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Crystallite Phase and Orientation Determinations of (Mn, Ga) As/GaAs-crystallites using Analyzed (Precession) Electron Diffraction Patterns

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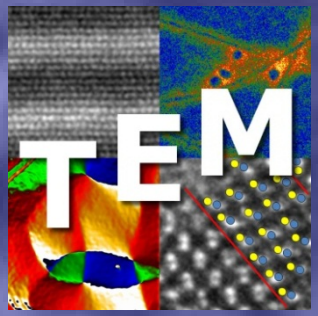
Crystallite phase and orientation determinations of (Mn,Ga)As/GaAs-crystallites using analyzed (precession) electron diffraction patterns



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Outline

1. Material system: (Mn,Ga)As/GaAs-crystallites
2. Structure analysis using

   Nano-beam Diffraction (NBD)

   Precession Electron Diffraction Technique (PED)

   → Structure type I + II
3. Phase and orientation mapping using ASTAR
4. Conclusion

Material system: MnAs/GaAs

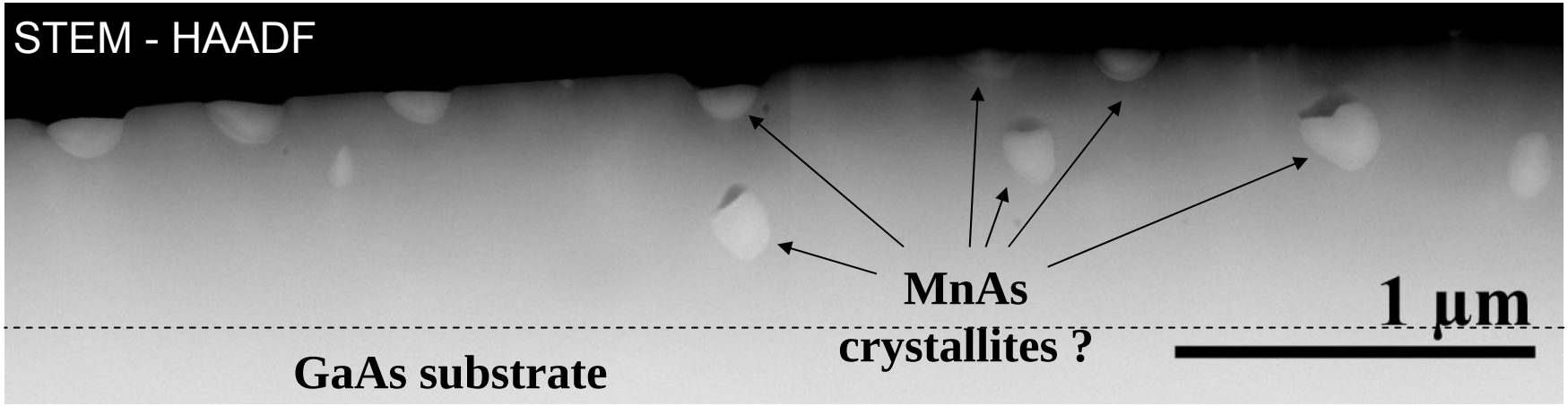
Motivation

- α-MnAs: **ferromagnetic** properties (Curie temperature above room temp.)
- combination of α-MnAs and paramagnetic semiconductor materials (e.g. GaAs) for **spintronic devices**

→ fast **information transport** basing on the intrinsic electron spin

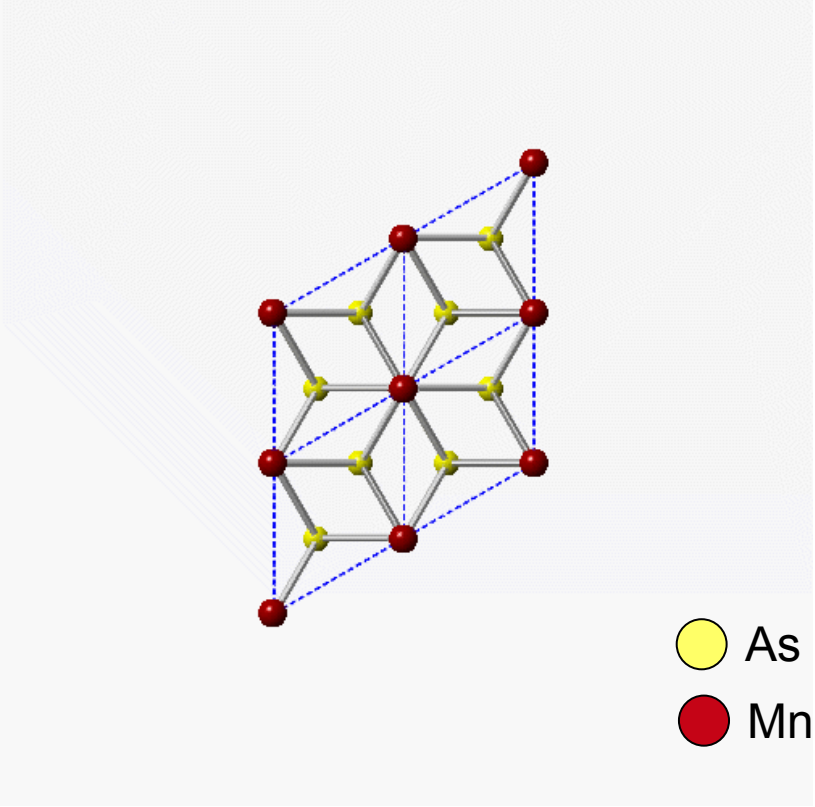
Growth process

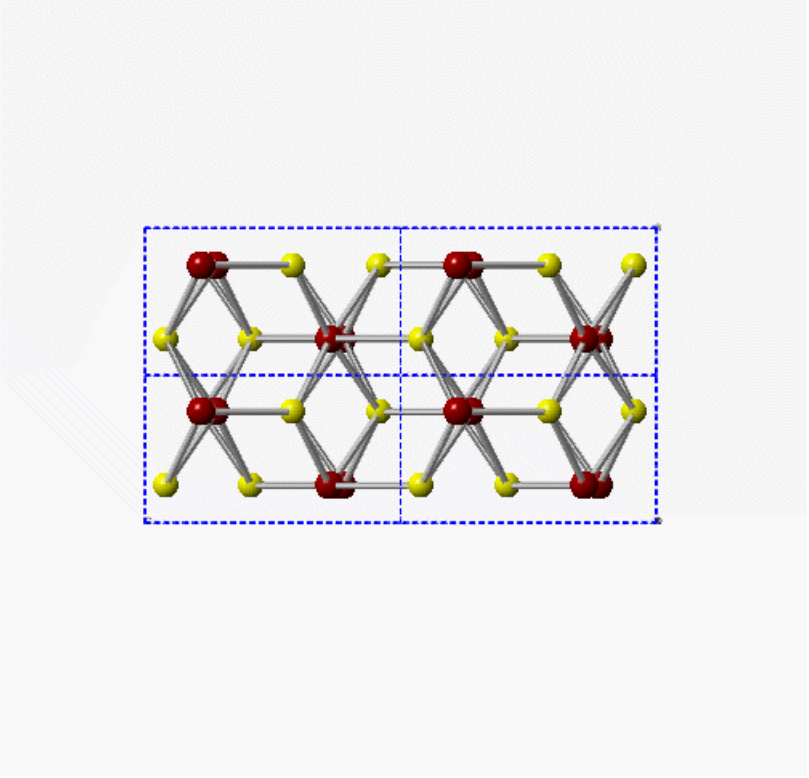
- Metal-organic chemical vapor deposition (**MOCVD**)
- [001]-oriented GaAs substrate
- Deposition of Ga, Mn and As at **870K**
- Formation of **crystallites during cooling** process



Phases of MnAs

α–MnAs		β–MnAs
hexagonal ferromagnetic	313 K ⟷	orthorhombic paramagnetic
Space group: $P6_3/mmc$		Space group: Pnma





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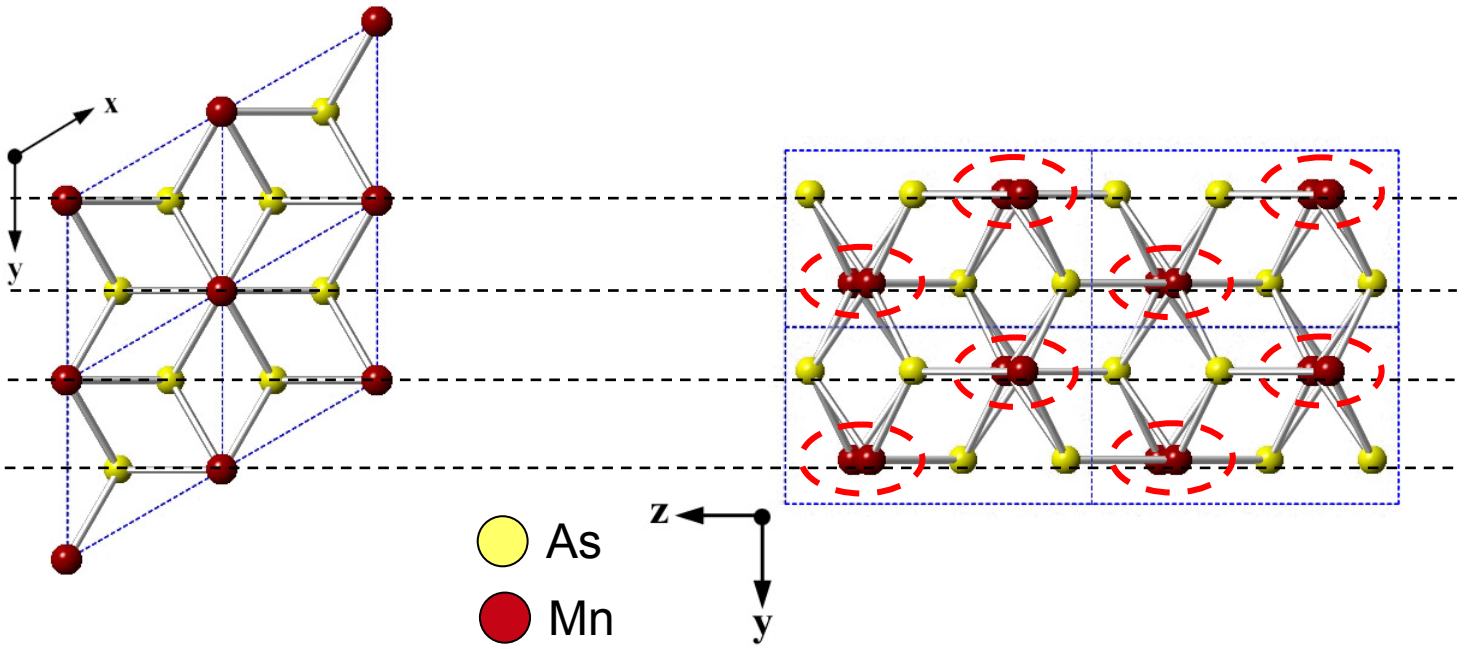
[00.1] **[100]**



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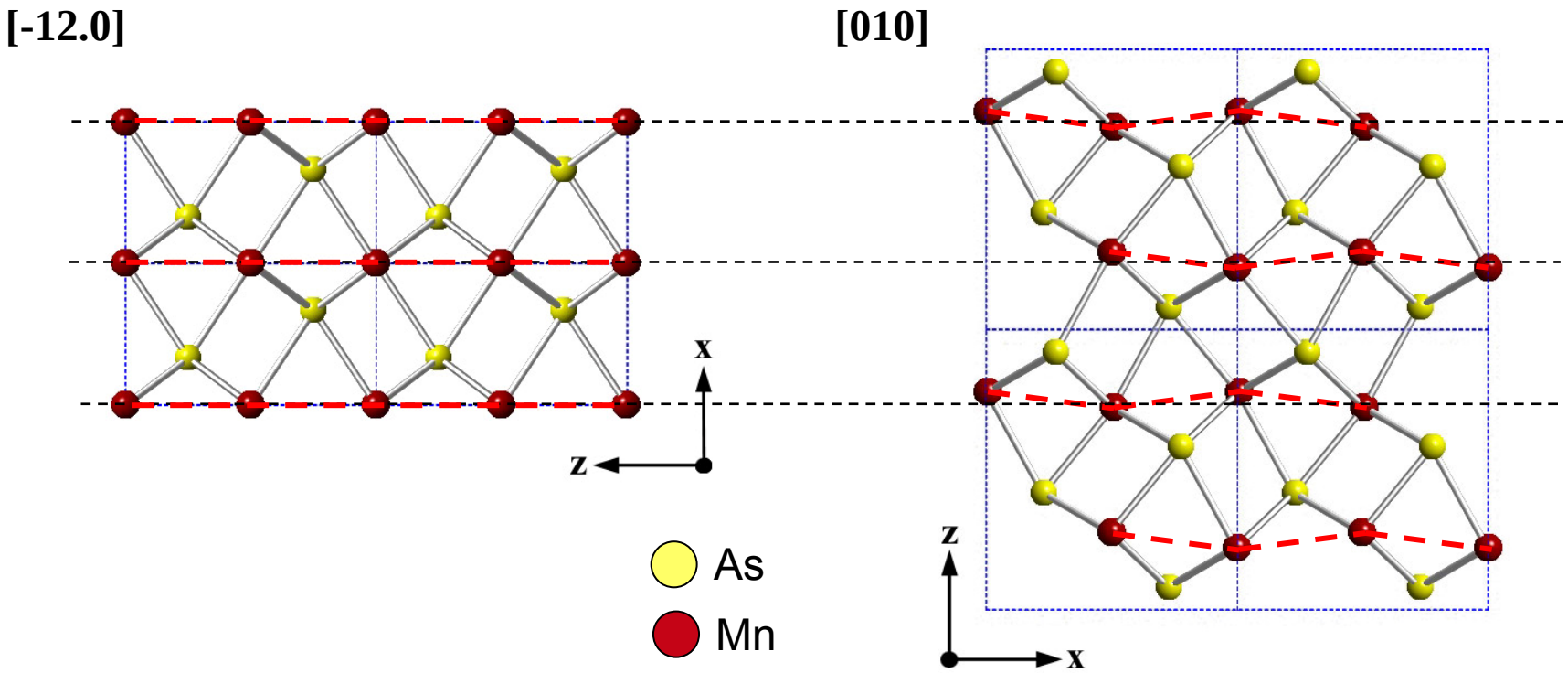
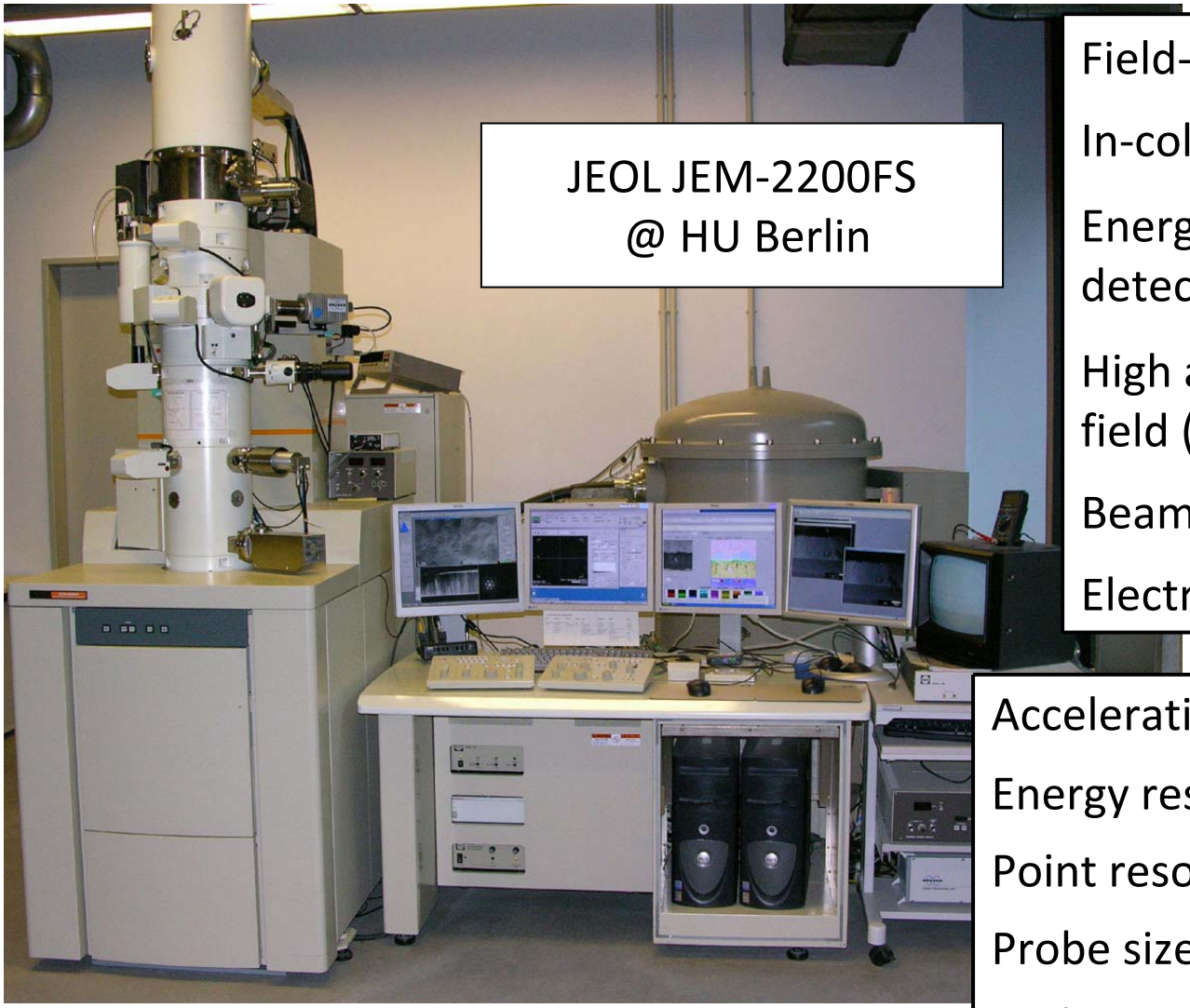


Instrumentation



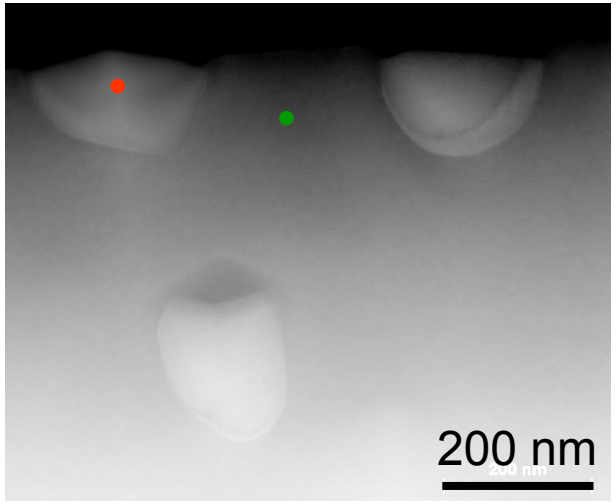
JEOL JEM-2200FS
@ HU Berlin

- Field-emission gun
- In-column energy filter
- Energy dispersive X-ray detector (EDXS)
- High angle annular dark-field (HAADF) detector
- Beam precession unit
- Electron biprism

