Kinetics of diffusion-controlled reactions in crystals with defects

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An investigation is made of the kinetics of diffusion-controlled reactions in crystals with defects such as dislocations and interfaces. Asymptotic relationships are derived for the decrease of the concentration of a reagent in the case of parallel and randomly oriented dislocations. The characteristics of interfaces in the cases when the active particles are distributed at random at defects are determined. The influence on the reaction kinetics of fluctuations in the defect density and the concentration of active particles is analyzed.

INTRODUCTION

Real crystals are characterized by a high concentration of paths for accelerated diffusion of crystal lattice defects such as dislocations, grain boundaries, boundaries between phases, microcracks, etc.[1–3] Defects are usually linked to form characteristic networks along which the diffusion process is much faster than through the undeformed part of a crystal. Moreover, the interaction of the stress fields of defects with impurity particles results in the segregation of the latter at the defects. It is natural to expect the kinetics of diffusion-controlled reactions in crystals with defects to exhibit some characteristic features because of a reduction in the diffusion stage of the reaction when the reagent particles travel along accelerated diffusion paths and also when particle segregation occurs at defects.

According to a theory of diffusion-controlled reactions first developed by Smoluchowski,[4] the experimentally observed rate constant $k_{\text{ex}}(t)$ of an irreversible reaction

$$A+B\xrightarrow{k_{ex}}B, \tag{1}$$

which occurs in a spatially homogeneous medium, is equal to the flux $\Phi^d(t)$ of the concentration of a reagent A reaching a reaction sphere of radius $a=R_A+R_B$, surrounding a particle B at rest, divided by the equilibrium concentration c_A^0 at infinity:

$$k_{ex}^{(d)}(t)=\frac{\Phi^{(d)}(t)}{c_A{}^0}=\frac{S_a^{(d)}D}{c_A{}^0}\cdot\frac{\partial c_A}{\partial r}\bigg|_{r=a}, \tag{2}$$

where R_A and R_B are the radii of the particles A and B; D_A and D_B are the diffusion coefficients of these particles; $D=D_A+D_B$; d is the dimensionality of space; $S_a^{(d)}=2\pi^{d/2}a^{d-1}\Gamma^{-1}(d/2)$ is the surface area of a d-dimensional sphere of radius a; $\Gamma(x)$ is the gamma function. The concentration $d_A(r,t)$ is found from the diffusion equation

$$\frac{\partial c_A(r,t)}{dt}=D\,\Delta c_A(r,t), \tag{3}$$

where Δ is the d-dimensional Laplace operator. The boundary and initial conditions for this equation are

$$c_A(a,t)=0, \tag{4}$$

$$c_A(r,t)\,|_{r=0}=c_A{}^0, \tag{5}$$

$$c_A(r,0)=c_A{}^0. \tag{6}$$

After a time $t\gg a^2/D$ the rate constant $k_{\text{ex}}^{(d)}(t)$, calculated using the Smoluchowski theory, is given by the following expressions for $d=1$, 2, and 3:

$$k_{ex}^{(1)}(t)=4(D/\pi t)^{1/2}, \tag{7}$$

$$k_{ex}^{(2)}(t)=4\pi D/\ln(Dt/a^2), \tag{8}$$

$$k_{ex}^{(3)}(t)=4\pi aD\{1+a(\pi Dt)^{-1/2}\}. \tag{9}$$

The rate $k_{\text{ex}}^{(d)}(t)$ reaches its steady-state value in the limit $t\to\infty$ only in the three-dimensional systems:

$$k_D=4\pi aD. \tag{10}$$

It is shown in Refs. 5–11 that the solution of the Smoluchowski equation describes only the intermediate asymptotic form of the reaction, because in the limit $t\to\infty$ the kinetics is governed entirely by fluctuations of the concentration of the initial (i.e., at $t=0$) reagent distribution.

In Refs. 6, 9, and 10, for the problem of A particles carrying a random walk on a lattice containing immobile B traps, was tackled and the following fluctuation dependence, asymptotically accurate for large values of t, was obtained:

$$\ln\left(c_A(t)/c_A{}^0\right)\propto -t^{d/(d+2)}. \tag{11}$$

The concentration asymptotically satisfies a relation of the form (11) because A particles survive in the limit $t\to\infty$ only in sufficiently large fluctuation-generated voids free of traps.

The kinetics of reactions such as annihilation at traps, occurring in subthreshold percolation lattice systems in which in the absence of a reaction the particles of a reagent A are localized in finite free-volume voids right from the beginning, was investigated in Ref. 11. In the case when the localization of a reagent is due to relatively ineffective traps (obstacles), a large number of such particles is annihilated in accordance with the law

$$\ln c_A(t)/c_A{}^0\propto -t^{d/(d+1)}. \tag{12}$$

The fluctuation asymptotes of Eqs. (11) and (12) describe a slower—compared with the laws of formal kinetics (7)–(9)—decrease of the reagent concentration.

A classification of the diffusion regimes in crystals with defects was made in Ref. 12 as a function of the depth of penetration of particles into the interior, i.e., as a function of values of a parameter $L=(D_A^{(V)}t)^{1/2}$, where $D_A^{(V)}$ is the

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bulk diffusion coefficient. The cases when L is larger, equal to, or shorter than the characteristic length l were considered specifically in Ref. 12 (here, l is the average grain size in the case of a network of grain boundaries or the average distance between two points at which dislocations are pinned). In accordance with the terminology adopted in Ref. 13, if $L \gg l$ we have regime A (Harrison's classification), when the diffusion fields of the adjacent accelerated-diffusion paths overlap and the effective diffusion coefficient is[14]

$$D_A^{eff}=fD_A'+(1-f)D_A^{(V)}, \tag{13}$$

where f is the relative number of the lattice sites belonging to the accelerated-diffusion paths and D_A' is the accelerated-diffusion coefficient. A regime labeled B occurs for $L \ll l$, when the diffusion along adjacent paths is independent. If the bulk diffusion is negligible compared with the diffusion along defects and the depth of penetration is high ($L \gg l$), then we have a regime labeled C when the concentration profile of the penetrating particles is the same as the profile established by bulk diffusion with the coefficient D_A' instead of $D_A^{(V)}$.

An analysis of the diffusion in a medium with an ensemble of parallel dislocation tubes in the regime B was made in Refs. 15–18. Estimates of the effective diffusion coefficient were obtained there from the concentration profile of penetrating particles and the absorption and desorption diffusion coefficients were determined for a system of this kind.

In spite of the fact that diffusion in crystals with defects has been investigated theoretically on a number of occasions, a theory of diffusion-controlled reactions in such systems is not yet available. We shall show that substitution of the effective diffusion coefficient into standard relationships of the type described by Eqs. (7)–(9) does not solve the problem.

We analyze the kinetics of the reaction (1) in crystals with defects in the form of dislocations and interfaces (for example, grain boundaries, boundaries between phases, etc.). We find the relationships describing the decrease of the concentration of a reagent A diffusing in the crystal matrix and reacting in accordance with Eq. (1) when in contact with active particles B, which are distributed at random at defects representing accelerated-diffusion paths. We also consider the diffusion stage of the reaction in the case of various diffusion regimes.

