Paul Scherrer Institut, Swiss Light Source

Armin Kleibert
X-ray microscopy (and PEEM)
Surface Science, FS 2013

Repetition VIII

- Near Edge X-ray Absorption Fine Structure
  reflects density of unoccupied states
- Absorption processes and decay (soft X-rays)
- Sampling depths (total electron yield, secondary, Auger, Fluorescence)
- Multiplet structure (chemical, electronic sensitivity)
- XMCD (sum rules)
- XMLD
- Magnetism (spin and orbital moment, magnetocrystalline anisotropy)
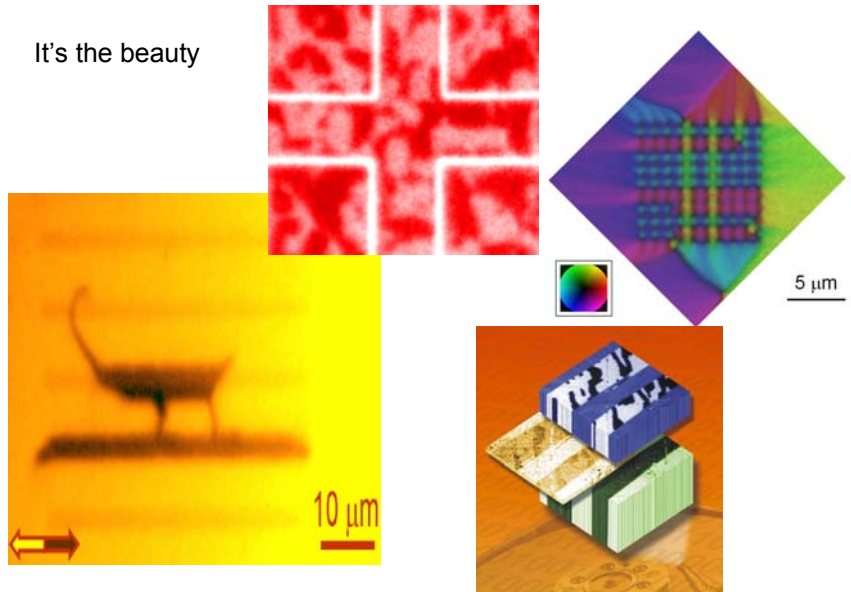
X-ray Absorption Spectra in a Nutshell

atom

tabulated
Henke-Gullikson

molecule

molecular
resonces
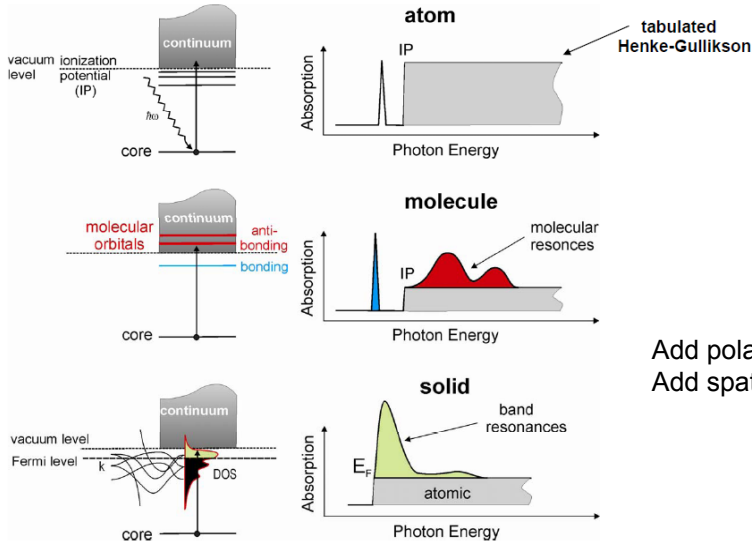
Add polarization
Add spatial resolution

solid

band
resonances

Why do we care

It's the beauty

5 µm

10 µm

2

Why do we care

It's the function

Hysteresis loop

hard axis
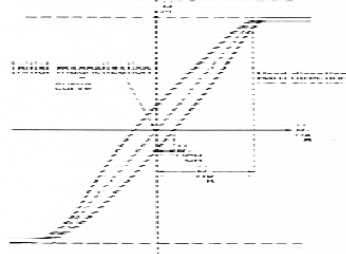
easy axis

Why do we care

It's the function

Co

Py

Substrate
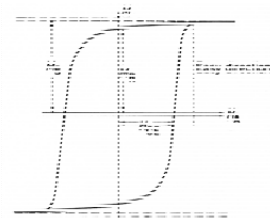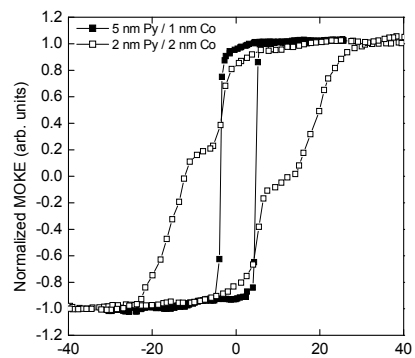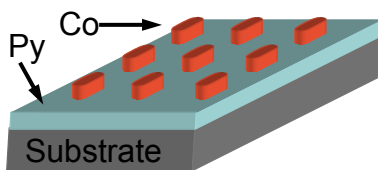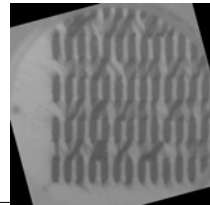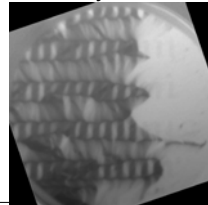
Magnetic domain configuration in the Py film

■ 5 nm Py / 1 nm Co   □ 2 nm Py / 2 nm Co

10 μm

A. Fraile Rodríguez, L. J. Heyderman, F. Nolting, A. Hoffmann, J. E. Pearson, L. M. Doeswijk, M. A. F. van den Boogaart, and J. Brugger, Appl. Phys. Lett. **89**, 142508 (2006).

Outline

The magnetic domain (crash class II)

Photoemission Electron Microscope (PEEM)
   Electron optic
   XMCD/XMLD image
   Aberration correction

The X-ray source
   Röntgen
   Storage ring
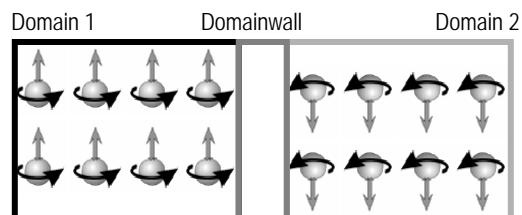   Polarized X-rays

Research example
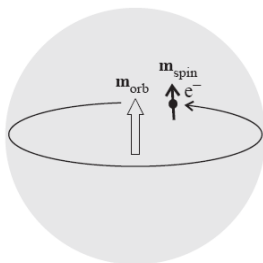   Nanocrystals

PEEM without X-rays

Switching on the interaction

Atoms have an magnetic moment

With interaction they can align to each other and can create macroscopic magnetic field

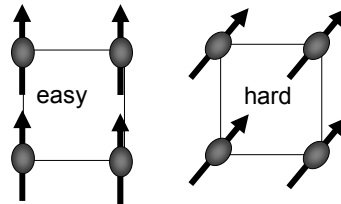Domain 1   Domainwall   Domain 2

Exchange energy:
ferromagnet   parallel spins
antiferromagnet   antiparallel spins
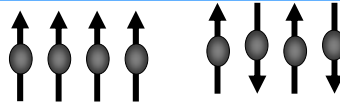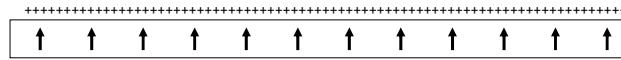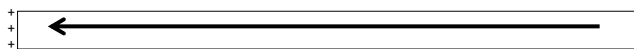
Magnetostatic energy
Closure
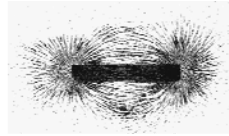
Magnetic Anisotropy
preferential magnetization along axes
easy / hard axis

easy   hard

Zeeman :
spin alignment in the external magnetic field

Magnetostatic energy

Costs more energy

REVIEWS OF
MODERN PHYSICS

VOLUME 21, NUMBER 4   OCTOBER, 1949

Physical Theory of Ferromagnetic Domains

CHARLES KITTEL
Bell Telephone Laboratories, Murray Hill, New Jersey
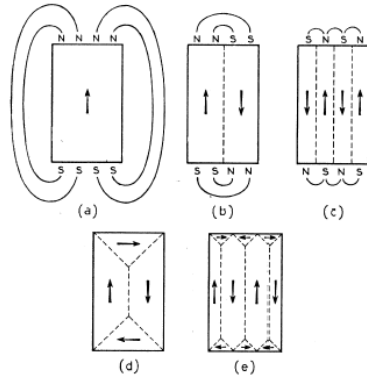
FIG. 9. The origin of domains.

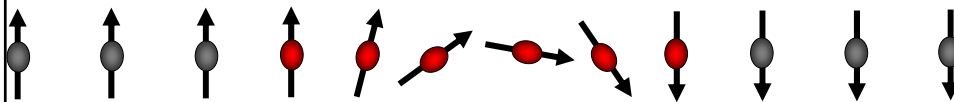| 1907 | Weiss |
1931	Sixtus and Tonks
1932	Bitter
1935	Landau and Lifshitz

Reviews
C. Kittel Rev. Mod. Phys **21** (1949) 541
A. Hubert and R. Schäfer "Magnetic Domains" (Berlin: Springer) 1998

Domain Walls

Exchange energy favors wide walls:

Anisotropy energy favors narrow walls:
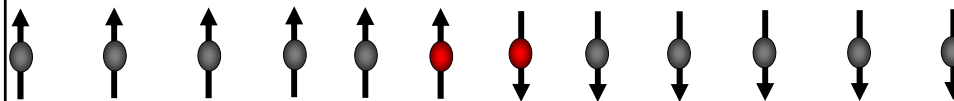
Domain wall width

$$\lambda \sim a \left(\frac{E_{exchange}}{E_{anisotropy}} \right)^{1/2}$$

one dimension below critical length scale
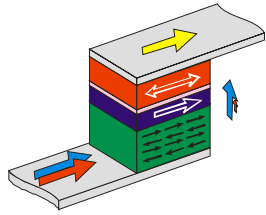
Domain size, domain wall width, Exchange length
Spin diffusion length, Spin precession length

Effect of shape
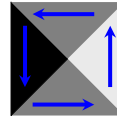
Effect of size
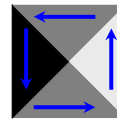
Effect of composition, coupling …

Dealing with multielements, ferromagnetic, antiferromagnetic

X-ray microscope

source

optics

detector

X-ray tube
Synchrotron
      Bending magnet
      Insertion device

Mirrors
Refractive elements
Diffractive elements
Electron optic

Photodiode
Phosphorscreen
…

sample

Detecting methods

Photon in / Photon out   **Photon in / Electron out**

Fluorescence
Escape depth
~ 50 - 100 nm

secondary electrons
Escape depth ~ 5 nm

Auger electrons
Escape depth ~ 0.5 nm

$h\nu$

vacuum

sample surface

sample

X-ray penetration depth
~ 50 - 100 nm

How?

