Long-term asymptotic migration in disordered systems with exchange interaction

T. T. Basiev and V. V. Murav'ev

Institute of General Physics, Russian Academy of Sciences, 117942 Moscow, Russia

(Submitted 28 June 1991)
Zh. Eksp. Teor. Fiz. **105**, 1342–1356 (May 1994)

The results of computer modeling of intercenter exchange-interaction-mediated incoherent migration of electronic excitations in a disordered system of donor centers in doped crystals are presented. The long-term asymptotic migration process is studied. It is established that at long times the migration process in these systems considered is diffusive. The dependence of the diffusion coefficient on the concentration of centers and on the parameters characterizing the intercenter interaction is determined.

1. INTRODUCTION

Incoherent transport processes in disordered systems play an important role in diverse physical phenomena. Incoherent transport of electronic excitations in disordered systems is at the basis of a large class of energy relaxation and transfer phenomena, such as spectral migration, depolarization, concentration quenching, and others.[1] Incoherent electron transport determines the hopping conductivity in doped semiconductors.[2] Thus the study of transport processes is important for fundamental and applied physics.

The incoherent character of transport processes means, first, that at each moment an excitation (or electron) is localized on a definite center (donor ion, impurity, and so on) and, second, that the probability of excitation transfer at a given moment does not depend on how and when the excitation arrived at a given center. It is well known that such an excitation transfer process is described by a system of rate equations. For a fixed configuration of centers the ith equation has the form

$$dP_i(t)/dt=\sum_j [W_{ji}P_j(t)-W_{ij}P_i(t)], \quad (1)$$

where $P_i(t)$ is the probability of finding an excitation on the ith center (occupation number of the center) at time t and W_{ij} is the rate of excitation transfer from the ith to the jth center. In this paper we consider only completely reversible migration of excitations, in which excitations are not annihilated and the rates of direct and reverse transfer between two centers are equal:

$$W_{ij}=W_{ji}.$$

For the most important types of excitations, the dependence of the excitation transfer rate on the intercenter distance R_{ij} is either an inverse power-law function for the electrostatic interaction[3,4]

$$W_{ij}=C_{DD}/R_{ij}^S, \quad (2)$$

where C_{DD} is the microeefficiency of the interaction and S is the degree of multipolarity ($S=6$, 8, and 10 for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions), or an exponential function for the exchange interaction[4]

$$W_{ij}=W_0\exp(-R_{ij}/l), \quad (3)$$

where W_0 is the amplitude and l is the radius of the interaction.

The experimentally observed characteristics of migration in disordered systems with prescribed parameters (concentration, type of interaction, and so on) are described by the solutions of the system (1), averaged over all possible configurations of the centers. It is extremely difficult to perform this averaging correctly, and this is still an unsolved mathematical problem. For this reason, even if the elementary transfer mechanism is known, migration processes are still very difficult to describe theoretically, and this problem is still far from being completely solved.

It has been found that the initial stage of migration can be described accurately by a small number of terms of the exact concentration expansion of the average delocalization radius[5] or by the population kinetics of the initial site[6–8] [the pair model, which has a simple and clear physical meaning, is identical to the linear term of the cumulant (exponential) form of this expansion[9]]. However, the existing theoretical models of the later stages of the migration process incorporate assumptions which are difficult to check, so that these assumptions must be checked independently in an experiment.

Virtually all authors of theoretical works now agree (though this has not been rigorously proved) that at sufficiently long times, migration is of a diffusion-like character. This means that the mean squared delocalization radius $\langle r^2\rangle$ of an excitation is directly proportional to the time

$$\langle r^2\rangle=6Dt, \quad (4)$$

and the population kinetics of the initial site is described by the expression

$$P(t)=(W_d t)^{-3/2}, \quad (5)$$

where W_d is the rate of migration at the diffusion stage and is related to the diffusion coefficient D by the expression

$$W_d=4\pi n^{2/3}D, \quad (6)$$

where n is the concentration of centers. The expression (6) is obtained from the seemingly obvious considerations of normalization of the solution of the diffusion equation $\partial P/$

1063-7761/94/050723-08$10.00

$\partial t = D\Delta P$ in a volume corresponding to a single center, and can be proved rigorously with help of the averaging procedure performed in Ref. 8.

It is well known[10] that the diffusion kinetics of the form (5) is obtained for disordered systems in the limit of very long times $t \to \infty$ in the continuous random walk (CRW) model.[7,11] In an earlier work[12] employing the CRW method, as well as in other theoretical approaches—percolation theory,[13] the coherent-potential method,[14] and the self-consistent diagrammatic method[15]—the diffusion stage appears as a linear time dependence of the mean-square delocalization radius.

A system with multipole interactions is characterized by only two dimensional parameters (the concentration n and the microefficiency C_{DD} of the interaction), so that all theoretical models give the same concentration dependence

$$W_d = 4\pi\alpha C_{DD} n^{S/3} \tag{7}$$

which is confirmed by real[16,18] and numerical[18] experiments. The difference between the experimental and theoretical kinetics appears only in the magnitude of the numerical factor α, and it can indicate how accurately the theory takes reversibility of the transfer process into account (see Ref. 18).

The situation becomes more complicated for the exchange interaction. Because there are three dimensional parameters—the concentration n, the amplitude W_0, and the interaction radius l—even the very form of the functional dependence is different in different theories.

