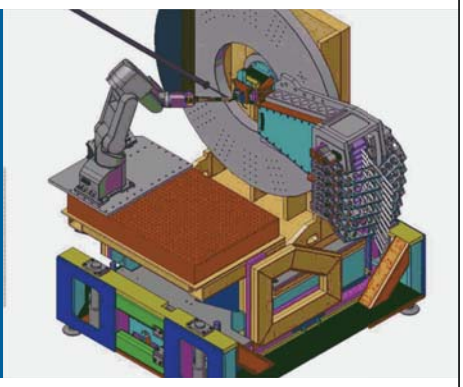
INTRODUCTION TO POWDER DIFFRACTION INSTRUMENTATION



BRIAN TOBY
Senior Scientist

OUTLINE

- Powder diffraction basics: why it's harder
- Laboratory instrumentation
- Differences between X-ray & neutron diffraction
- CW and TOF neutron diffraction
- Synchrotron x-ray diffraction
  - APS instrumentation
- How to get neutron/synchrotron time

SINGLE CRYSTAL DIFFRACTION: THE MOVIE

Video from Diamond synchrotron (U.K.)

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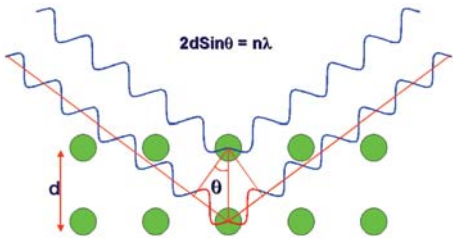
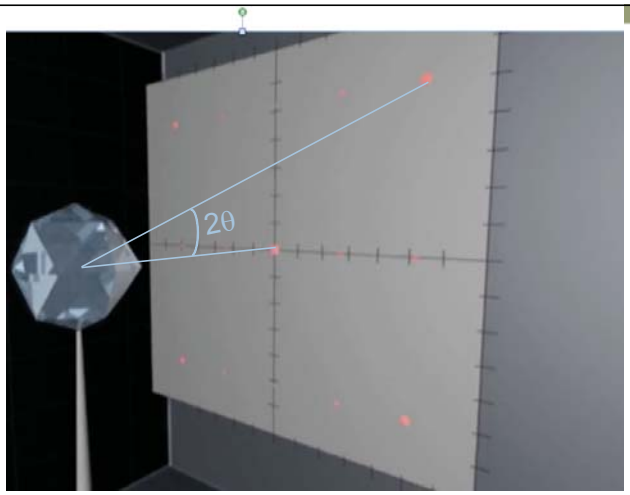
Bragg scattering in single crystals: 1) Reflection positions

Bragg's law:





$\lambda = 2\ d \sin\theta$

Note that d really should be considered a reciprocal space quantity (d = 1/d*), $\underline{\mathbf{d^*}} = h\underline{a^*} + k\underline{b^*} + \ell\underline{c^*}$

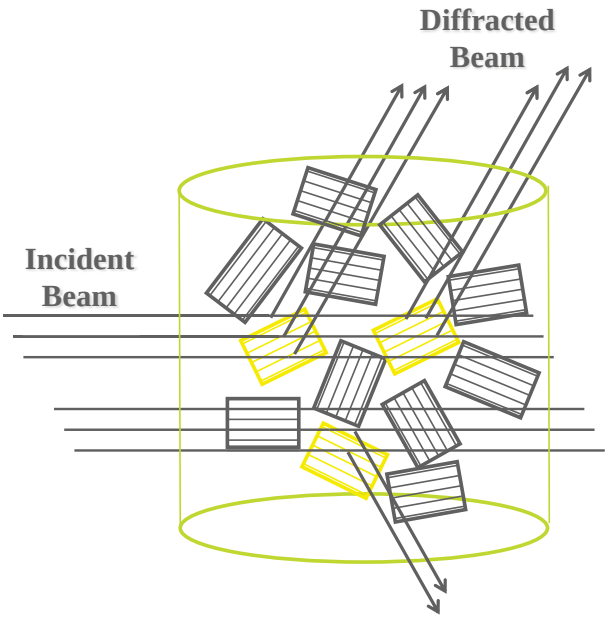
Better (IMHO): $\lambda = 4\ \pi \sin\theta\ /\ Q$

Diffraction from random polycrystalline material

In a sufficiently large, randomly oriented polycrystalline sample (e.g. a powder) contains a very large number of crystallites.

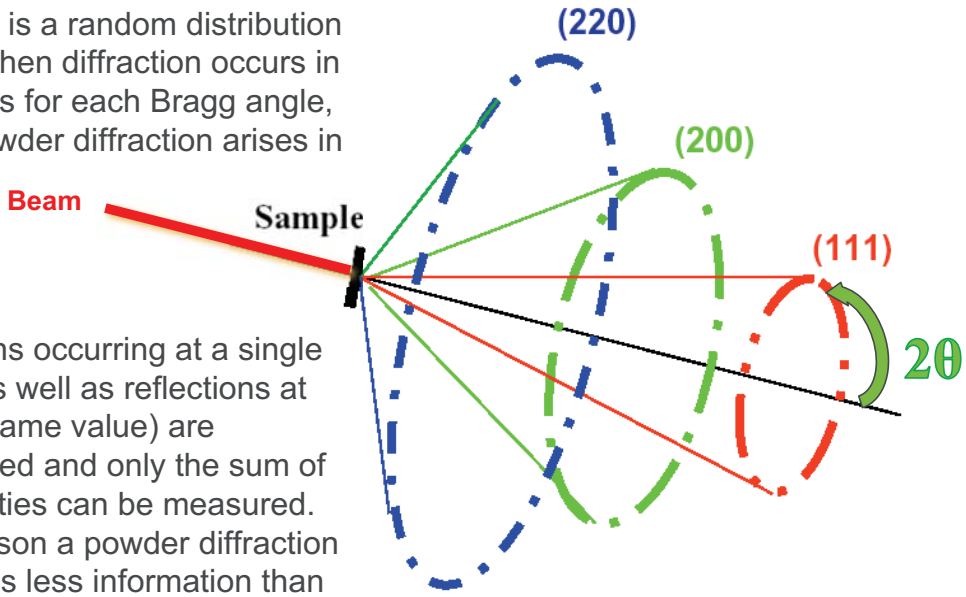
A beam impinging on the sample will find a representative number of crystallites in the right orientation for diffraction

Diffraction occurs only at specific angles, those where Bragg's Law is satisfied.



BRAGG CONES IN POWDER DIFFRACTION

Since there is a random distribution of crystals then diffraction occurs in all directions for each Bragg angle, 2θ, thus powder diffraction arises in cones



All reflections occurring at a single 2θ value (as well as reflections at nearly the same value) are superimposed and only the sum of their intensities can be measured. For this reason a powder diffraction pattern gives less information than a single crystal measurement

SIMPLEST APPROACH TO POWDER DATA COLLECTION: LARGE-AREA 2D DETECTION

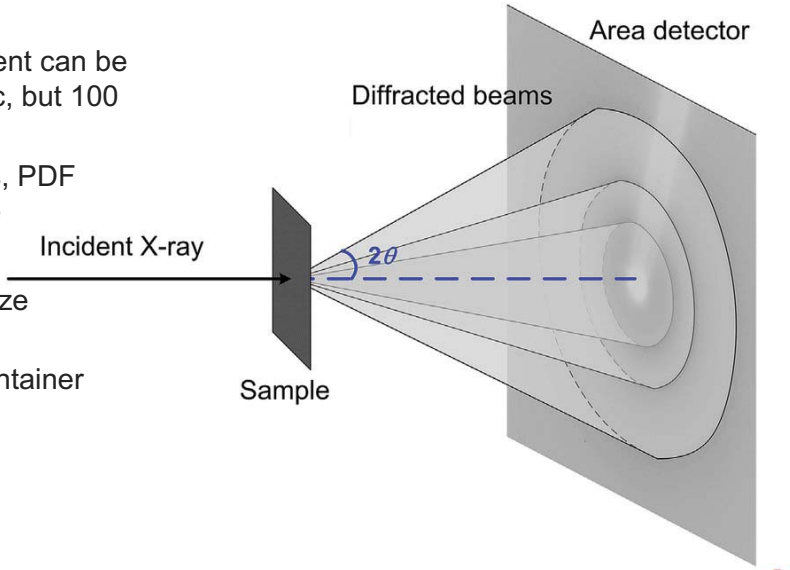
Good:

- Radial integration avoids low-angle asymmetry
- Full pattern measurement can be very fast (typical ~1 sec, but 100 ns possible!)
- With short wavelengths, PDF data collection possible

Not so good:

- Finite sample & pixel size degrades resolution
- No rejection of air & container scatter or fluorescence

https://www.researchgate.net/publication/325207552
(DOI: 10.1016/j.compscitech.2018.05.028)



