

Free-carrier effects in gallium nitride epilayers: Valence-band dispersion

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The dispersion of the A -valence-band in GaN has been deduced from the observation of high-index magnetoexcitonic states in polarized interband magnetorefectivity and is found to be strongly nonparabolic with a mass in the range 1.2 – $1.8m_e$. It matches the theory of Kim *et al.* [Phys. Rev. B **56**, 7363 (1997)] extremely well, which also gives a strong k -dependent A -valence-band mass. A strong phonon coupling leads to quenching of the observed transitions at about an LO-phonon energy above the band gap and a strong nonparabolicity. The valence band was deduced from subtracting from the reduced dispersion the electron contribution with a model that includes a full treatment of the electron-phonon interaction.

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Cyclotron resonance experiments have yet to shed significant light on the valence band structure of gallium nitride,¹ despite using magnetic fields up to 700 T. Therefore, less direct methods are required to experimentally determine the effective mass parameters. Several techniques have been employed (see Ref. 2 for review), but the significant scatter of the resulting hole masses varying from 0.5 – $2.2 m_e$ illustrates their limitations. In contrast, the magneto-optics of GaN in the last few years has been successful in providing an accurate mass for the conduction band.^{3,4}

Interband magneto-optics has made significant progress recently as a result of the improvements in the luminescence linewidths in the bandgap region. Beyond successfully examining the impurity bound states, so far the analysis has centered on the properties of the strongly bound excitonic states such as the $1s$ and $2s$ free excitons. The properties of these are considerably complicated by the proximity of the split valence bands where it has been pointed out that a full description of the magnetic-field dependence of these states requires account to be taken of the interaction of all the excitonic states belonging to the different valence bands.⁵

In order to find out more about the valence band and to avoid this problem, we present a study of magnetorefectivity data from high-order Landau level transitions that have energies that are considerably greater than the excitonic binding energy. By looking at the high index levels the magnetoexcitonic corrections become less significant, so that the transitions are dominated by the contributions from the free carriers. Then, by considering in detail the properties of the conduction band, now accurately known to have a mass of $0.2220(5) m_e$,³ the valence band properties can be deduced with reasonable confidence.

The polarized magnetorefectivity experiments were performed in a continuous magnetic field up to 20 T and at 4.2 K. The sample, G889, was grown by the ELOG method by MOVPE on a sapphire substrate.⁶ The hexagonal c axis was parallel to the magnetic field and perpendicular to the electric

field vector of the light. Fiber optics were used to guide the 75W Xenon light source to the sample, also taking the reflected light to a quarter meter spectrometer fitted with a UV-enhanced CCD detector.

The reflectivity spectra were analyzed by identifying peaks in the first derivative, $-dR/dE$ (Refs. 7 and 8) to give the transition energies, as shown in Fig. 1. This approximates to a Kramers-Kronig analysis for the case of weak, well-separated transitions and has been already successfully applied to describe the Zeeman shifts of the $1s$ excitonic states.⁷

The data for the two different polarizations were analyzed separately and it was found that for all of the higher index transitions it was possible to take account of the Zeeman splitting by using a single value of the g factor. A term $\pm \frac{1}{2}g\mu_B B$ was subtracted with $g_{band} = -1.8(2)$, which was then found to give coincident results for the two polarizations. For comparison this is significantly different to that determined for the A excitonic states, where we find the weak field g factor is $g_{A1s} = +0.254$. Using a value of $g^e = 1.95$ for the electron g factor^{9,10} gives $g_{1s}^{h(A,\parallel)} = 2.2(2)$ as the apparent hole g factor for the $1s$ exciton in agreement with Ref. 5, where \parallel means the field is parallel to the c axis, but which is then quenched to the much lower value of $g_{band}^{h(A,\parallel)} = 0.2(2)$ for the higher transitions. The large difference in the g factors for the different states confirms the conjecture by Rodina *et al.*⁵ that there are large differences between the apparent g factors of the holes when they are involved in different states, as a result of intervalence band coupling.

