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Tight-binding calculation of the properties of the *F* center and of isoelectronic defects in ZnS

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Using a tight-binding parametrization of the band structure of ZnS, we calculate the energy levels of the *F* center associated with a vacancy of S, and of some isoelectronic defects on Zn and S sites. The calculation is performed in a Koster-Slater scheme, using the Haydock, Heine, and Kelly recursion method to generate the Green's functions. The theoretical results agree reasonably well with the experimental data.

I. INTRODUCTION

Recently there has been a renewed interest in tight-binding parametrizations of the band structure of semiconductors.[1-3] Most of this work is concerned with surface properties but these parametrizations can also be used to calculate the localized deep levels associated with point defects.[4] In the present paper we focus our attention on the properties of the simplest point defects in ZnS: the sulphur vacancy and isoelectronic traps, as there is a large number of experimental data for such levels, obtained by[5] EPR and luminescence[6] measurements.

These results are generally interpreted using molecular or purely ionic models. The classical point-ion approximation appropriated to purely ionic crystals has been used by Wruck[7] to investigate the properties of the *F* center. Such a model is very useful for a qualitative understanding of the *F* center associated with a vacancy but it cannot be taken too seriously in a band semiconductor like ZnS. The purpose of the present paper is to perform a Koster-Slater[8] calculation of vacancy and impurity states in ZnS and to show how the experimental results can be interpreted. We will also improve on the description of isoelectronic traps in ZnS by Baldereschi and Hopfield[9] who use a one-band one-site model.

Our calculation is semiempirical: the matrix elements of the Hamiltonian are determined without explicit use of the wave functions in both perfect and imperfect crystals. We perform a second-nearest-neighbor Slater-Koster[10] fit to the dispersion curves obtained using a self-consistent band-structure calculation. This procedure leads to a fairly accurate representation of the valence bands and a reasonable agreement for the first four conduction bands, while such interpolations cannot fit accurately the higher conduction bands in purely covalent semiconductors.[2,4] This difference is apparently due to the ionicity of the II-VI compounds and gives us some confidence that the method can be used to describe semiquantitatively the impurity states originating from the conduction bands (S vacancy and isoelectronic traps on the cation site) as well as those originating from the valence bands (isoelectronic traps on the anion site).

In Sec. II of the present paper, we give our results for the band structure and the corresponding density of states of pure ZnS. Sections III and IV are devoted to the sulphur vacancy and isoelectronic traps, respectively, and to comparisons of our results with experimental data and with other theoretical calculations.

II. BAND STRUCTURE OF ZnS

A. Tight-binding (TB) parametrization

Two tight-binding parametrizations of the band structure of ZnS have been already published by Kraut,[3] one including third-neighbor interactions and the other with only second-neighbor interactions.

The first type of parametrization provides a better fit to the dispersion curves but (i) it involves seven more parameters than the second one, (ii) it leads to second-neighbor transfer integrals that are largely smaller than the third-neighbor ones. On the other hand, the diagonal elements $E_{ss}(000)$ and $E_{pp}(000)$ in the second-neighbor parametrization lead to an ionic picture of the band structure of ZnS: the *s* and *p* levels of sulphur generate the lower and upper valence bands when the *s* and *p* levels of zinc correspond to the lower and upper conduction bands. Therefore we consider that the second-neighbor parametrization is more realistic than the third-neighbor fit. However, as the calculation of Kraut leads to a very small coupling parameter between the "*s*" orbitals on Zn and S, we preferred to perform a new second-neighbor fit to the dispersion curves of Stuckel *et al.*[11] using the values of Kraut for the transfer integrals as a starting point.

The calculation of the parameters is performed

TABLE I. Slater-Koster transfer integrals obtained in our parametrization, compared with those of Kraut (Ref. 3).

	Parameter	Present work	Kraut	Parameter	Present work	Kraut
Zn	$E_{ss}(0\,0\,0)$	4.917 31	5.1751	$E_{ss}(1\,1\,0)$	−0.1041	−0.102 21
	$E_{xx}(0\,0\,0)$	7.608 31	7.9147	$E_{sx}(1\,1\,0)$	0.001 06	0.034 05
S	$E_{ss}(0\,0\,0)$	−10.079 69	−10.649	$E_{sz}(1\,1\,0)$	0.034 94	0.130 77
	$E_{xx}(0\,0\,0)$	−0.382 39	−0.604 54	$E_{xx}(1\,1\,0)$	0.2109	0.220 92
	$E_{ss}(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$	0.5224	0.004 77	$E_{zz}(1\,1\,0)$	−0.3230	−0.337 69
	$E_{sx}(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$	−0.7322	−0.176 35	$E_{xy}(1\,1\,0)$	0.1174	0.105 34
	$E_{xs}(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$	0.7322	0.176 35	$E_{xz}(1\,1\,0)$	0.0000	
	$E_{xx}(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$	−0.079 83	−0.2305			
	$E_{xy}(\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2})$	1.229	1.2821			

using the nonlinear least-square-fitting method of Mattheiss.[12]

