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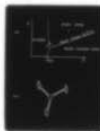PREPRINT-4

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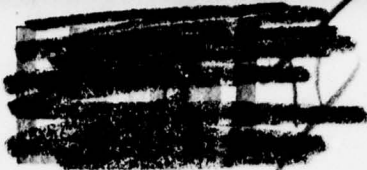
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ELECTRONIC PROCESSES IN GLASSY SEMICONDUCTORS

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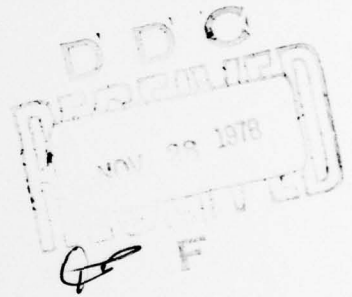
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October, 1978   - Preprint (Les Houches Lectures)

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) ELECTRONIC PROCESSES IN GLASSY SEMICONDUCTORS		5. TYPE OF REPORT & PERIOD COVERED Preprint
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) D.C. Licciardello		8. CONTRACT OR GRANT NUMBER(s) N00014-77-C-0711
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Physics Princeton University Princeton, N.J. 08540		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 318-058
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research (Code 427) Arlington, Va. 22217		12. REPORT DATE
		13. NUMBER OF PAGES 10 + Figures
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Lecture   presented at Les Houches Summer School (1978)   France

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Amorphous Semiconductors
Chalcogenide Glasses

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Electronic Processes in Glassy Semiconductors[*]

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Although the theory of microscopically disordered solids is in its embryonic stages compared with that of crystalline systems, some very general principles have begun to emerge, tempting theorists to venture into the glassy state. The most obvious property of glasses requiring attention is the presence, almost universally, of a well defined absorption edge (indeed, it is commonly true that the gap is sharper than in the crystalline phase of the same material). The problem is a fundamental one because the transparency of glassy systems suggests a smaller role for the intrinsic randomness than is indicated from very general considerations.

The thrust of modern ideas on the nature of disordered systems have illucidated two main principles: 1) that for many quantities of interest, probability distributions play a more important role than their averaged or most probable values; that is, from information about the latter only, one often misses the essential feature describing the way microscopic processes effect the system behavior. 2) The eigenstates of the system divide into two classes, localized and extended, which are <u>qualitatively</u> different. These states are separated, within the spectrum, by sharp energies (on the scale of 1/N) called mobility edges. This dichotomy is specific to disordered systems and has no crystalline analogue. The interesting point is that both these theoretically well founded conceptions seem particularly difficult to establish experimentally in glasses.

Thus, in amorphous semiconductors, for example, in addition to having a sharp optical gap, there exists no firm experimental evidence for the existence of a localization edge. This has persuaded many workers to treat these materials as "effective crystals" where the absence of long-range structural order leaves the system, for most processes, qualitatively unchanged. Weaire has shown[1], for instance, within a simple model of covalent bonding,

how real gaps can occur without invoking long-range order. This model arbitrarily truncates the range of the matrix elements which, of course, begs the effect and so leaves the more general question open.

Anderson[2] has attempted to preserve the general principles by introducing a third: strong lattice coupling. Basically it is argued that lattice relaxation near localized carriers leads to a net attraction between electrons in the same state (site). The model is further discussed by Anderson in these Les Houches lectures. Stein et al.[3] have shown how this model can lead to specific defects in chalcogenide glasses and the topology of these centers as well as the nature of the low-energy excitations is discussed.

In this lecture, we examine some important consequences of the approach taken in references 2 and 3. In particular, we reconsider the question of the presence of sharp phenomena, e.g. absorption edges, in a model which presumes a continuous distribution of states. We ask where are the gap states and how can they be observed experimentally? Anderson has taken the view[2] that since a mobility edge is the only sharp energy which exists in a disordered system, the observed band edge must be a mobility edge. It is argued that localized states are eliminated by phonon self-trapping to below the gap.

