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# Giant oscillator strength of free excitons in GaAs

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The radiative lifetime of free excitons in GaAs is unambiguously determined for the first time using ultrapure material grown by molecular-beam epitaxy. Its value amounts to $3.3 \pm 0.5$ ns in the limit of very low temperatures. Consequently, the oscillator strength of free excitons is on the order of unity, in contrast to what commonly is deduced from the total absorption cross section. At excitation densities above 0.5 W/cm$^2$ we have observed the radiative recombination of excitonic molecules (biexcitons) at 1.5146 eV in accordance with theoretical considerations.

In this Rapid Communication we report on our findings concerning the transition probability of Wannier excitons in a semiconductor. GaAs is taken as a test case. We will show that the radiative lifetime is small and, consequently, the transition probability large. This is in contrast to theoretical considerations and unexpected from the strength of the absorption line.

The strength of an optical transition is commonly expressed in terms of a dimensionless quantity, $f$, the oscillator strength. Experimentally, the oscillator strength can be deduced from the total absorption cross section. For excitonic transitions in semiconductors the appropriate relation is[1,2]

$$Nf = \frac{4m_0\epsilon_0 c\tilde{n}}{e^2 h} \int \alpha(E)dE \; . \tag{1}$$

Here $\tilde{n}$ is the refractive index, $\alpha$ is the absorption coefficient, $E$ is the photon energy, and $N$ is the number of unit cells per volume; $m_0$, $\epsilon_0$, $c$, $e$, and $h$ are fundamental physical constants with their usual meaning. Segall and Marple[2] have made a systematic study of the oscillator strength for II-VI compounds. They obtained values on the order of $10^{-3}$–$10^{-4}$. The transition probability per molecule is thus quite low, but because of the large concentration the absorption coefficient can still be around $10^4$–$10^5$ cm$^{-1}$. For GaAs we obtain in this way a value of $7\times10^{-5}$ for the oscillator strength. The small values for $f$ have been attributed to the small probability of finding the electron at the position of the hole, e.g., at a particular unit cell.[3,4] The transition probability is thus proportional to the ratio of unit-cell volume and exciton volume $(a/a_{\mathrm{ex}})^3$. The values for $f$ cited above correspond to this ratio. For GaAs, for instance, the unit-cell length $a = 5.6$ Å and the excitonic Bohr radius $a_{\mathrm{ex}} = 120$ Å so that $(a/a_{\mathrm{ex}})^3 = 1\times10^{-4}$.

Apart from the absorption lines of free excitons, other sharp lines near the fundamental band edge of semiconductors have been observed in numerous experiments. They are assigned to excitons bound to donors or acceptors. However, the concentration of impurities is generally many orders of magnitude smaller than that of regular molecules. The appearance of bound-exciton lines in absorption spectra is thus unexpected. This controversy was explained for the first time by Rashba and Gurgenishvili,[5] who introduced the concept of giant oscillator strength $f_{\mathrm{BE}}$ for bound excitons. This concept implies that

$$f_{\mathrm{BE}} = \left(\frac{a_{\mathrm{ex}}}{a}\right)^3 f \; . \tag{2}$$

Thus, the oscillator strength of bound excitons almost equals unity and is 4 or 5 orders of magnitude larger than that for free excitons.

The transition probability is related not only to the strength of the absorption lines but also to the radiative lifetime $\tau$ of the excited state:[1]

$$\tau = \frac{2\pi\epsilon_0 m_0 c^3}{\tilde{n}e^2\omega^2 f} \; . \tag{3}$$

For bound excitons with an oscillator strength of unity the radiative lifetime is expected to be in the nanosecond time domain. Henry and Nassau[6] have verified this for CdS and have found a lifetime of 0.5 ns for donor-bound excitons and 1.0 ns for acceptor-bound excitons. In contrast, free excitons having low oscillator strength are expected to exhibit very long lifetimes. In the case of GaAs, using Eq. (3) one calculates a value of 40 $\mu$s for the radiative lifetime of the free exciton. However, the measured lifetime will usually be much shorter due to trapping of the free excitons by impurities and subsequent fast recombination. The measured lifetime is an effective and not a radiative one and will depend on the amount of impurities present in the sample. Hwang[7] found indeed that the effective free-exciton lifetime in GaAs decreased progressively from 2.9 to 1.1 ns when the mobility at 77 K decreased from $1.28\times10^5$ to $1.0\times10^5$ cm$^2$/Vs.

