Random-Bethe-lattice model applied to the electronic structure of amorphous and liquid silicon

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Bethe lattices of arbitrary number of nearest-neighbor atoms and geometrical configurations are defined for the standard sp^3s^* tight-binding Hamiltonian that gives correctly both valence and conduction bands of crystalline Si. Averaged densities of states are obtained through a well-grounded extension of the coherent-potential approximation to random Bethe lattices with off-diagonal disorder. In that way, a unified picture of the electronic structure of Si in amorphous and liquid phases is obtained. Formation energies of dangling and floating bonds are estimated within Chadi's tight-binding scheme.

I. INTRODUCTION

Since the pioneering work done by Weaire and Thorpe in 1971 on the electronic structure of amorphous silicon (a-Si),[1] many calculations on the same topic have been published. References to the original contributions can be found in reviews written on this subject.[2–4] Although the field is not closed, as the recent controversy on the nature of native defects in hydrogenated good-quality a-Si has shown,[5–18] almost all the interesting features related to the electronic structure are well established. On the other hand, it is also clear that *ab initio* methods like the one implemented by Car and Parrinello[19] based on the Hohenberg-Kohn-Sham local-density approximation for the electron-electron interaction give *state-of-the-art* results for the electronic structure of the condensed phases of Si.[20,21] Consequently, the aim of an empirical approach to the electronic structure of amorphous and liquid Si cannot be an improvement of the mentioned results but a stimulus for people that must describe the nature of the electronic states in amorphous semiconductors in order to study more particular topics such as hydrogenation of the material, doping of the semiconductor, alloying, coordination defects, and, more generally, whatever kind of deviation from the ideal structure or composition of the semiconductor. In other words, our approach to the condensed phases of Si—Bethe lattices and a self-consistent definition of an effective medium—provides quite powerful and versatile tools for studying the electronic structure of materials that have been actually synthesized in the laboratory. As the experience of people dealing with crystalline semiconductors has shown recurrently, both kinds of method—*ab initio* and empirical—are not contradictory but complementary. On the other hand, our work is closely related to the cluster–Bethe-lattice approach,[22] which has been extensively used to study semiconducting amorphous compounds;[23] sometimes our cluster is reduced to one atom connected to five instead of four branches of an ideal Si Bethe lattice to simulate a fivefold-coordinated atom,[24,25] whereas random instead of ideal Bethe lattices[26] are used to simulate a material with a finite density of overcoordinated atoms.

In this paper, we collect our last experience dealing with amorphous semiconducting alloys based on Si,[27–30] and, in particular, studying coordination deviations of a-Si.[24,25] Since previous publications dealing with compounds contain enough information to be easily reproduced, we will restrict ourselves to pure Si, the simplest and better-studied system. As we have said, the main ingredients of our approach are random Bethe lattices[26] and a self-consistent definition of an effective medium that describes, on the average, the effect of random branches of the Bethe lattice attached to some atom.[31,32] Although both approximations have been described and successfully employed in the study of a variety of topics, we will give here a self-contained version as it is needed for the present study.

The format of the paper is the following. The main ingredients of the theoretical method are given in Sec. II. Then Sec. III contains the results of the application of our scheme to the study of the electronic structure of dangling and floating bonds—both localized states and formation energy—the modifications introduced into the electronic spectrum by the presence of finite amounts of defects, and, finally, the electronic structure of a liquid-silicon (l-Si) model in which atoms are frozen, i.e., the movement of electrons and Si ions is completely uncoupled in this model. Some additional equations are given at places where it is necessary to complete the theoretical method. Section IV is devoted to some general conclusions.

II. METHOD

For the sake of concreteness, let us introduce our scheme as it is used to study a-Si. Later, we will show

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how to extend our methodology to the study of more-complex structures, such as the one shown by liquid silicon (l-Si). First of all we need a structural model. It is well known[2-4] that good-quality hydrogenated a-Si is a fourfold-coordinated material in which bond lengths are close to the value they have in the diamond phase of crystalline Si (c-Si) with fluctuations of about 1% and bond-bond angles that fluctuate about 10% around the ideal tetrahedral angle. H saturates dangling bonds (or native defects of pure a-Si, whatever they are) producing a relaxation of strain as the main structural effect. On the other hand, gap states are removed and the possibility of effective doping is reached. Although the existence of some kind of intermediate-range order has been discussed in the literature, we keep only short-range order in our structural model; intermediate-range order could in principle be included, but it would complicate the calculation considerably. Based on these facts, our structural model for a-Si is a fourfold-coordinated Bethe lattice showing a *perfect* tetrahedral environment about Si atoms. Neither bond length and bond-bond angle fluctuations nor rings are included in our idealized structure of a covalent amorphous semiconductor. All deviations from this model are defects in our terminology: geometrical defects (fluctuations of the nearest-neighbor configuration), coordination defects (atoms having more or less than four nearest-neighbor atoms), chemical defects (the explicit inclusion of H atoms or atoms of a different chemical element), topological defects (the systematic existence of some kind of rings or correlations between dihedral angles), etc. All of these types of defects or combinations of them can be included in our scheme in a second step. In fact, some of them have been considered in previous publications; for example, H was randomly incorporated within a Si Bethe lattice.[26,31] Summarizing, we use as a starting structural model an ideal continuous random network in which the only random variable is the dihedral angle. Interactions among ions and electrons moving through the Bethe lattice are given by a standard sp^3s^* tight-binding Hamiltonian.[33] Although somewhat artificial by the inclusion of a fifth additional orbital s^*, this Hamiltonian is able to reproduce quite precisely not only the whole set of valence bands but also the lowest conduction band. That characteristic allows, for example, finding the correct energy of localized states.

A. Complex Bethe lattices

We denote as complex Bethe lattices those Bethe lattices (BL's) in which sites are occupied by atoms having more than one valence orbital. A Green-function formalism is used to get the local density of states (local DOS) that is everywhere the same in an ideal BL. Within this formalism, the effect of attaching one BL branch to an atom is entirely contained in a local self-energy that is added to the intra-atomic terms of the Hamiltonian. Local self-energies are represented by matrices having the size of the atomic orbital basis: five for the standard sp^3s^* Hamiltonian. The self-energy matrix produced by a branch of a Cayley tree connected to a reference atom along the [100] direction has the following irreducible form:

$$\underline{\Sigma}_{(1,0,0)}=\begin{pmatrix} \sigma_{ss} & \sigma_{sp} & 0 & 0 & \sigma_{ss^*} \\ \sigma_{sp} & \sigma_{pp\sigma} & 0 & 0 & \sigma_{s^*p} \\ 0 & 0 & \sigma_{pp\pi} & 0 & 0 \\ 0 & 0 & 0 & \sigma_{pp\pi} & 0 \\ \sigma_{ss^*} & \sigma_{s^*p} & 0 & 0 & \sigma_{s^*s^*} \end{pmatrix}, \quad (1)$$

