# X-ray Absorption Fine Structure Spectroscopy

## National School on Neutron and X-ray Scattering

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Bruce Bunker
Physics Department
University of Notre Dame

# In this talk …

- Reminder about x-ray techniques
- A bit of history
- A bit of physics
- Related techniques
- The challenge of analysis
- Examples
- Related topics in this summer school

# X-ray Techniques

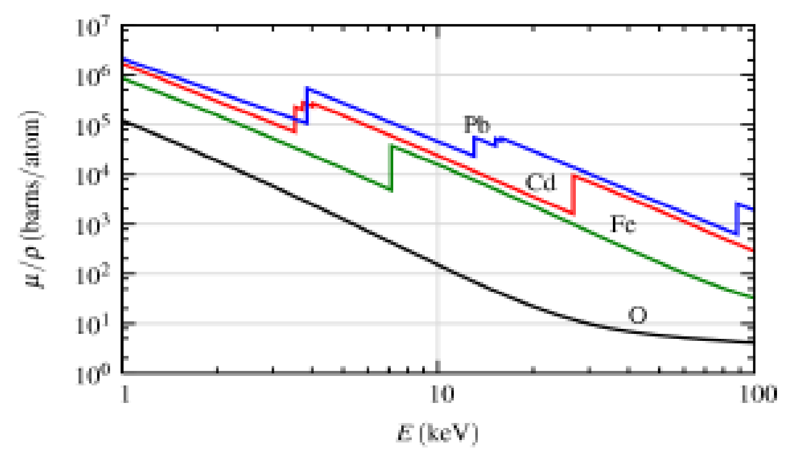
- X-ray diffraction
  - **Long-range crystalline order**
- X-ray diffuse scattering
  - **Short range order**, info on alloys, vibrations, etc.
  - Sees all possible atom pairs
- X-ray reflectivity (or reflectometry)
  - Measure specular-reflected beam intensity as function of incidence angle
  - Reveals **electron density as function of depth** near surface or interface
- X-ray absorption spectroscopy (XAFS) …

# What is XAFS?

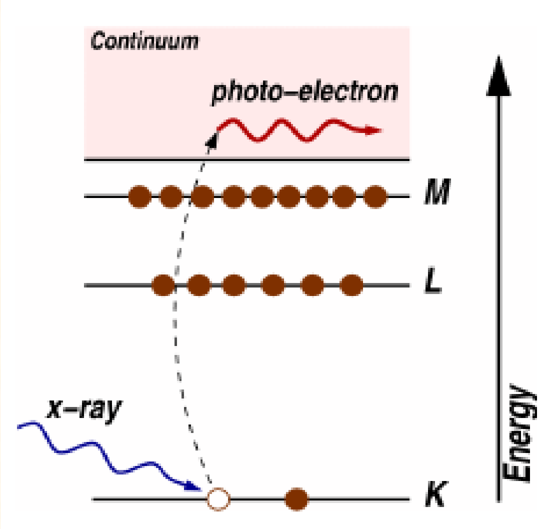
- X-ray Absorption Fine Structure spectroscopy uses the **x-ray photoelectric effect** and the **wave nature of the electron** to determine **local structures around selected atomic species** in materials
- Unlike x-ray diffraction, it does not require long range translational order – it works equally well in amorphous materials, liquids, (poly)crystalline solids, and molecular gases.
- XANES (near-edge structure) can be sensitive to charge transfer, orbital occupancy, and symmetry.

# X-ray Absorption

Many contributions to absorption, but largest in x-ray region is the **photoelectric effect: Ionization of inner-shell atomic electrons**



**Absorption Edge:**
High enough energy for excitation of **atomic core electrons** to **unoccupied states** (either bound or continuum)



Figures courtesy Matt Newville, University of Chicago / CARS

# If monatomic gas, generally smooth spectrum above edge. If molecules, liquid, or solid, see oscillatory structure.

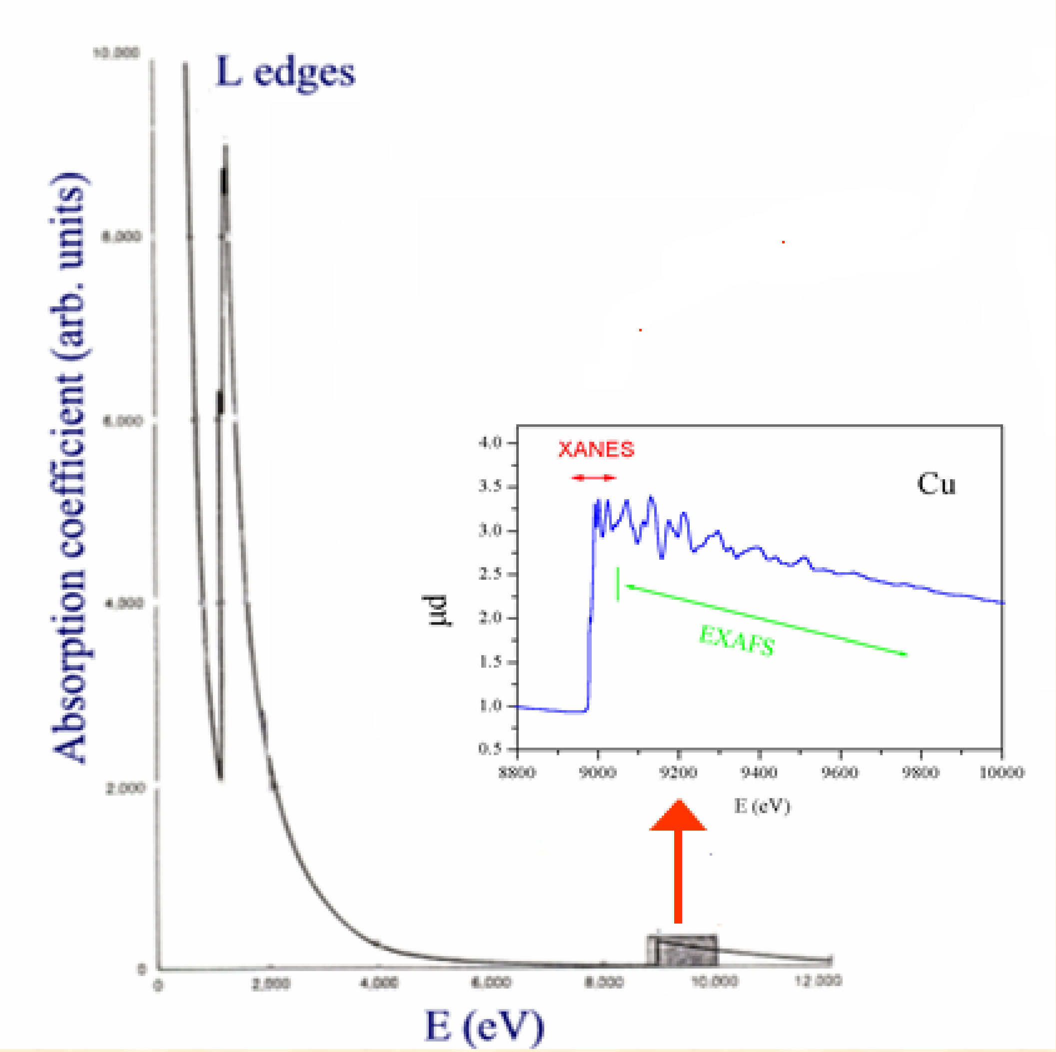
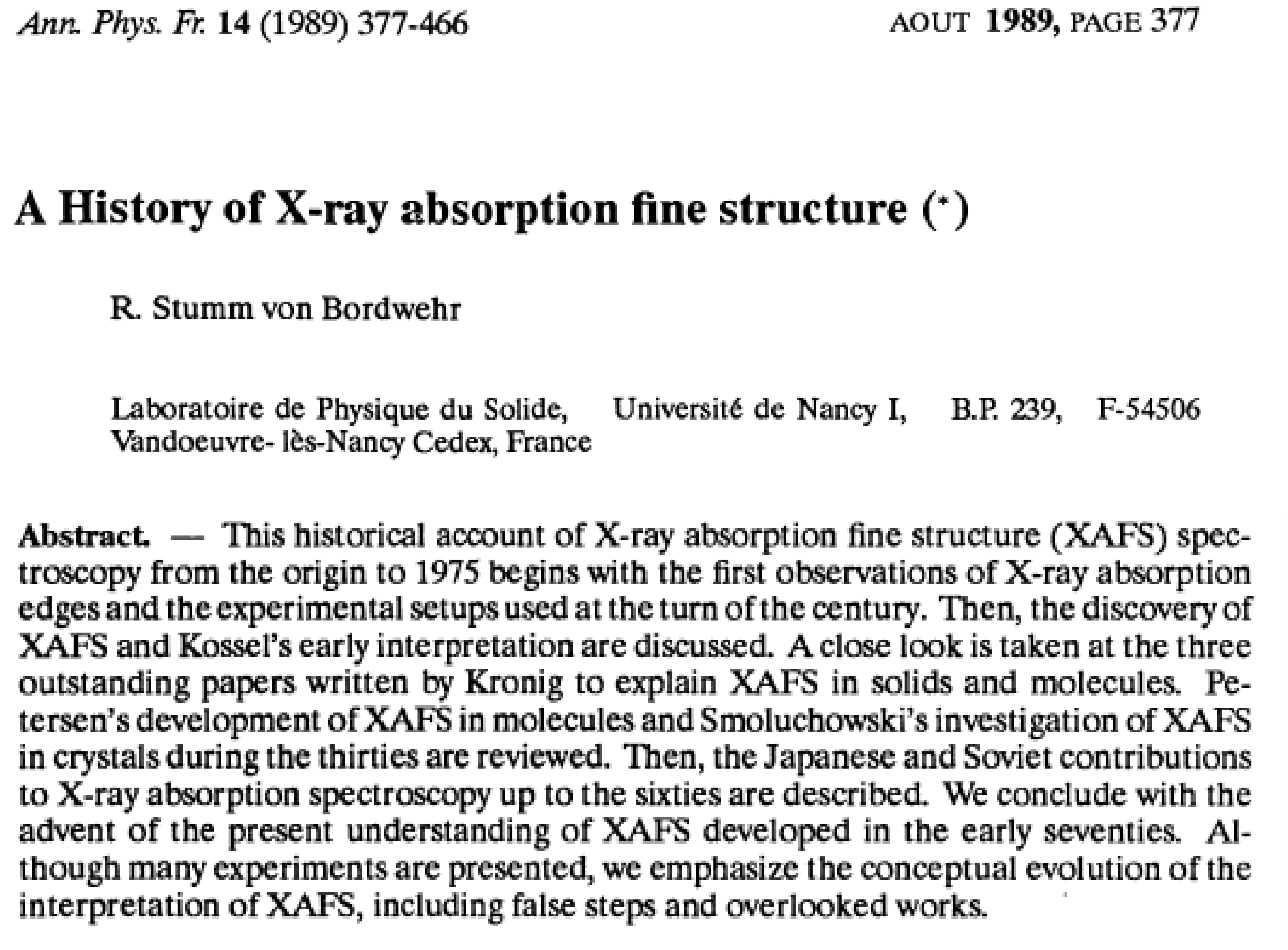


Figure courtesy Matt Newville, University of Chicago / CARS

That’s the observed effect.

Now, a bit of history…

# A nice paper on the history of the technique…



*Ann. Phys. Fr.* **14** (1989) 377-466 AOUT **1989,** PAGE 377

## A History of X-ray absorption fine structure (*)

R. Stumm von Bordwehr

Laboratoire de Physique du Solide, Université de Nancy I, B.P. 239, F-54506
Vandoeuvre- lès-Nancy Cedex, France

**Abstract.** — This historical account of X-ray absorption fine structure (XAFS) spectroscopy from the origin to 1975 begins with the first observations of X-ray absorption edges and the experimental setups used at the turn of the century. Then, the discovery of XAFS and Kossel's early interpretation are discussed. A close look is taken at the three outstanding papers written by Kronig to explain XAFS in solids and molecules. Petersen's development of XAFS in molecules and Smoluchowski's investigation of XAFS in crystals during the thirties are reviewed. Then, the Japanese and Soviet contributions to X-ray absorption spectroscopy up to the sixties are described. We conclude with the advent of the present understanding of XAFS developed in the early seventies. Although many experiments are presented, we emphasize the conceptual evolution of the interpretation of XAFS, including false steps and overlooked works.

# Early Development of XAFS

- First noted in literature by students of Manne Siegbahn in Lund: Wilhelm Stenström, Hugo Fricke 1918-1920
- Lots of early experimental and theoretical work around the world in the first 60 years of the 20th century:

  **Cauchois, Kossel, Yoshida, Kronig, Hayasi, Hanawalt, Petersen, Bogdanovich, Kostarev, Smoluchowski, Kurylenko, Izraileva**, **many more**

# Modern History

- 1960s and later: XAFS as a routine x-ray technique: **Lytle, Stern, Sayers, Kincaid, Eisenberg, Vedrinskii, Mazalov, Schaich, Pendry, Lee, Rehr, many more**
- Web of Science Search (last year): "EXAFS" or "XAFS" (but not "XAS" – too many false hits)
  - 1971-1975: **8 Publications**
  - Last year: **743 Publications**
  - Last 10 years: **7,199 Publications**
- Applications in **materials research, catalysis, molecular physics, biology/life sciences, environmental and geosciences, astronomy**, others

Now a little physics:

What do we know from quantum mechanics?

# Reminder about optical/x-ray excitation:

- Result from time-dependent perturbation theory: "Fermi's Golden Rule": Transition rate (and absorption) between two states in external $\vec{E}$ field proportional to

$$\mu \propto | \int \psi_f^* \boxed{\hat{\epsilon} \cdot \vec{r}\, e^{i\vec{k}\cdot\vec{r}}}\, \psi_i \, d^3r |^2$$

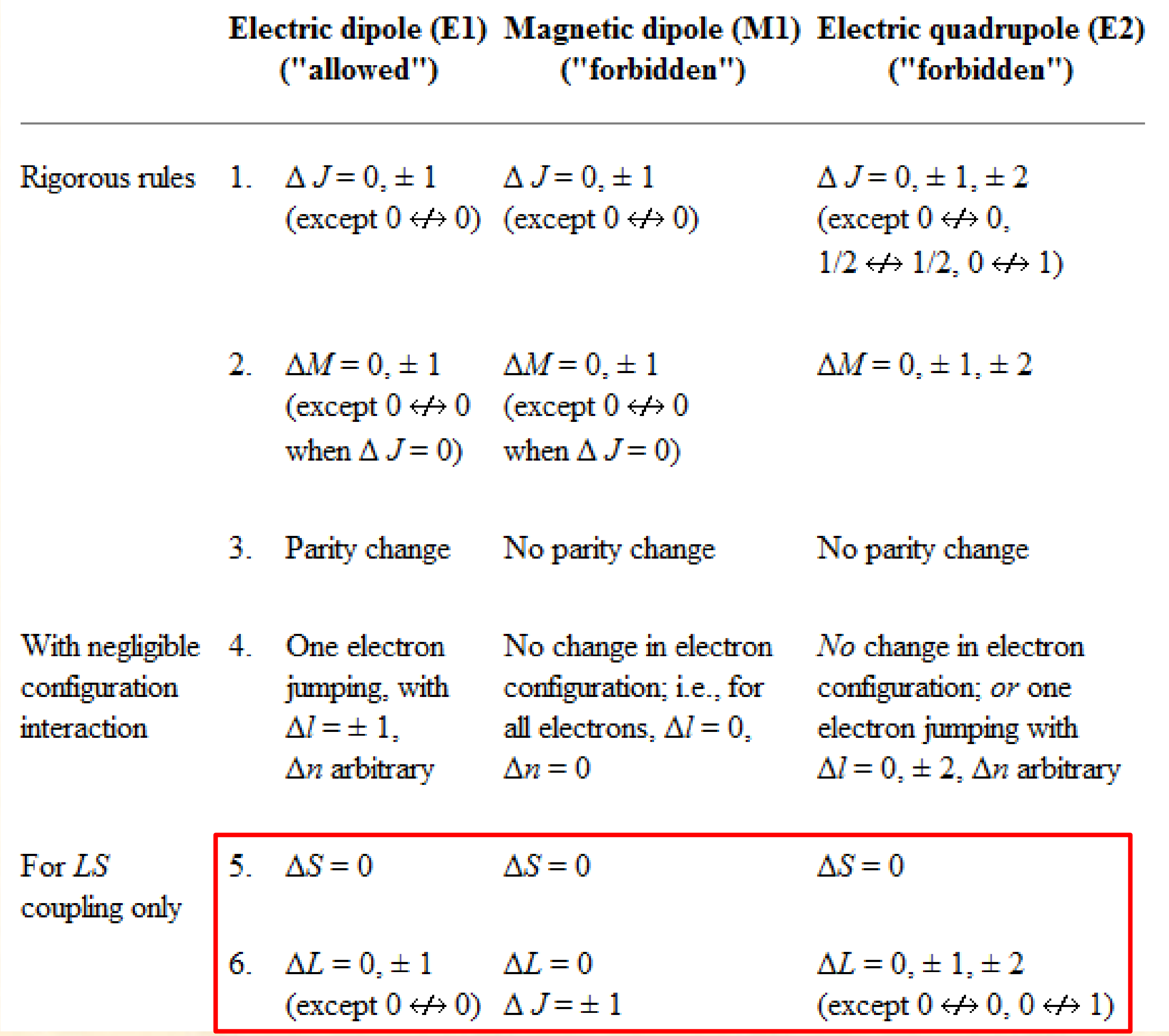
$\hat{\epsilon}$ = polarization vector

- Expand exponential, find multipole series with leading **dipole** and **quadrupole** terms

$$\approx | \int \psi_f^* \, (\hat{\epsilon} \cdot \vec{r} \; + i(\hat{\epsilon} \cdot \vec{r})(\vec{k} \cdot \vec{r})) \; \psi_i \, d^3r |^2$$

