Structural disorder and electronic properties of amorphous silicon*

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We have performed a first-principles calculation of the electronic energies for amorphous Si using the method of orthogonalized linear combinations of atomic orbitals. The basis functions are the $3s$, $3p$ Bloch sums for each atom in the large quasi-unit-cell orthogonalized to all $1s$, $2s$, $2p$ Bloch sums. All the multicenter integrals and Hamiltonian matrix elements are computed exactly by the Gaussian technique with no empirical parametrization. Applied to a recently constructed periodic random-network structural model, the method yields a band gap of 0.67 eV. An alternative scheme is to employ as basis functions orthogonalized $3s$, $3p$ orbitals centered at sites within a cluster to obtain energy levels and to configurationally average the results over several clusters. This scheme is applied to make similar analyses for the nonperiodic networks of Polk and Boudreaux (as refined by Steinhardt, Alben, and Weaire) and of Connell and Temkin; the calculated band gaps are 2.19 and 1.24 eV, respectively. The general profiles of the density of states for different nets show relatively little variation, but the band gap depends quite sensitively on the details of the structural disorder.

I. INTRODUCTION

The theoretical study of the electronic density of states of amorphous group-IV semiconductors has advanced quite rapidly in the past few years.[1-4] The use of continuous random tetrahedral networks (CRTN)[5-8] to represent the amorphous material enables us to specify the positions of the atoms in the solid and makes it possible to perform theoretical studies at a microscopic level.[9,10] In the pioneer work of Weaire, Thorpe, and Alben,[11] the tetrahedrally coordinated structure is described by a simple model Hamiltonian where four basis functions (corresponding to the four tetrahedral bonds) are associated with each atom, and the only nonvanishing matrix elements of the Hamiltonian consist of (i) a constant matrix element between two different basis functions on the same atom, and (ii) another constant element between two basis functions of the same bond. Since the atomic positions do not enter explicitly and because interactions between orbitals on unbonded pairs of atoms are neglected, the spectrum of this Hamiltonian is dictated by the bond pattern, i.e., by the topological disorder. Positional disorder or structural disorder *per se* is important only indirectly through the topological disorder that produced it. As a result, a CRTN is primarily characterized by its ring statistics, whereas less attention is directed to the effects of bond-length and bond-angle distortion.[5] However,

to acquire a more quantitative understanding of the electronic properties, calculations based on more realistic Hamiltonians are necessary.

Recent advances in computational technique for band structure of solids now allow the calculation of the electronic energies of a CRTN of atoms from first principles (instead of from empirical model Hamiltonians), once the positions of the atoms are given. Such a calculation has been performed[9,10] for the electronic structure of amorphous silicon (a-Si), based on Henderson's periodic CRTN (H-61).[8] For a periodic CRTN, the procedure is the same as that for the energy bands of a crystal. Using the method of orthogonalized linear combinations of atomic orbitals (OLCAO) recently developed for band-structure calculation it was possible[10] to take into account the detailed positional disorder, and thus to characterize the electronic properties of an amorphous solid realistically. Of course, structural disorder and topological disorder are not independent of each other. Nevertheless, we regard the structural disorder as the more fundamental way of charaterizing the CRTN: Given a set of atomic positions that are consistent with the known static structure, the electronic structure must be such as to correspond to a topologically disordered scheme of covalent bonds joining each atom to its four nearest neighbors.

The OLCAO calculation for a-Si using the H-61 structure led to a theoretical density of states

(DOS) for the valence band in fair agreement with the experimental result, but it predicted no intrinsic band gap although the DOS near the Fermi level was low. Since the size of the band gap undoubtedly is related to details of the structural disorder, the absence of a band gap in the H-61 CRTN could have been peculiar to that network. Additional calculations based on other CRTN were needed to clarify this point. Very recently one of us (LG) has constructed a periodic CRTN containing 54 atoms in a unit cell (G-54) which has somewhat smaller distortions than H-61.[12] A comparison of the electronic energy structures derived from these two periodic CRTN would be very instructive. In addition it would also be desirable to study the electronic energies for some of the nonperiodic CRTN structural models. This indeed can be done as techniques for applying the OLCAO method to nonperiodic solids have been described in the literature.[13] Accordingly we have performed first-principles calculations of the electronic energies of a-Si using the G-54 and two nonperiodic CRTN. Comparison of the results for the various CRTN enables us to analyze quantitatively how the electronic states are affected by different degrees of structural disorder.

II. DESCRIPTION OF THE CRTN STRUCTURAL MODELS

There exist two classes of CRTN structural models of a-Si. Finite networks, containing typically 200–500 atoms, have been built by hand, sometimes with computer assistance. Examples are those of Connell and Temkin[6] (CT) and of Polk and Boudreaux.[5] The coordinates of the latter were subsequently refined by Steinhardt, Alben, and Weaire[14] to give the minimum energy under the Keating potential. We refer to this refined version of the model of Polk and Boudreaux as RPB. In the existing models, construction has stopped at a point where a large fraction of the atoms is still close to the surface, with effects on the properties that may be large and are difficult to estimate.

In the other class of CRTN, designed to eliminate surface effects, a certain number of atoms is disposed within a unit that satisfies periodic boundary conditions, i.e., repeats indefinitely in three (usually orthogonal) directions. The first of these to be made is due to Henderson and Herman,[7] later modified by Henderson.[8] This is the H-61 structural model referred to in Sec. I. More recently a prescription has been given for systematic construction of such periodic CRTN by computer simula-

TABLE I. Atomic coordinates of the G-54 CRTN. All distances are expressed in units of R_0, the nearest-neighbor distance in the silicon lattice. Cell size is $4.3197 R_0$.

