# Dynamic Studies of the Optical Absorption Associated with Trapped Electrons*

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Studies of electron traps in fused silica, populated via x irradiation, are reported. The silica was doped with several concentrations of the rare earths Tb, Tm, and Dy in order to measure thermoluminescence, which was correlated with the radiation-induced optical absorption. The traps were found to be host associated, rather than dopant associated. The absorption spectrum was obtained both under static conditions (at room temperature) and under dynamic conditions (at elevated temperatures) for which, in addition to thermal broadening, the densities of the populated traps change with time. The dynamic measurements were made using a rapid-scan monochromator, designed to obtain the spectrum in ~1 msec. The results of these measurements demonstrated unambiguously the existence of a redistribution of electrons among the traps at elevated temperatures, implying the existence of nonlocalized intermediate states.

## I. INTRODUCTION

The study of defects in solids provides much useful information, not only about the defects themselves, but also about the properties of the structure in which they exist. Such defects are often studied by x irradiation of the solid, the energy of the radiation being chosen to be sufficient to produce internal ionization (electronic rearrangements) in the solid, but none of the ionic displacements which complicate similar investigations of high-energy radiation damage. Upon cessation of the irradiation, the solid relaxes to a metastable state in which electrons are weakly bound ("trapped") at impurity or defect sites. The manifestations of this electronic rearrangement are numerous; e.g., one finds additional optical absorption and electron spin resonances, thermoluminescence, and, in some cases, thermally stimulated electrical conduction and photoconductivity, all of which were absent prior to irradiation. Studies of the optical absorption make up the bulk of the literature in the field of color centers in the alkali halides,[1] while electron spin resonance finds predominant use in studies of high-energy radiation damage. The remaining phenomena are mainly of interest to those who study phosphors, which differ slightly in that they involve the doping of a material with a luminescent impurity.[2] Unfortunately these phenomena are seldom intercorrelated for a given sample.

The interpretation of experimental studies in phosphors commonly invokes one or the other of two models for the physical processes involved (models A and B in Fig. 1). Both models involve the trapping of electrons in a spectrum of long-lived states. In model A, both the trapping and subsequent luminescence take place in the same center, while in model B these occur at different sites. Thus, for model A, trap depletion and subsequent luminescence proceed through localized intermediate states, while model B assumes nonlocalized intermediate states (such as a "conduction band") involving the transport of charge, and implying some persistent internal ionization of the material. The final stage of the luminescence process can take place through a variety of mechanisms, such as recombination of an electron with a previously ionized luminescent ion, recombination at a host site with resonant energy transfer to the luminescent ion, and so on. For both models the mathematical description of the dynamics can be made quite similar, involving parameters describing the occupancies of various states, characteristic times, and intrinsic absorption cross sections. Differences are found in the details of the rate equations and their solutions. Workers in the field generally rely upon two related measurements for the interpretation of thermoluminescence phenomena[3]: thermal "glow curves" and the transient response of thermoluminescence. The first involves measurements of thermoluminescent intensity versus temperature, when the sample is heated at a prescribed rate; the second determines thermoluminescent intensity as a function of time, with the sample at a constant temperature. In any event, the testing of the rate equations for a given model is overly dependent upon curve fitting. In view of the variety of adjustable parameters to be determined it is difficult, if even possible, to distinguish model A (with a distribution of traps) from model B. This is pointed out strikingly in the work of W. L. Medlin[4] who was able to fit his data on thermoluminescent decay to either model. The ambiguities inherent in glow-curve analysis have also been emphasized recently by Kelly and Bräunlich.[5] It is clear that, in order to apply these techniques to investigations of defect sites in solids, one must be able to distinguish unambiguously between these physically different situations (see Fig. 1).

