PHYSICAL REVIEW B VOLUME 40, NUMBER 18 15 DECEMBER 1989-II

Correlation between electronic structure and local ordering in hydrogenated amorphous silicon

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(Received 21 December 1988; revised manuscript received 25 July 1989)

Nonparametrized calculations of the electronic structure of hydrogenated amorphous silicon are presented. The method of calculation is based on the cluster Bethe-lattice approximation. The Hamiltonian matrix elements and the equilibrium atomic distances are obtained via *ab initio* cluster calculations. The calculations are performed for isolated and clustered Si-H units in the silicon Bethe lattice. A two-peak structure in the hydrogen-related electronic density of states is found for dihydride and trihydride bonding. A three-peak structure in the density of states is found for different clustered arrangements of monohydride units. The position and assignment of the structure in the density of states is in qualitative agreement with ultraviolet-photoemission-spectroscopy data. It is shown that the finite-cluster calculations produce spurious structure in the density of states, and therefore they are not suited to obtain reliable densities of states. The charge transfer to hydrogen is found to be 0.16, 0.15, and 0.11 electron for the monohydride, dihydride, and trihydride configurations, respectively. The need for a nonparametrized calculation in infinite systems is discussed.

I. INTRODUCTION

In the last 15 years there has been continuing interest in the study of the electronic structure of hydrogenated amorphous silicon from both experimental and theoretical points of view.[1] Better and more realiable preparation techniques as well as better methods of calculation have led to an overall understanding of the main features found in the electronic spectra of *a*-Si:H. Nevertheless, some subtle details still remain, and the interpretation based on theoretical calculations is in some cases contradictory. In Fig. 1 we reproduce the ultraviolet photoemission spectra (UPS) of samples prepared in two different ways.[2] The different hydrogen-related peaks are labeled. The hump at -3 eV is a silicon *p*-like peak.

Cluster calculations[3-5] support the idea that the origin of the three-peak structure in the annealed samples [curve labeled (b) in Fig. 1] is due to single Si-H units, whereas other authors identify these peaks as being due to local ordering such as sixfold rings of bonds or clustering of hydrogen atoms.[6,7] The two-peak structure in the nonannealed samples [curve labeled (a) in Fig. 1] has been interpreted as being due to electronic-correlation effects at the hydrogen atom by some authors.[8] Others claim that this structure is due to the presence of the dihydride and trihydride units.[7]

We believe that some of these discrepancies are due to the fact that the calculations are performed for either finite systems or else using parametrized tight-binding Hamiltonians in infinite systems. To try to clarify the issue, we have developed a method that deals with infinite systems and a nonparametrized Hamiltonian such that its matrix elements depend on the specific atomic configuration. A realistic basis-function set is used, and the Hamiltonian matrix elements as well as the equilibrium atomic distances are obtained from *ab initio* calculations performed in large enough clusters of atoms. The transferability of these interactions to continuous structures is well justified as will be shown below. The advantage of such a method is that there are no adjustable pa-

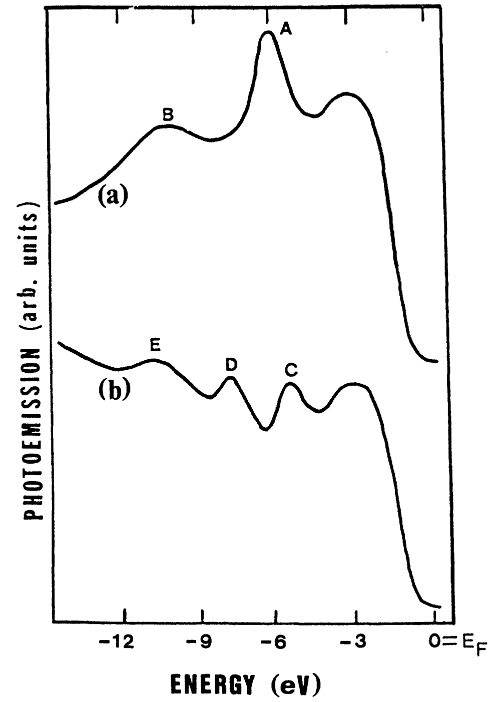

FIG. 1. UPS spectra of hydrogenated amorphous silicon (Ref. 1). Curve (a) stands for a glow-discharge sample deposited at a substrate of 250°C. Curve (b) refers to a sample sputtered with hydrogen at a substrate temperature of 350°C. Similar results are obtained by annealing (at 350 °C) the sample corresponding to curve (a) (see Ref. 1).

rameters, and the variation of the Hamiltonian matrix elements for different atomic configurations are included. We hope that with this method we can provide a unifying picture of the electronic structure of *a*-Si:H.

