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Molecular-cluster studies of defects in silicon lattices. III. Dangling-bond reconstruction at the core of a 90° partial dislocation in silicon

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The energetics of bond reconstruction at the core of a 90° partial dislocation in silicon has been studied by means of Hartree-Fock-Roothaan molecular-orbital linear-combination-of-atomic-orbitals self-consistent-field (HFR-MO-LCAO-SCF) computations on Si_5H_{10}, Si_9H_{18}, and $Si_{10}H_{18}$ model molecular clusters. These studies show the reconstructed geometry to be the most favorable one. On the basis of these tentative results, the electronic structure and charge distribution of the Si_5H_{10} model cluster are analyzed and correlated to those of the dislocations in the solid.

I. INTRODUCTION

In silicon and germanium, 60° dislocations, dissociated into 90° and 30° partials separated by a stacking fault, are known to play an important role in determining the structural and electronic properties of the deformed material.[1–3]

In a previous paper[4] the structure and the associated bands of a 90° partial dislocation had been studied by means of an empirical valence force field (VFF) model and the extended-Hückel-theory large-unit-cell approach (EHT-LUCA) method.[4–6] Two different core geometries were considered in that work: one derived assuming dangling-bond reconstruction, Fig. 1, and the other built on the opposite hypothesis (i.e., unreconstructed dangling bonds), Fig. 2.

The energies derived for the two core geometries from the VFF treatment favor the reconstructed geometry by 2.66 eV per lattice vector, the bond-formation energy being the most important term in minimizing the total energy.[4] Chelikowsky and Spence[7] faced the same problem by means of an anharmonic version of the Keating force field and they found the reconstructed geometry as the minimum energy one; nevertheless, the question of incomplete coordination present in the unreconstructed geometry, leaves, in the opinion of the same authors, some open questions. It is, then, desirable to pay further attention to the analysis of dangling-bond reconstruction within the core of the dislocation in order to confirm or otherwise the trends given by the force field methods.

The methods of *ab initio* molecular quantum chemistry can be very valuable when dealing with structural and electronic properties of atoms localized within the dislocation region, if small clusters representing the defect[8–16] can be extracted from the lattice.

In the present paper the choice of cluster shape will be considered first. The reconstructed and unreconstructed cluster total energies, derived by *ab initio* methods, will then be discussed, after which the electron eigenvalues of the energetically favored model and their relation to the band structure of the defective material will be examined. Finally, the electron density of the reconstructed and unreconstructed clusters will be compared by means of contour plots of total and difference electron density maps.[17]

II. METHODS OF CALCULATION

All the *ab initio* Hartree-Fock-Roothaan molecular-orbital linear-combination-of-atomic-orbitals self-consistent-field (HFR-MO-LCAO-SCF) calculations were carried out by means of GAUSSIAN-80 (Ref. 18) on the IBM 4361/4 computer of the Istituto di Teoria e Struttura Elettronica, Consiglio Nazionale delle Ricerche, Italy.

The extended basis set[19] was adopted with the silicon basis set taken from Snyder and Wasserman;[20] this basis set describes the core orbitals of the silicon atoms by a combination of four Gaussians and the valence orbitals of the silicon atoms and of the hydrogens are split into two different shells described, respectively, by a combination of three Gaussian functions and by a single Gaussian function; hereafter, the simple HFR-SCF calculations performed by means of this basis set will be referred to as 4-31g, unless otherwise stated. This particular combination was thoroughly tested against the structural and electronic properties of saturated silanes[21] and unsaturated SiH_n ($n = 1,3$) fragments.[16]

An estimate of the electron correlation energy is useful when dealing with a bond formation problem, where it is known to play a very important role. This energy contribution was estimated by means of the Moller-Plesset[22] perturbation treatment extended to the second order (hereafter referred to as MP2) and by means of a configuration interaction treatment including all double excited electronic configurations, keeping the core orbitals frozen[23] (hereafter referred to as CID).

Unfortunately, because of the inherent limitations of the GAUSSIAN-80 program, the 4-31g basis set expansion is such that it does not allow correlation energy calculations to be performed on the chosen clusters. This limitation was overcome by the use of the minimal basis set by Hehre *et al.*[24] by means of which the MP2 and CID calculations were performed. This basis set describes all the orbitals of a given atom by a combination of three Gaussian functions obtained by least-square fitting to a Slater-type orbital (STO); hereafter, the simple HFR-SCF calculations performed by means of this basis set will be referred to as STO-3g, unless otherwise stated. The STO-3g basis set is less accurate than the 4-31g one. Although they do partially account for bond stretching and angular correlation; nevertheless, correlation energy contributions computed by means of STO-3g wave functions could be slightly underestimated (see Ref. 25 for a comprehensive discussion of this point); but the STO-3g-MP2 and STO-3g-CID calculations are good enough to give an estimate of the general influences on the total energy due to electron correlation. The Pople and Nesbet[26] open-shell treatment was employed where unpaired electrons were found.

In order to bring out the effects of electron migration on bond formation, the difference electron density $\Delta p(\mathbf{r}) = p(\mathbf{r}) - p_A(\mathbf{r})$ is calculated, where $p(\mathbf{r})$ is the standard total electron density and $p_A(\mathbf{r})$ is the electron density at the same point in space obtained by superposition of the electron densities of isolated, "spherically averaged," atoms placed at the corresponding position in the molecule.[17,27]

III. RESULTS

A. Choice of the cluster geometry

The model geometries have been extracted from the VFF calculations performed on two different 500-atom clusters containing two 90° partial dislocations with opposite Burgers vectors.[4] Two different minimum-energy geometries, shown in Figs. 1 and 2, had been then generated on the basis of the reconstructed and unreconstructed topologies, respectively. The dangling-bond reconstruction takes place on each of the (10$\bar{1}$)-periodic planes shown in Figs. 1(a) and 2(a), which contains the pairs of silicon atoms carrying the dangling bonds. It is therefore possible to limit the search for a significant cluster shape to one of the above-mentioned planes, neglecting interplanar interactions as a first approximation. The lattice strain energy has to be considered as the other important term in determining if the dangling bonds reconstruct, in addition to the bond formation energy. As a consequence, three different cluster shapes have been chosen (considering one of the two equivalent dislocation cores appearing in Figs. 1 and 2) so that both energy terms appear in them.