In Table I we compare the parameters obtained in this way with those of Kraut and Table II compares the energy eigenvalues we obtained for different points in $\vec{k}$ space with the values of Stuckel *et al.*

B. Density of states

Once the parameters of the band structure are calculated, the density of states is determined using the method of Haydock, Heine, and Kelly[13] in a cluster of 2545 atoms. This procedure, particularly well suited to the description of localized levels, amounts to developing the partial density of states $n^{\Gamma,X}(E)$ (where X= Zn or S and Γ refers to the symmetry mode considered: $\Gamma = A_1$ or T_2 in the tetrahedral symmetry) in a continued fraction:

$$n^{\Gamma,X}(E) = -(1/\pi)\,\mathrm{Im}\,G_{00}^{\Gamma,X}(\omega)$$
$$= -(\alpha_\Gamma/\pi)\,\mathrm{Im}[\omega - a_1 - b_1 G_{11}^{\Gamma,X}(\omega)]^{-1},$$

where

$$G_{11}^{\Gamma,X}(\omega) = [\omega - a_2 - b_2 G_{22}^{\Gamma,X}(\omega)]^{-1},$$

$$\cdot$$
$$\cdot$$
$$\cdot$$

$$G_{n-1,n-1}^{\Gamma,X}(\omega) = [\omega - a_n - b_n g(\omega)]^{-1},$$

$$\omega = E + i0^+, \quad \alpha_\Gamma = 1 \text{ for } A_1, \quad \alpha_\Gamma = 3 \text{ for } T_2.$$

The coefficients a_n and b_n are determined using the recursion method of Haydock *et al.* and the continued fraction is terminated by the function $g(\omega)$ such that

$$g(\omega) = [E - a - bg(\omega)]^{-1},$$

TABLE II. Energies (in eV) obtained by Stuckel *et al.* (Ref. 11) and in our parametrization model (TB) for selected symmetry points in $\vec{k}$ space.

	TB	Stuckel		TB	Stuckel		TB	Stuckel
L_{1V}[a]	−10.58	−10.66	Λ_{1V}[b]	−11.11	−11.00	Γ_{1V}[c]	−11.61	−11.77
L_{1V}	−4.13	−4.20	Λ_{1V}	−2.22	−2.5	Γ_{15V}	0.00	0.00
L_{3V}	−0.53	−0.61	Λ_{3V}	−0.25	−0.45	Γ_{1C}	3.95	3.77
L_{1C}	5.03	4.96	Λ_{1C}	4.66	4.8	Γ_{15V}	8.02	7.99
L_{3C}	8.69	8.62	Λ_{1C}	8.95	8.0			
L_{1C}	9.87	9.88	Λ_{3C}	8.34	8.8			
Δ_{1V}[d]	−11.44	−11.50	Δ'_{1V}[e]	−10.85	−11.0	X_{1V}[f]	−10.24	−10.29
Δ_{3V}	−0.60	−0.8	Δ'_{3V}	−2.41	−3.0	X_{3V}	−4.26	−3.93
Δ_{5V}	−0.23	−0.2	Δ'_{5V}	−0.88	−0.7	X_{5V}	−1.43	−1.61
Δ_{1C}	4.32	4.2	Δ'_{1C}	5.31	5.5	X_{1C}	5.21	5.01
Δ_{3C}	7.68	7.5	Δ'_{3C}	6.5	6.3	X_{3C}	6.23	5.95
Δ_{5C}	8.46	8.2	Δ'_{5C}	9.85	9.7			

[a] $L = (\pi/a)(1,1,1)$.
[b] $\Lambda = (\pi/a)(0.48,0.48,0.48)$.
[c] $\Gamma = (\pi/a)(0,0,0)$.
[d] $\Delta = (\pi/a)(0.44,0,0)$.
[e] $\Delta' = (\pi/a)(1.04,0,0)$.
[f] $X = (\pi/a)(2,0,0)$.

where a and b are related to the energies E_1 of the top of the conduction band and E_2 of the bottom of the valence band:

$$a=\tfrac{1}{2}(E_1+E_2), \quad b=\tfrac{1}{16}[(E_1-E_2)^2].$$

The size of the cluster leads to exact values of a_n and b_n up to $n=12$ when only first-nearest-neighbor interactions are taken into account and to $n=6$ when second-nearest-neighbor interactions are included.

