LEEM and PEEM for Surface Science

Juan de la Figuera

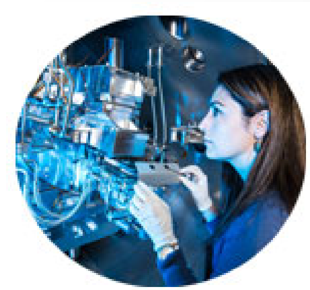
http://www.iqfr.csic.es
http://surfmoss.iqfr.csic.es

Instituto de Quimica-Física “Rocasolano”, CSIC

19 Junio 2015

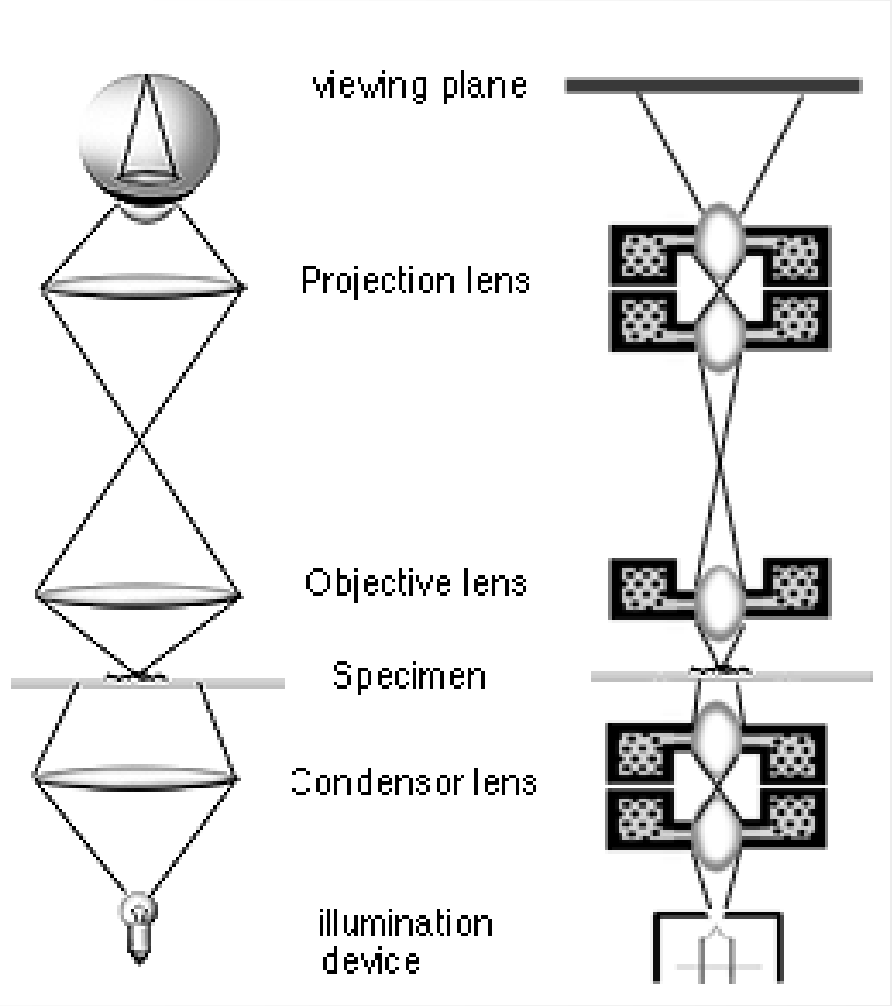
ALBA

AUSE
Asociación
Usuarios
Sincrotrón
España



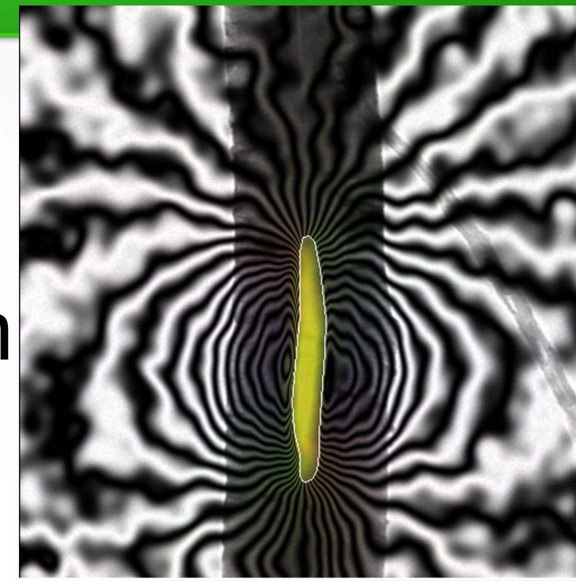
Transmission Electron Microscopy

- Workhorse of Material Science
  - Basic tool for understanding microstructure
  - Allows diffraction
  - Down to atomic resolution

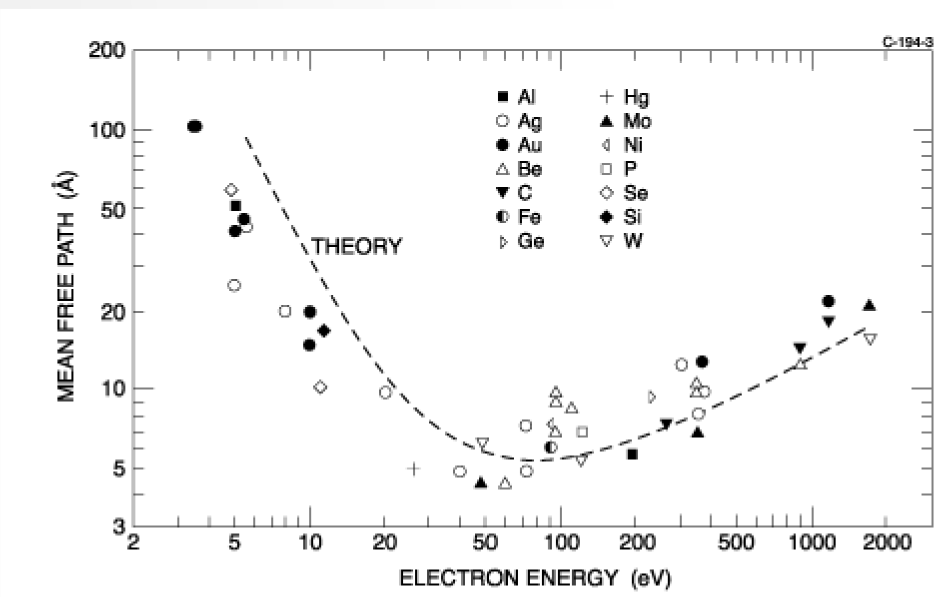


Transmission Electron Microscopy

- Requieres special samples (thickness <100nm is some cases)
- Not very sensitive to surfaces*: high energy electrons (100-2000 keV)
- No magnetic contrast**



Magnetic field around a carbon nanotube filled with Fe
T Kasama et al, Cambridge

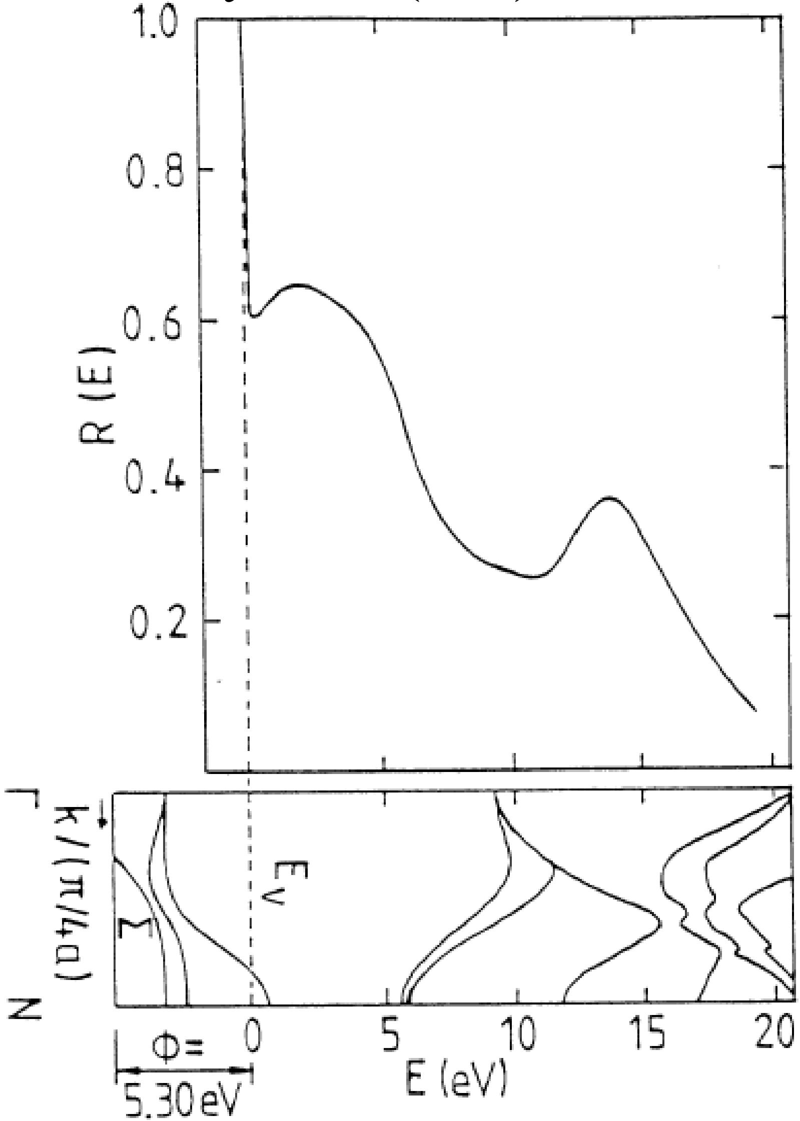


* Not withstanding the Si(7x7) determination by Takayanagi *et al.*

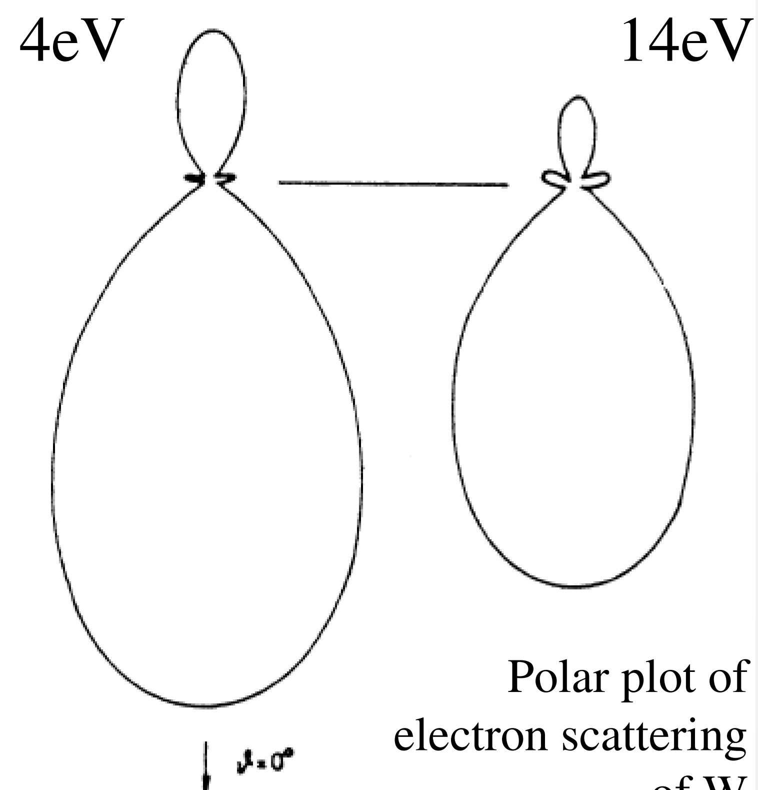
** Lorentz Microscopy is sensitive to magnetic fields.

Reflectivity of low energy electrons

Reflectivity of W(110)

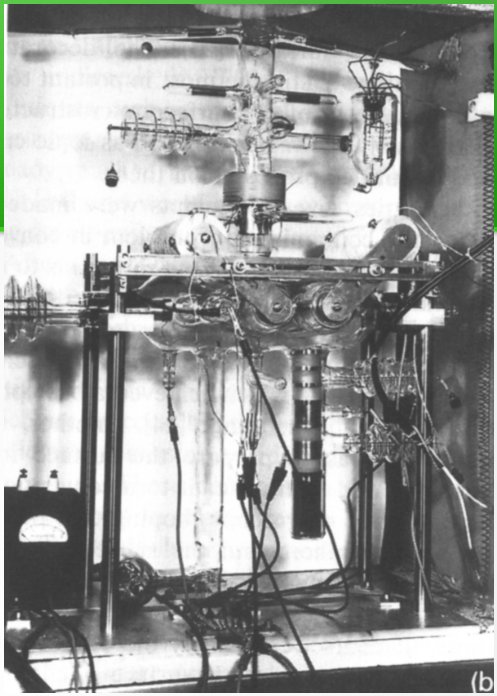


There are more than enough backscattered electrons to allow for video-rate image adquisition in *crystalline* samples:

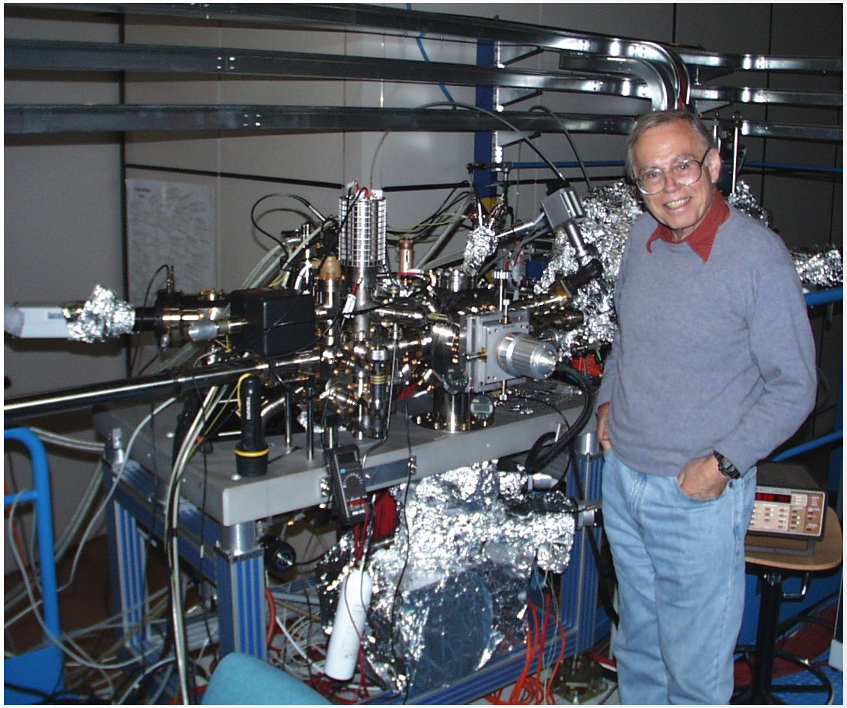


Polar plot of electron scattering of W

Low Energy Electron Microscope: a long road to the nanoscale

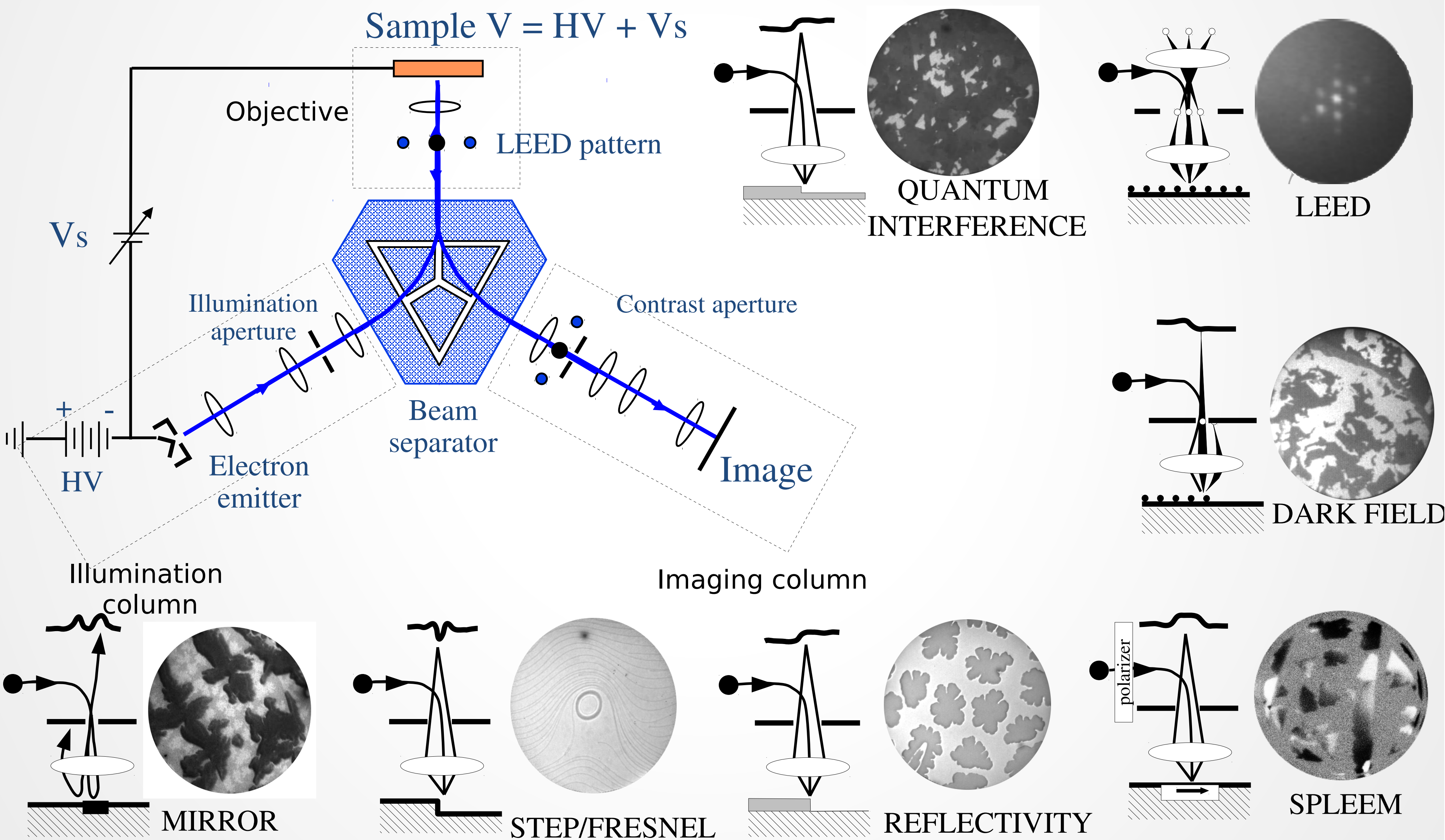


- 1962 Invention by Ernst Bauer
  - Glass-Based Vacuum Apparatus
- 1985 First Operational LEEM Instrument
  - Telieps and Bauer
- 1991 Spin polarized LEEM
  - Bauer and others
- 1991 IBM LEEM-I
  - Tromp and Reuter
- 1993 Elmitec LEEM
  - Former Coworkers of E. Bauer
- 1994 Spin manipulator
  - Duden and Bauer
- 2005 Specs/IBM commercial system
- 2009 Aberration correction

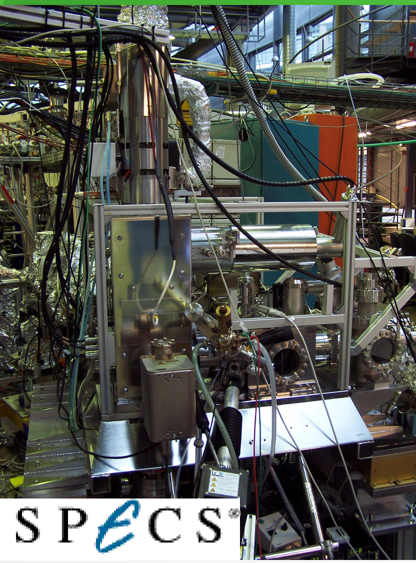


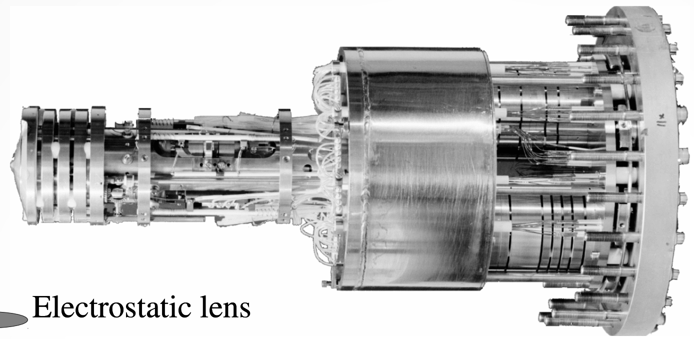
Now there are about 30 instruments in the world,
about 4 with spin polarized e-guns

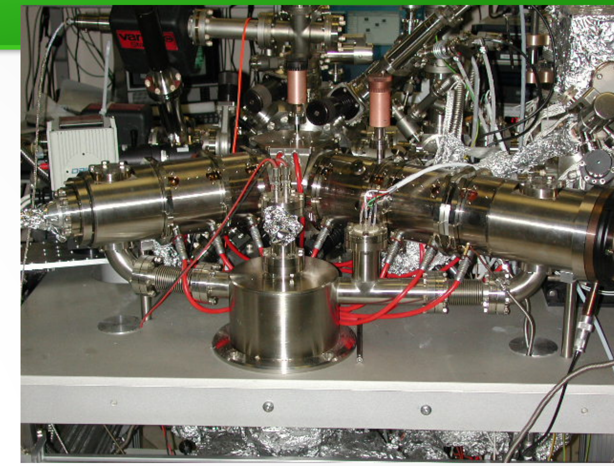
How a LEEM works



Different LEEM designs

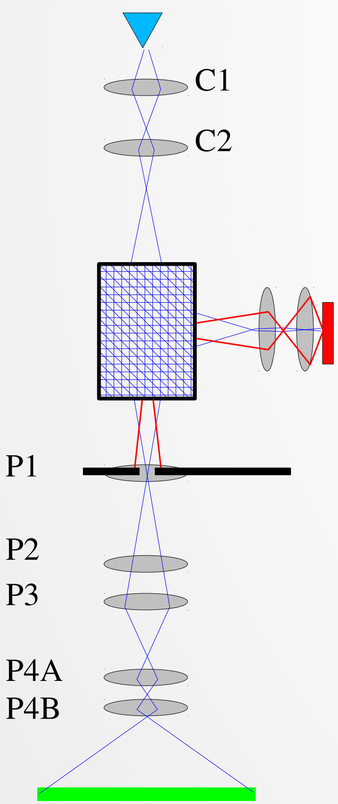


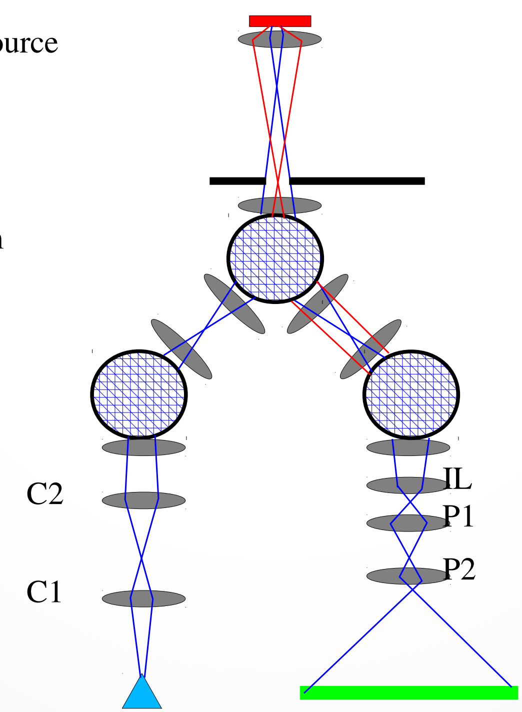


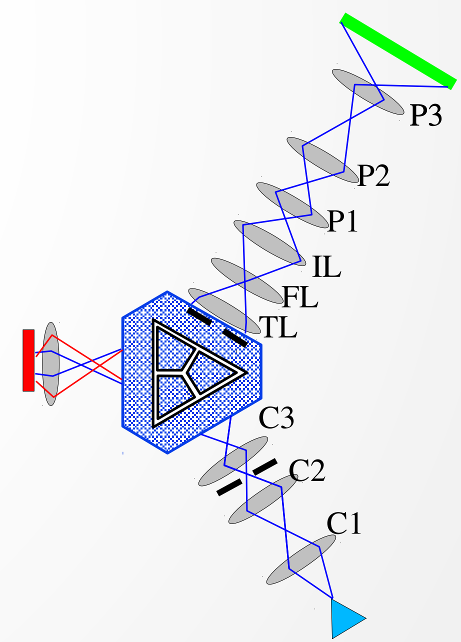


ELMITEC

Electrostatic lens
Magnetostatic lens
screen
electron source
sample
Field beam
Axial beam

