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Optical absorption edge in liquid semiconductor alloys $Se_{1-x}Tl_x$

F. G. Bell and M. Cutler
Department of Physics, Oregon State University, Corvallis, Oregon 97331-6507

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Measurements are presented of the optical absorption edge in the liquid semiconductor system $Se_{1-x}Tl_x$ for $0 \le x \le 0.009$ and for the temperature range $220\,^{\circ}C < T < 480\,^{\circ}C$. The absorption edge is approximately exponential in the photon energy and increases linearly with Tl concentration. The absorption coefficient has an activation energy of 0.5 eV in the alloys and 1.0 eV in pure selenium, for photon energies $h\nu \le 1$ eV. This constant activation energy is in contrast to the temperature dependence implied by the Urbach rule. These results are explained with an ionic model based on the Dow-Redfield theory of optical absorption in an electric field. It is proposed that the sources of the electric fields are ionic bond defects which are thermally generated. A calculation of the absorption is given which is in good agreement with the data. The ionic model may provide a universal explanation of the optical absorption edge in liquid semiconductors having ionic defects.

I. INTRODUCTION

It is known that some of the liquid semiconductors have an optical absorption edge which decays exponentially.[1–5] An exponential tail, generally known as the Urbach edge,[6] is common in the alkali halides and many of the amorphous semiconductors.[7–9] In the liquid semiconductors, the absorption edge shifts toward longer wavelengths with increasing temperature, and in the case of Se-Te,[3] it shifts to longer wavelengths with increasing Te concentration. The absorption has been suggested to be associated with transitions between extended states in the bands and tail states within the mobility gap.[3,4] It has also been suggested that the temperature shift may be due to narrowing of the gap or an increase in the density of tail states as the temperature increases.[3,4] The lack of a satisfactory explanation of the exponential absorption tail in the liquid semiconductors is partly due to the small amount of experimental data for this phenomenon.

We report here measurements of the optical absorption edge in the liquid alloys $Se_{1-x}Tl_x$ for $x \le 0.009$ at temperatures from the melting point, 220 °C, up to 475 °C. This system was chosen for several reasons. The alloys are easily prepared. Tl is soluble in Se over most of the temperature and composition range, and much of the absorption edge is within the experimentally accessible range of photon energies and absorption magnitudes. In addition, information is available[10] based on a study of the thermoelectric properties of the alloy system for low Tl concentrations. The optical measurements reported here cover the photon range from 0.3 to 1.3 eV, and over this range the absorption varies from 1 to 10^3 cm^{-1}. Because our interest has centered on the temperature dependence of α and its interpretation in terms of activation energies, special care was taken to measure the temperature accurately. We have also studied the influence of Tl concentration on the absorption coefficient.

On the basis of the concentration and thermal effects, we have been able to obtain a specific model for the absorption mechanism. We have found that the absorption coefficient is thermally activated, the activation energy being independent of the photon energy for energies $h\nu \le 1$ eV (1 eV$\approx E_g/2$). We have related this activation energy to the activation energy for the creation of positive and negative ions. The absorption tail is interpreted as due to the field-assisted excitation of electron-hole pairs, in the regions near ions where especially high electric fields occur.

In Sec. II we present experimental results for the absorption edge, and in Sec. III we analyze the absorption data in terms of the energy, concentration, and thermal effects. In Sec. IV we present a calculation of the absorption expected from a model based on field-assisted photogeneration of virtual excitons. Finally we discuss the implications and interpretations of the model in Sec. V.

II. EXPERIMENTAL RESULTS

The alloys used in this study were prepared from 99.999%-purity Se and Tl. Master alloys of 0.1, 0.05, and 0.01 at. % Tl were prepared by combining Se and Tl in a fused silica tube, which was then evacuated and sealed. The tube was heated to 600 °C for 5 h and rotated to ensure mixing. At the end of the heating period, the sample tubes were quenched in water at room temperature. The master alloys were then ground to a fine powder and these were added to selenium to make the sample alloys in the same way as the master alloys. The optical cell and the optical system used in this experiment have been described elsewhere.[11] The cell-window material for these measurements was sapphire, and so the low-energy limit of the measurements is approximately 0.3 eV.

The absorption coefficient α for 100% Se is shown in Fig. 1, where we have plotted $\ln\alpha$ versus $h\nu$ for several isotherms. In this figure the solid symbols are the present work and the open symbols are from the work of Rabit and Perron,[4] included here for comparison. Our measurements on liquid Se extend the lower range of energies to about 0.3 eV. The uncertainty[11] in the magnitude of α depends upon both the magnitude of α and the cell thick-

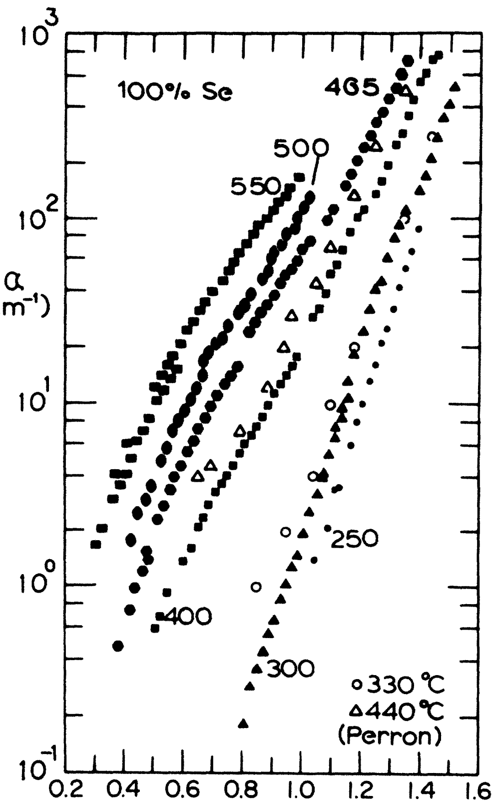

FIG. 1. Absorption coefficient isotherms in 100 at. % Se. Solid symbols are this work, open symbols are from Rabit and Perron (Ref. 4).

ness, but is about 5% of α near $\alpha = 1\ \mathrm{cm}^{-1}$, and decreases with increasing α.

