Nondiffusive excitonic transport in GaAs and the effects of momentum scattering

A. C. Schaefer, J. Erland,* and D. G. Steel
The Harrison M. Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan 48109
(Received 15 July 1996)

Measurements of exciton transport using frequency-domain nearly degenerate four-wave mixing (NDFWM) show a failure of Fick's law and near-ballistic excitonic motion for scale lengths less than 10 μm. A solution of the Boltzmann transport equation assuming a simple momentum-changing collision model is in agreement with the observed NDFWM line shapes and apparent subquadratic dependence on inverse scale length. The measurements show the surprising result that exciton-exciton interactions lead to a large increase in exciton linewidth with little corresponding change in exciton center-of-mass momentum, unlike exciton interactions with phonons and impurities.

The nature of exciton motion in crystals such as semiconductors has been a topic of great interest for over six decades. Although it is clearly established that exciton motion results in significant transfer of energy in a lattice,[1] the understanding of the microscopic details of the dynamics involved remains incomplete. Several theoretical pictures have been developed to describe exciton motion in crystals,[2] beginning with the early ideas of Frenkel[3] based on coherent transfer between lattice sites. The transport properties of the exciton polariton, the coupled exciton-photon mode which is an eigenstate of an ideal crystal, have also been considered in detail.[4]

Because of the numerous strong interactions of excitons with the crystal environment (e.g., phonons, impurities, etc.), the consideration of classical transport equations provides a useful formalism for describing the motion, irrespective of the underlying microscopic transfer mode.[2] The description of the exciton as a diffusing particle, obeying Fick's law, has proved especially relevant. In semiconductors, the study of exciton diffusion has furthered understanding of exciton interactions with interface roughness in multiple quantum wells,[5–8] exciton scattering with phonons and impurities in bulk materials,[9–12] and the dynamics of biexcitons.[13]

In the consideration of classical transport, it is known that the diffusive limit is valid only when the mean free path is much less than any spatial variation in the density.[2] It is expected that a regime of near-ballistic transport will be observed if the scale length resolution of the experiment approaches the mean free path. In this paper we report the observation of such transport for excitons using a traveling-wave grating technique based on frequency domain (cw) nearly degenerate four-wave mixing (NDFWM) in GaAs at low temperature. In this case, description of the motion by the Boltzmann transport equation is more appropriate. It is found that the observed motion is sensitive to the amount of momentum scattering, and that for increased scattering the transport becomes diffusive. Moreover, it is shown that exciton interactions with phonons and impurities lead to an increase in both the exciton linewidth (which measures the dephasing rate of the dipole coherence) and exciton momentum scattering rate, unlike exciton-exciton interactions, which appear to lead to large dephasing with little corresponding effect on exciton momentum. This observation leads to questions of the fundamental relationship between momentum scattering and exciton dephasing.

Exciton transport was investigated in several high-quality molecular-beam-epitaxy grown GaAs layers (surrounded by two $Al_{0.3}GaAs_{0.7}As$ layers and a multiple-quantum-well structure) of various thicknesses (200, 300, and 500 nm). The samples were mounted on a sapphire disk and placed in a helium immersion cryostat (the temperature was varied from 4 to 60 K). The light-hole–heavy-hole (lh-hh) degeneracy was lifted by uniaxial strain.[11] The typical full width at half maximum (FWHM) linewidth of the homogeneously broadened absorption spectrum at the 1s lh exciton is 0.3 meV at 4 K. The experiments employed argon-ion pumped frequency-stabilized Styryl 9 dye lasers (linewidths <5 neV) tuned to the exciton resonance. Exciton densities were approximately 10^{15} cm^{-3} (estimated with a 400-μm spot radius, intensity of 10 W/cm^2 and 1 ns radiative lifetime).

