

THEORY OF RESONANCE ENERGY TRANSFER BETWEEN IMPURITIES IN SOLIDS

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A new mechanism of resonance energy transfer between impurity atoms (or molecules) in a solid is considered. The excitation level of the impurity is assumed to be close to the exciton excitation band in the crystal matrix. It is shown that the transfer probability is $W_{da} \sim R^\alpha \exp(-\gamma R)$, where R is the distance between the impurities, W_{da} is calculated for one-dimensional and three-dimensional cases and for interstitial as well as substantial impurities. The physical basis for such a mechanism is delocalization of the wave function of the impurity excited state with decrease of Δ which is the difference between the excitation energies of the impurity and exciton. The probability W_{da} as a function of Δ passes through a maximum. If the exciton band possesses several minima for $k \neq 0$ then interference terms from different minima enter W_{da} and for an ordered distribution of impurities this may lead to a nonmonotonous dependence of the energy transfer rate on the impurity concentration. If the exciton band is due to dipole-dipole interaction between the crystal atoms (molecules) then at large distances $W_{da} \sim R_{da}^{-6}$. The mechanism studied here may be especially effective in the case of triplet-triplet excitation transfer.

1. INTRODUCTION

RESONANT excitation transfer from one molecule to another plays an important role in the mechanism of luminescence quenching, in the absorption of light by impurities in condensed media, etc. Förster proposed a mechanism for resonant energy transfer from an excited donor molecule to an acceptor molecule.^[1] If the ground and excited states of the donor and acceptor molecules are coupled by a dipole transition, then the matrix element of the excitation transfer from the donor D to the acceptor A turns out to be $d_{D^*D^0} d_{A^0A^*} / R_{da}^3$, where $d_{D^*D^0}$ and $d_{A^0A^*}$ are the matrix elements of the electric dipole moment for the transition of the donor D from the excited electronic state to the ground state and respectively of the acceptor A from the ground state to the excited state, and R_{da} is the distance between the molecules D and A . Then the probability of excitation transfer from D to A turns out to be

$$W = \alpha / R_{da}^6, \quad (1)$$

where α is a coefficient that can be calculated if the emission spectrum for the molecule D and the absorption spectrum for A are known. If the matrix element of the dipole transition D or A is equal to zero, and only the probability of the electric quadrupole or magnetic dipole transitions differs from zero, then the corresponding probability is $\sim 1/R_{da}^8$.^[2]

In the cited papers, and in others devoted to resonant energy transfer between impurities in condensed media, the properties of the medium were taken into account only by introducing the static dielectric constant of the medium ϵ . However, starting with the experimental investigations of Robinson and co-workers^[3,4] on triplet-triplet energy transfer between isotopically substituted impurities in solid ben-

zene (in^[4] there are many references to papers published to date concerning this question), it has become clear that allowance for the exciton excitation band of the solvent crystal, which is closely adjacent to the excited levels of the impurities, changes radically the character of the energy transfer. In these experiments, the shift of the triplet level of the impurity relative to the level of the solvent molecule is $\Delta \gg \epsilon_0$, where ϵ_0 is the width of the triplet electronic band. The probability of energy transfer is then $W \sim (\epsilon_0/\Delta) \exp(R_{da}/a)$, where a is the interatomic distance in the crystal. An exact result was obtained in this case only for a one-dimensional system (polymer) for interstitial impurities, when the interaction between the impurity molecules and the polymer molecules is $V \ll \Delta$, was considered theoretically in^[5]. The calculation was based on perturbation theory in terms of the small parameter V/Δ . The energy transfer probability was then found to be $W \sim \exp(-\gamma R_{da})$, where γ is a coefficient that depends strongly on the arrangement of the energy levels of the impurities and of the solvent substance.

In the case of a three-dimensional crystal, the exponential dependence of the excitation-transfer probability on the distance between impurities is obtained only if the interaction between the atoms of the crystal, leading to the presence of the exciton band, is of the short-range type (excitons with short-range action). In the case of dipole-dipole excitons at larger distances, $W \sim \alpha R_{da}^{-6}$, where the coefficient α is strongly anisotropic and depends on the characteristics of the exciton band.

In this paper we present an exact solution of the problem of energy transfer in both the one-dimensional and three-dimensional cases, for interstitial and substitutional impurities with $\Delta < \epsilon_0$. This inequality is frequently satisfied under experimental conditions (see, for

example, ^[6]), and it is precisely in this case that the investigated energy-transfer mechanism is most effective.

2. SYSTEM HAMILTONIAN. ENERGY TRANSFER MATRIX ELEMENT

We are considering the following system: atom¹⁾ of the main substance situated at the crystal-lattice sites, a donor atom D, and an acceptor atom A. As will be shown below, the exponential character of the dependence of the excitation-transfer probability on the distance between the donor and acceptor atoms does not depend on whether the impurities are of the interstitial or of the substitutional type, all that changes is the method of calculating the constants. We write down the Hamiltonian of the system with interstitial impurities in the second-quantization representation:

$$\hat{\mathcal{H}} = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} b_{\mathbf{k}}^+ b_{\mathbf{k}} + \epsilon_d b_d^+ b_d + \epsilon_a b_a^+ b_a + \sum_{\mathbf{k}} [V_d(\mathbf{k}) b_{\mathbf{k}}^+ b_d + V_a(\mathbf{k}) b_{\mathbf{k}}^+ b_a + \text{h.c.}] \quad (2)$$

