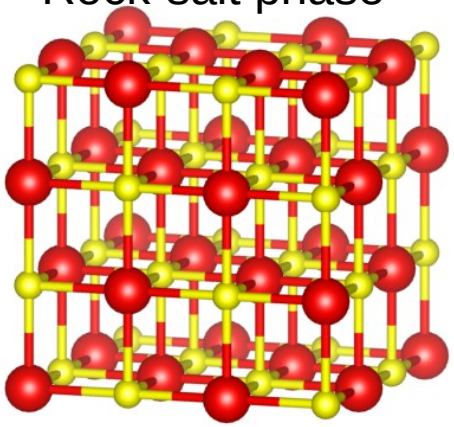
Growth of cobalt iron oxides on Ru(0001) by real-time LEEM and real-time PEEM

Juan de la Figuera

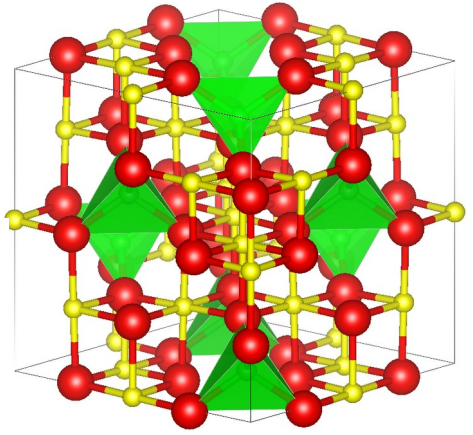
Cobalt-iron oxides

- Cobalt iron oxides show a mixture of spinel and rock salt phases
  - Rock salt (aka halite) phases: only octahedral sites, occupied by divalent cations. **Antiferromagnetic.**
  - Spinel phases: octahedral and tetrahedral sites, with divalent and trivalent cations. Mostly **ferrimagnetic**, some antiferromagnetic

Rock-salt phase

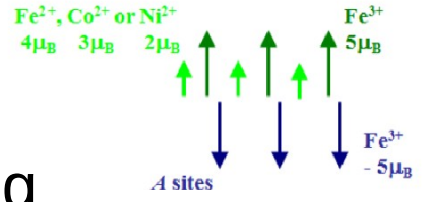


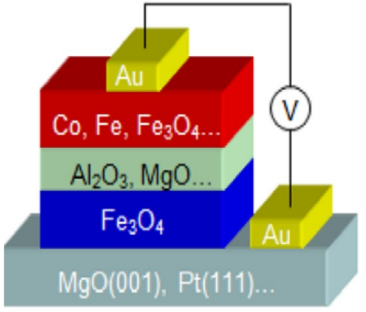
Spinel phase



They can be used for:

- Spin filters
- Conductive *or* insulating ferrimagnetic layers





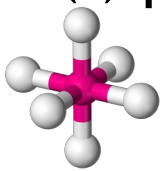
Moussy, J.Phys.D 46(2013) 143001

Magnetism in mixed cobalt and iron oxides

Spinel phases

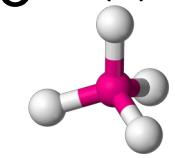
Co_3O_4:
$(Co^{2+})[Co^{3+}]_2O_4$
Insulating **AFM**
T_{Neel}=40 K
Normal Spinel

$Co^{3+} \leftrightarrow Fe^{3+}$



$CoFe_2O_4$:
$(Fe^{3+})[Co^{2+}Fe^{3+}]_2O_4$
Insulating **Ferrim**
T_{Curie}=800 K
Inverse Spinel

$Co^{2+} \leftrightarrow Fe^{2+}$

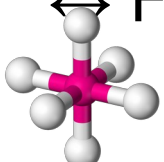


Fe_3O_4:
$(Fe^{3+})[Fe^{2+}Fe^{3+}]_2O_4$
Conducting **Ferrim**
T_{Curie}=850 K
Inverse Spinel
Half-metal
Verwey Transition

Rock-salt phases

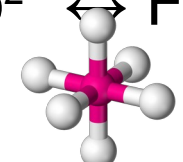
CoO:
Insulating **AFM**
T_{Neel}=300 K
Mott insulator

$Co^{2+} \leftrightarrow Fe^{2+}$



$Co_xFe_{1-x}O$:
Insulating, ??
T_{neel}= ?? K

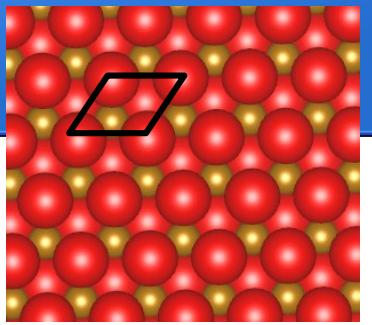
$Co^{2+} \leftrightarrow Fe^{2+}$



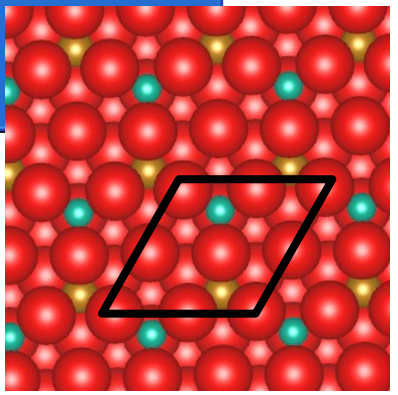
FeO:
Insulating **AFM**
T_{Neel}= 200 K
Mott insulator?

Spinel vs rock-salt along the (111) orientation

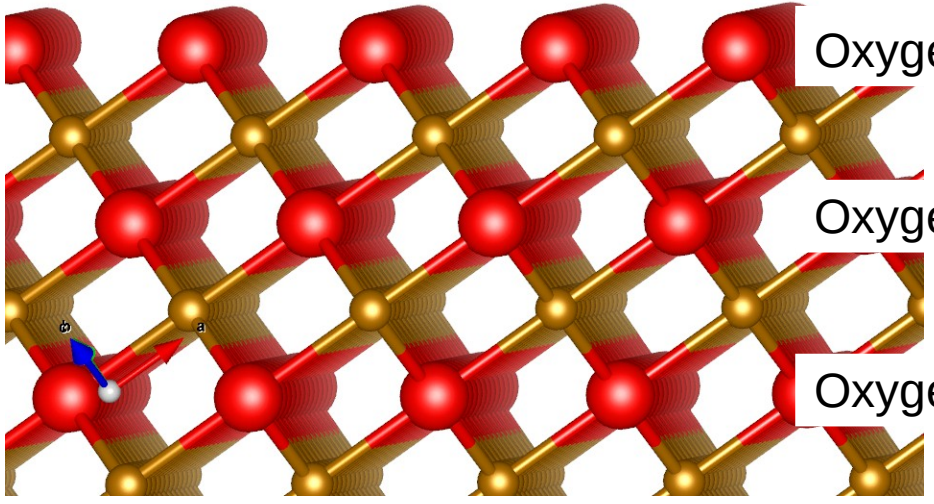
Red- oxygen anions
Yellow- Fe in octahedral sites
Blue- Fe in tetrahedral sites



Rock-salt unit cell



Full spinel unit cell

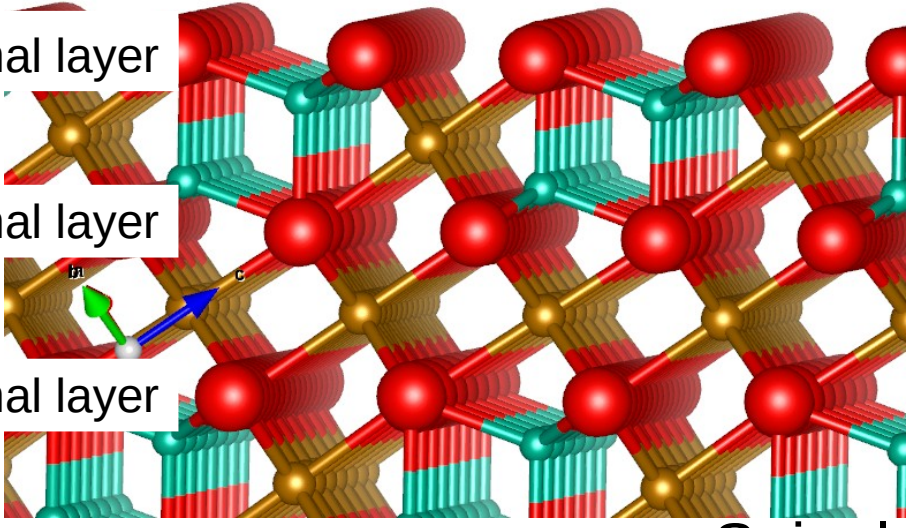


Rocksalt

Oxygen hexagonal layer

Oxygen hexagonal layer

Oxygen hexagonal layer

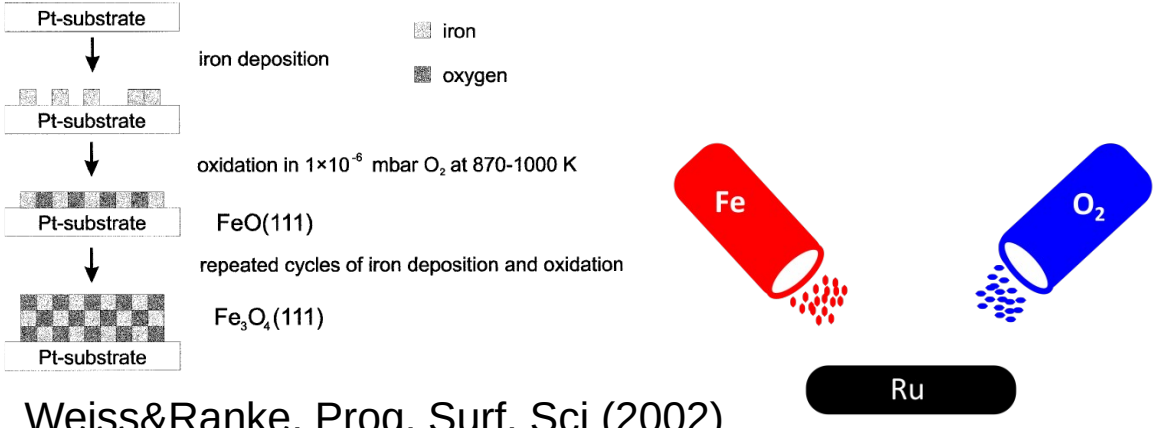


Spinel

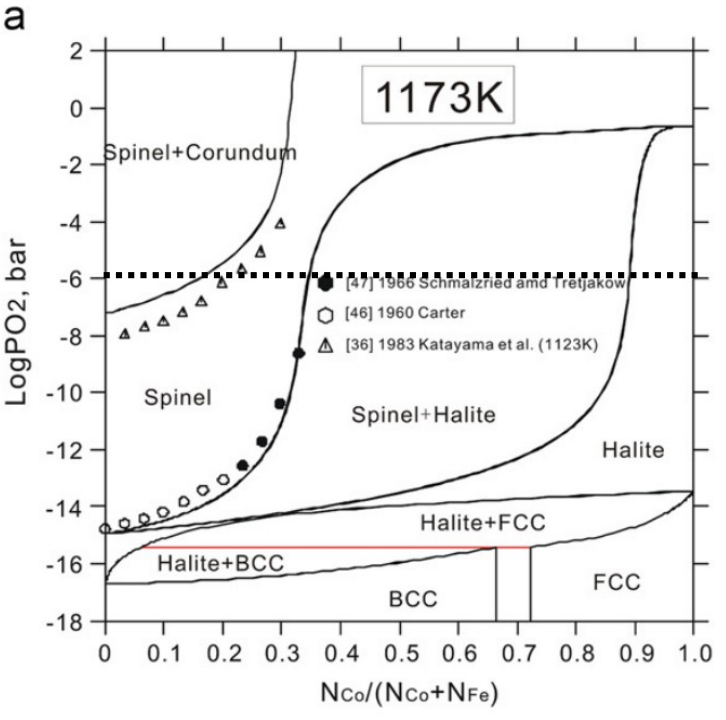
Easily distinguishable by LEED

Growing oxides in UHV: lets look!