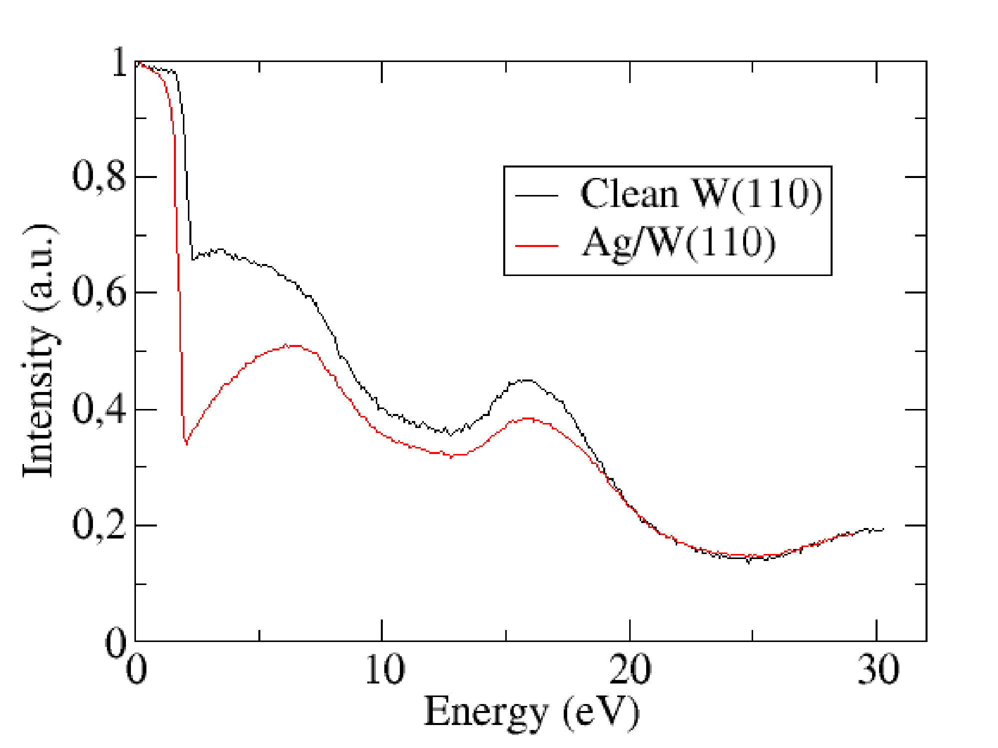


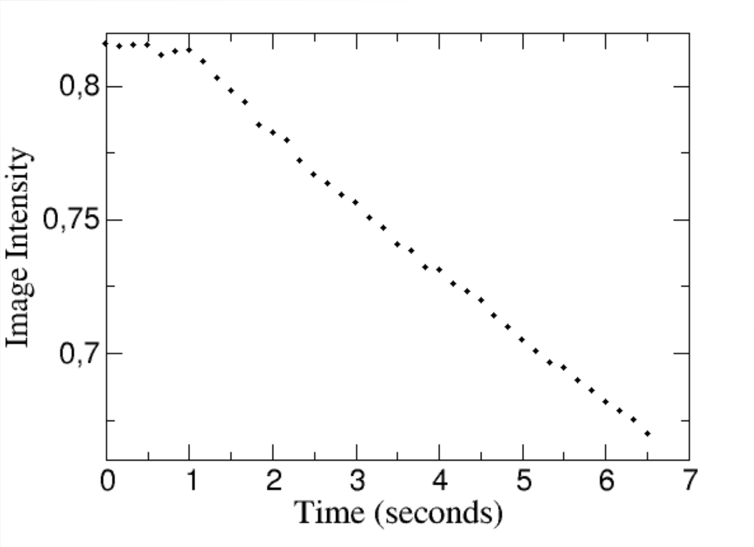


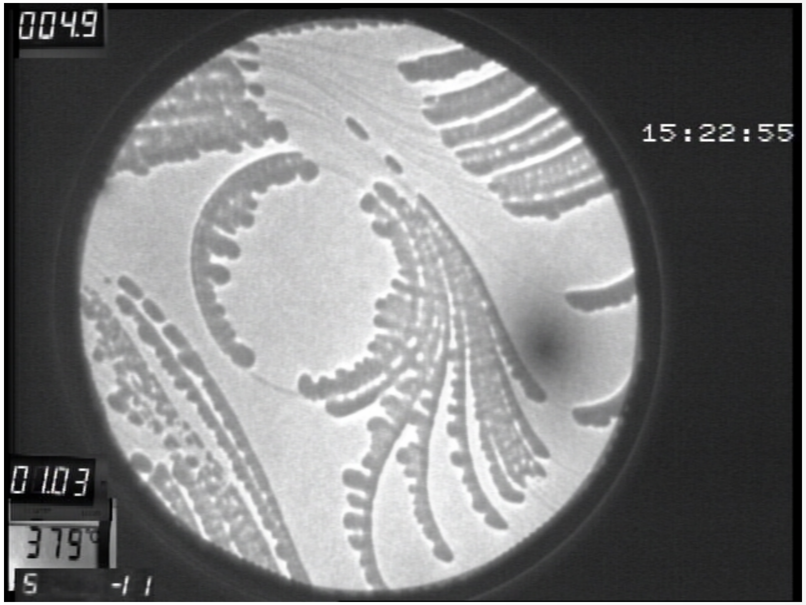


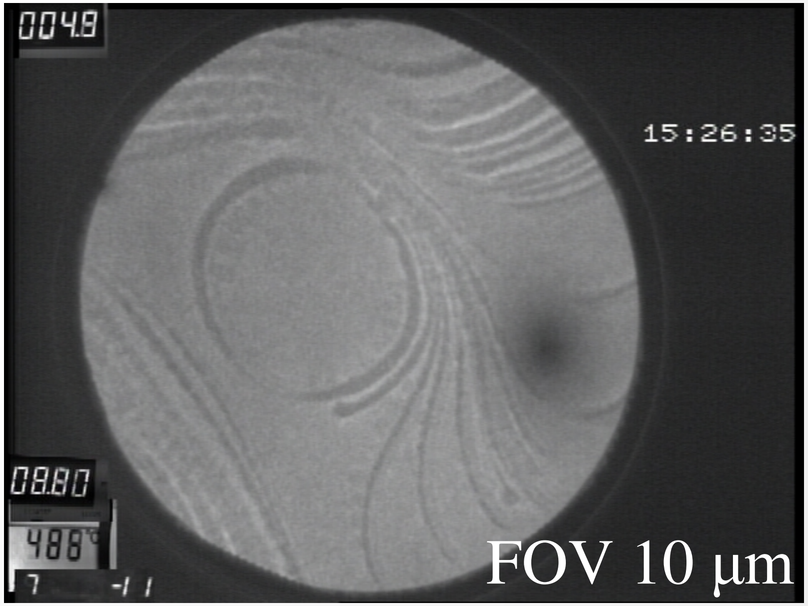
Reflectivity contrast

De la Figuera, *Surf. Sci.* 2006









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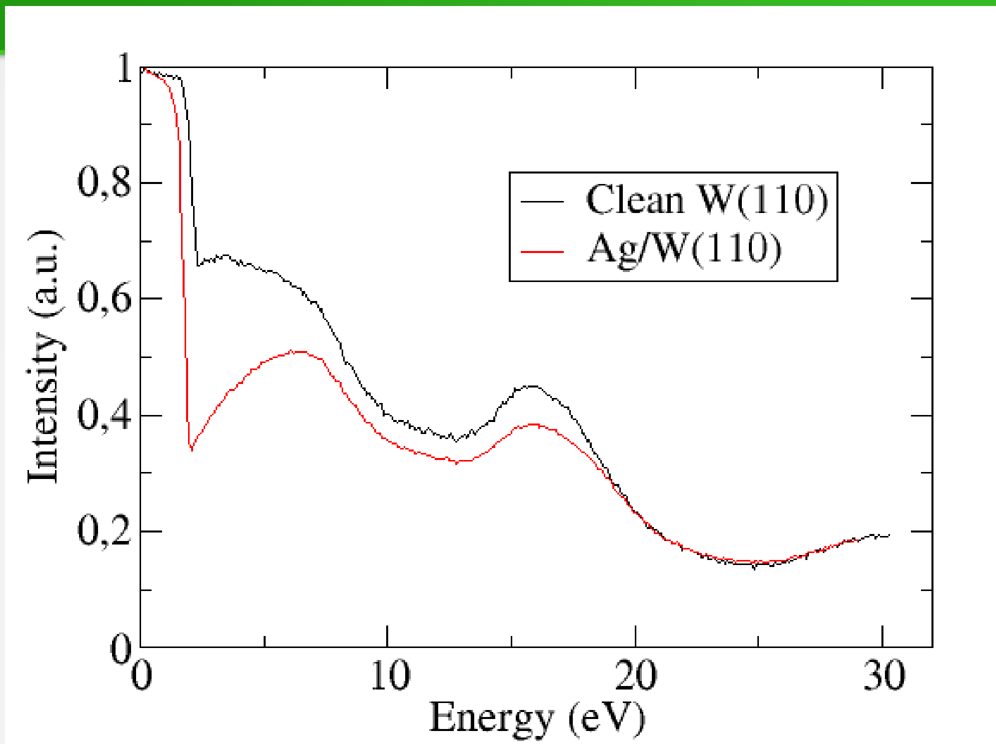
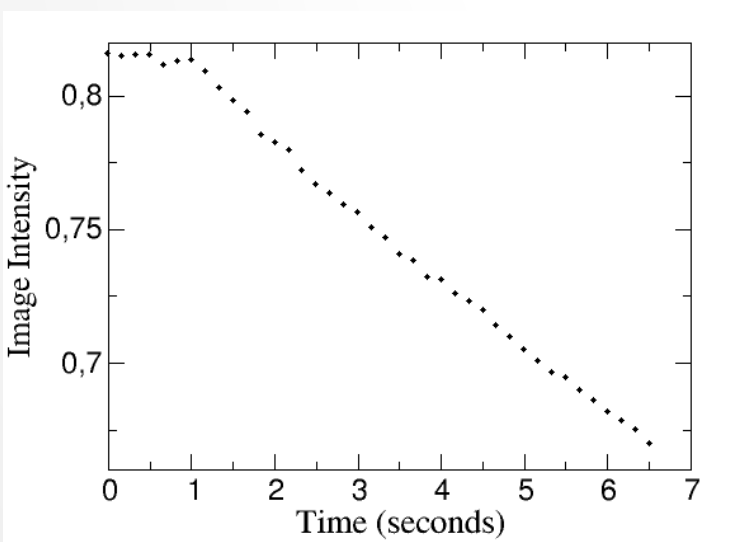
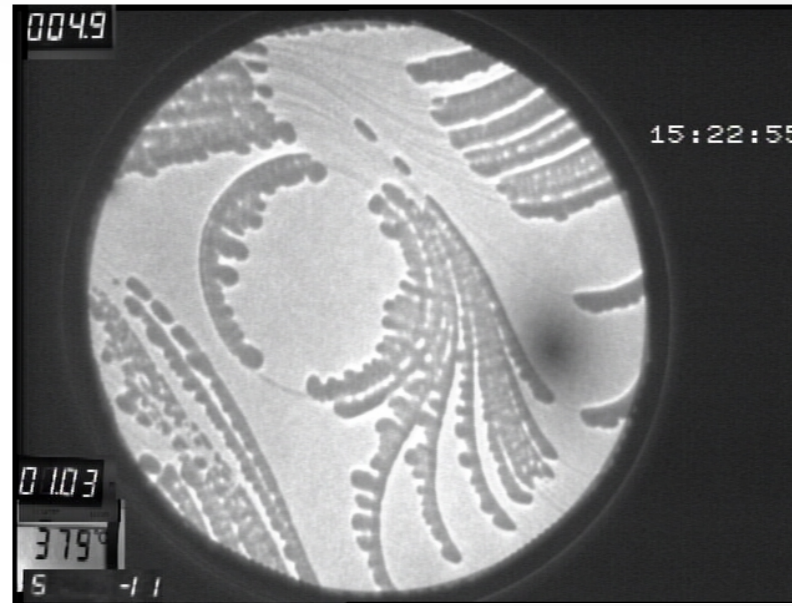




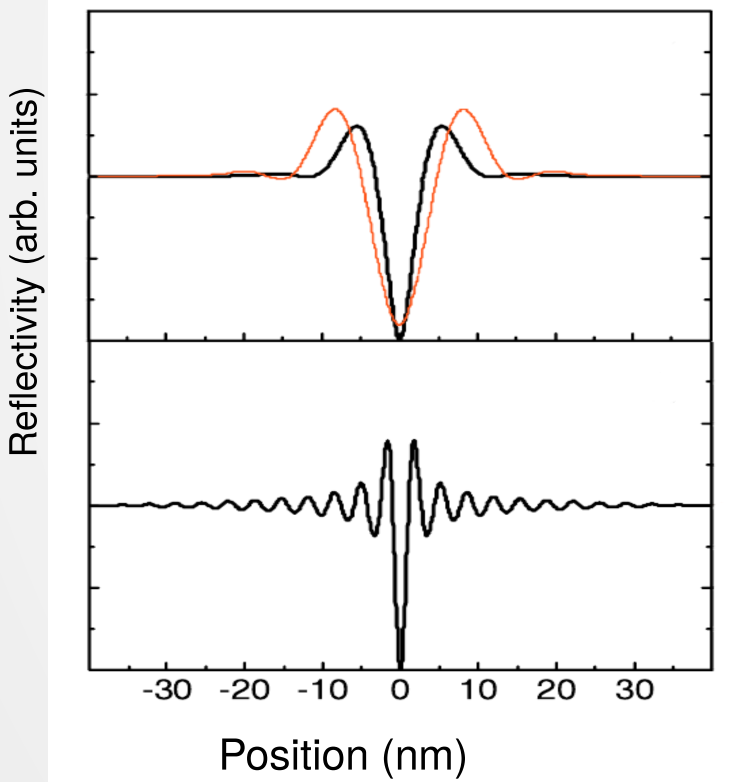


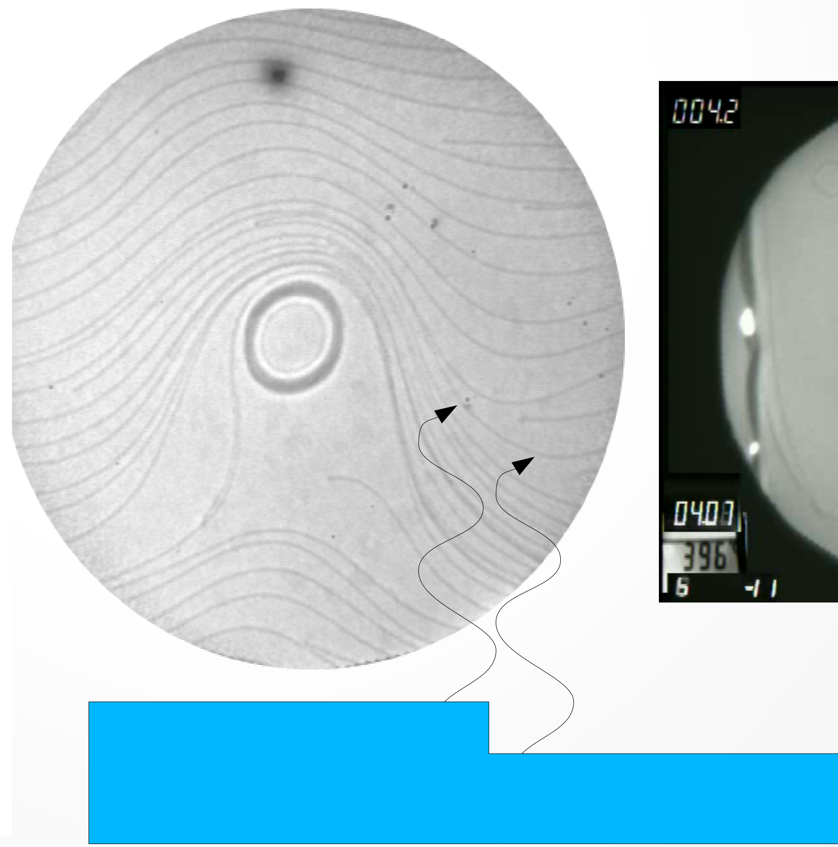
Phase Contrast: see atomic steps

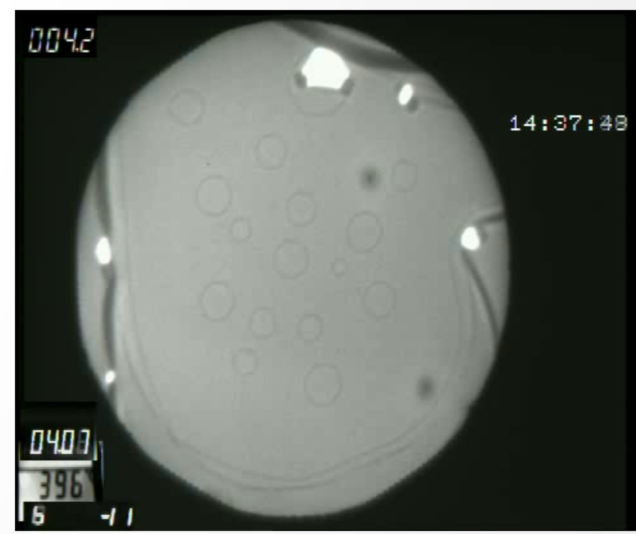
- Spatial resolution is ~ 10nm
- But vertical resolution can be much better!
  - Use interference effects
  - electron wavelength in Å is

For 10 eV, $\lambda = 3.87$ Å

$$\lambda = \frac{h}{\sqrt{2mE}} = \sqrt{\frac{150}{E(eV)}}$$







W(110), 10 µm FOV

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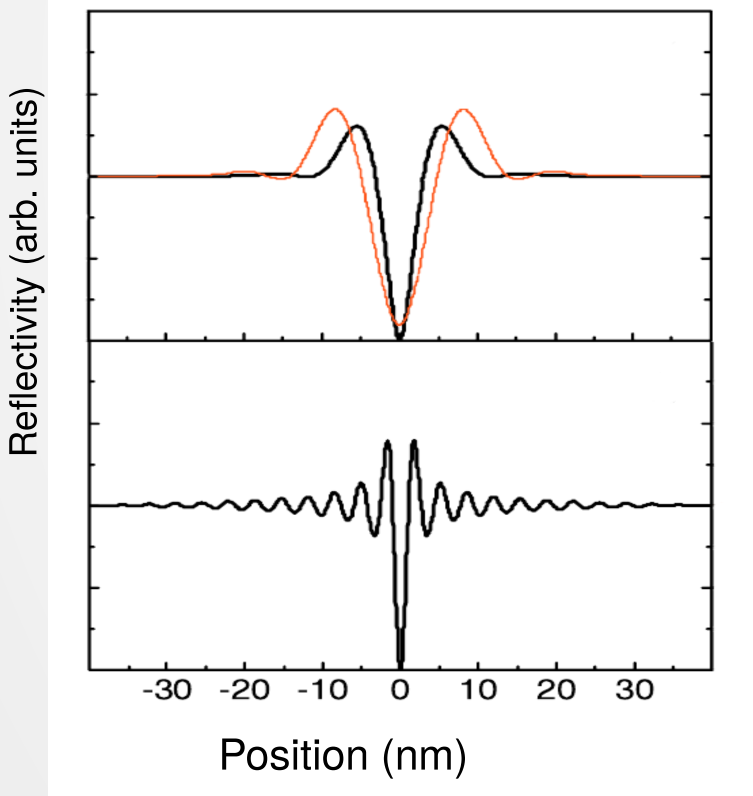
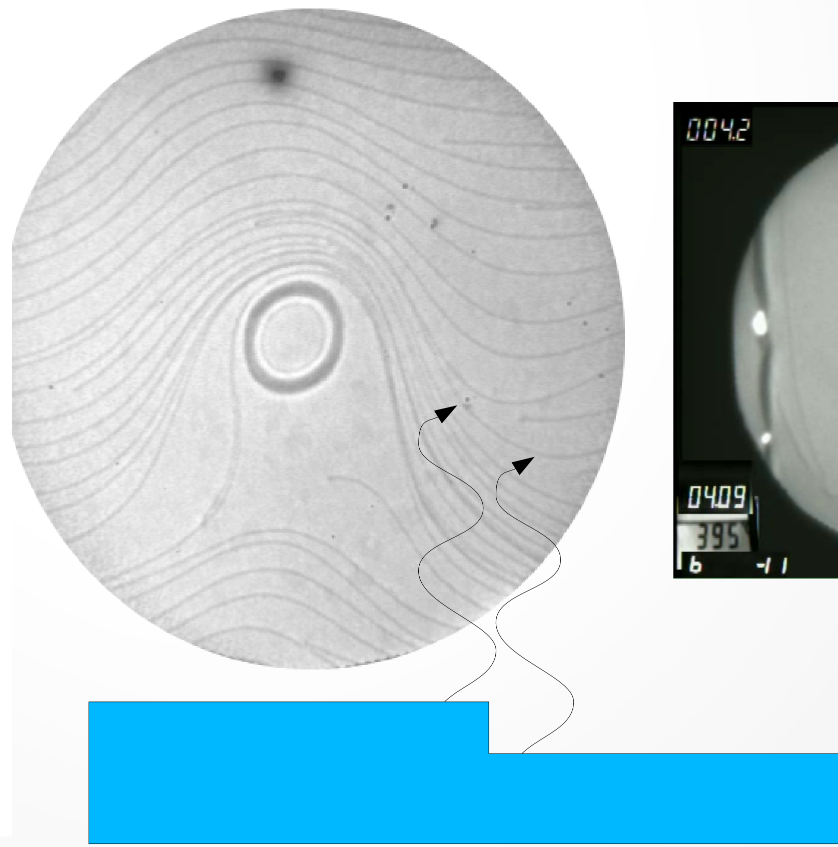
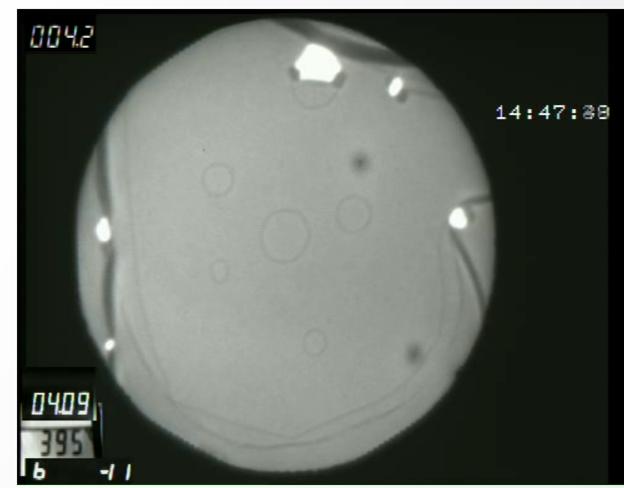
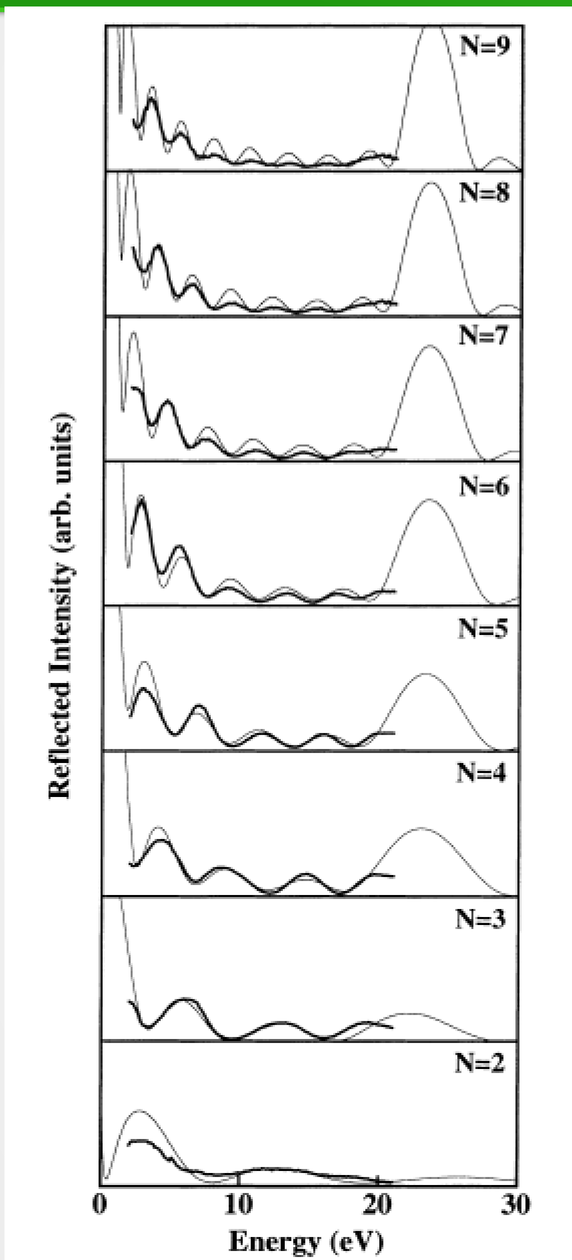




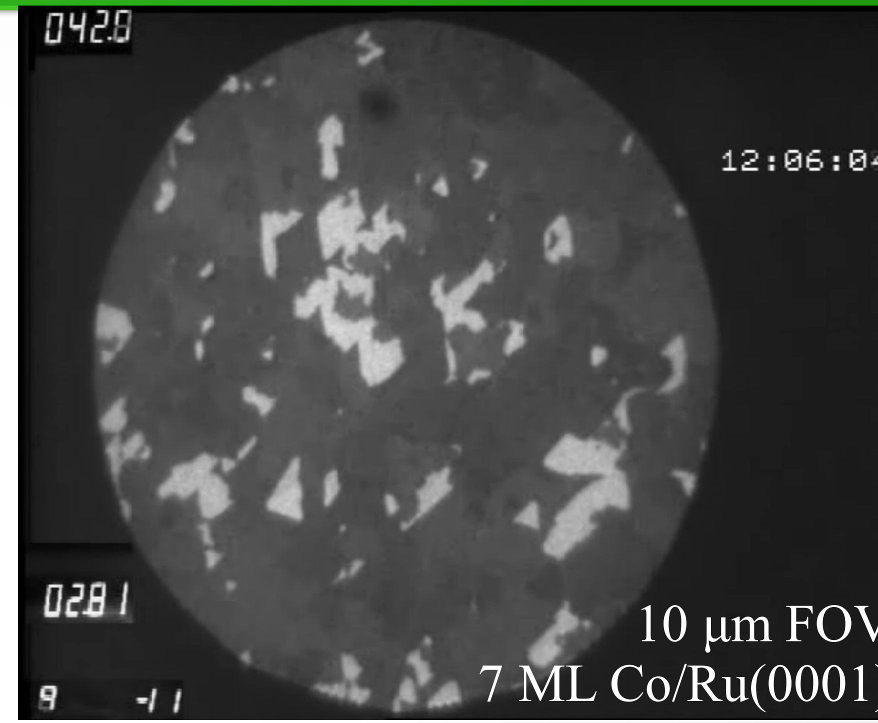


W(110), 10 µm FOV

Phase contrast:Quantum size effect

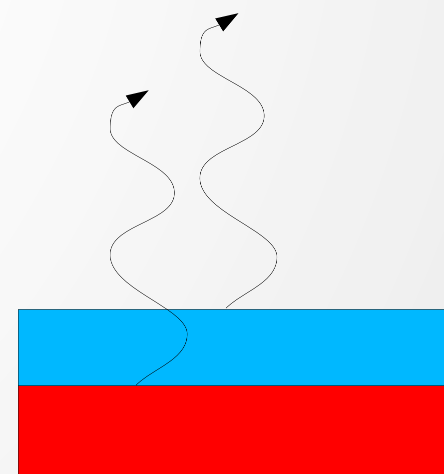


Interference between waves reflected at the outer interface and waves reflected at the film/substrate interface



Cu/W(110)

M.S. Altman, W.F. Chung, Z.Q. He, H.C. Poon, S.Y. Tong *Quantum size effect in low energy electron diffraction of thin films,* App. Surf. Sci. **169-170** (2001) 82



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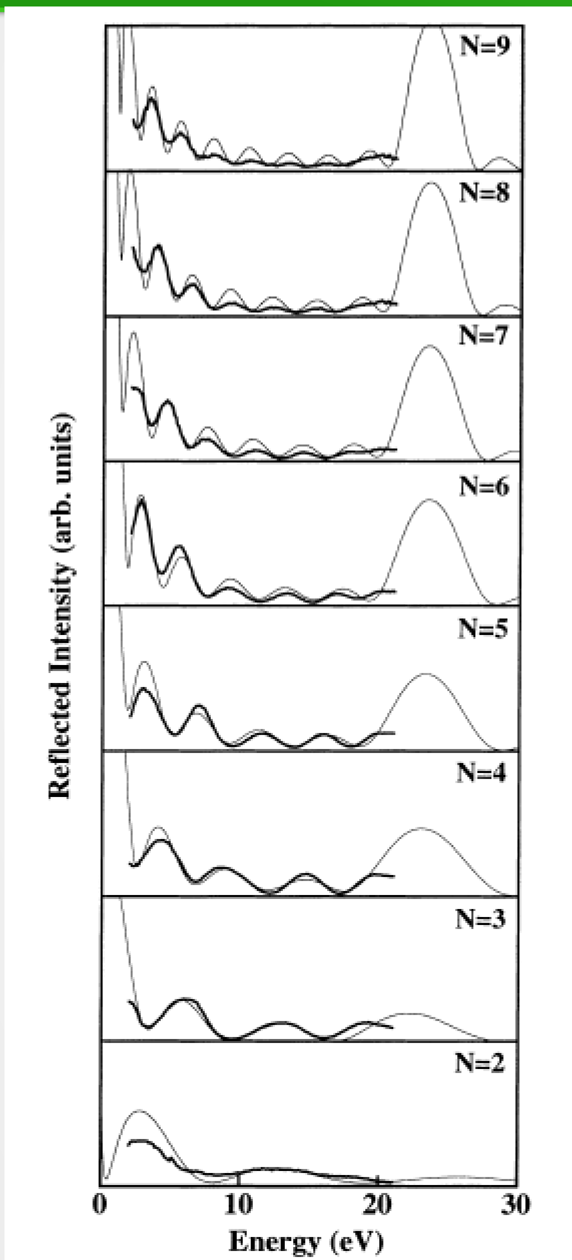

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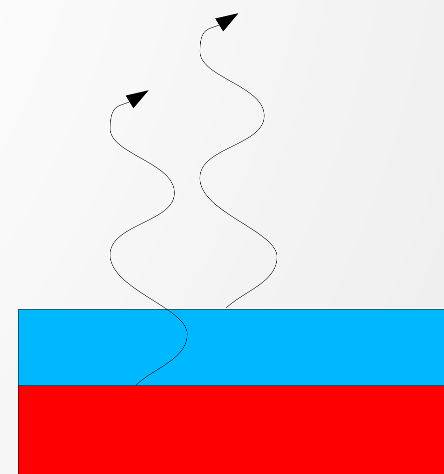
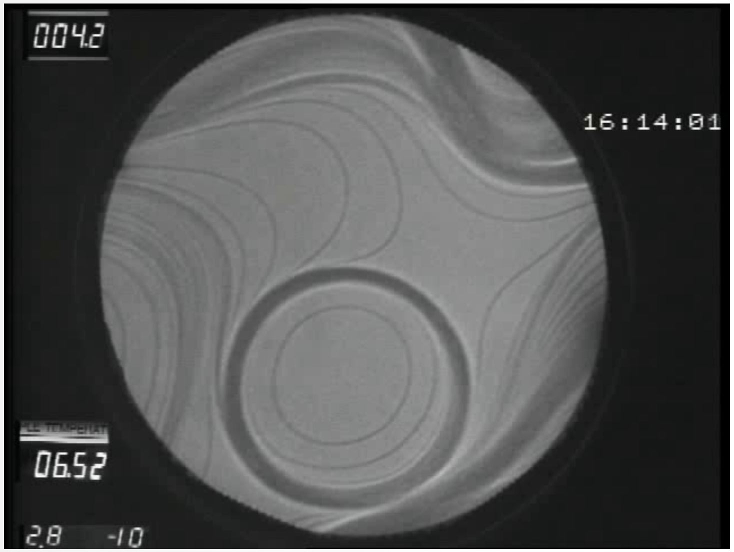


Real time imaging of growth processes

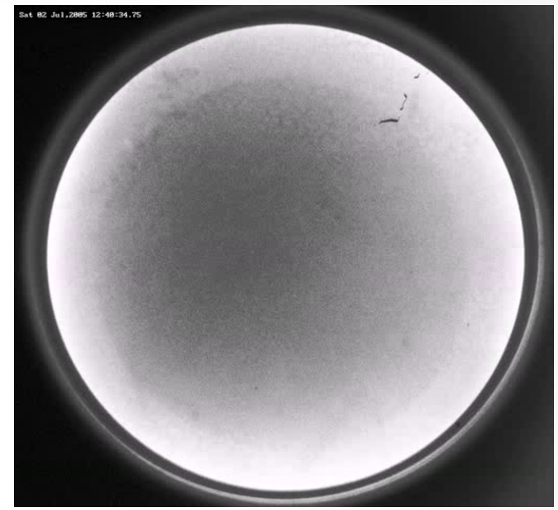
Step-flow. Cr/W(110)



B Santos
New J Phys 2008

FOV 7μm

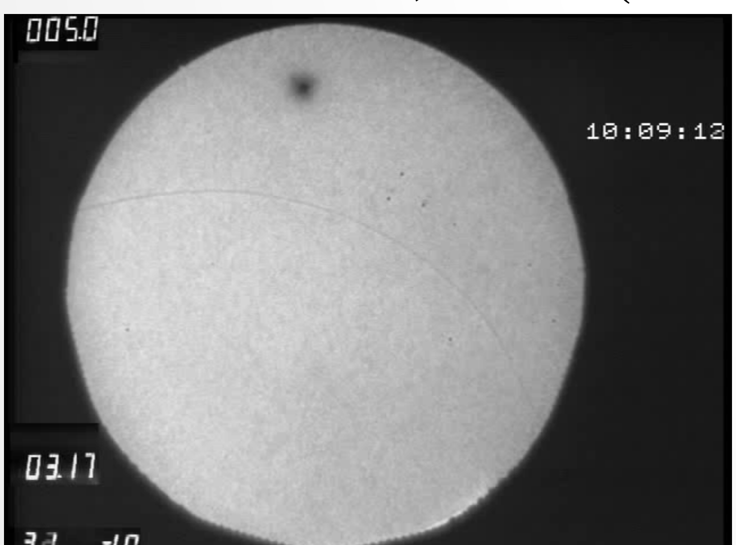
Kinetic labyrinth, Pd/Ru(0001)



N Rougemaille
Phys Rev Lett
2008

FOV 8μm

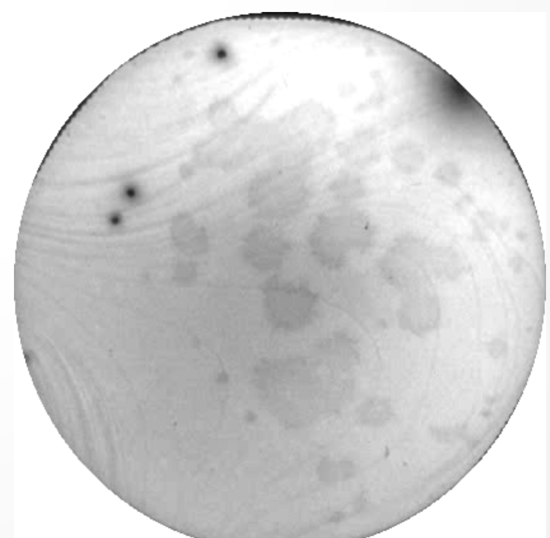
Island nucleation, Co/Ru(0001)



El Gabaly,
Phys Rev Lett 2006

FOV 10μm

Oxide growth, magnetite/Ru(0001)



M. Monti,
PRB 2013

FOV 10μm

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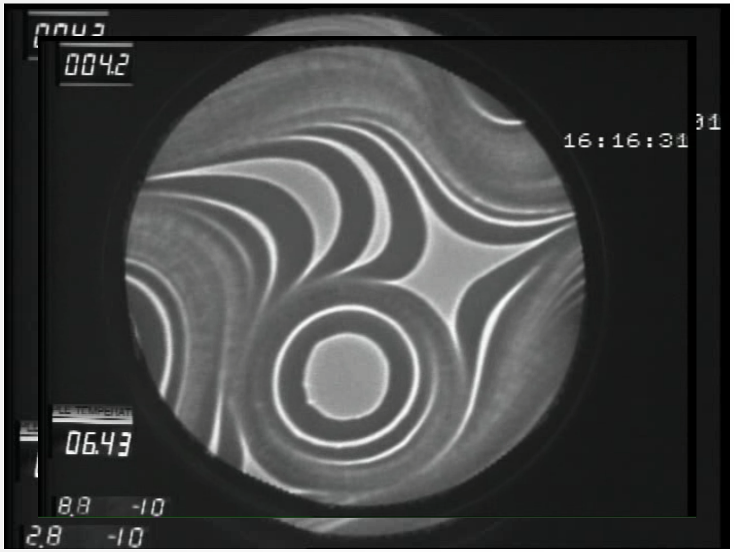

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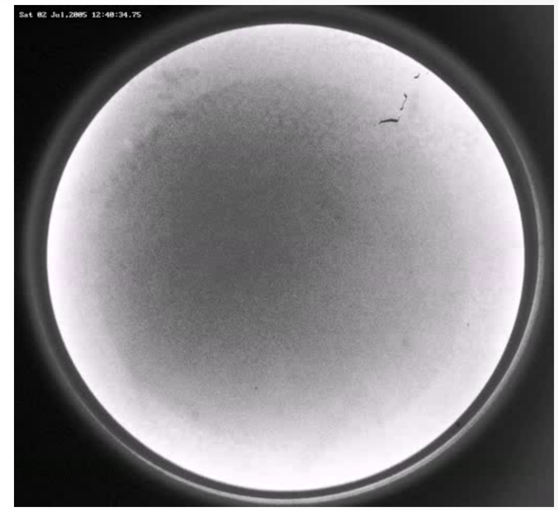

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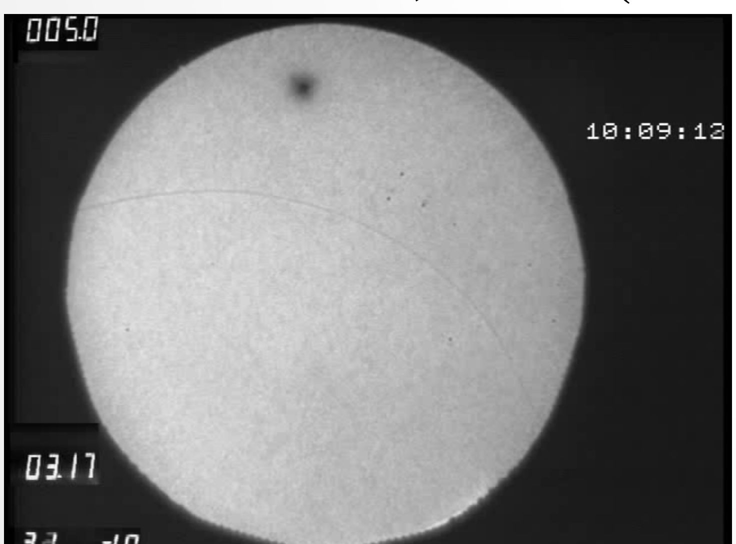

