X-ray Microscopy and Spectroscopy

at Synchrotron Light Sources

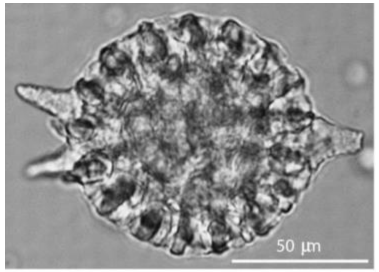
Emma-Elizabeth Cating-Subramanian, Postdoctoral Researcher, Kapteyn-Murnane group at CU Boulder

Vanessa Schoeppler, Postdoctoral Researcher, Falcone group, UC Berkeley and Advanced Light Source (LBNL)

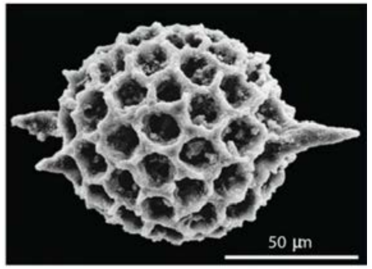
Last Months Tutorial: Electron Microscopy

Light microscope

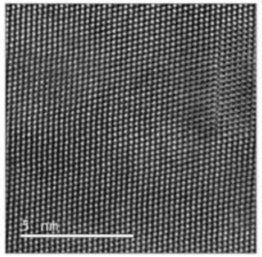
- Uses visible light
- Minimum sample prep
- Inexpensive equipment
- Live or dead samples
- No screen/camera needed
- Resolution ~ 10^{-7}m



(a) Radiolarian under light microscope



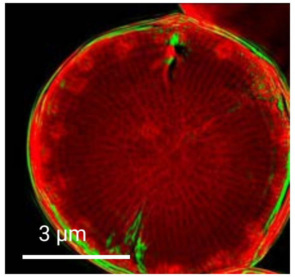
(b) Radiolarian under electron microscope



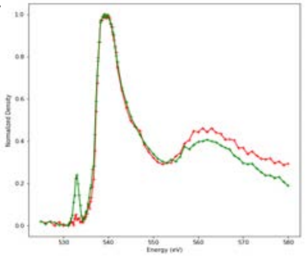
High resolution TEM Pt crystal

Electron microscope

- Uses electrons
- Thin, clean sample
- Expensive, high maintenance
- Dead samples
- Screen/camera is required
- Resolution < 10^{-10} m



Chemical map of a diatom acquired with x-ray spectromicroscopy

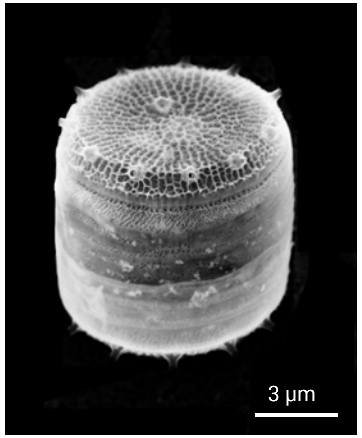


X-rays

- Minimum sample prep
- Do not interact strongly with light elements
- Large field of view
- Average structure atomic structure
- Real-space resolution ~ 10^{-9} m

Electrons

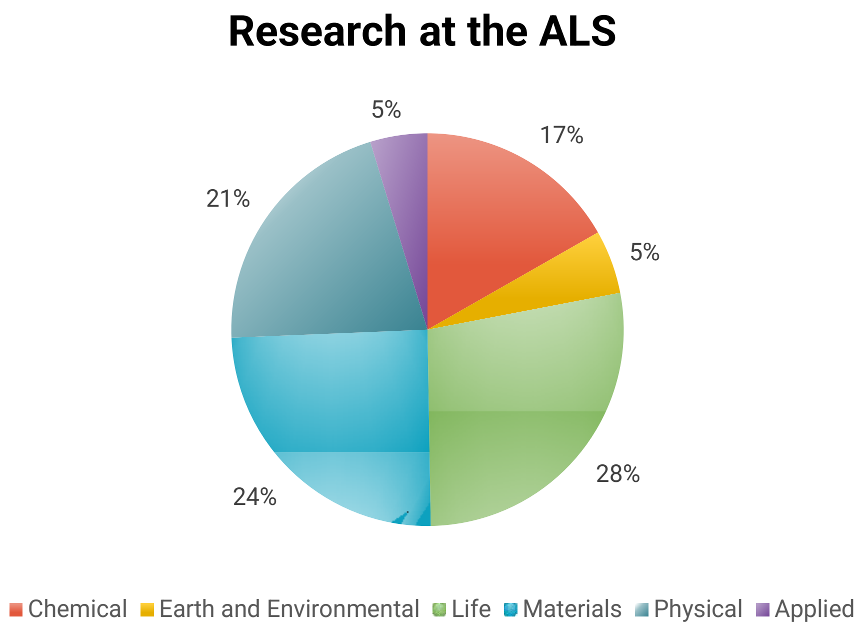
- Sample must be thin, clean
- Interact strongly with light elements
- Small field of view
- Probe local structural changes
- Resolution < 10^{-10} m

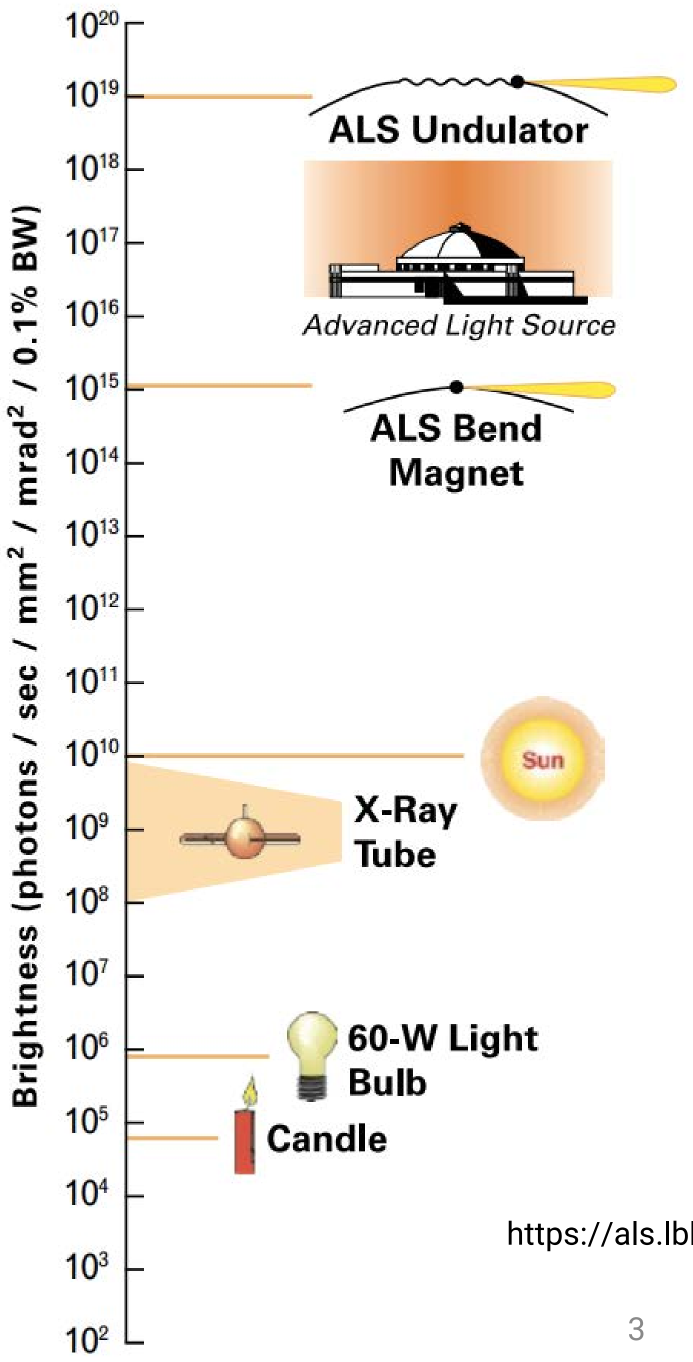


SEM image of a diatom

Synchrotron Facilities

- Circular particle accelerators
- Produce particularly bright x-rays
  - Billion times brighter than the sun
  - Trillion times brighter than medical x-rays
- Interaction of x-rays with materials is used to perform state-of-the-art research in:
  - Biology
  - Chemistry
  - Physics
  - Materials Sciences
  - Energy Sciences
  - Environmental Sciences





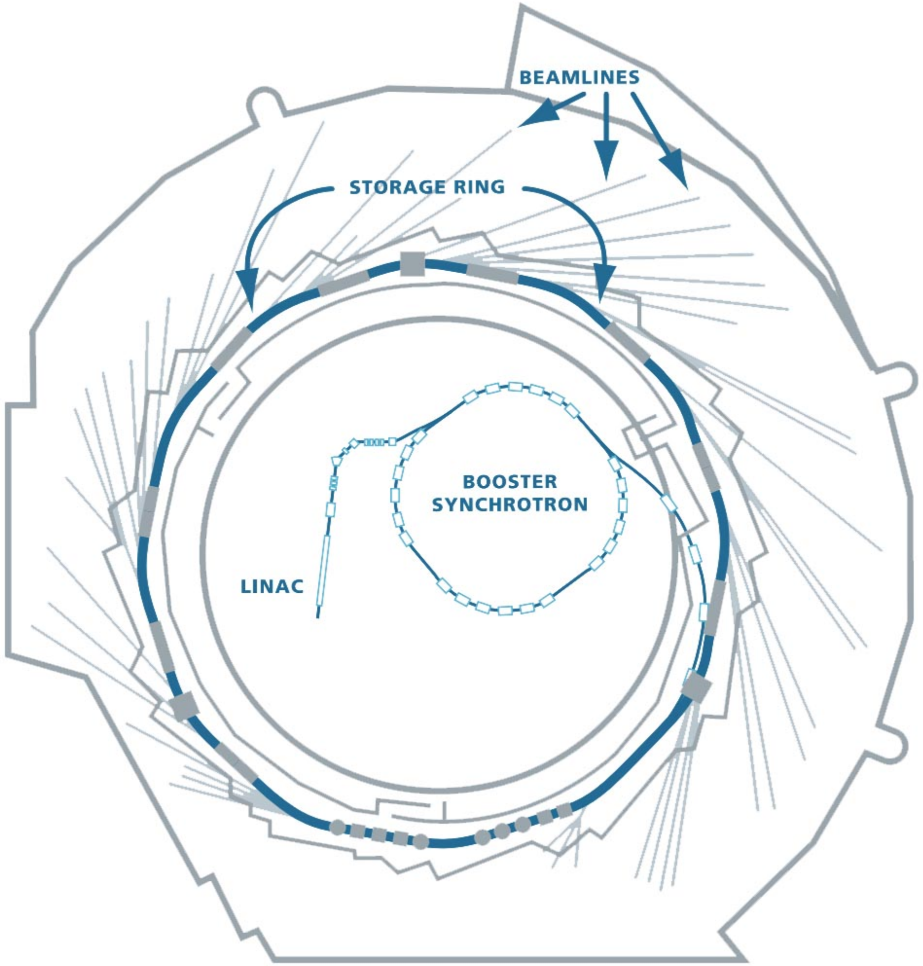
https://als.lbl.gov/

The Synchrotron

When a moving electron changes direction, it emits energy. When the electron is moving fast enough, the emitted energy is at x-ray wavelength.

- **LINAC**: electrons are produced in an electron gun, packed in bunches and accelerated to an energy of 50MeV
- **Booster Ring**: pre-accelerator that increases the speed of the electrons to 1.9 GeV
- **Storage Ring**: hair thin electron beam is stored in a 200 m ring where they travel at 99.99996 % the speed of light – 299,792,447 m/s
- **Beamlines**: the x-ray beams emitted by the electrons are directed toward the "beamlines". Each beamline is designed for use with a specific technique or for a specific type of research.

The Advanced Light Source

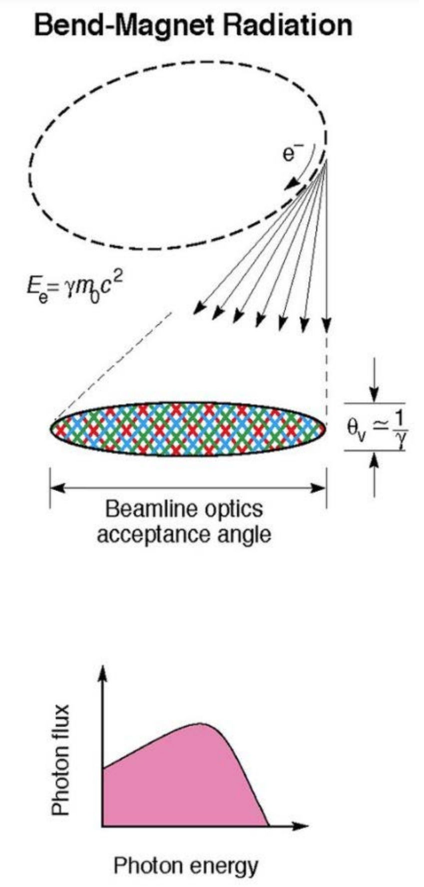


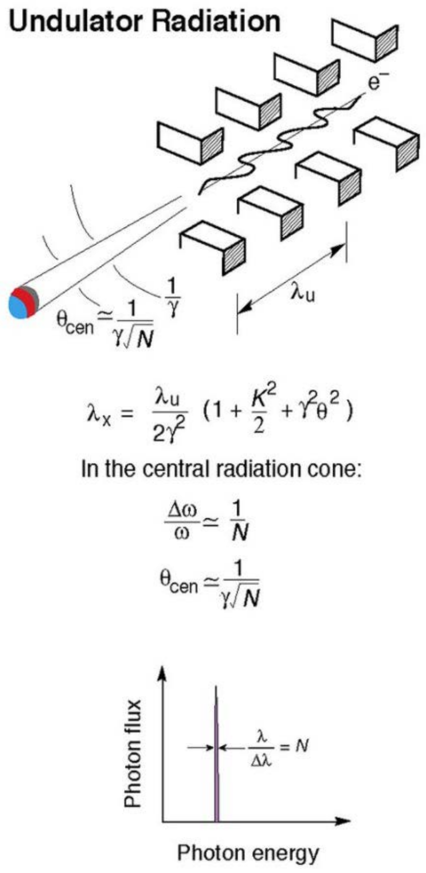
https://als.lbl.gov/

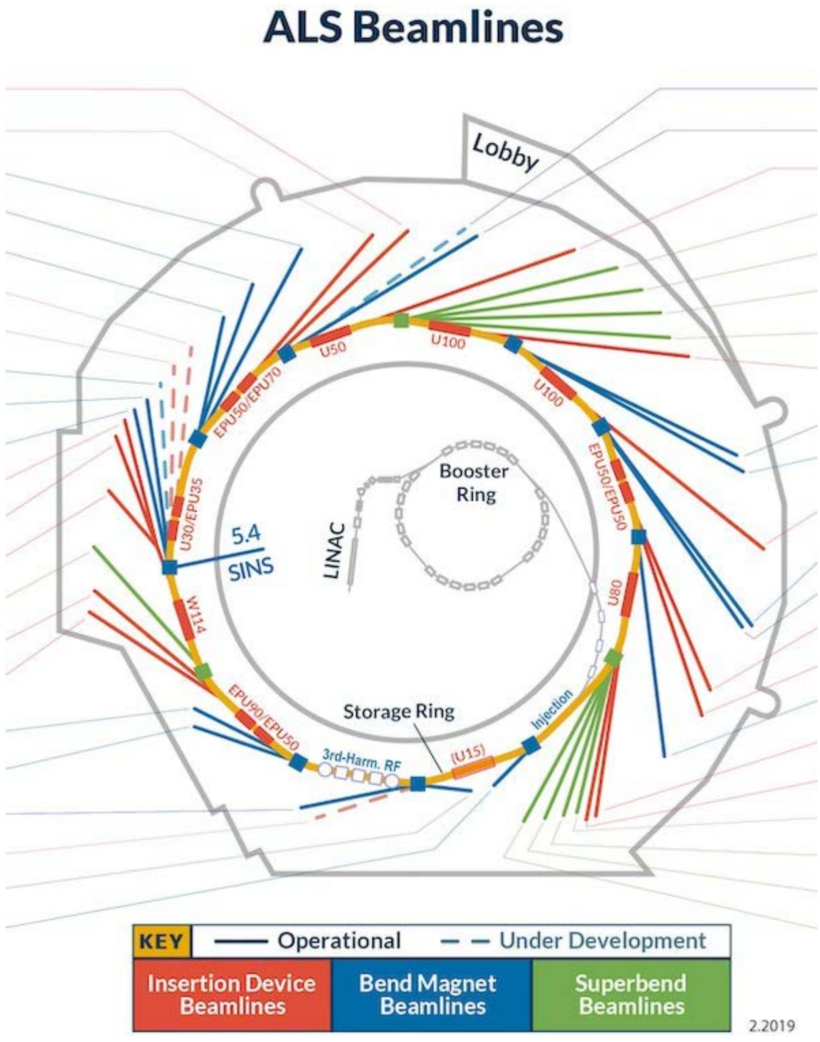
Storage Ring

Linear segments and curved with special magnets

- Bending magnets force the electrons into their orbital path
- Insertion devices create high energy x-rays



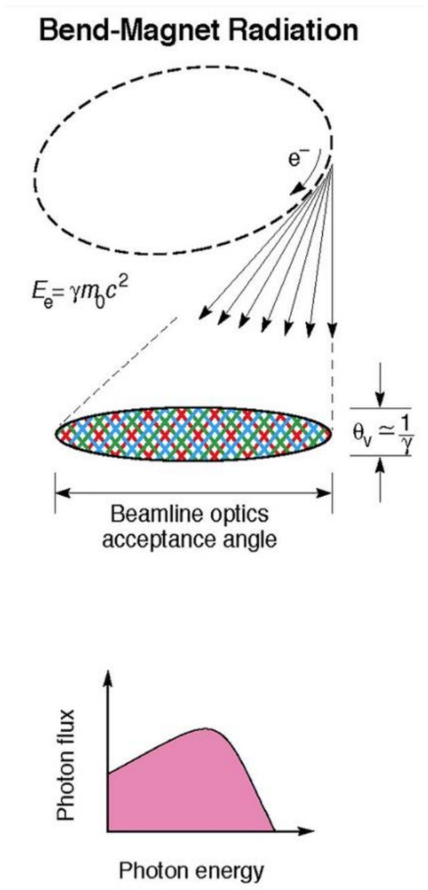


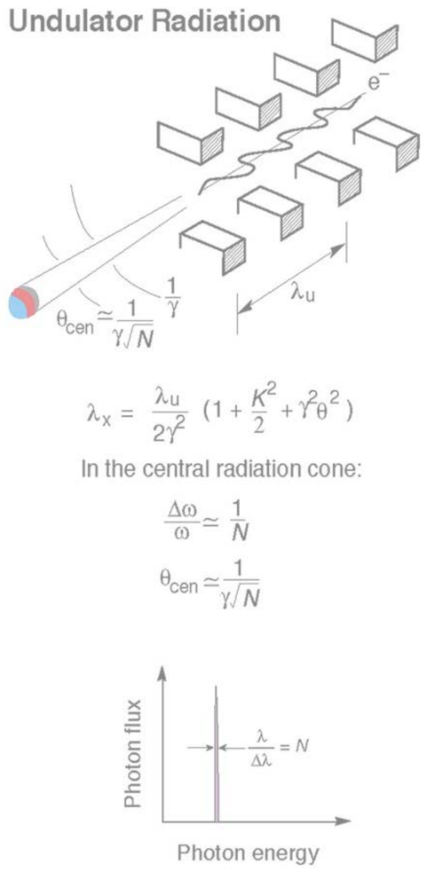


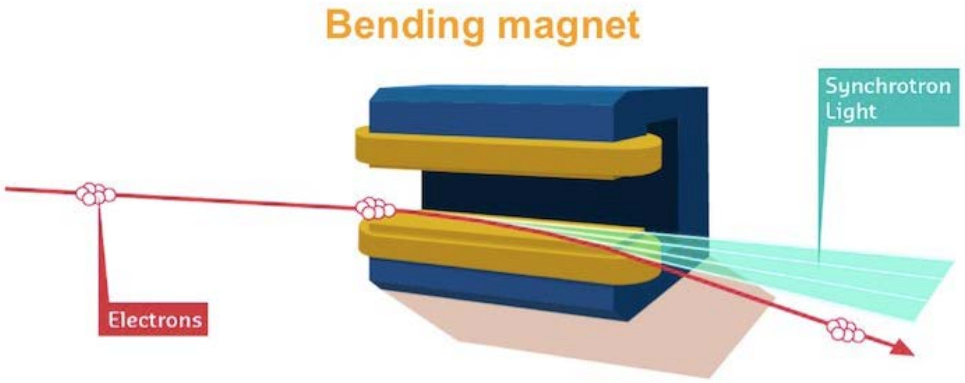
https://als.lbl.gov/

Storage Ring

Bending Magnets: Force electrons into orbital path and emit a spray of x-rays tangentially to the plane of the electron beam