A systematic study on clusters of increasing size has shown however that even in this last case, the coefficients a_n and b_n are obtained with a very good precision up to $n=12$, which corresponds to 24 correct moments of the density of states.

Our results for the partial density of states on sulphur and zinc sites are displayed on Fig. 1. These results compare favorably with those obtained by Herman[14] who used the classical Gilat-Raubenheimer method.[15] Our tight-binding parametrization leads to a gap of 3.95 eV when Herman obtains 3.77 eV. It is to be noticed however that in our description the position of the band edges is somewhat arbitrary: our termination procedure replaces the true gap by a region of low density of states which is not apparent on Fig. 1 because of the scale used. It is comforting that, although we use a moment method, the critical points are clearly exhibited in the valence band.

The lower valence band is almost entirely accounted for by the s orbitals on sulphur, and the p orbitals on S give the main contribution to the upper valence bands. The conduction band originates from the orbitals on zinc, its lower part being of A_1 symmetry. This result does not imply that the hypothetical conduction charge density is concentrated on Zn atoms (which is not actually the case[16]) because our (implicit) basis wave functions are not atomic orbitals: (i) as shown by first-principle tight-binding calculations on diamond,[17] considering short-range interactions implies the use of truncated atomic orbitals; (ii) neglecting the overlaps amounts, through the orthogonalization process, to define basis functions which are actually linear combinations of these.

In fact the first-principles calculation[17] shows that in diamond second-neighbor interactions are not sufficient to describe correctly the conduction band. As mentioned in the Introduction the situation is probably less critical for partially ionic semiconductors. It has been shown[16] that the hypothetical charge density of the first conduction band of ZnSe has a clear antibonding character, while that of Ge is rather free-electron-like. Moreover the empirical adjustment performed in the present paper may correct somehow this drawback of the method. Let us stress that we do not make explicit use of the wave functions in the following defect calculations.

From the partial density of states, we obtain a transfer of charge of 1.15 electron from Zn to S, in good agreement with the values obtained semiempirically by Suchet[18] and by simple calculations by Bailly[19] and Hubner.[20] Let us notice however

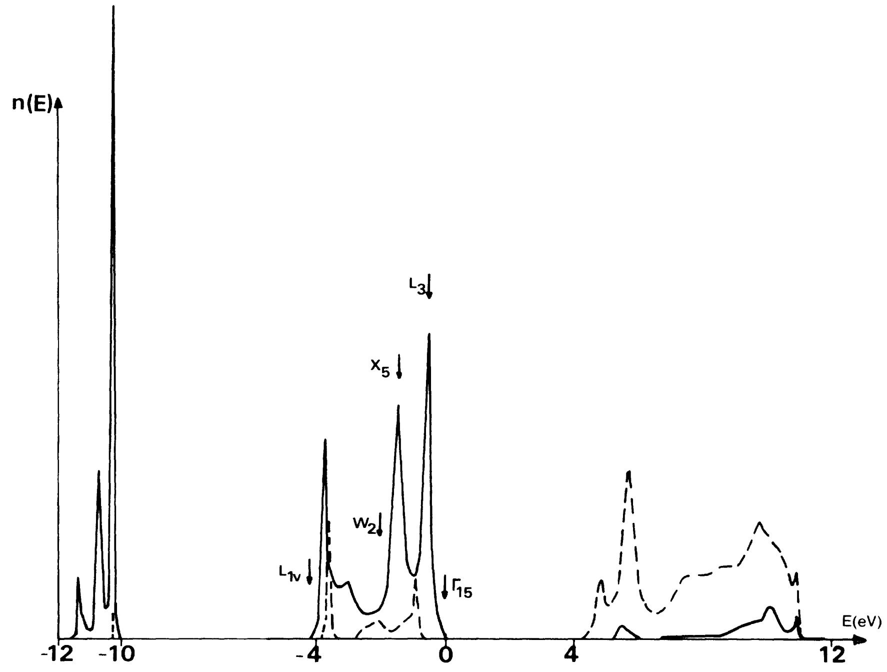

FIG. 1. Partial density of states in ZnS. Solid line, sulphur; dashed line, zinc.

that the charge transfer calculated in this way does not correspond to the excess charge on the sulphur cell as the orbitals extend up to second neighbors of an S atom. Then part of this charge is actually located on the neighboring Zn cells so that the true charge on the S cell is in fact much weaker.

