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

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HFML Science in High Magnetic Fields

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Radboud University Nijmegen, The Netherlands

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University of British Columbia, Vancouver, Canada

Ann Arbor, July 16th

Outline

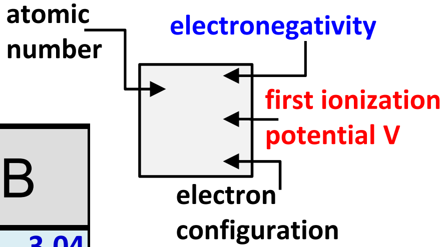
Bismuth in GaAs:

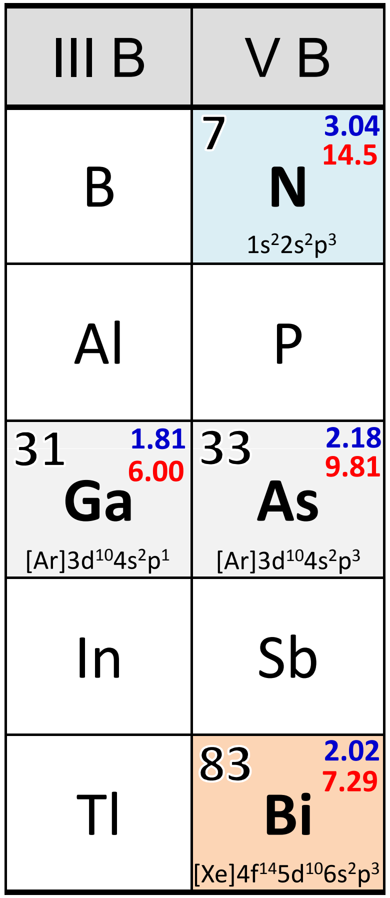
- electronic properties

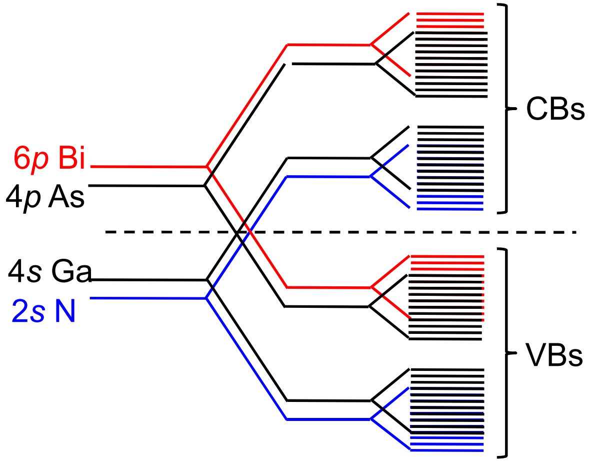
- magneto-photoluminescence (0-30 T) and
  exciton reduced mass determination

- evidence for a largely perturbed band structure

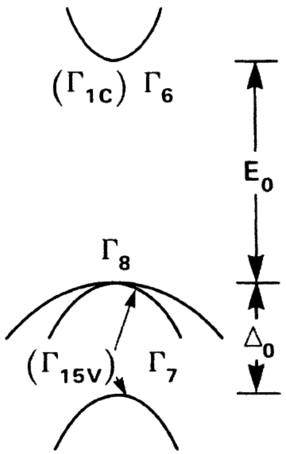
Ga(As,Bi) expected trends

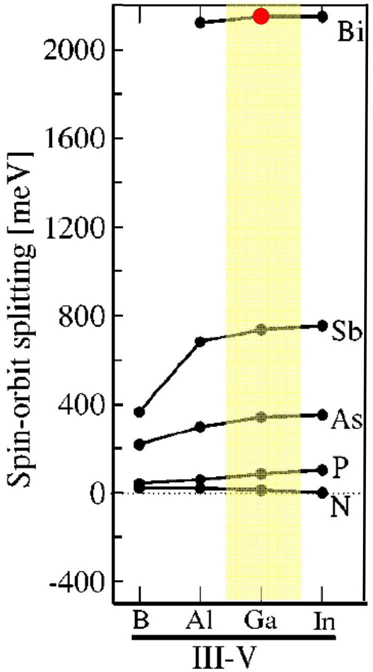






Bi is expected to influence the valence band





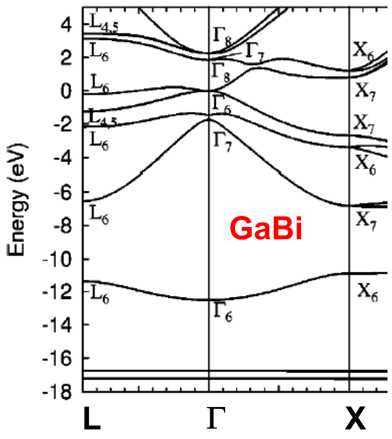
Large relativistic corrections are expected due to Z_{Bi} → *large SO splitting* Δ_0 of VB anion *p*-states

Δ_0(GaBi)=2.15 eV

P. Carrier and S.-H. Wei, Phys. Rev. B **70**, 035212 (2004)

Ga(As,Bi) expected trends

A. Janotti, S.-H. Wei, and S. B. Zhang, Phys. Rev. B **65**, 115203 (2002)

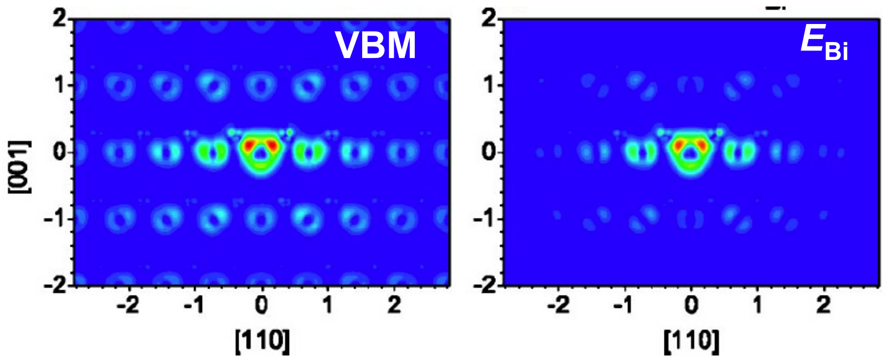


Predicted E_g= -1.45 eV for GaBi

density functional formalism and LDA (64-atom cell calculation)

Expected *band gap reduction* following (heavier anion)-(smaller gap) rule

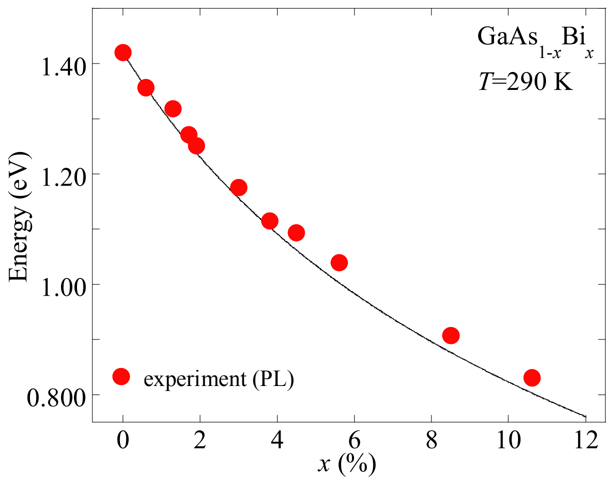
Y. Zhang, A. Mascarenhas, and L. –W. Wang, Phys. Rev. B **71**, 155201 (2005)



- 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

density functional formalism and LDA

Ga(As,Bi) observed trends



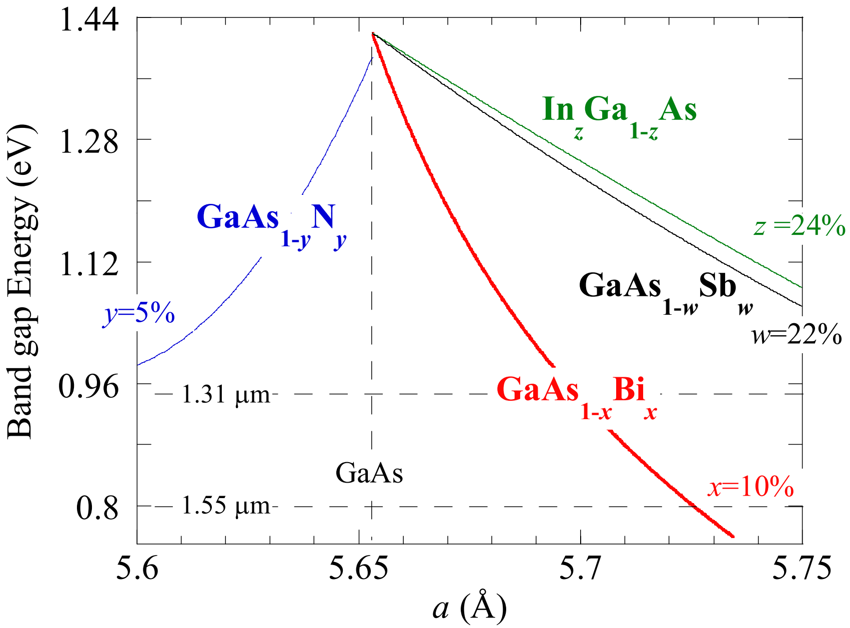
$$E_{GaAs_{1-x}Bi_x} = x\,E_{GaBi} + (1-x)E_{GaAs} - \boldsymbol{b}x\,(1-x)$$

$$b(x) = \alpha/(1+\beta\,x) \qquad E_{GaBi} = -0.36\,\text{eV} \quad \alpha = 9.5\,\text{eV} \quad \beta = 10.4$$

Kunishige Oe and Hiroshi Okamoto, Jpn. J. Appl. Phys. **37**, L1283 (1998)
X. Lu *et al.*, Appl. Phys. Lett. **95**, 41903 (2009)

x=(0-5)% ΔE_g≈-80 meV/%Bi

($GaAs_{1-x}N_x$; ΔE_g≈-100 meV/%N; b~16-20 eV)

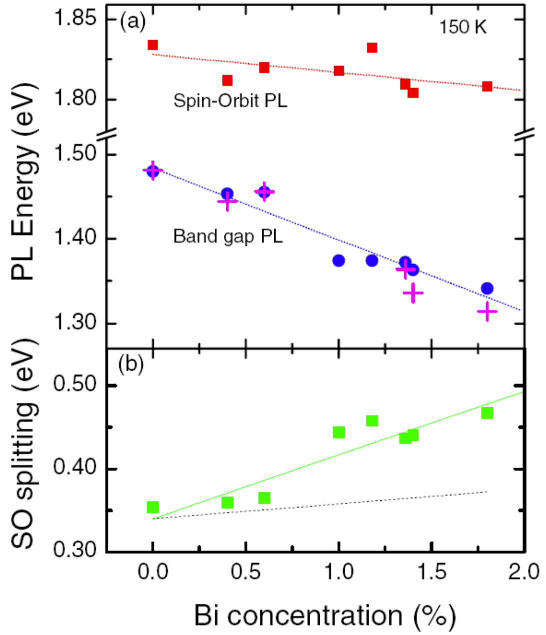


A larger band gap reduction is observed for the same increase in lattice constant

Potential for
- Heterojunction bipolar transistors
- Solar cells
- Telecom

Ga(As,Bi) observed trends

B. Fluegel *et al.*, Phys. Rev. Lett. **97**, 067205 (2006)



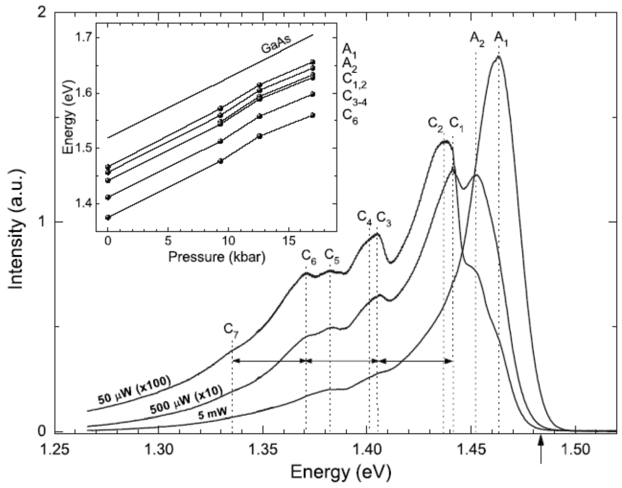
$$\Delta_0(\mathrm{GaAs}_{1-x}\mathrm{Bi}_x) = x\,\Delta_0^{\mathrm{GaBi}} + (1-x)\Delta_0^{\mathrm{GaAs}} - \boldsymbol{b}x\,(1-x)$$

$$\Delta_0^{\mathrm{GaBi}} = 2.15\,\mathrm{eV} \quad \Delta_0^{\mathrm{GaAs}} = 0.34\,\mathrm{eV}$$

b = -6.0 eV

($GaAs_{1-x}N_x$; Δ_0 constant)

