The use of synchrotron and neutron facilities in modern research

X-ray Crystallography

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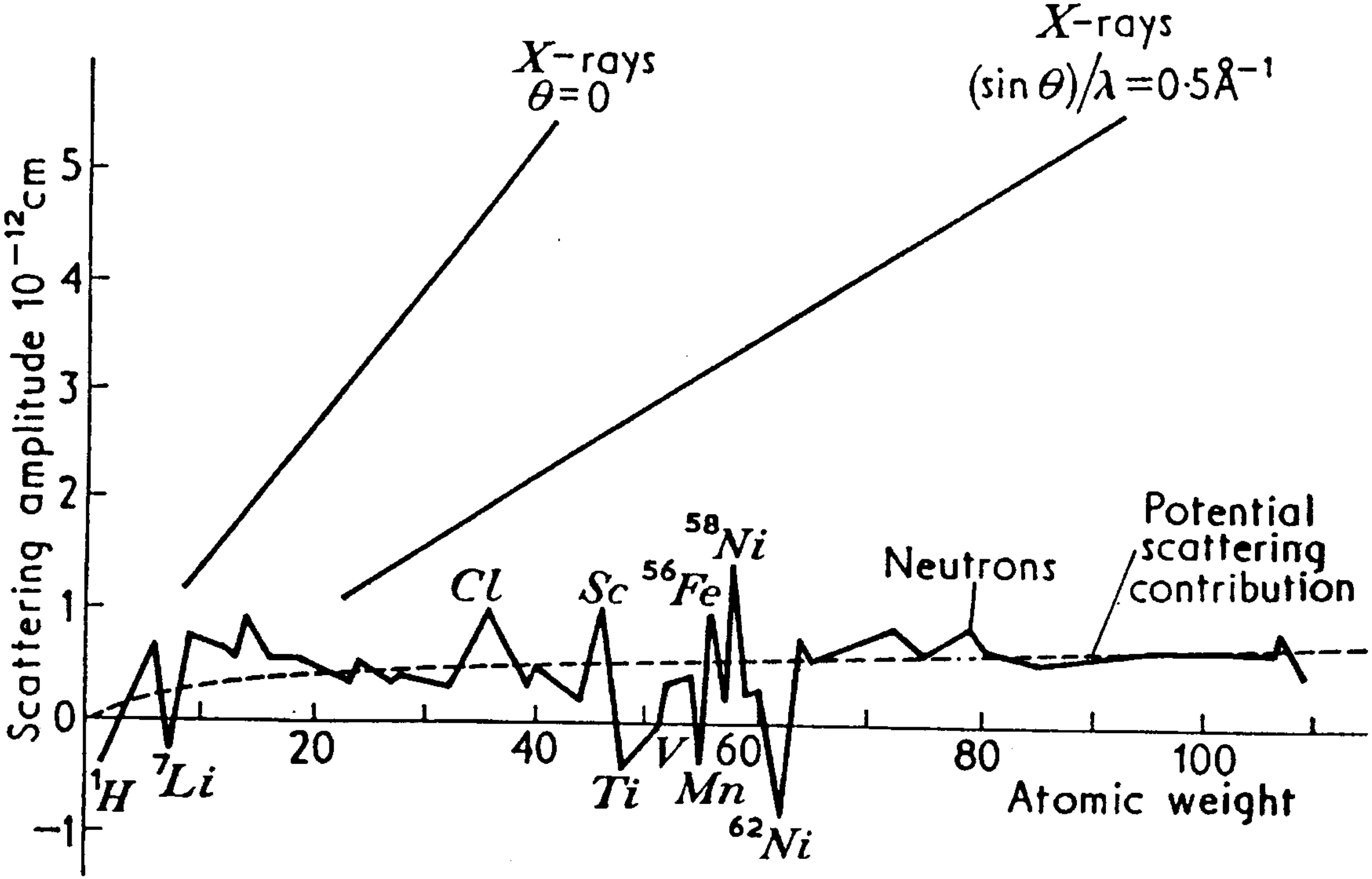
Outline

- Historical development of synchrotrons
- Insertion devices
- Advantages of synchrotron radiation over "traditional sources"
- Possible applications of synchrotron radiation in research
- Neutron sources and experimental setups

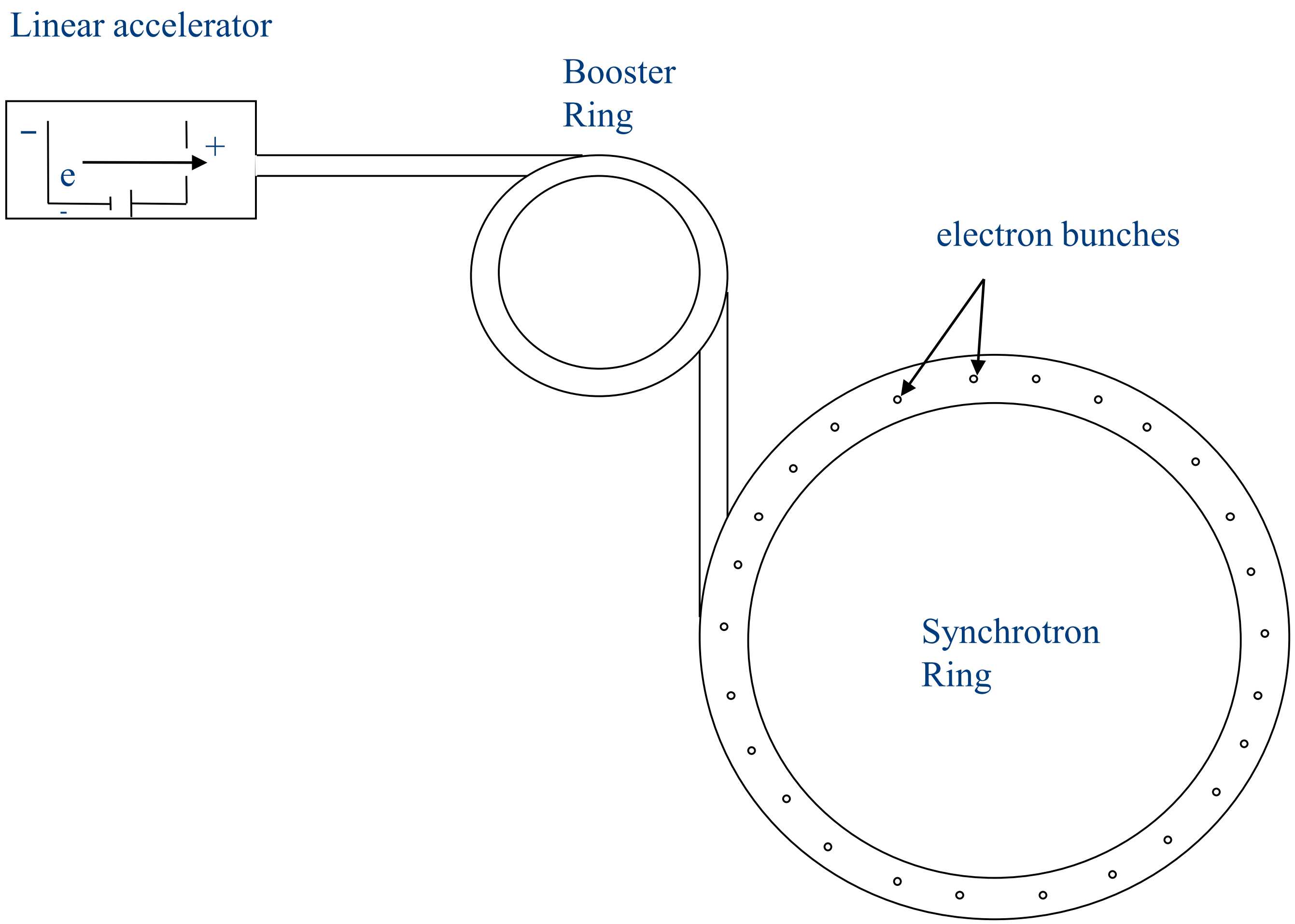
X-rays and neutrons in comparison

X-rays	Neutrons
Atomic scattering power varies smoothly with atomic number	Atomic scattering power varies randomly with atomic number
Atomic scattering power decreases with increasing scattering angle	Atomic scattering power remains approximately constant with angle
Mostly insensitive to magnetic moments	Strong interaction (scattered) with magnetic moments
High intensity beams	Low intensity beams
Strong absorption, especially by heavier elements	Weakly absorbed by most materials

Neutron scattering lengths



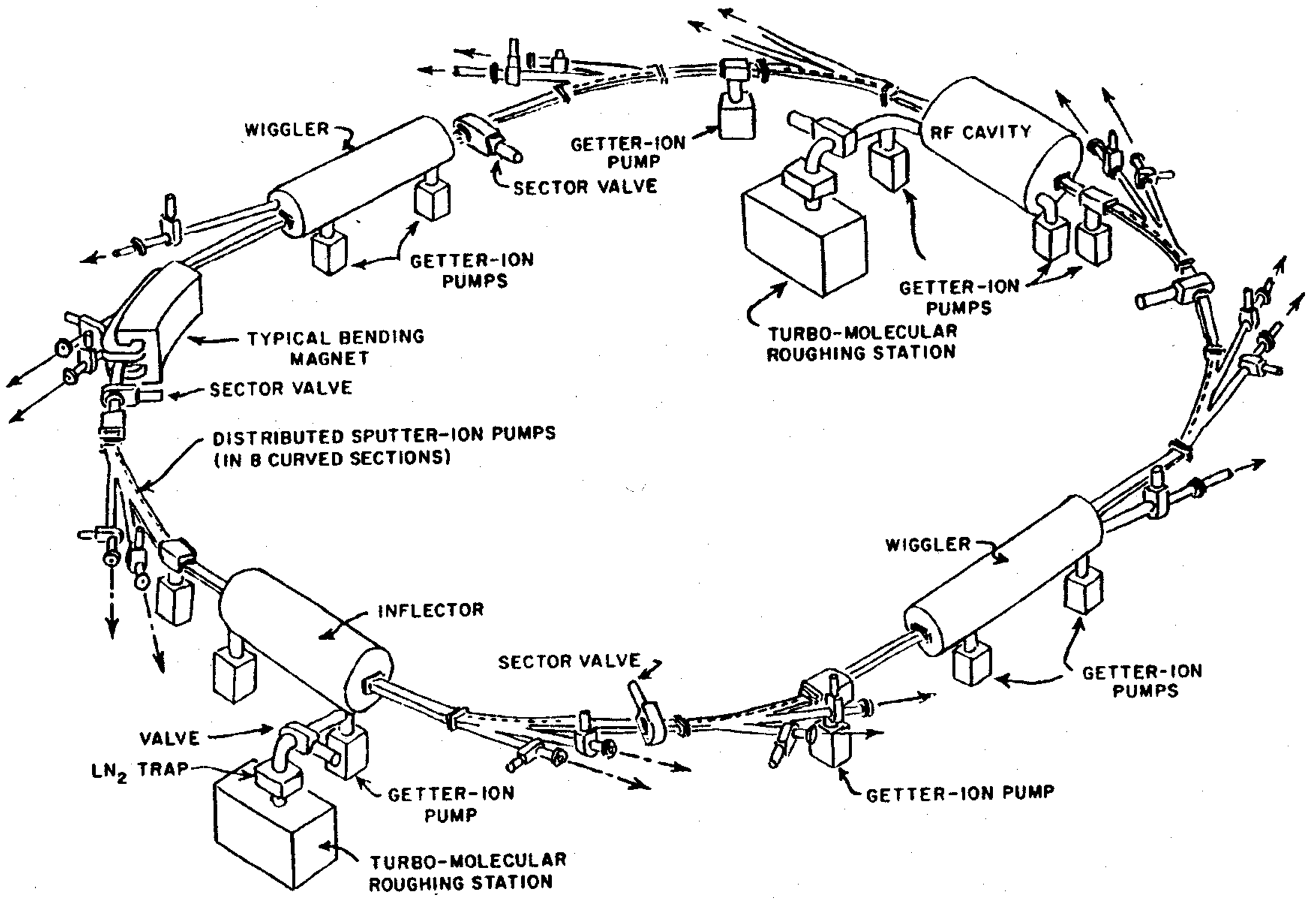
What is a synchrotron?



Synchrotron Radiation

- To keep electrons on a circular path: Constant acceleration necessary (bending magnets)
- Acceleration of particles produces radiation
- Emission of white radiation in X-ray region
- Emission properties can be modified by the use of insertion devices like wigglers and undulators

Producing Synchrotron Radiation



Winick, Doniach; “Synchrotron Radiation Research”

The Advanced Photon Source

http://www.aps.anl.gov/About/APS_Overview/

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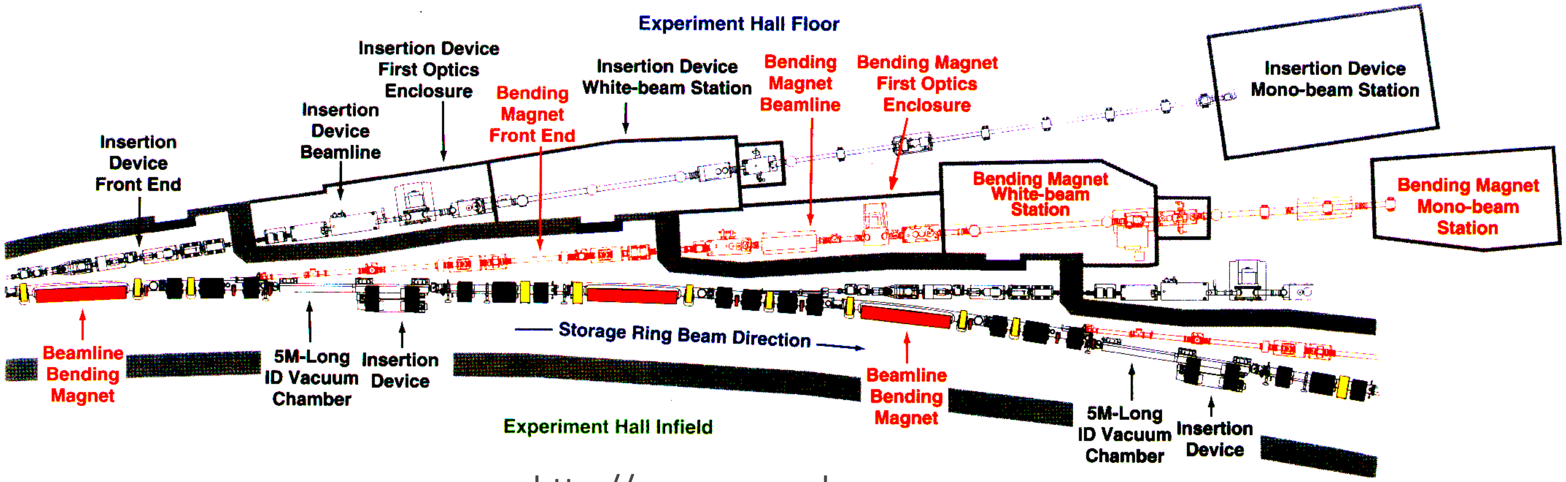
The Advanced Photon Source



http://www.aps.anl.gov

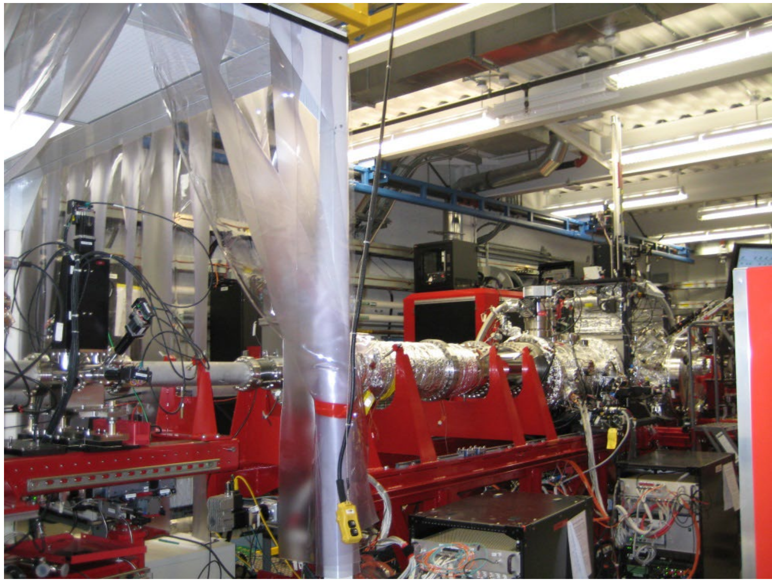
Synchrotrons - historical development

- **First generation:**
    - Used for high energy physics research on elementary particles
    - Radiation was only rarely - “parasitically” - used for spectroscopy or diffraction experiments
    - Investigation of frog muscle contraction (1967) motivated use of synchrotron radiation
    - Unstable/unreliable machines
    - Spectroscopic/diffraction experiments had different operational requirements from high energy physics

