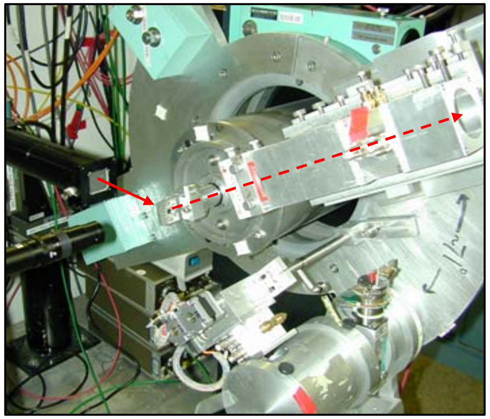
Introduction to Synchrotron X-ray Scattering Techniques

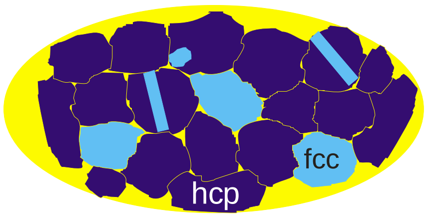
Mike Toney, (SSRL)

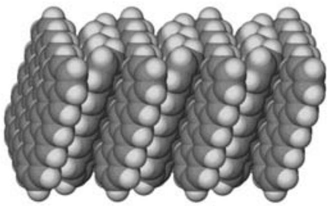
1. Why do x-ray scattering?
2. Typical SR x-ray scattering experiment
3. Stuff we will cover (SAXS, Powder, Amorphous, Thin Films: random, textured, epitaxial, Surfaces)
4. Some examples
   a. SAXS: porous films
   b. Powder: Mn oxides
   c. Textured thin films: pentacene
   d. Epitaxial Film: oxidzed Fe
5. Summary



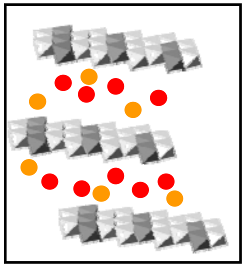
Why do SR X-ray scattering?

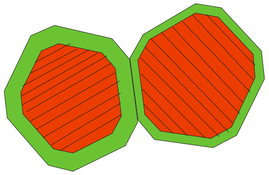
➢ Really interesting materials with really great properties. Want to understand properties (structure – property). Improve your materials.

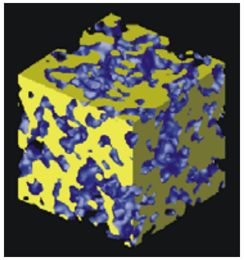


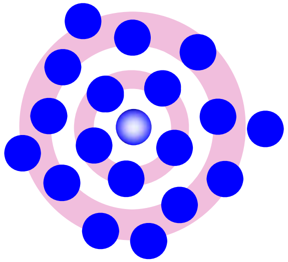


- Phase identification & quantify
- Where are the atoms: Atomic or molecular arrangement, crystal & surface structure
- Strain, lattice parameters (unit cell size)
- Grain/crystallite size (diffraction)
- Pore/particle size (SAXS)
- Other defects & disorder (faults)
- Crystallite orientation or texture
- Atomic environment (amorphous)

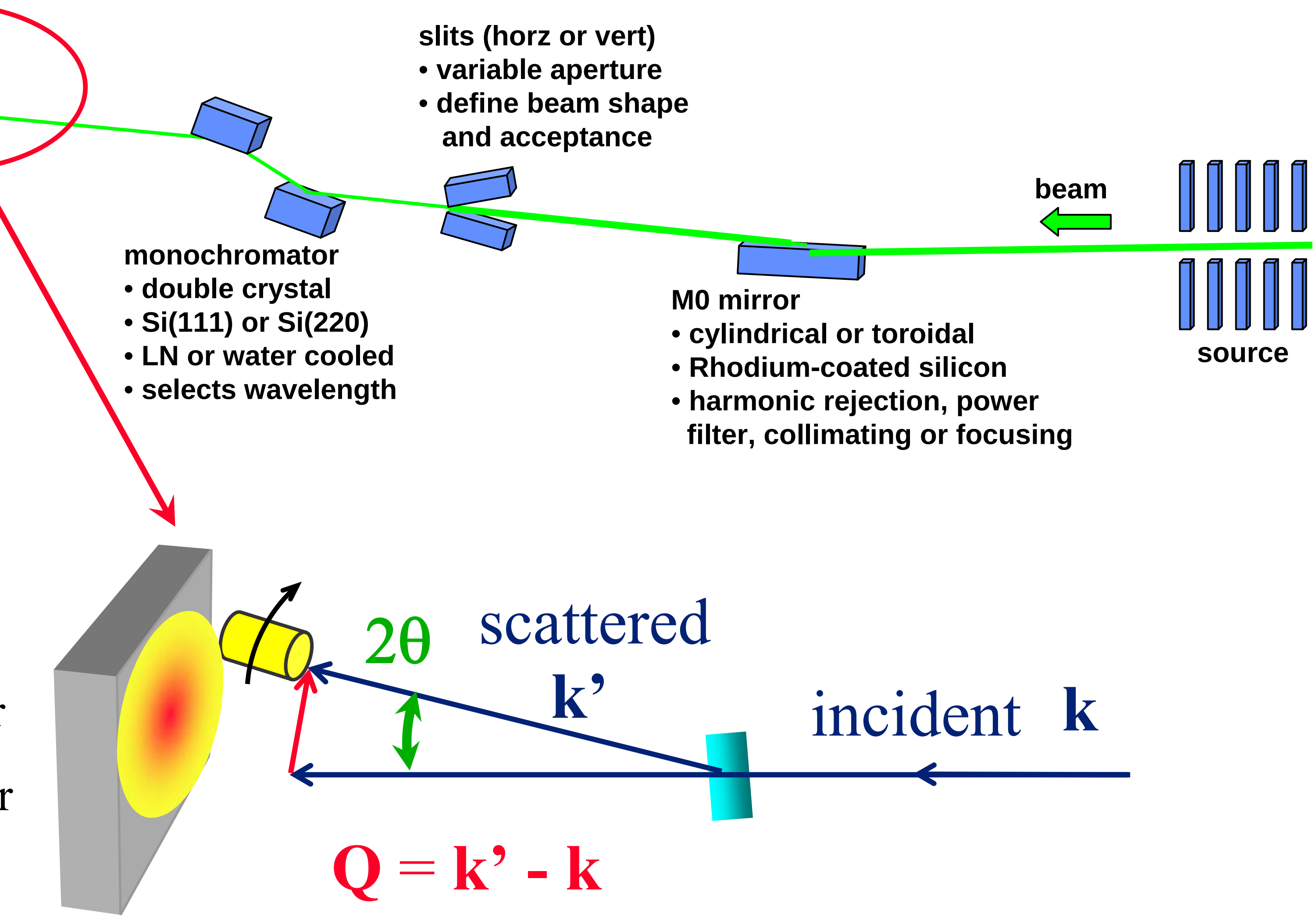








SR Scattering Experiment

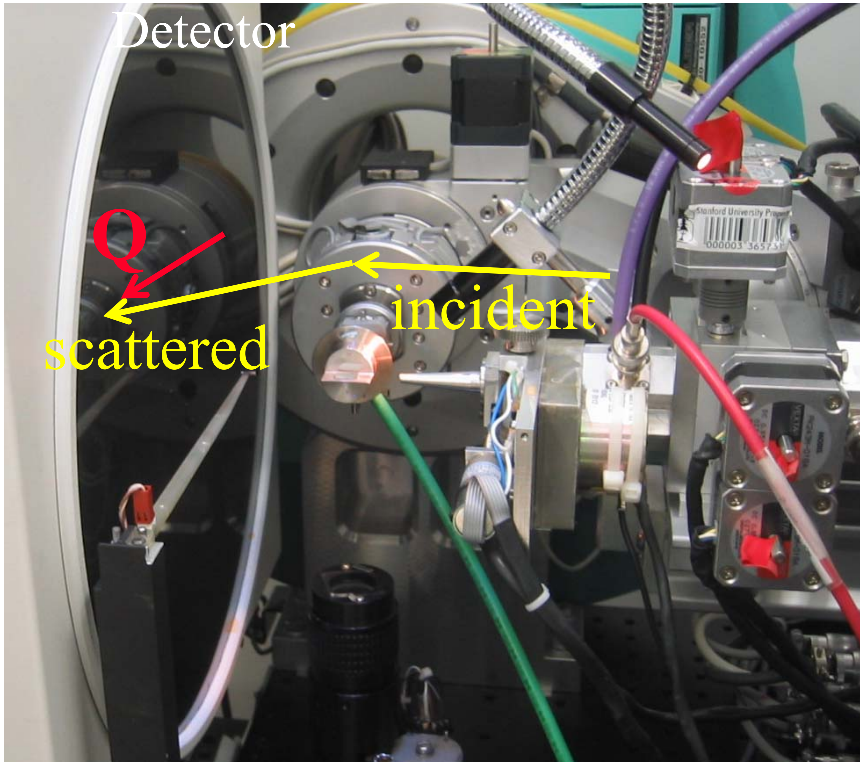


collect I(Q)

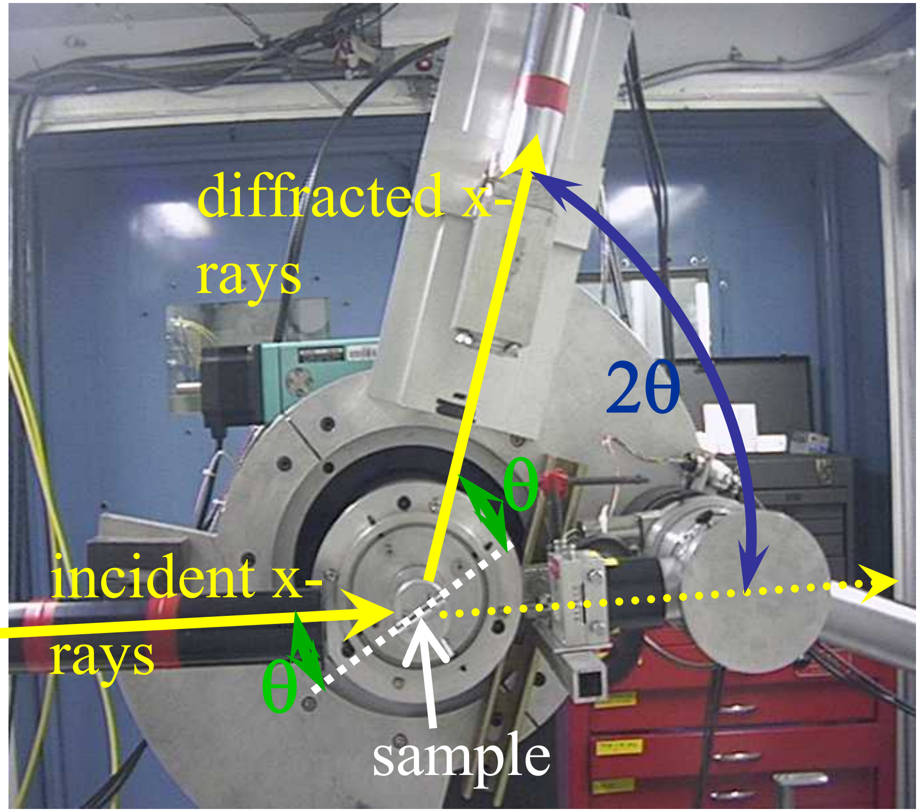
All you care about is **Q**

SR Scattering Experiment

Area (11-3)



Point (2-1, 7-2)



2θ = scattering angle

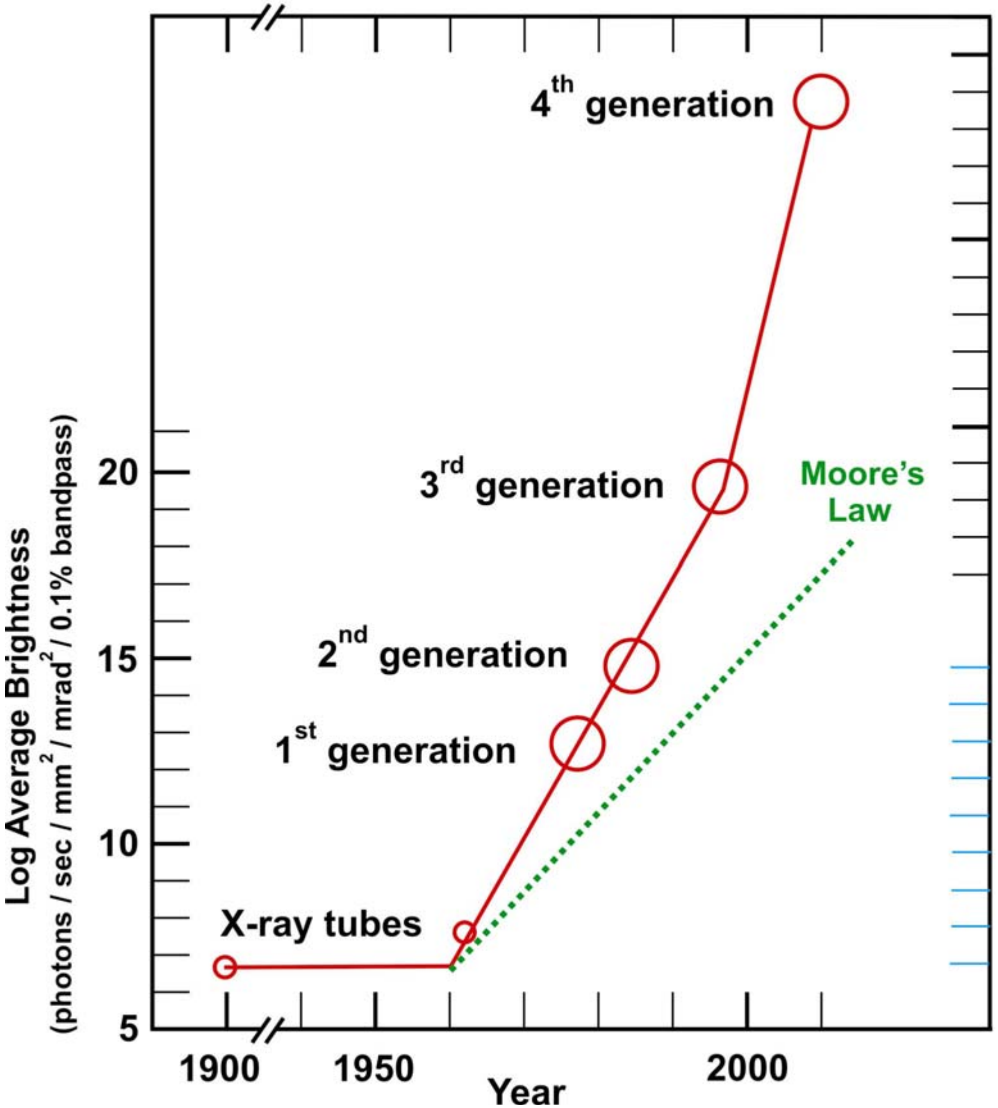
Q = (4π/λ) sin θ

Which to use?