In addition to the Zeeman energy there is also the small Coulomb correction due to the finite binding of the higher excitonic states that causes the transitions to lie just below the corresponding Landau level energies. Unfortunately there are no numerical values available for the higher level states in the field range used here so it is necessary to make some approximations. The binding energies are usually expressed as a function of the dimensionless parameter $\gamma = \hbar\omega/2R$,

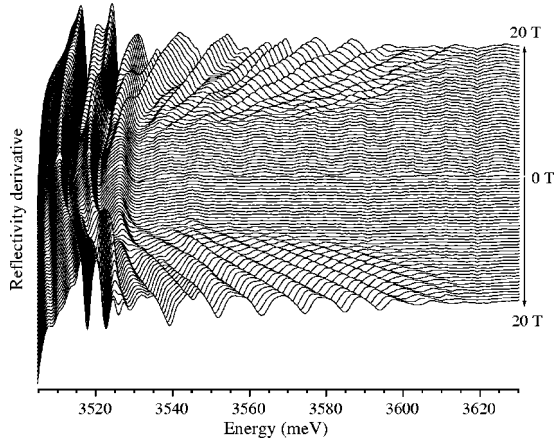


FIG. 1. The derivative of the reflectivity, $-dR/dE$, is shown for the two circular polarizations for magnetic fields up to 20 T. The energy range includes the excited $n=2$ exciton states as well as the “free carrier” Landau levels. The transitions are quenched around 3620 meV, as a result of possible LO phonon emission above this energy. σ^+ : top, σ^- : bottom.

where $\hbar\omega$ is the cyclotron energy and R is the effective Rydberg energy. For InSb it was found that for the high field regime, $\gamma > 5$, the binding energy was described accurately by^{11–13}

$$E_{ex} \approx \lambda R \left[\frac{\gamma}{2n+1} \right]^{1/3}, \quad (1)$$

where the prefactor $\lambda=1.6$ and n is the Landau level index. For GaN $\gamma=0.11 \rightarrow 0.27$ for $B=8 \rightarrow 20$ T. Despite these small values of γ for the $1s$ state, we still expect the excited states to be dominated by the magnetic energy in the high-field regime, as a result of the reduced effective binding energy for higher Landau levels. We, therefore adopt, the functional form of Eq. (1) but adjust the value of the prefactor λ . Numerical calculations do exist for a Landau level index of $n=3$,¹⁴ so by comparing Eq. (1) with a weighted average of the multiple bound states associated with any one Landau level, we expect a prefactor of $\lambda \sim 0.5$.

Once stripped of the Landau level quantization and the Coulomb corrections that depend on this, one expects the transition energies from all LL indices to reduce to a single simple $E-k$ dispersion relation. This provides us with an empirical method of fine-tuning the Coulomb correction by optimizing the colinearity of the different Landau index contributions to the dispersion relations. We find that the optimum results are obtained with a value of $\lambda=0.4$ which gives a typical binding energy for the higher levels of order 2–3 meV.

In order to analyze the transition energies in terms of a single free carrier $E(k)$ dispersion we use a semiclassical quantization of the Landau levels with

$$\langle k^2 \rangle = eB(2n+1)/\hbar. \quad (2)$$

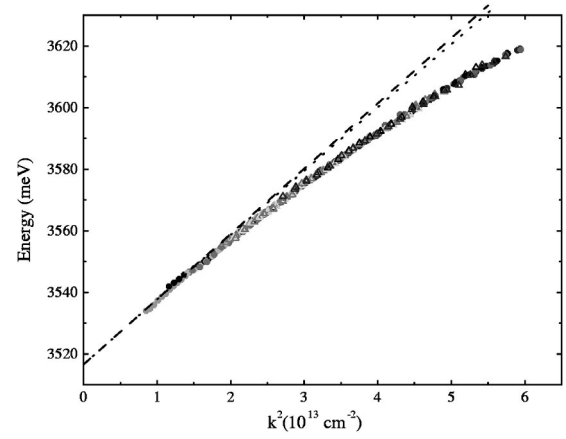


FIG. 2. The reduced dispersion formed from free carrier Landau levels. For polarization σ^- (closed circles) LL indices $n=3-13$ were used, whereas for polarization σ^+ (open triangles) $n=5-10$. Reduced dispersion without polaron corrections are shown (dashed line), and including $k \cdot p$ induced band nonparabolicity (dotted line).

This requires the assumption that the Landau quantization is the dominant effect, which is easily satisfied for the magnetic fields used.

The reduced dispersion determined from the magnetoexcitonic transitions by taking into account both the Coulomb correction and Landau quantization is shown in Fig. 2. In order to reduce the significance of the excitonic Coulomb interactions we have excluded the lowest transitions, leaving LL indices $n=3-13$ for σ^- , along with $n=5-10$ for σ^+ .

