

## Interaction Between Dangling Bonds in Vacancy-Defects in Silicon

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**Abstract** We review the "defect-molecule" model in the simplest scheme (without configuration interaction) and explore the concept of "delocalized dangling-bonds" in the study of the interaction between the unsaturated hybrids of the mono and divacancy in silicon. The "defect-molecule" hamiltonian is written in parametric form, and the parameters are extracted from full self-consistent calculations for both systems carried out through the MS-Xa molecular cluster model.

### 1. INTRODUCTION

The "defect molecule" model<sup>1,2</sup> has played a pioneering role in the study of vacancy-type defects in covalent semiconductors<sup>3</sup> and the more modern molecular cluster models<sup>4-10</sup> arised, in a way, due to the partial success the old model achieved in a difficult theoretical field<sup>11</sup>. In the original "defect molecule" model, the study is restricted to the interactions between the dangling bonds, while the back-bonds are included at most as fixed charge densities (i.e., they do not participate in the self-consistent procedure). For the single vacancy, for instance, one would study only the interactions between the hybrids  $a_1, a_2, a_3, a_4$ , as in Fig.1 in the simplest scheme, and then one would assemble the spectrum of global states for the "molecule" composed of these hybrids.

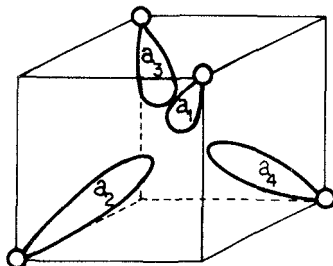


Fig.1 - Scheme of the directional dangling bonds in a single vacancy in a tetrahedral crystal.

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The defect-molecule model is subject to severe restrictions, the first being the fact that the defect levels cannot be located relative to the band structure of the crystal<sup>2,3</sup>. Furthermore, as the defect is forced to an extreme degree of localization, the model tends to superestimate many-electron effects.

On the other hand valuable physical insight can be gained from this simple modelling of the defect. Recently Lannoo<sup>12</sup> introduced the notion of "delocalized" dangling bonds, in the sense that results from more sophisticated models, which really take into account the interaction defect-lattice, could be interpreted within the simplified defect-molecule model. A major advantage would be that, if for a particular set of defects there could be discovered a trend for the behavior of the dangling bonds, such an unified picture can be of great value when studying problems of a more complex nature.

## 2. SIMPLIFIED "DEFECT MOLECULES" FOR THE MONO AND DIVACANCY IN DIAMOND STRUCTURE CRYSTALS

In the one-electron approximation the interaction matrix for the defect molecule is built from the integrals  $(a_i | V | a_j) = V_{ij}$ . For the single vacancy the local symmetry dictates that the interaction between any two hybrids has one and the same value:  $(a_i | V | a_j) = \gamma, j \neq i = 1 \dots 4$  thus,

$$V = \begin{pmatrix} 0 & \gamma & \gamma & \gamma \\ \gamma & 0 & \gamma & \gamma \\ \gamma & \gamma & 0 & \gamma \\ \gamma & \gamma & \gamma & 0 \end{pmatrix} \quad \text{with } \vec{\psi} = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{pmatrix}$$

and we can easily solve the eigenvalue equation in terms of the "parameter"  $\gamma$  using group theory, noting that the representation formed by the four hybrids can be reduced, within the  $T_d$  point group, to  $1A_1 + 1T_2$ . Using the appropriate transformations, we obtain

$$\varepsilon_{a_1} = Q + 3Y \quad , \quad \phi_{a_1} = \frac{1}{2} (a_1 + a_2 + a_3 + a_4)$$

$$\varepsilon_{t_2} = Q - Y \quad , \quad \phi_{t_2} = \frac{1}{2} \begin{cases} (-a_1 + a_2 + a_3 + a_4) \\ (a_1 - a_2 + a_3 + a_4) \\ (a_1 + a_2 - a_3 - a_4) \end{cases}$$

not including the overlap integrals in the normalization of the  $\phi$ 's. The common term  $Q$  comes from the diagonal elements of the secular matrix (the hybrids degenerate energy before interaction) and the resulting level scheme is shown in Fig. 2 supposing  $Y < 0$ .

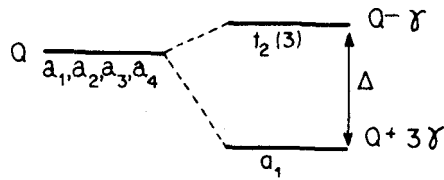


Fig.2 - Scheme of the level splitting for the "molecule" composed of the dangling bonds of the single vacancy.

