# Quantum diffusion in irregular crystals

Yu. Kagan and L. A. Maksimov

*I. V. Kurchatov Institute of Atomic Energy*

(Submitted 17 August 1982)
Zh. Eksp. Teor. Fiz. **84**, 792–810 (February 1983)

Quantum below-barrier diffusion of atoms is considered in a crystal with arbitrary shift of the energy levels. The theory is developed within the framework of the density-matrix formalism with account taken of static fluctuations as well as of dynamic ones due to interaction with phonons. Diffusion is investigated under conditions of localization and induced phonon delocalization. A special analysis is made of quantum diffusion under conditions when the interaction between the particles ceases to be weak. The low-temperature recombination of atoms in a crystal, when the kinetics is restricted by below-barrier diffusion of the particles, is considered. A comparison is made with the experimental results obtained by Katunin *et al.* [JETP Lett. **34**, 357 (1981)] and Mikheev *et al.* [Sov. J. Low Temp. Phys. **8**, 505 (1982)].

PACS numbers: 66.30.Dn

## 1. INTRODUCTION

The problem of quantum below-barrier diffusion of atomic particles into crystals has recently attracted much theoretical and experimental attention. A distinguishing feature of this class of phenomena is the extremely weak tunnel bonds between the equivalent positions for the diffusing particles, which are realized against the background of strong interaction with the dynamic and static fluctuations of the medium. The latter cause a strongly pronounced tendency to localize the particle, a tendency overcome in principle only to the extent that the tunneling is weak.

In an ideal crystal at $T=0$ any defect should in principle be delocalized. This concept was methodically developed by Andreev and Lifshitz[1] on the basis of the concept of quasiparticle band motion of the defects in a quantum crystal. Allowance for scattering by phonons in this motion made it possible for them to find the low-temperature dependence of the diffusion coefficient $D$ on $T$.

In view of the very narrowband width $\Delta$, however, the level shift in neighboring equivalent wells begins to exceed $\Delta$, because of the interaction with the phonons, even at quite low temperatures. Dynamic destruction of the band sets in. The particle motion loses completely the band character and a tendency to particle localization arises.[2,3] This localization, however, is only virtual. A general solution of the problem was found in Refs. 2 and 3 for arbitrary temperatures and demonstrated the conservation of the coherent diffusion (particle tunneling without excitation of the phonon system) in dynamic destruction of the band; the solution described also the diffusion transport under conditions when the mean free path $\lambda$ is small compared with the interatomic distance $a$.

The small bandwidth makes the low-temperature kinetics anomalously sensitive to deviations of the crystal from ideal. Even at a low impurity density the level shift becomes comparable with $\Delta$ and static destruction of the band takes place. Consequently, as $T\to 0$, a true particle localization of the Anderson type appears. Now, as the temperature is raised, the interaction with the phonons should, on the contrary, eliminate the localization and consequently the localization should increase rather than decrease with $T$. However, when the scale of the dynamic level shift begins to exceed the characteristic static shift, the diffusion picture becomes the same as in the dynamic destruction of the band of an ideal crystal. The diffusion coefficient now decreases with increasing $T$, going through a maximum at a certain intermediate temperature. The qualitative aspect of this picture can be deduced even from the results of Ref. 4, devoted to two-well kinetics in a phonon field, and is expounded explicitly in Ref. 5.

We develop in this paper a general theory of quantum diffusion in nonideal crystal with static level shift. The analysis is based on the formalism of the equation for the density matrix, a formalism similar to that used earlier in Refs. 2 and 4, with thorough account taken of the distinguishing features of the inhomogeneous problem. Even at this point we wish to note two results that follow from the general analysis. We find that in a wide range of low temperatures, at an arbitrary level shift the coherent diffusion is found to be larger (or at least not smaller) than the incoherent diffusion (tunneling with simultaneous excitation of the phonons). According to the second result, at a fixed scale of the level shift, when the temperature is lowered the two-phonon kinetics typical of the problem with an extremely narrow band gives way to one-phonon kinetics, and this entails a radical change in the dependence of $D^{\rm coh}$ on $T$ and $\delta\varepsilon$, and in many cases also in the very picture of the kinetics.

Among the typical problems of quantum diffusion there exists a large class of phenomena suggesting that the diffusing particles approach one another to within interatomic distance. In this case the particle must inevitably pass through a region in which, by virtue of the interaction between the particles, the level shift $|\delta\varepsilon|\gg\Delta$. Clearly, as the particles come closer the local diffusion coefficient will decrease strongly. However, after a certain critical distance $r_*$ is reached, when the level shift $\delta\varepsilon(r_*)$ exceeds a certain critical value, the leading role is assumed by one-phonon interaction. The latter, however, is characterized by an increase of $D$ with increasing $\delta\varepsilon$, meaning acceleration of the diffusion

0038-5646/83/020459-11$04.00

in the region $r < r_*$. It turns out as a result that the kinetics is determined by the rate of passage through the critical radius $r_*$, a rate proportional to $D(r_*)$. According to the results above, at low temperature this diffusion coefficient increases with increasing $T$. The theory of such a process, which establishes in particular the temperature dependence of the kinetics in this case, is developed in Sec. 5 of the present article. Recently (see Ref. 6), quantum below-barrier diffusion of atomic hydrogen in a matrix of molecular hydrogen, with a power-law increase with increasing temperature, was observed for the first time. The kinetics of recombination of atomic hydrogen was experimentally investigated in the case when the limiting process is just the diffusion occurring when the particles come close together.

A special role is played in the problem of quantum diffusion by the interaction of the diffusing particles with one another. By virtue of the smallness of $\Delta$, even at low particle density conditions are realized when the interaction at an average distance exceeds $\Delta$. In the case of random particle distribution, a level-shift picture is produced similar to that in the case of point defects, and the band character of the motion of the individual particles is suppressed. As a consequence, in a defect-free crystal strong localization takes place as $T \to 0$ at a certain particle density $x_p^c$. The possibility of collective effects does not negate this statement, since the transition amplitude for a cluster of $n$ particles inevitably contains the individual-particle overlap integral raised to the power $n$. The elimination of the localization on account of interaction with phonons should lead in this case to a sharp increase of the diffusion coefficient with increasing temperature (see Ref. 5). This problem is analyzed in detail in Sec. 4, with a solid solution of $He^3$ in $He^4$ as an example. In a just-published paper by Mikheev and co-workers[7] are cited results that demonstrate for the first time the localization of $He^3$ at $x_p \gtrsim 4\%$ and the $D \sim T^9$ dependence predicted earlier in Ref. 5.

Many aspects of quantum diffusion in irregular crystals were clearly revealed recently in experiments on depolarization of $\mu^+$ mesons in matter (see, e.g., Refs. 8, 9 and 10). The comparatively small mass of the particles made it possible to observe quantum diffusion in metallic matrices with large potential barriers (Coulomb interaction) and to observe the manifestation of both localization and motion under conditions of strong static and dynamic level shifts and finally, pure band motion. We shall not discuss these experiments in the present article. A partial analysis can be found in Ref. 5.

## 2. COLLISION MATRIX

In the eigenfunction representation of the particle Hamiltonian

$$\hat{H}|m\rangle = \varepsilon_m |m\rangle \tag{2.1}$$

the particle motion is described by the kinetic equation for the particle density matrix

$$f_{mn} = \mathrm{Sp}\, \rho \hat{a}_n{}^+ \hat{a}_m,$$

which takes the form

$$\frac{\partial}{\partial t} f_{mn} + i(\varepsilon_m - \varepsilon_n) f_{mn} = -J_{mn}, \tag{2.2}$$

in which the "collision matrix" is a linear functional, nonlocal in time, of $\hat{f}$ (see, e.g., Refs. 2 and 11):

$$J_{mn} = \mathrm{Sp}_0 \left\{ [\hat{a}_n{}^+ \hat{a}_m, \hat{V}] \int_0^t d\tau e^{-i\hat{H}_0\tau} [\hat{V}, \hat{f}(t-\tau)\hat{\rho}_{\mathrm{ph}}] e^{i\hat{H}_0\tau} \right\}. \tag{2.3}$$

Here $\hat{H}_0 = \hat{H} + \hat{H}_{\mathrm{ph}}, \hat{\rho}_{\mathrm{ph}} \sim \exp(-\beta \hat{H}_{\mathrm{ph}}), \beta = 1/T$; the index ph pertains to the phonon subsystem; the summation $\mathrm{Sp}_0$ extends over all the states of the Hamiltonian $\hat{H}_0$. Here and elsewhere $\hbar = 1$.

