SOME ASPECTS OF THE ELECTRONIC DENSITY OF STATES OF AMORPHOUS SEMICONDUCTORS

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Recent progress in the analysis of the properties of a simple tight binding Hamiltonian, appropriate to the study of the role of topological disorder in determining properties of amorphous semiconductors, is reviewed. The band structure generated by such a Hamiltonian for the diamond cubic structure is compared with a more realistic calculation for Ge.

The generalisation that the electronic properties of solids depend chiefly on the nature and degree of the short range order and are little affected by the loss of long range order has in recent years achieved a proverbial status without being at all well understood in theoretical terms. It has of course for long been an important component of the chemist's rather empirical point of view. On the other hand, solid state theorists, accustomed to dealing with systems with essentially perfect long range order, have been somewhat dismayed to be reminded that this does not seem to play a very important role in most physical properties, however important it may be in facilitating their mathematics. In particular, this point has been driven home by the observation of band gaps in amorphous semiconductors 1), equal to or even greater than those of corresponding crystals, despite the fact that "the conventional methods of band theory have not yet succeeded in calculating a density of states with a band gap" 2) for such systems. The conventional methods of band theory are founded on Bloch's Theorem. Without this powerful first step in the mathematics we might appear to be doomed to be cast adrift in a sea of approximations. This is however not entirely so -- as always, some elegant, exact, and quite simple mathematical truths lie behind the empirical generalisation. We shall review below some exact results for a Hamiltonian which provides a somewhat idealised model of an amorphous semiconductor such as Si or Ge. The Hamiltonian is not capable of giving a really accurate description of these semiconductors. On the other hand it is not so oversimplified as to be irrelevant to a qualitative consideration of their properties. Our approach is therefore complementary to that of Klima and McGill3), since we have sought exact results for a crude Hamiltonian while they have sought approximate results for a more accurate Hamiltonian.

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The Hamiltonian that we use involves four basis functions 4 per atom. There is a matrix element V1 between functions associated with the same atom i (but different bonds) and V2 between functions associated with the same bond./ (but different atoms). Implicit in this definition is the assumption that the structure in which these atoms are arranged is such that each atom is tetrahedrally coordinated with its nearest neighbors. This perfect four fold coordination is a feature of the random network model of amorphous semi-conductors 4). In deriving most of our results we do not use, implicitly or explicitly, any further details of the structure, which is just as well since these are not precisely specified experimentally or theoretically at present. The structure can therefore be any four fold coordinated network, whether periodic or disordered. If it is disordered, we call this "topological disorder" to emphasize the fact that we have a Hamiltonian whose matrix elements are the same everywhere in the structure but the connectivity of the structure is disordered.

For $V_2 = 0$ such a Hamiltonian describes an array of decoupled atoms each having an "s-state" at $E = 3 V_1$ and triply degenerate "p-states" at $E = - V_1$. For $V_1 = 0$ it describes decoupled bonds, each with bonding and antibonding states and $E = \pm V_2$. When both matrix elements are nonzero, it may be shown 5) that the eigenstates still fall into two separate bands with zero density of states between them. For $| V_1/ V_2, | < 1/2$ the bands are of bonding and antibonding character, containing 2 states per atom (not counting spin), and are the familiar valence and conduction bands. There is a gap between them of magnitude (at least)

Gap = $2|V_2| - 4|V_1|$ (1)

Thus the gap is not destroyed by topological disorder.

Further results which have been obtained[6-9]) for this Hamiltonian are briefly summarised below.

(1) The bounds are all attained for the case of the diamond cubic structure so the gap takes its minimal value for this case).

(2) There are delta functions of weight unity in the density of states at the top of the valence and conduction bands, for any structure [6]).

(3) The average fractional s-like (p-like) and bonding (antibonding) character of wave functions may be derived as a function of the energy [6, 7]).

(4) The density of states may be related to that generated by a much simpler Hamiltonian, involving only one basis function per atom. This simplifies calculations and provides a proof that when the delta functions are discarded, what remains is symmetric about the center of the gap?).

(5) The existence of the band gap can also be proved when the Hamiltonian is generalised to include a further matrix element V3 which connects functions (/),; for neighboring atoms and different bonds, one of the latter being the bond connecting the atoms [8]). The alternative proof [8]) which provides this generalisation also goes through without the assumption of the orthogonality of the two orbitals associated with a given bond.

(6) The proof may be generalised to the case of a Hamiltonian appropriate to a compound semiconductor, having diagonal matrix elements + Vo associated with the atoms of one type and — V0 for the other type?). It is necessary to further assume that these lie on interpenetrating sublattices, which is not compatible with the existence of five fold rings in the amorphous structure. This point will merit further consideration when the structures of amorphous III—V compounds are more accurately characterised. The gap for the compound is?)

$$\text{Gap} = 2\,(V_2^2 + V_0^2)^{1/2} - 4|V_1| \qquad\qquad (2)$$

It bears an intriguing resemblance to the semi-empirical formula which is central to the recent work of Phillips 10) on crystalline semiconductors.

(7) For any of the above Hamiltonians, the density of states is the same for diamond cubic, wurtzite, and all the related "polytype" structures obtained by arranging close packed layers of diatomic molecules in a close packed structure 9).

(8) For the Hamiltonian in its simplest form, the total energy of the valence band is lower for the random network than for the above crystal structures 9).

While all these results appear to be new, perhaps the last is the only really startling one. Note however that it is derived for a Hamiltonian with purely topological disorder. Bond stretching and bending, which raise the energy of the amorphous solid, are not represented in the model.

