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Effect of frustration on the band edge in amorphous semiconductors

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The existence of odd-membered rings leads to an erosion of antibonding states in a simple tight-binding Hamiltonian on a random network. We obtain better estimates of the magnitude of this erosion by systematically introducing fivefold rings into a diamond lattice with a supercell containing 8000 atoms. It is shown that the position of the band edge moves roughly linearly with the number of fivefold rings and that the slope agrees with that obtained from perturbation theory.

I. INTRODUCTION

There has been much interest in the past decade in the electronic[1-3] and vibrational[4] properties of continuous random networks,[5] the prototype of which is fourfold coordinated and is believed to describe the structure of amorphous Si (a-Si) well. In the very simplest theories ("sp^3" orbitals with nearest-neighbor overlaps only, and nearest-neighbor central forces only[6]) the eigenvalues of two separate problems, the electronic band structure and the vibrational density of states, can be related to the eigenvalues of the Hamiltonian

$$H=\sum_{\langle i,j\rangle} |i\rangle\langle j| . \tag{1}$$

This is the simplest Hamiltonian that contains the topology of the network. The state $|i\rangle$ is defined at a site i and has an overlap (set equal to 1) with the four neighboring sites in the network. This is denoted by the angular brackets in the summation. Because of the intimate connection between (1) and the electronic and vibrational states in these networks, it is important to have a good understanding of the properties of the Hamiltonian (1).

Rewriting (1) in matrix form leads to a semipositive real symmetric matrix with all zero entries except for four entries of 1 in each row and column. It is sometimes called the connectivity matrix of the network. Using the theorem of Frobenius,[7] it can be shown that the eigenvalues ϵ of (1) are bounded by

$$-4 \leq \epsilon \leq 4 . \tag{2}$$

The state at +4 corresponds to the "bonding" state with equal amplitudes, for example 1, on every site. The "antibonding" state at −4 corresponds to alternating amplitudes +1, −1, +1, etc., from site to site. It is clear that such a state can only be constructed on a bichromatic network (i.e., one that can be divided into two sublattices A and B such that all the four neighbors of A are on B and vice versa). Examples of such networks are the diamond structure itself, wurtzite, and the Connell-Temkin[8] continuous random network. It is generally believed that a-Si contains odd rings, the smallest of which involves five bonds. We thus expect an erosion of the states around the antibonding band edge at $\epsilon = -4$.

This problem has received a considerable amount of attention that we will review briefly as it is not all easily accessible. We will use the symbol n_5 for the average number of fivefold rings through a site in the network. It was shown[9] that if the network can be dissected into fivefold rings of bonds so that each bond is included in such a ring exactly once ($n_5 = 2$), then the lower band edge occurs at

$$\epsilon = -4\cos(\pi/5) = -3.236 . \tag{3}$$

While no real networks are known to have this property, it was shown by direct calculation that Ge III has its lower band edge at the position given by (3). Ge III is a metastable high pressure form of Ge (Refs. 9 and 10) that has $\frac{1}{3}$ of its sites with four fivefold rings and $\frac{2}{3}$ of its sites with three fivefold rings so that $n_5 = 3.33$.

The fact that the erosion in these two networks is identical, even though they have differing numbers of fivefold rings, led to a notion that as the number of fivefold rings in a network increases the lower band edges move from −4 to −3.236, with −3.236 being an asymptote that is reached when the number of fivefold rings becomes sufficiently large ($n_5 \geq 2$). It is interesting to note that the original Polk continuous random network[11,12] has $n_5 \simeq 1.9$. Subsequent continuous random networks have shown similar values except, of course, for the Connell-Temkin network that has $n_5 = 0$.

In order to test these ideas, it was convenient to have a network in which n_5 could be varied continuously. This was done by Goldstein[13] by introducing "defects" into the diamond lattice. Although somewhat artificial, this was a convenient way to construct a network in which n_5 could be varied. This calculation showed that the lower band edge did move more or less monotonically with the number of fivefold rings. However, the calculation encountered two problems. (a) The initial slope at small n_5 did not seem to be correct, and (b) it was unclear whether the speculated asymptotic behavior did indeed occur.

