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Phonon interactions in the tail states of *a*-Si:H

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Many experimental data on the 1.4-eV photoluminescence of *a*-Si:H have been interpreted by the assumption of a Stokes shift of up to 0.5 eV. We show that the evidence for a Stokes shift may be satisfactorily explained by a distribution of zero-phonon energies only. This suggests that the radiative states may be rigid and so that there is no evidence for a significant disorder-induced electron-phonon interaction in the tail states of amorphous silicon.

I. INTRODUCTION

Amorphous semiconductors differ from crystalline semiconductors primarily in having a high density of localized states at the band edges. These band-tail states dominate the transport properties, and so an understanding of their nature is of technological as well as of physical interest. Nevertheless, their origin and nature is not yet clear. The model which is, perhaps, the most generally accepted attributes the tail states to Anderson localization; in this model, due to Mott, states may be delocalized at the center of a band but a mobility edge will separate a tail of localized states at the band edge. Other authors, however, have emphasized the importance of long-range fluctuations of the band-edge energy. For a discussion and references, see a recent review by Mott.[1]

It is generally agreed that the 1.4-eV photoluminescence (PL) band in *a*-Si:H is due to the recombination of carriers trapped in the conduction- and valence-band tail states (see Street's recent review[2]). Consequently, studies of the PL should be of considerable help in elucidating the nature of the band-tail states. However, the mechanism of the PL is itself still controversial. It is not yet agreed whether its kinetics are geminate[2–4] or distant pair,[5,6] nor whether it is significantly Stokes shifted[2,7] or is due to essentially zero-phonon transitions.[8–11] Both questions are important, the kinetics of the luminescence being related to the kinetics of the photoconductivity, photoabsorption, and light-induced EPR, and the Stokes shift, related to the nature of the tail and its density of states. We have discussed the kinetics elsewhere[6,12,13] and established that under quasicontinuous excitation the recombination is distant pair; here we consider the question of the Stokes shift.

Many of the features of the 1.4-eV PL band may be interpreted either in terms of a distribution of zero-phonon energies, or in terms of a Stokes shift of about 400 meV, with, of course, a correspondingly much narrower distribution of zero-phonon energies. Nevertheless, many of these features have been used to support the Stokes-shift model. In particular, the following four features of the luminescence have been quoted as evidence for a Stokes shift; it is the purpose of this article to show that they are also consistent with a zero-phonon model:

(1) The peak energy of the band is some 400 meV below the optical (Tauc) band gap, and the width of the (roughly Gaussian) band is 200—300 meV.[7]

(2) The emission peak energy shifts to the red when the excitation energy is reduced below the band gap.[14–16]

(3) Essentially the same temperature dependence of the PL intensity is observed at all emission energies.[7]

(4) The absorption strength at the emission energies is some three decades weaker than would be expected from considerations of detailed balance, on the assumption that the zero-phonon energies are the same as the emission energies.[7]

However, there is also direct evidence against a Stokes shift. The PL bandwidth does not show the expected temperature dependence; the excitation spectrum is temperature independent below the postulated zero-phonon energies[11] and is exponential in form rather than Gaussian as expected if it is due to phonon broadening; and finally, the Urbach edge (which in the Stokes-shift model is due to phonon broadening of the intrinsic absorption edge) is very similar in systems with widely different values of the Stokes shift, such as chalcogenide glasses and *a*-Si:H.[1]

In the Stokes-shift model, (1) is attributed largely to the Stokes shift. Street[7] showed that the spectrum is very similar to that expected from a zero-phonon energy of 1.5—1.55 eV and a Stokes shift of 0.4—0.5 eV (for a band gap of 1.7—1.8 eV and an emission peak energy of 1.3 eV). In Sec. II, we obtain the emission spectrum from a physically plausible distribution of zero-phonon energies, with fewer fitting parameters than in the Stokes-shift model.

