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.\textsuperscript{1–4} Bismuthides are, therefore, than that achieved for a same mismatch of the lattice constant semiconductor alloys with very peculiar properties. Bismuth for \( \text{Bi} \) concentrations. Thus, the present FIR absorption measure-

\[ P_{\text{exc}}(B) \sim 30 \text{ mW/cm}^2 \] was directed onto the sample to increase the signal from the impurity levels.\textsuperscript{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,\textsuperscript{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.\textsuperscript{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.\textsuperscript{16,17} 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.\textsuperscript{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 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 \( \text{LL}_2 \) and \( \text{LL}_3 \) 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 \( \text{LL}_n \) 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.\(^{18}\) 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.\(^{23}\) 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, \( g_{\text{Bi}} = 14.9 \), is one order of magnitude larger than that predicted for a normal substitutional shallow acceptor in GaAs \((g_{\text{eff}} = 1.93)^{22}\) and observed for Be and C.

of the common substitutional acceptors in GaAs matches this value \((E_{\text{Bi}}^\pm = 26.9 \text{ meV}, E_{\text{Mg}}^\pm = 28.7 \text{ meV}, E_{\text{Si}}^\pm = 30.6 \text{ meV}, E_{\text{Bi}}^z = 34.8 \text{ meV})\),\(^{16}\) the observed absorption spectra ought to involve some different Bi-related acceptor state \(~25 \text{ meV}\) above the valence band maximum.\(^{21}\) 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.\(^{22,23}\) As a matter of fact, the \( E_x \) absorption peak splits into a series of transitions related to free-hole Landau levels of increasing energy \((\text{LL}_n)\),\(^{24}\) whose linear dependence on \( B \) is well resolved at high fields as soon as these transitions emerge from the GaAs reststrahlen band.\(^{25,26}\) The Landau level model gives a free-hole effective mass \( m_b^* \approx 0.47 m_0 \), where \( m_0 \) is the electron mass in vacuum.
COMPOSITIONAL EVOLUTION OF Bi-INDUCED . . .

\( g_{\text{eff}}^{\text{C}} = 1.83 \). 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 \( B \) \((14.1 \text{ cm}^{-1}/T)\). The latter transition dominates all absorption spectra for \( x > 5.6\% \) (not shown here) and extrapolates to 32.7 \text{ cm}^{-1} (4.1 \text{ meV}) for zero magnetic field. The effective mass of the involved carrier, estimated from the slope of the transition energy vs \( B \), is \( m^*_e = 0.066 m_0 \). 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)].\(^{30}\) 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 \( [\Delta \alpha = -\ln (\alpha_{\text{exc}}/\alpha_{\text{dark}})]^{31} \) where \( \alpha \) 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 \((110–220 \text{ cm}^{-1})\); 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 \( 10^{21} \text{ cm}^{-3} \). The Mott’s criterion \( (n/\rho_{\text{IMT}} \geq 0.25) \) predicts \( n_{\text{IMT}} = 5 \times 10^{18} \text{ cm}^{-3} \) 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 $y = 3\%$, 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. 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. 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. Alternatively, Bi complexes involving 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. 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 ($E_A \sim 25$ 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 ($g_{\text{Bi}} = 14.9$) 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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* g.pettinari@science.ru.nl
1 X. Lu et al., Appl. Phys. Lett. 95, 041903 (2009).
17 We use the notation for acceptors first employed in Ge and commonly used in GaAs; see Ref. 16. Acceptor energy states are labeled $n\Gamma_k^{\pm}$, where $\Gamma_k^{\pm}$ 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, $1s_{\Gamma_6} (\Gamma_5^+)$, to the first three odd-parity excited states, $2p_{\Gamma_2} (\Gamma_5^+), 2p_{\Gamma_2} (2\Gamma_5^+)$, and $2p_{\Gamma_2} (\Gamma_6^-)$, respectively (the atomic notation with the subscript giving the total angular momentum is also indicated).
21 Under 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.