Depends on sample (more latter)

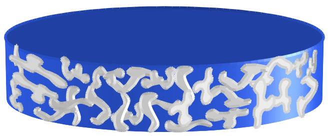
Synchrotron Radiation Advantages

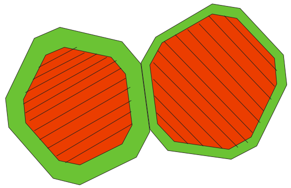
- Lots more flux
- High Collimation
- Tunable Energy (Wavelength)

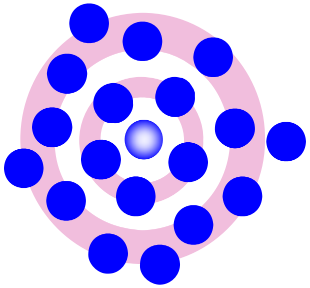


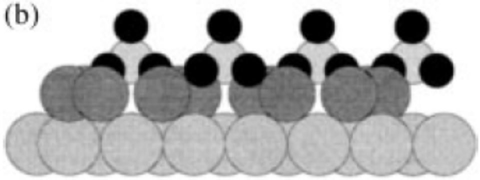
What we will cover today

- Small Angle X-ray Scattering (SAXS)
  - probes structures 1-100 nm
- Powder Diffraction includes in-situ
  - random or isotropic; nanoparticles
- Amorphous Materials
  - no crystalline order
- Thin Films: random, textured, epitaxial
  - wide variety
- Surface Scattering
  - atomic structure at surface or interface



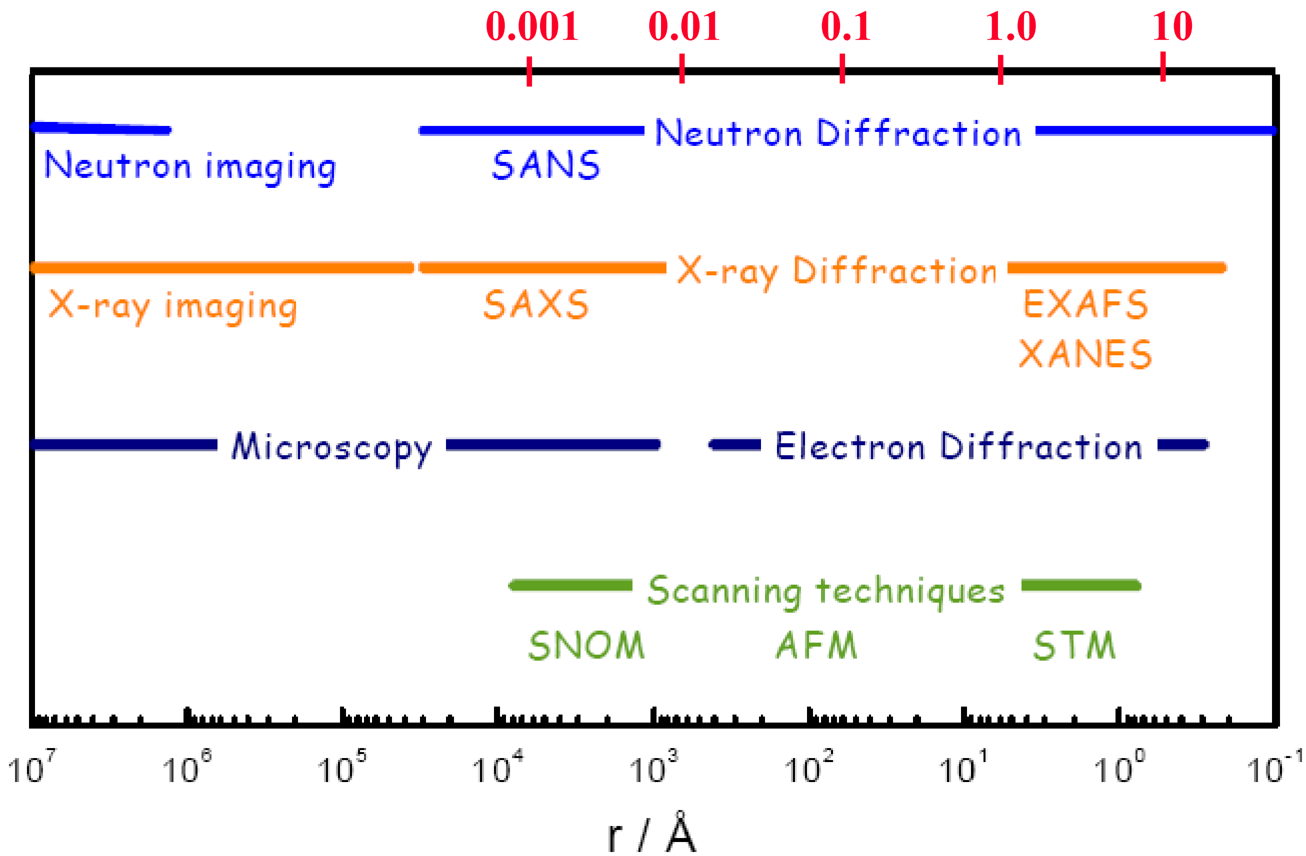






Lengths Accessed by Probes

$Q \sim (2\pi/r)$



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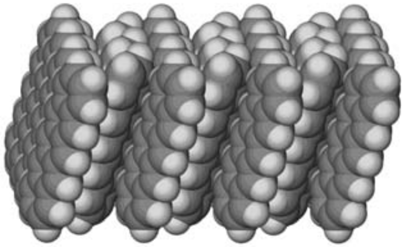
Summary: SR Scattering

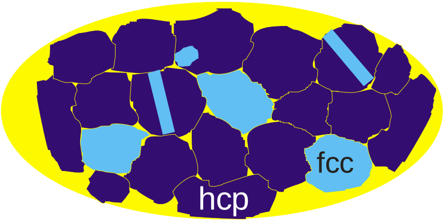
SR Scattering:

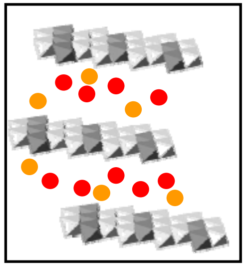
- **Q** is important variable: measure I(**Q**)
- choose Q to match length scale
- variety of materials

What can we learn:

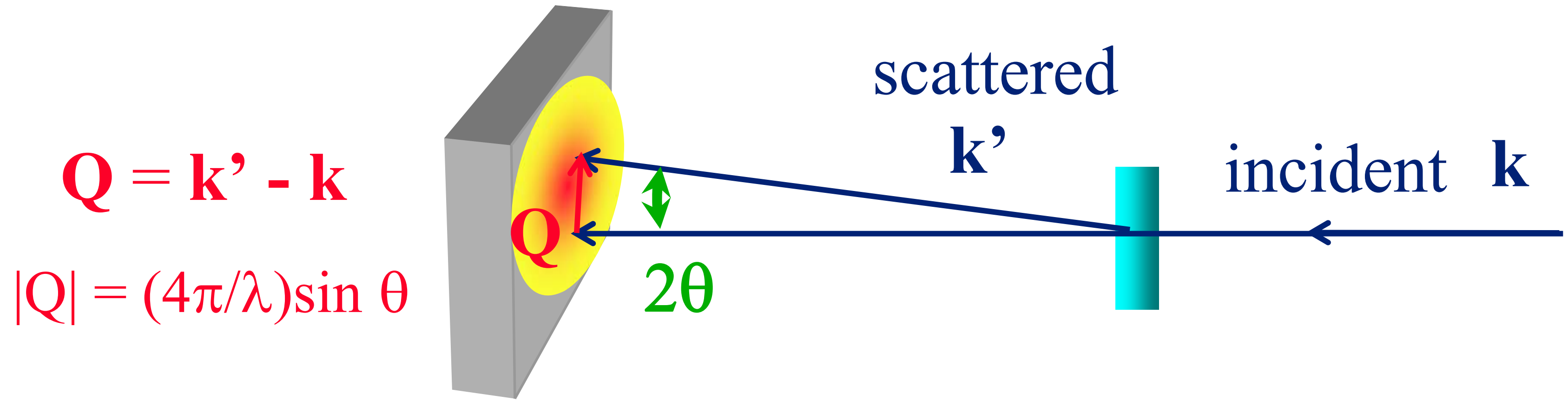
- Phase identification & quantify
- Where are the atoms: crystal & surface structure
- Strain, lattice parameters
- Grain/crystallite size
- Pore/particle size
- Other defects & disorder
- Crystallite orientation or texture
- Atomic environment (amorphous)



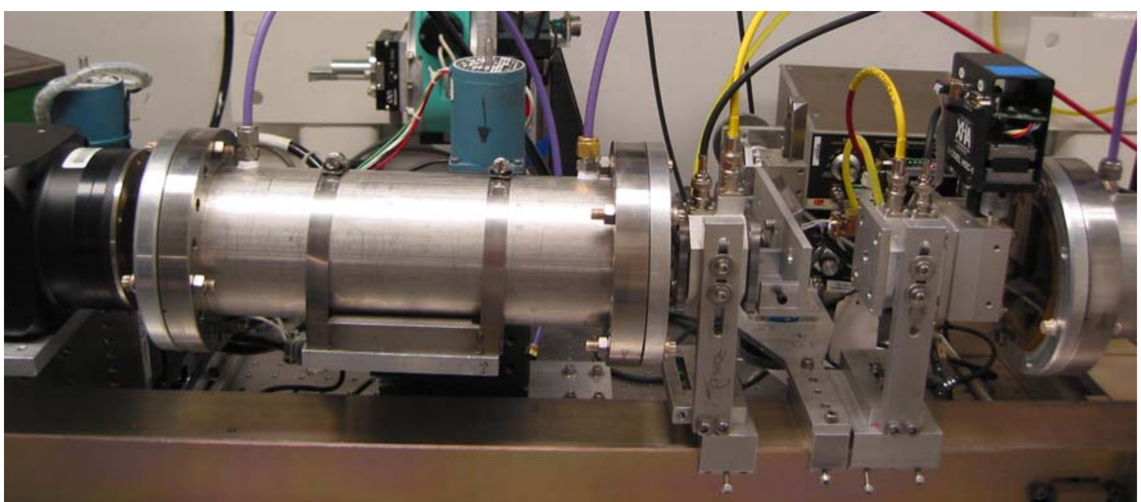




Small Angle Scattering

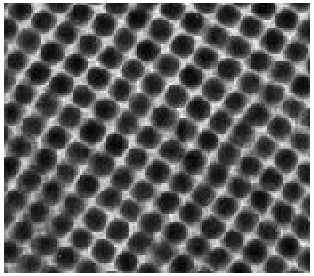


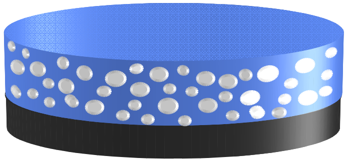
- Measure I(Q) with Q ~ 0.0001 – 1 $Å^{-1}$
- Scattering from 1-100 nm density inhomogeneities



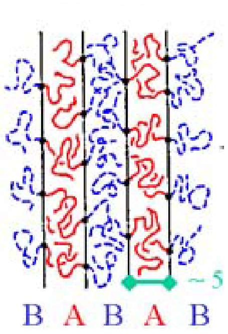
Small Angle Scattering

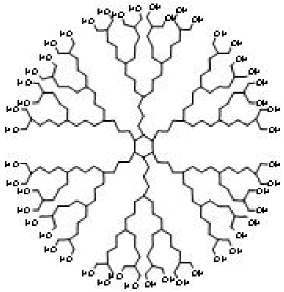
Scattering from density inhomogeneities with sizes 1-100 nm

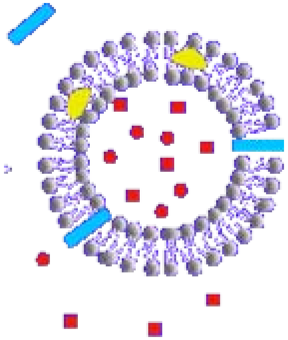


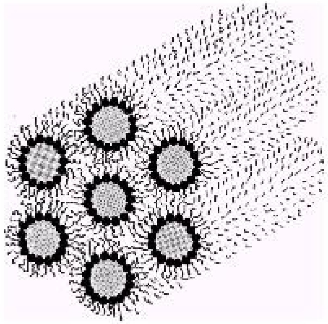


- nanoparticles (catalysts, bio-oxides, geo-oxides)
- nanoporous materials
- co-polymers
- dendimers
- supramolecular assemblies
- micelles
- colloids
- metallic glasses



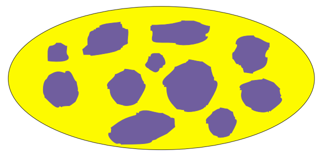




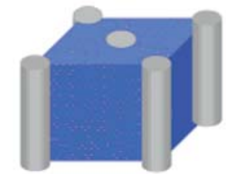


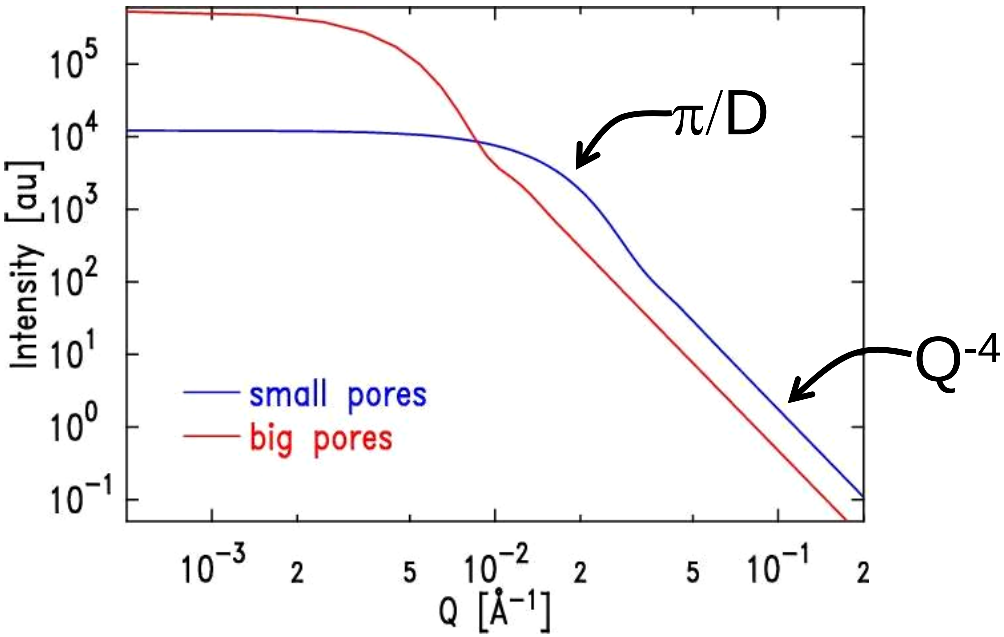
Small Angle Scattering

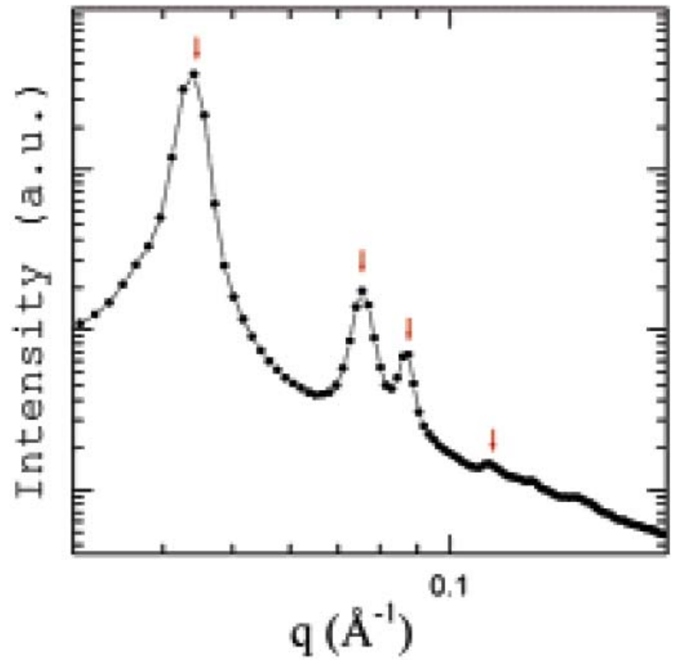
Isolated particles or pores with diameter D



Hexagonal packed cylinders

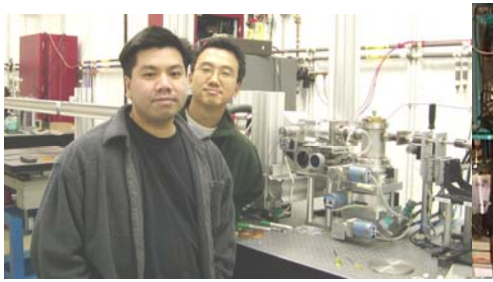






- Need large Q range: $1/D \lesssim Q \lesssim 10/D$

Nanoporous Films



Matrix: Methyl Silsesquioxane (MSSQ), $CH_3SiO_{1.5}$

Porogen (thermally labile polymer):
copolymer poly(methyl methacrylate-co-dimethylaminoethyl methacrylate) or P(MMA-co-DMAEMA)

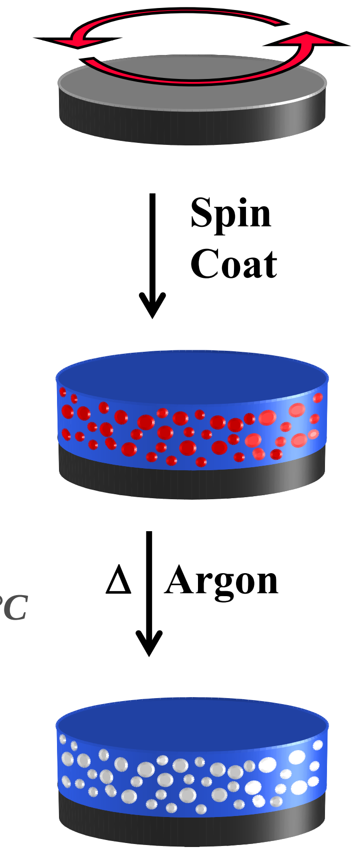
<u>IBM</u>
Elbert Huang
Jonathan Hedstrom
Ho-Cheol Kim
Teddie Magbitang
Robert Miller
Willi Volksen