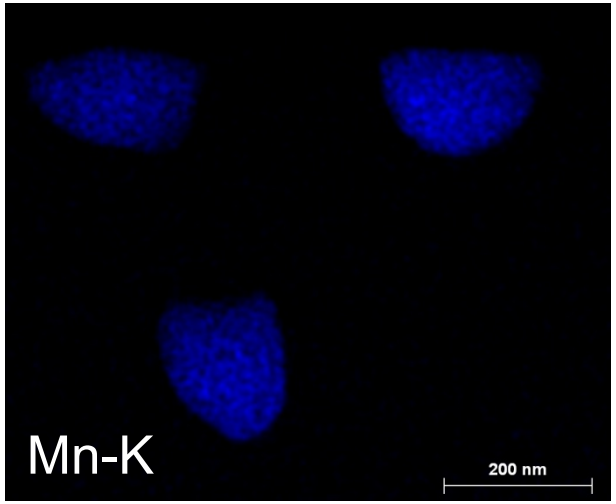
Accelerating voltage:	**200 kV**
Energy resolution:	**0.7 eV**
Point resolution:	**0.19 nm**
Probe size STEM:	**0.14 nm**
Probe size NBD:	**0.5 nm**

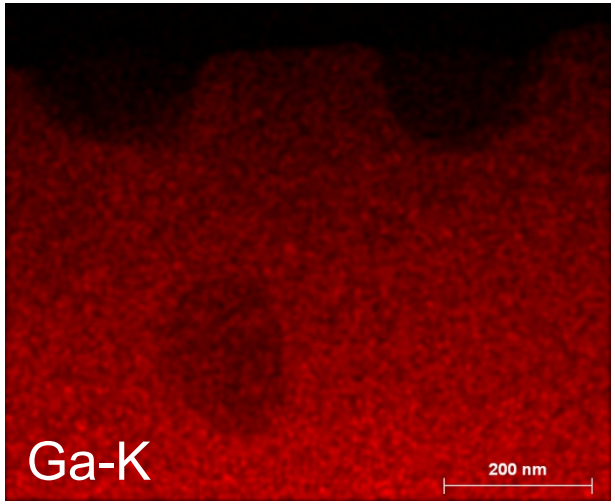
Energy dispersive X-ray spectroscopy

HAADF STEM

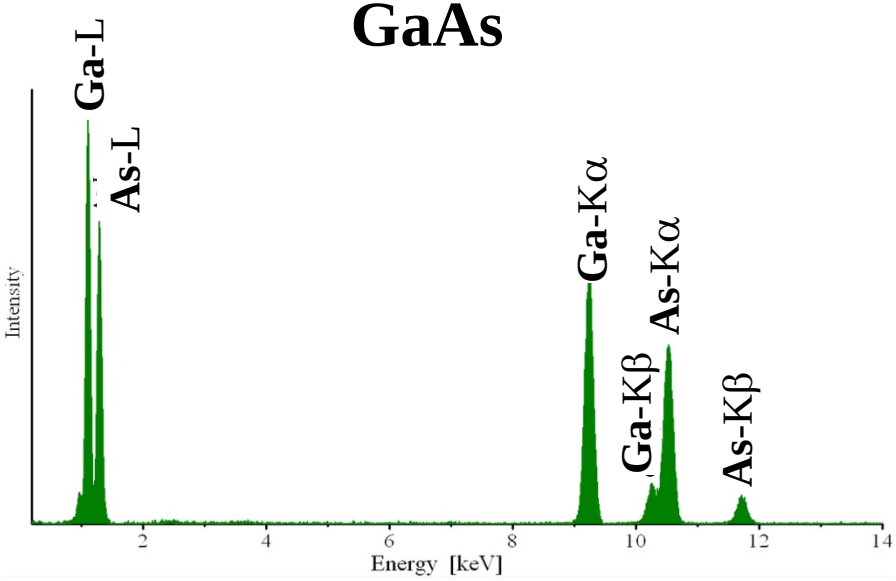


Elemental mapping

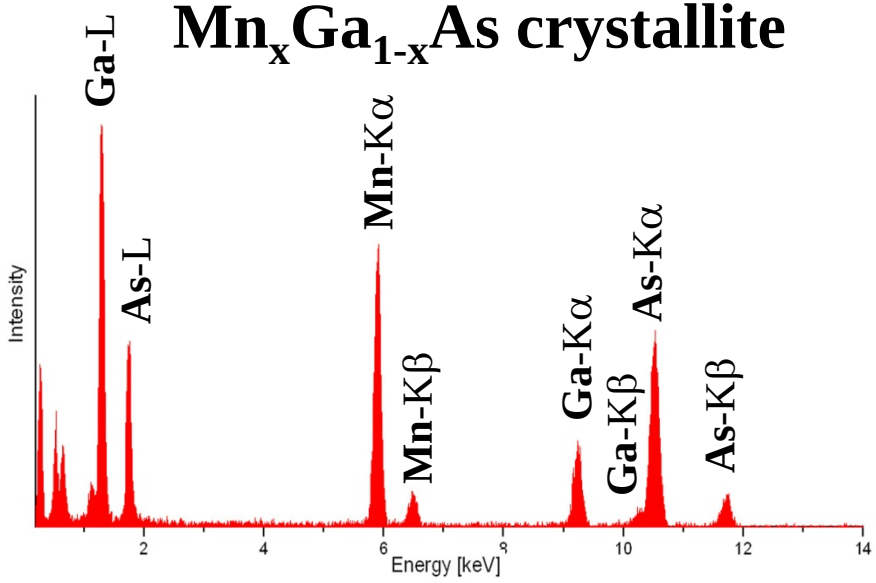




GaAs



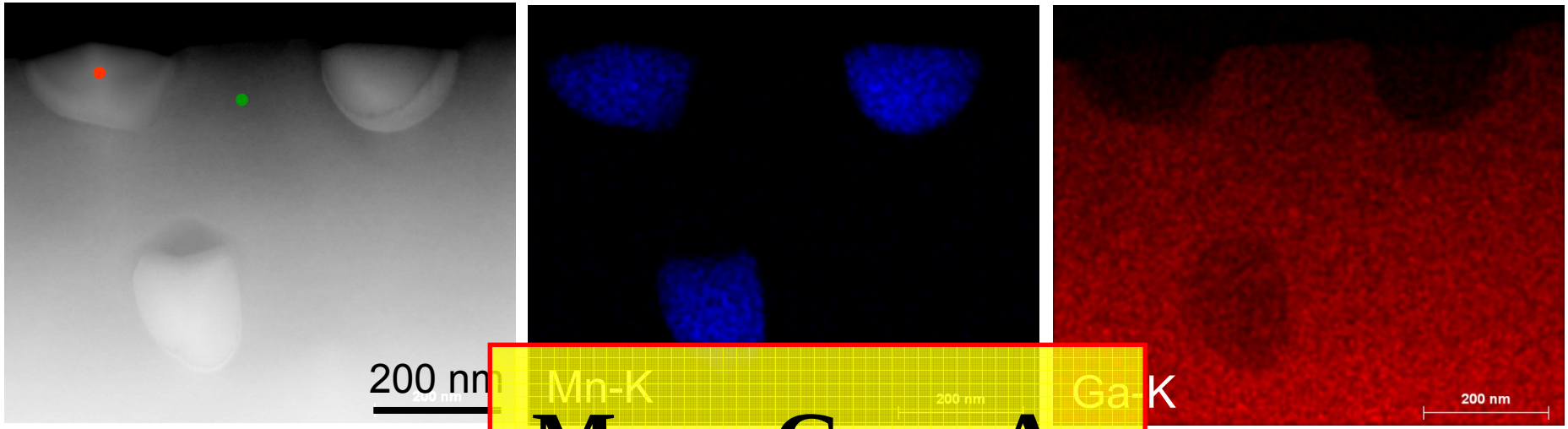
$Mn_xGa_{1-x}As$ crystallite



Energy dispersive X-ray spectroscopy

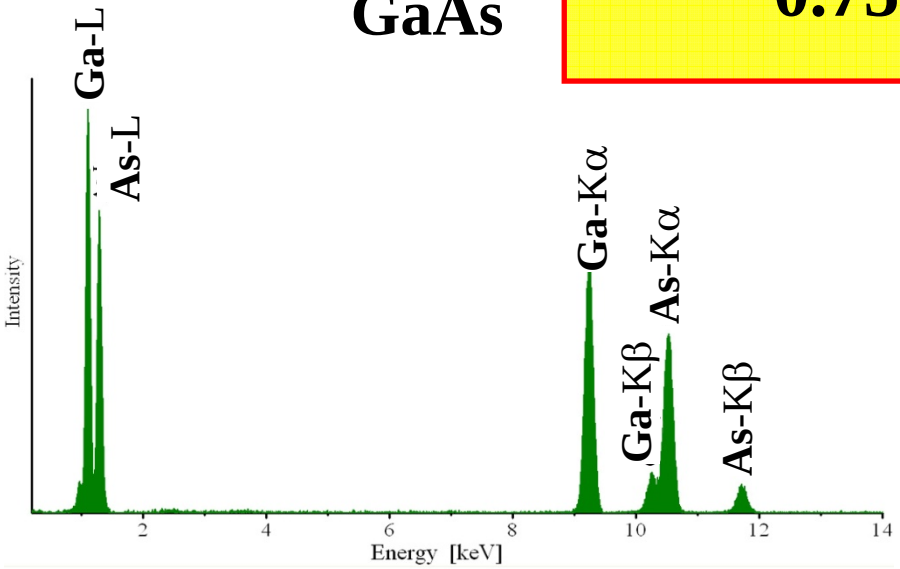
HAADF STEM

Elemental mapping

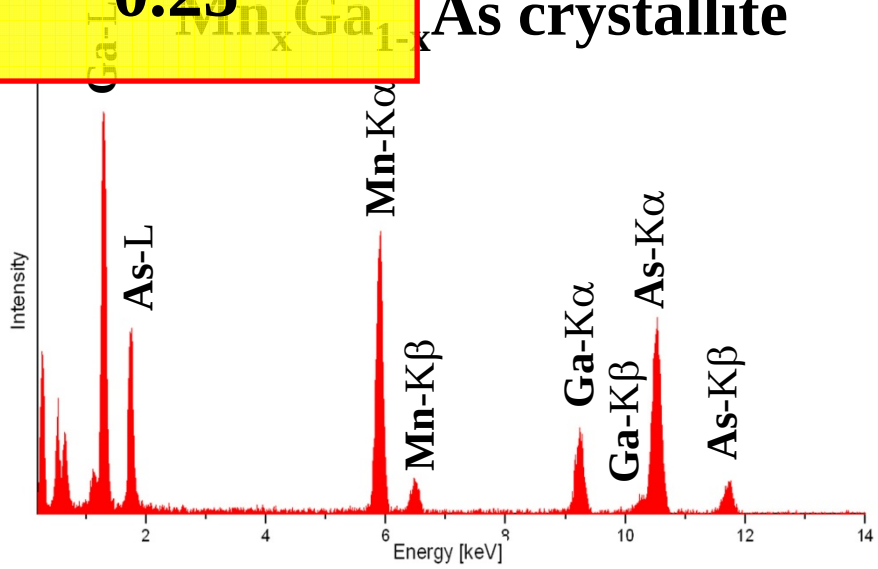


$Mn_{0.75}Ga_{0.25}As$

GaAs



$Mn_xGa_{1-x}As$ crystallite



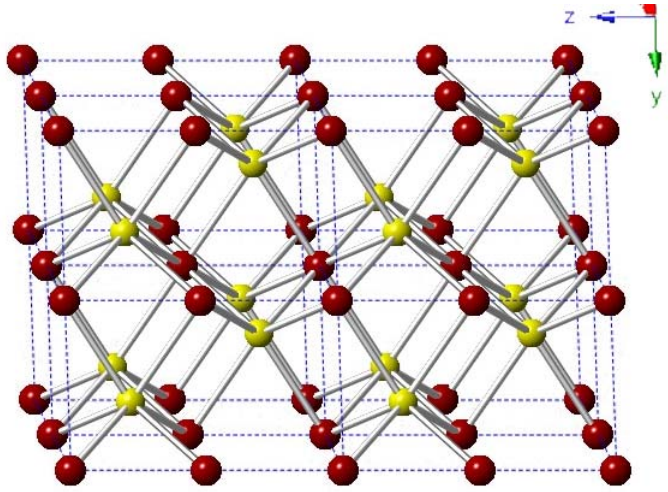
$Mn_{0.75}Ga_{0.25}As$ Structure Type I

Assumption: Statistically distribution of Manganese atoms (75%) and Gallium atoms (25%) at cation positions

α–$Mn_{0.75}Ga_{0.25}As$

hexagonal
Space group: $P6_3/mmc$

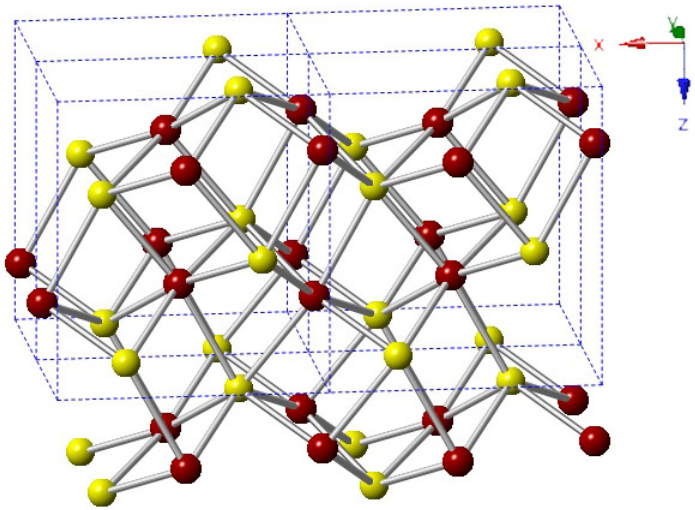
Short: **α–$Mn_{0.75}Ga_{0.25}As$ (hex)**

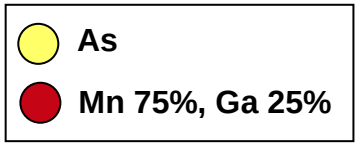


β–$Mn_{0.75}Ga_{0.25}As$

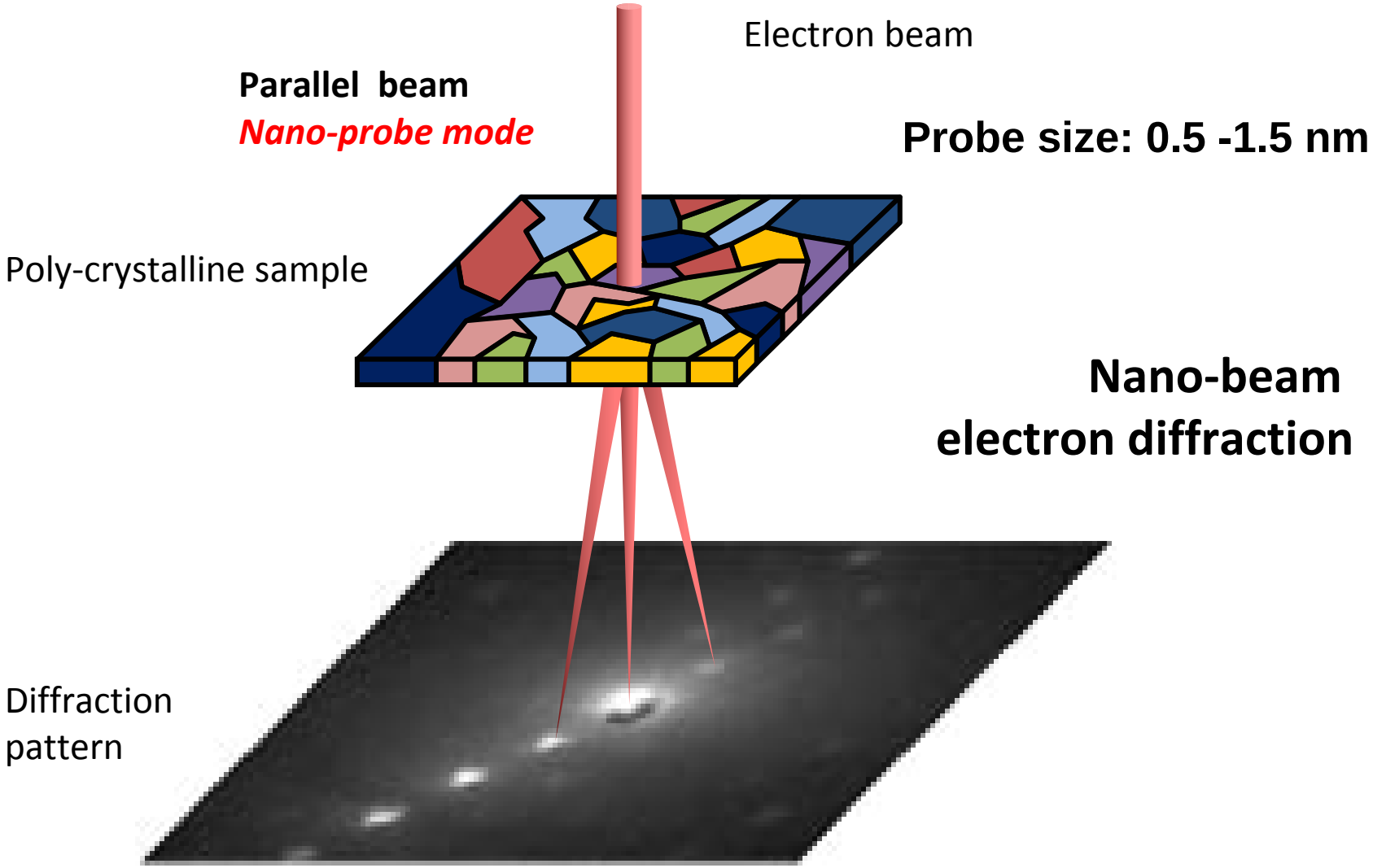
orthorhombic
Space group: Pnma

Short: **β–$Mn_{0.75}Ga_{0.25}As$ (orth)**

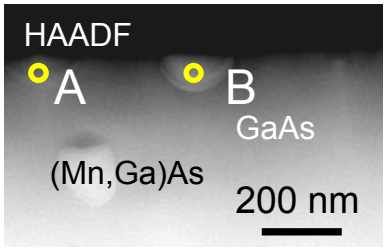




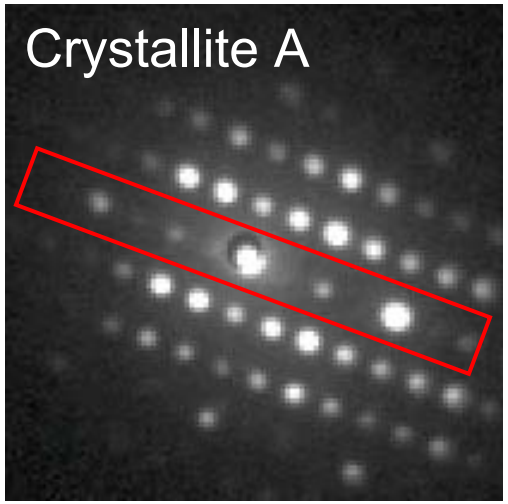
Nano-beam electron diffraction (NBD)

