

XAFS Experimental Methods

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- Firouzeh Tannazi (IIT/BCPS) (recent results on fluorescence in complex materials)
- Suggested References:
 - Steve Heald's article "designing an EXAFS experiment" in Koningsberger and Prins and early work cited therein (e.g. Stern and Lu)
 - Rob Scarrow's notes posted at http://cars9.uchicago.edu/xafs/NSLS_2002/

Outline of talk

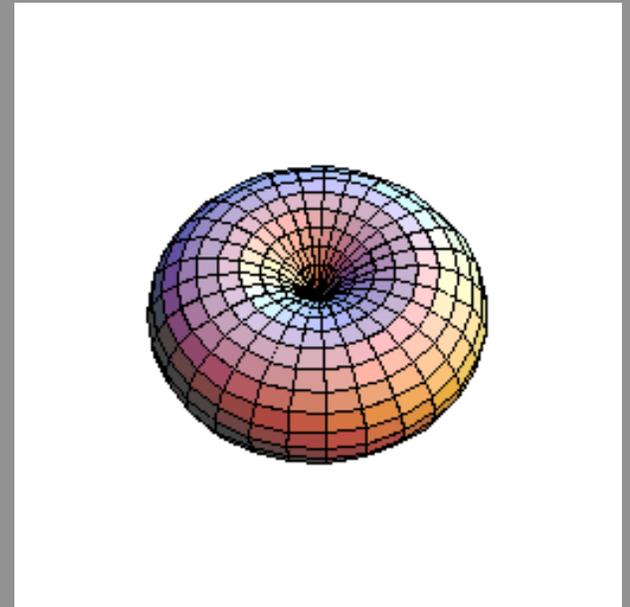
- ① Synchrotron Radiation Sources
- ① Beamlines and optics
- ① Experimental modes and samples
- ① Detectors and Analyzers
- ① Conclusion

Sources

- Dipole Bend Magnets
- Insertion Devices
 - Wigglers
 - Undulators

Light Emission

- Accelerating charged particles emit electromagnetic radiation
 - radio, microwave, infrared, visible, UV, X-rays, gammas
 - These are emitted in a dipole pattern
 - Not collimated - frequency is same as oscillation frequency - radio waves?

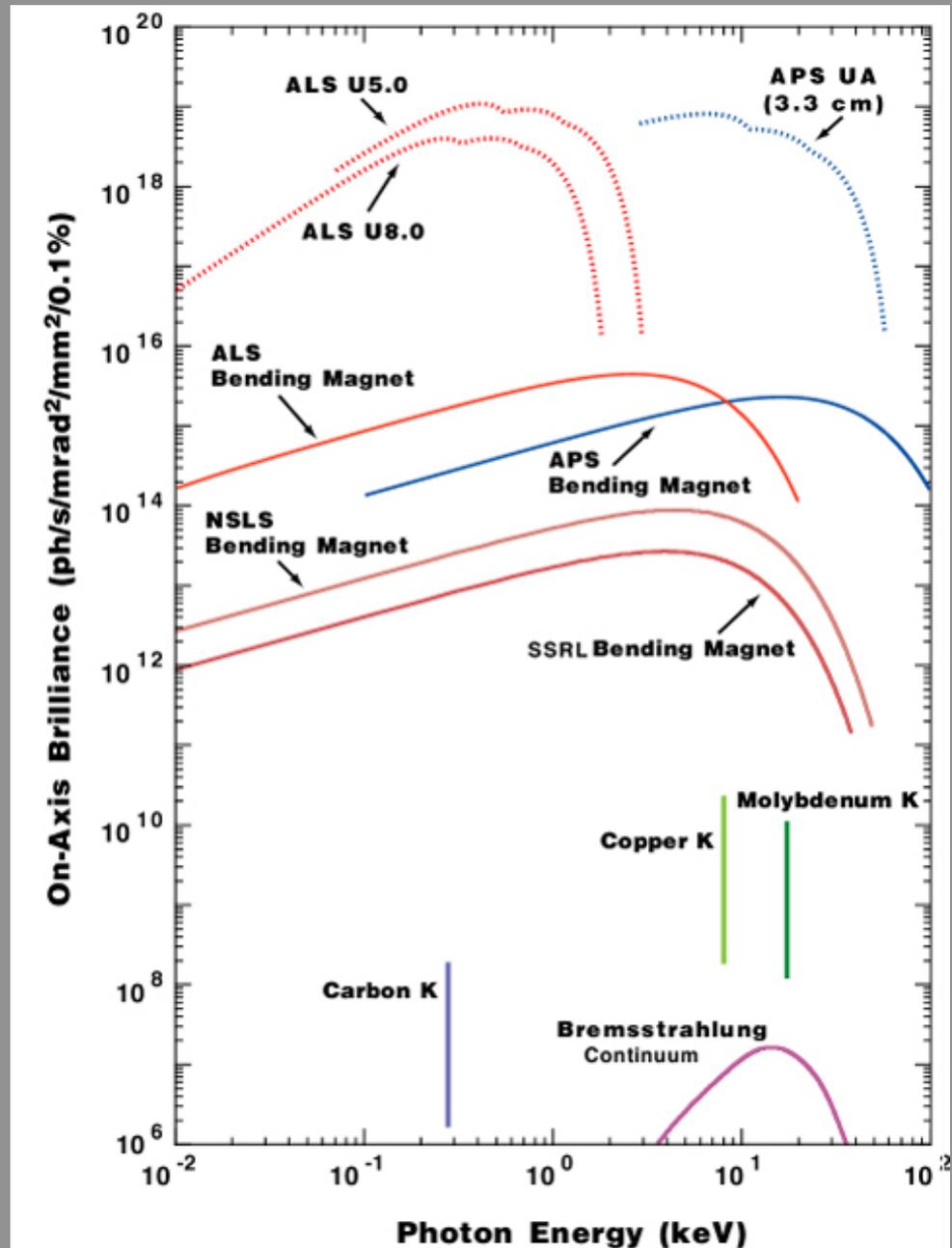


No radiation along
acceleration vector

Relativity changes everything

- When particles move at speeds close to the speed of light
 - it's still a dipole pattern in their instantaneous rest frame
 - but in lab frame, radiation pattern tilts sharply into the forward direction "headlight effect"
- Frequency of emitted light measured in lab frame is dramatically higher -> x-rays

Brilliance of X-ray Sources



graphic courtesy of APS

Advanced Photon Source



graphic courtesy of APS

Inside the Ring:

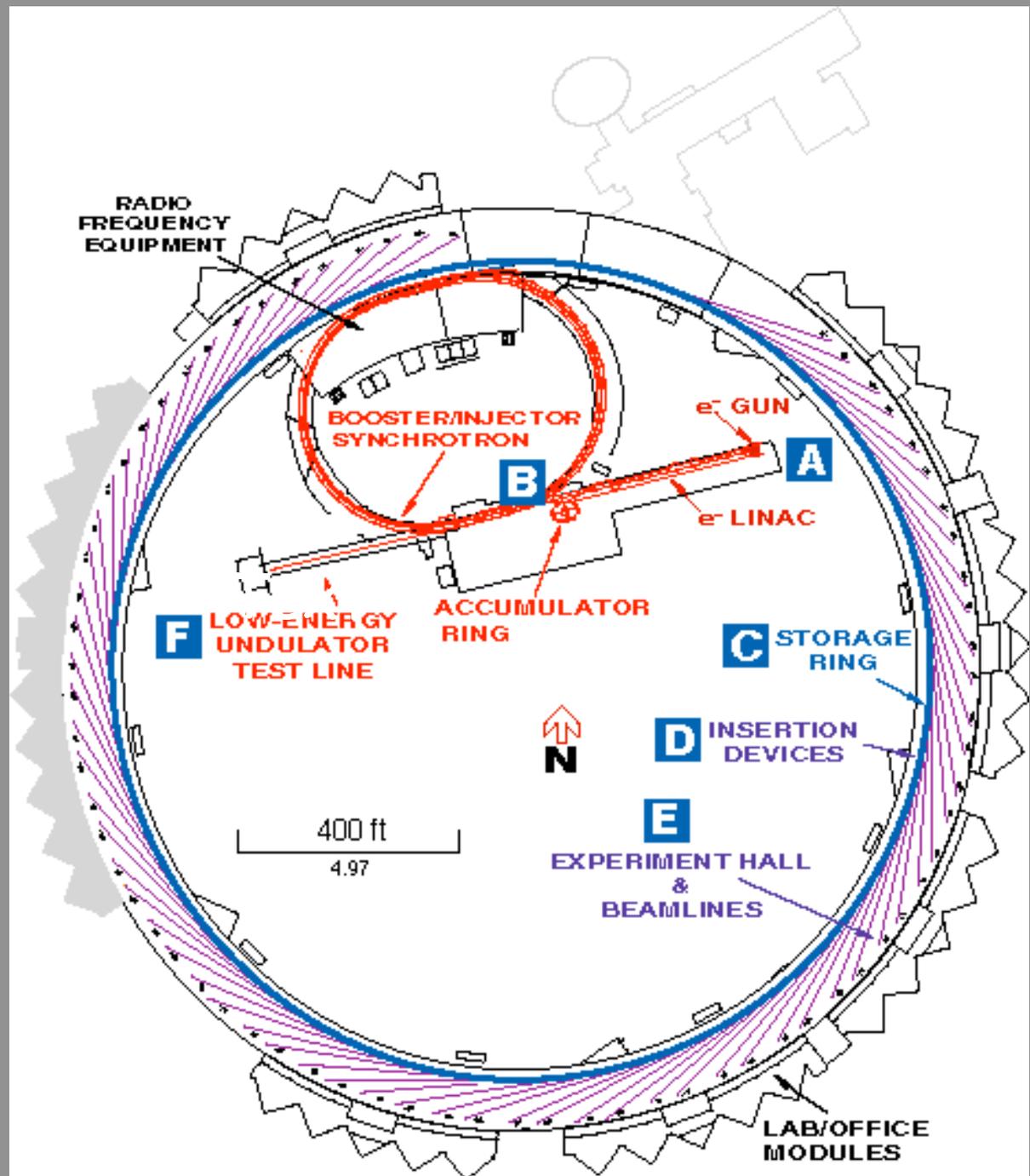
Linac

Synchrotron

Storage
Ring

Insertion
Devices

Beamlines!



