

# Major Synchrotron Techniques

## SPECTROSCOPY

→ Paul Northrup

- Infrared spectroscopy
- Photoelectron spectroscopy
- X-ray absorption spectroscopy
- X-ray emission spectroscopy

## DIFFRACTION/SCATTERING

→ Elaine DiMasi

- Protein crystallography
- Small molecule crystallography
- Powder diffraction
- Small-angle x-ray scattering
- X-ray microdiffraction
- High momentum resolution x-ray scattering

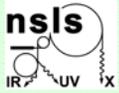
## IMAGING

→ Lisa Miller

- Infrared microspectroscopy
- Soft X-ray scanning microscopy
- Hard X-ray microprobe
- X-ray microtomography
- Diffraction-enhance imaging

## OTHER

- Micro-machining
- X-ray footprinting



# Welcome to Scattering! *Elaine DiMasi, NSLS*

## It's all scattering!

Photons interact with sample, are re-radiated, and detected.  
X-ray *momentum transfer* provides structural information.

## The building blocks:

Scatter photon from one electron ...

... x-rays interact *weakly* with materials.

Scatter from an atom ...

... integrate over electron distribution.

Atomic sensitivity!  $f = f_0 + f'(q) + if''(E)$

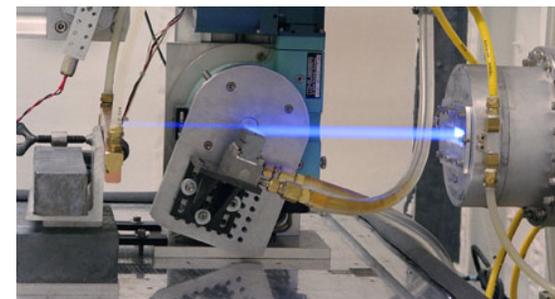
Scatter from organized electron density distribution ...

... *crystals* or *other*, i.e., your samples.

$$I = I_0 \frac{e^4}{m^2 c^4 R^2} \left( \frac{1 + \cos^2 \phi}{2} \right)$$

$$f = \sum_n \int_0^\infty 4\pi r^2 \rho_n(r) \frac{\sin qr}{qr} dr$$

**X-ray scattering probes structure in a huge variety of ways.**



# Scattering: outline of topics

## Structure measurement from diffraction

crystallography  
powder diffraction  
texture, strain, and disorder

## Other scattering methods

surface scattering and reflectivity  
small angle x-ray scattering  
pair distribution function

## Energy considerations and electronic structure topics

surface / bulk sensitivity  
resonance: elemental specificity, orbital ordering  
adjust  $q$  and scattering angle range  
inelastic x-ray scattering, magnetic x-ray scattering

## Not covered!

beamlines, optics, spectrometers, detectors, ancillary eqpt, labs ...

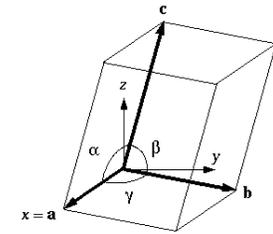


# Structure measurement from diffraction

**Crystallography: atoms have regular long range order.**

When you define atomic positions in a unit cell, the summation of scattering from every atom leads to the Bragg law:  $\mathbf{q} = (h,k,l)$

By measuring scattered intensity at these  $\mathbf{q}$  values, the structure factor can be measured and the atomic positions can be *deduced*.



$$I(\mathbf{q}) \sim |F(\mathbf{q})|^2$$

**Typical objectives:**

determine structure of a new compound

examine how structure depends on conditions ( $T, P, H\dots$ )

$$F = \sum_n f_n \exp [(2\pi i/\lambda) \mathbf{q} \cdot \mathbf{r}_n]$$

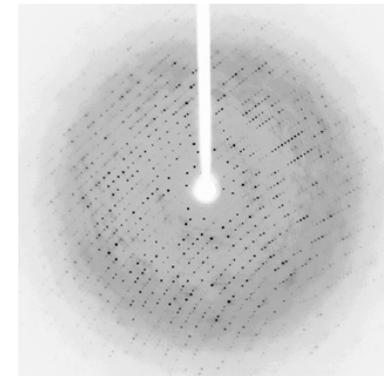
**Synchrotron especially useful for:**

microcrystals

high throughput

obstructive sample environment (anvil cell, water)

*macromolecular crystallography*



# Diffraction from powders

**Powder diffraction: good crystals, but micron sized grains.**

An ideal powder contains grains with crystalline long range order, but the grains are distributed among all orientations.

Only the magnitude of  $q$  is known, but with good knowledge of the sample chemistry new structures can routinely be discovered.