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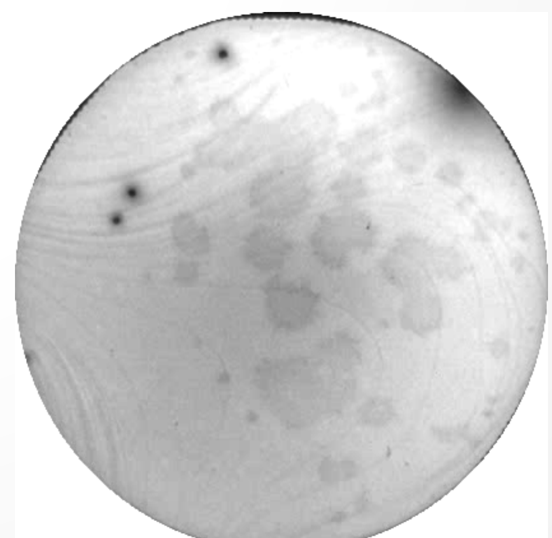

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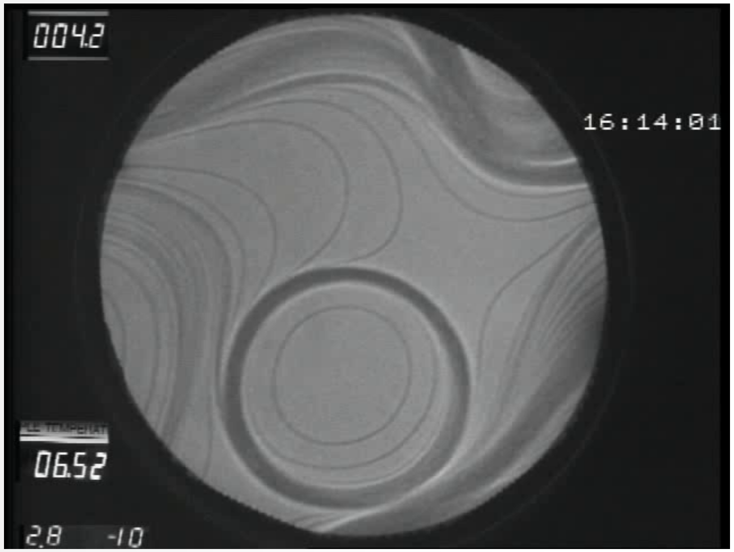

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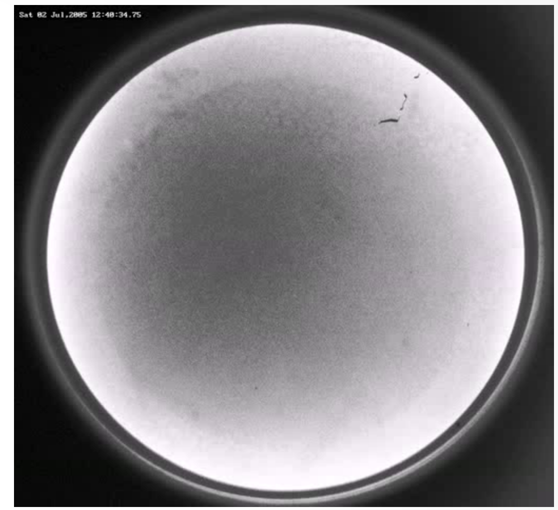

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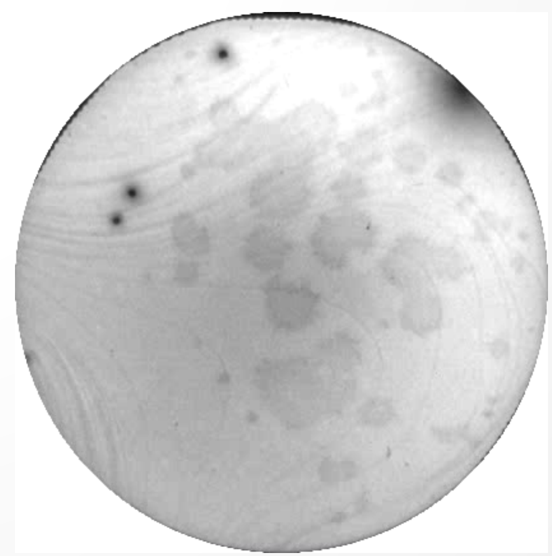

M. Monti,
PRB 2013

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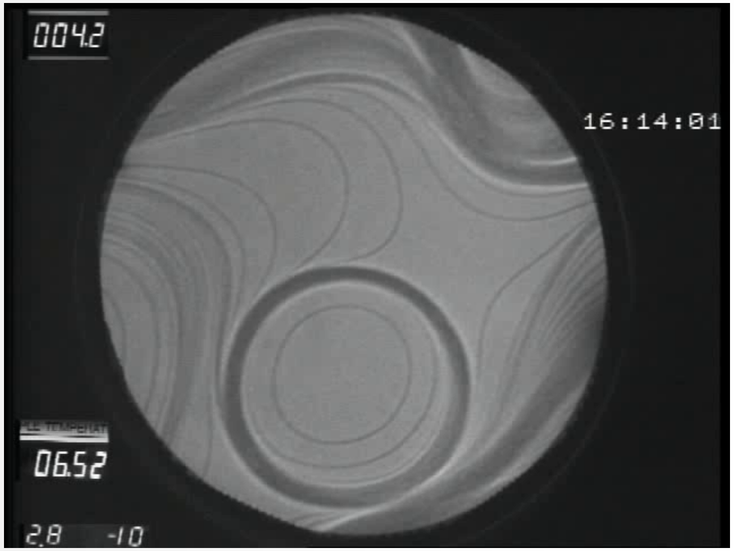

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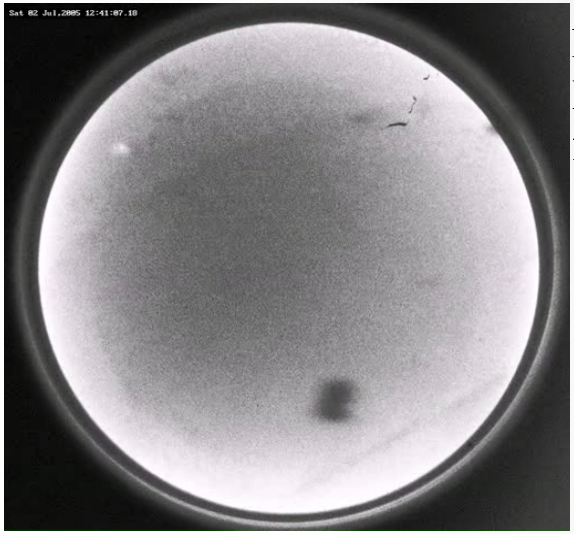

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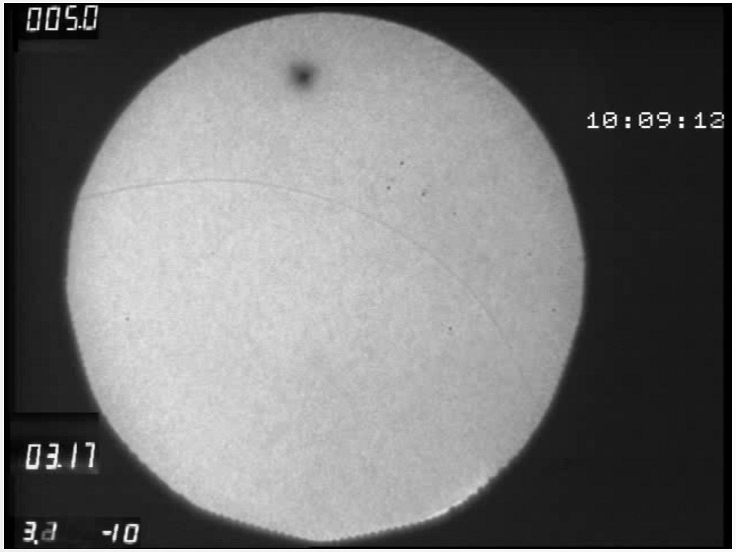

El Gabaly,
Phys Rev Lett 2006

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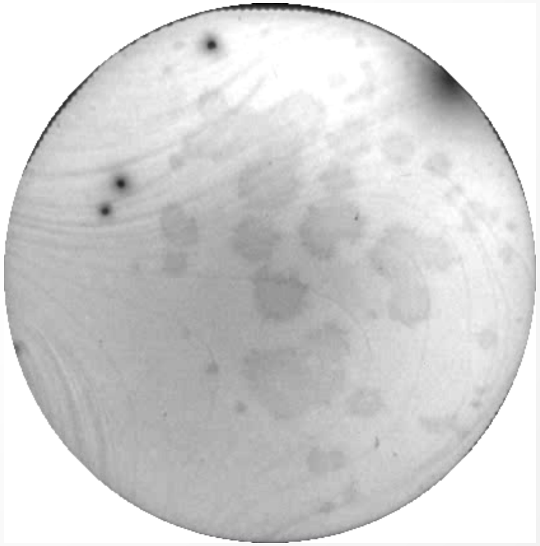

M. Monti,
PRB 2013

FOV 10µm

Real time imaging of growth processes

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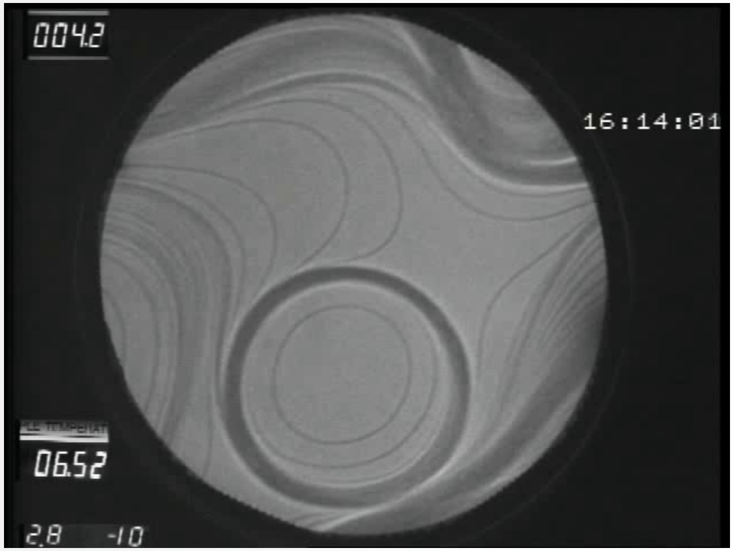

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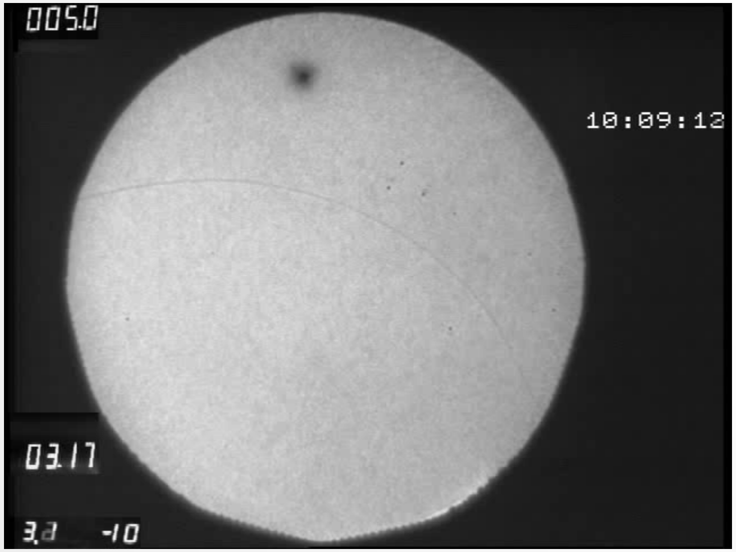

El Gabaly,
Phys Rev Lett 2006

FOV 10µm

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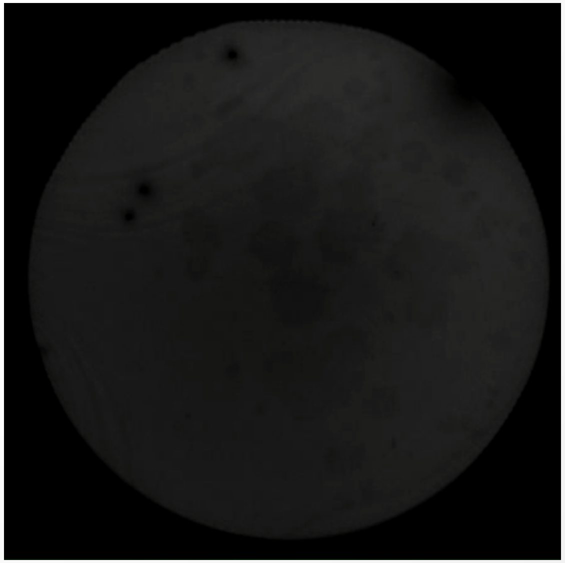
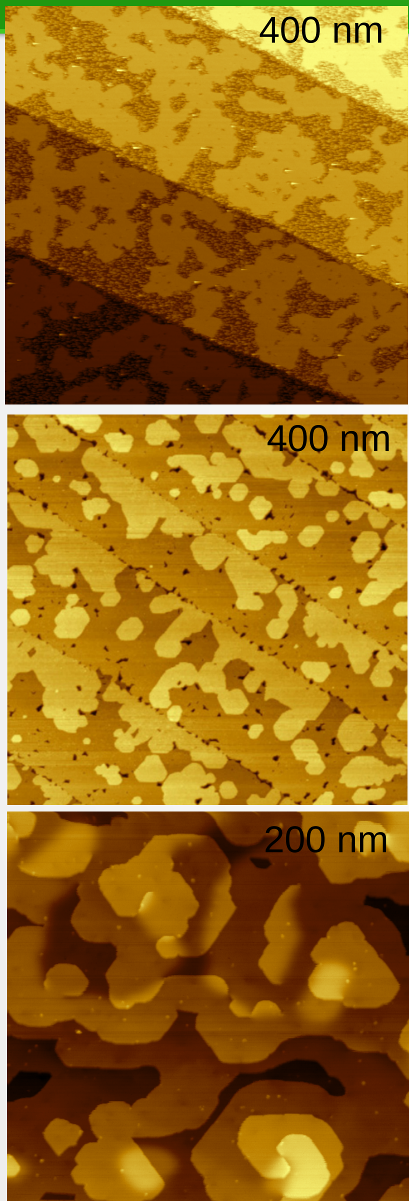


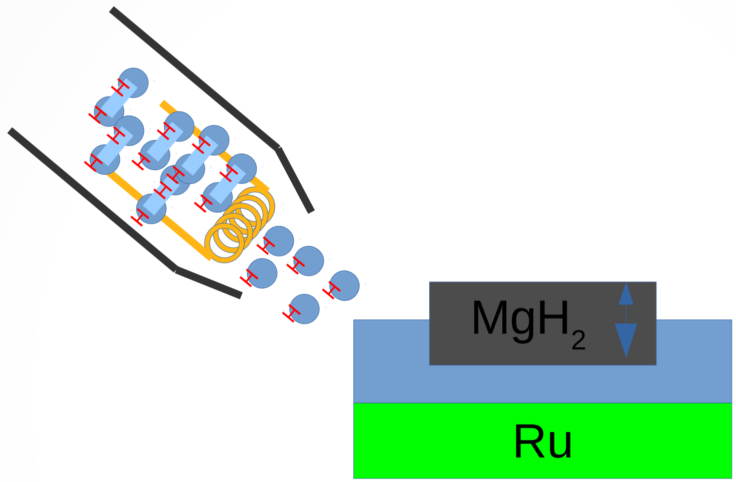
M. Monti,
PRB 2013

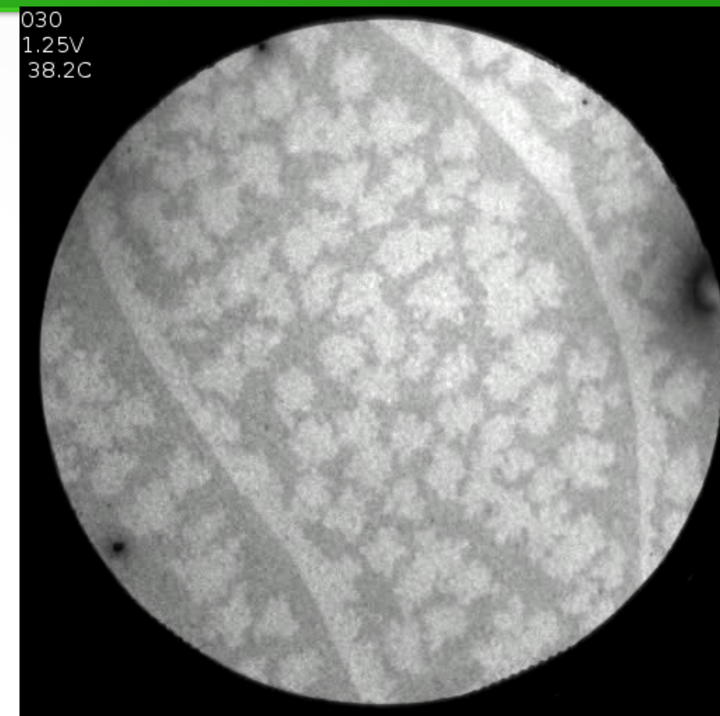
FOV 10µm

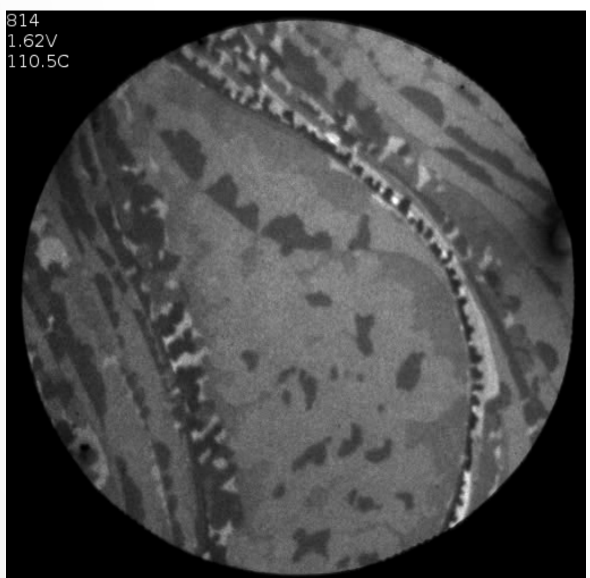
Mirror Mode: for delicate surfaces H/Mg/Ru

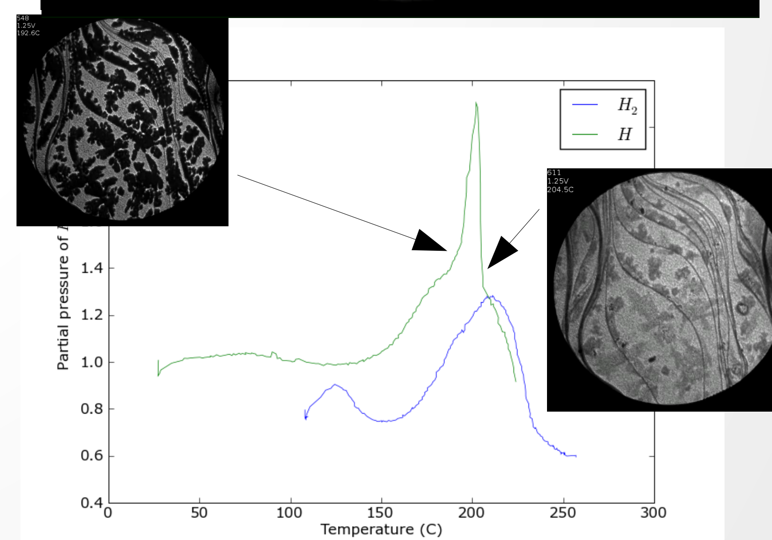


B. Santos et al., Chem Mat (2010)

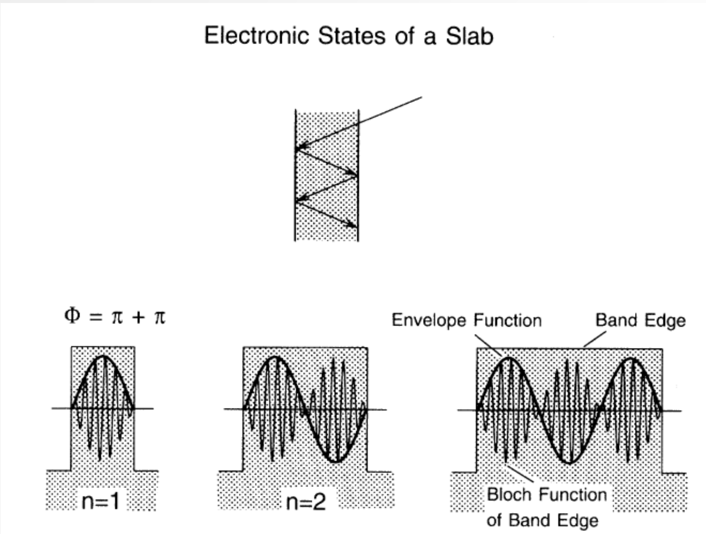


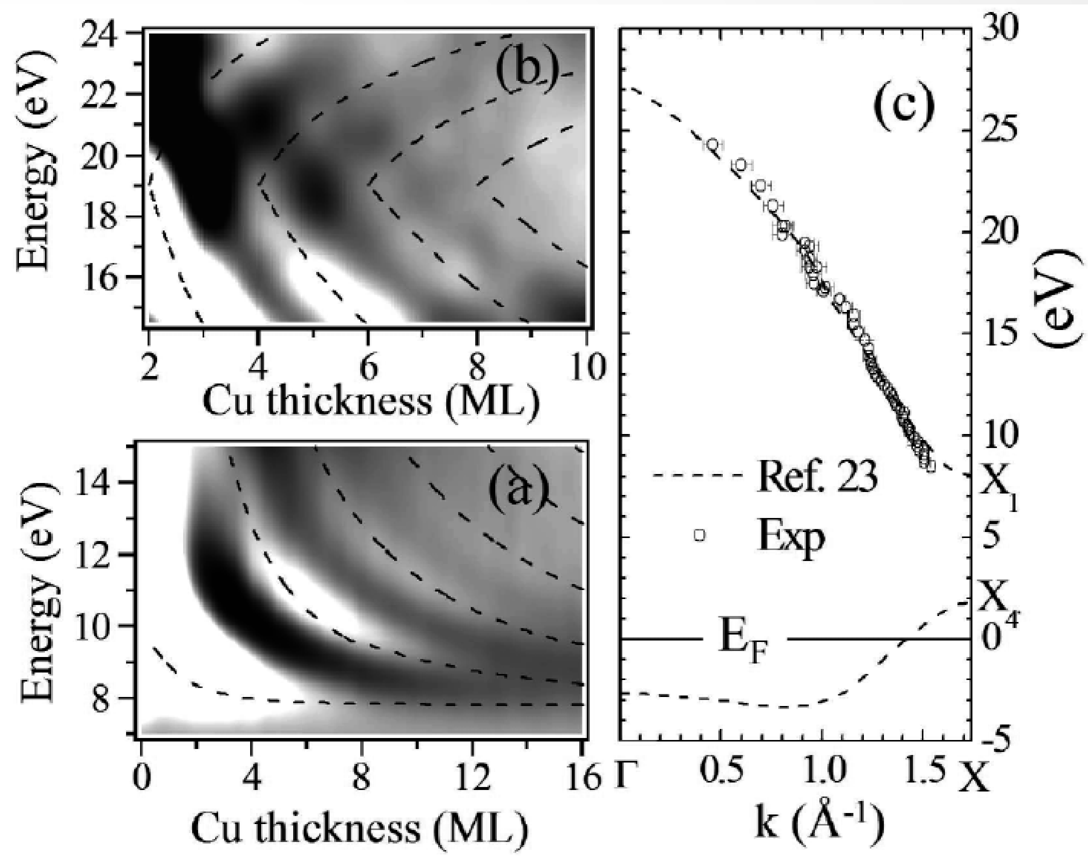






Reflectivity +QWS: band structure mapping





Cu/Co(100)

YZ Wu, AK Schmid, MS Altman, XF Jin, ZQ Qiu, *Phys. Rev. Lett* **94** (2005) 027201

$$if\ k < \frac{k_{BZ}}{2}$$

$$2k\,d_{Cu} + \Phi = 2\pi n$$

$$if\ k > \frac{k_{BZ}}{2}$$

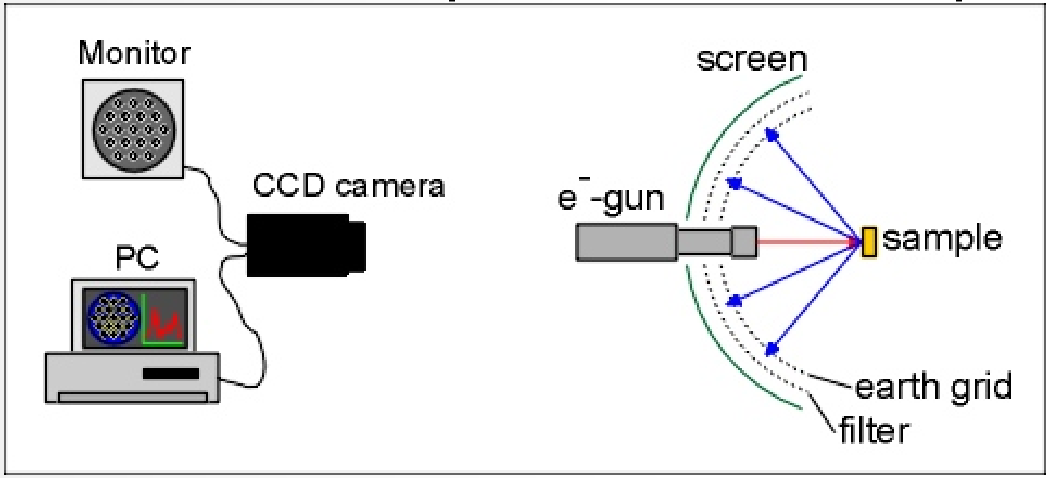
$$2(k_{BZ} - k)\,d_{Cu} - \Phi = 2\pi\nu$$

Directly from the periodicity at constant energy, the band structure can be extracted

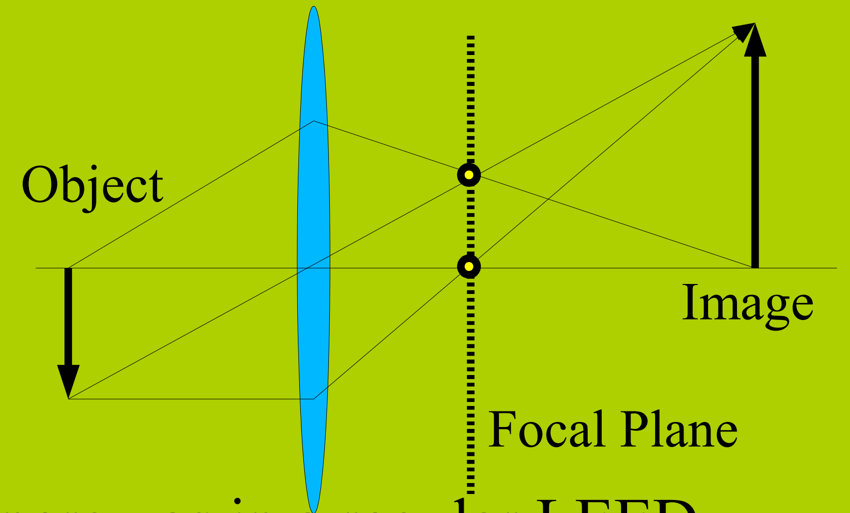
Low Energy Electron Diffraction

- Change energy, measure intensity of diffracted spots
- Multiple scattering calculations required
- Well understood, error sources known, error below the 1% range

Traditional experimental setup

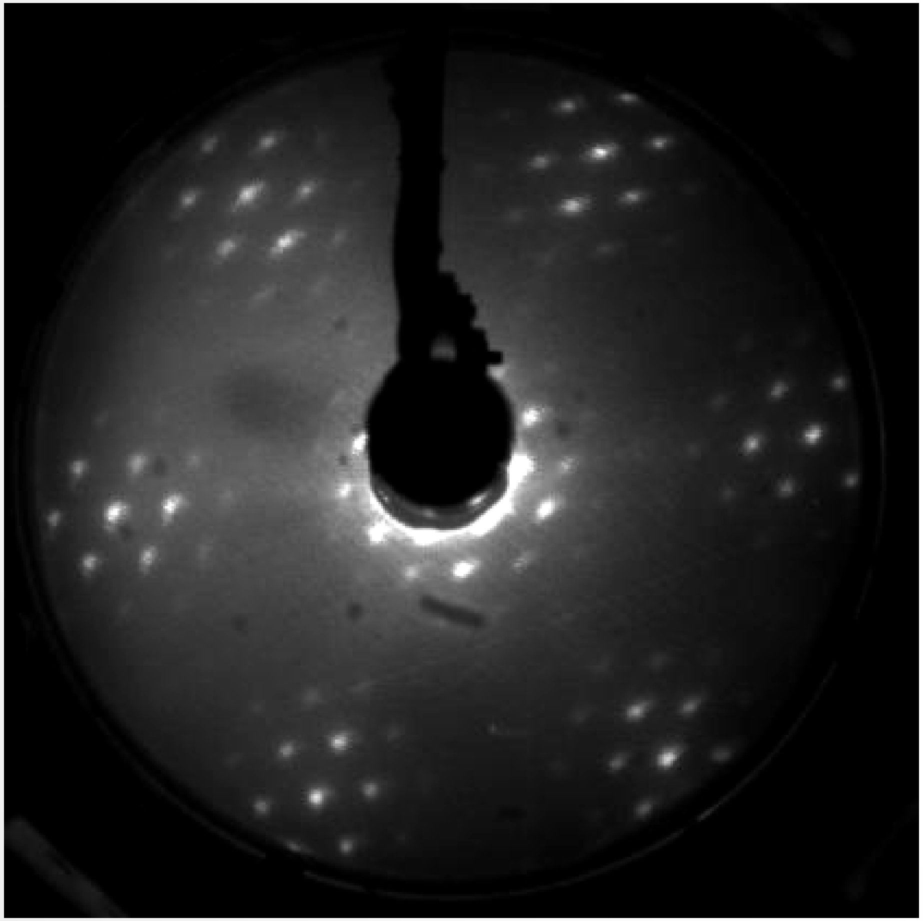


With LEEM

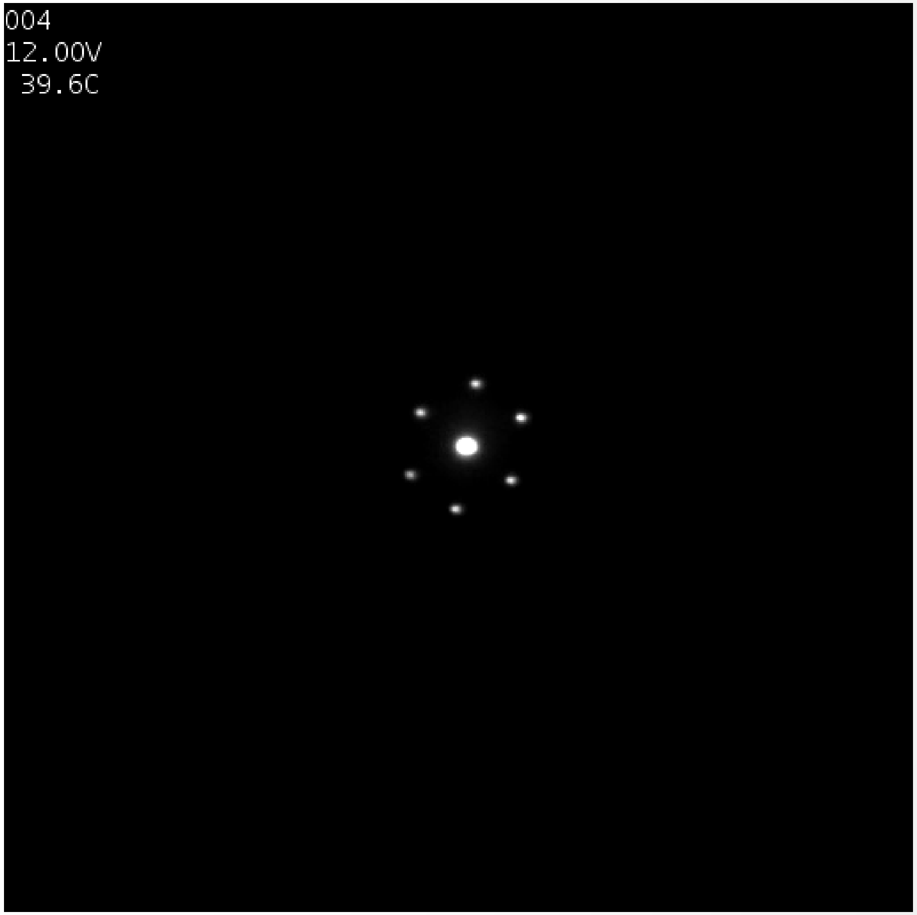


- The spots do NOT move changing the energy as in a regular LEED spectrometer!
- The spots can be amplified (~SPALEED)
- The specular beam (0,0) can be recorded at normal incidence
- No problem heating the sample (screen is not in line of sight of sample)
- Unless energy filtering is used, inelastic electrons are included

