Model for the Electronic Structure of Amorphous Semiconductors

P. W. Anderson*

Bell Laboratories, Murray Hill, New Jersey 07974, and Cavendish Laboratory, Cambridge CB3 0HE, England
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It is pointed out that a model which agrees well with the observed properties of semi-conducting glasses is an attractive Hubbard model of localized states. Such a model has no gap for two-electron excitations but an energy gap for one-electron ones. The suggested physical model for a two-electron excitation is a new covalent bond in the structure, which is severely localized. It is also proposed that the one-electron excitation spectrum is wholly, or almost wholly, extended, and all observed gaps are identical with the mobility gap.

The usually accepted models for semiconduction in amorphous materials involving localized states in the gap[1] are deficient in two related ways: They do not come to grips with the problem of the interactions of electrons in localized states, and they do not attempt to discuss what can be argued to be the most fundamental experimental fact about these states, i.e., their magnetic properties. In the best-attested example of localized states, impurity bands in covalent semiconductors, the localized electrons show Curie-law paramagnetism due to repulsive Coulomb interactions.[2] In a wide variety of other materials, especially the semiconducting glasses, paramagnetism appears to be either absent or not simply related to densities of localized states. For these no simple modification of the conventional model is possible—even noninteracting electrons must show Pauli paramagnetism if there is a Fermi level in the localized region —and I propose the following new model. I envisage a random lattice of "sites" i, which may be occupied by up- and down-spin electrons, and which have a spectrum of energies E_i with density $\rho(E_i)$ in energy, the energy being a random function of position. These may be thought of as representing the totality of possible covalent bonds between nearby atoms in the random glass structure.

The unique feature of the model is that it is assumed to have a strong *attractive* Hubbard interaction $-U^{\text{eff}}$ between up-spin (designated by $\uparrow$)

and down-spin ($\downarrow$) electrons on the same bond site i. That is, I assume that we deal with one of the great majority of all substances which are naturally *diamagnetic*, preferring paired electrons to single ones. This attractive interaction U^{eff} can be further modeled, if we like, as the sum of a repulsive Coulomb interaction U and an attractive interaction caused by the drawing together of the two atoms in the bond. In a Holstein model[3] for this attractive interaction, we can introduce a bond length coordinate x_i and assume a potential energy

$$V = \tfrac{1}{2} c \, x_i^2 - \lambda x_i (n_{i\uparrow} + n_{i\downarrow}),\tag{1}$$

which, when eliminated via $\partial V/\partial x_i = 0$, gives

$$U^{\text{eff}} = -U + \lambda^2/c.\tag{2}$$

The reader will recognize that this assumes quite a large electron-phonon coupling, but he is reminded that, as I remarked, in most real materials, and even more in characteristic glass-forming ones such as silicates and polymers, diamagnetism is the rule and thus electrons usually prefer to pair up in bonds. Even in most metals the existence of superconductivity demonstrates that the normal net electron-electron coupling is attractive because of phonons outweighing the repulsive pseudopotential U. Finally, I assume that electrons may hop from site to site by a random hopping interaction T_{ij}. Our model Hamiltonian including the Holstein coordinates x_i is, then,

$$H^{\text{tot}} = \sum_{i\sigma} E_i n_{i\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{ij\sigma} T_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_i [\tfrac{1}{2} m \dot{x}_i^2 + \tfrac{1}{2} c x_i^2 - \lambda x_i (n_{i\uparrow} + n_{i\downarrow})].\tag{3}$$

For very low-frequency processes for which $\omega \ll \omega_0$ and $\omega_0^2 = c/m$, we may eliminate x_i in favor of the n's and we have

$$H_{\text{low freq}}^{\text{eff}} = \sum_i E_i^{\text{eff}} n_{i\sigma} - U^{\text{eff}} n_{i\uparrow} n_{i\downarrow} + \sum_{ij\sigma} T_{ij}' c_{i\sigma}^\dagger c_{j\sigma},\tag{4}$$

where U^{eff} is given by (2),

$$E_i^{\text{eff}} = E_i - \lambda^2/2c , \qquad (5)$$

and T_{ij}' is very much reduced from T_{ij} because of phonon overlap factors; i.e., it is of order

$$T_{ij}'/T_{ij} \sim \exp(-\lambda^2/2c\omega_0) . \qquad (6)$$

Considering (6), it is certain that eigenstates of (4) will be strongly localized, so that, aside from small renormalizations, we may neglect the T_{ij} term. In that case for each bond i we have three possible eigenenergies:

$$n_i = 0 , \quad E = 0 ; \qquad (7a)$$

$$n_i = 1 , \quad E = E_i^{\text{eff}} ; \qquad (7b)$$

$$n_i = 2 , \quad E = 2E_i^{\text{eff}} - U^{\text{eff}} . \qquad (7c)$$

It is clear that all sites will be, for $kT \ll U^{\text{eff}}$, either in (7a) or (7c):

$$E_i^{\text{eff}} > \tfrac{1}{2}U^{\text{eff}} , \quad \text{i.e.,} \quad E_i > \lambda^2/c - \tfrac{1}{2}U , \quad n_{i\sigma} = 0 ;$$
$$E_i^{\text{eff}} < \tfrac{1}{2}U^{\text{eff}} , \quad n_{i\sigma} = 2 . \qquad (8)$$