Potential for spintronics



S. Francoeur *et al.*, Phys. Rev. B **77**, 085209 (2008)

Bi-related states form with pressure coefficient similar to GaAs

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

K. Bertulis *et al.*, Appl. Phys. Lett. **88**, 201112 (2006)

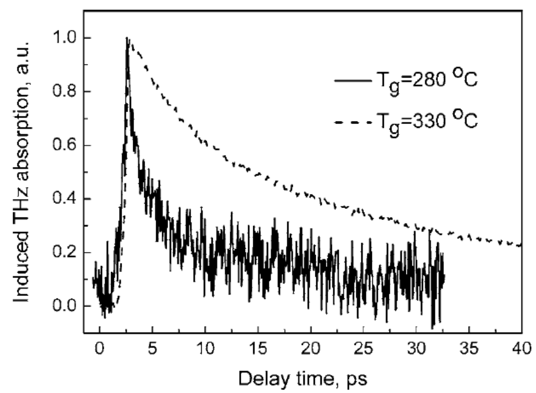
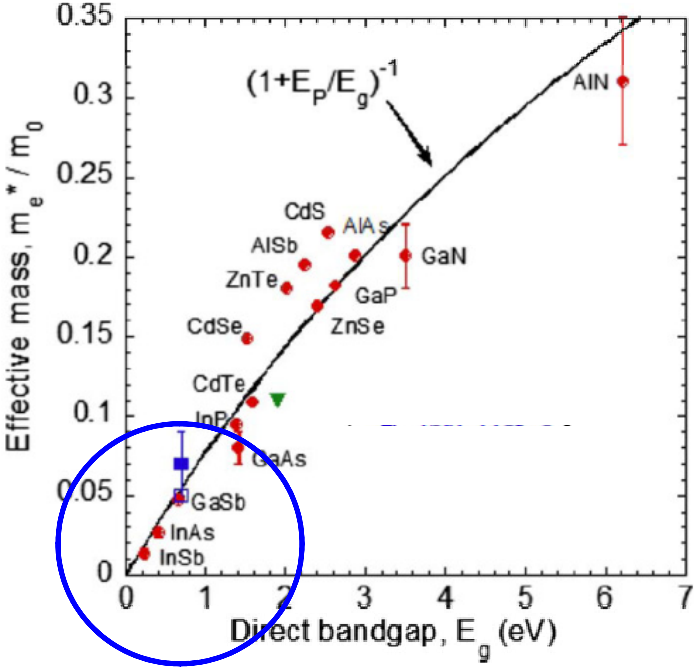


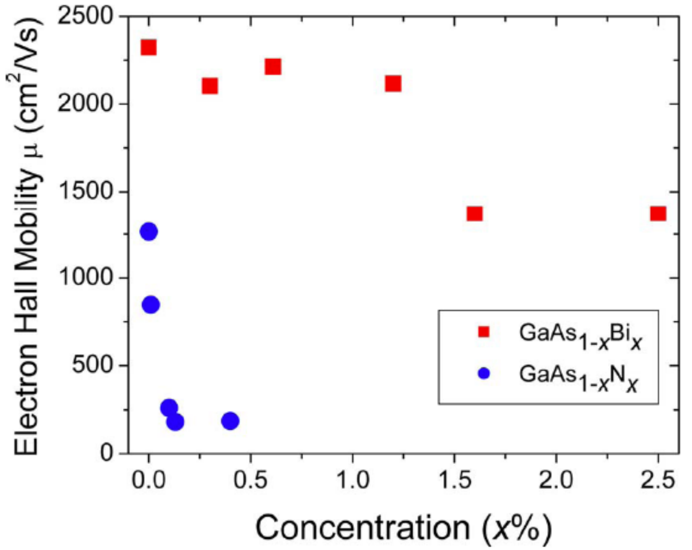
FIG. 3. Optical pump induced temporal changes of the transmitted THz field magnitude measured on two different GaBiAs samples.

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

J. Wu *et al.*, J. Appl. Phys. **105**, 011101 (2009)



R. N. Kini *et al.*, J. Appl. Phys., **106**, 043705 (2009)



Bi incorporation affects the electron mobility

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

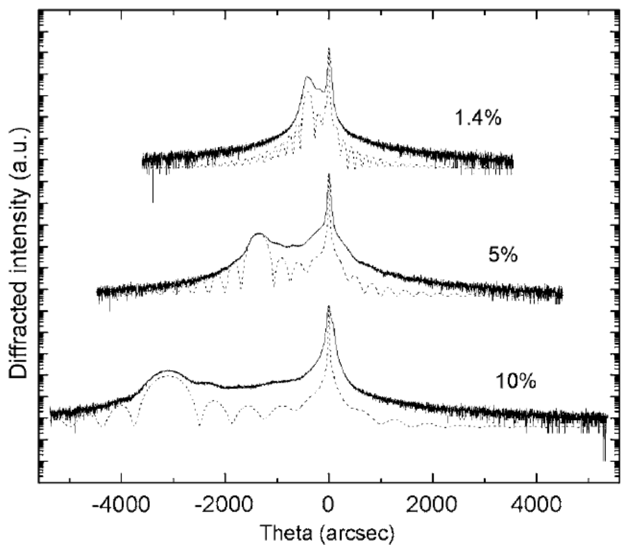
The samples

Grown on (100) GaAs by molecular beam epitaxy

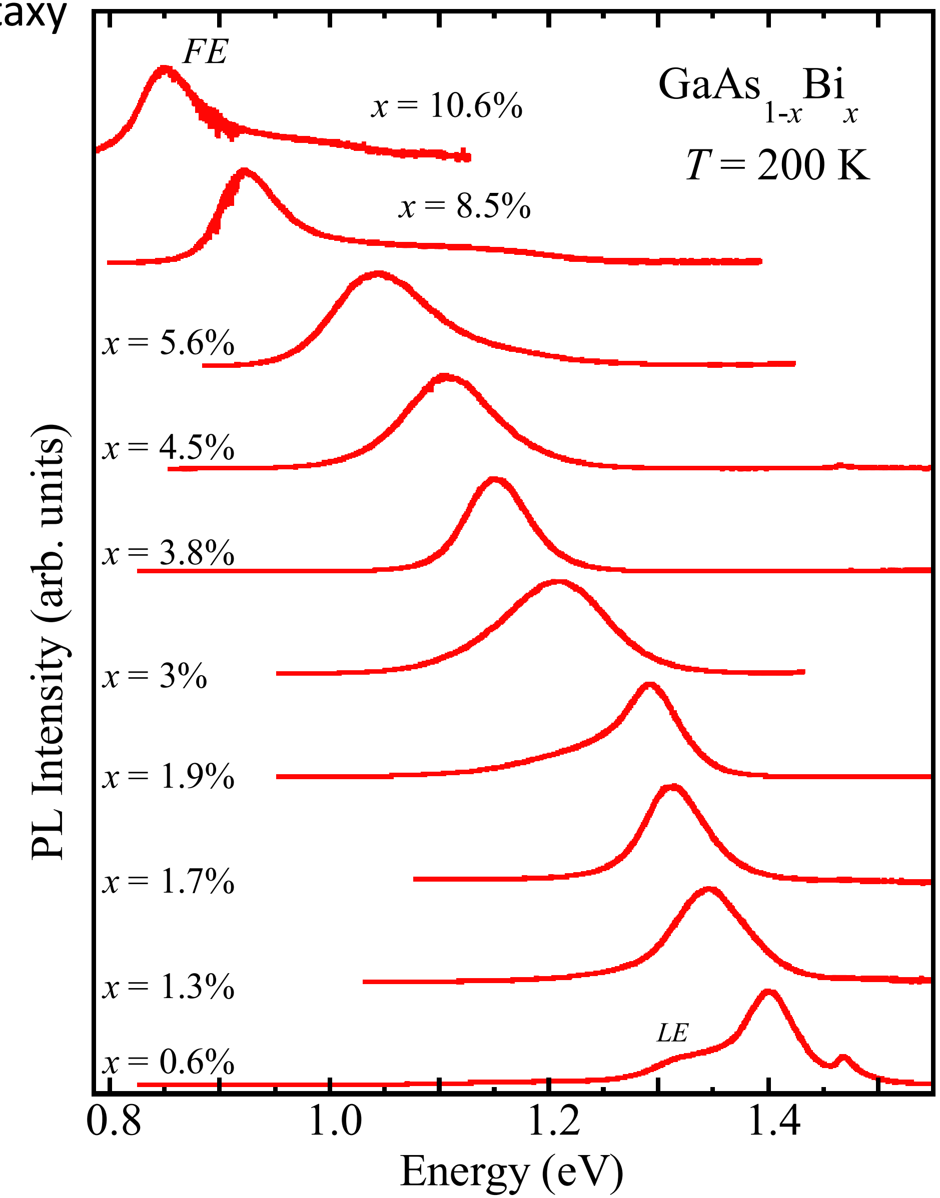
x =0, 0.6, 1.3, 1.7, 1.9, 3.0, 3.8,
4.5, 5.6, 8.5 and 10.6%

T_G=(270 – 380) °C, thickness *t*=(40-350) nm

X. Lu *et al.*, Appl. Phys. Lett. **92**, 192110 (2008)



Good structural properties



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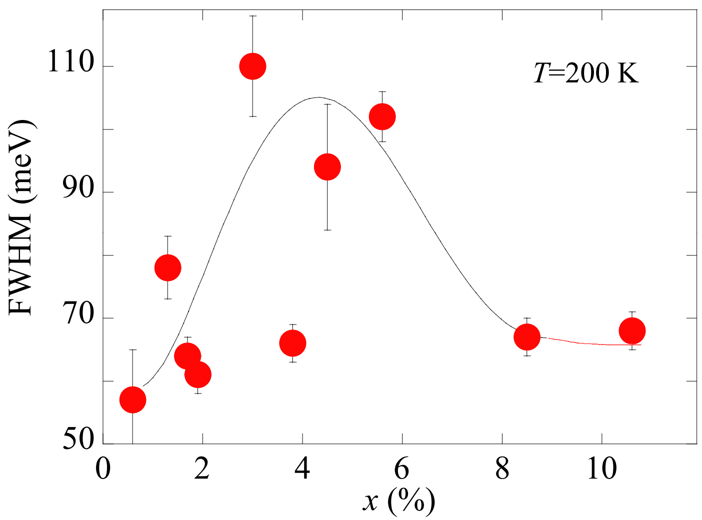
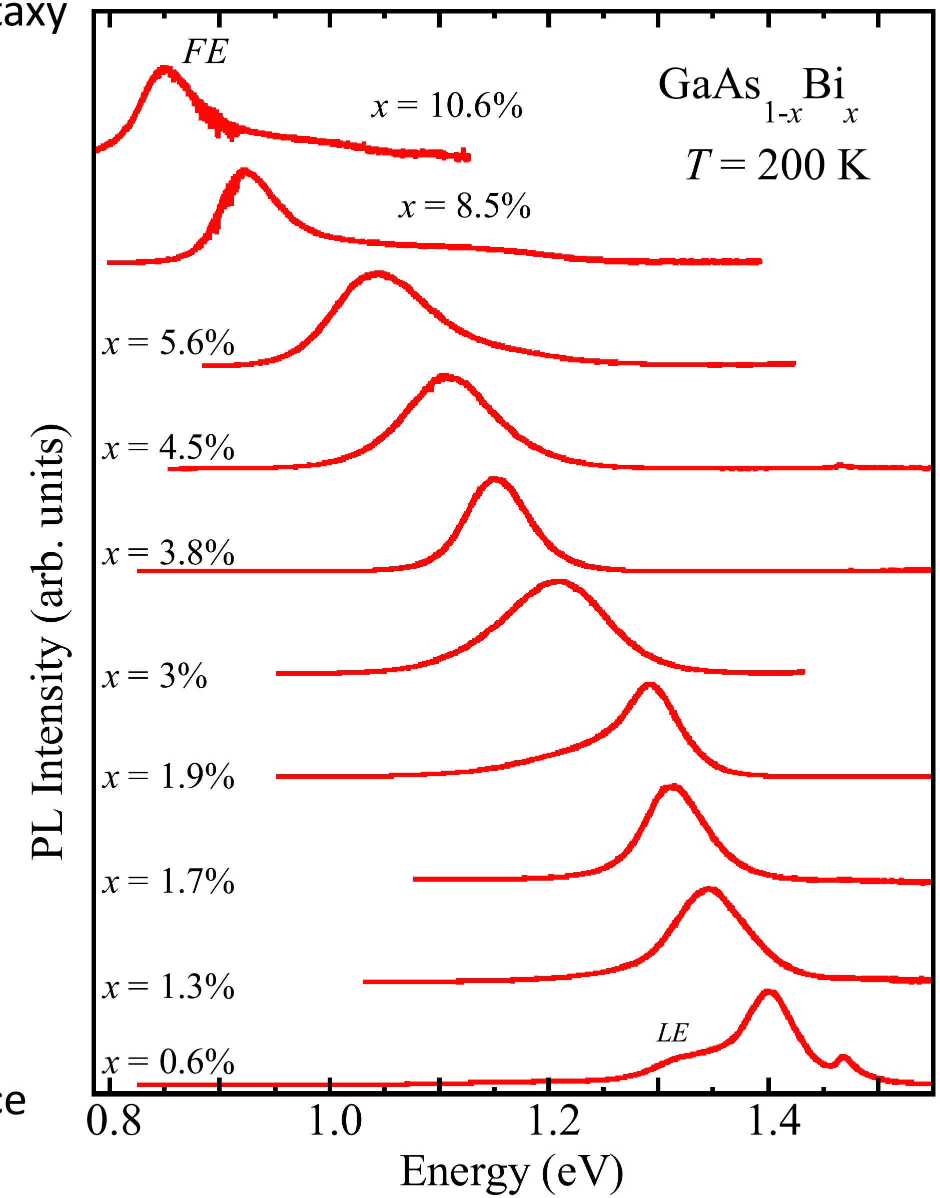
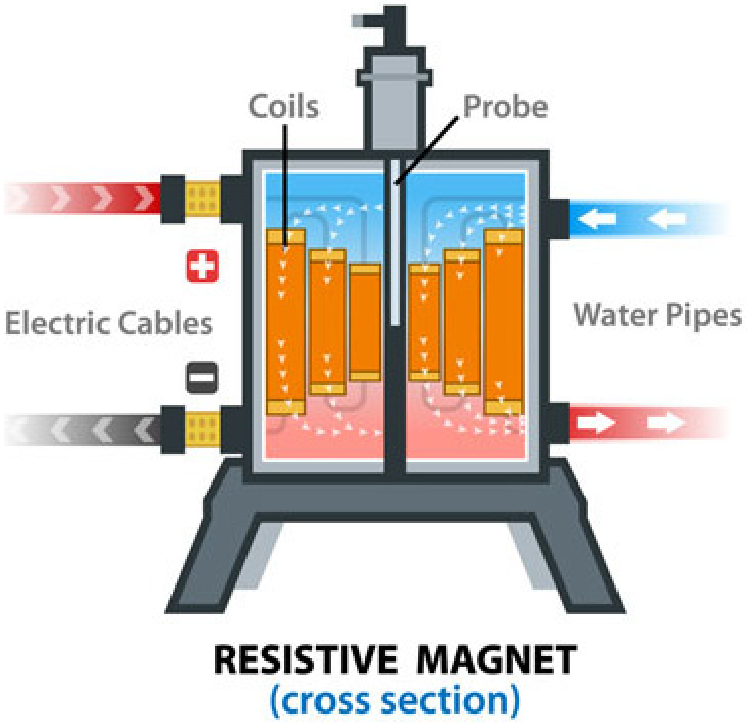


