

## Electron Mass in Dilute Nitrides and its Anomalous Dependence on Hydrostatic Pressure

G. Pettinari, A. Polimeni,<sup>\*</sup> F. Masia,<sup>†</sup> R. Trotta, M. Felici,<sup>‡</sup> and M. Capizzi

*CNISM and Dipartimento di Fisica, Sapienza Università di Roma, P.le A. Moro 2, 00185 Roma, Italy*

T. Niebling and W. Stolz

*Department of Physics and Material Sciences Center, Philipps-University, Renthof 5, 35032 Marburg, Germany*

P. J. Klar

*Institute of Experimental Physics I, Justus-Liebig-University, Heinrich-Buff-Ring 16, 35392 Giessen, Germany*

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The dependence of the electron mass on hydrostatic pressure  $P$  in N-diluted GaAs<sub>1-x</sub>N<sub>x</sub> ( $x = 0.10\%$  and  $0.21\%$ ) is investigated by magnetophotoluminescence. Exceedingly large fluctuations (up to  $60\%/kbar$ ) in the electron mass with increasing  $P$  are found. These originate from a pressure-driven tuning of the hybridization degree between the conduction band minimum and specific nitrogen-related states. Present results suggest a hierarchy between different nitrogen complexes as regards the extent of the perturbation these complexes exert on the electronic properties of the GaAs host.

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Nitrogen-diluted III-V alloys, such as Ga(AsN), have strikingly unusual physical properties [1]. These latter include a giant reduction in the band-gap energy [2] and a puzzling compositional dependence of the parameters governing transport (i.e., the electron mass [3,4]) and spin-related (i.e., the electron gyromagnetic factor [5]) properties of the material. Such features are due to the strongly perturbed conduction band structure of Ga(AsN) [6] originating from the interaction of the GaAs extended states with localized electronic levels related to single and multiple N complexes (e.g., pairs, triplets, and clusters) [7], which modify the host properties already at N concentrations as small as  $10^{19} \text{ cm}^{-3}$  and whose formation is still a matter of debate [8]. These peculiar characteristics of dilute nitrides offer novel design opportunities for a widespread number of applications, which range from photovoltaics [1] to optoelectronic communications [9] and terahertz sources [10], including hydrogen-assisted defect engineering [8,11].

Great attention has been dedicated to the extraordinary behavior of the electron effective mass  $m_e$  in Ga(AsN) [3,4,10]. Indeed, this fundamental band structure parameter determines the transport properties and affects the density of states in solids. In the case of dilute nitrides,  $m_e$  turns out to be tremendously sensitive to sample composition and/or external perturbations. Electron mass becomes negative when carriers are accelerated by a high electric field ( $> 10^6 \text{ V/m}$ ) in the nonparabolic conduction band (CB) of GaAs<sub>1-x</sub>N<sub>x</sub> [10] and exhibits a strongly nonmonotonic dependence on  $x$  [3,4]. In order to fully understand (and exploit) the peculiar behavior of  $m_e$  in GaAs<sub>1-x</sub>N<sub>x</sub>, when the N concentration varies, one has to take into account the *concomitant* modifications in the statistical distribution of N complexes *and* in the relative alignment between the CB and N-related electronic levels. These two effects can be disentangled by the application of

a hydrostatic pressure  $P$ , which finely tunes the energy position of the conduction band edge in the same sample while maintaining fixed the type and number of nitrogen complex states. A modified  $\mathbf{k} \cdot \mathbf{p}$  model successfully describes the dependence of  $m_e$  on composition [3] and predicts a highly nonmonotonic behavior of  $m_e$  with increasing  $P$  [4]. Quite surprisingly, however, this prediction is in strong disagreement with the experimental monotonic dependence of  $m_e$  on pressure found by magnetotunneling spectroscopy in GaAs<sub>1-x</sub>N<sub>x</sub> quantum wells [12], an analysis of the excitonic radiative recombination line shape in In<sub>y</sub>Ga<sub>1-y</sub>As<sub>1-x</sub>N<sub>x</sub> thin layers [13], and calculations [14].