The absorption coefficients (isotherms) for several alloy concentrations x are shown in Figs. 2–7. These data represent all the concentrations studied and about half of the isotherms obtained.[12] In the alloys, the absorption is approximately exponential in the photon energy, and it increases as the concentration x and the temperature increase. In some of the curves for the alloys, in particular at lower temperatures, the absorption appears to level off somewhat as the photon energy decreases. This occurs close to a temperature range where phase separation occurs due to a miscibility gap.[13,14] We believe the leveling off of α was due to scattering from small droplets of a Tl-rich alloy which formed on entering the miscibility gap. Consequently, we have excluded from our analysis data which were possibly affected by this phenomenon.

III. ANALYSIS OF THE ABSORPTION DATA

A. Extrapolation to the band gap

In the past it has been suggested that the increase in the absorption coefficient with temperature and concentration might be due to a decrease in the optical band gap.[3,4] As a check on this hypothesis, we have extrapolated the α curves to find the photon energy at which α has a magnitude expected for interband absorption. The value 10^5

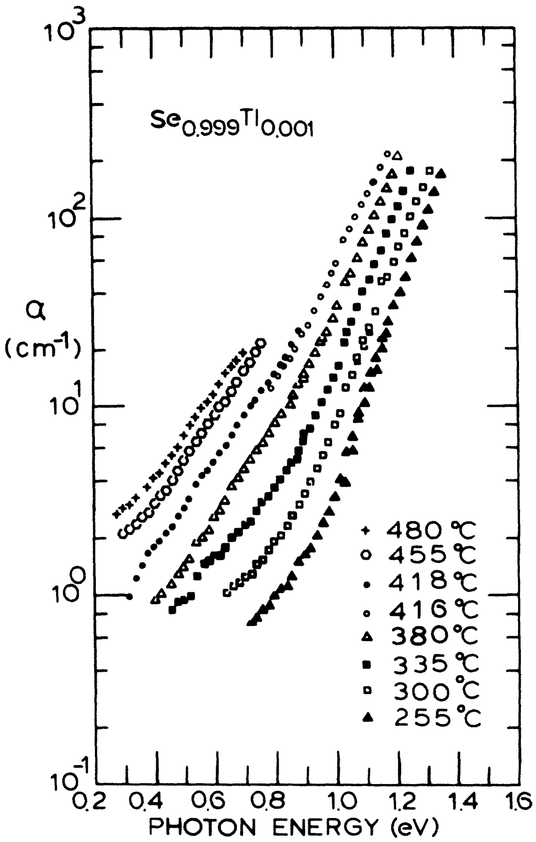

FIG. 2. Absorption coefficient isotherms in $\mathrm{Se}_{0.999}\mathrm{Tl}_{0.001}$.

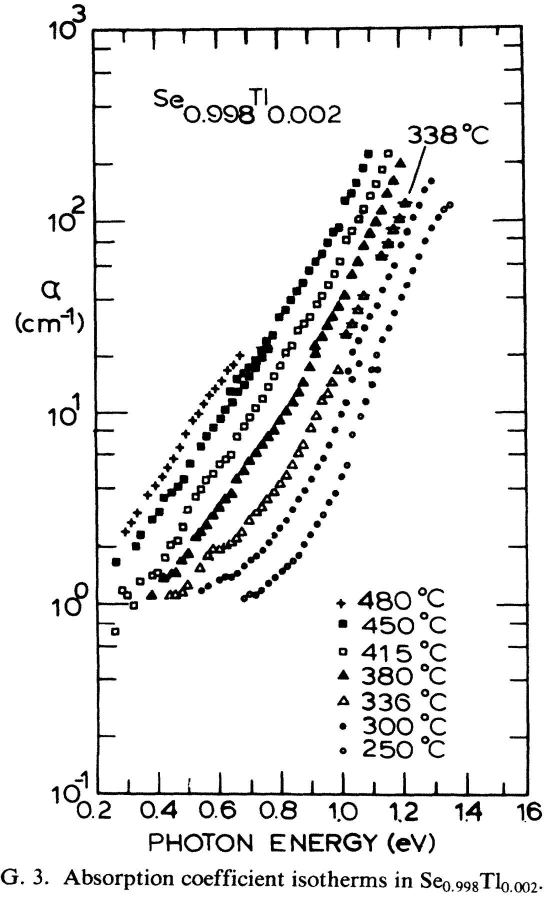

FIG. 3. Absorption coefficient isotherms in $\mathrm{Se}_{0.998}\mathrm{Tl}_{0.002}$.

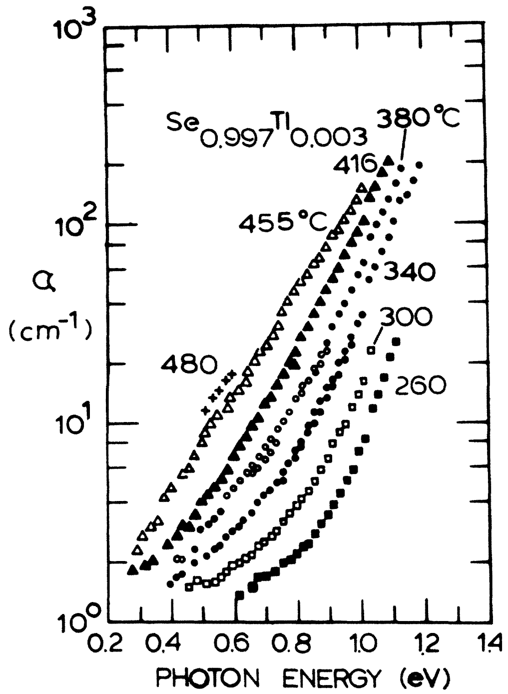

FIG. 4. Absorption coefficient isotherms in $Se_{0.997}Tl_{0.003}$.

cm^{-1} was chosen for this purpose. This was done for 30 curves representing all compositions and temperatures from 250 to 450 °C. The photon energies obtained in this way showed no trend with x or T and had an average value 2.0 ± 0.1 eV. We take this as evidence that the band gap does not decrease significantly with temperature and has the value 2.0 eV. This value agrees well with the value 2.05 eV obtained by Davis[15] for the absorption edge in amorphous Se.

