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Multiplet splittings and Jahn-Teller energies for the vacancy in silicon

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The question of the relative importance of multiplet-splitting effects and Jahn-Teller distortion energies is discussed in detail for the vacancy in silicon. The calculations are done within the self-consistent local-density approximation. It is demonstrated that the dominant contribution comes from the magnetic or exchange splitting, which for the free atom is the origin of the Hund's-rule ground state. The calculated value of this splitting is an appreciable 0.35 eV for the neutral-vacancy case. However, if multiplet and Jahn-Teller splittings are combined, the ground state is dominated by Jahn-Teller distortions while multiplet effects are practically quenched. The general results of the negative-U system formed by the three charge states V^{2+}, V^{+}, and V^{0} remain thus basically unaltered.

I. INTRODUCTION

There has been a long controversy concerning the relative importance of correlation effects and Jahn-Teller (JT) distortions for vacancy centers in silicon. The first theoretical models,[1,2] all based on the defect-molecule approximation, pointed out that many-electron effects were essential for a correct description of the electronic properties of these defects. On the other hand, Watkins[3] was able to show that very simple one-electron models combined with local Jahn-Teller distortions can account quite successfully for the results of EPR experiments. This was interpreted to imply that the Jahn-Teller distortion is the dominant effect and that the defect-molecule grossly overestimates correlation effects. A plausible explanation for this is that the bound states of the vacancy (which have a dangling-bond character) are in fact quite delocalized, and that this delocalization is likely to reduce considerably the relevant Coulomb interactions. However, the magnitude of this effect is still subject to uncertainty. Coulson and Larkins[4] increasing the size of the defect molecule, concluded that this reduction was weak, while Messmer and Watkins, using the scattered wave $X\alpha$ method,[5] arrived at the opposite conclusion, namely, that the Coulomb terms almost tend to zero as the size of the cluster is increased.

Two other papers have dealt in some detail with this subject. The first one by Surratt and Goddard[6] is based on the generalized valence-bond model for clusters C_4H_{12} or Si_4H_{12}. The straight application of their method leads to results essentially similar to those of the defect-molecule model, i.e., an overestimate of the electron-electron interactions. These authors then, used modified values corresponding to reduced interactions, which improved their numerical results. The second paper by Lannoo[7] reviewed these calculations on the basis of a two-parameter model, one for the hopping between dangling bonds and the other for the Coulomb interaction. He found that plausible values for the Coulomb interactions should be much smaller than in the defect-molecule model, but by no means small enough that the resulting multiplet splitting could be neglected.

It is thus of interest to obtain the best possible estimate of the multiplet-structure parameters and to make a systematic study in which these effects are combined with Jahn-Teller distortions. To do this we shall use the local-density formalism which, when used with some care,[8,9] has been shown to predict correct multiplet structure for free atoms. We use here an extension of this formulation, whose details are published elsewhere,[10] and in which the total energy of the system is expressed to second order in the changes in occupation numbers of the orbitals, in terms of a minimal number of independent parameters. These correspond to the self-energies of fluctuations of either charge densities or spin densities. They can readily be obtained from the results of one-electron self-consistent calculations. These energies are characteristic of the multiplet splitting occurring at the ground-state configuration, and will then be compared to Jahn-Teller energies.

In Sec. II we give a brief account of Watkins's one-electron linear combination of atomic orbitals (LCAO) picture, discussing its relation with the results of more sophisticated recent calculations by Baraff and Schlüter[11] and Bernholc, Lipari, and Pantelides.[12] We also recall characteristic features of tetragonal and trigonal distortion modes which can occur in the neighborhood of the vacancy site and the splitting of the vacancy states they induce. Section III is devoted to a brief account of the general method used to handle the multiplet-structure problem and gives a detailed application to the neutral-vacancy case. The question of the relative importance of multiplet

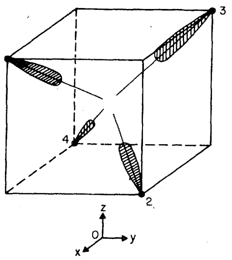

FIG. 1. The vacancy defect molecule with its four dangling bonds.

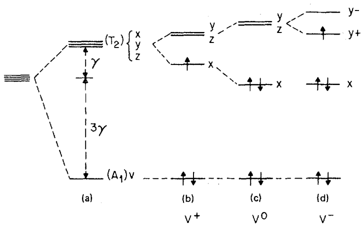

FIG. 2. Splitting of the molecular levels under the Jahn-Teller distortion for V^+, V^0, and V^-.

and Jahn-Teller splittings is analyzed in Sec. IV for arbitrary strength of their relative parameters. Finally these results are discussed in terms of the negative-U centers formed by V^{2+}, V^+, and V^0.

