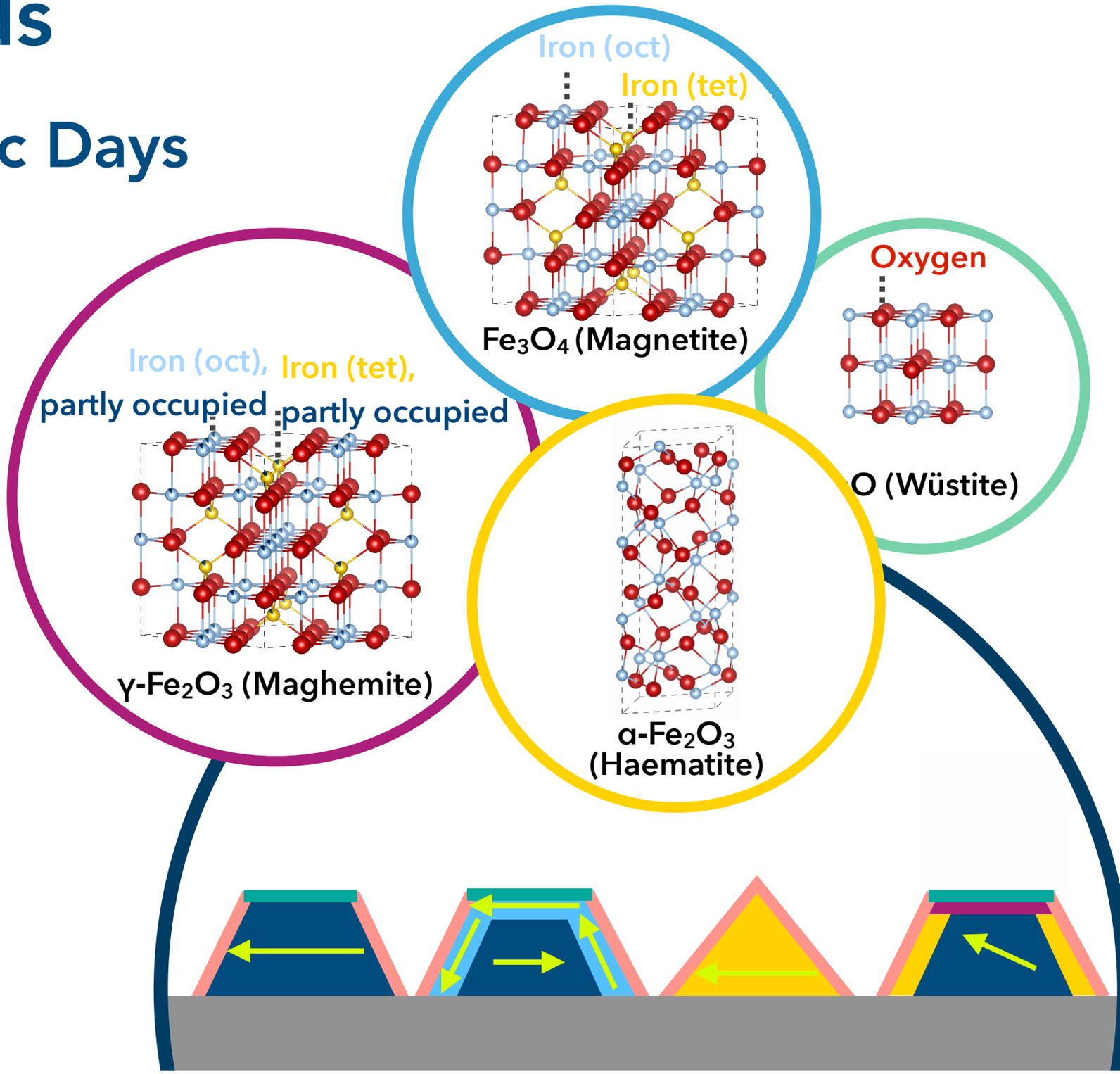
Growth and redox properties of Fe_xO_y nanoislands

JCNS-2 PhD & Postdoc Days
Spring 2024



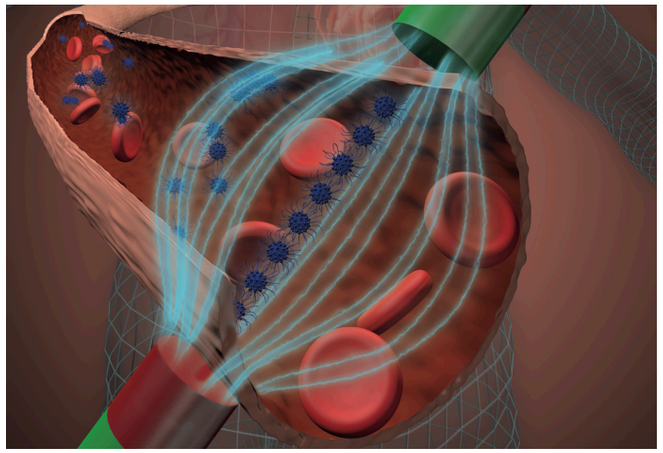
Steffen Tober

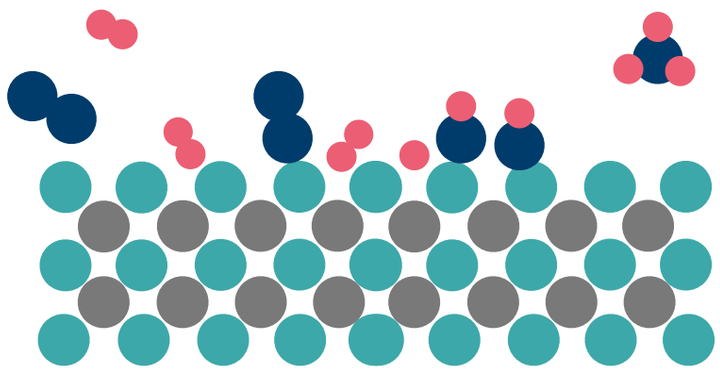
February 15th 2024

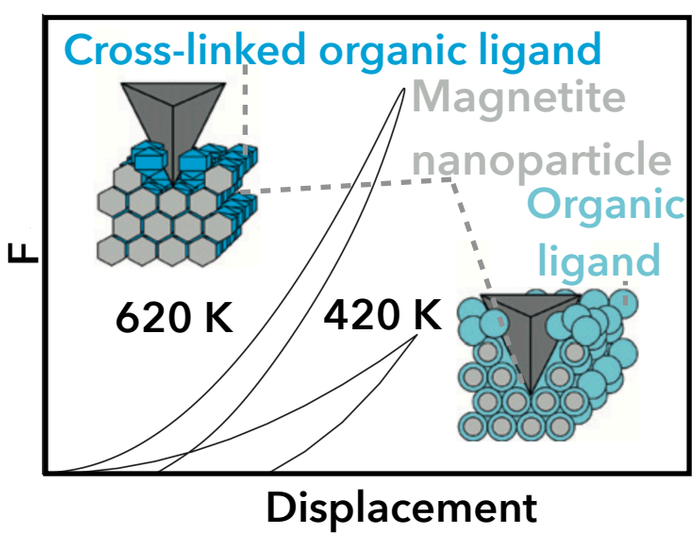
Jülich Centre for Neutron Science

Iron Oxide Nanostructures

Applications







Medicine

- Contrast agent for magnetic imaging
- Cancer treatment by hyperthermia

Catalyst or catalyst precursor

- Precursor for Haber-Bosch synthesis
- Active component in water-gas shift catalysts

