Evidence for Dipole-Dipole Hopping of GaAs Quantum Well Excitons

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We present measurements of the energy relaxation of quasi-two-dimensional excitons in the hopping regime. Under a variety of experimental conditions, the mean energy decays in proportion to $\ln t$. We interpret this result naturally in a model based on the dipole-dipole mechanism for energy loss hops. The model achieves semiquantitative agreement with the observed energy loss rates. [S0031-9007(97)03243-2]

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The slow relaxation of quantum particles through a system of localized states offers a test of accepted models of hopping and is central to the understanding of transient photoconductivity and the optical properties of disordered systems [1–4]. Specific examples include hydrogenated amorphous silicon and III-V or other heterostructures in which long recombination lifetimes are achieved through band gap engineering. At low temperatures an electron hops only to sites of lower energy. The rate of direct, tunneling-type hopping Γ for single electrons depends exponentially on the distance R between localized sites according to

$$\Gamma(R) = \Gamma_1 \exp(-2R/a), \tag{1}$$

where Γ_1 is the attempt-to-escape frequency and a is the larger of the localization lengths of the initial and final states. With each additional hop, the number of sites available for the next hop drops and, on average, the hops grow in length. Since more distant hops proceed more slowly, the relaxation has the property of slowing over ever-lengthening time scales. For example, if the density of localized states is a simple exponential

$$g(E) = \frac{N}{E_0} \exp(-E/E_0), \tag{2}$$

the energy of the particle evolves [1] according to

$$E(t) \approx 2E_0 \ln\ln \Gamma_1 t. \tag{3}$$

In Eqs. (2), (3), E_0 is the energy which characterizes the band tailing, N is the total concentration of localized states, and the localization energy E is measured in the positive sense from the mobility edge to the gap center. The very slow energy relaxation of Eq. (3) results from the combined effects of exponentially fewer available sites at low energies, together with the exponentially small rate of hopping over long distances.

The situation is different for composite particles such as excitons. For those particles, hopping may be mediated by the direct mechanism outlined above and expressed in Eq. (1), or may proceed via an exchange coupling. In particular, excitons may hop via exchange of a virtual photon (dipole-dipole coupling) [2,3]. The probability of this hop scales with distance as

$$\Gamma(R) = \Gamma_2 (R_0/R)^6. \tag{4}$$

A comparison of Eqs. (1) and (4) shows that the dipole-dipole mechanism should dominate for large hopping lengths. However, if the intersite distance R is comparable to the exciton Bohr radius or the localization length, wave function overlap between localized excitons is not negligible, and the tunneling-type transfer can be relevant. It is not possible to calculate theoretically from first principles which of Eqs. (1) or (4) should be applied for a particular experimental situation [3].

Dipole-dipole hopping is well documented in organic crystals, and figures in theories of exciton relaxation in semiconducting structures based on III-V and II-VI compounds. (See references in [2].) Nevertheless, there has been no clear experimental verification of this effect in, e.g., GaAs quantum wells, in spite of the enormous literature on exciton dynamics in such structures. Here, we present data on the slow energy relaxation of excitons in GaAs quantum structures, and compare to theoretical predictions based on the direct tunneling and dipole-dipole hopping mechanisms.

The principle prediction for excitonic energy relaxation mediated by the tunneling mechanism is contained in Eq. (3). The corresponding result for dipole-dipole hopping is obtained as follows. At an observation time t, excitons have relaxed within the tail states via some number of hops. The average hopping time of each of these hops is considerable shorter than t. The excitons form a distribution around an average energy E_d below the mobility edge [1]. The hopping time for the next hop is, on average, larger than t. The energy E_d of the packet is thus related to the time t by the condition

$$\Gamma(R(E_d)) \approx t^{-1}, \tag{5}$$

where, in the two-dimensional system under study,

$$R(E_d) \approx [\pi N(E_d)]^{-1/2} \tag{6}$$

is the average distance between states with localization energies greater than E_d, and having an interface concentration

$$N(E_d) = \int_{E_d}^{\infty} g(E)\, dE. \tag{7}$$

Using Eqs. (4)–(7), we obtain a relation between the energy E_d and the corresponding time t

$$E_d(t) = (E_0/3)\ln(\pi^3 R_0^6 N^3 \Gamma_2 t). \quad (8)$$

Equation (8) is the result for the dipole-dipole mechanism, and contains two main predictions. The first is a much faster $\ln t$ energy decay compared to the $\ln\ln t$ decay of Eq. (3). This faster relaxation results from the power law decay of the hopping rate with hop length, compared to the exponential form of Eq. (1). Equation (8) also makes a specific connection between the rate of energy loss and the density of states parameter. In particular, we have

