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Simulation of electronic states in the band gap of ZnS: Cu, Cl crystallophosphors

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Abstract. The results of calculations of the valence band top, conduction band bottom, optical band gap, gap states formed by the homopolar bonds and clusters in ZnS: Cu, Cl crystallophosphors have been presented. The calculation procedure has been based on the linear combination of atomic orbitals and pseudo-potential methods. The energy values have been determined in the centre of the Brillouin zone. The atomic terms determined within Herman-Skillman and Hartree-Fock approximations have been used in the calculations. The quantitative agreement between theoretical and experimental data on the band gap and photoemission threshold for this type of materials has been shown. The energy values for the optical transitions have been determined (1.77; 2.41; 2.65 and 2.95 eV) and correlated with the experimental emission spectra for the samples processed under different conditions.

Keywords: photoemission threshold, LCAO, gap states, ZnS: Cu, Cl crystallophosphor, electroluminescence

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1. Introduction

The use of reliable theories giving insight into the basic fundamental physical properties of solids gives possibility to predict the band gap structure and properties for the novel materials, and to make correct interpretation of the effect of preparation techniques and external factors on these properties.

The methods of the linear combination of atomic orbitals and pseudo-potential are known to be used for the calculation of physical parameters of solids [1]. This method now is being used for the calculations of the band gap structure and properties for a number of materials [2–7]. The calculations have also been carried out for ZnS crystals. Bearing in mind that this method being still under development (see, [8–9]) enables the calculation of the radiative transitions from the electronic structure of the solid. It can be used for the simulation of electronic states in the band gap and the fundamental properties of ZnS: Cu, Cl phosphors within the same model. In this method of calculations, the intratomic parameters (terms), determined within the Hartree-Fock approximation are applicable. In this work, the calculations have been performed for different approximations, since the

results of the calculations in different specified cases can coincide or differ. The interatomic distance dependence of the matrix element characterising the covalent bonding energy requires the detailed analysis of the correlation of solid body properties with this parameter. For the analysis, the compounds of A^{II}B^{VI} type (ZnS, ZnSe, and ZnTe) have been chosen.

Zinc sulphide doped with Cu and/or Cl manifests the electronic states inherent to Cu₂S and CuCl compounds. These electronic states are responsible for the changes in the luminescence spectra and physical properties of the doped ZnS. Thus, the calculations should be done for these compounds as well.

This work is devoted to the simulation of the electronic structure for ZnS: Cu, Cl crystallophosphors and its correlation with the known experimental results.

2. Simulation of optical properties for chalcogenides of zinc and activator and co-activator based compounds

To calculate the positions of the electronic states in the band gap for semiconductors, it is necessary to know

the energy position of the upper part of the valence band (E_v) and the bottom of the conduction band (E_c) with respect to the vacuum level. These values can be calculated following the formulae given in the works by W.A. Harrison [1, 10–13]:

$$E_v = \frac{\varepsilon_p^c + \varepsilon_p^a}{2} - \sqrt{V_2^2 + V_3^2} + 1.11V_1 + E_{relax}, \quad (1)$$

$$E_c = \frac{\varepsilon_p^c + \varepsilon_p^a}{2} + U/2, \quad (2)$$

where ε_p^c and ε_p^a are the atomic terms of the cation (Zn, Cu) and anion (S, Cl) p -states. The metallic bond energy (V_1) and ionic bond energy (V_3) have been found from the equations:

$$V_1 = \frac{V_1^c + V_1^a}{2} = \frac{\varepsilon_p^a - \varepsilon_s^a + \varepsilon_p^c - \varepsilon_s^c}{8}, \quad (3)$$

$$V_3 = \frac{\varepsilon_p^c - \varepsilon_p^a}{2}, \quad (4)$$

where ε_s^c and ε_s^a are the atomic terms of the anion and cation s -states. The values for the atomic terms have been taken from Ref. [1].

The covalent bonding energy (V_2) has been determined from the equation:

$$V_2 = \frac{\eta \hbar}{md^2}, \quad (5)$$

where $\eta = 2.16$ is the dimensionless coefficient that derives the approximate values of the interatomic interaction matrix elements for the Γ -point, the centre of the Brillouin zone, $\hbar = h/2\pi$ is the Planck constant, m is the electronic mass.

