The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

1936-39

Advanced School on Synchrotron and Free Electron Laser Sources and their Multidisciplinary Applications

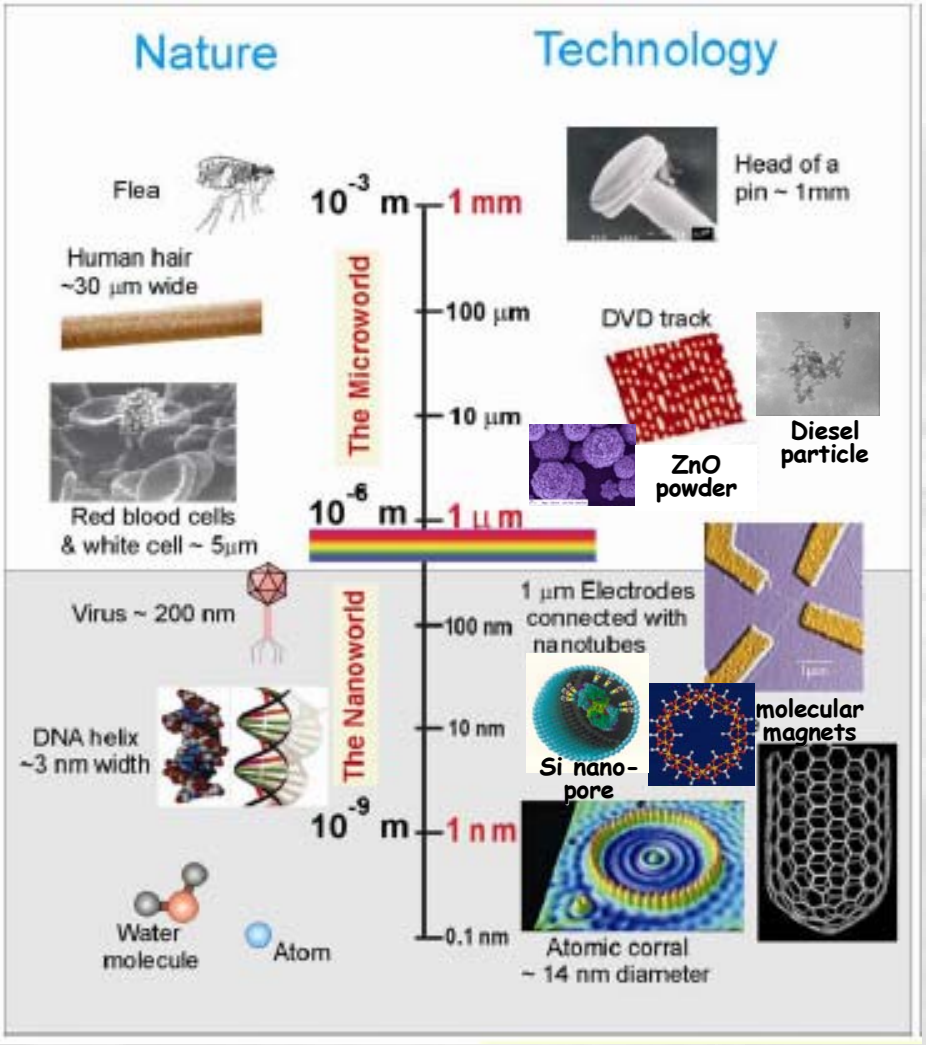
7 - 25 April 2008

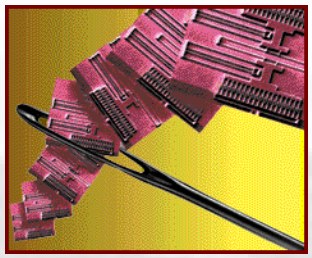
X-ray Micro-spectroscopy.

Maya Kiskinova
Sincrotrone Trieste
Italy

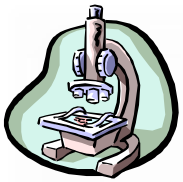
X-ray Micro-spectroscopy

Maya Kiskinova, Sincrotrone Trieste, Italy





1. Introductory remarks.
2. Principle of microscopy approaches using spectroscopic methods.
3. Outlook on 'microscopic' future.



Why we need x-ray microscopy?

elettra

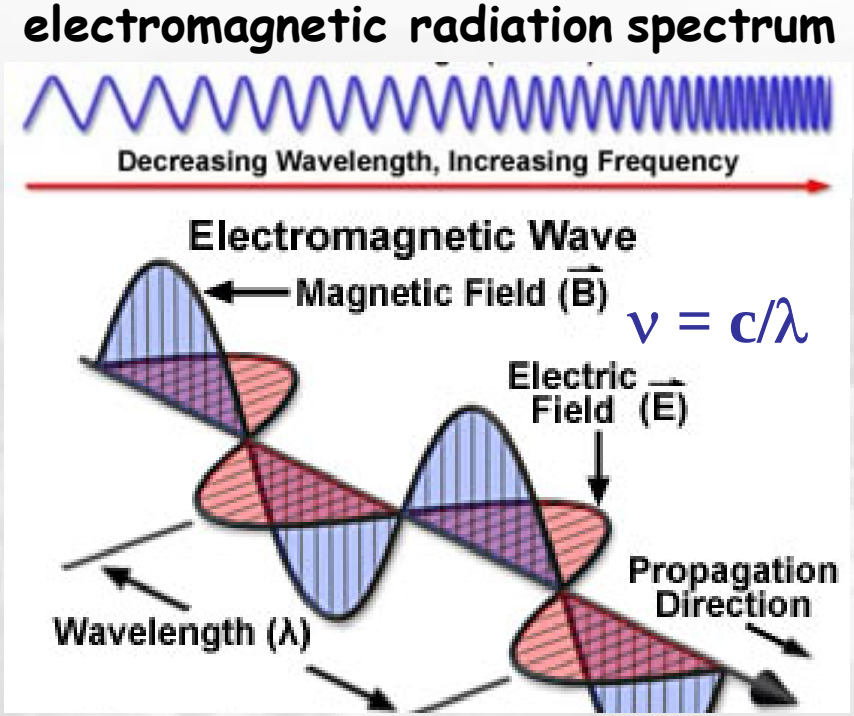
There's Plenty of Room at the Bottom

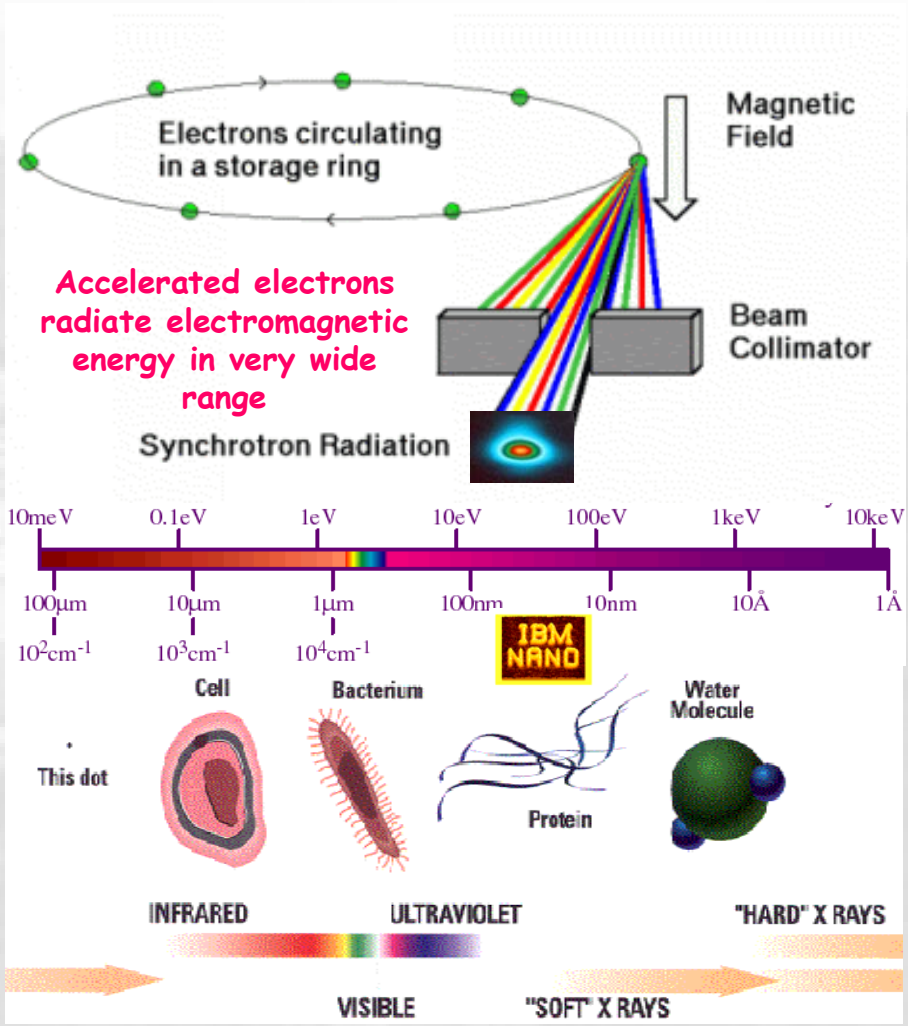
An Invitation to Enter a New Field of Physics & Material Science

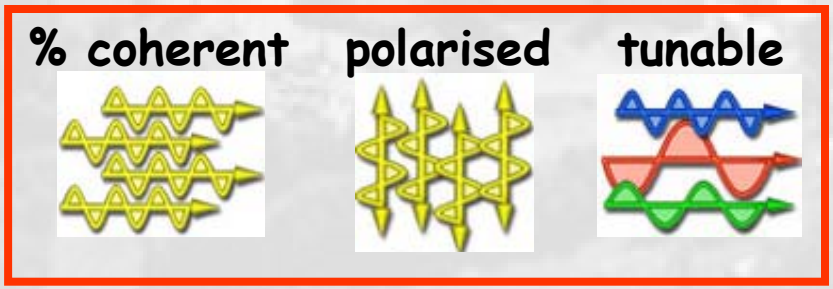
Richard P. Feynman - 1959!!!

1) STATIC: Heterogeneity by nature (e.g. phase separation), by design (e.g. μ and nanostructures), generated in reactive environment by local radiation or heat.
2) STATIC: Reduced dimensionality and unique properties, e.g. structural and electron confinement effects.
3) MASS TRANSPORT: thermal and electro-migration, reorganizations in reactive environment, segregation

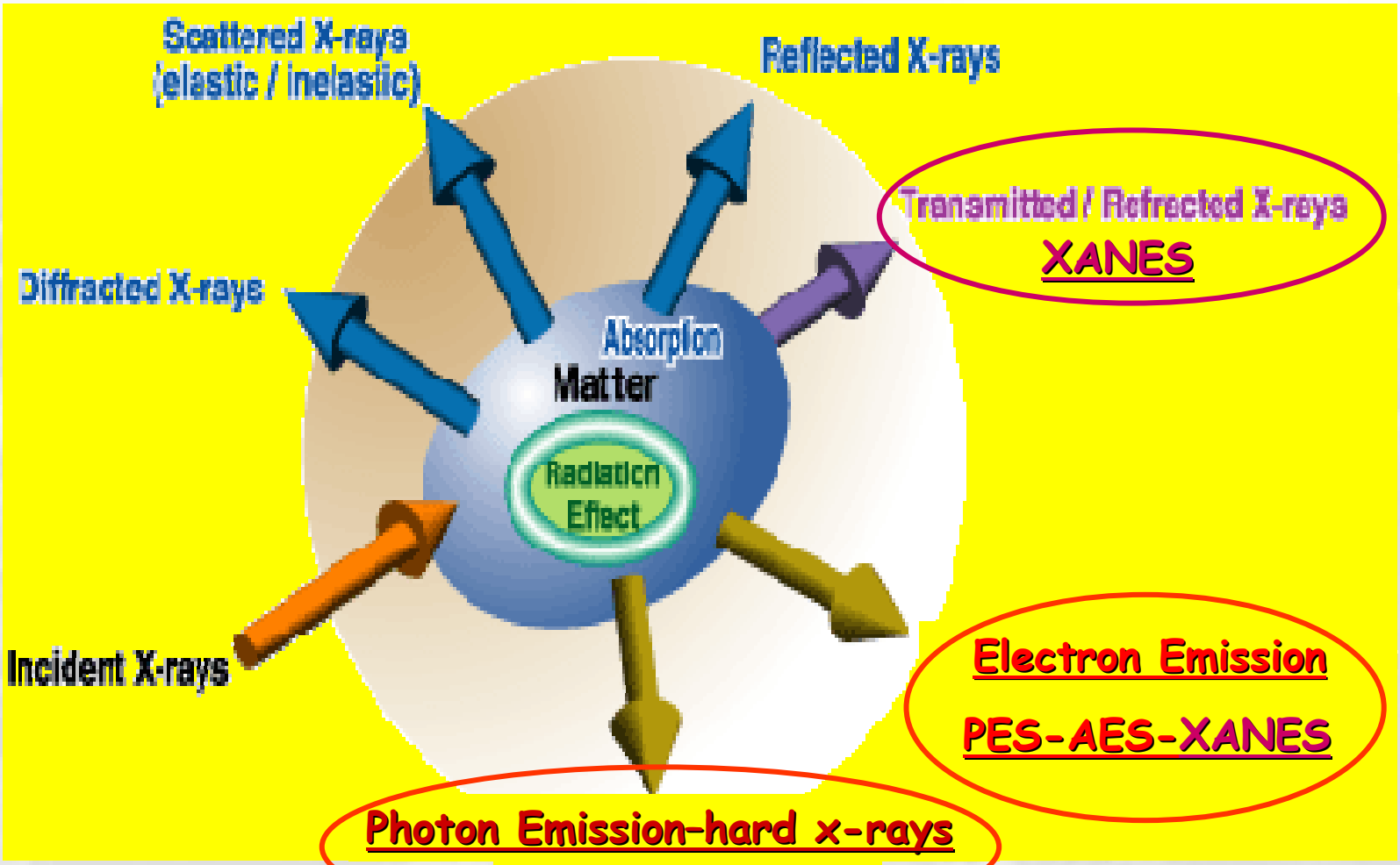
Only 'LIGHT'
with comparable wavelength, λ, can visualize the micro- and nano-structured world