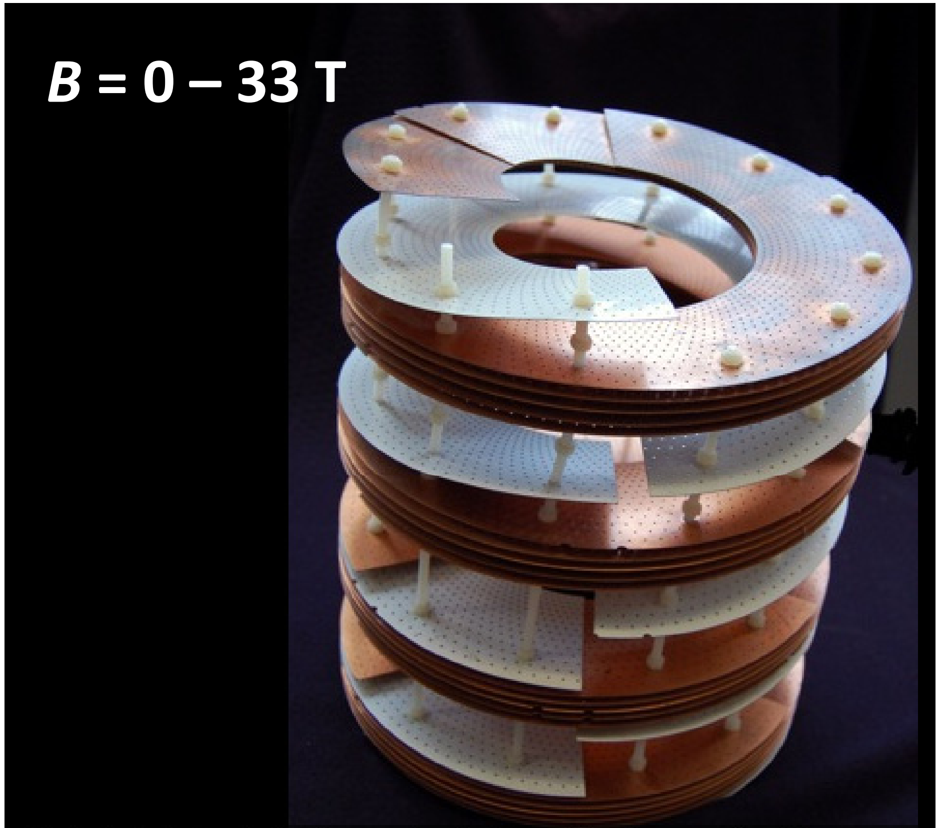
Unusual compositional linewidth dependence



High-magnetic field measurements

HFML
Science in High Magnetic Fields
Nijmegen
The Netherlands





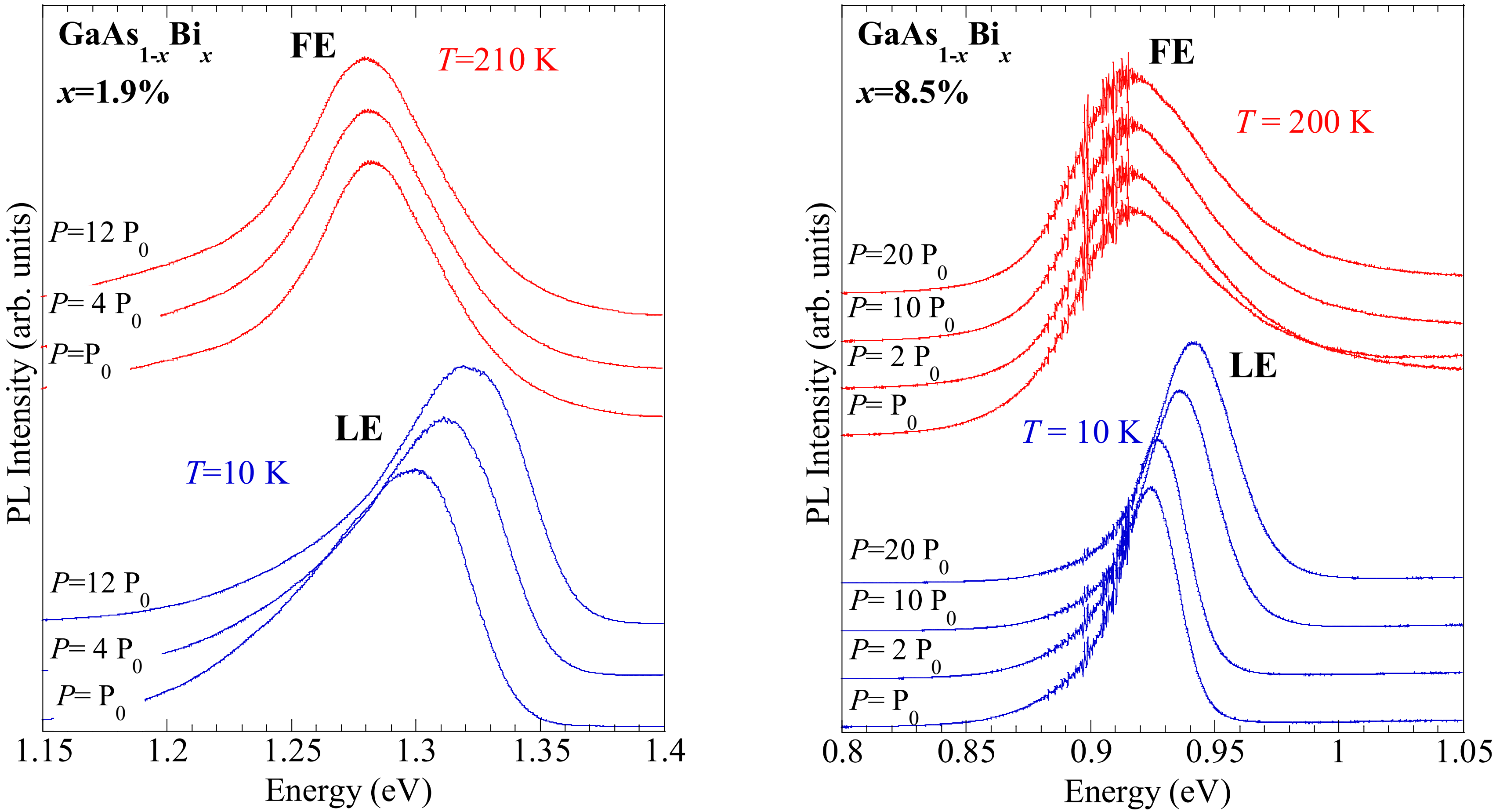
Model of a helix-stacked magnet coil. The white discs are insulators.

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

- Chilled by 10^4 l/min deionised water at 30 atm at 10 °C.

1 hour magnet time costs 1,000 €

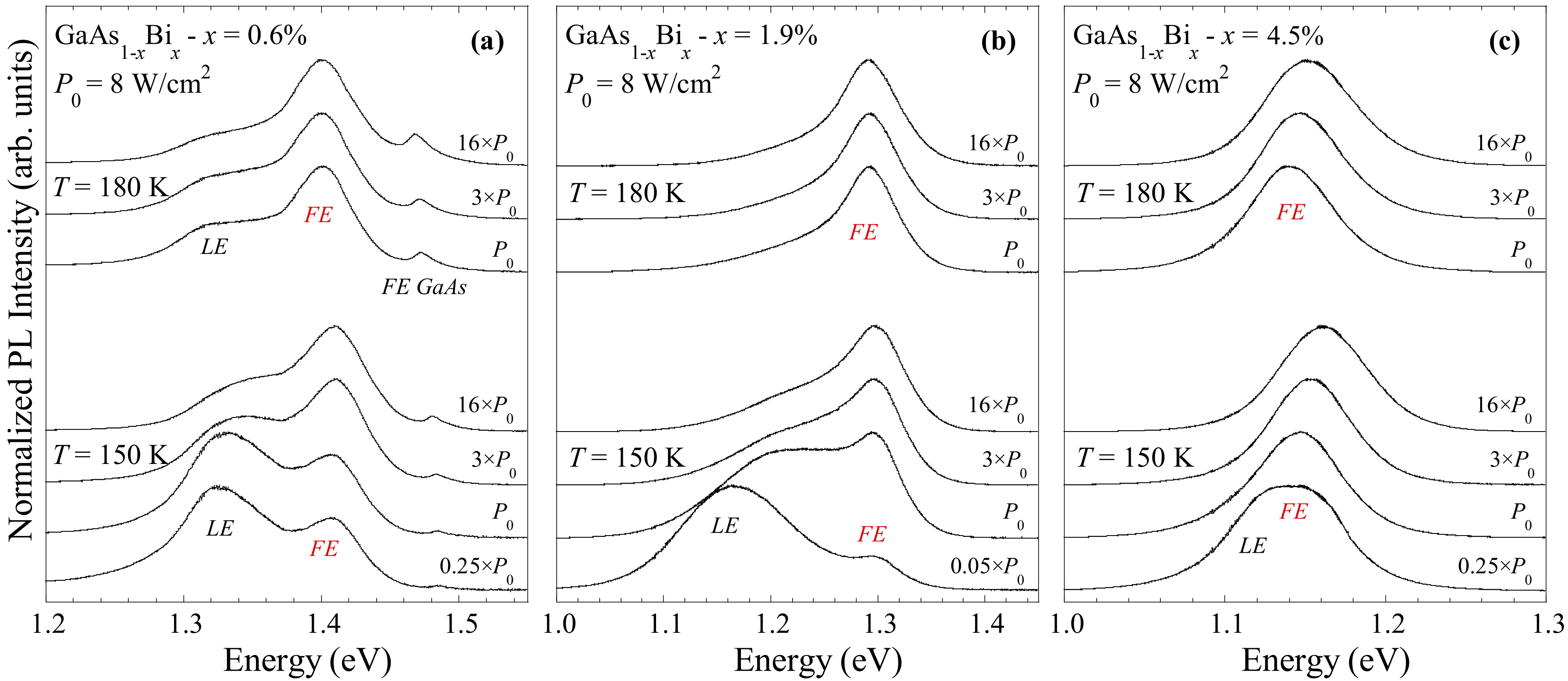
Why 200 K?



Localized excitons dominate low-*T* photoluminescence

G. Pettinari *et al.*, Appl. Phys. Lett. **92**, 262105 (2008)

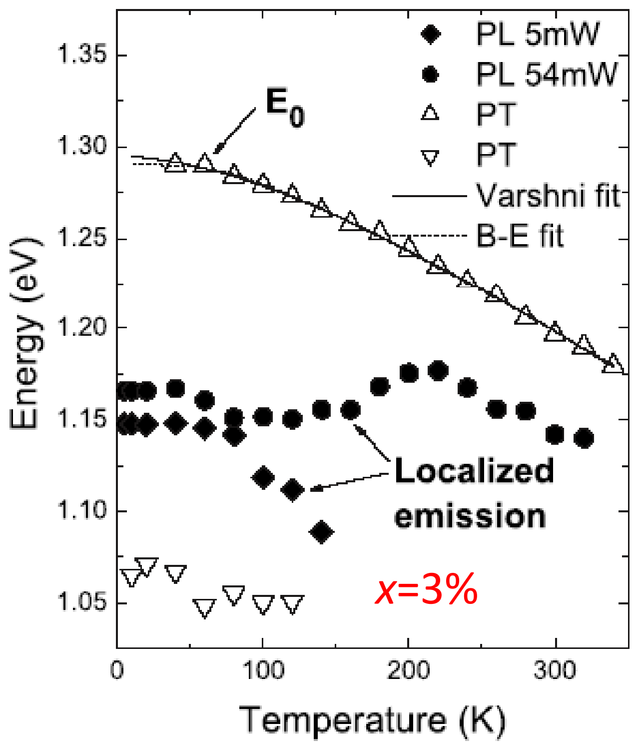
Why 200 K?



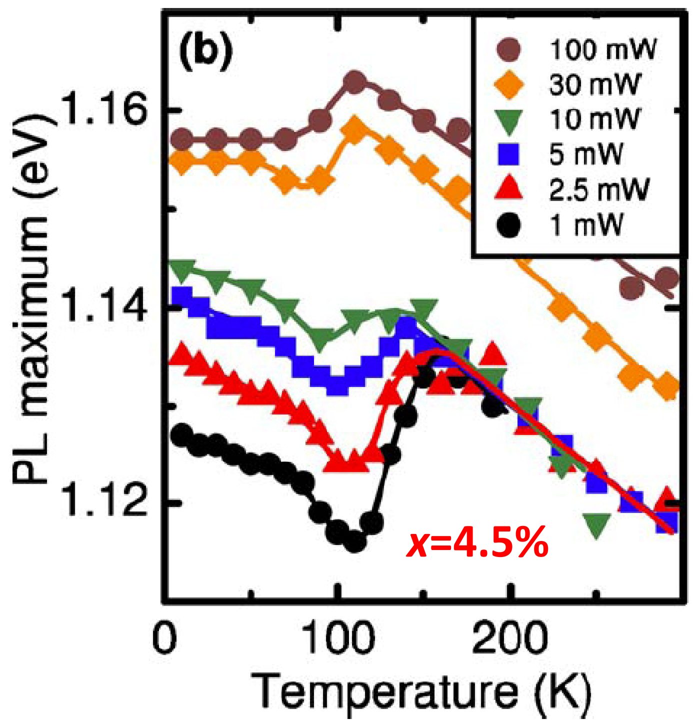
Accurate choice of measurement power and temperature

Why 200 K?

