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The electronic structure and conductivity of large models of amorphous silicon

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Abstract. Calculations of the electronic properties of very large models of amorphous silicon are presented using Chadi's tight-binding model and the equation-of-motion method. The electronic density of states and the conductivity are calculated for structures containing up to 13 824 atoms generated using molecular dynamics techniques. The structures contain defects, but the importance of this work is that we can make comparisons with earlier calculations using pseudopotentials, work with larger structures, use longer run times and lay the basis for calculations on hydrogenated a-Si and calculations of more complex properties, such as the Hall coefficient which is a long-standing problem.

1. Introduction

The quantitative understanding of amorphous semiconductors has remained a major unsolved problem for many years despite, the high level of activity especially concerned with device development.

Progress in computer simulations of electronic and structural properties has made it possible to clarify some issues, albeit for structural models which usually consist of hundreds of atoms. We have used the www model (Wooten *et al* 1985), pseudopotentials and the equation-of-motion method (Alben *et al* 1975, Weaire and Williams 1977, Kramer and Weaire 1978, Kramer *et al* 1981, Hickey *et al* 1985, Hickey and Morgan 1986, Hickey *et al* 1990a) to study a number of properties. On the other hand, the tight-binding models are often used for studies of the electronic properties of amorphous systems (Ding and Andersen 1987, Nichols and Winer 1988, Bose *et al* 1988, Biswas *et al* 1989, Mercer and Chou 1991). Localization in fully bonded models of amorphous silicon was studied by Nichols and Winer (1988), while a tight-binding muffin-tin orbitals scheme and the recursion method were also used for studies of properties of the www model (Bose *et al* 1988). Recently Biswas *et al* (1989) applied the simple tight-binding model of Chadi (1984) for studies of the electronic structure of defects in a model of amorphous silicon composed of 216 atoms. They found a large density of gap states arising from threefold coordinated atoms.

In a very recent paper (Mercer and Chou 1991) studies of the electronic structure of amorphous silicon using tight-binding models were presented. The structure consisted of 588 atoms and was generated by molecular dynamics. The main drawback of the structure they used was a very high percentage of fivefold coordinated atoms

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(22%), which is much higher than would be expected or is reasonable. They also obtained a high density of states in the gap, mainly due to threefold coordinated atoms. The results were not very sensitive to the tight-binding models they used.

In our previous paper (Holender and Morgan 1991) we generated a wide range of a model structures of amorphous silicon which were composed of up to 10^5 atoms. We are now able to present the results of calculations of the electronic conductivity for some of these structural models. Because we are dealing with large structures (up to 13 824 atoms in this study) we have to use a method which enables us to calculate the electron density of states and the electrical conductivity of such systems with reasonable accuracy. We can then make comparison with previous calculations using pseudopotentials, but for only 216 atoms.

We apply the nearest-neighbour tight-binding model of Chadi (1984), combined with the equation-of-motion method and compare the results for the smaller systems and pseudopotential method. The importance of this work is that the two types of calculations are in reasonable agreement, but we are able to perform much more precise calculations for larger models and also demonstrate some useful features of the equation-of-motion method. This work enables us to extend the method to other properties and materials of more applied importance, such as hydrogenated a-Si.

2. The amorphous silicon models

We have recently published details of various models of amorphous silicon (Holender and Morgan 1991) where a common feature is the presence of about 2% of threefold-coordinated atoms and a similar fraction of atoms is fivefold coordinated.

In this paper we will use some of our models and compare results with those obtained for the www model. The original www models are fully bonded, i.e. all atoms are fourfold coordinated. From EPR experiments it is thought that the number of coordination defects is about 10^{19} – 10^{20} cm^{-3} (Brodsky 1985), so there are about 0.1% defected atoms in a real network of amorphous silicon, but it is not clear what kind of defect gives the EPR signal. It was believed that threefold-coordinated atoms are responsible for the signal, but Pantelides (1986,1987) suggested that the fivefold-coordinated atoms might be the major defect. Our structures (Holender and Morgan 1991) contain about 6% of coordination defects of both types, i.e. an order of magnitude more than that indicated by experimental data, but the main point of this paper is to demonstrate the power of the equation-of-motion method and the usefulness of a simple tight-binding scheme. In this paper we also present results for a structure composed of 1728 atoms having only two defected atom, so that the concentration of defects approaches the experimental value. An important point is that real structures composed only of Si are thought to contain voids or internal surfaces which are not present in our model structures.