Funded by NSF-ATP

1. Spin coat MSSQ/Porogen solution
2. Heat to 450°C, at 5°C/min under argon

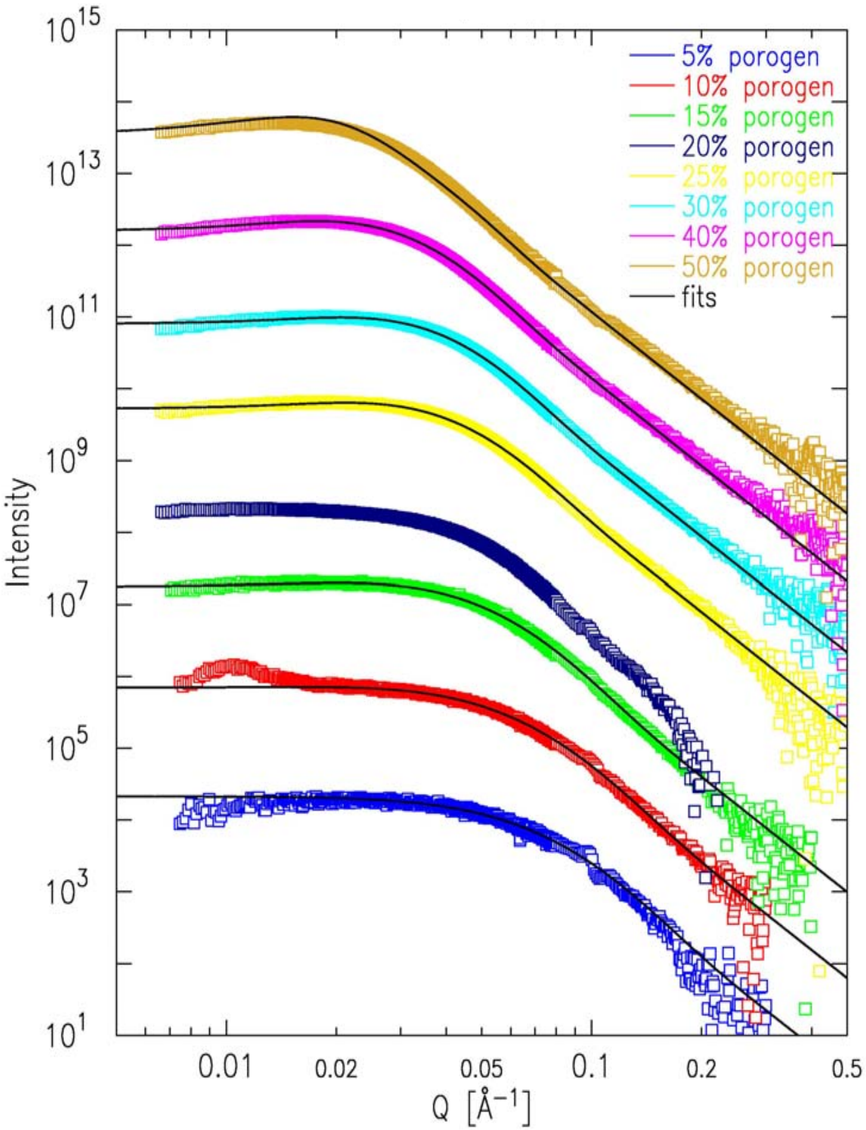
MSSQ crosslinks at 200°C
Poragen fully degrades at 400°C

3. Cool to room temperature

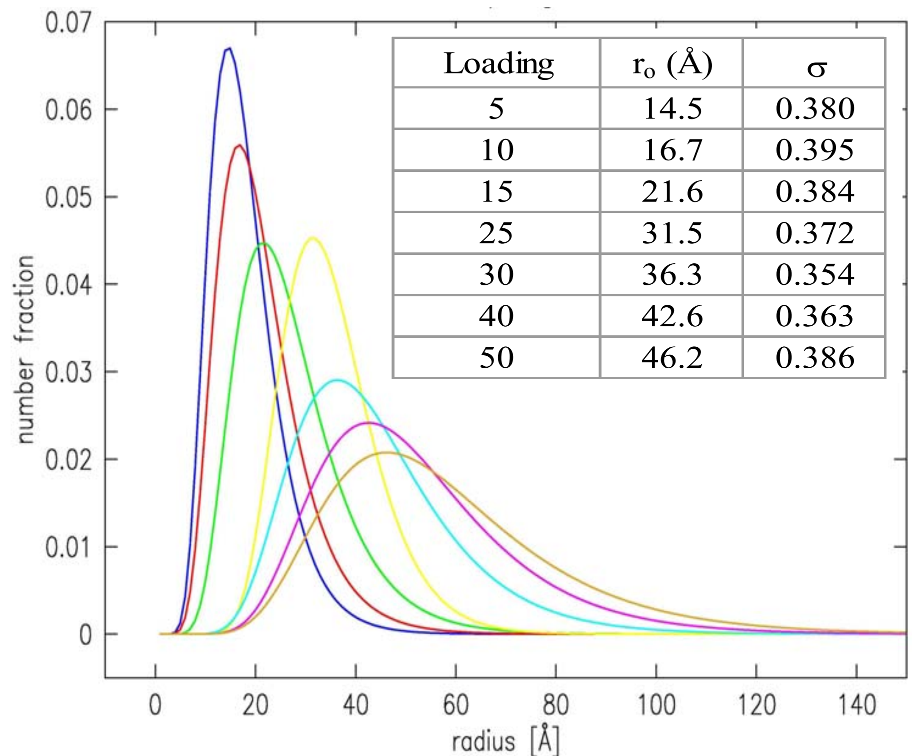


- Huang et al, Appl. Phys. Lett. **81**, 2232 (2002)
- Huang et al., Chem. Mater. **14**, 3676 (2002)
- Magbitang, Adv. Materials. **17**, 1031 (2005)

Nanoporous Films: SAXS



Huang et al, Appl. Phys. Lett. 81, 2232 (2002)

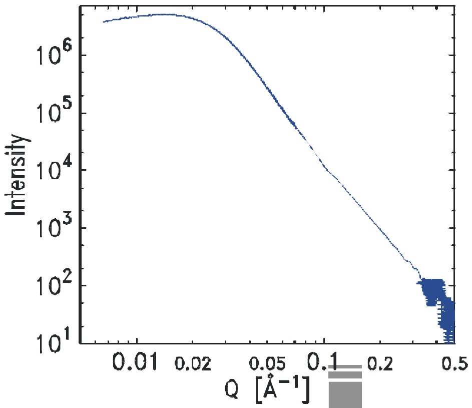


Loading	r_o (Å)	σ
5	14.5	0.380
10	16.7	0.395
15	21.6	0.384
25	31.5	0.372
30	36.3	0.354
40	42.6	0.363
50	46.2	0.386

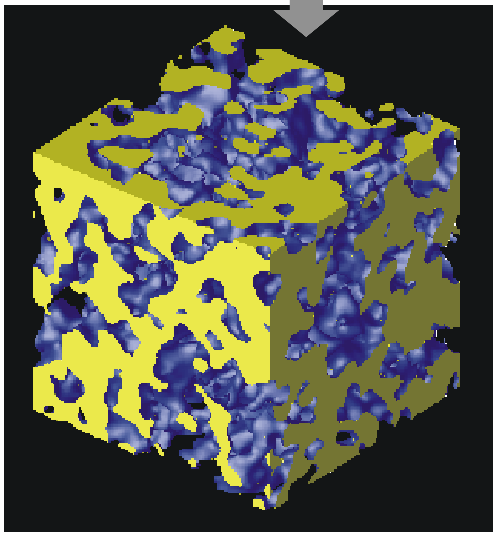
Find:

- reasonably small pores (good)
- board distribution of pore sizes (bad)
- size increases with loading => agglomeration (bad)

Nanoporous Film Morphology



Goal: obtain representative real space picture (correct size scale and extent of interconnection)



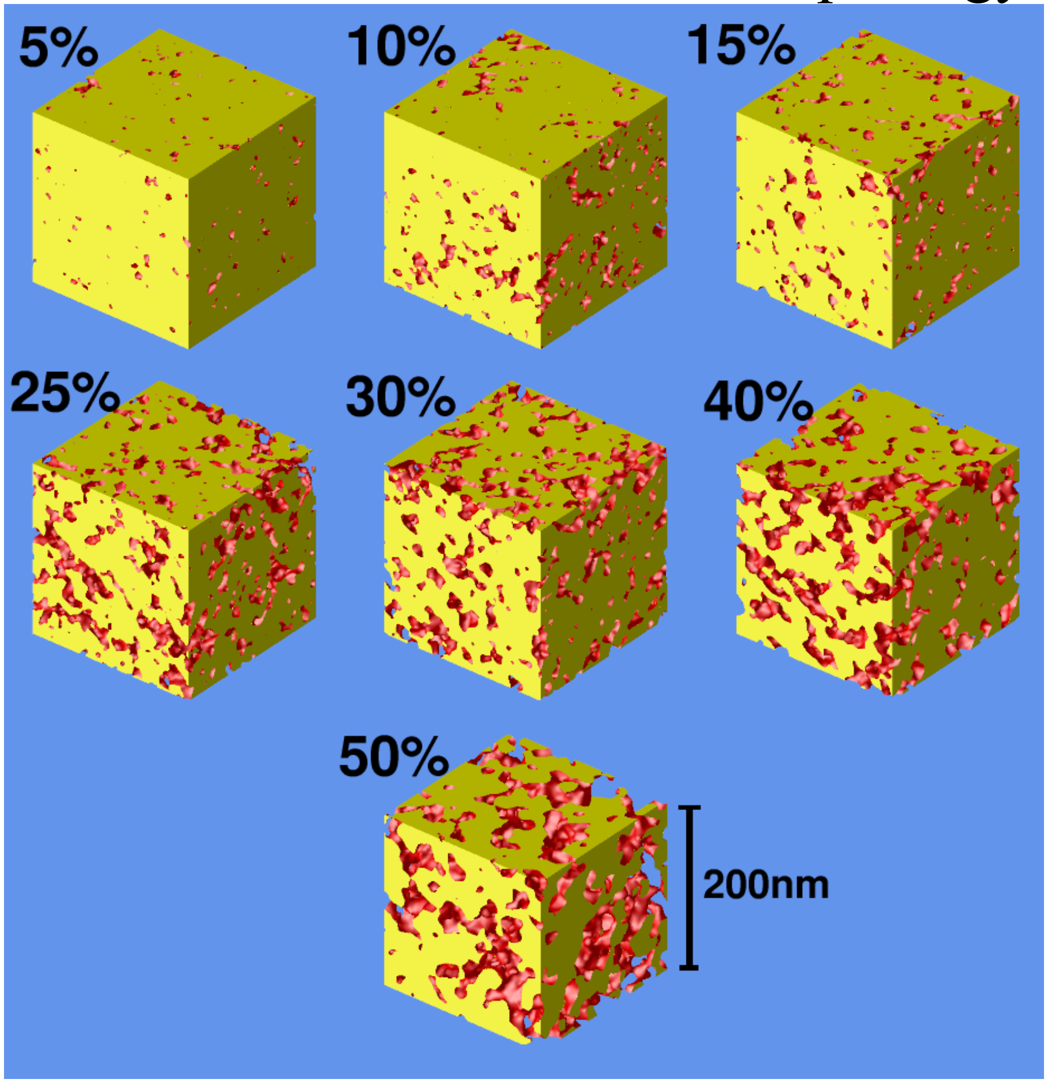
Approximations:

- morphology is "disordered" or random with no preferred direction
- morphology described by cosine waves:
  - with random phase and direction
  - non-random distribution of wavelengths (from SAXS)

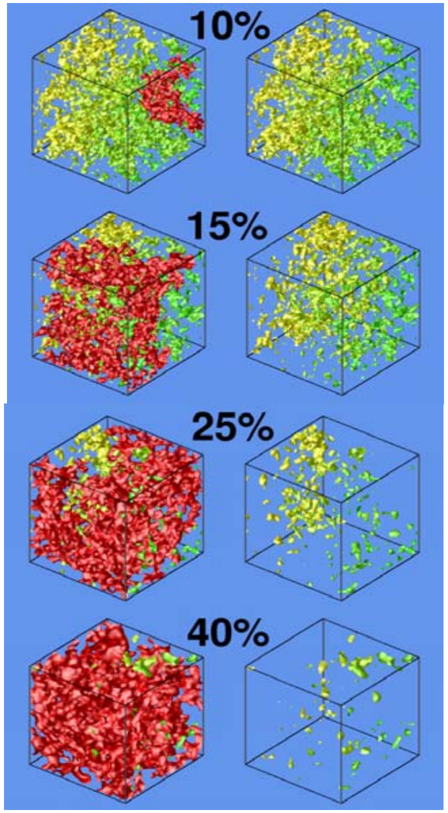
- Cahn, J.W., *J. Chem. Phys.* **42**, 93 (1965).
- Berk, N.F. *Phys. Rev. Lett.* **58**, 2718 (1987) & *Phys. Rev. A* **44**, 5069 (1991).
- Jinnai, H., et al., *Phys. Rev. E* **61**, 6773 (2000).
- Teubner, M., *Europhys. Lett.* **14**, 403 (1991).
- Hedstrom et al., Langmuir 20, 1535 (2004)

Nanoporous Film Morphology

Reconstruction of Pore Morphology



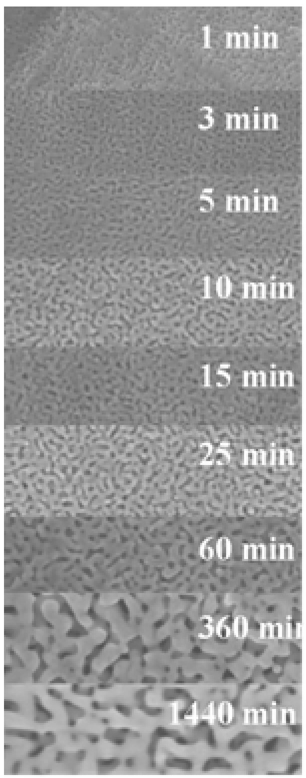
Determine transition from closed pores (5-10%) to interconnected (15%) pores to bicontinuous (>25%)



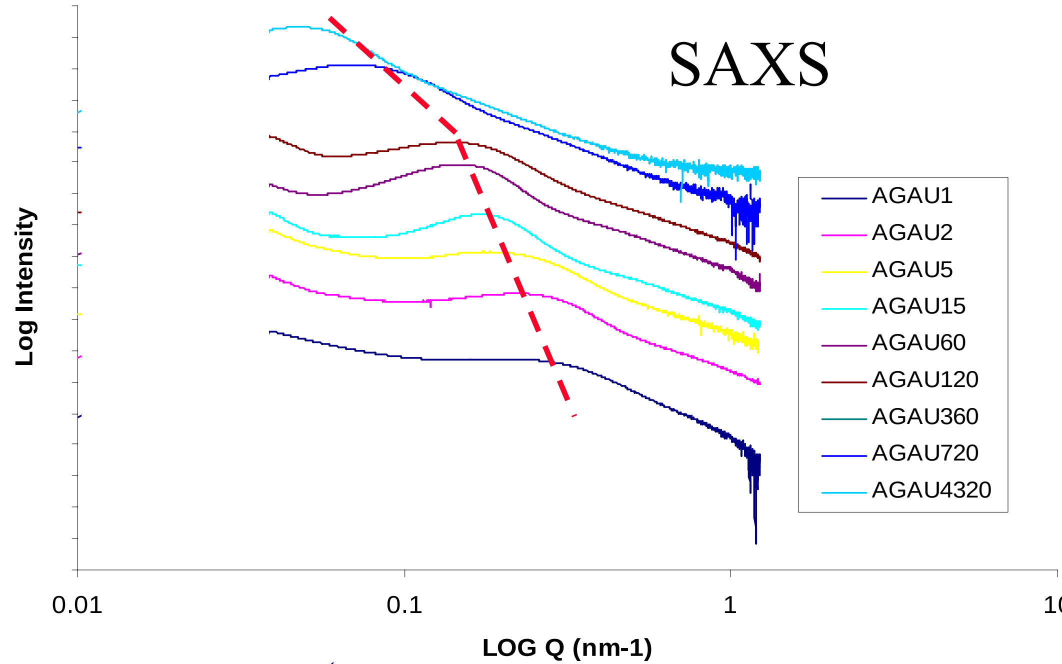
Hedstrom et al, Langmuir **20**, 1535 (2004)

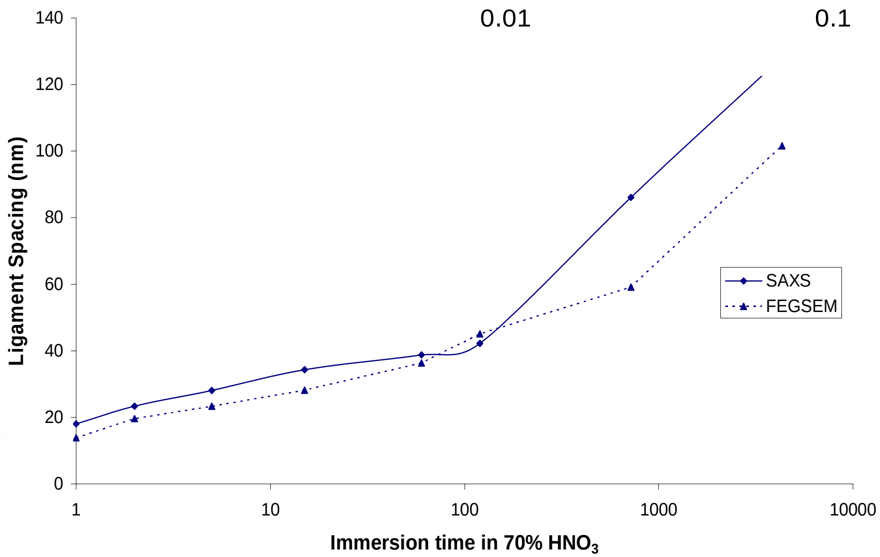
AgAu dealloyed films: SAXS

- removal of a less noble element from an alloy via selective dissolution
- AgAu → Au
- how does process occur?
- what is left?