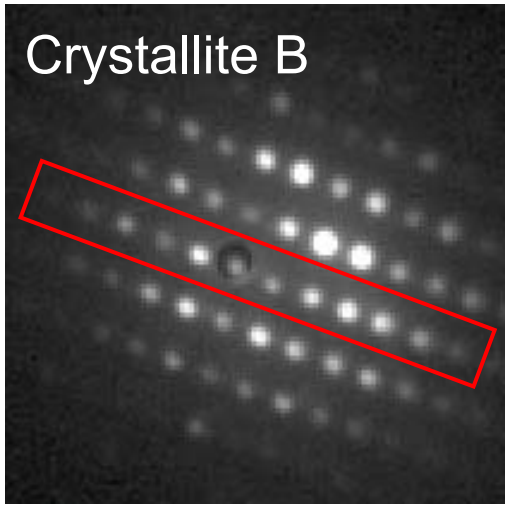


Structure analysis of $Mn_{0.75}Ga_{0.25}As$
Nano-beam electron diffraction

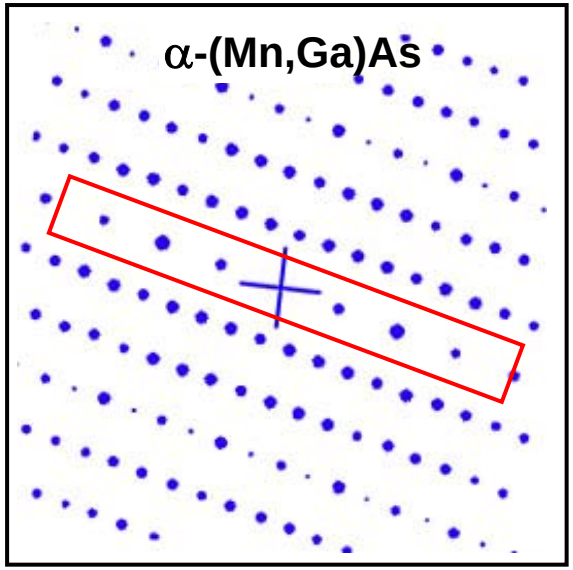


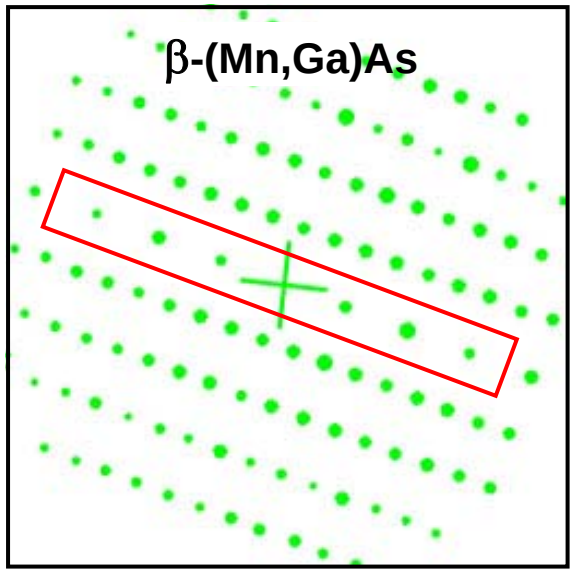
Nano-beam mode
Spot size: 1.0 nm





Templates





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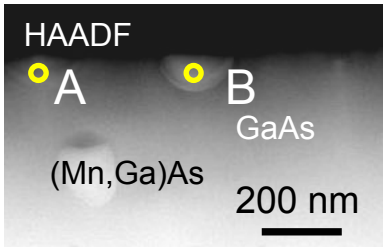

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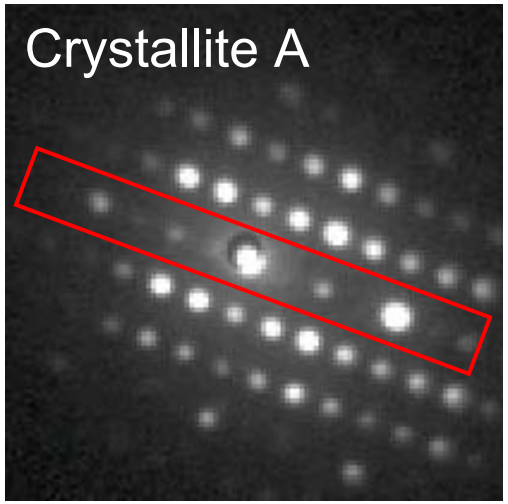

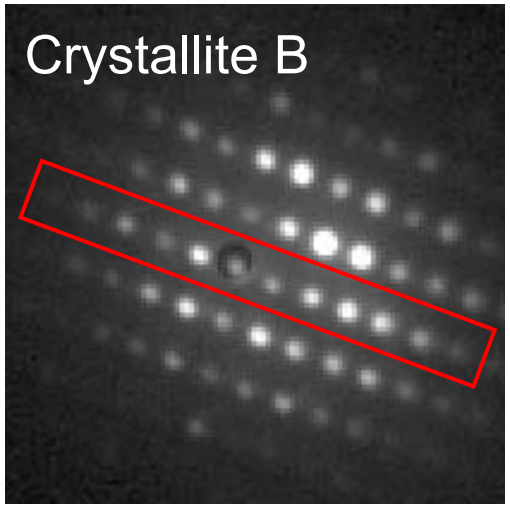

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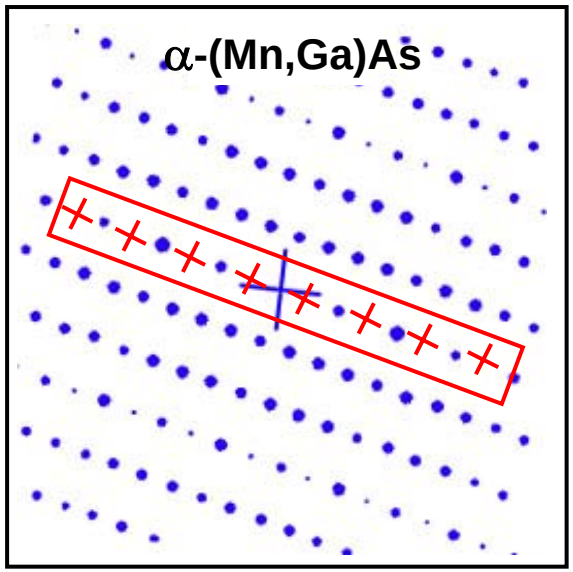
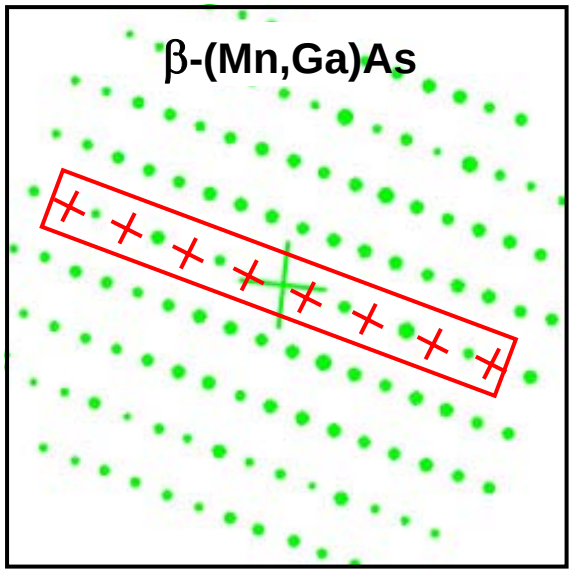




Reflection conditions (kinematic)

Hexagonal

$P6_3/mmc$

No. 194

$P\ 6_3/m\ 2/m\ 2/c$

Reflection conditions*

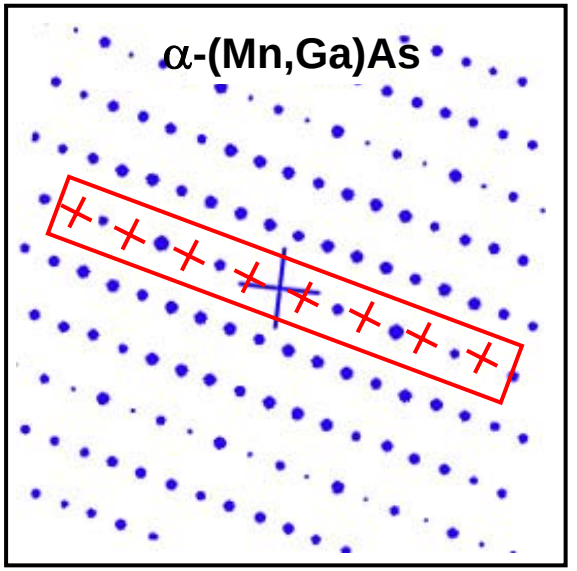
General:

$hh\bar{2}hl:\ l = 2n$

$000l\ :\ l = 2n$

✗

0001
0003
...
000(2n-1)



Orthorhombic

$Pnma$

No. 62

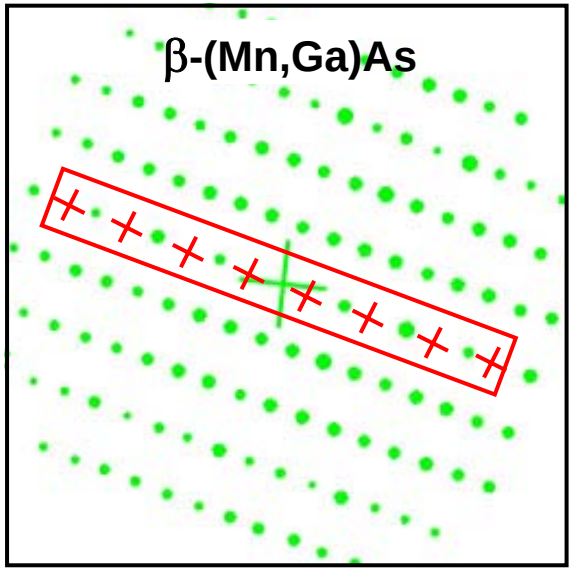
$P\ 2_1/n\ 2_1/m\ 2_1/a$

General:

$0kl\ :\ k+l = 2n$
$hk0:\ h = 2n$
$h00:\ h = 2n$
$0k0:\ k = 2n$
$00l\ :\ l = 2n$

✗

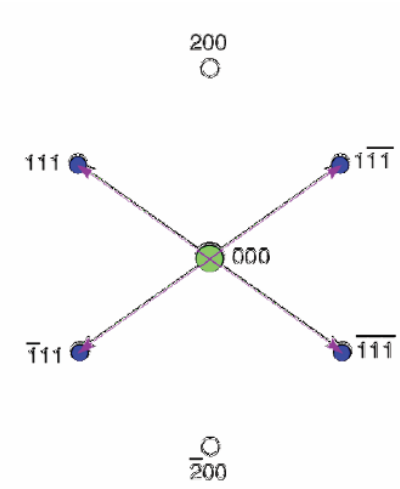
100
300
...
(2n-1)00



* International Tables for Crystallography: Volume A – space group symmetry; ed. Th. Hahn

Kinematic versus Dynamic ED

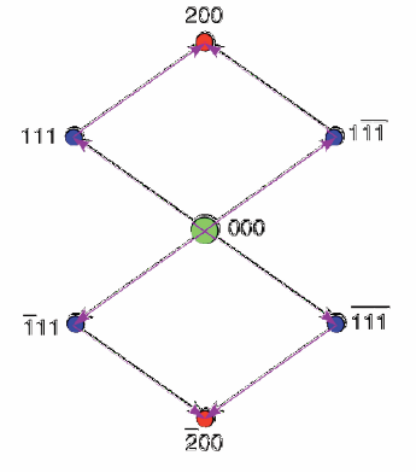
Kinematic Electron Diffraction:



- Only single scattering processes take place
- No double diffraction
- Each individual diffraction event acts independently of the others
- Two-beam condition (just the undiffracted beam and one diffracted beam are only excited)

→ Very thin crystals

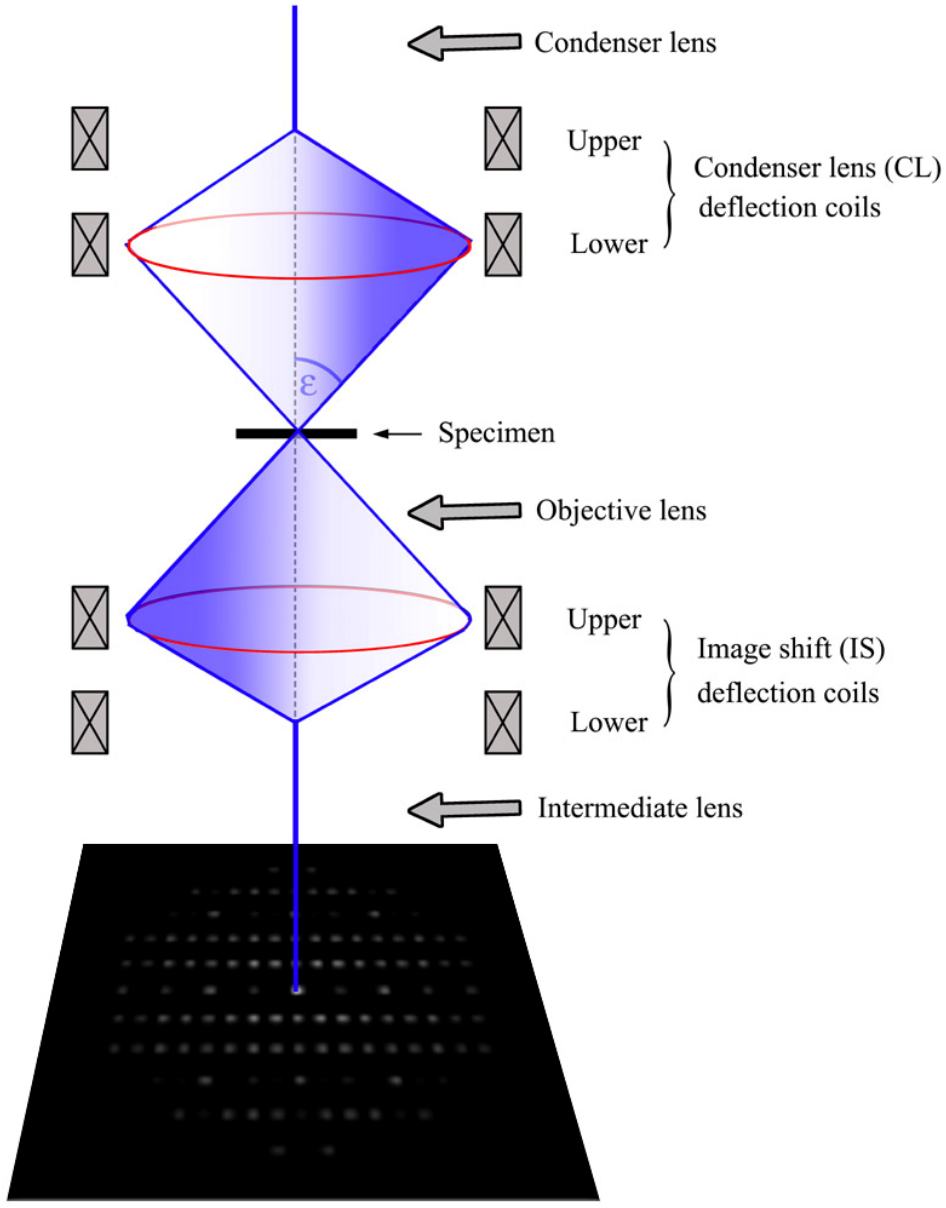
Dynamic Electron Diffraction:



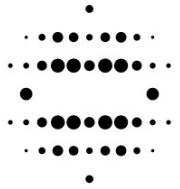
- Interaction of waves
- Multiple scattering effects
- Double diffraction possible (strong reflections behave like new primary beams)
- Dynamical effects increase with the number of excited reflections

→ Thick crystals

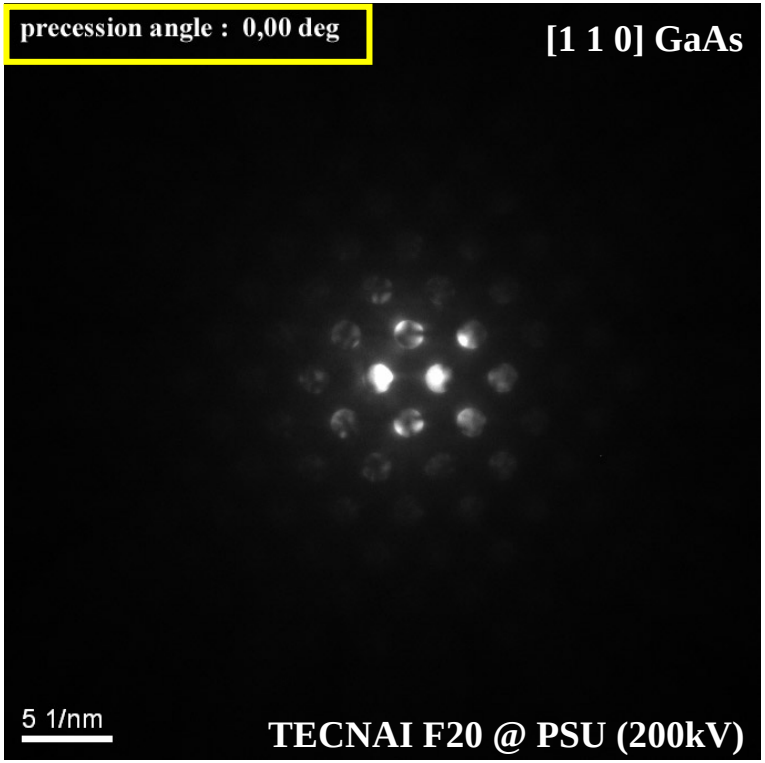
Precession Electron Diffraction (PED)

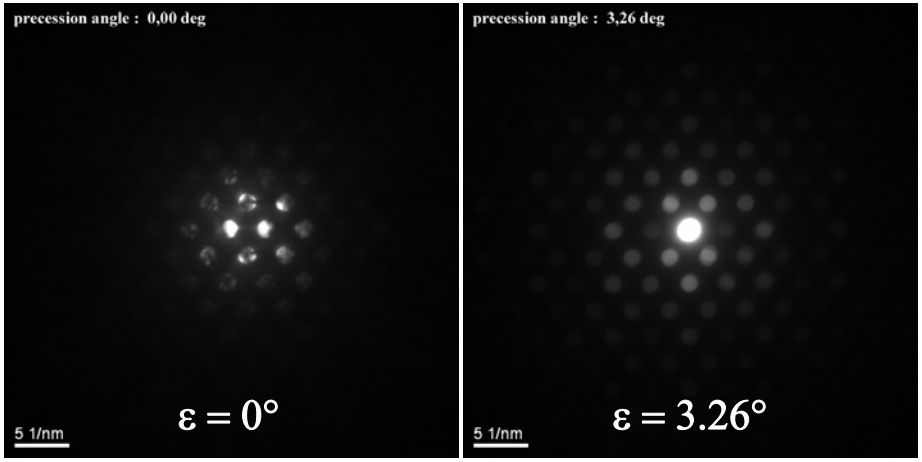


- Tilting the incident electron beam away from the zone axis (tilting angle = **precession angle ε**, typically 1°-3°)
  → less beams are simultaneously excited
- Continuous integration of the reflections over the entire range of angle ω



Precession Electron Diffraction (PED)