Different ways of measuring X-ray absorption
=
Different ways of magnetic imaging with X-rays

Scanning Transmission X-ray Microscopy STXM

Zone Plate Focusing Lens

Photoelectrons

Fluorescence Photons

Scanning Sample Stage

X-Ray Detector

Transmission X-ray Microscopy TXM

Condenser Lens

Sample

Monochromator Pinhole ~20μm

Micro Zone Plate

CCD Camera

X-Ray Photoemisson Electron Microscopy XPEEM

Phosphor Screen

Magnified Image

Projection Lens

Objective Lens

Aperture

Photoelectrons

Monochromatic X Rays

Sample

Courtesy J. Stöhr

Outline

The magnetic domain (crash class II)

Photoemission Electron Microscope (PEEM)
Electron optic
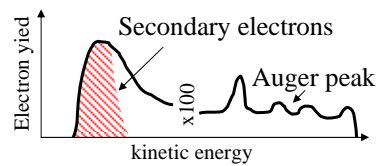XMCD/XMLD image
Aberration correction

The X-ray source
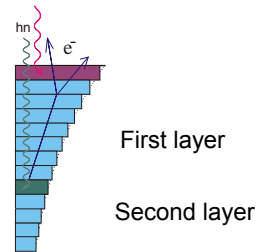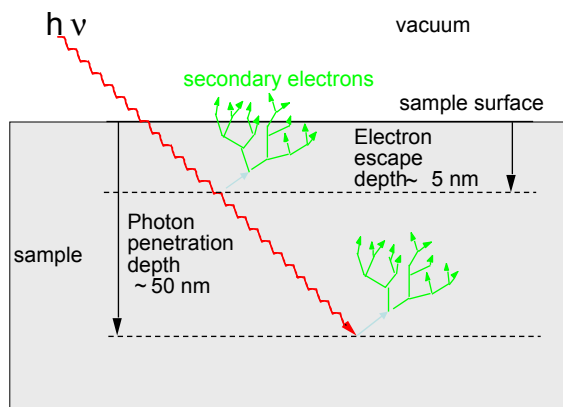Röntgen
Storage ring
Polarized X-rays

Research example
Nanocrystals

PEEM without X-rays

Probing surface/interface

Photoemission Electron Microscope - PEEM

Energy analyzer

Lenses
(magnetic)

MCP
Phosphor

X-rays

16°

20kV
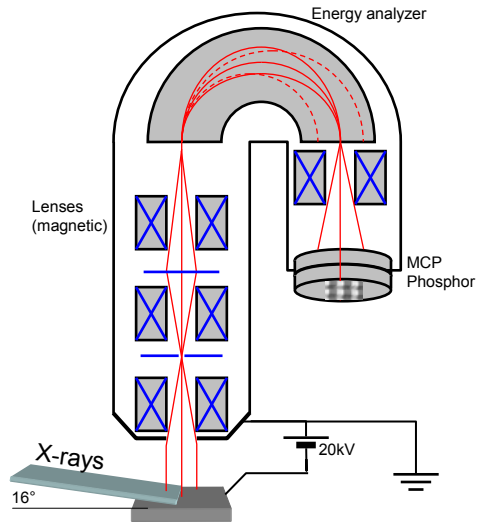
Slow electrons

Probe   :   slow electrons

Imaging :   high energy electrons
             (more stable and maintain spatial information)

0 eV   20 keV   20 keV

Sample   High Voltage
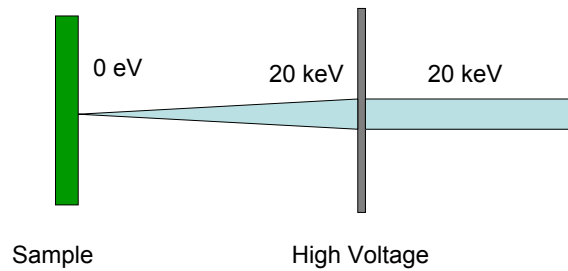
Immersion lens: electrons have before and after the lens different
                          velocity (different wavelength)

Cathode lens: Sample is cathode
                          electron microscope is anode

Just another lens?

Classical: electron in homogenous electric field
calculate electron trajectory

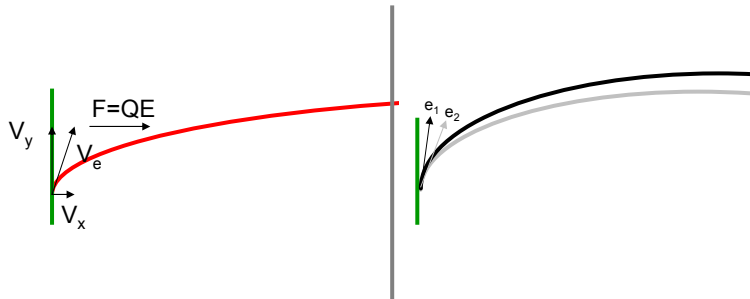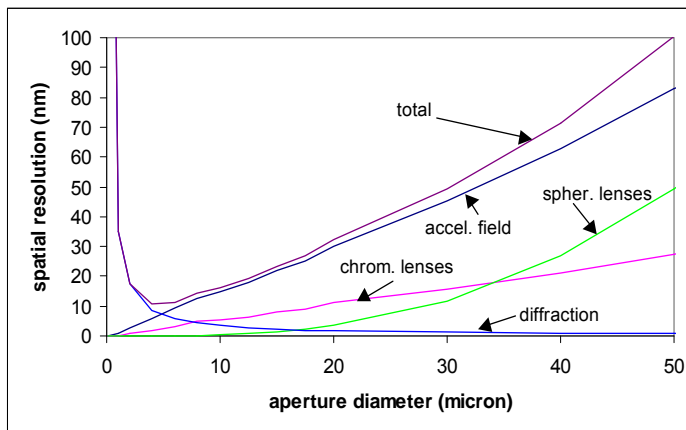
Trajectory depends on emission angle and velocity

No, it is a very important lens in a PEEM, dominating the spatial resolution due to its spherical and chromatic aberrations.
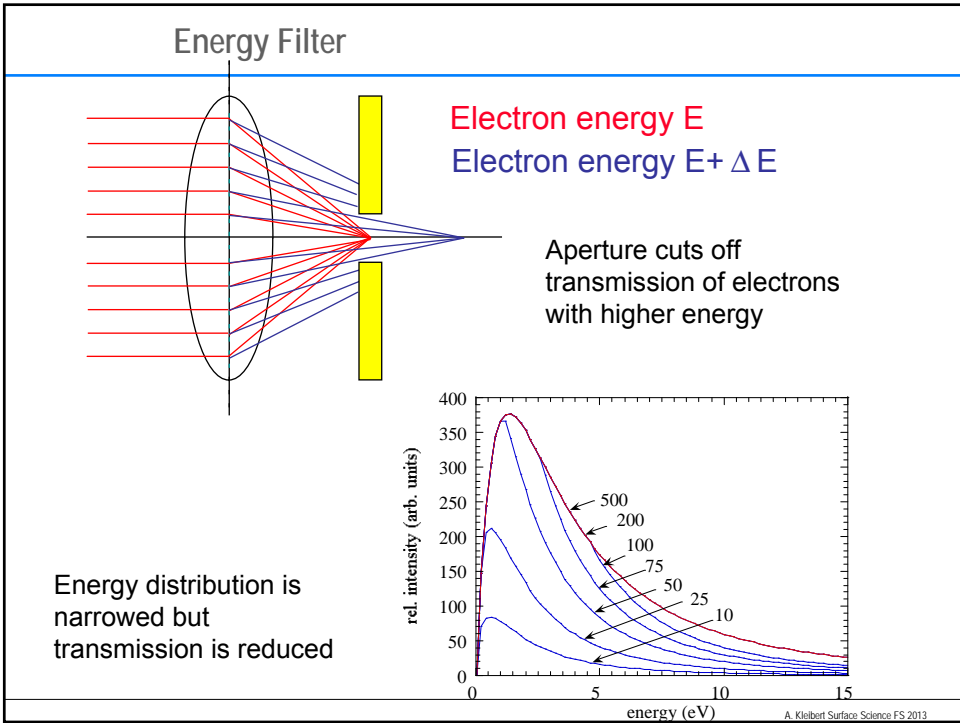
Calculated Spatial Resolution

PEEM 2 at the ALS, Simone Anders
Work function 4 eV, sample voltage 30 kV, X-rays

Energy Filter

Electron energy E
Electron energy E+ΔE

Secondary electrons

Auger peak

x100

Electron yied

kinetic energy

Energy Filter

Electron energy E
Electron energy E+ΔE

Aperture cuts off
transmission of electrons
with higher energy

Energy distribution is
narrowed but
transmission is reduced

rel. intensity (arb. units)