This paper is organized as follows. In Sec. II we describe the method of calculation and discuss its applicability to pure silicon. In Sec. III the method is applied to different configurations of hydrogen bonded to the silicon Bethe lattice. The results are compared with experimental data. Also, the vibrational modes of the different atomic arrangements are calculated. In Sec. IV the results are compared with other calculations. Finally, in Sec. V the conclusions of our work are drawn.

II. METHOD OF CALCULATION

Before discussing the case of amorphous silicon, we will describe how the calculation procedure works in crystalline silicon. We will assume a basis set formed by one *s* and three *p* atomic orbitals per silicon atom.[9] Each orbital is formed by four Gaussian functions. The effect of the core electrons is simulated with the appropriate pseudopotential[10] $V_{\rm ps}$ of the form[11]

$$V_{\rm ps} = -Z/r + \sum_l W_l(r) P_l \ , \tag{1}$$

where P_l is the projection operator on the wave functions of angular momentum l and W_l has the form

$$W_l(r) = \exp(-\alpha r^2) \sum_i C_i / r^{n_i} , \tag{2}$$

where the coefficients C_i and n_i are obtained from molecular calculations.

In order to obtain the matrix elements between atomic orbitals and the equilibrium distance between the atoms, we have performed total-energy calculations in finite silicon clusters with the surface orbitals saturated with hydrogenlike atoms.[12] The calculation is done in the closed-shell Hartree-Fock approximation.[13] The Fock-operator matrix elements are of the form

$$H_{ij} = H_{ij}^{\rm core} + \sum_{k,l} P_{kl} (\langle ij|kl \rangle - \tfrac{1}{2} \langle ik|jl \rangle) \ , \tag{3}$$

where P_{kl} is the matrix element of the density operator between orbitals k and l and

$$P_{ij} = 2 \sum_n^{\rm occ} c_i^n c_j^n \ . \tag{4}$$

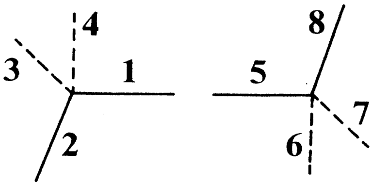

FIG. 2. Labeling of the silicon sp^3 orbitals in the diamond structure.

The c's are the coefficients of the atomic wave functions in the expansion of the total wave function. $\langle ij|kl \rangle$ stands for the double integral given by

$$\langle ij|kl \rangle = \int \int \phi_i(r_1) \phi_j(r_1) |r_1 - r_2|^{-1} \times \phi_k(r_2) \phi_l(r_2) dr_1 \, dr_2 \ . \tag{5}$$

The one-electron part of the Hamiltonian has the form

$$H^{\rm core} = \tfrac{1}{2} \nabla^2 - \sum_A Z_A / |r - r_A| \ . \tag{6}$$

The calculation is done self-consistently until the stable electronic configuration for a given distribution of atoms is obtained. In the finite-cluster calculations the sum in (6) includes all the atoms, and all the integrals (5) are included in the calculation. The total (electronic plus nuclear) energy is calculated for different atomic distances to obtain the stable configuration. We have done these calculations for different cluster sizes and have found that the results, as far as charge distributions and equilibrium distances are concerned, are fairly stable provided the silicon atom we are looking at has four silicon neighbors in the cluster.

To show how the method works we describe here a $\rm Si_5H_{12}^*$ cluster (H* stands for the hydrogenlike saturator) such that the silicon atoms are in the tetrahedral configuration. The equilibrium distance between silicon atoms is found to be 2.39 Å which compares well with the crystalline distance of 2.35 Å. We then extract from the cluster calculation the Hamiltonian matrix elements needed for the calculation of the infinite system. The overlap between sp^3 orbitals and the Hamiltonian matrix elements obtained in this way are given in Table I. The labeling of orbitals corresponds to Fig. 2. We will assume, throughout this work, interactions only between nearest-neighbor silicon atoms.

