Intercenter carrier transitions in partly disordered silicon: calculations

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A nonadiabatic approximation is used in a calculation of the probabilities of transitions involving one- and two-electron states. An analysis is made of the field dependences of the frequency factor and of the activation energy of intercenter transitions. Necessary calculations are made of the parameters of a model of generation-recombination transitions in disordered silicon.

Difficulties are frequently encountered in unambiguous interpretation of the characteristics of electron transitions occurring in generation-recombination processes in semiconductors or in semiconductor structures with a complex spectrum of localized states in the band gap. This applies also to real surfaces of semiconductors, amorphous and polycrystalline semiconductors, semiconductors with a high dislocation density, interfaces between a metal and a semiconductor and at a junction, etc. An analysis of the recent experimental data on generation-recombination processes shows that the main recombination channel in these materials usually includes intercenter electron transitions.

Information on the spin states of carriers has extended greatly the scope of investigations of characteristics of electron transitions in such semiconductors. There are several models \(^{1-3}\) that account for the dependence of the rate of recombination of nonequilibrium carriers on the spin states of free and localized electrons. The Kaplan–Solomon–Mott model\(^{3}\) allows for the recombination of carriers via pair states and has been confirmed by direct experiments.\(^{3-5}\) Figure 1 shows schematically the generation–recombination transitions in this model. It was reported in Ref. 6 that each of the centers in a pair in most of the investigated objects can be in one or two-electron states.

There is much which is not yet clear about the origin and physics of two-electron states and little is known about the pair states themselves, such as the radius of the electron wave functions of the states, the distance between the partners in a pair, and the methods suitable for the determination of the parameters of such states.

We shall try to tackle most of the problems mentioned above in the present and following papers. The present paper reports calculations of transitions involving one- and two-electron states, gives an analysis of the field dependences of the frequency factor and the activation energy of intercenter transitions, and derives relationships necessary for the determination of the parameters of a model of generation-recombination transitions in disordered silicon. In the following paper we shall give the experimental data for partly disordered silicon and discuss them using the results given below: we shall estimate the radii of electron wave functions (4-7 Å) and the separation between the pair partners (25-40 Å), and we shall also account for the field dependences of the frequency factor and the activation energy.

1. ELECTRON STATES LOCALIZED AT STRUCTURE DEFECTS AND THE POLARON EFFECT

We shall consider a structure defect in an ideal periodic lattice, for example, a vacancy in silicon. Among the various types of local vibrations of atoms associated with this defect we shall select the "softest" mode and we shall label its con-
Figurational coordinate $X$. Following Holstein\textsuperscript{7,8} and Anderson,\textsuperscript{9} we shall assume that the distortion of the atomic system of a defect (which results, for example, because of the capture of an electron) is due to this softest mode. We shall try to obtain the simplest description of such a defect which has captured $n = 0, 1, 2$ electrons and, following tradition,\textsuperscript{7-11} we shall confine our treatment to the harmonic approximation for the energy of the atomic subsystem $kX^2/2$ and to the linear approximation for the energy of its interaction with captured electrons $-nQX$, where $Q$ is the deformation potential.

The total energy of the system

$$W (X, n) = h X^2/2 - nQX + nU_{ac}$$

includes also the one-electron energy $n\epsilon$ and the energy of the Coulomb repulsion $U_C$, which is "activated" only if $n = 2$.

Minimization of Eq. (1) with respect to $X$ allows us to find the equilibrium energies of the system $E(n)$ and the equilibrium displacements $X^0(n)$

$$E(n) = n\epsilon - nQW + nU_{ac}, \quad X^0(n) = nX^1, \quad X^0 = Q/k,$$

as well as the polaron shift $W$

$$W = Q^2/2k,$$

If the polaron shift is sufficiently large, so that the Hubbard energy

$$U = E(2) - 2E(1) = -2W + U_C$$

becomes negative, then two electrons are more likely to occupy one center than two different centers.