Here $\epsilon_{\mathbf{k}}$ is the exciton energy reckoned from the ground (electronically unexcited) state of the crystal, the summation over the wave vector \mathbf{k} is within the limits of the first Brillouin zone, ϵ_d and ϵ_a are the excitation energies of the donor and of the acceptor reckoned from the ground states of the corresponding atoms, $b_{\mathbf{k}}^+$ and $b_{\mathbf{k}}$ are the operators of creation and annihilation of the excited state of the crystal, b_d^+ , b_d , and b_a^+ , b_a are the operators of creation and annihilation of the excited states of the donor and acceptor, respectively. The vacuum wave function is assumed to be the wave function of the ground state of the system $\Psi_0 = \Phi_0 \varphi_{d0} \varphi_{a0}$. The wave function of the exciton is then $\Psi_{\mathbf{k}} = b_{\mathbf{k}}^+ \Psi_0$, and the wave function of the excited state of the donor (or acceptor) is $\Psi_d = b_d^+ \Psi_0$ ($\Psi_a = b_a^+ \Psi_0$).

The program of the subsequent analysis is as follows: we find the distribution of the energy levels of the impurity atoms due to the interaction via the excitons. This enables us to find the matrix element of the excitation transfer from the donor to the acceptor, and then also the total transfer probability.

We call attention to the fact that ϵ_d and ϵ_a in formula (2) are not observable quantities. Indeed, we have retained in (2) only the matrix elements of the interaction between the impurity atoms and the atoms of the main substance, of the type $\langle \Psi_{\mathbf{k}} | \hat{V} | \Psi_d \rangle$, i.e., those connecting the excited states of the impurities and of the crystal. On the other hand, all the "diagonal" matrix elements of \hat{V} , which connect the wave functions of the crystal only, or else of the impurity only, are included in the zeroth Hamiltonian, the diagonalization of which leads to the first three terms of the right side of formula (2). But whereas a local perturbation leaves the quasicontinuous spectrum in the excitation band of the crystal practically unchanged, the levels ϵ_d and ϵ_a can differ greatly from the excitation levels of the isolated atoms, without being at the same time excitation levels of the impurity atoms in the crystal, so that a part of the interaction with the crystal atoms (the last term in

the right side of Eq. (2)) is not taken into account in their calculation. However, we shall show below that the final expression for the energy transfer probability will contain the true excitation energies of the impurity atoms in the crystal.

Let us examine in greater detail the structure of the expression

$$V_d(\mathbf{k}) = \langle \Psi_{\mathbf{k}} | \hat{V}_d | \Psi_d \rangle. \quad (3)$$

The operator \hat{V}_d is the operator of the Coulomb interaction of the valence electrons of the donor atom with the valence electrons of the crystal atoms:

$$\hat{V}_d = \sum_j \sum_i \frac{e^2}{|r_i - r_j|} \quad (4)$$

where the index i pertains to the electrons of the donor atom, and j to the crystal electrons. That part of the operator \hat{V}_d , which leads to the transfer of excitation, can be written as the sum of different multipole terms and of the exchange interaction (see, for example, ^[7]). Retaining from among the multipole terms only the dipole-dipole interaction (the higher multipole terms, being short-range, can be effectively included in the exchange term), we obtain

$$\hat{V}_d(\mathbf{k}) = \frac{1}{\sqrt{N}} \exp(i\mathbf{k}\mathbf{R}_d) \sum_{\mathbf{R}_m'} \exp(i\mathbf{k}\mathbf{R}_m') \frac{(\boldsymbol{\mu}_d^* \boldsymbol{\mu}) \mathbf{R}_m'^2 - 3(\boldsymbol{\mu}_d^* \mathbf{R}_m')(\boldsymbol{\mu} \mathbf{R}_m')}{R_m'^5} + \frac{1}{\sqrt{N}} \exp(i\mathbf{k}\mathbf{R}_s) V_{ex} = \frac{1}{\sqrt{N}} \exp(i\mathbf{k}\mathbf{R}_d) v_d(\mathbf{k}), \quad (5)$$

where $\mathbf{R}_m' = \mathbf{R}_m - \mathbf{R}_d$, $\boldsymbol{\mu}_d$ and $\boldsymbol{\mu}$ are the matrix elements of the dipole transition in the impurity atom and in the crystal, respectively, V_{ex} is the exchange integral, \mathbf{R}_s is the radius vector of the atom closest to the impurity, and is assumed approximately equal to \mathbf{R}_d , and N is the number of atoms in the sample.

We now proceed to determine the exact energy levels of the system. We seek a wave function that diagonalizes the Hamiltonian (2) in the form

$$\Psi = \sum_{\mathbf{k}} \alpha_{\mathbf{k}} b_{\mathbf{k}}^+ | \Psi_0 \rangle + \alpha_d b_d^+ | \Psi_d \rangle + \alpha_a b_a^+ | \Psi_a \rangle. \quad (6)$$

We then obtain in the usual manner the following system of equations for the determination of the energy levels of the system and of the coefficients $\alpha_{\mathbf{k}}$, α_d , and α_a :

$$\begin{aligned} \alpha_{\mathbf{k}}(\epsilon_{\mathbf{k}} - E) + \alpha_d V_d(\mathbf{k}) + \alpha_a V_a(\mathbf{k}) &= 0, \\ \sum_{\mathbf{k}} \alpha_{\mathbf{k}} V_d^*(\mathbf{k}) + \alpha_d(\epsilon_d - E) &= 0, \\ \sum_{\mathbf{k}} \alpha_{\mathbf{k}} V_a^*(\mathbf{k}) + \alpha_a(\epsilon_a - E) &= 0. \end{aligned} \quad (7)$$

