Temperature dependence of the self-trapping rate

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A theory is derived for the temperature dependence of the self-trapping rate. At high temperatures an Arrhenius law $w \propto \exp(-W/T)$ holds, where W is the height of the self-trapping barrier. At low temperatures tunneling is predominant. In the exponential approximation, the behavior $\ln w \propto [a + b\exp(\omega/T)]$ holds for optical phonons, while $\ln w \propto (a + bT^4)$ holds for acoustic phonons.

In several crystals, quasiparticles (excitons and charge carriers) can exist in either free or self-trapping states. These states are separated by a self-trapping barrier.[1] Excitons are produced in the free state by light, but before they decay some of them manage to undergo a self-trapping by overcoming the barrier. The fraction of the luminescence accounted for by self-trapping states is determined by the self-trapping rate w. In this letter we propose a general method for calculating w for arbitrary temperatures T. We show that the mechanism for overcoming the self-trapping barrier at high temperatures is completely different from that at low temperatures. At high temperatures it is an activation mechanism, and the Arrhenius law holds. At low temperatures a tunneling mechanism operates, and the temperature dependence of w is determined by the temperature dependence of the optimum tunneling path in configuration space (i.e., by the time evolution of the shape of the instanton).

This problem is related to several other problems of current interest: quantum nucleation,[2,3] the decay of the false vacuum in quantum field theory,[4] and tunneling in the case of friction.[5–7] An important point for the problem at hand is that the self-trapping barrier is not determined from without and is instead produced by the tunneling lattice itself. As a result, the dynamics of the barrier depends on T. The method proposed below is based on Ref. 8, where w was calculated for $T=0$, and on Ref. 9, where a theory for edge absorption at $T\neq 0$ was derived with allowance for self-trapping.

The rate of exciton self-trapping, w, determined in terms of the secondary-emission spectrum, can be expressed in terms of the Fourier transform of the two-particle correlation function:

$$\begin{aligned} F(tt_1t_2) &= \mathrm{Sp}\,\{ K_0(-i\beta,0)K(0,t_2)K_0(t_2,t+t_1)K(t+t_1,t)K_0(t,0)\} \\ &= \int d\{\mathbf{r}\}\int \mathcal{D}\Psi\,\mathcal{D}Q\,\Psi_1(t+t_1)\,\Psi_1^*(t)\,\Psi_2(0)\,\Psi_2^*(t_2)\exp\{iS\}\ . \end{aligned} \tag{1}$$

Here $\beta = T^{1}$, and K_0 and K are the exact propagators of the free lattice and of the system consisting of the lattice plus the exciton. These propagators are written as a functional path integral over Q [under the condition $Q(0) = Q(-i\beta)$] and as a field integral over the exciton wave functions Ψ; here $\{\mathbf{r}\}$ is the set of spatial coordinates of the Ψ functions. The action S is given by

$$S = \sigma \int_{(\Gamma)} dt \int d\mathbf{r} \left\{ \frac{i}{\sigma} \Psi^* \frac{\partial}{\partial t} \Psi + \frac{1}{2} \Psi^* \nabla^2 \Psi + \frac{1}{2}\left(\frac{\partial Q}{\partial t}\right)^2 - \frac{1}{2} Q^2 - Q \Psi^* \Psi \right\}. \qquad (2)$$

For definiteness, the action is written for the case of an exciton which has interacted with nonpolar, dispersion-free, optical phonons, and we are using dimensionless units.[8] The parameter σ is $\sigma = W/W_0\omega$, where W is the height of the self-trapping barrier, ω is the phonon frequency, and $W_0 \approx 44$. Figure 1a shows the integration path Γ. The heavy segments of the path correspond to the propagators K, and the light segments to the propagators K_0. The terms with Ψ in (2) must be omitted on the light segments. The arrows show the time sequence. After a Gaussian integration over Q in (1), we find