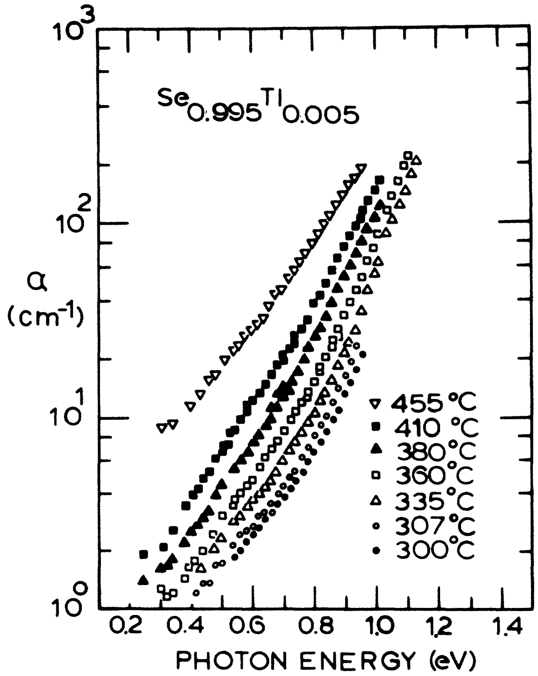

FIG. 5. Absorption coefficient isotherms in $Se_{0.995}Tl_{0.005}$.

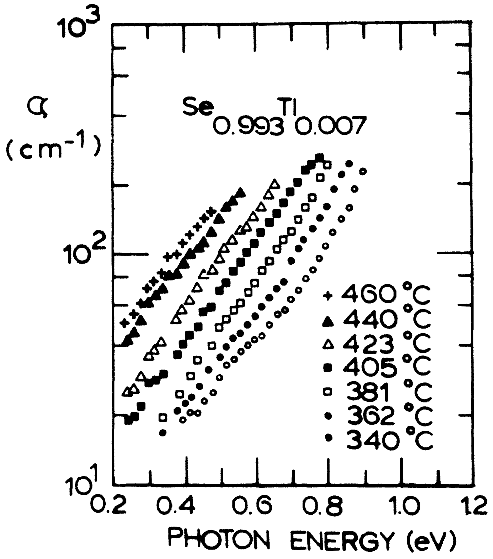

FIG. 6. Absorption coefficient isotherms in $Se_{0.993}Tl_{0.007}$.

B. Concentration dependence

The absorption coefficient in the alloys was found to increase linearly with Tl concentration. This was generally true for all the temperatures and photon energies, but some deviation occurred for $x=0.005$. We believe this deviation to be a result of uncertainty in this particular concentration. A representative plot of α versus x for $T=400$ °C is shown in Fig. 8. In this plot, data for $x=0$ has been omitted. The lines represent linear least-squares

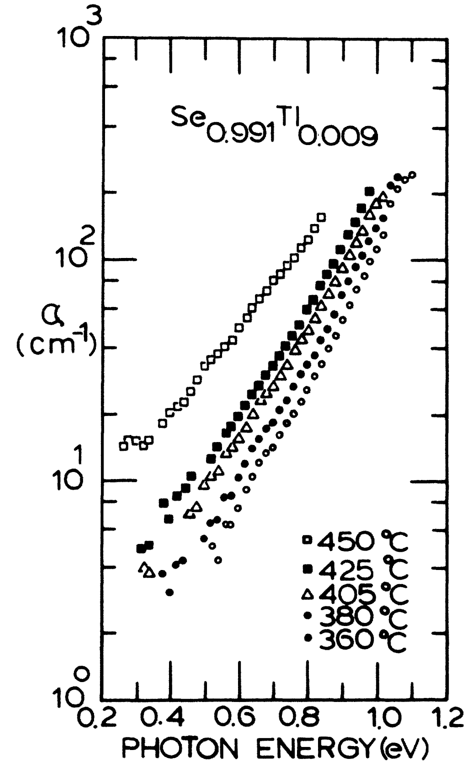

FIG. 7. Absorption coefficient isotherms in $Se_{0.991}Tl_{0.009}$.

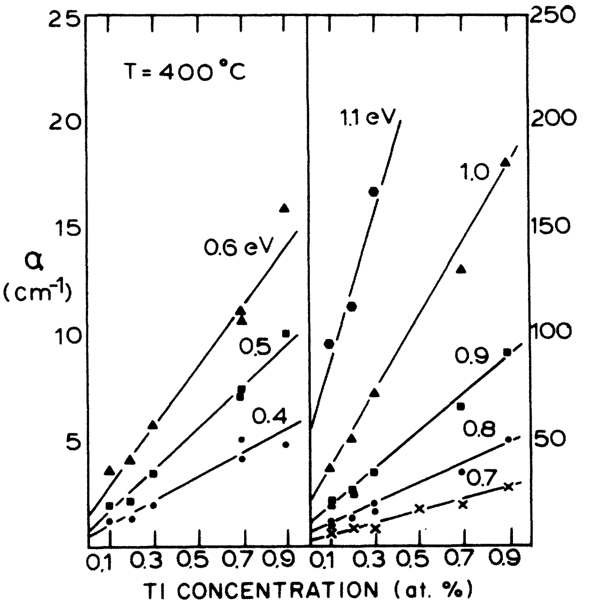

FIG. 8. Absorption coefficient vs Tl concentration for several photon energies at $T=400\,^{\circ}\mathrm{C}$.

fits to the data. It can be seen from this figure that the intercept of α at $x=0$ is nonzero. The relationship between α and x in the alloys may therefore be written

$$\alpha_{\mathrm{tot}}(h\nu,x,T)=\alpha_1(h\nu,T)+x\alpha_2(h\nu,T)\ , \qquad (1)$$

where α_{tot} is the total absorption at photon energy $h\nu$, concentration x, and temperature T, α_1 is the intercept at $x=0$, and α_2 is the slope of the α-versus-x curves. The intercept α_1 in the alloys agrees well with the absorption in 100 at. % Se at corresponding temperatures and energies. Similar results were obtained for other temperatures. This suggests that the absorption in the alloys is a combination of the absorption in pure Se and an absorption mechanism characteristic of Tl, and that the two are noncompetitive.

C. Temperature dependence

First, we shall consider the thermal dependence of the absorption in 100% Se. It has been reported by Rabit and Perron[4] that the logarithm of the absorption coefficient in liquid Se decreases linearly with T^{-1}. Consequently, the slope can be expressed as an activation energy,

$$E_{\mathrm{Se}}=-k_B\partial\ln\alpha_{\mathrm{Se}}/\partial(1/T)\ \mathrm{eV}\ , \qquad (2)$$

where k_B is the Boltzmann constant (8.62×10^{-5} eV/K). Over the range $1\le\alpha\le10^4\ \mathrm{cm}^{-1}$ and $0.5\le h\nu\le1.8$ eV, Rabit and Perron found that E_{Se} decreased with photon energy according to $E_{\mathrm{Se}}=1.29-0.59h\nu$. In the present results, we have also found a T^{-1} dependence in $\ln\alpha$, but the activation energy is not linear in $h\nu$. In Fig. 9 we show $\ln\alpha$ versus $1000/T$ in liquid Se for photon energies $0.4\le h\nu\le1.2$ eV. The slopes of these lines increase for photon energies between 1.5 and 0.9 eV according to $E_{\mathrm{Se}}=1.38\ \mathrm{eV}-0.71h\nu$, but approach a constant value of about 1 eV for photon energies less than 0.9 eV.