In Sec. 1 we discuss the kinetics of the reaction (1) in a system with one dislocation at which there is a single particle of type B. Generalization to a system with one dislocation, but with randomly distributed B particles on this dislocation is given in Sec. 2; Sec. 3 is devoted to an analysis of the kinetics in the case of an ensemble parallel dislocations distributed at random in a system, whereas Sec. 4 deals with an ensemble of dislocations parallel to one another and carrying B particles. An ensemble of randomly oriented dislocations is considered in Sec. 5 and an analysis is made of the effects associated with fluctuations of the dislocation density and the reagent concentrations; Sec. 6 deals with the kinetics in a crystal when a single B particle is at an interface, whereas Sec. 7 is concerned with the problem of the kinetics in the same system but with many active B particles.

In most cases (Secs. 2–5 and 7) such an investigation is carried out using the concept of an effective medium developed for diffusion-controlled reactions in Refs. 19 and 20, which makes it possible to obtain the solution of the many-particle problem on the basis of the initial solution $G(r,t)$ of the one-particle diffusion problem. The solution of the Laplace-transformed diffusion equation (3) can be represented by a linear combination

$$\bar c_A(\mathbf r,s)=\frac{c_A^0}{s}+\sum_{i=1}^{N}c_i(\varkappa)G(\varkappa|\mathbf r-\mathbf R_i|), \tag{14}$$

with

$$\bar c_A(r,s)=\int_0 \exp(-st)c_A(r,t)\,dt,$$

where $\varkappa^2=s/D$, and $G(x)$ is the Green function of the one-particle problem, for example, the absorption at one sink or motion in a crystal containing one dislocation etc; $\mathbf R_i$ is the radius of the vector of an ith B particle or a dislocation, $c_i(\varkappa)$ are the weighting coefficients found from the boundary conditions and N is the total number of B particles or dislocations in the system. To first order in the small gas parameter $\alpha = na^d \ll 1$, equal to the fraction of the volume occupied by dislocations or active particles, the functions $c_i(\varkappa)$ are equivalent to one another:

$$c_i(\varkappa)=c(\varkappa)\quad(i=1,\ldots,N),$$

where n is the dislocation density or the concentration of B particles and a is their characteristic size. The criterion for this approximation to be valid sometimes contains time, i.e., after a long time the criterion may be fail (Sec. 5).

In the case of a homogeneous distribution of dislocations or B particles in the reaction space we find that averaging Eq. (14) with respect to r allows us to go from summation over the index i to integration over the volume V of the system:

$$\bar c_A(s)=\frac{c_A^0}{s}+nc(\varkappa)\int_V G(\varkappa r)\,dV, \tag{15}$$

where $\bar c_A(s)$ is the Laplace-transformed average concentration of the reagent A in the system.

1. REACTION IN A SYSTEM WITH ONE DISLOCATION AND A SINGLE *B* PARTICLE

We consider the simplest case when the reaction occurs in a crystal with a single dislocation. We shall assume that such a dislocation is an infinite tube of radius R which contains one active particle B. The diffusion along this dislocation is much faster than the regular part of the crystal: $D_A^{(V)}/D_A^{(d)}=\zeta \ll 1$, where $D_A^{(d)}$ is the diffusion coefficient of A particles in this dislocation tube (in the case of real crystals we usually have $\zeta \sim 10^{-3}-10^{-6}$). In the absence of a reaction an equilibrium distribution of the reagent A is established in the volume V and at a dislocation $\mathscr{D}$ characterized by homogeneous concentrations c_{0v} and $c_{od}=p_Ac_{oV}$, where p_A is the segregation coefficient of the A particles equal to the concentration of A at the boundary between the dislocation tube and the undeformed part of the crystal: $p_A=(c_d/c_V)|_{r=R}$. Usually $p_A \gg 1$. We consider the most typical case when all the B particles are on the dislocation ($p_B \to \infty$). Generalization of these results to the $p_B \sim 1$ case presents no difficulties. In the system under consideration the parameters obey $\zeta \ll 1$ and $p_A \gg 1$, the transport of A to B occurs mainly along the dislocation, and we can assume that

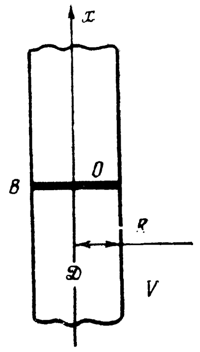

FIG. 1. Dislocation D with a particle B.

the height h of a sink B in the form of a cylinder of radius R is zero (Fig. 1). Concentration of the reagent A, given by the expressions $\rho_V(r,x,t)$ and $\rho_d(r,x,t)$ in the regions V and $\mathscr{D}$, is described by the relevant diffusion equations when the reaction (1) begins. For convenience, we shall calculate the quantities

$$c_{V(d)}=\rho_{V(d)}-c_{0V(d)}.$$

After the Laplace transformation the diffusion equations for c_v and c_d become

$$D_A^{(V)}\left\{\Delta_r\bar{c}_V(r,x,s)+\frac{\partial^2\bar{c}_V(r,x,s)}{\partial x^2}\right\}=s\bar{c}_V(r,x,s),\qquad r\geqslant R, \tag{16}$$

$$D_A^{(d)}\left\{\Delta_r\bar{c}_d(r,x,s)+\frac{\partial^2\bar{c}_d(r,x,s)}{\partial x^2}\right\}=s\bar{c}_d(r,x,s),\qquad 0\leqslant r<R, \tag{17}$$

where

$$\Delta_r=\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right)$$

is the radially symmetric Laplace operator. The boundary conditions are

$$D_A^{(V)}\frac{\partial\bar{c}_V}{\partial r}\Big|_{r=R}=D_A^{(d)}\frac{\partial\bar{c}_d}{\partial r}\Big|_{r=R}, \tag{18}$$

$$\frac{c_{0d}}{s}+\bar{c}_d\Big|_{r=R}=p_A\left(\frac{c_{0V}}{s}+\bar{c}_V\big|_{r=R}\right), \tag{19}$$

$$\bar{c}_d\big|_{x=0}=-c_{0d}/s, \tag{20}$$

$$\bar{c}_d\big|_{x=\pm\infty}=0, \tag{21}$$

$$\bar{c}_V\big|_{x=\pm\infty}=\bar{c}_V\big|_{r=\infty}=0. \tag{22}$$

It is shown in Ref. 15 that for $\zeta\ll 1$ the average concentration $\bar{c}_d$ depends weakly on r and we have $\bar{c}_d(r,x,s)\approx\bar{c}_d(R,x,s)$. Averaging Eq. (17) with respect to r between 0 and R, we obtain

$$D_A^{(d)}\frac{\partial^2\tilde{\bar{c}}_d}{\partial x^2}(x,s)+\frac{2}{R}D_A^{(d)}\frac{\partial\bar{c}_d}{\partial x}(R,x,s)=s\bar{c}_d(x,s), \tag{23}$$

where

$$\tilde{\bar{c}}_d(x,s)=\frac{2}{R^2}\int_0^\infty\bar{c}_d(r,x,s)\,r\,dr-$$

is the average concentration of the A particles in the dislocation tube. In view of the symmetry of the system with respect to the $x=0$ plane, it is sufficient to solve the problem for the half-space $x>0$. If we Fourier-transform Eqs. (16) and (23) with the kernel $\cos k_x$ and bear in mind that the flux across the $x=0$ plane vanishes, we find that $(\partial\bar{c}_V/dx)|_{x=0}=0$, i.e., we obtain

$$D_A^{(d)}\left\{-\frac{\partial\tilde{\bar{c}}_d}{\partial x}(0,s)-k^2\tilde{\bar{\bar{c}}}_d(k,s)\right\}+\frac{2D_A^{(V)}}{R}\frac{\partial\bar{\bar{c}}_V}{\partial r}\Big|_{r=R}=s\tilde{\bar{\bar{c}}}_d(k,s), \tag{24}$$