In the next section we repeat this calculation using 8000 atoms rather than 64. The problem with (a) is cleared up but (b) remains obscure. However, it seemed to us useful to publish this work to make it available in the open literature. We note that since the work of Goldstein in 1974, the word "frustration" has been coined by workers in the spin glass area.[14] We note that this is also a manifestation of frustration. The inability to fit spins pointing alternately up and down around an odd plaquette or polygon is similar to the inability to fit amplitudes +1, −1, etc., around an odd ring. The major difference is that we are interested in a density of states rather than a thermodynamic quantity.

II. THE CALCULATION

A defect that creates four fivefold rings can be created by removing a site and its four bonds[3] shown by dashed lines in Fig. 1. Although a single defect of this kind cannot shift the band edge in an infinite network, it does change the nature of the local density of states at the band edge from $\sim(E+4)^{\gamma}$ to $\sim(E+4)^{\gamma-1}$ where $\gamma=\frac{1}{2}$ and, as we will show later in this section, the magnitude of the shift for a small finite fraction of defects can be inferred from the behavior of a single defect.

The numerical computation proceeds as follows. An N-site cubic network is chosen with periodic boundary conditions so that the fourfold connectivity is maintained. The diamond structure can be described with a cubic unit cell with 8 atoms/unit cell. We used a large cube with 10 unit cells in each direction to give $8\times10^3=8000$ atoms. We also reproduced the original calculation of Goldstein with a large cube with 2 unit cells in each direction to give $8\times2^3=64$ atoms. A convenient labeling scheme is chosen for the sites (1 through N) and a register of the four neighbors of each site is generated. A random number generator is used to provide an integer in the range 1 to N to determine which site is to be removed. Another random number is used to choose one of the two possible reconnections between the neighbors of the removed site (see Fig. 1). A register is kept of both sites removed and of sites that are now on a fivefold ring as a result of the reconnections. The original labeling is now modified to go from 1 to $N-1$ and the procedure repeated, except that if an atom already has one or more fivefold rings through it, it is not removed as this would create a fourfold ring. The procedure is repeated until the required number of defects has been created. It was found possible to remove up to about 15% of the sites in this way. The register of remaining sites and their four neighbors defines a real symmetric sparse matrix. The extreme negative eigenvalue was obtained using a block Lanczos routine developed by Scott.[15] Indeed it was the existence of this routine that encouraged us to reexamine this problem.

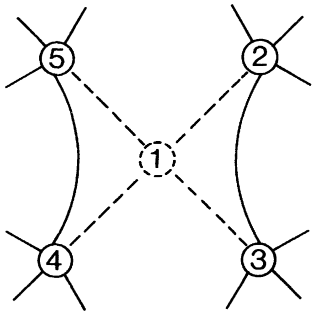

FIG. 1. Showing a defect atom and its four bonds by dashed lines. When atom 1 is removed, the host lattice is reconnected by the solid curve bonds, joining atoms 2 and 3 and atoms 4 and 5 so that every site remains fourfold coordinated but four fivefold rings are introduced into the network.

The results for the position of the lower band edge against fraction of sites removed are shown in Fig. 2. It can be seen that the results for 8000 atoms (crosses) lie above these for 64 atoms (triangles) and are rather monotonic. At a number of places, crosses lie vertically above one another. This is because even though the same fraction of sites were removed, different random configurations of the defects were produced leading to different extreme negative eigenvalues.

The initial slope in Fig. 2 can be calculated by perturbation theory. The definition of the Green's function g for the Hamiltonian (1) is given by

$$g=(\epsilon-H)^{-1}\,. \tag{4}$$

The defect matrix for a single defect as shown in Fig. 1 is given by[3]

$$\begin{array}{c c} \begin{array}{ccccc} |1\rangle & |2\rangle & |3\rangle & |4\rangle & |5\rangle \end{array} & \\ \left[\begin{array}{ccccc} 0 & -1 & -1 & -1 & -1 \\ -1 & 0 & 1 & 0 & 0 \\ -1 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 1 & 0 \end{array}\right] & \begin{array}{c} |1\rangle \\ |2\rangle \\ |3\rangle \\ |4\rangle \\ |5\rangle \end{array} \end{array}\,, \tag{5}$$

