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Photoluminescence Excitation Spectra in Chalcogenide Glasses

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The intensity of the photoluminescence in glassy As_2Se_3, As_2S_3, and $As_2Se_3 \cdot As_2Te_3$ has been measured as a function of the wavelength of the exciting light at a temperature of 6 K. The resulting excitation spectra are sharply peaked in the vicinity of the optical-absorption edge and indicate that the photoluminescence in these glasses is excited by interband optical absorption. For thick samples the most efficient excitation occurs for exciting photons with penetration depth of about 100 μm. The excitation of the photoluminescence is primarily a bulk effect and excitation efficiency decreases rapidly when the penetration depth of exciting light falls below a few microns. An analysis of the line shapes of the excitation spectra in terms of interband optical absorption and surface-recombination effects yields values for the carrier diffusion length in these glasses of the order of 1 to 3 μm. The measured response times for the photoluminescence in these glasses are in the range 0.10–0.84 msec. The functional dependence of the photoluminescence intensity upon chopping speed, the observation of a lifetime independent of excitation intensity, and the linear dependence of photoluminescence upon the intensity of the exciting light all indicate that the radiative recombination in the $As_2Se_3 \cdot As_2Te_3$ glass obeys monomolecular recombination statistics. These results are consistent with the recombination of carriers at one band edge with carriers trapped in a band of recombination centers near midgap.

I. INTRODUCTION

Photoluminescence (PL) in a semiconducting chalcogenide glass was first reported by Kolomiets *et al.*[1] in bulk samples of glassy $As_2Se_3 \cdot As_2Te_3$ using what was described as ultraviolet excitation. Subsequently these same workers observed PL in crystalline and glassy As_2S_3 and As_2Se_3 using 2–3-eV exciting photons from a mercury vapor lamp.[2,3] The broad PL spectra observed in all of these materials had maxima well below the forbidden-gap energy in the spectral range corresponding to high transparency. The midgap position of the PL spectra was explained on the basis of radiative recombination through impuritylike levels lying deep in the forbidden gap. Although these experiments were carried out on both freshly fractured and polished and etched samples, the effects of surface recombination on PL line shapes or efficiency were not discussed.

Fisher *et al.*[4] studied PL in thin films of amorphous $As_2Se_3 \cdot 2As_2Te_3$ using 1.06-μm exciting radiation from a Nd:YAG (yttrium aluminum garnet) laser. Again, the observed broad PL spectrum had its maximum well below the forbidden-gap energy. These workers interpreted the midgap position of the spectrum in terms of simultaneous radiative recombination and phonon emission in a continuum of states in the gap.[4,5] The 0.4-μm penetration depth of the exciting light was considered sufficient to effectively eliminate surface effects. It was, however, speculated that diffusion of photoexcited carriers to the surface with subsequent nonradiative recombination could constitute a competitive nonradiative-recombination mechanism.

It was the intention of the present work to study the dependence of the PL intensity in chalcogenide glasses upon the photon energy of the exciting radiation. Such excitation spectra provide information about the energy transfer between the interband-absorption process and the radiative-recombination process. The PL in the chalcogenide glasses is ideally suited to such measurements since the PL spectrum is well separated from the intrinsic absorption edge, thereby minimizing the problem of separating exciting light from emitted light. In addition, the effects of self-absorption on the emitted light are minimal because of the high transparency in the spectral range of the PL.

The experimental results presented here include PL spectra and PL-excitation spectra for glassy $As_2Se_3 \cdot As_2Te_3$, As_2Se_3, and As_2S_3, and measurements of the response time (lifetime) of the PL in these materials. It is demonstrated that carrier diffusion lengths of the order of microns are required if the shape of the PL-excitation spectra is to be explained on the basis of interband optical absorption and nonradiative surface recombination effects. The PL-lifetime measurements in conjunction with the measurements of the dependence of the PL intensity upon the excitation intensity indicate that the radiative recombination in the $As_2Se_3 \cdot As_2Te_3$ glass is governed by monomolecular recombination statistics.