Although, in the system discussed here, neither

the measurements of thermally stimulated conductivity[6] nor the kinetics of trap depletion suffice to distinguish model A from model B, this can be done by another method. In particular, it will be shown here that studies of the energy dependence of the transition rates associated with the x-ray-induced optical absorption at various temperatures can provide this information. The problem of distinguishing localized and nonlocalized intermediate states reduces to that of determining, in detail, the effects of temperature on the *shape* of this spectrum. For model A one expects, at worst, a superposition of "lines" which broaden symmetrically with increasing temperature and decrease in intensity on the low-energy side due to preferential depletion of traps with energies closer to that of the intermediate state(s). In the system discussed here, quite a different situation is found. At elevated temperatures the shape of the spectrum is unchanged on the high-energy side, while the peak is shifted slightly toward lower energies and intensities increase, rather than decrease, for lower energies. This is interpreted as arising from a redistribution of electrons among the spatially isolated traps, implying a coupling of traps through nonlocalized intermediate states (model B).

There are several advantages to studying optical absorption rather than thermoluminescent phenomena. It appears more desirable to obtain information about the traps and intermediate levels from studies of the initial transitions ($t{\rightarrow}i$, in Fig. 1) rather than to infer this information from studies of the final transitions ($i{\rightarrow}f$ and $f{\rightarrow}g$). These may involve a variety of different mechanisms, and could contribute to the temperature dependence of the eventual light output. In addition, these measurements allow one to study the host material directly without requiring the incorporation of a luminescent impurity which could conceivably affect the trap distribution being studied. Finally, the measurements of glow for the deeper traps could involve temperatures which are sufficiently high to produce some annealing of the samples, with concomitant changes in the trap distribution.

Since the emphasis of this study was upon discriminating between the physically different situations pictured in models A and B, little effort was made to identify the trapping sites involved. In addition, it was thought desirable to avoid any assumptions concerning the kinetics or the physical parameters involved in the thermoluminescent mechanism. It was assumed that the traps involved are localized and isolated, at least to the extent that electron "hopping" between traps need not be considered. This assumption can be justified for the system studied here, as is indicated in a later section.

The fundamental distinction between the two models considered rests with the question of whether or not there exist excited bound states for the trapping sites. If so, the appropriate description of the optical
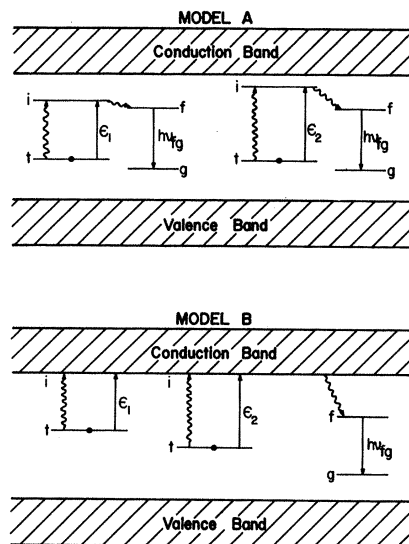


FIG. 1. Schematic representation of models. In each case an electron may be stimulated from the trapping state $t$ to an intermediate state $i$ via optical ($\uparrow$, $\downarrow$) or thermal excitation, subsequently relaxing to state $f$, from which it undergoes the luminescent transition $f{\rightarrow}g$.

transitions is the usual treatment in terms of a configuration coordinate,[7] which serves to describe the perturbation of localized states due to interactions with the surrounding lattice. In this case, the spectral distribution of absorption due to a single trapping level is Gaussian, with a width proportional to the square root of an appropriate effective temperature. If there is a distribution of trap depths due to differences in environment for different trapping sites, the absorption spectrum should contain a superposition of symmetrical, thermally broadened lines.