400
350
300
250
200
150
100
50
0

500
200
100
75
50
25
10

0   5   10   15
energy (eV)
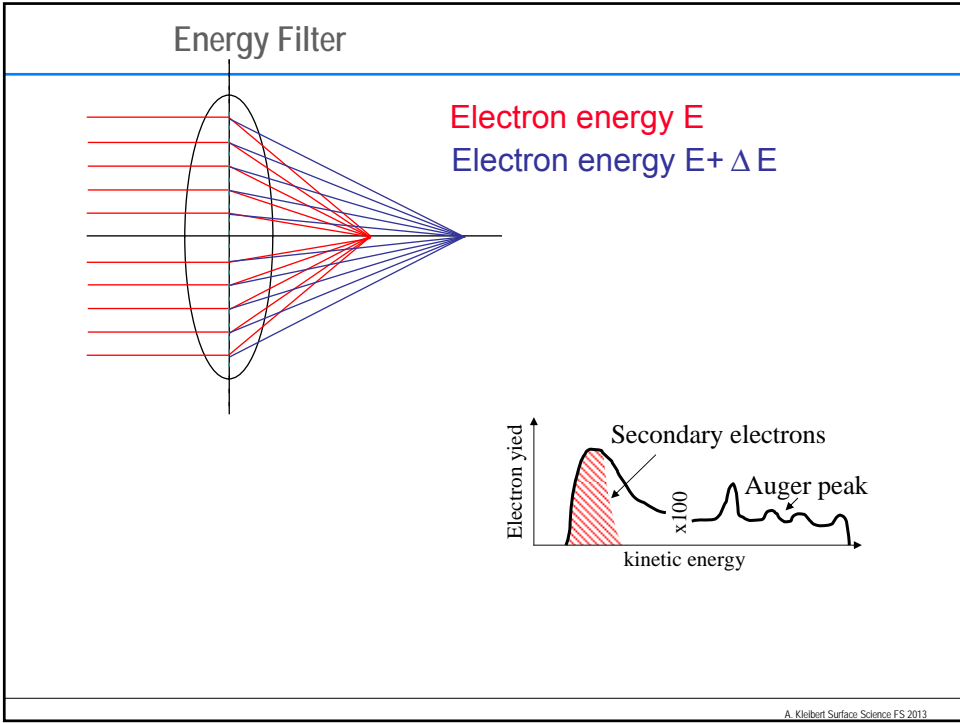
Effect of Aperture Size on Resolution

Spatial resolution depends on aperture size - limits pencil angle of transmitted electrons and transmission
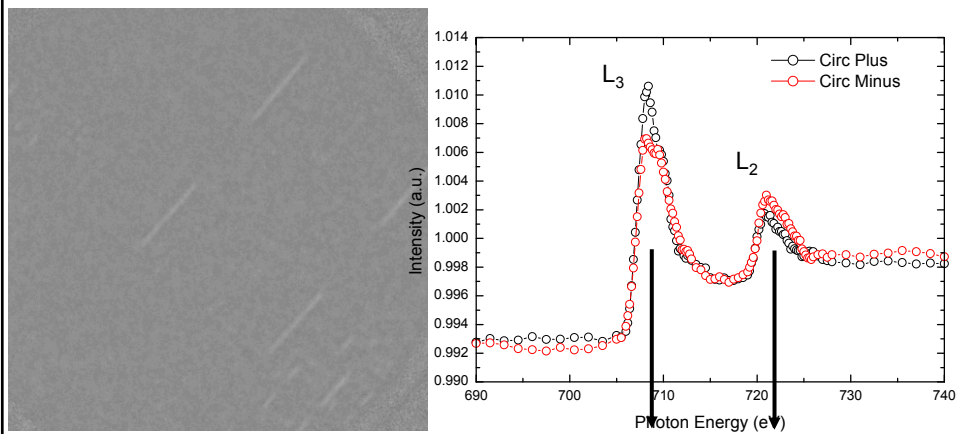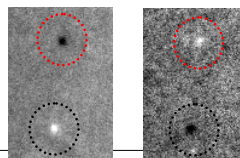Highest resolution is achieved with 12 μm aperture for PEEM2, ALS
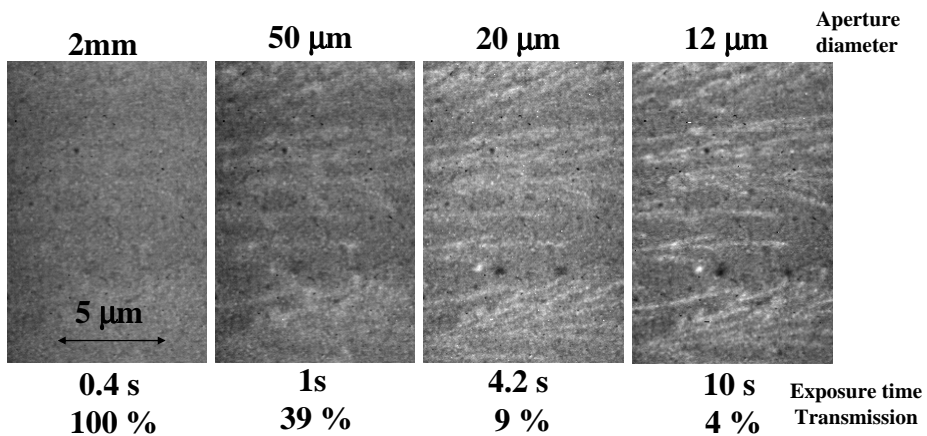
2mm	50 μm	20 μm	12 μm	Aperture diameter

5 μm

0.4 s	1s	4.2 s	10 s	Exposure time
100 %	39 %	9 %	4 %	Transmission

Spectra of individual Fe nanoparticles

Sample: Fe nanoparticles with diameter = 9 nm

L_3

L_2

— Circ Plus
— Circ Minus

Intensity (a.u.)

Photon Energy (eV)

Images with increasing Photon Energy

XMCD image

A. Fraile Rodríguez et al. PRL 104, 127201 (2010)

X-ray Magnetic Circular Dichroism (XMCD)

XMCD ~ <**M**> cos(**M**,**L**)

L_3
L_2

TEY (a.u.)

Photon energy (eV)

A/B ≈ (A-B)/(A+B)
magnetization direction
Domain shape

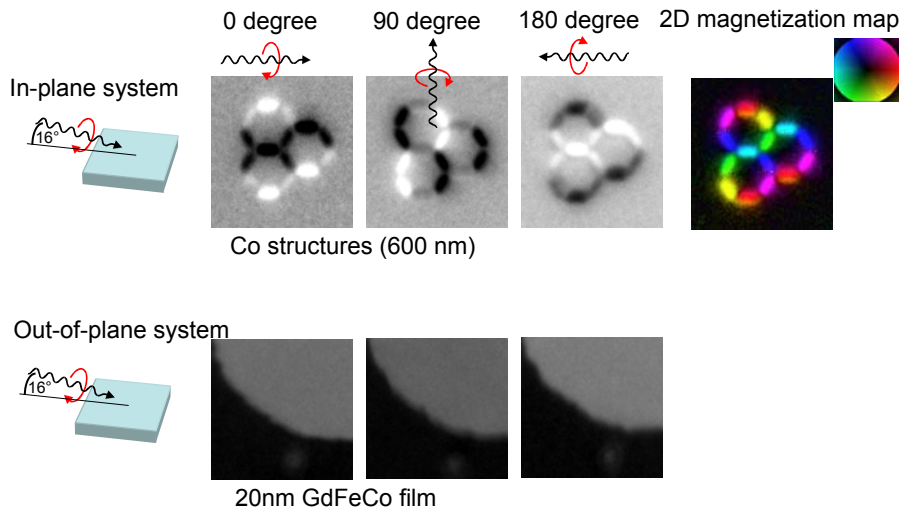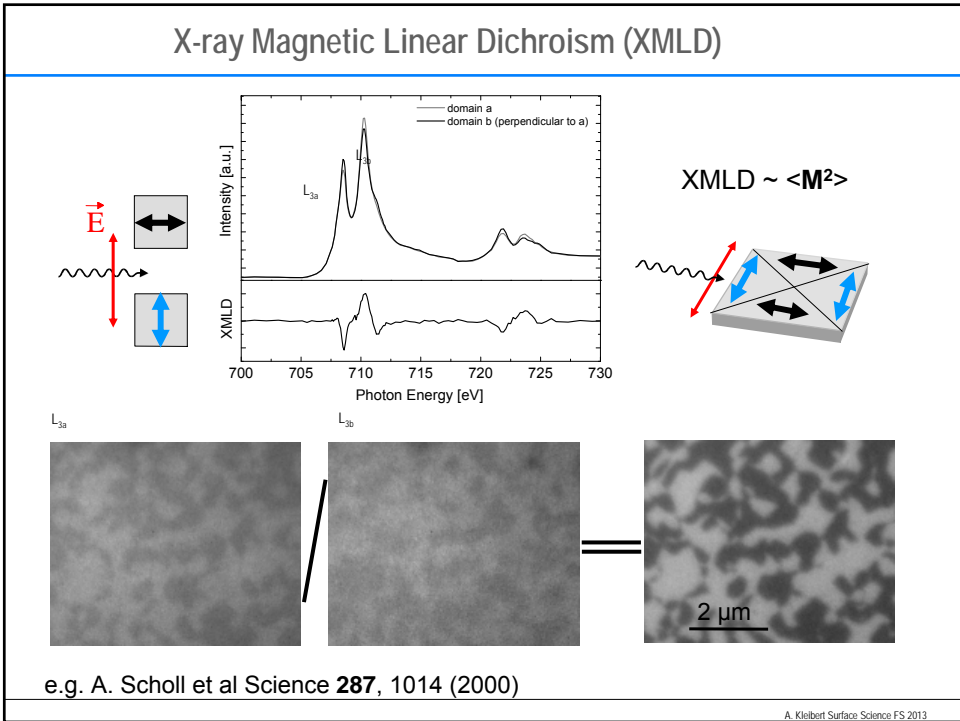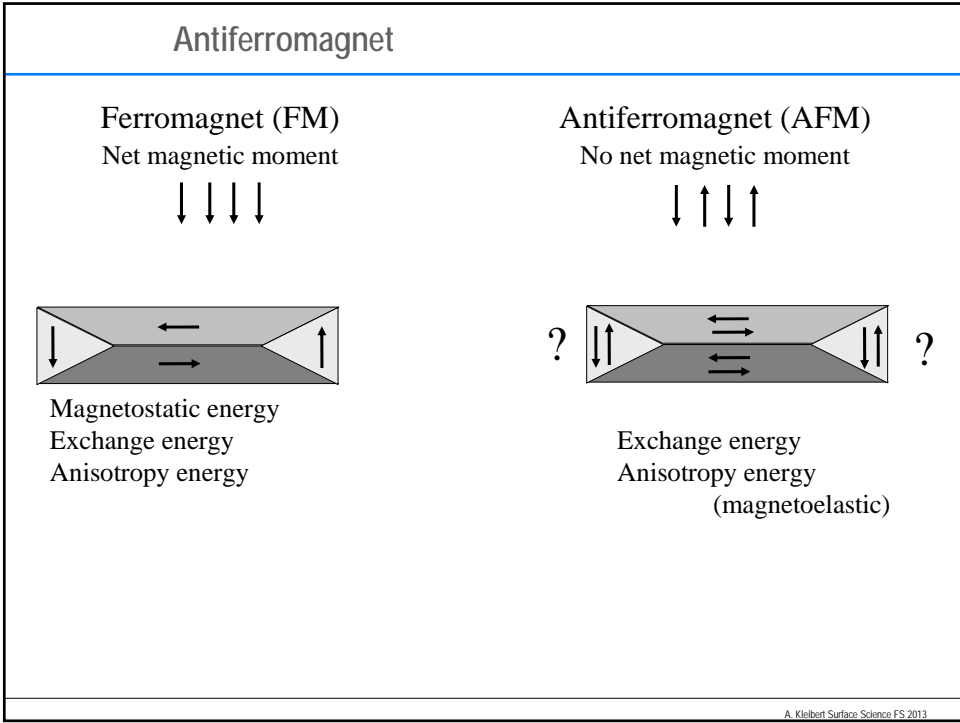Circular right / Circular left =

4 µm

e.g. J. Stohr et al Surface Rev. Lett. **5**, 1297 (1998).