In percolation theory and the coherent-potential theory, the dependence of the migration rate W_d at the diffusion stage in a system with an exponential potential on the parameters of the system is described [taking into account Eq. (6)] by the expression[13,14]

$$W_d = 4\pi\kappa W_0 \exp(-z/\beta), \tag{8}$$

where $z = \bar{R}/l = 1/ln^{1/3}$ characterizes the slope of the interaction potential at the average distance between centers $\bar{R} = (n)^{-1/3}$, the parameter $\beta = 1.15$ for both methods, and κ is a dimensionless parameter. In percolation theory[13] κ has the concentration dependence $\kappa = \kappa_0 z^{-3.87}$, and in the coherent-potential method κ is a constant. Expressions similar to Eq. (8) but with different values of β were also obtained in Ref. 10 ($\beta = 1.61$) on the basis of very simple approximate considerations and in Ref. 19 ($\beta = 1.28$) by a diagrammatic method first proposed in Ref. 15.

The CRW method[20] yields a diffusional migration rate with a concentration dependence that is different from Eq. (8). According to Ref. 20 this dependence has the form [using the expression (6)]

$$W_d = 4\pi\kappa(z) W_0 \exp(-bz^{3/2}), \tag{9}$$

where $b = 0.19$ and the function $\kappa(z)$ is a weak function of z (the explicit form of this function is not given in this work). A concentration dependence similar to Eq. (9) is derived for the diffusion coefficient in Ref. 21, where the relation obtained by a diagrammatic method in Ref. 15 between the population kinetics at the initial site and the diffusion coefficient is employed. We note that although the leading-order exponential terms for large z in Eqs. (8) and (9) have a significantly different form, due to the specific choice of the parameters β and b and the preexponential factors $\kappa(z)$, these z dependences will be similar over some range of z.

2. MODELING METHOD

Due to the significant experimental difficulties that arise in the investigation of the population kinetics $P(t)$ of the initial site at great depth $P \lesssim 10^{-2}$ (Refs. 9, 18, and 22) and the impossibility of choosing the form of the interaction potential a priori, we used computer modeling to investigate incoherent migration of excitation.

Our modeling method was initially proposed in Refs. 9 and 23. In Ref. 18 we determined the method's limits of applicability and accuracy, which are associated with the finiteness of the number N of centers in the model system. We modeled migration owing to multipole interaction between the centers in three-dimensional[18] and two-dimensional[24] impurity crystals. In the present work the computer modeling was extended to migration of excitations in three-dimensional systems with an exponential dependence of the excitation transfer rate between centers. Our method consists of constructing a random configuration of centers, distributed randomly among the sites of, in our case, a simple cubic lattice with spacing R_0 and fixed specific concentration c, i.e., having the concentration $n = c/R_0^3$, and calculating the kinetics on a computer as the arithmetic mean of the time dependences of the populations of the initially excited site with excitation of each site in a given configuration:[9,23]

$$P(t) = \frac{1}{N} \sum_{i=1}^{N} P_i^{(i)}(t). \tag{10}$$

Here $P^{(i)}(t)$ is the solution of the system (1) for a given configuration of centers with the ith site excited initially, i.e., with the boundary conditions $P_j^{(i)}(0) = \delta_{ij}$.

As we have shown previously in Ref. 18, the range of initial-site populations accessible to investigation is determined mainly by the finiteness of the number of centers in the model system. By comparing the initial-site population kinetics in systems with different numbers of centers, we found that the error introduced by the finiteness of the number N of centers in the model system is less than 10% as long as $P > 3/N$. For the results presented in the present paper, the number of centers falls in the range $N = 640$–850, which makes it possible to investigate initial-site population kinetics up to depths $P(t) = 0.0035$–0.0047.

In Ref. 24 we compared the results of modeling of migration in ordered systems with a contact interaction to the exact solution known for these systems (see Fig. 1). As one can see from the figure, the modeling result (dashed curve) differs from the exact solution (solid curve) by not more than 3% over the given range $P(t) > 3/N$ (horizontal dashed straight line) and by not more than 10% over the range $P(t) > 2/N$. This is a less stringent restriction than that indicated above and employed in the present work.

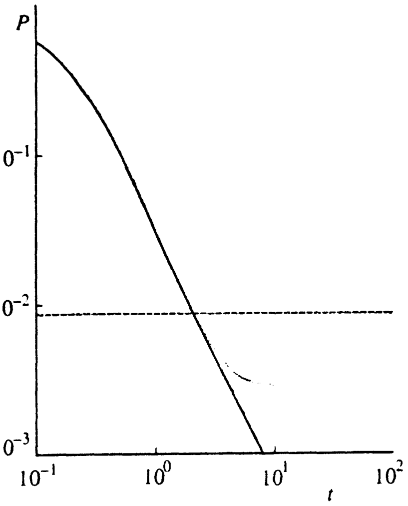

FIG. 1. Comparison of the results of computer modeling of excitation migration in a three-dimensional ordered system of centers with a short-range interaction potential (dashed curve) to the exact solution for this system (solid curve). The dashed straight line indicates the lower limit of the range where the modeling results are correct.

For some of the systems modeled, the modeling was conducted in several different configurations of the centers with the same parameters n, l, and W_0 in order to check the statistical interconfigurational spread. It was shown that the population kinetics of the initial site, averaged over a single configuration, over the entire investigated range of values of the parameters n, l, and W_0 remain virtually unchanged from one configuration to another and, at least for most of the systems investigated, they exhibit the same functional behavior. This enabled us to do without configurational averaging of initial-site population kinetics. Some differences of the functional behavior of the kinetics in different random configurations (presence or absence of the diffusion stage in the range of initial-site populations $P(t)$ accessible to modeling) are observed only at the later stages of migration and only for systems with interaction potentials having the largest slopes. These differences will be discussed below.

3. RESULTS AND DISCUSSION

We performed computer modeling of the excitation migration in systems with an exponential interaction potential for a wide range of specific concentrations: from $c=0.01$–0.08 up to $c=0.1$–0.2. For a number of values of the interaction radius, modeling was also performed for systems with concentrations close to the limiting values: $c=0.5$ for $l=R_0$, $R_0/2$, and $R_0/5$ and $c=0.75$ for $l=R_0$.

