

## Theory of diffusion-controlled tunnelling recombination incorporating Coulomb interaction and annihilation

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**Abstract.** The theory of diffusion-controlled defect recombination incorporating the tunnelling transfer of electrons between spatially well-separated defects, an annihilation of close defects and their Coulomb electrostatic interaction is developed. The estimates of the quasi-steady reaction radius is given employing the variational principle. The estimates obtained have been applied to attraction and repulsion cases, namely to pairs  $V_K-A^0$ , in alkali halides, and the di-pair model in semiconductors. The problem of interpretation of the fractional glow technique spectra is discussed.

### 1. Introduction

At present there is extensive literature on the tunnelling recombination (TR) of defects in solids (both ionic and covalent crystals and disordered systems) and solvated electrons with ions in solutions.

The probability that a pair of defects will recombine per unit time is (Döhler 1971, Jefferson *et al* 1975, Zamaraev *et al* 1977)

$$W(r) = W_0 e^{-r/r_B}, \quad (1)$$

where  $r$  is the distance between defects,  $r_B$  half the Bohr radius of more delocalised defects,  $W_0$  is constant. At sufficiently high temperatures certain defects become mobile and their recombination has to be described in terms of diffusion-controlled tunnelling reactions.

TR, i.e., the spontaneous spatial electron transfer, leads to the transformation of the initial defect pair into *another* one instead of annihilation, which occurs when defects approach each other at a short distance  $\rho$  and leads to their disappearance (e.g., the recovery of perfect lattice).

A corresponding theory of diffusion-controlled tunnelling recombination for uncharged defects has been developed quite recently (Fabrikant and Kotomin 1974, 1975, Pilling and Rice 1975, Berlin 1975, 1976).

However, the defects are often charged, which necessitates taking into account the Coulomb interaction.

The preliminary results concerning the quasi-steady diffusion-controlled tunnelling recombination incorporating the Coulomb interaction (and neglecting annihilation)

have been discussed by Fabrikant and Kotomin (1974, 1975, 1977). The purpose of the present paper is to provide *strict* estimates of this reaction radius, also taking into account the annihilation process.

## 2. Variational estimates of quasi-steady tunnelling recombination radius

### 2.1. Statement of the problem

The quasi-steady recombination constant we are concerned with is:

$$k = \int u(r) W(r) dV, \quad (2)$$

where  $u(r)$  is the spherically symmetric solution of the steady-state diffusion equation for pair probability density as follows:

$$D \left\{ \Delta u + \frac{1}{kT} \nabla(u \nabla \phi) \right\} = Wu, \quad (3)$$

with the boundary conditions:

$$\begin{aligned} u(\rho) &= 0 && \text{(annihilation)} \\ u(r \rightarrow \infty) &= 1 - b/r, \end{aligned} \quad (4)$$

$b$  is the asymptotic coefficient,

$$\phi(r) = \frac{e_1 e_2}{\epsilon r}.$$

Equations (2) and (3) hold for sufficiently low defect concentrations, when only pair interactions are important.

To combine the TR and the annihilation the recombination probability of (1) can be rewritten as:

$$W(r) = \begin{cases} \infty, & r \leq \rho & \text{annihilation part} \\ W_0 e^{-r/r_B} & r > \rho & \text{TR part.} \end{cases} \quad (5)$$

Let us now introduce the quasi-steady tunnelling recombination radius  $R_{\pm}$  via:

$$k \equiv 4\pi D R_{\pm},$$

$R_{\pm}$  means an average distance, approaching which a pair of defects are sure to recombine.

For  $R_{\pm}$  from (3) one obtains†

$$R_{\pm} = b - g, \quad (6)$$

$g = e_1 e_2 / \epsilon k T$ —the effective radius if only an annihilation is taken into account (Debye 1942).

One can see that the problem is now reduced to calculating the asymptotic coefficient  $b$ .

Making use of the substitution:

$$u(r) = (y(r)/r) e^{-g/2r},$$

† Subscripts +, - hereafter indicate the Coulomb attraction and repulsion as distinct from the case of its absence (subscript 0).

