Exciton diffusion and energy transport in cryogenic xenon, krypton, and argon crystals

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The diffusion kinetics of free excitons in cryogenic Xe, Kr, and Ar crystals is analyzed. Experiments proving the fundamental role played by "hot" excitons in the transport of excitation energy are described.

The simultaneous existence of free and self-localized excitons complicates the picture of the transport of electron energy in Xe, Kr, and Ar lattices, making it nontrivial in comparison with that for other crystals.[1,2] Experiments[3] on the concentration dependence of the sensitized luminescence in a Kr matrix have yielded convincing evidence that energy is transported by free electrons in the course of a diffusive motion at low impurity concentrations, $c \lesssim 0.1\%$. However, an urgent question as to which group of excitons—thermal or hot (nonthermalized)—dominates the energy transport has not been resolved. After analyzing the diffusion kinetics of free excitons theoretically, we formulated an experiment which has answered this question.

The motion of excitons in a regular lattice is controlled by scattering by acoustic phonons. A small dimensionless parameter of this scattering is[4] $\lambda = 4m^2C^2/3\pi\rho s\hbar^3$, where m is the mass of an exciton, C is the strain energy, ρ is the density, and s is the sound velocity in the cryogenic crystal. A direct calculation of the exciton diffusion time for one-phonon scattering, $\tau_{\rm ph}$, leads to the following result for an arbitrary quasimomentum k and an arbitrary temperature T (Ref. 1):

$$\hbar/\tau_{ph} = \frac{6}{5}\lambda\epsilon_k\,[1+\psi(z)], \qquad \psi(z) = \frac{10}{z^5}\int_0^z \frac{x^4\,dx}{\exp x - 1}\quad . \tag{1}$$

Here ϵ_k and v_k are the energy and velocity of an exciton in the band, and $z = 2msv_k/T$. The diffusion coefficient is introduced by $D(k,T) = \frac{1}{3}\tau_{\rm ph}v_k^2$. At small values of z, expression (1) is dominated by the integral $1+\psi(z) \simeq 5/2z$, and we find

$$\hbar/\tau_{ph}(k,T) = \frac{3}{4}\lambda T\frac{v_k}{s}\ , \qquad l_{ph}(T) = \frac{4}{3}\,\frac{\hbar s}{\lambda T}\ . \tag{2}$$

Relation (2) leads to a linear dependence $D(z)$ at $z < 1$:

$$D(z) = D_0 \frac{2}{5} z , \qquad D_0 = \frac{5}{9} \frac{\hbar}{\lambda m} . \tag{3}$$

At large values of z, the function $\psi(z)$ is small, telling us that the contribution from induced scattering by thermal phonons is inconsequential in comparison with spontaneous emission by a factor on the order of the parameter $1/z < 1$. In this case the diffusion coefficient does not depend on T or k:

$$D^* = D_0 = \text{const}\,(k, T). \tag{4}$$

Figure 1 is a schematic plot of the diffusion coefficient against the two variables v_K and T. The line $z = 1$ divides the (v_k, T) into two regions, corresponding to the asymptotic results in (3) and (4). Shown in the same plane is the temperature dependence of the thermal velocity $v_T = (3T/m)^{1/2}$, which intersects the line $z = 1$ at the point[1] $T_c^0 = 12ms^2 \lesssim 6K$[1]. At $T > T^\circ$ the temperature dependence of the diffusion along the v_T curve corresponds to the familiar behavior $D(T) \propto T^{-1/2}$ for thermalized quasiparticles. The diffusion coefficient for hot excitons, with a characteristic velocity v_k and energy ϵ_k, becomes a different function of T, in accordance with (3) and (4), at temperatures

$$T_c(\epsilon_k) \simeq 2msv_k = 2(2ms^2\epsilon_k)^{1/2} . \tag{5}$$

The conclusions found from this analysis lead to a systematic and natural interpretation of experiments on the temperature dependence of the sensitized luminescence.

The luminescence intensity in the band of an impurity center is determined by the number of excitons participating in the transport of excitation, $N(\epsilon_k)$, and their diffusion coefficient: $I_{\text{imp}} \propto N(\epsilon_k) D_{\text{ph}}(T, \epsilon_k)$. The exciton distribution function over the band for energies $\epsilon_k \gg T$ has a weak temperature dependence, so that $I_{\text{imp}}(T)$ is controlled essentially by diffusion. We studied the energy transport in cryogenic Xe, Kr, and Ar crystals containing an O_2 impurity with a low concentration ($c \lesssim 10^{-3}\%$), so that the mean free path with respect to scattering by the impurity was greater in all cases than the corresponding mean free path for scattering by phonons: $l_{\text{imp}} \gg l_{\text{ph}}$. The excitons are excited by an electron beam with an energy $E \approx 0.5$ keV and a low current density, to avoid the creation of radiation-induced defects. An O_2 impurity in an inert host gives rise to a variety of emission centers: molecular excitations (Herzberg bands)