II. INTERPRETATION OF EXCITATION SPECTRA

In crystalline semiconductors the form of the excitation spectrum for PL (or photoconductivity) closely follows the intrinsic absorption spectrum at low energies, while at higher energies where the absorption process saturates, the excitation spectrum usually decreases monotonically due to the increasing influence of strong nonradiative surface recombination.[6,7] The exact shape of the excitation spectrum will be determined by the absorption spectrum, the sample thickness, the carrier diffusion length, and the ratio of surface-to-volume recombination rates.[6]

Initially, it seemed unlikely that surface-recombination effects could be responsible for the observed shape of the PL-excitation spectra to be presented here. The inherently low mobilities of carriers in chalcogenide glasses would appear to make diffusion of photoexcited carriers to the surface improbable. However, attempts to fit the observed spectra on the basis of the known absorption curves and an energy-dependent quantum efficiency which is a bulk property of the glass (and is independent of sample thickness) have been unsuccessful. Careful measurements of the excitation spectra for various sample thicknesses and subsequent analysis of these data have demonstrated that the observed spectra can only be fitted by an energy-dependent quantum efficiency which is itself a function of sample thickness. Nonradiative surface-recombination effects can provide just such a mechanism since the relative importance of radiative volume recombination and nonradiative surface recombination is a strong function of the relative sizes of the sample thickness and the carrier diffusion length. The theoretical treatment of these effects is well developed and, as will be shown, can be applied successfully to the description of the observed PL-excitation spectra for chalcogenide glass samples of varying thickness.

The problem of explaining the observed shape of photoconductive or PL-excitation spectra on the basis of surface-recombination effects has been analyzed in detail by DeVore.[6] His analysis is carried out for a semiconductor in the form of a large sheet with thickness d. The sample is illuminated on one face and carrier pairs are continuously generated at each point in the sample volume at a rate proportional to the intensity of the absorbed radiation at that point. Because of the gradient in the density of the photoexcited carriers, the carriers will undergo diffusion. The carriers will recombine in the volume at a rate governed by a volume lifetime τ, while those that diffuse to the surface will recombine at a rate which may be represented by a surface-recombination velocity S.

DeVore's theoretical analysis results in an expression for the shape of the excitation spectrum which uses the minority-carrier diffusion length L and the quantity $A = S(\tau/D)^{1/2}$ as adjustable parameters; S is the surface-recombination velocity, τ is the volume-recombination time, and D is the diffusion constant for the photoexcited carriers. The quantity A is proportional to the ratio of surface-to-volume recombination rates. If λ is defined as the ratio of sample thickness d to diffusion length L ($\lambda = d/L$) and α is the absorption coefficient, DeVore's theory yields the following expression for the excitation spectrum:

$$P(\alpha) = \frac{2}{(1+\coth\frac{1}{2}\alpha d)(1+A\coth\frac{1}{2}\lambda)} \times \left(1 + \frac{A(\frac{1}{2}\lambda)\left[(\frac{1}{2}\lambda)\coth\frac{1}{2}\lambda - (\frac{1}{2}\alpha d)\coth\frac{1}{2}\alpha d\right]}{(\frac{1}{2}\lambda)^2 - (\frac{1}{2}\alpha d)^2}\right) . \tag{1}$$

For strong surface recombination ($A \gg 1$), and for λ and αd greater than about 3, Eq. (1) reduces to the form

$$P(\alpha) = \frac{1 - e^{-\alpha d}}{A}\left(1 + \frac{A\lambda}{\lambda + \alpha d}\right) . \tag{2}$$

Equation (2) is applicable for the analysis of most of the data to be presented here. For relatively thick samples (~ 1 mm), the excitation spectra predicted by the DeVore theory show a peaked form and approach an asymptotic value in the high-absorption region. For very thin samples ($\lesssim 1\ \mu$m), no peak or a very broad peak is predicted with little or no drop in the high absorption (see Figs. 2–7 of Ref. 6).

In commenting on the comparison of the theory with experimental results, DeVore states that the general prediction of a peaked form for thick samples and no peak or a very broad peak for thin samples is confirmed by experiment. However, on the low-absorption (long-wavelength) side of the excitation peak, experimental curves generally show less photoconductive or photoluminescent response for a given value of α than is expected on the basis of the DeVore theory.[6]

III. EXPERIMENTAL PROCEDURE

The glass samples studied in these experiments were prepared from the appropriate elemental materials, all of 99.999% purity. The constituents were sealed in evacuated quartz ampoules, melted and fired in a rocking furnace, and air quenched. None of the compositions exhibited any tendency to devitrify and an examination of selected specimens with a scanning electron microprobe revealed no evidence of crystallinity.

