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Electronic structure of vacancies in Si(111) unreconstructed surfaces

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The electron states at vacancies in Si(111) unreconstructed surfaces are calculated by means of a tight-binding scheme. Vacancies at the surface layer and at the second and third layers are considered. The results for a vacancy at the surface layer show one state of A_1 symmetry below the surface dangling-bond band, and a doubly degenerate state of E symmetry above it. Then, it is argued that as the Fermi level is fixed by the surface, the doubly degenerate state is empty and, as a consequence, the Jahn-Teller effect cannot take place. By means of a simplified version of the model, the possibilities for a local distortion of the Jahn-Teller type are examined. It is shown that the charge redistribution in the electronic spectrum caused by the eventual distortion leads to a gain in electronic energy proportional to the square of the displacements of the ions. The elastic energy is also estimated and shown to dominate the electronic energy. Thus it is concluded that vacancies in Si(111) surfaces are very likely stable to local distortions of the Jahn-Teller type.

I. INTRODUCTION

The crucial role played by vacancies in determining the bulk properties of semiconductors has long been recognized.[1,2] More recently, vacancies have been invoked in order to explain various phenomena specific to surfaces or interfaces. For instance, a model based upon the existence of vacancies has been suggested to describe the reconstruction of Si(111) surfaces.[3] Also, such a topical problem as Schottky-Barrier formation has been studied by assuming that defects created in the semiconductor when the metal-semiconductor junction is formed[4] were responsible for the pinning of the Fermi level and other properties of the junction.

An unavoidable step on the way to understanding the properties of vacancies in semiconductors is the description of their electronic structure. The electron states at bulk vacancies of semiconductors have been long studied by means of a wide variety of methods.[5-15] Recently, very accurate self-consistent calculations of the ideal bulk vacancy in Si (Refs. 13 and 14) and of the Jahn-Teller distorted vacancy,[15] have been reported. Although these calculations have provided a detailed knowledge of the electronic structure of bulk vacancies in Si, the essential characteristics have been obtained by means of simpler tight-binding schemes.[10,12] The main difficulty of the bulk Si vacancy is the strong Jahn-Teller distortion that takes place. The self-consistent calculation recently reported solves only, in fact, a particular model for the displacements of the ions.[15] Vacancies in other semiconductors have been also studied by means of parametrized models.[9,12,16,17]

Calculations of the electronic structure of surface vacancies in semiconductors are just beginning to be performed. In fact, only the GaAs(110) and (100) surfaces[16,17] and the Si(111) surface[18,19] have been studied, and both by means of non-self-consistent tight-binding models. Although self-consistent calculations are desirable, it seems worthy to start with simpler studies which can eventually throw light on the role of vacancies in many interesting surface phenomena which still lack a satisfactory explanation.

The purpose of this paper is to discuss in detail a recently reported calculation[19] of the electronic structure of vacancies at and near Si(111) surfaces. The model used here has been previously applied to the study of nonideal semiconductor[20] and metal[21] surfaces, in particular to Si(111) stepped surfaces. It is based upon the cluster-Bethe lattice method,[22] whereby the defect is included exactly by means of an *ad hoc* cluster and then the Bethe lattice (bulk or surface) is attached to its ends. In order to check the reliability of the model we first compute the electronic structure of the bulk vacancy and compare with self-consistent calculations. Then we turn to analyze the surface vacancy. The most interesting aspect of our results is that vacancies at this surface are not expected to undergo a Jahn-Teller-type distortion, as suggested previously by Andreoni and Tosatti.[18] The implications of these results on the reconstruction of this surface will be outlined.

The rest of the paper is organized as follows. In Sec. II we present the model and the results for the bulk and the surface vacancies. In Sec. III a simplified version of that model is used to examine in detail the possibility of a Jahn-Teller-type distortion around the vacancy in the surface layer. Finally some concluding remarks are included in Sec. IV.

II. ELECTRON STATES AT VACANCIES IN Si(111) UNRECONSTRUCTED SURFACES

In order to describe the method used in this section and, at the same time, to check its validity, we begin with the bulk vacancy in Si. We first consider the simplest model one can imagine, namely, we take the four atoms around the vacancy with three of their bonds connected with the bulk Bethe lattice and a dangling bond. As the Bethe lattice is solved for a nearest-neighbor Hamiltonian (as in Ref. 20), the four atoms around the vacancy will be decoupled. The basis used here is the four hybridized sp^3 orbitals. Then the local Green's function of one of the atoms neighboring the bulk vacancy (BV) is written in a straightforward fashion as

$$\underline{G}_{1,1}(E)=[\underline{1}E-\underline{U}_0^{\mathrm{BV}}-\underline{U}_2\underline{T}_2-\underline{U}_3\underline{T}_3-\underline{U}_4\underline{T}_4]^{-1}\,, \quad (1)$$

where we call 1, 2, 3, 4 the four bond directions of the diamond structure and $\underline{T}_1, \underline{T}_2, \underline{T}_3, \underline{T}_4$ the corresponding transfer matrices in the Bethe lattice.[20] The matrices $\underline{U}_i$ ($i=1,2,3,4$) are formed by the matrix elements of the Hamiltonian between the sp^3 orbitals in one atom and those in its nearest-neighbor atom along the i bond. The first-nearest-neighbor parameters used here are those of Ref. 19. The matrix $\underline{U}_0^{\mathrm{BV}}$ contains the intra-atomic interaction between sp^3 orbitals in an atom neighboring the vacancy. The diagonal elements of this matrix are nothing but the energy of the free sp^3 orbitals. We shall change these energies with respect to their bulk values (chosen as the zero of energies) to obtain local charge neutrality. Notice that in Eq. (1) we have taken bond 1 as the one pointing to the vacancy.

This simple model leads, of course, to a fourfold degenerate state. To remove this degeneracy we introduce the second-nearest-neighbor interaction between the four atoms around the vacancy. Then, we solve this problem according to the cluster–Bethe-lattice method. In this case the cluster is formed by the four atoms interacting through the second-nearest-neighbor interaction, and to the ends of the cluster we attach the Bethe lattice solved within a first-nearest-neighbor approximation. The set of equations which describes this system, from which the local Green's function of one of the four atoms is obtained, is the following:

$$\begin{aligned}
\Big(\underline{1}E-\underline{U}_0^{\mathrm{BV}}\sum_{i=2,3,4}\underline{U}_i\underline{T}_i\Big)\underline{G}_{1,1}&=1+\underline{V}_{1,2}\underline{G}_{2,1}+\underline{V}_{1,3}\underline{G}_{3,1}\\
&\quad+\underline{V}_{1,4}\underline{G}_{4,1}\,,\\
\Big(\underline{1}E-\underline{U}_0^{\mathrm{BV}}\sum_{i=1,3,4}\underline{U}_i\underline{T}_i\Big)\underline{G}_{2,1}&=\underline{V}_{2,1}\underline{G}_{1,1}+\underline{V}_{2,3}\underline{G}_{3,1}\\
&\quad+\underline{V}_{2,4}\underline{G}_{4,1}\,,\\
\Big(\underline{1}E-\underline{U}_0^{\mathrm{BV}}-\sum_{i=1,2,4}\underline{U}_i\underline{T}_i\Big)\underline{G}_{3,1}&=\underline{V}_{3,1}\underline{G}_{1,1}+\underline{V}_{3,2}\underline{G}_{2,1}\\
&\quad+\underline{V}_{3,4}\underline{G}_{4,1}\,,\\
\Big(\underline{1}E-\underline{U}_0^{\mathrm{BV}}-\sum_{i=1,2,3}\underline{U}_i\underline{T}_i\Big)\underline{G}_{4,1}&=\underline{V}_{4,1}\underline{G}_{1,1}+\underline{V}_{4,2}\underline{G}_{2,1}\\
&\quad+\underline{V}_{4,3}\underline{G}_{3,1}\,.
\end{aligned} \quad (2)$$

Here and after the atoms are numbered by their corresponding bonds pointing to the vacancy, i.e., in atom 1 bond 1 is a vacancy dangling bond. $\underline{G}_{i,j}$ involves the matrix elements of the Green's function between the sp^3 orbitals of atom i and those of atom j. The matrices $\underline{V}_{i,j}$ $(=\underline{V}_{j,i})$ include the second-nearest-neighbor interactions between atoms i and j. This set of equations can be easily solved for $\underline{G}_{1,1}$. As regards the second-nearest-neighbor parameters, we keep only the $pp\sigma_2$ interaction and adjust its value to get the splitting between the A_1 and T_2 states obtained in self-consistent calculations.[13,14] In the calculations we shift the energies of the sp^3 orbitals of the atoms neighboring the vacancy by −0.5 eV; this gives approximate local charge neutrality.