where matrix indices correspond to atomic orbitals in the order $\{s,p_x,p_y,p_z,s^*\}$. The only supposition needed to get this form is that the Cayley tree has cylindrical symmetry around the [100] axis or, in other words, that an average over dihedral angles is needed to obtain the correct BL symmetry. Now, it is a simple geometrical matter to obtain the self-energy matrix corresponding to the same Cayley tree attached along an arbitrary (l,m,n) direction. It suffices to use the unitary matrix that rotates the atomic orbitals from the x,y,z axis to a system x',y',z' in which x' lies on the (l,m,n) direction and y' and z' are orthogonal to it. We take

$$\underline{R}_{(l,m,n)}=\begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & l & m & n & 0 \\ 0 & m/\Gamma & -l/\Gamma & 0 & 0 \\ 0 & ln/\Gamma & mn/\Gamma & -\Gamma & 0 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}, \quad (2)$$

where $\Gamma=[(l^2+m^2)]^{1/2}$. The rotated self-energy matrix is given by

$$\underline{\Sigma}_{(l,m,n)}=\underline{R}^{\dagger}_{(l,m,n)}\underline{\Sigma}_{(1,0,0)}\underline{R}_{(l,m,n)} . \quad (3)$$

The relevant elements of the resulting symmetric matrix are the following:

$$\begin{aligned}
&\underline{\Sigma}_{(l,m,n)}(1,1)=\sigma_{ss} ,\\
&\underline{\Sigma}_{(l,m,n)}(1,2)=l\sigma_{sp} ,\\
&\underline{\Sigma}_{(l,m,n)}(1,3)=m\sigma_{sp} ,\\
&\underline{\Sigma}_{(l,m,n)}(1,4)=n\sigma_{sp} ,\\
&\underline{\Sigma}_{(l,m,n)}(1,5)=\sigma_{ss^*} ,\\
&\underline{\Sigma}_{(l,m,n)}(2,2)=l^2\sigma_{pp\sigma}+(1-l^2)\sigma_{pp\pi} ,\\
&\underline{\Sigma}_{(l,m,n)}(2,3)=lm(\sigma_{pp\sigma}-\sigma_{pp\pi}) ,\\
&\underline{\Sigma}_{(l,m,n)}(2,4)=ln(\sigma_{pp\sigma}-\sigma_{pp\pi}) ,\\
&\underline{\Sigma}_{(l,m,n)}(2,5)=l\sigma_{s^*p} ,\\
&\underline{\Sigma}_{(l,m,n)}(3,3)=m^2\sigma_{pp\sigma}+(1-m^2)\sigma_{pp\pi} ,\\
&\underline{\Sigma}_{(l,m,n)}(3,4)=mn(\sigma_{pp\sigma}-\sigma_{pp\pi}) ,\\
&\underline{\Sigma}_{(l,m,n)}(3,5)=m\sigma_{s^*p} ,\\
&\underline{\Sigma}_{(l,m,n)}(4,4)=n^2\sigma_{pp\sigma}+(1-n^2)\sigma_{pp\pi} ,\\
&\underline{\Sigma}_{(l,m,n)}(4,5)=n\sigma_{s^*p} ,\\
&\underline{\Sigma}_{(l,m,n)}(5,5)=\sigma_{s^*s^*} .
\end{aligned} \quad (4)$$

Notice the close resemblance between the elements of the

self-energy matrix and the matrix elements of a tight-binding Hamiltonian coupling two atoms lying in the (l,m,n) direction.[34,35] Larger basis sets containing d orbitals, for example, would produce a larger number of irreducible self-energy elements. Also the construction of the rotation matrix is a bit more involved. Nevertheless, the analogy with Slater-Koster theory for the rotation of the Hamiltonian matrix is still valid.

The equation defining a simple effective medium is easily written as the following self-consistency equation:

$$\underline{\Sigma}_{(1,0,0)}=\underline{V}[E\mathbb{1}-\underline{E}_0-(\underline{\Sigma}_T-\underline{\Sigma}_{(-1,0,0)})]^{-1}\underline{V}^{\dagger} , \quad (5)$$

where $E\mathbb{1}$ is the energy times the identity matrix, $\underline{E}_0$ is a diagonal matrix containing the orbital levels, $\underline{\Sigma}_T$ is the sum of the self-energy matrices entering through all the Cayley-tree branches attached to an atom, and $\underline{V}$ is the interatomic interaction matrix through the [100] direction:

$$\underline{V}=\begin{bmatrix} V_{ss} & V_{sp} & 0 & 0 & V_{ss^*} \\ -V_{sp} & V_{pp\sigma} & 0 & 0 & -V_{s^*p} \\ 0 & 0 & V_{pp\pi} & 0 & 0 \\ 0 & 0 & 0 & V_{pp\pi} & 0 \\ V_{ss^*} & V_{s^*p} & 0 & 0 & V_{s^*s^*} \end{bmatrix} . \quad (6)$$

Equation (5) contains the unknown variables $\sigma_{ss},\sigma_{sp},\ldots$ on both sides but it can be solved numerically by iteration in a very efficient way.[36] Notice that *all* the structural information enters into Eq. (5) through the sum done to obtain $\underline{\Sigma}_T$. Usually, ideal short-range order is assumed and the set of nearest-neighbor directions suffices to construct $\underline{\Sigma}_T$. For example, the ideal a-Si Bethe lattice is obtained for

$$\underline{\Sigma}_T=\sum_{i=1}^{4}\underline{\Sigma}_{\tau_i} , \quad (7)$$

where the four nearest neighbors are placed at ideal tetrahedral directions:

$$\begin{aligned} \tau_1&=\frac{1}{\sqrt{3}}(1,1,1) ,\\ \tau_2&=\frac{1}{\sqrt{3}}(1,-1,-1) ,\\ \tau_3&=\frac{1}{\sqrt{3}}(-1,1,-1) ,\\ \tau_4&=\frac{1}{\sqrt{3}}(-1,-1,1) . \end{aligned} \quad (8)$$

Alternatively, one bond can lie on the x axis to make the use of Eq. (5) more transparent:

$$\begin{aligned} \tau_1&=(-1,0,0) ,\\ \tau_2&=\tfrac{1}{3}(1,2\sqrt{2},0) ,\\ \tau_3&=\tfrac{1}{3}(1,-\sqrt{2},\sqrt{6}) ,\\ \tau_4&=\tfrac{1}{3}(1,-\sqrt{2},-\sqrt{6}) . \end{aligned} \quad (9)$$

In any case, the total self-energy $\underline{\Sigma}_T$ results:

$$\underline{\Sigma}_T=4\begin{bmatrix} \sigma_{ss} & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{3}(\sigma_{pp\sigma}+2\sigma_{pp\pi}) & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{3}(\sigma_{pp\sigma}+2\sigma_{pp\pi}) & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{3}(\sigma_{pp\sigma}+2\sigma_{pp\pi}) & 0 \\ 0 & 0 & 0 & 0 & \sigma_{s^*s^*} \end{bmatrix} . \quad (10)$$