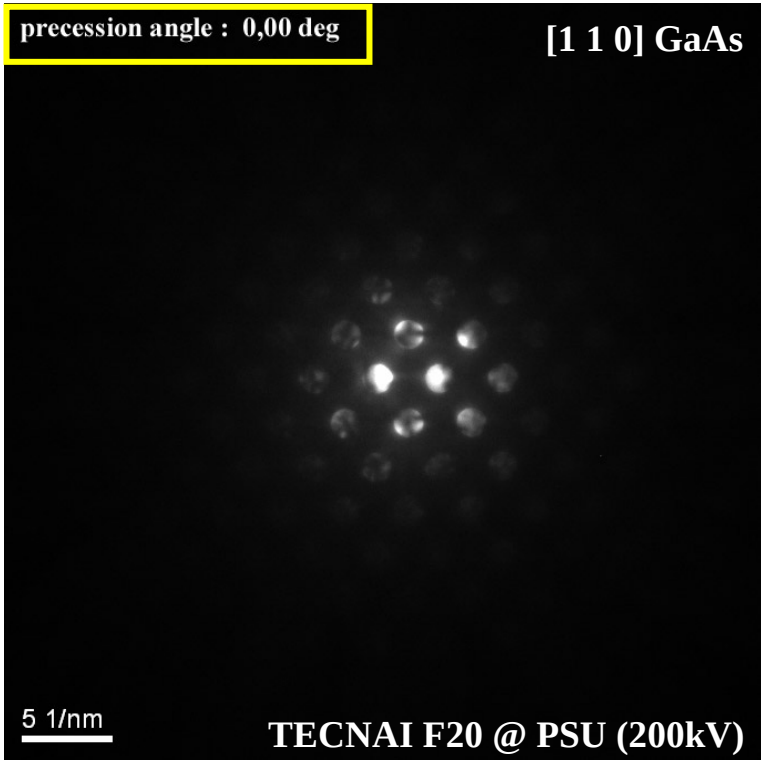


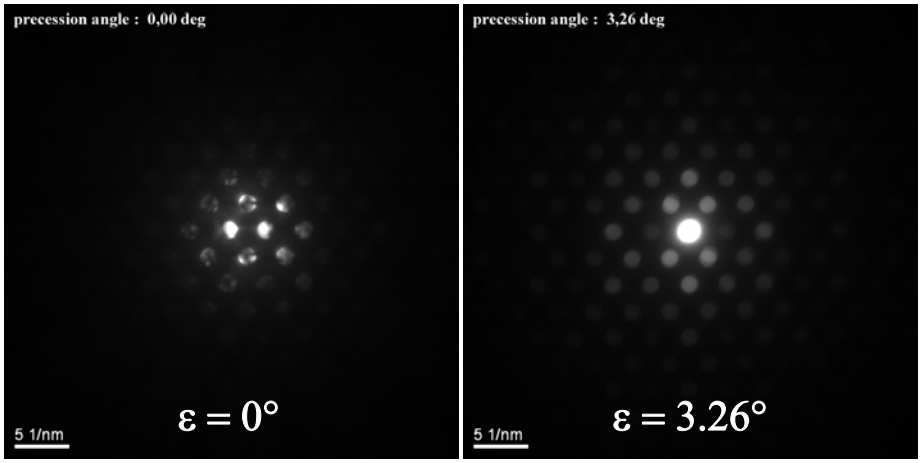


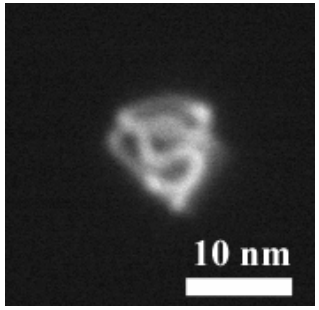
Advantages:

- Symmetrical precession patterns are obtained also for off-zone orientation tilted by less than 1°
- Dynamical effects are reduced due to the off-axis beam inclinations because less beams are simultaneously excited
- The number of reflections is higher than in conventional electron diffraction

Precession Electron Diffraction (PED)







JEOL JEM 2200 FS
Unprecessed: 1nm
Precessed (ε=1°): 10nm

Problems:

- The loss of the spatial resolution (depends on the precession angle and spherical aberation)
- Overlaps between Laue zones are possible for high precession angles
- Information about the shape of the reflections is lost by integration over ω
- Reflections at low angle stay in Bragg condition for longer time than reflections at high angles (Lorentz effect)

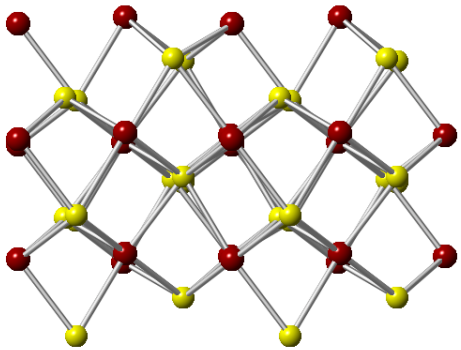
Instrumentation – ASTAR

PED Simulation of $Mn_{0.75}Ga_{0.25}As$ Structure Type I

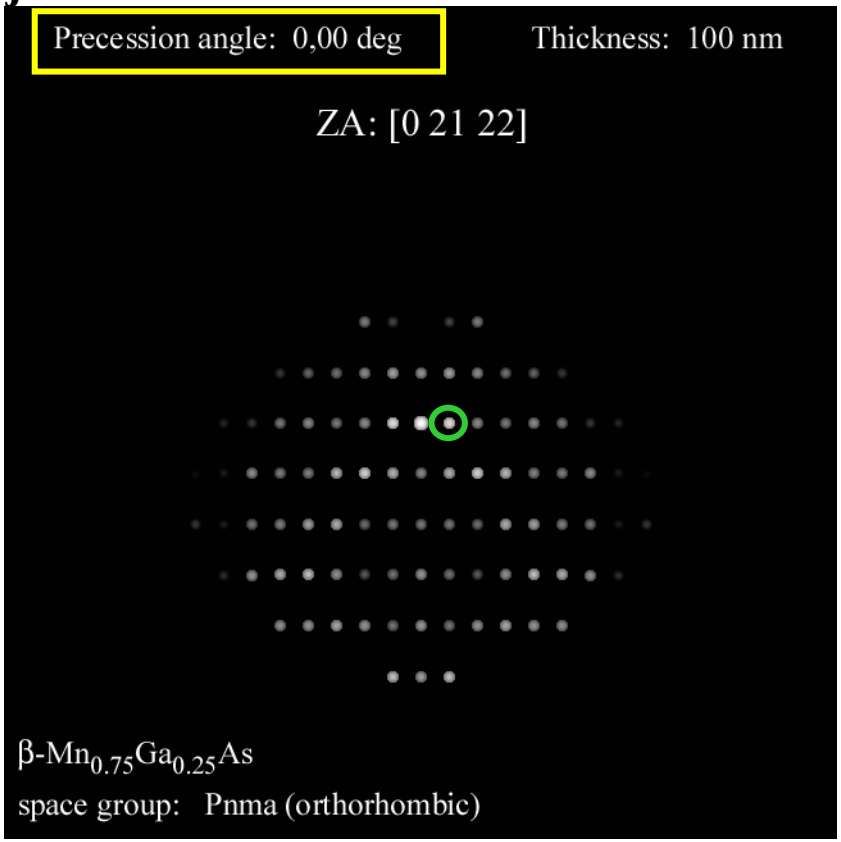
ZA: [0 21 22]

As

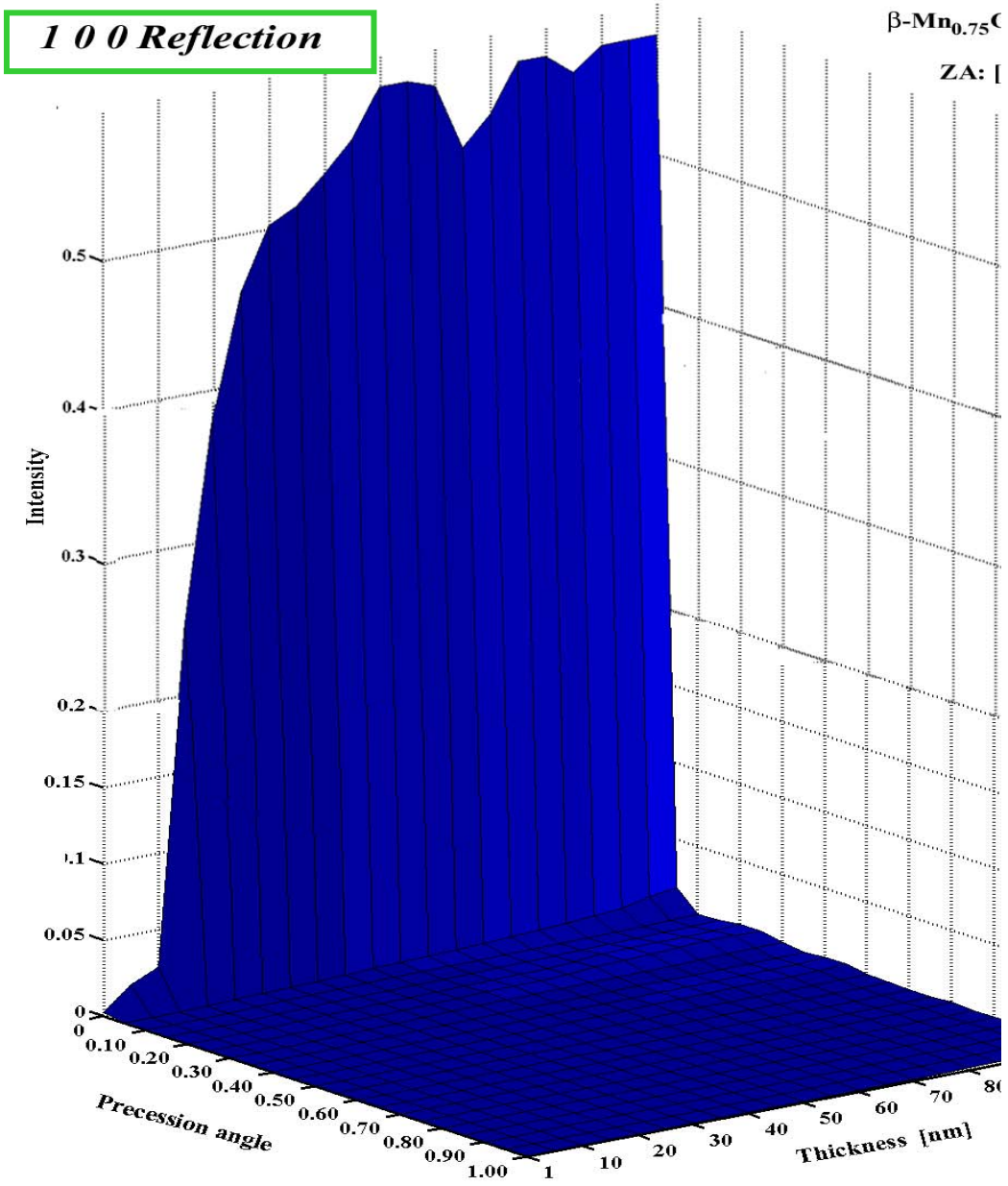
Mn 75%, Ga 25%



jems - Simulation



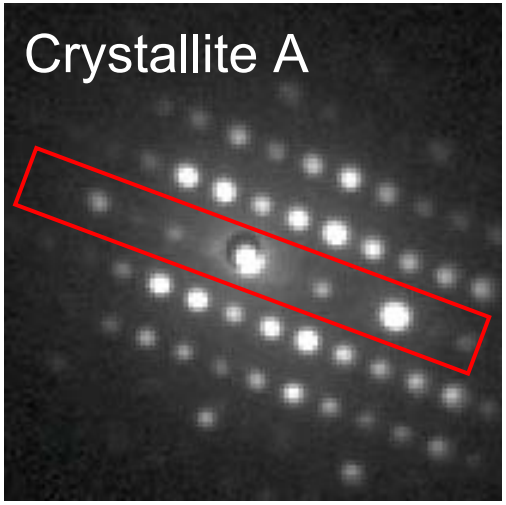
1 0 0 Reflection

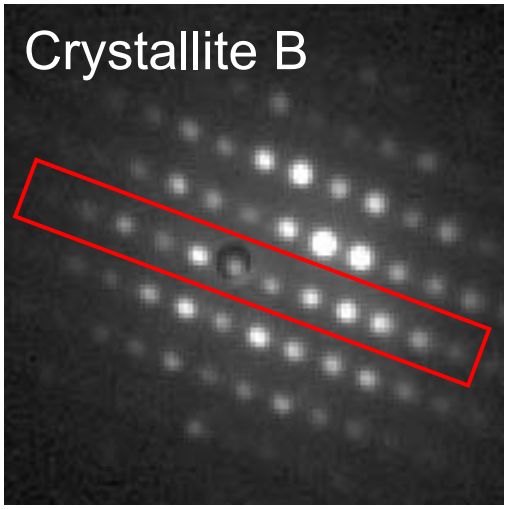


Structure analysis of (Mn,Ga)As

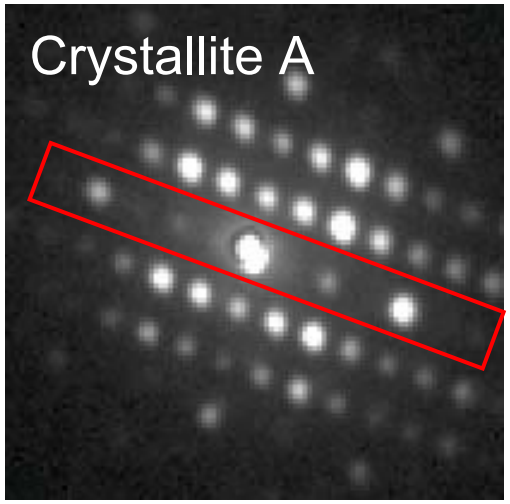
Nano-beam mode, spot size: 1.0 nm

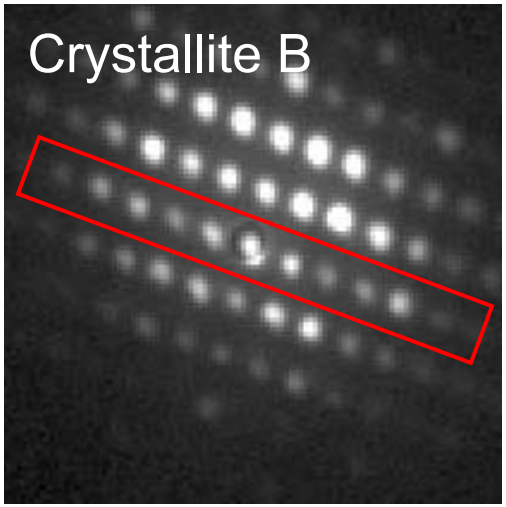
Precession **OFF**





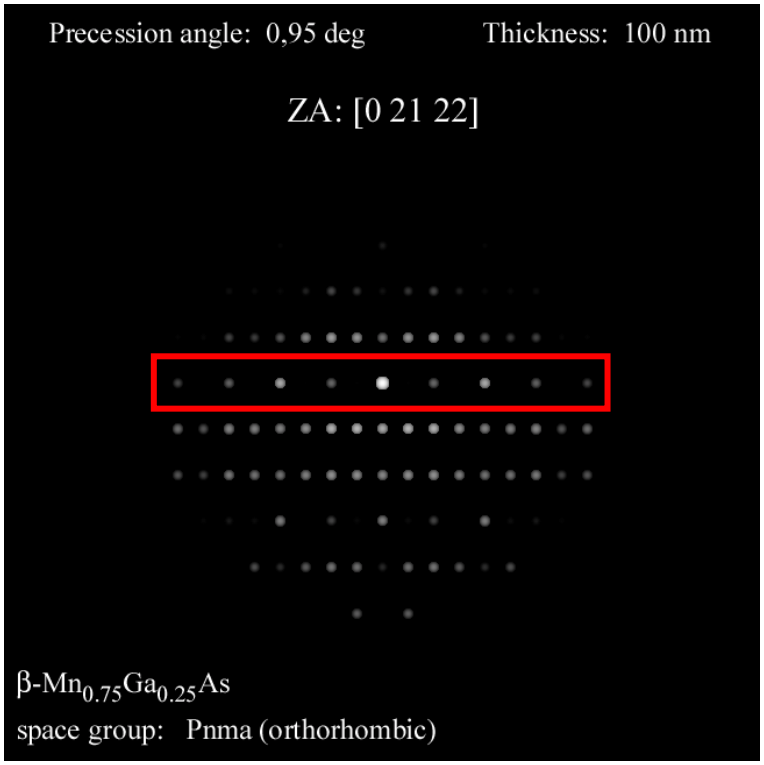
Precession **ON**: 0.96°





Simulation

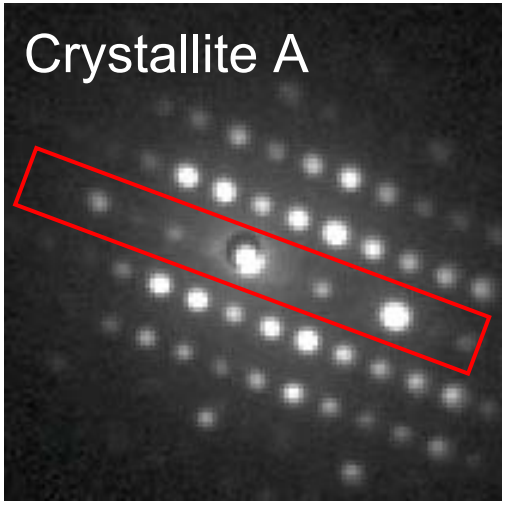
Precession **ON**: 0.95°

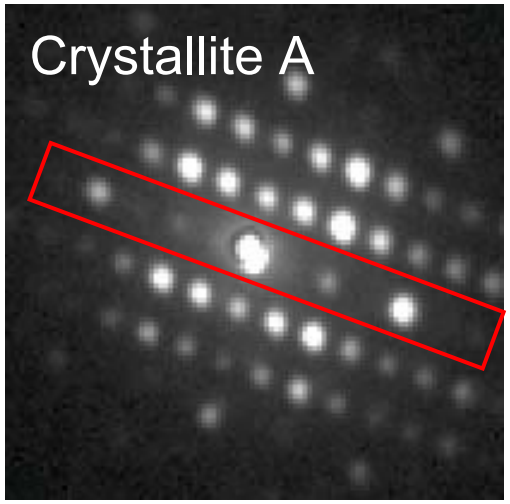


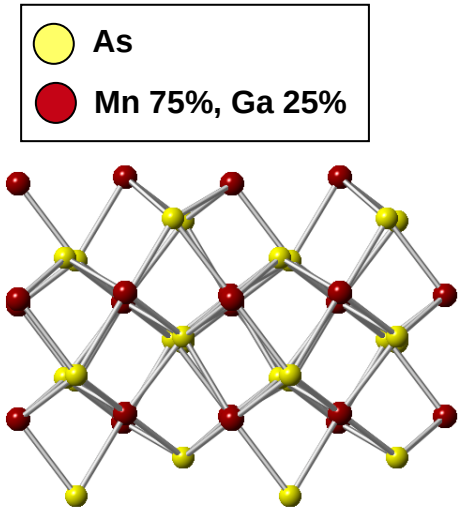
Structure analysis of (Mn,Ga)As

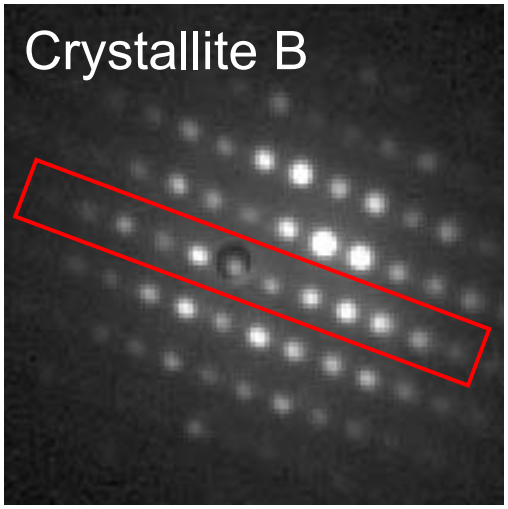
Nano-beam mode, spot size: 1.0 nm

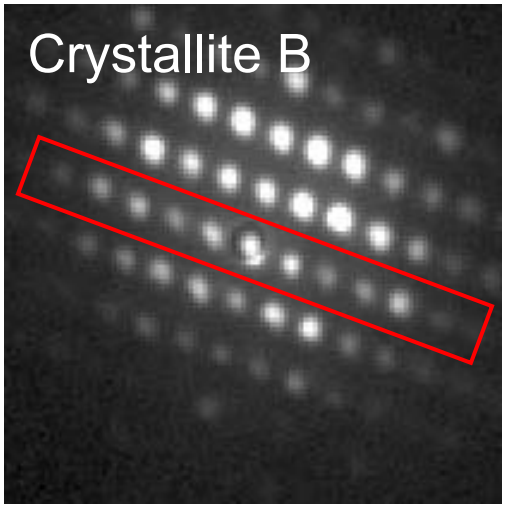
Precession **OFF** Precession **ON**: 0.96°