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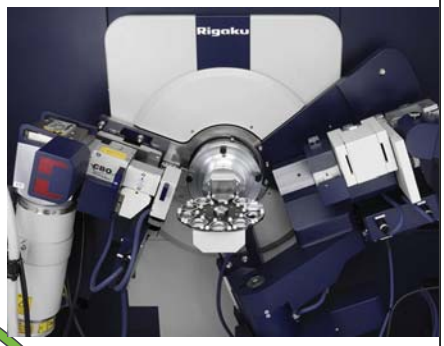
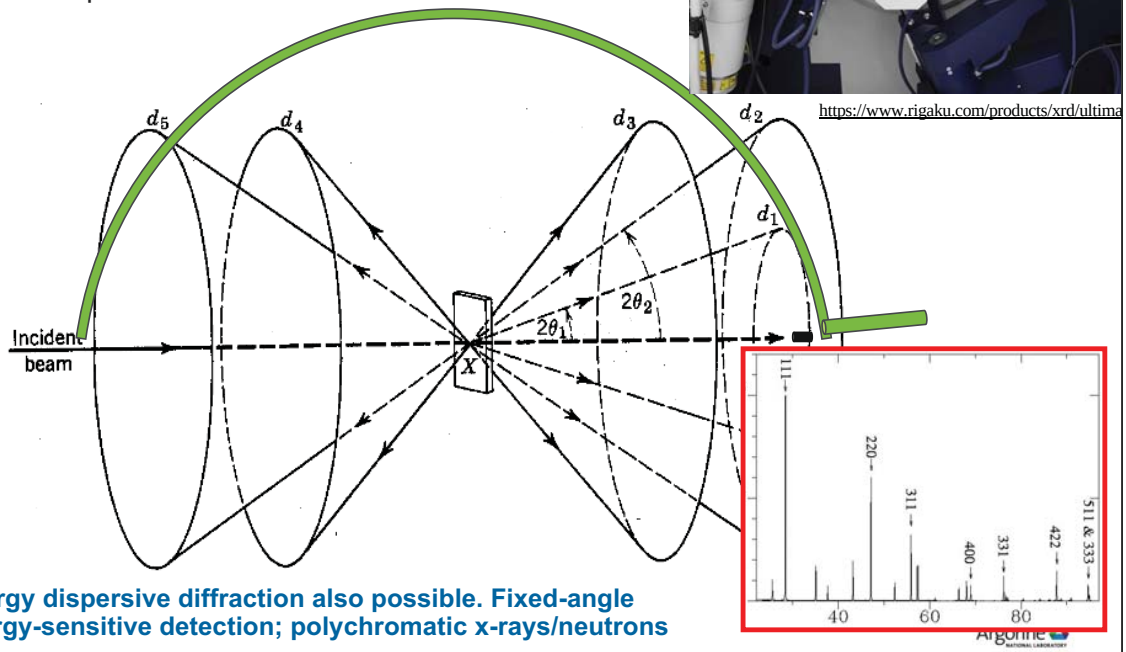
POWDER DIFFRACTION MEASURMENTS

Angular dispersion: a single detector is moved over a range of 2θ angles.

– Sample irradiated with monochromatic radiation



https://www.rigaku.com/products/xrd/ultima



Energy dispersive diffraction also possible. Fixed-angle energy-sensitive detection; polychromatic x-rays/neutrons

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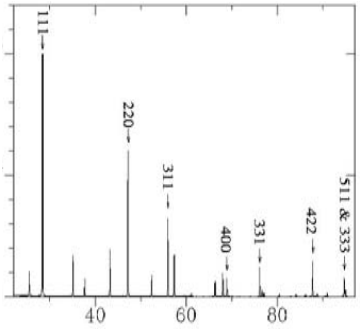
WHY IS POWDER DIFFRACTION HARD?

- In a single-crystal experiment, background is spread out over a sphere, but in powder diffraction the same scattering is concentrated into a single line
  - ➢ powder backgrounds are higher and weak peaks are harder to see



- Powder reflections overlap, sometimes due to lack of resolution, but sometimes because different lattice planes have the same Q values
  - ➢ All that can be measured is the sum of overlapped reflections (phase problem + overlap problem)

Powder diffraction experiments tend to be “information starved”

- It tells us information about our sample, but not always all that we want to know.
- Some determinations (absolute configuration, some magnetic moment directions) not possible from powders

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WHY DO WE DO POWDER DIFFRACTION?

- Learn where the atoms are (when appropriate single crystals are not available)
- Determine the chemical phase(s) in a sample
- Measure lattice constants
- Quantify the components of a mixture
- Learn about physical specimen characteristics such as stress, texture, microstrain or crystallite sizes
- Occupancies of elements amongst crystallographic sites (needs high-Q data, often from neutrons)

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LAB-BASED INSTRUMENTATION

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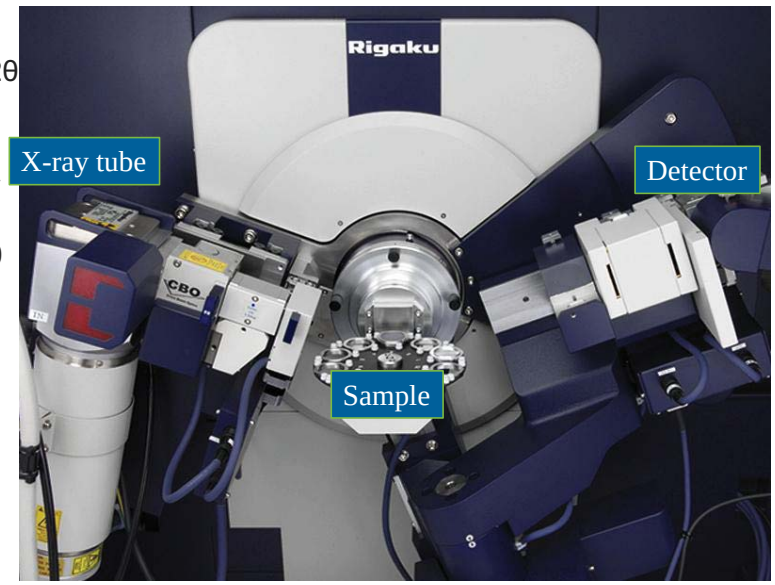
BRAGG-BRENTANO DIFFRACTOMETER

Basic lab diffractometer

- This is a θ-2θ instrument
  - Tube is stationary
  - Stage rotates to θ
  - Detector rotates to 2θ
- Also possible:θ-θ
  - Sample is stationary
  - Tube rotates to θ
  - Detector rotates to θ (*more expensive but keeps sample horizontal)*



https://www.rigaku.com/products/xrd/ultima?index=1

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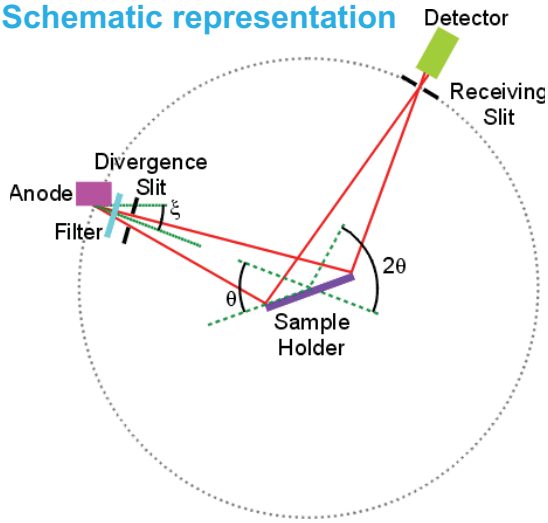
BRAGG-BRENTANO PARAFOCUSING

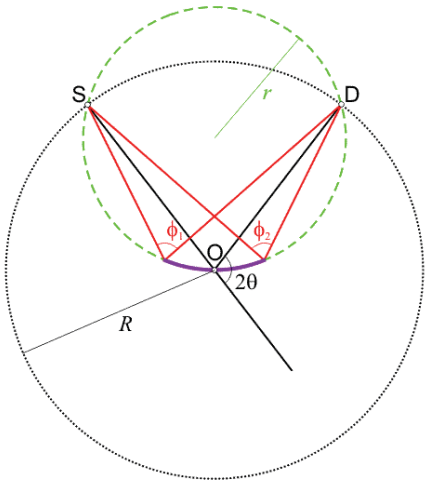
By focusing divergent beam from x-ray tube, parafocusing allows use of more x-rays

Schematic representation



http://pd.chem.ucl.ac.uk/pdnn/inst1/optics1.htm

Focusing concept



http://pd.chem.ucl.ac.uk/pdnn/inst1/focircle.htm

Note that the Source (S) and Detector (D) stay on the black circle (fixed sample to source/detector distance, R) independent of 2θ but the radius of the focusing circle (green) changes with 2θ. For ideal focusing the sample curvature would need to change with 2θ (impossible) or the R must change with 2θ (Seeman-Bohlin geometry)

Images from Jeremy Cockcroft's Advanced Certificate in Powder Diffraction, School of Crystallography, Birkbeck College, University of London

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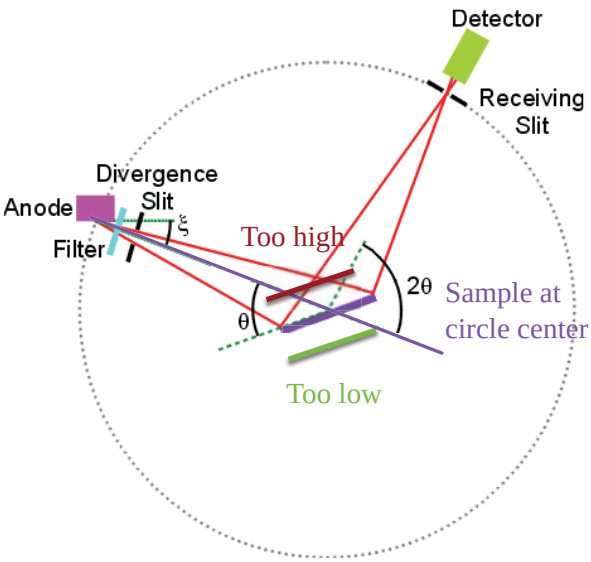
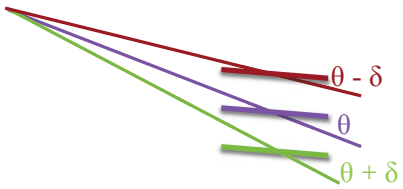
BRAGG-BRENTANO GEOMETRY IS VERY SENSITIVE TO SAMPLE HEIGHT