Atoms	x	y	z	Atoms	x	y	z
1	1.5993	1.9516	0.2758	28	3.0155	3.6403	3.6018
2	2.8552	2.4957	1.3041	29	3.6866	2.4962	4.4207
3	0.6000	1.1139	2.0043	30	3.7541	3.9404	5.6255
4	2.3054	2.9208	3.7796	31	2.8937	4.3085	1.3405
5	0.8947	2.3160	3.9904	32	4.2391	4.6158	0.7854
6	1.9306	2.6392	5.2053	33	2.5173	5.5780	2.1852
7	1.3976	2.7086	1.6906	34	4.0124	5.1599	2.2183
8	2.1379	3.0076	2.2638	35	2.8295	4.5094	4.1125
9	1.6450	2.8133	3.0608	36	3.2182	5.9581	4.4713
10	1.8471	3.4011	4.5413	37	4.7732	1.0681	1.0753
11	0.7744	4.1126	5.1433	38	5.2166	2.0131	2.2433
12	2.3273	4.1956	4.8827	39	5.5788	1.9274	3.1535
13	1.5981	4.6786	0.9955	40	5.3020	3.8740	4.2398
14	3.2189	5.2288	1.6073	41	2.9593	0.8416	2.9583
15	2.4220	3.9699	2.1242	42	4.3743	2.7479	5.7607
16	2.3420	5.2870	3.6712	43	4.4525	2.5732	2.3927
17	1.4341	5.2644	3.2987	44	5.0715	3.4285	1.5184
18	1.2288	5.3809	4.8000	45	4.7411	3.1816	3.8097
19	3.3387	1.6870	1.0638	46	5.1906	4.8726	3.9980
20	5.0561	3.1919	2.9152	47	3.5969	3.0384	5.2768
21	3.7704	2.9969	3.6059	48	3.9742	4.1695	6.5798
22	3.8094	1.3216	3.0455	49	3.6250	5.0255	0.0993
23	2.4057	1.9116	4.0232	50	6.2348	4.8090	1.9364
24	4.3153	1.8858	5.3062	51	4.9268	3.9532	2.3656
25	2.7866	2.2520	2.2542	52	5.4607	4.7817	2.4885
26	3.1287	4.1723	2.7786	53	4.3175	5.3605	3.8508
27	3.6298	2.3049	2.8555	54	4.4380	6.2228	4.3497

TABLE II. Comparison of the root-mean-square bond-length and bond-angle distortion ($\Delta R/R$ and $\Delta \theta$), number of n-fold rings per atom, and density relative to the density of the perfect crystal (ρ/ρ_0) for several CRTN. The ring statistics figures for the CT and ST-12 CRTN are given in Ref. 32 and the paper by M. F. Thorpe and D. Weaire in Ref. 2, respectively.

CRTN	Type	No. of atoms	$\Delta R/R$	$\Delta \theta$	n-fold rings/atom $n=5$	$n=6$	$n=7$	ρ/ρ_0
G-54	periodic	54/cell	0.025	13.0°	0.57	0.630	0.35	1.03
H-61	periodic	61/cell	0.038	12.3°	0.44	0.803	0.51	1.03
RPB	finite	519	0.011	7.1°	0.38	0.93	1.04	0.995
CT	finite	238	0.012	11.5°	0	2.432	0	0.99
ST-12	periodic	12/cell	0.014	15.7°	0.556	0.333	0	1.11

tion.[12] Briefly, the method is to start from a finite region of a crystal, to join each atom randomly to four others so as to satisfy periodic boundary conditions, and then to modify the bond pattern progressively in order to lower the strain energy as much as possible. An example has been produced in this way (the G-54 CRTN referred to in Sec. I), starting from a cubical region containing 27 unit cells of the body-centered-cubic lattice (54 atoms). Its radial distribution, after relaxation under the Keating potential with $\beta/\alpha = 0.2$, is in good agreement with the experimental function for amorphous Ge. The coordinates of this CRTN are given in Table I.

In addition to the two kinds of CRTN referred to in the preceding paragraphs, the crystalline structures of polymorphs of Si and Ge have been suggested as possible structural models for a-Si.[15,16] These polymorphs are stable at high pressures.[17] Silicon III has a body-centered-cubic structure with 8 atoms per unit cell (BC-8), whereas Ge III has a simple tetragonal structure with 12 atoms per unit cell (ST-12). The electronic structures of silicon in the BC-8 and ST-12 structure have been calculated.[15,16,18-20] The valence-band DOS of ST-12 Si shows a fair degree of resemblance to the experimental data for a-Si, but a much larger difference is found for BC-8. Moreover, the polymorphic forms have too high a density and their computed radial distribution functions (RDF), especially that of BC-8, show considerable departure from the observed results for the amorphous phase.[16] For these reasons the BC-8 and ST-12 structures do not make very realistic models for a-Si. Nevertheless they are useful as intermediates between the crystalline and the amorphous state.

The RPB model (519 atoms) has the smallest distortion of bond length and bond angle and contains five-fold rings. The CT model is unique in having only evenfold rings. In Table II some parameters

describing the structural and topological disorder for several CRTN and ST-12 are given.