$$D_A^{(V)}\{\Delta_r\bar{\bar{c}}_V(r,k,s)-k^2\bar{\bar{c}}_V(r,k,s)\}=s\bar{\bar{c}}_V(r,k,s), \tag{25}$$

where $\bar{\bar{c}}(k,s)$ is the Fourier transform of the function $\bar{c}(x,s)$. It follows from Eqs. (24) and (25) that

$$\tilde{\bar{\bar{c}}}_d(k,s)=\left(k^2+\frac{s}{D_A^{(d)}}\right)^{-1}\left\{\frac{2\xi}{R}\frac{\partial\bar{\bar{c}}_V}{\partial r}\Big|_{r=R}+\frac{\partial\tilde{\bar{c}}_d}{\partial x}\Big|_{x=0}\right\}, \tag{26}$$

$$\bar{\bar{c}}_V(r,k,s)=MK_0(\varkappa r), \tag{27}$$

where $\varkappa^2=k^2+s/D_A^{(V)}$, $M=\text{const}$, and $K_0(x)$ is the modified Bessel of the second kind. The Laplace-transformed boundary condition (19) becomes

$$(\tilde{\bar{\bar{c}}}_d-p_A\bar{\bar{c}}_V)\big|_{r=R}=(p_Ac_{0V}-c_{0d})\pi\delta(k)/2s, \tag{28}$$

where $\int_0^\infty\cos kx\,dx=\pi\delta(k)/2$ and $\delta(k)$ is the Dirac delta function. It follows from the condition (28) that

$$M=-\frac{(p_Ac_{0V}-c_{0d})(k^2+s/D_A^{(d)})\pi\delta(k)/2s+(\partial\tilde{\bar{c}}_d/\partial x)\big|_{x=0}}{p_A(k^2+s/D_A^{(d)})K_0(\varkappa R)+(2\xi/R)\varkappa K_1(\varkappa R)}. \tag{29}$$

When the initial condition is selected in a special manner, so that $p_Ac_{0V}=c_{0d}$, the first term in the numerator of Eq. (29) responsible for the process of relaxation of the distribution of the **A** particles between the undeformed bulk and the dislocation tube vanishes. The inverse Fourier transformation applied to $\tilde{\bar{\bar{c}}}_d$ and $\tilde{\bar{\bar{c}}}_v$ yields

$$\bar{c}_V(r,k,s)=-\frac{\partial\tilde{\bar{c}}_d}{\partial x}\Big|_{x=0}\cdot\frac{2}{\pi}\int_0^\infty f(r,k,s)\cos kx\,dk,\qquad r\geqslant R, \tag{30}$$

$$\bar{c}_d(x,s)=-p_A\frac{\partial\tilde{\bar{c}}_d}{\partial x}\Big|_{x=0}\cdot\frac{2}{\pi}\int_0 f(R,k,s)\cos kx\,dk,$$

$$0\leqslant r<R, \tag{31}$$

where

$$f(r,k,s)$$

$$=K_0(\varkappa r)\left[p_A\left(k^2+\frac{s}{D_A^{(d)}}\right)K_0(\varkappa R)+\frac{2\xi}{R}\varkappa K_1(\varkappa R)\right]^{-1}.$$

It follows from the boundary condition (20) that

$$\frac{\partial\tilde{\bar{c}}_d}{dx}\Big|_{x=0}=\pi c_{0d}/2p_As\int_0^\infty f(R,k,s)\,dk. \tag{32}$$

The reaction rate constant $k_{\text{ex}}(t)$ is governed by the fluxes of the concentration of the reagent A to a particle B along a dislocation from the positive and negative directions of x, and also by the flux of A to B directly from the regular (undisturbed) part V of the investigated crystal. The latter flux vanishes in the limit $\zeta\ll 1$, $p_A\gg 1$ and $h\to 0$. In this approximation we can find $\bar{k}_{\text{ex}}(s)$ from Eq. (2):

$$\bar{k}_{ex}(s)=(\pi R)^2 D_A^{(d)}/s\int\limits_0^\infty f(R,k,s)\,dk. \qquad (33)$$

For short times $t\ll R^2/D_A^{(V)}$ the inverse Laplace transformation of Eq. (33) gives the following result which is of the same type as the one-dimensional solution of the Smoluchowski equation (7):

$$k_{ex}(t)\,|_{t\to 0}\propto R^2(D_A^{(d)}/t)^{1/2}. \qquad (34)$$

Consequently, in the limit $t\to 0$ the reaction involves only those A particles present in the dislocation tube at $t=0$ and the diffusion stage of the reaction occurs in the C regime, i.e., mainly along the dislocation. We can easily show that in the case when a B particle diffuses along a dislocation with the diffusion coefficient $D_B^{(d)}$, the constant $k_{\text{ex}}(t)$ is given by Eq. (34) provided we replace $D_A^{(d)}$ with $D_A^{(d)}+D_B^{(d)}$.

After a long time $t\gg R^2/D_A^{(V)}$ the constant $k_{\text{ex}}(t)$ reaches its steady-state value

$$k_{ex}(t)\,|_{t\to\infty}=4\pi RD_A^{eff}=k_D(D_A^{eff}/D_A^{(V)}) \qquad (35)$$

which has the form of the three-dimensional Smoluchowski constant of Eq. (10) for a spherical trap of radius R and with the effective diffusion coefficient for the A particles given by

$$D_A^{eff}=\pi D_A^{(d)}/4\int\limits_0^\infty\frac{\mathrm{K}_0(x)\,dx}{p_A x^2\mathrm{K}_0(x)+2\xi x\mathrm{K}_1(x)}$$

$$\approx\frac{\pi}{4}\left(\frac{p_A D_A^{(V)}D_A^{(d)}}{\ln(p_A/2\xi)}\right)^{1/2}.$$

The solution (35) can be represented also in the form

$$k_{ex}(t)\,|_{t\to\infty}=4\pi D_A^{(V)}RF_p, \qquad (36)$$

where

$$F_p\approx\frac{\pi}{4}\left[\frac{p_A/\xi}{\ln(p_A/2\xi)}\right]^{1/2},$$

which is identical with the solution of the problem of the absorption in a homogeneous medium containing an ellipsoidal sink elongated along a dislocation and characterized by the semiaxes b and c (Ref. 21). The corresponding steric factor F_p is given by

$$F_p=(c^2-b^2)^{1/2}a^{-1}\ln^{-1}\frac{1+[1-(b/c)^2]^{1/2}}{1-[1-(b/c)^2]^{1/2}}.$$

In our problem the parameters of this effective ellipsoid of revolution are

$$b=R,\qquad c\sim R\left(\frac{p_A}{\xi}\right)^{1/2}\ln^{1/2}\frac{p_A}{2\xi}.$$

Therefore, when the transport of a reagent A to a particle B occurs in the diffusion regime A ($t\to\infty$), the reaction kinetics obeys the familiar law (10) with the effective diffusion coefficient D_A^{eff} which differs considerably from the value established earlier and given by Eq. (13). It readily follows from Eqs. (35) and (36) that if $\zeta/p_A\ll 1$, we have $k_{\text{ex}}(t)|_{t\to\infty}\gg k_D$ i.e., the presence of a dislocation in the regular structure of a crystal may considerably increase the diffusion-controlled reaction rate constant.

If we consider the limit $\zeta\sim 1$ and $p_A\sim 1$, we find the expected result $k_{\text{ex}}(t)|_{t\to\infty}\sim k_D$, as in the case of a system without dislocations.

