The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific
and Cultural Organization

International Atomic
Energy Agency

SMR.1825 - 5

Advanced Workshop on

Recent Developments in Nanomaterials

15 - 19 January, 2007, ICTP, Trieste, Italy

Total Scattering: A "Complete" Structural Fingerprint of Nanoparticles Experimental Aspects

T. Proffen
Los Alamos National Laboratory
New Mexico
Los Alamos
USA

Total Scattering and Nanomaterials

Experimental

Thomas Proffen

NPDF instrument scientist
Lujan Neutron Scattering Center
Los Alamos National Laboratory
tproffen@lanl.gov

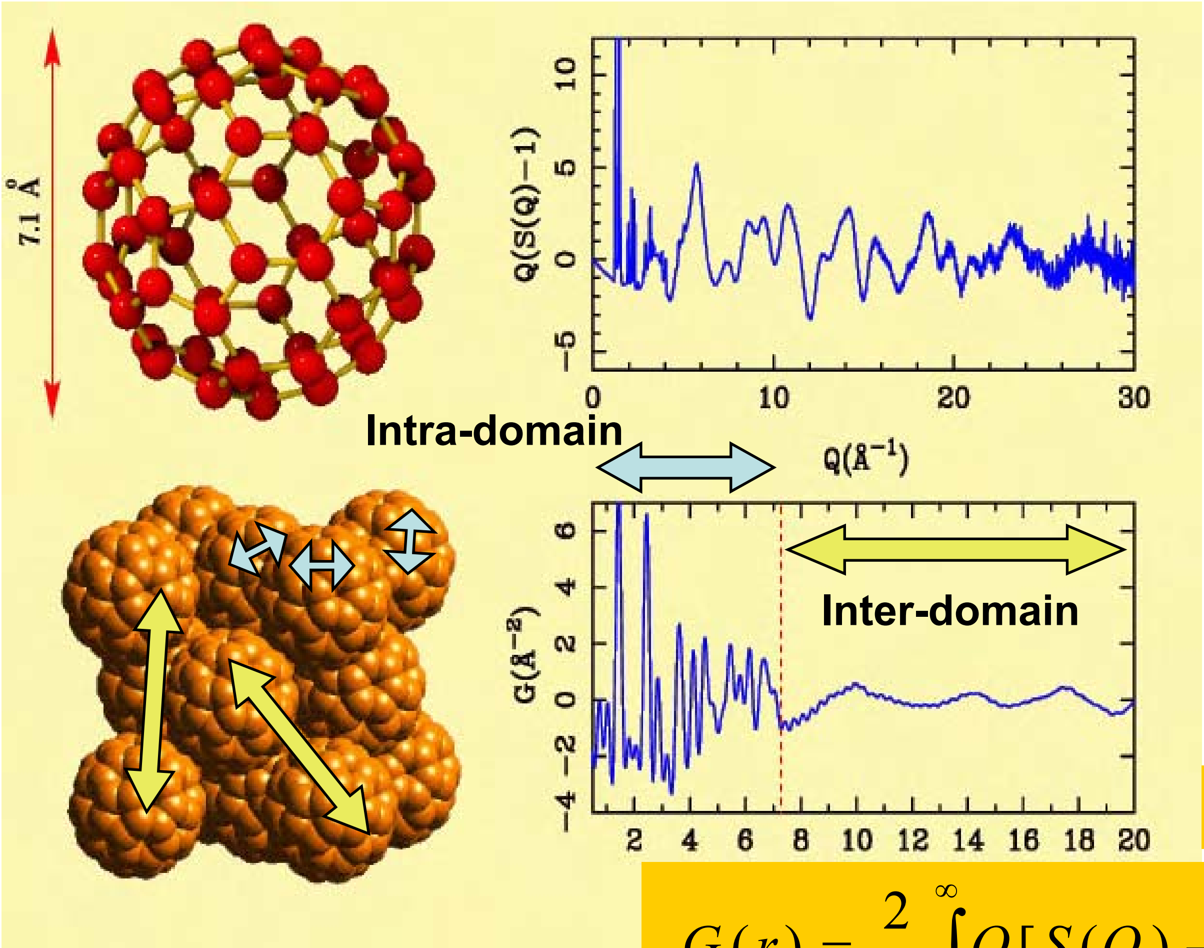
LA-UR 07-0197

Outline

- Experimental considerations
- Facilities and Instruments
- Data Reduction Steps and Software

Operated by the Los Alamos National Security, LLC for the DOE/NNSA

REMINDER: What is a PDF?



$$Q = 4\pi \sin\theta / \lambda$$

$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin(Qr)\,dQ$$

Experimental considerations

or

What makes a good PDF ?

What is required to obtain high quality PDFs ?

The PDF (similar to the Patterson) is obtained via Fourier transform of the normalized total scattering S(Q):

$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin(Qr)\,dQ$$

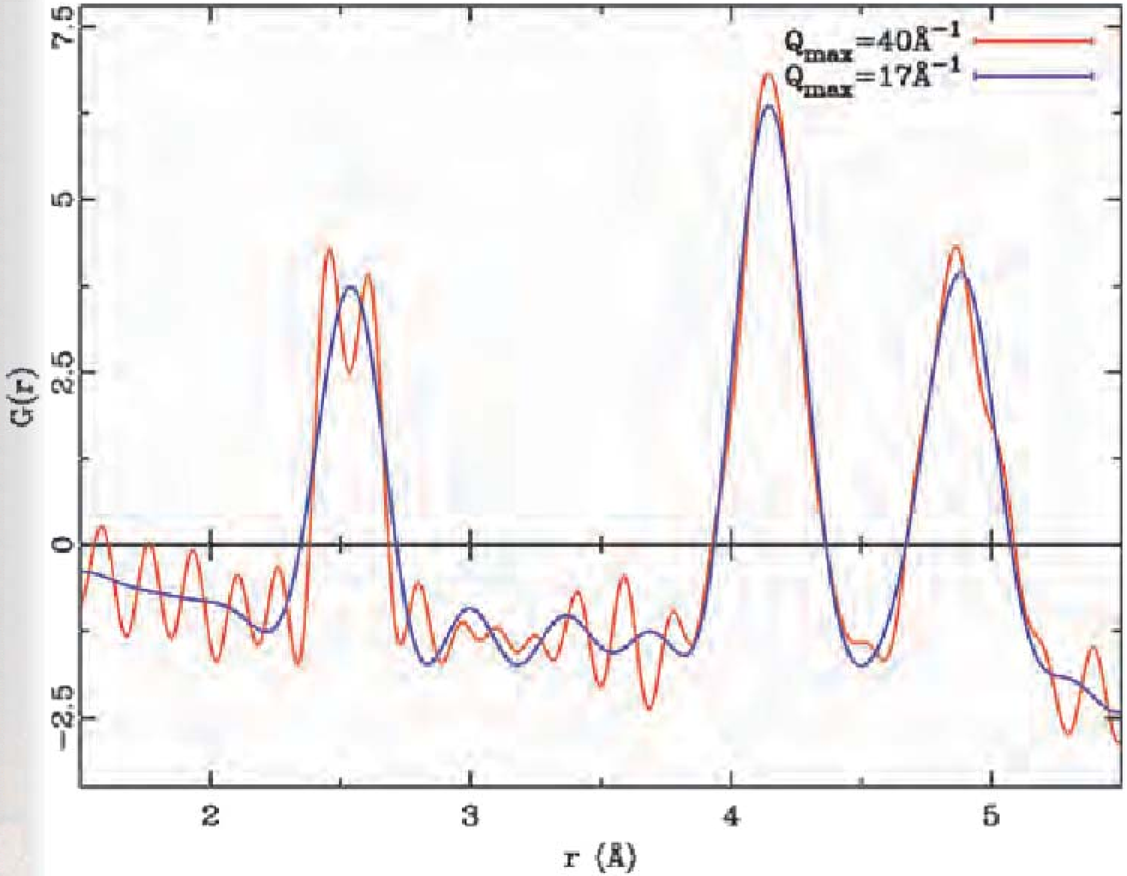
Requirements to obtain 'good' PDF:

- High momentum transfer, Q_{max}.
- High Q-resolution.
- Good counting statistics @ high Q.
- Low instrument and stable background

Where ?

Synchrotron sources (high energy X-rays) or spallation neutron sources (reactor neutron energies are too low)

What makes a good PDF: Influence of Q_{max} …

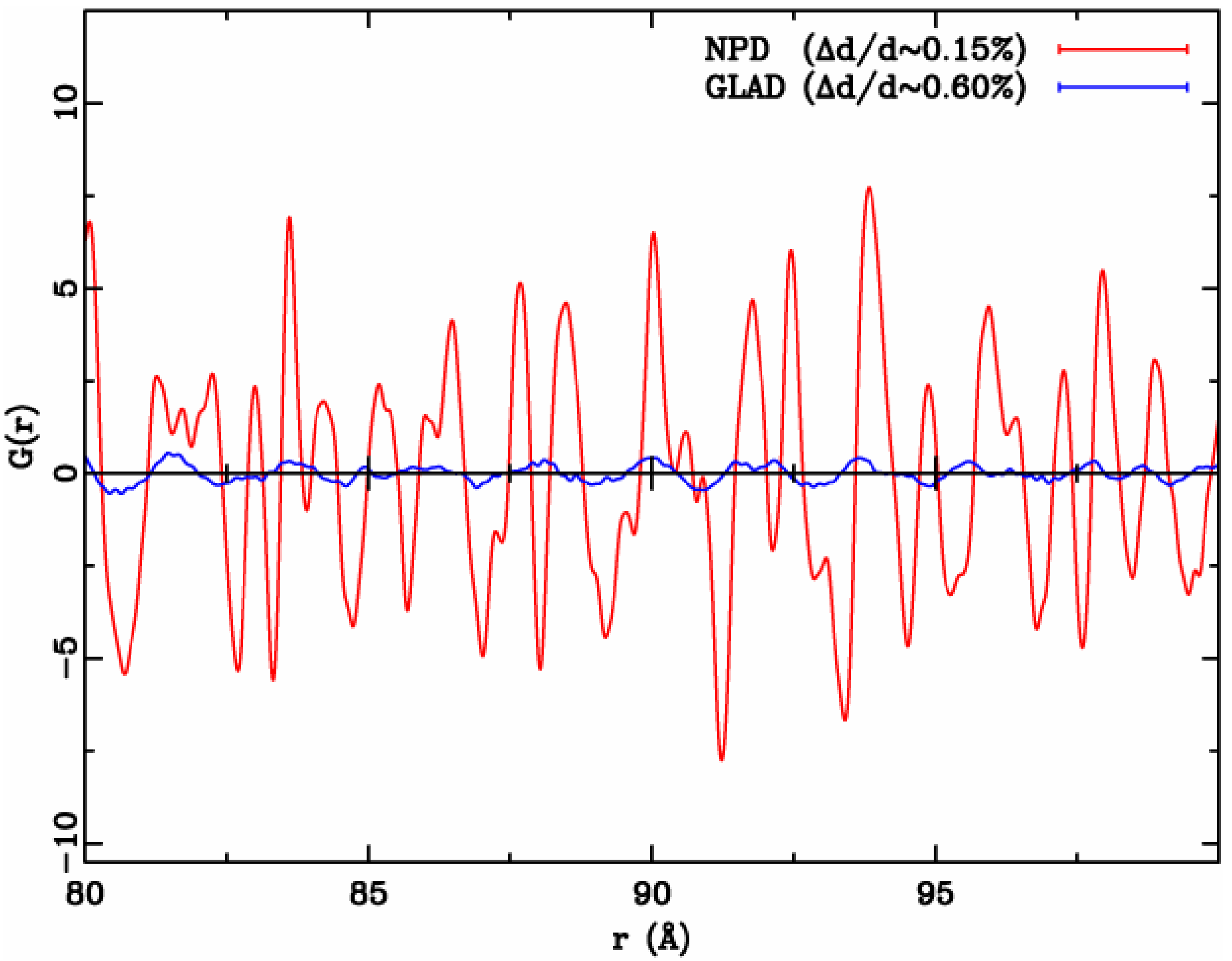


Termination of integral at Q_{max} results in convolution of G(r) with $\sin(Q_{max}\, r)/r$.