On the other hand, an ideal Bethe lattice for metallic sixfold-coordinated Si can be built using

$$\underline{\Sigma}_T=\sum_{i=1}^{6}\underline{\Sigma}_{\tau_i} , \quad (11)$$

where the six nearest neighbors are placed along the Cartesian axis:

$$\begin{aligned} \tau_1&=(1,0,0) ,\\ \tau_2&=(-1,0,0) ,\\ \tau_3&=(0,1,0) ,\\ \tau_4&=(0,-1,0) ,\\ \tau_5&=(0,0,1) ,\\ \tau_6&=(0,0,-1) . \end{aligned} \quad (12)$$

In this case, the total self-energy describing the whole effect of six Bethe lattices attached to any atom of the system is

$$\underline{\Sigma}_T=6\begin{bmatrix} \sigma_{ss} & 0 & 0 & 0 & 0 \\ 0 & \frac{1}{3}(\sigma_{pp\sigma}+2\sigma_{pp\pi}) & 0 & 0 & 0 \\ 0 & 0 & \frac{1}{3}(\sigma_{pp\sigma}+2\sigma_{pp\pi}) & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{3}(\sigma_{pp\sigma}+2\sigma_{pp\pi}) & 0 \\ 0 & 0 & 0 & 0 & \sigma_{s^*s^*} \end{bmatrix} . \quad (13)$$

As before, Eq. (5) determines the unknown irreducible elements of the self-energy matrix.

B. Self-consistent effective-medium approximation

The construction of an effective medium corresponding to more complex systems is also possible. We have in mind systems showing deviations from perfect short-range order either because the continuous random network (CRN) is formed by more than one atomic species or because several kinds of short-range configurations are possible in the neighborhood of the same chemical element (Si, in this work). An example of the first kind of system is amorphous-silicon nitride:[28,29] Si atoms show tetrahedral bonding to random atoms, whereas N atoms are surrounded by three Si atoms in a planar or somewhat pyramidal configuration. Ill-coordinated *a*-Si belongs to the second class of materials: Si is the only chemical element, but more than one nearest-neighbor configuration should be taken into account. In these cases, Eq. (5) must be substituted by some averaging procedure that takes into account all possible configurations about an arbitrary atom and the corresponding configuration probabilities. It has been proved[31,32] that a very convenient way to obtain an averaged effective medium is the definition of self-energy matrices through averages over *local* Green functions. We define as many different self-energy matrices as there are different kinds of atoms belonging to the complex system: two for silicon nitride (the first saturating Si atoms and the second playing the same role about N atoms) and three for ill-coordinated Si if coordinations 3, 4, and 5 are taken into account.

Let us write the equations describing more or less ill-coordinated Si. Later (subsection III D), similar averaging equations are used for liquid Si. A CRN is taken as the structural model, and the presence of threefold- and fivefold-coordinated Si atoms in addition to standard fourfold-coordinated Si atoms is considered. We define three irreducible self-energy matrices $\underline{\Sigma}^3_{(1,0,0)}$, $\underline{\Sigma}^5_{(1,0,0)}$, and $\underline{\Sigma}^4_{(1,0,0)}$ that simulate the average effect of random Cayley trees connected along the (1,0,0) direction to threefold-, fourfold-, and fivefold-coordinated Si atoms, respectively. Now, the self-consistency equations defining the effective medium are the following:

$$(E\underline{1}-\underline{E}_0-\underline{\Sigma}^3_T)^{-1}=\sum_{i=3}^{5} p_{3i}\{E\underline{1}-\underline{E}_0-(\underline{\Sigma}^3_T-\underline{\Sigma}^3_{(1,0,0)})-\underline{V}_{3i}[E\underline{1}-\underline{E}_0-(\underline{\Sigma}^i_T-\underline{\Sigma}^i_{(-1,0,0)})]^{-1}\underline{V}^\dagger_{3i}\}^{-1}\ , \tag{14a}$$

$$(E\underline{1}-\underline{E}_0-\underline{\Sigma}^4_T)^{-1}=\sum_{i=3}^{5} p_{4i}\{E\underline{1}-\underline{E}_0-(\underline{\Sigma}^4_T-\underline{\Sigma}^4_{(1,0,0)})-\underline{V}_{4i}[E\underline{1}-\underline{E}_0-(\underline{\Sigma}^i_T-\underline{\Sigma}^i_{(-1,0,0)})]^{-1}\underline{V}^\dagger_{4i}\}^{-1}\ , \tag{14b}$$

$$(E\underline{1}-\underline{E}_0-\underline{\Sigma}^5_T)^{-1}=\sum_{i=3}^{5} p_{5i}\{E\underline{1}-\underline{E}_0-(\underline{\Sigma}^5_T-\underline{\Sigma}^5_{(1,0,0)})-\underline{V}_{5i}[E\underline{1}-\underline{E}_0-(\underline{\Sigma}^i_T-\underline{\Sigma}^i_{(-1,0,0)})]^{-1}\underline{V}^\dagger_{5i}\}^{-1}\ , \tag{14c}$$

where p_{ij} is the probability that an atom of coordination i is bonded to an atom of coordination j and V_{ij} is the corresponding interatomic interaction matrix [$\underline{V}$ is given by Eq. (6) for a standard Si—Si bond]. Pair probabilities p_{ij} are normalized,

$$\sum_{j=3}^{5} p_{ij}=1\ ,$$

and are compatible with the site distribution.

In the absence of experimental information about first-neighbor configurations around threefold- and fivefold-coordinated Si atoms, the total self-energy matrices are constructed assuming tetrahedral configurations for threefold-coordinated atoms and the *canonical* configuration[5] for fivefold-coordinated atoms:

$$\underline{\Sigma}^5_T=\sum_{i=1}^{5}\underline{\Sigma}^5_{\tau_i}\ , \tag{15}$$

with τ vectors given by

$$\begin{aligned} \tau_1&=(-1,0,0)\ ,\\ \tau_2&=\tfrac{1}{3}(1,2\sqrt{2},0)\ ,\\ \tau_3&=\tfrac{1}{3}(1,-\sqrt{2},\sqrt{6})\ ,\\ \tau_4&=\tfrac{1}{3}(1,-\sqrt{2},-\sqrt{6})\ ,\\ \tau_5&=(1,0,0)\ . \end{aligned} \tag{16}$$

A subtle point must be considered whenever Eq. (14a) is used. When a (3,3) pair is studied, the local Green function on each of both atoms is a function of the dihedral angle defined by the two dangling bonds on nearest-neighbor atoms. Therefore, an additional averaging over dihedral angles must be done in order to obtain a $\underline{\Sigma}^3_{(1,0,0)}$ matrix showing the irreducible form. This means that Eq. (14a) is a formal equation in which the (3,3) term is actually an average over dihedral angles. Although the irreducible form of $\underline{\Sigma}^3_{(1,0,0)}$ is recovered summing a small number of dihedral angles, good convergence of the averaging needs the consideration of several hundreds of terms. That means that, finally, the average is not done over three short-range-order configurations but over several hundreds of configurations.

