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Abstract (cont'd.)

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consideration of their relaxation leads to the existence of long lived
states in a narrow region of the spectrum near the Fermi level.

A Theory of Glassy Semiconductors[*]

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ABSTRACT

A model for glassy semiconductors is discussed which provides for a generic description of a wide range of materials. The theory is based on the premise that the underlying disorder of the amorphous state requires a qualitatively different description. The major consequence of the lack of long-range structural symmetry is the enhancement of the electron-phonon interaction and the localization of the eigenstates. Strong enough interaction leads to an effective attraction between localized electrons which accounts for both diagmagnetism and optical transparency. The excitations on the ground state are derived and consideration of their relaxation leads to the existence of long lived states in a narrow region of the spectrum near the fermi level.

We describe here a simple theory of amorphous semiconductors which, we believe, is applicable to a wider range of glassy materials. The approach is substantially different from the generally accepted point of view[1] in which defects in an otherwise ideal material play the dominant role. Described elsewhere[2] in these proceedings, the defect model supposes that an ideal random network (for a covalently bonded material, for example) would give rise to a similar electronic structure to the corresponding crystal except for small band tailings at band extrema. The real material, however, is interrupted by a set of thermodynamically stable defects where the valence requirements are not satisfied. The corresponding states will lie in the gap and thus determine much of the observed electrical and optical properties. In our picture, disorder is assumed to be severe so that the fundamental electronic energy distribution, in the gound state, contains no structure. More precisely, we do not a priori suppose the existence of an energy gap in the electronic spectrum. Thus the optical gap observed in these materials will follow from a different mechanism.

Our model[3] bears at least a family resemblance to the Cohen-Fritsche-Ovshinski (CFO) band picture for amorphous semiconductors described some years ago.[4] These authors assumed that band tailings from the conduction and valence bands would be significant enough to completely wipe out the gap. The density of states at the fermi level $N(E_F)$ was supposed finite due to band tail overlap. Indeed, experimentally it remains a more or less universal property of virtually all glassy semiconductors that the fermi level is pinned : that the states in the conduction or valence band do not control the position of E_F . Thus such materials generally give rise to a large density of states at E_F . Hydrogenated amorphous silicon

provides the one counter-example where the material has been shown to be dopable to a limited extent. This, of course, is why there is a current flurry of interest in this system. We shall argue that even in this case, however, many of the considerations we discuss are relevant.

Perhaps the most convincing evidence exists in the class of chalcogenide glasses where, for a wide range of materials, the optical gap roughly equals twice the conductivity activation energy.[1] This implies that E_F is pinned near mid-gap which is easy to understand within the CFO picture. The defect model would, by contrast, require a surprising correlation of defect energies to explain this effect.

The main consequences of an approach which assumes severe randomness is twofold: 1) electron localization and associated mobility edge phenomena, and 2) the enhancement of the electron phonon interaction. The first follows from well established theoretical considerations, first elucidated by Anderson for a simple model.[5] Although there is no similar first principles evidence for a disorder induced electron-phonon coupling, even within a simple model, Emin[6] and Mott and Davis[1] have argued that much of the transport data on glassy systems can be understood in terms of a polaronic picture. The enhancement of the lattice interactions is due, in part, to the reduced electron mobility observed generally in these materials.

We describe some of the implications of a model, first introduced by Anderson,[7] in which both localization and a strong lattice coupling are explicitly included. We consider a spatially random distribution of localized eigenstates characterized by an energy ϵ_i (also random) for the ith state. Each state may be occupied by up to two electrons. The coulombic repulsion at double occupancy is treated by a Hubbard-like term

characterized by an energy U_i for the ith site. We ignore the intersite electrostatic interaction. The coupling of the electron to <u>local</u> phonon modes is taken explicitly through terms linear in the electron occupation operator n_i and the phonon field b_i^+ for creating a phonon at the ith site. In the absence of an intersite transfer matrix element for the phonons or the electrons, this term is easily diagonalized[3]and gives attractive terms quadratic in the occupation n_i . Thus for the ith site occupied by n_i electrons, the energy E_{n_i} is given by

$$E_{n_i} = n_i \varepsilon_i + U_i \delta_{2,n_i} - \frac{1}{2} C_i n_i^2 \qquad (1)$$

Here C_i describes a lattice-mediated attractive interaction energy between two electrons at the site i which occurs in the Hamiltonian on the same footing as the Hubbard U_i . The factor $1/2$ accounts[3] for the renormalization of the energy term ε_i due to the lattice coupling.

