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Invited Lecture

Radiative lifetime of excitons in chalcogenide glasses

JAI SINGH
Lawrence Berkeley National Laboratory, Berkeley, CA94720, USA
(On leave from School of Engineering and Logistics, B-41, Faculty of Technology, Charles Darwin University, Darwin, NT 0909, Australia)

The radiative lifetime of triplet excitons, is studied here for the first time theoretically in chalcogenide glasses. A new time-dependent exciton-spin-orbit-photon interaction operator is derived and rates of radiative recombination of triplet excitons and corresponding radiative lifetimes are calculated in three chalcogenide glasses, a-As_2S_3, a-As_2Se_3 and a-Se. Results agree quite well with the experimental results. The theory is quite general and can be applied to any amorphous materials, including organics.

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1. Introduction

Photoluminescence and electroluminescence have recently become very active areas of research for their applications in light emitting devices (LEDs) [1]. Photoluminescence (PL) from singlet excitons has been studied extensively in inorganic crystalline [2-4] and amorphous semiconductors [5-8] but not as much from triplet excitons. However, there has been much research interest in studying the triplet states and their optical properties in organic semiconductors about four decades ago [9-13]. In inorganic crystals, like Si, Ge, GaAs, etc., excitons are regarded to be the long radii orbital excitons so the exchange interaction between the excited electron and hole being of short range nature is neglected. It is the exchange interaction that contributes to the additional binding energy to the triplet excitons. Therefore, its neglect in inorganic crystals gives the same binding energy for both singlet and triplet excitons. and triplet excitons are not distinctively observed in crystalline inorganic semiconductors except in alkali halide crystals [14-15]. In inorganic amorphous semiconductors, like a-Si:H , a-Ge:H and chalcogenide glasses, however, triplet excitons have been observed [1] and also they have been observed in organic light emitting devices [16-18].

Recently Aoki et al. [19-20] have used the dual phase and double lock (DPDL) quadrature frequency resolved spectroscopy (QFRS) technique to measure PL spectra in chalcogenide glasses, like a-As_2Se_3, g-As_2S_3 and a-Se. Three peaks have been observed at a temperature of 37 K on the time resolved scale in amorphous As_2S_3 (a-As_2S_3 also called granular denoted by g-As_2S_3) and a-Se , one in the short time range of 10^{-9} – 10^{-7} s, second in the time range of 10^{-4} s and the third in the seconds range. Only two peaks have been observed in a-Se_2Se_3 ; one at 10^{-4} s and the other in the seconds time range. The short-time peak has not been observed in this material. A PL of three peaks structure has also been observed in a-Si:H and a-Ge:H [21]. The short-time peak is assigned to the PL from the singlet excitons. As the radiative transition from a singlet is spin allowed the rate of spontaneous emission becomes quite high, resulting into a shorter lifetime. The second peak, in the 10^{-4} s time range, is assigned to PL from triplet excitons. A triplet exciton recombination is spin forbidden, so the rate of spontaneous emission becomes very small and the corresponding radiative lifetime becomes longer. This recombination can only occur through the involvement of the spin-orbit interaction. The third peak is assigned to the PL from non-geminate (distant) pair recombination. It is well established that the occurrence of such peak structures in the PL cannot be explained on the basis of the RT model [8,22]. A theory for the radiative recombination of singlet excitons has recently been developed [23-24] and also the radiative lifetime of geminate and non-geminate (or distant) pairs have been calculated theoretically [25-26]. However, to the author’s knowledge no theoretical attempts have been made in calculating the rate of radiative recombination of triplet excitons in amorphous chalcogenide glasses.

In this paper, a theory for calculating the rate of spontaneous emission from the radiative recombination of a triplet exciton in amorphous chalcogenides (a-Chs) glasses is presented. A new time dependent exciton-spin-orbit- photon interaction operator derived recently [27] is used for amorphous solids and the rate of spontaneous emission is calculated by applying the first order perturbation theory. Assuming that the observed PL peak and the maximum of the rate of spontaneous emission occur at the same energy, the radiative lifetime is calculated from inverse of the rate of spontaneous emission calculated at the PL peak energy. The theory is then applied to a-As_2Se_2, a-As_2S_3 and a-Se chalcogenides where the radiative lifetime has been measured experimentally. It is found that the calculated results agree very well with the experimental ones. The theory is general and can be applied to any amorphous semiconductors, including organic materials.

2. Exciton-photon-spin orbit interaction operator

The spin-orbit interaction operator for an electron in an atom can be written as [28]:

$$\hat{H}_{so}^{at} = -\frac{eg}{2m_e^2c^2}\mathbf{s}\cdot\mathbf{p}\times\mathbf{E} \quad , \tag{1}$$

where g is the gyromagnetic ratio (g = 2), **s** and **p** are the spin angular momentum and orbital momentum of the electron, respectively, and **E** is the electric field on the electron generated by the nucleus. If we shine light on the atom then the electron's linear momentum and electric and magnetic fields acting on the electron get modified due to the presence of the electromagnetic field and thus Eq. (1) modifies to:

$$\hat{H}_{so}^{at} = -\frac{eg}{2m_e^2c^2}\mathbf{s}\cdot(\mathbf{p}+\frac{e}{c}\mathbf{A})\times(-\frac{1}{c}\frac{\partial\mathbf{A}}{\partial\mathbf{t}}-\nabla V_n)+\frac{eg}{m_ec}\mathbf{s}\cdot\mathbf{H}\,, \tag{2}$$

where **A** is the vector potential of photons, V_n is the scalar potential of the nucleus and $\mathbf{H} = \nabla\times\mathbf{A}$ is the magnetic field of the electromagnetic radiation. The effect of radiation on the electron has been studied about four decades ago (see, e.g., review by Hameka [29]), but the change in the linear momentum due to the radiation was ignored.