2. REACTION IN A CRYSTAL WITH ONE DISLOCATION CHARACTERIZED BY A RANDOM DISTRIBUTION OF *B* PARTICLES

We consider a system with a single dislocation in which there are N particles of type B distributed at random at position x_i ($i=1,\ldots,N$) and characterized by an average linear concentration c_B^0 (Fig. 2). The solution $\bar{c}_d(x,s)$ of the many-particle problem can be represented, in accordance with the concept of an effective medium described in the Introduction, by a linear combination of the solutions of the type given by Eq. (31) for dislocations with one B particle:

$$\tilde{c}_d(x,s)=$$

$$-p_A\sum_{i=1}^N c_i\frac{\partial\tilde{c}_d}{\partial x}\bigg|_{x=x_i}\cdot\frac{2}{\pi}\int\limits_0^\infty f(R,k,s)\cos k(x-x_i)\,dk. \qquad (37)$$

When the concentration of the B particles distributed on a dislocation is low, then in the first approximation involving a small parameter $\alpha=c_B^0R\ll 1$ we find that the functions c_i and $(\partial\bar{c}_d/dx)|_{x=x_i}$ are the same for all the particles

$$c_i=c,\qquad\frac{\partial\tilde{c}_d}{\partial x}\bigg|_{x=x_i}=\frac{\partial\tilde{c}_d}{\partial x}\bigg|_{x=0},\qquad i=1,\ldots,N.$$

The substitution of the solution (37) into the boundary condition (20) and a change from summation over i to integration with respect to x between the limits $-\infty<x<\infty$ gives the following expression for the experimentally observed reaction rate constant $\bar{k}_{\text{ex}}(s)$:

$$\bar{k}_{ex}(s)=(\pi R)^2D_A^{(d)}\bigg/\left(s\int\limits_0^\infty f(R,k,s)\,dk+\pi s\alpha R^{-1}f(R,0,s)\right). \qquad (38)$$

For short times $t\ll\min\{R^2/D_A^{(V)},R^2/(D_A^{(d)}\alpha^2)\}$, the constant $k_{\text{ex}}(t)$ decreases in accordance with the one-dimensional law

$$k_{ex}(t)\,|_{t\to 0}\propto R^2\left(\frac{D_A^{(d)}}{t}\right)^{1/2}\left\{1-2\alpha\left(\frac{\pi D_A^{(d)}t}{R^2}\right)^{1/2}\right\}, \qquad (39)$$

which, to within a quantity on the order of the small gas parameter α, is identical over this time interval with Eq. (34), i.e., it corresponds to the diffusion regime C. Hence, the absorption of the reagent A by each of the B particles is an independent process.

The kinetics of the next stage of the reaction is governed by the value of the gas parameter α. At times $t\gg R^2/D_A^{(V)}$ Eq. (38) for the reaction rate constant $\bar{k}_{\text{ex}}(s)$ is given by

$$\bar{k}_{ex}(s)=\frac{2\pi RD_A^{(d)}}{s}\left[\frac{1}{p_A\xi}\left(\ln\frac{p_A}{2\xi}\right)^{1/2}+\frac{\alpha}{\xi}\ln\frac{1}{R}\left(\frac{D_A^{(V)}}{s}\right)^{1/2}\right]^{-1}. \qquad (40)$$

(40)

If the parameter α is sufficiently large,

$$\left(\frac{\xi}{p_A}\ln\frac{p_A}{2\xi}\right)^{1/2}=\alpha_1\ll\alpha\ll 1,$$

then the value of $k_{\text{ex}}(t)$ per unit dislocation length decreases in accordance with the law

$$k_{ex}(t)=4\pi D_A^{(V)}/\ln(D_A^{(V)}t/R^2). \qquad (41)$$

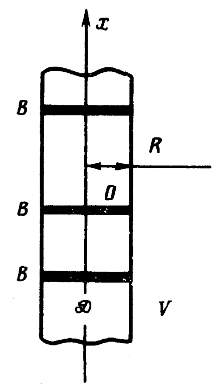

FIG. 2. Dislocation D with B particles.

This dependence is exactly the same as the two-dimensional solution of the Smoluchowski equation (8) in the problem of absorption of a reagent by an ideal sink of radius R. This regime is established because by the time $t \sim R^2/(D_A^{(d)}\alpha^2) \ll R/D_A^{(V)}$ the particles of the reagent B initially present on a dislocation are lost and the A particles reaching the dislocation at times $t \gg R^2/D_A^{(V)}$ are annihilated at the B particles with a probability close to unity (because $\zeta \ll 1$). In this regime the reaction is controlled by the transport of the reagent A to a dislocation tube from the undeformed bulk of the crystal.

For a sufficiently small gas parameter $\alpha \ll \alpha$, a steady-state dependence described by Eq. (34) is established at times $t \gg R^2/D_A^{(V)}$ and after a very long time

$$t \gg \tau_1 \propto (R^2/D_A^{(V)}) \exp(2\alpha_1/\alpha)$$

it changes to the relationship (41). Since the concentration B is low, the particles A penetrating a dislocation can leave it so that the process in which the dislocation acts as an ideal sink [see Eq. (41)] competes with the regime when the A particles are lost independently at single B particles [see Eq. (34)]. The change in the dominant regime after an exponentially long time $t \sim \tau_1$ is due to logarithmic factors and does not have clear limits on the time scale.

It therefore follows that in the course of the transformation the diffusion stage of the reaction follows consecutively in the regimes C and A (when the average distance between the B particles is $1/c_B^0$) and is characterized by a change of the asymptotic relationships governed by a change in the effective dimensionality of the system in accordance with $d^{\text{eff}} = 1 \to 3 \to 2$ if $\alpha \ll \alpha_1$, but in accordance with $d^{\text{eff}} = 1 \to 2$ for higher values of α. The observed reaction rate constant $k_{\text{ex}}(t)$ cannot be found by simple substitution of the effective diffusion coefficient from Eq. (16) into Eq. (10).

3. REACTION IN A SYSTEM WITH PARALLEL DISLOCATIONS

In many cases we can expect dislocations in a crystal to have a preferential orientation along crystallographic axes.[2,13] Let us consider an ensemble of M parallel dislocations with an average density σ and assume that each of them contains active B particles (Fig. 3).

The concentration $\tilde{\bar{c}}_d(x, s)$ inside a selected dislocation $\mathscr{D}_1$ can be represented, in accordance with the concept of an effective medium, by a linear combination of the solutions (37) for isolated dislocations

$$\tilde{\bar{c}}_d(x, s) = -p_A \sum_{j=1}^{M} \sum_{i=1}^{N_j} c_{ij} \frac{\partial \tilde{\bar{c}}_d}{\partial x}\bigg|_{x=x_{ij}} \cdot \frac{2}{\pi} \int_0^\infty f(R_j - R, k, s) \cos k(x - x_{ij})\, dk, \tag{42}$$

where N_j is the number of the B particles at the jth dislocation; $R_j - R \geqslant R$; $j = 1, \ldots, M$. The quantities c_{ij} and $(\partial \bar{c}_d/\partial x)|_{x=x_{ij}}$ to first order in the small parameters $\alpha \ll 1$ and $\sigma R^2 \ll 1$, can be regarded as having the same values for all cases defined by $i \leqslant j \leqslant M$, $1 \leqslant i \leqslant N_j$. If we modify Eq. (42) so that integration is carried out in the plane $0 \leqslant r < \infty$ in the range $0 < \varphi \leqslant 2\pi$ and if we use the boundary condition (20), we obtain the following expression for $\bar{k}_{\text{ex}}(s)$:

$$\bar{k}_{ex}(s) = \frac{2\pi R^2 D_A^{(d)}}{s} \bigg/ \left\{ \frac{2}{\pi} \int_0^\infty f(R, k, s)\, dk + 2\alpha R^{-1} f(R, 0, s) \left[1 + 2\pi\sigma R^2 \frac{K_1(\beta)}{\beta K_0(\beta)} \right] \right\} \tag{43}$$

where $\beta = R(s/D_A^{(V)})^{1/2}$. Compared with Eq. (38) for one dislocation, we find that the denominator of Eq. (43) now has an additional term because the diffusion flux is redistributed between dislocations.