In this paper we do not analyze the behavior of the kinetics at the initial stage of migration in systems with an exponential potential. These results are presented in detail in our paper Ref. 25. We merely note that the initial stage of migration is described, to an adequate degree of accuracy, by the well-known pair model[9] (as in the case of systems with a dipole–dipole interaction[18]), but for a number of systems with an exponential interaction potential the pair model ceases to work an order of magnitude earlier (with respect to the population of the initial center) than the onset of the diffusion stage of migration.

In this paper we consider only the long-term asymptotic behavior of the initial-site population kinetics obtained by computer modeling.

In order to analyze the long-term asymptotic behavior of the computed-modeled kinetics, we constructed the kinetics in the coordinates $[\log(W_0 t), \log P]$, in which the expected diffusion approximation function (5) becomes linear:

$$\log P = (-3/2)[\log(W_0 t) + \log(W_d/W_0)].$$

The diffusion stage of migration was observed in systems of centers for which the values of the slope parameter $z=(l\cdot\sqrt[3]{n})^{-1}$ of the interaction potential span a wide range (approximately from $z=3$ to $z=11$). The existence of this stage was ascertained on the basis of the computer-generated kinetics $P(t)$ becoming rectilinear in the indicated coordinates with the tangent of the slope angle being $-3/2$ (see Fig. 2).

The diffusion migration rate W_d determined from the results of computer modeling in the range $z=4.6$–12.1, where W_d varies by more than three orders of magnitude, are described well by a straight line in the coordinates $[z, \log(W_d/W_0)]$, which corresponds to the function (8) with $\kappa=\text{const}$.

Least-squares analysis of the experimental results under the assumption that the preexponential factor κ in Eq. (8) is constant gives the values $\beta=0.870\pm0.009$ and $\kappa=2.84\pm0.32$ [continuous straight line in Fig. 3(a)]. If, however, it is assumed that the factor κ in Eq. (8) is a power-law function of z of the form $\kappa=\kappa_0 z^{\gamma}$, then least-squares analysis of the results gives $\beta=1.10\pm0.04$, $\gamma=-1.7\pm0.4$, and $\kappa_0=12\pm4.7$ [dashed curve in Fig. 3(a)].

The best approximation of the computer modeling results by an expression of the type (9) with a power-law preexponential factor $\kappa=\kappa_0 z^{\gamma}$ is obtained with the parameters $b_e=0.15$ and $\gamma_e=-3.7$ [dashed curve in Fig. 3(a)]. It is obvious from the figure that an expression like (9) with the given parameters describes the modeling results quite well. The parameter $b_e=0.15$ is close to the value $b_t=0.19$ obtained in the continuous random–walk theory.[20] Unfortunately, since no explicit expression for the factor κ is given in Ref. 20, we were not able to make a more detailed comparison between the CRW theory and our results. In a function of the form (9), obtained in Ref. 21, the parameter $b_t=0.27$ is significantly larger than $b_e=0.15$, and this theoretical model therefore describes the modeling results poorly [see the solid curve in Fig. 3(b)].

The dashed curve in Fig. 3(b) represents the concentration dependence of the diffusion-migration rate according to the percolation theory[13] [a function of the form (8) with $\kappa=\kappa_0 z^{\gamma}$, $\beta=1.15$ and $\gamma=-3.87$, and the value of κ_0, not determined within the theory of Ref. 13, was obtained by least-squares approximation]. It is evident from Fig. 3(b) that the percolation theory describes the computer modeling data poorly. As is evident from the same figure,

