Influence of nitrogen-cluster states on the gyromagnetic factor of electrons in GaAs$_{1-x}$N$_x$

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The effective gyromagnetic factor of electrons, g_e^*, has been determined by Zeeman splitting measurements in a large number of GaAs$_{1-x}$N$_x$/GaAs ($x < 0.7\%$) samples. Upon N incorporation, g_e^* shows first a sign reversal with respect to that of GaAs, then increases abruptly for a nitrogen concentration of order of 0.04%, and finally displays a nonmonotonic dependence on composition for higher x values. This behavior is well reproduced by a modified **k·p** model taking into account a nonmonotonic loss of Γ character of the conduction band minimum due to multiple crossings between the redshifting conduction band edge and N-cluster states.

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I. INTRODUCTION

A small fraction of nitrogen atoms incorporated isovalently in GaAs and GaP produces major modifications of the electronic properties of these compounds.[1] A dramatic band gap reduction is observed in GaAs$_{1-x}$N$_x$ and GaP$_{1-x}$N$_x$ as a result of the mixing between different conduction bands of the host crystal induced by the incorporation of single and multiple nitrogen complexes,[2] which break the lattice translational symmetry.[3] In GaAs$_{1-x}$N$_x$, the pressure[4] and temperature[5] coefficients of the band gap are reduced sizably with respect to the N-free case and the electron effective mass displays a rather unusual dependence on N concentration.[6–8]

Standard **k·p** models need to be modified for parametrizing the band structure changes of GaAs$_{1-x}$N$_x$ with composition[9] and even then cannot fully account for all the details of the band formation processes, e.g., the unusual dependence of the conduction band effective mass on N concentration. As a matter of fact, a satisfactory quantitative description of such dependence could be achieved only after including the effect of different N-cluster states on the GaAs$_{1-x}$N$_x$ band structure.[8]

The study of the evolution of the effective gyromagnetic factor of electrons, g_e^*, with increasing N concentration may provide additional information on the degree of interaction between the N levels and the conduction and valence bands and a further test of the different theoretical models aimed at describing the band structure of dilute nitrides.[3,10,11]

In this work, we measured by magnetophotoluminescence the Zeeman splitting of the free-electron to neutral-carbon acceptor transition, (e,C), in a wide series of GaAs$_{1-x}$N$_x$ samples. With increasing N concentration, x, the value of the electron gyromagnetic factor undergoes first a sign reversal with respect to that of GaAs, rapidly increases for $x = 0.04\%$, and finally exhibits a rather nonmonotonic

behavior at higher values of x. A modified **k·p** model reproduces this behavior well in terms of hybridization effects between N-cluster states and the conduction band (CB) edge.

II. EXPERIMENT

We studied a set of GaAs$_{1-x}$N$_x$ epilayers grown on GaAs by molecular beam or metal-organic vapor-phase epitaxy. The composition and layer thickness of the as-grown samples were determined by x-ray diffraction. *Nominal* N concentrations range from $x = 0.043\%$ to 0.7%. Additional N concentrations have been achieved by H irradiation of the samples, which permits a fine tuning of the effective N concentration due to the formation of stable nitrogen-dihydrogen complexes passivating N atoms.[2,12–14] The *effective* nitrogen concentration (ranging from 0.005% to 0.6%) was estimated in each case from the free-exciton energy (see Ref. 8) and it will be used hereafter to indicate the composition of the samples. Photoluminescence (PL) measurements were carried out in a liquid He optical cryostat. A magnetic field ($|B| = 0-12$ T) was applied in a Faraday configuration with $B < 0$, namely, parallel to the growth axis of the samples and opposite to the luminescence detection direction. Photoluminescence was excited by the 532 nm line of a vanadate-Nd laser, dispersed by a 3/4 m monochromator, and detected by a liquid-nitrogen cooled InGaAs linear array. Left and right circular polarization states of the luminescence were selected by using a liquid crystal variable retarder and a linear polarizer. The variation of g_e^* with x is also calculated by modeling the wave function of the CB edge of GaAs$_{1-x}$N$_x$ with a linear combination of randomly distributed isolated nitrogen states (LCINS model).[8,11]