In this Letter, by a combined use of magnetic field  $B$  (0–12 T) and hydrostatic pressure  $P$  (1 bar–10 kbar) we determine the variation of the electron mass as a function of  $P$  in steps of 1 kbar, or less, in bulk GaAs<sub>1-x</sub>N<sub>x</sub> ( $x = 0.10\%$  and  $0.21\%$ ). The fine-tuning of the applied pressure allows observation of successive decreases and increases in the electron effective mass, not reported previously. This strikingly unusual dependence of  $m_e$  on hydrostatic pressure is attributed to a  $P$ -induced variation of the relative energy distance between the upward-shifting CB edge and *specific* N-related states. These results shed light on the role played by different N complexes and their relative importance in GaAs<sub>1-x</sub>N<sub>x</sub>, a debated issue of interest also for the optoelectronic and transport properties of dilute nitrides.

We studied three  $0.5 \mu\text{m}$ -thick GaAs<sub>1-x</sub>N<sub>x</sub> samples grown by metal-organic vapor-phase epitaxy on (001) GaAs substrates ( $x = 0.043\%$ ,  $0.10\%$ , and  $0.21\%$  as measured by high-resolution x-ray diffraction).  $m_e$  values were determined at different hydrostatic pressures by photoluminescence (PL) under a magnetic field directed along the [001] growth axis of the samples. Pressures were applied by means of a Cu:Be clamp cell filled with a 1:4 ethanol-methanol mixture, and  $P$  values were determined from the

shift of the characteristic fluorescence lines ( $R_1$  and  $R_2$ ) of a ruby crystal mounted in the pressure cell along with the sample [15]. We found a pressure coefficient for the band-gap exciton energy of a GaAs reference sample equal to 11.1 meV/kbar, in good agreement with previous measurements ( $10.8 \pm 0.3$  meV/kbar) [16]. GaAs $_{1-x}$ N $_x$  photoluminescence was excited by the 532 nm line of a frequency-doubled Nd:vanadate laser, dispersed by a single 3/4 m monochromator, and detected by a liquid nitrogen-cooled InGaAs linear array (spectral resolution of 0.1 nm). The ruby fluorescence was spectrally analyzed by the same 3/4 m monochromator in a doubled configuration and detected by a Peltier-cooled GaAs:Cs photomultiplier operating in a single-photon counting mode with a spectral resolution of 0.01 nm ( $P$  uncertainty =  $\pm 0.3$  kbar).

Figures 1(a) and 1(b) show the PL spectra at  $T = 90$  K of the  $x = 0.10\%$  and  $0.21\%$  samples, respectively, at different hydrostatic pressures. At ambient pressure, the free-exciton recombination band (FE) dominates the PL spectrum for both concentrations. As  $P$  approaches 6 kbar, nitrogen complex (NC) states (labeled  $C_i$ ,  $i = 0, \dots, 6$  in the figure), which are resonant with the CB continuum at ambient pressure, emerge into the band gap [17–19]. In turn, these NC levels provide low-energy recombination channels competing with the FE recombination, which indeed loses intensity [19]. The energy shift with  $P$ ,  $\beta_{P,E}$ , of the NC states depends on the type of complex considered and varies between 4.0 and 4.9 meV/kbar, in agreement with previous work [17,19]. In the case of the free exciton, instead,  $\beta_{P,E} = 10.5$  ( $x = 0.043\%$ ), 10.0 ( $x = 0.10\%$ ), and 9.1 meV/kbar ( $x = 0.21\%$ ). These values differ by  $\sim 15\%$  from those reported previously [17], likely due to the different measurement temperature ( $T =$

