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Optical vs. Transport Processes in Chalcogenide Glasses†

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ABSTRACT

A model for amorphous chalcogenide semiconductors predicts an intrinsic photoinduced paramagnetic band of metastable states which may absorb light and give rise to an electron spin resonance. It is shown that these centers are unrelated to those responsible for limiting carrier mobility in accord with recent experiments on doped $a - As_2Se_3$.

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Our current understanding of the observed properties of amorphous chalcogenide semiconductors is based on models in which charged defect centers in the gap are responsible for many of the optical electronic properties. Among these models, those of Mott, Davis, and Street¹ (MDS) and Kastner, Adler, and Fritzsche² (KAF) have attracted widespread attention. According to their picture, charged defect states arise in the gap when a chalcogen atom deviates from its normal twofold coordination, leading to centers with threefold coordination (C_3^+ , or D^+) and singly coordinated chain ends (C_1^- , or D^-). When excited, these states may transfer electrons to form a band of paramagnetic states (C_3^0 , or D^0) at the Fermi level. The defect states are supposed responsible for pinning the Fermi energy, providing traps for mobile carriers³, explaining photoluminescence (PL) spectra and induced electron spin resonance⁴ (ESR) experiments. Recently, however, transport and optical measurements were performed by Pfister et al.⁵ on a - As_2Se_3 doped with thallium; it was found that the centers responsible for hole trapping differed from those associated with PL and photoinduced ESR, in sharp contrast to the predictions of defect models. In this Letter, we show how a simple model which presumes only a distribution of localized states which are strongly lattice-coupled resolves these apparent discrepancies. The model has been described in great detail elsewhere⁶; here we summarize briefly some of its main points which are relevant to the experiment of Pfister et al.⁵

The approach rests on two assumptions: We adopt the old Mott-CFO model in which there is disorder-induced "tailing" into the semiconductor gap. The disorder is likely to be severe (for a glass); we presume the level density, even near the Fermi level, to be high ($\sim 10^{20}$ states/cm³ eV).

This picture is in sharp disagreement with the electronic structure usually presented in the defect models. The second assumption follows from Anderson's⁷ original proposal in which strong electron-phonon coupling is present, leading to a negative correlation energy between electrons at the same site.

The Hamiltonian for one site is ($\kappa = 1$ throughout the text)

$$H = E(n_{\sigma} + n_{-\sigma}) + U n_{\sigma} n_{-\sigma} + \omega b^{\dagger} b + g(n_{\sigma} + n_{-\sigma})(b + b^{\dagger}) \quad (1)$$

where E is the energy of an electron at the center, n_{σ} the number of electrons with spin σ at the center, U the Hubbard electronic repulsion between two electrons at the same site, b^{\dagger} and b are phonon creation and annihilation operators, ω the phonon frequency and g the electron-phonon coupling. If $C \equiv \frac{2g^2}{\omega}$, then $C \gg U$ for strong coupling and soft phonons. Let $\tilde{E}_i \equiv E_i - \frac{1}{2} C_i$, $\tilde{U}_i \equiv C_i - U_i > 0$, where i is a site index; \tilde{E}_i and \tilde{U}_i are random variables, since the unrenormalized parameters are presumed to be randomly distributed. The Hamiltonian for the entire system may be written^{6,7}

$$H = \sum_{i,\sigma} \tilde{E}_i n_{i\sigma} - \sum_i \tilde{U}_i n_{i\sigma} n_{i-\sigma} + \sum_{i>j,\sigma} T_{ij} C_{i\sigma} C_{j\sigma} \quad (2)$$

where we introduce T_{ij} , a transfer matrix element from site i to j .

Neglecting for the moment the T_{ij} term, the equation (2) leads to a ground state in which all levels are doubly occupied or unoccupied. The density of states spectrum $\rho(E_2)$ for two-electron states is, by construction of the \tilde{E} distribution, continuous with only a small reduction near μ_2 (here μ_2 is the chemical potential for adding a pair of electrons to the ground state). Both energy and entropy considerations⁶ support the correctness of such a picture for the two-electron spectrum.