The strong polaron effect in disordered semiconductors is due to anomalously low rigidity $k$ of stretched bonds. For our purpose it is important that stretched bonds appear at dislocations and, consequently, U centers with a large polaron effect may concentrate around dislocations. Therefore, even in the case of relatively weakly deformed semiconductors in which the total number of such centers is small, the probability of their close distribution in the coordinate space may be high. This in turn may induce transitions between the U centers and consequently give rise to spin-dependent effects in the generation and recombination of carriers.

2. NONADIABATIC ELECTRON TRANSITIONS BETWEEN U CENTERS

In the range of parameters of interest to us the activation energy (or the barrier height) for a transition of an electron between two U centers is much greater than the energy $T$. Therefore, these transitions are of multiphonon nature. The excitation of the atomic subsystem can then be considered classically using the configurational coordinates of the centers $X_1$ and $X_2$ of interest to us.

We can say that mechanical vibrations of frequencies not exceeding the Debye value are induced by the influence of temperature and the electron states in the defects adjust themselves adiabatically to the current states of the configurational coordinates $X_1(t)$ and $X_2(t)$. For certain displacements corresponding to crossing of the electron terms we can expect a transition of an electron between centers and the frequency of such transitions is $\gamma(X_1, X_2)$. The value of $\gamma$ can be found simply using quantum-mechanical perturbation theory\textsuperscript{12}

$$\gamma_{\pm}(X_1, X_2) = \frac{2n!}{2n} [W_-(X_1, X_2) - W_+(X_1, X_2)].$$

Here, $W_+(X_1, X_2)$ and $W_-(X_1, X_2)$ are the energies of two centers before and after the transfer of an electron from the first to the second center at fixed values of the configurational coordinates $X_1$ and $X_2$; the energy interval of the overlap $\gamma$ is the matrix element in the Hamiltonian of the transition

$$\mathcal{H} = \gamma \left( \delta d_4 + \vec{d} \vec{d} \right).$$

If the probability of a transition during the time of one passage through a $W_+ = W_-$ resonance is low (nonadiabatic conditions), the interference between different passages through the resonance can be ignored and the total transition frequency is found by averaging $\gamma(X_1, X_2)$ over different configurations of the system of two centers $X_1$ and $X_2$ with a Boltzmann probability function\textsuperscript{13}

$$f(X_1, X_2) = Z^{-1} \exp \left[ \frac{W_-(X_1, X_2) - W_+(X_1, X_2)}{T} \right].$$

Here, $X^0_1$ and $X^0_2$ are the equilibrium displacements of the centers 1 and 2, respectively; $Z$ is the partition function governed by the probability normalization condition. We therefore have

$$\gamma = \int f(X_1, X_2) \gamma(X_1, X_2) dX_1 dX_2.$$

3. DEPENDENCE OF THE OVERLAP INTEGRAL ON THE CONFIGURATIONAL COORDINATES

In calculation of the transition frequency $\gamma$ it is usual to ignore the dependence of $\gamma$ on $X_1$ and $X_2$ (see, for example, Ref. 14). We shall show that this approximation may be incorrect.

We shall consider a defect with a characteristic size $a$ of the order of several lattice constants $a_S$. At a distance $r > a$ from the center of a defect the field of the defect vanishes so that the electron function $\Psi$ falls on increase in $r$ in a universal manner independent of the nature of the defect. In the effective mass approximation when an electron "sees" the crystal as a continuous medium, the function $\Psi$ in the range $r > a$ satisfies the free Schrödinger equation. In the spherically symmetric case, we have\textsuperscript{12}

$$\Psi \approx r^{-1} \exp (-r).$$

The localization radius $r_0 = 1/\kappa$ of an electron depends only on the electron energy $\epsilon$ measured from the bottom of the conduction band:

$$\kappa^2 \epsilon^2/2m = -\epsilon, \quad \epsilon < 0.$$
Calculations of the matrix element of the kinetic energy operator of an electron using the functions \( \psi (r) \) and \( \psi (r^{m}) \) of Eq. (9) gives the familiar asymptotic (for large values of \( R \)) dependence of the energy of an overlap integral on the distance between the centers \( R 
ash 0 \approx 0.1-0.2 \text{ eV}.

