Bismuthides form a new class of highly mismatched semiconductor alloys with very peculiar properties. Bismuth alloying in GaAs produces a band gap reduction sizably larger than that achieved for a same mismatch of the lattice constant by alloying N, Sb, or In in GaAs.\(^1\)-\(^4\) Bismuthides are, therefore, promising candidates for photovoltaic and telecommunication applications based on GaAs technology.\(^5,6\) Moreover, large relativistic corrections reduce the Bi chemical valence from 5 to 3, e.g., in Bi\(_2\)Te\(_3\) and Bi\(_2\)Se\(_3\), giving rise to intriguing phenomena in the incorporation of Bi in a GaAs lattice.

In GaAs\(_{1-x}\)Bi\(_x\), the exciton reduced mass\(^7,8\) and the short range ordering of Bi atoms\(^9\) display an anomalous compositional dependence. For \(x < \sim 5\%\), the exciton reduced mass increases\(^7,8\) with \(x\) and Bi atoms display a short range ordering (SRO).\(^9\) For \(x > \sim 5\%\), the exciton reduced mass largely decreases and begins to follow a regular \(k\cdot p\) behavior, while a random anion distribution is restored. These results support theoretical predictions\(^10,11\) that a simple virtual crystal approximation cannot account for the electronic properties of GaAs\(_{1-x}\)Bi\(_x\) and that more complex Bi-related states should play a key role in this alloy. However, these states have been scarcely investigated and their presence,\(^12,13\) energy position,\(^10,11\) and compositional evolution are still debated issues.

In this work, far-infrared (FIR) absorption measurements as a function of magnetic field in nominally undoped GaAs\(_{1-x}\)Bi\(_x\) show transitions belonging to the Lyman series of Bi-related acceptor states. The Lyman series dominates the absorption spectra for \(x < 5\%\), while it suddenly disappears at higher Bi concentrations. Thus, the present FIR absorption measurements confirm a transition in the material electronic properties for \(x \sim 5\%\) and provide a clue about the sudden changes observed in the exciton reduced mass and SRO of GaAs\(_{1-x}\)Bi\(_x\) for \(x \sim 5\%\).

GaAs\(_{1-x}\)Bi\(_x\) epitaxial layers (thickness \(t = 30–125\) nm; \(x = 0.6\%, 1.9\%, 3.8\%, 4.5\%, 5.6\%, 8.5\%,\) and 10.6\%) grown by solid source molecular beam epitaxy on a GaAs substrate were investigated; see elsewhere for details on the growth procedure and sample parameters.\(^1,6,8\) The Bi concentration was determined by combining x-ray diffraction and optical data. Far-infrared absorption at \(T = 2\) K was measured in the 50–500 cm\(^{-1}\) spectral region by means of a Fourier transform interferometer (Bruker IFS-113v) with an unapodized spectral resolution of 1 cm\(^{-1}\). The FIR radiation coming from an evacuated beam line was partially transmitted through the sample and detected by a liquid-helium-cooled Si-composite bolometer. A secondary optical illumination (HeNe laser, \(P_{\text{exc}} \sim 30\) mW/cm\(^2\)) was directed onto the sample to increase the signal from the impurity levels.\(^14\) The signal dependence on magnetic field \(B\) was determined in the Faraday geometry with the sample in a 33-T water-cooled Bitter magnet.

