X-ray photogeneration in amorphous selenium: Geminate versus columnar recombination

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Amorphous selenium (*a*-Se) is a photoconductor used for both optical and x-ray imaging. Its optical photogeneration efficiency has been understood in terms of the Onsager theory of geminate recombination. However, x-ray photogeneration in *a*-Se has not been understood well. A previous argument has dismissed the Onsager theory of geminate recombination in the context of carrier generation in *a*-Se by high-energy radiation. Instead, columnar recombination has been proposed. In this paper we examine this argument and the predictions of the two recombination mechanisms. We find that the argument which dismissed the Onsager theory of geminate recombination is unwarranted, and that the Onsager theory is generally consistent with available experimental data. On the other hand, the columnar recombination theory is inconsistent with experiment. We have extended the Onsager theory in a form appropriate for x-ray photogeneration in *a*-Se to reflect that there should be a broad distribution of electron-hole separations.

I. INTRODUCTION

Amorphous selenium (*a*-Se) is a semiconductor which photoconducts upon irradiation of optical or x ray photons, and is employed in photocopy technology[1] and medical x-ray imaging.[2,3] Its application in photocopy technology has led to extensive studies of its properties in the optical-photon energy range. In comparison, the properties of *a*-Se in the x-ray photon energy range are much less understood, and the recent applications of *a*-Se in medical x-ray imaging have created the need to understand these properties much better.

When a semiconductor is exposed to high-energy radiation, electron-hole pairs are created in the material. As discussed by Klein,[4] the number of pairs created is proportional to the energy deposited in the semiconductor, and is independent of the characteristics of the radiation. The average energy required to create an electron-hole pair in a semiconductor using high-energy radiation is denoted as W_0 in this paper. Klein derived a formula which states that W_0 should be about three times the band gap of the semiconductor. A large number of semiconductors have been found to agree with this formula.[5] For *a*-Se, which has a band gap of about 2.3 eV (Ref. 6) (some authors have used the value 2.4 eV), Klein's formula predicts a W_0 of about 7 eV. (2.3 eV corresponds to the energy of a photon with a wavelength of 540 nm). However, experiments have found that the average energy required to create a free electron and a free hole in *a*-Se is not only much larger than 7 eV, but also depends on the applied electric field E.[7] For example, at $E=10$ V/μm, each measured electron-hole pair corresponds to about 50 eV deposited x-ray energy. This apparent disagreement with Klein's formula can be reconciled by assuming that, in *a*-Se, some of the electron-hole pairs recombine before they have a chance to separate into a free electron and a free hole, and hence are not measured by experiments. Indeed, electron-hole pairs created in *a*-Se by optical photons are known to have a tendency to recombine, probably within 10^{-11} s,[8] through the so-called geminate recombination mechanism,[9–12] and the probability of recombination is a function of applied electric field. It is reasonable to expect that in *a*-Se electron-hole pairs created by x-rays or other high-energy radiations will also recombine. A difference between optical and x-ray photons is that, due to its limited energy, an optical photon can create only a single electron-hole pair in *a*-Se, while an x-ray photon can create thousands of electron-hole pairs through an electron cascade. In the optical regime the photogeneration efficiency η is usually defined as the number of measured electron-hole pairs per absorbed photon. More generally, we can define the photogeneration efficiency η as the fraction of electron-hole pairs which do not recombine relative to all the electron-hole pairs created. This more general definition of η can apply to both optical and x-ray photons. We denote W as the average energy deposited per freed electron-hole pair, to distinguish from W_0, which is the average energy deposited per created electron-hole pair. They are related by

$$W=\frac{W_0}{\eta}\ . \tag{1}$$

The large value of W and its dependence on the electric field E for x-ray photogeneration in *a*-Se are consistent with the assumption that, similar to the optical photogeneration in *a*-Se, the presence of recombination leads to a photogeneration efficiency η less than 1 and dependent on electric field.

While there should be no dispute that recombination of electron-hole pairs created by x rays is present in *a*-Se, the mechanism by which the electron-hole pairs recombine is not well understood. In the optical regime, the recombination mechanism is known to be the geminate

recombination described by the Onsager theory.[9-12] It seems natural to assume that the same recombination mechanism also applies to electron-hole pairs created by x rays. After all, geminate recombination has been found to be responsible for the recombination of electron-hole pairs created by both optical and x-ray photons in at least one other material, i.e., anthracene.[13,14] However, it has been argued that geminate recombination is not applicable to electron-hole pairs created in *a*-Se by high-energy radiations, and another mechanism called the columnar (or track) recombination has been invoked.[15-17] In this paper we examine this argument and the predictions of the two recombination mechanisms. We find that the argument which dismissed the Onsager theory of geminate recombination is unwarranted, and that the Onsager theory is generally consistent with experimental data, while the columnar recombination theory is not.