In the NDFWM configuration, as shown in Fig. 1(a), two laser beams, represented by fields $\mathbf{E}_1(\omega_1,\mathbf{k}_1)$ and $\mathbf{E}_2(\omega_2,\mathbf{k}_2)$ $(|\omega_2-\omega_1|=|\delta|\ll\omega_1,\omega_2)$, intersect in the sample at a small angle θ, producing a traveling wave modulation of absorption and dispersion. The resulting exciton population grating is probed by a third beam, $\mathbf{E}_3(\omega_3,\mathbf{k}_3)$ $(\omega_3=\omega_1)$, giving rise to a nonlinear signal propagating in the $-\mathbf{k}_2$ direction (the contribution from the grating formed by $\mathbf{E}_1$ and $\mathbf{E}_3$ was minimized by setting $\mathbf{E}_3\perp\mathbf{E}_1,\mathbf{E}_2$.[14]) For small angles, the grating spacing is given by $\Lambda=\lambda/2\sin(\theta/2)$ (λ is the wavelength). One of the powerful features of the NDFWM optical-grating experiment is that a large range of scale lengths can be probed for the study of exciton transport along the grating (in the direction $\mathbf{k}_1-\mathbf{k}_2$) by simply varying θ; in these experiments grating spacings from 2 to 40 μm were accessed. The population grating decays by energy relaxation, radiative recombination, and spatial motion that washes out the grating. These dynamics are studied by measuring the nonlinear signal as a function of the frequency difference δ.

In the limit of purely diffusive motion, the cw nonlinear signal for a single excitation grating is a Lorentzian with a full width given by 2Γ (Γ is the grating decay rate), where $\Gamma=\gamma_{rec}+4\pi^2D/\Lambda^2$ (D is the diffusion coefficient and γ_{rec} is the recombination rate) and Γ is quadratic with the inverse grating spacing (Λ^{-1}) (for examples of diffusion studies us-

0163-1829/96/54(16)/11046(4)/$10.00

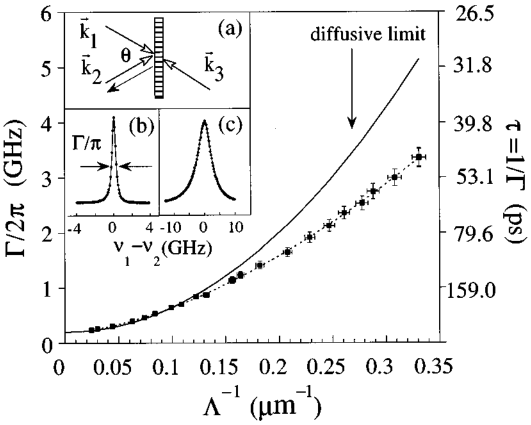

FIG. 1. Decay rate of the optical grating signal Γ as a function of Λ^{-1}. Data taken at the lh (1*s*) exciton in GaAs at 4 K with an exciton density of 8×10^{14} cm^{-3}. Dashed line, the illustrative power-law fit mentioned in the text with $n=1.6$ (nondiffusive behavior). Solid line, a quadratic fit, shown for comparison. Insets: (a) Optical grating experiment in the cw-phase conjugate geometry. (b) FWHM signal as a function of $(\nu_1-\nu_2)=\delta/2\pi$ for $\Lambda=23$ μm and (c) for $\Lambda=3$ μm. Solid lines are a fit to a Lorentzian.