one gets the equation:

$$\frac{d^2 y}{dr^2} - y[(g^2/4r^4) + (W(r)/D)] = 0, \quad (7)$$

with boundary conditions  $y(\rho) = 0$ ,  $y(r \rightarrow \infty) = r - a$ , from which:

$$R_{\pm} = a - g/2. \quad (8)$$

The exact analytical solution of equation (7) is not known and hence some approximations have to be used. Two extreme cases are evident here: a *drift-controlled* reaction takes place if the second term in brackets in equation (7) is small as compared to the first one, in the opposite case a TR-controlled reaction occurs. For small  $D$  values one obtains the estimate for the radius of a TR-controlled reaction (cf Fabrikant and Kotomin 1974, 1975)

$$R_{\pm} = R_0 - g/2 + O(g^2), \quad \rho \neq 0, R_0 \gg |g|, \quad (9)$$

where the tunnelling recombination radius for neutral defects is:

$$R_0 = 2r_B \left[ \ln(\alpha/2) + 0.577 + \frac{K_0[z(\rho)]}{I_0[z(\rho)]} \right], \quad (10)$$

$$\alpha = 2r_B(W_0/D)^{1/2}, \quad z = \alpha e^{-r/2r_B}.$$

## 2.2. Drift-controlled reaction

To obtain the radius estimates for the drift-controlled reaction a variational principle has to be employed. We used Kohn variational principle to get an upper estimate (e.g., Mott and Massey 1965) and Spruch and Rosenberg (1975) method for a lower bound estimate.

When using the trial function which is the solution of (7) with  $W(r) = 0$ ,  $\rho = 0$ , one gets an upper estimate:

$$R_{\pm}^{(0)} \leq (|g| - g)/2 + 2(W_0/D)(|g|r_B)^{3/2} K_3[2(|g|/r_B)^{1/2}], \quad (11)$$

where  $K_3$  is a modified third-order McDonald function. It is easily seen that the right-hand side of (11) results from the first-order perturbation theory employing the parameter  $\alpha^2/4 = W_0 r_B^2/D$  if  $\rho = 0$ . (For  $\rho \neq 0$  the estimate is more complicated (cf Fabrikant and Kotomin 1977)).

When employing the above-mentioned trial function, one gets two *lower* bound estimates:

$$R_{\pm}^{(1)} \geq R_{\pm}^{(0)} - \frac{W_0^2 |g|^{3/2} r_B^{7/2}}{D^2 \sqrt{2}} K_7[2(|g|/r_B)^{1/2}], \quad (12)$$

$$R_{\pm}^{(2)} \geq (|g| - g)/2 + 2(W_0/D)(|g|r_B)^{3/2} K_3[2(|g|/r_B)^{1/2}] \{1 - (W_0/\lambda D)\} \quad (13)$$

where  $\lambda = (g^2/4)(e/4r_B)^4 + (W_0/D)$ .

If  $W_0/\lambda D \ll 1$ , the right-hand side of (13) coincides with that of (11).

The upper (equation (11)) and lower bound estimates (equations (12), (13)) obtained coincide if the second term in (12) is small compared to the first one, which is the case if either  $|g| \gg r_B$ ,  $\alpha^2 \lesssim 1$  or  $|g| \simeq r_B$ ,  $\alpha^2 \ll 1$ . These conditions obviously mean a negligible TR as compared to the drift effect.

It is important that the TR correction in the estimate (11)  $\Delta R_{\pm}$  is proportional to  $W_0/D$ , which consequently yields a correction to the rate constant  $\Delta k$  independent of  $D$ . For the case of repulsion and  $g \gg \rho$  the  $\Delta k$  coincides with the total  $k$ , i.e., the Arrhenius relation does not hold (Fabrikant and Kotomin 1974, 1975). From (11) the conclusion can be drawn that, however,  $k$  remains temperature dependent via  $g(T)$  and here  $k \propto \exp \{E^*/kT\}$  with:

$$E^* = 2kT(|g|/r_B)^{1/2}. \quad (14)$$

The third kind of diffusion-controlled reactions are those controlled by annihilation for which one easily obtains:

$$R_{\pm} \leq \rho - g/2 + g^2/12\rho. \quad (15)$$

This estimate presents a first-order correction of the perturbation theory, where the Coulomb and TR terms are regarded as a perturbation.

For obtaining more accurate estimates more flexible trial functions are required, which leads to rather lengthy relations. Some results are supplied by Fabrikant and Kotomin (1977).

### 3. Theory applications

#### 3.1. Radii estimates

Let us apply the above-obtained variational estimates to concrete systems.

In alkali halides TR of positively charged  $V_K$  centres (and their products) with (un-charged)  $F$  centres and negatively charged mercury-like activator atoms ( $A^0$ ) has been well investigated (e.g., Delbecq *et al* 1966, 1974; Bogan *et al* 1973).

