Étude de l'ordre locale autour d'impuretés magnétiques dans les semiconducteurs pour l'électronique de spin

Thèse pour obtenir le grade de
Docteur en Sciences de l'Université Joseph Fourier - Grenoble I
Spécialité Physique de la Matière Condensée et du Rayonnement

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6 Octobre 2009

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M. Rovezzi
Introduction
Spintronics
XAFS
Fe in GaN
Incorporations
Series
Co-doping
Mn in Ge
Models
NCs results
Mn in GaAs
Models
Surface study
Etch-anneal
Conclusions

Study of the local order around magnetic impurities in semiconductors for spintronics

Mauro Rovezzi[1]

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BM08 c/o ESRF - Grenoble, France

October 6th, 2009

Outline

The whole work:

I. Fe in GaN
II. Mn in Ge
III. Mn in GaAs
IV. Mn in GaAs/InAs NanoWires

Additional work:

A. GIXAS exp. set-up
B. CARD software
C. Mn in ZnSe and CdSe

This talk:

1 Introduction
- Semiconductor spintronics
- XAFS

2 Fe in GaN
- Incorporations
- Series
- Co-doping

3 Mn in Ge
- Models
- NCs results

4 Mn in GaAs
- Models
- Surface study
- Etch-anneal process

5 General conclusions and outlook

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Semiconductor spintronics

Combination of semiconductor technology (charge) with magnetism (spin)

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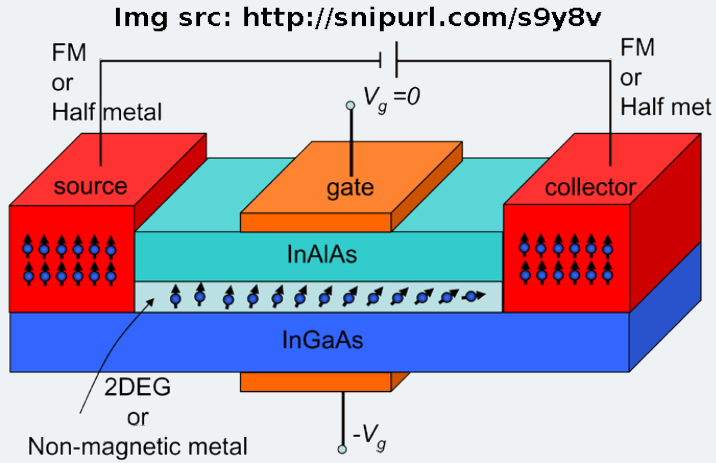
Spin-polarized field-effect transistor [Datta & Das, Appl. Phys. Lett. (1990)]

1. Efficient spin injection
2. Long spin diffusion (nm–μm) and efficient spin manipulation
3. Reliable spin detection



Magnetic semiconductors (MS)

- Electric spin injection better than optical for real devices
- Injection by ferromagnetic metals is inefficient (conductivity mismatch) $\Rightarrow$ tunnel juctions or ferromagnetic semiconductors
- Advantage in MS: control electric properties using a magnetic field and *vice versa* their magnetic properties using an electric field
- Need high Curie temperature (T_C), beyond room temperature

Diluted Magnetic Semicondutors (DMS)

Mechanism of magnetic order

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Semiconductor ($A_{1-x}B_x$) where a fraction x of the cations (few %) is randomly substituted by magnetic elements as transition metals (TMs)

Origin of ferromagnetism $\Rightarrow$ exchange interactions

- TMs introduce localized energy levels (in the band gap for III-V)
- Magnetic order: interplay between spin degree of freedom, Coulomb interactions and Fermi statistics; not crucial for magnetic order: dipole-dipole and spin-orbit (relativistic effect)
- *s*(*p*)-*d*, and *d*-*d* exchage: former direct between band states and TM, latter indirect (mediated by valence/conduction band states)

"low"-T_C FM DMS: electronic nanoscale phase separation

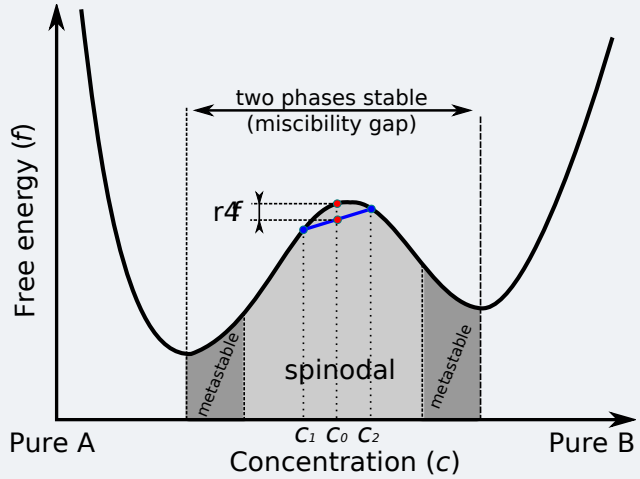
- Zener mean field model [Dietl *et al.*, Science (2000)]
  $\mathcal{H} = \mathcal{H}_0 + \sum_{i \in I} J_{pd} S_i \cdot s_i \rightarrow T_C \propto J_{pd}^2 x_{eff} p^{1/3}$ increasing p and x_{eff}!
- Disorder $\Rightarrow$ need to consider defects of compensation (E.g. in III-V):
  - Anti-sites affect the density of carriers
  - Interstitials affect also the density of magnetically active TMs

Non-uniform magnetic semiconductors

"high"-T_C FM: chemical nanoscale phase separation

Spinodal decomposition [Cahn and Hilliard works ('60s)]

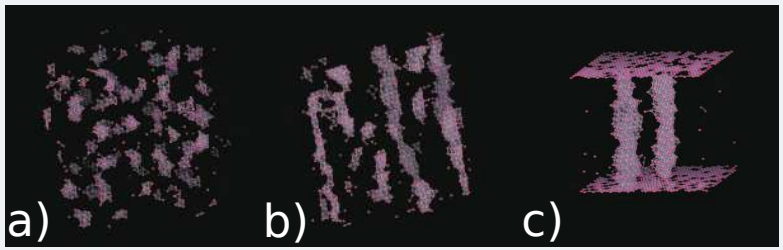
- $\partial^2 f/\partial c^2 < 0 \Rightarrow$ decompose spontaneously; phase transition small in degree (composition change) but large in extent (size)
- $\partial^2 f/\partial c^2 > 0 \Rightarrow$ nucleation and growth; phase transition large in degree but small in extent



- TM-rich and TM-poor regions with the structure of the host crystal
- TM-rich region is high T_C and accounts for magnetization at RT
- Controlled by Fermi level during growth (Coulomb repulsion)

Magnetism: *ab initio* approach [Katayama-Yoshida *et al.* (2007)]

- No semi-phenomenological $\mathcal{H}$
- DFT + Monte Carlo
- GaMnN: a,c) high-T_C; b) low-T_C



XAFS in the study of (D)MS

Why?

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Advantages

- Element-selective (x-ray absorption edges of the elements)
- Local probe (< 10 Å from the absorbing atoms)
- No need long-range order (complementary to XRD)
- Sensitive to impurities (detection limit: $\approx 10^{14}$ at/cm^2)
- Accurate bond distances (resolution: $\approx 1\%$)
- Charge state (from near-edge region)

Disadvantages

- Average signal (difficult to resolve mixed phases if present in small quantities, limit: $\approx 20\%$)
- No spatial resolution in the sample (bulk probe)

X-ray Absorption Fine-Structure

Measurements and theory basics

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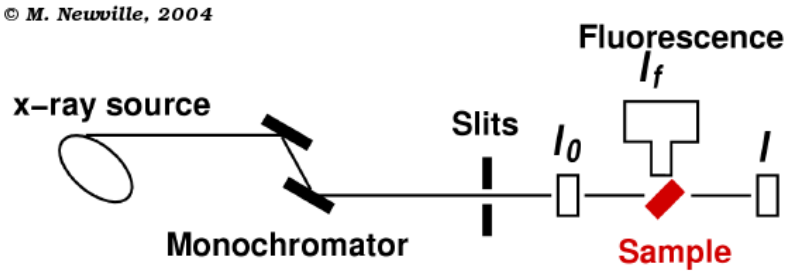
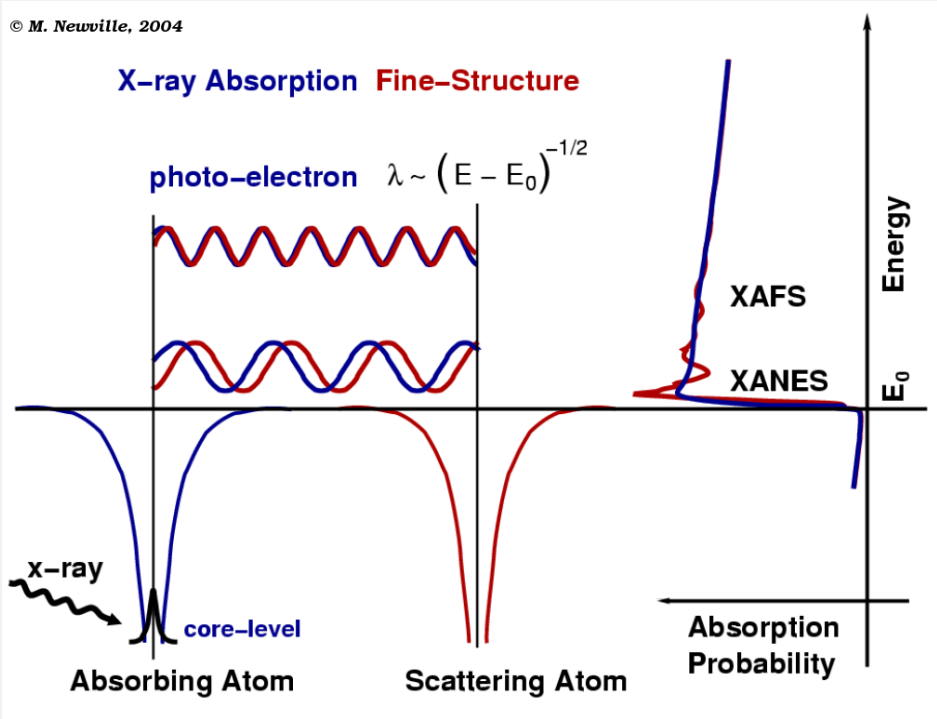


Absorption coefficient $\mu(E)$

$\mu(E)t = -ln(I/I_0)$, transmission

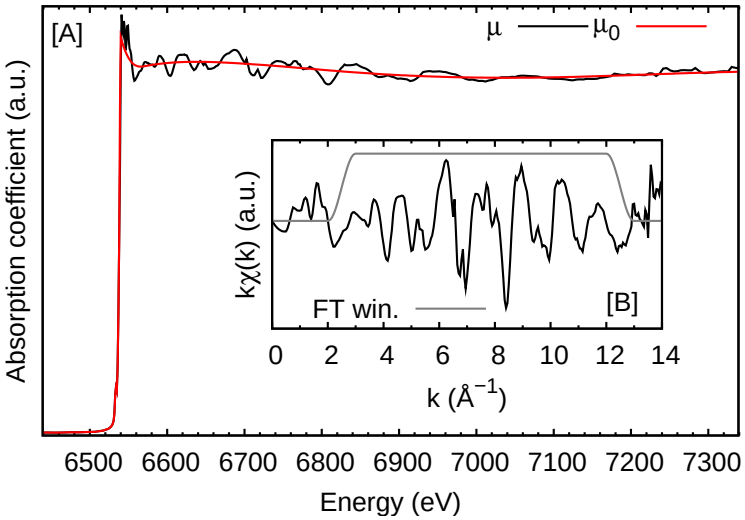
$\mu(E) \propto I_f/I_0$, fluorescence

1. Absorption through photo-electric effect
2. Photo-electron scattering and interference with itself
3. Core-hole filled and fluorescent x-ray emitted

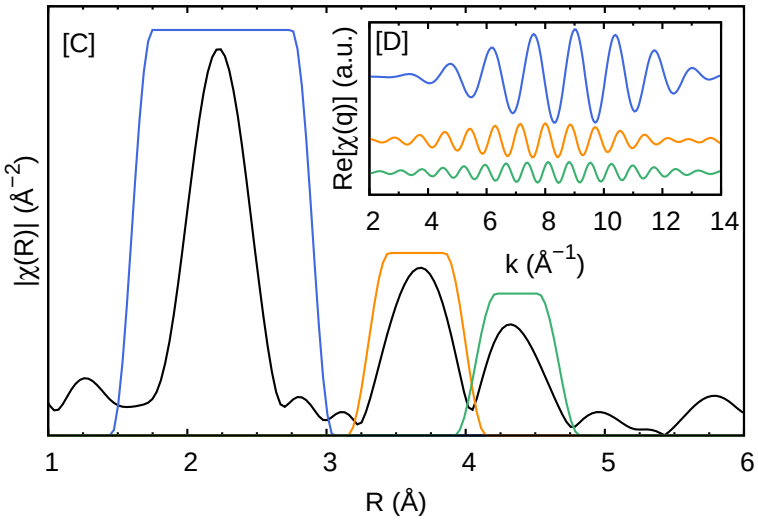


X-ray Absorption Fine-Structure

Overview of the quantitative analysis

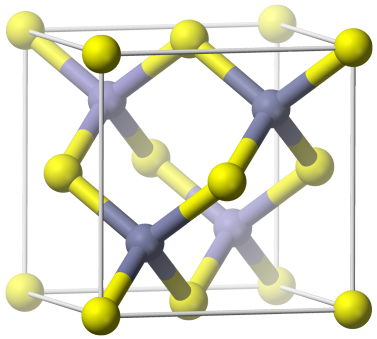


FT →



$$\chi(k) = \sum_j \frac{N_j S_0^2 f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{kR_j^2} sin[2kR_j + \delta_j(k)]$$

From "scattering paths" → distances, coodination numbers and mean-square disorder around absorber



GILDA: BM08 @ ESRF

General purpose Italian beamLine for Diffraction and Absorption

- Source: bending magnet
- Monochromator: double crystal with sagittal focusing (horizontal)
- Mirrors (for harmonics rejection): Pd/Pt with bending (vertical focusing)
- Energy range: 4 – 80 KeV
- Energy resolution ($\Delta E/E$): 10^{-4}
- Flux on the sample: 10^{8} – 10^{11} ph/s
- Minimum beam-size (vertical): 30 μm
- Detector for reflectivity and monitoring: ion chambers
- Detector for fluorescence: 13 elements high purity Ge
- Detection modes: transmission, normal fluorescence, total electron yield, grazing-incidence (ReflEXAFS)