In the linear model employed by Anderson the local lattice coupling energy W_i is quadratic in the occupation:

$$W_i = -n_i^2 \, C_i/2 \qquad (1)$$

where $C_i \equiv 2g^2/\omega_i$. Here n_i is the occupation at the site i , g is the electron-phonon coupling and ω_i is the local phonon frequency. Each center or bond is characterized by an electronic energy ε_i and a phonon

frequency ω_i . The local lattice modes are displaced on occupation (with one or two electrons according to Eq. (1)) and so the electron energies are renormalized. For $n_i = 1$, the effective electronic energy is, from Eq.(1)

$$E_i = \varepsilon_i - \frac{1}{2} C_i \tag{2}$$

and for $n = 2$ the level eigenvalue is

$$2\varepsilon_i + U_i - 2C_i = 2E_i - (C_i - U_i) \tag{3}$$

where U_i is the contribution from the Coulomb interaction between the electrons. Thus we may recharacterize the local parameters with the effective electronic energy E_i and the effective electronic <u>attraction</u> $\tilde{U}_i \equiv C_i - U_i$ which acts when the site i is doubly occupied. Note that $\tilde{U}_i$ includes the Coulomb repulsion U_i between the particles which, of course, reduces the effect of the lattice interaction. It is presumed that for diamagnetic glasses the distribution funtion $P(\tilde{U}_i)$ favors positive values of $\tilde{U}_i$ for most sites near the Fermi level.

It is clear from Eq. (3) that for $\tilde{U}_i > 0$ all sites are doubly occupied up to $E_i = \tilde{U}_i/2$; sites with larger energies are empty. Assuming a distribution of site energies which does not deplete appreciably near $E_i = \tilde{U}_i/2$, the Fermi level for the pair states is pinned at this value.

Absorption edges arise from one-electron excitations so to study this question we consider the process by which we break a pair. One may think of the process as the creation of two particle states (as opposed to a particle and a hole) each of energy E_i out of a doubly-occupied state of energy $2E_i - \tilde{U}_i$. (Here we presume the two states are each characterized by the same parameters E_i, $\tilde{U}_i$, for simplicity, but we relax this restriction

below.) The total energy for the process is $\tilde{U}_i$ and we remark that these considerations only apply to low frequency processes $(\omega \ll \omega_i)$ when the two singly-occupied states have had time to relax to their effective energies E_i . For optical processes (Franck-Condon) there is no time for relaxation and the single-particle energies take the unrenormalized values ε_i . In this case the gap energy $2\varepsilon_i - (2E_i - \tilde{U}_i) = \tilde{U}_i + C_i$ which is larger by an amount C_i . Thus we see that an optical gap will occur even in the case of weak diamagnetism, i.e. $C_i \gtrsim U_i$.

Up to now, we have not introduced any correlations between the site parameters E_i and $\tilde{U}_i$. In Figure 1, we define the space of the parameters; in this diagram each bond (site) is represented by a point and, in general, no region is excluded. For simplicity, however, we examine the strongly-coupled case where some minimum $\tilde{U}_{min}$ exists below which there are no states.[*] The line $E = \tilde{U}/2$ divides the existing states into ones which are doubly occupied and those which are empty. A one-electron process involves the excitation of an electron from a state i with $E_i < \tilde{U}_i/2$ and $\tilde{U}_i > \tilde{U}_{min}$ to a state j with $E_j > \tilde{U}_j/2$ and $\tilde{U}_j > \tilde{U}_{min}$. The energy for the process is $\Delta E = E_j + \tilde{U}_i - E_i$ and the absorption edge occurs at $\min(\Delta E)$. If the entire space is accessible, with the proviso that $\tilde{U} > \tilde{U}_{min}$ for all i , the minimum will occur for two states at the Fermi level with absorption energy $\Delta E = (\tilde{U}_i + \tilde{U}_j)/2$.

We assume for the moment that the space of Figure 1 is not uniformly

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[*]This can be approximately so in glasses of low-averaged coordination number (e.g. amorphous chalcogenides) but a wider range of values of $\tilde{U}_i$ (extending into the negative region) is expected in the highly coordinated systems a-Si and a-Ge.