✗ Superlattice reflections

Modification of structure

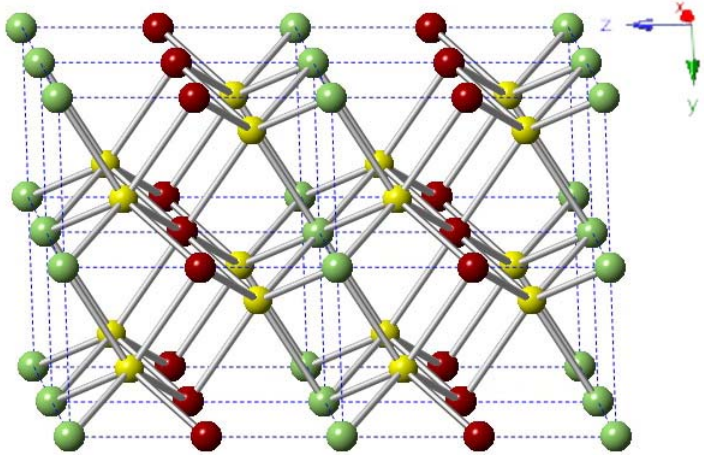
$Mn_{0.75}Ga_{0.25}As$ Superstructure Type II

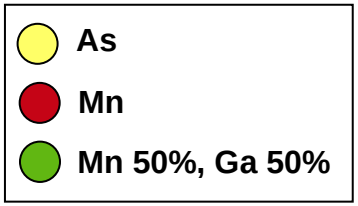
Assumption: **Superstructure**

Each second cation lattice plane of the superlattice is completely occupied with Manganese atoms. 50% of Manganese and 50% of Gallium are statistically distributed on the other cation lattice planes.

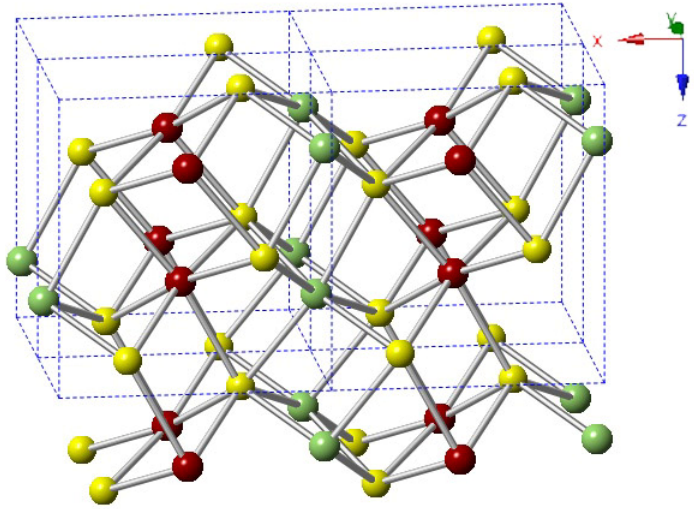
α–superstructure $Mn_{0.75}Ga_{0.25}As$	**β–superstructure $Mn_{0.75}Ga_{0.25}As$**
trigonal	monoclinic
Space group: $P\bar{3}m1$	Space group: $P2_1/m$

Short: **α–$Mn_{0.75}Ga_{0.25}As$ (tri)**



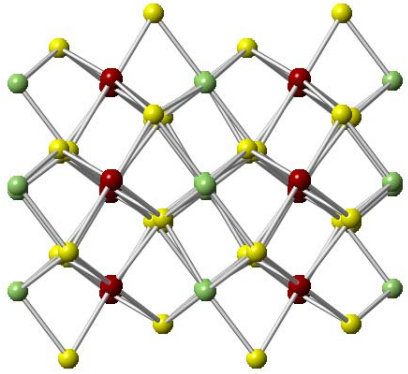


Short: **β–$Mn_{0.75}Ga_{0.25}As$ (mono)**



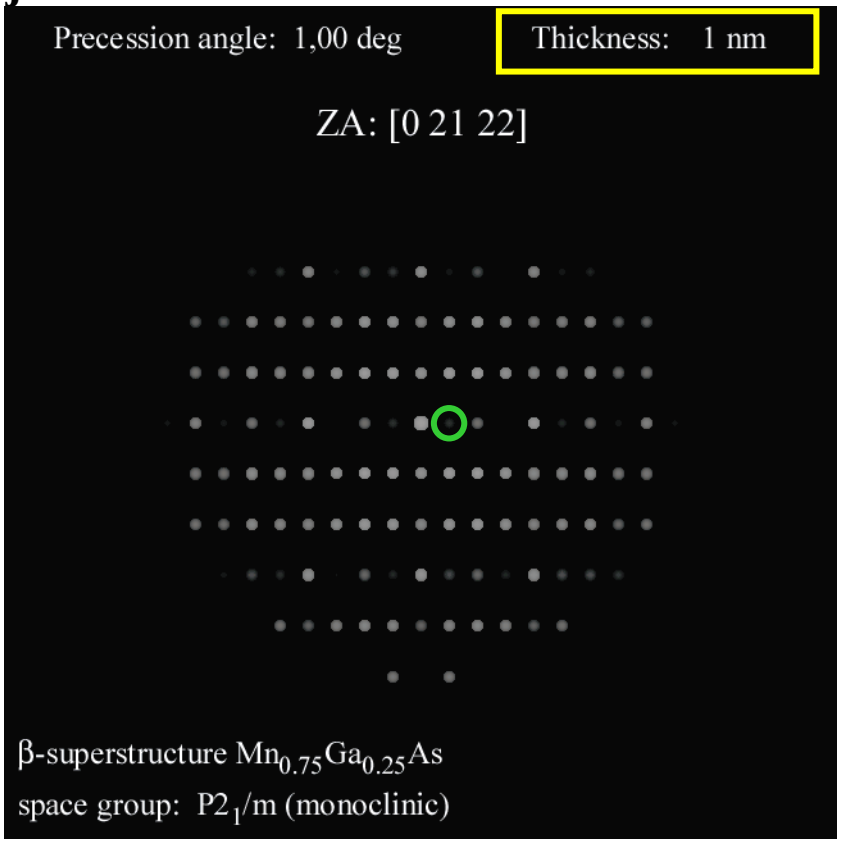
PED Simulation of $Mn_{0.75}Ga_{0.25}As$ Superstructure Type II

ZA: [0 21 22]

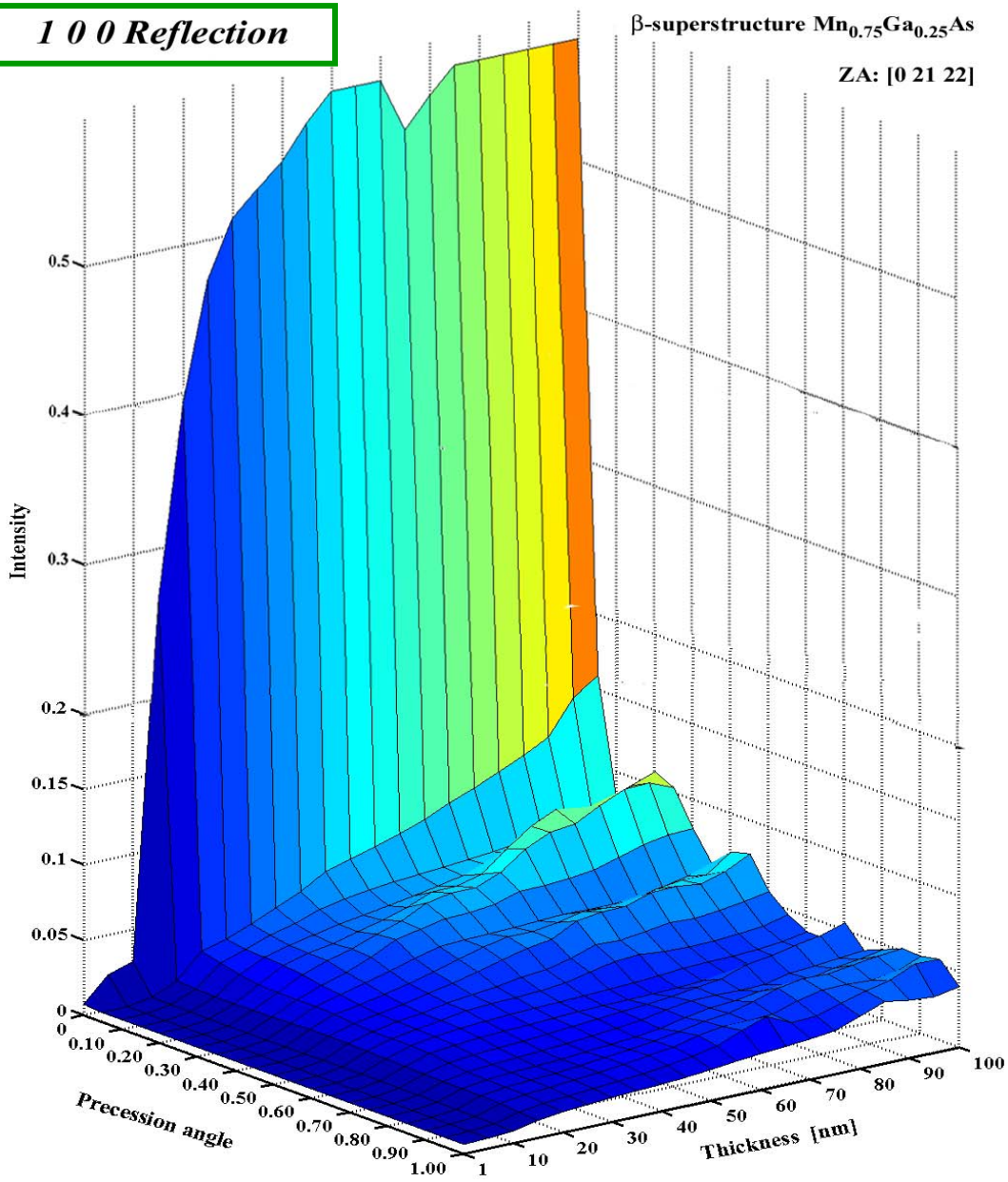


As
Mn
Mn 50%, Ga 50%

jems - Simulation



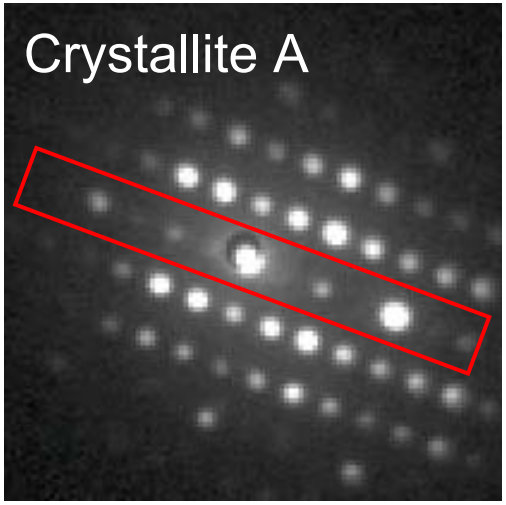
1 0 0 Reflection

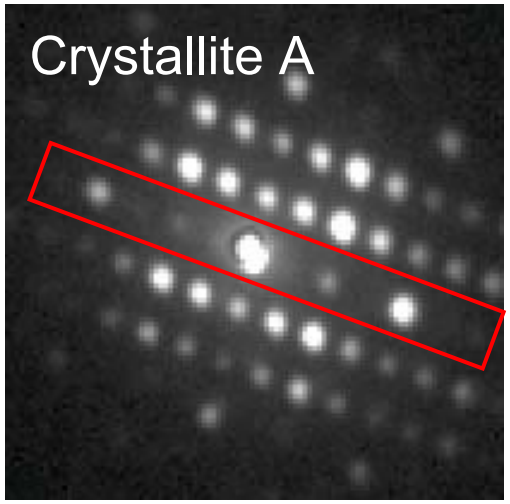


Structure analysis of (Mn,Ga)As

Nano-beam mode, spot size: 1.0 nm

Precession **OFF** Precession **ON**: 0.96°

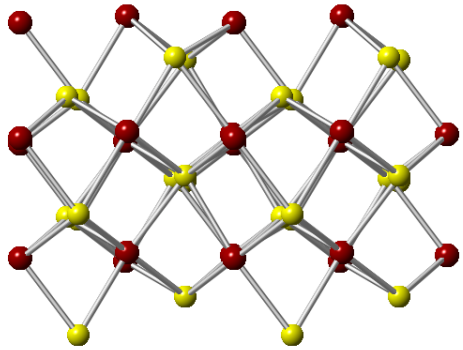


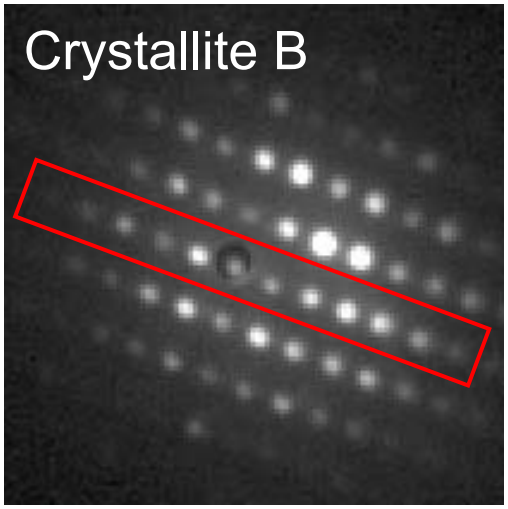


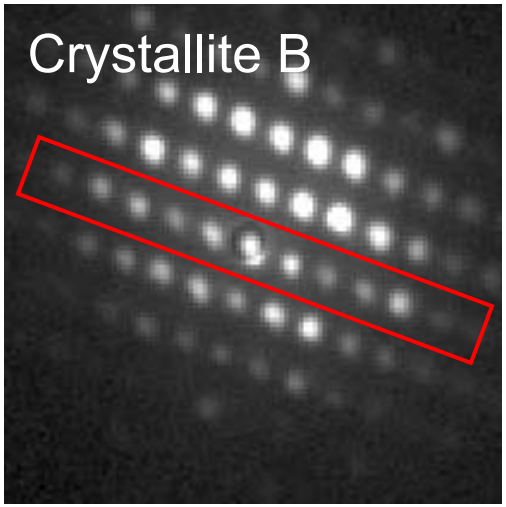
As

Mn 75%, Ga 25%

Structure type I





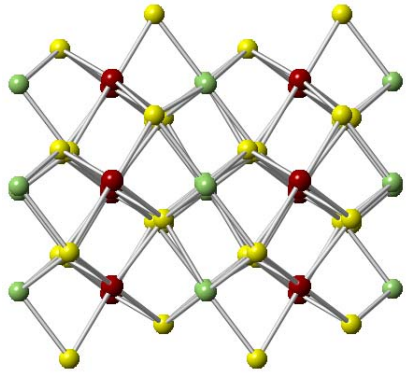


As

Mn

Mn 50%, Ga 50%

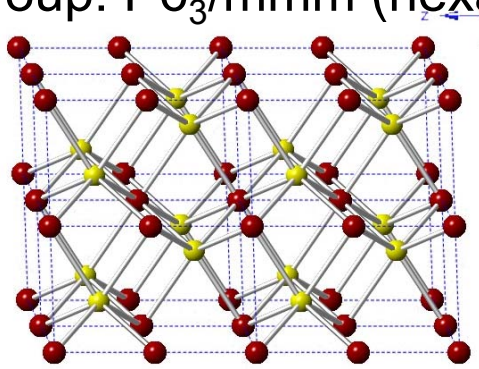
Superlattice structure type II



Phases of $Mn_{0.75}Ga_{0.25}As$

α–$Mn_{0.75}Ga_{0.25}As$(hex)

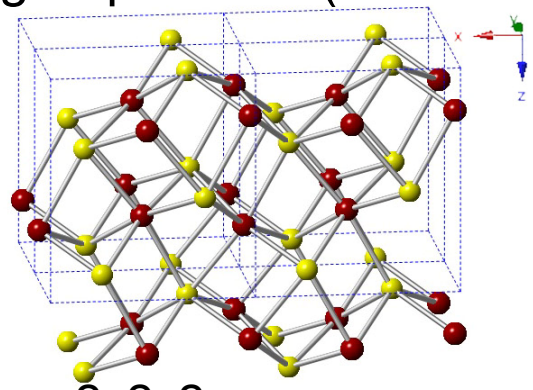
space group: $P6_3/mmm$ (hexagonal)



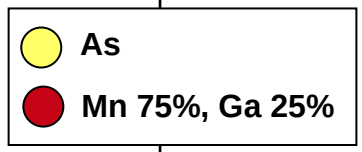
Laue class: $\frac{6}{m}\frac{2}{m}\frac{2}{m}$ → 2701 templates

β–$Mn_{0.75}Ga_{0.25}As$(orth)

Space group: Pnma (orthorhombic)

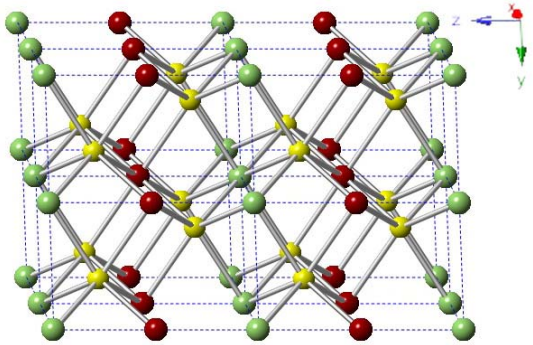


Laue class: $\frac{2}{m}\frac{2}{m}\frac{2}{m}$ → 8001 templates



α–$Mn_{0.75}Ga_{0.25}As$(tri)

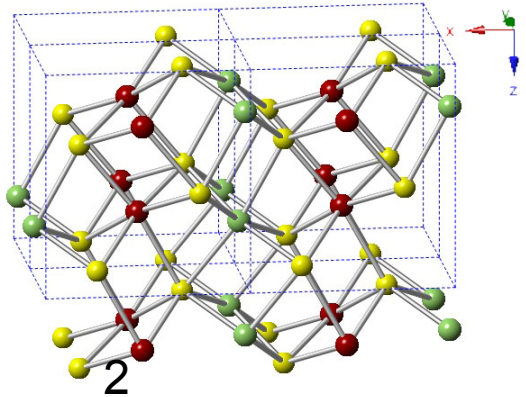
space group: $P\bar{3}m1$ (trigonal)