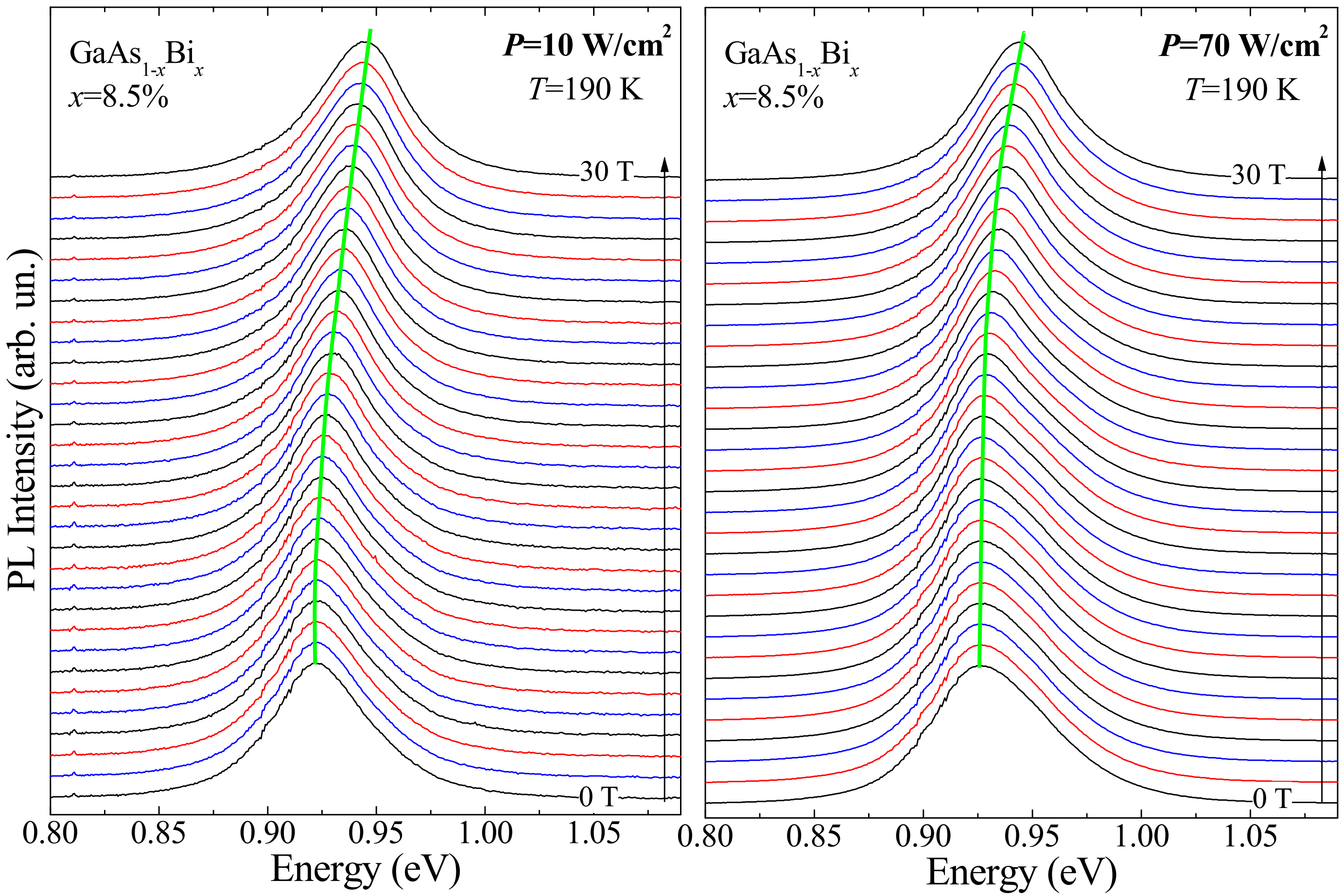
R. Kudrawiec *et al.*, J. Appl. Phys. **106**, 023518 (2009)



S. Imhof *et al.*, Appl. Phys. Lett. **96**, 131115 (2010)



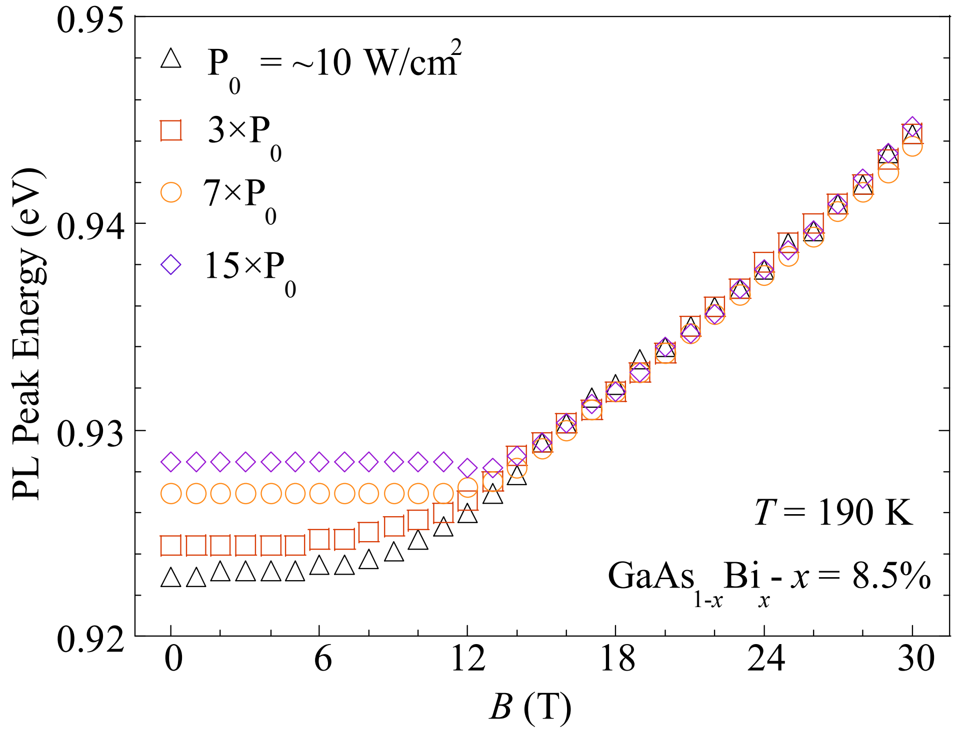
Magneto-PL: data



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

G. Pettinari *et al.*, Phys. Rev. B **81**, 235211 (2010)

Magneto-PL: data



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G. Pettinari *et al.*, Phys. Rev. B **81**, 235211 (2010)

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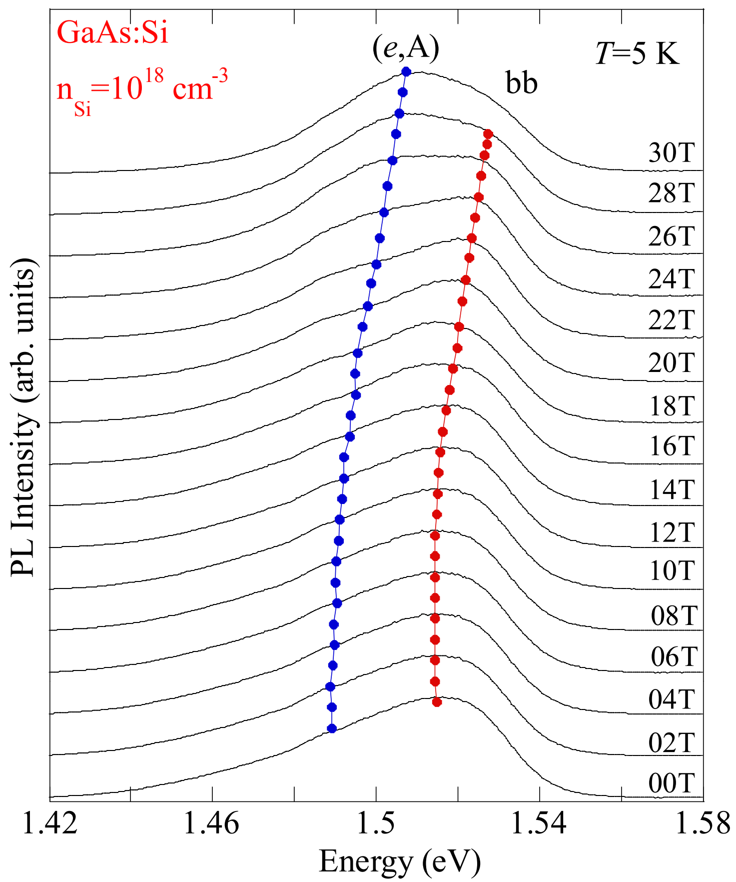
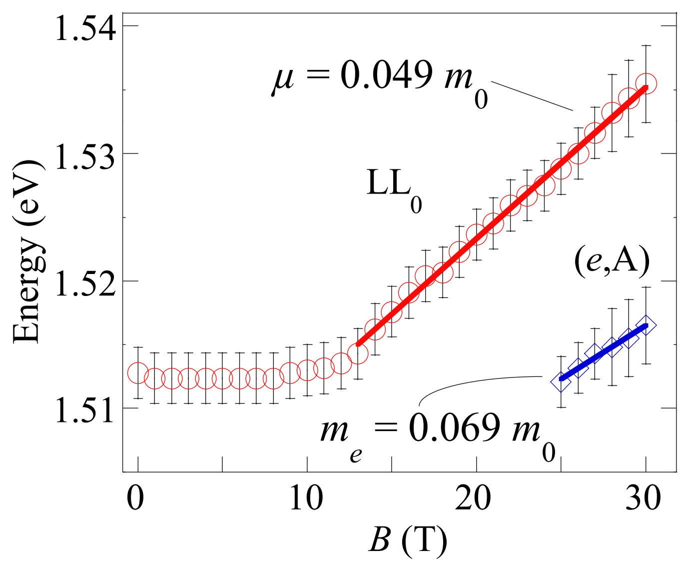
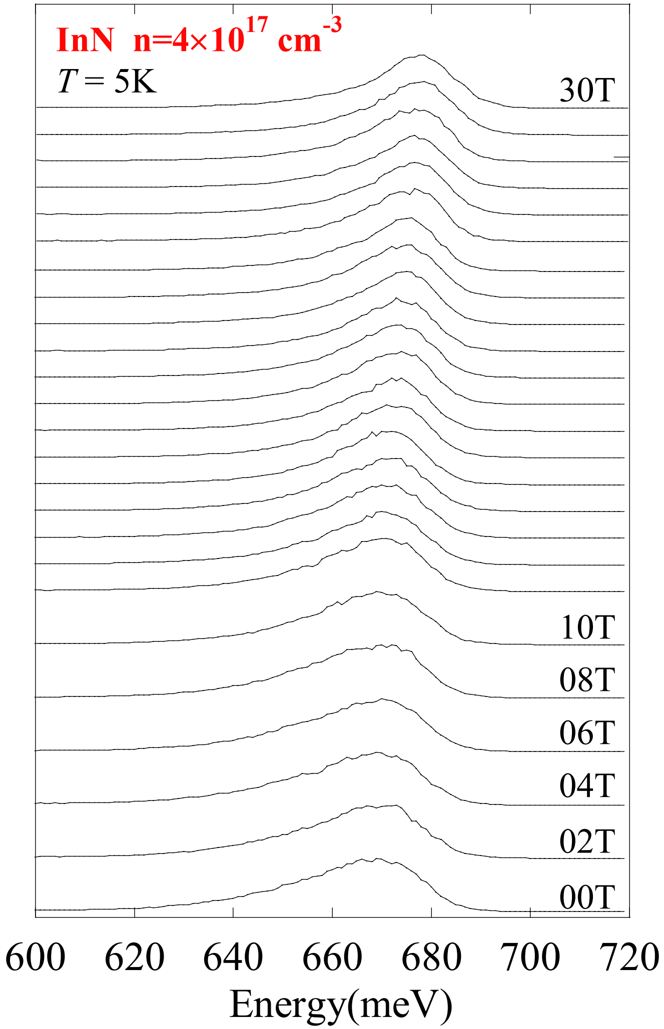


At high power carrier scattering disrupts the coherence of the electron/hole cyclotron orbit as found in degenerate **GaAs** and InN



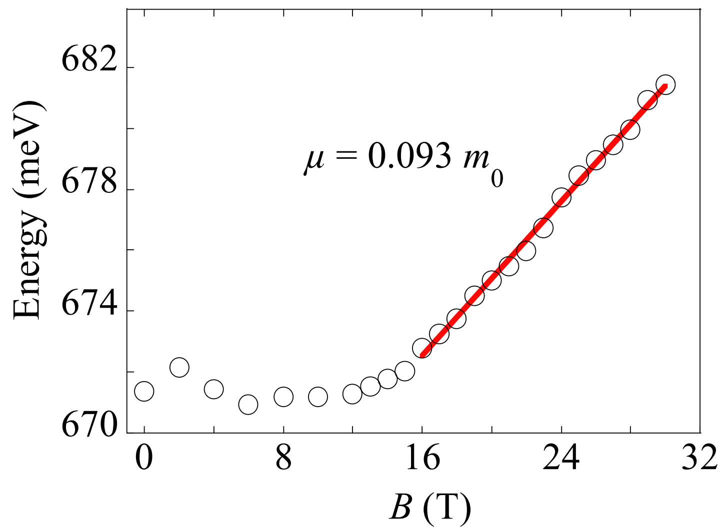
G. Pettinari *et al.*, Phys. Rev. B **79**, 165207 (2009)