The interaction $V$ of the particle with the phonons, after separating the polaron effect (which can be taken into account in the definition of the parameters of the particle Hamiltonian) is assumed weak, and it is this which enables us to confine ourselves in the collision matrix (2.3) to an approximation quadratic in $V$. We retain in the expression for $V$ only the one-phonon and two-phonon interactions. It is convenient then to write the one-phonon interaction in the form

$$\hat{V}_{\mathrm{I}} = \sum_q \hat{A}_{\mathrm{I}}{}^q \hat{B}_{\mathrm{I}}{}^q, \tag{2.4}$$

$$\hat{A}_{\mathrm{I}}{}^q = \sum_{mn} \hat{a}_m{}^+ A_{mn}{}^q \hat{a}_n, \quad \hat{B}_{\mathrm{I}}{}^q = (\omega_q \omega_D / N_0)^{1/2} (\hat{b}_q + \hat{b}_{-q}{}^+), \quad q \equiv \mathbf{k}, s, \tag{2.5}$$

where $\omega_D$ is the limiting frequency, $N_0$ is the number of sites in the lattice, $\mathbf{k}$ is the phonon momentum, and $s$ is its polarization. The two-phonon interaction is written in similar form, but

$$\hat{B}_{\mathrm{II}}{}^q = {}^1/_2 (\omega_{q_1} \omega_{q_2})^{1/2} N_0^{-1} (\hat{b}_{q_1} + \hat{b}_{-q_1}{}^+)(\hat{b}_{q_2} + \hat{b}_{-q_2}{}^+), \quad q \equiv q_1, q_2. \tag{2.6}$$

The integral with respect to time in (2.3) converges on the interval $\Delta\tau = \beta$. The density remains practically unchanged over such times. Neglecting the retardation in (2.3) and integrating with respect to time we obtain

$$J_{mn} = \sum_{PQ} \pi\delta(E_P - E_Q) [\hat{a}_n{}^+ \hat{a}_m, \hat{V}]_{PQ} [\hat{V}, \hat{f}(t) \hat{\rho}_{\mathrm{ph}}]_{QP}. \tag{2.7}$$

Here $P$ and $Q$ number the states of the Hamiltonian $\hat{H}_0$. We have left out the terms that contain integration in the sense of the principal value; these terms reduce to a renormalization of the particle energy. By writing the interaction in the form (2.4) we are able to sum in (2.7) over the states of the phonon subsystem. Introducing the notation

$$M^q(E) = \sum_{\alpha\alpha'} (\rho_{\mathrm{ph}})_{\alpha\alpha} |B^q_{\alpha\alpha'}|^2 \pi\delta(E_\alpha - E_{\alpha'} + E), \tag{2.8}$$

we reduce the collision matrix (2.7) to the form

$$J_{mn} = \sum_{qm'n'} [\hat{a}_n{}^+ \hat{a}_m, \hat{A}^q]_{m'n'}$$

$$\times \{ (\hat{A}^{-q} \hat{f})_{n'm'} M^q(\varepsilon_{m'n'}) - (\hat{f} \hat{A}^{-q})_{n'm'} M^q(\varepsilon_{n'm'}) \}, \tag{2.9}$$

where $\varepsilon_{mn} = \varepsilon_m - \varepsilon_n$. All the elements of the matrix (2.9), including the off-diagonal ones, vanish for the equilibrium distribution $f_{mn} \propto \delta_{mn} \exp(-\beta \varepsilon_m)$. This can be easily verified by using the detailed-balancing principle

$$M^q(-E) = M^q(E) e^{-\beta E}. \tag{2.10}$$

The diagonal element of the matrix (2.9) goes over into the usual collision integral in the particular case when the density matrix is diagonal, i.e., $f_{mn} = \delta_{mn} f_m$:

$$J_{mm}=\sum_n \{f_m W_{mn}-f_n W_{nm}\}, \qquad W_{mn}=2\sum_q |A_{mn}{}^q|^2 M^q(\varepsilon_{mn}). \tag{2.11}$$

The collision matrix takes the form (2.11) only in the eigenfunction representation (2.1). It is more convenient, however, to describe the particle diffusion through an irregular crystal in the site representation $|\mathbf{r})$, in which the coordinate $\mathbf{r}$ has a direct physical meaning and in which such concepts as tunneling and the intra- and intersite interactions $A^q_{\mathbf{rr}}$ and $A^q_{rr'}$ with the phonons are distinctly defined. In the site representation the particle Hamiltonian is

$$\hat{H}=\sum_{\mathbf{r}} \varepsilon_{\mathbf{r}} \hat{a}_{\mathbf{r}}{}^{+}\hat{a}_{\mathbf{r}}+\sum_{\mathbf{rr}'} h_{\mathbf{rr}'}\hat{a}_{\mathbf{r}}{}^{+}\hat{a}_{\mathbf{r}'}, \tag{2.12}$$

where $\varepsilon_{\mathbf{r}}$ is the ground-state energy of a particle in a potential well with center at the crystal lattice site $\mathbf{r}$ and $h_{\mathbf{rr}'}$ is the amplitude particle tunneling from the state $|\mathbf{r}')$ to the state $|\mathbf{r})$. We neglect the excited states of the particles in the potential wells, and regard the states $|\mathbf{r})$ as orthonormalized:

$$(\mathbf{r}|\mathbf{r}')=\delta_{\mathbf{rr}'}.$$

We assume that the amplitude $h_{\mathbf{rr}'}$ differs from zero only for a jump into the nearest neighboring wells, and does not depend on the location of the site $r$ at an arbitrary configuration of the particles and of the defects

$$h_{\mathbf{r},\,\mathbf{r}+\mathbf{g}}=\Delta_0\delta_{|\mathbf{g}|,\,a}, \qquad \Delta_0{}^*=\Delta_0. \tag{2.13}$$

Here and elsewhere a cubic symmetry of the crystal is assumed for simplicity.

In this model, the irregularity of the crystal reduces only to a dependence of the energy $\varepsilon_r$ on the particle position.

The basic interaction of the particle with the phonons is that part of the interaction $\hat{V}$ (2.4) which is independent of the overlap integral, is diagonal in the site number, and is responsible for the shaking of the level. In this case

$$(\mathbf{r}|A^q|\mathbf{r}')=A^q(0)e^{i\mathbf{qr}}\delta_{\mathbf{rr}'}, \tag{2.14}$$

where $q = \mathbf{k}$ for one-phonon processes and $q = \mathbf{k}_1 + \mathbf{k}_2$ for two-phonon processes. We assume that the amplitude $A_q(0)$ does not depend on the number of the site. The part of the interaction $A^q_{\mathbf{rr}'}$ ($\mathbf{r}\neq\mathbf{r}'$) that is not diagonal in the sites leads to a noncoherent hopping $\mathbf{r}'\to\mathbf{r}$ of the particle. This process will be considered at the end of this section.

An expression for the collision matrix in the site representation can be obtained directly from (2.9) when

$$T\gg\Delta,\,\delta\varepsilon, \qquad \Delta=z\Delta_0 \tag{2.15}$$

($\delta\varepsilon$ is the scale of the level shift in neighboring sites and $z$ is the number of nearest neighbors) at an arbitrary relation between $\Delta$ and $\delta\varepsilon$. In this case the function (2.8) is equal to

$$M^q(E)=M^q(0)\,(1+{}^1\!/_2\beta E) \tag{2.16}$$

and, substituting (2.16) and (2.14) in (2.9) we get

$$J_{\mathbf{rr}'}=\sum_q M^q(0)\,\mathrm{Sp}\{[\hat{a}_{\mathbf{r}'}{}^{+}\hat{a}_{\mathbf{r}},\hat{A}^q][\hat{A}^{-q},f]\}$$

$$+\frac{1}{2}\beta\sum_q M^q(0)\,\mathrm{Sp}\{[\hat{H},[\hat{a}_{\mathbf{r}'}{}^{+}\hat{a}_{\mathbf{r}},\hat{A}^q]](\hat{A}^{-q}\hat{f}+\hat{f}\hat{A}^{-q})\}. \tag{2.17}$$

The trace (Sp) denotes here summation over the particle states. Since the trace of the matrix is independent of the choice of the representation, this summation can be carried out in the site representation:

$$J_{\mathbf{rr}'}=\Omega_{\mathbf{rr}'}(0)\,\{f_{\mathbf{rr}'}+{}^1\!/_2\beta h_{\mathbf{rr}'}(f_{\mathbf{r}}+f_{\mathbf{r}'})\}, \tag{2.18}$$

where

$$\Omega_{\mathbf{r},\mathbf{r}+\mathbf{g}}(E)=2|A^q(0)|^2\sum_q M^q(E)\,(1-e^{i\mathbf{qg}}). \tag{2.19}$$

In the calculation of the second term of (2.17) we have left out corrections that contain off-diagonal density-matrix elements, inasmuch as generally speaking $f_{\mathbf{rr}'} \propto (\Delta_0)^n$, where $n$ is the number of the coordination sphere corresponding to the difference $\mathbf{r} - \mathbf{r}'$.

If the inequality (2.15) is violated so that the expansion (2.16) can no longer be used, the matrix $J_{\mathbf{rr}'}$ is equivalent to the general expression (2.9) in which the projection operator $\hat{a}_n^+\hat{a}_m$ is replaced by the operator $\hat{a}_{\mathbf{r}'}^+\hat{a}_{\mathbf{r}}$, and the summation must be carried out in the representation of the eigenfunctions of the Hamiltonian (2.12). In the general case, the latter are unknown.