Fe in GaN

In collaboration with

Part of the present work published in

- A. Bonanni *et al.*, Phys. Rev. Lett. **101**, 135502 (2008)
- M. Rovezzi *et al.*, Phys. Rev. B **79**, 195209 (2009)

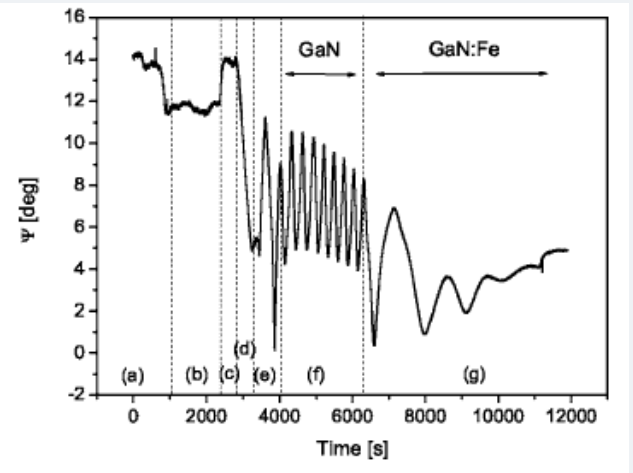
GaN:Fe(Mg,Si)

[A. Bonanni *et al.*, Phys. Rev. B 2007]

- Metalorganic vapour phase epitaxy (MOVPE)
- *c*-plane Al_2O_3 (sapphire) substrates
- Precursors: TMGa (trimethilgallium), NH_3 (ammonia), Cp_2Fe (ferrocene), Cp_2Mg (bis-cyclopentadienyl-magnesium), SiH_4 (silane)
- In-situ monitoring: ellipsometry, XRD, laser reflectivity

Growth procedure

1. Substrate nitridation
2. LT (540 °C) GaN nucl. layer
3. Annealing/recrystallization
4. 1 μm HT (1050 °C) GaN
5. 0.5 – 1 μm GaN:Fe(:Mg,Si)
   - 800 – 950 °C
   - 50 – 400 sccm[a] Cp_2Fe

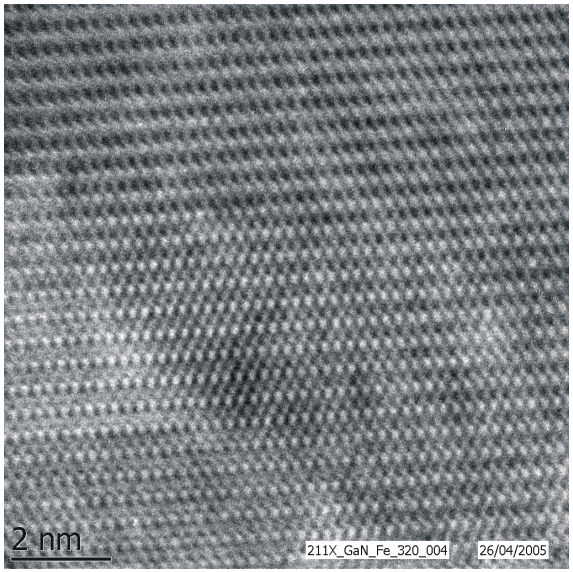


[a] standard cubic centimeters per minute

Ex-situ characterizations

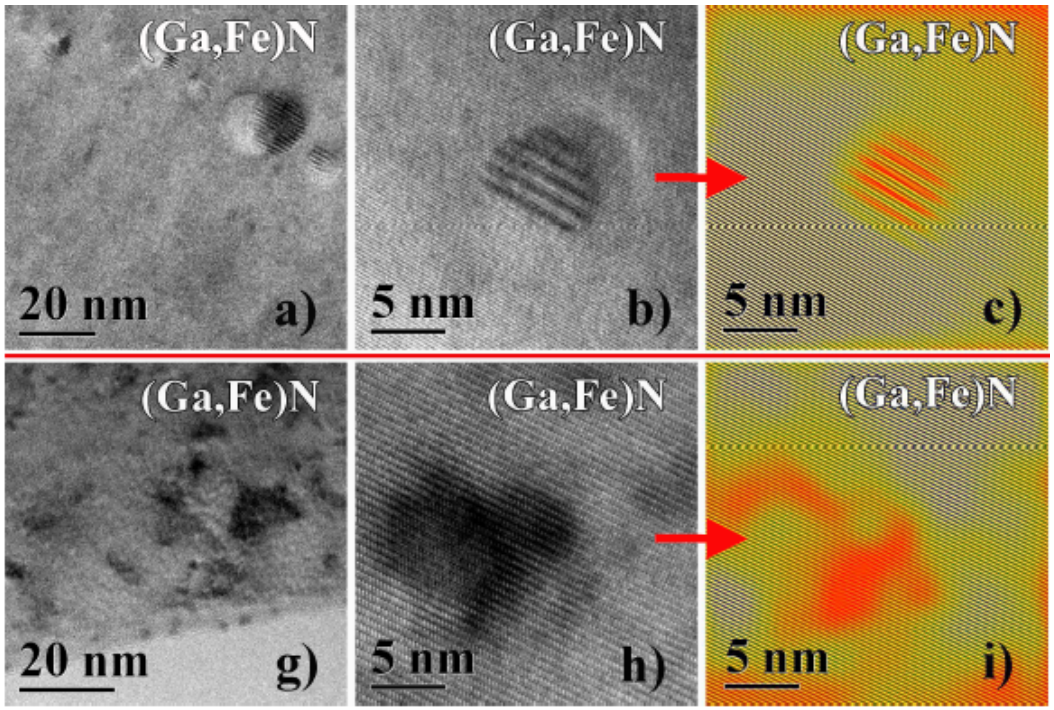
(HR)TEM, SQUID, synchrotron XRD

Random substitutional



- Low temp. Curie paramagnetism from Fe^{3+} (d^5)

Chemical and crystallographic separation



- Enhanced ferromagnetic response
- Persisting at high temperature

Solubility limit[1] at 200 sccm Cp_2Fe ($\approx$ 0.4% Fe)

[1] in our growth conditions

EXAFS
Measurements

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Samples characterized at Fe K-edge (7112 eV)

GILDA at ESRF

- Bending magnet source
- Linear polarization: out-of-plane (90°)
- Standard geometry
- High-purity 13-elements Ge detector

LUCIA at SLS (now at SOLEIL)

- Insertion device source
- Linear polarization: in-plane (0°) and out-of-plane (90°)
- Grazing incidence geometry
- Silicon drift fluorescence detector

Characterized samples

Overview of the parameters space

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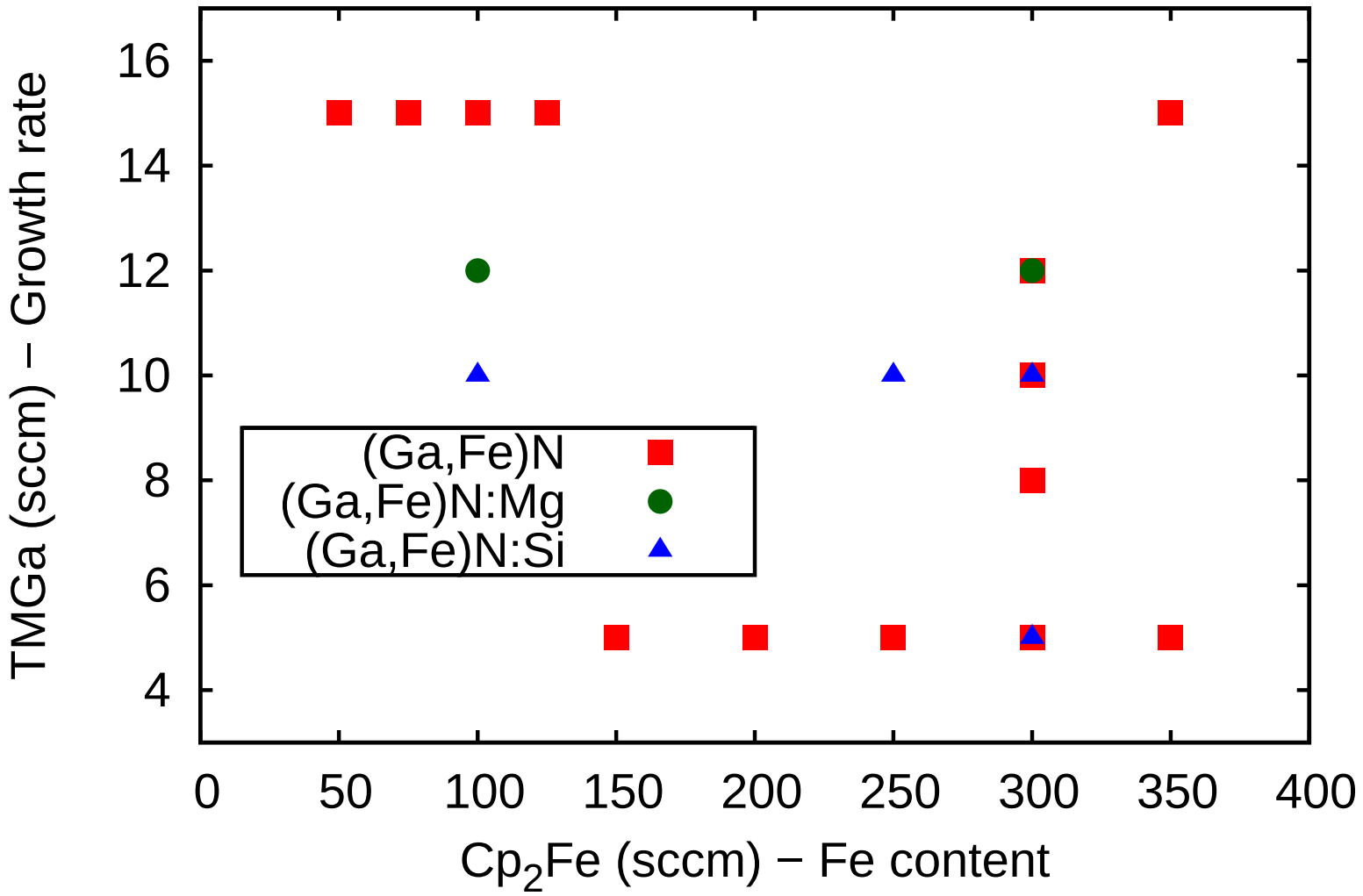
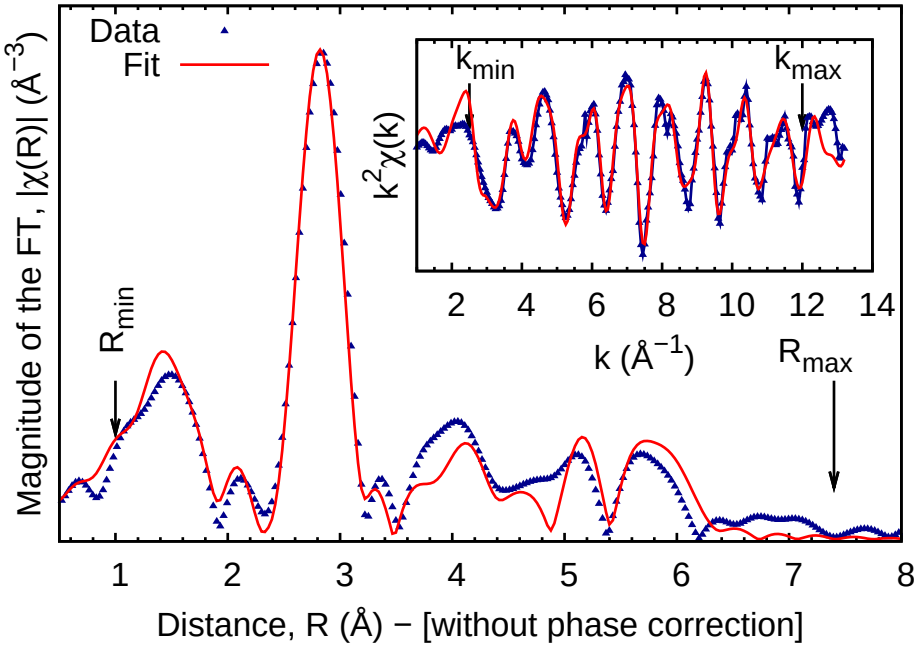
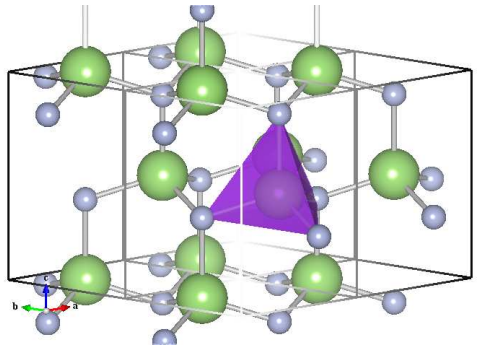


Low Fe content

Fe_{Ga} as relaxed by Density Functional Theory



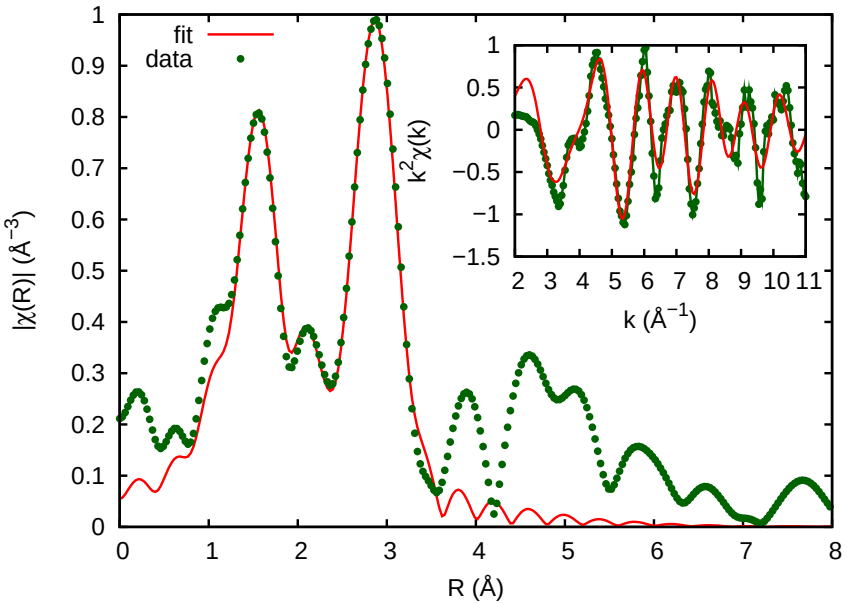


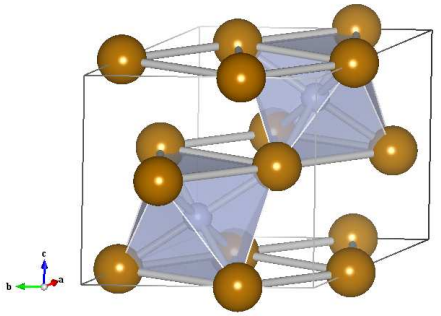
Fe_{Ga}

- Possible to fit up VI coordination shell with a minimum set of variables (Debye correlated model for σ^2) $\Rightarrow$ low local structural disorder
- Global 1% expansion to respect GaN [$d_{Fe-N} = 1.98(1)$ Å and $d_{Fe-Ga} = 3.19(2)$ Å]
- Experimental results in line with the Fe^{3+}_{Ga} DFT relaxed structure (LSDA+U, 72-atoms supercell): $d_{Fe-N} = 1.99(1)$ Å and $d_{Fe-Ga} = 3.22(1)$ Å