Expressing $\alpha_{\mathbf{k}}$ with the aid of the first equation (7) in terms of α_d and α_a , and substituting in the second and third equations, we obtain a system of equations:

$$\begin{aligned} \alpha_d \left[\sum_{\mathbf{k}} V_d^*(\mathbf{k}) \frac{1}{E - \epsilon_{\mathbf{k}}} V_d(\mathbf{k}) + \epsilon_d - E \right] + \alpha_a \sum_{\mathbf{k}} V_d^*(\mathbf{k}) \frac{1}{E - \epsilon_{\mathbf{k}}} V_a(\mathbf{k}) &= 0, \\ \alpha_d \sum_{\mathbf{k}} V_a^*(\mathbf{k}) \frac{1}{E - \epsilon_{\mathbf{k}}} V_d(\mathbf{k}) + \alpha_a \left[\sum_{\mathbf{k}} V_a^*(\mathbf{k}) \frac{1}{E - \epsilon_{\mathbf{k}}} V_a(\mathbf{k}) + \epsilon_a - E \right] &= 0. \end{aligned} \quad (8)$$

Equating the determinant of the system (8) to zero, we obtain an equation for the eigenvalues of E . We are interested only in the energy level outside the limits of

¹⁾We say "atoms" for simplicity, but these can be either atoms or molecules.

the exciton band, which is interpreted as the impurity excitation level E_d (or E_a).

We call attention to the fact that by equating to zero the expression in the square brackets in the first or second equations of (8), we obtain an equation for the determination of the experimentally observed impurity level E_d' in the case of large dilution, for only in such a case is it possible to consider a single impurity atom. Let the impurity level lie below the bottom of the exciton band. The largest contribution to the sums in (8) will obviously be made by the terms having $\epsilon_{\mathbf{k}}$ near the bottom of the band. Assuming that the change of the excitation energy of the impurity atom due to the interaction with the other impurity atom is

$$|\delta E_d| = |E_d - E_d'| \ll |E_d' - \epsilon_{\mathbf{k}}|, \quad (9)$$

we can expand the sums in the square brackets of (8) in terms of the small quantity $\delta E_d / (E_d - \epsilon_{\mathbf{k}})$. It is then possible to put in the remaining sums $E_d = E_d'$, since these sums themselves, as will be shown below, are small. We assume also that $E_d = E_a$. This simplifies the derivations without affecting the magnitude of the calculated excitation-transition matrix element. Owing to the interaction via the excitons, the doubly-degenerate impurity level (either the donor or the acceptor is excited) is split. Taking (9) into account and equating to zero the determinant of the system (8) we obtain for the splitting δE_d

$$|\delta E_d| = 2 \left[1 + \sum_{\mathbf{k}} \frac{|V_d(\mathbf{k})|^2}{(E_d - \epsilon_{\mathbf{k}})^2} \right]^{-1/2} \left[1 + \sum_{\mathbf{k}} \frac{|V_a(\mathbf{k})|^2}{(E_a - \epsilon_{\mathbf{k}})^2} \right]^{-1/2} \left| \sum_{\mathbf{k}} \frac{V_d^*(\mathbf{k}) V_a(\mathbf{k})}{E_d - \epsilon_{\mathbf{k}}} \right|. \quad (10)$$

On the other hand, if there is some interaction \hat{v} that leads to the transition of the excitation from a donor to an acceptor, then the matrix element of the transition is

$$|v_{da}| = |\langle \Psi_{da} | \hat{v} | \Psi_{a0} \rangle| = 1/2 |\delta E_d|. \quad (11)$$

Substituting (10) in (11), we obtain for the matrix element of the transition

$$|v_{da}| = \left[1 + \sum_{\mathbf{k}} \frac{|V_d(\mathbf{k})|^2}{(E_d - \epsilon_{\mathbf{k}})^2} \right]^{-1/2} \left[1 + \sum_{\mathbf{k}} \frac{|V_a(\mathbf{k})|^2}{(E_a - \epsilon_{\mathbf{k}})^2} \right]^{-1/2} \times \left| \sum_{\mathbf{k}} \frac{V_d^*(\mathbf{k}) V_a(\mathbf{k})}{E_d - \epsilon_{\mathbf{k}}} \right|. \quad (12)$$

The dependence of $|v_{da}|$ on the distance R_{da} is determined principally by the energy spectrum in the exciton band near the minimum of the band (if E_d lies below the exciton band), or near the maximum (if E_d lies above the exciton band). As will be shown in the next section, if $\epsilon(\mathbf{k})$ has no singularities at the minimum of the band, then $v_{da} \sim \exp(-\gamma R_{da}/2)$. The exponential character of the dependence of v_{da} on R_{da} is due to the last factor in the right side of (12), and the closer the excitation impurity level to the exciton band, the smaller γ . The physical reason for this dependence is as follows:

When E_d approaches $\epsilon_{\mathbf{k}}$, the excitation becomes more and more delocalized, and spreads over the closely-lying atoms of the host matrix. This can be readily verified by calculating a wave function of type (6) for one impurity atom. Such a "swelling" of the

wave function of the excited state leads to the so-called Rashba effect, namely a sharp increase of the coefficient of light absorption by the impurity when the impurity excitation energy approaches the exciton band of the crystal.^[8,9] In our case, the "swelling" of the wave function of the excited state of the donor leads its overlap with the unexcited wave function of the acceptor, and increases the excitation transition probability. However, the first two factors in (12) decrease with decreasing $|E_d - \epsilon_{\mathbf{k}}|$, and this decreases v_{da} . The reason is that as the wave function Ψ_d "swells out" its amplitude near the acceptor atom may decrease, since the region where Ψ_d is significantly different from zero ($R \lesssim 1/\gamma$) increases, and Ψ_d is normalized to unity: $\int |\Psi_d|^2 d\mathbf{R} = 1$. Therefore the probability of excitation transfer as a function of $|E_d - \epsilon_{\mathbf{k}}|$ passes through a maximum.

In the case of a dipole-dipole interaction between the crystal atoms (three-dimensional case), $\epsilon_{\mathbf{k}}$ has a singularity at $\mathbf{k} = 0$,^[7] due to the appearance of a long-range character of the interaction, leading to the presence of an exciton. Then v_{da} in (12) depends on R_{da} in a much more complicated manner, and at large distances we get $v_{da} \sim R_{da}^3$.

3. EXCITATION TRANSFER VIA EXCITONS WITH SHORT-RANGE ACTION

We now proceed to the calculation of v_{da} by means of formula (12) in those cases when the interaction that leads to the appearance of the exciton band is short-range. We consider the one-dimensional and three-dimensional cases.

In the one-dimensional case (physical realization—a polymer chain) it is reasonable to confine oneself only to the nearest-neighbor interaction, both in determining the exciton-band structure and in the calculation of the interaction between the impurity and the polymer links.

Then

$$\epsilon_{\mathbf{k}} = E_0 - \epsilon_0 \cos(kd), \quad (13)$$

where $2\epsilon_0$ is the width of the exciton band, $-\pi/d \leq k \leq \pi/d$, d —period of the one-dimensional structure (polymer), and

$$V_d(k) = \frac{1}{\sqrt{N}} e^{ikR_{da}} v_d, \quad V_a(k) = \frac{1}{\sqrt{N}} e^{ikR_a} v_a, \quad (14)$$

where v_d, v_a is the term in (5) corresponding to the polymer link closest to the impurity. Replacing in (12) summation over \mathbf{k} by integration and assuming

$$\epsilon_0 \gg \Delta, \quad (15)$$

where $\Delta = E_0 - \epsilon_0 - E_d$ is the energy difference between the bottom of the exciton band and the impurity level, we obtain, in accordance with (12),

$$|v_{da}| = \frac{|v_a| |v_d|}{\sqrt{2\epsilon_0\Delta}} \left[1 + \frac{|v_a|^2}{2\sqrt{2}\epsilon_0^{1/2}\Delta^{3/2}} \right]^{-1/2} \left[1 + \frac{|v_d|^2}{2\sqrt{2}\epsilon_0^{1/2}\Delta^{3/2}} \right]^{-1/2} \times \exp \left\{ -\frac{R_{da}}{d} \sqrt{2\Delta/\epsilon_0} \right\}. \quad (16)$$

If v_d and v_a are sufficiently large,

$$v_a, v_d \gg \epsilon_0^{1/2}\Delta^{3/2}, \quad (17)$$

we obtain for v_{da} the simple expression

$$|v_{da}| = 2\Delta \exp\left\{-\frac{R_{da}}{d}\sqrt{2\Delta/\epsilon_0}\right\}, \quad (18)$$

i.e., the probability of excitation transfer does not depend at all on the character of the interaction v_a and v_d (provided, however, that (17) is satisfied). In the case of small v_a and v_d

$$v_a, v_d \ll \epsilon_0^{1/2}\Delta^{3/4}, \quad (19)$$

we obtain for $|v_{da}|$

$$|v_{da}| = \frac{|v_d v_a|}{\sqrt{2\epsilon_0}\Delta} \exp\left\{-\frac{R_{da}}{d}\sqrt{2\Delta/\epsilon_0}\right\}, \quad (20)$$

In the three-dimensional case, to describe the structure of the exciton band we confine ourselves to the effective-mass approximation of the exciton near the bottom of the band. This approximation is physically justified if the condition (15) is satisfied, since the integrals in (12) contain only those exciton states, whose energies are close to the bottom of the band. Near the bottom of the band ($\mathbf{k}_{\min} = \mathbf{k}_0$)

$$\epsilon_{\mathbf{k}} = \epsilon_{\mathbf{k}_0} + \sum_{\alpha=x, y, z} \frac{\hbar^2}{2\mu_{\alpha}} (\mathbf{k} - \mathbf{k}_0)_{\alpha}^2, \quad (21)$$

where μ_{α} are the principal values of the exciton effective-mass tensor. Using (15), we can extend the integration with respect to \mathbf{k} in (12) to $\mathbf{k} = \infty$, and we then obtain