Based on http://pd.chem.ucl.ac.uk/pdnn/inst1/optics1.htm

If sample is not at exact center of circle, 2θ angles will not be correct



Effective sample position is determined by mounting and penetration of beam

Sample displacement causes largest shifts at low angles

Sample offset as small as ~microns produces significant peak displacement

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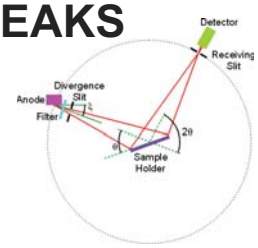
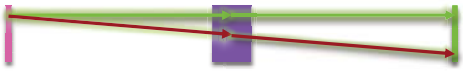
ANGULAR DIVERGENCE BROADENS PEAKS

Typical line-focus tube is 12 mm

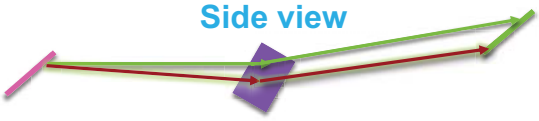


- Uncertainty from where x-ray originates could allow for a range of 2θ angles to be seen (causes peak broadening). Addressed by collimation.

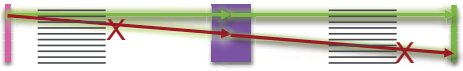
Above



Side view



Soller "slits" limit divergence



https://www.jjxray.dk/p/neutron-soller-collimator/

Soller collimators work like venetian blinds to restrict x-rays to a narrow angular range

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OPTIONAL LAB INSTRUMENT COMPONENTS

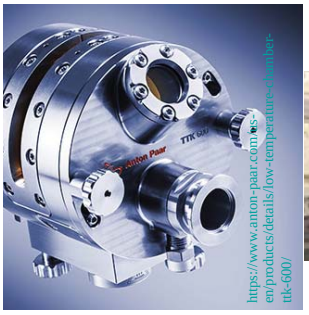
https://www.rigaku.com/products/sources/multimax

Rotating anode source for more flux

http://pd.chem.ucl.ac.uk/pdnn/inst1/optics1.htm

Incident beam monochromator rejects $K\alpha_2$

Mirrors can improve flux



https://www.anton-paar.com/es-en/products/details/low-temperature-chamber-ttk-600/

Sample stages can control temperature, humidity or provide sample changing

https://kemi.uu.se/angstrom/research/inorganic-chemistry/x-ray-laboratory/3-siemens-d5000/

Graphite analyzer (diffracted beam monochromator) rejects fluorescence & Kβ ($K\alpha_2$ remains)

Significant speed-up can be obtained, at the expense of resolution and fluorescence sensitivity, through use of linear (position-sensitive) detectors or an area detector

https://www.d2phaser.com/en/#139-lynxeye

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RECOGNIZING WHEN TO LOOK BEYOND YOUR LAB

Tough problems require the best available data (and sometimes not even that will do)

Reasons to use a synchrotron/neutrons: **resolution, speed, spot size, special environments,** or **wavelength control**

- Synchrotrons and neutrons usually provide data with better resolution, faster, and/or with better sensitivities
- Some problems (**indexing, structure solution, complex structure** fitting) may be tough (sometimes impossible) with lab data
- Measurement under “exotic” conditions (temperature, pressure, chemistry…)
- Site occupancy measurement usually needs neutrons or short-λ x-rays
- “Light atoms” & magnetism require neutrons
- Powder diffraction is an “information starved” technique, better data = more structural information. Some problems need neutrons and x-rays.
- But note:
  - Sample and instrumental broadening convolute (add), if your peaks show significant sample broadening on a lab instrument they will not be sharp with a synchrotron – but still consider an area detector instrument
  - Sometimes 11-BM data are too good
    - Phase purity: ~1% (lab), ~0.5% neutrons ~0.1% (synchrotron)
    - Broad peaks can hide sample issues

Non-commercial access is free, but much use (mail-in excepted) requires travel

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X-RAYS VS NEUTRONS

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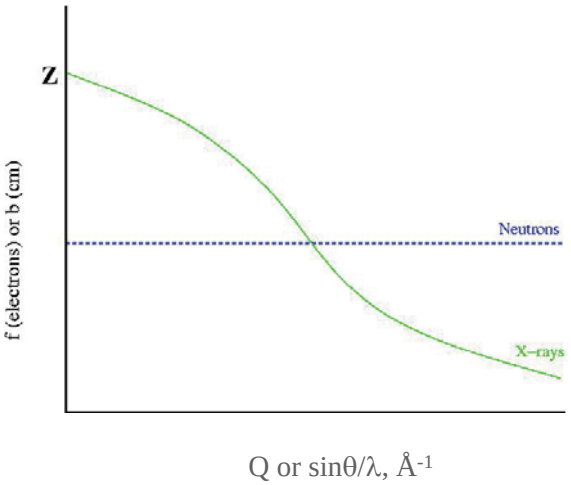
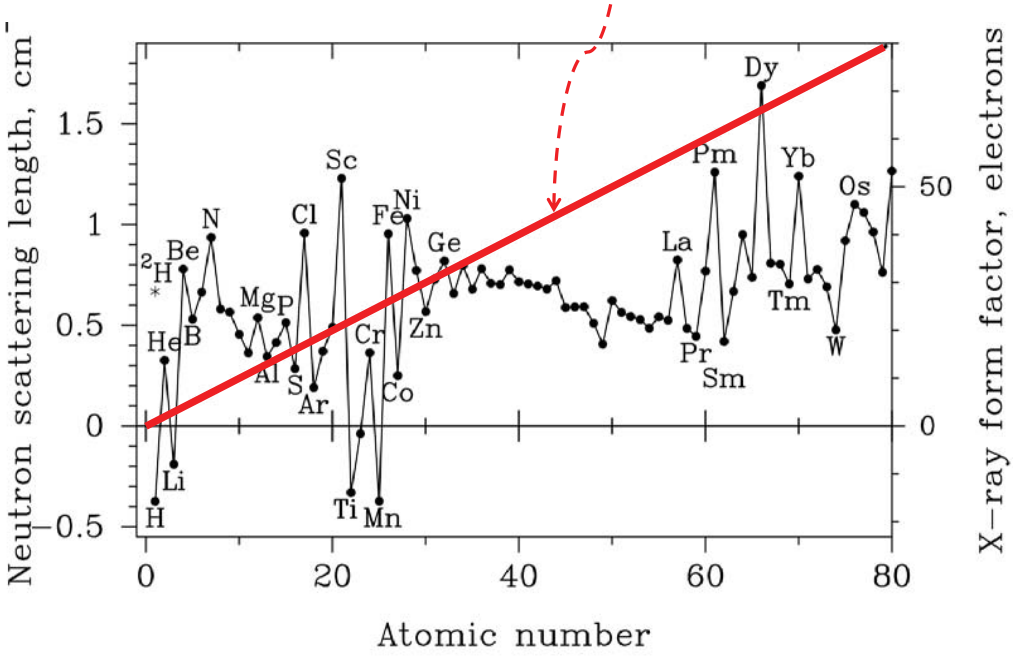
Bragg scattering: Reflection Intensities

Structure factors: $F_{hkl} = n\sum f_i \exp[2\pi i(hx_i + ky_i + \ell z_i)] \exp(-U_i Q^2/2)$