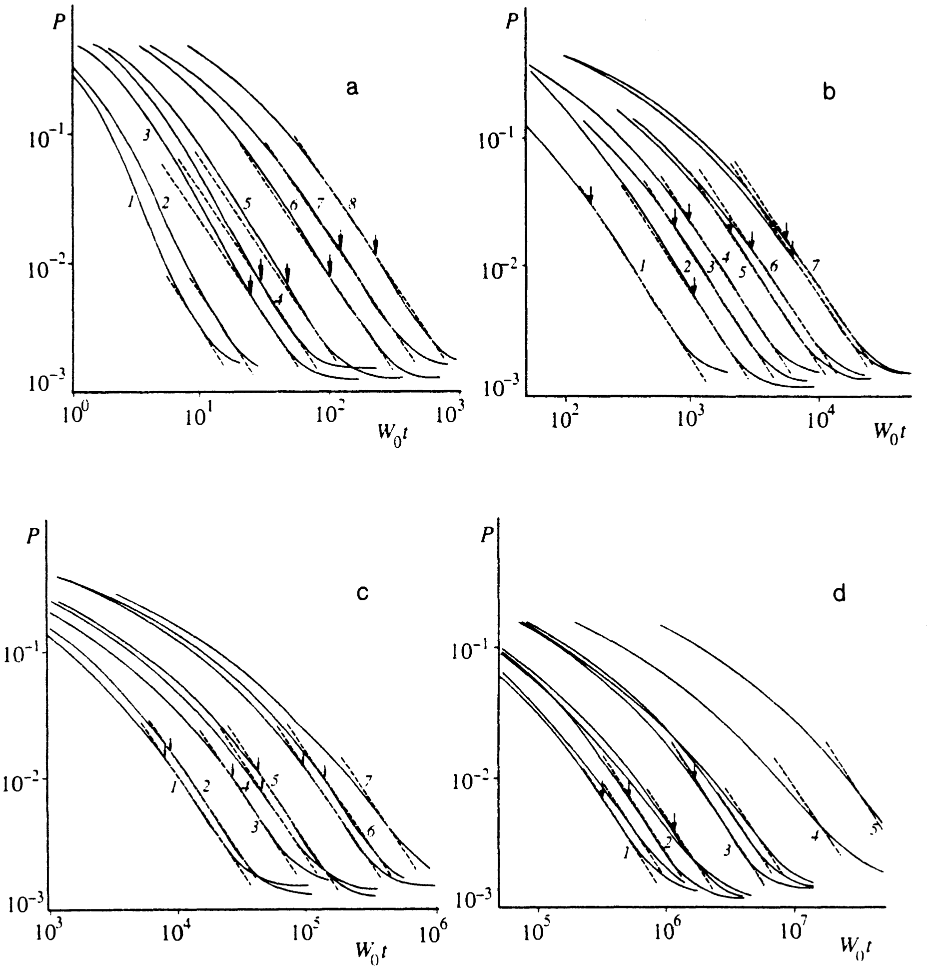

FIG. 2. Results of computer modeling (solid curves) and analytical approximations (dashed straight lines) of long-term asymptotic behavior for different slopes of the interaction potential: (a) small slope: 1—$z=2.52$ ($l=R_0/2$, $c=0.5$), 2—$z=2.71$ ($l=R_0$, $c=0.05$), 3—$z=3.22$ ($l=R_0$, $c=0.03$), 4—$z=3.42$ ($l=R_0/2$, $c=0.2$), 5—$z=3.68$ ($l=R_0$, $c=0.02$), 6—$z=4.31$ ($l=R_0/2$, $c=0.1$), 7—$z=4.64$ ($l=R_0$, $c=0.01$), 8—$z=5.13$ ($l=R_0/3$, $c=0.2$); (b) average slope: 1—$z=5.43$ ($l=R_0/2$, $c=0.05$), 2—$z=6.30$ ($l=R_0/5$, $c=0.05$), 3—$z=6.46$ ($l=R_0/3$, $c=0.1$), 4—$z=6.84$ ($l=R_0/4$, $c=0.2$), 5—$z=7.20$ ($l=R_0/3$, $c=0.07$), 6—$z=7.37$ ($l=R_0/2$, $c=0.2$), 7—$z=8.14$ ($l=R_0/3$, $c=0.05$); (c) large slopes: 1—$z=8.55$ ($l=R_0/5$, $c=0.2$), 2—$z=8.62$ ($l=R_0/4$, $c=0.1$), 3—$z=9.28$ ($l=R_0/2$, $c=0.01$), 4—$z=9.66$ ($l=R_0/3$, $c=0.03$), 5—$z=9.70$ ($l=R_0/4$, $c=0.07$), 6—$z=10.9$ ($l=R_0/4$, $c=0.05$) (two configurations), 7—$z=11.1$ ($l=R_0/3$, $c=0.02$); (d) largest slope: 1—$z=11.7$ ($l=R_0/5$, $c=0.08$) (two configurations), 2—$z=12.1$ ($l=R_0/5$, $c=0.07$) (three configurations), 3—$z=13.6$ ($l=R_0/5$, $c=0.05$) (three configurations), 4—$z=13.9$ ($l=R_0/3$, $c=0.01$), 5—$z=14.6$ ($l=R_0/5$, $c=0.04$). The arrows mark the onset of the diffusion stage.

the theoretical coherent potential and diagrammatic methods[14,19] (dashed straight lines) also describe the modeling results poorly.

Within the limits of accuracy of our experimental results we cannot determine reliably whether or not the preexponential factor κ is constant or is a power-law function of z. The choice of one or another form of the function $\kappa(z)$ substantially changes the value of the parameter β (by 25%): while for $\kappa=\text{const}$ the experimentally obtained value $\beta_e=0.87\pm0.009$ is significantly less than the theoretical value, for $\kappa=\kappa_0 z^\gamma$ the quantity $\beta_e=1.10\pm0.04$ is less than but close to the theoretical value $\beta_t=1.15$ obtained in the percolation theory[13] and the coherent potential theory[14] (though the exponent $\gamma_e=-1.7$ is substantially different from the value predicted by the percolation theory,[13] $\gamma_t=-3.87$). Analysis of the results under the assumption of a power law $\kappa=\kappa_0 z^\gamma$ shows that the parameters κ_0 and γ depend strongly on one another. A strong dependence of the parameters on one another usually indicates that there are too many fitting parameters, and for subsequent analysis we therefore choose a simpler form of the expression (8) with $\kappa=\text{const}$.

The value $\beta_e=0.87$ obtained in this work from the computer results is less than the values $\beta_t=1.15$–1.61 obtained theoretically.[10,13,14,19] We note that according to Ref. 2, the values of the coefficient $\beta_e=1.0$–1.14 obtained in experiments on hopping conductivity in semiconductors are also less than the theoretical values β_t. To analyze the discrepancy indicated above, we rewrite Eq. (8) in the form

$$W_d=4\pi\kappa W_0\exp(-1/l\sqrt[3]{n\beta^3}). \tag{11}$$

The fact that the theoretically predicted value β_t is higher than the experimental value (result of modeling) β_e can be attributed to too high a value of the effective concentration

