Compositional dependence of the exciton reduced mass in $GaAs_{1-x}Bi_x$ ($x=0-10\%$)

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We report the compositional dependence of the exciton reduced mass, μ_{exc}, of $GaAs_{1-x}Bi_x$ in a very large Bi concentration range ($x=0$–10.6%). Photoluminescence under high magnetic fields (B up to 30 T) shows that μ_{exc} *increases* rapidly until $x\sim 1.5\%$ and then *oscillates* around $\sim 0.08\ m_0$, m_0 being the electron mass in vacuum, up to about $x=6\%$. Surprisingly, for $x>8\%$ the exciton reduced mass *decreases below* the GaAs value, in agreement with the expectations of a $k\cdot p$ model. Such a behavior reveals the existence of different concentration intervals, where continuum states of the valence and conduction band hybridize with Bi-related levels at different extents, thus conferring to the band edges a localized or bandlike character for $x<6\%$ and $x>8\%$, respectively.

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I. INTRODUCTION

Recently, there has been much interest in the science and applications of highly mismatched semiconductor alloys. In these materials, the substitutional isovalent impurities have size and atomic potential largely different from those of the atoms being replaced. Quite often, these alloys exhibit uncommon compositional dependences of their fundamental band structure parameters (e.g., band-gap energy and carrier effective mass) thus boosting the number of opportunities for materials engineering. The unusual properties of highly mismatched semiconductors stem from the impuritylike localized character that the host band edges acquire as a consequence of the hybridization with the impurity wave function.[1] Among other effects, this causes a largely nonlinear and unexpected variation of the band-gap energy with composition, as found in GaAs:N[2] and ZnTe:S.[3] Within this class of nonconventional materials, $GaAs_{1-x}Bi_x$ has attracted much curiosity because of a series of interesting characteristics that include a large band gap reduction[4–6] and a giant spin-orbit bowing.[7,8] Despite the relevance of these effects for Terahertz[9] and telecom optoelectronics, solar cells, and spintronics, very little is known about the $GaAs_{1-x}Bi_x$ transport properties.[10,11] In particular, this applies to the carrier effective mass, which has a relevant applicative interest and can provide insightful information about nature and extent of the interaction between Bi-related levels and the conduction band (CB) and valence band (VB) states of the host crystal.

In this work, we find by magnetophotoluminescence measurements that the exciton reduced mass, μ_{exc}, of $GaAs_{1-x}Bi_x$ shows an unexpected dependence on Bi concentration when it is measured in a wide concentration range ($x=0$–10.6%). μ_{exc} first increases rapidly by 50% ($0\leq x<\sim 1.5\%$), then fluctuates around 0.08 m_0 ($1.5\%<x<\sim 6\%$, m_0 being the electron mass in vacuum), eventually decreases below the GaAs value ($x>8\%$). Such behavior unveils a complex and unexpected evolution of the nature of the band edges. In the low Bi-concentration interval, the large value of the exciton reduced mass (about 0.08 m_0) indicates that the Bloch states of *both the valence and conduction bands* are affected on an equal footing as a consequence of Bi incorporation, although Refs. 10 and 11 report that the electron mobility is not affected largely by Bi incorporation. Instead, for $x>8\%$ we find that a conventional $k\cdot p$-like behavior (i.e., a carrier mass *decreasing* with decreasing band-gap energy) is restored. This behavior has not observed in the concentration range investigated in the better known alloy $GaAs_{1-y}N_y$. These results are discussed highlighting the role that the distribution of Bi atoms may play on the alloy band structure.