The first model is based on a five-member ring shape,

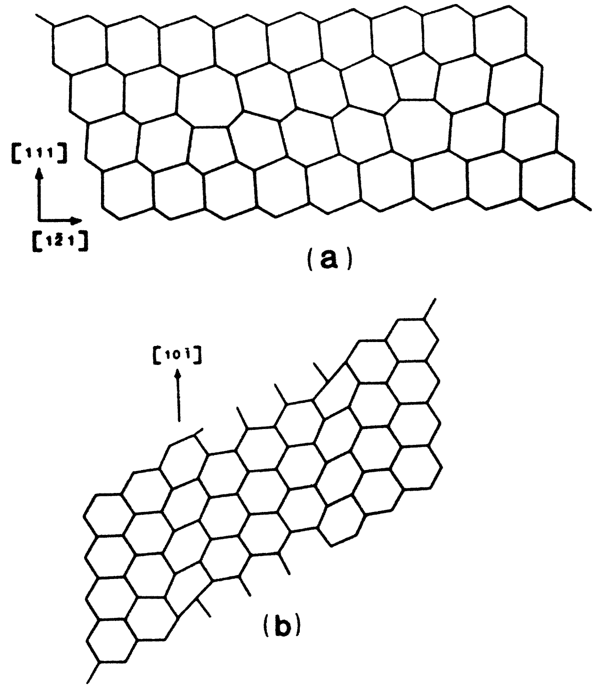

FIG. 1. Projected view of the 500 silicon atom cluster generated by the VFF method with the reconstructed bonding topology (see Ref. 4). (a) [10$\bar{1}$] projection. (b) [111] projection of glide plane double layer.

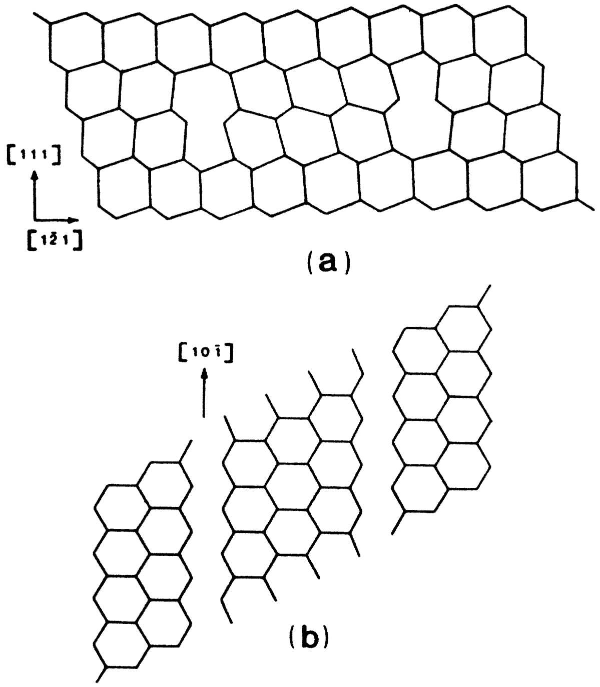

FIG. 2. Projected view of the 500-atom cluster generated by the VFF with the unreconstructed topology (see Ref. 4). (a) [10$\bar{1}$] projection. (b) [111] projection of the glide plane double layer.

Si_5H_{10}, extracted from the planes shown in Figs. 1(a) and 2(a) by taking the silicon atoms around a five-member ring; Figs. 3(a) and 3(b) show the reconstructed and unreconstructed structures, respectively. The calculations were performed on this model by means of the 4-31g and STO-3g basis sets, the MP2 and CID post-SCF treatments have been performed on the STO-3g wave function only.

The second model is based on the same five-member ring shape in which the four hydrogen atoms bonded to the silicon atoms 1 and 5 [see Figs. 3(a) and 3(b)], have been substituted by four silyl fragments producing a Si_9H_{18} cluster; Figs. 4(a) and 4(b) show the reconstructed and unreconstructed structures, respectively. This kind of shape ensures a better description of the environment of the two atoms between which the dangling-bond reconstruction takes place; the silyl geometries have been taken, as usual, from the 500-atom clusters.

The third model is based on a ten-member ring shape, $Si_{10}H_{18}$, extracted from the planes shown in Figs. 1(a) and 2(a) by taking the silicon atoms of two adjoining five- and seven-member rings; Figs. 5(a) and 5(b) show the reconstructed and unreconstructed structures, respectively.

This model, including within itself those atoms more severely affected by deformation, allows a first rough estimate of the difference in strain energy contribution per lattice vector between the reconstructed and unreconstructed models by means of the quantum-mechanical computations. The calculations on the last two proposed molecular shapes were performed by means of the STO-3g basis set.