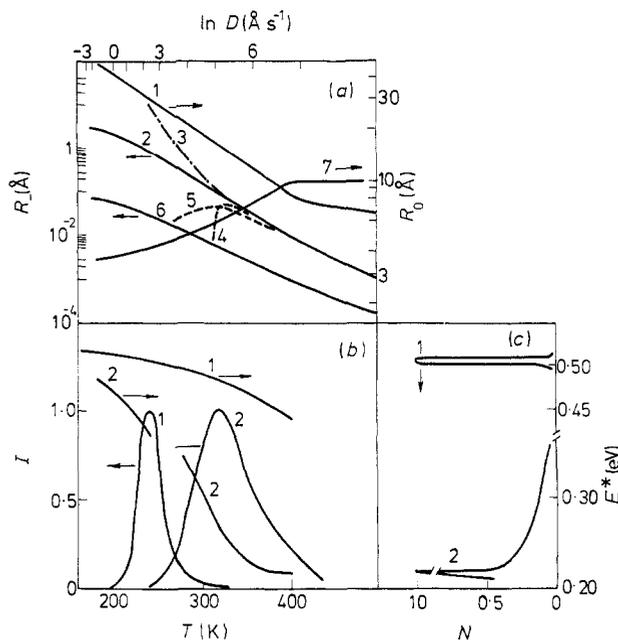
The typical Debye radius  $|g|$  is of the order of hundred Å at temperatures above that of  $V_K$  delocalisation ( $\approx 170$  K, hereafter for concreteness we consider KCl), which appreciably exceeds the  $R_0$  values (equation (10), curve 1, figure 1(a)) that is TR-controlled reaction does not take place in alkali halides (see equation (9)). Its appearance, however, is much more possible in liquids and semiconductors with large dielectric constant  $\epsilon$  (reducing  $g$ ) and typical for shallow defects, large  $r_B$ .

It should be mentioned that an elastic interaction of defects can be neglected because our estimates for both neutral and attracting defects indicate large reaction radii (figure 1(a)) at which an elastic interaction is very small.

Using the estimates of §2.2 the conclusion can be drawn that the drift-controlled reaction occurs at  $T \gtrsim 360$  K. The corresponding variational estimates of the radius for repulsion,  $R_-$ , are given in figure 1(a) by curves 3, 4, 5, the latter is of the order of  $10^{-1}$ – $10^{-3}$  Å. From (8) one can conclude that at *all*  $D$   $R_+ - R_- = |g|$ . This means that in particular in the drift-controlled region  $R_+$  equals  $|g|$  with great accuracy.

The analytical estimates of  $R_{\pm}$  for the intermediate temperature region are rather complicated. Curve 2 shows computer-calculated  $R_-$  temperature dependence obtained by numerical integration of (7). One can conclude that  $R_-$  remains rather small even at low temperatures close to  $V_K$ -delocalisation, i.e., in alkali halides  $R_+ = |g|$ , i.e., the recombinational process is drift-controlled at *all* temperatures and contribution of TR is negligible. It should be stressed that the calculated  $R_{\pm}$  is independent of the annihilation radius (given a few Å).

Curves 6, 7 in figure 1(a) show the temperature dependence of ratios  $R_-/R_0$  and



**Figure 1.** (a) quasi-steady tunnelling recombination radii in KCl against temperature: curve 1, absence of Coulomb interaction; curve 2, Coulomb repulsion (computer calculated); curve 3, upper estimate of equation (11); curves 4 and 5, lower bounds of equations (12) and (13), respectively. (b) TL curves and effective energies; (c) FGT spectra for absence of Coulomb interaction (curves 1) and repulsion (curves 2). Parameters employed:  $E_a = 0.54$  eV,  $W_0 = 10^7$  s $^{-1}$ ,  $r_B = 2$  Å,  $D_0 = 4 \cdot 10^{-3}$  cm $^2$  s $^{-1}$ ,  $C = 10^{18}$  cm $^{-3}$ .

$R_+/R_0$ , indicating that the reaction with repulsion is very ineffective and the efficiency of that with attraction increases with temperature as compared to the case of the absence of Coulomb interaction. It should be noted that TR of neutral defects becomes inefficient at  $T \geq 400$  K, where  $R_0$  becomes close to the annihilation radius  $\rho$  (see curve 1). Ueta (1967) estimated roughly the  $R_+(F)/R_0(F)$  to be about two at room temperature, which is appreciably less than the above-mentioned estimate. Unfortunately, the corresponding temperature dependence has not been reported.

The diffusion-controlled tunnelling recombination incorporating Coulomb attraction also holds for the so-called isoelectronic donor-acceptor (DA) pairs in semiconductors (e.g., Dean 1973), but for usual DA pairs *repulsion* takes place. According to the DA di-pair model (Gunsul *et al* 1970, Williams 1973) thermoluminescence arises due to TR after successive electron and hole transfer from a distant DA pair to an associated (close) one. The TR rate is controlled by the first particle transfer, say, of an electron, because it is delayed by repulsion from a bare acceptor core. The electron motion from a distant donor to an associated one through unoccupied donors can be considered as a phonon-assisted tunnelling diffusion, where an activation energy in  $D$  arises from ionic relaxation around a donor after an electron has occupied it, the pre-exponential factor,  $D_0$ , is strongly dependent on donor concentration.

