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Quantum diffusion: effect of defect-localized phonon dynamics

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Abstract. The quantum diffusion of lattice defects is considered on the basis of the non-perturbative description of the quadratic defect-lattice coupling. This allows to take explicitly into account the effect of defect-localized phonon dynamics. This effect is especially important in the case of diffusion of vacancies and self-interstitials while a defect displacement to a nearest site is accompanied by a breaking and reconstitution of bonds of nearest atoms. It is shown that the local softening of the lattice by a vacancy due to the breaking of bonds produces an enhancement of the contribution of the low frequency phonons while the local hardening of the lattice by an interstitial atom leads to the opposite effect. As a consequence, at low temperatures the diffusion coefficient of vacancies is much smaller than that of interstitial atoms; the temperature dependences of these coefficients are also different. The obtained results are compared with experimental data for diffusion of vacancies in solid helium.

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1 Introduction

The diffusion of defects in crystals is one of the fundamental dynamical processes in solids. At high temperatures $T \gtrsim T_D$, where T_D is the Debye temperature, diffusion takes place as thermal-activated jumps from site to site; it decreases for decreasing temperature and can be described classically on the basis of the Arrhenius law. At low temperature, however, the classical dynamics is not applicable, and strong deviations from the Arrhenius law are expected because of quantum effects [1].

As shown by Andreev and Lifshitz [2] there exists the cross-over temperature T_0 below which the diffusion coefficient increases for decreasing temperature. The reason of this is the change in the mechanism of the diffusion motion: at $T \ll T_D$ the quantum diffusion occurs as a sequence of tunnelling transitions of a defect between lattice sites and is characterized by the coherence time τ which is large as compared to the mean period of vibrations and increases for decreasing temperature.

One of the basic parameters of the quantum regime of the diffusion is the width ϵ of the energy band of the coherent motion. Usually ϵ is rather small, - much smaller than the characteristic phonon energy of the lattice $\hbar\bar{\omega}$ [2–7]. Another essential characteristic of the quantum diffusion is the rather strong interaction of the defect with phonons. This has the two following important consequences.

a. The value of the band width ϵ for the coherent motion is strongly reduced [4–7]. The main reduction comes from the linear interaction with phonons: due to this interaction, only the zero-phonon transition leads to the coherent tunnelling (i.e., a tunnelling without creation or annihilation of phonons). Usually even at low temperatures $T \ll \hbar\bar{\omega}/k_B$ the reduction factor (Debye-Waller factor) e^{-f} spans many orders of magnitude. With regard to the above-mentioned relationships, we note that there exists one special case, vacancies in He crystals, where due to large amplitude of the zero-phonon motion and a remarkable softening of the lattice around the vacancy the bandwidth ϵ is unusually large and comparable to $\hbar\bar{\omega}$ [8]. However, with account of the Debye-Waller factor $e^{-f} \sim 0.3$ [9], also in this case the renormalized bandwidth $\bar{\epsilon}$ is smaller than $\hbar\bar{\omega}$.

b. The quadratic interaction with phonons causes at non-zero temperature a total switching-off of the zero-phonon tunnelling. This is due to the fact that this interaction yields a vibrational modulation of the energy difference between the initial and final levels [4]. As a result, the quantum diffusion takes place as a phonon-assisted tunnelling (see, e.g. [4–7]), i.e. with the assistance of quasi-elastic scattering of phonons. Therefore the time τ of the coherent motion becomes finite as well as the width $\gamma = 1/\tau$ of the involved energy levels. At low temperatures τ is large (according to Andreev and Lifshitz [2] in the $T \ll T_D$ limit $\tau \propto (T_D/T)^9$, where T_D is the Debye temperature). However, due to the smallness of the tunnelling matrix element $\Delta \sim \epsilon/4$, already at reasonably low temperatures $\Delta < \gamma$. This means that at such temperatures the quantum diffusion can be considered as a

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sequence of non-correlated jumps between nearest neighbor (nn) sites. This situation is known as the dynamical destruction of the band of the coherent motion [4]. The diffusion coefficient in this regime of motion is given by the equation $D = za^2\Delta^2/\gamma$ [2], where a is the shortest distance between two equivalent positions of the defect, z is the number of the nn sites. The main temperature dependence of D at low temperatures comes from that of ϵ and f.

Although the quadratic interaction with phonons plays a key role in the quantum diffusion, till now it was not properly described. The typical assumption which is usually made is that this interaction can be taken into account within the perturbation theory. However, already in some early publications on the subject (see, e.g. [3–7,10–12]) it was pointed out that this assumption may not be correct. This is especially clear in the case of diffusion of vacancies and self-interstitials, where a defect displacement to a nearest site is accompanied by a breaking and reconstitution of bonds. This implies a large perturbation of phonons in the vicinity of a defect – an effect which cannot be treated on the basis of the perturbation theory.

Accounting for the local perturbation of the phonon structure is very important in the theory of quantum diffusion. This especially holds in the case of diffusion of vacancies at low temperatures, when, as a result of the breaking of bonds, low-frequency resonant (pseudo-local) modes may appear. Low frequency phonons play an essential role in the quantum diffusion process, notably in changing the usual very strong temperature dependence $D \propto T^{-9}$ of the diffusion coefficient at low temperatures $T \ll T_D$ to a much weaker one. Moreover, they may be important also at higher temperatures. For example, it was demonstrated by Dick [6] that the presence of a low-frequency resonant mode can extend the range of Arrhenius behavior of diffusion to temperatures substantially lower than those predicted by models which use a phonon spectrum unaltered by the presence of defects.