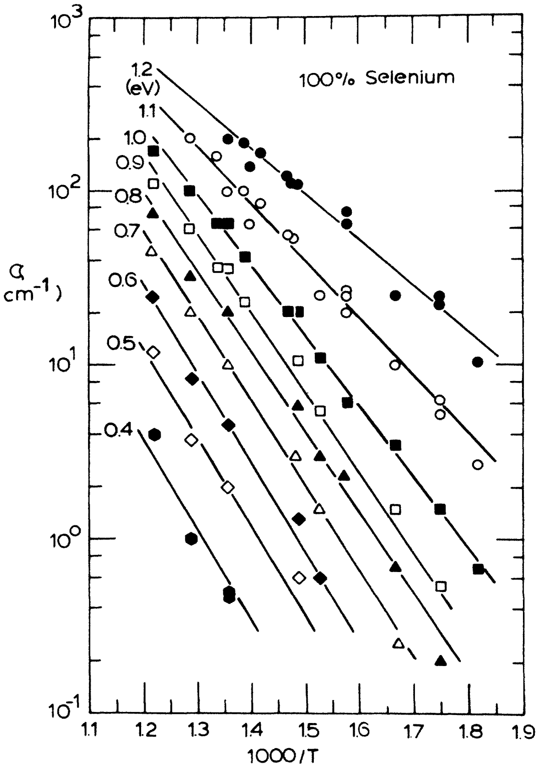

FIG. 9. Logarithm of absorption coefficient vs $1000/T\ \mathrm{K}^{-1}$ in 100 at. % Se. Curves are for different photon energies.

In the alloys, since α_1 is found to equal α_{Se}, we have analyzed the temperature dependence of the part of the absorption due to the addition of Tl, $\Delta\alpha=\alpha_{\mathrm{tot}}-\alpha_{\mathrm{Se}}=x\alpha_2(h\nu,T)$. We find that $\ln\Delta\alpha$ also varies linearly with T^{-1}, so that the slope can also be expressed by an activation energy E_t defined by an equation similar to Eq. (2). We show a representative plot of $\ln\Delta\alpha$ versus T^{-1} for $x=0.001$ in Fig. 10. The values of E_t were found to be independent of x, in keeping with Eq. (1). Figure 11 shows the values of E_t averaged over the various compositions, plotted against the photon energy. Similar to the case of 100 at. % Se, the slopes E_t increase as the photon energy decreases below 1.2 eV, and approach a constant value of about 0.5 eV for photon energies below 0.9 eV. Also shown in the figure are corresponding slopes E_{Se} from this work and, for comparison, from the work of Siemsen and Fenton.[2]

The empirical Urbach equation[16] is

$$\alpha_U(h\nu,T)=\alpha_0\exp[\sigma(h\nu-E_g)/k_BT]\ , \qquad (3)$$

where α_0 and σ are fitting parameters, E_g is the band-gap energy, and k_B is Boltzmann's constant. The Urbach rule has been used to describe the exponential absorption tail in cases where the thermal dependence and the spectral dependence are interrelated. In the present case, the Urbach rule is satisfied for photon energies greater than 0.9 eV. However, for photon energies less than 0.9 eV, the spectral dependence and the thermal dependence are very nearly independent, and the Urbach rule is not a consistent representation of the absorption edge. For photon

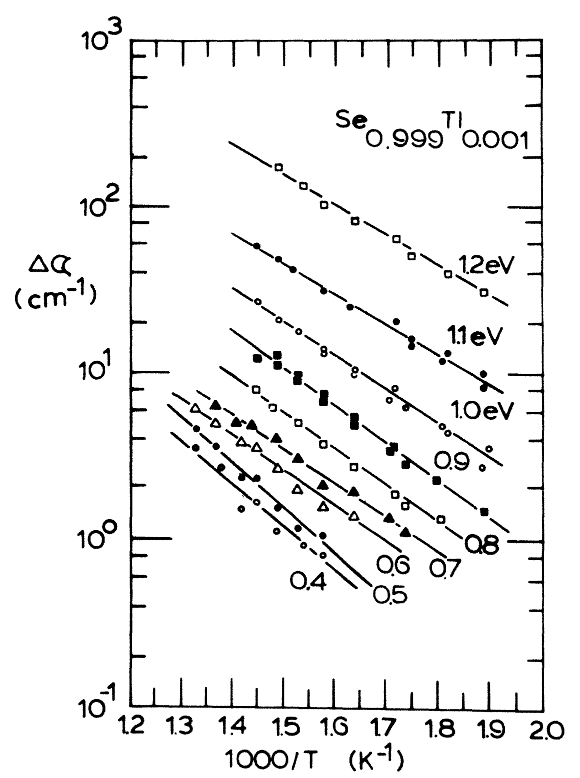

FIG. 10. Logarithm of $\Delta\alpha$ vs $1000/T$ K^{-1} in Se$_{0.999}$Tl$_{0.001}$. Curves are for different photon energies.

energies less than 0.9 eV, the absorption coefficient in the alloys follows the empirical equation

$$\Delta\alpha(h\nu,T)=x\alpha(h\nu)e^{-E_t/k_BT}, \tag{4}$$

where x is the Tl concentration and

$$\alpha(h\nu)\approx\exp[\gamma(h\nu-E_0)] . \tag{5}$$

Similar equations may be written for the case of 100 at. % Se. The parameter $E_0\approx2.0$ eV and can be identified as the band gap, in agreement with the value obtained by extrapolation of the $\ln\alpha$-versus-$h\nu$ curves. In the alloys, the parameter γ is a function of temperature, and varies from 5 eV^{-1} at the highest temperatures (near 500 °C) to 10 eV^{-1} at the lowest temperatures (near 250 °C).