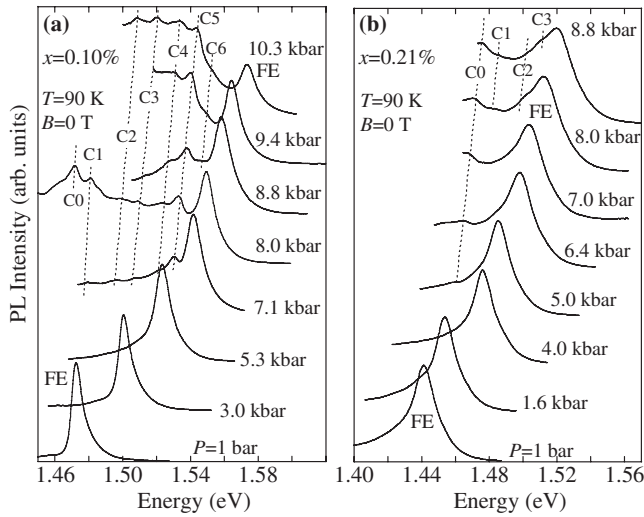


FIG. 1. (a) PL spectra at  $T = 90$  K and  $B = 0$  T of a GaAs $_{1-x}$ N $_x$  sample with  $x = 0.10\%$  recorded at different hydrostatic pressures  $P$ . FE and  $C_i$  indicate the free exciton and nitrogen complex-related recombinations, respectively. (b) Same as (a) but  $x = 0.21\%$ .

2 K) in that work. Hereafter, we restrict our analysis to magneto-PL measurements taken at a moderately high temperature (90 K), because we found that, at a low temperature (5 K), NC bands dominate the emission spectra as soon as  $P > 1$  kbar (not shown here; see also Ref. [19]).

Figures 2(a) and 2(b) show typical magneto-PL spectra for different  $P$ 's. The NC bands visible for  $P > 6$  kbar do not shift with increasing  $B$ , while the FE energy displays a nonlinear  $B$  dependence characteristic of Coulomb bound states [20]. In Figs. 2(c) and 2(d), the FE diamagnetic shift  $\Delta E_d$  is shown for different applied pressures. The dashed lines are best fits to  $\Delta E_d$  data by a numerical method [20], where the exciton reduced mass  $\mu_{\text{exc}}$  is the only fitting parameter. Within this approach, the exciton Hamiltonian in the presence of a magnetic field  $B$  is solved numerically by expanding the exciton wave function in terms of spherical harmonics. The only external parameter entering in the Hamiltonian is the exciton reduced mass  $\mu_{\text{exc}}$ , on which the size of both the exciton energy and the wave function depend. Following this method, in a GaAs reference we derived  $\mu_{\text{exc}} = 0.054m_0$ , in excellent agreement with previous determinations. Figures 2(c) and 2(d) show that  $\mu_{\text{exc}}$  (which decreases with increasing  $\Delta E_d$  curvature) and,