In additon, there is the usual phonon contribution to the energy. Recalling that we only consider local phonon modes we may represent all the contributions on an energy-configuration diagram shown in Figure 1 . The diagram refers to a single site occupied by $n = 0, 1,$ or 2 electrons with energies given according to eq. (1). The case shown assumes $E > \frac{1}{2} C$ and $C > U$ where the i index has been suppressed. We observe that the local configuration is displaced according to occupation due to the lattice copuling. For a given occupation, however, corresponding to a particular configuration, the energy is increased quadratically in the presence of a coordinate displacement. Thus the model includes local minima leading to metastabilities as discussed below.

The model is constructed from a collection of such sites in which the parameters U_i, C_i, and E_i vary randomly from site to site. It is

easy to show[3] for a strongly coupled system in which $C_i > U_i$ for all i that, in the ground state, all sites contain $n_i = 2$ or 0 electrons according to their energy. It is convenient to set the energy scale so that the pair with the highest energy, which occurs at site j , satisfies

$$2\varepsilon_j + U_j - 2C_j = 0 \ .$$

Our assumption on the electronic structure requires that the density of pairs with energies close to this is large. We may define a density of pair states $\rho(E_2)$ in which the energy E_2 of such a state refers to two electrons and is given through eq. (1). The chemical potential μ for adding a pair of electrons to the system vanishes according to our energy scale. This spectrum is displayed in the non-shaded region of Figure 2 and we note that there is no gap for pair excitations. Anderson has already pointed out that the absence of any gap in this spectrum can lead to a linear temperature term in the specific heat which has been observed generally in glassy systems.

In addition to this spectrum we may consider single-particle excitations which are relevant for optical absorption. For simplicity, we ignore the distributions in C_i and U_i and take them equal to some average value keeping $<C_i> > <U_i>$. We consider the process in which an electron is transferred from site i to site j through the absorption of a single photon. Thus each site will change its occupation by one particle. Since the absorption will occur on a time scale which is much faster than the period of a typical phonon oscillation, the configuration of each of the two sites will not change during the process. Thus each site, at its final occupation, will be displaced to the configuration of its initial occupation and this requires an additional energy $\frac{1}{2} C$. The energy for the process in which an electron is transferred from site i to

site j requires the contributions from an electron excitation at site j,
Δ_j^e and a hole excitation at site i , Δ_i^h , given by

$$\Delta_j^e = E_{n_j+1} - E_{n_j} + \frac{1}{2} C \tag{2a}$$

$$\Delta_i^h = E_{n_i-1} - E_{n_i} + \frac{1}{2} C \tag{2b}$$

where the energies E_n are obtained from (1). In the ground state, the only
allowable sites correspond to $n_i = 2$ and $n_j = 0$. The minimum energy
for this occurs for sites at the fermi level of the $\rho(E_2)$ distribution
(Figure 2) where $E_2 = 2\varepsilon + U - 2C = 0$ or $\varepsilon = C - U/2$. Substituting
in eq. (2) we find

$$\Delta_i^e = \Delta_j^h = C - U/2 . \tag{3}$$

which gives particle hole symmetry. Thus an optical gap exists and
we predict that the fermi level will be pinned at midgap. This situation
is observed generally in the class of chalcogenide glassy semiconductors.

We include both particle and hole excitations on a single particle
excitation spectrum, shown in Figure 3, in which electron excitations
appear for excitation energies $\Delta > 0$ and hole excitation energies are
displayed with energies $\Delta < 0$. The solid curve represents the ground
state excitations described above and the gap is evident with full width
2C - U . Note that this is larger than the absolute gap in the single
particle excitation spectrum (not shown) which must be equal to C - U
or just the effective binding of the two electrons in the pair. This, of
course, is due to our requirement of an optical process in the analysis
above.

