

DYNAMICS OF THE OPTICALLY INDUCED PROPERTIES
OF A SMALL-POLARONIC GLASS*

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The relaxation and recombination of an electronic excitation created by the absorption of a super-band-gap photon is considered for a system in which excitons and charge carriers find it energetically favorable to self-trap. The notions of a barrier to self-trapping, a short-range repulsion between electrons and holes, and the electromodulation of the small-polaron absorption band play a central role in this discussion. The results are consistent with experiments on chalcogenide glasses.

INTRODUCTION: ITINERANT AND LOCALIZED MODELS

In this discussion the absorption of a photon of energy in excess of the absorption edge is presumed to create either a pair of separated charges or an exciton which self-traps. Since electronic adjustment and transfer times ($\sim 10^{-15}$ sec) are very often orders of magnitude shorter than lattice relaxation times ($> 10^{-12}$ sec), a carrier which is initially severely localized can spread out or diffuse from its initial location before the atoms can respond to its presence. In such a situation, self-trapping only occurs when, by virtue of their vibrations, the atoms of the material assume a configuration that corresponds to a potential well which confines the excitation sufficiently so that further localization and ultimate small-polaron formation readily ensues. The time delay for self-trapping involved in this process is associated with a barrier to self-trapping, which is depicted in Fig. 1.¹ This figure shows three plots of the (adiabatic) energy of the system comprising an electronic charge in a three-dimensional deformable continuum characterized by a local electron-lattice interaction, against a normalized variable proportional to the spatial extent (radius) of the carrier. These three curves successively correspond to either an increasing carrier mass ($M_c = M_0/2 = M_0/3$) or an increasing electron-lattice coupling strength. The small- R cut-off at $R = R_0$ occurs at the small-polaron state, where the carrier is confined within a region of interatomic dimensions. Curves a, b, and c, respectively, correspond to self-trapping at $R = R_0$ being energetically unstable, metastable, and stable. With the situation depicted in curve c, a carrier inserted (optically excited) into an undeformed system ($R \rightarrow \infty$) will not be driven to localize unless atoms in its vicinity assume a configuration corresponding to a potential well which confines the carrier within a radius less than R^{MAX} . Having achieved this condition the system will then find it energetically favorable to shrink to the small-polaron situation, $R = R_0$ in $\sim 10^{-12}$ sec. A barrier to the deep small-polaron trapping of excitons and charge carriers can also occur for excitations initially localized by defects and disorder.¹ Here, the barrier and time delay decrease with increasing initial (nonpolaronic) localization.

If one or both of the charge carriers of the unrelaxed system have mobilities comparable to those in a crystal (an itinerant picture), the absorption of a super-band-gap photon produces an electron and hole which tend to diffuse far apart from one another before relaxing to form small polaronic carriers. Thus, if the unrelaxed

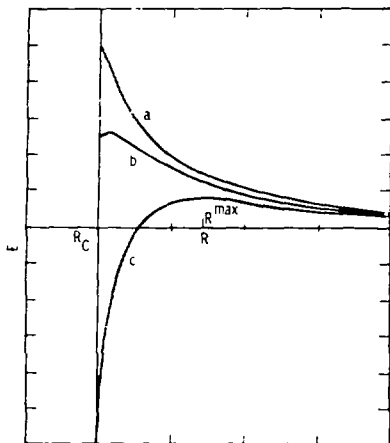


Fig. 1. E-versus-R curves for three carrier effective masses.

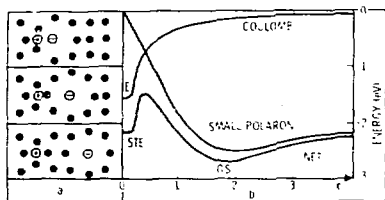


Fig. 2. a) Equilibrium displacement patterns for three separations of electron and hole small polarons; b) The coulomb, polaronic, and net energy of the polaron pair as a function of separation.

carriers are itinerant, optical excitation will efficiently produce electron-hole pairs which typically escape from each other's coulombic field and contribute to the photoconductivity. The mobility associated with photoconductivity is the average of the relatively high nonpolaronic mobility and the much lower small-polaronic mobility weighted by the fraction of the photoconductivity lifetime during which the carrier is in each of the two states. Thus with a sufficiently long time delay for self-trapping the photoconductivity may even manifest high-mobility itinerant behavior while the dc transport indicates low-mobility small-polaron hopping.