- Two methods used in the field:
  - Sequential metal growth and oxidation
    - Oxidation (O_2) while depositing



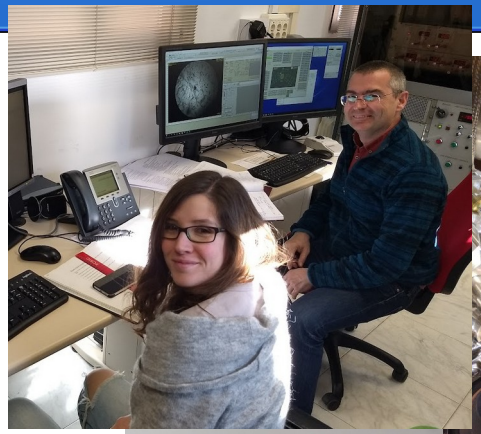
Weiss&Ranke, Prog. Surf. Sci (2002)

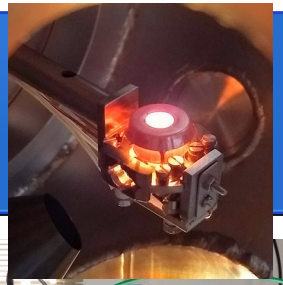


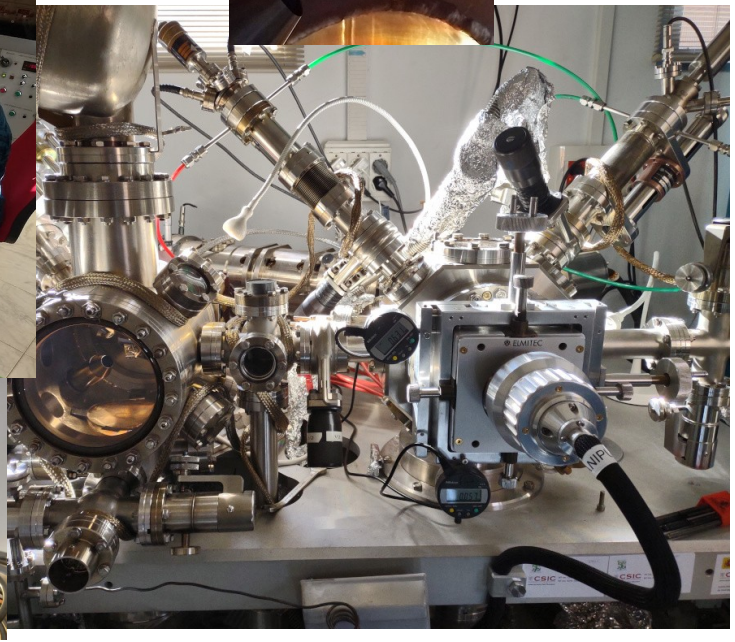
Zhang & Chen, CALPHAD 41 (2013) 76

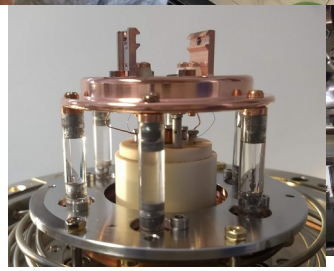
In LEEM we can image in p<10^{-5} Torr O_2

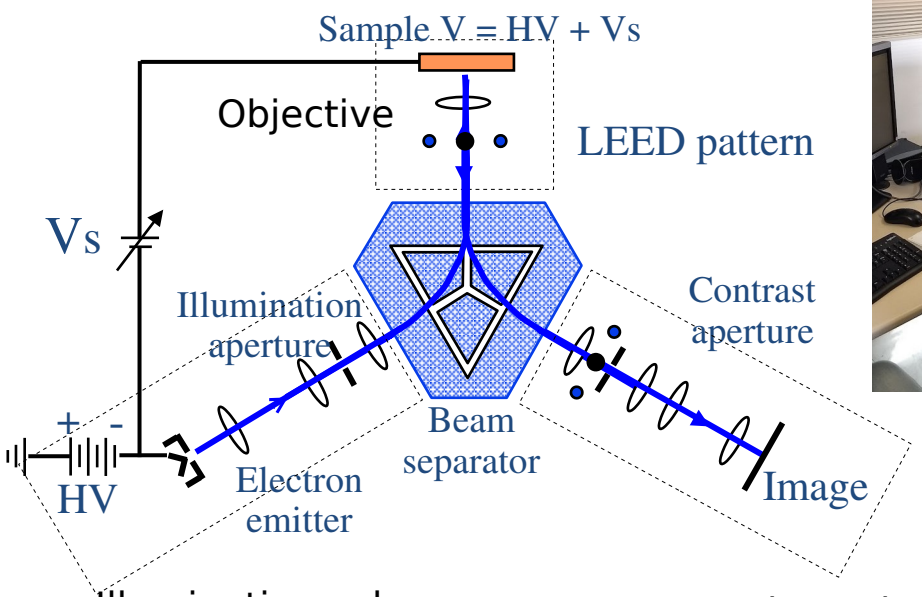
Low-Energy Electron Microscopy

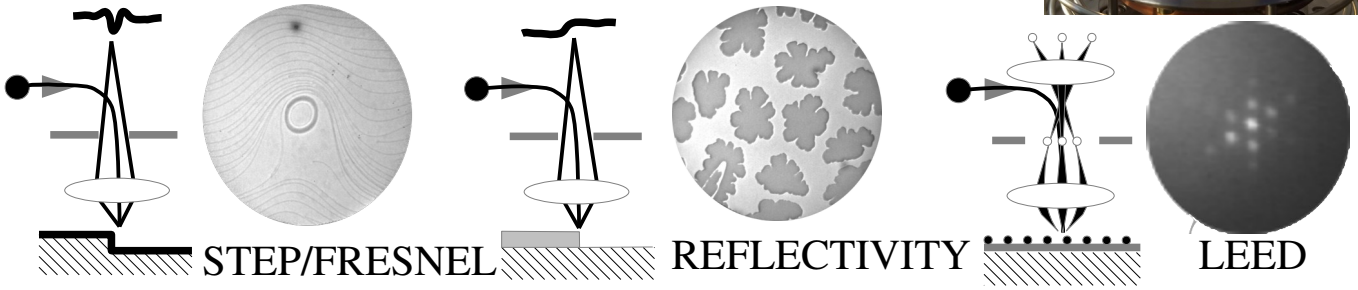










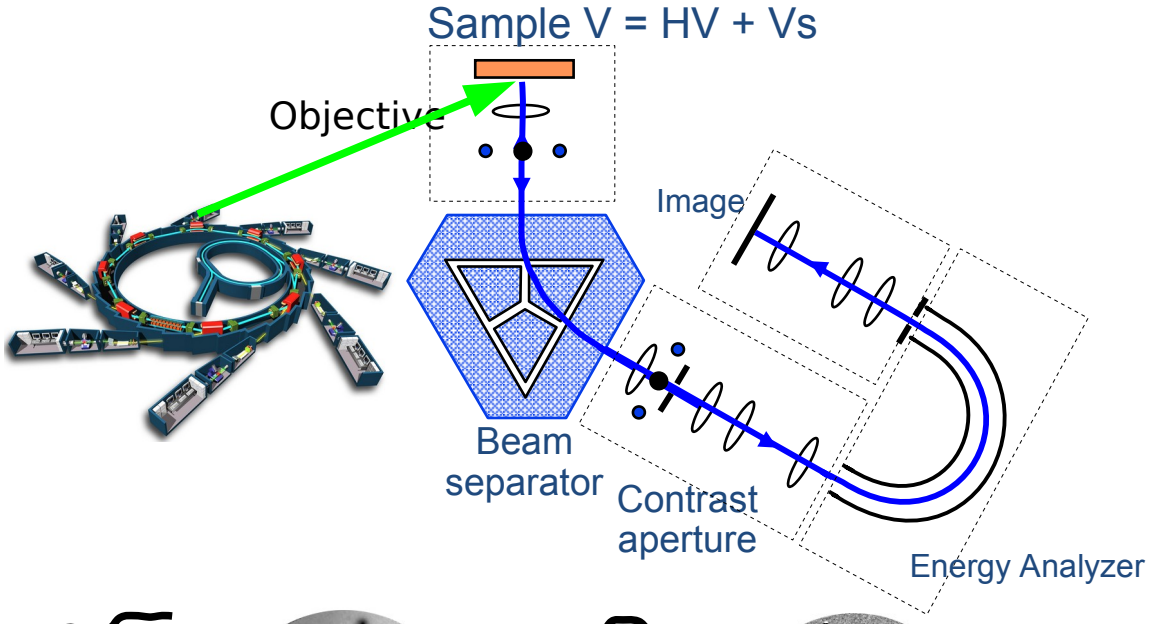


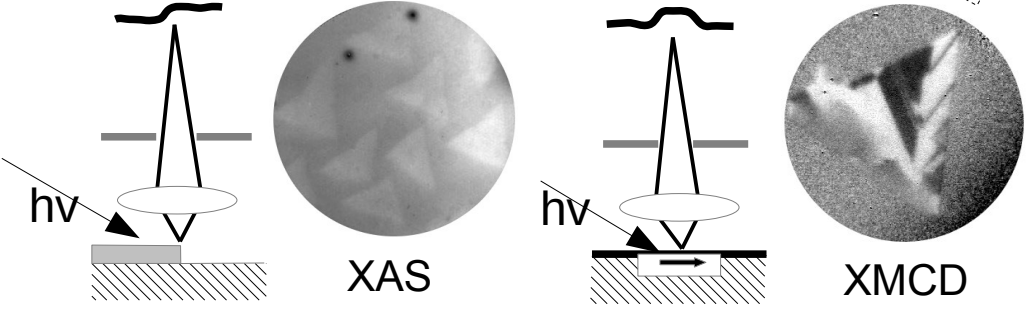
Elmitec III LEEM at
Instituto de Química Física
“Rocasolano”, CSIC (Madrid)

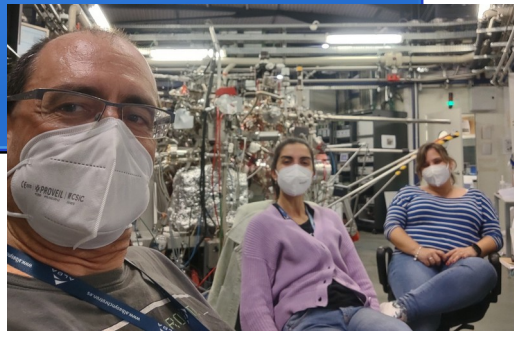
http://labrg.iqfr.csic.es

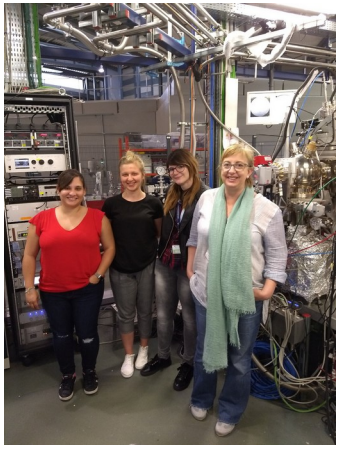
Elmitec SPLEEM, CIRCE Beamline

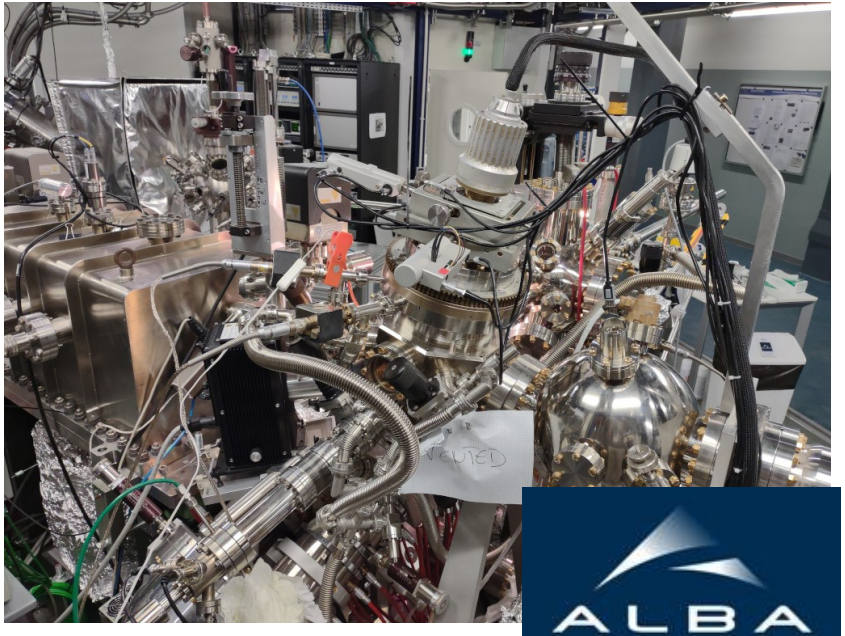
Adding x-rays: PEEM





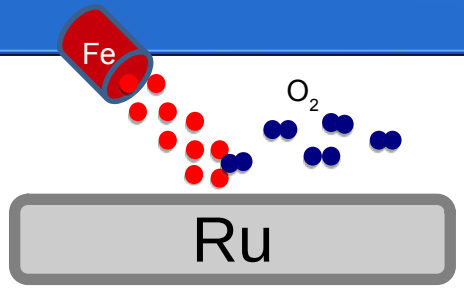






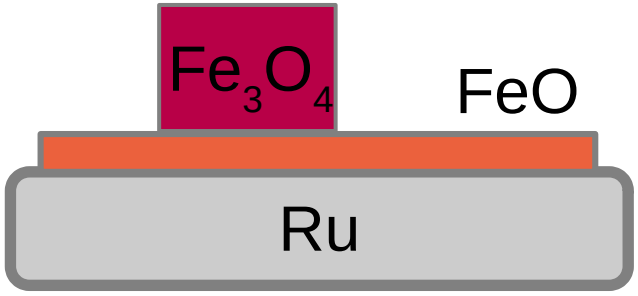
ALBA

Growth of magnetite crystals on Ru(0001)