Our results for $pp\sigma_2=1.0$ eV (used also in the surface vacancies calculation) are shown in Table I and Fig. 1. First, it is worth remarking that in the atom neighboring the vacancy only the local density of states at the dangling bond differs greatly from the bulk density of states (see Fig. 7 of Ref. 20). The main changes take place in the region of energies around the gap, where the bound states of A_1 and T_2 symmetries lie. We notice that in other calculations the A_1 state appears as a resonance in the valence band. In our calculation it lies in the gap (just above the top of the valence band) due to the narrowing of the bands introduced by the Bethe lattice approximation. There is another resonance of A_1 symmetry, deep in the valence band (at approximately −8.0 eV), found by other authors,[10-14] which does not appear in our results (Fig. 1). As it has been stressed by several authors that this resonance is highly delocalized, we have calculated the phase shifts by using the technique proposed by Bernholc and Pantelides.[12] Noticing that this resonance should not be strongly affected by the second-nearest-neighbor interaction, we have neglected this inter-

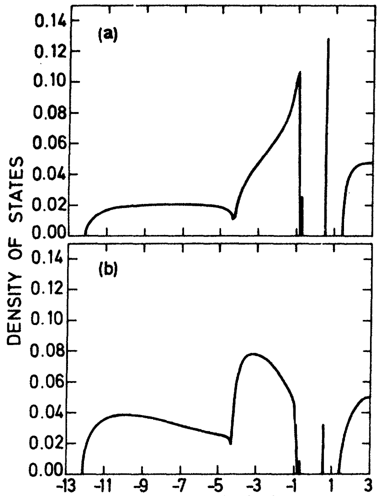

FIG. 1. (a) Local density of states at the sp^3 orbital pointing to the bulk vacancy in Si. (b) Local density of states at the atom neighboring the bulk vacancy. Bound states are represented by vertical lines of heights proportional to the weights of the states. Symmetries and weights of the bound states are given in Table I. All densities are normalized to one state per spin.

action in the calculation. A further simplification is obtained by taking the energies of the sp^3 orbitals at the atoms around the vacancy equal to their bulk values. Then the phase shift is obtained directly from the bulk local Green's function. Again there is not any excess of states in this region of energies. In fact, it can be shown[23] that this resonance comes from the rings' characteristics of the diamond lattice. The rings introduce also the two peaks (s- and sp-like) in the density of states of silicon,[22] which are not described by the Bethe lattice approximation.

Finally, we comment on the localization of the A_1 and T_2 states. We notice that less than 50% of the bound states are localized at the atoms neighboring the vacancy (Table I). We have also calculated the weights of both states at the second shell of atoms, obtaining 0.108 and 0.708 for the A_1 and T_2 states, respectively. Summing up the contributions of the first and second shells of atoms around the vacancy, we obtain 0.416 (42%) and

TABLE I. Energies and weights (states per spin) of the bound states in the fundamental gap introduced by the bulk vacancy in Si. Energies (eV) refer to the energy of the free sp^3 hybrid. The weights of the states are given for the different bonds on the atoms neighboring the vacancy. The total weights correspond to the sum over the atoms next to the vacancy. The atoms are numbered by their corresponding bonds pointing to the vacancy, and the bonds by means of two numbers i-j, the first indicating the atom (i) and the second the orbital (j).

Symmetry	Energy (eV)	Weights		
		1-1	1-2	Total
A_1	−0.79	0.074	0.001	0.308
T_2	0.4	0.367	0.001	1.480

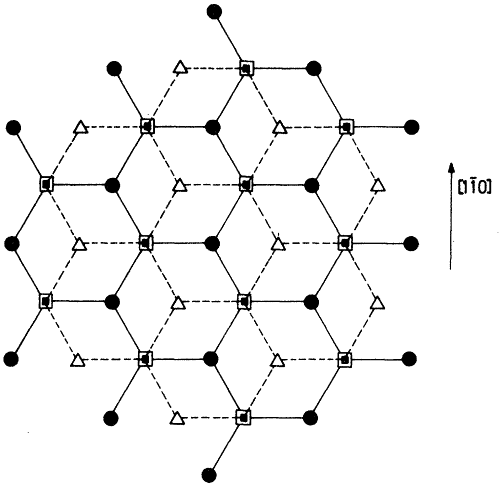

FIG. 2. Stacking of the layers in Si(111) surfaces. The [1$\bar{1}$0] direction is indicated. The atoms at the top layer are represented by circles.

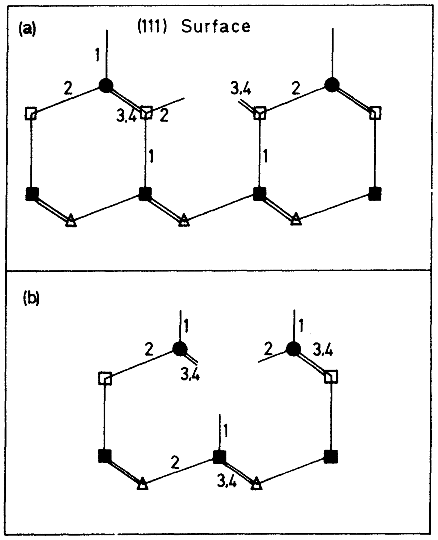

FIG. 3. Sketch of the geometry around vacancies in the first layer (a) and second layer (b) of Si(111) surfaces. The sp^3 orbitals around the vacancies are numbered. In the captions of the following figures the atoms will be numbered by their bonds pointing to the vacancy (dangling bonds), and the bonds by means of two numbers i - j, the first indicating atom and the second orbbital. The view is along direction [1$\bar{1}$0]. See also Fig. 2.

2.188 (73%) for the A_1 and T_2 states, respectively. This result is in line with those obtained in self-consistent calculations.[13,14] We turn now to discuss our results for vacancies at and near Si(111) surfaces.

A. Vacancy at the surface layer

In Fig. 2 we show the stacking of layers in the (111) surface of the diamond structure viewed along the [111] direction. The arrangement of atoms around a vacancy in the surface layer, viewed along the $[1\bar{1}0]$ direction, is shown in Fig. 3(a). To calculate the local Green's function of the atom next to the vacancy we use the approximation described above. In this case the cluster is formed by three atoms having two bonds connected with the surface Bethe lattice and one bond with the bulk Bethe lattice [see Fig. 3(a)]. The Green's function is then obtained from the following set of equations:

$$\begin{aligned}
&(\underline{1}E-\underline{\mathrm{U}}_0^{s1}-\underline{\mathrm{U}}_1\underline{\mathrm{T}}_1-\underline{\mathrm{U}}_3\underline{\tau}_3^{\mathrm{out}}-\underline{\mathrm{U}}_4\underline{\tau}_4^{\mathrm{out}})\underline{\mathrm{G}}_{2,2}\\
&\quad=\underline{1}+\underline{\mathrm{V}}_{2,3}\underline{\mathrm{G}}_{3,2}+\underline{\mathrm{V}}_{2,4}\underline{\mathrm{G}}_{4,2}\,,\\
&(\underline{1}E-\underline{\mathrm{U}}_0^{s1}-\underline{\mathrm{U}}_1\underline{\mathrm{T}}_1-\underline{\mathrm{U}}_2\underline{\tau}_2^{\mathrm{out}}-\underline{\mathrm{U}}_4\underline{\tau}_4^{\mathrm{out}})\underline{\mathrm{G}}_{3,2}\\
&\quad=\underline{\mathrm{V}}_{3,2}\underline{\mathrm{G}}_{2,2}+\underline{\mathrm{V}}_{3,4}\underline{\mathrm{G}}_{4,2}\,,\\
&(\underline{1}E-\underline{\mathrm{U}}_0^{s1}-\underline{\mathrm{U}}_1\underline{\mathrm{T}}_1-\underline{\mathrm{U}}_2\underline{\tau}_2^{\mathrm{out}}-\underline{\mathrm{U}}_3\underline{\tau}_3^{\mathrm{out}})\underline{\mathrm{G}}_{4,2}\\
&\quad=\underline{\mathrm{V}}_{4,2}\underline{\mathrm{G}}_{2,2}+\underline{\mathrm{V}}_{4,3}\underline{\mathrm{G}}_{3,2}\,,
\end{aligned}\tag{3}$$

where τ_i^{out} are the surface transfer matrices defined in Ref. 19, and the remaining symbols have been already defined. This set of equations can be easily solved for $\underline{\mathrm{G}}_{2,2}$ from which the local density of states is obtained. In the calculations we have also shifted the energies of the sp^3 orbitals at the atoms neighboring the vacancy (contained in $\underline{\mathrm{U}}_0^{s1}$) by -0.5 eV; this also gives approximate local charge neutrality. We also remark that, as in Ref. 20, the energies of the sp^3 orbitals at the surface atoms are shifted by -0.5 eV.