II. WATKINS'S LCAO ONE-ELECTRON PICTURE (REF. 3)

This picture is based on the simplest possible version of molecular-orbital theory. The atomic orbitals are taken to be one s and three p orbitals per atom. As usual in tetrahedral covalent structures one builds sp^3 orbitals which, in the perfect crystal, pair to form strong covalent bonds. Upon forming a vacancy by removal of one atom (Fig. 1) four such bonds are broken, leaving four dangling bonds ψ_i, $i=1$ to 4. From symmetry, one has only two independent parameters, the self-energy of these orbitals:

$$\overline{E}=\langle\psi_i|h|\psi_i\rangle \tag{1}$$

and their overlap interaction

$$-\gamma=\langle\psi_i|h|\psi_j\rangle \quad \text{for } i\neq j\,. \tag{2}$$

The 4×4 Hamiltonian matrix can be easily diagonalized and gives the one-electron level splitting of Fig. 2(a), with a nondegenerate A_1 state at -3γ and a threefold-degenerate T_2 state at $+\gamma$. The corresponding eigenfunctions (which will be needed later) are

$$\begin{aligned} A_1:&\ v=\tfrac{1}{2}(\psi_1+\psi_2+\psi_3+\psi_4)\,,\\ &\ x=\tfrac{1}{2}(\psi_1+\psi_2-\psi_3-\psi_4)\,,\\ T_2:&\ y=\tfrac{1}{2}(\psi_1+\psi_2+\psi_3-\psi_4)\,,\\ &\ z=\tfrac{1}{2}(\psi_1-\psi_2+\psi_3-\psi_4)\,. \end{aligned} \tag{3}$$

Let us begin with the V^{2+} charge state. There are two available electrons which will fill the lower level A_1. In the V^+ case, one extra electron has to be in the T_2 state. This one being degenerate is subject to a Jahn-Teller distortion which by removing the degeneracy lowers the energy. The general theory of the Jahn-Teller effect on a T_2 state[13,14] predicts two possibilities: either a tetragonal distortion [lowering the symmetry to D_{2d} with three equivalent possibilities, the $\langle100\rangle$ being pictured in Fig. 3(a)] or a trigonal distortion [lowering the symmetry to C_{3v} with four equivalent possibilities, the $\langle111\rangle$ being pictured in Fig. 3(b)]. On these figures we also give the coordinates of the atomic displacements in terms of the normalized symmetry mode amplitudes Q_E and Q_T. The experimental results for V^+ are consistent with a tetragonal distortion, as shown on Fig. 2(b). Going to V^0 one adds another electron to the lowered level, thereby increasing the Jahn-Teller distortion. Finally, for V^-, the fifth electron must be added to the twofold-degenerate state. Again the Jahn-Teller theorem applies, but now the splitting can only occur through a trigonal distortion superimposed on the tetragonal one [Fig. 2(d)]. This situation is in agreement with the experimental observation[3] of a mixed tetragonal and trigonal distortion for V^-.

We may ask how such a simple model compares with the results of more elaborate calculations? Let us first compare one-electron energies. In the LCAO picture, the defect molecule formed by the four dangling bonds must be embedded in the

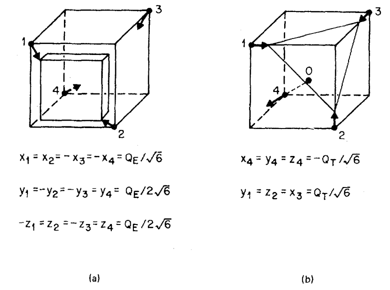

FIG. 3. (a) Tetragonal distortion along the x axis and (b) trigonal distortion along the $\langle111\rangle$ direction.

crystal, i.e., the four-dangling-bond states are coupled with neighboring bonding and antibonding states of the valence and conduction bands. The molecular states A_1 and T_2 of Eq. (3) can be found either as localized states in the forbidden gap or resonant states within the bands. With the A_1 state being lower self-consistency requires that the T_2 level be localized within the forbidden gap. Thus the A_1 level is likely to be found as a resonance in the valence band. This picture is confirmed by the local-density calculations of Baraff and Schlüter[11] and Bernholc, Lipari, and Pantelides[12] (where the A_1T_2 splitting is of the order of 1.7 eV in silicon). The picture is also confirmed by empirical tight-binding treatments.[15] The important point is that the A_1 and T_2 states are now somewhat delocalized. However, it is instructive to still consider them as being built from the four equivalent wave functions ψ_i (with $=1$ to 4) which can now be considered as *delocalized* dangling bonds. The Jahn-Teller coefficients have been calculated by Baraff, Kane, and Schlüter[16] and found to give good agreement with experimental results for the charge states V^{2+}, V^{+}, and V^0 which form from a negative-U system. We shall discuss these numerical values later.

A way to go beyond the simple one-electron picture is to include many-electron effects. This has been done first in the spirit of the molecular treatment. There one only considers the defect molecule of Fig. 1 and builds determinants from the individual spin orbitals which are v, $\bar{v}$, x, $\bar{x}$, y, $\bar{y}$, z, and $\bar{z}$ (here the bar denotes spin down). For the neutral vacancy, for instance, one has three possible configurations: $A_1^2T_2^2$ (two electrons each in the A_1 and T_2 state), $A_1T_2^3$ (one and three), and T_2^4 (zero and four). One builds all possible Slater determinants belonging to each configuration [for instance, the determinant $|v\bar{v}x\bar{x})$ belongs to $A_1^2T_2^2$] and finally diagonalizes the many-electron Hamiltonian in the corresponding basis, allowing for the interaction between configurations. It is this procedure which led to the conclusion that many-electron effects were important enough that they could not be neglected. From this point of view however, it is still hard to understand why these effects seem to disappear so completely in experiment so that, in fact, the simple one-electron picture works well. As we shall see, the argument that the *delocalization* of the dangling-bond states leads to vanishingly small many-electron effects is *not* valid. It is the aim of this paper to analyze simultaneously the many-electron and Jahn-Teller effects and to show why only the second effect seems to be important.