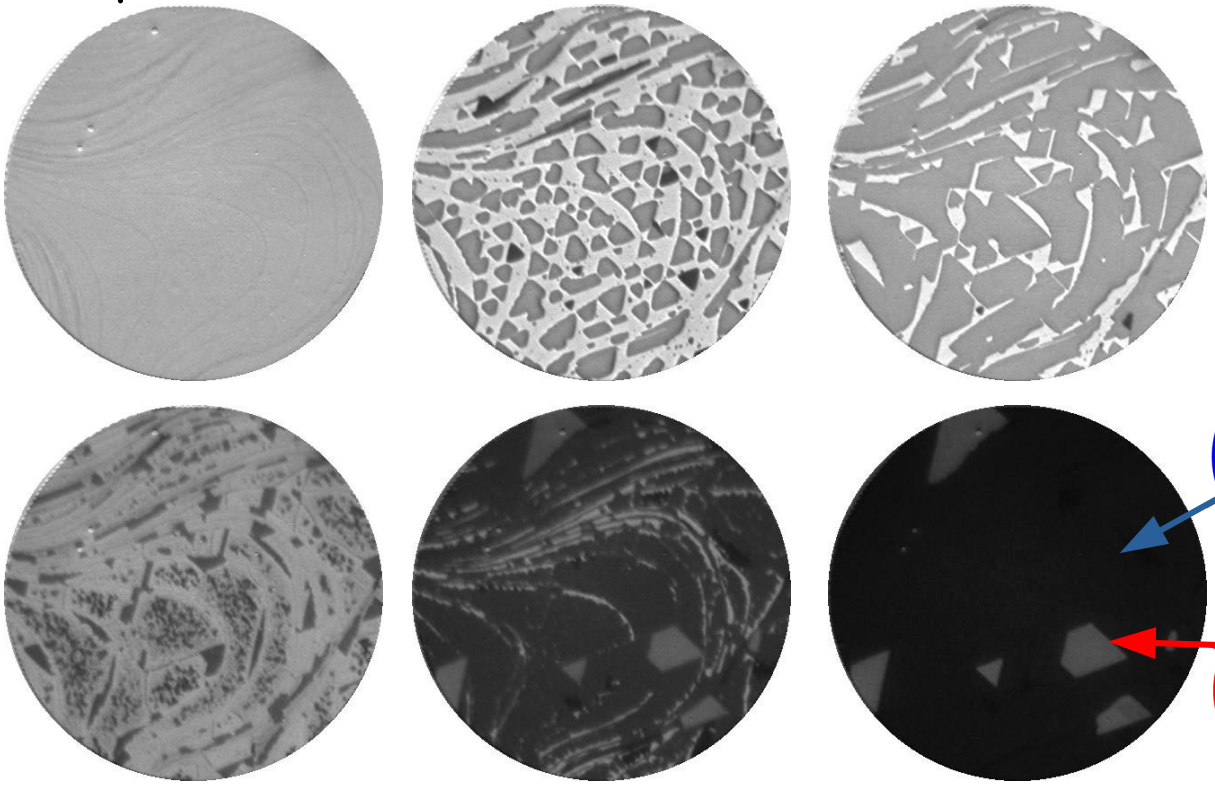
Reactive-MBE

O_2 pressure~ 10^{-6} Torr
Fe flux~ 1 ML/10
Temperature ~ 600-800ºC



FOV 10 μm

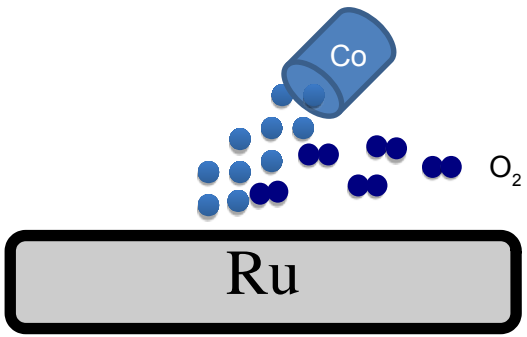
LEEM



M. Monti et al., Phys. Rev. B 85 (2012) 020404(R)

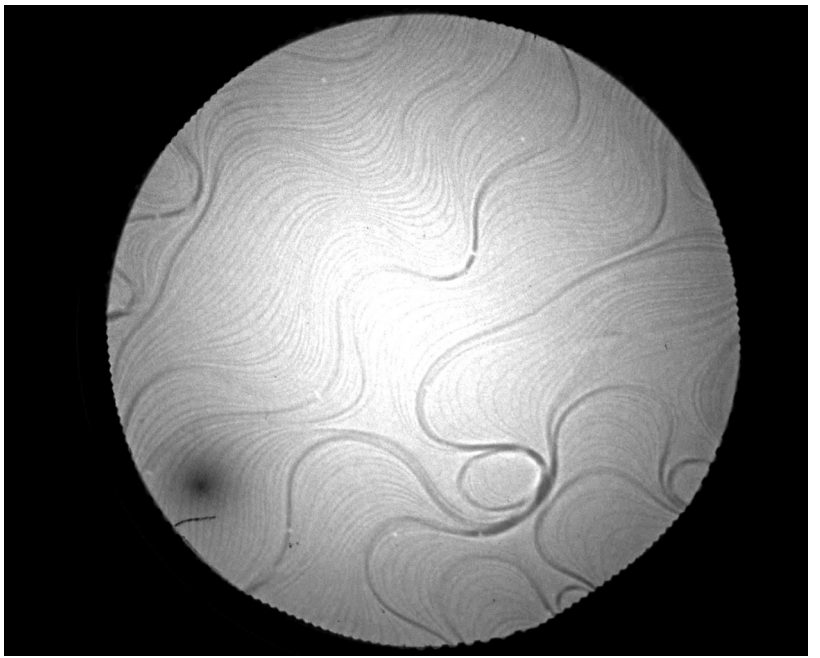
Growth of Co oxides on Ru (0001)

- Growth by HOMBE (High-Temperature, O-assisted MBE):
- Thermal evaporation of Co in O_2 (p = 1.0 ×10^{-6} mbar) atmosphere.
- Ru(0001) substrate, T ~ 850 ºC



CoO / Ru(0001); FoV: 20 µm

In-situ monitoring by LEEM



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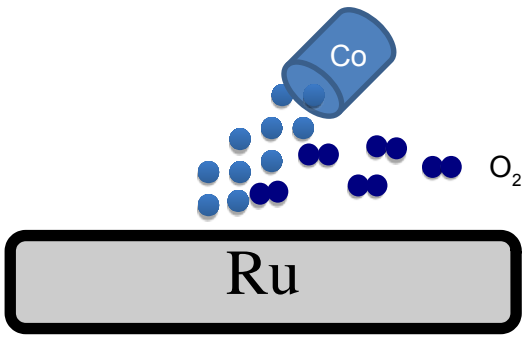
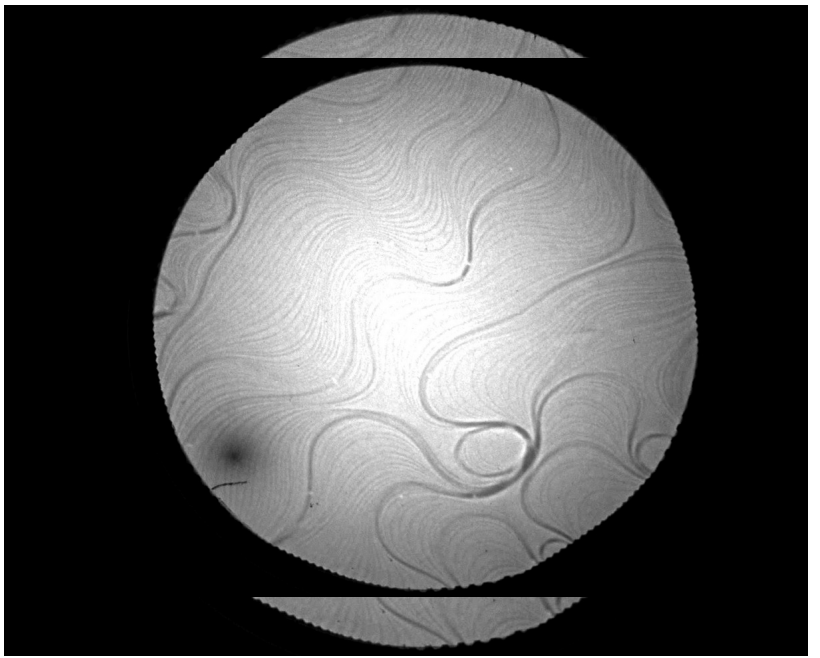


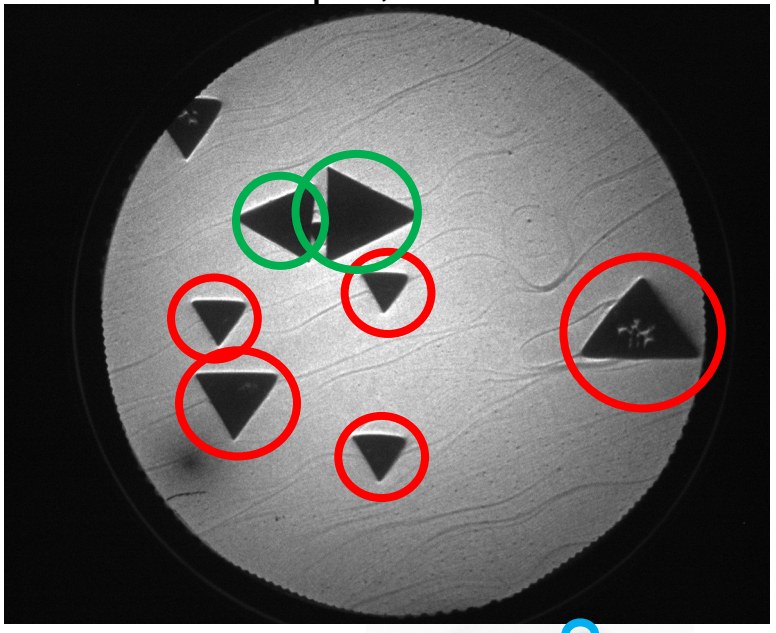
CoO / Ru(0001); FoV: 20 µm

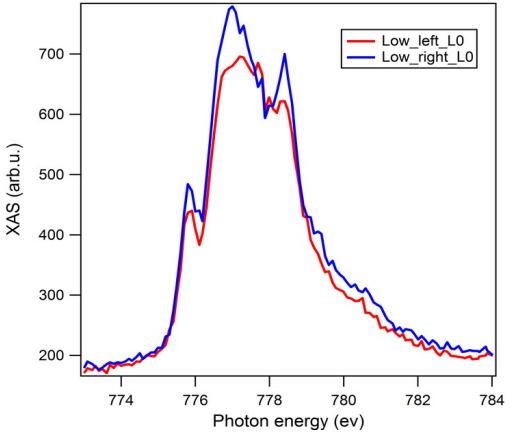
In-situ monitoring by LEEM

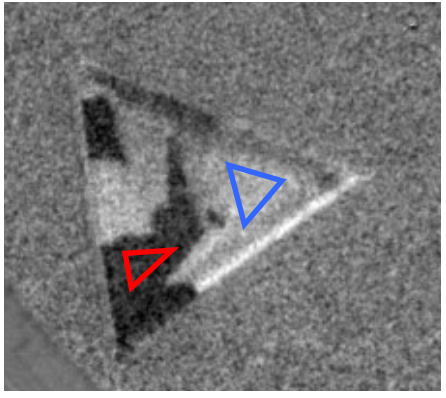


Epitaxial CoO islands on Ru(0001)

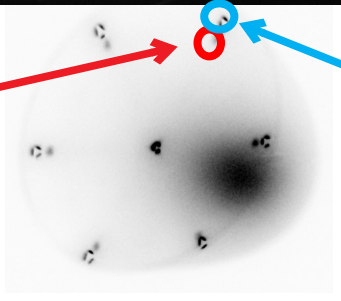
FoV = 20 µm, SV = 50 eV



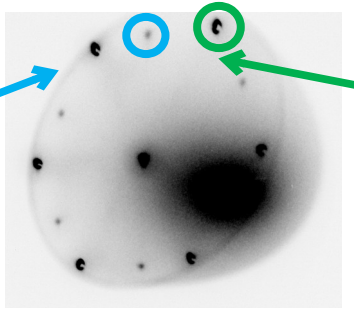




"majority" island

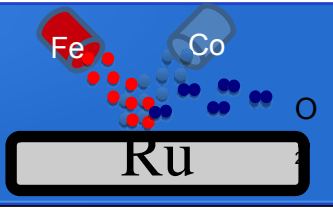


Spots of substrate

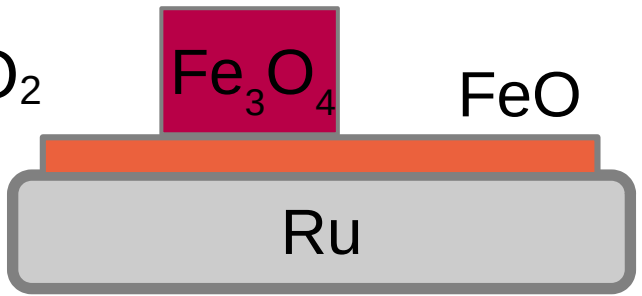


"30º rot." island

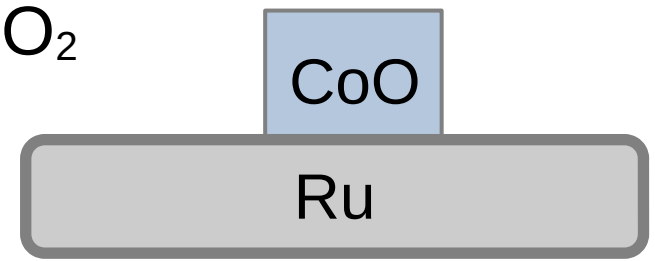
Does it work for ternary spinels?