Historical development

- **Second generation:**
  - Built during the 1980’s
  - Designed for use of the radiation produced
    - Many beamlines and hutches with different equipment
    - Number of users increased drastically
- **Third generation:**
  - Characterized by high brilliance, mostly achieved with large rings
  - Three largest ring facilities:
    - European Synchrotron Radiation Facility (Grenoble, 1995, 6 GeV)
    - Advanced Photon Source (Argonne, 1996, 7 GeV)
    - Spring-8 (Himeji, 1997, 8 GeV)
  - Also, a number of smaller rings with high brilliance (~20 worldwide)

Recent developments



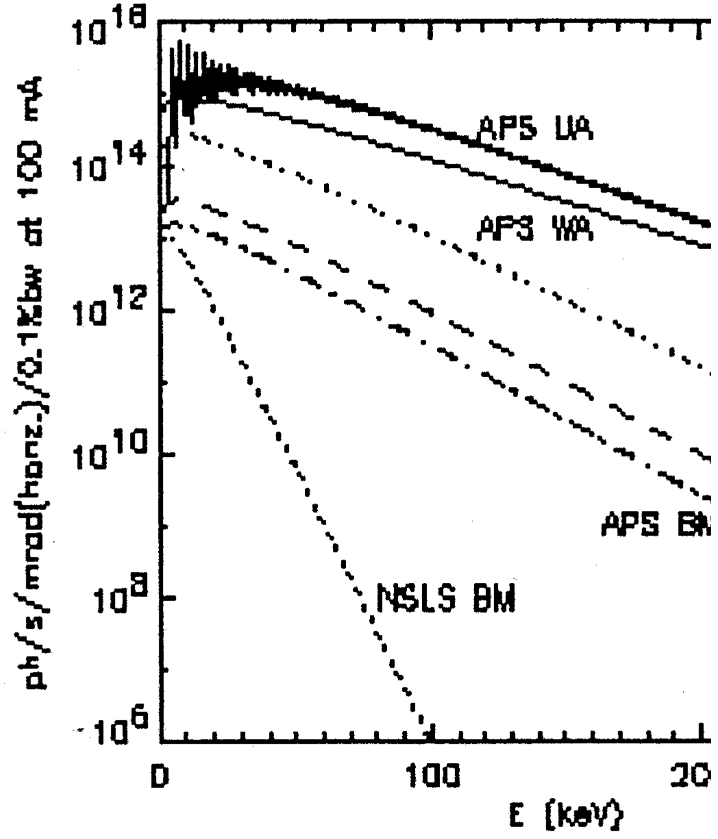
- **X-ray free electron laser (FEL)**
  - Linac Coherent Light Source at SLAC
    - World’s most powerful X-ray laser
    - 2 mile long linear accelerator
    - 100 fs pulses, 8 orders of magnitude brighter than synchrotrons!
    - “Diffract and destroy”
    - First beam in 2009
  - European XFEL at DESY
  - SACLA at Riken Harima Institute
  - …and about a handful more
- **Fourth generation: Characterized by even higher brilliance**
  - Achieved by using multi-bend achromat magnets
  - First facility: MAX IV in Sweden (2015); APS-U upgrade starting soon

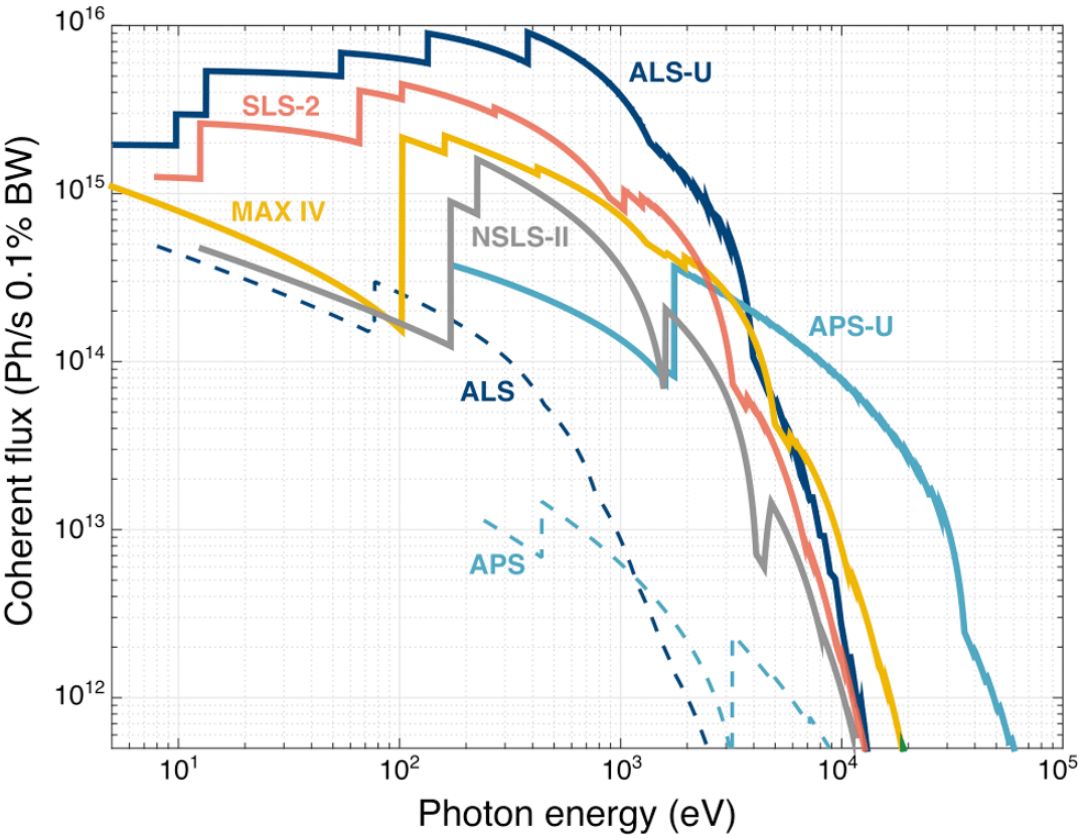
https://www.aps.anl.gov/sites/www.aps.anl.gov/files/APS-Uploads/ASD/2019-03KJKFest/Presentations/Hettel%20%20The%20Evolution%20of%204th%20Generation%20Storage%20Ring%20Light%20Sources.pdf

Synchrotron Radiation Properties

- **Intensity**
  - Number of photons
- **Flux**
  - Number of photons per second (ph/s)
- **Brilliance**
  - Flux per unit area (ph/s/mm^2)
- **Brightness**
  - ph/s/mm^2/mrad^2
    - Takes into account divergence of beam (synchrotrons have low divergence)

Energy spectrum of synchrotron radiation

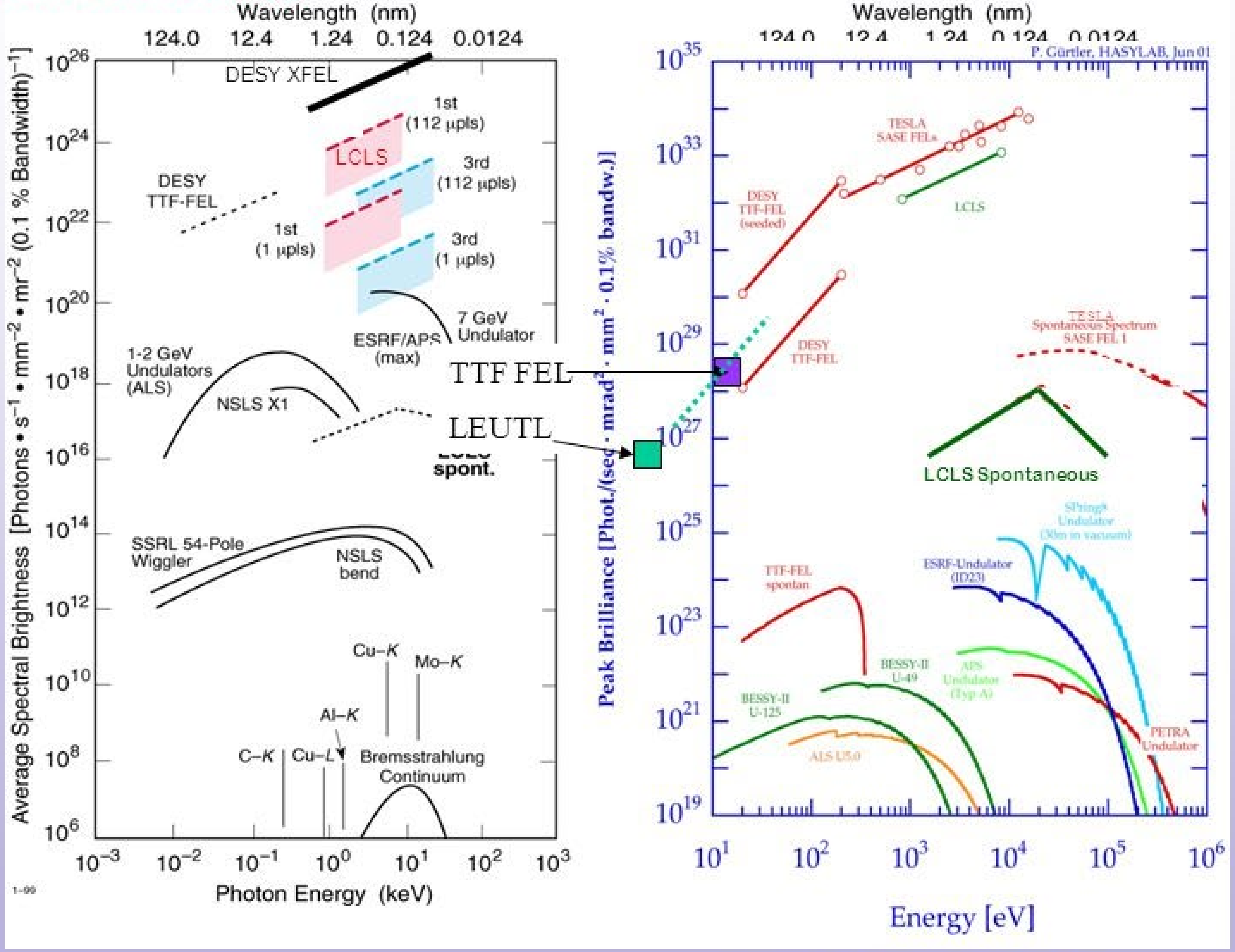




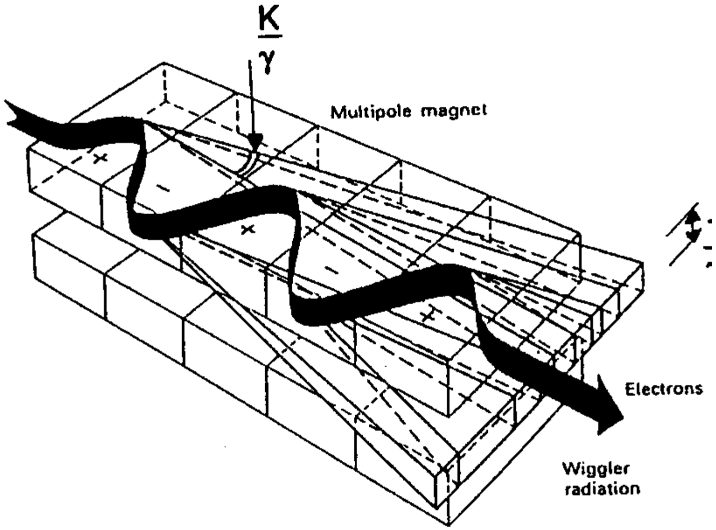
http://atap.lbl.gov/wp-content/uploads/sites/22/2016/10/ALSUcoherentflux1000x779y.png

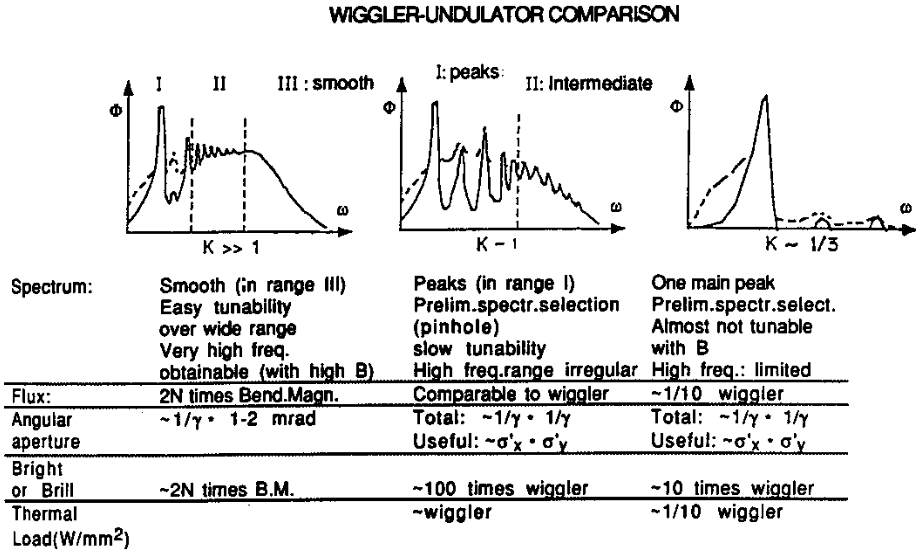
Performance Characteristics

Peak and time averaged brightness of the LCLS and other facilities operating or under construction



Wigglers and Undulators





WIGGLER-UNDULATOR COMPARISON

	$K >> 1$	$K \sim 1$	$K \sim 1/3$
Spectrum:	Smooth (in range III) Easy tunability over wide range Very high freq. obtainable (with high B)	Peaks (in range I) Prelim.spectr.selection (pinhole) slow tunability High freq.range irregular	One main peak Prelim.spectr.select. Almost not tunable with B High freq.: limited
Flux:	2N times Bend.Magn.	Comparable to wiggler	~1/10 wiggler
Angular aperture	$\sim 1/\gamma \cdot$ 1-2 mrad	Total: $\sim 1/\gamma \cdot 1/\gamma$ Useful: $\sim \sigma'_x \cdot \sigma'_y$	Total: $\sim 1/\gamma \cdot 1/\gamma$ Useful: $\sim \sigma'_x \cdot \sigma'_y$
Bright or Brill	~2N times B.M.	~100 times wiggler	~10 times wiggler
Thermal Load(W/mm^2)		~wiggler	~1/10 wiggler

- **Wigglers and undulators “wiggle” the electron path back and forth between multipole magnets**
  - Emission of radiation whenever the direction is changed
  - Wigglers: Large pole spacing, incoherent interference
  - Undulators: Short spacing, coherent interference

What’s special about synchrotron radiation?