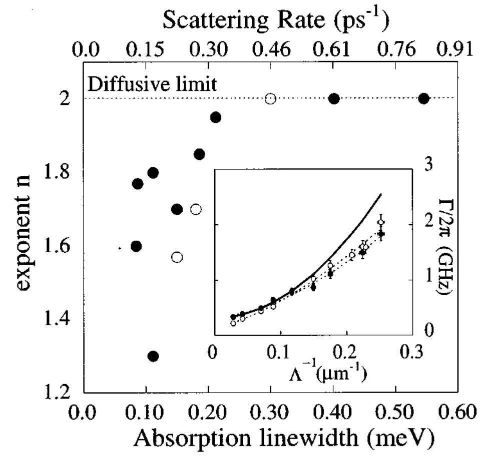

FIG. 2. Dependence fo the exponent n of the power-law fit on the absorption linewidth (half width at half maximum). Note the transition to diffusive behavior for larger linewidths (assumed as a measure of scattering rates). Solid circles, linewidth variations due to sample variations in impurity scattering rates. Open circles, linewidth variations by an increase in temperature from 4 to 60 K (acoustic-phonon scattering). Inset, dependence of transport behavior at 4 K on increased exciton-exciton interactions. Solid circles, data taken at lh at density of 2×10^{14} cm^{-3} with no pump. Dotted line, a fit with $n=1.6$. Open circles, with strong incoherent, resonant pump (at lh), increasing density to 1×10^{15} cm^{-3} (and dephasing rate by 70%). Dotted line, a fit with $n=1.4$. Solid line is a quadratic fit, for comparison.

ing optical gratings, see Refs. 7 and 10–12).The experimental nonlinear signal, fitted with a Lorentzian, is shown in Figs. 1(b) and 1(c), where the dependence on grating spacing is clearly seen. It is observed, however, as shown in Fig. 1, that the dependence of Γ on Λ^{-1} deviates from quadratic for small Λ ($\Lambda<10$ μm).[15] The subquadratic dependence on Λ^{-1} is clearly shown in Fig. 1 with the illustrative power-law fit (not related to any model) of $\Gamma=A+B(1/\Lambda)^n$, with $n=1.6$. The deviation from quadratic dependence indicates that the scale length resolution of the experiment is approaching the mean free path and the diffusive limit is no longer valid.

The observation of near-ballistic transport is dependent on the momentum scattering rate (which determines the mean free path). For example, when the exciton-phonon scattering rate was increased by raising the temperature from 4 to 60 K, a transition was observed from the near-ballistic behavior to diffusive behavior (with $D=120$ cm^2/s at 60 K). This dependence on momentum scattering rate is a general trend, as shown in Fig. 2, where the exponent n of the power-law fit is shown as a function of exciton linewidth, and a clear transition between the near-ballistic and diffusive regimes is seen.

It is found, however, that not all interactions which increase the linewidth contribute strongly to exciton-momentum scattering. As shown in the inset of Fig. 2, when the exciton density was increased by a fourth resonant laser beam, increasing the exciton linewidth and dephasing rate by about 70% through exciton-exciton interactions,[16] the transport behavior changes little. In fact, where a transition from near-ballistic to diffusive behavior is expected, the motion becomes slightly *more* ballistic, most likely due to a saturation of impurity scattering.[6]

To phenomenologically and qualitatively understand these experiments we consider the Boltzmann transport equation for excitons as a dilute gas of particles with center-of-mass velocities **v** undergoing momentum- (or velocity) changing collisions (with unspecified perturbers). The optically excited exciton density is described by

$$\left[\frac{\partial}{\partial t}+\mathbf{v}\cdot\nabla\right]N(\mathbf{v},\mathbf{r},t)=-\gamma_{\mathrm{rec}}(\mathbf{v})N(\mathbf{v},\mathbf{r},t)+G(\mathbf{v},\mathbf{r},t)+\left(\frac{\partial N}{\partial t}\right)_{\mathrm{coll}},\qquad(1)$$

where $\gamma_{\mathrm{rec}}(\mathbf{v})$ is the recombination rate and $G(\mathbf{v},\mathbf{r},t)\propto|\mu|^2E_1E_2^*e^{i[(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{r}+(\omega_2-\omega_1)t]}F(\mathbf{v})$ is the generation rate of the optical grating (to lowest order in the applied fields). The velocity-dependent recombination and generation rates account for momentum conservation (in the dipole approximation only excitons with $|\mathbf{v}|=|\hbar\mathbf{K}_{\mathrm{ex}}/m_{\mathrm{ex}}^*|=0$ are optically accessible). For the following solution it is assumed that $\gamma_{\mathrm{rec}}(\mathbf{v})=\gamma_{\mathrm{rec}}$ and $F(\mathbf{v})=1$ when $|\mathbf{v}|\leqslant\Delta v$ and $\gamma_{\mathrm{rec}}(\mathbf{v})=F(\mathbf{v})=0$ when $|\mathbf{v}|>\Delta v$ (Δv represents a small spread in velocity around $|\mathbf{v}|=0$ due to a relaxation in the momentum selection rule).[17] The consideration of other forms of $\gamma_{\mathrm{rec}}(\mathbf{v})$ and $F(\mathbf{v})$ does not change the predicted form for the exciton transport obtained below.