High Fe content

Crystallities appears





ϵ-Fe_3N

- $\approx$ 60(10)% Fe_{Ga}: $d_{Fe-N} = 2.02(1)$ Å $d_{Fe-Ga} = 3.22(4)$ Å
- $\approx$ 40(10)% ϵ-Fe_3N (Bainite): $d_{Fe-Fe} = 2.71(2)$ Å

Polarized measurements

Linear dichroism sensitive to simmetry

[Data from LUCIA]

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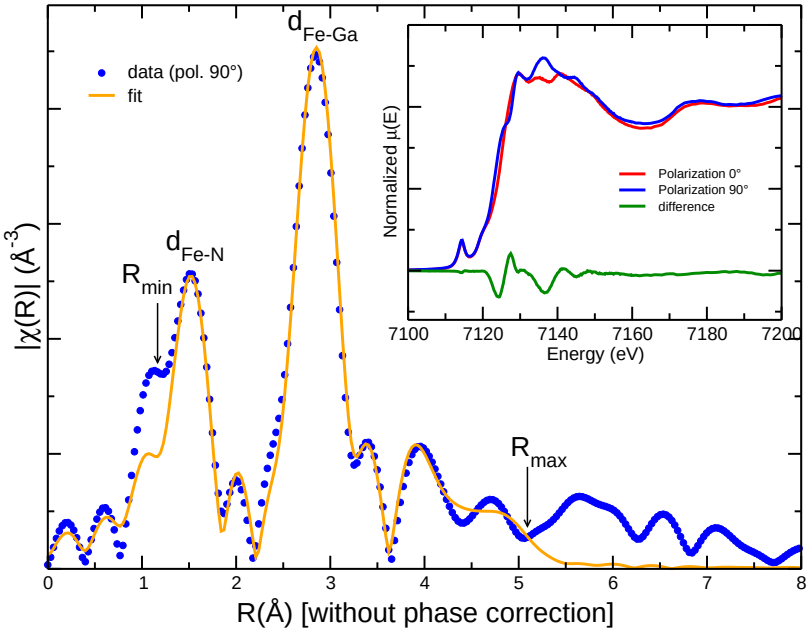
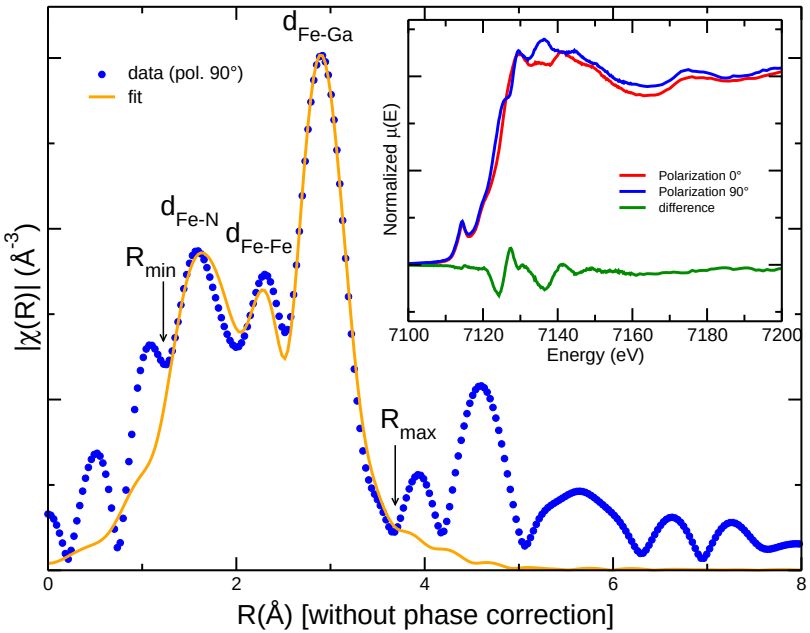
Fe_{Ga}



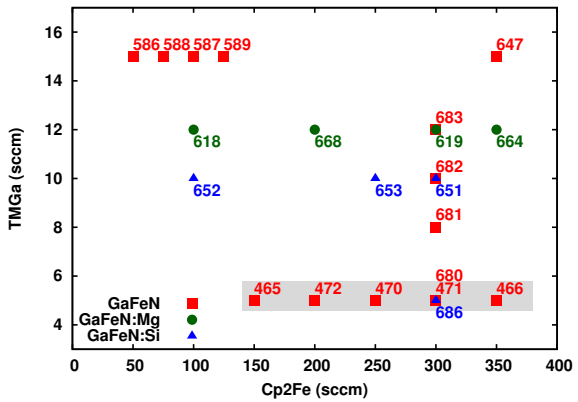
Fe_{Ga} + precipitates (α-Fe)



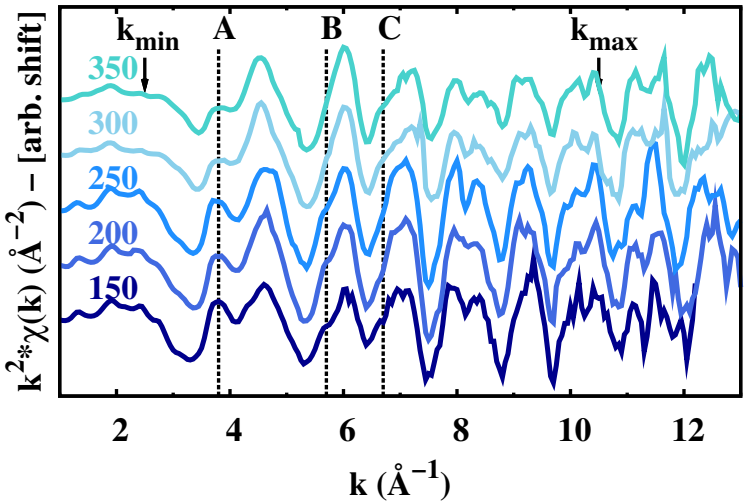
- Double polarization (changed at the source): in-plane (0°) and out-of-plane (90°)
- Linear dichroism $\Rightarrow$ incorporation in non-cubic site
- Cubic precipitates do not contribute to the dichroic signal $\Rightarrow$ additional information by EXAFS

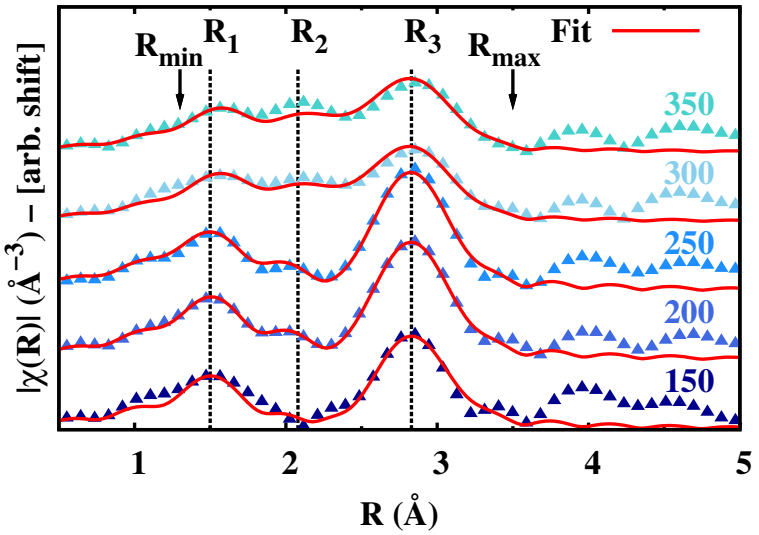
Solubility limit as function of Fe content

Low growth-rate



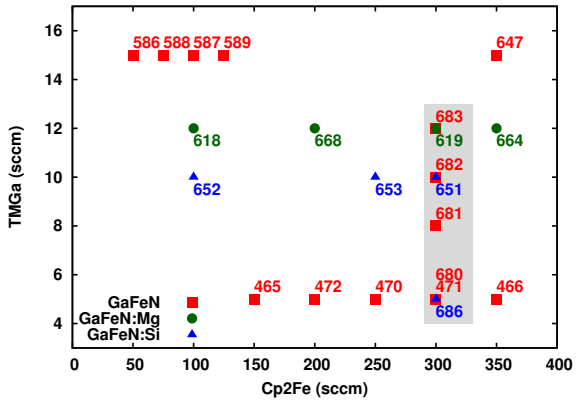
- TMGa @ 5 sccm $\Rightarrow$ solubility limit at $\approx$ 0.4% Fe (in our growth conds.)
- Fe $<$ 200 sccm $\Rightarrow$ Fe substitutional in wurtzite GaN (Fe_{Ga})
- Fe $\geq$ 200 sccm $\Rightarrow$ Fe_{Ga} + ϵ-Fe_3N precipitates



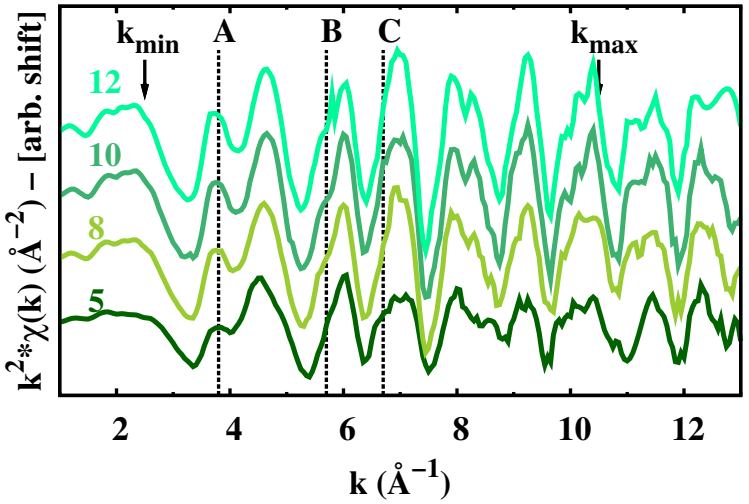


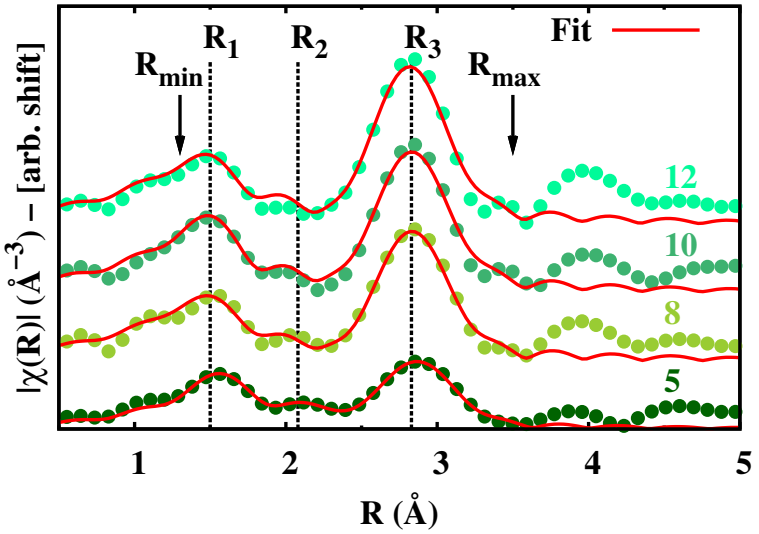
Increasing growth-rate

Increases the Fe solubility limit



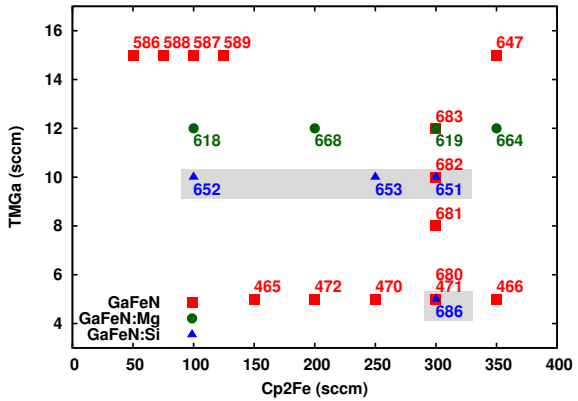
- Fe_{Ga} for TMGa $\geq$ 8 sccm
- 100(10) % Fe_{Ga} still for 350 sccm Cp_2Fe and TMGa 15 sccm (max!)
- Solubility limit improved from $\approx$0.4% to $\approx$1% Fe