III. COMPUTATIONAL METHOD

A. Periodic networks

The general procedure for calculating the electronic energy levels of a periodic CRTN of an amorphous system by means of the first-principles LCAO method is just that for the band-structure calculation of a complex crystal,[21] and extension of this method to a periodic network is conceptually straightforward. The only difficulty is a practical one of having to handle extraordinarily large energy matrices. Even with a minimal basis set of nine orbitals $(1s, 2s, 2p, 3s, 3p)$ per Si atom, one would have to use $9N$ Bloch-sum basis functions for a periodic lattice with N atoms in a unit cell. Since we are mainly interested in the valence-type states, a large reduction of the basis functions can be effected if the core states can be deleted with no loss in accuracy. This indeed can be accomplished by the recently developed OLCAO scheme[10,18] in which the $3s, 3p$ Bloch sums are orthogonalized to the $1s, 2s, 2p$ core Bloch sums. Specifically let us denote by $b_{i\alpha}(\vec{k}, \vec{r})$ the Bloch sum which is associated with the $\vec{k}$ point in the quasi-Brillouin-zone and is formed by the atomiclike orbital ϕ_i centered at the point $\vec{p}_\alpha$, the site of the αth atom in the νth unit cell, i.e.,

$$b_{i\alpha}(\vec{k}, \vec{r}) = \sum_\nu e^{i\vec{k}\cdot\vec{R}_\nu} \phi_i(\vec{r} - \vec{p}_\alpha - \vec{R}_\nu) \ . \tag{1}$$

The orthogonalized Bloch sum $b'_{i\alpha}$ is related to the unorthogonalized ones as

$$b'_{i\alpha}(\vec{k}, \vec{r}) = b_{i\alpha}(\vec{k}, \vec{r}) + \sum_{l,\gamma} a_{i\alpha,l\gamma} b_{l\gamma}(\vec{k}, \vec{r}) \ , \tag{2}$$

where

$$\alpha, \gamma = 1, 2, 3, \ldots, N, \quad i = 3s, 3px, 3py, 3pz \ ,$$
$$l = 1s, 2s, 2px, 2py, 2pz \ . \tag{3}$$

The coefficient $a_{i\alpha,l\gamma}$ can be determined from the condition that $b'_{i\alpha}$ be orthogonal to $b_{l\gamma}$. The new orthogonalized basis set $b'_{i\alpha}$ covers $4N$ functions. The energy levels are obtained by calculating the Hamiltonian and overlap matrix elements in the orthogonalized basis and diagonalizing a $4N \times 4N$ matrix for each $\vec{k}$ point.

In the one-electron Hamiltonian, the potential function is taken as a superposition of atomic potentials V_a centered at each site. Each V_a is calculated from the Hartree-Fock wave function of a free Si atom using a Slater-type local exchange with $\alpha = \frac{2}{3}$. (This overlapping-atomic-potential approximation for constructing the crystal potential has been widely used for energy-band calculation of crystals. For example, when applied to crystalline Si, it gives energy bands in good agreement with the self-consistent-field results of Stukel and Euwema.[22]) To facilitate the evaluation of multicenter integrals, the atomic potential is fitted to a Gaussian form

$$V_a(r) = -\frac{Z}{r}e^{-Cr^2} + \sum_m \xi_m e^{-b_m r^2} . \qquad (4)$$

The parameters of the Gaussian fit are given in Ref. 18. Although the ϕ_i in Eq. (1) are often identified with the free-atom wave functions, we find it more advantageous to take the ϕ_i as some localized functions which are qualitatively similar to the true atomic orbitals, but are somewhat distorted in the crystal. A set of such optimized orbitals determined by the technique of contracted Gaussians[23] has been given in Ref. 18. With both ϕ_i and V_a expressed in Gaussian form, a typical Hamiltonian matrix element can be decomposed into a multiple series, summed over the CRTN lattice, of multicenter integrals that can be either evaluated analytically or expressed in terms of the error function. More details of the computational procedure have been described previously.[10,13,18]

Once the Hamiltonian and overlap matrix elements are computed, the energy levels are obtained by solving the secular equations. For a crystal with a large unit cell like the G-54 CRTN, the quasi-Brillouin-zone is very small. Thus we can get a good sampling of the energy states from eight non-equivalent points of the zone, i.e., $\pi(0,0,0)/a$, $\pi(1,0,0)$, $\pi(0,1,0)/a$, $\pi(0,0,1)/a$, $\pi(1,1,0)/a$, $\pi(1,0,1)/a$, $\pi(0,1,1)/a$, and $\pi(1,1,1)/a$.

B. Finite networks

Even in the absence of any periodicity of the CRTN, one can apply the LCAO method to calculate the electronic energy. Here the basis functions are simply the atomic (or optimized) orbitals located at each site, instead of being in the Bloch-sum

form. The technique of orthogonalization can also be applied, viz., the $3s$, $3p$ orbitals at one site are orthogonalized to the $1s$, $2s$, $2p$ core orbitals at all other sites. The major consideration is how many atoms can be included in the calculation. With four orthogonalized orbitals per atom, it becomes difficult to go much beyond, say, 100 atoms. One practical procedure is to calculate the energy levels for a cluster of 100 atoms from the CRTN and to repeat the calculation for several different 100-atom clusters so as to get a statistical average. The drawback of this procedure is that even for a 100-atom cluster a good fraction of the atoms are on the surface, and hence the energy levels would contain a number of surface states. Menzel et al.[13] have introduced a method to eliminate the surface states. They take the Hamiltonian of an infinite solid but use as the basis functions atomiclike orbitals centered at sites within a cluster. Although their LCAO basis set covers only a limited number of atoms, there is no physical surface present in the Hamiltonian which includes the potential terms of all atoms in the infinite solid. Indeed Menzel et al. found no surface states in their cluster-basis calculation of crystalline Si and LiF. However, one important point must be kept in mind in using a finite cluster-type basis set in conjunction with the Hamiltonian of an infinite solid. The Hamiltonian is capable of yielding an infinite number of core-state eigenvalues, but with a finite basis set, one expects the eigenvalues to include the core states of only the atoms inside the cluster. If the $3s$ and $3p$ orbitals inside the cluster penetrate appreciably into the sites outside, the minimum-seeking nature of the linear variational method would attempt to reproduce the core states of the exterior atoms and therefore produce some spurious roots. This complication can be avoided if the cluster-type basis functions are supplemented by the $1s$, $2s$, $2p$ core orbitals around the sites of the next few exterior shells. Such a core-state cushion has been used successfully.[24]