In the most important case, however, of a strongly inhomogeneous crystal, when

$$\delta\varepsilon\gg\Delta, \tag{2.20}$$

the eigenfunctions of the Hamiltonian (2.12) have the site nomenclature and are equal to

$$|\mathbf{r}\rangle=|\mathbf{r})+\sideset{}{'}\sum_{\mathbf{r}'}|\mathbf{r}')H_{\mathbf{r}'\mathbf{r}}, \qquad H_{\mathbf{r}'\mathbf{r}}\equiv h_{\mathbf{r}'\mathbf{r}}/\varepsilon_{\mathbf{r}'\mathbf{r}}. \tag{2.21}$$

Using (2.20) we can transform in the matrix $J_{\mathbf{rr}'}$, in the approximation linear in $\Delta_0$, to summation over the site states, if it is recognized that in this approximation the eigenvalues of (2.12) remain unchanged, and the matrix elements in the eigenfunction representation (2.21) are connected with the matrix elements in the site representation by the relation

$$\langle\mathbf{r}|X|\mathbf{r}'\rangle=(\mathbf{r}|X|\mathbf{r}')+(\mathbf{r}|[H',X]|\mathbf{r}'). \tag{2.22}$$

Substituting this expansion in (2.9), we obtain

$$J_{\mathbf{rr}'}=J^{(0)}_{\mathbf{rr}'}+J^{(a)}_{\mathbf{rr}'}+J^{(b)}_{\mathbf{rr}'}, \tag{2.23}$$

where

$$J^{(0)}_{\mathbf{rr}'}=\sum_{qmn}[\hat{a}_{\mathbf{r}'}{}^{+}\hat{a}_{\mathbf{r}},\hat{A}^q]_{mn}\{(\hat{A}^{-q}\hat{f})_{nm}M(\varepsilon_{mn})-(\hat{f}\hat{A}^{-q})_{nm}M(\varepsilon_{nm})\},$$

$$J^{(a)}_{\mathbf{rr}'}=\sum_{qmn}[H',[\hat{a}_{\mathbf{r}'}{}^{+}\hat{a}_{\mathbf{r}},\hat{A}^q]]_{mn}$$

$$\times\{(\hat{A}^{-q}\hat{f})_{nm}M(\varepsilon_{mn})-(\hat{f}\hat{A}^{-q})_{nm}M(\varepsilon_{nm})\},$$

$$J^{(b)}_{\mathbf{rr}'}=\sum_{qmn}[\hat{a}_{\mathbf{r}'}{}^{+}\hat{a}_{\mathbf{r}},\hat{A}^q]_{mn}$$

$$\times\{[H',\hat{A}^{-q}\hat{f}]_{mn}M(\varepsilon_{mn})-[H',\hat{f}\hat{A}^{-q}]_{nm}M(\varepsilon_{nm})\}.$$

We emphasize that all the matrix elements in these expressions correspond to the site representation. The formula for $J^{(a)}$ [or $J^{(b)}$] is the result of the correction (2.22) to the first (or second) factor in $J(0)$.

For the intra-site interaction (2.14) of a particle with phonons, $J^{(0)}$, $J^{(a)}$, and $J^{(b)}$ are equal to

$$J_{\mathbf{r}\mathbf{r}'}^{(0)}={}^1/_2[\Omega(\varepsilon_{\mathbf{r}\mathbf{r}'})+\Omega(\varepsilon_{\mathbf{r}'\mathbf{r}})]f_{\mathbf{r}\mathbf{r}'},\qquad J_{\mathbf{r}\mathbf{r}'}^{(a)}=0,$$
$$J_{\mathbf{r}\mathbf{r}'}^{(b)}={}^1/_2H'_{\mathbf{r}\mathbf{r}'}[\Omega(\varepsilon_{\mathbf{r}\mathbf{r}'})-\Omega(\varepsilon_{\mathbf{r}'\mathbf{r}})](f_{\mathbf{r}}+f_{\mathbf{r}'}).\tag{2.24}$$

In the course of the calculation of the corrections $J^{(a)}$ and $J^{(b)}$, only the diagonal density-matrix elements were retained. The subscripts of the functions $\Omega_{\mathbf{r}\mathbf{r}'}(\varepsilon_{\mathbf{r}\mathbf{r}'})$ were left out for brevity.

It is important that at $T\gg\delta\varepsilon$ the matrix (2.23),(2.24) goes over into (2.18).

Thus, expressions (2.23),(2.24) are applicable in a much wider range than that defined by the inequality (2.20). This range remains valid also when (2.20) is violated, provided that the inequality (2.15) holds.

We now take into account the contribution made to the collision matrix by the noncoherent hops of the particle from site to site in the course of the interaction of the particle with the phonons:

$$(\mathbf{r}|\hat{A}^q|\mathbf{r}+\mathbf{g})=A^q(\mathbf{g})e^{i\mathbf{q}\mathbf{r}},\qquad A^q(\mathbf{g})\approx\Delta_0/\omega_D,\qquad|\mathbf{g}|=a.\tag{2.25}$$

Since this amplitude is proportional to the overlap integral, it suffices to calculate its contribution to the diagonal element $J_{\mathbf{r}\mathbf{r}'}$, with account taken of only the diagonal part of the density matrix. The answer is given by Eq. (2.11), in which the indices $m$ and $n$ should be taken to mean the site representation:

$$J_{\mathbf{r}\mathbf{r}}^{(\mathrm{incoh})}=\sum_q\{f_{\mathbf{r}}\gamma(\varepsilon_{\mathbf{r},\mathbf{r}+\mathbf{g}})-f_{\mathbf{r}+\mathbf{g}}\gamma(\varepsilon_{\mathbf{r}+\mathbf{g},\mathbf{r}})\},\tag{2.26}$$

where

$$\gamma(\varepsilon_{\mathbf{r},\mathbf{r}+\mathbf{g}})=\sum_q|A^q(\mathbf{g})|^2M^q(\varepsilon_{\mathbf{r},\mathbf{r}+\mathbf{g}}).\tag{2.27}$$

## 3. QUANTUM-DIFFUSION EQUATION

The kinetic equation (2.2) takes in the site representation the form

$$\frac{\partial}{\partial t}f_{\mathbf{r}\mathbf{r}'}+i\varepsilon_{\mathbf{r}\mathbf{r}'}f_{\mathbf{r}\mathbf{r}'}+i[h,f]_{\mathbf{r}\mathbf{r}'}=-J_{\mathbf{r}\mathbf{r}'}.\tag{3.1}$$

We write down in explicit form the equations for $f_{\mathbf{r}}$ and $f_{\mathbf{r},\mathbf{r}+\mathbf{g}}$ ($\mathbf{g}$ is the distance to one of the nearest neighbors), using the explicit collision integral in the form (2.24),(2.26)

$$\frac{\partial f_{\mathbf{r}}}{\partial t}+2\sum_{\mathbf{g}}\mathrm{Im}(f_{\mathbf{r},\mathbf{r}+\mathbf{g}}h_{\mathbf{r}+\mathbf{g},\mathbf{r}})=-J_{\mathbf{r}\mathbf{r}}^{(\mathrm{incoh})},\tag{3.2}$$

$$\frac{\partial}{\partial t}f_{\mathbf{r},\mathbf{r}+\mathbf{g}}+i\varepsilon_{\mathbf{r},\mathbf{r}+\mathbf{g}}f_{\mathbf{r},\mathbf{r}+\mathbf{g}}+ih_{\mathbf{r},\mathbf{r}+\mathbf{g}}(f_{\mathbf{r}+\mathbf{g}}-f_{\mathbf{r}})$$
$$+{}^1/_2[\Omega(\varepsilon_{\mathbf{r},\mathbf{r}+\mathbf{g}})+\Omega(\varepsilon_{\mathbf{r}+\mathbf{g},\mathbf{r}})]f_{\mathbf{r},\mathbf{r}+\mathbf{g}}$$
$$+{}^1/_2H'_{\mathbf{r},\mathbf{r}+\mathbf{g}}[\Omega(\varepsilon_{\mathbf{r},\mathbf{r}+\mathbf{g}})-\Omega(\varepsilon_{\mathbf{r}+\mathbf{g},\mathbf{r}})](f_{\mathbf{r}}+f_{\mathbf{r}+\mathbf{g}})=0.\tag{3.3}$$

We have left out of (3.3) the term

$$i\sum_{\mathbf{g}'\neq\mathbf{g}}(h_{\mathbf{r},\mathbf{r}+\mathbf{g}'}f_{\mathbf{r}+\mathbf{g}',\mathbf{r}+\mathbf{g}}-f_{\mathbf{r},\mathbf{r}+\mathbf{g}'}h_{\mathbf{r}+\mathbf{g}',\mathbf{r}+\mathbf{g}}).\tag{3.4}$$

This is certainly justified if one of the following inequalities holds:

$$\Delta\ll\delta\varepsilon,\qquad\Delta\ll\Omega.\tag{3.5}$$

After a time of the order of $\Omega^{-1}$ the element $f_{\mathbf{r},\mathbf{r}+\mathbf{g}}$ relaxes to its quasistationary value that is adiabatically attuned to the values of the diagonal elements:

$$f_{\mathbf{r},\mathbf{r}+\mathbf{g}}=\frac{h_{\mathbf{r},\mathbf{r}+\mathbf{g}}}{\bar\Omega+i\varepsilon_{\mathbf{r},\mathbf{r}+\mathbf{g}}}\{i(f_{\mathbf{r}}-f_{\mathbf{r}+\mathbf{g}})-(2\varepsilon_{\mathbf{r},\mathbf{r}+\mathbf{g}})^{-1}$$
$$\times[\Omega(\varepsilon_{\mathbf{r},\mathbf{r}+\mathbf{g}})-\Omega(\varepsilon_{\mathbf{r}+\mathbf{g},\mathbf{r}})](f_{\mathbf{r}}+f_{\mathbf{r}+\mathbf{g}})\},$$

where $\bar\Omega=\frac{1}{2}[\Omega(\varepsilon_{\mathbf{r},\mathbf{r}+\mathbf{g}})+\Omega(\varepsilon_{\mathbf{r}+\mathbf{g},\mathbf{r}})]$. Substituting this expression in (3.2) we obtain the diffusion equation

$$\frac{\partial f_{\mathbf{r}}}{\partial t}+\sum_{\mathbf{g}}(f_{\mathbf{r}}W_{\mathbf{r},\mathbf{r}+\mathbf{g}}-f_{\mathbf{r}+\mathbf{g}}W_{\mathbf{r}+\mathbf{g},\mathbf{r}})=0.\tag{3.6}$$

Here

$$W_{\mathbf{r},\mathbf{r}+\mathbf{g}}=\frac{2|h_{\mathbf{r},\mathbf{r}+\mathbf{g}}|^2\Omega(\varepsilon_{\mathbf{r},\mathbf{r}+\mathbf{g}})}{\bar\Omega^2+(\varepsilon_{\mathbf{r},\mathbf{r}+\mathbf{g}})^2}+\gamma(\varepsilon_{\mathbf{r},\mathbf{r}+\mathbf{g}}).\tag{3.7}$$

This probability of the jump $\mathbf{r}\rightarrow\mathbf{r}+\mathbf{g}$ per unit time satisfies the detailed-balancing principle

$$W(-E)=W(E)e^{-\beta E}.\tag{3.8}$$

The first and second terms in (3.7) correspond respectively to coherent and noncoherent diffusion. In the first case the particle tunnels without participation of the phonons, and the inelastic interaction with the phonons takes place in the site wells. In the latter case, conversely, the tunneling itself is accompanied by excitation of the phonon subsystem.