While Collins and Paul[15] accounted for (2) by changes in the electron-hole pair separations, it has also been given as evidence for a thermalization gap.[14] In this model, carriers excited into the bands thermalize down through the tail states to an energy, the thermalization gap E_{0t}, below which further thermalization is too slow to compete with the radiative transitions. Thus the distribution of zero-phonon energies is sharply peaked about E_{0t} [about 1.6 eV in *a*-Si:H (Ref. 14)] and a Stokes shift is required to give the observed PL spectrum. Exciting with subgap illumination excites preferentially the tail states below E_{0t}, and so the band then shifts to the red. We show, in Sec. II, that the red shift follows directly from the distribution of zero-phonon energies used to account for (1), without the additional assumptions of a thermalization gap and a Stokes shift, or changes in pair separations.

Since the temperature quenching is considered to be due to thermal excitation to the bands—or to the mobility edges—Street interprets (3) as indicating that the spread of zero-phonon energies cannot be comparable with the width of the emission band, for if it were, then greater activation energies of quenching would be expected at the lower emission energies.[7] We find that our distribution of zero-phonon energies correctly gives the temperature dependence of the PL spectrum. However, we do not calculate temperature-quenching curves from our model, since, as we have shown elsewhere,[13] they are critically dependent on the lifetime distribution and its shifts with temperature and excitation energy; consequently, without a full knowledge of the recombination kinetics, temperature-quenching curves cannot in any case be correctly interpreted.

Finally, Street[7] gives the natural explanation of (4), that the inverse transition to the PL occurs at considerably higher energy, where the absorption coefficient is a factor of $\sim 10^3$ greater than at the emission energies. This point is not dealt with explicitly by our model, and so remains as the only real evidence for a Stokes shift.

We suggest, however, that undue reliance should not be placed on the argument from detailed balance, firstly, because of the direct evidence cited above against a Stokes shift, and, secondly, because of the comparison required in the detailed balance argument between the material close to equilibrium (in an absorption experiment) and under extremely intense optical excitation (the saturation experiment). Indeed, we show, in Sec. II, that the detailed balance argument is logically flawed in this respect.

However, since the points (1)—(3) have also been cited in the literature as primary evidence for Stokes-shift models, our principal concern here is to show that they are not; they arise equally naturally from a plausible no-phonon distribution of excited-state energies. This we show in Sec. II, and there we consider the detailed balance argument in more detail. In Sec. III, we discuss interpretations of the formalism of Sec. II.

It is important to note that we are not seeking to demonstrate that a no—Stokes-shift model is correct. Our purpose here is to take the simplest possibly correct model of the electronic structure of *a*-Si:H, and to show that it behaves similarly to the PL of *a*-Si:H. If there is not, in fact, a significant Stokes shift, then the exponential absorption tail implies an exponential density of excited states below the gap. We show, in Sec. II, that this is sufficient to account for the PL. Since we are not considering any *ad hoc* refinements of the model, minor quantitative discrepancies are not to be taken too seriously.

II. A NO—STOKES-SHIFT MODEL—COMPARISON WITH EXPERIMENT

A. The model and its emission spectrum

In this model, we assume that, below the band-gap energy, there is an exponentially decreasing density of states available for an optical excitation (an electron-hole pair):

$$N(E_0-\epsilon)\propto \exp(-\beta_L\epsilon)\ , \tag{1}$$

where ϵ is the energy below some suitably defined band gap E_0.

In contrast to the thermalization gap model, in which an excitation thermalizes down to a well-defined energy E_{0t} before radiative recombination occurs, we let thermalization occur to the lowest state among a number $N+1$ randomly chosen states. We consider the physical significance of this assumption, and of the value N, in the next section. Then the emission energy is given by the energy of this minimum state, and so the emission spectrum is given by the distribution in energy of the minimum states,[17(a)]

$$P_L(E_0-\epsilon)\propto \exp(-\beta_L\epsilon)(1-e^{-\beta_L\epsilon})^N\ . \tag{2}$$

Equation (2) gives a slightly asymmetrical, nearly Gaussian spectrum $P_L(h\nu)$ that is very similar to the experimental spectrum of the 1.4-eV PL in *a*-Si:H.[17(a)] The width at half-height is given by $\sim 2/\beta_L$ independent of N, and the depth below E_g is proportional to β_L^{-1} and increases logarithmically with N. Typical *a*-Si:H spectra are fitted with values of $\beta_L^{-1}\sim 100$—150 meV and $N\sim 50$ (Fig. 1).