For short times defined by $t \ll \min\{R^2/D_A^{(V)}, R^2/(D_A^{(d)}\alpha^2)\}$ the quantity $k_{\text{ex}}(t)$ decreases in accordance with the one-dimensional law (39) for B-type diffusion, exactly as in Sec. 2.

For

$$R^2/D_A^{(V)} \ll t \ll (4\pi\sigma D_A^{(d)})^{-1} \ln(4\pi\sigma R^2)^{-1} \sim \tau_2$$

the observed rate constant $k_{\text{ex}}(t)$ is described by Eqs. (35) and (41) under the conditions discussed in Sec. 2. Within the range of times defined above, we find that in the vicinity of each of the dislocations the reaction occurs in the diffusion regime A with respect to the average distance $1/c_B^0$ between the B particles and at the same time it occurs independently at each dislocation, i.e., in the B regime when the average distance between the dislocations is $(\pi\sigma)^{-1/2}$.

In the next stage of the reaction for $t \gg \tau_2$ in the diffusion regime A the competition between dislocations has the

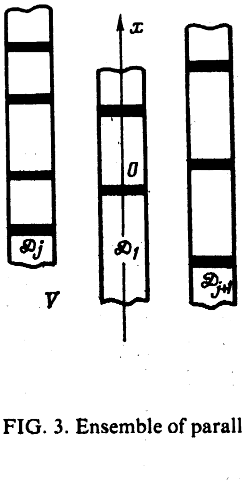

FIG. 3. Ensemble of parallel dislocations with B particles.

dominant influence on the distribution of the reagent flux A. After the inverse Laplace transformation, we find Eq. (43) becomes

$$k_{ex}(t) \approx u(t) R \exp[-u(t)\sigma t], \tag{44}$$

where

$$u(t) = 4\pi D_A^{(V)} / [2\alpha_1 + \alpha \ln (D_A^{(V)} t/R^2)].$$

We can easily see that for $t \gg \tau_2$, the average concentration in the system $\langle c_v(t) \rangle$ decreases in accordance with the law

$$\langle c_V(t) \rangle = c_{0V} \exp[-u(t)\sigma t]. \tag{45}$$

Consequently, the true value is $k_{ex}(t) = u(t)R$ and it is identical with the corresponding value for a single dislocation.

If the dislocation density is sufficiently low,

$$\sigma \ll (4\pi R^2)^{-1} \exp(-2\alpha_1/\alpha) = \sigma_1,$$

then in the interval $\tau_2 \ll t \ll \tau_1$ the average concentration $\langle c_v(t) \rangle$ is described by an exponential dependence of the Smochulowski solution form for $d = 3$

$$\ln(\langle c_V(t) \rangle / c_{0V}) \approx -k_D^{eff} n_B^{eff} t, \tag{46}$$

where k_D^{eff} is given by Eq. (35) and $n_{\text{B}}^{\text{eff}} = \sigma c_{\text{B}}^0$ is the effective concentration of the B particles in the system.

At times $t \gg \tau_1$ the reaction is limited by the diffusion of the A particles to dislocation tubes and is described by the dependence

$$\ln(\langle c_V(t) \rangle / c_{0V}) \approx -4\pi\sigma D_A^{(V)} t / \ln(D_A^{(V)} t/R^2). \tag{47}$$

The fractions of the reagent A annihilated in accordance with the laws (46) and (47) are Δ_1 and Δ_2. They are described by

$$-\ln \Delta_1 \sim \left(\frac{\xi\alpha}{\alpha_1}\right) \ln \frac{1}{4\pi\sigma R^2} \ll 1,$$

$$-\ln \Delta_2 \sim \frac{\sigma R^2 \alpha}{\alpha_1} \exp\left(\frac{2\alpha_1}{\alpha}\right) \gg -\ln \Delta_1.$$

A higher proportion of the reagent A is lost in accordance with the law (46).

If the dislocation density is relatively high ($\sigma \gg \sigma_1$), then at times $t \gg \tau_2$ the dependence (46) is not obtained and the bulk of the reagent disappears in accordance with the law (47).

As in Sec. 2, where we considered a system with one dislocation, a crystal with an ensemble of parallel dislocations exhibits a change in the effective dimensionality of the reaction system: $d^{\text{eff}} = 1 \to 3 \to 2$. This model describes more satisfactorily the kinetics of crystals than the treatments given in Secs. 1 and 2, because the dislocation density is not usually low. Calculations predict the decrease in the average concentration in the system $\langle c_V(t) \rangle$ in accordance with the laws (46) and (47), which can easily be observed experimentally, since in the case $D_A^{(d)} \sim 10^{18}$ cm^2/s. $R \sim 10^{-8}$ cm, and $\sigma \sim 10^{10}$–10^{12} cm^{-2}, the characteristic time when this change occurs is fairly long and represents a value from several minutes to tens of hours.

4. REACTION IN A SYSTEM WITH AN ENSEMBLE OF PARALLEL DISLOCATIONS IN ONE PLANE ("DISLOCATION WALL")

A group of dislocations can pile up in front of some obstacles under the action of stresses in a crystal; for example, this can happen in front of grain boundaries preventing the motion of the head of the dislocation. As a rule, dislocations become aligned head-to-tail.[2] We shall consider the kinetics of the reaction (1) when B particles are distributed in such a dislocation ensemble. As in Sec. 3, the concentration of these particles $\bar{\bar{c}}_d(x, s)$ inside a given dislocation $\mathscr{D}_1$ is given by Eq. (42) The observed rate constant of the reaction $\bar{k}_{ex}(s)$, calculated by the effective medium method, is then

$$\bar{k}_{ex}(s) = \frac{\pi R^2 D_A^{(d)}}{s} \Big/ \left[\frac{1}{\pi}\int_0^\infty f(R,k,s)\,dk + \alpha R^{-1} f(R,0,s) + \alpha\rho I(\beta)\beta^{-1}\right] \tag{48}$$

where ρ is the linear dislocation density in the ensemble ($\rho R \ll 1$), $\beta = R(s/D_A^{(V)})^{1/2}$, and

$$I(\beta) = \int_\beta^\infty f(x,0,s)\,dx\,|_{\beta\to 0} \approx \left(\frac{\pi}{2} + \beta \ln \beta\right)\frac{R^2}{2\xi}.$$

During the early stage of the reaction at times $t \ll \min\{R^2/D_A^{(V)}, R^2/(D_A^{(d)}\alpha^2)\}$ the inverse Laplace transformation of Eq. (48) gives the one-dimensional law (39) (see Secs. 2 and 3).

