these states (if they exist) do not account for a large fraction of the total number of states at $T = 0.1$ K since the long-time specific heat and the short-time specific heat are equal at this temperature.

To our knowledge, the time dependence of the specific heat in amorphous substances at low temperatures is the only prediction made by the tunneling model as presently formulated[4-6] which is specific to the tunneling process. For instance, the ultrasonic results[9] can also be explained with the assumption of low-energy nonharmonic oscillator states, which do not arise from tunneling. It is conceiveable that one of the basic assumptions of the tunneling model, i.e., that both the specific-heat anomaly and the thermal conductivity are caused by the same kind of defects, is responsible for the disagreement between theory and experiment found in the present investigation.

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[11] According to manufacturer specifications, GE No. 101 fused silica has 7 ppm by weight of Fe_2O_3 and Spectrosil *B* has less then 0.1 ppm. Low-temperature specific-heat anomalies due to magnetic impurities have been observed in a number of glasses (see Ref. 3).

Electronic Energy Structure of Amorphous Silicon by the Linear Combination of Atomic Orbitals Method*

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A first-principles linear combination of atomic orbitals calculation of the electronic energy structure of amorphous silicon based on Henderson's 61-atom quasiperiodic lattice model has been performed. The potential is constructed by a superposition of atomic potentials with interactions between all atoms included. The lattice summation of multicenter integrals, evaluated by the Gaussian technique, is performed to convergence. Results on energy levels and density of states are presented and compared with experiments.

The study of amorphous solids has been of great interest from both theoretical and experimental standpoints in the recent years.[1] Several continuous random-tetrahedral-network (CRTN) models for the structure of the amorphous Group-IV semiconductors[1,2] have been proposed and they have provided the foundation for numerous theoretical works. Most previous calculations of electronic structure either are based on a simple model Hamiltonian with the nearest-neighbor approximation[3] or resort to empirical or semiempirical means.[1] Discussions of the energy spectra of amorphous Si and Ge based on the band structures of the crystalline polytypes have also been given.[4] However, first-principles calculations of energy structure have not been reported and some of the very important issues such as band tailing are yet to be demonstrated from such calculations.

We have performed a first-principles calculation of the electronic structure of amorphous silicon (a-Si) by means of the method of linear combination of atomic orbitals (LCAO) which has recently been applied to crystals of different varieties.[5] A quasiperiodic lattice model due to Henderson,[2] with 61 atoms per unit cell, is used. Although Henderson's model may have larger distortions as compared to some of the others,[2] its radial distribution function is in very good agreement with experiment. Moreover, Henderson's model was found to be quite successful in lattice-vibration calculations.[6] The periodicity of the large cell of CRTN is especially convenient because of the absence of the surface states. The problem now becomes that of a band calculation for a quasicrystal with 61 atoms per unit cell and the general scheme of approach can be outlined as follows: The basis functions are the Bloch sums associated with the appropriate atomic orbitals (expanded in terms of Gaussians) for each atom in the unit cell. The crystal potential is expressed as a superposition of atomiclike potentials centered at each Si site. The numerical work is greatly facilitated by fitting the atomiclike potential to the form

$$V^{\mathrm{atom}}(r) = -(Z/r)\exp(-ar^2) + \textstyle\sum_i \xi_i \exp(-b_i r^2). \qquad (1)$$

A Hamiltonian matrix element may be decomposed into a series of three-center integrals containing a Gaussian at site A, another at B, and $V^{\mathrm{atom}}(r)$ centered at C; the integrals associated with the first member of Eq. (1) can be expressed in terms of the error function and those associated with the second member can be evaluated analytically.[5] Upon computing all the Hamiltonian (H_{ij}) and overlap (S_{ij}) matrix elements, the energy spectrum is obtained by solving the secular equations $|H_{ij} - ES_{ij}| = 0$ for various $\vec{k}$ points.

The atomiclike potential is approximated by the potential of a free Si atom which is computed from the atomic Hartree-Fock wave functions (using Slater's approximation for exchange with $\alpha = \frac{2}{3}$) and curve fitted to Eq. (1). To test this potential, we use it to calculate the band structure of the Si crystal with eleven s-type and nine p-type single-Gaussian Bloch sums[5] as basis, and the results are in good overall agreement with those of Stukel and Euwema[7] (the indirect band gap being 1.14 eV). In the crystal calculation we find it advantageous to suppress the very long-range tail of the atomic potential through curve fitting. This operation is found to produce virtually no change (less than 0.0005 a.u.) in the calculated crystal band structure, but has the benefit of bringing the vacuum level much closer to the experimental value and significantly reducing the computational work. This same procedure is adopted in the calculation for a-Si.