A. Kleibert Surface Science FS 2013

X-ray Magnetic Circular Dichroism (XMCD)

0 degree   90 degree   180 degree   2D magnetization map

In-plane system

Co structures (600 nm)

Out-of-plane system

20nm GdFeCo film

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Antiferromagnet

Ferromagnet (FM)
Net magnetic moment

$\downarrow \; \downarrow \; \downarrow \; \downarrow$

Magnetostatic energy
Exchange energy
Anisotropy energy

Antiferromagnet (AFM)
No net magnetic moment

$\downarrow \; \uparrow \; \downarrow \; \uparrow$

Exchange energy
Anisotropy energy
(magnetoelastic)

X-ray Magnetic Linear Dichroism (XMLD)

$\vec{E}$

XMLD ~ **<M²>**

domain a
domain b (perpendicular to a)

Intensity [a.u.]

L_{3a}

XMLD

700 705 710 715 720 725 730
Photon Energy [eV]

L_{3a}

L_{3b}

2 µm

e.g. A. Scholl et al Science **287**, 1014 (2000)
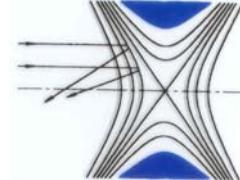
Microscopy with synchrotron light

Aberrations and their correction

Spherical aberrations
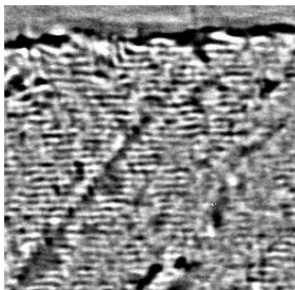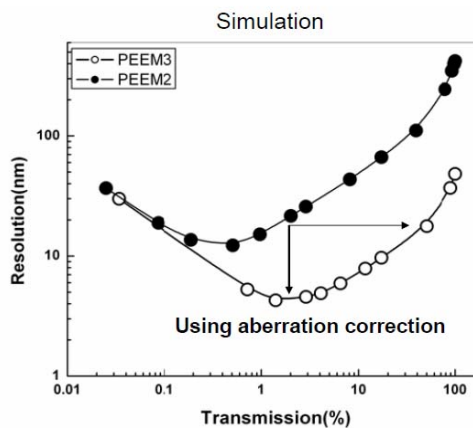
Lens
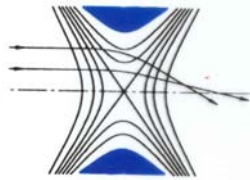
Mirror

Chromatic aberrations

Aberration corrected PEEM

Without aberration correction
Element-resolved X-PEEM image of
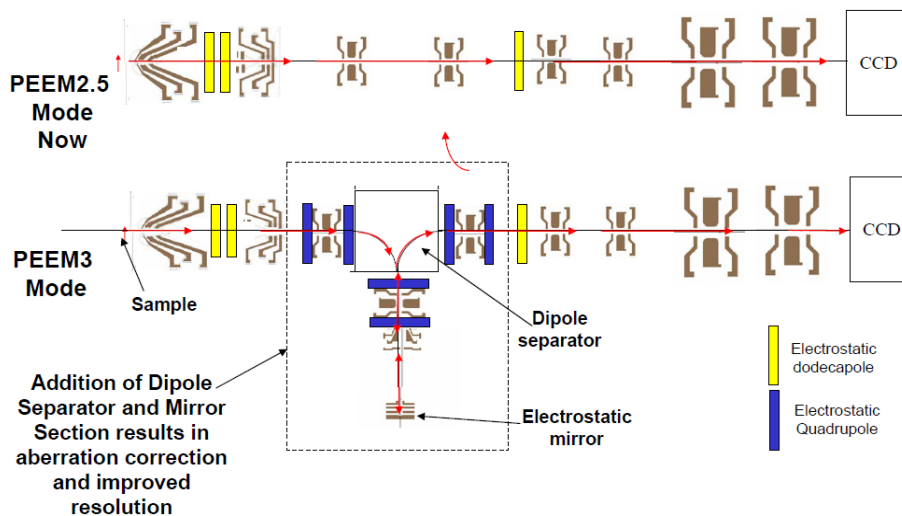25 nm thick Cr/Si layers.

Simulation

Aberration correction:

**4-fold improvement of
spatial resolution** at a few %
transmission (goal 10 nm)

**10-fold improvement of
transmission** at several 10
nanometer spatial resolution.

Courtesy A. Scholl (ALS)

A. Kleibert Surface Science FS 2013

Aberration corrected PEEM

**PEEM2.5
Mode
Now**

CCD

**PEEM3
Mode**

Sample

CCD

**Addition of Dipole
Separator and Mirror
Section results in
aberration correction
and improved
resolution**

**Dipole
separator**

**Electrostatic
mirror**

Electrostatic
dodecapole

Electrostatic
Quadrupole

Courtesy A. Scholl (ALS)

A. Kleibert Surface Science FS 2013

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Aberration-corrected instruments

SMART (SpectroMicroscope for All Relevant Techniques)
    at BESSY II, Berlin, Germany
    collaboration of seven Universities in Germany
    status: LEEM 3 nm, X-PEEM about 20 nm

PEEM III
    at ALS, Berkeley, USA
    aberration corrected not yet build

Companies with aberration correction:
ELMITEC
SPECS

Outline

The magnetic domain (crash class II)

Photoemission Electron Microscope (PEEM)
    Electron optic
    XMCD/XMLD image
    Aberration correction

The X-ray source
    Röntgen
    Storage ring
    Polarized X-rays

Research example
    Nanocrystals

PEEM without X-rays

1895 Discovery of X-rays by Wilhelm Röntgen
1901 Nobel prize in physics

Image of hand of Albert von Kölliker
this is the second image, the first one, very
similar is said to be the hand of his wife

Wilhelm Röntgen

27. März 1845 in Lennep geboren.

1861 bis 1863 Technische Schule in Utrecht. Aus disziplinarischen Gründen, weil er irrtümlich für den Urheber einer Karikatur seines Klassenlehrers gehalten wurde, verwies man ihn ohne Abitur von der Schule.

1864 - 1868 Eidgenössischen Technischen Hochschule Zürich (ETH Zürich) Maschinenbauingenieur
1869 promovierte Röntgen an der Universität Zürich in Physik mit „Studien über Gase".

1870 begleitete er August Kundt als Assistent nach Würzburg.
1874 Habilitation Universität Straßburg die ihm die Universität Würzburg zuvor wegen seines fehlenden Abiturs verweigert hatte.

1875 außerordentlicher Professor für Physik und Mathematik an der Landwirtschaftlichen Akademie Hohenheim.
1876 eine Stelle als außerordentlicher Professor für Physik in Straßburg.
1879 ordentliche Professur in Gießen
1888 Professor der Experimentalphysik Würzburg.
1900 Professor an der Universität München
1923 verstorben

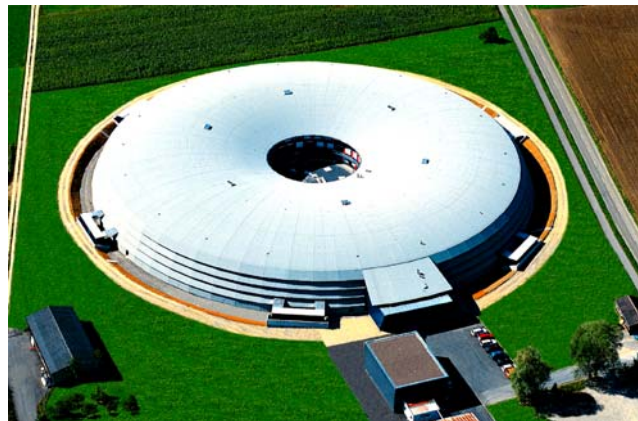## Creation of electromagnetic radiation

The *Liénard–Wiechert field* $\mathbf{E}(t)$ of a point charge q detected by an observer at a time t is determined by the distance r^*, the velocity v^*, and acceleration a^* of the charge at the emission or retarded time $t^* = t - r^*/c$. Defining $\beta^* = v^*/c$ we have

$$\mathbf{E}(t) = \frac{q}{4\pi\epsilon_0} \underbrace{\frac{1-(\beta^*)^2}{(r^*)^2\,(1-\mathbf{n}^*\cdot\boldsymbol{\beta}^*)^3}\,[\mathbf{n}^*-\boldsymbol{\beta}^*]}_{\text{velocity field}}$$

$$+ \frac{q}{4\pi\epsilon_0}\underbrace{\frac{1}{c^2\,r^*\,(1-\mathbf{n}^*\cdot\boldsymbol{\beta}^*)^3}\,\{\mathbf{n}^*\times([\mathbf{n}^*-\boldsymbol{\beta}^*]\times\mathbf{a}^*)\}}_{\text{acceleration field}}. \quad (4.58)$$