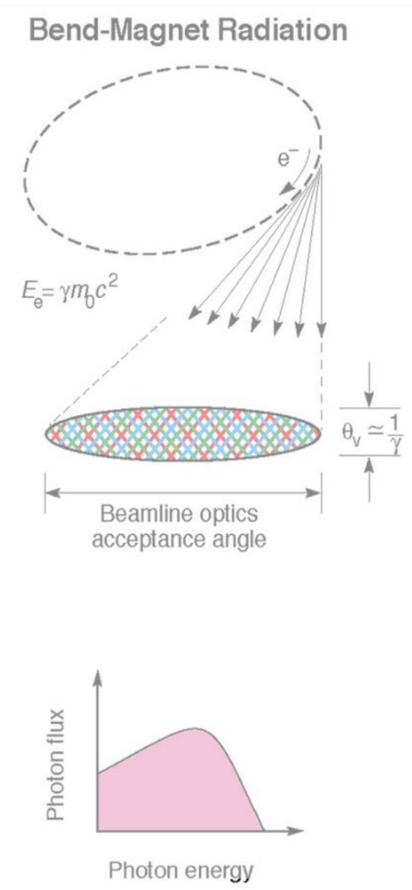


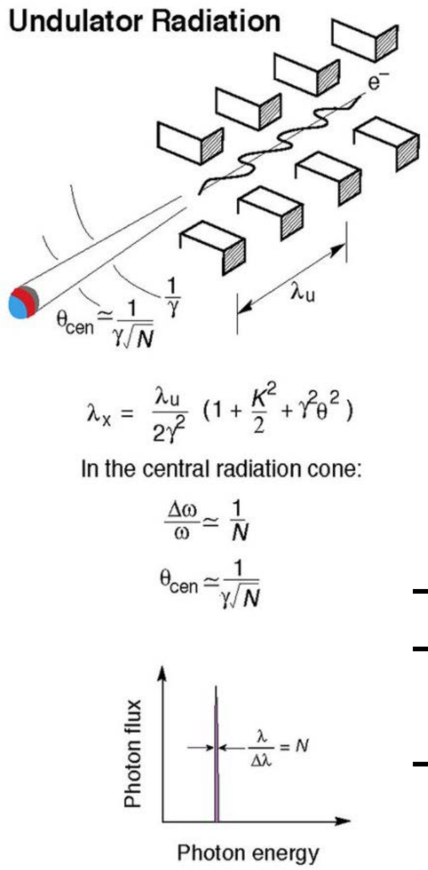
https://www.esrf.fr/

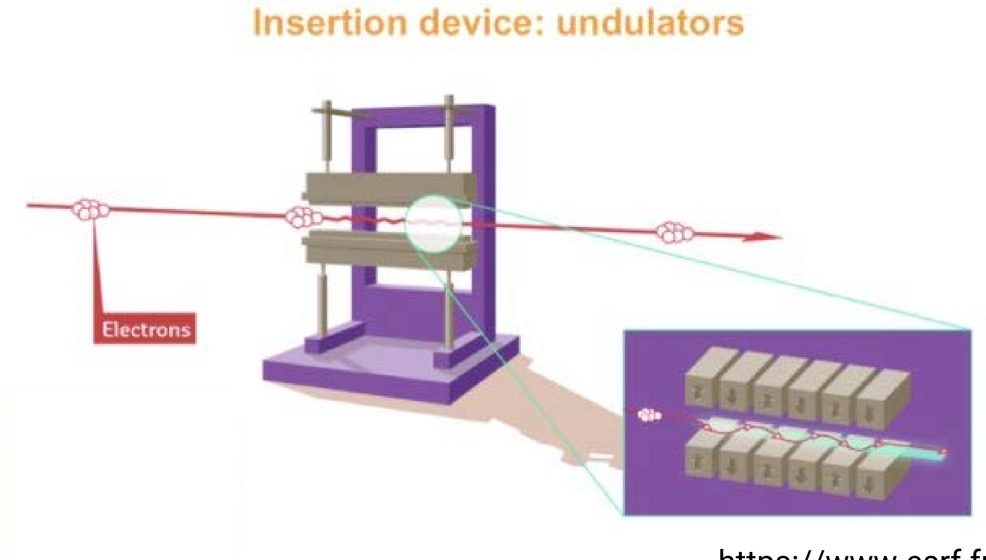
→ covers a less intense wide and continuous spectrum

Storage Ring

Undulator (Insertion Device): a complex array of small bending magnets with alternating polarity, force the electrons to follow an undulating, or wavy, trajectory. The radiation emitted at each consecutive bend overlaps and interferes







https://www.esrf.fr/

- → More focused and brilliant beam
- → The photons are concentrated at certain energies (the fundamental and harmonics)
- → Wavelength of the x-rays in the beam can be fine-tuned

Synchrotron Radiation

Soft x-rays:

wavelengths bigger than 0.10 nm or energies smaller than10 keV

→Higher absorption

→Higher chemical sensitivity

→Bonding states

→Magnetic sensitivity

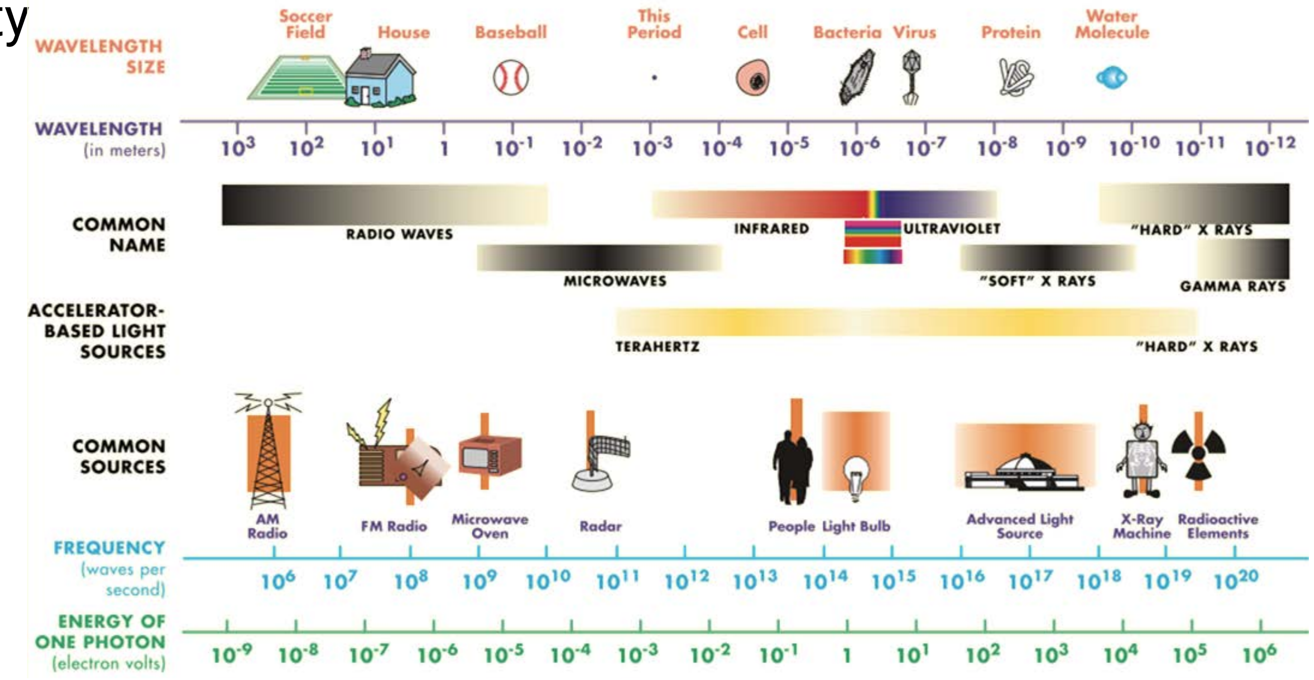
Hard x-rays:

wavelengths of 0.10 to 0.01 nm or energies in the range 10 to 120 keV

→Higher Penetration

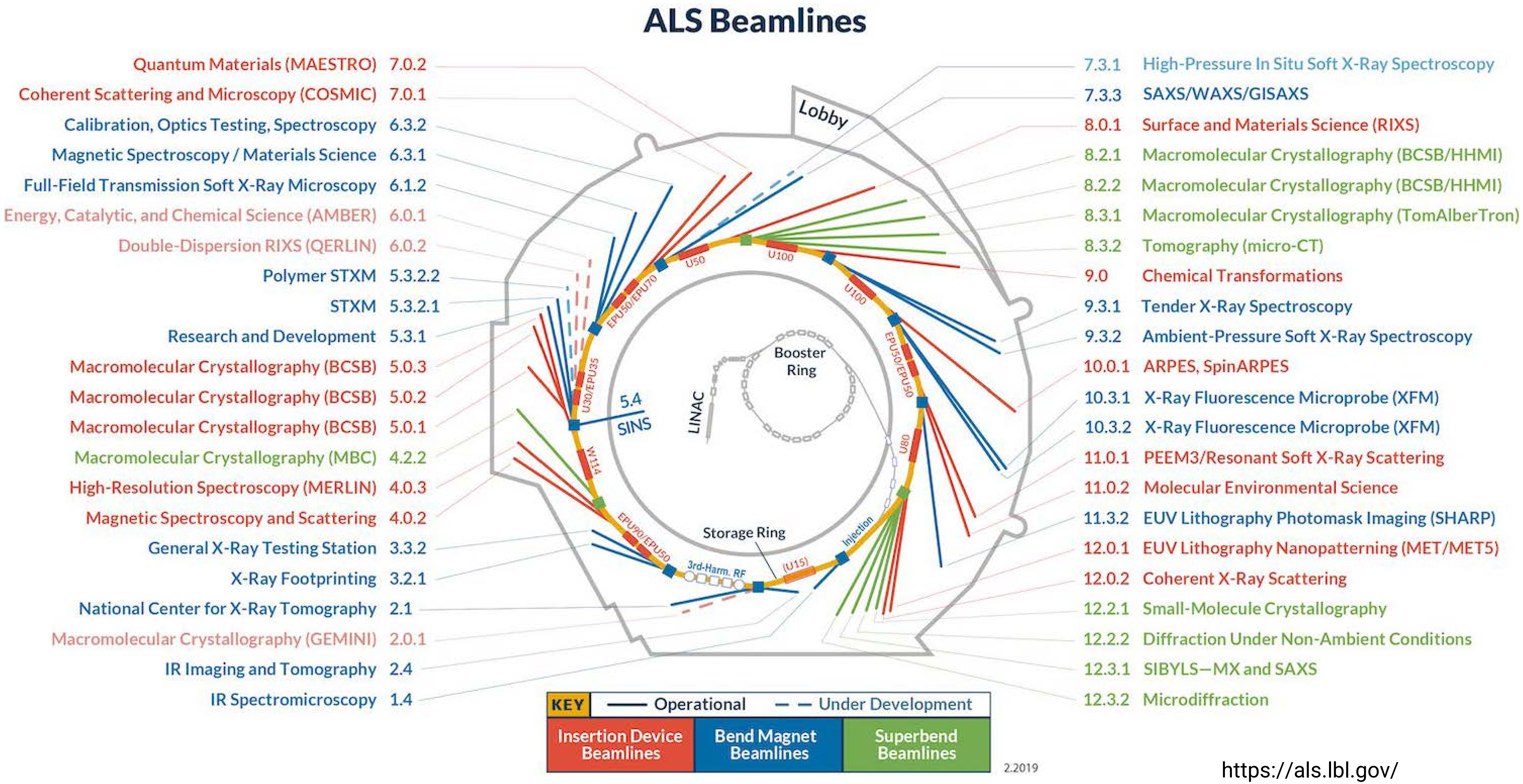
→Crystal lattice / strain information

→Fluorescence



https://als.lbl.gov/

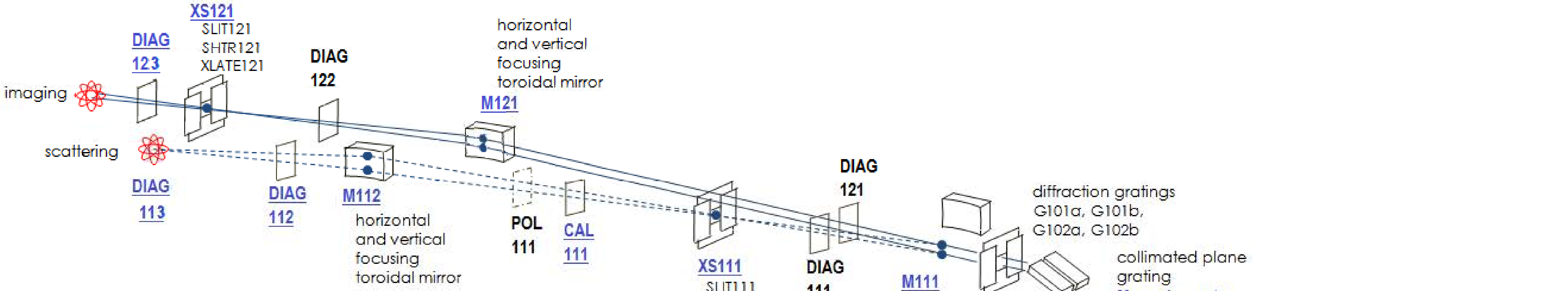
40 Beamlines at the ALS

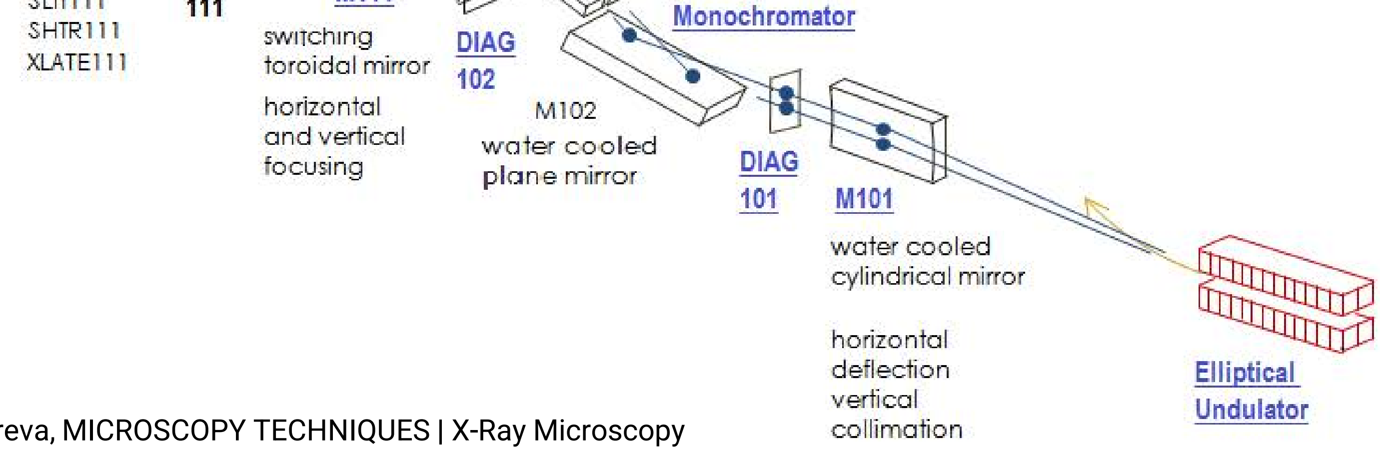


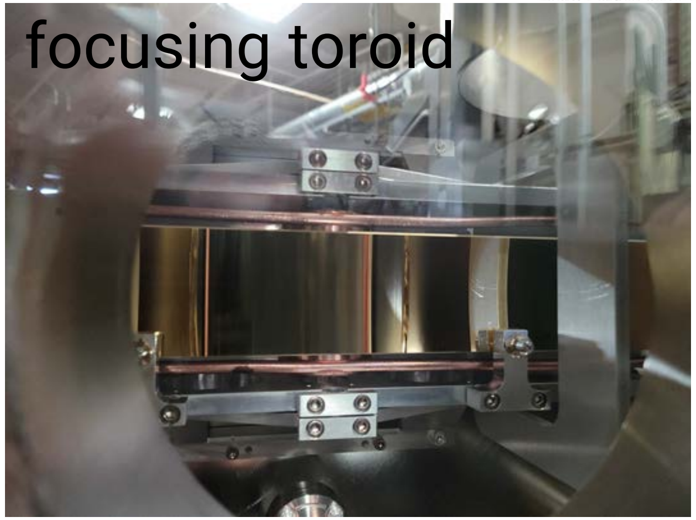
https://als.lbl.gov/

A Typical Beamline

X-ray optics: Modify the raw x-ray beam provided by the accelerator. Specialized mirrors and crystal optics may be used to focus the beam and to select the wavelength, energy, or coherence desired







I. Snigireva, A. Snigireva, MICROSCOPY TECHNIQUES | X-Ray Microscopy in Encyclopedia of Analytical Science (Second Edition), 2005

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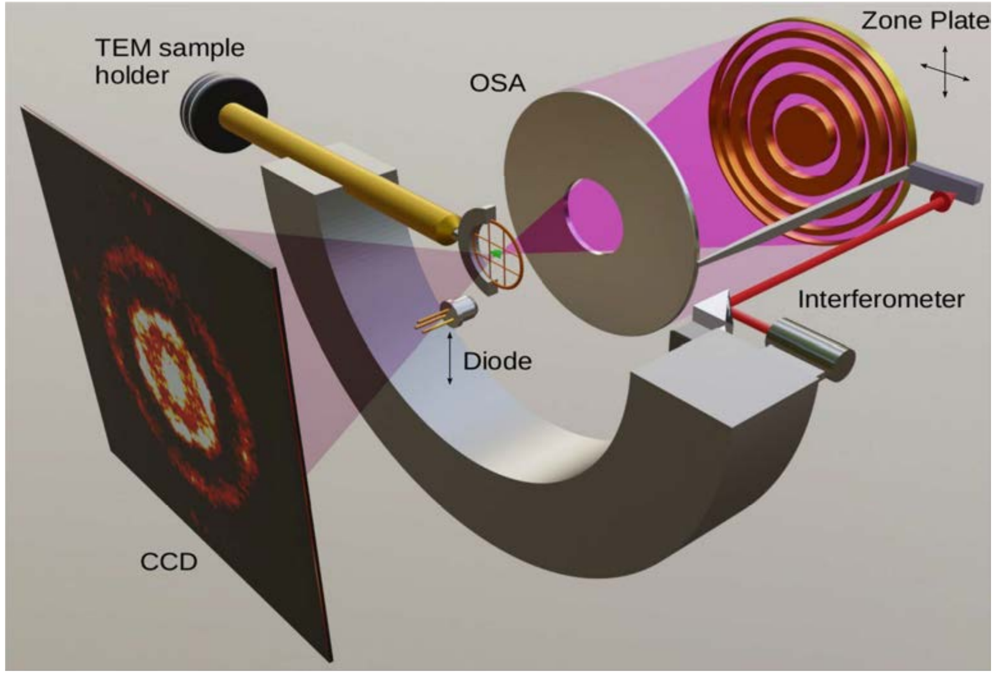
Experimental cabin: Beamline specific sample placement in open air, in vacuum or temperature controlled. Can be motorized. Equipped with detectors, such as diodes, scintillators or CCDs suitable for the corresponding technique



The Advanced Light Source -Techniques

Microscopy/Imaging

These techniques use the light-source beam to obtain pictures with fine spatial resolution of the samples under study and are used in diverse research areas such as cell biology, lithography, infrared microscopy, radiology, and x-ray tomography

Spectroscopy

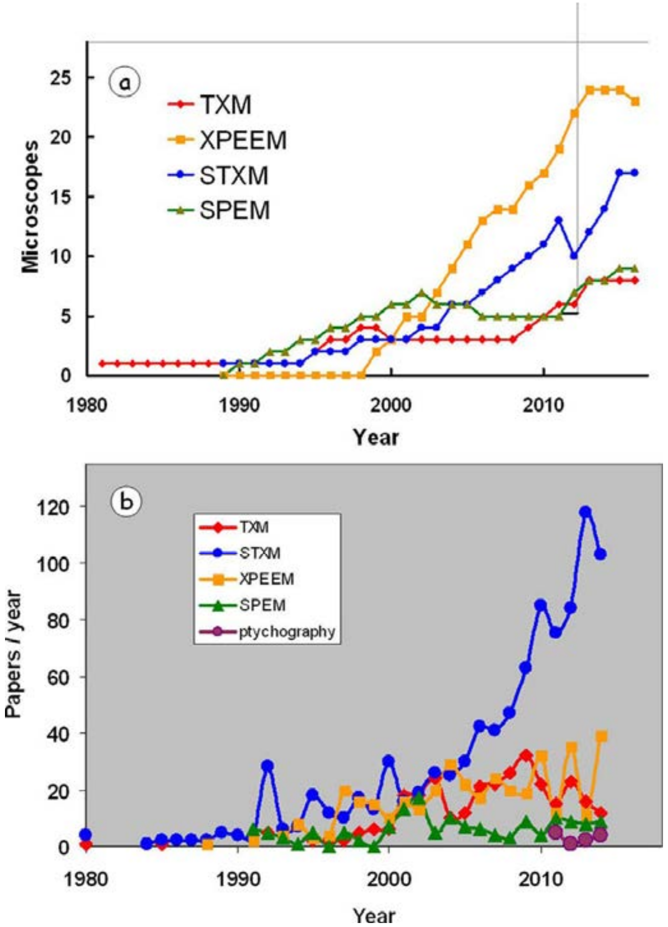
These techniques are used to study the energies of particles that are emitted or absorbed by samples that are exposed to the light-source beam and are commonly used to determine the characteristics of chemical bonding and electron motion