For amorphous solids a more economical orbital basis set must be selected. This is done by inspecting the eigenvectors of the Hamiltonian for several $\vec{k}$ points obtained from the single-Gaussian calculation for the Si crystal. Using the relative weightings of the single-Gaussian Bloch sums in these eigenvectors, we construct five linear combinations of Gaussians (contracted Gaussians), all at the same center, corresponding to modified versions of the $1s$, $2s$, $3s$, $2p$, and $3p$ atomic orbitals. The $1s$, $2s$, and $2p$ contracted-Gaussian orbitals are virtually identical to the true atomic orbitals, and the $3s$ and $3p$ contracted-Gaussian orbitals have the same general shape as their free-atom counterparts but are of shorter range. Basis sets consisting of contracted-Gaussian orbitals generated in this fashion give much more accurate energies than those of the true atomic orbitals.[8] When the Bloch sums of these contracted-Gaussian orbitals are used to calculate the band structure of the Si crystal, the results agree with those of the single-Gaussian basis to within typically 0.007 a.u. However, even with the $1s, \ldots, 3p$ contracted-Gaussian orbitals, we get a total of 549 basis functions for the amorphous problem. To reduce this number, the $1s$, $2s$, $2p$ core-type functions are excluded from the basis set. We have performed test calculations on the Si crystal to examine the validity of this step. With the chosen basis functions and potential, our calculations show a downward shift in energy when the core functions are dropped. This shift amounts to about 0.2 eV for states near the top of the valence band and becomes much larger for states close to the bottom of the valence band. A comparison of the valence-band densities of states of the Si crystal calculated with and without the core states is shown in the bottom of Fig. 1. The general features are similar although the peaks are shifted to lower energies.

With only the $3s$, $3p_x$, $3p_y$, and $3p_z$ orbitals (contracted Gaussians) for each atom, the 244 $\times$244 Hamiltonian matrices are manageable. A typical matrix element is expanded as a lattice-point summation of the multicenter integrals de-

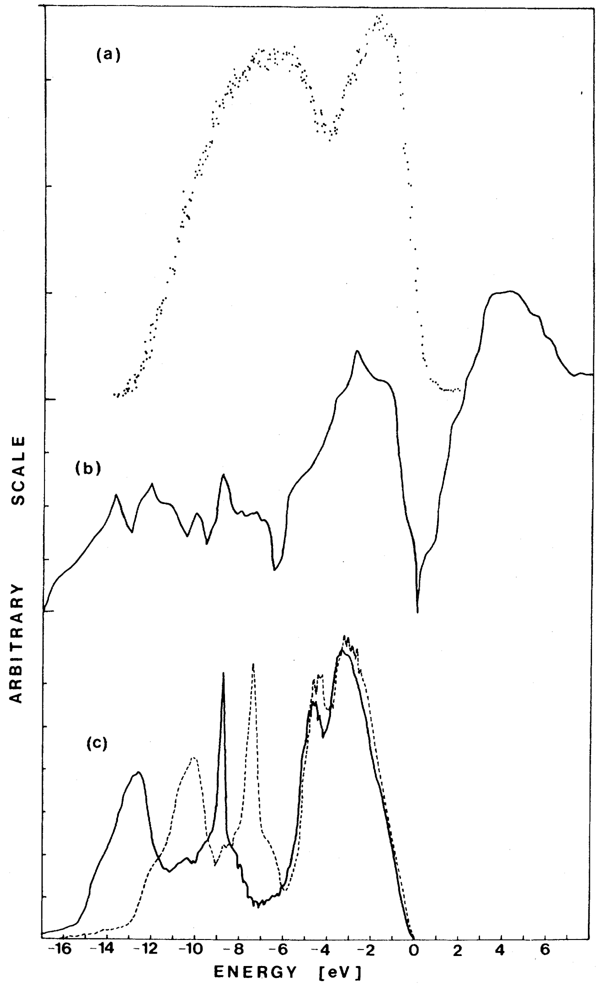

FIG. 1. (a) Experimental x-ray photoelectron valence-band spectra of a-Si (Ref. 9). (b) Calculated density of states of a-Si. (c) Calculated densities of states of Si crystal without core states (solid curve) and with core states (dotted curve). The energy of the top of the valence band is set equal to zero for each of the curves in (b) and (c).