We have further evaluated the excitations on a system prepared in a non-equilibrium metastable state. The state is determined by occupying all empty states above the fermi level with one or two electrons and all states below the fermi level (where $n = 2$ is the ground state) with one or two holes. Those states whose excited occupations require an absorption of a phonon or photon in order to relax to a state with a different occupation are termed metastable. States which will spontaneously change their occupation (with the absorption of any number of electrons or holes) with a phonon emission are unstable. If we ignore the energy of the absorbed particle, the condition for metastability for n particles (or holes) is given by

$$\Delta_n^{e,h} > 0 \tag{4}$$

where $\Delta_n^{e,h}$ is defined by equation 2. This is a somewhat conservative estimate for metastability since, as shown above, a gap exists in the single particle spectrum and thus for absorptions involving $n = 1$, the electron or hole is only available for energies above the gap. On the other hand, for a severely perturbed state there will be metastable single particle states occupied at the fermi level and so our estimate is self-consistent.

The metastable bandwidths are determined by setting

$$\Delta_n^{e,h} = 0 \tag{5}$$

For electron states we have

$$
\begin{aligned}
n &= 2 \quad, \quad \Delta n = -1, -2 \\
n &= 1 \quad, \quad \Delta n = -1
\end{aligned}
\tag{6a}
$$

and for hole states we have

$$n = 0 \quad , \quad \Delta n = +1, +2$$
$$n = 1 \quad , \quad \Delta n = +1 \tag{6b}$$

The solutions to (5) for each of these four conditions are shown in the shaded region of Figure 2. For electron states (with $E_2 > 0$) we may occupy the states between $0 < E_2 < 2C - U$ metastably with two electrons. The region is marked 2_0 where the subscript refers to the antecedent occupation (or ground occupation). Similar single electrons may persist in states in the range $0 < E_2 < U$ denoted by 1_0 . Single holes are metastable in the range $-U < E_2 < 0$ and two holes will metastably occupy those states in the range $-(2C-U) < E_2 < 0$ as denoted, respectively, by 1_2 and 0_2 . Thus the model is consistent with the observations of a photo induced spin.

More interesting is the effect of these metastabilities on the excitation spectrum. In the extreme case in which the least stable of the metastable states are occupied, that is, $|E_2| = 2C - U$ for $n = 2$, and $|E_2| = U$ for $n = 1$, we determine a complete collapse of the gap. This is shown in Figure 3 by the dashed region. The dashed density for excitation energies Δ in the range $0 < \Delta < U/2$ correspond to the process $1_2 + e \rightarrow 2_2$ (without relaxation), the range $U/2 < \Delta < U$ to the process $1_0 + e \rightarrow 2_0$ (without relaxation) and the dashed region $0 < \Delta < C - U/2$ corresponds to the process $0_2 + e \rightarrow 1_2$ (without relaxation). Fast hole excitations are also shown for $\Delta < 0$ and mirror the electronic ranges.

These metastabilities and the effect they have on optical excitations are consistent with a class of experiments performed on glassy chalcogenide semiconductors. These systems are well known to have photoinduced metastable states which give rise to a spin and a subgap absorption or photodarkening.

The lifetime of the metastability can be long ($\sim$ days) experimentally
which is entirely expected on the basis of the above considerations in
which the energy scale is electronic ($\sim$ eV) but the relaxation is
thermal.

These considerations are entirely general and should apply to
any diamagnetic glassy semiconductor including silicon-hydrogen alloys.
The observed spin quenching on alloying can be understood within a
negative-U model in which case the above analysis is relevant. The
reduced density of states will not, of course, qualitatively affect these
considerations. A specific negative-U configuration has already been
proposed.[8]

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Figure 1   Energy/configuration diagram for a single lattice-coupled site. The three levels shown correspond, respectively, to electron occupation $n = 0$, 1 and 2, which are displaced accordingly. For a given occupation, the energy of each level increases with change in configuration quadratically in the configuration parameter.