$ZnSe_{0.5}Te_{0.5}$ data collected on GEM terminated at 40 $Å^{-1}$ and 17 $Å^{-1}$

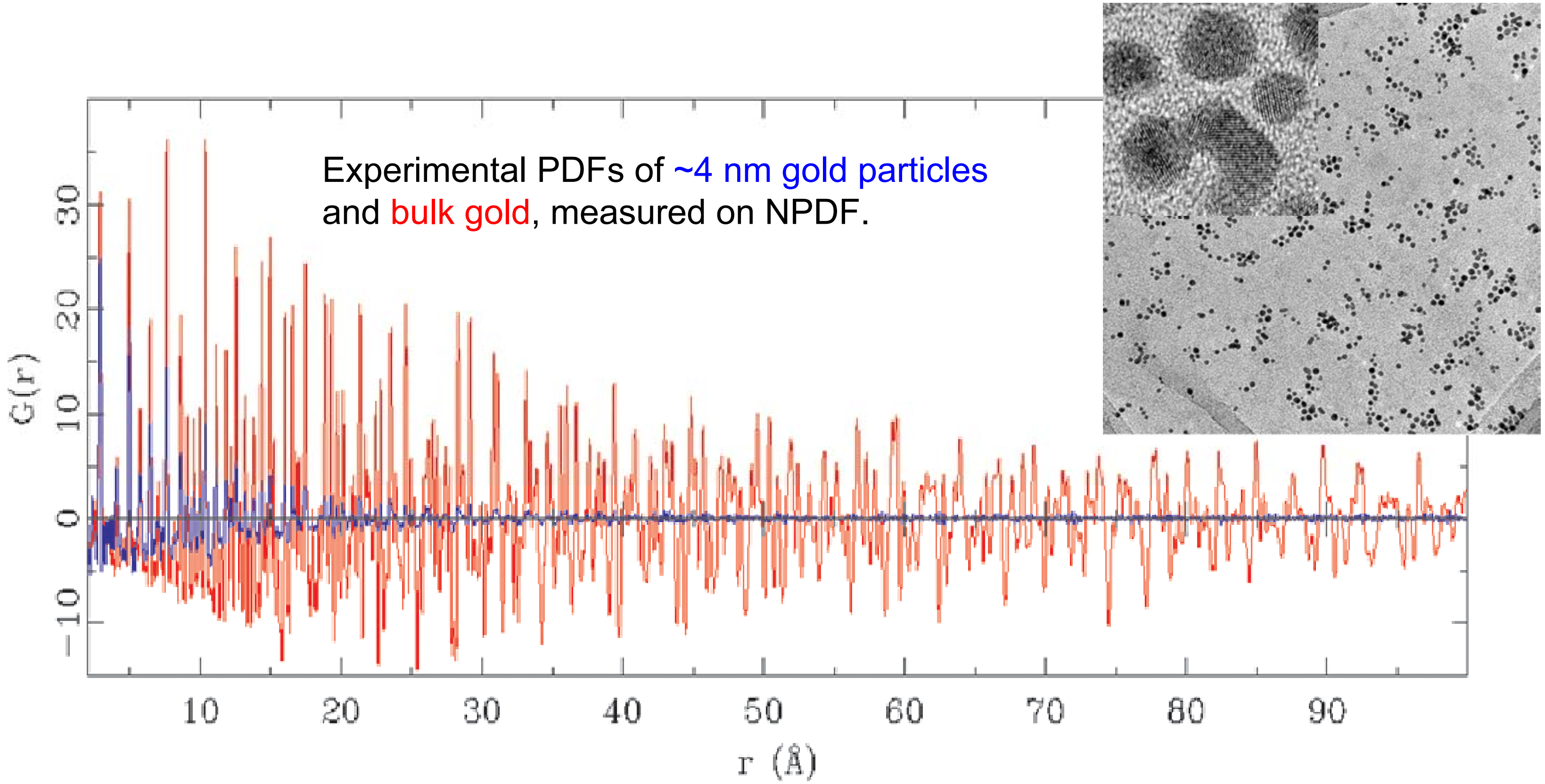
NN split unresolved at 17 $Å^{-1}$!

What makes a good PDF: Influence of Q resolution …



High Q resolution: Large *r* range (PDF dampened by *exp -(rΔQ)²/2)*)

Nano-PDF: Example gold nanoparticles



K.L. Page, Th. Proffen, H. Terrones, M. Terrones, L. Lee, Y. Yang, S. Stemmer, R. Seshadri and A.K. Cheetham, **Direct Observation of the Structure of Gold Nanoparticles by Total Scattering Powder Neutron Diffraction**, *Chem. Phys. Lett.* **393**, 385-388 (2004).

Experimental

Facilities

or

Where to measure a good PDF ?

Neutrons

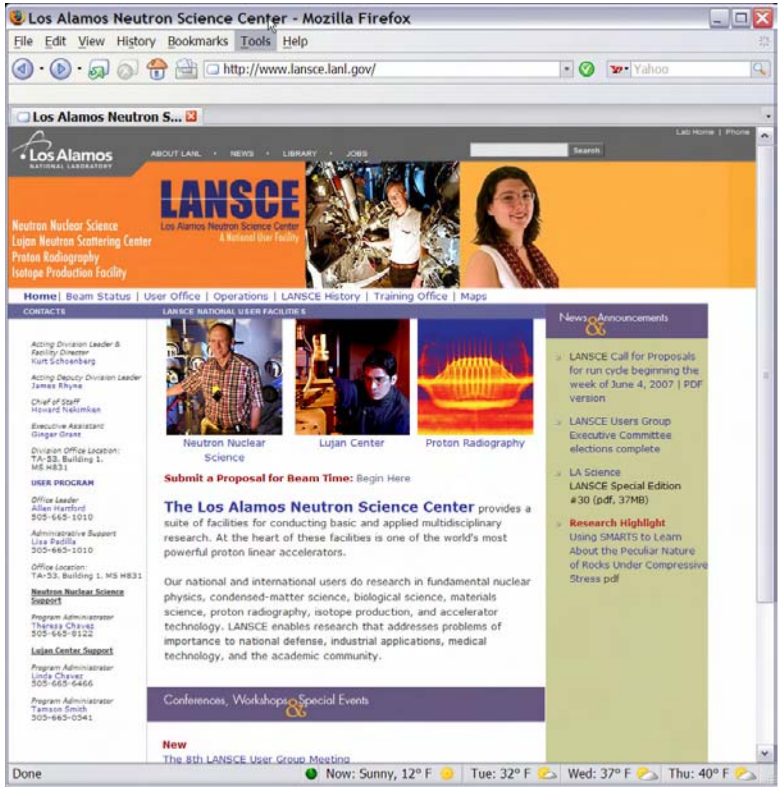
Facility overview

- **Spallation Neutron Sources**
  - Lujan Neutron Scattering Center, Los Alamos, USA
  - ISIS Pulsed Neutron and Muon Facility, Didcot, UK
  - IPNS, Argonne, USA
  - *Spallation Neutron Source, Oak Ridge, USA*
  - *Japan Proton Accelerator Research Complex, Tokai, Japan*
- **Synchrotron Sources**
  - Advanced Photon Source, Argonne, USA
  - ESRF, Grenoble, France
  - Many more ..

- **Links**
  - http://neutron.anl.gov/facilities.html
  - http://www-als.lbl.gov/als/synchrotron_sources.html

Facility Access

- Most facilities in the US (and Europe) run a open user program.
- Peer reviewed proposals.
- Tips for success:
  - **Check the facilities web sites.**
  - **Contact the instrument scientist before submitting a proposal online !**



Next LANSCE deadline
Feb. 18, 2007

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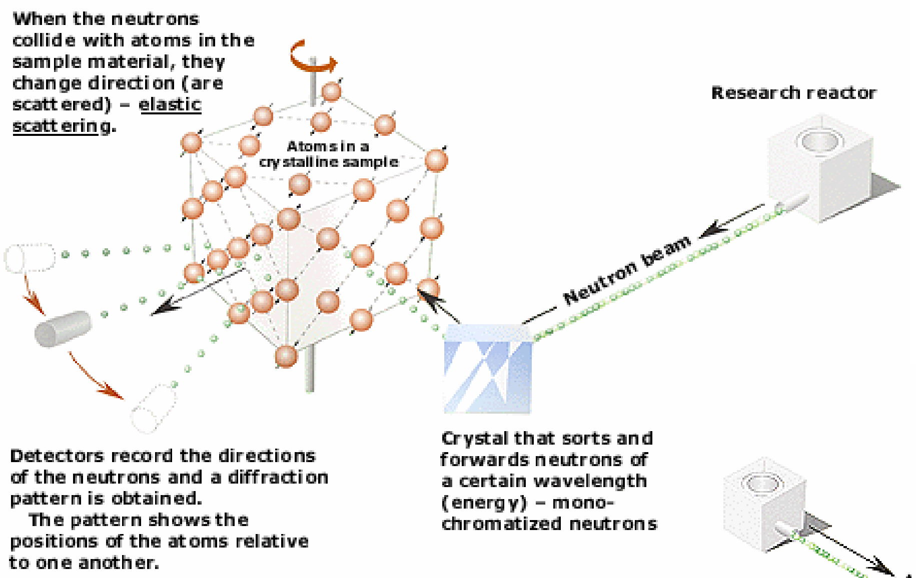
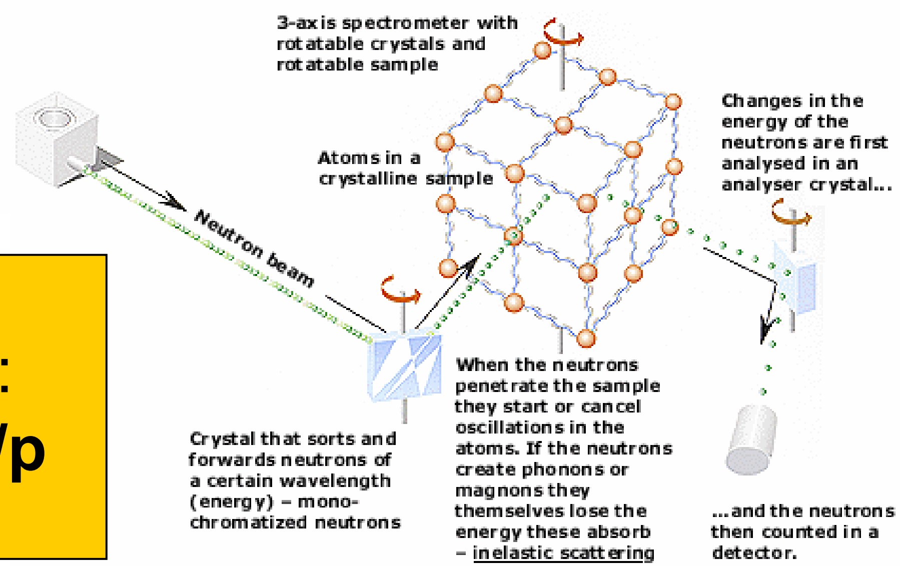
Neutrons ?