TABLE I. Hamiltonian matrix elements in eV between silicon sp^3 orbitals and the corresponding overlaps (third column). The first and second columns stand for the parameters corresponding to the $\rm Si_5H_{12}^*$ and the $\rm Si_8H_{18}^*$ clusters, respectively. The labeling of the orbitals is given in Fig. 2.

$\langle 1|H|1 \rangle = -10.2$	$\langle 1|H|1 \rangle = -10.5$	
$\langle 1|H|2 \rangle = -2.32$	$\langle 1|H|2 \rangle = -2.31$	
$\langle 1|H|5 \rangle = -12.39$	$\langle 1|H|5 \rangle = -12.39$	$\langle 1|5 \rangle = 0.5948$
$\langle 1|H|6 \rangle = -2.42$	$\langle 1|H|6 \rangle = -2.42$	$\langle 1|6 \rangle = 0.075\,31$
$\langle 2|H|7 \rangle = -0.51$	$\langle 2|H|7 \rangle = -0.57$	$\langle 2|7 \rangle = 0.040\,04$
$\langle 2|H|8 \rangle = 2.15$	$\langle 2|H|8 \rangle = 2.33$	$\langle 2|8 \rangle = -0.1285$

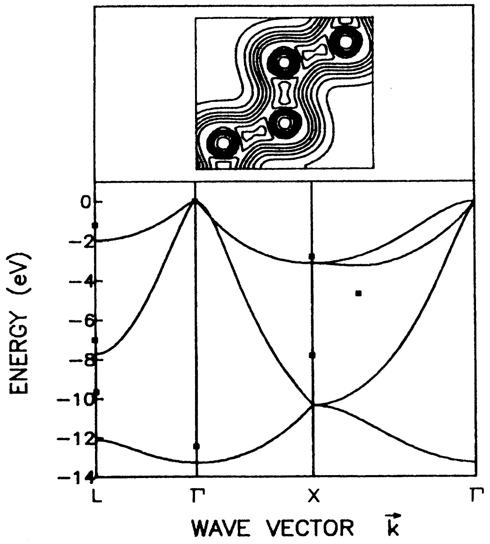

FIG. 3. Valence-band structure and total electronic charge distribution of silicon obtained with the parameters given in Table I. The origin of energies is the top of the band. The small squares at high-symmetry points indicate experimental values.

The band structure and charge distribution calculated with this approximation are shown in Fig. 3. There is a qualitative agreement with the experimental bands, the main discrepancy being the narrowness of the calculated p-like bands. This is due to the restriction to nearest-neighbor interactions.[14] This should be kept in mind when comparing the a-Si:H spectrum with experimental data. The calculated valence band is wider than found experimentally. This can be ascribed to the Hartree-Fock approximation. The total charge distribution is in agreement with other calculations, although there is a shallow dip in the charge at the middle of the bond characteristic of the Hartree-Fock approximation. We obtain an sp^3 hybridization corresponding to s- and p-orbital occupation of 1.44 and 2.56 electrons, respectively. These results are fairly satisfactory. It should be stressed that the above bands and charge distribution have been obtained without adjustable parameters and simply by assuming that the matrix elements between nearest neighbors are transferable from the cluster calculations. When changing the size or shape of the cluster, we obtain similar results to the above. For a $Si_8H^*_{18}$ the matrix elements are given in Table I. The calculations with these parameters are very similar to those reported above. These calculations show that although the electronic distribution for the cluster and for the crystal are different (in a cluster the energy spectrum is discrete, whereas in a crystal it is continuous), the Hamiltonian matrix elements are rather similar.

III. RESULTS FOR a-Si:H

To simulate the amorphous silicon network we will assume the Bethe-lattice configuration. This approximation has proven to be very useful for tight-binding Hamiltonians.[7,15] As indicated above, we will keep only interactions between orbitals in nearest-neighbor atoms.