200 nm



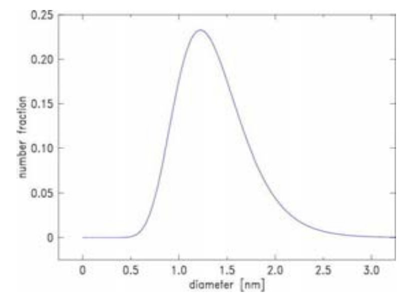


- "quasi-periodic": peak gives ligament spacing
- three dimensional morphology
- real time

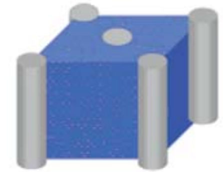
E Schofield, thesis

Summary: SAXS

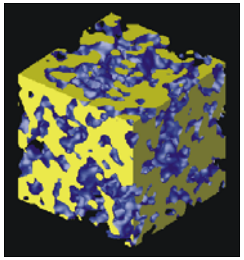
- Isolated Particles/Pores (not ordered)
  - ✓ Obtain average size & particle/pore size distribution (need large Q range)



- (More) Ordered Structures
  - ✓ particle/pore spacing and morphology



- Dense Network of Pores/Particles
  - ✓ Obtain representative morphology
  - ✓ Good for interconnected & bicontinuous morphologies



Mud, Dirt and Soils: Nanoparticles

Mn oxides

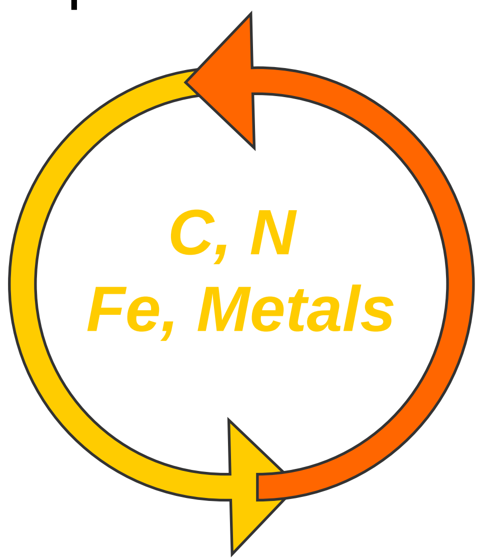
- Important constituent in soils & oceans
- Nutrient cycling
- Contaminant cycling
- Mn oxides dominant source/sink for bioavaliable Mn(II) in oceans

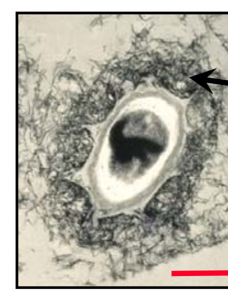
Mn Cycling in the biosphere:

Mn(II)

Mn(III)

Mn(IV)

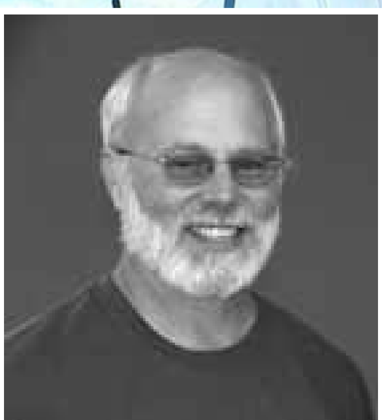




MnO_2

1 μm

Bacteriogenic Manganese Oxides



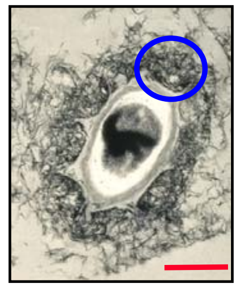
Mn(II)

↓

Mn(III)

↓

Mn(IV)



1 µm

Structure of products as function of reaction time & solution chemistry.

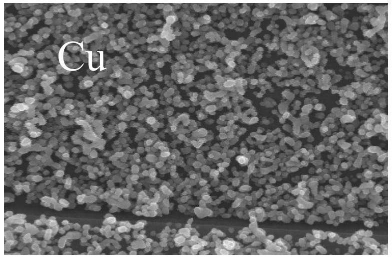
This study:

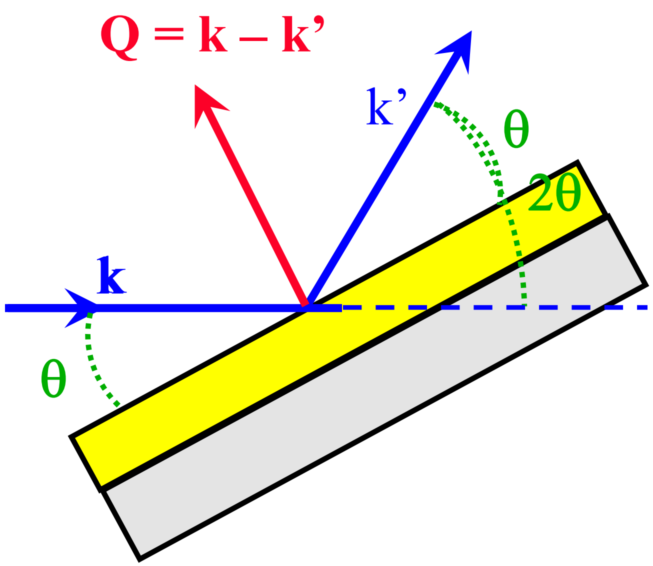
- Model organism: *Bacillus* sp., strain SG-1
- Mn(II) Oxidized by dormant spores

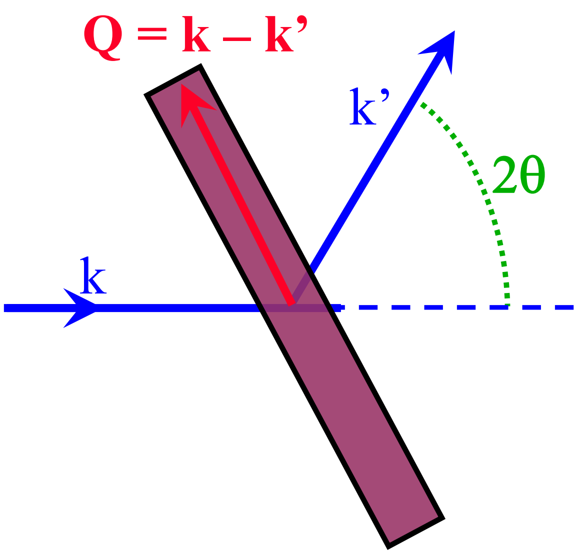
J.R. Bargar, S.M. Webb (SSRL), B.M. Tebo (Scripps), & C.C. Fuller (USGS)

Powder Diffraction

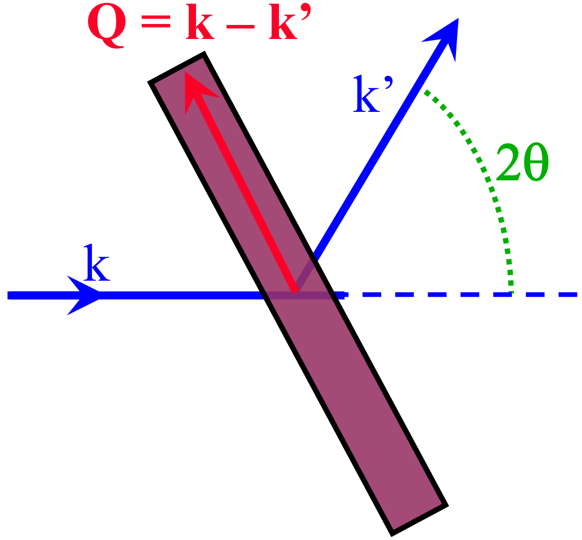
- lots of randomly crystallites (get for free with nanoparticles)
- collect I(Q)
- transmission or reflection
- analyze wet samples (*in–situ*)
- good statistics for background removal
- Tune energy to penetrate mud



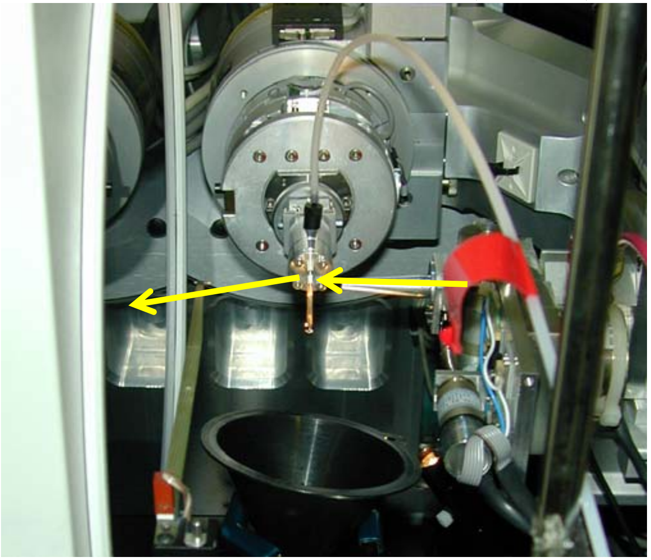




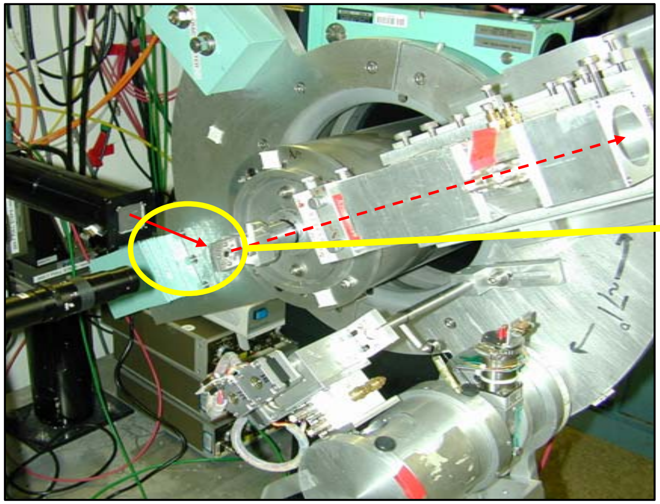
Powder Diffraction

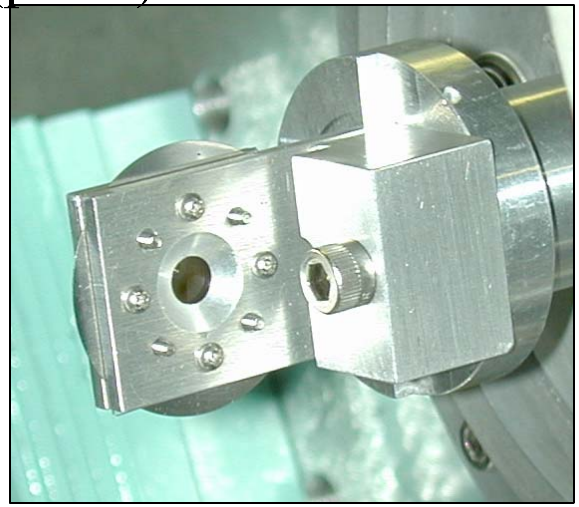


beam line 11-3 (area)

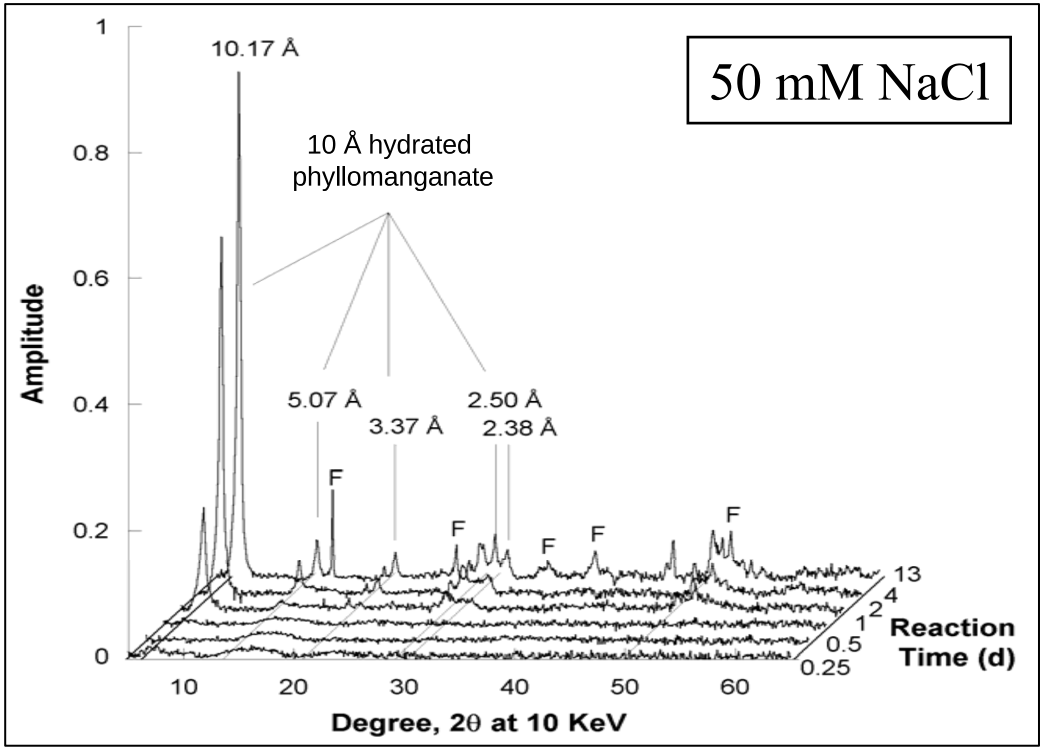


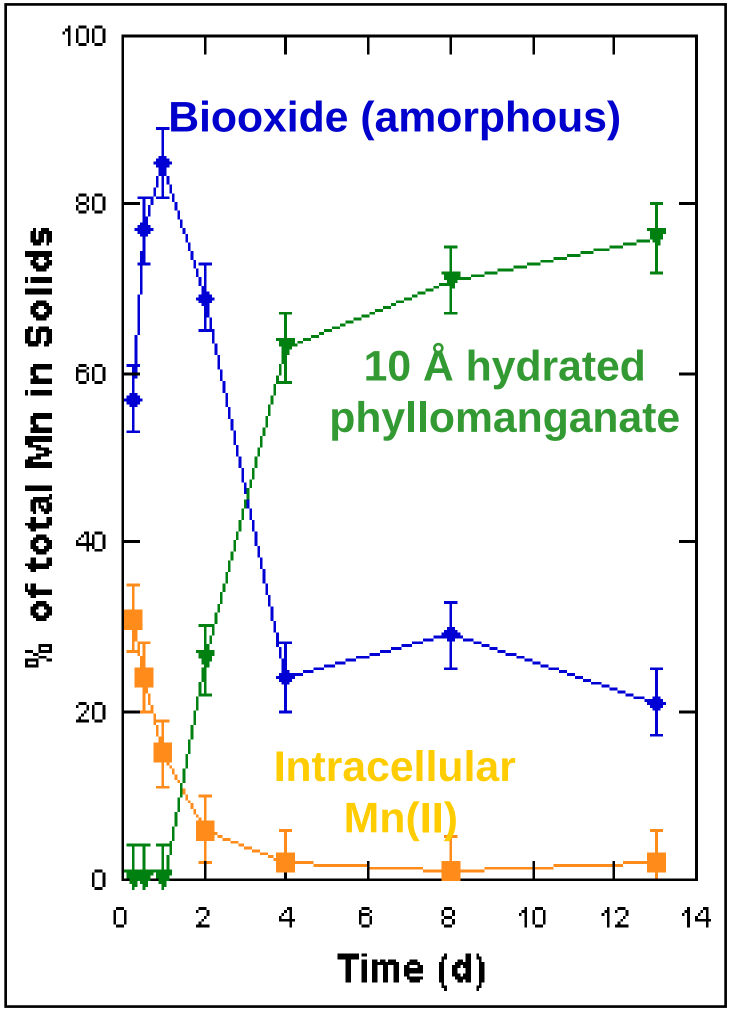
beam line 2-1(point)