In recent years, the preparation of GaAs has improved tremendously. We have studied the free-exciton lifetime in ultrapure GaAs in which the defect-related recombination can be saturated and thus the true radiative lifetime is obtained.

The material was grown by molecular-beam epitaxy with a Varian GEN II machine. The growth conditions were such that the arsenic flux was minimal to get an As-stable surface, and the substrate temperature was 630 °C. The growth rate was 1 monolayer/sec for GaAs and correspondingly higher for Al-containing layers. Under these circumstances, the upper limit for background impurity levels in GaAs is about $2\times 10^{14}$ $\mathrm{cm}^{-3}$ for both donors and acceptors. For more details on crystal growth, see Ref. 8. The structure was grown on a Si-doped (001)-oriented substrate and consisted of the following layers. After a 1-$\mu$m buffer layer and a 250-period superlattice of 10 monolayers GaAs and 33 monolayers $\mathrm{Al_{0.09}Ga_{0.91}As}$, the 1.5-$\mu$m-thick GaAs active layer was deposited followed by an 80-period superlattice of identical composition as the previous one. The active-layer thickness was chosen to be equal to the penetration depth of the exciting light, effectuating homogeneous excitation. The two cladding superlattices prevent the free excitons from diffusing to places with increased defect concentrations like substrates and/or free surfaces. Superlattices also help to minimize carrier spill over into the active layer from background impurities in the $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ layer. To a large extent these carriers will now spill over into the GaAs wells of the superlattice. Furthermore, the superlattices ensure that the interfaces around the active layer are of optimum quality.[9]

The experiments were performed using a picosecond dye laser synchronously pumped by a mode-locked krypton laser. The samples were placed in a variable-temperature, optical cryostat. The luminescence was dispersed through a $\frac{3}{4}$-m monochromator and detected by a cooled photomultiplier with GaAs cathode. Photoluminescence decays were measured via appropriate single-photon-counting equipment with a time resolution of 0.3 ns.

Some of the recorded photoluminescence spectra at 1.7 K are displayed in Fig. 1 for a few excitation densities. The features seen at low excitation density are the recombination of free excitons in the 2*s* excited state at 1.518 eV, the free-exciton line at 1.5151 eV, the line related to excitons bound to neutral donors at 1.5141 eV, the one related to excitons bound to neutral acceptors at 1.5124 eV, and the so-called *g* line of Kunzel and Ploog.[10] Even at excitation densities as low as 5 mW/cm$^2$ the free-exciton line is dominant and has a full-width at half maximum of only 0.36 meV, indicating the very high quality of our material. At excitation densities above 0.2 W/cm$^2$ an additional luminescence feature can be observed centered at 1.5146 eV. Above 1 W/cm$^2$ this spectral line broadens and becomes the dominant recombination mechanism. We attribute this line to the recombination of excitonic molecules (biexcitons) on the basis of its spectral position. A number of authors[11,12] have calculated the extra binding energy of the excitonic molecule in units of the excitonic Rydberg as a function of the ratio of the effective masses of electrons and holes. For GaAs the ratio is 0.14, implying that the extra binding energy is 0.08 excitonic Rydberg, i.e., approximately 0.35 meV. The actually observed energy difference between the free-exciton and biexciton lines is 0.5 meV. The agreement is reasonably good. Note that the biexciton line cannot be assigned to the formation of an electron-hole liquid or an electron-hole plasma, since the former is not stable and the latter occurs at much lower photon energies.[13]