We shall now estimate the magnitude of the energy integral for deep centers in silicon. It is worth noting that \( \epsilon \) in Eq. (11) depends on \( \epsilon \) in accordance with Eq. (10), and that \( \epsilon \) represents an energy of a transition between the centers 1 and 2 in a state which is adiabatically adjusted to fit the current values of the configurational coordinates \( X_{1} \) and \( X_{2} \). In the case of the \( |0, 2 > \rightarrow |1, 1 > \) transition (with two electrons at the first center and none at the other in the initial state and with one electron per center in the final state), we have

\[
\epsilon = -Q_{2} + U_{12} - U_{X_{1}}.
\]

(12)

We can see that the energy overlap integral depends exponentially (strongly) on \( X_{1} \) and \( X_{2} \) in Eq. (8) is carried out, this dependence can generally be ignored.

4. FREQUENCY OF \(|0, 2 > \rightarrow |1, 1 > \) TRANSITIONS IN NONADIABATIC CONDITIONS

We shall use the above framework to find the frequency of the \( \gamma (0, 2 \rightarrow 1, 1) \) transitions when in the initial state there are two electrons at the second center and the first is empty and in the final state each center has one electron. The nature of these centers may be different so that we shall distinguish the deformation potential \( Q \) and other phenomenological parameters of the centers by labeling them with the indices 1 and 2. It follows from Eqs. (1) and (2) that

\[
W_{1}, (X_{1}, X_{2}) = \left(k_{1}X_{1} + k_{2}X_{2}\right)^{2} - 2Q_{1}X_{1} + 2Q_{2} + U_{a_{1}} + U_{a_{2}}.
\]

(13a)
\[
W_{2} = \left(k_{2}X_{2} + k_{1}X_{1}\right)^{2} - 2Q_{1}X_{1} + 2Q_{2} + U_{a_{1}} + U_{a_{2}}.
\]

(13b)
\[
W_{s}, (X_{1}, X_{2}) = \left(k_{1}X_{1} + k_{2}X_{2}\right)^{2} - 2Q_{1}X_{1} - 2Q_{2} + U_{a_{1}} + U_{a_{2}}.
\]

(13c)

According to Eqs. (7) and (13) the probability function is Gaussian

\[
f = Z^{-1} \exp \{-\left(\sqrt{Z}X_{1}^{2} - 2X_{1}\right)\}. \]

(14)

where

\[
Z = 2\pi T \left|Q_{1}\right|^{1/2} \times \exp \left[-\Phi \left(X_{1}, X_{2}\right)\right] dX_{1}dX_{2},
\]

where

\[
\Phi = 2\pi \left(\sqrt{Z}X_{1}^{2} - 2X_{1}\right) / T.
\]

We can find the integral with respect to \( X_{2} \) with the aid of the \( \delta \) function, and that with respect to \( X_{1} \) by the saddle point method. The saddle point \( X_{1}, X_{2} \) is defined by the condition for the minimum of \( \Phi \):

\[
k_{1}X_{1} + k_{2}X_{2}/Q_{1} = Q_{1} \left[2 - \sqrt{Z} \epsilon \right]/\left(T1\right),
\]

(16a)

\[
t_{1} - Q_{1}X_{1} = -Q_{2}X_{1} + t_{1} + U_{a_{1}} = t_{1}, X_{1} \equiv t_{1}.
\]

(16b)

