$ will be found. It allows us to calculate the dipole matrix elements necessary to obtain the optical constants of crystals and the kinetic coefficients of semiconductors [16].

The presence of a subsystem of strongly correlated 3d Cr electrons determines the use of a hybrid exchange-correlation functional. We chose the latter in the form of PBE0 [17, 18], namely

$$E_{xc}^{\text{PBE0}}[\rho] = E_{xc}^{\text{PBE}}[\rho] + \beta(E_x^{\text{HF}}[\Psi_{3d}] - E_x^{\text{PBE}}[\rho_{3d}]). \quad (5)$$

In this functional, the exchange-correlation energy of the 3d electrons of the Cr atom, found in the GGA [17] approximation, is partially removed, and the exchange energy of the same electrons, found in the Hartree-Fock theory, is substituted in its place. Namely, the PBE0 functional includes the usual PBE term, which corresponds to electrons with a smooth change in space of their density. The second term of formula (5) leads to the partial elimination of self-interaction error of 3d electrons. The mixing factor β is recommended to be 0.25 [18].

3. RESULTS AND DISCUSSION

The calculated electronic properties of the ZnSeTe solid solution, at ambient conditions, in which the Cr atom replaces the Zn atom, are shown in Figures 1-3.

Fig. 1 shows the presence of 3d electrons at the Fermi level, which move in very narrow energy bands. Such a subsystem of electrons is poorly described by the exchange-correlation functional of the GGA, since the 3d electrons are characterized by very large self-interaction energy. This shortcoming is successfully eliminated with

the help of the hybrid exchange-correlation functional PBE0.

As can be seen from Figure 1 the material ZnCrSeTe is a narrow band semiconductor for a majority-spin direction. The optical band gap for the spin up carriers equals to 0.07 eV and the fundamental one is to be of 0.02 eV. And Fig. 2 shows a semiconductor nature of the the minority-spin carriers. The optical and fundamental band gaps are the same and equal to 1.03 eV.

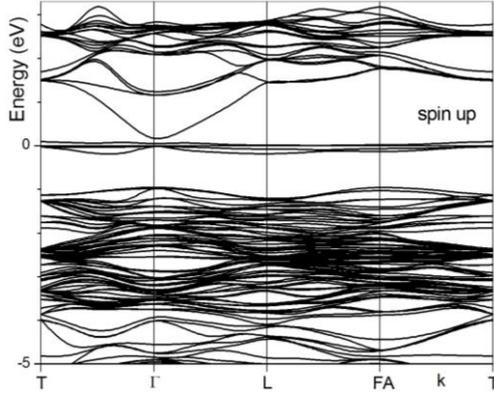


Fig. 1 – The majority-spin electronic energy bands, evaluated for supercell Zn₃₁Cr₁Se₂₄Te₈ at ambient conditions

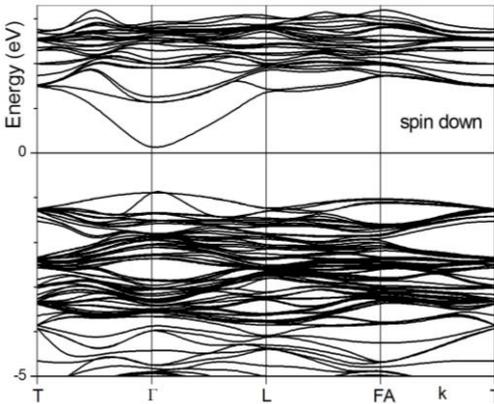


Fig. 2 – The minority-spin electronic energy bands, evaluated for supercell Zn₃₁Cr₁Se₂₄Te₈ at ambient conditions

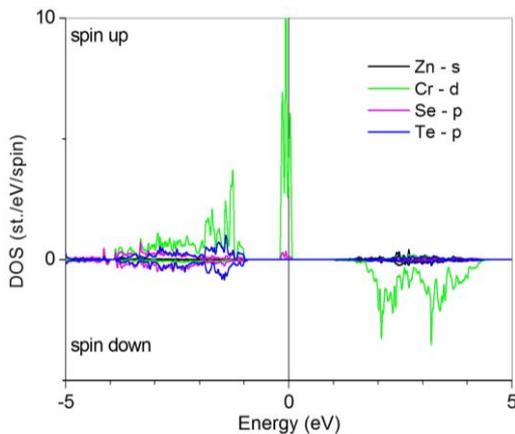


Fig. 3 – The majority- and majority-spin partial DOS, evaluated for supercell Zn₃₁Cr₁Se₂₄Te₈ at ambient conditions

The densities of states presented in Fig. 3 show that the top of the valence band is formed mainly by *p* states of Se and Te, as well as by *d* states of Cr.

Curves in Fig. 3 reveal a significant asymmetry of the Cr *d* states, which indicates the presence of a non-zero magnetic moment of the supercell. The latter equals to $4.0\mu_B$ and the Cr atom contribution is $3.04\mu_B$.