The PL specimens consisted of fractured fragments of the bulk ingots. Freshly fractured surfaces, polished surfaces, and hot-pressed surfaces were all subjected to PL study. The PL spectra, PL-excitation spectra, and luminescence efficiency did not exhibit any significant dependence upon surface condition. Samples were mounted on the cold finger of an optical Dewar and cooled to either 80 or 6 K. The PL spectra were excited by broadband radiation from a 650-W tungsten iodide lamp. Various combinations of a water filter and appropriate Corning glass filters were used to eliminate exciting light in the spectral range of the luminescence, and long-pass filters such as Si and Ge excluded all exciting radiation from the analyzing monochromator. The power density of exciting light incident upon the sample surface was typically 0.5 W/cm^2. The PL spectra were analyzed by a grating monochromator and detected by a room-temperature PbS photoconductor. The excitation light was chopped by a mechanical chopper and the resulting ac signal was processed by phase-sensitive detection with a lock-in amplifier.

In order to obtain the excitation spectra, the light from a tungsten source was passed through an auxilliary monochromator and the resulting monochromatic light was used to excite the luminescence. A mirror replaced the grating in the analyzing monochromator and all wavelengths of the PL were received simultaneously by the PbS detector. By this means the integrated intensity of the PL could be measured as a function of the photon energy of the exciting light. The resulting excitation spectra were corrected or normalized for equal photon flux at all photon energies.

The dependence of the PL intensity upon chopping speed was measured with a variable-speed chopper in the range 10–4000 Hz. For these measurements an InSb photovoltaic detector with a time constant of 1 μsec at an operating temperature of 77 K was used.

IV. EXPERIMENTAL RESULTS

A. Photoluminescence Excitation Spectra

In Fig. 1 the PL spectrum and the PL-excitation spectrum obtained at 6 K from a polished sample of $As_2Se_3 \cdot As_2Te_3$ glass 0.36-cm thick are shown, along with the optical-absorption spectrum. The optical-absorption spectrum was measured at room temperature and then corrected for low temperatures on the basis of the reported temperature dependence of the optical-absorption edge.[8–10] This figure clearly illustrates how far below the band edge or optical-absorption edge the broad PL peak occurs. Its peak position is in substantial agreement with the peak at 0.67 eV reported by Kolomiets *et al.*[1] for this glass at 77 K. The semilog plot of Fig. 2 demonstrates how the low-energy side of the excitation spectrum corresponds to the onset of strong interband absorption. The excitation spectra of Fig. 2 were obtained from samples of $As_2Se_3 \cdot As_2Te_3$ glass ranging in thickness from 0.36 to 10^{-3} cm. While both the peak position and the low-energy side of the spectrum shift to lower energy with increasing sample thickness, all of the spectra closely parallel the absorption curve on the low-energy side of the peak. Increasing the sample thickness increases the absorption of the longer-excitation wavelengths and enhances the low-energy side of the excitation spectrum.

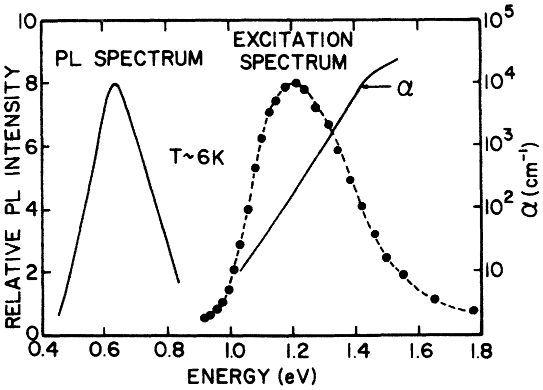

FIG. 1. Photoluminescence spectrum, excitation spectrum, and optical-absorption spectrum for glassy $As_2Se_3 \cdot As_2Te_3$. The closed circles and connecting dashed line represent the measured excitation spectrum for a 0.36-cm-thick polished sample. The excitation spectrum is normalized to the number of incident photons.

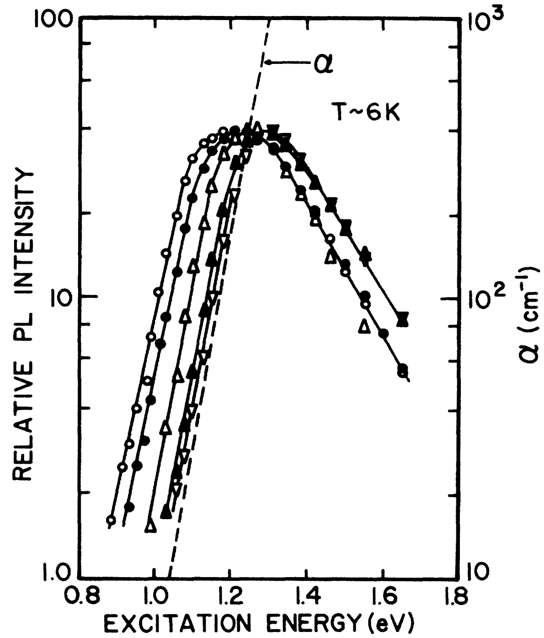

FIG. 2. Photoluminescence-excitation spectra for several samples of $As_2Se_3 \cdot As_2Te_3$ glass of varying thickness. Sample thicknesses in cm are: (O) 0.36, (•) 0.1, (Δ) 3.4 × 10^{-2}, (▲) 1.5 × 10^{-3}, and (∇) 1.0 × 10^{-3}. All spectra are normalized to the number of incident photons and to equal peak intensity. The optical-absorption spectrum is also shown.