We have indicated all retarded quantities by an asterisk.
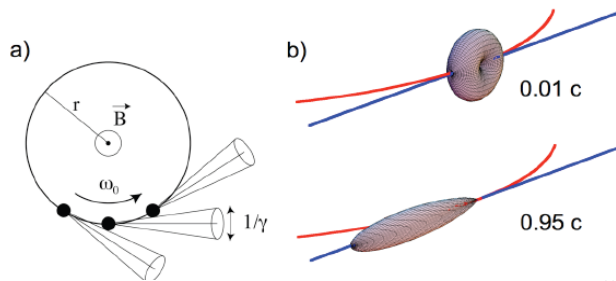
a)   b)   0.01 c   0.95 c

Swiss Light Source

Synchrotron

Polarized Photons
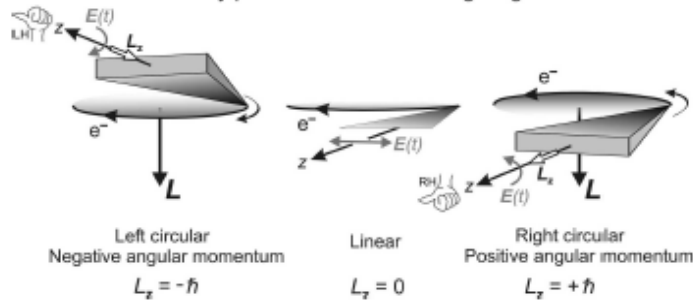
21
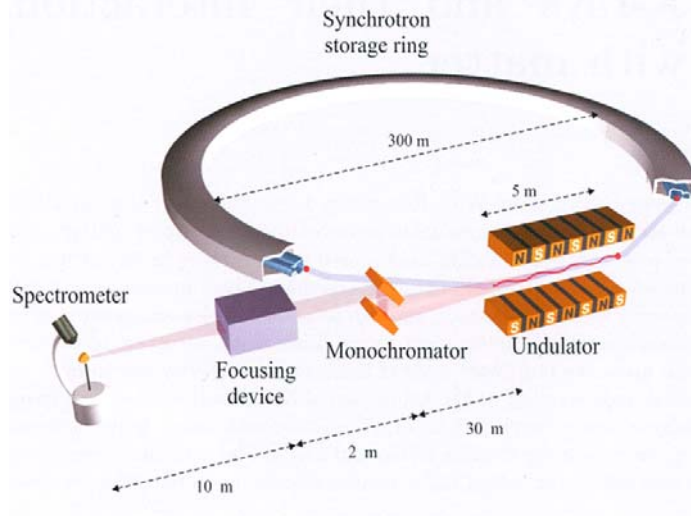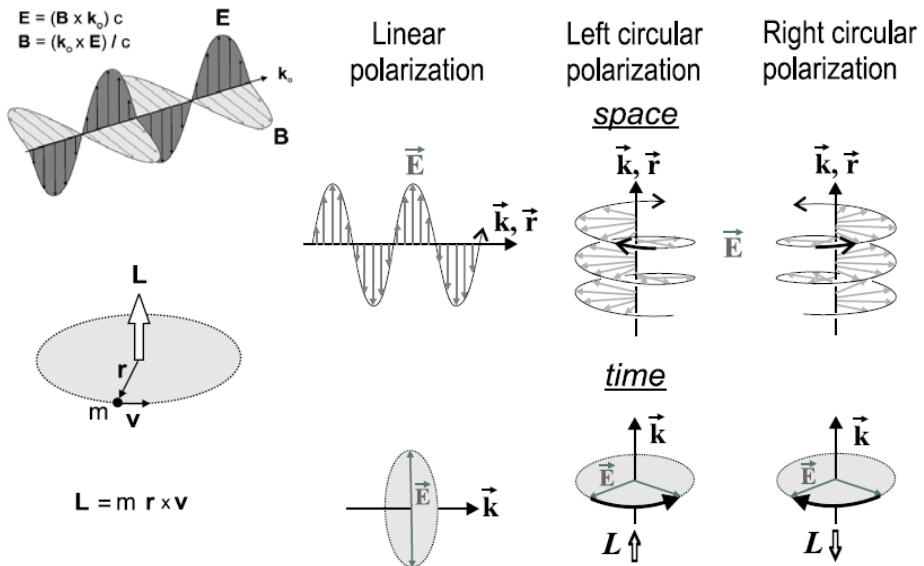
Creation of electromagnetic radiation - polarization
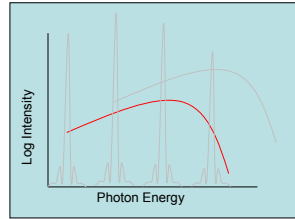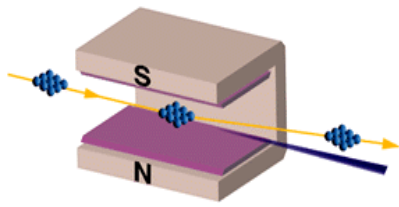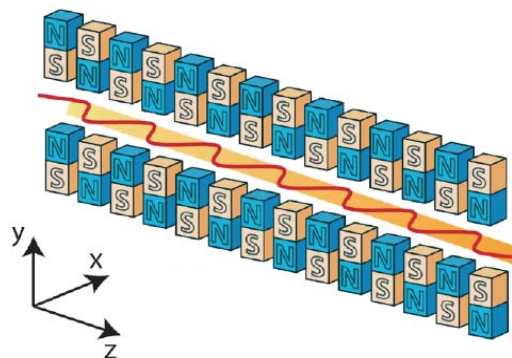
X-ray polarization from bending magnets
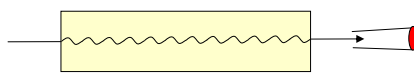
Left circular
Negative angular momentum
$L_z = -\hbar$

Linear
$L_z = 0$

Right circular
Positive angular momentum
$L_z = +\hbar$

Taken from J. Stöhr

Source: undulator

Undulator
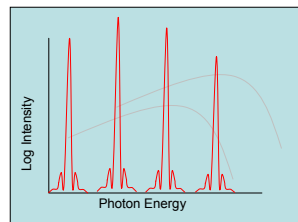
Outline

The magnetic domain (crash class II)

Photoemission Electron Microscope (PEEM)
Electron optic
XMCD/XMLD image
Aberration correction

The X-ray source
Röntgen
Storage ring
Polarized X-rays

Research example
Nanocrystals

PEEM without X-rays

Spectroscopy of individual nanoclusters

Size-dependent spin structures in iron nanoparticles

A. Fraile Rodríguez[1], A. Balan[1], A. Kleibert[1], J. Bansmann[2], A. Voitkans[2], L. J. Heyderman[1], and F. Nolting[1]

[1]Paul Scherrer Institut, Villigen PSI, CH-5232 Switzerland.
[2]Institute of Surface Chemistry and Catalysis, University of Ulm, D-89069 Ulm, Germany.
[3]Institute of Physics, University of Rostock, D-18051 Rostock, Germany.

Domainwall

A domainwall needs space

Domain 1   Domänenwand   Domain 2
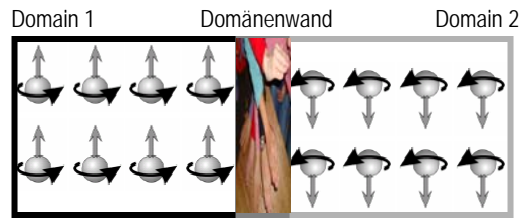
How stable?

finite temperature
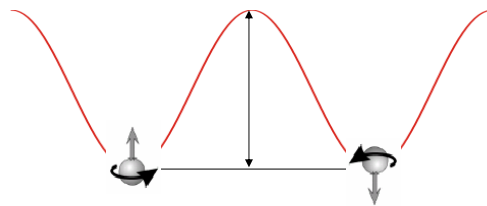
Energy

$\approx K_{ani} \cdot V_{particle}$

Temperature and Energy
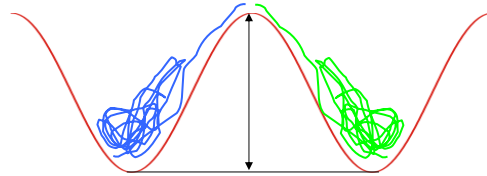
$\overline{E_{kin}} = \frac{3}{2} k_B T$ (Ideal Gas)

Thermal energy at room temperature: 1/40 eV (0.0258472 eV)

Flipping between two states

finite temperature

$$\frac{1}{\tau} = f \exp\left(-\frac{E_A V}{2kT}\right) \qquad f \sim 10^9\, s^{-1}$$

$V^{1/3} = 14\ \text{nm} \rightarrow \tau = 10^4\ \text{s}$
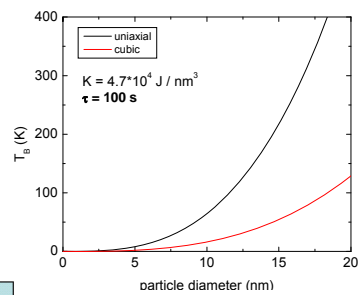$V^{1/3} = 10\ \text{nm} \rightarrow \tau = 10^{-5}\ \text{s}$

How small?

