

Electronic structure of $\text{ZnS}:[\text{Cu}_{z_n}, \text{V}_{z_n}]$

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Abstract We have developed a molecular cluster method for the calculation of defects in semiconducting materials by imposing proper crystalline embedding conditions to the well known multiple scattering X_α method. The proposed modification introduces a common energy reference for the clusters representing the crystal and the defect, which makes possible to compare the energy eigenvalues coming from both calculations. The method has been applied to determine the electronic structure of the copper substitutional impurity and the cationic vacancy in cubic zinc sulphide crystals with very satisfactory results.

1. Introduction

When considering the problem of a localized defect in an insulating matrix, one is mainly interested in those states (associated to the defect) whose energies lie into the host energy band gap. If the impurity gives rise to shallow energy levels, the effective mass approximation¹ provides a neat way of determining these states and those electronic properties related to them. However, the same does not hold

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for the deep defects, due to the highly localized behavior of their wavefunctions. Several procedures have been developed to describe these states, most of them based on the Green's function method². An alternative procedure is provided by the molecular cluster methods, which are also frequently used due to their greater computational speed and conceptual simplicity. In this type of procedure the defect and its immediate crystal environment are considered as if they form a large and isolated molecule or molecular ion³⁻⁸, assuming that such a small cluster of atoms can reproduce at least those crystal features that depend mainly on short range interactions. However, in some cases, the reduction of a crystal to a few atoms may not preserve the main crystal features. For instance, the finite cluster size can turn the cluster energy spectrum into a mixture of bulk and surface states³. These effects can be minimized, but not avoided, by using some art in the introduction of arbitrary embedding conditions⁴ or by increasing the number of atoms in the cluster⁵. Besides these inadequacies, the molecular cluster methods suffer from the lack of a unique energy reference for the cluster representing the crystal and the defect. The absence of this energy reference makes it very difficult to determine the position of the defect energy states with respect to the band edges or to decide among the several possible defect charge states.

A molecular cluster that avoids most of these inadequacies is the crystalline cluster model (CCM)^{9,10}. In this self-consistent-field procedure the Schrödinger equation is solved in a finite cluster of atoms, by using some quantum chemistry method for large molecules, but the self-consistent potential is obtained solving the Poisson equation in the infinite periodic crystal. Consequently, one avoids the potential surface effects and the calculated cluster energy spectrum provides a suitable description of the crystalline density of states¹⁰. Moreover, if a defect calculation is performed through this method, the localized energy states associated with the defect becomes properly located with respect to the crystal band edges because the reference used to define the potential for the cluster representing the defect is the same as that used in the crystal calculation.

In this work we have used the crystalline cluster method, within the framework of the multiple scattering X_α method¹¹, to perform first principle investigations

of the electronic structure of the ZnS crystal, as well as of the localized states associated to the copper cationic substitutional impurity and the zinc vacancy in that material.

2. Theory

We begin our discussion of the CCM following the Hamiltonian

$$\hat{H} = \hat{H}_0 + A\Theta(r - R) , \tag{1}$$

where \hat{H}_0 is the Hamiltonian of an electron in the infinite crystal, A is a large and positive constant, and Θ is the Heaviside step function. The effect of the second term on the right-hand side of eq.(1) is easy to understand. This term raises the energy of the electron if it ventiires outside the sphere of radius R . Consequently, each energy band of the spectrum of \hat{H}_0 is given by a set of discrete energy states herein designated as *cluster energy spectrum*, and a continuum of states shifted by A from the original band. This can be easily seen if one works in the Wannier representation. In this representation, the matrix elements of \hat{H} can be written in the form:

$$\hat{H} = \hat{H}_1 + \hat{H}_2 \tag{2}$$

where

$$\hat{H}_1 = \begin{pmatrix} \langle \vec{l}I \hat{H}_0 I\vec{l} \rangle & \vdots & 0 \\ \dots\dots\dots & \vdots & \dots\dots\dots \\ 0 & \vdots & \langle \vec{l}'I \hat{H}_0 I\vec{l}' \rangle + \\ & \vdots & A \langle \vec{l}'I \Theta(r - R) I\vec{l}' \rangle \end{pmatrix} \tag{3}$$