III. RESULTS AND DISCUSSION

Figure 1 shows the PL spectra of three GaAs$_{1-x}$N$_x$ epilayers in the spectral region of the free-electron to neutral-
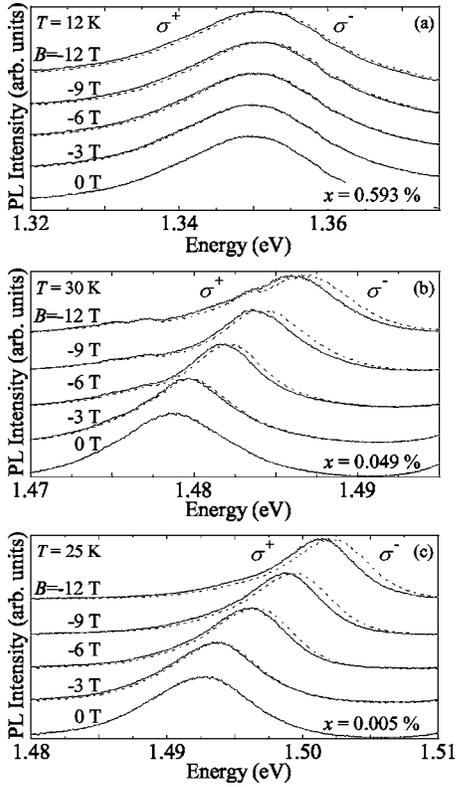
FIG. 1. Photoluminescence, PL, spectra in the region of the free-electron to neutral-carbon recombination, (e, C), under different magnetic field, B, values for GaAs$_{1-x}$N$_x$ samples with: (a) $x=0.593\%$; (b) $x=0.049\%$; (c) $x=0.005\%$. Solid (dashed) lines represent spectra for left circular polarized light corresponding to σ^+ transition (right circular light corresponding to σ^- transition). The negative sign for B indicates the Faraday configuration with B opposite to the luminescence detection direction. The spectra were taken at different temperatures and different laser-excitation power-densities to enhance the spectral contribution arising from the (e, C) transition.

carbon recombination band for different values of the magnetic field and opposite circular polarizations of the emitted photons. The spectra were taken at $T=10-30$ K in order to favor the (e, C) transition with respect to those related to N localized states. The g_e^* value of GaAs, though temperature dependent, varies only slightly in this temperature range.[15] With increasing B, the (e, C) band shifts to higher energy at a rate proportional to the inverse of the electron effective mass, whose value depends on x.[6–8] At the same time, the energy separation between the transitions leading to light emission with opposite circular polarization state increases (σ^+ and σ^- transitions are associated to left and right circular polarization, respectively). We will refer to this separation as the Zeeman splitting, $\Delta E_{\pm}$. Since the Zeeman splitting is much smaller than the PL linewidth, $\Delta E_{\pm}$ can be better estimated by

$$\Delta E_{\pm}(B) = \frac{I_{\sigma^+} - I_{\sigma^-}}{dI_{\sigma^+}/E}, \qquad (1)$$

where $I_{\sigma^{\pm}}$ is the peak-normalized luminescence intensity corresponding to $\sigma^{\pm}$ transitions, and $dI_{\sigma^+}(B)/dE$ is the first
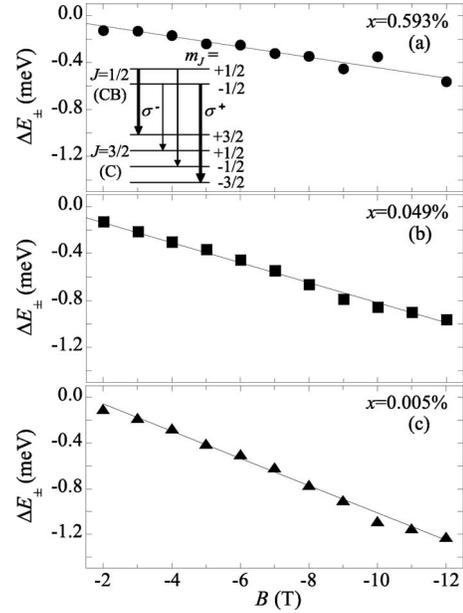