- **High photon flux**
- **Plane polarized**
- **Intrinsically collimated beam**
- **White radiation ⇒ energy (wavelength) can be changed**
    - Selection of “suitable” wavelength
    - Multiple experiments at different wavelengths are possible
    - White radiation experiments
    - Spectroscopy (changing the wavelength continuously)
- **Well defined time structure**

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Beam collimation

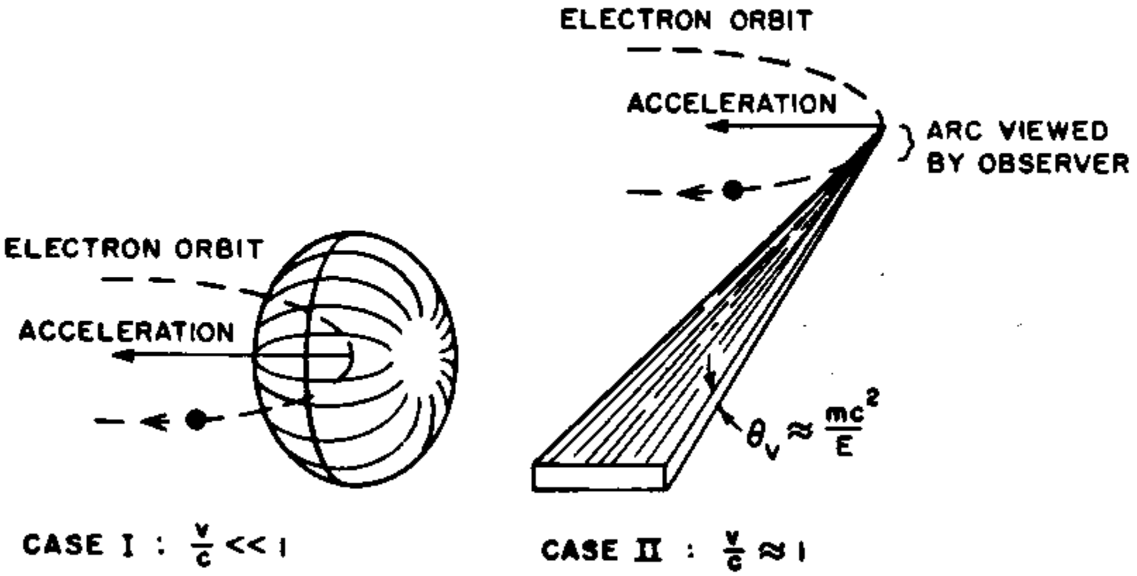


Figure 1. Radiation emission pattern of electrons in circular motion: Case I, nonrelativistic electrons. Case II, relativistic electrons.

Winick, Doniach; "Synchrotron Radiation Research"

Possible experiments

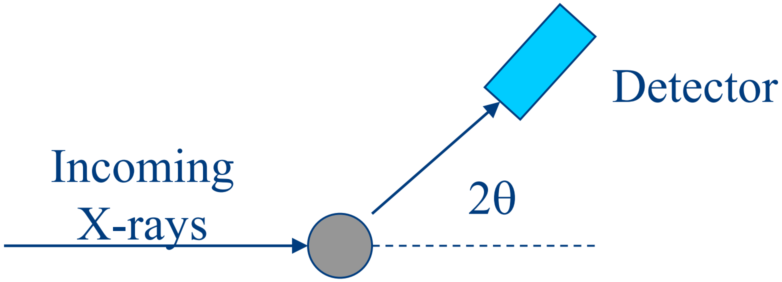
- **Crystallography**
  - powder
  - single crystal: down to 1 m possible in some cases
  - macromolecules
  - MAD - recovery of phase information
- **Spectroscopy**
  - absorption
  - x-ray emission
  - EXAFS
  - XANES

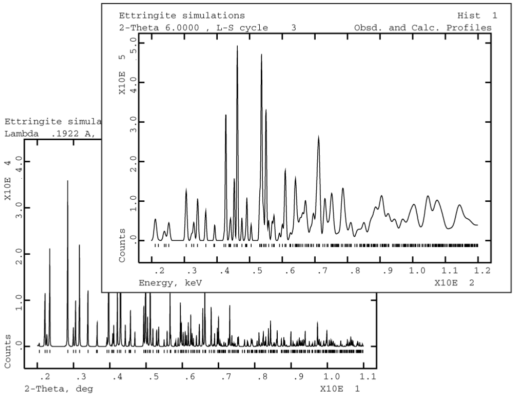
Possible experiments - cont’d

- **High pressure experiments**
  - in situ observation by diffraction
- **Imaging**
- **X-ray reflectivity**
- **Scattering**
  - small angle
  - inelastic
  - magnetic
  - surface
- **Time resolved x-ray studies**

Energy and angle dispersive diffraction

- **An X-ray diffraction pattern is a measurement of X-ray intensity versus d-spacing**
  - d-spacing, scattering angle and l are related by Bragg’s law
    - $2d \sin\theta = \lambda$





Energy dispersive diffraction
Fix 2q and vary l
Quick experiment with fixed sampling volume, but low resolution

Angle dispersive diffraction
Fix l and vary 2q
High resolution but slow and sampling volume varies

Powder diffraction with high energy X-rays

- **Can use complex sample environment due to penetrating nature of X-rays**
- **Can map out phase and stress distributions inside parts due to penetrating power**
- **Systematic errors due to absorption and extinction are eliminated**
- **Can work at high energy absorption edges in resonant scattering experiments**
- **Can make measurements to very high Q**
  - provides a lot of structural detail

Anomalous diffraction: The X-ray scattering factor

- **The elastic scattering is given by,**

$$f(E,Q) = f_o(Q) + f_o'(E,Q) + i f_o''(E,Q)$$

- **For a spherical atom,**

$$f_o(Q) = 4\pi \int_0^{\infty} \frac{r^2 \rho(r) \sin Qr}{Qr} dr$$

- **f ′ and f ″ undergo drastic changes close to the absorption edges**

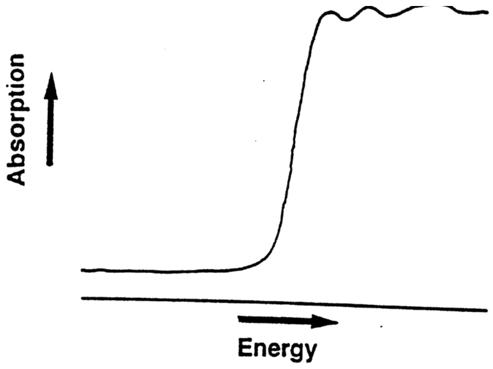
Absorption and anomalous scattering

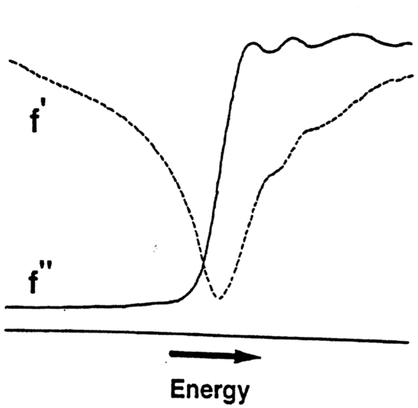
- **f ″ “mirrors” the absorption coefficient**

$$f''(E) = \left(\frac{2\pi m c \varepsilon_0}{e^2 h}\right) E \mu_a$$

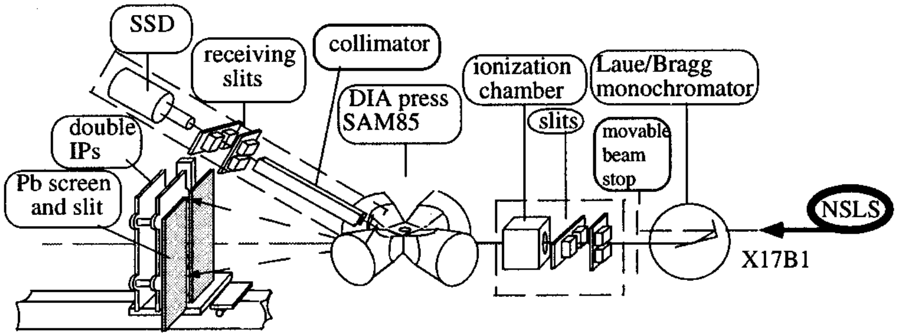
- **f ′ is intimately related to the absorption coefficient**

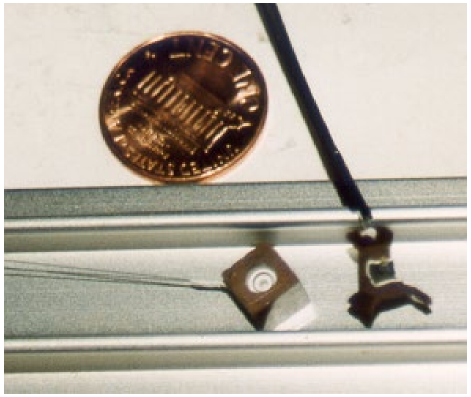
$$f'(E) = \left(\frac{2}{\pi}\right) \int_0^\infty \frac{E f''(E)}{(E_0{}^2 - E^2)} dE$$

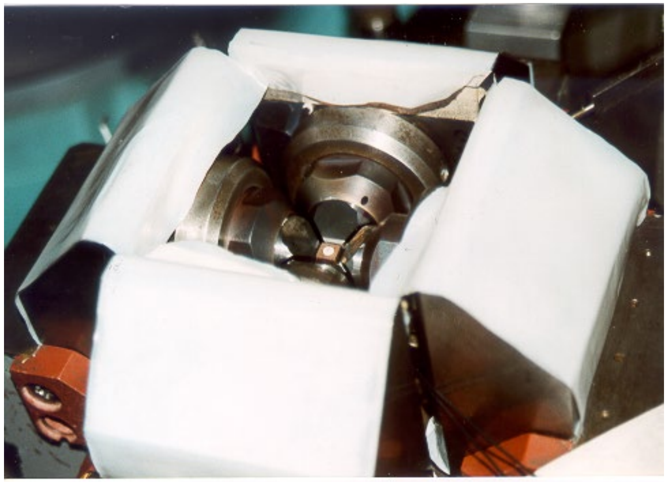


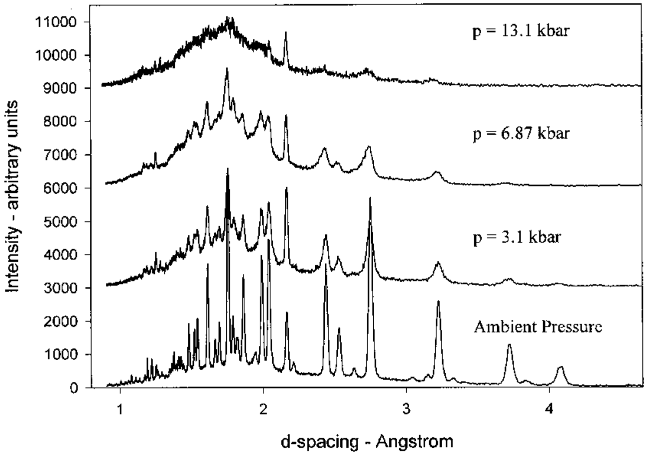


High pressure in situ diffraction studies

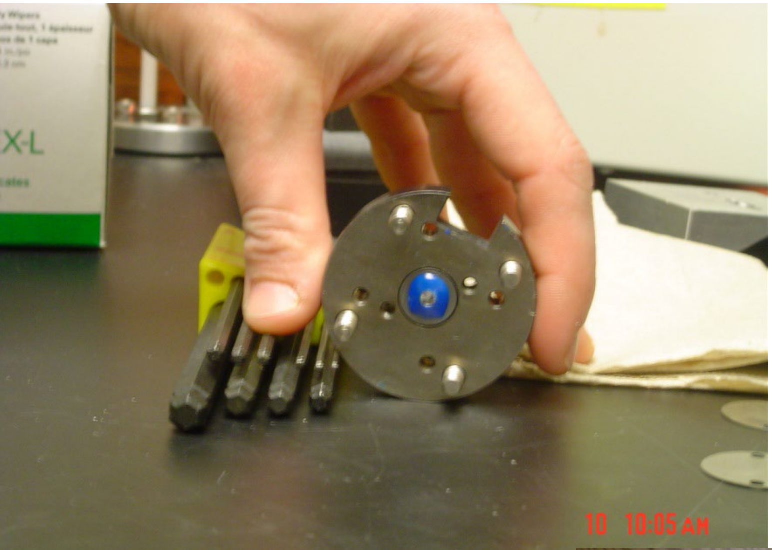


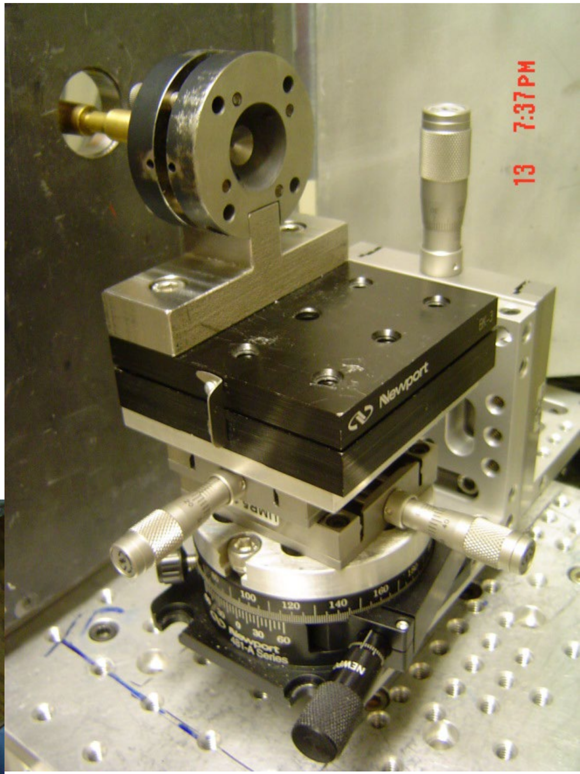




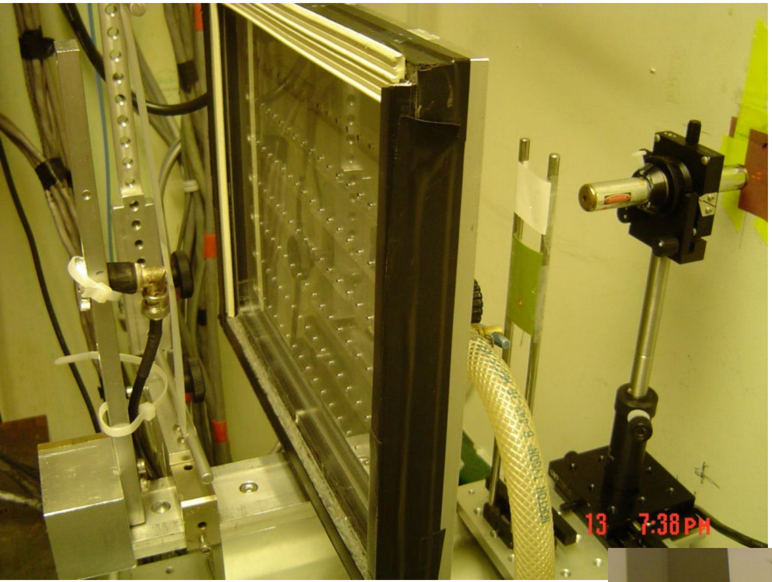


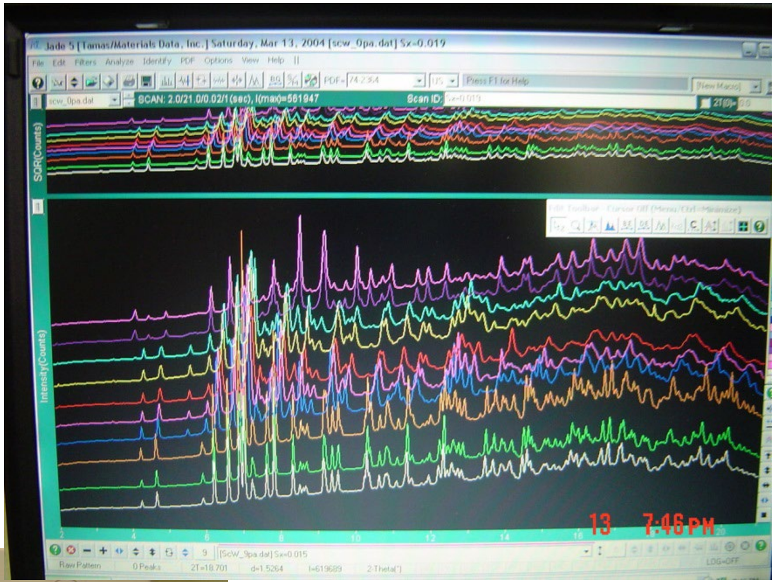
Even higher pressures: Diamond anvil cells