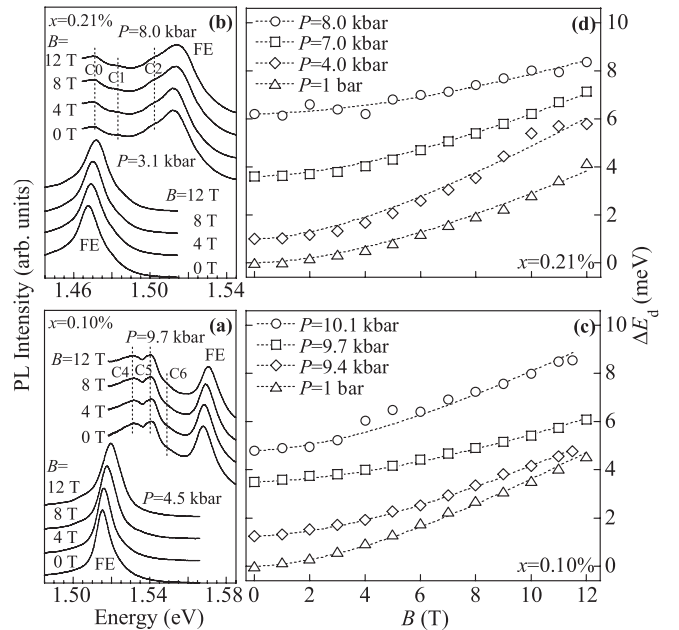


FIG. 2. (a) PL spectra at  $T = 90$  K for different magnetic fields  $B$  and two hydrostatic pressures on a GaAs $_{1-x}$ N $_x$  sample ( $x = 0.10\%$ ). FE and  $C_i$  indicate the free exciton and nitrogen complex-related recombinations, respectively. (b) Same as (a) but  $x = 0.21\%$ . Notice that in both cases the spectral weight of NC states increases with  $P$ . (c) Dependence of the free-exciton diamagnetic shift (open symbols)  $\Delta E_d$  on a magnetic field for different pressures in a GaAs $_{1-x}$ N $_x$  sample with  $x = 0.10\%$ . The dashed lines are a fit to the data by means of the model reported in Ref. [20]. The exciton reduced mass is the only fitting parameter. (d) Same as (c) but  $x = 0.21\%$ .  $\Delta E_d$  data are vertically shifted for clarity purposes.

hence,  $m_e$  do not depend monotonically on  $P$ . In the  $x = 0.10\%$  sample, an increase by only 0.3 kbar at  $\sim 9.7$  kbar causes a large difference in the  $\Delta E_d$  dependence on  $B$ . In the  $x = 0.21\%$  sample,  $\mu_{\text{exc}}$  (and  $m_e$ ) decreases sizably for  $P$  varying from 1 bar to 4 kbar, contrary to what was found in GaAs, where  $m_e$  increases with  $P$  at a rate  $\alpha_{P,m} = 5.2 \times 10^{-4} m_0/\text{kbar}$ ,  $m_0$  being the electron mass in vacuum [21].

Figures 3(a) and 3(b) show the pressure dependence of the electron mass, whose value is derived from the analysis described in the preceding figure using the hole mass obtained from independent measurements [3] and assuming that the hole mass does not change sizably with pressure [22] and temperature. At ambient pressure, in both samples  $m_e$  is much greater than the value it has in GaAs ( $0.067m_0$ ) because of an already strong admixing between