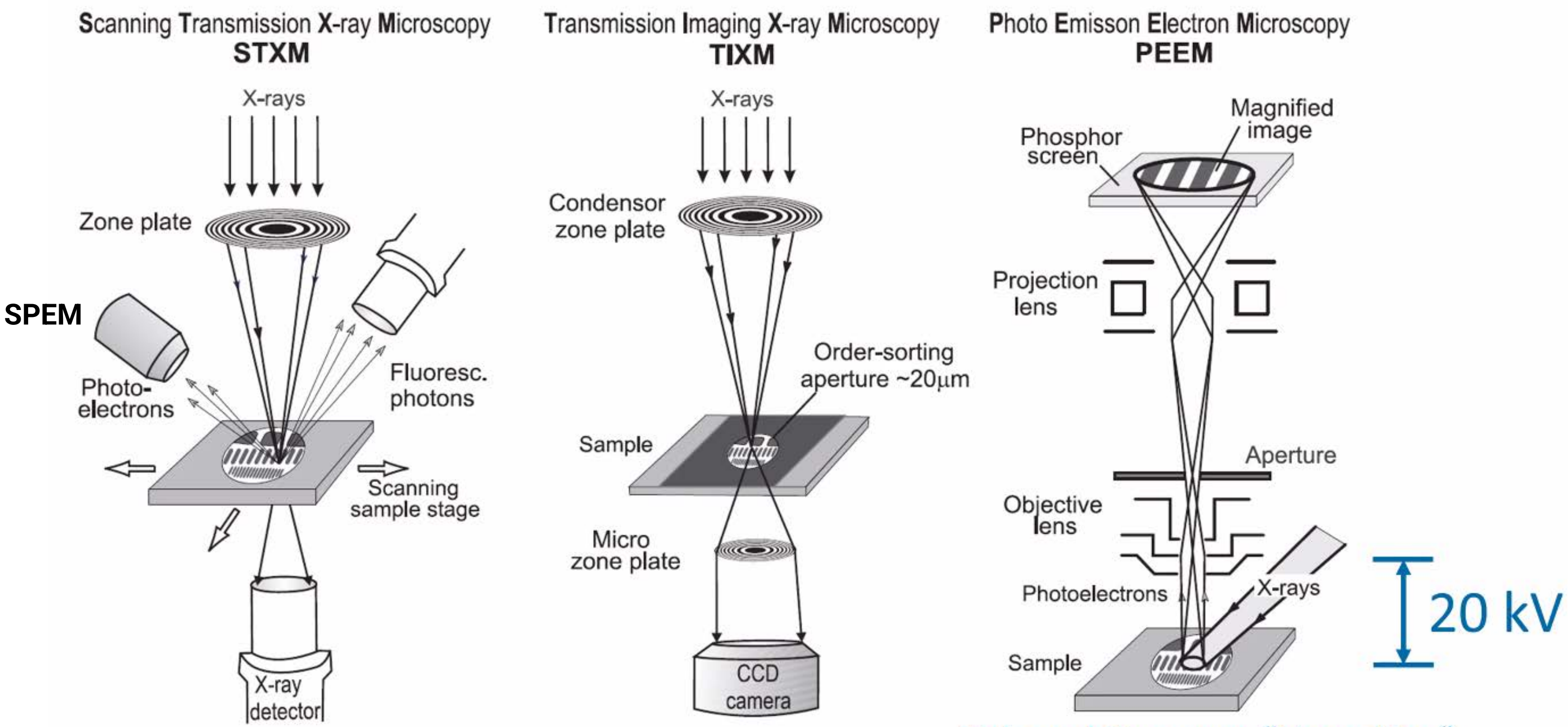
Scattering/Diffraction

These techniques make use of the patterns of light produced when x -ays are deflected by the closely spaced lattice of atoms in solids and are commonly used to determine the structures of crystals and large molecules such as proteins

X-Ray Microscopy

- “Nondestructive” imaging technique – image contrast determined by the difference in absorption of x-rays in different components of the sample
- First invented in the 1940s equipped with a photographic film





Stohr and Siegmann, “Magnetism”

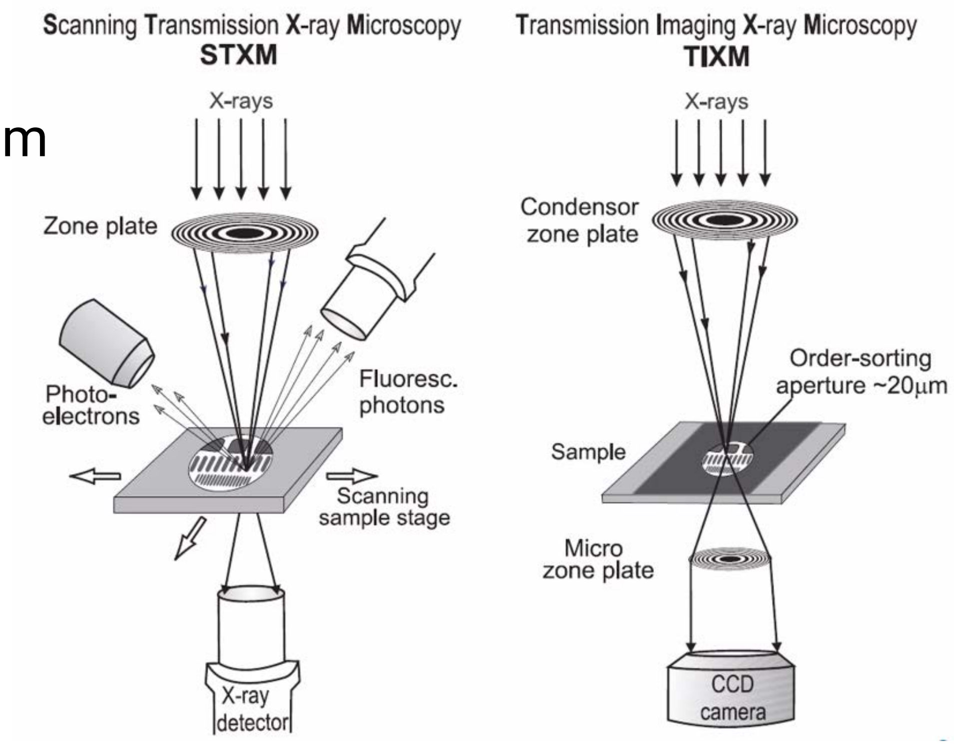
A.P. Hitchcock / Journal of Electron Spectroscopy and Related Phenomena 200 (2015) 49–63

X-Ray Microscopy

- Tunable soft x-rays: 50 – 3000 eV → spectrally sensitive imaging, based on systematic changes of the incident photon energy and/or polarization properties of the x-rays
- Synchrotron source or laser-produced plasma
- Higher penetration than electrons
- Resolution between light and electron microscopes ~ 30 nm
- In principle limited by the wavelength

$$\lambda = \frac{hc}{E} = \frac{1.24 \text{ keV nm}}{\text{photon energy (keV)}}$$

- **STXM**: focused beam is rastered over sample
- **TXM**: full field imaging -> faster, reduced brightness



X-rays are focused with **Fresnel Zone Plates**: circular diffraction grating that works as a lens for monochromatic light

I. Snigireva, A. Snigireva, MICROSCOPY TECHNIQUES | X-Ray Microscopy in Encyclopedia of Analytical Science (Second Edition), 2005

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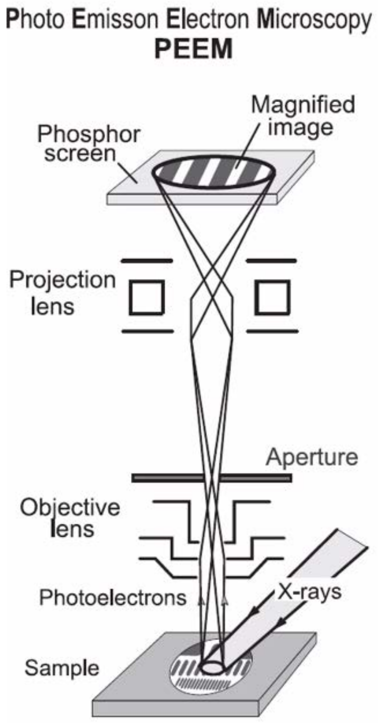


- **XPEEM**: full-field imaging in reflection geometry
- record electrons emitted from a sample in response to the x-ray absorption

→ Study chemistry, structure and magnetism of thin films and surfaces

Spectromicroscopy

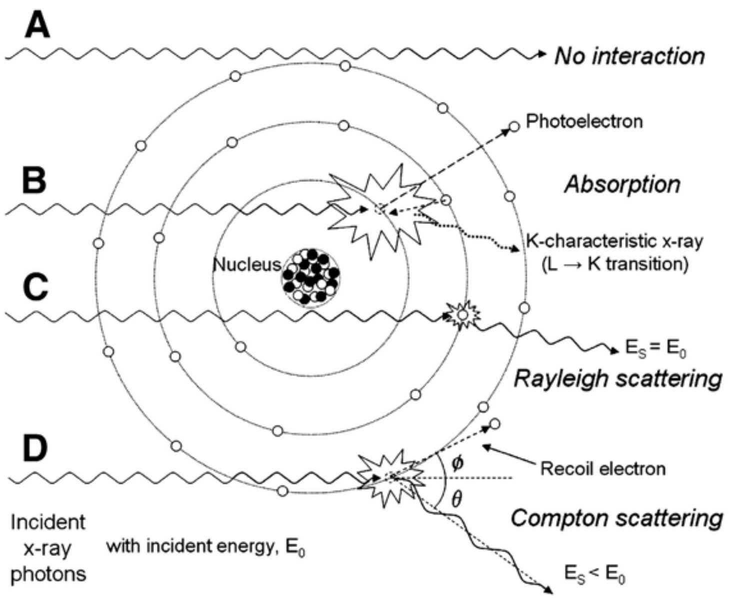
Inelastic scattering:
Many mechanisms/interactions with loosely bound electrons
→ Loss of energy

Coherent/elastic scattering:
Thomson and Rayleigh scattering/ interactions with strongly bound electrons
→ wavelength stays the same/ no loss in energy
→ Can change direction/phase

→ **Phase shift**

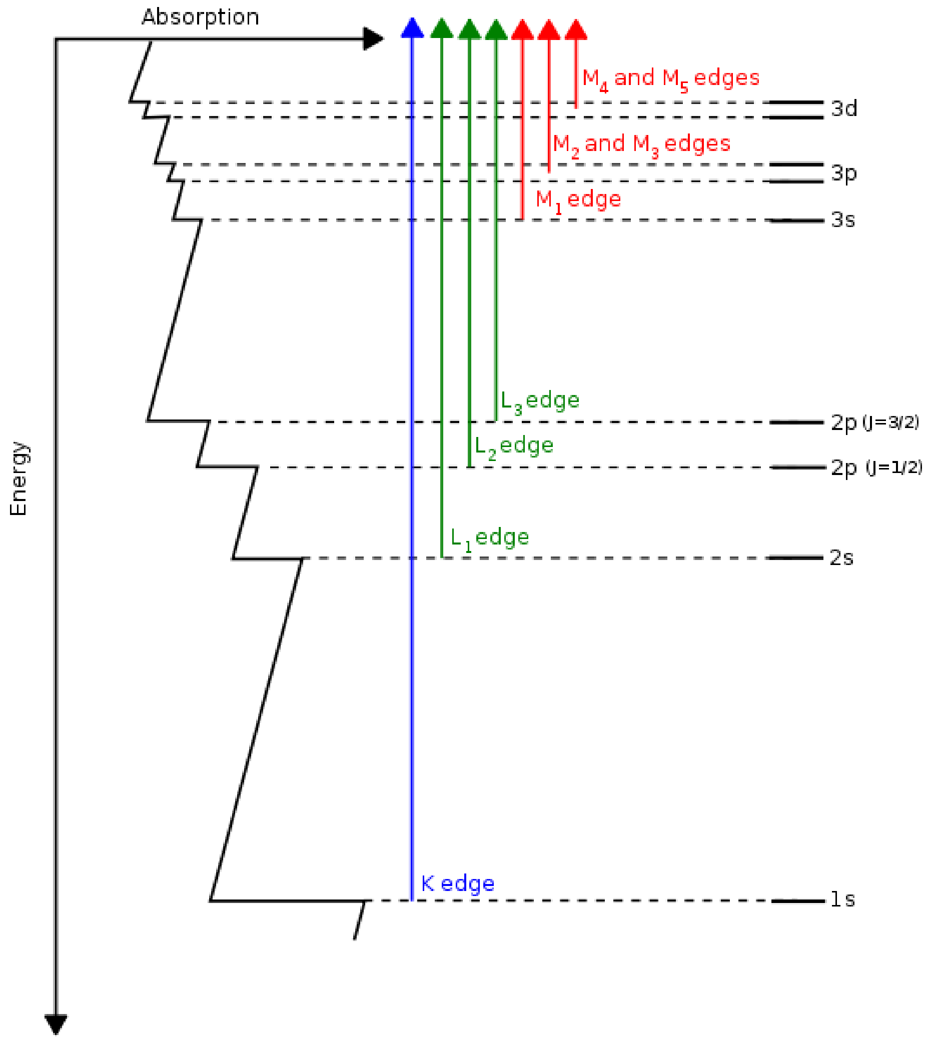
Absorption:
Energy is transferred to an inner atomic electron
→ Elements have different sets of core level energies
→ X-ray absorption near edge structure (XANES)
→ near edge X-ray absorption fine structure (NEXAFS)

→ **Amplitude**



J. A Seibert and J. M. Boone, Journal of Nuclear Medicine Technology March 2005, 33 (1) 3-18

Spectromicroscopy

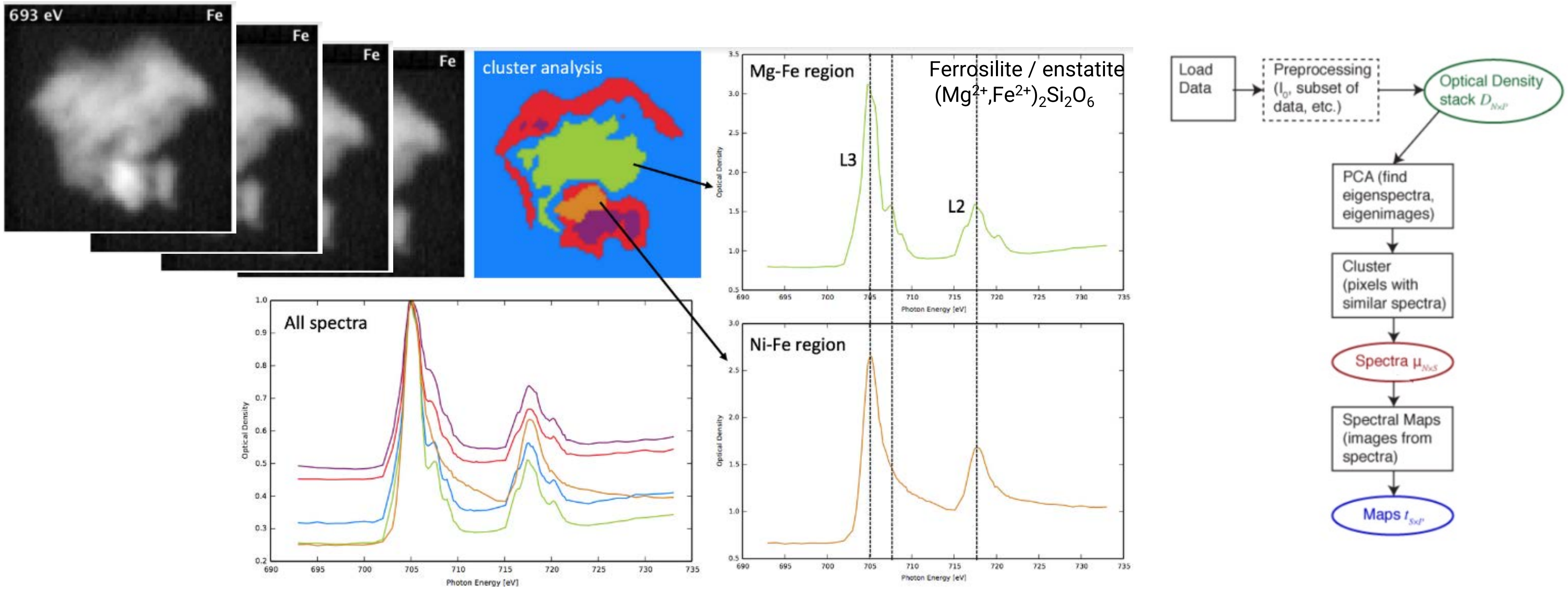


Absorption:
Energy is transferred to an inner atomic electron
→ Elements have different sets of core level energies
→ X-ray absorption near edge structure (XANES)
→ near edge X-ray absorption fine structure (NEXAFS)

Energy range of soft X-rays in STXM:
- 1s absorption edges of light elements such as C, N, O, Na, Mg, Al, Si, and P
- 2p absorption edges of elements of environmental relevance such as Fe, Mn, Cr, As, Zn, Ni, Ti, and Ca

J. A Seibert and J. M. Boone, Journal of Nuclear Medicine Technology March 2005, 33 (1) 3-18

Spectromicroscopy



(1) Applying principle component analysis (PCA):
PCA calculates ***eigenspectra*** and ***eigenimages*** from the image stack. The eigenspectra are an orthogonal set of spectra that, in linear combination, can describe any observed spectrum in the dataset. The eigenvalue associated with each eigenspectrum gives a typical weighting of that eigenspectrum in the entire data set, so that the later eigenspectra (with small eigenvalues) represent less and less common variations in the data.

(2) Applying cluster analysis:
The cluster analysis is used to classify data in the image stack according to spectral similarities. When searching for clusters, you are looking for pixels with similar weightings of eigenspectra.

MANTiS (Multivariate ANalysis Tool for Spectromicroscopy)
Lerotic *et al.*, MANTiS: a program for the analysis of X-ray spectromicroscopy data. J. Synchrotron Rad. 2014 Sep; 21(5); 1206–1212

COSMIC 7.0.1

Soft X-ray Spectroscopy:

Build in 2017

Energy range: 250-2500 eV:

High sensitivity for chemical and magnetic states

Higher spatial resolution

Scanning Transmission X-ray Microscopy (STXM):

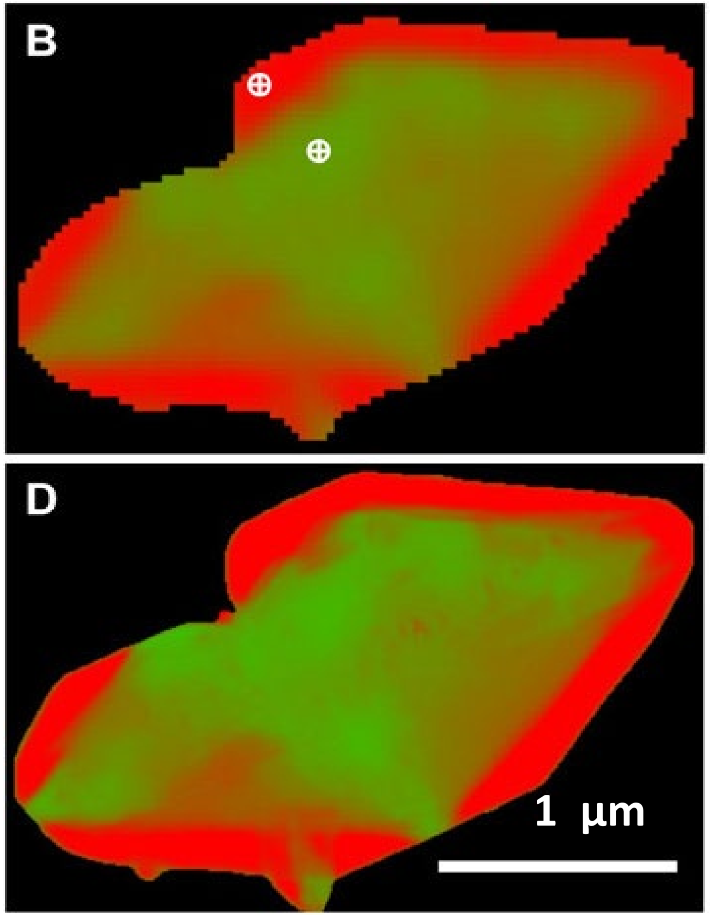
Scans the sample with focused X-ray beam and intensity is detected with a diode

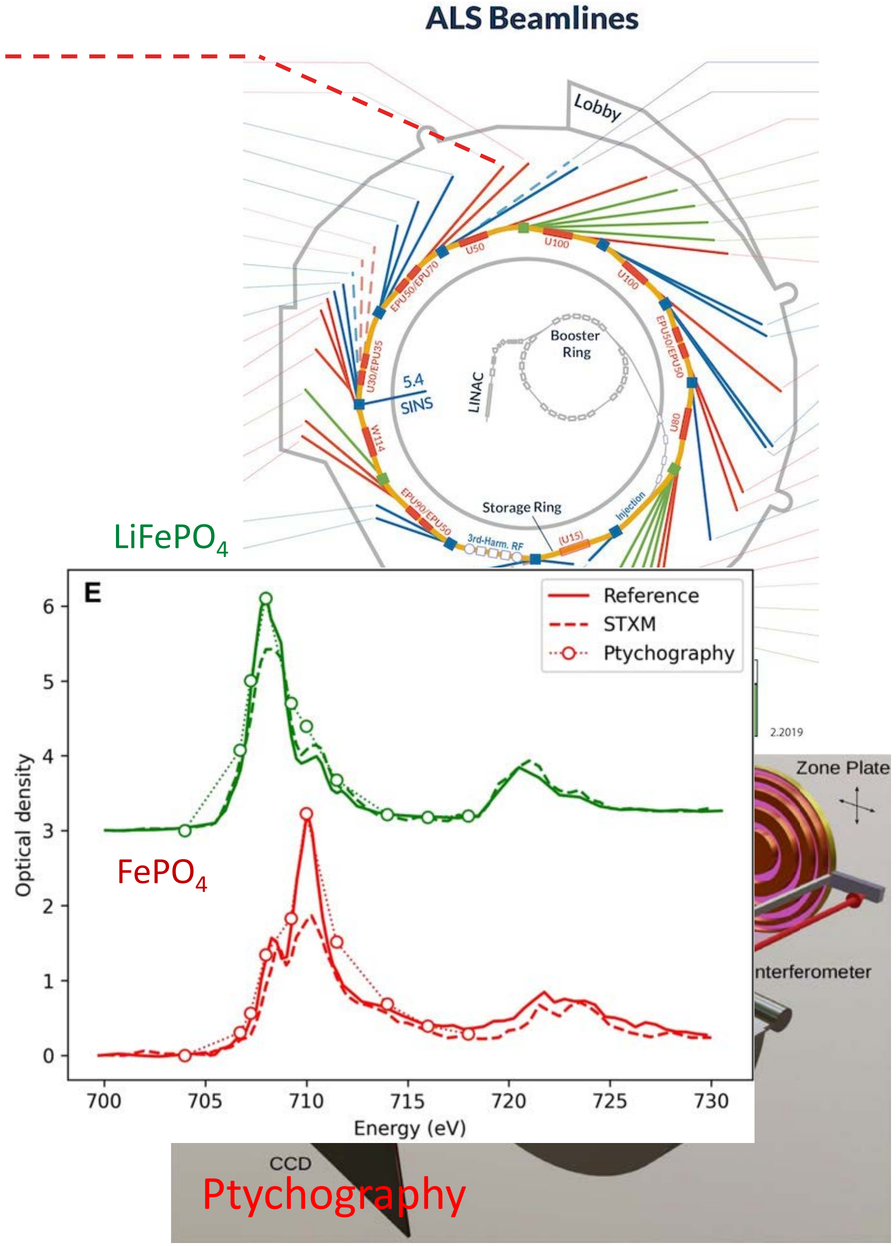
Resolution is limited by X-ray optics: ~ 50nm