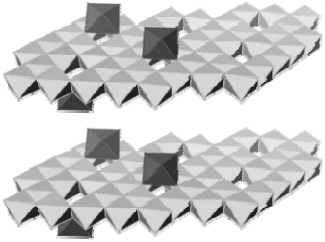


Bacterial Mn(II) Oxidation: 0.25–13 days



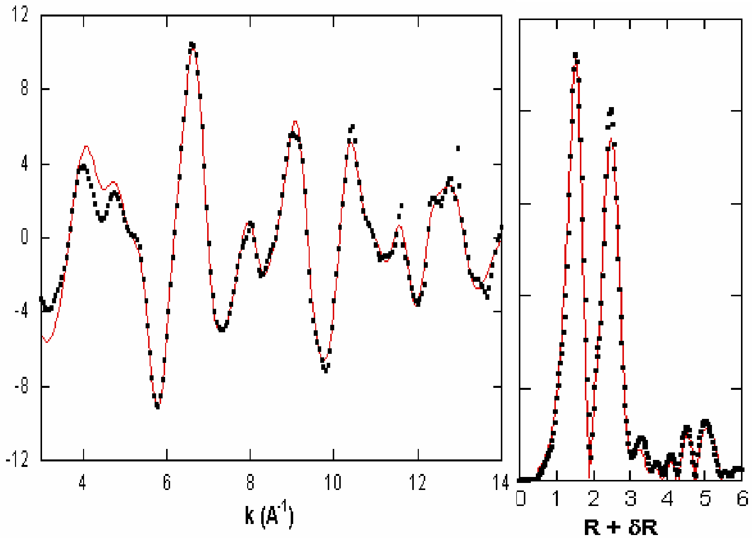


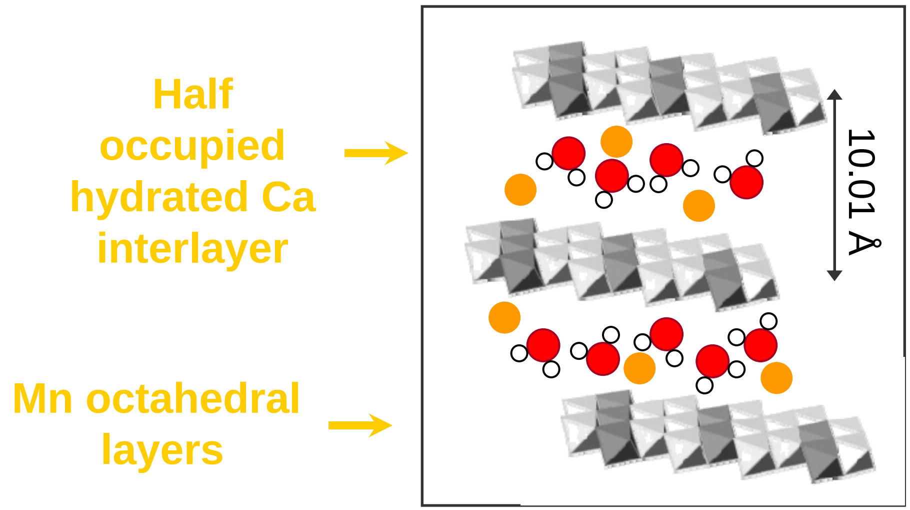
Products: "X-ray" amorphous hexagonal MnO2, then hydrated 10 Å phyllomanganate

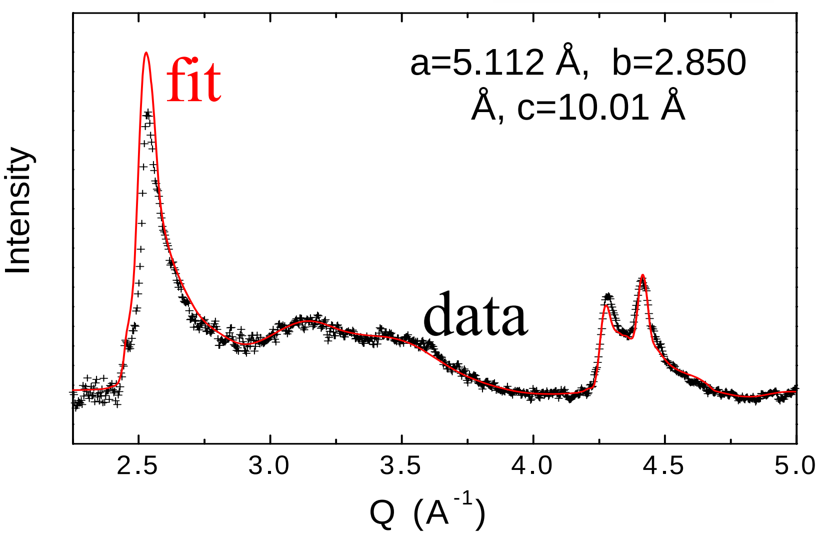


Bargar al (2004) Am Min.

Triclinic 50-hr Seawater Biooxide





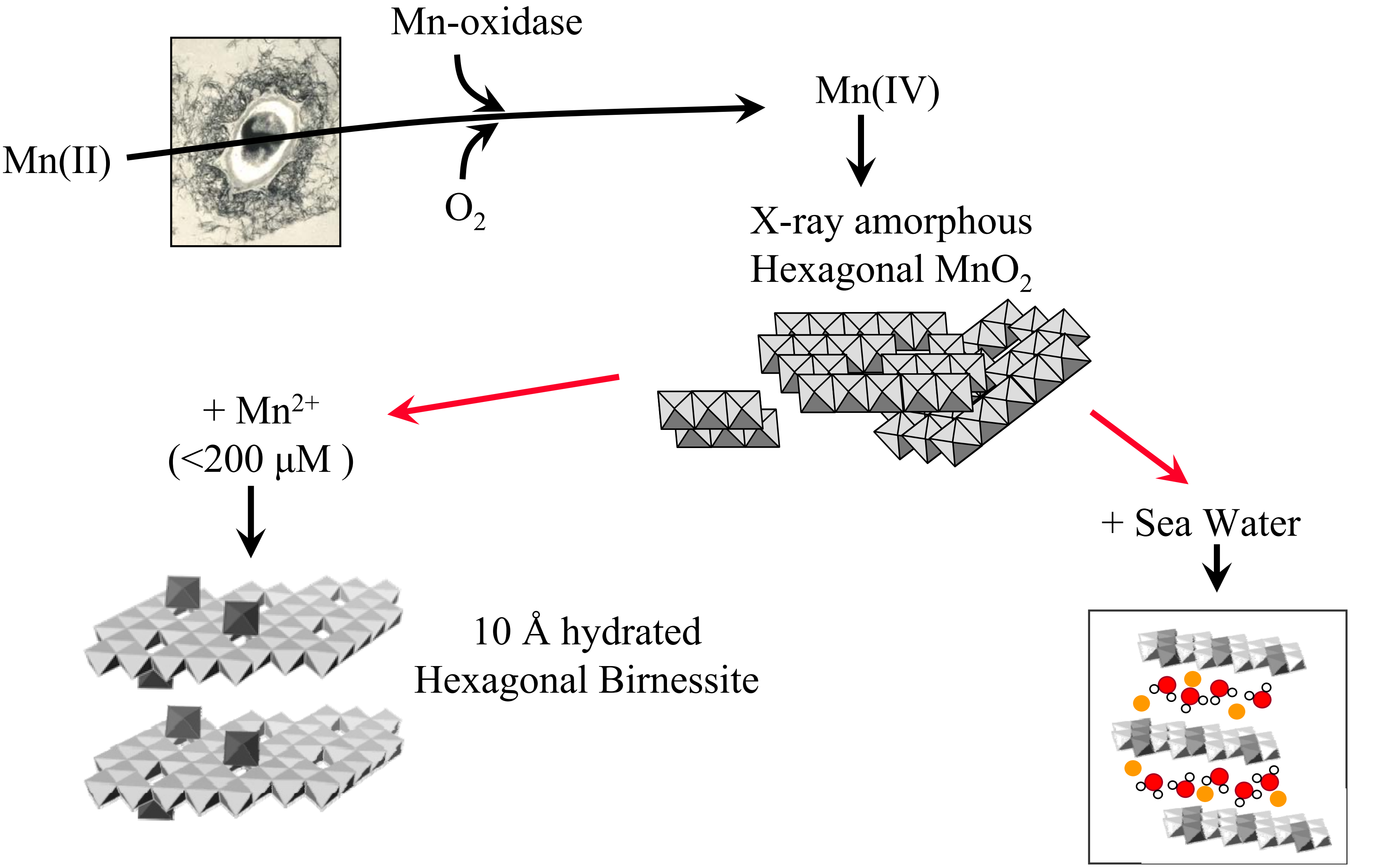


- Hydrated Ca^{2+} interlayer (XRD, EDS)
- Small particles: 3-layers thick (XRD)
- Disordered turbostratic stacking: 80 Å coherence length (XRD)
- 11% Mn layer vacancies (XRD, EXAFS)
- Mn^{3+} triple corner binding over vacancies (XRD)

EXAFS, XRD, and SEM give consistent results!

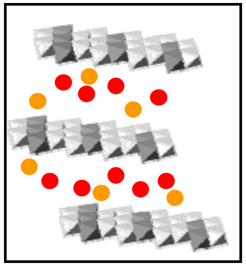
Webb, Bargar, Tebo, 2004

Oxidation and Transformations



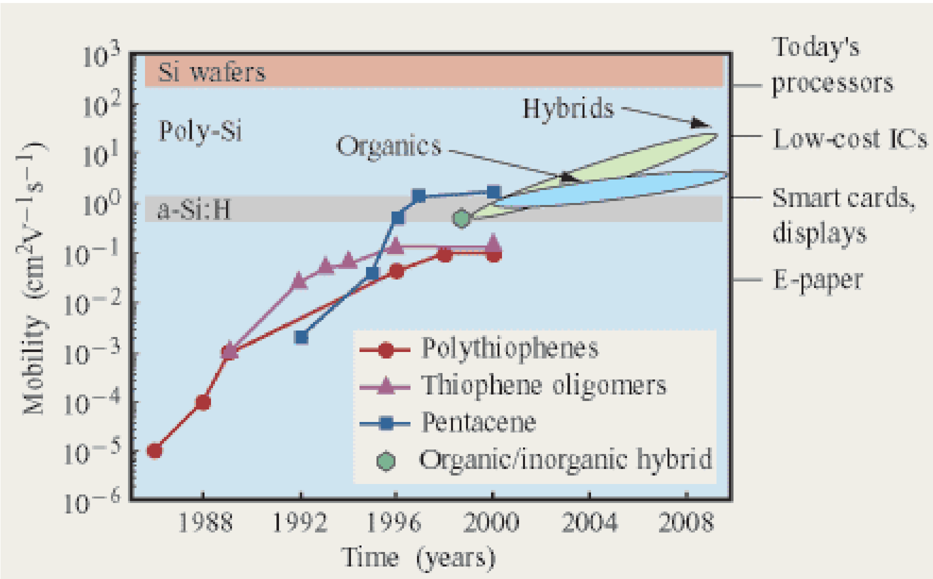
Summary: Powder

- Phase identification
  - ✓ 10 Å Birnessite
- Structure Determination
  - ✓ Hydrated Ca structure
- Crystallite size
- Defects
  - ✓ Turbostatic layering
- *In-situ* Measurements

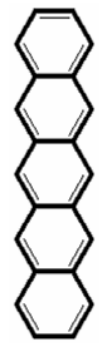


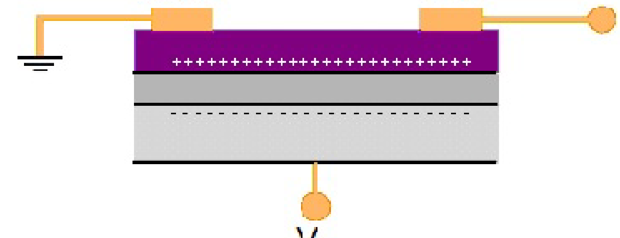
Apurva Metha, Sam Webb, me: this afternoon

Organic Thin Films



Organic FET





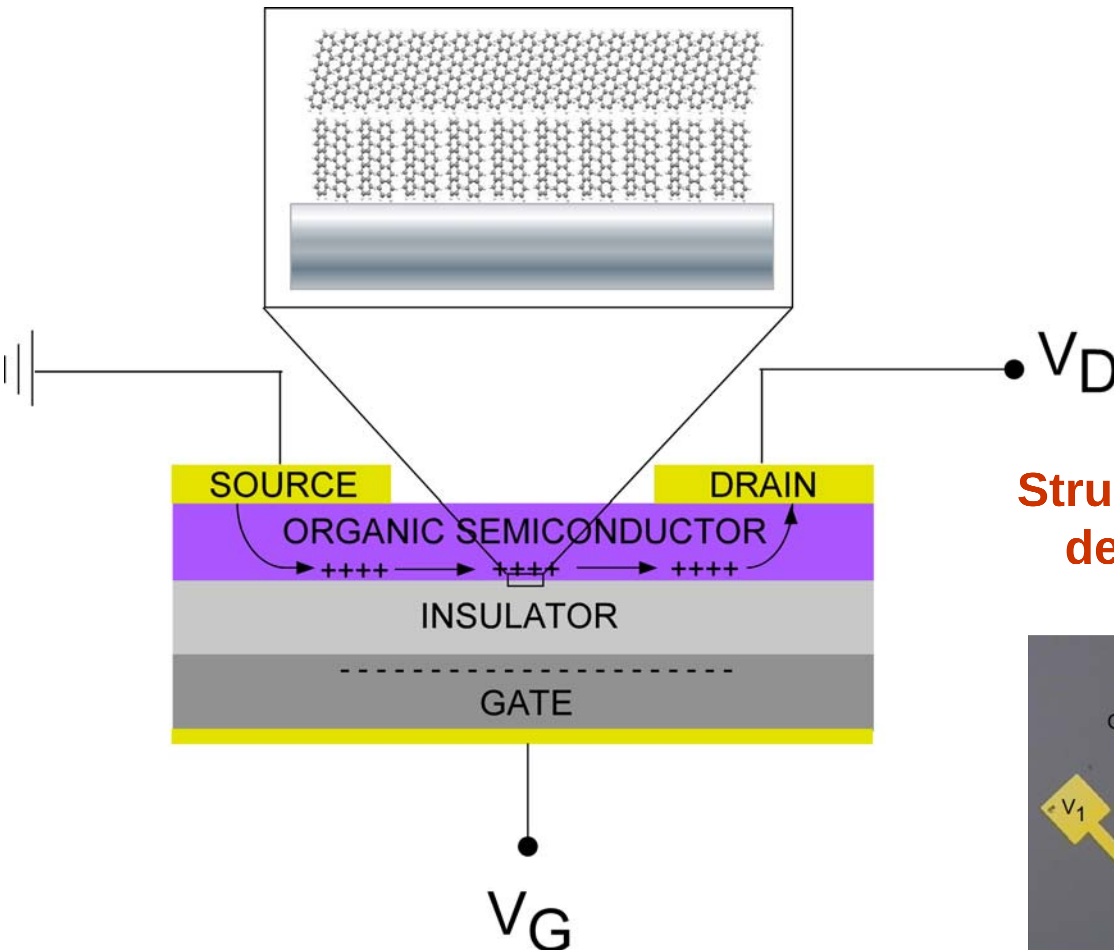
Sandra Fritz,
C. Daniel Frisbie,
Mike Ward,
Chemical Engineering and Materials Science
University of Minnesota

CEMS Chemical Engineering & Materials Science

150 YEARS 1851 2001
University of Minnesota

Organic Thin Films

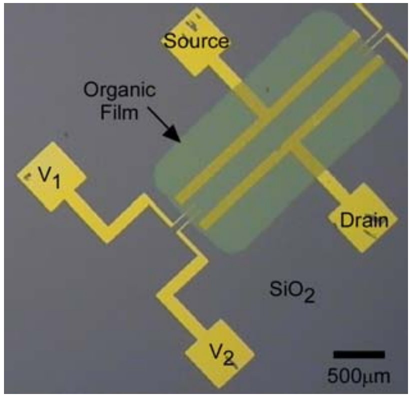
Organic FET



Goals:

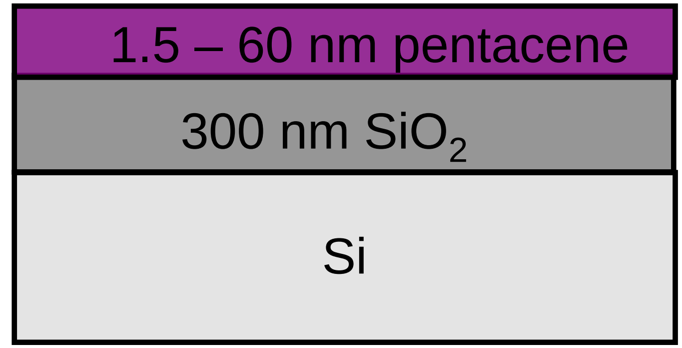
- lattice parameters
- structure (packing of molecules)
- changes in structure with thickness
- crystallite size

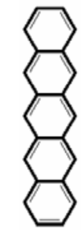
Structure (molecular packing; defects) => Transport

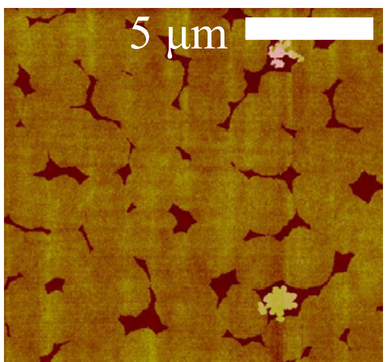


Pentacene Thin Films

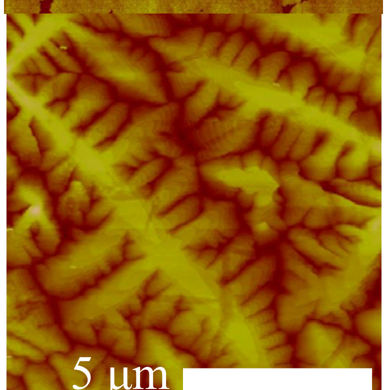
- Thermal evaporation of pentacene
- Film morphology and structure dependant on substrate temperature, deposition rate and film thickness





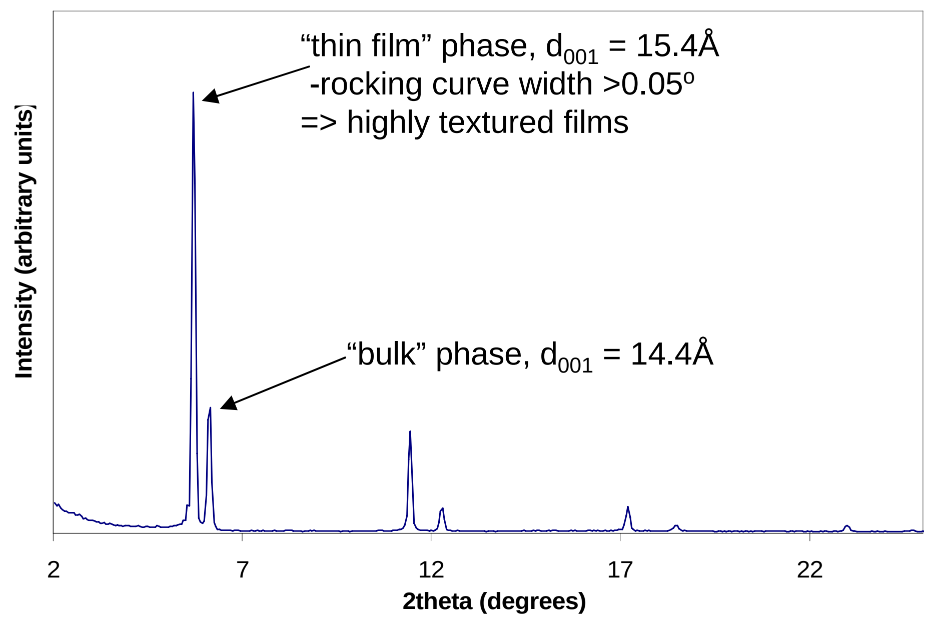


1.5 nm - one layer

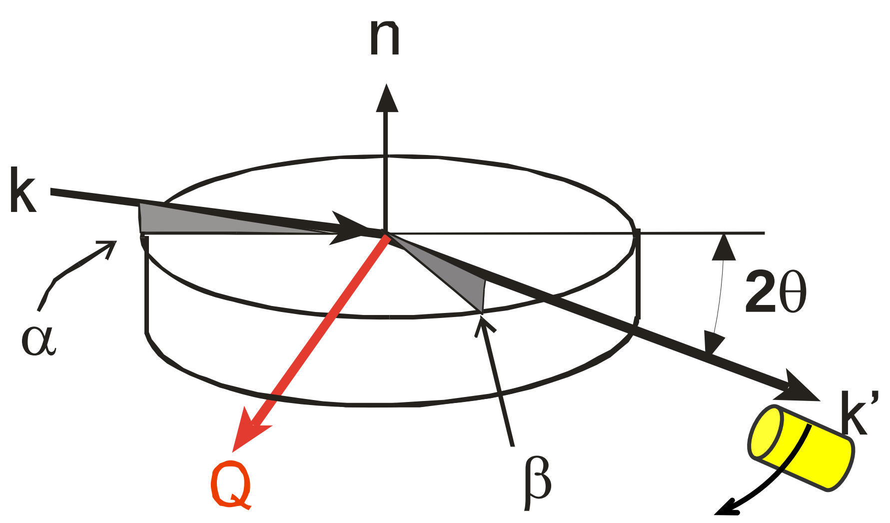


30 nm – ca 15 layers

θ/2θ XRD



Grazing Incidence Diffraction



2θ is scattering angle

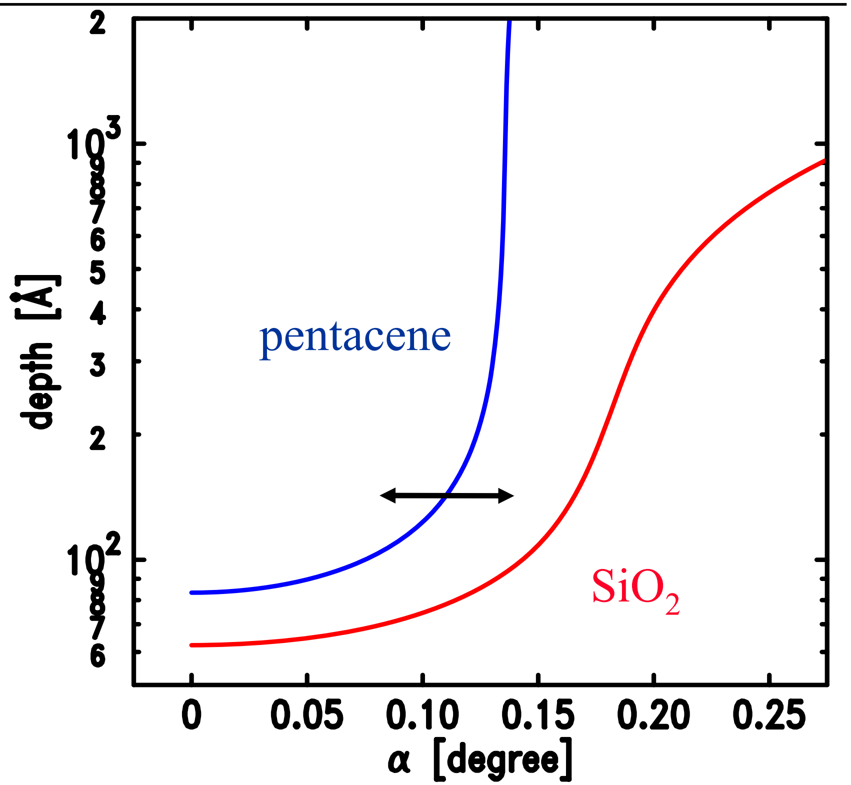
Q = scattering vector

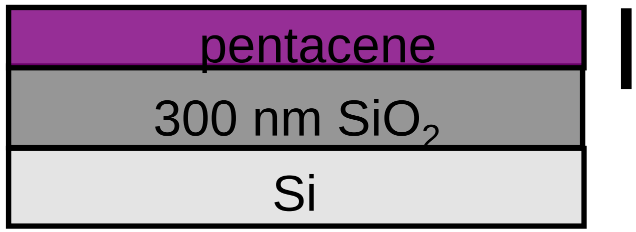
Q = k' - k

$Q = (4\pi/\lambda) \sin\theta$

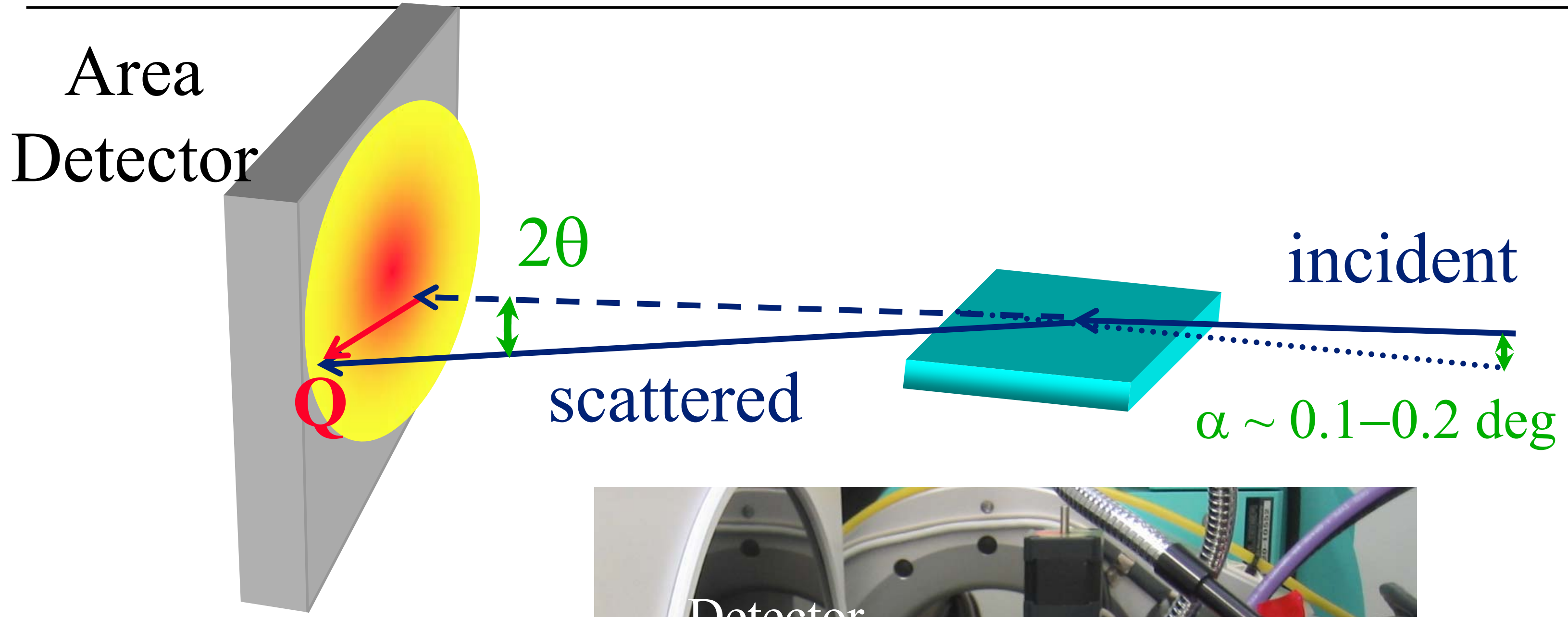
α = incidence angle (small)

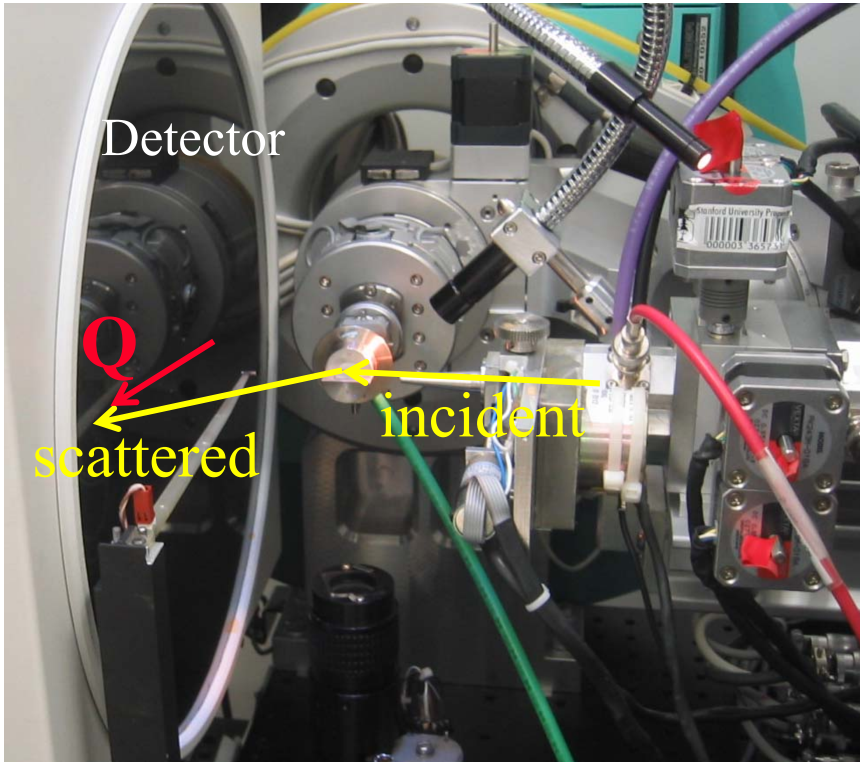
β = exit angle (small or large)





