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MOLECULAR CLUSTER MODEL OF COVALENT SEMICONDUCTORS

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ABSTRACT

A Multiple - Scattering - Cluster model of IV and III-V covalent semiconductors is proposed. The feasibility of the model is tested by carring out calculations on GaAs . The valence band width, the energy band gap and the location of the cationic and anionic *d* levels obtained are in fairly good agreement with the experimental results for the bulk crystal.

By using a localized description of the electronic structure of solids instead of the conventional band structure description, the molecular cluster model has been successfuly applied to study the properties of vacancies, interstitials and substitutional impurities in insulators and semiconductors (Messmer and Watkins 1973, Hemstreet 1975, Oliveira et al. 1976).

According to this method we start by first selecting a small part of the crystal. The electronic structure of this cluster of atoms is then obtained by solving the one electron Schroedinger equation through some Quantum Chemistry technique. The self-consistent statistical-exchange-correlation multiple scattering method ($MS - X_\alpha$) has been stablished as an useful and flexible tool to deal with these problems (Johnson 1975, Yu et al. 1976).

The $MS - X_\alpha$ - cluster method has recently been used by Cartling to study the electronic structure of Diamond, Silicon and Germanium, through a cluster of 17 atoms (Cartling 1975). The cluster model used consists of 5 crystal atoms, the central atom and its 4 nearest neighbours. In order to take care of the bonds dangling out of the cluster, a next shell of 12 Hydrogen atoms is included. The energy levels are classified according to the irreducible representations of the tetrahedral point group.

Although these calculations have interesting features, there are some elementary properties of the bulk electronic structure which the model fails to describe: The cluster

highest occupied orbital has a $t_1(\Gamma_{25})$ symmetry when is well known that the valence band top has a $t_2(\Gamma_{15})$ symmetry (Cheli kowsky and Cohen 1976). Furthermore, the cluster model leads to a valence band width for Diamond about a half of the value obtained for the bulk (Leite et al. 1975).

In this letter we propose a more realistic MS-X_α - cluster model to investigate the electronic structure of IV and III-V tetrahedrally coordinated semiconductors. We still keep the cluster with 17 atoms. The central atom is surrounded by its 4 nearest neighbours and 12 next-nearest neighbours, in tetrahedral configuration. If the electronic structure of the cluster is interpreted in terms of sp^3 hybrids and N is the number of valence electrons, there will be N - 32 electrons filling dangling bonds. Instead of saturate them by including an extra shell of atoms, we proceed by promoting these electrons to the Watson sphere (Watson 1958). No relevant extra diffi - culties are added to the calculations to transfer the electrons filling dangling bonds to the Watson sphere.

To test the feasibility of our cluster model for covalent solids we obtain the energy spectra for a cluster of GaAs. (1 As 4 Ga 12 As). The electronic structure of this material was already investigated through a non-self consistent calculation on a cluster of 35 atoms, supposing the tight-binding representation for the localized molecular orbitals (Lowther 1976).

The MS - X_α - cluster method is described with detail in the literature (Johnson 1975). The muffin-tin atomic spheres radii are the atomic radii 2.17 and 2.45 (au) for As

and Ga respectively (Slater 1965). These touching spheres corresponds to a lattice constant equal to 5.65 Å (Ley et al. 1974). The outer sphere radius is 9.74 au, which is supposed to be the same for the Watson sphere. The exchange parameters α utilized were 0.7069 and 0.70665 for Ga and As respectively (Schwarz 1972). The interstitial constant potential V_{II} was obtained by the usual procedure of volume averaging, with an exchange parameter equal to 0.70677. The frozen core state approximation (up to $3d$) was also utilized.

In Fig. 1 is shown the energy spectra obtained from the self-consistent calculations for the cluster when the dangling bonds are filled by 45 electrons (77 electrons - model) and when those electrons are transfered to the Watson sphere (32 electrons - model).

Insert Figure 1

The comparison between the two spectra emphasize that the most crucial approximation is that of the boundary condition. When the dangling bonds are occupied the model leads to a valence band width, $t_2 - t_1$ ($\Gamma_{15v} - \Gamma_{1v}$), equal to 6.54 eV. This value is 11.67 eV when the 45 electrons are promoted to the Watson sphere, which is in fairly good agreement with the experimental result from photoemission spectroscopy, 12.9 eV and the result of band structure calculation, 12.4 eV (Chelikowsky and Cohen 1976). In the 77 electrons-cluster model the dangling bonds are undesirable occupied surface states of the cluster. Most of these states penetrate well into the cluster, generating an electronic structure strongly deviated

from that of the ideal crystal.

The energy band gap, $a_1 - t_2\ (\Gamma_{1c} - \Gamma_{15v})$, of 0.93 eV for the 77 electrons-cluster model, increases to 1.17 eV for the 32 electrons-cluster model. The electron relaxation effects taken into account through the Slater transition state concept (Slater 1974) leads to a final value of 1.19 eV for the band gap. The experimental value is 1.5 eV approximately (Aspnes and Studna 1973). We do not expect an exact agreement between our calculated values and the experimental one, since in our model the relativistic effects (Chadi 1977) and the non muffin-tin corrections (Williams and Morgan 1974) are neglected.

