Defecton diffusion in quantum crystals

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Diffusion of defectons in quantum crystals at low temperatures is considered. The diffusion coefficients, mean free paths, and mobilities of the defectons are found in all limiting cases of interest. The theory is compared with the experimental results.

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As shown by Andreev and I. Lifshitz [1], the kinetic properties of point defects in quantum crystals at low temperatures are determined by the behavior of the quasiparticles corresponding to them, the defectons. The main kinetic characteristics of defectons and their dependences on the temperature were determined by the present author [2-5] on the basis of the microscopic theory. The experiments performed on the diffusion of He^3 impurities in solid He^4 [6-9] are in qualitative agreement with the predictions of the theory. The main results [1-5] were confirmed also in studies of the diffusion of light impurities [10,14]. In view of the increased interest in quantum kinetics of defects, it is necessary to consider more fully the main features of this kinetics, since failure to take these into account leads sometimes even to the wrong order of magnitude.

THE ROLE OF DEFECTS

At absolute zero temperature, a defecton moves through a crystal like a free particle, and is scattered mainly by lattice inhomogeneities and by other defectons. The gas of null phonons has time to adjust itself to the defecton, greatly altering its dynamic characteristics, but not leading to dissipation. Therefore, if the defect concentration x is small enough, then its diffusion coefficient can be calculated by using the gas approximation [4]. If we denote by σ the cross section for the scattering of a defecton by a defecton (in units of a^2, where a is the lattice constant), then the mean free path is $l = a/\sqrt{2}x\sigma$. The quasiparticle velocity can be determined from the velocity of the delocalization-wave front [4]: $v = Aa/\hbar$ (A is the amplitude of the probability of the transition of a defect into a neighboring equivalent position). The diffusion coefficient is then

$$D_0 = \frac{1}{3\sqrt{2}}\frac{a^2A}{x\sigma} \approx \frac{ac}{zx\sigma}\frac{\varepsilon}{\Theta}, \qquad (1)$$

where c is the speed of sound, z is the number of nearest neighbors, Θ is the Debye temperature, and $\epsilon = zA$ is the width of the defecton band.

In order for the defectons to be good quasiparticles, their mean free path should be larger than the lattice constant; this takes place at concentrations

$$x < \sigma^{-1}. \qquad (2)$$

It is important that the scattering cross section itself depends on the width of the band [2,4,5] and in the case of narrow bands it can turn out to be anomalously large. On the one hand, this imposes rather stringent requirements on the permissible concentrations and on the perfection of the employed crystals, and on the other hand it shows that one cannot put $D_0 \sim \epsilon$, as is frequently assumed in the reduction of the experimental results. To determine the dependence of D on ϵ it is necessary to know the interaction potential between the defects. We assume for simplicity that it takes the form $V(r) = V_0(a/r)^3$ (the case of isotropic interaction, $V \sim r^6$, is considered in [2]). As a rule, the width of the impurity band is small in comparison with V_0 ($\epsilon \ll V_0$). Then, if the defecton wavelength is not very large ($\lambda \lesssim aV_0/\epsilon$), the quasiclassical approximation $\sigma \sim V_0\lambda/\epsilon a$ is valid. If $T > \epsilon$, as is the case in practice, then $\sigma \sim V_0/\epsilon$ and $D \sim \epsilon^2$.

Owing to the small width of the energy band there are produced around the defects large regions that are inaccessible to the quasiparticle. Their linear dimension can be easily estimated from the relation $V_0(a/R)^n \sim \epsilon$, $R \sim a(V_0/\epsilon)^{1/n}$, and the cross section is $R^2 \sim a^2(V_0/\epsilon)^{2/n}$. We can thus expect a static "trapping" of the electron to take place at $x \gtrsim (\epsilon/V_0)^{3/n}$.