and

$$\hat{H}_2 = \begin{pmatrix} \langle \vec{I} I \Theta(\mathbf{r} - R) I \vec{I}' \rangle & \vdots & \langle \vec{I} I \hat{H}_0 I \vec{L}' \rangle + \\ \dots\dots\dots & \vdots & A \langle \vec{I} I \Theta(\mathbf{r} - R) I \vec{L}' \rangle \\ \langle \vec{L} I \hat{H}_0 I \vec{I}' \rangle + & \vdots & \dots\dots\dots \\ A \langle \vec{L} I \Theta(\mathbf{r} - R) I \vec{I}' \rangle & \vdots & 0 \end{pmatrix} \quad (4)$$

where $I \vec{I}' \rangle$ represents the minimal width Wannier function associated to the n-th crystal band and to the lattice vector \vec{I}^{12} . Each matrix of eqs. (3) and (4) breaks into four submatrices. The upper left submatrix refers to the internal Wannier states, namely

$$\| \vec{I} \|, \| \vec{I}' \| < R,$$

the lower right diagonal submatrices refer to Wannier functions outside the cluster, that is,

$$\| \vec{L} \|, \| \vec{L}' \| > R,$$

and the off-diagonal submatrices mix the internal and external Wannier functions. One can easily see that the cluster states are those states coming from the upper-left submatrix of \hat{H}_1 . Now, if A is large enough (later on one will see how large A must be), the effective cluster Hamiltonian becomes:

$$\begin{aligned} \hat{H}_C(\vec{I}, \vec{I}') = & \langle \vec{I} I \hat{H}_0 I \vec{I}' \rangle + \frac{1}{A} \sum_{L > R} \langle \vec{I} I \hat{H}_0 I \vec{L}' \rangle \langle \vec{L} I \hat{H}_0 I \vec{I}' \rangle \\ & + A \langle \vec{I} I \Theta(\mathbf{r} - R) I \vec{I}' \rangle \\ & A \sum_{L > R} \langle \vec{I} I \Theta(\mathbf{r} - R) I \vec{L}' \rangle \langle \vec{L} I \Theta(\mathbf{r} - R) I \vec{I}' \rangle \\ & \sum_{L > R} \{ \langle \vec{I} I \hat{H}_0 I \vec{L}' \rangle \langle \vec{L} I \Theta(\mathbf{r} - R) I \vec{I}' \rangle \\ & + \langle \vec{I} I \Theta(\mathbf{r} - R) I \vec{L}' \rangle \langle \vec{L} I \hat{H}_0 I \vec{I}' \rangle \} \end{aligned} \quad (5)$$

The second term in eq.(5) is of order B^2/A , where B is the width of the band one is dealing with. So, if A is much larger than the bandwidth B , this term becomes negligible when compared with the first term in eq.(5). One can readily see that the third and fourth terms in eq.(5) are of the order of the product of A by C , where C is the largest eigenvalue of the matrix:

$$\Theta(\vec{1}, \vec{1}') = \langle \vec{1} | \Theta(r - R) | \vec{1}' \rangle$$

Then, if A is much smaller than B/C , these terms can also be neglected. Finally, if the above conditions are satisfied, the last term in eq.(5) being of the order of the product of B by C can also be neglected. Summarizing the above results one can say that, of the constant A in eq.(1) can be chosen so that

$$B \ll A \ll B/C, \tag{6}$$

the effective Hamiltonian for the discrete states of H is reduced to the first term in eq.(5). In other words, the potential barrier at the cluster surface decouples the internal and external Wannier functions, and the cluster energy spectrum consists only of bulk states with energies lying between the top and the bottom of the crystal band to which they are related.

Since the cluster energy spectrum depends very little on the details of the electronic potential outside the sphere of radius R , the potential to be used in the cluster calculation can be rewritten in a more practical way as

$$V_c(\vec{r}) = \begin{cases} V_0(\vec{r}) - A; & \text{if } r < R \\ \omega(\vec{r}); & \text{if } r > R \end{cases} \tag{7}$$

where w is a smoothly decaying function of r , which has only been introduced to simplify the solution of the Schrödinger equation.

