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Self-Consistent Semi-Classical Dynamic Theory of Non-Radiative Capture and Emission Statistics in Defect Semiconductors

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A self-consistent, semi-classical theory of the non-radiative capture and emission rates of carriers in defect semiconductors is presented. The lattice is treated in the configuration coordinate approximation and thermal averages of transition rates and cross-sections are calculated in the experimentally important statistical limit. The semi-classical theory gives explicit expressions for the time-dependent transition rates following optical excitation of carriers initially trapped in defect states within the band-gap of the semiconductor. In the steady state and in the thermodynamic limit, the predicted rates are in agreement with experiment. The theory bridges the gap in the literature between rigorous but complex quantum-mechanical theories and rough but experimentally useful semi-classical calculations, while it makes apparent the connection to Shockley-Read statistics.

Une théorie exhaustive et semi-classique des taux d'absorption et d'émission des porteurs dans les semi-conducteurs (de défaut) est proposée. Le réseau est étudié dans l'approximation de coordonnées de configuration, les moyennes thermiques des taux de transitions ainsi que les sections efficaces étant calculés dans la limite statistique, importante experimentalement. La théorie semi-classique fournit des expressions explicites des taux de transition, dependant du temps, qui se produisent aprés excitation optique des porteurs initialement priégés dans des états en défaut dans le vide de la bande du semi-conducteur. Pour le cas indépendant du temps et dans la limite thermodynamique, les taux prédits sont en accord avec l'expérience. Tout en faisant apparaitre la relation avec la statistique de Shockley-Read, la théorie effectue la transition entre la démarche rigoureuse, mais complexe, de la mécanique quantique et les calculs semiclassiques grossiers souvent utilisés dans l'expérience.

1. Introduction

In recent years, a number of theoretical attempts have been made by several authors [1 to 6] to develop expressions for non-radiative transition rates in semiconductors. The impetus for this activity has been twofold: the intrinsic theoretical interest in the multifaceted and complicated problem of non-radiative transition mechanisms [3 to 6]; and the practical desire to understand the energetics of defect centres and degradation pathways in semiconductor materials used for the fabrication of direct energy conversion devices, such as light emitting diodes (LED's) and semiconductor lasers [1 to 7].

In the recent literature, there is general agreement that multiphonon capture and emission processes are consistent with observed material behaviour [1, 2, 4, 7, 8], however, the calculated transition rates and cross-sections are dependent on the type of approximation used by individual authors to describe the non-radiative transition process(es). In general, the adiabatic and the crude Born-Oppenheimer schemes have been popular for the description of the (lattice + defect state) Hamiltonian in crystalline solids [9].

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Henry and Lang [1] introduced a combined approach for the description of semiconductor non-radiative capture, which was very successful in predicting experimental capture cross-section data. They used adiabatic electronic wave functions away from the defect level–band edge crossing point in the configuration coordinate, and first-order time-dependent perturbation theory for values of the coordinate near crossing. Their semi-classical treatment was in agreement with a simple quantum-mechanical calculation in the Condon approximation, however, proper coupling of the bound defect state with the entire quasi-continuum of free states in the respective band was ignored. Further, the emission rate to the quasi-continuum was estimated using a formula due to Landau [10] and Zener [11], without further justification. The original derivation of that formula was made for transitions between electronic states of diatomic molecules and the conditions of its applicability to the solid state are not clear. These shortcomings of the semi-classical theory used by Henry and Lang have also been recognized by the authors themselves [1].

Pässler ([2] and references therein) developed a semi-empirical theory of Shockley and Read [12] processes in semiconductors, in the static carrier–lattice coupling limit. He was thus successful in deriving explicit expressions for the non-radiative capture and emission cross-sections associated with deep, charged or neutral traps in semiconductors. However, the static Condon approximations employed by that author have been shown to break down near the crossing point of the trap state and the respective lattice band edge potential curves [13].

Ridley also performed a detailed quantum-mechanical calculation of the non-radiative transition rate in semiconductors, using infinite-order perturbation theory in the non-Condon approximation [4]. The capture cross-sections which resulted from his treatment are higher at high temperatures than those calculated by Henry and Lang by a factor of $p^2/2S$, where p is the number of accepting phonons corresponding to the zero-phonon line energy, and S is the Huang-Rhys factor.

In this paper, a self-consistent semi-classical theory of the non-radiative capture and emission rates in defect semiconductors will be presented. The theory takes into account the dynamic response of the lattice following optical excitation, and results in time-dependent transition rates. Statistical averages depend on the density of states of the semiconductor, and lead to a capture cross-section expression similar to that in [1] but enhanced by a factor of $2(p - S)$, thus bridging the absolute magnitude gap between the expressions in [1, 4]. Explicit expressions for the net transition rates in the steady state will be derived. These fit reasonably well the experimental data at high temperatures and can be used to calculate true defect level depths within the band gap.

Finally, it will be shown that the theory presented in this paper is consistent with the statistical formalism of Shockley and Read [12] in the long-time limit as the lattice–defect system approaches equilibrium.

2. Lattice Relaxation and Non-Radiative Capture Rate

Fig. 1 shows a configurational coordinate model of a semiconductor conduction band edge $|c\rangle$ and a defect state $|d\rangle$ immediately after optical excitation of a trapped carrier from $|d\rangle$ to $|c\rangle$. The origin of the k-th mode of configurational space is coincident with the bottom of the (assumed harmonic) trapped state. The energies in Fig. 1 are given by [14]

$$U_c(Q) = E_0 + \sum_k \tfrac{1}{2} m_k^* \omega_k^2 (Q_k - \Delta_k)^2 , \tag{1a}$$

$$U_d(Q) = \sum_k \tfrac{1}{2} m_k^* \omega_k^2 Q_k^2 , \tag{1b}$$

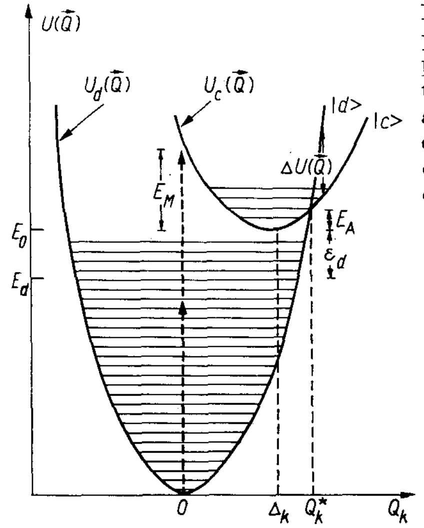

Fig. 1. Semiconductor configurational coordinate representation. Q_k is the accepting mode, E_0 the zero-phonon energy, E_{M} the lattice relaxation energy, E_{A} the thermal barrier height, E_{d} the defect energy level, and ε_{d} the minimum energy required for excitation of a trapped carrier to the conduction band. An entirely analogous diagram can be drawn for defects which act as traps of carriers excitable into the valence band