Generally speaking, when defectons are scattered by the lattice defects, a situation wherein $V_0 \ll \epsilon$ is possible (e.g., when a vacancion is scattered by an isotropic impurity). In this case the Born approximation is valid and the problem can be solved completely with account taken of the angular dependence of $V_0(\mathbf{n})$ ($\mathbf{n}$ is a unit vector in the direction of the line joining the interacting particles). The quantity $V_0(\mathbf{n})$ is of alternating sign, i.e., there are directions corresponding to attraction as well as directions in which the defects are repelled. Of course, its average over the angles is equal to zero. We consider for simplicity a primitive cubic lattice [12]

$$V_0(\mathbf{n}) = U_0\Gamma(\mathbf{n}), \quad \Gamma(\mathbf{n}) = n_x^4 + n_y^4 + n_z^4 - 3/5.$$

According to the general theory [13], the scattering amplitude is

$$F(\mathbf{n}) = a\frac{U_0}{2\pi A}\int \Gamma(\mathbf{n}')e^{-i\mathbf{f}\mathbf{r}'}\,dr',$$

where $\mathbf{f} = \mathbf{p}' - \mathbf{p}$ is the difference between the initial and final wave vectors of the defecton. The calculation of the integral that enters here is exceedingly complicated [4] and yields

$$F(\mathbf{n}) = -\frac{2a}{15}\frac{U_0}{A}\Gamma(\mathbf{n}).$$

It is seen that the scattering amplitude has the same angular dependence as the interaction potential, and that the scattering cross section is $\sigma \sim (U_0/\epsilon)^2$. Thus, if this mechanism turns out to be the principal one (e.g., owing to the very small defecton concentration), then $D \sim \epsilon^3$.

DIFFUSION IN PHONON GAS

At $T \neq 0$, owing to scattering by thermal phonons, the diffusion coefficients begins to depend strongly on the temperature. To determine this dependence, let us consider an individual collision of a phonon with a defecton. We start from the energy and momentum conservation laws:

$$\frac{\hbar^2 n^2}{2m^*}+\hbar ck=\frac{\hbar^2 n'^2}{2m^*}+\hbar ck', \tag{3}$$

$$\mathbf{p}+\mathbf{k}=\mathbf{p}'+\mathbf{k}'. \tag{4}$$

Here k is the wave vector of the phonon, m* is the effective mass of the defecton. The primed letters denote the quantities after the collision. For simplicity we use a quadratic dispersion law for the defecton and a linear one for the phonons, which is well satisfied at sufficiently low temperatures. If the phonon gas is assumed to be in equilibrium, then the mean thermal value of the phonon momentum is $\hbar k \sim T/c$. Thus, at temperatures $T \ll m^*c^3$ $T \ll m^*c^3$, which is almost always the case, we have $\hbar k \ll m^*c$. Taking this into account we obtain for the energy transfer in the collision the value $\Delta E = \hbar c\varkappa$, where

$$\varkappa \equiv k'-k=\frac{k}{p_0}\mathbf{p}(\mathbf{n}'-\mathbf{n})-\frac{k^2}{p_0}(1-\mathbf{n}\mathbf{n}'), \quad p_0=\frac{m^*c}{\hbar}, \tag{5}$$

$\mathbf{n} = \mathbf{k}/k$ and $\mathbf{n}' = \mathbf{k}'/k$ are the directions of the incident and scattered phonons. For the wave vector transferred during the collision we have similarly

$$\mathbf{q}=k(\mathbf{n}-\mathbf{n}')+\varkappa\mathbf{n}'.$$

It is easily seen that the relative changes of the energy and momentum of the defecton are small:

$$\frac{\Delta E}{\varepsilon(p)}\sim\frac{k}{p}\sim\left(\frac{T}{m^*c^2}\right)^{1/2}\ll 1, \quad \frac{q}{p}\sim\frac{k}{p}\leqslant 1.$$

As to the phonon momentum, its direction changes greatly in each collision, but its magnitude remains practically constant. The situation thus recalls the motion of a heavy particle in a gas of light particles. The difference lies in the dispersion laws and in the different statistics obeyed by the defectons and phonons. It is important also that the width of the defecton band is relatively small.