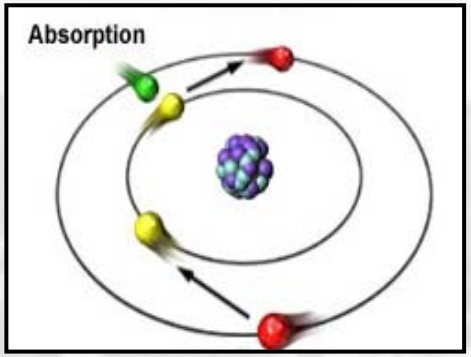


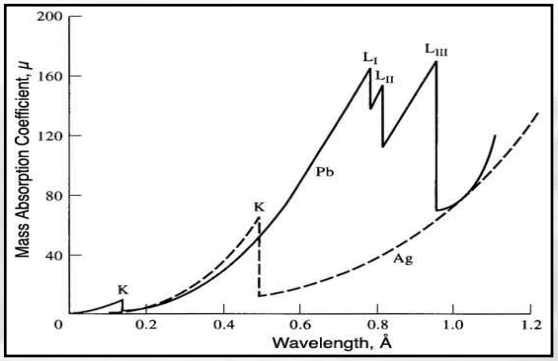


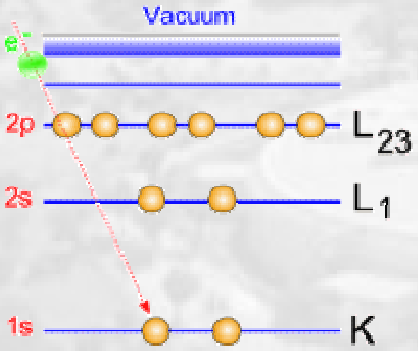
Interactions of x-rays with the matter: redirection & absorption: x-ray transmission and x-ray or electron emission

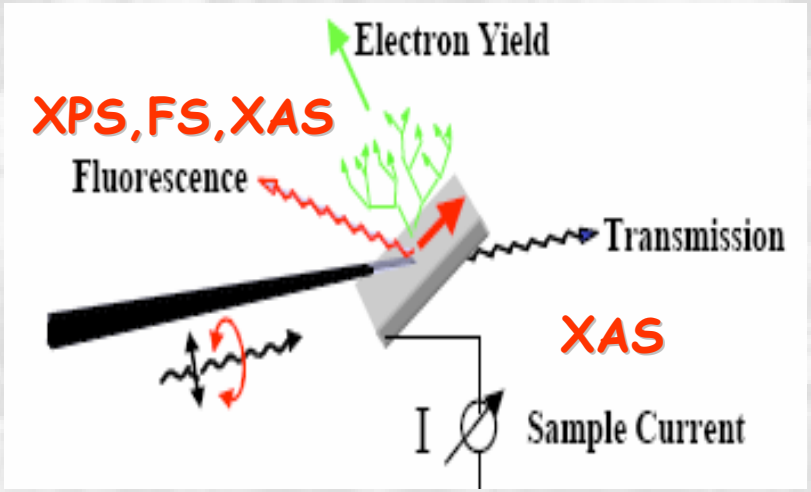


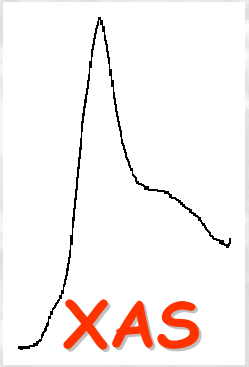
All chemical specific spectroscopies are based on absorption of the photons by the matter and following excitation & de-excitation processes

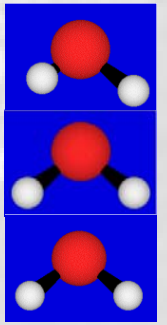


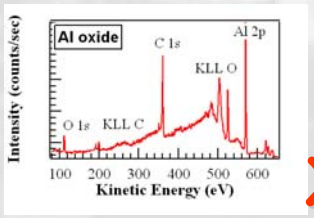






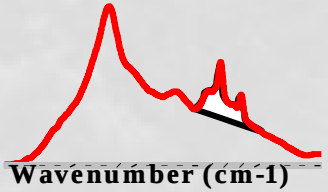




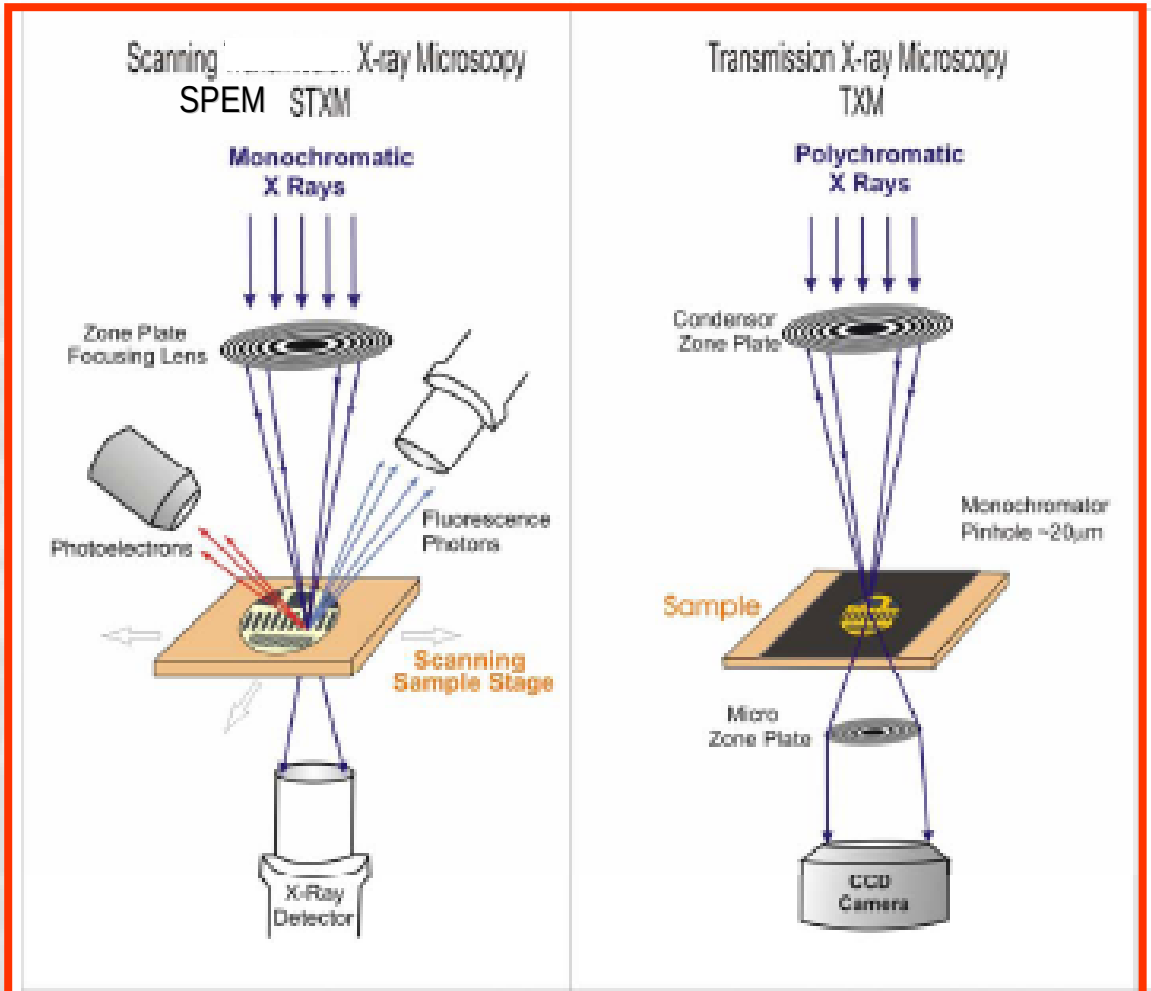


XPS & FS

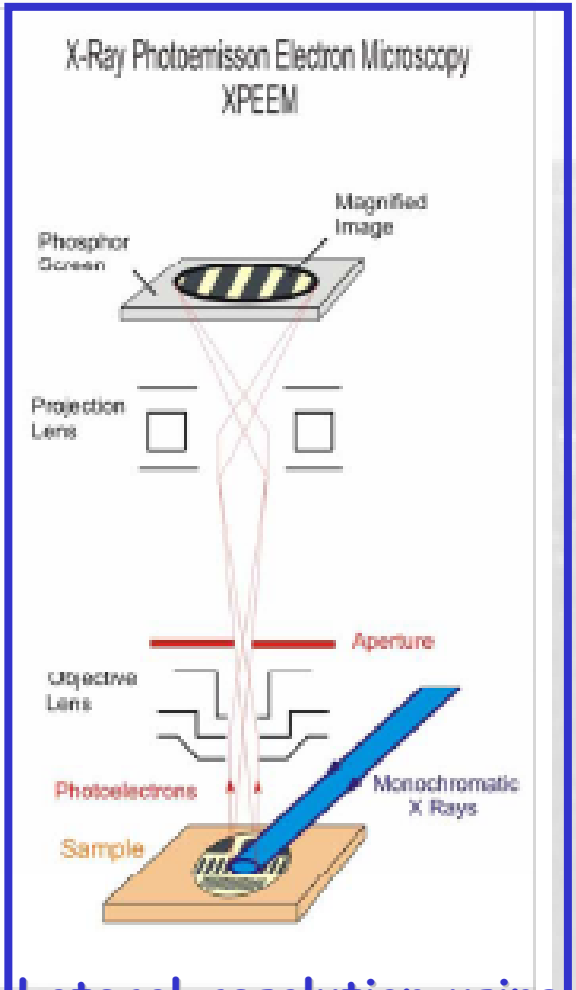
IR



Types of X-ray microscopes using x-rays

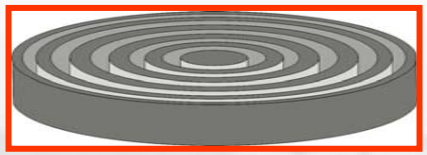


Lateral resolution provided by photon optics

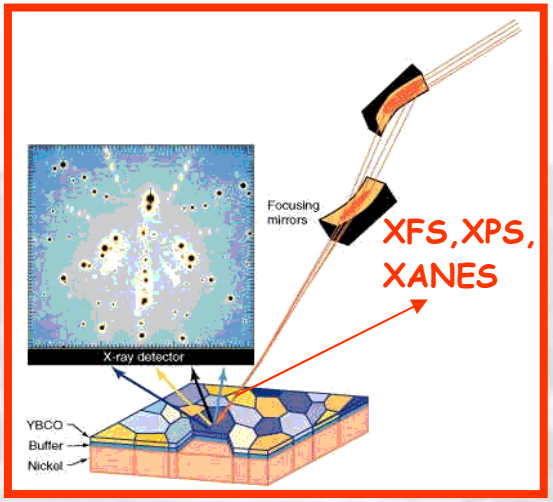


Lateral resolution using electron optics

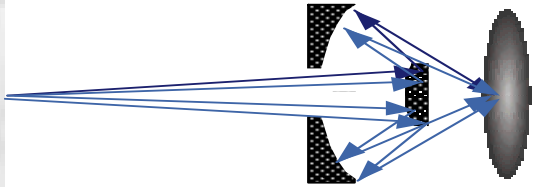
Focusing optics: zone plates, mirrors, capillaries