$$\begin{aligned} |v_{da}| = & \left[1 + \frac{\Omega}{2\sqrt{2}\pi\hbar^3} \sum_i \frac{(\mu_{ix}\mu_{iy}\mu_{iz})^{1/2}}{\Delta_i^{1/2}} |v_d(\mathbf{k}_{0i})|^2\right]^{-1/2} \\ & \times \left[1 + \frac{\Omega}{2\sqrt{2}\pi\hbar^3} \sum_i \frac{(\mu_{ix}\mu_{iy}\mu_{iz})^{1/2}}{\Delta_i^{1/2}} |v_a(\mathbf{k}_{0i})|^2\right]^{-1/2} \\ & \times \frac{\Omega}{\sqrt{2}\pi\hbar^3} \left| \sum_i (\mu_{ix}\mu_{iy}\mu_{iz})^{1/2} \frac{v_d^*(\mathbf{k}_{0i})v_a(\mathbf{k}_{0i})}{R_{i'}} \exp(-R_{i'}) \exp(i\mathbf{k}_{0i}\mathbf{R}_{da}) \right|, \end{aligned} \quad (22)$$

where Ω is the volume of the unit cell of the crystal, the sum over i is the sum over all the minima of the exciton band, $\Delta_i = \epsilon_{\mathbf{k}_{0i}} - E_d$,

$$R_{i'} = \frac{\sqrt{2}}{\hbar} \Delta_i^{1/2} \sqrt{X_{da}^2 \mu_{ix} + Y_{da}^2 \mu_{iy} + Z_{da}^2 \mu_{iz}}, \quad (23)$$

X_{da} , Y_{da} , and Z_{da} are the projections of R_{da} on the coordinate axes, chosen in such a way that the effective-mass tensor is diagonal close to the i -th minimum.

Formula (22) is difficult to interpret. If all the Δ_i are identical ($\Delta_i = \Delta$), the effective mass is isotropic ($\mu_{ix} = \mu_{iy} = \mu_{iz} \equiv \mu$, $v_d, v_a(\mathbf{k}_{0i})$ are the same for all \mathbf{k}_{0i} , and we assume that the inequality (17) is satisfied (in this case $\epsilon_0 \approx \hbar^2/\mu\Omega^{2/3}$), we obtain

$$|v_{da}| = \frac{2\hbar\sqrt{\Delta}}{\sqrt{\mu}} \frac{1}{n} \left| \sum_i e^{i\mathbf{k}_{0i}\mathbf{R}_{da}} \right| \frac{1}{R_{da}} \exp\left\{-R_{da} \frac{\sqrt{2\mu\Delta}}{\hbar}\right\} \quad (24)$$

where n is the number of minima of the exciton band.

We call attention to the fact that if there are several minima in the exciton band, the contributions from them interfere (the sum in the expression (24)). v_{da} may vanish at certain values of R_{da} . Thus, if there are two minima, such that $\mathbf{k}_{01} = -\mathbf{k}_{02} = \mathbf{k}_0$, then

$$\frac{1}{n} \left| \sum_i e^{i\mathbf{k}_{0i}\mathbf{R}_{da}} \right| = |\cos(\mathbf{k}_0\mathbf{R}_{da})|.$$

At values of R_{da} such that $(\mathbf{k}_0\mathbf{R}_{da}) = (2l+1)\pi/2$, we get $v_{da} = 0$. If the impurities are disposed in the crystal in

an orderly manner, i.e., if $\overline{\delta R_{da}}$ the average spread of the distances between the neighboring impurity atoms satisfies the condition $\overline{\delta R_{da}} < \pi/2k_0$, then the presence of such an interference can lead to a nonmonotonic dependence of the excitation transfer probability on the impurity density. The width of the impurity excitation band (when there is only one species of impurities) is also determined by formula (24). Then the width of the band as a function of the impurity density may have oscillations.

So far we have considered interstitial impurities. In the case of substitutional impurities, the physical reasons for the appearance of an excitation transfer probability that is exponentially dependent on the distance are the same as given above, but the mathematical approach is somewhat different. We present the results for the case when the impurity atom differs from the crystal atoms only in the magnitude of the excitation energy; the interaction between the impurity and the neighboring atoms is the same as for the atoms of the host matrix. It is easily seen that the Hamiltonian of the system then takes, in lieu of (2), the form^[8]

$$\hat{\mathcal{H}} = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} + \Delta \epsilon_d b_d^{\dagger} b_d + \Delta \epsilon_a b_a^{\dagger} b_a,$$

where $\Delta\epsilon_d$ is the difference between the excitation energies of the donor and crystal free atoms, $\Delta\epsilon_a$ is the same for the acceptor. Assuming the inequality (9) to be satisfied, we obtain for the one-dimensional case the result (18), and for the three-dimensional case, in lieu of (22),

$$|v_{da}| = 2 \left| \sum_i (\mu_{ix}\mu_{iy}\mu_{iz})^{1/2} \frac{e^{-R_{i'}}}{R_{i'}} \exp(i\mathbf{k}_{0i}\mathbf{R}_{da}) \right| \left[\sum_i (\mu_{ix}\mu_{iy}\mu_{iz})^{1/2} \Delta_i^{-1/2} \right]^{-1}. \quad (25)$$

If all the minima of the exciton band are the same, then v_{da} is determined by formula (24). Thus, in cases of practical interest (the satisfaction of the inequality (17), i.e., not too weak an interaction between the impurity and crystal atoms, and not too large a gap Δ , when v_{da} is not too small) the excitation transfer probability does not depend on whether we are dealing with substitutional or interstitial impurities.