**Data acquisition is fast with area detectors.**

Higher resolution may be needed for some samples.  
Mixed samples like soils can be studied.

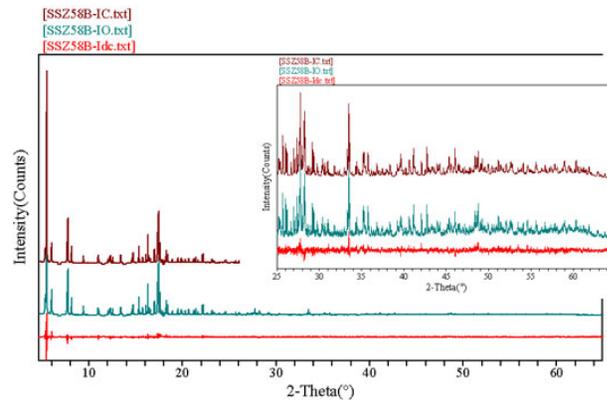
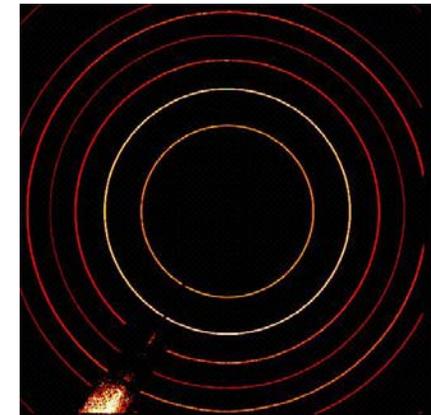
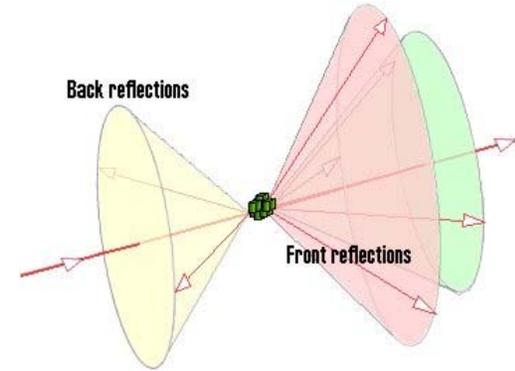


Figure 1. The simulated, experimental, and difference profiles of the synchrotron powder x-ray diffraction pattern ( $\lambda = 1.1996$  Angstrom) of SSZ-58.

# Diffraction from imperfect crystals

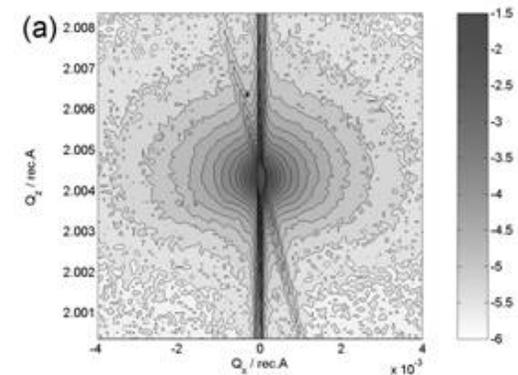
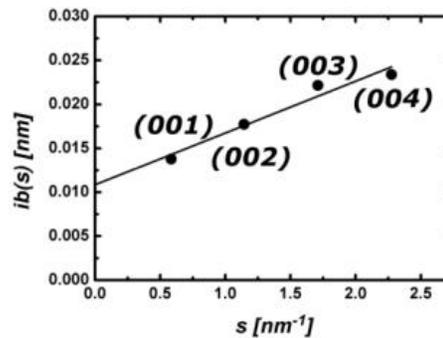
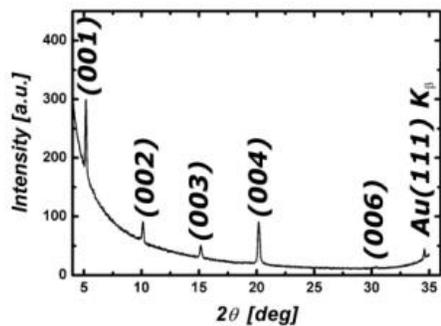
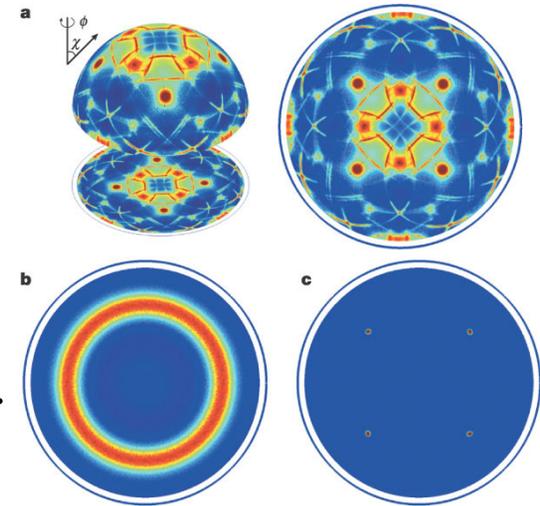
**Deviations from perfect crystalline order have specific signatures.**

*Texture*: can observe transitions and intermediates between perfect crystals and perfect powders.