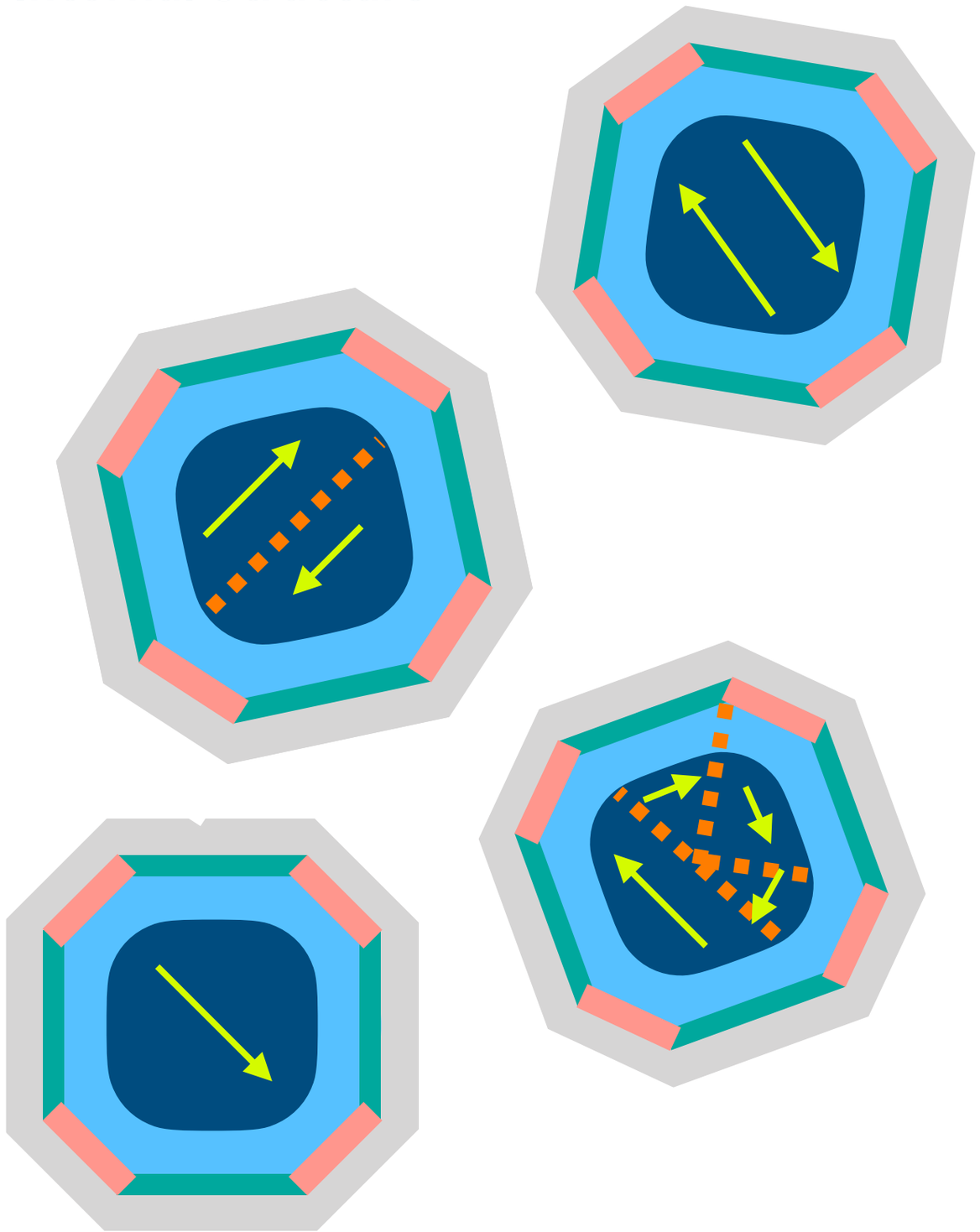
Materials science

- Nanoscale organic/inorganic building blocks in hard yet tough hierarchical materials

Nandakumaran *et al. Adv. Mater.* **33**, 2170189 (2021)
redrawn from Ind. Eng. Chem. Res. **60**, 18560 (2021)
modified from Dreyer *et al.*, Nat. Mater. **15**, 522 (2016)

Iron Oxide Nanoparticles

Internal Structure



Complex internal structure

- Facets with deviating properties
- Composition gradients in the particle
- Different oxide phases
  (FeO, Fe_3O_4, γ-Fe_2O_3 and α-Fe_2O_3)
- Grain boundaries
- Surface interaction with ligands

➡ Influecences magnetic structure

How to reduce the *number* and *interdependence* of these factors?

based on Zákutná *et al*, Phys. Rev. X. **10**, 031019 (2020)

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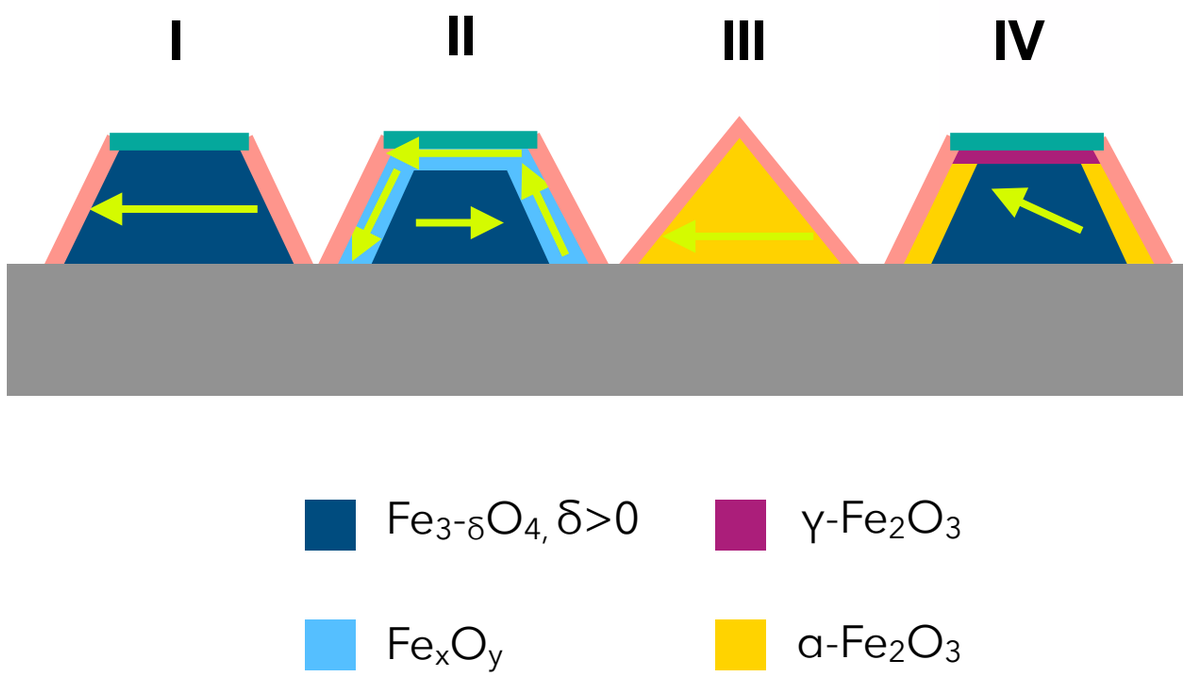
Epitaxial Fe_xO_y nanoislands

A model system with reduced complexity



MBE deposition

✓Well-defined crystal structure

✓Identical crystallographic orientation

✓Well-defined facets

- High polydisperisty
- Disorder at interfaces of nanoislands

➡ Modelling with layer approach

➡ Facet sensitive measurements

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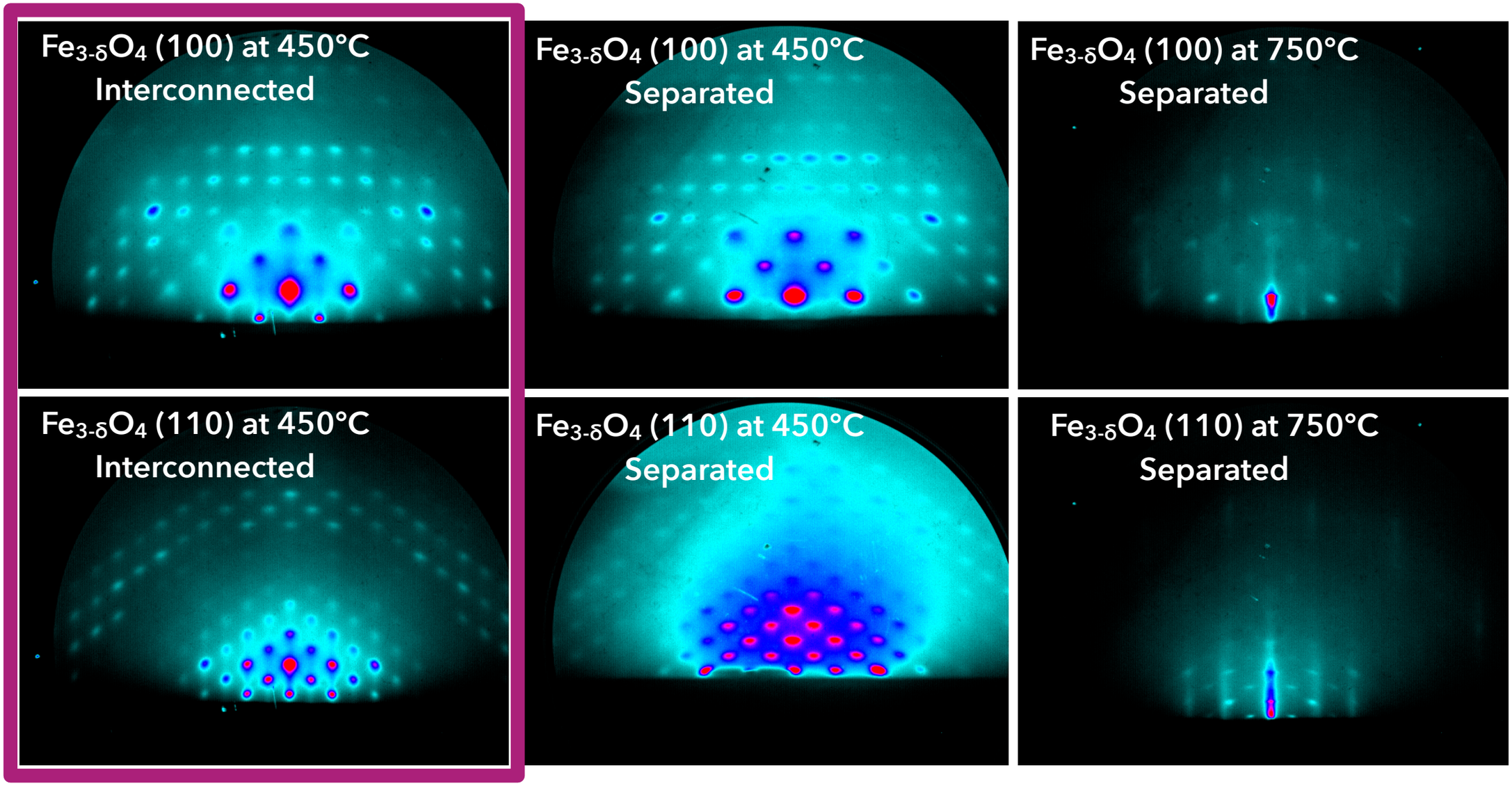
Growth and structure by RHEED