All of the excitation spectra decrease monotonically for energies above about 1.3 eV, with the peak occurring at an absorption constant of about

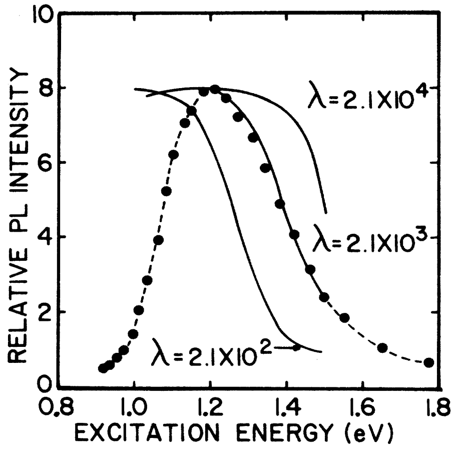

FIG. 3. Results of fitting the DeVore theory [Eq. (2)] to the measured excitation spectrum for the 0.36-cm thick sample of $As_2Se_3 \cdot As_2Te_3$ at 6 K. The best fit, $A = 10$ and $\lambda = 2.1 \times 10^3$, corresponds to a diffusion length of $(1.7 \pm 0.2) \times 10^{-4}$ cm.

$\alpha = 1 \times 10^2$ cm^{-1} in the 0.36-cm sample. This means that the most efficient excitation in the thick sample occurs for exciting photons with penetration depth of the order of 100 μm, while for the thin film the penetration depth at peak excitation is of the order of the sample thickness. Clearly the excitation of the PL is primarily a bulk effect since the excitation efficiency decreases rapidly as the penetration depth falls below a few microns. This decrease could be explained by the onset of strong nonradiative surface recombination at the higher absorption coefficients where the penetration depth of the exciting light becomes comparable to the diffusion length L of the photoexcited carriers. The decreasing high-energy side of the excitation spectrum (1.3–1.6 eV) is essentially unchanged for the relatively thick samples (0.36 cm to 3.4×10^{-2} cm) of Fig. 2. However, when the sample thickness is decreased to $\sim 10^{-3}$ cm the high-energy side of the spectrum shifts to higher energy. The 1.3–1.6-eV data of Fig. 2 for the 10- and 15-μm samples are displaced to higher energies relative to the thick-sample spectra by an amount well outside the experimental error in this spectral range. This shift is in agreement with the behavior predicted by the DeVore theory for this thickness dependence of the shape of an excitation spectrum in the case of strong surface recombination (see Sec. II.)

With the quantities A and λ (as defined in Sec. II) serving as adjustable parameters, the DeVore theory has been used to fit the measured excitation spectrum for the 0.36-cm thick sample of $As_2Se_3 \cdot As_2Te_3$ at 6 K. The results are shown in Fig. 3. As can be seen from Eq. (2), the asymptotic value of the excitation spectrum at high absorption constants yields the value of A, and the data of Fig. 1 indicate $A \geq 10$ for the $As_2Se_3 \cdot As_2Te_3$ glass. (Inspection of Fig. 3 in Ref. 6 reveals that $A = 10$ corresponds to rather strong surface recombination and increasing A above a value of 10 has relatively little effect upon the resulting excitation spectrum.) If A is set equal to 10, the DeVore theory yields the curves shown in Fig. 3 for $\lambda = 2.1 \times 10^2$, 2.1×10^3, and 2.1×10^4. The curve for $\lambda = 2.1 \times 10^3$ fits the data well in the spectral range 1.2–1.5 eV. This is the energy range for which the surface effects determine the shape of the excitation spectrum and for which the DeVore theory has been most successful in fitting excitation spectra.[7] As pointed out in Sec. II, on the low-energy side where the spectrum rises with increasing absorption, there are often disparities between theory and experiment.[6] The curves for $\lambda = 2.1 \times 10^2$ and 2.1×10^4 are included in Fig. 3 to illustrate graphically how sensitive the fit is to the value of λ. A value of $\lambda = 2.1 \times 10^3$ corresponds to a carrier diffusion length of $L = (1.7 \pm 0.2) \times 10^{-4}$ cm, where the error reflects the estimated uncertainty in the fit.