II. GEMINATE VS COLUMNAR RECOMBINATION

As pointed out by Hughes,[13] there has been a long history of controversy between the geminate and columnar recombination mechanisms in different circumstances. The initial controversy arose in the early years of this century in the explanation of the generation of ion pairs in high pressure gases by high-energy electrons or x rays. It was settled after Onsager's 1938 paper[12] demonstrated that the experimental results favored the geminate over the columnar recombination mechanism. In the late sixties and early seventies, the same controversy occurred in the study of the generation of electron-hole pairs in anthracene by ionizing radiation. It was settled after Hughes[13] performed an experiment using pulsed x rays and showed that the results supported the geminate recombination mechanism. Anthracene and *a*-Se both have low mobilities, a common signature for materials where the geminate recombination mechanism is applicable. The geminate recombination mechanism has also been found to be applicable to the x-ray photogeneration in poly-*n*-vinylcarbazole (PVK),[14] which, like *a*-Se, is an amorphous material.

Given the above context and that geminate recombination is the established recombination mechanism for electron-hole pairs created in *a*-Se by optical photons, it is alarming to see an argument which claims that geminate recombination is not the correct recombination mechanism for electron-hole pairs created in *a*-Se by high-energy radiations. This argument was presented in some detail by Hirsch and Jahankhani[15] in their paper on the experimental carrier yield in *a*-Se under electron bombardment. Others have developed theoretical models based on the assumption that geminate recombination is absent.[16,17] The theoretical argument was critical in the interpretation of Hirsch and Jahankhani's experimental data in relation to the Onsager theory of geminate recombination. Therefore it is important to examine the assumptions used in this argument.

An optical photon has enough energy to create only one electron-hole pair. The electron-hole separation is determined by the excess kinetic energy of the electron-hole pair, which in turn depends on how much energy the photon has above the minimum energy required to create an electron-hole pair. For optical photogeneration, the electron-hole separation r_0 is a key parameter in the Onsager theory of geminate recombination, and the photogeneration efficiency is a sensitive function of r_0.[9] Hirsch and Jahankhani[15] noted that, unlike excitation by monochromatic optical photons, where we can expect a δ-function-like distribution of the excess kinetic energy among electron-hole pairs, a high-energy radiation should result in a broad distribution. Physically, in the case of x-ray absorption, the x ray first creates a very energetic primary electron, which in turn creates many electron-hole pairs through random collisions. During each collision, the amount of energy transferred from the primary electron to the created electron-hole pair depends on such parameters as the energy and direction of the primary electron before the collision. These parameters vary from one collision to another, and therefore the created electron-hole pairs should have a broad distribution of excess kinetic energy. Hirsch and Jahankhani[15] also argued that (part of the argument comes from Alig and Bloom[5] in a different context) there is a nonzero minimum excess kinetic energy for electron-hole pairs. This translates to a minimum electron-hole separation, and sets a lower limit on the carrier generation efficiency in the Onsager theory of geminate recombination. Hirsch and Jahankhani's experimental data suggested a carrier generation efficiency lower than the expected limit, and the Onsager theory was dismissed.

The argument goes as follows. It is assumed that the primary electron, and the electron and hole created after collision, all have the same mass. If before collision the primary electron has momentum P, and its kinetic energy E_I corresponds to the ionization threshold, i.e., the minimum energy required to create an electron-hole pair, then by conservation of momentum in free space the momenta of the three particles after collision must be collinear and of magnitude $P/3$. Since the kinetic energy is proportional to the square of the momentum, it follows that after collision each particle has kinetic energy $E_I/9$, and the minimum kinetic energy of an electron-hole pair is $2E_I/9$. The electron-hole pair is created by exciting an electron in the valence band across the band gap E_g. By energy conservation, the total kinetic energy of three particles after collision plus the energy gap E_g must equal to the kinetic energy of the primary electron before collision, i.e., $E_I/3+E_g=E_I$, or

$$E_I=\tfrac{3}{2}E_g \ . \tag{2}$$

The minimum kinetic energy of the electron-hole pair $2E_I/9$ is then equal to $E_g/3$. Using 2.4 eV for E_g, Hirsch and Jahankhani noted that the minimum kinetic energy of the electron-hole pair is 0.8 eV, which corresponds to an electron-hole pair created by a 3.2-eV photon (390-nm wavelength) across a 2.4-eV band gap. However, as the electric field decreased, they found that the observed yield (which should be proportional to η) decreased much faster than the η curve of the Onsager theory[9] for a photon with comparable energy, leading to the dismissal of the Onsager theory of geminate recom-

bination.

The above argument used many assumptions. A serious flaw of the argument is the use of the momentum-conservation law in free space. This may be valid for a crystalline solid where the momentum is conserved within a reciprocal-lattice vector, but in an amorphous solid like a-Se the momentum is generally not conserved, because the wave vector is not a good quantum number for a nonperiodic lattice. If the need for momentum conservation is eliminated, the minimum kinetic energy of the electron-hole pair becomes zero, instead of $2E_I/9$. In the Onsager theory for optical photogeneration, the rate of decrease of η is very sensitive to the photon energy, or the kinetic energy of the electron-hole pair. As the kinetic energy of the electron-hole pair approaches zero, the rate of decrease of η becomes larger than the rate of decrease of the observed yield. The dismissal of the Onsager theory of geminate recombination then becomes unwarranted, because the rate of decrease of the observed yield is now within the range of possible values in the Onsager theory. Also, in general, the electron mass and the hole mass in a solid are different, and it is not known whether the masses are equal in a-Se. If they are not equal, the minimum kinetic energy of the electron-hole pair can be reduced even if the momentum is conserved as in free space.