Figure 1 shows the transmission \((T)\) spectra of the \(x = 4.5\%\) sample for different values of \(B\). In the displayed spectra, the transmitted FIR intensity under secondary optical illumination, \(I_{\text{exc}}(B)\), has been normalized to the transmission intensity at zero magnetic field without secondary optical illumination, \(I_{\text{dark}}(B = 0)\): \(T = I_{\text{exc}}(B)/I_{\text{dark}}(B = 0)\). The increase upon secondary illumination in the FIR absorption from carriers bound to impurity levels,\(^14\) shown in the inset of Fig. 1(a) for \(B = 0\) T, has allowed the observation of absorption peaks for transmissions as small as \(T \sim 1\%\). In the spectral region from 110 cm\(^{-1}\) to 240 cm\(^{-1}\), the transmission spectrum at \(B = 0\) T shows four main absorption peaks with energies and relative intensities characteristic of hole transitions from the ground to the excited states of shallow acceptors.\(^14\)-\(^16\) Transitions at 124.2 ± 0.5 cm\(^{-1}\), 156 ± 1 cm\(^{-1}\), and 172.7 ± 0.5 cm\(^{-1}\) are attributed to the three first parity-allowed transitions of the Lyman series, namely, the \(G, D,\) and \(C\) lines, in the order.\(^16\) The energy differences between \(C\) and \(D\) lines (16.7 ± 1.5 cm\(^{-1}\)) and \(G\) and \(D\) lines (31.8 ± 1.5 cm\(^{-1}\)) are in good agreement with those theoretically predicted and experimentally observed for shallow acceptors in GaAs.\(^14\),\(^16\),\(^18\)-\(^20\) The \(E_b\) absorption peak at 203 ± 1 cm\(^{-1}\) (25.2 ± 0.2 meV) is attributed to a hole transition from the ground state to the continuum (top of the valence band) in the Lyman series and directly gives the acceptor binding energy. Since none of the binding energy values
The increase in absorption peak intensity upon a secondary optical illumination (Ref. 25). The dashed line at high fields highlights the GaAs reststrahlen band. Landau-related series expected for given in the figure. Solid lines are visual guides; dotted lines give the absorption intensity in arbitrary units. Normalization factors are resolved; see text and Ref. 17 for the labeling. (b) Energy dependence on the absorption peaks shown in panel (a). Symbol size indicates the value \( E_b \) of the common substitutional acceptors in GaAs matches this value \( E_b^{\text{Ga}} = 26.9 \text{ meV}, E_b^{\text{Mg}} = 28.7 \text{ meV}, E_b^{\text{Si}} = 30.6 \text{ meV}, E_b^{\text{Bi}} = 34.8 \text{ meV} \), the observed absorption spectra ought to involve some different Bi-related acceptor state \( \sim 25 \text{ meV} \) above the valence band maximum. The dependence of the absorption peaks on \( B \) shown in Fig. 1(b) unveils the nature of this acceptor state. Different acceptor transitions split into components related to different magnetic moments and characterized by quadratic diamagnetic shifts. As a matter of fact, the \( E_b \) absorption peak splits into a series of transitions related to free-hole Landau levels of increasing energy \( (L_{n}) \), whose linear dependence on \( B \) is well resolved at high fields as soon as these transitions emerge from the GaAs reststrahlen band. The Landau level model gives a free-hole effective mass \( m_b^* = 0.47 m_0 \), where \( m_0 \) is the electron mass in vacuum.

The excellent agreement with heavy-hole values reported in the literature confirms the acceptor nature of the involved state. The absorption peak with energy intermediate between the \( L_1 \) and \( L_3 \) transitions (much more intense than neighboring peaks) cannot be attributed, however, to the Landau-related series. The diamagnetic shift of this peak has a slope \( (6.79 \text{ cm}^{-1}/T) \), much larger than that of the neighboring \( L_n \) transitions and extrapolates at \( B = 0 \) T at \( 171 \pm 1 \text{ cm}^{-1} \), namely, the energy of the \( C \) line. Therefore, this transition is attributed to the highest-energy component of the Zeeman multiplet related to the \( C \) line. The other two components of the Zeeman multiplet are clearly resolved at lower energies, for all magnetic fields (a scheme of the involved levels is shown in the inset of Fig. 2). The energy splitting of the \( C \)-line Zeeman multiplet is analyzed as done by Lewis et al. to determine the \( g \) factors of Be acceptors in GaAs. In the Faraday geometry of our experimental setup, only transitions between acceptor states differing by \( \Delta m_j = \pm 1 \) are measured, preventing an independent determination of the two parameters, \( g_1 \) and \( g_2 \), that define the linear Zeeman shift of the acceptor ground state. Nevertheless, an effective gyromagnetic factor \( g_{\text{eff}} \) can be estimated for the acceptor ground state. Indeed, the total energy splitting of the four ground-state sublevels, namely, the energy difference between the highest-energy and the lowest-energy components of the \( C \) line, is given by \( \Delta E = (4g_1 + 7g_2) \mu_B B = g_{\text{eff}} \mu_B B \). The value obtained by this analysis, \( g_{\text{eff}}^{\text{Bi}} = 14.9 \), is one order of magnitude larger than that predicted for a normal substitutional shallow acceptor in GaAs \( (g_{\text{eff}} = 1.93) \) and observed for Be and C.