We shall assume that, in accordance with Eq. (10), we have \( \kappa (\epsilon) = 1 - \epsilon \) and that \( \epsilon \) is given by Eq. (12). We shall calculate \( \phi \) at the saddle point:

\[
\phi \left(\epsilon \right) = d\phi /dX = \kappa \left(1, 1 \rightarrow 1, 1 \right) / \left(TW_{2} - XW_{4}/W_{2}\right).
\]

Our calculations are valid if the separation between the centers is not too high, so that \( \phi \left(\epsilon \right) > 0 \). This gives the condition

\[
\sqrt{\epsilon} < 1 / \left(TW_{2} + W_{4}\right).
\]

(17)

If we introduce a characteristic temperature

\[
T* = T \left(W_{1} + W_{4}\right) / \left(U_{1} + W_{4}\right)\left(TW_{2} + W_{4}\right),
\]

(18)

then the condition (17) can be rewritten in the form

\[
T* > 0.
\]

Assuming that this condition is satisfied, we find from Eqs. (15)-(18) that the frequency of the activated \( |0, 2 \rightarrow |1, 1 \) transitions is

\[
\gamma (0, 2 \rightarrow 1, 1) = \kappa \left(\epsilon \right) \phi \left(\epsilon \right) \exp \left[-\Delta E_{p} / T \right],
\]

(19)

Here, \( \phi \left(\epsilon \right) \) is the energy overlap integral of Eqs. (11) and (10) at the saddle value of \( \epsilon \) of the tunneling energy of Eq. (12):

\[
T = \frac{1}{W_{1} + W_{4}} \left(W_{1} + W_{4}\right) / \left(U_{1} + W_{4}\right) + 2W_{1}W_{4} + W_{2}T / \left|T1\right|,
\]

(20)

where \( \Delta E_{p} \) is the activation energy of the investigated \( |0, 2 \rightarrow |1, 1 \) transitions. This energy is

\[
\Delta E_{p} = \Delta E_{1} - \Delta E_{2},
\]

(21)

where

\[
\Delta E = t_{1} - t_{2} - U_{a_{1}} + 3W_{1} - W_{4}
\]

(22)

is the difference between the equilibrium (in respect of the configurational coordinates \( X_{1} \) and \( X_{2} \)) energies of Eq. (2) of two electrons after a transition (in the \( 1, 1 \) state) and before a transition (in the \( 0, 2 \) state); \( \Delta E_{1} = \Delta E_{p} - \Delta E_{p} \) is the energy of a configurational barrier. This energy consists of the already known term \( \Delta E_{p} \) of Ref. 15 and an additional term \( \Delta E_{p} \), which appears because of the energy dependence of the overlap integral

\[
\Delta E_{a} = t_{1} - t_{2} - U_{a_{1}} + 2W_{1} + 3W_{4}\left(W_{1} + W_{4}\right).
\]

(23a)
\[
\Delta E_{a} = \left(\epsilon \right) \exp \left(-\Delta E_{p} / T \right),
\]

(23b)

This energy occurs in the exponential temperature dependence of the frequency of the reverse (recombination) transition \( |1, 1 \rightarrow |0, 2 \).

\[
\gamma (1, 1 \rightarrow 0, 2) = \sqrt{\epsilon} \phi \left(\epsilon \right) \exp \left[-\Delta E_{p} / T \right],
\]

(24)

The dependence \( \phi \left(\epsilon \right) \) gives rise to several effects. Firstly, in the numerator of the preexponential factor we find that temperature is modified to \( T \rightarrow T^{*} > T \). Secondly, it follows from Eq. (20) that the energy of a tunneling electron in-
creases and so does the overlap integral \( J \).