Temperature dependence, growth in $1 \cdot 10^{-6}$ torr O_2



- Growth of well-defined, crystalline islands by iron deposition on $SrTiO_3$
- Cubic structures at 450 °C, yet unknown structure at 750 °C

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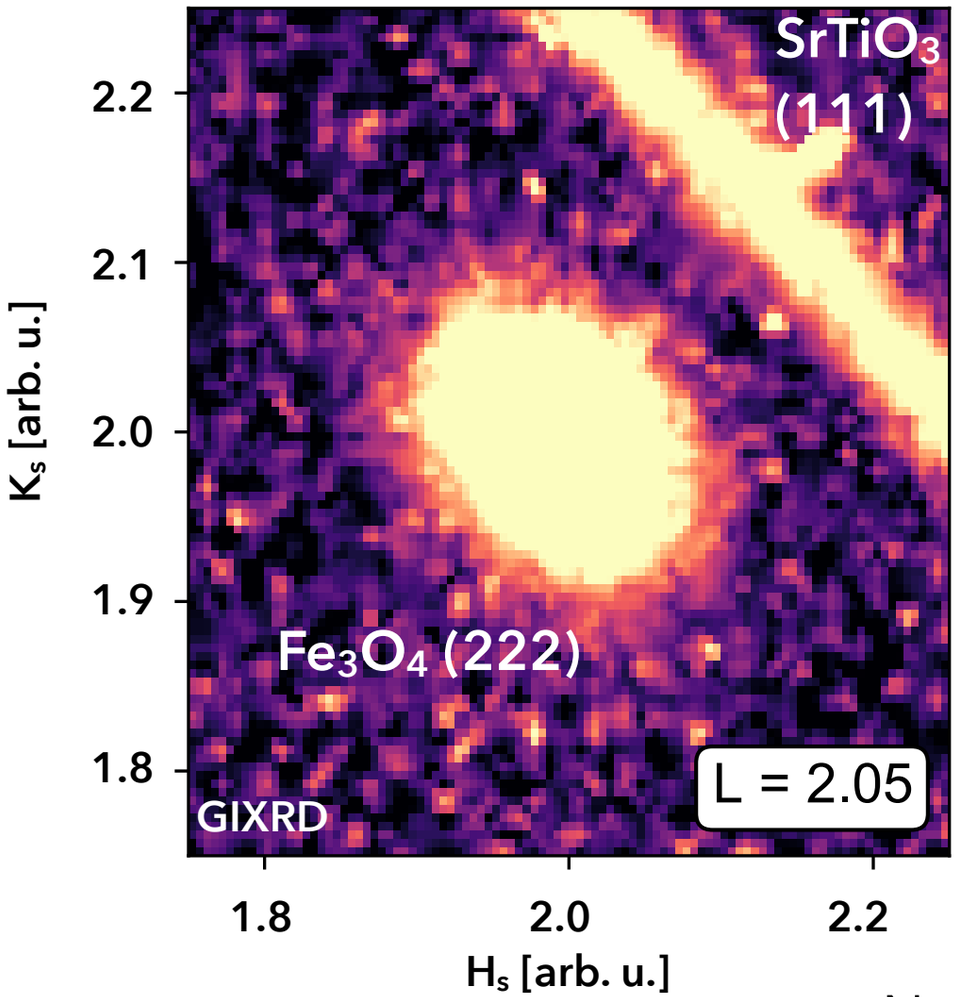
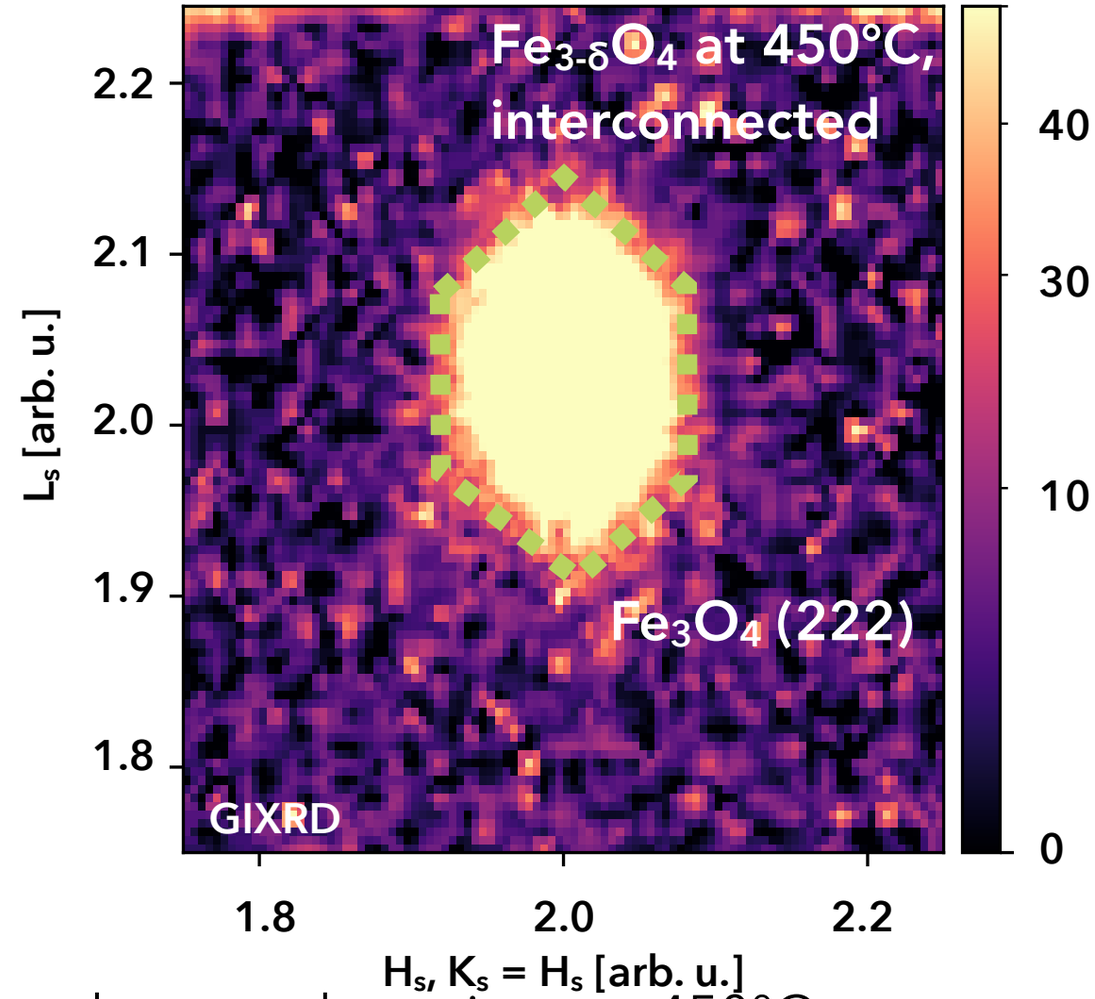
Structural Characterisation