In this model, the energy difference between the peaks of the excitation and emission spectra comes not from relaxation of an occupied excited state (a Stokes shift), but only from thermalization of the excitation among the tail

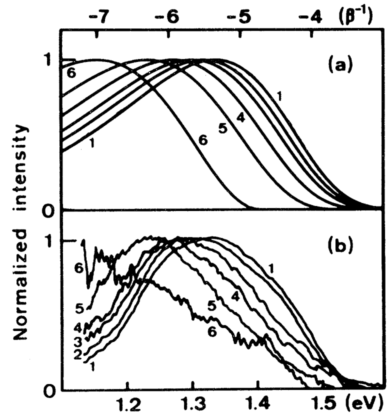

FIG. 1. (a) Theoretical spectra calculated from Eq. (3), and (b) experimental spectra (corrected for instrumental response), showing the red shift of the PL emission band as the excitation energy is reduced below the band gap. For the spectra 1—6, respectively, the excitation energies are 2.07, 1.91, 1.82, 1.72, 1.63, and 1.51 eV. The theoretical curves are calculated for $N=50$, $1/\beta_L=110$ meV, and $E_0=1.92$ eV.

states. It is therefore expected that the absorption and the excitation spectra will be similar. It would be natural to identify the slope β_L with β_α, the slope of the exponential absorption tail; however, the mechanisms of absorption and emission are not the same. The PL is a bound-to-bound transition, while the absorption is thought to be due to free-to-bound and free-to-free transitions only. Thus the emitting energy states available to the excitation are not directly accessible by absorption, only by absorption followed by thermalization, and there is no necessary relationship between β_L and β_α. Nevertheless, because the emission spectrum results from a convolution of electron and hole bound-state energy distributions, while absorption measures a superposition (not being bound to bound), we expect $\beta_L < \beta_\alpha$ (for a symmetrical band structure, $\beta_L = \frac{1}{2}\beta_\alpha$). Indeed, the absorption tail slope β^{-1} is typically ~60—70 meV, about half the value of β_L^{-1} found to fit the emission spectra.

The red shifts with excitation energy and with temperature are obtained very simply, by appropriately weighting the contributions to the PL intensity of the minimum states of different energy.

B. Excitation energy dependence of the emission spectrum

For the red shift with decreasing excitation energy, we take for the weighting function the same dependence on excitation energy above the energy of the minimum state as the absorption has on the energy above the band gap. In doing so, we ignore, for simplicity, the fact that much of the absorption feeding a given minimum state occurs through the nearby higher states (the "watershed" of the minimum). We discuss this choice of the weighting function in Sec. III; meanwhile we remark only that the exact form of the function is not critical. Omission of the watershed affects the weighting function somewhat, but does not change the result significantly, compared with the scatter in the experimental data (see below, Fig. 2).

The absorption above the gap E_{0g} in *a*-Si:H is given by

$$\alpha(h\nu) = \frac{\alpha_0}{h\nu}(h\nu - E_{0g})^2$$

so we obtain for the emission spectra as a function of the excitation energy $h\nu_{\rm ex}$

$$I(h\nu_{\rm ex}, h\nu_{\rm PL}) \propto P_L(h\nu_{\rm PL}) \frac{(h\nu_{\rm ex} - h\nu_{\rm PL})^2}{h\nu_{\rm ex}} . \qquad (3)$$

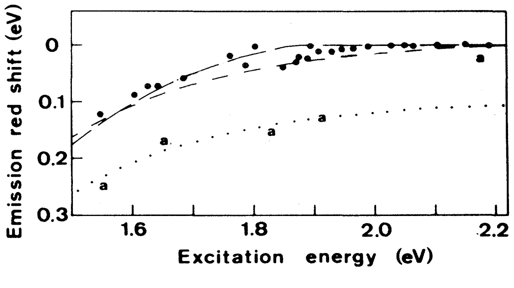

FIG. 2. Data points show the peak position red shifts as a function of excitation energy for *a*-Si:H (solid circles) taken from Fig. 1(b) and from the literature (Refs. 14—16), and for *a*-As_2Se_3 (a) taken from Depinna *et al.* (Ref. 18). The curves show theoretical results using a band gap $E_0 = 2$ eV, $1/\beta_L = 120$ meV, and $N = 45$. The broken curve is obtained from Eq. (3) and is repeated, shifted downwards 120 meV (dotted curve). The dotted-dashed curve is calculated for a watershed as described in the text.