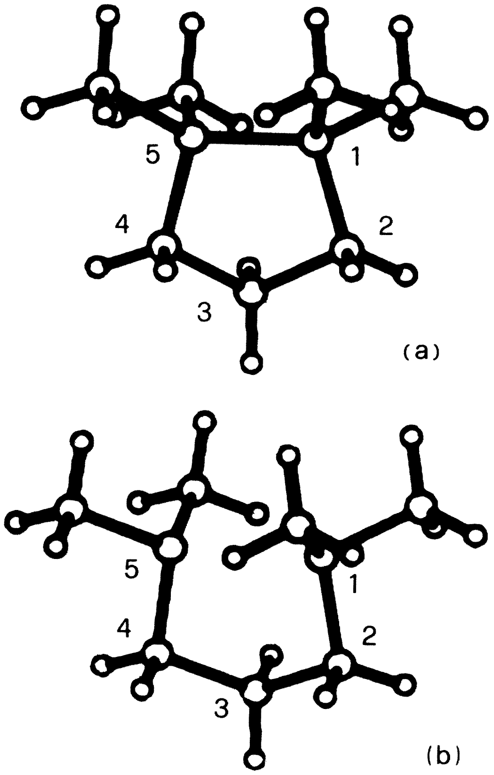

FIG. 4. Ball and stick model of the Si_9H_{18} cluster. (a) Reconstructed model, (b) unreconstructed model.

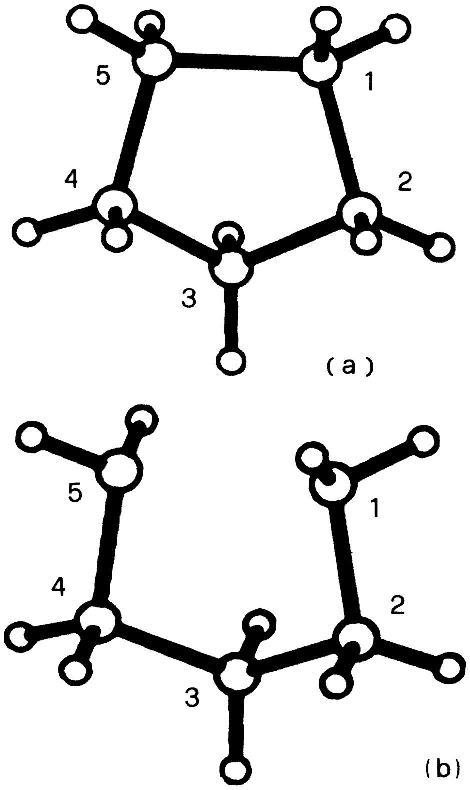

FIG. 3. Ball and stick model of the Si_5H_{10} cluster. (a) Reconstructed model, (b) unreconstructed model.

B. Choice of the saturating material

It is important in the molecular environment to set appropriate boundary conditions in order to avoid generating fictitious surface states which could couple with the real dangling-bond states connected with the defect core, thus severely affecting the final results. This problem has been present in all the cluster model calculations performed up to now and it has been approached in various ways (see Refs. 8–15 and 28–41). The most widely used choice has been followed in the present paper: hydrogen atoms were used as saturating material. The hydrogens were generated with the valence and torsional angles equal to those of the parent silicon atoms in the 500-atom clusters.

The value to be attributed to the Si—H bond length in cluster calculations has been the subject of much discussion in the literature (see Ref. 12 and references therein); in fact, the suggestion has been put forward to use this quantity as a parameter to be chosen in order to simulate the crystalline in the best possible way.[12] This proposal was tested in the present work on the $Si(SiH_3)_4$ model, Fig. 6, on using both the 4-31g and STO-3g basis sets; this molecule has been chosen by several authors as a good simulation of the perfect silicon crystal.[10,12,28]

The calculations were performed using the same procedure as that of Ref. 12: the Si—H bond distance was varied from 1.492 Å, the value found in gaseous disi-

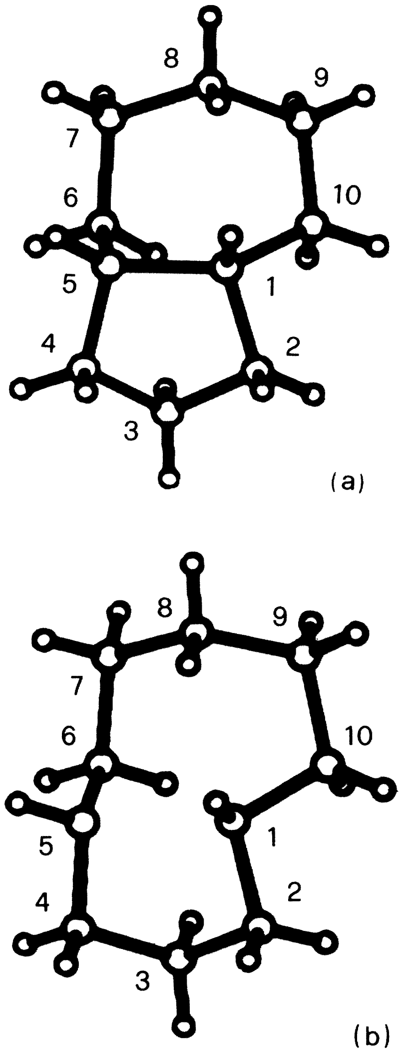

FIG. 5. Ball and stick model of the $Si_{10}H_{18}$ cluster. (a) Reconstructed model, (b) unreconstructed model.

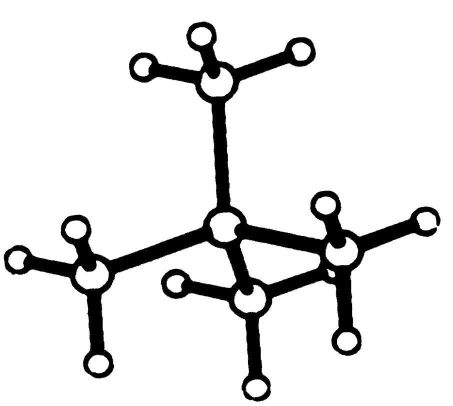

FIG. 6. Ball and stick model of the $Si(SiH_3)_4$ cluster reproducing a portion of the perfect silicon lattice.

lane,[42] to 2.351 Å, keeping the Si—Si distance fixed at the crystalline value (2.351 Å). The resulting 4-31g valence (occupied) and first unoccupied eigenvalues are shown in Fig. 7 for the two limiting bond distances, and they are compared with the data derived from one of the best calculations performed on a similar model.[28] In that work, the boundary conditions were implemented by means of sp^3 silicon hybrids whose center was kept fixed at 2.351 Å away from the silicon atoms to be saturated, a choice which clearly constitutes a more sophisticated solution of the saturing material problem than the use of hydrogen atoms.