Our results are reported in Table II and Fig. 4. As in the bulk vacancy, the most relevant changes occur in the energy region of the forbidden gap. We found two bound states, one of A_1 symmetry below the surface-state band and another doubly degenerate state of E symmetry above it, whose energies (which refer to the Fermi level which coincides with the energy of the sp^3 orbital in the bulk) and weights on different bonds are given in

TABLE II. Energies (eV) and weights of the bound states introduced in the fundamental gap by a vacancy in the surface layer of Si(111) surfaces. Energies refer to the energy of the free sp^3 hybrid in the bulk (which coincides with the Fermi level). See also Table I.

Symmetry	Energy (eV)	Weights 2-1	2-2	2-3	Total
A_1	-0.73	0.003	0.181	0.004	0.576
E	0.50	0.0	0.243	0.007	0.771

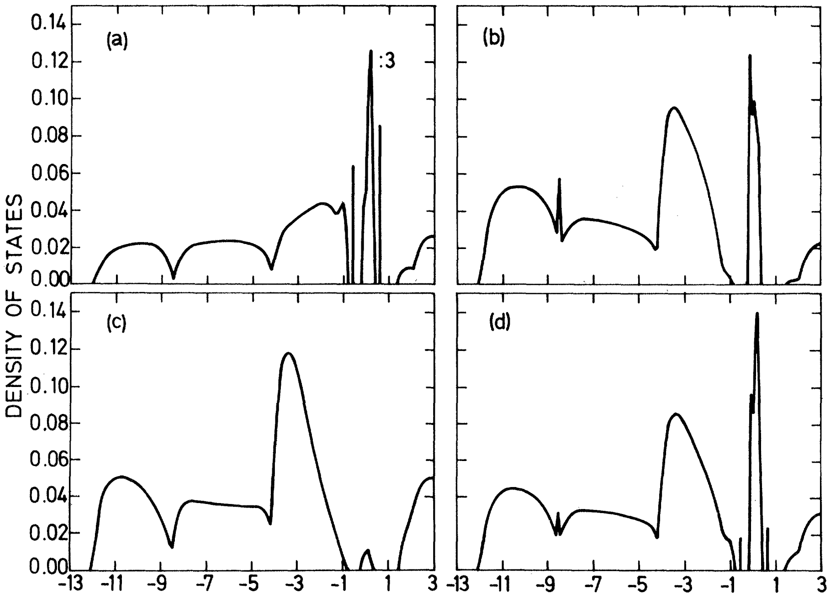

FIG. 4. Local densities of states at various sp^3 orbitals around a vacancy in the first layer of Si(111) surfaces [see Fig. 3(a)]: (a) bond 2-2, (b) bond 2-3, (c) bond 2-1, (d) atom 2. Symmetries and weights of the bound states are given in Table II. See also caption of Fig. 1.

Table II. The surface-state band lies in our calculation between −0.2 and 0.25 eV. We notice (Table II) that as in the bulk vacancy the bound states are quite extended, in fact, only 57%of the A_1 state and 40% of the E state are located at the atoms next to the vacancy. Regarding the s region of the valence band we should remark that our results cannot be trusted. In fact, in this region of energies a resonance of A_1 symmetry could be present due to the vacancy,[18] and on the other hand a back-bond surface state[20] will be very close to it. While our model accounts fairly well for the latter, it may surely fail in describing the former, as we have shown above that it does not give the A_1 state introduced by the bulk vacancy. To check this point we have again calculated the phase shift by performing approximations similar to those used for the bulk vacancy. We have found that at the energy of the back-bond surface state (−8.5 eV) a strong antiresonance is present, while no resonance appears close to it. The weak peaks at −8.5 eV shown in Figs. 4(b) and 4(d) are remainders of the strong back-bond surface resonance.[24] A complete description of the surface vacancy, while preserving the decrease of the surface state here discussed, might lead to a resonance of A_1 symmetry in the same energy region.[18]

We finally comment on the occupancy of the bound states. It is clear that as the Fermi level is fixed by the surface, the doubly degenerate level of E symmetry which lies above E_F will be empty. Therefore a Jahn-Teller effect is not expected. The Jahn-Teller effect occurs due to the gain of electronic energy associated with the splitting of a partially filled n-fold degenerate bound state, which is linearly proportional to the displacements of the atoms and therefore dominates the elastic energy, needed to produce the distortion, which is always proportional to the square of the displacements. Nevertheless, a local distortion of the Jahn-Teller type (distortions which reduce the point symmetry of the system) could also lead in the present case, to a gain in the electronic energy which have to be compared with the elastic energy in order to analyze the stability of the surface vacancy to Jahn-Teller-type distortions. These questions will be examined in Sec. III.

B. Vacancy at the second layer

The arrangement of the atoms around a vacancy in the second layer of Si(111) surfaces is shown in Fig. 3(b). Four atoms, three in the surface layer and one in the third layer are, in this case, next to the vacancy. Within the approximation discussed above, the local Green's function of atom 2 [Fig. 3(b)] is obtained from the following set of equations:

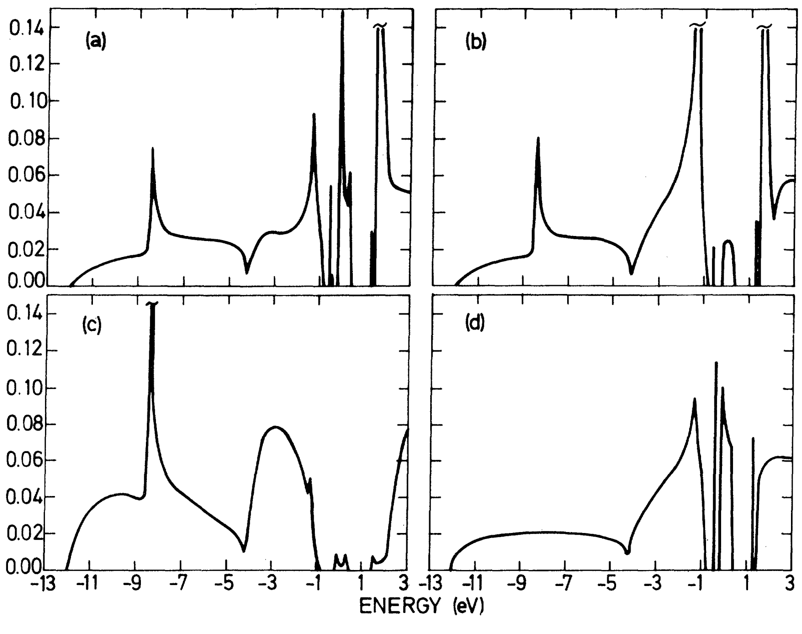

FIG. 5. Local densities of states at various sp^3 orbitals around a vacancy in the second layer of Si(111) surfaces [see Fig. 3(b)]: (a) bond 2-1, (b) bond 2-2, (c) bond 2-3, (d) bond 1-1. Symmetries and weights of the bound states are given in Table III. See also caption of Fig. 1.

$$\begin{aligned}
&(\underline{1}E-\underline{U}_0^{s2}-\underline{U}_3\underline{\tau}_3^{\text{in}}-\underline{U}_4\underline{\tau}_4^{\text{in}})\underline{G}_{2,2}\\
&\quad=\underline{1}+\underline{V}_{2,3}\underline{G}_{3,2}+\underline{V}_{2,4}\underline{G}_{4,2}+\underline{V}_{2,1}\underline{G}_{1,2}\,,\\
&(\underline{1}E-\underline{U}_0^{s2}-\underline{U}_2\underline{\tau}_2^{\text{in}}-\underline{U}_4\underline{\tau}_4^{\text{in}})\underline{G}_{3,2}\\
&\quad=\underline{V}_{3,2}\underline{G}_{2,2}+\underline{V}_{3,4}\underline{G}_{4,2}+\underline{V}_{3,1}\underline{G}_{1,2}\,,\\
&(\underline{1}E-\underline{U}_0^{s2}-\underline{U}_2\underline{\tau}_2^{\text{in}}-\underline{U}_3\underline{\tau}_3^{\text{in}})\underline{G}_{4,2}\\
&\quad=\underline{V}_{4,2}\underline{G}_{2,2}+\underline{V}_{4,3}\underline{G}_{3,2}+\underline{V}_{4,1}\underline{G}_{1,2}\,,\\
&(\underline{1}E-\underline{U}_0^{s2}-\underline{U}_3\underline{T}_3-\underline{U}_4\underline{T}_4-\underline{U}_2\underline{T}_2)\underline{G}_{1,2}\\
&\quad=\underline{V}_{1,2}\underline{G}_{2,2}+\underline{V}_{1,3}\underline{G}_{3,2}+\underline{V}_{1,4}\underline{G}_{4,2}\,,
\end{aligned}\tag{4}$$

where $\underline{\tau}_i^{\text{in}}$ are surface matrices defined in Ref. 20. An equivalent set of equations can be written for $\underline{G}_{1,1}$. In the calculations for this vacancy we have again shifted the energies of the free sp^3 orbitals of the four atoms around the vacancy by −0.5 eV. This might not be the right procedure, as three of the atoms have two dangling bonds while the fourth has only one. Nevertheless, we have not performed the cumbersome calculations needed to achieve local charge neutrality. See further comments below.