Figure 2   The density of pair states $\rho(E_2)$ as a function of pair energy E_2 in the ground state (solid curve). The shaded areas correspond to those regions of the spectrum where states occupied with N_m electrons (where m is the ground occupation) are metastable.

Figure 3   Single particle (fast) excitation spectrum. Electron excitations of energy Δ occur with $\Delta > 0$ and hole excitation with $\Delta < 0$. The ground states particle/hole excitation costs $\Delta = 2C - U$. The dashed region corresponds to excitations on metastable states. The dashed region $-U < \Delta < U$ defines fast processes on singly occupied metastable states and the dashed region in the range $-(C-U/2) < \Delta < C - U/2$ refers to metastable doubly occupied states.
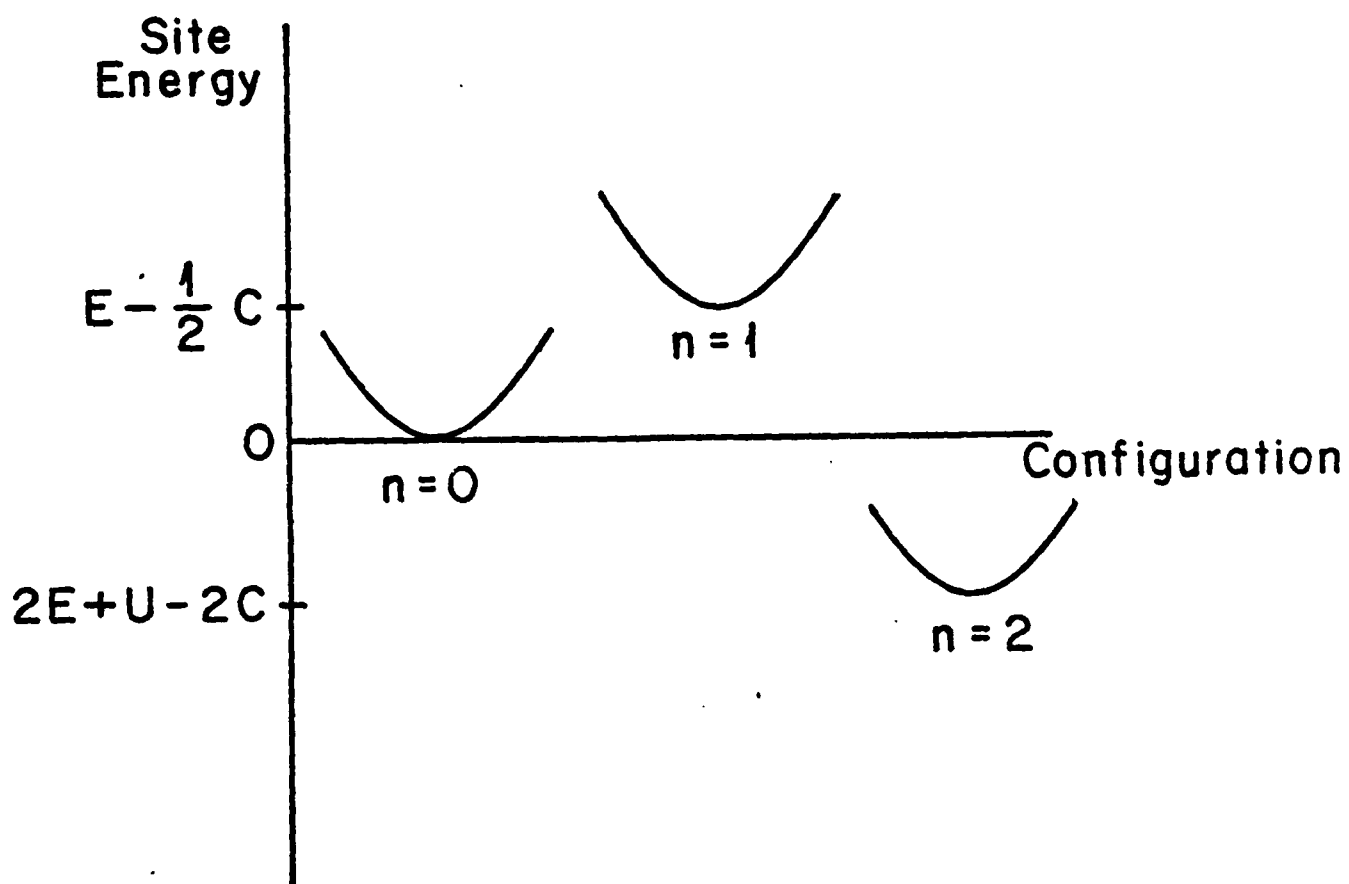
Fig. 1