We define a metastable state (MS) as one which requires the absorption of a phonon (or photon) in order to relax to a lower energy state with a different occupation. The linear electron-phonon coupling introduced in eq. (1) is easily shown⁸ (by diagonalizing the phonon terms) to lead to a quadratic dependence of the energy eigenvalue on the electron occupation. If we ignore the fluctuations in C_i, U_i (i.e. $C_i \equiv C, U_i \equiv U$) it may be demonstrated from (2) that excited metastable two-electron states will occur in the range

$$\mu_2 < E_2 < 2C - U + \mu_2 \quad , \quad (3)$$

metastable one-electron states in the range

$$-U + \mu_2 < E_2 < U + \mu_2 \quad (4)$$

and metastable zero-electron states in the range

$$\mu_2 - (2C-U) < E_2 < \mu_2 \quad . \quad (5)$$

Here E_2 is a two-particle energy, that is, the eigenenergy of Hamiltonian (1) for double occupation. Note in particular that we find a band of paramagnetic states of width $2U$ centered at μ_2 .

When considering optical processes one looks at the single particle excitation spectrum, which is the density of states available to add (without lattice relaxation) a single electron (or hole) of energy $\epsilon(-\epsilon)$ to the system in the ground or metastable configuration. Thus, both the energy required to remove an electron from one state and add it to another, plus the range of allowed ground or metastable states must be considered. One arrives at the single-particle excitation spectrum of Figure 1. The region $-\frac{1}{2}(2C-U) < E_2 < \frac{1}{2}(2C-U)$ of the spectrum corresponds to metastable states; the states with the energy range $-U < E_2 < U$ may be occupied by a single electron. Note that the density of paramagnetic states

is assumed larger than the density of metastable two-electron states since the latter requires trapping of two electrons in the same states after photoexcitation.

There are four possible absorptive mechanisms for this spectrum, represented as follows:

$$\alpha_1 : 2 \rightarrow 1 + 0 \rightarrow 1 \quad (6a)$$

$$\alpha_2 : 2 \rightarrow 1 + 1 \rightarrow 2 \quad (6b)$$

$$\alpha_3 : 1 \rightarrow 0 + 0 \rightarrow 1 \quad (6c)$$

$$\alpha_4 : 1 \rightarrow 0 + 1 \rightarrow 2 \quad (6d)$$

where 2, 1, 0 stand for a doubly occupied, singly-occupied, and unoccupied site. Hence (6a) represents the transfer of an electron from a doubly-occupied to an unoccupied site, leaving two singly-occupied sites. All centers may be ground states or metastable states. The minimum energy for each process is zero⁶, corresponding to photodarkening⁹ in the case of extreme fatigue. After only moderate illumination, however, few metastable two-electron states will be occupied, and paramagnetic states will dominate the metastable populations, having a density of approximately $10^{17}/\text{cm}^3$ according to ESR measurements⁴. In this case,

$$\min (\alpha_1) = 2C - U \quad (7a)$$

$$\min (\alpha_2) = \min (\alpha_3) = C - \frac{1}{2} U \quad (7b)$$

where $\min (\alpha_i)$ is the minimum energy allowable for process α_i . Process α_4 should not contribute, being proportional to matrix elements between paramagnetic levels, which will be exponentially small.

These results are summarized in Fig. 2 which is similar in many respects to the measured photoinduced absorption spectrum reported¹⁰ in chalcogenide glasses. We find the simple model of eqs. (1) and (2) predicts an

induced absorption edge at $E_g/2$ where E_g is the ground state gap. Also, the centers giving rise to the absorption are unambiguously paramagnetic (i.e. processes α_2 and α_3) involving initial states occupied by a single electron. Thus the model would predict a strong correlation between ESR and optical measurements.

Transport processes, on the other hand, are determined by mobilities in the extended state region of the spectrum and by trap densities. The traps providing the greatest capture cross section will occur near μ_2 where there must exist charged centers. These occur when anti-bonding-like states fall below μ_2 (and must pick up two electrons) and bonding-like states occur above μ_2 (and must give up two electrons). After local reconstruction, it is likely that some charge remains, examples of which are discussed in refs. 1 and 2. From hole transport measurements the inferred trap densities for undoped samples are in the range 10^{16} to 10^{17} cm^{-3} . This is 3-4 orders of magnitude below the density presumed pinning μ_2 .