In this connection, we remind that the T^{-9} temperature dependence of D for $T \ll T_D$ is connected with the T^9 temperature dependence of γ, which is explained as follows. According to the Rayleigh law, the cross-section of the non-resonant scattering of long-wave phonons by a small defect depends on their frequency ω as ω^4, which gives a factor $\propto T^4$. An additional T^2 temperature factor comes from the fact that the long-wave phonons poorly distinguish the difference in the position of a defect jumping from the initial to a nn site. Therefore the scattering cross-section σ, which leads to the phonon-assisted tunnelling, actually depends on ω as $\propto \omega^6$ which gives the factor $\propto T^6$. An additional factor $\propto T^3$ stands for the temperature dependence of the number of phonons at low temperatures. However, as it was already pointed out above, the defect (e.g., vacancy) may cause the appearance of low frequency resonant modes. In these cases the phonon scattering becomes resonant which, as it is shown below, results in the violation of the relation $\sigma \propto \omega^6$ already for $\omega \ll \bar{\omega} \sim k_B T_D/\hbar$ and in a strong change of the temperature dependence.

Here the physical situation is analogous to that of optical transitions in centers. Here we refer to the fact that the role of phonons in quantum diffusion is analogous to that for the zero-phonon electronic transition in an optical center. At low temperatures the probability of the latter transition is determined by the peak intensity of the narrow zero-phonon line $I \propto 1/\gamma_{ZPL}$, where γ_{ZPL} is the width of the line. The broadening mechanism of this line is analogous to that of γ, described above: it is the modulation of the energy of the electronic transition by phonons. However, due to difference of the initial and final states in optical transition, the additional factor $\propto T^2$ is absent. Therefore in crystals in the $T \ll T_D$ and in the weak quadratic coupling limit the width of the line, as a rule, increases (and the intensity decreases) with temperature as $(T/T_D)^7$ (Refs. [13–16]). However, as it was shown in [17–19], if a low frequency resonant mode exists then this temperature dependence is changed to a much weaker one.

In all the quoted investigations of the effects of quadratic interaction on diffusion the standard theory of quantum transitions (based on the Fermi Golden Rule) has been used. The quadratic interaction is taken into account to the second order of perturbation theory, which, as explained above, in many cases is not sufficient. In the classical limit a nonperturbative treatment of this interaction can be done by means of classical molecular dynamics (CMD) simulations [20]. At low temperature these simulations are not possible because the quantum effects become important. However in the case of intermediate temperatures $T \sim T_D$ these effects are moderate, and in some cases can be taken into account only for a limited number of degrees of freedom. For example, in the case of diffusion of a light particle at intermediate temperatures one can take quantum effects for the light particle into account and neglect them for the lattice vibrations. Then, as it was shown in reference [21], one can successfully perform the CMD simulations for the lattice vibrations in combination with the path integral-type description of the quantum motion of the light particle (see, e.g., [22–24]).

At very low temperatures the path-integral-type quantum simulations of diffusion seem to be at present very hard to accomplish. On the other hand, the standard quantum approach based on the calculation of the hopping probability of the defect does not definitely require the assumption of weak quadratic coupling. As shown in the next sections, this approach in the low temperature limit permits to find an exact analytical solution. Besides providing an interpretation to recent measurements of the vacancy diffusion coefficient in solid helium, this result may also constitute a reference for future path-integral simulations of quantum diffusion.

2 Model

We consider a single defect, which can jump from site to site in the lattice. The model we use to describe this motion of the defect has been discussed in a number of papers (see, e.g. [6,7,10]). In this model, as a basis one uses the localized states $|i\rangle$, where i labels a lattice site, which can

be occupied by the defect; these states are not mutually orthogonal: $\langle i|i'\rangle \neq 0$ if $i \neq i'$. In this representation the Hamiltonian of the system reads

$$H = \sum_{ii'} \left[\Delta_{ii'}(1-\delta_{ii'}) + H_i\delta_{ii'}\right]|i\rangle\langle i'|, \qquad (1)$$

where H_i is the Hamiltonian of phonons when the defect occupies the site i, $\Delta_{ii'}$ is the tunnelling Hamiltonian matrix element, which, in principle, may include phonon operators. Note, that one can also use for the basis the Wannier-type localized states, which are mutually orthogonal for the nuclear configuration corresponding to the ideal lattice (see, e.g. [4,5]). We prefer here to use the states $|i\rangle$ as the basis, because this allows one to apply the standard theory of defect lattice dynamics [25].

We take into account the linear and quadratic interaction of the defect with the lattice by expanding H_i into the configurational coordinate vectors of the lattice Q:

$$H_i = H_L + V_iQ + \frac{1}{2}QW_iQ. \qquad (2)$$

Here H_L is the phonon Hamiltonian of the perfect lattice (described in harmonic approximation), V_i is a vector whose elements are the parameters of the linear interaction, W_i is a tensor with the parameters of the quadratic interaction. The coordinates Q can be expressed by $Q = \sum_j e_jx_j$, where x_i are the normal coordinates of the lattice and e_i are polarization vectors. In the case of diffusion of an interstitial the local dynamics is solved with the Green's function method and the fictitious sublattice method [26], where the crystal lattice is enlarged by adding a sub-lattice defined by the interstitial equilibrium positions.

3 Transition rate

As explained above, we restrict ourselves to considering a transition between two nn sites $i = 1, 2$. To calculate the transition rate $\mathcal{P}$, we use the Fermi golden rule. Then (see, e.g. [6,7])

$$\mathcal{P} = 2Re\int_0^\infty F(t)dt,\ F(t) = \left\langle \Delta e^{itH_2}\Delta e^{-itH_1}\right\rangle_1. \qquad (3)$$

Here and below $\langle ...\rangle_i \equiv \mathrm{Tr}\{e^{-H_i/k_BT}...\}/\mathrm{Tr}\{e^{-H_i/k_BT}\}$ indicates the thermal averaging in the i site; we set $\hbar = 1$ (the subscripts $1, 2$ of Δ have been omitted) [27].