In order to further distinguish the geminate and columnar recombination mechanisms, we examine the predictions of the two recombination mechanisms in comparison with experiments. The Onsager theory of geminate recombination for optical photogeneration as presented by Pai and Enck[9] uses a δ-function distribution for the electron-hole separation. Before we can compare the predictions to experiments, the theory need to be extended to account for a broad distribution of electron-hole separations. This will be done in Sec. III. Here we examine the predictions of the columnar recombination theory.

The columnar recombination theory[18] predicts that the yield behaves differently at high and low electric fields. In a region below a critical field, the yield should be independent of the field, and approximately proportional to the temperature T. Above the critical field, the yield should vary linearly with both the field and energy of the radiation, and should be independent of the temperature T. Hence the yield versus field curve should have a corner which corresponds to the critical field. The critical field is expected to be

$$E_c \approx \frac{kT}{eR_0} , \tag{3}$$

where R_0 is the radius of the track of created charge carriers, k the Boltzmann constant, and e the unit charge. These predictions have the following inconsistencies with experiments.

First, from the value of the critical field, the value of R_0 can be estimated from (3). The yield versus field curve obtained by Hirsch and Jahankhani shows no corner, and the yield decreases approximately linearly with decreasing field all the way down to the lowest field data point, at about 2.5 kV/cm. This means that if the columnar recombination is applicable, the critical field must be less than 2.5 kV/cm, and the track radius R_0 in a-Se should be at least 1000 Å. This is to be compared with the R_0 value in anthracene, which is expected to be less than 160 Å.[19] However, we should expect the R_0 value in a-Se to be smaller than that in anthracene, which is an aromatic hydrocarbon solid, because a-Se has higher atomic number and density.

Second, if the columnar recombination is applicable, then the nearly linear yield obtained by Hirsch and Jahankhani suggests that the data points were taken in the high-field regime, where the yield is expected to be independent of temperature. In fact, Hirsch and Jahankhani observed that, from −77 to 20 °C, the yield more than doubled, varying with temperature slightly faster than linearly. However, they did not recognize that this disagrees with the prediction of the columnar recombination theory.

III. PHOTOGENERATION IN a-SE

In order to extend the Onsager theory of geminate recombination in a-Se from the optical regime to the x-ray regime, it is necessary to provide some background of the theory for optical photons. Each absorbed optical photon creates one electron-hole pair in a-Se. The excess kinetic energy carried by the electron or hole is not sufficient to generate secondary electrons or holes, and is presumed to be dissipated by exciting phonons.[20] The process by which the electron-hole pair loses excess energy and reaches an equilibrium state is called the thermalization process. After the electron-hole pair is thermalized, the electron and hole are separated by a distance r, at an angle θ with the applied electric field E. According to the Onsager theory, such a thermalized pair can either recombine (geminate recombination), or escape their mutual Coulomb attraction and separate into a free electron and a free hole. The probability of escaping geminate recombination is[9]

$$p(r,\theta,E)=e^{-A-D}\sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\frac{A^m}{m!}\frac{D^{m+n}}{(m+n)!} , \tag{4}$$

where $A=e^2/(\epsilon rkT)$, $D=eEr(1+\cos\theta)/(2kT)$, and ϵ is the relative dielectric constant. If there is a distribution of separation between the electron and the hole represented by $g(r,\theta)$, the photogeneration efficiency is given by

$$\eta=\int p(r,\theta,E)g(r,\theta)d^3r . \tag{5}$$

Pai and Enck[9] found that the experimental data on optical photogeneration in a-Se can be explained satisfactorily by using a δ-function distribution for the electron-hole separation,

$$g(r,\theta)=\frac{1}{4\pi r_0^2}\delta(r-r_0) , \tag{6}$$

where r_0 is a function of the photon energy, and is determined by fitting the calculated η with experimental data. From (4) to (6) η is found to be

$$\eta = e^{-a-b}\frac{1}{b}\sum_{m=0}^{\infty}\frac{a^m}{m!}\sum_{n=0}^{\infty}\sum_{l=m+n+1}^{\infty}\frac{b^l}{l!}\ , \tag{7}$$

where $a=e^2/(\epsilon r_0 kT)$ and $b=eEr_0/(kT)$. Que[21] has shown that the triple summation in Eq. (7) can be reduced to a single summation,

$$\eta = e^{-a-b}\frac{1}{b}\sum_{l=1}^{\infty} l\left[\frac{b}{a}\right]^{l/2} I_l(2\sqrt{ab})\ , \tag{8}$$

where I_l are modified Bessel functions. More generally, for any isotropic distribution $g(r,\theta)=g(r)$, Eq. (8) can be replaced by the formula[21]

$$\eta = 4\pi\frac{kT}{eE}\sum_{i=1}^{\infty} i\left[\frac{\epsilon E}{e}\right]^{i/2} I_i(2\sqrt{AB}) \times\int_0^{\infty} g(r)r^{i+1}e^{-A-B}dr\ , \tag{9}$$

where $B=eEr/(kT)$. To first order in E, Eq. (9) can be expanded as

$$\eta \approx 4\pi\left[1+\frac{e^3E}{2\epsilon k^2T^2}\right]\int_0^{\infty} g(r)r^2e^{-A}dr\ . \tag{10}$$