Normalized spectra $I(h\nu_{\rm PL})$ are shown in Fig. 1(a) for a range of values of $h\nu_{\rm ex}$ and we see that the experimental behavior [Fig. 1(b)] is well reproduced. For excitation well above the band gap, the emission spectrum is independent of the excitation energy, and when $h\nu_{\rm ex}$ is reduced below the gap, the emission shifts to the red while retaining the form of the spectrum. In Fig. 2, we compare the peak positions of the theoretical spectra of Eq. (3) with the experimental data of Fig. 1(b) and in the literature.[14—16,18] The data show some scatter; this is partly due to different experimental conditions, and partly due to differently prepared samples. The dashed curve in Fig. 2 is calculated from Eq. (3) using the parameters given in the figure caption, and is repeated, shifted downwards by 120 meV (dotted curve), for comparison with the *a*-As_2Se_3 data. The dotted-dashed curve shows the effect of a watershed only; to calculate this curve, the dependence of absorption on excitation energy has been ignored and we assume that the effective capture radius of a minimum decreases linearly from a constant value for excitation at the band edge to zero at the energy of the minimum.

A comparison of the data with the theoretical curves in Fig. 2 shows that we cannot decide between the different weighting functions used here; agreement is within the scatter of the data. Consequently, data showing a red shift as in Fig. 2 cannot be taken as evidence for a thermalization gap.

Data for *a*-As_2Se_3 taken from Depinna *et al.*[18] are also shown in Fig. 2. Although the recombination mechanisms are the same in *c*-As_2Se_3 and *a*-As_2Se_3,[18] the crystal shows no red shift. The shift in the glass, on the other hand, is very similar to that in *a*-Si:H, for excitation below the gap (1.9 eV), leading Depinna *et al.*[18] to propose an explanation along the lines of that given here. The large shift in peak energy for excitation above the gap is due to a change in emission mechanism[18] and so is outside the scope of our model.

C. Temperature dependence of the emission spectrum

Essentially similar temperature dependence of the PL is observed at all emission energies (3); this feature has been taken to support a Stokes-shift model[7] since it can be interpreted as indicating that the zero-phonon states are distributed over a much narrower range of energy than the emission. The temperature quenching is not, however, quite the same for all emission energies, for the PL shifts to lower energy as the temperature is increased.[3,8] Indeed, we have observed that the red shift is linear with the quenching $\log_{10}(I/I_0)$ and its value is the same whether the reduction in emission intensity I/I_0 is obtained by thermal quenching or by excitation below the gap

[Dunstan and Rosso, Ref. 17(b)]. Since the red shift with excitation energy is obtained by a different weighting of each minimum, it is plausible that the thermal red shift is likewise obtained. We write, as for Eq. (3), the emission spectrum as

$$I(h\nu,T)=\frac{\tau_r^{-1}}{\tau_r^{-1}+u(h\nu,T)}P_L(h\nu) \qquad (4)$$

with

$$u(h\nu,T)=u_0\left[\exp\left[\frac{\epsilon}{kT}\right]-1\right]^{-1}$$

and $h\nu=E_0-\epsilon$ and in Fig. 3(a) we show the spectra obtained for various values of the temperature. The behavior is similar to that of the experimental spectra [Fig. 3(b)]. In Fig. 4, the thermal red shifts of the experimental spectra are plotted against the extent of quenching, $\log_{10}(I/I_0)$; the linear behavior expected from moving a weighting function down an exponential is displayed except at very small values of the quenching. The solid curve is calculated from Eq. (4).