Alternatively, both carriers of the unrelaxed system may be localized or have their motion severely impeded. For example, this can occur if the material possesses structural localization which renders it similar to a molecular crystal. Then optically generated charge carriers may often not separate further than their coulomb capture radius before relaxing and the system will manifest geminate recombination: charge carriers recombine with their nascent partners and thereby avoid contributing to the dc photoconductivity.² Furthermore, since localization tends to reduce the barrier and time delay for small-polaron formation,¹ the photoconductivity will tend to be dominated by the small-polaron component. In addition, super-band-gap absorption can produce localized exciton-like excitations which, as in molecular crystals, may relax and degrade in energy very little compared with itinerant carriers ($\sim 10^{12}$ eV/sec for hot electrons). The observation of geminate recombination,³ small-polaronic dark transport and phototransport,⁴ and long-lived un-Stokes-shifted super-band-gap luminescence⁷ in chalcogenide glasses suggests that these materials are examples of this localized variety.

THE ENERGY OF AN OPTICALLY PRODUCED EXCITATION

In this localized picture, the unrelaxed electronic excitation generated by a super-band-gap photon is taken to be characterized by a distribution of charge-separation lengths. If the resulting electron and hole remain sufficiently close so that their wavefunctions overlap substantially they are regarded as a neutral entity, an exciton. Otherwise, whether or not they geminately recombine, charges whose wavefunctions do not overlap substantially are viewed as separated, or metastably separated, charges. Since the interaction of an exciton with the atoms in its immediate vicinity is typically much weaker than that of a single carrier, the

exciton is taken to be characterized by a much longer time delay toward small-polaronic relaxation than are separated charges. In this interpretation, the self-trapping of separated charges in the chalcogenide glasses appears to take place in about a picosecond.⁶

The kinetics of the hopping of separated electron-like and hole-like small polarons from their positions at creation to those from which they recombine reflects itself in the time dependence of the luminescence and induced absorption. To understand the dynamics of the recombination of the electron and hole small polarons involves considering the energy of the system as a function of the pair separation. As illustrated in Fig. 2a, in addition to their coulomb attraction, they interact via the overlap of their atomic displacement patterns. The coulomb, polaronic, and net potential energies of the pair as functions of their separation, r , in units of the interatomic spacing, are plotted in Fig. 2b; for like-signed small polarons one simply inverts the energy scale. The three pair-potential minima corresponding to the formation of an exciton (E), a self-trapped exciton (STE), and the ground-state of separated electron and hole small polarons (GS) are indicated on the figure.

LUMINESCENCE

Those carriers which do not separate ($r_{\text{initial}} < 1$) after excitation are viewed as forming excitons which ultimately self-trap to STE. Those charges which separate ($r_{\text{initial}} > 1$) rapidly ($\sim 10^{-12}$ sec) relax to form small polarons at $r > 1$. They then tend to hop toward their groundstate before recombining. Those that radiatively recombine before reaching GS will luminesce at a higher energy than those which reach GS. Furthermore, since the overlap and the matrix elements for recombination decrease with increasing separation, the luminescence will tend to shift to lower energy with time as the small- r pairs recombine first.

Three luminescence bands result. At the highest energy lies the simple exciton luminescence. Since there is little lattice relaxation about the localized exciton it manifests a minimal Stokes shift. In chalcogenide glasses, the parameters are such that the recombination is primarily radiative. The extreme smallness of the competing nonradiative rate results from the recombination energy ($\sim 2-3$ eV) greatly exceeding the exciton-lattice coupling energy ($\Delta E_{\text{EL}} = 2k_{\text{B}}T \approx 1$ eV).⁹ A lower-energy luminescence, manifesting a Stokes shift, is due to the self-trapped exciton. As indicated above, the nonradiative recombination associated with the STE, while larger than that for the simple exciton, will still not be able to effectively compete with the radiative recombination. For both excitons the luminescence decay rates at low temperatures will manifest little temperature dependence. However, at higher temperatures (comparable to the phonon temperature) thermally assisted tunneling through the self-trapping barrier from E to STE will enhance the STE luminescence at the expense of that of the simple exciton. Finally, the lowest-energy luminescence is associated with the recombination of separated small polarons. As indicated above, this Stokes shift increases in time as more luminescing carriers converge on their minimum energy separation. Furthermore, calculations⁹ show that as a result of reduced electronic energy separation and enhanced electron-lattice coupling strength, nonradiative recombination dominates recombination at the groundstate and its vicinity. In addition, reflecting both the predominance of nonradiative recombination and the thermally assisted motion of the separated charges, the small-polaron population and its associated luminescence will shift and decay with increasing rapidity as the temperature is raised above a fraction ($\sim 1/3$) of the phonon temperature. Also, since the decay rate of the luminescence decreases as the fraction of large initial separations of small polarons ($r \gg r_{\text{GS}}$) increases, a rise in the energy of the exciting photons which appropriately increases the initial separations will cause a decrease of the decay rate.