We calculate the matrix elements of the Green's function between the different orbitals in the atoms in the usual way, taking care of the subtleties introduced by the fact that we are using a nonorthogonal basis.[16–18] We therefore define a dual set of basis vectors $|\hat{\phi}\rangle$ such that

$$\langle \hat{\phi}_i|\phi_j\rangle=\delta_{ij} , \tag{7}$$

and

$$\sum_i |\hat{\phi}_i\rangle\langle\phi_i|=1 . \tag{8}$$

The matrix elements of the Green's function between these dual-basis orbitals satisfy the Dyson equation

$$\sum_i (E\langle\phi_j|\phi_i\rangle-\langle\phi_j|H|\phi_i\rangle)\langle\hat{\phi}_i|G(E)|\hat{\phi}_k\rangle=\delta_{jk} . \tag{9}$$

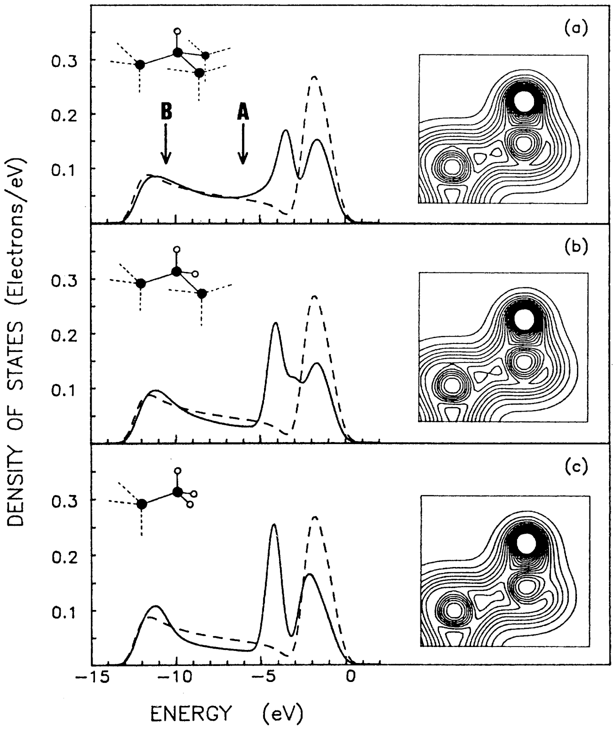

FIG. 4. Density of states and total charge distribution in the vicinity of hydrogen for the monohydride, dihydride, and trihydride configurations (a), (b), and (c), respectively. The densities of states have been obtained by adding up the densities of states of hydrogen and its nearest-neighbor silicon atoms. The dashed lines represent the pure silicon Bethe-lattice density of states. The spectra have been convoluted with a Gaussian function of 0.5 eV half-width at half maximum (HWHM). The charge distributions are plotted in a plane containing one Si—H bond and the Si—Si bonds in the "crystalline" (110) plane. In the dihydride and trihydride cases there are one and two hydrogen atoms out of plane, respectively. A and B stand for the peaks labeled in Fig. 1.

TABLE II. Hamiltonian matrix elements (in eV) between silicon sp^3 orbital and hydrogen s orbital at the vicinity of the hydrogen atom in the monohydride, dihydride, and trihydride configurations. The labeling corresponds to Fig. 5. In the dihydride and trihydride configurations the interaction between hydrogen atoms is indicated ($\langle 1|H|1'\rangle$).

Monohydride	Dihydride	Trihydride
$\langle 1\|H\|1\rangle=-11.64$	$\langle 1\|H\|1\rangle=-11.74$	$\langle 1\|H\|1\rangle=-11.88$
$\langle 2\|H\|2\rangle=-10.12$	$\langle 2\|H\|2\rangle=-10.11$	$\langle 2\|H\|2\rangle=-10.29$
$\langle 3\|H\|3\rangle=-10.09$	$\langle 3\|H\|3\rangle=-10.11$	$\langle 3\|H\|3\rangle=-10.23$
$\langle 1\|H\|2\rangle=-14.04$	$\langle 1\|H\|2\rangle=-14.11$	$\langle 1\|H\|2\rangle=-14.20$
$\langle 2\|H\|3\rangle=-2.31$	$\langle 2\|H\|3\rangle=-2.40$	$\langle 2\|H\|3\rangle=-2.33$
$\langle 3\|H\|4\rangle=-12.43$	$\langle 3\|H\|4\rangle=-12.50$	$\langle 3\|H\|4\rangle=-12.46$
	$\langle 1\|H\|1'\rangle=-2.53$	$\langle 1\|H\|1'\rangle=-2.54$