Magneto-PL: data



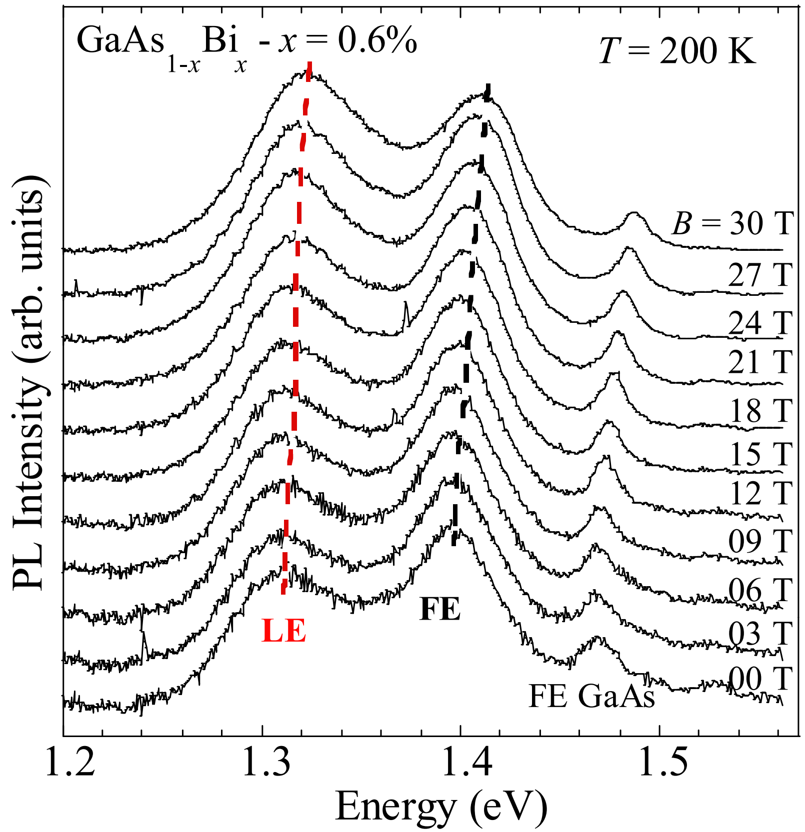
G. Pettinari *et al*., Phys. Rev. B **79**, 165207 (2009)

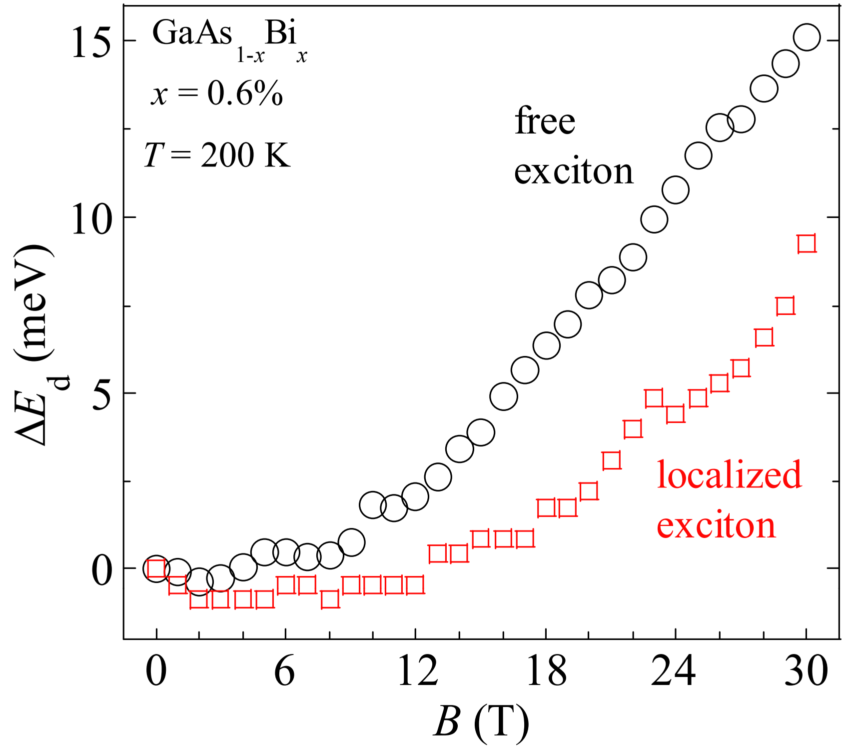
At high power carrier scattering disrupts the coherence of the electron/hole cyclotron orbit as found in degenerate GaAs and **InN**



Magneto-PL: data

. . . back to GaAsBi





Localized excitons behave differently

Magneto-PL: analysis

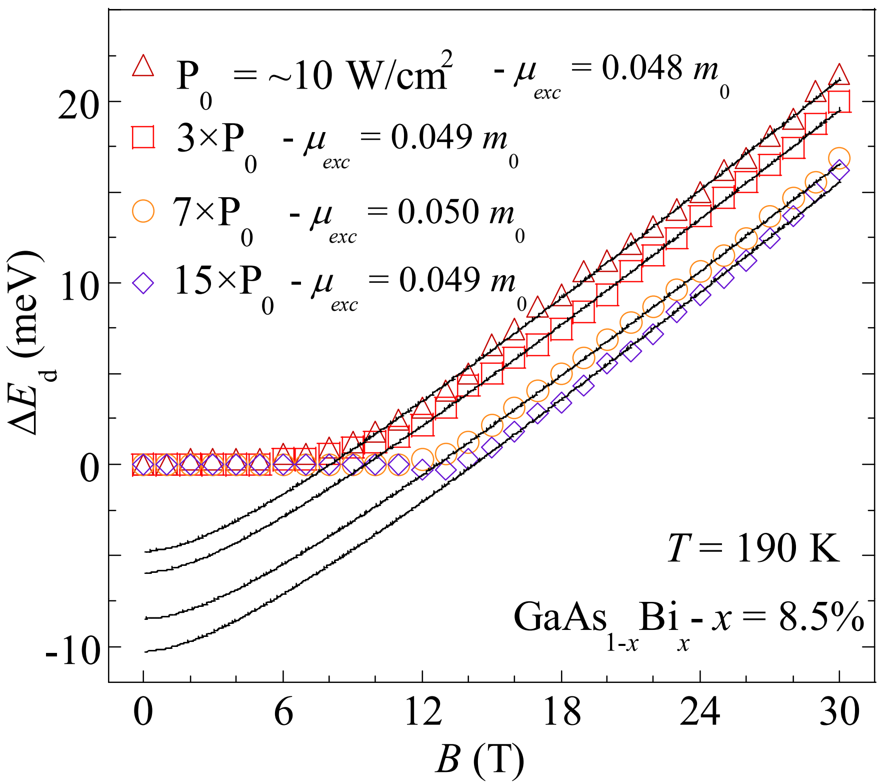
B-induced shift of given by

(see D. Cabib, E. Fabri, and G. Fiorio, Il Nuovo Cimento **10B**, 185 (1972))

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

$$\gamma = (e\hbar B)/(2\mu_{\mathrm{exc}} R^*)$$

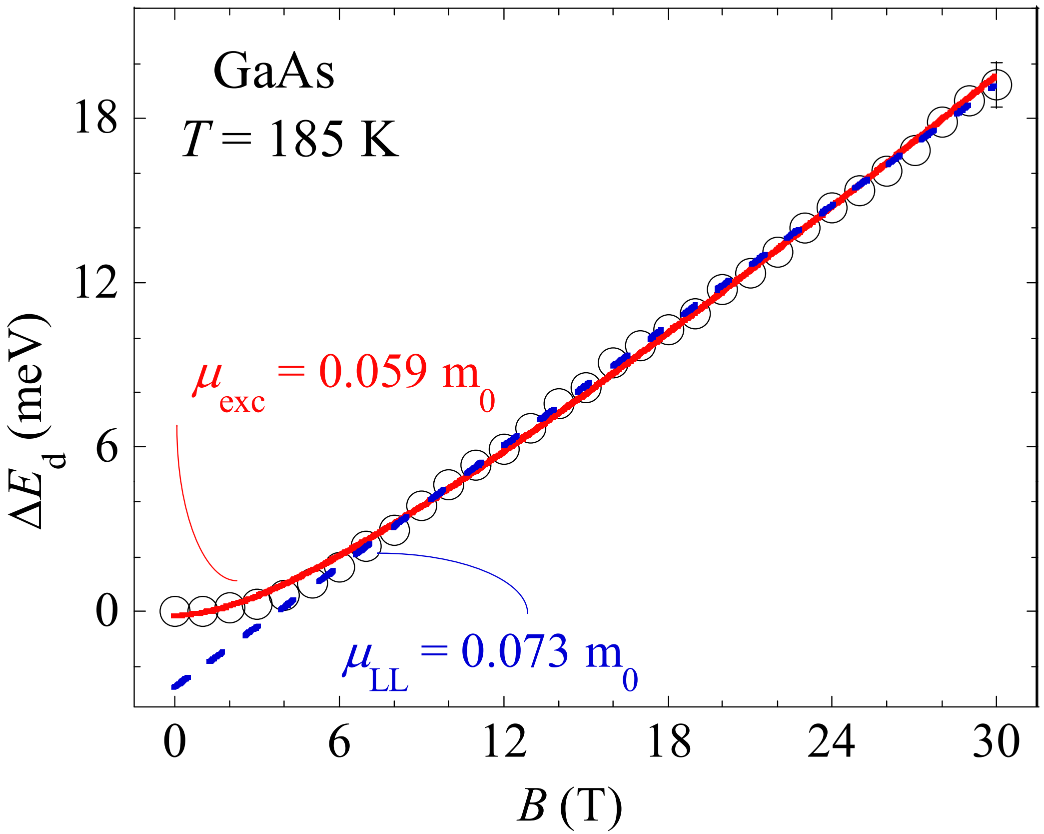
R^* Rydberg



The exciton reduced mass does not depend on excitation power

Magneto-PL: analysis

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



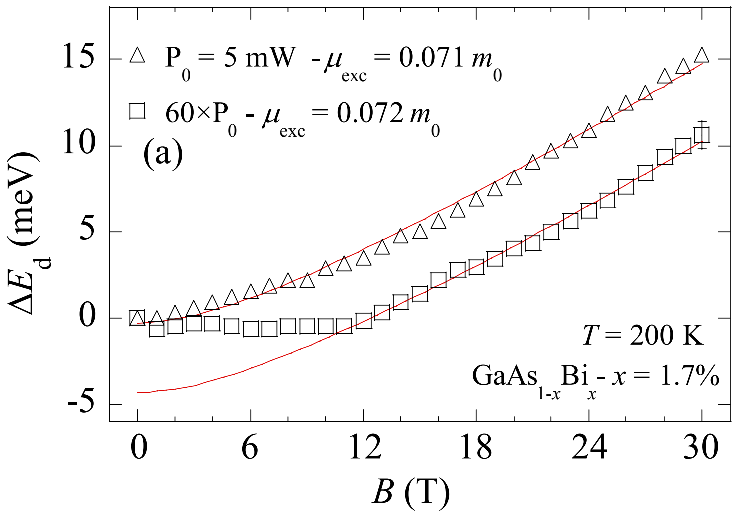
Free-exciton: quadratic-like

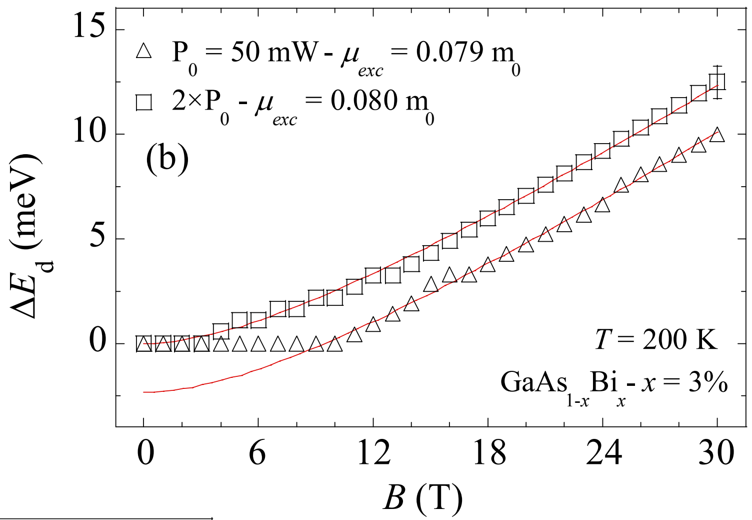
Free-carrier: Landau levels form

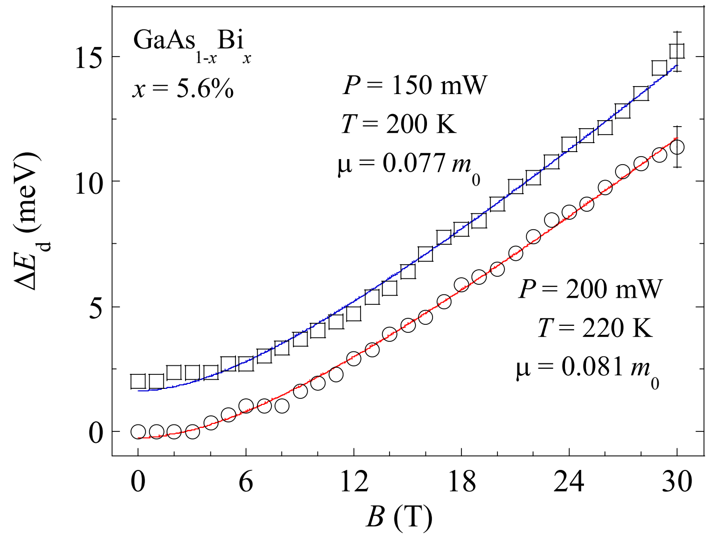
A more reasonable carrier reduced mass is found for exciton-like recombination