Finally, the configurational barrier described by the system (23) becomes higher. If we use \( \gamma_0 \) to denote the frequency of a transition ignoring the dependence \( J \), but only allowing for this factor, we obtain

\[
\gamma_0 \to \gamma = \gamma_0 \sqrt{\frac{FR}{F^2}} \exp \left[ \frac{(\alpha R)^2}{16(W_1 + W_2)} \left( 2 - \frac{W_2}{W_1 + W_2} \right) \right].
\]

(25)

This relationship is valid if the separation between the centers is not too large so that \( T^* \) does not correspond to a minimum, but to a maximum of the activation energy, which should be compared with the \( \alpha W \) between the centers gives rise to an addition to Eq. (26b) change in the activation energy, which should be compared with the \( \alpha R \) effect.

Therefore, in the expression (1) for the electric field we now have \( Q \) and \( \delta E \).

In the case of a vacancy in Si (Ref. 16) we find that \( Q \approx 1 \, \text{eV/Å} \).

In a field \( \delta E = 10^3 \, \text{V/cm} \), we obtain \( e \delta E / Q \approx 10^{-2} \).

It follows from Eq. (3) that the change in the polaron shift in the field is \( \delta W = 2\delta E / Q \).

The value of \( W \) is of the order of 0.2-0.3 eV, so that we have \( \delta W \approx 10^{-2} \, \text{eV} \).

The difference between the values of \( W \) between the two centers gives rise to an additional effect compared with Eq. (26b) in the activation energy, which should be compared with the \( \delta E \) effect.

The estimates made above show that, with the exception of the temperature range \( T < 10^k \), we can ignore the influence of the electric field on \( W \).

3. Generally speaking, a field \( \delta E \) alters the position of the center of gravity of an electron cloud at a center and, consequently, the effective distance between the centers. However, this effect is negligible: \( \delta R \approx e \delta E / k \) for \( |\delta E| > 10^{10} \, \text{V/cm} \) and \( k \approx 10 \, \text{eV/Å} \).

Even when \( 1/k = a_0 = 5 \) Å the relative change in the overlap integral is less than \( 10^{-2} \).

4. Finally, we must bear in mind that the electric field has a direct influence on the overlap integral when the distance between the centers is fixed. This important effect will be discussed in the next subsection.

b) Dependence of the overlap integral on the applied electric field

The application of an electric field influences the wave function \( \psi(\mathbf{r}) \) of an electron tunneling between the investigated centers. In the space between the centers the function \( \psi(\mathbf{r}) \) satisfies the following Schrödinger equation (\( z \) is the electric field direction):

\[
-H\Delta \psi/2m = (\mathbf{e} \cdot \mathbf{E} + \delta E) \psi.
\]

(27)

We shall seek the solution \( \psi(\mathbf{r}) \) in the semiclassical approximation

\[
\psi(\mathbf{r}) = \exp (-S(\mathbf{r})), \quad S = \hbar S_0 + \frac{1}{2} \mathbf{S}^2.
\]

(28)

Hence, in the axially-symmetric case we find that \( S_0 \) is described by

\[
(\delta S_0/\delta \rho)^2 + (\delta S_0/\delta \varphi)^2 = (1 - 2|\delta e|/|\rho|) \delta \varphi^2 = \varphi^2 (z).
\]

(29)

Here, \( \rho \) is the transverse coordinate and \( 1/k \) is the localization radius of an electron in the absence of the field (10). Equation (29) is the Hamiltonian–Jacobi equation for the time-independent part of the Euclidean action \( S_0 \) of a classical particle moving in imaginary time under the influence of a constant force. The path of such motion can be found in a trial manner by integrating the Lagrange function with respect to time and along a classical path, which gives the action, and then express \( S_0 \) in terms of the coordinates of the initial \( z = 0, \varphi = 0 \),
and final \( z, \rho \) points of motion. This gives

\[
S_0(\nu, z) = (2\pi |\delta| |m|)^{-1} \left[ e^{i(z/2)} + \delta |\delta| |m|^2 \right] - (e^{i(z/2)} - \delta |\delta| |m|^2),
\]

(30)

where

\[
x^{i(z/2)} = x^2 - \delta |\delta| m, r^2 = r^2 + \delta^2.
\]