Our results for this vacancy are shown in Figs. 5 and 6 and Table III. To get a clearer understanding of the electronic structure of this vacancy we first discuss what is obtained without considering the second-nearest-neighbor interaction. In this case all the atoms next to the vacancy are decoupled and the results are easily understood. On the atom at the surface layer there are two dangling bonds, one pointing to the vacancy and a surface dangling bond. The interaction between these two bonds is very strong (−2.0 eV) and two states appear, one in the conduction band (1.5 eV) and the other in the top of the valence band (−0.9 eV). As there are three equivalent atoms next to the vacancy both states are triply degenerated. The fourth atom introduces a singlet in the gap. When the second-nearest-neighbor interaction is switched on, an intricate interaction between the above-mentioned states and the surface states band takes place and leads to the bound states reported in Table III plus two resonances at −1.3 and 1.5 eV of A_1 and E symmetry, respectively. As the bound state introduced by the atom in the third layer lies at 0.05 eV, it interacts more strongly with the triply degenerate state at −0.9 eV leading to two singlets (at −1.3 and −0.4 eV) and a doublet (at −0.6 eV). The triplet at 1.5 eV is split into a singlet and a doublet. It can be shown that symmetry requires the E states to have zero weights on atom 1 (see Table III). As regards the s region on the spectrum we notice a strong peak at −8.4 eV [Fig. 5(c)]. The back-bond surface state characteristic of this surface, which lies at −8.5 eV, has been slightly shifted by the vacancy. This result could again be modified if the rings characteristic of the diamond lattice were introduced through either cluster or exact calculations.

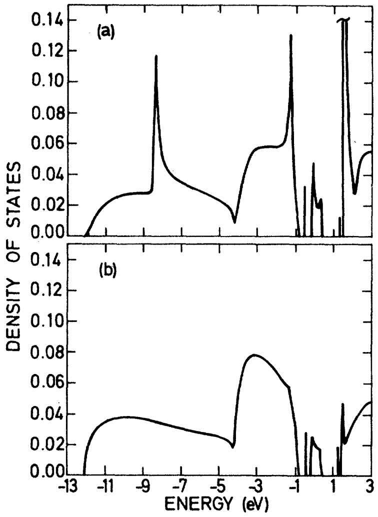

FIG. 6. Local densities of states at the two types of atoms neighboring a vacancy in the second layer of Si(111) surfaces [see Fig. 3(b)]: (a) atom 2, (b) atom 1. Symmetries of the bound states are given in Table III. See also caption of Fig. 1.

We again notice that there is no degenerate state partially filled. This would in principle preclude a Jahn-Teller effect. It should be noted that if we had taken a more negative value for the atomic energies of the sp^3 orbitals of the atoms, in the surface layer, around the vacancy, the E state would have appeared at lower energies; nevertheless, it lies at such high energies that very strong shifts (unphysical) would be required in order to place

TABLE III. Energies (eV) and weights of the bound states introduced in the fundamental gap by a vacancy in the second layer of Si(111) surfaces. See also Table II.

Symmetry	Energy (eV)	Weights 2-1	2-2	2-3	1-1	1-2	Total
A_1	−0.53	0.012	0.0	0.0	0.324	0.001	0.361
A_1	1.15	0.084	0.059	0.0	0.206	0.005	0.65
E	−0.69	0.157	0.097	0.014	0.0	0.0	0.846

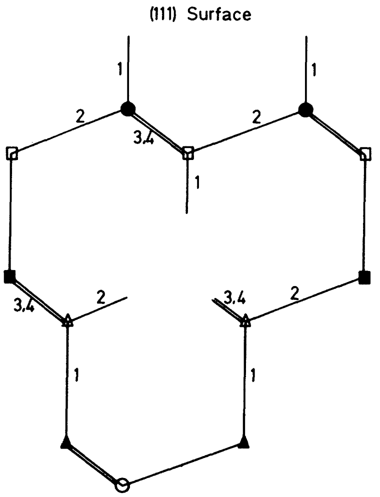

FIG. 7. Same as Fig. 3 for a vacancy in the third layer of Si(111) surfaces.

this state close to the Fermi level. Therefore we expect the present calculation to be at least a semiquantitative description of the vacancy in the second layer of Si(111) surfaces.

C. Vacancy at the third layer

The arrangement of atoms around a vacancy in the third layer of Si(111) surfaces is shown in Fig. 7. Again four atoms are neighboring the vacancy, one in the surface layer and three in the fourth layer. The approximation used in this section leads to the following system of equations for the local Green's function of atom 1:

$$
\begin{aligned}
&(\underline{1}E-\underline{U}_0^{s3}-\underline{U}_2\underline{\tau}_2^{\text{out}}-\underline{U}_3\underline{\tau}_3^{\text{out}}-\underline{U}_4\underline{\tau}_4^{\text{out}})\underline{G}_{1,1}\\
&\quad=\underline{1}+\underline{V}_{1,2}\underline{G}_{2,1}+\underline{V}_{1,3}\underline{G}_{3,1}+\underline{V}_{1,4}\underline{G}_{4,1}\,,\\
&(\underline{1}E-\underline{U}_0^{s3}-\underline{U}_1\underline{T}_1-\underline{U}_3\underline{T}_3-\underline{U}_4\underline{T}_4)\underline{G}_{2,1}\\
&\quad=\underline{V}_{2,1}\underline{G}_{1,1}+\underline{V}_{2,3}\underline{G}_{3,1}+\underline{V}_{2,4}\underline{G}_{4,1}\,,\\
&(\underline{1}E-\underline{U}_0^{s3}-\underline{U}_1\underline{T}_1-\underline{U}_2\underline{T}_2-\underline{U}_4\underline{T}_4)\underline{G}_{3,1}\\
&\quad=\underline{V}_{3,1}\underline{G}_{1,1}+\underline{V}_{3,2}\underline{G}_{2,1}+\underline{V}_{3,4}\underline{G}_{4,1}\,,\\
&(\underline{1}E-\underline{U}_0^{s3}-\underline{U}_1\underline{T}_1-\underline{U}_2\underline{T}_2-\underline{U}_3\underline{T}_3)\underline{G}_{4,1}\\
&\quad=\underline{V}_{4,1}\underline{G}_{1,1}+\underline{V}_{4,2}\underline{G}_{2,1}+\underline{V}_{4,3}\underline{G}_{3,1}\,,
\end{aligned}
\tag{5}
$$

An equivalent set of equations can be written for $\underline{G}_{2,2}$. Again we shift the atomic energies of the sp^3 orbitals of the atoms around the vacancy (included in U_0^{s3}) by −0.5 eV.

Our results are shown in Table IV and Figs. 8 and 9. It is most remarkable that the electronic structure of this vacancy is yet quite different from that of the bulk vacancy. The main reason for that is the strong interaction between the bond of atom 1 pointing to the vacancy (bond 1) and the surface dangling bonds of its three nearest neighbors in the surface layer. In fact, this interaction originates the two peaks at −1.3 and 1.5 eV in the local density of states of atom 1 (see Figs. 8 and 9). A further effect of this interaction is to diminish the importance of the second-nearest-neighbor interaction between atom 1 and the other three atoms around the vacancy. As a consequence the two bound states in the gap are completely localized on the three atoms 2, 3, and 4 of Fig. 7 (see Table IV). These states of A_1 and E symmetry lie at −0.56 and 0.37 eV, respectively, their localization being rather similar to those found for other vacancies here studied. Finally we should remark that the weak peak at −8.5 eV [Fig. 8(b) and Fig. 9(a)] is the back-bond surface state already mentioned; again our results for this energy region cannot be fully trusted.

As regards occupancy, it has to be noted that despite the very low density of states in the dangling-bond band localized at the atoms around the vacancy, the Fermi level is again fixed by the surface at $E=0$ and therefore, as the E bound state is empty, no Jahn-Teller effect is expected. Here we should remark that although we have not carried out the calculations necessary to achieve local charge neutrality it is approximately given (with the Fermi level at $E=0$) by the chosen shift of the energies of the orbitals at the atoms around the vacancy (−0.5 eV). Although we again expect the present calculation to give a semiquantitative description of this vacancy, we think that our analysis cannot answer an important question which emerges from our results. The question concerns the point where a change from bulklike behavior (in which the Jahn-Teller effect takes place) to a surfacelike behavior occurs. This question should surely require a self-consistent treatment of the problem.

TABLE IV. Energies (eV) and weights of the bound states introduced in the fundamental gap by a vacancy in the third layer of Si(111) surfaces. See also Table II.