Let us find first the diffusion coefficient in momentum space. Obviously, the change of the square of the wave vector per unit time is given by the integral

$$\langle q^2\rangle=\frac{3c}{(2\pi)^3a^3}\int d\mathbf{k}\, d\sigma_{\mathbf{k}\mathbf{k}'}n(k)\,(k-k')^2, \tag{6}$$

where $n(k) = [\exp(\hbar ck/T) - 1]^{-1}$ is the phonon distribution function and $d\sigma_{kk'}$ is the differential cross section for phonon scattering by the defecton. As shown in [2], this cross section is given by

$$d\sigma_{\mathbf{k}\mathbf{k}'}=\frac{\sigma_0 a^2}{(2\pi)^2}(ka)^4(\mathbf{n}\mathbf{n}')^2 d\Omega',$$

where σ_0 is a constant that depends on the type of defect. In the case of a vacancy, $\sigma_0 = 1$, and in the case of an isotopic impurity $\sigma_0 = ((M - m)/M)^2$, where M is the impurity mass and m is the mass of the main atoms of the crystal. At low temperatures ($T \ll \hbar c/a$) the integration limits in (6) can be extended to infinity, after which the result is expressed in terms of the Riemann ζ function

$$\langle q^2\rangle=\alpha\frac{\sigma_0 c}{a^3}\left(\frac{T}{\Theta_p}\right)^9, \tag{7}$$

where

$$\alpha=\frac{\pi^5\zeta(9)}{240\zeta(8)}\approx 1{,}27, \quad \Theta_p=\frac{\hbar c}{2a}=\frac{\Theta}{2(6\pi^2)^{1/3}}.$$

To calculate the diffusion coefficient in coordinate space we proceed as follows: We define the free path time of the defecton as the time during which the transferred momentum squared becomes of the order of the square of the initial particle momentum:

$$\tau=\frac{\tau_0}{\alpha\sigma_0}\frac{\varepsilon(p)}{\Theta_p}\left(\frac{\Theta_p}{T}\right)^9, \quad \tau_0=\frac{\hbar}{A}. \tag{8}$$

Then the mean free path is the path traversed during the time τ:

$$l=\frac{\sqrt{2}}{\alpha}\frac{a}{\sigma_0}\frac{\varepsilon(p)^{1/2}}{\sqrt{A}\,\Theta_p}\left(\frac{\Theta_p}{T}\right)^9, \tag{9}$$

and the coefficient of diffusion in the phonon gas is

$$D_{ph}=\frac{1}{3}\tau v^2=\frac{ac}{3\alpha\sigma_0}\left(\frac{\varepsilon(p)}{\Theta_p}\right)^2\left(\frac{\Theta_p}{T}\right)^9. \tag{10}$$

The presence of the temperature raised to the ninth degree has a lucid physical meaning—three degrees are connected with the number of phonons, four with the scattering cross section, and two with the ineffectiveness of the collisions. It is very important, however, that the temperature parameter is not the Debye temperature Θ but $\Theta_p \sim \Theta/8$. (In [2-3] we used the quantity $\Theta/8$ for convenience in the calculation.)

Defectons can satisfy both Fermi-Dirac statistics and Bose-Einstein statistics. We have accordingly for the two cases

$$D_F\sim\frac{ac}{\sigma_0}x^{4/3}\left(\frac{\varepsilon}{\Theta_p}\right)^2\left(\frac{\Theta_p}{T}\right)^9, \quad D_B\sim\frac{ac}{\sigma_0}\left(\frac{\Theta_p}{T}\right)^7.$$

But the degeneracy temperature of the defecton gas is unusually small, $T^* \approx Ax^{2/3}$. Therefore in almost the entire experimentally accessible range of temperatures we have $T > T^*$. If at the same time $T \leq \epsilon$, then Boltzmann statistics apply and the relation $\overline{\epsilon(p)} = 3T/2$ can be used to estimate the averages over the temperature. In this case we obtain for the free path time and for the diffusion coefficient, respectively,

$$\tau_B\approx 1.18\frac{\tau_0}{\sigma_0}\left(\frac{\Theta_p}{T}\right)^8, \quad D_B\approx 0.59\frac{ac}{\sigma_0}\left(\frac{\Theta_p}{T}\right)^7. \tag{11}$$