Within the so called dipole approximation ($e^{i\mathbf{k}_\lambda\cdot\mathbf{r}} \approx 1$), the vector potential is given by:

$$\mathbf{A} = \sum_\lambda A_0\hat{\varepsilon}_\lambda c_\lambda^+ e^{-i\omega_\lambda t} + c.c., \tag{3}$$

where $A_0 = \left[\frac{2\pi c^2\hbar}{\varepsilon_0\omega_\lambda V}\right]^{1/2}$, $\hat{\varepsilon}_\lambda$ is the unit polarization vector, c_λ^+ is the creation operator of a photon in mode λ, ε_0 is the vacuum permittivity, ω_λ is the photon's frequency and V is the illuminated volume. In Eq. (3), *c.c.* represents the complex conjugate of the first term and it corresponds to the absorption of a photon. As we are dealing with the emission of a photon due to the radiative recombination, the second term will not be considered here.

The scalar nuclear potential V_n is given by:

$$V_n = \frac{Ze\kappa}{r_e} \quad , \kappa = 1/4\pi\varepsilon_0\text{, and}$$

$$\nabla V_n = -\frac{Ze\kappa}{r_e^3}\mathbf{r}_e \ , \tag{4}$$

where $\mathbf{r}_e$ is the position vector of the electron from the nucleus and $\left|\mathbf{r}_e\right| = r_e$. For Z > 1, the interaction between the excited electron and other valence electrons in the atom is considered to be negligible [27,29]. Within the dipole approximation we get $\nabla\times\mathbf{A} = \mathbf{0}$ due to which the magnetic contribution vanishes and also two other terms vanish as shown below:

$$\frac{e}{c^2}\mathbf{s}\cdot(\mathbf{A}\times\frac{\partial\mathbf{A}}{\partial t}) = \mathbf{0}\,, \tag{5a}$$

and

$$\frac{1}{c}\mathbf{s}\cdot\mathbf{p}\times\frac{\partial\mathbf{A}}{\partial\mathbf{t}} = -\frac{i\hbar}{c}\mathbf{s}\cdot\nabla\times\frac{\partial\mathbf{A}}{\partial\mathbf{t}} = -\frac{i\hbar}{c}\mathbf{s}\cdot\frac{\partial}{\partial t}(\nabla\times\mathbf{A}) = 0 \ . \tag{5b}$$

Substituting Eqs. (4) and (5) in Eq. (2) the interaction operator reduces to the following two non-zero terms:

$$\hat{H}_{so}^{at} = -\frac{eg}{2m_e^2c^2}(-\frac{Ze\kappa\,\mathbf{s}\cdot\mathbf{L}}{r_e^3}-\frac{e}{c}\mathbf{s}\cdot(\mathbf{A}\times\nabla V))\,, \tag{6}$$

where $\mathbf{L} = \mathbf{r}_e$ x $\mathbf{p}$ is the orbital angular momentum of electron. The first term of Eq. (6) is the usual stationary spin-orbit interaction operator obtained in the absence of radiation. Its inclusion in the Hamiltonian as a perturbation can only split the degeneracy of a triplet state. Thus, only the last term, which depends on spin, radiation and time can be considered as the time-dependent perturbation operator and hence can cause transitions. Using Eqs. (3) and (4), the last term of Eq. (6), denoted by $\hat{H}_{so}^{at(t)}$, can be written as:

$$\hat{H}_{so}^{at(t)} = -\frac{e^3gZ\kappa}{2m_e^2c^2r_e^2}\sum_\lambda(\frac{2\pi\hbar}{\varepsilon_0\omega_\lambda V})^{1/2}e^{-i\omega t}\,\mathbf{s}\cdot(\hat{\varepsilon}_\lambda\times\hat{\mathbf{r}}_e)c_\lambda^+\,, \tag{7}$$

where $\hat{\mathbf{r}}_e = \frac{\mathbf{r}_e}{r_e}$ is a unit vector. For evaluating the triple scalar product of three vectors, without the loss of any generality we may assume that vectors $\hat{\varepsilon}_\lambda$ and $\hat{\mathbf{r}}_e$ are in the xy-plane at an angle ϕ_λ, then we get $\hat{\varepsilon}_\lambda\times\hat{\mathbf{r}}_e = \sin\phi_\lambda\,\hat{\eta}$, $\hat{\eta}$ being a unit vector perpendicular to the xy-plane. This gives $\mathbf{s}\cdot(\hat{\varepsilon}_\lambda\times\hat{\mathbf{r}}_e) = \mathbf{s}\cdot\hat{\eta}\sin\phi_\lambda = s_z\sin\phi_\lambda$, which simplifies Eq. (7) as:

$$\hat{H}_{so}^{at(t)} = -\frac{e^3gZ\kappa}{2m_e^2c^2r_e^2}\sum_\lambda(\frac{2\pi\hbar}{\varepsilon_0\omega_\lambda V})^{1/2}e^{-i\omega t}\sin\phi_\lambda\,s_z\,c_\lambda^+ \ . \tag{9}$$