The relaxation energy E_{relax} has been calculated from Eq. (13):

$$E_{relax} = \frac{U(\varepsilon - 1)}{2\varepsilon} \quad (6)$$

where ε is the dielectric constant. In the calculations, the following values for this magnitude have been used [14]: for ZnS – $\varepsilon = 5.3$, for ZnSe – $\varepsilon = 6.3$, for ZnTe – $\varepsilon = 7.8$, and for CuCl – $\varepsilon = 5.7$. For Cu₂S the calculated value of $\varepsilon = 3.7$ has been used.

The intratomic Coulomb repulsion U has been calculated following Eq. (13):

$$U = \frac{5}{4} e^2 \left(\frac{2\pi^2 m}{h^2} \right)^{1/2} \left(\frac{\varepsilon_p^c + \varepsilon_p^a}{2} \right)^{1/2} \quad (7)$$

where e is the electronic charge.

The photoemission threshold (Φ) corresponds to the energy of E_v , that is $\Phi = E_v$, and the band gap is $E_g = |E_c - E_v|$.

The procedure of going from the atomic p -orbitals to the energy bands for ZnS crystals has been illustrated in Fig. 1. The following designations have been made there: $V_1^* = 1.11V_1$; $E_{p\pi}$ is the energy corresponding to the non-bonding π -states S 3 p of sulphur atoms in ZnS band gap. The latter has been derived from the formula:

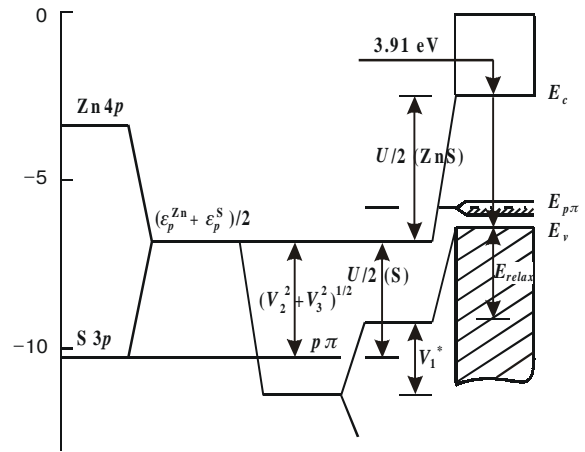


Fig. 1. Illustration to the procedure of using LCAO method to proceed from the atomic p -orbitals to the energy bands in zinc sulphide.

$$E_{p\pi} = \varepsilon_p + U/2(S). \quad (8)$$

When going from the atomic terms to the energy bands in solids non-bonding states have been splitted into a narrow (near ± 0.2 eV) band [15] the lower part of which is occupied with electrons.

The energy parameters V_1 , V_2 , V_3 , U and E_{relax} , calculated within Herman-Skillman and Hartree-Fock approximations, and experimental d , E_g and Φ values for ZnS, ZnSe, ZnTe, Cu₂S and CuCl compounds are given in the Table. Simulation of the internuclear distance d has been performed using the data on the covalent atomic radii by Pauling and Haggins [16]. From this Table, it is seen that the experimental and calculated d values are in agreement within the accuracy of ± 0.001 nm.

Theoretical and experimental dependences of the band gap and photoemission threshold for A^{II}B^{VI} compounds on the internuclear distance d are presented in Fig. 2 and Fig. 3. From Fig. 2 it is seen that for ZnS the experimental E_g values closest to the calculated ones have been obtained with the terms, calculated within the Herman-Skillman approximation. Thus, in simulation of the electronic states in ZnS band gap, this approximation is applicable. The variation of the photoemission threshold with the internuclear distance in the compounds of A^{II}B^{VI} type (Fig. 3) is in qualitative agreement with theoretical data. As it has been shown in examination, for the experimental Φ and d values the magnitude of $d \ln \Phi / d \ln d$ equals to -2 , while for those calculated within Herman-Skillman and Hartree-Fock approximations, these magnitudes are -3.0 and -2.5 , respectively.

3. Simulation of the electronic states in zinc sulphide band gap

The energy diagram illustrating the formation of the electronic states in the band gap for ZnS (a), ZnS: Cu (b), ZnS: Cl (c) and ZnS: Cu, Cl (d) is given in Fig. 4. In this figure, the