Symmetry	Energy (eV)	Weights 1-1	 1-2	 2-1	 2-2	 2-3	 Total
A_1	−0.56	0.007	0.0	0.002	0.128	0.0	0.397
E	0.37	0.0	0.003	0.0	0.297	0.0	0.9

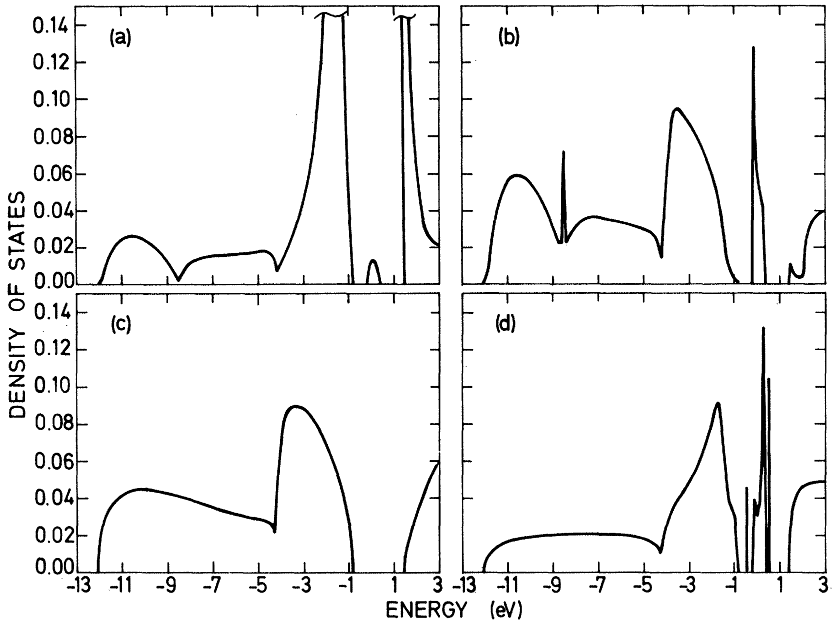

FIG. 8. Local densities of states at various sp^3 orbitals around a vacancy in the third layer of Si(111) surfaces (see Fig. 7): (a) bond 1-1, (b) bond 1-2, (c) bond 2-1, (d) bond 2-2. Symmetries and weights of the bound states are given in Table IV. See also caption of Fig. 1.

III. IS A VACANCY IN Si(111) SURFACES STABLE TO JAHN-TELLER-TYPE DISTORTION?

In the preceding section we have shown that, as in the electronic structure of a vacancy in the surface layer of Si(111) surfaces there is not any degenerate state partially filled, a Jahn-Teller effect, as it stands,[1] cannot occur. Nevertheless, a Jahn-Teller-type distortion would also rearrange the charge in the dangling-bond band. This rearrangement could lead to a gain of electronic energy, which has to be compared with the elastic energy in order to examine the stability of the surface vacancy to Jahn-Teller-type distortions. Thus, in this section we shall try to answer the question addressed in the heading. To this end we shall use a very simple description of the electronic structure of a vacancy in the surface layer.

A. Simple model of the electronic structure of a vacancy in the top layer of Si(111) surfaces

The simplest model one can use to describe the surface vacancy is the molecular one introduced by Watkins.[8] In this model the localized states at the vacancy are constructed, in analogy with the bulk vacancy, by means of a linear combination of the three sp^3 hybrids neighboring the vacancy. Once introduced, the interaction (second-nearest-neighbor interaction) between these three hybrids, a state of A_1 symmetry, and one of E symmetry (doubly degenerate) are obtained, whose energies and wave functions are given by

$$\begin{aligned} E_{A_1} &= E_h + 2W, \quad \psi_{A_1} = \frac{1}{\sqrt{3}}(|1\rangle + |2\rangle + |3\rangle), \\ E_E &= E_h - W, \quad \psi_E = \frac{1}{\sqrt{2}}(|2\rangle - |3\rangle) \\ &= \frac{1}{\sqrt{6}}(2|1\rangle - |2\rangle - |3\rangle), \end{aligned} \tag{6}$$

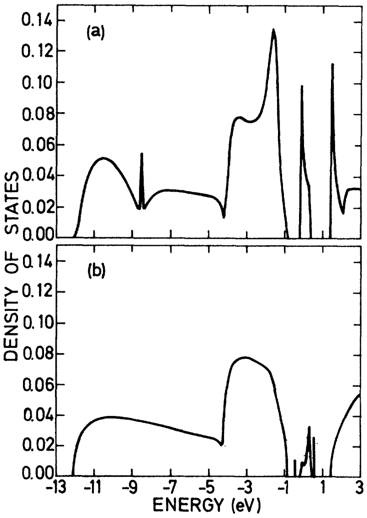

FIG. 9. Local densities of states at the two types of atoms neighboring a vacancy in the third layer of Si(111) surfaces (see Fig. 7): (a) atom 1, (b) atom 2. Symmetries of the bound states are given in Table IV. See also caption of Fig. 1.

where W (<0) is the interaction between the hybrids represented by $|1\rangle$, $|2\rangle$, and $|3\rangle$.

This simple model fails mainly for one reason (see Sec. II), namely, the interaction between the hybrids around the vacancy and the surface hybrids forming the surface dangling-bond band is very strong and has to be included. We shall call this interaction U (<0). On the other hand we shall not include the interaction of the vacancy hybrids with the bonding and antibonding states of the valence and conduction bands. Hence the interactions U and W have to be considered as "effective" interactions between all the hybrids.

The two-dimensional lattice of hybrids in the Si(111) surface has sixfold coordination and leads through a small interaction to a band 0.5 eV wide. We parametrize this band by means of a single first-nearest-neighbor interaction V (>0). In order to best simplify the model, we shall approximate the two-dimensional lattice by a Bethe lattice. By using the basis formed by the surface hybrids, the Green's function takes the following form:

$$\langle i|G_0(E)|i\rangle=\frac{1}{E-6VT}\,,\quad \langle i|G_0(E)|i+n\rangle=\frac{T^n}{E-6VT}\,, \tag{7}$$

where $|i+n\rangle$ indicates the nth neighbor of $|i\rangle$. The energy refers to the average value of the band. The transfer matrix T is given by

$$\begin{aligned} T&=[E-i(20V^2-E^2)^{1/2}]/(10V)\quad \text{for } |E|\leqslant\sqrt{20}\,|V|\,,\\ T&=[E-\operatorname{sgn}(E)(E^2-20V^2)^{1/2}]/(10V)\quad \text{for } |E|\geqslant\sqrt{20}\,|V|\,, \end{aligned} \tag{8}$$

and the band energy edges lie at $\pm\sqrt{20}\,|V|$, where the value of V is adjusted to give the width of the surface-state band obtained in full calculations (around 0.5 eV). The density of states is given by

$$N_0(E)=\frac{1}{\pi}\,\frac{3(20V^2-E^2)^{1/2}}{36V^2-E^2}\,. \tag{9}$$

$N_0(E)$ is symmetric around $E=0$ and therefore, as we have one electron per hybrid, $E_F=0$ (Fermi level).

To solve the problem of a vacancy in this lattice of hybrids, the best way to proceed is through the Dyson equation, i.e.,

$$G=G_0+G_0\hat{V}G\,, \tag{10}$$

where $\hat{V}$ defines the perturbation introduced in creating the vacancy. The potential $\hat{V}$ is more easily written by using the functions with the symmetry of the point group C_{3v} (the one appropriate to the surface vacancy). Thus $\hat{V}$ consists in cutting the bonds of the central atom with its six nearest neighbors and connecting the vacancy states ψ_{A_1} and ψ_E [Eq. (6)] with the Bethe lattice.

Then a phase shift can be defined as

$$\eta(E)=\arg\det(I-G_0\hat{V})\,, \tag{11}$$

from which the change in the density of states is calculated by means of the equation

$$\Delta N(E)=-\frac{1}{\pi}\frac{d}{dE}\,\eta(E)\,. \tag{12}$$

The following results are obtained:

$$\eta_E(E)=2\arg\frac{E-E_E-(2U^2/V)T}{E-E_E}\,, \tag{13a}$$

$$\eta_{A_1}(E)=\arg\frac{E}{E-6VT}+\arg\frac{E-E_{A_1}-(2U^2/V)T}{E-E_{A_1}}\,. \tag{13b}$$

Four spurious states are included in Eqs. (13). A bound state appears at $E=0$, which is nothing but the surface dangling bond (SDB) decoupled from the SDB band, and the states at E_E (double) and at E_{A_1} disappear as the levels of the vacancy states change their energies when the interaction with the surface band is switched on. In summary we have lost two states which have to be counted to satisfy Levinson's theorem. Then, the physically meaningful part of $\Delta N(E)$ is of the form

$$\begin{aligned} \Delta N_{A_1}&=-\frac{1}{\pi}\frac{d}{dE}\left[\arg\left(E-E_{A_1}-\frac{2U^2}{V}T\right)-\arg(E-6VT)\right],\\ \Delta N_E(E)&=-\frac{1}{\pi}\frac{d}{dE}\left[2\arg\left(E-E_E-\frac{2U^2}{V}T\right)\right], \end{aligned} \tag{14}$$

and the integral of both increments from $-\infty$ to $+\infty$ gives two states which compensate for the loss of the states previously mentioned.

