

CLUSTER CALCULATIONS OF TRANSITION-METAL IMPURITIES
 IN SEMICONDUCTORS

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Self-consistent calculations in the CNDO approximation of 17 atoms clusters representing Cu and Ag impurities in ZnS, CdS and ZnO crystals give satisfactory agreement with the experimental crystal field splitting 10 Dq. Correlation energy results in a considerable shift of energy levels and an important decrease of 10 Dq.

I. Introduction

The basic crystal field splitting parameter 10 Dq is calculated for transition metal ions in II-VI compounds with a LCAO formalism to take care of the covalent bonding in these crystals. The calculation is done with a self-consistent field method in the CNDO approximation developed by Pople et al. [1],[2],[3]. In case of one electron spectra like those of impurities with a d^9 configuration, the calculation gives the one electron energy level scheme, from which the crystal field splitting can be found from the relation

$$10 Dq = E(e^1 t_2^3) - E(e^2 t_2^2), \quad (1)$$

where e and t_2 are the molecular orbitals adapted to the tetrahedral symmetry group which represents the d-orbitals of the impurity and where the "different orbitals for different spin" formalism is used. The energies E are then corrected to include correlation energy.

II. Cluster Model and Boundary Conditions

To calculate the localized wave functions of the deep impurity states a cluster of 17 atoms CuS_4Zn_{12} with the impurity at the center is used. Figure (1) shows the impurity cluster: The cross-hatched atom is the transition metal impurity, hatched atoms are chalcogenides and dotted atoms are second neighbor host atoms. The cluster with the point symmetry of the impurity site is large enough to represent the localized states but too small to represent band states, though the energy gap comes out to be 4.9 eV for a ZnS_4Zn_{12} cluster compared with the experimental value of 3.77 eV for cubic ZnS.

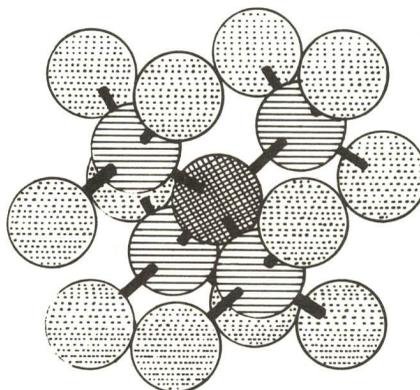


Fig. 1: The 17-atom impurity cluster

Because of the cut off of the covalent bonds at the surface of the cluster, special boundary conditions have to be used to keep the charge of the dangling bonds at the outermost atoms. To solve this, we first carried out a calculation of the ideal cluster ZnS_4Zn_{12} , i.e. the crossed hatched atom in Fig. 1 is replaced by a dotted one, and added an extra potential at the outermost Zn atoms. After every step of the iteration procedure to achieve self-consistency, the potential is modified to satisfy the condition of periodicity of the effective charges of the atoms. The effective charges are also determined this way and are used to include the long range ionic bonding by a Madelung-potential which is proportional to the effective charges of the ions outside the cluster. The same boundary condition is then used for the cluster CuS_4Zn_{12} .

III. CNDO-Approximation

The CNDO-approximation, described in the book of Pople and Beveridge [4], was used with the computer programs QCPE 119 and 223 [5] which were modified to include d-orbitals of the central transition metal ion and to allow calculations with different orbitals for different spins for the open shell calculation (41 electrons). In addition a closed shell calculation with 42 electrons has been performed which converged better. The details of the equations used are described in ref.[6] and [7]. The atomic orbitals included are 3d, 4s, 4p from the central transition metal, 3s, 3p for the next neighbor chalcogenide atoms and 4s only for the second next neighbor atoms. Special attention needs the choice of the β -parameters which have to be introduced into the nondiagonal Hartree-Fock-matrix elements:

$$h_{\mu\nu}^{AB} = \frac{1}{2} (\beta_A + \beta_B) S_{\mu\nu}, \quad (2)$$

where h is the one electron part of the Fock operator, $\mu\nu$ denote atomic orbitals located at atoms $A \neq B$ respectively and $S_{\mu\nu}$ is the overlap integral. We used β -parameters from other authors which were found by fitting to full LCAO calculations of other molecules. The β -parameter for S was taken from [2]. For copper we used β_{3d} and β_{4s} from [3]. Since no β -parameters were available for Zn we used the same β_{3s} parameter for Cu and Zn. It should be noted that our method does not fit any parameter to properties of the crystal or the impurity.