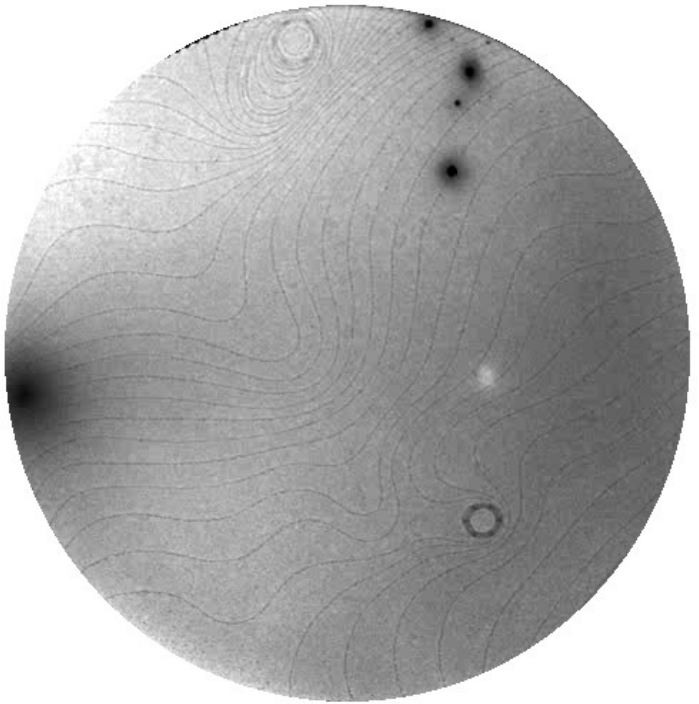
$Fe + O_2$



$Co + O_2$

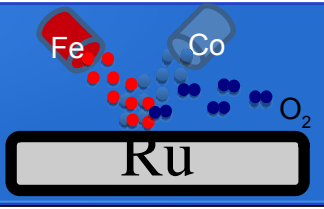


$Fe + Co + O_2$



Fe+Co (2:1), in 10^{-6} mbar O_2 on Ru(0001),
FOV 10 µm, 770ºC

Does it work for ternary spinels?



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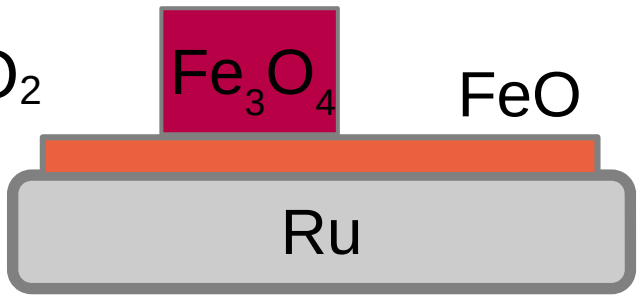
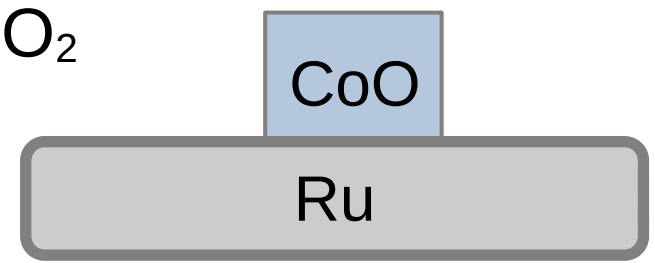
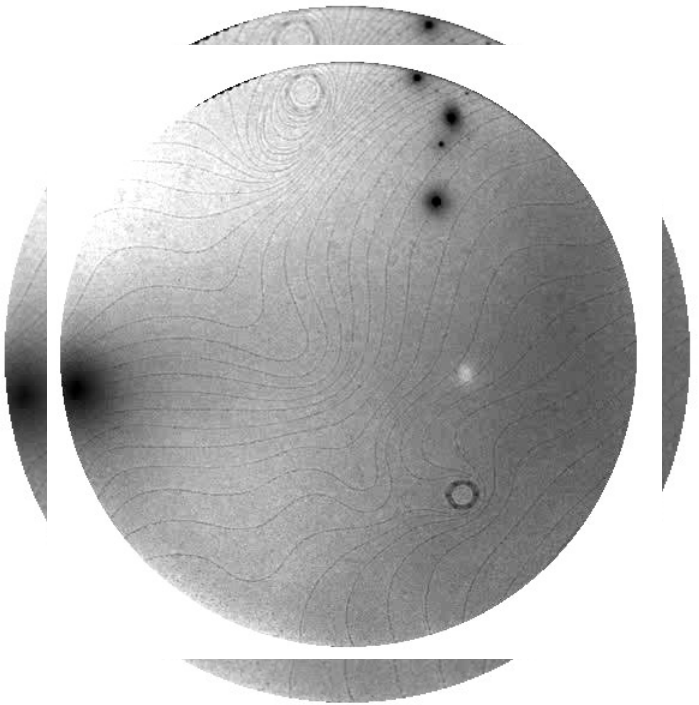


$Co + O_2$

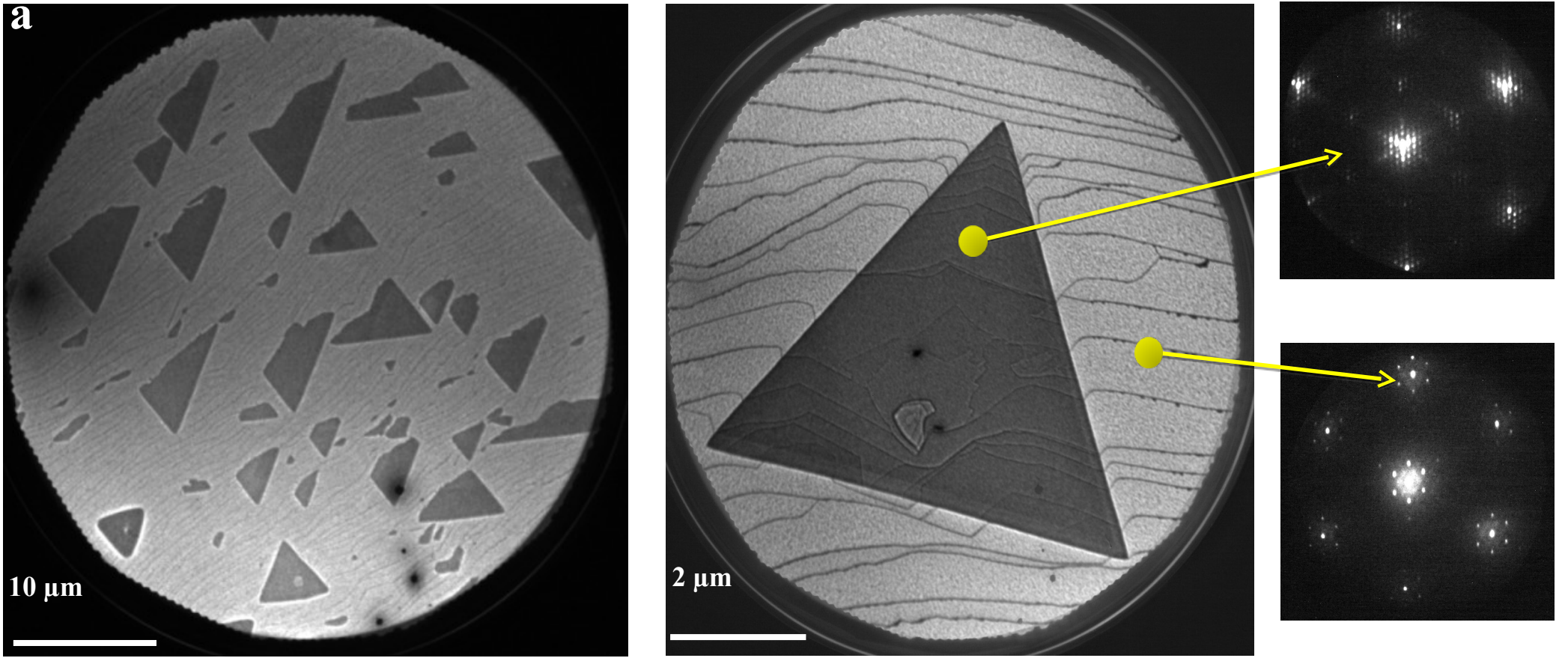


$Fe + Co + O_2$

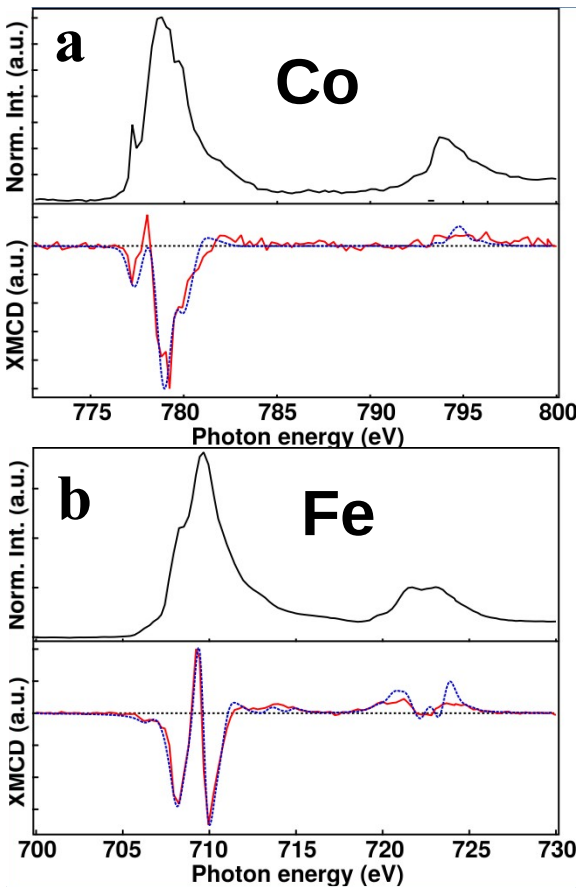


Fe+Co (2:1), in 10^{-6} mbar O_2 on Ru(0001),
FOV 10 µm, 770ºC

It works: wetting layer plus islands



XAS provides chemical characterization

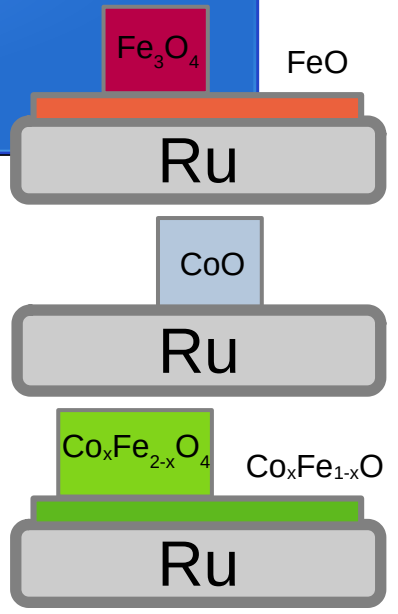


- Deposited ratio: Co:Fe 1:2
- Islands are spinel
- Wetting layer is a Co(II), Fe(II) oxide
- Experimental composition of:
  - Islands: $Co_{0.5}Fe_{2.5}O_4$
  - Wetting layer: $Co_{0.5}Fe_{0.5}O$

Composition does not match the deposited ratio

Too many questions...

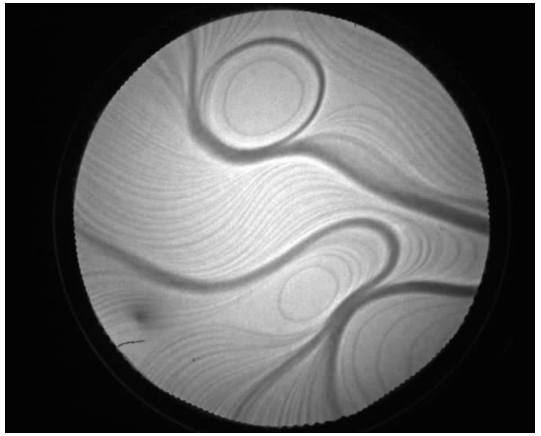
- Co+O2 gives Co 3D islands
- Fe+O2 gives Fe3O4 3D islands on FeO
- 1 Co: 2 Fe + O2 gives CoFeO4 3D islands plus CoFeO

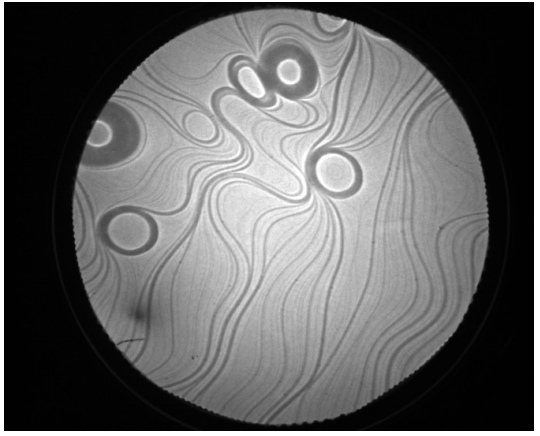


- How does the growth mode depend on the Co:Fe ratio?
- Is the composition of CFO islands and wetting layer constant for a given ratio?
- Can we engineer particular nanostructures?