At $\delta\varepsilon=0$, Eq. (3.7) goes over into the known expression of the theory of quantum diffusion in an ideal crystal[2,3]:

$$W=2\Delta_0^2(\Omega_{\mathrm{ph}})^{-1}+\gamma_0,\qquad\Omega_{\mathrm{ph}}=\Omega(\delta\varepsilon=0),\quad\gamma_0=\gamma(\delta\varepsilon=0),\tag{3.9}$$

with the quantity $W=W_{\mathbf{r},\mathbf{r}+\mathbf{g}}$ independent of both $\mathbf{r}$ and of the direction $\mathbf{g}$, and connected with the diffusion coefficient by the formula

$$D={}^1/_6za^2W,\tag{3.10}$$

where $z$ is the number of nearest neighbors. As shown in Refs. 2 and 3, this expression remains valid also when the second inequality of (3.5) is violated, provided that the weaker inequality

$$\Delta(a/L)\ll\Omega\tag{3.11}$$

holds, where $L$ is the scale of the distribution inhomogeneity [as before, it is possible here to discard (3.4)]. Actually the inequality (3.11) means the requirement that the mean free path be small

$$\lambda=a\Delta/\Omega\tag{3.12}$$

compared with $L$.

In a weakly nonideal crystal, when $\delta\varepsilon\ll\Delta$ but $\delta\varepsilon>\Omega_{\mathrm{ph}}$, expression (3.7) is incorrect even if the inequality (3.11) is satisfied. The reason is that by virtue of the quasi-band character of the particle motion the mean free path $\lambda$ is in this case much longer than $a$ and an averaging-out of the random level spread takes place over the scale $\lambda$. All that remains is the scattering effect which is quadratic in $\delta\varepsilon$.

The most direct way of taking this scattering into account is to transfer the second term of (3.1) to the right-hand side and to use the same iteration procedure[2,4] as in the derivation of the collision integral (2.3) due to the interaction with the phonons. The summation over the phonon variables is then replaced by averaging over the random configurations of the level shifts. It is convenient to carry out the direct calculation by changing over to the representation of the Bloch functions $|\mathbf{p}\rangle$. Using the results of Ref. 2 we have, after returning to the site representation

$$J^{\mathrm{im}}_{\mathbf{r},\mathbf{r}+\mathbf{g}}=\Omega_{im}f_{\mathbf{r},\mathbf{r}+\mathbf{g}}. \tag{3.13}$$

Here $\Omega_{\mathrm{im}}$ is the frequency, averaged over the band, of the scattering by the static inhomogeneities of the medium. The frequency of the damping of the off-diagonal elements of the density matrix is now equal to the sum $\Omega = \Omega_{\mathrm{ph}} + \Omega_{\mathrm{im}}$ and the mean free path (3.12) changes correspondingly. If it is assumed that the condition (3.11) is satisfied for the renormalized value of $\Omega$, we can still neglect (3.4) and the diffusion coefficient is given by Eq. (3.10) with

$$W=2\Delta_0^2/(\Omega_{\mathrm{ph}}+\Omega_{\mathrm{im}})+\gamma_0. \tag{3.14}$$

As $T\to0$ this quantity reaches rapidly the static limit

$$W_0=2\Delta_0^2/\Omega_{\mathrm{im}}. \tag{3.15}$$

In the case of point defects we have approximately

$$\Omega_{\mathrm{im}}\approx(a\Delta_0)(x/a^3)\sigma_{\mathrm{eff}}. \tag{3.16}$$

The first factor in this expression is the particle group velocity averaged over the band ($T>\Delta$), and $x$ is the relative density of the impurities. For extremely narrow bands, the effective cross section $\sigma_{\mathrm{eff}}$ is determined in fact by the size $R_0\gg a$ of the region around the defect, where the level shift exceeds the band width $\Delta$ (Ref. 3):

$$\sigma_{\mathrm{eff}}\approx\pi R_0^2,\quad |\varepsilon(R_0)|=\Delta. \tag{3.17}$$

At small values of $\Delta$ the dimensions $R_0$ are set by the most slowly decreasing interaction between the particle and the defect. In the case of point defects this interaction is an elastic-force that yields, at large distances from the defect,

$$|\varepsilon(r)|=u_0(a/r)^3, \tag{3.18}$$

where $u_0 = \varkappa\varepsilon_0$, $\varepsilon_0$ is an energy parameter of the order of the matrix binding energy per atom, and $\varkappa$ is a dimensionless factor proportional to the product of the relative changes of the unit-cell volume due to introduction of a defect and of a diffusing particle into the matrix. It is easily seen that in this case [bearing (3.15)—(3.18) in mind]

$$\Omega_{\mathrm{im}}\propto\Delta_0^{1/3},\quad D_0\propto\Delta_0^{5/3}. \tag{3.19}$$

By virtue of the inequality $R_0\gg a$ spheres of radius $R_0$ begin to overlap already at low defect density. We arrive at a picture that is typical of the percolation problem (see, e.g., Ref. 12): at a certain critical defect density $x^c\ll1$ the coherent band motion is blocked and spatial localization of the particles sets in in regions of limited size. For the law (3.18) we have

$$x^c=\nu(\Delta/u_0), \tag{3.20}$$

where $\nu$ is a numerical factor.

When the critical density is approached from below, the law that follows from (3.10), (3.15), and (3.16)

$$D_0\propto1/x, \tag{3.21}$$

is replaced by the relation

$$D_0\propto(x^c-x)^\sigma, \tag{3.22}$$

which is typical of the critical behavior near a localization point.

So far, we have paid no attention to the sign of the interaction of the particle with the defect. At the same time, in the case of attraction or of alternating-sign attraction (that depends on the direction relative to the crystallographic axes) there will exist in the system, even at $T\to0$, besides the strong elastic scattering, also a channel of weak inelastic scattering that leads to capture by a "trap." (The kinetics of motion towards such a trap is considered in Sec. 5.) The expressions given above then again describe adequately at $x<x^c$ the diffusion motion on a scale of the order of the so-called diffusion length.

In those cases when the level shift $\varepsilon(\mathbf{r})$ has a small-scale character with a correlation length of the order of the atom size, we have for $\Omega_{\mathrm{im}}$ an expression different from (3.16). If $\overline{\delta\varepsilon}$ denotes the mean square level shift, $\Omega_{\mathrm{im}}$ at $\overline{\delta\varepsilon}\ll\Delta$ is described by an expression of the form (3.16) with

$$\sigma_{\mathrm{eff}}\approx a^2(\overline{\delta\varepsilon}/\Delta)^2,\quad x=1. \tag{3.23}$$

In contrast to (3.19) we have then

$$\Omega_{\mathrm{im}}\approx\overline{\delta\varepsilon^2}/z\Delta,\quad D_0\approx{}^1/_3a^2\Delta^3/\overline{\delta\varepsilon^2}\propto\Delta^3. \tag{3.24}$$

When the parameter $\zeta = \overline{\delta\varepsilon}/\Delta$ increases and becomes comparable with unity, the band mechanism of diffusion is destroyed and relation (3.24) does not hold. The classical regime of Anderson localization sets in at a certain $\zeta_c>1$. Near this value, the diffusion coefficient should behave like

$$D_0\propto(\zeta_c-\zeta)^{\sigma'},\quad \zeta<\zeta_c. \tag{3.25}$$

We consider now the temperature dependence of the diffusion coefficient. We determine for this purpose in explicit form of the temperature dependences of $\Omega_{\mathrm{ph}}$ and $\gamma$. In an ideal or a weakly nonideal crystal ($\delta\varepsilon\ll\Delta\ll\omega_D$) only two-phonon interactions of the particle with phonons are possible, inasmuch as for one-phonon processes it is impossible to satisfy simultaneously at $\Delta\ll\omega_D$ the energy and momentum conservation laws in emission (absorption) of one phonon by a particle.

For two-phonon processes, the function (2.8) is equal to

$$M_{\mathrm{II}}^q(E)=\pi N_0^{-2}\omega_1\omega_2(N_1+1)N_2\delta(\omega_1-\omega_2-E),$$

where $N(\omega) = (e^{\beta\omega}-1)^{-1}$. Accordingly, in the Debye model the expressions (2.19) and (2.27) at $E=0$ are equal to

$$\Omega_{\mathrm{II}}(0,T)=10B_c\int_0^{\omega_D}d\omega(\omega/\omega_D)^8N(\omega)(1+N(\omega)), \tag{3.26}$$

$$\gamma_{\mathrm{II}}(0,T)=10B_h(\Delta/\omega_D)^2\int_0^{\omega_D}d\omega(\omega/\omega_D)^6N(\omega)(1+N(\omega)). \tag{3.27}$$

At low temperatures $T<0.1\omega_D$ we have

$$\Omega_{\mathrm{II}}(0,T)\approx10^6B_c\omega_D(T/\omega_D)^9,$$

$$\gamma_{\mathrm{II}}(0,T)\approx10^4B_h\omega_D(\Delta_0/\omega_D)^2(T/\omega_D)^7. \tag{3.28}$$

Here $B_c$ and $B_h$ are constants of the order of unity.