It is clear that the Fermi level is located at $E = 0$. This model then has two distinct spectra. The lowest possible localized single-particle and single-hole excitations are located at $\tfrac{1}{2}U^{\text{eff}}$ so that there is a gap U^{eff} in the single-particle excitation spectrum, while there is a continuum of strongly localized two-electron and two-hole excitations extending right down to zero energy. (One might think of these as particles and holes in a band of localized bipolarons.)[4] This latter spectrum cannot be excited optically or lead to ordinary electronic conduction, but it has two basic properties: (1) It pins the Fermi level very effectively near the middle of the one-electron gap; (2) it leads to a linear term γT in the specific heat with $\gamma \propto \tfrac{1}{2}\rho(E_i)|_{E_i = U^{\text{eff}}/2}$.

The one-electron spectrum may not be discussed properly within the low-frequency model (4) because, of course, I am assuming that $U^{\text{eff}} \gg \hbar\omega_0$. If the one-electron spectrum were of a localized type above U^{eff}, we would expect quite a number of complications, especially large discrepancies between E_g^{opt}, E_g^{thermal}, and $E_g^{\text{photoelectric}}$. We do not, however, expect any excitonic effects; since the net interaction of electrons and electrons is attractive, that of electron and hole is repulsive.

Life is much simpler if I assume, as I temporarily shall, that essentially

$$U^{\text{eff}} > \text{mobility gap } E_g \text{ of } H \text{ in Eq. (3).} \qquad (9)$$

That is, I adjust parameters so that the basic one-electron spectrum consists wholly of extended states. The localized states, within the model (3), are eliminated by a mechanism similar to that suggested earlier.[5] One may ask what E_i^{eff}, a localized state just below the upper mobility edge E_c, would initially have originated from. If

$$E_i^{\text{eff}}(E_c) < \tfrac{1}{2}U^{\text{eff}} , \quad \text{i.e.,}$$
$$E_i(E_c) < \lambda^2/c - \tfrac{1}{2}U , \qquad (10)$$

then that state is already occupied with electrons of both spins and cannot be used for the parentage of a state to be occupied by electrons. A similar mechanism will work for hole states: Their antecedents in the original Hamiltonian will come from above $\lambda^2/2c - \tfrac{1}{2}U$ and will hence be completely empty. Another way of saying it is that all localized states are also self-trapped to below the Fermi energy.

This then gives us optical, conductivity, and photoelectric gaps which are identical. All single-particle, single-hole excitations involve extended states for both and occur above a mobility gap energy E_g. The extended states of course do not cause large static deformations and the hopping matrix elements for these are T_{ij}, not T_{ij}'; this alone may spread their spectrum and permit E_g to be $< U^{\text{eff}}$.

It should not escape attention that the properties of this model agree well with those of pure, well-characterized, glassy semiconductors:

(1) The linear specific heat is found to be a general characteristic of glasses.[6] The present description is not totally orthogonal to that of Anderson, Halperin, and Varma (AHV)[7] and of Phillips[8]; we can describe the "tunneling states" of these authors as a tunneling of a covalent bond and its associated pair of electrons from one site to another near by. A density of $\sim 10^{19}$–10^{20} sites/eV cm^3, where an essentially free pair of electrons can form a new bond, would be a small fraction of the AHV-Phillips specific heat, and not unrelated to it.

(2) For purposes of pinning the Fermi energy near $\tfrac{1}{2}E_g$ it is essential to have a high density ($\sim 10^{19}$) of gap states, according to rectification and other experiments.[9] These are our two-electron states.

(3) There is nonetheless in pure glasses no observed magnetism, as, e.g., ESR,[10] and little if any optical absorption which may be ascribed to the gap states,[11] in agreement with this model.

(4) When magnetic gap states are introduced by

dopants in glasses, or by structural defects in amorphous Si and Ge, these remain near the Fermi level in the middle of the gap,[12] implying a high density of background states—see property (2). Hence $\sigma(T)$ is usually a good exponential, unless hopping conductivity is present.

(5) In spite of all this there is no good evidence for band tails and mobility edges, à la Cohen, Fritzche, and Ovshinsky[13]; all band gaps measured optically, photoelectrically, or from $\sigma(T)$ are fairly close to each other and quite sharp in many glasses.

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[1]For a summary, see N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Oxford Univ. Press, Oxford, England, 1971), Chaps. 2 and 7.

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[4]The bipolaron idea is not new: See T. D. Shultz, in *Polarons and Excitons,* edited by C. G. Kuper and G. D. Whitfield (Plenum, New York, 1962), p. 110; V. L. Vinetskii, Zh. Eksp. Teor. Fiz. **40**, 1459 (1961) [Sov. Phys. JETP **13**, 1023 (1961)]. But the connotation of interaction with "polar" modes is misleading, and the use of the idea is very different from the usual one.

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