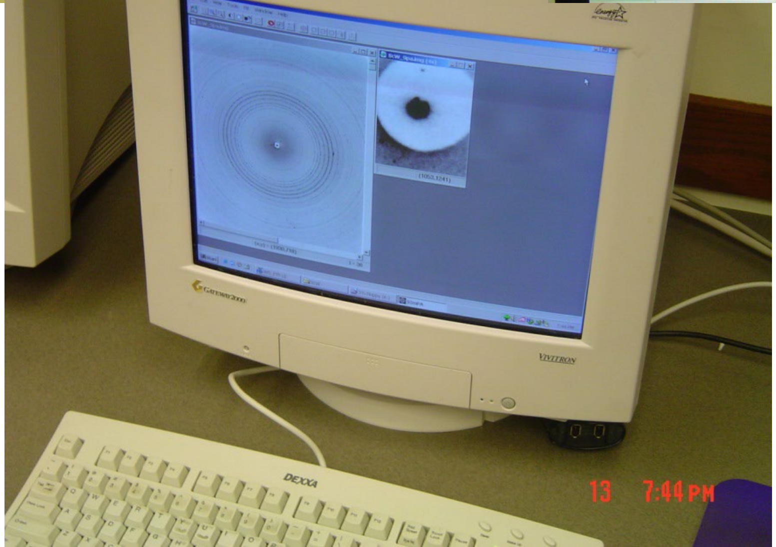




Data collection and processing







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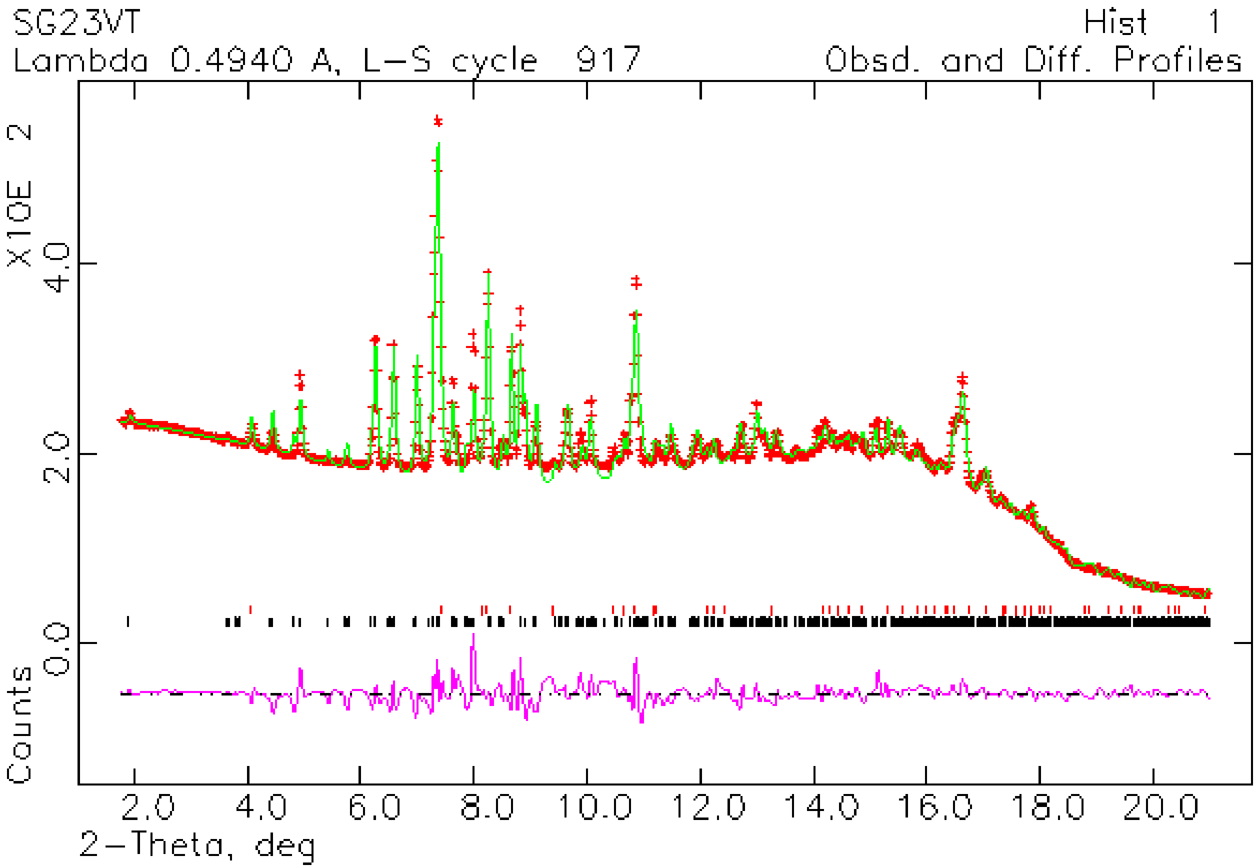
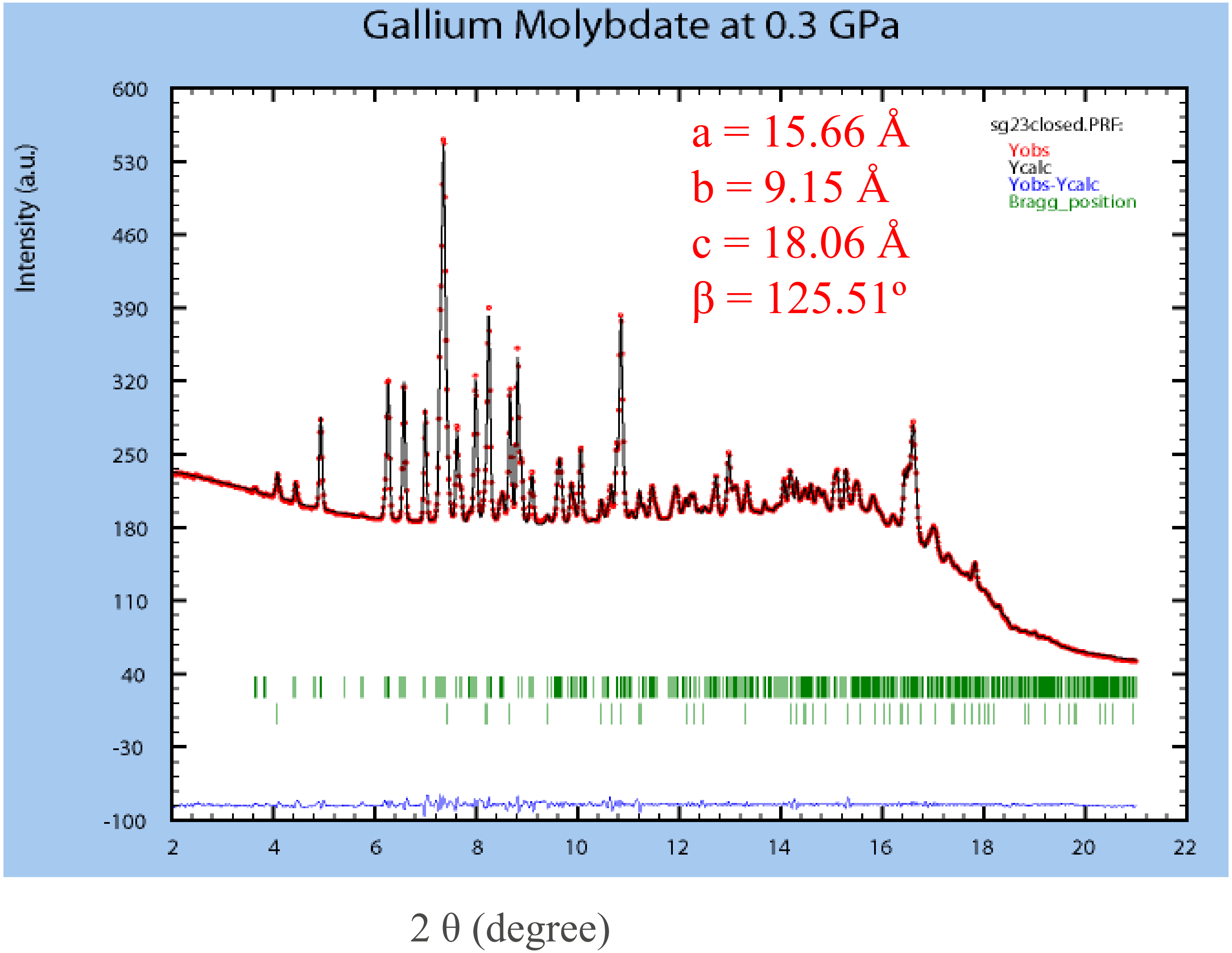
Refinements – structural model

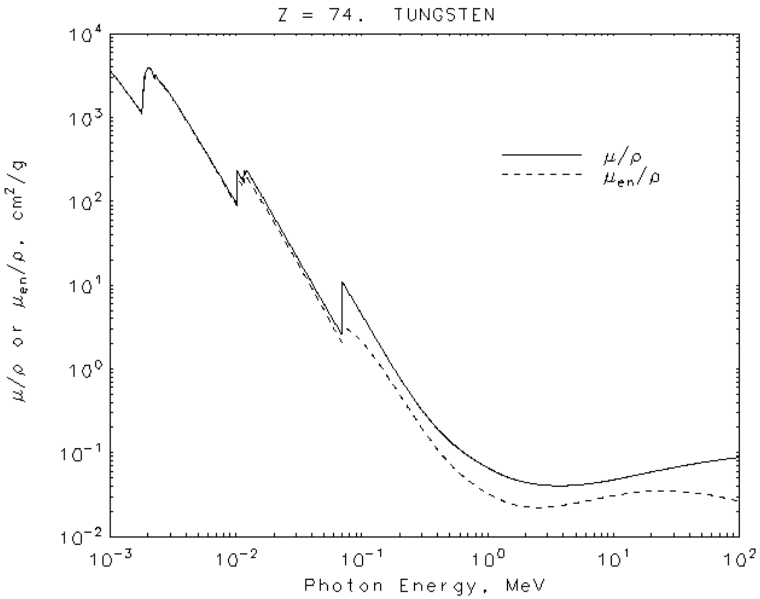


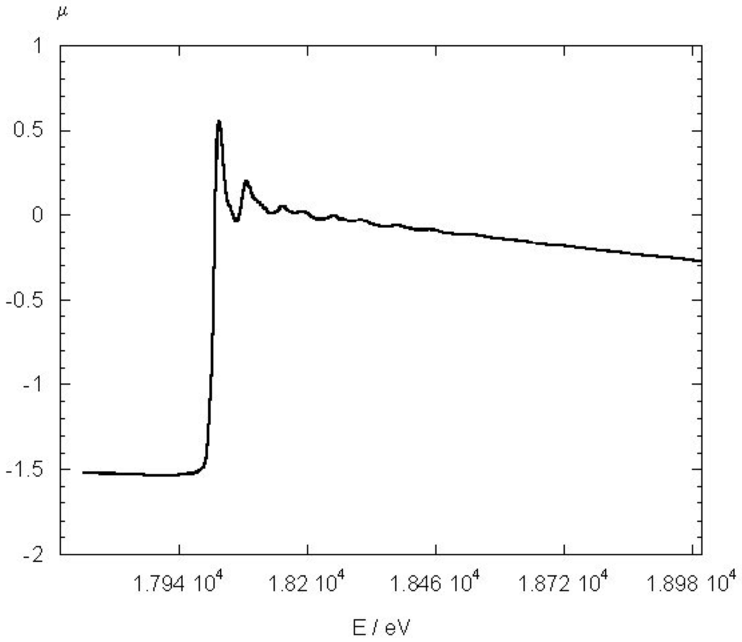
Refinements – Le Bail or Pawley Fits



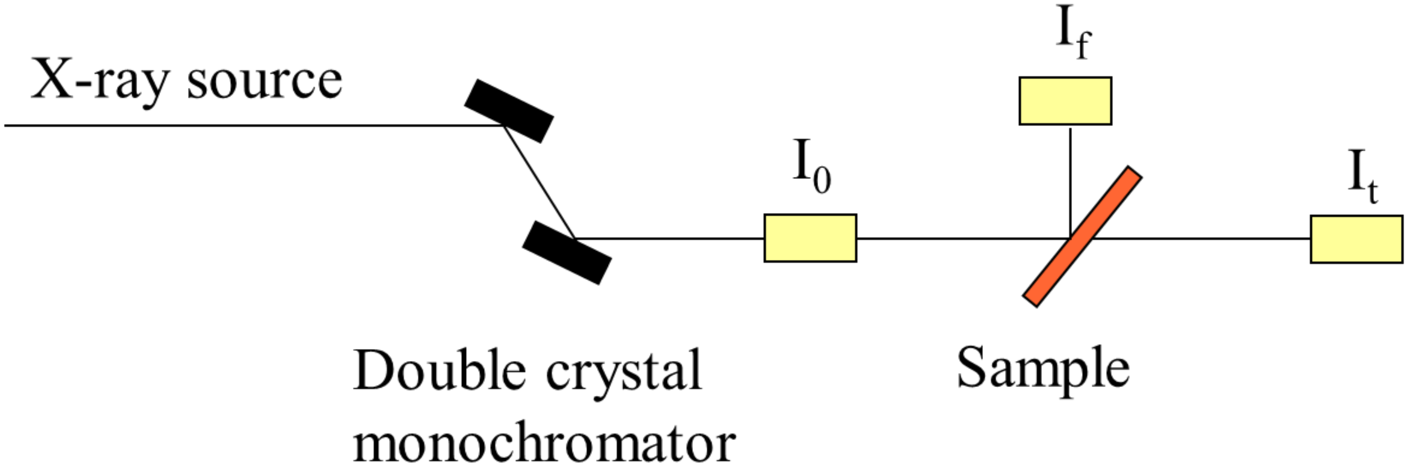
X-ray Absorption Spectroscopy

- **Based on excitation of core electrons by photons**
- **Element specific**
- **Usually carried out for edge energies 3 < E < 35 keV**