The same fitting procedure has been applied successfully to the excitation spectrum for the 15-μm thick sample. Since this sample was hot pressed on an aluminum foil backing of high reflectivity, an effective thickness of $2d = 30$ μm was used in the fitting procedure. In this case, the best fit was obtained for $\lambda = 20$ (again, it was assumed $A = 10$), which yields a diffusion length of $L = (1.5 \pm 0.2) \times 10^{-4}$ cm, in excellent agreement with the result for the thick sample. These diffusion lengths correspond to the average displacement distance of a photoexcited carrier during its lifetime for volume recombination.

The PL spectrum and the PL-excitation spectrum obtained at 6 K from a fractured sample of glassy As_2Se_3 are shown in Fig. 4 with the low-

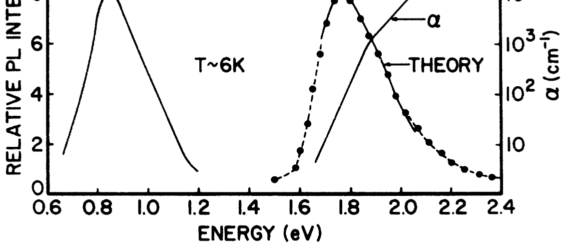

FIG. 4. Photoluminescence spectrum, excitation spectrum, and absorption spectrum (Refs. 11 and 12) for glassy As_2Se_3. The closed circles and connecting dashed line represent the measured excitation spectrum for a 0.15-cm thick sample. The theoretical solid-curve segment represents DeVore's theory for $A = 10$ and $L = (3.0 \pm 0.5) \times 10^{-4}$ cm.

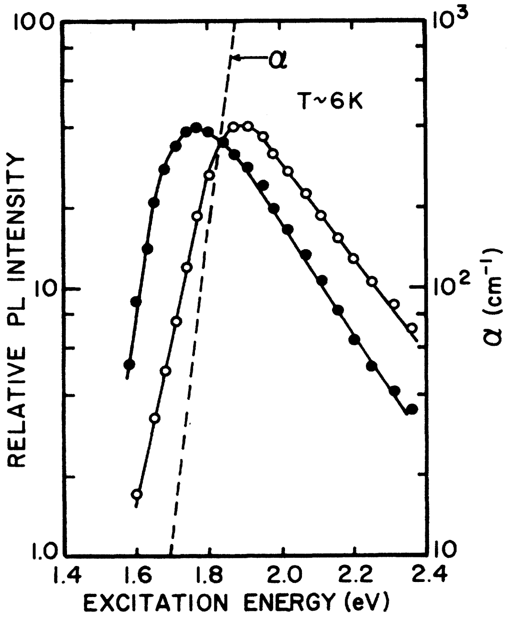

FIG. 5. Photoluminescence-excitation spectra for two samples of As_2Se_3 glass with thicknesses of (●) 0.15 cm and (○) 1.1×10^{-2} cm. Both spectra are normalized to the number of incident photons and to equal peak intensity. The optical-absorption spectrum is also shown (Refs. 11 and 12).

temperature optical-absorption data of Edmond and Shaw *et al.*[11,12] Again the PL spectrum with its peak near 0.85 eV falls well below the optical-absorption edge in the spectral range of relative transparency, in agreement with the earlier work of Kolomiets *et al.*[2,3] The sample was 0.15-cm thick and the penetration depth of the exciting photons at the maximum of the excitation spectrum (1.77 eV) was about 100 μm. In the spectral range 1.7–2.0 eV, the DeVore theory has been fitted to these data and the fit is indicated by the solid line drawn through the experimental points for these energies in Fig. 4. The adjustable parameters are $A = 10$ and $\lambda = 500$, which corresponds to a diffusion length of $L = (3.0 \pm 0.5) \times 10^{-4}$ cm.

In Fig. 5 the excitation spectra for the 0.15-cm sample and a second sample of As_2Se_3 glass 1.1×10^{-2}-cm thick at 6 K are plotted on a semilog scale along with the low-temperature optical-absorption curve. Just as in the case of the $As_2Se_3 \cdot As_2Te_3$ glass the low-energy side of the As_2Se_3 excitation spectrum roughly parallels the onset of strong optical absorption. In addition, the peak is shifted to lower energy and low-energy excitation is enhanced in the thicker sample, and in accord with the DeVore theory, the high-energy side of the spectrum shifts to higher energy in the thinner sample. The 1.1×10^{-2}-cm sample data are best fitted by the DeVore theory for $A = 10$ and $L = (1.0 \pm 0.5) \times 10^{-4}$ cm. Here the agreement of the diffusion lengths for the two different thicknesses is not as good as in the case of the $As_2Se_3 \cdot As_2Te_3$ glass. However, the results are certainly adequate to establish the order of magnitude of the required diffusion length of the photoexcited carriers.