So far we have disregarded direct interaction \hat{V}_{da} between the atoms D and A; if this interaction exists, it has a multipole character (since R_{da} is large). If R_{da} is so large that the exponential term in v_{da} becomes smaller than the power-law term due to \hat{V}_{da} , then it is easy to show that

$$v_{da} = \left[1 + \sum_{\mathbf{k}} \frac{|v_d(\mathbf{k})|^2}{(E_d - \epsilon_{\mathbf{k}})^2}\right]^{-1/2} \left[1 + \sum_{\mathbf{k}} \frac{|v_a(\mathbf{k})|^2}{(E_a - \epsilon_{\mathbf{k}})^2}\right]^{-1/2} |V_{da}|. \quad (26)$$

Only in the case of a weak interaction of the impurity atoms with the crystal atoms (19) do we have $v_{da} \approx |V_{da}|$,^[2] but in the case of a strong interaction between the impurity and the crystal (inequality (17)), the transfer by means of the Förster-Dexter mechanism decreases appreciably when $\Delta \ll \epsilon_0$. Assuming $v_d, v_a \approx \epsilon_0$, we get for v_{da}

$$v_{da} \approx (\Delta/\epsilon_0)^{1/2} |V_{da}|. \quad (27)$$

4. EXCITATION TRANSFER VIA DIPOLE-DIPOLE EXCITONS

We now consider the three-dimensional case, when the excitation level of the impurity is close to the di-

pole-dipole exciton band. Then $\epsilon(\mathbf{k})$ has a singularity at $\mathbf{k} = 0$, i.e., when $\mathbf{k} \rightarrow 0$ the value of the energy $\epsilon(\mathbf{k})$ depends on the direction of \mathbf{k} . Near $\mathbf{k} = 0$, the function $\epsilon(\mathbf{k})$ can be represented as a sum of a part that is regular when $\mathbf{k} = 0$, a part quadratic in \mathbf{k} , and an irregular part that depends only on the angles θ and φ that specify the direction of \mathbf{k} :^[10]

$$\epsilon(\mathbf{k}) = 1/2 \hbar^2 \mu_{\alpha\beta}^{-1} k_{\alpha} k_{\beta} + \bar{\epsilon} f(\theta, \varphi), \quad (28)$$

where $\bar{\epsilon}$ is a parameter with the dimension of energy, and as a rule $\bar{\epsilon} \sim \epsilon_0$ is the width of the band. (To simplify the derivations, we shall henceforth assume that $\mu_{\alpha\beta}^{-1} = \mu^{-1} \delta_{\alpha\beta}$).

Let us consider for concreteness a substitutional impurity. Then

$$|v_{da}| = \left| \int d\mathbf{k} \exp(i\mathbf{k} \mathbf{R}_{da}) [\Delta + \epsilon(\mathbf{k})]^{-1} \left[\int d\mathbf{k} [\Delta + \epsilon(\mathbf{k})]^{-2} \right]^{-1} \right| \quad (29)$$

The dependence of v_{da} on R_{da} is determined by the integral I in the numerator of (29). If we neglect the terms that decrease exponentially with increasing R_{da} , then we can show that after integration with respect to \mathbf{k} the integral I reduces to

$$I = \frac{\pi}{2} \int_{-1}^{+1} dx \int_0^{2\pi} d\varphi \{ a_1(x, \varphi) \exp[-a_1(x, \varphi) R_{da} |t|] - a_2 \exp[-a_2 R_{da} |t|] \}, \quad (30)$$

where

$$a_1(x, \varphi) = \frac{1}{\hbar} \sqrt{2\mu} [\Delta + \bar{\epsilon} f(x, \varphi)]; \quad a_2 = \frac{1}{\hbar} \sqrt{2\mu} \Delta, \quad (31)$$

$$t = x x_0 + \sqrt{1 - x^2} \sqrt{1 - x_0^2} \cos(\varphi - \varphi_0), \quad x \equiv \cos \theta, \quad x_0 \equiv \cos \theta_0,$$

θ_0 and φ_0 are the spherical angles of \mathbf{R}_{da} .

The integral (30) cannot be evaluated exactly. However, if we go over to integration variables \mathbf{x} and t , then we can readily see that the expansion of I in powers of R_{da} begins with R_{da}^{-3} . In the general case we obtain for this first term of the asymptotic expansion of v_{da} in terms of R_{da} the expression

$$|v_{da}| = \frac{1}{R_{da}^3} \frac{\hbar^3 \bar{\epsilon}^{3/2}}{\sqrt{2} \pi \mu^{3/2}} \left[\ln \frac{\sqrt{\bar{\epsilon} + \Delta} + \sqrt{\bar{\epsilon}}}{\sqrt{\Delta}} \right]^{-1} \times \left| \int_{-1}^{+1} dt \left[3 \frac{a_1'(x, t)}{a_1^4(x, t)} - \frac{a_1''(x, t)}{a_1^3(x, t)} \right]_{t=0} (1-t^2)^{-1/2} \right|. \quad (32)$$

Here a_1 is the function defined by (31), but with variables \mathbf{x} and φ replaced by $\tilde{\mathbf{x}}$, t and $\mathbf{x} = \sqrt{(1-x_0^2)(1-t^2)} + t x_0$,

$$a_1' = \frac{da_1(\tilde{\mathbf{x}}, t)}{dt}, \quad a_1'' = \frac{d^2 a_1(\tilde{\mathbf{x}}, t)}{dt^2}.$$