Laue class: $\bar{3}m$ → 10404 templates

β–$Mn_{0.75}Ga_{0.25}As$(mono)

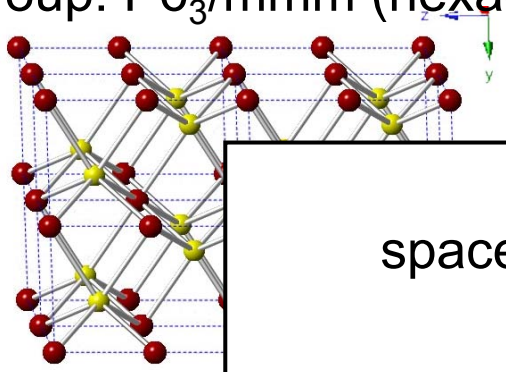
space group: $P2_1/m$ (monoclinic)



Laue class: $\frac{2}{m}$ → 16129 templates

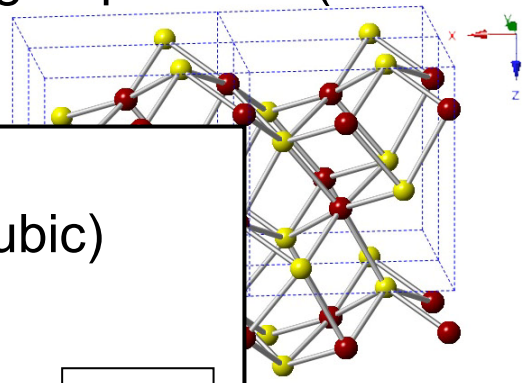
Phases of $Mn_{0.75}Ga_{0.25}As$

α–$Mn_{0.75}Ga_{0.25}As$(hex)
space group: $P6_3/mmm$ (hexagonal)



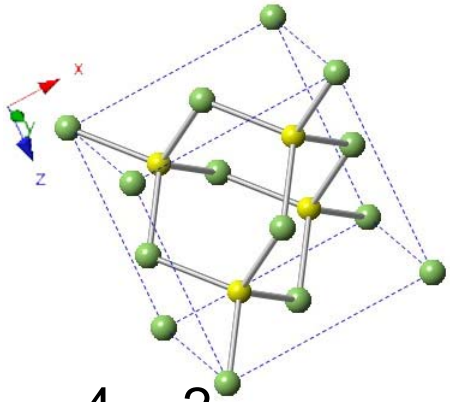
Laue class: $\frac{6}{m}\frac{2}{m}\frac{2}{m}$

β–$Mn_{0.75}Ga_{0.25}As$(orth)
Space group: Pnma (orthorhombic)



→ 8001 templates

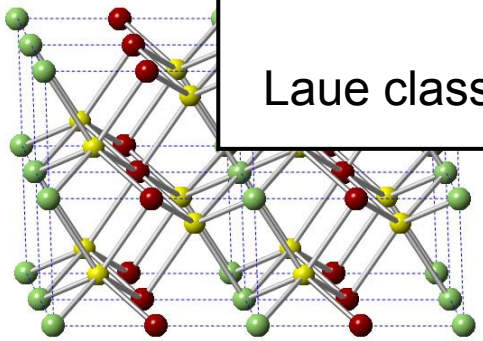
GaAs
space group: $F\bar{4}3m$ (cubic)



As
Ga

Laue class: $\frac{4}{m}\bar{3}\frac{2}{m}$ → 1326 templates

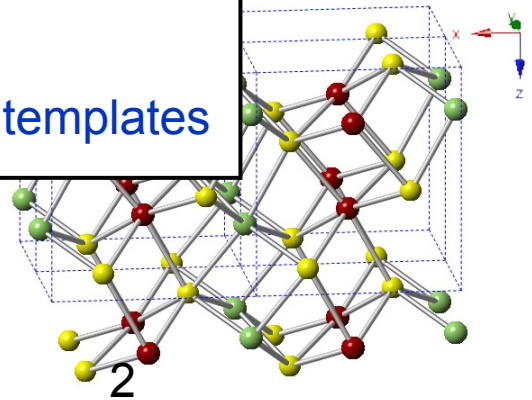
α–$Mn_{0.75}G$
space group: F



Mn
Mn 50%, Ga 50%

Laue class: $\bar{3}m$ → 10404 templates

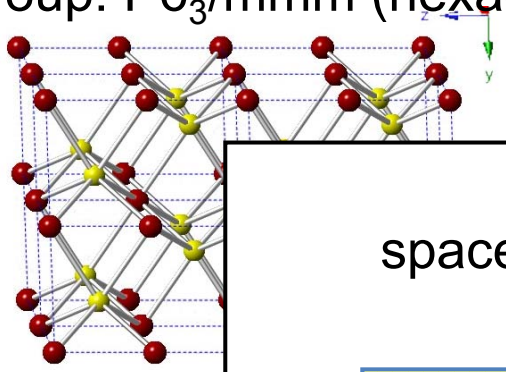
$_{25}As$(mono)
$_1/m$ (monoclinic)



Laue class: $\frac{2}{m}$ → 16129 templates

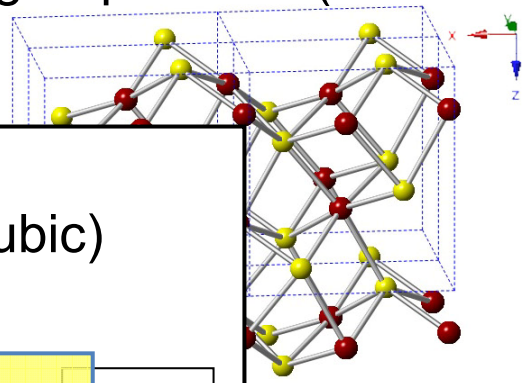
Phases of $Mn_{0.75}Ga_{0.25}As$

α–$Mn_{0.75}Ga_{0.25}As$(hex)
space group: $P6_3/mmm$ (hexagonal)



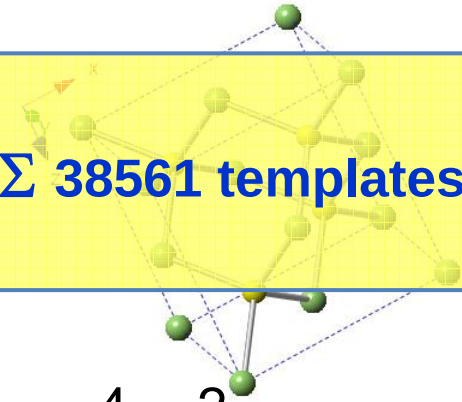
Laue class: $\frac{6}{m}\frac{2}{m}\frac{2}{m}$

β–$Mn_{0.75}Ga_{0.25}As$(orth)
Space group: Pnma (orthorhombic)



→ 8001 templates

GaAs
space group: $F\bar{4}3m$ (cubic)

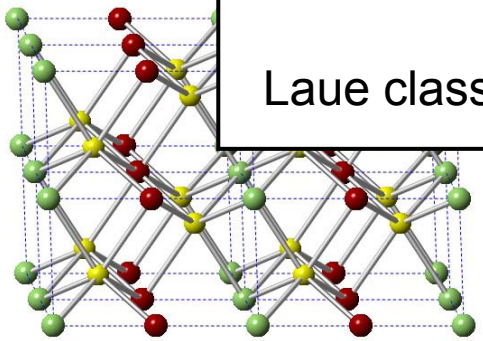


Σ 38561 templates !

As
Ga

Laue class: $\frac{4}{m}\bar{3}\frac{2}{m}$ → 1326 templates

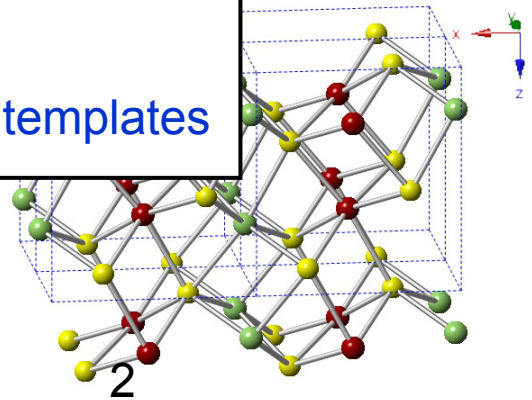
α–$Mn_{0.75}G$
space group: F



Mn
Mn 50%, Ga 50%

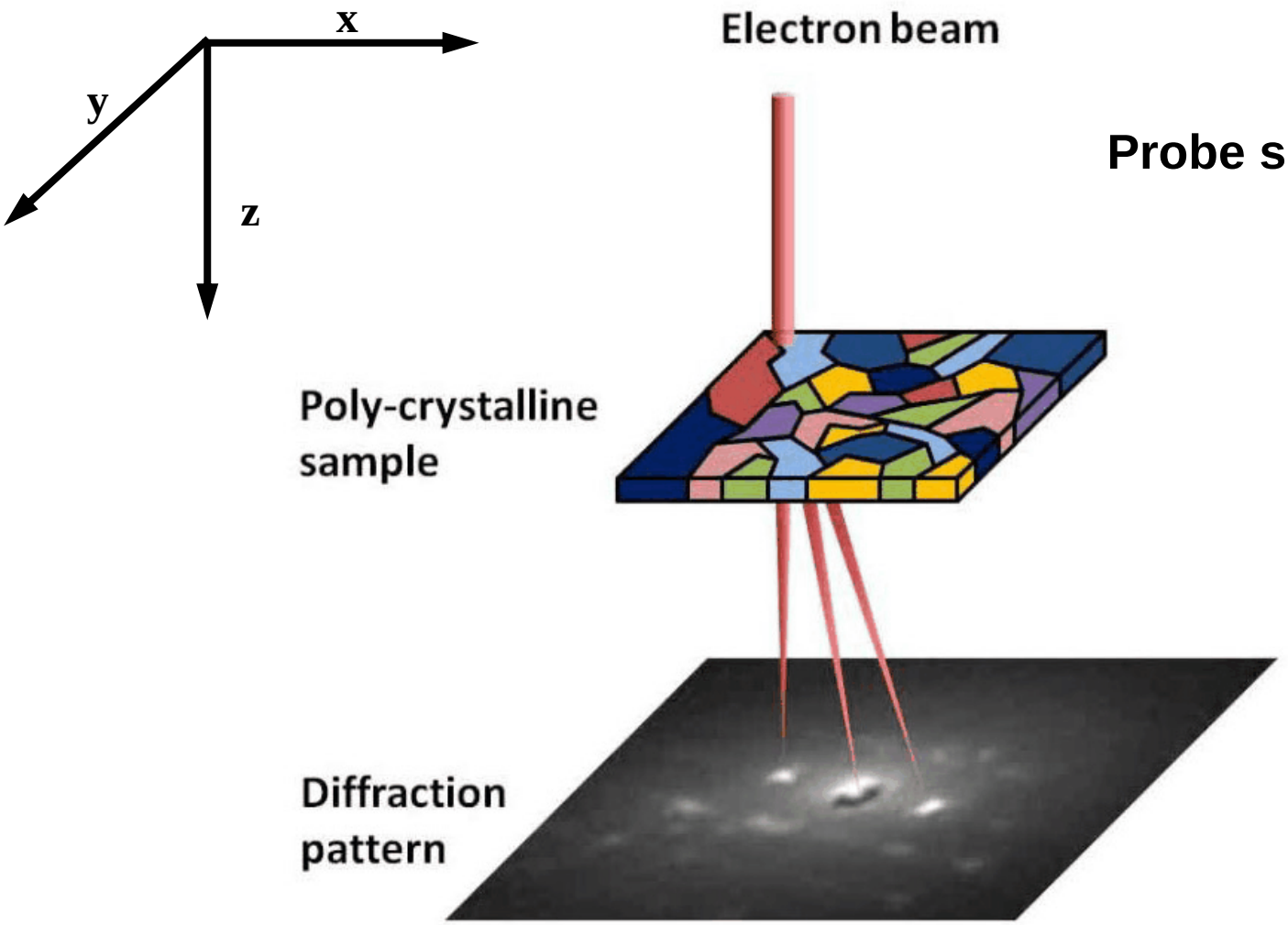
Laue class: $\bar{3}m$ → 10404 templates

$_{25}As$(mono)
$_1/m$ (monoclinic)



Laue class: $\frac{2}{m}$ → 16129 templates

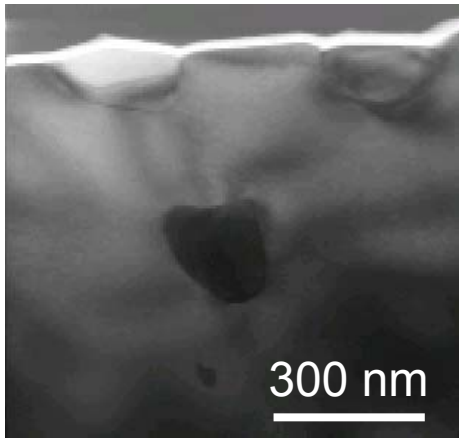
Scanning nano-beam diffraction (SNBD)



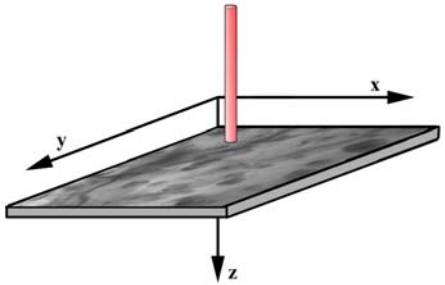
Probe size: 0.5 -1.5 nm

ASTAR: Phase and Orientation Maps

Virtual BF

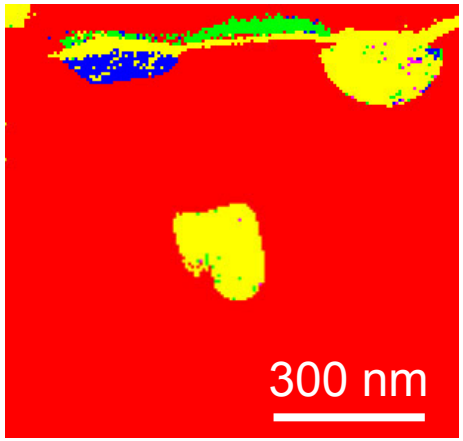


without precession



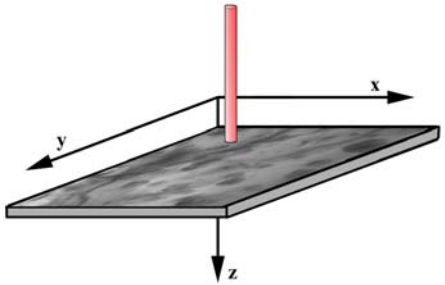
ASTAR: Phase and Orientation Maps

Phase map



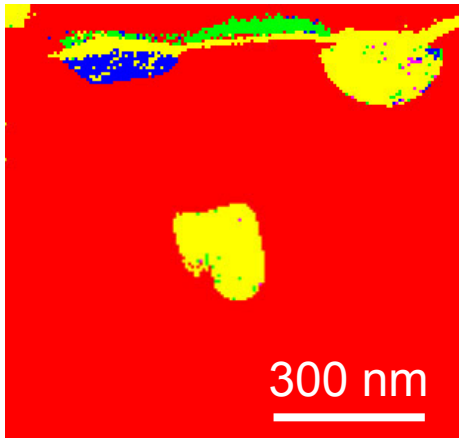
- GaAs (cubic)
- α–$Mn_{0.75}Ga_{0.25}As$(hex)
- β–$Mn_{0.75}Ga_{0.25}As$(orth)
- α–$Mn_{0.75}Ga_{0.25}As$(tri)
- β–$Mn_{0.75}Ga_{0.25}As$(mono)

without precession



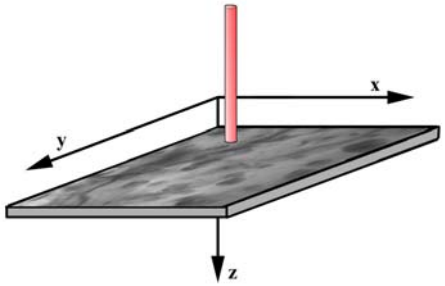
ASTAR: Phase and Orientation Maps

Phase map

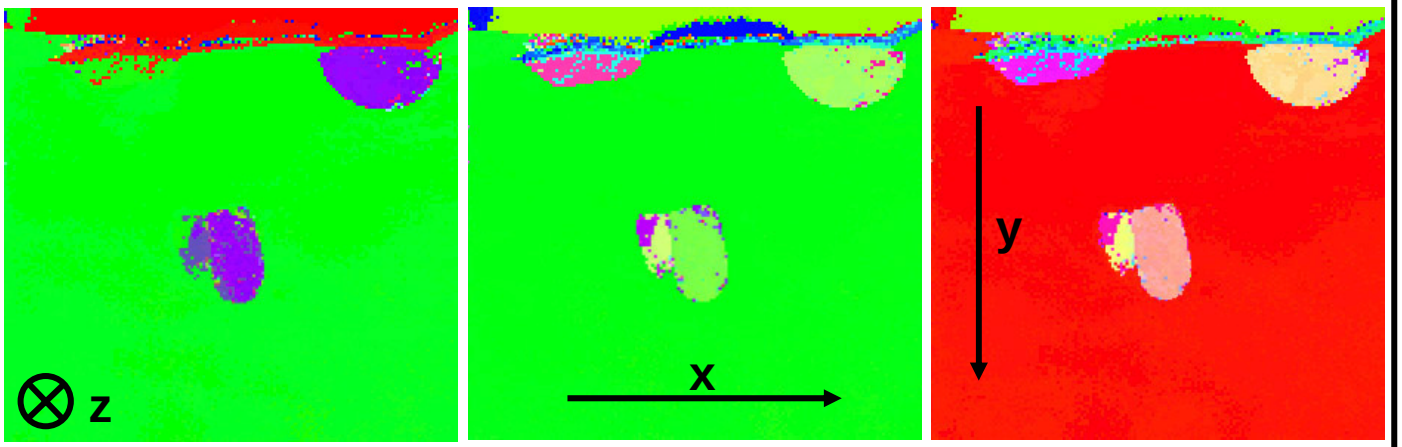


- GaAs (cubic)
- α–$Mn_{0.75}Ga_{0.25}As$(hex)
- β–$Mn_{0.75}Ga_{0.25}As$(orth)
- α–$Mn_{0.75}Ga_{0.25}As$(tri)
- β–$Mn_{0.75}Ga_{0.25}As$(mono)