3. Electronic structure calculations

3.1. Method

In order to carry out calculations for large systems we have used Chadi's nearest-neighbour tight-binding model (Chadi 1984). One should be very cautious when applying Chadi's parameters for structures other than the diamond structure of silicon,

but on the other hand the local environment in the amorphous silicon does not differ very much from those in the diamond structure. It is a semi-empirical approach, but, as can be found in the literature (Biswas *et al* 1939, Mercer and Chou 1991) and as will be shown in this paper, this model gives quite a good description of the electronic properties of amorphous silicon. We have verified its applicability for amorphous silicon ourselves by comparing with results for the same structure using the pseudopotential approach and we have obtained very good agreement (Hickey and Morgan 1986). The tight-binding model has also been applied successfully for studies of localization in amorphous germanium-molibdenum alloys.

Mercer and Chou (1991) compared Chadi's tight-binding model with another tight-binding model (Allen *et al* 1986) with much better justified transferability of parameters for amorphous silicon. However, the results obtained using both models for the same amorphous structure are very similar.

We apply the equation-of-motion method of solving the time-dependent Schrödinger equation. The initial wavefunction is chosen to be

$$\Phi = \sum_{j=1}^{4N} b_j \chi_j \quad (1)$$

where χ_j is a tight-binding basic function (four per site) when only s and p orbitals are used. The initial phases, b_j , are chosen randomly with the condition

$$\sum_{j=1}^{4N} b_j^*(0) b_j(0) = 1. \quad (2)$$

The time evolution of the initial random wavefunction Φ is calculated by numerical integration of the time-dependent Schrödinger equation using the simplest leapfrog algorithm. The matrix elements of the tight-binding Hamiltonian are calculated using Chadi's parameters with r^{-2} scaling as a function of distance r and a cutoff between the first and second nearest neighbours defined by the minimum in the pair distribution function. It is known that Chadi's parameters do not describe the details of the conduction band very accurately, but for our studies it is not a very serious drawback as we are concerned with broader issues. We will mainly concentrate on states in the vicinity of the gap.

The normalization of the wavefunction (2) is conserved throughout all runs (up to 10^6 iterations) with an accuracy better than one part in 10^6 .

3.2. Electronic density of states

The electronic density of states is obtained from the following formula

$$g(E) = \frac{1}{\pi \hbar} \text{Re} \int_0^T \sum_{j=1}^{4N} b_j^*(0) b_j(t) e^{-iEt/\hbar} e^{-t/\tau} dt \quad (3)$$

where $T \gg \tau$ (in our calculations $T = 5\tau$). The exponential damping compensates for the finite length of integration. Such calculations result in the density of states convoluted with a Lorentzian with a width inversely proportional to τ . One can deconvolute the resulting density of states (Hickey and Morgan 1986), but, due to the relatively fast calculations in the tight-binding approximation, we are able to run integrations for a very long time (over 100 000 iterations) and make the Lorentzian very narrow. The final density of states is obtained by averaging over at least ten sets of the initial random phases.

3.3. Conductivity

The conductivity as a function of energy is calculated from the Kubo–Greenwood formula (Kramer *et al* 1981, Hickey *et al* 1990a, Hickey *et al* 1990b):

$$\sigma_F(E) = \frac{2\pi e^2 (4N)^2}{\hbar \Omega} \sum_{i,j,k,l} (\mathbf{r}_{ij} \cdot \mathbf{e}) H_{ij} (\mathbf{r}_{kl} \cdot \mathbf{e}) H_{kl} \times ((b_i^F b_j^{F*} b_k^{F*} b_l^F) - \langle b_i^F b_j^{F*} \rangle \langle b_k^{F*} b_l^F \rangle) \quad (4)$$