This result means that, at low electric field, the η vs E curve should be approximately linear, with a slope to intercept ratio

$$R_{\rm SI}=\frac{e^3}{2\epsilon k^2T^2}\ . \tag{11}$$

Equivalently, from Eq. (1), the W versus E curve should have a slope to intercept ratio equal to minus the above $R_{\rm SI}$, because W_0 is independent of E. As has been noted previously, $R_{\rm SI}$ is independent of the electron-hole separation r,[14] or the form of the distribution function $g(r)$. The only parameters that affect $R_{\rm SI}$ are the dielectric constant ϵ and temperature T. It will become clear below that this prediction for the value of $R_{\rm SI}$ is applicable to both optical and x-ray photogeneration and can serve as a robust test for the theory. For a-Se the dielectric constant is $\epsilon=6.3$; at $T=300$ K the expression in (11) is equal to $R_{\rm SI}=1.7\times10^{-5}$ cm/V.

For photon wavelengths ranging from 400 to 620 nm, Pai and Enck[9] found that r_0 obtained by fitting experimental data varies from 7.0 to 0.84 nm. The electron-hole separation r_0 for a given photon energy can also be calculated using the approach of Knights and Davis.[20] Knights and Davis assumed that, during the thermalization process, the motion of the carriers is diffusive, and the rate of energy dissipation to phonons is $h\nu_p^2$, where ν_p is the phonon frequency. They deduced that the thermalization time is given by the excess kinetic energy, measured from the local Coulomb potential, divided by $h\nu_p^2$. On the other hand, the thermalization time t is related to the separation r_0 and the diffusion constant D through the relation $r_0=(Dt)^{1/2}$. Hence Knights and Davis arrived at the following equation for r_0:

$$t=\frac{r_0^2}{D}=\frac{h\nu-E_g+\dfrac{e^2}{\epsilon r_0}+eEr_0\cos\theta}{h\nu_p^2}\ . \tag{12}$$

Considering the simplifications in deriving the above equation to describe a complicated thermalization process, we can expect that r_0 and t calculated from Eq. (12) are only rough estimates. Pai and Enck[9] obtained order-of-magnitude agreement between r_0 calculated from (12) and that from fitting experimental data.

In passing, we note that in principle, r_0 is a function of θ, as (12) indicates. But in practice, the term $eEr_0\cos\theta$ is usually small. To be more specific, the order of magnitude of r_0 is typically a few nm, and a typical operating electric field used for a-Se is 10 V/μm. This implies that $eEr_0\cos\theta$ is of the order of 0.01 eV, while the $e^2/(\epsilon r_0)$ term is of the order of 0.1 eV. Hence, at this level of field

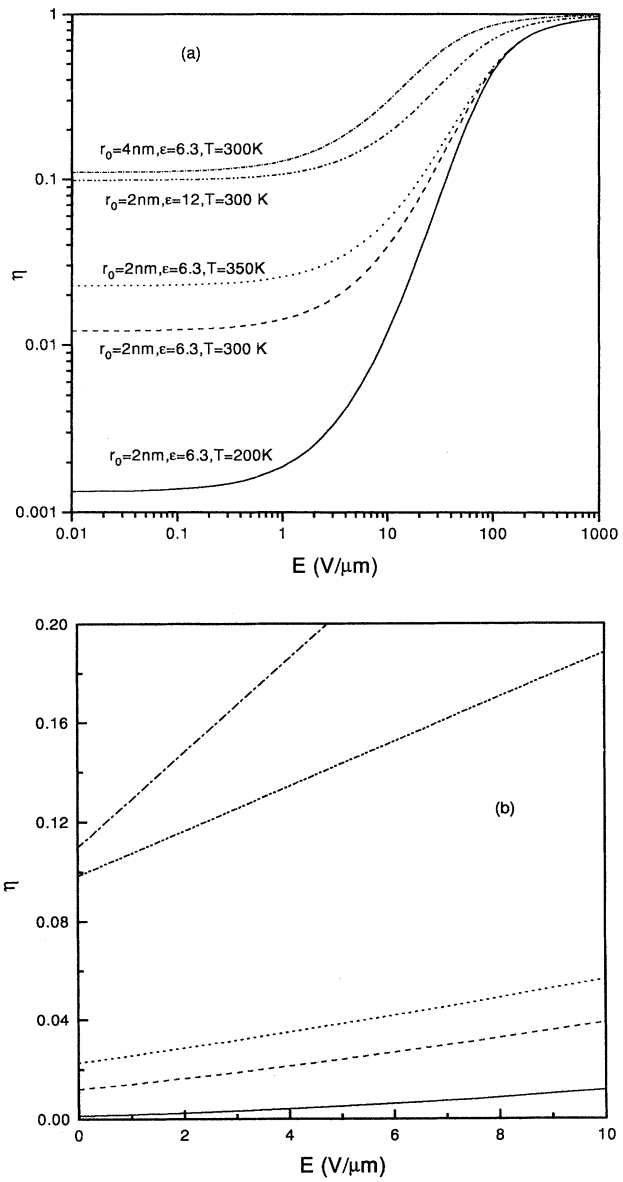

FIG. 1. (a) Optical photogeneration efficiency calculated from the Onsager theory. Note that $\epsilon=6.3$ corresponds to the dielectric constant of a-Se, while $\epsilon=12$ corresponds to the dielectric constant of Si. (b) Low-field part of (a) on linear scales.