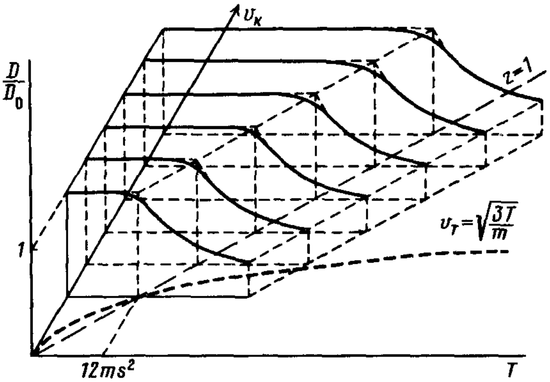

FIG. 1. Diffusion coefficient as a function of the velocity of free excitons and the crystal temperature.

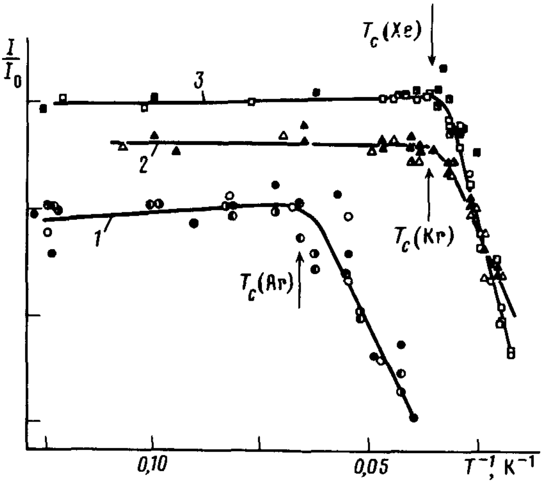

FIG. 2. Temperature dependence of the intensity of the impurity luminescence bands in the various lattices: 1— Ar; 2— Kr; 3— Xe.

and several excimer complexes (RO)*, where R is an atom of the inert element. Since the spectrum of the impurity and intrinsic emission of O_2-R systems spans a broad wavelength range, from the vacuum-UV to the IR, we used two spectral instruments for the measurements. All the conditions in the excitation and measurement of the spectra were strictly fixed over the entire series of experiments.

Figure 2 shows the relative intensity of the impurity-center luminescence as a function of the temperature for the three hosts: Xe, Kr, and Ar. We see that $I_{\rm imp}$ remains constant over a broad T range, while at certain temperatures above a characteristic $T^c_{\rm exp}$ there is a sharp decrease in the intensity with increasing temperature, described by $\sim T^{-1}$. We wish to emphasize that the $I_{\rm imp}(T)$ curves for the various types of impurity states are identical in each host. A change of host is accompanied by a change in $T^c_{\rm exp}$. A slight shift of the region of the slope change on the curves (toward a lower T_c) is observed in the samples with the higher defect concentrations.

The dependence $I_{\rm imp} \sim T^{-1}$ sets in at $T_c \gg T^0_c$, so it should be suggested, in accordance with (5), that hot excitons with $v_k \gg v_T$ are participating in the transport of electron energy. This conclusion is apparently closely related to the retarded thermalization of hot excitons in cryogenic crystals, where the band width $2B$ is substantially greater than the characteristic phonon energy: $2B \gg \overline{\omega}$. Another important point for explaining the special role played by hot excitons in cryogenic crystals is the self-localization of free excitons. As was shown in Ref. 5, at low temperatures the self-localization probability should reach a maximum at energies on the order of the height of the self-localization barrier, H. Self-localization leads to a significant decrease in the number of excitons with energies ϵ_k below the height of the barrier, $\epsilon_k \lesssim H$, so that "hot" quasiparticles with $\epsilon_k > H$ should dominate the energy transport. This conclusion has been varified experimentally: Using the value of H from Ref. 1, expression (5), and the relation $\epsilon_k \gtrsim H$, we find the following temperature regions for the change in slope on the curves: $T_c(\mathrm{Xe}) \gtrsim 22$ K, $T_c(\mathrm{Kr}) \gtrsim 21$ K, and $T_c(\mathrm{Ar}) \gtrsim 13$ K. The experimental results are $T^c_{\rm exp}(\mathrm{Xe}) \approx 30$ K, $T^c_{\rm exp}(\mathrm{Kr}) \approx 30\,K$, and $T^c_{\rm exp}(\mathrm{Ar}) \approx 17$ K.

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