Note that, while the experimental behavior is predicted qualitatively by Eq. (4), there are serious quantitative discrepancies. However, while the excitation energy dependence of the emission spectra can be successfully predicted without taking the kinetics into account (Sec. II B), this is not so for the temperature dependence, due to the lifetime τ_r appearing in Eq. (4). The radiative lifetime has a wide range of values, and furthermore its distribution is itself temperature dependent.[2] There is also a correlation between decay energy and decay time.[2] It is outside the scope of the present paper to consider the kinetics of recombination; we cannot expect, therefore, more than qualitative agreement between experiment and theory, such as is shown in Figs. 3 and 4. For the same reason, we do not attempt to calculate quenching curves $I(T)$.[13]

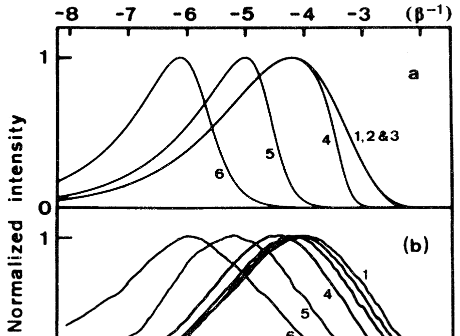

FIG. 3. Same as Fig. 1, but for thermal red shifts as calculated from Eq. (4). For the experimental spectra (b) the temperatures are (1, . . . , 6) $T=5$, 54, 96, 141, 200, and 256 K. The theoretical curves (a) are calculated for temperatures 40% higher, with $N=45$, $1/\beta_L=130$ meV, and $E_0=1.9$ eV at 0 K going to 1.8 eV at 300 K; $\mu_0\tau_r=10^8$.

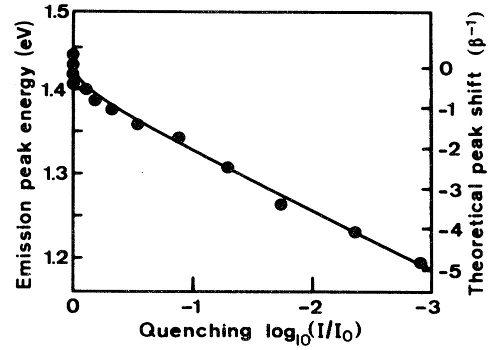

FIG. 4. Thermal red shift plotted against the extent of quenching expressed as $\log_{10}(I/I_0)$. The solid curve is calculated from Eq. (4) using the same parameters as for Fig. 3(a); the experimental data is from the same sample as in Fig. 3(b). Note that the scale of the theoretical shift is compressed; this is analogous to the error in the temperature scale in Fig. 3 and is due to the temperature dependence of the kinetics.

D. Detailed balance

Finally, we consider the argument from detailed balance for a Stokes shift.[7] Both the strength of the absorption due to the radiative centers and the intensity of emission at optical saturation are proportional to $N_r\tau_r^{-1}$; consequently without knowing either the number of radiative centers N_r, or their lifetime τ_r, a direct comparison can be made between the absorption and the saturated intensity. Street[7] found that optical saturation occurs at or above 3×10^{26} photons $\text{cm}^{-3}\,\text{s}^{-1}$ and deduced that the corresponding absorption strength should be some 10^3 cm^{-1}. Since the absorption at the PL energies, around 1.4 eV, is only of the order of 1 cm^{-1}, Street ruled out the possibility that the PL could be due to zero-phonon transitions.

The applicability of detailed balance has already been the subject of some controversy.[2,9] We believe that confidence in the argument would be justified if optical saturation were to be demonstrated—that is, the functional form of the dependence of the PL intensity on the excitation rate G were of the form $I(G)\sim G/(\text{const}+G)$, and bleaching of the absorption of the form $\alpha(G)\sim 1/(\text{const}+G)$ were to be observed. Neither are found to be so in *a*-Si:H; instead of photobleaching, photoabsorption is observed, and the form of $I(G)$ is roughly linear to the "saturation" level, at which a sharp cutoff occurs.[7] What actually happens as the excitation intensity is increased in *a*-Si:H is not clear; the application of detailed balance rests, however, on the assumption that once optical saturation is reached, then the observed emission intensity cannot increase further. This requires assumptions about the fate of the excess photoexcited carriers, and we now show that, in the standard model of *a*-Si:H, these assumptions are not justified.