strength, the anisotropy in $g(r,\theta)$ due to the field should be negligible. Indeed, all calculations of the Onsager photogeneration efficiency in the literature have used isotropic $g(r,\theta)$.[11]

Examples of the photogeneration efficiency η calculated from the Onsager theory using (7) or equivalently (8) are shown in Fig. 1. In the log-log plot in Fig. 1(a), a characteristic feature of the curves is that, at low electric fields, the photogeneration efficiency η saturates; in a linear plot, as in Fig. 1(b), this is reflected as nonzero intercepts of the curves on the vertical axis. This feature was in disagreement with early experiments on optical photogeneration in a-Se, but was confirmed by later experiments which were designed to eliminate surface effects.[9] We note from the figure that increasing the dielectric constant ϵ or the separation r_0 can both significantly enhance the photogeneration efficiency η. Raising the temperature can also improve η.

While an optical photon can produce only one electron-hole pair in a-Se, and hence a δ-function distribution for the electron-hole separation as in (6) is appropriate, an x-ray photon can produce thousands of electron-hole pairs with many different electron-hole separations. Thus we should use a distribution function $g(r,\theta)$ which reflects this point. We expect that the shape of the distribution function should not be sensitive to the x-ray photon energy, because the electron-hole pairs are created in a random fashion. This means that the x-ray photogeneration efficiency η or W should be insensitive to the x-ray photon energy, in contrast to the case of optical photons. Indeed, apart from one anomalous result,[22] which we will discuss in Sec. IV, all experiments[23,7] have found that W is independent of the x-ray energy.

In the x-ray regime, experiments usually measure W instead of η. W is found to be a function of the electric field E. At $E=10$ V/μm, most experiments seem to produce a W value around 50 eV.[7] Provided the value of W_0 is known, we can calculate W using Eqs. (1) and (9) to compare with experimental values. Klein's formula states that

$$W_0=2.8E_g+rh\nu_p \ , \tag{13}$$

where the last term is a phonon contribution and is between 0.5 and 1 eV. In this paper we use the intermediate value 0.75 eV for this term. Alig and Bloom[5] have presented a derivation of this formula as follows. Apart from the phonon contribution term, the average energy required to create an electron-hole pair W_0 should be equal to the band gap E_g plus the average kinetic energy of an electron-hole pair. The kinetic energy of an electron or a hole is assumed to vary from 0 to E_I, where E_I is the threshold energy required for creating an electron-hole pair. (Note that Alig and Bloom used 0, not $E_I/9$ as the minimum kinetic energy, in contrast to Hirsch and Jahankhani.) The density of states of the electron or hole is assumed to be proportional to $E_k^{1/2}$, where E_k is the kinetic energy. With these assumptions, W_0 is found to be

$$W_0=E_g+2\frac{\int_0^{E_I}E_k^{3/2}dE_k}{\int_0^{E_I}E_k^{1/2}dE_k}=E_g+\tfrac{6}{5}E_I \ , \tag{14}$$

where the factor of 2 in front of the integrals accounts for the number of particles in an electron-hole pair. Using $E_I=\frac{3}{2}E_g$ as in Eq. (2) derived by assuming momentum and energy conservation, (14) becomes $W_0=E_g+\frac{9}{5}E_g=2.8E_g$, or Eq. (13) before the phonon term is added.

As we mentioned above, for an amorphous solid the momentum does not need to be conserved. Hence $E_I=\frac{3}{2}E_g$ can be replaced by $E_I=E_g$, and we obtain

$$W_0=2.2E_g+rh\nu_p \tag{15}$$

for amorphous solids instead of Eq. (13). For $E_g=2.3$ eV, the bandgap for a-Se, Eq. (13) gives $W_0=7.19$ eV, while Eq. (15) gives $W_0=5.81$ eV. However, the derivation of Klein's formula is not a strict derivation and should not be taken literally, because it uses assumptions such as equal mass for electron and hole, a density of states proportional to the square root of energy, etc., which may not hold at all. As a result Klein's formula is generally viewed as an empirical relation rather than as a relation derived from first principles. From this viewpoint it is perhaps not necessary to replace Klein's formula by Eq. (15) in the case of amorphous solids. Alig and Bloom's paper[5] lists many solids well served by Klein's formula, generally crystalline solids. The only amorphous solid whose values of W_0 and E_g we are aware of is amorphous Si, with $W_0=4.8$ eV and $E_g=1.7$ eV.[24] With the phonon contribution in Eq. (13) assumed to be 0.75 eV, Klein's formula gives $W_0=5.5$ eV, while Eq. (15) gives $W_0=4.5$ eV, in better agreement with the experimental result. While we feel that this is a suggestive result, more evidence is needed before we can conclude that for amorphous solids (15) is generally better than Klein's formula.