graphic courtesy of APS

Inside the ring

- Electrons circulate through ultrahigh vacuum at very nearly the speed of light (at the APS, only 1.5 m/s slower than c !).
- Relativistic parameter $\gamma = E/mc^2$
- Their paths are made to bend using dipole bend magnets. The beams are focussed with quadrupole and sextupole magnets
- "insertion devices" (wigglers and undulators) can be placed in straight sections between dipole bend magnets



Synchrotron Radiation

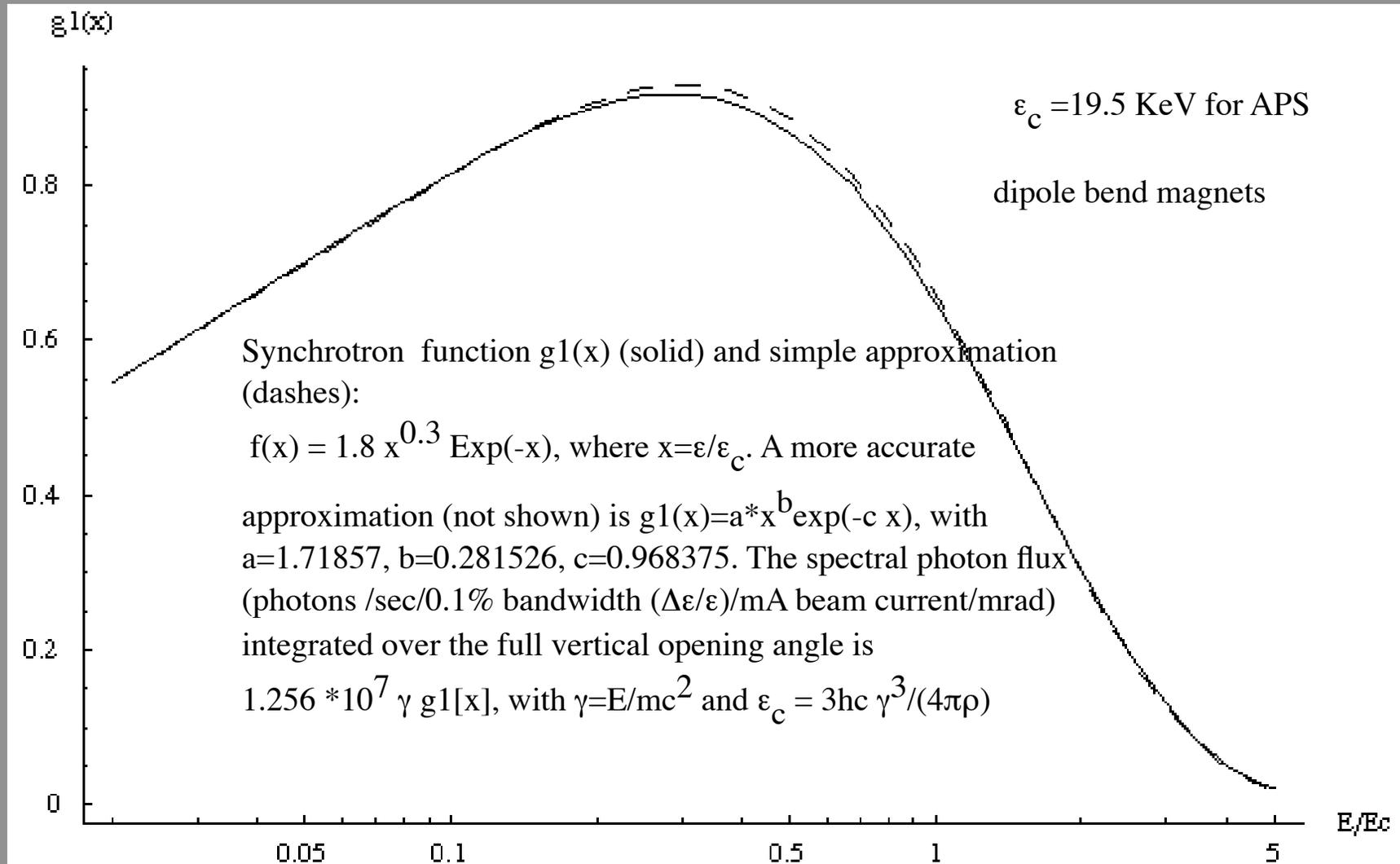
- Wherever the path of the electrons bends, their velocity vector changes
- This acceleration causes them to produce electromagnetic radiation
- In the lab rest frame, this produces a horizontal fan of x-rays that is highly collimated (to $\Delta\theta \approx 1/\gamma$) in the vertical direction and extends to high energies
- Energy is put back into electron beam by electrons "surfing" through radio frequency (RF) cavities

Properties of Synchrotron Radiation

- It's far more intense ($>10^6$) than lab sources
- Broad or tunable energy spectrum
- Naturally collimated in vertical plane - clean
 - well-matched to crystal monochromators
 - undulators produce pencil beam of x-rays
- Brilliance is much greater than other sources
 - photons/sec/source size/angular divergence
- Light comes in rapid pulses - useful for time resolution

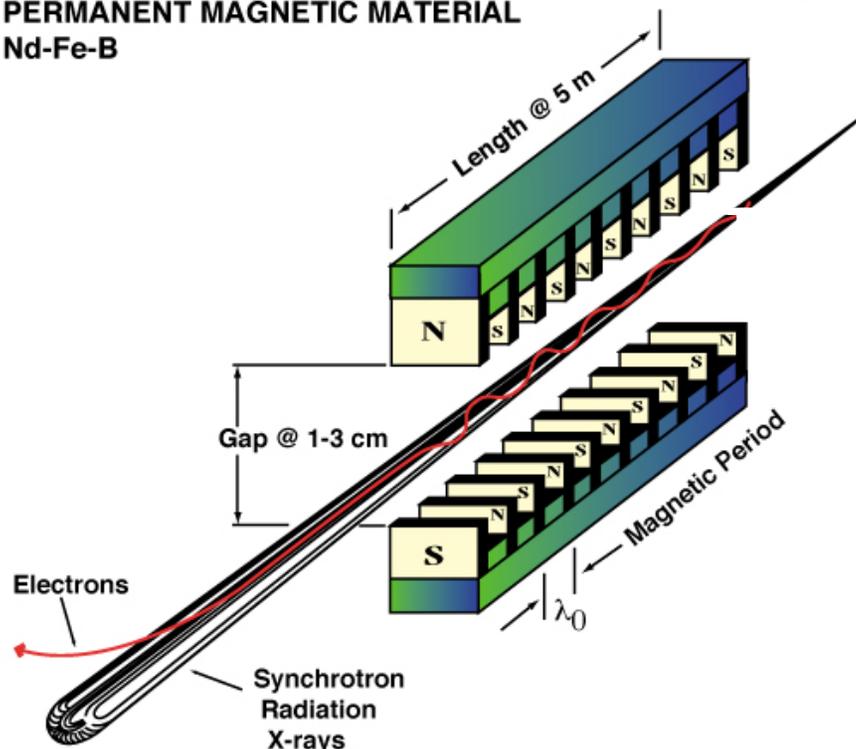
Universal Flux Curve

compute flux for bend magnets & wigglers



Insertion Devices

INSERTION DEVICE (WIGGLER OR UNDULATOR) PERMANENT MAGNETIC MATERIAL Nd-Fe-B



- arrays of magnets of alternating polarity between which the beam travels
- The alternating magnetic field causes the path of the electrons to wiggle back and forth
- Acceleration causes emission of radiation at each pole (typically 50-100 poles)
- Unlike bend magnets, ID properties can be chosen to optimize beam specifically for experiments
- Two main types: Wigglers and Undulators

Wigglers vs Undulators

- Wigglers cause the electron beam to oscillate with angular deviation that is large compared to $1/\gamma$
 - Wiggler spectrum follows universal curve (like bend magnet), scaled by number of poles
- Undulators use smaller deflections compared to $1/\gamma$
 - Light emitted at each pole interferes with that emitted from others
 - Energy spectrum is bunched up into harmonics
 - Radiation pattern is a pencil of light in forward direction

x-ray energy from undulator

We will take the average speed of the electron through the undulator as essentially c , with relativistic parameter

$$\gamma = \frac{1}{\sqrt{1-v^2/c^2}}.$$

The undulator period λ_0 in the lab frame appears to the electron as λ_0/γ , i.e. very much shortened by the Lorentz contraction.