occupied with sites but that states near the Fermi level have larger values of $\tilde{U}$ on average. This is indicated by the dotted boundary in the figure where the "no states" region protrudes to larger $\tilde{U}$ values near the Fermi energy. In this case, it is not clear that the first states to absorb will come from the Fermi level. In order to minimize the quantity $E_j + \tilde{U}_i - E_i$, larger values of $E_j - E_i$ may be necessary and a typical absorption process under such circumstances is indicated in the figure (labeled α). The possibility of strongly coupled pairs of electrons near E_F is an interesting one for two reasons. Firstly, the corresponding single-particle states could be pushed deep in the spectrum and may be in resonance with the mobile states of the valence band. Even more interesting is the possibility that probing deep into the spectrum for the minimum absorption pair E_i, E_j may reach the mobility edge of this spectrum. (It is presumed that some transfer matrix element T_{ij} operates to move an electron from site i to j.) Whether or not the minimum absorption energy ΔE equals the mobility gap depends entirely on the exponent describing the coupling of the lattice to a localized state near E_c. This problem has been discussed by Licciardello and Thouless.[4] The situation in which absorption between mobile states occurs would confirm Anderson's conjecture that the observed absorption edge is indeed/ a mobility edge. The effect is enhanced by the T_{ij} term, as discussed by Anderson, since the extended states may lower their energy gap/through kinetic broadening and thereby lower their absorption energy.

As yet no mechanism has been proposed to account for the enhanced coupling of pair states near E_F. Stein et al. have argued that the two-electron states near the Fermi level are chemically distinct from those deep in the valence band. An important effect not included in Anderson's strong

coupling theory of glass is the overwhelming preference for atoms to satisfy their local valence requirements. This leads to "phonon sharing" and so a model which introduces only one frequency ω_i for each bond does not take account of the possibility that some lattice modes may extend over several bonds. This effect tends to reduce the coupling to the electronic system and prevails in regions where the local coordination is satisfied.

During glass formation (quenching) most atoms, in fact, manage to find the requisite number of neighbors to satisfy valence and so minimize their local free energy. A few, depending on the temperature from which the system is quenched, do not, however, and the defect so formed has been termed valence alternation.[5,6] These atoms have more or fewer chemically bonded neighbors than is indicated from normal valency. It is worth pointing out that it is not necessary to restrict these considerations to lone-pair or chalcogenide semiconductors although for these systems coordination fluctuations are easier. For example, silicon can, in the amorphous phase, bind with only three neighbors.

Stein, et al. have shown[2] how the excess energy of formation may be compensated by the configurational entropy to account for their presence in significant numbers. More importantly, it is argued that these centers are responsible for pinning the Fermi level of the two-electron spectrum. Perhaps without doing an injustice to the idea of continuous distributions we can argue that the centers near E_F tend to be more defect-like than those near the true bonding energy.

Although these centers are the weakest two-electron states, we argue here that they have the strongest coupling, i.e. $C_i \gg U_i$. As an example, we consider elemental glassy selenium with four-valence electrons in the three $4p$ states. The atoms prefer two-fold coordination (in either eight-

member rings or N polymer chains) with the other two electrons in non-
bonding states. The coordination defect, then, is $z = 3$ or 1; the
trigonally bonded case is illustrated in figure 2. Here the orbitals of the
defect atom are exhausted (p levels) and so the atom has room for only three
electrons at the bonding energy with no non-bonding levels available. If
we require double occupancy in every state (as shown in the figure), the
center defect atom must divest itself of its fourth electron and so the
defect has charge $+ 1$ (called D^+). By charge neutrality we require an equal
number of defects in the (-) charge state (D^-) where a selenium atom has
only one bond and four electrons in non-bonding states. The defect illustrated
then, is an empty two-electron state and we imagine, according to the arguments
given above, that it exists at E_F . That is, the reaction $D^+ + 2e => D^-$
is a low-energy excitation as discussed by Stein, et al.

We now consider the process of adding <u>one</u> electron. Kastner, et al.
speculate[5] that the D^o center remains three-fold coordinated, although the
presence of the σ^* electron should certainly weaken the bonds. The impor-
tant point is that the addition of yet a second electron causes considerable
softening of ω_i because one of the bonds now certainly breaks leaving one
of the three neighbors with only one bond (it becomes the D^- center).
An elementary argument gives a factor 2-3 lower frequency for the center and
this softening could give rise to a large local distortion. No such
softening can be expected to occur at other two-electron centers where the
bonding is canonical and the phonons are large.

Thus we are left with strongly-coupled states in the gap which pins
the Fermi level against doping but which eludes optical probes. The pair
states, however, should be strongly localized especially near defect positions
and thus long relaxation times are expected for low energy two-particle

processes. Anderson has suggested[2] that out of equilibrium occupation of the pair states near E_F and the associated long times relaxation can provide explanations for photostructural effects including fatiguing and even switching phenomena.