The validity of this solution can readily be confirmed by direct substitution in Eq. (29). We shall analyze the resultant expression (30) for \( S_0 \) expanding it as a series in \( r \):

\[
S_0 = x^{i(z/2)} + (1 - x^{2i|\delta| |m|}) + \ldots, \quad z = x^{i(z/2)} |\delta| |m|.
\]

(31)

Here, \( z \) is the distance along the \( z \) axis from the point with the coordinate \( z/2 \) to the turning point, where \( x^2(z) = 0 \). It should be noted that the expansion of Eq. (31) converges well: even at the limit of validity at \( r = 0 \) it is valid.

To ensure that the precision is \( 1.5 \times 10^{-5} \); however, if \( r \gtrsim 2z_0 \), then to within \( 10^{-2} \) we need to consider only the first term of the expansion, i.e., we can assume that \( S_0 = x^{i(z/2)} r \). In this approximation the influence of the applied electric field on the argument of the exponential function reduces to renormalization of the localization radius \( x \rightarrow x(z/2) \). The result can be interpreted as follows: we can calculate the semi-classical shift of the phase of \( S_0 \) at a point at a certain coordinate \( z_1 \), \( r_1 = \sqrt{z_1^2 + z_0^2} \) by replacing in Eq. (29) \( x(z) \) with the average value of this quantity along a classical path, i.e., by replacing it with \( x(z/2) \). The resultant equation can be solved in a trivial manner. In the spherical case we have \( S_0 = x^{i(z/2)} r \), which agrees with the first term of the expansion in Eq. (31).

In the next order of the classical expansion (28) we have to calculate \( S_1 \), which determines the preexponential factor in the expression for the wave function \( \psi(r) \). Since in \( \delta = 0 \) this factor is independent of \( \kappa \), the influence of the field on the preexponential factor cannot be great; even if do not approach too closely the turning point, this influence can be ignored compared with the field dependence of the argument of the exponential function for \( \kappa \). In this way we obtain the following approximation for \( \psi(r) \), which replaces Eq. (9):

\[
\psi(r) = \exp [-S_1(z, \rho)] r.
\]

(32)

The saddle-point method is used to calculate the overlap integral containing the functions (32). The classical path is called the saddle path when it joins the points with the coordinates \( r_1 \) and \( r_2 \) at which the centers are located. The argument of the exponential function in the integrand \( \psi = \psi((r-r')^2 + \rho') \) contains a sum of the Euclidean actions and this sum is independent of the position of the point \( r \) on the classical path and is given by \( S_0(z_1, \rho_1) \) of Eq. (30) if \( z \) and \( \rho \) are the components of the vector \( R = r_1 - r_2 \) at \( z = z_1 + z_2 \), \( \rho = \rho_1 - \rho_2 \). This gives the argument of the exponential function in the overlap integral: \( \mathcal{J} \propto \exp [-S_0(z, \rho)] \). If \( R \) is less than the distance from the point \( r_1 + r_2/2 \) to the turning point, then - as demonstrated above - we can limit the expansion (31) to the first term: \( S_0(z, \rho) = \tau R, \tau \equiv \kappa(z_2/2) \). If we recall that Eqs. (30) and (31) are obtained on the assumption that \( p_1 = 0 \), it becomes clear that \( z_2/2 \) is the coordinate \( z \). In calculation of the preexponential factor in \( \mathcal{J} \) we ignore the dependence \( \kappa(z) \) and take \( \kappa(z) \) at this point: \( \kappa = \tau \). Consequently, \( \mathcal{J} \) is described by an expression similar to Eq. (11):

\[
\mathcal{J}(R) \simeq \mathcal{J}_0(\tau) \exp (-\tau R).
\]