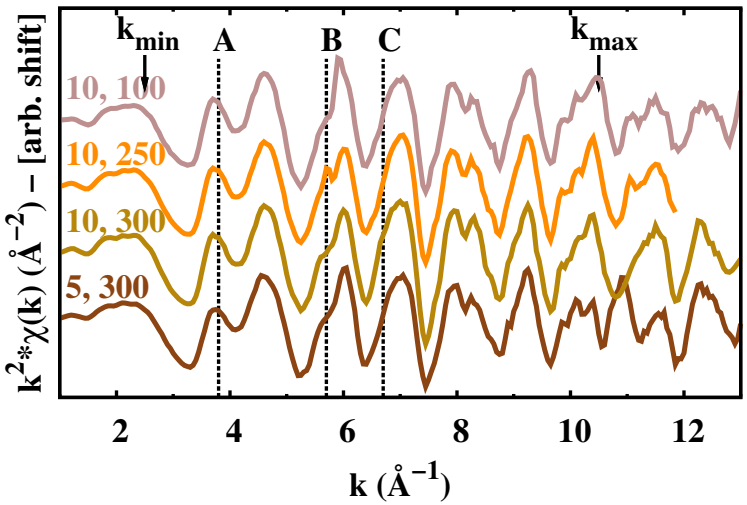


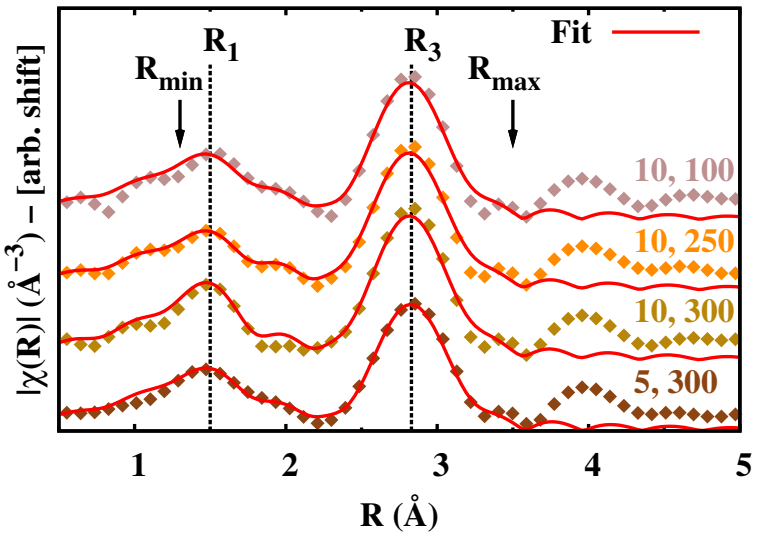
Si co-doping

n-type doping ⇒ promotes dilution



- 100(10)% Fe_{Ga}
- No additional phases are detectable
- Effect due to Fermi level shift





Fe charge state by XANES

Study of pre-edge peaks ($1s \rightarrow 3d$ transitions)

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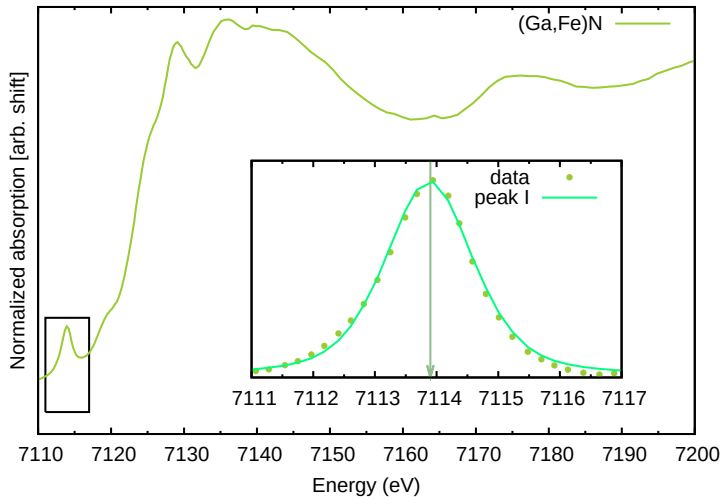
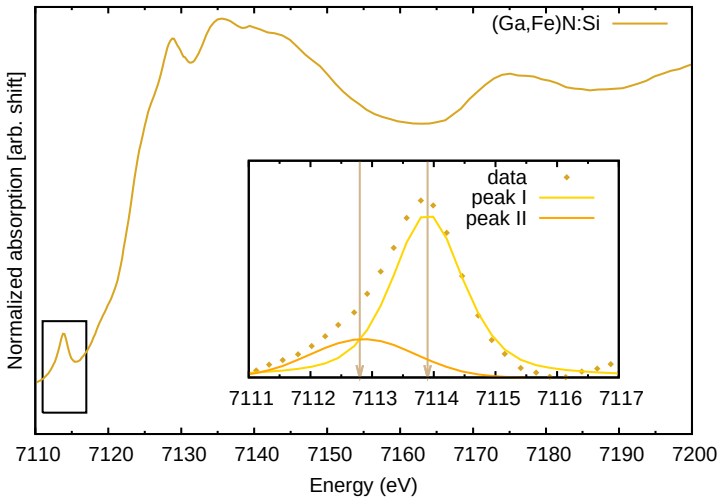
Comparing spectra with the same Fe_{Ga} incorporation





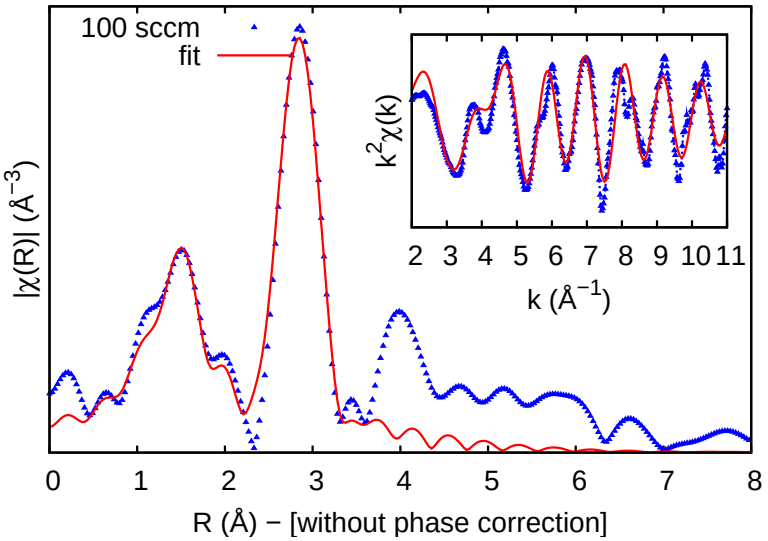
- I @ 7113.9(1) eV $\Rightarrow$ Fe^{3+}

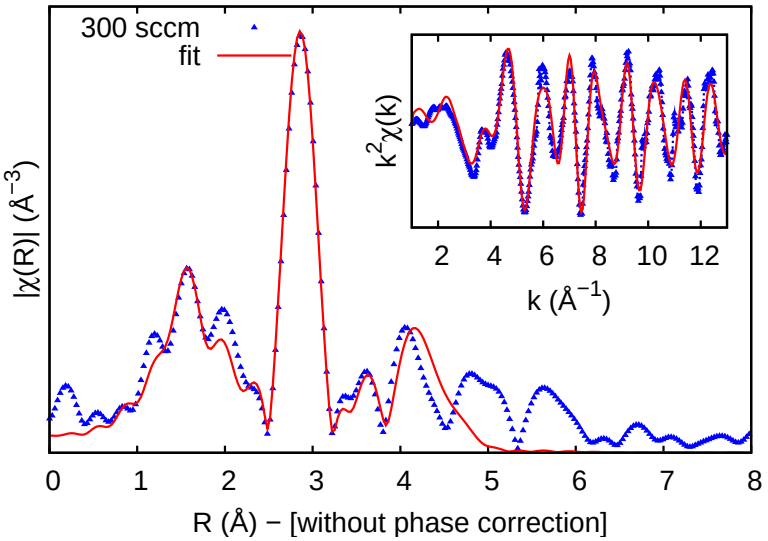
- I @ 7113.9(1) eV $\Rightarrow$ Fe^{3+}
- II @ 7112.8(1) eV $\Rightarrow$ Fe^{2+}

By affecting the Fe charge state, the Coulomb repulsion overcompensate the lowering of the free energy due to the nearest-neighbour bonding [Dietl, Nature Mat. (2006)]

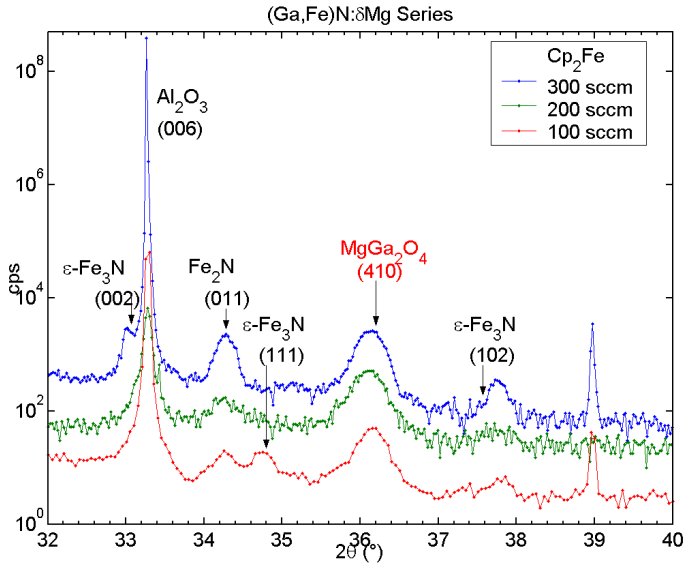
Mg co-doping

p-type doping ⇒ promotes aggregation





- No charge state change (Fe^{3+})
- Additional $d_{Fe-Fe} = 2.57(1)$ Å increasing in amplitude
- Closer to γ-Fe (fcc) or ζ-Fe_2N (orthorombic) than α-Fe (bcc)
- Precipitates visible by SXRD



Mn in Ge

In collaboration with

Part of the present work published in

- M. Rovezzi *et al.*, Appl. Phys. Lett. **92**, 242510 (2008)

$Ge_{1-x}Mn_x$ self-organized Nano-Columns

M. Jamet *et al.*, Nat. Mater. (2006) & T. Devillers *and al.* Phys. Rev. B (2007)

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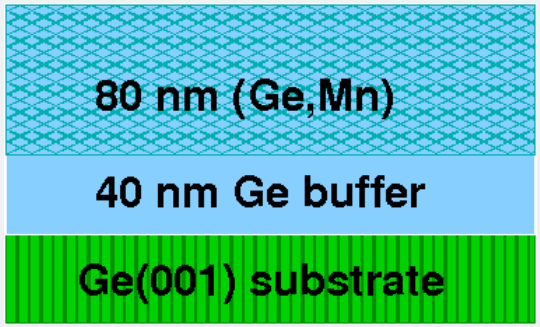
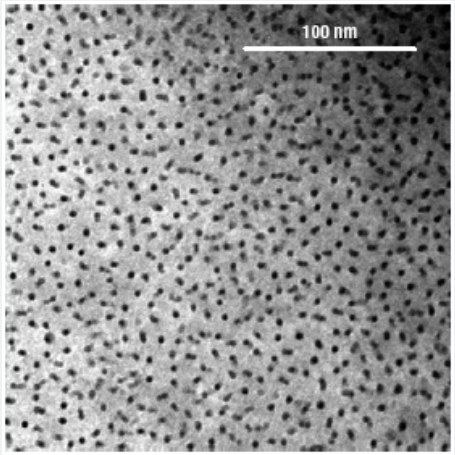
Sample growth

- LT-MBE, co-dep. of Ge and Mn
- Ge(001) substrate + Ge buffer
- Growth temp.: 80 °C – 200 °C
- Mn concentration: 0.1% – 20 % (Mn solubility in Ge is very low, $\approx 10^{-5}$ %)



2D spinodal decomposition

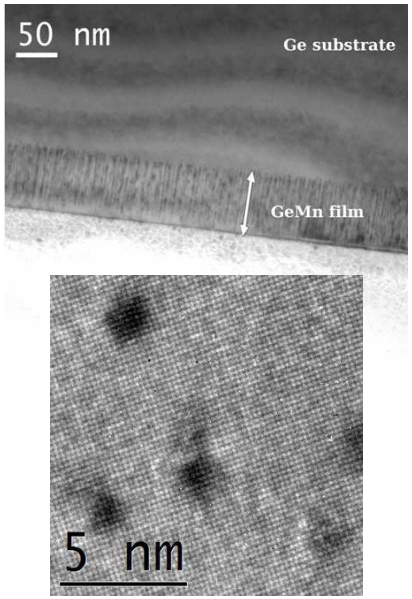
- High-T_C self-organized nanocolumns (> 400 K)
- Diameter 3 nm, volume fraction 16%



Nano-columns phase diagram

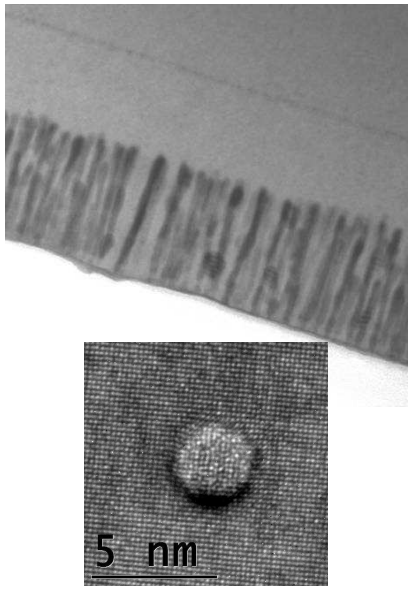
HRTEM and magnetic (SQUID) characterization

80–120 °C



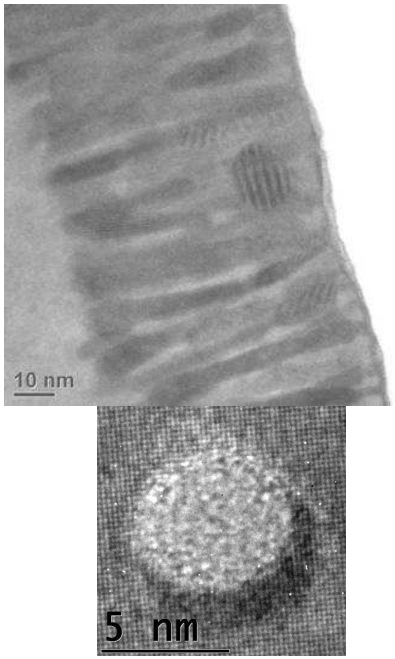
- Fully strained low-T_C NCs
- Narrow size distribution
- Superpara-magnetism

120–145 °C



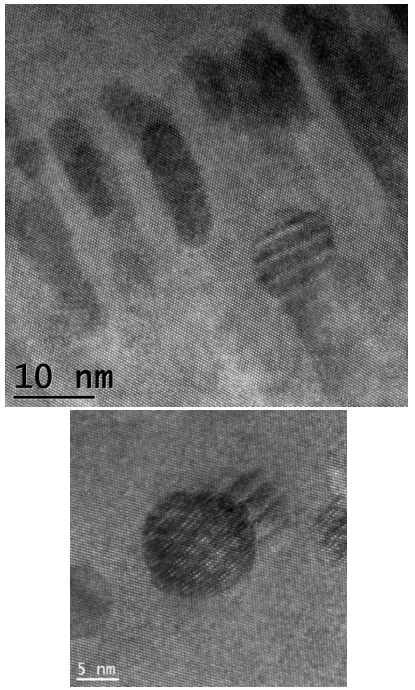
- Columns diameter increase
- Ferro-magnetism
- High-T_C NCs around 130 °C