- Matrix element projects out part of the final state of the right symmetry (e.g. p, d, etc., depending on edge)

# Evaluate matrix element , get **atomic selection rules**



| | | **Electric dipole (E1) ("allowed")** | **Magnetic dipole (M1) ("forbidden")** | **Electric quadrupole (E2) ("forbidden")** |
|---|---|---|---|---|
| Rigorous rules | 1. | $\Delta J = 0, \pm 1$ (except $0 \nleftrightarrow 0$) | $\Delta J = 0, \pm 1$ (except $0 \nleftrightarrow 0$) | $\Delta J = 0, \pm 1, \pm 2$ (except $0 \nleftrightarrow 0$, $1/2 \nleftrightarrow 1/2$, $0 \nleftrightarrow 1$) |
| | 2. | $\Delta M = 0, \pm 1$ (except $0 \nleftrightarrow 0$ when $\Delta J = 0$) | $\Delta M = 0, \pm 1$ (except $0 \nleftrightarrow 0$ when $\Delta J = 0$) | $\Delta M = 0, \pm 1, \pm 2$ |
| | 3. | Parity change | No parity change | No parity change |
| With negligible configuration interaction | 4. | One electron jumping, with $\Delta l = \pm 1$, $\Delta n$ arbitrary | No change in electron configuration; i.e., for all electrons, $\Delta l = 0$, $\Delta n = 0$ | *No* change in electron configuration; *or* one electron jumping with $\Delta l = 0, \pm 2$, $\Delta n$ arbitrary |
| For *LS* coupling only | 5. | $\Delta S = 0$ | $\Delta S = 0$ | $\Delta S = 0$ |
| | 6. | $\Delta L = 0, \pm 1$ (except $0 \nleftrightarrow 0$) | $\Delta L = 0$<br>$\Delta J = \pm 1$ | $\Delta L = 0, \pm 1, \pm 2$ (except $0 \nleftrightarrow 0$, $0 \nleftrightarrow 1$) |

From physics.nist.gov/Pubs/AtSpec/node17.html

# Final State Symmetry of Photoelectron

- K-edge: 1s initial state (n = 1,l=0,m=0)
- $L_1$-edge: 2s initial state (n=2,l=0,m=0)
- $L_2$-edge: 2p (j=1/2) initial state (n=2,l=1)
- $L_3$-edge: 2p (j=3/2) initial state (n=2,l=1)
- dipole selection rules project out specific symmetry components of final state wavefunction
  - **K, $L_1$ edges probe p part of final states**
  - **$L_{2,3}$ edges probe d (& s) part of final states**
- **Note:** These rules are for **atomic potentials**. In crystal field, can have violations/mixing near the absorption edge

# Absorption Spectrum

- The measured spectrum is an average of the "snapshot" spectra (~$10^{-15}$ sec) of all the atoms of the selected type that are probed by the x-ray beam
- In general XAFS determines the statistical moments of the distribution of atoms relative to the central absorbers.
  - In the case of single scattering the **pair correlation function** is probed.
  - Multiple scattering gives information on **higher order correlations**.
  - This information is encoded in the $\chi$ (**chi**) function: ($\mu_o$ = absorption for isolated or embedded atom)

$$\mu(E) = \mu_0(E)\big(1 + \chi(E)\big)\,;\ \chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)}$$

# Fine Structure Oscillations

- Just had

  $\mu(E) = \mu_0(E)\big(1 + \chi(E)\big)$ ; $\chi(E) = \dfrac{\mu(E) - \mu_0(E)}{\mu_0(E)}$

- Modulations in $\chi$ encode information about the local structure
- $\chi$ function represents the fractional change in the absorption coefficient that is due to the presence of neighboring atoms
- How to figure out $\chi(E)$?

# The x-ray spectroscopy acronym game

- X-ray Absorption Spectroscopy (**XAS**)
  - X-ray Absorption Fine-structure Spectroscopy **(XAFS)**
  - **Extended** X-ray Absorption Fine-structure Spectroscopy (**EXAFS**)
  - X-ray Absorption **Near-Edge** Spectroscopy (**XANES**) or
  - **Near-Edge** X-ray Absorption Fine Structure (**NEXAFS**)
  - And many more variations of techniques
- In all cases, variations in x-ray absorption coefficient as function of energy related to **structural or electronic properties** of sample

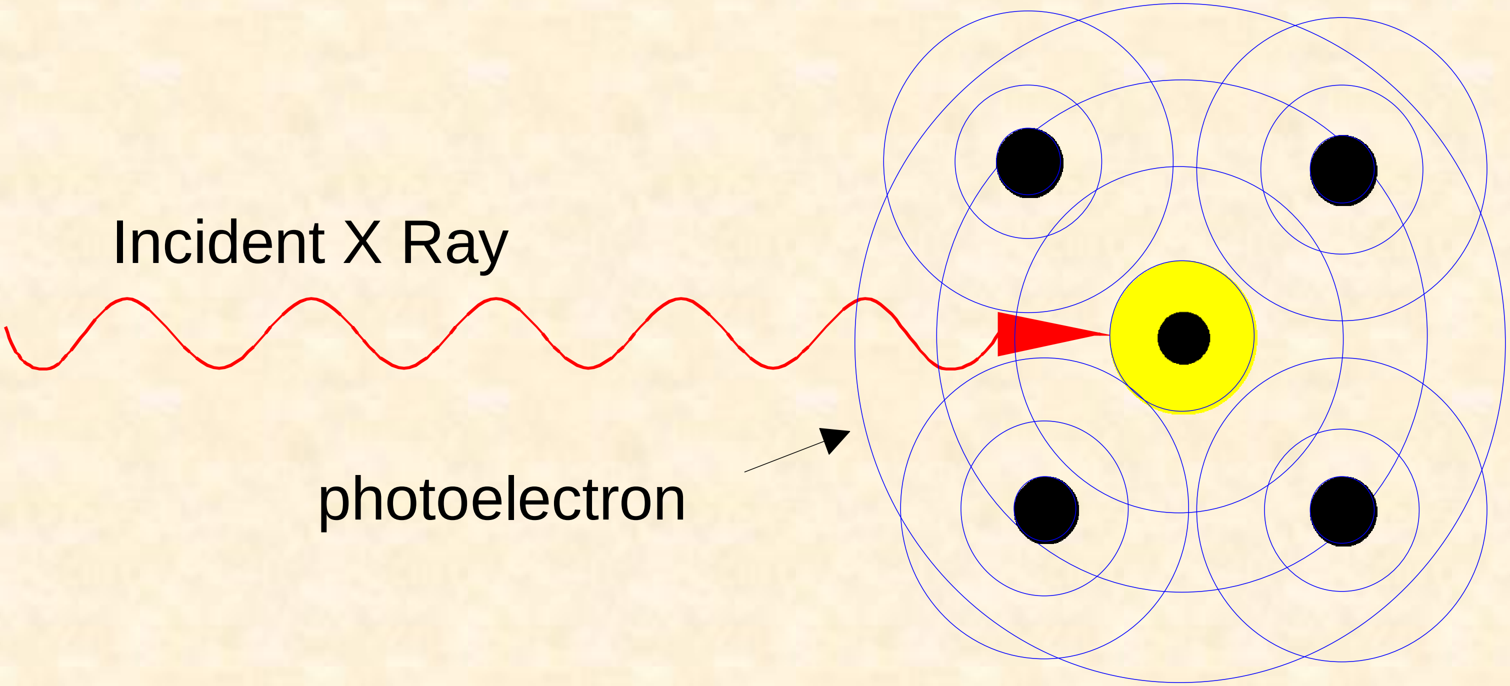
# Look more carefully at final state

- Absorbed x-ray photon induces transition of electron to unfilled final state of appropriate symmetry. Can be …
  - bound states for low energies near absorption edge
  - Continuum **outgoing spherical waves** for higher energies above threshold
    - Wave characterized by electron wavenumber

$$k = \frac{2\pi}{\lambda} = \sqrt{2m(E - E_0)/\hbar^2}$$

# Nearby atoms: origin of fine structure

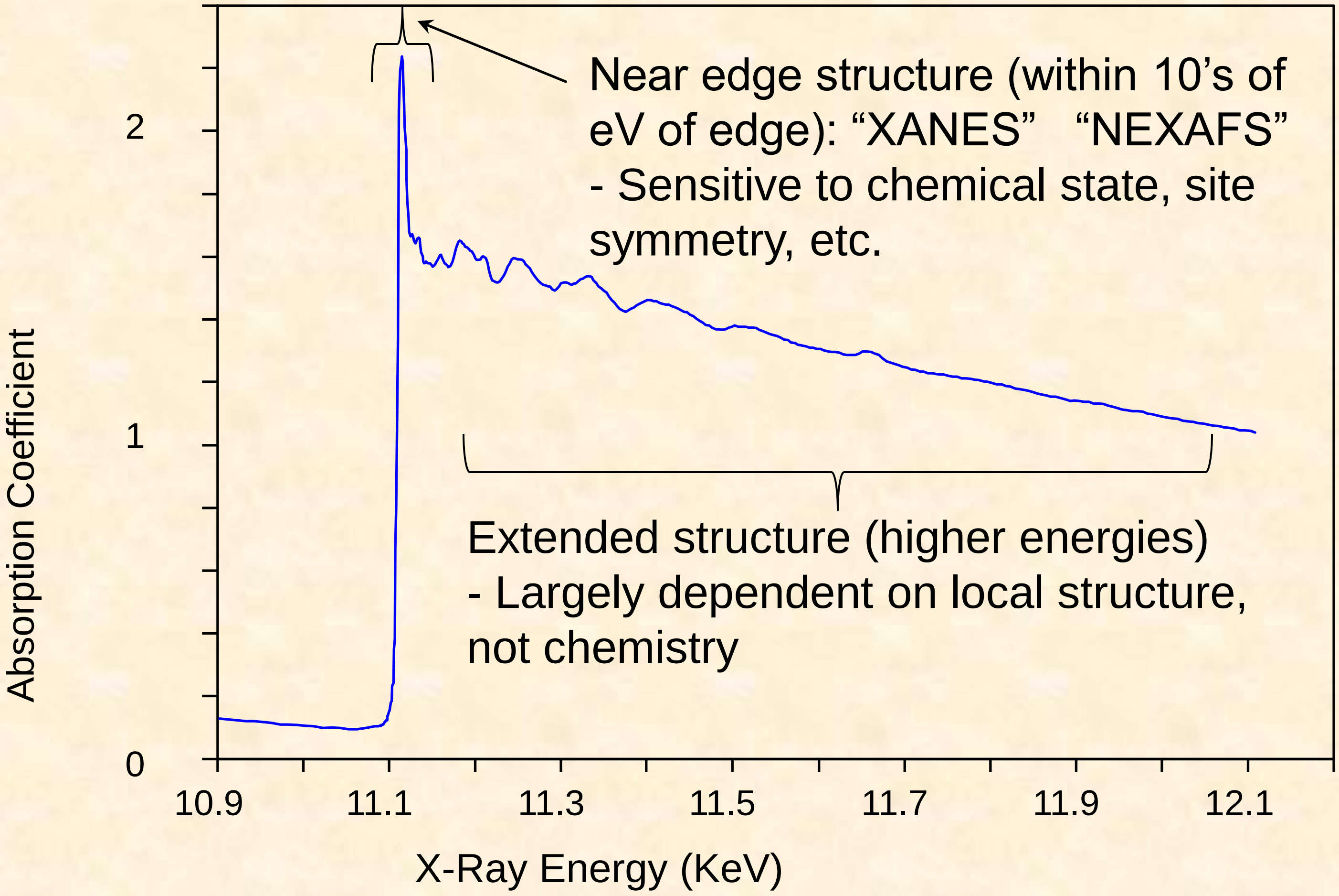
x-ray photon excites photoelectron from atom:



$$\psi_f = \psi_{\text{outgoing}} + \psi_{\text{backscattered}}$$

Maximum absorption when in phase with each other

# Energy regions of XAFS spectrum



Near edge structure (within 10's of eV of edge): "XANES" "NEXAFS"
- Sensitive to chemical state, site symmetry, etc.

Extended structure (higher energies)
- Largely dependent on local structure, not chemistry

# Fine Structure: Electron Interference

Absorption coefficient: $\mu \propto \left|\langle\psi_f|\mathcal{H}'|\psi_i\rangle\right|^2$

Where $\psi_f = \psi_{\text{outgoing}} + \psi_{\text{backscattered}}$

- Get constructive interference if outgoing and backscattered waves are in phase, destructive if $\pi$ out of phase
- Phase difference between waves for backscattering atom distance $R$ away from excited atom:

$$\Delta k = 2kR + \delta_{\text{atomic}}$$

- As photon energy changes, $k$ changes and move from destructive to constructive interference, etc.

# Extended fine structure (EXAFS)

- With some approximations, oscillations can be represented as sum of sine waves:

$$\chi(k) = \sum_R S_0^2 N_R \frac{|f(k)|}{kR^2} \sin(2kR + 2\delta_C + \phi) e^{-2R/\lambda(k)} e^{-2\sigma^2 k^2}$$

$R$: distance from central atom to surrounding atom

$N_R$: number of backscattering atoms at distance $R$

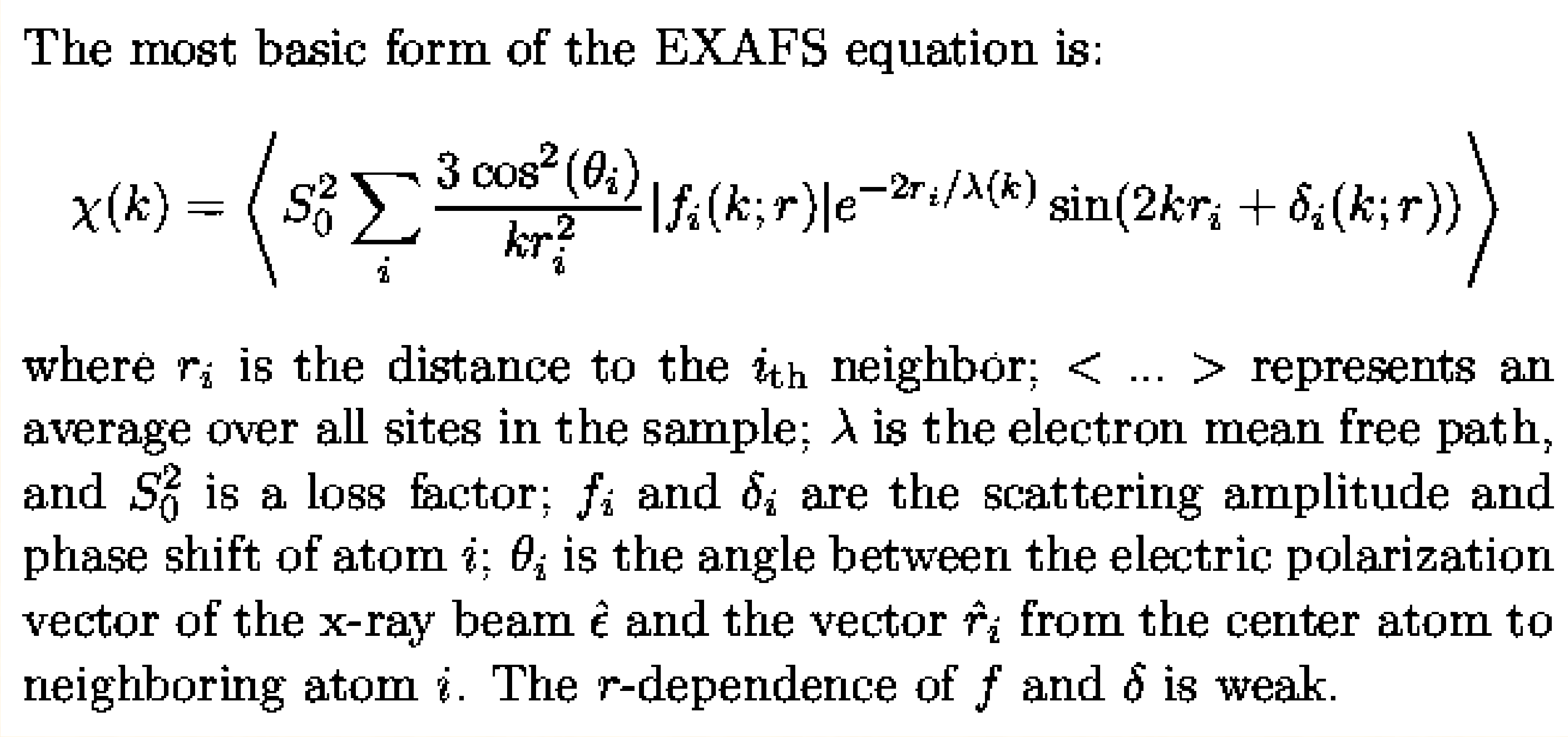
$\sigma^2$: Debye-Waller factor from multiple (but close) distances

