



Complimentary Methods

Today I'm going to briefly discuss some structural characterization techniques that are complimentary to X-ray powder diffraction.

- **Neutron Diffraction**
- **Electron Diffraction**
- **X-ray Fluorescence, EDAX and Electron Microprobe Analysis**
- **EXAFS and XANES**
- **Pair Distribution Function (PDF) Analysis**

Neutron Diffraction

We've talked about X-ray and neutron diffraction throughout the quarter as though they were interchangeable. The basic concept is the same though there are important distinctions between the two. Let's begin with the DeBroglie relationship.

$$\lambda = h/p = h/mv$$

but the kinetic energy, E , and velocity, v , of a particle are related by the expression

$$E = (1/2)mv^2 \rightarrow v = \text{sqrt}(2E/m)$$

combining the two relationships gives

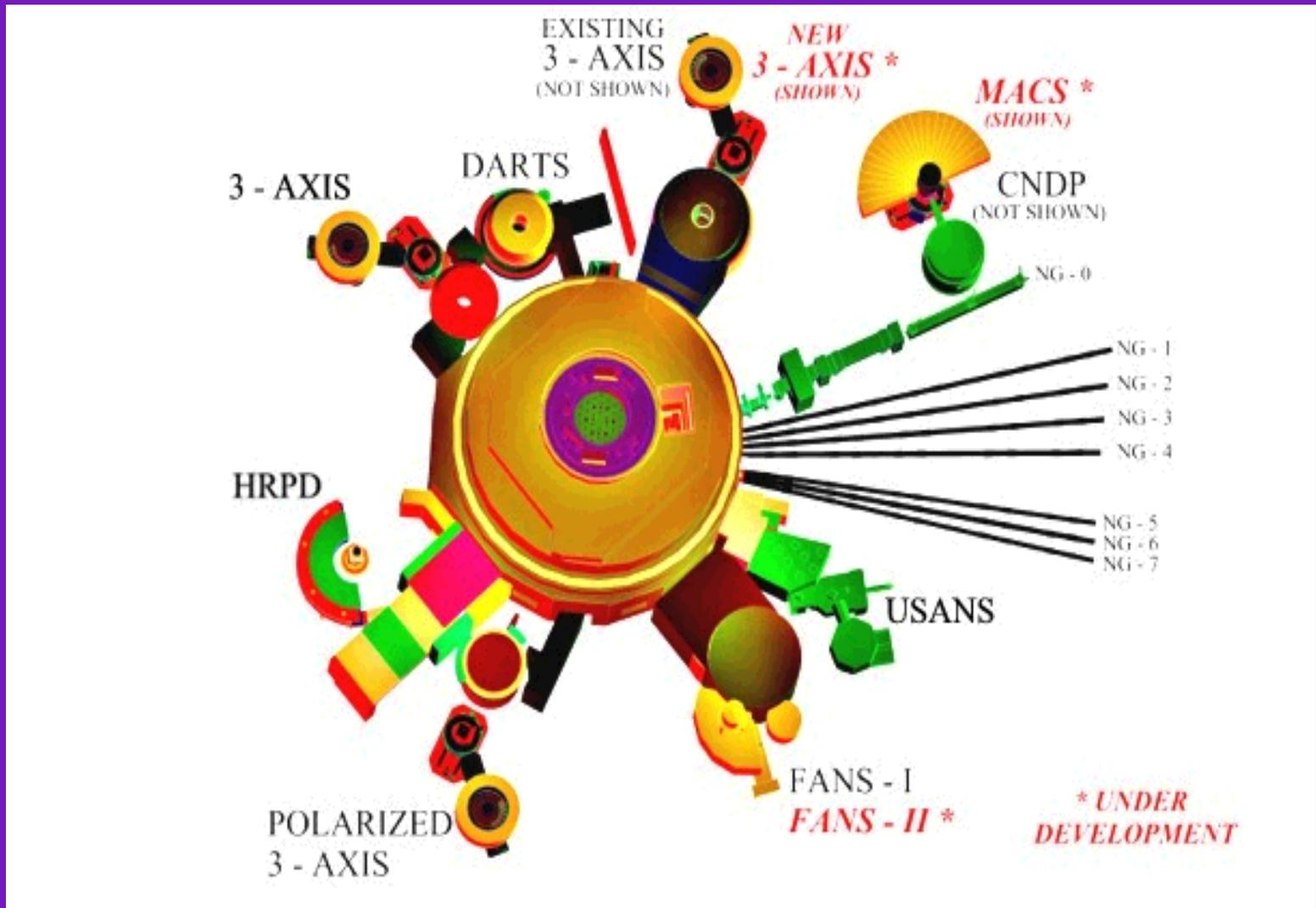
$$\lambda = h/\text{sqrt}(2mE)$$

finally for thermal neutrons from a reactor source the energy of an electron is $E = kT$ so that