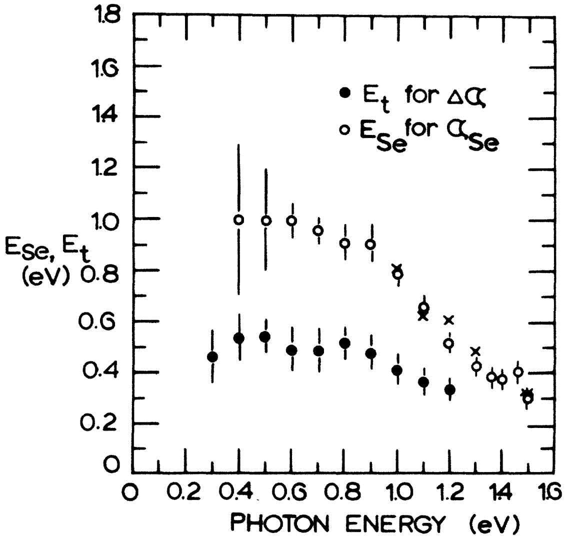

FIG. 11. Activation energies E_t and E_{Se} vs photon energy. Solid circles are E_t and error bars represent standard deviation in averaging over all concentrations. Open circles are E_{Se} and error bars represent uncertainties in the least-squares fit to $\ln\alpha_{\mathrm{Se}}$ vs $1/T$. Crosses are E_{Se} values calculated from the work of Siemsen and Fenton (Ref. 2).

IV. IONIC MODEL

The constant value of $E_t=0.5$ eV in the alloys suggests a thermal mechanism that is independent of photon energy. We propose that this thermal dependence is related to the thermal excitation of ions. There is experimental evidence of high concentrations of ions in Se$_{1-x}$Tl$_x$ alloys from the thermoelectric study of Rasolondramanitra and Cutler.[10] Although their work determined most directly the concentration of ions for $x\cong0.31$, the influence of ions at small Tl concentrations was established. The dominant ions are believed to be the Se-Tl$^-$ diatomic ion and the positively charged threefold selenium defect $D_{\mathrm{Se}}{}^+$. We believe the effect of ions on the optical properties of Se-Tl alloys is to produce large, local electric fields which shift the absorption edge to lower photon energies. This shift is responsible for the absorption tail at photon energies less than about 1 eV, and for much of the absorption at energies greater than 1 eV.

Ions are expected to occur in the liquid alloys at concentrations of the order $10^{-6}N_a$, where N_a is the number of atoms per unit volume ($N_a=2.7\times10^{22}$ cm^{-3}). The concentration of ions C_i is thermally activated according to[17]

$$C_i=C_{i0}\exp(-E_i/k_BT) , \tag{6}$$

where E_i is one half the sum of the enthalpies of the positive and negative ions (they are formed in pairs), and C_{i0} depends on the Tl concentration x. E_i is estimated from measurements of conductivity and thermopower to be about 0.52 eV.[18]

When ions are present, a large number of neutral atoms close to the ions will experience intense electric fields. This is due to the relatively low dielectric constant[19,20] of liquid Se, which is close to 5.4 at 250 °C and decreases linearly to about 4.2 at 700 °C. If we take a value of $\epsilon=5$ at 400 °C, then the electric field at a distance r in angstroms from an ion is $\mathscr{E}=2.86\times10^8/r^2$ V/cm. Therefore on the average there will be more than 10^4 atoms in a field greater than 10^5 V/cm within a volume of radius 50 Å surrounding a single ion. We believe that when absorption occurs at these neutral atomic sites, the absorption is shifted to longer wavelengths as in the Franz-Keldysh effect.[21,22] Because the number of atoms experiencing large fields is considerable, the magnitude of the resulting absorption is appreciable, as will be shown. The absorption will be calculated using a model based on the Dow-Redfield[23,24] theory of optical absorption in a strong electric field.

In the Franz-Keldysh effect a large electric field is applied across the semiconductor and the energy band tilt in space. Electronic transitions can occur from states in the valence band to states in the conduction band even if the photon energy is less than the band gap, for the extra energy is supplied by the field. This can be viewed as a photon-assisted tunneling process in which the electron tunnels across a barrier of height $e\mathscr{E}\Delta x$, where Δx is the tunneling distance. Normally, this effect is small for photon energies less than the band gap. The theory of Dow and Redfield (hereafter DR theory) is a calculation based on Elliot's theory[25] of optical absorption by Wannier excitons in the presence of a strong electric field, but with the electron-hole Coulomb interaction included. The DR theory shows an enhancement of the Franz-Keldysh effect by the excitonic Coulomb interaction between the photoexcited electron and the hole. The DR absorption coefficient, $\alpha_{\mathrm{DR}}(h\nu,F)$, which is a function of the electric field strength F and depends upon the exciton parameters, was found to decrease exponentially for energies less than the exciton peak, and to be at least 3 orders of magnitude greater than the field-only (Franz-Keldysh) effect. This result was used to argue the common origin of the exponential edge in ionic solids and also in covalent solids with large concentrations of ionic impurities. The electric fields derive from optical phonons in the ionic solids and from the average fluctuation field due to ionic impurities in the covalent solids. In the present case, we assume that ions are the source of the electric fields. Our calculation differs from the cases considered by DR in that the dominant effects are due to relatively large fields close to individual ions rather than fluctuating fields remote from individual ions.

The optical absorption coefficient for the liquid alloys can be calculated by averaging the DR result over a distribution of fields appropriate for discrete "ionic centers." It turns out that we will have a reason to consider two types of ionic centers, one of which is a discrete ion whose concentration is given by Eq. (6), and another involving a positive- and negative-ion pair in close proximity, which will be discussed later. In either case, we allot a volume V_0 to each ionic center, which is roughly given by the reciprocal of the total number of ionic centers per unit volume. Regarding this volume as a sphere about the ionic center, the field F in reduced units ($F=\epsilon\mathscr{E}/e$) is a unique function of the radial distance r as long as $r \ll r_0$, where $V_0=4\pi r_0^3/3$. In a region surrounding a single ion, the number of neutral atoms experiencing a field in the range between F and $F+dF$ is

$$n(F)=\left[\frac{dN}{dF}\right]dF=N_a\left[\frac{dV}{dF}\right]dF\ . \tag{7}$$

The differential quantity dV/dF is the volume per field magnitude, which can be calculated from electrostatics. For a discrete ion, the volume at a radius r is related to the field F at that distance as $V=4\pi/3F^{3/2}$. The volume per field is then

$$\frac{dV}{dF}=2\pi F^{-5/2}\ . \tag{8}$$

We now define an absorption coefficient $\alpha^*(h\nu,F)=\alpha_{\mathrm{DR}}(h\nu,F)/N_a$ which is the contribution per atom to the total absorption coefficient at $h\nu$ and F and $\alpha_{\mathrm{DR}}(h\nu,F)$ is the absorption coefficient as calculated in the DR model. The contribution per atom per field to the absorption is then $(dN/dF)\alpha^*(h\nu,F)dF$.