Interconnected islands grown at 450°C

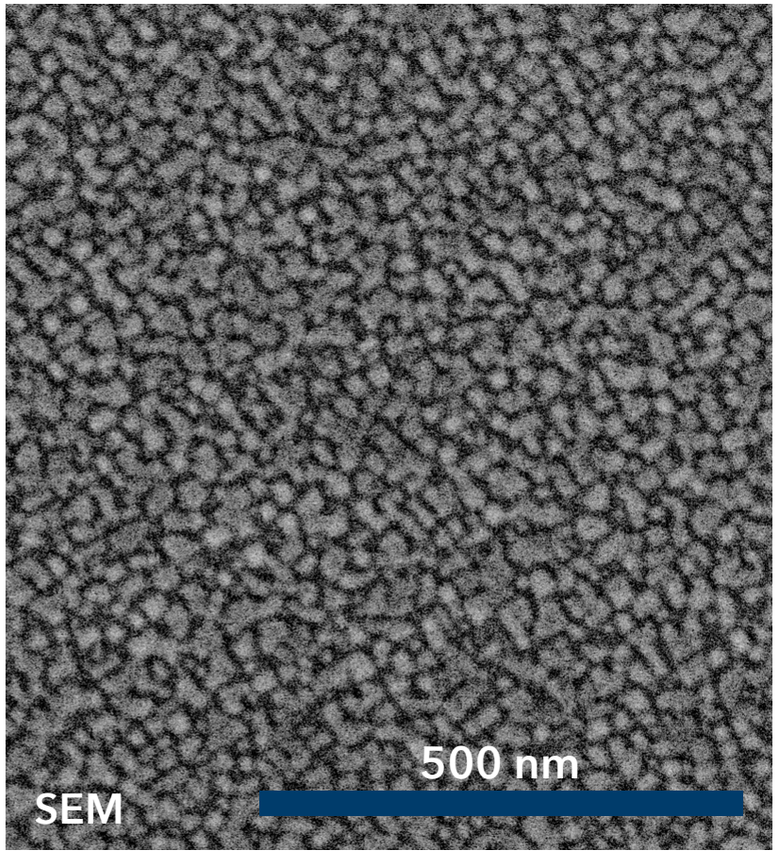


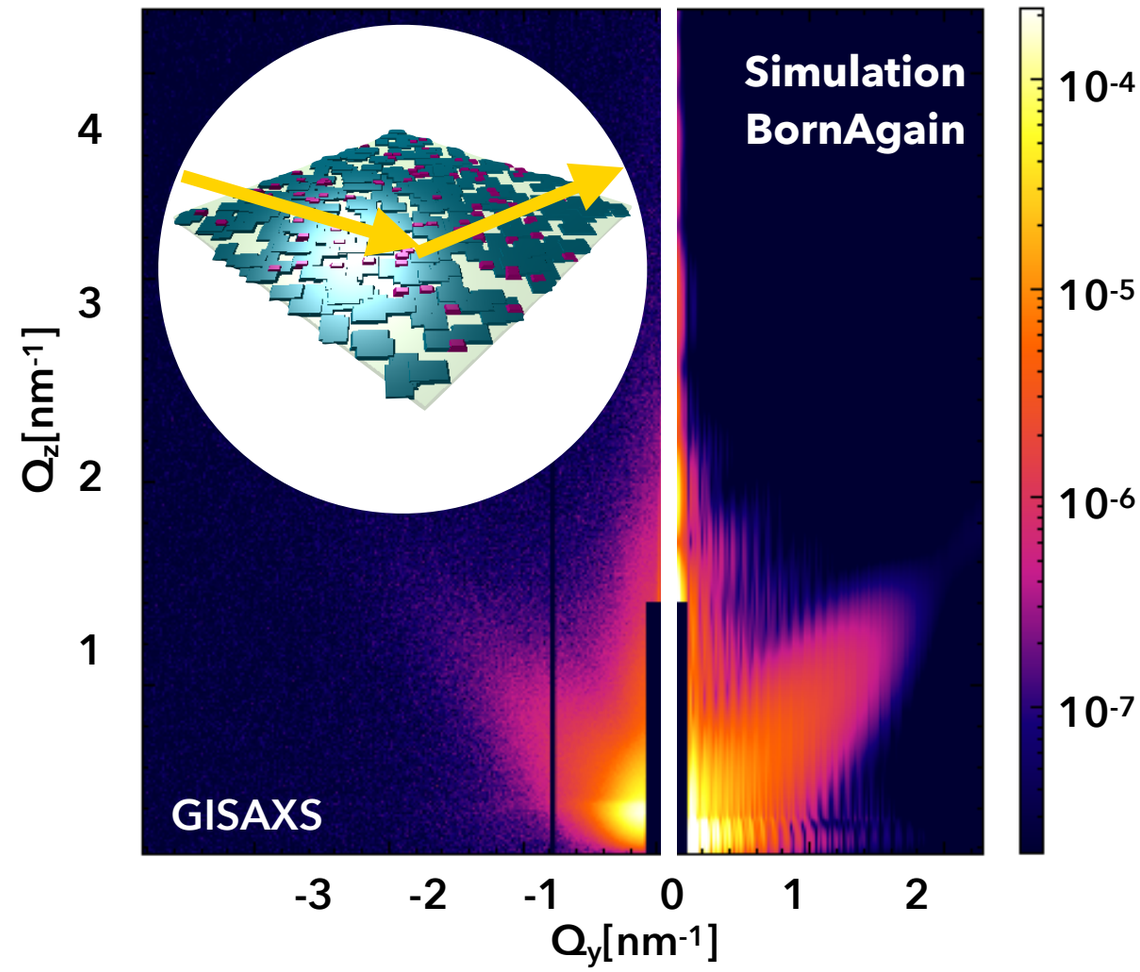


- Nanoislands with cube-on-cube epitaxy at 450°C
- crystalline island diameter ~14 nm, height 8-12 nm
- Weak facet signal for Fe_3O_4(100) top- and Fe_3O_4(111) side facets

Shape

Interconnected islands grown at 450°C





- Formation of polydisperse rectangular islands
- Edges along $SrTiO_3$ (110) ,Fe_3O_4 (111) side facets
- Height ~10 nm, lateral dimensions 40-120 nm