In the whole process we gain two electrons—we gained three electrons in the vacancy dangling bonds (VDB) and lost one electron in the SDB—therefore self-consistency is obtained by requiring that

$$\int_{-\infty}^{E_F}\Delta N(E)\,dE=1\,. \tag{15}$$

This condition can be fulfilled by varying the energy E_h which determines the energy of the VDB before switching the interaction with the SDB band [see Eq. (6)].

Our results for $V=0.075$ eV, which gives the correct value for the width of the SDB band, $U=-0.275$ eV, the only first-neighbor interaction (Phillips-Pandey value[10]), and $W=-0.315$ eV which gives the splitting between the E and A_1

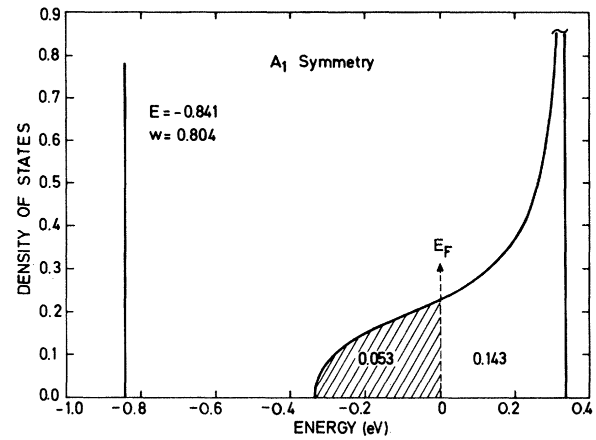

FIG. 10. Local density of states of A_1 symmetry at the sp^3 orbitals pointing to a vacancy in the first layer of Si(111) surfaces as calculated by means of the model of Sec. III. The energies (E) and weights (W) of the bound states are shown. The density is normalized to one. The Fermi level (E_F) is indicated by a vertical arrow.

states obtained in Sec. II, are shown in Figs. 10 and 11. We remark that self-consistency leads to $E_h = -0.023$ eV. We notice that the results are rather similar to those obtained in the full calculation, but for the E state just below the SDB band. This state is, in fact, very close to the band edge (0.05 eV below it) and in the full calculation remains within the band. We think that the results here obtained are good enough to analyze the question of the stability of the ideal surface vacancy.

B. Lattice distortions near the surface vacancy: Electronic and elastic energies

The three atoms neighboring the vacancy in the top layer of Si(111) surfaces have the following coordinates:

$$\text{Atom } a\text{:}\quad a\left(0,\ \frac{1}{\sqrt{6}},\ -\frac{1}{4\sqrt{3}}\right),$$

$$\text{Atom } b\text{:}\quad a\left(-\frac{1}{2\sqrt{2}},\ -\frac{1}{2\sqrt{6}},\ -\frac{1}{4\sqrt{3}}\right), \tag{16}$$

$$\text{Atom } c\text{:}\quad a\left(\frac{1}{2\sqrt{2}},\ -\frac{1}{2\sqrt{6}},\ -\frac{1}{4\sqrt{3}}\right),$$

where a is the lattice constant. Now, if we allow the atoms to move, the easiest way to handle the problem is to use a set of normal coordinates[25] instead of the nine Cartesian coordinates (x_i, y_i, z_i), $i=1,2,3$, namely,

$$Q_1=\frac{1}{\sqrt{3}}(x_a+x_b+x_c),$$

$$Q_2=\frac{1}{\sqrt{3}}(y_a+y_b+y_c),$$

$$Q_3=\frac{1}{\sqrt{3}}(z_a+z_b+z_c),$$

$$Q_4=\frac{1}{\sqrt{3}}(x_a-\tfrac{1}{2}x_b-\tfrac{1}{2}x_c)+\tfrac{1}{2}(y_b-y_c),$$

$$Q_5=\frac{1}{\sqrt{2}}(z_b-z_c), \tag{17}$$

$$Q_6=\frac{1}{\sqrt{6}}(2z_a-z_b-z_c),$$

$$Q_7=\tfrac{1}{2}(x_c-x_b)+\frac{1}{\sqrt{3}}(y_a-\tfrac{1}{2}y_b-\tfrac{1}{2}y_c),$$

$$Q_8=\frac{1}{\sqrt{3}}(x_a-\tfrac{1}{2}x_b-\tfrac{1}{2}x_c)+\tfrac{1}{2}(y_c-y_b),$$

$$Q_9=\tfrac{1}{2}(x_b-x_c)+\frac{1}{\sqrt{3}}(y_a-\tfrac{1}{2}y_b-\tfrac{1}{2}y_c).$$

The normal coordinates Q_1, Q_2, and Q_3 define three rigid translations of the three atoms. Similarly the coordinates Q_4, Q_5, and Q_6 define three independent rigid rotations. These six coordinates are not relevant for the purposes of the present work as they represent six degrees of freedom of the solid considered as rigid.

The coordinate Q_7 defines a breathing symmetrical distortion of A_1 symmetry around the vacancy and the associated Cartesian displacements of the atoms are the following:

$$\text{Atom } a\text{:}\quad (0,\ Q_7/\sqrt{3},\ 0),$$

$$\text{Atom } b\text{:}\quad (-Q_7/2,\ -Q_7/2\sqrt{3},\ 0), \tag{18}$$

$$\text{Atom } c\text{:}\quad (Q_7/2,\ -Q_7/2\sqrt{3},\ 0).$$

The pair of coordinates Q_8, Q_9 define a distortion of E symmetry around the vacancy, the corresponding Cartesian displacements being

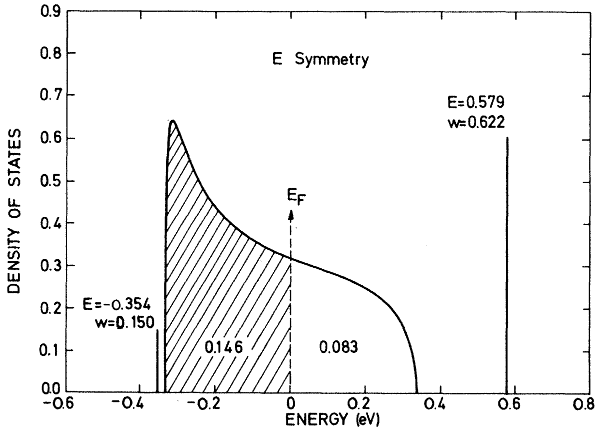

FIG. 11. Same as Fig. 10 for E symmetry.

$$\begin{aligned} &\text{Atom } a\text{: } (Q_8/\sqrt{3}, Q_9/\sqrt{3}, 0)\,, \\ &\text{Atom } b\text{: } (-Q_8/2\sqrt{3}+Q_9/2, -Q_8/2-Q_9/2\sqrt{3}, 0)\,, \\ &\text{Atom } c\text{: } (-Q_8/2\sqrt{3}-Q_9/2, Q_8/2-Q_9/2\sqrt{3}, 0)\,. \end{aligned} \tag{19}$$

The point symmetry around the surface vacancy is that of the point group C_{3v}. If a static distortion of E symmetry takes place, the point symmetry around the vacancy would be reduced. This distortion would be of the Jahn-Teller type.[1]

In order to study the stability of the surface vacancy to Jahn-Teller-type distortions we proceed as follows. We allow the atoms neighboring the vacancy to move according to the normal coordinates Q_8 and Q_9; meanwhile the rest of the atoms of the crystal are kept at their original sites. The energy of the system formed by the ions plus the electrons varies for two reasons:

(i) The nine bonds that the three atoms around the vacancy form with their neighbors change their length and, at the same time, the angles between those bonds are also modified. These lead to an increase in the elastic energy described in terms of bonds.

(ii) The interactions of the vacancy sp^3 hybrids with themselves and with the surface hybrids change their values. This leads to modifications of the electronic bound-state energies as well as a rearrangement of the charge in the SDB band. As a consequence the electronic energy is modified (in the term commonly called band structure). It should be noticed that although the ultimate reason for the change of the energy of the system is the same (modification of the electronic states) due to the model used here (see Sec. III A) the energy is split in two terms which correspond to changes in the valence-band states and in the surface and vacancy states, respectively. The first contribution will be handled by means of a model of forces adjusted to the bulk of the solid. This assumes that the bonds near the surface are identical to those of the volume, which is not exactly true. A somewhat similar procedure has been succesfully used by Chadi[26] in his studies of reconstructed surfaces. We shall show that as the Jahn-Teller effect does not occur (see Sec. II) the total change in the energy of the system is proportional to $(Q_8^2+Q_9^2)$, with a positive coefficient. Thus, a Jahn-Teller-type distortion is not energetically favorable. Nonetheless it has to be remarked that the negative contribution of (ii) greatly cancels that of (i). This will be of paramount relevance in the study of the vibrational modes of E symmetry.