where i, j, k, l denote the tight-binding states, $H_{ij} = \langle i|H|j \rangle$ denotes the matrix element of the Hamiltonian H , \mathbf{r}_{ij} is a vector from the site at \mathbf{r}_i to the site at \mathbf{r}_j , \mathbf{e} is the direction of the applied electric field, Ω is the volume, N is the number of atoms and $\langle \rangle$ denotes averaging over time. The symbol $b_j^F(t)$ denotes the amplitude of the j th phase as a function of time as it evolves from an initial random value and is filtered to retain only the states near to the required energy E . The filtering is carried out in a way described in Hickey *et al* (1990a).

The amplitudes are integrated numerically with the filter function

$$F_E(t) = (1/\pi)(1/\sqrt{2W})(1/t) \sin(Wt/\hbar) \exp(iEt/\hbar) \quad (5)$$

where W is a width of the filter function. In all calculations $W = 0.1$ eV. If the integration is carried out for sufficient time, then the filter function has a nearly rectangular shape. This function integrated over 100 000 iteration steps (the value used in our calculations) is shown in figure 1 (without a factor of $1/\sqrt{2W}$ which is required for calculations of the conductivity). This filter function is very useful, in general, for isolating a group of states and can be used, for example, in self-consistent calculations or calculations of the optical properties (Weaire *et al* 1991). Furthermore, a very important point is that it can be used to decrease the effective band width and then a larger time step can be used to perform calculations on larger systems.

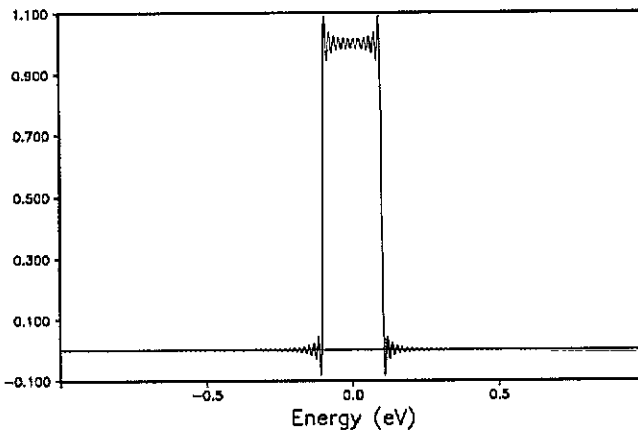


Figure 1. The filter function used in the calculations.

4. Calculations

4.1. Structures and parameters

We have chosen the following structures for our study:

- (i) The original www structure (216 atoms, fully bonded).
- (ii) The www structure relaxed with the Stillinger–Weber potential (Stillinger and Weber 1975) using molecular dynamics (216 atoms, fully bonded; denoted by S1).
- (iii) A structure composed of 216 atoms with two defected (undercoordinated) atoms generated using molecular dynamics starting from the Wooten and Weaire model (denoted by S2).
- (iv) A structure from our paper (Holender and Morgan 1991) having about 4% overcoordinated and 2% undercoordinated atoms (1728 atoms; B1).
- (v) A structure generated from www (as described by Holender and Morgan (1991)) by putting together eight www blocks. However, contrary to structure B1, only 12.5% of the randomly chosen atoms were given higher kinetic energy. The structure was later cooled to 0 K. This structure contains only two defected (not fourfold coordinated) atoms, so the number of defects roughly corresponds to the range of experimental values deduced from EPR measurements. The one drawback of this structure is that a degree of the initial periodicity is retained, but it should not be very important for the study of electronic properties. We will denote this structure B2.

Finally we used the structure M2 from our previous paper (Holender and Morgan 1991), composed of 13 824 atoms and having 2% threefold coordinated atoms and 4.5% fivefold coordinated ones.

The time step used in our integrations is $\Delta t = 0.005$ fs for the calculations of the density of states; for the filtered states the time step can be increased by a factor of up to ten to increase the speed of calculations. The calculations of the electronic density of states are carried out over the whole range of energies for the tight-binding model, i.e. from -15 eV to 15 eV. For systems of 216 atoms we carried out 25 000 iterations and used ten sets of initial random phases. We were able to run calculations for longer times, but then we got better resolution (τ is bigger) and very spiky curves because of the limited number of states (864).