As the level splitting is dependent on the interaction energy between hybrids,  $\varepsilon_{t_2} - \varepsilon_{a_1} = \Delta = -4Y$ , we can now proceed to revert the process: from a complete one-electron self-consistent procedure including defect-lattice interaction, we extract from the level splitting the value of  $Y$  for "delocalized" hybrids.

For the divacancy in diamond and silicon there are six dangling bonds, as in Fig. 3, and the local symmetry is  $D_{3d}$ .

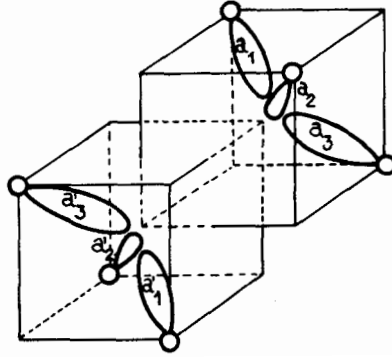


Fig.3 - Scheme of the directional dangling bonds in a divacancy in a crystal of the diamond structure; the vacancy sites are the centers of the interpenetrating cubes.

The interaction between "nearest-neighbor" hybrids must also have the same value for any two hybrids,  $(a_1|V|a_2)$  or  $(a_i|V|a'_2)$  for example, and we will still call it  $\gamma$ . For "second-neighbor" hybrids, i.e., neighbors across the divacancy  $(a_i|V|a'_j)$ , the local symmetry constrains the interactions between an hybrid in one of the mirror planes and the hybrids in the other two mirror planes to assume the same value, not necessarily equal to the interaction between hybrids in the same plane. Thus, in the notation of Fig. 3

$$(a_i|V|a'_j) = \begin{cases} \gamma' & , i = j \\ \mu\gamma' & , i \neq j \end{cases}$$

and the complete interaction matrix is

$$V = \begin{Bmatrix} 0 & \gamma & \gamma & \gamma' & \mu\gamma' & \mu\gamma' \\ \gamma & 0 & \gamma & \mu\gamma' & \gamma' & \mu\gamma' \\ \gamma & \gamma & 0 & \mu\gamma' & \mu\gamma' & \gamma' \\ \gamma' & \mu\gamma' & \mu\gamma' & 0 & \gamma & \gamma \\ \mu\gamma' & \gamma' & \mu\gamma' & \gamma & 0 & \gamma \\ \mu\gamma' & \mu\gamma' & \gamma' & \gamma & \gamma & 0 \end{Bmatrix} \quad \text{with } \vec{\psi} = \begin{pmatrix} a_1 \\ a_2 \\ a_3 \\ a'_1 \\ a'_2 \\ a'_3 \end{pmatrix}$$

According to the representations of the  $D_{3d}$  point group, the representation formed by these six hybrids can be reduced to  $1A_{1g} + 1A_{2u} + 1E_g + 1E_u$ , and after the corresponding unitary transformations we obtain the solution of the eigenvalue equation in terms of the parameters  $\gamma$ ,  $\gamma'$  and  $\mu$ :

$$\epsilon_{a_{1g}} = Q + 2\gamma + 3\gamma'(1+2\mu) \quad \phi_{a_{1g}} = \frac{1}{\sqrt{6}} (a_1 + a_2 + a_3 + a_1' + a_2' + a_3')$$

$$\epsilon_{a_{2u}} = Q + 2\gamma - 3\gamma'(1+2\mu) \quad \phi_{a_{2u}} = \frac{1}{\sqrt{6}} (a_1 + a_2 + a_3 - a_1' - a_2' - a_3')$$

$$\epsilon_{e_g} = Q - \gamma + \gamma'(1-\mu) \quad \phi_{e_g} = \begin{cases} \frac{1}{2} (a_1 - a_2 + a_1' - a_2') \\ \frac{1}{\sqrt{12}} (-a_1 + 2a_2 - a_3 - a_1' + 2a_2' - a_3') \end{cases}$$

$$\epsilon_{e_u} = Q - \gamma - \gamma'(1-\mu) \quad \phi_{e_u} = \begin{cases} \frac{1}{2} (a_1 - a_3 - a_1' + a_3') \\ \frac{1}{\sqrt{12}} (-a_1 + 2a_2 - a_3 + a_1' - 2a_2' - a_3') \end{cases}$$

where we again did not include the overlap integrals in the normalization, and  $Q$  has the same meaning. We note that setting  $\mu = 1$  would result in an accidental degeneracy of the  $e$  levels.

As for the single-vacancy, we can now obtain the magnitude of the hybrids interactions from the level splittings; from complete calculations on both systems for a chosen material we can assess the influence of the environment on the behavior of the dangling bonds.