The electronic transport in *a*-Si:H at low temperature displays a very low, activated mobility, which is usually attributed to trapping in the tail states. Since, in good quality samples, the PL quantum efficiency approaches 100%,[2] it follows that the traps which control the mobility must be identified with the radiative states. In this case, at optical saturation, the mobility is no longer controlled by the traps. It does not matter at what level of excitation saturation occurs; this will always be true. Consequently, the excess carriers, which cannot recombine in the saturated volume, will diffuse (presumably with Mott's minimum metallic mobility controlling the diffusion) and recombine elsewhere—whether radiatively or through nonradiative centers depends on the details of the nonradiative recombination mechanism, which is itself still in some doubt.[2,19,20] The optical saturation experiment uses a focused laser, exciting a volume of perhaps $10\times 10\times 0.1\ \mu\text{m}^3$; it is easy to calculate that, using Mott's minimum metallic conductivity to obtain the diffusion constant, not many of the carriers will remain in this small volume. Thus, *within* the standard model, one does not expect to observe optical saturation, whatever the value of G at which it occurs, and the experiment in which it is not observed gives no additional information. Thus the detailed balance argument is founded on an experiment that gives no relevant information; it therefore has no validity.

It may be argued that the dramatic increase in mobility predicted above could be observed, and that its absence would then confirm the detailed balance argument. This would be to miss the point. Firstly, the assertion that the detailed balance argument demonstrates either a Stokes shift or a massive increase in mobility at saturation is already a weaker proof of a Stokes shift than that which has been given in the literature. Secondly, we do not consider that the standard model gives a very satisfactory picture even at low excitation levels; detailed balance requires its uncritical extension to high excitation levels. There are many other possibilities, besides the one given above for the standard model, for high excitation rates.

E. Discussion

We conclude that a rigid tail-state model with an exponential distribution of no-phonon energies provides at least as good an account of the PL in *a*-Si:H as do the Stokes-shift and thermalization gap models. Indeed, while in the latter models the values of the Stokes shift, the phonon frequency, the zero-phonon energy, or the value of the thermalization gap, and the spread in energy due to disorder[3] are entirely free fitting parameters, we shall see in the next section that in our description the parameters β_L, N, and E_0 are not entirely free, but may be derived—at least in principle—from other considerations. Using only these parameters to fit the emission band, we then obtain quantitative agreement with the excitation energy dependence without any adjustable parameters. Qualitative agreement only is obtained with the temperature dependence of the emission; however, as remarked in Sec. II C, in view of the complexity of the kinetics of the recombination, quantitative agreement is not expected here.

We proceed in the next section to consider how the purely formal model presented here may be given a physical interpretation in two current models of the electronic structure of amorphous materials, and to what extent the parameters β and N may be derived from known quantities.

III. INTERPRETATION

In this section, we discuss two physical interpretations of the formalism of the preceding section. These interpretations are according to the Mott-Anderson model of the amorphous state (Sec. III A) and in the fluctuating band-gap model (Sec. III B).

A. Rigid-tail states in the Mott-Anderson model

According to the Mott-Anderson model, a band has a tail of localized states below a mobility edge. The theory is not explicit as to the form of the tail or its density of states[1]; however, the exponential absorption tail suggests an exponential density of states for the band tails and this is supported by the success of the multiple trapping model for the kinetics of photoinduced absorption.[21] It is generally supposed that the absorption is predominantly band-to-band and band-to-tail transitions, because tail-to-tail transitions are indirect in real space. On the other hand, the PL is due to tail-to-tail tunneling transitions.[7]

Consequently, we identify the exponential distribution of excited states with the Mott-Anderson tail states. For conduction- and valence-band tails given, respectively, by

$$N_i(E)\propto \exp(-\beta_i E),\quad i=c,v$$

the absorption spectrum shows a tail with a slope β_α given roughly by the smaller of the two values β_c and β_v.[22] The emission spectrum is given by the convolution of the two expressions of the form of Eq. (2), for each band:

$$I_{\text{PL}}(h\nu)\propto \int_0^{E_0-h\nu} R_c(E)R_v(E_0-h\nu-E)dE \qquad (5)$$

with

$$R_i(E)=\beta_i \exp(-\beta_i E)[1-\exp(-\beta_i E)]^N .$$

Numerical solutions of Eq. (5) give spectra very similar in form to the solutions of Eq. (2); in the case of $\beta_v \sim \beta_c$ then $\beta_L=(\beta_v+\beta_c)/4$. Thus β_L is not a free parameter: It is given roughly by $\frac{1}{2}\beta_\alpha$ in agreement with the fits given in Sec. II. The absorption tail is usually described by $\beta_\alpha \sim 16$ eV^{-1}; the fits in Sec. II were obtained with $\beta_L \sim 8$ eV^{-1} (i.e., $\beta_L^{-1} \sim 125$ meV).