Superparamagnetism

$K_{ani} \cdot V_{particle} \cong k_B \cdot T$

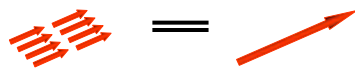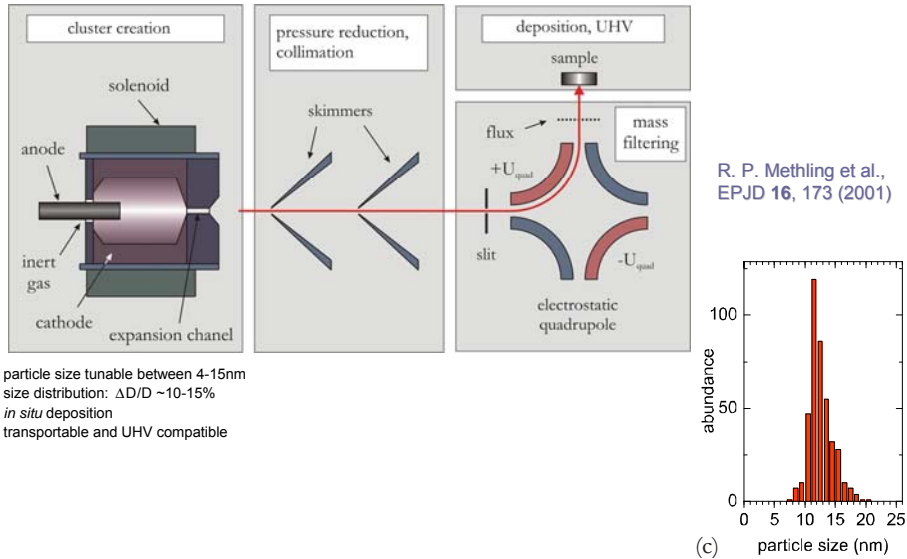$$\frac{1}{\tau} = f \exp\left(-\frac{E_A V}{2kT}\right) \qquad f \sim 10^9\, s^{-1}$$

$K = 4.7 \ast 10^4\ \text{J} / \text{nm}^3$
$\tau = 100\ \text{s}$

uniaxial
cubic

T_B (K)

particle diameter (nm)

$V^{1/3} = 14\ \text{nm} \rightarrow \tau = 10^4\ \text{s}$
$V^{1/3} = 10\ \text{nm} \rightarrow \tau = 10^{-5}\ \text{s}$

Single spin model
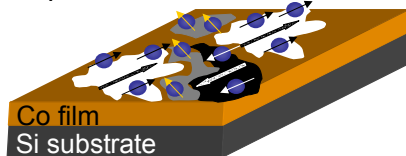For particles smaller than 20 – 100 nm (material dependent)

Mass-filtered nanoparticles: Arc-ion source

cluster creation

solenoid

anode

inert gas

cathode   expansion chanel

pressure reduction, collimation

skimmers

deposition, UHV

sample

flux

$+U_{quad}$

mass filtering

slit

$-U_{quad}$

electrostatic quadrupole

R. P. Methling et al., EPJD **16**, 173 (2001)

particle size tunable between 4-15nm
size distribution: $\Delta D/D \sim 10\text{-}15\%$
in situ deposition
transportable and UHV compatible

abundance

100

50

0

0 5 10 15 20 25

particle size (nm)

(c)

In-situ Fe particles deposited on cobalt surfaces

Fe particles (5-25 nm)

Co film
Si substrate

1. e-beam evaporation of cobalt thin films (2- 4 nm thickness)

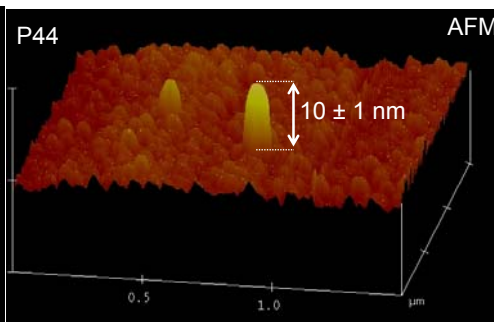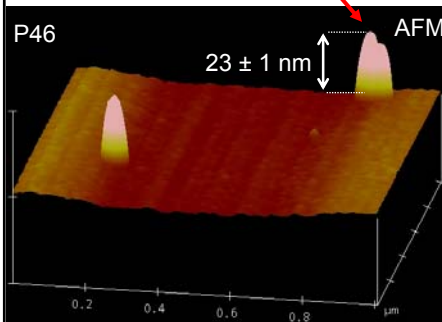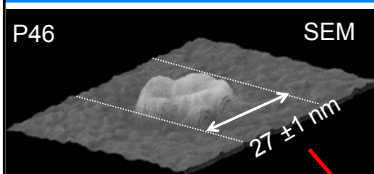2. in-situ deposition of Fe particles using arc-ion cluster source

Fe Elemental

SEM

$\Phi = 4.5 \pm 0.5$ nm

Line Profile

FOV = 20 micrometer

26

SEM, AFM

P46   SEM

27 ±1 nm

P46   AFM

23 ± 1 nm

P44   AFM

10 ± 1 nm
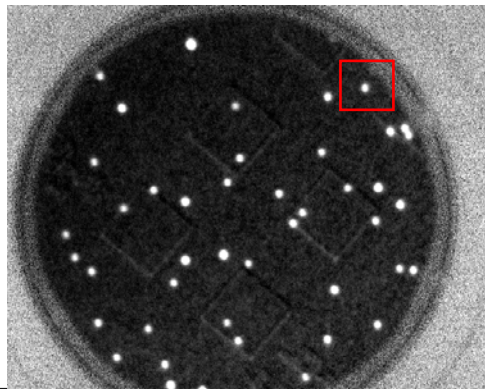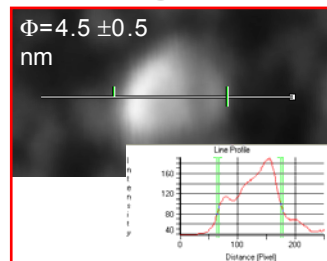
0.2   0.4   0.6   0.8   µm   0.5   1.0   µm

P46 (lateral size) = 27±1 nm   P44 (estimated lateral size) = 30±1 nm

P46 (height÷width)=0.85   P44 (height÷width)=0.33

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Spectra of individual Fe nanoparticles
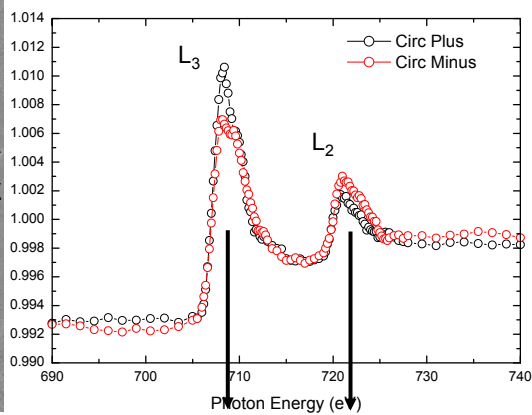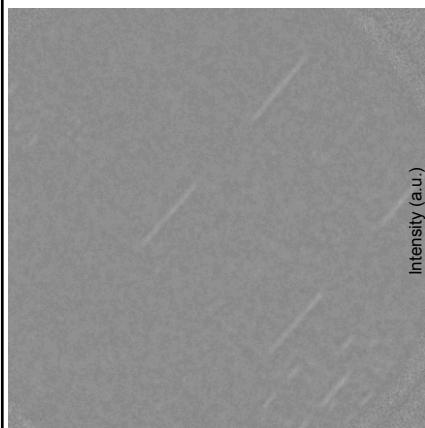
Sample: Fe nanoparticles with diameter = 9 nm

L_3

L_2

○— Circ Plus
○— Circ Minus

Intensity (a.u.)

Photon Energy (eV)

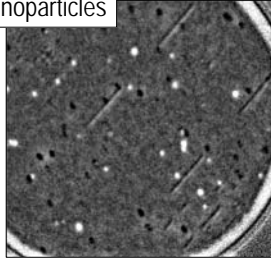Images with increasing Photon Energy

XMCD image
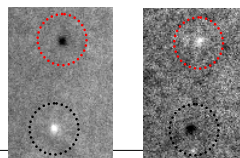
A. Fraile Rodríguez et al. PRL 104, 127201 (2010)
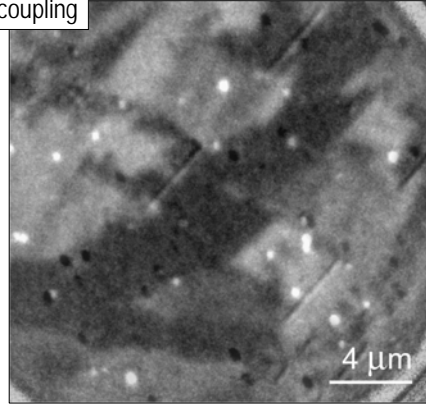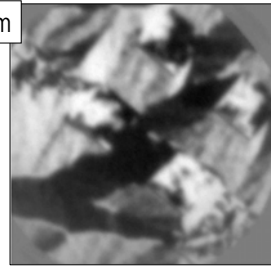
A. Kleibert Surface Science FS 2013

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Coupling

Fe Nanoparticles

coupling

Co film

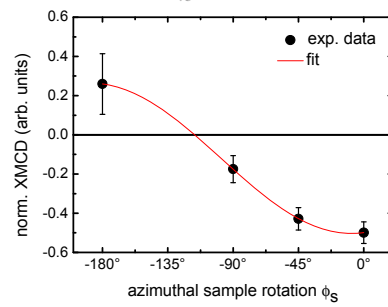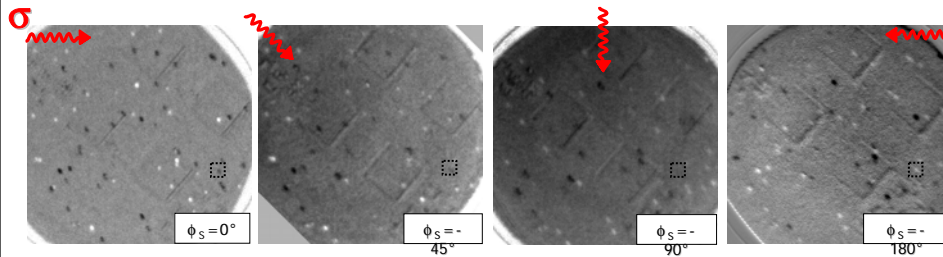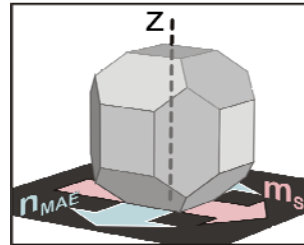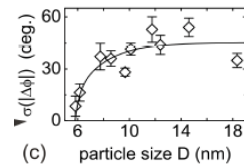4 µm

3D magnetization map

σ

$\phi_S = 0°$

$\phi_S = -45°$

$\phi_S = -90°$

$\phi_S = -180°$

norm. XMCD (arb. units)