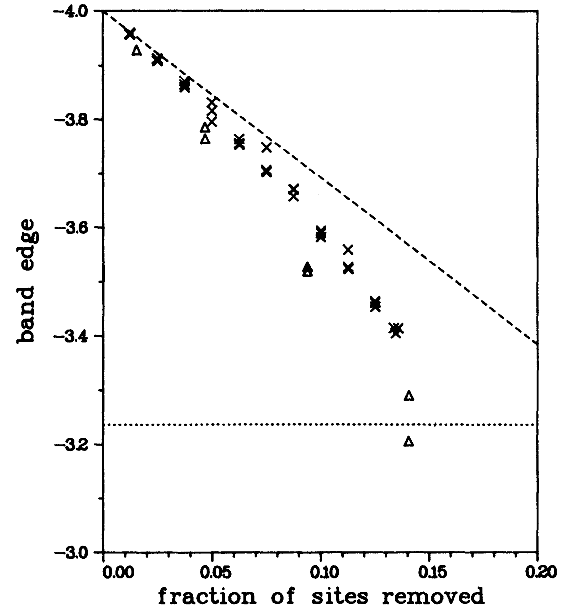

FIG. 2. Showing the shift in the lower band edge with the fraction of sites removed for the 8000-atom samples (crosses) and the 64-atom sample (triangles). The dotted line shows $-4\cos(\pi/5)=-3.236$ [see Eq. (3)] and the dashed line is the result of perturbation theory [Eq. (14)].

where the kets just designate the states associated with the atoms in Fig. 1. The Green's function with a single defect present G is then given by

$$G=g+gVG \tag{6}$$

and the *change* in the density of states is given by

$$\Delta\rho=-\frac{\operatorname{Im}}{\pi}\sum_i(G_{ii}-g_{ii})$$

$$=-\frac{\operatorname{Im}}{\pi}\frac{\partial}{\partial\epsilon}\ln\operatorname{Det}(1-gV)\,. \tag{7}$$

The Green's functions can be decomposed into the various symmetry types associated with the point defect in Fig. 1. *Near* the lower band edge at $\epsilon=-4$, only the s-like symmetry contributes and we find that

$$\Delta\rho=\frac{\partial\rho}{\partial\epsilon}\bigg|_{\epsilon=-4}\bigg/\left(\frac{1}{8}-W\right), \tag{8}$$

where W is the Watson integral[3] for the diamond lattice. It can easily be shown that this is the same as the Watson integral[16] for the fcc lattice and given by

$$W=0.44822\ldots\,. \tag{9}$$

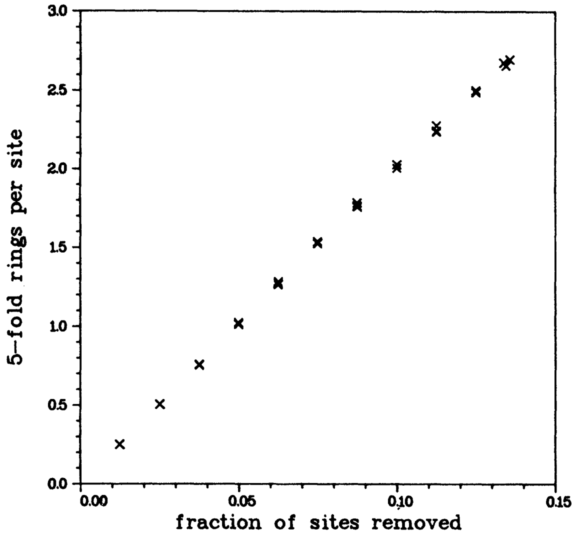

FIG. 3. Showing the number of fivefold rings per site (n_5) against the fraction of sites removed (c).

The initial slope can be obtained by the following argument which is nonrigorous but probably correct. Similar arguments exist for phase boundaries in thermodynamics.[17] We assume that *near* the lower band edge ϵ_0, the density of states can be written as

$$\rho=A(c)[\epsilon-\epsilon_0(c)]^{\gamma(c)}\,, \tag{10}$$

where c is the concentration of defects. Then

$$\frac{1}{\rho}\frac{\partial\rho}{\partial c}=\frac{1}{A}\frac{\partial A}{\partial c}+\frac{\partial\gamma}{\partial c}\ln(\epsilon-\epsilon_0)-\frac{\gamma}{\epsilon-\epsilon_0}\frac{\partial\epsilon_0}{\partial c}\,. \tag{11a}$$