➡Interconnected islands with multiple nuclei

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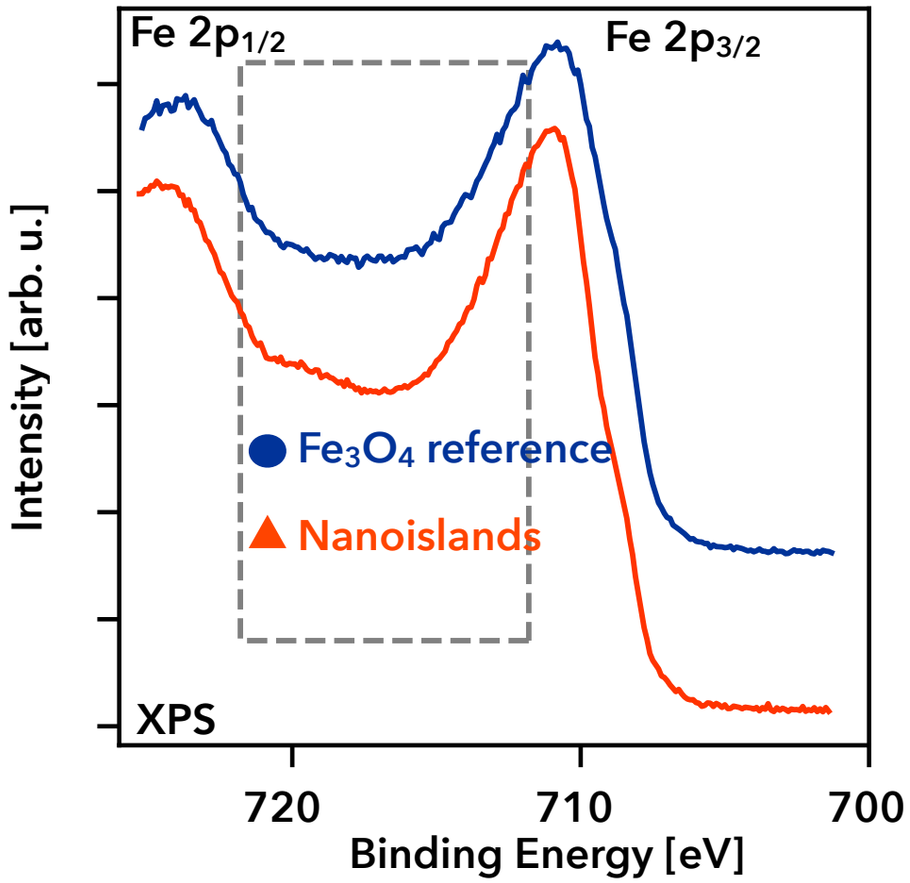
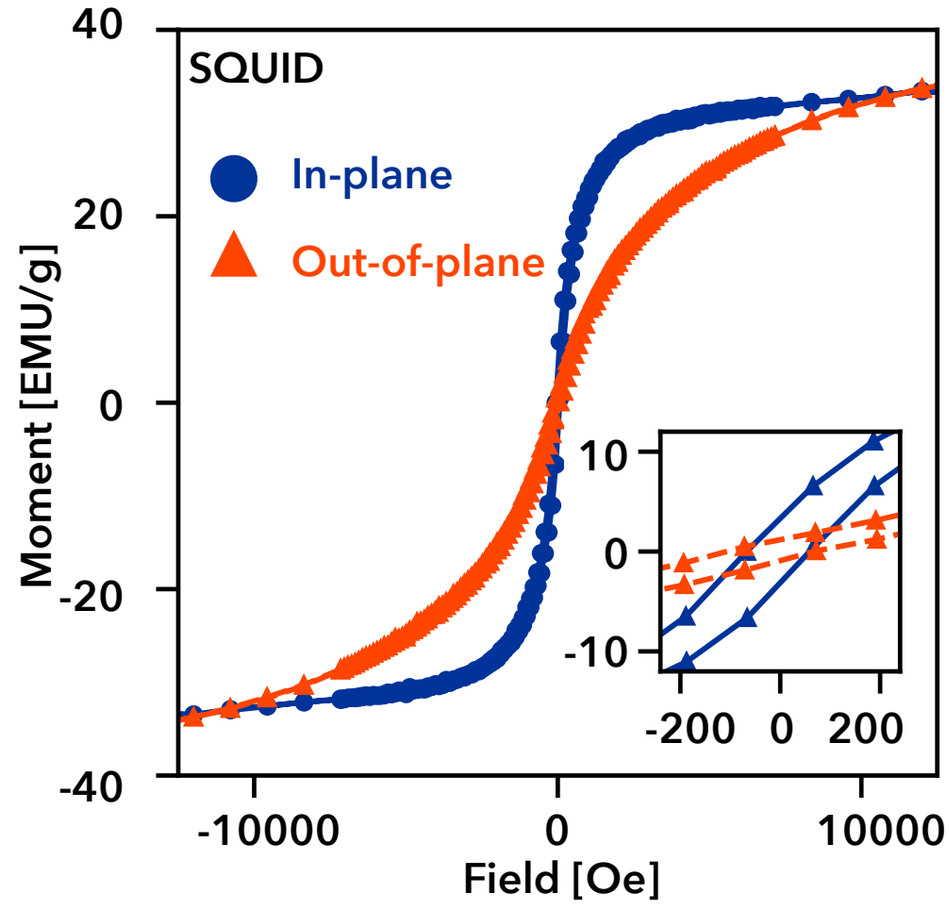
Composition and magnetic properties

Interconnected islands grown at 450°C



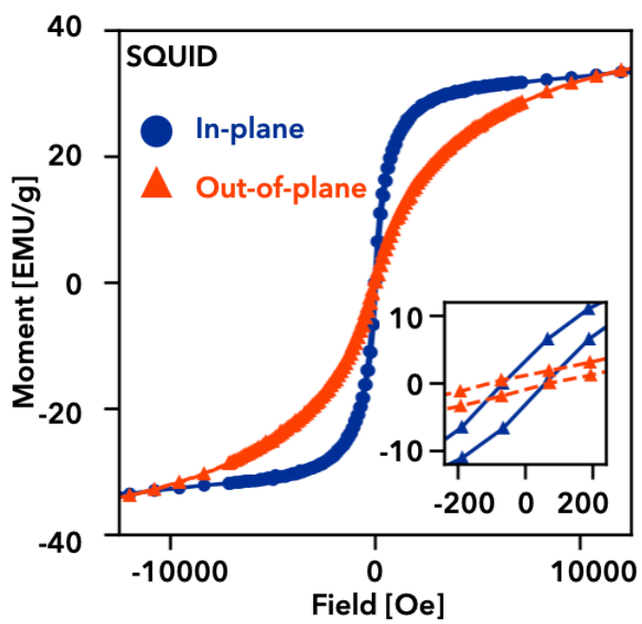


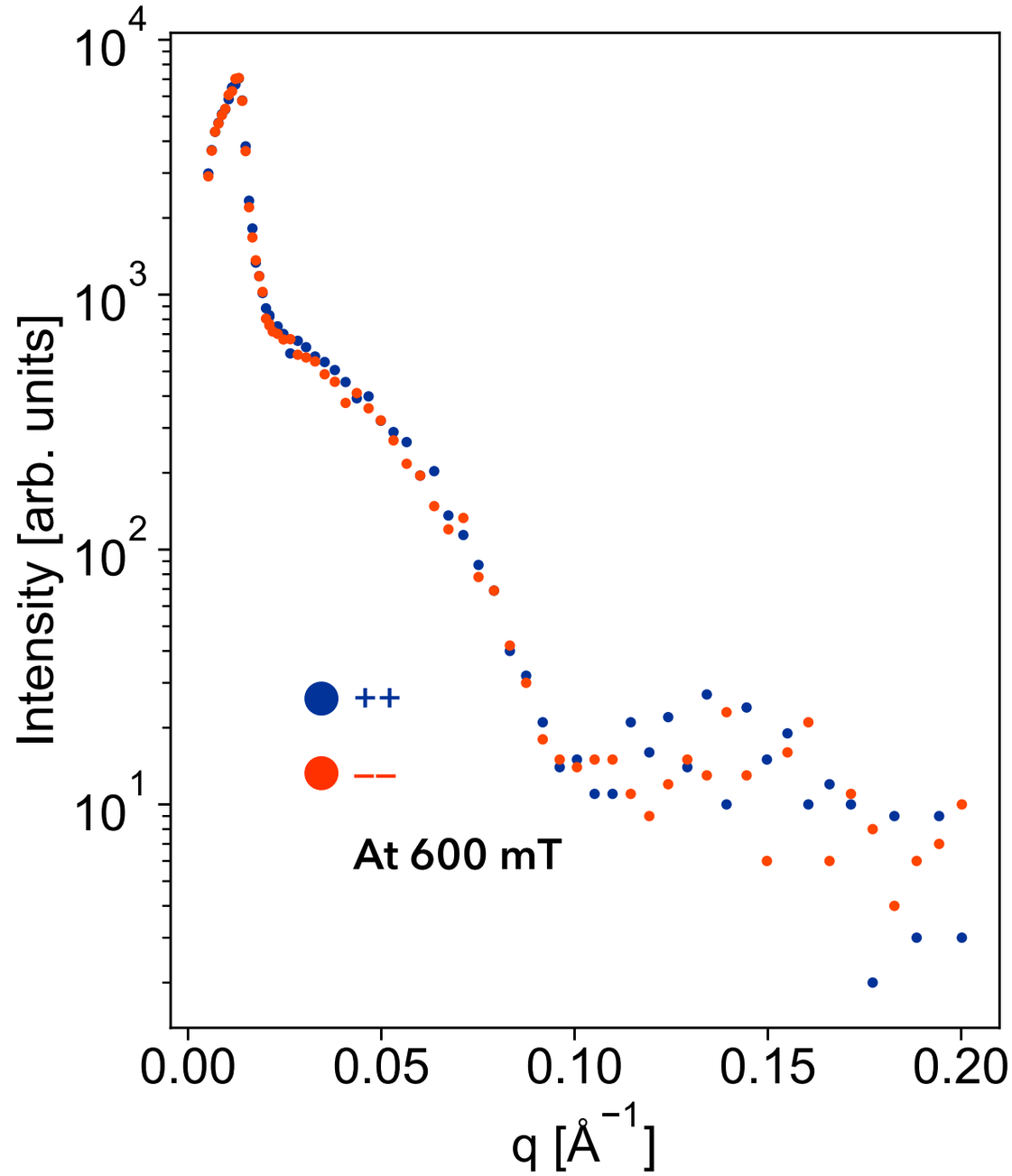
- $Fe_{3-\delta}O_4$ with high cation deficit after air transfer
- Ferro/ferrimagnetic oxide
- Harder hysteresis in in-plane direction due to aspect ratio

