Resolved Free-Exciton Transitions in the Optical-Absorption Spectrum of GaAs

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The optical-transmission spectrum of high-purity epitaxial GaAs has been studied at 2 K in the spectral region near the free exciton. Both resolved free-exciton transitions ($n = 1, 2$) and impurity-induced-absorption features are seen. The energy separation $E_x(1s) - E_x(2s)$ = 3. 15 ± 0. 15 meV observed for the $n = 1, 2$ states of the transverse exciton provides an unambiguous value for the exciton binding energy [$E_x(1s) = 4. 2 ± 0. 2$ meV], which agrees well with theory.

We report a new and reliable value of $4. 2 ± 0. 2$ meV for the free-exciton binding energy in GaAs obtained from a direct measurement of the resolved $n = 1$ and $n = 2$ exciton transitions in the optical-absorption spectrum of high-purity epitaxial layers. This value agrees well with the theoretical value based on the work of Baldereschi and Lipari.[1] Our data demonstrate that the recent assignments of photoluminescence transitions by Bimberg and Schairer[2] are in error: The feature that they assign as an $n = 2$ exciton is impurity induced; their $n = 3$ luminescence feature is probably associated with the $n = 2$ exciton state. We also report that the experimental exchange energy obtained from the stress dependence of the polariton reflectance is less than 0. 1 meV, in contrast to the value 0. 37 meV obtained in earlier luminescence results.[3]

The samples were prepared from n-type vapor-phase epitaxial layers with total impurity concentrations less than 10^{14} cm^{-3} and 77 K mobilities near 200 000 cm^2/V sec. The substrate was removed and both faces of the epitaxial layer were chemically polished to a final sample thickness of approximately 10 μ. Thinner samples were obtained by further etching. The sample was mounted over a 1-mm-diam hole (0. 5 mm for thinner samples) on a GaAs sample holder to minimize the strain due to differential thermal contraction. Reflectance and luminescence spectra were monitored after each step of surface preparation. In general, the spectra for the chemically polished surfaces were sharper, stronger, and more reproducible than those obtained with as-grown surfaces. The transmission data were obtained with a double-beam spectrophotometer.[4] The samples were immersed in pumped liquid helium.

Figure 1 illustrates the optical-density data for two samples. The optical density is given by

$$O. D. = - \log_{10} T$$

$$= - \log_{10}[(1 - R)^2(1 - R^2 e^{-2\alpha l})^{-1} e^{-\alpha l} + C] , \qquad (1)$$

where T is the ratio of transmitted to incident light,

R is the single-surface reflectance, α is the absorption coefficient, l is the sample thickness, and C accounts for extraneous light signals. For the thicker sample $l = 10 ± 1 \mu$. From Sturge's[5] value of the absorption coefficient just above the band edge ($\alpha_g \sim 10^4$ cm^{-1}), we estimate that $l = 2. 3$ μ for the thinner sample. The solid curve labeled $(1 - R)^2$ in Fig. 1 illustrates that the term $- \log_{10}[(1 - R)^2]$ has a negligible effect upon the spectral shape of the data. Similarly, the term $(1 - R^2 e^{-2\alpha l})$ is unimportant. When $e^{-\alpha l} \gg C$, the optical density is proportional to the absorption coefficient (O. D. $= \alpha l/2. 3$). The observed saturation of the optical density near the value 2. 7 is due to the factor C in Eq. (1) which arises from scattered light and from the photoluminescence (excited by the monochromatic transmission light) which traverses the sample and is detected by the photomultiplier (EMI 9659). This saturation is unimportant for optical densities less than 2. 0 in Fig. 1.

Here, we are concerned primarily with the stronger structure related to intrinsic-exciton absorption. Strong polariton reflectance structure and polariton luminescence have been reported by
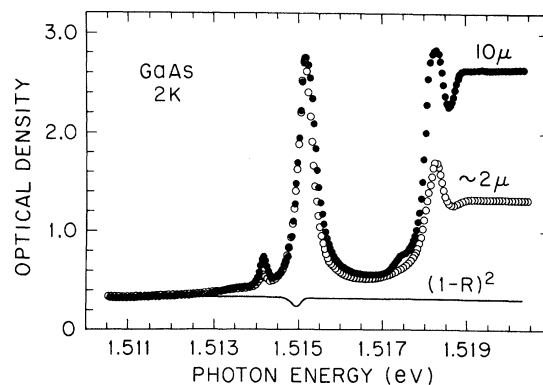

FIG. 1. Optical density of GaAs at 2 K for two sample thicknesses: 10 μ, solid circles; approximately 2 μ, open circles. The solid curve represents the structure in the optical density due to the $(1 - R)^2$ term in Eq. (1).