$$S = \sigma \int d\mathbf{r} \left\{ \sum_\alpha \int dt\, \Psi_\alpha^* \left(\frac{i}{\sigma} \frac{\partial}{\partial t} + \frac{1}{2} \nabla^2 \right) \Psi_\alpha - \frac{1}{4} \sum_{\alpha\beta} \iint dt\,dt'\, D_{\alpha\beta}(t-t') \, |\Psi_\alpha(t) \Psi_\beta(t')|^2 \right\}, \qquad (3)$$

where $\alpha, \beta = 1$ or 2; 1 refers to the upper segment of the contour, and 2 to the lowest segment. The integration in (3) runs over only the heavy parts of contour Φ (Fig. 1a) and goes in the direction shown by the arrows. The phonon Green's function is

$$D_{\alpha\beta}(t-t') = -i\{(N+1)\exp(-i[t-t']_\Gamma) + N\exp(i[t-t']_\Gamma)\}, \qquad (4)$$

where $[t-t']_\Gamma$ is equal to the difference between the later and earlier times (in the sense of their order on Γ), and $N = (\exp\beta - 1)^{-1}$ is the occupation number.

The integration over Ψ in (1) can be carried out by the method of steepest descent if Γ is deformed as shown in Fig. 1b. The point ξ corresponds to the time of self-

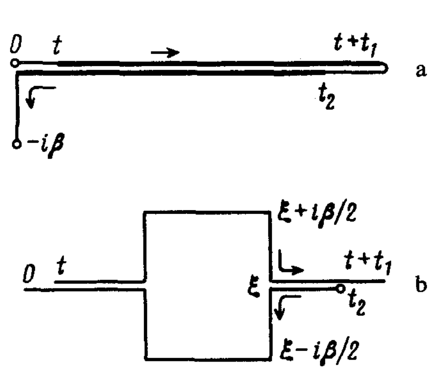

FIG. 1.

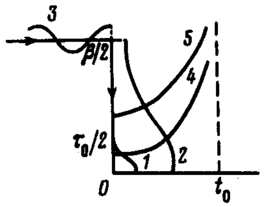

FIG. 2. Structure of a "short" instanton (at $\tau \geqslant 0$). Time evolution of the depth of the exciton level (1 and 4) and of the deformation at the center of the instanton (2, 3, 5). Curves 1–3 are plotted along the vertical from the two extreme regions of the time contour, while curves 4 and 5 are plotted along the horizontal from the central part of the contour.

trapping and can be chosen arbitrarily. To the left of ξ an exciton is free, while to its right it is self-trapped. Only the segment $(\xi - i\beta/2; \xi + i\beta/2$, which contains an instanton, contributes to S. After a transformation to the imaginary time τ, we can write the rate as $w \sim \exp(-S)$, where

$$S[\psi] = \sigma \int d\mathbf{r} \, \frac{1}{2} \int_{-\beta/2}^{\beta/2} d\tau \, |\nabla \psi(\mathbf{r}\tau)|^2 - \frac{1}{4} \iint d\tau d\tau' \left\{ (N+1) e^{-|\tau-\tau'|} + N e^{|\tau-\tau'|} \right\} |\psi| \psi(\mathbf{r}\tau) \psi(\mathbf{r}\tau')|^2 . \quad (5)$$

The function $\psi(\mathbf{r},\tau)$ is defined in the class of normalized functions by the conditon $\delta S[\psi] = 0$, the condition $\psi(\tau) = \psi(-\tau)$ holds.

Ioselevich[9] has shown that there are three types of extrema of the functional (5), all of which correspond to saddle points of $S[\Psi]$.