In order to obtain the electronic structure corresponding to the crystal, one has to solve simultaneously the Schrödinger and the Poisson equations. The Schrödinger equation is solved in the cluster for the potential defined in eq.(7)

and the resulting number density is put into a muffin-tin format. The crystal number density is then obtained according to Bressanini and Ferreira⁸. This model number density is used to solve the Poisson equation in the periodic lattice by means of standard Ewald techniques¹³. Now, as we have shown above, the cluster energy spectrum obtained in the CCM becomes a good sampling of the crystal density of states provided the self-consistent potential V_c is truly the crystalline potential, that is, if the model density of charge defined in the CCM reproduces that of the crystal. Populating all of the cluster states associated to a crystal band means to generate a number density given by

$$n(\vec{r}) = \sum_{\mathbf{I} < \mathbf{R}} \| a_n(\vec{r} - \vec{\mathbf{I}}) \|^2 \quad (8)$$

while the corresponding crystal number density would be

$$\rho(\vec{r}) = \sum_{\mathbf{I}} \| a_n(\vec{r} - \vec{\mathbf{I}}) \|^2 \quad (9)$$

Comparing eqs. (8) and (9) one observes that the cluster density leaves out the contribution coming from the Wannier functions outside the cluster. But, whenever inequality eq.(6) is satisfied, this contribution is very small and the crystal number density becomes well described by the cluster.

The Hamiltonian of a crystal containing a defect can always be decomposed into the Hamiltonian of the unperturbed host lattice plus an effective perturbation U introduced by the defect. If U is well localized inside the cluster, a condition that can be easily attained for deep defects in semiconductors, the only nonnegligible matrix elements of U are those corresponding to Wannier functions localized inside the sphere of radius R . Then, if a development similar to that used in the case of the crystal is performed, one can easily show that the effective Hamiltonian for the cluster representing the defect becomes

$$\hat{H}_D(\vec{\mathbf{I}}, \vec{\mathbf{I}}') = \langle \vec{\mathbf{I}} | \hat{H}_0 | \vec{\mathbf{I}}' \rangle + \langle \vec{\mathbf{I}} | U(\vec{r}) | \vec{\mathbf{I}}' \rangle \quad (10)$$

One can readily see from eq.(10) that \hat{H}_D preserves the same energy reference used in the crystal calculation. Thus, the cluster representing the defect provides energy levels which become properly localized with respect to the crystal band edges.

3. Results and Discussion

It is well known the the 11-VI semiconducting compounds have highly ionic bonds. This means that one can assume that the muffin-tin approximation can be used to properly describe their electronic properties. Thus, we have used the CCM within the framework of the multiple-scattering X_α method to perform investigations of the zinc sulphide electronic properties. One can also presume, from this ionic character, that even small clusters can be used to reasonably describe the electronic properties of these 11-VI compounds. Two clusters with seventeen atoms have been used in the present calculations of pure ZnS. These clusters, labelled as Zn_4S_{12} and S_4Zn_{12} , consist of a central atom surrounded by its four nearest neighbours and twelve next-nearest neighbour atoms, which are arranged in a tetrahedral configuration compatible with the undistorted host lattice geometry. The radii of the atomic muffin-tinspheres have been chosen to be $R_{Zn}=2.436$ a.u. and $R_S=1.988$ a.u., in such a way that they are proportional to the tabulated covalent radii for zinc and sulphur¹⁴ and their sum reproduces the crystal interatomic distance. The outer sphere radius has been chosen to be tangent to the outermost atomic spheres. The α exchange-correlation parameter inside the atomic spheres were chosen according to the atomic tables¹⁶ to be $\alpha_{Zn}=0.706$ and $\alpha_S=0.725$. Our experience has shown that, provided a value close to that of the atomic species is chosen, the cluster energy spectrum depends very little on the value of α in the inter-sphere region. On the other hand, in our model, the cluster energy spectrum does not depend on the α value outside the sphere of radius R. Thus, we choose an *ad hoc* value $\alpha=0.700$ for the exchange-correlation parameter in these inter-sphere and extramolecular regions. For all valence orbitals the basis functions include angular momenta up to $l = 2$ in the central sphere and up to $l = 1$ in the remaining atomic sites. The 3d orbitals for the outermost zinc atoms

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in the Zn, S₄Zn₁₂ cluster have been included in the self-consistent process but have been imposed to be confined inside their muffin-tin spheres.