In order to evaluate the first contribution we use the model proposed by Keating.[27] This model includes central and noncentral forces restricted to nearest neighbors. We have also used the model introduced by Born,[28] obtaining very similar results. For the values of the force constants we have chosen those reported by Weaire and Alben in their study of the vibrational properties of amorphous silicon.[29]

The analysis of the second contribution (ii) is more involved. Within the adiabatic approximation it is assumed that the electrons follow the ions in their displacements. As the ions change their original sites, the electronic levels are modified. We have considered two causes for the coupling between the electronic states and the distortion.

(1) The distance and therefore the interaction between the hybrids are modified. Following Chadi,[26] we assume that the new interaction is inversely proportional to the square of the new distance. For instance the interaction between the hybrids pointing to the vacancy is changed as follows: $W(d)=(d_0^2/d^2)W(d_0)$.

(2) As the first nearest neighbors move, the angles between the bonds that join these atoms with their neighbors (which remain in their original sites) cease to be equal to the tetrahedral angle (109°28′). We assume that these bonds become dehybridized[30] and will no longer be of the sp^3 type. As a consequence the whole electronic spectrum is modified. Nonetheless the coupling constants associated with these two causes are greatly different, namely,

$$\begin{aligned} &G_1 \sim \frac{2W}{(a\sqrt{2}/2)} = 0.165\,, \\ &G_2 \sim -\frac{1}{2\sqrt{3}}\left(-\frac{16\sqrt{2}}{\sqrt{3}}\,\frac{\frac{1}{4}(E_s-E_p)}{a}\right) = -1.39\,, \end{aligned} \tag{20}$$

where values are expressed in units of eV Å^{-1} and where a is the lattice constant and E_s and E_p are the energies of the s and p orbitals, respectively. Therefore the coupling due to the dehybridization is the most relevant, and its value is similar to the interaction which leads to the Jahn-Teller distortion in the bulk vacancy (see Ref. 1). Thus, we shall work out in detail this mechanism, using G_2 as a parameter which we assume to include also effects of the type described by G_1. On the other hand the dehybridization of the sp^3 orbitals is a cleaner and more elegant mechanism than the change of the interactions with distance. The latter needs to be corrected by considering the change of the Coulomb interactions between ions, which is of opposite sign and rather difficult to estimate, while the former (dehybridization) only depends upon angles and therefore changes of the electrostatic energy can be neglected.

Let us start by considering the atom around the vacancy which moves as $(X_a, Y_a, 0)$. In this case, the unit vectors which point to its three nearest neighbors are given by (to first order in the displacements)

$$\begin{aligned}
\vec{\tau}_2' &= \left(\frac{\sqrt{2}}{\sqrt{3}} - \frac{4}{3\sqrt{3}}\frac{X_a}{a} + \frac{8}{9}\frac{Y_a}{a}, \frac{\sqrt{2}}{3} + \frac{8}{9}\frac{X_a}{a} - \frac{28}{9\sqrt{3}}\frac{Y_a}{a}, \frac{1}{3} + \frac{8}{9\sqrt{2}}\frac{X_a}{a} + \frac{8}{9\sqrt{6}}\frac{Y_a}{a}\right), \\
\vec{\tau}_3' &= \left(-\frac{\sqrt{2}}{\sqrt{3}} - \frac{4}{3\sqrt{3}}\frac{X_a}{a} - \frac{8}{9}\frac{Y_a}{a}, \frac{\sqrt{2}}{3} - \frac{8}{9}\frac{X_a}{a} - \frac{28}{9\sqrt{3}}\frac{Y_a}{a}, \frac{1}{3} - \frac{8}{9\sqrt{2}}\frac{X_a}{a} + \frac{8}{9\sqrt{6}}\frac{Y_a}{a}\right), \qquad (21) \\
\vec{\tau}_4' &= \left(-\frac{4}{\sqrt{3}}\frac{X_a}{a}, -\frac{4}{\sqrt{3}}\frac{Y_a}{a}, -1\right),
\end{aligned}$$

the three $sp^{\lambda_\alpha^2}$ hybrids along these three directions being given by

$$\begin{aligned}
|h_2'\rangle &= \frac{1}{(1+\lambda_2^2)^{1/2}}\left(|s\rangle + \lambda_2 |p\rangle_{\vec{\tau}_2'}\right), \\
|h_3'\rangle &= \frac{1}{(1+\lambda_3^2)^{1/2}}\left(|s\rangle + \lambda_3 |p\rangle_{\vec{\tau}_3'}\right), \qquad (22) \\
|h_4'\rangle &= \frac{1}{(1+\lambda_4^2)^{1/2}}\left(|s\rangle + \lambda_4 |p\rangle_{\vec{\tau}_4'}\right),
\end{aligned}$$

where $|p\rangle_{\vec{\tau}_\alpha'}$ represents the p orbital which points in the direction $\vec{\tau}_\alpha'$. The three orthogonality relations between these three orbitals determine the coefficients λ_α. Then, the orbital $|h_1'\rangle$ pointing to the vacancy is the $sp^{\lambda_1^2}$ hybrid normalized and orthogonal to the hybrids of Eq. (22). The energies associated with the hybrids of Eq. (2) are given by

$$\langle h_\alpha' |H| h_\alpha'\rangle = \frac{1}{1+\lambda_\alpha^2}(E_s + \lambda_\alpha^2 E_p), \qquad (23)$$

which becomes the usual value $\frac{1}{4}(E_s + 3E_p)$ when the hybrid is the sp^3 ($\lambda_\alpha^2 = 3$). The atomic level of the fourth hybrid (h_1') can be obtained by assuming the invariancy of the trace under unitary transformations. Recalling that we have taken $\frac{1}{4}(E_s + 3E_p) = 0$, we obtain

$$\begin{aligned}
\langle h_1' |H| h_1'\rangle &= -E_s\left(\sum_{\alpha=2}^{4}\frac{1}{1+\lambda_\alpha^2}\right) - E_p\left(\sum_{\alpha=2}^{4}\frac{\lambda_\alpha^2}{1+\lambda_\alpha^2}\right) \\
&= -\frac{16\sqrt{2}}{\sqrt{3}}\frac{D}{a}Y_a \qquad (24)
\end{aligned}$$

to first order in the displacements, where it has been defined $D \equiv \frac{1}{4}(E_s - E_p) = -2$ eV.

Finally, the dehybridization of the hybrids pointing to the vacancy leads to the following atomic levels:

$$\begin{aligned}
E_a &= -\frac{16\sqrt{2}}{\sqrt{3}}\frac{D}{a}Y_a, \\
E_b &= -\frac{16\sqrt{2}}{\sqrt{3}}\frac{D}{a}\left(-\frac{\sqrt{3}}{2}X_b - \tfrac{1}{2}Y_b\right), \qquad (25) \\
E_c &= -\frac{16\sqrt{2}}{\sqrt{3}}\frac{D}{a}\left(\frac{\sqrt{3}}{2}X_c - \tfrac{1}{2}Y_c\right),
\end{aligned}$$

where E_a, E_b, and E_c give the energies of the hybrids, at the atoms a, b, and c, respectively, pointing to the vacancy. Then, if a displacement of the atoms, according to the normal coordinates Q_7, Q_8, and Q_9 occurs, the perturbation of the hybrids pointing to the vacancy ($|1\rangle$, $|2\rangle$, and $|3\rangle$) is described by

$$\hat{V} = E_a |1\rangle\langle 1| + E_b |2\rangle\langle 2| + E_c |3\rangle\langle 3| . \qquad (26)$$

This perturbation can be rewritten in terms of the normal coordinates and symmetrized orbitals, namely,

$$\begin{aligned}
\hat{V} = {} & \frac{C}{\sqrt{3}} Q_7\left(|\psi_{A_1}\rangle\langle\psi_{A_1}| + |\psi_{E_1}\rangle\langle\psi_{E_1}| + |\psi_{E_2}\rangle\langle\psi_{E_2}|\right) \\
& + \frac{C}{\sqrt{6}}\left(Q_8 |\psi_{A_1}\rangle\langle\psi_{E_1}| + Q_8 |\psi_{E_1}\rangle\langle\psi_{A_1}| + Q_9 |\psi_{A_1}\rangle\langle\psi_{E_2}| + Q_9 |\psi_{E_2}\rangle\langle\psi_{A_1}|\right) \\
& - \frac{C}{2\sqrt{3}}\left(Q_9 |\psi_{E_1}\rangle\langle\psi_{E_1}| - Q_9 |\psi_{E_2}\rangle\langle\psi_{E_2}| + Q_8 |\psi_{E_1}\rangle\langle\psi_{E_2}| + Q_8 |\psi_{E_2}\rangle\langle\psi_{E_1}|\right), \qquad (27)
\end{aligned}$$

where $C \equiv -(16\sqrt{2}/\sqrt{3}\,(D/a) = 4.82$ eV Å^{-1}. The wave functions $|\psi_{E_1}\rangle$ and $|\psi_{E_2}\rangle$ are the two orbitals of E symmetry and $|\psi_{A_1}\rangle$ the one of A_1 symmetry.