Magneto-PL: analysis

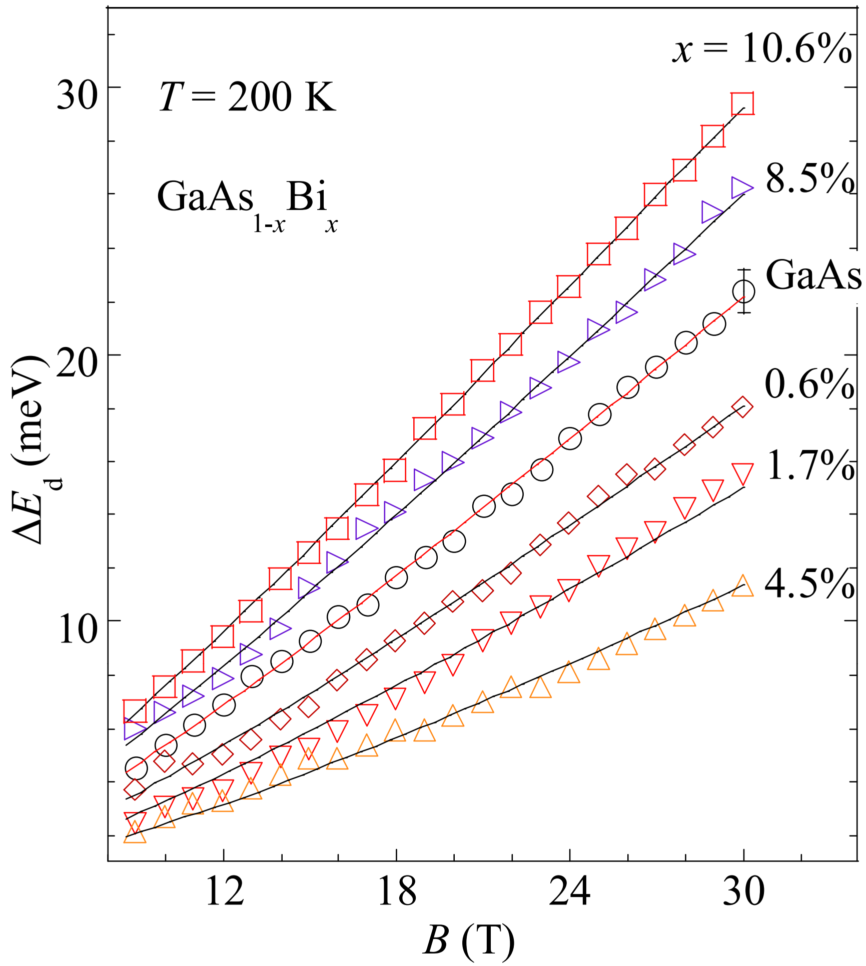
High- temperature PL: free-exciton or free-carrier ?







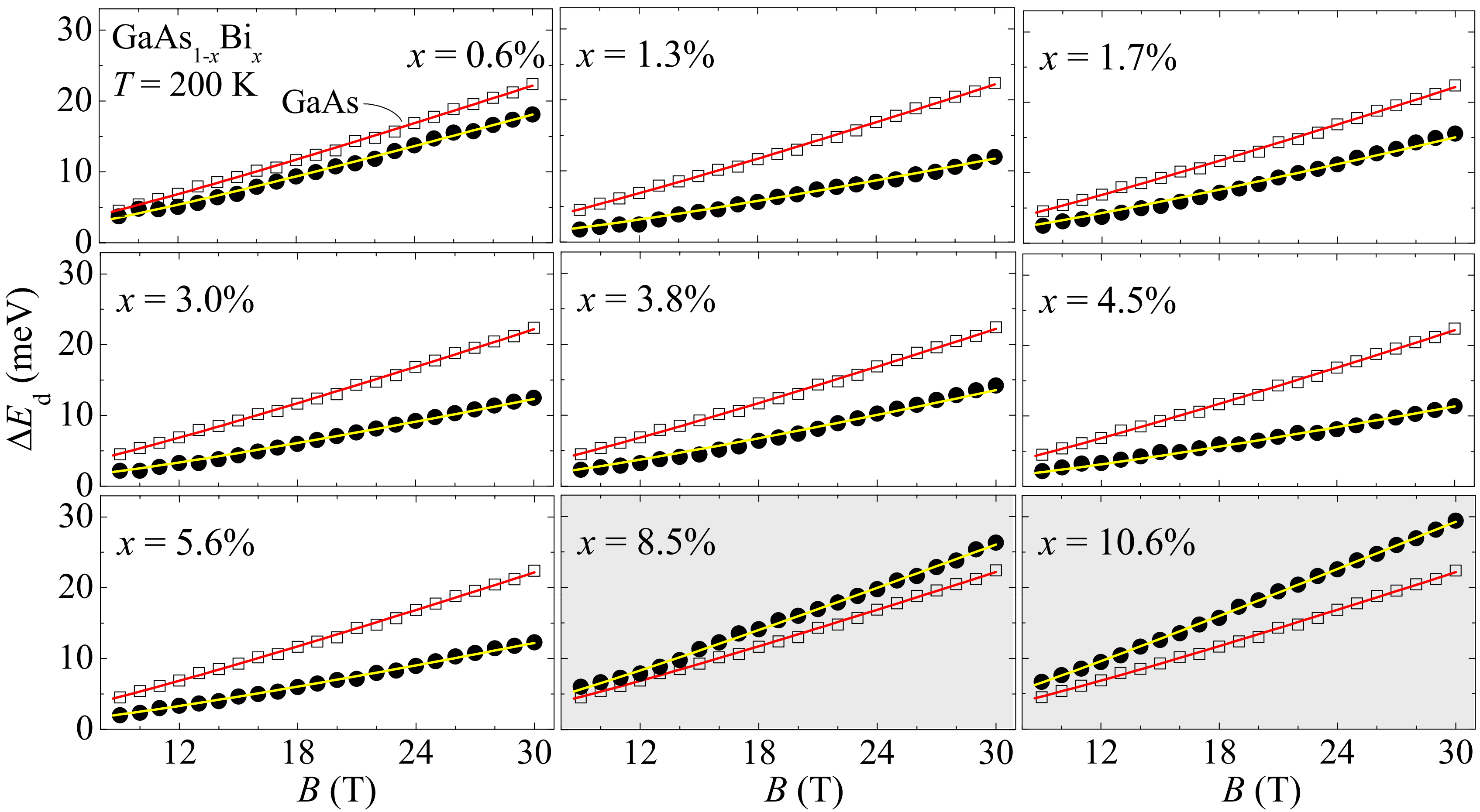
Magneto-PL: results



Non monotonic dependence of the exciton reduced mass on Bi concentration

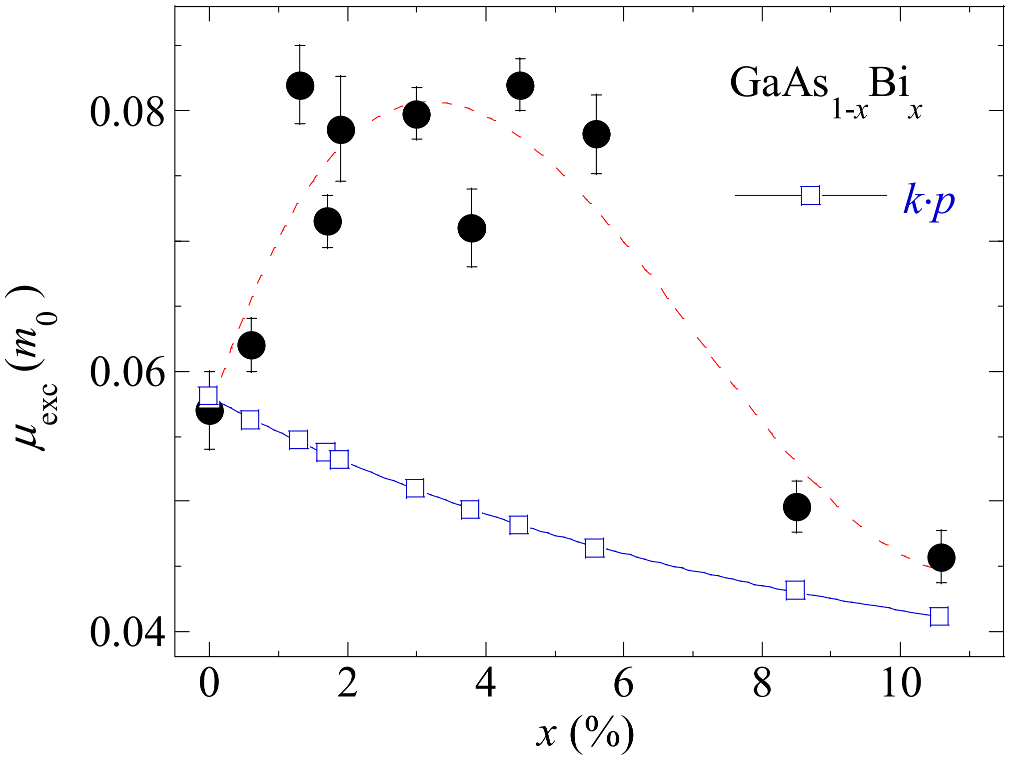
G. Pettinari *et al.*, Phys. Rev. B **81**, 235211 (2010)