II. EXPERIMENT

The investigated $GaAs_{1-x}Bi_x$ samples have Bi concentration $x=0$, 0.6, 1.3, 1.7, 1.9, 3.0, 3.8, 4.5, 5.6, 8.5, and 10.6%. The samples were grown on (100) GaAs by solid source molecular beam epitaxy. Bi concentration was determined by combining x-ray diffraction and optical data. The growth conditions were set differently for different groups of samples as to incorporate the wanted Bi content.[6,12] Table I reports the main growth parameters along with the relevant physical quantities determined in this work. All samples were characterized first by temperature- and power-dependent photoluminescence (PL) using a 532 nm laser for excitation and a 0.75 m monochromator and an InGaAs linear array or Si charge coupled device detector (depending on sample emission energy) for spectral analysis. Magneto-PL was performed in a 30 T water-cooled resistive magnet, the luminescence being spectrally analyzed by a 0.30 m monochromator and detectors similar to those mentioned above. For magneto-PL the optical path was purged of water vapor by nitrogen gas in order to make easier the determination of peak position, in particular for the $x=8.5\%$ and 10.6% samples. All spectra have been normalized by the system response.

III. RESULTS

At low temperature, T, and at almost any excitation power density, P_{exc}, PL spectra of disordered semiconductor alloys

TABLE I. List of the samples investigated in this work. x is the Bi concentration, determined by combining x-ray and optical data, t is the $GaAs_{1-x}Bi_x$ layer thickness, T_G is the $GaAs_{1-x}Bi_x$ layer growth temperature, FWHM is the full-width at half-maximum of the photoluminescence spectra recorded at 200 K under excitation power density P_{exc} ~10 W/cm^2, and μ_{exc} is the exciton reduced mass obtained by fitting the diamagnetic shift of the PL peak in the framework of an excitonic model (m_0 is the electron mass in vacuum).

x (%)	t (nm)	T_G (°C)	PL FWHM (meV)	μ_{exc} (m_0)
0.6	40	360	57 ± 8	0.062 ± 0.002
1.3	350	380	78 ± 5	0.082 ± 0.003
1.7	250	380	64 ± 3	0.072 ± 0.002
1.9	125	380	61 ± 3	0.079 ± 0.004
3.0	30	380	110 ± 8	0.080 ± 0.002
3.8	56	300	66 ± 3	0.071 ± 0.003
4.5	30	300	94 ± 10	0.082 ± 0.002
5.6	30	290	102 ± 4	0.078 ± 0.003
8.5	30	270	67 ± 3	0.050 ± 0.002
10.6	30	270	68 ± 3	0.046 ± 0.002

are dominated by the contribution of localized exciton (LE) states.[13–20] Therefore, PL measurements vs T and P_{exc} have been performed for each sample in order to determine the experimental conditions that maximize the contribution of free-excitons (FE) and of band-to-band (B-B) recombination, which eventually dominates PL spectra at high T, with respect to that of localized states. Measurements at $T=10$ K and ~200 K are shown in Fig. 1 for two $GaAs_{1-x}Bi_x$ samples with $x=3.8\%$ [panels (a) and (b), respectively] and 8.5% [panels (c) and (d), respectively]. In these as well as in all other samples, the low-T PL spectra show a marked blue shift of the PL peak with increasing P_{exc} and a low-energy skewed lineshape. These features are typical signatures of finite-density localized states.[13–20] On the contrary, the PL peak energy of spectra taken at $T \sim 200$ K does not depend on P_{exc} (but for a small blue shift due to band-filling effects) and the PL lineshapes are inhomogeneously and symmetrically broadened, that is typical of free excitons or of band-to-band transitions in disordered alloys. Consequently, magneto-photoluminescence measurements have been performed at relatively high power-density (P_{exc} =5–400 W/cm^2) and temperature ($T \sim 200$ K).

Then, it is worth discussing the dependence on excitation power density of the diamagnetic shift $\Delta E_d(B)$. Figure 2 shows the shift of the PL peak energy with applied magnetic field B in the $x=1.7\%$ sample for two excitation power densities differing by a factor 60. At lower power density and small fields, a quadratic behavior is observed thus indicating that excitons are involved in the transition considered. At higher power density, the creation of a rather large density of photogenerated carriers enhances the occurrence of carrier-carrier scattering events. In turn, this—along with likely carrier scattering from Bi clusters—disrupt the coherence of the electron/hole cyclotron orbit. Therefore, a diamagnetic shift