(33)

where \( \mathcal{J}_0(\tau) = \mathcal{J}_0 \tau^2/4m \). Therefore, in our approximation the influence of an electric field on the overlap integral reduces to the dependence \( \tau(\varepsilon) \). \( \mathcal{J} \) should be calculated from Eq. (10) in terms of the tunneling electron energy \( \varepsilon \) of Eq. (20) measured from the bottom of the conduction band at the point with the coordinate \( r = (r_1 + r_2)/2 \). Using Eqs. (10), (20), and (2), we obtain an expression which describes the change in the energy \( \varepsilon \) in an electric field \( \delta \):

\[
\varepsilon \rightarrow \varepsilon + \mathcal{E}_R + \mathcal{E}_E + h_0 \mathcal{E}_R.
\]

(34)

This change in \( \mathcal{E}_R \) results, in accordance with Eq. (39), in an additional [compared with Eq. (26)] change in the height of the configurational barrier:

\[
\mathcal{E}_E \rightarrow \mathcal{E}_E + \mathcal{E}_R + h_0 \mathcal{E}_R.
\]

(35)

where

\[
h_0 \mathcal{E}_R = \frac{3W_1 W_2 W_4 W_5}{2(W_1 + W_2)} \left[ \kappa(z_2/2) - \kappa(z_1/2) \right] \mathcal{E}_R.
\]

c) Influence of the applied electric field on the frequency of intercenter transitions

We shall estimate the general change in the frequency of the carrier-generation transition \( \nu \) due to the total change in the argument of the exponential function in an electric field. The change is due to the field dependence of the activation energy and of the configurational barrier [Eqs. (26) and (34)] and of the overlap integral [Eqs. (33) and (34)]

\[
\nu(\delta)/\nu(0) = \exp \left[ h_0 (A + B/T + C) + (h_0)^2 (D + F/T) \right].
\]

(36)

The term \( A \) is due to the change in the overlap integral in a field and is obtained by expanding \( \kappa(\varepsilon) \) as a series using Eqs. (34) and (18):

\[
A = \nu(W_1 + W_2 \varepsilon/R) 2 \varepsilon |W_1 + W_2| - W_1 W_2 R \varepsilon.
\]

(37)

The term \( B \) is due to the field dependence of the activation energy \( \Delta E_g \) of Eq. (26):

\[
B = -2W_1 + U_H |W_1 + W_2| = U_H |W_1 + W_2|.
\]

(38)

Here, \( U_H \) is the Hubbard energy. The term \( C \) is related to the additional change in the barrier \( \Delta \mathcal{E}_R \) represented by Eq. (35):

\[
C = \frac{3W_1 W_2 W_4 W_5}{2(W_1 + W_2)} \left[ \kappa(z_2/2) - \kappa(z_1/2) \right] \mathcal{E}_R^2.
\]

(39)

The term \( D \) is due to the change in the overlap integral and \( F \) caused by the change in the configurational barrier [Eq. (26)]:

\[
D = \nu R \varepsilon (W_1 + W_2) [I + \varepsilon (W_1 + W_2) - \nu R \varepsilon R].
\]

(40)

\[
F = -\nu \epsilon (W_1 + W_2).
\]

(41)

If we limit the treatment to the effects which are linear functions of the distance between the
centers, then
\[ A = \frac{z R}{2 t}, \quad B = \frac{U_2}{(W_1 + W_2)}. \]
\[ C = 0, \quad D = \frac{z R}{16 t^2}, \quad F = -\frac{1}{T} (W_1 + W_2). \]

The main qualitative conclusion that follows from Eqs. (36) and (42) is that the application of an electric field has different effects on the temperature-dependent part of the exponential function (terms B and F) and on the temperature-independent part which is a linear function of R (terms A and D \( \propto R \)). If \( \delta \xi < 0 \), the energy barrier height decreases and the probability of thermal fluctuations necessary for the transition increases. However, the tunneling probability falls. If the distance between the centers is not too large, the former effect predominates and the transition frequency increases on application of the field. It is easy to separate experimentally these two effects by determination of the temperature dependences of the transition frequency in different electric fields.


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