An important feature of small-polaron hopping is that the jump rates depend strongly

on the energy differences between initial and final sites.² As a result, pairs with separations on the relatively steep portions of the small-polaron E-versus-r curve hop toward the groundstate rather quickly, (10^{-8} sec per hop) while those that are sufficiently well separated so as to experience small energy gradients require extremely long times to move, $\sim 10^3$ sec per hop for $r \geq 4$. These metastably separated small-polaron pairs contribute a long slowly decaying tail to the lowest-energy (small-polaron) luminescence. They also produce the metastable induced absorption and e.s.r. These features are all in accord with recent observations of the luminescence of some chalcogenide glasses.^{7,8,10}

INDUCED ABSORPTION

A self-trapped charge carrier can be induced to hop by the absorption of a photon of energy roughly equal to the difference between the electronic energies of the initial and final states.¹⁰ In this process, the atoms remain essentially fixed during the excitation process (the Franck-Condon principle). Without electric fields (either applied or due to charges), the electronic energy difference is simply due to small-polaron formation. Then the centroid of the absorption band of an isolated small-polaron lies at about twice the small-polaron binding energy. However, in the case of oppositely charged small-polaron pairs the centroid of the absorption of each member of the pair is shifted (electromodulated) by the fields produced by its partner. As the distribution of pair separations changes in time due to recombination and hopping, the broadening of the small-polaron absorption band is thereby altered. Specifically, as illustrated in Fig. 3, the density of pairs of small-r, associated with large energy gradients and concomitantly great broadening, falls first (in $\sim 10^{-9}$ sec in a-As₂Se₃) leaving only the metastably separated (large-r) pairs at long times (~ 1 sec)². The small-polaron absorption bands thus narrow in time toward the field-free values of well-separated pairs. As shown in Fig. 4, the predicted small-polaron absorption band, with the hole-lattice coupling parameter determined independently from transport experiments on a-As₂Se₃, is similar to the observed metastable induced absorption.¹¹ Furthermore, consistent with the present work, short-time picosecond measurements of the induced absorption in a-As₂Se₃ indicate a very broad induced absorption band⁹, although the long-time metastable induced-absorption band is very much narrower.¹¹

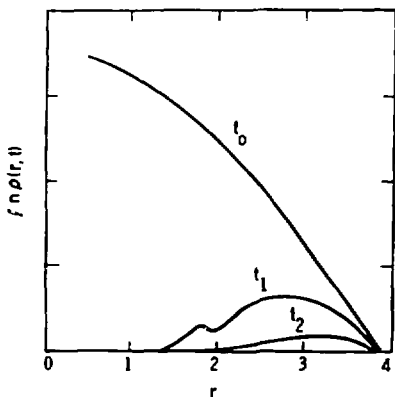


Fig. 3. Density of pairs versus r for three times, $t_2 > t_1 > t_0$.

$$E_A = 0.3 \text{ eV (a-As}_2\text{Se}_3), h\nu = 0.03 \text{ eV; } \alpha/n_p = 10^{16} \text{ cm}^{-2}$$

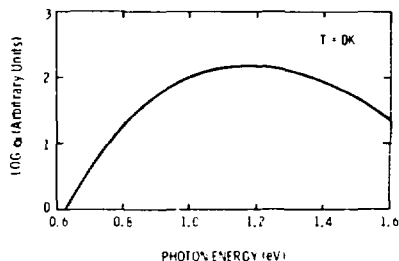


Fig. 4. Field-free (unbroadsened) hole small-polaron absorption band in a-As₂Se₃.

SUMMARY

The photoinduced properties of a defect-free system in which the charge carriers and excitons find it energetically favorable to self-trap have been discussed. The essential concepts involved are that: 1) The barrier and time delay for exciton self-trapping will significantly exceed that for small polaron formation; 2) Electron and hole small polarons experience short-range repulsion, barring their coalescence, which produces a dichotomy between self-trapped excitons and separated small polarons; 3) In this picture, three distinct luminescence bands, associated with the recombination of excitons, self-trapped excitons and small polarons, emerge; 4) The time scales for the motions of the separated charges depend strongly on their separations; 5) The kinetics of the recombination and recombination of separated charges is mirrored in the time dependence of the optically induced small-polaron absorption and luminescence. This model is consistent with both established transport^{3,4} and recent optical measurements^{7,8,10,11} on various amorphous semiconductors.

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