At times $t \gg R^2/D_A^{(V)}$ the kinetics is governed by the relationship between the small parameters α and ρR. When the first of these small parameters obeys $\alpha \ll \alpha_1$ and the dislocation density is sufficiently high that

$$\rho \gg (\alpha R)^{-1} \alpha_1 \exp(-\alpha_1/\alpha) = \rho_1$$

we find that in the time intervals defined by

$$R^2/D_A^{(V)} \ll t \ll (\alpha_1/\alpha)(\rho^2 D_A^{(V)})^{-1} = \tau_3$$

the constant $k_{ex}(t)$ is independent of time and is given by Eq. (35). For $t \gg \tau_3$ the reaction is controlled by the transport of the reagent A to a dislocation wall. The observed constant $k_{ex}(t)$ calculated per unit area for the dislocation ensemble is

$$k_{ex}(t) \sim [D_A^{(V)}/\pi t]^{1/2}. \tag{49}$$

The effective dimensionality of the reaction system again becomes unity, as in the $t \to \infty$ case when $k_{ex}(t)$ is described by (34), except that now the diffusion coefficient $D_A^{(V)}$ is smaller than $D_A^{(d)}$.

If the dislocation density is low ($\rho \ll \rho_1$), then for $R^2/D_A^{(V)} \ll t \ll \tau_1$ the rate constant $k_{ex}(t)$ is given by Eq. (35), whereas at times $\tau_1 \ll t \ll (\rho^2 D_A^{(V)})^{-1} \ln^2 \rho R$ an intermediate asymptote of Eq. (41) is established which changes for times $t \gg \tau_3$ to the law (49). If the gas parameter is relatively high ($\alpha_1 \ll \alpha \ll 1$), the dependence (35) is not obtained and the kinetics occurs in accordance with the laws (41) and (49) at times $R^2/D_A^{(V)} \ll t \ll \tau_3$ and $t \gg \tau_3$, respectively.

We conclude this section by noting that in the course of the reaction the effective dimensionality of the system changes nontrivial:

$$d^{eff}=1\rightarrow\left\{\begin{matrix}3; & \alpha\ll\alpha_1, & \rho\gg\rho_1\\ 3\rightarrow 2; & \alpha\ll\alpha_1, & \rho\ll\rho_1\\ 2; & \multicolumn{2}{c}{\alpha_1\ll\alpha\ll 1}\end{matrix}\right\}\rightarrow 1.$$

Therefore, after a long time a "dislocation wall" can absorb A particles in the same way as a perfectly absorbing plane.

5. REACTION IN A SYSTEM WITH RANDOMLY ORIENTED DISLOCATIONS SUBJECT TO FLUCTUATIONS OF THE CONCENTRATION OF *B* PARTICLES AND OF THE DISLOCATION DENSITY

We next consider the kinetics of the reaction (1) in a crystal containing M equiprobably oriented dislocations (i.e., we assume that a unit area of an arbitrary section of the system is crossed by σ dislocations). As in Sec. 4, the concentration $c_d(x, s)$ inside a selected dislocation is a superposition of the solutions of the form given by Eq. (42) for single dislocations carrying B particles, where x_{ij} are the coordinates of these B particles for the jth dislocation which is directed along a vector $\mathbf{1}_j$ and R_j is the distance from the origin of the coordinate system to the jth dislocation (Fig. 4). We now sum the contributions made to $\bar{\bar{c}}_d(0, s)$ due to ensembles of quasiparallel dislocations, i.e., of dislocations oriented along angles θ and φ within the intervals $[\theta, \theta + d\theta]$ and $[\varphi, \varphi + d\varphi]$, where θ and φ are the angles which vary from 0 to $\pi/2$ in a spherical coordinate system linked to a specific dislocation $\mathscr{D}_1$. Going over from summation to integration with a unit weight, because different directions of dislocations are equally probable, we find that in the case of small parameters obeying $\alpha \ll 1$ and $\alpha_\sigma = \sigma R^2 \ll 1$ the average concentration $\langle c_V(t)\rangle$ of the particles in the system decreases in accordance with the law given by Eq. (44), i.e., it decreases in exactly the same manner as in the case of an ensemble of parallel dislocations.

In the case of real crystals the dislocation density and the concentration of the impurity atoms are distributed homogeneously only on a macroscopic scale. It is of practical interest to analyze the kinetics allowing for fluctuations of the dislocation density and of the concentration of the active B particles, when the latter are also present in the regular part of a crystal ($p_B = c_B^0/\pi R^2 n_B^{(V)} \neq \infty$, where $n_B^{(V)}$ is the concentration of the B particles in the regular part of volume V). The concept of the effective medium yields the following dependence of the average particle concentration:

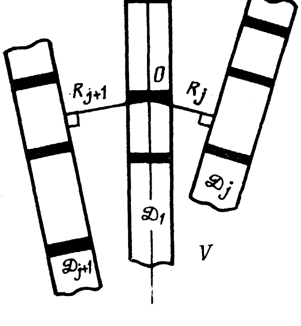

FIG. 4. Ensemble of randomly oriented dislocations with B particles.

$$\frac{\ln\langle c_V(t)\rangle}{c_{0V}}=-4\pi a D_A^{(V)}\,n_B^{(V)}t\left\{1+\frac{p_B\alpha_\sigma}{2\alpha_1+\alpha\ln(D_A^{(V)}t/R^2)}\right\} \tag{50}$$

where the coefficient in front of the expression enclosed in braces is equal to the volume of the reaction tube around the path of a particle A which lies in the regular part of the crystal and is traversed in an average time $(1-\alpha_0)t$.

Fluctuation effects appear also in the limit $t\rightarrow\infty$, when the reaction kinetics is governed by those A particles which are localized in large fluctuation voids free of the B particles and whose outer boundary is not crossed by dislocations. The solution of the diffusion equation (3) in a spherical void Ω subject on its surface Σ to the boundary condition

$$c_\Omega(r, t)\,|_{r\in\Sigma}=0 \tag{51}$$

and subject to the initial condition

$$c_\Omega(r,0)=\left\{\begin{matrix}c_{0V}, & r\in\Omega\\ 0, & r\notin\Omega\end{matrix}\right. \tag{52}$$

yields the following dependence, which applies to the average concentration $\langle c_\Omega(t)\rangle$ inside the cavity when the condition $D_A^{(V)}t\gg l^2$ is obeyed:

$$\frac{\ln\langle c_\Omega(t)\rangle}{c_{0V}}=-\left(\frac{\pi}{l}\right)^2 D_A^{(V)}t, \tag{53}$$

where l is the radius of the void. In this regime the reaction is controlled by the diffusion of A toward the internal boundary Σ. We average $\langle c_\Omega(t)\rangle$ over all the voids using the expression

$$\langle c_V(t)\rangle=\int_V \langle c_\Omega(t)\rangle p_\Omega(V_\Omega, S_\Omega)\,dV \tag{54}$$

subject to the weighting function

$$p_\Omega(V_\Omega, S_\Omega)=\exp(-n_B^{(V)}V_\Omega-\sigma S_\Omega), \tag{55}$$

equal to the probability for of a void of volume V_Ω with a surface area S_Ω to form free of B particles and uncrossed by dislocations. Using the steepest descent method, we find that the radius of the optimal void $l(t)$ is described by the following equation:

$$1+\frac{2\alpha_\sigma}{\pi\alpha_B^{(V)}}\gamma=\frac{\pi D_A^{(V)}t}{2\alpha_B^{(V)}a^2}\gamma^5, \tag{56}$$

where $\gamma = a/l(t)$ and $\alpha_B^{(V)} = n_B^{(V)}a^3$.