### 3. THE VACANCY AND DIVACANCY IN SILICON

We have studied the single vacancy and the divacancy in Si through a molecular cluster model, within the formalism of the self-consistent Multiple-Scattering method<sup>13</sup> in the  $X\alpha$  local density approximation (MS-X $\alpha$ ). The dangling bonds at the surface of the cluster

are kept from interfering in the electronic structure through the method of transference of electrons to a Watson sphere<sup>9</sup>.

The single vacancy (Si:V) was simulated by a cluster with a central empty sphere plus 16 Si atoms in  $T_d$  symmetry<sup>10</sup>; the self-consistent results, compared to the results for a "perfect" cluster with 17 Si atoms, permit us to identify the two levels associated to the dangling bonds as an  $a_1$  level slightly below the top of the valence band, and a  $t_2$  level near the middle of the band gap, as shown in Fig. 4. These results refer to the neutral unrelaxed system and compare very

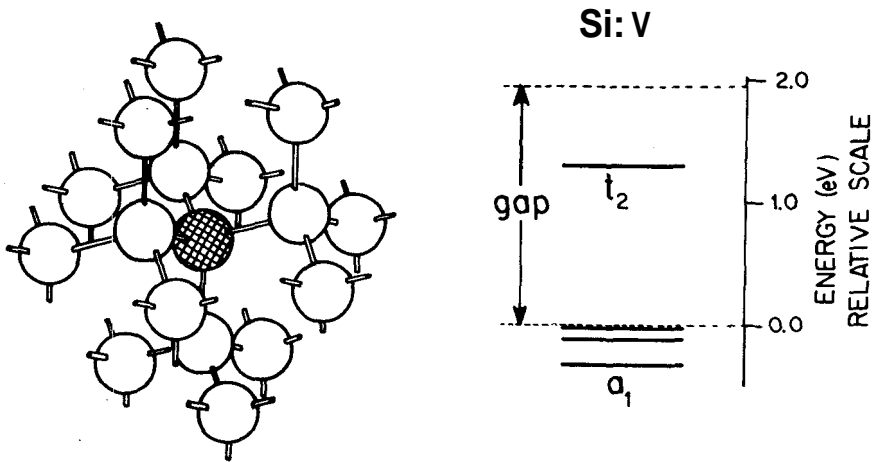


Fig.4 - a) representation of the molecular clusters used to study the single vacancy in Si: the cluster simulating the bulk crystal has 17 Si atoms in  $T_d$  symmetry, and the dashed sphere is the site of implantation of the vacancy. b) self-consistent energy spectrum for the cluster 16 Si+V, representing the system Si:V, in the gap region.

well with other theoretical results obtained through rigorous self-consistent pseudo-potential calculations<sup>14,15</sup>.

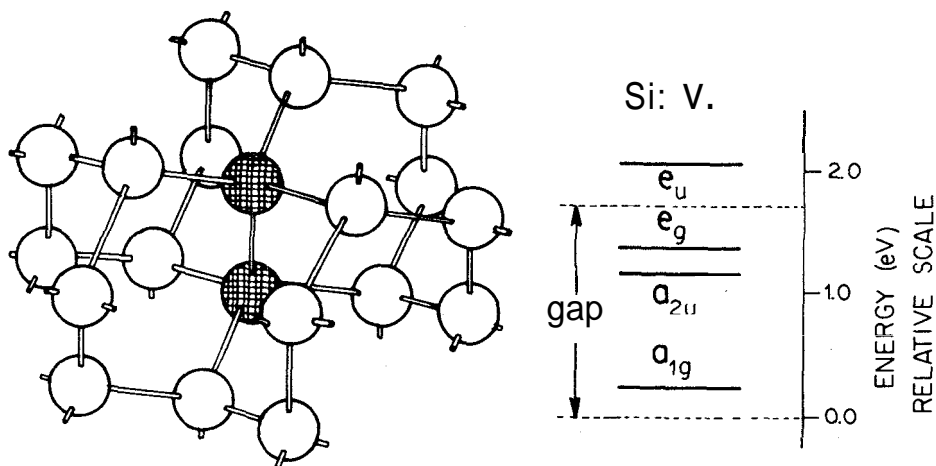


Fig.5 - a) representation of the molecular clusters used to study the divacancy in Si: the cluster simulating the bulk crystal has 20 Si atoms in  $D_{3d}$  symmetry, and the dashed spheres are the sites of implantation of the two vacancies. b) self-consistent energy spectrum for the cluster 18 Si+ $V_2$ , representing the system Si: $V_2$ , in the gap region.