For the Bethe lattice an infinite set of difference equations can be written and solved to obtain the matrix elements

$$\hat{G}_{ij}(E)=\langle\hat{\phi}_i|G(E)|\hat{\phi}_j\rangle\ . \tag{10}$$

The local density of states at a given orbital labeled i is then given by

$$n_i(E)=-(1/\pi)\mathrm{Im}G_{ii}(E)\ , \tag{11}$$

where

$$G_{ij}(E)=\sum_k S_{ik}\hat{G}_{kj}\ , \tag{12}$$

where S_{ik} stands for the overlap between orbitals ϕ_i and ϕ_k. In Fig. 4 we show the results for isolated Si-H units in the silicon Bethe lattice. The results are for monohydride, dihydride, and trihydride bonding as indicated. The Hamiltonian matrix elements have been obtained as indicated above from different finite clusters of atoms. The equilibrium distance found for the Si—H bond is 1.52 Å, whereas the experimental one is 1.48 Å. The Hamiltonian matrix elements for the monohydride, dihydride, and trihydride configurations are given in Table II. The labeling of the different orbitals is shown in Fig. 5.

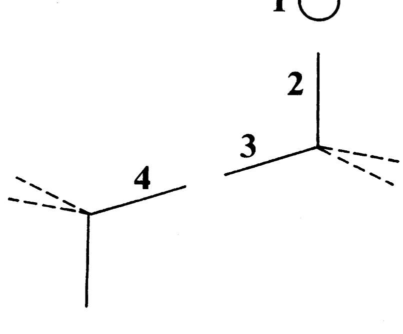

FIG. 5. Labeling of the silicon sp^3 orbitals and hydrogen s orbital at the vicinity of hydrogen. The dashed lines represent bonds pointing out of the plane of the page.. The circle represents the hydrogen s orbital.

Looking at the densities of states, we observe the following facts. In all three spectra there is a main hydrogen-related peak below the p-like silicon peak at approximately 4 eV below the the valence-band edge. This peak corresponds to that found experimentally[19] at around -6 eV (labeled A in Fig. 1). Its position in the calculation is higher in energy due to the narrowness of the silicon p-like bands due to the lack of second nearest-neighbor interactions. In despite of this error in the absolute position we find a shift of approximately 0.6 eV when going from the monohydride to the polyhydride configuration in agreement with the experimental results.[19] This shift is essentially due to the change in the matrix elements obtained in the cluster calculations. In the polyhydride configurations we obtain a second hydrogen-related peak (labeled B) at approximately -11 eV, again in fair agreement with the experimental data for nonannealed samples[19] (see Fig. 1).

We have also calculated the charge distribution and the atomic and bond charges in the vicinity of the defect. The total electronic charge distribution is given by

$$\rho(r)=\sum_{i,j}P_{ij}\phi_i(r)\phi_j(r)\ , \tag{13}$$

where

$$P_{ij}=-(2/\pi)\mathrm{Im}\int_{-\infty}^{E_F}\hat{G}(E)dE\ . \tag{14}$$

The atomic charge at atom labeled i is given by

$$Q_i=\sum_j P_{ij}\langle\phi_i|\phi_j\rangle\ . \tag{15}$$

The results for the total charge distribution are given in Fig. 4 and the atomic charges in Table III. The charge

TABLE III. Atomic charges near the hydrogen atom in the monohydride, dihydride, and trihydride configurations. Si* stands for the silicon atom attached to hydrogen and Q_{Si} is the total charge of the next silicon atom attached to it.

	Monohydride	Dihydride	Trihydride
Q_{H}	1.16	1.15	1.11
Q_{Si^*}	3.81	3.69	3.55
Q_{Si}	4.01	4.01	4.11

transferred to the hydrogen atom is in agreement with experiments.[20] Also, the charge at the silicon atom attached to it is in agreement with core-level-shift measurements that indicate that the charge transferred from the silicon atom is essentially proportional to the number of hydrogen atoms attached to it.[20]