LEED IV data on a LEEM

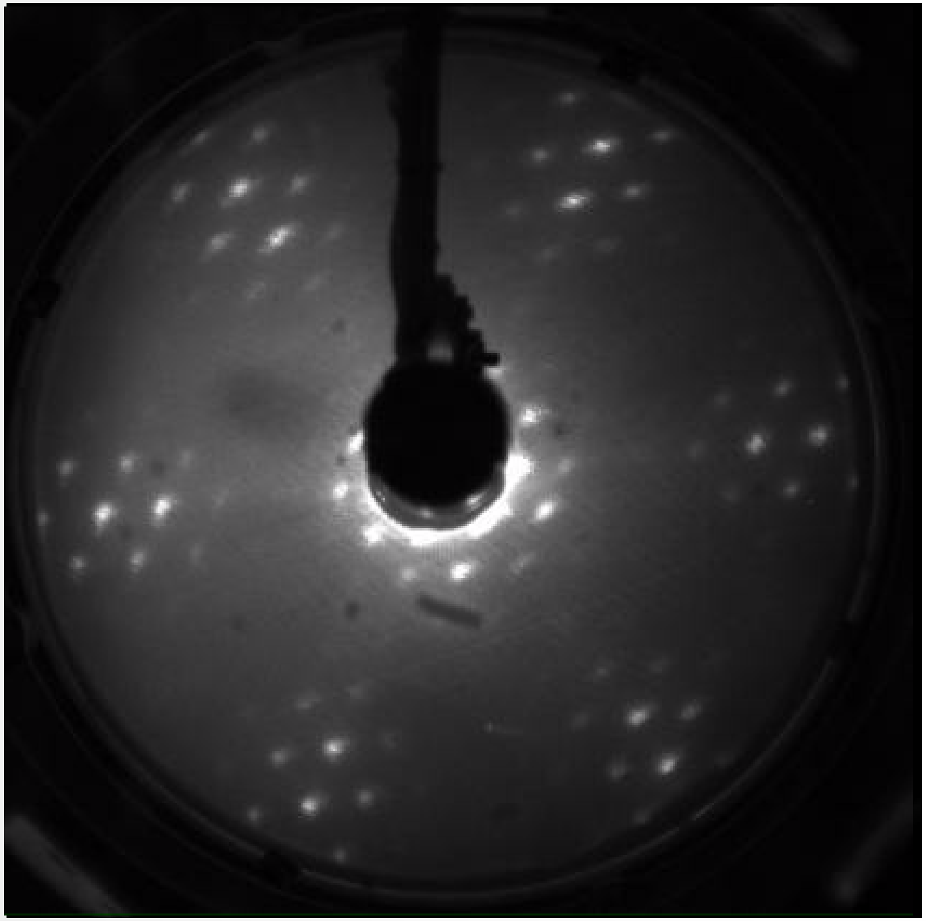


Regular diffractometer,
FeO/Ru(0001)

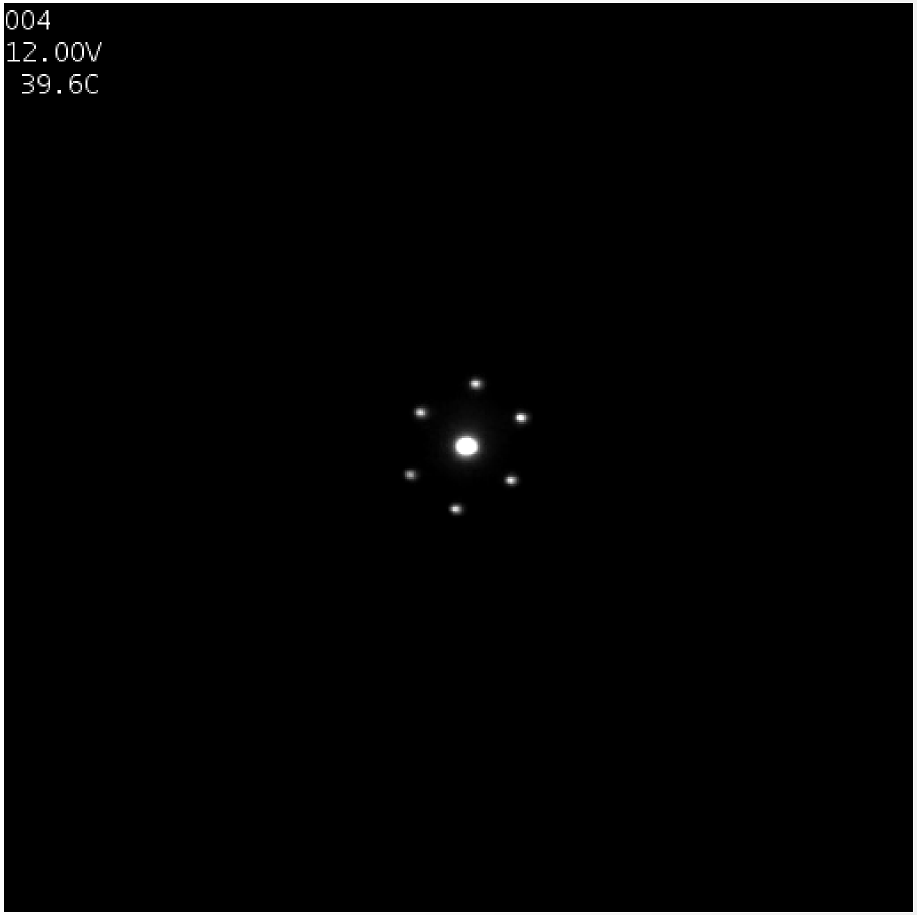


LEED on LEEM,
FeO/Ru(0001)

LEED IV data on a LEEM

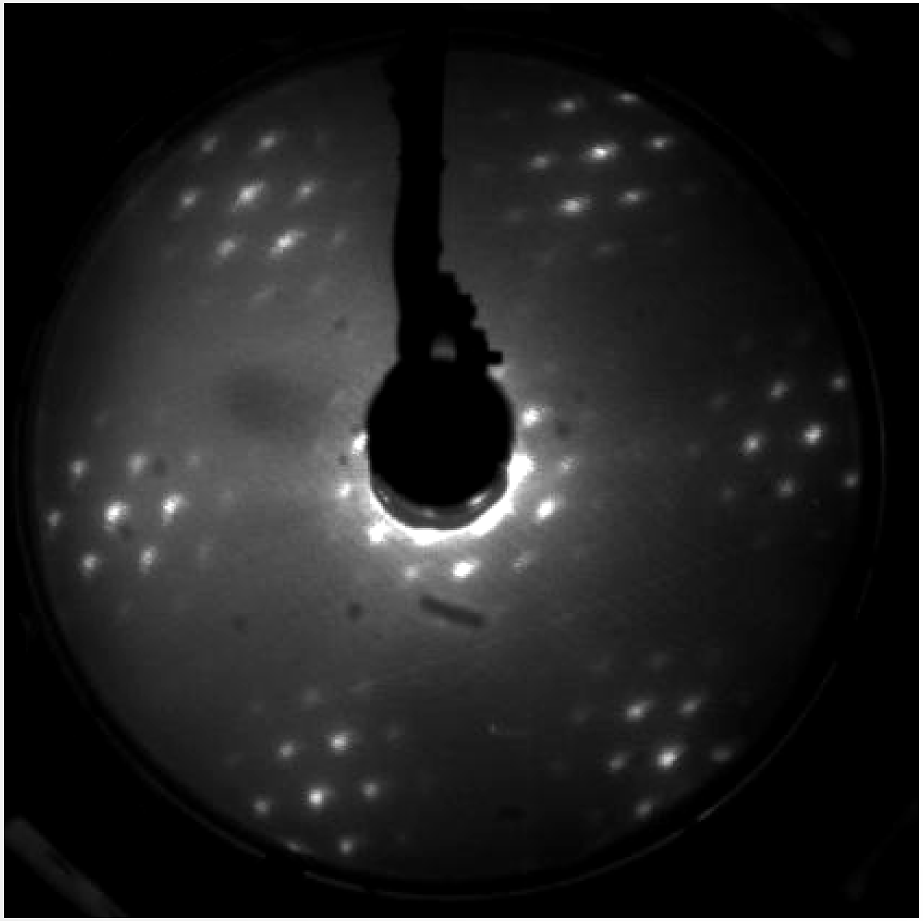


Regular diffractometer, FeO/Ru(0001)

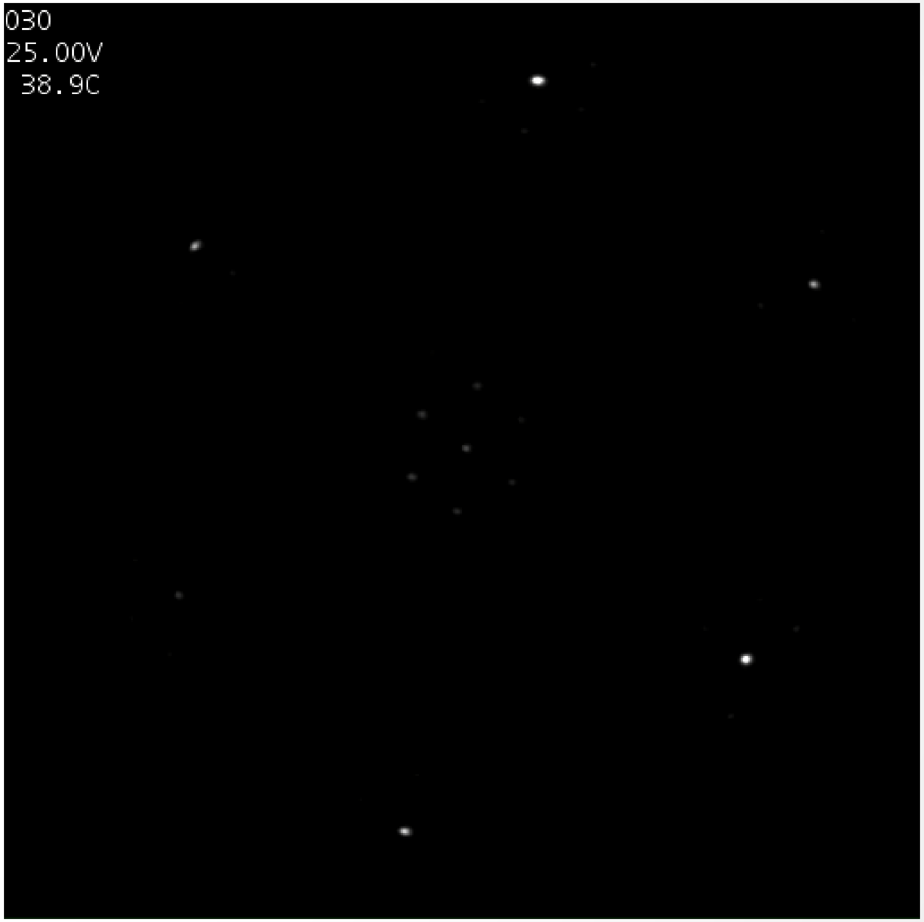


LEED on LEEM, FeO/Ru(0001)

LEED IV data on a LEEM

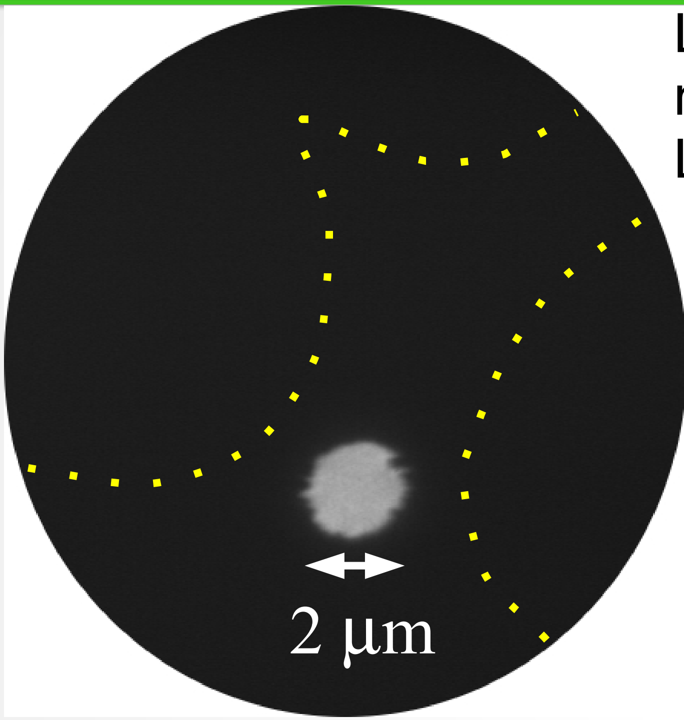


Regular diffractometer, FeO/Ru(0001)



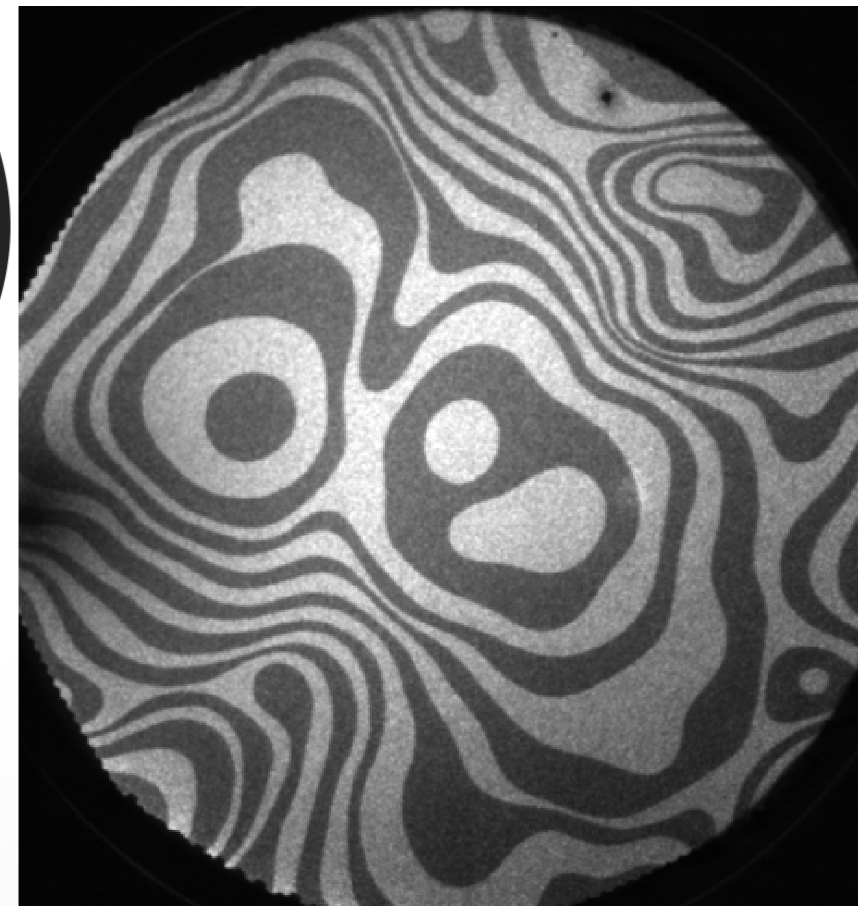
LEED on LEEM, FeO/Ru(0001)

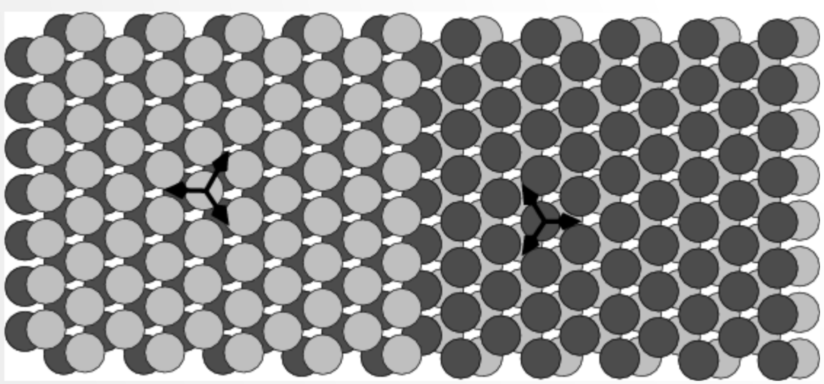
Doing LEED with LEEM: µLEED

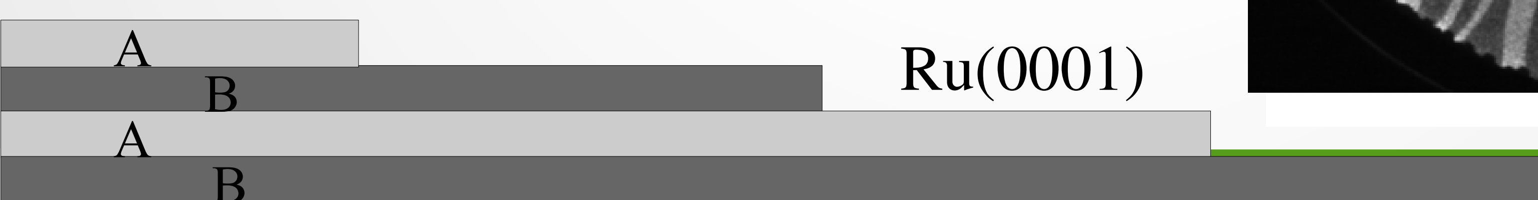


Limiting the beam size down to a fraction of a micrometer by means of an aperture give micro-LEED:

Take LEED data on a single terrace!

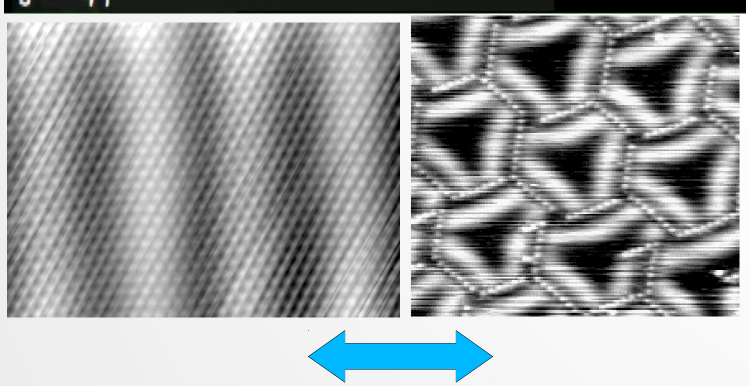






Better LEED for phase transitions!: "SPALEED"

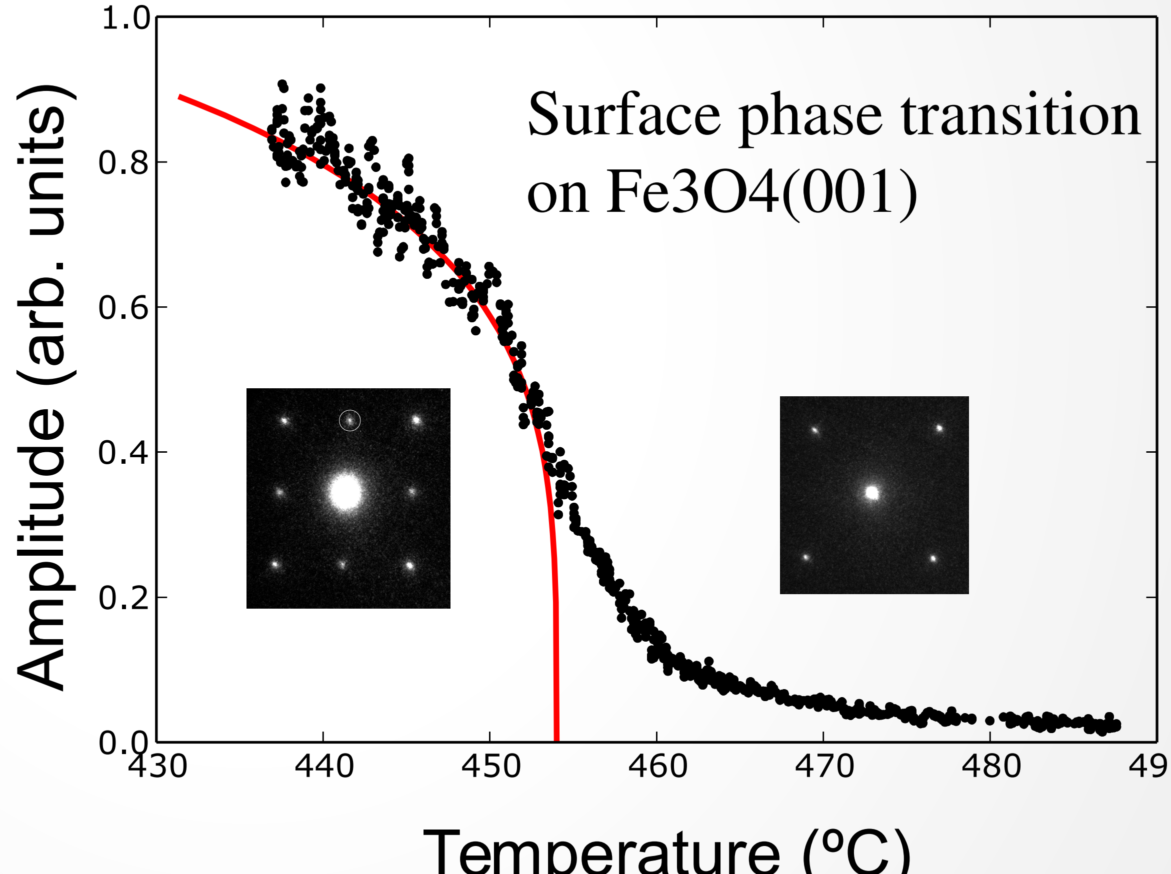
Structural transitions upon temperature changes of S/Cu/Ru(0001)



Unpublished

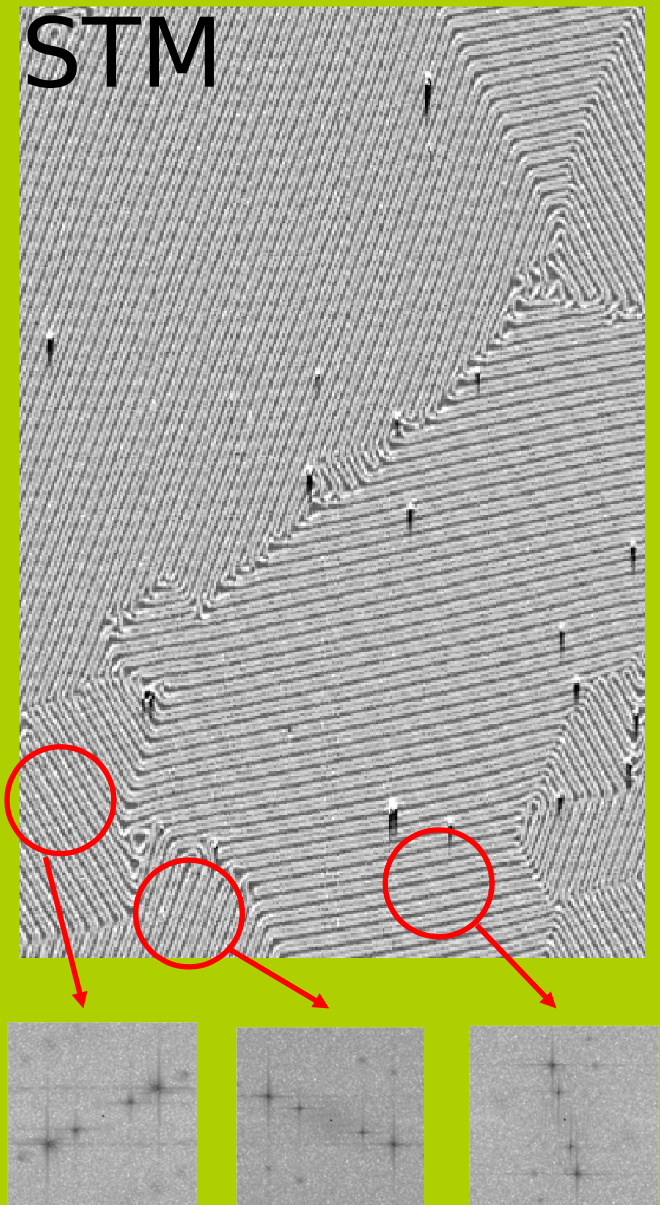
Order-disorder transition at the Fe3O4(001) surface

NC Bartelt et al., Phys Rev. B 88 (2013) 235436

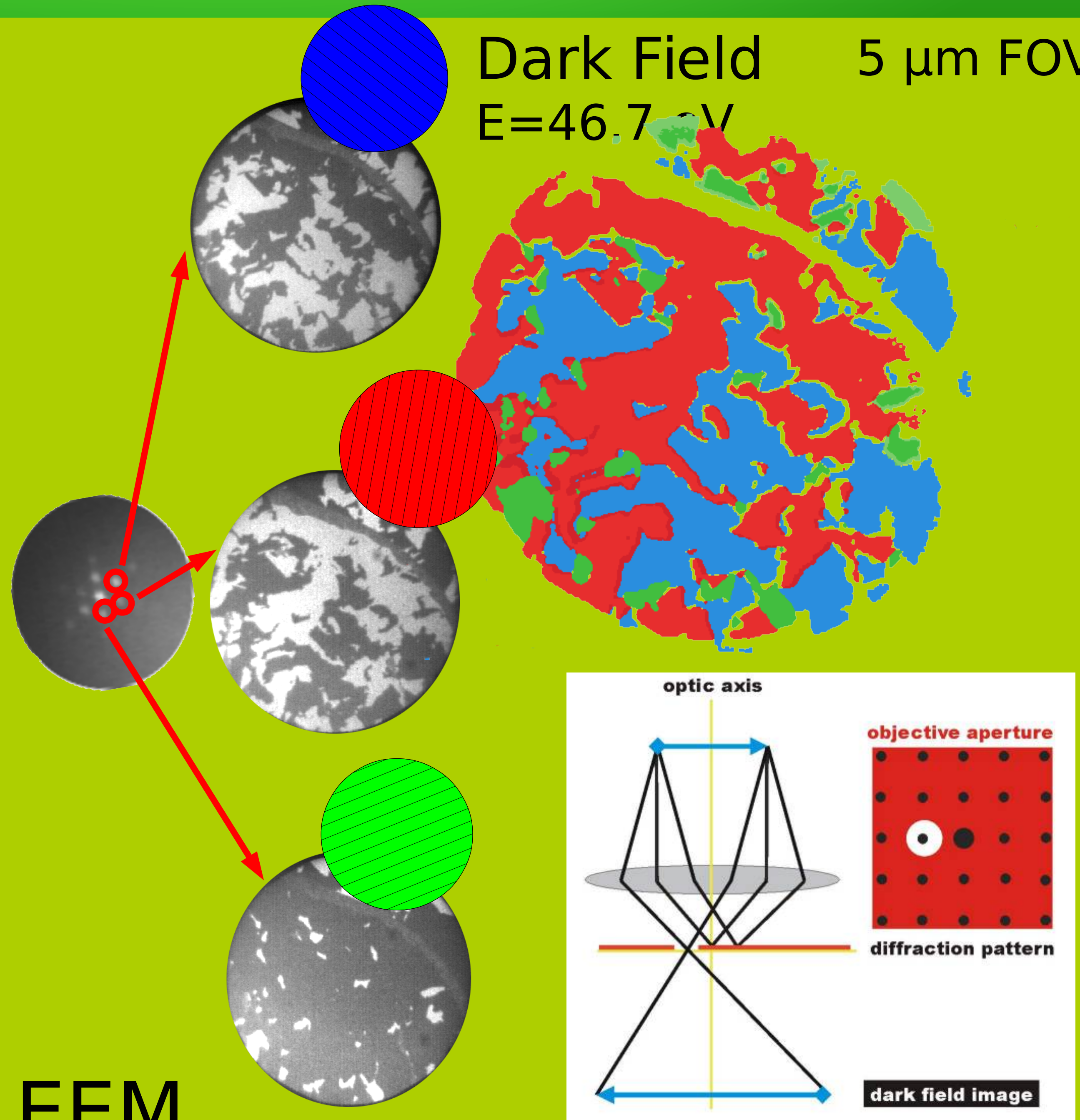


LEED can be performed at any temperature

Dark field imaging of 2ML Cu/Ru(0001)



FFT of selected areas

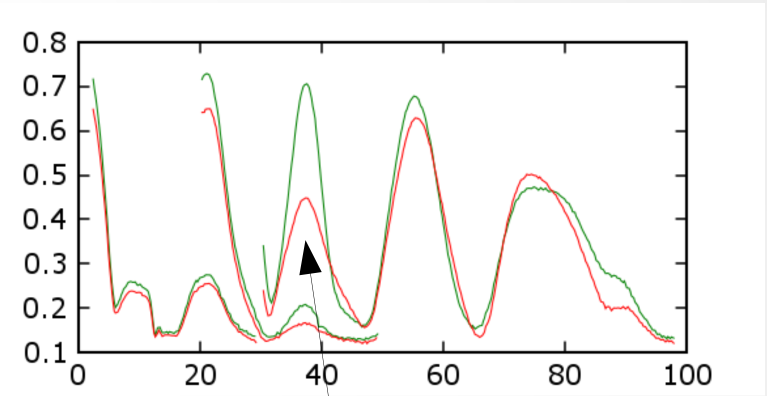


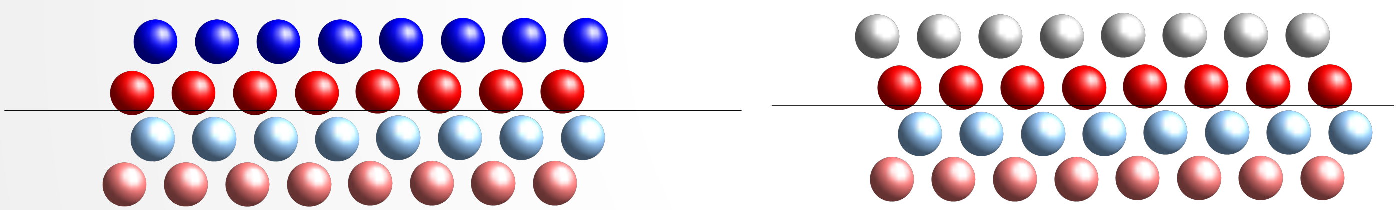
LEEM

Origin of stacking domains on 2 ML Cu/Ru(0001): use specular beam

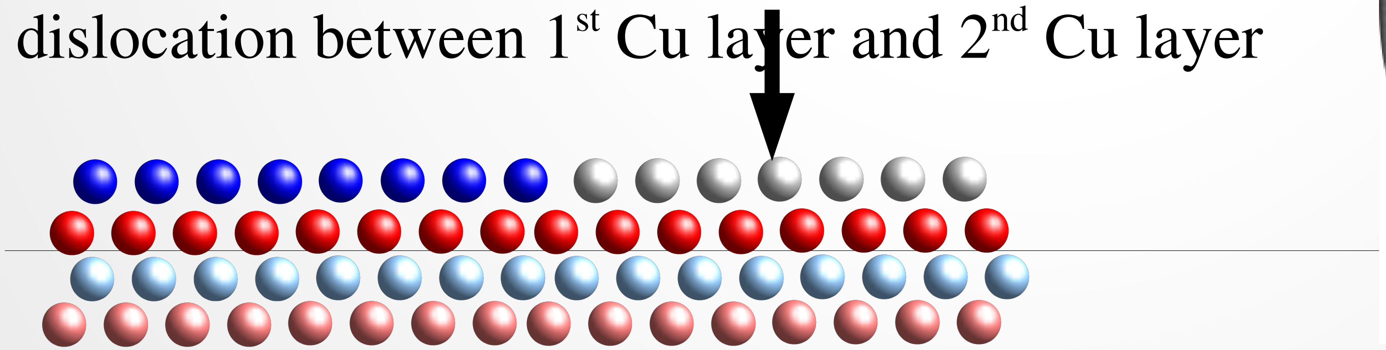
The Cu films are 2 ML high:

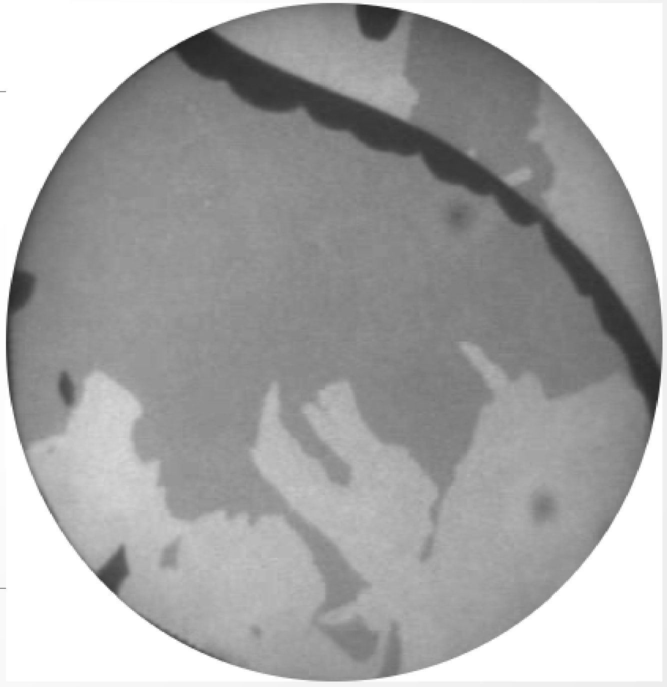
there are two ways of stacking the second layer on top of the first on 3-fold hollow sites





Boundary between stacking domains: partial dislocation between 1st Cu layer and 2nd Cu layer





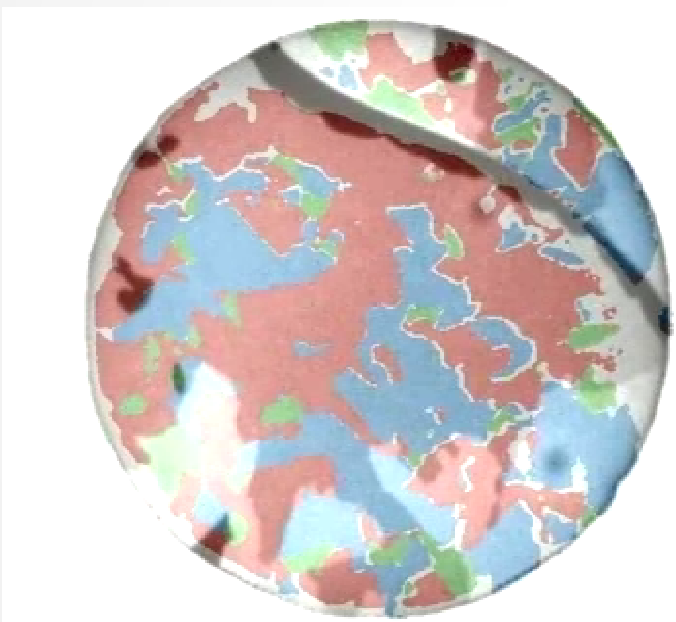
Full domain structure of 2 ML Cu/Ru: SIX domains= 3 rot x 2 stacking

Jerky motion:

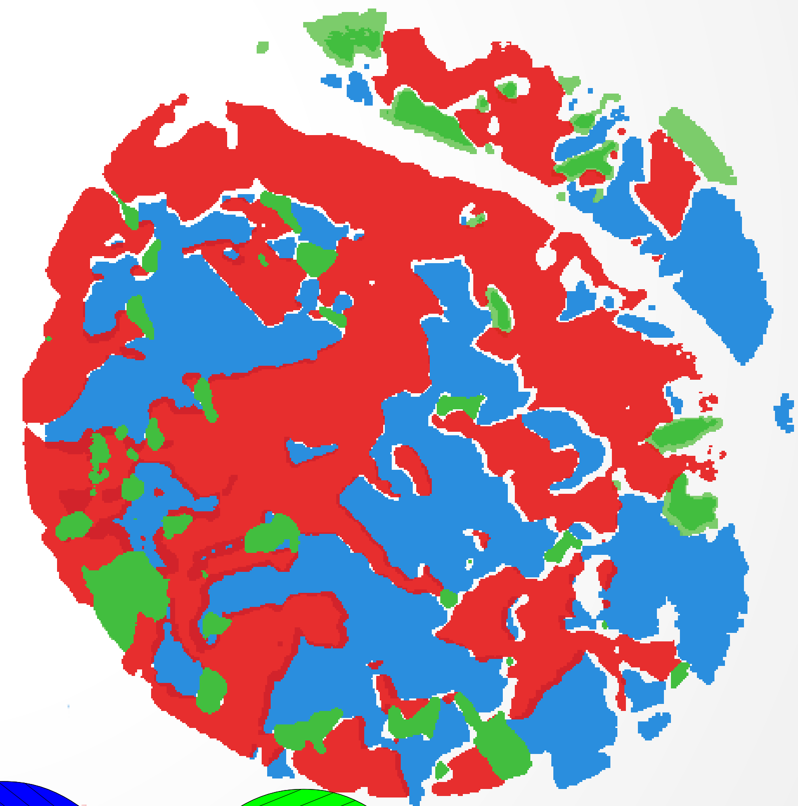
Fast within rotational domains

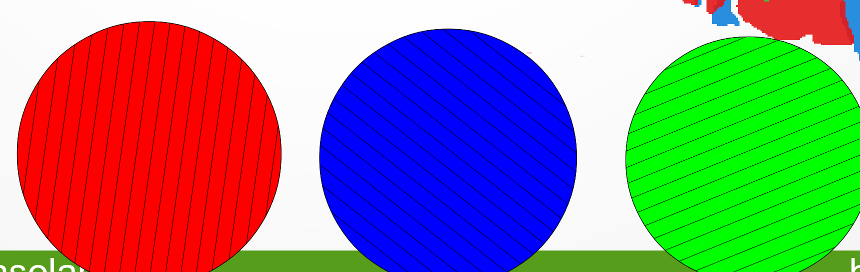
Slow at rot. boundaries

FOV 5 µm. The 260 frames correspond to 13 minutes of real time, with an initial temperature of 197 °C and a final one of 302 °C.



5 µm FOV





Evolution of Stacking Domain boundaries

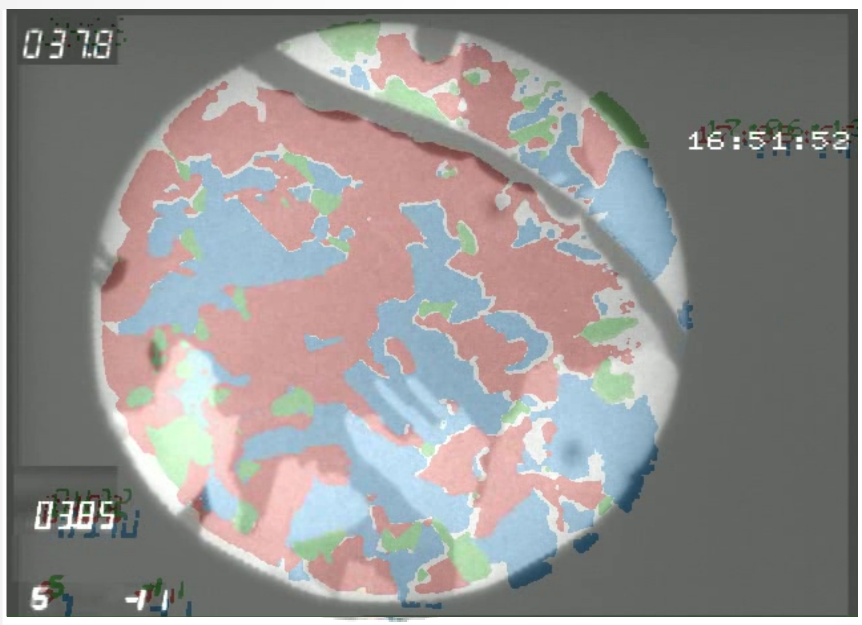
Science 308 (2005)1303

F. El Gabaly, Wai Li W. Ling,
K. F. McCarty, J. de la Figuera

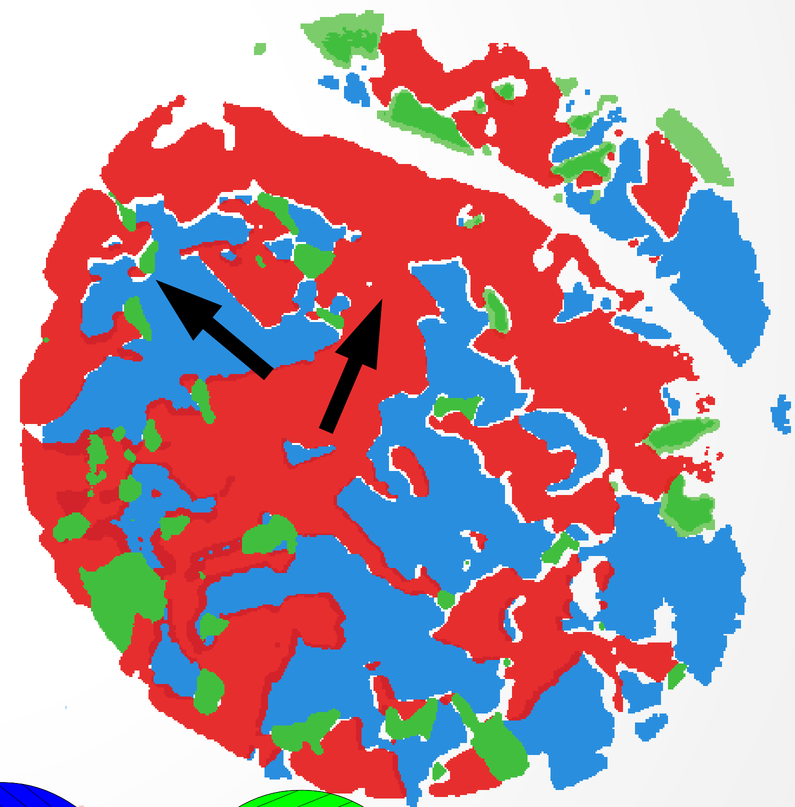
Jerky motion:

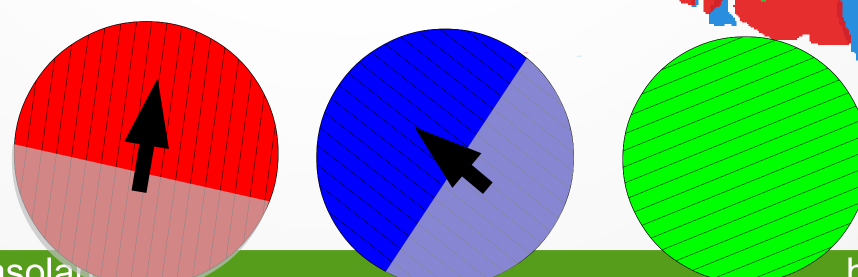
Fast within rotational domains

Slow at rot. boundaries



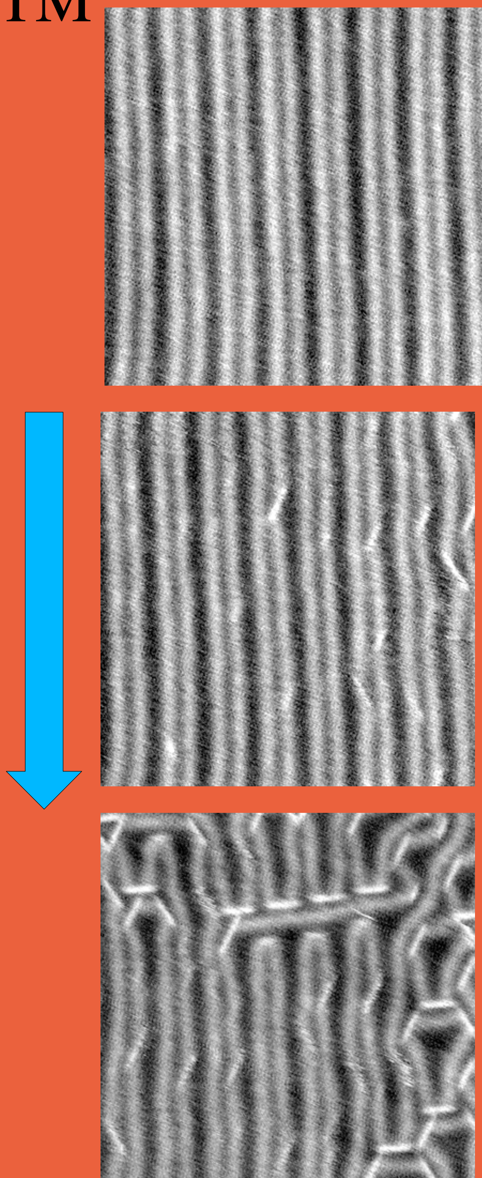
5 μm FOV



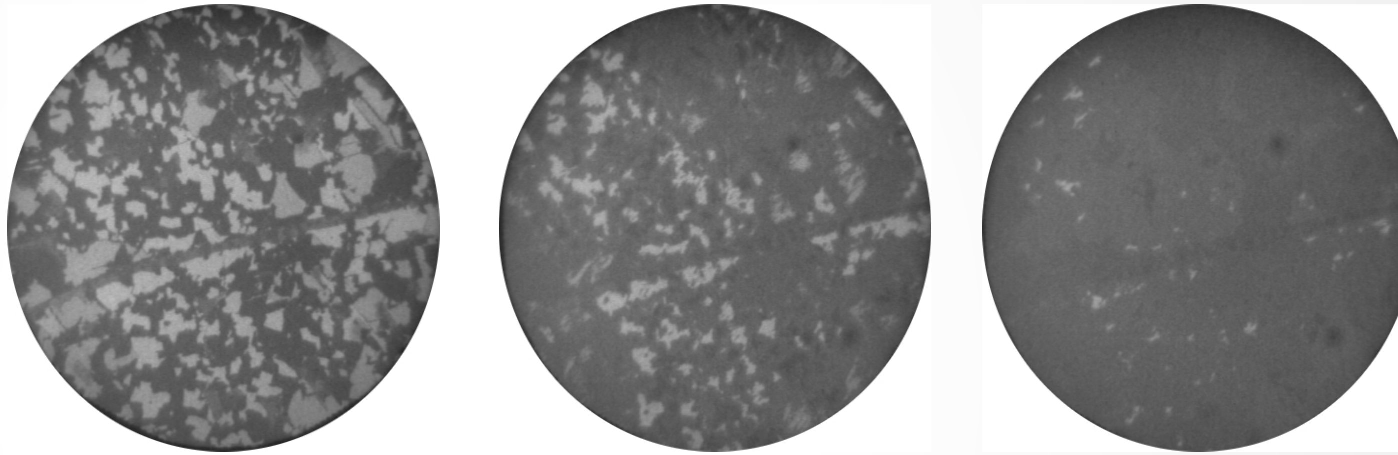


Effect of exposing 2ML Cu/Ru(0001) to sulfur

STM



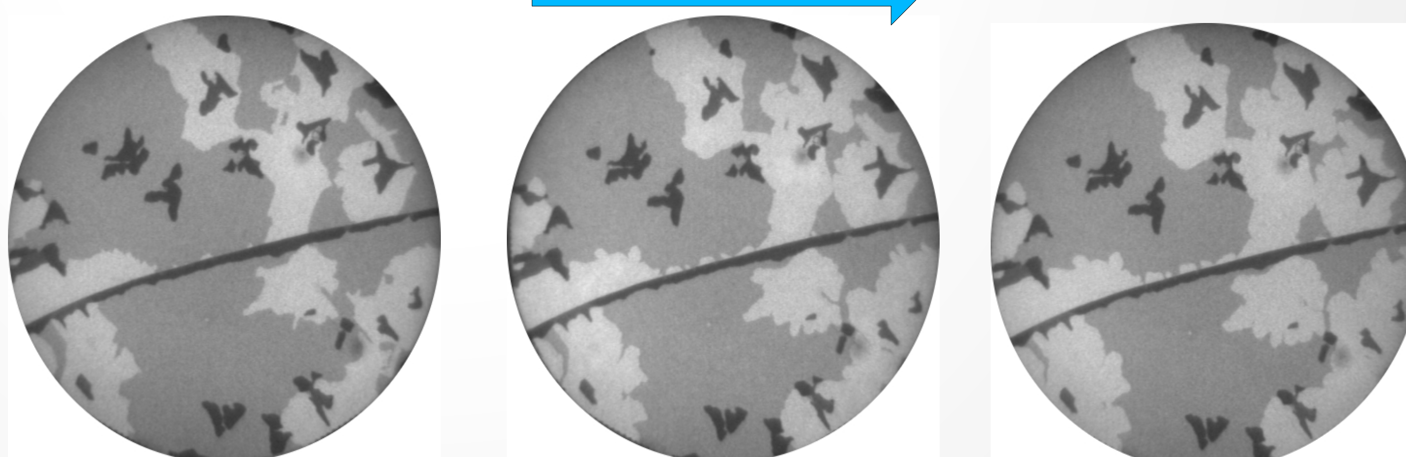
Rotational domains dissapear



θ= 0 ML_S

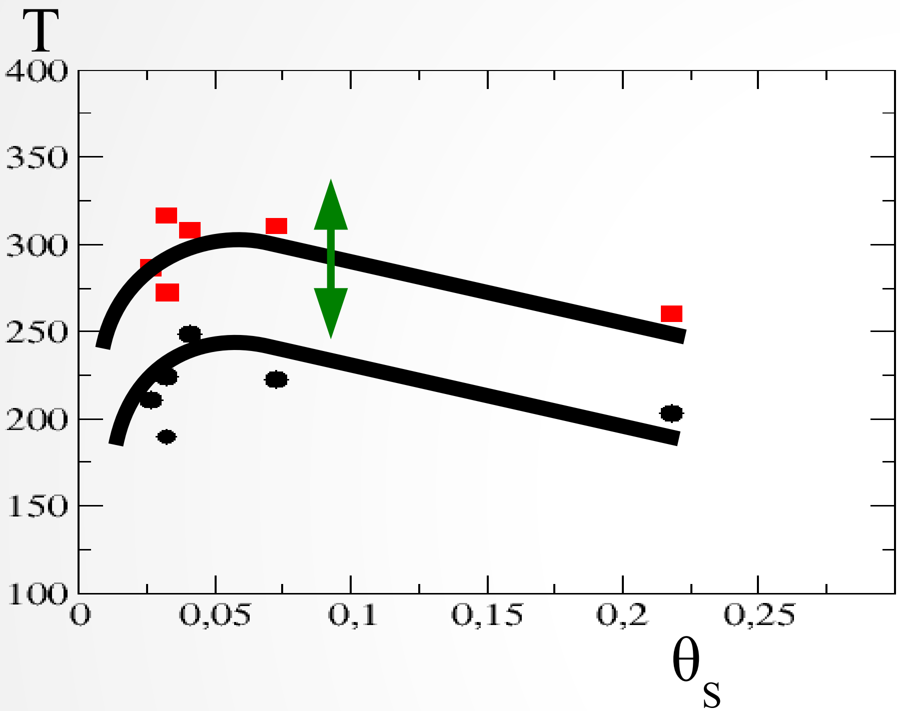
Sulfur exposure

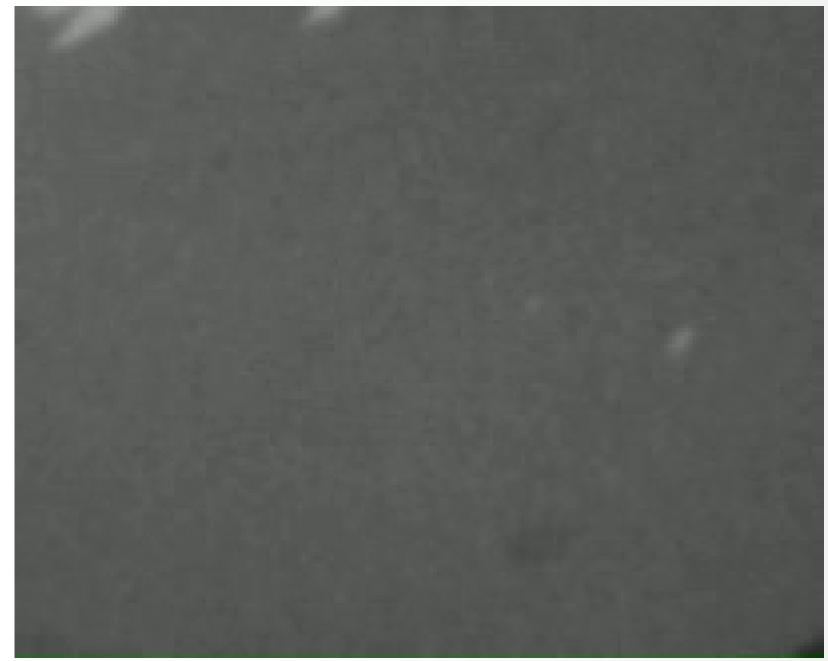
θ= 0.04 ML_S



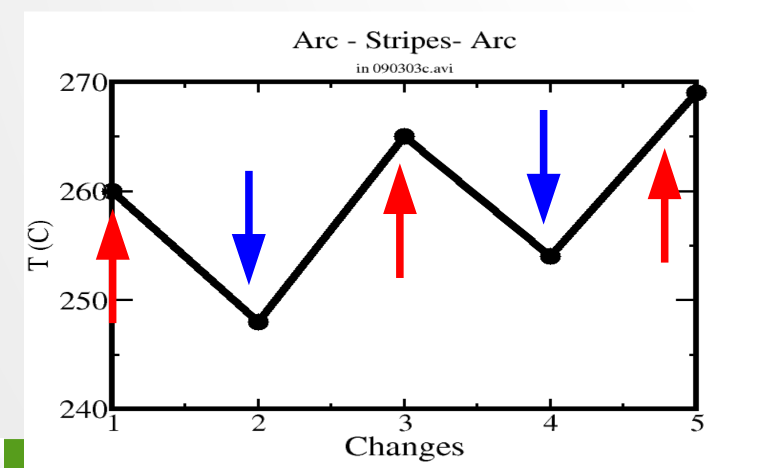
Stacking domains stay

Transition in real space between S/Cu structures





-arc phase -stripe phase



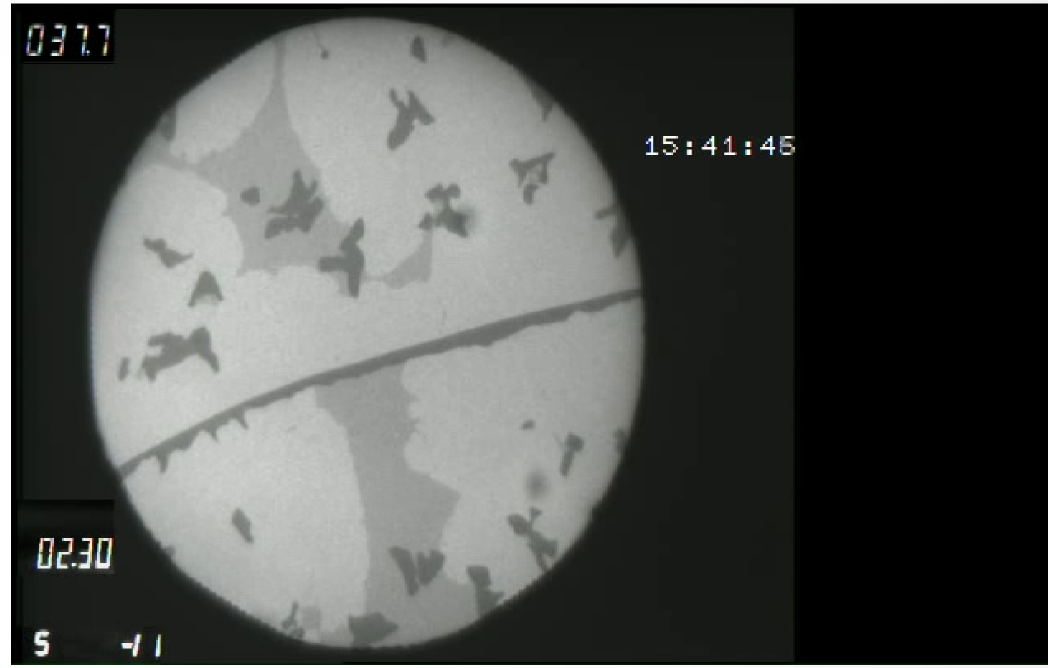
1st order transition evidences:

Nucleation and growth

Change of symmetry

Hysteresis

Evolution of domains in S/Cu/Ru(0001)

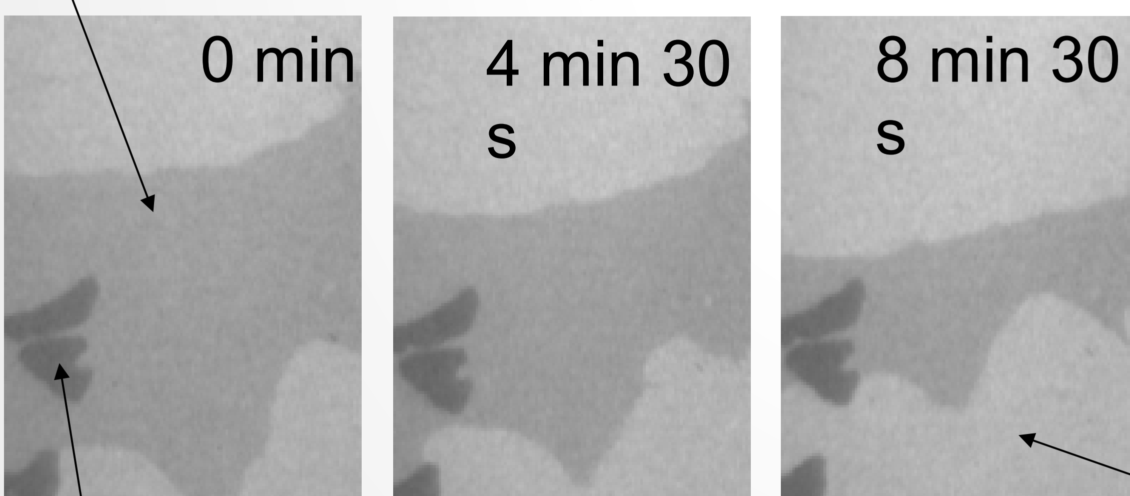


Evolution at 150 ºC

NO preferred directions

NO jerky motion

2 ML “dark” stacking domain



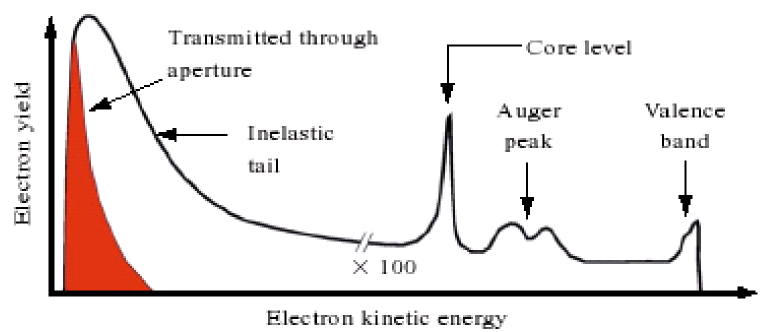
3ML

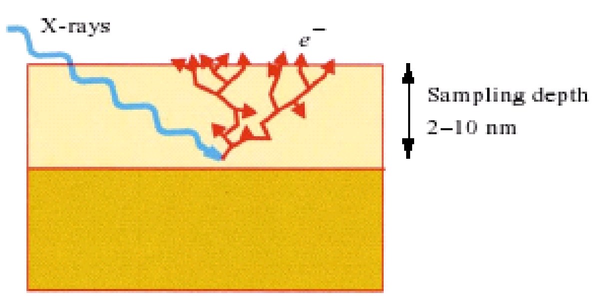
2 ML “bright” stacking domain

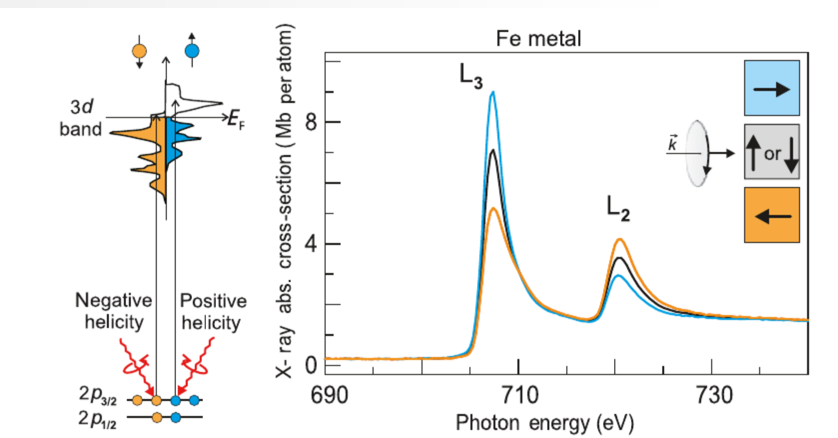
Science 308 (2005)1303

F. El Gabaly, Wai Li W. Ling, K. F. McCarty, J. de la Figuera

"Traditional" techniques using photoelectrons







x-ray absorption spectroscopy

Measure absorption of x-ray as a function of photon energy

Determine composition, chemical state

x-ray magnetic circular dichroism

Measure difference in absorption of x-ray as a function of helicity

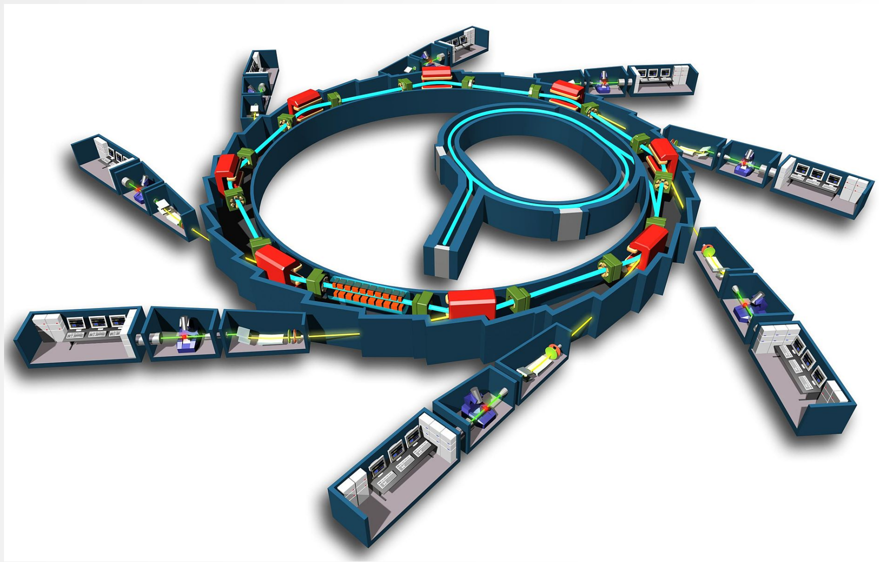
Determine magnetic moments

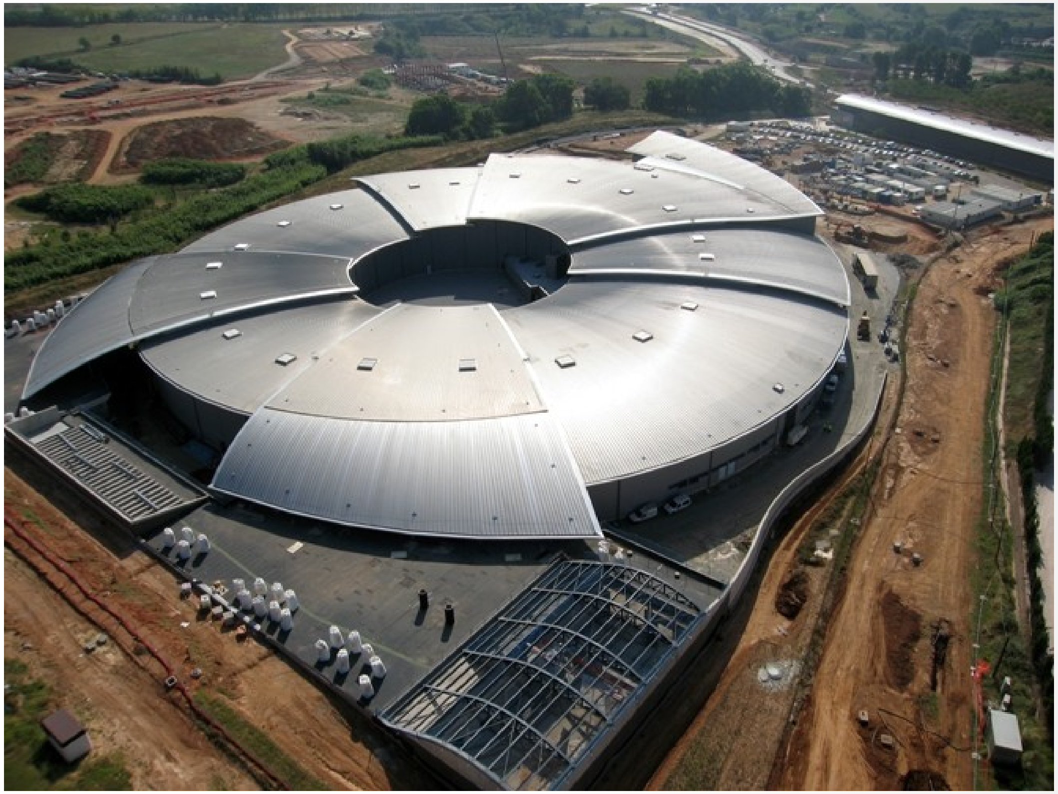
x-ray photoemission spectroscopy

Measure photoelectrons as a function of kinetic (binding) energy for a given photon energy