Zone Plate optics: from ~ 200 to ~ 10000 eV
Resolution: 25 nm in transmission

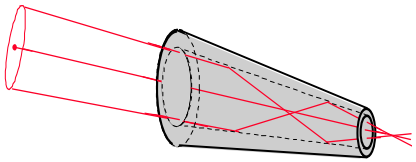


KP-B mirrors each focusing in one direction: soft & hard: ~ 1000 nm
Soft & hard x-rays!
chromatic focal point, easy energy tunability, comfortable working distance
Resolution ≤ 1000 nm



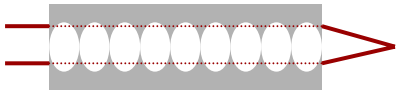
Normal incidence: spherical mirrors with multilayer interference coating (Schwarzschild Objective)
not tunable, E < 100 eV
Resolution: best ~ 100 nm

Capillary: multiple reflection concentrator



Hard x-rays ~ 8-18 keV
Resolution: > 3000 nm

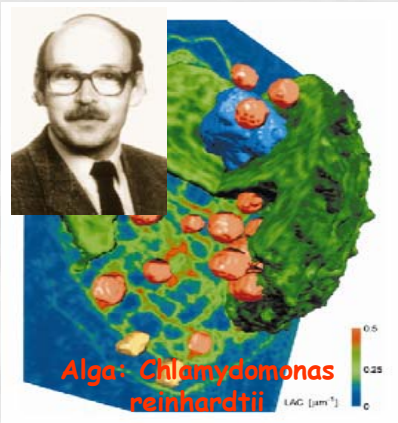
Refractive lenses

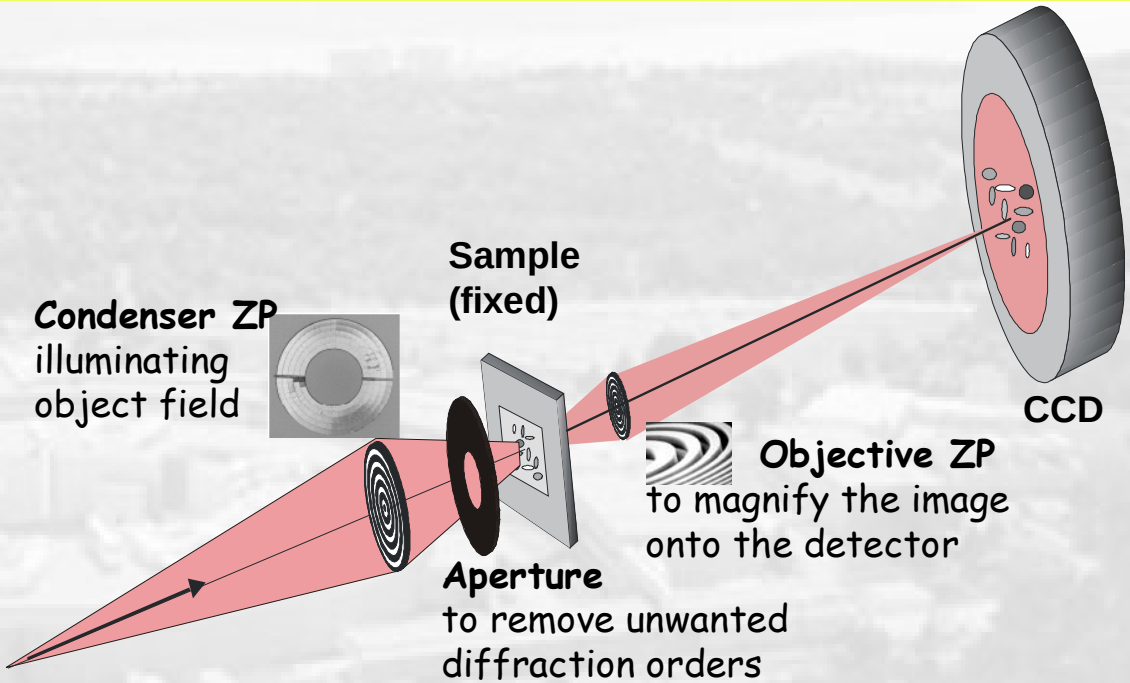


Hard x-rays ~ 4-70 keV
Resolution: > 1000 nm

Imaging x-ray transmission microscope (TXM)

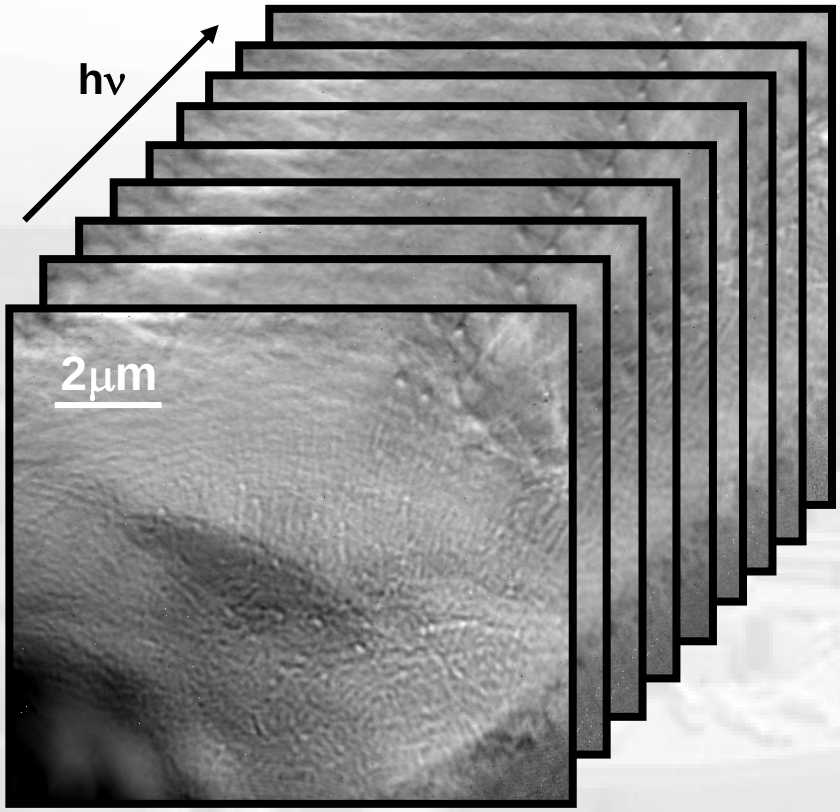
History: 1st experiments at DESY, 1976
Uni Göttingen, Günther Schmahl & Co
The first operating XTM – 1979 ACO, 1983 - BESSY I.





2006 - XTM (7+4): - ALS (2), APS (2), BESSY II (1), ELETTRA (1), ESRF (1), ASTRID (1), SPRING'8 (1), AURORA (1), DIAMOND (1),SOLEIL (1), ALBA (1), SLS (1). Resolution achieved 25 nm.

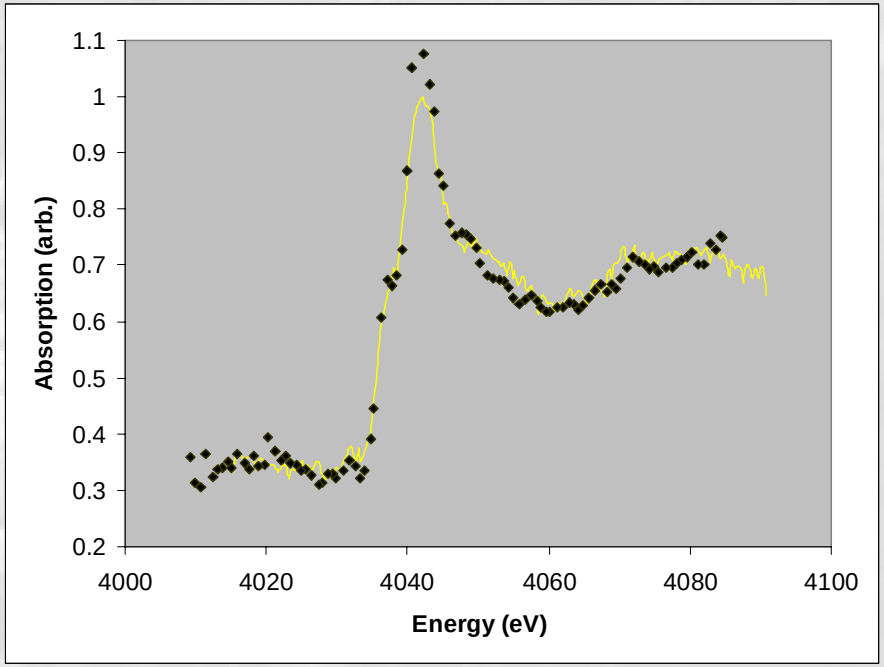
Spectro-microscopy with FFIM



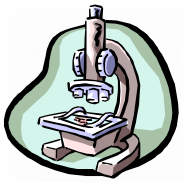
Trabecular bone of a mouse femur sample (10μm thick);
Image field is 27 x 21 μm^2

Study dealing with genetic determinism of immobilization induced bone loss with the FFIM at ID21, ESRF, France

M.Salome et al.



Hydroxy-apatite spectrum recovered from a stack of 200 images



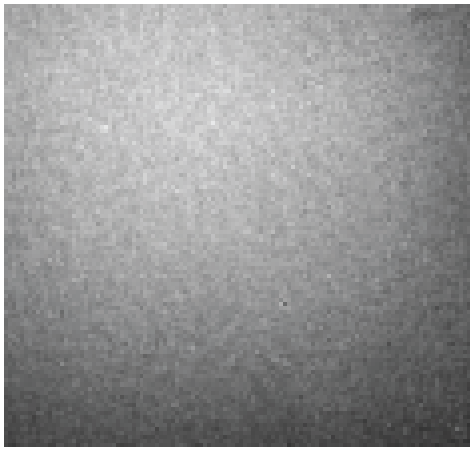
Magnetic imaging (XCMD) with x-ray transmission microscope: domain sizes and spatial distribution

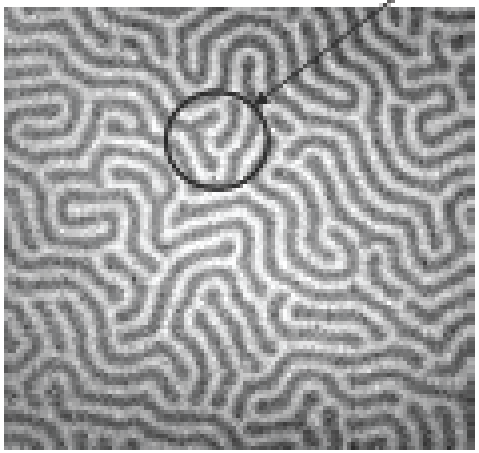
FeGd Multilayer

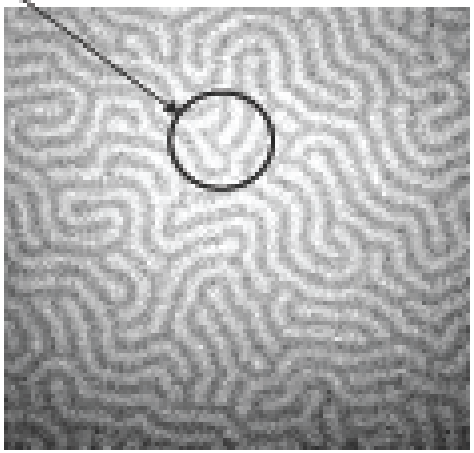
TXM

Contrast reversal

1 μm

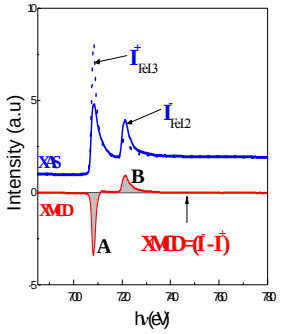






ħω = 704 eV
below Fe L-edges

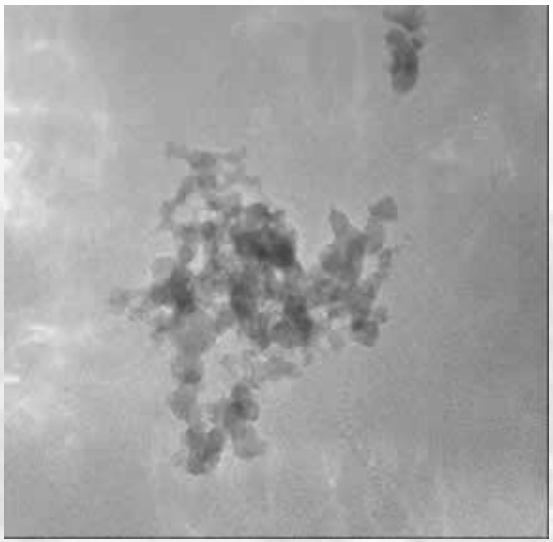
ħω = 707.5 eV
Fe L_3-edge

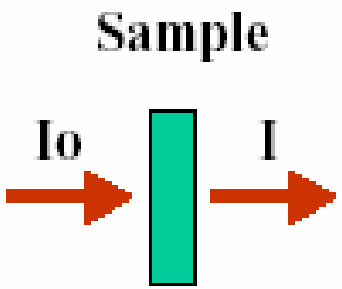


ħω = 720.5 eV
Fe L_2-edge

P. Fischer, T. Einmueller, M. Koehler (U. Wuerzberg)
S. Tsunashima (U. Nagoya) and N. Tagaki (Sanyo)
G. Denbeaux, L. Johnson, A. Pearson (CXRO-LBNL)

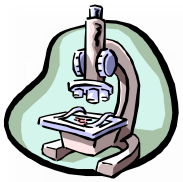
X-ray microscopy and Cell Biology: morphological information





$$= \lambda n\left(\frac{Io}{I}\right)$$

Cell imaging in their natural environment: the cells contain C and N and absorb an order of magnitude more strongly than the surrounding water when using x-rays below the O edge (540 eV, 'water window'). The resulting natural contrast generates unprecedented views of the internal cellular architecture in a natural, albeit frozen, state, information crucial for understanding the cellular function: Tomography!!!