As can be seen from **fig.1**, the **crystalline** electronic structure for the **full** occupation regime obtained in the present calculation agrees with previous self-consistent band structure **calculations**^{16,17}. One can also see from **fig. 1** that, as anticipated in the previous section, our model provides larger gaps and **smaller** bandwidths than those obtained in a band structure calculation. One can also conclude, by comparing our **results** with the calculations of **Ferreira and De Siqueira**¹⁸, that for materials like zinc sulphide the cluster energy spectrum is not very sensitive to the details of the exchange-correlation potential.

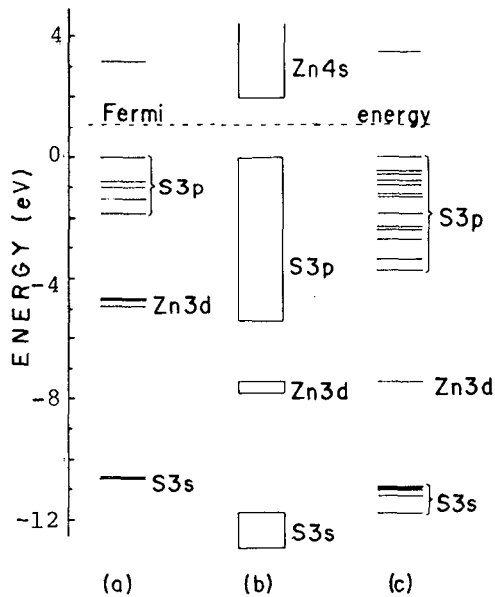


Fig.1 - Calculated one-electron energy spectrum for pure ZnS crystals in the filled shell configuration obtained in the present calculation. The band structure determinations by Bendt and Zunger (ref.16) are also presented for comparison. (a) - present calculations with Zn₁S₁Zn₁₂, (b) - Zunger and Cohen, (c) - present calculations with S₁Zn₄S₁₂ cluster.

According to Ferreira and De Siqueira¹⁸, the transition state concept has to be used to determine the electronic ionization potential whenever the electron self-energy is larger than the width of the band one is dealing with, while the energy eigenvalues have to be used to estimate the ionization potential if the bandwidth is much larger than the electron self-energy. In this work we have found that the electron self-energies for the Zn-3d and S-3s bands are 4.5 eV and 1.1 eV. These values are large compared to the respective bandwidths of 0.6 eV and 1.2 eV, obtained by means of band structure calculations^{16,17}, and our estimates of 0.2 eV and 0.9 eV. One can conclude from these results that the hole created in the ionization process of the Zn-3d band is highly localized around the zinc atom, so that its ionization potential can be obtained through the transition state concept by means of a cluster calculation. For the S-3s band we have that the created hole becomes more delocalized than that created in the former case. However, it is still localized enough to be properly described by means of a small 17-atom cluster such as that used in the present work. The self-energy for the S-3p band we obtained is about 2.5 eV, a value smaller than our estimate of 3.4 eV for the S-3p bandwidth, or the value determined by means of band structure calculations^{16,17}. We have also observed that the hole created has a much highly delocalized behavior in this case, that is, the cluster is too small to describe the excited state wavefunction, which becomes artificially confined inside the cluster volume, then increasing the electron self-energy. Thus, if it is non-negligible, this self-energy cannot be determined by means of a cluster calculation, unless a much larger cluster is used. The same does hold in the case of an electron promoted to the conduction band (Zn-4s). So, for the S-3p and Zn-4s energy bands, the best one can do is to use the electron energy eigenvalues to estimate the electron ionization energy.