The results for the 1.492 Å Si—H distance are in better agreement with the reference calculation[28] than those obtained using the crystalline bond distance (2.351 Å), especially when orbital ordering is considered. All the results obtained for intermediate distances are linearly disposed between the two endpoints. The valence-band width values, estimated for the two limiting bond distances by the difference between the $3t_2$ and $1a_1$ levels, are quite similar, 11.45 eV and 12.36 eV, respectively, and near to the value reported by pseudopotential band calculations.[43,44]

The rationale for the use of the longer Si—H employed in Fig. 7(c) is that the band gap, given by the distance between the $3t_2$ and $4t_2$ levels, is lower than in the two other calculations, and this is in better agreement with experiment. We do not consider this agreement, however, to be entirely sound. The level $3a_1$, which is basically a Si—H antibonding level, lies above the level $4t_2$ in Figs. 7(a) and 7(b), whereas it has dropped substantially in Fig. 7, the reason being that the longer bond length reduces the energy difference between bonding

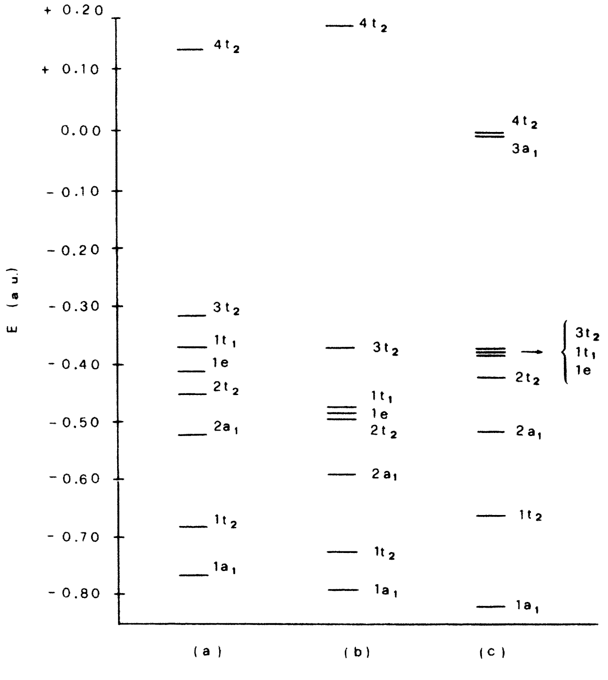

FIG. 7. $Si(SiH_3)_4$ 4-31g eigenvalues, in eV, computed for two Si—H bond length values, *B*, 1.492 Å, and *C*, 2.351 Å, respectively. The results pertaining to the Si_{17} cluster of Malvido and Whitten (see Ref. 28) are given for comparison in *A*.

and antibonding levels. Thus although the gap is better for the longer Si—H bond distance, the states which define the gap are entirely alien to those of interest in the solid: they are largely spurious surface states. For this reason, and in agreement with the discussion of Malvido and Whitten,[28] we have adopted throughout the present work the value 1.492 Å for the Si—H bond distance.

The STO-3g results reproduce the same trends of the results discussed above, although their numerical values are influenced by the smallness of the basis set.

C. Energetics of the reconstruction process

It can be said, on intuitive chemical grounds, that the energetics of dangling-bond reconstruction at the dislocation core is mainly determined by the interplay between two major competing energy contributions, the elastic and the bond-formation energies, acting on the two reconstructed and unreconstructed model geometries. The SCF calculations on the chosen clusters give total energies which contain within themselves a very good description of the bond-formation term and an estimate of the strain whose accuracy is directly related to dimensions of the chosen models. Therefore, a good basis for the discussion of the reconstruction problem is an analysis of the total-energy differences of the proposed reconstructed and unreconstructed models. The treatment of a bond-formation problem implies the possibility that the reacting species undergoes an electronic transition. Because of this reason, in the present case, the total energies for reconstructed and unreconstructed models were computed assuming two different electronic configurations: a singlet, closed shell configurations, and a triplet, open shell one.

The first cluster to be discussed is the Si_5H_{10} one, for which the most complete set of calculations is available, as shown in Table I. Examination of the first two rows of this table gives rise to an unambiguous picture: the absolute minimum energy is always coupled with the reconstructed models. Furthermore, the singlet electronic state is the most stable one for the reconstructed model whereas the triplet state is the favored one in the unreconstructed geometry. The relative stabilities of the singlet and triplet states of the unreconstructed model, as they come from the simple HFR-SCF calculations, should be reversed because the electron correlation influences, acting on the two weakly overlapping dangling-bond orbitals placed on the Si(1) and Si(5) atoms (see Fig. 3), would force the unreconstructed singlet below the unreconstructed triplet; the reconstructed Si(1)—Si(5) bond, instead, is short and strong enough to be correctly described by the simple HFR computation. The more accurate 4-31g basis, indeed, already gives a very small singlet-triplet energy difference in the unreconstructed cluster, 0.19 eV.

Then an estimate of the correlation energy, a factor which is important in a bond-formation problem, was attempted through a second-order post SCF perturbation treatment (MP2) of the STO-3g wave functions. The final MP2 results are shown in the third row of Table I. Once again the MP2 treatment gives the reconstructed structure as favorable and, furthermore, it is able to produce the expected inversion of the total energies of the singlet and triplet states of the unreconstructed Si_5H_{10} clusters. A STO-3g CID computation was, then, performed on the reconstructed and unreconstructed Si_5H_{10} singlets in order to confirm quantitatively the MP2 results, fourth row of Table I.