FIG. 1. (Color online) (a) Transmission spectra at \( T = 2 \) K of a GaAs\(_{1-x}\)Bi\(_x\) sample \((x = 4.5\%)\) for magnetic fields \( B \) up to 30 T applied in steps of 1 T. Dotted lines are visual guides. The vertical dashed line at \( \sim 151 \text{ cm}^{-1} \) indicates a spurious spectral feature. The increase in absorption peak intensity upon a secondary optical illumination (by a HeNe laser, \( P_{\text{Ne}} \sim 30 \text{ mW/cm}^2 \)) is shown in the inset for \( B = 0 \) T. Absorption peaks related to a shallow acceptor are clearly resolved; see text and Ref. 17 for the labeling. (b) Energy dependence on \( B \) of the absorption peaks shown in panel (a). Symbol size indicates the absorption intensity in arbitrary units. Normalization factors are given in the figure. Solid lines are visual guides; dotted lines give the Landau-related series expected for \( m_b^* = 0.47 m_0 \). A grey rectangle highlights the GaAs reststrahlen band (Ref. 25).

FIG. 2. Energy splitting of the four sublevels of the Bi-acceptor ground state \( |1S_{1/2}(1G^+_n)\rangle \); see Ref. 17 as deduced by the analysis of the \( C \)-line Zeeman splitting shown in Fig. 1 (circles). The solid line is a linear fit by the formula \( \Delta E = g_{\text{eff}} \mu_B B \). The linear dependences on \( B \) predicted (Ref. 22) for a conventional substitutional acceptor in GaAs and experimentally measured (Ref. 18) for C and Be are given, respectively, by a dotted and a dashed line. A scheme of the levels involved in the \( C \)-line recombination is sketched in the inset by following Ref. 23. The allowed transitions for magnetic field \( B \parallel [001] \) and Faraday geometry \( (E \perp B) \) are indicated by solid arrows. We resolve only three out of four expected components of the \( C \) line [the (8,7) and (7,8) components are merged in one broad absorption peak; see Fig. 1].
(\(g_{\text{eff}}^B = 1.83\)). Similar values of \(g_{\text{eff}}\) have been obtained in all other GaAs\(_{1-x}\)Bi\(_x\) samples with lower Bi concentration (\(x \leq 4.5\%\)). These high \(g_{\text{eff}}\) values characterize atoms with high atomic numbers and strong relativistic effects, thus strongly supporting the attribution of the observed lines to a Bi-related acceptor. So far, giant relativistic corrections in the GaAs\(_{1-x}\)Bi\(_x\) alloy have been theoretically predicted but experimentally inferred only by measurements of the spin-orbit bowing.\(^{27}\)

A drastically different behavior is observed for Bi concentration > 5%, as shown in Fig. 3 for the \(x = 5.6\%\) sample. The strongest components of the \(D\) and \(C\) transitions have the same energies but absorption intensities \(\sim 40\) times smaller than in the \(x = 4.5\%\) sample, as highlighted in the inset of Fig. 3(a).