$$\lambda = h/\text{sqrt}(2kT)$$

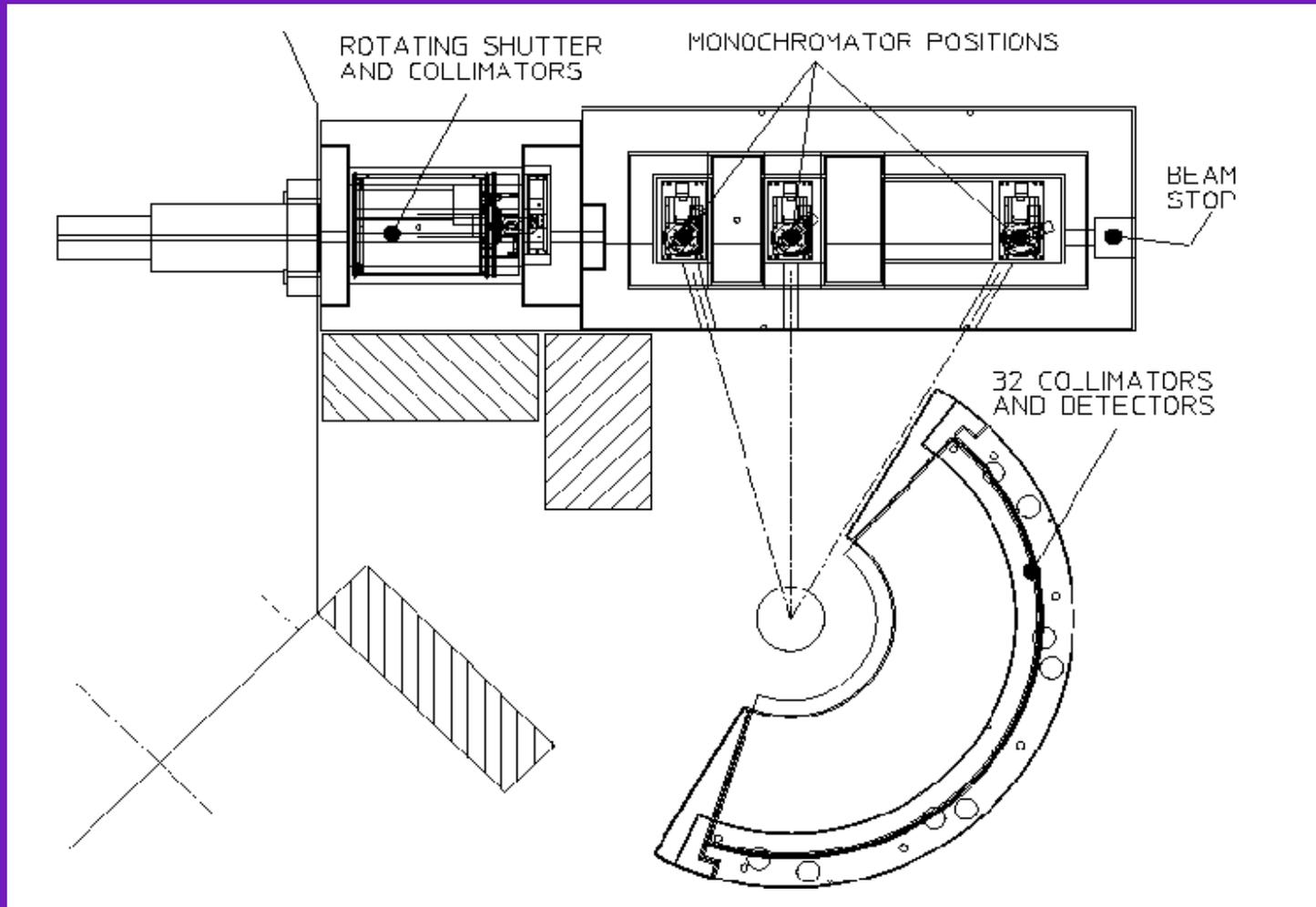
Typical values for a neutron reactor source are $300 < T < 400\text{K}$ and $1.0 \text{ \AA} < \lambda < 2.5 \text{ \AA}$.