The exact form of $g(r,\theta)$ for electron-hole pairs created in a-Se by x rays is not known. We have tried several different forms of $g(r,\theta)$ to see how sensitively the calculated results for η and W depend on the details of $g(r,\theta)$. In Fig. 2 we show a family of curves using the distribution function

$$g(r,\theta)=cr^n\exp[-r/R] \ , \tag{16}$$

where $c=1/[R^{n+3}4\pi(n+2)!]$ is determined from the normalizing condition

$$\int g(r,\theta)d^3r=1 \ . \tag{17}$$

For each n, parameter R is determined by fixing W to be 54 eV at $E=10$ V/μm. The value of W_0 is chosen to be 7.19 eV in all our calculations. As n increases from zero, the peak of the distribution in (16) located at $r=nR$ shifts to larger r values. We see that for different exponents n, the curves for W change very little, suggesting that the details of the shape of $g(r,\theta)$ are not critical to the W versus E curve.

The distribution in (16) has a long tail extending to

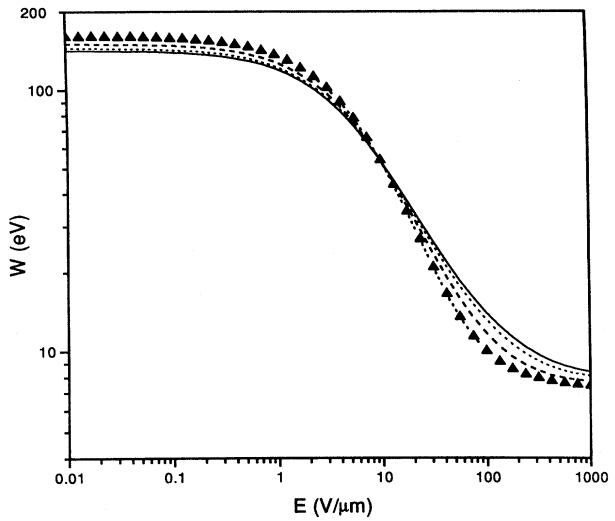

FIG. 2. Calculated W using the distribution function $g(r,\theta)=cr^n\exp(-r/R)$. Solid curve: $n=0$ ($R=0.862$); dotted curve: $n=1$ ($R=0.659$); dashed curve: $n=5$ ($R=0.3411$). For comparison, the triangle curve is obtained by using the δ-function distribution in (6) with $r_0=2.844$. $T=300$ K.

infinity in r. According to Knights and Davis,[15] r is the electron-hole separation resulting from the diffusion of carriers within a finite thermalization time. Therefore there should be an upper bound on the value of r, and $g(r,\theta)$ should be zero beyond the maximum possible r. Thus in order to perform a more realistic calculation of W, we calculate $g(r,\theta)$ from a given kinetic-energy distribution of electrons and holes by using a modified version of Knights and Davis's Eq. (12). The kinetic-energy distribution of electrons and holes is denoted by $G(E_k)$, and E_k runs between 0 and E_I. E_I is chosen to be $1.5E_g$.[4] Anisotropy in $g(r,\theta)$ is neglected by using an isotropic $g(r)$. The relationship between $G(E_k)$ and $g(r)$ is

$$g(r)=\frac{G(E_k)}{4\pi r^2}\frac{dE_k}{dr} . \tag{18}$$

Similar to (12), we determine r from E_k through the equation

$$\frac{r^2}{D}=\frac{E_k+\frac{e^2}{\epsilon r}+eEr}{h\nu_p^2}=t . \tag{19}$$

The diffusion constant D is calculated from the Einstein relation[25] $D=\mu kT/e$, and the hole mobility $\mu_h=0.14$ $\text{cm}^2/\text{s V}$ is used for μ because the electron mobility $\mu_e=5\times10^{-3}$ $\text{cm}^2/\text{s V}$ is negligible in comparison.[6] As for the phonon frequency ν_p, we note that experiments have reported phonon energies at 10.8, 15.3, and 32.4 meV.[26] We use the intermediate value $h\nu_p=15$ meV, and expect reasonable results.

For $G(E_k)$ we assume a Gaussian distribution

$$G(E_k)\propto\exp[-(E_k/E_c)^2] \tag{20}$$

for E_k between 0 and E_I, and 0 otherwise. By fixing $W=54$ eV at $E=10$ V/μm, the parameter E_c is determined to be 2.067 eV. The calculated W and η are shown in Fig. 3. Similar to Fig. 2, W saturates at low fields. Available experimental results on W in a-Se cover only a small range of electric field strength compared to Fig. 3; as a result experimental W versus E curves on a log-log plot can be approximated by a straight line, implying a power law $W\propto E^{-\alpha}$ with α in the range from 0.67 to 0.8.[7] If we use the power law $W\propto E^{-\alpha}$ to fit the section of our theoretical curve around $E=10$ V/μm in Fig. 3, we obtain $\alpha=0.613$, slightly smaller than experimental values but still within the error bars.