III. LOCAL-DENSITY TREATMENT OF MULTIPLET STRUCTURE

We follow here a method which has similarities with the procedure used, for free atoms, by Ziegler, Rauk, and Baerends[8] and von Barth.[9] The similarity lies in the fact that we use local-density theory to calculate the total energy of a state only when its charge density can be simulated by *one* single Slater determinant. This is because a state corresponding to a combination of Slater determinants must give rise to a state-dependent exchange-correlation potential and can thus not be simulated by the simple local-density functionals which are in current use. A new feature, not present in atomic problems, is that we are dealing with an extended system (composed of delocalized plus localized states).

In this case, it is considerably more difficult to calculate the total energy for various determinants. For this reason we have developed a theory in which the total energy is expanded to second order in *changes* in the occupation number of the one-electron spin orbitals. The advantages of this formulation are the following: (i) it reduces the problem to the calculation of the localized-electron states only, (ii) it allows one to express the multiplet splittings (i.e., the difference in energy between various determinantal states) in terms of the self-energy of self-consistently screened change- or spin-density fluctuations, and (iii) because each determinant is a given average over true multiplet states, a comparative study of different possibilities reduces the problem to the evaluation of a few independent parameters (e.g., two for the neutral vacancy).

A detailed account of this theory is given elsewhere.[10] Here we shall simply outline the essential steps, taking as an example the neutral-vacancy case (extensions to other charge states can be made trivially). We consider a configuration in which all the valence states are completely filled, in which the A_1 state (a resonance within the valence band) is filled with two electrons of opposite spin, and in which the two remaining electrons are localized in the T_2 state. This situation is the equivalent to the $A_1^2T_2^2$ configuration of the defect-molecule model. The problem here arises from the many different possibilities of distributing these two electrons on the orbitally triply degenerate level T_2 (the situation is in some respects analogous to the two equivalent p^2 electrons of a free carbon or silicon atom).[9] This leads to a splitting into different levels forming the multiplet structure for that configuration. This effect is important for localized states in semiconductors, as has been known for a long time for transition-metal ions in more or less ionic systems.[17]

To derive the second-order expansion of the energy, we have to start from a reference state, for which a complete self-consistent calculation has been performed. For the neutral vacancy V^0 in silicon, this was done for an average state in which the two electrons were distributed equally between the six T_2 spin orbitals. Then, the corresponding contributions $\rho_{0\uparrow}$ and $\rho_{0\downarrow}$ to the electron density were

$$\rho_{0\uparrow}=\frac{x^2+y^2+z^2}{3}=\rho_{0\downarrow}\ . \tag{4}$$

Starting from this reference state, we expand the total energy to second order in the changes $\Delta n_{i\sigma}$ in occupation numbers of the one-electron spin orbitals $\psi_{i\sigma}$. This expansion can be expressed as

$$E_{\text{tot}}(n_{i\sigma})=E_{\text{tot}}(n_{i\sigma}^0)+\sum_i \epsilon_{i\sigma}\Delta n_{i\sigma} + \tfrac{1}{2}\sum_i \epsilon_{i\sigma}\Delta n_{i\sigma}+\cdots\ , \tag{5}$$

where i stands for the orbital part and σ stands for the spin part. The first-order coefficient $\epsilon_{i\sigma}$, being the partial derivative of E_{tot} with respect to $n_{i\sigma}$, is the corresponding one-electron eigenvalue. The coefficient $\Delta\epsilon_{i\sigma}$ is the first-order change in $\epsilon_{i\sigma}$ induced by $\Delta n_{i\sigma}$. It can be calculated by first-order self-consistent perturbation theory. One can show (for details see Ref. 10) that this second-order term can be split into two different contributions: the first one comes from pure charge fluctuations $\Delta\bar{\rho}$ defined by

$$\Delta\bar{\rho}=\sum_i \frac{\Delta n_{i\uparrow}+\Delta n_{i\downarrow}}{2}\,|\psi_i|^2\ , \tag{6}$$

where ψ_i is the orbital part of the wave function. The associated energy is

$$E_{\Delta\bar{\rho}}=\tfrac{1}{2}\int[2\Delta\bar{\rho}(\vec{r})]\epsilon_d^{-1}(\vec{r},\vec{r}\,)\left(v(\vec{r}\,',\vec{r}\,'')-\frac{v_x'}{2}(\vec{r}\,')\delta_{r'r''}\right)[2\Delta\bar{\rho}(\vec{r}\,'')]\,d\tau\,d\tau'\,d\tau''\ , \tag{7}$$

where $\epsilon_d^{-1}(\vec{r},\vec{r}\,')$ is the inverse dielectric matrix, $v(\vec{r}\,',\vec{r}\,'')$ is the Coulomb potential $|\vec{r}\,'-\vec{r}\,''|^{-1}$, and v_x' the density derivative of the exchange potential in its local-density form (we use Slater's $X\alpha$ exchange with $\alpha=0.7$). Expression (7) can be extended to include more complex exchange-correlation functionals.[10]