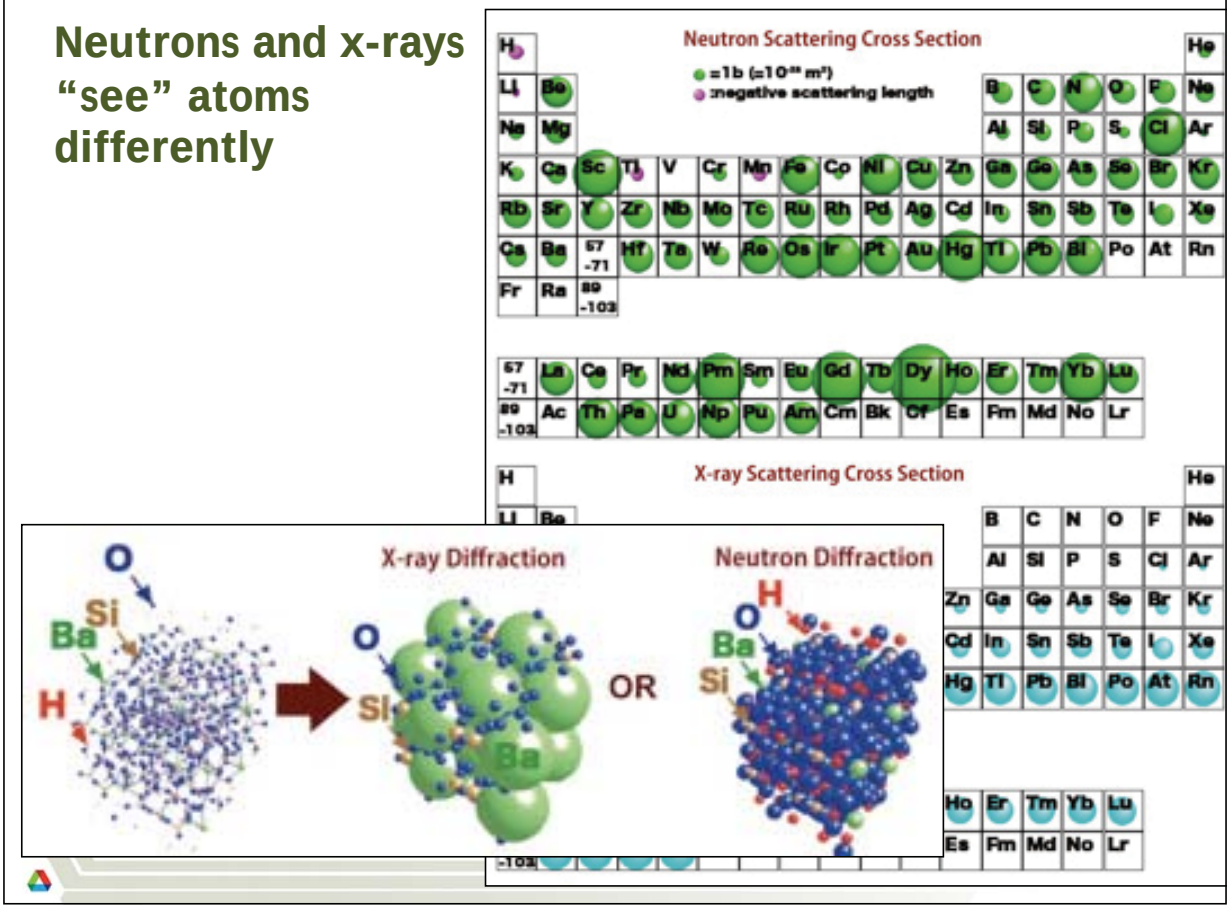
- **X-rays**: The scattering power (form factor, f_i) of an atom depends on the number of electrons in the atom and Q ($Q \propto \sin\theta/\lambda$)
  - X-ray scattering changes near absorption edges
- **Neutrons**: The scattering power (scattering length, b_i) of an atom depends on the isotope and is independent of Q
  - A few isotopes scatter with opposite phase to most, for these we write *b* (f) as negative
  - Some isotopes atoms have neutron resonances (similar to x-rays)
  - Magnetic scattering is from valence electrons; $f_M(Q)$ similar to x-rays, except fall-off is faster



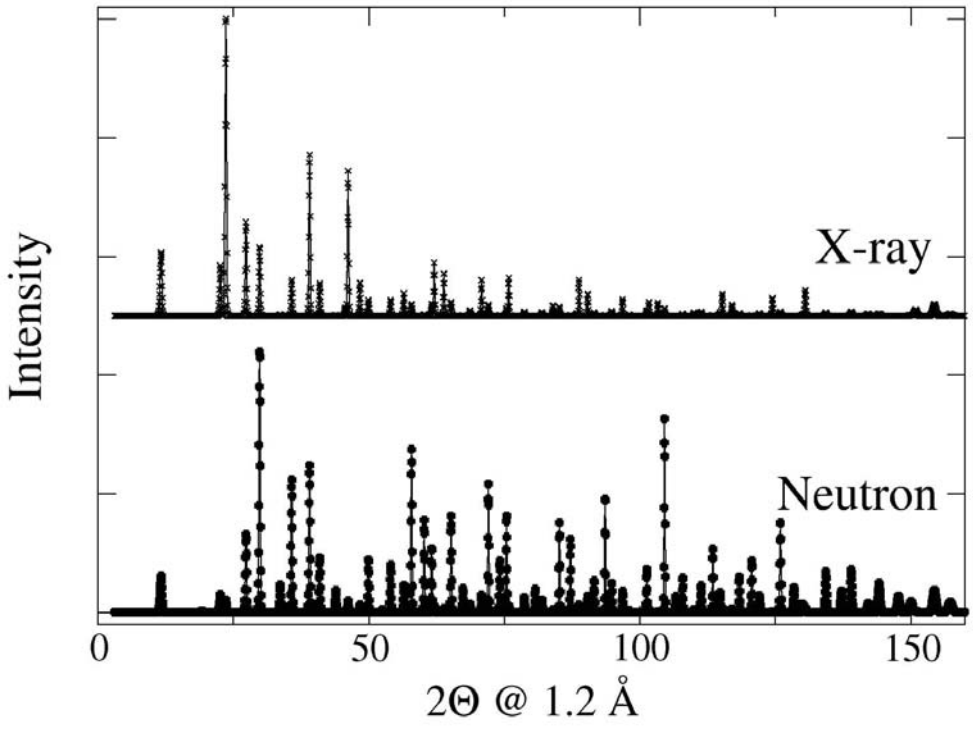
Comparison of Neutron and X-ray Atomic Scattering Powers



Neutrons and x-rays "see" atoms differently



Comparison of Tb_2TiO_7 with x-rays & neutrons

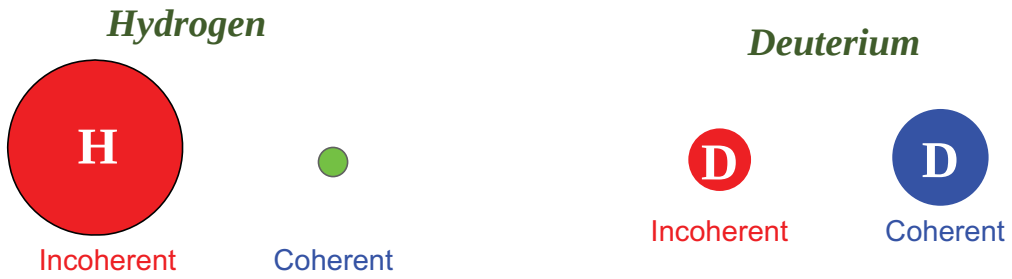


Incoherent and inelastic scattering

Incoherent and inelastic scattering create background. *This is usually significant only with neutrons and most commonly for powder (less so single crystal) diffraction*

With neutrons, some type of atoms have large incoherent cross sections (phase is lost during the scattering).

Hydrogen (not deuterium) is the poster child for this: it has a huge incoherent scattering cross-section (~80 barns) that tends to overpower coherent scattering (typically <1 barns for most atoms). Samples with more than a few atom % (not mass %!) will have a significant background.



Resonant scattering: scattering at a resonance edge causes atoms to "light up"

Experiments are sometimes performed at wavelengths close to absorption edges to enhance the scattering from particular elements

X-rays

The x-ray form factor has in fact three components:

- **f(Q) + f'(λ) + i f"(λ)**
  - f is determined by Q and the number of electrons in an atom and is independent of wavelength
  - f' and f" are small except at wavelengths very close to an atom's absorption edge

At wavelengths close to an edge absorption becomes high; fluorescence occurs above the edge.

Neutrons

Scattering lengths for most atoms are wavelength-independent.

A similar "resonant scattering" type experiment can sometimes be performed comparing samples containing different isotopes ($$ to $$$$$)

A few isotopes (mostly lanthanides and actinides) have adsorption edges at accessible wavelengths.

- This is usually a curse rather than a blessing: it makes TOF neutron scattering had to analyze

NEUTRON POWDER DIFFRACTION

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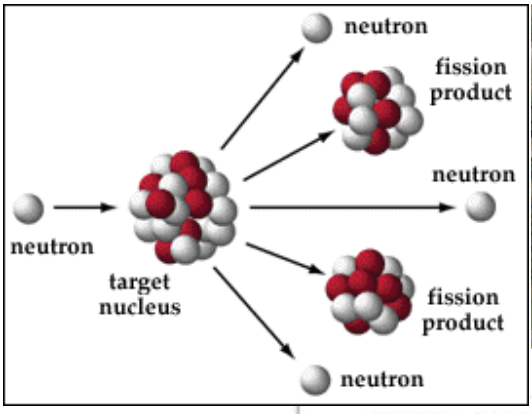
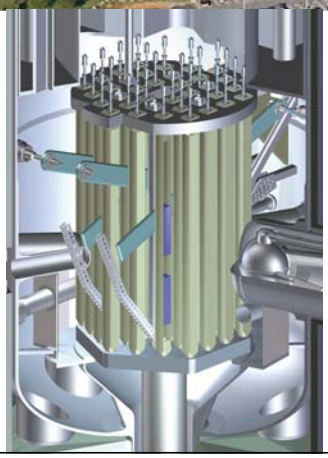
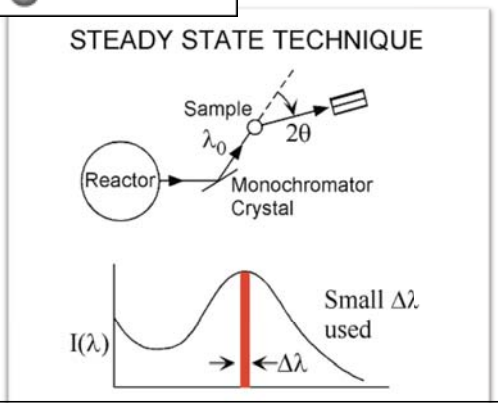
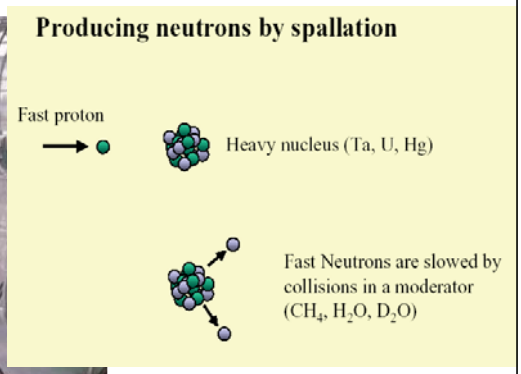
NEUTRONS ARE MADE USING A NUCLEAR REACTOR