TABLE I. The method (and notation) of Baldereschi and Lipari was used to calculate the exciton binding energies for the following parameters: $\epsilon_0 = 12.56 \pm 0.04$,[a] $m_e^*/m_0 = 0.06650 \pm 0.00007$,[a] $\gamma_1 = 7.2 \pm 0.6$, $\gamma_2 = 2.5 \pm 0.4$, $\gamma_3 = 2.9 \pm 0.3$, $\phi = 0.301$, and $R_0 = 3.88$. The small exchange energy has not been included in the calculation. Energy units are meV.

	$E_x(1s) - E_x(2s)$	$E_x(1s)$	E_G
Theory	3.05 ± 0.09	4.10 ± 0.12	
Present work	3.15 ± 0.15	4.2 ± 0.2	1519.2 ± 0.2[b]
Bimberg and Schairer	2.5 ± 0.2	3.4 ± 0.3[c]	1518.5 ± 0.3[d]
Sturge[e]		3.4 ± 0.2	1521.0 ± 1.5

[a]G. E. Stillman, D. M. Larsen, C. M. Wolfe, and R. C. Brandt, Solid State Commun. **9**, 2245 (1971).

[b]For the energy 1.5151 eV for the longitudinal exciton.

[c]Calculated from the experimental values in Ref. 2. The value 3.77 meV in Ref. 2 is a theoretical value which includes an exchange energy of 0.37 meV.

[d]The value 1.5189 eV in Ref. 2 is based on theoretical binding energy.

[e]Reference 5.

Sell et al.[6] in the energy region near the strong absorption peak at 1.5152 eV. Hence we identify this line in Fig. 1 with the polariton for the $n = 1$ exciton state. Reflectance and luminescence spectra on these transmission samples indicate that the longitudinal-exciton energy is 1.5153 eV. This energy shift from the value 1.5151 eV reported earlier[6] can be attributed partly to sample dependence (typically ± 0.1 meV for epitaxial layers on a substrate) and partly to strain introduced in mounting thin samples. The 0.5-meV broadening of the transmission data, which is an order of magnitude smaller than that seen by Sturge,[5] is probably caused by inhomogeneous strain introduced in mounting. As discussed in Ref. 6, the transverse exciton falls at an energy 0.1 to 0.2 meV below the longitudinal-exciton energy. Thus the peak of the absorption line at 1.5152 eV occurs at, or within 0.1 meV above, the transverse-exciton energy in agreement with recent theoretical work by Tait[7] on polariton absorption. In any case, since the observed linewidth is larger than the longitudinal-transverse splitting, the polariton interaction has very little effect upon the spectral shape of the absorption data in Fig. 1. Even for the thinner sample, the optical density for this line saturates near 2.7; thus we cannot compare its strength with theoretical predictions.

We associate the line at 1.5183 eV with the $n = 2$ exciton state. In agreement with the simple hydrogenic theory, this feature has a strength such that additional broadening would cause it to merge into the flat continuum absorption. This is seen most clearly for the thinner sample which is not affected in this spectral region by the saturation effect dis-

cussed above. Recently Bimberg and Schairer[2] have associated two weak photoluminescence features at 1.5176 and 1.5182 eV with the $n = 2$, 3 exciton states, respectively. This assignment is not consistent with the transmission data in Fig. 1. The weak absorption feature near 1.5175 eV has an oscillator strength that is a factor of 50 smaller than that predicted by the simple hydrogenic theory. Thus it seems reasonable to conclude that the luminescence at 1.5176 eV and the weak absorption near 1.5175 eV arise from an impurity-induced transition. The luminescence line at 1.5182 eV has the correct energy to be associated with the $n = 2$ exciton state.

The $n = 1$, 2 absorption peaks in Fig. 1 are separated by 3.1 meV. If we include the 0.1-meV ambiguity of the $n = 1$ transverse-exciton energy and neglect the small longitudinal-transverse splitting for the $n = 2$ exciton (~ 0.025 meV), we obtain the experimental value

$$E_x(1s) - E_x(2s) = 3.15 \pm 0.15 \text{ meV}$$

for the energy separation between the $n = 1$, 2 transverse excitons. This energy separation is the most accurate and reliable data currently available for the exciton binding energy in GaAs.