IV. Electron Correlation

In order to include electron correlation beyond the Hartree-Fock approximation the excitation energy $10 Dq$ has been expressed as a difference of ionization potentials in a parent system model [8], [9]:

$$10 Dq = I_e^{N+1} - I_{t_2}^{N+1}. \quad (3)$$

The ionization potentials I_k^{N+1} are calculated by the Green's function method in CNDO approximation [10]-[13], i.e. $I_k^{N+1} = -\omega_k^{N+1}$ where ω_k^{N+1} are solutions of the inverse Dyson equation

$$\omega_k^{N+1} = \epsilon_k^{N+1} + M_{kk}(\omega_k^{N+1}), \quad (4)$$

where ϵ_k^{N+1} are the CNDO orbital energies of the closed-shell cluster $(CuS_4Zn_{12})^-$ and M_{kk} is the second order irreducible self-energy part in diagonal approximation, i.e.:

$$M_{kk}(\omega) = \sum_{\substack{m \in \text{occ} \\ k, l \notin \text{occ}}} \frac{V_{imkl}(V_{kljm} - V_{klmj})}{\omega + \epsilon_m - \epsilon_k - \epsilon_l} + \sum_{\substack{m \notin \text{occ} \\ k, l \in \text{occ}}} \frac{V_{imkl}(V_{kljm} - V_{klmj})}{\omega + \epsilon_m - \epsilon_k - \epsilon_l}, \quad (5)$$

where V_{imkl} are the two-particle integrals, in CNDO approximation, and occ denotes the index set of occupied orbitals. Instead of the full calculation performed in [9] which was rather computer-time spending, we use here a limited basis set for the sums in eq. (5): In addition to the localized $2e$ and $4t_2$ we take only the next two occupied and the next two unoccupied orbitals into account. This is the smallest basis set which gives appreciable shifts of the energies.

V. Discussion of Results

Figure (2) shows the ionisation energies and electron affinities in a closed-shell calculation: (a) denotes the ZnS_4Zn_{12} cluster of the ideal crystal, (b) the $(CuS_4Zn_{12})^-$ cluster both in the CNDO approximation, while (c) shows the shifts due to inclusion of electron correlation.

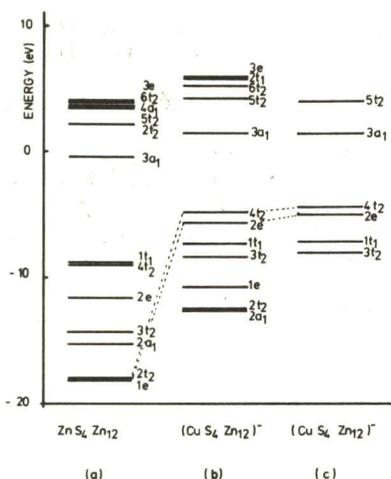


Fig. 2 Energy level schemes for different cluster calculations

	ZnS:Cu	CdS:Cu	ZnS:Ag	ZnO:Cu
10 Dq (exp)	0.77 ^a	0.69 ^a	0.88 ^b	0.70 ^c
10 Dq (CNDO)	0.84 ^d	0.81 ^d	0.60 ^d	0.95 ^e
10 Dq (corr)	0.65	0.67	0.51	--

Table 1 Crystal field splittings in eV a) [14], b) [15], c) [16], d) closed-shell calculation, e) open shell calculation

The first line of table 1 gives the experimentally determined crystal field splitting parameters 10 Dq and the second the results of

the calculation in the CNDO approximation. The third line gives 10 Dq corrected by the correlation energy. From this one can see that correlation energy plays an important role for 3d electrons and reduces the crystal field splitting. The correlation energy shifts the energy levels of the CNDO calculation of the order of magnitude of 1 eV and therefore the corrected energy level difference should be regarded as satisfactory. This is confirmed by comparison with similar calculations of excitation energies in molecular physics [17]. For ZnO:Cu the unperturbed value refers to an N electron (open shell) system and the parent system model is not applicable.

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