Model for the Electronic Properties of Amorphous Semiconductors

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The interaction of electrons and of holes with the two-level tunneling modes appearing in certain amorphous semiconductors is studied theoretically. An electron or a hole can be localized in the vicinity of a tunneling mode; a tunneling mode can also mediate an effective electron-electron or hole-hole attraction which gives rise to localized electron or hole pairs. These electronic states provide a unified explanation for numerous experimentally observed properties, some of which have not been discussed before.

It has recently been proposed that electrons (or holes) in the localized gap states of bulk amorphous semiconductors form bound pairs.[1,2] The latter provide an explanation for various puzzling experimental properties[1,2] (e.g., a pinned Fermi level, the absence of paramagnetism). The attraction required to overcome the Coulomb repulsion and to form the localized bound electron (or hole) pair has been attributed to local phonon exchange[1] or to processes involving both dangling-bond orbitals and phonons.[2]

We propose here a new mechanism which gives rise to both single-electron (-hole) localized and resonance states and also pair localized states. This mechanism has several desirable features: (i) It connects properties appearing in α semiconductors to excitations characteristic of the amorphous state; (ii) it accounts naturally for the large pair binding energies required by experiment; (iii) it connects structural and electronic properties of these amorphous systems, and thus it provides new insight into photostructural changes, photodarkening, and the Urbach absorption edge[3]; (iv) the resulting highly localized pair states include those previously proposed and also include further possibilities which give a more complete correlation with experiment; and (v) the character of the single-electron and single-hole resonance states in the lone-pair glasses such as SiO_2 leads to a lower mobility for holes than for electrons, consistent with experiment.

Our mechanism is based on electron (or hole) interaction with what we shall refer to as local rearrangement modes (LRM's). Each LRM is a *local* bonding or structural transformation from an initial stable state to a final metastable state of only slightly higher energy.[4] A potential barrier separates the two. The existence of LRM's (also called AHV-Phillips tunneling modes[4]) in amorphous semiconductors in now widely accepted in view of a variety of supporting experimental results[5] (e.g., an excess low-T specific heat, the saturation of ultrasonic attenuation, etc.). We expect LRM's to exist in appreciable numbers in materials which are easily deformable locally such as the chalcogenide glasses with their two-dimensional (2D), low-coordination structure. On the other hand, in α-Ge or α-Si, with their 3D, high-coordination structure, LRM's are expected to have less pronounced physical effects.

In the following we consider a simplified model of the carrier-LRM system. The Hamiltonian is $H = H_e + H_h + H_L + H_{e\text{-}L} + H_{h\text{-}L}$, where e refers to electrons in the conduction band and h to holes in the valence band. H_e is the usual tight-binding form

$$H_e = \sum_{is} \epsilon \hat{n}_{is} + V \sum_{ijs}{}' a_{is}^{\dagger} a_{js} + I \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow},$$

where i,j are nearest neighbors, and the last term is the direct Coulomb repulsion. The LRM is described by

$$H_L = \sum_{i=1}^{N^*} \omega_i \sigma_i^z,$$

where the Pauli matrix σ_i^z spans the two levels of the LRM at i,[6] the splitting of which is $2\omega_i$, and N^* is the total number of physically interesting LRM's. The electron-LRM interaction is[6]

$$H_{e\text{-}L} = \sum_i t_i f_1(\hat{n}_{i\uparrow}, \hat{n}_{i\downarrow}) \sigma_i^x + \sum_i \tau_i f_2(\hat{n}_{i\uparrow}, \hat{n}_{i\downarrow}) \sigma_i^z. \quad (1)$$

The first term describes electron-induced transitions between the LRM levels, and the second the renormalization of their splitting due to electrons at site i. A nonlinear dependence of f_1 on $\hat{n}_i$ is

physically likely because the electric field of the electron will alter the LRM potential barrier; this would imply an exponential dependence of f_1 on $\hat{n}_i$. The terms H_h and $H_{h\text{-}L}$ in H have the same form as these for electrons but may have different parameter values.[7]

We begin by showing that the interaction in Eq. (1) produces localized electron and hole states with energies in the gap. Consider a single electron in the conduction band (holes in the valence band are treated analogously) and a single LRM at site $i=0$. Take $f_1(\hat{n}_0)=f_2(\hat{n}_0)=\hat{n}_0$, which is their simplest form, and drop the site indices from ω, τ, and t. This problem is then solved exactly by a generalization of the method of Koster and Slater.[8] The Green's function $\hat{G}(E)=(E-\hat{H})^{-1}$ becomes

$$\langle 0|\hat{G}(E)|0\rangle = \begin{pmatrix} f_- & 0 \\ 0 & f_+ \end{pmatrix} + tf_+f_-(1-t^2f_+f_-)^{-1}\begin{pmatrix} tf_- & 1 \\ 1 & tf_+ \end{pmatrix}, \quad (2)$$