Baldereschi and Lipari[1] have calculated $E_x(1s)$ and $E_x(2s)$ including the effects of valence-band degeneracy and anisotropy. For GaAs the correction to the simple hydrogenic model is small; the correction to the binding energy $E_x(1s)$ is less than 6%. These authors do not include the exchange interaction in their calculation; however, as discussed below, Sell et al.[6] have obtained a reliable upper limit of 0.1 meV for the exchange energy. Thus, initially, we neglect exchange and make a direct comparison of our data with the results of Baldereschi and Lipari as shown in Table I. The Luttinger parameters for the valence band are an average of several experimental values (given in Refs. 8 and 9) and the semiempirical values of Lawaetz.[10] The uncertainties in the binding energies arise primarily from the uncertainty in the γ_1 parameter. The 4.2-meV value for the experimental binding energy $E_x(1s)$ is obtained by scaling the theoretical value $(4.1 \times 3.15/3.05)$. The good agreement with the theoretical binding energy together with the experimental evidence based upon the spectral shape and strength of the absorption data provides a strong case for the present interpretation. Table I also includes a comparison with other experimental values for the exciton binding energy and the band-gap energy E_G. Both of the earlier values for $E_x(1s)$ are 0.8 meV smaller than the value obtained here. Bimberg and Schairer obtained a smaller value because they assigned the 1.5176-eV rather than the 1.5182-eV luminescence line to the $n = 2$ exciton transition. Sturge's value

is based upon the slope of the continuum absorption in material with 10^{17}-cm^{-3} ionized impurities.

It should be noted that the theoretical value for the $E(2s) - E(3s)$ splitting is 0.6 meV. This agrees well with the experimental energy separation between the $n = 2$ peak and the onset of continuum (actually quasicontinuum) absorption which occurs at the $n = 3$ exciton energy.

Two modifications of the theory could be considered. Inclusion of a 0.1-meV exchange energy would decrease the theoretical value of $E_x(1s) - E_x(2s)$ to nearly 2.95 meV and give poorer agreement with experiment. We could also include the interaction with optical phonons as discussed by Mahanti and Varma.[11] If their interpolation scheme is used to obtain ϵ_{eff} for the $n = 1$, 2 states, the theoretical value for $E_x(1s) - E_x(2s)$ is increased to approximately 3.5 meV, which also gives poorer agreement with experiment.

Returning to the question of the exchange energy, Langer et al.[12] have shown theoretically and have demonstrated experimentally for several II-VI compounds that the stress dependence of the exciton reflectance provides a direct measure of the exchange energy. A uniaxial stress (along [001], for example) splits the Γ_5 (singlet, optically allowed) exciton and mixes it with the Γ_4 (triplet, optically forbidden) exciton. In general, three optically active states result: Two states (y_1 and y_2) couple to light for E perpendicular to the stress and one state (z) couples for E parallel to the stress. In GaAs both the exchange constant j defined in Ref. 12 and the stress splittings of interest are small compared with the spin-orbit splitting. At zero stress, the z-y_1 splitting (i.e., the $\Gamma_5 - \Gamma_4$ exchange splitting) is $4j/3$. As the stress increases, the z-y_1 splitting asymptotically approaches the value j. Sell et al.[6,13] reported that the z-y_1 splitting observed in reflectance as function of uniaxial stress is less than 0.1 meV. This provides a reliable upper bound of 0.1 meV for j.

In earlier work Gilleo et al.[3] obtained a larger value of 0.37 meV for the exchange energy from a study of the stress dependence of the luminescence. These authors also based their value upon the z-y_1 splitting argument for their lines $X_{1a}(\pi)$ and $X_{1b}(\sigma)$ in Fig. 2 of Ref. 3. They interpret the zero stress splitting of 0.37 meV as the exchange energy; however, their asymptotic splitting for large stress is only 0.12 meV. This stress dependence does not agree with the theoretical behavior discussed above. On the other hand, the reflectance data do follow the predicted behavior. Furthermore, given our present incomplete theoretical understanding of this luminescence, it is not clear whether such a splitting in the luminescence data can be interpreted to yield the exchange energy.