The above derivation for the atomic case can be easily extended to amorphous semiconductors. Here we consider a sample of amorphous semiconductor with N atoms and excited with a pair of electron and hole bound in a triplet spin configuration, electron being in the conduction band and hole in the valence band. In accordance with Eq. (1), the spin-orbit interaction for such an excited pair in a sample with N atoms can be written as:

$$\hat{H}_{so}^{a-sem} = -\frac{eg}{2\mu_x^2 c^2}\mathbf{s}_e \cdot (\mathbf{p}_e \times \sum_{n=1}^{N} \mathbf{E}_{ne}) + \frac{eg}{2\mu_x^2 c^2}\mathbf{s}_h \cdot (\mathbf{p}_h \times \sum_{n=1}^{N} \mathbf{E}_{nh}), \tag{10}$$

where $\mu_x^{-1} = m_e^{*-1} + m_h^{*-1}$ is the reduced mass of exciton, m_e^* and m_h^* are the effective masses of the electron in the conduction band and hole in the valence band, respectively. $\mathbf{E}_n = -\nabla V_n$ is the electric field on the excited electron (e) or hole (h) generated by the n^{th} nucleus in the solid. Here also the effects of electron-electron and spin-spin exchange interactions are considered to be negligible [29-30]. Other quantities with the subscript *e* represent the electron and with *h* represent the hole. In the presence of radiation, Eq. (10) becomes [27]:

$$\hat{H}_{so}^{a-sem} = -\frac{eg}{2\mu_x^2 c^2}\mathbf{s}_e \cdot (\mathbf{p}_e + \frac{e}{c}\mathbf{A}_e) \times (-\frac{1}{c}\frac{\partial \mathbf{A}_e}{\partial t} - \sum_{n=1}^{N} \nabla V_{ne}), \tag{11}$$
$$+ \frac{eg}{2\mu_x^2 c^2}\mathbf{s}_h \cdot (\mathbf{p}_h - \frac{e}{c}\mathbf{A}_h) \times (-\frac{1}{c}\frac{\partial \mathbf{A}_h}{\partial t} - \sum_{n=1}^{N} \nabla V_{nh})$$

where the zero magnetic contribution is neglected. Applying the results of Eq. (5), this can be expanded to give:

$$\hat{H}_{so}^{a-sem} = -\frac{eg}{2\mu_x^2 c^2}(-\sum_{n=1}^{N} \frac{Z_n e\kappa \mathbf{s}_e \cdot \mathbf{L}_{en}}{\varepsilon r_{en}^3} - \frac{e}{c}\mathbf{s}_e \cdot (\mathbf{A}_e \times \sum_{n=1}^{N} \nabla V_{ne})), \tag{12}$$
$$+ \frac{eg}{2\mu_x^2 c^2}(-\sum_{n=1}^{N} \frac{Z_n e\kappa \mathbf{s}_h \cdot \mathbf{L}_{hn}}{\varepsilon r_{en}^3} + \frac{e}{c}\mathbf{s}_h \cdot (\mathbf{A}_h \times \sum_{n=1}^{N} \nabla V_{nh}))$$

where ε is the static dielectric constant of the material. It may be pointed out here that the interaction operator as obtained in Eq. (12) is the same for a triplet exciton and for an excited pair of electron and hole in a triplet spin configuration. Here again we will consider only the last term within each summation to be responsible for a triplet radiative recombination. As explained earlier, the first term is only responsible for the splitting of a degenerate triplet state. In most semiconductors, usually the valence band arises from a *p*-state (l =1 and m_l = 1, 0, -1) which is triply degenerate. If one includes the first term of the hole operator in the Hamiltonian for calculating the energy eigenvalue, it splits this degeneracy [31,32]. Following the procedures applied in the atomic case and using $A_0 = (\frac{2\pi\hbar}{\varepsilon_0 \varepsilon \omega V})^{1/2}$ for a solid, the last terms of the electron and hole parts in Eq. (12) together can be denoted by $\hat{H}_{so}^{a-sem(t)}$ and written as:

$$\hat{H}_{so}^{a-sem(t)} = -\frac{e^3 g\kappa}{2\mu_x^2 \varepsilon c^2} \sum_{\lambda,n} [\frac{Z_n}{r_{en}^2}(\frac{2\pi\hbar}{\varepsilon_0 \varepsilon \omega_\lambda V})^{1/2} \sin\phi_{\lambda en}\, s_{ez} \;. \tag{13}$$
$$+ \sum_{\lambda,n} \frac{Z_n}{r_{hn}^2}(\frac{2\pi\hbar}{\varepsilon_0 \varepsilon \omega_\lambda V})^{1/2} \sin\phi_{\lambda hn}\, s_{hz}\,] e^{-i\omega_\lambda t} c_\lambda^+$$

The field operator of an electron in the conduction band can be written as:

$$\hat{\psi}_c(r_e) = N^{-1/2} \sum_{l,\sigma_e} \exp(i\mathbf{t}_e \cdot \mathbf{R}_l^e)\varphi_l(r_e, \sigma_e) a_{cl}(\sigma_e), \tag{14}$$

where $\mathbf{R}_l^e$ is the position vector of an atomic site at which the electron is created, $\varphi_l(r_e)$ is the atomic wave function of an electron at the site l , r_e is the position coordinate of the electron with respect to site l and $\mathbf{t}_e$ is given by [23]:

$$|\,\mathbf{t}_e\,| = t_e = \sqrt{\frac{2m_e^*(E_e - E_c)}{\hbar^2}}, \tag{15}$$

where E_e is the energy of the electron, E_c is that of the electron mobility edge, and $a_{cl}(\sigma_e)$ is the annihilation operator of an electron with energy E_e and spin σ_e at a site *l* in the conduction *c* band. According to Eq. (15), if the electron energy E_e is above the mobility edge, then the electron moves as a free particle in the conduction extended states but if $E_e < E_c$ the electron gets localized as t_e becomes imaginary and the envelope function becomes exponentially decreasing. Likewise the field operator, $\hat{\psi}_v(r_h)$, of a hole excited with an energy E_h and spin σ_h in the valence band can be written as:

$$\hat{\psi}_v(r_h) = N^{-1/2} \sum_{l,\sigma_h} \exp(-i\mathbf{t}_h \cdot \mathbf{R}_l^h)\varphi_l^*(r_h, \sigma_h) d_{vl}(\sigma_h),$$
$$d_{vl}(\sigma_h) = a_{vl}^+(-\sigma_h) \tag{16}$$

where

$$|\,\mathbf{t}_h\,| = t_h = \sqrt{\frac{2m_h^*(E_v - E_h)}{\hbar^2}}. \tag{17}$$

Here E_v is the energy of the hole mobility edge and $d_{vl}(\sigma_h)$ is the annihilation operator of a hole in the valence band *v* with energy E_h and spin σ_h. Here again if the hole energy is in the extended valence states ($E_h < E_v$) it moves like a free particle but if it is in the tail states ($E_h > E_v$) the hole gets localized.

