Quantum diffusion and recombination of atoms in a crystal at low temperatures

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The recombination kinetics of atoms in a crystal, when quantum sub-barrier diffusion is the limiting factor, is examined. The experimental results[4] on recombination of atomic hydrogen in a molecular hydrogen matrix are analyzed.

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1. There is a wide class of phenomena suggesting the convergence of particles which diffuse in crystals to interatomic distance. These phenomena include recombination of atomic particles and, in general, a chemical reaction in the solid phase or the formation of bound pairs, in particular, trapping of particles by defects. If we consider temperatures such that the kinetics are determined by the quantum sub-barrier particle diffusion, then the basic characteristic of such problems is the necessity for particles to traverse regions in which the levels in neighboring wells turn out to be strongly misaligned relative to each other. Such misalignment of levels $\delta\epsilon$ is unavoidable, since it is related to the interaction between particles, direct or indirect (via a strain field), while the amplitude of a tunneling transition Δ_0 or band width $\Delta \approx z\Delta_0$ (c is the number of nearest neighbors in the sublattice in which the particles are diffusing) is extremely small. In this situation, beginning already with comparatively large distances r_0, where $\delta\epsilon(r_0) \approx \Delta$, the band nature of the motion, turns out to be completely destroyed, and further convergence of particles can occur only due to interaction with phonons. The latter leads to a fluctuating dynamics shift in the levels in neighboring wells, which effectively compensates for the statistical misalignment and thereby removes localization.[1,2] At low temperatures T this process turns out to be very slow and for $nr_0^3 \ll 1$ (n is the particle density), the characteristic reaction time is determined by the time it takes to traverse the region $r < r_0$.

2. The microscopic equation describing quantum diffusion in an irregular crystal can be obtained by using the results in Refs. 1, 2, and 3. For this purpose, we construct the kinetic equation for the density matrix of particles interacting with the phonon subsystem and after eliminating the nondiagonal elements, we find an equation for the particle distribution function f_r in the lattice-site representation

$$\frac{\partial f_{\mathbf{r}}}{\partial t} + \sum_{\mathbf{g}} \{ f_{\mathbf{r}} W_{\mathbf{r},\,\mathbf{r}+\mathbf{g}} - f_{\mathbf{r}+\mathbf{g}} W_{\mathbf{r}+\mathbf{g},\,\mathbf{r}} \} = 0. \tag{1}$$

Here ($\hbar = 1$)

$$W_{\mathbf{r},\,\mathbf{r}+\mathbf{g}} = \frac{2\Delta_0^2\, \Omega\,(\epsilon_{\mathbf{r},\,\mathbf{r}+\mathbf{g}})}{(\epsilon_{\mathbf{r},\mathbf{r}+\mathbf{g}})^2 + \bar{\Omega}^2} \tag{2}$$

is the probability for coherent hopping (tunneling without phonon excitation) from site $\mathbf{r}$ to site $\mathbf{r}+\mathbf{g}$, and $\epsilon_{\mathbf{r},\mathbf{r}+\mathbf{g}} = \epsilon_{\mathbf{r}} - \epsilon_{\mathbf{r}+\mathbf{g}}$ is the relative level misalignment

$$\bar{\Omega} = \frac{1}{2}\, [\Omega(\epsilon_{\mathbf{r},\,\mathbf{r}+\mathbf{g}}) + \Omega(\epsilon_{\mathbf{r}+\mathbf{g},\mathbf{r}})]\,.$$

The function $\Delta\,(\epsilon_{\mathbf{r},\mathbf{r}+\mathbf{g}})$ contained in (2) represents teh damping rate of the nondiagonal elements of the density matrix $f_{\mathbf{r},\mathbf{r}+\mathbf{g}}$ due to the interaction with phonons. This is the basic kinetic characteristic which describes the mean-square relative vibration of levels in neighboring wells.

In (2), the probability for coherent hopping (tunneling involving phonons), whose contribution at $T \ll \omega_D$ to two-phonon processes is negligibly small and does not exceed (2) when single-phonon processes (large misalignment) become important, is omitted.

In deriving (1) and (2), we assumed that one of the following two inequalities is satisfied

$$\Delta \ll \delta\epsilon, \qquad \Delta \ll \Omega\,, \tag{3}$$

although for $\Omega \gg \delta\epsilon$ the equation remains valid when (3) breaks down (see Refs. 2 and 3).

3. We shall now examine the particle motion in the region $r < r_0$, assuming for simplicity that the second particle is stationary (in so doing we lose only a factor of 2 in the final results). In this region, the first inequality in (3) is valid.

When the misalignment scales are bounded, two-phonon interaction almost always plays the determining role. This leads to the following $\delta\epsilon$ dependent expression $(\delta\epsilon < T)^{1-3}$ for Ω

$$\Omega_{\mathrm{II}} \simeq B_{\mathrm{II}} 10^6\, \omega_D (T/\omega_D)^9, \tag{4}$$

where B_{II} is a dimensionless factor of order unity.