If we assume that the dislocation density is sufficiently low to satisfy the inequality $\alpha_0 \ll \gamma^{-1}\alpha_B^{(V)}$, we find that Eq. (56) yields $l(t)\propto t^{1/5}$, which gives rise to a fluctuation dependence (11), the establishment of which is governed by the inhomogeneity of the B particle concentration. The regime (11) alters the relationship (50) over times

$$t\gg\frac{a^2}{D_A^{(V)}(\alpha_B^{(V)})^{3/2}}\left(1+\frac{p_B\alpha_\sigma}{2\alpha_1+\alpha\ln z_1}\right)^{-1},$$

where

$$z_1^{-1}=(\alpha_B^{(V)})^{3/2}\left\{1+\frac{p_B\alpha_\sigma}{2\alpha_1+\alpha}\right\}.$$

If the dislocation density is high i.e., if $\gamma^{-1}\alpha_B^{(V)} \ll \alpha_0 \ll 1$, there is an intermediate asymptotic of $\langle c_V(t)\rangle$ which is characterized by $l(t) \sim t^{1/4}$ and by

$$\ln(\langle c_V(t)\rangle/c_{0V}) \propto (\sigma D_A^{(V)} t)^{1/2}. \tag{57}$$

The dependence (57) replaces the regime described by Eq. (50) for

$$t \gg \frac{a^2 p_B}{D_A^{(V)}\alpha_B^{(V)}}\left(1+\frac{p_B\alpha_\sigma}{2\alpha_1+\alpha\ln z_2}\right)^{-1} = \tau_0$$

where

$$z_2^{-1} = \frac{\alpha_B^{(V)}}{p_B}\left(1+\frac{p_B\alpha_\sigma}{2\alpha_1+\alpha}\right).$$

Since $l(t)$ increases over a time satisfying

$$t \gg (a^2/D_A^{(V)})\alpha_\sigma^5(\alpha_B^{(V)})^{-4} = \tau_*$$

the quantity $(2\alpha_\sigma/\pi\alpha_B^{(V)})\gamma$ in Eq. (56) associated with fluctuations of the dislocation density becomes less than unity. The intermediate asymptotic form of Eq. (57) is then replaced by the dependence described by Eq. (11). The changes of the time intervals τ_0 and τ_* are then

$$\Delta_1 = -\ln(\langle c_V(\tau_0)\rangle/c_{0V}) \sim (\alpha_\sigma\tau_0 D_A^{(V)}/a^2)^{1/2},$$

$$\Delta_2 = -\ln(\langle c_V(\tau_*)\rangle/c_{0V}) \sim \alpha_\sigma^3(\alpha_B^{(V)})^{-2} \gg \Delta_1.$$

It therefore follows that when the dislocation density is high compared with the concentration of the B particles, i.e., for $\gamma^{-1}\alpha_B^{(V)} \ll \alpha_\sigma \ll 1$, the law (57) indicates that a considerable fraction of the reagent A is annihilated; this is governed by the survival of A in dislocation-free fluctuation voids. At times $t \gg \tau_*$ the number of voids free of the B particles becomes larger than the number of voids which are not intersected by dislocations, so that the fluctuation regime changes. The laws (11) and (57) predict a slower reaction in the limit $t \to \infty$ than that which follows from the Smoluchowski theory.

6. REACTION IN A POLYCRYSTALLINE SAMPLE WITH A PARTICLE *B* AT AN INTERFACE

Diffusion along interfaces in a polycrystalline sample is, like that along dislocations, much faster than in the regular lattice,[3,13] so that in the case when the B particles are located at such interfaces the diffusion stage of the reaction is much shorter than the corresponding stage of the reaction in the undeformed crystal.

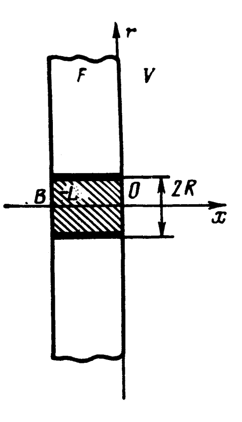

FIG. 5. Interface F with a localized B particle.

We first consider the simplest model in a single cylindrical particle B of radius R and of height L is located on an infinite plane boundary F of thickness L (Fig. 5). The particles of a reagent A diffuse along the regions F and V with the diffusion coefficients $D_A^{(f)}$ and $D_A^{(V)}$. The corresponding concentrations of these particles $\bar c_f\,(r,x,s)$ and $\bar c_V\,(r,x,s)$ obey the diffusion equation (16) subject to the boundary conditions

$$D_A^{(f)}\frac{\partial\bar c_f}{\partial x}\bigg|_{x=0} = D_A^{(V)}\frac{\partial\bar c_V}{\partial x}\bigg|_{x=0}, \quad r \geqslant R, \tag{58}$$

$$\frac{c_{0f}}{s}+\bar c_f|_{x=0} = p_A\left(\frac{c_{0V}}{s}+\bar c_V|_{x=0}\right), \quad r\geqslant R, \tag{59}$$

$$\bar c_V|_{x=0} = -c_{0V}/s,\ 0\leqslant r<R, \tag{60}$$

$$\bar c_f|_{r=R} = -c_{0f}/s,\ -L\leqslant x\leqslant 0, \tag{61}$$

$$\frac{\partial\bar c_f}{\partial x}\bigg|_{x=-L} = 0, \quad r\geqslant 0, \tag{62}$$

$$\bar c_f|_{r=\infty} = 0, \tag{63}$$

$$\bar c_V|_{x=\infty} = \bar c_V|_{r=\infty} = 0. \tag{64}$$

We apply the Fourier transformation to the diffusion equation for $\bar c_V(r,x,s)$ with a kernel cos kx and we shall average the equation for $\bar c_f\,(r,x,s)$ over x in the interval $[-L, 0]$ with a unit weight:

$$\Delta_r\bar{\bar c}_V(r,k,s) - \frac{\partial\bar c_V}{\partial x}\bigg|_{x=0} - k^2\bar{\bar c}_V(r,k,s) = \frac{sc_V(r,n,s)}{D_A^{(V)}}, \tag{65}$$

$$\Delta_r\bar c_f(r,s) + \frac{1}{L}\frac{\partial\bar c_f}{\partial x}\bigg|_{x=0} = \frac{s\bar{\bar c}_f(r,s)}{D_A^{(f)}}. \tag{66}$$

We now subject Eqs. (65) and (66) to the Hankel transformation

$$\tilde c_{f(V)}(a) = \int_a^\infty rJ_0(ar)c_{f(V)}(r)\,dr,$$

where $J_0\,(x)$ is a Bessel function of zeroth order. After the transformations we obtain

$$\tilde{\bar{\bar c}}_V(a,k,s) = -\frac{\partial\tilde{\bar c}_V}{\partial x}\bigg|_{x=0}\left(a^2+k^2+\frac{s}{D_A^{(V)}}\right)^{-1}, \tag{67}$$

$$\tilde{\bar{\bar c}}_f(a,s) = \left(a^2+\frac{s}{D_A^{(f)}}\right)^{-1}\left\{\frac{\chi}{L}\frac{\partial\tilde{\bar c}_V}{\partial x}\bigg|_{x=0} - R\frac{\partial\bar c_f}{\partial r}\bigg|_{r=R} J_0(aR) + aR\frac{c_{0f}}{s}J_1(aR)\right\}, \tag{68}$$

where $\chi = D_A^{(V)}/D_A^{(f)} \ll 1$. The inverse Fourier transformation applied to Eq. (67) gives

$$\tilde{\bar c}_V(a,x,s) = -\left(a^2+\frac{s}{D_A^{(V)}}\right)^{-1/2}\frac{\partial\tilde{\bar c}_V}{\partial x}\bigg|_{x=0} \times \exp\left[-x\left(a^2+\frac{s}{D_A^{(V)}}\right)^{1/2}\right]. \tag{69}$$