The quantities $\Omega_{\mathrm{II}}(E,T)$ and $\gamma_{\mathrm{II}}(E,T)$ satisfy the detailed-balancing principle. In particular, at $|E|\ll T$ we have

$$\Omega_{\mathrm{II}}(E,T)=\Omega_{\mathrm{II}}(0,T)(1+{}^1/_2\beta E),$$

$$\gamma_{\mathrm{II}}(E,T)=\gamma_{\mathrm{II}}(0,T)(1+{}^1/_2\beta E). \tag{3.29}$$

It follows from (3.14) and (3.27) that in a weakly noni-

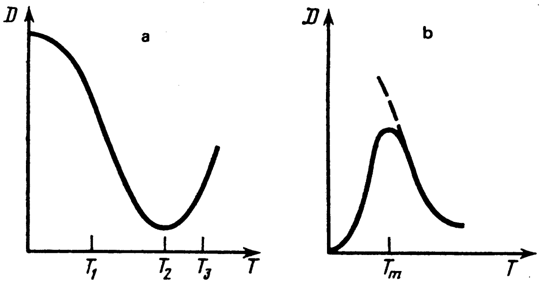

FIG. 1.

deal crystal ($x \ll x_c$ or $\overline{\delta\varepsilon} \ll \Delta$ ), when band motion takes place, the diffusion coefficient decreases with rising temperature from its value (3.15) and rapidly changes to the form[1-3]

$$D \propto T^{-9}. \tag{3.30}$$

By virtue of the small value of $\Delta$, the band character of the particle motion takes place only in a narrow temperature interval

$$T<T_1, \quad \Omega(0, T_1)=\Delta. \tag{3.31}$$

However, as shown in Refs. 2 and 3, this law is in fact preserved in a wide temperature interval also after the dynamic destruction of the band takes place ($\Delta < \Omega, T_1 < T$), see Fig. 1a. Moreover, the character of the coherent-diffusion temperature dependence, determined by the first term of (3.14), remains valid in the entire temperature interval, including temperatures $T \gtrsim \omega_D$.

We note that in an ideal crystal, at extremely low temperatures ($T \ll \Delta$ ) the $T^{-9}$ law gives way to $T^{-7}$ (cf. Ref. 13). This is due to the simple fact that at $T \ll \Delta$ it is necessary to take into account the temperature dependence of the particle velocity.

In the absence of the polaron effect the inequality

$$D^{\text{coh}} > D^{\text{incoh}} \tag{3.32}$$

remains in fact valid all the way to temperatures $T \approx \omega_D$. As a rule, however, at lower temperatures ($T > T_2$) an alternate particle-motion channel opens up and is connected either with classical above-the-barrier diffusion or, as in the case of quantum crystals, with the vacancion diffusion mechanism. In both cases the temperature dependence has (at $T > T_2$) an activation character. This leads to the diffusion-coefficient behavior shown in Fig. 1a.

So far we have considered in fact the problem in the absence of the polaron effect. The presence of a strong polaron effect introduces a temperature-dependent renormalization of $\Delta$ and enhances substantially the role of the incoherent processes (see, e.g., Ref. 3). In particular, even at limited temperatures, $\gamma$ acquires an activation dependence (see Refs. 14 and 3). Under these conditions there can appear two activation regions with different energies ($T < T_3$) and $T_3 < T$ in Fig. 1a).

We consider now the opposite case, when static destruction of the band takes place ($x > x^c$). We assume that the impurity density corresponds to the case of strong localization, when $\delta\varepsilon > \Delta$ for the overwhelming part of the space. Strong localization corresponds in principle to a certain critical density $x^{c'}(x^{c'} > x^c)$. In the case of point defects this density is obtained from the condition that there be an overlap of spheres of radius $R_0'$, defined by the condition[5]

$$a\left|(\partial\varepsilon/\partial r)_{r=R_0'}\right|=\Delta, \quad x^{c'}=\nu'(\Delta/3u_0)^{3/4}, \tag{3.33}$$

where the form of $\varepsilon(r)$ is set by expression (3.18).

In the case of a small-scale spread of the levels, the strong-localization condition coincides in fact with the localization condition

$$\overline{\delta\varepsilon}>\delta\varepsilon_c, \quad \delta\varepsilon_c=\nu''\Delta. \tag{3.34}$$

Under conditions of strong localization, the diffusion coupling of the sites $r$ and $r+g$ is governed by the probability (3.7).

If the level shift is due to point defects separated by distances $l \gg a$, the value of $\delta\varepsilon$ changes little over a distance $\sim a$. This makes it possible in principle to go over in (3.6) to the differential form (at $T \gg \delta\varepsilon$)

$$\frac{\partial f}{\partial t}+\operatorname{div}\mathbf{j}=0, \quad j_\alpha=-D_{\alpha\beta}\frac{\partial f}{\partial r_\beta}+V_\alpha f \tag{3.35}$$

with a local diffusion tensor

$$D_{\alpha\beta}(\mathbf{r})=\sum_{\mathbf{g}} g_\alpha g_\beta\left\{\frac{\Delta_0^2\Omega_{\text{ph}}}{\Omega_{\text{ph}}^2+(\varepsilon_{\mathbf{r},\mathbf{r}+\mathbf{g}})^2}+\frac{1}{2}\gamma\right\} \tag{3.36}$$

and with a "hydrodynamic" velocity

$$V_\alpha=\frac{1}{2}\sum_{\mathbf{g}} g_\alpha(W_{\mathbf{r},\mathbf{r}+\mathbf{g}}-W_{\mathbf{r}+\mathbf{g},\mathbf{r}}). \tag{3.37}$$

We note that the "hydrodynamic" term in the current ensures evolution to thermodynamic equilibrium and has at $T \gg \delta\varepsilon$ little effect on the diffusion process.

To describe particle diffusion over macroscopic distances it is necessary to change from the local tensor $D_{\alpha\beta}$ to the macroscopic diffusion coefficient $D$. The problem of diffusion under conditions of a strong shift reduces in fact to the problem of percolation on a three-dimensional regular grid with diffusion bonds (3.7) distributed in accordance with a definite law. It is clear that, just as in the classical percolation problem, we are interested in the minimum value of $\delta\varepsilon^*$ corresponding to an infinite cluster with $\delta\varepsilon^* \gtrsim |\delta\varepsilon|$.

We consider now the temperature range $\delta\varepsilon^* \ll T \ll \omega_D$. In this region, the incoherent diffusion is small compared with the coherent one, and we shall confine ourselves to an analysis of just the coherent diffusion. The character of the averaging of $D^{\text{coh}}$ depends substantially on the investigated problem. A number of general considerations can be advanced, however, from the very beginning.

The most radical change in the behavior of the diffusion coefficient takes place at sufficiently low temperatures, when $\Omega_{\text{ph}} \ll \delta\varepsilon^*$. In this case, in contrast to (3.9), expression (3.36) yields

$$D_{\alpha\beta}^{\text{coh}} \propto \Omega_{\text{ph}} \propto T^9. \tag{3.38}$$

Obviously, this temperature dependence is directly transferred to the macroscopic diffusion coefficient $D$ regardless of the character of the averaging. In a matrix of cubic symmetry, the macroscopic diffusion coefficient is

$$D^{\text{coh}}={}^1/_3 z a^2\Delta_0^2\Omega_{\text{ph}}/(\delta\varepsilon^*)^2. \tag{3.39}$$

Similarity considerations for the law (3.18) lead to the extremal value

$$\delta\varepsilon^* = \alpha u_0 x^{4/3}. \tag{3.40}$$

In the case of small-scale shifting of the levels

$$\delta\varepsilon^* = \alpha' \overline{\delta\varepsilon}. \tag{3.41}$$

Actually, only the factors $\alpha$ and $\alpha'$ depend on the character of the averaging.

In nonideal crystals, when $\delta\varepsilon \gtrsim \Delta$, not only two-phonon but also one-phonon processes can take place in the formation of $\Omega_{\text{ph}}$. The point is that, in contrast to the band case, under strong level-shift conditions the momentum conservation law no longer imposes any restrictions whatever.

According to (2.8) we have

$$M_{\text{I}}^{q}(E) = \pi \omega_D \omega_q N_0^{-1} [(N_q+1)\delta(\omega_q - E) + N_q \delta(\omega_q + E)]$$

and at $T \ll \omega_D$ the integral (2.19) is given in the Debye model by

$$\Omega_{\text{I}}(E, T) = B_{\text{I}} \omega_D (|E|/\omega_D)^5 [N(|E|) + \Theta(E)]. \tag{3.42}$$

We note that $\Omega_{\text{I}} \ll |E|$ always, and if $|E| < T$, then $\Omega_{\text{I}} \propto TE^4$.

The one-phonon and two-phonon scattering mechanisms make identical contributions to $\Omega_{\text{ph}} = \Omega_{\text{I}} + \Omega_{\text{II}}$ when [cf. (3.28),(3.42)]

$$\delta\varepsilon = \delta\varepsilon_T, \quad \delta\varepsilon_T \approx 30 T^2/\omega_D, \tag{3.43}$$

or

$$T = T_{\delta\varepsilon}, \quad T_{\delta\varepsilon} \approx (\omega_D \delta\varepsilon/30)^{1/2}. \tag{3.44}$$

In a system with a broad distribution of the level shifts, at a given temperature, the hops between sites with level shifts exceeding $\delta\varepsilon_T$ are of the one-phonon type, while those with $\delta\varepsilon < \delta\varepsilon_T$ are of the two-phonon type. Bearing in mind the extremal character of the transport picture, it can be assumed that the diffusion in the crystal is determined by two-phonon processes at $T > T^*$, where $T^* \equiv T_{\delta\varepsilon^*}$, and by one-phonon processes at $T < T^*$.