For low T and with motion toward the center, the condition $\delta\epsilon \gg \Omega_{\mathrm{II}}$, goes rapidly into effect and

$$W_{\mathbf{r},\,\mathbf{r}+\mathbf{g}} \approx 10^6\, \omega_D \frac{\Delta_0^2}{(\epsilon_{\mathbf{r},\,\mathbf{r}+\mathbf{g}})^2} \left(\frac{T}{\omega_D}\right)^9. \tag{5}$$

This probability drops very sharply with decreasing r. This continues until the misalignment at some distance r_* reaches the value

$$\delta\epsilon(r_*) \approx 30T^2/\omega_D, \tag{6}$$

when single-phonon relaxation frequency

$$\Omega_1(\epsilon) \simeq B_1\omega_D \left|\frac{\epsilon}{\omega_D}\right|^5 [N(|\epsilon|) + \theta(\epsilon)]; \qquad N(\epsilon) = \frac{1}{e^{\epsilon/T} - 1} \tag{7}$$

becomes comparable to Ω_{II}. For $r < r_*$ $[\delta\epsilon(r_*) < T]$

$$W_{r,\,r+g} \simeq \frac{\Delta_0^2\,(\epsilon_{r,r+g})^2}{\omega_D^4}\,T, \tag{8}$$

and now the opposite occurs: the hopping probability rapidly increases with decreasing r. Thus, $W(r)$ has the dependence shown in Fig. 1(a) with a very sharp minimum at the point $r = r_*$, if it is assumed that $\delta\epsilon$ drops rapidly and monotonically with increasing r. It is clear that the reaction kinetics is actually determiend by the time for passing through the "narrow neck" in the vicinity of $r = r_*$, where, in accordance with (5)–(8),

$$W^* \simeq 10^3\Delta_0^2\,T^5/\omega_D^6. \tag{9}$$

If during motion in the region $r < r_*$ the particle enters a region where $\delta\epsilon > T$, then the nature of further motion depends on the sign of $\epsilon_{r,r+g}$ or $\epsilon(r)$. For $\epsilon(r) < 0$ and $\delta\epsilon > T$, the probability for single phonon hopping in a direction toward the center no longer depends on T [see Eqs. (7) and (2)] and irreversible capture at a rate limited by (9) occurs. For $\epsilon(r) > 0$, the T dependence of the motion toward the center has an activation nature and the time for pair formation is determined by the competition between the time for passing through the narrow neck and the activation region.

Let us now examine, for simplicity, the problem of the capture of a particle by a system of stationary force centers, whose relative concentration coincides with the particle concentration x. The behavior $W(r)$ leads to the fact that the particle distribution is uniform outside a region of radius r_* around the centers. In the case of attraction toward a center, as follows from (1), the gradient of the distribution function is concentrated near the narrow region with a scale of the order of the atomic scale, and the characteristic reaction time can be estimated as

$$\frac{1}{\tau} \approx 4\pi\left(\frac{r_*}{a}\right)^2 W^* x \sim T^{5-4/n+1} \tag{10}$$

assuming that $\epsilon(r) \simeq U_0(a/r)^n$.

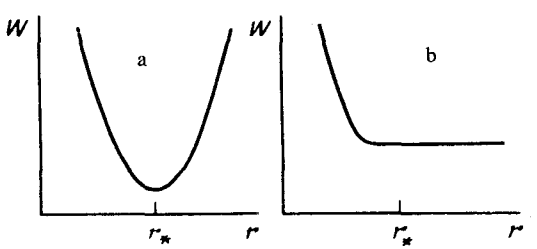

FIG. 1.

As T is decreased, the radius r_* continuously increases until it reaches the value r_0 at $T \simeq \sqrt{\omega_D \Delta}/30$, after which it remains constant. As a result, the temperature dependence of τ changes considerably [see Eq. (8)]

$$\frac{1}{\tau} \simeq 4\pi \left(\frac{r_0}{a}\right)^2 \frac{\Delta_0^4 x}{\omega_D^4} T, \qquad T < T_0 . \tag{11}$$

On the other hand, with the increase of T and hence $\delta\epsilon(r_*)$ (6), the radius r_* can enter the region of the nearest coordination spheres, where the discreteness of the structure is important. In this case, the radius r_* cannot hop into another coordination sphere in a finite temperature interval and a linear T dependence should again be observed in this interval.

In the presence of defects, if the scale of the misalignment induced by them $\delta\epsilon^{im} < \delta\epsilon(r_*)$, then all results remain essentially unchanged. In the opposite case, the picture changes considerably. Now single-phonon processes dominate in the entire range of r. For $r > r_*^{im}$, where r_*^{im} is determined from the equality $\delta\epsilon(r) = \delta\epsilon^{im}$, diffusion is determiend by the misalignment of levels due to defects. It is easy to understand [see Fig. 1(b)] that motion precisely in this region will be the limiting factor in this case and

$$\frac{1}{\tau} \simeq 4\pi \left(\frac{r_*^{im}}{a}\right) \frac{\Delta_0^2 (\delta\epsilon^{im})^2 x}{\omega_D^4} T \tag{12}$$

(the linear dependence on r_*^{im} arises due to the inclusion of the gradient of the function f_r near r_*^{im}).

4. In a recent paper,[4] in studying the kinetics of recombination of atomic hydrogen in solid H_2 with the help EPR, it was discovered that for $T < 4$ K the rate of recombination completely loses its activation nature (classical diffusion) and goes over into a regime with slow decrease with decreasing T. It was later established by Kafunin *et al.* that the decrease is nearly linear (in press). If we take into account the fact that the H concentration was $x = 10^{-3} - 10^{-4}$ and the reaction requires convergence to interatomic distance (after which it occurs very rapidly), then there is no doubt that the observed time scale $\sim 10^4$ s is related to the time for convergence of a particle pair and Katunin observed for the first time the picture described above. If we use the results obtained above, then we obtain the following estimate:

$$10^{-3}\,\mathrm{K} < \Delta_0 < 10^{-1}\,\mathrm{K}.$$

The upper limit is obtained by using (11), while the lower limit is obtained if it is assumed that the crystal is strongly defective. It is interesting that a direct estimate of the tunneling exponent, depending on the value of the activation energy of classical diffusion ($E \simeq 100$ K[4]), gives a value lying in this interval.

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