As in the simpler case of Eq. (5), the unknown variables $\sigma^3_{ss}, \sigma^4_{ss}, \ldots, \sigma^5_{s^*s^*}$ appear on both sides of Eq. (14) and again an iterative numerical procedure is necessary to get the solution.[36] Once the self-energy matrices have been determined, the averaged local Green function is given by

$$\underline{G}=\sum_{i=3}^{5} x_i(E\underline{1}-\underline{E}_0-\underline{\Sigma}^i_T)^{-1}\ , \tag{17}$$

where x_i is the concentration of i-fold-coordinated Si atoms.

III. RESULTS

After the introduction of random Bethe lattices and the effective-medium approach, let us proceed to the exposition of our calculations and main results.

A. Isolated undercoordinated and overcoordinated atoms in *a*-Si

Recently, Pantelides[5–8] introduced a new and quite original point of view regarding paramagnetic defect centers in amorphous silicon. According to his point of view, the existence of dangling bonds (threefold-coordinated Si atoms) in the continuous random network describing the atomic structure of *a*-Si is followed by the presence of floating bonds produced by overcoordination (fivefold-coordinated Si atoms). Both kinds of defects are primitive conjugate defects in *a*-Si and should be treated equally. Certainly, an undercoordinated atom can be transformed continuously into a regular fourfold-coordinated atom through a gradual bonding with a second atom of initial coordination equal to 4. In the *canonical* configuration[5] the fifth bond is formed just opposite to one of the four existing bonds. At the end of the process, i.e., when the distance between both atoms is more or less the equilibrium Si-Si distance, the second atom becomes overcoordinated whereas the initial undercoordinated atom becomes regular. Alternatively, Pantelides proposed a mechanism of bond switching that simultaneously produces a pair of undercoordinated and overcoordinated Si atoms. Total-energy calculations done for clusters[9] and crystals of huge unit cell[37] using a parametrized classical form for the interatomic interactions seem to favor the formation of fivefold-coordinated centers.

Four years after its introduction by Pantelides, overcoordination in amorphous silicon remains a very interesting but not yet confirmed prediction. This unsatisfactory situation is borne out of the difficulty of distinguishing between effects due to dangling and floating bonds. EPR experiments can be alternatively explained by both kinds of defects.[13,14] We suggest a new way to attack this problem based on the important differences between the wave functions of dangling- and floating-bond defect states: *while single defect states appear practically at the same energy, pairs of defects show a pronounced dispersion.* Therefore, the careful global analysis of *all* the states within the gap would allow, in principle, not only the confirmation of the existence of both kinds of conjugate defects but also the knowledge of their concentration in a particular specimen.

We have used Eqs. (1)–(13) in conjunction with the Vogl *et al.* Hamiltonian[33] in order to study isolated undercoordinated or overcoordinated Si atoms. The DOS of the ideal fourfold-coordinated Bethe lattice shows an energy gap of 1.91 eV between −0.955 and 0.955 eV relative to the sp^3-hybrid level (see Fig. 1). It will be considered as the pseudogap or mobility gap of good-quality hydrogenated *a*-Si. Once the irreducible $\underline{\Sigma}_{(1,0,0)}$ is known, the local density of states on Si atoms of i coordination is given by

$$N_i(E) = -\frac{1}{\pi}\,\mathrm{Im}\,\mathrm{Tr}[(E\underline{1}-\underline{E}_0-\underline{\Sigma}_T^i)^{-1}]\;, \tag{18}$$

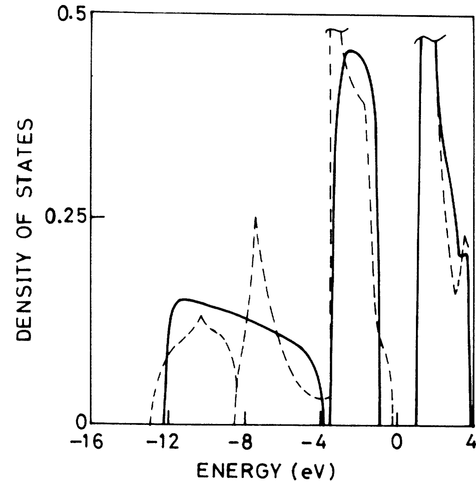

FIG. 1. Density of states of the diamond phase of crystalline Si as given by the sp^3s^* tight-binding Hamiltonian compared with the density of states of an ideal tetrahedrally coordinated Si Bethe lattice described by the same tight-binding parameters. The energy origin is the orbital sp^3-hybrid level.

where the i superindex of the total self-energy means that i branches of the ideal Bethe lattice are used to saturate the atom under study. Undercoordinated Si has been saturated along tetrahedral directions while configurations showing the greatest symmetry have been used for overcoordinated Si except for fivefold-coordinated Si. In this case, the *canonical* configuration [Eqs. (15) and (16)] has been used. Nevertheless, we have realized that the energy of the defect level produced by a floating bond is weakly dependent on the precise atomic configuration around it. The total number of nearest-neighbor atoms is

TABLE I. Localized states introduced into the pseudogap by isolated undercoordinated or overcoordinated Si atoms and by isolated pairs of nearest-neighbor Si atoms with coordination different from 4. Energies relative to the top of the valence band are given in eV. Weights on the defect atom and on its nearest-neighbor atoms appear in the third and fourth columns, respectively.

Center	Gap states	On-site weight	N-n weight
1			
2	0.01	0.10	0.06
3	1.21	0.67	0.06
5	1.21	0.0	0.09
6	1.21	0.0	0.22
7	1.21	0.0	0.31
	1.89	0.0	0.02
8	1.21	0.0	0.39
	1.81	0.19	0.04
(3,3)	Two bands between	Ranging from	
	0.84 and 1.58	0.34 to 0.41	
(3,5)	0.97	(0.40,0.02)	
	1.44	(0.34,0.02)	
(5,5)	0.81	(0.06,0.06)	
	1.37	(0.03,0.03)	
	1.89	(0.06,0.06)	

the relevant magnitude in this case. On the other hand, Fedders and Carlsson[16,17] discuss the dependence of energy levels and wave functions for threefold- and fivefold-coordinated Si atoms embedded in a Bethe lattice described by a more-complex tight-binding Hamiltonian: next-nearest-neighbor interactions are included. In that case, the s or p character of the dangling-bond wave function shows a strong dependence on relaxation, whereas the energy level introduced by the floating bond into the Si gap is in agreement with the detailed atomic configuration. While our calculations show the same behavior for the dangling bond, we do not find strong dependence for the floating-bond level. This fact suggests that next-nearest-neighbor interactions are playing a major role in the shift of the defect level through a large part of the mobility gap found by Fedders and Carlsson.