For the divacancy we used a cluster with 2 central empty spheres plus 18 Si atoms in  $D_{3d}$  symmetry, as in Fig. 5, referenced to a "perfect" cluster with 20 Si atoms<sup>16</sup>. Of the 4 defect orbitals 3 introduce levels within the band gap, and only the  $e_u$  level is found lying above the bottom of the conduction band. These results (also shown in Fig. 5) refer to the unrelaxed defect in the neutral charge state.

Summarizing the relevant results, we have for the systems

Si: $V$

$$\epsilon_{t_2} - \epsilon_{a_1} \approx 1.62 \text{ eV}$$

$$\gamma_v = -0.40 \text{ eV}$$

and

Si:V<sub>2</sub>

$$\epsilon_{a_{2u}} - \epsilon_{a_{1g}} = 0.92 \text{ eV}$$

$$\epsilon_{e_u} - \epsilon_{e_g} = 0.66 \text{ eV}$$

$$\frac{1}{2} (\epsilon_{e_u} + \epsilon_{e_g}) - \frac{1}{2} (\epsilon_{a_{2u}} + \epsilon_{a_{1g}}) = 1.00 \text{ eV}$$

$$\gamma_{v_2} = -0.33 \text{ eV}$$

$$\gamma'_{v_2} = -0.37 \text{ eV}$$

$$\mu = 0.12$$

The first information provided by these models is that, as the  $\gamma$  integrals have **negative** values, the rebonding between these hybrids is energetically favorable.

The interaction between nearest-neighbor hybrids for both systems is of the same order of magnitude, but the surprising result is that the interactions across the defect between opposite hybrids (in the same mirror plane) is also of this order of magnitude. Furthermore, there's a strong **asymmetry** as concerns interactions out of the mirror plane that is patent in the value of  $\mu = 0.12 \ll 1$ .

These results indicate firstly that the second neighbor hybrids interaction cannot reasonably be neglected, and so for more distant hybrids a complete study is still necessary. Also, besides the fact that the magnitude of these interactions cannot yet be thought convergent with the size of the defect, the use of these values in other systems does not **seem** to be straightforward due to possible asymmetries, the degree of which is not known "a priori".

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## REFERENCES

1. C.A.Coulson and M.J.Kearsley, *Proc.Roy.Soc.* 241, A 433 (1957).
2. T. Yamaguchi, *J.Phys.Soc. Japan* 17, 1359 (1962).
3. F.P.Larkins, *J.Phys.Chem.Solids* 32, 965 (1971).
4. F.P. Larkins and A.M. Stoneham, *J.Phys. C. Solid St. Phys.* 4, 143 (1971).
5. G.T. Surratt and W.A.Goddard III, *Solid St. Commun.* 22, 413 (1977).
6. R.P. Messmer and G.D. Watkins, *Phys. Rev. B* 7, 2568 (1973).
7. C.A.J. Ammerlaan and J.C.Wolfrat, *Phys. Stat. Sol. B* 89, 541 (1978).
8. L.A. Hemstreet, *Phys. Rev. B* 15, 834 (1977).
9. A. Fazzio, J.R. Leite and M.L. de Siqueira, *J.Phys. C: Solid St. Phys.* 12, 346 9 (1979).
10. A. Fazzio, M.J.Caldas and J.R.Leite, *Int. J. Quantum Chem. S* 13, 349 (1979).
11. S.T. Pantelides, *Rev. Mod. Phys.* 50, 797 (1978) and references therein.
12. M. Lannoo, *Physica B (special issue): "12<sup>th</sup> Int.Conf.Defects in %i-conductores"*, Amsterdam, 1982 - to be published.
13. K.H. Johnson, *J.Chem.Phys.* 45, 3085 (1966).
14. G.A. Baraff and M. Schlüter, *Phys. Rev. Lett.* 41, 892 (1978); *Phys. Rev. B* 19, 4965 (1979).
15. J. Bernholc, N.O. Lipari and S.T. Pantelides, *Phys. Rev. Lett.* 41, 895 (1978); *Phys. Rev. B* 21, 3545 (1980).
16. A.Fazzio, M.J.Caldas and J.R.Leite, *Physica B (special issue): "12<sup>th</sup> Int. Conf. Defects in Semiconductors"*, Amsterdam, 1982 - to be published.

## RESUMO

Fazemos uma breve revisão do esquema mais simplificado do modelo da "molécula de defeito" (sem interação de configuração), e exploramos o conceito de orbital flutuante "deslocalizado" no estudo da interação dos híbridos não saturados da mono e divancância em silício. O hamiltoniano da "molécula de defeito" é escrito em forma paramétrica, sendo os parâmetros então extraídos de cálculos autoconsistentes completos para os dois sistemas, realizados através do modelo de aglomerados moleculares no formalismo do Espalhamento Múltiplo - Xa.