$f(k), \delta_C, \varphi$: backscattering amplitude, phase shifts from central and backscattering atoms. (Only depend on atomic species)

$S_0^2, \lambda$: reduction factor, mean-free path due to inelastic processes, core-hole lifetime

This is for an **isotropic average** (e.g. solution or unoriented powder)

# With angular dependence (K edges)



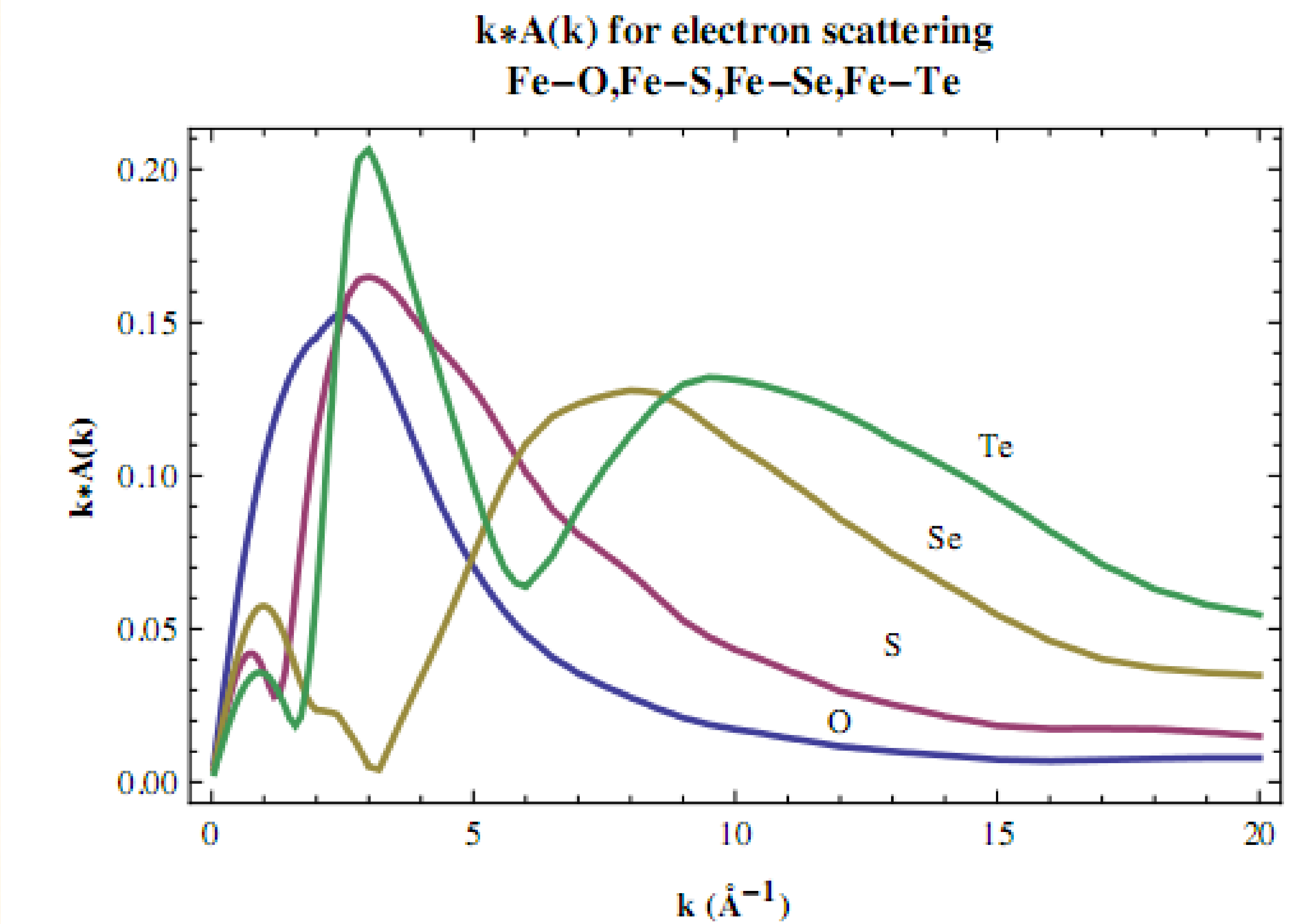
The most basic form of the EXAFS equation is:

$$\chi(k) = \left\langle S_0^2 \sum_i \frac{3\cos^2(\theta_i)}{kr_i^2} |f_i(k;r)| e^{-2r_i/\lambda(k)} \sin(2kr_i + \delta_i(k;r)) \right\rangle$$

where $r_i$ is the distance to the $i_{\mathrm{th}}$ neighbor; $< \ldots >$ represents an average over all sites in the sample; $\lambda$ is the electron mean free path, and $S_0^2$ is a loss factor; $f_i$ and $\delta_i$ are the scattering amplitude and phase shift of atom $i$; $\theta_i$ is the angle between the electric polarization vector of the x-ray beam $\hat{\epsilon}$ and the vector $\hat{r}_i$ from the center atom to neighboring atom $i$. The $r$-dependence of $f$ and $\delta$ is weak.

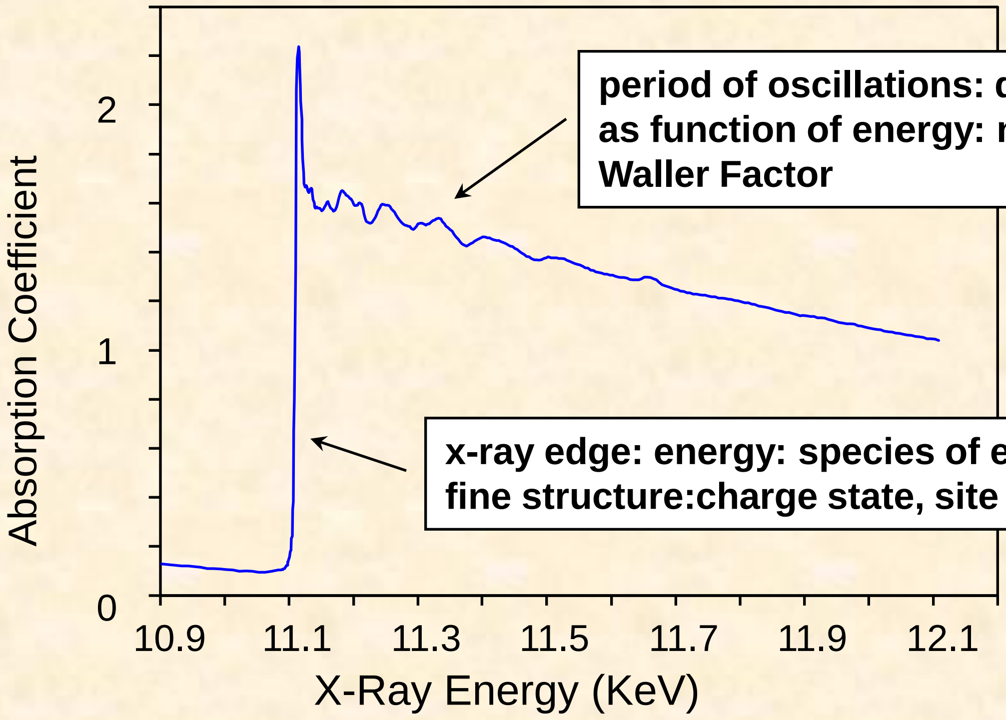
- Angular dependence useful for single-crystal, surface, interface studies (more later)

# *k* dependence of scattering helps identify types of scattering atoms



Courtesy Grant Bunker

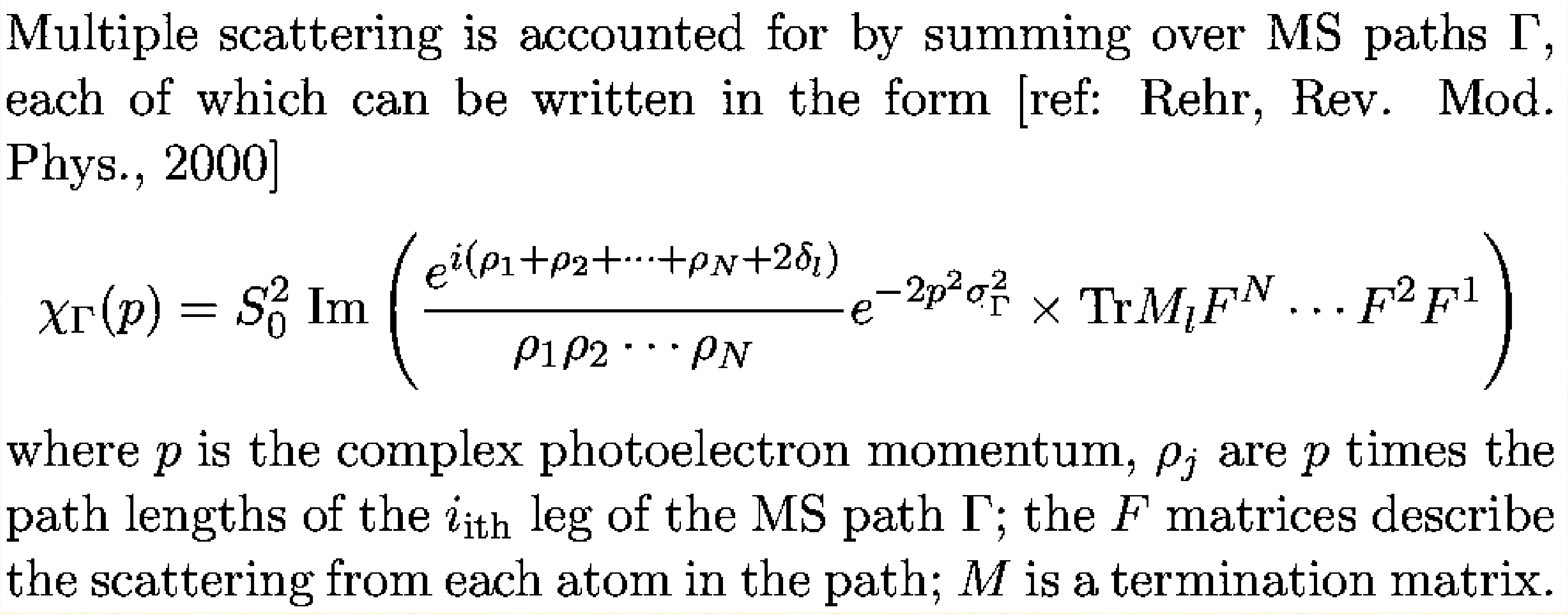
# Structural information from XAFS spectrum



**period of oscillations: distance to nearby atoms; amplitude as function of energy: number, types of neighbors; Debye-Waller Factor**

**x-ray edge: energy: species of excited atom;**
**fine structure:charge state, site symmetry**

# Sometimes need to worry about multiple scattering as well…

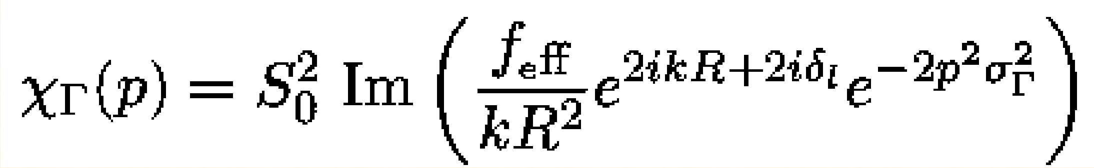


Multiple scattering is accounted for by summing over MS paths $\Gamma$, each of which can be written in the form [ref: Rehr, Rev. Mod. Phys., 2000]

$$\chi_\Gamma(p) = S_0^2 \,\mathrm{Im}\left(\frac{e^{i(\rho_1+\rho_2+\cdots+\rho_N+2\delta_l)}}{\rho_1\rho_2\cdots\rho_N} e^{-2p^2\sigma_\Gamma^2} \times \mathrm{Tr} M_l F^N \cdots F^2 F^1\right)$$

where $p$ is the complex photoelectron momentum, $\rho_j$ are $p$ times the path lengths of the $i_{\mathrm{ith}}$ leg of the MS path $\Gamma$; the $F$ matrices describe the scattering from each atom in the path; $M$ is a termination matrix.

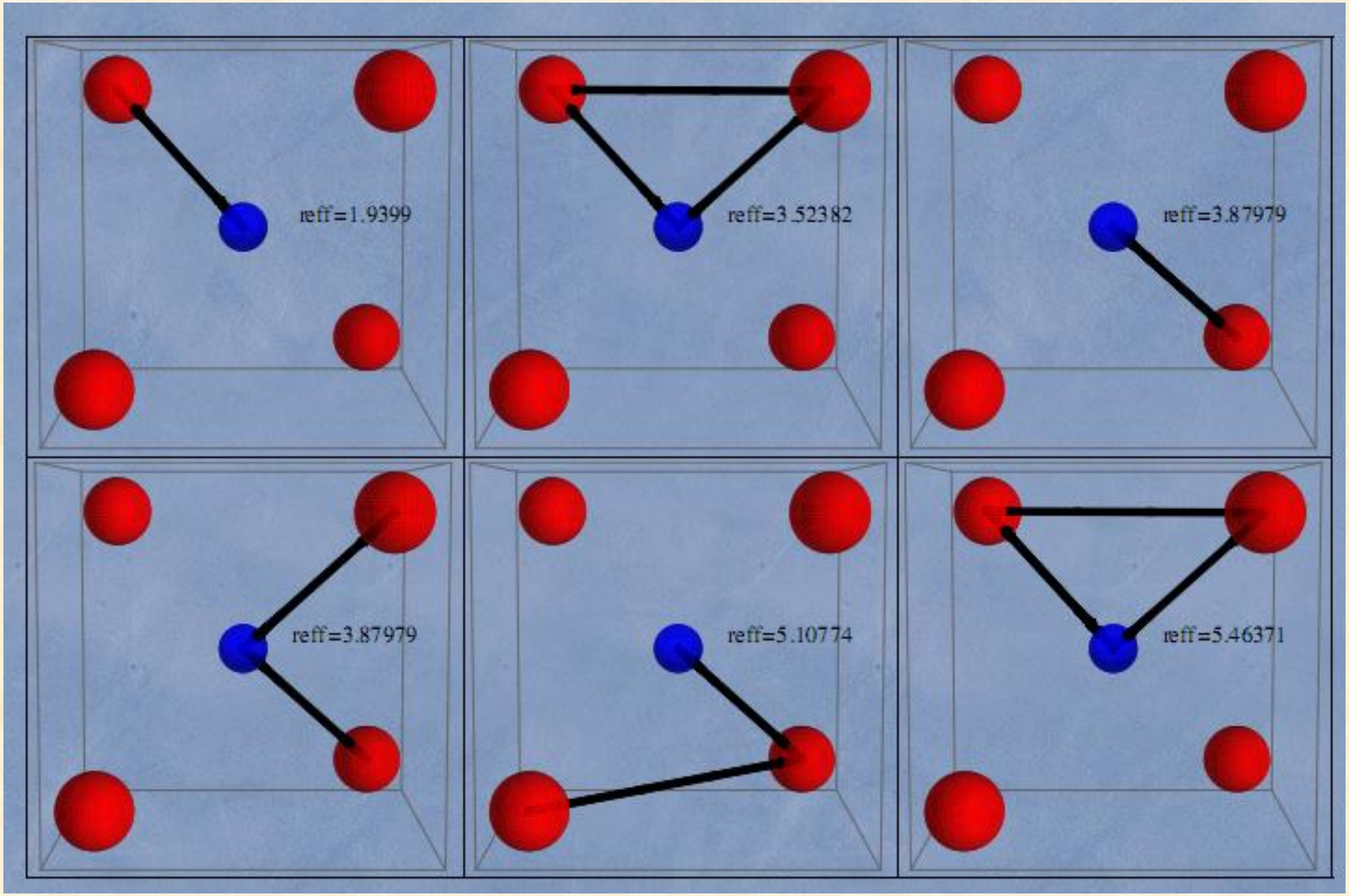
Compare to single-scattering expression:



$$\chi_\Gamma(p) = S_0^2 \,\mathrm{Im}\left(\frac{f_{\mathrm{eff}}}{kR^2} e^{2ikR+2i\delta_l} e^{-2p^2\sigma_\Gamma^2}\right)$$