In order to understand the origin of the three-peak structure of the spectrum found for the annealed samples (see Fig. 1), we have to restrict ourselves to monohydride configurations as indicated experimentally. As shown before [Fig. 4(a)], a single isolated Si-H unit gives rise to a single-peaked spectrum. We then look at possible clustered configurations of monohydride units. The results of the calculation for hydrogen bonded at a microsurface formed by seven atoms is given in Fig. 6(a). We observe the existence of three peaks in fair agreement with the experimental data (see Fig. 1). The reason for the presence of the new peaks *D* and *E* in the spectrum is the existence of silicon atoms bonded to hydrogen alternating with silicon atoms bonded to four silicon neighbors. This alternating structure opens a "pseudogap" as in binary compounds. This can be easily checked using simplified model Hamiltonians like the Weaire-Thorpe

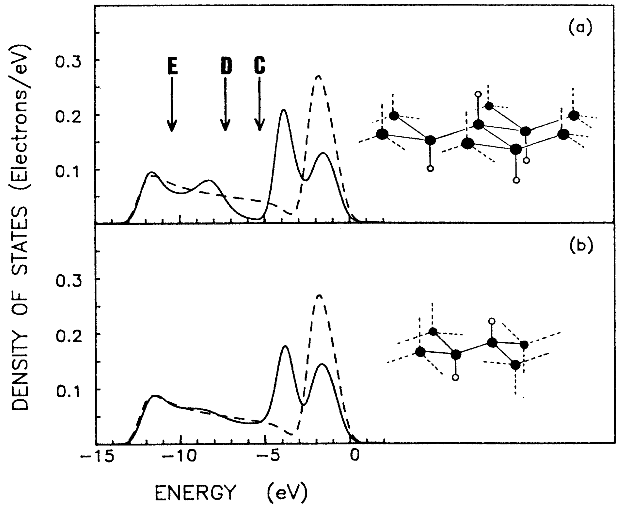

FIG. 7. Densities of states for two different clusterings of monohydride bonding. Notice that in both clusterings the hydrogen atoms are bonded to nearest-neighbor silicon atoms. The arrows indicate the position of the UPS observed peaks (see Fig. 1). The dashed line represents the silicon Bethe lattice. The spectra have been convoluted with a Gaussian function of 0.5 eV HWHM.

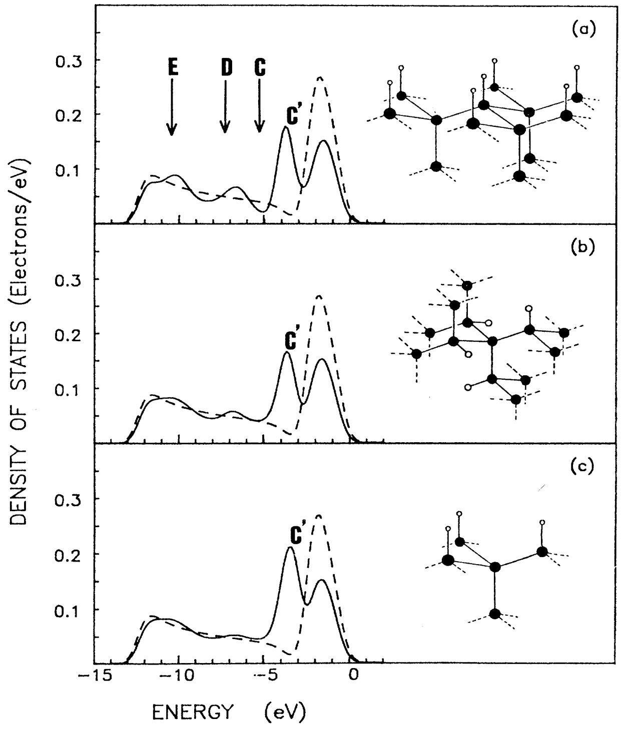

FIG. 6. Densities of states for three different clusterings of monohydride bonding. Notice that in all three configurations the hydrogen atoms are bonded to second-nearest-neighbor silicon atoms. The arrows indicate the position of the UPS observed peaks (see Fig. 1). The dashed line represents the pure silicon Bethe lattice. The spectra have been convoluted with a Gaussian function of 0.5 eV HWHM.