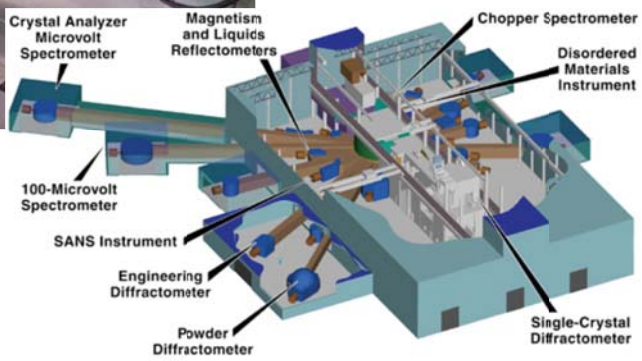




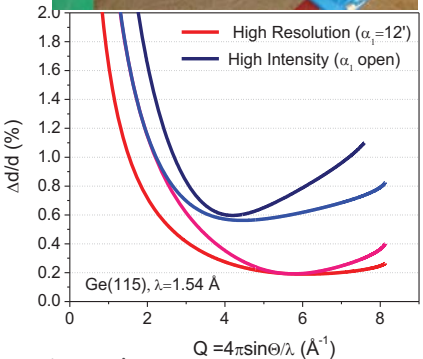


OR BY SPALLATION: A BEAM OF PROTONS IS COLLIDED WITH A METAL TARGET

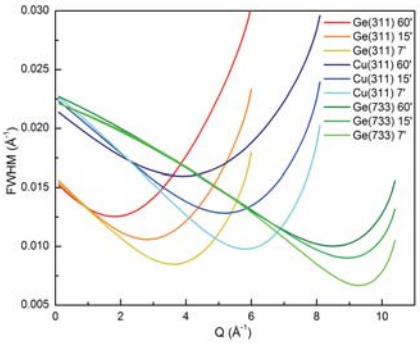




CONSTANT WAVELENGTH (REACTOR) POWDER INSTRUMENTS



beamline HB2a at HFIR



beamline BT1 at NIST (NCNR)

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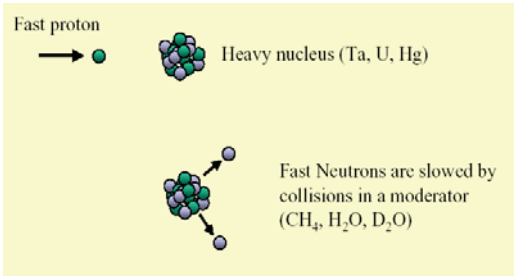
SPALLATION SOURCES MAKE NEUTRON PULSES

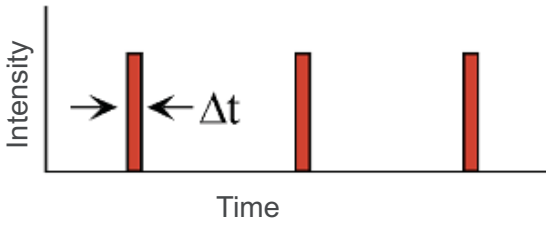
An accelerator makes a pulse of protons ~30 times/sec.

The protons impact the target producing a shower of fast neutrons (short λ)

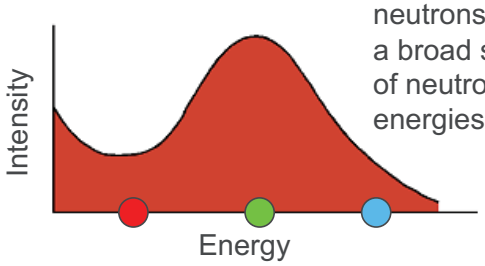
The neutrons are slowed down (longer λ) in a moderator.

Neutrons separate by λ as they travel to the instruments





Each pulse of neutrons contains a broad spectrum of neutron energies



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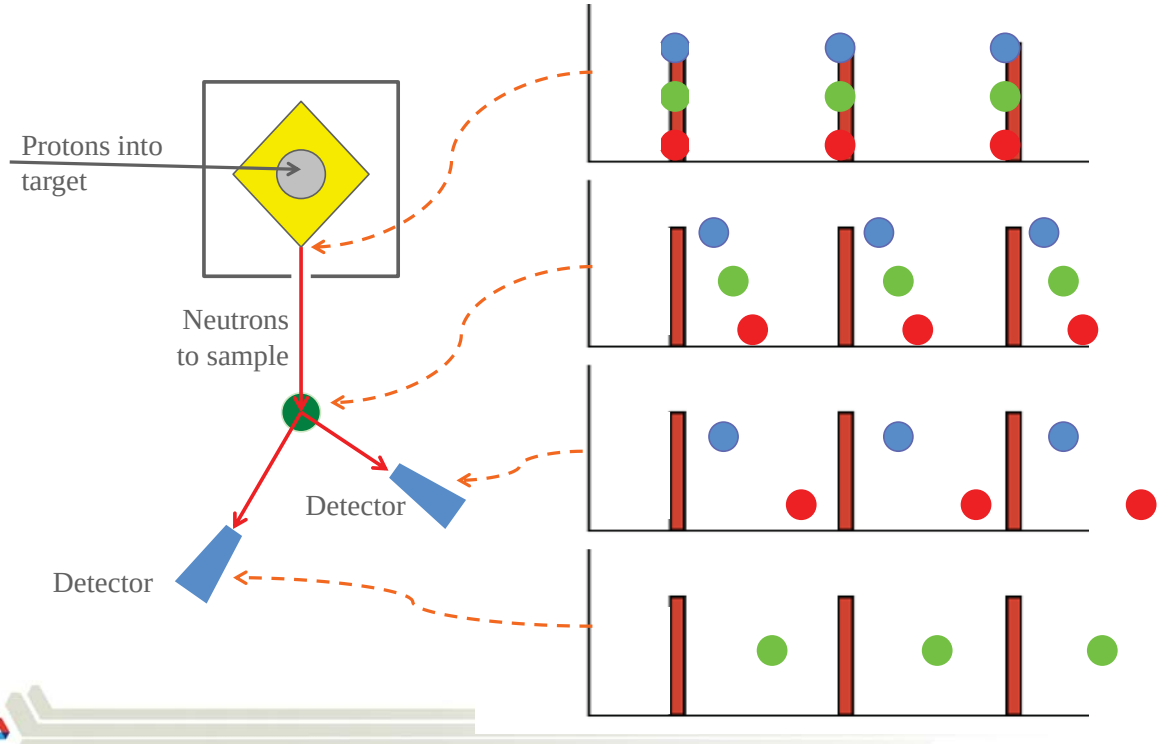
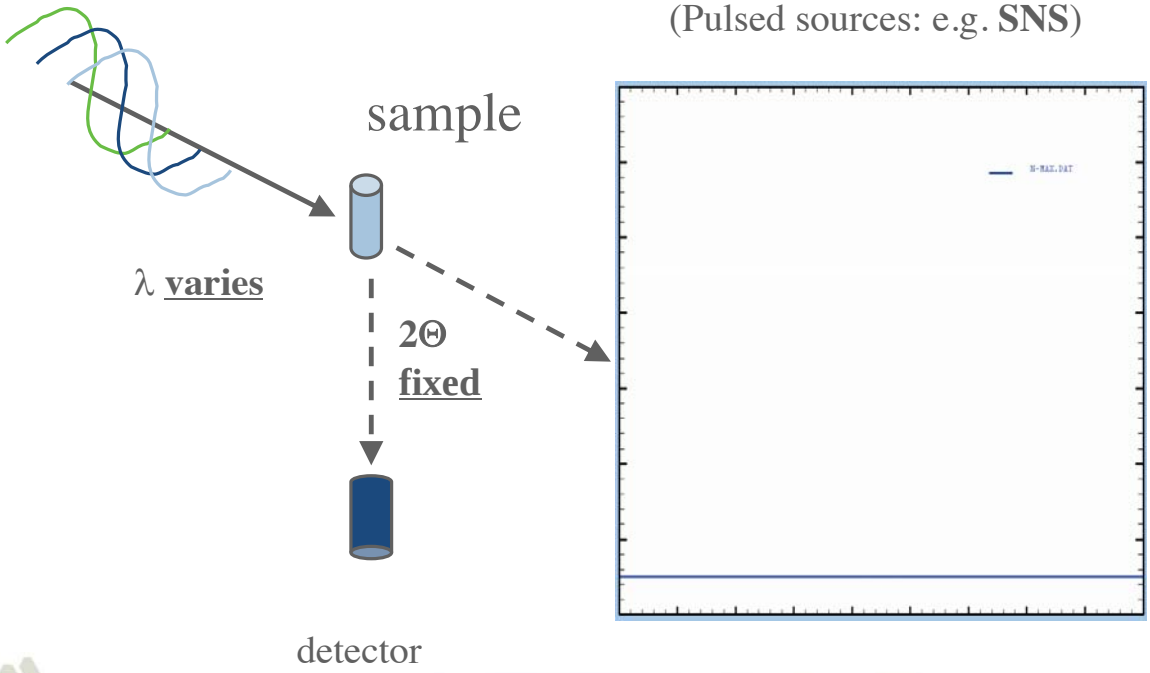
Time of Flight Diffraction

Time of flight diffraction uses the fact that neutrons with different energies (velocities) have different wavelengths, $\lambda=h/mv$ (de Broglies relationship)