We find that no matter what $G(E_k)$ or $g(r)$ we use, as long as W is normalized to 54 eV at $E=10$ V/μm, all W versus E curves are very similar. As we have pointed out in Sec. II, the slope to intercept ratio of the W versus E

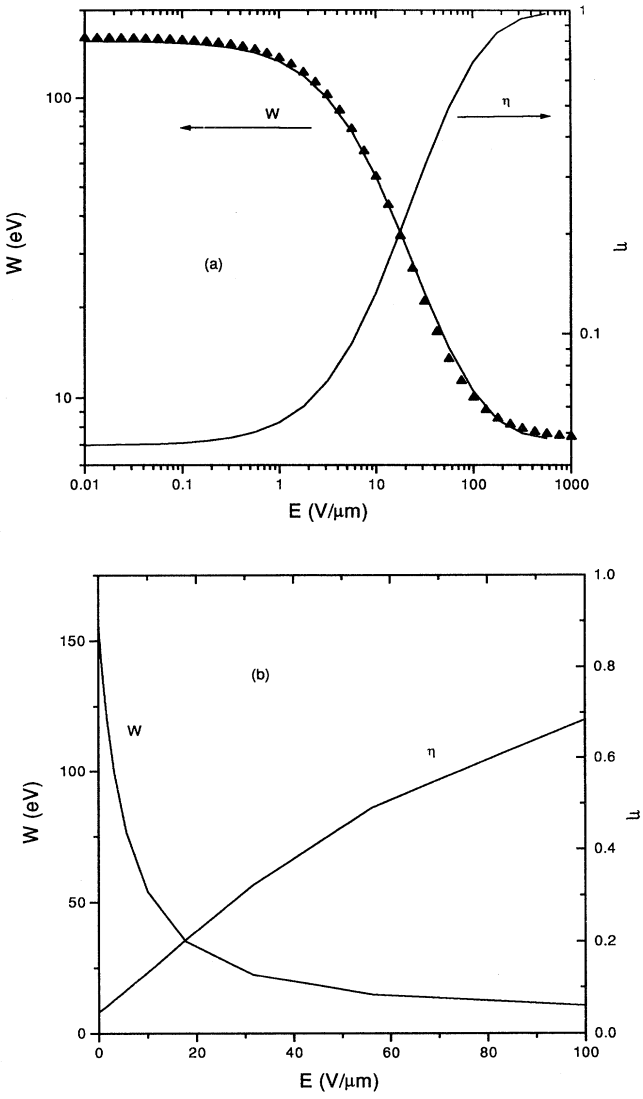

FIG. 3. (a) Calculated W and η using (19) and (20). For comparison, the triangle curve is W obtained by using the δ-function distribution in (6) with $r_0=2.844$. $T=300$ K. (b) The low electric-field part plotted on linear scales.

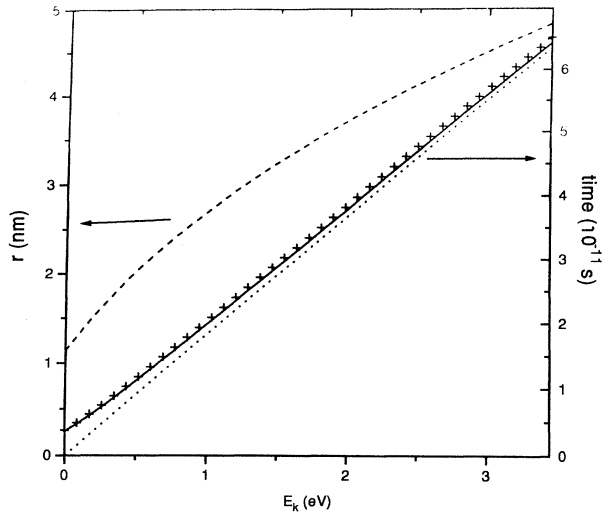

FIG. 4. The electron-hole separation r (upper dashed curve) and the thermalization time at $E=0$ (solid curve) and 10 V/μm (cross curve) calculated from (19). The dotted line corresponds to $E_k/h\nu_p^2$ to show the effect of the terms $e^2/(\epsilon r)+eEr$ in (19). $T=300$ K.

curve is independent of the form of $g(r)$. This suggests that the Onsager theory can be tested in two ways: by comparing the experimental slope to intercept ratio with theory if reliable low-field data can be obtained, or by comparing the experimental W versus E curve with Fig. 3 over a wide range of electric-field strengths.

Figure 4 shows the electron-hole separation r, and the thermalization time $t=r^2/D$ from $E_k=0$ to E_I, calculated using (19). We see that r is a few nm in magnitude, in comparison with the fitted r_0 by Pai and Enck[9] ranging from 0.84 to 7 nm for optical photons. The calculated thermalization time is of the order of 10^{-11} s. We also see in Fig. 4 that the thermalization time is almost a linear function of E_k.