Ptychography:

Overlapping scattered signals are detected on CCD

High spatial resolution based on instrument precision and scattering of the sample: ~ 8 nm





David Shapiro, *et al.* SCIENCE ADVANCES, 2020

Versatile Ultrahigh-Resolution Soft X-ray Microscope

Tunable:

- Energy range → chemical information
- Tilt angles → 3D information
- X-ray polarization → orientational information

Combinable:

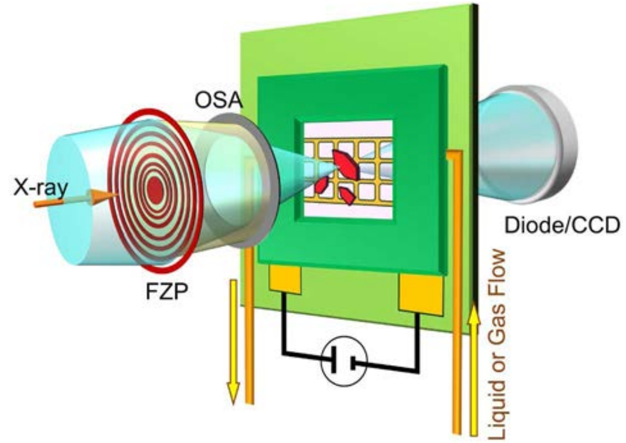
- Commercial TEM holders and cells (e.g. Hummingbird Scientific)
- Custom made environmental cells (Prof. Will Chueh of Stanford)

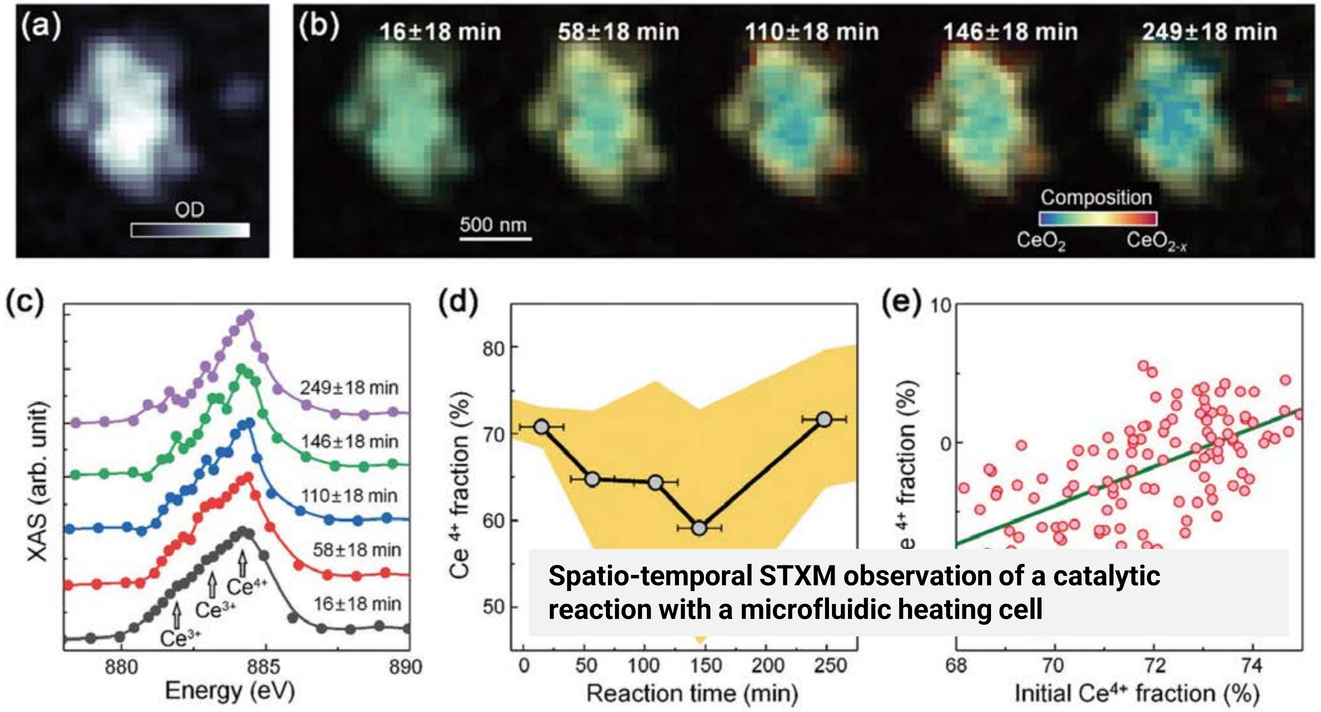
Adjustable (Time Resolved):

- Liquid-flow
- Heating
- Gas-flow
- Electrochemistry
- **Cryogenics**

Samples:

- Chemically heterogenous samples
- Morphologically heterogenous samples
- Geological samples
- Catalysts, Magnetic & Battery materials
- Biominerals
- Biological samples (Cryo)





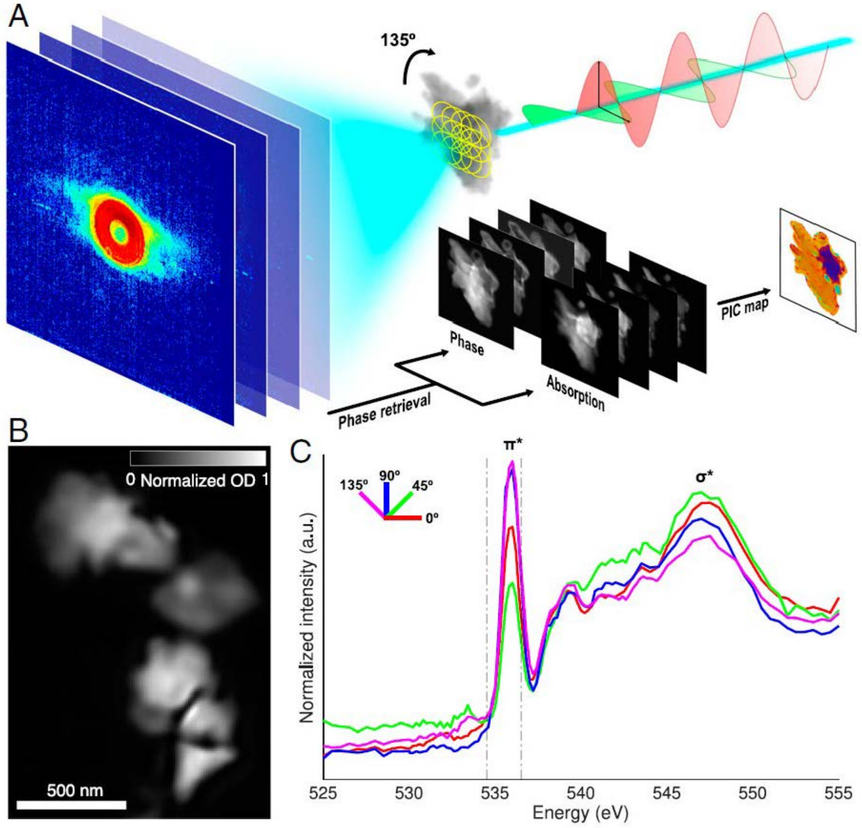
Spatio-temporal STXM observation of a catalytic reaction with a microfluidic heating cell

Mi Yoo *et al.* Energy Environ. Sci. 2020

Linear Dichroic Ptychography – 7.0.1

- Provides orientational information of optically anisotropic materials
- Contrast changes as a function of incident beam polarization and energy

→ **Orientation information of certain chemical bonds**

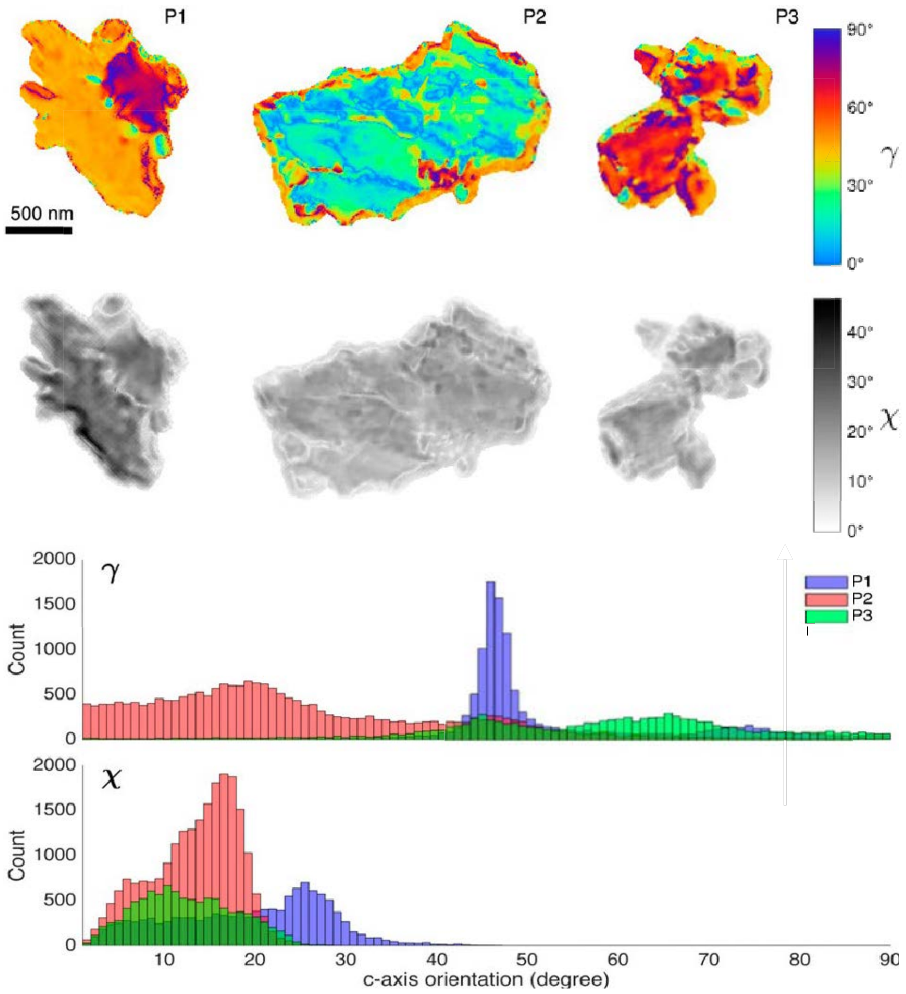


Yuan Hung Lo, *et al*. PNAS 118(3), e2019068118 (2021)

→ in-plane/out-plane orientations of crystallographic c-axis in $CaCO_3$

Change sample orientation in respect to monochromatic x-ray beam

Typical Misorientation in Coral Fragments < 35°



Yuan Hung Lo, *et al*. PNAS 118(3), e2019068118 (2021)

→ **Implementation of automated EPU control, data acquisition and analysis & 3D**

→ **Determination of precision, resolution and thickness limitation**

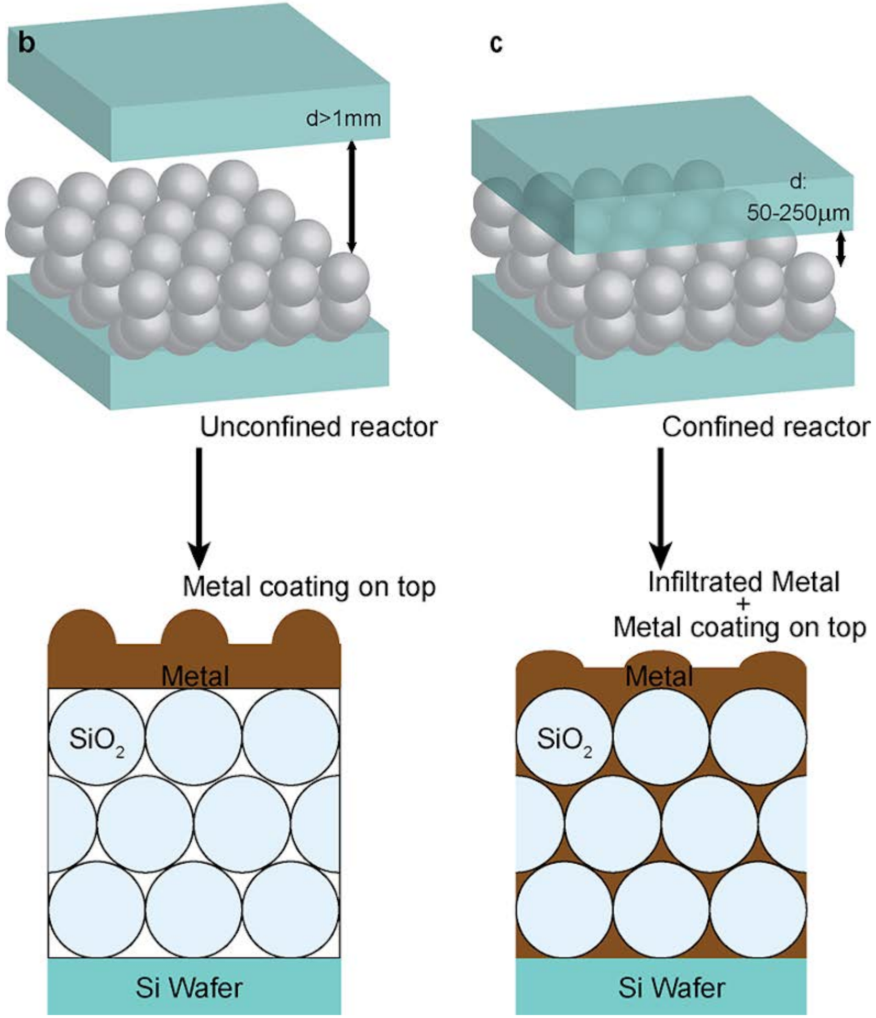
References

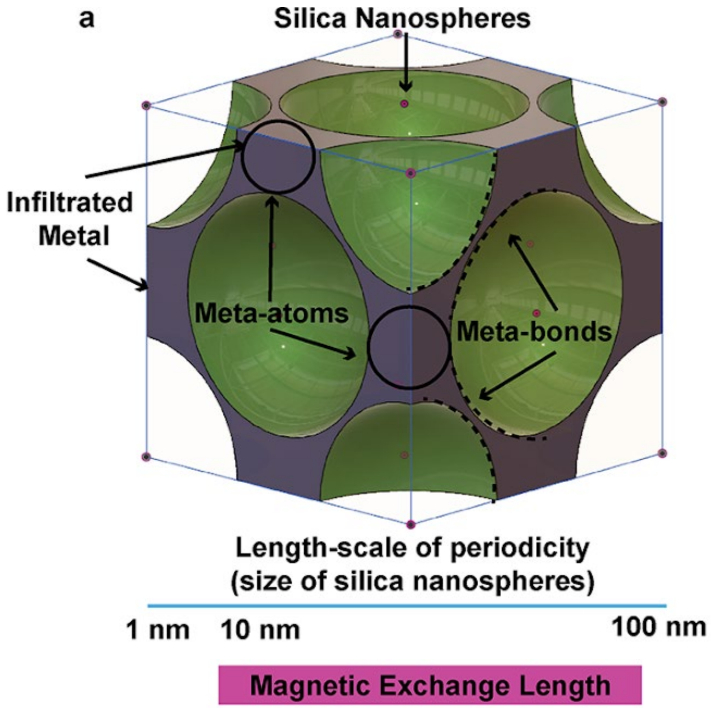
- X-ray Microscopy – An Overview, Encyclopedia of Interfacial Chemistry, 2018
- David A. Shapiro, et al., An ultrahigh-resolution soft x-ray microscope for quantitative analysis of chemically heterogeneous nanomaterials, Science Advances 2020; 6 : eabc4904
- I. Snigireva, A. Snigireva, MICROSCOPY TECHNIQUES | X-Ray Microscopy, Encyclopedia of Analytical Science (Second Edition) 2005
- A.P. Hitchcock / Journal of Electron Spectroscopy and Related Phenomena 200 (2015) 49–63

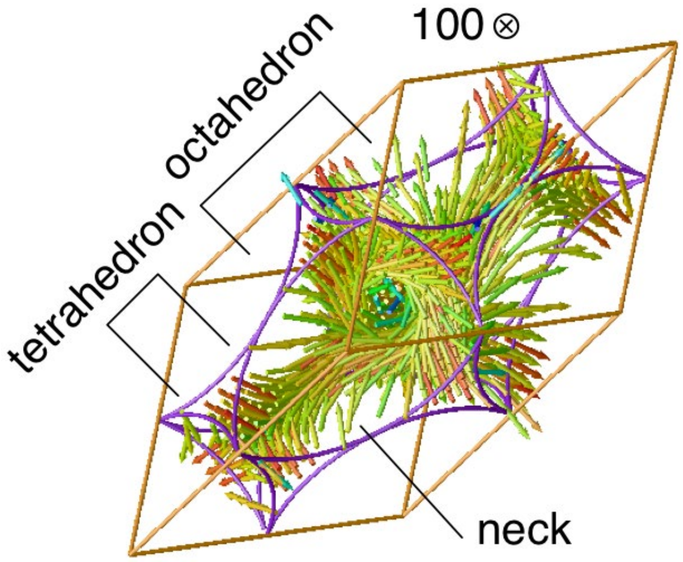
Ni metalattice

Han, Crespi, *Phys. Rev. Lett.* 2002

Liu, Y. *et al. Nano Letters* **18**, 546–552 (2018).