For a bigger system (1728 atoms) we carried out 100 000 iterations. When calculating the electrical conductivity we concentrated on the states in the vicinity of the gap. During the 100 000 iterations we filtered states with width (W) equal to 0.1 eV and calculated the electrical conductivity from (4) by averaging over the final 10 000 iterations from the total of 25 000. We repeated this procedure for at least ten different sets of the initial random phases and we have checked that changing the orientation of the electric field has little effect. We found that this procedure gives extremely reasonable accuracy, which we tested by using 30 different sets of phases for selected samples. The electrical conductivity is calculated for energies around a gap at intervals of 0.1 eV.

All the calculations are carried out at the densities derived from constant-pressure molecular dynamics using the Andersen method (Andersen 1980) and the Stillinger–Weber interatomic potential.

4.2. Results

In figures 2–6 the density of states is shown for the structures described above and,

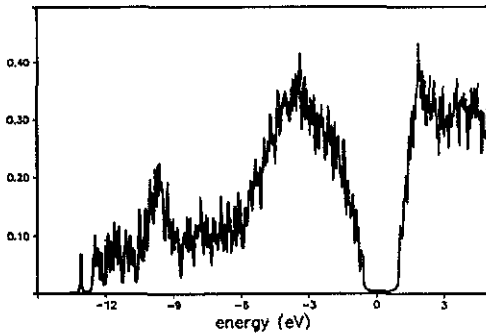


Figure 2. The electronic density of states (spin eV atom)⁻¹ for the www model (216 atoms).

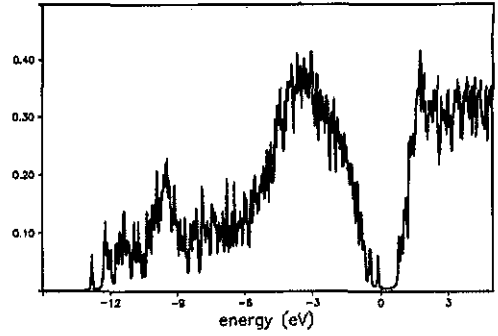


Figure 3. The electronic density of states (spin eV atom)⁻¹ for structure S2 (216 atoms).

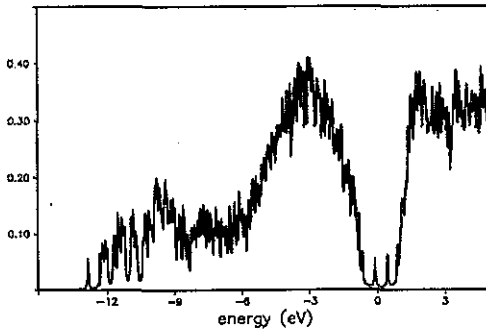


Figure 4. The electronic density of states (spin eV atom)⁻¹ for structure S3 (216 atoms).

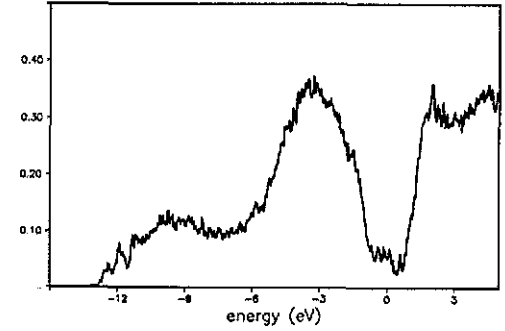


Figure 5. The electronic density of states (spin eV atom)⁻¹ for model B1 (1728 atoms).

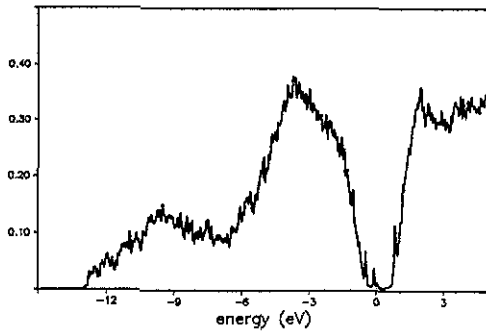


Figure 6. The electronic density of states (spin eV atom)⁻¹ for model B2 (1728 atoms).