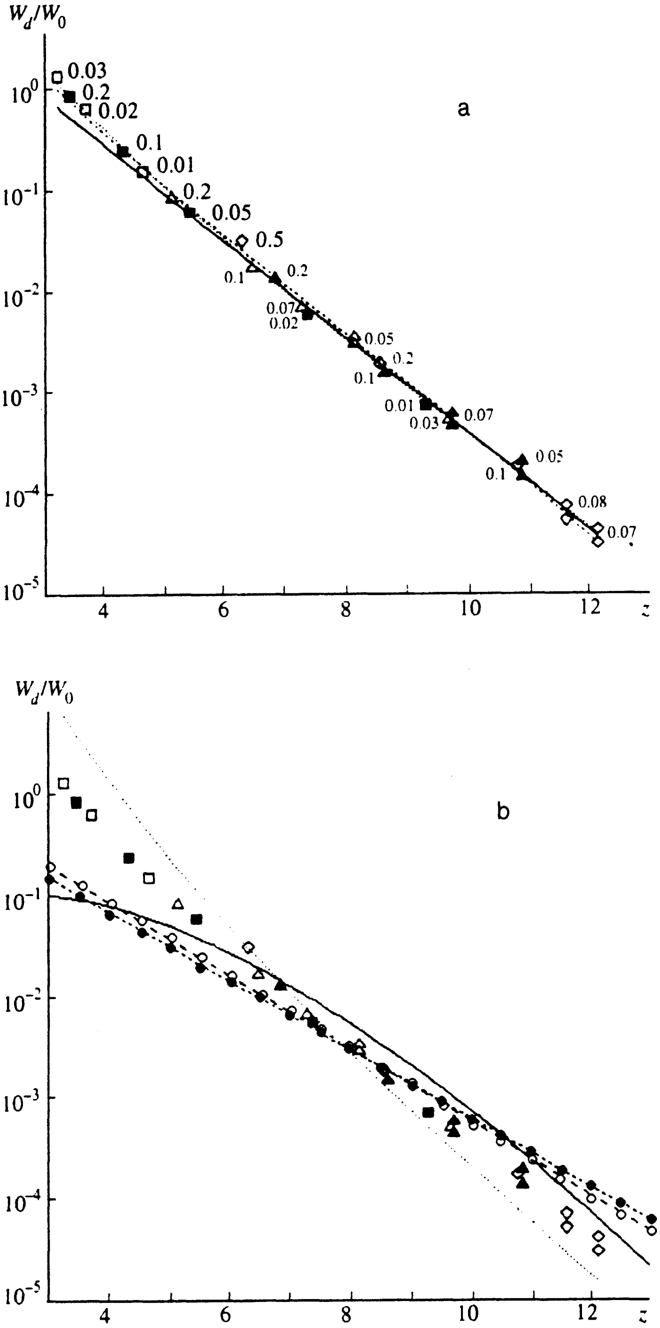

FIG. 3. (a) Concentration dependence of the migration rate at the diffusion stage: dots–data from computer modeling for different values of the interaction radius: □—$l=R_0$, ■—$l=R_0/2$, △—$l=R_0/3$, ▲—$l=R_0/4$, ◆—$l=R_0/5$; the numbers near the points indicate the specific concentrations. Solid straight line—approximation by an expression of the type (8) with κ=const. Dotted straight line—approximation by an expression of the type (8) with a power law function $\kappa(z)$. Dashed straight line—approximation by an expression of the type (9) with a power-law function $\kappa(z)$. (b) Comparison of the theoretical concentration dependences of the migration rate at the diffusion stage to the results of computer modeling; the labeling of the points is the same as in Fig. 3a. Solid curve—dependence from Ref. 21; dotted curve—dependence obtained with the percolation theory;[13] dashed straight lines—dependences obtained by the coherent-potential method[14] (○) and the diagrammatic method[19] (●).

$n\beta^3$ of centers—excitation carriers—capable of delocalizing the excitation. In our view this indicates that because the multistep random-walk trajectories are not taken into account adequately, the reversibility of the transport process may not be taken into account completely in the theory, thus lowering the concentration of effective carrier centers. A similar situation occurs in the dipole–dipole interaction.[18] In that case

$$W_d=4\pi C_{DD}(n\sqrt{\alpha})^2,$$

and the fact that the experimental values[18] $\alpha_e=1.5$–1.9 are lower than the theoretical values $\alpha_t=2.2$–3.4 likewise suggests that the reversibility of the transport process is not adequately taken into account in the theory, and this is manifested as a weak decrease in the effective concentration of carrier-centers $n\sqrt{\alpha}$. The replacement of the disordered system by an effective ordered system in the theoretical models in order to simplify the computations could also result in values of α_t that are too high.[26]

For a system with a sufficiently high specific concentration of centers $c=0.5$, the migration rate W_d deviated from the values obtained from Eq. (8) in the direction of higher values. This can be interpreted as an increase in the diffusion coefficient with increasing degree of ordering of the system. Deviations from the law (8) in the direction of higher values of W_d are also observed for $z\leqslant 4.5$. This indicates that the pre-exponential factor in Eq. (8) has a significant concentration dependence for small values of z. Both enhancements of the rate W_d (for large c and for small z) can be understood in terms of an increase in the parameter κ and the diffusion coefficient D, occurring with increasing degree of ordering in a discrete system (large c) or quasicontinuous system with long-range action (small z). This is analogous to the behavior of the concentration dependence of W_d in systems with multipole interaction.[18]

To compare the diffusion stage in systems with exchange interaction to the analogous stage in systems with electrostatic interaction of different multipolarity, it is convenient to represent the concentration dependence of the migration rate at the diffusion stage in logarithmic coordinates $[\log(nl)^3, \log(W_d/W_0)]$ (see Fig. 4, curve *1*). It is evident from Fig. 4 that when the concentration changes by 1.5 orders of magnitude, the migration rate changes by almost five orders of magnitude, but the increase in migration rate with increasing concentration is not uniform: The migration rate rises steeply for small nl^3, i.e., for interaction potentials with a large slope, and slows down as nl^3 increases (i.e., with decreasing z). Thus the behavior of the concentration dependence of the migration rate in systems with exchange interaction is reminiscent of the behavior of the analogous dependences in systems with electrostatic interaction of different multipolarity in different ranges of values of z. In order to find these ranges we equate the derivatives $d\ln W_d/d\ln n$ of the corresponding concentration dependences of the migration rates at the diffusion stage:

$$-S/3=-z/3\beta. \tag{12}$$

It is evident from Eq. (12) that the concentration dependence (8) of the migration rate at the diffusion stage for