It is certainly clear that any Fermi level smearing in the two-particle spectrum will induce lower energy absorption processes. After prolonged optical pumping, free electrons and holes will fall into available gap states, doubly occupying some two-electron centers above E_F . In addition, some centers will trap single particles which may relax to the effective energy $E_i = \varepsilon_i - \frac{1}{2} C_i$. If this particular center has an effective energy E_i which is smaller than the ground occupancy (n=0,2) in the same deformation configuration, the singly occupied state will be metastable. An explicit calculation using the same strong coupling model gives a band of paramagnetic metastable defects near the Fermi level:

$$E_F - \frac{U_i}{2} < E_i < E_F + \frac{U_i}{2} \tag{4}$$

Note that the bandwidth is the Coulomb repulsion U_i and not the effective energy $\widetilde{U}$. Thus if we presume that the Fermi level is pinned by 10^{19} states/cm^3 and take[5] a few tenths of eV for the Coulomb term in amorphous chalcogenide glasses, we predict some 10^{18} spins/cm^3 should be observable in photo-induced ESR. A typical fatigued spectra is shown in figure 3. Thus we witness the reappearance of the missing gap states.

Acknowledgement

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FIGURES CAPTIONS

Fig. 1   Phase space for two-electron centers characterized by an effective
energy E and an effective electronic attractive coupling $\tilde{U}$ which
acts when the site is doubly occupied. There are no sites
characterized by parameters to the left of the dashed boundary.
The arrow indicates a possible minimum energy absorption process.

Fig. 2   The D^{+} defect present in amorphous chalcogenide semiconductors.
All sites (bonds) are occupied by electrons of both spin. The
central ion in the defect is three-fold coordinated and has charge
+ 1.

Fig. 3   The single-particle excitation spectra for a material in equilibrium
(top sketch) and after considerable photo excitation (lower sketch).
The gap fatiguing is due to the occupation of metastable
two-particle states. Metastable paramagnetic states occur in a
possibly narrow band (order U, the site Coulomb repulsion) near
the Fermi level.