Reactor Diffractometers



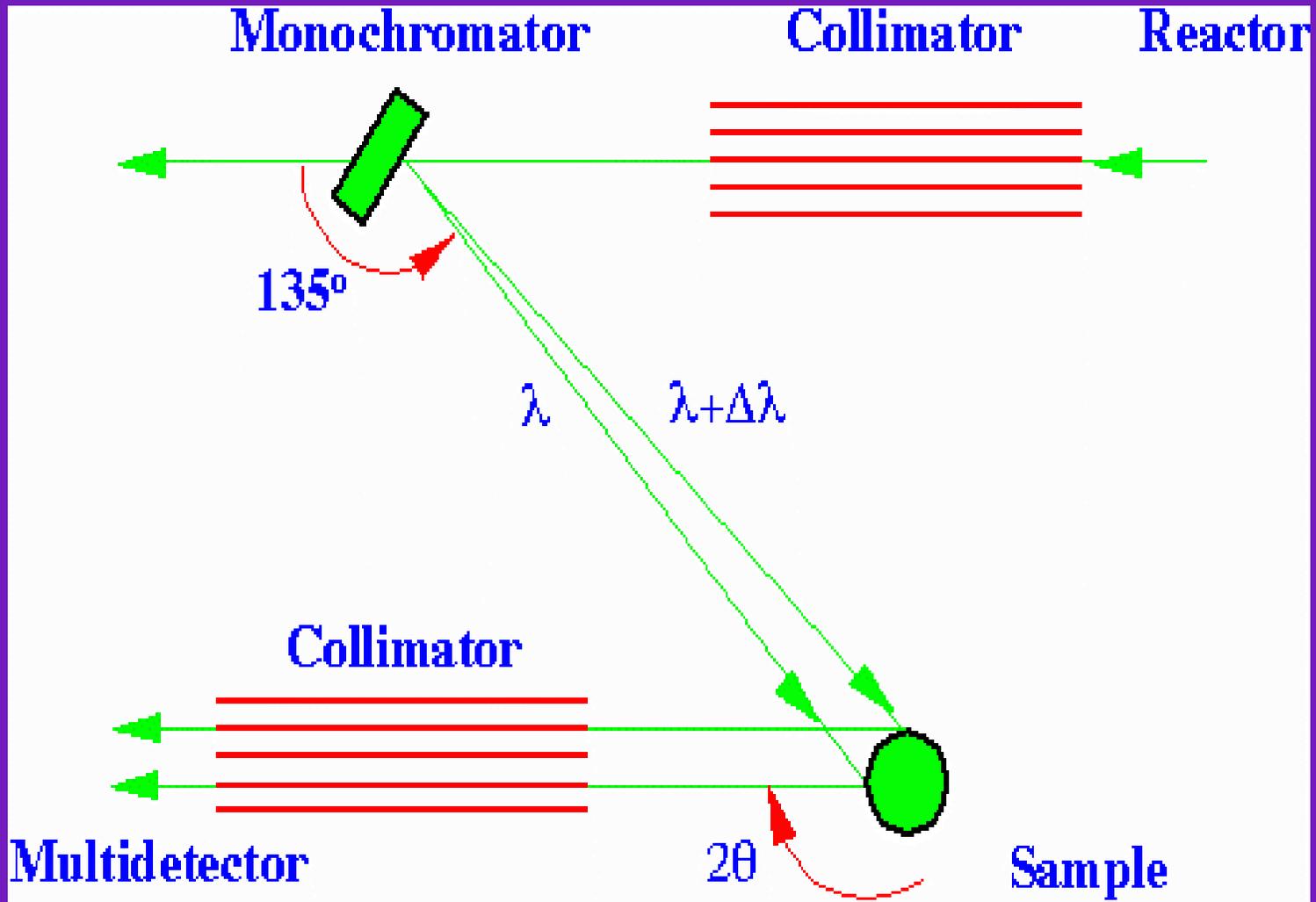
Thermal Neutron Instruments at NIST

BT1 Powder Diffractometer



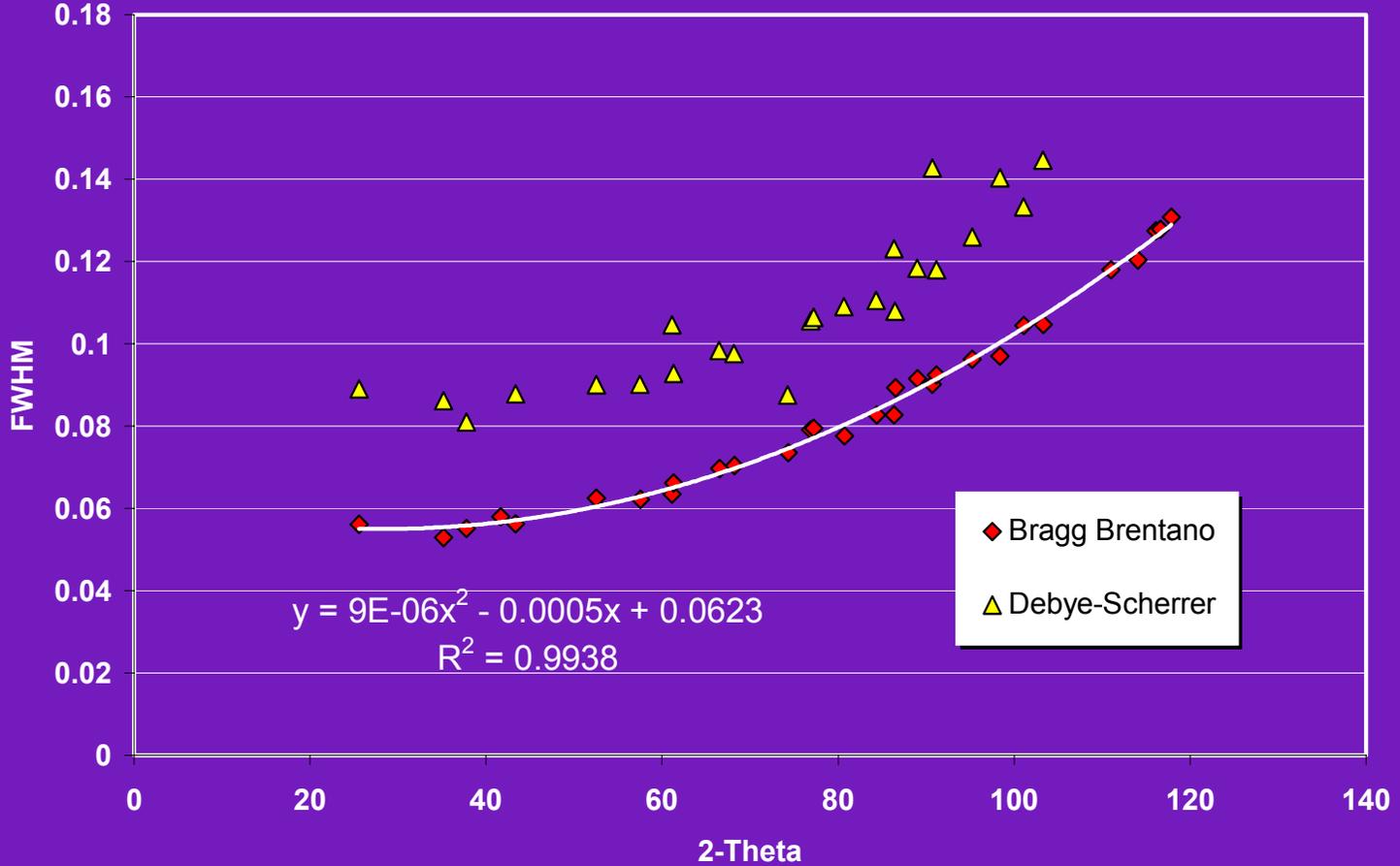
BT1 Powder Diffractometer at NIST

D2B Powder Diffractometer



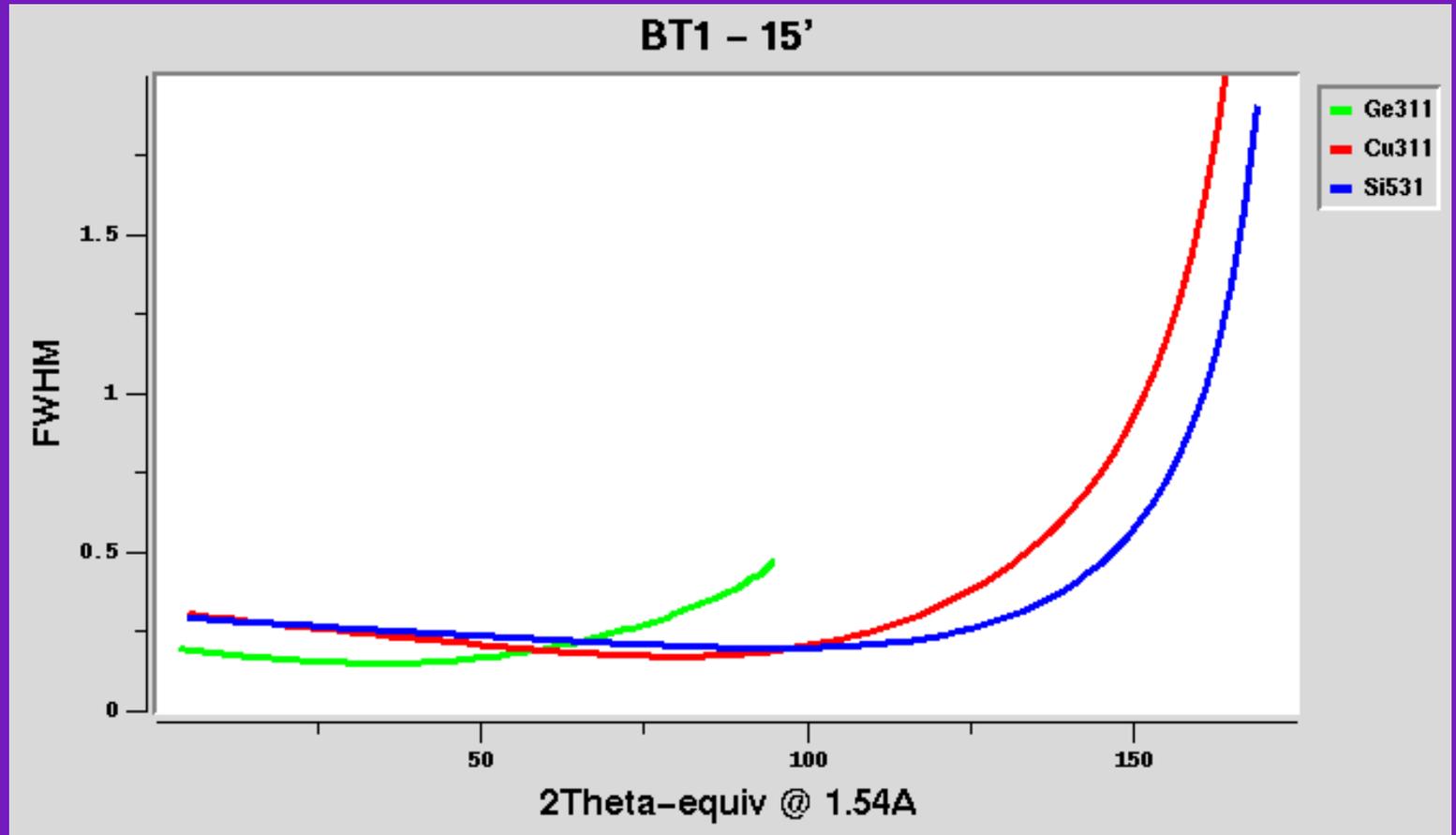