The appropriate value of N in the Mott-Anderson model may be obtained as follows. As a carrier thermalizes down through the tail states, it diffuses spatially as it tunnels from one state to another. The tunneling probability τ_t^{-1} will be given by an expression of the form

$$\tau_t \sim \omega_0^{-1}\exp\frac{2r}{r_0}$$

with $\omega_0 \sim 10^{12}$ Hz where r_0 is the Bohr radius of a tail state, 10—12 Å.[3] The radiative recombination probability τ_r^{-1} is similarly given by

$$\tau_r=\tau_0\exp\frac{2r}{r_0}$$

with $\tau_0=10^{-8}$ s.[3] We assume that the carrier continues to thermalize until $\tau_t > \tau_r$. Since the mean radiative lifetime τ_{rm} may be taken as about 1 ms,[6] we obtain a critical radius r_c given by

$$r_c = \ln(\tau_{rm}\omega_0)\frac{r_0}{2} \sim 100\ \text{Å} .$$

Thus the states from which radiative recombination occurs are those which are the lowest within volumes $\sim r_c^3$. The total tail-state density is not accurately known; taking a value of $10^{19}\ \text{cm}^{-3}$ we find that the radiative states are the lowest of groups of about 42 tail states. This is then the value of N, in reasonable agreement with the values $N \sim 50$ used in Sec. II.

The red shift with excitation energy in this interpretation is to be obtained not from Eq. (3) but from the convolution, Eq. (5), and using the free-to-bound transition rate as the weighting function. The calculation would be much more tedious than that using Eq. (2); it is readily seen, however, that it would give a result similar to Fig. 2. The thermal red shift is also more complex to calculate, since carriers in one band will detrap more readily than those in the other[13] and retrapping must then also be taken into account. Here, it is sufficient to note that the position, width, and form of the emission spectrum of *a*-Si:H are in quantitative agreement with a model of rigid band-tail states with an exponential distribution in energy, and that the model predicts qualitatively the dependence of the spectrum on excitation energy and on temperature.

It is also worth noting a couple of predictions of the model as described here. First, the thermalization into the tails proceeds through a considerable number of tunneling transitions between tail states, over distances up to ~ 100 Å. It is then not to be expected that a carrier will remain within a few tens of angstroms of its origin, as required by the geminate model of the recombination kinetics.[3] Instead, we expect diffusion over distances $> \sim 100$ Å, leading to distant-pair kinetics, as observed.[6,12] Second, given distant-pair kinetics, the average lifetime decreases as the excitation rate G is increased, roughly as $G^{-0.8}$.[12,23] From Eq. (6), this will result in a roughly logarithmic shift of the emission band to higher energy with G, corresponding to a decrease in the value of N. This, too, is observed.[24]

B. The band-gap fluctuation model

The fluctuating band-gap model was proposed in order to account for the absorption spectrum in amorphous semiconductors.[25] We discussed it in connection with the PL spectrum of *a*-Si:H in Ref. 17, and so will treat it only briefly here. A similar model, of quantum wells,[26] also accounted for the absorption and the PL without invoking a Stokes shift.

It is assumed that the band-edge states are dominated by long-range fluctuations in energy, so that the values of the band gap found locally are distributed in energy:

$$P(E_g) = P(E_0 - \epsilon) \propto \exp(-\beta\epsilon) .$$

Then the distribution of values of local minima is obtained as in Sec. II. It is assumed that carriers are trapped only in the minima, giving Eq. (2) for the PL spectrum; the value of N is expected to be about twelve.[17(a)]

Only an antiparallel component of the fluctuations will be observed in absorption; we assume that the local value of the chemical potential will also vary spatially, giving a parallel component. Assuming that this component is not correlated with the band-gap fluctuations, we may express the fluctuations either in terms of a β_p and a β_{ap}, or in terms of a β_c and a β_v for the conduction- and valence-band edges separately. Then

$$\beta_p^{-1} + \beta_{ap}^{-1} = \beta_c^{-1} + \beta_v^{-1} \sim \beta_L^{-1} .$$

We do not know β_p, but we expect β_L^{-1} to be greater than the β_{ap}^{-1} $(=\beta_\alpha^{-1})$ that we observe in absorption (~ 60 meV) and the results of Sec. II are consistent with $\beta_p \simeq \beta_{ap}$.