Figure 6 shows the PL spectrum and the PL-excitation spectrum at 6 K for a 2.5×10^{-2}-cm thick sample of As_2S_3 glass. The PL spectrum is in reasonable agreement with that reported by Kolomiets *et al.*[2] and lies well below the forbidden-gap energy, with its peak near 1.18 eV. The low-temperature optical-absorption data of Kosek and Tauc[13] are also shown and have been used in the application of the DeVore theory to the PL-excitation data. For the As_2S_3 glass a somewhat larger high-energy asymptotic value of the excitation spectrum is inferred from the data of Fig. 6 and, accordingly, a value of $A = 2.7$ was used along with $\lambda = 83.3$ to obtain the theoretical curve depicted by the solid line in the range 2.34–2.66 eV in Fig. 6. This corresponds to a diffusion length of $(3.0 \pm 0.5) \times 10^{-4}$ cm which is consistent with the results obtained for the other two glasses.

The excitation spectrum for As_2S_3 glass occurs in a rather high-energy spectral range where the output of the tungsten source is rapidly diminishing. Consequently, the PL signal was weaker than in the case of the other two glasses and a thickness study was not undertaken.

B. Response Times

In Fig. 7 the intensities of the PL observed at 6 K in glassy $As_2Se_3 \cdot As_2Te_3$, As_2Se_3, and As_2S_3 are plotted as a function of chopping frequency. The intensities decrease with increasing chopping frequency (roll off) in all cases with some charac-

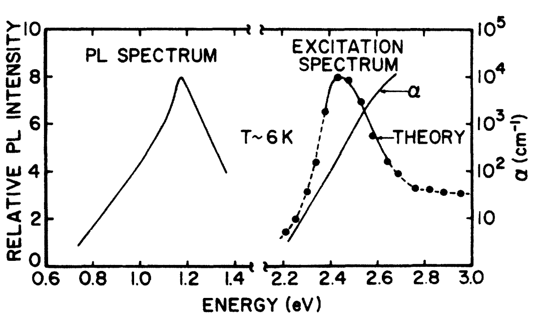

FIG. 6. Photoluminescence spectrum, excitation spectrum, and absorption spectrum (Ref. 13) for glassy As_2S_3. The closed circles and connecting dashed line represent the measured excitation spectrum for a 2.5×10^{-2}-cm thick sample. The theoretical solid-curve segment represents DeVore's theory for $A = 2.7$ and $L = (3.0 \pm 0.5) \times 10^{-4}$ cm.

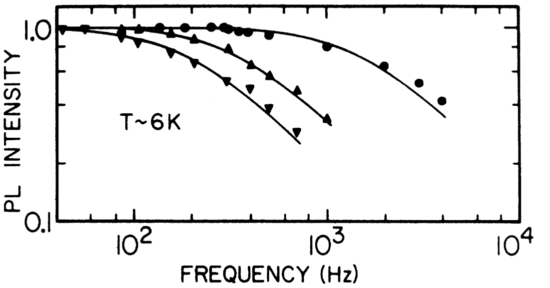

FIG. 7. Photoluminescence intensities for glassy $As_2Se_3 \cdot As_2Te_3$(●), As_2Se_3(▲), and As_2S_3 (▼) as a function of chopping frequency. The solid curves represent the function $1/(1+\omega^2\tau^2)^{1/2}$ for $\tau = 0.10$ msec ($As_2Se_3 \cdot As_2Te_3$), $\tau = 0.46$ msec (As_2Se_3), and $\tau = 0.84$ msec (As_2S_3).