D2B Powder Diffractometer at ILL

Instrumental Broadening: X-rays



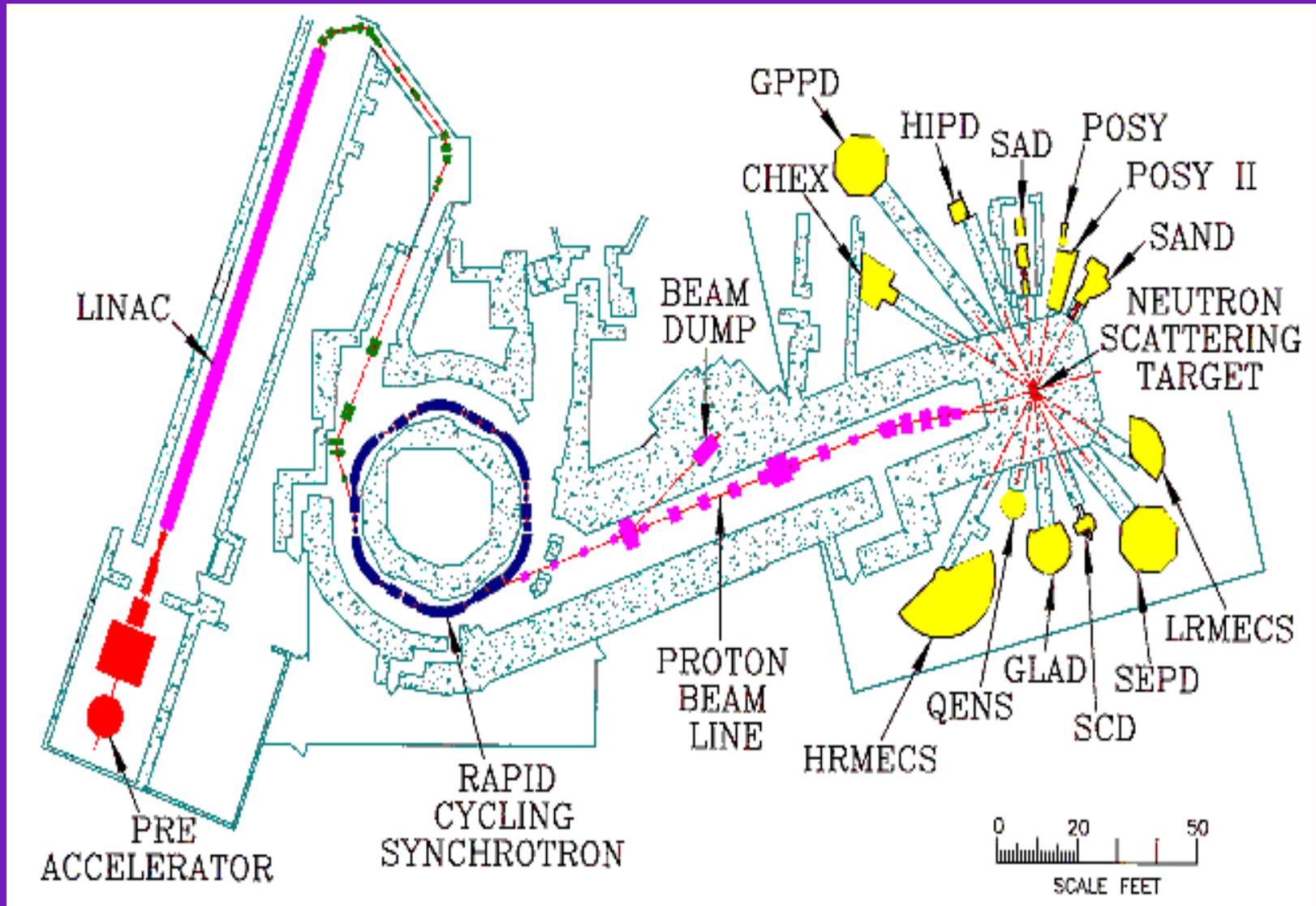
This data corresponds to a Bruker D8 Diffractometer, equipped with an incident beam Ge monochromator and Braun Position Sensitive Detector (masked to use $\sim 4^\circ 2\theta$)