and

$$E_{\mathrm{M}} = \sum_k \tfrac{1}{2}\, m_k^* \omega_k^2 \Delta_k^2\,, \tag{1c}$$

where m_k^* is the effective mass of the free carrier in the k-th mode of configuration space. In this work, it will be assumed for simplicity that the value of the effective mass in the trapped state is also m_k^*. ω_k is the characteristic vibrational angular frequency of the k-th mode, and Δ_k is the Frank-Condon displacement of the conduction band with respect to the equilibrium position of the trapped carrier, if captured at the cross-over of $|c\rangle$ and $|d\rangle$. E_0 and E_{A} are the zero-phonon energy and thermal activation energy for non-radiative decay, respectively. Assuming that modes j and k are affected to the same extent by the optical excitation, in the sense that

$$\Delta_j Q_k^* \approx \Delta_k Q_j^*\,, \tag{2}$$

then it can be shown that E_0 and E_{A} are related by

$$E_{\mathrm{A}} = \frac{1}{4}\,\frac{(E_0 - E_{\mathrm{M}})^2}{E_{\mathrm{M}}}\,. \tag{3}$$

In the harmonic approximation, we can set

$$Q_k(t) = [Q_k(\max)] \cos \omega_k t = \Delta_k \cos \omega_k t\,, \tag{4}$$

where the maximum vibrational excursion of the lattice from its equilibrium point was assumed to be Δ_k. Thus the level separation of the conduction band state $|c\rangle$ and the defect state $|d\rangle$ can be written as

$$\Delta U(t) \equiv U_{\mathrm{c}}(\boldsymbol{Q}; t) - U_{\mathrm{d}}(\boldsymbol{Q}; t) = E_0 + E_{\mathrm{M}} - 2 \sum_k \tfrac{1}{2}\, m_k^* \omega_k^2 \Delta_k^2 \cos \omega_k t\,. \tag{5}$$

Equation (5) can be simplified considerably using its average in the statistical limit [14], which is an excellent approximation in the case of optical excitations, where E_0 is large compared to the lattice phonon energies:

$$\Delta U(t) \approx E_0 + E_{\mathrm{M}} - 2E_{\mathrm{M}} \cos \omega t\,, \tag{6}$$

where

$$\cos \omega t \equiv \langle \cos \omega_k t \rangle_k = \frac{\sum\limits_k \frac{1}{2}\, m_k^* \omega_k^2 \Delta_k^2 \cos \omega_k t}{\sum\limits_k \frac{1}{2}\, m_k^* \omega_k^2 \Delta_k^2}\,. \tag{7}$$

In the statistical limit, also

$$E_{\mathrm{M}} = S\hbar\omega\,. \tag{8}$$

Equation (6) shows that the time τ_{c} after excitation, at which a carrier in the conduction band will cross the defect state $|\mathrm{d}\rangle$, and therefore is most likely to be captured, is given by

$$\tau_{\mathrm{c}} = \frac{1}{\omega} \cos^{-1} \frac{E_0 + E_{\mathrm{M}}}{2E_{\mathrm{M}}}\,. \tag{9}$$

In the semi-classical adiabatic approximation, which is valid for motion far from the crossing point Q^* in Fig. 1, the Hamiltonian of the system can be written [1]

$$H(\boldsymbol{r}, \boldsymbol{Q}; t) = H^{(0)}(\boldsymbol{r}, \boldsymbol{Q}) + H^{(1)}(\boldsymbol{r}; \boldsymbol{Q})\,. \tag{10}$$

In (10), $\boldsymbol{r}$ and $\boldsymbol{Q}(t)$ are the electronic and nuclear coordinates, respectively. Nonradiative transitions occur due to the presence of the non-adiabaticity (perturbation) operator $H^{(1)}(\boldsymbol{r}; \boldsymbol{Q})$, which mixes the states $|\mathrm{c}\rangle$ and $|\mathrm{d}\rangle$. $H^{(0)}$ denotes the kinetic energy operators of the electrons and nuclei, and vibrational potentials. The wave function $\psi(t)$ describing the system (quasi-continuum + defect state) at all times, including $t \sim \tau_{\mathrm{c}}$, is assumed to be expandable in terms of eigenstates of $H^{(0)}(\boldsymbol{r}, \boldsymbol{Q})$ evaluated at $Q = Q_1(t = t_1)$ [1]:

$$\psi(t) = \sum_{\mathrm{c}} A_{\mathrm{c}}(t)\, u_{\mathrm{c}}(t_1) \exp\left[\frac{1}{i\hbar}\int\limits_0^t U_{\mathrm{c}}(x)\,\mathrm{d}x\right] + B_{\mathrm{d}}(t)\, v_{\mathrm{d}}(t_1) \exp\left[\frac{1}{i\hbar}\int\limits_0^t U_{\mathrm{d}}(x)\,\mathrm{d}x\right], \tag{11}$$

where $\psi(t)$ satisfies the Schrödinger equation

$$H(\boldsymbol{r}, \boldsymbol{Q}; t)\, \psi(t) = i\hbar \frac{\partial}{\partial t} \psi(t) \tag{12}$$

and $u_{\mathrm{c}}(t)$, $v_{\mathrm{d}}(t)$ are eigenstates of $H^{(0)}$ describing the motion of carriers in the conduction band quasi-continuum and in the defect state, respectively. The coefficients $A_{\mathrm{c}}(t)$ and $B_{\mathrm{d}}(t)$ can be calculated using the orthonormality of the states $|\mathrm{c}\rangle$ and $|\mathrm{d}\rangle$. They are given by the coupled equations

$$\frac{\mathrm{d}}{\mathrm{d}t} A_{\mathrm{c}}(t) = \frac{H_{\mathrm{cd}}^{(1)}}{i\hbar} \exp\left[-\frac{1}{i\hbar}\int\limits_0^t \Delta U(x)\,\mathrm{d}x\right] B_{\mathrm{d}}(t) \tag{13a}$$

and

$$\frac{\mathrm{d}}{\mathrm{d}t} B_{\mathrm{d}}(t) = \sum_{\mathrm{c}'} \frac{H_{\mathrm{dc}'}^{(1)}}{i\hbar} \exp\left[\frac{1}{i\hbar}\int\limits_0^t \Delta U(x)\,\mathrm{d}x\right] A_{\mathrm{c}'}(t) \tag{13b}$$

with

$$H_{\mathrm{cd}}^{(1)} \equiv \int u_{\mathrm{c}}^*(\boldsymbol{r}, \boldsymbol{Q})\, H^{(1)}(\boldsymbol{r}, \boldsymbol{Q})\, v_{\mathrm{d}}(\boldsymbol{r}, \boldsymbol{Q})\,\mathrm{d}^3 r\,.$$