PNR at SuperADAM

Magnetic depth profiling

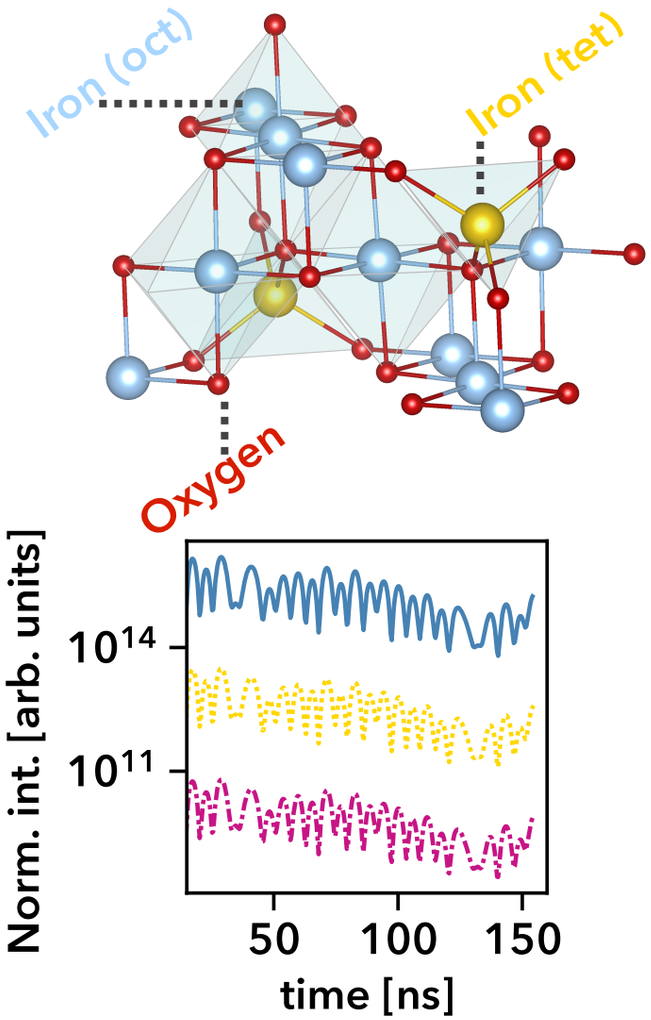
- Distinct oscillations visible
- ➡ Thin-film approach could work
- Slight splitting at 600 mT, no splitting at 0 mT or 200 mT
- No obvious remanence after returning to 0 mT

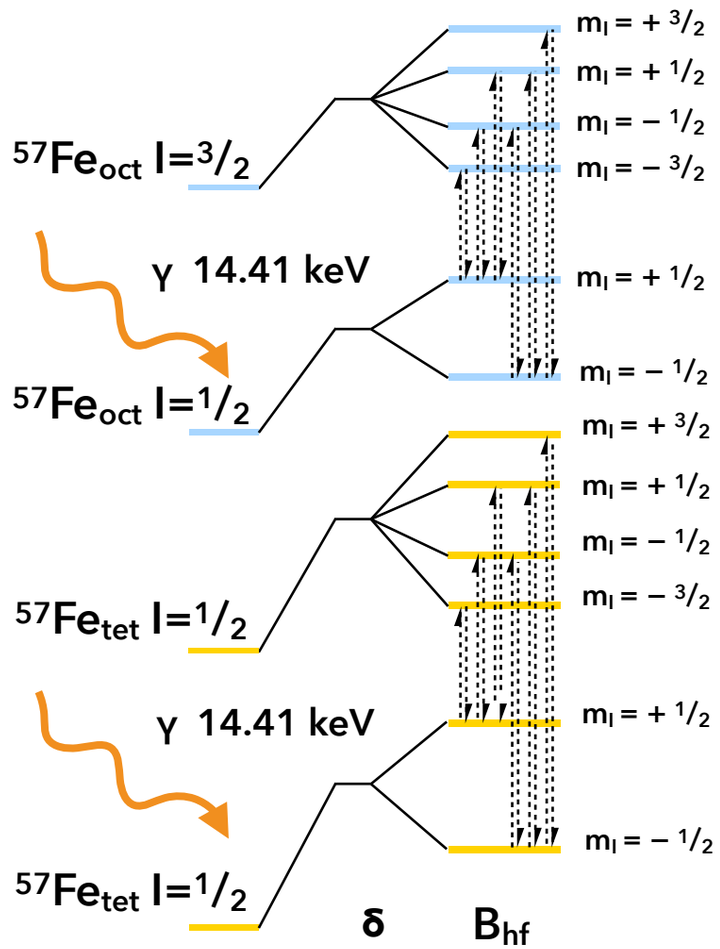




Nuclear forward scattering

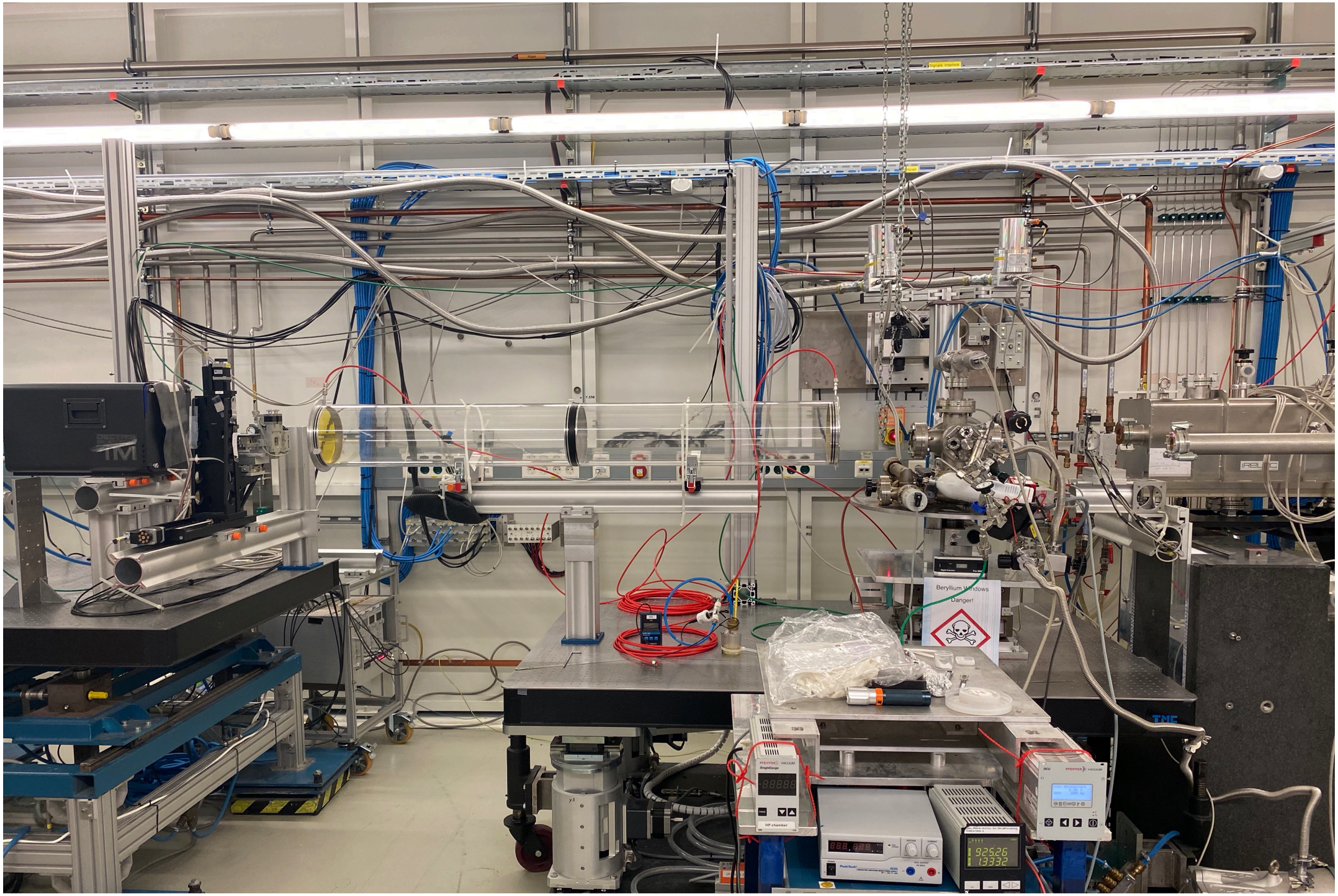
Near-surface composition and surface magnetisation