- exp. data
— fit

azimuthal sample rotation ϕ_S
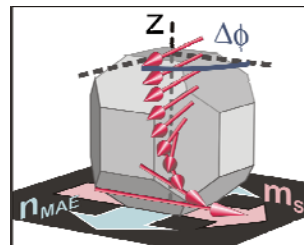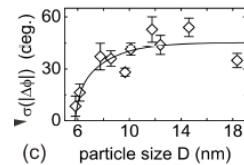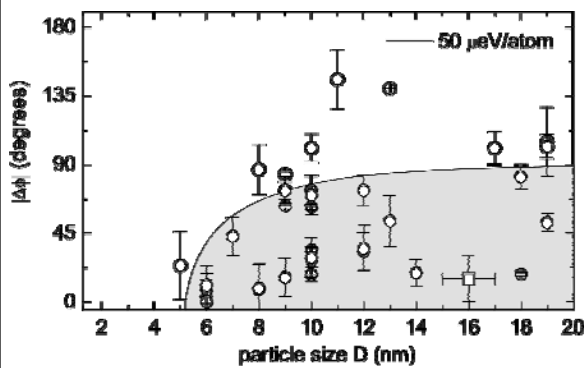
What is acting on the nanoparticle
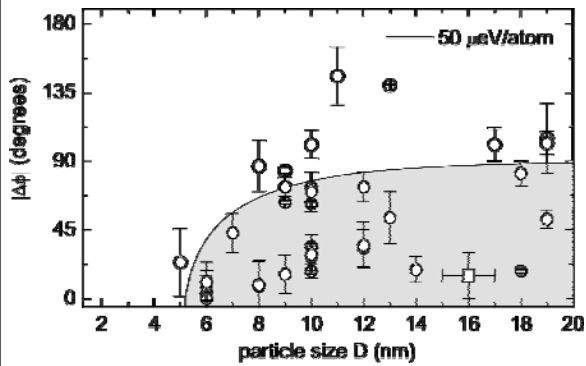
Exchange energy with ferromagnetic Co-film
Magnetocrystalline energy of the Fe-nanoparticle

A. Fraile Rodríguez, A. Kleibert, J. Bansmann, A. Voitkans, L. J. Heyderman, and F. Nolting PRL 104, 127201 (2010)

The smallest domainwall in a nanoparticle

Already for particles larger than 6 nm is the
single-spin model not correct anymore

A. Fraile Rodríguez, A. Kleibert, J. Bansmann, A. Voitkans, L. J. Heyderman, and F. Nolting PRL 104, 127201 (2010)

Outline

The magnetic domain (crash class II)

Photoemission Electron Microscope (PEEM)
    Electron optic
    XMCD/XMLD image
    Aberration correction

The X-ray source
    Röntgen
    Storage ring
    Polarized X-rays

Research example
    Nanocrystals

PEEM without X-rays

A. Kleibert Surface Science FS 2013

Not only with X-rays

PEEM with UV light
    10 nm spatial resolution
    workfunction and topography contrast
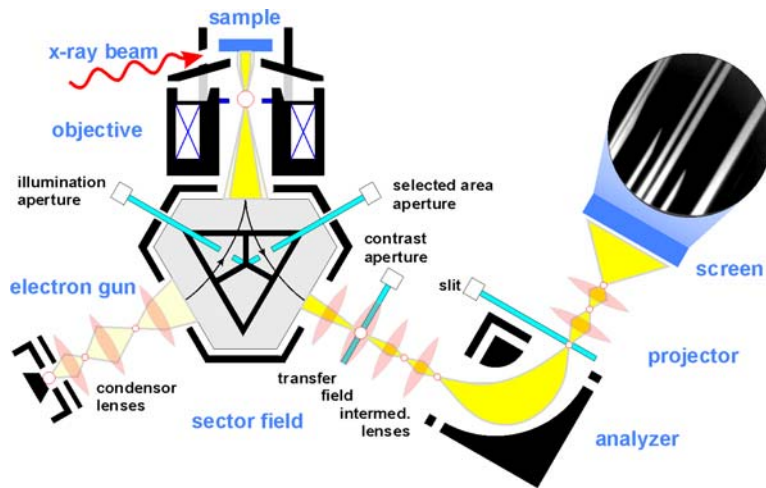
PEEM with slow electrons
    8 nm spatial resolution
    LEED, LEEM, MEM ….

PEEM with X-rays
    50-20 nm spatial resolution
    spectromicroscopy

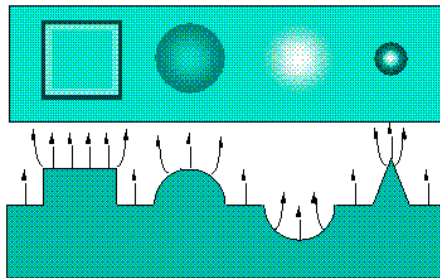A. Kleibert Surface Science FS 2013

Spectromicroscope

L.H. Veneklasen: Ultramicroscopy 36 (1991), 76
Image courtesy of S. Heun (ELETTRA)

Elmitec Elektronenmikroskopie GmbH
Clausthal-Zellerfeld, Germany

Topographical Contrast

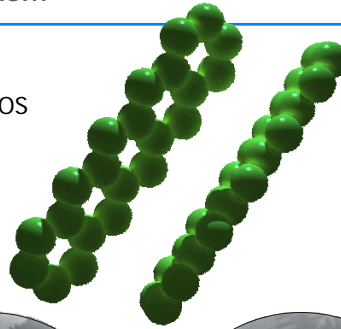Distortion of the electric field due to topography

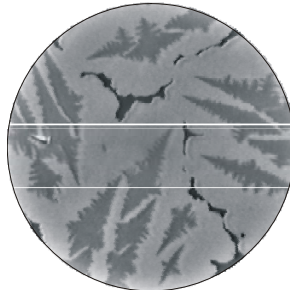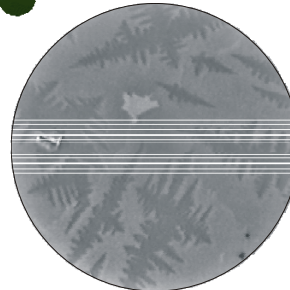## PEEM Contrast Mechanism

- Mercury lamp (5eV)
- Contrast either by Work Function or DOS
- Pentacene: 5 Benzene Rings
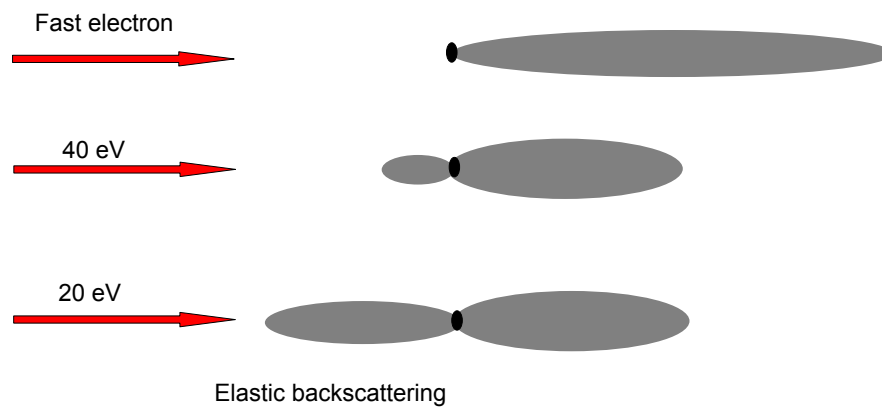- Contrast Changes During Deposition
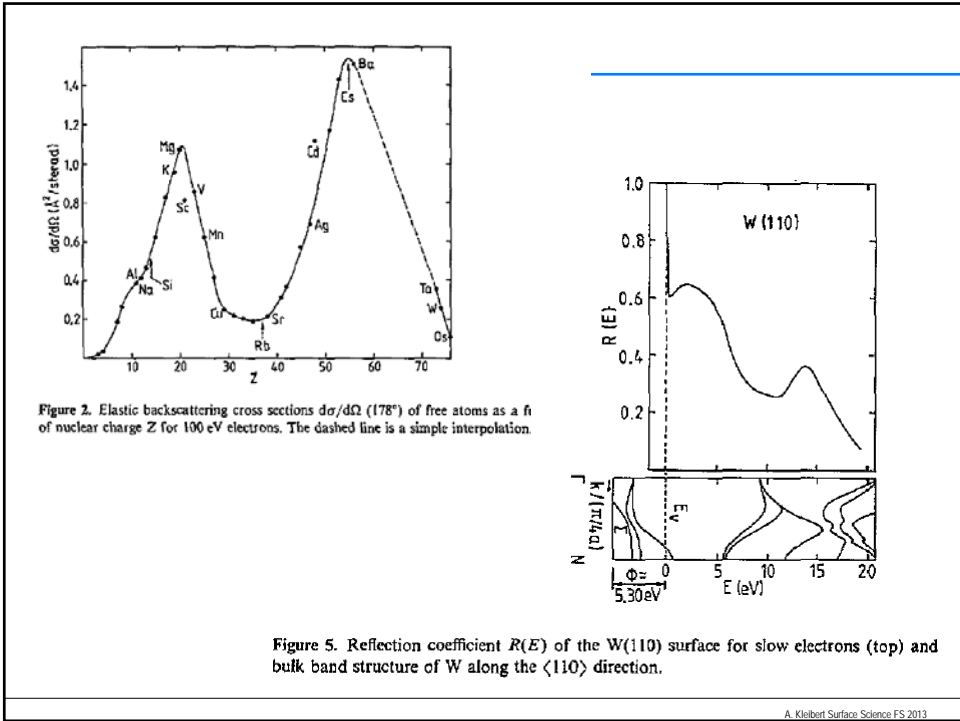- FoV = 65µm
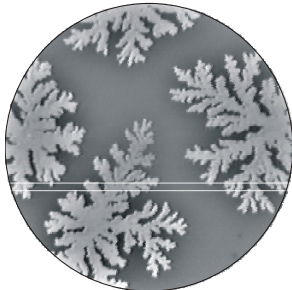
1 Layer   2 Layers   3 Layers

Source: slow electrons

How slow electrons interact with matter

Fast electron

40 eV

20 eV

Elastic backscattering

Figure 2. Elastic backscattering cross sections $d\sigma/d\Omega$ (178°) of free atoms as a function of nuclear charge Z for 100 eV electrons. The dashed line is a simple interpolation.

Figure 5. Reflection coefficient $R(E)$ of the W(110) surface for slow electrons (top) and bulk band structure of W along the $\langle 110 \rangle$ direction.