3.1 Renormalization of tunnelling matrix element

By applying to H_2 the shift transformation e^{∇} one can exclude the linear term in the transformed operator:

$$e^{\nabla}H_2e^{-\nabla} = H_1 + QWQ/2 \equiv \mathcal{H}_2.$$

Here $W = W_2 - W_1$, ∇ is the linear differential operator with the property $[\nabla, Q] = \mathrm{const}$. Then

$$F(t) = \left\langle \Delta e^{\nabla}e^{-\nabla(t)_2}\Delta(t)_2e^{it\mathcal{H}_2}e^{-itH_1}\right\rangle_1, \qquad (4)$$

where the notation $\nabla(t)_2$ stands for $e^{it\mathcal{H}_2}\nabla e^{-it\mathcal{H}_2}$.

At low temperatures the largest contribution to $\mathcal{P}$ comes from the asymptotic value of $F(t)$ for large time t. In this limit the factors containing the operator ∇ are decoupled:

$$F(t) = \left\langle \Delta e^{\nabla}\right\rangle_1 \left\langle e^{-\nabla(t)_2}\Delta(t)_2\right\rangle_1 \left\langle e^{it\mathcal{H}_2}e^{-itH_1}\right\rangle_1,\ t\to\infty.$$

As shown in [28], in the $t \to \infty$ limit $\langle e^{-\nabla(t)_2}\Delta(t)_2\rangle_1 = \langle e^{-\nabla}\Delta\rangle_2$. Taking into account the existing symmetry with respect to the exchange of $i = 1$ with $i = 2$, we get $\langle e^{-\nabla}\Delta\rangle_2 = \langle e^{-\nabla}\Delta\rangle_1$.

Let us expand Δ with respect to displacements and take into account first three terms: $\Delta = \Delta_0 + \Delta^{'}Q + Q\Delta^{"}Q$. Using the Bloch-DeDominicis theorem on pair correlations, we get $\langle e^{\nabla}\Delta\rangle_1 = \tilde{\Delta}_0e^{-f}$, where e^{-f} is the Debye-Waller factor with $f = -\langle\nabla^2\rangle_1$,

$$\tilde{\Delta}_0 = \Delta_0^{'} + \Delta^{"}\langle Q^2\rangle_1,$$

where $\Delta_0^{'} = \Delta_0 + \Delta^{'}C + \Delta^{"}C^2$; $C = [Q, \nabla]/2$ is a constant vector. Thus, in the large t limit

$$F(t) = \tilde{\Delta}^2\langle e^{it\mathcal{H}_2}e^{-itH_1}\rangle_1, \qquad (5)$$

where $\tilde{\Delta} = \tilde{\Delta}_0e^{-f}$ is the renormalized tunnelling matrix element.

3.2 Quadratic coupling

Let us consider first the last factor in (5), which can be presented in the form (see, e.g. [29])

$$\tilde{F}(t) = \left\langle \hat{T}_- \exp\left[i\int_0^t H'(s)\,ds\right]\right\rangle_1,$$

where $H' = \mathcal{H}_2 - H_1 = (1/2)QWQ$ is the Hamiltonian of the quadratic coupling and $\hat{T}_-$ is negative time ordering operator (the subscript 1 for the time and temperature dependence has been omitted). Usually this factor is calculated using the cumulant expansion with respect to the quadratic coupling, taking into account up to second order terms. This is correct only if this coupling is weak. However, as it was found in [30,31], the $t \to \infty$ asymptotic behavior of this factor can be found also for an arbitrary quadratic coupling. Here we use the formulation of this case as given in reference [18] in connection with the nonperturbative description of the quadratic vibronic coupling in optical transition.

As a first step, we can diagonalize the quadratic form $H' = (1/2)\sum_{mm'}W_{mm'}Q_mQ_{m'}$ by means of a diagonal transformation $Q_m = \sum_l S_{ml}q_l$. We get $H' = (1/2)\sum_l w_lq_l^2$. We can redefine the coordinates q_l so that their pair correlation functions will be orthogonal. This allows one to present $\tilde{F}(t)$ in the form $\tilde{F}(t) = \prod_l \mathcal{F}_l$, where

$$\mathcal{F}_l = \left\langle \hat{T}_- \exp\left\{iw_l\int_0^t q_l^2(s)\,ds\right\}\right\rangle_1.$$

As it was shown in [18] (see also [30,31]) the factor $\mathcal{F}_l$ in the $t \to \infty$ limit gets the form $\mathcal{F}_l(t) = e^{-\gamma_l t}$, where

$$\gamma_l = -\frac{1}{2\pi}\mathrm{Im}\int_0^\infty d\omega \ln\left(1 - w_l d_l(\omega)\right), \tag{6}$$

$$d_l(\omega) = \int_{-\infty}^{\infty} e^{-i\omega t} d_l(t) dt$$

is the Fourier transform of the pair causal correlation function $d_l(t) = i\,\langle \hat{T}_- q_l(t) q_l(0)\rangle_1$.