The method of Menzel et al. can be adapted to the case of a finite CRTN provided there are many more atoms in the CRTN than in the cluster. For our application we start with a cluster C' for the basis functions (both core and valence) as illustrated in Fig. 1. Enclosing C' is a region designated as A which usually contains several hundred atoms. The potential-energy function in the Hamiltonian includes the contribution from all the atoms inside A. Thus A must cover at least several shells of atoms outside of C' and its size must be such that an enlargement of A would not affect the Hamiltonian matrix elements between two basis functions inside C'. Surrounding C' and inside A we choose a core-cushion region B as shown in Fig. 1. The
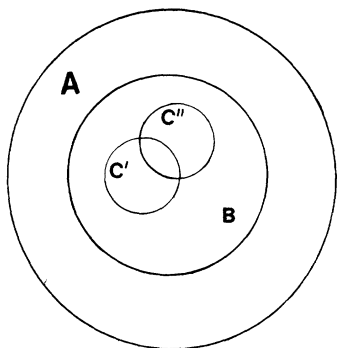
FIG. 1. Schematic diagram for regions A and B and the various clusters C', C'', etc.

region B serves as the core-state cushion, but instead of adding the core orbitals of the cushion atoms to the basis set we orthogonalize the $3s$ and $3p$ orbitals within C' to all the core orbitals in B. The latter serves the same purpose as the core cushion but does not result in an enlargement of the basis set. The valence orbitals inside C' are also orthogonalized to the core functions of all atoms inside C'. The orthogonalized $3s, 3p$ functions inside C' constitute the basis set. To compute the necessary matrix elements, we again express the potential function as a superposition of atomic potentials at each Si site and evaluate the relevant three-center integrals using Eq. (4). After obtaining the energy levels we repeat the calculations using different clusters $C'', C''', \ldots$ for configuration averaging in order to get a better sampling in cal-

culating density of states (DOS). Ching et al. applied this procedure to perform a cluster-type calculation with H-61 and the DOS so obtained is in good agreement with the result derived from the quasicrystal calculation.[10]

Other methods for removing the surface states in cluster-type calculations have been used. One way is to introduce hydrogen atoms to saturate the dangling bonds of the surface Si atoms.[25] The calculated energy states, however, may include some which are largely associated with the Si-H bonds. More recently, a new cluster approach has been proposed.[26-29] It consists of attaching a Bethe lattice to the surface of a finite cluster to simulate an infinite solid. Solution of the Bethe-lattice problem can be obtained by parametrizing the matrix elements. Since the Bethe lattice does not correspond to a real system, it is more suitable for model study than first-principles calculations.

IV. RESULTS FOR AMORPHOUS SILICON

A. G-54 network

In Fig. 2 is shown the theoretical DOS of a-Si using the G-54 lattice based on the energy levels of eight points in the quasi-Brillouin-zone. To facilitate comparison of the general shape of curves for different CRTN we have applied a Gaussian broadening of full width 0.1 eV to smooth out the very sharp spikes. For comparison, the DOS derived from the H-61 CRTN (with the same broadening) is reproduced in Fig. 3. The general shape is similar to the G-54 result except that the H-61 lattice gives
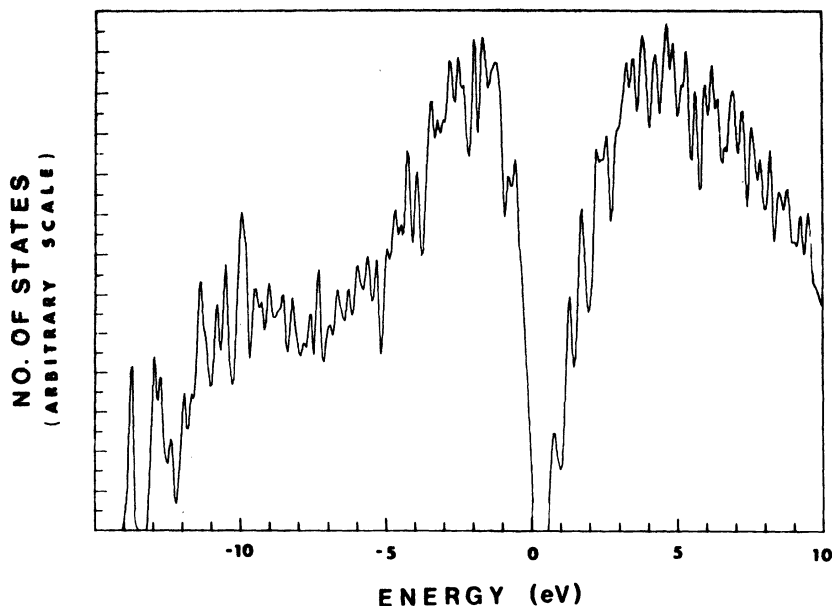