Low Energy Electron Diffraction

LEED

Electron Gun Visible
High Linearity
Spots move with Energy

http://www.vgsysj.co.jp/sipic.jpg

LEEM
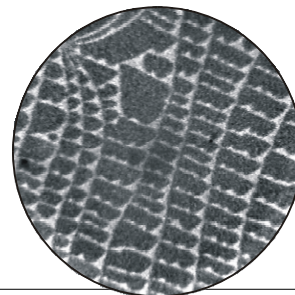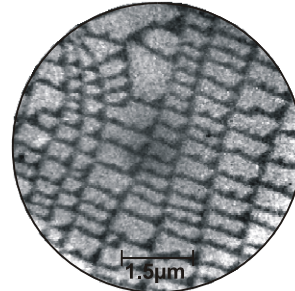
No Apparent Electron Gun
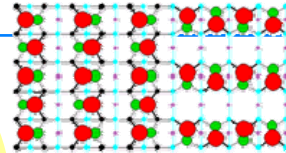Secondary Electrons
Spots Don't Move

Bright Field Imaging of Si (111)
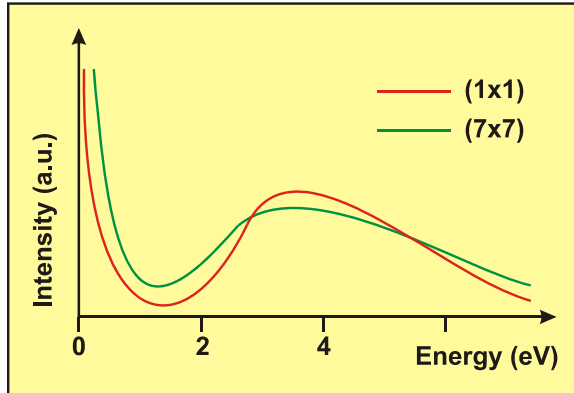
- Different Reflectivity of (1x1) and (7x7)
- Reflectivity Energy Dependent
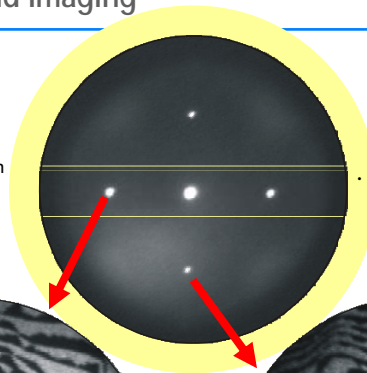- Contrast Reversal Dependent on Imaging Conditions

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Dark Field Imaging

Si (001)

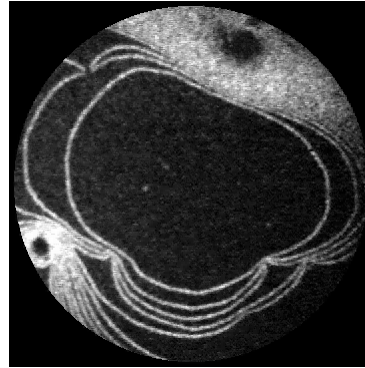

- Creator of the LEED Spots Lights up in Bright

- The Rest of the Surface Remains Dark

**Direct Observations of Nanoscale Self-Assembly and
Pattern Formation Solid Surfaces**
by R. Plass, N. C. Bartelt, and G. L. Kellogg

LEEM-Movie of the growth of Pb on a
Cu(111) surface.

Nature, 412 (2001) 875

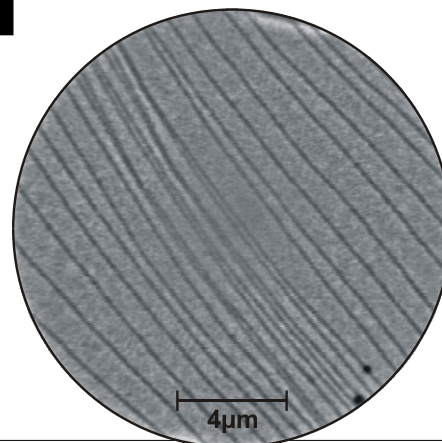## Phase Contrast Imaging
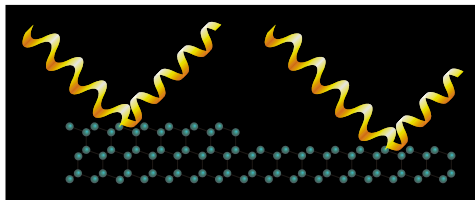
Analogue LEED
Electrons from Different
Terraces have a Phase Shift at
Out-of-Phase Conditions

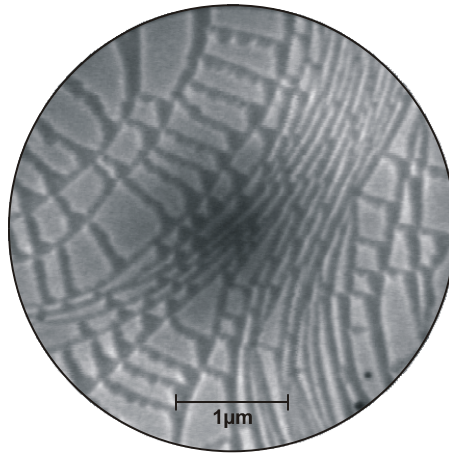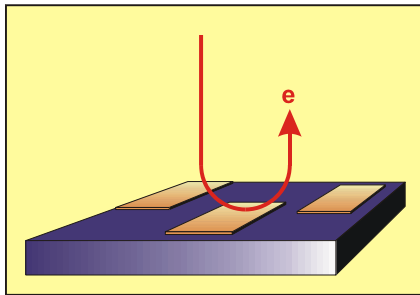**Localized Phase Shift**
Defocusing of the Image turns Steps
into Dark Lines, i.e. Centers of
Destructive Interference.

4µm

Mirror Imaging of Si(111)

Electron Energy is 0eV
- Electrons Return Before they Hit the Sample

Contrast created by outer Potential
- Workfunction

Image appears Blurred

Brief History

1930s   Electron lenses/electron microscopy
        Photoemission electron microscope   (PEEM)
              E. Brueche, Z. Phys. (1933) 448
        Low Energy Electron Diffraction (LEED)
              W. Ehrenberg, Philos. Mag. **18** (1934) 878

1960s   improved LEED
        E.J. Scheibner, L.H. Germer and C.D. Hartman,
        Rev. Sci. Instrum. **31** (1960) 112
        Invention of Low energy electron microscop (LEEM) by Ernst Bauer
        Glass-Based Vacuum Apparatus (1962)

1985   First Operational LEEM Instrument
        Telieps and Bauer, Ultramicroscopy **17** (1985) 57

1991   IBM LEEM-I
        Tromp and Reuter

Brief History

Since 1990 several groups and companies:
> Elmitec LEEM (Former Coworkers of E. Bauer)
> Staib, Omicron
> Schoenhense, Kirschner
> De Stasio

> Synchrotron based PEEM
> pioneering G. Harp and B. Tonner, Rev. Sci. Instrum. **59** (1988) 853
> Magnetism: Stöhr et al, Science **259** (1993) 658

Since 2000
> world wide several beamlines for PEEM

Future
> Aberration-corrected instruments (SMART / Germany, PEEMIII / USA)
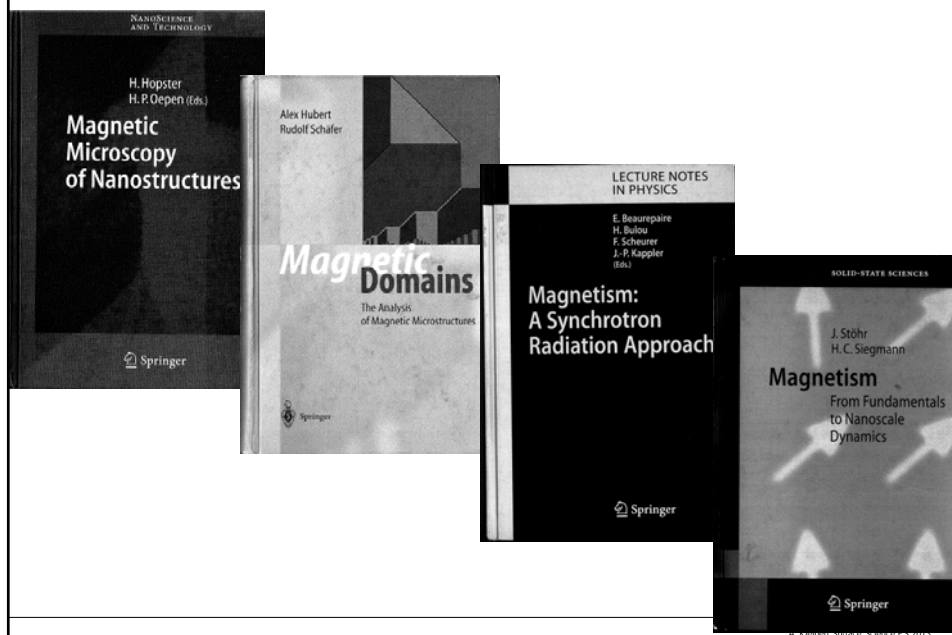> spatial resolution ~ nm

Reviews (X-PEEM)
J. Stöhr et al., Surf. Rev. Lett. **6** (1998) 1297
E. Bauer, J. Phys.: Condens Matter **13** (2001) 11391
Th Schmidt et al., Surf. Rev. Lett. **9** (2002) 223

Some good books

Some good review papers

Magnetic imaging,
F U Hillebrecht, J. Phys.: Condens. Matter 13, 11163 (2001)

Photoelectron microscopy and applications in surface and materials science,
S. Günther, B. Kaulich, L. Gregoratti, M. Kiskinova, Progress in Surface
Science 70, 187 (2002)

Recent advances in chemical and magnetic imaging of surfaces and interfaces
by XPEEM,
A Locatelli and E Bauer J. Phys.: Condens. Matter 20, 093002 (2008)

Principles of X-ray magnetic dichroism spectromicroscopy,
J. Stöhr, S. Anders, T. Stammler, and M.R. Scheinfein, Surface Review and
Letters, 5, 1297 (1998)

Repetition VIII

- Magnetic domains
- Slow electrons (surface/interface sensitivity)
- PEEM with soft X-rays as source (XMCD image)
- Polarized X-ray source
- PEEM with slow electrons as source
- Research example nanocrystals