The second term comes from pure spin fluctuations $\delta\Delta\rho(\vec{r})$ given by

$$\delta\Delta\rho(\vec{r})=\sum_i \frac{\Delta n_{i\uparrow}-\Delta n_{i\downarrow}}{2}\,|\psi_i|^2 \tag{8}$$

and has a second-order energy $-E'_{\delta\Delta\rho}$ given by

$$-E'_{\delta\Delta\rho}=-\int \delta\Delta\rho(\vec{r})\epsilon_m^{-1}(\vec{r},\vec{r}\,')v_x'(\vec{r}\,')\delta\Delta\rho(\vec{r}\,')\,d\tau\,d\tau'\ , \tag{9}$$

where now ϵ_m^{-1} describes *magnetic* first-order screening of the system.

For the application of this theory to the natural-vacancy case, we consider the $A_1^2T_2^2$ configuration discussed above. This means that we include in our treatment all the possibilities of distributing the two T_2 electrons over the six T_2 spin orbitals x, $\bar{x}$, y, $\bar{y}$, z, and $\bar{z}$, i.e., only the occupation numbers of these spin orbitals will be varied. As they all belong to the same degenerate T_2 level, the first-order term in Eq. (5) will vanish, since the sum of the $\Delta n_{i\sigma}$ has to be zero.

As we have seen, the second-order terms require a first-order self-consistent calculation. The need for self-consistency can be understood simply. In our example we consider Slater determinants such as $|x\bar{x}\rangle$, $|xy\rangle$, etc., where x, $\bar{x}$, etc., are the localized T_2 states. In this condensed notation we do not specify the other filled extended states which form a closed shell. However, these states influence the result, since they become polarized by the perturbation which is induced by the change in occupation number of the localized states. This means that they tend to screen that perturbation. The result is that the energy of the system, instead of being simply the self-energy of the bare perturbation, is now the corresponding screened quantity given by Eqs. (7) and (9). It turns out here, however, that terms involving ϵ_d^{-1} will be negligible because of small wave function overlap. Moreover we shall take $\epsilon_m^{-1}=1$, so that we avoid the calculation of the self-consistent response. However, this is not valid in general and self-consistency can certainly play an important role in some cases.

Once the electrostatic and magnetic contributions to the energy [given by Eqs. (7) and (9)] are known the question arises of how to obtain the complete multiplet structure from these results. This can be done in many cases by using the fact that the many-electron eigenstates have a definite space symmetry and a given total spin (ignoring spin-orbit-coupling effects). This allows one to know *a priori* the correct *combinations* of Slater determinants defining one given eigenstate. These combinations are given for V^0 in Table I, with their symmetry label and their spin multiplicity. One can see that, except for the $M_s=\pm 1$ components of the triplet state ${}^3T_1$, all other states are *combinations* of Slater determinants.

TABLE I. Eigenstates of V^0 in terms of single Slater determinants.

$^1A_1$	$\frac{\lvert x\bar{x}) + \lvert y\bar{y}) + \lvert z\bar{z})}{\sqrt{3}}$		
^1E	$\frac{2\lvert x\bar{x}) - \lvert y\bar{y}) - \lvert z\bar{z})}{\sqrt{6}}$		
	$\frac{\lvert y\bar{y}) - \lvert z\bar{z})}{\sqrt{2}}$		
$^1T_2$	$\frac{\lvert y\bar{z}) - \lvert \bar{y}z)}{\sqrt{2}}$		
	$\frac{\lvert z\bar{x}) - \lvert \bar{z}x)}{\sqrt{2}}$		
	$\frac{\lvert x\bar{y}) - \lvert y\bar{x})}{\sqrt{2}}$		
$^3T_1$	$\lvert yz)$	$\frac{1}{\sqrt{2}}[\lvert \bar{y}z) + \lvert y\bar{z})]$	$\lvert \bar{y}\bar{z})$
	$\lvert zx)$	$\frac{1}{\sqrt{2}}[\lvert \bar{z}x) + \lvert z\bar{x})]$	$\lvert \bar{z}\bar{x})$
	$\lvert xy)$	$\frac{1}{\sqrt{2}}[\lvert \bar{x}y) + \lvert x\bar{y})]$	$\lvert \bar{x}\bar{y})$

Let us now examine in more detail the case of V^0. In Table II we give for different determinants the following characteristic quantities:

(i) Its pure charge- ($\Delta\bar{\rho}$) and pure spin- ($\delta\Delta\rho$) density fluctuations;

(ii) its energy in terms of a few independent-energy parameters of the type $E_{\Delta\bar{\rho}}$ [Eq. (7)] and $E_{\delta\Delta\rho}$ [Eq. (9)];

(iii) the average over multiplets which the single determinant represents.