145–180 °C



- Large and amorphous columns
- Major contribution from Ge_3Mn_5

180–200 °C

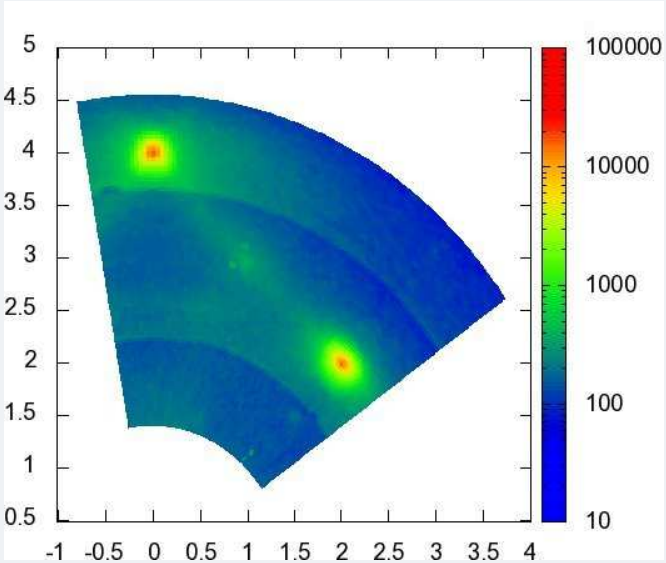


- Ge_3Mn_5 clusters

Structural characterization

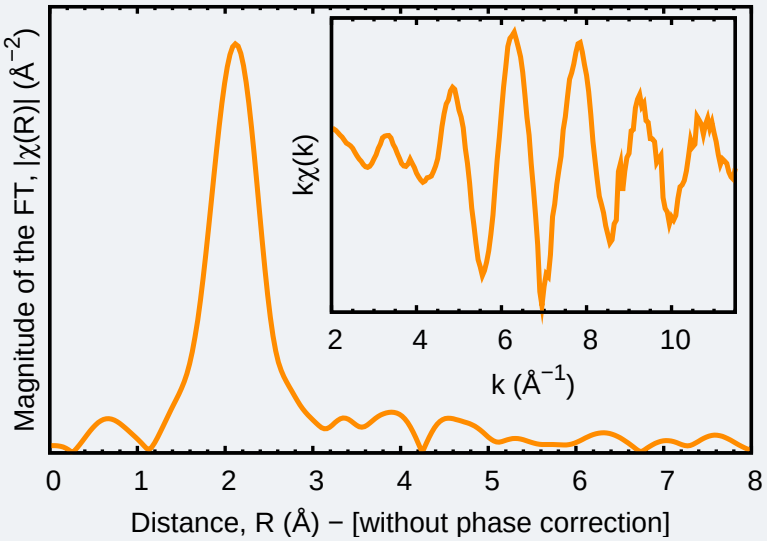
A challenging system

Long range ⇒ crystalline



GIXRD map of $\{hk0\}$

Short range ⇒ disordered



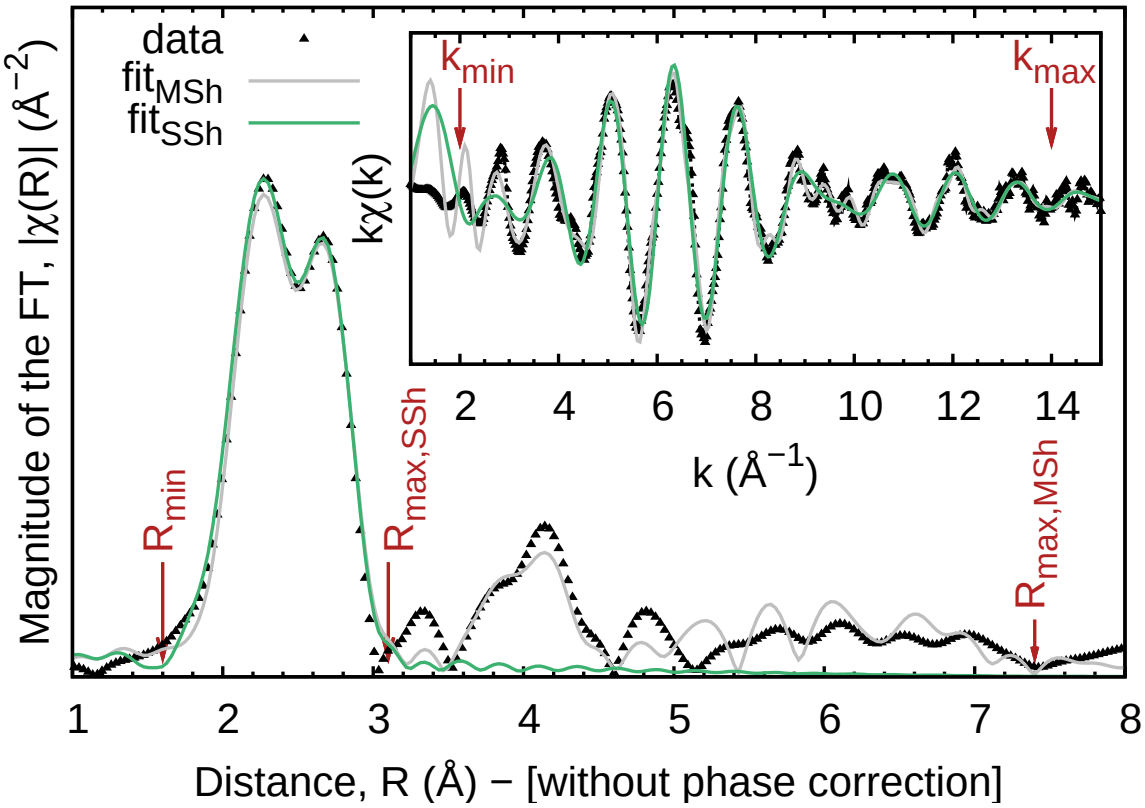
XAFS data @ Mn K-edge

Data analysis

- Comparison with reference samples: Ge_3Mn_5 and GeMn(0.1%)
- Fits using multiple data sets (to compensate the reduced information content in EXAFS)
- Assisted by *ab initio* DFT calculations (in the limit of LSDA approx.)

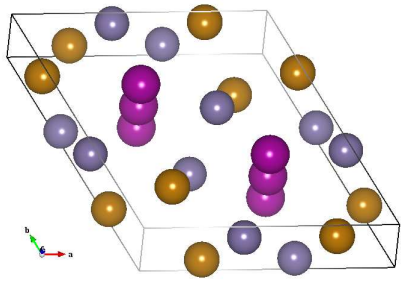
Model sample: Ge_3Mn_5

Thin film (≈10 nm) grown on Ge(111) at 350 °C

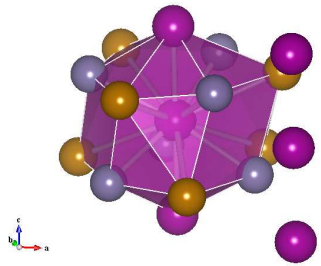


	Mn$_1$		Mn$_2$		Average	
	coord.	dist. (Å)	coord.	dist. (Å)	coord.	dist. (Å)
d_2	2 Mn$_1$ 6 Ge	2.526 2.538	2 Ge	2.488	4.4 Ge&Mn	2.507
d_3			1 Ge 2 Ge	2.610 2.768	1.8 Ge	2.715
d_4	6 Mn$_2$	3.065	2 Mn$_2$ 4 Mn$_2$ 4 Mn$_1$	2.983 3.058 3.065	8.4 Mn	3.053

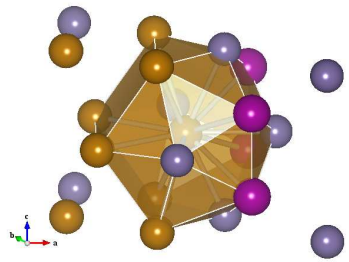
Crystallographic (Ge_3Mn_5) distances



Unit cell



Mn$_1$ (40% of the sites)



Mn$_2$ (60% of the sites)

Model sample: Mn “diluted” in Ge

Minimum Mn concentration reachable (≈0.1 %) grown at 125 °C

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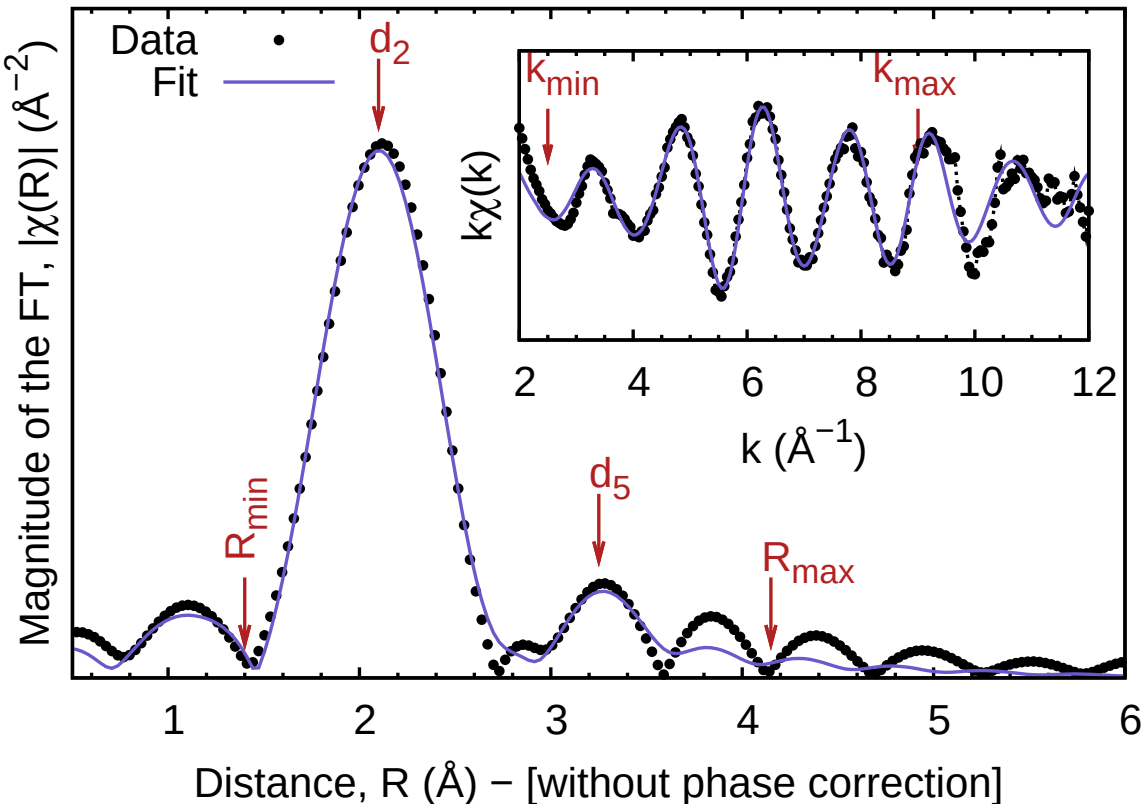
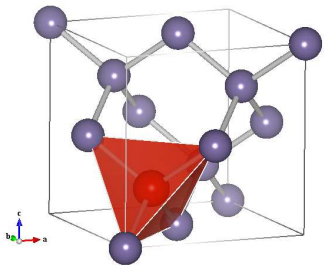


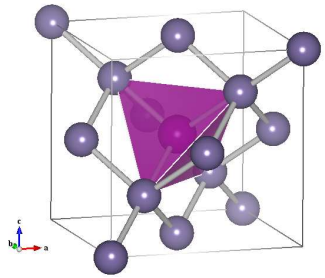
Site	Distance (Å) / Coordination									
	d_1		d_2		d_3		d_5		d_6	
Mn_S	–	–	2.45	4	–	–	–	–	4.00	12
Mn_T	–	–	2.45	4	2.83	6	–	–	–	–
Mn_H	2.35	6	–	–	–	–	3.67	8	–	–