Neutrons show where the atoms are….



The 1994 Nobel Prize in Physics – Shull & Brockhouse

…and what the atoms do.

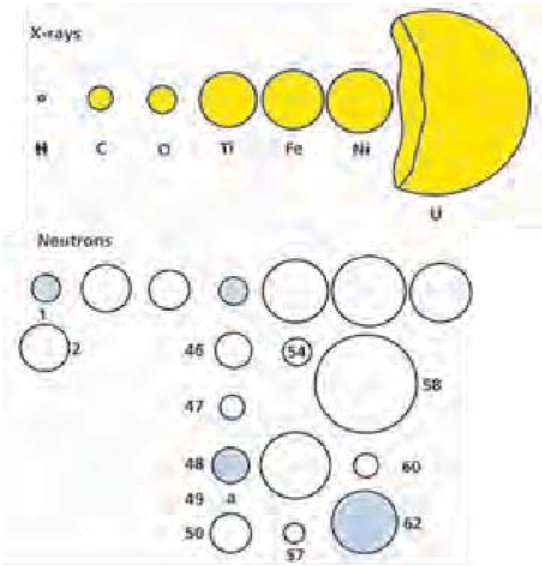


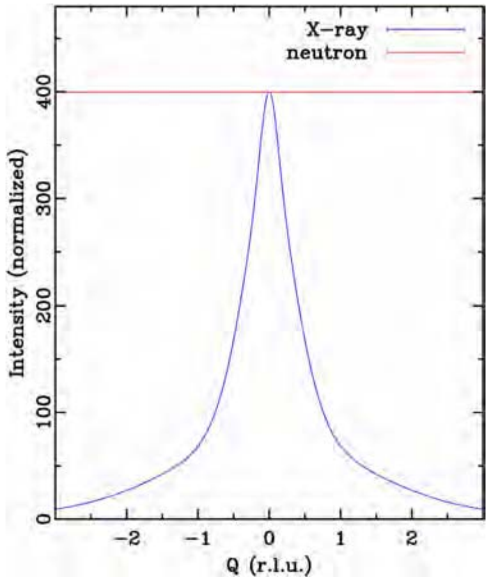
Wave nature of neutron:
de Broglie relation: λ**=h/p**

Neutrons vs. X-rays

- Sensitive to light atoms (e.g. H)
- Contrast by isotope substitution
- Easy sample environment (T,p,..)
- No ‘formfactor’ (good for PDF)
- Weak ⇒ large samples & long measuring times ..

X-ray and neutron scattering Lengths for selected elements.

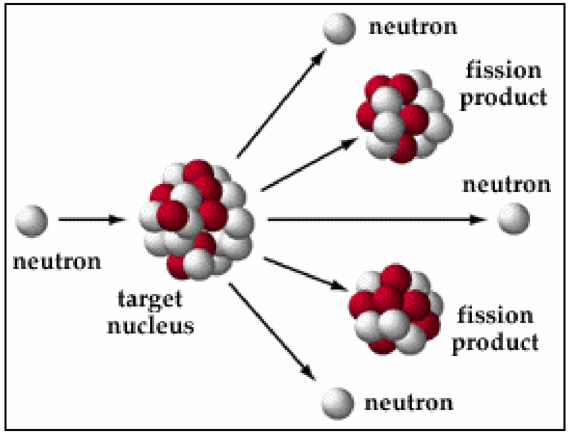




Scattering from single atom

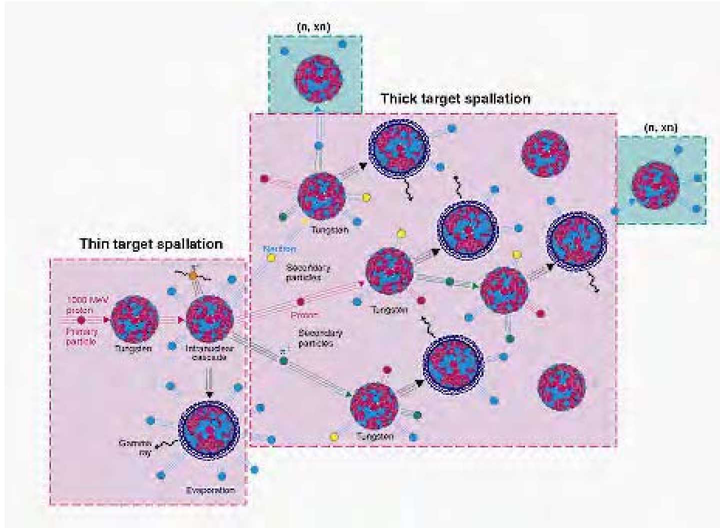
Neutron sources

- ***Reactor sources***



- Steady state
- Powder diffraction done using constant wavelength (**angle dispersive**)

- ***Spallation sources***



- Pulsed
- Powder diffraction done using time-of-flight technique (**energy dispersive**)