where $f_\mp(E)=\langle 0|(E-\hat{H}_e\mp\omega\mp\tau\hat{n}_0)^{-1}|0\rangle$, and $|0\rangle$ is the Wannier function at site 0. By standard techniques,[8] $f_\pm(E)=\hat{g}_{00}(E\pm\omega)/[1\pm\tau\hat{g}_{00}(E\pm\omega)]$, and $\hat{g}_{00}=\langle 0|(E-\hat{H}_e)^{-1}|0\rangle$, which is the usual Green's function for $\hat{H}_e$. All of the information about the system is now obtained from $\hat{G}(E)$. The partial density of states for site 0 is

$$N_0(E)=-\pi^{-1}\lim_{s\to 0^+}\mathrm{Im}\{[f_+(E')+f_-(E')]/[1-t^2f_+(E')f_-(E')]\},$$

where $E'=E+is$, and the condition for a discrete, localized state is

$$f_+(E)f_-(E)=t^{-2}. \quad (3)$$

When $\omega=0$, Eq. (3) simplifies to $g_{00}^{-2}=t^2+\tau^2$.

It should be noted that the localized eigenstates are linear combinations of the two LRM states, i.e., they are composite electron-LRM states. Thus electron localization alters the local LRM configuration. $N_0(E)$ may exhibit a peak within the band resulting from a small value of $1-t^2f_+f_-$. States corresponding to such peaks are called resonances; they describe particles being trapped around the LRM for a relatively long time before diffusing away. Resonances contribute much less to transport than do ordinary band states.

Considering for simplicity the case $\omega=0$, we have the following picture: As $(t^2+\tau^2)^{1/2}$ increases from zero, resonances start appearing within the band near the edge. The formation of resonances is favored by high values of the unperturbed density of states (DOS), $-\mathrm{Im}g_{00}/\pi$, near the band edge. As $(t^2+\tau^2)^{1/2}$ continues to increase, a critical value is reached[9] for which a local level is split off from the continuum thus creating a state in the gap. Further increase in $(t^2+\tau^2)^{1/2}$ pushes this level farther away from the band edge; however, as we shall discuss below, for such large values of $(t^2+\tau^2)^{1/2}$ it is energetically favorable for the local level to be doubly occupied, forming a bound diamagnetic pair.

In order to treat the physically important question of an effective electron-electron (hole-hole) attraction, we consider two electrons and one LRM (at site 0). We have found that it is important to include a nonlinear dependence of f_1 on $\hat{n}_0$ (discussed above). We choose

$$f_1(\hat{n}_{0\uparrow},\hat{n}_{0\downarrow})=\exp[W(\hat{n}_{0\uparrow}+\hat{n}_{0\downarrow})]/\exp W \quad (4)$$

and $f_2=\hat{n}_{0\uparrow}+\hat{n}_{0\downarrow}$, where W is a constant. The electronic energies for this system were calculated for the Bethe lattice, and they are obtained variationally by choosing for the localized one-electron (I) and two-electron (II) wave functions $\Psi_I\dagger(\vec{r})=(\varphi_I(\vec{r}), C_I\varphi_I(\vec{r}))$ and $\Psi_{II}\dagger(\vec{r}_1,\vec{r}_2)=(\varphi_{II}(\vec{r}_1)\varphi_{II}(\vec{r}_2), C_{II}\varphi_{II}(\vec{r}_1)\varphi_{II}(\vec{r}_2))$. Here $\varphi_\alpha(\vec{r})=\sum_m B_m{}^\alpha|m\rangle$, $\alpha=$ I, II, and the coefficients are $B_m{}^\alpha=B_0{}^\alpha\exp(-\gamma_\alpha l)$ where l is the number of nonretracing steps between 0 and m on the Bethe lattice. Note that the spatial dependence of $\varphi_\alpha(\vec{r})$ is of the same form as that obtained from the exact solution of the one-electron problem. The electron-spin part of Ψ_{II} is a singlet, like that of the He ground state.

The energies of the one-electron and of the two-electron states are expressed in terms of the variational parameters (C_α,γ_α) by $E_\alpha(C_\alpha,\gamma_\alpha)=\langle\Psi_\alpha|\hat{H}|\Psi_\alpha\rangle/\langle\Psi_\alpha|\Psi_\alpha\rangle$, $\alpha=$ I, II, and the values of the energies are obtained by minimizing E_α with respect to C_α and γ_α. Explicit results will be given elsewhere. The conclusion is that the dynamic electron-LRM interaction can mediate an effective attractive interaction between the electrons which overcomes the direct Coulomb repulsion, and therefore it produces a localized two-electron state which lies lower than the one-electron state. The effective binding energy is found to depend fairly strongly on t, W, and I, but it is weakly dependent on τ and on K; the latter means that it is almost independent of the unperturbed DOS.