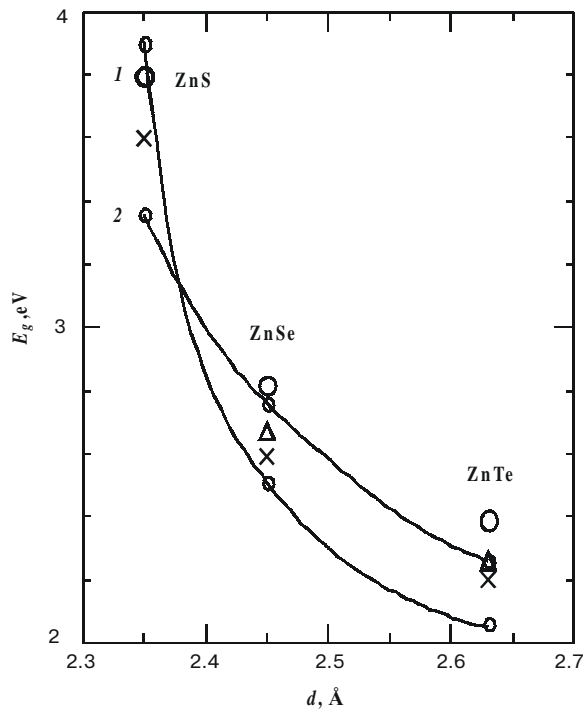


Fig. 2. Band gap (E_g) versus internuclear distance (d) for ZnS, ZnSe and ZnTe semiconductors. Curves 1 and 2 correspond to theoretical dependences constructed using the atomic terms within Herman-Skillman (1) and Hartree-Fock (2) approximations. Symbols (O), (Δ) and (\times) show the experimental E_g values taken from Refs [1], [18] and [17].

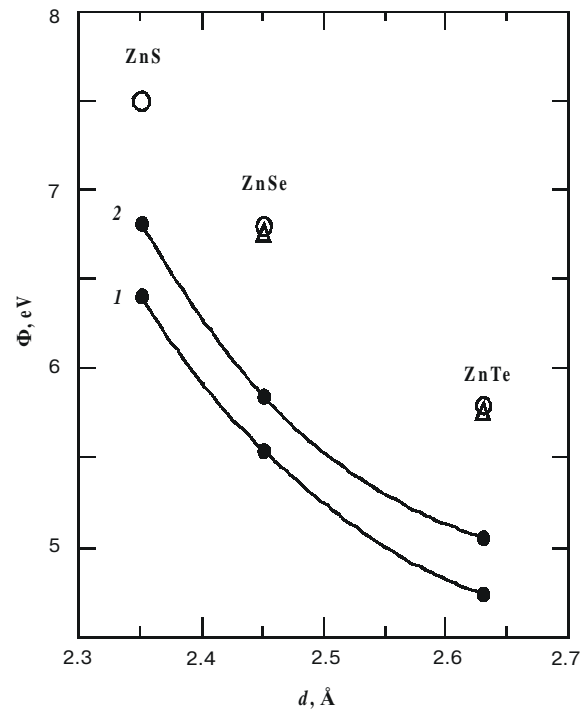


Fig. 3. Photoemission threshold (Φ) versus internuclear distance (d) for ZnS, ZnSe and ZnTe semiconductors. Curves 1 and 2 correspond to theoretical dependences constructed using the atomic terms within Herman-Skillman and Hartree-Fock approximations, respectively. Experimental values are designated similarly to those in Fig. 2.

Table. Parameters of the semiconductors along with the calculated and experimental values for the internuclear distances, band gaps and photoemission thresholds. The values predicted within the Hartree-Fock approximation are given in parentheses

	ZnS	ZnSe	ZnTe	Cu2S	CuCl	Reference
d, nm (theory)	0.235	0.245	0.263	0.239	0.234	
d, nm (exper.)	0.234–0.236*	0.245	0.264	–	0.234	[1], [18]
V_1, eV	1.95 (2.06)	1.98 (2.03)	1.70 (1.70)	1.95 (1.57)	2.18 (2.33)	
V_2, eV	2.96	2.74	2.36	2.88	3.01	
V_3, eV	3.45 (3.81)	3.08 (3.35)	2.61 (2.78)	4.21 (4.15)	5.24 (5.24)	
$U/2, \text{eV}$	3.46 (4.33)	3.42 (4.23)	3.31 (3.96)	2.70 (3.93)	3.37 (4.34)	
E_{relax}, eV	2.80 (3.51)	2.87 (3.55)	2.88 (3.45)	1.97** (2.87**)	2.78 (3.58)	
E_g, eV (theory)	3.91 (3.36)	2.51 (2.76)	2.06 (2.26)	3.91 (3.08)	4.45 (4.47)	
E_g, eV (exper.)	3.80 – 3.6	2.82 2.67 2.6	2.39 2.26 2.2	– – –	– – –	[1] [18] [17]
Φ, eV (theory)	6.41 (6.82)	5.55 (5.86)	4.74 (5.06)	7.26 (7.84)	7.13 (8.68)	
Φ, eV (exper.)	7.5 –	6.8 6.76	5.8 5.76	– –	– –	[1] [18]