Crystallographic (Ge diamond) distances

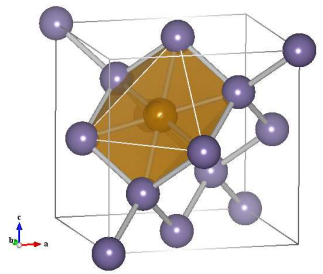
Elementary defects in Ge



Substitutional, Mn_S



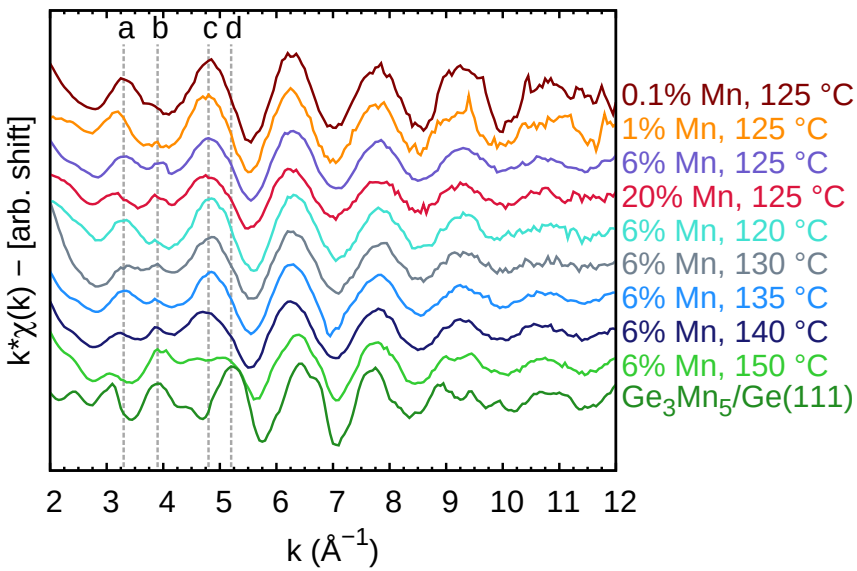
Tetrahedral interstitial, Mn_S

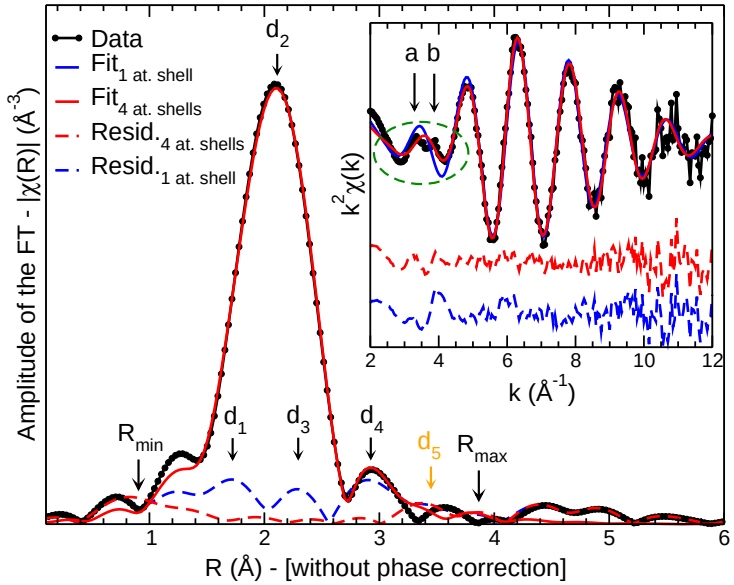


Hexagonal interstitial, Mn_H

GeMn nanocolumns

Temperature and concentration dependence results





Sample	Distance (Å) / Coordination							
	d_2		d_3		d_4		d_5	
T_G = 125 °C:								
GeMn(0.1%)	2.47(1)	4.2(5)^a	–	–	–	–	3.57(2)	1.2(4)^a
GeMn(1%)	2.48(1)	4.0(5)^a	–	–	–	–	3.60(4)	0.8(5)^a
GeMn(6%)	2.49(1)	4.0(5)^a	2.82(4)	0.8(4)^c	3.09(4)	0.8(4)^c	–	–
GeMn(20%)	2.49(1)	4.0(5)^a	2.82(2)	1.6(2)^b	3.10(2)	1.4(3)^b	–	–
Mn 6 %:								
GeMn(120 °C)	2.48(1)	4.2(5)^a	–	–	–	–	3.57(4)	0.7(3)^a
GeMn(130 °C)	2.49(1)	4.0(5)^a	2.86(5)	1.2(4)^c	3.10(5)	1.3(4)^c	–	–
GeMn(135 °C)	2.49(1)	4.0(5)^a	2.80(2)	1.0(2)^c	3.07(2)	1.2(2)^b	–	–
GeMn(140 °C)	2.49(1)	4.0(5)^a	2.80(2)	1.4(2)^c	3.06(2)	1.1(3)^b	–	–
GeMn(150 °C)	2.49(1)	4.0(5)^a	2.81(2)	3.7(7)^b	3.01(2)	2.2(4)^b	–	–
Reference sample on Ge(111):								
Ge$_3$Mn$_5$	2.52(1)	5.0(5)^d	2.70(5)	1.2(4)^a	3.04(5)	8.4(5)^b	–	–

Backscatterer: ^{a} Ge; ^{b} Mn; ^{c} Ge or Mn; ^{d} Ge and Mn.

GeMn nanocolumns

Proposed atomic models

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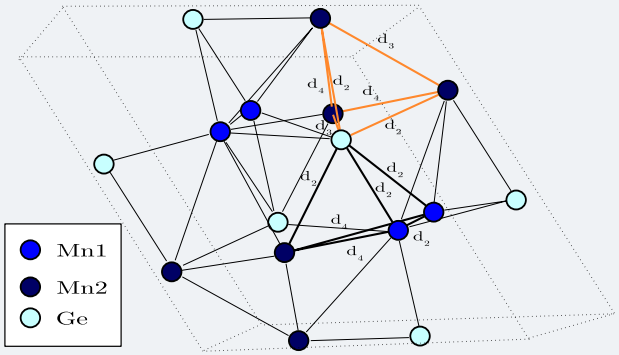
Building block

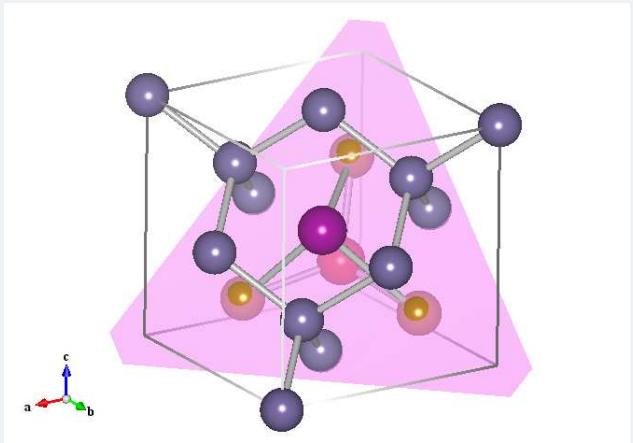


- Only the Ge-3Mn_2 tetrahedron fits with experimental results
- NCs are precursors of Ge_3Mn_5 $\Rightarrow$ increase of d_4 coordination number with temp. and conc.

Linking block

[Ahlers, PhD Thesis (2009)]

- Pure ball-and-stick model (not relaxed!) $\Rightarrow$ links Ge_3Mn_5 to Ge(111) with native defects
- 3 Mn_2 as Mn_H on Ge(111) + 2 Mn_1 $\perp$ as Mn_T and Mn_S
- Compatible with present results



Mn in GaAs

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UNIVERSITY OF NOTRE DAME College of Science DEPARTMENT OF PHYSICS

Growth

$Ga_{0.94}Mn_{0.06}As$

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- Low-temperature Molecular Beam Epitaxy $\Rightarrow$ non-equilibrium growth (increase Mn incorporation into GaAs host)
- Riber 32 R&D chamber, sources: standard effusion cells
- Growth procedure (monitored by RHEED):
  1. GaAs buffer layer on semi-insulating (001) GaAs substrate at 590 °C + cooled to 200–300 °C
  2. LT-GaAs (0–100 nm)
  3. $Ga_{1-x}Mn_xAs$ at 250 °C (x=6%, 133 nm)
  4. LT-GaAs capping layer (0–6 nm)
- Annealing: at ≈285 °C for 70 min in N_2

Curie temperature

From ≈60 K in *as deposited* samples to ≈110 K with annealing $\Rightarrow$ surface migration of $Mn_{interstitial}$ defects and neutralization with oxide

[Kirby *et al.*, Phys. Rev. B 2006]

ReflEXAFS measurements

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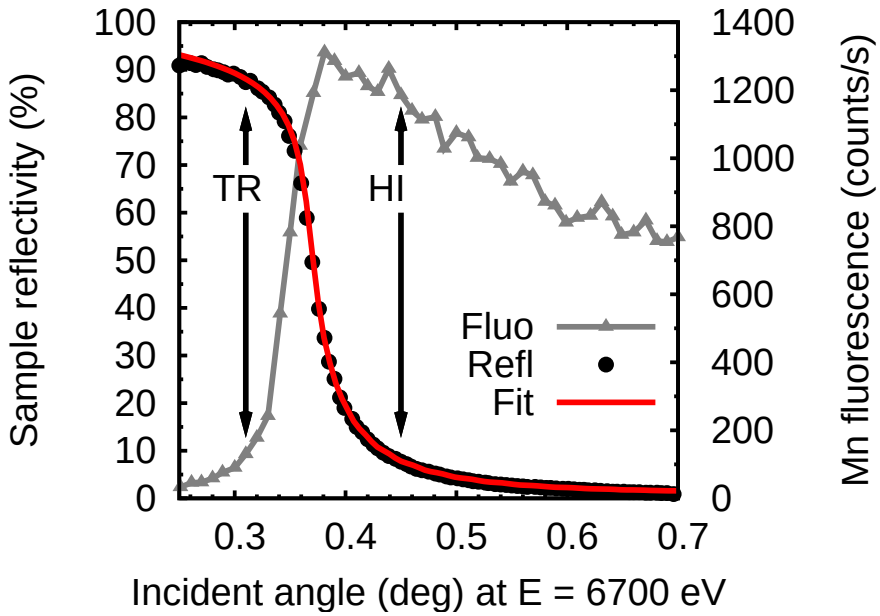
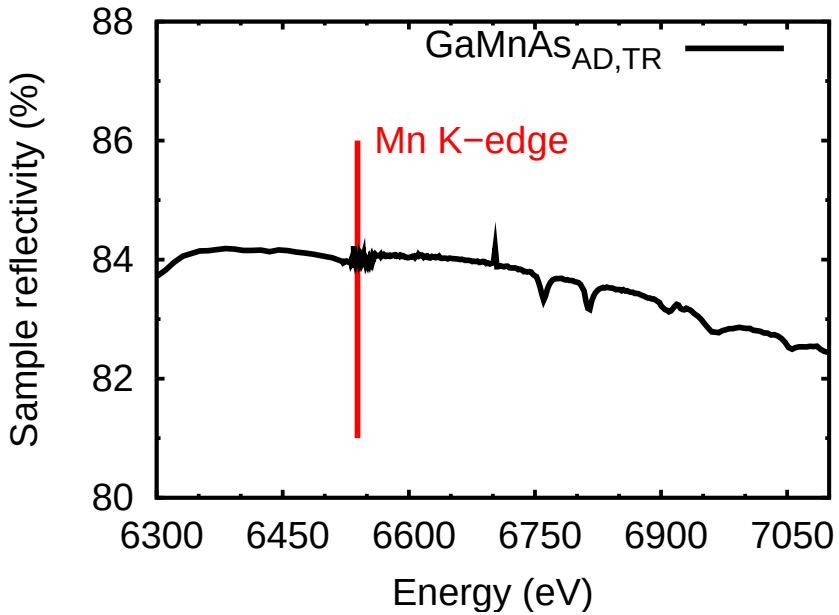
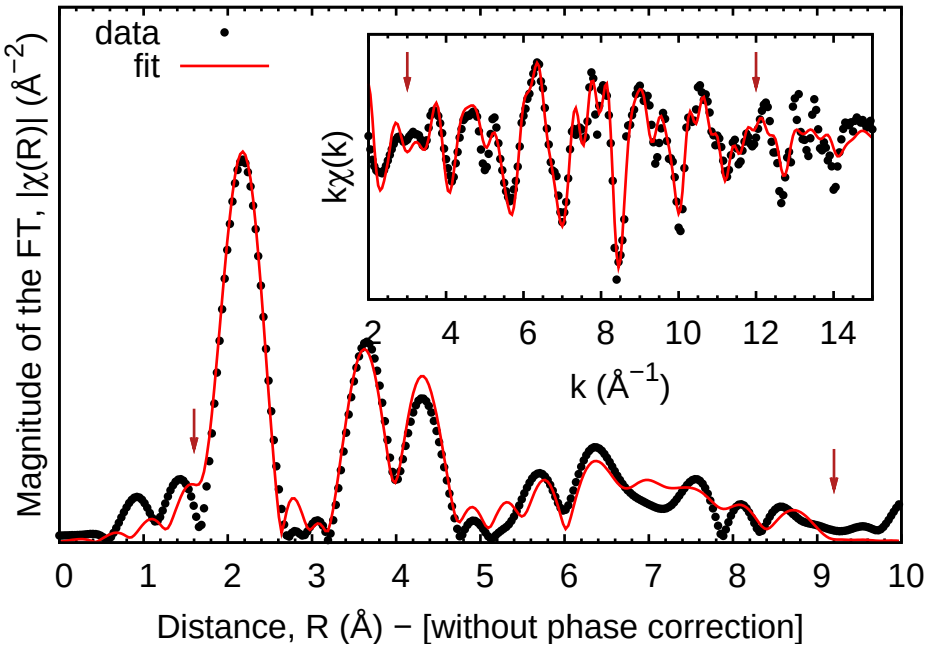
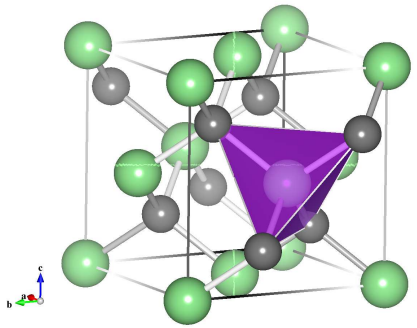




- Mn K-edge fluorescence in grazing-incidence mode
- Working around critical angle $\theta_c \approx 0.35°$
- Total reflection ($0.80\theta_c$): probing the surface (< 10 nm)
- High incidence ($1.2\theta_c$): probing the whole doped layer
- Reflectivity monitored during the energy scan

Mn substitutional (Mn_{Ga})

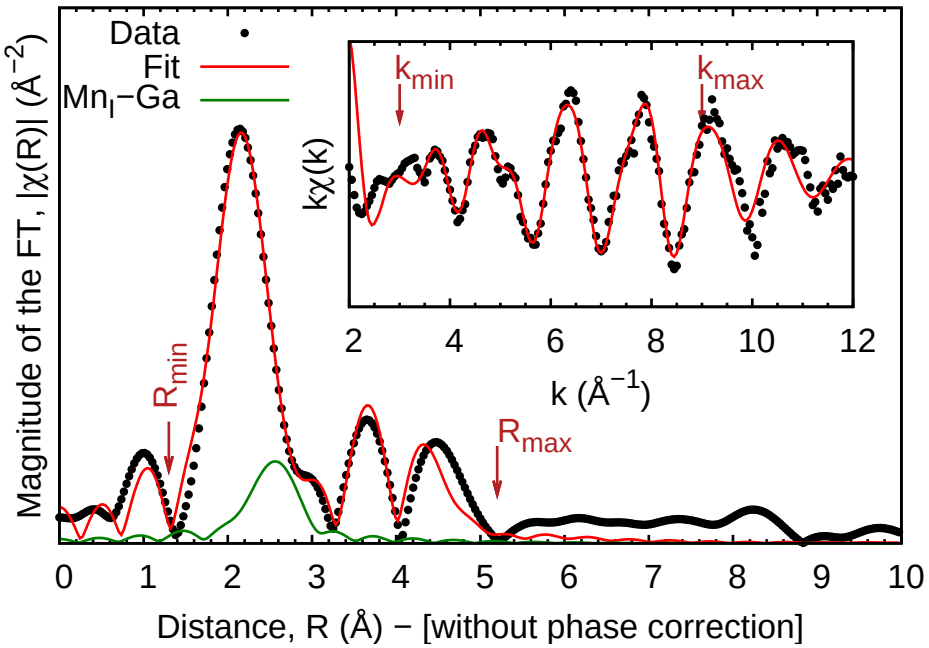


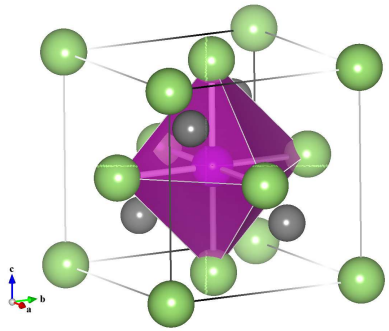


Mn_{Ga}

- First shell expansion: Mn-As @ 2.50(1) Å, typical 2% exp.
- Local structure well fitted up to VI coordination shell
- Model with minimum set of variables and Debye correlated model for σ^2