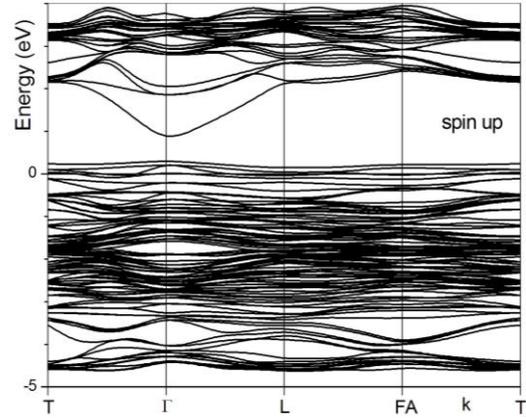


Fig. 4 – The majority-spin electronic energy bands, evaluated for supercell Zn₃₀Cr₁Se₂₄Te₈ with cationic vacancy V_{Zn}

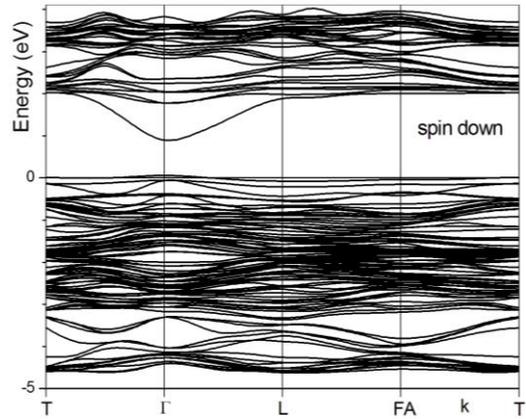


Fig. 5 – The minority-spin electronic energy bands, evaluated for supercell Zn₃₀Cr₁Se₂₄Te₈ with cationic vacancy V_{Zn}

The results shown in Figures 4-6 allow us to reveal the effect of a cationic vacancy V_{Zn} on the electronic structure of the ZnCrSeTe material. The spin-polarized electron energy spectra shown in Figures 4, 5 reveal a metallic state at the Fermi level for electrons in spin-up and spin-down states, respectively. Both of the latter graphs show that the Fermi level crosses the dispersion curves within the upper energy region of the valence band.

As can be seen from fig. 6, at the Fermi level dominate the Cr 3d electrons in spin-up and spin-down states. Narrow bands in which Cr 3d electrons move, as well as large values of the density of states in them, indicate a subsystem of strongly correlated electrons. The most appropriate approach for describing such systems is the use of hybrid exchange-correlation energy functionals [18].

The total magnetic moment of the supercell equals to $2.87\mu_B$ and the contribution of the Cr atom dominates and amounts of $2.84\mu_B$.

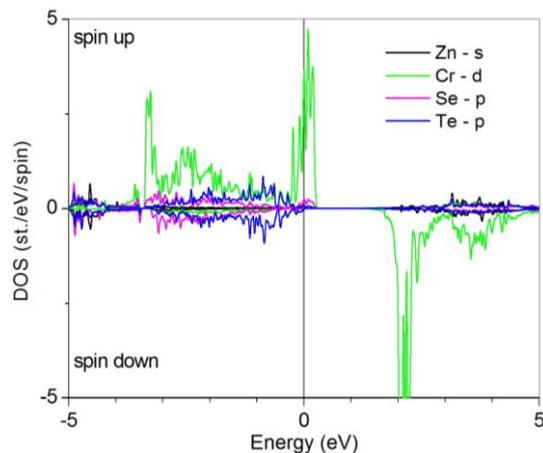


Fig. 6 – The majority- and majority-spin partial DOS, evaluated for supercell $Zn_{30}Cr_1Se_{24}Te_8$ with cationic vacancy V_{Zn}

4. CONCLUSIONS

This study consists of the following two main stages. At the first one, the spin-polarized electronic structure of the Cr:ZnSeTe solid solution is investigated. The second part of the study is devoted to the study of changes in the parameters of the electronic structure

under the influence of the V_{Zn} cation vacancy.

Electronic energy bands were evaluated for $Zn_{31}Cr_1Se_{24}Te_8$ supercell in which the Zn atom is replaced by the Cr atom. The calculation results revealed significant changes in the electronic structure due to the presence of chromium impurity. Thus, the electronic energy spectrum of charge carriers with spin up is characterized by a narrow interband optical gap of 0.07 eV. And for carriers with an opposite spin states, this parameter is equal to 1.03 eV.

A cationic vacancy V_{Zn} fundamentally changes the parameters of the electronic structure of the material, represented by the supercell $Zn_{30}Cr_1Se_{24}Te_8$. The Fermi level is now localized at the upper part of the valence band for both values of the spin moment. That is, for both spin orientations, the metallic state is realized. The magnetic moments of the supercell are almost the same for both spin orientations. We can consider such a material as a magnetic metal.