We allot to the volume V_0 of an ionic center a number of neutral atoms $N_0=N_aV_0=1/C$ for the purpose of calculating the influence of the ion field distribution on the optical absorption for atoms close to an ionic center. This will be accurate at the largest values of the field for which the atoms are representative, but inaccurate at the low-field limit at a distance $\approx r_0$ from the ion. As it turns out, the absorption is mainly due to transitions on atoms close to the ions. The total absorption due to the N_0 atoms within the volume V_0 is obtained by integrating the absorption per atom per field over the expected range of fields,

$$\begin{aligned}\alpha_0(h\nu)&=\int_{F_0}^{F_m}\left[\frac{dN}{dF}\right]\alpha^*(h\nu,F)dF\\ &=\int_{F_0}^{F_m}\left[\frac{dV}{dF}\right]\alpha_{\mathrm{DR}}(h\nu,F)dF\ ,\end{aligned} \tag{9}$$

where Eq. (7) has been used. F_m is the maximum field, and this is approximately the field at the interatomic spacing. The minimum field is F_0 and is taken to be the field at r_0. The absorption coefficient is obtained by multiplying Eq. (9) by the number of ionic centers per unit volume. Finally, by using the discrete-ion field distribution, Eq. (8), we have

$$\alpha_0(h\nu,T)=2\pi CN_a\int_{F_0}^{F_m}F^{-5/2}\alpha_{\mathrm{DR}}(h\nu,F)dF\ . \tag{10}$$

By comparing Eq. (10) with Eq. (4) it is clear how the temperature and spectral effects are independent. The exponential behavior in $h\nu$ comes about through the DR absorption mechanism. The increase in absorption with temperature is a result of the thermal excitation of ions, with a concomitant increase in the number of atoms experiencing high fields. The shift of the absorption curves with increasing temperature is better regarded as a vertical shift on a plot of $\ln\alpha$ versus $h\nu$, rather than a shift of the curves to lower energies.

The $\alpha_{\mathrm{DR}}(h\nu,F)$ may be written[23]

$$\alpha_{\mathrm{DR}}(h\nu,F)=\frac{4\pi^2e^2p^2}{m^2cn\omega\mathscr{R}a^3}S(E_r,F)\ , \tag{11}$$

where ω is the photon frequency and n is the index of refraction. p is the interband matrix element for the optical transition given by

$$p^2=|\langle v,k_0|\mathbf{e}\cdot\mathbf{p}|c,k_0\rangle|^2$$

and is evaluated at the $k_0=0$ band minimum. $S(E_r,F)$ is the dimensionless "absorption strength," numerically calculated by Dow and Redfield, and given in Fig. 2(a) of Ref. 23. It is related to the tunneling probability. E_r is the shift from the band gap in units of the exciton Rydberg energy $\mathscr{R}$: $E_r=-(E_g-h\nu)/\mathscr{R}$.

The results calculated by DR for $S(E_r,F)$ are a family of curves for different values of the electric field. They are indexed by a dimensionless parameter f which is the ratio of the potential drop across the excitonic radius to the exciton Rydberg: $f=|e\mathscr{E}a/\mathscr{R}|$. In the present calculation, the integration was carried out numerically by taking the values $S(E_r,F)$ from the DR plots. The curves given by Dow and Redfield give limited information for the absorption strength $S(E_r)$. For values of f less than unity, the strength can be interpolated, but for values of f greater than unity, no information is given. This corresponds to fields larger than about 2×10^7 V/cm, which fortuitously, is approximately the maximum field F_m.

By putting in the values of the fundamental constants in Eqs. (10) and (11) the absorption may be written

$$\alpha_0(h\nu,T)=2.8\times10^7(\mu^2C/n\epsilon h\nu) \times \int_{F_0}^{F_m} S(E_r,F)F^{-5/2}dF\ \text{cm}^{-1}\ , \qquad (12)$$

where ϵ is the dielectric constant and μ is the electron-hole reduced mass in units of the electron rest mass m_0. In this expression, $h\nu$ is in eV and F is in Å^{-2}. In order to obtain a numerical result, a value for C must be chosen. In keeping with Eq. (6) we write the concentration of ionic centers in the form

$$C=C_0e^{-E_0/k_BT}\ . \qquad (13)$$

Upon comparing Eqs. (13), (9), and (10) with Eq. (4), we identify $E_0=E_t$, C_0 with x, and $\alpha(h\nu)$ with $\alpha_0(h\nu)$, and so an estimate of the concentration of ions obtains from the experimental result for E_t. In Fig. 12 we show the result of the absorption calculation for $T=400\,^\circ\text{C}$, $x=0.003$, $E_t=0.52$ eV, and $\mu=1.75$. Also shown in the figure are experimental data for the same temperature and concentration. The exciton Rydberg energy is $\mathscr{R}=0.96$ eV. The DR calculations do not extend above $E_g-\mathscr{R}$ and so the calculation is not continued above this energy.

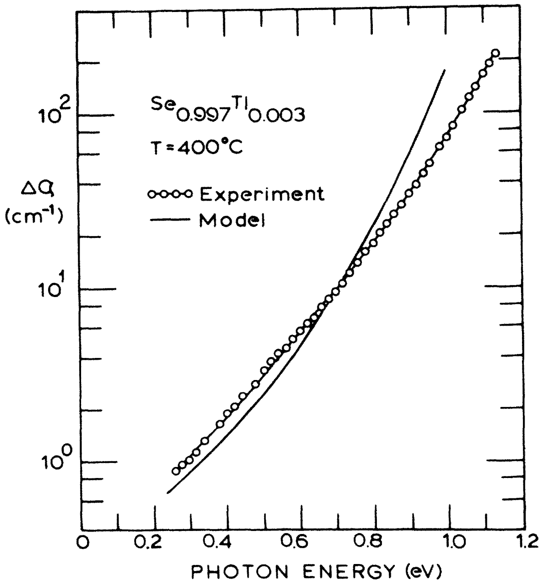

FIG. 12. Comparison of the absorption in $Se_{0.997}Tl_{0.003}$ for $T=400\,^\circ\text{C}$ as calculated in the ionic model and the experimental result.