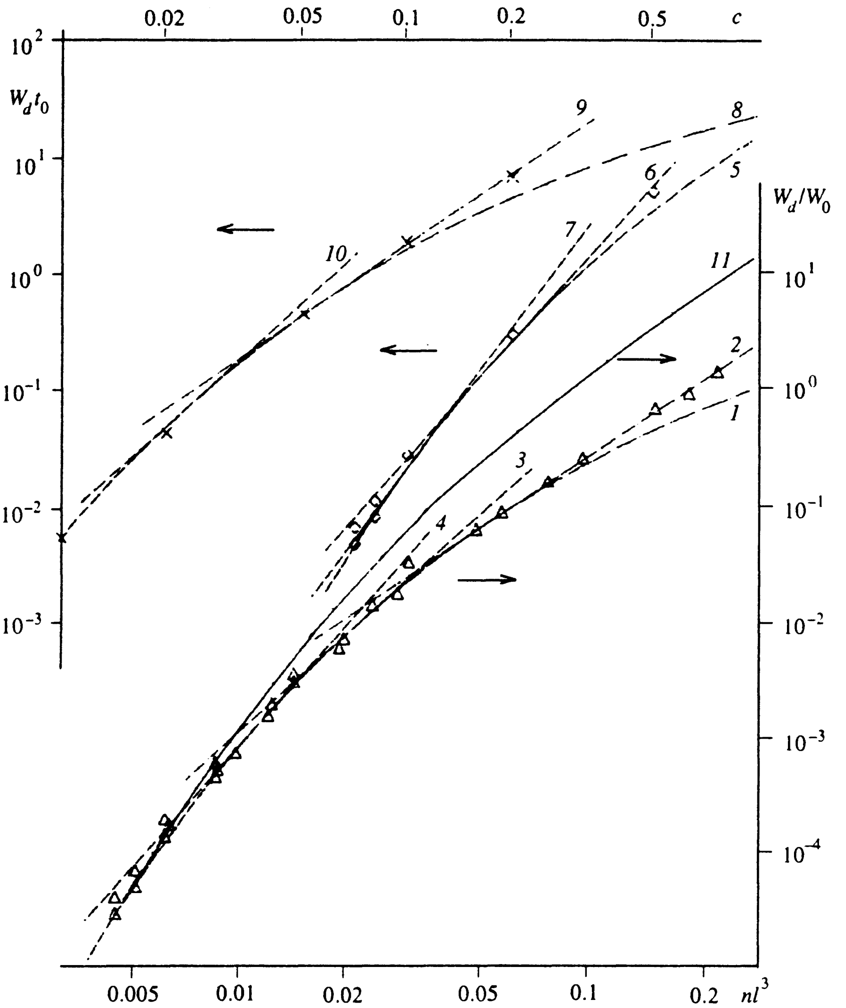

FIG. 4. Concentration dependences of the migration rate at the diffusion stage. Solid lines—theoretical dependences. Dots—results of computer modeling: 1—exchange interaction (8), 2–4—dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively; 11—exchange interaction within the simplest model [see the expression (17)]; 5, 8—exchange interaction for $l=R_0/2$ and $l=R_0/5$, respectively; 6, 7, 9, 10—interactions with degree of multipolarity 6, 8, 10, 12, respectively.

systems with exchange interaction is close to the analogous dependence for systems with electrostatic interaction with degree of multipolarity S near the values

$$z=S\beta. \tag{13}$$

Thus, using our value $\beta=0.87$, exchange diffusion near $z=5$ is similar to dipole–dipole diffusion ($W_d \propto n^2$), dipole–quadrupole diffusion ($W_d \propto n^{8/3}$) near $z=6.7$, and quadrupole–quadrupole diffusion ($W_d \propto n^{10/3}$) near $z=8.3$ (see Fig. 4, straight lines 2–4). It is also evident from Fig. 4 that starting at $z=5$, the function $W_d(n)$ found by computer modeling becomes quadratic, deviating, as has already been mentioned, from the theoretical exponential dependence (8) [compare also Fig. 3(a)].

The concentration dependences of the diffusion migration rate, presented in the standard coordinates ($\log c, \log W_d$) for analyzing the concentration dependences of migration rates in systems with multipole interaction [in units of t_0, where $t_0=W_{ij}^{-1}(R_0)$], for different interaction radii $l=R_0/2$ and $l=R_0/5$ (see Fig. 4, curves *5* and *8*), show that over the investigated range of specific concentrations $c=0.01$–0.50, the dependence for the system with the smallest slope of the interaction potential is close to the dependences for the dipole–quadrupole interaction for low concentrations and the dipole–dipole interaction for high concentrations (straight lines *6* and *7*). In addition, the concentration dependence for the system with the highest slope of the potential ($l=R_0/5$) in the experimental concentration range is close to that for interactions with multipolarity $S=10$–12 (straight lines 9 and 10 in Fig. 4).

The similarity of the dependences of the migration rate at the diffusion stage for systems with exchange and multipole interactions can be understood if it is assumed that delocalization is caused by hops over distances close to some R_{eff} and these distances are such that both types of interactions have the same slope near them. This representation can make sense physically, since, on the one hand, the intercenter excitation transfer rate $W_{ij}(R_{ij})$ drops rapidly with increasing intercenter distance R_{ij} and, on the other hand, hops over small distances, though they are significantly more frequent, do not lead to significant delocalization of excitation from the starting point.[10]

