served tend to have the same line shape independent of the particular orbit on the Fermi surface which gives rise to the signal. When the signal is weak, as, for example, W_2 in Fig. 1, its dR/dH line shape closely resembles that predicted by Chambers[11] for the Azbel'-Kaner signals from regions of the Fermi surface where the cyclotron effective mass m^* is locally constant with varying k_H. For the stronger signals, such as L_1 and W_1 in trace a of Fig. 1, this line shape is distorted by the presence of a broad, deep minimum on the high-field side of the resonance. We speculate that the basic line shape for the field-normal signals is the Chambers constant-m^* line shape, and that the broad minimum on the high-field side of the stronger signals is associated with a wave propagation phenomenon of the type discussed by Walsh.[12] If one had to choose a line shape for the field-normal signals from among Chambers's three basic Azbel'-Kaner line shapes, it would be reasonable to pick the constant-m^* line shape, since little mass variation is to be expected over the band of orbits that contribute to a field-normal signal.

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Nonhydrogenic Exciton and Energy Gap of GaAs

D. Bimberg and W. Schairer*
Physikalisches Institut der Universität Frankfurt am Main, Frankfurt am Main, Germany
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The free-exciton series $n=1,2,3$ in high-purity GaAs has been observed in photoluminescence and photoconductivity. The $n=1$ peak shifts upon changing the excitation level because of free-carrier screening. Anisotropy and exchange effects as well as two valence bands must be included to interpret the series spectrum of this Wannier-like exciton. New values are derived for the band gap at 1.6 K ($E_g=1.5189\pm0.0001$ eV) and for the $n=1$ excitonic binding energy [$E_X(1s)=3.77\pm0.05$ meV].

Free-exciton states have been calculated by several authors for the Frenkel and Wannier cases.[1] These calculations do not apply directly to zinc-blende semiconductors because of their degenerate valence bands at Γ. Recently Baldereschi and Lipari[2] (BL) considered this degeneracy and also determined the effect of valence-band anisotropy upon the states of free excitons. Rohner[3] treated exchange interaction; earlier Abe[4] calculated numerically this energy for GaAs. In high-purity materials experimental tests for these calculations are still lacking.[5]

This Letter presents spectra of near-band-gap photoluminescence (PL) and photoconductivity (PC) of high-purity GaAs, including data at *very low* excitation levels. The $n=1$ free-exciton emission is found to shift towards higher energies with increasing excitation intensity because of screening by free carriers.[6] We measure a definitive energy for the $n=1$ state at vanishing

screening and thus resolve discrepancies between results of previous authors.[5] The $n=2$ and 3 lines are established for the first time in a III-V semiconductor.[7] These data entail new values for band-gap and excitonic binding energies of GaAs. A naive hydrogenic model is an inadequate description of the excitonic series; anisotropy and exchange effects are required for the interpretation of the spectra.

The GaAs crystals investigated have been grown by liquid-phase epitaxy at the Fernmeldetechnisches Zentralamt, Darmstadt, Germany. Typical carrier concentrations and mobilities at 77 K were $n \approx 2\times10^{13}$ cm^{-3} and $\mu \approx 170\,000$ cm^2/V sec. The specimens were immersed directly in liquid He. Luminescence and photoconductivity were excited by a Kr laser (647.1 nm) and a tungsten lamp, respectively. The laser intensity could be varied by the discharge current and calibrated neutral density filters. The detecting system consisted of a 2-m Jarrell-Ash spectrometer with a Jarrell-Ash grating blazed at 750 nm with 1180 grooves/mm and a ghost intensity of 0.002% in the first order of 5461 Å, a cooled photomultiplier with an S-20 extended red cathode, and a lockin amplifier. Control measurements of the spectra were made with a $\frac{3}{4}$-m Spex spectrometer with a Bausch and Lomb grating with 1200 grooves/mm using the same and some previously investigated crystals.[8]

Figure 1 shows PL and PC data for two different samples at 1.6 K and excitation intensities of approximately 5×10^{15} photons/cm^2 sec (PL) and 1×10^{13} photons/cm^2 sec (PC). This Letter concerns only peaks $X_{1,2,3}$. Recombination from the $n=1$ free-exciton state is known to cause X_1.[9] This peak shifts with increasing excitation intensity toward the blue as shown in Fig. 2. The low-excitation asymptote lies at 8180.6 ± 0.2 Å $=1.5151\pm0.000\,04$ eV $=E(X_1)$ in PL as well as in PC.[10] We claim this to be a trustworthy value of the $n=1$ free-exciton recombination energy, because it is measured at low excitation and at small impurity content, becoming independent of these two parameters at low parameter values.