At $T < T^*$ the temperature dependence of the local diffusion coefficient (3.36) takes in place of (3.38) the linear form

$$D_{\alpha\beta}^{\text{coh}} \propto \Omega_{\text{I}}(\delta\varepsilon, T)/\delta\varepsilon^2 \propto T\delta\varepsilon^2, \tag{3.45}$$

where $\delta\varepsilon = |a\partial\varepsilon/\partial r|$. A fundamental circumstance is that now the diffusion coefficient is proportional to $\delta\varepsilon^2$ and consequently the transport accelerates with increasing level shift. Consequently the diffusion picture changes at $T < T^*$. The particles move primarily towards larger shifts, up to shifts of the order of $|\delta\varepsilon| \approx T$, after which, according to (3.7) and (3.42), the sign of $\varepsilon_{r,r+g}$ becomes significant in $W_{r,r+g}$ and an important role is assumed in the expression (3.35) for the particle flux by the "hydrodynamic" velocity (3.37). Under these condition the diffusion proceeds in different manners, depending on the character of the interaction between the particle and the defects.

If the defects act as repulsion centers, we again encounter in the calculation of the macroscopic diffusion coefficient the problem of percolation of an infinite cluster with $|\delta\varepsilon| > \delta\varepsilon^{**}$, but now already with the maximum permissible $\delta\varepsilon^{**} (\delta\varepsilon^* < \delta\varepsilon^{**} < T)$, so that

$$D \approx {}^1/_3 z a^2 \Delta_0^2 (\delta\varepsilon^{**})^2 T/\omega_D^4. \tag{3.46}$$

With further lowering of the temperature, the value of $\delta\varepsilon^{**}$ joins up with $T$, after which $\delta\varepsilon^{**}$ depends on $T$, and the diffusion coefficient acquires a stronger than linear dependence on the temperature. For motion over large distances at $T < \delta\varepsilon^*$ it is necessary to overcome shifts $\delta\varepsilon < T$, and according to (3.42) the diffusion coefficient should decrease exponentially as $T \to 0$.

A diffusion of an entirely different kind takes place at $T < T^*$ in the case of attraction of the particle to defects. An important role is assumed by the capture of the particles by the defects (see Sec. 5), especially if it is assumed that $T \ll |\delta\varepsilon_{\text{max}}|$, where $\delta\varepsilon_{\text{max}}$ is the shift in the coordination sphere nearest to the defect. Obviously, in this case the diffusion has in this case the usual activation character with an activation energy equal to the energy of binding the particle to the defect.

At $T < T^*$ the one-phonon processes are of decisive significance also in incoherent particle transport, for which a direct calculation of (2.27) in the Debye model yields

$$\gamma_{\text{I}}(E, T) = B_{\text{I}}' \omega_D (\Delta_0/\omega_D)^2 (|E|/\omega_D)^3 [N(|E|) + \Theta(E)]. \tag{3.47}$$

Comparing this value with the first term in (3.36) (we recall that $\Omega_{\text{I}} \ll \delta\varepsilon$), we see that in the case of one-phonon processes the probabilities of coherent and noncoherent hops are of the same order and must be taken into account simultaneously. Since, however, both hopping mechanisms depend exactly in the same way on the temperature (and incidentally on the remaining parameters), allowance for the noncoherent hops reduces in fact to a renormalization of the numerical coefficient in (3.46).

Thus, in a relatively large interval of low temperatures, where two-phonon processes predominate, the interaction with the phonons eliminates the localization and leads to the power-law increase (3.38) of the diffusion coefficient with increasing $T$. In the region of extremely low temperatures, a transition to the one-phonon regime takes place and the diffusion coefficient becomes linearly dependent on the temperature [see (3.46)]. With further decrease of temperature this dependence becomes exponential. If the defect attracts the particle, irreversible capture by the defect becomes significant at sufficiently low $T$.

Conversely, with increasing $T$, when $\Omega_{\text{ph}}(T)$ becomes larger than $\delta\varepsilon$, the dynamic level shift exceeds the static one, and the diffusion coefficient (3.36) acquires the same temperature dependence (3.9) as in a defect-free crystal. Now the diffusion coefficient decreases with increasing temperature like $T^{-9}$ and this dependence has again a universal character. In the intermediate temperature range the diffusion coefficient goes through a maximum (see Fig. 1b) at a temperature $T_m$ determined approximately from the relation

$$\Omega_{\text{II}}(T_m) = \delta\varepsilon^*. \tag{3.48}$$

The position of the maximum changes little with density: $T_m \propto x^{4/27}$, and the maximum value of the diffusion is $D_{\text{max}} \propto x^{-4/3}$. The behavior itself is not universal near the maximum, since the result of the averaging depends on the temperature. In particular, on sections with small $\delta\varepsilon$ the transition from the $T^9$ to the $T^{-9}$ law takes place earlier than on sections with larger $\delta\varepsilon$, and this obviously flattens the $D(T)$ plot in the region of $T_m$. Disregarding this, we can write a general expression for $D$ at $x > x^c$:

$$D \approx \frac{1}{3} za^2 \frac{\Delta_0^2 \Omega_{ph}(T)}{\Omega_{ph}^2(T) + [\delta\varepsilon^*(x)]^2}. \tag{3.49}$$

## 4. LOCALIZATION AND PHONON DELOCALIZATION IN A SYSTEM OF INTERACTING PARTICLES. DIFFUSION OF He$^3$ IN SOLID He$^4$

In systems with extremely small tunneling amplitudes, as is typical of atomic particles, the interaction between particles begins to exceed $\Delta$ at an average distance $\bar{\varepsilon}$ even at quite low densities $x_p$ of the diffusing particles. If the particles are randomly distributed, the picture of the level shift for each individual particle is similar to that in a crystal with point defects. It is clear that, just as in the last case, there should exist a critical density $x_p^c$ above which there is no band motion and localization sets in[5] (see also Ref. 3). The difference is that as $T \to 0$ a thermodynamic-equilibrium state should correspond either to phase decay or to spatial ordering of the particles. For ordering to be absent, however, even temperatures $T \gg \Delta$ (more accurately, $T \gg \bar{\varepsilon}$) are already sufficient, and if the phase-decay temperature is at the same time low enough, we should observe to full degree a picture of quasilocalization ($\Omega(T) \ll \delta$) and phonon delocalization similar to that described in the preceding section.

The most adequate system for revealing such a quasilocalization is a weak solid solution of He$^3$ in He$^4$. In this system, according to Ref. 15, the bandwidth is $\Delta \approx 10^{-4}$ K and the interaction between two He$^3$ atoms is asymptotically described by relation (3.18) with $|u_0| \approx 10^{-2}$ K (see, e.g., Ref. 16). At these values of the parameters the localization condition (3.20) should correspond to a concentration $x_p^c$ of the order of several percent. It is known that at such He$^3$ concentrations the temperature stratification of the phases in a solid solution of He$^3$ in He$^4$ is of the order of tenths of a degree. This means that even at very low temperatures there will be neither ordering nor decay of the phases. Since $T \gg |u_0|$ in this case, all the particle configurations turn out to be practically equiprobable, and the problem of bound-pair production is at the same time totally nonexistent. Thermodynamically speaking, the He$^3$ subsystem will remain a weakly interacting lattice gas also at $x_p > x_p^c$. From the kinetic point of view, however, this system is strongly interacting, a fact predetermined by close-to-critical character of the behavior of this system at $x_p \approx x_p^c$. It must be noted that in the temperature region in question we always have $T_{\delta\varepsilon} \ll T$, where $T_{\delta\varepsilon}$ is defined in accord with (3.44), and the kinetics is determined exactly by two-phonon processes.

At $x_p \ll x_p^c$, in the absence of defects, the motion of the He$^3$ atoms is of the band type. The diffusion coefficient is described then by expressions (3.10) and (3.14), with $x$ in expression (3.16) for $\Omega_{im}$ replaced by $x_p$, and with $R_0$ determined from (3.17) using parameters typical of the interaction of the He$^3$ atoms. The corresponding dependence of the diffusion on $x_p$ and $T$ was observed in Refs. 15, 17, and 18, in which band quantum diffusion of He$^3$ atoms in a solid He$^4$ matrix was observed for the first time, and the initial ideas of the paper by Andreev and Lifshitz[1] were confirmed.

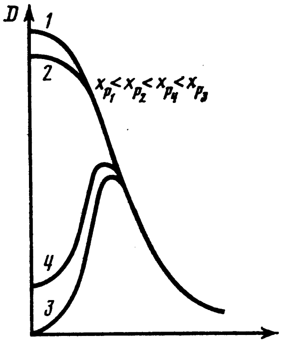

FIG. 2.

At $x_p > x_p^c$ the picture of the quantum diffusion could change radically. In accord with the results of the preceding section, the diffusion coefficient $D$ will obey relations (3.39) and (3.40) with $x \to x_p$ in the large interval $0.2 < T < 1.5$ K, where $\Omega_{ph} \ll \delta\varepsilon_*$ and the activation diffusion still plays a very small role. In place of the rapid decrease with rising temperature in accord with (3.30) (curves 1 and 2 of Fig. 2), an abrupt increase of the diffusion coefficient should be observed

$$D \propto T^9 (x_p)^{-8/3} \tag{4.1}$$

(curve 3 of Fig. 2).