*Pole figures* are commonly used to study alloys and material processing.

*Peak lineshapes* are affected by grain size, strain, and by the way that molecular subunits are correlated.

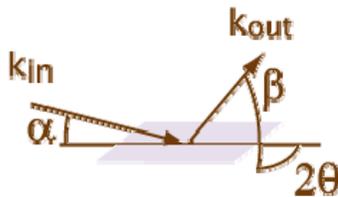
*Thermal diffuse scattering* patterns are signatures of disorder, structural phase transitions, etc.



# Non-crystalline scattering methods

**We do not always analyze data in terms of a crystal structure.**

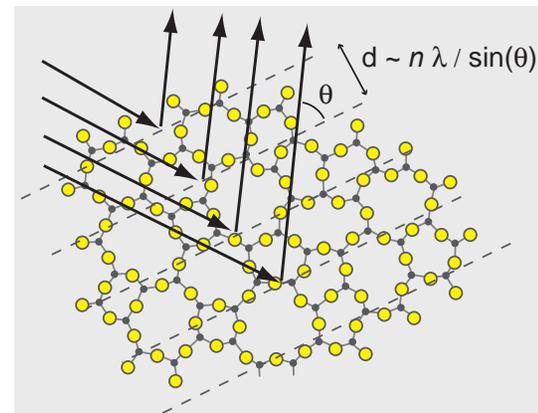
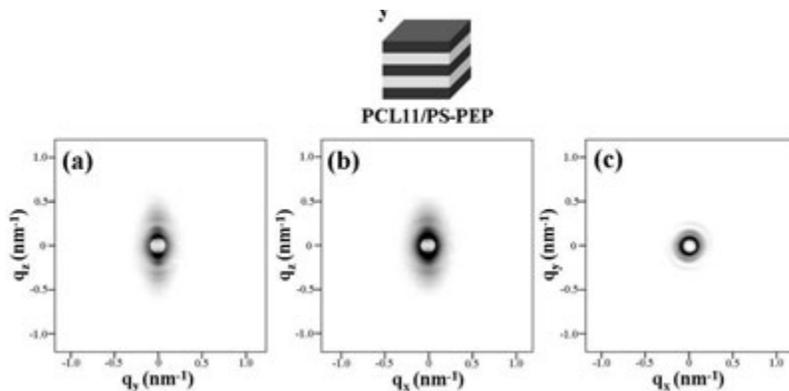
*Reflectivity.* The electron density distribution is an infinite half plane. Density and profile of thin films, surfaces, multilayers, liquid interfaces.



$$R(q_z) = R_F \left| \frac{1}{\rho_{\text{avg}}} \int dz (\partial\rho/\partial z) e^{-iq_z z} \right|^2$$

*Small angle scattering.* Homogeneous regions on 50 nm to micron scales. Colloids, polymers, membranes, proteins in solution.

*Pair distribution function.* Glassy materials, liquids.



## More about surface scattering

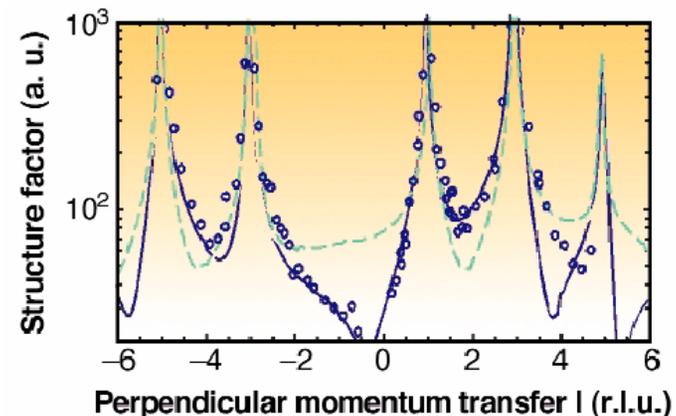
**X-ray scattering can be sensitive even to atomic monolayers.**

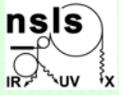
*Grazing-incidence* techniques take advantage of the total external reflection of x-rays from materials. X-rays incident below the critical angle do not penetrate more than 50 Å into the bulk. Diffraction from surface monolayers will not be swamped by background scattering.