Los Alamos Neutron Science Center

Lujan Neutron Scattering Center

Proton Radiography

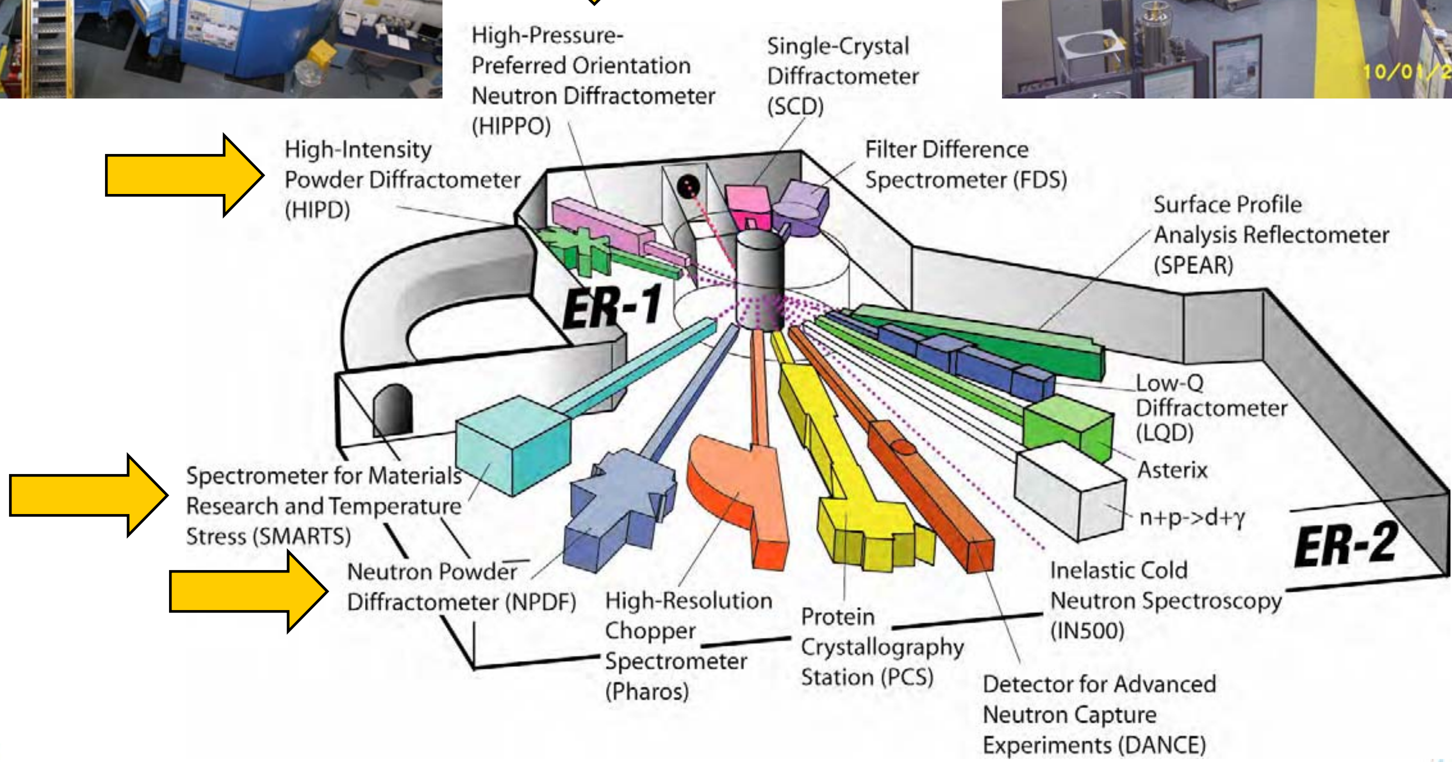
Proton Storage Ring

Weapons Neutron Research

800-MeV Linear Accelerator

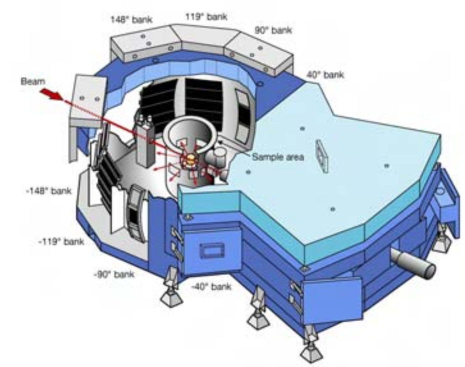
LANSCE Visitor's Center

Lujan Center: Powder diffractometers

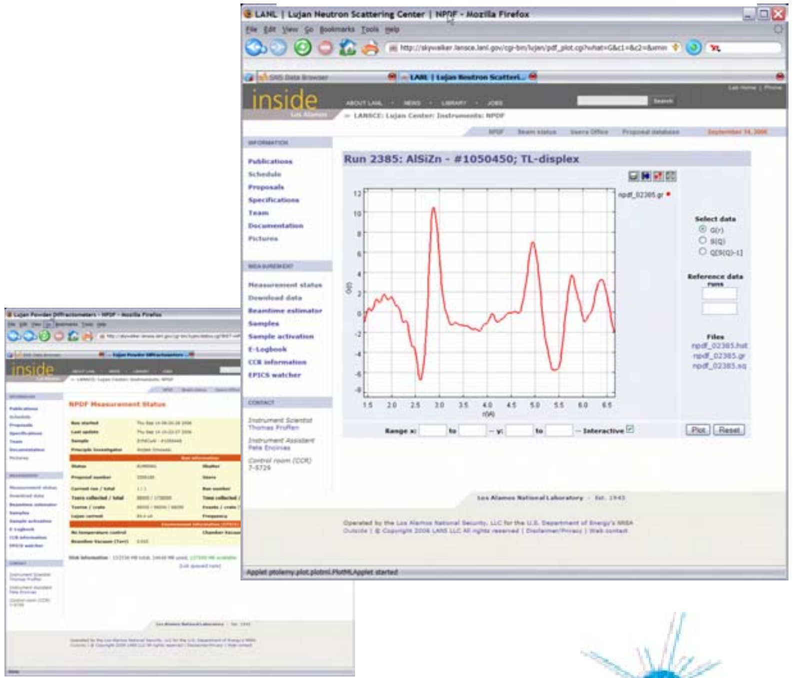


NPDF: Specialized for total scattering

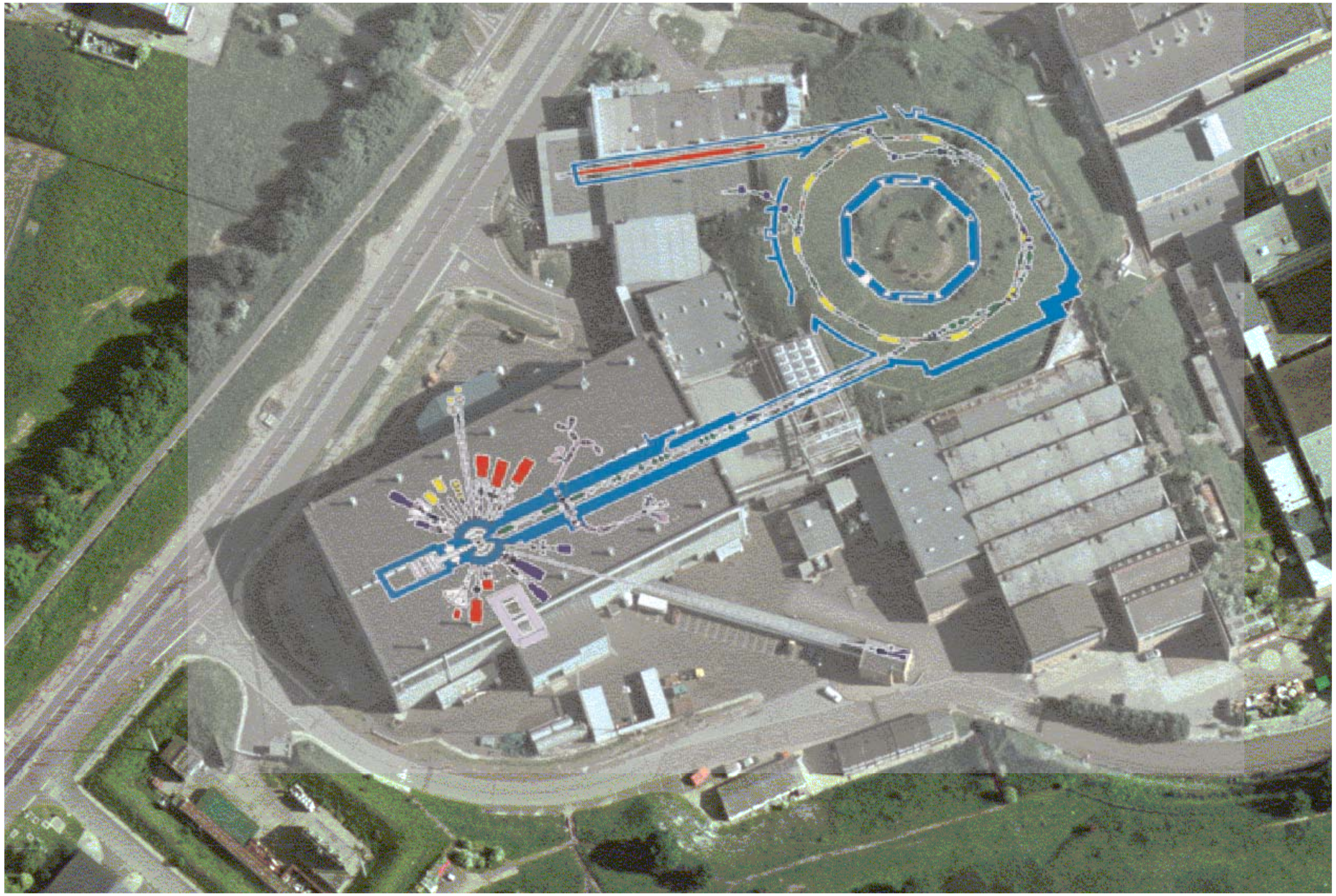
- Specifications
  - Upgrade finished Sep. 2002
  - L1: 32m, Q_{max}=50Å^{-1}, Δd/d=0.15%
  - Typical PDF measurement 1 - 4 hrs
  - Sample amounts down to 200 mg
  - Ancillary: 10K-1500K, soon: 0.5K, 11T



- Science
  - 95% PDF studies, hard matter
  - Many users *new* to PDF
  - Oversubscription in 2006: ~1.6
- Software
  - Web based instrument interface
  - Automatic creation of PDF
  - Integration in SNS data portal

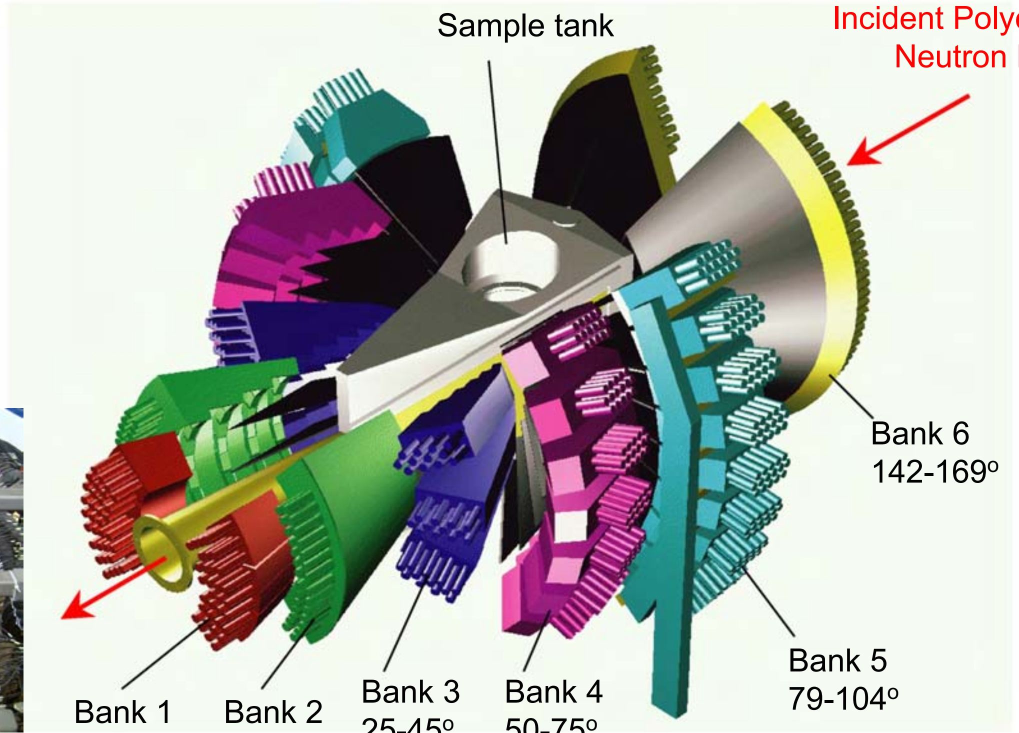


The ISIS Neutron Facility



ISIS: Powder diffractometers

- GEM
- POLARIS
- SANDALS



Neutron Instruments Summary

Instrument	*Resolution Δd/d*	*Q range*
Lujan Neutron Scattering Center http://www.lansce.lanl.gov/		
NPDF	0.15 – 0.8 %	0.85 – 51.1 Å^{-1}
HIPPO	0.40 – 5.0 %	0.13 – 52.4 Å^{-1}
HIPD	0.30 – 3.0 %	0.20 – 60.0 Å^{-1}
Intense Pulsed Neutron Source http://www.pns.anl.gov/		
GPPD	0.26 – 0.8 %	1.10 – 60.4 Å^{-1}
SEPD	0.34 – 4.7 %	0.60 – 47.3 Å^{-1}
GLAD	0.60 – 5.0 %	0.20 – 45.0 Å^{-1}
ISIS http://www.isis.rl.ac.uk/		
GEM	0.34 – 4.7 %	0.60 – 100 Å^{-1}
POLARIS	0.50 – 1.0 %	0.30 – 31.5 Å^{-1}
SANDALS	?	0.05 – 50.0 Å^{-1}

Experimental

Facilities

or

Where to measure a good PDF ?