Determine composition, chemical state, do band mapping

Where to do microscopy with photoelectrons

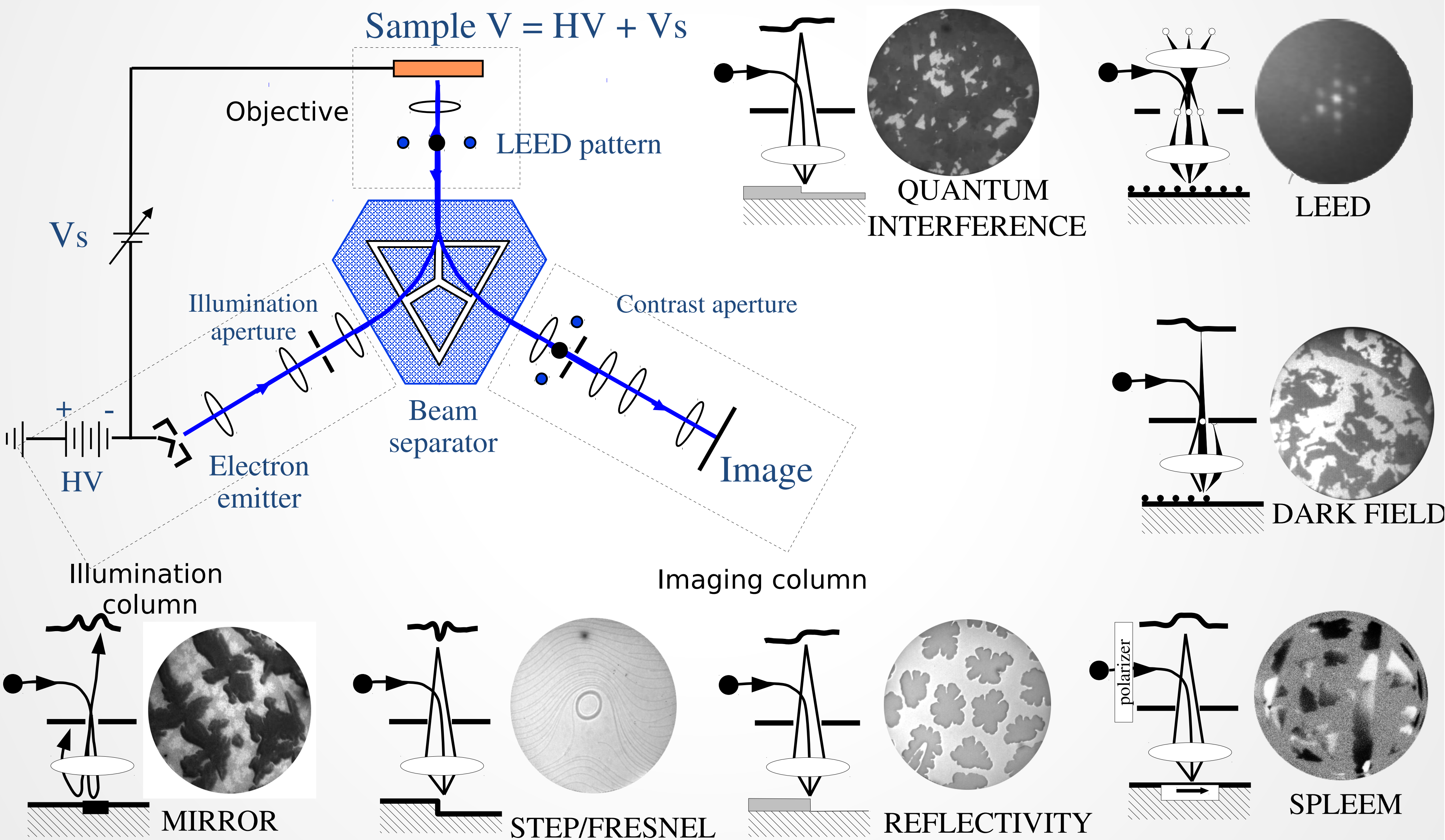




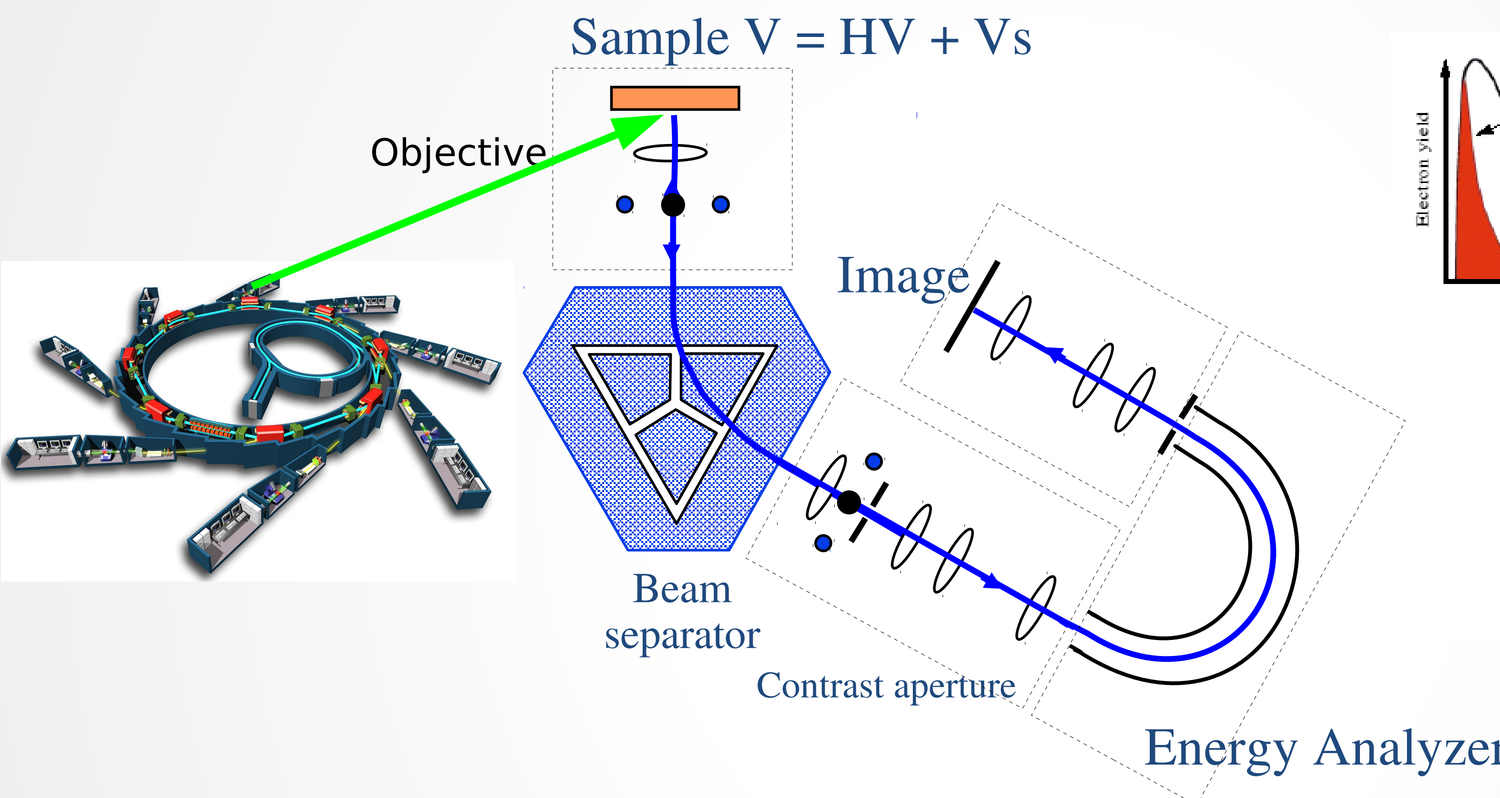
Alba, Barcelona

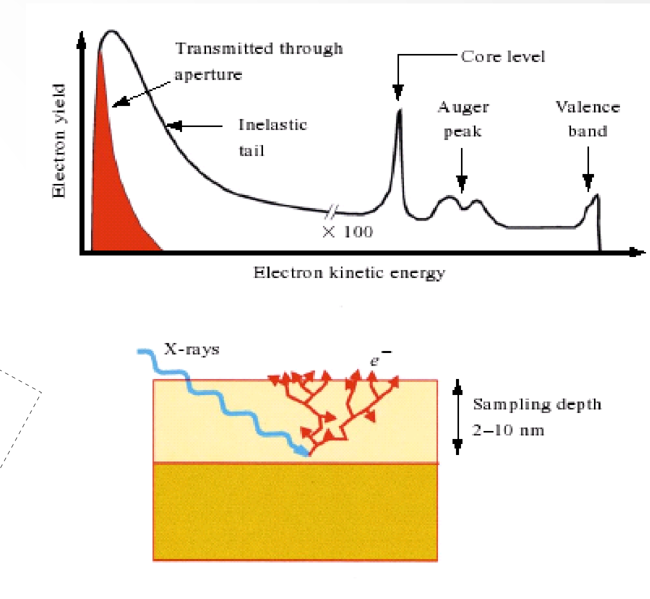
Need lots of photons: go to a synchrotron!

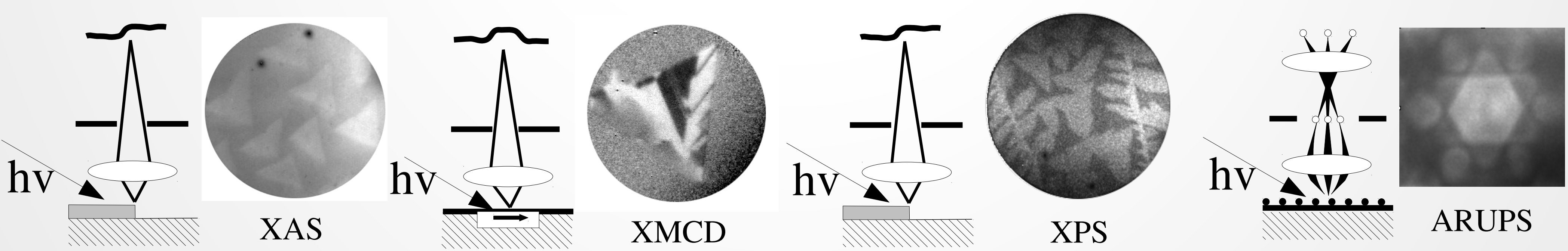
How a LEEM works



How to do microscopy with photoelectrons: PEEM







Typical specs to be expected

- Energy resolution 0.4-0.1 eV
- Selected area 50-10 um
- Reciprocal space resolution
- Transmission falls down with kinetic energy
  - Excellent for secondary electrons (~eV)
  - Ok for 50-100 eV
  - Hard for higher kinetic energies
- In XPS: adjust photon energy as close as possible!
- XAS images: ~seconds-minutes
- XPS images: ~minutes-hours

Different approach for LEEM and PEEM components

Rule of thumb (there are always exceptions):

- LEEM:
  - fast, seconds per image, real-time, use during preparation/growth, surface evolution, **dynamics**, atomic structure
- PEEM:
  - slower, minutes-hours, **characterization** of already-grown samples, electronic structure, chemical and magnetic analysis

L_{23} X-ray absorption on thick Co film

15 µm FOV

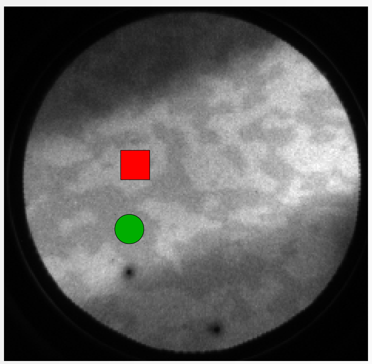


Image at L3

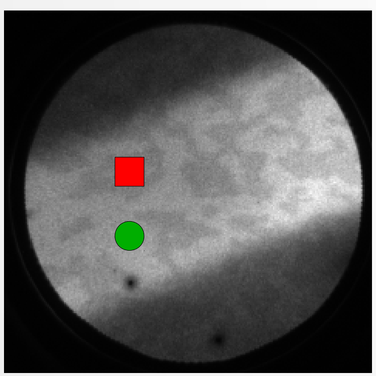
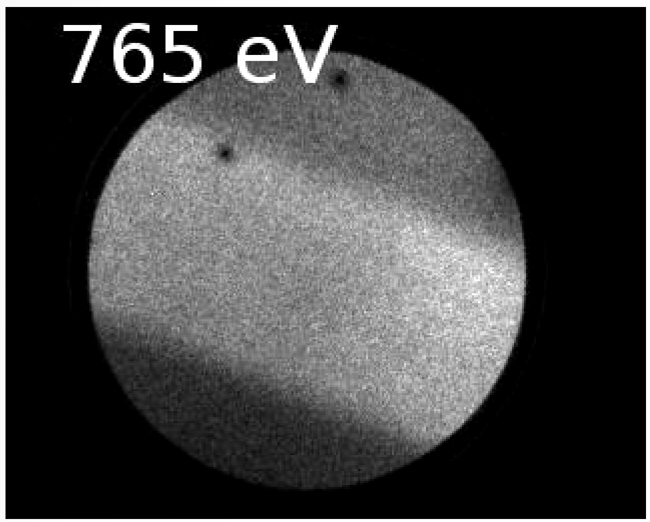
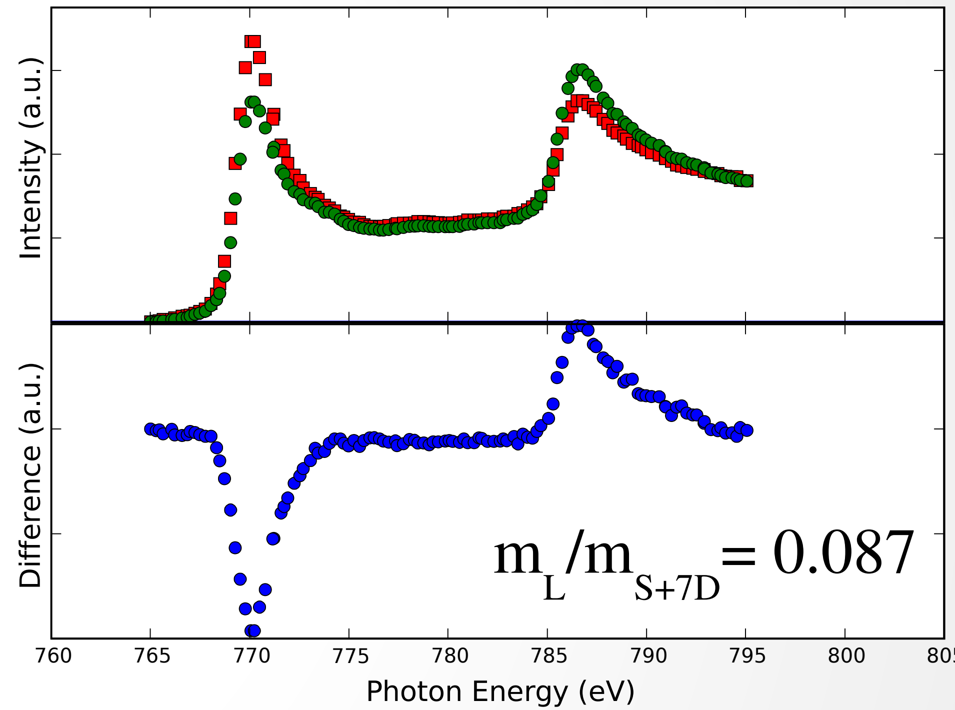


Image at L2

Au/ 10 ML Co /W(110)





Two ways to perform our XMCD-PEEM experiment:

- measure intensity in different domains with opposite domain orientation (=switch M)
- magnetize the sample and measure with different photon helicities (=switch P)

L_{23} X-ray absorption on thick Co film

15 µm FOV

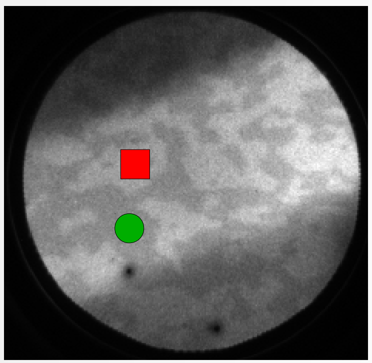


Image at L3

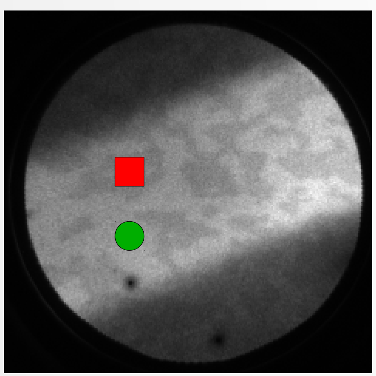
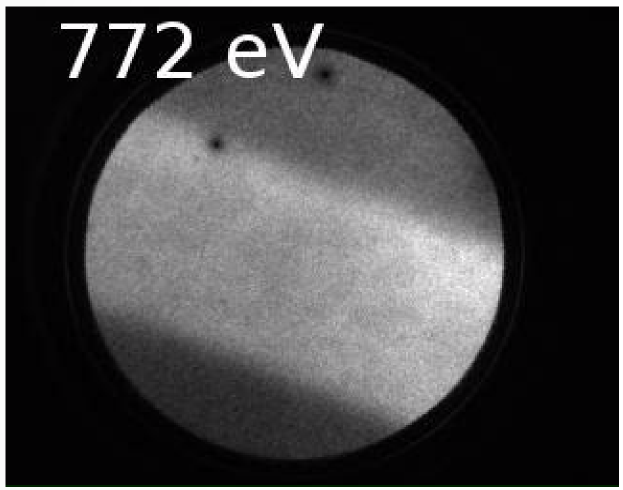
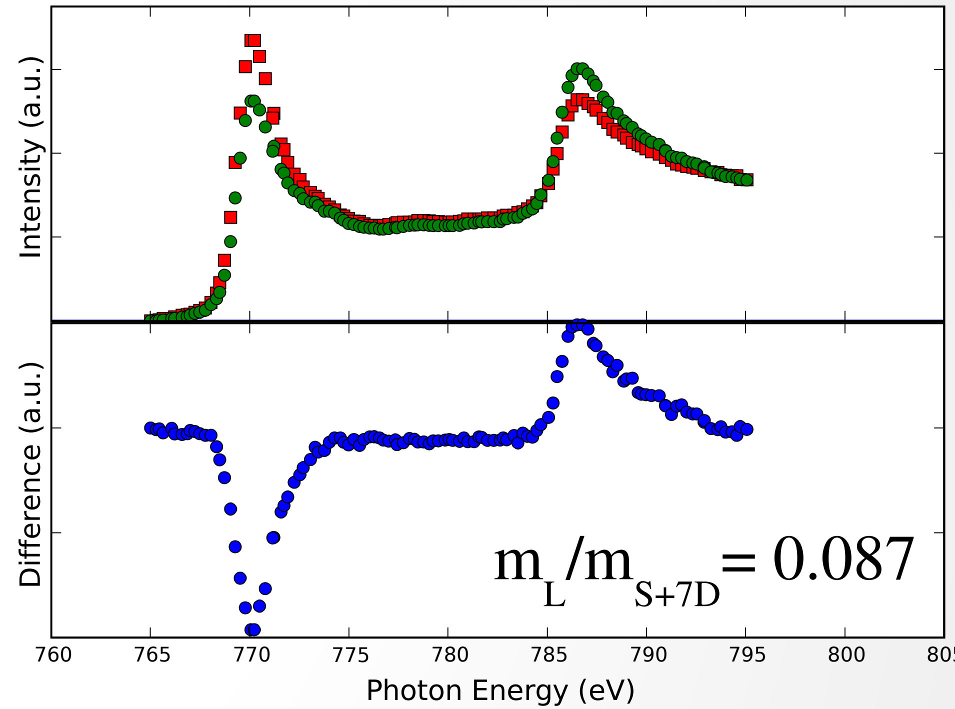


Image at L2

Au/ 10 ML Co /W(110)





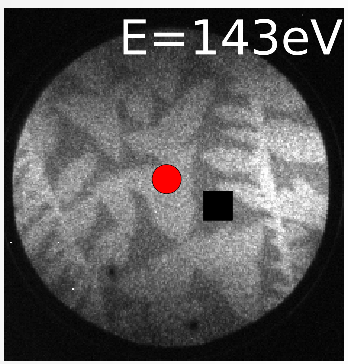
Two ways to perform our XMCD-PEEM experiment:

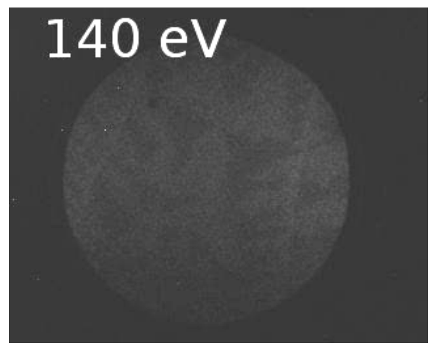
do XAS images using secondary electrons (E~2.5eV)

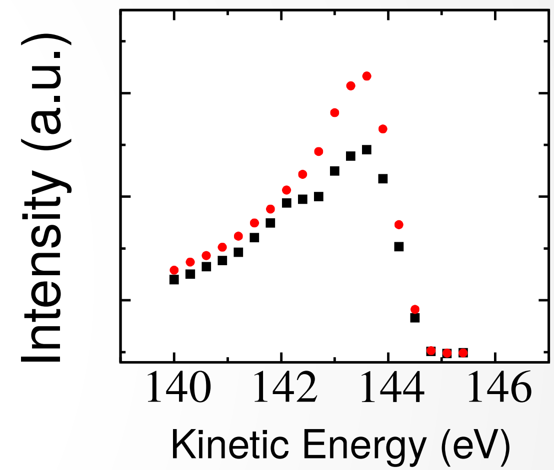
Photoemission with PEEM

Normal incidence (θ~2º)

hν= 150eV



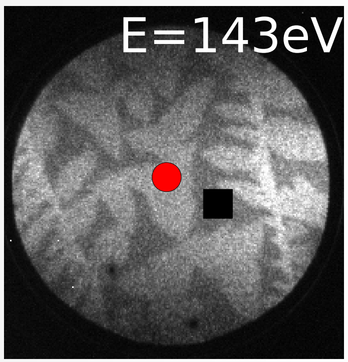


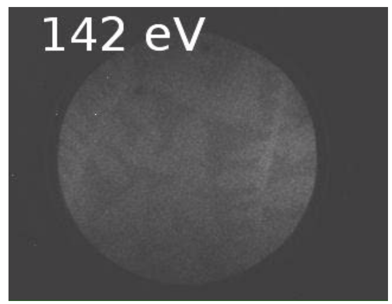


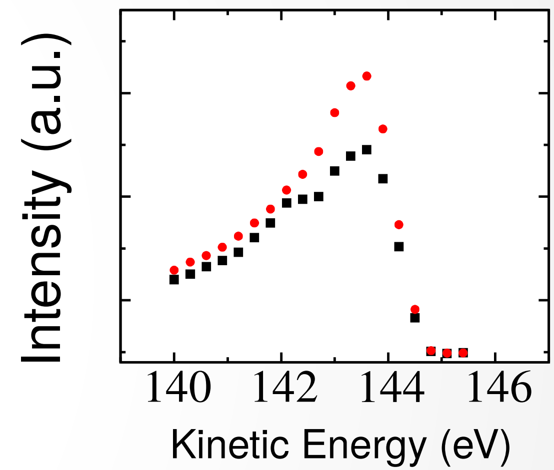
UPS Photoemission with PEEM

Normal incidence (angular resolution θ~2º)

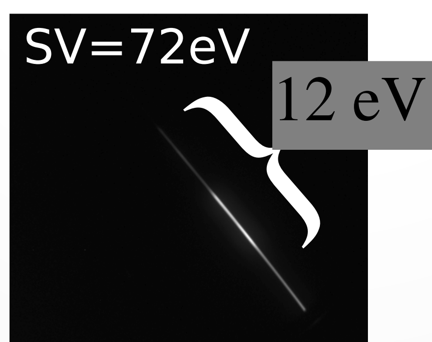
hν= 150eV

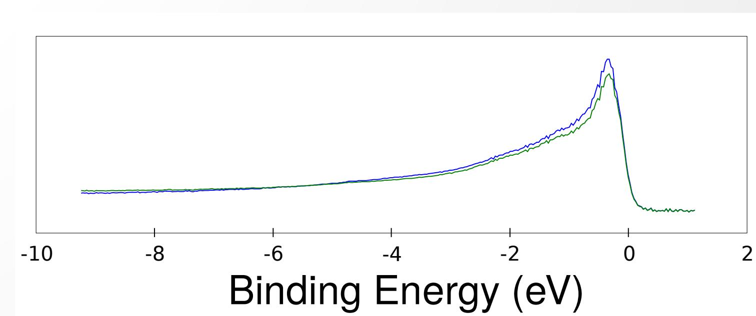






hν= 80eV
Area on sample: ~2μm



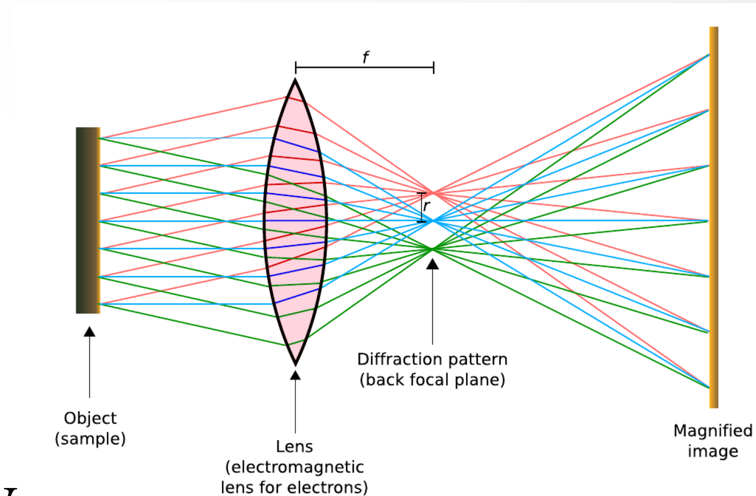


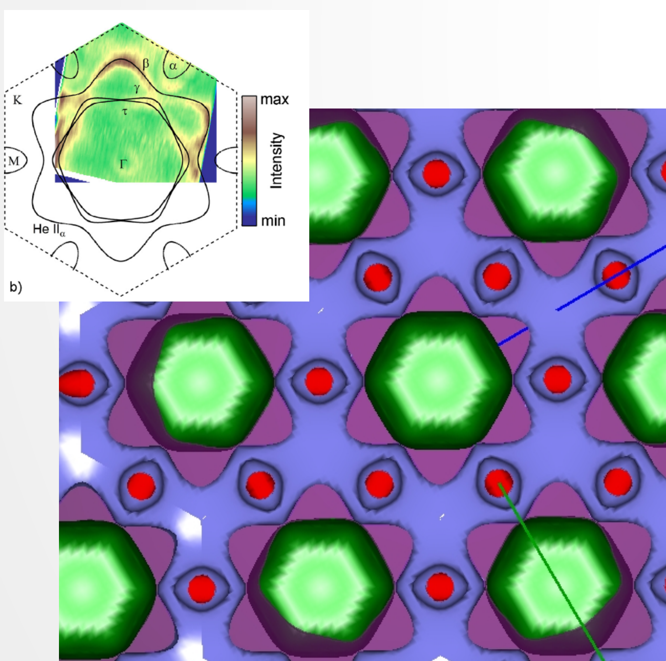
Imaging photoelectrons in reciprocal space

The LEEM can image fast photoelectrons in an angle resolved way by imaging the back focal plane (line doing LEED in LEEM):

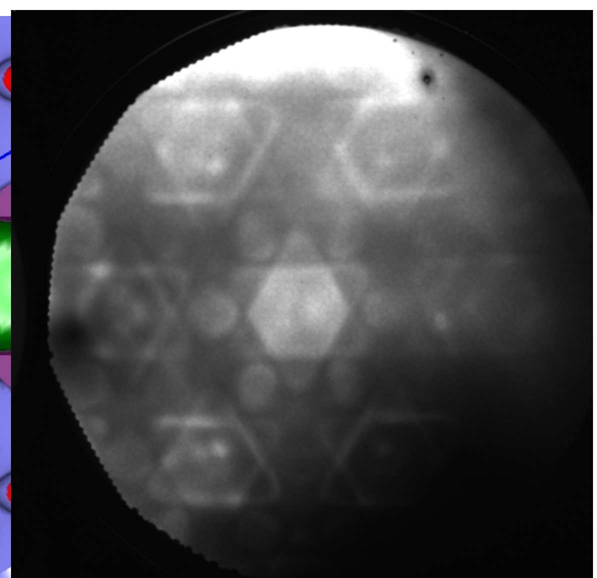
Angle-resolved photoemission:

- Band mapping
- Fermi surface imaging

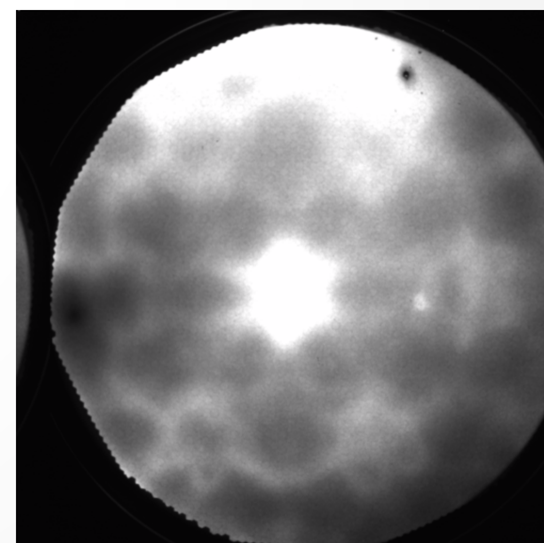




Photon energy 140 eV



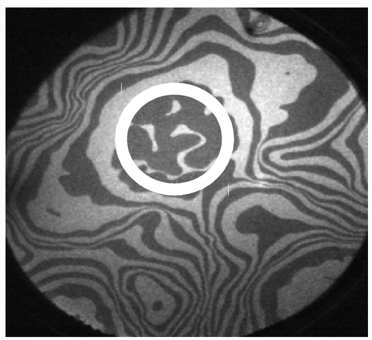
Ru(0001) Fermi Surface



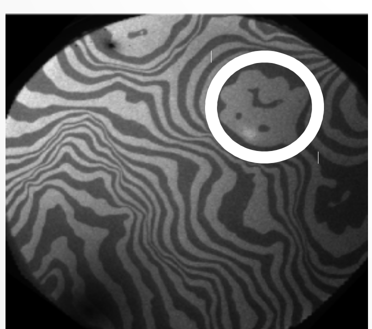
ARPES scanning energy

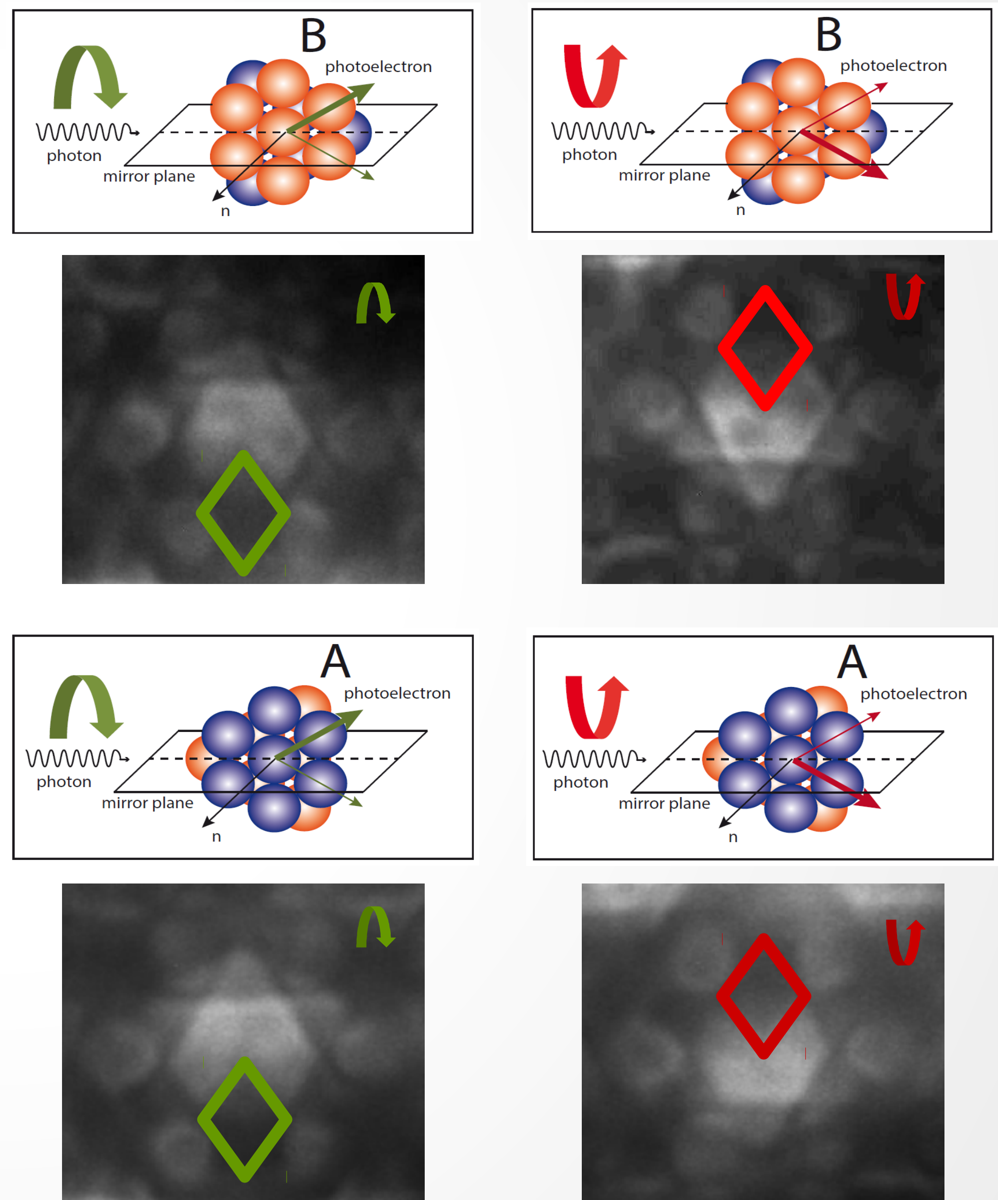
Unique advantages of ARPES in LEEM/PEEM instruments

ARPES images taken with positive and negative helicity at the selected area
(Energy photon = 140 eV)

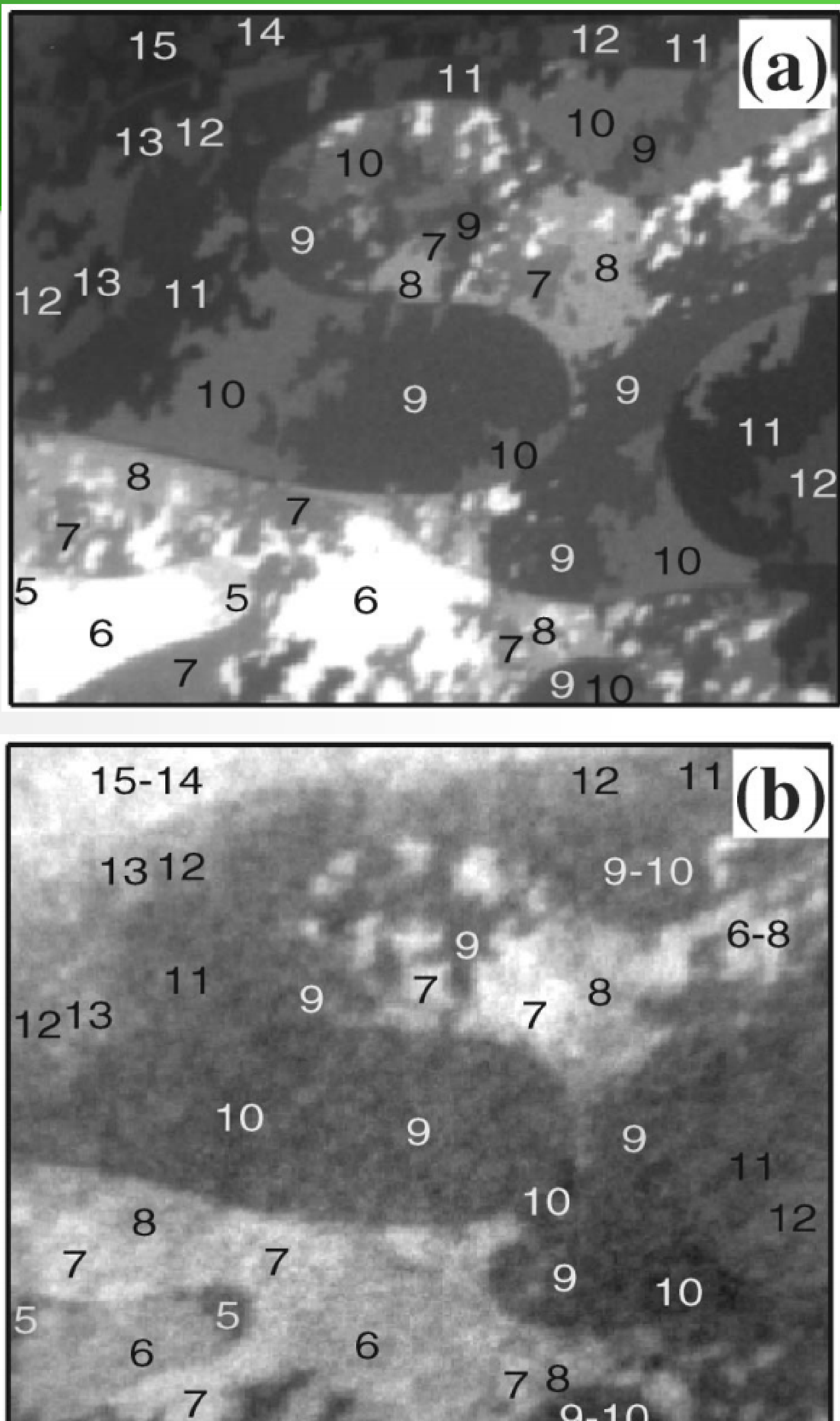


Dark field
FOV = 50μm



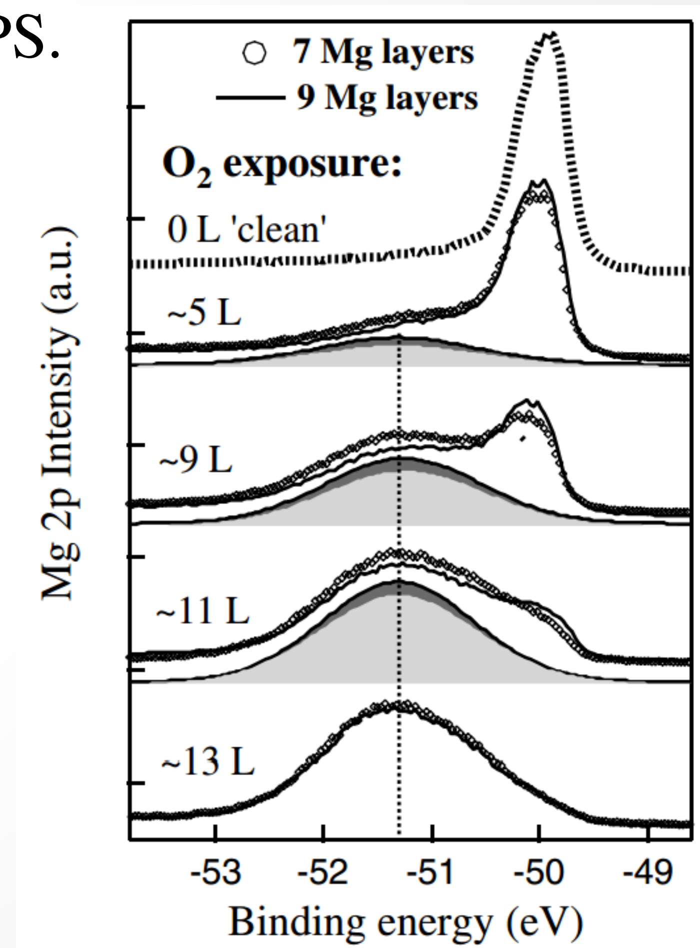


Layer dependent reactivity



6 um wide

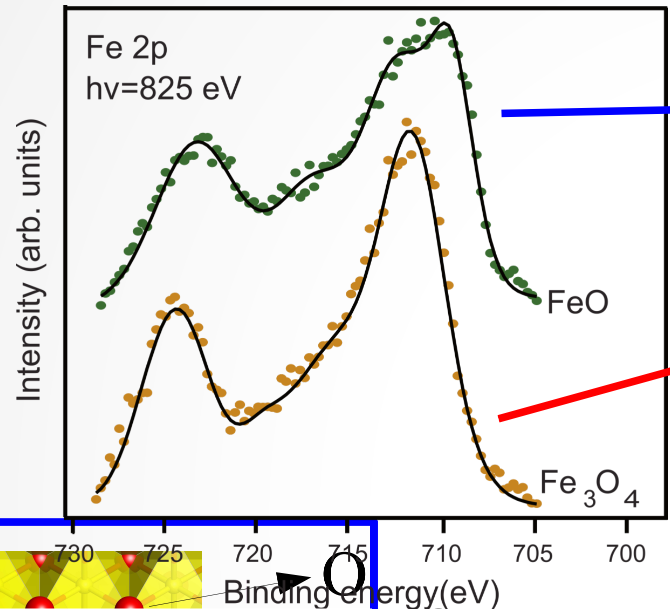
Grow in LEEM a multilayer film of Mg. Then measure XPS Mg 2p spectra. Select an energy which corresponds to the Mg-oxide. Do imaging in XPS.

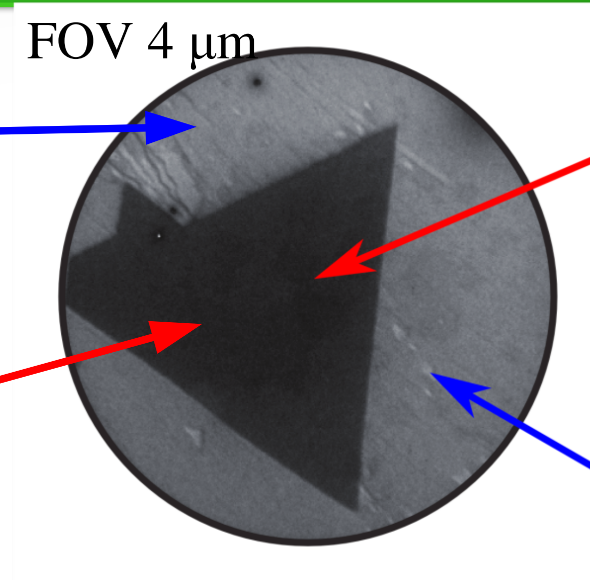


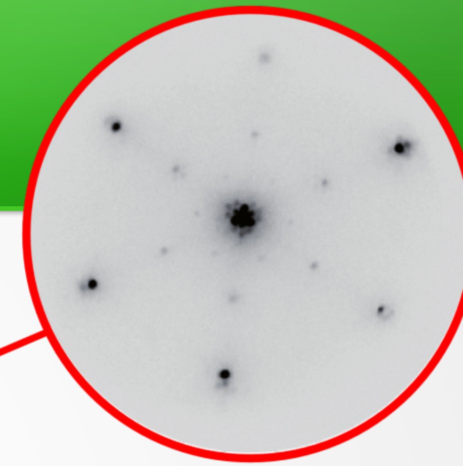
L. Aballe, Phys. Rev. B 93 (2004) 196103

Multitechnique characterization

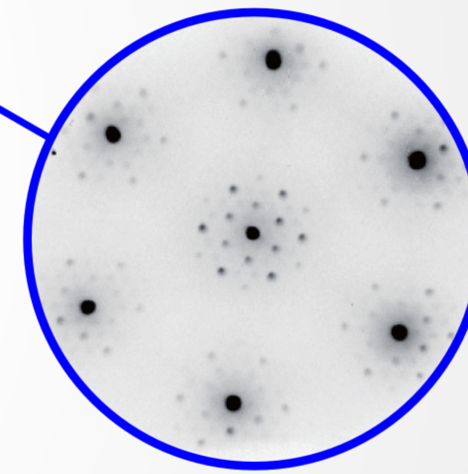
XPS

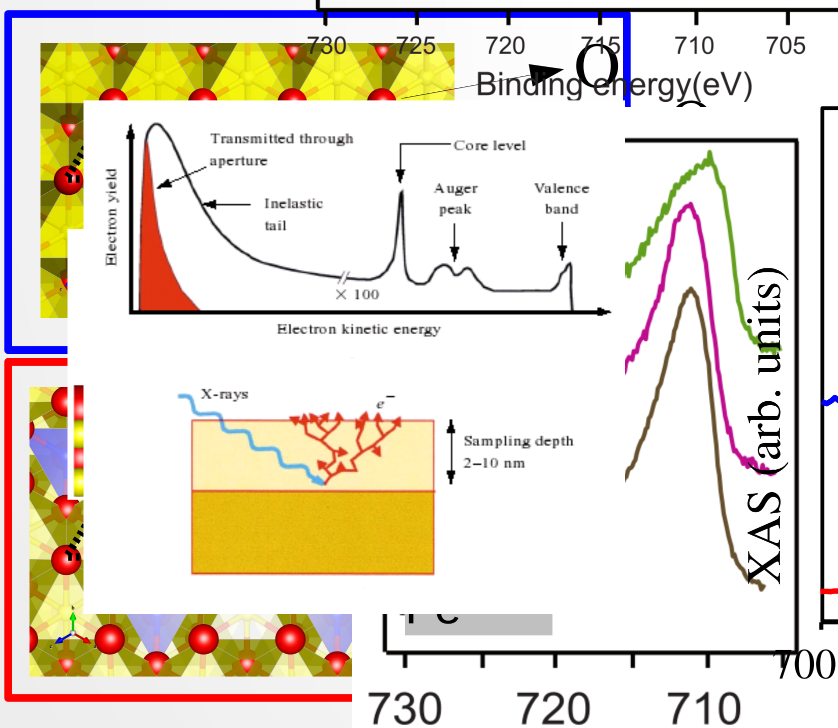


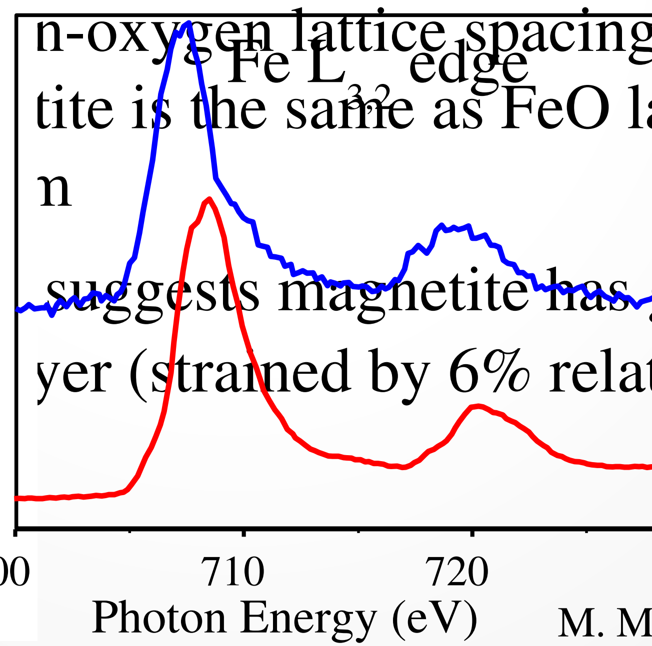




LEED



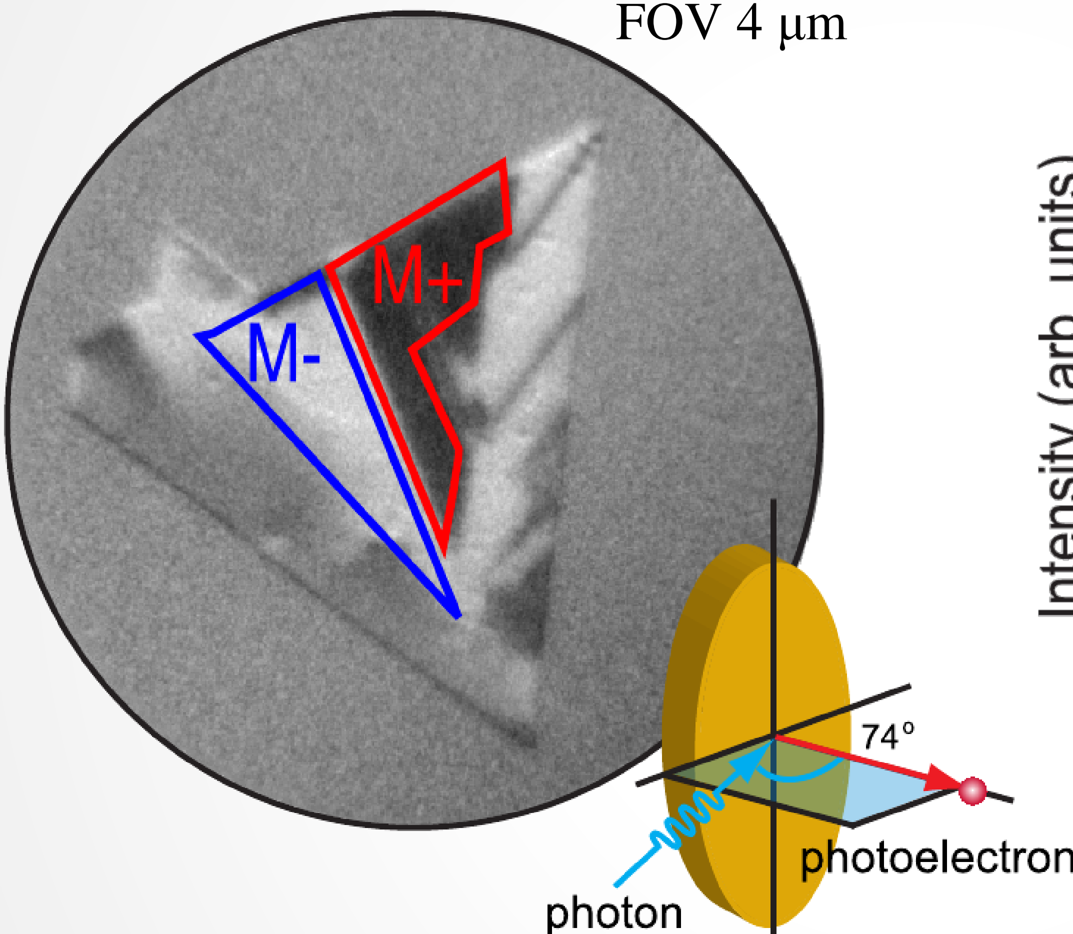


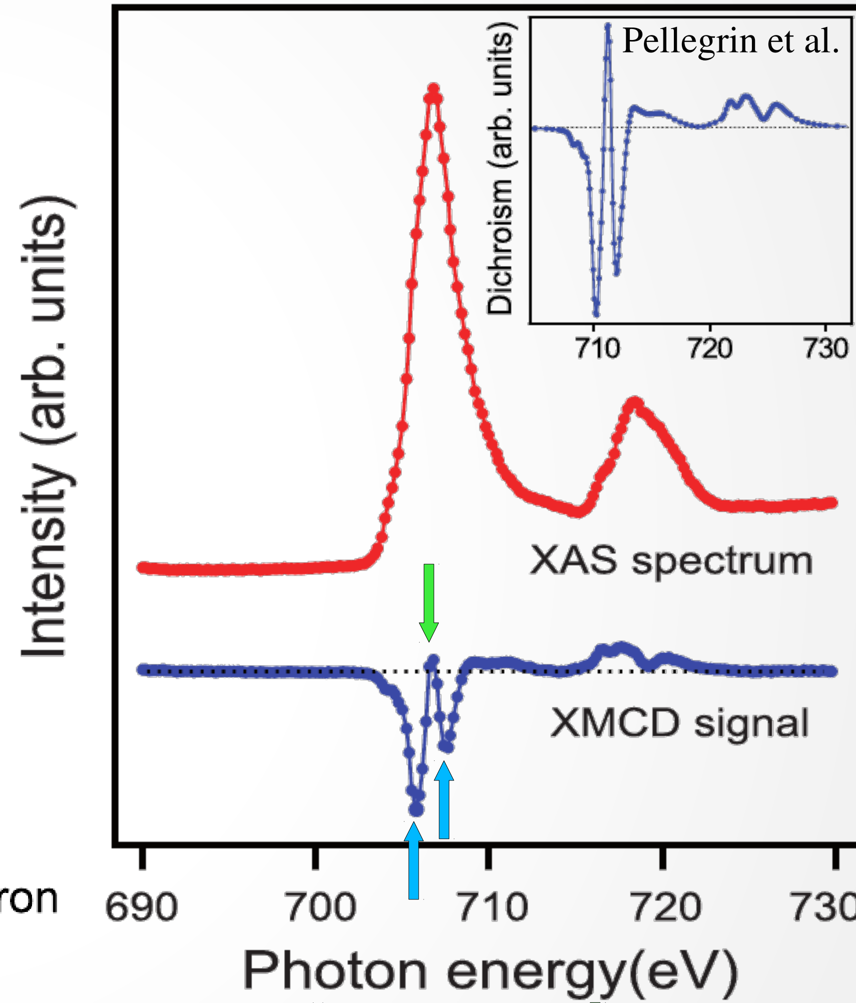


n-oxygen lattice spacing of
tite is the same as FeO layer:
n
suggests magnetite has grown **on top of** the
yer (strained by 6% relative to bulk magnetite)

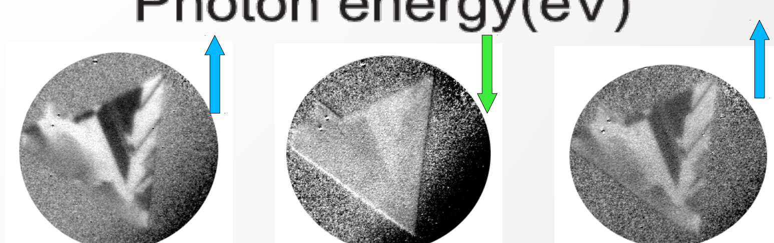
M. Monti, Phys. Rev. B 85 (2012) 020404

X-ray magnetic circular dichroism



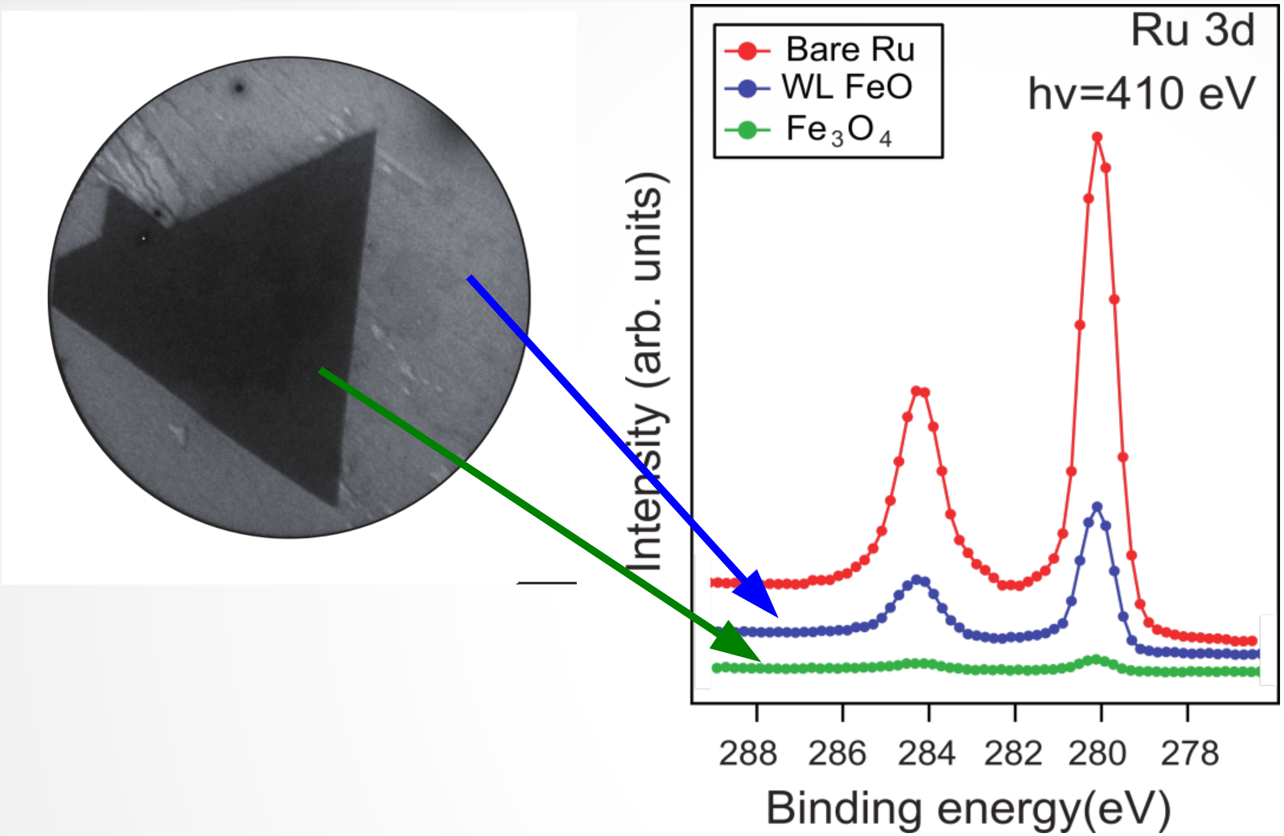


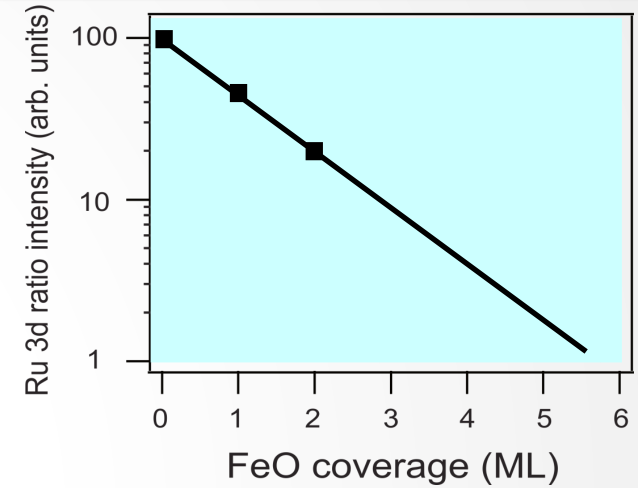
Three peaks XMCD spectra further confirms magnetite. Also it shows antiferromagnetic coupling between iron in octahedral (↑) and tetrahedral positions (↓) and robust magnetic domains (up to 520 K).



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

How to measure the islands thickness?





Magnetite islands are ~3 FeO layers thick

For estimating the thickness we need **an accurate value** of the mean free path of the electrons. But we have it!