Summations over spins in Eqs. (14) and (16) can be expressed for a triplet configuration between an electron and a hole as:

$$a_{cl}(+1/2)d_{vm}(+1/2) = a_{cl}(+1/2)a_{vm}^+(-1/2) \tag{18a}$$

$$\frac{1}{\sqrt{2}}[a_{cl}(+1/2)d_{vm}(-1/2) - a_{cl}(-1/2)d_{vm}(+1/2)] =$$
$$\frac{1}{\sqrt{2}}[a_{cl}(+1/2)a_{vm}^+(+1/2) - a_{cl}(-1/2)a_{vm}^+(-1/2)] \tag{18b}$$

$$a_{cl}(-1/2)d_{vm}(-1/2) = a_{cl}(-1/2)a_{vm}^+(+1/2) \tag{18c}$$

Using Eqs. (14), (16) and (18) the interaction operator in Eq. (13) can be written in second quantisation as:

$$\hat{H}_{so}^{a-sem(t)} = -\frac{\hbar e^3 g\kappa}{4\mu_x^2\,\varepsilon c^2} N^{-1} \sum_{l,m} \exp[i\mathbf{t}_e \cdot \mathbf{R}_l^e]\exp[-i\mathbf{t}_h \cdot \mathbf{R}_m^h]$$
$$\times \sum_{\lambda,n} Z_n (\frac{2\pi\hbar}{\varepsilon_0 \varepsilon \omega_\lambda \varepsilon V})^{1/2} [\sin\phi_{\lambda en} < \varphi_m(r_h)|\, r_{en}^{-2}\,|\varphi_l(r_e) >$$
$$+\sin\phi_{\lambda hn} < \varphi_m(r_h)|\, r_{hn}^{-2}\,|\varphi_l(r_e) >]e^{-i\omega_\lambda t}$$
$$\times[\frac{1}{\sqrt{2}}(a_{cl}(+1/2)d_{vm}(-1/2)+a_{cl}(-1/2)d_{vm}(+1/2))]c_\lambda^+ \tag{19}$$

In deriving Eq. (19), the property of the spin operator $s_z a_e(\pm\frac{1}{2}) = \pm\frac{1}{2}\hbar a_e(\pm\frac{1}{2})$ has been used and thus only the integral from Eq. (18b) is non-zero.

3. Rate of spontaneous emission

We now consider a transition from an initial state with a triplet excitation whose spin has been flipped by the spin-orbit interaction but it has no photons to a final state with no excitation (ground state) and one photon created in a mode λ. Within the occupation number representation, such initial $|\,i>$ and final $|\,f>$ states can be respectively written as:

$$|\,i> = |\frac{1}{\sqrt{2}}[a_{cl}^+(+1/2)d_{vm}^+(-1/2) + a_{cl}^+(-1/2)d_{vm}^+(+1/2)]\,|\,0>|\,0_p> \tag{20}$$

$$|\,f> = c_\lambda^+\,|\,0>|\,0_p> \tag{21}$$

where |0> and $|0_p>$ represent the vacuum states of electrons (no excitations) and photons (no photons), respectively. Using Eqs. (19) - (21) and the usual anti-commutation rules for fermion and commutation rules for boson operators, the transition matrix element is obtained as [27]:

$$< f\,|\,\hat{H}_{so}^{a-sem(t)}\,|\,i> = -\frac{\hbar e^3 g\kappa}{4\mu_x^2\,\varepsilon c^2} N^{-1} \sum_{l,m} \exp[i\mathbf{t}_e \cdot \mathbf{R}_l^e]\exp[-i\mathbf{t}_h \cdot \mathbf{R}_m^h]$$
$$\times \sum_n Z_n (\frac{2\pi\hbar}{\varepsilon_0 \varepsilon \omega_\lambda V})^{1/2} [\sin\phi_{\lambda en} < \varphi_m(r_h)|\, r_{en}^{-2}\,|\varphi_l(r_e) >$$
$$+\sin\phi_{\lambda hn} < \varphi_m(r_h)|\, r_{hn}^{-2}\,|\varphi_l(r_e) >]e^{-i\omega_\lambda t}\delta_{l,m} \tag{22}$$

where $\delta_{l,m}$ ensures that at the time of recombination both particles are on the same site. In Eq. (22), the two integrals depend on the inverse squares of the electron and hole distances from a nucleus and therefore only the nearest nucleus is important and the influences of other nuclei can be neglected as an approximation. In a pure material, the atomic number will be the same for all atoms and hence it is site independent. In a compound or doped semiconductor, the atomic number of the heaviest atom will contribute the most and hence can be used. In semiconductors, where the constituting atoms do not differ much in their atomic numbers, the average atomic number may be used. Incorporating the above points in Eq. (22), the transition matrix element is obtained as:

$$< f\,|\,\hat{H}_{so}^{a-sem(t)}\,|\,i> \approx -\frac{\hbar e^3 gZ\kappa}{4\mu_x^2\,\varepsilon c^2} (\frac{2\pi\hbar}{\varepsilon_0 \varepsilon \omega_\lambda V})^{1/2} N^{-1} \sum_{l,m} \exp[i\mathbf{t}_e \cdot \mathbf{R}_l^e]\exp[-i\mathbf{t}_h \cdot \mathbf{R}_m^h]$$
$$\times [\sin\phi_{\lambda em} < \varphi_m(r_h)|\, r_{em}^{-2}\,|\varphi_l(r_e) >$$
$$+\sin\phi_{\lambda hm} < \varphi_m(r_h)|\, r_{hm}^{-2}\,|\varphi_l(r_e) >]e^{-i\omega_\lambda t}\delta_{l,m} \tag{23}$$