In all the above quoted calculations the absolute minimum energy is always coupled with the singlet reconstructed model.

The actual ΔE_{R-U}'s ($E_{\text{recon}} - E_{\text{unrecon}}$), evaluated by taking into account the minimum-energy electronic configurations, are -2.11 eV (singlet-triplet), -2.46 eV (singlet-triplet), -2.61 eV (singlet-singlet), and -2.20 eV (singlet-singlet) for the 4-31g, STO-3g, STO-3g MP2, and STO-3g CID calculations, respectively. All the quantitative ΔE_{R-U} estimates are in substantial agreement among themselves and they clearly indicate that the reconstructed geometry is the favored one. The STO-3g basis is able to reproduce the same trends generated by the more accurate 4-31g one; which means that it can be used with some confidence whenever the 4-31g calculations are unavailable.

Furthermore, if one assumes that the major source of the correlation energy correction is coming from a correct treatment of the elongation of the Si(1)—Si(5) bond on going from the reconstructed to the unreconstructed model, it is possible to derive from the STO-3g and STO-3g CID calculations a factor to be used in order to correct for correlation energy effects the ΔE_{R-U}'s of all those clusters for which the MP2 or CID results are unavailable. The STO-3g ΔE_{R-U} between singlet states is equal to -3.30 eV, the same quantity drops down to -2.20 eV in the STO-3g CID calculation, which gives the correct ordering of the singlet and trip-

TABLE I. Total energies (in a.u.) of the Si_5H_{10} cluster in the reconstructed and unreconstructed model geometries for all the computational procedures employed.

	Reconstructed singlet	Reconstructed triplet	Unreconstructed singlet	Unreconstructed triplet
4-31g	−1448.569 12	−1448.401 20	−1448.484 68	−1448.491 64
STO-3g	−1433.844 83	−1433.651 58	−1433.723 68	−1433.751 41
STO-3g MP2	−1434.040 99	−1433.833 15	−1433.945 22	−1433.927 38
STO-3g CID	−1434.125 75		−1434.044 79	

let states either in the unreconstructed and reconstructed models; the difference between these two results, 1.1. eV, gives the correction factor to be added to the single-singlet STO-3g ΔE_{R-U}'s of all those clusters for which the post SCF treatments are unavailable. It would be useful to derive a similar correction factor to be applied to 4-31g wave function results. Unfortunately, 4-31g MP2 and 4-31g CID calculations on a Si_5H_{10} molecule are not available, it was, then, that a smaller model system was chosen i.e., Si_2H_6, in which the Si—Si bond length was alternatively set at the values found in the reconstructed and unreconstructed models for the Si(1)—Si(5) bond, see Fig. 3 (2.42 Å and 3.04 Å), respectively[4]). The differences between the 4-31g ΔE_{R-U} and the 4-31g CID ΔE_{R-U} for the singlet Si_2H_6 molecule is equal to 0.48 eV and, once more, the 4-31g CID computations give the correct ordering between singlet and triplet states in the unreconstructed Si_2H_6 molecule (i.e., the singlet lies below the triplet). It was, then, possible to derive an estimate, corrected for correlation energy effects, for the 4-31g ΔE_{R-U} between singlet states in Si_5H_{10}. The addition of the above-quoted 0.48 eV correlation energy correction factor to the -2.30 eV 4-31g ΔE_{R-U} (singlet-singlet) brings the final ΔE_{R-U} estimate down to -1.82 eV, a value which indicates reconstruction.

The second batch of computations were performed on the Si_9H_{18} cluster, Fig. 4. This model has one main additional feature with respect to the Si_5H_{10} one: the silicon atoms carrying the dangling bonds are totally surrounded by Si—Si backbonds. Table II shows the STO-3g total energies for the reconstructed and unreconstructed models in the singlet and triplet electronic configurations. The results parallel those obtained for the Si_3H_{10} cluster: the absolute minimum energy corresponds to the reconstructed model in the singlet electronic configuration and ΔE_{R-U} equals -1.6 eV (singlet-triplet). If one takes the singlet-singlet ΔE_{R-U}, -2.36 eV, and adds to it the above mentioned 1.1 eV STO-3g correlation energy correction factor, one arrives at a final ΔE_{R-U} equal to -1.26 eV, a value which still indicates reconstruction. It must be noted that the difference of 1.0 eV or so compared with the previous Si_3H_{10} STO-3g CID estimate is accounted for by the inclusion here of strained silyls whose contribution to the strain energy ranges over more than one lattice vector.

The last set of calculations have been performed on $Si_{10}H_{18}$ clusters, Fig. 5. In this case the most strained silicon atoms, correctly contributing to the energy per lattice vector, are included in the model. It was only possible to perform the calculations on the singlet states by means of the STO-3g basis set for these molecules and the final total energies are $-2866.600\,87$ a.u. and $-2866.502\,75$ a.u. for the reconstructed and unreconstructed geometries, respectively. This led to ΔE_{R-U} equal to -2.67 eV. It is, however, possible to estimate a final ΔE_{R-U} of -1.57 eV, thus supporting the dangling-bond reconstruction, by adding to the abovementioned value the previously obtained 1.1 eV STO-3g correlation energy correction factor.