Experimental setup



🟨 = ion chambers

-I_0 = incident intensity

-I_t = transmitted intensity

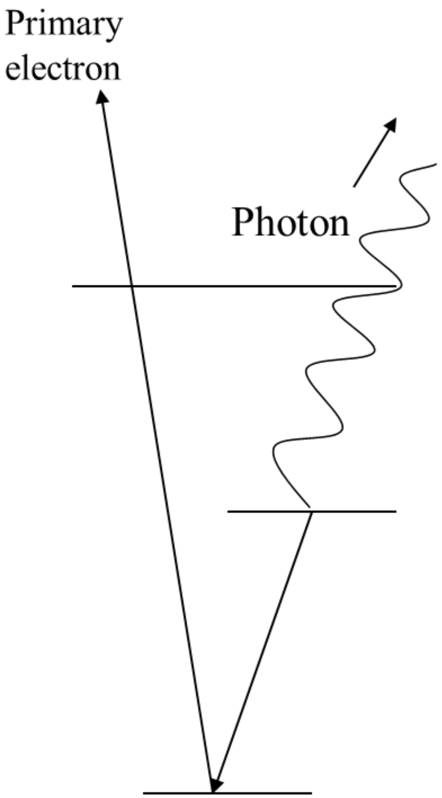
-I_f = fluorescence intensity

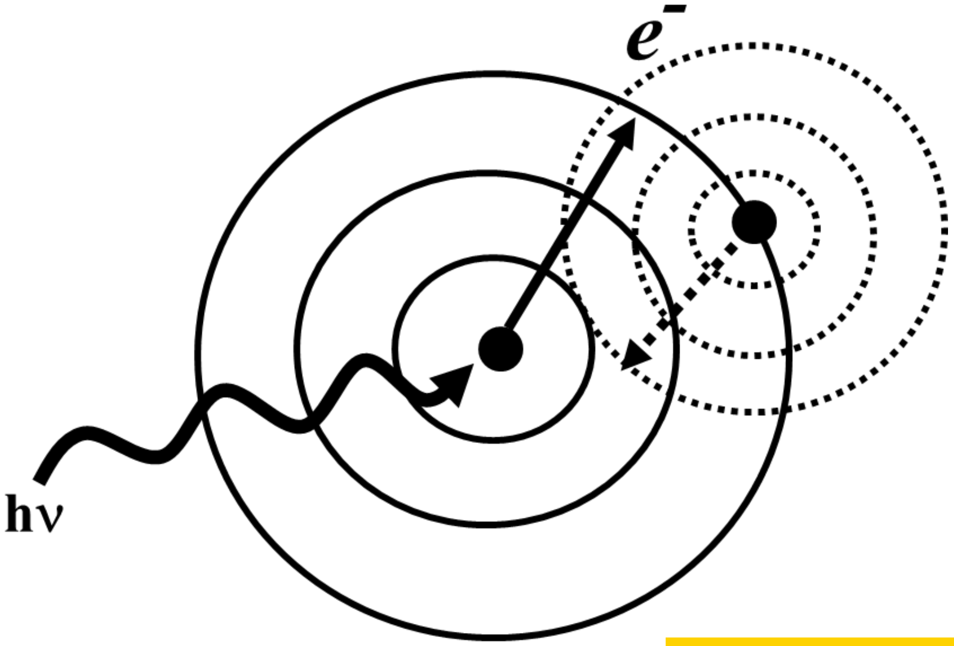
XANES experiments

- X-ray Absorption Near Edge Spectroscopy
- Region starting below the absorption edge up to ~30-40 eV above the edge
- Contains information about the absorber
    - Oxidation state
    - Symmetry of coordination environment
- Works for very low concentrations
- Conclusions are often drawn by comparison with model compounds that possess known, distinct environments

The EXAFS experiment

Extended X-ray Absorption Fine Structure





Information from EXAFS experiments

- **Quantitative information can be extracted from the oscillations above the absorption edge**
  - Use model compound to fix some fundamental parameters
- **Contains information about the surrounding atoms**
  - Number of nearest neighbors
  - Type of neighboring atoms
  - Distance from absorber
- **Information out to ~4 Å distance can be extracted from high quality data**
  - Fit several shells of neighboring atoms

EXAFS

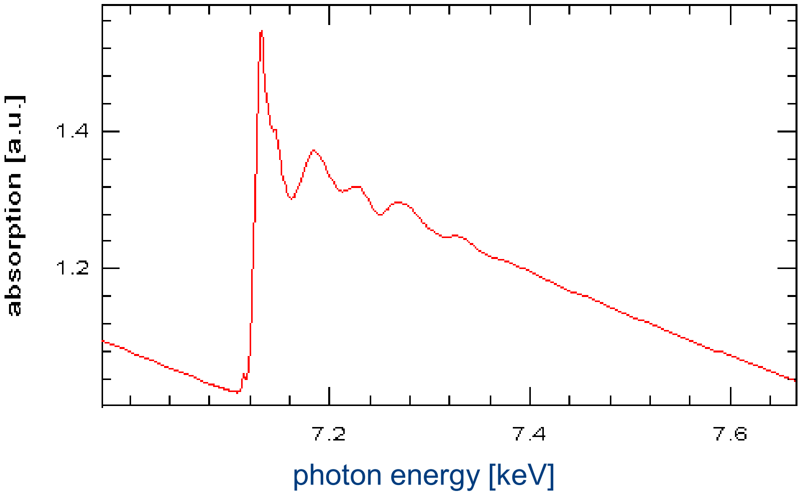
- **Element specific**
- **Can be applied to any kind of sample**
  - Crystalline or amorphous, solids, liquids, gases
- **EXAFS equations:**
  - Absorption: $\mu \cdot t = \ln \frac{I_0}{I}$, $\mu = \mu_0 (1 - \chi)$
  - Oscillations:

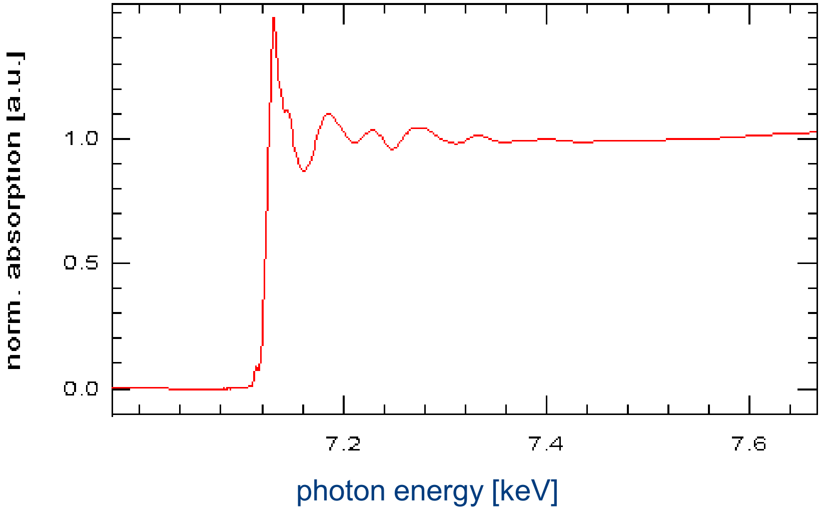
$$\chi(k) = \sum_j \frac{N_j f_j(k) \exp(-2k^2\sigma_j^2 - 2r_j/\lambda(k))}{k r_j^2} \sin(2kr_j + \varphi_j(k))$$

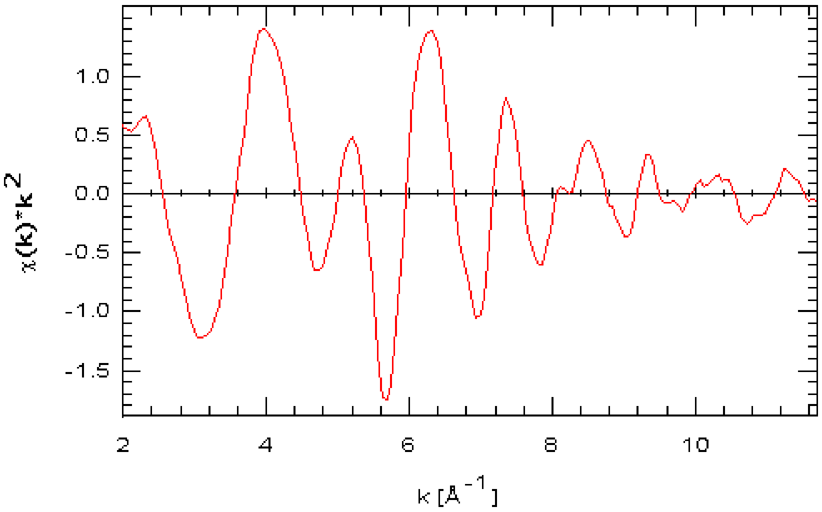
$$k = \sqrt{\frac{2m(E - E_0)}{\hbar^2}}$$

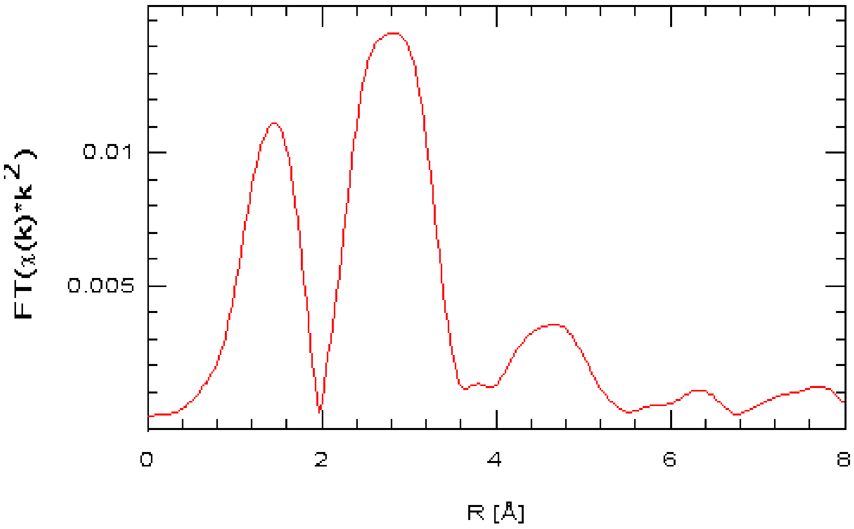
photoelectron wave vector

An example of EXAFS data processing

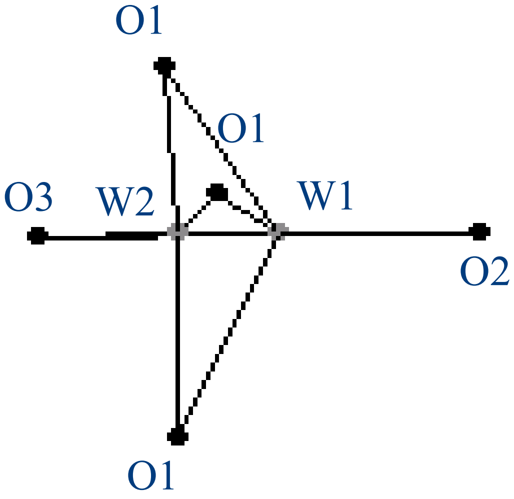


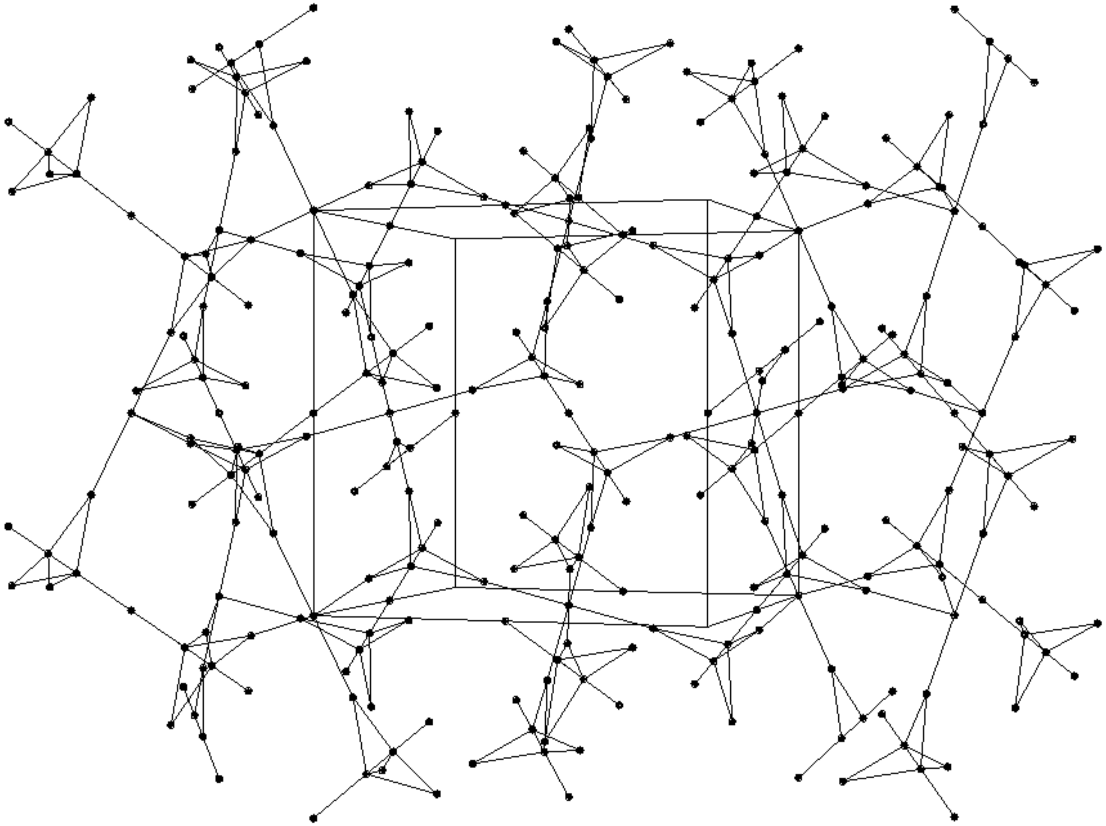






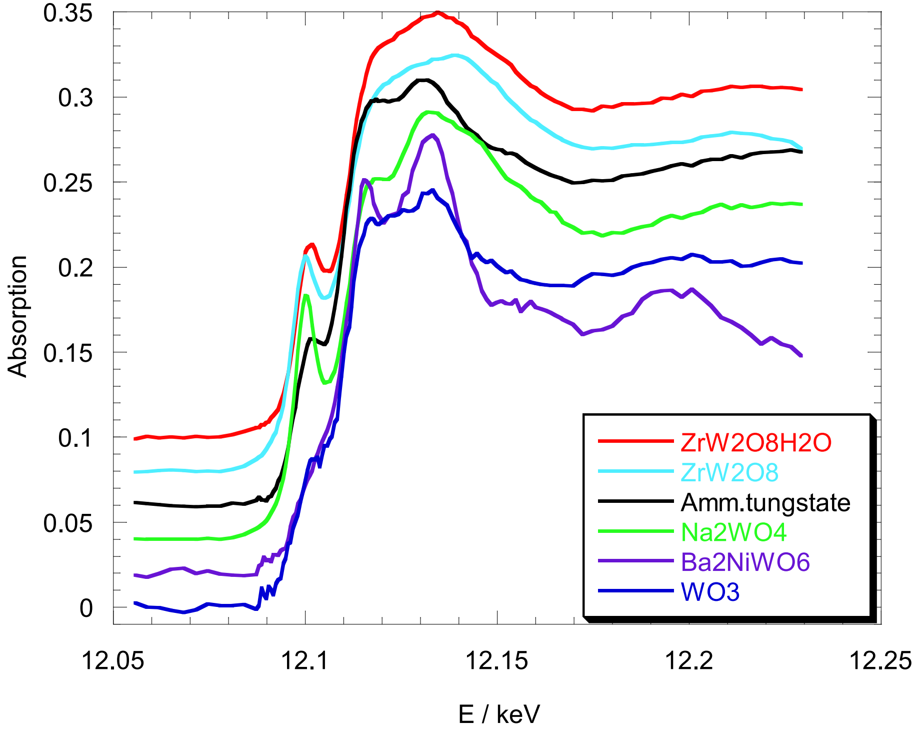
Partial solution of $ZrW_2O_8 \cdot xH_2O$