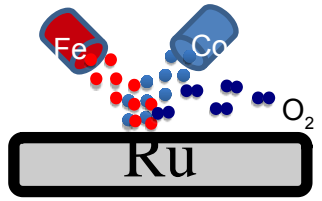
Initial growth with different Co:Fe ratios

Co:Fe 2:1

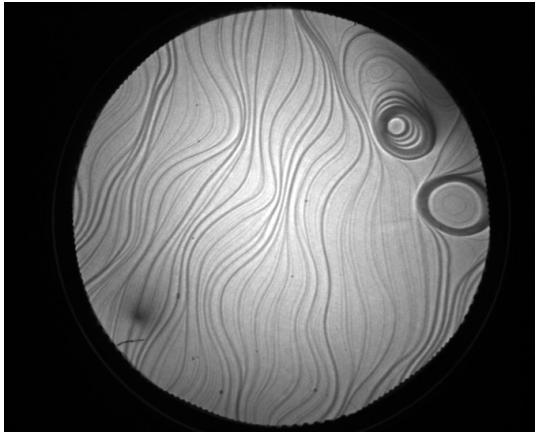


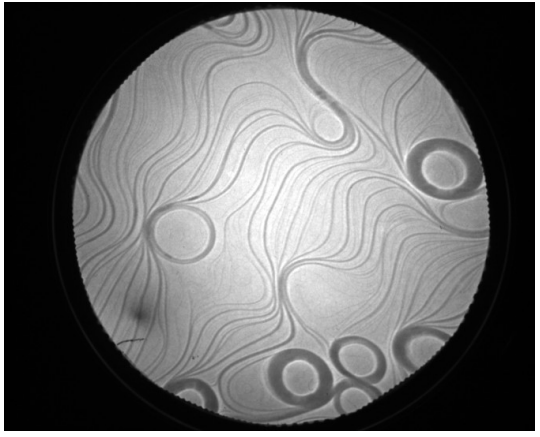


Co:Fe 5:1



Co:Fe 3:1





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FOV 10 um
Substrate 850 ºC
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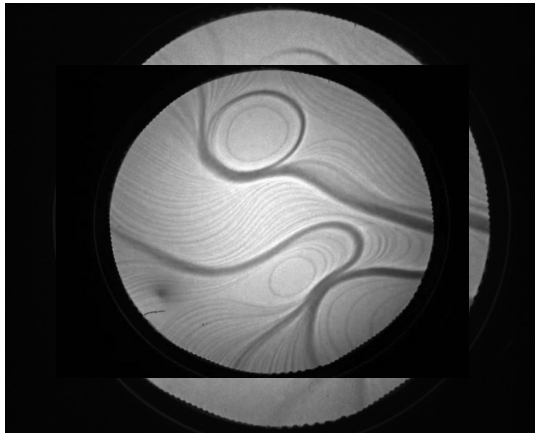
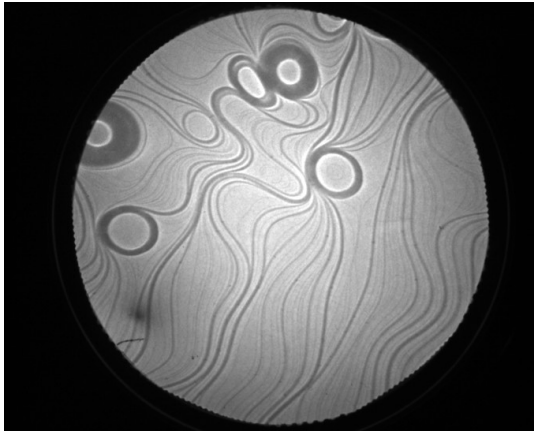
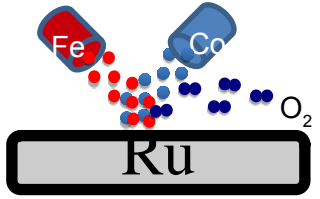
Initial growth with different Co:Fe ratios

Co:Fe 2:1





Co:Fe 5:1



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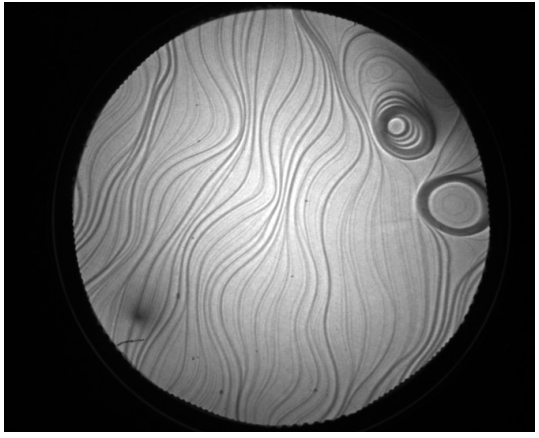

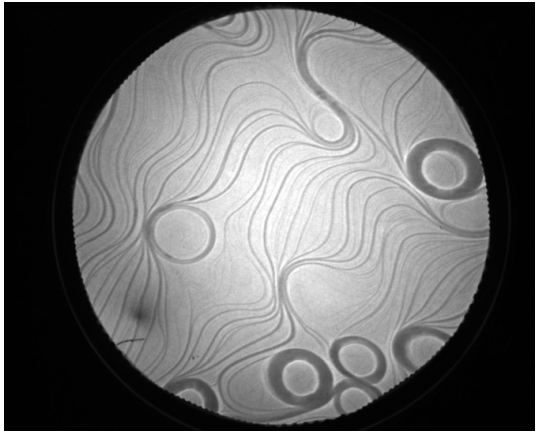

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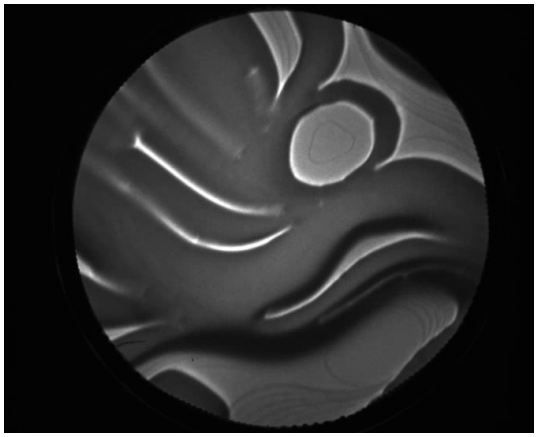
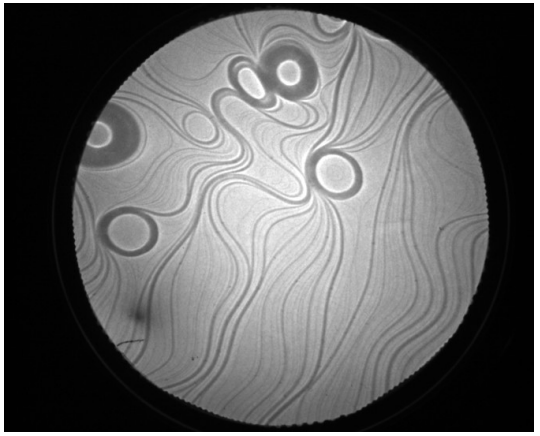
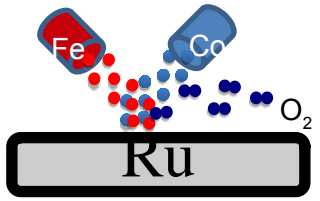




Co:Fe 5:1



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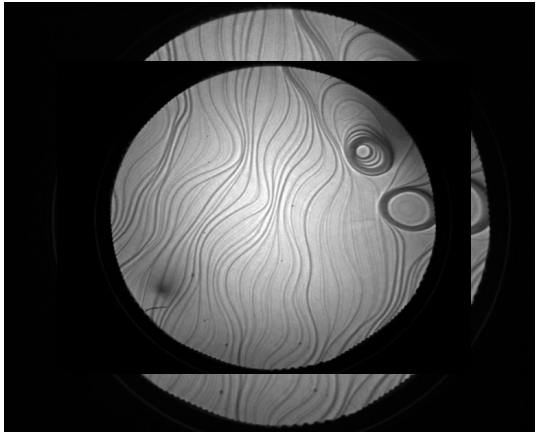

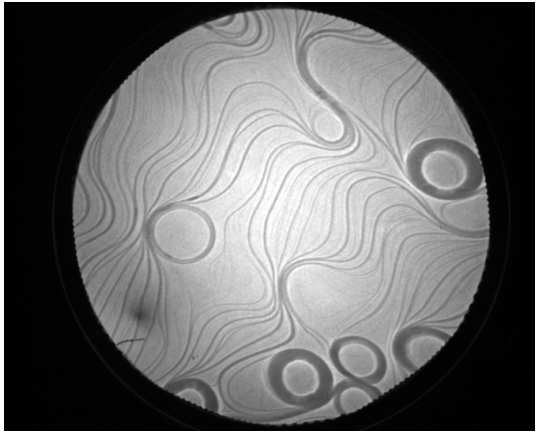

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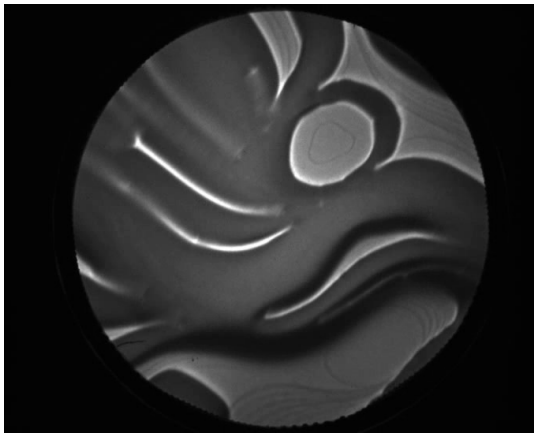
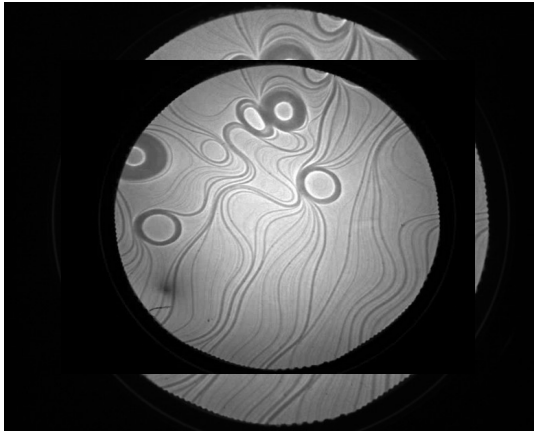
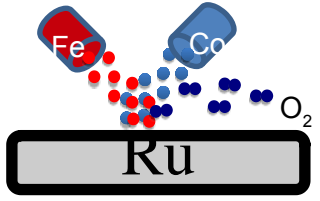
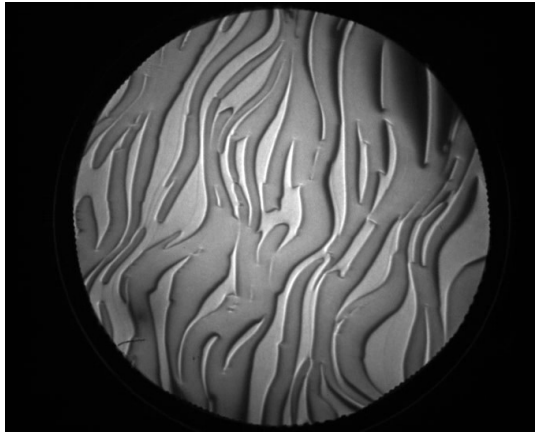


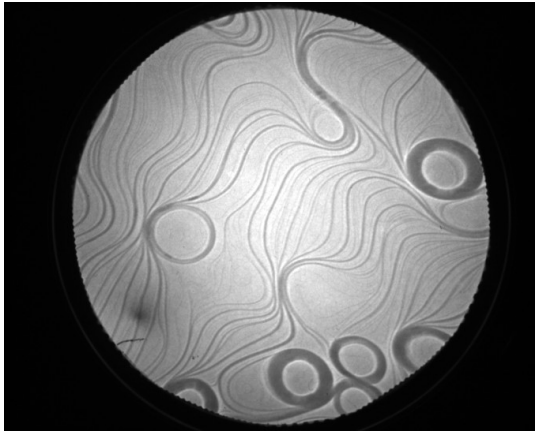


Co:Fe 5:1



Co:Fe 3:1





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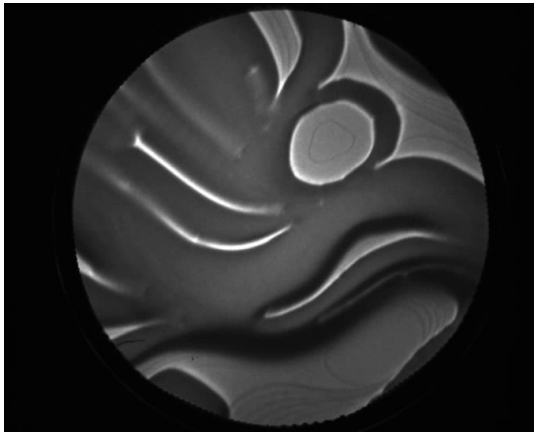

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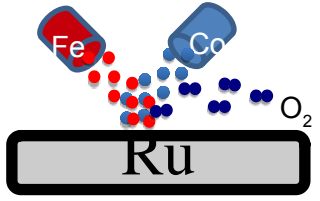

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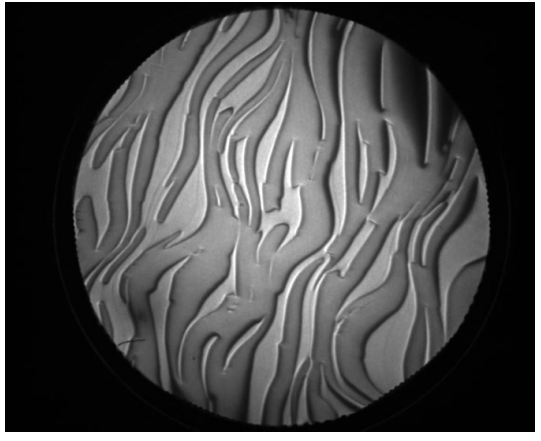

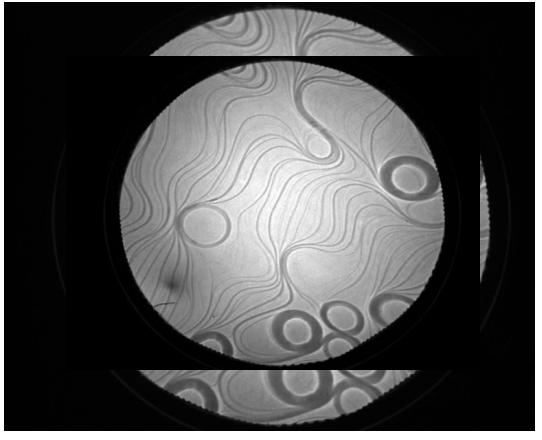

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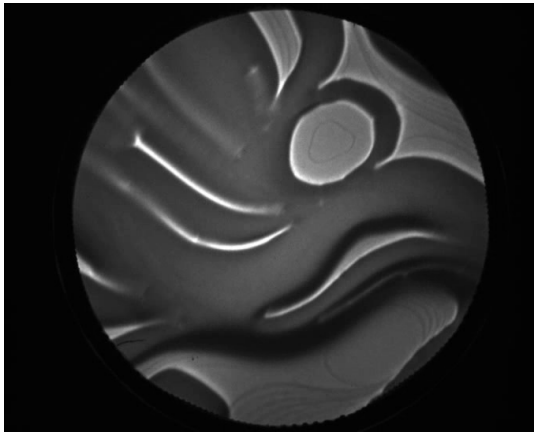