None of the previous calculations show any appreciable degree of charge separation, so that that it was not felt necessary to apply corrections due to the polarization in an infinite solid, as done by Surratt and Goddard III.[45]

All the ΔE_{R-U}'s computed up to now clearly indicate the reconstructed model as the energetically favorable one, but several problems must be solved before the reconstruction problem could be considered completely solved. These are mainly connected with the small size of the proposed model clusters as compared with that of the deformed solid. It is, however, possible to apply a correction for the finiteness of the proposed clusters. Even the $Si_{10}H_{18}$ cluster does not contain within itself all those silicon atoms whose deformed environments contribute to the strain energy. It is possible, however, to obtain a rough estimate of cluster size effects by merging the present results with those coming from the VFF work.[4] If one takes the 4-31g ΔE_{R-U} (singlet-singlet), -1.82 eV, computed for the Si_5H_{10} cluster as a good estimate of the bond-formation energy, and adds to it the VFF value, 0.85 eV,[4] for the difference in strain energy per lattice vector between the reconstructed and unreconstructed 500-atom clusters, one arrives to a final -0.97 eV total energy difference per lattice vector, a value which still indicates reconstruction. Manipulating in the same way the STO-3g CID results, one arrives at the same conclusion (total STO-3g energy per lattice vector equal to -1.35 eV).

It must be noted in the above argument that the strain-energy contribution of the silicon atoms within the five-members ring is accounted for twice, clearly affecting quantitatively the previous energy estimate, but if this bias could be taken into account, it would modify the estimated values above by making the reconstructed model even more favorable, because all the ΔE_{R-U} values used above for the bond-formation energy should be even more negative.

Some further open questions could be answered if it were possible to equate ideally the ΔE_{R-U} obtained for the Si_5H_{10} model (i.e., the cluster which is least affected by strain amongst the proposed shapes) with the bond-energy contribution only. On the basis of this assumption, it is possible to derive an *ab initio* HFR rough estimate of the difference in strain energy between the reconstructed and unreconstructed models. This results

TABLE II. Total energies (in a.u.) of the Si_9H_{18} cluster in the reconstructed and unreconstructed model geometries for the STO-3g basis set.

	Reconstructed singlet	Reconstructed triplet	Unreconstructed singlet	Unreconstructed triplet
STO-3g	$-2580.943\,33$	$-2580.784\,53$	$-2580.856\,48$	$-2580.884\,56$

from the following consideration: only the strain energy contributes to the difference between the STO-3g ΔE_{R-U}'s of the $Si_{10}H_{18}$ and Si_5H_{10} models, respectively (−1.57 eV and −2.20 eV), the bond energy contribution being roughly equal in both clusters.

Therefore, the difference between those two energies, 0.63 eV, represents the *ab initio* quantum-mechanical estimate of the difference in strain-energy contribution per lattice vector. It must be noted that this value is of the same order as the difference in strain energies between the reconstructed and unreconstructed structures, 0.85 eV,[4] computed by the VFF, a method which is known to be highly reliable when dealing with elastic deformation energies.

Clearly, the above mentioned assumption, on whose basis this rough estimate is made, is far from accurate (the attempt to partition the total energy derived from *ab initio* quantum-mechanical calculations into different energy contributions based on intuitive chemical concepts is always questionable) and the trends deduced from its use have to be taken as no more than plausible.

D. Electronic structure of the clusters

A general problem in defect physics is the identification of the band states associated with a particular defective situation. The cluster electronic structure can give qualitative suggestions about the band structure even if the extrapolation of the molecular results towards the solid state is somewhat questionable. In this approach, the fundamental quantity is the cluster band gap, which is defined as the energy difference required for a localized excitation of an electron between the highest occupied molecular orbital (HOMO) of the cluster to the lowest unoccupied molecular orbital (LUMO) in it.[12] It is possible in our case to obtain in this way some indications about the band structure of the 90° dislocation by comparing the cluster band gap of the Si_5H_{12} model, simulating the perfect lattice, with those of the clusters (Si_5H_{10} and Si_9H_{18}), simulating the reconstructed defect.

Two different methods are used in order to estimate the cluster band gap: (1) the SCF total energy difference, ΔSCF, between the singlet and triplet electronic configurations computed for both the perfect crystalline Si_5H_{12} cluster and the reconstructed models, Si_5H_{10} and Si_9H_{18}; (2) the differences between the singlet and triplet HOMO eigenvalues computed for both above-mentioned situations, keeping in mind that the triplet HOMO is obtained by populating the antibonding singlet LUMO.

The ΔSCF cluster band gap estimate is, clearly, the more correct one because it takes partially into account electron relaxation effects. The second method gives a rougher estimate of the cluster band gap but it is an improvement with respect to the simple HOMO LUMO singlet eigenvalue difference and it helps in extrapolating the cluster results toward the solid state.

TABLE III. SCF singlet-triplet energy differences (in eV), ΔSCF, computed for the perfect silicon Si_5H_{12} cluster and the reconstructed derivative Si_5H_{10} and Si_9H_{18} clusters.

	Si_5H_{12}	Si_5H_{10}	Si_9H_{18}
4-31g	−7.52	−4.57	
STO-3g	−11.20	−5.26	−4.32

Table III shows the ΔSCF results for the crystalline perfect Si_5H_{12} cluster and the reconstructed defective Si_5H_{10} and Si_9H_{18} clusters by means of the 4-31g and STO-3g basis sets.

Both the 4-31g and STO-3g cluster band gap values for Si_5H_{12} are considerably higher than the crystalline indirect band gap, 1.12 eV,[46] showing that a cluster with five silicon atoms is too small to quantitatively reproduce solid-state levels, especially when excited states are involved.

Indeed it is more reasonable to accept that the cluster is too small to contain a level anything like that at the crystalline conduction band minimum, and to compare the $3t_2 \rightarrow 4t_2$ cluster band gap transition with the $\Gamma'_{25} \rightarrow \Gamma_{15}$ crystalline transition, 3.45 eV,[46] since the levels thus associated have the same symmetries and similar forms locally. Using the 7.52 eV 4-31g value, which is in good agreement with a similar calculation,[28] the comparison is still poor, the difference is again due to the smallness of the cluster. This is a major problem in any attempt to correlate cluster and crystalline levels in general and, as a result, only very rough correlations can be made.