With consideration of all the configurational coordinates q_l, the factor $1 - w_l D_l(\omega)$ in equation (6) is replaced by $\prod_l \left(1 - w_l d_l(\omega)\right) = |I - WD(\omega)|$, where $|\cdots|$ denotes the determinant of the matrix. In the last equation W and $D(\omega)$ are diagonal matrices with diagonal elements w_l and $d_l(\omega)$. As it is well known, the determinant of a matrix is an invariant which does not change with unitary (orthogonal) transformations of the matrix. This allows one, when calculating the determinant, to use the initial representation. Therefore in the case of an arbitrary number of configurational coordinates, contributing to the quadratic coupling one gets in the large t limit $\mathcal{F}(t) = e^{-\gamma t}$, where

$$\gamma = \frac{1}{2\pi}\int_0^\infty d\omega \ln\left|I - WD(\omega)\right|. \tag{7}$$

Here $W = W_2 - W_1$, the matrix $D(\omega)$ equals [18]

$$D(\omega) = G_1(\omega) + 2in(\omega)\mathrm{Im}G_1(\omega),$$

where

$$G_1(\omega) = \int_{-\infty}^{\infty} e^{-i\omega t} G_1(t) dt$$

is the Fourier transform of the causal Green's function matrix $G_1(t) = \langle 0|\hat{T}_- Q(t) Q(0)|0\rangle_1$ in the lattice perturbed by the defect occupying the site 1, $|0\rangle_1$ is the zero-point state of the perturbed lattice, $n(\omega) = 1/(e^{\hbar\omega/k_B T} - 1)$ is the Bose population factor.

Should one single nearest neighbor be considered, the long-time limit of $\tilde{F}(t)$ would just be $e^{-\gamma t}$. For the actual case of z nearest neighbors the structure of equation (7) suggests that $\tilde{F}(t) = ze^{-\tilde{\gamma} t}$, where $\tilde{\gamma} = z\gamma$, and the diffusion coefficient is given by [2]

$$D = a^2 \tilde{\Delta}^2/\gamma, \tag{8}$$

subject to the condition $\tilde{\Delta} < z\gamma$. In this case the perturbation matrix W accounts only for $i = 1 \to i = 2$ transition of the defect.

3.3 Relation to the Green's function of the perturbed lattice

The Green's function matrix for the defect occupying the site i satisfies the Dyson (Lifshitz) equation (see, e.g. Ref. [25])

$$G_i(\omega) = G^{(0)}(\omega) + G^{(0)}(\omega) W_i G_i(\omega),$$

where $G^{(0)}(\omega)$ is the Fourier transform of the Green's function $G^{(0)}(t)$ of the ideal lattice. Note that G_1 and G_2 also satisfy the Dyson equation

$$G_2(\omega) = G_1(\omega) + G_1(\omega) W G_2(\omega).$$

This gives $[I - WG_1]^{-1} = I + WG_2$. Taking this identity into account and keeping in mind that the indices $i = 1$ and $i = 2$ can be interchanged we get the relations

$$\ln\left|I - WG_1\right| = 0,$$

where $|\cdots|$ denotes the determinant of the matrix. This permits to rewrite equation (7) in the form

$$\gamma = \mathrm{Re}\int_0^\infty \frac{d\omega}{2\pi} \ln\left|I - 2in(\omega)(I + WG_2(\omega)) W \mathrm{Im}G_1(\omega)\right|.$$

At low temperatures only the linear term with respect to $n(\omega)$ may be retained. In this case

$$\gamma \approx \frac{1}{\pi}\int_0^{\omega_M} d\omega\, n(\omega) \mathrm{Tr}\left[W\mathrm{Im}G_2(\omega) W \mathrm{Im}G_1(\omega)\right]. \tag{9}$$

Here ω_M is the maximal phonon frequency. Note that the imaginary parts of the perturbed Green's functions $G_1(\omega)$ and $G_2(\omega)$ in equation (9) are not equal to each other because the local perturbation of phonon spectrum depends on the position of the defect.

4 Diffusion of vacancies

As a first example we consider the diffusion of a vacancy in a simple cubic lattice. The phonon-assisted tunnelling transition takes place to the nearest site in any of the $\langle 100\rangle$ directions. By assuming that only nn central forces are broken at the vacancy site, the essential contribution of phonons to the diffusion process comes from vibrations of 11 atoms – the atom, which jumps into the vacancy site, the 5 atoms surrounding this atom and the 5 atoms surrounding the vacancy. However, as it follows from the consideration of the local dynamics of KCl (where the ion masses are almost equal and vibrational dynamic is close to the simple-cubic lattice) given in [32] (see also below) only a two-fold degenerate mode of E_g symmetry associated with the vacancy has a low frequency resonance. At low temperature only four configurational coordinates are relevant to the quadratic interaction: the two E_g components Q_1 and Q_1' which are linear combinations of central nn atom displacements with respect to the vacancy in the initial position and the two analogous E_g components Q_2 and Q_2' referred to the vacancy in the final (shifted) position.

The configurational coordinate Q_1' is chosen so as to be, in the long-wave limit, orthogonal to Q_2, and similarly Q_2' is chosen to be orthogonal to Q_1. In this way the contributions to the process of the configurational coordinate pairs Q_1, Q_2 and Q_1', Q_2' can be considered independently. In this approximation the contribution of Q_1

and Q_2 to the change of the potential energy due to vacancy jump equals

$$H' = -\frac{1}{2} w \left(Q_1^2 - Q_2^2\right). \tag{10}$$

Then in equation (9) $W = w\sigma_z$, and

$$W\mathrm{Im}G_i = -w \begin{pmatrix} \mathrm{Im}G_{i,11} & \mathrm{Im}G_{i,12} \\ -\mathrm{Im}G_{i,21} & -\mathrm{Im}G_{i,22} \end{pmatrix},$$