FIG. 2. Density of states of the valence and conduction bands of a-Si calculated by using the G-54 CRTN. A 0.1-eV Gaussian broadening has been applied.
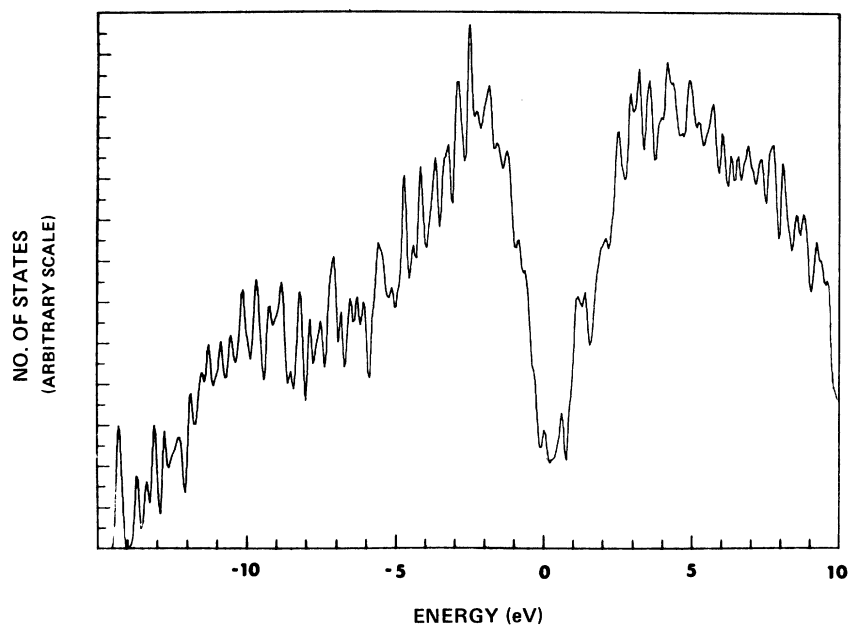
FIG. 3. Density of states of the valence and conduction bands of a-Si calculated by using the H-61 CRTN. A 0.1-eV Gaussian broadening has been applied.

no band gap.

It is interesting to see how well the band gap and the energy-level pattern near the gap can be reproduced by cluster-type calculations based on the same CRTN. Accordingly, we select a large spherical aggregate of some 600 atoms from the G-54 lattice as region A of Fig. 1. Energy levels are calculated using orthogonalized $3s$, $3p$ basis orbitals within a cluster of 75 atoms, and the procedure is repeated for seven other 75-atom clusters. The resulting DOS [Fig. 4(d)] agrees well with the quasicrystal result of Fig. 2, not only in its general shape, but also in the band gap (0.7 eV in Fig. 4(d) vs 0.67 eV in Fig. 2), and in the detailed structure near it. In a cluster calculation, one invariably gets more valence-band states than con-
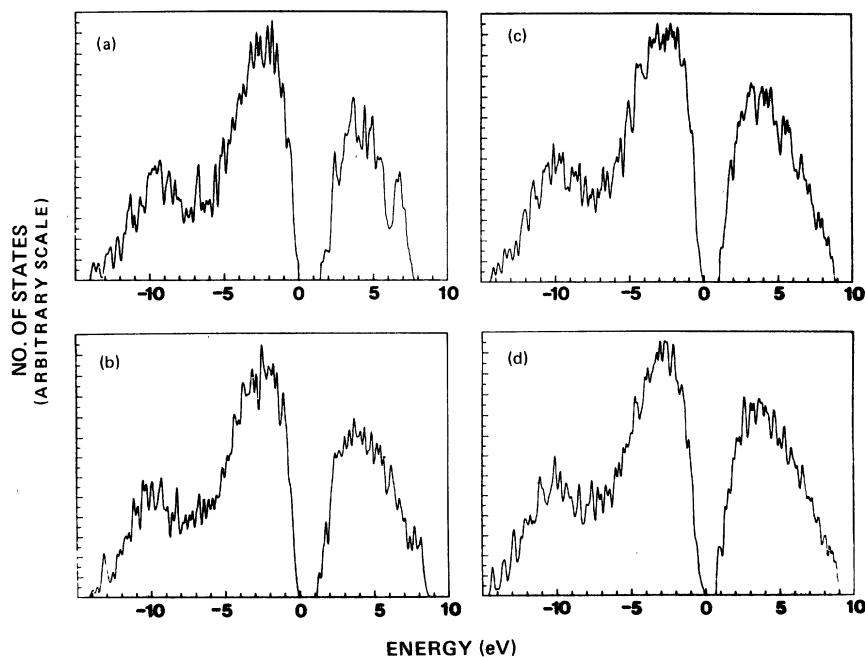

FIG. 4. Calculated density of states of the valence and conduction bands of a-Si based on the G-54 CRTN using the average of (a) 36 17-atom clusters, (b) 18 35-atom clusters, (c) 13 47-atom clusters, and (d) 8 75-atom clusters. A 0.1-eV Gaussian broadening has been applied.

duction-band states because of the dangling orbitals of the boundary atoms.[30] Consequently we find a smaller area under the conduction-band DOS as compared to the valence band. Furthermore, the higher conduction states obtained here are not as accurate as the valence states because to reproduce the former properly by a cluster-type calculation, single-Gaussian basis functions would have to be added.[13] To examine the effect of the cluster size, we have also tried clusters of 60, 47, 35, 25, 20, 17, and 13 atoms. The numbers of configurations averaged for these clusters were 10, 13, 18, 24, 30, 36, and 47, respectively, so as to maintain about the same degree of statistical sampling. The calculated DOS for some of these clusters are included in Fig. 4. Comparison with Fig. 3 shows that as far as the valence band is concerned, the 47-atom clusters are practically as good as the 75-atom ones, but that to reproduce the conduction-band-edge behavior and the band gap, clusters with more than 47 atoms are needed.