Thin Film Diffraction

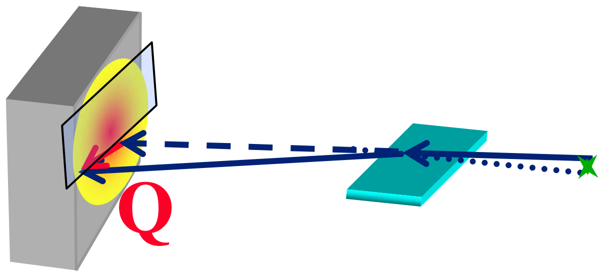


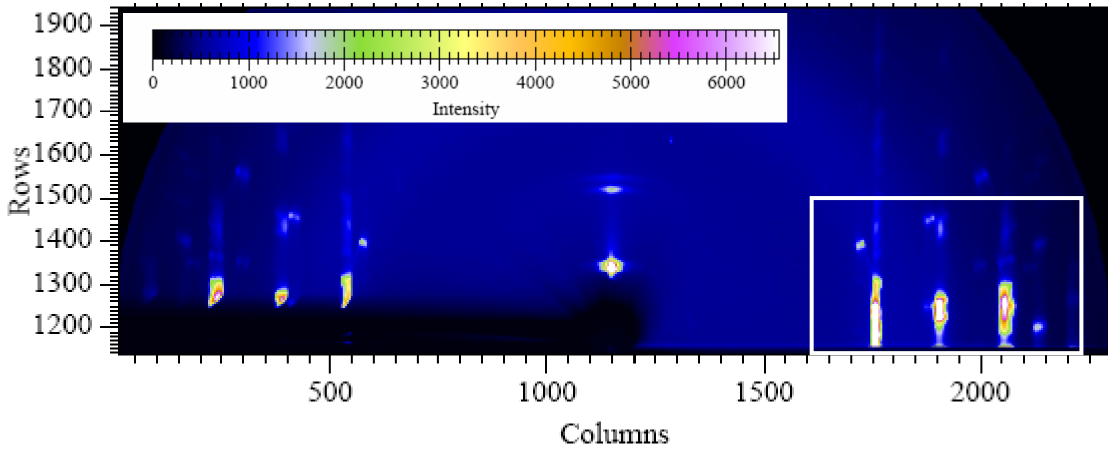


Beam line
11-3

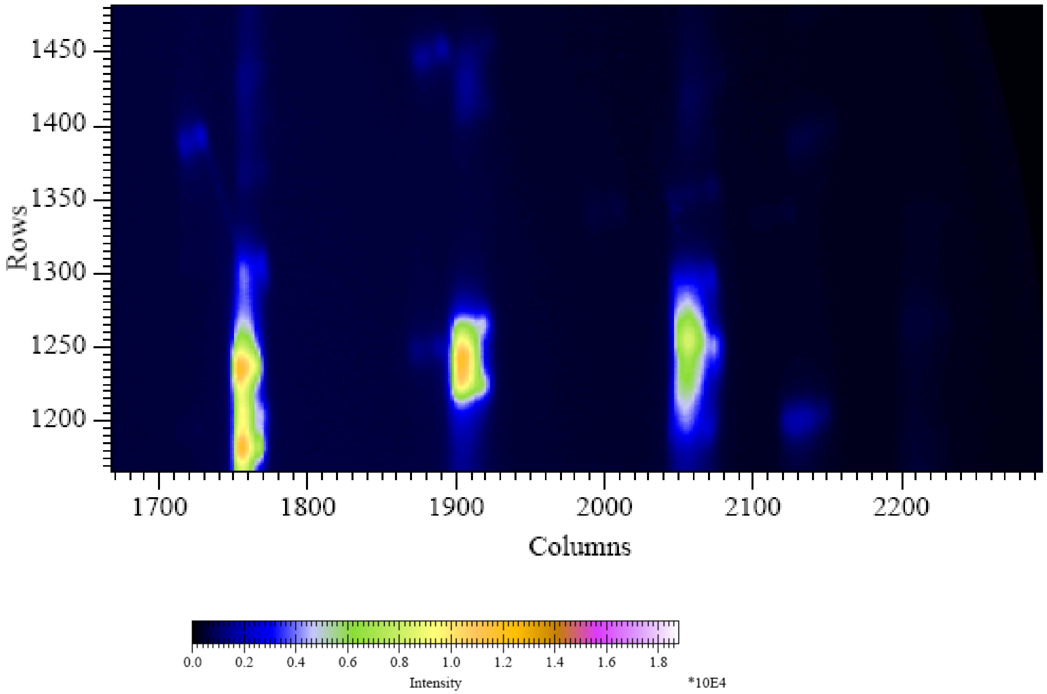
Pentacene Thin Films

20 nm film

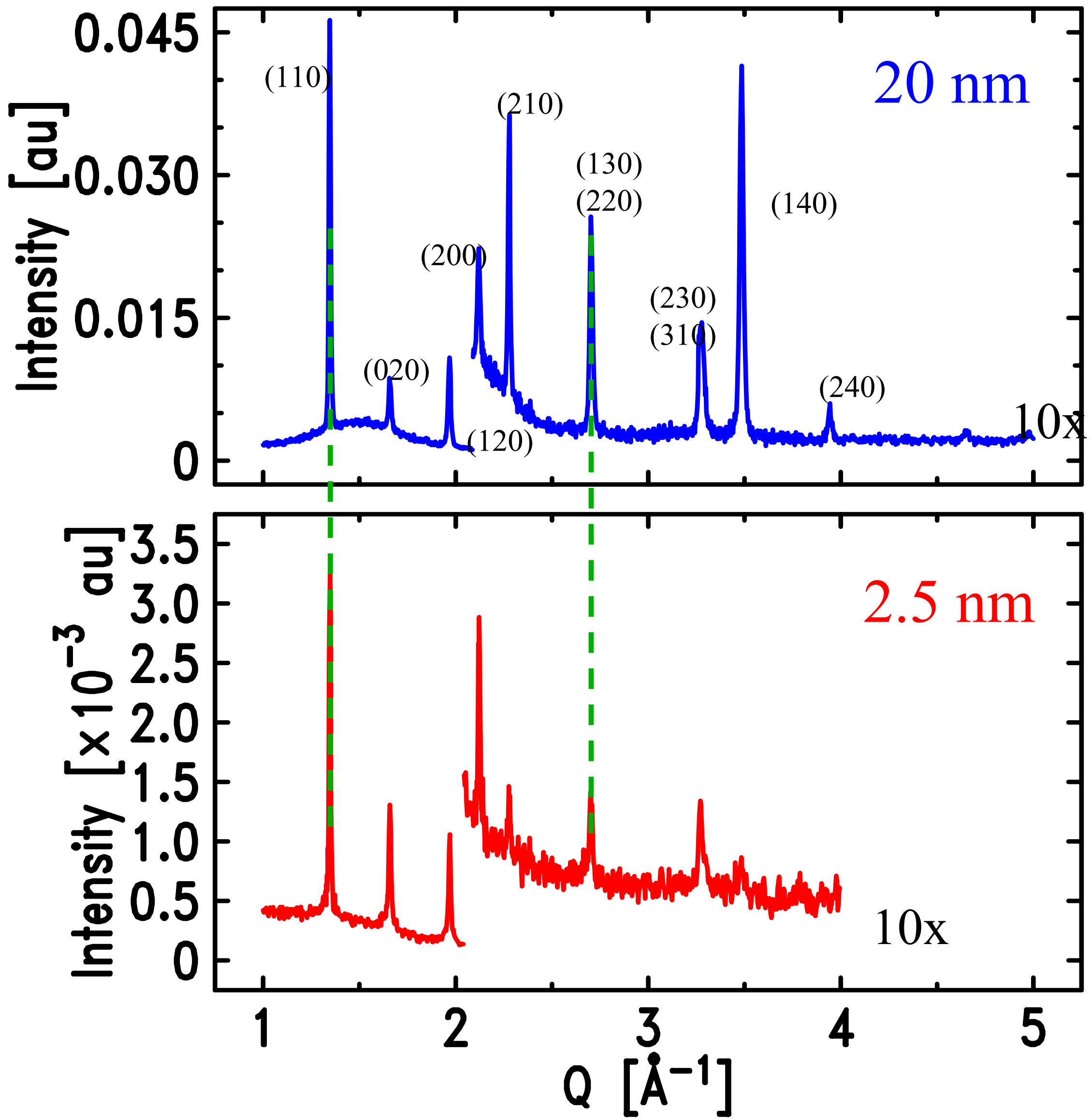


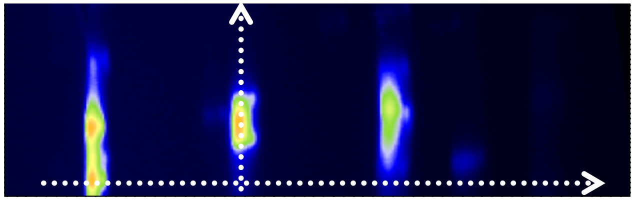


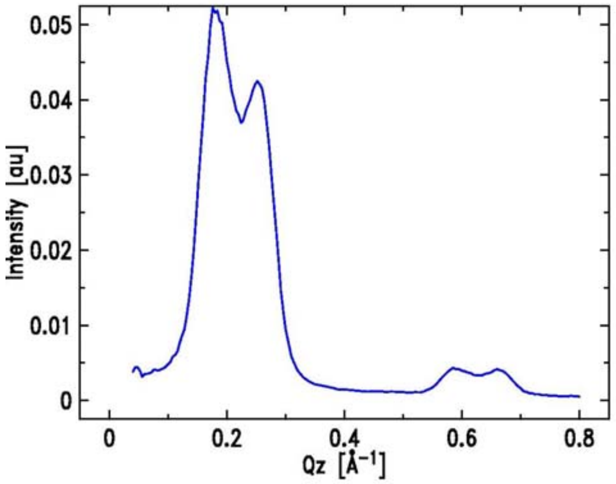
- quick
- complete diffraction pattern => index peaks
- rough lattice parameters
- misses details (poor resolution)
- weak peaks hard to detect



Pentacene Thin Films





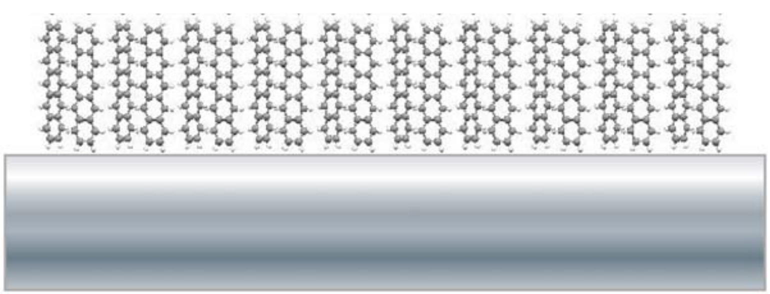


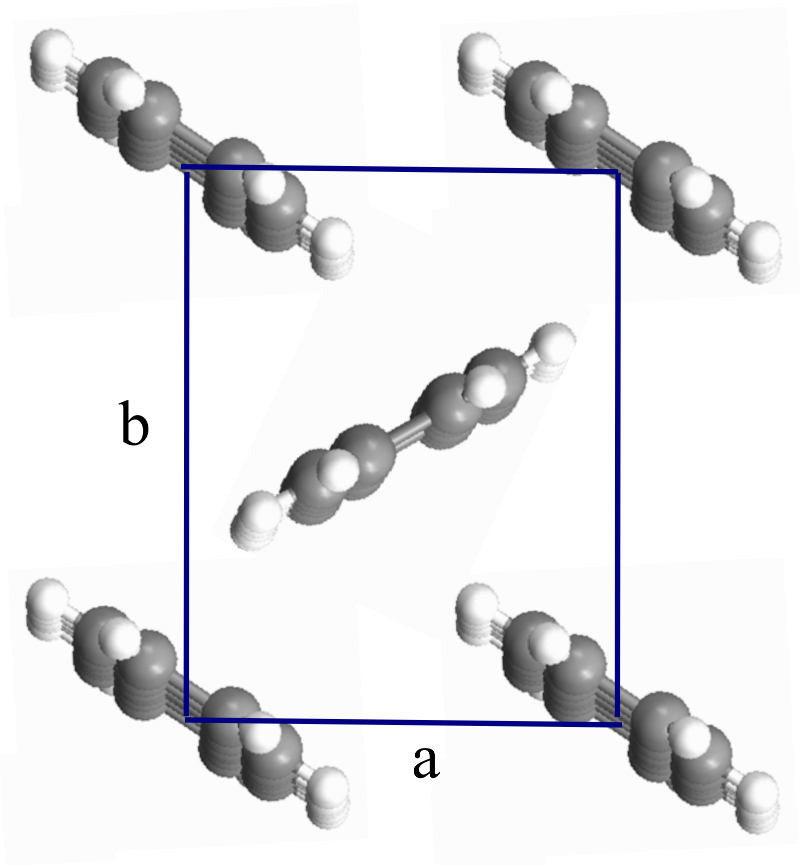
- Deduce unit cell and lattice parameters as function of thickness
- Determine monolayer and 'thin film' crystal structure

Fritz et al., unpublished

Pentacene Monolayer

- Rectangular unit cell:
  a= 5.905 Å &
  b= 7.562 Å
- centered symmetric structure
- molecules vertical
- herringbone angle is 63 deg

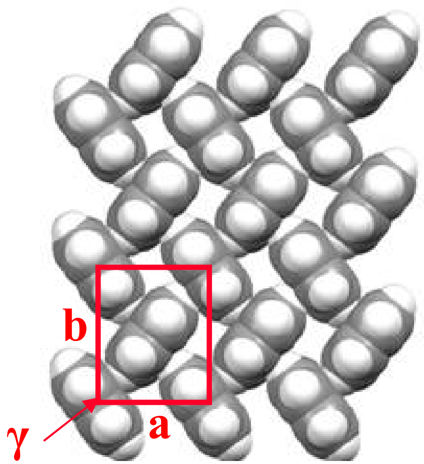


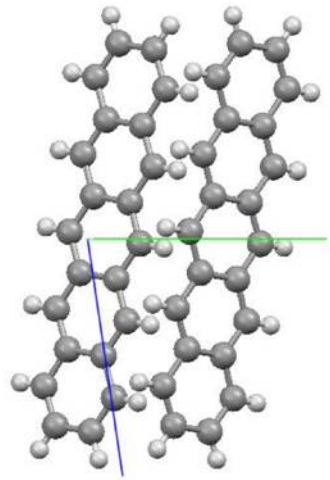


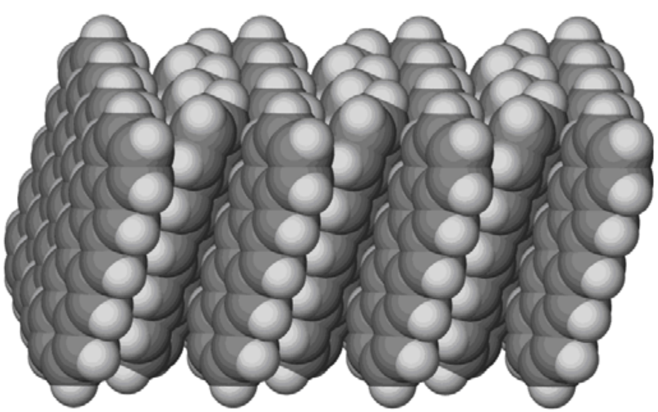
Fritz et al., unpublished

Pentacene Thin Films

Thin Film: herringbone motif with molecules tilted 10-20 degrees





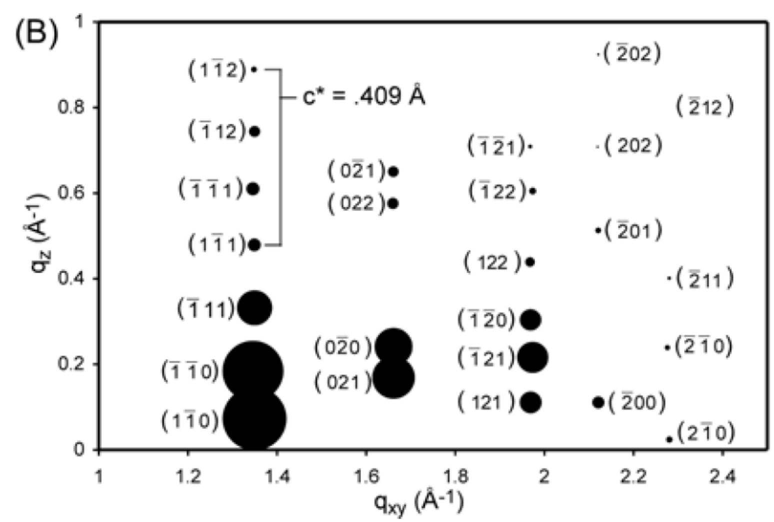


a = 5.919 Å, b = 7.556 Å, c = 15.54 Å

α = 81.6 deg, β = 87.2 deg, γ = 89.8 deg

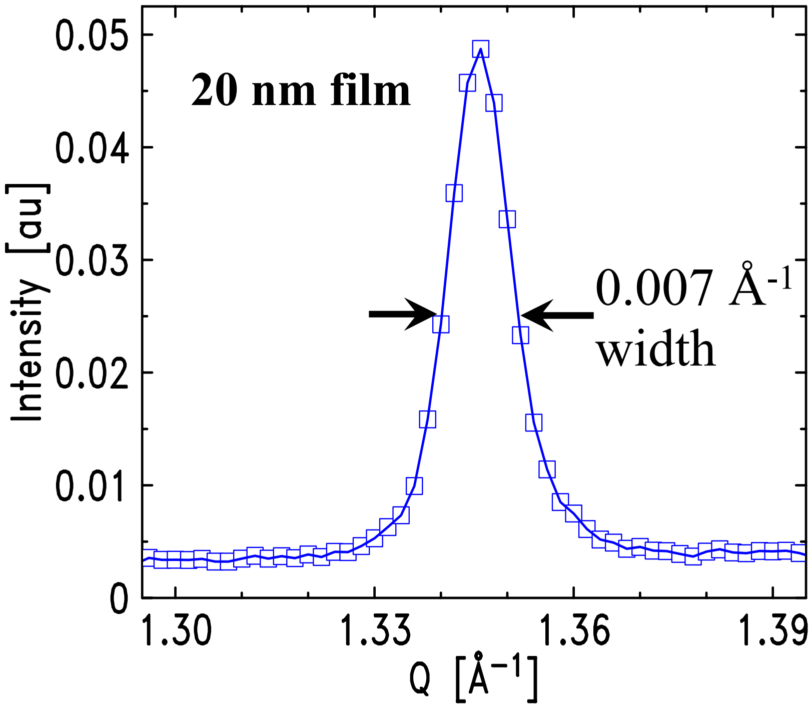
tilt = 20 deg

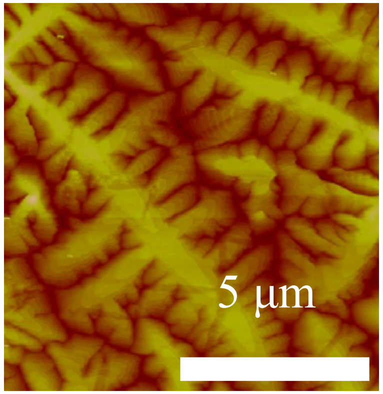
herringbone angle = 50-60 deg



Fritz et al., unpublished

Pentacene Films: Crystallite Size





$\Delta Q \approx 2\pi * 0.9/D$

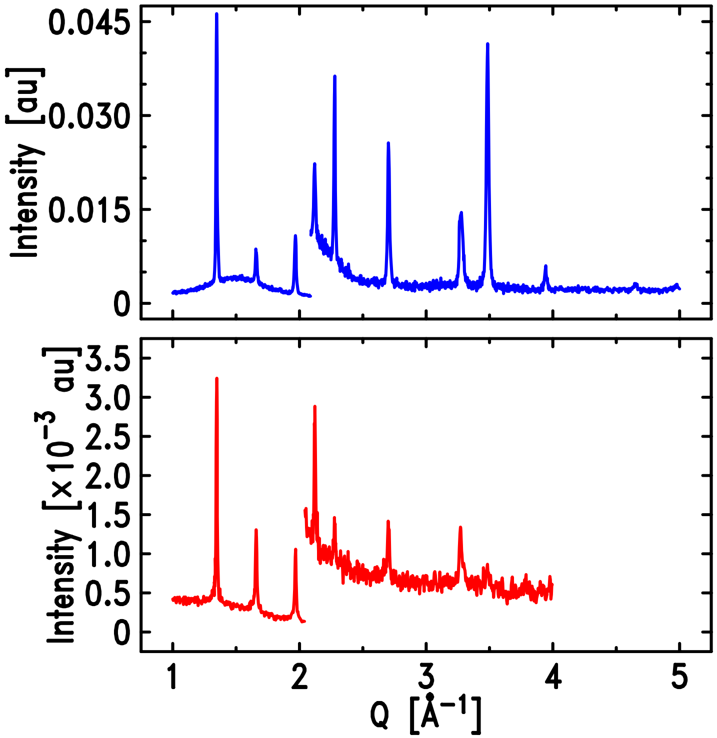
=> Crystallite size is large (D > 30 nm)