Magnetite island thickness is 1.0±0.4 nm

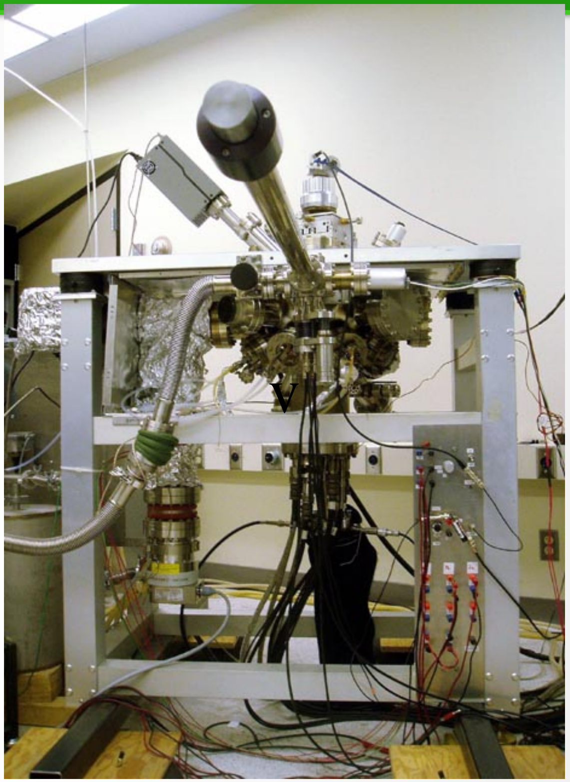
1 nm thick magnetite is magnetic

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

(SP)LEEM main points

- Time resolution:
  - milliseconds in LEEM mode (video taped)
  - seconds in SPLEEM mode (can be improved)
- Real-space resolution:
  - 10 nanometers resolution (2 nm with ab. corr.)
  - Typical field of view 3-25 μm
  - Atomic steps can be detected, thickness using QSE
- Diffraction data (no energy filtering):
  - μLEED ,Nanometer scale LEED (in imaging mode)
  - Dark field imaging
- Limitations:
  - In-situ UHV technique (not a post-mortem characterization technique)
  - Only for flat, (poly or mono)**crystalline**
  - Electrons used for imaging: only magnetic fields ⊥ sample can be applied
- Cost:
  - Full commercial systems around ¾ M€, a system should be available below 200k€

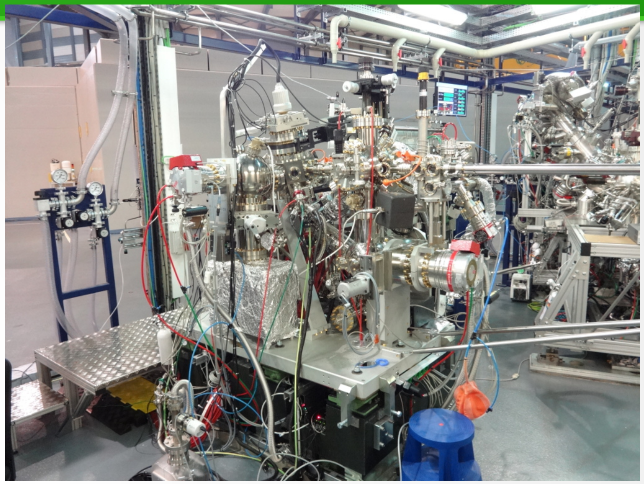
LEEM-on-a-flange from E. Bauer at AZU



Dynamics

PEEM main points

LEEM/PEEM at Alba, Barcelona



- Advantage over LEEM
  - Good for non crystalline samples, chemical analysis
- Time resolution:
  - 10s minutes (electron energy scan or photon energy scan)
- Real-space resolution:
  - 40 nanometers resolution (10 nm with ab. corr.)
  - Typical field of view 3-25 μm
- Reciprocal space data:
  - Selected area x-ray photoelectron diffraction, ARUPS
  - "Dark field" in band structure
- Limitations:
  - Energy resolution is often less than dedicated non-microscopy instruments
  - Electrons used for imaging: only magnetic fields ⊥ sample can be applied
  - Need a synchrotron as x-ray source (not strictly true, but still)

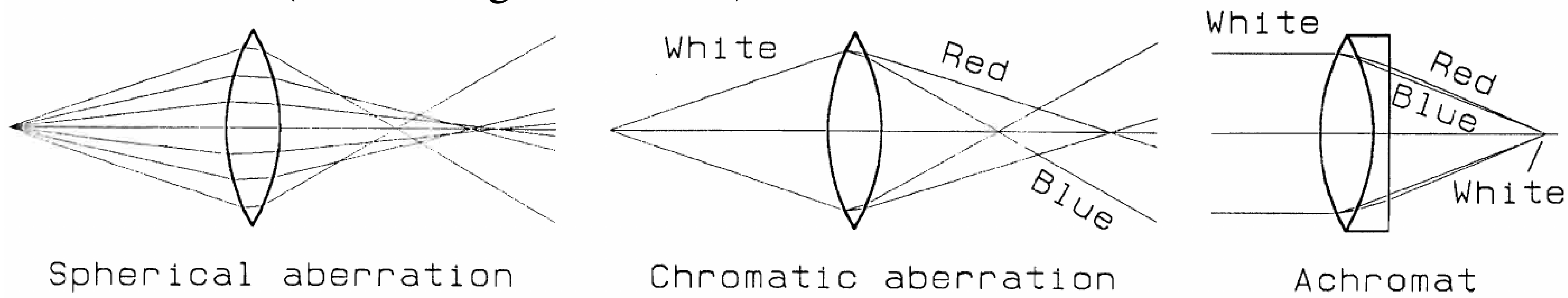
Spatially resolved chemical contrast and identification

Near future?

- More instruments, generalization of aberration correction (resolution down to 1 nm)
- Full image spin-analysis
- Cooling down to He
- Motorized sample stages

How to improve resolution

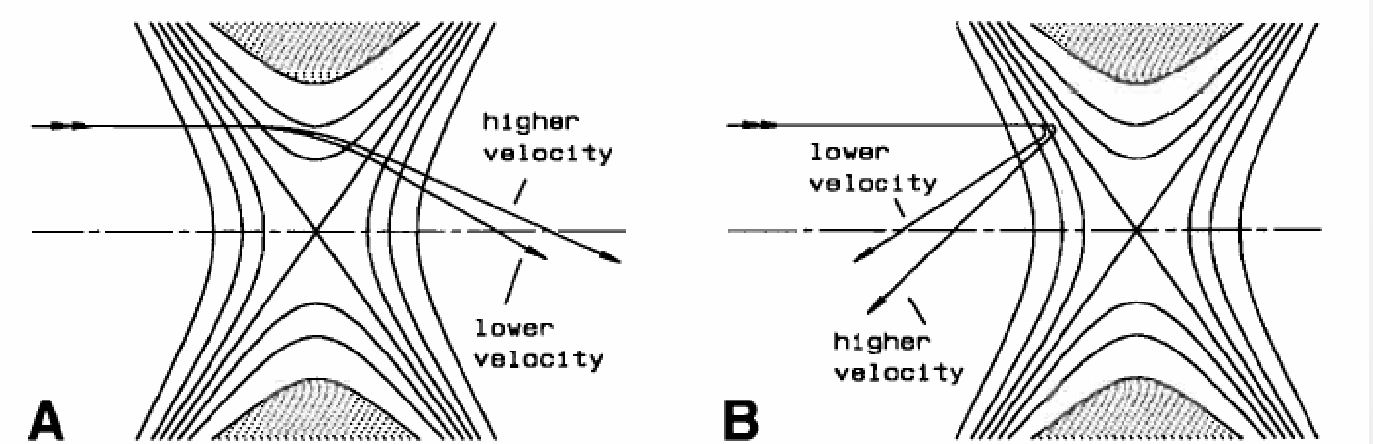
Problem with (electromagnetic or not) lenses:



But all simple electromangetic lenses have the same sign of the aberrations

No way to make an "achromatic" set only with lenses.

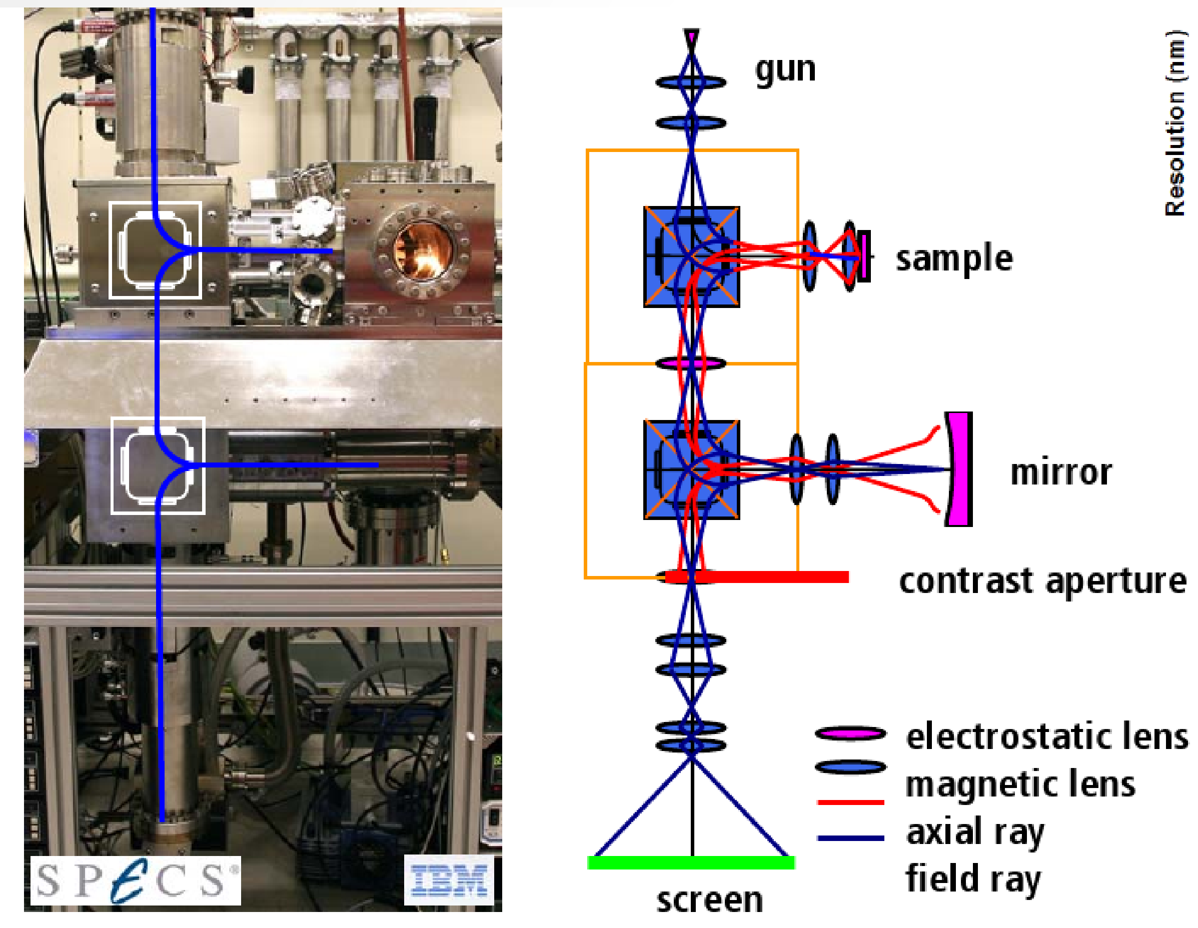
Needs other "devices", ex. Mirrors

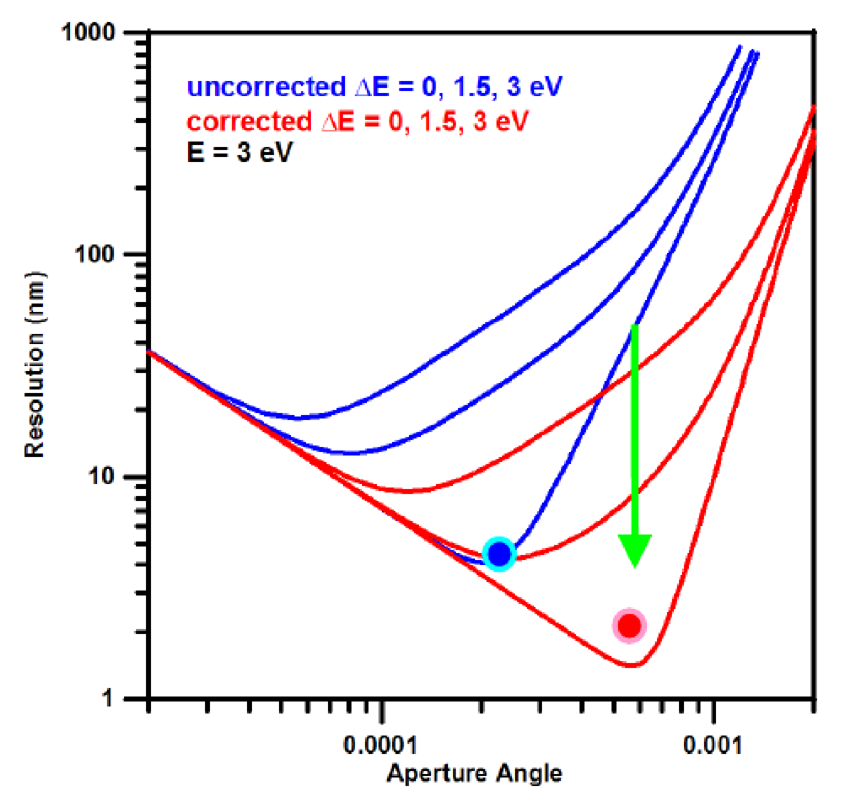


Gertrude Rempfer et al, Microscopy&microanalisis 3 (1997) 14

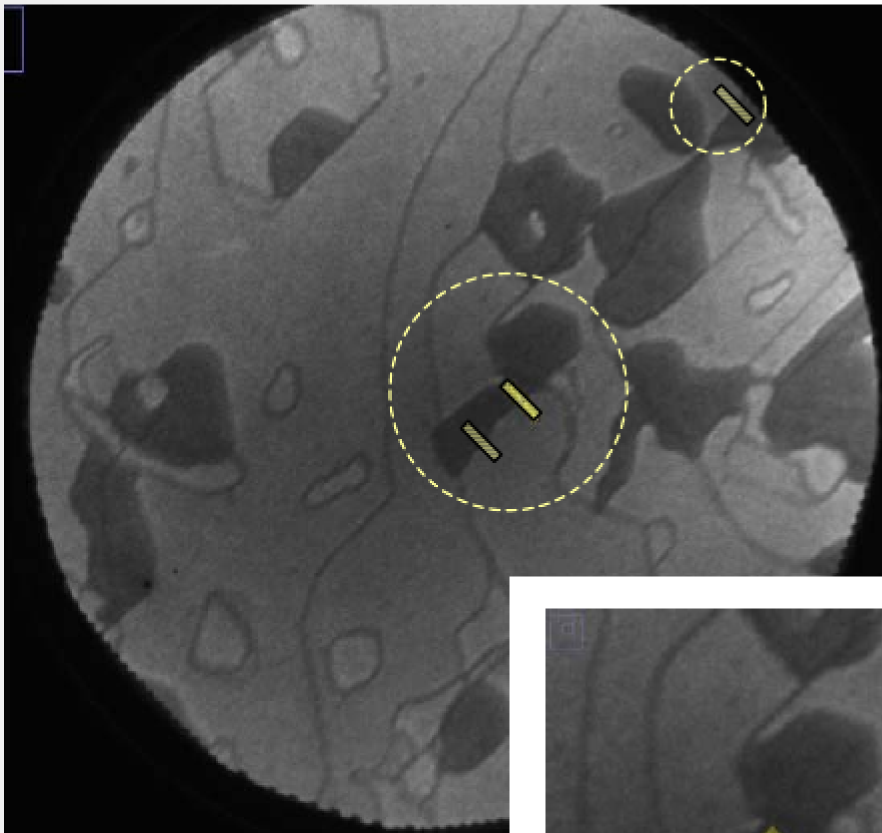
Future (now in LEEM!): aberration correction

(Spherical) aberration correction can be achieved with electron mirrors





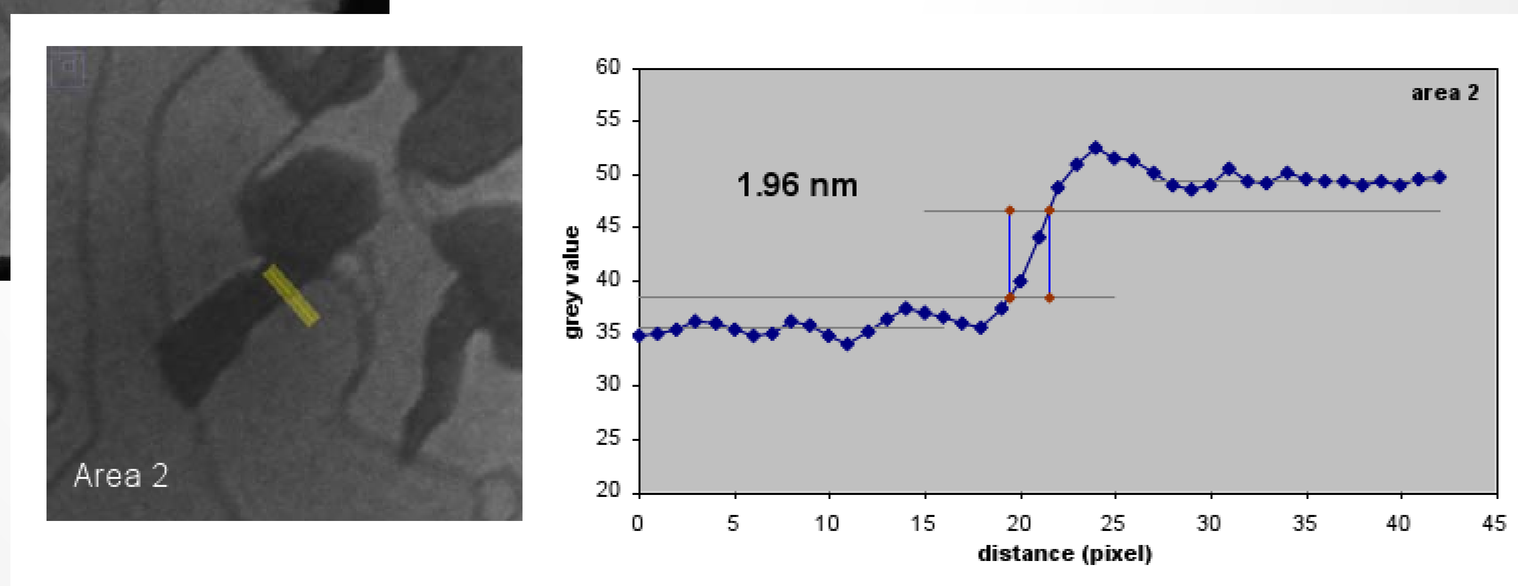
Future (now in LEEM!): aberration correction



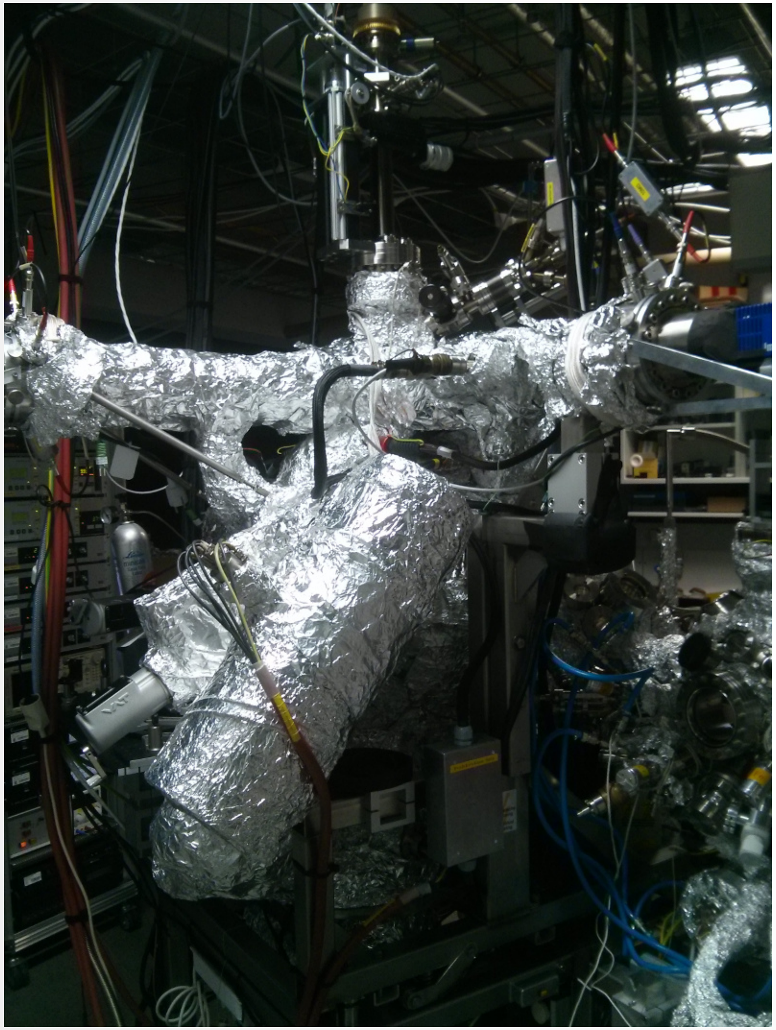
Graphene/SiC **FOV 0.75 µm**

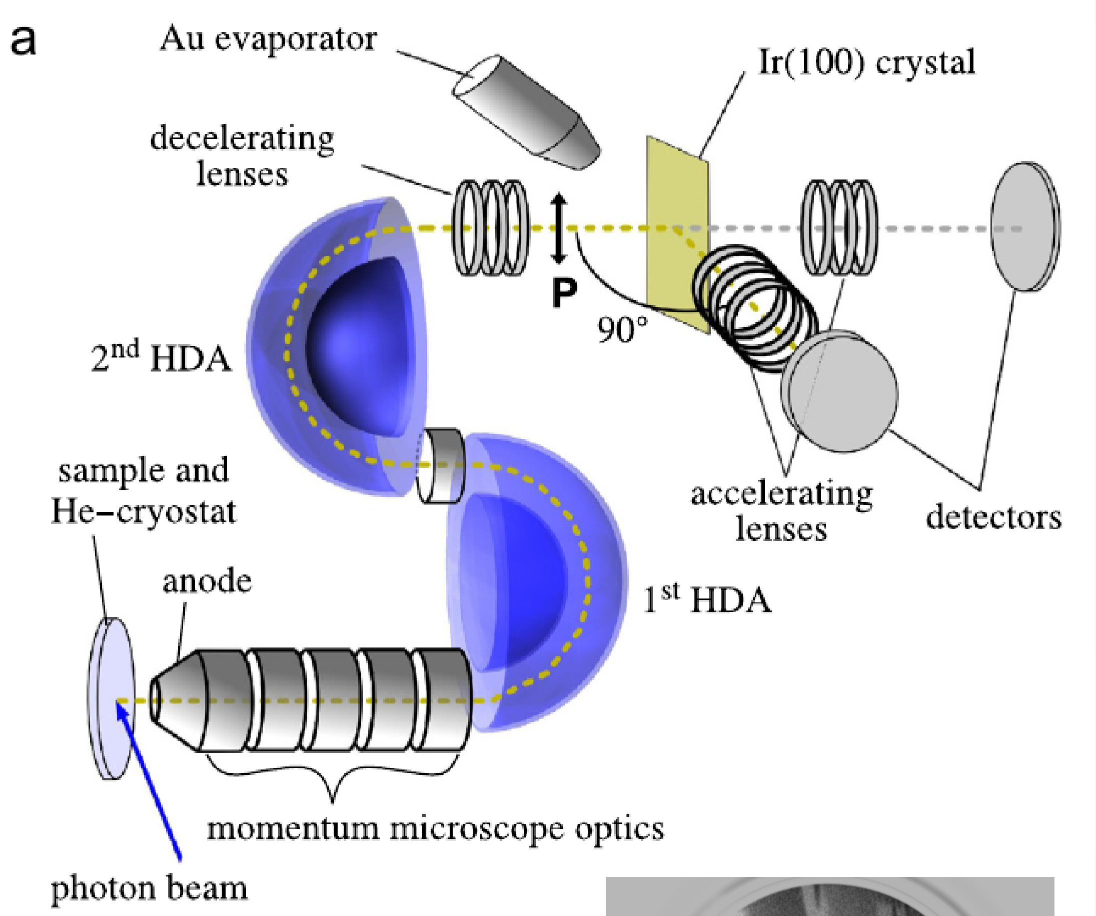
In addition to resolution down to 2 nm, transmission is x6!

This is with a field-emission cold-cathode

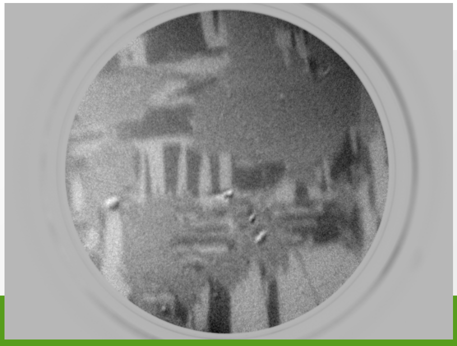


Spin-analysis in PEEM



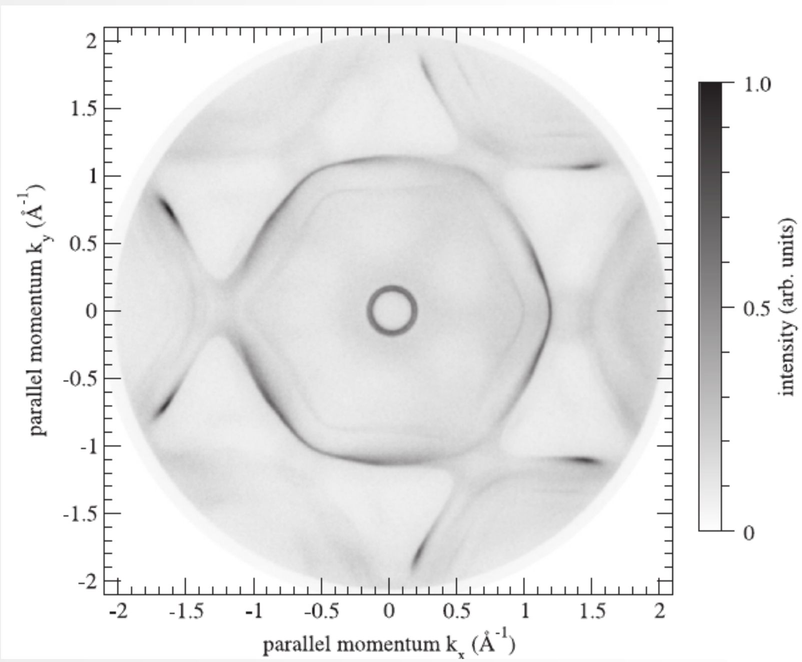


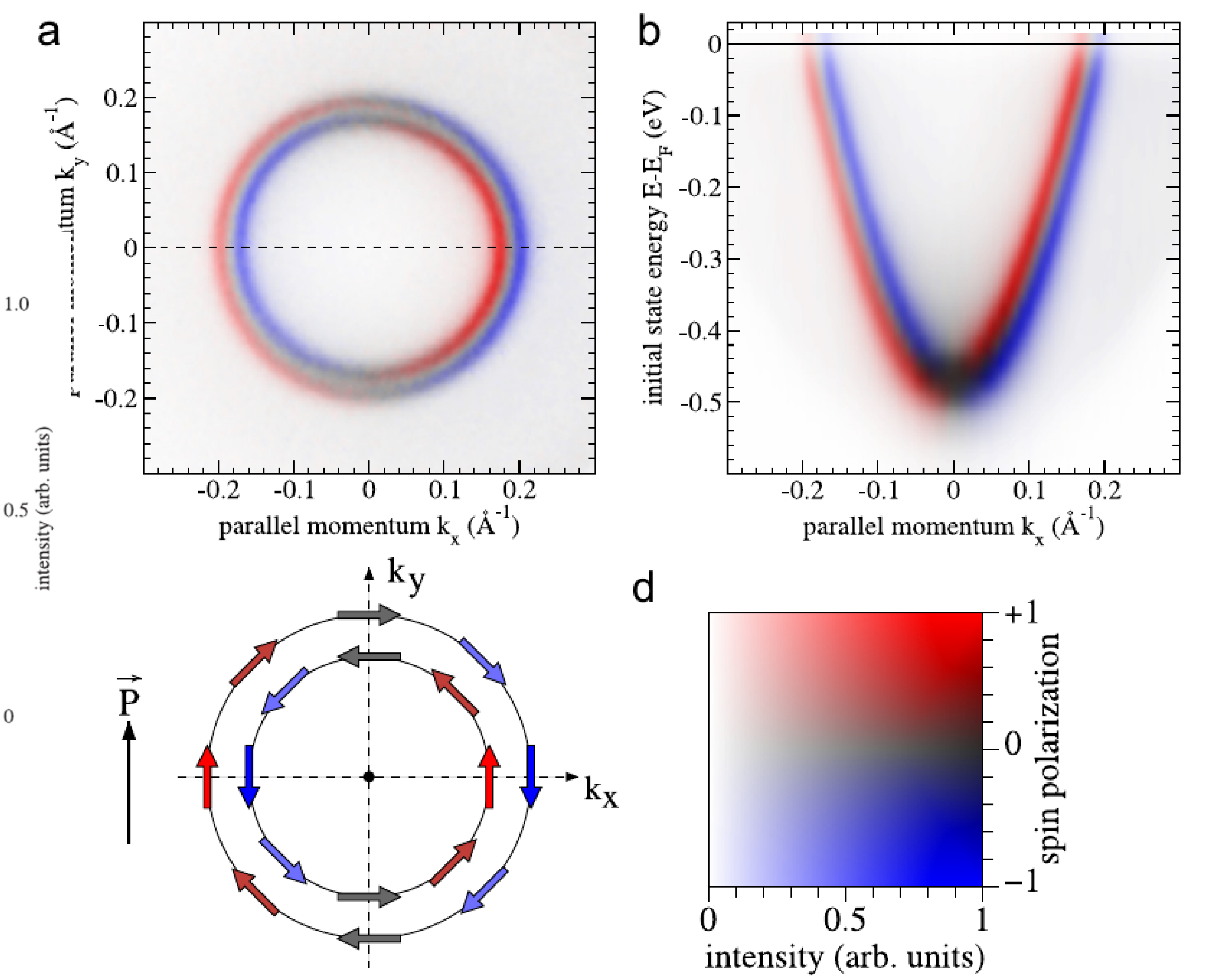
Imaging: domain in Fe3O4



Spin-analysis in ARPES

Au(111)





What to know more?

- E. Bauer: Surface electron microscopy: the first thirty years, Surf. Sci 299/300 (1994) 102
- E. Bauer, Low energy electron microscopy, Rep. Prog. Phys. 57 (1994) 895
- R.M. Tromp, Low Energy electron microscopy, IBM J. of Res. Dev. 44 (2000) 503
- E. Bauer, Cathode lens electron microscopy: past and future, J. Phys: cond. Mat. 21 (2009) 314001
- M.S. Altman, Trends in low energy electron microscopy, J. Phys: cond. Mat. 22 (2010) 084017
- K.F. McCarty and J. de la Figuera, Low-energy electron microscopy, "Surface Science Techniques", Eds. G. Bracco and B. Holst, Springer Series in Surface Sciences, 51 (2013) 531

http://surfmoss.iqfr.csic.es/leem

The most important part: the people

LEEM/PEEM

Lucia Aballe

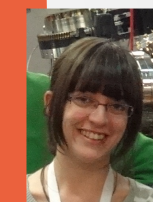
Michael Foerster

LEEM

Norm C. Bartelt

Farid El Gabaly

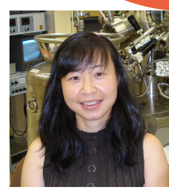
Jose F. Marco



Raquel Gargallo

Laura Martin

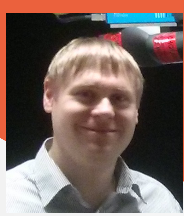
Former members of LEEM group



Shu Nie, Elena Loginova
Kevin F. McCarty

Spin-PEEM

Christian Tusche



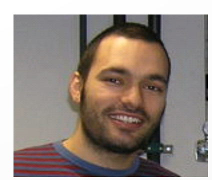
Arantzazu Mascaraque,
Manu Rodriguez
Beatriz Martínez
Oscar Rodríguez de la Fuente,

SPLEEM

LBL,USA

Andreas K. Schmid, Alpha N'Dyale,
Gong Chen

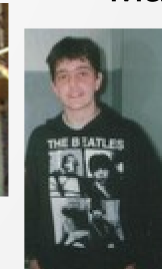
Farid El Gabaly

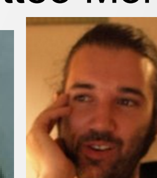


Former members of our group

Tirma Herranz

Matteo Monti





Benito Santos

Lucia Vergara

LEEM/PEEM

Andrea Locatelli,
Tevfik Onur Mentes
Benito Santos