The $3s$ and $3p$ orbitals used in this work are "optimized" in the sense that the band structure (including the band gap) *for the normal Si crystal* obtained by using only the orthogonalized $3s, 3p$ Bloch sums as basis functions is nearly the same as that derived from an extended basis set containing eleven s-type and nine p-type single-Gaussian Bloch sums. When applied to a-Si and the polymorph forms of Si, this $3s$-$3p$ basis set is not expected to reproduce so closely the results of an extended-basis calculation. For instance, augmentation of the $3s$-$3p$ basis set by adding single-Gaus-

sian Bloch sums changes the band gap of the BC-8 Si by 0.07 eV.[18] While we have not performed extended-basis calculations for a-Si because of the size of the secular equation, it is reasonable to take the number cited above for BC-8 as an indication of the effect of augmenting the basis set on the band gap of a-Si.

B. Finite networks

Cluster-type calculations of the energy levels have been made for the RPB and CT networks. The DOS obtained from the averages of eight different 75-atom clusters are presented in Figs. 5 and 6. The CT network contains 238 atoms, which is sufficient to provide eight different clusters but not enough to cover region A. In other words, some of the 75-atom clusters are too close to the boundary of the network. Therefore to the peripheral atoms we connect tetrahedrally some 130 atoms to extend the CRTN. No special effort was made to minimize the energy in the enlargement process. The added atoms do not appear in any of the eight clusters but are included in the Hamiltonian in order to eliminate the surface effects. Thus the fact that the addition of the extra atoms was not done to the same degree of refinement as the construction of the original CRTN is not believed to have much effect on the calculated DOS.

Both models give an intrinsic band gap, 2.19 eV for RPB and 1.24 eV for CT. The gap of the RPB model is much larger than the experimental value for crystalline Si (1.13 eV). In view of the close agreement between the band-gap values of G-54
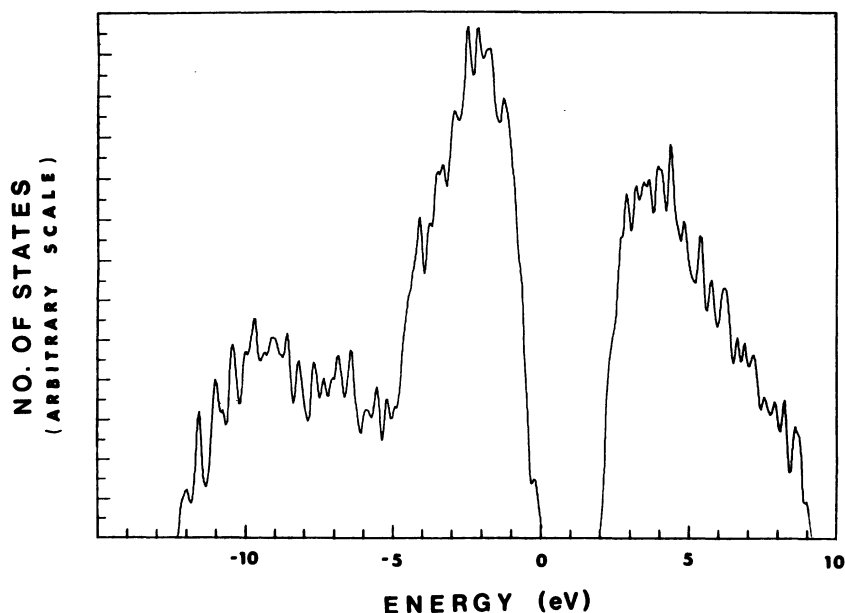

FIG. 5. Calculated density of states of the valence and conduction bands of a-Si based on the RPB CRTN. A 0.1-eV Gaussian broadening has been applied.
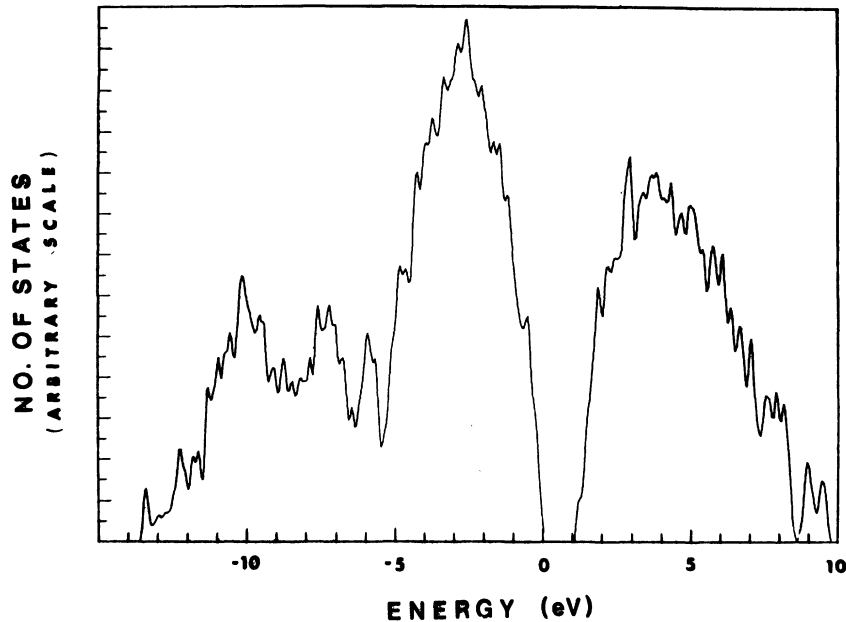
FIG. 6. Calculated density of states of the valence and conduction bands of a-Si based on the CT CRTN. A 0.1-eV Gaussian broadening has been applied.

derived from the 75-atom cluster and from the quasicrystal calculation, we expect the two gap values cited above to be quite close to, though somewhat larger than, the infinite-cluster limit. Although further increases in the cluster size are expected to decrease the gap only a little, larger effects would result from supplementing the $3s, 3p$ basis orbitals by some single-Gaussian orbitals[13] (within the cluster) to increase the variational freedom. However, it is not likely that this change would be more than several tenths of an eV. Along this line, we may mention that the calculated band gap for ST-12 Si (with single-Gaussian supplement to the basis set) is 1.31 eV which is larger than the band gap of crystalline Si. The valence-band DOS of the RPB network has the usual two-peak structure, whereas in the case of CT the lower half of the valence band shows some well-developed structures. The RPB lattice has the smallest distortion

and the CT lattice is intermediate between RPB and G-54. The results of calculations with four different CRTN are summarized in Table III.