When account is taken of (3.28), practically complete localization takes place on the low-temperature end of the indicated interval of $T$. When the temperature rises above 1.5 K, the diffusion coefficient, after passing through a maximum, goes over into the regime of dynamic band destruction, so that $D \propto T^{-9}$ on the right-hand slope of curve 3. The entire behavior is described by relation (3.49).

Phonon delocalization, however, should manifest itself already when $x_p$ approaches $x_p^c$ from the region of lower concentrations. The point is that when the difference $x_p^c - x$ decreases a sharp decrease of the relative number of the particle configurations $A(x_p)$ that ensure the possibility of long-scale diffusion at $T = 0$ begins in the immediate vicinity of $x_p^c$. At finite $T$, the diffusion for these configurations satisfies Eq. (3.14), but at the same time diffusion sets in for the remaining configurations and is described already by relations of the type (3.49). As a result, the general expression for the diffusion coefficient can be approximately written in the form

$$D^{coh} \approx \frac{1}{3} za^2 \Delta_0^2 \left\{ \frac{Q(x_p)}{\Omega_{ph}(T) + \Omega_{im}(x_p)} + \frac{[1 - Q(x_p)]\Omega_{ph}(T)}{[\Omega_{ph}(T)]^2 + [\delta\varepsilon_*(x_p)]^2} \right\}. \tag{4.2}$$

The function $Q(x_p)$ vanishes at $x_p = x_p^c$, and it is just its behavior which ensures a critical behavior of $D(x_p)$ of the form (3.22) at $T = 0$. With increasing difference $x_p - x_p^c$ the function $Q$ reaches rapidly its limit, equal to unity, and (4.2) goes over into a formula that describes the band motion. At $x_p > x_p^c$ the diffusion coefficient takes on the value (3.49), as it should. It is important that when the dynamic level spread becomes predominant, i.e., at $\Omega_{ph} > \delta\varepsilon_*$, and $\Omega_{ph} > \Omega_{im}$, Eq. (4.2) takes at arbitrary $x_p$ the form (3.9),(3.10) which is typical of the diffusion of isolated particles, a behavior with a

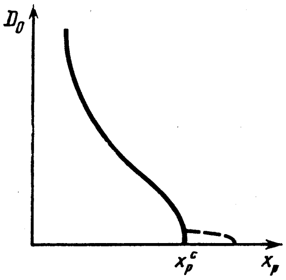

FIG. 3.

lucid physical meaning. Thus, relation (4.2) provides a reasonable description of the coherent quantum diffusion coefficient on the entire plane of the parameters $x_p$ and $T$.

At $x_p$ close to $x_p^c (x_p^c - x_p > 0)$ the dependence of $D^{\mathrm{coh}}$ on $T$, as follows from (4.2), takes the form shown by curve 4 of Fig. 2. It is interesting that with increasing $x_p$ the role of the interaction with the phonons varies continuously even in the subcritical region, from the onset of additional resistance (curves 1 and 2) to the formation of parallel channels of motion (curve 4). Equation (4.2) is least accurate, in all likelihood, when going from one regime of $x_p$ to another. We note that although the second term in (4.2) differs from zero in only a very limited interval $x_p^c - x_p > 0$, the quantity $\alpha$ in relation (3.40) for $\delta\varepsilon_* (x_p)$ is not universal and can vary in this interval. It must be taken into account here, however, that $(\delta\varepsilon_*)_{\min} \approx \Delta$, The reason is that the second term pertains to configurations on which the band character of the motion is suppressed. We note also that in a solid solution of $\mathrm{He}^3$ in $\mathrm{He}^4$ the difference between $x_p^c$ and $x_p^{c'}$ (see the preceding section) is not very pronounced.

The form of the function $Q(x_p)$ can be established from the $D(x_p)$ dependence at $T = 0$. A general form of this dependence is shown in Fig. 3.

The change from the $1/x_p$ law to a sharper decrease with concentration near $x_p^c$ is due to destruction of the band motion on the average and to the progressive decrease of the number of configurations on which the remnants of such a motion are still preserved. In this sense is clear that the plot of $D^{\mathrm{coh}}(T)$ will be close in this case to that of the diffusion coefficient near $x^c$ in the case of level shifts on account of static defects. At the same time one cannot exclude the possibility that in a system of interacting diffusing particles there will remain, in a certain interval $x_p > x_p^c$, a small tail (dashed line in Fig. 3) due to the weakly pronounced effects of the collective motion.

In a just-published interesting paper by Mikheev and co-workers,[7] quasilocalization of $\mathrm{He}^3$ atoms in an $\mathrm{He}^4$ matrix was observed in experiment ($x_p^c \gtrsim 4\%$) and it was confirmed that phonon localization obeys the law (4.1).

## 5. PARTICLE CAPTURE BY A FORCE CENTER. DIFFUSION RECOMBINATION OF ATOMIC HYDROGEN IN AN $H_2$ MATRIX

There exists an entire class of phenomena connected with capture of a particle by a potential center or with the need for particles to approach each other to within interatomic distance. In the latter case one can speak of a chemical reaction in the solid phase, in particular, of recombination at low temperatures, or of formation of cluster states, which are readily detected by methods such as, e.g., NMR. The main feature of such problems is that the particle must inevitably pass through the strong shift produced by the potential center itself. It is physically obvious that the characteristic time of the reaction is determined in such a case by the time of passage through the strong shift. Therefore, when considering the kinetics of the falling on the center, it is possible to disregard the time of meander of the particle far from the force center (trap) and, on the other hand, one can study the kinetics of falling on an individual center without considering the remaining centers.

We assume for simplicity that the potential $\varepsilon(r)$ produced by the trap is spherically symmetrical. At large distances from the center there is always a slowly varying part of the potential, connected with the deformation field (3.18). At close distances an important role is played by direct interaction of the particle with the center. The small value of $\Delta$, typical of motion of atomic particles in a crystal, makes the particle to subject to the conditions of a strong shift of the levels $\delta\varepsilon > \Delta$ even at large distances from the center. At $T > T_{\delta\varepsilon}$ [Eq. (3.44)] the motion in this region is determined by two-phonon processes and is described by the local hopping probability (3.7) with $\Omega_{\mathrm{II}}$ determined in accord with (3.28). On moving to the center at low $T$, the condition $\delta\varepsilon \gg \Omega_{\mathrm{II}}$ is realized rapidly and

$$W_{\mathbf{r},\, \mathbf{r}+\mathbf{g}} \approx 2\Delta_0^2 \Omega_{\mathrm{II}} / (\varepsilon_{\mathbf{r},\, \mathbf{r}+\mathbf{g}})^2. \tag{5.1}$$

This probability decreases sharply with decreasing distance $r$ to the center. Once the shift at a certain distance $r_*$ reaches the value

$$\delta\varepsilon(r_*) \approx 30 T^2/\omega_D, \tag{5.2}$$

the condition $T > T_0$ is violated and the one-phonon interaction becomes decisive.

Replacing in (5.1) $\Omega_{\mathrm{II}}$ by $\Omega_{\mathrm{I}}$ (3.42) we obtain

$$W_{\mathbf{r},\, \mathbf{r}+\mathbf{g}} \approx \Delta_0^2 (\varepsilon_{\mathbf{r},\, \mathbf{r}+\mathbf{g}})^2 T/\omega_D^4. \tag{5.3}$$

It is seen therefore that with further decrease of $r$ the hopping probability increases rapidly. Thus $W(r)$ behaves as shown in Fig. 4a, with a very sharp minimum at the point $r = r_*$. Indeed, if the level spread depends on $r$ like $\delta\varepsilon \propto r^{-n-1} (\varepsilon(r) = u_0 (a/r)^n, n \geqslant 3)$, then

$$W(r) \propto \begin{cases} r^{-2(n+1)}, & r < r_* \\ r^{2(n+1)}, & r > r_* \end{cases}. \tag{5.4}$$

It is physically clear that the kinetics of the falling on

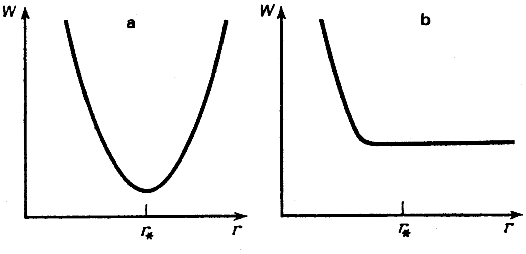

FIG. 4.

the center is actually determined by the time of passage through the bottleneck in the vicinity $r = r_*$, where, in accord with (5.2) and (5.3)

$$W^* \approx 10^3\,\Delta_0^2 T^5/\omega_D^6. \tag{5.5}$$

This expression is valid at sufficiently low temperature, when the inequality $\delta\varepsilon(r_*) < T$ is satisfied (see (5.2)).

When moving in the region $r < r_*$, the particle ends up under conditions of so strong a shift, that $\delta\varepsilon > T$. In this case the subsequent motion depends substantially on the sign $\varepsilon_{r,r+g}$ and in final analysis on the sign of $\varepsilon(r)$. At $\varepsilon(r) < 0$ and $\delta\varepsilon < T$ the probability of a one-phonon hop towards the center ceases to depend on the temperature [see (3.42)] and a really irreversible capture takes place, at a rate limited by expression (5.5). At $\varepsilon(r) > 0$, further motion to the center has an activation dependence on $T$ and the time of capture by the center is determined by the competition between the time of passage through the bottleneck and the activation region.