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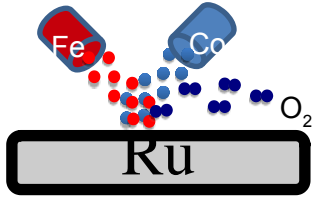

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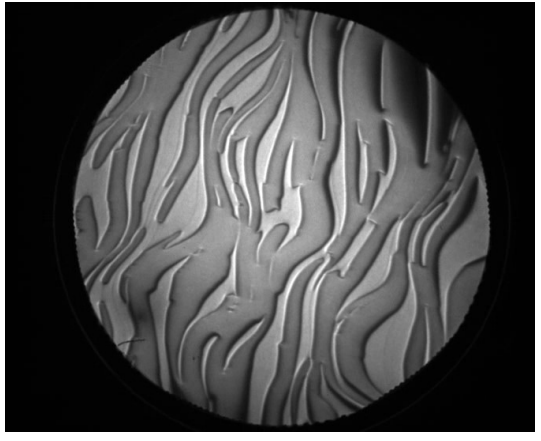
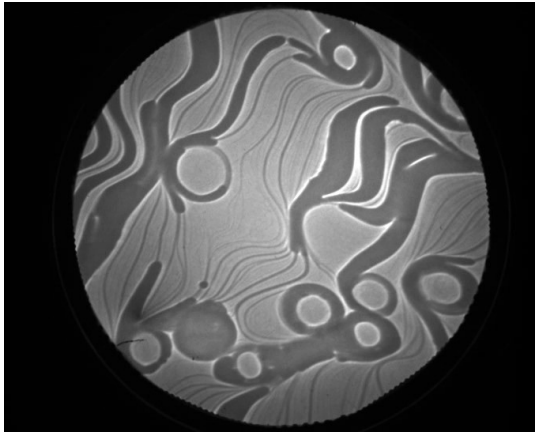
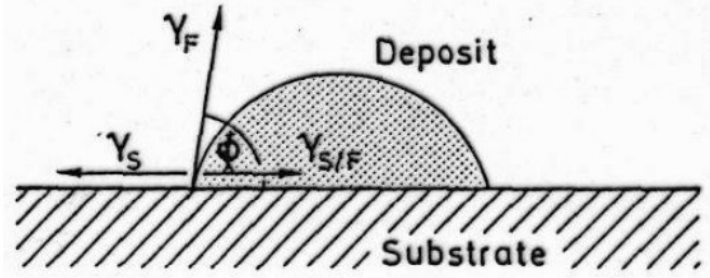


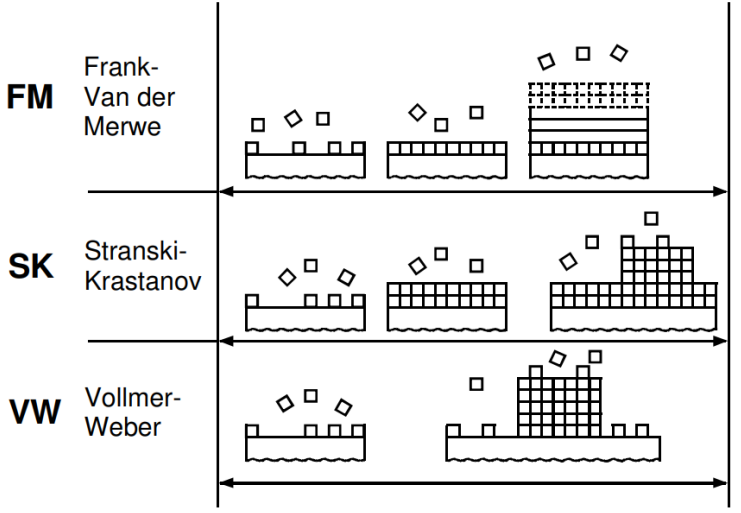


Co:Fe 17:1

Depositing 1ML Co in 8 min
FOV 10 um
Substrate 950 ºC
Pressure oxygen $1x10^{-6}$ mbar

Why the transition from layer-by-layer to 2D growth?





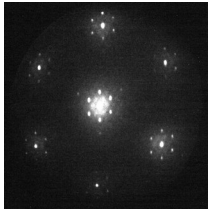
Layer-by-Layer (FM): $\Phi = 0$, $\gamma_S \geq \gamma_F + \gamma_{S/F}$

3D growth (VW): $\Phi > 0$, $\gamma_S < \gamma_F + \gamma_{S/F}$

Bulk CoO/FeO: lattice 0.301/0.305 nm

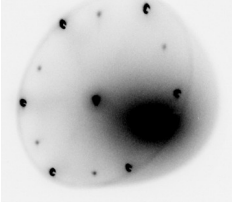
$Co_xFe_{1-x}O$, with $0<x<0.95$

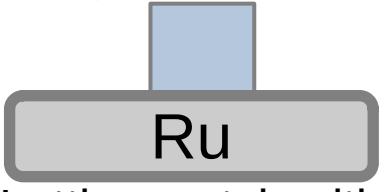
Lattice 0.32 nm



Moiré underneath

CoO

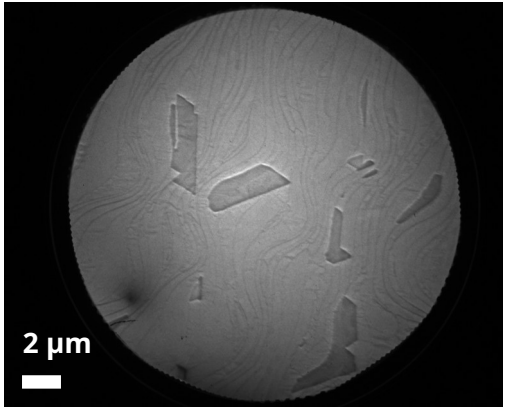




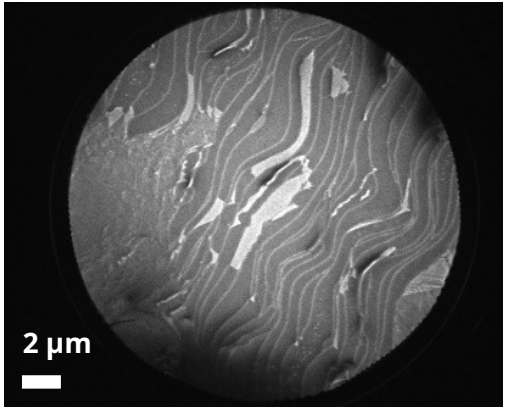
Lattice match with Ru, 0.27 nm

But at later stages things differ strongly!!!

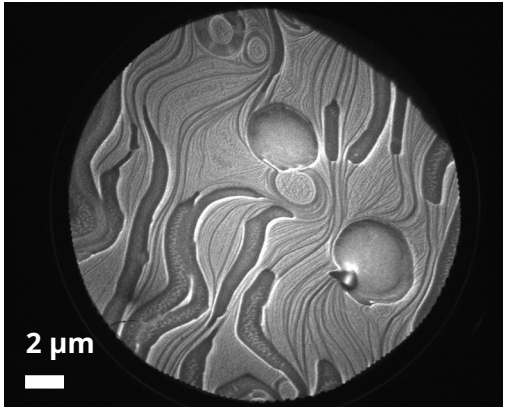
Work in progress



Co:Fe 2:1



Co:Fe 3:1

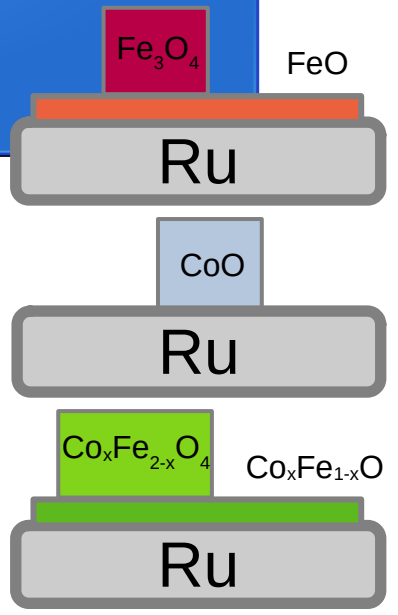


Co:Fe 17:1

- 5 % Fe enough to favor initially a 2D-growth (pure FeO) over a 3D-growth (pure CoO)
- 30% Fe required to grow a homogeneous film

Too many questions...

- Co+O2 gives Co 3D islands
- Fe+O2 gives Fe3O4 3D islands on FeO
- 1 Co: 2 Fe + O2 gives CoFeO4 3D islands plus CoFeO



- How does the growth mode depend on the Co:Fe ratio?
- Is the composition of CFO islands and wetting layer constant for a given ratio?
- Can we engineer particular nanostructures?

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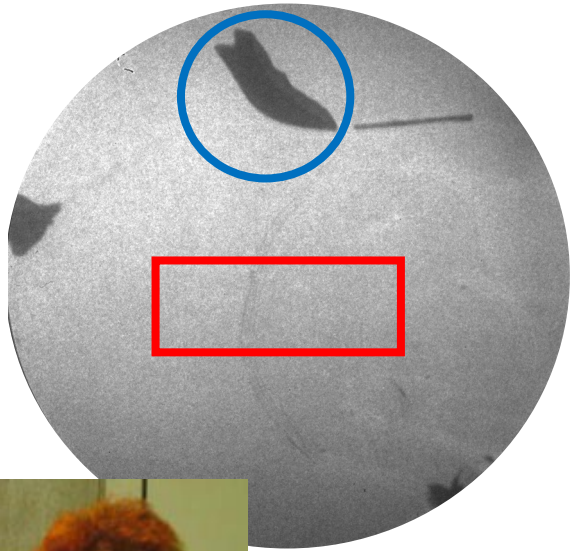
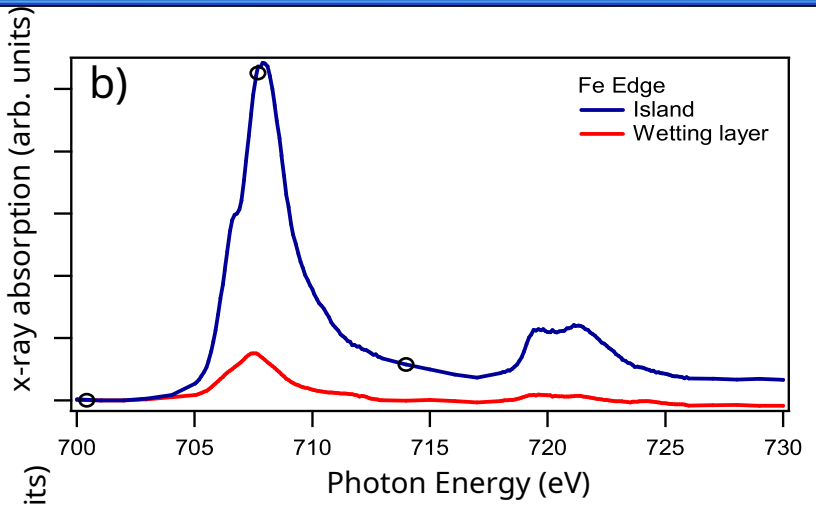
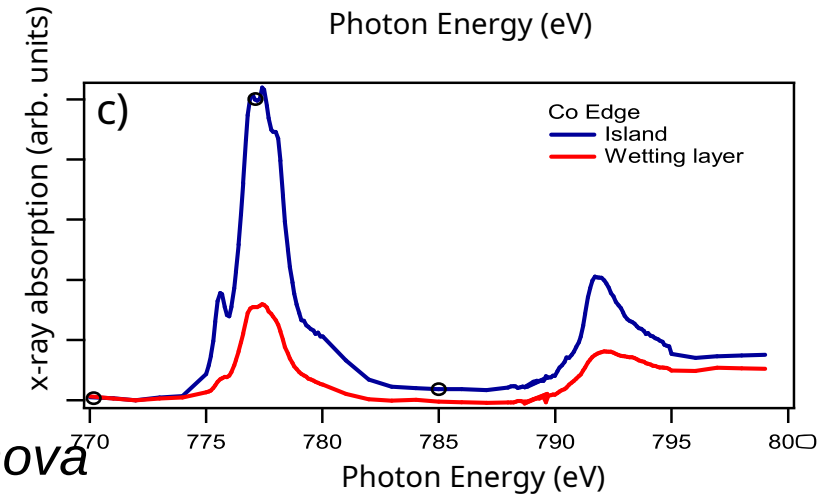
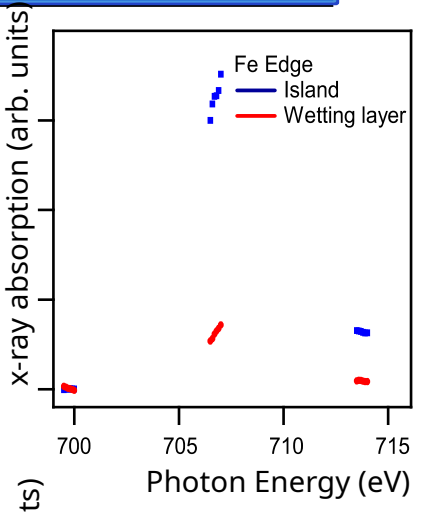
How to follow growth in PEEM