Courtesy Grant Bunker

# Leading paths in $MnO_4$



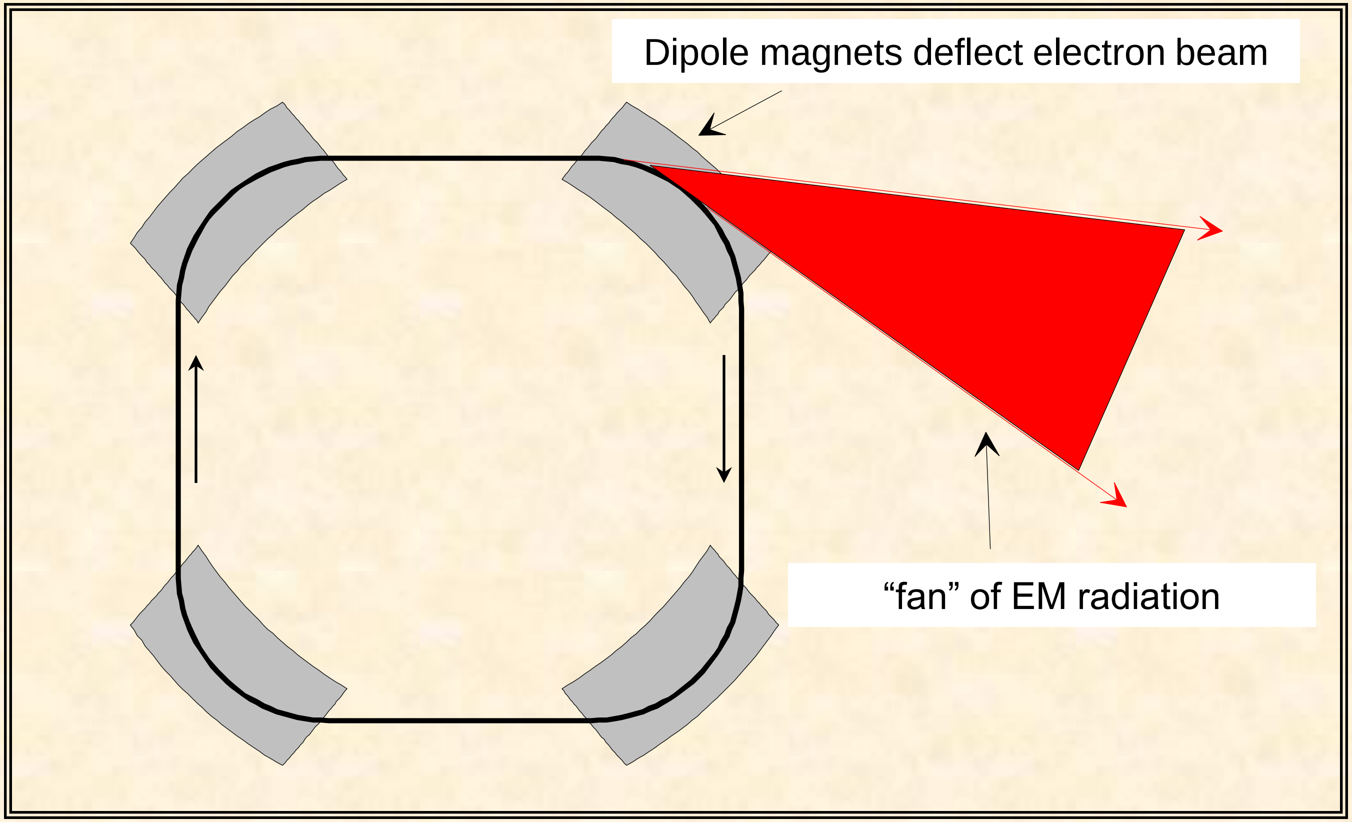
Courtesy Grant Bunker

# Back in to analysis to extract structural information in a minute, first…

- These experiments require x-ray beam that is
  - **extremely intense**
  - **well-collimated** (for some experiments)
  - **broad-spectrum** so that we can tune x-ray energy
- By far best source is **synchrotron radiation**

# Synchrotron Radiation

electron storage ring: Relativistic electrons in “racetrack”



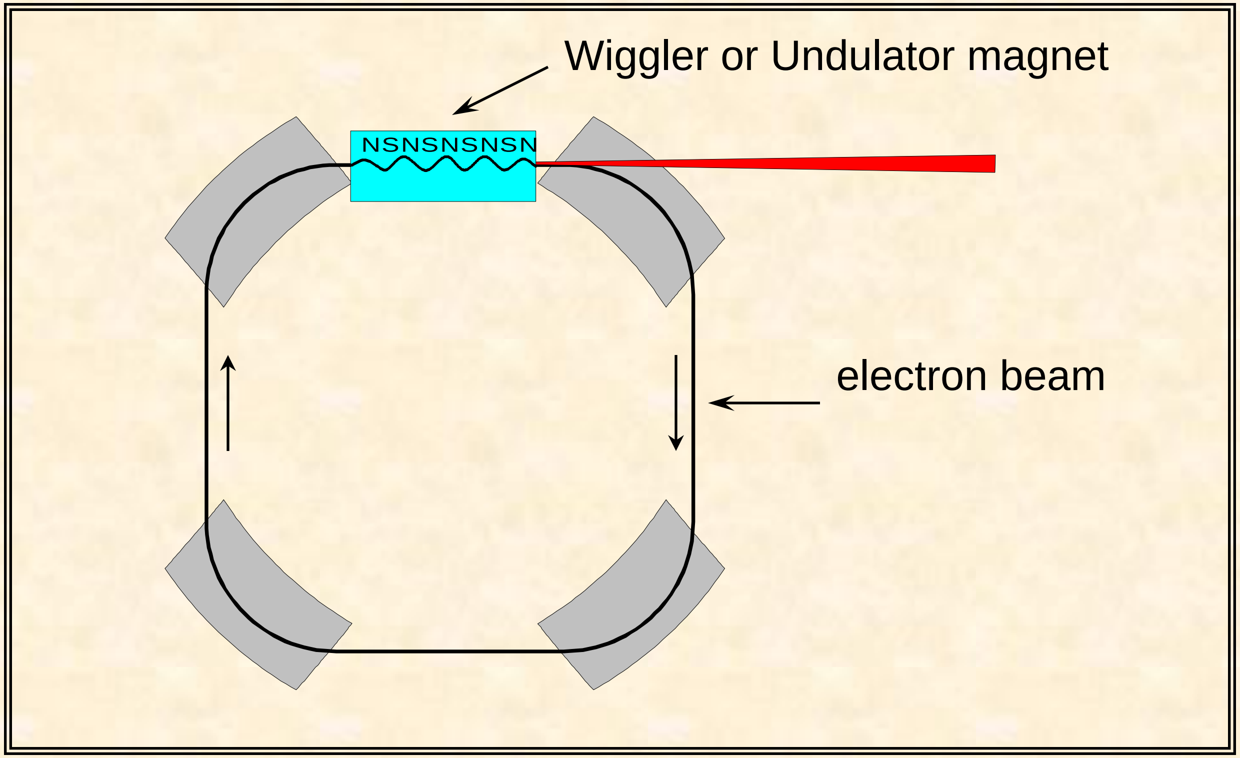
Dipole magnets deflect electron beam

“fan” of EM radiation

In real storage ring, **many** bending magnets with **small angle change**

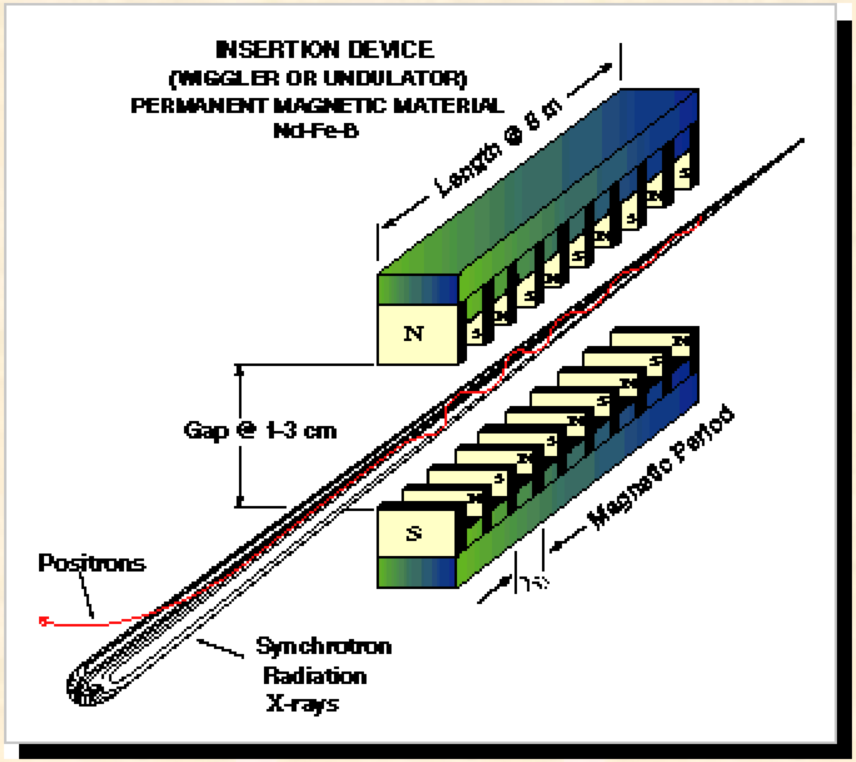
**Source of extremely intense x rays with broad energy spectrum**

# “Insertion Devices”



Extra magnetic poles, stronger magnetic field, *interference* between radiation from each pole give extremely **“brilliant”, highly coherent** x-ray beam

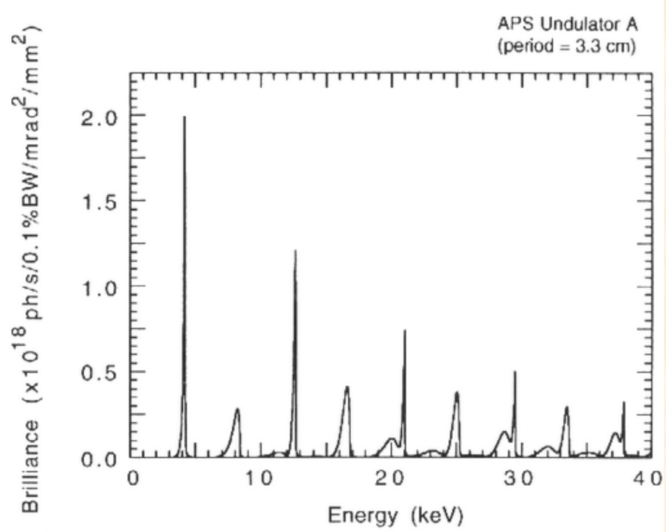
# Undulator Magnets



Extremely “bright” beam (small source size, small divergence)

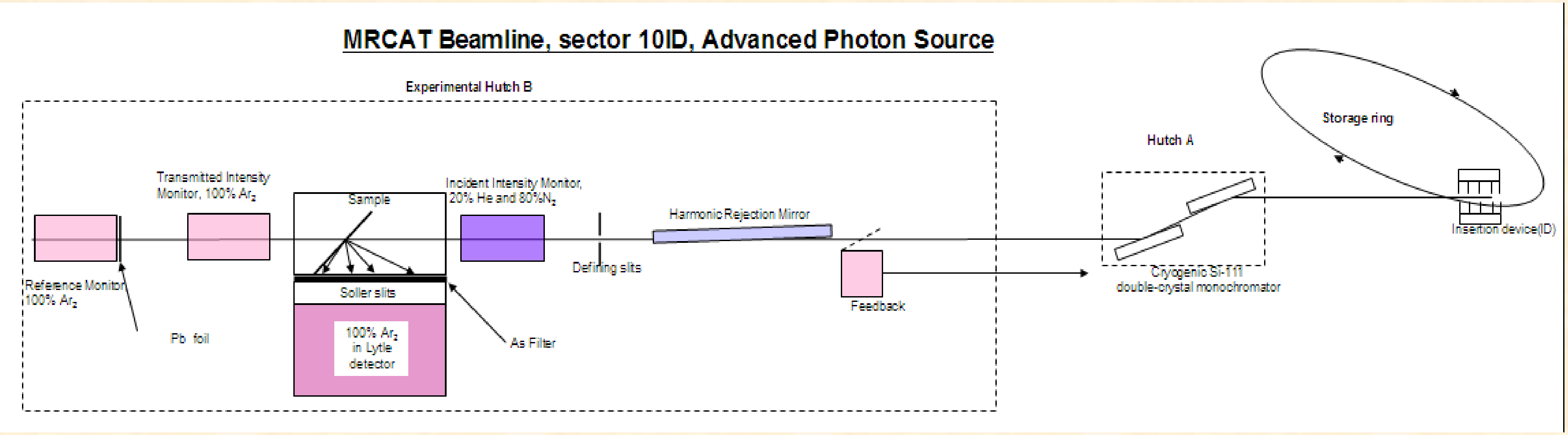
Great for spatial resolution, angular resolution, etc.

**Undulators** have sharp peaks in spectrum that can be tuned by changing gap
**Wigglers** have stronger field, broad spectrum



APS Undulator “A”
on-axis brilliance

# Schematic of beamline Instrumentation



X-ray beamline components include…

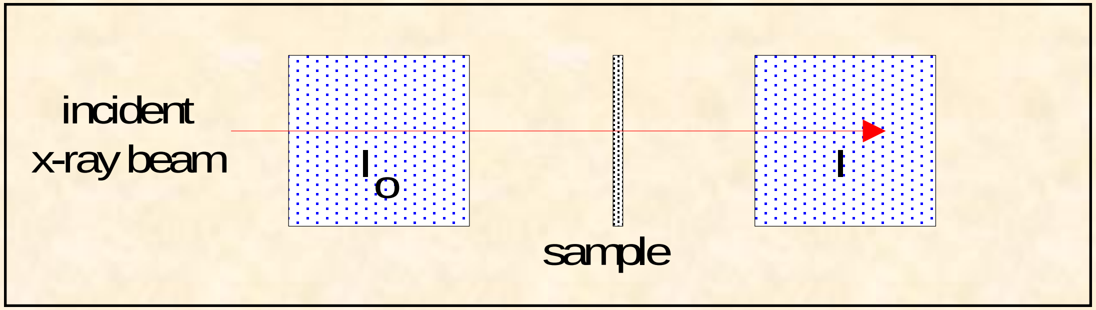
- “Front-end” components (cooled slits, etc.)
- Bragg Crystal Monochromator (two Si crystals, first cooled with liquid nitrogen)
- Harmonic-rejection mirror (monochromator lets through not only energy of interest, but harmonics)
  - Alternative: detune monochromator
- Detectors (several different types)
- Goniometers, etc., for sample positioning

# What makes a good XAFS beamline?

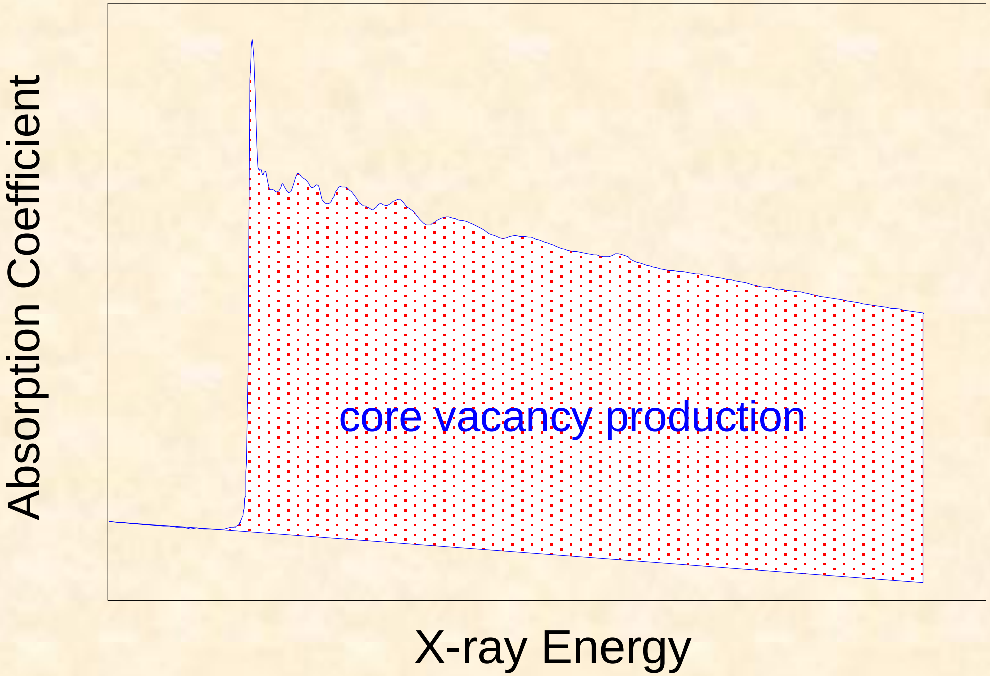
- Monochromator explicitly designed for **continuous energy scanning** (pretty uncommon for lines optimized for scattering), with approximately 1 eV or $10^{-4}$ relative energy resolution
- Smooth spectrum into monochromator
  - Bending magnet – naturally broadband
  - Wiggler – naturally broadband, but heat load can be tricky to deal with
  - Undulator – peaked spectrum, need to either scan with monochromator or “taper”
- Harmonic elimination (mirror or detuning mono)
- Detectors optimized for the different detection modality, particularly linearity with intensity