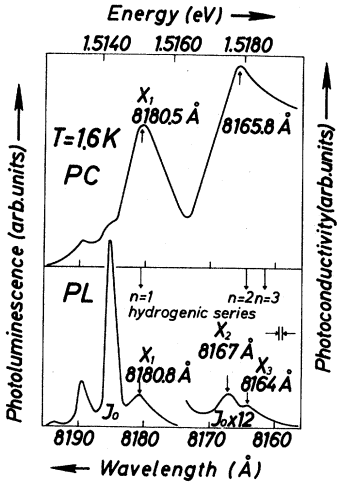

FIG. 1. Photoconductivity and photoluminescence spectra near the band gap of high purity GaAs at very low excitation. The excitation intensity is approximately 5×10^{15} photons/cm^2 sec for PL, and 1×10^{13} photons/cm^2 sec for PC. $X_{1\text{-}3}$ are the free-exciton lines. The arrows in the lower part show the theoretical predicted position of a purely hydrogenic exciton series.

Older experiments yielded higher energies for $E(X_1)$ and also were scattered considerably.[5] First, these discrepancies are caused by the previously neglected dependence on excitation intensity. With increasing excitation intensity I the free-carrier density N increases $\sim I^{0.6}$ in the investigated range. This increase of free-carrier concentration causes a blue shift by screening of the Coulombic attraction between hole and electron. This screening of the excitonic interaction was treated by Albers,[6] who considered the solution of the effective-mass equation

$$[-(\hbar^2/2\mu)\nabla^2 + U(r)]F(r) = E_X(1s)F(r) \qquad (1)$$

for a Thomas-Fermi potential

$$U(r) = \exp(-\alpha r)/\epsilon_0 r \qquad (2)$$

with the screening length

$$\alpha = (4\pi Ne^2/\epsilon_0 kt)^{1/2}, \qquad (3)$$

where $E_X(1s)$ is the energy of the $n=1$ state of the free exciton and N is the free-carrier density. The other symbols have the usual meaning.[6] We find that Albers's theory gives a qualitatively

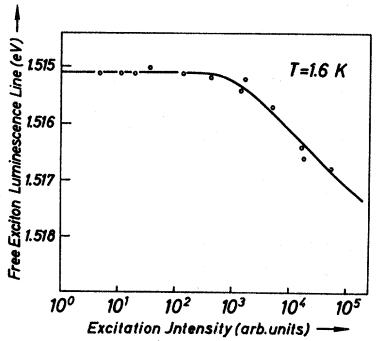

FIG. 2. Excitation intensity dependence of the peak position of the $n=1$ free-exciton recombination line. The straight line is a fit of the experimental points (dots).

correct picture of our experiments as shown in Fig. 2. A more recent theoretical approach[11] to the screening predicts beyond it a remarkable shift of the band edge due to self-screening. This should cause a simultaneous shift of other luminescence lines which could not be observed. Details of this will be discussed elsewhere.[12]

Secondly, previous discrepancies might stem from less pure samples, in which the line X_1 is easily masked by recently identified neutral donor-exciton complexes.[13]

Before proceeding to further experimental results, we evaluate a new band-gap energy E_g for GaAs from the energy $E(X_1)$, using the results of BL. The valence-band maximum at Γ in zinc-blende crystals consists of two degenerate bands, spin degeneracy neglected. Earlier exciton calculations ignored this degeneracy, although it exceeds other perturbations, such as anisotropy, missing inversion symmetry, or exchange interaction. Only recently BL deduced an explicit formula for the excitonic binding energies including degeneracy, spin-orbit splitting, and anisotropy of the valence bands. We evaluate the binding energies $E_B(ns)$ of the states $n=1,2,3$ as proposed by BL using new cyclotron-resonance masses for the two valence bands.[14] Table I lists these energies as obtained via the mass parameters $\mu_{0,1,2}$ as defined by BL; the subsequent rows show the result for some older mass values.[15-17] Electron mass $m_e{}^+=0.066\,50m_0$ and dielectric constant $\epsilon_0=12.5$ were used to calculate $E_B(ns)$, $n=1,2,3$.[18] Effects of missing inversion symmetry and of the split-off valence band are not included in this calculation, because they are too small in GaAs.[2] The effect of exchange interaction is larger. It was not considered by BL, but by Rohner[3] and Abe.[4] Abe calculated a correction of $E_{\text{exch}}=-0.38$ meV for the $1s$ exciton state in GaAs. Gilleo, Bailey, and Hill[9] proved this value to be correct by means of uniaxial strain effects on the $n=1$ line; they got $E_{\text{exch}}=-0.37\pm0.04$ meV. This energy decreases approximately as $1/n^3$.[3] The corrected binding energies are $E_X(ns)=E_B(ns)+E_{\text{exch}}(n)$. They are listed in the three last columns of Table I for the states $n=1,2,3$. The two most recent hole-mass data,[13,14] when averaged, yield