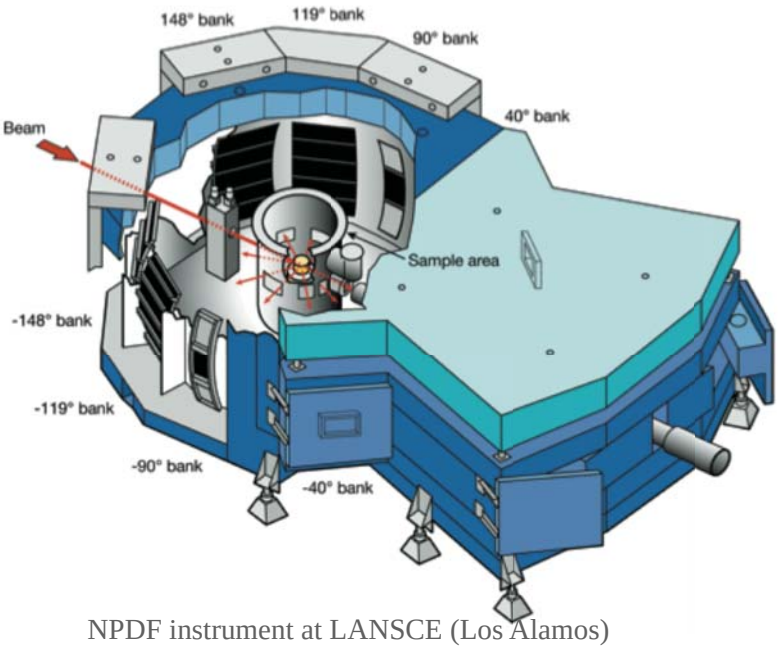
Time-of-flight ($2d\sin\Theta=\lambda$)

(Pulsed sources: e.g. **SNS**)



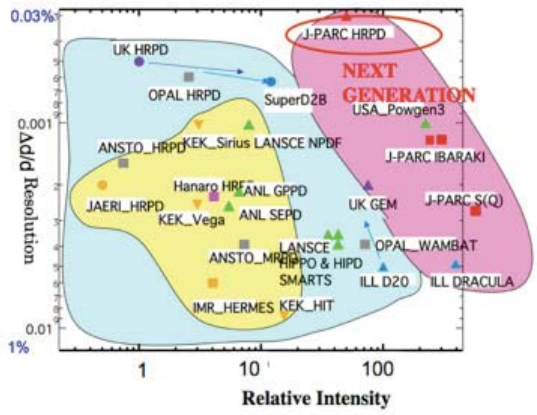
Neutron Powder Diffraction with Spallation Source

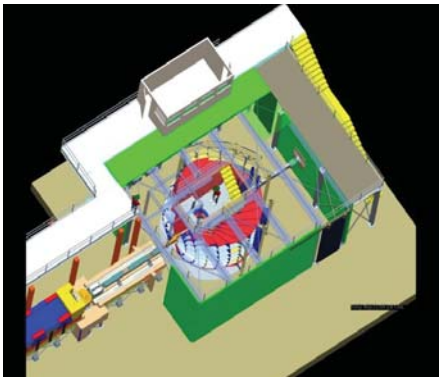
- Spallation source provides a broad band of wavelengths in sharp pulses
  - TOF detection allows measurement of intensity versus wavelength
  - Each detector provides a full diffraction pattern
  - Data collection times:
    - Seconds to hours



NPDF instrument at LANSCE (Los Alamos)

3rd Generation TOF Instruments: High Intensity and High Resolution

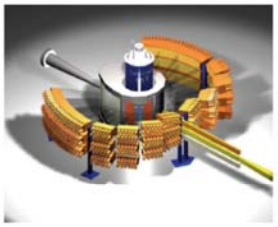




SNS: POWGEN[-3]

GEM (ISIS TS-I)

WISH
A high-resolution magnetic diffractometer for TS-II



Super HRPD (JSNS)

SYNCHROTRON POWDER DIFFRACTION

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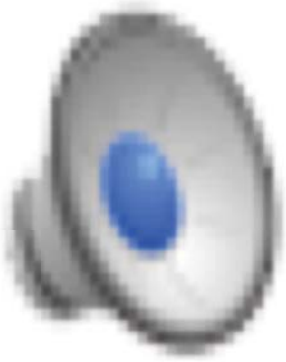
THE DIAMOND (U.K.) SYNCHROTRON



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LIGHT IS MADE AT THE SYNCHROTRON BY DEFLECTING (ACCELERATING) ELECTRONS

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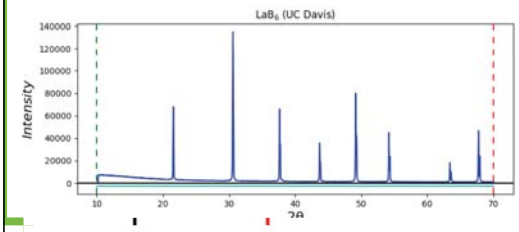
WHY USE A SYNCHROTRON FOR POWDER DIFFRACTION?

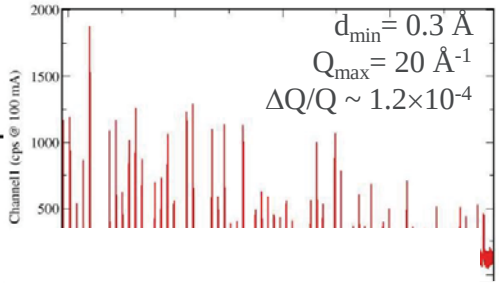
Synchrotrons offer very bright, low divergent x-rays with tuneable wavelengths. This allows x-ray diffraction measurements that can be (but not all at the same time)

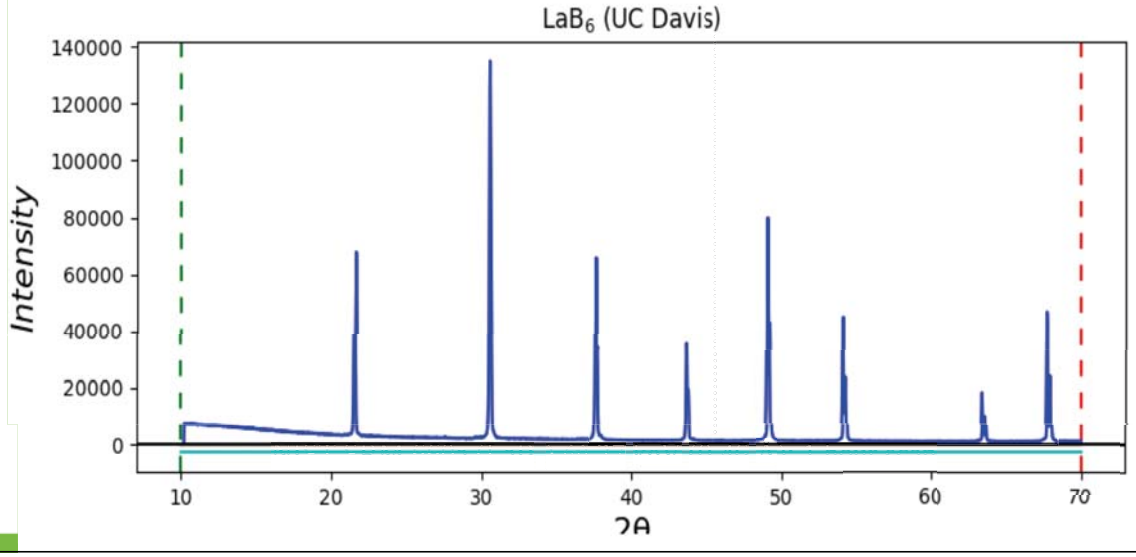
- Very quick (typical 0.1 sec., but with a single x-ray pulse, ~0.1 microsec possible)
- Short λ (high energy):
  - Extreme environments, requiring container penetration
  - Very high Q: needed for PDF
- With perfect-crystal monochromator and analyzers: Very high resolution, complete fluorescence rejection, very low backgrounds
- Resonant scattering (anomalous dispersion): differentiate scattering by element by measuring diffraction just below an element's absorption edge
- Very small spot size: diffraction imaging and high-pressure (diamond anvil) measurements

Argonne NATIONAL LABORATORY

LAB DATA VS. HIGH RESOLUTION SYNCHROTRON DATA







WHY USE THE APS?