Eq. (23) can be simplified further with two approximations. 1) Considering that the two integrals give the inverse squares of the distance between the electron and its nearest nucleus and the hole and its nearest nucleus, respectively, we may approximately write as:

$$< \varphi_m(r_h)|\, r_{em}^{-2}\,|\varphi_l(r_e) > = < \varphi_m(r_h)|\, r_{hm}^{-2}\,|\varphi_l(r_e) > \approx (r/2)^{-2} \tag{24}$$

where r is the average separation between the pair of excited charge carriers, electron and hole, and 2) assume that $\sin\phi_{\lambda em} = \sin\phi_{\lambda hm} \approx \sin\phi_\lambda$. With these two approximations, Eq. (23) becomes:

$$< f\,|\,\hat{H}_{so}^{a-sem(t)}\,|\,i> \approx -\frac{2\hbar e^3 gZ\kappa}{\mu_x^2 c^2 \varepsilon r^2} (\frac{2\pi\hbar}{\varepsilon_0 \varepsilon \omega_\lambda V})^{1/2} \sin\phi_\lambda e^{-i\omega_\lambda t} p_{eh}, \tag{25}$$

where

$$p_{eh} = N^{-1} \sum_{l,m} \exp[i\mathbf{t}_e \cdot \mathbf{R}_l^e]\exp[-i\mathbf{t}_h \cdot \mathbf{R}_m^h]\delta_{l,m}\,. \tag{26}$$

Although the above two approximations may not alter the magnitude of the transition matrix element, they have simplified the expression considerably.

In the case of amorphous solids we have to consider the conduction and valence bands consisting of the corresponding delocalized extended and localized tail states within the band gap. This creates four possibilities [23,26]: i) both the excited electron (e) and hole (h) are in their respective extended states, ii) e is in the extended and h in the tail states, iii) e is in the tail and hole in extended states and iv) both e and h are in their respective tail states. p_{eh} for these four possibilities have already been evaluated [23, 27]. For possibilities (i) to (iii), the square of the transition matrix element is obtained as:

$$|< f\,|\,\hat{H}_{so}^{a-sem(t)}\,|\,i>|^2 \approx [-\frac{2\hbar e^3 gZ\kappa\sqrt{\varepsilon}}{\mu_x^2 c^2 a_{ex}{}^2}]^2 (\frac{2\pi\hbar}{\varepsilon_0 \omega_\lambda V}) \sin^2\phi_\lambda\,. \tag{27}$$

Here $r = a_{ex}/\varepsilon$ is used with the triplet exciton's Bohr radius $a_{ex} = \frac{\mu\varepsilon}{\mu_x} a_0$ [16], where a_2 = 0.529 Å is the Bohr radius and μ is the reduced mass of electron in the hydrogen atom. As the effective masses of e and h are different in the extended and tail states, the excitonic Bohr radius is also different for the extended and tail states.

For the possibility (iv), when both excited charge carriers are localized in their tail states, the square of the transition matrix element is obtained as:

$$|< f \,|\, \hat{H}_{so}^{a-sem(t)} \,|\, i >|^2 \approx [-\frac{2\hbar e^3 gZ\kappa\sqrt{\varepsilon}}{\mu_x^2 c^2 a_{ex}{}^2}]^2 (\frac{2\pi\hbar}{\varepsilon_0 \omega_\lambda V}) \sin^2\phi_\lambda \exp(-2t'_e a_{ex}) \tag{28}$$

where

$$|\mathbf{t}'_e| = t'_e = \sqrt{2m_e^*(E_c - E_e)}/\hbar, \tag{29}$$

and the exponential factor in Eq. (28) arises from the localization of the electronic wave functions.

Once the transition matrix elements are determined the rate of spontaneous emission, R_{sp}^{a-sem} (s^{-1}), can be derived using Fermi's golden rule as:

$$R_{sp}^{a-sem} = \frac{2\pi}{\hbar}\sum_{\lambda}\sum_{E'_c, E'_v} |< f \,|\, \hat{H}_{so}^{at(t)} \,|\, i >|^2 \; f_c f_v \delta(E'_c - E'_v - \hbar\omega_\lambda)\text{'} \tag{30}$$

where f_c and f_v are the probabilities of occupation of an electron in the conduction and a hole in the valence bands. $E_c^{'}$ and $E_v^{'}$ are the energies in the conduction and balance bands to which an electron and hole can respectively be excited. Substituting Eq. (27) in (30), the rate for the possibilities (i) to (iii) are obtained as [23,26]:

$$R_{sp} = \frac{16\pi^2\hbar^2 e^6 g^2 Z^2 k^2 \varepsilon}{\varepsilon_0 \mu_x^4 c^4 a_{ex}^4 \omega_\lambda V} \sin^2\phi_\lambda \sum_{E'_c, E'_v} f_c f_v \delta(E'_c - E'_v - \hbar\omega_\lambda) \tag{31}$$