C. Comparison with experiment

Experimental measurement of the DOS of the valence band of a-Si has been reported by Ley et al.[31] In order to compare with the experimental DOS, a Gaussian broadening of 0.5 eV (full width) has been applied to all the theoretical curves. Since only relative values of the measured DOS are given in Ref. 31, we normalize all the theoretical curves to the same area as the experimental one. The results are shown in Fig. 7. In all four theoretical curves, the energy of the upper peak is quite close to the observed value but their lower peaks are shifted to lower energies and show more structure than is observed. Furthermore, the experimental maxima are more nearly equal in height than any of those calculated.

V. DISCUSSION

We have obtained the DOS of a-Si based on four different CRTN, the H-61, G-54, CT, and RPB structural models. All four reproduce quite well the experimental RDF but have different amounts of distortion. To a less extent reference can be made of the ST-12 and BC-8 models. Their DOS curves are reproduced in Fig. 8. The BC-8 structure gives a RDF markedly different from the experimental data of a-Si and therefore is not a realistic structural model.[16] The ST-12 is somewhat

TABLE III. Calculated band gap and valence-band width for four CRTN.

CRTN	Band gap (eV)	VB width (eV)
H-61	None	15.1
G-54	0.67 (0.70)[a]	14.2 (14.6)[a]
RPB	2.19	12.5
CT	1.26	13.8

[a]The values in parentheses are obtained by using cluster-type basis functions and the values outside by Bloch-sum basis functions.
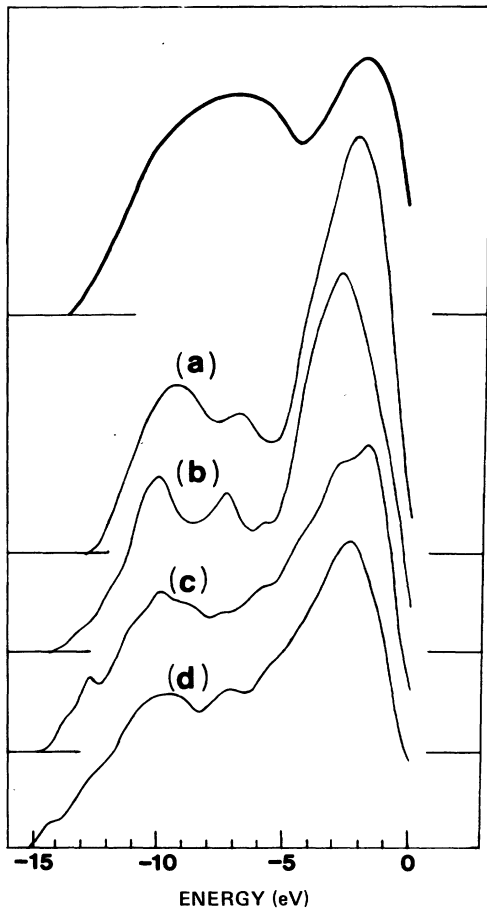
FIG. 7. Comparison of the experimental valence-band density of states of a-Si (top curve) with the theoretical ones based on four different CRNT: (a) RPB, (b) CT, (c) G-54, (d) H-61. All four theoretical curves were smoothed by a 0.5-eV Gaussian broadening and normalized so as to cover the same area as the experimental curve.

iment.

(iii) The width of the valence band increases as the band gap decreases.

(iv) The size of the band gap appears to have a somewhat more direct correlation with the root-mean-square bond-length distortion $(\Delta R/R)$ than with the root-mean-square bond-angle distortion $(\Delta\theta)$. For instance $\Delta R/R$ for H-61 is 0.038 as compared to 0.025 for G-54, which is in turn much larger than those of CT and RPB; indeed $\Delta R/R$ is in reverse order of the band-gap values. On the other hand, G-54 has a slightly larger bond-angle distortion than H-61. Although our analysis is made in terms of the two root-mean-square distortion parameters, it is in no way implied that the band gap is dictated only by these two quantities. In fact the detailed distribution of each positional distortion may well play an important role so that two CRTN having similar $\Delta R/R$ and $\Delta\theta$ but different distribution of the individual distortion could have appreciably different band gaps. Neverthe-

better but will be considered only in an auxiliary way. Comparison of their DOS results leads us to the following observations:

(i) The general shape of the valence-band DOS is insensitive to the detailed distortion since all four CRTN give similar results which are in accord with experiment. Even the ST-12 DOS for the valence band is in fair agreement with the other four.