- Mössbauer resonance of ^{57}Fe excited at 14.41 keV
- Excited states split due to hyperfine interactions
- Temporal evolution of decay of excited nuclei measured as time spectrum
- Depends on composition and thickness

UHV chamber at P01

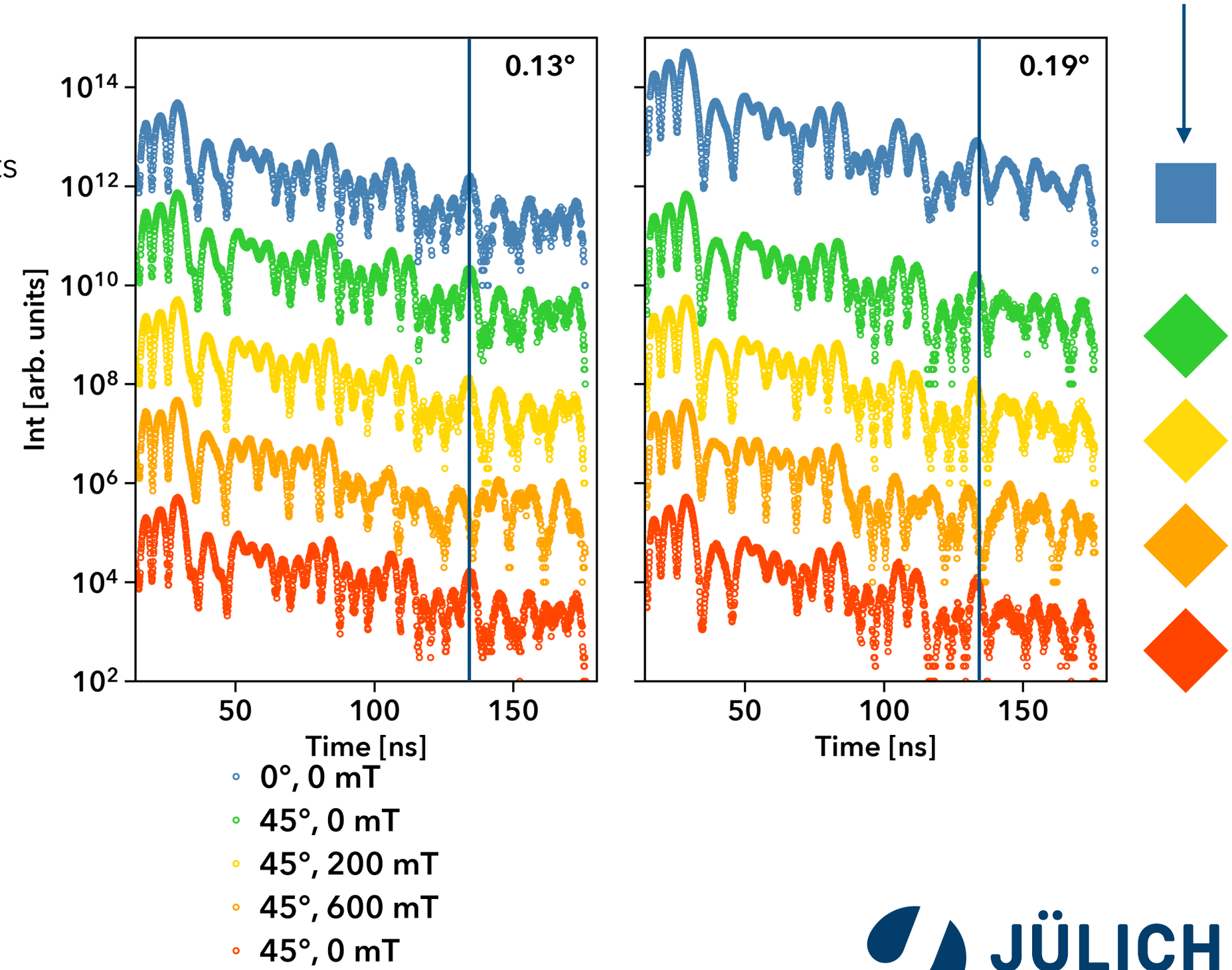


Iron Oxide Nanoislands

Field dependence

PETRA III.

- In-plane random distribution of the magnetic moments
- Hyperfine field increases with applied magnetic field
- No obvious remanence



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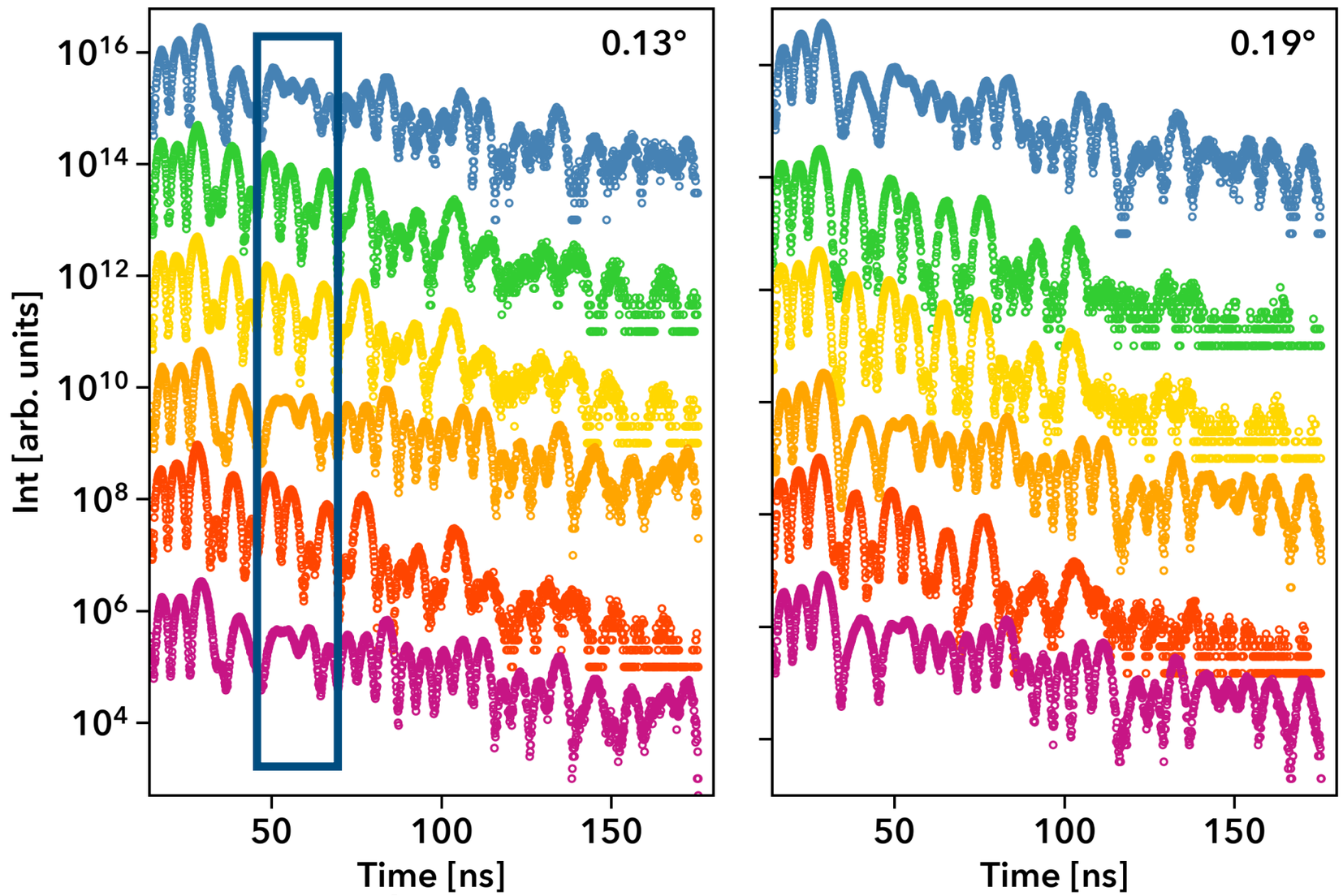
Iron Oxide Nanoislands

Redox behaviour

PETRA III.

