LETTER TO THE EDITOR

A note on band gaps in amorphous semiconductors†

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Abstract. It is argued that the band gap in amorphous semiconductors is maximized if the structure is as homogeneous as possible.

There has been much recent interest in the existence and size of the band gap in amorphous semiconductors. It has been discussed from the point of view of a varying potential (see for example Fritzche 1971), which leads to rather sharp mobility edges with a small number of states in the ‘gap’. Weaire (1971) on the other hand took a tight binding model with constant matrix elements and showed that a gap existed for all topologies. Indeed, subsequent work (Weaire and Thorpe 1971, Thorpe and Weaire 1971, Thorpe et al 1973) has shown that the band gap may actually be larger in amorphous Si and Ge due to the existence of five-membered rings in the Polk structure (Polk 1971). The connection between these two models is not clear but certainly non-constant matrix elements must be included in the tight binding model.

This leads to a most interesting question. What is the relationship between the structure and the band gap of amorphous semiconductors? Phillips (1971) has suggested that there is a very important connection and that the free energy is minimized by a ‘selfconsistent arrangement of atoms which maximizes the bond energies by ejecting states that would otherwise fall in the “tail” region to above the band edge.’ This idea is very appealing but hard to pursue further in quantitative calculations. We set up a model below to show how these states may be ejected by choosing an optimum structure.

The tight binding Hamiltonian of Weaire (1971) uses ‘sp³’ orbitals |i⟩ where i labels the atom and j the bond

\[ H = \sum_{ij} V_{ij} |i⟩⟨j| + \sum_{ij} V_{ij} |i⟩⟨j|. \] (1)

We assume that \( V_{ij} \), being essentially an atomic parameter, is constant throughout the solid but that \( V_2 \) has a distribution that is related to bond lengths. In this note we assume that \( V_2' \) may take one of two values, \( V_2' = \pm 9 \). This simulates a distribution of width 2 δ in the \( V_2 \) and makes the mathematics tractable. Generalizations of this are clear but it is essential to the argument below that the distribution be of finite extent.

We define the sum of the amplitudes \( A_i \) of the four wavefunctions |i⟩ associated

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with atom \( i \)\(^{\dagger} \). After two equations of motion we find

\[
\left(1 - \sum_{i'} \frac{V_{1}E}{E^2 - (V_{2}^{0})^2}\right) A_{i} = \sum_{i'} \left( \frac{V_{1}V_{2}^{0}}{E^2 - (V_{2}^{0})^2} \right) A_{i'}
\]

where \( i, i' \) are neighbouring atoms. If atom \( i \) has \( x \) bonds with overlap \( V_{2}^{0} + \delta \) and \((4 - x)\) with \( V_{2}^{0} - \delta \), then the regions of zero density of states are given by

\[
F(E) < 0
\]

\[
F(E) = \frac{|xV_{1}(V_{2}^{0} + \delta)|}{E^2 - (V_{2}^{0} + \delta)^2} + \frac{|(4 - x)V_{1}(V_{2}^{0} - \delta)|}{E^2 - (V_{2}^{0} - \delta)^2}
- \left| 1 - \frac{xV_{1}E}{E^2 - (V_{2}^{0} + \delta)^2} - \frac{(4 - x)V_{1}E}{E^2 - (V_{2}^{0} - \delta)^2} \right|
\]

for all atoms and all configurations.\(^{\dagger}\) Choosing values for the parameters that are appropriate for Si and Ge (Thorpe and Weaire 1971); \( V_{1} = -2.5 \) eV, \( V_{2} = -6.75 \) eV and putting \( \delta = 1 \) eV; we plot the functions \( F(E) \) in figure 1 for all values of \( x \). There are three cases we may consider.

A. We allow all configurations to occur; that is, all values of \( x \). The band gap is 1.5 eV. This result may also be obtained from Thorpe and Weaire (1971) who show that the gap is 2 min \( |V_{2}| - 4 \max\{V_{1}\} \).

\[\text{Figure 1. The function } F(E) \text{ plotted against } E \text{ for } x = 0, 1, 2, 3, 4. \text{ The regions where all these functions are negative give the regions of zero density of states.}\]

\(^{\dagger}\) This technique allows all the energies to be examined except those for which \( A_{i} = 0 \). These are states that are entirely p-like atomically and occur only at energies \( V_{2}^{0} \pm \delta \). These do not affect the size of the gap.

\(^{\dagger}\) This result is obtained from the following theorem due to Gerschgorin (1931) and quoted by Varga (1962). Let \( A = (a_{i,j}) \) be an arbitrary \( n \times n \) complex matrix, then all the eigenvalues \( \lambda \) of \( A \) lie in the union of the discs

\[|\lambda - a_{i,i}| < \sum_{j \neq i} |a_{i,j}|.\]

Equation (2) in the text corresponds to the special case of a hermitian matrix. The theorem may easily be extended to cover the case where the matrix elements are energy dependent as in (2).
B. We allow all configurations except $x = 0.4$. This makes the structure more homogeneous and increases the gap to 1.88 eV.

C. We only allow $x = 2$. This means that every atom has exactly two bonds with overlap $V_2^0 = \delta$ and two with $V_3^0 = \delta$. The gap increases to 2.35 eV.

These three cases are shown graphically in figure 2. It should be noted that these gaps are the ‘minimum gaps’ and apply to all topologies. We see that the size of the gap is correlated with the homogeneity of the solid.

We expect that the degree of homogeneity is related to the size of the total free energy. The entropy will be largest for case C which also represents the situation where we expect the strains to be minimized. When an amorphous film is grown by rapid cooling we expect a somewhat random distribution of bonds like A to exist. Upon annealing the film goes to a local minimum in the free energy which is the more homogeneous distribution of bonds as in C. We hope that this note will encourage more work on the intriguing possibility of an interplay between structure and the size of the band gap in amorphous semiconductors.

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References

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