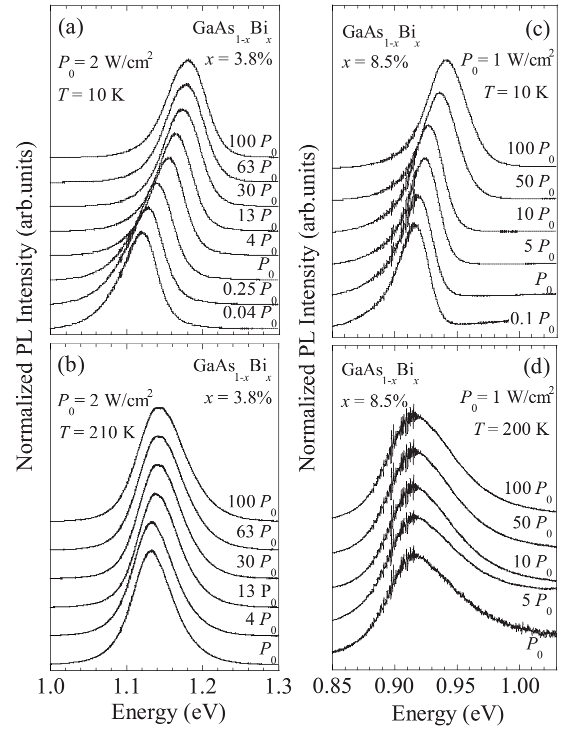

FIG. 1. Peak-normalized photoluminescence (PL) spectra of two $GaAs_{1-x}Bi_x$ samples with different bismuth concentration [x =3.8%: panels (a) and (b), and 8.5%: panels (c) and (d)] recorded at different values of excitation power density for $T=10$ K and T ~200 K.

begins to be observed at high P_{exc} only at magnetic fields higher than a critical field B_0, as reported previously in degenerate GaAs and InN.[21] It should also be noticed here that the *dependence* of ΔE_d on B does not change with photogenerated carrier density once $B > B_0$. This warrants that the values of the carrier mass that can be derived by the ΔE_d vs B dependence do not depend on P_{exc} within the experimental uncertainty. In addition, this confirms a vanishing contribution of localized states to the PL spectra under the chosen experimental conditions. A situation similar to that shown in Fig. 2 has been observed in other samples too.

Panels (a) to (d) of Fig. 3 show the PL spectra of some of the $GaAs_{1-x}Bi_x$ samples recorded for different magnetic

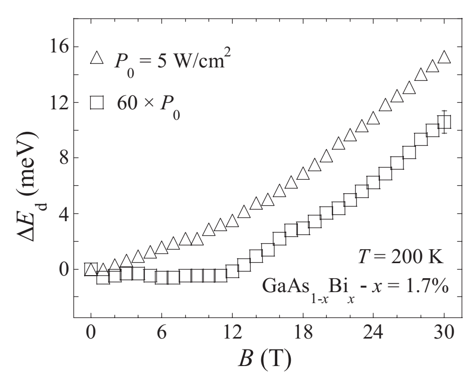

FIG. 2. Free-exciton diamagnetic shift (ΔE_d) as a function of magnetic field B and different power densities for a $GaAs_{1-x}Bi_x$ sample with $x=1.7\%$. The typical error bar is shown for one point.