Finally, we briefly consider the weaker structure at 1.5135, 1.5142, and 1.5175 eV. The two most intense photoluminescence features in these samples at 4.2 K occur near 1.5134 and 1.5142 eV; a weaker feature is seen near 1.5175 eV. The weak transmission features appear to be associated with these same transitions. The line at 1.5142 eV is reasonably well identified with excitons bound to neutral donors.[14] The identities of the other two lines have not been firmly established; however, we note that these features have the correct energies with respect to the new value of the band gap to be free-hole–bound-electron transitions ($D^+ + h\nu \rightarrow D^0 + h$) with both $n = 1$ and $n = 2$ final neutral-donor states. The sample in these transmission experiments remains essentially in thermal equilibrium, in contrast to the case of luminescence. Hence, the centers which give rise to the observed weak absorption must exist in the equilibrium state of these n-type crystals. For the case of the excitons bound to neutral donors, the theory of Rashba and Gurgenishvili[15] as modified by Henry and Nassau[16] predicts a very large oscillator enhancement ($f \approx 10^6 f_{ex}$) which is in reasonable agreement with the strength of the 1.5142-eV line.

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Configuration Interaction in Donor-Acceptor Pairs[*]

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The effect of configuration interaction on the electronic states of donor-acceptor pairs in semiconductors is reported. Both the radial and angular dependences of electron- and positive-hole effective-mass functions are varied to minimize the total energy, corresponding to mixing higher *s* and *p* states into the eigenstates. The orbits are delocalized and intercore electron and hole densities reduced as a consequence of pairing. A substantial improvement in agreement between theory and experiment is found on including configuration interaction in the calculation of the pair spectra of gallium phosphide. Also, the effect on radiative lifetimes is calculated. The Coulomb overlap, correlation, and anisotropy of the effective masses are also considered, as well as changes in the coupling with the lattice.

I. INTRODUCTION

The electronic states of donor-acceptor pairs in semiconductors have previously been considered rigorously only to first order (Heitler–London approximation)[1] or with a second-order van der Waals term added with an adjustable parameter.[2] The availability of extensive fine structure in the emission spectra of III-V semiconductors and the explanation of these spectra by Hopfield, Thomas, and Gershenzon[2] in terms of radiative recombination at specific pairs indicate a need for an improved theory. The usual theory accounts for the general features of these spectra; however, a substantial discrepancy between theory and experiment exists in the dependence of radiative transition energy on donor-acceptor distance for the nearer-neighbor pairs.

Distant donor-acceptor pair emission spectra are usually fitted with

$$E_{\mathrm{ph}}(R) = E_{\mathrm{gap}} - (E_D + E_A) + \frac{e^2}{K_s R} - \frac{e^2}{K_s}\left(\frac{b}{R}\right)^6 \quad (1)$$

assuming no overlap of the electronic distributions. R is the donor-acceptor separation, K_s the static dielectric constant, E_D and E_A the isolated donor and acceptor electronic binding energies, and b an arbitrary parameter in the van der Waals term used to improve the fit to experimental data. In Equation (1), K_s is the proper dielectric constant for the condition $\tau_0 \gg \tau_J$, where τ_0 is the orbital period for electronic motion and τ_J is the period for lattice vibrations.

The van der Waals term is the electronic correlation energy term for large R and is only valid

for $R \gg a_A$, a_D. Assuming $1s$-type wave functions,

$$a_A = e^2/2K_s E_A \quad \text{and} \quad a_D = e^2/2K_s E_D \quad , \quad (2)$$

this term represents the interaction of a neutral occupied donor and acceptor, without overlap of electronic distributions. To obtain the best fit to the data, Hopfield *et al.* found b to be the same magnitude as a_A or a_D.

Williams's[1] equation contains the effect of overlap, and does have the right dependence on R to improve somewhat the agreement between the observed spectrum and the theoretical spectrum,

$$E_{\mathrm{ph}}(R) = E_{\mathrm{gap}} - (E_A + E_D) + \frac{e^2}{K_s R}$$

$$- \frac{e^2}{K_s R} e^{-2\rho_0}(1 + \tfrac{5}{8}\rho_0 - \tfrac{3}{4}\rho_0^2 - \tfrac{1}{6}\rho_0^3) \quad . \quad (3)$$

Here $\rho_0 = R/a_0$, and it is assumed $a_0 = a_A = a_D$.

II. THEORETICAL ANALYSIS OF TRANSITION ENERGY

We have now obtained a significant improvement using methods previously applied to the hydrogen molecule. A variation of parameters of the one-electron wave functions in a configuration-interaction treatment of the hydrogen molecule can be applied with equal validity to the donor-acceptor pair system. Wang's[3] and Rosen's[4] treatment of the hydrogen molecule results in the wave function being localized and rendered nonspherical with electronic density piling up between the nuclei. Adapting this to the excited donor-acceptor pair results in the electron and hole effective-mass functions being delocalized and rendered non-spherical with the electronic density thinning out