Magneto-PL: results



G. Pettinari *et al.*, Phys. Rev. B **81**, 235211 (2010)

Exciton reduced mass

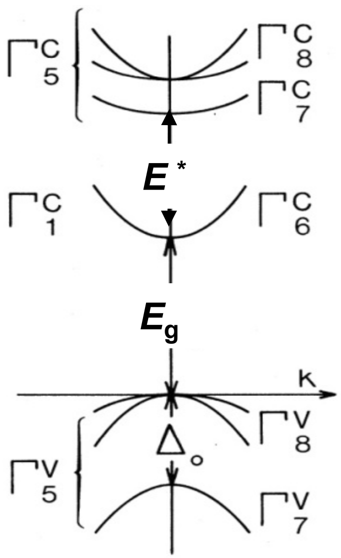


Non conventional compositional dependence followed by a *k·p*-like behavior

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

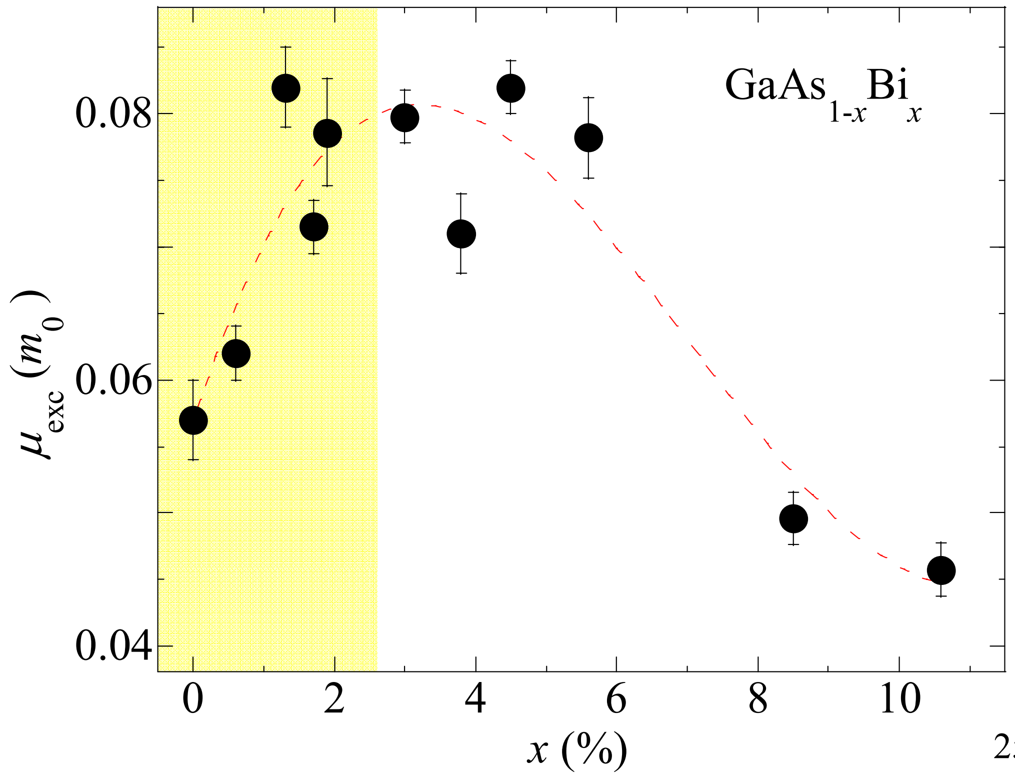
$m_{hh} \propto m_0(2Q^2/E^*-1)^{-1}$

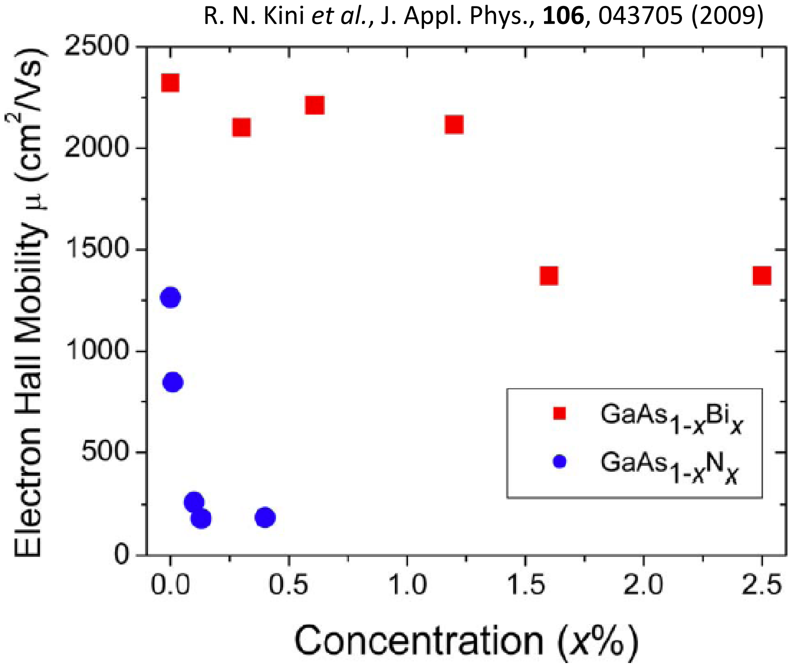
P^2=28.9 eV, Q^2=8 eV



G. Pettinari *et al.*, Phys. Rev. B **81**, 235211 (2010)

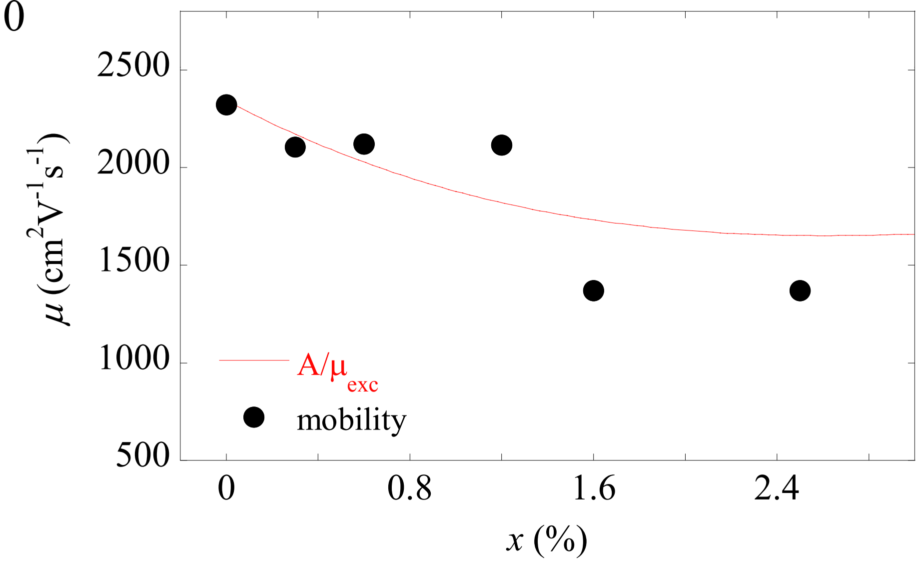
Exciton reduced mass: what we learn



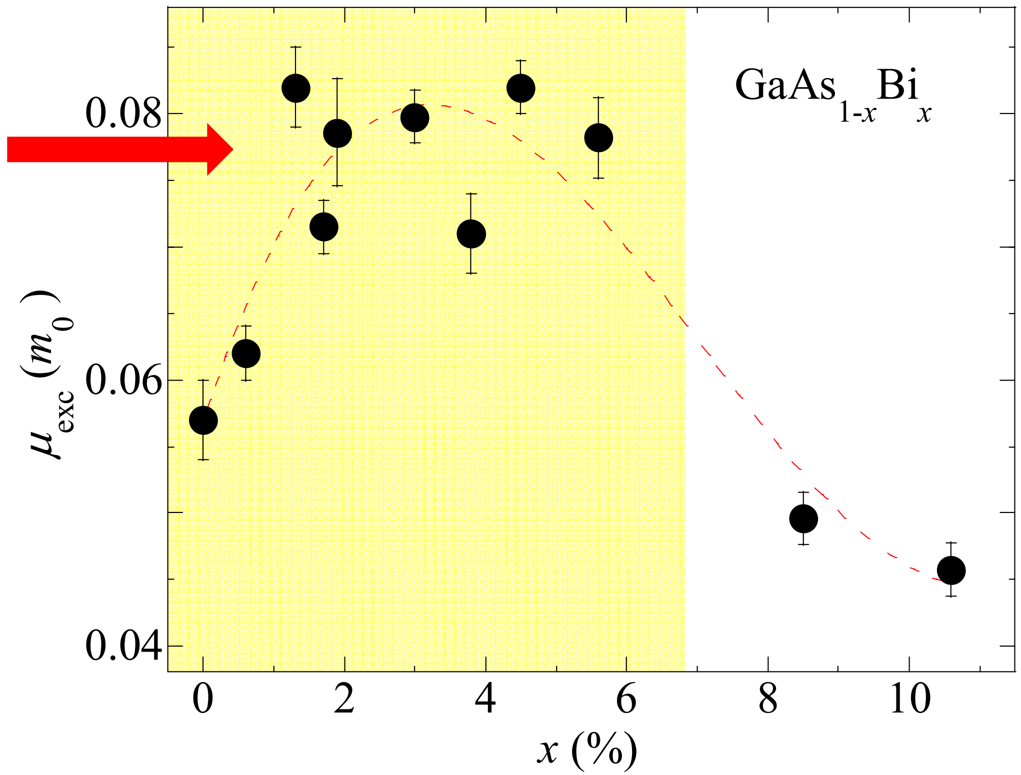


Consistent with mobility data

$\Delta\mu/\mu \approx \Delta m/m \approx 30\%$



Exciton reduced mass: what we learn



The *unexpected* increase of the carrier mass indicates a highly perturbed band structure.

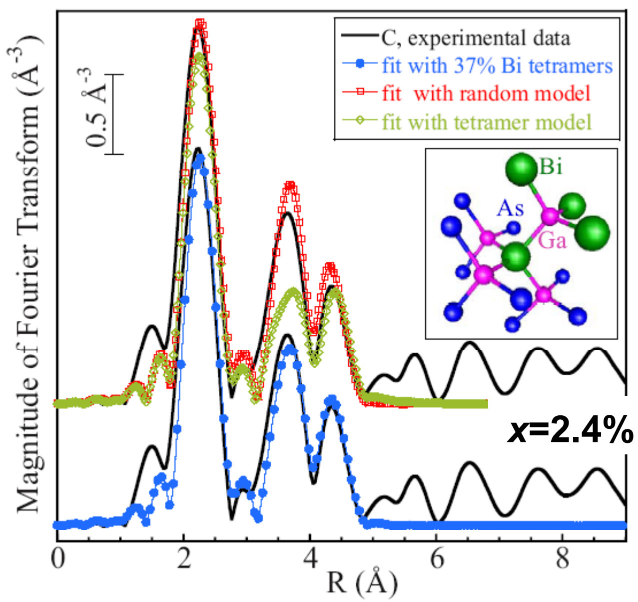
The plateau value (0.08 m_0) is not conceivable with a perturbation exerting on the VB only.

$1/\mu_{exc}=1/m_e+1/m_h$

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

The CB has to be perturbed, too

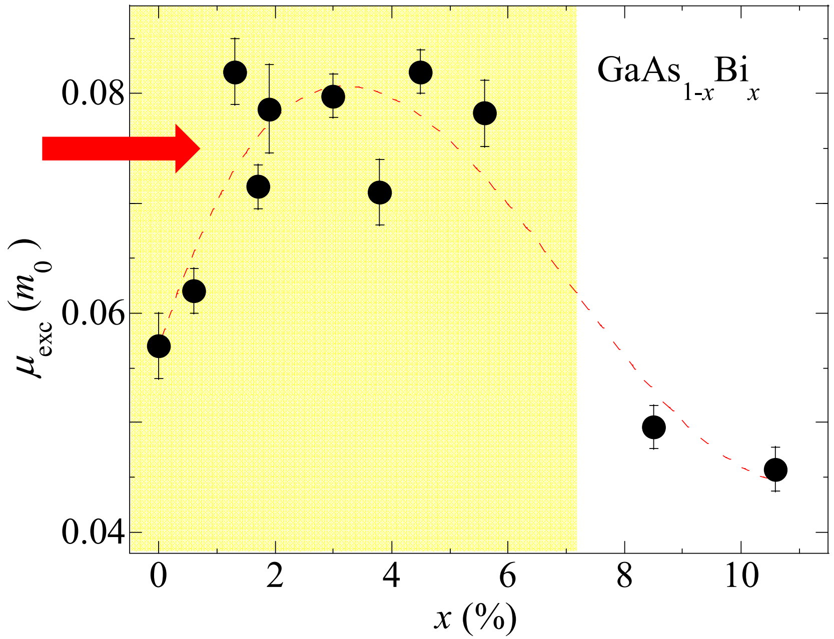
G. Ciatto *et al.*, Phys. Rev. B **78**, 035325 (2008)



Tendency to Bi atom clustering may perturb CB structure

G. Pettinari *et al.*, Phys. Rev. B **81**, 235211 (2010)

. . . alternatively



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

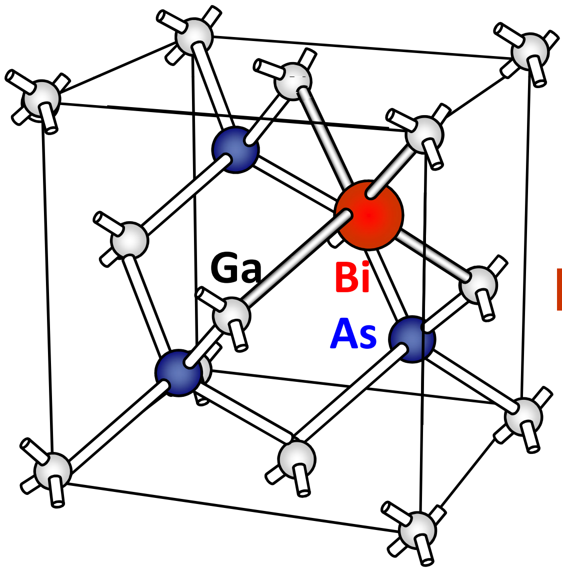
$m_h \rightarrow \infty$, μ_{exc}=0.067 m_0

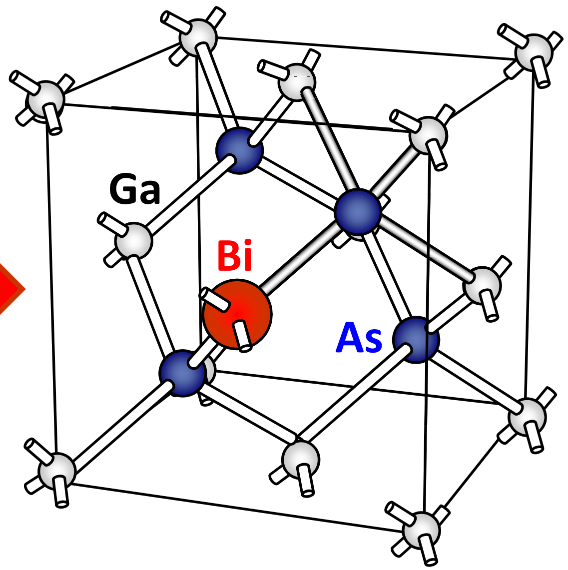
Bi is assumed to substitute As (valence 5)

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, . . .

Exciton reduced mass: what we learn

PHYSICAL REVIEW B VOLUME 48, NUMBER 7 15 AUGUST 1993-I

Identification of the Bi_{Ga} heteroantisite defect in GaAs:Bi

M. Kunzer, W. Jost, and U. Kaufmann
Fraunhofer-Institut für Angewandte Festkörperphysik, Tullastrasse 72, W-7800 Freiburg, Federal Republic of Germany

H. M. Hobgood and R. N. Thomas
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 $Bi_{Ga}{}^{+}$.

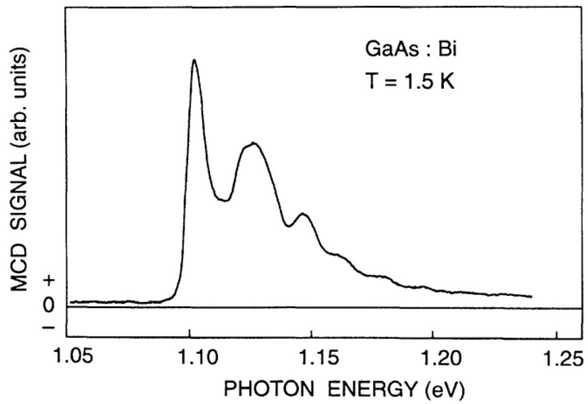


FIG. 2. The $Bi_{Ga}{}^{+}$ MCD absorption band following quenching of the As_{Ga} $EL2^{+}$ MCD band.

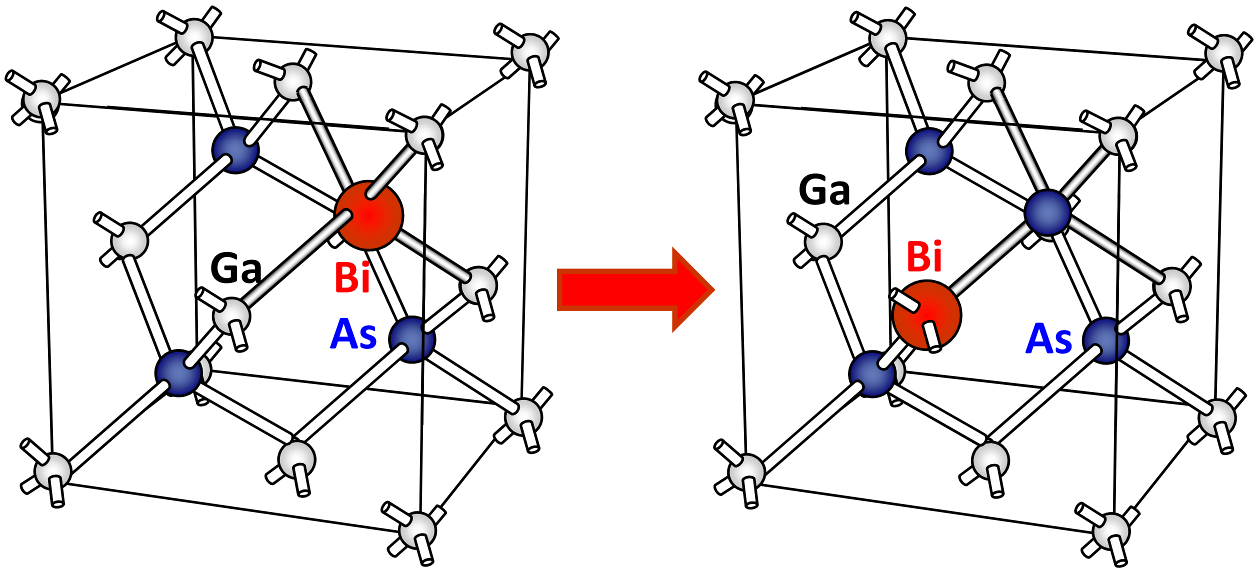
Exciton reduced mass: what we learn

IDENTIFICATION OF THE Bi_{Ga} HETEROANTISITE DEFECT . . .