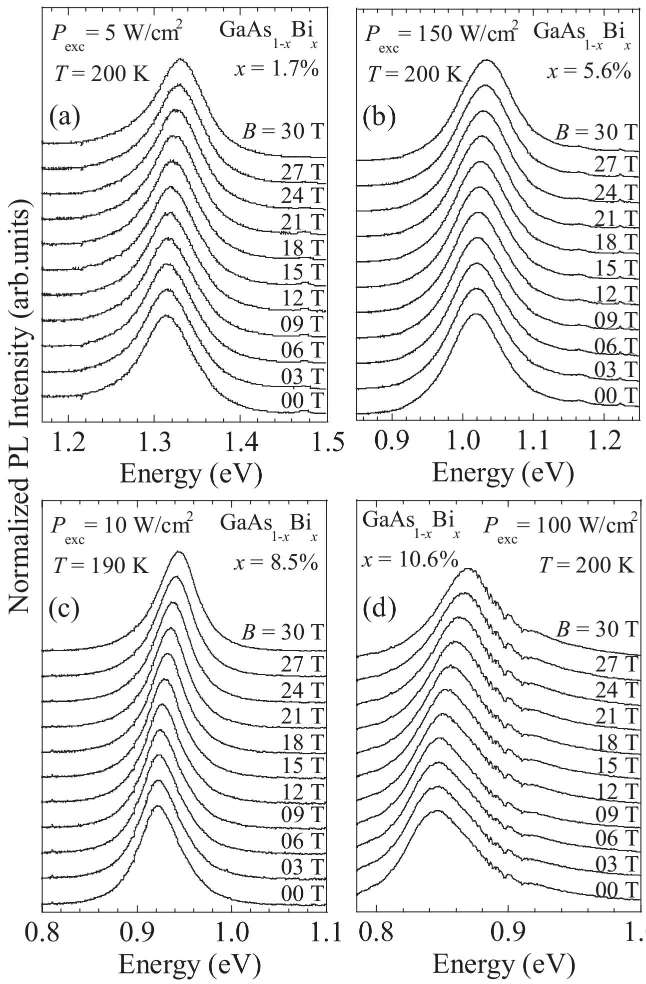

FIG. 3. Peak-normalized photoluminescence (PL) spectra of a selection of $GaAs_{1-x}Bi_x$ samples with different bismuth concentration [(a): x=1.7%, (b): x=5.6%, (c): x=8.5% and (d): x=10.6%] recorded at different values of magnetic field (B up to 30 T). Spectra of different samples were taken at $T \sim 200$ K with a different value of the excitation power density (indicated in the figure).

fields at $T \sim 200$ K. All samples show a clear blue shift with magnetic field and a quite symmetrical broadening typical of disordered alloys. The dependence of the PL linewidth on x is shown in Fig. 4 for spectra recorded at T=200 K under

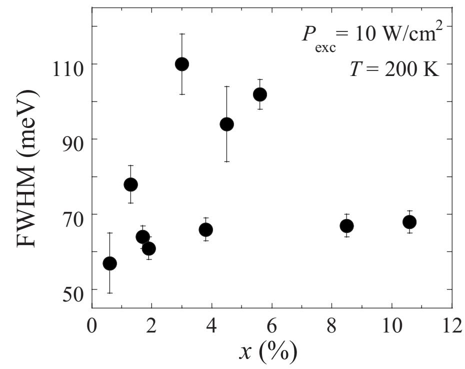

FIG. 4. Dependence on Bi concentration of the full-width at half-maximum (FWHM) of PL spectra recorded at 200 K under a same excitation power density ($P_{exc} \sim 10$ W/cm^2).

similar excitation power densities ($P_{exc} \sim 10$ W/cm^2): It cannot be accounted for by different growth conditions of the samples, at least on the ground of data reported in Table I.[12] We will further comment on the significance of these data in the Conclusions section.

An overview of the magneto-PL results is displayed in Fig. 5. The diamagnetic shift of $GaAs_{1-x}Bi_x$ (full symbols) is directly compared with the same quantity determined in GaAs (open symbols) under similar experimental conditions of P_{exc} and T. The slope (and extent at fixed B) of $\Delta E_d(B)$ is roughly proportional to the inverse of the exciton reduced mass, μ_{exc}. It is then evident at first glance that this slope displays a quite surprising behavior with increasing B: it *rapidly decreases* with respect to that of GaAs (for x=0.6 and 1.3%), then it *remains roughly constant* and well below that of GaAs (up to 5.6%), finally, it *goes greater* than that found in GaAs (for x=8.5 and 10.6%). The same figure shows also the analysis (lines) of the data by a numerical method[22–24] that applies to excitons under arbitrary magnetic fields. In this method, the exciton reduced mass and the zero-field energy are the only fitting parameters.[23] It could be questioned, however, whether FE or B-B transitions are involved in PL spectra taken at a temperature as high as $T \cong 200$ K. As regards this question, magneto-PL measurements have been performed in a GaAs sample under the same experimental conditions of P_{exc} and T of the measurements done in $GaAs_{1-x}Bi_x$. The GaAs carrier masses are known and an