X – r a y s

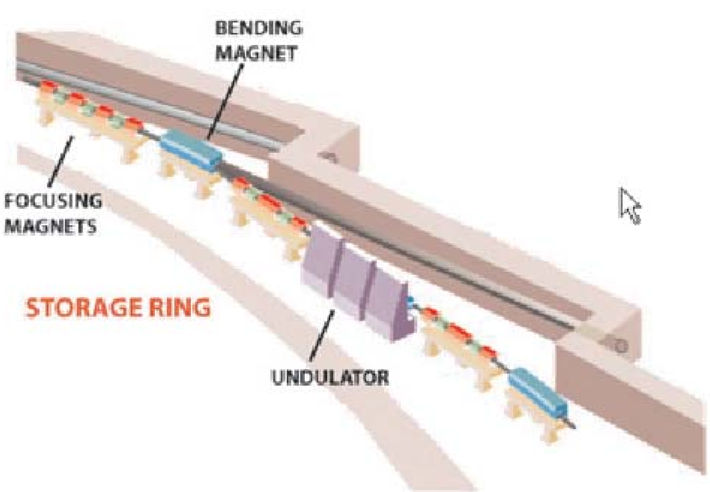
Searching for information on synchrotrons

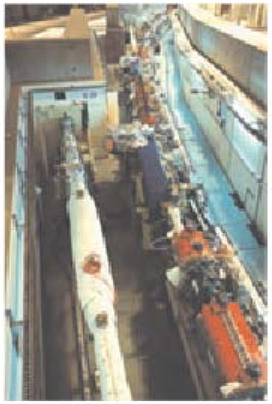
Advanced Photon Source
Argonne National Laboratory, USA

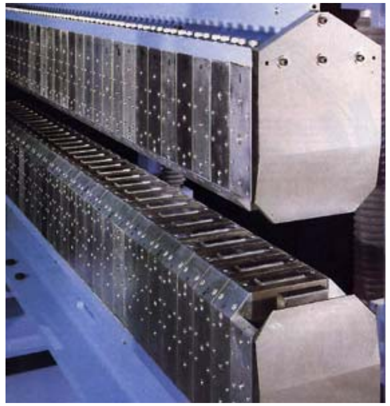
Wiggler

Synchrotron sources

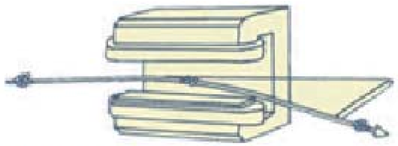
http://www.esrf.eu/AboutUs/GuidedTour/





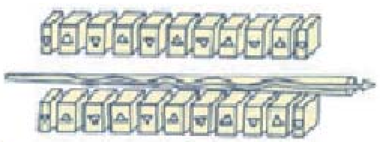


Bending magnets



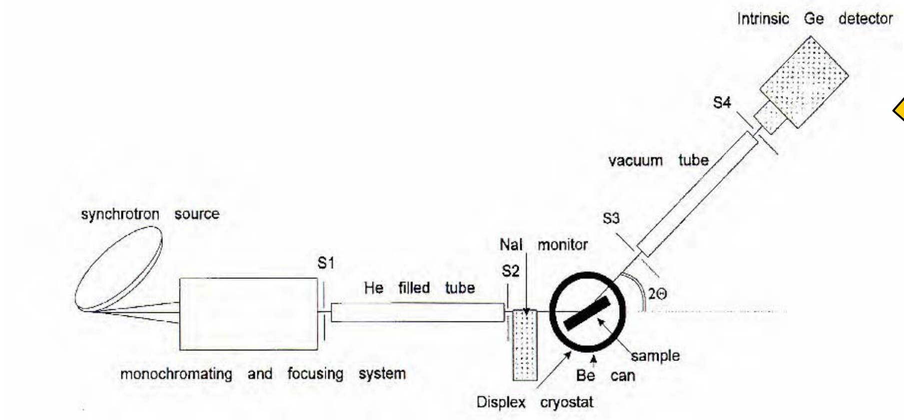
When the electrons pass through these magnets, they are deflected from their straight path by several degrees. This change in direction causes them to emit synchrotron radiation.

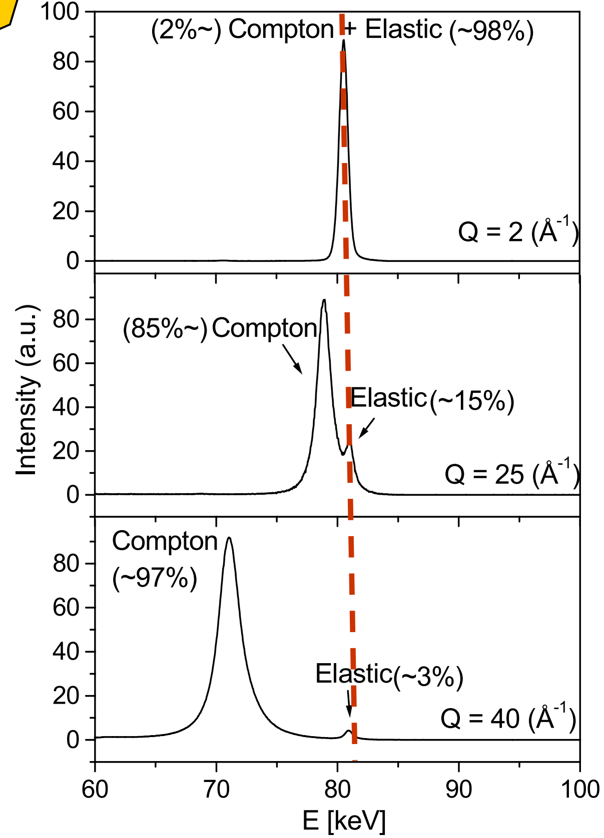
Undulators

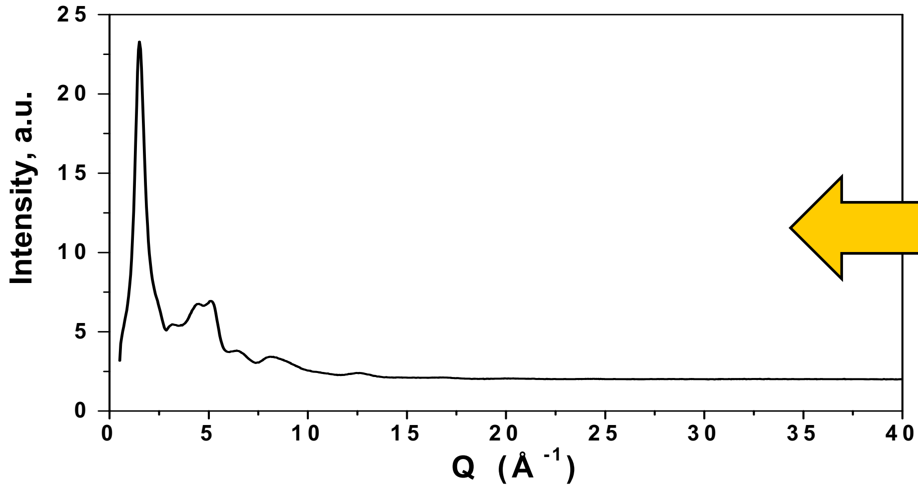


These magnetic structures, made up of a complex array of small magnets, force the electrons to follow an undulating, or wavy, trajectory. The beams of radiation emitted from the different bends overlap and interfere with each other to generate a much more intense beam of radiation than that generated by the bending magnets.

X-ray PDF: The traditional way







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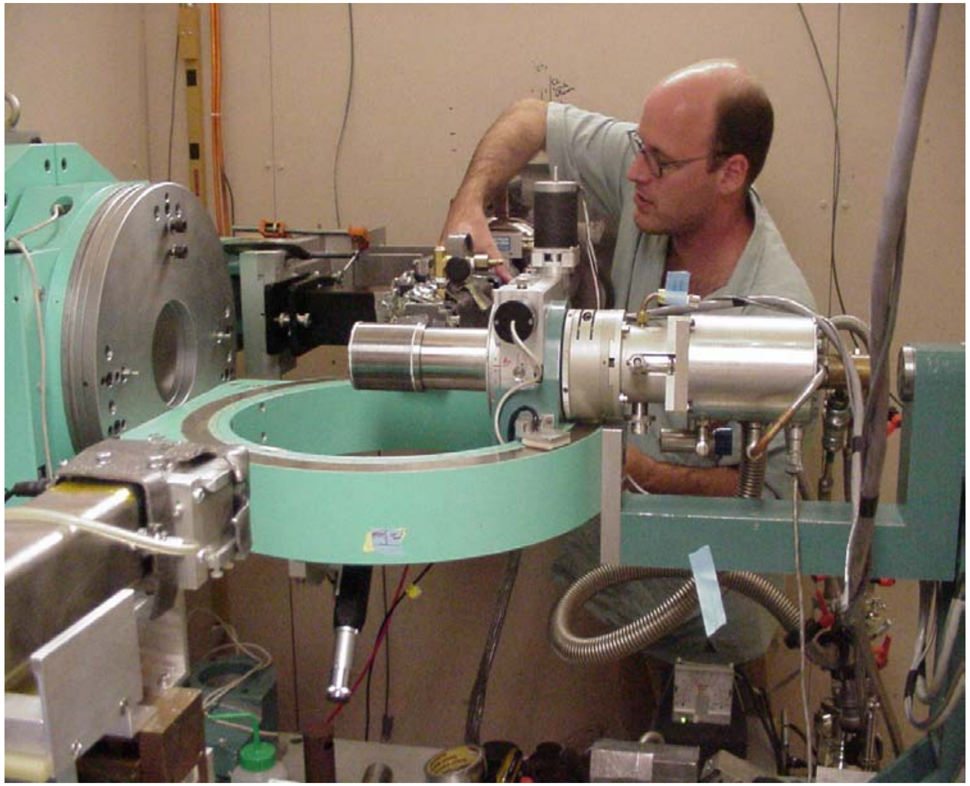
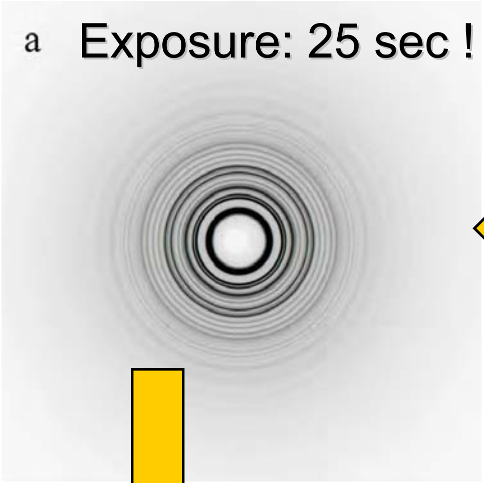
Valeri Petkov