Instrumental Broadening: Neutron



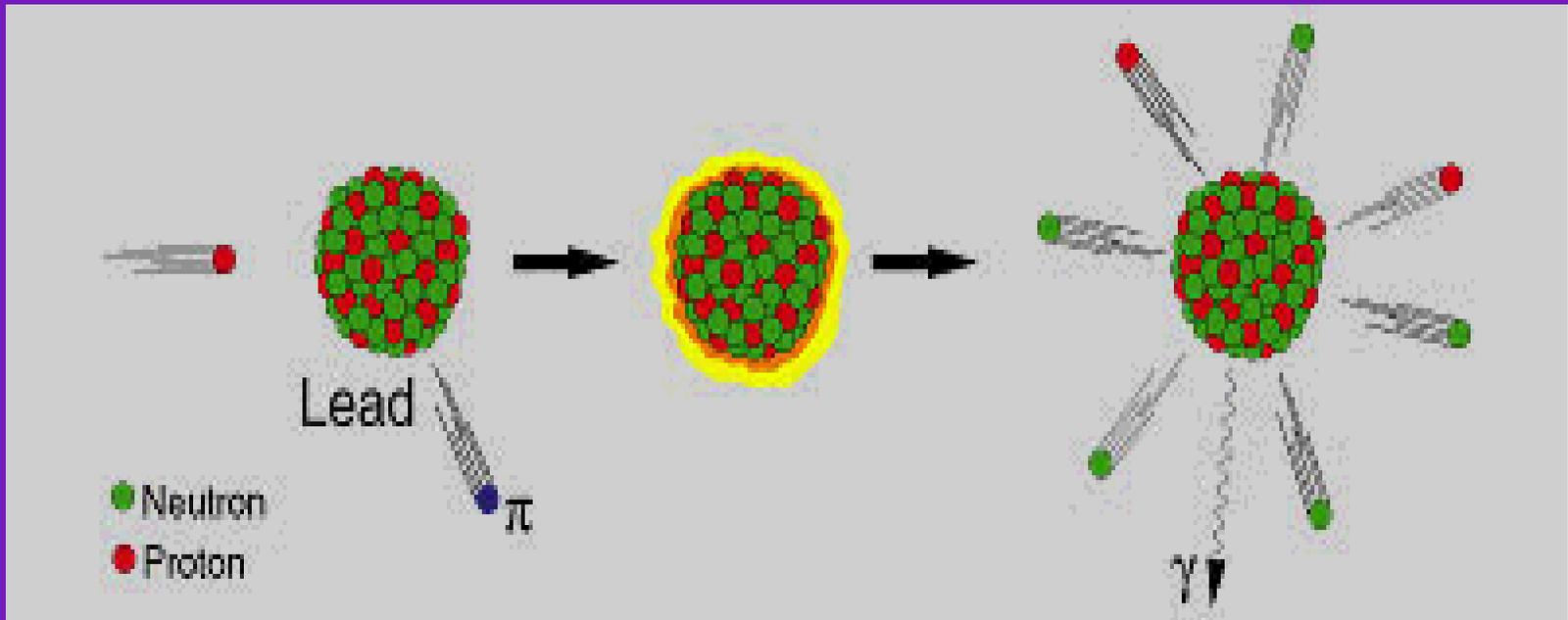
This data corresponds to a High Resolution Powder Neutron Diffractometer located on Beamline BT1 at NIST. See http://www.ncnr.nist.gov/instruments/bt1/bt1_for_xtal.html for more information.

Spallation Sources



IPNS Facility <http://www.pns.anl.gov/ipnsmap.htm>

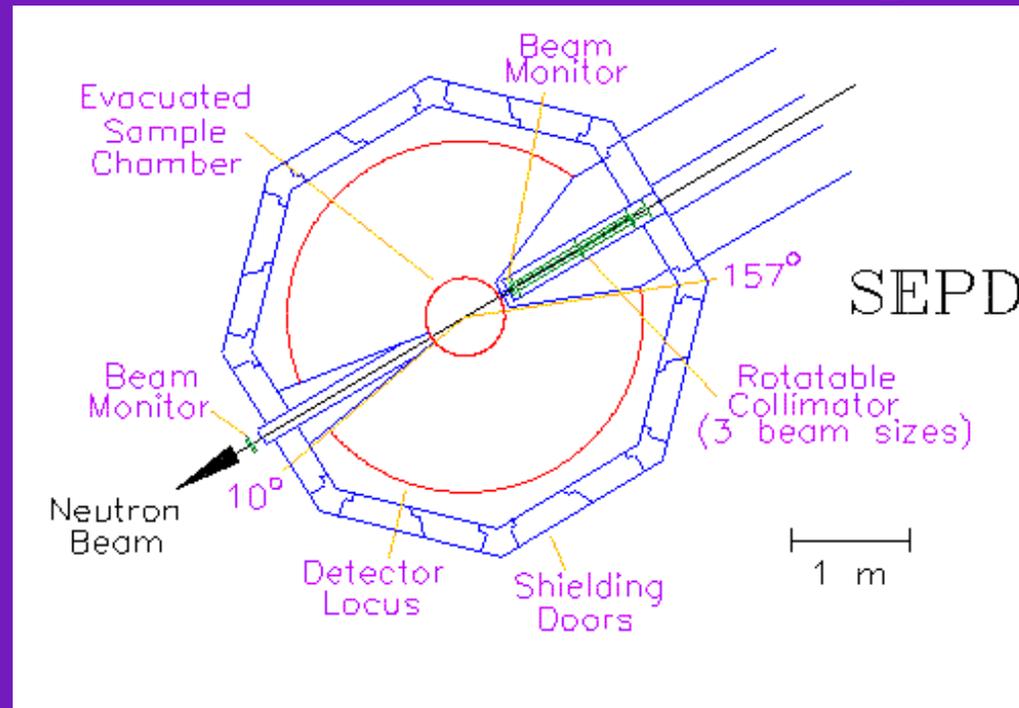
Spallation Sources



The interaction between the accelerated proton and the neutron target (Pb). Typically each proton generates 10-15 neutrons. These neutrons then pass through a moderator (often water or liquid methane) to reduce their energy to a level comparable with thermal neutrons from a reactor. This image was taken from the website of the Paul Scherrer Institute.