Assuming that the excited charge carriers are in thermal equilibrium with the lattice, f_c and f_v can be given by the Maxwell-Boltzmann distribution functions and then their product is obtained as:

$$f_c f_v \approx \exp[-(\hbar\omega_\lambda - E_0)/\kappa_B T], \tag{32}$$

where E_0 is the energy of the lowest state within the conduction band from where the radiative recombination occurs. In crystalline solids, it is equal to the minimum energy gap plus the binding energy of an exciton in the triplet state. However, in amorphous solids, depending on where the recombination originates from (extended or tail states), there are more than one possible values of E_0. Using Eq. (32) and product of the individual density of states of electrons and holes, the summations over E'_c and E'_v in Eq. (31) can be evaluated by converting these in integrals. One thus obtains [23, 26-27]:

$$R_{sp}^{a-sem} = \frac{4e^6 g^2 Z^2 k^2 \varepsilon V}{\pi\varepsilon_0 \mu_x c^4 a_{ex}^4 (\hbar\omega_\lambda)\hbar^3} (\hbar\omega - E_0)^2 \sin^2\phi_\lambda$$
$$\exp[-(\hbar\omega_\lambda - E_0)/\kappa_B T]. \tag{33}$$

Integrating Eq. (33) over the solid angle $\sin\theta_\lambda d\theta d\phi_\lambda$, we get the total rate of spontaneous emission as:

$$R_{sp}^{a-sem} = \frac{16e^6 g^2 Z^2 k^2 \varepsilon}{\varepsilon_0 \mu_x c^4 a_{ex}^4 (\hbar\omega_\lambda)\hbar^3 \nu\rho_A} (\hbar\omega - E_0)^2$$
$$\exp[-(\hbar\omega_\lambda - E_0)/\kappa_B T]\Theta(\hbar\omega - E_0), \tag{34}$$

where $V = \dfrac{2}{\nu\rho_A}$ has been used [23, 27, 34-35], ν is the number of coordinating valence electrons per atom and ρ_A is the atomic density per unit volume. In Eq. (34), a step function $\Theta(\hbar\omega - E_0)$ is used to indicate that there is no radiative recombination for $\hbar\omega < E_0$.

For the possibility (iv), let us denote the spontaneous emission rate in the tail-states by R_{spt}^{a-sem} and then use the transition matrix element of Eq.(28) in Eq. (31) to get:

$$R_{spt}^{a-sem} = R_{sp}^{a-sem} \exp[-2t'_e a_{ex}], \tag{35}$$

where the pre-exponential factor is the same as the rate in Eq. (34). Here again one has to use the corresponding reduced mass and exciton Bohr radius.

It is important to determine the value of E_0 for calculating the rates of spontaneous emission from Eqs. (34) and (35). This is done by maximising the rate in Eq. (34) with respect to $x = \hbar\omega - E_0$ and then one obtains E_0 as:

$$E_0 = \frac{(1+\beta)E_{mx} - 2}{(1+\beta)}, \tag{36}$$

where $\beta = 1/\kappa_B T$ and E_{mx} is the energy at which the peak of the triplet PL is observed. We get the same expression for E_0 from Eq. (35) as well.

4. Results

Here the above theory will be applied to calculate the rates of spontaneous emission and the corresponding radiative lifetimes of triplet excitons in a-As_2Se_3 , a-As_2S_3 and a-Se. However, before we can calculate the rates from Eqs. (34) and (35), we need the values of reduced exciton mass μ_X, E_0, E_{mx}, a_{ex}, atomic density ρ_A, coordination number ν and the dielectric constant. ε for each of these materials. Let us first discuss the effective mass of charge carriers in a-Chs.

4.1. Effective mass of carriers in a-Chs

The effective mass of charge carriers in amorphous solids has been derived by the author and it is found to be inversely proportional to the width of their energy bands

[8]. Thus, the effective mass of an electron in the conduction extended states is obtained as:

$$m^*_{ex} \approx \frac{E_L}{2(E_2 - E_c)a^{1/3}} m_e, \tag{37}$$

and in the conduction tail states as:

$$m^*_{et} \approx \frac{E_L}{(E_c - E_{ct})b^{1/3}} m_e \tag{38}$$

where:

$$E_L = \frac{\hbar^2}{m_e L^2}. \tag{39}$$

Here $a = \frac{N_1}{N} < 1$, N_1 is the number of atoms contributing to the extended states, $b = \frac{N_2}{N} < 1$, N_2 is the number of atoms contributing to the tail states, such that $a + b = 1$ ($N = N_1 + N_2$) and m_e is the free electron mass. The energy E_2 in Eq. (37) corresponds to the energy of the middle of the conduction extended states at which the imaginary part of the dielectric constant becomes maximum and E_{ct} is the energy corresponding to the end of the conduction tail states. L is the average bond length between nearest neighbours in the sample.

Likewise, the hole effective masses m^*_{hx} and m^*_{ht} in the valence extended and tail states are obtained, respectively, as:

$$m^*_{hx} \approx \frac{E_L}{2(E_v - E_{v2})a^{1/3}} m_e, \tag{40}$$

and

$$m^*_{ht} \approx \frac{E_L}{(E_{vt} - E_v)b^{1/3}} m_e, \tag{41}$$

where E_{v2} and E_{vt} are energies corresponding to the half width of valence extended states and the end of the valence tail states, respectively. In sp^3 hybrid semiconductors, the electron's effective mass in the conduction band equals the hole's effective mass in the valence band [8]. In a-Chs considered here, the valence band has the lone pair electron bands on its top and hence gets broadened. In this case, Eq. (40) for the effective mass of the hole in the valence extended states can be modified to:

$$m^*_{hx} \approx \frac{E_L}{(2(E_2 - E_c) + E_{lp})a^{1/3}} m_e, \tag{42}$$

where E_{lp} is the width of the lone pair band on the top of the valence band. This clearly illustrates that the effective mass of holes in the extended states is less than that of electron in the conduction extended states and hence holes move faster than the electrons in these materials which is well established experimentally [8]. In the tail states, however, as these are localized states the effective masses are large and can be regarded to be the same for electrons and holes.