The electron oscillates back and forth and emits radiation with frequency $\omega \approx \frac{c}{(\lambda_0/\gamma)} = \gamma c/\lambda_0$ in the rest frame of its average motion through the undulator.

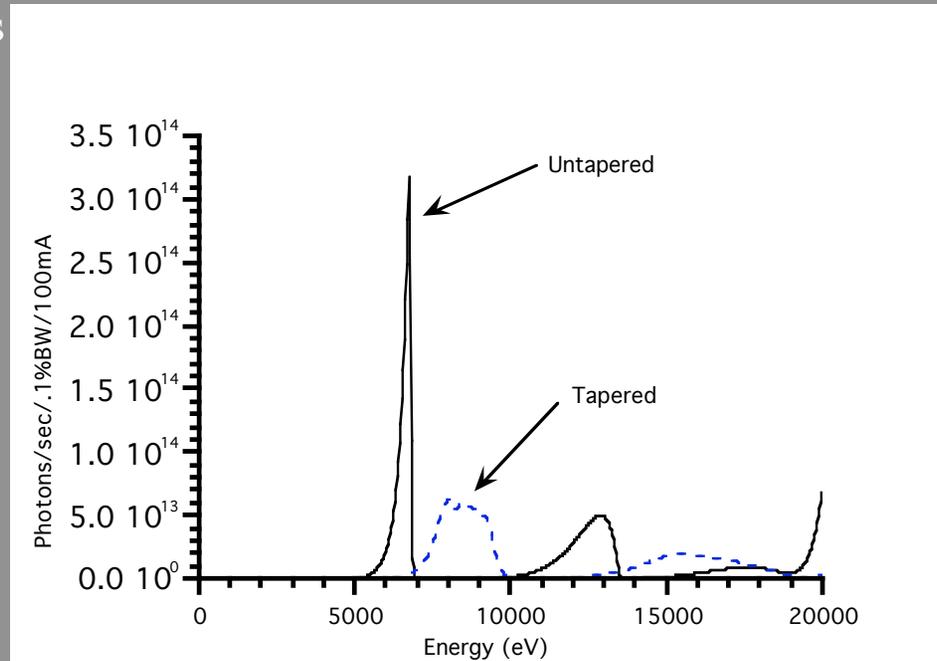
In the lab frame, the frequency of the light is increased by the relativistic doppler shift $\sqrt{\frac{1+v/c}{1-v/c}} = \gamma(1+v/c) \approx 2\gamma$.

Therefore the frequency of radiation observed in the lab frame is then $2\gamma^2 c/\lambda_0$. At the APS, $\gamma^2 \approx 2 \times 10^8$.

Calculated Flux from Undulator A

The position of undulator peaks can be tuned by adjusting the undulator gap, which varies the strength of the magnetic field felt by the electrons.

Decreasing the gap increases the field, causing a larger deflection, and slightly slowing down the electron's average speed through the undulator. This shifts the spectrum to lower energy.



The x-ray frequency of the fundamental is given approximately by $2 \gamma^2 \Omega_w / (1 + K^2/2 + \gamma^2 \theta_0^2)$. Here $K = \gamma \delta_w$, where $\delta_w = \lambda_0 / 2\pi\rho_0$, λ_0 is the undulator period, and ρ_0 is the bend radius corresponding to the peak magnetic field.

X-ray Polarization

- In the orbital plane, the radiation is nearly 100% linearly polarized
- This can be used for polarized XAFS (x-ray linear dichroism) experiments on oriented specimens
- Out of the orbital plane, bend magnet radiation has some degree of left/right circular polarization
- Wiggler/undulator radiation is not circularly polarized (planar devices)

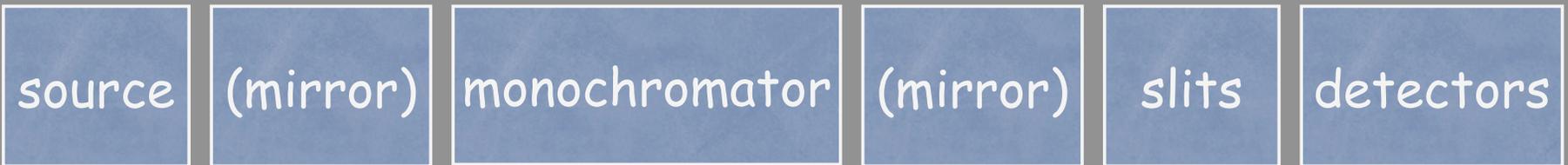
Beamlines

- Beamlines are complex instruments that prepare suitable x-ray beams for experiments, and protect the users against radiation exposure.
- They combine x-ray optics, detector systems, computer interface electronics, sample handling/cooling, and computer hardware and software.

Beamline Functions

- Radiation shielding and safety interlock
- Select/scan energies/wavelengths using monochromators.
Stability during scanning is important for XAFS
- Focus the beams with x-ray mirrors, bent crystals, fresnel zone plates, or refractive optics
- Define the beams with x-ray slits
- Measure beam intensity, scan monochromator, and record data with suitable detectors
- Electronics amplify/process signal and interface to the computers
- Computer control and data acquisition system orchestrates motion of the monochromator and other optics, controls readout of detectors, and facilitates remote control alignment of samples.

Basic Beamline Components for XAFS



Collimating mirror is sometimes used to match source to acceptance of mono

mirror following mono is often used for harmonic rejection or focussing

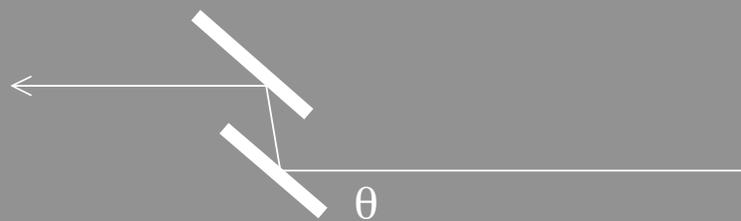
BioCAT beamline panorama



Double-crystal monochromators

The “white” x-ray beam impinges on a perfect single crystal of silicon at a specified orientation. Those X-ray photons that are of the correct wavelength and angle of incidence θ to meet the Bragg diffraction condition $n\lambda=2 d_{hkl} \sin(\theta)$ are diffracted through an angle 2θ ; the rest are absorbed by the crystal. Here λ is the x-ray wavelength; the photon energy $\epsilon=hc/\lambda$; and n is the harmonic number.

The spacing between diffracting atomic planes in the crystal for "reflection" hkl is $d_{hkl} = a_0/(h^2+k^2+l^2)^{1/2}$, where a_0 is the lattice constant (0.5431 nm for Si).



Si double crystal monochromator

The second crystal simply redirects the diffracted beam parallel to the incident beam. If bent, it can be used for horizontal “sagittal” focussing.

Heat Load

- Undulators pose special challenges for optics
 - high power density makes silicon at room temperature unsuitable (mostly): need higher thermal conductivity or lower thermal expansion coefficient
 - Cooling silicon to $\sim 100\text{K}$ improves both properties
 - Diamonds are excellent thermal conductors and synthetic diamonds are suitable monochromator crystals