where σ_z is the Pauli matrix, $G_{i,nm}$ is the Greens's function associated with the configurational coordinates Q_n and Q_m in the case of the vacancy being in the position i. In the problem under consideration there is the symmetry with respect to change of the numbers of the initial and final sites with simultaneous change of the numbers of the coordinates:

$$G_{1,11} = G_{2,22},\ G_{1,22} = G_{2,11},\ G_{2,12} = G_{1,21}.$$

This allows one to replace the elements of $G_{i=2}$ by the elements of $G_{i=1}$ and then omit the subscript $i = 1$. Then we get

$$\mathrm{Tr}\left[W\mathrm{Im}G_2 W\mathrm{Im}G_1\right] = 2w^2 \left(\mathrm{Im}G_{11}\mathrm{Im}G_{22} - \mathrm{Im}G_{21}^2\right). \tag{11}$$

Applying now the Dyson equation one gets

$$G_{11} = \frac{G_{11}^{(0)}}{1 + wG_{11}^{(0)}}, \quad G_{21} = \frac{G_{21}^{(0)}}{1 + wG_{11}^{(0)}}, \tag{12}$$

$$G_{22} = G_{11} + \frac{w(G_{11}^{(0)\,2} - G_{21}^{(0)\,2})}{1 + wG_{11}^{(0)}}, \tag{13}$$

where $G_{nm}^{(0)}$ are the unperturbed Green's functions associated with the coordinates Q_n and Q_m.

At low temperatures only phonons of low frequencies $\omega \ll \omega_D$ contribute to γ (here $\omega_D = k_B T_D/\hbar$ is the Debye frequency). In this case $\mathrm{Im}G_{21}^{(0)} \approx (1 - \omega^2 a^2/c^2)\mathrm{Im}G_{11}^{(0)}$, where c is the velocity of sound. This gives

$$\mathrm{Im}G_{11}\mathrm{Im}G_{22} - \mathrm{Im}G_{21}^2 \approx 2\chi(\omega a/c)^2 \big(\mathrm{Im}G_{11}(\omega)\big)^2, \tag{14}$$

where $\chi = 1 + wG_{11}^{(0)}(0)$ and

$$\mathrm{Im}G_{11}(\omega) = \frac{\mathrm{Im}G_{11}^{(0)}(\omega)}{\left|1 + wG_{11}^{(0)}(\omega)\right|^2}. \tag{15}$$

The simple-cubic model assumed in the above derivation can be applied to a vacancy in an ionic lattice like KCl (where the ion masses are almost equal) in the nn effective force-constant approximation [32]. By means of the defect Green's functions plotted in reference [32] it is found for KCl that a low-lying resonance of E_g symmetry falls at $\omega_R \approx -\chi[wdG_{11}^{(0)}(0)/d\omega]^{-1} \approx 0.3\omega_D$, corresponding to $\chi \approx 0.17$. (No such resonances of other representations exist in this lattice.) Obviously for $\chi = 0$ a resonance occurs at $\omega = 0$. In general the condition $|\chi| \ll 1$ implies that a vacancy leads to the appearance of a low-frequency peak in $\mathrm{Im}G_{1,nn'}(\omega)$ due to a resonant mode. In the central force approximation the value of this parameter is expected to be of the same order also for other cubic lattices and to lead, for a vacancy, to a low-frequency resonant mode which provides, at low temperatures, the main contribution to quantum diffusion.

In general in 3-dimensional lattices the Green's function $G_{11}^{(0)}$ for E_g modes at small Ω can be expanded as

$$G_{11}^{(0)} \simeq G_{11}^{(0)}(0)\left(1 + \beta\Omega^2 + i\delta\Omega^3\right), \quad \Omega \ll 1, \tag{16}$$

where $\Omega = \omega/\omega_D$, and β and δ are positive dimensionless parameters. In this approximation

$$\mathrm{Im}G_{1,11} = \frac{\delta\Omega^3/\omega_D^2}{\beta^2(1-\chi)^2\left(\alpha + \Omega^2\right)^2}.$$

Typical values of β and δ are between 2 and 6. For example, in the Debye model $\beta = 3$ and $\delta = (\pi/2)\beta$.

From equation (16) one gets for $\Omega \ll 1$

$$\mathrm{Tr}\big[W\mathrm{Im}G_2 W\mathrm{Im}G_1\big] \simeq \frac{4\pi^2\alpha\delta^2(1+\alpha\beta)^2\Omega^8}{\beta^3\left(\alpha + \Omega^2\right)^4}, \tag{17}$$

where $\alpha = \chi/\beta(1-\chi) \ll 1$. Thus for the E_g-mode contributions and for $T \ll T_D$ it is found

$$\gamma \approx \frac{2\pi^3\alpha\omega_D}{3}\int_0^1 \frac{n(\Omega)\Omega^8 d\Omega}{(\alpha + \Omega^2)^4}. \tag{18}$$

where $n(\Omega) = 1/\big(e^{\,\Omega T_D/T} - 1\big)$.

One sees that only at very low temperatures $T \ll \sqrt{\alpha}\,T_D$ one gets the usual low temperature dependence $\gamma \propto T^9$. At intermediate temperatures γ is larger and the T-dependence is weaker as compared to a standard theory which does not take into account the effect of the defect-induced change in the localized phonon dynamics. For $\sqrt{\alpha}\,T_D < T < T_D$ the dependence of γ on T is practically linear.