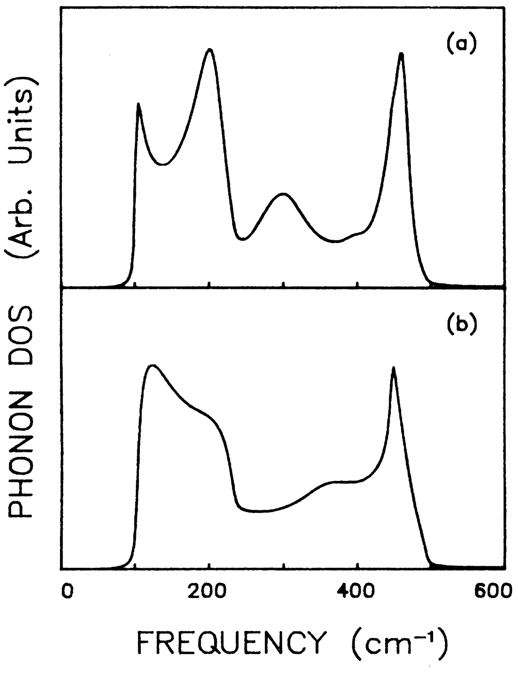

FIG. 8. Phonon densities of states for two different configurations of monohydride clustering. The density of states of (a) corresponds to the distribution of hydrogen as in Fig. 6(a). Similar results are obtained for the other clusterings shown in Fig. 6. The density of states at (b) corresponds to the clustering of Fig. 7(a). Notice in (a) the peak at 200 cm^{-1}. The peak at 100 cm^{-1} in (a) is due to the Bethe-lattice band edge.

one.[21] It is important to notice that if this is the origin of the double structure in the lower part of the valence band, it should be independent of the atomic configuration as long as the alternating structure prevails. To show this we have performed calculations for other configurations shown in Fig. 6. We observe again the three-peak structure at almost exactly the same positions. Also, for all the atomic arrangements, the peak labeled C' is about 0.6 eV higher than in the polyhydride case (Fig. 4), in agreement with experiments[19] (compare peaks labeled A and C in Fig. 1). Joannopoulos *et al.*[7] have argued that peaks labeled D and E are due to the presence of hydrogenated dimers in the bulk material. We have therefore performed similar calculations for hydrogenated dimers and clustered Si-H units such that hydrogen is singly bonded to adjacent silicon atoms. As in previous cases, the Hamiltonian parameters are obtained from the appropriate cluster calculations. The results are shown in Fig. 7. We obtain a double structure in the lower part of the spectrum which resembles the UPS curve. However, it seems that the structure near the bottom of the valence band is not an actual peak, but rather a band-edge feature. It is difficult, however, from these spectra to assess which atomic configuration is responsible for the appearance of peaks D and E in the UPS spectrum of annealed samples.

To gain more insight into the relevance of the above-discussed clustering of Si-H units, we have obtained the corresponding phonon density of states using the Born model. Results of the calculation for two representative clusterings are shown in Fig. 8. It is interesting to note that whereas the bonding of Si-H units in second-neighbor atoms reproduces the ir (Ref. 22) and neutron-scattering[23] observed peak at 200 cm^{-1}, the bonding in nearest-neighbor does not. The existence and the infrared activity of this peak has been already discussed.[24] This is an indication of the more plausible arrangement of Si-H units probably in microvoids. This type of monohydride clustering is present in the actual samples as ir data indicate.[25,26]

IV. COMPARISON WITH OTHER CALCULATIONS

Joannopoulos *et al.*[7] performed a calculation using a tight-binding parametrized Hamiltonian including up to second-neighbor interactions. The results of these calculations favor hydrogen dimer-type arrangement to explain the UPS spectrum of annealed samples. Our calculation, however, tends to support an explanation based on hydrogen bonded to second-neighbor silicon atoms. It is very difficult from these calculations to rule out either type of clustering, the actual sample being probably a mixture of both.

It has been suggested[3–5,7] that the hydrogen-related three-peak structure in the UPS spectrum of annealed samples is just due to isolated Si-H units. This has been based on finite-cluster calculations. As seen in Fig. 4, we do not obtain this three-peak structure. To clarify this point we have performed calculations of the density of states for clusters of increasing size up to infinite atoms in the Bethe-lattice configuration. Results of the calculations are shown in Fig. 9. We indeed observe the three-peak structure in the H-Si_4 saturated cluster in agreement with previous calculations. However, when increasing the size of the cluster, this structure is washed out with only the main hydrogen-induced peak remaining as shown in Fig. 4. This clearly demonstrates the inadequacy of using finite clusters of atoms to reproduce infinite systems densities of states and stresses again that isolated Si-H units do not reproduce the three-peak structure of the spectrum.