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REFERENCES

- I.A. Rybalka, S.N. Galkin, E.F. Voronkin, V.D. Ryzhikov, *Crystallography Rep.* **53**, 1163 (2008).
- T. Mahalingam, V. Dhanasekaran, Suganthi Devadason, J.P. Chu, *ECS Trans.* **45**, 19 (2013).
- C.-H. Su, Y.-G. Sha, M.P. Volz, P. Carpenter, S.L. Lehoczyk, *J. Crystal Growth* **216**, 104 (2000).
- J. Suthagar, N.J.S. Kissinger, G. M.S. Nath, K. Perumal, *J. Korean Phys. Soc.* **64**, 58 (2014).
- V. Fedorov, T. Carlson, S. Mirov, *Opt. Mater. Exp.* **9**, 2340 (2019).
- J.R. Sparks, S.C. Aro, R. He, M.L. Goetz et al., *Opt. Mater. Exp.* **10**, 1843 (2020).
- S.V. Syrotyuk, V.M. Shved, *Condens. Matter Phys.* **16**, 13701 (2013).
- V. Tsiumra, A. Zhyshkovich, T. Malyi, Y. Chornodolsky, V. Vistovskyy, S. Syrotyuk, Ya. Zhydachevskyy, A. Suchocki, A. Voloshinovskii, *Opt. Mater.* **89**, 480 (2019).
- M. Labair, H. Rached, D. Rached, S. Benalia, B. Abidri, R. Khenata, R. Ahmed, S. Bin Omran, A. Bouhemadou, S.V. Syrotyuk, *Int. J. Mod. Phys. C* **27**, 1650107 (2016).
- J. Wu, W. Walukiewicz, K.M. Yu, W. Shan, J.W. Ager, E.E. Haller, I. Miotkowski, A.K. Ramdas, Ching-Hua Su, *Phys Rev B* **68**, 033206 (2003).
- S.V. Syrotyuk, M.K. Hussain, *J. Nano- Electron. Phys.* **15** No 5, 05002 (2023).
- X. Gonze, F. Jollet, F. Abreu Araujo, D. Adams, B. Amadon, T. Applencourt, C. Audouze, J.-M. Beuken, J. Bieder, A. Bokhanchuk, E. Bousquet, F. Bruneval, D. Caliste, M. Cote, F. Dahm, F. Da Pieve, M. Delaveau, M. Di Gennaro, B. Dorado, C. Espejo, G. Geneste, L. Genovese, A. Gerossier, M. Giantomassi, Y. Gillet, D. R. Hamann, L. He, G. Jomard, J. Laflamme Janssen, S. Le Roux, A. Levitt, A. Lherbier, F. Liu, I. Lukacevic, A. Martin, C. Martins, M. J. T. Oliveira, S. Ponce, Y. Pouillon, T. Rangel, G.-M. Rignanese, A. H. Romero, B. Rousseau, O. Rubel, A. A. Shukri, M. Stankovski, M. Torrent, M. J. Van Setten, B. Van Troeye, M. J. Verstraete, D. Waroquier, J. Wiktor, B. Xu, A. Zhou, J. W. Zwanziger, *Comput. Phys. Commun.* **205**, 106 (2016).
- E. Sjöstedt, L. Nordström, D.J. Singh, *Solid State Commun.* **114**, 15 (2000).
- P.E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- A.R. Tackett, N.A.W. Holzwarth, G.E. Matthews, *Comput. Phys. Commun.* **135**, 348 (2001).
- O.P. Malyk, S.V. Syrotyuk, *J. Nano- Electron. Phys.* **14**, 01014 (2022).
- J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- F. Tran, P. Blaha, K. Schwarz, P. Novák, *Phys. Rev. B* **74**, 155108 (2006).

Електронні та магнітні властивості твердого розчину Cr: ZnSeTe з катіонною вакансією

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У фокусі даного дослідження – структурні, електронні та магнітні характеристики твердого розчину ZnSeTe з домішкою хрому. Структуру цього твердого розчину визначали у два етапи. На першому етапі оптимізовано внутрішні координати атомів, а на другому проведено повторну релаксацію параметрів ґратки, включаючи повторну оптимізацію внутрішніх координат. Далі, після введення до-

мішки заміщення Cr, розраховували електронні енергетичні спектри та густини електронних станів. Виявлено суттєві зміни параметрів електронної структури та магнітних властивостей, зумовлені катіонною вакансією. Встановлено, що легований твердий розчин Cr:ZnSeTe є напівпровідником для обох електронних спінових поляризацій. Дослідження суперкомірки з катіонною вакансією виявило суттєві відмінності параметрів електронних енергетичних зон, а також магнітних властивостей порівняно з кристалом без дефектів.

Ключові слова: Твердий розчин ZnSeTe, Домішка Cr, Катіонна вакансія, Електронні енергетичні зони, ГЕС (DOS), Магнітний момент.