teristic response time τ. The curves drawn through the data points represent the best fits of the expression

$$I(\omega) = I(0)/(1+\omega^2\tau^2)^{1/2} . \tag{3}$$

This expression is valid for the case of monomolecular recombination kinetics[14] and assumes that the roll off (or decay) of the PL is governed by a single response time or time constant. In the case of bimolecular recombination kinetics, the decay of PL is not characterizable by a single exponential decay constant and the roll off will not be described by Eq. (3). Furthermore, for bimolecular recombination kinetics the response time for the PL is a function of the intensity of the exciting light.[15] The response time for the $As_2Se_3 \cdot As_2Te_3$ glass was measured over a factor of 30 change in exciting lamp intensity and within the experimental error was found to remain constant. The facts that the roll-off data obey Eq. (3) reasonably well and the response time in at least one of the glasses is independent of the intensity of the exciting light strongly indicate that the radiative recombination is governed by monomolecular kinetics. In addition, the intensity of the PL in the $As_2Se_3 \cdot As_2Te_3$ glass exhibited a linear dependence upon the intensity of the exciting light at both 6 and 80 K. This behavior is also consistent with monomolecular recombination kinetics.[15]

The time constants which result from fitting Eq. (3) to the roll-off data (Fig. 7) are 0.10 msec for $As_2Se_3 \cdot As_2Te_3$, 0.46 msec for As_2Se_3, and 0.84 msec for As_2S_3.

V. DISCUSSION AND CONCLUSIONS

The most obvious conclusion to be drawn from the observed excitation spectra is that the PL in these chalcogenide glasses is excited by the absorption of light with photon energy in the vicinity of the band-gap energy, that is, by interband absorption. Kolomiets *et al.*[3] had pointed out the possibility that the PL might be excited by absorption involving transitions from recombination levels near midgap to one band edge. The excitation spectra of Figs. 1, 4, and 6 demonstrate that this is clearly not the case. In addition, the excitation of the PL is a bulk effect since (i) the excitation efficiency decreases rapidly at higher energies when the penetration depth of the exciting light falls below a few microns, and (ii) the measurable low-energy limits of the excitation spectra extend to absorption constants of 10 cm^{-1} and below.

The discussion of Sec. IV A demonstrated that both the thickness dependence of the excitation spectra in Figs. 2 and 5 and the shape of the high-energy fall off in excitation efficiency conform quite well to the DeVore theory[6] of nonradiative surface recombination. It is true that the ~ 1-μm diffusion lengths required to fit the DeVore theory to the data may seem implausible on the basis of the inherently low mobilities of carriers in chalcogenide glasses. For this reason an alternative explanation of the data, such as an energy-dependent quantum efficiency which is a bulk property of the glass, might seem attractive. However, it must be emphasized that the excitation spectra for various thicknesses presented in Fig. 2 cannot be explained on the basis of a single energy-dependent quantum-efficiency curve and the absorption curves. The observed spectra can only be fitted by an energy-dependent quantum efficiency which changes as a function of sample thickness. Nonradiative surface-recombination effects do produce just such a thickness-dependent quantum-efficiency curve and the DeVore theory would appear to be the only presently available analysis which can successfully explain the excitation spectra in these chalcogenide glasses. Mott and Davis[16] have drawn the conclusion that very similar rates of recombination obtain at the surface and in the bulk of glasses. This conclusion was based on the assertion that photoconductivity spectra in the chalcogenide glasses rise at the optical-absorption edge and remain constant at higher energies, exhibiting no fall off. This is true of some published photoconductivity spectra for chalcogenide glasses but in most cases (including the data[17] which they cite), these spectra are obtained from samples less than one micron thick. As stated previously, excitation spectra from thin samples show no peak or only very little drop in the high-absorption region, even for the case of strong surface recombination (see Ref. 6). Furthermore, there are many published photoconductivity spectra for chalcogenide glasses which do exhibit a fall off at high energies.[18–23] Hence the observation of surface-recombination effects in PL-excitation spectra is by no means anomalous.

It was pointed out in Sec. IV A that increasing the value of the parameter A in the DeVore theory above the value of 10 has relatively little effect upon the excitation spectrum. The fact that the observed excitation spectra are in most cases best fitted by $A \geqq 10$ may explain why surface condition had no observable effect upon the excitation spectra (fractured, polished, and hot-pressed surfaces were used). If for each surface condition strong surface recombination occurs, $A \geqq 10$ would hold in each case and variations in A from surface to surface would have no manifest effect upon the observed excitation spectrum.

The measurements of the PL response times described in Sec. IV B were carried out on relatively thick samples with exciting light whose penetration was sufficient to assure bulk excitation. Under these conditions surface recombination, if it occurs, would not have an effect upon the measured response time. Surface effects can shorten the measured response time only if the sample thickness is smaller than the diffusion length.[24] Consequently, the measured response times represent the bulk lifetimes of the photoexcited carriers.