4.1 Effect of soft vibrations on the tunnelling matrix element

A strong local softening of the lattice leads also to a strong enhancement of the temperature effect on the tunnelling matrix element $\tilde{\Delta} = \tilde{\Delta}_0 e^{-f}$ at low temperatures. It appears that the main temperature dependence of $\tilde{\Delta}$ comes from $\tilde{\Delta}_0$, whereas the temperature dependence of the Debye-Waller factor at low temperatures remains relatively weak.

To show that, we take into account only soft E_g vibrations Q_1, Q_1', Q_2 and Q_2'. Then $f = -2\langle\nabla^2\rangle_1$ is calculated from $\nabla = 2(\nabla_1 - \nabla_2)$, where ∇_i is the logarithm of the shift operator for the relaxation with respect to the ideal

lattice position of the coordinate Q_i induced by the vacancy in the starting position. A simple calculation gives

$$f \propto \int_0^{\omega_D} d\omega (2n(\omega)+1)\mathcal{F}(\omega)/\omega^2,$$

where

$$\mathcal{F}(\omega) = \mathrm{Im}\big[G_{1,11}(\omega) + G_{1,22}(\omega) - 2G_{1,21}(\omega)\big].$$

From equations (12) and (13) it follows, for small ω that

$$\mathcal{F}(\omega) \approx 2\chi\,(\omega a/c)^2 \mathrm{Im}G_{1,11}(\omega).$$

Due to the small factor χ, the contribution of the low-frequency phonons to the Debye-Waller factor f is rather small despite the local softening of the lattice. This is in agreement with [9], where the value of f was found to be of the order 0.3 to 0.4. The temperature dependence of the Debye-Waller factor at low temperatures is also relatively weak.

Let us consider now the temperature dependence of $\tilde{\Delta}_0$. Taking into account the E_g vibrations, one gets

$$\left\langle Q\ddot{\Delta} Q\right\rangle_1 = 2\int_0^{\omega_D} d\omega (2n(\omega)+1)\mathrm{Im}\phi(\omega),$$

where

$$\phi(\omega) = \ddot{\Delta}_{11} G_{11}(\omega) + \ddot{\Delta}_{22} G_{22}(\omega) + 2\ddot{\Delta}_{21} G_{21}(\omega).$$

From the equations (12) and (13) for the Green's functions one finds that for small Ω

$$\mathrm{Im}\phi \approx \frac{\delta\left(\ddot{\Delta}_{11} + \ddot{\Delta}_{22} + 2\ddot{\Delta}_{21}\right)\Omega^3}{\beta^2\omega_D^2(1-\chi)^2\left(\alpha+\Omega^2\right)^2}.$$

One can see that at $T > \alpha T_D$ $\langle Q\Delta Q\rangle_1 \sim T/\sqrt{\alpha}$. For small α this term gives the largest contribution to $\tilde{\Delta}$. Consequently in this case $\tilde{\Delta} \propto T$. As a consequence also $\gamma \propto T$ and therefore the diffusion coefficient $D = \tilde{\Delta}^2 a^2/\gamma$ for $T > \alpha T_D$ depends linearly on T: $D \propto T$. This means that the local softening of the lattice results in a strong decrease of the characteristic cross-over temperature T_0 of the quantum diffusion of vacancies.

5 Diffusion of self-interstitials

As a second example we consider the diffusion of self-interstitials in a fcc lattice. In this case interstitials have cubic symmetry; the nn sites are in (110) and in other 11 equivalent positions. Following [26] we enlarge the crystal lattice by adding a fictitious sublattice containing the sites at the equilibrium positions of interstitials. The sites are considered to be occupied by fictitious atoms whose mass is equal of the interstitial mass and which are completely uncoupled to all the atoms of the lattice. We take into account only nn central forces at the interstitial site. In this case the potential energy change due to the interstitial occupying the fictitious site i reads:

$$\delta U_i = \frac{1}{2} w \sum_\alpha \left[(q_{i0\alpha} - q_{i\alpha})^2 + (q_{i0\alpha} - q_{i-\alpha})^2\right].$$

Here $q_{i0\alpha}$ is the α component of the reduced displacement of the interstitial, $q_{i\alpha}$ and $q_{i-\alpha}$ are the α components of the reduced shifts of the two nn atoms in the positive and negative α direction, $w = v/M$, v is the central elastic spring between the interstitial and an nn atom, M is the mass of the atom.

Let us take into account the relations

$$(q_{i0\alpha} - q_{i\alpha})^2 + (q_{i0\alpha} - q_{i-\alpha})^2 = \tilde{q}_{\alpha i}^2 + 3Q_{i\alpha}^2,$$

$$\sum_\alpha \tilde{q}_{i\alpha}^2 = \sum_j Q_{ij}^2,$$

where $\tilde{q}_{i\alpha} = (q_{i\alpha} - q_{i-\alpha})/\sqrt{2}$, $Q_{i\alpha} = (2q_{i0\alpha} - q_{i\alpha} - q_{i-\alpha})/\sqrt{6}$, $j = 0, 1, 1'$, $Q_{i0} = (\tilde{q}_{ix} + \tilde{q}_y + \tilde{q}_{iz})/\sqrt{3}$, $Q_{i1} = (2\tilde{q}_{ix} - \tilde{q}_{iy} - \tilde{q}_{iz})/\sqrt{6}$ and $Q_{i1'} = (\tilde{q}_{iy} - \tilde{q}_{iz})/\sqrt{2}$. Here the configurational coordinates Q_{ij} in the symmetry operations with respect to the site i transform according to the A_{1g} (Q_{i0}) and E_g (Q_{i1} and $Q_{i1'}$) representations, while the coordinates $Q_{i\alpha}$ transform according to T_{1u} representation. The change of the potential energy by the interstitial can now be presented in the form:

$$\delta U_i = \frac{1}{2} w \left(\sum_j Q_{ij}^2 + 3\sum_\alpha Q_{i\alpha}^2\right).$$

Therefore the change of the potential energy of the lattice due to the jump of the interstitial from the site $i = 1$ to the nearest site $i = 2$ equals

$$H' = \frac{1}{2} w \left[\sum_j \left(Q_{2j}^2 - Q_{1j}^2\right) + 3\sum_\alpha \left(Q_{2\alpha}^2 - Q_{1\alpha}^2\right)\right]. \quad (19)$$

To calculate the Green's functions associated with the coordinates Q_{ij} and $Q_{i\alpha}$, one can use the equations (12) and (13) with w replaced by $-w$ (for Q_{ij}) or by $-3w$ (for $Q_{i\alpha}$).