If A, ϵ, and γ are continuous functions of c, then the last term in (8) dominates as $\epsilon\to\epsilon_0$ so that

$$\frac{1}{\rho}\frac{\partial\rho}{\partial c}\simeq-\frac{\gamma}{\epsilon-\epsilon_0}\frac{\partial\epsilon_0}{\partial c}\,, \tag{11b}$$

but from (10) we have

$$\frac{1}{\rho}\frac{\partial\rho}{\partial\epsilon}=\frac{\gamma}{\epsilon-\epsilon_0}\,. \tag{12}$$

Combining Eqs. (8), (11b), and (12),

$$\frac{\partial\rho}{\partial c}=-\frac{\partial\epsilon_0}{\partial c}\frac{\partial\rho}{\partial\epsilon}=\left(\frac{\partial\rho}{\partial\epsilon}\right)\bigg/\left(\frac{1}{8}-W\right) \tag{13}$$

so that

$$\frac{\partial\epsilon_0}{\partial c}=(W-\tfrac{1}{8})^{-1}$$

$$=3.094\ldots\,, \tag{14}$$

where we have used the equivalence between $\Delta\rho$ and $\partial\rho/\partial c$ for one defect.

The argument above allows us to go from a single defect to a small but thermodynamically significant number of defects. The initial slope (14) is shown in Fig. 2 as a dashed line. It agrees well with the results for the 8000-atom sample but

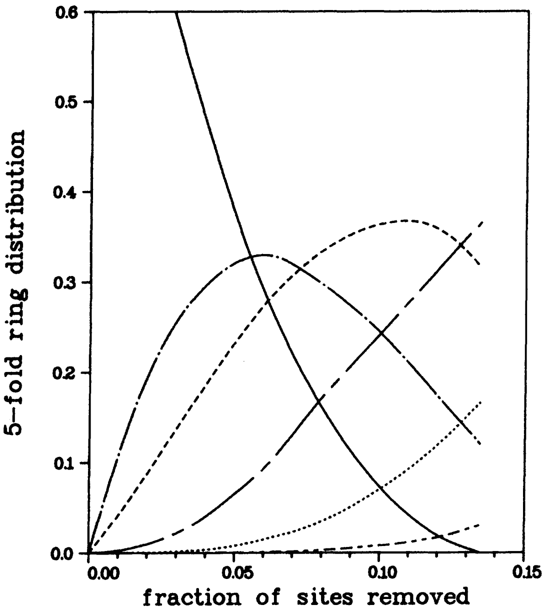

FIG. 4. Showing the fivefold ring distribution against the fraction of sites removed (c). ——, —·—·, -----, —— ——, · · ·, and — — — are the probability that a site has 0, 1, 2, 3, 4, or 5 fivefold rings passing through it. The graph is obtained by averaging over three different ensembles. The fraction of sites with six fivefold rings is too small to show.

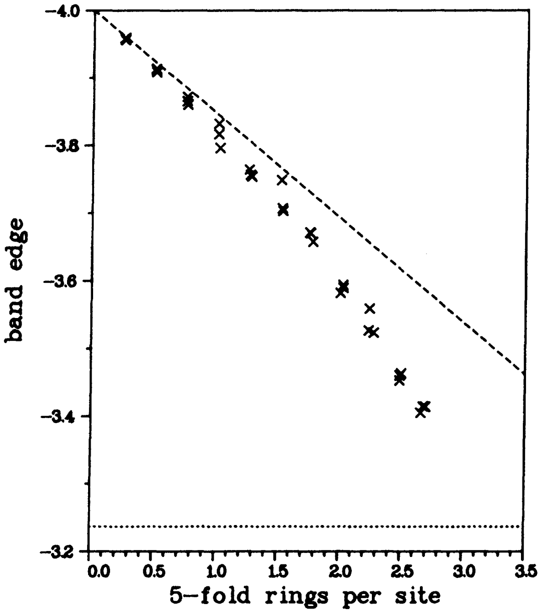

FIG. 5. Showing the shift in the lower band edge of the 8000-atom sample with n_5 (the average number of fivefold rings going through a site). The dotted line shows $-4\cos(\pi/5) = 3.236$.

less well with those for the 64-atom sample as the defects are not sufficiently far apart (because of the periodic boundary conditions).