As might have been expected from the strained bonds in the models simulating the dislocation core, their cluster band gaps are much smaller than for the model simulating the perfect lattice. Further insight is obtained from the shifts of the singlet and triplet HOMO eigenvalues in going from the perfect to the defect clusters, Fig. 8. In the strained clusters the smaller band gaps result from pushing the singlet HOMO "bonding" state up and the triplet HOMO "antibonding" state down. Also

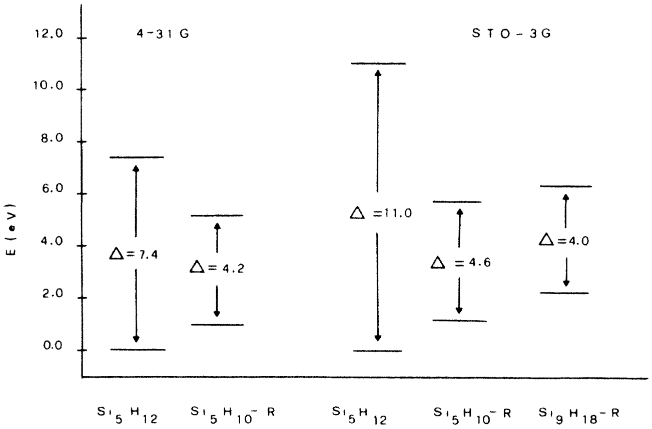

FIG. 8. Singlet and triplet HOMO's eigenvalues, in eV, computed for perfect, $Si(SiH_3)_4$, and defective reconstructed, Si_5H_{10}, clusters. (a) 4-31g eigenvalues, (b) STO-3g eigenvalues. The singlet HOMO eigenvalue of the $Si(SiH_3)_4$ cluster has been taken as the reference value in each one of the two sets of computations, (a) and (b). In every case the lower level is the singlet HOMO closed-shell state and the upper one is the triplet occupied HOMO open-shell state.

from either basis set calculations, this strain effect is twice as large on the antibonding states as on the bonding states.

A tentative extrapolation of these results toward the solid state might be based on the reduction of the perfect cluster band gap toward the crystalline one with increasing cluster size. In such a process the form of the band edge level can change; this occurs with the $4t_2$ level of Si_5H_{12} which is eventually left behind in the conduction continuum whereas the $3t_2$ level evolves into the valence-band edge.

Similarly, for clusters of increasing size built about the models simulating the dislocation one, the cluster band gap must eventually reduce at least as far as the perfect crystal band gap, and the major point of interest is the evolution of levels that are strongly associated with the dislocation one. In principle these dislocation levels could evolve either into localized states in the gap or into resonances in the valence- or conduction-band continuums.

The singlet and triplet HOMO levels of the defect clusters are prime candidates for dislocation levels which evolve into localized states in the gap. The large reduction in the cluster band gap in going from the perfect model to the defect models strongly indicates this as a possibility. This is especially true of the triplet HOMO antibonding state where the shift is most pronounced.

However there are equally strong arguments to the contrary. It must be remembered that the above comparison involves the $4t_2$ level which evolves into a state 2.33 eV above the conduction-band minimum. Also, the approach towards the perfect crystalline band gap with increasing cluster size is very slow[47] due to the extended nature of the states.

By contrast, levels that evolve into localized states must become independent of the boundary conditions more quickly and so must reach their limiting energies sooner. This implies that they must start much closer to the perfect crystalline band gap if they are to remain localized.

In consequence the results of the present calculations cannot be used to determine if the defect states associated with straight 90° reconstructed dislocation in silicon lie in the gap of if they are merged with the valence and conduction bands. We can only say that the defect states are expected to be roughly in the regions of the band edges.

E. Charge and spin density analysis of the clusters

The analysis of the electron density of the reconstructed and unreconstructed models gives useful auxiliary data which enrich the overall picture of these systems. The total electron charge density contour maps for the Si_5H_{10} clusters, described in a previous section, have been computed using the 4-31g wave functions of the minimum energy end points (i.e., reconstructed singlet, unreconstructed triplet).[48]

A preliminary analysis was carried out in order to identify the spatial plane on which the more significant electron density charges take place. This was chosen to be the plane containing the two silicon atoms 1 and 5 (see Fig. 3), which are involved in the bond reconstruction, plus atom number 2.

The total electron density maps for the reconstructed and unreconstructed models are shown in Figs. 9(a) and 9(b), respectively. The contour line marked with an asterisk in Figs. 9(a) and 9(b) is the one most sensitive to the reconstruction process, since it embraces the three atoms 1, 2, and 5 in the reconstructed model, indicating that the electron charge density cloud is equally distributed among the three atomic centers, whereas, in the unreconstructed model, it passes between atoms 1 and 5, indicating a decrease in electron density in that region.

The described displacements in total electron density are clearly related to the state of the covalent bonding across the dislocation core; the decrease in charge density between atoms 1 and 5 in the unreconstructed model being a clear indication of the weakening of the covalent Si—Si bond.

The total electron density maps could mask some of the details of the charge displacements, because the fraction of the electrons which are responsible for the bond formation are usually a very small percentage of the total.[17,49]

The difference electron density maps, which have been defined in Sec. II, are instead a good tool to unambigu-