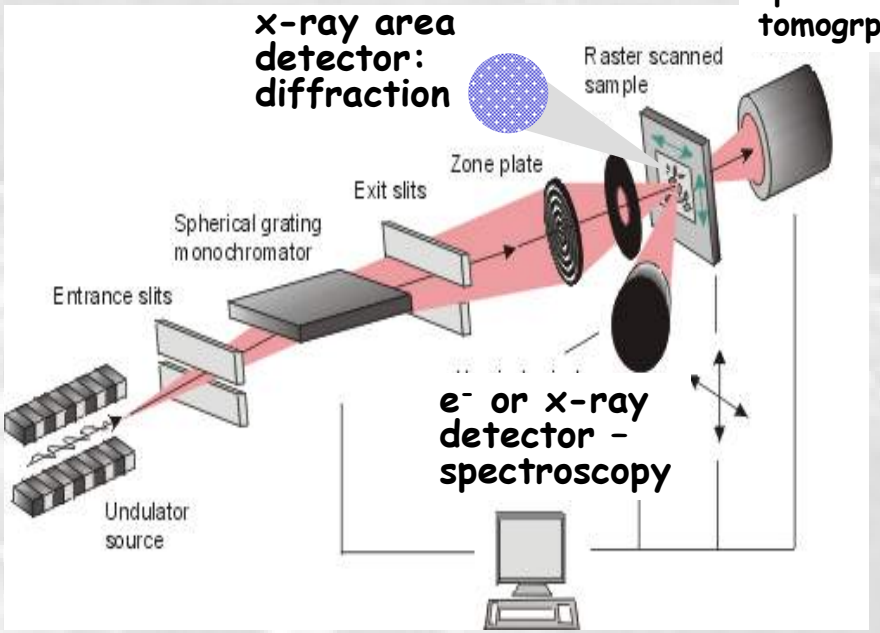


X-ray Scanning microscopy: uses focusing x-ray optics (preferred zone plates)

History: 1st experiments with lab source and at SSR late 1970s

NSLS-Stony Brook: Janos Kirz & Co.

The first operating STXM - 1983, SPEM – 1990.

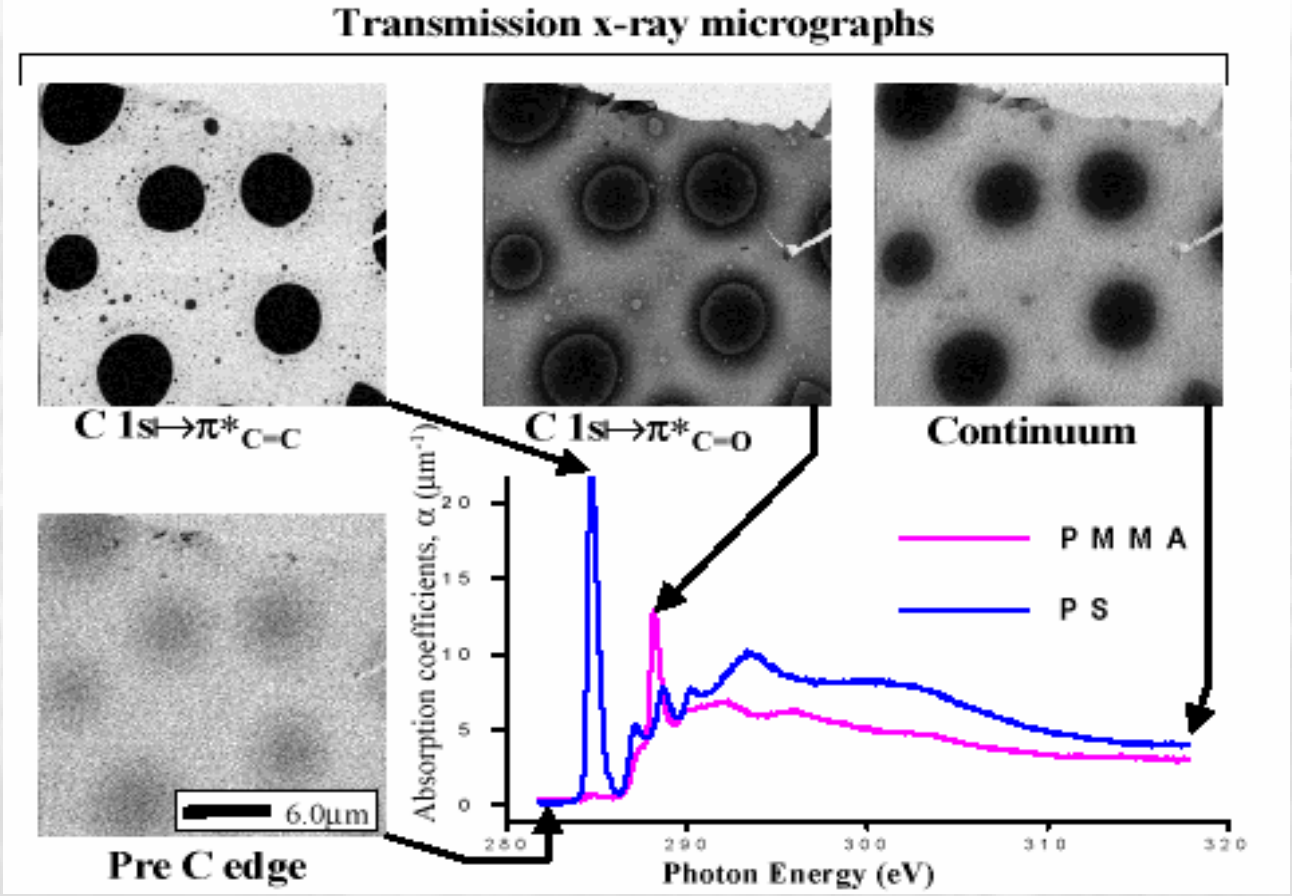


2008 - STXM and/or SPEM (17): - ALS (3), APS (2), BESSY2 (1), ELETTRA (3), ESRF (1), PLS (1), NSLS (1), SLS (1), SPRING'8 (1), SRRC (1), CLS (1), DIAMOND (1), Soleil (1) Resolution achieved 25 nm.

XANES imaging and spectroscopy with STXM

Polymer science: outlining the lateral distribution of PS/ PMMA using the XANES fingerprints

STXM

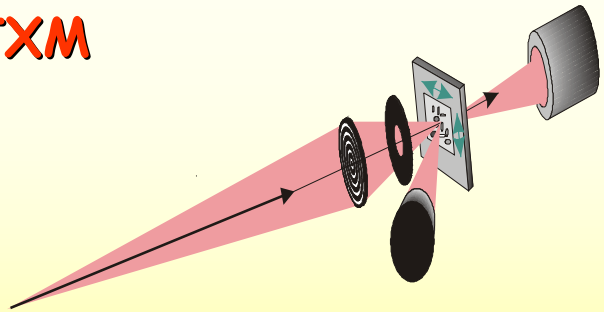


H. Ade et al, STXM at NSLS

Transmission Microscopes

scanning & full-field imaging

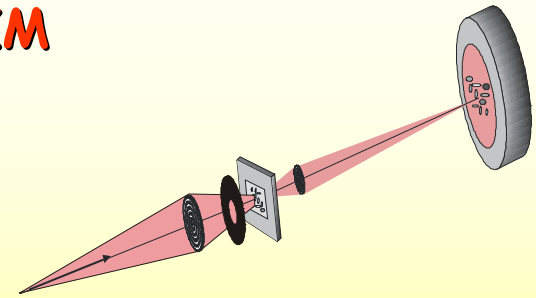
STXM



+ versatile detectors can run simultaneously;
+ easier optics set-up;
- long exposure time;
- complex electronics.

Ideal for spectromicroscopy

TXM

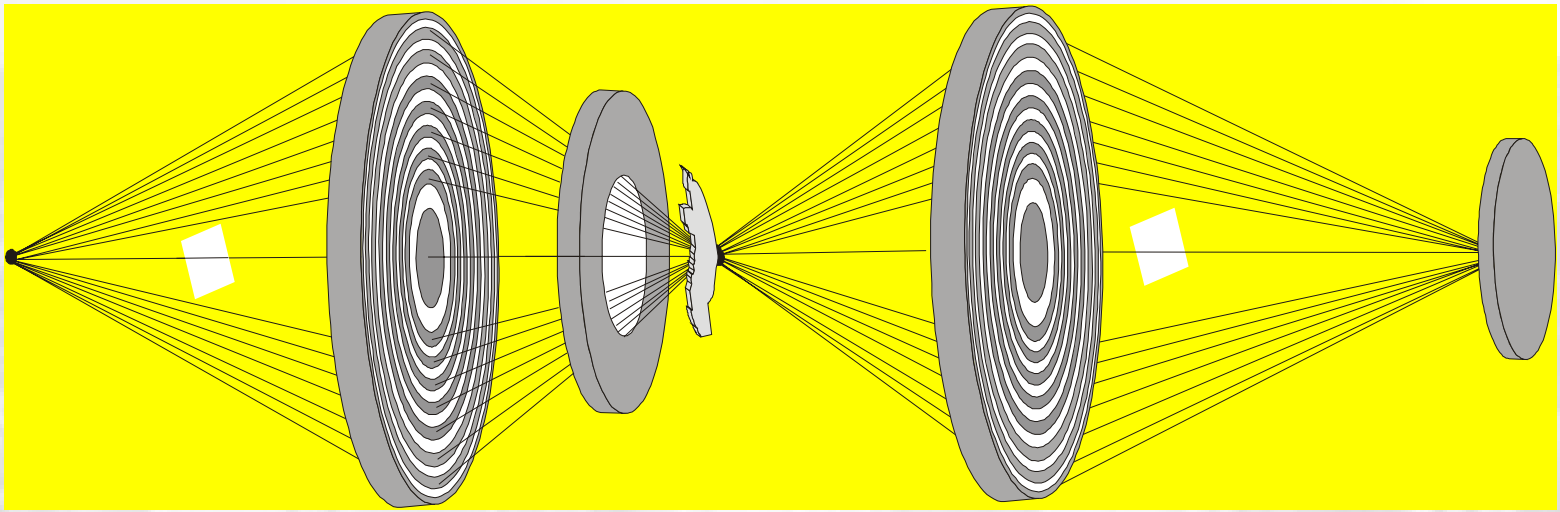


+ short exposure time;
+ higher resolution - static system;
- complex optical alignment.