If, on the other hand, the optical transitions are from localized bound states to a band of nonlocalized final states, the shape of the absorption spectrum may depend sensitively on the details of the wave functions, which are not well known. For this reason, a study of the detailed shape of the absorption spectrum under static conditions cannot distinguish between the two types of transition. When the optical absorption is measured under dynamic conditions (while the population of trapping levels is changing) the distinction is more easily made. While thermal broadening is expected to produce symmetrical effects on the high- and low-energy sides of absorption maxima, the effects of population changes are not symmetric. For model A, for example, one expects a relative decrease in intensity at lower energies resulting from preferential depletion of traps with lower activation energies. For model B, however, retrapping of electrons from the nonlocalized intermediate state can occur, and the resulting redistribution of electrons among the trapping sites can produce an increase in low-energy
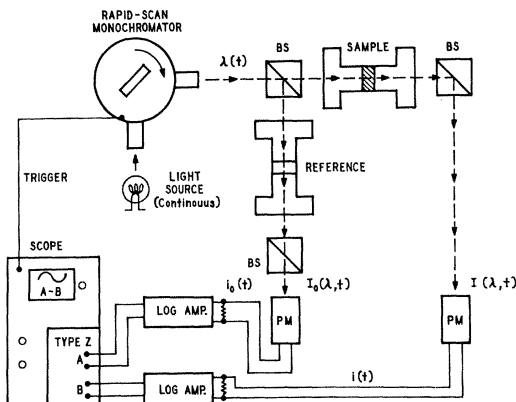
FIG. 2. Schematic diagram of absorbance apparatus. By direct measurement of the difference between the logarithms of the intensity transmitted by the reference and sample beams, the apparatus obtains (to within a subtractable constant) the absorbance directly.

absorption relative to that at higher energies. The crucial point is that once an electron has left a shallow trap in model A, that trap can make no further contribution to the low-energy optical absorption. In contrast, a depleted shallow trap in model B could retrap other electrons from the nonlocalized intermediate state. Thus an observed shift in absorption toward lower energies demonstrates unambiguously the presence of nonlocalized intermediate states.

## II. EXPERIMENT

The system chosen for the experimental studies was silica, doped with various concentrations of three different rare earths: terbium, thulium, and dysprosium. The use of rare earths as luminescent impurities provides for a well-characterized set of final transitions ($f \rightarrow g$, in Fig. 1) which occur in a time which is short compared to other characteristic times involved in the thermoluminescence mechanism.[8]

The samples were fabricated from O-I silica, a commercially available material[9] consisting of silica, either undoped (LO) or homogeneously doped with various concentrations (viz., 40, 70, 140, 250, and 400 ppm atomic, relative to Si) of the trivalent rare-earth ions: Tb($L9$), Dy($L10$), or Tm($L13$). After careful selection for optical quality, $\frac{3}{8}$-in.-diam rods were sliced into 4-mm-thick discs which were mechanically ground and polished on both surfaces. Midway between the polished faces of each disc, a $\frac{1}{16}$-in.-diam hole was sonically drilled radially inward $\frac{1}{10}$ in. from the periphery in order to provide for potting a thermocouple into the sample.

Since it had been established that curing a sample for 20 min at 700°C is a completely satisfactory way of producing a "fresh" sample (i.e., it removes all the effects of irradiation, but does not cause any

changes in the effects of subsequent irradiation), a variety of measurements could be made on the same sample. This approach was most appealing since it completely eliminates the effects of any variations (within a given rod) in dopant concentration, impurities, light scattering, etc. Although this treatment showed no evidence of causing changes in the effects of irradiation, each of the samples was heat treated for one hour at 900°C prior to its use. They were then x irradiated on a General Electric (model XRD-3) x-ray diffraction unit using a copper target, CA-7 Coolidge gun at 40 kV and 12 mA to produce an x-ray induced absorbance within $\sim 0.7\%$ of the value at saturation.

Measurements of the absorbance were made at room temperature, using a Beckman (Model DK-2A) ratio recording spectrophotometer, from wavelengths slightly larger than those corresponding to the onset of x-ray-induced absorption to wavelengths for which internal absorption in the rare earth becomes significant, viz., 1.15 $\mu \rightarrow$ 0.275 $\mu$. The absorbance measurements were made both *before* and *after* x irradiation. All other things being constant, the difference between these represents the *x-ray induced absorbance* $A(\lambda)$.