$$\frac{\partial E_d}{\partial \ln t} = \frac{1}{3} E_0 . \quad (9)$$

Equations (3) and (8) describe only the long-time behavior. This behavior is probably not accessible using ordinary quantum structures in which the radiative lifetime of excitons is less than one nanosecond. Here, we employ a double well structure to create spatially indirect excitons whose radiative lifetime can be varied between nanoseconds and microseconds. Using these long-lived excitons, we can track the energy relaxation deep into the band tails. Specifically, the sample consists of 15 nm and 10 nm GaAs quantum wells separated by a 3 nm $Al_{0.3}Ga_{0.7}As$ barrier, and embedded in the 1 μm thick intrinsic layer of an $Al_{0.3}Ga_{0.7}As$ pin diode. This arrangement allows for the application of an electric field along the growth direction. As described elsewhere [5], this electric field permits us to bias the system to a type II (spatially indirect) condition in which the lowest lying interband excitations consist of electron and hole confined to separate well layers. In this case, the small electron-hole overlap assures a long radiative lifetime. The sample was held in an optical cryostate at temperature $T = 1.4$ K and excited using 1.0 nsec pulses from a laser diode operated at 100 kHz repetition rate. The photon energy 2.0 eV exceeded the band gap of the $Al_{0.3}Ga_{0.7}As$ layers. The pair density is estimated to be 10^9 cm^{-2}. Time-resolved luminescence spectra were acquired using the time-correlated photon counting technique. The average energy per particle is taken as the centroid of the time-resolved spectrum. The emission rate is determined as the spectrally integrated signal.

Figure 1 shows the time evolution of the emission rate for the bias $V = -3.5$ V (electric field ≈ 50 kV/cm). The emission is exponential over the 5 μsec range studied. As discussed in detail elsewhere [6], this exponential feature is characteristic of excitonic recombination. Slower, power law decay at longer times and/or weaker electric fields correspond to distant pair recombination and is not the subject of this work.

Figure 2(a) shows the time dependence of the mean energy over 2.5 decades of time. Each data point is labeled by an error bar which indicates a >50% confidence interval. The error bars are determined by the shot noise inherent to the detection process, and are calculated as $\Delta E/N^{1/2}$, where ΔE is the full width at half maximum of the corresponding time-resolved spectrum, and N is the number of counts in the spectrum. A best fit to Eq. (8) is obtained for a slope parameter 0.419 meV/e-fold corresponding [throufgh Eq. (9)] to a density of states parameter $E_0 = 1.26$ meV. The goodness of fit may be estimated using the normalized

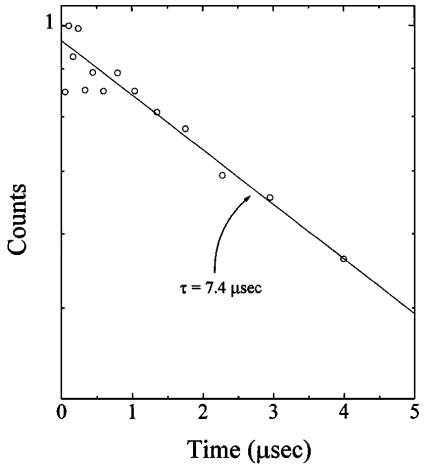

FIG. 1. Spectrally integrated photoluminescence decay.

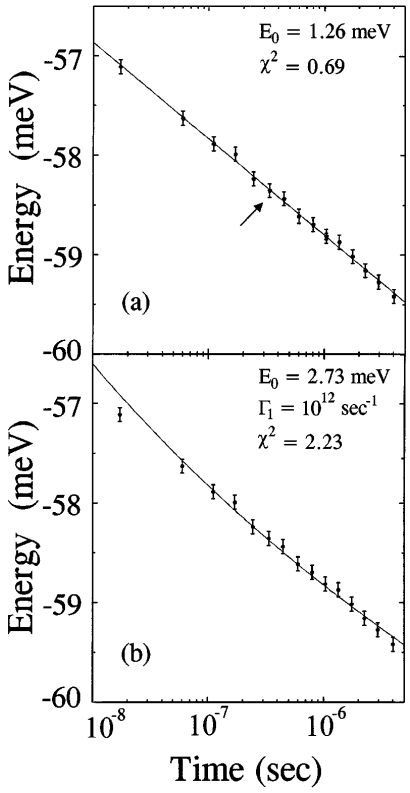

FIG. 2. Time evolution of the mean energy references to 1.519 eV. In (a), the data are compared to a best fit to Eq. (8). In (b), the same data are compared to a fit based on Eq. (3). The parameters are discussed in the text. The arrow in (a) indicates the time corresponding to the spectrum of Fig. 3.

chi-squared (χ^2) statistic [7] using the reciprocal confidence intervals as weights. The result is $\chi^2 = 0.69$. The χ^2 statistic is distributed in a well known way [7], and has been tabulated. In the present case of 13 degrees of freedom (= number of data points − fitting parameter) a χ^2 at least as large as 0.69 is 77% probable. We conclude that the data follow Eq. (8) very closely, with small, random deviations at a statistically reasonable level.

Figure 2(b) compares the same experimental data to Eq. (3) for the case $\Gamma_1 = 10^{12}$ sec^{-1}. Equation (3) is concave up when plotted versus $\ln t$, and deviates from the data systematically. A best fit is obtained for $E_0 = 2.73$ meV. The normalized χ^2 statistic in this case is $\chi^2 = 2.23$ and is less than 1% likely. That is, there is less than 1% change that Eq. (3), together with random error at a statistically reasonable level, could result in the present data. The χ^2 statistic essentially rules out the model of Eq. (3).