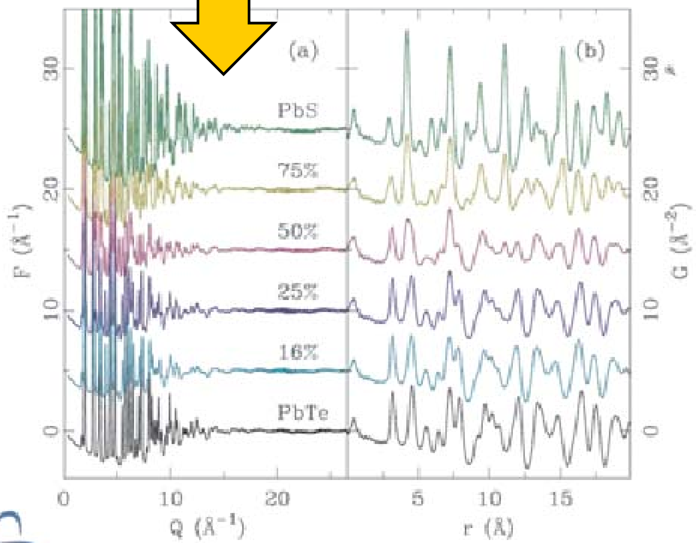
X-ray PDF: The traditional way

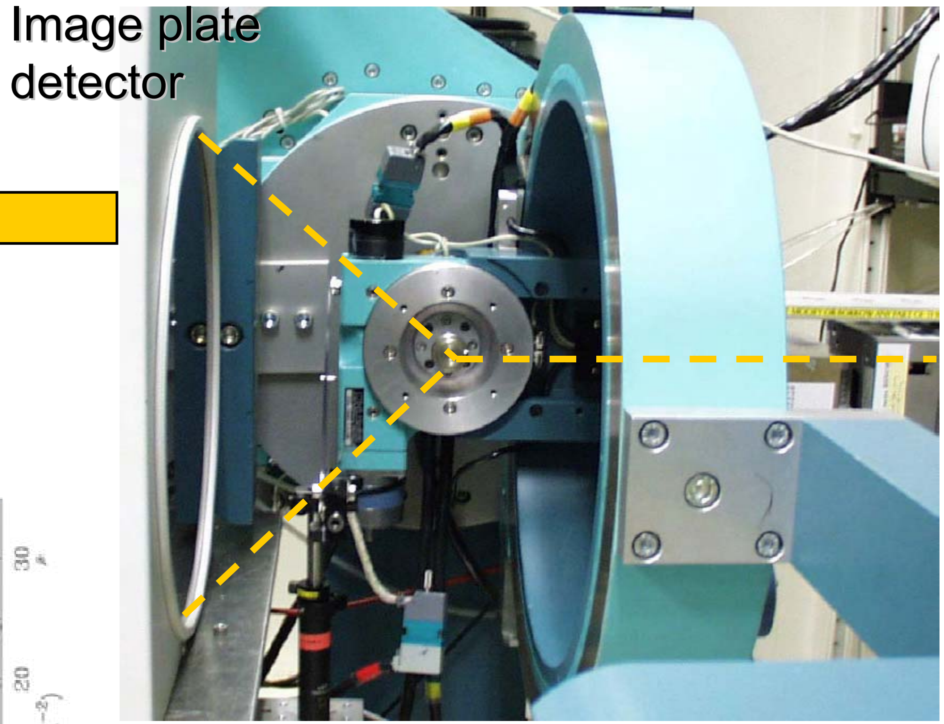
- Energy dispersive detector
- Step scans in Q
- Long counting times, especially at high Q.
- Typical collection time: **12-24 h**



X-ray PDF: The fast way





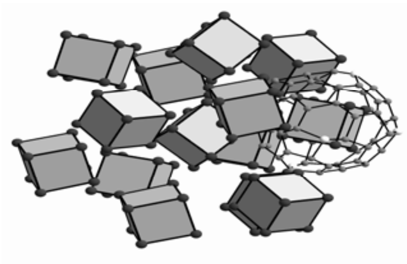


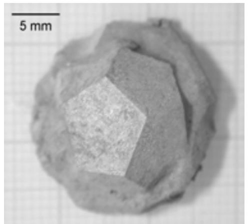
P.J. Chupas, X. Qiu, J.C. Hanson, P.L. Lee, C.P. Grey and S.J.L. Billinge, **Rapid-acquisition pair distribution function (RA-PDF) analysis**, *J. Appl. Cryst.* **36**, 1342-1347 (2003).

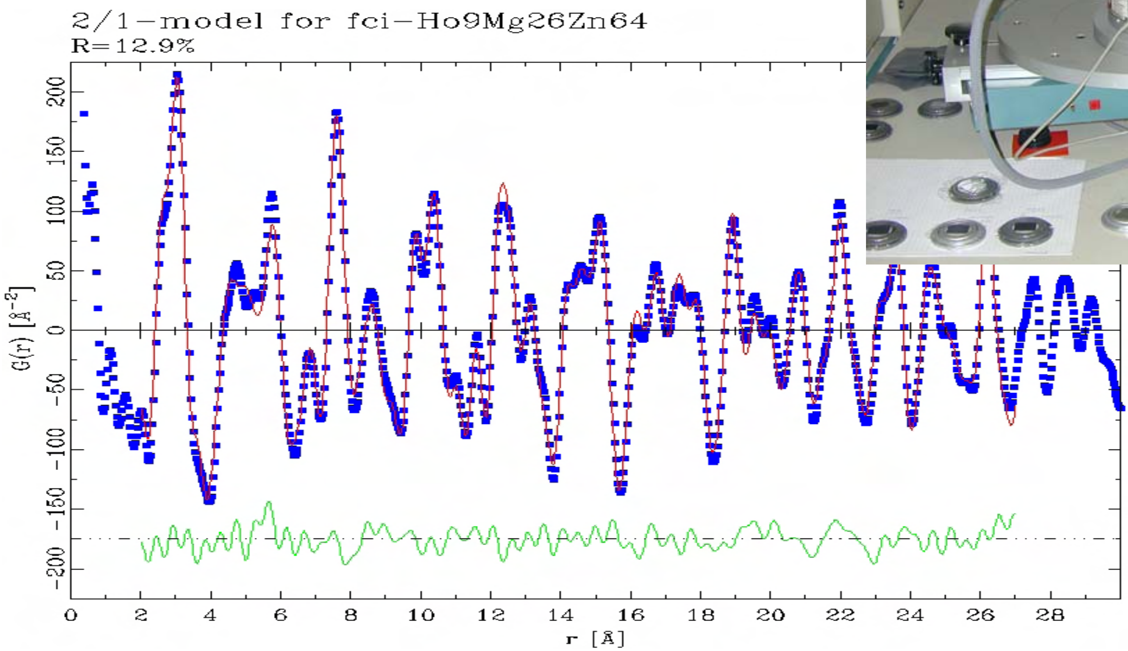
X-ray PDF: In house measurements

fci-Ho-Mg-Zn

Huber Gunier diffractometer
$Q_{max} = 13.5 Å^{-1}$







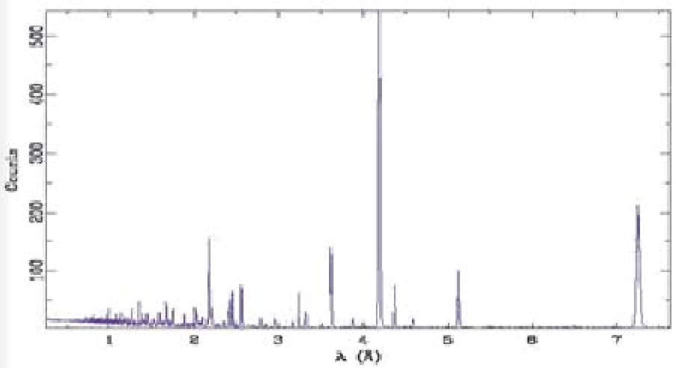
Brühne et al., *Z. Kristallogr.* **219** (2004) 245-258

Data Reduction

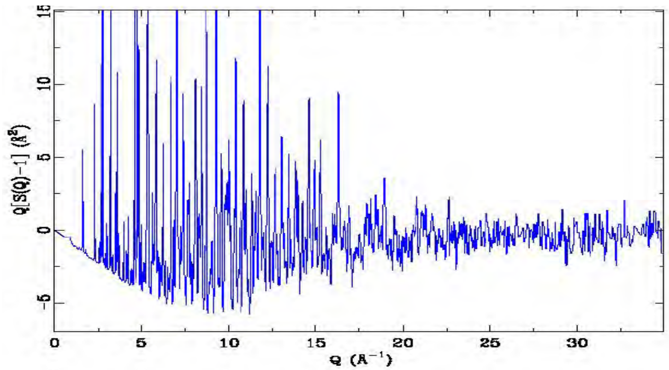
or

How difficult is the processing of total scattering data ?

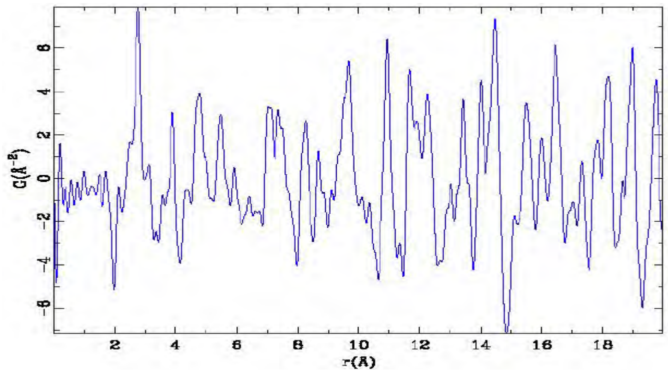
Neutron data processing



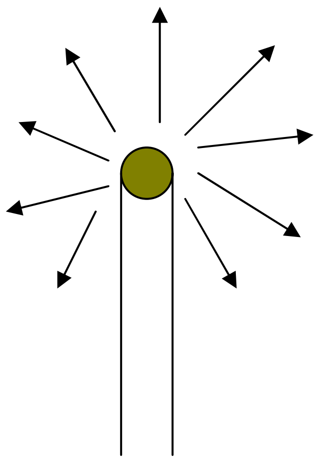
Corrections



$$G(r) = \frac{2}{\pi}\int_0^\infty Q[S(Q)-1]\sin Qr dQ$$



Cylindrical Time-Of-Flight geometry (energy dispersive)



Typical characterization runs

- Empty instrument (B)
- Empty Container (C)
- Empty Container background (CB)
- Vanadium (V)
- Vanadium background (VB)
- Sample (S)

S_{corr}=[(S-SB)-α(C-CB)]/[V-VB]

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Neutron corrections

- TOF $\rightarrow$ Q conversion
- Deadtime correction
- Absorption
- Multiple scattering
- Normalization
- Placzek correction
- Parasitic scattering

Conversion from time of flight to Q depends on path lengths. Can be refined, e.g. GSAS:

$$TOF = DIFC\ d + DIFA\ d^2 + T_0$$

$$DIFC = 252.816 \cdot 2\sin\theta\left(L_1 + \sqrt{L_2^2 + L_3^2/16}\right)$$

L_1: primary flight path (source – sample)
L_2: secondary flight path (sample – detector)
L_3: detector height

Neutron corrections

- TOF → Q conversion
- Deadtime correction
- Absorption
- Multiple scattering
- Normalization
- Placzek correction
- Parasitic scattering

> After an event is recorded the detector generally needs some time to reset itself and the detector electronics to process the pulse. Neutrons arriving during this dead-time are not recorded.

> Count-rate dependent.

> Important at high count-rates.

> Corrected analytically.

Neutron corrections

- TOF $\rightarrow$ Q conversion
- Deadtime correction
- Absorption
- Multiple scattering
- Normalization
- Placzek correction
- Parasitic scattering

> Depends on wavelength and elements present.