The boundary condition of Eq. (59) subject to the additional condition $p_A c_{0V} = c_{0f}$ leads to

$$\left.\frac{\partial \tilde{\bar{c}}_V}{\partial x}\right|_{x=0}(a,s)=\varphi(a,s)R\left(a^2+\frac{s}{D_A^{(V)}}\right)^{1/2}\left\{\left.\frac{\partial \bar{c}_f}{\partial r}\right|_{r=0}J_0(aR)\right.$$

$$\left.-a\frac{c_{0f}}{s}J_1(aR)\right\}, \tag{70}$$

where

$$\varphi(a,s)=\left\{p_A\left(a^2+\frac{s}{D_A^{(f)}}\right)+\frac{\chi}{L}\left(a^2+\frac{s}{D_A^{(V)}}\right)^{1/2}\right\}^{-1}.$$

Substituting the derivative $(\partial c_V/\partial x)|_{x=0}$ from Eq. (70) in the boundary condition (61), we obtain

$$\left.\frac{\partial \bar{c}_f}{\partial r}\right|_{r=R}=\frac{c_{0f}}{s}\left[1+p_AR\int_0^\infty a^2\varphi(a,s)J_0(aR)J_1(aR)\,da\right]\Big/$$

$$p_AR\int_0^\infty a\varphi(a,s)J_0^2(aR)\,da. \tag{71}$$

The reaction rate constant $k_{\text{ex}}\ (f)$ is equal to the sum of the fluxes of the reagent A to B arriving from the interface and from the regular lattice, divided by A the concentration at infinity, c_{0V}: $k_{\text{ex}}(t)=k_{\text{ex}}^{(f)}(t)+k_{\text{ex}}^{(V)}(t)$. The quantity $\bar{k}_{\text{ex}}^{(f)}\ (s)$ deduced from Eq. (2) is

$$\bar{k}_{ex}^{(f)}(s)=\frac{2\pi LD_A^{(f)}p_A}{s}\left\{\left(1+\int_0^\infty\frac{x^2J_0(x)J_1(x)\,dx}{x^2+\beta_f^2+z(x^2+\beta_V^2)^{1/2}}\right)\right.$$

$$\left.\times\left(\int_0^\infty\frac{xJ_0^2(x)\,dx}{x^2+\beta_f^2+z(x^2+\beta_V^2)^{1/2}}\right)^{-1}\right\}, \tag{72}$$

where $\beta_f\ =R(s/D_A^{(f)})^{1/2}$, $\beta_V\ =R(s/D_A^{(V)})^{1/2}$, and $z=\chi R(p_AL)^{-1}\ll 1$. At sufficiently short times $R^2/D_A^{(f)}\ll t\ll R^2/(zD_A^{(V)})$ the inverse Laplace transformation applied to Eq. (72) gives the following time dependence $k_{\text{ex}}^{(f)}\ (t)$:

$$k_{ex}^{(f)}\propto LD_A^{(f)}p_A/\ln(D_A^{(f)}t/R^2), \tag{73}$$

which corresponds to a solution of the type given by the two-dimensional solution of the Smoluchowski equation (8).

For $t\gg R^2/zL_A^{(V)}$, the constant $k_{\text{ex}}^{(f)}(t)$ is given by

$$k_{ex}^{(f)}\ (t)\,|_{t\to\infty}\approx 4\pi RD_A^{(V)}\Delta_0, \tag{74}$$

where $\Delta_0=\frac{3}{4}z^{-1}\ln^{-2}z^{-1}\gg 1$, i.e., the quantity $k_{\text{ex}}^{(f)}\ (t)$ in the limit $t\to\infty$ reaches a steady-state regime described by Eq. (74) of the same type as the three-dimensional solution of the Smoluchowski equation (10) for a spherical particle B of radius R and with the effective diffusion coefficient $D_A^{(V)}\ \Delta_0$.

In the limiting case $p_A\sim 1, \chi\sim 1$, we find $\Delta_0\sim 1$, and the constant $k_{\text{ex}}^{(f)}(t)$ of Eq. (74) is identical with the solution for a regular crystal free of defects.

We now consider the constant $k_{\text{ex}}^{(V)}(t)$. The flux of particles A to B from the region V when the interface represents an impermeable surface at $r\geqslant R$ and an ideal sink at $0\leqslant r<R$ is proportional to $D_A^{(V)}R$. This is easily demonstrated in the case discussed in Sec. 1 for $D_A^{(V)}=D_A^{(d)}$, and $p_A=1$. When the boundary conditions are described by Eqs. (58) and (59), this flux is even less because of penetration of the A particles into the region F so that under these conditions we have $k_{\text{ex}}^{(V)}\ll k_{\text{ex}}^{(f)}$. Annihilation of the reagent A occurs mainly on a side surface of B, i.e., within the interface. The positioning of the active B particles at such defects accelerates greatly the reaction.

We can show that after a long time a system in which the B traps are distributed at random on a plane interface absorbs in the same way as an ideally absorbing plane, by analogy with the system investigated earlier[20] and considered also in Sec. 4 above.

CONCLUSIONS

We have analyzed the kinetics of a reaction of the $A+B\to B$ type in crystals in the presence of accelerated-diffusion paths in the form of dislocations and interfaces. When active B particles are distributed in an ensemble of parallel dislocations, the observed reaction rate constant $k_{\text{ex}}\ (t)$ decreases for short times in accordance with the one-dimensional law (34), which is determined by the flux of the A particles to B when the latter are located at dislocations at $t=0$. During the subsequent stages of this reaction we can expect the A particles arriving at the dislocation from the regular bulk of the crystal to participate also. If the linear concentration of B at dislocations is sufficiently low, then $k_{\text{ex}}\ (t)$ assumes a steady-state value given by Eq. (35), which is considerably higher than the corresponding Smoluchowski solution for $d=3$: $k_D^{\text{eff}}\gg k_D$. This dependence then changes to that described by Eq. (47), when the process is controlled by the transport of A to dislocation tubes. At high values of α the steady-state relationship of Eq. (35) does not apply and a considerable fraction of the reagent A is annihilated in accordance with the law (47).

When the B particles are on a wall of parallel dislocations, the kinetics is characterized consecutively by (34), (46), and (47). In the limit $t\to\infty$ the reaction is limited by the diffusion of the A particles to a dislocation wall and the rate constant $k_{\text{ex}}\ (t)$ is described by the one-dimensional dependence (49).

The consecutive changes in the kinetics in accordance with the sequences $d=1\to 3\to 2$ and $d=1\to 3\to 2\to 1$ are due to changes in the effective dimensionality of the system. The physical reasons for these changes are analyzed above.

We also considered fluctuation effects associated with an inhomogeneous distribution of the dislocation orientation. If the dislocation density is sufficiently high, a considerable fraction of the reagent A is annihilated in accordance with the fluctuation law (57).

We also considered the kinetics of a system in which a B particle is located at an interface. At early times the observed rate constant for a cylindrical B particle is given by Eq. (73) when the flux of a reagent A to a particle B consists of A particles present initially at the interface. In the limit $t\to\infty$ the constant $k_{\text{ex}}\ (t)$ is independent of time and is greater by a factor than the Smoluchowski rate constant of Eq. (10) which applies to a homogeneous medium free of defects.

It therefore follows that the presence of active B particles along accelerated-diffusion paths can reduce greatly the diffusion stage of such a diffusion-controlled reaction and can alter greatly the kinetic relationships.

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