Monochromator: example

BioCAT
ID-18

Fixed exit;
bent second
crystal for
focussing

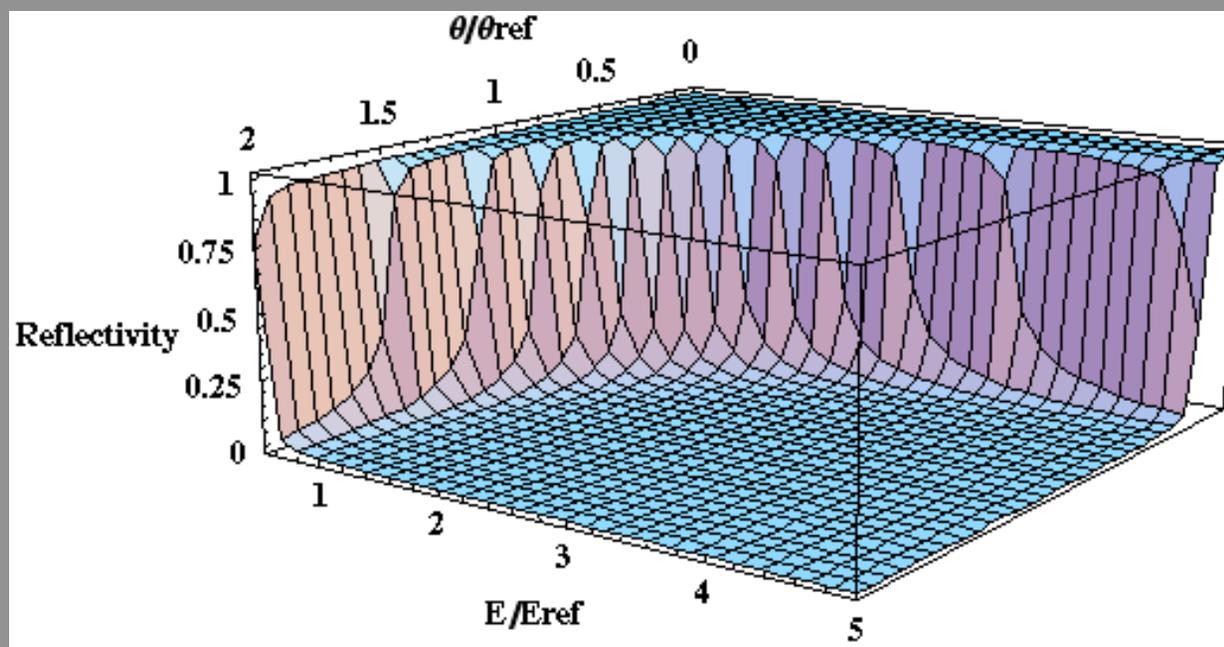
Design by
Gerd Rosenbaum
& Larry Rock



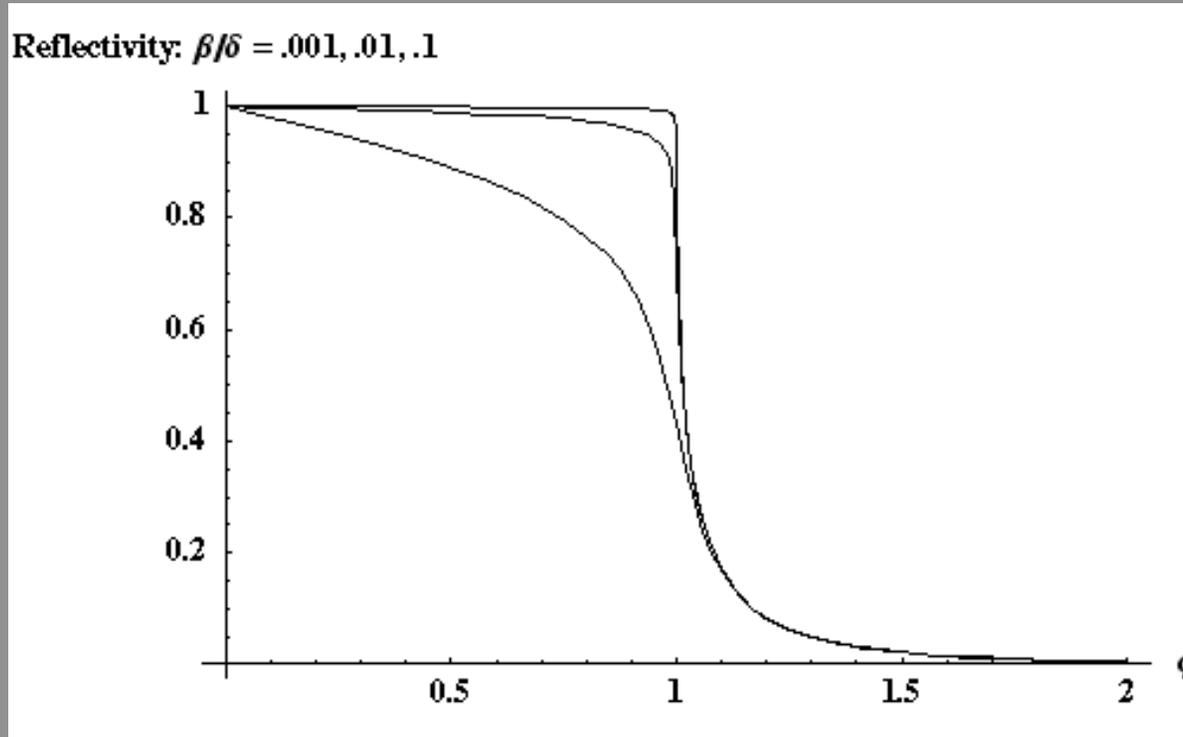
Grazing incidence mirrors

For most materials, the index of refraction at x-ray energies is a complex number $n=1-\delta-i\beta$. The real and imaginary parts describe dispersion and absorption. Total external reflection occurs at angles $\theta < \theta_c$, where the "critical angle" $\theta_c=(2\delta)^{1/2}$, which is typically 5-10 milliradians, i.e. grazing incidence. Higher atomic number coatings (e.g. Pt, Pd, Rh) allow the mirror to reflect at greater angles and higher energies, at the cost of higher absorption. To a good approximation $E_c \theta_c = \text{constant}$ for a given coating. For ULE ~ 30 KeV mrad; Pd, Rh ~ 60 KeV mrad; Pt ~ 80 KeV mrad.

Surface plot of reflectivity vs angle and photon energy

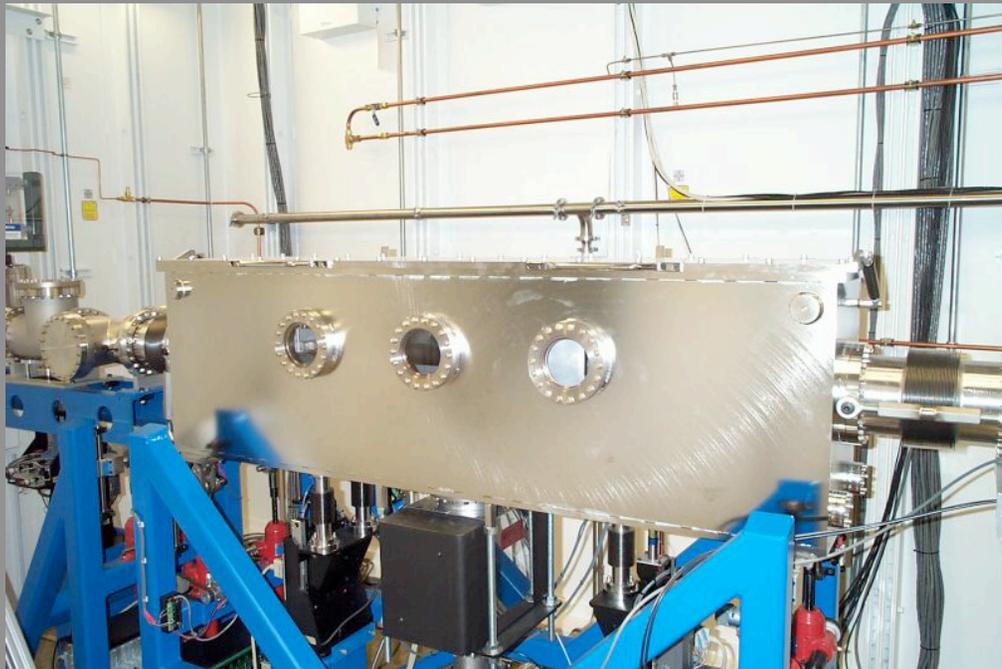


Mirror reflectivity vs absorptivity of surface coating



$$\phi = \Theta / \Theta_c$$

Focussing Mirror (example)



This is a one meter long ULE titanium silicate. It is polished to $\sim 2\text{\AA}$ RMS roughness; it was measured at ~ 1 microradian RMS slope error before bending. It has Pt, Rh, and uncoated stripes to allow the user to choose the coating.

The mirror is dynamically bent and positioned.
Design by Gerd Rosenbaum and Larry Rock Automation.

Harmonics

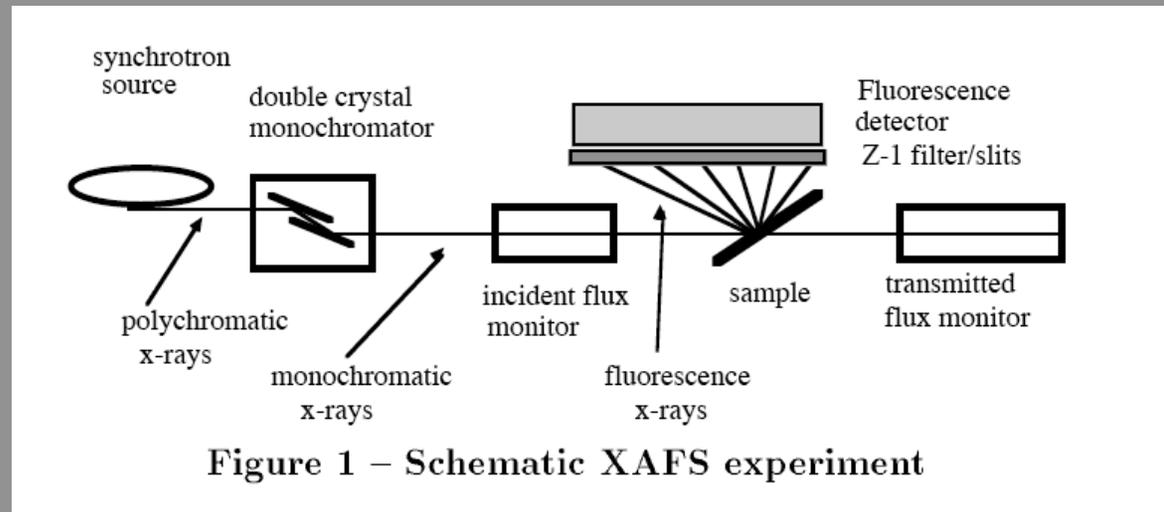
- Monochromators transmit not only the desired fundamental energy, but also some harmonics of that energy. Allowed harmonics for Si(111) include 333, 444, 555, 777...
- These can be reduced by slightly misaligning "detuning" the second crystal using a piezoelectric transducer ("piezo"). Detuning reduces the harmonic content much more than the fundamental.
- If a mirror follows the monochromator, its angle can be adjusted so that it reflects the fundamental, but does not reflect the harmonics.
- We have developed devices called "Beam Cleaners" can be made to select particular energies

Experimental Modes

- Modes:
 - Transmission
 - Fluorescence
 - Electron yield
- Designing the experiment requires an understanding of sample preparation methods, experimental modes, and data analysis
- Comparison to theory requires stringent attention to systematic errors - experimental errors don't cancel out with standard

Experimental Setup

- Transmission is the simplest XAFS measurement
- Fluorescence can give better sensitivity
- Both methods are vulnerable to systematic errors from sample prep and instrumental effects



uniform sample

Uniform, homogeneous sample:

$$\frac{I}{I_0} = \exp(-\mu(E)x)$$

x is the sample thickness

$\mu(E)$ is the linear x-ray absorption coefficient
at x-ray energy E

Decreases roughly as $1/E^3$ between absorption edges

Absorption Length

$$\text{"Absorption Length"} \equiv 1/\mu$$

- distance over which x-ray intensity decreases by factor $1/e \sim 37\%$
- sets the fundamental length scale for choosing sample thickness, particle size, and sample homogeneity
- You should calculate it when designing experiments

Absorption Coefficient

Single substance:

$$\mu = \rho\sigma$$

ρ is the density; σ is the cross section.