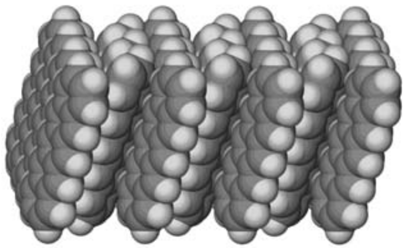
More sophisticated approaches possible (Apurva)

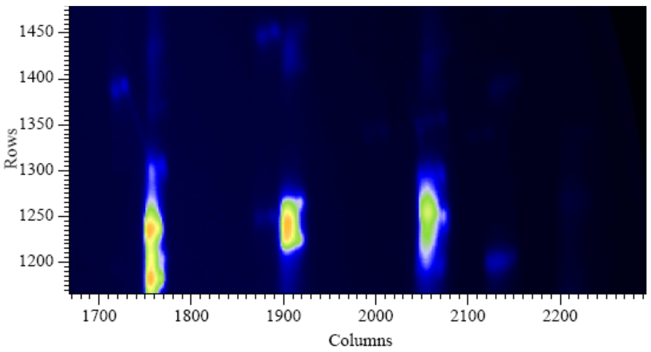
Fritz et al., unpublished

Summary: Pentacene

- Detectors to use: area, point
- Pentacene thin films on SiO_2 are crystalline, but distinct from bulk
- Monolayer: centered rectangle cell with herringbone motif and molecules vertical
- Thin Film: triclinic cell with herringbone motif and molecules tilted 10-20 degs
- Domain size is large (> 30 nm)





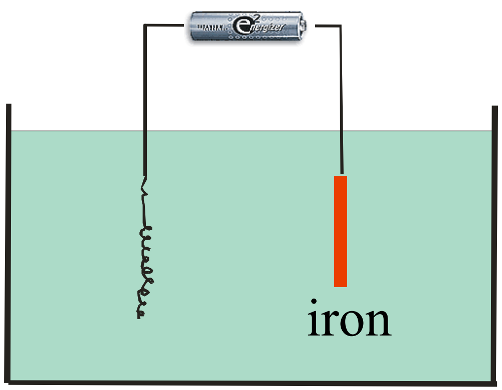


In-Situ Reaction: Oxidation

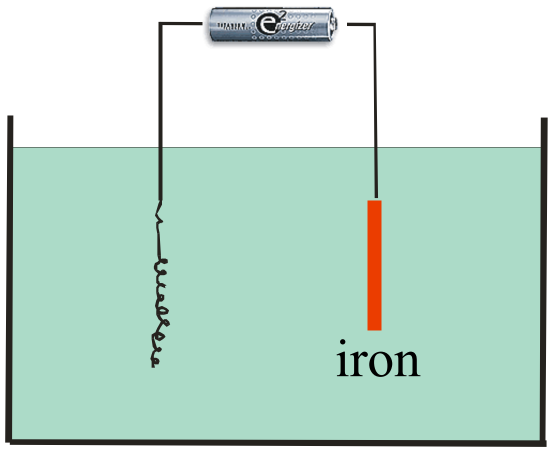
In-situ reactions

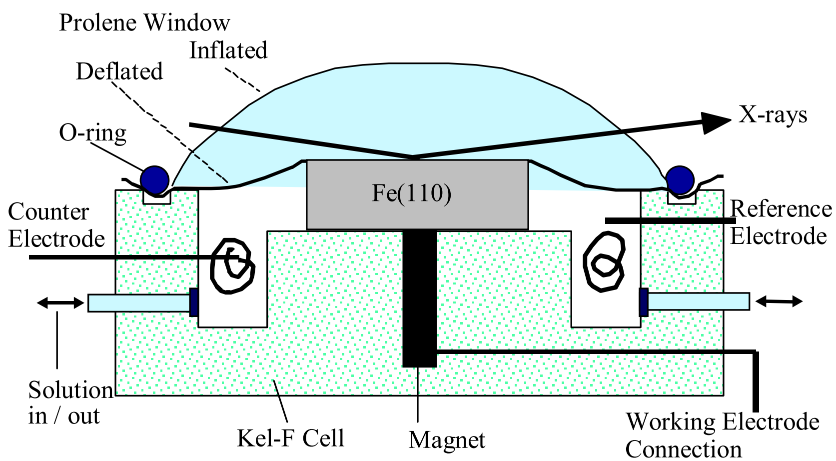
- High Pressure
- High Temperature
- Low Temperature
- During Film Growth
- Wet Environments

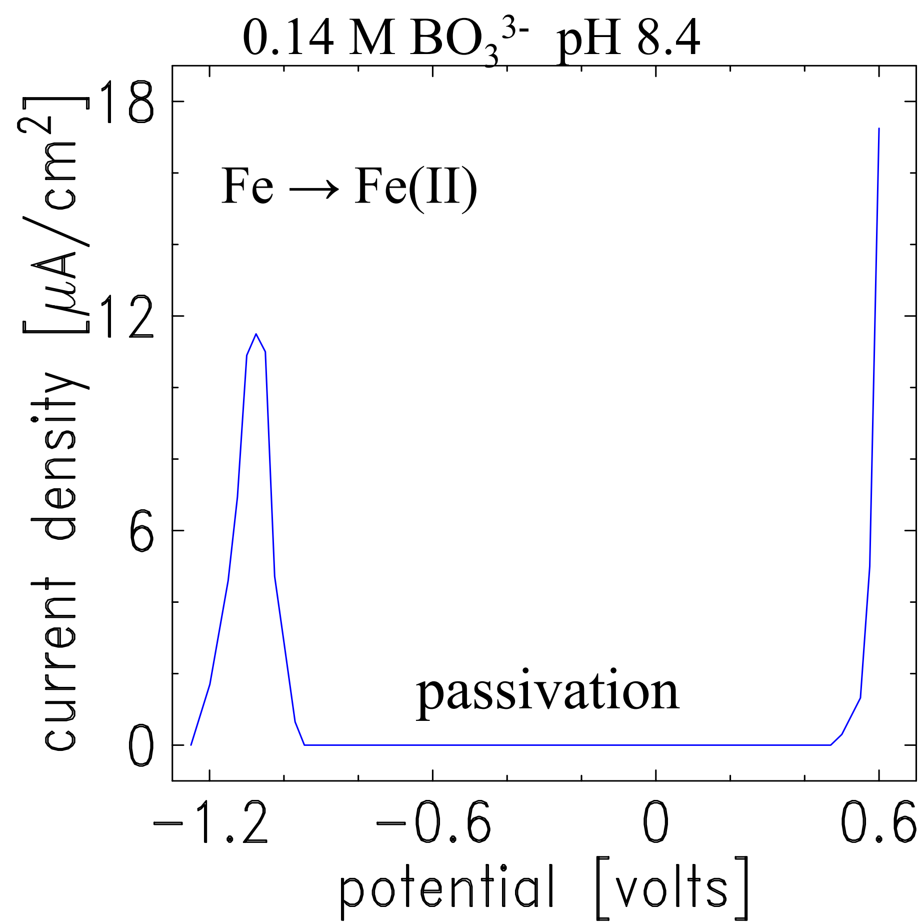
Alison Davenport
University of Birmingham
Mary Ryan
Imperial College London



In-Situ Reaction: Oxidation



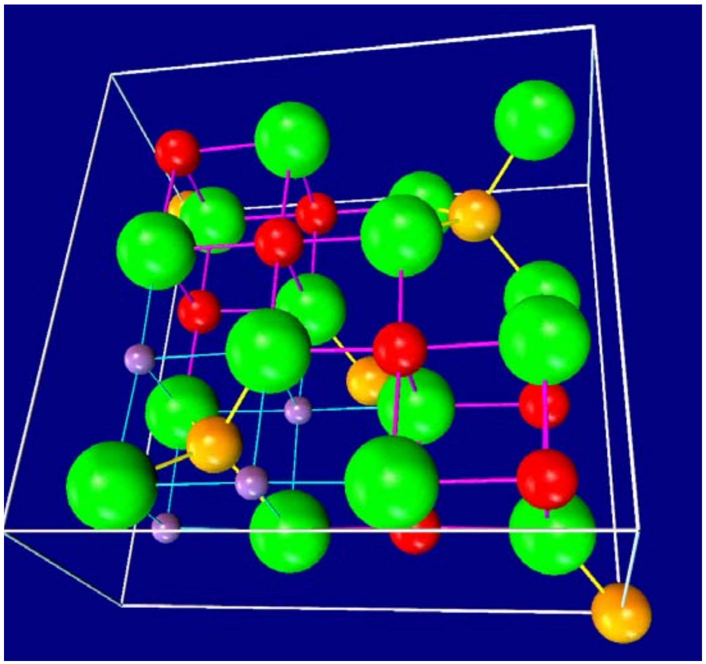




Davenport et al., J Electrochem Soc 147 2162 (2000)
Ryan et al., MRS Bull 24 29 (1999)

In-Situ Reaction: Oxidation

Passive film is defective Fe_3O_4

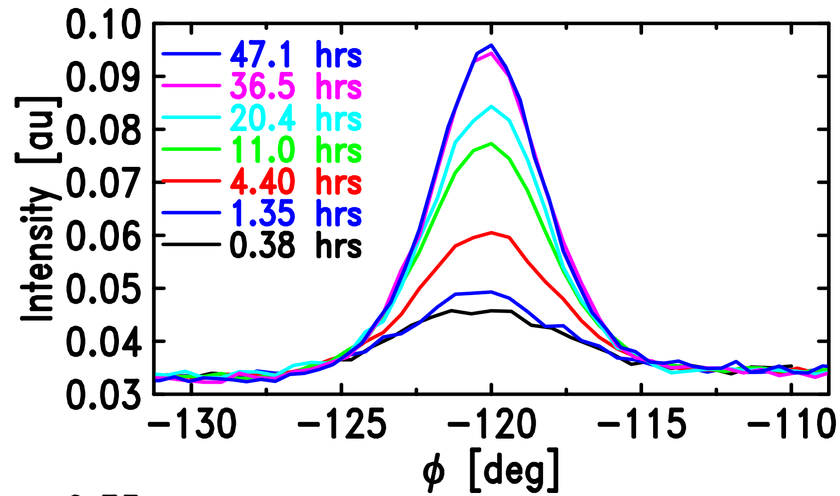


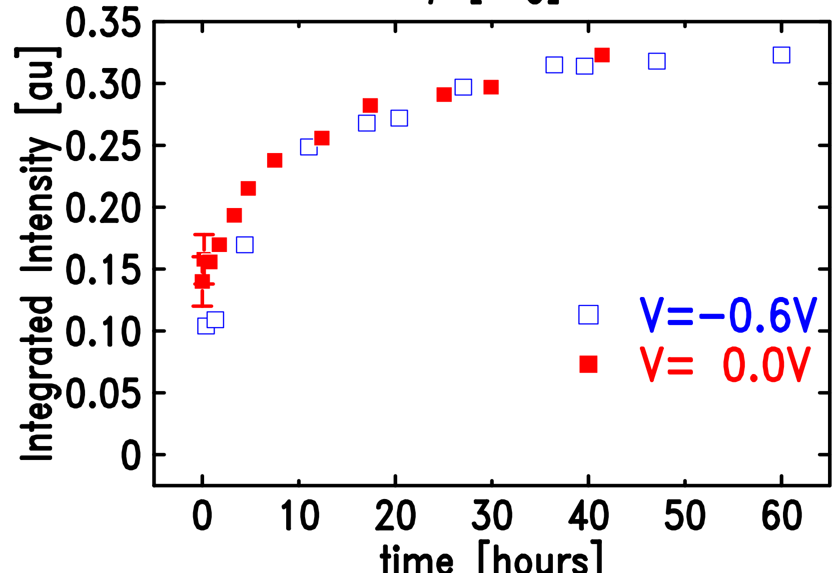
oxide ions: 100% occupancy

tetrahedral cation sites: 66% occupancy

octahedral cation sites: 80% occupancy

octahedral interstitial sites 12% occupancy



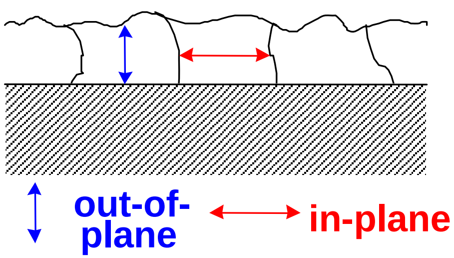


- No grain growth
- Thickness increase?

In-Situ Reaction: Oxidation

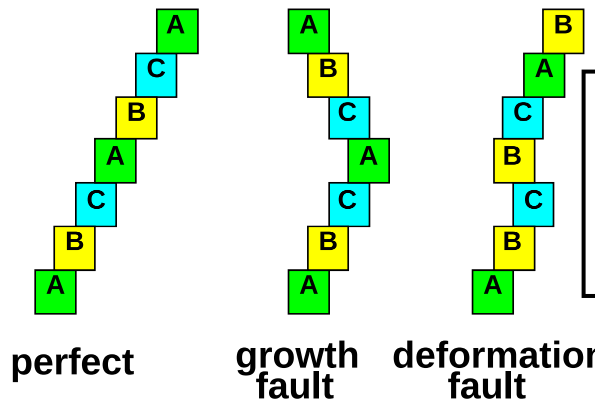
Defects in the passive oxide

Crystallite Size



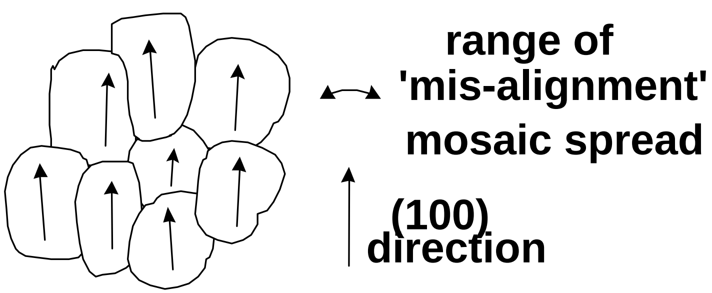
Fe(001)	Fe(110)
~35 Å	~25Å
~60Å	~45 Å

Stacking Faults



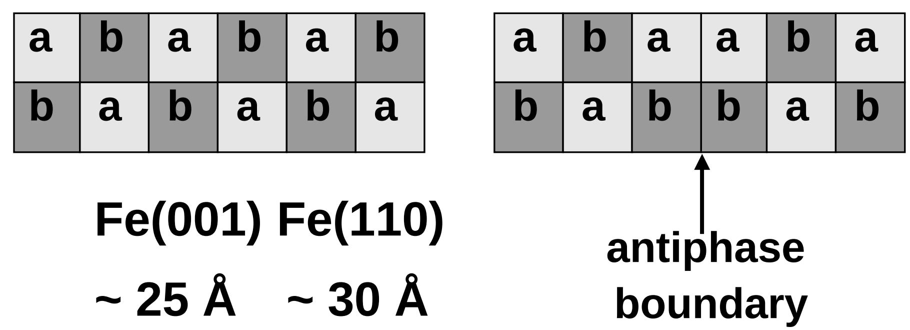
Fe(001)	Fe(110)
???	along (111)

Mosaic Spread



Fe(001)	Fe(110)
2.5°	3.7°

Antiphase Boundaries



Fe(001)	Fe(110)
~ 25 Å	~ 30 Å

Davenport et al., J Electrochem Soc 147 2162 (2000); Ryan et al., MRS Bull 24 29 (1999)

Summary

- Typical SR x-ray scattering experiment & some examples: porous films, bio-oxides, pentacene, oxidized Fe
- Stuff we will cover:

  SAXS

  Powder

  Amorphous

  Films: random, textured, epitaxial

  Surfaces