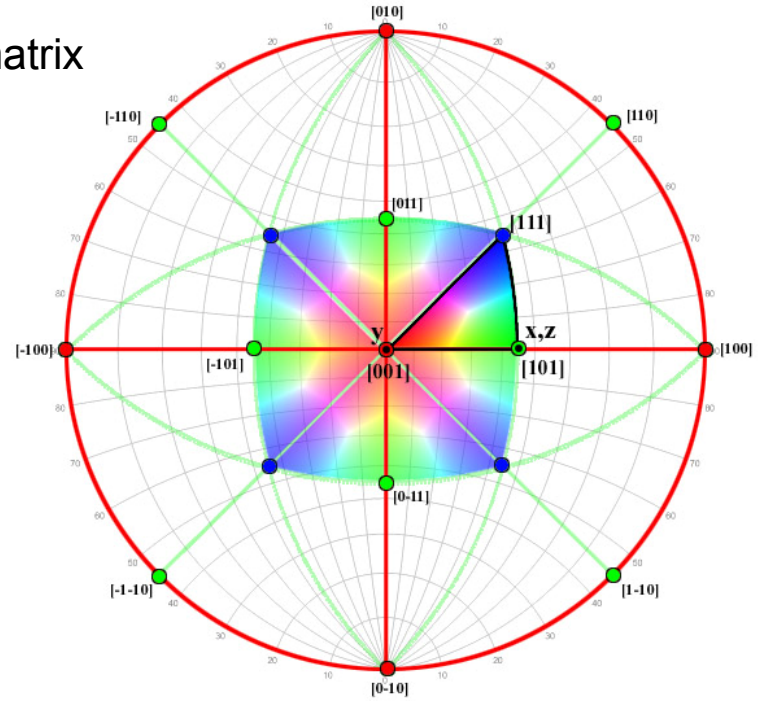
without precession



Orientation maps

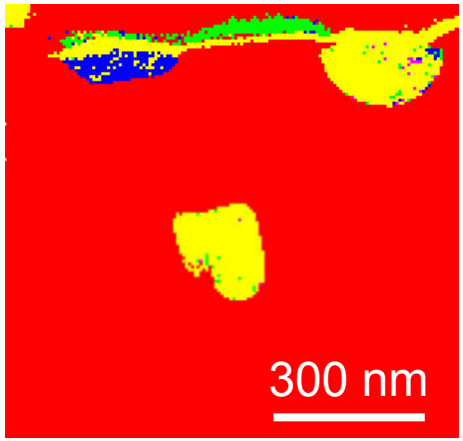


GaAs matrix (cubic)



ASTAR: Phase and Orientation Maps

Phase map



- GaAs (cubic)
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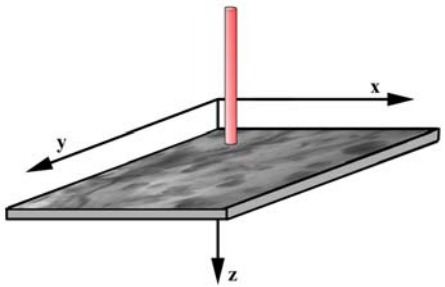
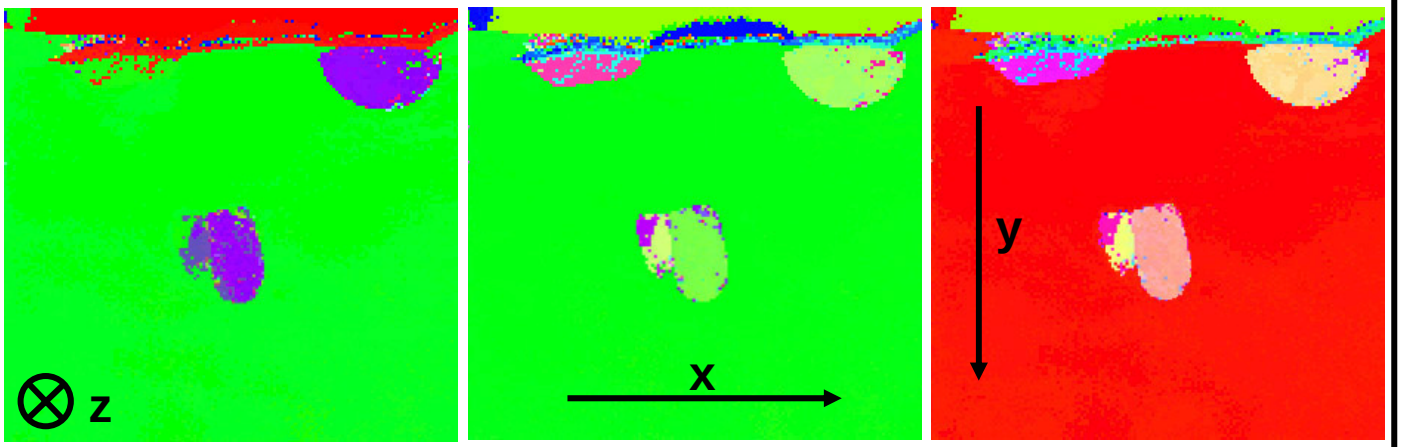
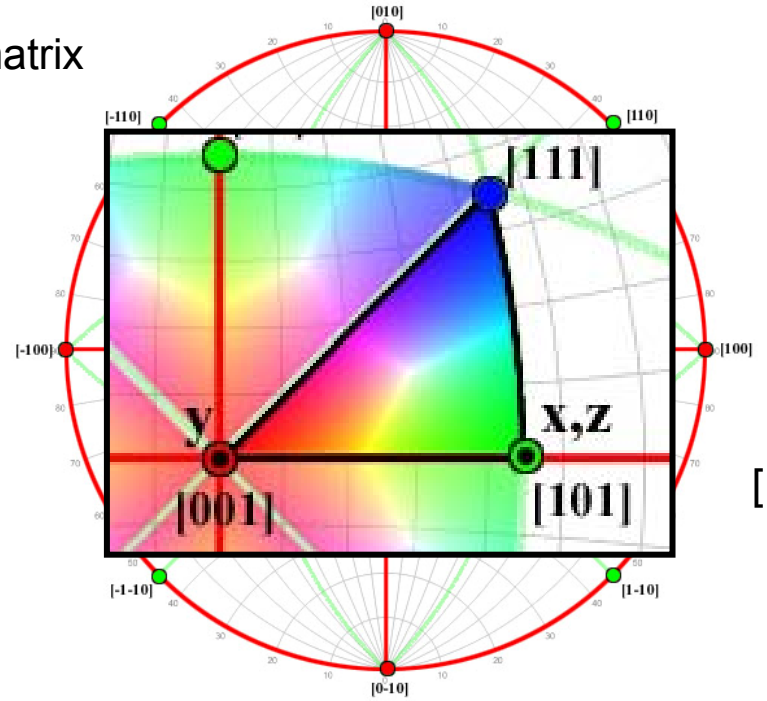
without precession

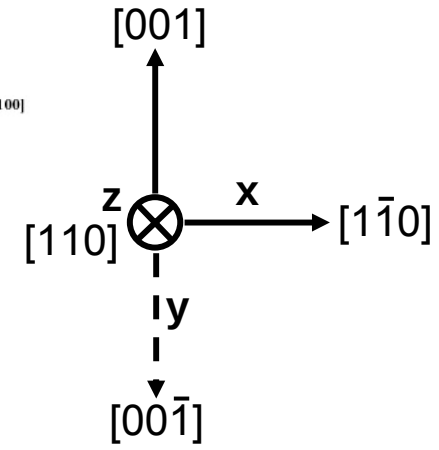


Orientation maps



GaAs matrix (cubic)





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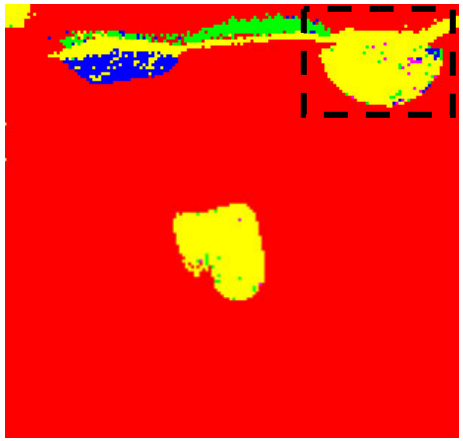

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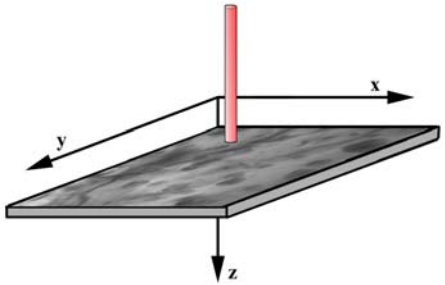
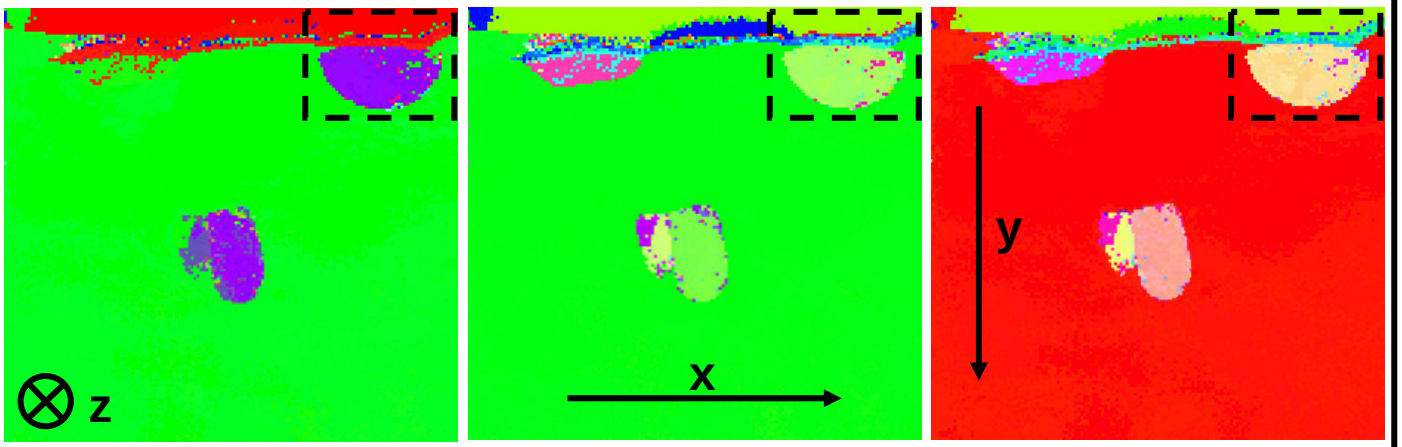
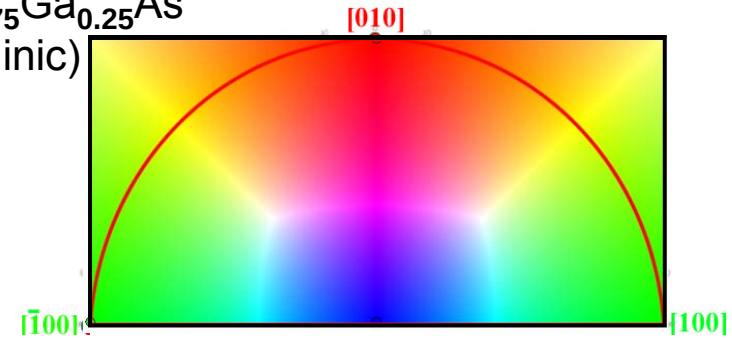


Orientation maps



β–$Mn_{0.75}Ga_{0.25}As$ (monoclinic)



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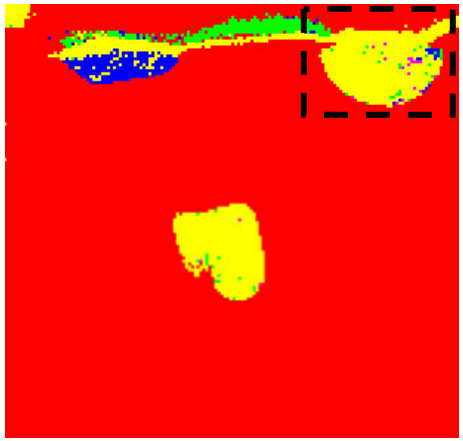
Phase map



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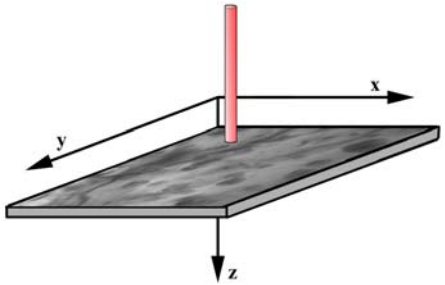
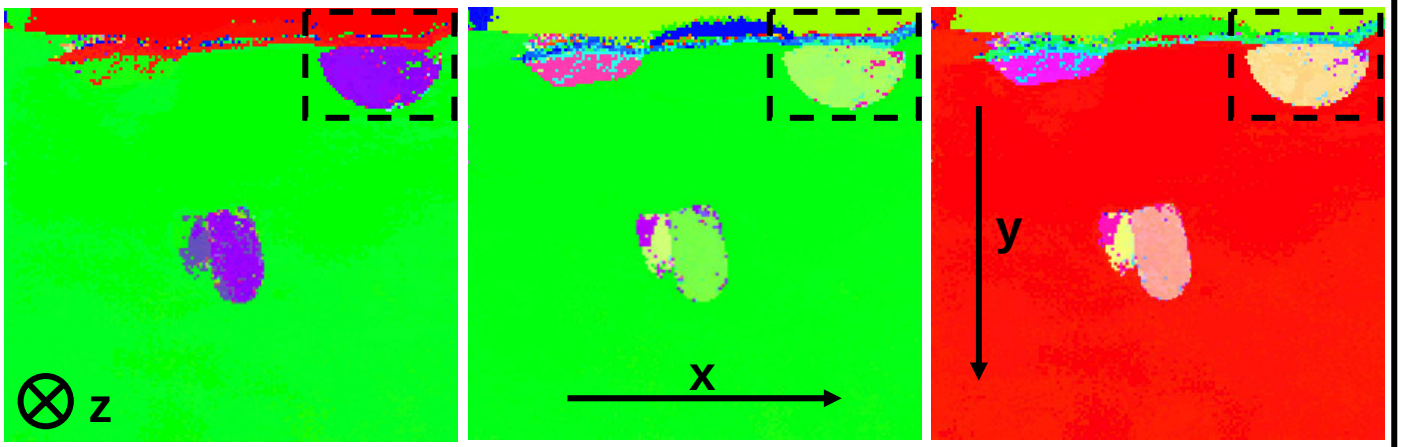
without precession



Orientation maps



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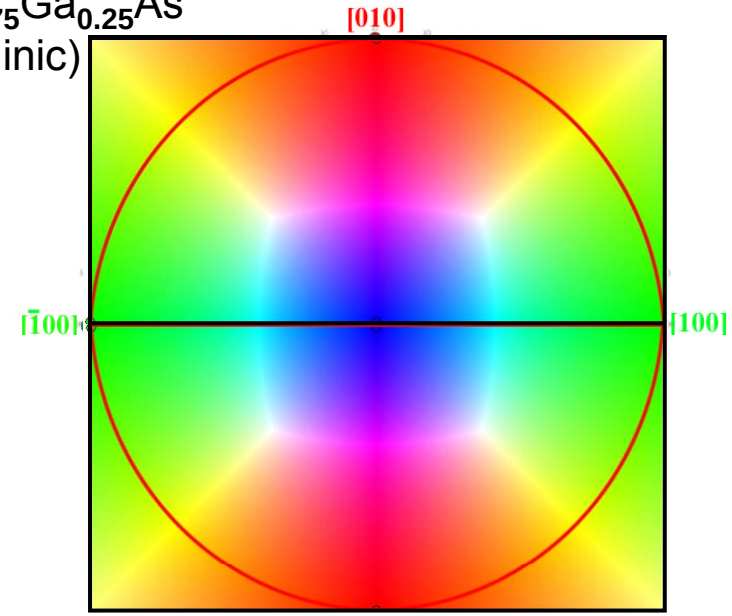
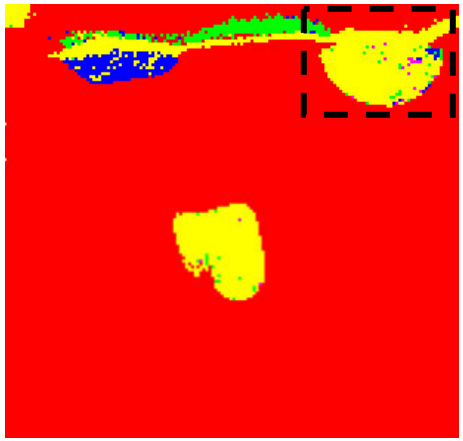


ASTAR: Phase and Orientation Maps

Phase map



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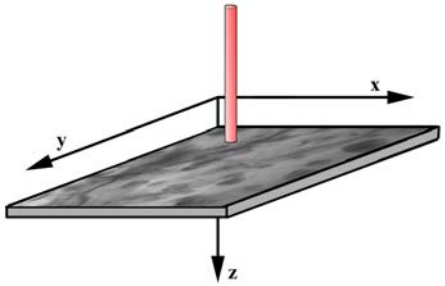
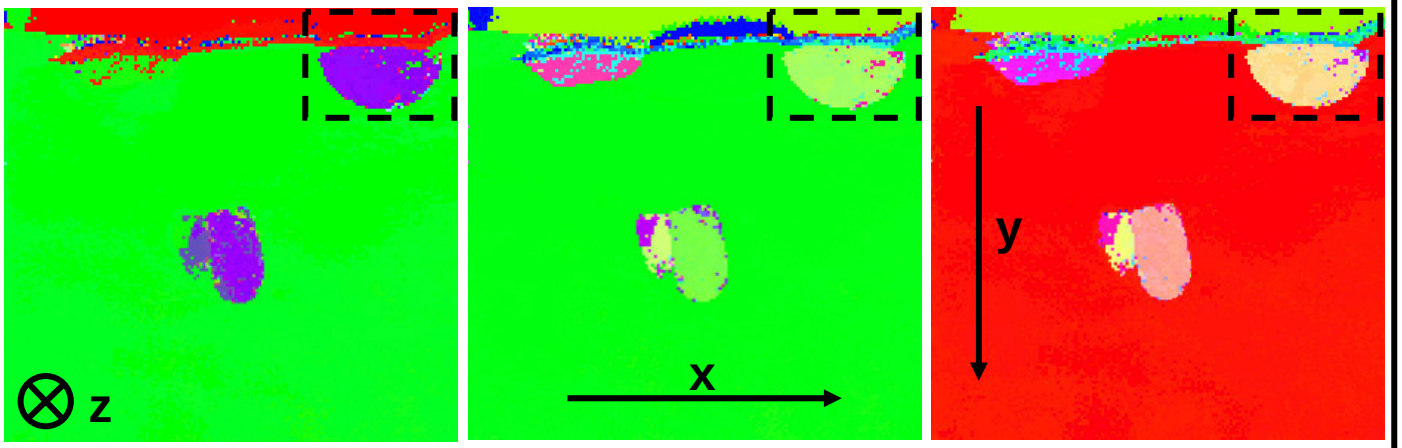
without precession



Orientation maps



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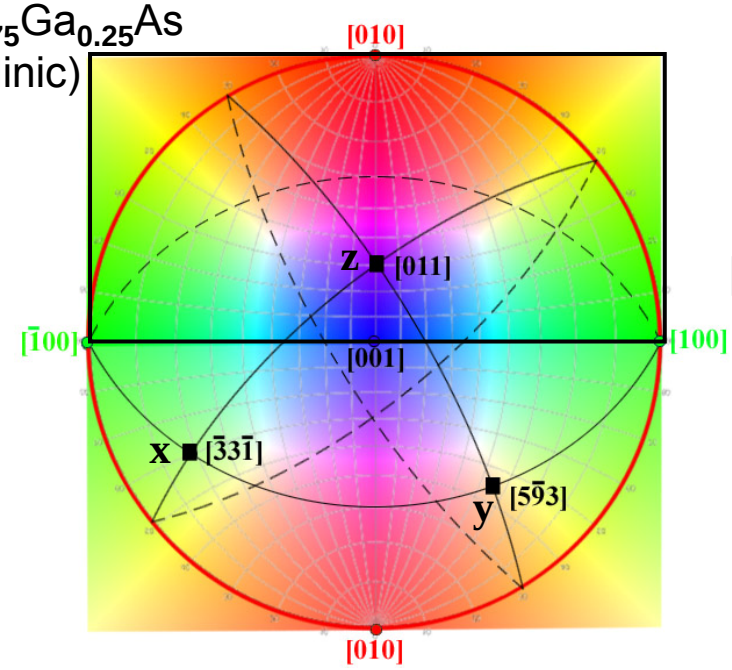