1. First, there is the "short" instanton shown schematically in Fig. 2. In it we have $\psi(\mathbf{r}\tau) \neq 0$ only on a part of the imaginary axis of width $\tau_0 \sim 1$ (or, in dimensional units, ω^{-1}; curve 1) and on the real axis to the right of ξ. The deformation of the lattice, $Q = \hat{D}\,|\psi|^2$, however, is nonzero everywhere: It oscillates on the left horizontal part of the contour (curve 3) and increases monotonically toward the center of the instanton on the vertical part (curve 2). We can draw the following physical picture of the process: At one of the times at which the kinetic energy of a lattice undergoing thermal vibrations vanishes, the lattice experiences a quantum fluctuation, i.e., tunneling begins. The deformation grows, and at the time $\tau_0/2$ a discrete level arises in the potential well that the fluctuation creates, and an exciton is trapped at this level. This point is the beginning of the instanton region. Subsequently, both the deformation and the depth of the level continue to increase, and by the time $\tau = 0$ the system emerges from beneath the barrier, and the motion becomes classical again (curves 4 and 5). The $S(\beta)$ dependence for this instanton is shown by curve 1–1′ in Fig. 3. At low temperatures ($\beta \gg 1$), we have

$$S \approx \frac{W}{\omega} (s_0 - s_1 \exp(-\beta)), \qquad s_1 = \frac{1}{2W_0} \int d\mathbf{r} \left(\int_{-\tau_0/2}^{\tau_0/2} d\tau \, \psi^2(\mathbf{r}\tau) \right)^2 , \quad (6)$$

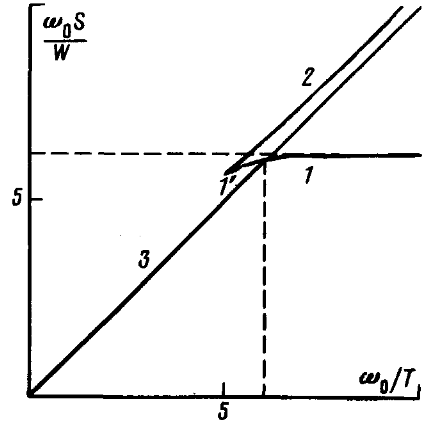

FIG. 3. Temperature dependence of the action for the various solutions. The heavy lines show solutions that result in the least action.

where s_0 and ψ are determined by (5) at $N=0$. A two-parameter variational calculation yields $\tau_0 \approx 2.15$, $s_0 \approx 6.2$, and $s_1 \approx 64$.

2. Next, there is the "long" instanton. At $\beta \gg 1$, its length is $\tau_0 \approx \beta - \ln 2$. The action is shown by curve 2 in Fig. 3. Since the action is always greater than for the short instanton, this solution does not contribute to the tunneling. At $\beta \approx 5$, the two instantons merge and disappear.

3. The last type of extrema is the static solution. Over the entire part of the contour $(-i\beta/2, i\beta/2)$ we have $\psi = \psi(\mathbf{r})$; i.e., this function is independent of τ. In this case, $S = W/T$ is shown by curve 3 in Fig. 3. This solution corresponds to a classical surmounting of the barrier by activation and gives us the Arrhenius law. This solution holds at all temperatures but is the primary solution up to the intersection with curve 1–1′. At low temperatures, the short instanton prevails in the competition.

For numerical reasons, the transition is displaced to temperatures low in comparison with ω:$T_{cr} \approx \omega/6$. Furthermore, the relative change in S in region 1 is small ($\approx 2.5\%$) and is described well by Eq. (6).

After the system emerges from beneath the barrier, the level depth and the deformation grow rapidly. In harmonic approximation the system collapses in a time $t_0 \sim \omega^{-1}$ (Fig. 2). The kinetic energy of the lattice increases in proportion to $W/(t_0 - t)^4$ and reaches a value near the self-trapping energy. Since the kinetic energy is distributed among a few atoms, the collapse may terminate in defect formation.

Although this discussion has dealt with a specific model, several of the conclusions are of general applicability. At high T we always have a law $w \propto \exp(-W/T)$. At low T an instanton mechanism operates, but the precise temperature correction to S depends on the type of phonon. For acoustic phonons it is proportional to T^4. The T dependence of the coefficient of the exponential function is apparently strongest at low temperatures; this question will be studied separately.

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