To illustrate the method let us work out the determinant $\lvert x\bar{x})$. Its spin densities are

$$\rho_\uparrow = x^2 , \qquad (10)$$
$$\rho_\downarrow = x^2 ,$$

leading to

$$\Delta\bar{\rho} = x^2 - \frac{x^2 + y^2 + z^2}{3} = 2\nu_1 , \qquad (11a)$$

$$\delta\Delta\rho = 0 . \qquad (11b)$$

Using (11a) in (7) gives an energy which is four times the energy due to the function ν_1. There is no magnetic contribution from (9) because $\delta\Delta\rho$ is zero, and so the total second-order change in energy is found to be $4E_{\nu_1}$. In Table II this is written as $4E_\nu$ because of the symmetry relations given in this table. Finally, as indicated in Table I, $\lvert x\bar{x})$ represents an average over $^1A_1$ and ^1E given by the expression in column five of Table II.

Clearly, in Table II the number of relations between the multiplet levels is greater than the number of levels itself. This implies that there exist relations between the fundamental parameters. These are found to be

TABLE II. Energies of single Slater determinants for the neutral vacancy V^0. The charge and spin fluctuations (columns 2 and 3) are expressed in terms of the following symmetry components:

$$\nu_1 = \frac{2x^2 - (y^2 + z^2)}{6}, \quad \nu_2 = \frac{y^2 - z^2}{2\sqrt{3}}, \quad \rho_0 = \frac{x^2 + y^2 - z^2}{3}, \quad \theta_1 = yz , \theta_2 = zx, \quad \theta_3 = xy .$$

There are no cross terms in $E_{\Delta\bar{\rho}}$ and $E'_{\delta\Delta\rho}$ between these elementary fluctuations. Owing to symmetry, one has $E_{\nu_1} = E_{\nu_2} = E_\nu$, $E_{\theta_1} = E_{\theta_2} = E_{\theta_3} = E_\theta$, and the same relations for E'.

Determinant	$\Delta\bar{\rho}$	$\delta\Delta\rho$	Energy in terms of fundamental parameters	Energy as an average over multiplets
$\lvert x\bar{x}\rangle$	$2\nu_1$	0	$4E_\nu$	$\frac{1}{3}(E_{^1A_1} + 2E_{^1E})$
$\lvert y\bar{z}\rangle$	$-\nu_1$	$\sqrt{3}\nu_2$	$E_\nu - 3E'_\nu$	$\frac{1}{2}(E_{^1T_2} + E_{^3T_1})$
$\left\lvert \frac{y+iz}{\sqrt{2}}, \frac{\bar{y}+i\bar{z}}{\sqrt{2}} \right\rangle$	$-\nu_1$	0	E_ν	$\frac{1}{2}(E_{^1E} + E_{^1T_2})$
$\left\lvert \frac{y+iz}{\sqrt{2}}, \bar{x} \right\rangle$	$\frac{\nu_1}{2}$	$-\frac{3}{2}\nu_1$	$\frac{E_\nu}{4} - \frac{3}{4}E'_\nu$	$\frac{1}{2}(E_{^1T_2} + E_{^3T_1})$
$\lvert y, z\rangle$	$-\nu_1$	$\rho_0 - \nu_1$	$E_\nu - E'_{\rho_0} - E'_\nu$	$E_{^3T_1}$
$\left\lvert \frac{y+iz}{\sqrt{2}}, x \right\rangle$	$\frac{\nu_1}{2}$	$\rho_0 + \frac{\nu_1}{2}$	$\frac{E_\nu}{4} - E'_{\rho_0} - \frac{E'_\nu}{4}$	$E_{^3T_1}$
$\left\lvert \frac{y+z}{\sqrt{2}}, x \right\rangle$	$\frac{\nu_1}{2} + \frac{\theta_1}{2}$	$\rho_0 + \frac{\nu_1}{2} + \frac{\theta_1}{2}$	$\frac{E_\nu}{4} + \frac{E_\theta}{4} - E'_{\rho_0} - \frac{E'_\nu}{4} - \frac{E'_\theta}{4}$	$E_{^3T_1}$

$$E_\nu = E'_\nu \,, \qquad E_\theta = E'_\theta \,. \tag{12}$$

These relations tell us that some asymmetrical density fluctuations do not change the total energy to second order. This comes from the condition which we have imposed, namely, that any single determinant which can be expressed as a linear combination of other determinants, members of a degenerate set, must have the same energy as these basis determinants. The degree to which relations (12) are obeyed is a measure of the validity of this statement.

The use of relations (12) allows us to express all the multiplet levels, in terms of only two fundamental parameters, i.e., E_ν and E'_{ρ_0}. One finds

$$\begin{aligned} E_{{}^3T_1} &= -E'_{\rho_0} \,, \\ E_{{}^1E} &= 6E_\nu - E'_{\rho_0} \,, \\ E_{{}^1T_2} &= E'_{\rho_0} - 4E_\nu \,, \\ E_{{}^1A_1} &= 2E'_{\rho_0} \,. \end{aligned} \tag{13}$$

We have calculated E'_{ρ_0} for the neutral vacancy by assuming the magnetic-screening effect to be negligible [i.e., taking $\epsilon_m = 1$ in Eq. (9)]. In this case we only have to integrate the square of the density $\rho_0 = (x^2 + y^2 + z^2)/3$ multiplied by the density derivative of the exchange potential which we take to the Slater $X\alpha$ form, with α equal to 0.7. Using the wave-functions results of Ref. 11 we find for E'_{ρ_0} a value of 0.33 ± 0.03 eV. In principle one should correct this value for magnetic screening which, opposite to dielectric screening, should increase the value of E'_{ρ_0}. We thus give here a lower bound for this quantity. However, we believe the correction to be small, for reasons which are detailed in Ref. 10, and thus neglect it in what follows.