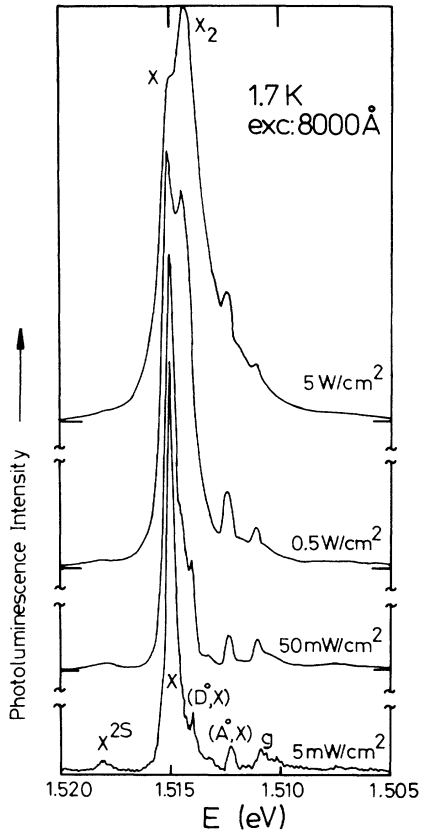

FIG. 1. Photoluminescence spectra of a 1.5-$\mu$m-thick GaAs layer at 1.7 K for various excitation power densities. The excitation wavelength was 800 nm. The spectra are scaled to have the same height for the main peak and are shifted for the sake of clarity.

To verify whether the defect concentration in our sample is low enough, we have measured the dependence of the luminescence on excitation density. The results are given in Fig. 2. Below 0.5 W/cm$^2$ the free-exciton recombination is strictly linear with power density. This is the first time that such a linear behavior for GaAs has been recorded. It demonstrates that the material is ultrapure and that the lifetime of free excitons is governed by radiative processes. For excitation densities above $\sim 1$ W/cm$^2$ the biexciton recombination takes over the linear power dependence and the free-exciton line more or less saturates.

We measured the lifetime of the free excitons as a function of power density, excitation photon energy, and lattice temperature. We found that the lifetime remains constant for power densities up to $\sim 1$ W/cm$^2$. For higher power densities the lifetime progressively decreases, as expected from the appearance of the parallel radiative process of biexcitonic recombination.

For excitation photon energies above 1.53 eV the lifetime of the free excitons is found to have increased by some 20%. This is probably due to the higher energy of the excited carriers and the slow cooling rate of the car-

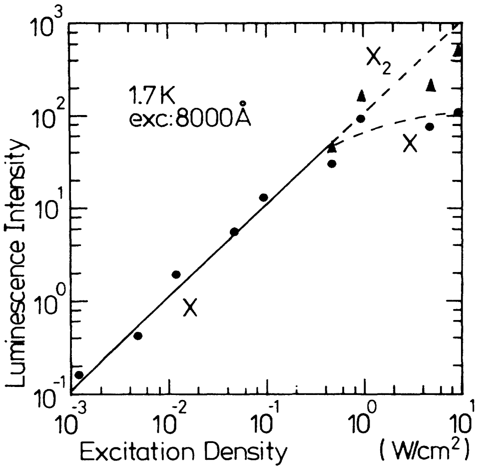

FIG. 2. Double logarithmic plot of the photoluminescence intensity of the free exciton line ($X$) vs excitation density for the GaAs sample of Fig. 1. At high excitation densities the intensity of the biexciton line ($X_2$) is also indicated.

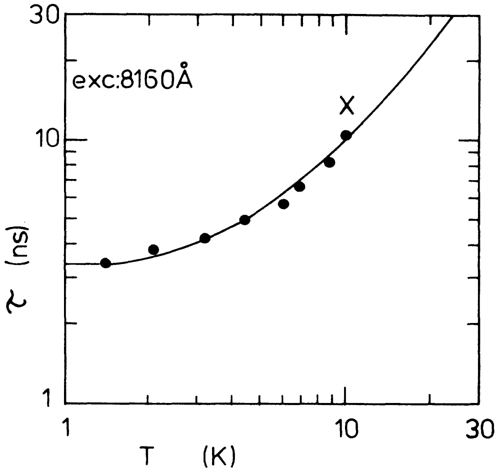

FIG. 3. Double logarithmic plot of the radiative lifetime of the free exciton in GaAs vs temperature. Excitation is resonant at the band edge of GaAs with a power density of ~0.1 W/cm².