> Depends on path sample $\Rightarrow$ *PDFgetN corrects for cylindrical geometry !*

Neutron corrections

- TOF $\rightarrow$ Q conversion
- Deadtime correction
- Absorption
- Multiple scattering
- Normalization
- Placzek correction
- Parasitic scattering

> Neutrons that are scattered twice or more in the sample need to be corrected.

> Effect can be as big as 10% !

> Corrected theoretically.

Neutron corrections

- TOF $\rightarrow$ Q conversion
- Deadtime correction
- Absorption
- Multiple scattering
- Normalization
- Placzek correction
- Parasitic scattering

- Incident beam is monitored to normalize for the total neutron flux.
- Incident neutron spectrum is corrected via vanadium characterization run.
- The condition $S(Q) \rightarrow 1$ for high Q is used to normalize for sample size and density.

Neutron corrections

- TOF $\rightarrow$ Q conversion
- Deadtime correction
- Absorption
- Multiple scattering
- Normalization
- Placzek correction
- Parasitic scattering

> Inelastically scattered neutrons are counted in the incorrect Q-bin in the time of flight neutron method.
> Corrected theoretically (?)
> Strictly only valid for liquids.
> Needs new approach !

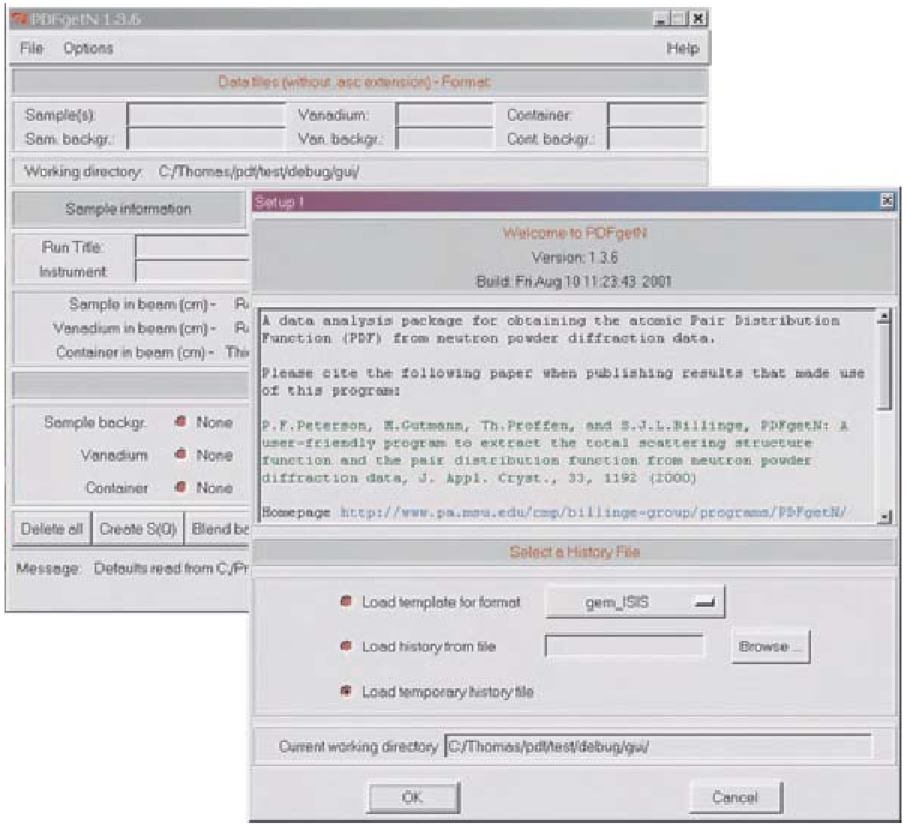
Neutron corrections

- TOF $\rightarrow$ Q conversion
- Deadtime correction
- Absorption
- Multiple scattering
- Normalization
- Placzek correction
- Parasitic scattering

- Measured (background and empty can) and subtracted after suitable normalization.
- Reproducible background key to success !

Software: PDFgetN

- Based on GLASS package.
- Graphical users interface & integrated plotting.
- Supports most TOF neutron powder file formats.
- Records all processing parameters as part of output files G(r) and S(Q).
- Runs on Windows 95/98/NT/2000 and UNIX

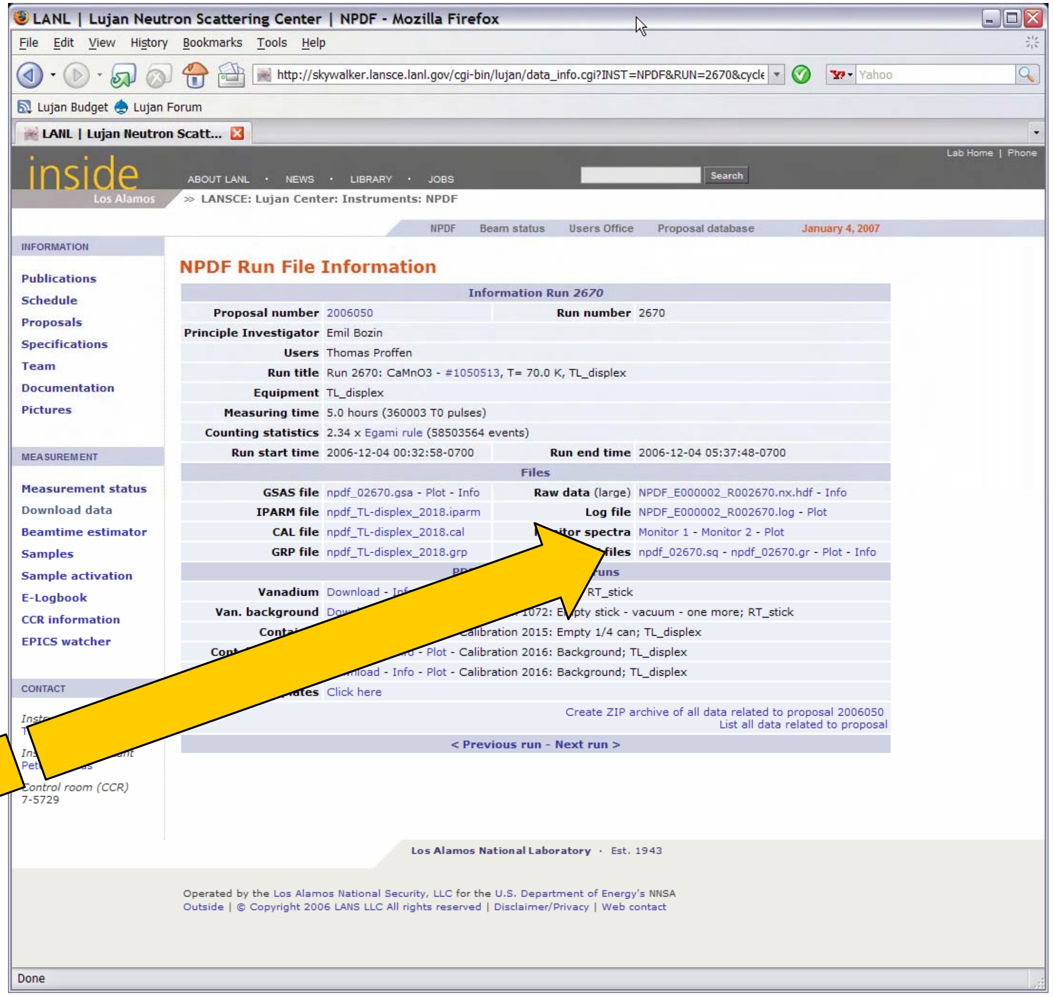


http://pdfgetn.sourceforge.net

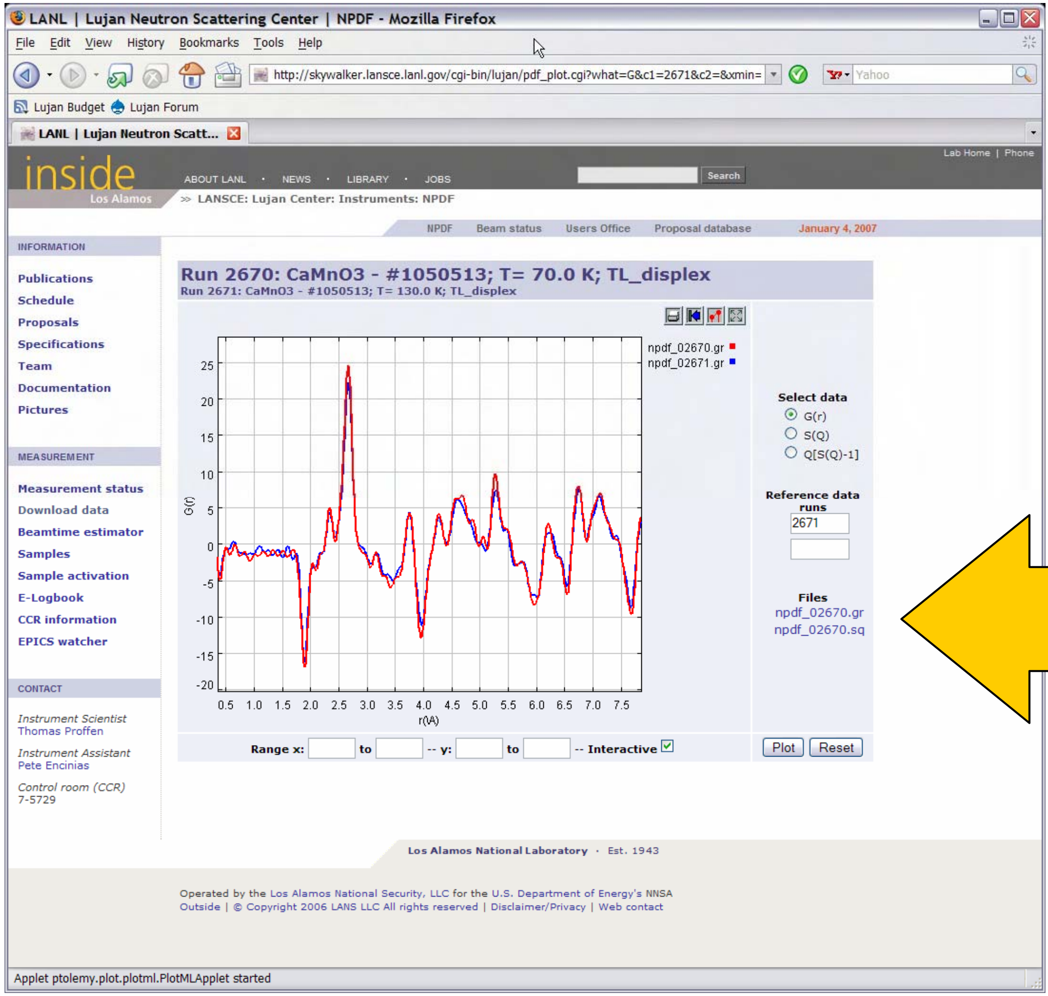
P.F. Peterson, M. Gutmann, Th. Proffen and S.J.L. Billinge, **PDFgetN: A User-Friendly Program ..**, *J. Appl. Cryst.* **33**, 1192 (2000).