Equation (13a) can be extended to include other possible defect levels upon summing over the index d, however, we are assuming here for simplicity that only one non-degenerate level of the state $|\mathrm{d}\rangle$ can be occupied by a carrier trapped at the defect. Equation (13b) can then be solved by using the initial conditions [15]

$$B_\mathrm{d}(t = 0^+) = 0 \tag{14a}$$

and

$$A_{\mathrm{c}'}(t \geqq 0^+) = \delta_{\mathrm{c}'\mathrm{c}}\,, \tag{14b}$$

where 0^+ indicates any positive time, including $t = 0$, after optical excitation. Equations (6), (13b), and (14a), (14b) give

$$B_\mathrm{d}(t) = \left[\frac{H^{(1)}_{\mathrm{dc}'}}{i\hbar}\right] \int\limits_0^t \exp\left\{-\frac{i}{\hbar}\left[(E_0 + E_\mathrm{M})\,t' - \frac{2}{\omega}\,E_\mathrm{M} \sin \omega t'\right]\right\} \mathrm{d}t'\,. \tag{15}$$

Equation (15) can be written more compactly using (8) and the definition [14]

$$p \equiv \frac{E_0}{\hbar\omega} = \frac{\omega_0}{\omega}\,. \tag{16}$$

With these definitions, (15) becomes

$$B_\mathrm{d}(t) = \left[\frac{H^{(1)}_\mathrm{dc}}{i\hbar\omega}\right] F_{p+S}(2S;\, \omega t)\,, \tag{17}$$

where

$$F_\nu(z;\, \omega t) \equiv \int\limits_0^{\omega t} \exp\left[i(z \sin x - \nu x)\right] \mathrm{d}x\,. \tag{18}$$

The transition probability, $W_{\mathrm{c}\to\mathrm{d}}$, for capture within one vibrational period by the defect state is equal to $|B_\mathrm{d}(t)|^2$, or

$$W_{\mathrm{c}\to\mathrm{d}}(U_\mathrm{c}, U_\mathrm{d};\, t) = \frac{|H^{(1)}_\mathrm{dc}|^2}{(\hbar\omega)^2}\, |F_{p+S}(2S;\, \omega t)|^2\,. \tag{19}$$

The experimentally important quantity is, however, the capture transition rate, $R_{\mathrm{c}\to\mathrm{d}}$, as it can be simply related to the experimentally measurable capture cross-section σ_c. The transition rate can be determined from (19) as follows:

$$R_{\mathrm{c}\to\mathrm{d}}(U_\mathrm{c}, U_\mathrm{d};\, t) = \frac{|H^{(1)}_\mathrm{dc}|^2}{(\hbar\omega)^2}\, \frac{\partial}{\partial t}\, |F_{p+S}(2S;\, \omega t)|^2\,. \tag{20}$$

In (20), use of Leibnitz's rule [16] for the time derivative gives

$$R_{\mathrm{c}\to\mathrm{d}}(U_\mathrm{c}, U_\mathrm{d};\, t \leqq \omega^{-1}) \approx \frac{2\omega\,|H^{(1)}_\mathrm{dc}|^2}{(\hbar\omega)^2}\, \frac{\sin\left[(p - S)\,\omega t\right]}{p - S} \tag{21a}$$

and, for long times after the optical excitation, i.e. for $t \gg \omega^{-1}$

$$R_{\mathrm{c}\to\mathrm{d}}\left(U_\mathrm{c}, U_\mathrm{d};\, t \sim \frac{\pi}{\omega}\right) \approx \frac{2\pi\omega\,|H^{(1)}_\mathrm{dc}|^2}{(\hbar\omega)^2}\, \Big(\mathrm{j}_{p+S}(2S) \cos\left[\pi(p + S)\right] + {} + \mathrm{e}_{p+S}(2S) \sin\left[\pi(p + S)\right]\Big)\,, \tag{21b}$$

where $\mathrm{j}_\nu(z)$ and $\mathrm{e}_\nu(z)$ are Anger's and Weber's functions, respectively [17]. Equations (21 a), (21 b) show that the non-radiative transition rate increases linearly with time immediately following the excitation, then becomes oscillatory, and finally saturates at long times. In the special case that $p + S$ equals an integer, (21 b) reduces to the rate expression derived in [1]. Using Schläfli's representations of Bessel's and Neumann's functions [17], we can write a more tractable form of (21 b) in the limit of large, but otherwise unrestricted p,

$$R_{\mathrm{c}\to\mathrm{d}}\left(U_\mathrm{c}, U_\mathrm{d}; t \sim \frac{\pi}{\omega}\right) \approx \frac{2\pi\omega\,|H^{(1)}_{\mathrm{dc}}|^2}{(\hbar\omega)^2}\left(\mathrm{J}_{p+S}(2S)\cos\left[\pi(p+S)\right] - \mathrm{N}_{p+S}(2S)\sin\left[\pi(p+S)\right]\right), \tag{21 c}$$

where J_{p+S} and N_{p+S} are Bessel and Neumann functions, respectively.