If the units of ρ are g/cm^3 the cross section is in cm^2/g .

If the units of ρ are atoms/cm^3 the cross section is in cm^2/atom .

$$1\text{barn} = 10^{-24}\text{cm}^2.$$

Cross section

Interaction between a beam of particles (photons) and a target

Definition of "cross section" σ :

$$R\left[\frac{\text{photons}}{\text{s}}\right] = \Phi\left[\frac{\text{photons}}{\text{s} * \text{cm}^2}\right] * \sigma\left[\frac{\text{cm}^2}{\text{atom}}\right] * N[\text{atom}],$$

alternatively

$$R\left[\frac{\text{photons}}{\text{s}}\right] = \Phi\left[\frac{\text{photons}}{\text{s} * \text{cm}^2}\right] * \sigma\left[\frac{\text{cm}^2}{\text{g}}\right] * M[\text{g}]$$

Sources of Cross Section Data

- S. Brennan and P.L. Cowan, Rev. Sci. Instrum, vol 63, p.850 (1992).
- C. T. Chantler, J. Phys. Chem. Ref. Data 24, 71 (1995)
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<http://www.csrrri.iit.edu/periodic-table.html>

compounds

Absorption coefficient approximately given by

$$\mu \approx \sum_i \rho_i \sigma_i = \rho_M \sum_i \frac{m_i}{M} \sigma_i = \rho_N \sum_i \frac{n_i}{N} \sigma_i$$

where ρ_M is the mass density of the material as a whole, ρ_N is the number density of the material as a whole, and m_i/M and n_i/N are the mass fraction and number fraction of element i .

Sample Calculation

Fe₃O₄ (magnetite) at 7.2 KeV;

<http://www.csrri.iit.edu/periodic-table.html>

density $5.2 \frac{\text{g}}{\text{cm}^3}$

$$\text{MW} = 3 * 55.9 \frac{\text{g}}{\text{mol}} + 4 * 16.0 \frac{\text{g}}{\text{mol}} = 231.7 \frac{\text{g}}{\text{mol}}$$

$$\sigma_{\text{Fe}} = 393.5 \frac{\text{cm}^2}{\text{g}}; M_{\text{Fe}} = 55.9 \frac{\text{g}}{\text{mol}};$$

$$f_{\text{Fe}} = 55.9/231.7 = .724;$$

$$\sigma_{\text{O}} = 15.0 \frac{\text{cm}^2}{\text{g}}; M_{\text{O}} = 16.0 \frac{\text{g}}{\text{mol}};$$

$$f_{\text{O}} = 16.0/231.7 = .276;$$

$$\begin{aligned} \mu &= 5.2 \frac{\text{g}}{\text{cm}^3} (.724 * 393.5 \frac{\text{cm}^2}{\text{g}} + .276 * 15.0 \frac{\text{cm}^2}{\text{g}}) \\ &= 1503/\text{cm} = .15/\text{micron} \end{aligned}$$

$$\text{Absorption Length} = 1\mu\text{m}/.15 = 6.7 \text{ microns}$$

Even if you don't know the density exactly you can estimate it from something similar. It's probably between 2 and 8 g/cm³

Transmission nonuniform sample

What's the
problem with
nonuniform
samples?

Characterized by thickness distribution $P(x)$

$$\mu x_{\text{eff}}(E) = -\ln \int_0^{\infty} P(x) \exp(-\mu(E)x) dx$$

$$= -\sum_{n=1}^{\infty} \frac{C_n (-\mu)^n}{n!},$$

where C_n are the cumulants of the thickness distribution ($C_1 = \bar{x}$, $C_2 = \text{mean square width, etc.}$)

A Gaussian distribution of width σ has

$$\mu x_{\text{eff}}(E) = \mu \bar{x} - \mu^2 \sigma^2 / 2$$

ref gb dissertation 1984

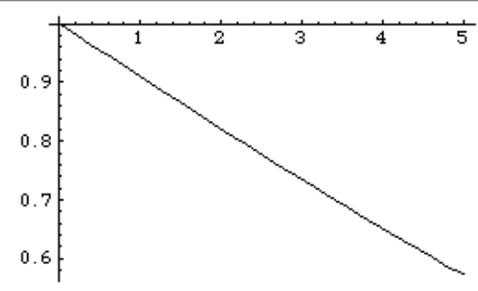
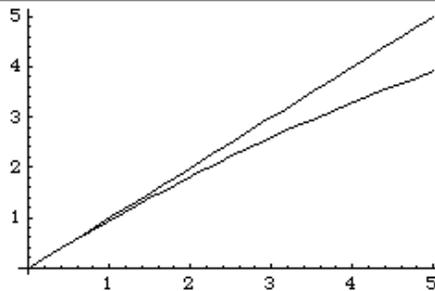
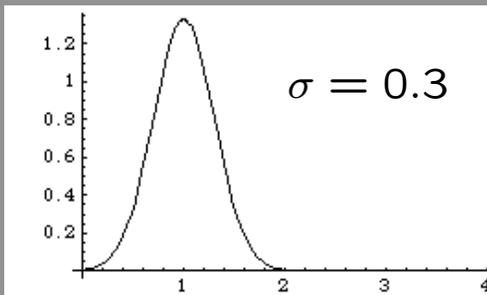
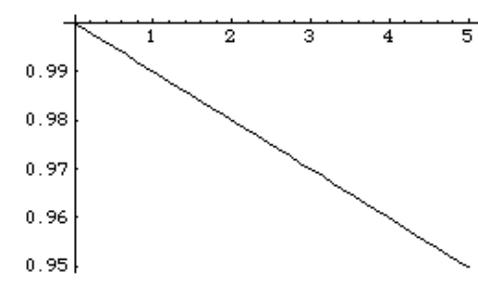
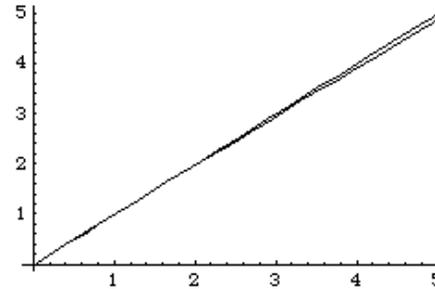
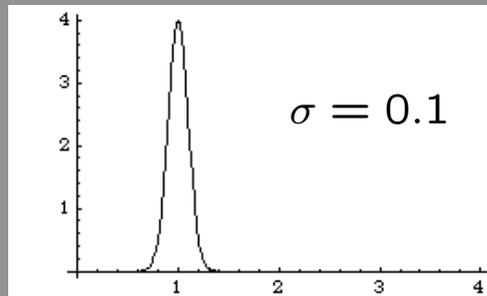
Effect of Gaussian thickness variation

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(x - \bar{x})^2}{2\sigma^2}\right)$$

$P(x)$

μx_{eff} and $\mu \bar{x}$ vs μ

$\mu x_{\text{eff}}'$ vs μ



Effect of leakage/harmonics

Leakage (zero thickness) fraction a , together with gaussian variation in thickness centered on x_0 with width σ :

$$P(x) = a\delta(x) + (1 - a) \frac{1}{\sigma\sqrt{2\pi}} \exp\left(\frac{-(x - \bar{x})^2}{2\sigma^2}\right)$$

$$\mu x_{\text{eff}}(E) = -\ln(a + (1 - a) \exp(-\mu x_0 + \mu^2 \sigma^2 / 2))$$