The other term E_ν (which should be equal to E'_ν) can be determined by two methods. Comparing E'_ν to E'_{ρ_0}, we find a considerable difference. The fluctuation ν integrates to zero, while ρ_0 integrates to one. Viewing x, y, z as combinations of delocalized dangling bonds, ν is only an overlap charge density which allows us to estimate that $E'_\nu = \frac{1}{100} E'_{\rho_0}$, i.e., completely negligible. The same reasoning applies to E_ν leading to a similar conclusion.

We are then left with only one significant parameter E'_{ρ_0}. With this our predicted multiplet structure is given in Fig. 4, with splittings which are by no means negligible. It is interesting to notice that our present result for ${}^1E$, ${}^3T_1$ and ${}^1T_2$ is extremely close to the one estimated in Ref. 7, while our conclusion about the relatively important value taken by the singlet-triplet splitting parameter E'_{ρ_0} seems at variance with the conclusion of Messmer and Watkins[5] for diamond. We shall come back to an explanation of this difference later.

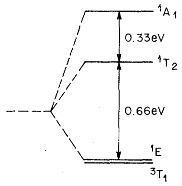

FIG. 4. Multiplet splitting for the neutral vacancy.

IV. THE RELATIVE IMPORTANCE OF MULTIPLET AND JAHN-TELLER SPLITTINGS

We have shown in the previous section that the singlet-triplet splitting of the undistorted vacancy state V^0 is of order 0.33 eV. It is thus not obvious that this energy can be neglected compared to Jahn-Teller energies of the order of 0.2 eV (see Ref. 16). It is thus important to study the two effects combined in order to obtain a correct answer to that problem. We shall consider here the problem of the multiplet structure for the *tetragonally* distorted neutral vacancy V^0 (we simply drop the trigonal mode which is not observed experimentally for V^+).

In principle, the problem has to be treated by the same methods as used in Sec. III. One starts from a reference one-electron calculation performed for one given amplitude of the distortion mode Q_E. The one-electron levels are now split, so that one has the X level

$$\epsilon_x = \epsilon_{T2} + V_E Q_E \,, \tag{14}$$

where V_E has a value[16] of -1.12 eV/Å while the twofold-degenerate state is shifted by $-\frac{1}{2}V_E Q_E$. One then considers all possible determinants as was discussed before and expresses their energies in terms of the self-energy of fluctuations like ρ_0, ν_1, ν_2, θ_1, etc. Some of the equalities which were valid by symmetry (e.g., $E_{\nu_1} = E_{\nu_2}$) will now break down leading to a much more complicated problem. However, the main difference resides in the energy of small asymmetrical charge fluctuations which, as was the case before, are likely to be negligible compared to the dominant term E'_{ρ_0}. We can thus consider that the many-electron effects are still described, in the distorted situation, by the same parameter E'_{ρ_0} as in the undistorted one. In other words we write the total perturbation due to many electron effects plus the Jahn-Teller distortions, as the sum of two Hamiltonians H_m and $H_{\rm JT}$. The parameters of each perturbation are taken to be independent of the other one (i.e., H_m is calculated at zero distortion and H_{JT} in the one-electron model).

To go further one has to express H_m and H_{JT} in the same many-electron basis. This is obvious for H_m which is diagonal in the many-electron basis of Table I, with diagonal terms equal to $2E'_{\rho_0}$, E'_{ρ_0}, $-E'_{\rho_0}$, for the ${}^1A_1$, ${}^1T_2$ and ${}^1E$, ${}^3T_1$ states, respectively. This is not so trivial for H_{JT} whose effect is given by Eq. (14) in a one-electron calculation. However, this can be readily extended to the many-electron basis. One first notices that the determinant $|x\bar{x})$ corresponding to two electrons in the ϵ_x state will have a Jahn-Teller energy of 2δ, if δ stands for $V_E Q_E$. Any determinant like $|xy)$, $|xz)$, etc., corresponding to only one electron in ϵ_x will have an energy $\delta/2$ and, finally, any determinant with no electron in ϵ_x will have an energy $-\delta$. This defines H_{JT} in the single determinant's basis, from which it is simple to express it in the basis of Table I. In this basis, we obtain for $H_m + H_{JT}$, the corresponding matrix, which is built from the following three independent blocks:

$$
\begin{aligned}
{}^1A_1 + {}^1E &\Rightarrow \begin{pmatrix} 2E'_{\rho_0} & \sqrt{2}\delta & 0 \\ \sqrt{2}\delta & \delta - E'_{\rho_0} & 0 \\ 0 & 0 & -\delta - E'_{\rho_0} \end{pmatrix}, \\
{}^1T_2 &\Rightarrow \begin{pmatrix} -\delta + E'_{\rho_0} & 0 & 0 \\ 0 & \frac{\delta}{2} + E'_{\rho_0} & 0 \\ 0 & 0 & \frac{\delta}{2} + E'_{\rho_0} \end{pmatrix}, \\
{}^3T_1 &\Rightarrow \begin{pmatrix} -\delta + E'_{\rho_0} & 0 & 0 \\ 0 & \frac{\delta}{2} + E'_{\rho_0} & 0 \\ 0 & 0 & \frac{\delta}{2} + E'_{\rho_0} \end{pmatrix}.
\end{aligned}
\tag{15}
$$