The last term in Eq. (1) describes the evolution of the population due to momentum (velocity)-changing collisions and is given by

$$\left(\frac{\partial N}{\partial t}\right)_{\mathrm{coll}}=-\Gamma_M(\mathbf{v})N(\mathbf{v})+\int A(\mathbf{v}'\to\mathbf{v})N(\mathbf{v}')d^3v'$$
$$\cong-\Gamma_MN+\Gamma_MW(\mathbf{v})\overline{N},\qquad(2)$$

where $A(\mathbf{v}'\to\mathbf{v})$ is the collision kernel and Γ_M is the momentum (velocity)-changing collision rate. For the solution below, the final form of Eq. (2) is taken in the so-called strong collision limit,[18] where Γ_M is independent of **v**,

$\overline{N}=\int N(\mathbf{v})d^3v$ and $W(\mathbf{v})=(\sqrt{\pi}u)^{-3}e^{-v^2/u^2}$ is a Maxwellian distribution with $u=\sqrt{2kT/m_{\rm ex}^*}$. A full consideration of the scattering kernel for excitonic interactions with various perturbers (i.e., phonons) would be a refinement of this model; however, the basic qualitative features of the transport data are adequately described with the limiting assumption of an effective collision rate Γ_M.

The third-order contribution to the cw polarization in the phase-conjugate geometry is proportional to $N(\mathbf{v},\mathbf{r},t)$ integrated over the optically accessible states. While the complete expression is complex, it simplifies considerably in the limit that $\Gamma_M \gg \gamma_{\rm rec}$ as in GaAs (essentially, only the quasithermalized population contributes significantly to the polarization). In this limit,

$$P^{(3)}(\delta)\approx \frac{K|\mu|^4E_1E_2^*E_3}{\left\{\gamma_{\rm rec}^{\rm eff}+\Gamma_M\left[1+\Gamma_M\left(\frac{i}{ku\theta}\right)Z(\xi)\right]\right\}}, \qquad (3)$$

where $\gamma_{\rm rec}^{\rm eff}=(\Delta v/\sqrt{\pi}u)^3\gamma_{\rm rec}$ is an effective recombination rate of the quasithermalized population,[19] k is a constant, and

$$Z(\xi)=\frac{1}{u\sqrt{\pi}}\int_{-\infty}^{+\infty}\frac{e^{-(v_x/u)^2}}{(v_x/u)-\xi}\,dv_x$$

is the plasma dispersion function with $\xi=(-\delta+i\Gamma_M)/ku\theta$ (v_x is the velocity component parallel to $\mathbf{k}_1-\mathbf{k}_2$ and $|\mathbf{k}_1|\approx|\mathbf{k}_2|=k$).

The important parameter determining the nature of the detected spatial motion is $\Gamma_M/ku\theta=\Lambda/2\pi l$, or the ratio of the grating spacing to the effective collisional scale length defined by $l=u/\Gamma_M$. This can be seen by an asymptotic expansion of $Z(\xi)$ in Eq. (3), which gives (including the first three terms in the expansion)

$$P^{(3)}(\delta)\approx\frac{K|\mu|^4E_1E_2^*E_3}{\left\{i\delta+\gamma_{\rm rec}^{\rm eff}+\Gamma_M\left[\frac{1}{2}\left(\frac{2\pi l}{\Lambda}\right)^2-\frac{3}{4}\left(\frac{2\pi l}{\Lambda}\right)^4\right]\right\}}. \qquad (4)$$