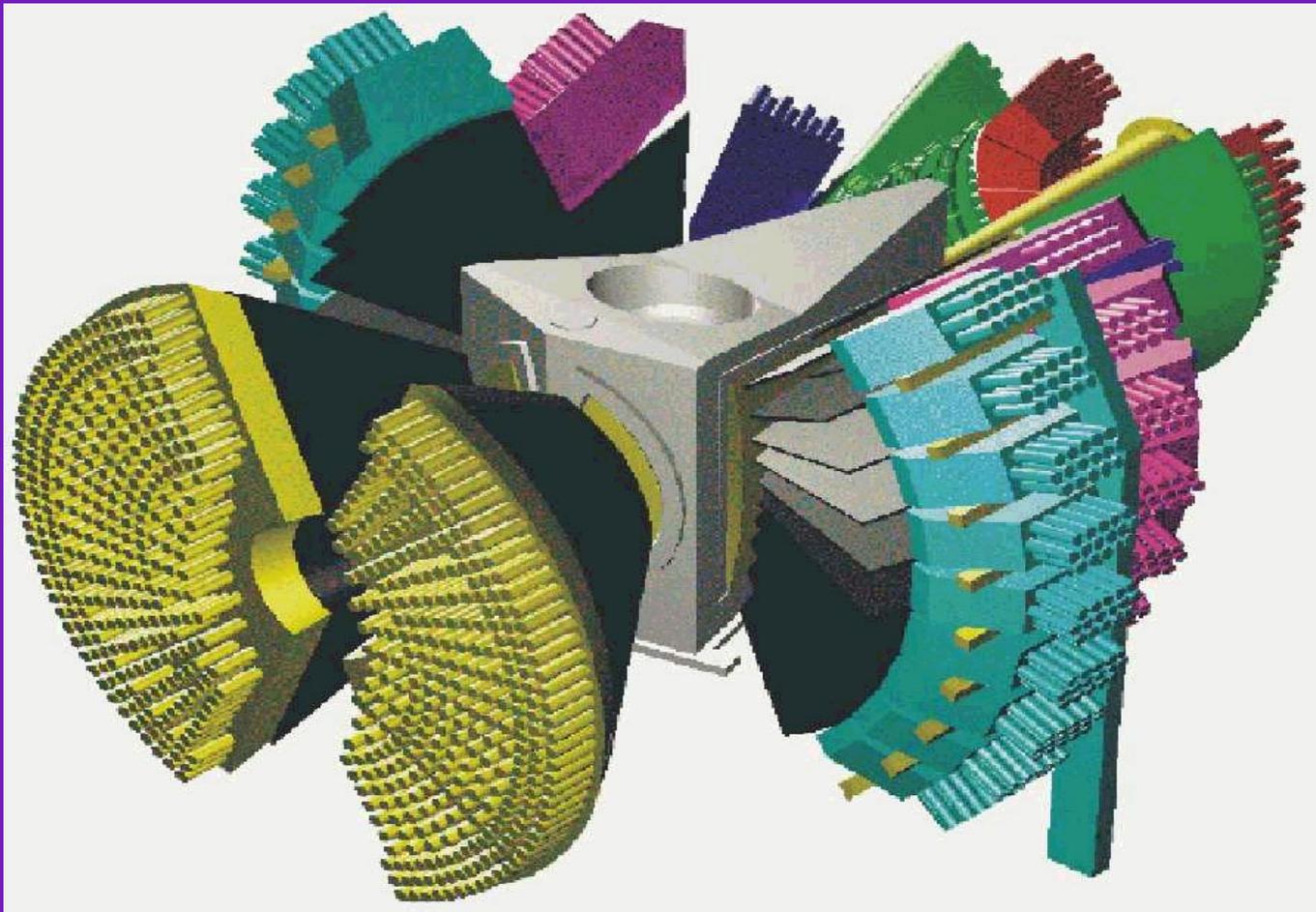
http://www.psi.ch/index_e_sinq.shtml

TOF Diffractometer (SEPD)

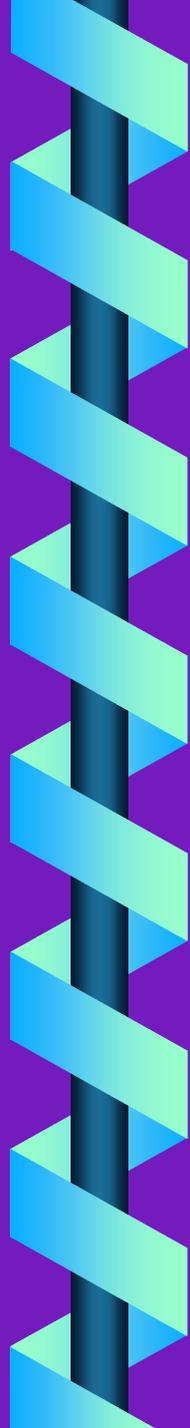


Since the neutrons come in pulses their energy (and hence wavelength) can be determined by measuring the time it takes for the neutron to hit the detector. Hence the spectra come out in Time-of-Flight (TOF) rather than 2θ . The geometry of the experiment is still transmission and there are sets of detector banks that record the diffracted neutrons. Typically the only moving parts will be choppers that let through the neutron pulses. This diagram shows the layout of the SEPD diffractometer at IPNS.

TOF Diffractometer (GEM)



Schematic Drawing of the GEM Diffractometer at the ISIS source in the UK. For more information see: http://www.isis.rl.ac.uk/disordered/gem/gem_home.htm



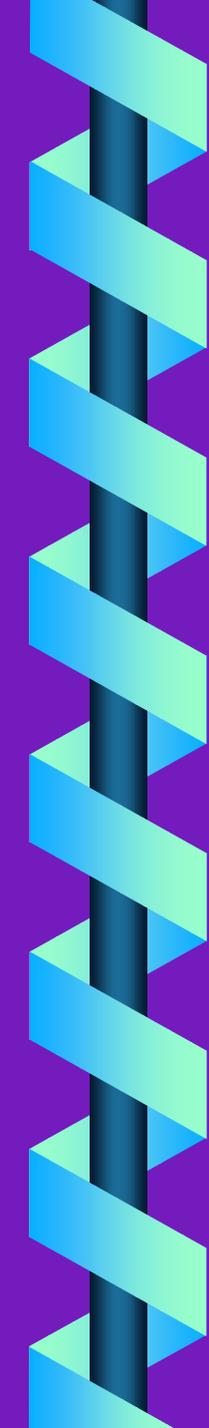
Spallation vs. Reactor Sources

- ◆ **Advantages of TOF instruments on spallation sources**
 - **Better resolution at low d-spacings (high angle). This is good for accurate structure refinements.**
 - **Higher neutron flux, which translates to smaller samples and faster collection times.**
 - **Politically feasible to build a spallation neutron source in the US.**
- ◆ **Advantages of diffractometers at reactor sources**
 - **Better resolution at high d-spacings (low angle). This is good for magnetic studies, compounds with large unit cells, ab-initio structure solution.**
 - **Data analysis and background modeling is more straightforward.**



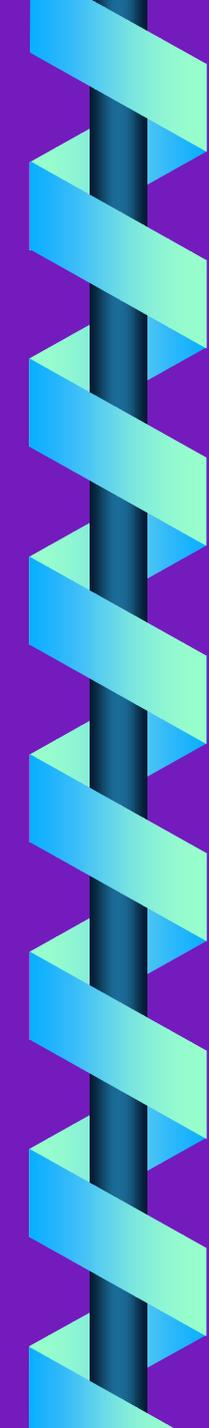
X-rays vs. Neutrons

- ◆ Neutron beams are highly penetrating (penetration depths of centimeters-decimeters),
- ◆ **X-rays are highly attenuated by matter (penetration depths of microns-millimeters).**
- ◆ Neutrons are scattered from nuclei
- ◆ **X-rays are scattered by electrons**
- ◆ Neutron scattering power varies irregularly with atomic number and mass number
- ◆ **X-ray scattering power varies smoothly with atomic number**
- ◆ Neutrons have an intrinsic magnetic moment
- ◆ **X-rays have no magnetic moment**