We may inquire as to the effect of doping with Tl, an electropositive atom, as performed by Pfister, et al.⁵ The electrons contributed by Tl^+ will occupy states at μ_2 , increasing the density of hole traps, but will not affect the position of μ_2 . Thus we predict no significant change in the activation energy for transport (essentially a measure of μ_2 relative to the mobile hole states). The hole transit time should be increased significantly, reflecting the increased trap density. This situation must prevail until doping densities approach the pinning density $> 10^{19}$. The results of Pfister, et al.⁵ are essentially in agreement with all of these qualitative predictions.

By contrast, doping will have no effect on the optical excitation spectrum of the model (of Fig. 1). The width of the

paramagnetic band is determined by the coulomb repulsion parameter U characteristic of states at μ_2 . The number which can be excited depends on rate processes which are not taken into account by the model but which are intrinsic to the material. The occupation of the paramagnetic band by optical pumping is rate limited by 1) photon absorption by the metastable state causing relaxation to the ground state, 2) phonon absorption or annealing, and 3) second electron capture producing a metastable two-electron state, thereby reducing the spin density.

Summarizing, we find that within a simple model there is no connection between the centers which control ESR, photoluminescence, photoinduced absorption and the "defects" which limit transient hole transport in doped samples.

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Figure Captions

- Fig. 1. Excitation spectrum for model described in text. Here μ_2 is taken to be zero for simplicity. Metastable two-electron states appear to the right of the Fermi level and metastable zero-electron states to the left. The narrow band at center consists of one-electron states.
- Fig. 2. Photoinduced absorption spectrum derived from equations (7). Absorption begins at an energy equal to half the gap (processes α_2 and α_3) and increases at full gap, when process α_1 begins to contribute.