Results of our calculations are compiled in Table I, where the weight of the wave function on the defect and nearest-neighbor atoms is also given. These weights provide a rough indication of the localization character of the wave function. For example, the defect state produced by fivefold-coordinated Si has no weight on the overcoordinated atom and only 45% on the shell of nearest-neighbor atoms, confirming the relative delocalization argued by Pantelides[5-8] in his applications of floating bonds.

Perhaps the most surprising result contained in Table I is the equality of the energy levels of defect states produced by both threefold- and fivefold-coordinated Si atoms. For a better understanding of this point we have studied a continuous transformation from one defect to the other. To this end, we consider a (3,4) pair that is initially uncoupled. Then, we switch on gradually the interaction through an interaction matrix $\lambda \underline{V}$. Finally, we have a (4,5) pair when λ reaches 1. The result is quite surprising and reinforces the point of view of conjugation: a defect state is always introduced into the semiconducting gap at an energy $E_v + 1.21$ eV that *does not depend on* λ. Simultaneously, the wave function changes gradually between the extreme values given in Table I. Fedders and Carlsson[17] give a very nice and quite general proof of this property. Of course, that result is model dependent and some shift is expected after including rings, atomic relaxations, next-nearest-neighbor interactions, or orthogonalization effects into the model. On the basis of the present experience, we believe that these changes would be small in any case (say less than 0.2 eV). This approximate independence of the defect level shows the great difficulty of differentiating between both kinds of defects or even between a continuous distribution of defects going from undercoordination to overcoordination on the basis of energy levels.

Next, we have studied pairs of undercoordinated or overcoordinated Si atoms to learn about the effects of interference between different pairs of defect states. As before, we use the ideal Si Bethe lattice [Eqs. (1)–(13)] to saturate small clusters formed by a couple of nearest-neighbor Si atoms of coordination different from 4. We call the pair (i,j), where i and j are the coordinations. In that case, Eq. (18) should be generalized as follows to give the local DOS on the i atom:

$$N_{ij}(E) = -\frac{1}{\pi}\,\mathrm{Im}\,\mathrm{Tr}\{E\mathbb{1} - \underline{E}_0 - (\underline{\Sigma}_T^{i} - \underline{\Sigma}_{(1,0,0)}) - \underline{V}_{ij}[E\mathbb{1} - \underline{E}_0 - (\underline{\Sigma}_T^{j} - \underline{\Sigma}_{(-1,0,0)})]^{-1}\underline{V}_{ij}^{\dagger}\}^{-1}\ , \tag{19}$$

where superindices of $\underline{\Sigma}_T$ do not indicate different effective mediums [as they do in Eqs. (14)] but only different local configurations constructed as a sum of rotations of the same irreducible $\underline{\Sigma}_{(1,0,0)}$ matrix. As discussed in Refs. 24 and 25, defect states produced by (3,3) pairs, i.e., by pairs of dangling bonds on nearest-neighbor atoms, depend on the dihedral angle defined by them. There, the dispersion of the defect states as a function of the dihedral angle was given. The results for (3,5) and (5,5) pairs are similar. They are given in Table I together with a summary concerning (3,3) bands. We avoided averages over dihedral angles for (3,5) and (5,5) pairs selecting the [100] direction as the fifth bond direction of fivefold-coordinated atoms. Our choice is based on topological constraints for (5,5) pairs and on convenience for (3,5) pairs. Nevertheless, we have checked that different (3,5) configurations give negligible dispersion compared with the one showed by (3,3) pairs. While the bands produced by (3,3) pairs can be understood easily as bonding and antibonding linear combinations of the localized states introduced by separate dangling bonds, the (5,5) defect produces besides bonding and antibonding states a quite different state that lies very close to the bottom of the conduction band. This third state becomes localized by the large potential well around a couple of overcoordinated Si atoms.

B. Formation energy of coordination defects in *a*-Si

In spite of the limitations inherent to an empirical method like tight-binding, we have studied how large is the energy needed to get an isolated defect. To this end, we have used the scattering method[38] to calculate the *total* variation of the density of states following the coupling of a dangling bond and a fourfold-coordinated atom to produce a floating bond. Then, the energy change has been calculated within Chadi's tight-binding scheme.[39]

For the sake of completeness, let us collect all the needed formulas. The total energy is written as the sum of two terms:

$$E_T = E_{bs} + U\ , \tag{20}$$

where the first term is a sum over occupied one-electron energy levels

$$E_{bs} = \sum_{\substack{\text{occupied}\\ \text{levels}}} E_\alpha \tag{21}$$

and the second term is a short-range term taking into account ion-ion Coulomb repulsion and the double counting of the electron-electron interaction included in the sum over occupied energy levels; it is approximated as a sum over all system bonds and expressed as a Taylor ex-

pansion around the equilibrium bond length. Usually, the leading first three terms are retained:

$$U=\sum_{\text{bonds}}(U_0+U_1\varepsilon+U_2\varepsilon^2)\ , \tag{22}$$

where ε is the relative bond stretching defined by

$$\varepsilon=(d-d_0)/d_0\ . \tag{23}$$

Now, total-energy changes are given as the sum of the changes of both energy contributions:

$$\Delta E_T=\Delta E_{bs}+\Delta U\ . \tag{24}$$

Scattering theory is used to obtain the total change of the DOS when a *new* interaction $\underline{V}$ is switched within a system described by the Green function $\underline{G}_0$. A phase shift is defined:

$$\eta(E)=\arg[\det(\underline{1}-\underline{G}_0\underline{V})]\ , \tag{25}$$

from which the DOS variation is obtained:

$$\Delta N(E)=-\frac{1}{\pi}\frac{d\eta(E)}{dE}\ . \tag{26}$$

In our case, a bond is broken removing one of the Si-Si interactions given by matrix $\underline{V}$ of Eq. (6) and a new bond is formed connecting through the same matrix two parts of the system that were uncoupled until this moment. Once the total DOS is known, the change of the band-structure term is given by the following integral:

$$\Delta E_{bs}=\int_{-\infty}^{E_F}E\,\Delta N(E)dE\ . \tag{27}$$

Contributions coming from the short-range term are twofold. A quantity U_0 should be added whenever a new bond is formed, whereas the same quantity is substracted when a bond is removed. In addition to them, contributions are expected from the relaxation of bonds that are close to the defect. The last contributions enter through the U_1 and U_2 terms of Eq. (22).

The relevant features of our calculations are the following.

(i) The value of the structural parameters that reproduce cohesive energy, lattice constant, and bulk modulus of crystalline Si are $U_0=5.36$ eV, $U_1=-20.26$ eV, and $U_2=61.66$ eV.