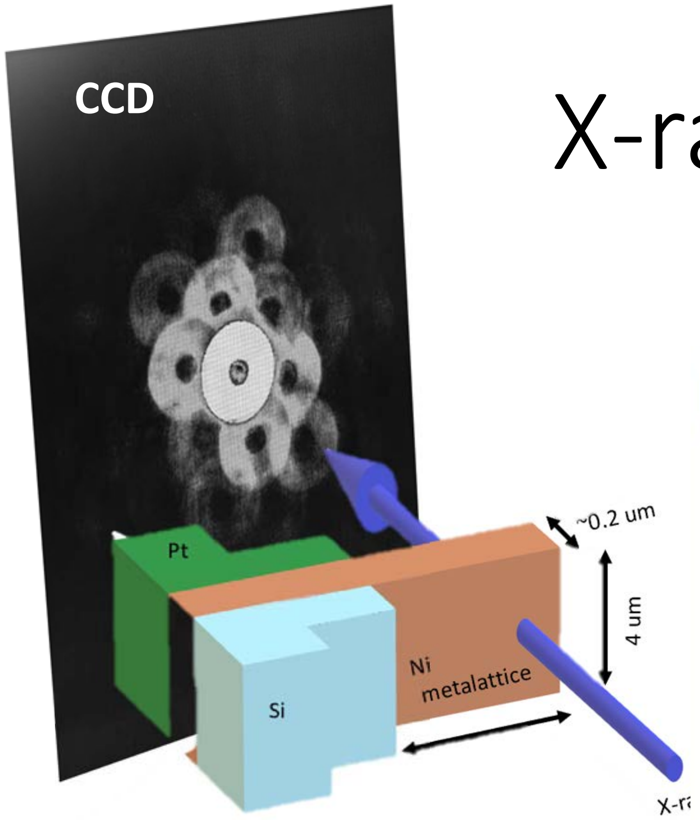


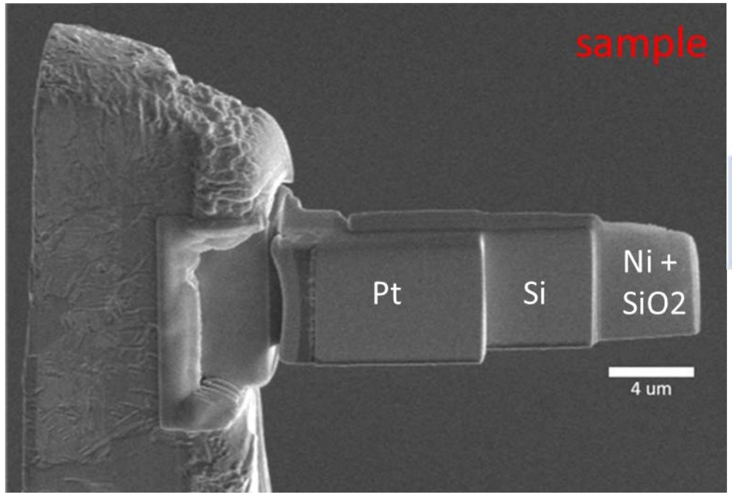


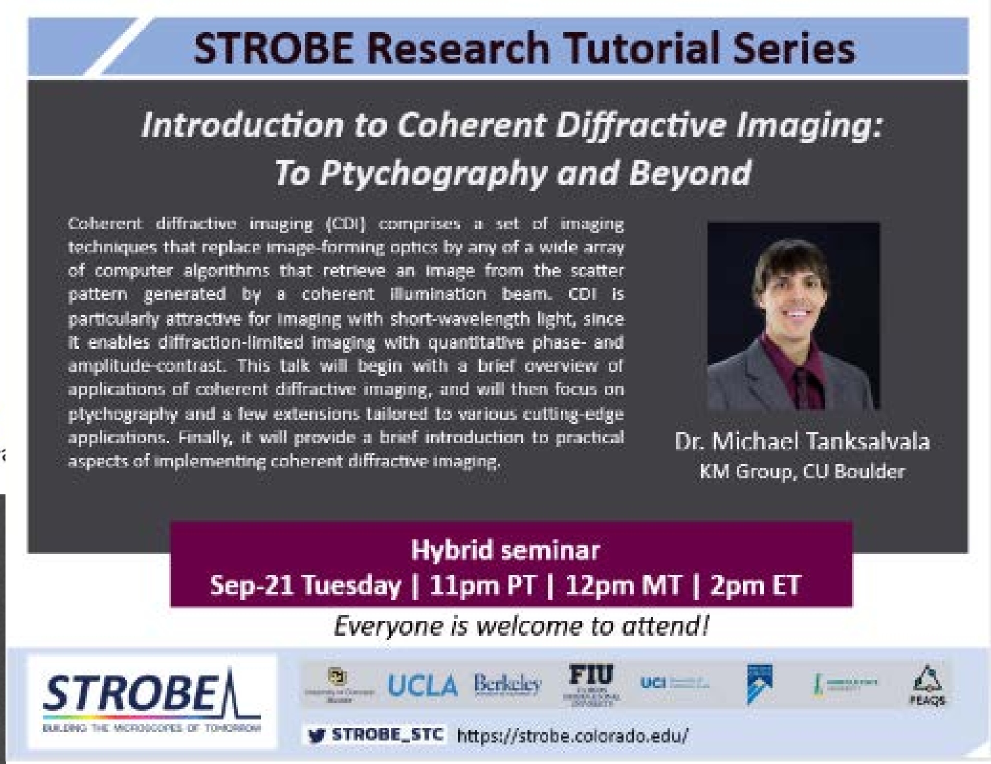


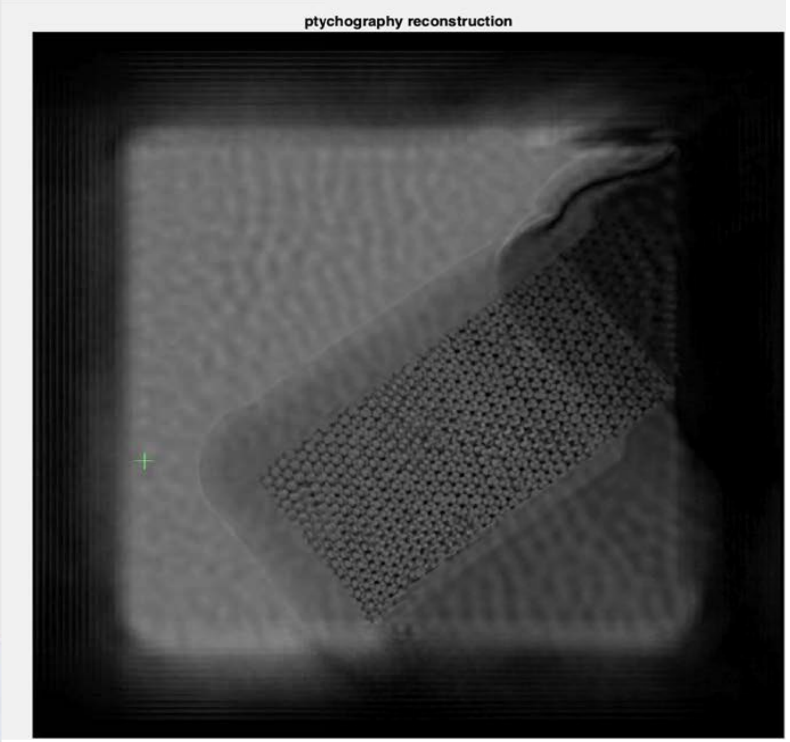
Goal: Image the magnetic field of nanostructured Ni in 3D.

X-ray ptychography of a Ni metalattice









https://strobe.colorado.edu/members/tutorials/2021/tutorial-introduction-to-coherent-diffractive-imaging-to-ptychography-and-beyond/

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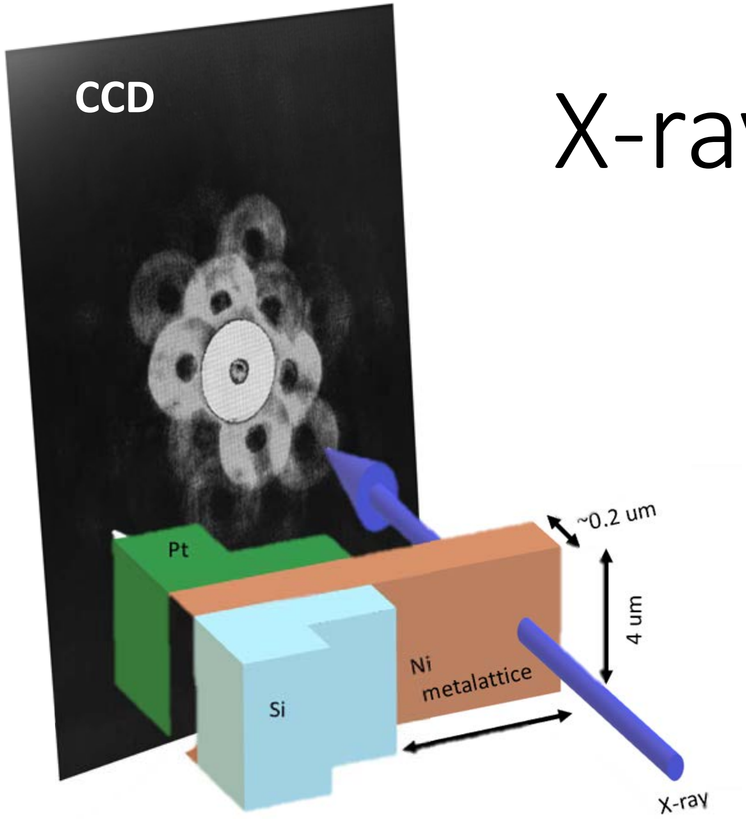
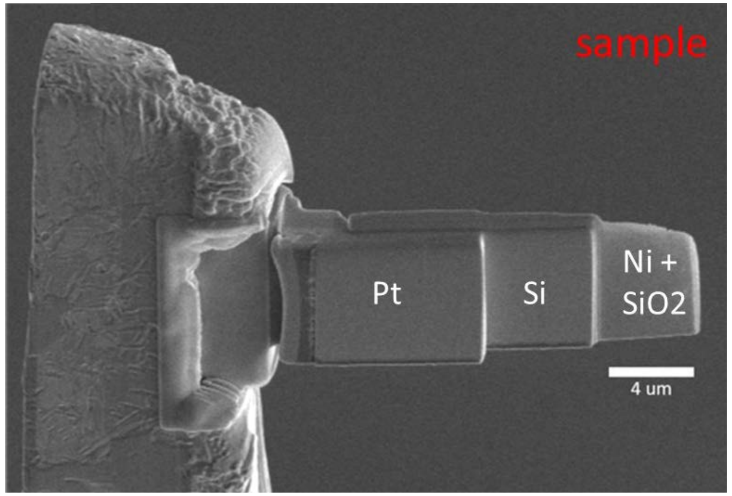
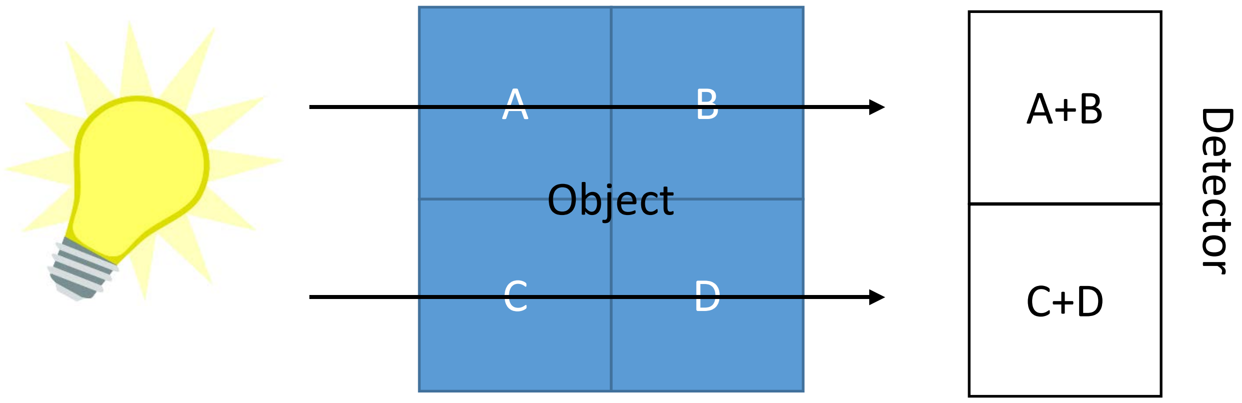




This is still only 2D – What if we want to image the internal structure?

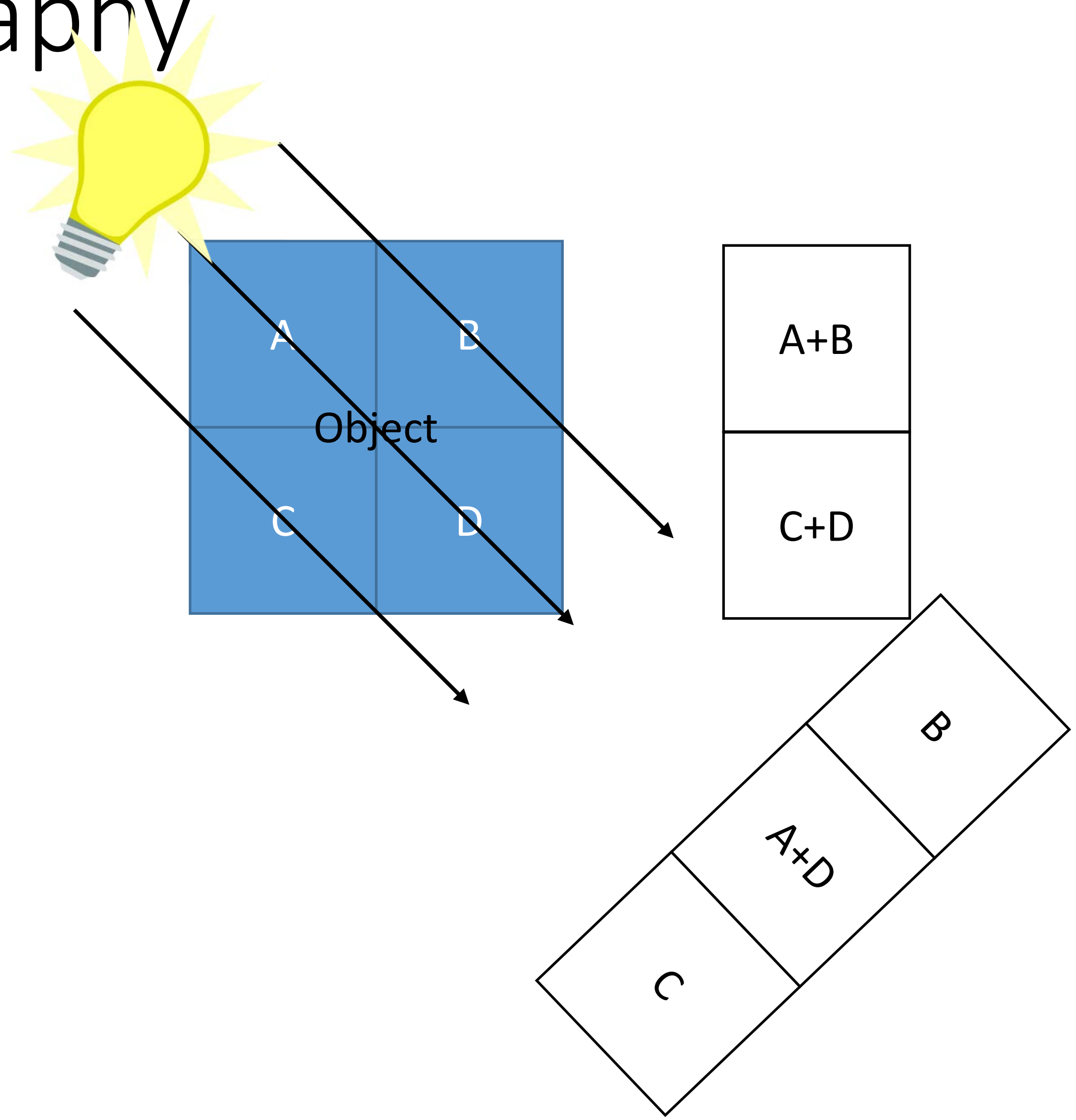
Let's try tomography!

Scalar Tomography



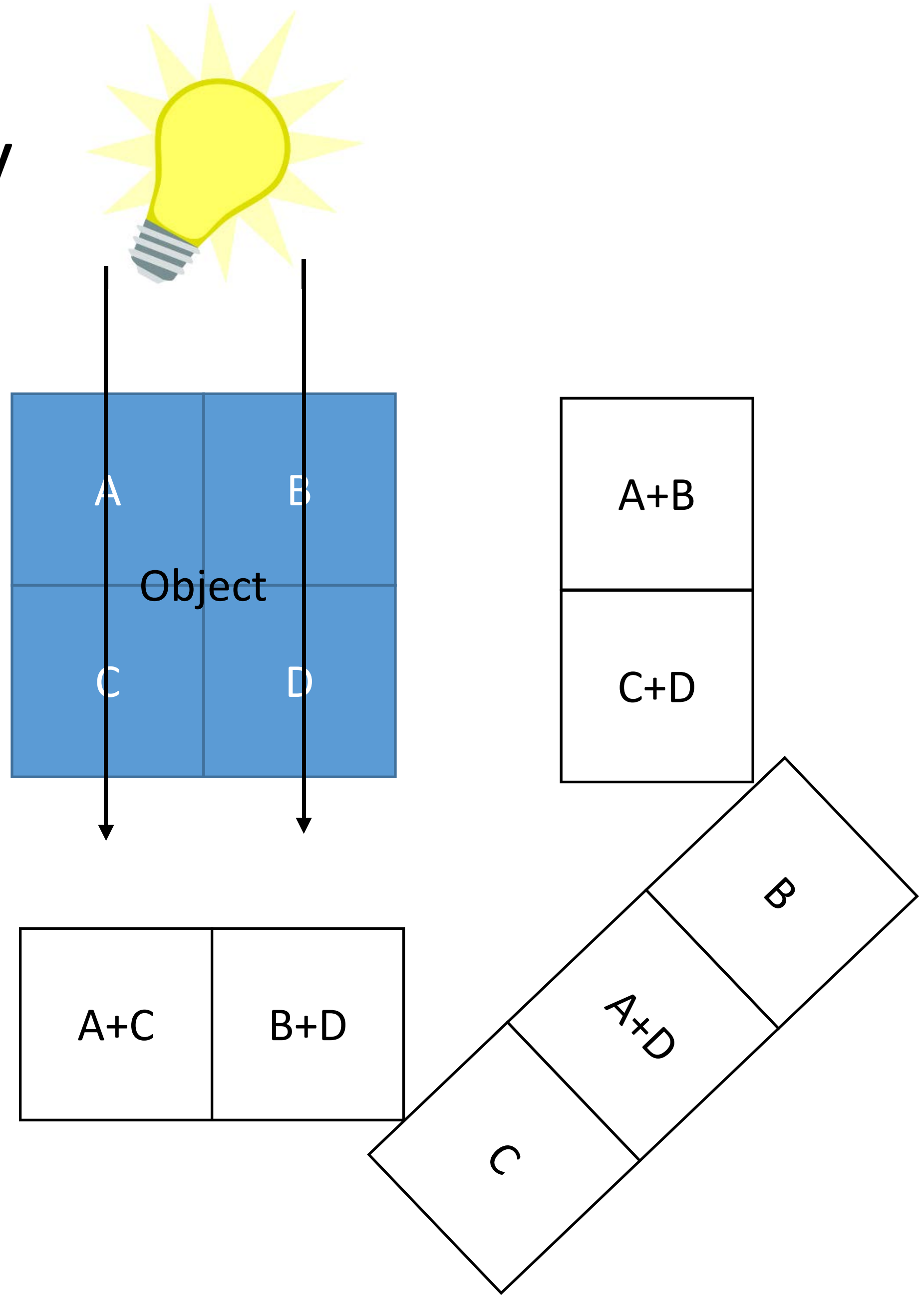
http://www.desy.de/~garutti/LECTURES/BioMedical/Lecture7_ImageReconstruction.pdf

Scalar Tomography



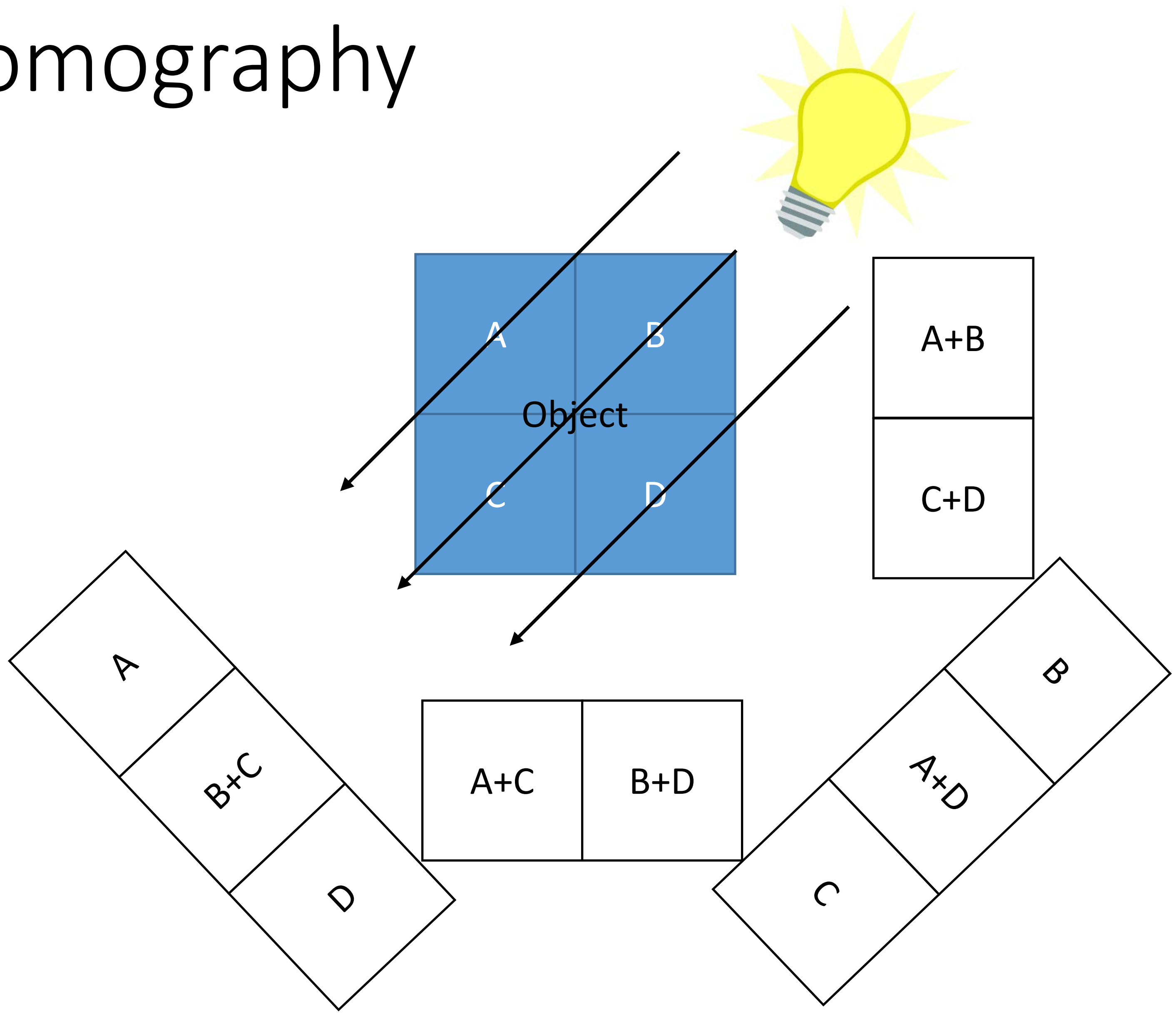
http://www.desy.de/~garutti/LECTURES/BioMedical/Lecture7_ImageReconstruction.pdf