METASTABLE BANDS

$\rho(E_2)$

Ground | State

n = 2

n = 0

1_2 1_0
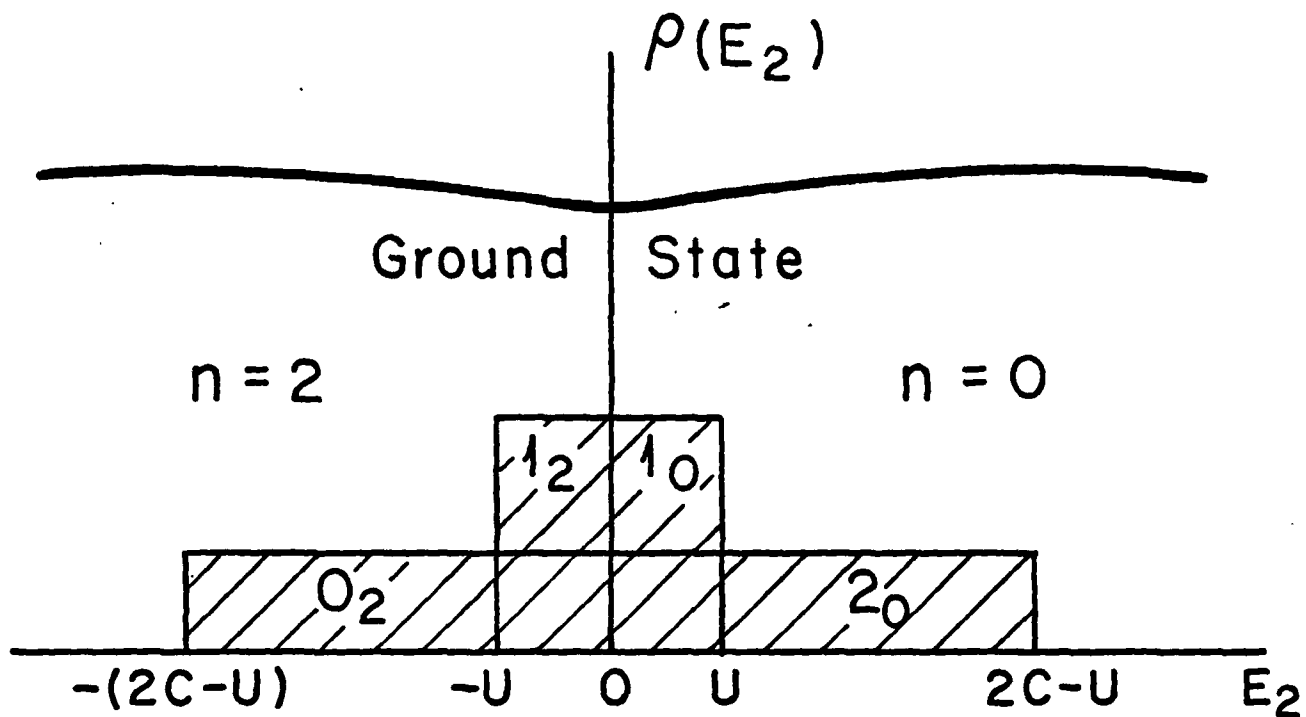
0_2

2_0

$-(2C-U)$ $-U$ O U $2C-U$ E_2

Fig. 2

SINGLE PARTICLE EXCITATION SPECTRUM

Fig. 3