(ii) The phase shift produced by the formation of a bond is given in Fig. 2: two states are removed from the gap and introduced into the upper part of the valence band. On the other hand, the formation of a 4-5 pair of atoms starting from a 3-4 pair produces the phase shift given in Fig. 3: localized states appear at the bottom of both parts of the valence band. Nevertheless, these states do not come from the gap but from the upper parts of the valence band. In conclusion, the number of gap states is not changed by this structural transformation.

(iii) The energy needed to break a bond, i.e., to form two dangling bonds, is 2.38 eV [this energy is very close to half of the cohesive energy of Si—4.63 eV—that corresponds to two bonds (four dangling bonds)]. This accurate result gives credit to the tight-binding estimation.

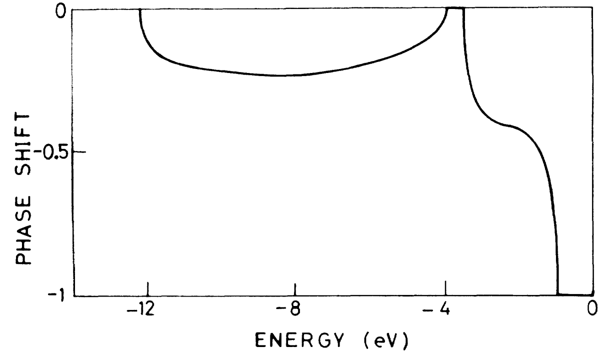

FIG. 2. Phase shift produced by the formation of a bond starting from two isolated dangling bonds.

(iv) The formation of a fivefold-coordinated Si atom starting from a threefold-coordinated atom requires 0.13 eV.

(v) We have estimated the energy gained through atomic relaxation around the defect. Relaxation around a dangling bond in *a*-Si is very small: a geometry optimization around a dangling bond allows a reduction of 0.03 eV in formation energy of an undercoordinated atom. The minimum is obtained when backbonds are 1.5% shortened and bond angles between the dangling bond and backbonds are reduced by 3°. Relaxation of further atoms is meaningless within our structural short-range-order model.

(vi) Finally, an ideal fivefold-coordinated Si atom in the *canonical* configuration needs 1.32 eV to be formed, whereas the formation of a dangling bond requires only 1.19 eV (1.16 eV if relaxation is allowed). Our estimates are much larger than the mean formation energies of 0.3 eV (fivefold-coordinated atom) and 0.6 eV (threefold-coordinated atom) obtained by Kelires and Tersoff[37] and, also, the values of 0.6 and 0.8 eV quoted by Pantelides.[7] Presently, it is not possible to decide among these values: some *ab initio* local-density-functional calculation would be needed. On the other hand, Phillips[11] has argued against the relevance of an equilibrium property (forma-

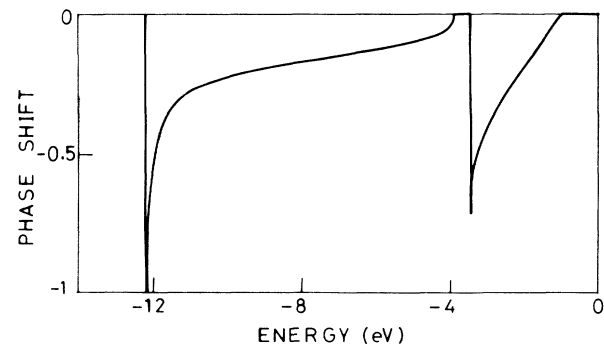

FIG. 3. Phase shift produced by the formation of a 4-5 pair starting from a 3-4 pair. The total variation of the DOS is obtained from this phase shift [Eq. (25)] and it gives (apart from a U_0 term) the difference of formation energies between a floating bond and a dangling bond.

tion energy) for the description of a nonequilibrium process like chemical vapor deposition.

C. Electronic structure of ill-coordinated amorphous silicon

In this subsection, we consider an effective medium including finite concentrations of both dangling and floating bonds, or in a different nomenclature, a continuous random network with finite amounts of both threefold- and fivefold-coordinated Si atoms. Equation (14) has been employed assuming random bonding among atoms belonging to the network; that means that probabilities p_{ij} are proportional to the number of bonds participated by j-fold-coordinated Si atoms: jx_jN, x_j being the percentage of j-fold-coordinated atoms and N the whole number of atoms. Since the sum of probabilities is 1 for every bond in the system, the following normalization condition is obtained:

$$\sum_{j=3}^{5} p_{ij} = \sum_{j=3}^{5} C(jx_jN) = 1 \ .$$

Once the normalization constant C is known,

$$C = \frac{1}{N}\left[\sum_{j=3}^{5} jx_j\right]^{-1} ,$$

the probability p_{ij} is given by

$$p_{ij} = jx_j\left[\sum_{k=3}^{5} kx_k\right]^{-1} .$$

All $\underline{V}_{ij}$ matrices have been set equal to $\underline{V}$ [Eq. (4)], i.e., bond-length fluctuations have not been considered. We have taken $x_3 = x_5 = 0.001$ and $x_4 = 0.998$ to work with values that give measurable effects. This concentration of paramagnetic defects is close to values found in *technologically uninteresting* a-Si samples but far from defect concentrations of *good-quality* hydrogenated a-Si samples. Local densities of states on threefold-, fourfold-, and fivefold-coordinated atoms are given in panels (a), (b), and (c) of Fig. 4, respectively. Perhaps, the most interesting feature is the broadening appearing about the main defect band centered at $E_v + 1.21$ eV due to the explicit inclusion within our configurational average of a continuous distribution of dihedral angles for (3,3) pairs. The form of the band is quite relevant, showing a clear decrease when the band limits are approached. Besides this feature, bands introduced by (3,5) and (5,5) pairs appear about the energies of the corresponding defect states of the isolated pairs. The identification is possible thanks to the previous study (see Table I). These new bands coming from interference effects between the different types of coordination defects are mainly localized on threefold- and fivefold-coordinated atoms (top and bottom panels of Fig. 4, respectively) whereas their weight on fourfold-coordinated atoms is negligible (central panel of Fig. 4). It is very easy to understand this feature: while the probability of the appearance of a pair of defects is of order $x_3 = x_5 = 0.001$ in the neighborhood of a defect, the same probability decreases to an order of $x_3^2 = x_5^2 = 10^{-6}$ in the neighborhood of a regular atom. The appearance of new bands within the mobility gap due to the presence of ill coordination in the random network opens the possibility of a clear experimental detection of floating bonds. In principle, an unambiguous detection of these new states would suffice to decide between undercoordination or overcoordination, or even to know the precise combination of both types of defects.