The resulting nonlinear signal, $|P^{(3)}|^2$, is a Lorentzian with a width given by

$$\Gamma=\gamma_{\rm rec}^{\rm eff}+\Gamma_M\left[\frac{1}{2}\left(\frac{2\pi l}{\Lambda}\right)^2-\frac{3}{4}\left(\frac{2\pi l}{\Lambda}\right)^4\right],$$

which has an obvious deviation from quadratic dependence on Λ^{-1} when $\Lambda\leqslant 2\pi l$. When $\Lambda\gg 2\pi l$, the quadratic dependence on Λ^{-1} is recovered and *diffusive motion* is described [with an effective $D=(u^2/2\Gamma_M)$]. A fit of the data shown in Fig. 1 to the expansion in Eq. (4) (fit not shown) gives an approximate measure of $\Gamma_M=0.3$ ps^{-1} and $l=0.2$ μm (this gives an estimate of $u=6\times10^6$ cm/s, which is close to the expected thermal value at 4 K).

Given an effective critical length scale of $2\pi l\approx 1$ μm, it is surprising that a deviation from diffusive behavior is so clearly seen for experimental lengths over several micrometers. This result, however, which is described by the transport equation, illustrates the sensitivity of the optical grating experiment. Figure 3 shows the experimental behavior is described in general by the unexpanded solution (3), including the subquadratic dependence of Γ on Λ^{-1} for $\Gamma_M/ku<1$ and the continuous transition to diffusive behavior with increasing momentum scattering.

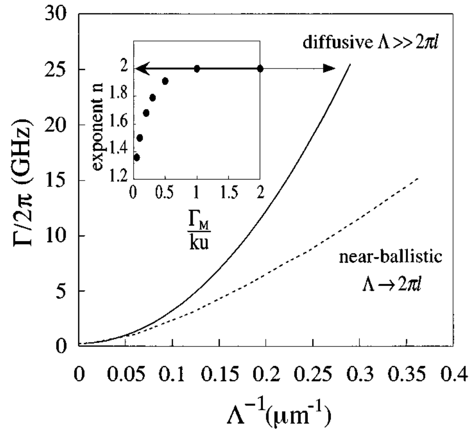

FIG. 3. Decay rate of the optical grating as a function of Λ^{-1}, predicted by a solution of the transport equation (3), with $\Gamma_M/ku=0.1$ (dashed line). Solid line is a quadratic (diffusive limit), for comparison. Inset: calculated dependence of the exponent n of a power-law fit of grating decay rates for various ratios Γ_M/ku. In these plots, $ku=0.46$ ps^{-1}.

It should be noted that Wong and Kenkre predict similar nondiffusive behavior for an optical grating experiment using a discrete space master equation.[20] Their model, derived for molecular crystals, considers incoherent transport over a characteristic distance a, and also gives nonquadratic dependence of Γ on Λ^{-1} for $\Lambda\leqslant 2\pi a$ and a transition to diffusive behavior as $a\to 0$.

The observation that increasing exciton density greatly effects the dephasing but does not change the qualitative behavior of the transport raises questions about the connection between dephasing and momentum scattering. It has been previously observed that the dephasing rate is not equal to the momentum scattering rate measured through transport. Oberhauser *et al.* reported a momentum scattering rate due to interface roughness much greater than the dephasing rate in GaAs quantum wells, attributed to different scattering mechanisms dominating the thermalization and transport processes.[7] Wang *et al.* also observed a greater momentum scattering rate than dephasing rate, which they attributed to a breakdown of the impact approximation.[21] Our observation, however, may indicate that the dephasing mechanism due to exciton-exciton interactions is only weakly correlated to exciton momentum scattering.[22]

In conclusion, traveling wave optical grating experiments in GaAs show a significant deviation from diffusive behavior. These measurements illustrate that a regime of near-ballistic exciton transport can be observed in high-quality semiconductors and the behavior is adequately described by the Boltzmann transport equation.

We acknowledge P. Berman and D. Citrin for helpful discussions. This work was supported by the Air Force Office of Scientific Research and the Army Research Office. J.E. acknowledges support from the Danish Research Academy.

*Present address: Grundfos A/S Afd. 3800, Poul Due Jensen's Vej 7, DK-8850 Bjerringbro, Demark

[1] See, for example, P. L. Gourley and J. P. Wolfe, Phys. Rev. B **20**, 3319 (1979).