# Types of Measurements

**Transmission:**
directly measure absorption as function of incident energy

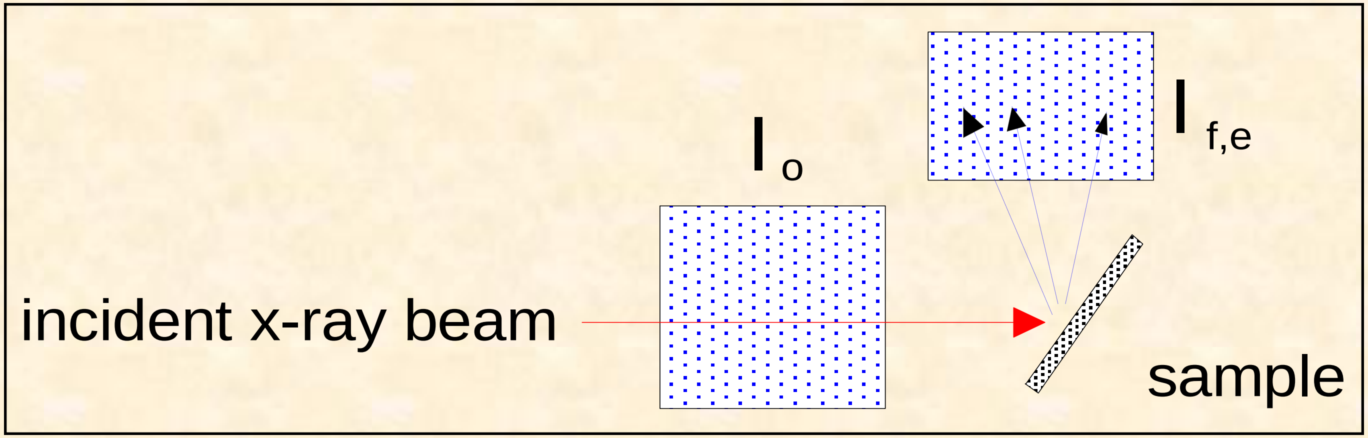


Note: Extra absorption above edge due to excitation of core electron, and creation of atomic "core vacancies" that later decay



# “Indirect” XAFS Detection Methods: (proportional to absorption)

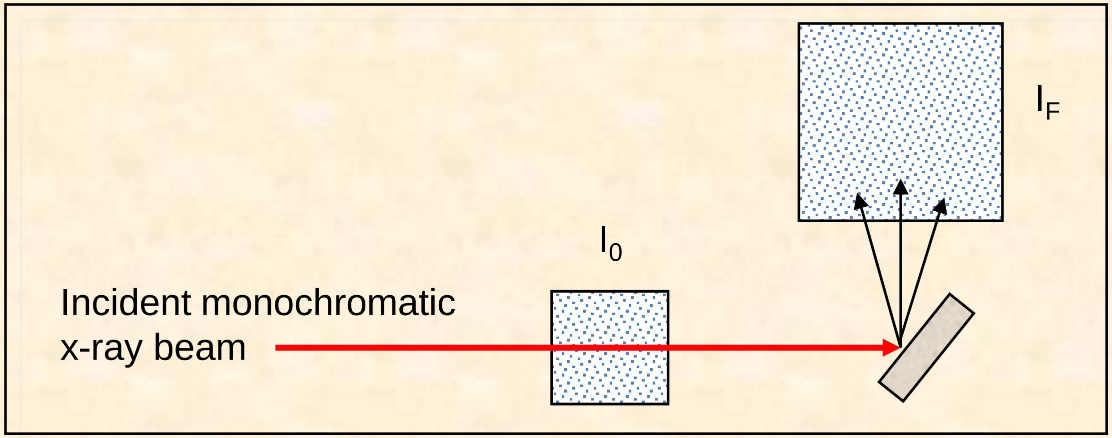
- x-ray fluorescence
- emitted electrons (“total electron yield”)



Measure **emitted flux** as function of **incident beam energy**

# X-ray Fluorescence Detection

- Proportional to absorption
- More sensitive for dilute atomic species



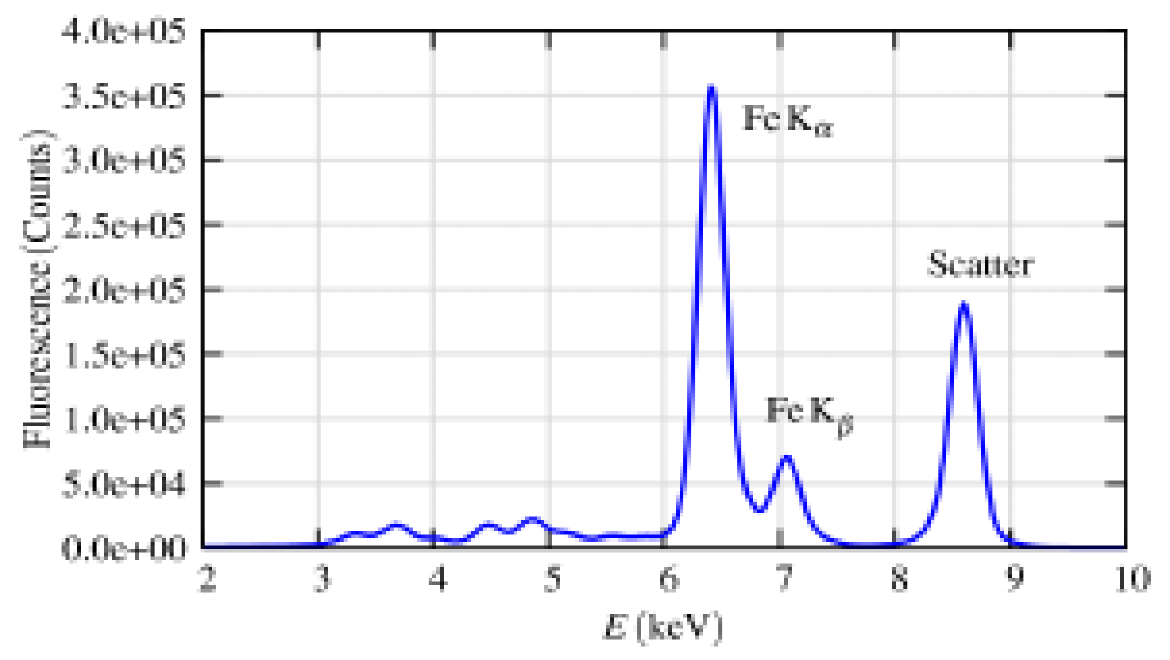
Measure emitted flux as function of incident beam energy

# Standard XAFS detectors

- Integrating (non-energy resolving)
  - Ionization chambers
  - Fluorescence ionization chambers (Stern/Heald)
  - PIN diodes/PIPS detectors
- Pulse counting (energy resolving)
  - Solid State (Ge/Si) detectors
  - Silicon Drift Detectors (SDD)
  - Scintillator/Photomultiplier (PMT)
  - Proportional Counters (PC)
  - Avalanche Photodiodes (APD)

# More on Fluorescence Measurements

- X-rays from sample include not only fluorescence signal, but also background:
  - Elastic and Compton scattered x-rays
  - Fluorescence from other atomic species



For many systems, background can be 10-100 times larger than desired fluorescence

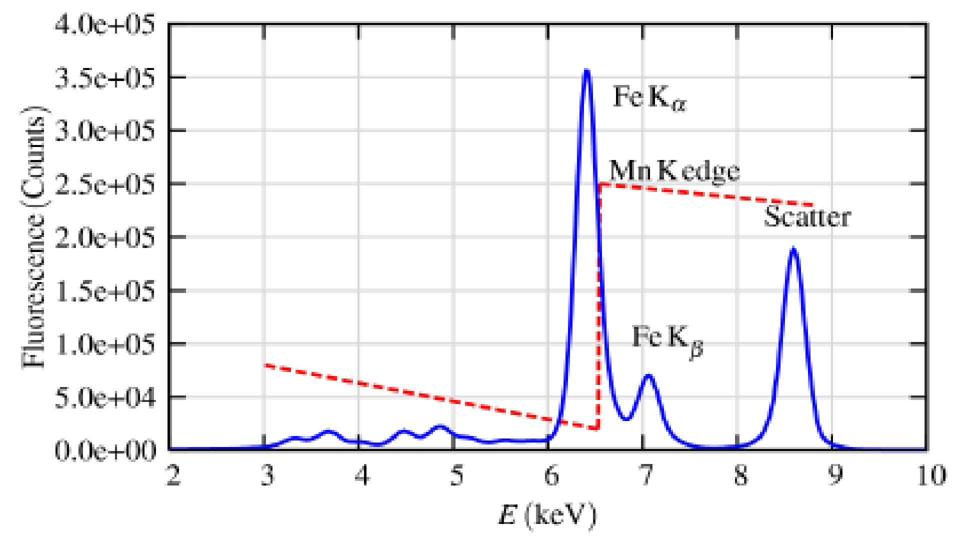
Figures pillaged from Matt Newville, University of Chicago / CARS

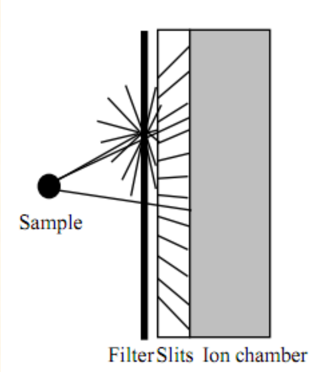
# Minimization of X-ray Background

- Scattered x-ray background at higher energy than fluorescence
- Two common methods:
  - Can use x-ray “filters” that have more absorption for background than fluorescence signal
  - Use energy-resolving detector to choose just desired energy

Screen clipping taken: 6/8/2011 5:07 PM

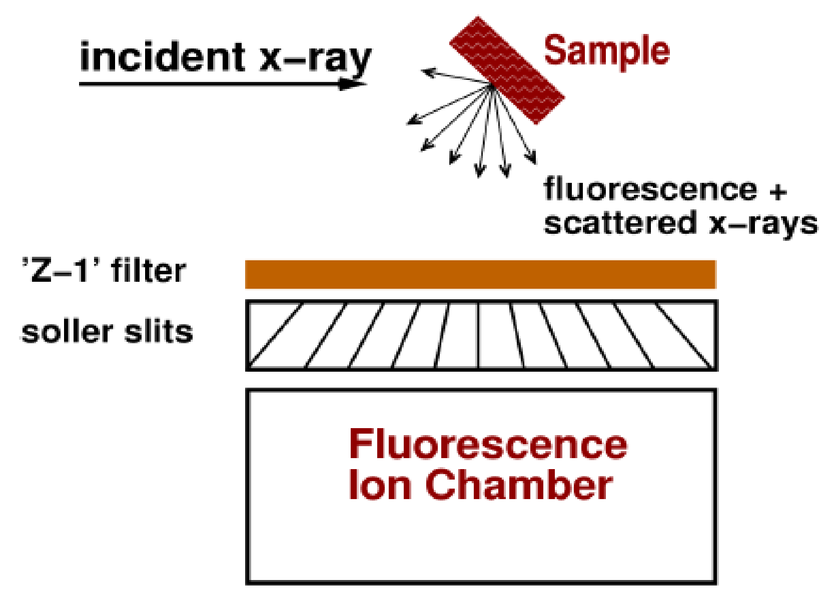
# For high fluorescence flux: X-ray Filters





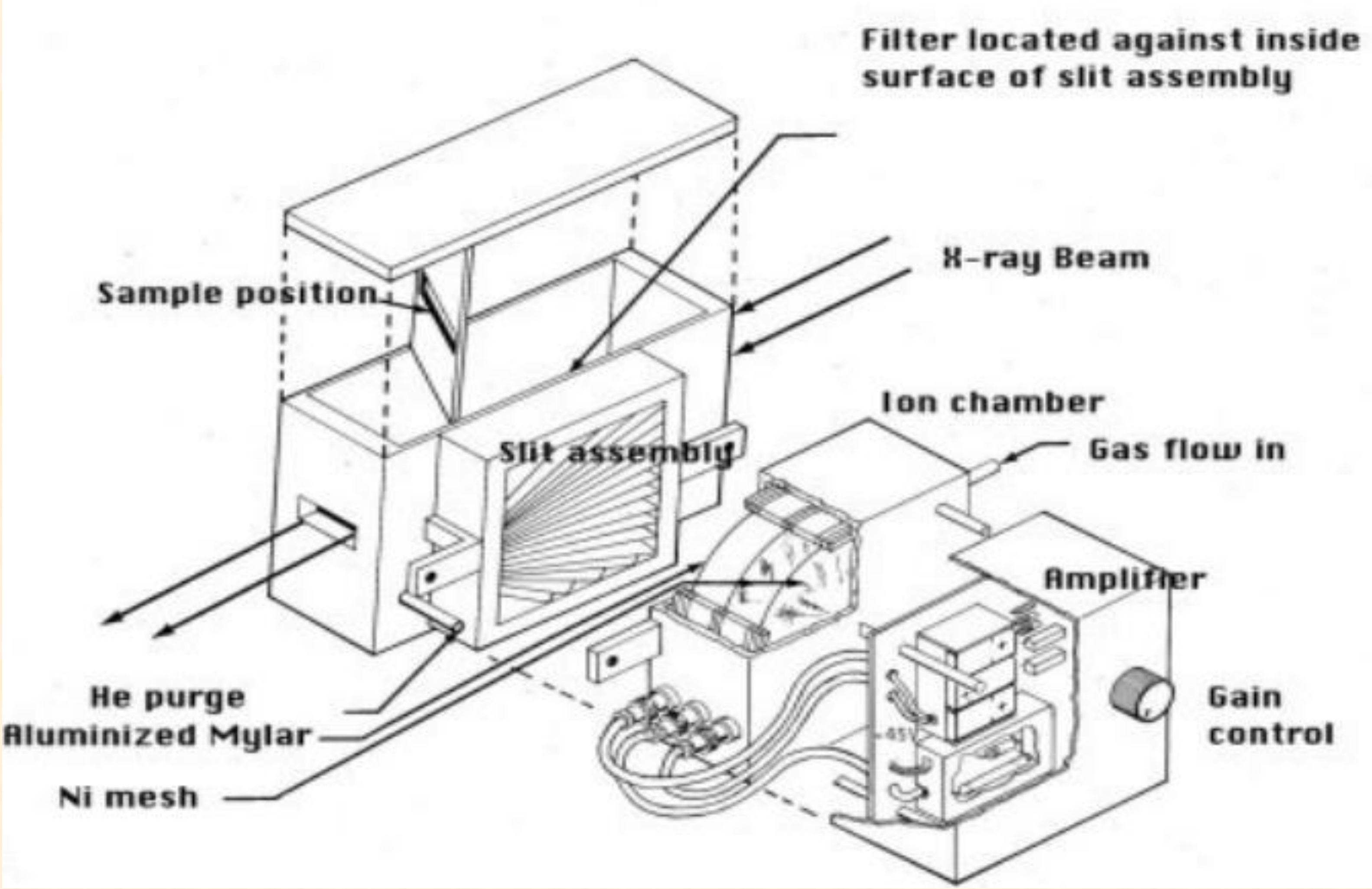
Use Z-1 filter (e.g. Mn for Fe fluorescence). Use Soller slits to minimize re-fluorescence from filter.