When the first defect is created four separate fivefold rings are made. If the defects are well separated the number of fivefold rings per sites should be

$$n_5 = 20c/(1-c)\,, \tag{15}$$

where c is the fraction of sites removed. The factor $(1-c)$ in the denominator arises because the total number of sites is reduced. In fact we see from Fig. 3 that n_5 is linear in c and very nearly given by

$$n_5 \simeq 20c \tag{16}$$

to a very good approximation. This occurs because sometimes fewer than four fivefold rings are made when a defect is created. On the average it appears that $4(1-c)$ fivefold rings are created. In Fig. 4 we show the fivefold ring distribution as a function of the fraction of sites removed. In Fig. 5 we have replotted the data from the 8000-atom sample against the number of fivefold rings per site. The dotted line is at -3.236 [see Eq. (3)] and the dashed line is the result of perturbation theory [Eq. (14), with the factor of 20 from Eq. (16) incorporated to give an initial slope of 0.015 47].

III. CONCLUSION

If we assume that each pair of fivefold rings around a defect introduces a single "frustrated" bond into the network, then there are a fraction $n_5/20 \simeq 0.10$ of such bonds in Polk-type continuous random networks. This leads to an erosion of the lower band edge.

This has important consequences for the size of the gap in amorphous semiconductors. To estimate the size of the effect we use the one-band–two-band transformation[2,3]

$$E = V_1 \pm (V_2^2 + 4V_1^2 + V_1 V_2 \epsilon)^{1/2}\,, \tag{17}$$

with values of the parameters ($V_1 = -2.5$ eV, $V_2 = -6.75$ eV) appropriate for Si and Ge. Taking $n_5 = 1.9$ which, from Fig. 5, gives a shift of ~0.35 in the band edge, we find that the bottom of the conduction band moves up by about 1.24 eV. The top of the valence band is dominated in this model by a δ function (broadened into a band in a more realistic model), whose position is unaffected by the topology. Thus the band gap is *increased by 1.24* eV *by frustration*. Put another way for every additional 1% of frustrated bonds the band gap increases by ≃1/10 eV. (Of course, in reality, by band gap we mean the gap between the mobility edges.) This is a large effect and must be taken into account in any realistic attempt to understand the size of the band gap in amorphous materials.

This effect is important because essentially all other effects, such as dangling bonds, variation of overlap parameters, etc., will go in the other direction and tend to close the band gap or at least produce Lifshitz tails.

ACKNOWLEDGMENTS

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[1] D. Weaire and M. F. Thorpe, Phys. Rev. B 4, 2508 (1971).

[2] M. F. Thorpe and D. Weaire, Phys. Rev. B 4, 3518 (1971).

[3] M. F. Thorpe, D. Weaire, and R. Alben, Phys. Rev. B 7, 3777 (1973).

[4] For a review see M. F. Thorpe, in *Vibrational Spectroscopy of Molecular Liquids and Solids*, NATO Advanced Study Series, edited by S. Bratos and R. M. Pick (Plenum, New York, 1980), p. 341.

[5] For a review see W. Paul and G. A. N. Connell, in *Physics of Structurally Disordered Solids*, NATO Advanced Study Series, edited by S. S. Mitra (Plenum, New York, 1974), p. 45.

[6] P. Sen and M. F. Thorpe, Phys. Rev. B 15, 1600 (1977).

[7] See, for example, R. Bellman, *Introduction to Matrix Analysis* (McGraw-Hill, New York, 1960), p. 278.

[8] G. A. N. Connell and R. J. Temkin, Phys. Rev. B 9, 5323 (1974).

[9] R. Alben, S. Goldstein, M. F. Thorpe, and D. Weaire, Phys. Status Solidi A 53, 545 (1972).

[10] J. S. Kasper and S. M. Richards, Acta Crystallog. Sect. A 17, 752 (1964).

[11] P. Steinhardt, R. Alben, and D. Weaire, J. Non-Cryst. Solids 15, 199 (1974).

[12] D. Weaire and M. F. Thorpe, in *Computational Methods for Large Molecules and Localized States in Solids*, edited by F. Herman, A. D. McLean, and R. K. Nesbet (Plenum, New York, 1972), p. 295.

[13] S. Goldstein, Ph.D. Thesis, Yale University, 1974 (unpublished).

[14] See, for example, G. Toulouse, Commun. Phys. 2, 115 (1977).

[15] D. S. Scott, Oak Ridge National Laboratory Technical Report No. ORNL/CSD-48, 1979 (unpublished).

[16] G. N. Watson, Q. J. Math. (Oxford) 10, 266 (1939).

[17] See Appendix A of M. F. Thorpe and A. R. McGurn, Phys. Rev. B 20, 2142 (1979).