The character (5.4) of the behavior of $W$ leads in fact to a homogeneous distribution of the particles in the region $r > r_*$. In the case of attraction to the center the gradient of the distribution function is directly concentrated near the bottleneck on a scale that is most frequently of the order of interatomic, and the time of capture by the center can be estimated at

$$1/\tau \approx 4\pi (r_*/a)^2 W^* x_p \propto T^{5-4/(n+1)}, \tag{5.6}$$

where $x_p$ is the relative concentration of the particles. It is always assumed here that $x_p(r_*/a)^3 \ll 1$.

With rise in temperature, the radius $r_*$ increases continuously until $\delta\varepsilon(r_*)$ decreases to a value equal to $\Delta$. This takes place at $T_\Delta \approx 0.1(\omega_D \Delta)^{1/2}$; as before, we have here $\Omega_{\rm ph} \ll \delta\varepsilon(r_*)$ and $\Delta \ll T$. From this instant on, further lowering of $T$ leaves this radius $r_* = r_0$ unchanged—at $r > r_0$ the diffusion remains fast all the time. As a result, a change takes place in the temperature dependence of the reciprocal time of capture by the center:

$$1/\tau \approx 4\pi (r_0/a)^2 \Delta_0^4 T x_p/\omega_D^4, \qquad T < T_\Delta. \tag{5.7}$$

If, conversely, the temperature is raised, an increase of $\delta\varepsilon(r_*)$ (5.2) can cause $r_*$ to decrease to a distance corresponding, for example, to the second coordination sphere. In this case the discrete character of the structure becomes significant, and $r_*$ remains rigidly tied to a definite coordination sphere when $T$ is increased in a certain temperature interval. In this $T$ interval, relation (5.7) will again be valid. Thus, the law (5.6) is replaced on both ends of the low-temperature region by a linear dependence on $T$.

It is of interest to trace the influence of the extraneous defects on the considered process. It is readily understood that if the characteristic scale of the shifts $\delta\varepsilon^{\rm im}$ due to the defects is less than $\delta\varepsilon(r_*)$, all the results remain practically unchanged. If, however $\delta\varepsilon^{\rm im} > \delta\varepsilon(r_*)$, the picture is significantly changed. One-phonon processes now predominate in the entire $r$ interval. We denote by $r_*^{\rm im}$ the value of $r$ obtained from the relation $\delta\varepsilon(r) = \delta\varepsilon^{\rm im}$. Naturally, at $r > r_*^{\rm im}$ the diffusion of the particles is determined in practice by the level shifts on account of the defects. It is easy to imagine (see Fig. 4b) that the limit for capture by the center will be imposed by just the motion in this region, and for the reciprocal capture time we have approximately

$$1/\tau \approx 4\pi (r_*^{\rm im}/a)\,\Delta_0^2 (\delta\varepsilon^{\rm im})^2 T x_p/\omega_D^4 \tag{5.8}$$

(a linear dependence on $r_*^{\rm im}$ rather than a quadratic is due to allowance for the gradient of the particle distribution function near $r_*^{\rm im}$). It is important that in the presence of a random level shift on account of extraneous defects, with $\delta\varepsilon^{\rm im} > \Delta$, lowering the temperature will always cause a transition to a regime described by relation (5.8), and by the same token to a linear dependence on $T$.

The results above, to within a factor of 2, are fully applicable to the case when the force centers are the particles themselves. It follows from these results that at sufficiently low temperatures the reaction between the particles in a solid neutral matrix will be limited by below-barrier diffusion under conditions of a level shift that is due primarily to interaction within an individual pair of reacting particles.

Such a picture was first observed in experiment in Ref. 6, in a study of the recombination of a weak solid solution of atomic hydrogen in a matrix of molecular hydrogen. By investigating the kinetics in such a system with the aid of ESR, the authors have observed that at $T < 4$ K the recombination rate loses its activation character (classical diffusion) and goes over into regime of slow decrease with decreasing $T$. The same authors (to be published) have established later, that the decrease is very close to linear. If it is taken into account that the relative concentration of the hydrogen was $x_p \approx 10^{-3}$ to $10^{-4}$ and that the reaction calls for approach to within interatomic distance (after which it proceeds very rapidly), there is no doubt that the observed characteristic recombination-time scale, $\sim 10^4$ sec, is connected just with the time of approach of the individual particle pairs. It is clear from the foregoing discussion that a linear dependence on $T$ occurs in principle in several cases. If it is assumed that the condition $T < T_\Delta$ holds for the experimental interval 1.5 K $< T <$ 4 K, it is possible, using (5.7), to obtain the estimate $\Delta_0 \approx 0.1$ K, which in turn leads to a noncontradictory estimate of $T_\Delta$. If, however, it is assumed that in this interval of $T$ the radius $r_*$ is practically fixed on the third or second coordination sphere, or that the kinetics is limited by the level shift on account of the defects (in particular, since the matrix is a mixture of ortho- and parahydrogen), we arrive similarly to the estimate $(\Delta_0 \delta\varepsilon)^{1/2} \approx 0.1$ K. In the first case the shift $\delta\varepsilon$ will be of the order of several degrees on account of the direct interaction of the two atoms, and as the lower-bound estimate we have $\Delta_0 \approx 10^{-3}$ K. It is little likely that $\delta\varepsilon^{\rm im}$ can cause a large shift. It can therefore be assumed that actually $\Delta_0$ lies in the interval

$$10^{-3}\ {\rm K} < \Delta_0 < 0.1\ {\rm K}.$$

It is interesting that a direct estimate of the tunnel exponential, which takes into account the obtained values of the activation energy for classical diffusion ($E_A \sim 100$ K, Ref. 6) and the geometry of the crystal matrix, yields values that lie inside this interval.

We note in conclusion that at the obtained scale of $\Delta_0$ a pure band diffusion would yield for the estimate of the recombination time a value smaller by many orders of magnitude than observed in experiment. In this case the experiment reveals very vividly the peculiarities of quantum diffusion in an inhomogeneous system, when the delocalization exists at all only to the extent that there is interaction with phonons.

[1] A. F. Andreev and I. M. Lifshitz, Zh. Eksp. Teor. Fiz. **56**, 2057 (1969) [Sov. Phys. JETP **29**, 1107 (1969)].

[2] Yu. Kagan and L. A. Maksimov, Zh. Eksp. Teor. Fiz. **65**, 622 (1973) [Sov. Phys. JETP **38**, 307 (1974)].

[3] Yu. Kagan and M. I. Klinger, J. Phys. C 7, 2791 (1974).

[4] Yu. Kagan and L. A. Maksimov, Zh. Eksp. Teor. Fiz. **79**, 1363 (1980) [Sov. Phys. JETP **52**, 688 (1980)].

[5] Yu. M. Kagan, Defects in Insulating Crystals, Proc. Intern. Conf., Riga, May, 1981, Springer.

[6] A. Ya. Katunin, I. I. Lukashevich, S. T. Orozmamatov, V. V. Sklyarevskiĭ, V. V. Suraev, V. V. Filippov, N. I. Filippov, and V. A. Shevtsov, Pis'ma Zh. Eksp. Teor. Fiz. **34**, 375 (1981) [JETP Lett. **34**, 357 (1981)].

[7] V. A. Mikheev, V. A. Maĭdanov, and I. P. Mikhin, Fiz. Nizk. Temp. **8**, 1000 (1982) [Sov. J. Low Temp. Phys. **8**, 505 (1982)].

[8] V. G. Grebennik, I. I. Gurevich, V. A. Zhukov, A. I. Klimov, V. N. Maĭorov, A. P. Manych, E. V. Mel'nikov, B. A. Nikol'skiĭ, A. V. Pirogov, A. I. Ponomarev, V. I. Selivanov, and V. A. Suetin, Pis'ma Zh. Eksp. Teor. Fiz. **25**, 322 (1977) [Sov. Lett. **25**, 298 (1077)].

[9] Muon Spin Rotation, Proc. First Intern. Topical Meeting, 1978. Hyperfine Interactions, **6**, Nos. 1–4 (1979).

[10] Muon Spin Rotation, Proc. Second Intern. Topical Meeting, 1980, Hyperfine Interactions **8**, Nos. 4–6 (1981).

[11] C. V. Heer, Statistical Mechanics, Kinetic Theory, and Stochastic Process, Academic, 1972 [Russ. transl. Mir, 1976], p. 491.

[12] B. I. Shklovskiĭ and A. A. Efros, Elektronnye svoistva legirovannykh poluprovodnikov (Electronic Properties of Doped Semiconductors), Nauka 1979.

[13] A. A. Gogolin, Pis'ma Zh. Eksp. Teor. Fiz. **32**, 30 (1980) [JETP Lett. **32**, 28 (1980)].

[14] C. P. Flynn and A. M. Stoneham, Phys. Rev. **B1**, 3966 (1970).

[15] V. A. Mikheev, B. N. Esel'son, V. N. Grigor'ev, and N. P. Mikhin, Fiz. Nizk. Temp. **3**, 385 (1977) [Sov. J. Low Temp. Phys. **3**, 186 (1977)].

[16] V. A. Slyusarev, M. A. Strzhemechnyĭ, and I. A. Burakhovich, Fiz. Nisk. Temp. **3**, 1229 (1977) [Sov. J. Low Temp. **3**, 591 (1977)].

[17] V. N. Grigor'ev, B. N. Esel'son, and B. A. Mikheev, Fiz. Nizk. Temp. **1**, 5 (1975) [Sov. J. Low Temp. Phys. **1**, 1 (1975)].

[18] A. R. Allen and M. G. Richards, Phys. Lett. **65A**, 36 (1978).

Translated by J. G. Adashko