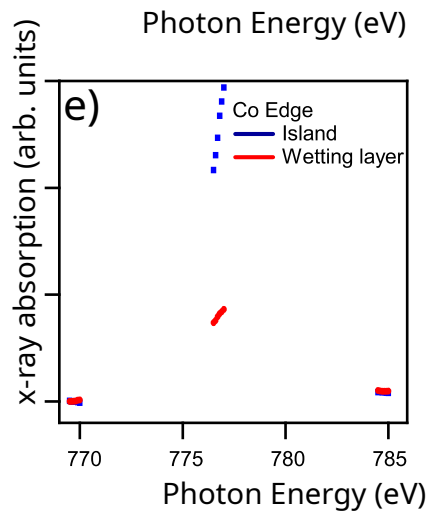


Suggested by Maya Kiskinová









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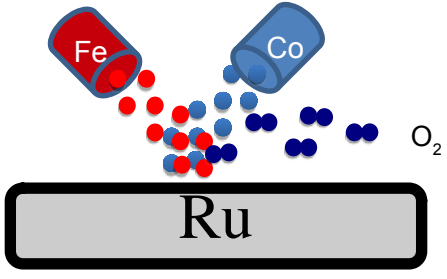
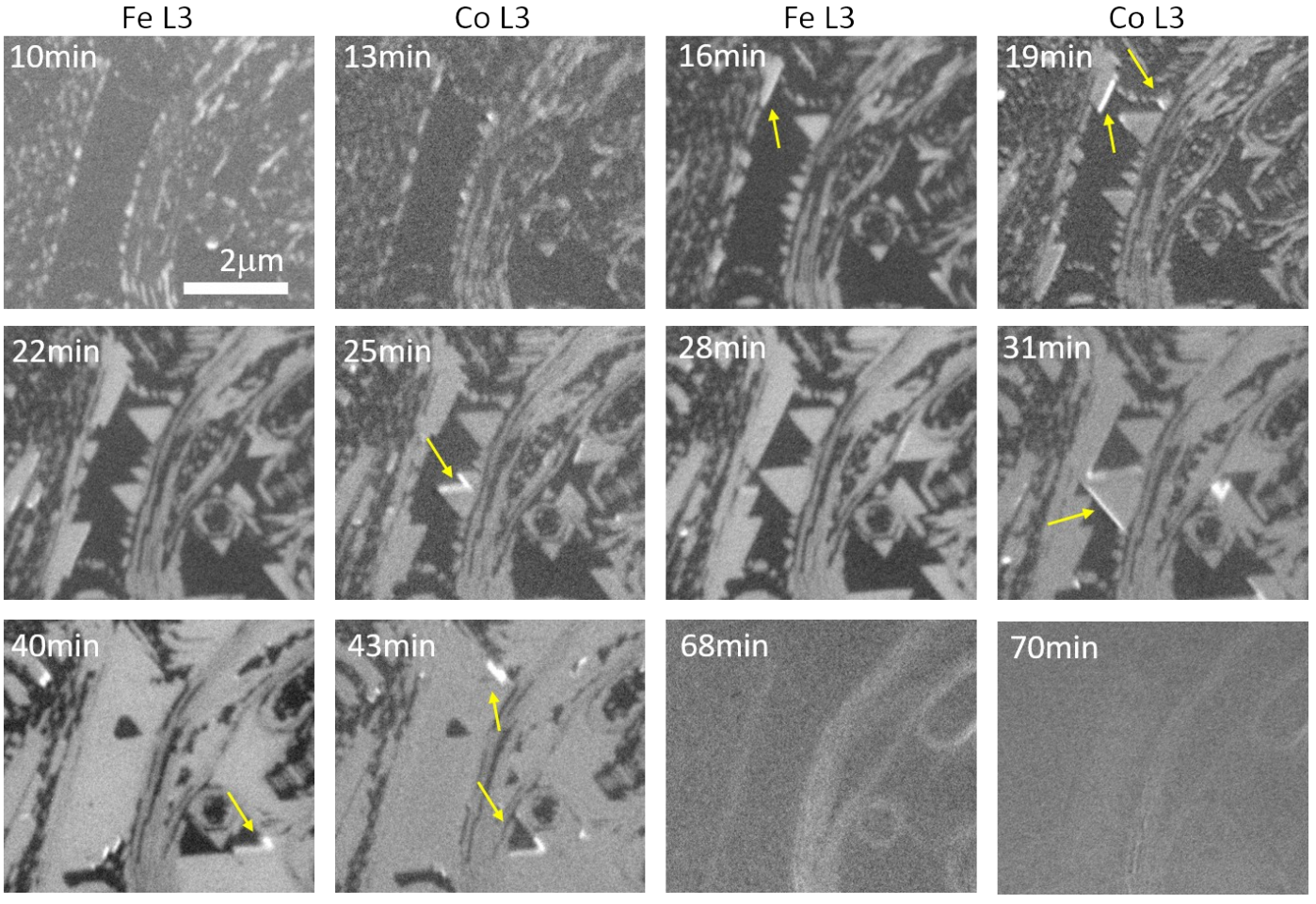
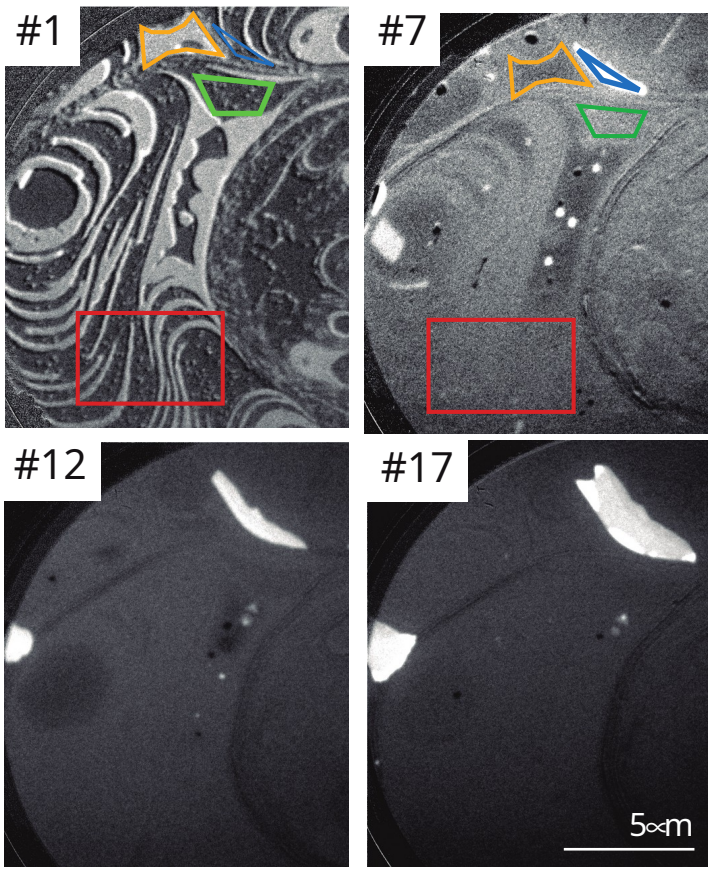
A PEEM growth movie

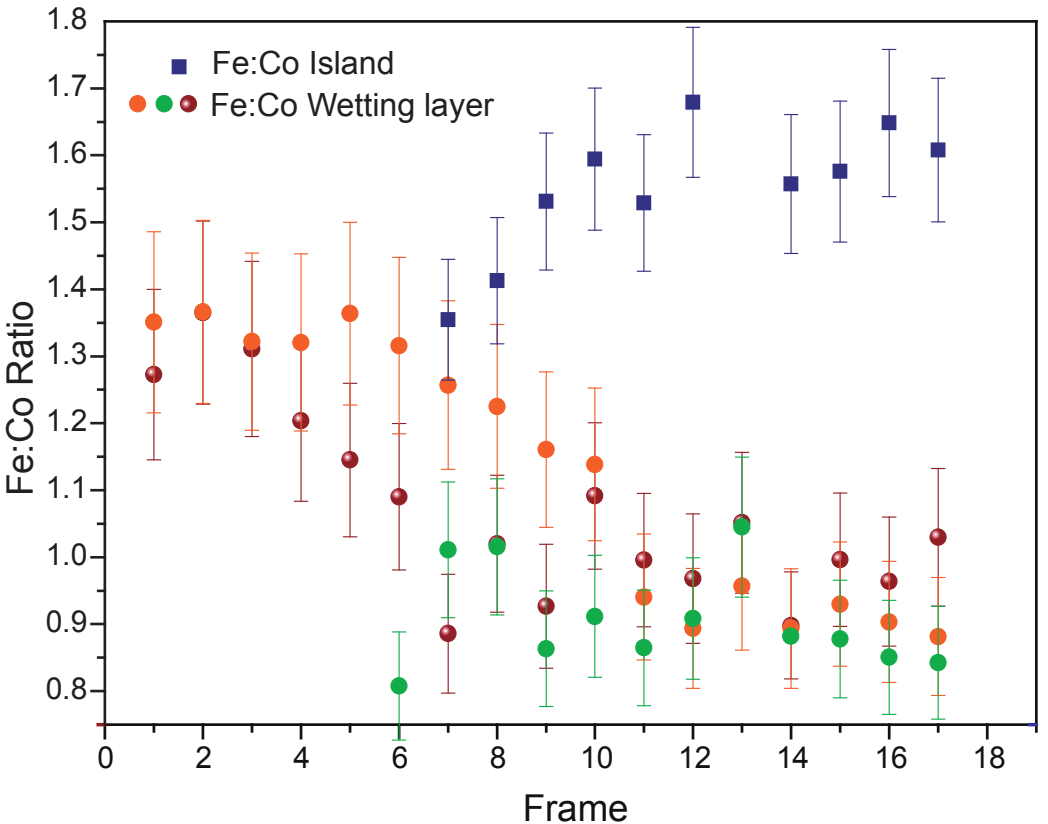
Following growth in PEEM, switching between Fe and Co XAS edges





Evolution of the composition of the film





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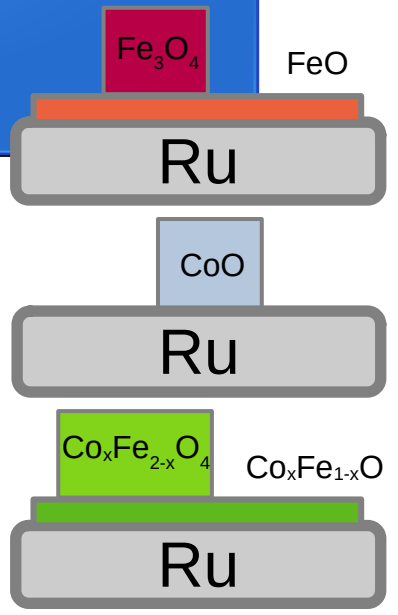
- Fe+O2 gives Fe3O4 3D islands on FeO
- 1 Co: 2 Fe + O2 gives CoFeO4 3D islands plus CoFeO



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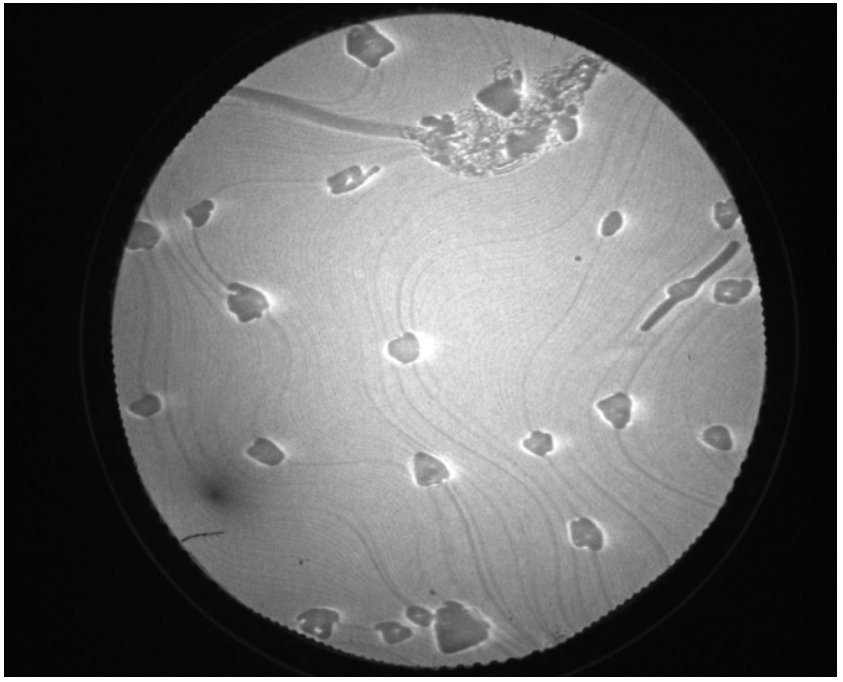
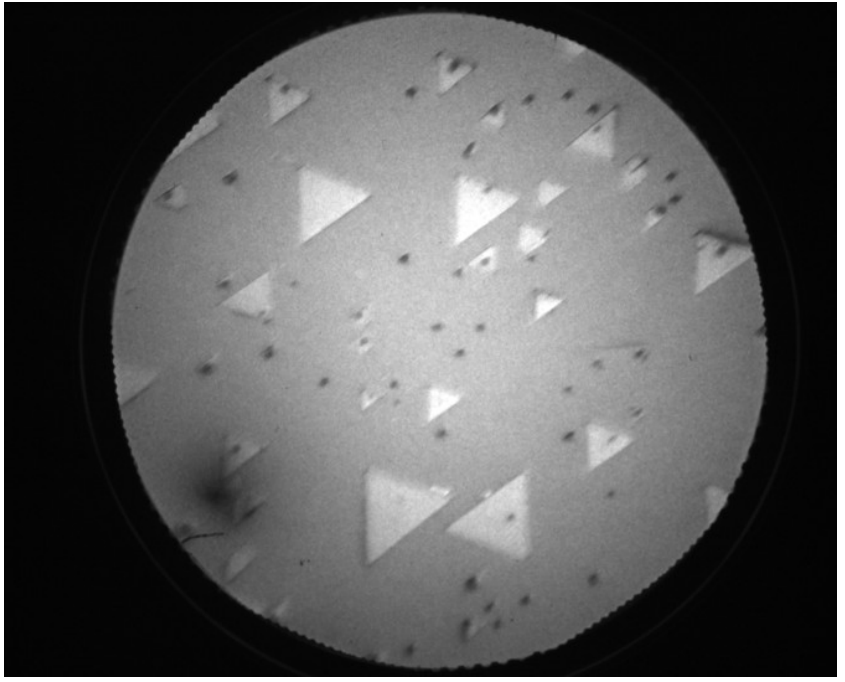
CoO/Fe3O4 nanostructures

grow CoO, then Fe3O4



growth Fe3O4, then CoO



CoO islands disolved upon Fe deposition

CoO islands covered Fe3O4 ones???