Thermoluminescence measurements were made at a constant heating rate (45°C/min) in the temperature range 0–480°C. For these measurements, the sample was friction fitted in the center of a 2 in. length of thin-walled platinum tubing (0.005-in. wall) and heated by passing a large current ($\sim 100$ A, $\sim 1$ V) through the tubing. A Chromel P-Alumel thermocouple was inserted into the hole provided and was insulated from the surroundings by packing with powdered
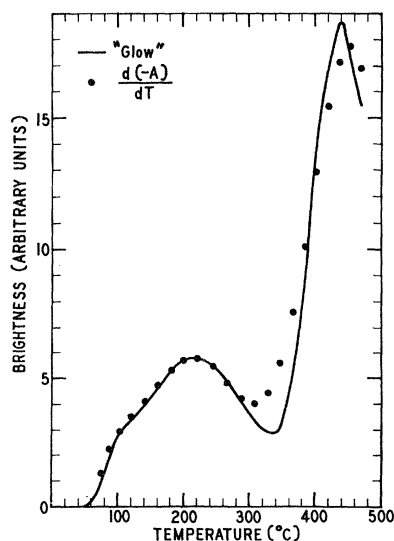


FIG. 3. Correlation of radiation-induced optical absorption with thermal "glow." Simultaneous measurements of absorption and glow were made (at a constant heating rate) on a silica sample doped with 400 ppm Tb. The curves were normalized at $T = 220°$C.

ceramic. This arrangement provided the "fastest" possible furnace, the time constant of which was limited by the sample ($\simeq$2 sec). The constant heating rate was obtained by using an SCR phase-sensitive controller[10] which compares a given input signal (provided by a precision potentiometer, rotated at a constant rate) to the actual sample temperature via a retransmitting slidewire attached to a Brown recorder directly monitoring the thermocouple output. The thermocouple output was also connected to the $x$ axis of an $xy$ recorder whose $y$ axis monitored the thermoluminescence via the output of an E.M.I. 9558Q photomultiplier terminated with 100 k$\Omega$. For each of the dopants, transitions originating from a single excited state were selected using the appropriate Corning-glass filters.

Measurements of the x-ray-induced absorbance were made at elevated temperatures by heating the sample using the same method (and at the same rate) as previously described for thermoluminescence measurements. Since, at elevated temperatures, the number of filled traps decreases with time and changes during the time required for a conventional scan of the spectrum, it was necessary to design and construct a rapid-scan monochromator having a scanning rate which is large compared to trap depletion rates. The scan of the entire visible portion of the spectrum in $\sim$1 msec was achieved by rapidly rotating a grating, producing a temporally analyzed "spectrum" which was detected by a photomultiplier and displayed on an oscilloscope. Using the rapid-scan monochromator, which was capable of resolving spectral detail of $\sim$2 nm, the absorption measurements were obtained
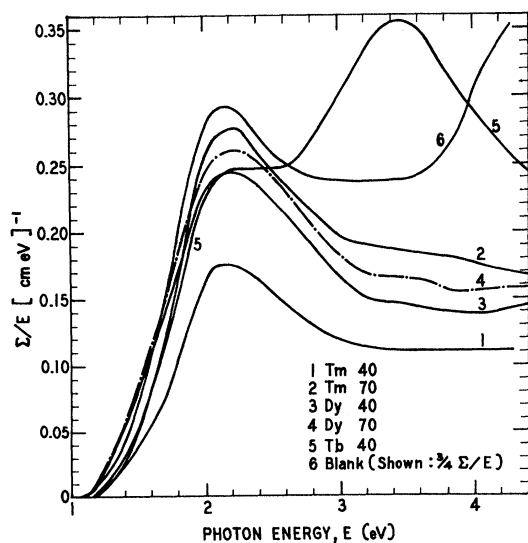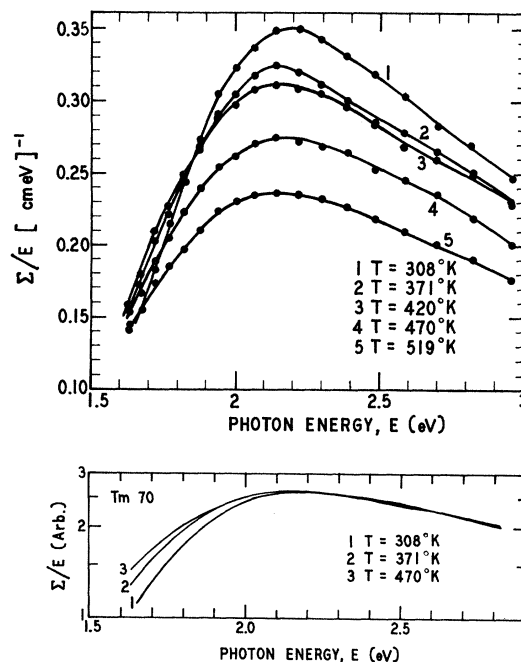