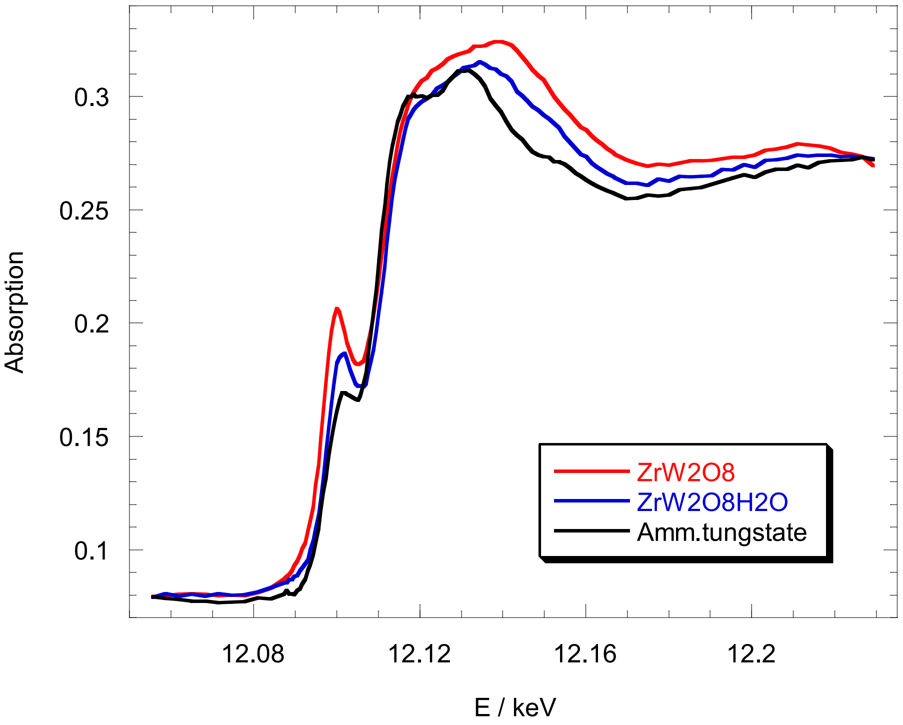




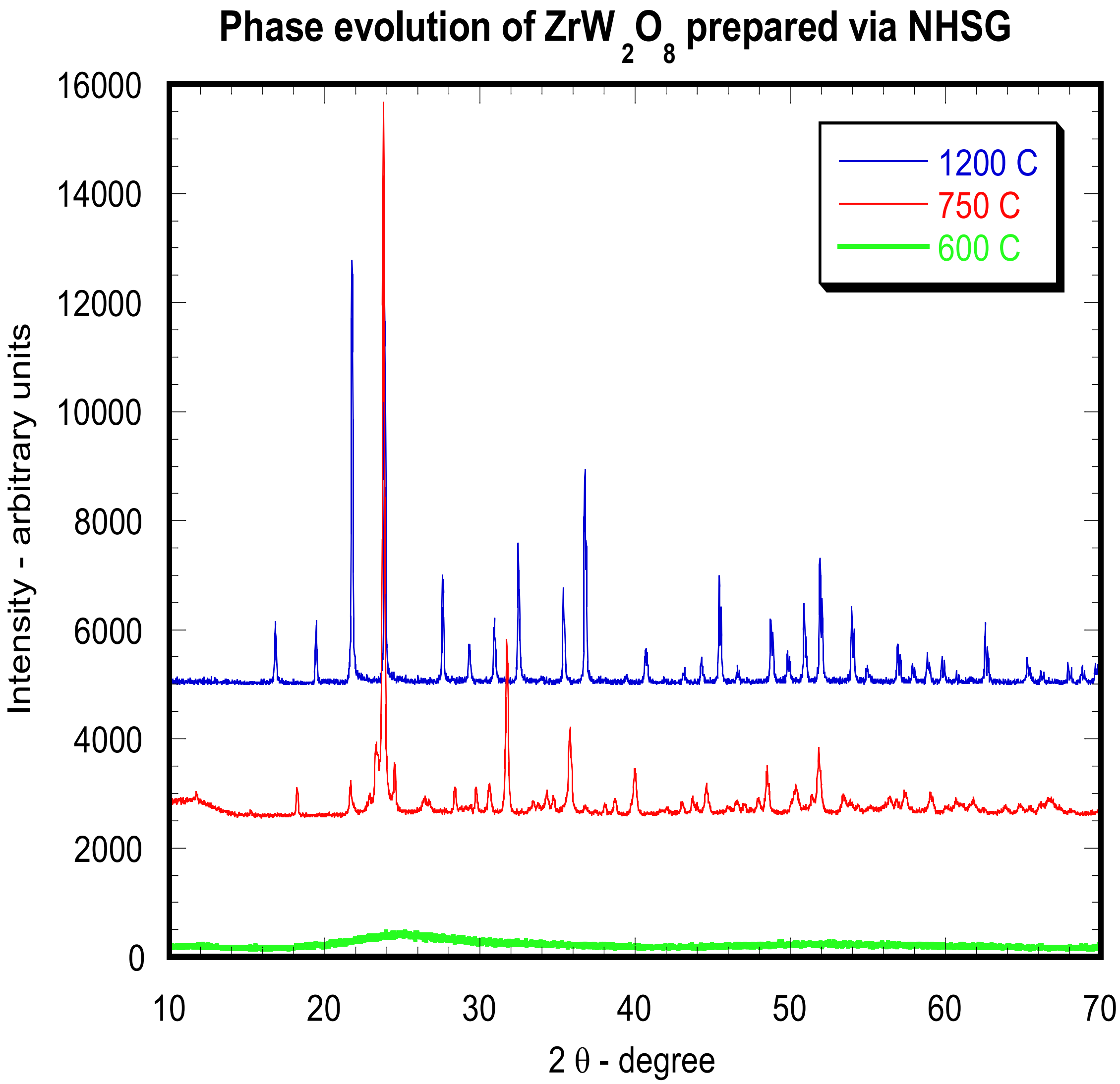
Highly disordered structure, but partial solution suggests increase in tungsten coordination number.

XANES measurements on the hydrate





ZrW_2O_8 prepared by NHSG chemistry



EXAFS study on ZrW_2O_8

- **Goal 1: Investigate the changes in local metal environments during heat treatment of amorphous gels and compare them to the local environments of crystalline phases**
  - Is the gel structure responsible for the crystallization of trigonal ZrW_2O_8?
- **Goal 2: Compare the local metal environments in cubic and trigonal ZrW_2O_8**
  - How different are they? Could seeding favor the desired phase?

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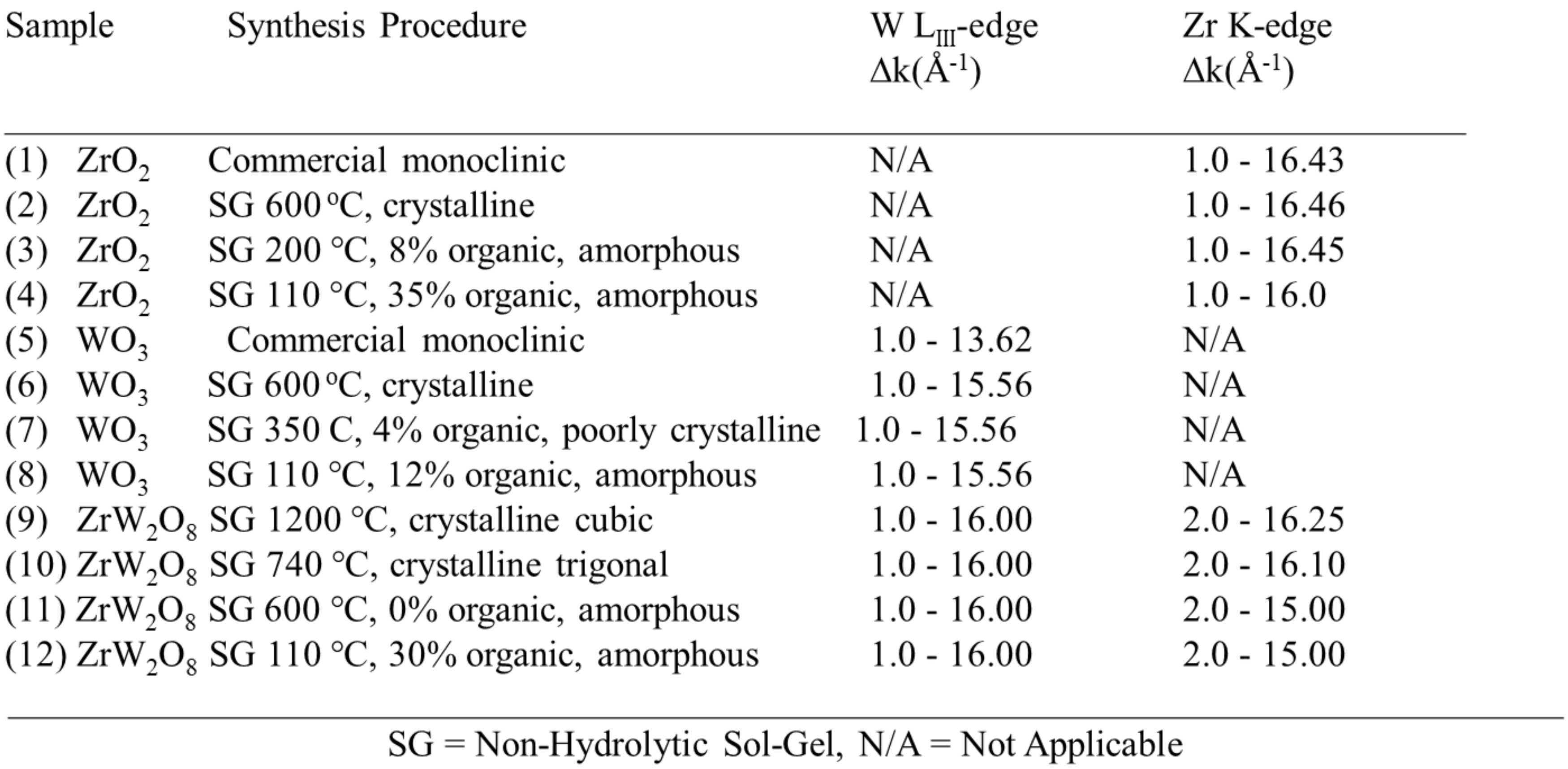
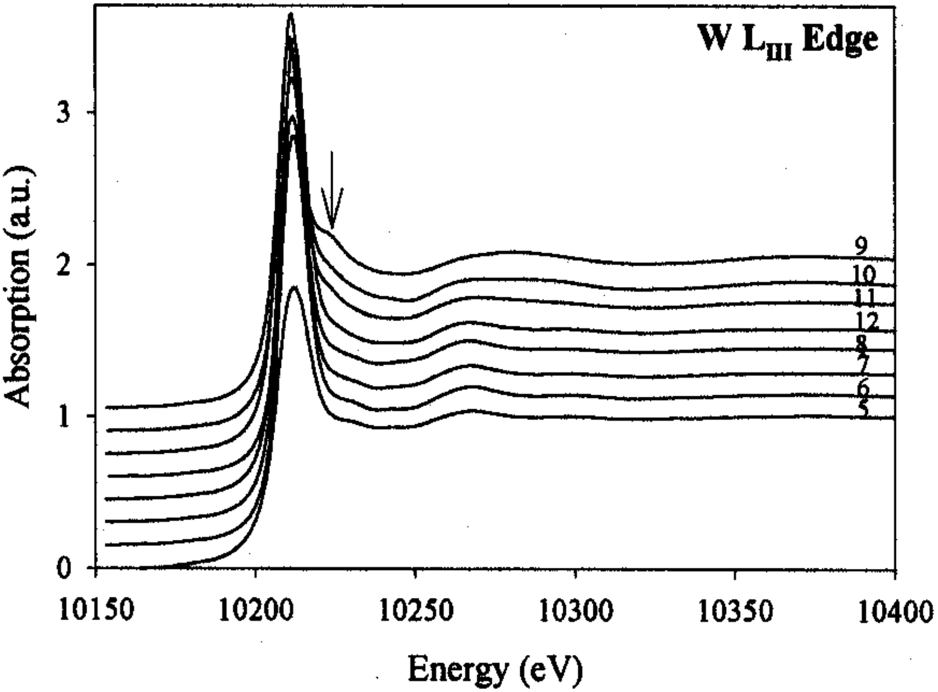
EXAFS samples

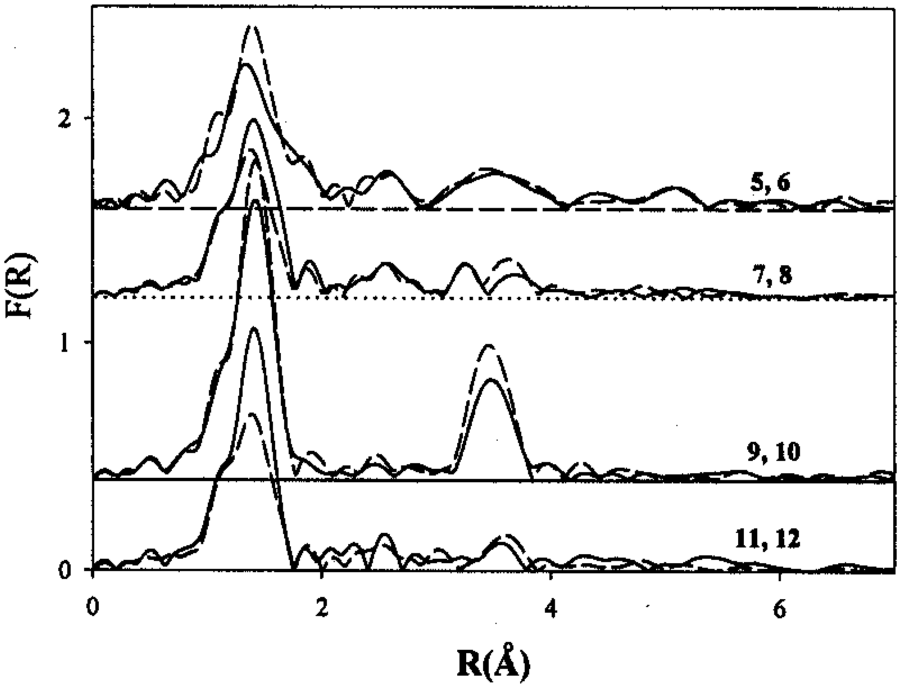


Sample	Synthesis Procedure	W L_{III}-edge $\Delta k(Å^{-1})$	Zr K-edge $\Delta k(Å^{-1})$
(1) ZrO_2	Commercial monoclinic	N/A	1.0 - 16.43
(2) ZrO_2	SG 600 °C, crystalline	N/A	1.0 - 16.46
(3) ZrO_2	SG 200 °C, 8% organic, amorphous	N/A	1.0 - 16.45
(4) ZrO_2	SG 110 °C, 35% organic, amorphous	N/A	1.0 - 16.0
(5) WO_3	Commercial monoclinic	1.0 - 13.62	N/A
(6) WO_3	SG 600 °C, crystalline	1.0 - 15.56	N/A
(7) WO_3	SG 350 C, 4% organic, poorly crystalline	1.0 - 15.56	N/A
(8) WO_3	SG 110 °C, 12% organic, amorphous	1.0 - 15.56	N/A
(9) ZrW_2O_8	SG 1200 °C, crystalline cubic	1.0 - 16.00	2.0 - 16.25
(10) ZrW_2O_8	SG 740 °C, crystalline trigonal	1.0 - 16.00	2.0 - 16.10
(11) ZrW_2O_8	SG 600 °C, 0% organic, amorphous	1.0 - 16.00	2.0 - 15.00
(12) ZrW_2O_8	SG 110 °C, 30% organic, amorphous	1.0 - 16.00	2.0 - 15.00