3. Non-Radiative Emission Rate

In principle, an exact expression for the emission rate can be obtained from combining (13 a), (13 b) and solving for $A_\mathrm{c}(t)$. The mathematical difficulty involved in that straightforward procedure suggests that an alternative solution method would be desirable. In this section, we present such a method, which is consistent with the assumptions used in Section 2. In the limit of large $t(\sim \pi/\omega)$, i.e. for times near those required for thermodynamic equilibrium in the electron system both in the conduction band states and in the defect state, equation (15) can be written

$$B_\mathrm{d}\left(t \sim \frac{\pi}{\omega}\right) \approx \frac{\pi H^{(1)}_{\mathrm{dc}}}{i\hbar\omega}\,\mathrm{H}^{(1)}_{p+S}(2S)\,, \tag{22}$$

where

$$\mathrm{H}^{(1)}_\nu(z) = \mathrm{J}_\nu(z) + i\mathrm{N}_\nu(z)$$

is the first Hankel function, and Schläfli's representations of J_ν and N_ν were used. Appendix A shows that for phonon energies $\hbar\omega \sim k_\mathrm{B}T$, equation (22) becomes to within a phase factor

$$B_\mathrm{d}\left(t \sim \frac{\pi}{\omega}\right) \approx \exp\left\{-\frac{U_\mathrm{c}\left(t \sim \frac{\pi}{\omega}\right) - E_\mathrm{d}}{2k_\mathrm{B}T}\right\}; \tag{23}$$

where E_d is the particular defect level considered, cf. Fig. 1.

Inserting (23) in (13a) and keeping in mind that for $t > \omega^{-1}$ any change in the lattice energy is slow, we find

$$A_\mathrm{c}\left(t \sim \frac{\pi}{\omega}\right) \approx \frac{H^{(1)}_{\mathrm{dc}}}{i\hbar\omega}\exp\left[-\frac{1}{i\hbar}\int_0^t \Delta U(x)\,\mathrm{d}x\right]\exp\left[-\frac{U_\mathrm{c} - E_\mathrm{d}}{2k_\mathrm{B}T}\right]. \tag{24}$$

The transition probability, $W_{\mathrm{d}\to\mathrm{c}}$, for emission within one vibrational period to the conduction band is equal to $|A_\mathrm{c}(t)|^2$, or for $t \sim \pi/\omega$

$$W_{\mathrm{d}\to\mathrm{c}}(U_\mathrm{c}, U_\mathrm{d}; t) = \frac{|H^{(1)}_{\mathrm{cd}}|^2}{(\hbar\omega)^2}\,|G_{p+S}(2S; \omega t)|^2\exp\left[-\frac{U_\mathrm{c} - E_\mathrm{d}}{k_\mathrm{B}T}\right], \tag{25}$$

where

$$G_\nu(z; \omega t) \equiv \int_0^{\omega t}\exp\left[-i(z\sin x - \nu x)\right]\mathrm{d}x\,. \tag{26}$$

The emission rate, $R_{d\to c}$, can be calculated in a manner similar to that used for (21 b). Using Schläfli's representations of J_ν and N_ν, we can write

$$R_{d\to c}\left(U_c, U_d; t \sim \frac{\pi}{\omega}\right) = \frac{2\pi\omega\,|H_{cd}^{(1)}|^2}{(\hbar\omega)^2}\,(\mathrm{J}_{p+S}(2S)\cos[\pi(p+S)] - \\ - \mathrm{N}_{p+S}(2S)\sin[\pi(p+S)])\exp\left[-\frac{U_c - E_d}{k_B T}\right]. \tag{27}$$

From (21 c) and (27), using the Hermitean property of the matrix element $H_{cd}^{(1)}$, we find

$$\frac{R_{d\to c}}{R_{c\to d}} = \exp\left(-\frac{U_c\left(t \sim \frac{\pi}{\omega}\right) - E_d}{k_B T}\right). \tag{28}$$

Equation (28) shows that the infinitesimal adiabatic, Frank-Condon emission and capture rates are in agreement with the principle of detailed balance [12] for large times after excitation.

4. Calculation of $H_{cd}^{(1)}$ and Rate Statistical Averages

A more realistic evaluation of the matrix element $H_{cd}^{(1)}$ than the one presented in [1] can be made using an extension of the method described in [1].

Defining effective wave vectors $\boldsymbol{K}_d$ and $\boldsymbol{k}$ for the trapped and free carriers, respectively, and assuming the same effective masses for both kinds of carriers, we can write

$$K_d^2 = \frac{2m_e^*}{\hbar^2}\,E_d \tag{29a}$$

and

$$k^2 = \frac{2m_e^*}{\hbar^2}\,(E_0 + U_c)\,. \tag{29b}$$

From Fig. 1, it can be seen that for the capture of a carrier at a level U_c in the conduction band, the quantity $\varepsilon_d + U_c$ will be the energy of the trapped carrier

$$\langle d|H^{(1)}|\,d\rangle = \varepsilon_d + U_c\,. \tag{30}$$

In the special case that the defect level E_d lies close to the bottom of the conduction band, and the optical excitation does not raise the carrier much above the conduction band edge, we can approximate

$$K_d^2 \approx k^2\,. \tag{31}$$

In this case, the bound well method of [1] and (29 a), (29 b) yield the following expression for the matrix element responsible for non-radiative transitions:

$$|H_{cd}^{(1)}|^2 = 2\pi\left(\frac{\hbar^2}{2m_e^*}\right)^{3/2}(U_c + \varepsilon_d - E_0)^{1/2}\,. \tag{32}$$

Equation (32) reduces to the matrix element of Henry and Lang ([1], equation (88)) upon setting $U_c = E_0$, i.e. for excitations to the bottom of the conduction band.

Experimentally, it is extremely difficult to know with reasonable certainty the exact quantum levels in a solid between which non-radiative transitions occur, especially at elevated temperatures (e.g. room temperature). High temperatures are efficient in inducing thermally activated transitions to and from many levels in the quasi-continuum of the conduction band. Therefore, any semi-classical formalism which considers transitions solely between two specific energy levels tends to underestimate the magnitude of the transition rate which can be observed experimentally. To be interpreted properly, the infinitesimal rates obtained in (21 c) and (27) must be thermally averaged over the entire distribution of the quasi-continuum excited states.

The processes involved are non-equilibrium, though for times $t \sim \pi/\omega$, it is reasonable to assume that internally the conduction band states, as well as the defect states, have achieved equilibrium and can therefore be described by quasi-Fermi levels or imrefs [18].