From the last expression and the Einstein relation we easily obtain the mobility b of the defecton in the phonon gas

$$b=D_B/T=1.18\frac{a^2}{\hbar\sigma_0}(\Theta_p/T)^8. \tag{12}$$

Naturally, the same value of the mobility can be obtained by direct calculation of the force experienced by a quasiparticle moving in the gas. Indeed, in the system in which the defecton is at rest, the phonon distribution function takes the form $\tilde{n}(k) = n(\epsilon - \hbar\mathbf{k}\cdot\mathbf{v})$, and the force acting on the defecton can be expressed as the change of the momentum per unit time:

$$\mathbf{F}=\frac{3c\hbar}{(2\pi)^3}\int d\mathbf{k}\, d\sigma_{\mathbf{k}\mathbf{k}'}\tilde{n}(k)\,k(\mathbf{n}-\mathbf{n}')=b^{-1}\mathbf{v}.$$

In first order in the small ratio $v/c \ll 1$, the mobility calculated in this manner coincides with (12).

If $T > \epsilon$, then the band is filled uniformly and $\overline{\epsilon(p)} = \epsilon$. Thus, we obtain the well-known result [3-5]:

$$\tau=\frac{\tau_0}{\alpha\sigma_0}\frac{\varepsilon}{\Theta_p}\left(\frac{\Theta_p}{T}\right)^9, \quad D=\frac{ac}{3\alpha\sigma_0}\left(\frac{\varepsilon}{\Theta_p}\right)^2\left(\frac{\Theta_p}{T}\right)^9. \tag{13}$$

Such a temperature dependence was obtained later in [11] for the diffusion coefficient of light impurities.

Of course, the derived formulas are valid so long as $\tau > \tau_0$, i.e., if the free path time is longer than the time required to produce the defecton. This condition reduces to $T < T_c$, where

$$T_c=\Theta_p(\varepsilon/\alpha\sigma_0\Theta_p)^{1/9}. \tag{14}$$

At temperatures $T > T_c$, the mean free path becomes smaller than the interatomic distances. As a result, the defecton begins to spend a greater part of the time within the cell, and only rarely does it execute individual tran-

sitions (tunnel or activation) to a neighboring equivalent positions. At $T = T_c$ the diffusion coefficient is $D \sim a^2\epsilon/\hbar$. Its behavior at higher temperatures calls for a special analysis. It appears that situations are possible [11] when the T^{-9} law is valid also at $T > T_c$.

COMPARISON WITH EXPERIMENT

For the comparison with the experimental results let us consider the diffusion of He^3 impurities in solid He^4 at temperatures $T > \epsilon$. If the mechanisms of scattering by phonons and by defectons are regarded to be independent, then, using the Matthiessen rule, we can represent the diffusion coefficient in the form [5]

$$D^{-1} = \frac{1}{ac}\frac{\Theta_p}{\varepsilon}\left\{8x\sigma + 3\alpha\sigma_0\frac{\Theta_p}{\varepsilon}\left(\frac{T}{\Theta_p}\right)^9\right\}. \quad (15)$$

The experimental value is

$$D^{-1} = 6.25\cdot 10^{10}\, x + 4.6\cdot 10^6\, T^9 \ \text{cm}^{-2}\text{sec} \quad (16)$$

Comparing (15) and (16) and recognizing that $\sigma_0 = 1/9$ in this case, we obtain $\epsilon \approx 10^{-4}$ °K and $\sigma \gtrsim 10^2$. Substituting the value determined in this manner for the band width in (14), we obtain for the critical temperature the value $T_c = 1.3$°K, in very good agreement with experiment [7]. The lower temperature limit to which the D(T) law (13) can be observed follows from (15):

$$T_1 < T < T_c, \quad T_1 = T_c(x\sigma)^{1/9}.$$

At $x = 10^{-3}$ and $\sigma = 10^2$ we obtain $T_1 = 1$°K, which is also in good agreement with the experimental curves [7-9]. Unfortunately, there is still no experimental answer to the question of the behavior of the diffusion coefficient at $T > T_c$.

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