The main optical transition energies associated with bulk ZnS are summarized in table 1. The first transition corresponds to the ground state energy band gap, namely the promotion of an electron from the uppermost valence state to the lowest conduction state. Our predictions of 3.13 eV and 3.96 eV, obtained by means of the $Zn_1S_4Zn_{12}$ and $S_1Zn_4S_{12}$ clusters are in good agreement with previous theoretical calculations¹⁶⁻¹⁸ and the 3.91 eV experimental value¹⁹. The other

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optical **transitions** correspond to the position of the Zn-3d and S-3s bands with respect to the top of the S-3p valence band. These energies have been determined to be 9.4 eV and 12.9 eV, respectively, while the experimental values are²⁰ 9.5 eV and 13.5 eV. Thus, one can conclude that our 17-atom cluster calculations **provide** a good description of the pure ZnS electronic structure. These results also suggest that these clusters can be used to describe the localized states associated with deep defects in this material.

Table 1 – Theoretical estimatives of pure ZnS crystal obtained in the present calculations. All energies are quoted in eV.

optical transition	cluster used	present calculation	Ferreira De Siqueira ^a	Bendt and Zunger ^b	Stukel et ali ^c	experim.
energy band gap	Zn ₁ S ₄ Zn ₁₂	3.13	4.46	1.95	3.77	3.91 ^d
	S ₁ Zn ₄ S ₁₂	3.96				
position Zn-3d band	Zn ₁ S ₄ Zn ₁₂	9.4	7.6	7.4	14.1	9.5 ^e
position S-3s band	S ₁ Zn ₄ S ₁₂	12.9	14.1	12.9	11.8	13.5 ^e

a - ref.18, b - ref.16, c - ref. 17, d - ref. 19, e - ref.20.

The cluster **used** to represent ZnS:Cu has been labelled Cu₁S₄Zn₁₂ and has been obtained by replacing the central zinc atom of the Zn₁S₄Zn₁₂ cluster by a copper one. In this cluster we kept the same atomic radii and a exchange-correlation parameters we have **used** in the crystal calculation for **all** cluster regions. **According** to our calculations the substitutional copper (Cu²⁺) **impurity** in zinc sulphide gives **rise** to a resonant state with e symmetry, which is localized in the **uppermost valence band**, and a partially **fills** *t*₂ **orbital** that appears in the fundamental gap. Since these defect states associated to copper in zinc sulphide have **wavefunctions** that are well localized within the cluster volume, one can assume that the **transition** state concept should be **used** to determine the energies of the optical

transitions associated with **such** a defect. Two main absorption **lines** have been observed in copper-doped **ZnS**. The first consists of an **internal** $e \rightarrow t_2$ transition from the resonant state with e symmetry to the t_a acceptor state **localized** in the gap. According to our calculations this transition **occurs** at an energy of 0.97 eV, in agreement with the experimental **data**^{21,22} and previous theoretical **calculations**^{18,23}. The second absorption **line** corresponds to the ionization of the defect, that is, the promotion of an electron from the top of the uppermost valente band to the **half-filled** t_2 state in the gap. **We** obtained for this transition an excitation energy of 1.17 eV which is in good agreement with the experimentally obtained values (1.25 eV²¹, 1.44 eV²⁴).

Table 2 - Optical transition energies associated with the substitutional Cu **impurity** in zinc sulphide. All energies are in eV.

Transition	Chacham et ali ^a	Ferreira and De Siqueira ^b	Ours	Experimental
$e \rightarrow t_2$	-	0.71	0.97	0.77^c, 0.85^d
$(v^0, t_2^5) \rightarrow (v^{-1}, t_2^6)$	0.57	2.28	1.17	1.15^d, 1.44^e
green luminescence	-	-	2.5	2.4^f

a - ref.23, b - ref.18, c - ref. 22, d - ref. 21, e - ref.24, f - ref. 25.

