Unusual compositional dependence of the exciton reduced mass in GaAs$_{1-x}$Bi$_x$ (x=0-10%)
Outline

Bismuth in GaAs:

- electronic properties

- magneto-photoluminescence (0-30 T) and exciton reduced mass determination

- evidence for a largely perturbed band structure
Ga(As,Bi) expected trends

<table>
<thead>
<tr>
<th>III B</th>
<th>VB</th>
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<tbody>
<tr>
<td>B</td>
<td>7</td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>11</td>
</tr>
<tr>
<td>Ga</td>
<td>31</td>
</tr>
<tr>
<td>In</td>
<td>33</td>
</tr>
<tr>
<td>Tl</td>
<td>83</td>
</tr>
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Bi is expected to influence the valence band

Large relativistic corrections are expected due to $Z_{Bi} \rightarrow$ 

### large SO splitting $\Delta_0$ of VB anion $p$-states

$\Delta_0(GaBi)=2.15$ eV

Ga(As,Bi) expected trends

Predicted $E_g = -1.45$ eV for GaBi density functional formalism and LDA (64-atom cell calculation)
Expected **band gap reduction** following (heavier anion)-(smaller gap) rule

- Localization of *valence band* states at Bi atoms
- Bi generates an impurity state ($E_{Bi}$) 80 meV *below* the VBM
- Pressure coefficient of $E_{Bi}$ similar to GaAs, no Bi state emerging from the VB
**Ga(As,Bi) observed trends**

\[ E_{\text{GaAs}_{1-x}\text{Bi}_x} = x E_{\text{GaBi}} + (1-x)E_{\text{GaAs}} - bx (1-x) \]

\[ b(x) = \alpha/(1+\beta x) \]

\[ E_{\text{GaBi}} = -0.36 \text{eV} \quad \alpha = 9.5 \text{eV} \quad \beta = 10.4 \]


\[ x=(0-5)\% \quad \Delta E_g \approx -80 \text{meV/\%Bi} \]

(GaAs\(_{1-x}\)N\(_x\); \(\Delta E_g \approx -100 \text{meV/\%N}; b\sim 16-20 \text{eV}\))

A larger band gap reduction is observed for the same increase in lattice constant

Potential for

- Heterojunction bipolar transistors
- Solar cells
- Telecom
**Ga(As,Bi) observed trends**


\[
\Delta_0(GaAs_{1-x}Bi_x) = x\Delta_0^{GaBi} + (1-x)\Delta_0^{GaAs} - bx(1-x)
\]

\[
\Delta_0^{GaBi} = 2.15 \text{eV} \quad \Delta_0^{GaAs} = 0.34 \text{eV}
\]

\[b = -6.0 \text{ eV}\]

(GaAs\(_{1-x}\)N\(_x\); \(\Delta_0\) constant)

Potential for spintronics

**Bi-related states form with pressure coefficient similar to GaAs**

Ultrafast photoresponse in the NIR for emitters and detectors of pulsed THz radiation


**Ga(As,Bi): what about the carrier mass?**

We address the carrier effective mass in Ga(As,Bi) by magneto-photoluminescence.

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**Graphical Representation:**

- **Left Graph:**
  - Label: Effective mass, \( m_e^* / m_0 \)
  - X-axis: Direct bandgap, \( E_g \) (eV)
  - Y-axis: Effective mass, \( m_e^* / m_0 \)
  - Various materials are plotted, including GaAs, InAs, GaSb, and InSb.

- **Right Graph:**
  - Title: Electron Hall Mobility \( \mu \) (cm²/Vs)
  - X-axis: Concentration (x%) for \( x = 2.5 \%
  - Data points for GaAs\(_{1-x}\)Bi\(_x\) and GaAs\(_{1-x}\)N\(_x\)

**Citations:**


**Bi Incorporation Affects:**

- Electron mobility
The samples

Grown on (100) GaAs by molecular beam epitaxy

\( x = 0, 0.6, 1.3, 1.7, 1.9, 3.0, 3.8, 4.5, 5.6, 8.5 \) and 10.6%

\( T_G = (270 - 380) \)^\text{°C}, thickness \( t = (40-350) \) nm

\[ \begin{align*}
\text{PL Intensity (arb. units)} \\
0.8 & \quad 1.0 & \quad 1.2 & \quad 1.4 \\
0.6\% & \quad 1.3\% & \quad 1.7\% & \quad 3.0\% & \quad 3.8\% & \quad 5.6\% & \quad 8.5\% & \quad 10.6\%
\end{align*} \]