Ideal for dynamic studies and tomography

Transmission microscopes are hv-in/hv-out instruments

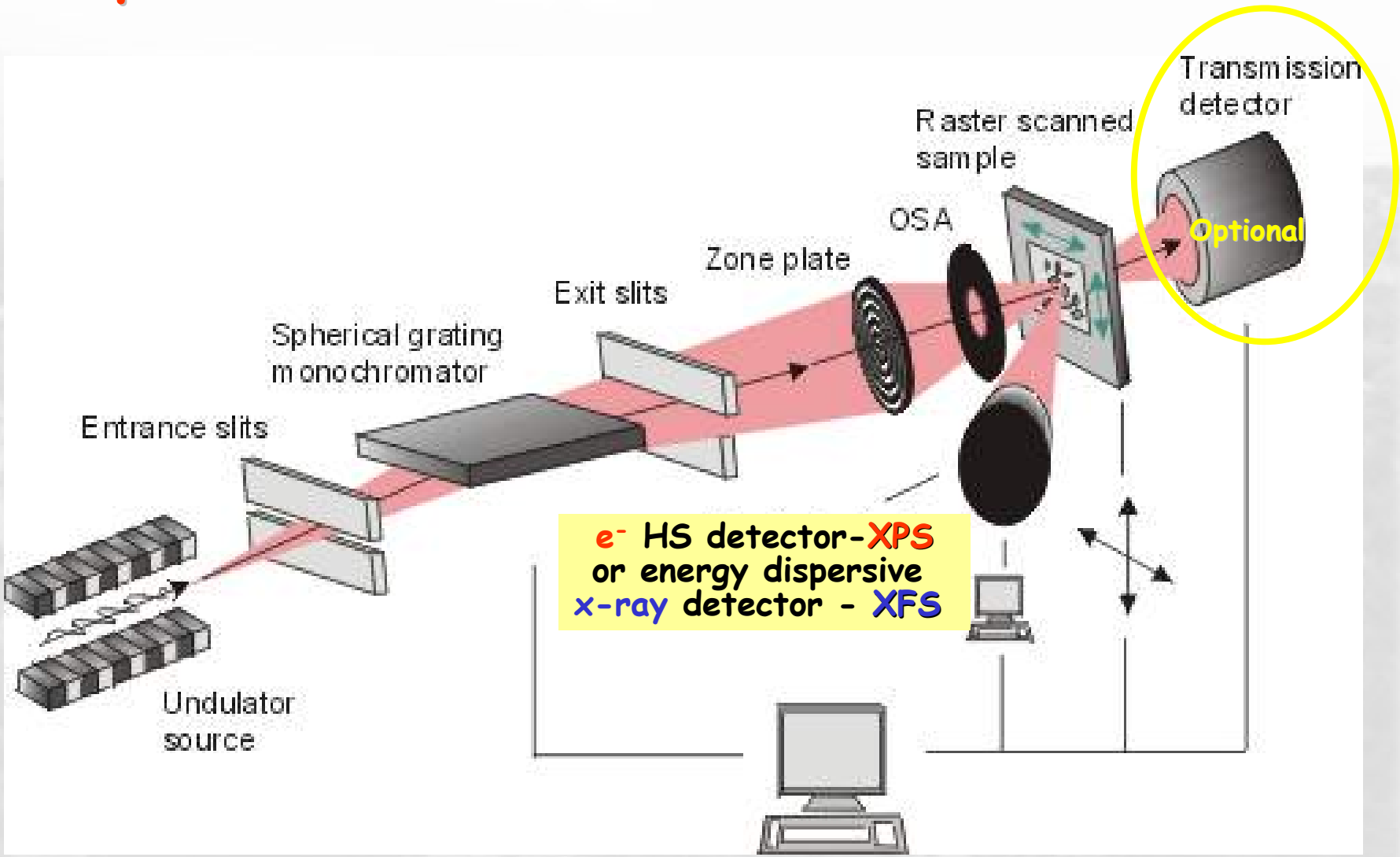
Transmission Microscopes
scanning & full-field imaging



EU-"TwinMic" at ELETTRA (Kaulich et al)

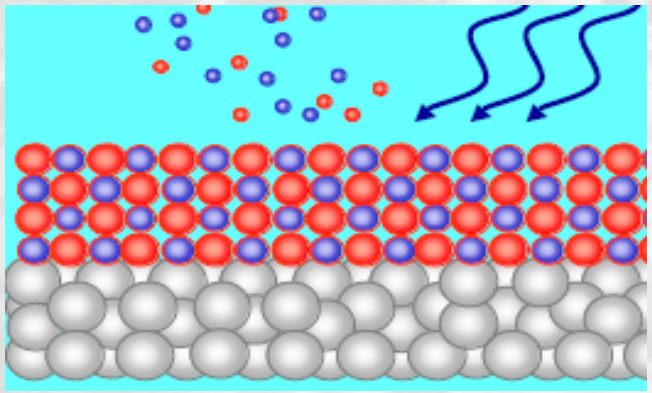
Versatile instrument for dynamic studies, 3D imaging and spectroscopy: with easy switch between two microscopy modes

Scanning photoemission microscopy: photoelectron, fluorescence and XANES

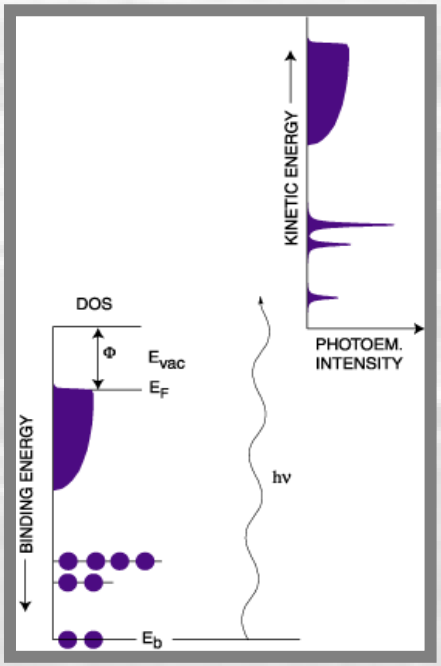


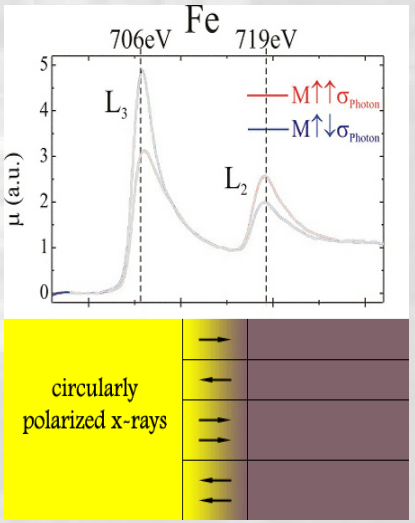
What does photon-induced electron emission provide

- Qualitative and quantitative elemental information: CL
- Chemical composition and chemical bonding:CL & VB
- Electronic and magnetic structure (VB, ARUPS, PED, XMCD-XMLD with secondary electrons (XANES).
- Information depth < 10 nm (surface sensitive)

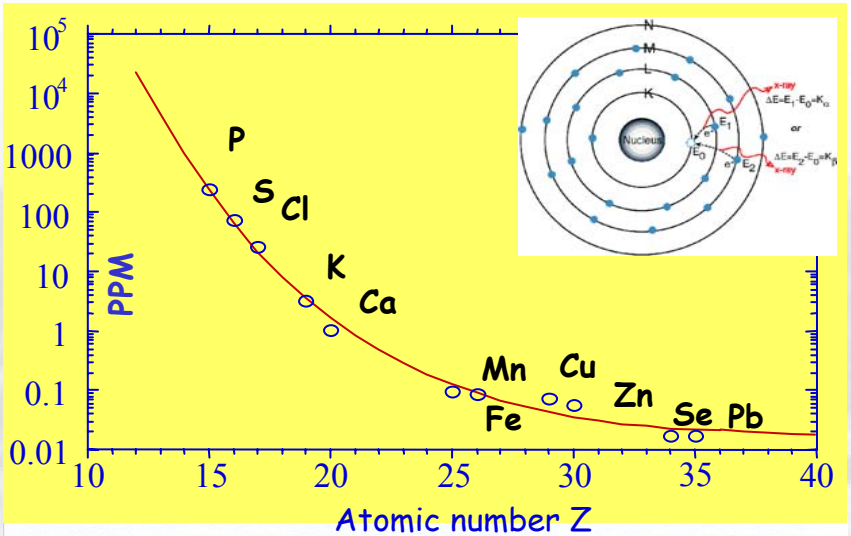


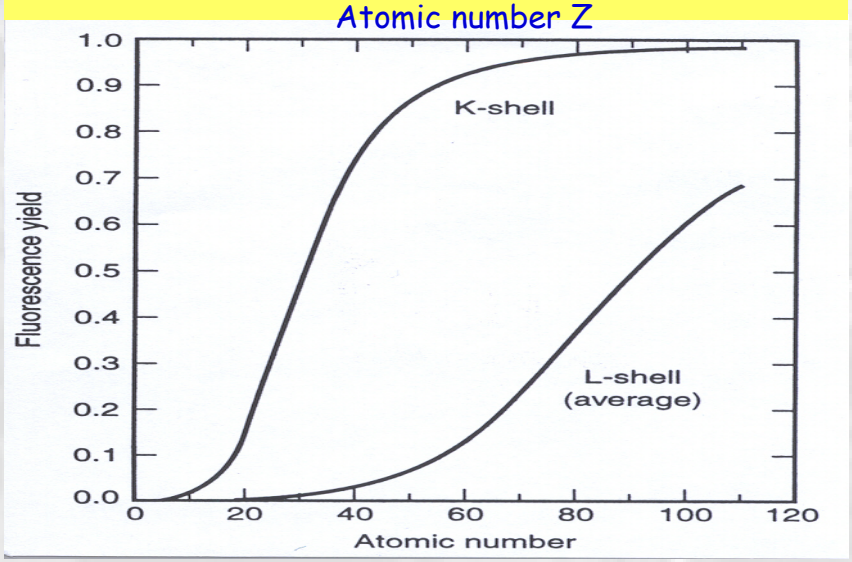
Information depth = dsinθ
d = Escape depth ~ 3 λ
θ = Emission angle relative to surface
λ = Inelastic Mean Free Path





Hard X-ray Microscopy: lower spatial resolution but X-ray fluorescence





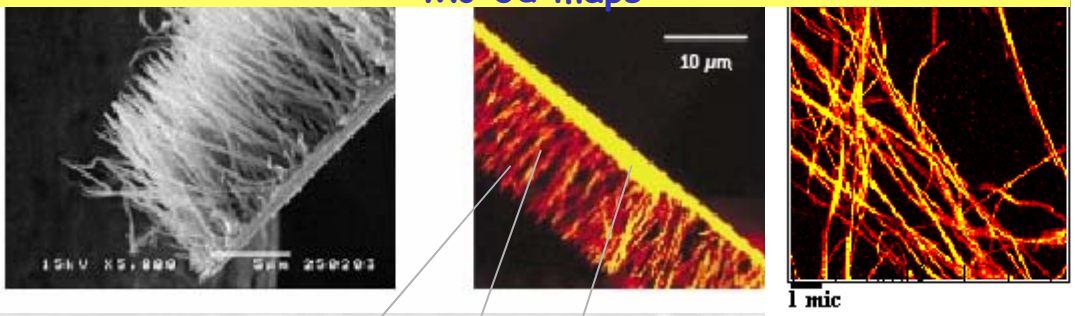
- Penetration depth: > 50μm
- Fluorescence yield.
- All type of samples
- μ-XANES (S, P, K, Ca, Fe..)

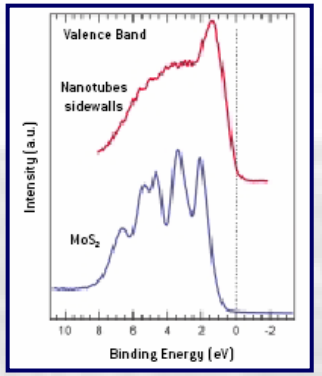
XRF (Scanning + energy/wavelength dispersive detection)

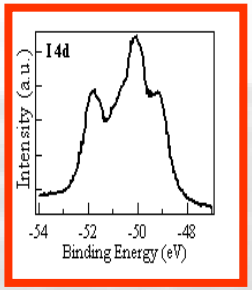
- Element specific (no labelling)
- Co-localisation
- Low detection limit (trace element).
- High signal-to-background ratio (low dose)

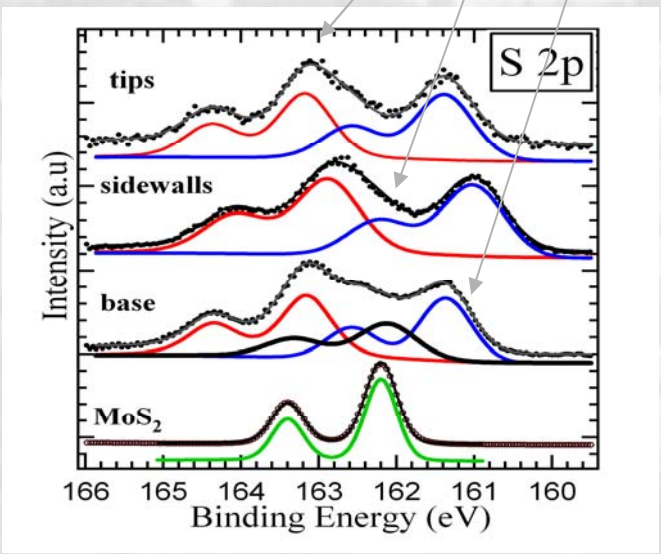
SPEM characterization of MoS_2-nanotubes