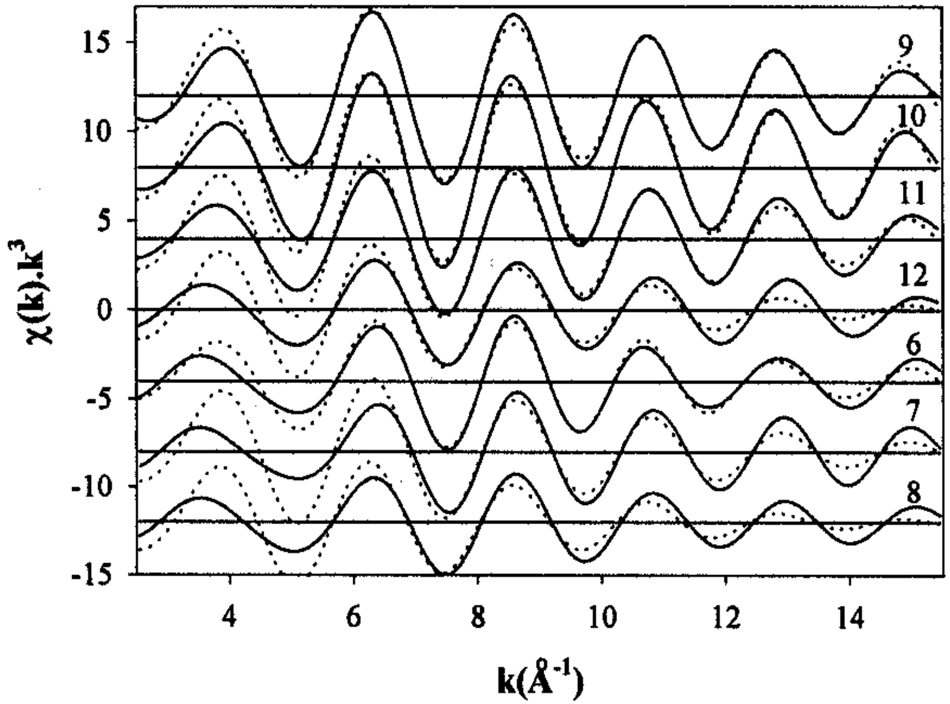
SG = Non-Hydrolytic Sol-Gel, N/A = Not Applicable

W L_{III}-edge data





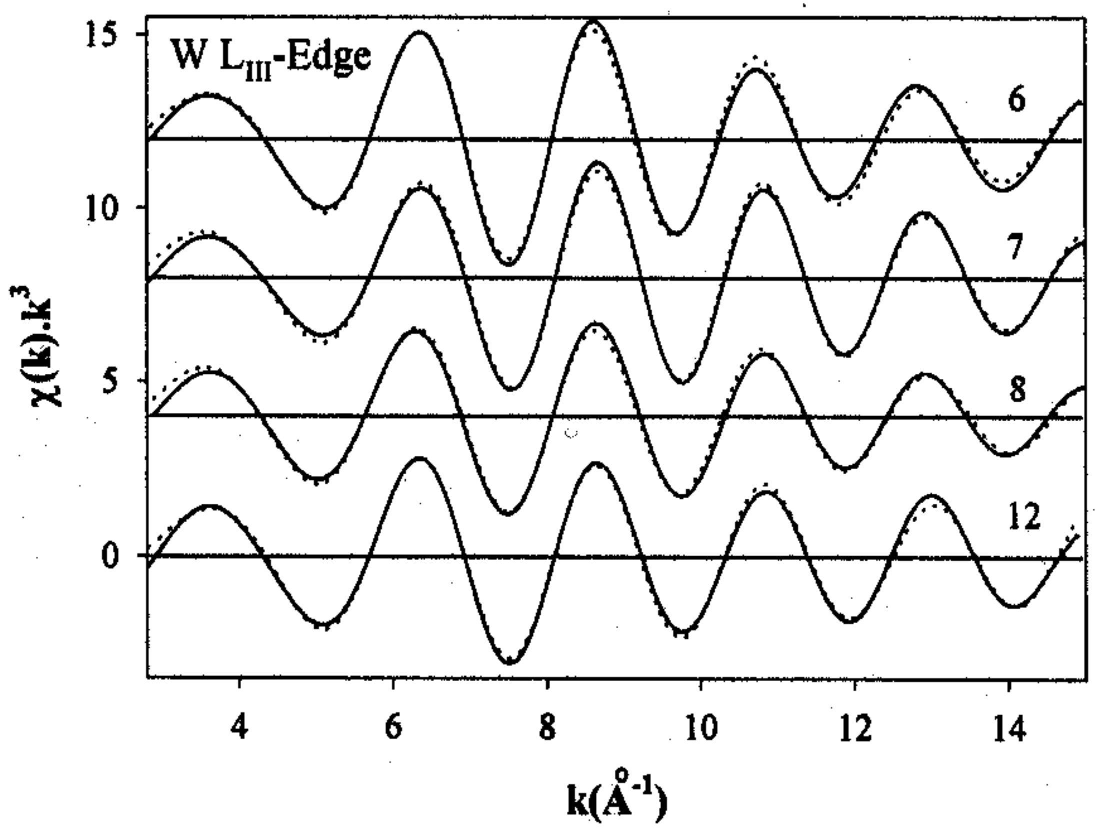
W L_{III}-edge data analysis



Sample		R(Å)	σ^2(Å^2)	N
(9) ZrW_2O_8, cubic	W-O1	1.72	0.0019	1
	W-O2	1.80	0.0019	3
(10) ZrW_2O_8, trigonal	W-O1	1.73	0.0015	1
	W-O2	1.80	0.0015	3
(11) ZrW_2O_8, 600 °C, am.	W-O1	1.75	0.0037	1
	W-O2	1.80	0.0037	3
(12) ZrW_2O_8, 110 °C, am.	W-O1	1.75	0.0066	1
	W-O2	1.79	0.0066	3

Fits using a 3+1 coordination model:
Only good for crystalline ZrW_2O_8 samples

W L_{III}-edge data analysis



Fits using an octahedral coordination model

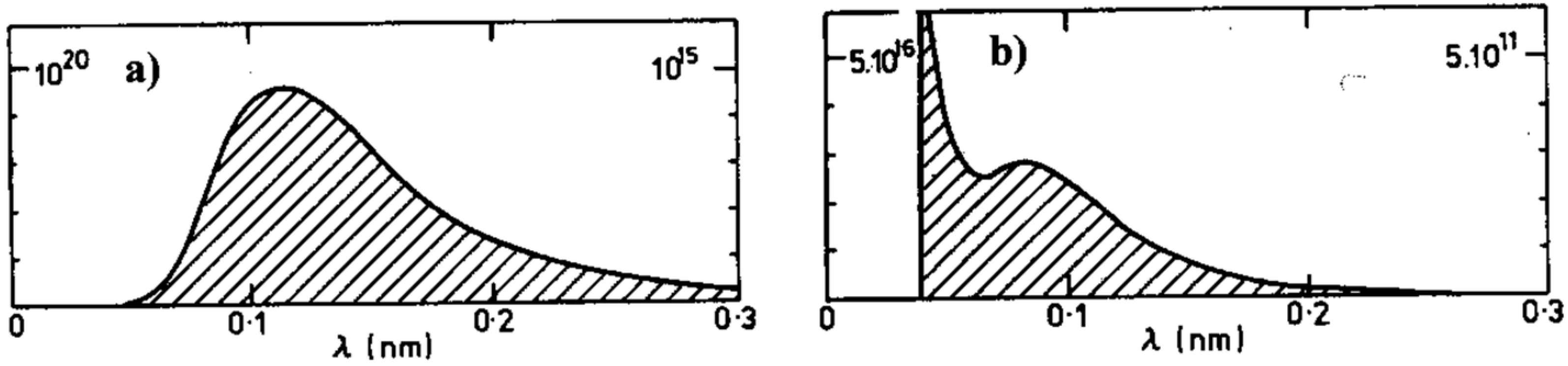
Neutron sources

Reactor sources

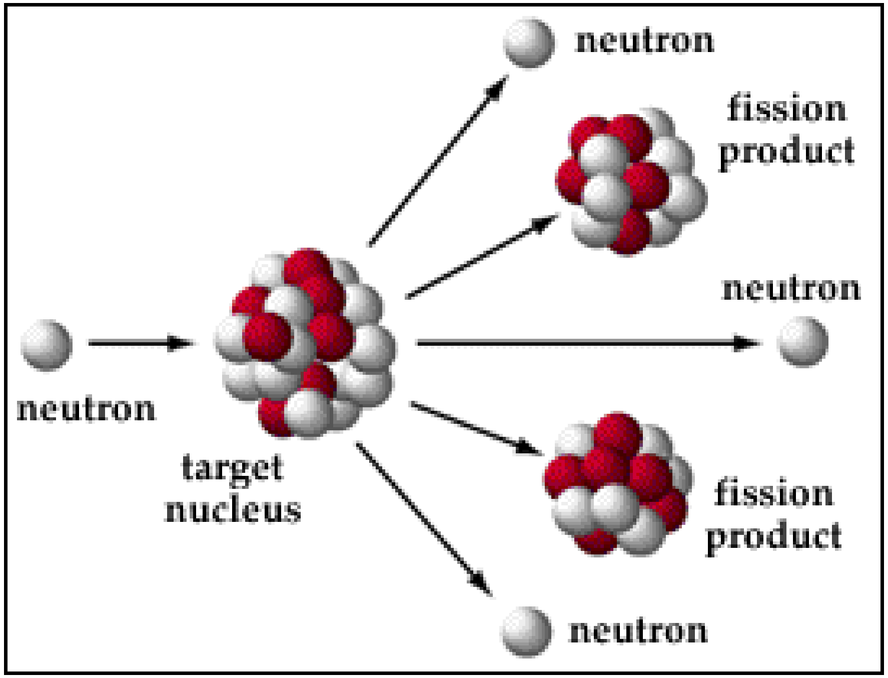
- Neutrons are produced by nuclear chain reaction
- Neutrons must be slowed down by moderator for use in diffraction
- Neutron wavelength distribution is thermal equilibrium distribution from moderator
- Monochromator needed => uses only small portions of the produced neutrons

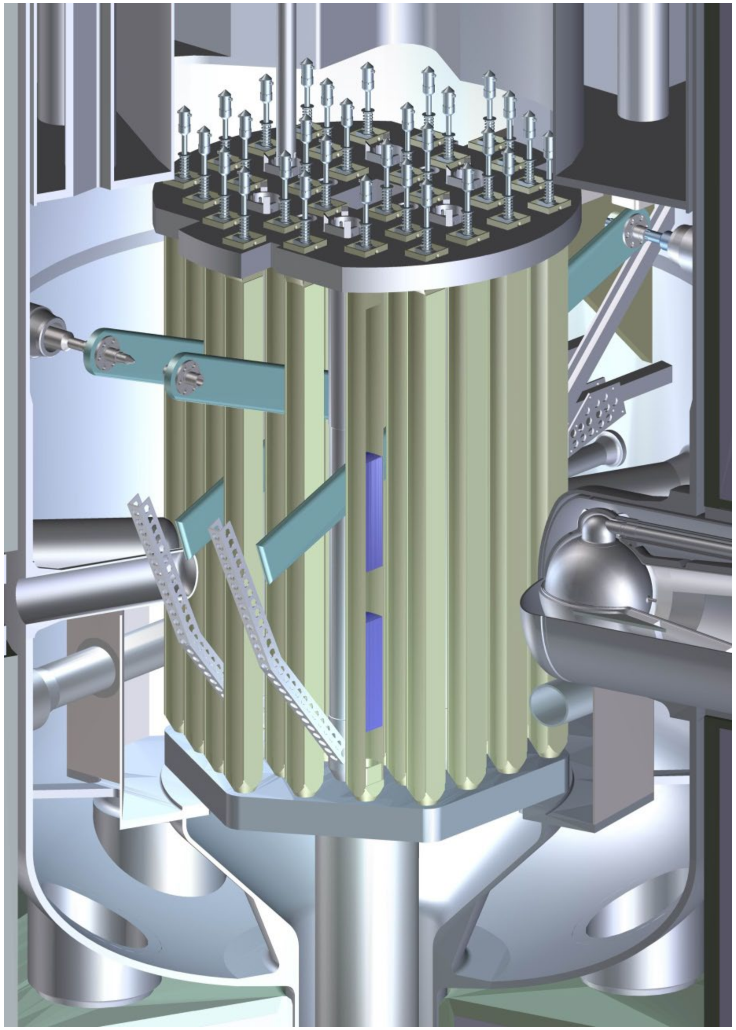
Spallation sources

- Neutrons are produced by bombarding a metal target with protons
- Different wavelength distribution from reactor
- High peak flux, low average flux
- Due to time structure, all neutrons can be used