It can be noted in Eq. (27) that the third term is of the form characteristic of the coupling between a vibrational mode and an electron state both of E symmetry (see, for instance, Ref. 1). This term and the second of Eq. (27) give a contribution of second order in the displacements. Instead, the first term which is of A_1 symmetry gives a contribution of first order, and therefore it necessarily takes place. Nonetheless we shall not consider this contribution to $\hat{V}$ as it only leads to a rigid shift (to lower energies) of the three atomic levels of the hybrids pointing to the vacancy and consequently it does not preserve charge neutrality. This does not necessarily mean that the Q_7 distortion does not occur; it only means that this distortion cannot be treated by using the zero-order approximation which assumes that only the atoms neighboring the vacancy can move. Then by taking $Q_7=0$ in $\hat{V}$, we obtain the following value for the determinant of $I-G_0\hat{V}$:

$$\det(I-G_0\hat{V}) \simeq 1-\frac{C^2}{12}(\langle\psi_E|G_0|\psi_E\rangle^2+2\langle\psi_E|G_0|\psi_E\rangle\langle\psi_{A_1}|G_0|\psi_{A_1}\rangle)(Q_8^2+Q_9^2)\,, \tag{28}$$

valid up to second order in the displacements. $\langle\psi_E|G_0|\psi_E\rangle$ is one of the diagonal elements (both are equal) of G_0 corresponding to ψ_{E_1} or ψ_{E_2}.

The effect of the perturbation in the energy region outside the SDB band is to shift the bound states and split the doubly degenerate states of E symmetry. In the band the Green's function G_0 is analytic and the following approximation can be made:

$$\eta(E)=\arg\det(I-G_0\hat{V}) \simeq -\frac{C^2}{12}\,\mathrm{Im}(\langle\psi_E|G_0|\psi_E\rangle^2+2\langle\psi_E|G_0|\psi_E\rangle\langle\psi_{A_1}|G_0|\psi_{A_1}\rangle)(Q_8^2+Q_9^2)\,. \tag{29}$$

This phase shift does not give charge neutrality and, in order to solve this problem, we add a constant diagonal term (μ) to the perturbation $\hat{V}$. The phase shift is then given by

$$\eta(E)=-\frac{C^2}{12}\,\mathrm{Im}(\langle\psi_E|G_0|\psi_E\rangle^2+2\langle\psi_E|G_0|\psi_E\rangle\langle\psi_{A_1}|G_0|_{A_1}\rangle)(Q_8^2+Q_9^2)-\mu\,\mathrm{Im}(2\langle\psi_E|G_0|\psi_E\rangle+\langle\psi_{A_1}|G_0|\psi_{A_1}\rangle)\,, \tag{30}$$

valid in the continuum. The charge neutrality condition, i.e.,

$$\eta(E_F)=\eta(0)=0 \tag{31}$$

determines μ, and finally the change in the electronic energy is given by

$$\Delta E_{\mathrm{BS}}=\int_{-\infty}^{E_F} dE\,E\,\Delta N(E)\,, \tag{32}$$

which is clearly of second order in the displacements. Note that (i) the occupied bound state of E symmetry is split in two states, and although the splitting is of first order the energy only changes in second order as both states are occupied, and (ii) in the continuum $\Delta N(E)$ is proportional to $(Q_8^2+Q_9^2)$.

Finally, by using the parameters of the model described in Sec. III A, the following result expressed in eV is obtained:

$$\Delta E_{\mathrm{BS}}=-3.364(Q_8^2+Q_9^2)\,, \tag{33}$$

with the lattice constant in Q_8 and Q_9 [see Eq. (17)] given in Å. Therefore as far as the surface sp^3 hybrids are concerned, the distortion of E symmetry is favorable.

We turn now to estimate the variation of the elastic energy due to the movement of the atoms neighboring the vacancy. We have used the model proposed by Keating[27] with the following force constants, in eV Å^{-2}:

$$\alpha=2.968,\quad \beta=0.2\alpha=0.594\,.$$

We obtain the following changes in the elastic energy, in eV, associated with modes of E or A_1 symmetry:

$$\begin{aligned}\Delta E^{A_1}_{\mathrm{elastic}}&=(\tfrac{2}{3}\alpha+\tfrac{1}{3}\beta)Q_7^2=2.178Q_7^2\,,\\ \Delta E^{E}_{\mathrm{elastic}}&=(\tfrac{4}{3}\alpha+\tfrac{5}{12}\beta)(Q_8^2+Q_9^2)=4.206(Q_8^2+Q_9^2)\,,\end{aligned} \tag{34}$$

where again the lattice constant in the normal coordinates—Eq. (17)—is given in Å. The results are more easily understood if we rewrite the response of the whole system (ions and electrons) to the discussed distortions, by introducing an effective frequency defined from the total change of the energy, namely,

$$\begin{aligned}\Delta E_{A_1}&\equiv\tfrac{1}{2}M\omega_{A_1}^2Q_7^2\,,\\ \Delta E_E&\equiv\tfrac{1}{2}M\omega_E^2(Q_8^2+Q_9^2)\,.\end{aligned} \tag{35}$$

By using the mass of the silicon atoms and the results for the increments of the total energy given above (we remark again that there is not a quadratic term in the modes of A_1 symmetry due to the surface hybrids) the result is the following, expressed in radians per second:

$$\omega_{A_1}=0.386\times10^{14}\,,$$

$$\omega_E=0.24\times10^{14}\,.$$

We notice that if we had only considered the elastic energy, the frequency of the E mode would have been 0.536×10^{14} (rad/s)$^{-1}$. Therefore the effect of the change in the electronic energy associated with surface and vacancy states is to reduce the frequency of the E mode. In fact, the resulting frequency is lower than the transverse branch of the acoustic mode in the vibrational spectrum of Si. This frequency would be even lower if all the ions were allowed to move (see Larkins and Stoneham[25]). If we had obtained a negative energy increment associated with the E symmetry, the surface vacancy would have been unstable to Jahn-Teller-type distortions. Nevertheless, for the two models here considered,[27,28] the elastic energy dominates.

IV. CONCLUDING REMARKS

In the present paper we have discussed the electronic structure of vacancies at and near Si(111) surfaces. The tool used has been a well tested model previously applied to the study of nonideal metal and semiconductor surfaces. Vacancies at the three successive surface layers have been examined. The main result is that, as in none of these vacancies is there a partially filled degenerate state, a Jahn-Teller effect is not expected. We have found that, in contrast with the results obtained by Daw and Smith[16] for GaAs(110) surfaces, the electronic structure at a vacancy in the third layer is not yet similar to that of the bulk vacancy, the reason for this being the different geometries of both surfaces. We have not been able to answer a question which arises from our results, namely, when a vacancy diffuses from the bulk to the surface or vice versa, at which point does a change from a bulklike behavior (in which the Jahn-Teller effect takes place) to a surfacelike behavior take place? This question surely requires a self-consistent treatment of the problem.

Then we have argued that although the Jahn-Teller effect, as it stands,[31] cannot occur, a local distortion of the Jahn-Teller type (a distortion which lowers the point symmetry of the system) would also rearrange the charge in the surface and vacancy states leading to a gain in electronic energy which can favor the distortion. We have then examined this question in detail for a vacancy in the surface layer concluding that this vacancy is very likely to be stable to Jahn-Teller-type distortions.

The results here reported can be relevant to the analysis of the reconstruction of Si(111) surfaces. In fact, it could be argued that, although a Jahn-Teller effect at the surface vacancy would, of course, only lead to a local distortion, if the number of vacancies is high, Jahn-Teller instabilities would aid to trigger some kind of long-range reconstructuion of the surface. This argument is ruled out by the results of the present work. Then, it would be interesting to analyze whether or not a vacancy at a 2×1 Si(111) surface would undergo a Jahn-Teller effect. It is clear that if we assume a widely accepted model of 2×1 reconstruction such as that suggested by Haneman,[32] the local symmetry of the problem leads to three singlets. Preliminary results[33] indicate that for a vacancy in the top layer no bound states lie in the gap open by the reconstruction, and that the E state at 0.5 eV splits in two singlets 0.05 eV appart. As the Fermi level lies in the gap, once again a Jahn-Teller instability is not expected.

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[24] It has to be remarked that there is an erratum in the caption of Fig. 7(c) of Ref. 20. In fact, the local density of states shown in that figure corresponds to the bonds joining the second-layer atoms to the third-layer ones. The back-bond surface states have some weight on the bonds joining the atoms in the second layer to those in the first layer. The peak shown in Fig. 4(b) is weaker than the peak displayed by the local density of states at the same energy in the absence of vacancies.

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