This technique works well for relatively concentrated samples

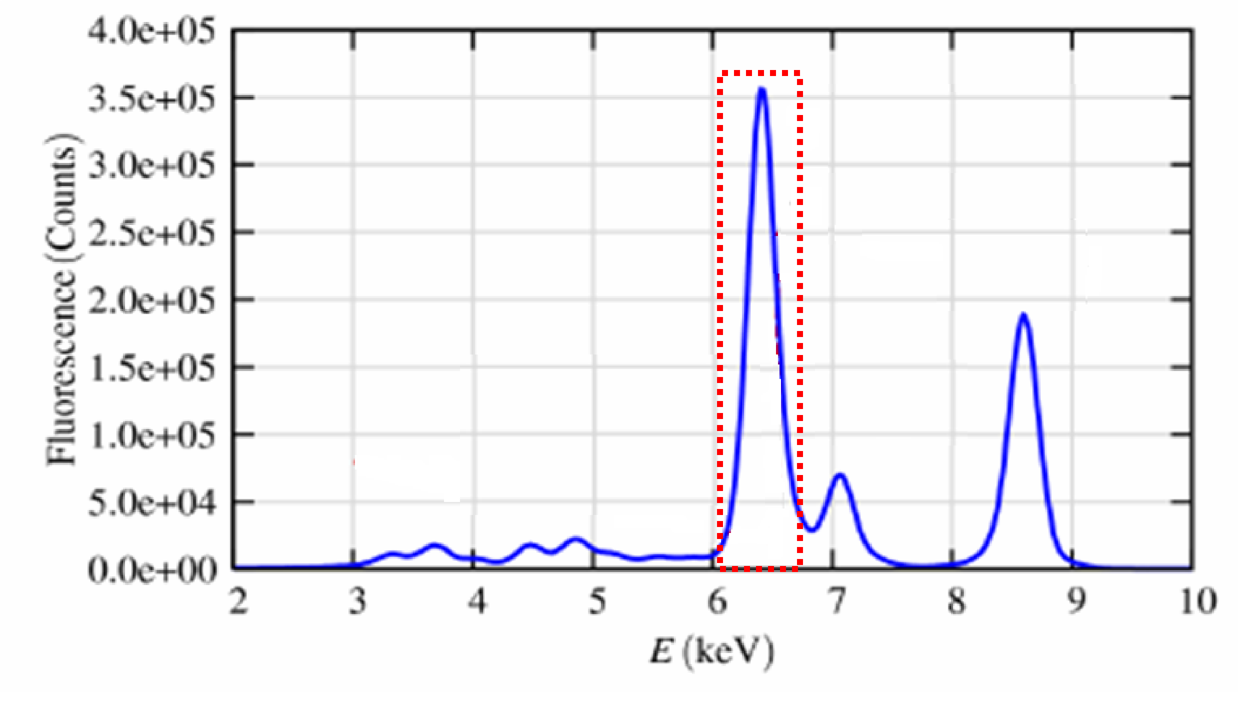


Figures courtesy Matt Newville Grant Bunker

# Stern/Heald/Lytle Detector



# Multi-element solid-state detectors (usually either Ge or Si)



- Select just energy region of interest
- Problems: Relatively low count rate, possible non-linearity

Figure courtesy Matt Newville

# Multi-element Ge detector

- e.g. Detector → preamp → shaping amp → multichannel analyzer or single channel analyzer + scaler
- Biggest problem: low count rate for each element (which is the reason for more elements; back up for lower flux)
- Can use with Z-1 filter

13-element Canberra

# Si Drift Detector

- Much higher count rate than Ge detectors $\sim 10^6$ cps vs. $\sim 2 \cdot 10^5$ cps / element
- Poor efficiency at higher energies because of less absorption by Si compared to Ge

Vortex-60EX®

# Another Approach:
# Energy discriminate with crystal analyzer

- If *lots* of background/signal, easy to get enough signal to saturate detector
  - → Get rid of background **before** detector
- Conventional approach: flat or Johansson bent/cut crystal analyzer
  - High energy resolution
  - Each crystal has small acceptance, so typically need to form array of them, all precisely aimed
- Bent Laue analyzer
  - More next slide
- In both cases, can use non-energy analyzing detector, e.g. ion chamber or integrating scintillator

# Bent-Laue analyzer

- Extreme bending of crystal in particular log-spiral shape broadens rocking curve and acceptance angle, so can get significant collection with single crystal
- Poorer resolution, but good enough to remove elastic and other fluorescence peaks

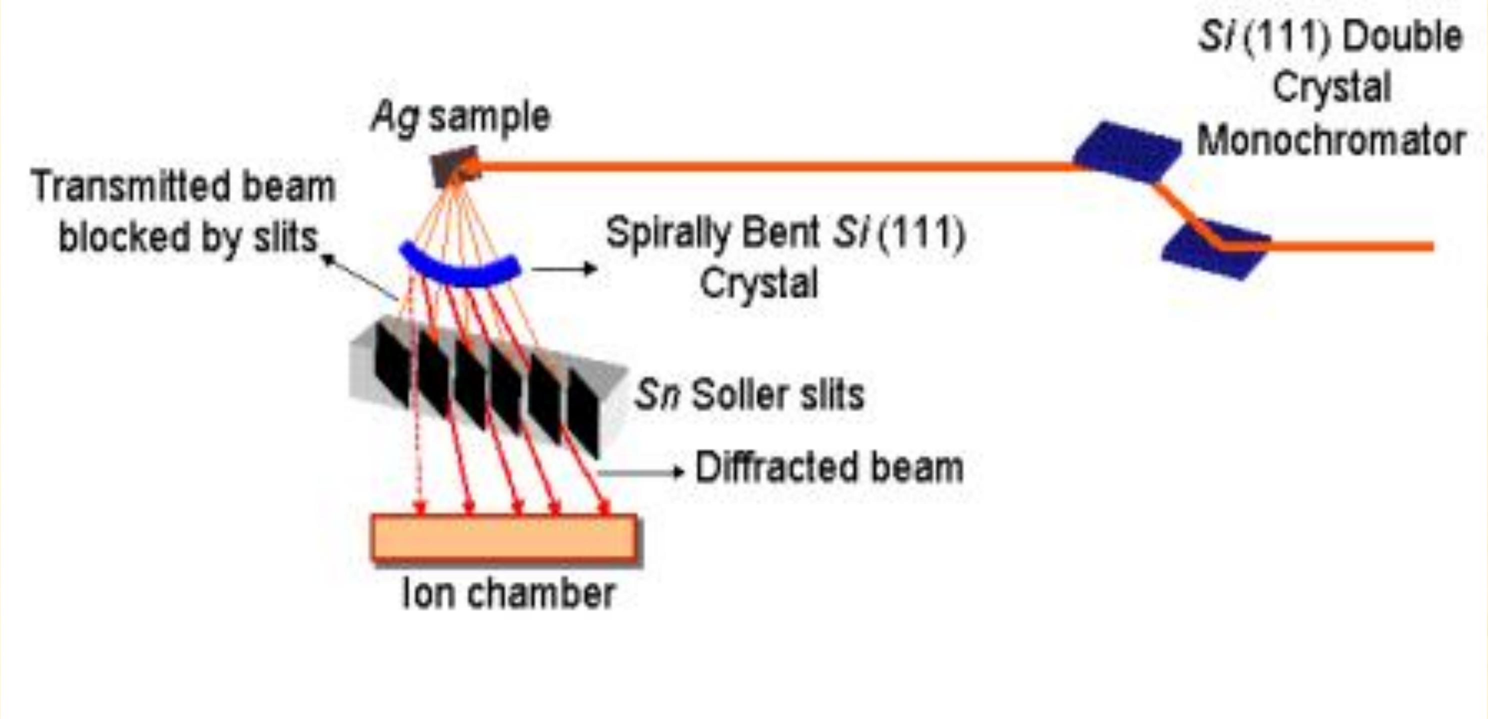
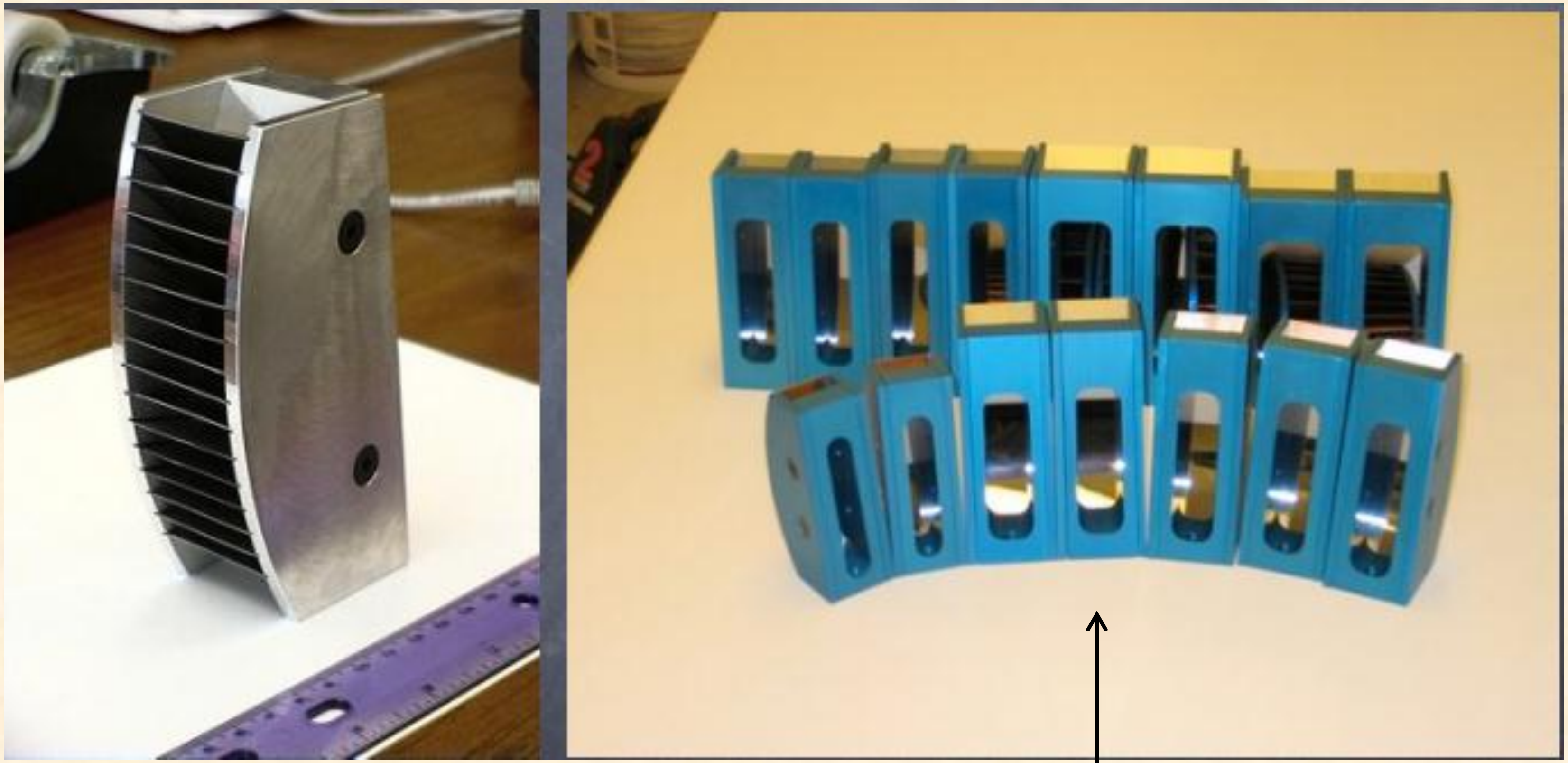


Figure courtesy Grant Bunker

# Bent-Laue analyzer



Different analyzers optimized for
different energy ranges

# Which detection method to use?

- concentrated, not too thick: use transmission
  want edge step ~1.0 (>0.1, <2.0)
- concentrated, thick: use electron yield, low-angle x-ray emission, total external reflection fluorescence, or apply fluorescence corrections numerically
- dilute samples: (< .1 absorption length edge step) use use fluorescence detection
- microbeams can used to measure small grains which may be concentrated even if sample is dilute on average (still must worry about particle size effects though)

# When performing experiments, need to keep track of (depending on beamline)

- **Undulator** (optimization for your energy region: choose taper and/or scanning parameters)
- **Monochromator** (optimize scanning, feedback stabilization, glitches)
- **Harmonic rejection mirror** (optimize for your energy range)
- **Detectors** ($I_0$, $I_t$, fluorescence; optimize for your samples)
- **Samples** (design for optimum thickness, uniformity, etc. During measurements need to monitor temperature, radiation damage, etc.)

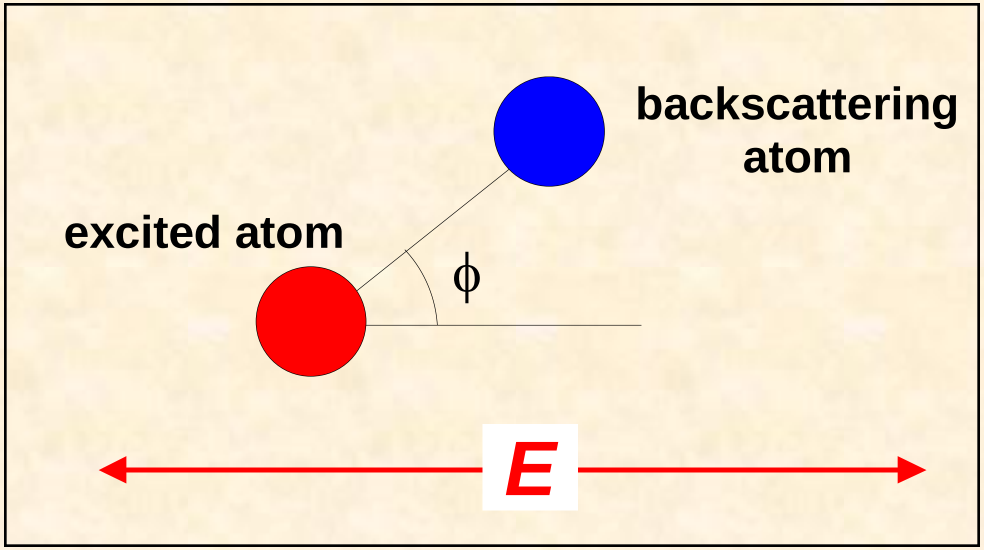
# Other variations on experimental methods …

# Polarization Dependence in XAFS

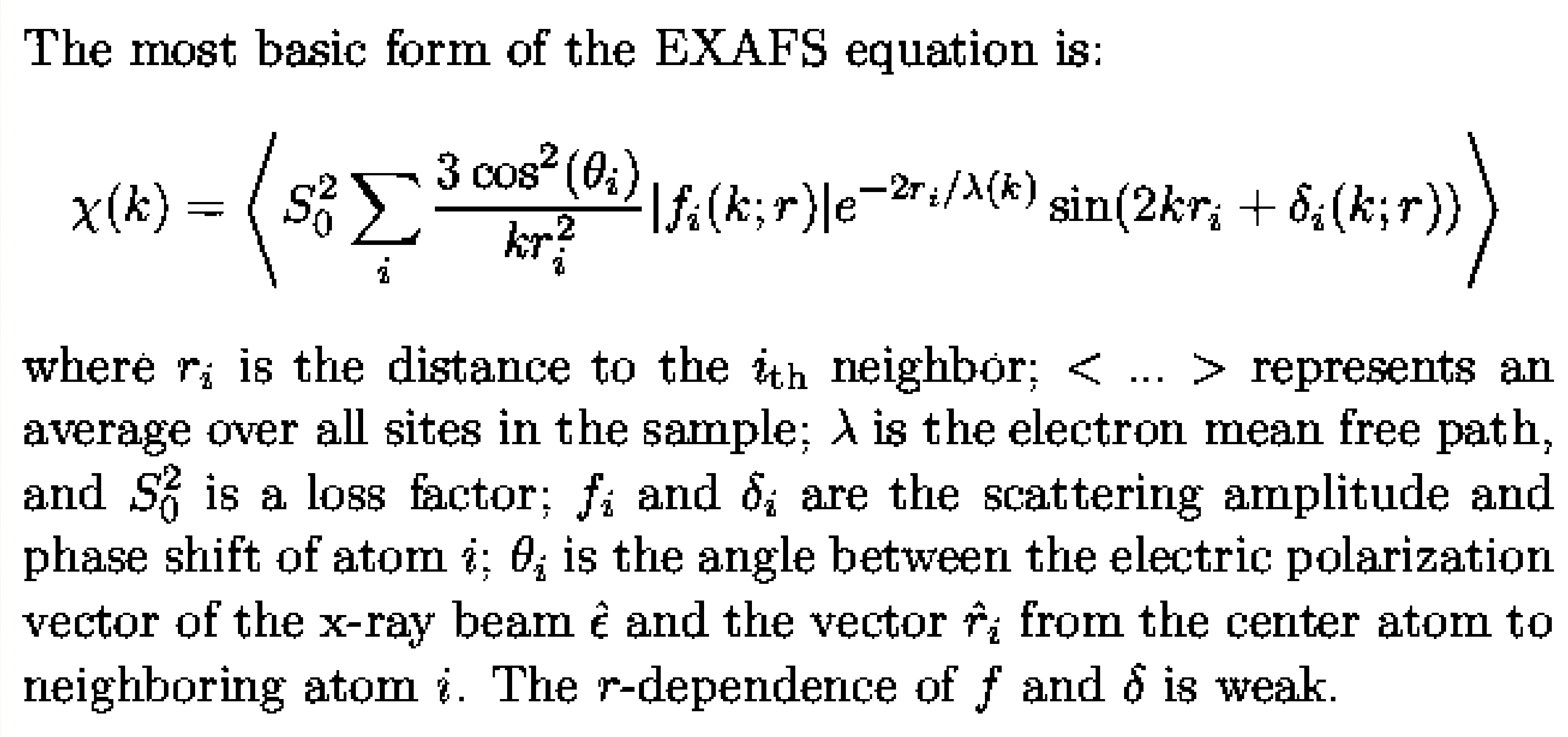
- X-rays from synchrotron source (usually) polarized in **horizontal** plane
- For ***s*** initial electron state (e.g. K or $L_1$ edge), final electron state will have ***p*** symmetry