V. DISCUSSION

Two of the parameters in the model, the exciton reduced mass and the maximum field F_m, are poorly known and are adjustable. The location of the calculated absorption edge in Fig. 12 are determined mainly by the value of the exciton Rydberg, which depends upon the dielectric constant ϵ and the choice of the reduced mass μ. Due to the lack of experimental information for the effective masses in liquid Se, the reduced mass must be estimated from measurements of the effective masses in amorphous or crystalline Se. Hartke and Regensburger[26] have estimated the exciton Rydberg energy in amorphous Se at about 0.1 eV. The dielectric constant[27] of amorphous Se is about 6.25, so this gives a reduced mass of $\mu\approx0.3$. Siemsen and Fenton[2] estimate the exciton Rydberg in amorphous Se at about 0.1 eV, with an uncertainty of a factor of 2 or 3. These estimates result in a reduced mass of 0.9 to 0.1. Measurements of Faraday rotation[28] in crystalline Se give estimates of effective masses $m^*\approx2.7m_0$, and this implies a reduced mass $\mu\approx1.4$. From bandwidth considerations,[29] the effective mass can be estimated, and this method gives $m^*\approx6m_0$. Moss[30] estimated the effective masses for amorphous Se from the drift-mobility studies of Spear[31] and in this way obtained $\mu\approx7$. Electroabsorption also provides a means of measuring m^*, and for amorpohous Se a value $m^*=4.5m_0$ can be estimated.[32] In view of the large differences in these values, and the lack of information on the effective masses in liquid Se, we treat the effective mass as an adjustable parameter. The best fit to the experiment was found for a value of $\mu\approx1.75$. Assuming equal electron and hole effective masses, this gives $m^*=3.5m_0$.

The slope of the calculated absorption curve is mainly determined by the range of fields over which the integration is carried out. The larger fields will contribute more to the absorption at lower photon energies. The resulting shape of the absorption curve is sensitive to the maximum field F_m. It was found that the best fit to the experimental data was obtained for a value of F_m corresponding to a minimum distance from an ion of $r_{\min}=2.6$ Å. This is intermediate between the interatomic distance within the chain (2.36 Å) and the interatomic distance between chains (4.5 Å).

There are two difficulties with the model as it stands, both of which can be removed by assuming that the electric field involves two ions in close proximity. One difficulty is that the activation energies decrease with increasing photon energy when the latter exceeds ~1.0 eV. This is not readily explained in terms of a single-ion mechanism for generating high-field regions. The second difficulty lies in the requirement that the initial state for the optical transition be below the Fermi energy E_F, and the final state, above. If E_F is near the middle of the band gap, as expected, interband absorption cannot occur for $h\nu<E_g/2$ (~1.0 eV).

To resolve the latter difficulty, we propose that the transitions for $h\nu<E_g/2$ occur in regions between oppositely charged ions as illustrated in Fig. 13. In this figure the unperturbed energy levels are shown by horizontal

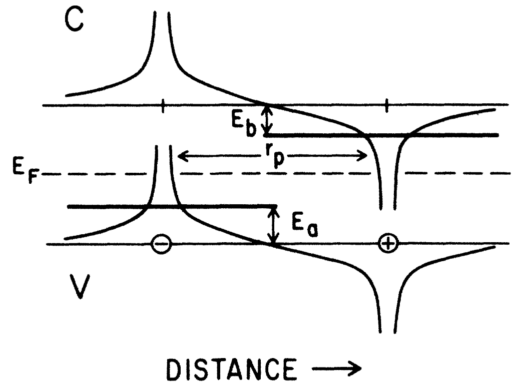

FIG. 13. Energy levels at a location in the semiconductor near a pair of oppositely charged ions having a separation distance r_p. The light horizontal lines are the valence and conduction edges in the absence of ions. The curved lines represent the potential excursions due to the ions. The Fermi energy is expected to lie near midgap. The initial- and final-state energies of the electronic transition are E_a and E_b, respectively. The states E_a and E_b have a small overlap.

lines, and the ions are expected to give rise to potential excursions as shown by the curved lines. The energy levels of the initial- and final-state wave functions, which are believed to have a coherence length[33] of about 30 Å, are represented by the heavy horizontal lines E_a and E_b. In order that there be enough overlap between wave functions centered on the two ions, the separation distance between the ions, r_p, must be much smaller than the average separation distance r_i given by $4\pi r_i^3/3=1/N_a C_i$. Consequently, the expression given for C in Eq. (13) must be interpreted in terms of the proposed ion-pair mechanism. The concentration of ion pairs at a separation energy distance r_p is given by

$$C_p=C_i^2\exp(e^2/\epsilon r_p k_B T) , \tag{14}$$

so that $E_t=2E_i-e^2/\epsilon r_p$, where E_i is the activation energy for ions of either charge. Using the estimate of 0.5 eV for E_i gives a value of 6 Å for r_p, which seems reasonable.

For $h\nu>E_g/2$, one expects an increasing contribution to α from transitions due to atoms near a single ion. Since the activation energy for a single ion is E_i, one expects E_t to decrease when $h\nu$ exceeds $E_g/2$ (or an energy somewhat less than $E_g/2$ if E_F is not quite in the center of the band gap). Thus we have a natural explanation for the decrease in E_t at $h\nu\geq 1.0$ eV. The ion-pair mechanism also improves the interpretation of the prefactor C_0 in Eq. (13). Rasolondramanitra and Cutler proposed that the dominant molecular ions in $\mathrm{Se}_{1-x}\mathrm{Tl}_x$ are selenium $D_{\mathrm{Se}}{}^{+}$ bond defects and diatomic molecular ions TlSe^{-}. In that case, one expects $C_0\propto x^{1/2}$, so that $\Delta\alpha$ due to regions near isolated ions would be proportional to $x^{1/2}$, whereas $\Delta\alpha$ due to regions near ion pairs is proportional to x. Due to experimental limitations, we were unable to obtain information about the dependence of $\Delta\alpha$ on x at photon energies above $E_g/2$ sufficient to test this conclusion.