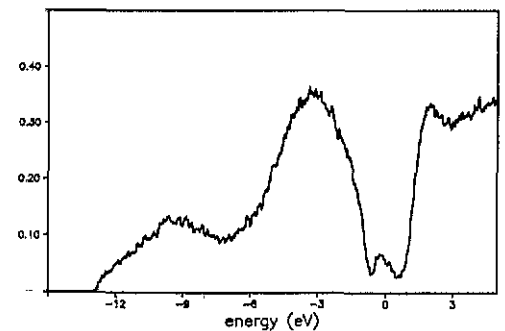


Figure 7. The electronic density of states (spin eV atom)⁻¹ for a structure composed of 13 728 atoms (model M2 from Holender and Morgan (1991)).

to demonstrate the efficiency of our algorithm, in figure 7 we show the density of states for a larger system consisting of 13 824 atoms.

When calculating the electrical conductivity from (4), the expressions $\langle b_k^{F*} b_l^F \rangle$ are not needed in the limit of large times, since these terms approach zero rapidly. Let us define

$$S_1 = \sum_{i,j} (\mathbf{r}_{ij} \cdot \mathbf{e}) H_{ij} \langle b_i^{F*} b_j^F \rangle$$

and

$$S_2 = \sum_{i,j,k,l} (\mathbf{r}_{ij} \cdot \mathbf{e}) H_{ij} (\mathbf{r}_{kl} \cdot \mathbf{e}) H_{kl} (b_i^F b_j^{F*} b_k^{F*} b_l^F)$$

then the electrical conductivity has the form

$$\sigma_F(E) \propto S_2 - S_1 S_1^*$$

Because of the symmetry of H_{ij} , S_1 is an imaginary number and S_2 is a real one. In figure 8 an example of the time dependences of $S_1 S_1^*$, S_2 and $S_2 - S_1 S_1^*$ is shown for a single set of phases, illustrating the decreases of S_1 and the remarkable constancy of $\sigma_F(E)$. When the density of states is low then the fluctuations in the asymptotic limit for a single set of phases is more pronounced because each eigenstate within the filter function does not receive exactly the same weight. The amplitudes only have the same modulus on average, which makes it important to average over phases near the gap to obtain accurate results.

Figures 9–13 show the conductivity and the electronic density of states for energies around the gap.

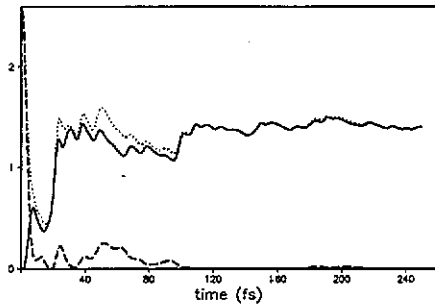


Figure 8. The time dependence of S_2 (dotted line), $S_1 S_1^*$ (dashed line) and $S_2 - S_1 S_1^*$ (in arbitrary units) for structure S2 and states filtered at an energy of -2 eV.

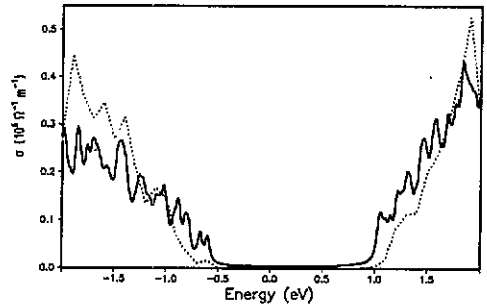


Figure 9. The electronic density of states (solid line) and conductivity (dotted line) for states close to the gap for the www model.