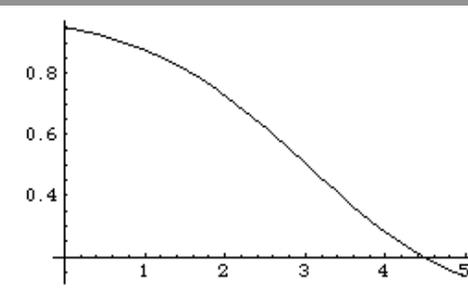
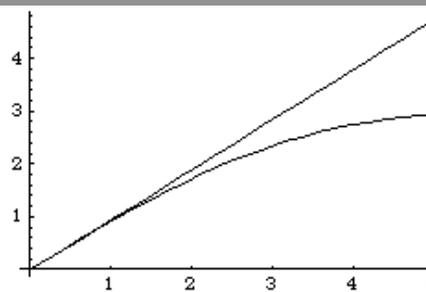
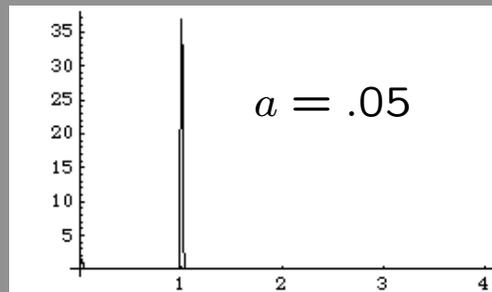
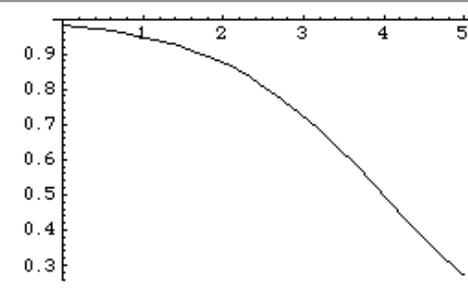
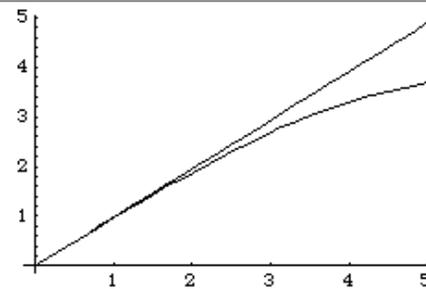
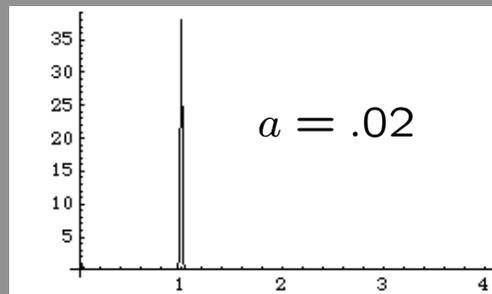
Effect of pinholes (leakage) or harmonics

$$P(x) = a\delta(x) + (1 - a)\frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(x - \bar{x})^2}{2\sigma^2}\right)$$

$P(x)$

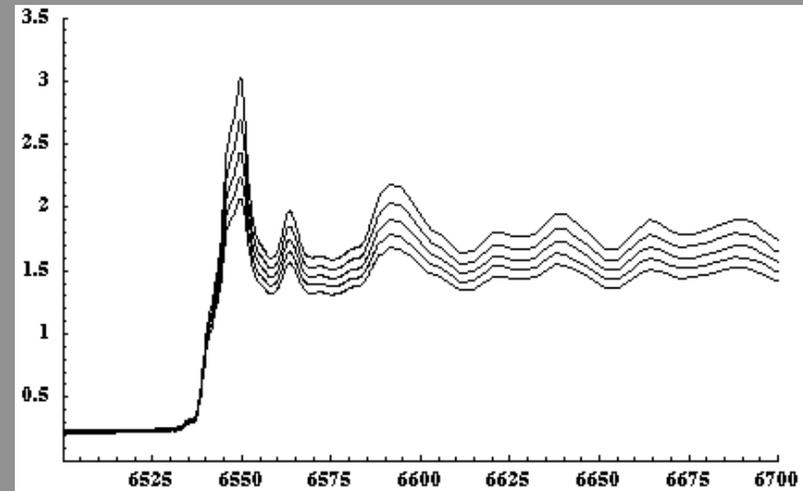
μx_{eff} and $\mu \bar{x}$ vs μ

$\mu x_{\text{eff}}'$ vs μ



Effect of Leakage on spectra

- MnO 10 micron thick
- ~2 absorption lengths
- leakage varied from 0% to 10%
- Edge jump is reduced
- EXAFS amplitudes are reduced
- white line height compressed
- thickness effects distort both XANES and EXAFS - screw up fits and integrals of peak areas
- If you are fitting XANES spectra, watch out for these distortions



Simple model of thickness distribution

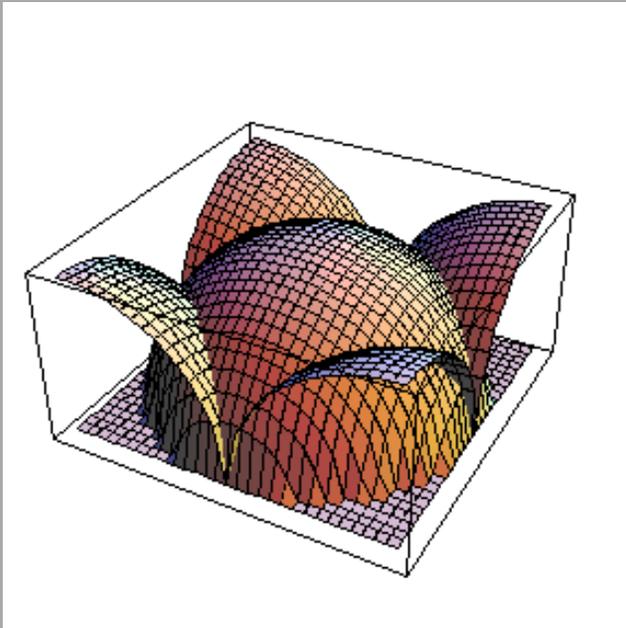
Thickness distribution is a sum of gaussians of weight a_n , thickness x_n , and width σ_n :

$$P(x) = \sum_n \frac{a_n}{\sigma_n \sqrt{2\pi}} \exp\left(-\frac{(x - x_n)^2}{2\sigma_n^2}\right)$$

$$\mu x_{\text{eff}}(E) = -\ln\left(\sum_n a_n \exp(-\mu x_n + \mu^2 \sigma_n^2 / 2)\right)$$

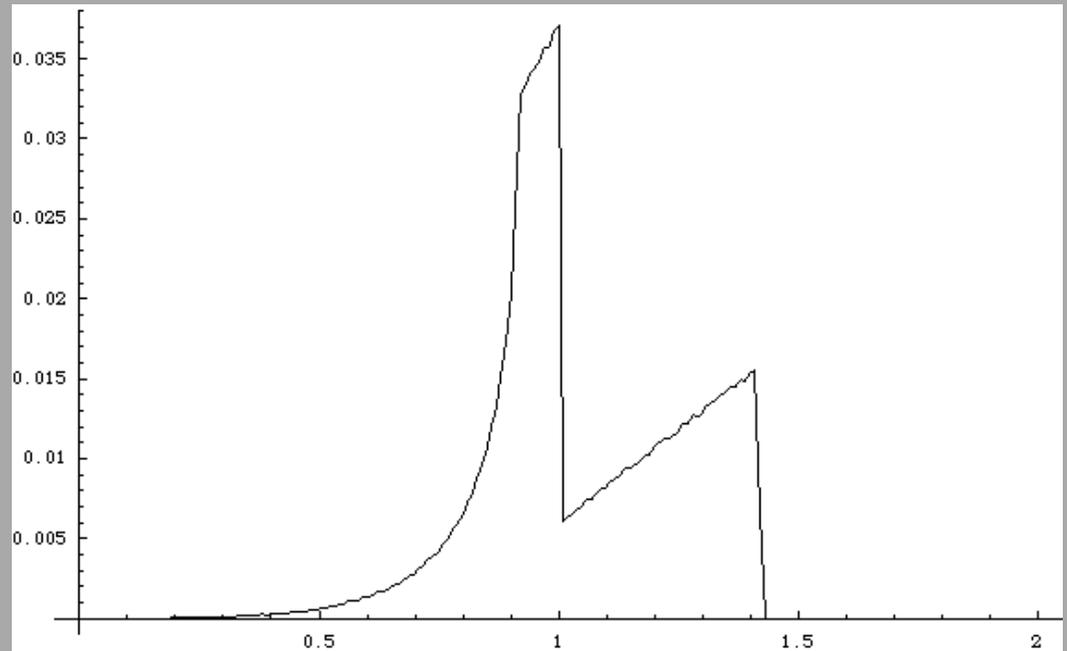
This expression can be used to estimate the effect of thickness variations

Example - Layers of spheres



square lattice - holes in one layer covered by spheres in next layer

Thickness
Distribution



Transmission mode -Summary

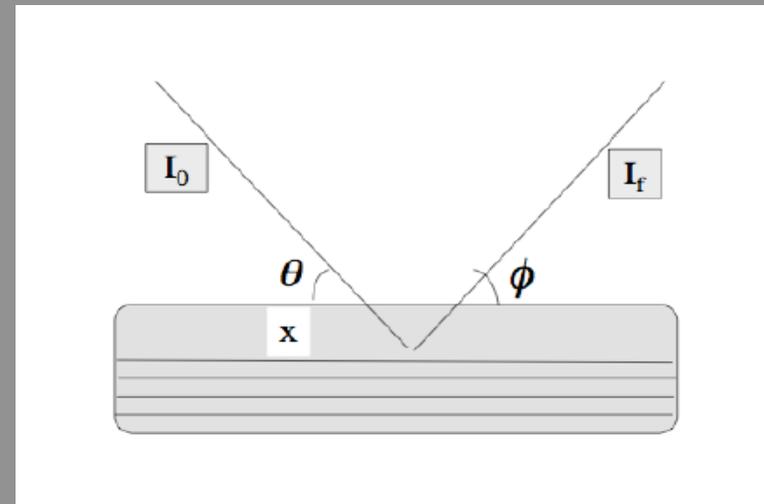
- Samples in transmission should be made uniform on a scale determined by the absorption length of the material
- Absorption length should be calculated when you're designing experiments and preparing samples