*Grazing-incidence SAXS* makes use of the same principle. Nanoparticle coatings are a recent application.

*Crystal truncation rods.*

Similar to reflectivity, but looking at the intensity between Bragg rods of a crystal surface, where surface reconstruction, relaxation, or adlayers modify the scattering.





# Energy considerations

**X-ray energy can be selected from 1 to 100 keV.**

10 keV is typical to study length scales of 1 Å.

**Reasons to tune energy:**

Futzing with Bragg's law,  $q = (4\pi/\lambda) \sin(\theta) \sim 2\pi/d$

High energy to *penetrate dense bulk samples*, or sample chambers.

Can adjust energy to distinguish bulk and surface effects.

*Resonance*: elemental specificity,  $f = f_0 + f'(q) + if''(E)$

Contrast between elements can be changed in the diffraction patterns.

Order/disorder in alloys, superstructures, surface phase behavior.

Routinely used in macromolecular crystallography to solve structures.

*Resonance* with special terms in certain electronic and magnetic structures.

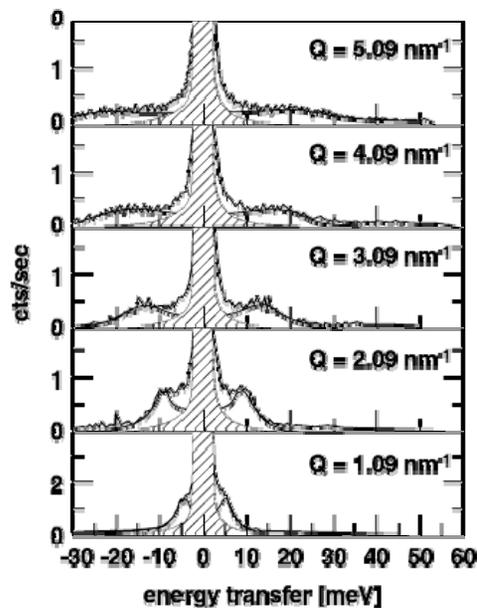
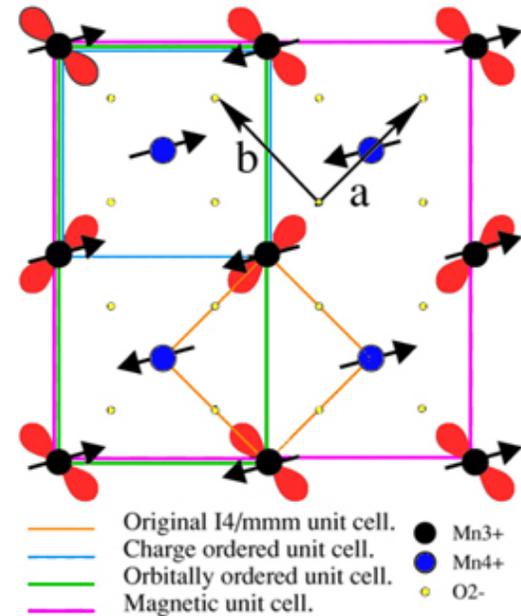
X-rays couple to magnetic structure and unlike neutrons, can distinguish spin and orbital terms.

# Electronic and magnetic structure

## Charge, orbital, and magnetic ordering

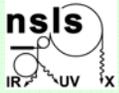
Supercells arising from the electronic structure can be detected by resonance in soft and hard x-ray ranges.

Common in layered perovskites; used to explore phase diagrams.



## Inelastic x-ray scattering

For measurement of the electronic structure in otherwise inaccessible momentum and energy regimes. Applied to liquids and solids, measure acoustic modes and electronic structure.



# Welcome to Scattering! *Elaine DiMasi, NSLS*

## It's all scattering!

Photons interact with sample, are re-radiated, and detected.  
X-ray *momentum transfer* provides structural information.

## The building blocks:

Scatter photon from one electron ...

... x-rays interact *weakly* with materials.

Scatter from an atom ...

... integrate over electron distribution.

Atomic sensitivity!  $f = f_0 + f'(q) + if''(E)$

Scatter from organized electron density distribution ...

... *crystals* or *other*, i.e., your samples.

**X-ray scattering probes structure in a huge variety of ways.**

$$I = I_0 \frac{e^4}{m^2 c^4 R^2} \left( \frac{1 + \cos^2 \phi}{2} \right)$$

$$f = \sum_n \int_0^\infty 4\pi r^2 \rho_n(r) \frac{\sin qr}{qr} dr$$