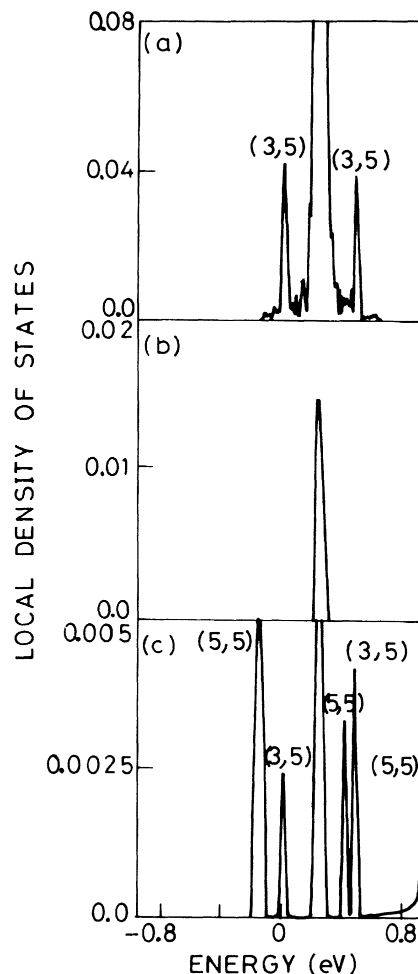

FIG. 4. Local densities of states of amorphous silicon modeled by a continuous random network containing 0.1% of dangling bonds (threefold-coordinated Si atoms), 0.1% of floating bonds (fivefold-coordinated Si atoms), and 99.8% of regular Si atoms. (a), (b), and (c) show the local density of states on threefold-, fourfold-, and fivefold-coordinated Si atoms, respectively. All the bands coming from interference effects between defects have been labeled accordingly. The band centered at 0.25 eV ($E_v + 1.21$ eV) is a superposition of both dangling- and floating-bond defect levels and, also, of (3,3) pairs (see Table I). The energy origin is the same as in Fig. 1.

Further, we have increased the concentration of ill-coordinated atoms up to the values shown by a-Si clusters *grown* by computer simulation.[37,18] These structures are very deficient from the point of view of connectivity, i.e., the quasiperfect short-range order present in good-quality a-Si samples is absent from the quenched liquid

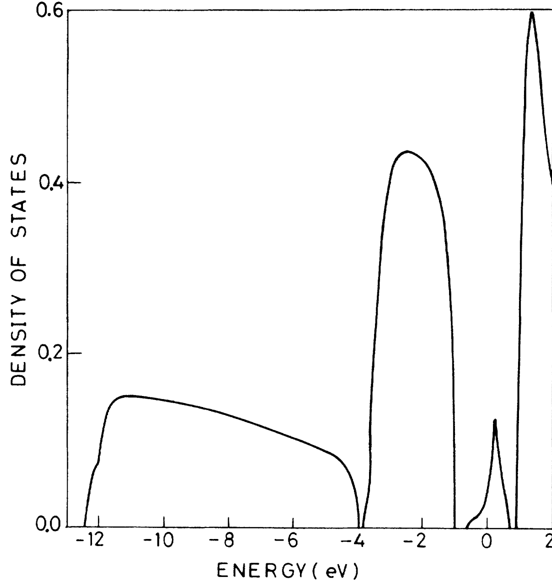

FIG. 5. Average density of states of amorphous silicon modeled by a continuous random network containing 2% of dangling bonds (threefold-coordinated Si atoms), 6% of floating bonds (fivefold-coordinated Si atoms), and 92% of regular Si atoms. The energy origin is the same as in Fig. 1.

obtained through numerical simulation. Both undercoordinated and overcoordinated atoms appear very frequently within the atomic structure. Applying our theory to a random Bethe lattice containing 6% floating bonds and 2% dangling bonds, a broad band of 1.3-eV width is obtained. This band contains 0.115 states per atom and practically closes the mobility gap (Fig. 5). The Fermi level lies at 0.35 eV, very close to the energy at which the defect DOS reaches its maximum value, a situation that suggests a metallic behavior for such a system. Although a quite presumable result, that is the first quantitative determination within mean-field theory of the catastrophe happening to the mobility gap when some percentage of Si atoms are allowed to have coordination different from 4.

D. Electronic structure of liquid silicon

State-of-the-art results for both the atomic and electronic structure of *l*-Si have been reported by Stich *et al.*[21] Molecular dynamics is done within a density-functional formalism in the local-density approximation and using norm-conserving pseudopotentials. Beside this sophisticated calculation, a mean-field approach that uses an empirical Hamiltonian solved for a model structure seems to be out of place. Nevertheless, we think that a tight-binding theory of the electronic structure of *l*-Si is relevant, both because of its simplicity (our program codes can usually be run in a few hours on a microcomputer) and versatility. For example, local deviations from homogeneity and their consequences on the DOS can be studied very carefully, as in standard applications of the cluster–Bethe-lattice method.[23] Moreover, it is interesting to know how the tools that are being used in current research on the solid phases of Si work for *l*-Si.

Structural information on the liquid phase of Si is given in the experimental works reported by Waseda and Suzuki[40] and Gabathuler and Steeb.[41] After melting, the coordination number of Si increases to an average value of 6.4, indicating a partial collapse of the tetrahedral network; this important structural change is strongly reflected in the electronic properties, which show a transition from semiconducting to metallic behavior. First-principles calculations[21] show that both coordination and bond-angle distributions are rather broad. Therefore, it is not very useful to interpret the local order of *l*-Si in terms of the high-pressure metallic phases of *c*-Si. Instead of such a structural model showing larger but fixed coordination, a network showing random coordination about a mean value close to 6 is more appropriate. In what follows, we focus on the consequences of Si overcoordination on the electronic properties of *l*-Si. The atomic structure of liquid silicon is modeled by a continuous random network containing fivefold-, sixfold-, and eightfold-coordinated Si atoms appearing in equal parts. In this way the average Si atom coordination of the model (6.3) is similar to the reported experimental result (6.4). Connections among them are random but the neighborhood of each kind of atom is always the same.