  → dipole pattern for emitted electron wave

Atoms in direction of ***E*** will be emphasized in XAFS spectrum, weighted by $\cos^2(\phi)$



# Angle Dependence in XAFS Equation
# more detail:

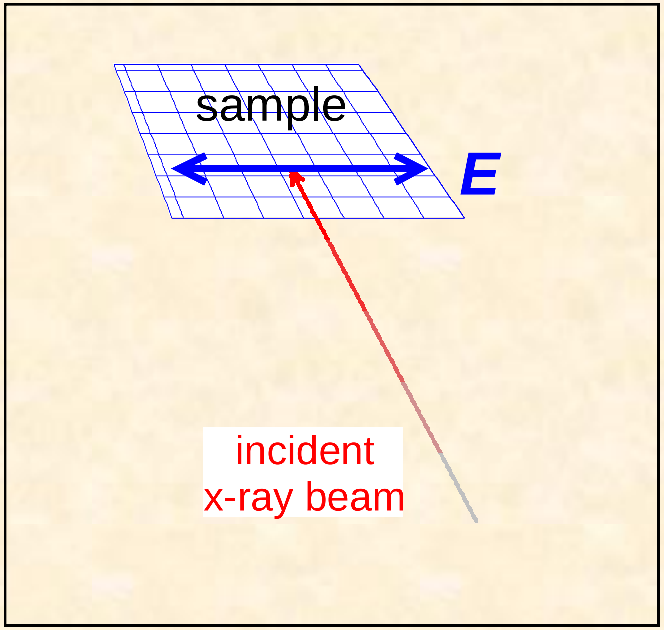


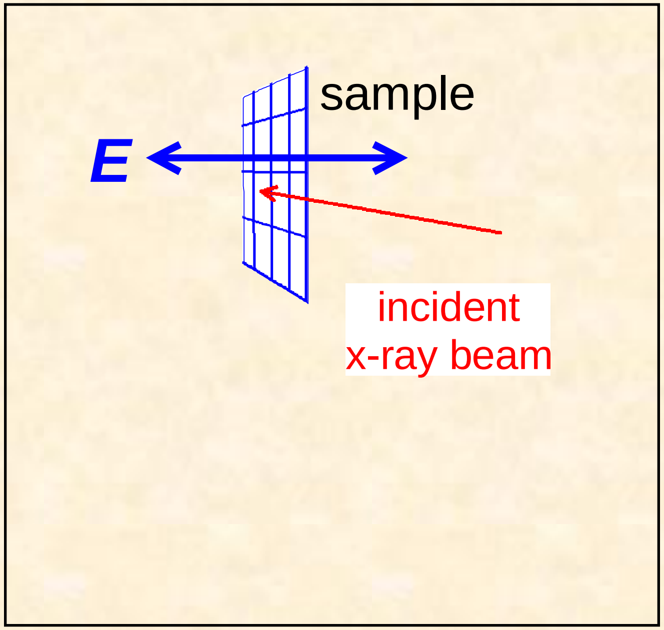
The most basic form of the EXAFS equation is:

$$\chi(k) = \left\langle S_0^2 \sum_i \frac{3\cos^2(\theta_i)}{kr_i^2} |f_i(k;r)| e^{-2r_i/\lambda(k)} \sin(2kr_i + \delta_i(k;r)) \right\rangle$$

where $r_i$ is the distance to the $i_{\mathrm{th}}$ neighbor; $< \ldots >$ represents an average over all sites in the sample; $\lambda$ is the electron mean free path, and $S_0^2$ is a loss factor; $f_i$ and $\delta_i$ are the scattering amplitude and phase shift of atom $i$; $\theta_i$ is the angle between the electric polarization vector of the x-ray beam $\hat{\epsilon}$ and the vector $\hat{r}_i$ from the center atom to neighboring atom $i$. The $r$-dependence of $f$ and $\delta$ is weak.

# Can use polarization of x-rays to emphasize atoms parallel or perpendicular to surface plane

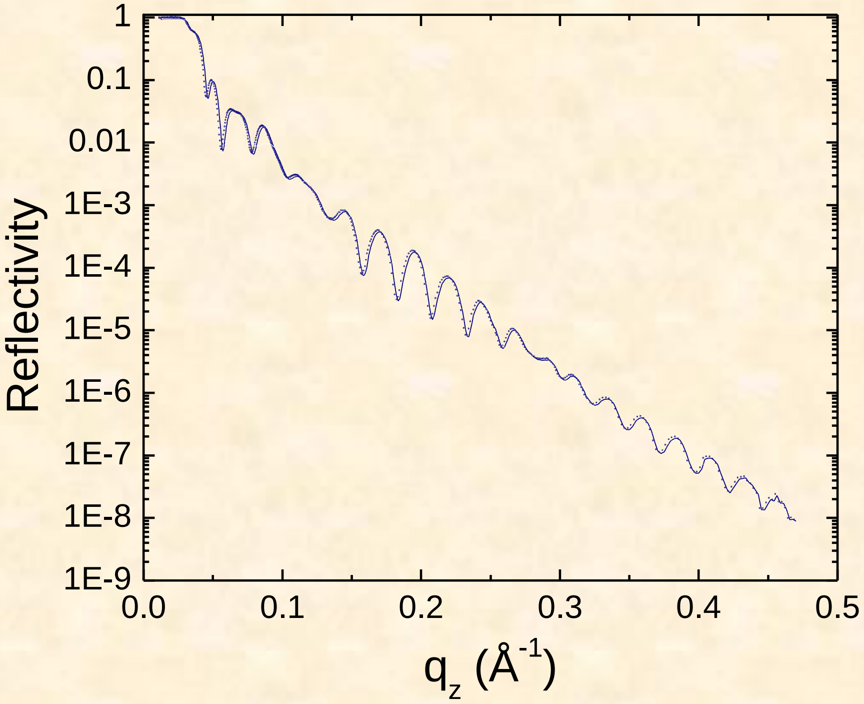




Makes no difference for isotropic samples, but can be very useful for studying surfaces and interfaces, layered materials, etc.

# Another technique: X-ray Reflectivity

- Normally, measure specular reflected intensity as function of incidence angle
- Data can be inverted to determine optical constants as function of depth
- Have to be careful about background subtraction, etc.: Need to do a lot of off-specular scans as well



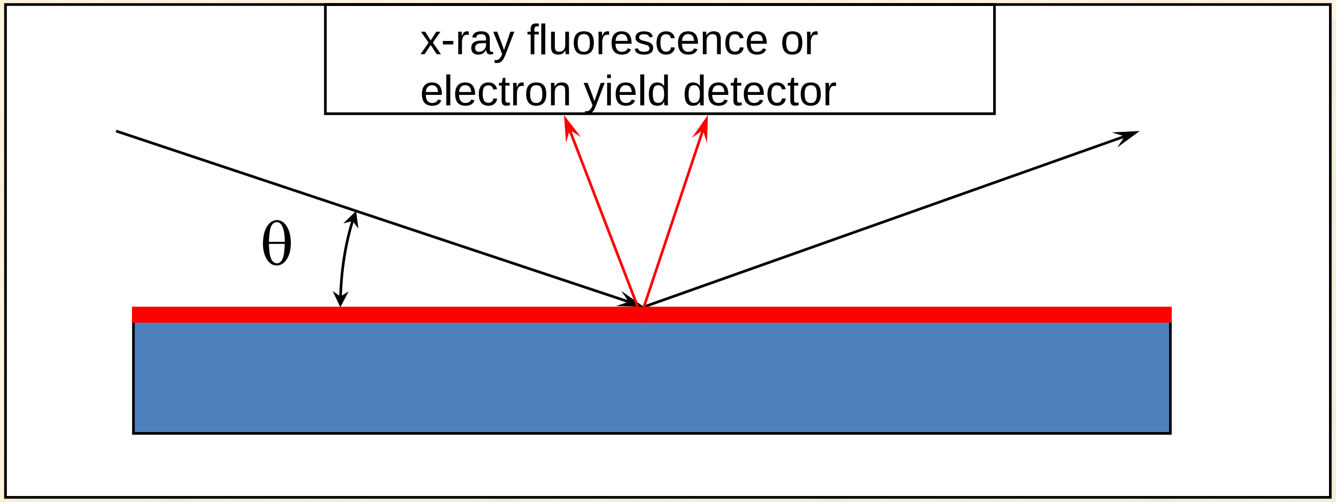
- Although useful to reveal electron density, can't directly give detailed information about particular atomic species or short-range order

# Reflection-Mode Techniques: surface sensitivity

At small incidence angles, transmitted beam kinematically forbidden:

Results in **total external reflection of x ray beam**

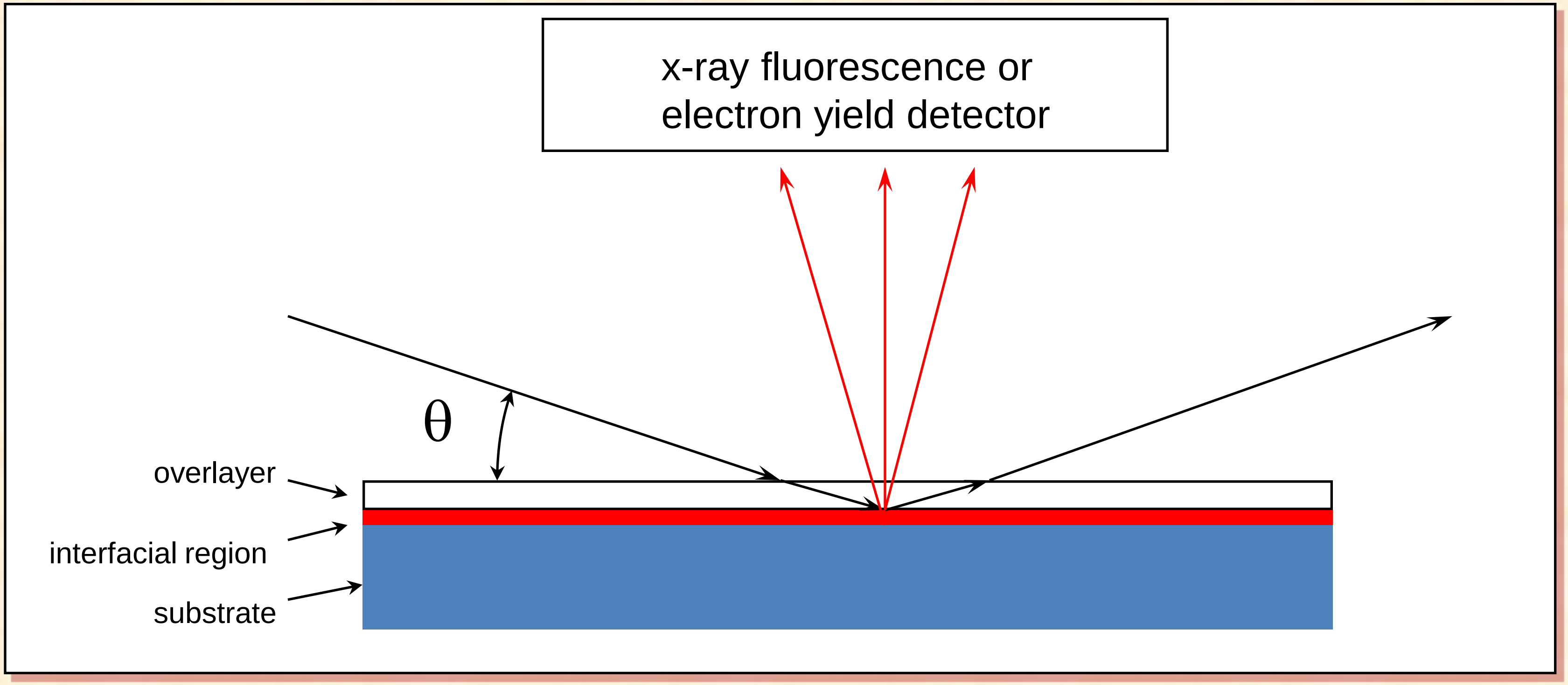
Only ***evanescent wave*** penetrates into sample: ~10-50Å



If fluorescence or electron-yield measurement performed in this geometry, only atoms within ~10-50Å of surface excited, detected

# Reflection-Mode Techniques: buried interfaces

If low-Z material overlies high-Z material, critical angle may be adjusted to penetrate overlayer, **reflect off of buried interface**. Fluorescence comes from **substrate atoms near interface**, even if 1000Å beneath surface!



# Related techniques – same physics!

- Detection of absorption by
  - X-ray Fluorescence
  - Auger or secondary electron emission
  - Optical luminescence
  - Electrical conductivity
  - others …
- Diffraction Anomalous Fine Structure (DAFS)
- Electron energy loss spectroscopy (e.g. in TEM)
- X-ray Raman spectroscopy (“x-ray energy loss”)
- X-ray magnetic circular dichroism
  (look at difference between RHS and LHS polarization for sample in magnetic field)

# Now a glimpse at data analysis…

- First steps:
  - removal of smoothly varying (as function of energy) background, normalization of data to edge step
  - Usually interpolate from original data points to equally-spaced in *k*
  - (optional) Fourier transform to separate out contributions from different distances in local structure
- More subtle: data fitting / data interpretation

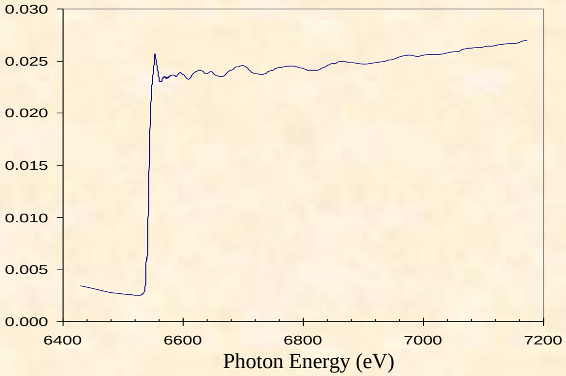
# Analysis: A big simplification

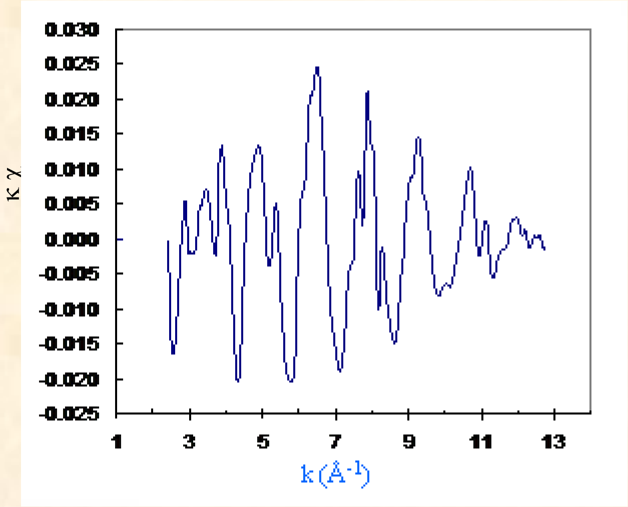
- Spectrum is dominated by sinusoidal oscillations $\sin\left(2kR + 2\delta_C + \phi\right)$