Possibly, the fit to Eq. (3) could be improved by allowing other attempt frequencies. Table I shows the results of fits to Eq. (3) using a series of Γ_1's. As Γ_1 is increased, the χ^2 improves until it reaches a minimum near $\Gamma_1 = 10^{15}$ sec^{-1}. Even this minimum value is only 15% likely, however, and it entails the use of an attempt frequency which is unphysically large.

The density of states parameter provides an additional point for comparison of the two models. E_0 was determined independently from the time-resolved photoluminescence spectrum shown in Fig. 3. The spectrum is taken at $t = 0.36$ μsec, corresponding to the point marked by the arrow in Fig. 2(a). The low energy tail of the photoluminescence spectrum is well described by Eq. (2) with $E_0 = 1.0$ meV. While there is no theory of the transient emission line shape [8], we expect the tailing parameter to be close to this value.

The fit to the dipole-dipole model [Fig. 2(a)] gives $E_0 = 1.26$ meV and is in good agreement with the photoluminescence result. The fit to the tunneling hopping model [Fig. 2(b)] gives $E_0 = 2.73$ meV which, though not impossible, is not in good agreement with the photoluminescence result. Table I shows that as the fit to Eq. (3) is adjusted to improve the χ^2 statistic, the resulting E_0 grows and agrees less and less well with the PL result. For $\Gamma_1 \leq 10^{14}$ sec^{-1}, Eq. (3) is rejected because of poor fit, while for $\Gamma_1 \geq 10^{15}$ sec^{-1}, is it rejected by reason of unphysical parameters.

TABLE I. Various fits of Eq. (3) to the data shown in Fig. 2 are given. For each set of parameters E_0 and Γ_1, the χ^2 statistic is given, together with is probability.

Γ_1 (sec^{-1})	E_0 (meV)	χ^2	Probability (%)
10^{10}	1.74	4.11	<0.1
10^{11}	2.24	2.86	0.1
10^{12}	2.73	2.23	1
10^{13}	3.24	1.87	3.5
10^{14}	3.72	1.63	7
10^{15}	4.22	1.47	15

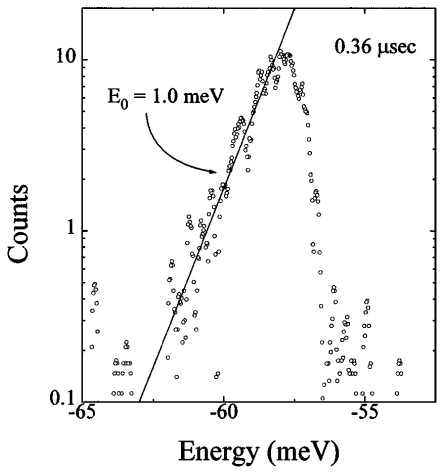

FIG. 3. Photoluminescence spectrum at $t = 0.36$ μsec. The low energy side of the peak is well described by an exponential with (reciprocal) slope 1.0 meV/e-fold.

We next mention an alternative explanation of the present data using the tunneling hopping mechanism characterized by Eq. (1). The $\ln t$ relaxation of the energy is predicted if we adopt the density of states

$$g(E) \sim E^{\sim 3}, \tag{10}$$

together with Eq. (1). However, this choice is contradicted by data such as Fig. 3, and has no apparent theoretical basis.

In conclusion, we have exploited the long radiative lifetime of spatially indirect excitons to explore the energy dynamics in the hopping regime. Under a variety of conditions, we find that the mean energy decays with the logarithm of the time. This result is explained easily in a model which includes an exponential density of localized states and dipole-dipole hopping. The exponential density of states is supported by the time-resolved photoluminescence data. An alternative explanation, based on direct hopping and a $1/E^3$ density of states is unsupported. The dipole-dipole model also achieves semiquantitative agreement with the observed energy loss rates.

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[1] D. Monroe, Phys. Rev. Lett. **54**, 146 (1985).
[2] T. Takagahara, Phys. Rev. B **31**, 6552 (1985).
[3] T. Takagahara, J. Lumin. **44**, 347 (1989).
[4] There is a very large literature on the energy relaxation of excitons. Here, we have given only a few references directly relevant to the issue of dipole-dipole versus direct tunneling-type hopping.

[5] J. E. Golub, P. F. Liao, Y. Prior, D. J. Eilenberger, J. P. Harbinson, and L. T. Florez, Appl. Phys. Lett. **53**, 2584 (1988).
[6] J. E. Golub, S. D. Baranovskii, and P. Thomas (to be published).
[7] P R. Bevington, *Data Reduction and Error Analysis for the Physical Sciences* (McGraw-Hill, New York, 1969).
[8] A theory of the emission line shape under continuous excitation conditions is given in A. Reznitsky, S. D. Baranovskii, A. Tsekoun, and C. Klingshirn, Phys. Status Solidi B **184**, 159 (1994).