riers when their excess energy is smaller than the optical-phonon energy. For above-band-edge excitation the electron ($J=\frac{1}{2}$) and hole ($J=\frac{3}{2}$) may form an exciton in either the singlet or the triplet state. Excitons in the triplet state cannot recombine radiatively and their occurrence might influence the lifetime. However, for photon energies equaling the $1s$ or the $2s$ state of the free exciton or equaling the band-edge energy, the radiative lifetime remains constant (3 ns at 1.7 K) within the limits of the experimental accuracy. The influence of the forbidden triplet state is thus negligible.

The influence of polariton effects is also ruled out on the basis of the small interaction energy of 0.08 meV between photons and excitons.[14] The polariton changes from exciton to photon character and vice versa in a time of $\hbar/(0.08\ \text{meV}) \simeq 8$ ps. Within this time the particle has already been scattered by acoustic phonons and the coherent coupling with the radiation field is lost.[15]

The influence of the lattice temperature on the radiative lifetime of the free excitons has been investigated. The results for band-edge excitation with 0.1 W/cm² are given in Fig. 3. The lifetime exhibits an increase from 3.3 ns at very low temperatures to almost 11 ns at 10 K. The center-of-mass system of the free excitons will have an increased average kinetic energy with increasing lattice temperature. Because of momentum conservation, only those free excitons close enough to the Brillouin-zone center can recombine radiatively. For a parabolic exciton band and an assumed Maxwell-Boltzmann distribution, the fraction, $r$, of free excitons with a kinetic energy smaller than $\Delta E$ is given by

$$r(T)=\frac{2}{\sqrt{\pi}}\int_0^{\Delta E/k_BT}\sqrt{\varepsilon}e^{-\varepsilon}d\varepsilon\ . \qquad (4)$$

The temperature-dependent radiative lifetime averaged over the ensemble is then

$$\tau(T)=\tau_0/r(T)\ . \qquad (5)$$

The theory of Eqs. (4) and (5) is fitted to the experimental points of Fig. 3 with $\tau_0$ and $\Delta E$ as parameters. The solid curve of Fig. 3 shows a perfect agreement for $\tau_0=3.3$ ns and $\Delta E=0.7$ meV, i.e., twice the linewidth of the free exciton.

In summary, we have shown unambiguously that the radiative lifetime of free excitons in GaAs is quite small, viz., $3.3\pm0.5$ ns in the low-temperature limit. The evidence that the lifetime is governed by radiative recombination consists of the dominant recombination band of free excitons in luminescence spectra, its linear behavior with power density, and the agreement between theory and experiment for the temperature dependence of the lifetime.

The oscillator strength associated with the lifetime must, therefore, be of the order of unity according to Eq. (3). To reconcile this with the total absorption cross section as stated in Eq. (1), one might take for the density of absorbing entities the concentration of excitons in a closed packed lattice instead of the density of GaAs molecules. This increases the oscillator strength by exactly a factor of $(a_{\text{ex}}/a)^3$. The oscillator strength is then per excitonic volume instead of per molecule. The existence of bound-exciton lines in absorption spectra merely reflects the probability of finding an impurity within the volume of the exciton. This probability is proportional to the number of unit cells per excitonic volume: $(a_{\text{ex}}/a)^3$. In the limit that the impurity concentration is so large that within every exciton volume an impurity is located, only bound-exciton absorption will be observed. This concentration is $(a/a_{\text{ex}})^3$ times the concentration of GaAs molecules.

Furthermore, we have observed for the first time excitonic molecules (biexcitons) in three-dimensional GaAs. In quantum wells they have been reported by Miller, Kleinman, Gossard, and Munteanu.[16]

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