III. PROPERTIES OF THE SULPHUR VACANCY

The vacancy is created by removing a sulphur ion from site 0; owing to the charge transfer from Zn to S, this introduces a positive effective charge of $1.15|e|$. As this charge is almost completely screened by the electron localized in the F center, we can describe it by a matrix element V_2 on the first neighbors of the S vacancy.

In a first approximation, we assume that V_2 is the Coulombic potential created by the positive effective charge of $+1.15|e|$ centered on the S vacancy ($V_2 = -7.08$ eV). The removing of the sulphur ion is accomplished by putting on site 0 a potential V_1 and letting it tend to infinity. This is equivalent to cut all bonds between this ion and the crystal.[21]

In practice we introduce the potential V_2 in an otherwise perfect crystal and we calculate the perturbed Green's functions $G_{00}^{\Gamma,S'}$ using the recursion method of Haydock, Heine, and Kelly in a cluster of 2545 atoms. This is possible because the method does not make use of the Bloch theorem. The F-center levels are then given by the usual scattering formula[22]:

$$\lim_{V_1 \to \infty} \det(1 - G_{00}^{\Gamma,S'} V_1) = 0 \quad \text{or} \quad G_{00}^{\Gamma,S'} = 0.$$

In this way, we find a level of A_1 symmetry located 2.65 eV below the edge of the conduction band and a T_2 level located at 1.25 eV above the A_1 level.

Experimentally[5] the absorption spectra associated with the F center in ZnS are very similar to those obtained in alkali halides like RbCl. The absorption spectrum is made of two bands: a strong Gaussian band centered at 2.27 eV (F band); and a weaker asymmetric one at 2.88 eV (K band).

These bands can be interpreted as follows:

(i) The K band, which leads to photoconductivity and the disappearance of the F center, is due to transitions from the ground level of the F center to excited levels close to the edge of the conduction band, an interpretation suggested previously by Schneider.[5] As the experimental value of 2.88 eV is very close to the theoretical value of 2.65 eV, this shows that our calculation is reliable for determining the location of the ground state of the F center.

(ii) As it does not lead to photoconductivity nor disappearance of the F center, the F band can be interpreted as due to transitions from the ground level of the F center to the first-excited T_2 level. The disagreement between our calculated value of 1.25 eV and the experimental data can be attributed, at least in part, to our imperfect description of the conduction bands.

In the spirit of this interpretation, it is not necessary to appeal to the Watanabe mechanism as suggested by Schneider, to explain the absorption band at 2.27 eV.

Let us notice that in our simple model for the S vacancy we do not take into account the polarization and distortion of neighboring atoms. These are usually thought to be weak for the ground state and the unrelaxed T_2 level which are calculated here.[23] In fact the potentials $V_1(\to\infty)$ and $V_2(=-7.08 \text{ eV})$ are certainly much larger than the perturbation introduced by the relaxation.

IV. PROPERTIES OF ISOELECTRONIC TRAPS

Using our parametrization we have also studied the properties of crystals of ZnS containing Se or Te substituted for S. These defects have already been studied by Baldereschi and Hopfield[9] in a Koster-Slater scheme but in a one-band, one-site model. We maintain the one-site approximation which seems reasonable for isoelectronic defects but we relax the one-band approximation which cannot be justified for localized defects. The perturbing potential U_Γ in the mode of Γ symmetry is estimated using two different methods. In the first one [(a) in Table III] we identify U_Γ with the difference of the energies of the atomic levels as given by Herman and Skillman.[24] In the second method, we perform a tight-binding parametrization of ZnSe and ZnTe using the values obtained for ZnS as a starting point and changing only the diagonal elements on the anion. In this process the U_Γ perturbing potential is identified with the change of these diagonal elements, the relative positions of the different band structures being fixed using the experimental ionization energy tabulated by Van Vechten.[25] We compare in Table III the values we obtain with those of Baldereschi and Hopfield (BH).

A level appears in the gap when

TABLE III. Values of the impurity potential U_p (eV) for Se and Te in ZnS; (a) from Herman and Skillman (Ref. 24). (b) from a parametrization of ZnSe and (c) values of Baldereschi and Hopfield (Ref. 9) (BH).