How accurate is the Hamiltonian on which this study has been made? This question can best be answered by comparing the band structure which it gives for the diamond cubic structure with a more realistic calculation. Figs. 1 and 2 present such a comparison for the

case of Ge. The valence band is reproduced rather well but the conduction band is not. Note that the delta function in the density of states in the valence band corresponds to a sub-band which although not flat in reality is confined to a width of a few eV. Inciden-tally the transfer of the delta function 8, 7) (or flat band) from one side of the gap to the other on increasing I V1/1721 through the value has a simple counterpart in nature
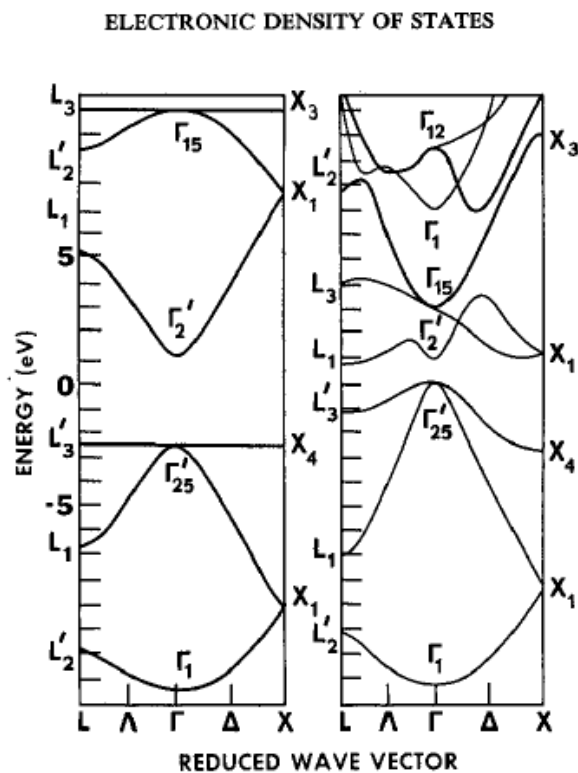

Fig. 1. Band structure of diamond cubic Ge as calculated using the Hamiltonian of ref. 5 (left-hand side) with VI = — 2.5 eV and V2 = — 6.75 eV is compared with the calculation of Herman et al.11) (right-hand side). In our previous works) the topmost X level was incorrectly labelled Xi. We wish to thank F. Herman for pointing this out.
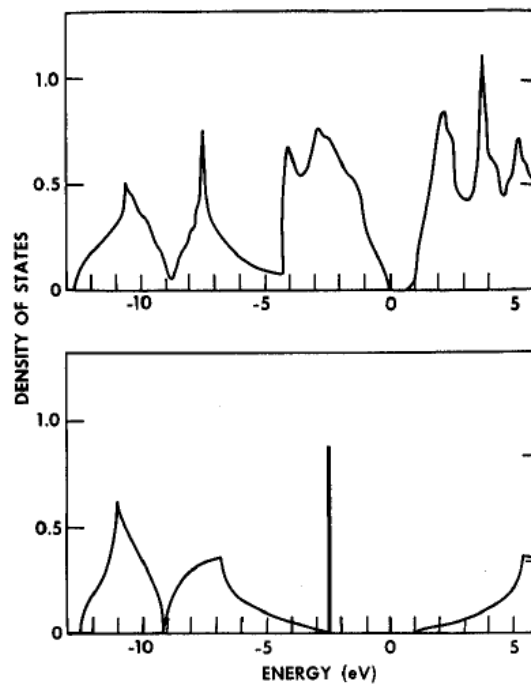
Fig. 2. Densities of states corresponding to band structure calculations of fig. 1. Top — Herman's calculation[13]); bottom — our calculation.

It produces the type of band structure which obtains in grey Sn 12). It is very evident in the present model why dilation of a crystal should change the band structure in that direction13) (since (V_2 should decrease) and why introduction of a heteropolar component in the Hamil-tonian produces the opposite effect[14]) [since $|V_2|$ effectively increases[7])]. In this and other ways we have found that this Hamiltonian, as well as providing insight into properties of amorphous systems, actually helps in the un-derstanding of the qualitative features of crystalline band structure, by virtue of its transparent simplicity.

We now turn to the question of the implications of these results for the interpretation of the properties of real amorphous systems. One should not jump to the conclusion that a zero density of states in the gap has been fully explained or predicted. The Hamiltonian that we have used provides insight into the effects of topological disorder at the expense of the neglect of quantitative disorder (the variation of matrix elements such as V_1 and V_2 throughout the structure). When this is taken into account, a tailing of the bands into the gap region seems likely. At this point two conclusions are possible to escape a dilemma. Either the experiments should not be interpreted as implying a zero density of states, or there is still some important element missing from our theoretical picture. Phillips [15]) suggests the latter conclusion, and further [advances] the hypothesis that the equilibrium of the

structure is the missing element. This is an intriguing idea and it would seem that the recent work of Connell and Paul [16] on the pressure dependence of optical properties lends it some support. If, as Phillips suggests 15), the amorphous structure relaxes into a configuration such as to exclude states from the gap, thereby lowering the free energy, then the effect of pressure should be to cause these states to encroach upon the gap, since the strong nearest neighbor repulsion increasingly constrains the structure to a particular configuration. Thus there should be a significant anomalous negative contribution to the change of the gap under increasing pressure, without much change in the broader features of the density of states. The measurements of Connell and Paul[14] reported at this conference would appear to be in accord with such a picture.

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