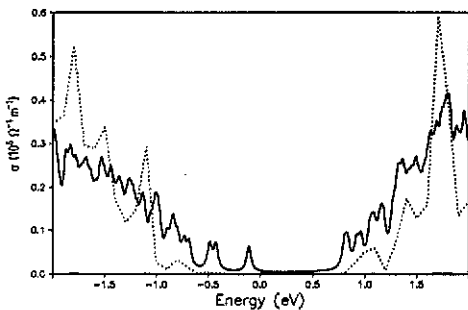


Figure 10. The electronic density of states (solid line) and conductivity (dotted line) for states close to the gap for structure S2.

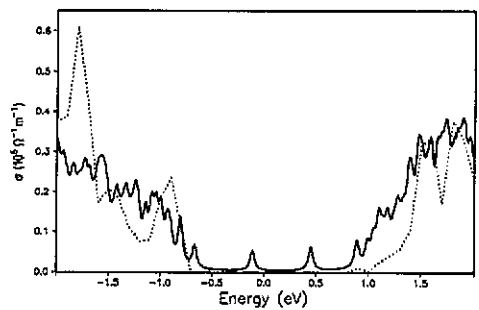


Figure 11. The electronic density of states (solid line) and conductivity (dotted line) for states close to the gap for structure S3.

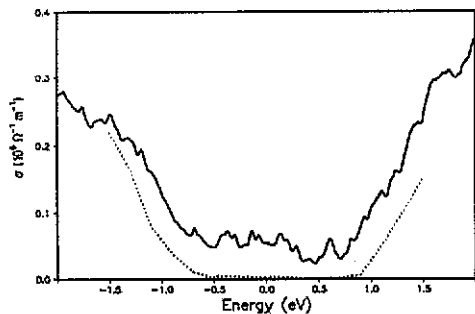


Figure 12. The electronic density of states (solid line) and conductivity (dotted line) for states close to the gap for structure B1.

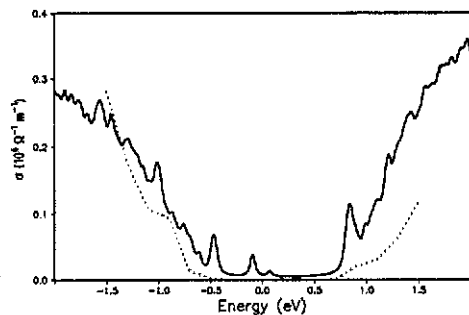


Figure 13. The electronic density of states (solid line) and conductivity (dotted line) for states close to the gap for structure B2.

5. Discussion

Before starting any discussion we should comment on the definition of the nearest neighbour. If the radial distribution function is equal to zero after the first peak then any atom closer in distance than this zero point can reasonably be defined as a nearest neighbour (NN). The situation is far more complex if $g(r) > 0$ between NN and NNN, or if there are small additional peaks. This is the case for defected structures and probably for the real material as well. In this case it is clear that we are dealing with defected structures, but there is some ambiguity in assigning the number of nearest neighbours for any particular atom.

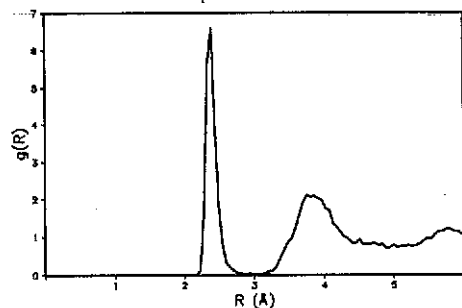


Figure 14. The radial distribution function for structure M2.

We consider, for example, our structure B2; the radial distribution function is shown in figure 14. It is very close to zero in the range from 2.70 Å to 3.10 Å. If we define NN by 2.75 Å, then we get 5 atoms with 2NN, 75 with 3NN, 1605 with 4NN and 43 with 5NN. If we define NN by 3.0 Å, then we get, respectively, 1, 48, 1599, 80. So if we have a continuous distribution of interatomic distances, then the concept of 3, 4 or 5 coordinated atoms is not very clear. It also perhaps casts some doubt on the interpretation of EPR results in terms of the coordinations of atoms, but, on the other hand, the nearest-neighbour concept is very useful when discussing structures, so we will use it, bearing in mind the above comments.