CoO/Fe3O4 nanostructures

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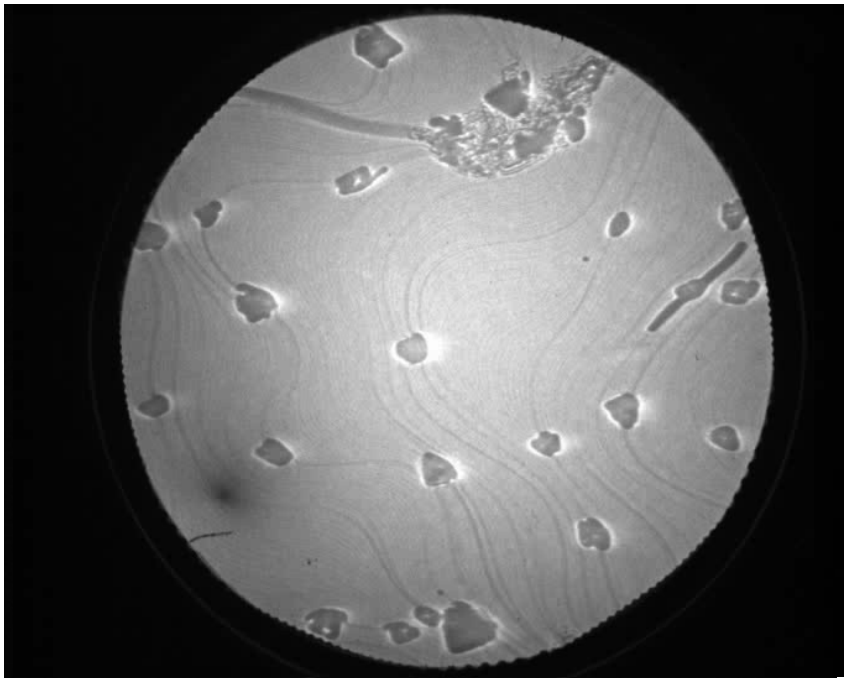

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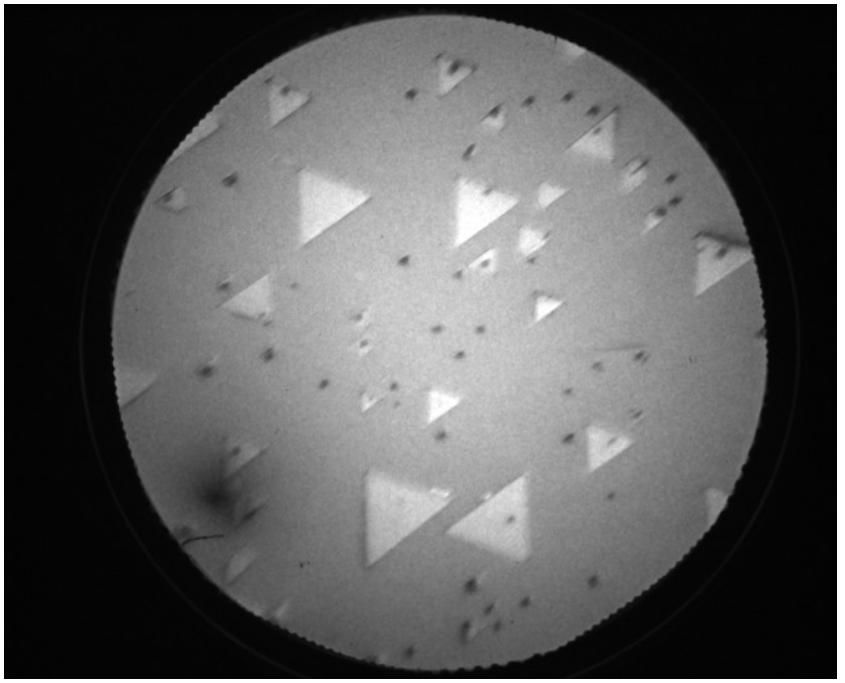
growth Fe3O4, then CoO



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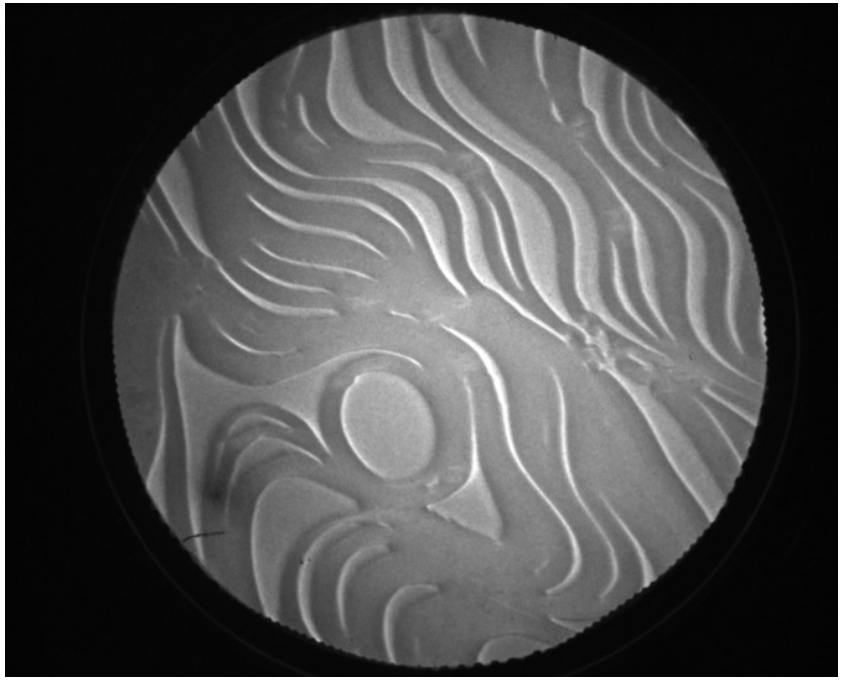
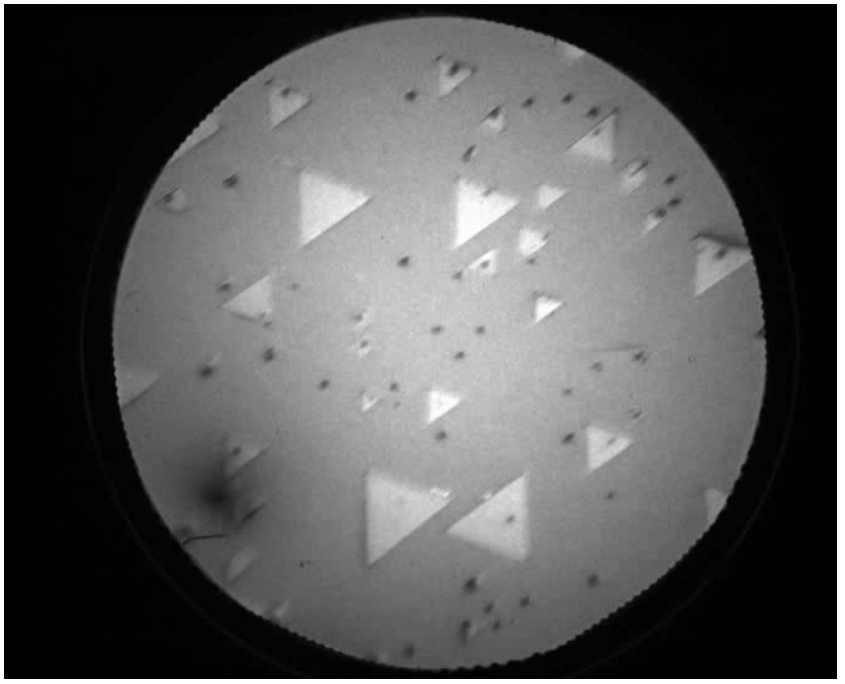


growth Fe3O4, then CoO



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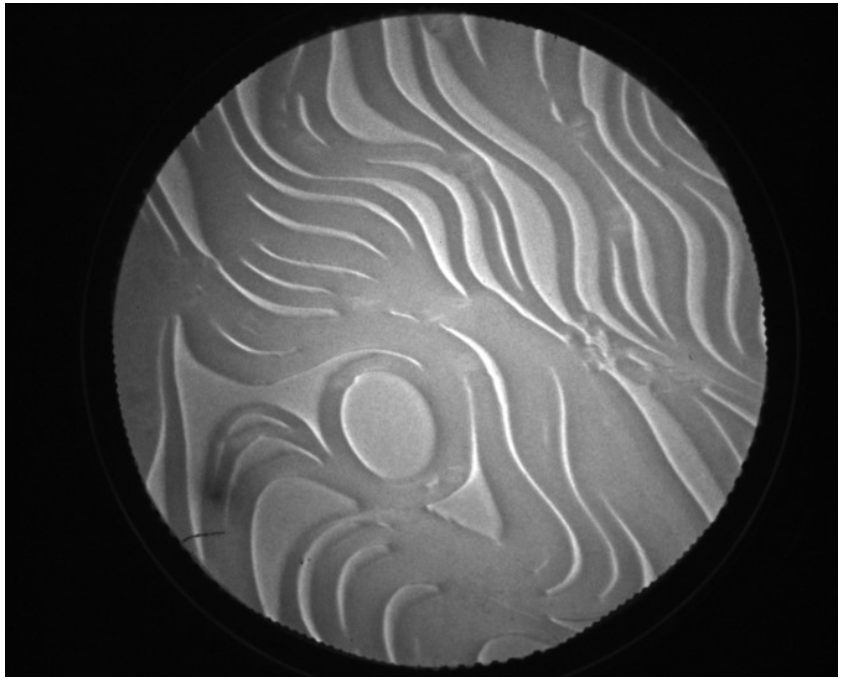

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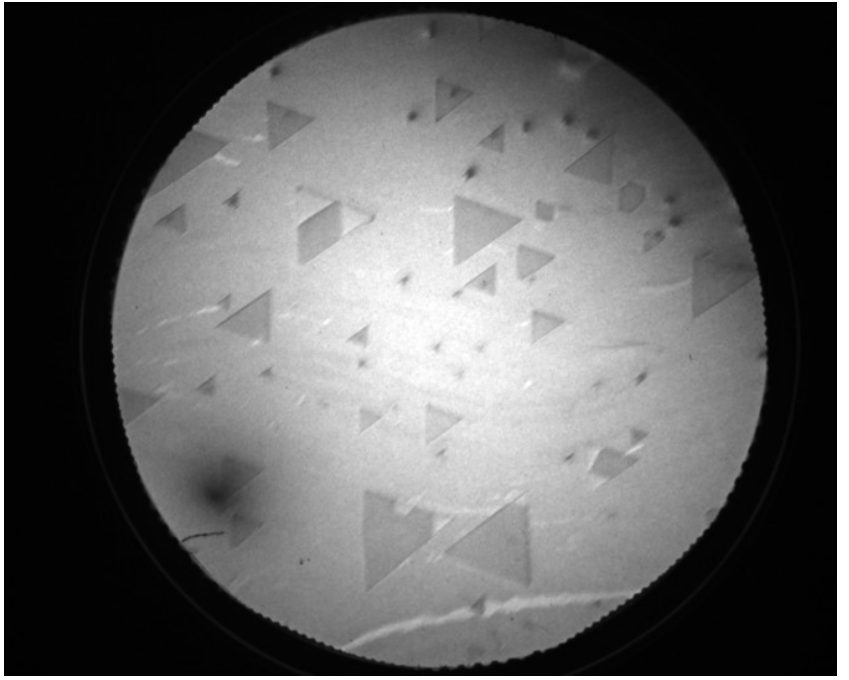

CoO islands disolved upon Fe deposition

CoO islands covered Fe3O4 ones???

Conclusions

- Electron microscopies are great for growth charaterization:
  - LEEM gives a real-space view of the growth front
  - PEEM gives composition. With some effort, it can be used in real time also.
- Co-Fe oxides are a fascinating playground of different phases with different magnetic properties
  - Simultaneous deposition of 2:1 Fe/Co in O2 produces a rock-salt wetting layer and 3-dimensional spinel islands.
  - The growth mode can be tuned by changing the Fe/Co ratio
  - The composition evolves with time even upon a given Fe/Co deposition ratio when there are several phases present. ***MORE PEEM MOVIES?***
- Combined CoO/Fe3O4 structures promise highly perfect systems to study AFM/FM magnetic coupling

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