FIG. 2. Dependence of the Zeeman splitting, $\Delta E_{\pm}$, on magnetic field for the same samples shown in Fig. 1. Full symbols refer to experimental data (a) ($\bullet$, $x=0.593\%$), (b) ($\blacksquare$, $x=0.049\%$), (c) ($\blacktriangle$, $x=0.005\%$). Solid lines are fits of Eq. (2) to the data, where g_e^* is the only fitting parameter. Inset: Scheme of the levels involved in the (e, C) transition under a magnetic field. CB and C indicate, respectively, the conduction band and the carbon-related levels. J and m_J are, respectively, the total angular momentum and its projection along the magnetic field direction. Vertical arrows indicate dipole-allowed transitions in Faraday configuration (thicker-line arrows are transitions actually resolved in the experiment).

derivative of the PL signal with respect to the photon energy. In each sample, we applied Eq. (1) to the high-energy side of the (e, C) band in order to avoid the contribution from bands related to N cluster states, which in some cases appear on the low-energy side of the PL spectra.

Now, we address the origin of the transitions involved in the spectra shown in Fig. 1. The energy levels responsible for the (e, C) recombination are the conduction band minimum, with total angular momentum $J=1/2$, and the carbon acceptor level, with $J=3/2$. The four transitions allowed between these levels, in a dipole approximation for a Faraday configuration, are sketched in the inset of Fig. 2. Transitions may occur between states whose projection of J along the growth direction differs by $\Delta m_J=+1$ or -1 with right (σ^- transition) or left (σ^+ transition) circular polarization of the emitted photons, respectively.[16] However, only two PL components differing in the polarization state are resolved in our GaAs$_{1-x}$N$_x$ samples, as shown in Fig. 1, instead of the four components reported in GaAs.[16] In the N-containing samples studied here the linewidth of the (e, C) band is $5-10$ meV, i.e., much broader than that ($\leqslant 1$ meV) reported in N free, almost intrinsic GaAs.[16] Moreover, the density of states of the light-hole components of the C level ($m_J=\pm 1/2$) is three times smaller than that of the heavy-holes ($m_J=\pm 3/2$),[16] thus hampering the spectral resolution of transitions to the $m_J=\pm 1/2$ carbon states.[17] Consequently, only heavy-hole states will be considered in the analysis of Zeeman splitting measurements,[18] namely
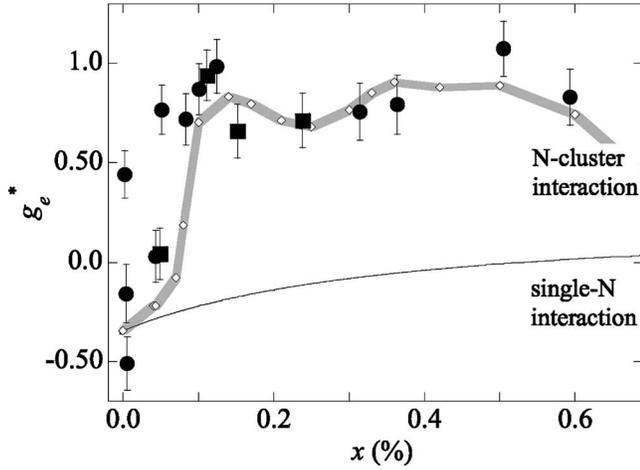
FIG. 3. Dependence of the electron gyromagnetic factor, g_e^*, on effective N concentration. Full squares (full circles) refer to as-grown (hydrogenated) samples. Open small diamonds connected by a solid gray line are the result of a modified three band $\mathbf{k \cdot p}$ calculation of g_e^* by Eq. (3). The solid thin line is the result of a three band $\mathbf{k \cdot p}$ calculation of g_e^* by Eq. (3) without including N-cluster states.

$$\Delta E_\pm(B) = (-g_e^* + 3g_{C3/2}^*)\mu_B B, \qquad (2)$$

where μ_B is the Bohr magneton and $g_{C3/2}^*$ is the gyromagnetic factor of the $m_J = \pm 3/2$ carbon state (we recall that in our case $B < 0$).