Let us consider a concrete example. Let the crystal contain one atom per unit cell and let the excited level of the crystal atoms, causing the exciton band, be nondegenerate. Then^[10]

$$f(\theta, \varphi) = \cos^2 \theta, \quad (33)$$

where θ is the angle between \mathbf{k} and the dipole moment of the transition. We then obtain for parallel transfer ($\theta_0 = 0$)

$$v_{da} = \frac{1}{\sqrt{2}} \frac{\hbar^3 \bar{\epsilon}^{3/2}}{\mu^{3/2} \Delta^2} \left[\ln \frac{\sqrt{\bar{\epsilon} + \Delta} + \sqrt{\bar{\epsilon}}}{\sqrt{\Delta}} \right]^{-1} \frac{1}{R_{da}^3}. \quad (34)$$

and for perpendicular transfer ($\theta_0 = \pi/2$)

$$v_{da} = \frac{1}{2\sqrt{2}} \frac{\hbar^3 \bar{\epsilon}^{3/2}}{\mu^{3/2} \Delta^2 (1 + \bar{\epsilon}/\Delta)^{3/2}} \left[\ln \frac{\sqrt{\bar{\epsilon} + \Delta} + \sqrt{\bar{\epsilon}}}{\sqrt{\Delta}} \right]^{-1} \frac{1}{R_{da}^3}. \quad (35)$$

The power-law dependence of v_{da} on R_{da} is valid at distances $R_{da} \gg d\sqrt{\epsilon_0/\Delta}$, where d is the crystal-lattice period. When $R_{da} \lesssim d\sqrt{\epsilon_0/\Delta}$, formula (24) holds true, but since the argument of the exponential is $\lesssim 1$, v_{da} is practically constant at these distances. The fact that at large distances $v_{da} \sim R_{da}^{-3}$ in the case of a dipole-dipole exciton band has a simple physical meaning. So long as we have dealt with short-range action, the excitation transfer was due to the overlap of the "blown up" wave functions and the acceptor, and since the wave functions decrease exponentially with increasing distance, v_{da} also had an exponential dependence on R_{da} . The "blown up" wave function of the impurity contains, with a large weight, excited states of the crystal atoms that lie close to the impurity. If the overlap is small, then the presence of the dipole-dipole interaction between the crystal atoms makes possible excitation transfer between the impurities via the dipole-dipole mechanism. The number of crystal atoms whose excited states enter in the "blown up" impurity function increases with decreasing Δ . Therefore the matrix element of the dipole-dipole transition increases with decreasing Δ (see (34) and (35)).

In the case of substitutional impurities, the interaction of which with the crystal atoms is large (17), formula (32) is valid. But if the interaction is small (19), then

$$v_{da} = |v_{dv}| \frac{2\pi}{R_{da}^3} \left| \int_{-1}^{+1} dr \left(3 \frac{a_1'^2}{a_1^4} - \frac{a_1''}{a_1^3} \right) (1-r^2)^{-1/2} \right|. \quad (36)$$

The calculations in this section are valid only when $R_{da} < \lambda$, where λ is the wavelength of the electromagnetic radiation, corresponding to the excitation of the exciton. Indeed, the decisive values in the calculation of I are $k \sim R_{da}^{-1}$. When $k < \lambda^{-1}$, it is necessary to take into account in the calculation of the exciton band also the delayed interaction.^[7-10] Thus, Eqs. (32), (34), and (35) are valid only when $R_{da} < \lambda$, when I is determined by $\epsilon(\mathbf{k})$ at $k \sim R_{da}^{-1} > \lambda^{-1}$. Since $\lambda \gtrsim 10^3 \text{ \AA}$, formulas (32)-(36) are valid for all practically interesting applications (impurity concentration $> 10^{15} \text{ cm}^{-3}$).

5. CALCULATION OF THE TRANSFER PROBABILITY

We proceed now to calculate the probability of excitation transfer from the donor to the acceptor. We make the assumption, which is almost always satisfied in experiments, that the rate of excitation transfer with a given energy E_d is much smaller than the rate of establishment of the equilibrium populations over all vibrational states of the given electronic level, owing to the interaction with the lattice phonons.^[2] Thus, no matter how the excited state of the donor is obtained, we should average over all the possible energies of the donor transition from the excited to the ground electronic state (at the given temperature) and over all the possible energies of the acceptor transition from the ground electronic state to the excited state. The accep-

tor has excited states with energies lower than those of the donor. Therefore the acceptor atom, once excited, goes over very rapidly (owing to the interaction with the phonons) to these lower states, and if the temperature is sufficiently low, the population of the acceptor excited states with higher energies is close to zero. We can therefore disregard the inverse transition from the acceptor to the donor. Then, using the procedure described in [2], we obtain the total transition probability

$$W_{da} = \frac{2\pi}{\hbar} \int |v_{da}|^2 \rho_d(\Delta) \rho_a(\Delta) d\Delta, \quad (37)$$

where $\rho_d(\Delta)$ and $\rho_a(\Delta)$ are the numbers of transitions produced when the donor becomes deactivated and the acceptor becomes excited, respectively, per unit energy interval.