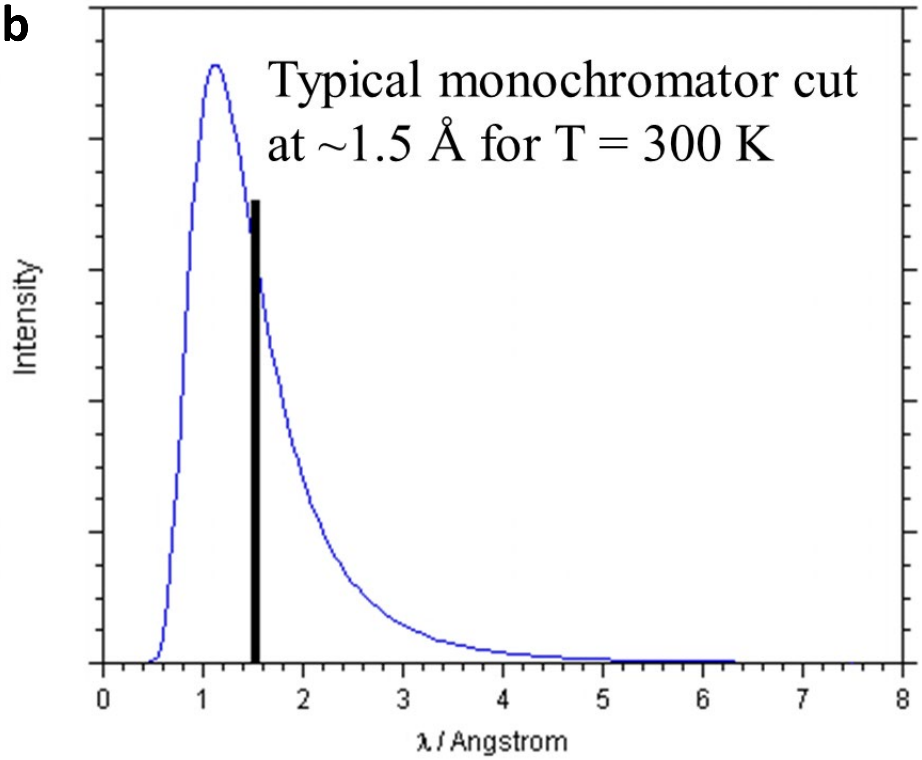
Nuclear Reactors



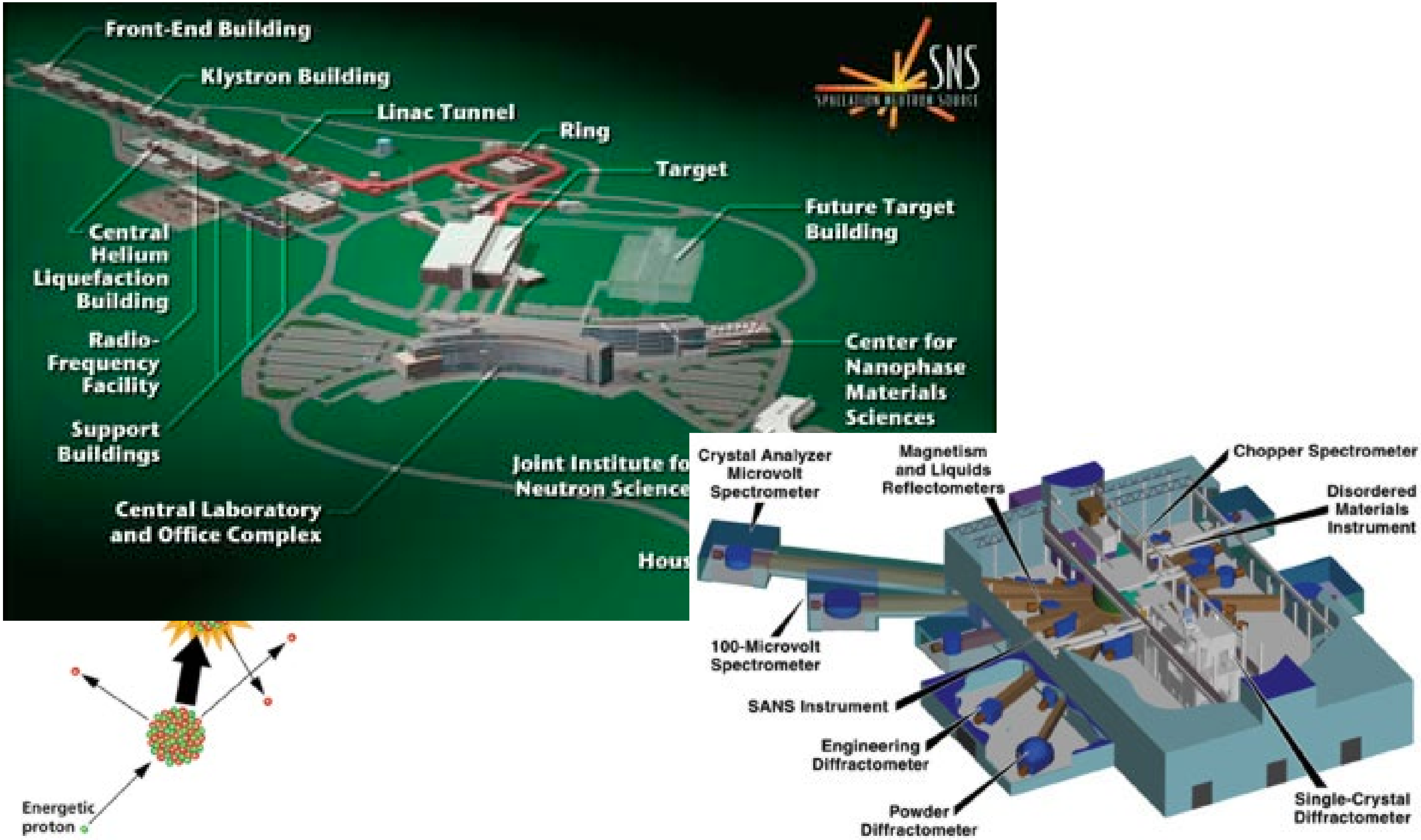


Reactor sources

- **Experimental setup very similar to lab X-ray diffraction**
- **Large samples needed**
    - low intensity beams
- **Powder data: Peak shape is often simple and thus easy to model**
- **No form factor fall-off gives good quality data at small d-spacings**
    - but d_{min} is often similar to a lab X-ray experiment



Spallation Sources



Spallation source – TOF experiments

- **Neutrons are particles with mass, so wavelength and speed are correlated (de Broglie)**

$$m \cdot v = \frac{h}{\lambda} \qquad \text{with} \qquad v = (L + L_1) / t$$

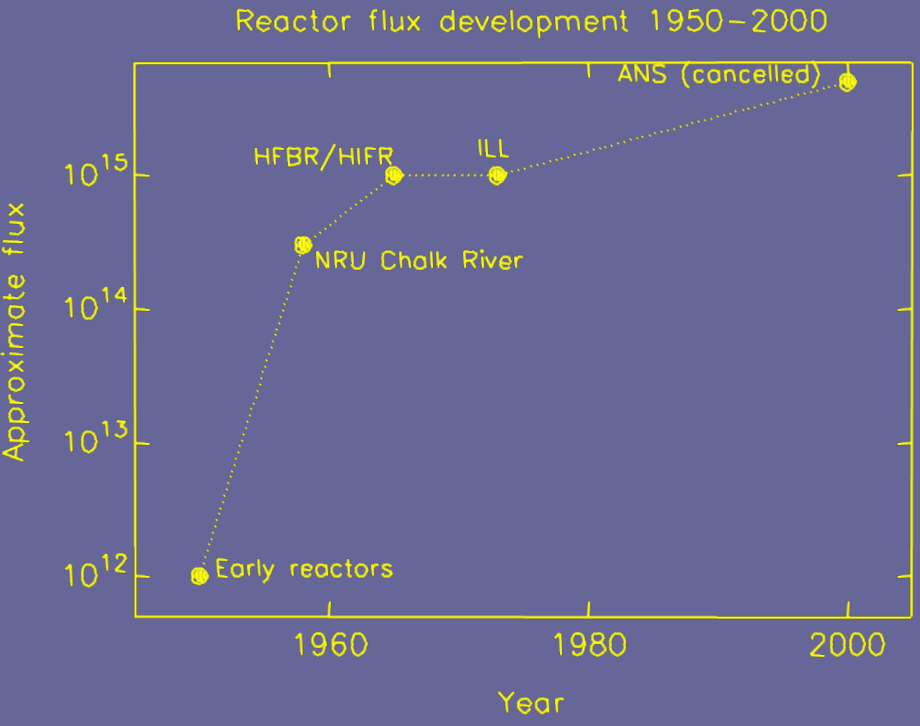
$$\text{so} \qquad t = \frac{m(L + L_1)\lambda}{h}$$

- **Data are plotted as a function of t (TOF)**
- **Originally: Detectors are combined in "banks" at fixed angles**
  - Accessible d-spacing range depends on angle of bank

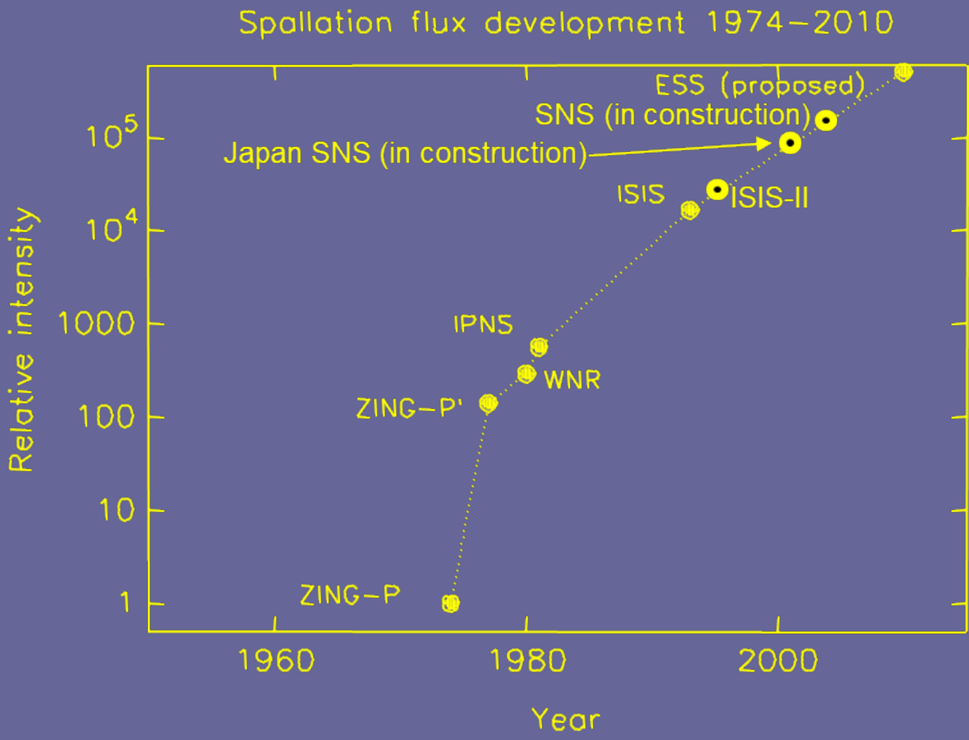
Neutron flux evolution

(Courtesy of Simon Billinge)

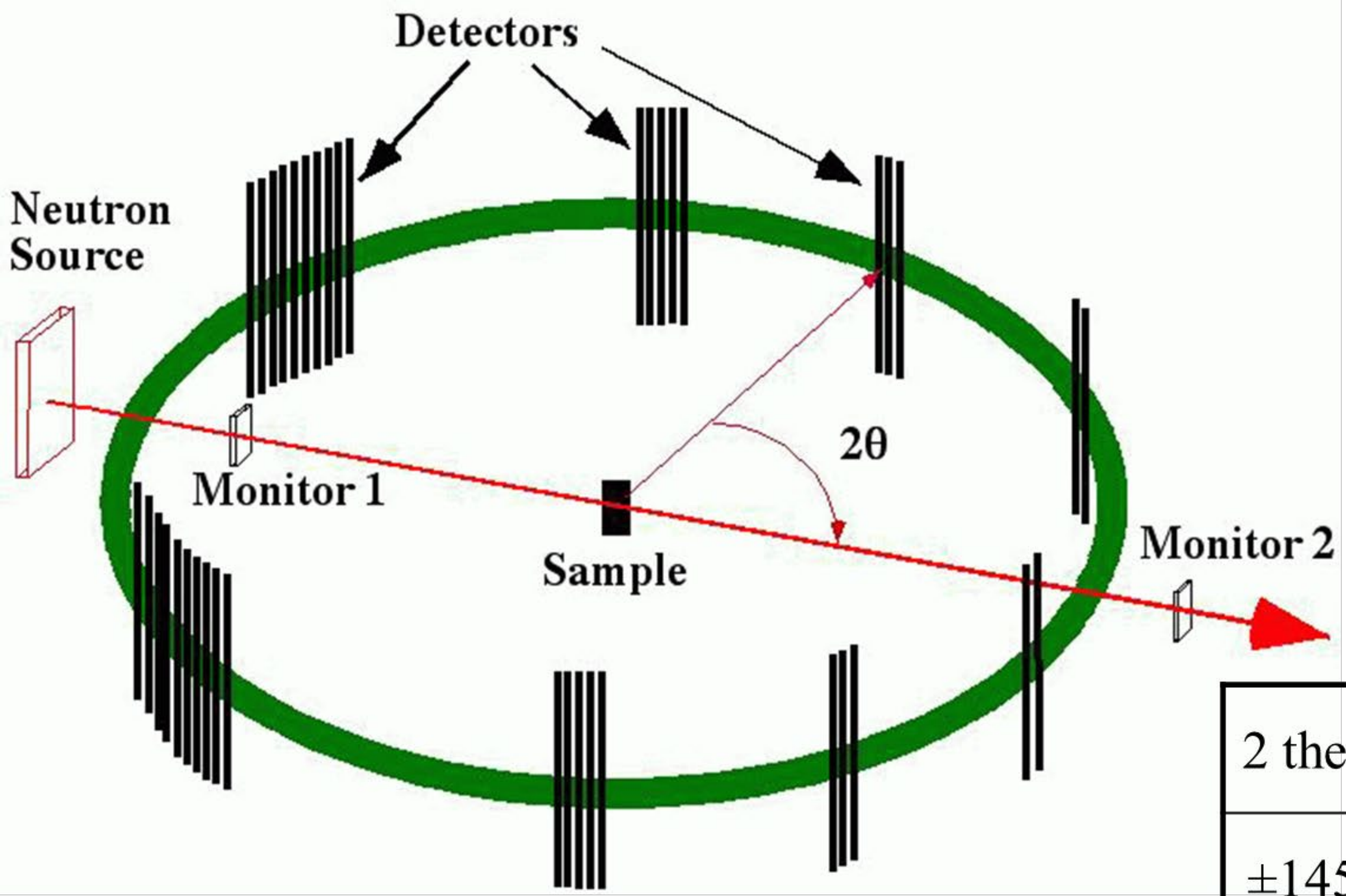
Reactor sources



Spallation sources

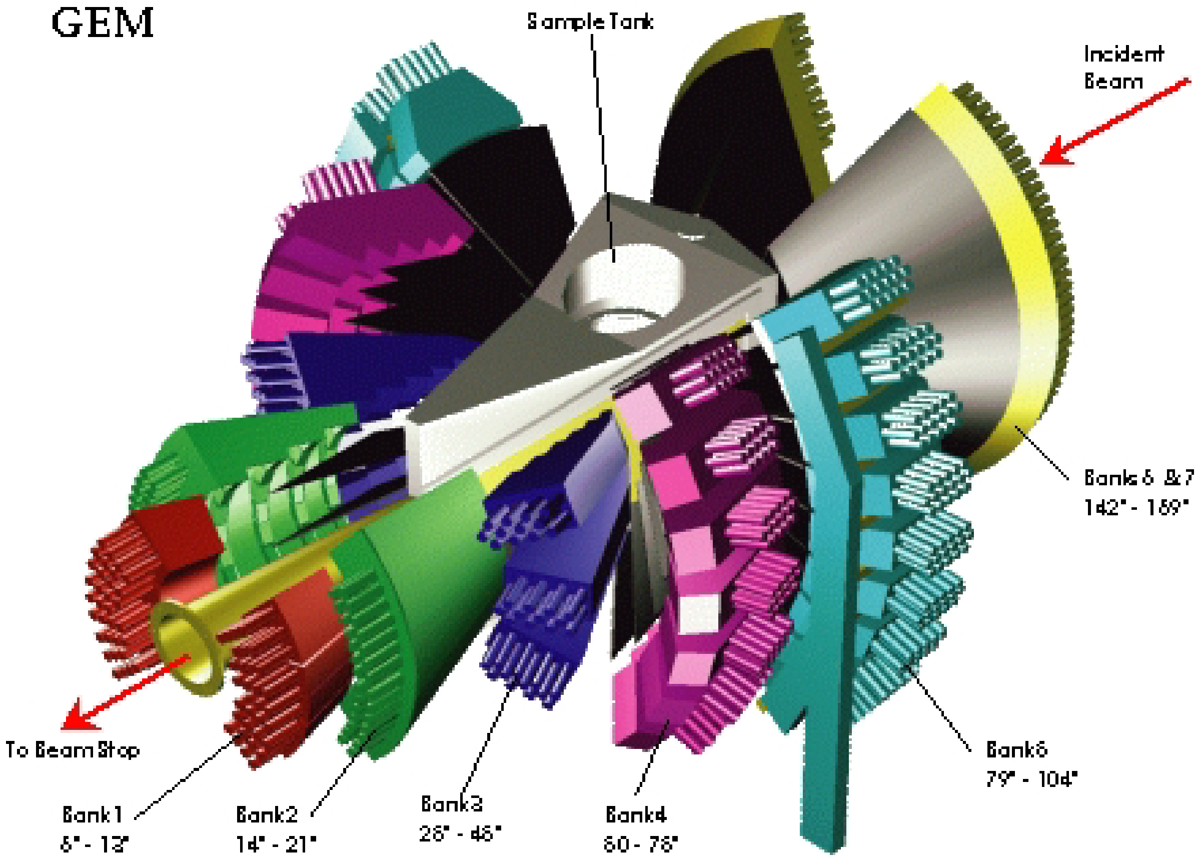


SEPD — Special Environment Powder Diffractometer



2 theta	d_{min}/Å	d_{max}/Å
±145°	0.33	4.02
±90°	0.45	5.41
±44°	0.85	10.21
±22°	1.7	20.25

Modern detector setups - GEM



Modern detector setups - POWGEN