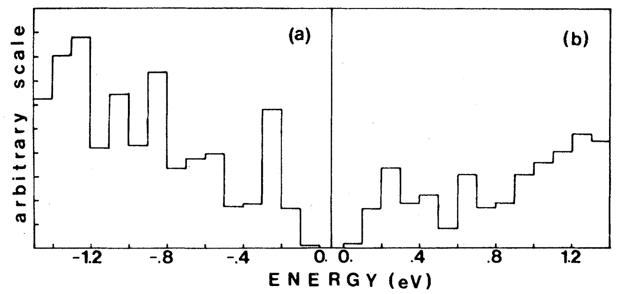

FIG. 2. Calculated density of states of a-Si near the gap region. (a) Valence band, (b) conduction band.

scribed earlier. This lattice summation must be carried out to full convergence.[5] In the present calculation an overlap integral still makes a nontrivial contribution[10] to the matrix elements when the two atoms are separated by even three times the bond length (corresponding to a distance of the eighth-neighbor shell), reflecting the inadequacy of the nearest-neighbor or next-nearest-neighbor approximations for this case. We have calculated the energy levels by solving the 244×244 secular equations for four high-symmetry $\vec{k}$ points (real matrices) and four additional interior $\vec{k}$ points (complex matrices). Because of the large unit cell, the Brillouin zone (BZ) is very small and there are 244 levels for each $\vec{k}$. Thus it is not necessary to sample a large number of $\vec{k}$ points in order to obtain a representative energy spectrum.

The calculated density of states (DOS) of the filled levels and empty levels of a-Si is shown in Fig. 1. Included in this figure are also the DOS of the Si crystal valence band and the experimental results of Ley *et al.* for a-Si.[9] The most prominent peak in the DOS of the crystal valence band is preserved in the amorphous solid, while the two lower peaks are less pronounced. Had it been possible to include the core states in our calculation, these two lower peaks would be somewhat higher because the energy levels at the lower part of the valence band will be pushed up slightly. This would bring the calculated DOS curve closer to the experimental data. The DOS near the Fermi level are shown in more detail in Fig. 2. There is a local maximum at 0.25 eV below the Fermi level and also one 0.25 eV above it. Examination of the DOS calculated by using a four-point and a seven-point sampling of the BZ shows that these two local maxima persist whereas the other structures (farther away from the Fermi level) in Fig. 2 do vary and therefore may be attributed partly to statistical fluctuation. Recently Engeman and Fischer[11] found that such local maxima in DOS are necessary to explain their experiment on luminescence spectra. Results of earlier experimental work by Spear and LeComber indicate a maximum in the distribution function of the localized states at energies somewhat above the Fermi level.[12] At present we are not able to comment about the nature of the states associated with the local maxima in Fig. 2, e.g., whether they are localized or not. For such an analysis one would have to determine not only the eigenvalues but also the eigenvectors

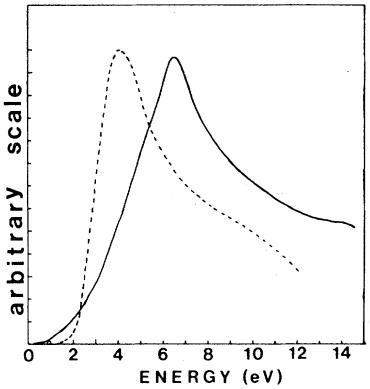

FIG. 3. Comparison of the calculated joint density of states of *a*-Si (solid curve) with the experimental optical-transition strength (dotted curve) from Ref. 13. The two curves were adjusted to have the same maximum height.

of the 244×244 Hamiltonian matrices. This is beyond our presently available computing capability.

The highest filled state and the lowest empty state are separated by 0.032 eV; however, little quantitative significance should be attached this band gap value. The magnitude 0.032 eV is well within the error incurred by neglecting the core states, and thus it may change vastly when the core states are reinstated. Aside from this uncertainty and the uncertainty associated with the lattice model, the DOS are very low in the region between the two local maxima so that experimental measurements would most likely lead to a much higher band gap.

Under the approximation of constant optical-transition matrix elements, the joint density of states (JDOS) is proportional to the optical absorption spectrum. Our calculated JDOS curve which has a peak at 6.5 eV is shown in Fig. 3 together with the optical-transition curve for *a*-Si obtained by Pierce and Spicer.[13] Inclusion of core states and the variation of the optical-transition matrix elements, however, may cause a change in the shape of the theoretical curve. Because of the local maxima in the DOS (Fig. 2), a small bump in the JDOS near 0.5–0.8 eV is found. Structures in the optical absorption spectra at energies below 1 eV have been observed, but the results reported by authors from different laboratories are not always consistent.[14]

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