In the fan plot of all observed lines, shown in Fig. 3(b), circles label the \(D\) and \(C\) lines of the Bi-related Lyman series and a relatively weak absorption with a linear dependence on \(B\) (14.1 cm\(^{-1}\)/T). The latter transition dominates all absorption spectra for \(x > 5.6\%\) (not shown here) and extrapolates to 32.7 cm\(^{-1}\) (4.1 meV) for zero magnetic field. The effective mass of the involved carrier, estimated from the slope of the transition energy vs \(B\), is \(m^*_e = 0.066m_0\). This absorption is attributed, therefore, to the \(1s \rightarrow 2p^+\) transition of a donor level in the GaAs substrate,\(^{28,29}\) as also confirmed by a comparison with data reported in the literature [crosses in Fig. 3(b)].\(^{28,30}\) Notice that the GaAs substrate contributes to the FIR absorption spectra with a single peak, visible only for \(x \geq 5.6\%\), relatively weak, and well separated from the Bi-induced peaks. Therefore, the substrate does not influence the analysis of Bi-induced acceptor levels.

The peculiar dependence of the acceptor state absorption on Bi concentration is shown in Fig. 4. First, the change in the absorption coefficient (\(\Delta\alpha\)) on going from dark to secondary optical illumination conditions has been calculated at zero field [\(\Delta\alpha = -\ln(I_{\text{exc}}/I_{\text{dark}})\)]\(^{31}\) where \(I\) is the GaAs\(_{1-x}\)Bi\(_x\)-layer thickness; see Table I in Ref. 8]. Then, \(\Delta\alpha\) has been integrated over the spectral region of Bi-acceptor levels (110–220 cm\(^{-1}\); see Fig. 4, inset) and shown on a semilog scale as a function of \(x\). The acceptor density (which is proportional to \(\Delta\alpha\)) is high for low \(x\), with a maximum at \(x = 4.5\%\), then it suddenly decreases down to the detection limit for \(x \geq 5.6\%\).

This Bi behavior recalls an insulator to metal transition, IMT. A Bi concentration of 5% in GaAs corresponds to a Bi atom density of \(10^{23}\) cm\(^{-3}\). The Mott’s criterion (\(a_p^0n_{\text{IMT}} \sim 0.25\)) predicts \(n_{\text{IMT}} = 5 \times 10^{19}\) cm\(^{-3}\) assuming hydrogenic impurity state at the acceptor sites and using the hole effective mass deduced by the Landau-related transition analysis. Therefore, only a fraction of \(\sim 0.5\%\) of the total Bi atoms is estimated to contribute to form acceptor states in the present GaAs\(_{1-x}\)Bi\(_x\) samples. It should be mentioned that in
Ga$_{1-x}$Mn$_x$As epilayers an IMT has been observed for $y = 3\%$.\textsuperscript{32} namely, a concentration of Mn acceptors very close to that of Bi in our samples.

The possible origin of acceptor states in nominally undoped GaAs$_{1-x}$Bi$_x$ is now discussed. In the impurity limit of GaAs:Bi (Bi concentration $\sim 3 \times 10^{16}$ cm$^{-3}$), electron spin resonance measurements have estimated that $\sim 10\%$ of Bi atoms occupy the Ga site, therein acting as double donors.\textsuperscript{33} On the other hand, the substitution of As atoms with isovalent Bi atoms cannot give rise to acceptors. However, strong relativistic effects lead to a large energy separation between $6s^2$ and $6p^3$ atomic orbitals in heavy atoms.\textsuperscript{34} Therefore, Bi assumes also a valence of 3, e.g., in Bi$_2$Te$_3$ and Bi$_2$Se$_3$, and should behave as an “isoelectronic” impurity in a group-III sublattice site or as a “substitutional double acceptor” in a group-V sublattice site.