Then, the statistically averaged non-radiative capture and emission rates are given by [12]

$$\langle R_{c\to d}(E_d; t > \omega^{-1})\rangle = \int_{E_0}^{\infty} g(U_c)\, f_{FD}(U_c)\, N_d(E_d)\, [1 - f_{FD}(E_d)] \times \\ \times R_{c\to d}(U_c, E_d; t > \omega^{-1})\, dU_c \tag{33a}$$

and

$$\langle R_{d\to c}(E_d; t > \omega^{-1})\rangle = \int_{E_0}^{\infty} g(U_c)\, [1 - f_{FD}(U_c)]\, N_d(E_d)\, f_{FD}(E_d) \times \\ \times R_{d\to c}(U_c, E_d; t > \omega^{-1})\, dU_c\,, \tag{33b}$$

where $g(U_c)$ is the density of states in the semiconductor, given by

$$g(U_c) = \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} (U_c - E_0)^{1/2}; \tag{34}$$

f_{FD} is the Fermi-Dirac statistical distribution for free and trapped carriers. Using the assumption of local equilibria, we can write

$$f_{FD}(U_c) = \frac{1}{1 + \exp\left[\dfrac{U_c - F_c}{k_B T}\right]} \tag{35a}$$

for conduction band states with F_c the imref for free electrons; and

$$f_{FD}(E_d) = \frac{1}{1 + \exp\left[\dfrac{E_d - F_d}{k_B T}\right]} \tag{35b}$$

for electrons trapped at defect levels with no degeneracies. The captured electron imref is F_d. In (33a, (33b), $N_d(E_d)$ is the defect density. It has been assumed that only the level E_d can be occupied by trapped carriers. This assumption is generally valid for deep impurities in the ground state, as well as for shallow, isolated, square-well type traps [19].

The expression (33a) for the statistically averaged non-radiative capture rate can be integrated explicitly in the case of non-degenerate semiconductors with $U_c - F_c > > k_B T$ with less than 10% error [18],

$$\langle R_{c\to d}(E_d; t > \omega^{-1})\rangle = 2N_d(E_d)\, [1 - f_{FD}(E_d)]\, \frac{\omega}{(\hbar\omega)^2} \exp\left(\frac{F_c}{k_B T}\right) \times \\ \times \{Q_1 \cos[\pi(p + S)] - Q_2 \sin[\pi(p + S)]\}\,, \tag{36}$$

where

$$Q_1 \equiv \int_{E_0}^{\infty} (U_\mathrm{c} - E_0)^{1/2} (U_\mathrm{c} + \varepsilon_\mathrm{d} - E_0)^{1/2} \mathrm{J}_{p+S}\left[(p + S)\left(\frac{U_\mathrm{c}}{E_\mathrm{A}}\right)^{1/2}\right] \exp\left(-\frac{U_\mathrm{c}}{k_\mathrm{B}T}\right) \mathrm{d}U_\mathrm{c} \quad (37\,\mathrm{a})$$

and

$$Q_2 \equiv \int_{E_0}^{\infty} (U_\mathrm{c} - E_0)^{1/2} (U_\mathrm{c} + \varepsilon_\mathrm{d} - E_0)^{1/2} \mathrm{N}_{p+S}\left[(p + S)\left(\frac{U_\mathrm{c}}{E_\mathrm{A}}\right)^{1/2}\right] \exp\left(-\frac{U_\mathrm{c}}{k_\mathrm{B}T}\right) \mathrm{d}U_\mathrm{c}. \quad (37\,\mathrm{b})$$

In Q_1, Q_2, we used equation (A2) of Appendix A. Details of the integrations (37 a), (37 b) are found in the Appendix B. Upon insertion of (B8) and (B12) in (36) and use of the identity

$$\cos\left[\pi(p + S)\right] + \sin\left[\pi(p + S)\right] \tan\left[\frac{\pi(p + S)}{2}\right] = 1 \quad (38)$$

we find the capture rate statistical average

$$\langle R_{\mathrm{c}\to\mathrm{d}}(\varepsilon_\mathrm{d}; E_\mathrm{A})\rangle = \frac{2\omega k_\mathrm{B}T}{(\hbar\omega)^2} N_\mathrm{d}(E_\mathrm{d}) (\varepsilon_\mathrm{d}E_\mathrm{A})^{1/2} \left[1 - f_\mathrm{FD}(E_\mathrm{d})\right] \exp\left[-\frac{E_\mathrm{A} - F_\mathrm{c}}{k_\mathrm{B}T}\right]. \quad (39)$$

The statistically averaged emission rate (33 b) can also be written in terms of the integrals Q_1 and Q_2,

$$\langle R_{\mathrm{d}\to\mathrm{c}}(E_\mathrm{d}; t > \omega^{-1})\rangle = 2N_\mathrm{d}(E_\mathrm{d}) f_\mathrm{FD}(E_\mathrm{d}) \frac{\omega}{(\hbar\omega)^2} \exp\left(\frac{E_\mathrm{d}}{k_\mathrm{B}T}\right) \times$$

$$\times \left\{Q_1 \cos\left[\pi(p + S)\right] - Q_2 \sin\left[\pi(p + S)\right]\right\}. \quad (40)$$

The emission rate statistical average can be found in a manner identical to the procedure above which led to (39),

$$\langle R_{\mathrm{d}\to\mathrm{c}}(\varepsilon_\mathrm{d}; E_\mathrm{A})\rangle = \frac{2\omega k_\mathrm{B}T}{(\hbar\omega)^2} N_\mathrm{d}(E_\mathrm{d}) (\varepsilon_\mathrm{d}E_\mathrm{A})^{1/2} f_\mathrm{FD}(E_\mathrm{d}) \exp\left[-\frac{E_\mathrm{A} - E_\mathrm{d}}{k_\mathrm{B}T}\right]. \quad (41)$$

5. Discussion and Conclusions

The experimentally measurable capture cross-section σ_c can be obtained from the theory presented above, upon taking the thermal average of the statistical rate (39),

$$\langle R_{\mathrm{c}\to\mathrm{d}}(E_\mathrm{d}; E_\mathrm{A})\rangle_T = \frac{\langle R_{\mathrm{c}\to\mathrm{d}}(E_\mathrm{d}; E_\mathrm{A})\rangle}{N_\mathrm{d}(E_\mathrm{d}) \left[1 - f_\mathrm{FD}(E_\mathrm{d})\right] \int_{E_0}^{\infty} g(U_\mathrm{c}) f_\mathrm{FD}(U_\mathrm{c}) \,\mathrm{d}U_\mathrm{c}}. \quad (42)$$

The capture cross-section per unit volume is given by [1]

$$\sigma_\mathrm{c} = \frac{\langle R_{\mathrm{c}\to\mathrm{d}}(E_\mathrm{d}; E_\mathrm{A})\rangle_T}{\left(\dfrac{8k_\mathrm{B}T}{\pi m_\mathrm{e}^*}\right)^{1/2}}. \quad (43)$$