$$E_X(1s)=3.77\pm0.05\ \text{meV} \tag{4}$$

for the ionization energy of the $1s$ state. Since the energy gap is $E_g=E(X_1)+E_X(1s)$, we obtain for the new value

$$E_g=1.5189\pm0.0001\ \text{eV}. \tag{5}$$

Our PC spectra contain another peak at ≈ 1.518 eV, which in PL is resolved into a doublet X_2, X_3 with a separation of 0.5 to 0.6 meV. These lines could only be found at low excitation intensities. The intensity ratio of the lines X_1, X_2, X_3 follows approximately a $1/n^3$ rule, if self-absorption is taken into account. We suggest that the lines $X_{2,3}$ result from recombinations from the $n=2,3$ states of the free exciton.

The spectral positions of the $n=2,3$ free-exciton recombination radiation can be predicted by means of Table I and Eq. (5) to be $E(X_2)_{\text{th}}=E_g-E_X(2s)=1.5178_5\pm0.0002$ eV and $E(X_3)_{\text{th}}=E_g-E_X(3s)=1.5184_5\pm0.0002$ eV. The experimental peak energies of the lines $X_{2,3}$ are $E(X_2)_{\text{exp}}=1.5176\pm0.0002$ eV and $E(X_3)_{\text{exp}}=1.5182\pm0.0002$ eV. There is good agreement between theory and experiment, except for a difference of 0.2 meV, which is within experimental error. The differences $E(X_2)_{\text{exp}}-E(X_3)_{\text{exp}}$ and $E_X(2s)-E_X(3s)$ are exactly equal to each other. The doublet $X_{2,3}$ is not caused by exchange splitting of the $n=2$, $l=0,1$ states, because the separation between the s and

TABLE I. Valence-band parameters μ_0, μ_1, μ_2, as defined by BL (Ref. 2), used to calculate the binding energies $E_B(ns)$ of the states $n=1,2,3$ of the free exciton as proposed by BL. $E_X(ns)$, $n=1,2,3$, are the ionization energies of the free-exciton states which result from the $E_B(ns)$ when the exchange energy is included. The energy unit is meV.

μ_0/m_0	μ_1/m_0	μ_2/m_0	$E_B(1s)$	$E_B(2s)$	$E_B(3s)$	$E_X(1s)$	$E_X(2s)$	$E_X(3s)$
0.046[a]	0.426[a]	0.123[a]	4.18	1.07	0.45	3.80	1.02	0.44
0.045[b]	0.401[b]	0.115[b]	4.12	1.04	0.44	3.74	0.99	0.43
0.048[c]	0.444[c]	0.129[c]	4.36	1.13	0.46	3.98	1.08	0.45
0.048[d]	0.823[d]	0.148[d]	4.28	1.08	0.46	3.90	1.03	0.45

[a]See Ref. 12.
[b]See Ref. 13.
[c]See Ref. 14.
[d]See Ref. 15.

p states should only be 0.05 meV, which is 10 times less than the measured difference. Also it cannot be explained by excited states of an effective-mass donor or an exciton bound to a neutral donor because these recombination lines should have another spectral position or another half-width, respectively. Thus lines $X_{2,3}$ should be indeed caused by the $n=2,3$ free-exciton states.

Our interpretation of the $X_{1,2,3}$ lines has an important consequence. A naive hydrogenic model has been shown to fail, not only in alkali halides, where the effect of exchange interaction is well known,[18] or in II-VI compounds with their Bohr radii between 18 and 53 Å,[3] but now also in the case of seemingly pure Wannier-like excitons such as in GaAs with a Bohr radius >100 Å. Anisotropy as well as exchange effects must be included here, and the resulting corrections do not show the hydrogenic $1/n^2$ behavior. To give an impression of the deviation from hydrogenic character, the theoretical spectral positions of the appropriate hydrogenic exciton recombinations lines which result from the spectral position of the $n=1$ line are marked with arrows in Fig. 1

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Note added in proof.—With respect to most recent work by Sell *et al.*,[20] we believe that we observe only emission from the lower polariton branch. A detailed discussion is in preparation.

*Present address: IBM Thomas J. Watson Research Center, Yorktown Heights, N. Y. 10598.

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