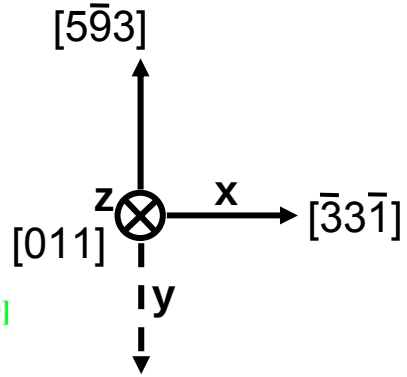

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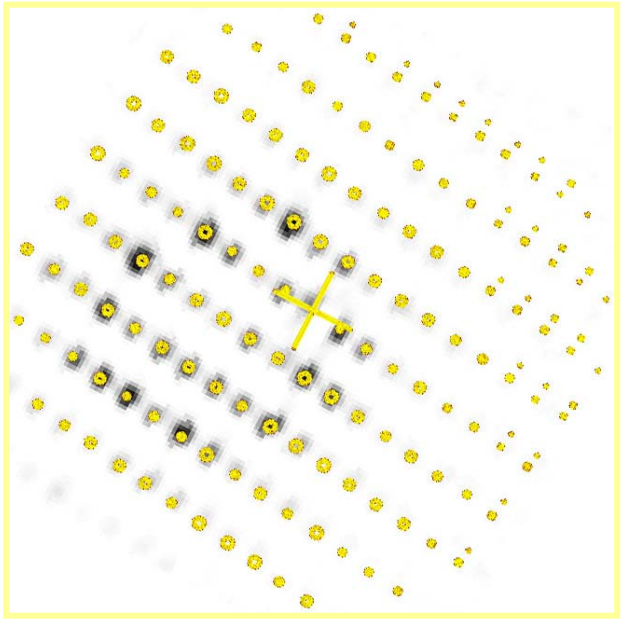
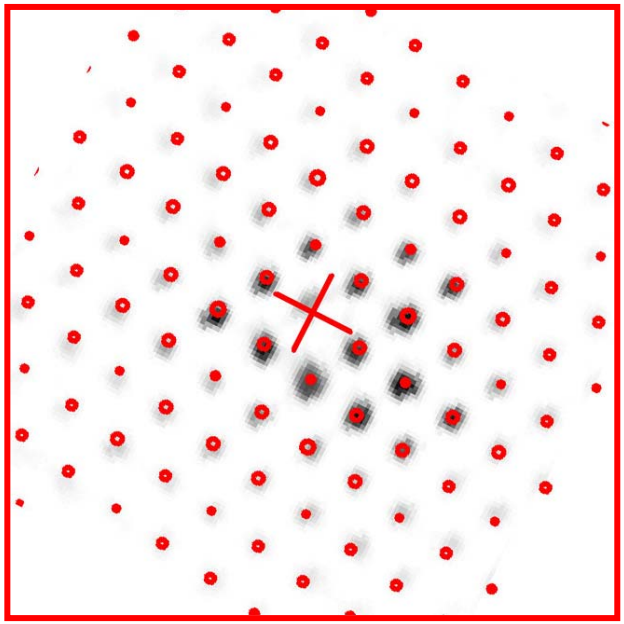
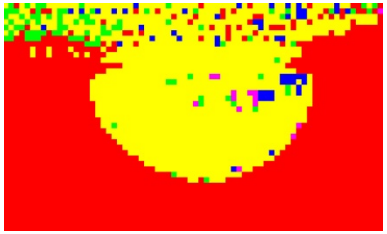
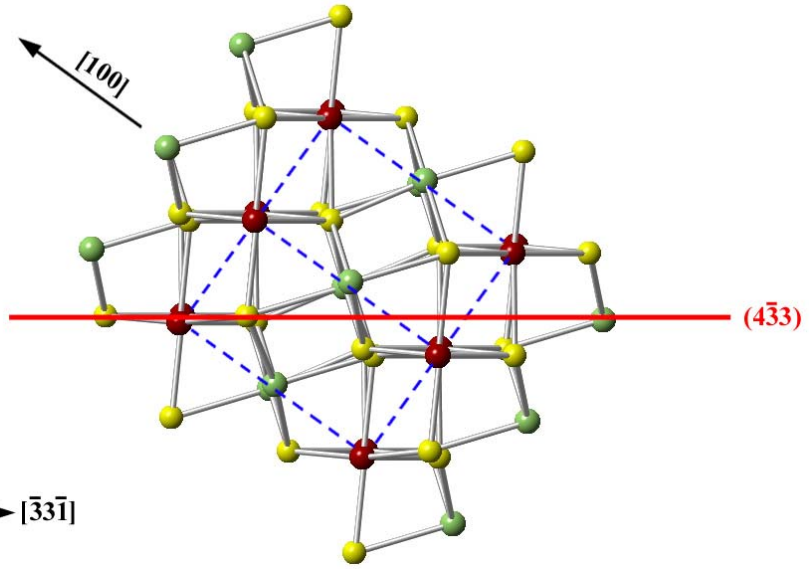


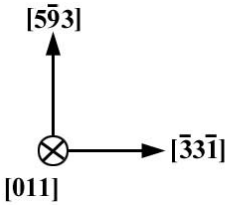




As
Mn
Mn 50%, Ga 50%

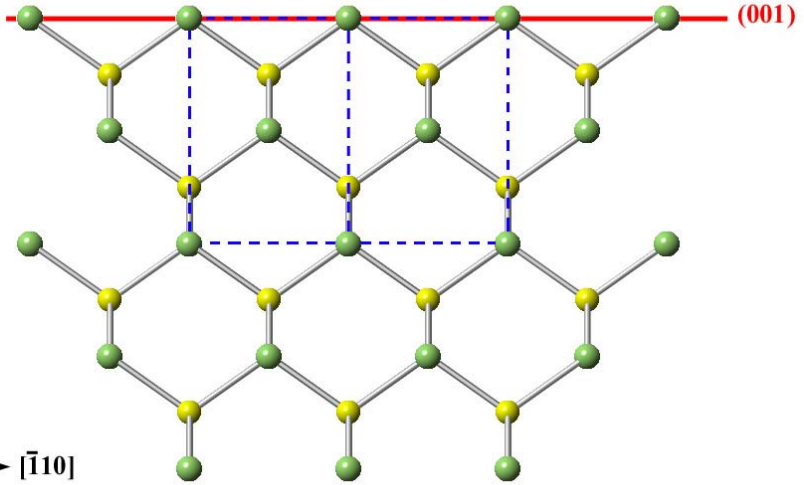
β–$Mn_{0.75}Ga_{0.25}As$ (monoclinic)

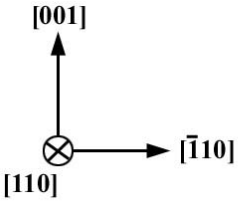




GaAs matrix (cubic)

As
Ga





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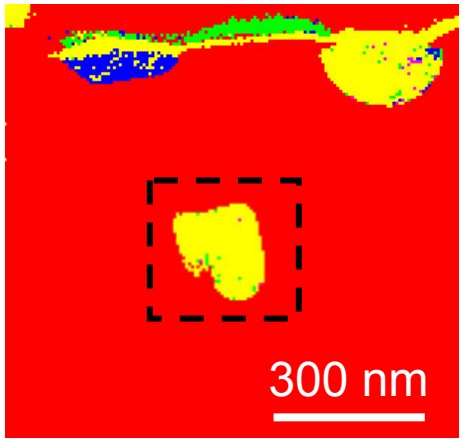

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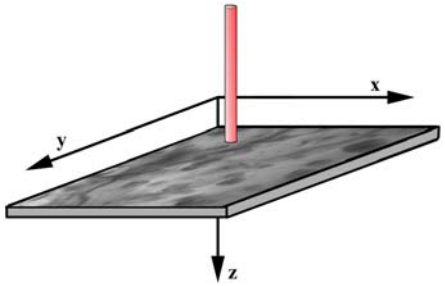
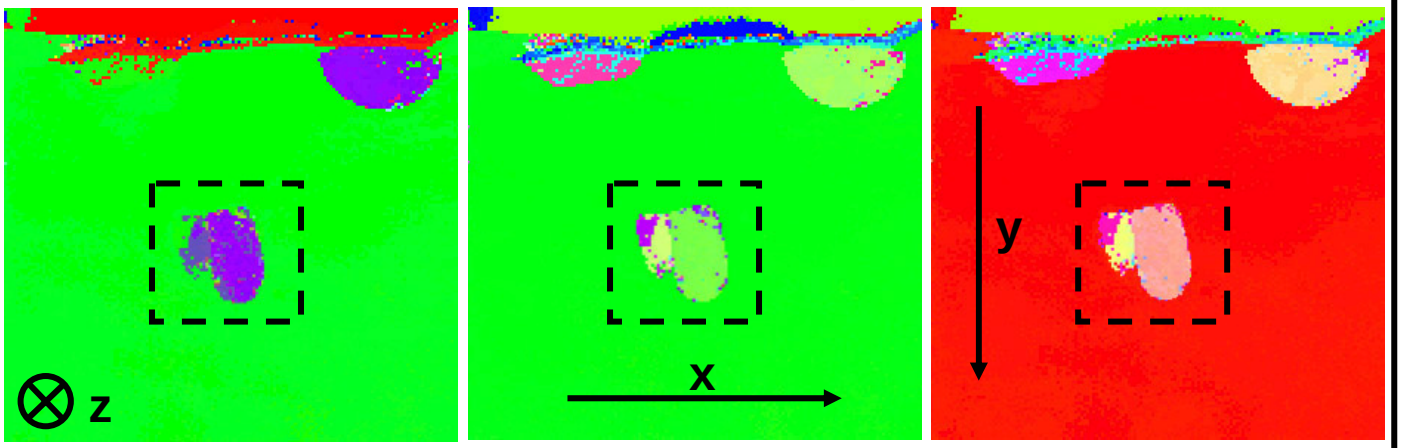
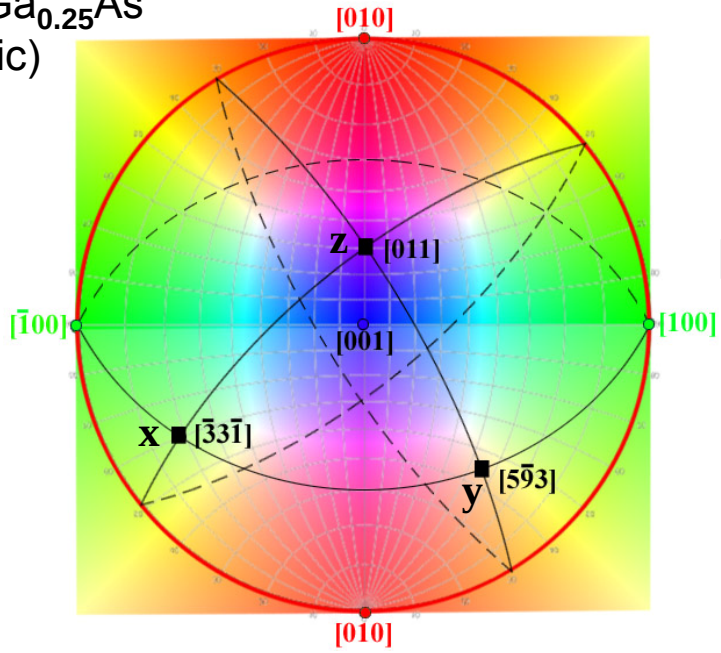
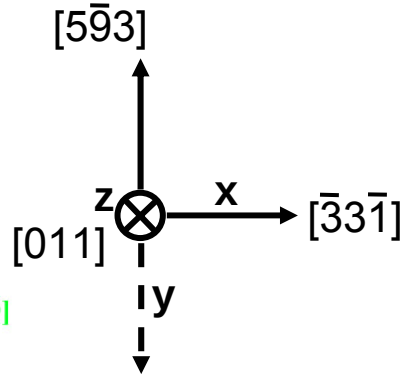


Orientation maps



β–$Mn_{0.75}Ga_{0.25}As$ (monoclinic)





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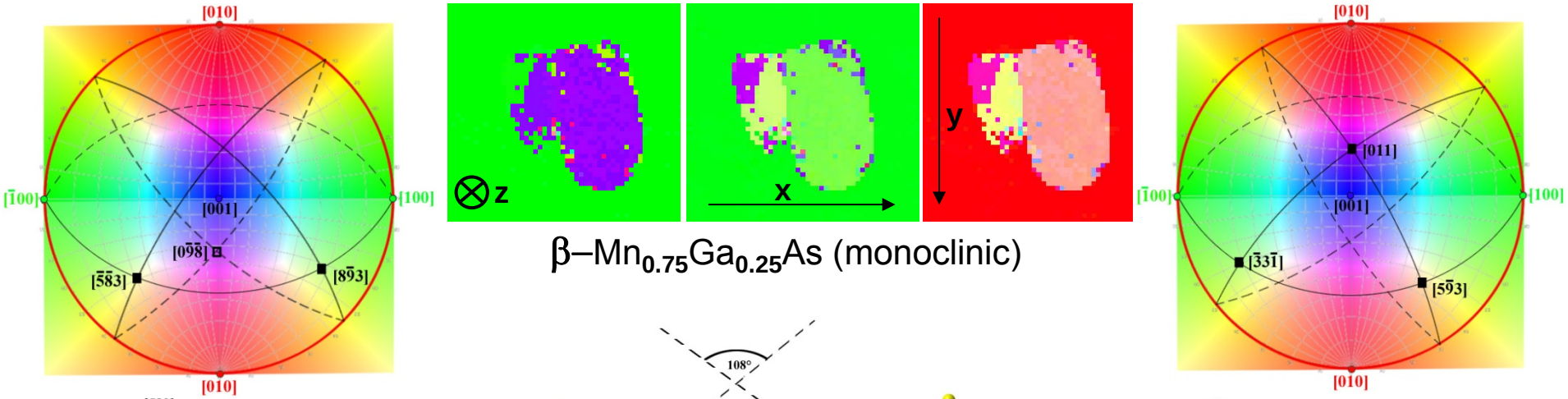

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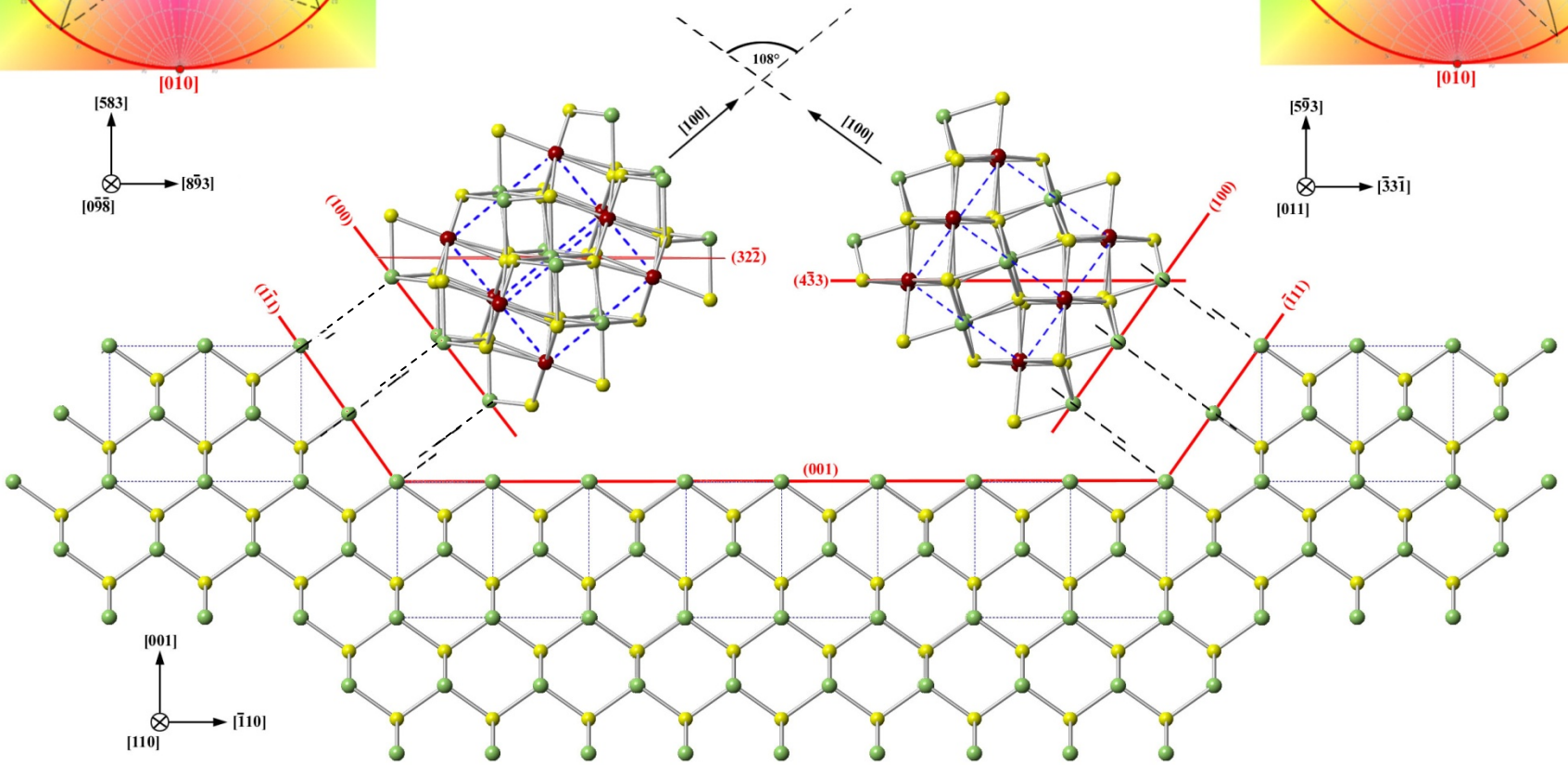

(Mn,Ga)As - Conclusion

Materials analysis:

- Chemical composition of crystallites as found by EDXS: **$Mn_{0.75}Ga_{0.25}As$**
- Formation of **superstructure** in $Mn_{0.75}Ga_{0.25}As$ as revealed by PED
- **Proposal of structure models** of a trigonal phase (derived from the hexagonal α-phase of $Mn_{0.75}Ga_{0.25}As$) and of a monoclinic phase (derived from the orthorhombic β-phase of $Mn_{0.75}Ga_{0.25}As$)
- Phase and orientation mapping
  - Identification of **two phases** within the crystallites:
    monoclinic β-$Mn_{0.75}Ga_{0.25}As$
    hexagonal α-$Mn_{0.75}Ga_{0.25}As$
  - **Oriented growth** of (Mn,Ga)As with respect to the GaAs matrix
  - **Multi-grain** growth found for individual crystallites

Acknowledgements

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Thank you

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