The extrapolation of the reduced dispersion to $k=0$ indicates that the Landau levels are derived from the A valence band. The Rydberg energy of 24.1 meV was estimated from the $1s-2s$ exciton separation in the same sample as used in this work¹⁵ using a hydrogenic model. Then from the calculated $2s$ binding energy, the band edge can be known to within ± 1 meV, despite not including the polaron corrections to the binding energy.⁵ No Landau levels can be seen from the B band, but its mass is expected to be considerably smaller, $m_B^\perp \sim 0.35$.¹⁶ This will give both a reduced oscillator strength and larger cyclotron splittings that will be difficult to see underneath the strong A band transitions.

The reduced dispersion is strongly nonparabolic, even after including the band contribution using Kane’s $k \cdot p$ framework in the two-band approximation¹⁷

$$E - E_g = \frac{\hbar^2 k^2}{2m^*} \left[1 - \frac{1}{E_g} \frac{\hbar^2 k^2}{2m^*} \left(\frac{m^*}{m_0} - 1 \right)^2 \right]. \quad (3)$$

The additional nonparabolicity is due to the importance of resonant polaron coupling in this material which is strongly polar.¹⁸ Further evidence for this idea comes from the rapid disappearance of observable transitions at an energy of 3620 meV, which corresponds to an energy where resonant coupling will occur for the electrons, $\sim (1 + m_e/m_h)E_{LO} + E_g$. This resonant polaron effect has a strong influence on the electron energy-momentum relation, $E(k)$, particularly when

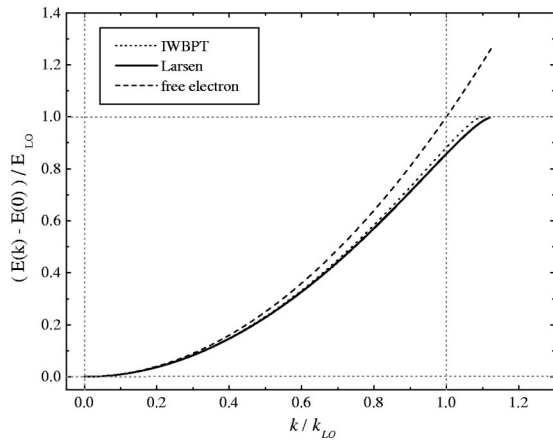


FIG. 3. The polaron energy spectrum calculated with perturbation theory (IWBPT) and variational techniques (Larsen), for $\alpha = 0.49$, compared with the free electron.

the LO-phonon energy is approached. A calculation of the electron-polaron dispersion relation is shown in Fig. 3.

The electron-phonon coupling constant in GaN is sufficiently large,¹⁸ i.e., $\alpha=0.49$, that perturbation theory is no longer valid. In order to calculate polaron effects, and in particular the energy-momentum relation,¹⁹ one has to go beyond the widely used “improved Wigner-Brillouin perturbation theory” (IWBPT). A suitable theory, which is valid for the intermediate electron-phonon coupling regime ($\alpha \leq 1$), is provided by the variational ansatz approach of Larsen²⁰ which is a combination of the one-phonon Tamm-Dancoff approximation²¹ and the Lee-Low-Pines transformation.²² The polaron energy-momentum relation is obtained from a solution of the secular equation²⁰

$$\Delta E = k^2 + \left(1 + \frac{\Delta E - k^2}{2k^2} \right) A(\Delta E),$$

with

$$A = \frac{\alpha}{2\pi k} \left(\pi(1+c)k - \int_0^1 dx \frac{1}{x} [D(c,x,p) + D(c,1/x,p)] \right),$$

where $D(c,x,p) = [(c+x^2)/(1+x^2)]^2 \ln[(c+x^2+2xp)/(c+x^2-2xp)]$ with $c = 1 + k^2 - \Delta E$. The above energy is in units of $\hbar\omega_{LO}$, the LO-phonon energy, and the electron wave vector is in units of $k_{LO} = \sqrt{2m\omega_{LO}/\hbar}$ where m is the electron band mass. In the limit of small polaron momentum one finds $\Delta E = E(k) - E(0) = k^2 [(1 - \alpha/12)/(1 + \alpha/2)]$ and consequently the small momentum polaron mass becomes $m^*/m = (1 + \alpha/12)/(1 - \alpha/12)$ which equals $m^*/m = 1.085$ for GaN ($\alpha = 0.49$).