- The APS is the country's brightest x-ray source and only one of four high-energy rings in the world.
- The APS has ~30 operating sectors and 68 beamlines that each have a variety of instruments; typically two or more can operate simultaneously.
  - Sectors may be operated by external collaborative access teams (CATs) or by the APS (XSD – X-ray Science Division)
- The APS has instruments that offer virtually all types of x-ray measurements
  - Nearly all instruments are best-in-class or are closely comparable to the best
  - Instruments can be accessed by scientists from across the world on a competitive proposal system
    - Externally reviewed
  - No costs for non-proprietary research
- Other North American synchrotrons: CLS (Saskatoon, Canada), NSLS-II (Long Island, NY), ALS (Berkeley, CA), SSRL & LCLS (Palo Alto, CA), CHESS (Cornell Univ., NY)

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APS MEASUREMENT CAPABILITIES

- X-ray Spectroscopy (DAFS, EXAFS, XPCS, X-ray Raman, XPS, dichroism…)
- Imaging/Microscopy:
  - Microfluorescence, Radiography, Phase Contrast, Tomography, Diffraction, Photoemisson, Ptychography
- Diffraction
  - Small angle (SAXS, GISAX, μSAXS)
  - High pressure diffraction (DA/MA, SX/Powder, Mono/Laue/ED)
  - Surface diffraction (Reflectivity, COBRA, Crystal Truncation Rods, Standing waves,…)
  - Liquids diffraction
  - Single crystal
    - Macromolecular
    - Small cell
  - Fiber diffraction
  - Powder diffraction (high resolution, Pair Distribution Function, *in situ & operando,* protein…)
  - HEDM & Laue grain microscopy
  - Bragg coherent diffraction imaging

- Dynamics
  - X-ray Photon Correlation Spectroscopy (XPCS)
  - Mössbauer Spectroscopy

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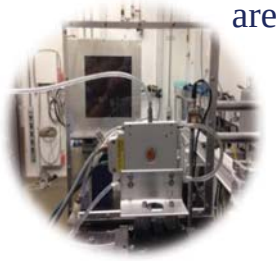
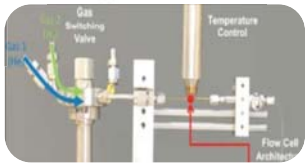
In Situ

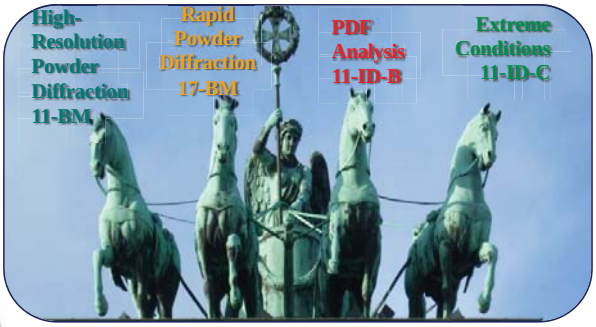


Most APS Powder Diffraction Capabilities are in the **Structural Science (SRS) Group**

Leader: Dr. Uta Ruett uruett@anl.gov

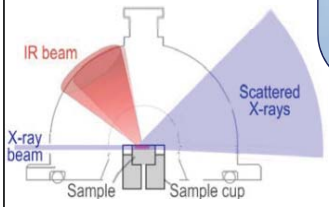
Operando





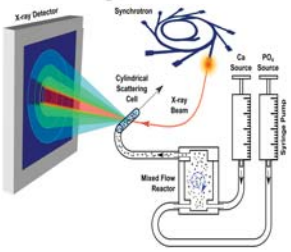
Extreme Conditions

Multimodal

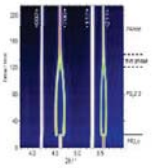


Mail-in

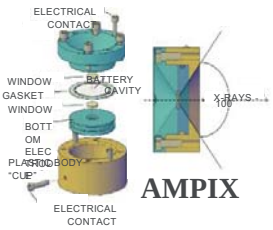
Synthesis



Time Resolved

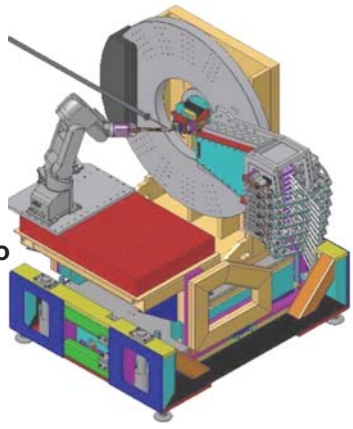


Sample Environments

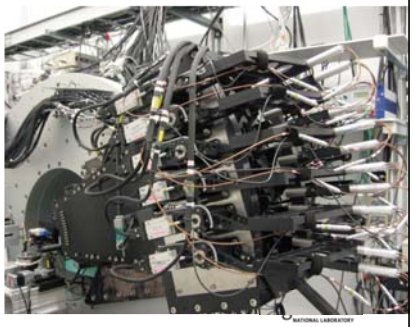


BEAMLINE 11-BM: HIGH RESOLUTION POWDER DIFFRACTION

- **Mail-in access:**
  - **Free for non-proprietary experiments**
  - **Measurements between 90K and 400 C**
  - **Standardized sample holder**
  - **Fast Turn around time: Proposal to Data in 3-6 weeks**
  - **30 KeV (standard) and 27 keV (for Sn containing samples)**
  - **Proposal is good for 2 years and can be utilized in batches**



- **On-Site measurements**
  - **5 K to 1600 C**
  - ***In-situ* and *in-operando conditions***
  - **Large numbers of samples or complex protocols**
  - **Allows for feedback to adjust measurement protocol**



http://11bm.xray.aps.anl.gov

11-BM Robotic Data Collection

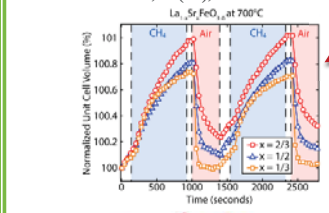
(Matt Suchomel: http://youtu.be/sowojskY7c4 or search APS 11-BM on YouTube)

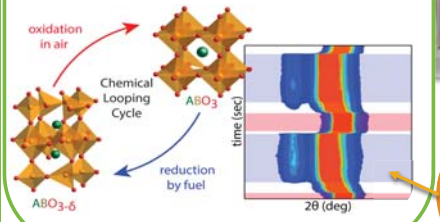
RAPID-ACQUISITION POWDER DIFFRACTION BEAMLINE 17-BM

In situ and operando at 27-51 keV

Example:

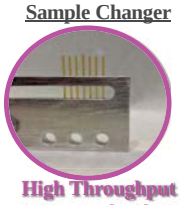
"Oxygen Storage Properties of $La_{1-x}Sr_xFeO_{3-\delta}$ ..."
Chem. Mater. **2016**, *28*(11), 3951.





RGA/Mass Spec

Sample Changer



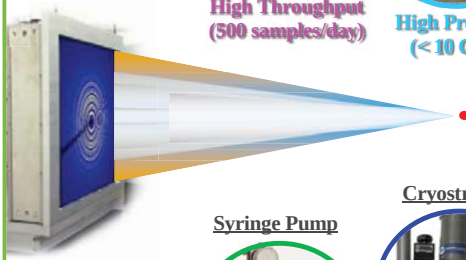
High Throughput (500 samples/day)

DAC

High Pressure (< 10 GPa)

AMPIX Cell

Electrochemistry



Incident X-ray beam

Raman Spectrometer

Cryostream

Temperature: 100 -500K

Syringe Pump

Gas Pressure (< 600bar)

Flow Cell/Furnace

Gas Atmosphere
Temperature: 25 -1000° C

Now with mail-in program

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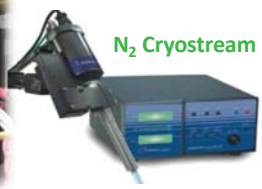
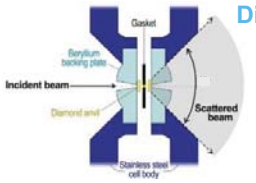
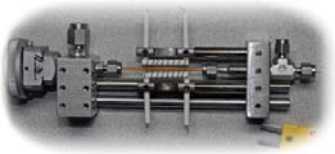
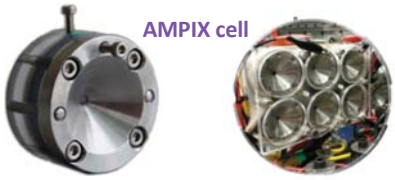
11-ID-B: DEDICATED PDF BEAMLINE

Specializing in *operando* and *in situ* measurements:









- High-throughput ambient measurements:
  - Sample changers with data acquisition automation
- Variable temperature
  - Oxford cryostream 700 plus (80-500 K)
  - Wire-wound furnace (RT-1000 C)
  - Capillary block heater furnaces (RT-800 C)
- Variable pressure
  - Diamond Anvil Cells (0-10 GPa)
  - Large volume, fluid cell (0-0.6 GPa)
- Chemical environments
  - Modular flow-cell/furnace apparatus
  - Inert and hazardous gas handling system
  - Rapid gas switching valves
  - Programmable mass-flow controllers
  - Residual gas analyzer (with advanced notice)
- Specialized environments:
  - Integrated setup for multi-sample electrochemical cell (AMPIX) operations
  - Combined PDF/DRIFT spectroscopy measurements

Now with mail-in program

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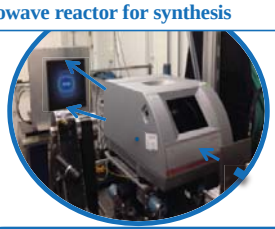
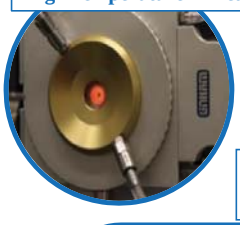
DIFFRACTION AT EXTREME CONDITIONS BEAMLINE 11-ID-C

General diffraction at 106 keV

Microwave reactor for synthesis



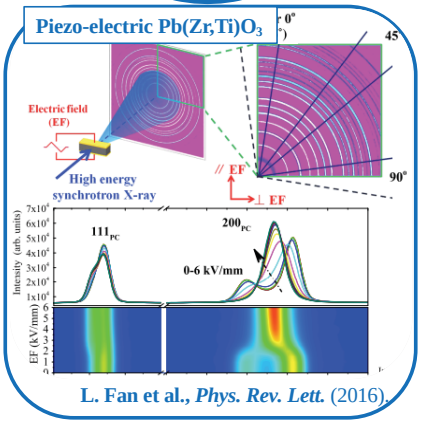
High Temperature Annealing



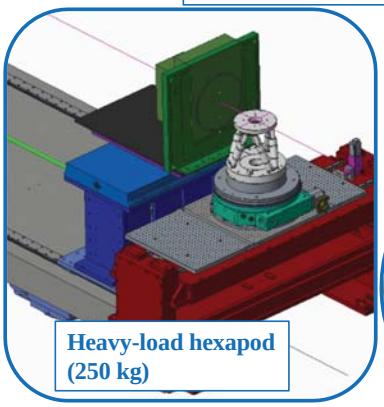
High temperature high pressure with pure H_2 reaction/storage