The diffusion-controlled tunnelling recombination incorporating both the Coulomb attraction and repulsion occurs often in diluted liquid solutions between solvated electrons and scavenger molecules (Zamaraev and Khairutdinov 1974, Pilling and Rice

1975). It would be of great interest to compare the previous estimates for  $R_{\pm}(D)$  with the experimental data obtained for a series of  $D$  values (e.g., varying a solution viscosity).

### 3.2. Interpretation of fractional glow technique data

One of the most popular methods to investigate recombination processes in solids for many decades was thermoluminescence (TL), recently its generalisation, the fractional glow technique (FGT) has been developed by Gobrecht and Hofmann (1966) (see also Tále 1974). In the FGT, using the temperature dependence of recombination intensity  $J(T)$ , the effective energy is determined:

$$E^* = \partial \ln J(T) / \partial (-1/kT) \quad (16a)$$

and the energy distribution function (so-called FGT spectrum):

$$N(E^*) = dS(E^*[T]) / |dE^*[T]|, \quad (16b)$$

where  $S$  is the light-sum emitted during warming a specimen up to temperature  $T$ .

In the case of the recombination process controlled by thermal ionisation of defects due to electron release to the conduction band (band model) and so well-separated discrete energy spectrum that corresponding TL peaks do not appreciably overlap, it can be seen from equation (16) that  $N(E^*)$  is very close to the original  $\delta$  like energy spectrum  $N(E)$ . (This is also the case in the other extreme case of continuous distribution (Tále 1974)). If the recombination process is a bimolecular-diffusion controlled one:

$$J \propto k \propto D(T)R(T),$$

in a clear-cut recombination radius approximation,  $R(T) = \text{constant}$ , one also finds a  $\delta$ -like FGT spectrum peaked at the diffusion energy.

However, another result is observed if  $R$  depends on temperature, which is the case for the diffusion-controlled tunnelling reaction. Curves 1 in figures 1(b) and (c) indicate for comparison the TL peak, the effective energy and the resulting FGT spectrum for the case of second-order reaction without the Coulomb interaction ( $R = R_0(T)$ ) with parameters corresponding to  $V_K-F$  pairs in KCl. The conclusion can be drawn that the FGT spectrum as compared to diffusion energy  $E_a = 0.54$  eV shifts 0.035 eV to lower energies and diffuses (the halfwidth 0.01 eV) which is in accord with actual experimental FGT data. For the Coulomb attraction case ( $V_K-A^0$  pairs) the TL peaks shifts about 20 K to lower temperatures and the FGT spectrum 0.015 eV to higher energies as compared to the absence of interaction.

For Coulomb repulsion there exist two extremes, depending on whether  $g e^{-g/\rho} \gg R_-$  or the opposite holds. In the first case

$$E^* = E_0 - kT + e^2/\epsilon\rho. \quad (17)$$

For many semiconductors, however,  $g \gg \rho$ , i.e., the second extreme is the case. Curves 2 in figures 1(b) and (c) have sense analogous to the curves 1 and correspond to  $R_-$  of figure 1(a). (The  $E_a$  employed is of the order of that estimated by Gunsul *et al* (1970) in ZnS). The simulated FGT spectrum is extended over a few tenths eV and peaks at  $E^* \simeq 0.22$  eV (which coincides with the estimate of equation (14)). Such a FGT spectrum looks like that in the band model for *continuous* trap distribution and additional information is required to distinguish between these cases.

#### 4. Conclusion

In the present paper the variational estimates of the effective radii of diffusion-controlled quasi-steady tunnelling recombination radius for the Coulomb attraction and repulsion (also taking into account annihilation) have been obtained. It is shown in particular that for attraction in alkali halides, occurring for  $V_K-F'$ , and  $V_K-A^0$  pairs, the radius equals  $e^2/\epsilon kT$  with great accuracy, i.e., the drift effect here is much more efficient than the tunnelling recombination. This conclusion justifies estimates of energy transport duration carried out by Dietrich and Murray (1972). The tunnelling recombination of neutral defects at high temperatures ( $\approx 400$  K in KCl) in turn becomes inefficient as compared to annihilation.

Temperature dependence of tunnelling recombination radii causes a shift and broadening of fractional glow technique spectra as compared to actual diffusion energy which has to be taken into account in its interpretation.

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