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

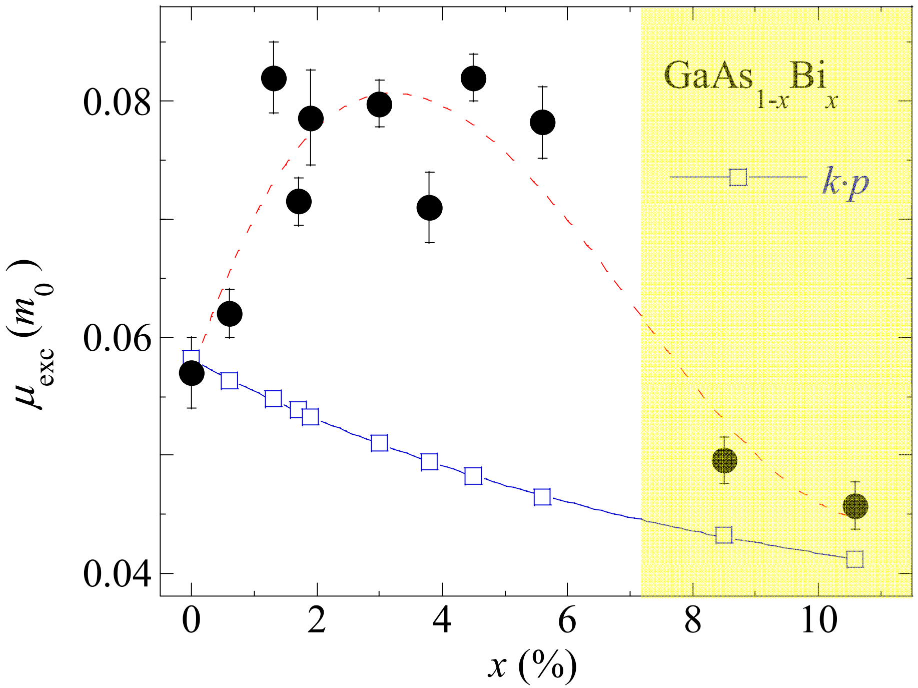
	g	A (GHz)	A/A_f	Formation probability f	(0/+) level below E_c (eV)
P_{Ga}	1.99	1.80	0.140		
As_{Ga}	2.04	2.70	0.184	$\sim 10^{-6}$	0.75
$^{121}Sb_{Ga}$	2.02	6.61	0.188	$\sim 10^{-3}$	0.48
Bi_{Ga}	2.055	10.96	0.141	$\sim 10^{-1}$	0.35–0.50

M. Kunzer *et al.*, Phys. Rev. B **48**, 4437 (1993)

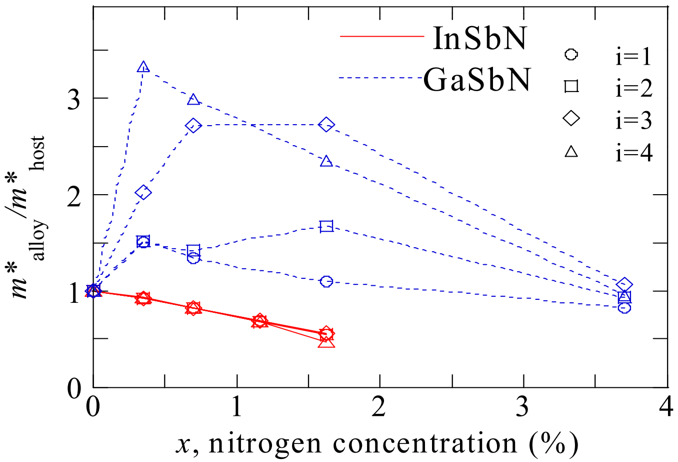


Then, what CB structure is expected for (GaBi)As?

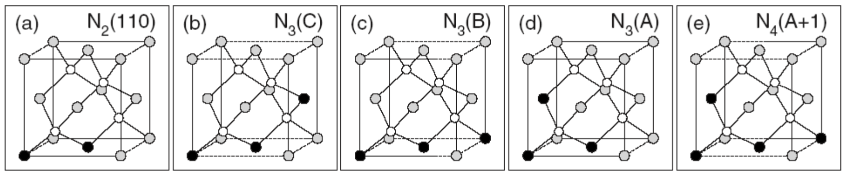
Exciton reduced mass: what we learn



A. Lindsay *et al.*, Phys. Rev. B **77**, 165205 (2008)

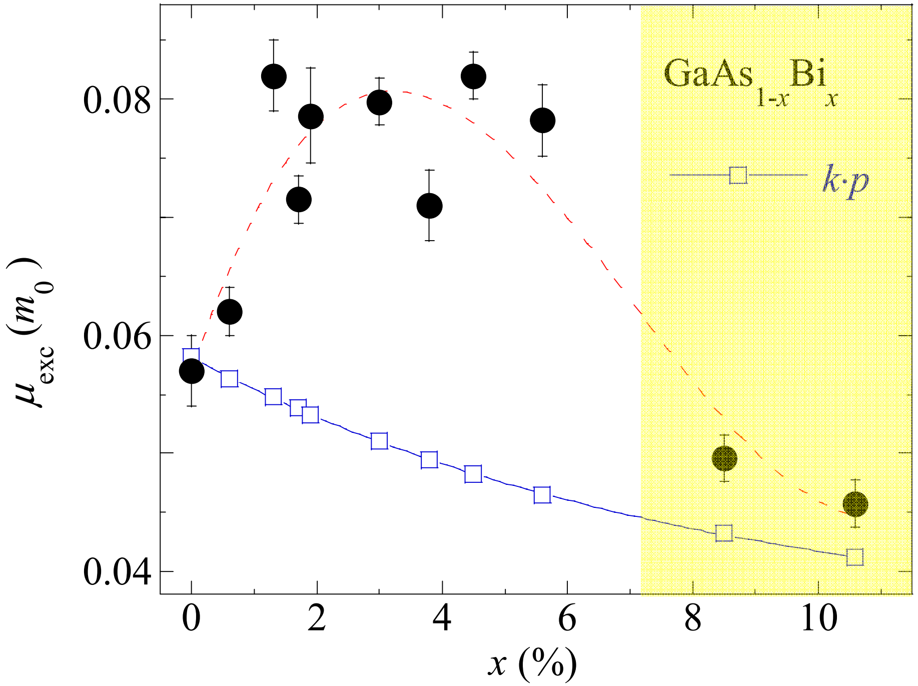


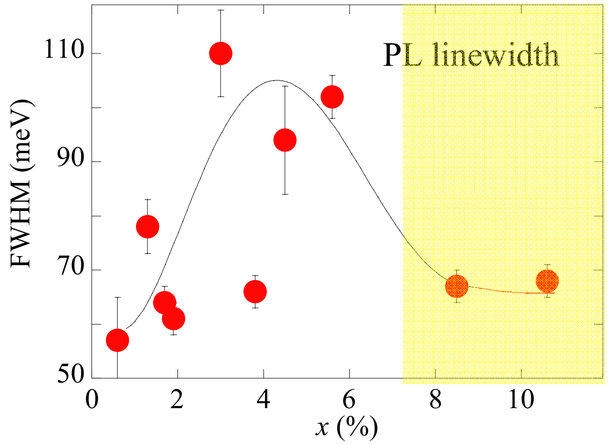
The recovery of a conventional-alloy behaviour above *x*>8% points toward a restoration of a random atomic distribution of Bi atoms.



G. Ciatto *et al.*, private communication

Exciton reduced mass: what we learn





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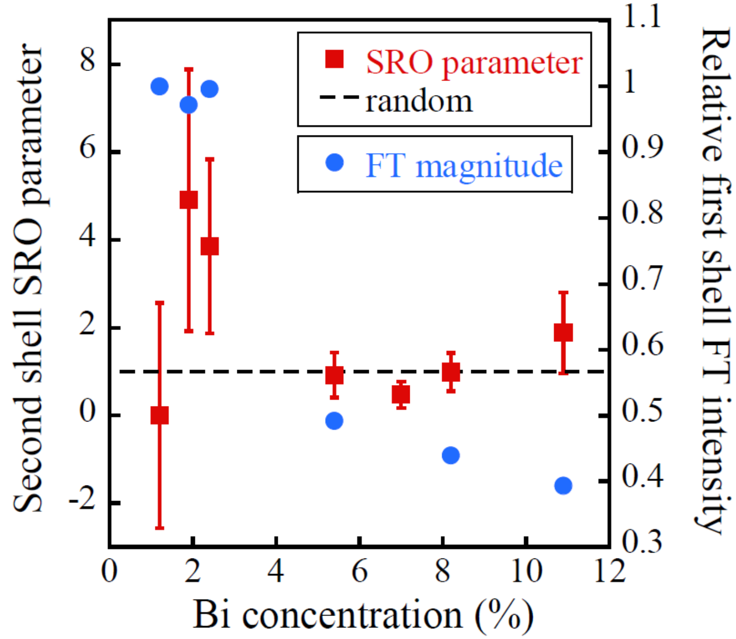
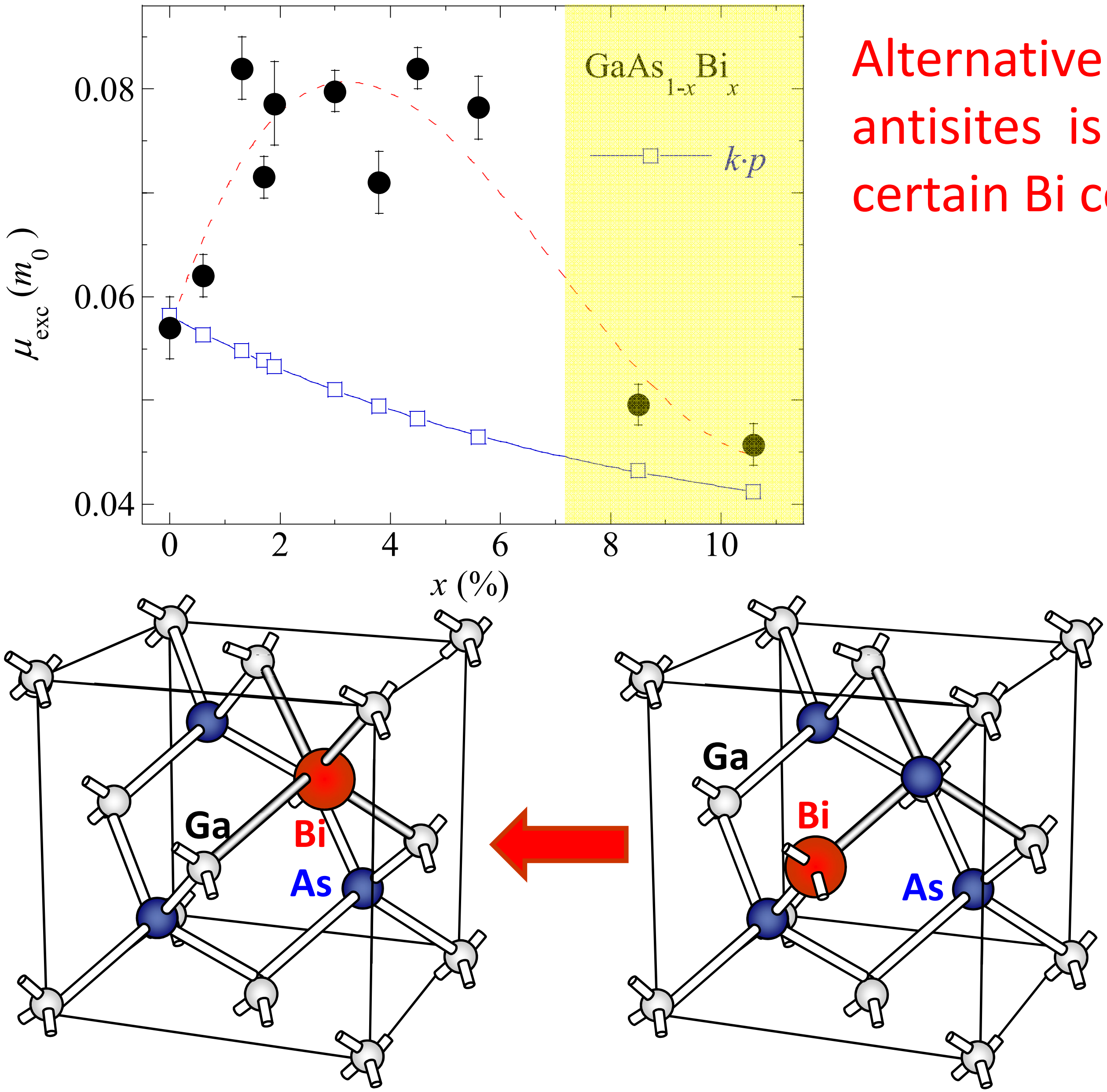


G. Ciatto *et al.*, private communication

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.