(ii) The band gap depends very strongly on the degree of distortion of the network. Of the four CRTN studied, three exhibit a band gap ranging from 2.19 to 0.67 eV. While our calculations are not able to provide a precise answer to the question of the magnitude of the band gap for a-Si, they do indicate the existence of an intrinsic band gap for certain CRTN (both periodic and nonperiodic) whose static structures are consistent with exper-
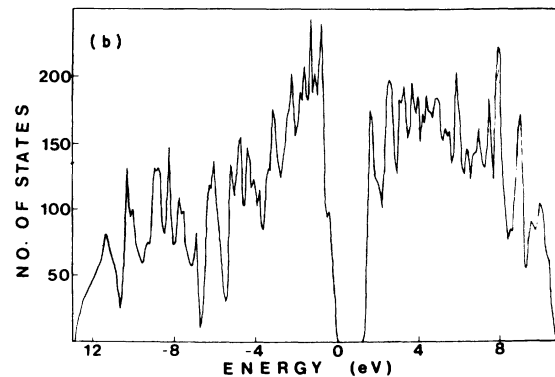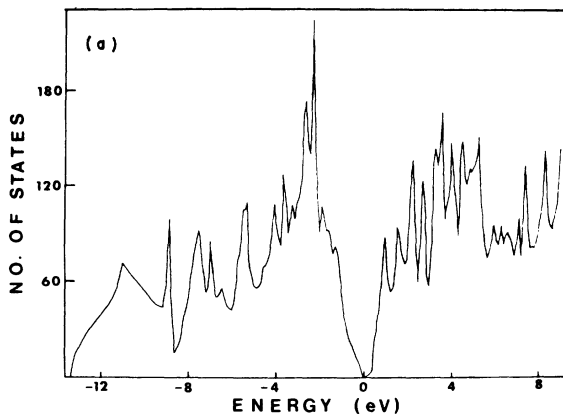

FIG. 8. Calculated density of states (in units of number of states per unit cell per a.u. of energy) of the valence and conduction bands of (a) BC-8 Si and (b) ST-12 Si.

less, we choose the two root-mean-square values as the zeroth-order parameters for describing the structural disorder. The results for the four CRTN studied here do reveal some correlation between the band gap and the mean distortion, but at this stage we do not know quantitatively to what extent the band gap and other electronic-energy properties are governed by these two parameters. The importance of details of the distortion can be discerned only by a more extensive study involving many different CRTN.

(v) In the early theoretical works on a-Si, because of the nature of the empirical approach adopted, the only way that the disorder enters into the Hamiltonian is through the connectivity of the lattice (see Sec. I). Thus it has been a common practice to regard the statistics of five- and sixfold rings, etc. as the measure of the disorder of the structure and to emphasize the roles they play in the electronic properties of amorphous Si. With the OLCAO scheme it is now possible to calculate, in an ab $initio$ manner, the electronic energies of a-Si using a realistic CRTN to represent the atomic positions. This allows us to probe into the effects of structural disorder such as bond-length and bond-angle distortion. For instance, the CT network is intermediate between G-54 and RPB as far as bond-length and bond-angle distortion are concerned, but differs from both G-54 and RPB in having no fivefold rings. Since the band gap and valence-band width of the CT network do fall between the G-54 and RPB counterparts, we see the fivefold rings per se are not a key factor in controlling these two properties. In Fig. 7 we note that the CT network shows the clearest double-maxima feature in the secondary peak of the DOS. Whether this is directly related to the absence of fivefold rings, we are not able to comment at this time.

VI. CONCLUDING REMARKS

The use of CRTN to describe the structure of a-Si and other amorphous group-IV semiconductors in terms of the position coordinates of the individual atoms has proved to be very successful in recent years. Based on a CRTN description it is now possible to perform first-principles calculations of the electronic energy states of a-Si by means of the OLCAO method. Since the Hamiltonian includes the contribution from all atoms in the entire CRTN, the complete detailed structural disorder is incorporated into the problem and treated in an ab $initio$ fashion without empirical parametrization. A disordered system has a great many degrees of freedom as far as structural distortion is concerned, and it is not clear whether the effect of disorder on

the electronic properties can all be absorbed into a few parameters. A first-principles approach that takes into account the full positional disorder gives a more basic view and reliable results. The first ab $initio$ calculation of the electronic energies for a-Si was done by using the H-61 structure.[9,10] In this paper we extend the study to three other CRTN.

Comparison of the DOS derived from the various CRTN indicated that while the general shape of the valence-band DOS shows little variation in going from one CRTN to another, the band gap does decrease markedly with increasing bond-length distortion. Likewise, the valence-band width is found to increase with higher distortion. Although it has been customary to correlate the electronic structure of a-Si with statistical distribution of fivefold rings in the CRTN, we find that the relative abundance of fivefold rings per se does not have much direct influence on the band gap. The structural disorder as a whole must be considered in studying the electronic properties.

A theoretical calculation of the electronic energy states of a-Si, in the spirit of this work, requires (i) construction of a suitable CRTN, and (ii) calculation of the energy levels based on a given CRTN. Although there is room for improvement for the second task, such as augmenting the basis-function sets by single-Gaussian orbitals and proceeding to self-consistency as discussed in Ref. 10, the method for calculating energy states of a given CRTN as employed in this paper is sufficiently refined that the accuracy of our results for a-Si is mainly limited by the uncertainty of the positions of the atoms in the amorphous solid. Thus we feel that more efforts should be devoted to obtaining better CRTN structural models. In this connection one wonders what is the "correct" amount of distortion. There are suggestions that the RPB model does not have enough distortion.[8,32] On the other hand the distortion in the H-61 model is probably too large. In many ways periodic CRTN structures are appealing because there is no inherent limit in the size of the network. It would be desirable to have periodic structural models of about 64–100 atoms per unit cell with distortion smaller than that of G-54. The requirement of periodic boundary condition does make the construction of periodic networks more difficult than the finite nonperiodic ones. Since one can apply the OLCAO method to nonperiodic systems as well, additional nonperiodic CRTN containing 600 or so atoms with varying degrees of distortion would be valuable. Furthermore, one can also study point defects in amorphous semiconductors such as vacancies and impurities provided suitable CRTN for the defect solid are available.

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