To make practical use of (37), it is necessary to know $\rho_d(\Delta)$ and $\rho_a(\Delta)$. However, $\rho_d(\Delta)$ and $\rho_a(\Delta)$ cannot be determined directly from experiment. The observed donor emission intensity or acceptor absorption coefficient at a definite frequency depend not only on $\rho_d(\Delta)$ and $\rho_a(\Delta)$, but also on the oscillator strengths of the corresponding transitions. Since at small values of Δ an important role is played in the absorption and emission intensities by the solvent parameters (in accordance with the Rashba effect), the determination of $\rho_d(\Delta)$ and $\rho_a(\Delta)$ from the spectral intensities of the absorption and emission becomes even more difficult. In order of magnitude we have

$$\rho_d(\Delta) \approx 1/\delta E_{em}^d, \quad \rho_a(\Delta) \approx 1/\delta E_{abs}^a, \quad (38)$$

where δE_{em}^d and δE_{abs}^a are the characteristic energy widths of the donor emission band and of the acceptor absorption band, respectively. Expressions (38) can be substituted in (37) if the edges of the donor emission band and the acceptor absorption band are weakly diffuse, i.e., v_{da} should change little in the frequency region $\delta\omega$ in which the absorption or emission intensity changes in order of magnitude. From (24) we can obtain

$$\delta\omega < \epsilon_0 c^{1/3} / \hbar, \quad (39)$$

where c is the relative impurity concentration. A similar inequality should be satisfied also by the diffuseness of the lower edge of the exciton absorption band, in order to be able to determine the quantity Δ . If (39) is not satisfied, then an exact calculation of W_{da} by means of (37) calls for exact knowledge of the behavior of $\rho_d(\Delta)$ and $\rho_a(\Delta)$.

If (39) is satisfied, then formula (37) can be rewritten in the form

$$W_{da} = C \frac{2\pi}{\hbar} \frac{1}{\delta E_{em}^d \delta E_{abs}^a} \int_{\Delta_{min}}^{\Delta_{max}} |v_{da}(\Delta)|^2 d\Delta. \quad (40)$$

Here Δ_{min} and Δ_{max} are the energy distances from the exciton absorption-band edge to the limits of the overlap of the donor emission band and the acceptor absorption band, and C is a coefficient of the order of unity. In the one-dimensional case, substituting (22) in (40), putting $2\sqrt{2}(R/d)(\Delta_{min}/\epsilon_0)^{1/2} > 5$, and assuming that $\Delta_{max} = \infty$, we obtain

$$W_{da} = C \frac{4\sqrt{2}\pi}{\hbar} \left(\frac{d}{R_{da}}\right)^{1/2} \frac{\Delta_{min}^{3/2} \epsilon_0^{1/2}}{\delta E_{em}^d \delta E_{abs}^a} \exp\left\{-2\sqrt{2} \frac{R_{da}}{d} \left(\frac{\Delta_{min}}{\epsilon_0}\right)^{1/2}\right\}. \quad (41)$$

In the three-dimensional case, under the same assumptions, we obtain

$$W_{da} = C \frac{\pi\hbar^2}{2\sqrt{2}\mu^{1/2}} \frac{\Delta_{min}^{3/2}}{\delta E_{em}^d \delta E_{abs}^a} \frac{1}{R_{da}^3} \exp\left\{-2\sqrt{2} \frac{R_{da}}{\hbar} \sqrt{\mu\Delta_{min}}\right\}. \quad (41a)$$

6. CONCLUSION

The investigated excitation-transfer mechanism can be quite effective in the case of triplet-triplet transfer.^{13, 41} In this case the usual (Förster) mechanism does not operate and if Δ is sufficiently small the transfer can proceed principally via virtual collective excitations of the medium, and is determined by formulas (22), (32), and (37). In the presence of a dipole-dipole exciton band, if the interactions \hat{V}_a and \hat{V}_d are sufficiently large, the energy transfer probability at large distances is proportional to R_{da}^{-6} , but the coefficient of R_{da}^{-6} is determined by formula (32) and not by the Förster-Dexter overlap integral.

The efficiency of the excitation energy transfer, in the case of excitons with short-range action, does not depend on whether the minimum of the exciton band is located at $k = 0$ or $k \neq 0$, if we disregard the interference between several minima. The triplet excitons are not excited by electromagnetic radiation. But if Δ is sufficiently small, the presence of an exciton band can be revealed by the increased rate of excitation transfer between impurities, even if it makes no contribution to the absorption spectrum of the crystal.

We have considered a case in which the impurity level lies below the exciton band. It is possible to consider in exactly the same manner the case when the impurity level lies above the exciton band. All the formulas remained unchanged, but Δ must be taken to mean the difference between the energies of the excited state of the impurity and the upper edge of the band.

Inasmuch as the transfer of excitation is not accompanied by the formation of real excitons—excited states of the solvent atoms, the presence of different defects in the lattice, which scatter or capture real excitons, cannot exert an appreciable influence on the probability of excitation transfer between the impurity atoms. These defects influence W_{da} only to the extent that they can distort the exciton spectrum, and such a distortion is as a rule small. In general, the main factor in the excitation transfer was not the ordered character of the medium, but the presence, near the excited impurity level, of a collective excitation of the atoms of the medium, which is delocalized as a result of the strong interaction between these atoms. In an ordered crystal these excitations are exciton, and in a liquid these are excited states for which k is a poor quantum number, but which nonetheless are delocalized. The described mechanism should then take place also in a disordered medium, but to calculate W_{da} it is necessary to know the probability characteristics of the excitation spectrum of the medium.

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