Good structural properties

\[ \begin{align*}
E_x & = 0.8, 1.0, 1.2, 1.4 \\
\text{Energy (eV)} & \\
0.8 & \quad 1.0 & \quad 1.2 & \quad 1.4 \\
\text{PL Intensity (arb. units)}
\end{align*} \]
The samples

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\( T_G = (270 - 380) ^\circ C \), thickness \( t = (40-350) \) nm

Unusual compositional linewidth dependence
High-magnetic field measurements

The Netherlands

$B = 0 - 33 \, T$

- Powered by $2 \times 10 \, MW$ at $500 \, V$ ($4 \times 10^4 \, A$)

- Chilled by $10^4 \, l/min$ deionised water at $30 \, atm$ at $10 \, ^\circ C$.

1 hour magnet time costs 1,000 €
Why 200 K?

Localized excitons dominate low-T photoluminescence

Why 200 K?

Accurate choice of measurement power and temperature
Why 200 K?


At high power carrier scattering disrupts the coherence of the electron/hole cyclotron orbit.

**Magneto-PL: data**

At high power carrier scattering disrupts the coherence of the electron/hole cyclotron orbit.

![Graph showing PL peak energy vs. magnetic field](image)

- $P_0 = \sim 10 \text{ W/cm}^2$
- $3 \times P_0$
- $7 \times P_0$
- $15 \times P_0$

$T = 190 \text{ K}$

$\text{GaAs}_{1-x} \text{Bi}_x \quad x = 8.5\%$

Magneto-PL: data

At high power carrier scattering disrupts the coherence of the electron/hole cyclotron orbit as found in degenerate GaAs and InN.

Magneto-PL: data

At high power carrier scattering disrupts the coherence of the electron/hole cyclotron orbit as found in degenerate GaAs and InN.

Magneto-PL: data

... back to GaAsBi

Localized excitons behave differently
Magneto-PL: analysis

B-induced shift of given by
(see D. Cabib, E. Fabri, and G. Fiorio, Il Nuovo Cimento 10B, 185 (1972))

\[ \Delta E_d (B; \mu_{\text{exc}}) = R^* \sum_{i=1}^{5} c_i \gamma^i \]

\[ \gamma = \frac{(e\hbar B)}{(2\mu_{\text{exc}} R^*)} \]

\[ R^* \text{ Rydberg} \]

The exciton reduced mass does not depend on excitation power

\[ T = 190 \text{ K} \]

GaAs$_{1-x}$Bi$_x$ - $x = 8.5\%$
Magneto-PL: analysis

High-temperature PL: free-exciton or free-carrier?

GaAs
$T = 185$ K

Free-exciton: quadratic-like

Free-carrier: Landau levels form

A more reasonable carrier reduced mass is found for exciton-like recombination
Magneto-PL: analysis

High-temperature PL: free-exciton or free-carrier?

(a) \[ \Delta P_0 = 5 \text{ mW} \quad \mu_{\text{exc}} = 0.071 m_0 \]
\[ 60 \times P_0 - \mu_{\text{exc}} = 0.072 m_0 \]

(b) \[ \Delta P_0 = 50 \text{ mW} \quad \mu_{\text{exc}} = 0.079 m_0 \]
\[ 2 \times P_0 - \mu_{\text{exc}} = 0.080 m_0 \]
Magneto-PL: results

Non monotonic dependence of the exciton reduced mass on Bi concentration

Magneto-PL: results

Exciton reduced mass

Non conventional compositional dependence followed by a $k \cdot p$-like behavior

$m_e \propto m_0 (1 + P^2/E_g)^{-1}$

$m_{hh} \propto m_0 (2Q^2/E^* - 1)^{-1}$

$P^2 = 28.9$ eV, $Q^2 = 8$ eV

Exciton reduced mass: what we learn

Consistent with mobility data
\[
\frac{\Delta \mu}{\mu} \approx \frac{\Delta m}{m} \approx 30\%
\]
**Exciton reduced mass: what we learn**