Selecting the experimental mode

- For transmission you need to get x-rays through the sample
 - Total thickness should be kept below < 2 absorption lengths including substrates to minimize thickness effects
 - “beam hardening” - choose fill-gases of back ion chamber to minimize absorption of harmonics; get rid of harmonics by monochromator detuning, harmonic rejection mirrors, etc.
 - Element of interest must be concentrated enough to get a decent edge jump (> 0.1 absorption length)
 - Pinholes and large thickness variations should be minimized
 - If you can't make a good transmission sample, consider using fluorescence or electron yield

Fluorescence Radiation in the Homogeneous Slab Model

- Probability the photon penetrates to a depth x in the sample
- and that is absorbed by the element i in a layer of thickness dx
- and as a consequence it emits with probability ϵ a fluorescence photon of energy E_f
- which escapes the sample and is radiated into the detector



- Thin Sample

$$dI_f = I_0 \epsilon_a \frac{\mu_a(E)}{\sin \theta} e^{-\frac{\mu(E)x}{\sin \theta}} e^{-\frac{\mu(E_f)x}{\sin \phi}} dx$$

$$I_f = \frac{I_0 \epsilon_a \left(\frac{\mu_a}{\sin \theta} \right)}{\frac{\mu_T}{\sin \theta} + \frac{\mu_f}{\sin \phi}} \left[1 - e^{-\left(\frac{\mu_T}{\sin \theta} + \frac{\mu_f}{\sin \phi} \right) d} \right]$$

$$\left[\left(\frac{\mu_T}{\sin \theta} + \frac{\mu_f}{\sin \phi} \right) d \right] \ll 1$$

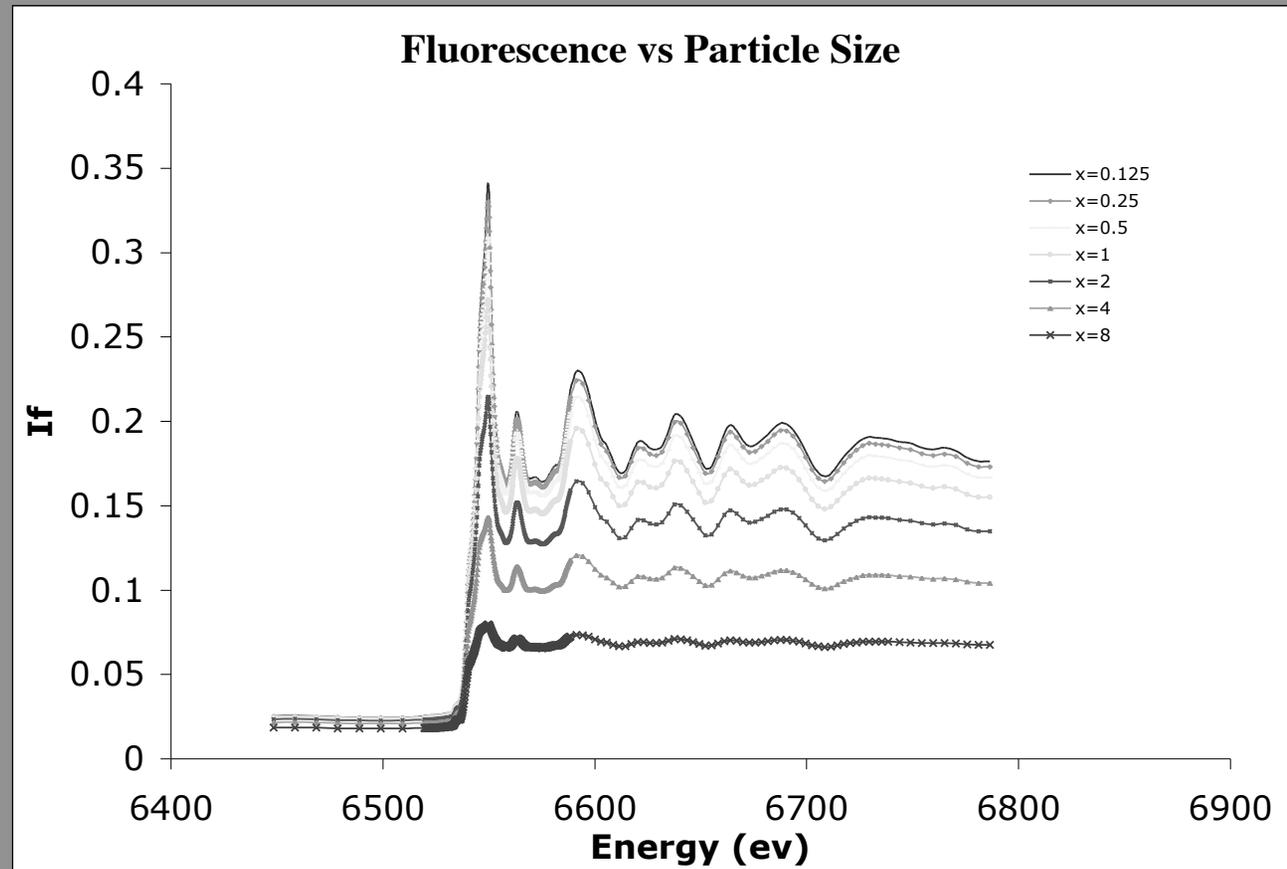
$$(I_f)_{thin} = I_0 \epsilon_a \left(\frac{\mu_a}{\sin \theta} \right) d$$

Fluorescence samples

- Simple in thin concentrated and thick dilute limits
- Thick concentrated requires numerical corrections (e.g. Booth and Bridges, XAFS 12). Thickness effects can be corrected also if necessary by regularization (Babanov et al).
- Sample Requirements
 - Particle size must be small compared to absorption lengths of particles (not just sample average). Can be troublesome for in situ studies
 - Homogeneous distribution
 - Flat sample surface preferred
- Grazing incidence external reflection gives surface sensitivity

Speciation problems

Nonlinear distortions of the spectra depend on particle size and distribution. This affects speciation results



Dilute samples

- “dilute”: absorption of element of interest is much less than average absorption of sample
- Even if the sample is dilute on average you may not be really in the dilute limit
- Each individual particle must be small enough, otherwise you will get distorted spectra
- Don't just mix up your particles with a filler and think it's dilute. First make particles small compared to one absorption length in the material of which the particles are composed.

Summary – Fluorescence

- Particle size effects are important in fluorescence as well as transmission
- The homogeneous slab model is not always suitable but other models have been developed
- If the particles are not sufficiently small, their shape, orientation, and distribution can affect the spectra in ways that can influence results
- Particularly important for XANES and chemical speciation, but also important for EXAFS

Electron yield detection

- sample is placed atop and electrically connected to the cathode of helium filled ion chamber
- electrons ejected from surface of sample ionize helium – their number is proportional to absorption coefficient
- The current is collected and it represents the signal, just in like an ionization chamber
- Surface sensitivity of electron detection eliminates self-absorption problems but does not sample bulk material
- Charging effects can be a problem

Sample Inhomogeneities

- Importance of inhomogeneity also can depend on spatial structure in beam
 - bend magnets and wiggler beams usually fairly homogeneous
- Undulator beams trickier because beam partially coherent
 - coherence effects can result in spatial microstructure in beam at micron scales
- Beam Stability
- Samples must not have spatial structure on the same length scales as x-ray beam. Change the sample, or change the beam.

- Foils and films often make good transmission samples
 - stack multiple films if possible to minimize through holes
 - check for thickness effects (rotate sample)
- Foils and films can make good thin concentrated or thick dilute samples in fluorescence
- Consider grazing incidence fluorescence to reduce background and enhance surface sensitivity (see mirror equations later in this document)

Solutions

- Usually solutions are naturally homogeneous
 - Can make good transmission samples if concentrated
 - Usually make good fluorescence samples (~1 millimolar and 100 ppm are routine), lower concentrations feasible
- They can become inhomogeneous during experiment
 - phase separation
 - radiation damage can cause precipitation (e.g. protein solutions)
 - photolysis of water makes holes in intense beams
 - suspensions/pastes can be inhomogeneous

Particulate samples

- First calculate the absorption length for the material
- prepare particles that are considerably smaller than one absorption length of their material, at an energy above the edge
- Many materials require micron scale particles for accurate results
- Distribute the particles uniformly over the sample cross sectional area by dilution or coating

Making Fine Particles

- During synthesis → choose conditions to make small particles
- Grinding and separating
 - sample must not change during grinding (e.g. heating)
 - For XAFS can't use standard methods (e.g. heating in furnace and fluxing) from x-ray spectrometry, because chemical state matters
 - Have to prevent aggregation back into larger particles

Checking the sample

- check composition by spectroscopy or diffraction
- visually check for homogeneity
 - caveat: x-ray vs optical absorption lengths
- tests at beamline: move and rotate sample
- digital microscope (Olympus Mic-D \$800 US)
- particle size analysis (Image/J free)
- If you have nice instruments like a scanning electron microscope or light scattering particle size analyzer, don't hesitate to use them

Preferred Orientation

- If your sample is polycrystalline, it may orient in non-random way if applied to a substrate
- since the x-ray beams are polarized this can introduce an unexpected sample orientation dependence
- Test by changing sample orientation
- Magic-angle spinning to eliminate effect

Control samples

- In fluorescence measurements always measure a blank sample without the element of interest under the same conditions as your real sample
- Many materials have elements in them that you wouldn't expect that can introduce spurious signals
- Most aluminum alloys have transition metals
- Watch out for impurities in adhesive films
- Fluorescence from sample environment excited by scattered x-rays and higher energy fluorescence

Effective Counts

Experimental conditions should be optimized to maximize "effective counts" = $(S/N)^2$

$$\text{signal} = N_s$$

$$\text{noise} = \sqrt{N_b + N_s}$$

$$S/N = N_s / \sqrt{N_b + N_s}$$

$$N_{\text{eff}} = N_s^2 / (N_b + N_s) = N_s / (1 + N_b / N_s)$$

This is usually easy to do; just take the edge jump (fluor. above- fluor. below) as the signal, and the fluorescence below the edge as the background.