Scalar Tomography



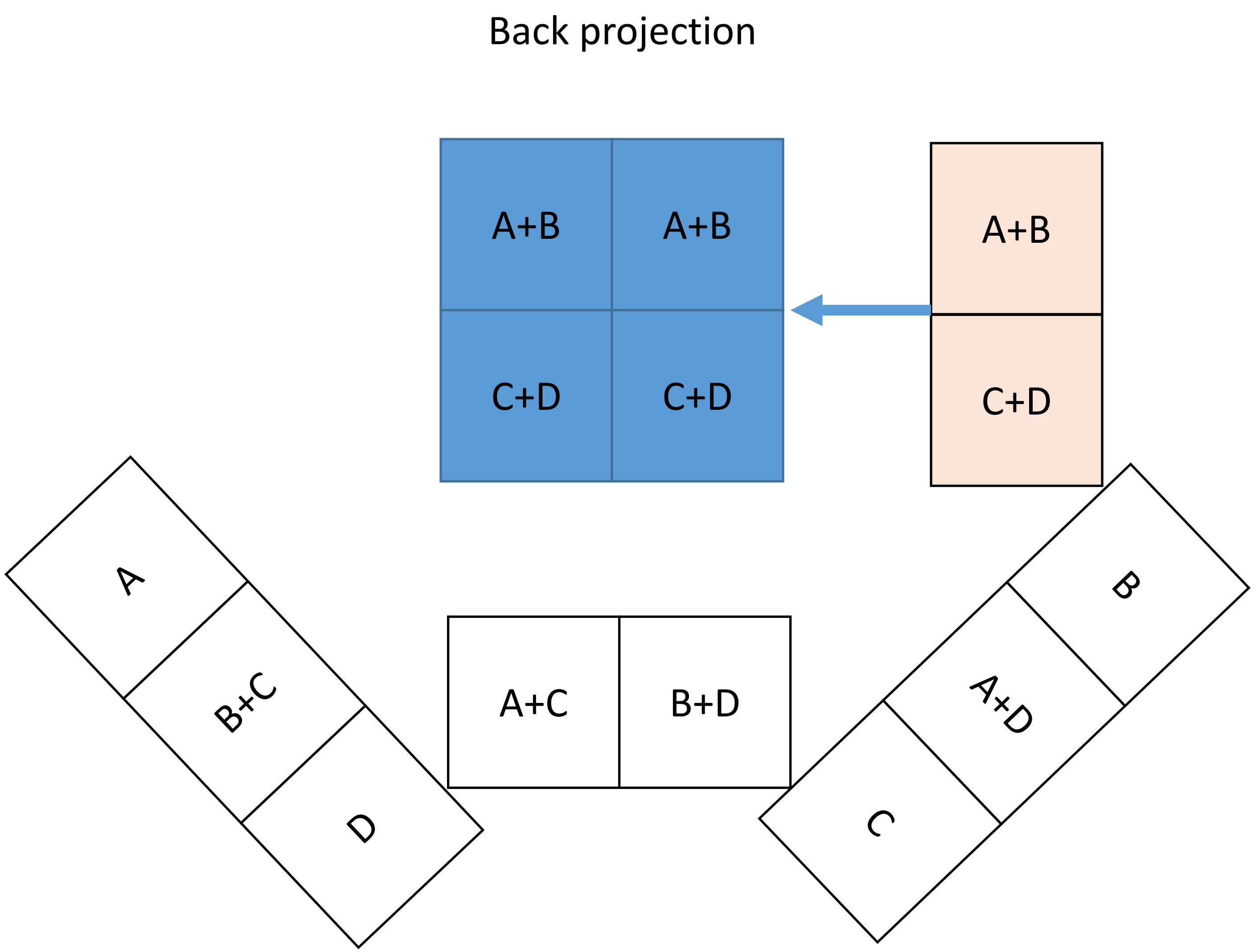
http://www.desy.de/~garutti/LECTURES/BioMedical/Lecture7_ImageReconstruction.pdf