In a-As_2Se_3, the average bond length L = 0.24 nm (As-Se = 0.24 nm, Se-Se = 0.23 nm and As-As = 0.24 nm [36], which gives E_L = 1.31 eV from Eq. (39), E_2 is not known in any of these materials and therefore taken to be the same as known for a-Si:H, which is E_2 = 3.6 eV [8] for all the three materials, E_c = 2.0 eV [20] and E_{ct} = 0.5 E_c = 1.0 eV, and it may be assumed that E_{lp} = E_{ct} = 1.0 eV. Using these for a sample, for example, with the density of weak bonds contributing to the tail states as 1 at.%, i.e. b = .01 and a = .99, we get , m^*_{ex} = 0.41 m_e from Eq. (37), m^*_{hx} = 0.31m_e from Eq. (42) and $m^*_{et} = m^*_{ht}$ = 6.1 m_e. These give the reduced excitonic masses for the possibility (i) both e and h in the extended states, denoted by μ^*_{exhx} = 0.18 m_e , for the possibility (ii) e in extended and h in the tail denoted by μ^*_{exht} = 0.38 m_e , for the possibility (iii) μ^*_{ethx} = 0.30 m_e and for the possibility (iv) μ^*_{etht} = 3.05 m_e .

In a-As_2S_3 (or g-As_2S_3), L = 0.28 nm (As-S = 0.28 nm [37,38]) which gives E_L = 0.97 eV, E_c = 2.7 [20], E_{ct} = 0.5 E_c = 1.35 eV and E_{lp} = E_{ct} = 1.35 eV. Using these and E_2 = 3.6 eV for a similar sample as of a-As_2Se_3 , i.e. a = 0.99 and b = 0.01, we get m^*_{ex} = 0.54 m_e from Eq. (37), m^*_{hx} = 0.31m_e from Eq. (42) and $m^*_{et} = m^*_{ht}$ = 3.32 m_e. These give the reduced excitonic masses as μ^*_{exhx} = 0.20 m_e , μ^*_{exht} = 0.46 m_e , μ^*_{ethx} = 0.28 m_e and μ^*_{etht} = 1.66 m_e .

For a-Se, L = 1.43 nm (Se-Se = 0.23 nm [38,39]) which gives E_L = 1.43 eV, E_c = 2.2 [20], E_{ct} = 0.5 E_c = 1.1 eV and E_{lp} = E_{ct} = 1.1 eV. Using these and E_2 = 3.6 eV for a similar sample with a = 0.99 and b = 0.01, we get m^*_{ex} = 0.51 m_e from Eq. (37), m^*_{hx} = 0.37m_e from Eq. (42) and $m^*_{et} = m^*_{ht}$ = 6.04 m_e. These give the reduced excitonic masses for the four possibilities as μ^*_{exhx} = 0.21 m_e , μ^*_{exht} = 0.47 m_e , μ^*_{ethx} = 0.35 m_e and μ^*_{etht} = 3.02 m_e .

4.2 Rates of spontaneous emission

Having determined the effective masses, we will calculate the rate of spontaneous emission in the three materials here.

a-As$_2$Se$_3$: The peak energy, E_{mx} of triplet PL has been measured by Aoki et al. [20] and found to be at E_{mx} = 1.1 eV at 3.7 K. Using this in Eq. (36), we get E_0 = 1.099 eV. For this material we have $\varepsilon = 8.0$ [8], which gives the triplet exciton Bohr radii for the four possibilities as (i) a_{exhx} = 2.35 nm, (ii) a_{exht} = 1.11 nm, (iii) a_{ethx} = 1.41 nm and (iv) a_{etht} = 0.14 nm. As the PL peak appears at a Stokes shift of E_c -E_{mx} = 0.9 eV , it is obvious that this radiative recombination does not occur through the possibility (i). The non-radiative relaxation is much faster (ps time range) and hence the excited charge carriers in triplet excitons relax down very fast. Therefore, here we consider calculating the rates of recombination only through the possibilities (ii) to (iv). Using these values in Eq. (34), we get the maximum rate calculated at $\hbar\omega = E_{mx}$ for the possibility (ii) as R_{sp}^{a-sem} = 1140 s^{-1} and the corresponding radiative lifetime $\tau_{exht}^{a-sem} = 1/R_{sp}^{a-sem} = 0.88$ ms and for the possibility (iii) R_{sp}^{a-sem} = 554.6 s^{-1} and $\tau_{ethx}^{a-sem} = 1.8$ ms. For the possibility (iv), we need to calculate t'_e from Eq. (29) at $E_e = 0.5E_c$ and $m_e^* = m_{et}^* = 6.1m_e$, which gives $t'_e = 13.2\times 10^9$ m^{-1}. Using this and the corresponding exciton Bohr radius in Eq. (35), we get $R_{spt}^{a-sem} = 1.3\times 10^4$ s^{-1} and the corresponding radiative lifetime as: $\tau_{etht}^{a-sem} = 1/R_{spt}^{a-sem} = 0.7\times 10^{-4}$ s. Except for the possibility (iii), these radiative lifetimes are in the range of 10^{-4} s and agree very well with that measured by Aoki et al. [20].