FIG. 5. "Absorbance" at elevated temperatures. Linear (upper) and normalized semilogarithmic (lower) plots of the probability spectrum, obtained while heating at a constant rate of 45°C/min, are shown for silica, doped with 70 ppm Tm.

as shown in Fig. 2. Corrections for differences in spectral response of the two photomultipliers, coloration due to beam splitters, and so on, could be determined by running a "zero-absorbance" curve (without sample) and this could be directly subtracted from the measured absorbance of the sample; i.e., one deals with additive, rather than multiplicative, contributions. In this way, errors in shape are less pronounced. A "wavelength" scale was established for the oscilloscope trace by means of a low-pressure Hg source. The absorbance spectra were obtained in the wavelength range 400–800 nm (40 nm/cm deflection), with a vertical scale deflection of 1 cm corresponding to an absorbance change of 0.1.

In order to test the correlation of radiation-induced absorbance and thermal "glow," simultaneous measurements of glow and absorption were made on a sample doped with 400 ppm. Tb. The observed glow curve was corrected for measured variations of the fluorescence efficiency with temperature. For first-order kinetics the glow $I(t)$ is given in terms of the density of filled traps $n$ by $I(t) \propto |dn/dt|$. Assuming that the radiation-induced absorbance $A$ is proportional to $n$, a one-to-one correspondence between the traps responsible for the glow and those responsible for the absorbance would result (for a linear heating rate, $(dT/dt)$ in $I(t) \propto d(-A)/dT$. This correspondence was unambiguously demonstrated, as shown in Fig. 3.
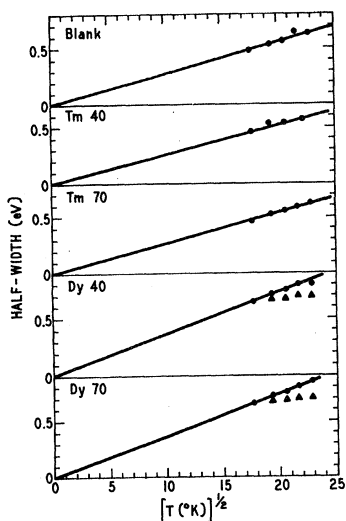


FIG. 4. Probability spectrum for optical transitions. The dependence, at room temperature, of a quantity $(\Sigma/E)$ proportional to the transition probability upon incident photon energy is shown for selected samples.

FIG. 6. Temperature dependence of absorbance half-widths. The results shown were obtained from the linear plots of $(\Sigma/E)$ versus $E$, using the low-energy side of each curve. Values were obtained by measuring (for each temperature) from a fixed energy, corresponding to the position of the maximum at room temperature (dots) *and*, for Dy 40 and 70, from the observed position of the maximum at each temperature (triangles).

## III. RESULTS AND DISCUSSION

The dependence of the radiation-induced absorption cross section at room temperature $\Sigma$ (absorbance/unit thickness) upon incident-photon energy $E$ was compared for the entire set of samples. No meaningful correlation was found between the amplitudes of the various spectra and the dopant concentrations, indicating that the traps responsible for the optical absorption are not intimately associated with the dopants.