Superconducting magnet:
T: 2 ~ 325K
H: 0 ~ 7 Tesla

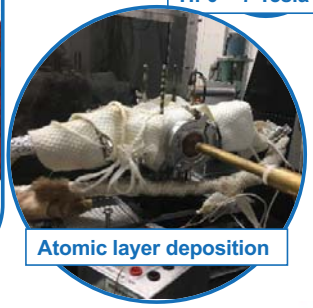
Piezo-electric $Pb(Zr,Ti)O_3$



L. Fan et al., *Phys. Rev. Lett.* (2016).



Heavy-load hexapod (250 kg)



Atomic layer deposition

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WIDE RANGE OF SAMPLE ENVIRONMENTS AVAILABLE AT SRS BEAMLINES

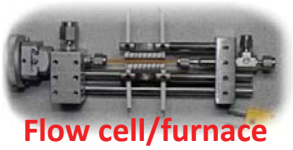
High-throughput
- Magnetic base, robotic arm sample changer
- Multi-sample cassette
- Multi-cassette changer*

Variable temperature
- N_2 Cryostream (80-500 K)
- Wire-wound furnace (≤1000 C)
- Linkam THS1500 (≤1500 C)
- Linkam THS600 (-200 – 600 C)
- He Cryostat (10 K - RT)
- Hot air blower (≤1000 C)
- High-temperature capillary heater

Variable temperature
- Flow-cell/furnace
- Rapid gas switching
- Non-hazardous gases
- Hazardous gases
- Mass flow controllers
- Vapor saturator
- Residual gas analyzer

Pressure
- Diamond anvil cell (DAC)
- Large volume fluid cell
- Syringe pump

Multimodal
- Combined DRIFT/PDF
- In situ Raman spectrometer



Electrochemistry
- AMPIX cell
- RATIX cell*

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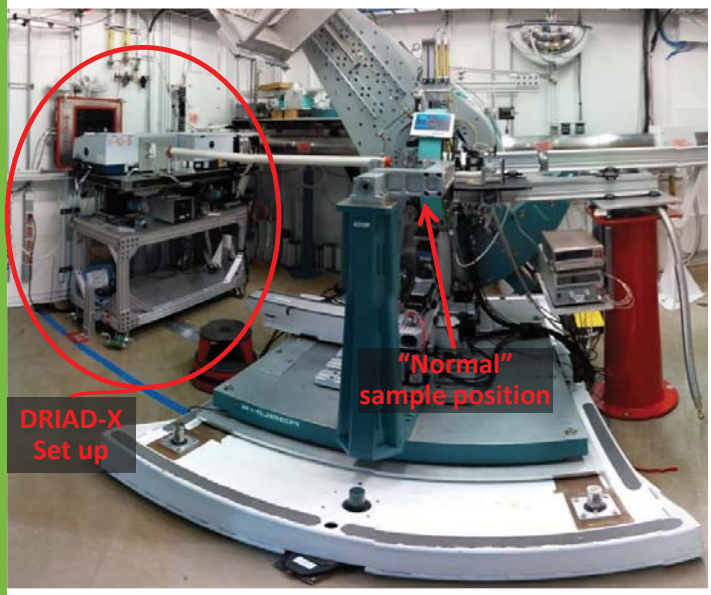
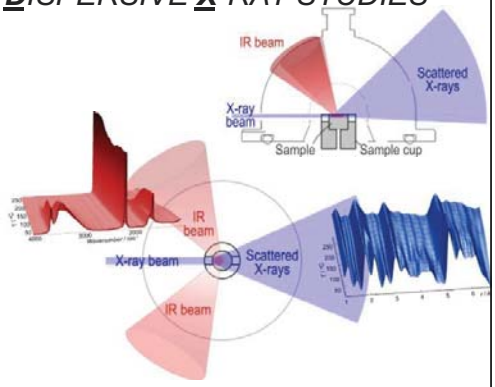
DRIAD-X: COMBINED DRIFTS/PDF

DIFFUSE REFLECTANCE INFRARED ANGULAR DISPERSIVE X-RAY STUDIES





Standard Bruker spectrometer with through hole in the external sample compartment

J. Appl.Cryst., **2014**, 47 (1), 95-101

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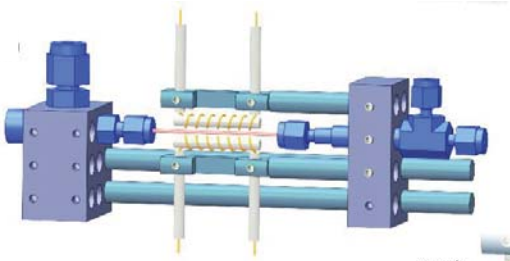
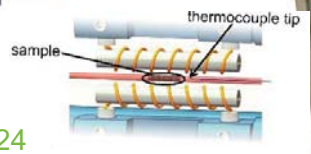
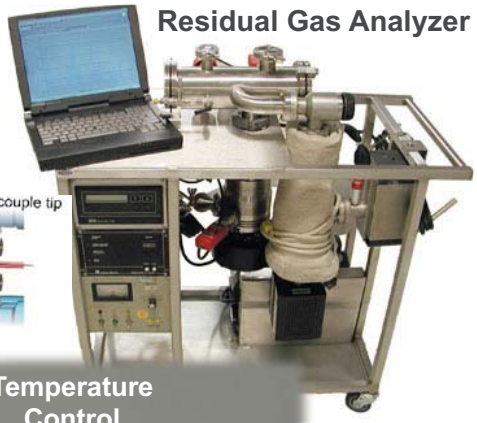
IN-SITU TIME-RESOLVED MEASUREMENTS

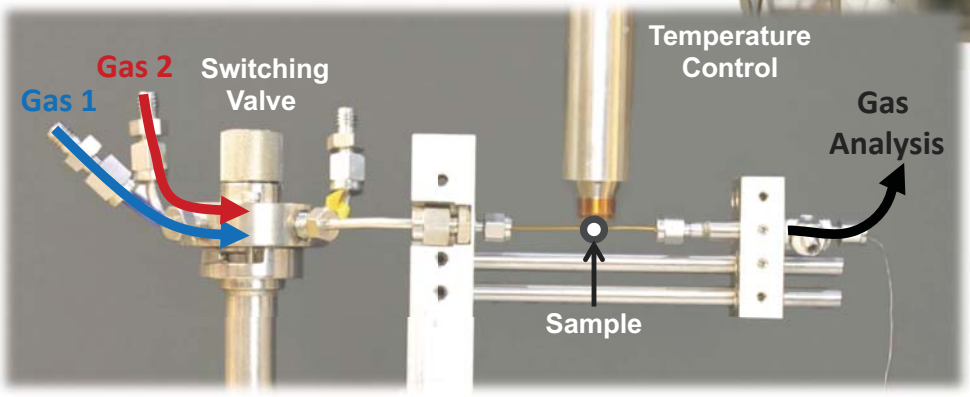




Residual Gas Analyzer



J. Appl.Cryst., **2008**, 41 (4), 822-824



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THE APS HAS A NUMBER OF OTHER DIFFRACTION INSTRUMENTS

- For single crystal, ChemMatCARS (or ALS, Berkeley) for crystals too small for a conventional instrument or for resonant scattering (anomalous dispersion)

Most powder diffraction is done with beamlines run by the SRS Group, but other choices:

- 6-ID-D for very high temperature (1000-2000+ C)
- 1-ID for high energy diffraction energy
- 1-ID & 11-ID-C for applied stress

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GETTING BEAMTIME TIME

- Usually beamtime access requires a proposal due with a specific deadline (APS & NSLS-II, 3x/year; SNS, HIFR & NIST 2x/year).
  - Plan ahead: ~6 months from proposal to beamtime
  - 1st time users: ask for some help from beamline staff/user office (professors…)
- Mail-in: proposals may be submitted at any time (3-6 week turnaround, if you avoid end of cycle)
- Rapid-access: proposals may be submitted at any time, but not all beamlines will put time aside
  - Needs a justification for why a proposal could not be planned and why it will not wait

Sometimes beamline scientists will "sneak in" a short measurement as a favor or for a "proof of concept" (treat such data as a collaboration, include them as co-authors on pubs)

Coauthorships for beamline staff: consider their input and involvement, but "European model" (beamtime=collaboration) is not followed. If in doubt, ask group leader

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BASICS OF PROPOSAL WRITING

- Briefly explain why you are doing the science (relates to energy storage, catalysis, materials discovery, targeted curiosity…)
- What materials you want to study and what you want to learn
- Why does the work need a synchrotron (or neutrons)
  - Resolution or sensitivity (for 11-BM)
  - Speed, *in situ*/*operando* for 17-BM, etc.
  - Specific element scattering (neutrons)
  - Expanded Q-range
  - Sample penetration
  - Temperature range/environmental control
- How will the data be used (intended publication, thesis,..)
- How many samples/temperatures; total time needed

These instruments are typically fully or over-subscribed, so you need to make your proposed use appear to be valuable

Contacting a beamline scientist can save you a lot of time or from proposing an impossible measurement (but understand they are <u>way</u> overworked)

Argonne