Scalar Tomography



http://www.desy.de/~garutti/LECTURES/BioMedical/Lecture7_ImageReconstruction.pdf

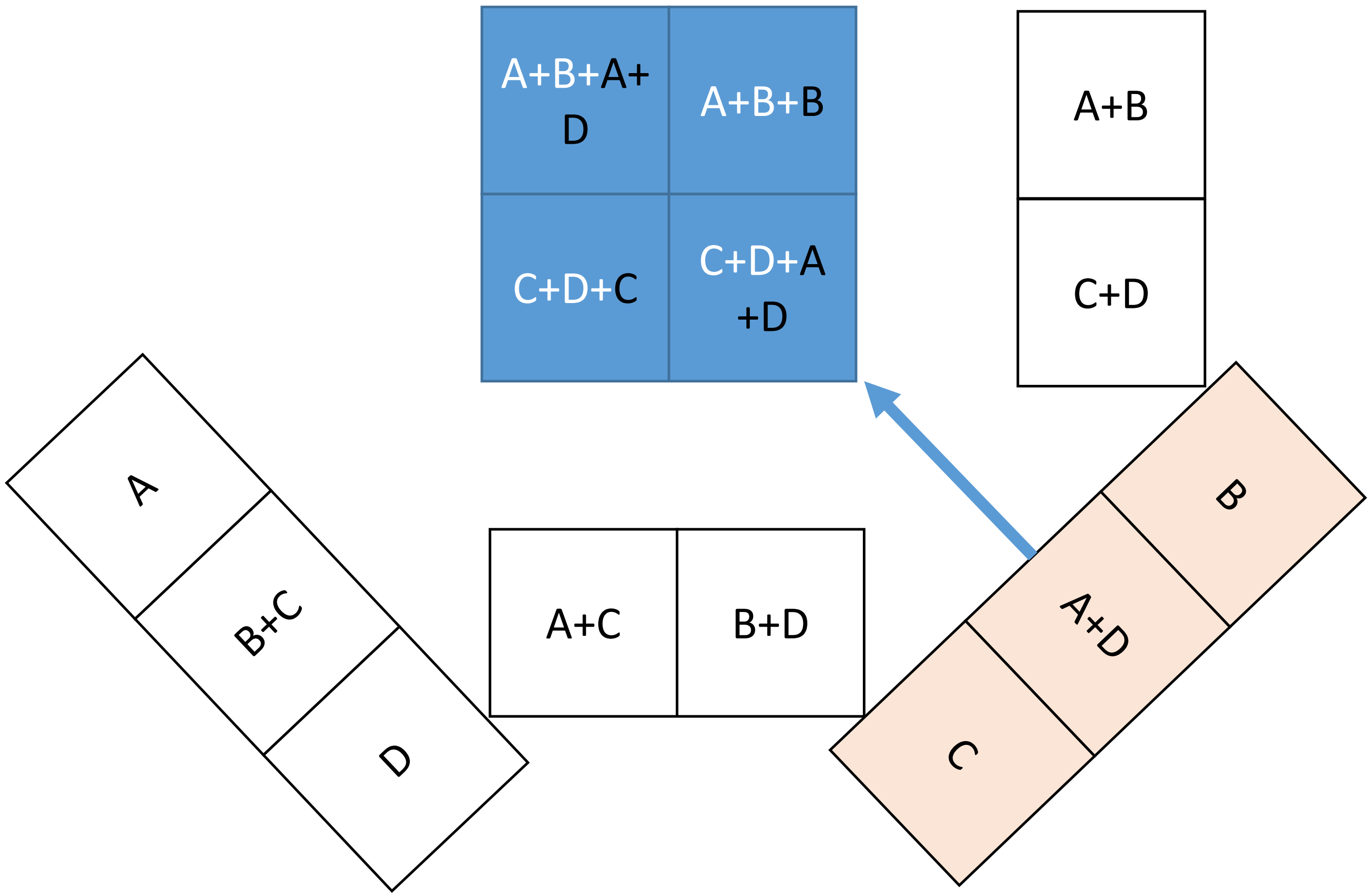
Scalar Tomography



http://www.desy.de/~garutti/LECTURES/BioMedical/Lecture7_ImageReconstruction.pdf

Scalar Tomography

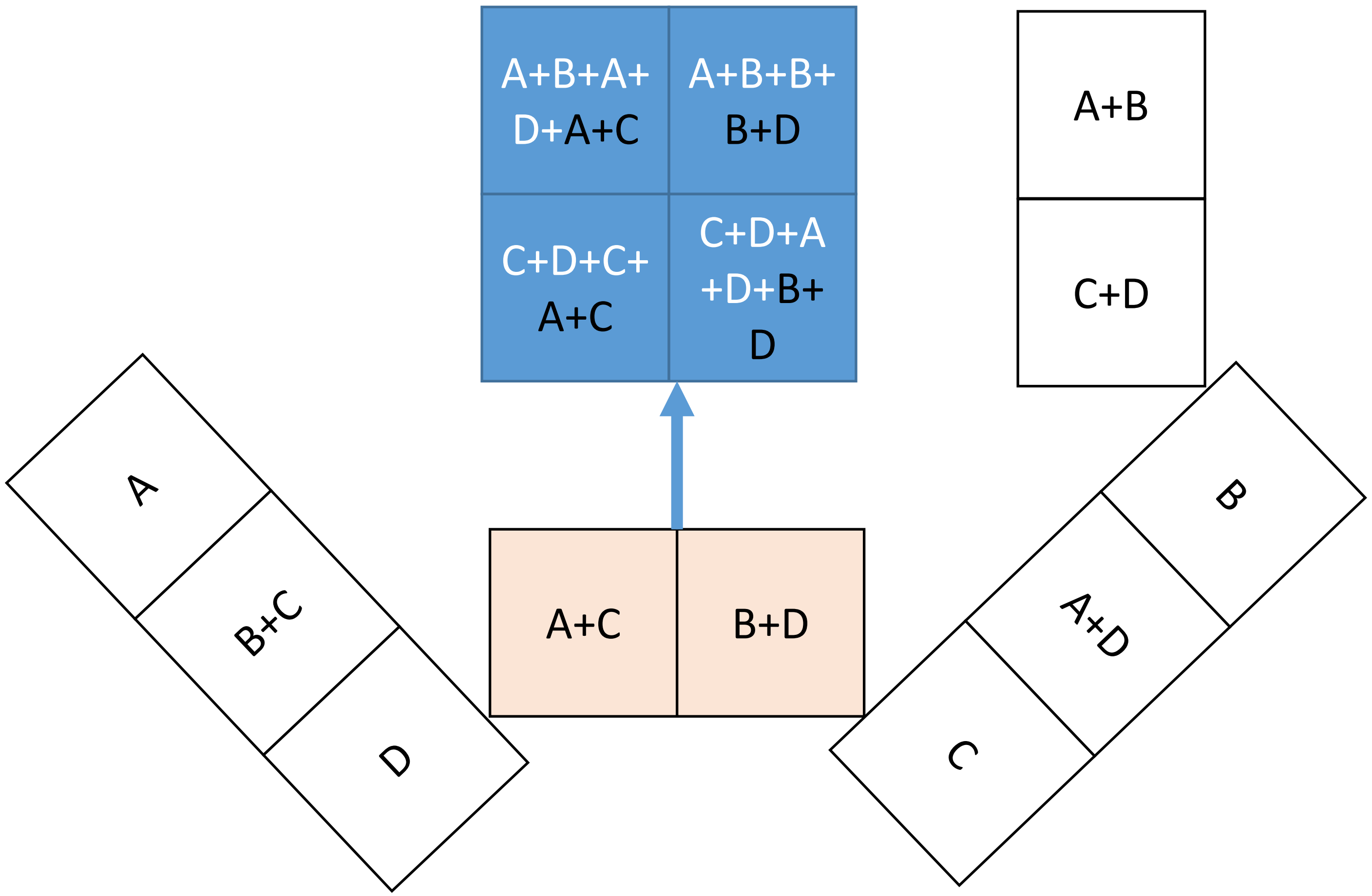
Back projection



http://www.desy.de/~garutti/LECTURES/BioMedical/Lecture7_ImageReconstruction.pdf

Scalar Tomography

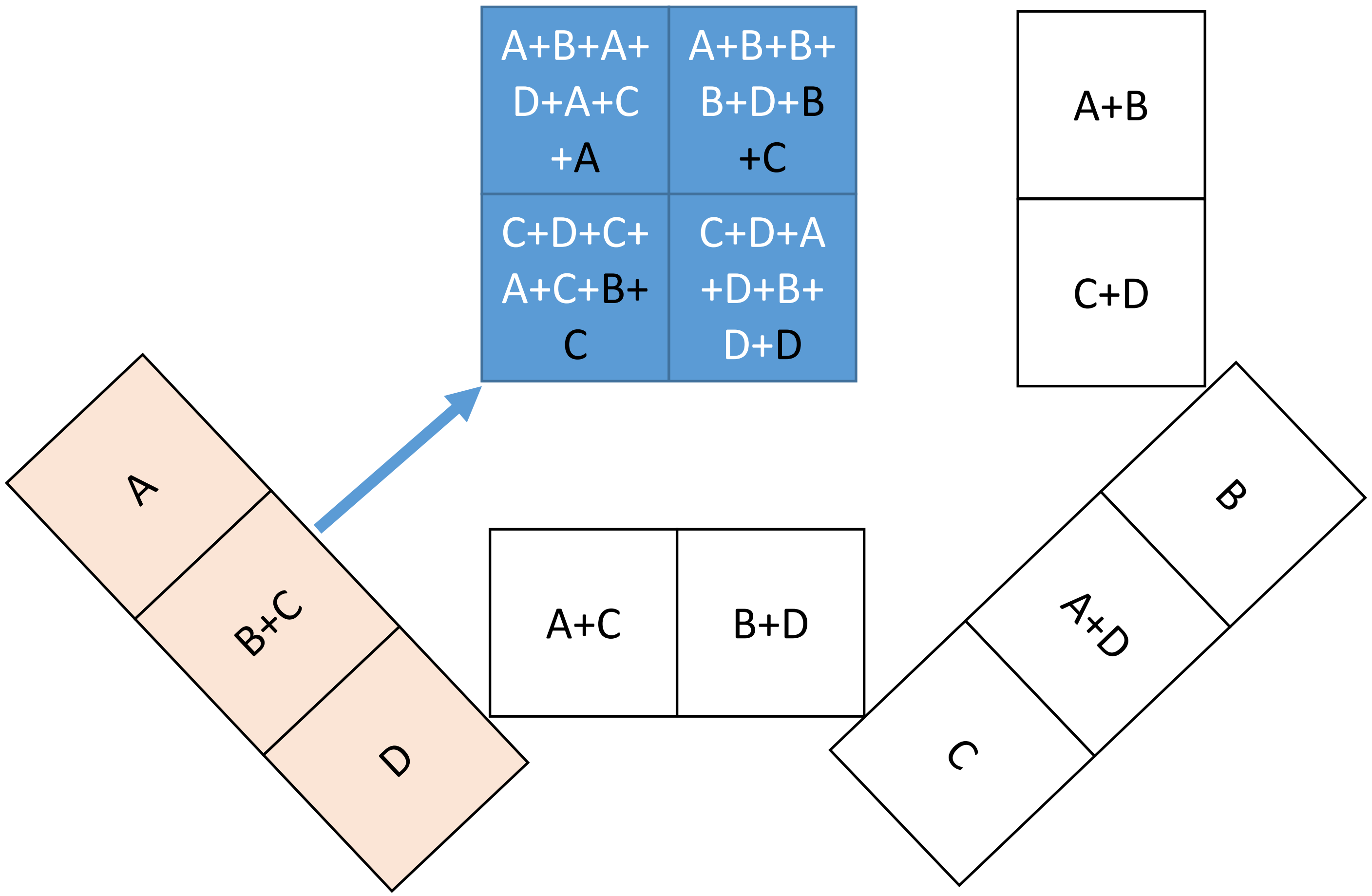
Back projection



http://www.desy.de/~garutti/LECTURES/BioMedical/Lecture7_ImageReconstruction.pdf

Scalar Tomography

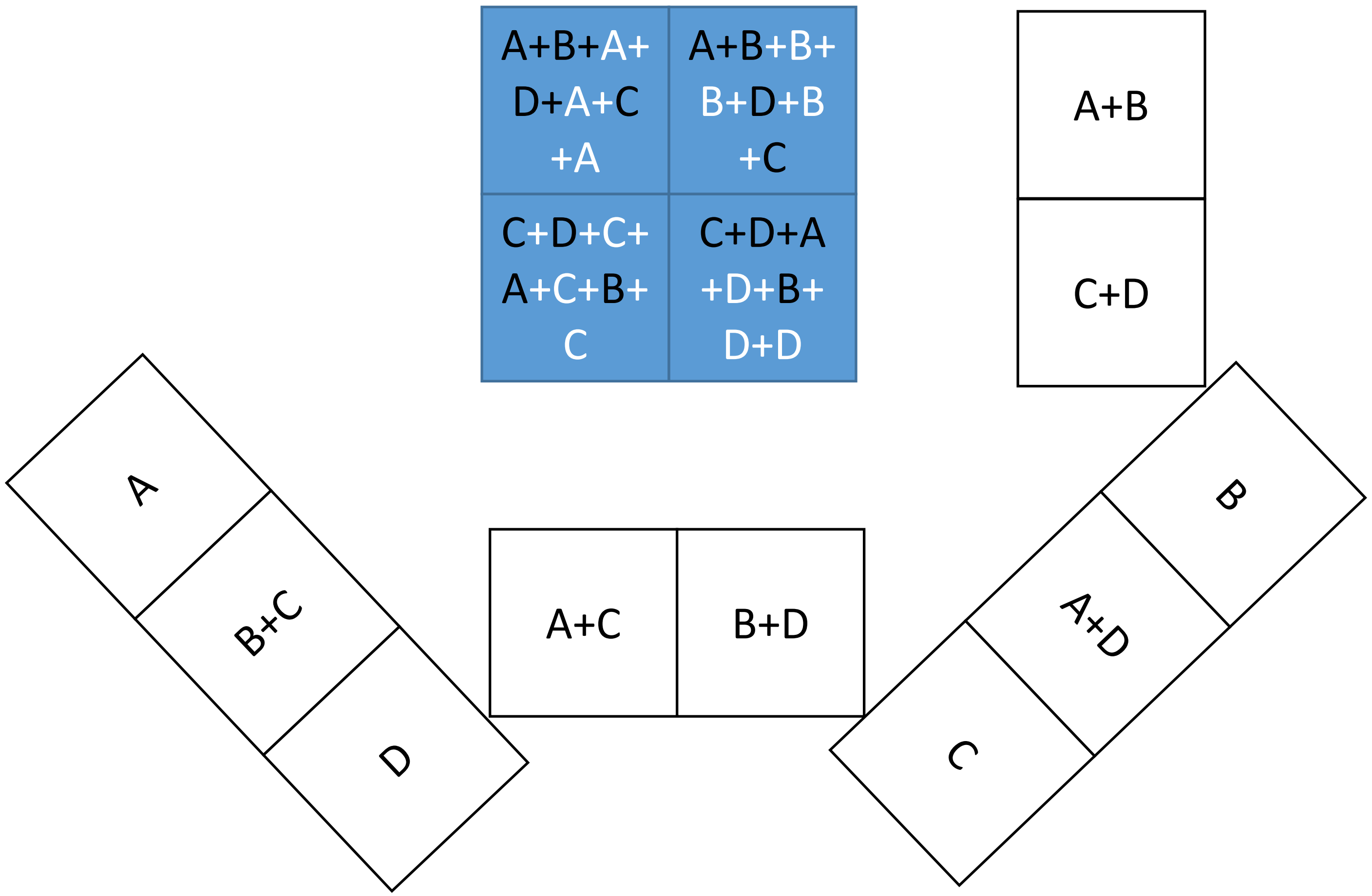
Back projection



http://www.desy.de/~garutti/LECTURES/BioMedical/Lecture7_ImageReconstruction.pdf

Scalar Tomography

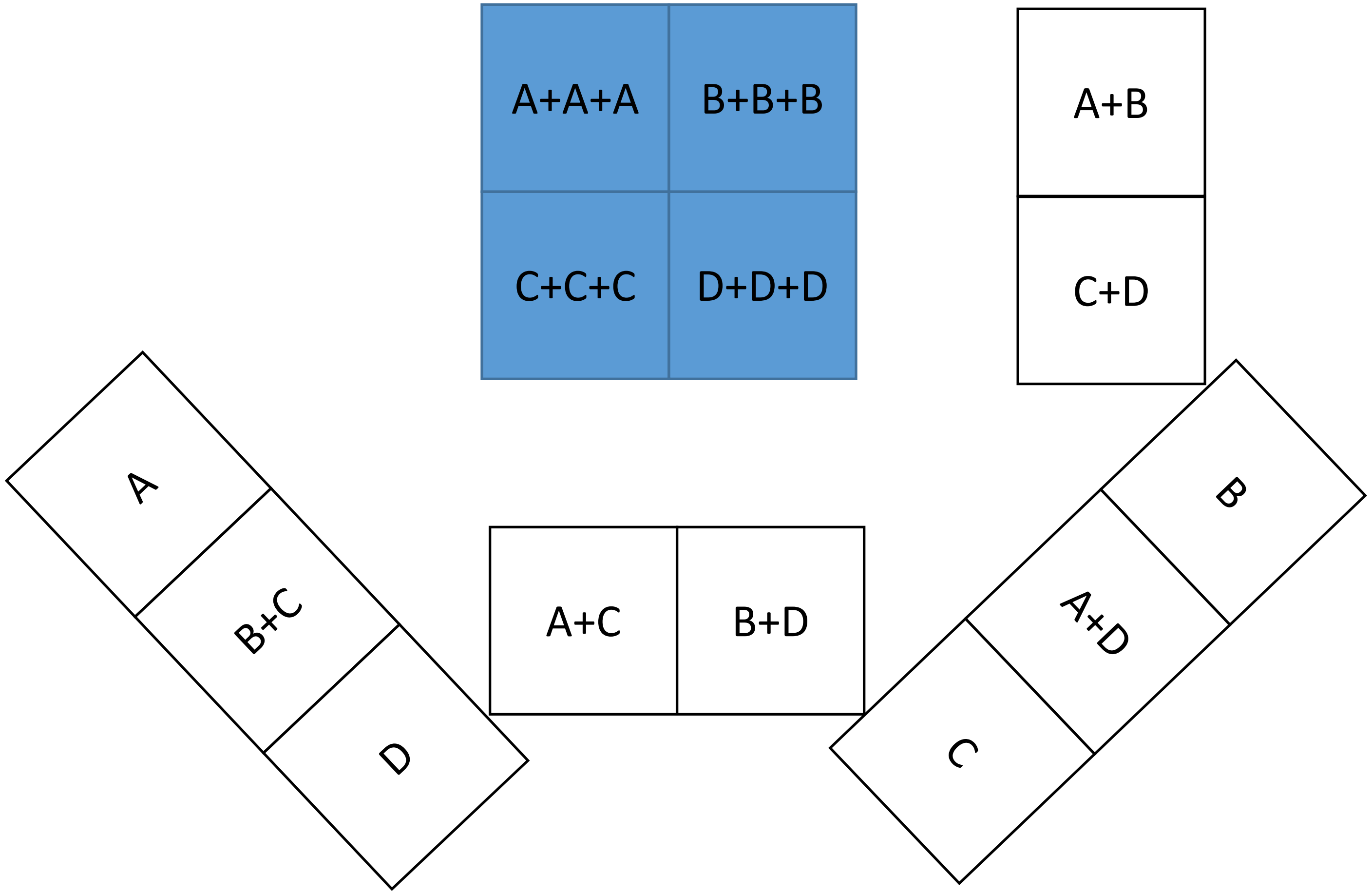
Subtract projection sum



http://www.desy.de/~garutti/LECTURES/BioMedical/Lecture7_ImageReconstruction.pdf

Scalar Tomography

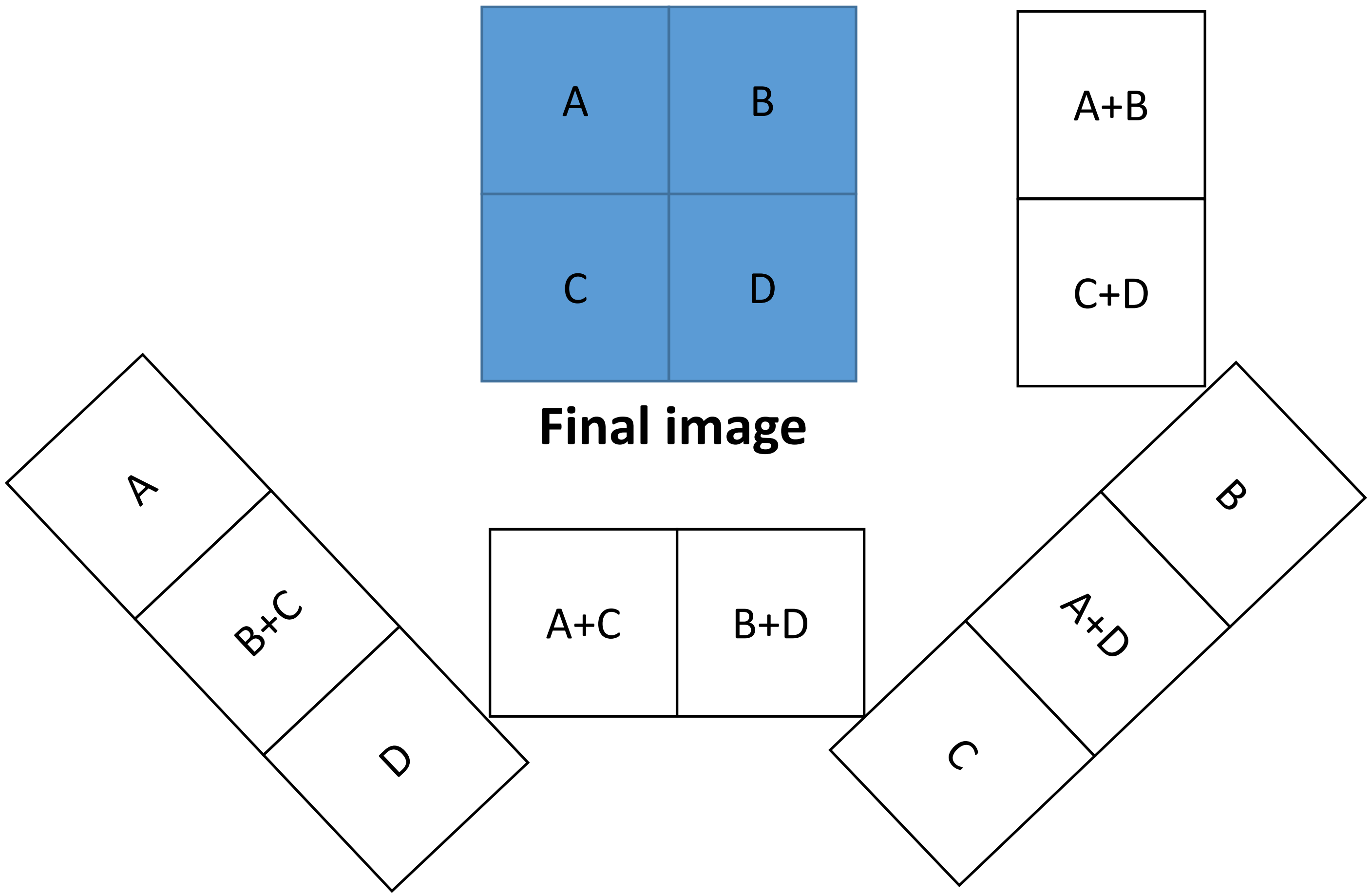
Subtract projection sum



http://www.desy.de/~garutti/LECTURES/BioMedical/Lecture7_ImageReconstruction.pdf

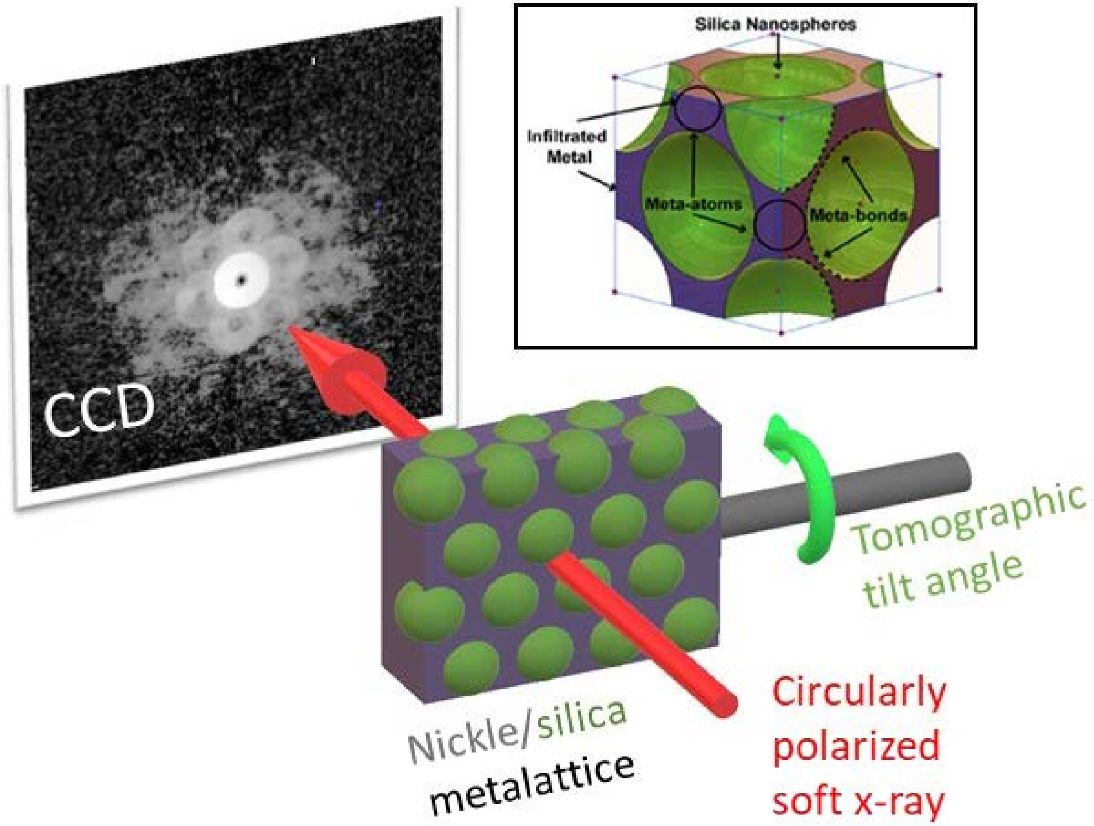
Scalar Tomography

Divide by (N-1)
N = # projections

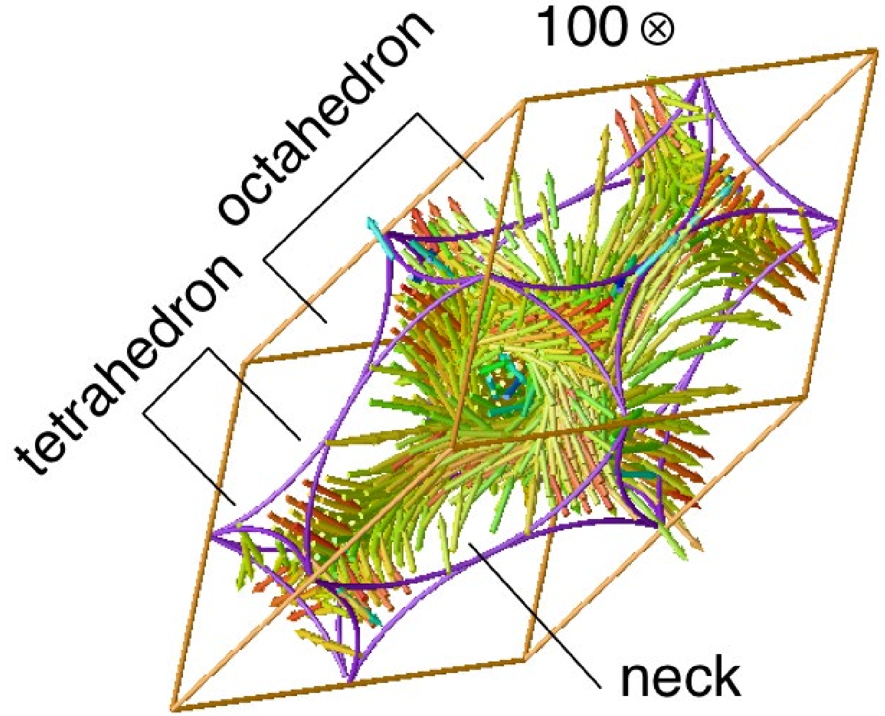


http://www.desy.de/~garutti/LECTURES/BioMedical/Lecture7_ImageReconstruction.pdf

Scalar tomography of Ni metalattice



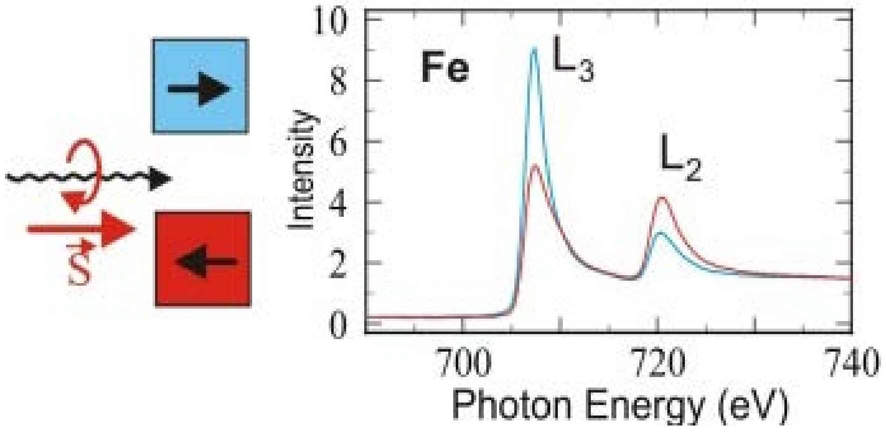
Scalar tomography of Ni metalattice



Han, Crespi, *Phys. Rev. Lett.* 2002

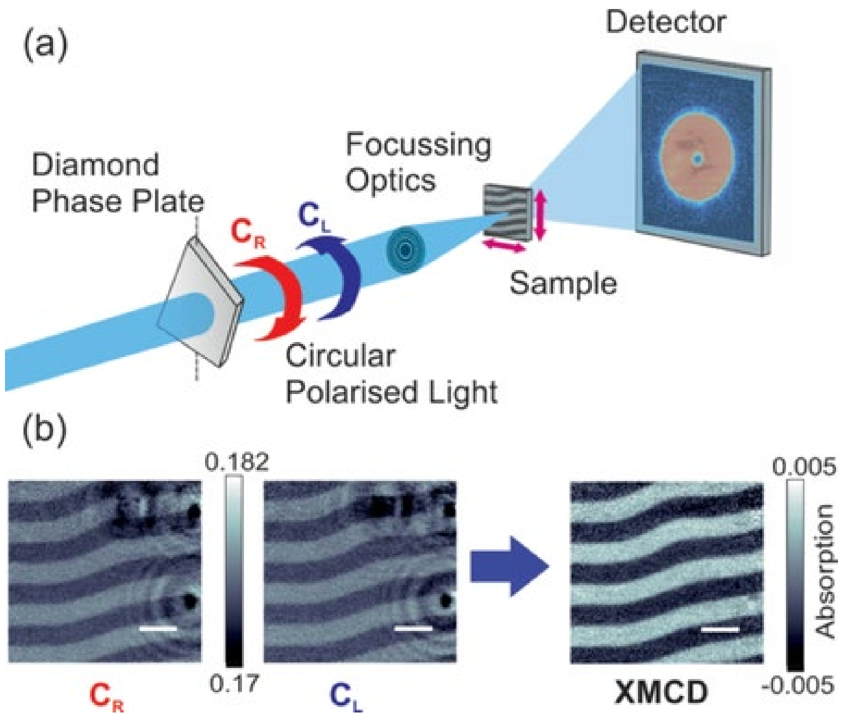
Imaging magnetism – XMCD ptychography

XMCD Spectroscopy



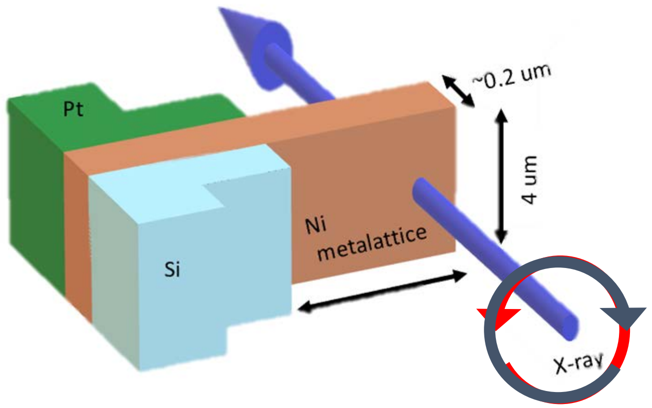
https://www-ssrl.slac.stanford.edu/stohr/xmcd.htm

Imaging: Combine XMCD with STXM or ptychography



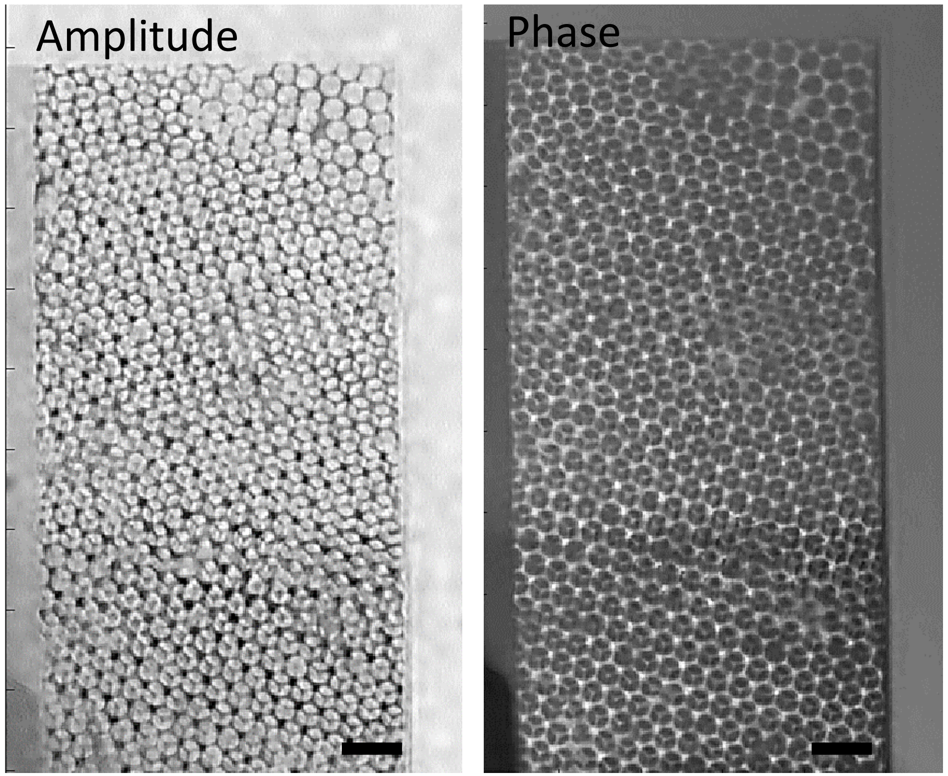
https://www.psi.ch/en/lmx-mesosys/scientific-highlights/high-resolution-hard-x-ray-magnetic-imaging-with-dichroic

Imaging magnetism in Ni metalattice



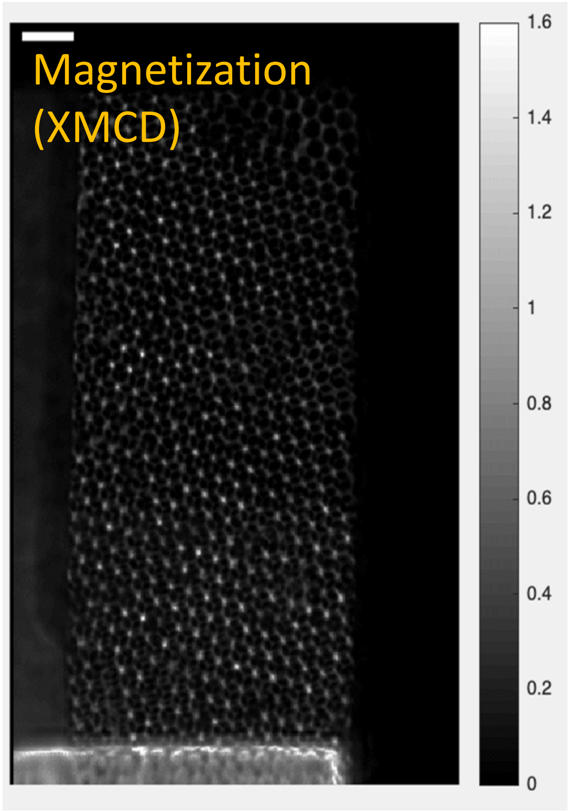
2 types of data

Electron density (absolute absorption)

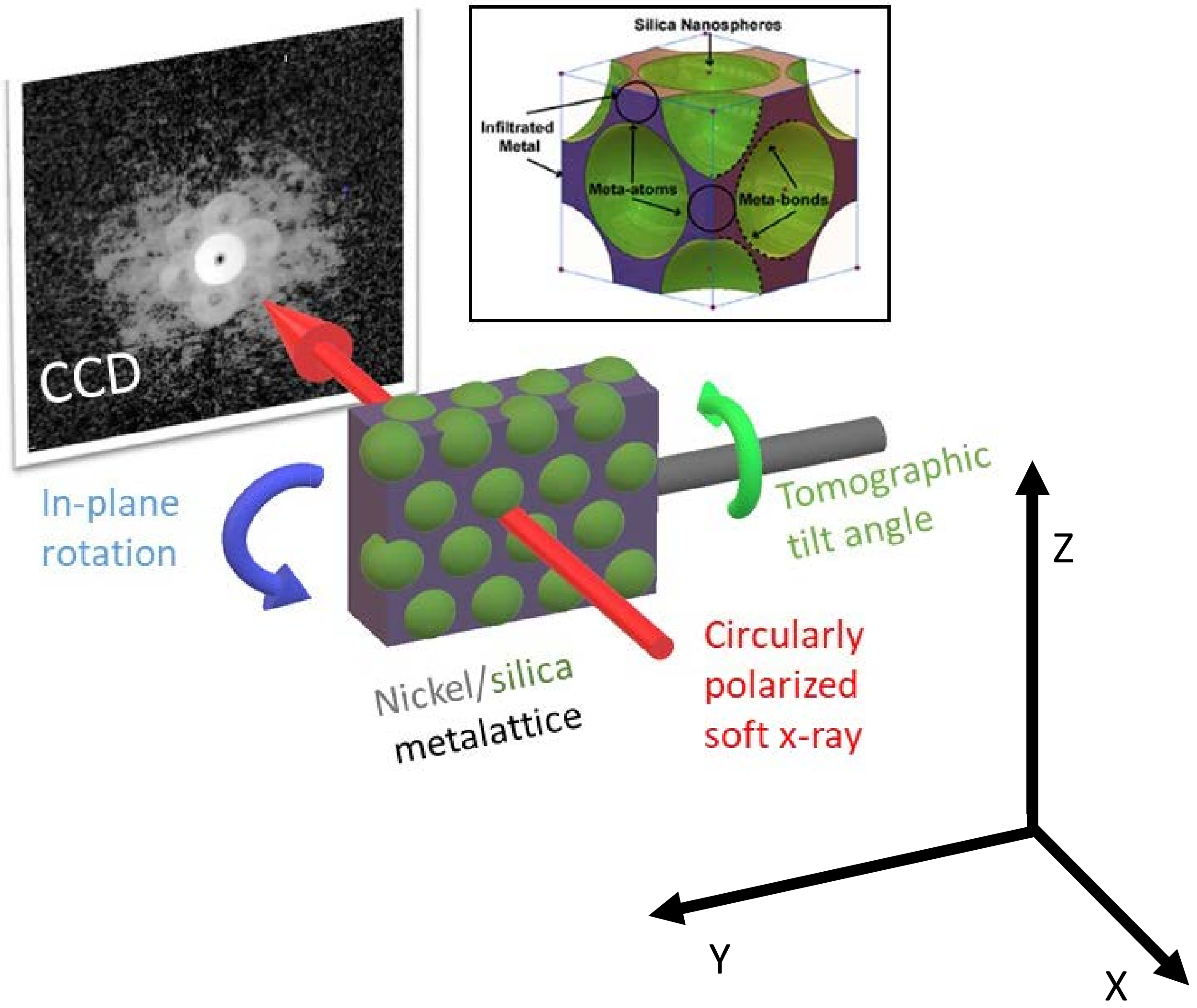


200 nm

Magnetic field intensity
(differential absorption)