The measured carrier lifetimes, which are of the order of fractions of a millisecond, may seem somewhat long in comparison to the lifetimes obtained in photoconductivity measurements in chalcogenide glasses which are of the order of 10^{-8} or 10^{-9} sec.[23,25,26] It should be pointed out, however, that the photoconductivity measurements are carried out at much higher temperatures and they do not distingiush radiative from nonradiative lifetimes. The 10^{-8}-sec τ might represent a relatively high-temperature nonradiative lifetime which could be much shorter than the radiative lifetime at 6 K.

It is interesting to speculate upon the implications that the occurrence of 1-μm diffusion lengths would have for the mobilities of the diffusing carriers. Under equilibrium conditions, the measured diffusion length L and bulk lifetime can be related to an effective mobility through the Einstein relation.[27] This relationship applies for the case of nondegenerate statistics and its use here could be considered rigorous only in the absence of band tail states which extend more than kT below the mobility edge, or if the tail states or traps are saturated by photoexcited carriers so that the diffusing carriers are in conduction- or valence-band states. Under these assumptions the values of the effective mobility listed in Table I are obtained from the values of L and τ obtained at 6 K. These values (0.21–0.55 cm^2/V sec) are so large as to be typical of those for delocalized carriers at room temperature in chalcogenide glasses,[28] and they illustrate how surprisingly long the inferred diffusion lengths are.

The experimental evidence presented in Sec. IV B strongly indicates that the radiative recombination is governed by monomolecular kinetics. This would be consistent with recombination through a band of recombination centers lying deep in the gap. For example, electrons at the conduction-band mobility edge might recombine radiatively with holes trapped at recombination levels near midgap. The linear dependence of PL intensity upon exciting light intensity implies that the occupation of the recombination levels does not change appreciably over the experimental range of intensities.[15,29] The most obvious way from this condition to hold is for the occupation of the recombination levels or traps to be saturated even at the lowest intensity of the exciting light. This is in direct contradiction to the assumptions made in the model of Kolomiets *et al.*[3] Their model assumes such a large density of radiative recombination levels that the number of occupied radiative levels (or recombination centers) is always negligible in comparison to the total number of radiative levels. In addition, it is assumed that the lifetime of the nonequilibrium or photoexcited carriers in the bands (delocalized states) is small compared to the lifetime at the radiative levels, i.e., there is no appreciable concentration of carriers in delocalized states. It would be difficult to explain the occurrence of 10^{-4}-cm diffusion lengths on the basis of this model.

It would also be difficult to reconcile the details of the symmetric recombination-edge model[4] with the observation of 10^{-4}-cm diffusion lengths for the photoexcited carriers. In this model it is assumed that carriers which are optically injected at or above the mobility edge relax to lower energies in a continuum of states in the gap by phonon emission at a rate r_{rel} while at the same time recombination is occurring at a rate r_{rec}. Both r_{rel} and r_{rec} decrease as the density of states decreases; however, r_{rel} decreases faster than r_{rec} and the peak of the luminescence spectrum is fixed by the crossover of these two rates.[4] As the carriers relax to lower energy they become increasingly localized. Since the model is symmetric, this localization process occurs in both conduction and valence bands. The localized nature of the states through

TABLE I. Measured values of the diffusion length L and the response time τ, and the effective mobility estimated from these data through the use of the Einstein relation (Ref. 27).

Glass	L (cm)	τ (msec)	μ(cm^2/V sec)
$As_2Se_{1.5}Te_{1.5}$	1.7×10^{-4}	0.1	0.55
As_2Se_3	3.0×10^{-4}	0.46	0.38
As_2S_3	3.0×10^{-4}	0.84	0.21

which the radiative recombination presumably occurs would make it unlikely that the recombining carriers could diffuse a distance as large as 10^{-4} cm.

In summary, photoluminescence in the chalcogenide glasses is excited by interband optical-absorption processes, with a quantum efficiency that decreases rapidly for absorption coefficients greater than about 10^{-4} cm^{-1}. The energy dependence of the quantum efficiency, as exhibited by the excitation spectra, is itself a function of sample thickness. Analysis of the line shapes of the excitation spectra on the basis of nonradiative surface-recombination effects yields diffusion lengths for the photoexcited carriers of the order of 10^{-4} cm. The inferred long diffusion lengths, the below-the-band-edge positions of the luminescence spectra, and the apparent monomolecular recombination kinetics are all consistent with the radiative recombination of delocalized carriers at one band edge with carriers trapped in a band of recombination centers near midgap.

Note added in proof. Subsequent to submission of this manuscript, Street *et al.*[30] have reported the observation of similar photoluminescence excitation spectra in glassy As_2S_3. These workers interpret the shape of the excitation spectrum in terms of an energy-dependent quantum efficiency which is a bulk property of the glass.

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