Adjust conditions to maximize $(A-B)^2/B$

Avoiding problems: "HALO"

- Harmonics:
 - Eliminate them by detuning mono, choosing mirror angle, or other optics
- Alignment
 - beam should only see uniform sample, nothing else
- Linearity
 - plateau ion chambers, dead time corrections
- Offsets
 - subtract dark currents regularly $(I+C)/(I_0+C) \neq I/I_0$

Detector Linearity

- Using “matched” but nonlinear detectors is not a good solution because detectors don’t measure identical signals
- Each detector individually must be linear, or corrected numerically to give linear response
- Keeping IO at a fixed level just hides detector nonlinearity but doesn’t eliminate all the problems. It may also vary the harmonic content.
- Intentionally varying IO and checking for correlated signals in I/IO is a good diagnostic

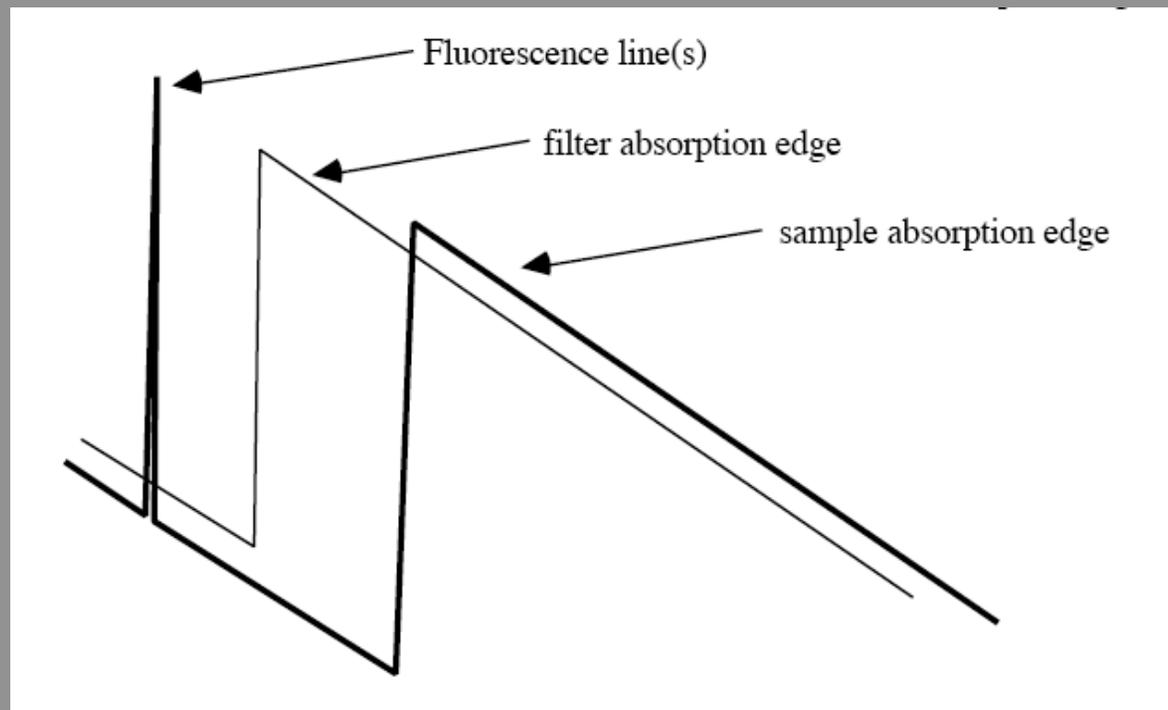
Integrating Detectors

- ④ Ionization chambers: choose fill gas to have appropriate absorption at energy of interest. Operate IC at high enough voltage that it's in the plateau region (I independent of V). Stern/Heald (Lytle) detectors offer large area for fluorescence detection.
- ④ Photodiode (e.g. PIPS) Detectors: do not require bias voltage, linear. Must keep shielded from light.
- ④ Scintillator/Photomultiplier in current mode – intrinsic gain, needs high stability high voltage supply. Magnetic fields may be problem.
- ④ Current output is amplified with transimpedance amplifier (e.g. Keithley) and typical fed into Voltage to Frequency converter. The resulting pulses are counted in a scaler for given time. The number of pulses is proportional to the current.

Pulse Counting Detectors

- Solid state (biased diode) detectors
- Multielement Ge and Si diode detectors (e.g. Canberra 13 element, NSLS detector integrated electronics)
- Silicon drift detectors -> faster, arrays becoming available
- Scintillator/Photomultipliers
- Proportional counters - need multiwire for speed
- Avalanche photodiodes - solid state geiger counter - fast
- Typical electronics: preamplifier -> shaping amplifier
-> discriminator -> scaler, one full electronics chain per detector element. Multichannel analyzer useful for observing energy spectrum
 - XIA digital x-ray processor handles these functions digitally using field programmable gate arrays

Z-1 Filters for scatter rejection

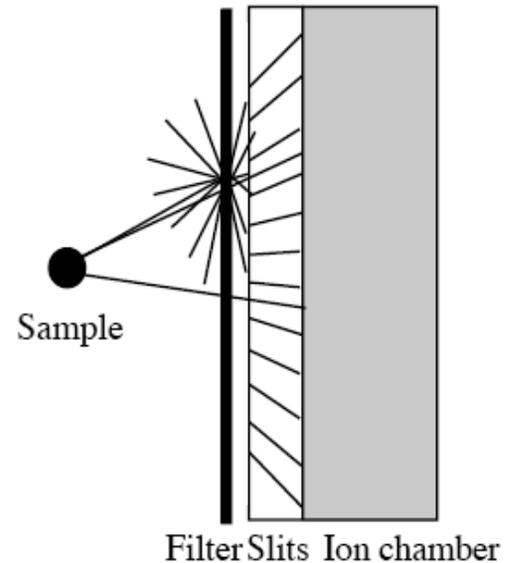


see http://gbxafs.iit.edu/training/filter_optimize_revised.pdf
http://gbxafs.iit.edu/training/filter_optimize_plots.pdf

Slits

Stern and Heald

Slits permit the fluorescence signal photons to travel from the sample to the detector, but block most of the filter refluorescence.



http://gbxafs.iit.edu/training/filter_optimize_revised.pdf
http://gbxafs.iit.edu/training/filter_optimize_plots.pdf

Z-1 filters/slits

- Can collect large solid angle with suitable detector (e.g. Stern/Heald ion chamber (Lytle detector))
- Can be used a pre-filter for solid state detector arrays
- Low pass filter only
 - Mostly useful for rejecting elastic scatter
- Need good quality filters and effective slits
- Inefficient for high background/signal ratios
- No suitable filter for some elements

Crystal Analyzers

Small beam sizes required; instruments have varied acceptance, tunability, solid angle, reflectivity characteristics

- Rowland circle instruments (e.g. Oxford Instruments WDXRF)
- LiF analyzers for x-ray spectrometry
- Graphite “barrel” monochromator (Bell Labs)
- Log spiral HOPG analyzers (Pease et al, www.ifg-adlershof.de)
- Log spiral bend analyzer (Attenkofer et al)
- Multilayer Array Analyzer (K. Zhang, G. Rosenbaum, G. Bunker, www.hdtechinc.com)
- Bent Laue Crystal Analyzers (e.g. C. Karanfil, G. Bunker, D. Chapman, Z. Zhong, G. Knapp, J. Kropf, www.quercustech.com)

Some Fluorescence Analyzers



HOPG
log spiral
Bragg



Multilayer Array Analyzer
20 element (Bragg)



assorted BCLAs
(Laue)

Conclusion

- Calculate the absorption coefficients of your sample so you know what you are dealing with at the energies you care about. Think like an x-ray. Know what to expect.
- Choose a beamline that can produce the kind of beam you need (flux, beam size, detectors available, etc). Choice of beamline/mode/sample/question_posed are interrelated decisions. Design the experiment iteratively with these in mind.
- Make particles small compared to absorption length and make samples homogeneous
- Check experimentally for thickness, particle size, and self absorption effects. Check a "blank" sample and a good reference sample.
- Maximize your effective counts by choice of detector and experimental geometry. Quality of filters and slits matters. Do deadtime corrections.
- "HALO" - check harmonics, alignment, linearity, offsets