Values of $\Delta E_\pm$, as obtained from the PL spectra displayed in Fig. 1, are shown in Fig. 2 as a function of the applied magnetic field. The Zeeman splitting has a linear dependence on B up to -12 T with a slope depending strongly on nitrogen concentration.[19]

By taking for $g_{C3/2}^*$ the value it has in GaAs (0.52 ± 0.04),[16] namely, assuming that the valence band gyromagnetic factor is not affected by N incorporation, the dependence of g_e^* can be derived by fitting Eq. (2) to the Zeeman splitting data. The values of the electron gyromagnetic factor are shown in Fig. 3, where untreated and hydrogenated samples are indicated by different symbols. g_e^* exhibits a sign reversal for $x \gtrsim 0.04\%$ and increases abruptly in a very narrow compositional window between $x = 0.04\%$ and $x = 0.1\%$. For $x > 0.1\%$, the electron gyromagnetic factor has a not well-defined behavior and fluctuates around 0.7 for the highest x values. These results indicate highly nonlinear changes in the GaAs$_{1-x}$N$_x$ conduction band. It should be mentioned here that a steep increase in the electron effective mass, m_e^*, at $x = 0.1\%$ as well as a nonmonotonic compositional dependence for $0.1\% < x \leqslant 1.8\%$ was observed recently in these same samples.[8] This dependence on N concentration was accounted for quantitatively in terms of a strong hybridization between N localized levels and the CB edge. Such level admixing occurs whenever the CB minimum, redshifting for increasing N concentration, crosses through a set of N states. As discussed in the framework of a model which incorporates a linear combination of randomly distributed isolated nitrogen states,[8,11] the Γ character of the CB minimum, f_Γ^c, decreases under such resonance conditions and

the electron mass increases accordingly. f_Γ^c is calculated by $f_\Gamma^c = |\langle \psi_{\mathrm{GaAsN}} | \psi_{\mathrm{GaAs}} \rangle|^2$, where $|\psi_{\mathrm{GaAsN}}\rangle$ and $|\psi_{\mathrm{GaAs}}\rangle$ are the electron wave functions of GaAs$_{1-x}$N$_x$ and GaAs at the conduction band minimum, respectively. The first large loss of Γ character for $0.05\% \leqslant x \leqslant 0.1\%$ can be attributed to a crossing of the CB minimum with N pairs at $E \sim 1.49$ eV, occurring for $x \sim 0.1\%$. As x increases, the band edge redshifts and interacts with other cluster states located at lower energy. These states are due to N triplets mainly and concur in keeping f_Γ^c around 50–60 %, with fluctuations due to the discreteness of the N cluster density of states itself.[8]

In a three band $\mathbf{k \cdot p}$ model, g_e^* is given by[20]

$$\frac{g_e^*(x)}{g_0} - 1 = -\frac{P^2(x)}{3}\left(\frac{1}{E_g(x)} - \frac{1}{E_g(x) + \Delta_0}\right), \qquad (3)$$

where $g_0 = 2$ is the gyromagnetic factor of the electron in vacuum, $E_g(x)$ is the band gap energy of GaAs$_{1-x}$N$_x$, and Δ_0 is the split-off energy. The optical matrix element $P^2(x)$ measures the coupling between the CB minimum (Γ_1^c) and the valence band (Γ_5^v) maxima. In turn, this coupling depends mainly on nitrogen concentration via f_Γ^c. The variation of $E_g(x)$ with x is calculated by the model of Ref. 11, while the split-off energy is kept fixed at the GaAs value ($\Delta_0 = 0.341$ eV), as observed experimentally.[4,10] $P^2(x)$ is obtained from the GaAs value (=28.9 eV) (Ref. 20) corrected by the fractional Γ characters f_Γ of the involved band wave functions

$$P^2(x) = \frac{2}{m_0}|\langle \Gamma_1^c | \hat{p} | \Gamma_5^v \rangle|^2 f_\Gamma^c(x) f_\Gamma^v(x), \qquad (4)$$