- Notable change of hyperfine interactions by O_2 annealing
- New phase stable in UHV
- Partly reversible by UHV annealing
- Change throughout the probed depth



- Initial
- After 450°C in 5×10^{-5} mbar O_2 in O_2
- After 450°C in 5×10^{-5} mbar O_2 in UHV
- After 550°C in UHV
- After 450°C in 1 mbar O_2 in O_2
- After 550°C in UHV

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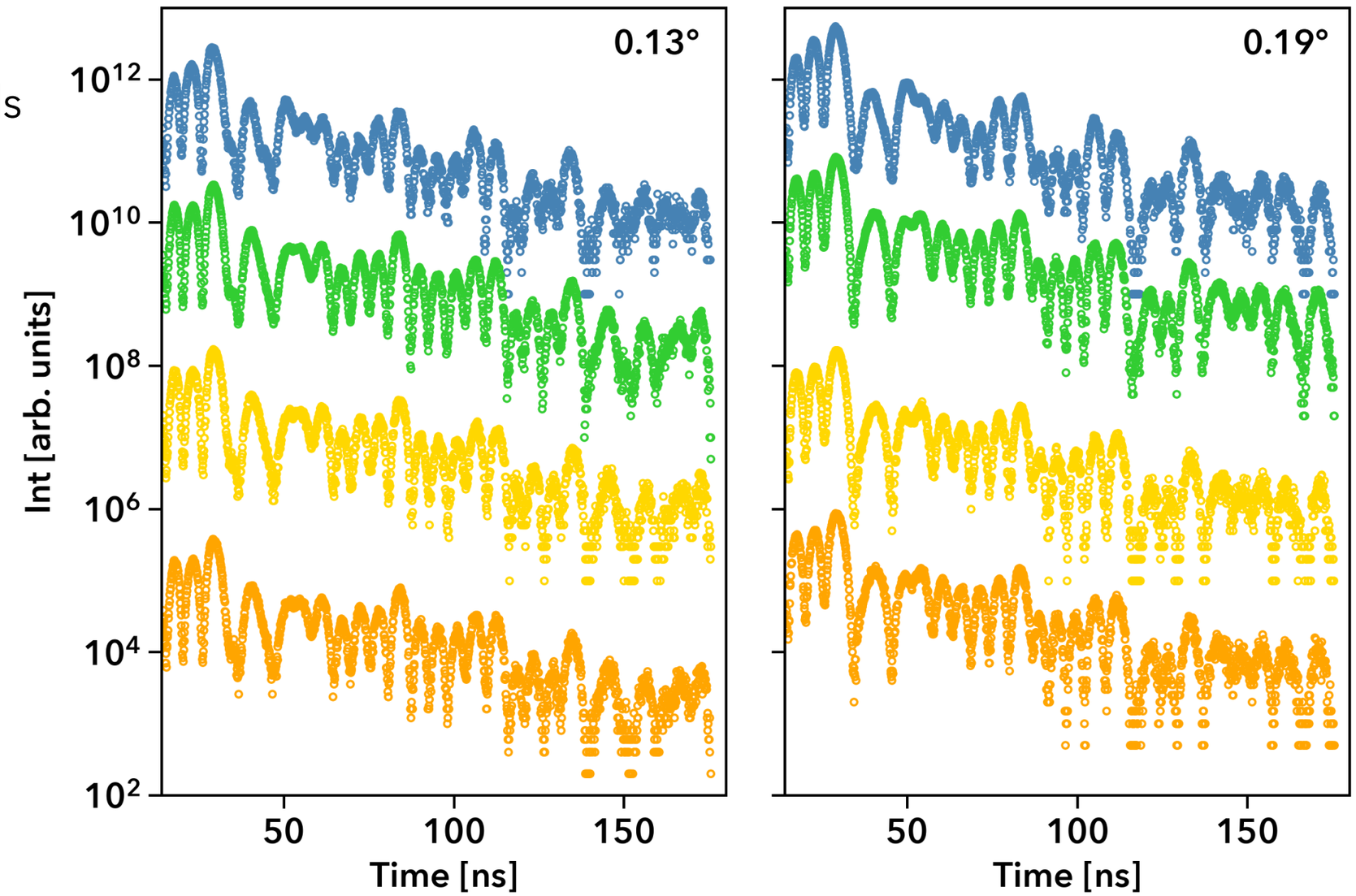
Iron Oxide Nanoislands

Redox behaviour

PETRA III.

- H_2 annealing to reduce nanoislands after annealing/ oxidation experiments
- No visible change after H_2 annealing



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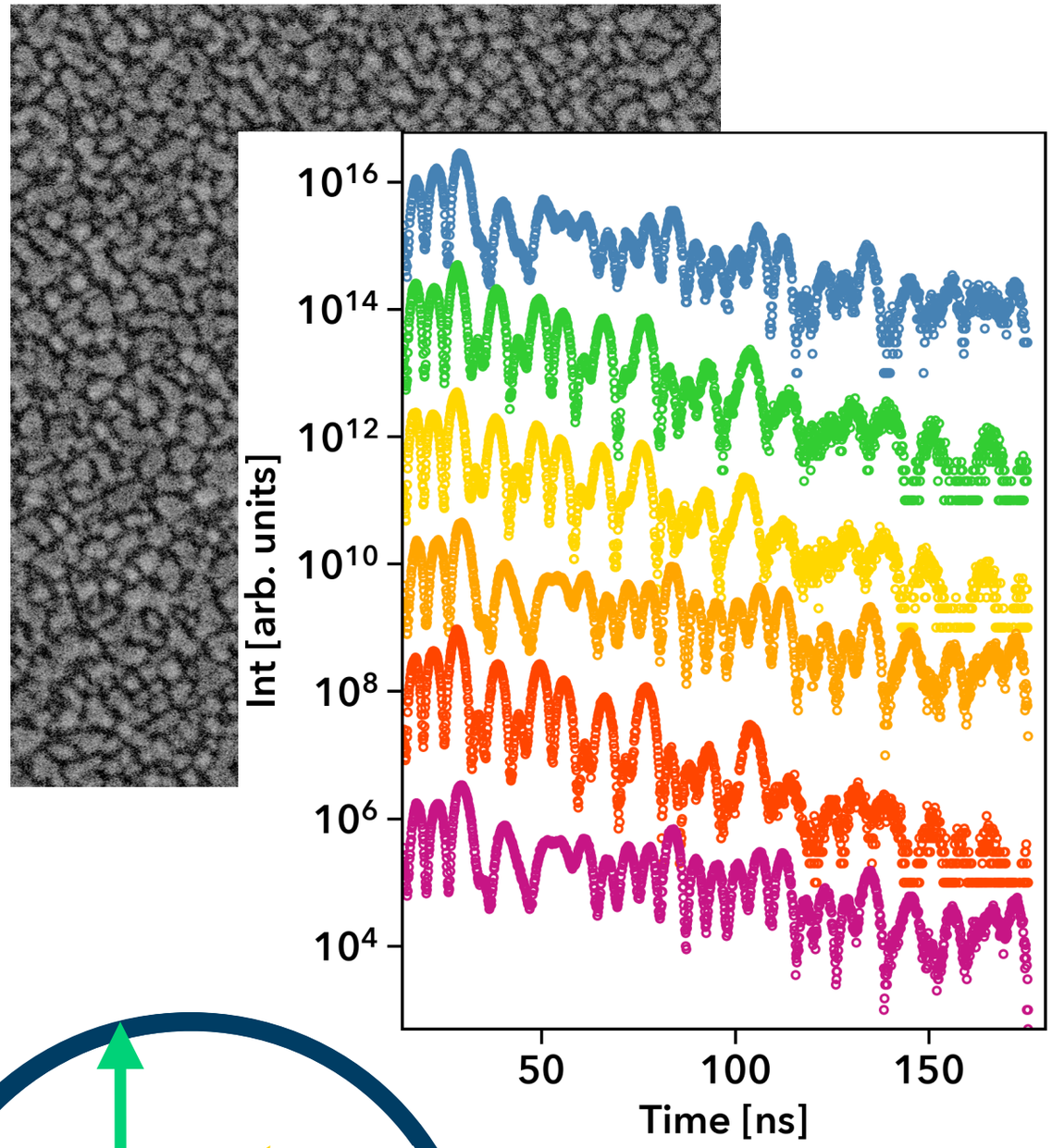
Summary and Outlook

Probing the properties of magnetic nanostructures



- Regular $Fe_{3-\delta}O_4$ islands with cube-on-cube epitaxy on $SrTiO_3(100)$
- Preferentially (100)- and (111) facets
- Weak ferrimagnetism with in-plane random orientation of magnetic moments
- Partly reversible redox behaviour
- Inert against H_2 reduction
- TEM charactersiation planned

Thank you!

JCNS 2
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Emmanuel Kentzinger
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PETRA III P01
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Deepak Prajapat

ILL SuperADAM
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