Rigorously, it would be more correct to take the convolution of the conduction- and valence-band distributions of minima to obtain the PL spectrum; however, as pointed out in Sec. III A, this does not lead to significantly different results. In particular, since the distribution of chemical potential is not known, and may be expected to be Gaussian rather than exponential, it would not be meaningful to go beyond the simple calculations of Sec. II.

In this interpretation, there is a considerable discrepancy between the value of N found to describe the data (~ 50) and that expected from the model (12). The result is that the emission is at a lower energy than predicted, by about 200 meV. We do not consider this to be a serious problem for the model. The radiative states are likely to be bound states below the local band edge; the binding energy would reduce the emission energy below that calculated from the model. On the other hand, N becomes a free fitting parameter. Nor do we exclude a Stokes shift of up to 200 meV. The purpose of this paper is not to show that there is no Stokes shift, only that there is no evidence for one. Finally, it should be noted that tunnelling between adjacent band-gap minima would increase the value of N, from 12 to about 50 (the number of second-nearest neighbors in random close packing.)

C. Discussion

It is clear that the formal model of Sec. II can be given a physical interpretation. Indeed, both models described in this section fit satisfactorily, and so the PL data cannot be used to determine between them. Nonetheless, the PL data do give information on the tail states; we suggest that the results given here show that the PL can be explained with fewer free fitting parameters in a rigid tail-state model than with a Stokes shift. There are some numerical discrepancies in the fit between the data and the models; we note that this is also the case in the Stokes-shift model. For example, Street[7] deduces a Stokes shift of 0.4—0.5 eV from the low-temperature spectrum, while Alvarez and Williams[27] obtain twice that value from the temperature dependence of the PL emission bandwidth; in contrast, our samples show very little change in bandwidth with temperature (Fig. 3). Tsang and Street[3] confirm the value of 0.4—0.5 eV for the Stokes shift and find additionally a disorder-induced spread in the zero-phonon energies of 0.2—0.25 eV, from the temperature dependence of the peak energy.

It is probable that these quantitative problems, both in our model and in the Stokes-shift model, are due to the experimental difficulties in studying incompletely resolved bands. Below the 1.4-eV band which is the subject of this paper, there is at least one other broad band, which partially overlaps with the 1.4-eV band. Under these circumstances, we believe that it is not possible—or meaningful—to have exact quantitative agreement between experiment and an essentially correct theory.

As for a decision as to which model is correct, we believe that the data are not sufficient to give a definitive answer. Mere agreement between a model and the data is not to be taken as sufficient evidence for the model, for more than one model is consistent with the data. It may be helpful, however, to conclude by summarizing the main points remaining which favor one model rather than the other. For the Stokes-shift model, this is the argument from detailed balance. For a no—Stokes-shift model, fewer free fitting parameters are required.

IV. CONCLUSIONS

We have shown that the 1.4-eV PL emission band in *a*-Si:H can be satisfactorily accounted for without recourse to a Stokes shift. Furthermore, our description requires fewer free parameters than the Stokes-shift model. This does not prove the complete absence of any Stokes shift, and we do not rule out the possibility that there may be a Stokes shift; even within the framework of our model there may be a Stokes shift of as much as 200 meV. On the other hand, there is no justification for attributing the PL energy and spectral width to electron-phonon interaction, nor for postulating a thermalization gap.

Since our interpretation explains the dependence of the PL spectrum on excitation energy solely in terms of the distribution of tail states, it explains the similar behavior in this respect of systems as different as the PL in *a*-Si:H and in *a*-As_2Se_3 (Fig. 2).

There is no evidence that disorder, of itself, induces an increase in the electron-phonon interaction [cf. the remarkable similarity of the PL spectra in *a*-As_2Se_3 and in *c*-As_2Se_3 (Ref. 18)]. There would be, then, no significant Stokes shift in the band-edge states in *a*-Si:H because in *c*-Si band-edge carriers do not self-trap.

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