For quantitative comparisons of the shapes of the absorption spectra, however, the relevant parameter to be compared is the transition probability $P(E)$, which yields a Gaussian dependence for the familiar bound-bound transitions. The absorption cross section is proportional[7] to the product $EP(E)$, so that one really wants to compare $\Sigma/E$ versus $E$ for the various samples. Representative results are compared in this manner in Fig. 4. Each of the spectra exhibit a maximum near 2.2 eV, and the shapes are strikingly similar for Tm 40,70 and Dy 40,70. There is clearly additional absorption, in Tb, centered at $\sim$3.5 eV, which increased for increasing Tb concentration. The results obtained for the blank are not understood. In addition to the over-all increase in the magnitude of the absorption (which, for host-associated traps, depends upon the thermal history of the sample), there is added absorption at energies above $\sim$3.6 eV.

Qualitative comparisons of thermoluminescence were made for the entire set of samples. The glow curves for Tm and Dy were in reasonable qualitative agreement, the numbers and locations of maxima being comparable. A detailed comparison of the shapes

was not legitimate, since the curves had not been corrected for the dependence of fluorescence efficiency upon temperature (photoluminescence in these dopants being negligible). The glow curves for Tb differed markedly from the others, again suggesting (as did the radiation-induced absorbance) the existence of dopant-associated traps in this case.

The glow curves were compared to those obtained by Yokota[11] for samples of fused quartz. The present results for Tm and Dy were in good qualitative agreement with Yokota's results for samples prepared under mildly oxidizing conditions. Calculation of the thermal activation energy for the traps, using Urbach's formula,[12] yields the value, $E_T \equiv 0.9$ eV. The onset of radiation induced optical absorption occurs at energies slightly larger than $E_T$. This is normally the case when the initial-state configurational coordinate curve is displaced (horizontally) relative to that for the final state.[13]

Representative results of measurements of the absorption at elevated temperatures are shown in Fig. 5. These were obtained for the entire range of photon energies available with the rapid-scan monochromator, and include a reasonable range about the maxima in the $(\Sigma/E)$ versus $E$ curves. In order to facilitate comparison of the *shapes* of the absorption spectra, the data are also presented on semilogarithmic plots, the curves being normalized by superimposing those regions of the spectra which have the same shape.
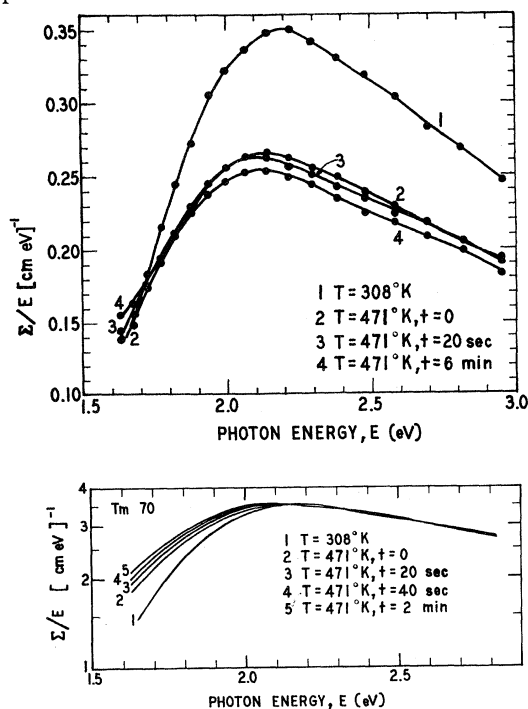


FIG. 7. Absorbance at elevated temperature. Linear (upper) and normalized semilogarithmic (lower) plots indicating the temporal changes in the probability spectrum (at constant temperature) are shown for silica, doped with 70 ppm Dy.

The linear plots of $(\Sigma/E)$ versus $E$ exhibit the decrease in x-ray-induced absorbance with increasing temperature (and time, as the samples were heated at a constant rate). In addition to the decrease in absorbance, a general broadening occurs with increasing temperature $T$. The half-width, as measured from the energy corresponding to the half-maximum on the low-energy side of the $\Sigma/E$ versus $E$ curves to a fixed energy, corresponding to the position of the maximum at room temperature, increases proportional to $T^{1/2}$. This would be the case, e.g., for a spectrum consisting of a superposition of Gaussian "lines" (with fixed centroids), since the thermal broadening of each "line" is proportional to $T^{1/2}$. The observed asymmetry, however, is *not* consistent with thermal broadening of a spectrum consisting of Gaussian "lines." In addition, the half-width, as measured from the position of the maximum observed at each temperature to the half-maximum point, is essentially independent of temperature. This indicates that the enhanced absorption at lower energies does not result from thermal broadening alone (see Fig. 6).