A similar interpretation applies to the behavior of the activation energy E_{Se} for selenium. In this case a different species of negative ion is believed to be present, the onefold-bonded $D_{\mathrm{Se}}{}^{-}$ ion. Using a value $E_{\mathrm{Se}}\approx 0.95$ eV yields a lower limit 0.48 eV for the ionization energy of $D_{\mathrm{Se}}{}^{-}$-$D_{\mathrm{Se}}{}^{+}$ pairs. The value of $r_p=6$ Å inferred from E_t leads to an estimate of 0.73 eV for the ionization energy.

According to the ionic field model, the activation energy should decrease to a lower limit equal to the ionization energy when $h\nu$ increases above $E_g/2$: 0.5 eV for E_t and a value >0.4 eV for E_{Se}. Where information is available at larger $h\nu$, from measurements of thin-film samples in the amorphous phase, E_{Se} decreases linearly with $h\nu$ to zero at $h\nu\approx E_g$. This is the behavior expected for the Urbach band edge, and it has been explained by Siemsen and Fenton[2] in terms of Toyozawa's theory[34–36] of phonon-assisted excitonic absorption. This mechanism has been shown to also lead to an exponential increase of α with $h\nu$, but the theory requires[2] that the activation energy of α decrease linearly with $h\nu$, and it is inconsistent with the leveling off at $h\nu<1.0$ eV shown in Fig. 11. It should be noted that the DR theory does not make provision for the effects of thermal disorder on the optical transition, and these can be expected to be large in a liquid at high temperature. As $h\nu$ approaches the exciton energy, these effects can be expected to have increasing importance; and conversely, the effect of tunneling is expected to be less important when $h\nu$ approaches the exciton energy. Consequently, we suggest that both single-ion field effects and phonon-mediated processes play a role at $h\nu>E_g/2$, with the latter becoming more important as $h\nu$ approaches the exciton energy.

There are several assumptions of the ionic model which are difficult to justify. First, the DR theory is based on the Elliot theory of optical absorption by excitons in the Wannier representation. In the present situation, the rather large value of μ and the value of the dielectric constant lead to an exciton Rydberg energy $\mathscr{R}_E=0.96$ eV, and an excitonic radius $a=2.65$ Å. These values are not very consistent with the Wannier representation of a loosely bound exciton, and this is one of the approximations of the present model. However, the use of the Wannier representation may not be as bad for the larger tunneling distances considered here, which result when the electron-hole pair is excited at relatively large separation distances (when $h\nu$ is far from the exciton peak). Another approximation of the model is use of the static dielectric constant. For smaller values of the field, which occur at larger distances from the ions, this is a fair approximation. However, for the largest values of the fields, which occur at distances of the order of the interatomic spacing, this is not valid, and it is certainly one of the poor assumptions of the model.

Another approximation is the use of a theory based on extended wave functions in situations where the electronic states are localized because of the Coulomb potential wells. The short correlation length (≈ 30 Å) of the extended states has been mentioned already, so the localization distinction is largely formal if the Coulomb well is wide in comparison. It seems to come down to a question of whether the high degree of disorder and the resulting short correlation length of the wave functions cause significant changes from the results of the DR theory.

The DR theory was derived for a uniform electric field, but it has been applied to ionic fields which are spherical near the ions. However, the tunneling process occurs in a relatively small region, so that the curvature of the field is significant only if the radius of curvature is comparable to the tunneling distance. The transitions involving the two-ion mechanism occurs mainly in regions between the ions, where the curvature is less pronounced, so we do not expect this idealization in the model to be as significant as some of the others. The two-ion field distribution will, of course, be different from the single-ion distribution, and it will be expected that the factor dV/dF in Eq. (9) will be somewhat different. We have calculated the absorption using a distribution appropriate for an extended dipole, but the result is not significantly different from the single-ion result.

VI. CONCLUSIONS

We have presented an explanation for the low-energy optical absorption tail in the liquid semiconductor system $\mathrm{Se}_{1-x}\mathrm{Tl}_x$ in terms of a field-assisted ionization model of excitonic absorption. Strong, local electric fields due to ions cause a shift in the absorption edge similar to the Franz-Keldysh effect. For photon energies less than the exciton peak, the exponential absorption is a consequence of the electron-hole Coulomb interaction modifying the usual $[\exp(h\nu)]^{3/2}$ behavior in the Franz-Keldysh effect, to produce the $\exp(h\nu)$ spectral dependence, with an accompanying enhancement of the absorption. The temperature dependence in the absorption arises from the thermal excitation of ions in the liquid, and this is the reason for the observed constant activation energy of the absorption for photon energies less than half the band gap.

The conventional interpretation of the temperature shift of the absorption edge has been that it reflects narrowing of the band gap. The results of our measurements are in disagreement with this interpretation, as the extrapolated band-gap energies do not vary with temperature. In the ionic model, the temperature shift of the absorption is explained as an increase in the absorption due to an increasing density of ions.

For photon energies greater than half the band gap, the activation energy of the absorption decreases with increasing photon energy. It is suggested that this decrease indicates a region of absorption associated with single ions. It is also likely that phonon broadening of the exciton absorption becomes important when the energies approach the exciton peak. It is possible that an energy boundary exists below which ionic effects are more important and above which phonon broadening is dominant. If this is the case, it is expected that this boundary will move to lower photon energies as the temperature is raised, and the phonon density increases. This is a question that could be examined theoretically.

Another theoretical question raised by this work is the character of the localization of states near the band edges which is induced by the presence of ions. The issue raised is the proper description in a situation where the width of the potential wells causing localization is comparable to the correlation length resulting from thermal disorder. This problem is ubiquitous to the systems where large concentrations of ions exist, particularly the liquid semiconductors and possibly also some amorphous semiconductors.

The Dow-Redfield model has been suggested previously as a possible explanation for the exponential absorption edge in liquid semiconductors.[4] However, there has been a question of the origin of the strong electric fields and how to represent such a field distribution. The present work proposes that the origins of these fields are the regions in the immediate vicinity of ions. Although some of the assumptions in the ionic model are idealized and perhaps have a questionable basis, we feel that the model captures some of the essential physics of the optical absorption edge in liquid semiconductors. The results of the model agree well with the data, and resolve the questions of the origin of the temperature shift and the exponential behavior. It is possible that the model may also be extended to the other liquid semiconductors, thus providing a universal explanation of the exponential edge in liquid semiconductors where charged defects are present. It also provides a direct experimental method for obtaining information about the presence of ions.

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