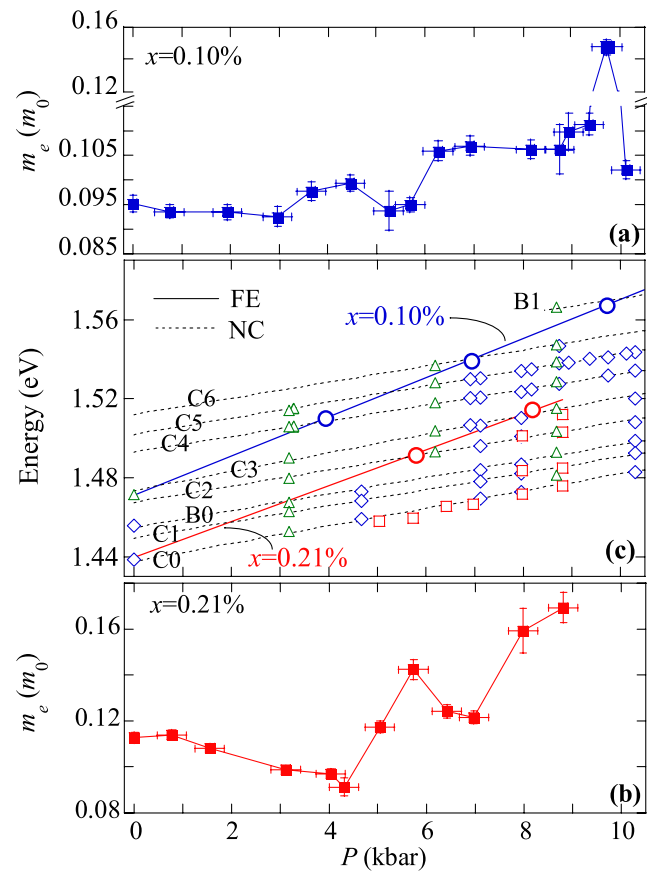


FIG. 3 (color online). (a) Dependence of the electron effective mass at  $T = 90$  K on hydrostatic pressure for a  $\text{GaAs}_{1-x}\text{N}_x$  sample with  $x = 0.10\%$ . (b) Same as (a) but  $x = 0.21\%$ . (c) Free-exciton energy vs pressure (solid lines) at  $T = 90$  K for the investigated samples. Symbols indicate the energy dependence on pressure of recombination bands related to N complexes in different samples (green  $\triangle$ :  $x = 0.043\%$ ; blue  $\diamond$ :  $x = 0.10\%$ ; red  $\square$ :  $x = 0.21\%$ ). Dashed lines are linear fits to the NC data.  $C_i$  label complexes shown in Figs. 1 and 2.  $B_i$  label complexes not observed in the spectra shown in the previous figures. Open larger circles highlight pressure values related to a marked increase of the electron mass as shown in (a) and (b).

N pair states and the CB edge [3,4]. We now discuss in detail the dependence of  $m_e$  on  $P$ . For  $x = 0.10\%$ ,  $m_e$  slightly decreases up to  $\sim 5.6$  kbar, except for a slight increase between 3.0 and 5.0 kbar. Then, after an increase by  $\sim 10\%$  at 6.3 kbar,  $m_e$  remains constant until  $P \sim 8.7$  kbar, suddenly increases by  $\sim 60\%$  at 9.7 kbar, and finally decreases at 10.1 kbar. For  $x = 0.21\%$ ,  $m_e$  decreases with increasing  $P$  up to 4.2 kbar, then increases by more than 25% at  $P = 5.8$  kbar, displays a second minimum at 7.0 kbar, and finally gets over  $0.16m_0$  at the highest applied pressure. It should be pointed out that, for some pressure intervals, these variations of  $m_e$  with  $P$  are almost 2 orders of magnitude greater than the linear increase usually observed in conventional semiconductors, about  $0.8\%/kbar$  [21].

The results shown in Figs. 3(a) and 3(b) differ from those reported in two previous studies of the electron mass dependence on pressure in  $\text{In}_y\text{Ga}_{1-y}\text{As}_{1-x}\text{N}_x$ . In the first study [13] ( $x = 1\%$  and  $2\%$ , and  $y \sim 3x$ ), the exciton reduced mass  $\mu_{\text{exc}}$  was derived from the linewidth of a PL band attributed to a bound exciton recombination. Pressure was varied in large steps up to  $\sim 110$  kbar—the 0–10 kbar range being covered by three pressures only.  $\mu_{\text{exc}}$  was found to increase steadily, and no peculiar pressure dependence was highlighted, as in Ref. [14]. In the second work [12] on  $\text{GaAs}_{1-x}\text{N}_x$  quantum wells ( $x = 0.10\%$  and  $0.20\%$ ), magnetotunneling measurements were performed at three pressures in the range investigated here. The concentrations of the samples studied in Ref. [12] are very close to those reported here; however, the achieved results appear to be noticeably different. In Ref. [12], the ratio of the electron mass with respect to its value at ambient pressure increases monotonically with  $P$  at a rate  $\alpha_{P,m} \sim 3 \times 10^{-3} m_0/\text{kbar}$ , in rough agreement with the predictions based on a band anticrossing model [2]. Moreover, this rate is independent of the N concentration.

Conversely, a much more complicated picture emerges from the data of Fig. 3, where the behavior of  $m_e$  on applied pressure shows marked differences on going from the  $x = 0.10\%$  sample to the  $x = 0.21\%$  sample. These differences are qualitatively accounted for by the fast evolution in the kind and density of nitrogen complexes forming in the N concentration range  $x = 0-0.5\%$ , where  $\text{GaAs}_{1-x}\text{N}_x$  exhibits strong and sudden changes in its physical properties [3–5,7,23]. As anticipated in the introductory section, for  $x$  varying between 0% and 0.6%, the compositional dependence of  $m_e$  is quantitatively reproduced by a theoretical model [3,4], which includes hybridization effects between different NC states and the conduction band edge. A behavior of  $m_e$  with hydrostatic pressure similar to that experimentally found here is predicted for  $x = 0.2\%$  by that same model [4] in terms of a variation in the  $\Gamma$  character of the CB minimum as soon as it resonates with NC states upon an applied pressure. In Fig. 3(c), we plot as a function of  $P$  the energy of the NC states (symbols and dashed lines; labels  $C_i$  refer to preced-