The most striking feature of the semilogarithmic plots is the pronounced asymmetry of the broadening (at elevated temperatures) on the high- and low-energy sides of the spectra. There is also a slight, but observable, shift (toward lower energies) in the energy corresponding to the maximum as temperature is increased. Furthermore, the excellent correspondence of the shapes on the high-energy side (at various temperatures) indicates that the absorption at lower energies is enhanced relative to that at higher energies.

These results are not consistent with bound-bound optical transitions (model A, Fig. 1), for which there are two physical situations of interest: isolated, *identical* traps (all traps in the same environment, resulting in a single trap depth), and isolated, *nonidentical* traps (traps in differing environments, resulting in a distribution of trap depths). In both of these cases, one expects enhancement of the absorption (at elevated temperatures) on both the low- *and* high-energy sides of the maximum. This was not observed. Furthermore, since both the transition probabilities *and* the numbers of filled traps could be changing with temperature (and time), one must also consider the effects of redistribution of electrons among traps. For model A, this redistribution would result in depletion of the shallower traps relative to the deeper traps, with a concomitant (relative) decrease in absorption at lower energies. This is entirely contradictory to the experimental results.

The results *are* consistent, however, with an increase in the relative number of filled shallow traps. In order to investigate this further, it was desirable to separate temporal and thermal effects on the absorption. For this reason a measurement was made in which the temperature was held constant and the temporal change in the absorption monitored. The results of
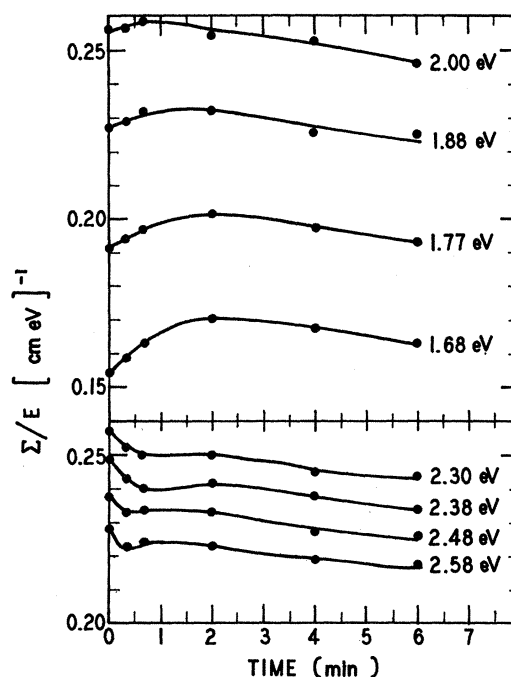


FIG. 8. Temporal changes in absorbance at elevated temperature. The temporal changes (at constant temperature) in $(\Sigma/E)$ are shown for several energies above and below the absorption maximum. The results were obtained for the Dy 70 sample, at a temperature of 471°K (see Figure 7).

this measurement are shown in Fig. 7, exhibiting both a decrease in over-all absorbance and an increase in low-energy absorption (relative to that at higher energies) with time. After the attainment of a steady-state temperature (with a time constant of $\sim$2 sec), the remaining effects are attributable directly to redistribution of electrons among traps and loss of electrons to recombination with other sites. The relative increase in the density of filled shallow traps is apparent. Figure 8, in which the temporal changes in the absorption are shown for several energies above and below the maximum, indicates that the shallow traps are initially filled at the expense of the deeper traps. At later times, the absorption decreases uniformly for all photon energies plotted. These results are consistent with an initial redistribution of electrons among the traps (as determined by the temperature) and an eventual decrease in the total number of trapped electrons (with constant relative distribution) due to recombination with other sites.