Notes: *) The value of $d = 0.236 \text{ nm}$ corresponding to sphalerite structure has been used in the simulation of the parameters
 **) The calculated value for the dielectric constant $\epsilon = 3.7$ has been used in the simulation of E_{relax}

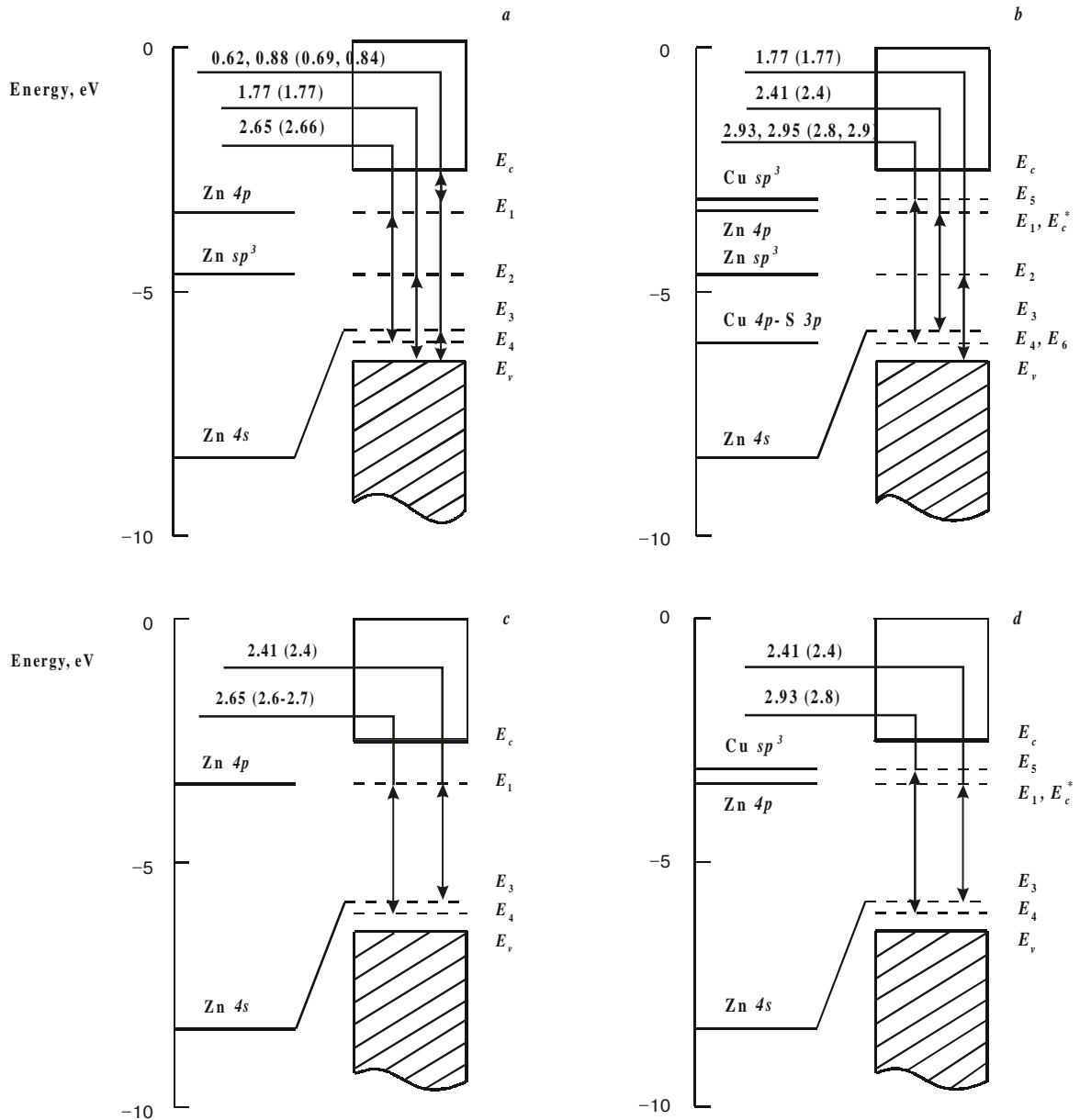


Fig. 4. Tentative electronic states in the band gap for ZnS (a), ZnS: Cu (b), ZnS: Cl (c) and ZnS: Cu, Cl (d). Arrows show the optical radiative transitions and corresponding energy values (in electron-volts). Experimental energy values related to the peak in emission spectrum are given in parentheses.

arrows show the possible optical radiative transitions and corresponding energy values. Experimental energy values related to the peak in the emission spectrum are given along with these values in parentheses [19, 20].