E

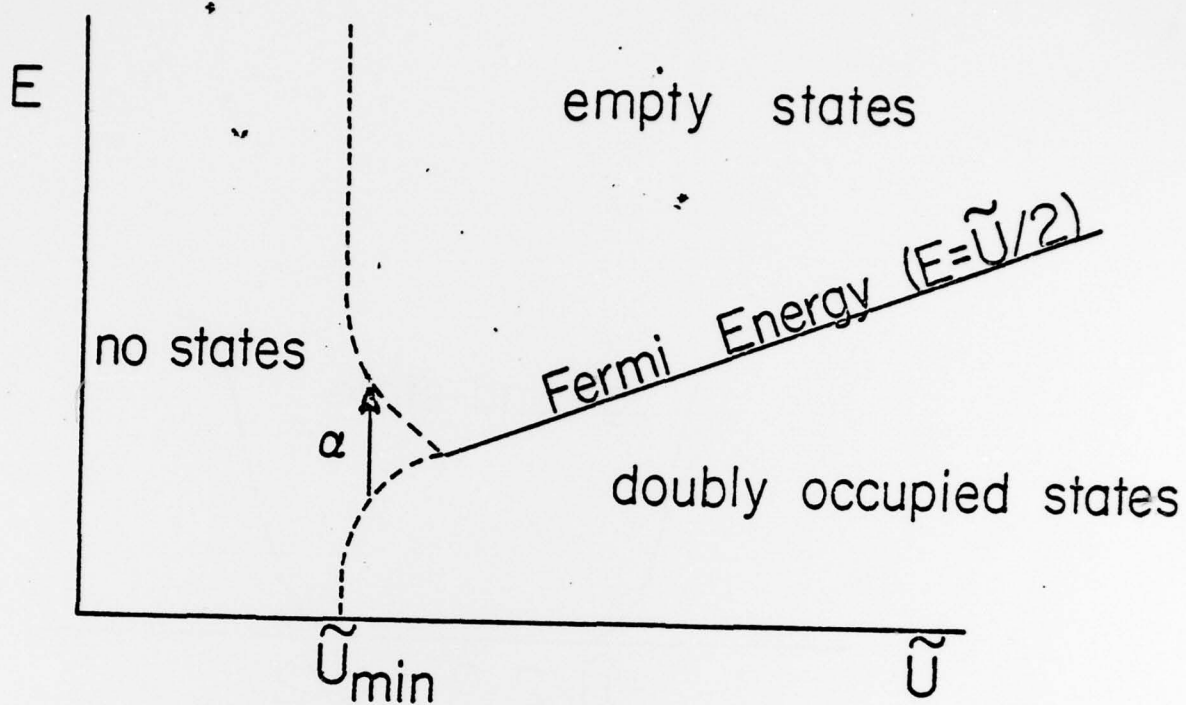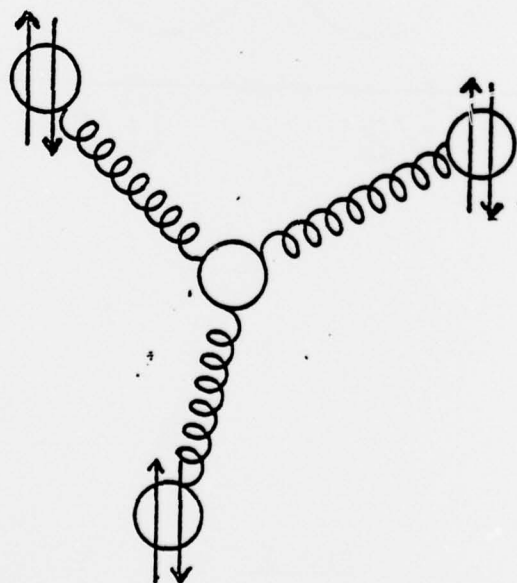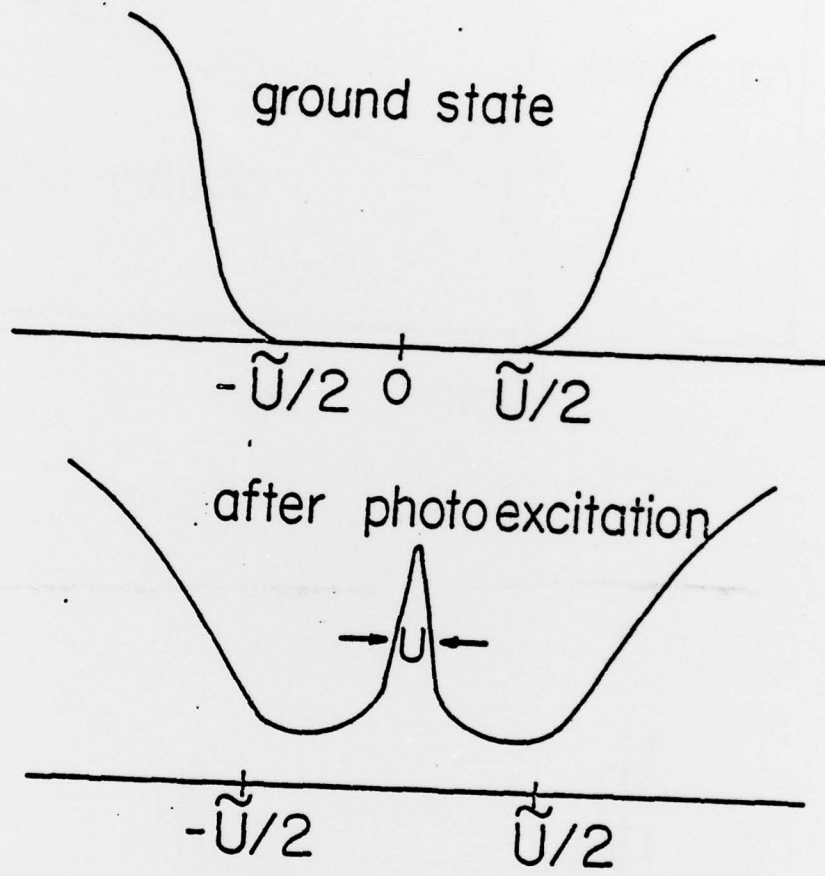empty states

no states

Fermi Energy $(E = \tilde{U}/2)$

α

doubly occupied states

$\tilde{U}_{min}$

$\tilde{U}$

Fig. 3