This matrix can easily be diagonalized for any value of the Jahn-Teller parameter δ and of the multiplet-splitting parameter E'_{ρ_0}. The corresponding energy E in units of E'_{ρ_0} is plotted in Fig. 5 versus the dimensionless parameter $x = |\delta|/E'_{\rho_0}$ (we consider here only negative values of δ). For high values of x the Jahn-Teller effect clearly dominates and all curves reduce to their straight-line asymptotes. For x tending to zero, one recovers the multiplet splitting at zero distortion. In this limit we give on Fig. 5, the straight lines which are tangent at $x = 0$ to the exact curve. The ${}^1E$ level becomes the most stable over the whole range of values and Fig. 5 shows that the line between the two different regimes where either multiplet or Jahn-Teller effects dominate, corresponds to $|\epsilon_x| = E'_{\rho_0}$ (i.e., the intersection of the dashed lines which represent the limiting behavior).

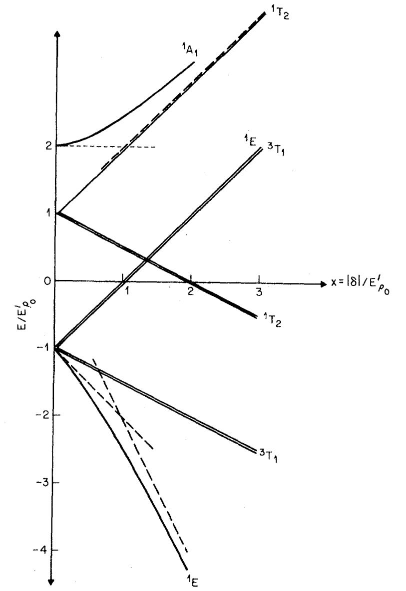

FIG. 5. Energy (in units of E'_{ρ_0}) versus the relative strength $x = |\delta|/E'_{\rho_0}$ of the Jahn-Teller tetragonal coupling, for the neutral vacancy V^0.

Let us now investigate the actual situation for V^0 in silicon. The total energy is obtained by adding to the energy given in Fig. 5 an elastic term $\frac{1}{2}k_E Q_E^2$ and by minimizing with respect to Q_E to find the stable configuration. This was done in Ref. 16 for the limit of vanishing multiplet effects, i.e., for

$$
\begin{aligned}
E &= 2\delta + \tfrac{1}{2}k_E Q_E^2 \\
&= 2V_E Q_E + \tfrac{1}{2}k_E Q_E^2 \,.
\end{aligned}
\tag{16}
$$

After minimization, the energy change was found to be −0.68 eV. At the minimum, the term $2V_E Q_{E_m}$ is equal to twice this value, and thus, δ is equal to $V_E Q_{E_m}$, i.e., −0.68 eV. As E'_{ρ_0} was found to be 0.33 eV, we are in a case where $|x|$ is equal to two, i.e., in a region where the Jahn-Teller effect dominates. In fact, for $|x| = 2$, the relative error introduced by the neglect of E'_{ρ_0} is only 6% compared to the Jahn-Teller stabilization of the level, which is 2δ, i.e., −1.36 eV. Inclusion of the many-electron effects only introduces a small further stabilization amounting to 0.25 E'_{ρ_0}, i.e., about 0.08 eV.

The important conclusion of this section is that, although the multiplet-splitting parameter E'_{ρ_0} is not small, its importance is very minimal for the *ground state* ${}^1E$ of V^0, which it tends to further stabilize by an amount of 0.08 eV. The multiplet splitting is, however, much more important for the structure of *excited levels*. Figure 5 shows, for instance, that the first allowed optical transition would be ${}^1E \rightarrow {}^1T_2$. The zero-phonon line for this transition is the difference in energy between the two absolute minima. For the ground state ${}^1E$, the minimum energy is at -0.76 eV. For the nondegenerate component of the ${}^1T_2$ state, the minimum will occur at positive values of δ. The linear term is $-\delta$. Thus minimization with respect to Q_E gives a Jahn-Teller energy of -0.17 eV, which has to be added to E'_{ρ_0} yielding 0.16 eV. The first excited state should then occur at 0.92 eV above the ground state at <0.05 eV. This puts the optical transition energy close enough to the band gap to make the detection difficult. Experimentally no absorption line is observed for the neutral vacancy.

V. DISCUSSION

One of the main results of this study is that only *one* parameter is important in determining the multiplet splitting associated with the vacancy in silicon. For the neutral case V_0 this parameter corresponds exactly to the singlet-triplet splitting calculated by Messmer and Watkins[5] (in Fig. 4, the average energy of zero-spin states is zero, compared to -0.33 eV for the ${}^3T_1$ state). However, Messmer and Watkins arrived at the conclusion that this splitting was decreasing rapidly with the size of the cluster they used, such that this parameter would in fact be negligible for a vacancy in an infinite crystal. However, our finding shows that this is not true and that the value of the splitting we find for silicon, i.e., 0.33 eV, is larger than what they have obtained for a C_{16} cluster in diamond, i.e., about 0.25 eV.