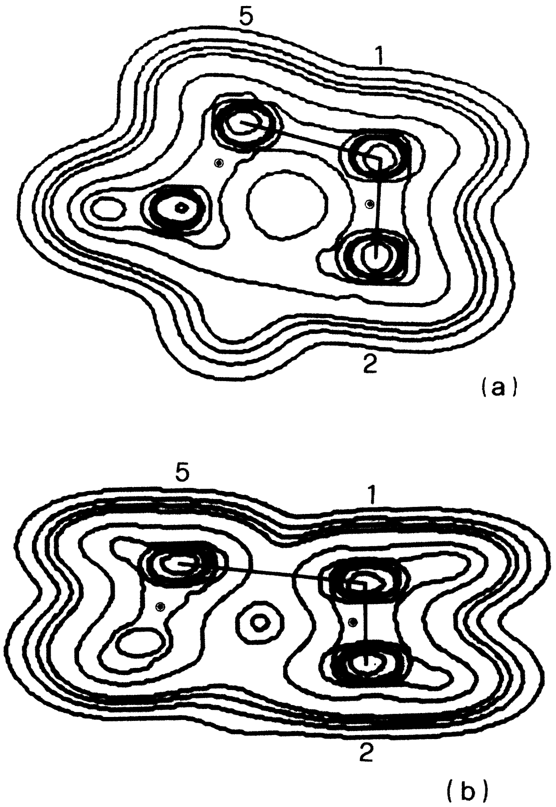

FIG. 9. Total electron density contour maps, in electron/bohr^3, computed by means of the 4-31g basis set in the Si_5H_{10} defective clusters. (a) Reconstructed model, (b) unreconstructed model. In every case the maps are oriented in exactly the same way as Figs. 3(a) and 3(b), with which they should be compared.

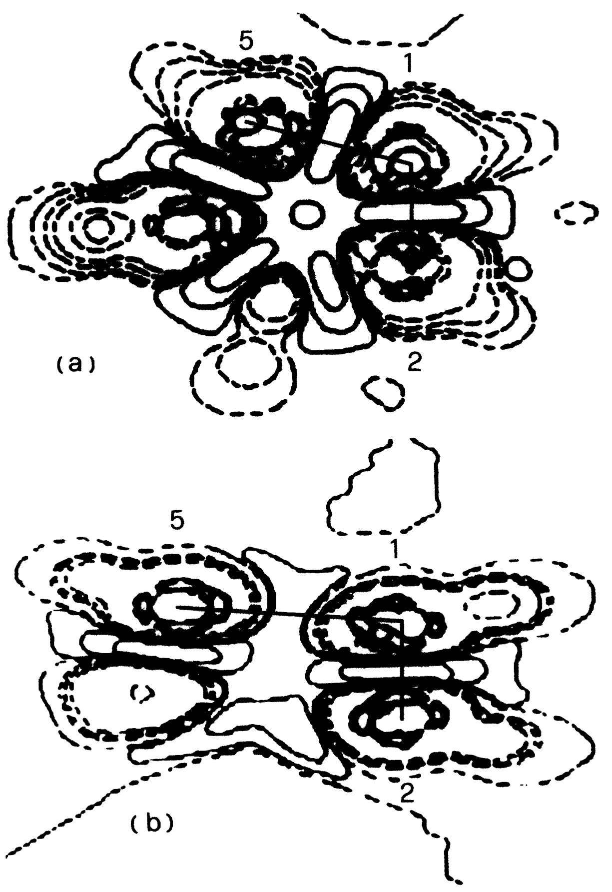

FIG. 10. Difference electron density contour maps, in electron/bohr^3, computed by means of the 4-31g basis set in the Si_5H_{10} defective clusters. (a) Reconstructed model, (b) unreconstructed model. The solid and dashed lines indicate positive and negative difference densities values, respectively.

ously determine the bonding electron charge densities. Figures 10(a) and 10(b) show the difference density maps computed for the reconstructed and unreconstructed models, respectively.

Five regions of positive difference densities given by solid lines in Fig. 10, appear clearly in those portions of the space placed in the middle of the five σ Si—Si bonds for the reconstructed models, Fig. 10(a). It is possible to handle all five bonds together because the conformation of the five-member ring is flattened by the reconstruction process. A closer inspection of these five positive difference density regions indicates that the five Si—Si bonds are almost equivalent and that the strain slightly changes the shape of the positive electron difference density cloud associated with the 1—5 bond.

Furthermore, the association of the midbond region with a positive maximum in difference density qualitatively matches the x-ray experiment[50,51] which finds a maximum in electron density along the Si—Si bond.

Only three positive difference density regions are found in the unreconstructed model, Fig. 10(b), and this is a consequence of the breaking of the 1—5 bond, which allows the five-member ring to pucker, thus relaxing the strain. The positive difference density region is still present between atoms 1 and 5, but it is more smeared out and smaller in contour line values than the one present in the reconstructed cluster, indicating that a bond breaking process had taken place.

The last interesting result regarding charge densities comes from the spin density results of the triplet, energetically unfavorable, unreconstructed model. In that situation the two unpaired spins are almost totally localized on the dangling bonds associated with atoms 1 and 5, see Fig. 3, which are facing each other across the dislocation core, as in the traditional picture which shows a dislocation as an infinitive row of facing dangling bonds, but this is not realistic if it is remembered that this particular state is energetically unfavorable.

IV. SUMMARY

Total energy calculations on clusters reproducing the reconstructed and unreconstructed cores of a 90° partial dislocation in silicon have been computed by means of the HFR MO LCAO SCF method using two different basis sets. Different molecular shapes and electronic configurations have been taken into account in order to reach a reliable description of the dangling-bond reconstruction. An estimate of the influence of the electron correlation on the whole phenomenon has been accounted for by means of MP2 and CID post SCF treatments.

The resulting energetics confirm the hypothesis of reconstruction put forward by previous VFF calculations[4] and even the semiquantitative agreement is satisfactory.

The electronic structure of a reconstructed cluster has been compared with that one computed for a model reproducing the perfect silicon lattice.

The modification in electron distribution, happening upon reconstruction, has been studied by means of total and difference electron density maps.

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[48]As a matter of fact, one would need the singlet correlated electron density for the unreconstructed model. Unfortunately, this is unavailable and we have used the minimum energy 4-31g results. The very small singlet-triplet energy difference between the unreconstructed Si_5H_{10} 4-31g wave functions, $+0.19$ eV, shows the the error made in adopting the triplet unreconstructed electron density is such that it does not alter the general considerations made in this section.

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