The polaron correction to the energy-momentum relation is twofold. First, there is a renormalization of the electron mass into the polaron mass, m^* for small momentum/energy. Second, for larger energies close to the LO-phonon energy, a resonant interaction occurs between the electron and the crystal, resulting in a flattening of the $E(k)$ relation which leads ultimately to $\partial E/\partial k = 0$ at some critical $k^* > k_{LO}$. This resonant polaron-induced nonparabolicity correction to the

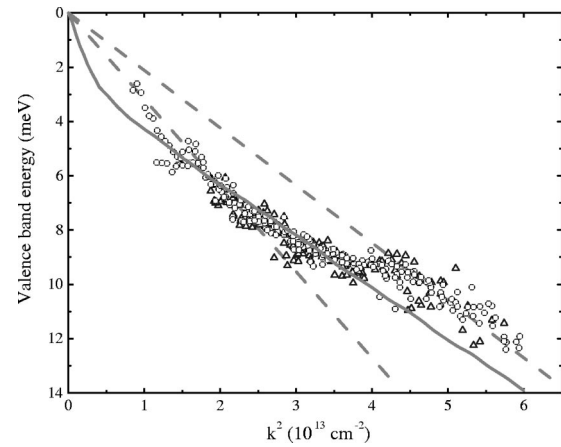


FIG. 4. The valence band dispersion of the A band deduced from the reduced dispersion with the electron contribution determined by the Larsen approach. Solid line from Kim *et al.* (Refs. 16,23). Dashed lines show constant masses of $m_h = 1.2$ and 1.8 . Circles: σ^- , Triangles: σ^+ .

$E(k)$ relation is particularly important as the LO phonon energy is approached as is apparent in both experiment (Fig. 2) and theory (Fig. 3). In accounting for this effect, we use the value for the low-energy polaron mass of $0.2220(5)m_e$,³ from which we deduce a bare band edge mass of $m = 0.204 m_e$.

Having taken proper account of the polaron corrections to the electron dispersion relation, it can now be subtracted from the reduced dispersion to give the valence band dispersion. This is shown in Fig. 4 as a function of k^2 . The data shows that the valence band is considerably nonparabolic as can be seen by the straight lines corresponding to parabolic masses of 1.2 and 1.8 in Fig. 4. However, theoretically this is expected as a result of the spin-orbit interaction,¹⁶ which splits the bands and leads to a much lighter mass at $k=0$ and strongly energy-dependent hole masses. The results from this theory,²³ for a slightly different value of the biaxial strain (and hence A-B separation), are also shown in Fig. 4. The agreement between the experimental data points and the

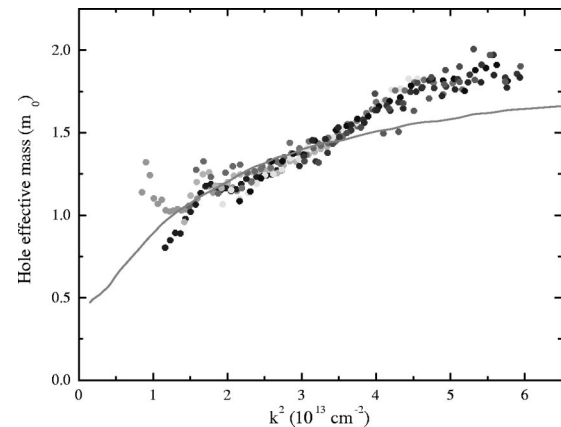


FIG. 5. The k -dependent effective A-hole mass for the σ^- polarization. Solid line from Kim *et al.* (Refs. 16,23).

theory is quite good, although it is not possible to access the very light mass region predicted by the theory very close to the band edge.

In order to determine the k -dependent effective masses, we define the quantity, $m(k) = k^2/E_k$, and these results are shown in Fig. 5. The effective masses can be seen to increase approximately linearly with k^2 from ~ 1.2 – $1.8m_e$, suggesting a band-edge mass value of $m_h \approx 0.8$, although we cannot exclude a value lower than this in the range $E \lesssim 5$ meV. When comparing these values with theory, however, it should be remembered that these values are measured at low frequency and will therefore represent the “hole” values with additional polaron dressing from the valence band and will therefore be somewhat higher than the bare band edge values.

To conclude, the results described show clearly the quite large mass values and strong nonparabolicity of the A -valence band in the direction perpendicular to the c axis. Consideration of the spin-orbit interaction is essential to understand this effect. It has been confirmed that whereas the band might be light at the band edge,^{16,5} this no longer holds for energies $\gtrsim 5$ meV into the band as also suggested by theory.¹⁶

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¹⁰The A valence band does not split for $B \perp c$, giving the electron g value in the free exciton. Our value of 2.00 ± 0.05 agrees with the value 1.95 deduced from electron spin resonance (Ref. 9).

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²³The spin-split A band dispersion from Fig. 7(a) of Kim *et al.* (Ref. 16) has been averaged to compare with the experimental data in Figs. 4 and 5.