X-rays vs. Neutrons-Implications

- ◆ Neutron beams are highly penetrating (penetration depths of centimeters-decimeters),
 - **Diffraction comes from entire sample. Values are less susceptible to surface and absorption effects.**
 - **Displacement (temperature) factors tend to be more accurate.**
 - **Larger samples are needed (optimal sample volume is on the order of 10 cm³, roughly the size of your finger)**
- ◆ Neutrons are scattered from nuclei
 - **Neutron scattering factors do not fall off with increasing 2-theta.**
 - **More reliable intensities for high angle peaks allow for more reliable structure determinations.**



X-rays vs. Neutrons-Implications

- ◆ Neutron scattering power varies irregularly with atomic number and mass number
 - Neutrons are more sensitive to light elements (H, N, O, F, C, etc.)
 - Neutrons are sensitive to isotope distributions
 - See <http://www.ncnr.nist.gov/resources/n-lengths/> for more information
 - Some elements strongly absorb neutrons and cannot be easily studied (B, Cd, Sm, Eu, Gd, Dy, Hf, Ir, Hg)
 - Some elements are essentially transparent to neutrons (V) or have negative scattering lengths (Ti, Mn)
- ◆ Neutrons have an intrinsic magnetic moment
 - Neutrons are used to determine ordered magnetic structures (Ferro-, Ferri-, and Antiferromagnetic materials)

Electron Diffraction

Just as with neutrons, electrons accelerated to a high velocity can have a wavelength in the Angstrom range, through the DeBroglie relationship.

$$\lambda = h/p = h/mv$$

but the kinetic energy, E , and velocity, v , of a particle are related by the expression

$$E = (1/2)mv^2 \rightarrow v = \text{sqrt}(2E/m)$$

combining the two relationships gives

$$\lambda = h/\text{sqrt}(2mE)$$

The energy of an electron is related to the accelerating voltage, V , by the relationship $E = eV$. Upon correcting for relativistic effects we get an approximate relationship between the wavelength (in Angstroms) and the Voltage

$$\lambda = \text{sqrt}(150/V)$$

Typical values for a electron microscope are $V \sim 100$ kV and $\lambda \sim 0.04$ Angstroms

Transmission Electron Microscope



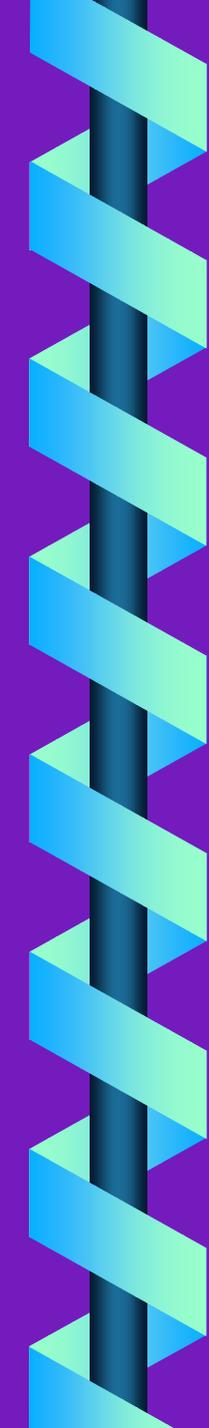
This is the CM300 Ultra-Twin Field Emission Gun TEM.

It is located in the Campus Center for Electron Optics (CEOF) in the MSE department



X-rays vs. Electrons

- ◆ Electrons are highly attenuated by matter (penetration depth of nanometers)
- ◆ **X-rays are strongly attenuated by matter (penetration depths of microns-millimeters).**
- ◆ Electrons beams can be highly focussed
- ◆ **X-rays are difficult to focus**
- ◆ Electron scattering power drops off strongly as a function of 2θ
- ◆ **X-ray scattering power drops off smoothly as a function of 2θ**
- ◆ Diffracted electrons can interact strongly with the lattice making it difficult to get reliable intensities
- ◆ **X-ray intensities and peak positions can be determined with a great deal of accuracy**



X-rays vs. Electrons-Implications

- ◆ **Differences between collecting X-ray and electron diffraction data**
 - **Data collection done under high vacuum**
 - **Data collection is usually transmission measurement (TEM) on a thin sample or crystal**
 - **Diffraction patterns can be collected in short periods of time (seconds)**
 - **Data sets are often collected over a very limited angular range ($\pm 4^\circ$ 2-theta)**
 - **Electron beam is usually focused onto a very small micro-single crystal**
- ◆ **Uses of Electron diffraction**
 - **You can obtain single crystal photographs from a microcrystalline substance**
 - **To determine unit cell dimensions and space group symmetry (good for finding superstructure peaks)**
 - **Can be used to get single phase information from a multiphase sample**

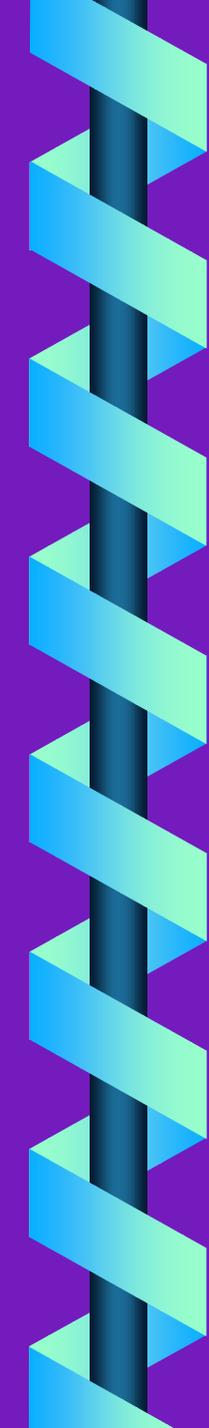
Chemical Analysis

- ◆ When an element is excited by either X-rays or high energy electrons above its absorption edge it will lead to the fluorescent emission of x-rays of a specific energy. This is the principle upon which the sealed Cu X-ray tube operates (Cu is bombarded by electrons and emits $K\alpha_1$, $K\alpha_2$ and $K\beta$ x-rays).
- ◆ Since each element fluoresces X-rays of a specific wavelength we can determine the elements present in a sample by analyzing the energy and intensity of the emitted X-rays.
- ◆ It's fairly straightforward to use this technique for qualitative and semiquantitative analysis.
- ◆ Using standards it is possible to develop a calibration curve and use this technique for quantitative elemental analysis.