Electronic states with the energies of E_1 and E_2 correspond to Zn $4p$ and Zn sp^3 atomic terms. Electronic states with the energy of E_3 are formed by the bonding Zn $4p$ states of Zn-Zn homopolar bonds. For these states, the splitting value can be found from Eq. (5) and is $V_2 = 2.35$ eV. The internuclear distance d for Zn-Zn bond equals to 0.266 nm [21]. E_4 electronic states correspond to the energy of the bottom of the non-bonding p -band.

In ZnS: Cu phosphors (Fig. 4, b) additional E_5 electronic states corresponding to the hybridized states of

copper atoms (Cu sp^3) can be formed in the band gap. The electronic states forming the bottom of the conduction band in Cu₂S fall into the band gap of these materials too. They are denoted as E_v^* in Fig. 4, b.

In ZnS: Cl phosphors (Fig. 4, c) no new electronic states are formed in the band gap. One can suppose that Cl atoms compensate Zn sp^3 electronic states, and thus the red emission band in these phosphors fades out.

Doping of ZnS with Cu and Cl atoms results in blue (2.8 eV) and green (2.4 eV) emission of these phosphors only (Fig. 4, d). The shift of the blue band towards lower energies is liable to stem from the occupation of the lower part of p -band by the electrons. The shift of the green band

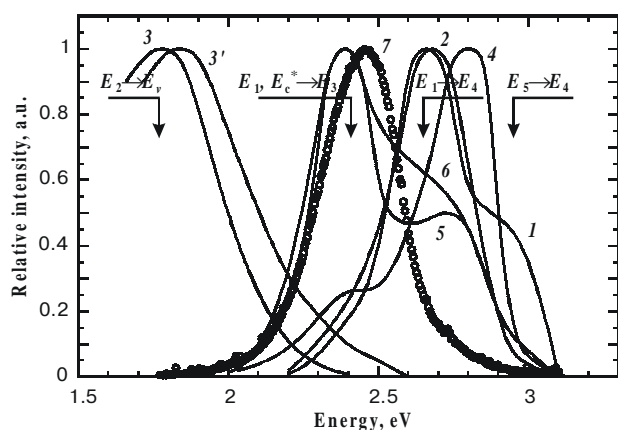


Fig. 5. Emission spectra for 1 – pure ZnS treated in zinc during 30 hours [22]; 2 – hexagonal ZnS: Cl at 80 K [20]; 3, 3' – hexagonal ZnS: 10^{-3} Cu at 80 K and 300 K [20]; 4 – hexagonal ZnS: 1.5×10^{-4} Cu: 10^{-4} Cl at 80 K (heating at 1473 K in H_2S with subsequent annealing during 74 hours at 448 K in air) [20]; 5 – cathodoluminescence spectrum at 83 K (15 kWt, 10^{-8} A cm^{-2}) for ZnS: 2×10^{-3} Cu annealed with $MgCl_2$, NaCl at 1223 K [23]; 6 – electroluminescence spectrum for ZnS: Cu, Cl powder annealed during 6 hours at 1073 K with CuCl (1.25 %) and $CuCl_2$ (1.25 %) [24]; 7 – ZnS: Cu, Cl powder phosphor (sample No. 1579a).

can originate from the reduction of the Cu-S bonds number due to formation of more efficient Cu-Cl bonds.

Fig. 5 shows emission spectra of photoluminescence, electroluminescence and cathodoluminescence for pure and doped ZnS single crystals reported by different authors [20–24] and powders doped with copper and chlorine (curve 7) obtained in these studies. The arrows in this figure show the energy values corresponding to the optical transitions in visible spectral range given in Fig. 4. As seen, these energy values (1.77; 2.41; 2.65 and 2.95 eV) are in good agreement with positions of the peaks in emission spectra observed experimentally.

4. Conclusions

The energy band diagram for ZnS: Cu, Cl phosphors has been calculated. The applicability of the modified LCAO method for the calculation of the electronic states in the band gap has been demonstrated.

The quantitative agreement between theoretical and experimental data on the band gap and photoemission threshold has been shown. The possible optical transitions responsible for the position of the peaks in experimental emission spectra have been determined.

The method can be used as a new approach to the modelling of the luminescence centres and thus understanding of the nature of degradation processes.

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