	(a)	(b)	(c)	
			BH ($X=0$)	BH ($X=1$)
Se	0.7	1.1	0.24	1.63
Te	1.3	3.4	1.19	4.21

$$1 - G_{00}^{p,S}(0)U_p > 0 \quad \text{or} \quad U_p > 1.25 .$$

Therefore a localized state appears on Te and a resonant one on a Se impurity. Notice that our threshold energy (1.25 eV) is somewhat larger than that obtained by Baldereschi and Hopfield (0.9 eV) with their generalized one-band one-site approximation. Let us investigate the approximations made in the one-band treatment to which this discrepancy could be traced.

(i) The trace $G(\omega)$ of the Green's function over an elementary cell is actually

$$G(\omega) = 3G_{00}^{p,S}(\omega) + G_{00}^{s,S}(\omega) + 3G_{00}^{p,Zn}(\omega) + G_{00}^{s,Zn}(\omega) ,$$

and the numerical values of the four terms entering this expression are, respectively, 2.4, 0.09, -0.09, and -0.12 eV for $\omega = 0$. This shows that it is a good approximation to assume that $3G_{00}^{p,S}(0) = G(0)$ as done in the calculation of Baldereschi and Hopfield.

(ii) In our calculation we calculate the true Green's function $G(\omega)$, including valence and conduction bands. In a rough approximation, the conduction bands contribute

$$G_c(\omega) = 1/(\omega - E_{ss}^{Zn}) + 3/(\omega - E_{pp}^{Zn})$$

to the total Green's function, which is negative for $\omega = 0$.

Therefore neglecting $G_c(\omega)$ overestimates the Green's function $G(\omega)$ and leads to a smaller threshold energy. In the present case for instance, the threshold energy is reduced from 1.25 to 1.04 eV if such an approximation is made, which could explain the discrepancy between our results and those of Baldereschi and Hopfield.

In order to obtain the energy of the level associated with a Te impurity, we follow Baldereschi and Hopfield and introduce the relaxation factor.

$$X = R/(R_i - R_h) ,$$

where R is the displacement of the first neighbors with respect to their crystallographic positions and $(R_i - R_h)$ is the difference between the bond lengths in ZnTe and ZnS. We may assume that $X = 0$ (no relaxation) corresponds to our choice (a) of the perturbing parameters and that $X = 1$ corresponds to the second choice (b). Using a linear interpolation and the value of $X = 0.5$ given by Baldereschi and Hopfield, the impurity level on Te appears located at 0.64 eV.

This result is in good agreement with the experimental result of Fukushima and Shionoya[26] (0.4 eV), in view of the approximations introduced in the calculation.

TABLE IV. Value of the impurity potential U_S for cation isoelectronic defects in ZnS (eV).

	Cd	Be	Mg	Ca	Sr	Ba
U_S (a)	+0.24	0.56	1.84	3.26	3.51	3.83
U_S (b)	0.46					

Turning now to the case of substitutional impurities on the cation site, we must explain why no isoelectronic traps have been found on them, in spite of many experimental investigations.[27] This feature can be understood using the preceding method: in order to extract a localized state from the conduction band, an attractive potential larger than 1.6 eV is necessary. It is shown in Table IV that all elements isoelectronic to zinc are actually repulsive or weakly attractive impurities. Then no localized level is to be expected on such centers.

V. CONCLUSION

Our results for the F center, obtained in a band model, give a reasonable account for the ground-state level, and predict the correct sequence: ground state, T_2 level and edge of the conduction band. This appears interesting since even in the case of purely ionic crystals it is difficult to obtain the relative position of the ground-state level and the band edges. For isoelectronic traps, our results give no localized level for Se, and a Te level in reasonable agreement with the experimental data. We also show that the one-band–one-site model may underestimate the threshold energy for the appearance of a bound state.

As already indicated the major weakness of the method lies in the description of the conduction band. This could be the reason for our underestimate of the A_1-T_2 transition. Unfortunately in this semiempirical scheme it does not seem reasonable to take into account longer-range interactions or higher l orbitals because this would introduce a large number of new parameters.

As it stands such a tight-binding analysis could be useful in II-VI compounds to describe more complicated defects semiquantitatively (for instance the zinc vacancy) especially when combined with the method of Haydock, Heine, and Kelly which does not appeal to the Bloch theorem.

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