Twisted chiral bundles of Mo-S individual cylinders: Mo 3d maps









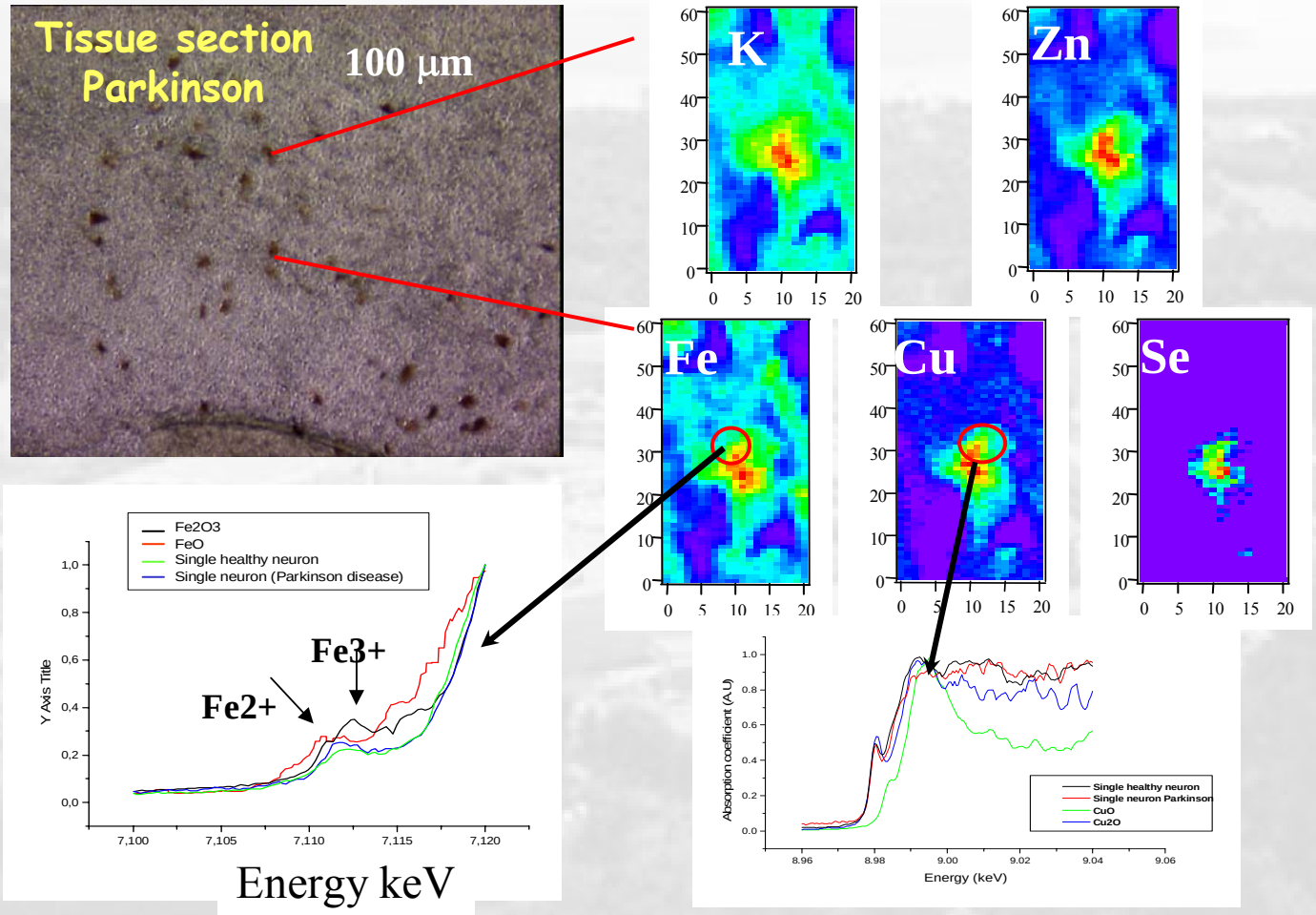
SPEM revealed I (used as a carrier) in interstitial positions between the tubes bonded to the outer S atoms.

Due to the low dimensionality the S 2p, Mo 3d and VB spectra are position-dependent and reflect electronic properties significantly different those of the MoS_2 crystal.

J. Kovac, A. Zalar, M. Remaskar et al, Elettra highlights, 2003

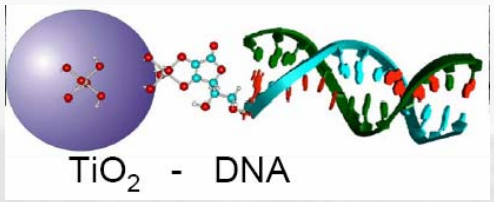
μ-XANES of single neuron:

role of metals in processes leading to degeneration and atrophy of nerve cells in Parkinson's disease (PD) & Amyotrophic Lateral Sclerosis (ALS)



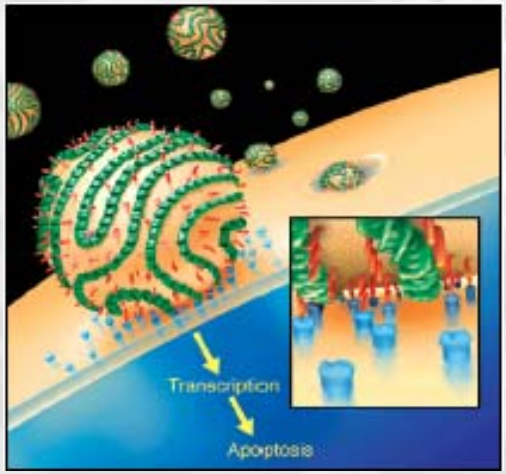
Courtesy J. Susini, ESRF

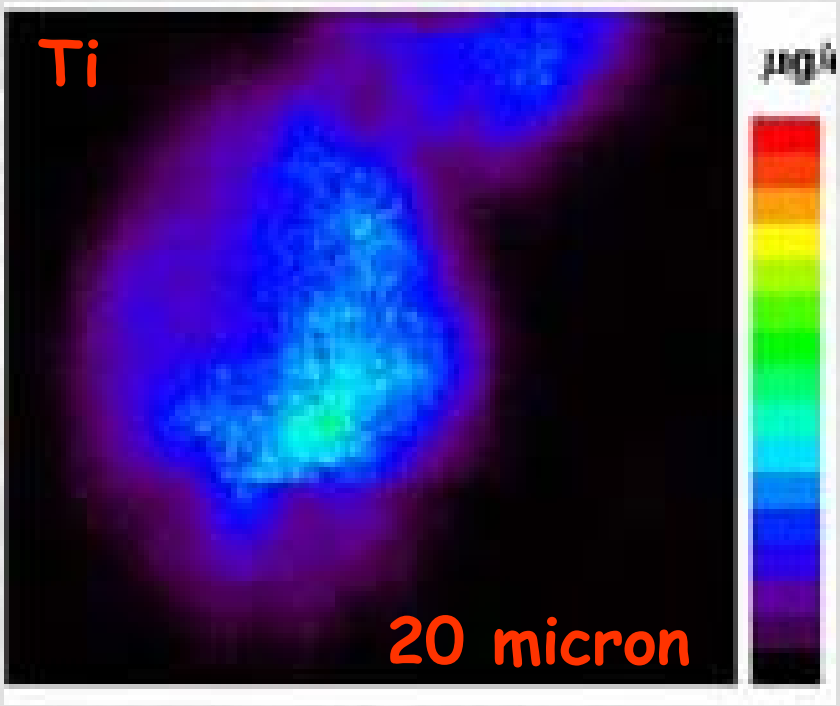
TiO2-DNA nano-composites for in-vivo Gene Surgery: XRF maps



Chemical FS imaging is crucial to quantify the success rate and reveal the location of the single stranded nanoparticle in the cell chromosome

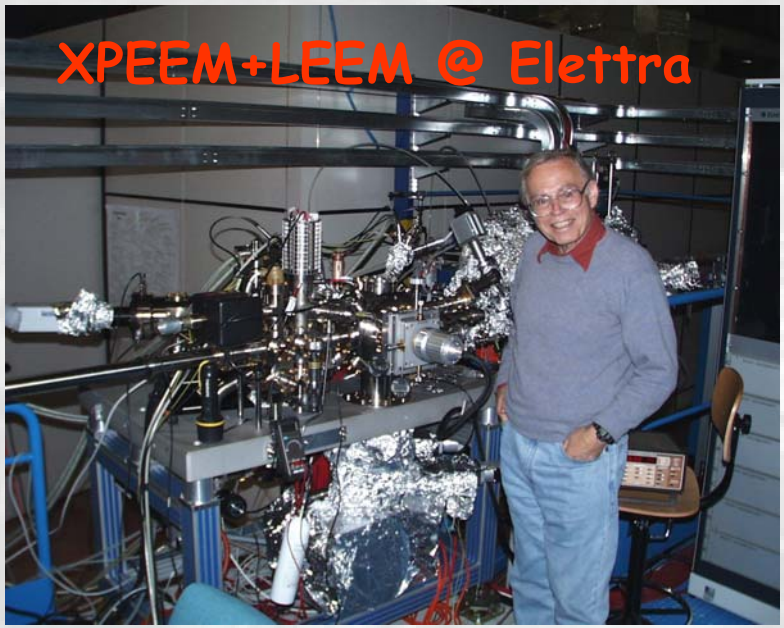
DNA-TiO2 particle crossing cell walls

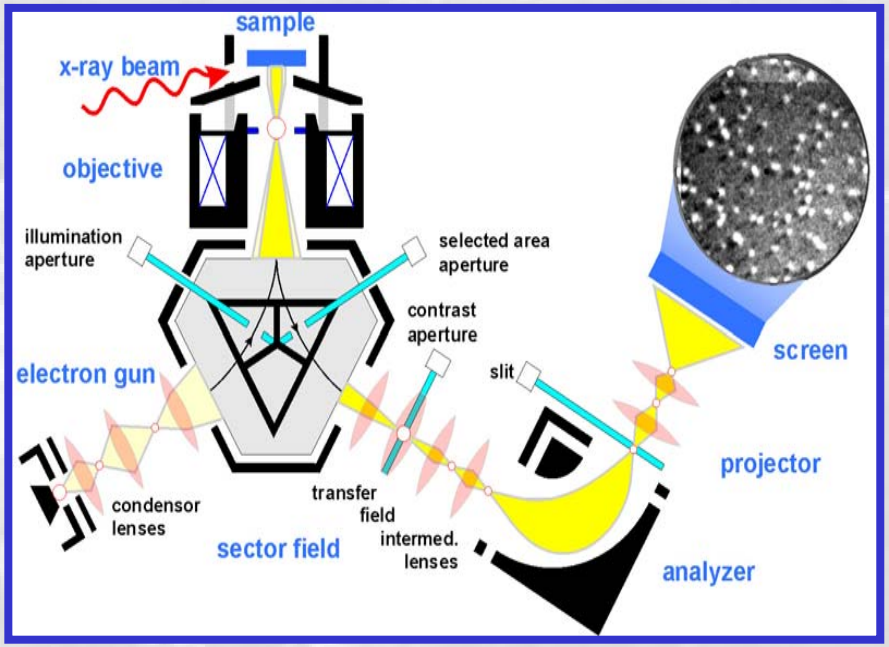




X-ray Imaging PhotoEmission Electron Microscopy (XPEEM) (+ LEEM)

History: PEEM-early 1930s, XPEEM late 1980s
Ernst Bauer (Uni Claustal), W. Engel (FHI-Berlin).B. Tonner (SRC)
The 1st XPEEM with energy analyser (XPS&XAS) – early 1990s

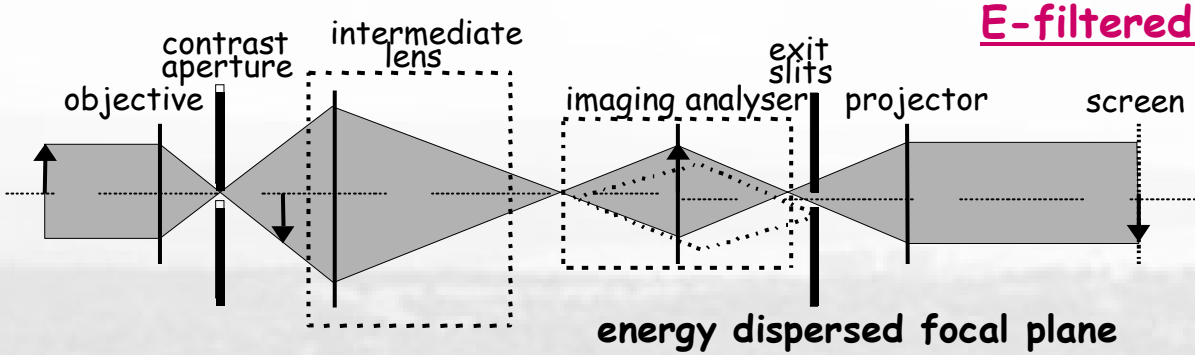


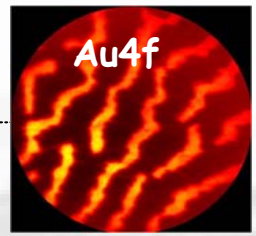


2006- XPEEM (19): – ALS(2), APS(1), BESSY II(2*), ELETTRA (1*), NSLS (1*), PLS(1), SPRING'8 (2), SLS (1*), SRRC (1), SRS(1), MAXLab (1*), CLS (1*), SOLEIL(1*), DIAMOND (1*), APS (1), Alba (1). Resolution achieved 20 nm.