Averaging of the CRN leads to the following self-consistency equations:

$$(E\underline{1}-\underline{E}_0-\underline{\Sigma}_T^5)^{-1}=\sum_{i=5,6,8} p_{5i}\{E\underline{1}-\underline{E}_0-(\underline{\Sigma}_T^5-\underline{\Sigma}_{(1,0,0)}^5)-\underline{V}_{5i}[E\underline{1}-\underline{E}_0-(\underline{\Sigma}_T^i-\underline{\Sigma}_{(-1,0,0)}^i)]^{-1}\underline{V}_{5i}^\dagger\}^{-1}\,, \quad (28a)$$

$$(E\underline{1}-\underline{E}_0-\underline{\Sigma}_T^6)^{-1}=\sum_{i=5,6,8} p_{6i}\{E\underline{1}-\underline{E}_0-(\underline{\Sigma}_T^6-\underline{\Sigma}_{(1,0,0)}^6)-\underline{V}_{6i}[E\underline{1}-\underline{E}_0-(\underline{\Sigma}_T^i-\underline{\Sigma}_{(-1,0,0)}^i)]^{-1}\underline{V}_{6i}^\dagger\}^{-1}\,, \quad (28b)$$

$$(E\underline{1}-\underline{E}_0-\underline{\Sigma}_T^8)^{-1}=\sum_{i=5,6,8} p_{8i}\{E\underline{1}-\underline{E}_0-(\underline{\Sigma}_T^8-\underline{\Sigma}_{(1,0,0)}^8)-\underline{V}_{8i}[E\underline{1}-\underline{E}_0-(\underline{\Sigma}_T^i-\underline{\Sigma}_{(-1,0,0)}^i)]^{-1}\underline{V}_{8i}^\dagger\}^{-1}\,, \quad (28c)$$

where p_{ij} is the probability that an atom of coordination i is bonded to an atom of coordination j and $\underline{V}_{ij}$ is the corresponding interatomic interaction matrix [$\underline{V}$ is given by Eq. (6) for a standard Si—Si bond]. The total self-energy matrices are constructed assuming the following fixed configurations around each kind of atom (each kind of coordination). Fivefold-coordinated atoms are described by[42]

$$\underline{\Sigma}_T^5=\sum_{i=1}^{5}\underline{\Sigma}_{\tau_i}^5\,, \quad (29)$$

with τ vectors given by

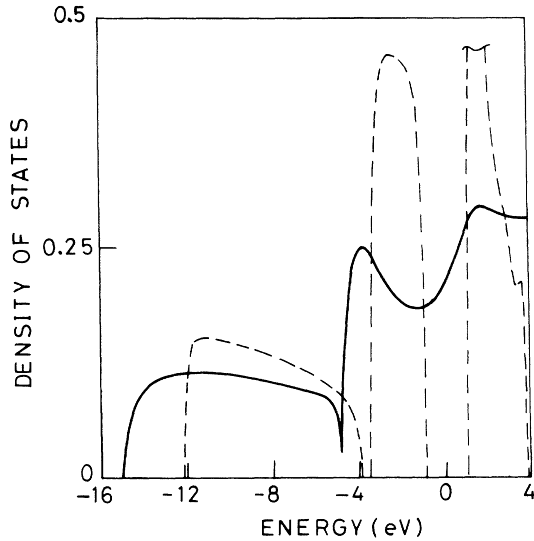

FIG. 6. Average density of electronic states of liquid silicon modeled by a continuous random network containing 33.3% of fivefold, 33.3% of sixfold, and 33.3% of eightfold Si atoms (solid line). The corresponding curve for amorphous Si (ideal fourfold network) is given to allow a direct comparison (dashed line). The energy origin is the same as in Fig. 1.

$$\begin{aligned}\tau_1&=(1,0,0)\ ,\\ \tau_2&=(-1,0,0)\ ,\\ \tau_3&=(0,1,0)\ ,\\ \tau_4&=\tfrac{1}{2}(0,-1,\sqrt{3})\ ,\\ \tau_5&=\tfrac{1}{2}(0,-1,-\sqrt{3})\ .\end{aligned} \tag{30}$$

Sixfold-coordinated atoms are described by

$$\underline{\Sigma}_T^6=\sum_{i=1}^{6}\underline{\Sigma}_{\tau_i}^6\ , \tag{31}$$

with τ vectors given by

$$\begin{aligned}\tau_1&=(1,0,0)\ ,\\ \tau_2&=(-1,0,0)\ ,\\ \tau_3&=(0,1,0)\ ,\\ \tau_4&=(0,-1,0)\ ,\\ \tau_5&=(0,0,1)\ ,\\ \tau_6&=(0,0,-1)\ .\end{aligned} \tag{32}$$

Finally, eightfold-coordinated atoms are described by

$$\underline{\Sigma}_T^8=\sum_{i=1}^{8}\underline{\Sigma}_{\tau_i}^8\ , \tag{33}$$

with τ vectors given by the eight possible (1,1,1) directions.

Figure 6 contains the more relevant information: the average DOS in which the Fermi level lies at $E=0$, just the sp^3-hybrid orbital energy. Comparison with the DOS of a fourfold-coordinated Bethe lattice (dashed curve on Fig. 6) shows that while the lower s-p part of the valence band does not change very much, the upper p part mixes completely with the p states of the conduction band. Consequently, the gap shown by a-Si appears now completely filled by states, in agreement with the very sophisticated calculations by Car and Parrinello[20] and Stich *et al.*[21] The width of the occupied part of the valence band now reaches 15.3 eV. Comparison of this widening with the one obtained in Ref. 21 is very interesting. A value of about 14 eV is obtained within local-density-functional theory: the valence band of l-Si is wider than the one of a-Si, but the widening does reach the tight-binding value. The reason for this is quite simple: Si—Si bonds stretch as coordination increases; accordingly, tight-binding parameters should decrease and balance up to some extent the widening of the valence band produced by the larger coordination number.

IV. CONCLUDING REMARKS

We now summarize the main findings achieved.

(i) Inclusion of undercoordinated and overcoordinated Si atoms within a continuous random network modeling ideal hydrogenated amorphous silicon introduces a wealth of defect states within the mobility gap.

(ii) Unfortunately, it is not possible to distinguish floating from dangling bonds on the basis of the level of the defect state they introduce into the semiconducting gap.

(iii) Moreover, even a continuous distribution of isolated coordination defects, i.e., weak bonds of different strengths, will produce gap levels with the same binding energy.

(iv) Nevertheless, interference effects between states originating in different defect centers are critically dependent on the extension of wave functions. That makes a major difference between floating and dangling bonds.

(v) Therefore, we propose an experimental search to find some or all of these interference states in order to confirm or discard the presence of floating bonds in a-Si samples.

(vi) Formation energies have been obtained for coordination defects within standard tight-binding methods. After relaxation, 1.16 eV are needed for the formation of a dangling bond whereas 1.32 eV are necessary to produce a floating bond.

(vii) Average densities of states have been calculated for ill-coordinated a-Si. Small percentages of coordination defects are enough to fill the spectral gap.

(viii) The density of electronic states has been calculated for a very simple structural model of liquid Si. A metallic DOS and a broader valence band are obtained.

ACKNOWLEDGMENTS

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[42]Notice that we choose the most symmetric distribution of nearest neighbors around fivefold-coordinated Si atoms instead of the *canonical* configuration used to describe overcoordinated atoms in *a*-Si [compare Eq. (30) with Eq. (16)]. Firstly, there is no reason to maintain the *canonical* configuration in melted Si and, secondly, we have checked that the influence of the exact geometry on the DOS is almost negligible: coordination number is the relevant magnitude. Consequently, we keep the calculation as simple as possible and use the most symmetric configuration for *all* types of Si atoms.