Vector ptycho-tomography



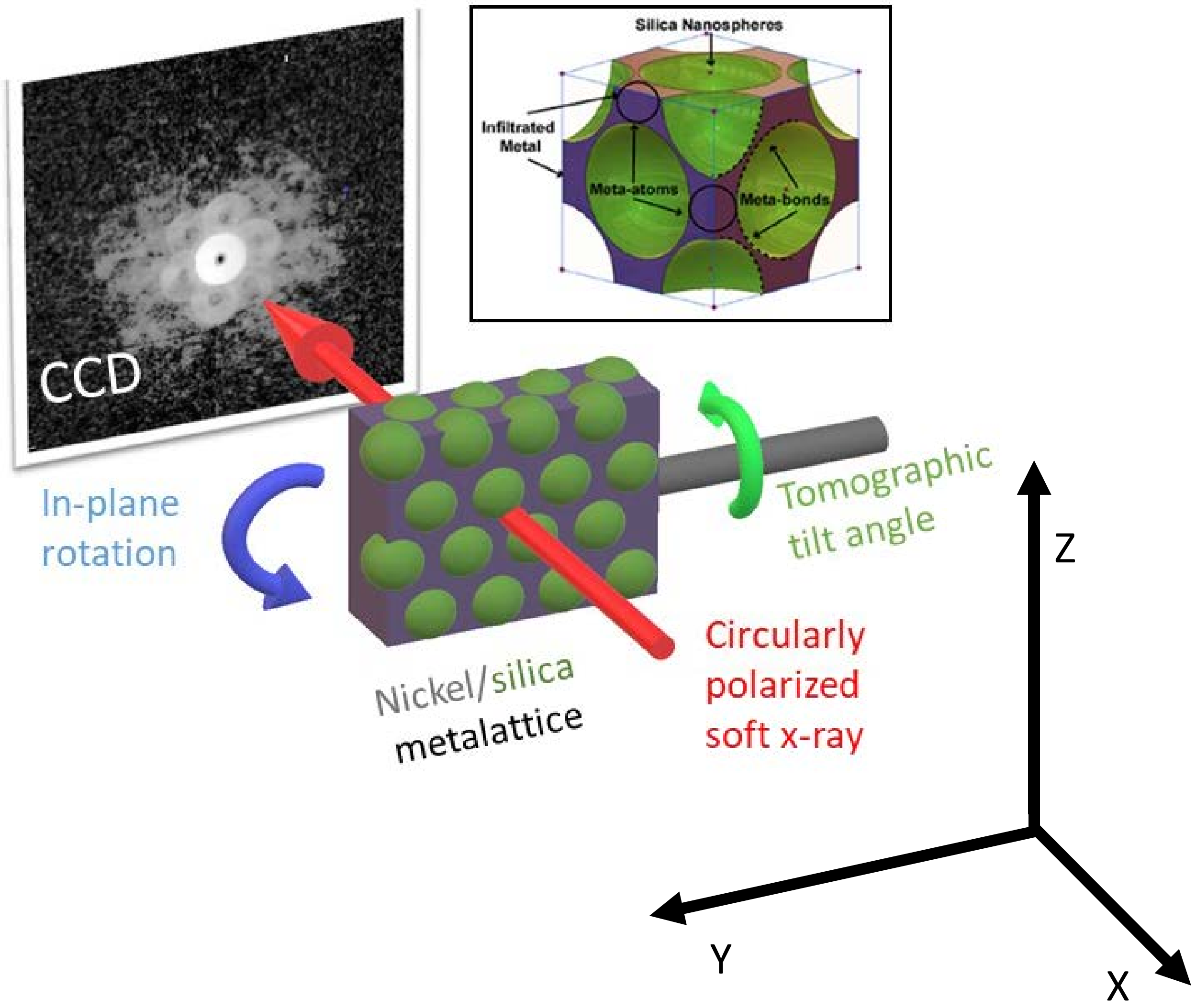
Scalar tomography only sees the intensity in a voxel.

XMCD provides the portion of the magnetic field vector that is parallel to the incoming light.

In this configuration, by rotating around the Y axis, we can learn about X and Z axis magnetization, but nothing about Y axis.

By rotating around the X axis we can learn about the Y component of the vector.

Vector ptycho-tomography



Data collection:

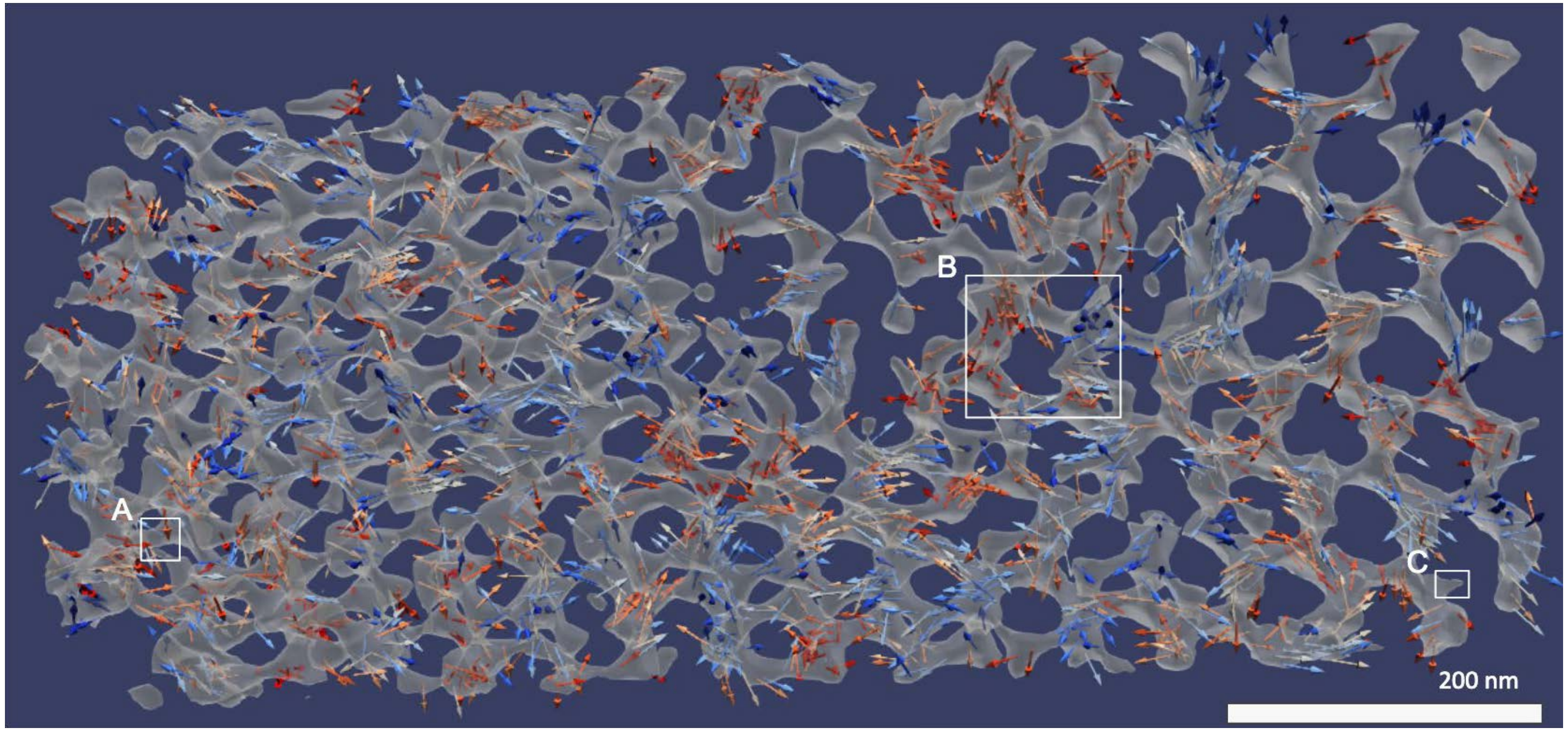
At each of 3 in-plane rotations

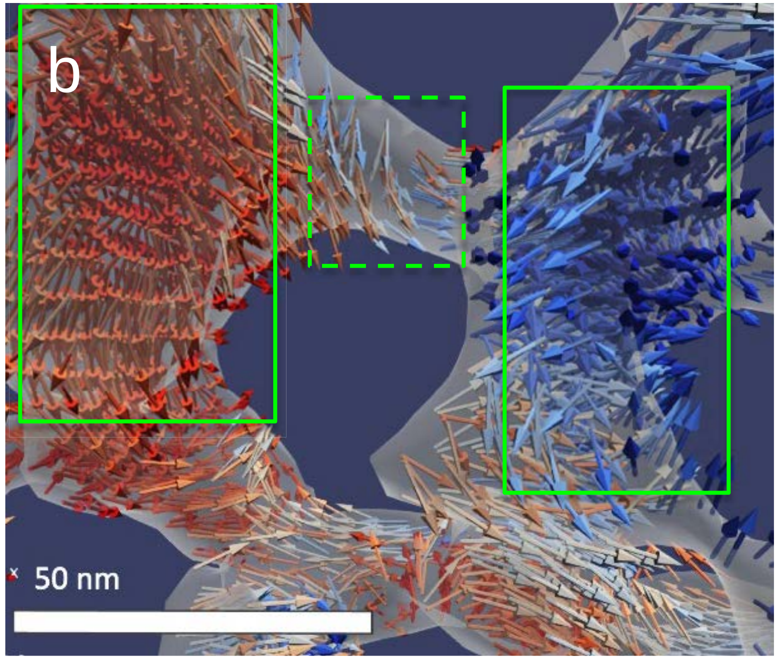
↳ At each of 40 tilt angles

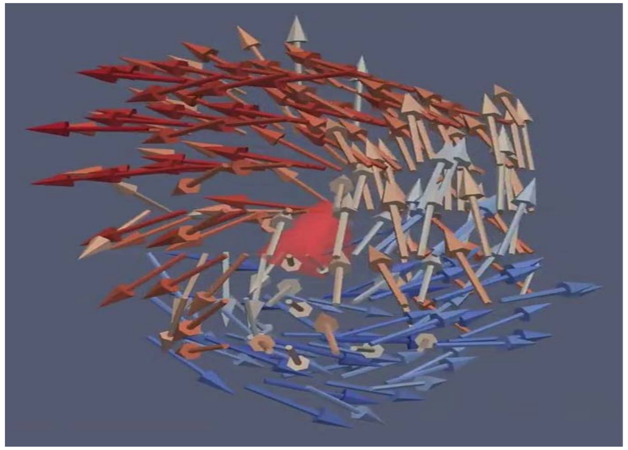
↳ Ptychographic imaging with L and R polarized light to calculate XMCD

Note that 3 in-plane rotations are not strictly necessary for vector tomography, but redundant data aids our reconstruction.

Vector ptycho-tomography

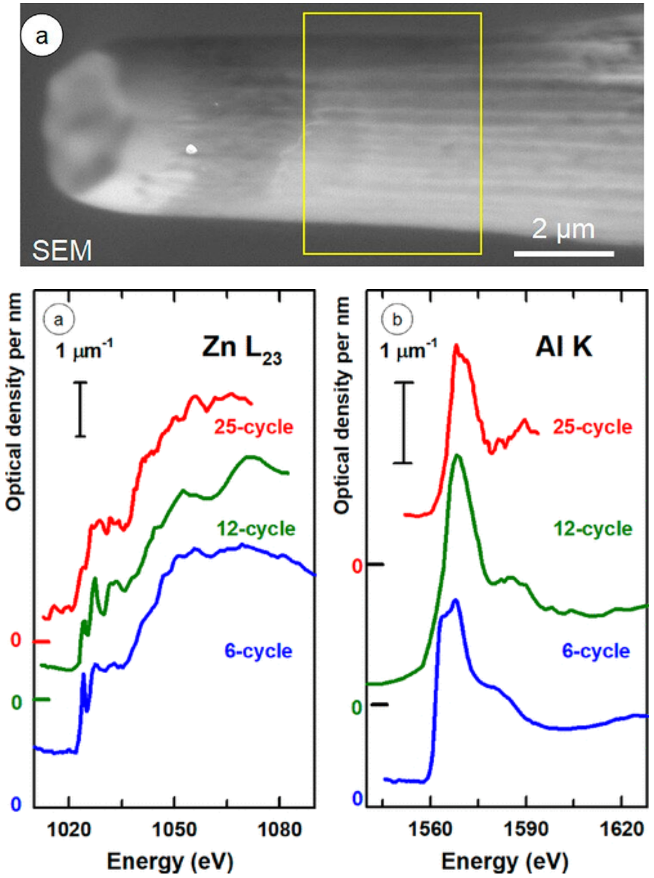


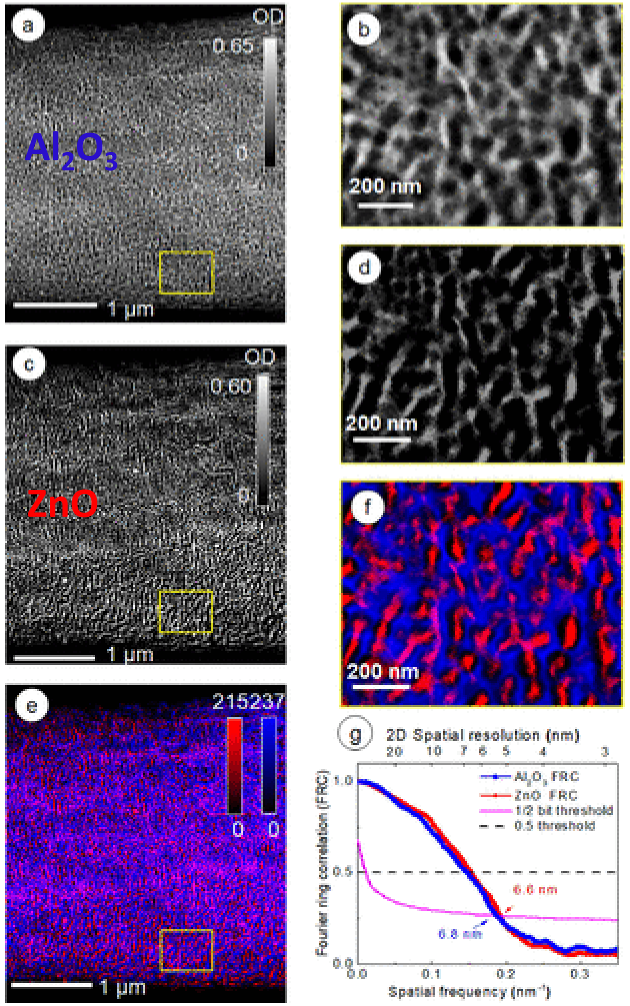




4D Spectromicroscopy

ZnO Loaded Al_2O_3 Aerogel Catalyst:



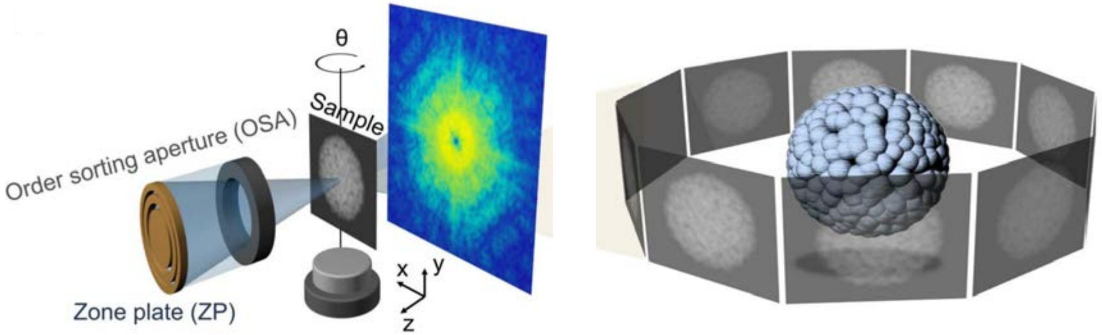


Ptychographic Image Sequence:

Varying energies and tilt angles

Hao Yuan, *et al. ACSANM 2021*

Ptychographic Tomography:



Jungjin Park, Young-Sang Yu, Jang-Wook Choi (Seoul National Univ.), *in preparation*

Chemically Sensitive Ptychographic Tomography:

Quantitative chemical information in 3D

Structure

Porosity

Reconstructed voxel size: $5 \times 5 \times 5$ nm^3

3D resolution : 9 nm

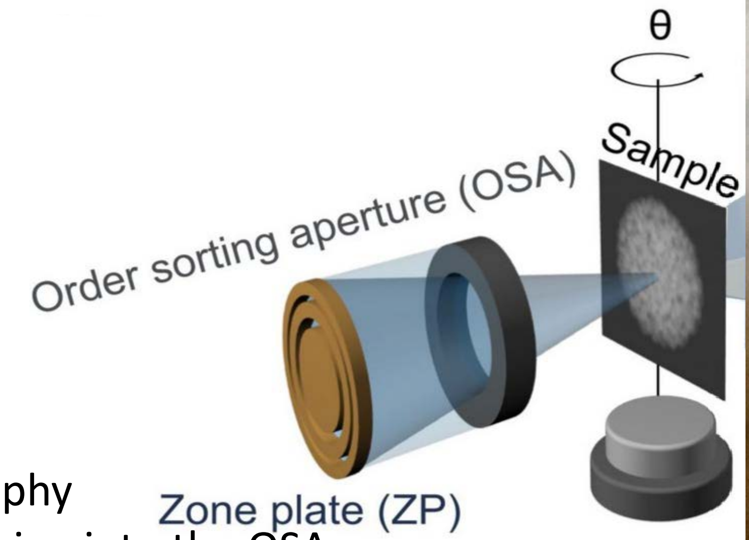
Challenges

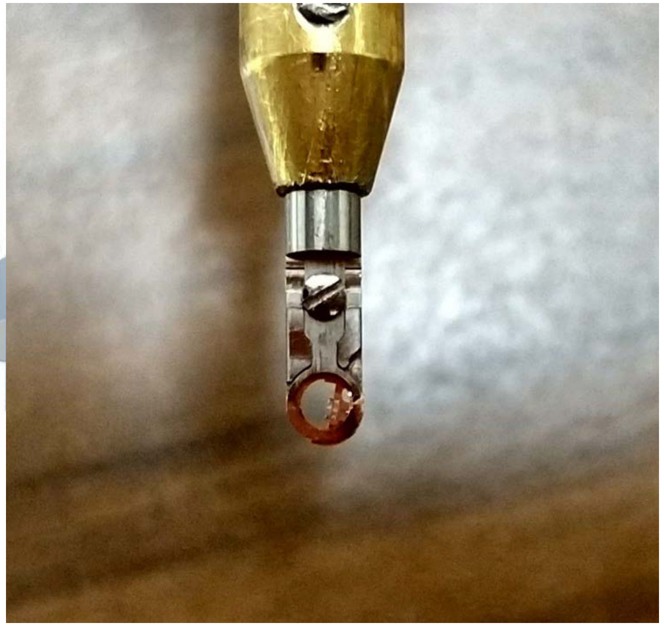
Stage stability
- Depending on sample holder, motor may require some settling time

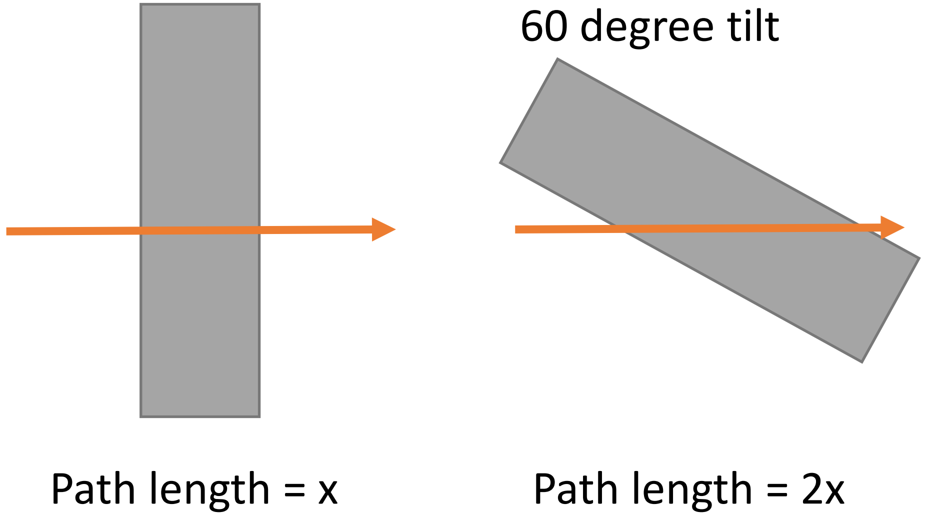
Sample preparation
- Need at minimum +/- 50 degrees of tilt for tomography
    - Many holders cannot achieve this without running into the OSA, sample must be on 3 mm TEM grid
    - System designed for **transmission** samples: sample must not be too thick or have features that block the light at high tilt angles

Spectroscopic concerns
- Substrate must be transparent to your desired wavelengths
    - This often gives a wider range of options than electron microscopy, however (material and sample holder dependent)
- For magnetic samples, need to ensure magnetization direction is parallel to beam propagation

DATA
- Single tomographic image can take ~10 TB of data to produce







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U.S. DEPARTMENT OF ENERGY Office of Science