Equations (39), (42), and (43) give the following expression for the capture cross-section:

$$\sigma_\mathrm{c}(E_\mathrm{d}; E_\mathrm{A}) = \left(\frac{\varepsilon_\mathrm{d}}{S\hbar\omega}\right)^{1/2} \frac{\pi^2}{2k_\mathrm{B}T} \left[\frac{\hbar^2(p - S)}{m_\mathrm{e}^*}\right] \exp\left(-\frac{E_\mathrm{A}}{k_\mathrm{B}T}\right), \quad (44)$$

where (3) was used in the form

$$E_{\mathrm{A}} = \frac{\hbar\omega(p - S)^2}{4S}. \tag{45}$$

Equation (44) is similar to equation (91) of [1], however, the present capture cross-section is larger than that derived by Henry and Lang by a factor of $2(p - S)$. This factor can be quite large in the case of strong electron–phonon coupling ($p \gg S$). The cause of the discrepancy between (44) and [1] is that Henry and Lang considered only transitions between two definite states and ignored the energy level distributions in the conduction (or valence) bands. The result of their approximation was an underestimation of σ_{c} by $2(p - S) \approx 20$ for typical values of p and S in the strong coupling limit [4]. In that same limit, the semi-classical equation (44) underestimates the infinite-order perturbation quantum-mechanical capture cross-section by a factor of $\approx p/S$ [4].

The net rate of capture at temperature T is

$$\begin{aligned} \langle r\rangle &\equiv \langle R_{\mathrm{c}\to\mathrm{d}}(E_{\mathrm{d}};\, E_{\mathrm{A}})\rangle - \langle R_{\mathrm{d}\to\mathrm{c}}(E_{\mathrm{d}};\, E_{\mathrm{A}})\rangle \\ &= \frac{2\omega k_{\mathrm{B}}T}{(\hbar\omega)^2}\, N_{\mathrm{d}}(E_{\mathrm{d}})\, (\varepsilon_{\mathrm{d}} E_{\mathrm{A}})^{1/2} \exp\left[-\frac{E_{\mathrm{A}} - E_{\mathrm{d}}}{k_{\mathrm{B}}T}\right] \left\{\frac{\exp\left[(F_{\mathrm{c}} - F_{\mathrm{d}})/k_{\mathrm{B}}T\right] - 1}{1 + \exp\left[(E_{\mathrm{d}} - F_{\mathrm{d}})/k_{\mathrm{B}}T\right]}\right\}. \end{aligned} \tag{46}$$

Equation (46) is applicable to non-degenerate semiconductors. It reduces to an explicit form of the general result of the statistical theory by Shockley and Read ([12], equation (2.10)) for the special case $E_{\mathrm{d}} - F_{\mathrm{d}} \gg k_{\mathrm{B}}T$. If the system (lattice + defect) is in thermodynamic equilibrium, then the imrefs are equal,

$$(F_{\mathrm{c}})_{\mathrm{eq}} = (F_{\mathrm{d}})_{\mathrm{eq}}, \tag{47}$$

and

$$\langle r\rangle = 0. \tag{48}$$

At, or near, steady state (i.e. for $t \geq \pi/\omega$), the net capture cross-section is given by

$$(\sigma_{\mathrm{c}})_{\mathrm{net}} = \frac{\langle r\rangle_T}{\left(\dfrac{8k_{\mathrm{B}}T}{\pi m_{\mathrm{e}}^*}\right)^{1/2}}. \tag{49}$$

Using (39), (40), and (42) in (49), and the following approximations, which are valid for shallow defect states with effective masses equal to those of free carriers [12, 18]

$$F_{\mathrm{c}} \approx \tfrac{1}{2}(E_0 + E_{\mathrm{d}}), \tag{50a}$$

$$F_{\mathrm{d}} \approx E_{\mathrm{d}}, \tag{50b}$$

we obtain

$$(\sigma_{\mathrm{c}})_{\mathrm{net}} \approx \left(\frac{\varepsilon_{\mathrm{d}}}{S\hbar\omega}\right)^{1/2} \frac{\pi^2}{2k_{\mathrm{B}}T} \left[\frac{\hbar^2(p - S)}{m_{\mathrm{e}}^*}\right] \exp\left(-\frac{E_{\mathrm{A}}}{k_{\mathrm{B}}T}\right) \left[\exp\left(\frac{\varepsilon_{\mathrm{d}}}{2k_{\mathrm{B}}T}\right) - 1\right] \tag{51}$$

or

$$(\sigma_{\mathrm{c}})_{\mathrm{net}} = \sigma_0(T) \exp\left[-\frac{E_{\mathrm{A}} - \varepsilon^*}{k_{\mathrm{B}}T}\right], \tag{52}$$

where

$$\sigma_0(T) \equiv \left(\frac{\varepsilon_{\mathrm{d}}}{S\hbar\omega}\right)^{1/2} \pi^2(p - S)\, \frac{\hbar^2}{2m_{\mathrm{e}}^* k_{\mathrm{B}}T} \tag{53a}$$

and

$$\varepsilon^*(T) \equiv k_B T \ln \left[\exp \left(\frac{\varepsilon_d}{2k_B T} \right) - 1 \right]. \tag{53b}$$

Equations (52) and (53) are the results of the self-consistent semi-classical theory presented in this work and should be compared with [1], equations (90) to (94) and (111) to (113). The main differences are (i) the σ_0 in (53a) is a function of T, whereas $\sigma_{\infty c}$ of [1] is not; and (ii) the exponent of (52) is a complicated function of T due to the inclusion of the emission component. The shape of the data curve for the electron capture cross-section of level B in n-GaAs versus T^{-1} given in Fig. 2 (Fig. 3 of [1]) indicates that the temperature dependence is not purely exponential. The slight curvature observed could be due to either the T-dependence of the pre-exponential factor, or some more complicated behaviour. The solid line A in Fig. 2 is a fit of (52) to the data, and the dashed line B corresponds to (91) of [1]. The parameters used for the two theoretical lines were $p = 20$ [4], $S = 1$ [4], $\varepsilon_d = 0.06$ eV [1], $E_A = 0.28$ eV (from the average slope of the data curve). At $T = 300$ K, equation (53b) gives $\varepsilon^* = 0.019$ eV. This value is to be compared with 0.012 eV calculated from the Landau-Zener model in [1]. Fig. 2, curve B shows that the T^{-1}-dependence of the pre-exponentials in (52) and (91) of [1] has little effect on the curvature of these lines. The observed departure from linearity of the solid curve A in the direction of the data points is due to the presence of $\varepsilon^*(T)$ in (52) and is most pronounced at $T < 250$ K. This curve deviates significantly from the data line at $T \leq 200$ K, which is expected in view of the semi-classical approach adopted in this work. Nevertheless, the fit is good at higher temperatures, and resolves the consistency problem presented in the fit of [4], Fig. 1 of a quantum-mechanical formula strictly valid at low temperatures, fit to the high-temperature data of Fig. 2.