According to the 32 electrons-cluster model, the Ga and As *d* levels are located at 18.10 eV and 39.14 eV, below the top of the valence band, respectively. These results are in good agreement with the experimental values of the binding energies obtained for the cationic (18.82 eV) and anionic (40.76 eV) *d* levels of the GaAs (Ley et al. 1974).

It is worth mentioning that the 32 electrons--cluster model should be well suitable to studying the properties of localized impurities in the lattice, since it reproduces realistically the main features of the bulk electronic structure.

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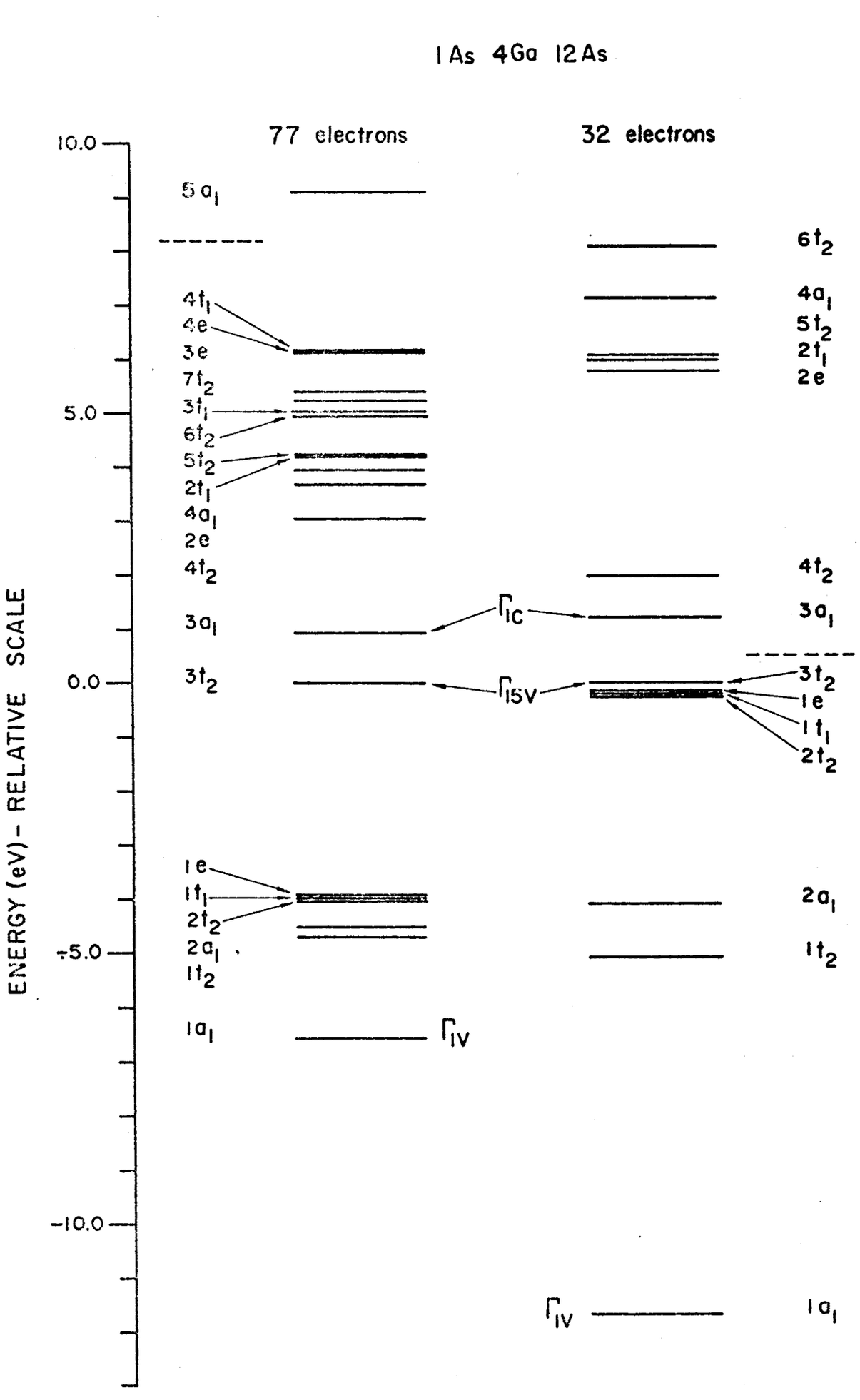
FIGURE CAPTIONS

Figure 1 - Orbital energies from the MS-X_α - cluster model for GaAs. The As is the central atom. The unoccupied energy levels are located above the dashed line. The absolute values of the energy level Γ_{15v} are 12.09 eV and 41.63 eV for the 77 and 32 electrons-cluster models respectively ("c" means conduction and "v" means valence).


1 As 4 Ga 12 As
77 electrons
32 electrons
ENERGY (eV) - RELATIVE SCALE
10.0
5.0
0.0
-5.0
-10.0
5a1
4t1
4e
3e
7t2
3t1
6t2
5t2
2t1
4a1
2e
4t2
3a1
3t2
1e
1t1
2t2
2a1
1t2
1a1
Γ1C
Γ15V
Γ1V
6t2
4a1
5t2
2t1
2e
4t2
3a1
3t2
1e
1t1
2t2
2a1
1t2
1a1