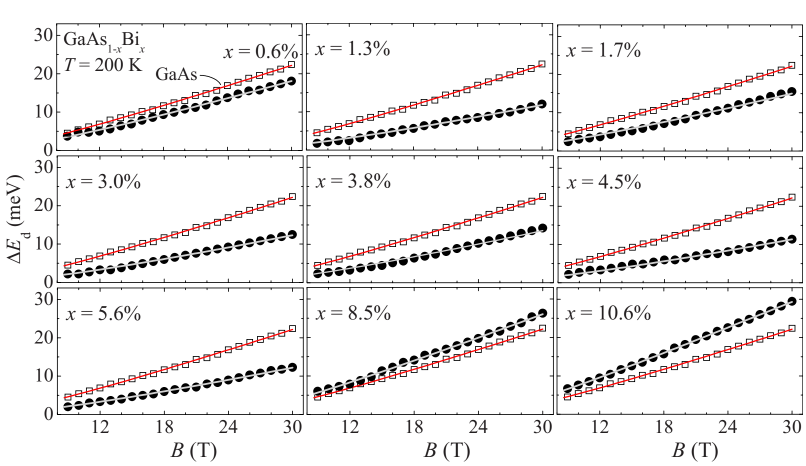

FIG. 5. (Color online) Free-exciton diamagnetic shift (ΔE_d) as a function of magnetic field for $GaAs_{1-x}Bi_x$ samples (full symbols) with different bismuth concentration (indicated in the figure). Lines are fits to the data by means of the model reported in Refs. 22–24. The diamagnetic shift of GaAs bulk (recorded under similar experimental conditions) is displayed by open symbols. Notice the change of slope with respect to GaAs for x=8.5 and 10.6%.

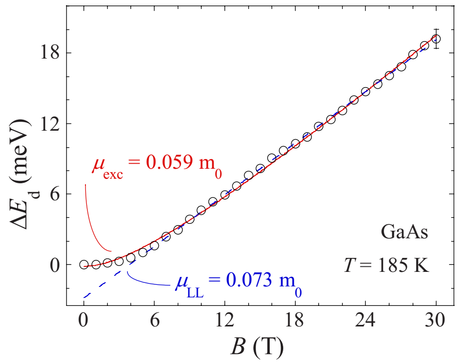

FIG. 6. (Color online) Free-exciton diamagnetic shift (ΔE_d) as a function of magnetic field for the GaAs buffer layer (full symbols). Lines are fits to the data by means of the excitonic model (solid line) reported in Refs. 22–24 and of the Landau level model (dashed line). The values of the electron and hole reduced mass obtained within the two models are shown in the figure. The typical error bar is shown for one point.

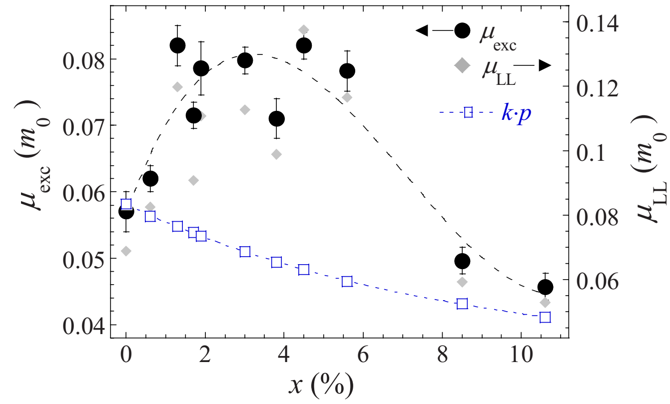

FIG. 7. (Color online) Estimated values of the electron and hole reduced mass as a function of Bi concentration as obtained in two different approaches: bound (full black circles) or unbound (full gray diamonds) electrons and holes. Notice the double *y* plot. Error bars indicating the uncertainty on μ_{exc} are shown. The open squares are the result of $k \cdot p$ calculations following Refs. 29–31. The lines are guides to the eye.