Anda *et al.*[8] have indicated that the two-peak structure in the nonannealed samples is due to the electronic correlation at the hydrogen atom. In our calculation the electron-electron interaction is incorporated through the integrals (ij/kl) which are all included explicitly in our cluster calculations. As indicated above, the single S-H units give rise to a single-peaked spectrum indicating a weak point in this interpretation.

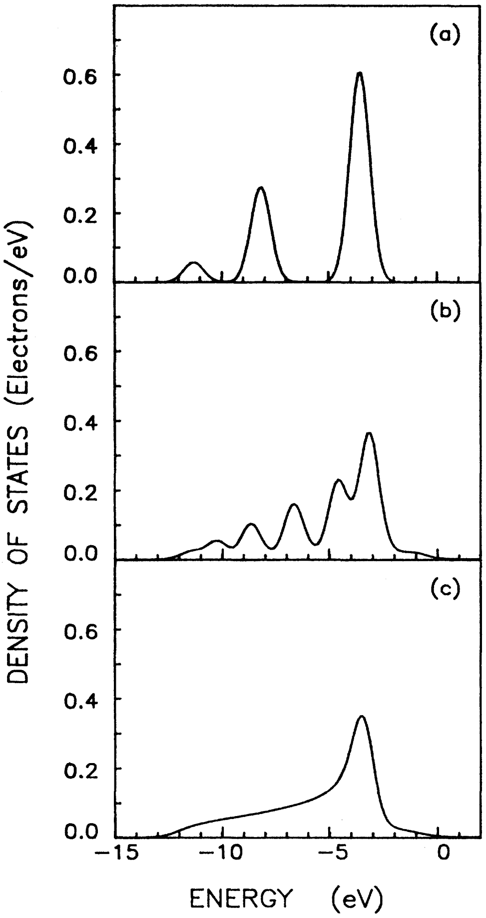

FIG. 9. Density of states at the hydrogen atom in the monohydride phase for different cluster sizes. (a) Local density of states in the H-Si_4 saturated cluster. (b) Local density of states for the H-Si_{364} saturated cluster. (c) Local density in the infinite system H–Bethe-lattice. The spectra have been convoluted with a Gaussian function of 0.5 eV HWHM.

V. CONCLUDING REMARKS

We have performed a detailed calculation of the electronic structure of hydrogenated amorphous silicon. The main ingredients of the calculations are the following.

(a) A realistic nonorthogonal atomic orbital basis.

(b) The Hamiltonian matrix elements between the basis functions are obtained from *ab initio* calculations in finite clusters of atoms.

(c) The amorphous network is simulated by a Bethe lattice such that only nearest-neighbor interactions are considered, and no rings of bonds are included in the atomic structure.

The calculations we have presented here have provided us with a unifying picture of the electronic structure of *a*-Si:H. The fact that we do not use parametrized Hamiltonians, as is usually done, enables us to reach more sound and realiable conclusions. Also, the use of a realistic, nonorthogonal basis, allows us to calculate charge distributions as well as charge transfers between the atoms.

The main results of the calculations are as follows.

(i) For equilibrium distances between silicon atoms as well as between silicon and hydrogen atoms, the results are in excellent agreement with experimental data.

(ii) For densities of states, the experimentally found two- and three-peak UPS structures are unambiguously assigned to single-polyhydride and clustered-monohydride atomic configurations, respectively. We have found that to obtain the three-peak structure in the UPS spectrum, clustering of monohydride units has to be considered.

(iii) For charge distribution and charge transfers, the calculated charge transfer between silicon atoms and hydrogen is in excellent agreement with the core-level-shift experimental results. We find that the charge transferred from the silicon atom attached to the hydrogen is proportional to the number of hydrogen atoms attached to it, in agreement with the experimental findings.

ACKNOWLEDGMENTS

Part of this work has been supported by a Spanish Comisión Interministerial Científica y Técnica (CICyT) grant. This support is gratefully acknowledged.

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