PEEM-LEEM with energy filter: imaging modes

E-filtered Imaging:LEEM-XPEEM





Res. <10-20 nm

Imaging Dispersive plane Spectroscopy

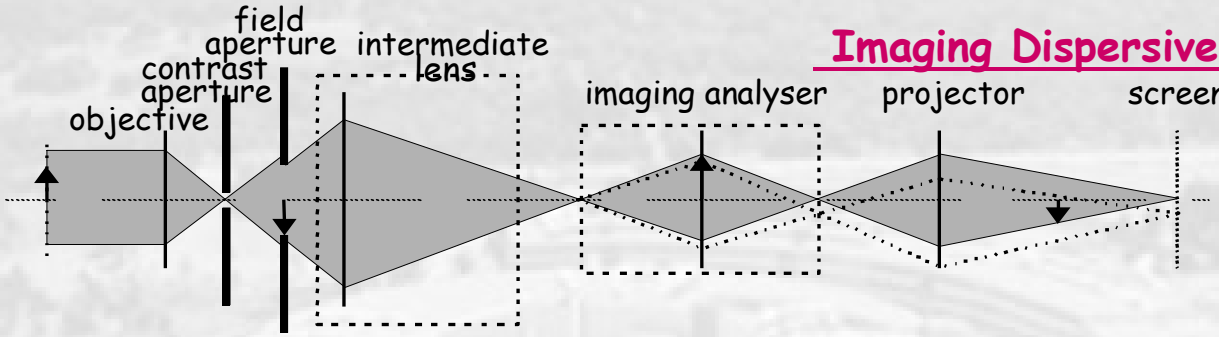
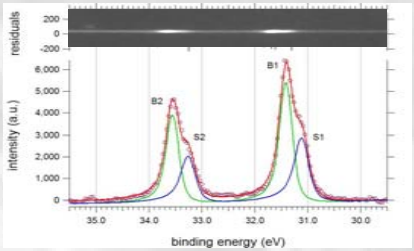
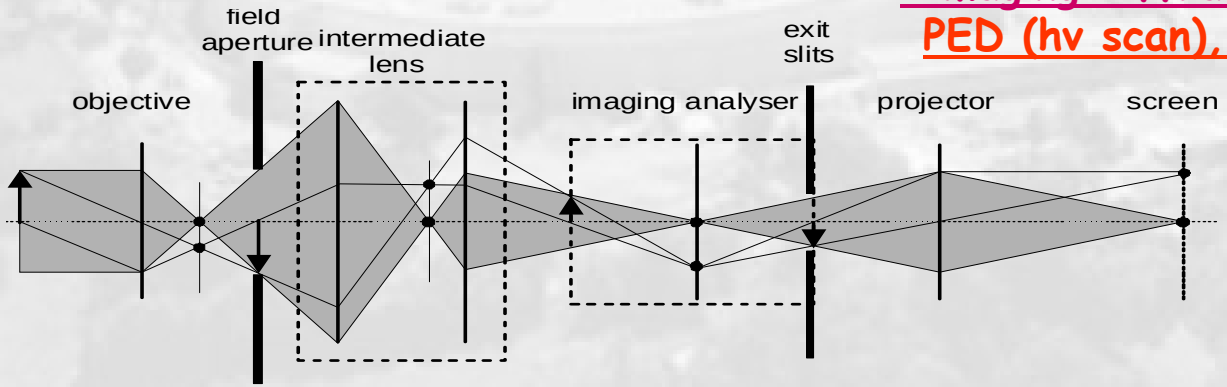


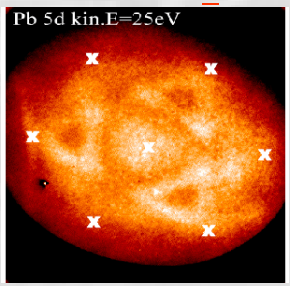
image energy dispersion



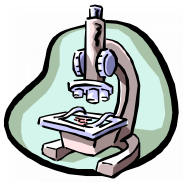
Res. 0.5-1 μm

Imaging diffraction plane: LEED, PED (hv scan), ARUPS (E_k scan)





T. Schmidt et al, Surf. Rev. Lett. 5, 1287, S. Günther et al Prog. Surf. Sci. 70 (2002) 187.



X-ray SPECTRO-microscopy and imaging

soft (< 1500 eV) *hard (2-20 keV)*

SURFACES & INTERFACES:
PHOTON IN/ELECTRON OUT
(probing depth=f(E_{el}) max ~ 20 nm)

BULK SAMPLES
PHOTON IN/PHOTON OUT
(probing depth = f (E_{ph}) > 1000 nm)

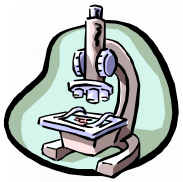
PE spectroscopy (XPS-AES)
ONLY CONDUCTIVE SAMPLES
Chemical surface sensitivity:
Quantitative μ-XPS (0.01 ML)
chemical & electronic (VB) structure

X-ray Fluorescence spectroscopy (XFS)
Chemical bulk sensitivity
Quantitative μ-XFS
Trace element mapping
(ppm 0.01/Pb - 200/S)

Total e^- yield
(sample current)

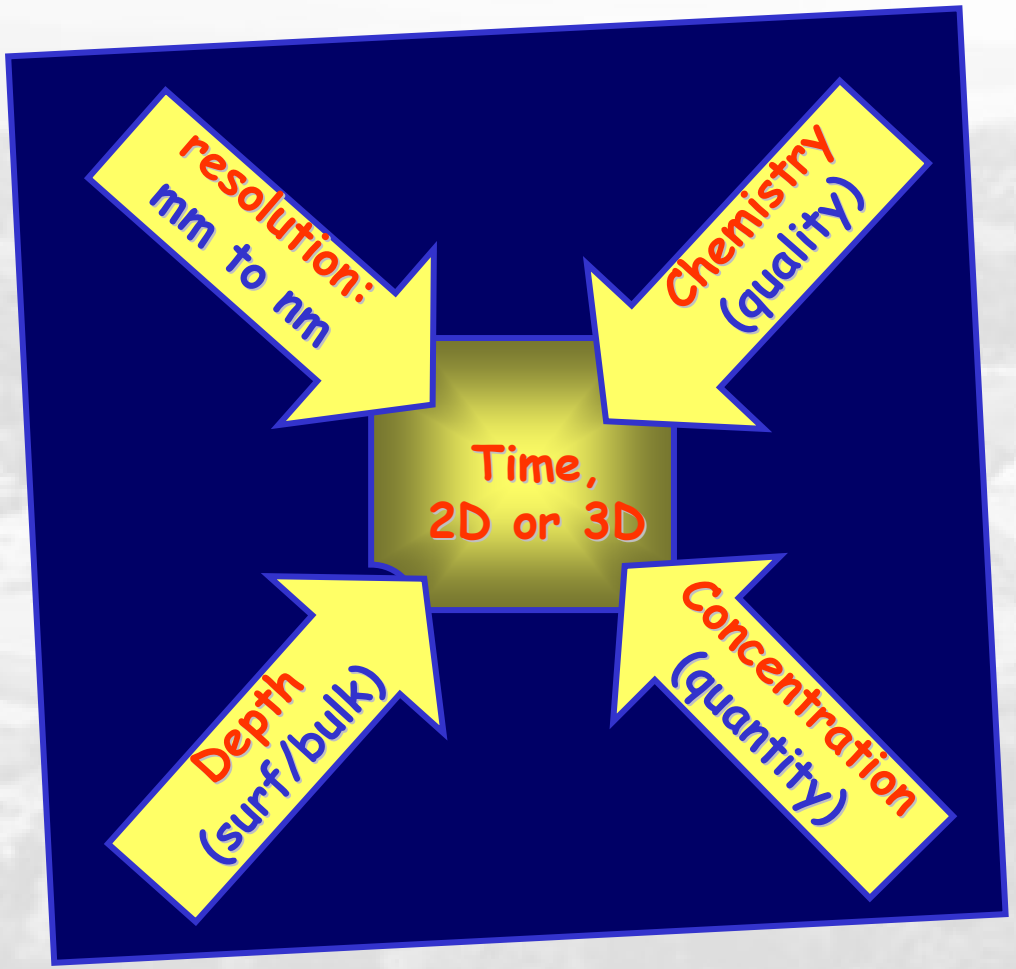
Absorption spectroscopy XANES
Transmitted x-rays