a-As$_2$S$_3$: Here we have E_{mx} = 1.4 eV at 3.7 K [20]. Using this in Eq. (36), we get E_0 = 1.399 eV. For this material $\varepsilon = 5.8$ [8], which gives the triplet exciton Bohr radii for the four possibilities as (i) a_{exhx} = 1.53 nm, (ii) a_{exht} = 0.67 nm, (iii) a_{ethx} = 1.10 nm and (iv) a_{etht} = 0.18 nm. Here also the PL peak appears at a Stokes shift of E_c – E_{mx} = 1.3 eV , which excludes the occurrence of this radiative recombination through the possibility (i). Using these values in Eq. (34), we get the maximum rate calculated at $\hbar\omega = E_{mx}$ for the possibility (ii) as R_{sp}^{a-sem} = 4138.2 s^{-1} and the corresponding radiative lifetime $\tau_{exht}^{a-sem} = 1/R_{sp}^{a-sem} = 2.4\times 10^{-4}$ s and for the possibility (iii) R_{sp}^{a-sem} = 9135.7 s^{-1} and $\tau_{ethx}^{a-sem} = 1.0$ ms. For the possibility (iv), we get t'_e from Eq. (29) at $E_e = 0.5E_c$ and $m_e^* = m_{et}^* = 3.3m_e$ as $t'_e = 6.4\times 10^9$ m^{-1}. Using this and the corresponding exciton Bohr radius in Eq. (35), we get $R_{spt}^{a-sem} = 3521.4$ s^{-1} and the corresponding radiative lifetime as: $\tau_{etht}^{a-sem} = 1/R_{spt}^{a-sem} = 2.8\times 10^{-4}$ s. Here again, except for the possibility (iii), these radiative lifetimes are in the range of 10^{-4} s and agree very well with that measured by Aoki et al. [20].

a-Se: In this case, we have E_{mx} = 0.74 eV at 3.7 K [20]. Using this in Eq. (36), we get E_0 = 0.739 eV. For this material $\varepsilon = 6.5$ [8], which gives the triplet exciton Bohr radii for the four possibilities as (i) a_{exhx} = 1.64 nm, (ii) a_{exht} = 0.73 nm, (iii) a_{ethx} = 0.98 nm and (iv) a_{etht} = 0.11 nm. Here the PL peak appears at a Stokes shift of E_c –E_{mx} = 1.46 eV , which also excludes the occurrence of this radiative recombination through the possibility (i). Using these values in Eq. (34), we get the maximum rate calculated at $\hbar\omega = E_{mx}$ for the possibility (ii) as R_{sp}^{a-sem} = 6093.3 s^{-1} and the corresponding radiative lifetime $\tau_{exht}^{a-sem} = 1/R_{sp}^{a-sem} = 1.6\times 10^{-4}$ s and for the possibility (iii) R_{sp}^{a-sem} = 2519.2 s^{-1} and $\tau_{ethx}^{a-sem} = 0.4$ ms. For the possibility (iv), we get t'_e from Eq. (29) at $E_e = 0.5E_c$ and $m_e^* = m_{et}^* = 6.04m_e$ as $t'_e = 13.2\times 10^9$ m^{-1}. Using this and the corresponding exciton Bohr radius in Eq. (35), we get $R_{spt}^{a-sem} = 77786.3$ s^{-1} and the corresponding radiative lifetime as: $\tau_{etht}^{a-sem} = 1/R_{spt}^{a-sem} = 0.1\times 10^{-4}$ s, this is about 2 orders of magnitude shorter than the experimental radiative lifetime of triplets in a-Se being 1 ms.

5. Discussion

Rates of spontaneous emission from the radiative recombination of triplet excitons in amorphous chalcogenides are calculated using a new time-dependent spin-orbit-photon interaction operator derived recently by the author [27]. Assuming that the maximum rate occurs at the same energy as the energy of the triplet PL peak, the maximum value of these rates can be calculated and the radiative lifetime is then calculated from the inverse of the maximum rate. The theory is then applied to calculate the rates of spontaneous emission in three amorphous chalcogenides, a-As$_2$Se$_3$, a-As$_2$S$_3$ and a-Se. In the first two a-Chs the calculated lifetime from the possibility (ii) and (iv) are found to be about 10^{-4} s which agrees very well with the radiative lifetime recently measured by Aoki et al. [20]. From this agreement, one may think that it is not possible to distinguish whether the PL occurs through the possibility (ii) with the excited electron being in the extended states and hole in the tail states or possibility (iv) where both the excited e and h are in their tail states. In these two materials, a-As$_2$Se$_3$, a-As$_2$S$_3$, the Stokes shift is 0.9 ev and 1.3 eV, respectively. Such a large Stokes shift is not possible due only to the binding energy of a triplet exciton. This suggests that the excited triplet excitons have relaxed to the tail states. As these materials are flexible the charge carrier-phonon interaction is large; much larger than in a-Si:H, and hence the non-radiative relaxation is very fast (in ps time range). It is therefore expected that both carriers are relaxed to the tail states and become type II triplet geminate pairs. The lifetime is about the same as only one of them is relaxed to the tail states, the possibility (ii). The possibility (iii) predicts theoretically a longer radiative lifetime. This may be due to the fact that holes move faster in these materials as a result the excitonic Bohr radius is slightly larger than that in the possibility (ii). As the rate of spontaneous emission from triplet excitons [Eqs. (34) and(35)] depends on the inverse of the fourth power of the Bohr radius, the possibility (iii) gives a slower rate and hence longer radiative lifetime. This means that before the exciton can radiatively recombine through the possibility (iii) it relaxes and radiates through the possibility (iv).

However, the case of a-Se is somewhat different and the triplet PL occurs at a much lower energy of 0.74 eV with a Stokes shift of 1.46 eV. This gives a much smaller exciton Bohr radius in this material and hence larger rate of spontaneous emission and shorter theoretical radiative lifetime. It may also be noted that this material may be regarded to have the strongest charge carrier-phonon interaction. It is therefore possible that when both the carriers have relaxed to the tail states they recombine non-radiatively without giving any PL from the possibility (iv). Therefore, the only possible channels of the radiative recombination in this material may be through the possibilities (ii) and (iii), which give the theoretical radiative lifetime of fraction of a mille second, in reasonable agreement with the ms time range measured experimentally.

The radiative lifetime of singlet excitons has also been calculated in these materials but it will be published elsewhere.

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Corresponding author: jai.singh@cdu.edu.au