ing figures) and the energy of the band-gap exciton (solid lines), which is a few meV smaller than the CB-edge energy. Different symbols refer to NC bands measured in the  $x = 0.21\%$  and  $0.10\%$  samples as well as in a  $x = 0.043\%$  sample, where the same NC states of the two other samples are observed and the same pressure coefficients are found indeed (see dashed lines).

For the  $x = 0.10\%$  sample, the increases in  $m_e$  observed at  $P \sim 4.0, 6.3,$  and  $9.7$  kbar correspond to a crossing between the CB edge and N complex levels C4, C6, and B1, respectively [see open circles in Fig. 3(c)]. Importantly, quantitative differences between different complexes can be observed with respect to the extent of the increase in  $m_e$ . The crossing with C3 at  $\sim 0.5$  kbar produces no sizable change in the electron mass. A *minimum* in  $m_e$  is observed instead when the CB edge resonates with C5 at 5.0 kbar. In the case of the  $x = 0.21\%$  sample, the initial decrease in  $m_e$  for  $0 < P \leq 4.0$  kbar should be related to the CB minimum moving away from level C0, as well as to the absence of interaction with cluster levels C1 and B0. The two increases in  $m_e$  at  $P \sim 5.8$  and  $\sim 8.0$  kbar can be attributed to a mixing between the CB edge and complex levels C2 and C3, respectively [evidenced by open circles in Fig. 3(c)] [24].

These results highlight a few, yet important, aspects concerning the interplay between extended and localized states in  $\text{GaAs}_{1-x}\text{N}_x$ . First, every increase in  $m_e$  induced by pressure can be traced back to a crossing of the CB edge with an NC state, in agreement with the model presented in Ref. [4]. However, such a crossing appears as a “necessary but not sufficient condition” for having an electron mass variation, as observed for C1, B0, and C5 complexes. This suggests that the degree of mixing between NC and CB states likely depends on the N complex symmetry, thus justifying the absence of a strong interaction with some specific N complex, whose wave function has an odd symmetry [25]. Furthermore, the amount of this levels’ admixing should increase with the density of a given NC state. As an example, the strong interaction between the CB minimum and cluster C3 observed in the  $x = 0.21\%$  sample is not noticeable for  $x = 0.10\%$  likely because of the lower C3 density in the latter sample. In fact, for a random distribution, the density of N clusters containing  $n$  nitrogen atoms varies as  $x^n$  (or faster if N atoms segregate, as observed in  $\text{GaAs}_{1-x}\text{N}_x$  for  $x \sim 5\%$ ), thus resulting in a relative increase of the population of higher-order clusters (e.g., N triplets and chains) faster than that of lower-order ones (e.g., N pairs).

In conclusion, we investigated the effects of hydrostatic pressure on the electron effective mass of  $\text{GaAs}_{1-x}\text{N}_x$  for  $x = 0.10\%$  and  $0.21\%$ . The application of an external pressure induces large and highly nonmonotonic variations of  $m_e$ . Despite being exceedingly larger than those observed in conventional semiconductors, these variations are qualitatively consistent with a modified  $\mathbf{k} \cdot \mathbf{p}$  model based on the pressure-driven modulation of the  $\Gamma$  character of the conduction band as on- and off-resonance conditions

occur between the conduction band minimum and *specific* N complex levels. In particular, the selective character of this hybridization process provides guidance to identify which N complexes contribute most to modify the band structure of  $\text{Ga}(\text{AsN})$  and to what extent the symmetry and the relative population of the N complexes matter.

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\*Electronic address: polimeni@roma1.infn.it

†Present address: School of Physics and Astronomy, Cardiff University, 5 The Parade, Cardiff, CF243AA, United Kingdom.

‡Present address: Laboratory of Physics of Nanostructures, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.

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