It has been **well** established in the literature²⁶ that the green **luminescent** emission in copper-doped **ZnS** is due to a donor-acceptor transition, from a single shallow substitutional donor, **say** chlorine on **aluminium**, to a **single** acceptor, **usually** copper or silver. **It can be shown**²⁶ that, neglecting the **electron-phonon** interaction, one has that the donor-acceptor density of states **has a maximum** at the energy

$$h \nu_m = E_G - E_D - E_A - \frac{e^2}{\epsilon} (\pi N_D)^{1/3} \quad (11)$$

where E_G is the host energy band gap, E_D and E_A are the donor and acceptor ionization energies, e is the electronic charge, N_D is the concentration of donor

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unities, and ϵ is a proper dielectric constant²⁷ which, for convenience, will be taken as the crystal static dielectric constant²⁸. Since the single donor states associated to the green emission are shallow, they cannot be determined by means of a cluster calculation¹⁰, so that we have assumed for E_D the experimental value²⁹ $E_d = 0.24$ eV. We have also assumed the experimental data¹⁹ for the energy band gap, and our theoretical estimates for E_g . Thus, for a typical donor concentration of $N_D \sim 10^{16} - 10^{18}$ cm⁻³, one has that the green emission line has a maximum at about 2.5 eV, in remarkably good agreement with the experimental value of 2.4 eV²⁵. Thus, one can conclude that our cluster calculation provides a neat description of the localized states associated to the copper impurity in zinc sulphide.

We have also performed calculations on the neutral Zn²⁺ cationic vacancy (V_{Zn}^0) in zinc sulphide. The cluster representing the cationic vacancy has been defined in a similar way as that used to obtain the cluster used in the copper impurity calculation, the only difference being the value of α in the defect spheres which has been chosen to be $\alpha = 1$. According to the atomic tabulations¹⁵, α increases as the atomic number Z decreases, and the vacancy can be considered as an atom with null Z . In this case we obtained that a filled a_1 orbital and a t_2 state occupied with only four electrons, that correspond to the dangling bonds associated to the vacancy, are introduced into the host gap. The Zn-3d states associated to the outermost cluster atoms for the cluster representing the vacancy become shifted by about 0.4 eV, when compared with those of the cluster representing the crystal. This shift suggests that the perturbation potential spreads out over a region larger than that defined by the cluster. On the other hand, our calculations indicate that the vacancy wavefunctions have a spread larger than that observed in the case of the copper impurity. So, one can conclude that the 17-atom cluster used in the present calculations is too small to properly describe the zinc vacancy. We have also observed that when the singly (V_{Zn}^+) and doubly (V_{Zn}^{2+}) ionized vacancy states are determined, the t_1 and e valence states also merge into the gap as this defect becomes ionized. So, one can conclude that clusters with more than 17 atoms must be used if one intends to obtain a proper description of the zinc vacancy.

4. Summary

When performing first-principle calculations of localized defects in semiconductors by means of a cluster calculation one usually suffers from the lack of a unique energy reference for the clusters representing the crystal and the defect. This makes the localization of the defect states with respect to the band edges a matter of free interpretation. Such a shortcoming can be avoided by using the crystalline cluster method. In this work we have applied that method in the study of $\text{ZnS}:[\text{Cu}_{\text{Zn}}, \text{V}_{\cdot}]$ by means of calculations performed with small 17-atom clusters. We have shown that, due to the highly localized behavior of the Cu-related wavefunctions, these clusters provide a good description of $\text{ZnS}:\text{Cu}_{\text{Zn}}$, with the theoretical predictions closely reproducing the experimentally determined optical transition energies. In the case of zinc vacancy we have been unable to determine the stability of the many charge states of the defect because the cluster used was too small to properly describe this defect.

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Resumo

Nós desenvolvemos um método de agregado molecular para o cálculo de defeitos em materiais semicondutores impondo condição de contorno cristalino ao conhecido método do espalhamento múltiplo X_α . A modificação proposta introduz um referencial de energia único para os agregados representando o cristal e o defeito, o que possibilita comparar os autovalores de energia proveniente de ambos os cálculos. O método foi aplicado para determinar a estrutura eletrônica de uma impureza substitucional de cobre e de uma vacância de cation no sulfeto de zinco com resultados bastante satisfatório.