In the latter case, the secondary optical illumination under which the FIR absorption spectra have been recorded could partially neutralize the double acceptors, thus accounting for observed spectra and a binding energy resembling those of single acceptors.\textsuperscript{35} Alternatively, Bi complexes involving two or more Bi atoms may give rise to acceptors. In this scenario, the acceptor states so far discussed offer a hint about the origin of the concomitant drastic changes occurring in the compositional evolution of the carrier effective mass and lattice ordering.\textsuperscript{8,9} The Bi acceptor state’s disappearance could then be regarded as the cause of the transition from a highly clustered to a truly random alloy.

In summary, we have given evidence of a Bi-related acceptor level ($E_B \sim 25$ meV) in nominally undoped GaAs$_{1-x}$Bi$_x$ and of its composition dependence that mirrors those reported in the same Bi concentration range for the electronic and structural properties. The giant effective $g$ factor ($g_{\text{eff}}^{Bi} \sim 14.9$) measured for the acceptor ground state indicates the involvement of Bi atoms with strong relativistic corrections. This study represents an important input to a further theoretical and experimental investigation of Bi inclusion in GaAs, as well as of the peculiar properties of GaAs$_{1-x}$Bi$_x$ alloys.

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17We use the notation for acceptors first employed in Ge and commonly used in GaAs; see Ref. 16. Acceptor energy states are labeled $n\Gamma^\pm_k$, where $\Gamma^\pm_k$ are irreducible representations of the $O_h$ group, $+\ or\ -$ is the parity, $k$ takes on the values $6, 7, or 8$, and $n = 1, 2, 3, \ldots$ is the sequence number for states of a given parity and $k$ in order of energy. Then $G, D$, and $C$ indicate the transitions from the ground state, $1S_{1/2}(\Gamma^+_{1s})$, to the first three odd-parity excited states, $2P_{1/2}(\Gamma^+_{3p})$, $2P_{3/2}(\Gamma^+_{3p})$, and $2P_{5/2}(\Gamma^+_{3p})$, respectively (the atomic notation with the subscript giving the total angular momentum is also indicated).


21Under a biaxial compressive strain, as for GaAs$_{1-x}$Bi$_x$ on GaAs, the shallow acceptor binding energy increases with respect to the stress-free case due to the removal of the valence band degeneracy. The valence band edge, indeed, acquires a greater heavy-hole character [see e.g., K. S. Kim et al., J. Appl. Phys. \textbf{82}, 5103 (1997) and references therein]. The value of acceptor binding energy ($\sim 25$ meV) we obtain in our samples is therefore greater than that in a stress-free layer. This increases the true energy difference between the binding energy of the acceptor state we observe and that of the most common substitutional acceptors in GaAs.


25In GaAs, the reststrahlen band, namely the energy region in which radiation is totally reflected ($\bar{\omega}_{\text{RO}} \leq \bar{\omega} \leq \bar{\omega}_{\text{LO}}$, with $\bar{\omega}_{\text{RO}}$ and $\bar{\omega}_{\text{LO}}$ the transverse and longitudinal optical phonon energy of the crystal, respectively), ranges from $\sim 273$ to $\sim 296$ cm$^{-1}$ (at $T \approx 4$ K). However, phonon-phonon interaction makes the region of zero transmittance broader [J. Yang et al., J. Appl. Phys. \textbf{98}, 043517 (2005)].

26A small deviation from a linear behavior shown by transitions LL$_0$ and LL$_1$ for $B > \sim 15$ T is accounted for by the variation of the Coulomb interaction with field and by nonparabolicity effects in the valence band.


29The behavior of the $1s \rightarrow 2p^+$ transition for energies above the GaAs reststrahlen band is due to magnetopolaron effects; see Ref. 28.


35Neutral double acceptors [e.g., Be$^{2+}$, Zn$^{2+}$, and Hg$^0$ in Ge] have spectra similar to those of single acceptors [see e.g., J. W. Cross et al., Phys. Rev. B \textbf{28}, 6953 (1983) and references therein].