Mn interstitial (Mn_I) and oxide (MnO)





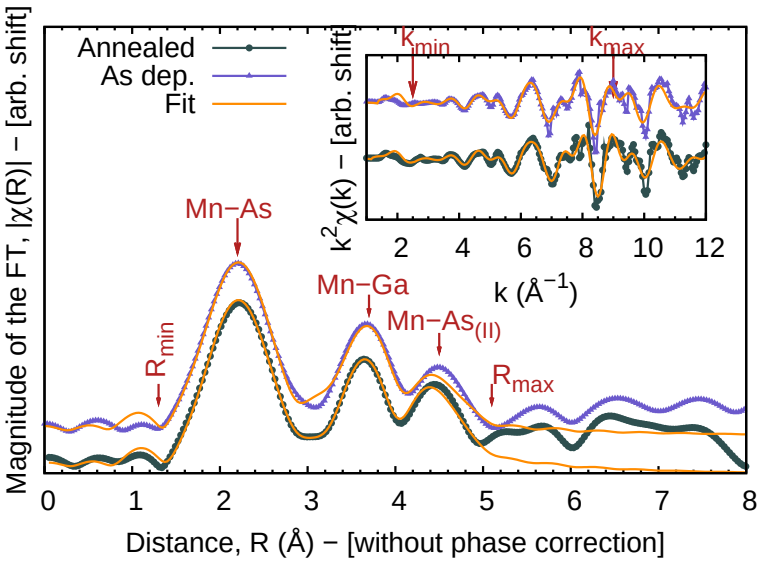
Mn_I

- Model: $\Xi Mn_I + (1-\Xi) Mn_{Ga}$
- Fingerprint: 6 Mn-Ga at 2.827 Å (crystallographic)
- First shell ≈2% exp., ≈1% upper distances
- $10(5)\% < \Xi < 20(5)\%$ in selected samples (χ^2-tested)

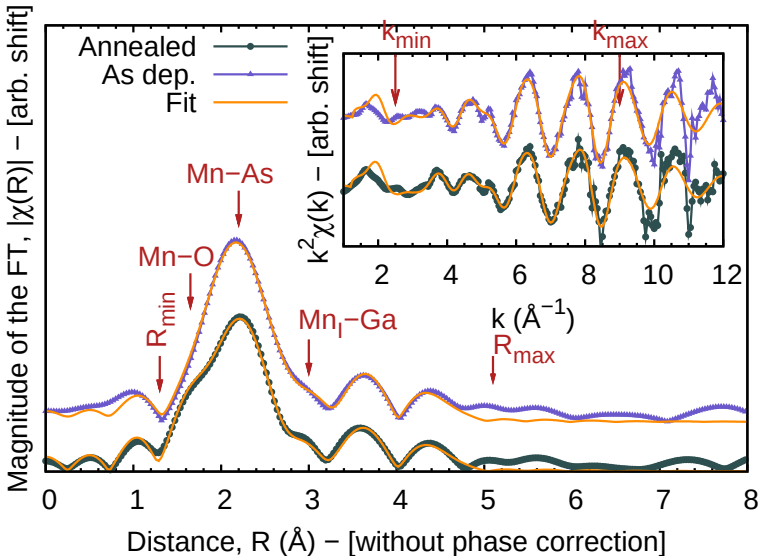
- Oxide contribution by 6 Mn-O at 2.222(1) Å (cryst.)
- MnO detectable only in RefleEXAFS (< 6 nm GaAs CL)

Standard versus grazing-incidence geometry

Standard geometry



ReflEXAFS at HI



- The same parameters for the extraction and the fits
- Only Mn_{Ga} is detected in the first case while in the second also Mn_I and MnO are visible
- The surface study is crucial in understanding Mn_I mobility and interaction with the thin surface oxide layer

Surface systematic study

As function of annealing and GaAs capping layer

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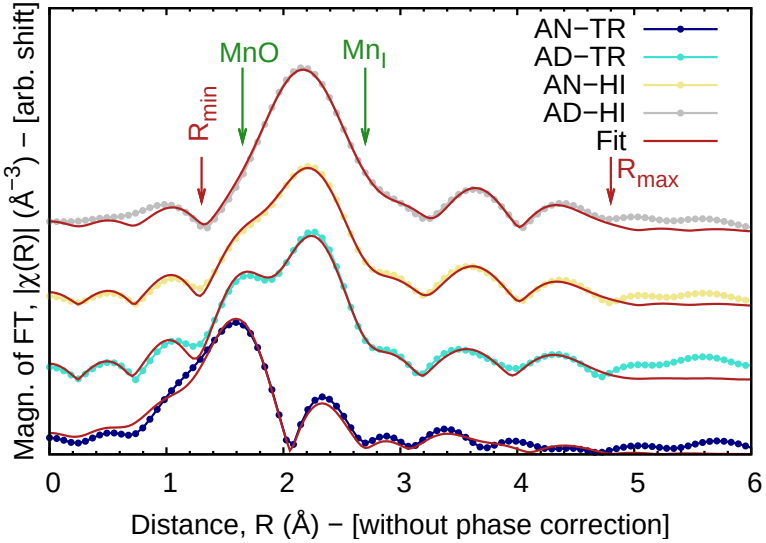
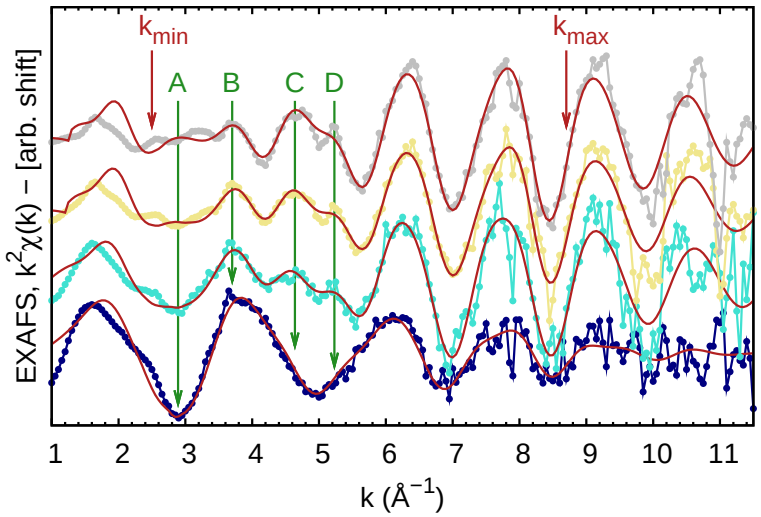
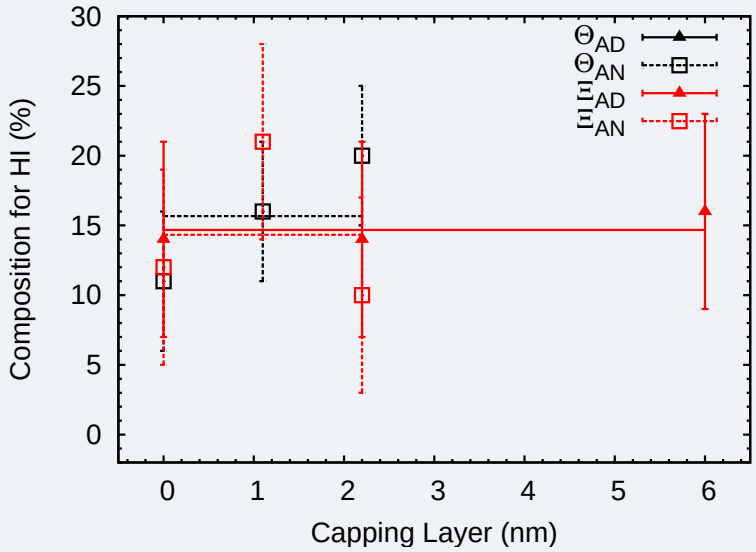
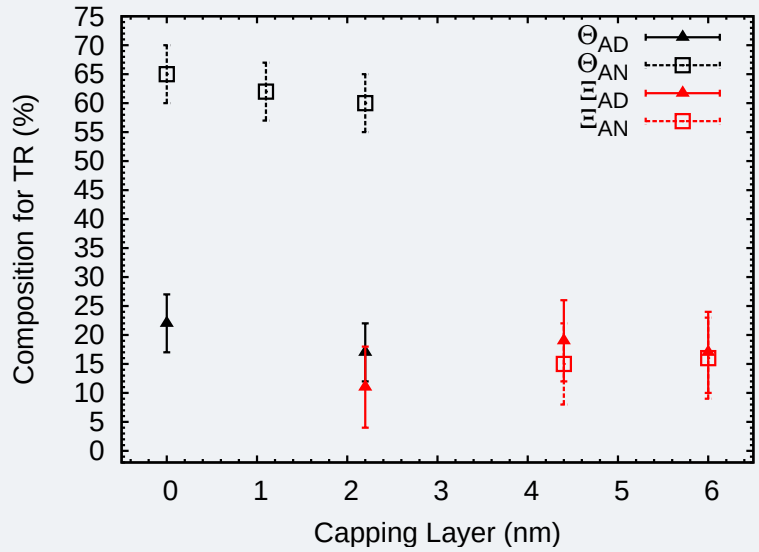




Results





Etch-anneal process

Permits to optmize the ferromagnetic film after growth

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[Olejnik *et al.*, Phys. Rev. B (2008)]

In situ post-growth etch-anneal procedure

1. (E)XAFS
2. Etching
   - 30s in 35% HCl
   - rinsing in water + blow dry by N_2 gas
   - transfer to vacuum chamber
3. (E)XAFS
4. Annealing
   - 20 min at 200 °C on hotplate under N_2 gas flow
   - rapid quench to room temperature under N_2 gas flow
   - tranfer to vacuum chamber
5. (E)XAFS
6. Steps 2–5 repeated

Etching/Annealing
Results

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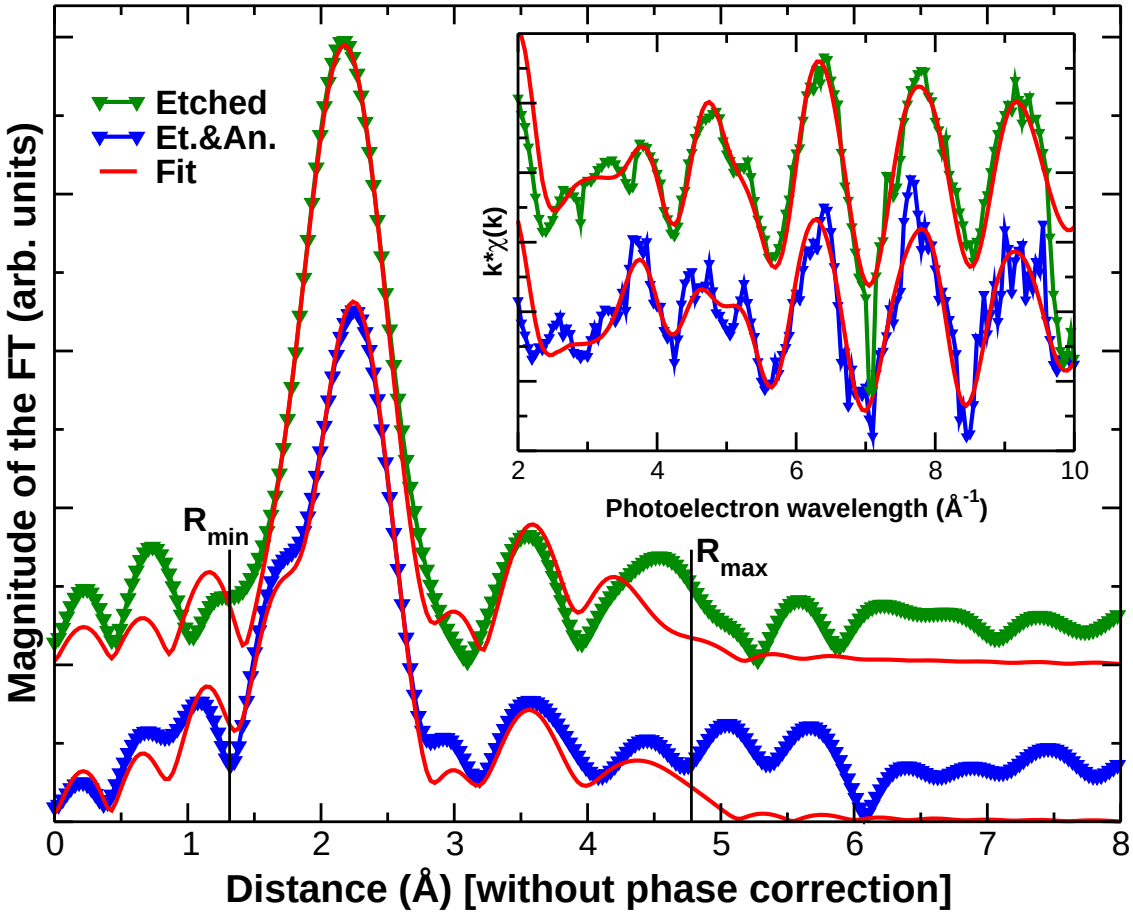

	ϕw	MnO		Mn_I		Mn_{Ga}			
		Θ (%) ±5	R_O (Å) ±0.02	Ξ (%) ±7	R_{Ga} (Å) ±0.06	R_{As} (Å) ±0.01	σ^2_{As} (Å^2) ±0.002	R_{Ga} (Å) ±0.05	σ^2_{Ga} (Å^2) ±0.005
Et.	HI	–	–	–	–	2.50	0.007	4.06	0.017
	TR	12	2.14	19	2.94	2.50	0.007	4.02	0.014
Et.&An.	HI	7	2.14	–	–	2.51	0.006	4.03	0.025
	TR	12	2.15	14	2.82	2.49	0.004	4.04	0.018

Summary
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Models
NCs results
Mn in GaAs
Models
Surface study
Etch-anneal
Conclusions