The present theory has the advantage over static theories [2, 21] that it treats the dynamic transition rates at the crossing points in a self-consistent manner, i.e. without resorting to the Condon approximation in a configurational coordinate region of rapid wave function change. It is also valid for shallow defect levels and yields relatively simple, analytical expressions for electron capture and emission cross-sections at room and higher temperatures. The static theories, however, have successfully treated the possibility of charged centers as a straightforward extension of the transition rates involving neutral traps in the thermodynamic equilibrium limit [21]. This task is, in principle, feasible using the present theory, albeit mathematically more involved.

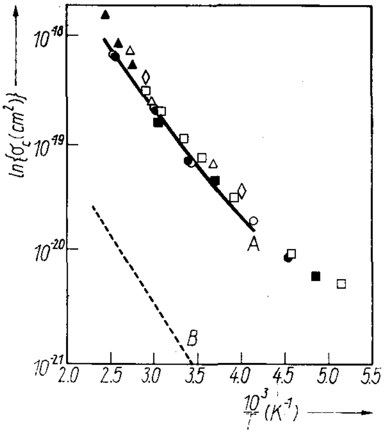

Fig. 2. Temperature dependence of the electron capture cross-section of level B in n-GaAs for various electron concentrations (after Fig. 3 of [1]). A: fit of (52) to the following data: $p = 20$, $S = 1$, $\varepsilon_d = 0.06$ eV, $E_A = 0.28$ eV. B: (91) in [1]. The discrepancy between the two lines is due to (i) the statistical approach, and (ii) the self-consistent consideration of the emission rate from the defect level in solid line A. △ 4.2×10^{15}, ○ 4.5×10^{15}, ◇ 2.0×10^{16}, □ 2.2×10^{16}, ▲ 3.0×10^{16}, ● 6.0×10^{16}, ■ 9.5×10^{16} cm^{-3}

The main advantage of the static [2, 21] and fully quantum-mechanical [4] theories is their ability to treat consistently low-temperature non-radiative processes. This is not feasible within the framework of a semi-classical formulation, as purely quantum effects become important at low-temperatures (e.g. quantum-mechanical tunnelling of the lattice oscillators [2]). The substantial deviation of the experimental data curve from the theoretical line A below $\approx$ 200 K in Fig. 2 is a practical manifestation of the non-quantum nature of the present semi-classical theory at low temperatures.

Appendix A

Derivation of expression (23) for $B_d(t \sim \pi/\omega)$

Equation (3) can be written in terms of p and S as follows:

$$2S = (p + S)\frac{(U/E_A)^{1/2}}{1 + (U/E_A)^{1/2}}, \tag{A1}$$

where $U(\equiv E_M)$ is the conduction band energy level to which the optically excited carrier has been raised. For the usual experimental case where $E_A > U$, we can simplify (A1):

$$2S \approx (p + S)\left(\frac{U}{E_A}\right)^{1/2}. \tag{A2}$$

For thermal emission to take place, a carrier must have enough thermal energy to cross the thermal barrier height E_A, i.e.

$$E_A \approx k_B T \tag{A3}$$

and

$$U \approx U_c - E_d \tag{A4}$$

for shallow defect levels. Equations (A2) to (A4) give

$$2S \approx (p + S)\left(\frac{U_c - E_d}{k_B T}\right)^{1/2}. \tag{A5}$$

In (2.2), $2S < p + S$ in view of (A5), so that the first Hankel function $H^{(1)}_{p+S}(2S)$ can be written in its asymptotic form ([17], Chapter 7.13.2):

$$\pi H^{(1)}_{p+S}\left[(p + S)\left(\frac{U_c - E_d}{k_B T}\right)^{1/2}\right] \approx \frac{-i\sqrt{2\pi}}{\left[(p + S)^2\left(1 - \frac{U_c - E_d}{k_B T}\right)\right]^{1/4}} \times$$
$$\times \exp\left[-(p + S)\left(1 - \frac{U_c - E_d}{k_B T}\right)^{1/2} + (p + S)\cosh^{-1}\left(\frac{k_B T}{U_c - E_d}\right)^{1/2}\right]. \tag{A6}$$

For $(U_c - E_d)/k_B T < 1$, the expression in the exponent of (A6) can be written approximately

$$\exp\left\{-(p + S)\left(1 - \frac{U_c - E_d}{2k_B T} - \ln\left[2\left(\frac{k_B T}{U_c - E_d}\right)^{1/2}\right]\right)\right\} \tag{A7}$$

and, upon expanding the logarithm and inserting back into (A6), we find

$$\pi \mathrm{H}^{(1)}_{p+S}\left[(p+S)\left(\frac{U_\mathrm{c}-E_\mathrm{d}}{k_\mathrm{B}T}\right)^{1/2}\right] \approx -i\left(\frac{2\pi}{p+S}\right)^{1/2} \exp\left[-\frac{p+S}{2}\left(\frac{U_\mathrm{c}-E_\mathrm{d}}{k_\mathrm{B}T}\right)^{1/2}\right]. \tag{A8}$$

Finally, substituting (A5) in (A8) and using the fact that along each configurational coordinate of Fig. 1 the Huang-Rhys factor S corresponds to one residual vibrational degree of freedom [4]

$$S\hbar\omega \approx \tfrac{1}{2}\, k_\mathrm{B}T \rightarrow S \approx 0.5$$

we can write

$$\pi \mathrm{H}^{(1)}_{p+S}(2S) \approx -i\left(\frac{2\pi}{p+S}\right)^{1/2} \exp\left[-\frac{U_\mathrm{c}-E_\mathrm{d}}{2k_\mathrm{B}T}\right]. \tag{A9}$$