In applying our approach to a glassy semiconductor, one must distinguish the effects of LRM's with a large t from those with a small t. LRM's with a large t ($\gtrsim B$) pull states from the conduction and the valence band to form two-electron

(2e) and two-hole (2h) sub-bands, respectively. In an amorphous chalcogenidelike semiconductor the 2e and the 2h sub-bands are located around the center of the gap and consequently they overlap appreciably. This picture is consistent with a variety of experimental results: (1) The overlap of the localized two-electron and two-hole states gives a pinned Fermi level, and the almost symmetric[10] occurrence of electron and hole states gives a Fermi energy near midgap.[11] (2) In the ground state the system is diamagnetic because only pair states are occupied[12]; this also predicts the absence of a variable-range hopping regime in the dc conductivity.[12] (3) The optical gap, which is due both to excitation from valence to conduction band and also to the breaking of pair states, is roughly equal to the energy difference between the valence- and conduction-band edges. (4) There are two different kinds of contributions to the linear term in the specific heat capacity,[5] one from the renormalized LRM's and the other from excitation of the electron (or hole) pair states. (5) Band-gap optical excitation will result in occupation of localized single-electron or single-hole states; this gives photoinduced localized ESR centers and also photoinduced midgap absorption.[13]

Specific examples of the possible electronic ground states of the chalcogenides including α-SiO_2 based on the present model are now given.[14] In the usual crystalline case the bonding (B) states are lower in energy than the nonbonding or lone-pair states (NB), which in turn lie below the antibonding (AB) states. The overlap of 2e and 2h sub-bands, which as noted above occurs at sites with large t, results in an inversion of the usual ordering of the B, NB, and AB states. For example, the states proposed by Street and Mott[2] (D^+ and D^-) for, say, Se result from an overlap of the NB sub-band with the B sub-band (giving their D^-) and a further overlap of the interchain B sub-band with the NB sub-band (giving their D^+).

Other possible diamagnetic ground states which have not been suggested previously can be obtained in a similar manner. Examples for Se include those obtained from the overlap of the NB and AB sub-bands with or without an accompanying overlap of the NB (in a neighboring chain) and the interchain B sub-bands. For As_2Se_3 examples include those arising from (a) the overlap of the (As-Se) B and the (As) NB sub-bands with or without an accompanying overlap of the (Se in a neighboring layer) NB with the interlayer (Se-Se) B sub-band, (b) the overlap of the (As-Se) B with the (Se) NB sub-bands with or without an accompanying overlap of the (Se in a neighboring layer) NB with the (As-Se) interlayer B sub-band, (c) overlap of the (Se) NB and the (As-Se) AB sub-bands with or without an accompanying overlap of the (Se in a neighboring layer) NB and the interlayer B sub-bands. We have straightforwardly obtained similar models for α-SiO_2 and α-As. Photoexcited paramagnetic states have also been obtained and will be reported elsewhere. It is worthwhile to point out that for As_2Se_3 we readily have ESR centers at both As and Se in agreement with experiment.[13]

The present model also gives new insight into photostructural and photodarkening effects[15] and the exponential absorption edge.[16] Carriers photoexcited by band-gap radiation can be trapped in single or pair (possibly metastable) localized states, and thereby modify nearby LRM's which give local structural changes. These changes are reversible if only a few electrons are involved, but for substantial excitation, LRM's with high barriers (or collective groups) may be modified leading to irreversible changes. In addition these modifications in the LRM's are accompanied by changes in the energies of their electronic constituents (e.g., lone-pair valence states) which lead to a shifted band gap.

The absorption edge of some amorphous and other glassy semiconductors exhibits an exponential or Urbach edge[16] which is independent of T at low T and goes as $\exp(1/T)$ at higher T. The present model gives such a T-independent edge at low T as a result of the interaction of electrons with local "microfields" of the LRM's,[17] and it gives an edge which is exponentially dependent on T at higher T as a result of the thermal excitation of the valence electron plus LRM.

Let us now discuss the effects due to LRM's with small $(t^2+\tau^2)^{1/2}$ ($\lesssim 0.2B$). In lone-pair semiconductors these LRM's leave the conduction band almost unaffected, while they create strong resonances near the top of the valence band. The source of this asymmetry is a peak in the unperturbed DOS near the top of the valence band which is created by the lone-pair orbitals, and which strongly favors formation of resonances.[18] Thus there are hole resonances and almost no electron resonances. This explains immediately why the hole mobility is much lower than the electron mobility in α-SiO_2[19] and also in some chalcogenide glasses. It further implies that holes in the valence band (created, e.g., by photoexcitation) will behave like local ESR or paramagnetic centers

with various lifetimes.

In summary we have proposed a new mechanism for the origin of localized and resonance electron (hole) states and for localized electron (hole) pair states in the gap of glassy semiconductors. The resulting picture is consistent with a variety of important experimental observations some of which have not been treated before. One can experimentally distinguish the present mechanism from the alternative phonon mechanism by changing the number of LRM's through careful preparation techniques, and monitoring this change by low-temperature specific-heat measurements. The present model, in contrast to the phonon mechanism, predicts that the electronic gap states should be reduced as the number of LRM's is decreased.

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