Software: NPDF creates PDF automatically !

- S(Q) and G(r) automatically generated.
- Access via instrument web site.
- Click PDF information

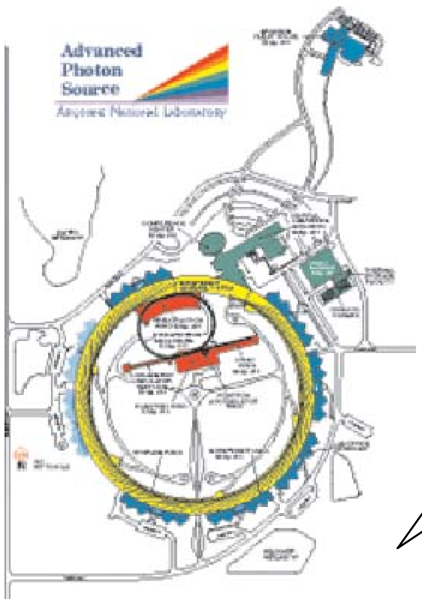


Software: NPDF creates PDF automatically !

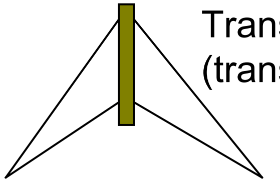


Download

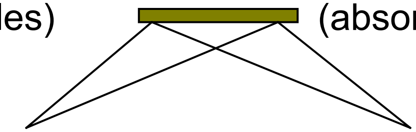
X-ray data processing



- **In house X-ray experiments**:
  - Easy.
  - Low *r* resolution, slow (and/or poor statistics).
  - *Mo*: Q_{max} ~ 17Å^{-1}, *Ag*: Q_{max} ~ 20Å^{-1}.
  - Flat plate transmission or reflection geometry.



Transmission
(transparent samples)



Reflection
(absorbing samples)

- **Synchrotron experiments**:
  - Little precious beamtime.
  - High energy X-rays (Q_{max} > 60Å^{-1}).
  - High intensity (x 10,000 times stronger).
  - Parallel beam optics.
  - Generally flat plate transmission geometry.
  - New rapid PDF setup (PDF in seconds).

X-ray corrections

- $2\Theta \rightarrow Q$ conversion
- Deadtime correction
- Absorption
- Multiple scattering
- Normalization
- Compton scattering
- Polarization correction
- Parasitic scattering

> Data from some diffractometers might require a conversion from scattering angle 2Θ to momentum transfer Q !

> Uncertainties: Offset 2Θ, wavelength

X-ray corrections

- $2\Theta \rightarrow Q$ conversion
- Deadtime correction
- Absorption
- Multiple scattering
- Normalization
- Compton scattering
- Polarization correction
- Parasitic scattering

➢ Incident beam is monitored to normalize for the total X-ray flux (especially at the synchrotron).

➢ Normalization for angle depended change of illuminated sample volume.

➢ The condition $S(Q) \rightarrow 1$ for high Q is used to normalize for sample size and density.

X-ray corrections

- $2\Theta \rightarrow Q$ conversion
- Deadtime correction
- Absorption
- Multiple scattering
- Normalization
- Compton scattering
- Polarization correction
- Parasitic scattering

> Compton scattering is inelastic incoherent scattering.

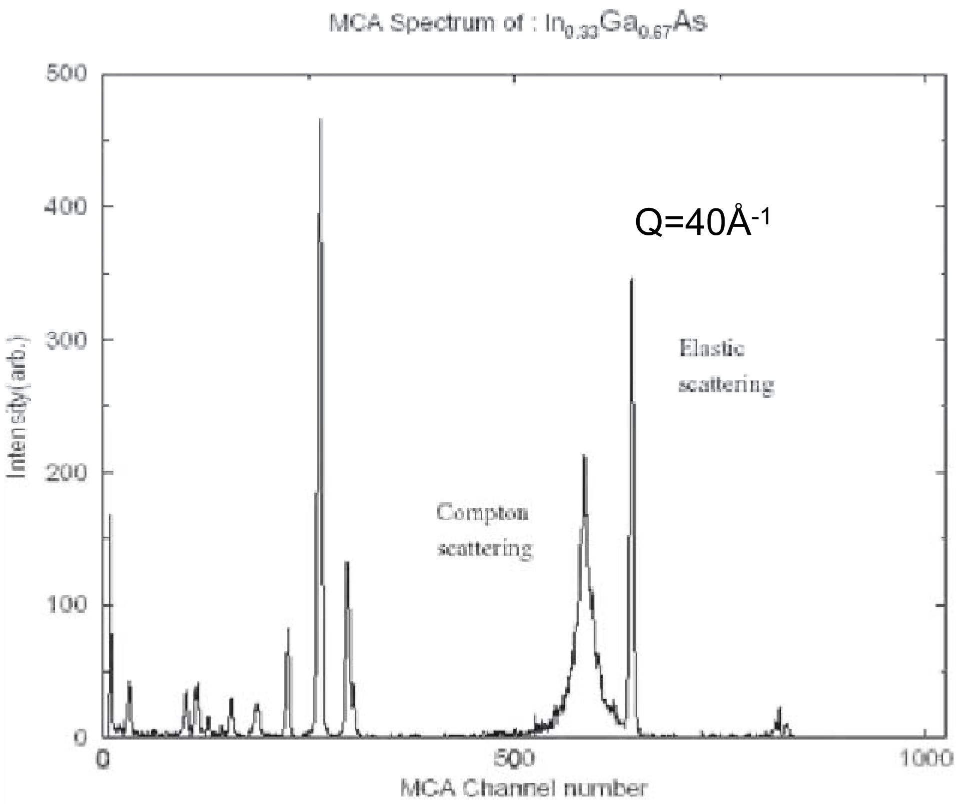
> Calculated theoretically or measured and subtracted.

X-ray corrections

- $2\Theta \rightarrow Q$ conversion
- Deadtime correction
- Absorption
- Multiple scattering
- Normalization
- Compton scattering
- Polarization correction
- Parasitic scattering

➢ Intensity depends on beam polarization which depends on beamline optics (monochromators etc.) and angle.

X-ray corrections: Removal of Compton scattering

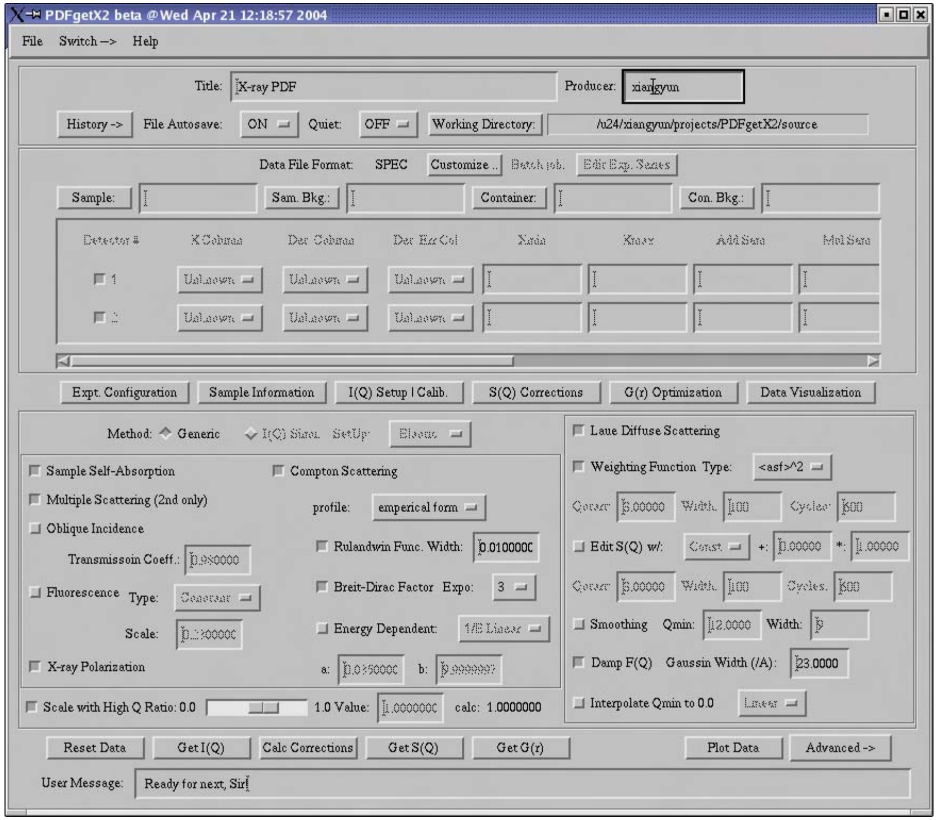


- Energy sensitive detector (e.g. Ge detector) allows separation of Compton scattering at higher Q.
- **Modes:**
  - SCA: Electronic windows to separate elastic channel
  - MCA: recording of complete spectrum at each measured point → software integration.

Software: PDFgetX2

X. Qiu, J. W. Thompson, and S. J. L. Billinge, *J. Appl. Cryst.* **37**, 678-678

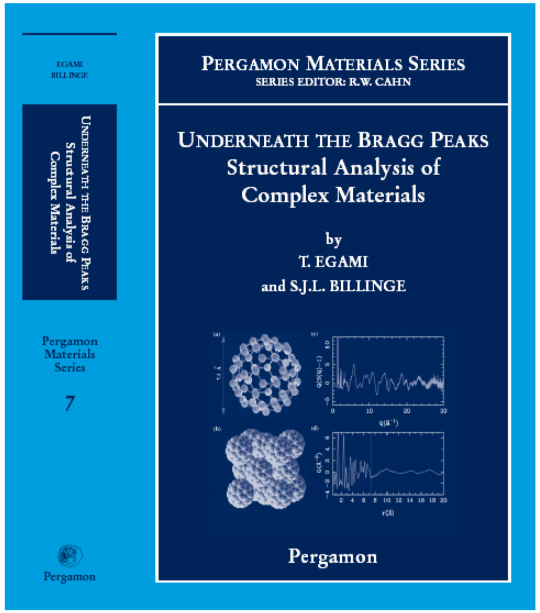
- Reads SPEC files.
- Supports MCA and SCA data.
- Integrated plotting of various corrections applied.
- Tools for merging scans.
- Runs on Windows and UNIX. Based on IDL.



http://www.pa.msu.edu/cmp/billinge-group/programs/PDFgetX2/

Summary

- Total scattering data processing is becoming routine.
- ‘Normal’ powder diffraction experiment can yield PDF as well.
- Dedicated instruments
  - NPDF
  - RA-PDF at APS



http://www.totalscattering.org


Thank you