analysis of the diamagnetic shift can be performed in terms of excitonic transitions, as for $GaAs_{1-x}Bi_x$ data, and of transitions between Landau levels of free electrons and holes. In the latter case, $\Delta E_d(B)$ should increase linearly with the applied field B and the reduced masses, μ_{LL}, would be directly proportional to the inverse of the slope of the diamagnetic shift. $\Delta E_d(B)$ values measured in GaAs and their theoretical fits in terms of both the excitonic and Landau level models are shown in Fig. 6. At a glance is clear that a linear fit poorly reproduces the experimental data in the whole magnetic field range. Moreover, the known value of the reduced electron and hole mass in GaAs (μ_{exc}=0.057 m_0) (Ref. 25) is much nearer to the value we find in the excitonic model (μ_{exc}=0.058±0.002 m_0, as derived by an average value over different measurements) than to the value found in the Landau level model (μ_{LL}=0.074±0.01 m_0).[26] In conclusion, present GaAs PL spectra seem to be dominated by free exciton recombination at $T \sim 200$ K. Similar conclusions have been previously obtained in GaAs by reflectivity measurements at room temperature[27] and PL measurements[28] (the latter measurements show that the PL peak position coincides with the FE peak energy even at room temperature).

As a final check, we have applied the Landau level model to the analysis of the diamagnetic shifts for $B > B_0$ in $GaAs_{1-x}Bi_x$ (linear fits to data are not shown in Fig. 5 for clarity purposes). Eventually, the best fit values of μ_{exc} (full black circles) and μ_{LL} (full gray diamonds) are shown as a function of Bi concentration in a double *y*-axis plot in Fig. 7. The μ_{exc} values are averages over similar mass values obtained for different temperatures and laser power densities (as long as the experimental conditions guarantee the absence of localized states), which has allowed an estimate of the experimental uncertainty shown in the figure. In agreement with the qualitative analysis of diamagnetic shift data in Fig. 5, μ_{exc} undergoes a rapid increase (from 0.058 m_0 for x=0% to 0.082 m_0 for x=1.3%), then oscillates (around a mean value equal to 0.078±0.005 m_0), finally it decreases below the GaAs value (for $x > 8\%$). The reduced masses μ_{LL}, roughly 50% higher than μ_{exc}, strictly mimic the dependence of μ_{exc} on Bi concentration. However, as found in the GaAs case, the diamagnetic shifts in Fig. 5 do not display a well defined linear dependence on B even at the high magnetic fields $B > B_0$ required by the use of high excitation powers; see Fig. 2. In conclusion, all experimental evidences indicate that at $T \sim 200$ K the PL spectra are dominated by free exciton in GaAs as well as in $GaAs_{1-x}Bi_x$.

IV. DISCUSSION

Since similar values of μ_{exc} are found in samples grown under different conditions (and sometimes even exhibiting sizably different PL linewidth; see, e.g., data for x=1.9, 3.0, and 4.5% samples reported in Table I), the dependence of μ_{exc} on Bi concentration is a genuine material feature, not related to the sample growth details. μ_{exc} values first indicate that the *electron* effective mass increases up to a value of 0.08 m_0, at least, in a wide Bi concentration range (1.3% $\leq x \leq$ 5.6%). Indeed, if the electron effective mass kept the value of 0.067 m_0 it has in GaAs, the reduced exciton mass μ_{exc} would never exceed that value, even in the limiting case that the hole effective mass m_h got an infinite value upon Bi insertion in the GaAs lattice. On the contrary, in the whole range 1.3% $\leq x \leq$ 5.6% μ_{exc} is equal to $\sim$0.08 m_0, as already shown by us in the case of the x=1.9% sample.[19,32] In turn, this greatly supports a strong effect of Bi insertion on *the GaAs conduction band*, independently of the choice of an excitonic or band-to-band recombination model. As a matter of fact, the value found for the electron effective mass in the Landau level model is higher by a factor $\sim$1.5 than the value found in the excitonic model, even for an infinite hole effective mass.