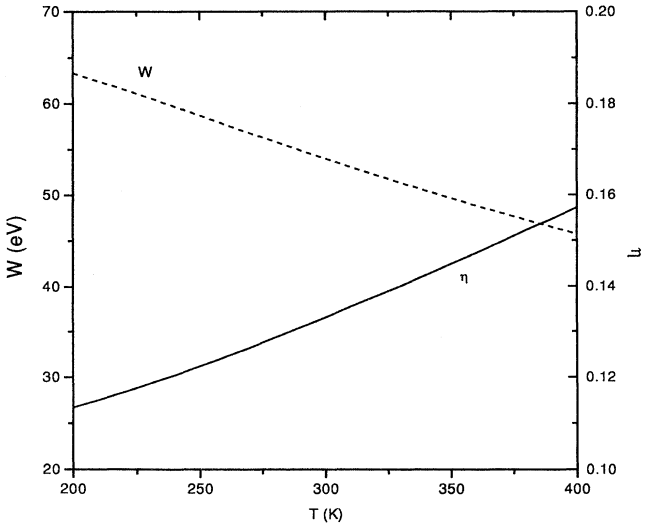

FIG. 5. Temperature dependence of W and η at $E=10$ V/μm.

In Fig. 5 we show the temperature dependence of W and η at $E=10$ V/μm. In our calculation we have assumed that the mobility has a temperature dependence[10] $\mu \propto T^{-3/2}$. As the temperature increases, η increases slightly faster than linearly, consistent with the experimental data on the carrier yield[15] which should be proportional to η.

IV. DISCUSSION

The theoretical results of the geminate recombination theory presented in Sec. III are generally consistent with experiments, with one exception. If geminate recombination is applicable, we expect W to be insensitive to the x-ray energy. Fiedler and Laugwitz[22] reported that they found W to be inversely proportional to the x-ray energy. When the x-ray energy increased from 30 to 200 keV, their measured W decreased by an order of magnitude. However, their results also disagree with other experiments,[23,7] which found that W was independent of the x-ray energy. Although the other experiments covered a smaller energy range, W still should have changed by a factor about 2–3 if Fiedler and Laugwitz's results are real. In any case, further experiments on the energy dependence of W would be useful. If the results of Fiedler and Laugwitz are confirmed, the Onsager theory of geminate recombination can be ruled out. However, this will not automatically save the columnar recombination theory. Although the columnar recombination theory does predict that in the high-field regime W is inversely proportional to the x-ray energy, it also predicts that W is independent of temperature, in contradiction with Hirsch and Jahankhani's data which implied that W is roughly inversely proportional to temperature. Further experiments to determine the temperature dependence of W would be welcome. From all the evidence currently available, the geminate recombination theory appears more convincing.

We can summarize our understanding of the x-ray photogeneration in a-Se as follows. An x-ray photon absorbed in a-Se creates many electron-hole pairs. The electrons and holes have a distribution of excess kinetic energy. This excess kinetic energy is dissipated through phonons during the thermalization time of about 10^{-11} s, during which the motion of the carriers is diffusive. The electron-hole separation of each pair at the end of the thermalization period is dependent on the amount of the initial excess kinetic energy. The average energy required to create an electron hole pair is W_0, which is about 7 eV in a-Se according to Klein's formula. Hence a 70-keV x-ray photon should create about 10 000 electron-hole pairs. However, due to geminate recombination, only a fraction of the pairs, represented by the photogeneration efficiency η, dissociate to become free carriers and contribute to photoconductivity. The average energy required to create a pair of free electron and hole is $W=W_0/\eta$, which is dependent on the electric field and temperature. The pairs that undergo geminate recombination first form charge neutral excitons,[27,28] which then recombine nonradiatively (through interaction with

phonons) with a lifetime of about 10^{-11} s.[8]

According to our understanding of x-ray photogeneration in *a*-Se, the sensitivity, which is inversely proportional to W, could possibly be improved in several ways: (a) enhancing the hole mobility to achieve larger thermalization distance r, e.g., through doping; (b) enhancing the dielectric constant through material engineering; (c) increasing the temperature; and (d) increasing the operating electric field. Among these, (d) has the potential of reducing W from about 50 eV at $E = 10$ V/μm to a W value about 12 eV at $E = 80$ V/μm, enhancing the sensitivity by a factor of 4. (For $E > 80$ V/μm, avalanche starts to occur in *a*-Se.) However, to achieve this, one must overcome the problem of dark current which also increases with electric field.

In conclusion, we have found that currently available experimental data on carrier generation in *a*-Se by high-energy radiation are generally consistent with the Onsager theory of geminate recombination, and that the previous argument which dismissed this theory is unwarranted. Experimental data on the temperature dependence of the yield in *a*-Se are inconsistent with columnar recombination. The energy dependence of W reported by Fiedler and Laugwitz is inconsistent with the Onsager theory of geminate recombination, but is also inconsistent with the experimental results of others. More experiments on the energy and temperature dependence of W will help clarify the controversy among the two competing theories. It will be particularly useful to obtain an experimental W versus E curve and its slope to intercept ratio to compare to the predictions of the Onsager theory of geminate recombination.

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