The average of $B_\mathrm{d}(t \sim \pi/\omega)$, equation (23), can be obtained upon squaring (22), using (32) and (A9), and weighing (multiplying) by an integral over the entire distribution of conduction band states:

$$\left\langle\left|B_\mathrm{d}\left(t \sim \frac{\pi}{\omega}\right)\right|^2\right\rangle = \left|B_\mathrm{d}\left(t \sim \frac{\pi}{\omega}\right)\right|^2 \int\limits_{E_0}^{\infty} g(E)\, f_\mathrm{FD}(E)\, \mathrm{d}E \approx \exp\left[-\frac{U_\mathrm{c}-E_\mathrm{d}}{k_\mathrm{B}T}\right]. \tag{A10}$$

Thus

$$B_\mathrm{d}\left(t \sim \frac{\pi}{\omega}\right) \equiv \sqrt{\left\langle\left|B_\mathrm{d}\left(t \sim \frac{\pi}{\omega}\right)\right|^2\right\rangle} = \exp\left[-\frac{U_\mathrm{c}-E_\mathrm{d}}{2k_\mathrm{B}T}\right] \tag{A11}$$

to within an arbitrary phase factor. $U_\mathrm{c} = U_\mathrm{c}(t \gg \omega^{-1})$ is the value of the excited carrier energy long after excitation, when the conduction band states are close to internal equilibrium.

Appendix B

The integrals Q_1 and Q_2 of (37a) and (37b)

1. The integral Q_1 can be simplified using the approximations

$$U_\mathrm{c} - E_0 \approx \varepsilon_\mathrm{d} \tag{B1}$$

and

$$U_\mathrm{c} + \varepsilon_\mathrm{d} - E_0 \approx U_\mathrm{c} \tag{B2}$$

which are valid for low excitation energies and for shallow defect levels. Under these conditions,

$$Q_1 \approx (k_\mathrm{B}T)^{3/2}\, \varepsilon_\mathrm{d}^{1/2} \int\limits_{\varepsilon_\mathrm{d}/k_\mathrm{B}T}^{\infty} \sqrt{x}\, \mathrm{e}^{-x}\, \mathrm{J}_{p+S}\left[(p+S)\left(\frac{k_\mathrm{B}T}{E_\mathrm{A}}\right)^{1/2}\sqrt{x}\right] \mathrm{d}x$$

or, for $\varepsilon_\mathrm{d} \ll k_\mathrm{B}T$ as is the case for shallow defects,

$$Q_1 \approx 2(k_\mathrm{B}T)^{3/2}\, \varepsilon_\mathrm{d}^{1/2} \alpha^{3/2} \int_0^\infty y^2\, \mathrm{e}^{-\alpha y^2}\, \mathrm{J}_{p+S}(y)\, \mathrm{d}y\,, \tag{B3}$$

where

$$\alpha \equiv \left[(p+S)^2 \frac{k_\mathrm{B}T}{E_\mathrm{A}}\right]^{-1}. \tag{B4}$$

Using the equality [20]

$$M_1(\alpha) \equiv \int_0^\infty e^{-\alpha y^2} J_{p+S}(y)\,dy = \frac{1}{2}\left(\frac{\pi}{\alpha}\right)^{1/2} \exp\left(-\frac{1}{8\alpha}\right) I_{1/2(p+S)}\left(\frac{1}{8\alpha}\right),$$

where $I_{1/2(p+S)}$ is the modified Bessel function of order $(p+S)/2$, we can express Q_1 as follows:

$$Q_1 = -2(k_B T)^{3/2}\, \varepsilon_d^{1/2} \alpha^{3/2} \frac{\partial}{\partial\alpha} M_1(\alpha) = \tag{B5}$$

$$= 2(k_B T)^{3/2} (\pi\varepsilon_d)^{1/2} \exp\left(-\frac{1}{8\alpha}\right) \times$$

$$\times \left[\left(\frac{1+p+S}{2} - \frac{1}{8\alpha}\right) I_{1/2(p+S)}\left(\frac{1}{8\alpha}\right) + \frac{1}{8\alpha} I_{1+1/2(p+S)}\left(\frac{1}{8\alpha}\right)\right]. \tag{B6}$$

Equation (B6) can be simplified further, upon writing the modified Bessel functions in their asymptotic forms ([17], Chapter 7.13.2) for $(p+S)/2 \gg 1$:

$$I_\nu(x) = \frac{1}{\sqrt{2\pi}\,(\nu^2+x^2)^{1/4}} \exp\left[(\nu^2+x^2)^{1/2} - \nu \sinh^{-1}\left(\frac{\nu}{x}\right)\right]. \tag{B7}$$

Using (B7) in (B6), we obtain

$$Q_1(\varepsilon_d, E_A; T) \approx 2(E_A\varepsilon_d)^{1/2}\, k_B T \exp\left(-\frac{E_A}{k_B T}\right). \tag{B8}$$

2. The integral Q_2 can be handled in exactly the same manner as Q_1:

$$Q_2 = -2(k_B T)^{3/2}\, \varepsilon_d^{1/2} \alpha^{3/2} \frac{\partial}{\partial\alpha} M_2(\alpha) \tag{B9}$$

with [20]

$$M_2(\alpha) = \int_0^\infty e^{-\alpha y^2} N_{p+S}(y)\,dy =$$

$$= -\frac{1}{2}\left(\frac{\pi}{\alpha}\right)^{1/2} \exp\left(-\frac{1}{8\alpha}\right)\left\{\tan\left[\frac{\pi(p+S)}{2}\right] I_{1/2(p+S)}\left(\frac{1}{8\alpha}\right) +\right.$$

$$\left. + \frac{1}{\pi} \sec\left[\frac{\pi(p+S)}{2}\right] K_{1/2(p+S)}\left(\frac{1}{8\alpha}\right)\right\}, \tag{B10}$$

where $K_{1/2(p+S)}$ is Basset's function, or the modified Bessel's function of the third kind of order $\frac{1}{2}(p+S)$.

Differentiating (B10) and retaining only terms consistent with the $(p+S)/2 \gg 1$ condition, we can write the asymptotic form for $K_{1/2(p+S)}$ [17]:

$$K_\nu(x) = \frac{\sqrt{\pi/2}}{(\nu^2+x^2)^{1/4}} \exp\left[-(\nu^2+x^2)^{1/2} + \nu \sinh^{-1}\left(\frac{\nu}{x}\right)\right]. \tag{B11}$$

From (B11), (B10), and (B9), we obtain

$$Q_2(\varepsilon_d, E_A; T) \approx -2(E_A\varepsilon_d)^{1/2}\, k_B T \tan\left[\frac{\pi(p+S)}{2}\right] \exp\left(-\frac{E_A}{k_B T}\right). \tag{B12}$$

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