Here we are interested in the low temperature case when only long-wave phonons contribute to γ. In this limit the reduced displacements of different representations and different rows of the same representation are mutually orthogonal also if they correspond to the nn sites. Therefore the given above description of contribution of the E_g coordinates Q_1 and Q_2 to the diffusion of a vacancy, holds also here for any of pairs of the coordinates Q_{1j}, Q_{2j} and $Q_{1\alpha}$, $Q_{2\alpha}$. Besides, here also one can express all Green's functions only through the Green's functions for the defect in the initial site $i = 1$ and then to omit the subscript i. However, as it follows from the comparison of equations (10) and (19), the value of w is different here: for A_{1g} and E_g coordinates one has w instead of $-w$, for T_{1u} modes

one has $3w$ instead of $-w$. The change of the sign w stands here for the replacement of the local softening of the lattice (due to a vacancy) by the local stiffening (due to an interstitial). Besides, the Green's functions of the coordinates of the T_{1u} representation of the ideal lattice are different, they include the Green's function at the fictitious site.

For A_{1g} and E_g vibrations equation (15) holds, which gives for small ω/ω_D for the Green's function being associated with the coordinate Q_{1j} the following equation:

$$\mathrm{Im}G_{11;j}(\omega) \approx \chi_j^{-1}\mathrm{Im}G^{(0)}_{11;j}(\omega) \propto \omega^3,\ j=0,1,2, \quad (20)$$

where $\chi_j = 1 - w\mathrm{Im}G^{(0)}_{11;j}(0)$. In this case $\chi > 1$ (differently to the vacancy case, when $\chi \ll 1$). This is due to the local hardening of the lattice by the interstitial. From equations (17) and (20), it follows that all three even modes give at low temperatures the following contribution to γ:

$$\gamma \approx \frac{\pi^3\omega_D}{9}\int_0^1 d\Omega n(\Omega)\Omega^8 \sum_{i=0}^{2}\chi_i \sim \omega_D(T/T)^9.$$

Let us consider now contribution of odd (T_{1u}) modes. From Dyson equation it follows that the Green's function associated with the coordinate $Q_{1\alpha}$, equals

$$G_{11;\alpha}(\omega) = \frac{G^{(0)}_{11;\alpha}(\omega)}{1 - 3wG^{(0)}_{11;\alpha}(\omega)},$$

where $G^{(0)}_{11;\alpha}(\omega)$ is the Green's function of the perfect lattice containing the fictitious atoms. Taking into account that fictitious atoms are fully decoupled from all other atoms of the lattice, we get

$$G^{(0)}_{11;\alpha} = \frac{2}{3}\mathcal{G}^{(0)}_{11;\alpha}(\omega) + \frac{1}{3}\tilde{G}^{(0)}_{11;\alpha}(\omega),$$

where $\mathcal{G}^{(0)}_{11;\alpha}(\omega) = \omega^{-2}$ [26] is the Green's function, which corresponds to the coordinate $q_{0\alpha}$ of the fictitious atom, $\tilde{G}^{(0)}_{11;\alpha}(\omega)$ is the Green's function, which corresponds to the symmetrized coordinate $Q_{1\alpha} = (q_{1\alpha} + q_{1-\alpha})/\sqrt{2}$ of the nn atoms in the ideal lattice. The imaginary part of the Green's function $G_{\alpha,11}$ then, equals

$$\mathrm{Im}_{11;\alpha}(\omega) = \frac{\mathrm{Im}\tilde{G}^{(0)}_{11;\alpha}(\omega)}{|1 - 2w/\omega^2 - w\tilde{G}^{(0)}_{11;\alpha}(\omega)|^2}.$$

Analogously one gets the Green's function associated wits the coordinates $Q_{1\alpha}$ and $Q_{2\alpha}$

$$G_{12;\alpha}(\omega) = \frac{\tilde{G}^{(0)}_{12;\alpha}(\omega)}{1 - 2w/\omega^2 - w\tilde{G}^{(0)}_{11;\alpha}(\omega)},$$

$$\mathrm{Im}G_{22;\alpha}(\omega) = \mathrm{Im}G^{(0)}_{11;\alpha}(\omega) - 3w\mathrm{Im}\frac{G^{(0)\,2}_{11;\alpha}(\omega) - G^{(0)\,2}_{12;\alpha}(\omega)}{1 - 3wG^{(0)}_{11;\alpha}(\omega)}.$$

For small ω

$$\mathrm{Im}\tilde{G}^{(0)}_{11;\alpha}(\omega) \approx \omega^4\mathrm{Im}\tilde{G}^{(0)}_{11;\alpha}(\omega)/12w^2 \propto \omega^7;$$

$$\mathrm{Im}G_{12;\alpha}(\omega) \approx -\omega^2\mathrm{Im}\tilde{G}^{(0)}_{12;\alpha}(\omega)/2w \propto \omega^5;$$

$$\mathrm{Im}G_{22;\alpha}(\omega) \approx \mathrm{Im}\tilde{G}^{(0)}_{11;\alpha}(\omega)/3 \propto \omega^3.$$

In this case the right-hand side of the equation (11) may contain only $\propto \omega^{12}$ or higher order terms with respect to ω. This means that odd vibrations give at low temperatures negligibly small contribution $\propto T^{13}$.