It turns out that R_{eff} for the exchange interaction can be determined on the basis of the assumption made above. Equating the derivatives $d \ln W_{ij}/d \ln R_{ij}$ for the exchange and multipole interactions at R_{eff} under the assumption that the parameters of both types of interactions are such that at this point ($R_{ij}=R_{\text{eff}}$) both interaction potentials have the same slope (see Fig. 5), we obtain

$$-S=-R_{\text{eff}}/l. \tag{14}$$

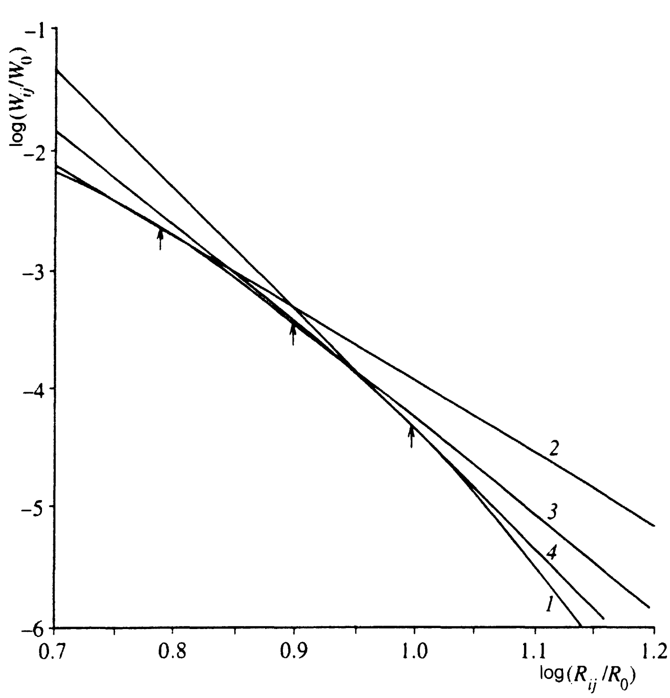

FIG. 5. Excitation transfer rates W_{ij} as a function of the intercenter distance R_{ij} for different types of interactions: 1—exchange, 2—dipole–dipole, and 3—dipole–quadrupole. The arrows mark the values of R_{ij} near which the transfer rates for the exchange and multipole (with different degree of multipolarity) interactions are close.

We note that the left-hand side of Eq. (14) (for multipole interaction) does not contain R_{eff}. Since the assumption made above implies that at this point the concentration dependences of the exchange and multipole migration rates at the diffusion stage must be the same, which, as the foregoing analysis of the concentration dependences showed, happens for $z=S\beta$ [see Eq. (13)], we have from Eqs. (13) and (14)

$$R_{\text{eff}}=n^{-1/3}/\beta. \tag{15}$$

It is interesting to note that substituting the value obtained for R_{eff} into the lower limit of integration in the expression[10]

$$W_d=4\pi\, n^{2/3}D=4\pi n^{2/3}\int_{R_{\text{eff}}}^{\infty}4\pi W_0 r^4\exp\left(-\frac{r}{l}\right)\frac{dr}{6}, \tag{16}$$

which determines the concentration dependence of the diffusion coefficient and migration rate at the diffusion stage on the basis of the simplest approach,[10] gives the expression

$$\begin{aligned}W_d&=\kappa(z)\exp\left(-\frac{z}{\beta}\right)\\&=\frac{8}{3}\pi^2\left(24z^{-5}+24\frac{z^{-4}}{\beta}+12\frac{z^{-3}}{\beta^2}+4\frac{z^{-2}}{\beta^3}+\frac{z^{-1}}{\beta^4}\right)\\&\quad\times W_0\exp\left(-\frac{z}{\beta}\right),\end{aligned} \tag{17}$$

whose exponential term $\exp(-z/\beta)$ (leading-order term for large z) is identical to the concentration dependence that we obtained by computer modeling for the migration rate at the diffusion stage (8). This proves the applicability of the assumption, made above, that hops over distances close to R_{eff} predominate in the delocalization process. Comparing the plots of the function (17) to the modeling results in Fig. 4 shows that in spite of the fact that they agree for large values of z, the expression (17) does not give an accurate description of the concentration dependence of the migration rate obtained by computer modeling. For small z, however, when the purely exponential formula (8) no longer describes the computer modeling results, the preexponential factor in Eq. (17) intensifies the concentration dependence, increasing the rate W_d, as actually happens according to the results of computer modeling (see Fig. 4, curves *1, 2,* and *11*). The form of the concentration dependence [expression (17), Fig. 4, curve *11*] is found to be close to the experimental (computer-modeled) dependence $W_d \propto n^2$ (Fig. 4, curve *2*), though the magnitude of the correction is much too large.

It is interesting that for small values $z<4.5$, the plots of the population kinetics $P(t)$ at the prediffusion stage are steeper than the fitted straight line of the diffusion stage, i.e., "overshoot" is observed[7] [see Fig. 2(a)], similar to that observed in the case of ordered systems with a multipole interaction.[18] The amplitude of this overshoot increases with decreasing z, and the limiting initial-site population corresponding to the onset of the diffusion stage (marked by arrows in Fig. 2) decreases and reaches for $z<3$ a value such that the minimum degree of the change in the kinetics $P \sim 3/N$ acceptable for modeling, which is limited by the number of centers in the model system $N \sim 800$ (see Ref. 18 for a more detailed discussion), does not permit observing the diffusion stage.

For larger values $z>4.5$, i.e., with increasing slope of the potential, overshoot is not observed [see Figs. 2(b)–2(d)], except for the system with high concentration and degree of ordering $c=0.5$ and $l=R_0/5$ [Fig. 2(b), curve *2*]. As z increases in the range $z>7.5$, the diffusion stage is observed [see Figs. 2(c) and 2(d)] at increasingly smaller values of the limiting initial-site population P_b.

For systems with large z and different randomly generated configurations of centers with the same parameters n, l, and W_0, the amplitudes of the initial-site population have a significant spread [see Figs. 2(c) and 2(d)], caused by fluctuations of the spatial distribution of the centers. The increase in the spread with increasing z is probably associated with the fact that the migration kinetics is more sensitive to fluctuations in the intercenter distance in systems with a larger ratio of the intercenter distance to the interaction radius (large slope of the interaction potential at the average intercenter distance). This spread is also manifested in fluctuations of the limiting population. Because of it, for a number of systems with large $z \sim 11$–14, the diffusion stage is not observed in some configurations, but is observed in other randomly generated configurations with the same parameters [see, for example, Fig. 2(d), curves *1, 2,* and *3*]. In addition, the fraction of configurations in which the diffusion stage is observed decreases as z increases from 11.7 to 13.6.