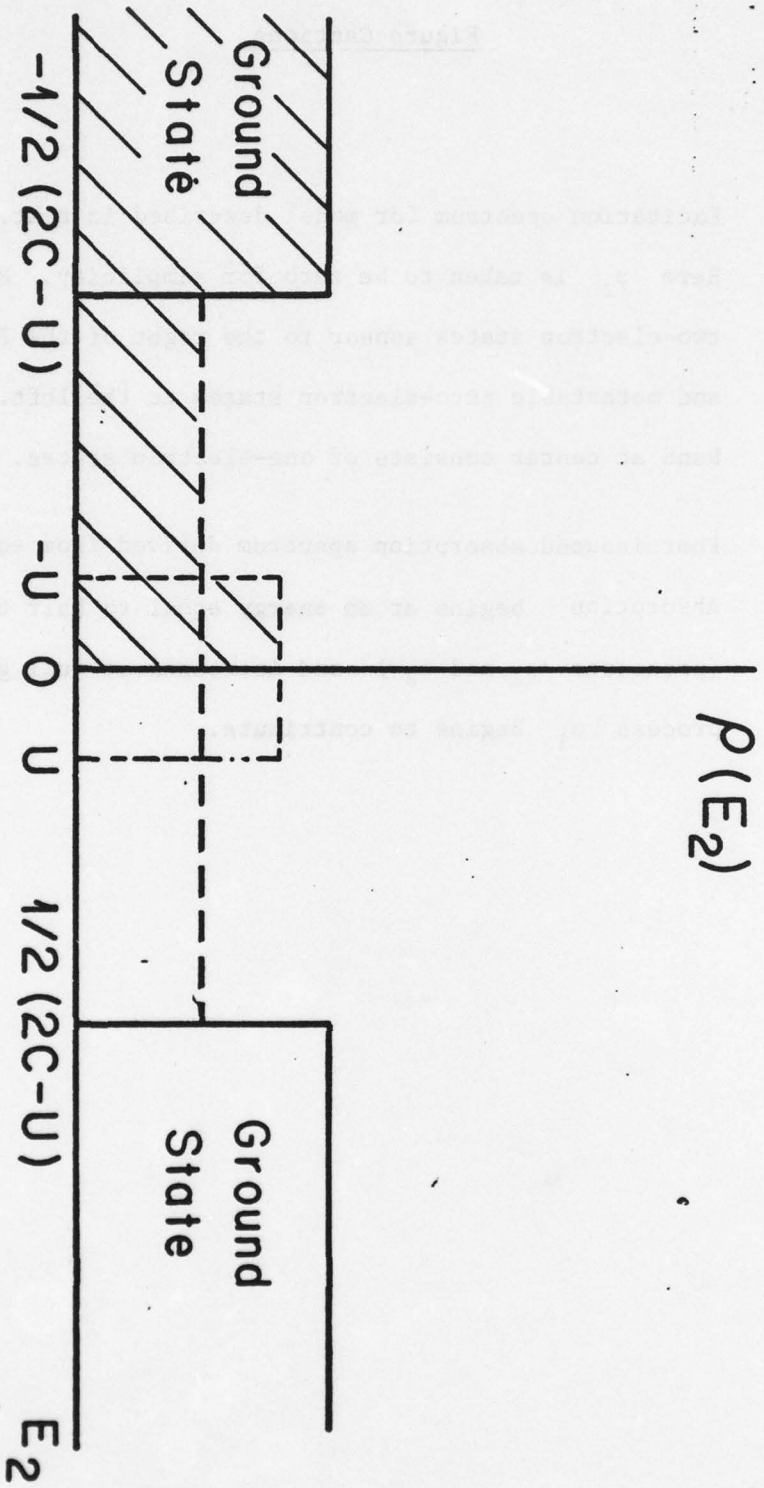


Fig. 1

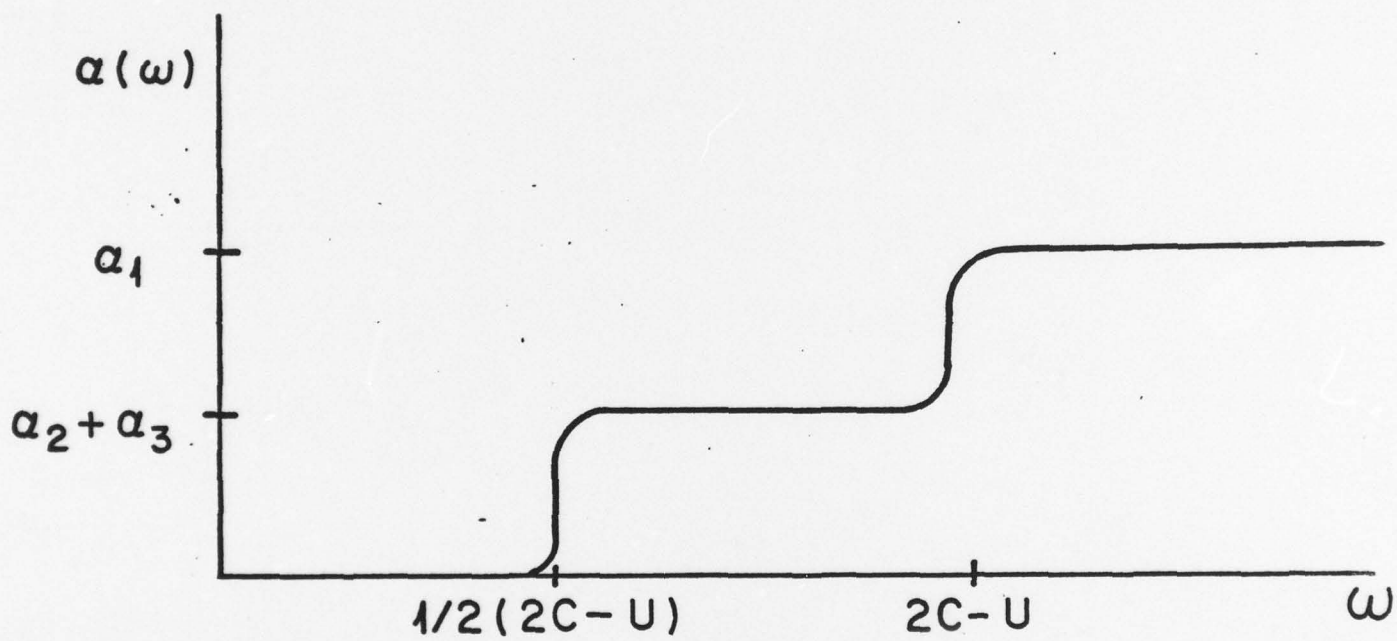


Fig. 2

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