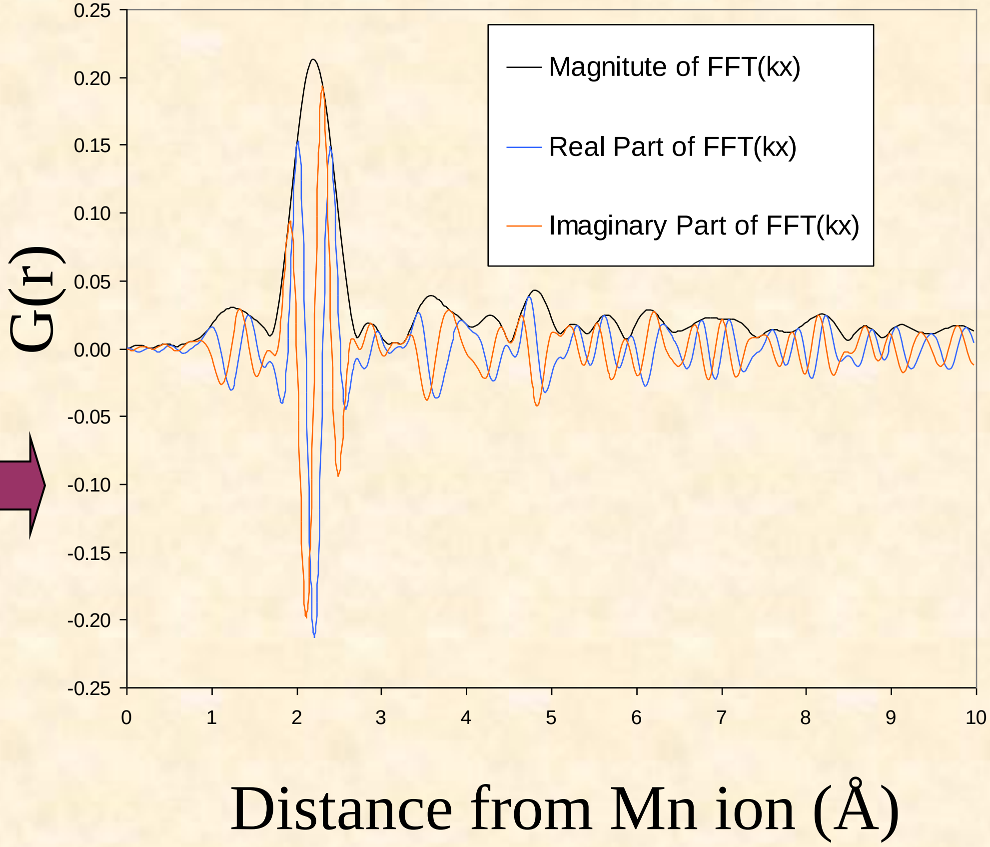
  modulated by other slowly-varying factors $\dfrac{\left|f(k)\right|}{kR^2} e^{-2\sigma^2 k^2}$

- Different distances have different oscillation periodicity
- Can use **Fourier transform techniques**

# Schematic of XAFS data processing







Fourier transform fit to determine structural parameters and uncertainties

# How about the unknown parameters?

- Remember those backscattering amplitudes and phase shifts, inelastic parameters? How do you figure them out?
  - Theoretical calculations
  - Empirical standards
- Luckily, these are largely dependent on just the atomic species, not detailed chemistry

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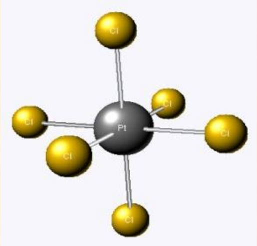
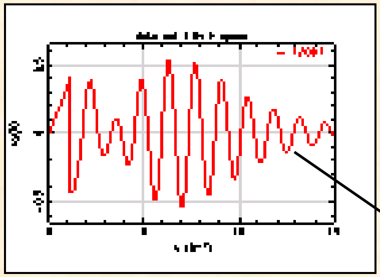
- How to determine parameters for complex system?

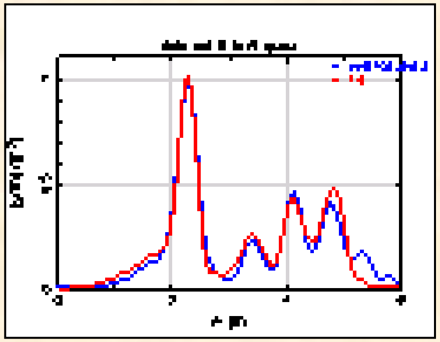
# Structural information from XAFS using model-dependent fitting



Theoretical Model

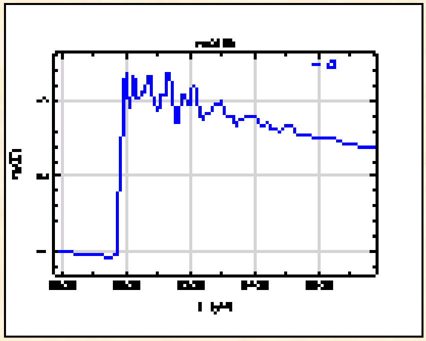


Numerical calculation



Fit with data

Data from standard compound with similar structure



Extract structural information from the fit based on the generalized EXAFS equation (curved wave)

$$\Delta\mu = \sum_j \frac{f(k)S^2(k)}{2k^2R_j^2}\sin\left(2kR_j + \delta_j(R,k)\right)\exp(-2k^2\sigma^2)\exp\left(\frac{2kR_j}{\lambda_j}\right)$$

# Things to worry about in analysis…

- Remember: See all atoms of that species in the sample!
- For simple systems (e.g. single type of atom in a shell, small disorder) interpretation generally straightforward
- For more complicated systems:
  - **multiple inequivalent sites**
  - **large non-Gaussian disorder**, etc.
  - may need **complex modeling**

  →Have to remember that your interpretation depends completely on your **how good your model is**! (this is true for any data fitting)

# Challenges of analysis and interpretation

- Ideally, would like analysis to be **model-independent**, with straightforward (and foolproof) determination of **uncertainties**
  - Probably not going to happen!
  - Except for Monte Carlo simulations, most rely on some sort of model-dependent fitting
- Would also like to **systematically include other sources of information** (e.g. x-ray PDF, etc.)
- Will always have problems with multiple inequivalent sites, etc.

# Things to worry about in analysis…

- For simple systems (e.g. single type of atom in a shell, small disorder) interpretation straightforward
- For complicated systems: multiple sites, larger non-Gaussian disorder, etc. may need complex modeling
  - Have to remember that your interpretation depends completely on your how good your model (this is true for any data fitting)

# Resources: XAFS Analysis Software

- ESRF EXAFS Software Catalog
- Many choices, including free, commercial, and licensed. Alphabetically:

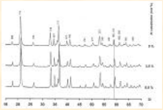
  CDXAS, Cerius2 XAFS, CHOOCH, DARESBURY, EDA, EXAFS (for Mac), EXAFSPAK, Excurv98, **FEFFIT**, GNXAS, LASE, MURATA, NPI, SEDEM, TT-MULTIPLETS, UWXAFS, VIPER, WINXAS, XAFS, XAID, XANES dactyloscope, XDAP, XFIT
- International XAFS Society (now the International X-ray Absorption Society, www.i-x-s.org/
- XAFS.ORG - open Wiki for XAFS users

# Simple Example: Environmental Nanoparticles

(with Zhen Song, Patricia Maurice)

- **Goethite** (α-FeOOH) is the most widespread Fe(III) (hydr)oxide mineral and the most common ingredient of iron rust
- Natural Goethite often exhibits Al substitution for Fe; up to 33 mol% of the Fe may be replaced by Al
- Morphology of nanoparticles changes dramatically with Al concentration (long needles with little Al, plates with lots of Al)
- Where is Al going?

# Use Array of Techniques…

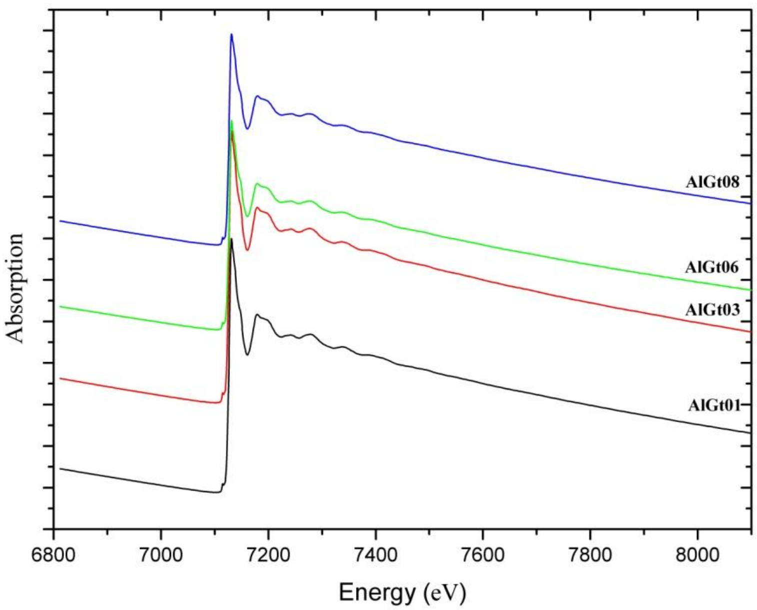


- X-ray diffraction to get average structure
- TEM/AFM to get particle morphology
- XAFS: Ideally would like to study Fe and Al edges, but not possible at the APS
  - Study Fe with XAFS, but what if Al in some sort of occlusions not involving Al?
  - indirectly look at Al with **x-ray diffuse scattering / pair distribution** function measurements

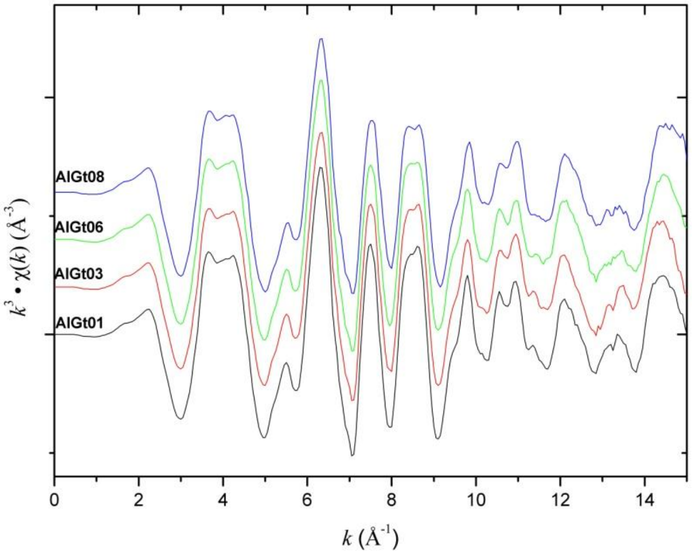
# Fe-edge XAFS

- Measurements at 10-BM (pretty concentrated samples, enough material, so no need to use undulator line)
- Particles in powders already much less than one x-ray absorption length so no need to further reduce size
- Powders put on Kapton adhesive tape for room temperature measurements
- Measure in both transmission and fluorescence (best results in transmission)

# Fe-edge Spectra



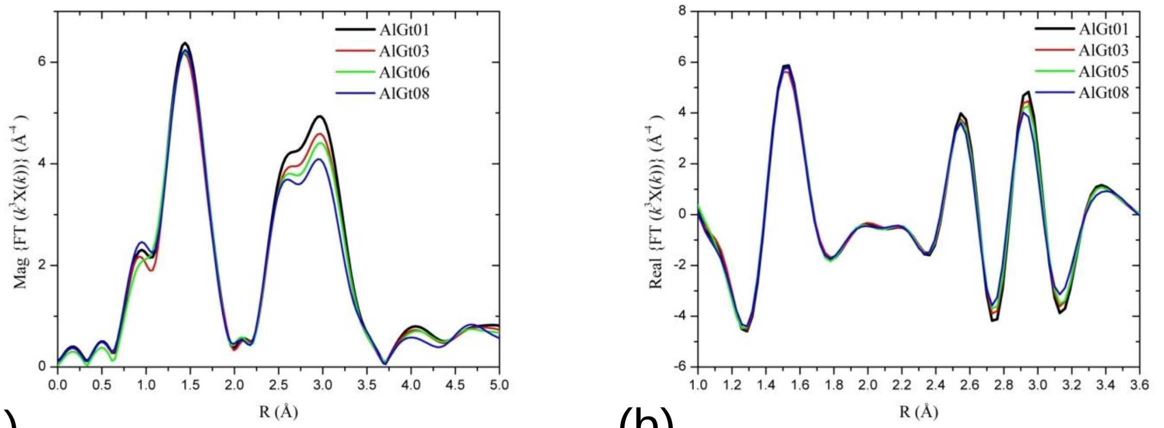
"raw" absorption data
(transmission)
x $\mu$(E) or "XMU"



Oscillations with
background removed and
normalized to edge step
$\chi$(k) or "CHI"

# FE-edge XAFS - results

- Around Fe atoms, no change in first shell, but systematic change in 2nd shell
- Consistent with Al substituting for Fe



(a) (b)

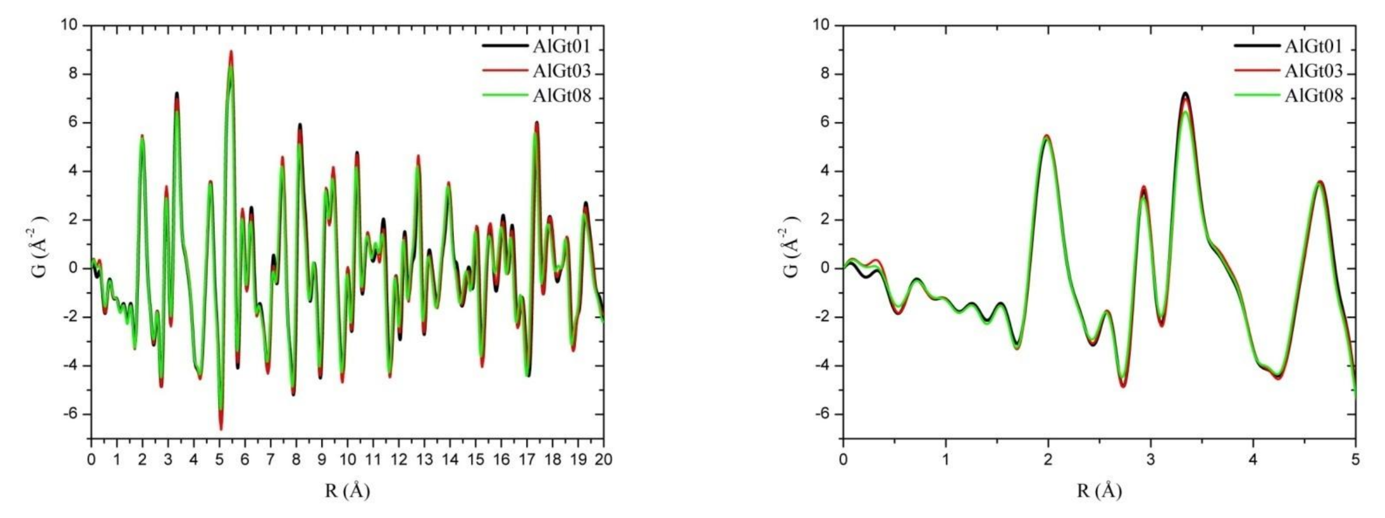
Magnitude (a) and real part (b) of the Fourier transformed (FT) data (FT k range 2.0-11.2 (Å$^{-1}$)) for Al-Goethite samples with 0%, 1.9%, 4.2%, and 8.8% Al, respectively.

# More careful modeling of data

- Use R-space fitting (using FEFFIT) over 1.1 - 3.6Å spectral range
- Find Al substituting pseudo-randomly on Fe sub-lattices, with coordination numbers consistent with Al concentration
- XAFS looks good for “solid solution” description of nanoparticles, but would be nice to double check about $Al_2O_3$ or other possible inclusions
  - Can’t see Al inclusions with Fe-edge XAFS!

# Complement XAFS with PDF Measurements (with Peter Chupas, APS Sector 11)

- Measure high-energy x-ray diffuse scattering to get $S(q)$
- After background removal, Fourier transform to get complete PDF (all possible atomic pairs)
- Difficult to analyze to get full structure, but easy to see that no extra pairs from other phases



Experimental PDF for Al substituted Goethite data
for samples with 0%, 1.9%, and 8.8% Al, respectively.

# XAFS Strengths and Limitations

- XAFS good for amorphous, liquid, molecular systems as well as crystalline
- X-ray & Neutron PDF …
  - have higher resolution, but can be difficult to separate contributions from different species
- Spatial resolution important for many problems these days
  - Resolution much lower than TEM
  - Typically about 10μm for EXAFS, 1μm for XANES, down to about 10 nm for mapping
  - Changing fast!
- These and other tools complementary: Use as many as you have access to!

# Related lectures this week

- **Magnetic spectroscopy**
  - Overlaps with XANES
- **X-ray imaging**
  - Overlaps with micro-spectroscopy: XANES or EXAFS with micron-sized beams
- **Pair-distribution function** (PDF) scattering measurements
  - Complementary to XAFS, often use together
- **X-ray inelastic scattering** (medium resolution)
  - Core electron excitation, similar physics and analysis to XAFS. Useful for low-energy edges