This effect of Bi on the GaAs conduction band is unexpected and quite surprising on the ground of current theoretical models and experimental results.[33] Phenomenological models[34] and calculations based on the local density approximation[7,35] find that Bi alloying of GaAs leads to the formation of energy levels either resonant with[7] or above[35] the *valence* band of the host. As the Bi concentration increases and the energy gap decreases, the band edges shift and cross the energy-pinned Bi-complex levels. In turn, this should give rise to sizable changes only of the *hole* effective mass m_h. These expectations are supported by the results reported for the dependence on N concentration of the free electron/exciton effective mass[23,36–38] and localized exciton reduced mass[39] in GaAs:N, a system somewhat similar to $GaAs_{1-x}Bi_x$ once the roles of electron and holes (of conduction and valence bands) are exchanged. In GaAs:N, N introduces a level resonant with the conduction band, which only slightly affects the valence band states.[40] On the ground of this similarity, therefore, no major change should be expected for the electron effective mass in $GaAs_{1-x}Bi_x$, contrary to present results. It could be worth mentioning that recent structural measurements in samples similar to those studied here report on strong pairing and clustering of Bi atoms up to $x=2.4\%$,[41] also evidenced by low-temperature PL measurements.[20] Bi pairs and clusters may then strongly affect the $GaAs_{1-x}Bi_x$ electronic properties, as found[38,42] in the case of N pairs in $GaAs_{1-x}N_x$.

The inversion of the compositional dependence of μ_{exc} for $x>8\%$, namely, the remarkable decrease of the exciton reduced mass below the GaAs value, is even more intriguing. This "reversed" trend of μ_{exc} would be expected for a "conventional" alloy, where the carrier effective mass decreases with the energy band gap E_g. Indeed, for $x>8\%$ the predictions of the $k\cdot p$ model[29,30] (open squares in Fig. 7) are in good agreement with the experimental values.[31] Therefore, in this concentration range the localized character of the band extrema following Bi incorporation (and leading to an increase of μ_{exc}) should lose importance with respect to the energy gap reduction, which causes, instead, a decrease of the carrier effective mass in a $k\cdot p$ framework. We speculate that either the energy distance between the VB and CB edges and the Bi levels increases as to render negligible their interaction and/or the alloy recovers progressively a random atomic distribution of Bi for $x>8\%$ (thus following more closely the expectations of a "regular" alloy). This latter hypothesis relates with recent theoretical calculations showing that in nitride semiconductors the band gap bowing[43,44] and the carrier effective mass[43] as well as electronic properties[45] depend dramatically on details of disordered potential. Specifically, for a fixed N concentration in GaSb:N, the electron effective mass may increase *or decrease* with respect to that of N-free GaSb.[43] Within this scenario, we point out the decrease of the PL full-width at half-maximum observed in the $x=8.5$ and 10.6% samples that suggests an increased alloy ordering consistent with the reduced mass data shown in Fig. 7.

V. CONCLUSIONS

In summary, we investigated by magneto-PL the electronic properties of $GaAs_{1-x}Bi_x$ alloys over a wide compositional range ($x=0$–10.6%). The peculiar dependence of the exciton reduced mass on x reveals a rather fascinating evolution of the nature of the band extrema that change their character from impuritylike to bandlike. Indeed, depending on the Bi concentration we observe an exciton reduced mass greater ($x<6\%$) or smaller ($x>8\%$) than the same quantity measured in the Bi-free material. Moreover, conduction band states too are strongly affected by Bi incorporation, contrary to common expectations of an effect mainly restricted to the valence band states, only. These features should guide the theoretical modeling seemingly required to reformulate the electronic properties of $GaAs_{1-x}Bi_x$. Finally, the decrease in the carrier effective mass we find for $x>8\%$ turns out to be of particular interest in all those applications where carrier mobility is a relevant issue.

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[32] The different value found here for x=1.9% with respect to that reported in Ref. 19 in the same sample is due to a more refined study involving measurements at different laser powers and temperatures.

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