Excitation Sources

- ◆ **X-rays (Fluorescence Analysis)**
 - Gives an accurate analysis of bulk stoichiometry
 - High vacuum is not utilized, so that it is easy to change samples
 - Can be difficult to detect light elements, lower limit of stability depends upon atmosphere
 - Air ($Z > 22$ {Ti})
 - He ($Z > 13$ {Al})
 - Vacuum ($Z > 9$ {F})
- ◆ **Electrons (EDAX, Electron Microprobe Analysis)**
 - Electrons can be focused which allows one to carry out elemental analysis on a specific spot or crystalline grain in a sample
 - Done under high vacuum



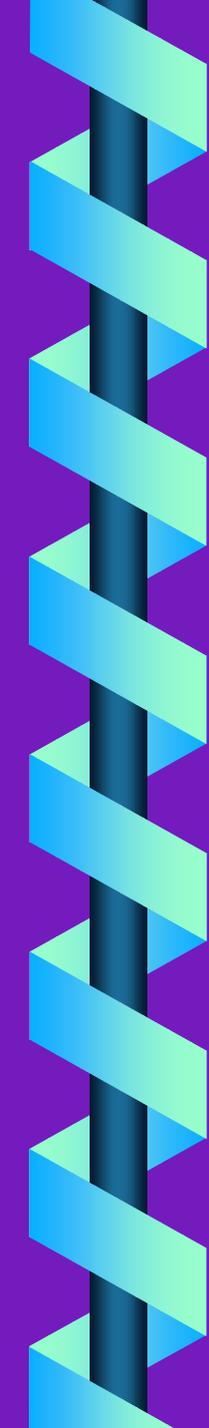
Energy Resolution

◆ Wavelength Dispersive

- **Fluorescent radiation is diffracted off of a crystal and various wavelengths are separated via Bragg's Law ($\lambda=2d\sin\theta$)**
- **This technique gives very good resolution, but longer counting times are needed in order to collect the data over the necessary 2-theta range.**

◆ Energy Dispersive

- **The fluorescent radiation passes directly from the sample to an energy sensitive detector (typically a Si(Li) detector)**
- **Often used with electron excitation sources. It is very common to have such an analyzer attached to an electron microscope.**
- **Lower resolution, but much faster collection times.**
- **Semiquantitative**



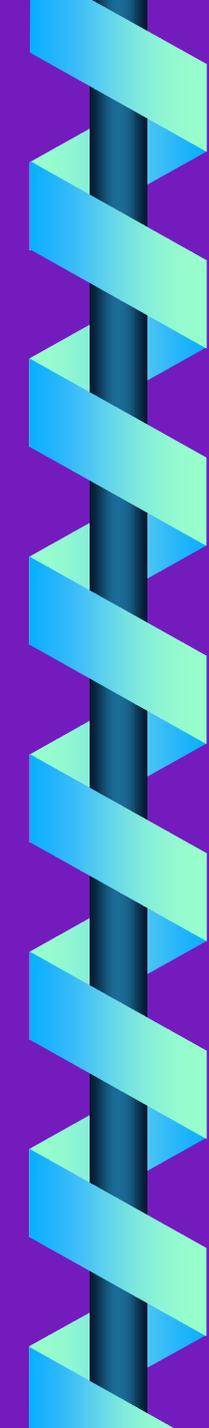
Issues with Quant. Analysis

- ◆ Reliable quantitative analysis using fluorescence methods usually requires generation of a calibration curve using appropriate standards. The similarity of your standards and the unknown sample determine the ultimate accuracy of the analysis. The need for standards comes about because of the following effects.
- ◆ **Matrix Absorption**
 - **The absorption of X-rays coming into and out of the crystal varies with composition.**
- ◆ **Enhancement**
 - **Fluorescent radiation from one element (i.e. Ni) can be absorbed and induce fluorescence in other elements contained in the sample (i.e. Fe)**



Elemental Analysis using an SEM

- ◆ The following specifications are taken from the MARC center in geology at Ohio State University (<http://www.geology.ohio-state.edu/marc/sem1.htm>)
 - High resolution (**4 nm**) imaging of surfaces
 - Nondestructive analysis of large samples (up to 8" x 8" x 1.5")
 - **Energy dispersive detector**
 - Low voltage operation for analysis of insulating samples
 - Quantitative chemical microanalysis with **0.1% detection limits** if no spectral overlaps
 - Extensive automated image analysis based on size, shape and chemical composition



Electron Microprobe Analysis

- ◆ The following specifications are taken from the MARC center in geology at Ohio State University (<http://www.geology.ohio-state.edu/marc/ema1.htm>)
 - Quantitative chemical microanalysis with **0.01% detection limits routinely**; 0.003% for some elements
 - Four high selectivity wavelength dispersive spectrometers operate simultaneously
 - Rapid spectral acquisition with **energy dispersive analyzer**
 - Analysis of elements from boron to uranium
 - High-resolution (**1 um beam diameter**) nondestructive analysis



Disordered Materials

- ◆ **Many materials contain some type of disorder on the atomic scale. For example this is true of any solid solution. Some classes of materials where disorder is an important element of the structure include:**
 - **Compound semiconductors**
 - **High Temperature Superconductors**
 - **Ferroelectrics and Piezoelectrics**
 - **Magnetoresistant Materials**
 - **Alloys**
- ◆ **In such systems the crystal structure that one obtains from powder or single crystal diffraction gives an average structure. Other techniques are needed to determine the local coordination environment of atoms.**

Methods of Extracting Local Structural Information

◆ Spectroscopic methods

- **Magic Angle Spinning - Solid State NMR**
- **Mossbauer Spectroscopy (Fe, Sn, Eu, ...)**
- **ESR (need an odd # of unpaired electrons)**
- **μ Sr**

◆ X-ray and Neutron Methods

- **X-ray absorption fine structure (EXAFS)**

http://www.lure.u-psud.fr/sections/chimie/xafsmac/cours_hercules.html

- **Pair Distribution Function (PDF) Analysis**

<http://www.pa.msu.edu/cmp/billinge-group/docs/home/overview.htm>