- Fe incorporation in GaN can be efficiently controlled by Fe flow, growth rate, and co-doping with Si
- EXAFS well identify the substitutional phase (Fe_{Ga}) and the presence of precipitates (ϵ-Fe_3N)
- The aggregation of Fe cations can be minimized by increasing the growth rate and by co-doping with Si, shifting the solubility limit towards higher Fe content at given growth conditions
- Detailed informations about Fe charge state are obtained from XANES: from Fe^{3+} (isoelectronic impurity) to partial reduction Fe^{2+} upon Si addition (Fermi level engineering)
- Co-doping with Mg do not introduce charge shift but promotes precipitation (difficult to distinguish by XAFS)
- Exploiting the complementarity of XAFS with XRD and TEM permits a fine structural characterization of this system at the nano-scale

Summary
Mn in Ge

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M. Rovezzi
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- The high local disorder reduces the information content in the EXAFS spectra (like Mn in Si [A. Wolska *et al.*, Phys. Rev. B 2007])
- Mn-rich NCs present a complex local structure that cannot be described only with a substitutional model
- Additional interatomic distances have to be considered in the EXAFS analysis which are in good qualitative and quantitative agreement with the structure of one of the Ge-3Mn building block tetrahedron found in Ge_3Mn_5 crystal
- Samples grown at low temperature or low Mn content present additional hexagonal interstitial-like defects ($\approx$10 %)

Summary
Mn in GaAs

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- LT-MBE permits the fabrication of a good DMS system with Mn main incorporation as Mn_{Ga} in a crystalline environment
- Enrichment of Mn_I at the surface: detected in grazing-incidence and not in standard geometry $\Rightarrow$ GIXAFS/ReflEXAFS is powerful local probe to study surface phenomena
- The effects of post-growth annealing on Mn_I surface migration are investigated but it is not possible to link the observed efficacy of this method to the interaction with the surface oxide
- The presence of the oxide phase reduces the sensitivity to Mn_I, even with the use of a GaAs capping layer of different thickness
- The etch-annealing process is fruitful in removing Mn_I $\Rightarrow$ first direct evidence of the neutralization process induced by this method

General conclusions

- The present work has permitted to find out the potentialities and limits of XAFS spectroscopy in the study of semiconductor spintronics
- A wide spectrum of the most promising materials in this field has been examinated (keeping apart semiconductor oxides while Mn-doped II-VI class investigated in the early times)
- Experimental work: implementation of a new sample holder for measurements in grazing-incidence geometry and a new data analysis method for ReflEXAFS measurements
- XAFS combined with complementary advanced characterization tools helps in the fine tuning of the deposition parameters and post-growth treatments

Outlook

- Fermi level engineering to increase the solubility limit (demostrated here for GaFeN) on GaMnAs [Cho *et al.*, Appl. Phys. Lett. (2008)] and GeMn [Chen *et al.*, Phys. Rev. B (2009)] via *n*-type counter-doping
- Fine tune the temperature parameter and adopt Fe doping in δ-fashion to obtain Fe-rich nanocolumns in GaN
- High-level doping with shallow acceptors to reach the metal-insulator transition and have high-T_C ferromagnetism (moving from weak to strong coupling regime) [Dietl, Phys. Rev. B (2008)]

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Direct collaborators

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Fe:GaN Alberta Bonanni[2], Andrea Navarro-Quezada[2], Tian Li[2], Bogdan Faina[2], Tomasz Dietl[3], Piotr Bogusławski[3], Paweł Jakubas[3], Aldo Amore Bonapasta[4] and Francesco Filippone[4]

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Thank you for your attention!

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- *Consiglio Nazionale delle Ricerche* (financial support)
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- ESRF (synchrotron radiation and stimulating research infrastructure)

Bibliographic databases

My personal collection (≈600 refs.):

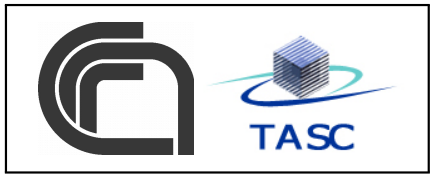
http://www.mendeley.com/profiles/mauro-rovezzi

Ferromagnetic Semiconductor Spintronics Web Project:

http://unix12.fzu.cz/ms/

Mn in III-V nanowires

In collaboration with

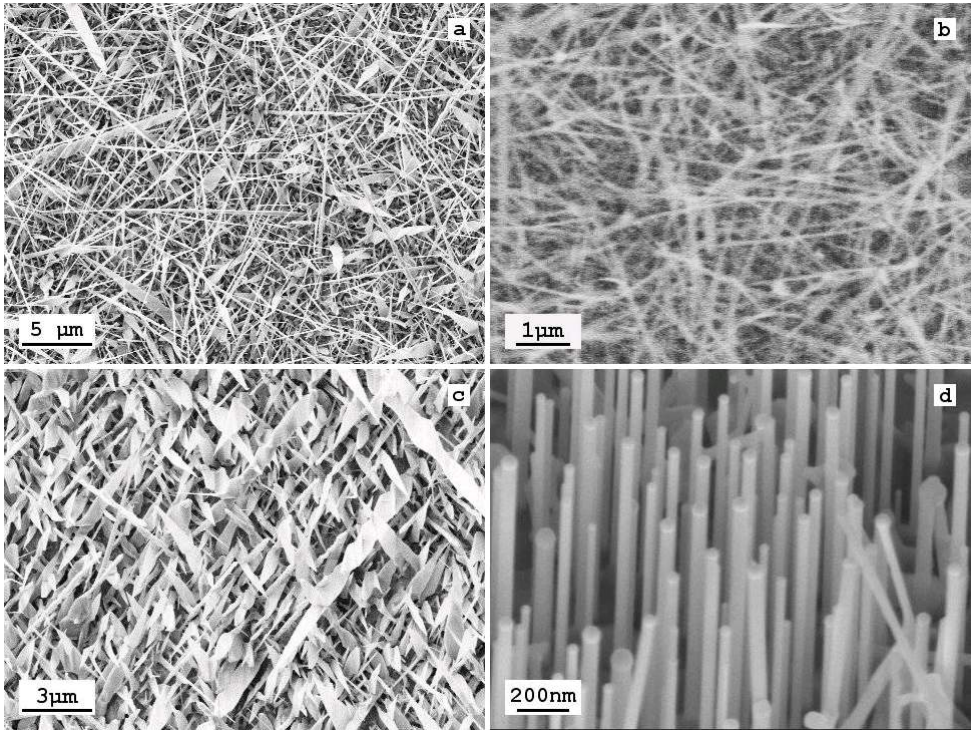


Growth of GaAs and InAs NWs

F. Martelli *et al.*, Nano Lett. (2006)

- Solid-state molecular beam epitaxy (VLS growth)
- Catalyzed by Mn (5 ML, 1 nm) and Au (10 ML, 2 nm) [+doped with Mn]
- Growth temperature: 535 °C – 620 °C
- Different substrates: GaAs and SiO_2

Electron microscopy



SEM images: (a) Mn-cat GaAs on SiO_2; (b) Mn-cat InAs on SiO_2; (c) Mn-cat GaAs on GaAs; (d) Au-cat GaAs on GaAs(111)

EXAFS measurements

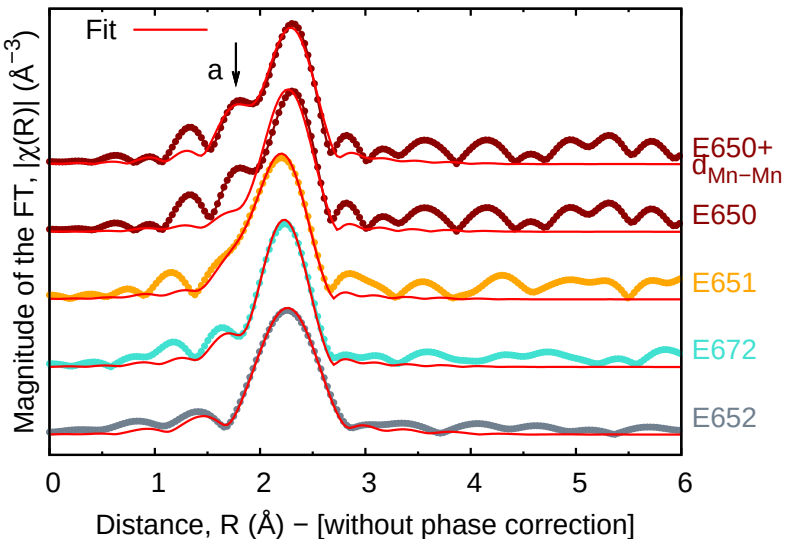
- Mn K-edge in fluorescence mode @ GILDA [standard geometry, low temp.: 10 K]
- All samples etched *in-situ* and transferred to vacuum chamber to avoid oxide formation
- Systematic study varying deposition parameters

Characterized samples

Sample	Wire	Cat.	Temp. (°C)	Time (min)
E650	GaAs	Mn	540	30
E651	GaAs	Mn	580	30
E672	GaAs	Mn	610	30
E652	GaAs	Mn	620	30
E656	GaAs	Au	540	30
E697	GaAs	Au	580	30
E683	InAs	Mn	390	60

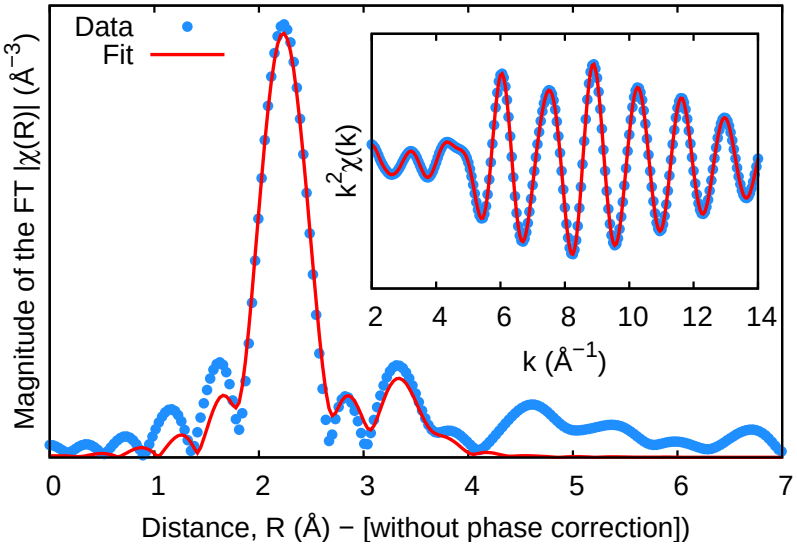
Mn-catalyzed

GaAs NWs



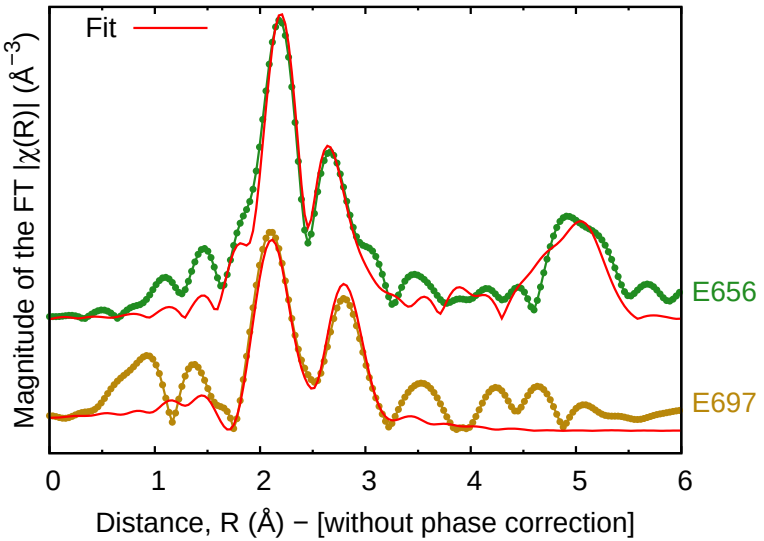
- High local disorder
- Mn_{Ga} but Mn-As at 2.58 Å ⇒ MnAs clusters
- Mn-Mn at 2.15 Å (no Mn-O!)

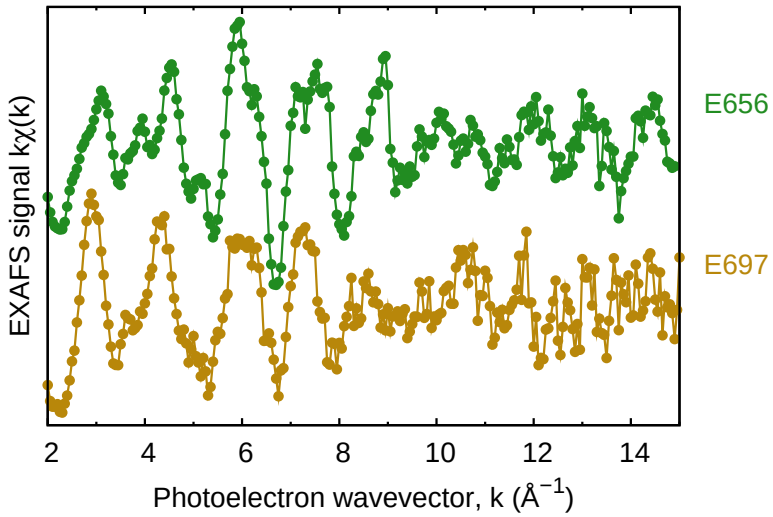
InAs NWs



- Low local disorder
- No Mn substitutional in wz-InAs
- Mn in hexagonal MnAs Mn-Mn at 2.85 Å and 3.72 Å

Au-catalyzed + Mn-doped





- Mn_{Ga} with Mn-As at 2.58 Å
- + cubic MnAu [Mn-Au at 2.79 Å]
- Fingerprint: Mn-Au-Mn collinear scattering path

Summary

Mn in InAs and GaAs NWs

- Mn-As bond distance of 2.56–2.58 Å, longer than the expected value for a substitutional site and probably due to the occupation of defect sites $\Rightarrow$ seeds for the formation of hexagonal MnAs precipitates
- Hexagonal MnAs clearly forms in Mn-cat. InAs NWs (well ordered local structure)
- Mn-Mn dimers at 2.15 Å found in Mn-cat. GaAs NWs (also reported by other groups: Mn-doped InAs at 2.19 Å, Mn-doped Ge at 2.04 Å)
- Mn in Au-catalyzed NWs forms an intermetallic alloy with Au resulting in a well ordered cubic MnAu