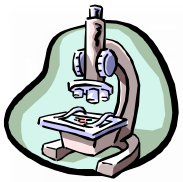
Total hν yield



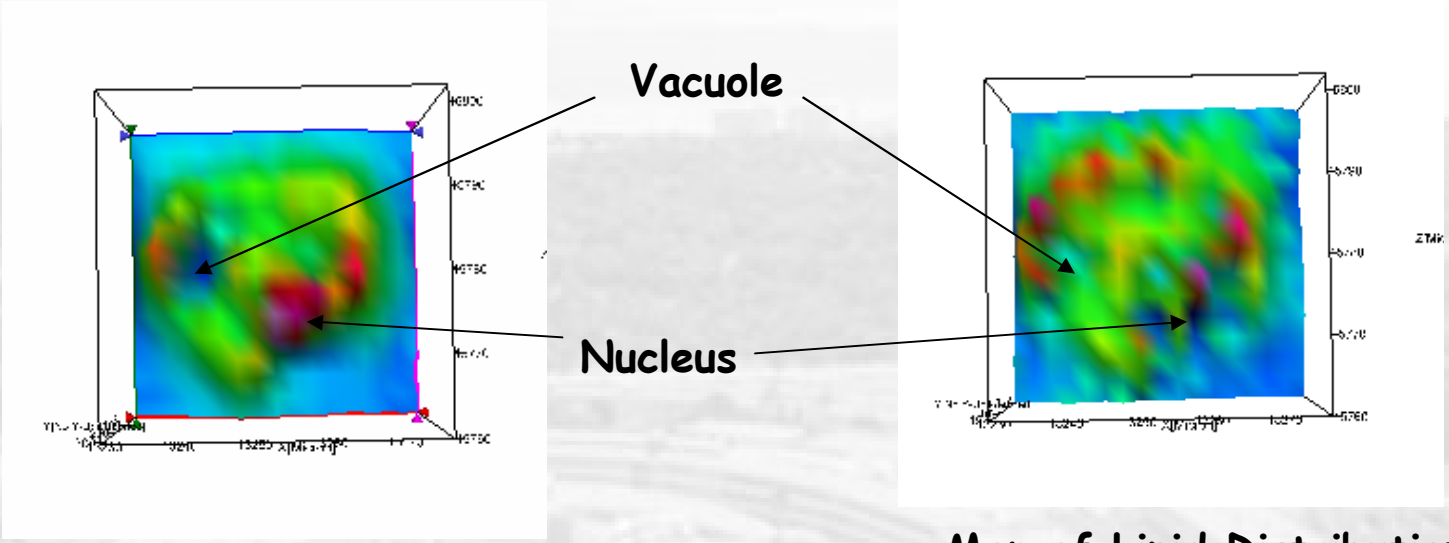
X-ray SPECTRO-microscopy and imaging

soft (< 1500 eV) *hard (2-20 keV)*





High-resolution IR Mapping of Single Cells



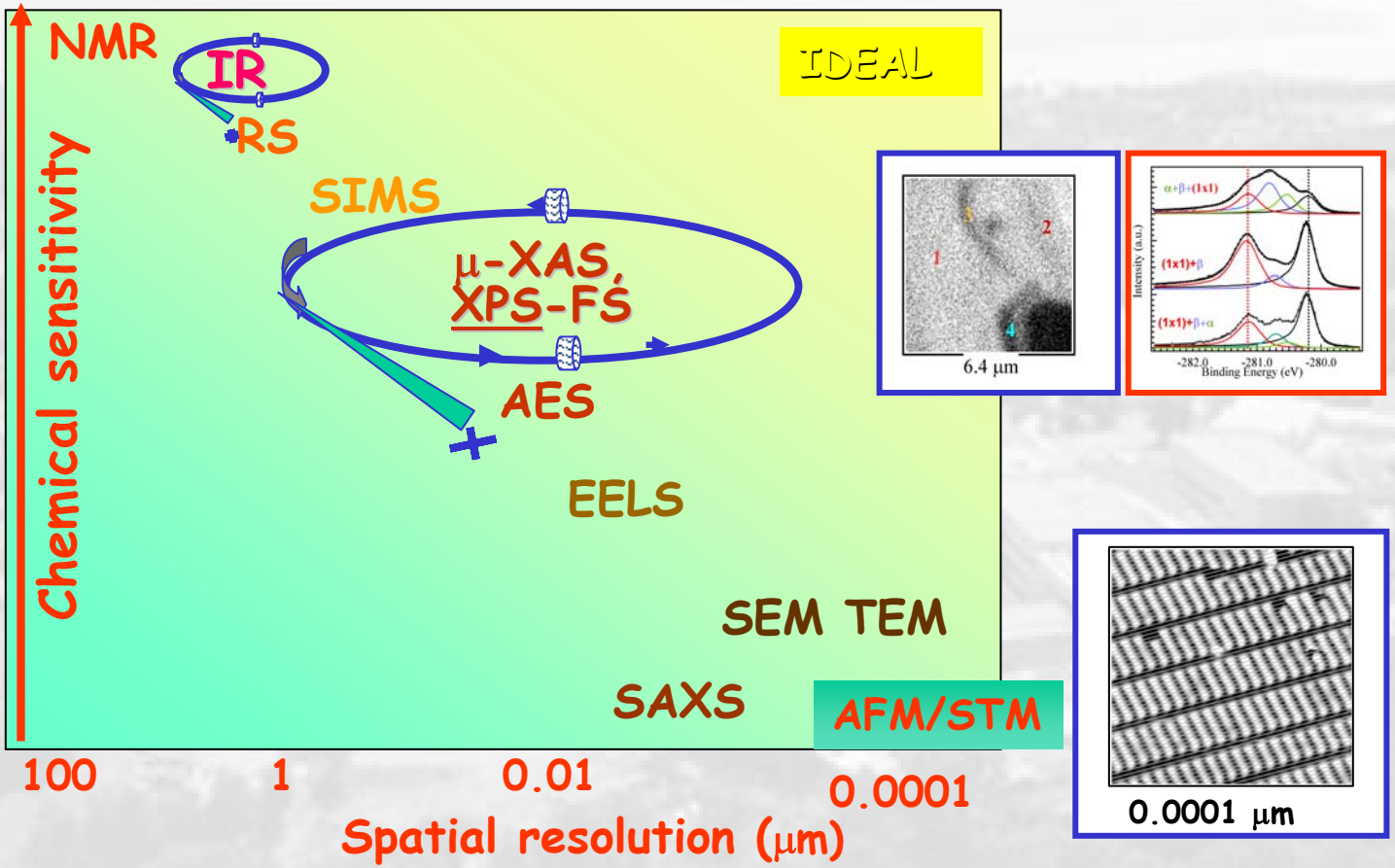
Map of Hydroxyl groups (water, sugars and nucleic acids)

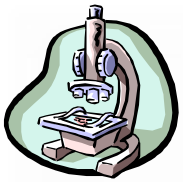
Map of Lipid Distribution

Aperture: 3 μm x 3 μm, SISSI@Elettra

Formalin Fixed Cells, Quaroni & Burrone et al ICGEB

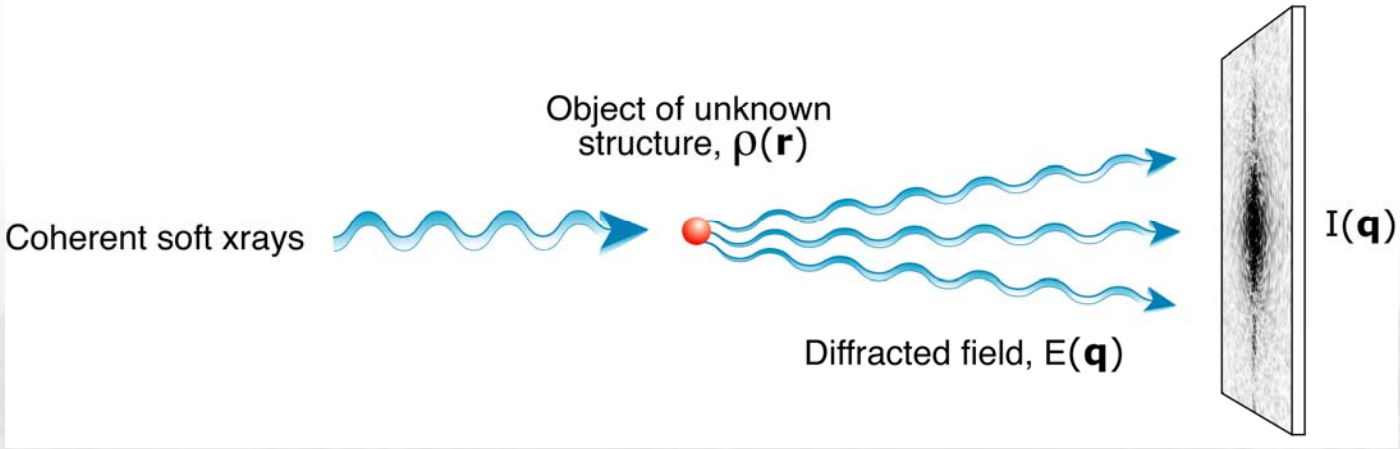
Chemical specificity and resolution using SR





Exploiting the coherence = 'Flash' imaging

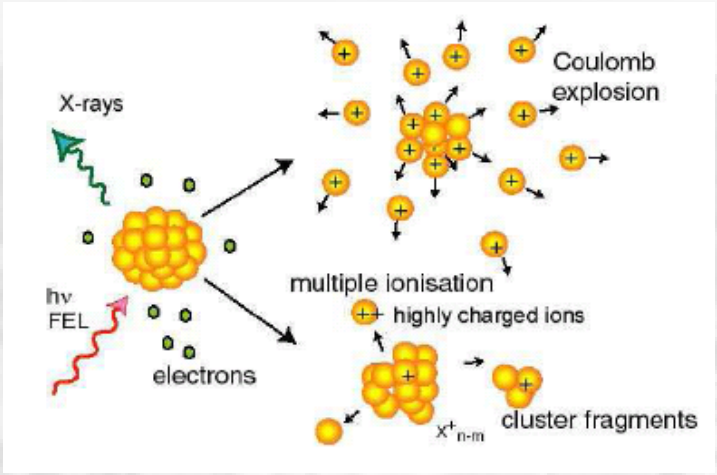
elettra

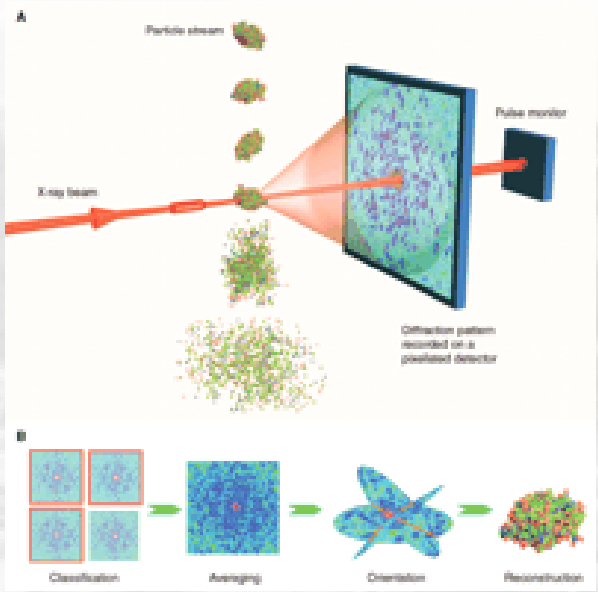


- **Diffraction pattern can be recorded with no optics-imposed resolution limits:** scattered amplitude is Fourier transform of (complex) electron density f(**r**): $F(\mathbf{k}) = \int f(\mathbf{r})\, e^{-2\pi i\, \mathbf{k}\cdot\mathbf{r}}\, d\mathbf{r}$
- J. Miao, D. Sayre & H. N. Chapman, *J. Opt. Soc. Am. A* 15, 1662.
- **Phase information retrieved by iterative algorithms applied to oversampled diffraction pattern, or through a mask-based holographically formed interference pattern.**

- Avoids ~100x signal loss of lenses and can go beyond numerical aperture limit of available optics?
- Challenge: algorithms for reconstruction of the holography patterns

Time scales for 'non-destructive' imaging: get information in one shot!

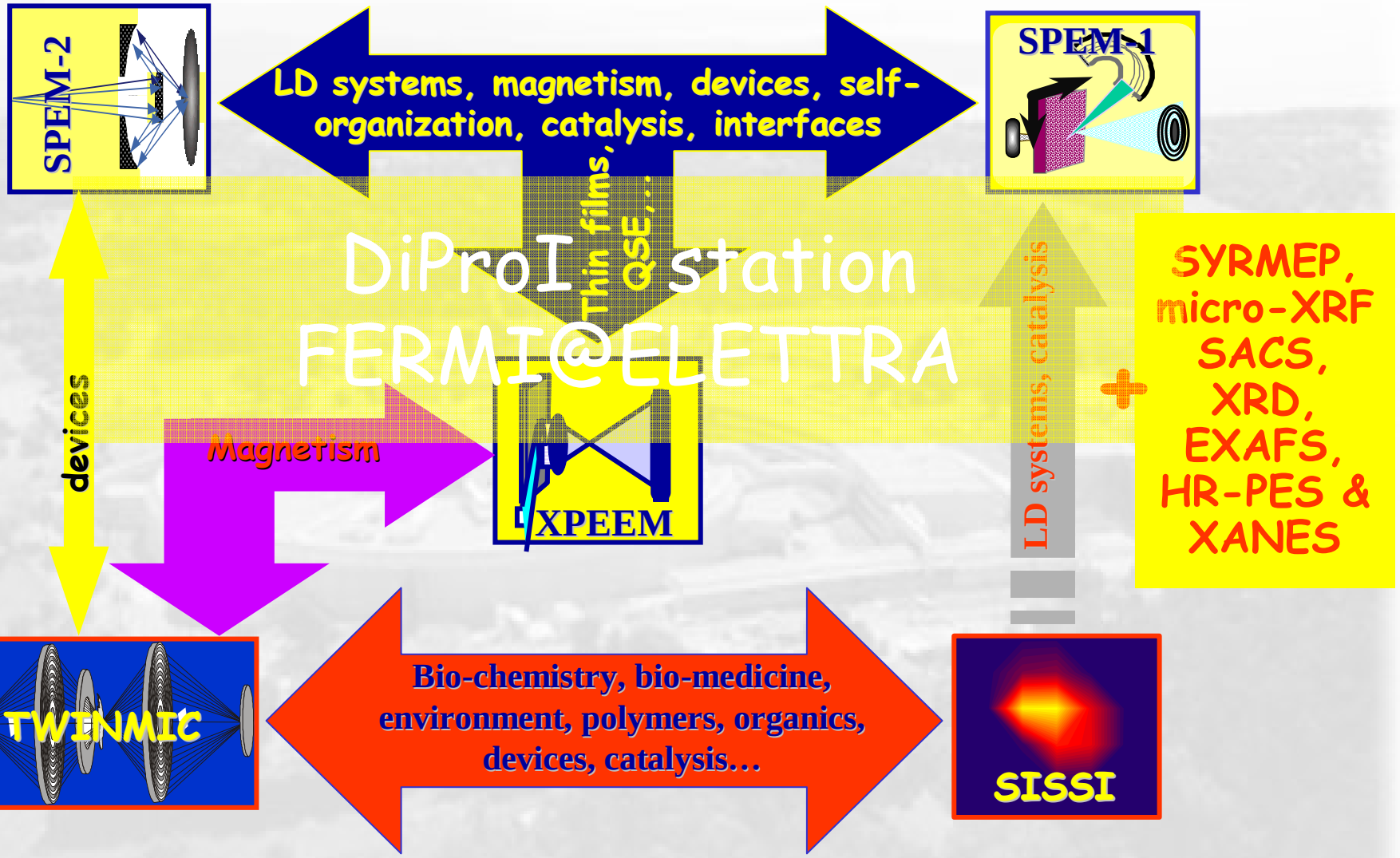




N.Neutze, et al , *Nature* 400, 752-757 (2000).

⇒ With an X-FEL of pulse length < 50 fs and 3 x 10^{12} photons focused down to a spot of ~ 0.1 μm, a 2D diffraction pattern could be recorded from a biomolecule before the radiation damage manifests itself.

At present Elettra has one of the most expanded microscopy programs in Europe allowing complementary research



Enjoy forthcoming Lectures