As is expected for the www model, we get a well defined gap of about 1.5 eV (figure 2), which is in very good agreement with others calculations (e.g. Hickey *et al* 1985, Hickey and Morgan 1986, Biswas *et al* 1989). Relaxation of the www

structure using the Stillinger-Weber potential makes the gap slightly narrower (figure 3), so even if the structure is still fully bonded there are states in a gap region due to the distortion of the network. The structure composed of 216 atoms, which has two defected atoms, has states in a gap (figure 4). Furthermore, calculations of the density of states using the pseudopotential method give identical results (Hickey B J, private communication). When we project out the density of states associated with these atoms it is found that they give the dominant contribution to the gap states; this has also been reported by others (Biswas *et al* 1989, Mercer and Chou 1991).

The larger defected structure (figure 5) has a high density of states in the gap, presumably because a band of defected states is formed. On the other hand it is worth noticing that the structure factor for this structure agrees very well with the experimental one (Holender and Morgan 1991). This structure factor has been used recently in a test of a new theory of gap formation (Burr *et al* 1992), which also results in only a very low minimum in the gap region. This illustrates how a defected structures can have a very similar structure factor to a real solid containing voids, if one ignores low-angle scattering from voids which are probably always present in pure amorphous Si.

The structure B2 with a low concentration of coordination defects (closer to that thought to be the experimental case) retains a gap only slightly narrower (figure 6) than the fully coordinated small model. Finally in figure 7 we show the results for the structure composed of 13 824 atoms (structure M2 in Holender and Morgan (1991)). It illustrates the efficiency of our method, which enables us to calculate the electronic density of states for over 10^4 atoms in a reasonable time. This structure also has many states in the gap region.

Because of some doubts about the definition of NN, we also checked the role of the cutoff in Chadi's tight-binding model. We found that the electronic properties are not sensitive to a change in the cutoff in the calculations of the matrix elements in the range from 2.75 Å to 3.00 Å. As far as the conductivity is concerned, the states in a gap give almost zero conductivity and they are almost certainly localized. From figures 9-13 it is clear that the conductivity drops more rapidly than the density of states, giving a clear indication of the probable position of mobility edges.

The conductivity is equal to about $5 \times 10^5 \Omega^{-1} \text{ m}^{-1}$ for energies away from a gap. It corresponds to resistivity of 200 $\mu\Omega \text{ cm}$, while typical values for liquid or amorphous metals are about 100 $\mu\Omega \text{ cm}$. This is an indication of free-electron-like behaviour away from the gap, as was suggested by Hickey *et al* (1990a). It is remarkable that calculations using plane waves and pseudopotentials on smaller models give such good qualitative agreement with these tight-binding calculations. This is especially noteworthy when one remembers that the results of the Ziman theory for simple liquids can be very sensitive to details of the pseudopotential and structure factors. Perhaps it is the case that, in the situations considered here, the density of states is the most important factor. The random-phase model predicts that the conductivity σ is proportional to $(g(E))^2$ and also that, if two models yield similar density of states, then the conductivities might agree quite well.

The *really* important thing about these calculations is that they show how accurate results can be obtained for large models. This opens the way for studies of hydrogenated amorphous silicon using model structures (Mousseau and Lewis 1991) and a tight-binding basis. It seems almost certain that hydrogen atoms with a tetrahedral arrangement of Si atoms around them at undercoordinated defect sites will pull states out of the gap region (Jones B, private communication). Furthermore, we are now

able to evaluate the Hall conductivity using the forms given by Morgan and Howson (1985) and settle the long-standing puzzles about the anomalous behaviour observed by LeComber *et al* (1977) (Holender and Morgan 1992).

All calculations were carried out using the Amdahl VP1200 supercomputer. The density of states calculations are rather fast; for 13824 atoms about 90 minutes of CPU time were needed. For smaller models calculations are much faster, but we have to average over more sets of initial phases. The conductivity calculations are much more time-consuming; at least 15 min of CPU time were required in order to get the the conductivity value for one energy.

All structures used in this study and those discussed in Holender and Morgan (1991) are available on request on a floppy disk or via E-mail (phy6jan@uk.ac.leeds.cms1).

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