[2] For a review, see V. M. Agranovich and M. D. Galanin, *Electronic Excitation Energy Transfer in Condensed Matter* (North-Holland, New York, 1982); R. S. Knox, in *Collective Excitations in Solids*, edited by B. D. Bartolo and J. Danko (Plenum, New York, 1983).

[3] J. Frenkel, Phys. Rev. **37**, 17 (1931).

[4] See, for example, C. Flytzanis, G. M. Gale, and F. Vallee, in *Frontiers in Nonlinear Optics*, edited by H. Walther, K. Koroteev, and M. O. Scully (Institute of Physics, Philadelphia, 1993), pp. 107. See also reference in Ref. 17.

[5] J. Hegarty and M. D. Sturge, J. Opt. Soc. Am. B **2**, 1143 (1985).

[6] H. Hillmer, S. Forchel, S. Hansmann, M. Morohashi, E. Lopes, H. P. Meier, and K. Ploog, Phys. Rev. B **39**, 10 901 (1989).

[7] D. Oberhauser, K.-H. Pantke, J. M. Hvam, G. Weimann, and C. Klingshirn, Phys. Rev. B **47**, 6827 (1993).

[8] S. T. Cundiff, H. Wang, and D. G. Steel, Phys. Rev. B **46**, 7248 (1992).

[9] N. N. Zinov'ev, L. P. Ivanov, I. G. Lang, S. T. Pavlov, A. V. Prokaznikov, and I. D. Yaroshetskii, Zh. Eksp. Teor. Fiz. **84**, 2153 (1983) [Sov. Phys. JETP **57**, 1254 (1983)].

[10] J. Erland, B. S. Razbirin, K.-H. Pantke, V. G. Lyssenko, and J. M. Hvam, Phys. Rev. B **47**, 3582 (1993).

[11] M. Jiang, H. Wang, R. Merlin, M. Cardona, and D. G. Steel, Phys. Rev. B **48**, 15 476 (1993).

[12] V. Mizeikis, V. G. Lyssenko, J. Erland, and J. M. Hvam, Phys. Rev. B **51**, 16 651 (1995).

[13] J. C. Kim, D. R. Wake, and J. P. Wolfe, Phys. Rev. B **50**, 15 099 (1994).

[14] In GaAs, the grating contribution from interactions between copolarized fields is at least an order of magnitude greater than that for orthogonally polarized fields; see H. Wang, K. Ferrio, D. G. Steel, Y. Hu, R. Binder, and S. Koch, Phys. Rev. Lett. **71**, 1261 (1993).

[15] Initial measurements of the nonquadratic behavior were first reported by H. Wang *et al.*, *Proceedings for the International Quantum Electronics Conference* (Optical Society of America, Anaheim, 1990), Vol. 8.

[16] L. Schultheis, J. Kuhl, A. Honold, and C. W. Tu, Phys. Rev. Lett. **57**, 1635 (1986).

[17] For a discussion of optically accessible momentum distributions, see L. C. Andreani, in *Confined Electrons and Photons: New Physics and Applications*, edited by E. Burstein and C. Weisbuch (Plenum, New York, 1995), p. 57.

[18] This assumption is functionally equivalent to taking the relaxation time approximation. For an application of the strong collison limit in an atomic gas, see M. Gorlicki, G. Khitrova, and P. R. Berman, Phys. Rev. A **37** 4340 (1988).

[19] Even with the simplified assumptions of this model, the consideration that only a finite range of velocity states is available for radiative decay leads to a modified recombination rate for the quasithermalized population. A more accurate treatment of the scattering kernels and form of the optically created velocity distribution may quantitatively describe the radiative recombination rate. For a general discussion of the connection between thermalization and radiative recombination, see Ref. 17.

[20] Y. M. Wong and V. M. Kenkre, Phys. Rev. B **22**, 3072 (1980).

[21] H. Wang, J. Shah, T. C. Damen, and L. N. Pfeiffer, Phys. Rev. Lett. **74**, 3065 (1995).

[22] C. Lonsky, P. Thomas, and A. Weller, Phys. Rev. Lett. **63**, 652 (1989).