Due to the local stiffening of the lattice by an interstitial, the tunnelling matrix element $\tilde{\Delta}$ at low temperatures does not essentially depend on T. Therefore taking into account the local stiffening of the lattice leads to an increase of the characteristic cross-over temperature T_0 of the quantum diffusion of self-interstitials. Since the diffusivity due to phonons became so large, the actual limiting factor at low temperatures is the scattering of self-interstitials by other impurities or defects [2] (see also [4]). Therefore, in good quality crystals with small amount of defects at temperatures $\sim \alpha T_D$ the diffusion coefficient of interstitials should be larger than the diffusion coefficient of vacancies. Note that the above arguments for self-interstitial also applies to other forms of impurities.

6 Comparison with experiment

It is interesting to apply these results to the diffusion of vacancies and interstitials in quantum crystals such as solid He, for which experimental data are available. A vacancy in bcc-^{4}He leads to the appearance of soft modes of T_{2g} symmetry. Therefore in the present approximation the only difference is that a vacancy in the bcc lattice produces three soft modes instead of two, as in the simple cubic lattice, and there are 8 nearest neighbours. This results in an additional 3/2 factor in the equation (18) for γ. Therefore at intermediate low temperatures $\alpha T_D < T \lesssim \sqrt{\alpha}\,T_D$ one should expect to observe in the bcc-^{4}He crystal the $D \propto T$ temperature dependence. Indeed the bcc-^{4}He diffusivity observed by Zuev et al. [34], in the existence interval $1.43\ \mathrm{K} < T < 1.8\ \mathrm{K}$ for a pressure close to the melting line, can be expressed by the law $D \simeq (5.8 \times 10^{-5}\ \mathrm{cm^2\ s^{-1}})T$. This allows one to suppose that in bcc-^{4}He $\alpha \lesssim 10^{-2}$. With $\omega_D \sim 3.4 \times 10^{11}\ \mathrm{s^{-1}}$ for bcc-^{4}He [35], one can first estimate the value of γ at $T \sim \sqrt{\alpha}\,T_D$ for $\alpha \sim 0.01$ as $\gamma \sim 0.3k_BT/\hbar \sim 6 \times 10^{10}\ \mathrm{s^{-1}}$. Then from $a \approx 3.56$ Å $\Delta_0 \sim 10^{10}\ \mathrm{s^{-1}}$ [8] and with a Debye-Waller factor of the order of 0.3 [9] the diffusion coefficient in the above temperature region is given by $D \sim 7 \times 10^{-5}\ \mathrm{cm^2\ s^{-1}}$. Taking into account the roughness of the Debye model, this estimation is in reasonable agreement with Zuev et al. data. Note that a vacancy diffusion in the range of a few $10^{-5}\ \mathrm{cm^2\ s^{-1}}$ is also found for the hcp-phase ^{4}He both from Zuev et al. data [34] and from the fitting of solid ^{4}He vacuum expansion measurements [36].

As it was shown above, the account of the local distortion of the phonon spectrum in case of self-interstitials leads to the opposite effect as compared to vacancies, because the lattice is stiffened around the interstitial atom. This eventually causes a rapid power-law increase of the diffusion coefficient for decreasing temperature. This means that at low temperatures the diffusion of vacancies is expected to be much slower than the diffusion of interstitials. In recent experiments based on the expansion into vacuum of solid ^{4}He through an orifice of micrometric diameter, the vacancy diffusion coefficient and life-time at given temperatures and pressures could be observed [36]. The vacancy diffusion coefficient was determined to be in the range of 10^{-5} cm^2/s, in agreement with Zuev et al. [34], while the vacancy recombination lifetime was found to be macroscopic (40 s). Such a large value was considered to be consistent with an interstitial concentration of about 10^{10} cm^{-3}, which is far smaller than the equilibrium concentration of thermally activated vacancies (10^{18} cm^{-3} for the parameters considered in Ref. [36]). This indicates an almost complete segregation of interstitial atoms to surface or extended defects, in agreement with the statistical model by Guyer [37] and Hetherington [38]. The present result, which indicates an interstitial diffusion (mobility) much larger than for vacancies, may well account for the observed lack of interstitials in the quoted experiments, where the powerful pressure gradient near the orifice ensures a quick sweeping away of thermally generated interstitials [36]).

7 Summary

We have studied the effect of the quadratic interaction of a defect with phonons on quantum diffusion. The standard assumption which is usually made is that this interaction can be taken into account within the perturbation theory. Here we proposed an analytical approach showing that this assumption is invalid if the diffusing defect causes a large local distortion of the phonon spectrum. Actually this is the case of intrinsic defects since their diffusion is accompanied by the breaking and reconstitution of strong bonds. We have demonstrated that the local softening of the lattice caused by breaking of bonds, leads to a drastic decrease of the characteristic cross-over temperature T_0 of the quantum diffusion of vacancies; as a result the Andreev and Lifshitz $D \propto T^{-9}$ law already at rather low temperatures is replaced by a much weaker dependence. On the opposite, the local stiffening of the lattice by interstitials leads to an increase of the cross-over temperature T_0. These conclusions are found to be in agreement with recent experiments on vacancy diffusion in solid ^{4}He.

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