If one assumes that the traps are *isolated*, precluding a direct transfer of electrons between traps, then the redistribution must occur via nonlocalized intermediate states, as described in model B. The assumption of *isolated* traps can be justified. For example, the density of traps can be estimated from the room-temperature radiation induced absorbance using the (classical) relation[14]

$$N = (9.1 \times 10^{15}) \Sigma_0 \Delta E,$$

where $N$ (cm$^{-3}$) is the density of traps (for a single

electron/trap), and $\Delta E$ (eV) is the width and $\Sigma_0$ (cm$^{-1}$) the height obtained by approximating the $\Sigma$ versus $E$ curve with a rectangular profile. Since $\Sigma$ was not measured over its entire (nonzero) range, this can at best provide only an estimate. For $\Sigma_0 \simeq 1$ cm$^{-1}$ and $\Delta E \simeq 3$ eV, for example, one obtains $N \simeq 3 \times 10^{16}$ traps/cm$^3$, implying a rather large average separation between traps ($\sim 300$ Å). In addition, the existence of narrow trap "bands," as determined from laser-bleaching measurements, is consistent with isolated traps. For this purpose, a high-concentration Tb sample was exposed to the 5145 Å (2.4 eV) emission from an argon laser, using a beam diameter which was less than the diameter of the sample. Visual inspection indicated *complete* bleaching of the exposed region of the sample only (implying that the bleaching was not thermally induced). Thus, irradiation with 2.4 eV light (near the onset of absorption) depleted traps responsible for absorption in the region from $\sim 1.8$ to 3.1 eV (and above, since no "tailing" into the visible remained), implying that the rather broad absorption band observed ($\sim 100 k T_0$, $T_0$ being room temperature) must result from a broad set of final states, the initial states being of the order of several $k T_0$ broad. This observation also argues against the possibility that the x-ray-induced absorption results from optical transitions originating in a "valence" band and terminating on trapped "holes".

## IV. SUMMARY AND CONCLUSIONS

Two models, relevant to the mechanism of thermoluminescence and the radiation-induced optical absorption, have been investigated for electron traps (filled via x irradiation) in silica. Both models involve relatively "deep" isolated traps and either localized (model A) or nonlocalized (model B) intermediate states. Since these physically different situations cannot be distinguished by measurements involving thermoluminescence alone (either "glow" curves or transient response), and measurements of thermally stimulated conductivity are inconclusive in the system discussed here, emphasis was placed upon studies of the radiation-induced optical absorption. This optical absorption was correlated with thermoluminescence in order to establish that the same traps were responsible for both. In addition, it was shown that the traps responsible for the optical absorption are host associated, rather than dopant associated (with the possible exception of Tb in silica).

Measurements of the optical absorption, both as a function of temperature, while heating the samples at a constant rate, and as a function of time at a given elevated temperature, were clearly inconsistent with the bound-bound optical transitions implied by model A and demonstrated unambiguously (and qualitatively) the existence of a redistribution of electrons among the traps at elevated temperatures. For isolated traps, this redistribution can occur only as a result of coupling of the traps via a nonlocalized intermediate state(s), involving electron transport.

Dynamic studies of the radiation-induced optical absorption provide a novel experimental approach to the problem of electron traps in solids. The various models can be distinguished, for a given system, without requiring any inferences regarding the details of the trapping sites or the kinetics involved in the thermoluminescence mechanism. There exist, for example, none of the ambiguities associated with curve fitting, adjustable parameters, and so on. Moreover, the fact that the redistribution of electrons among the traps can be seen in these data indicates that this redistribution takes place at a rate which is not small compared with the rate at which the total number of filled traps decreases. This suggests that, by making more detailed measurements of the kinetics of this redistribution, one might obtain useful information about parameters such as trap-depletion rates and recombination cross sections.

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[13] Reference 2, p. 162.

[14] See, e.g., Max Garbuny, *Optical Physics* (Academic, New York, 1965), p. 101.