The *unexpected* increase of the carrier mass indicates a highly perturbed band structure. The plateau value (0.08 $m_0$) is not conceivable with a perturbation exerting on the VB only.

$$\frac{1}{\mu_{\text{exc}}} = \frac{1}{m_e} + \frac{1}{m_h}$$

$m_h \to \infty$, $\mu_{\text{exc}} = 0.067 m_0$

The CB has to be perturbed, too

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**Tendency to Bi atom clustering may perturb CB structure**

The plateau value (0.08 $m_0$) is not conceivable with a perturbation exerting on the VB only. The CB has to be perturbed, too

$$m_n \to \infty, \mu_{\text{exc}} = 0.067 \, m_0$$

Bi is assumed to substitute As (valence 5)

But, Bi is usually trivalent due to large separation between 6s$^2$ and 6p$^3$ electrons (A. Zunger, private communication)

A rather strong tendency of Bi to substitute for Ga could be expected

In fact, . . .
Identification of the Bi$_{Ga}$ heteroantisite defect in GaAs:Bi

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Westinghouse Science and Technology Center, Pittsburgh, Pennsylvania  
(Received 8 December 1992)

GaAs lightly doped with the heaviest group-V atom, bismuth (Bi), has been studied by conventional electron-spin resonance (ESR) and by ESR detected via the magnetic-circular-dichroism (MCD) absorption. A new Bi-related sharp-line MCD band has been observed on which two MCD-ESR lines have been discovered. They are shown to arise from the singly ionized Bi$_{Ga}$ double donor. Most remarkably, a substantial fraction, about 10%, of the total Bi content is found to occupy the Ga site. The Bi$_{Ga}$ MCD absorption band is tentatively assigned to an exciton deeply bound to the singly ionized double donor Bi$_{Ga}^+$.  

![MCD Signal Graph](image)  
FIG. 2. The Bi$_{Ga}^+$ MCD absorption band following quenching of the As$_{Ga}$ $EL2^+$ MCD band.
Exciton reduced mass: what we learn

IDENTIFICATION OF THE Bi$_{Ga}$ HETEROANTISITE DEFECT . . .

TABLE I. Parameters for group-V antisites in GaAs.

<table>
<thead>
<tr>
<th></th>
<th>g</th>
<th>A (GHz)</th>
<th>$A / A_f$</th>
<th>Formation probability $f$</th>
<th>(0/+) level below $E_c$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{Ga}$</td>
<td>1.99</td>
<td>1.80</td>
<td>0.140</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_{Ga}$</td>
<td>2.04</td>
<td>2.70</td>
<td>0.184</td>
<td>$\sim 10^{-6}$</td>
<td>0.75</td>
</tr>
<tr>
<td>$^{121}Sb_{Ga}$</td>
<td>2.02</td>
<td>6.61</td>
<td>0.188</td>
<td>$\sim 10^{-3}$</td>
<td>0.48</td>
</tr>
<tr>
<td>$Bi_{Ga}$</td>
<td>2.055</td>
<td>10.96</td>
<td>0.141</td>
<td>$\sim 10^{-1}$</td>
<td>0.35–0.50</td>
</tr>
</tbody>
</table>


Then, what CB structure is expected for (GaBi)As?
Exciton reduced mass: what we learn

The recovery of a conventional-alloy behaviour above \( x > 8\% \) points toward a restoration of a random atomic distribution of Bi atoms.


G. Ciatto et al., private communication
The recovery of a conventional-alloy behaviour above $x>8\%$ points toward a restoration of a random atomic distribution of Bi atoms.
Exciton reduced mass: what we learn

Alternatively, the formation of Bi antisites is less likely above a certain Bi concentration.
Conclusions

The peculiar dependence of the exciton reduced mass reveals an transition of the nature of the band extrema from impurity-like to band-like.

The compositional dependence of the carrier effective mass mirrors major changes occurring in the structural properties of the lattice:
- disorder to order transition
- formation of $Bi_{Ga}$ antisites highlighting the competing characteristics of Bi as a metal and a group V element

The decrease in the carrier effective mass for $x>8\%$ turns out to be of particular interest in all those applications where carrier mobility is a relevant issue.