To study this discrepancy we have made an estimate of the result we would obtain for diamond, using our technique. When we apply a simple scaling argument to E'_{ρ_0} it is easy to show that this quantity scales as $1/R$, resulting in a value of 0.5 eV for diamond. This result also depends on the delocalization of the wave function varying roughly as the square of this quantity. The fact that the T_2 bound state is more localized in diamond will then still increase this value, perhaps up to 0.7 or 0.8 eV, which is in agreement with other estimates.[7] How can one then explain the discrepancy with Messmer and Watkins's result? The point is that they have plotted a curve going from the free carbon atom to the clusters C_4, C_4H_{12}, and C_{16} for which the singlet-triplet splitting parameters was decreasing dramatically. The comparison between the clusters C_4, C_4H_{12}, and C_{16} gives respective splittings which are 0.8, 0.6, and 0.25 eV. We believe that the problem arises from the clusters C_4 and C_{16} where the T_2 state interacts with dangling-bond surface states falling in the same energy range. This leads to an artificial delocalization factor of about 50%. This is not too serious for C_4 where this represents the only cause of delocalization, but becomes worse when going from C_4H_{12} to C_{16} where the effect is clearly seen. We thus think that C_{16} represents an underestimate of the limiting value and that it should be at least in the 0.5-eV range in agreement with our estimate.

We shall now discuss the effect of the multiplet splitting on the parameters of the negative-U system formed by V^{2+}, V^+ and V^0. Baraff, Kane, and Schlüter[16] calculated the ionization energies by the transition-state argument, for states with a symmetrical charge distribution and equal up and down spin densities. The difference in energy between V^+ and V^{2+} (plus one electron at the Fermi energy) was denoted $\epsilon_L - \mu$, while the difference between V^0 and V^+ (plus one electron at the Fermi energy) was written as $\epsilon_L + U - \mu$ where U is the electron-electron interaction parameter. To these values were added the distortion and relaxation energies of each state. For V^{2+} there is obviously no contribution. For V^+ there is a contribution due to the fact that the unpaired electron has a definite spin, while in the self-consistent calculation of Ref. 16 the spin density was half-spin up, half-spin down. The corresponding change in energy can be calculated using the method discussed above to be equal to $-E'_{\rho_0}/4$, where in principle E'_{ρ_0} has to be determined for V^+. This value should, however, be only slightly larger than for V^0, in view of the reduced charge density. Finally, for V^0, we have found that the extrastabilization energy amounted to -0.08 eV. From this we can infer that the difference in energy between V^+ and V^{2+} has to be reduced by $E'_{\rho_0}/4$, i.e., about 0.08 eV, corresponding to a reduction of 0.08 eV of ϵ_L and $\hat{\epsilon}_L$ in Ref. 16. The difference between V^+ and V^0 is not affected. However, since it is equal to $\epsilon_L + U$, and since ϵ_L is reduced by 0.08 eV, U has to be increased by the same amount.

All other parameters are unchanged, so that it is easy to work out the modifications of the relevant energies derived in Ref. 16. This is done in Table III where we have modified the two sets of values given in Ref. 16 and compared them to experiments. Clearly the numbers of calculation 1 (including a breathing-mode component) are improved by our corrections, while those of calculation 2 become too small on the average. The best agreement can be obtained with a breathing relaxation halfway between the two sets of values. It

TABLE III. Comparison between theoretical values from Ref. 16, our modified values and experiment (see Ref. 16).

Quantity	Calc 1 unmodified	Calc 1 modified	Calc 2 unmodified	Calc 2 modified	Expt
Activation energy (eV) $V^+ \rightarrow V^0$	0.13	0.13	0.05	0.05	0.057
Activation energy (eV) $V^{2+} \rightarrow V^+$	0.25	0.17	0.13	0.07	0.13
$E(0/2+)$	0.18	0.14	0.06	0.02	>0.065
V^+ excitation	0.21	0.13	0.09	0.01	0.006
$\hat{\epsilon}_L$	0.44	0.36	0.32	0.24	<0.35
η	0.13	0.05	0.13	0.05	V^+ not stable

$\eta > 0$ implies that V^+ is always metastable

is also important to notice that the parameter η, which measures the degree to which the system is a negative-U center, is decreased to 0.05 eV compared to the previous value 0.13 eV. However, as there is no change in sign, the qualitative conclusion that V^+ is always metastable remains unaltered.

VI. CONCLUSION

We have shown that many-electron effects *per se* are not negligible for the vacancy in silicon. We have calculated the multiplet structure for V^0 and shown that it could be described in terms of one single parameter, equal to the singlet-triplet splitting, with a value of 0.33 eV. We have then worked out in detail the case of V^0, treating multiplet effects and tetragonal Jahn-Teller splitting on an equal footing. The results show that the Jahn-Teller effect dominates the behavior for the *ground state*. Excited states, on the other hand, can be strongly affected by multiplet effects. We have finally included these effects to calculate the parameters of the negative-U system formed by V^{2+}, V^+, and V^0, obtaining only small overall changes over previous estimates.

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