where m_0 is the electron mass in vacuum, $\hat{p}$ is the momentum operator, and f_Γ^v is the valence band fractional Γ character, assumed to depend on N concentration as $(1-x)$ as reported in Ref. 11. The theoretical values of g_e^*, as obtained with no adjustable parameters from Eqs. (3) and (4), are shown by the thick gray line in Fig. 3. The overall agreement between the theoretical and the experimental values of g_e^* is very good. Therefore, the details of the conduction band modifications induced by nitrogen in dilute nitrides cannot just be described in terms of the interaction between the host CB and a single nitrogen level resonant with the conduction band, as assumed in the 2-level band-anticrossing (BAC) model.[10] The result of calculations performed within the same $\mathbf{k \cdot p}$ model but including the effects only of the single-N level (according to the BAC model) are shown by the thin line in Fig. 3. Clearly, a smooth variation of g_e^* with x is found if one neglects the effect of N clusters, in strong disagreement with the experimental data. As mentioned before, the compositional dependence of the electron gyromagnetic ratio shown in Fig. 3 resembles that of the electron effective mass previously reported in the same system. In the framework of a three band $\mathbf{k \cdot p}$ model, this is expected on the basis of Roth's formula[21]
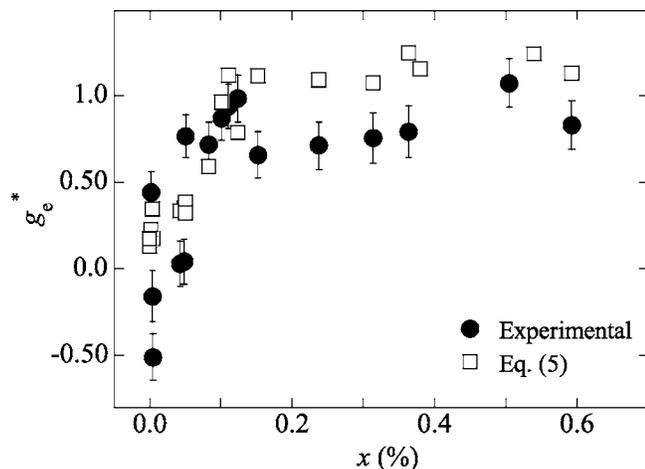
FIG. 4. Comparison between the compositional dependence of the electron gyromagnetic factor, g_e^*, as derived from Zeeman splitting experiments (full circles) and as determined by Roth's formula (open squares).

$$\frac{g_e^*(x)}{g_0} - 1 = -\frac{\Delta_0}{3E_g(x) + 2\Delta_0}\left(\frac{m_0}{m_e^*(x)} - 1\right), \qquad (5)$$

which establishes a relationship between m_e^* and g_e^*. In Fig. 4, the dependence on nitrogen concentration of the experimental g_e^* values shown in Fig. 3 is compared with the dependence predicted by Eq. (5), where the electron effective mass values employed were obtained in the same samples from the shift of the first electron Landau level induced by a magnetic field.[6–8] The agreement between the two sets of data is very good, especially if one considers that no free parameter is present in Eq. (5). This suggests a few considerations. First, since the gyromagnetic ratio and effective mass of electrons are derived from two independent measurements, the experimental consistency provided by Fig. 4 further supports the importance of the nitrogen cluster states in determining the electronic properties of $GaAs_{1-x}N_x$ as described by the LCINS model. Second, the **k·p** model is

based on a perturbative approach, which provides explicit expression for several physical quantities in solids.[22,23] In particular, this model predicts that the electron effective mass and gyromagnetic factor are *smaller* for the smaller band gap compounds and alloys. For $GaAs_{1-x}N_x$ this decrease is counteracted by the diminished value of the coupling parameter P^2 [see Eq. (4)], which follows the loss of Γ character of the CB minimum. In addition, the success of a "modified" **k·p** approach to account for the data of Figs. 3 and 4 indicates that the $GaAs_{1-x}N_x$ electronic states can be described in terms of coherent Bloch waves with a well-defined **k** vector, at least at the band extrema, where the Hamiltonian expansion is performed in the **k·p** model framework. Therefore, despite the loss of full translational symmetry deriving from the potential disorder induced by N clusters, a description of $GaAs_{1-x}N_x$ in terms of conventional semiconductor alloy concepts (such as electron effective mass) is still applicable for N concentrations as large as about 1%.[8]

IV. CONCLUSIONS

In summary, the electron gyromagnetic factor g_e^* turns out to be an insightful parameter particularly sensitive to the band structure of $GaAs_{1-x}N_x$. Indeed, its dependence on N concentration reflects the strong CB changes taking place when the CB minimum hybridizes with discrete N cluster states. This dependence is quantitatively backed by a modified 3 band **k·p** model and is qualitatively similar to that found for the electron effective mass. This confirms that a detailed description of the electronic properties of dilute nitrides cannot be achieved just by including the interaction between the host conduction band and a single N level, but must instead explicitly include the effects of the distribution of N states found in such alloys.

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