We note that for the experimental systems with an exponential interaction potential, the maximum limiting initial-site population $P_b \sim 0.03$ at the onset of the diffusion stage is reached for $z \sim 7$.

CONCLUSIONS

1. Diffusion asymptotic kinetics of excitation migration has been observed for the first time for a large group of disordered three-dimensional systems with a different slope of the exponential (exchange) interaction potential (ratio of the average distance between centers to the interaction radius for z ranging from 3 to 12).

2. It was established that at the diffusion stage, the migration rate decreases exponentially with increasing slope of the potential (ratio of the average interparticle distance to the interaction radius); the numerical parameters of this dependence were determined; the fact that the values of the parameters obtained in the numerical experiment are higher than the theoretical values indicates that the reversibility or stochasticity of the migration process in the previously existing analytical models was not taken into account fully.

3. For low values of the ratio of the average interparticle distance to the interaction radius (with long-range interaction), overshoot of the plot of the kinetics in logarithmic coordinates was observed at the prediffusion stage, and it was found that the amplitude of the overshoot decreases as this ratio increases (decreasing concentration, decreasing range of the interaction in the system). Overshoot was also observed for a strongly ordered system (specific concentration of 50%) with a large value of this ratio.

4. It was established that the limiting initial-site population corresponding to the onset of the diffusion stage has a maximum for a ratio of the average distance to the interaction radius of about 7, and decreases with both increasing (due to the later onset of the diffusion asymptotic behavior) and decreasing (due to an increase in overshoot) values of this ratio.

5. It was found that the migration rate at the diffusion stage and the diffusion coefficient increase with the degree of ordering of the system for both quasicrystalline ($c=0.5$) and quasicontinuous ($c \ll 1, z<4.5$) systems. The concentration dependence of the migration rate for small $z<4.5$ (high concentrations) is quadratic in the quasicontinuous system.

[1] V. M. Agranovich and M. D. Galanin, *Electron Excitation Energy Transfer in Condensed Media* [in Russian], Nauka, Moscow (1978).

[2] B. I. Shklovskii and A. L. Efros, *Electronic Properties of Doped Semiconductors* [English translation], Springer-Verlag, New York (1984).

[3] T. von Forster, Ann. Phys. **2**, 53 (1948).

[4] D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).

[5] S. W. Haan and H. Zwanzig, J. Chem. Phys. **68**, 1879 (1978).

[6] F. S. Dzheparov, V. S. Smelov, and V. E. Shestopal, Pis'ma Zh. Eksp. Teor. Fiz. **32**, 51 (1980) [JETP Lett. **32**, 47 (1980)].

[7] F. S. Dzheparov, *Proceedings of Schools of Higher Learning on Radio Spectroscopy* [in Russian], Perm' University, Perm' (1980), Vol. 13, p. 135.

[8] F. S. Dzheparov, S. V. Stepanov, and V. E. Shestopal, Preprint No. 133 [in Russian], Institute of Theoretical and Experimental Physics (1987).

[9] D. L. Huber, D. S. Hamilton, and B. Barnet, Phys. Rev. B **16**, 4642 (1977).

[10] A. I. Burshtein, J. Luminescence **34**, 167 (1985).

[11] J. Klafter and R. Silbey, J. Chem. Phys. **72**, 843 (1980).

[12] B. E. Bugmeister, Fiz. Tverd. Tela **18**, 819 (1976) [Sov. Phys. Solid State **18**, 469 (1976)].

[13] B. I. Shklovskii and A. L. Efros, Usp. Fiz. Nauk **117**, 401 (1975) [Sov. Phys. Usp. **18**, 845 (1975)].

[14] V. V. Bryksin, Fiz. Tverd. Tela **22**, 2441 (1980) [Sov. Phys. Solid State **22**, 1421 (1980)].

[15] C. R. Gouchanour, H. C. Anderson, and N. D. Fayer, J. Chem. Phys. **70**, 4254 (1979).

[16] M. Kh. Ashurov, T. T. Basiev, A. I. Burshtein *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **40**, 98 (1984) [JETP Lett. **40**, 841 (1984)].

[17] L. Gomez-Jahn, J. Kasinski, and R. J. D. Miller, J. de Phys. **46**, 85 (1985).

[18] O. K. Alimov, M. Kh. Ashurov, T. T. Basiev *et al.*, Trudy IOFAN **9**, 50 (1987).

[19] E. N. Bodunov and V. A. Malyshev, Izv. Akad. Nauk. Latv. SSR, Ser. Fiz. Tekhn. Nauk, No. 1, 98 (1988).

[20] H. Sher and M. Lax, Phys. Rev. B **7**, 4491 (1973).

[21] A. Blumen, J. Klafter, and R. Silbey, J. Chem. Phys. **72**, 5320 (1980).

[22] O. K. Alimov, M. Kh. Ashurov, T. T. Basiev *et al.*, Preprint No. 160 [in Russian], Physics Institute, USSR Academy of Sciences (1983).

[23] W. Y. Ching, D. L. Huber, and B. Barnet, Phys. Rev. B **17**, 5025 (1978).

[24] T. T. Basiev and V. V. Murav'ev, Preprint No. 37, IOFAN, 1989.

[25] T. T. Basiev and V. V. Murav'ev, Preprint No. 15, IOFAN, 1991.

[26] T. T. Basiev, Izv. Akad. Nauk SSSR, Ser. Fiz. **52**, 711 (1988).

Translated by M. E. Alferieff