Atomic Structure of Materials with Nano-Scale Coherence

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Advances in Neutron and X-ray Facilities

- Source intensity and brightness greatly improved.
- Not only the sources but detector systems have through a dramatic change.
- By using large detector arrays (PSD) a large portion of total angle is covered.
- Amount of data are 10^{6-9} bytes, producing a revolutionary improvement in data quality and statistics.
- We should focus on extracting more information from this vast amount of data, particularly on the **medium-range order**.

Nano-scale probes

- Small angle scattering
  - Only the size and density difference; attractive properties often originate from different structure
- Scanning probes (STM-AFM)
  - Only 2-d surface structure
- TEM
  - Averaged over the sample thickness
- Local probes (EXAFS, NMR)
  - Only the nearest neighbors
- Conventional diffraction
  - Above 5 nm
- **This leaves a gap for 0.5 – 5 nm range**

Atomic pair distribution function (PDF) Method.

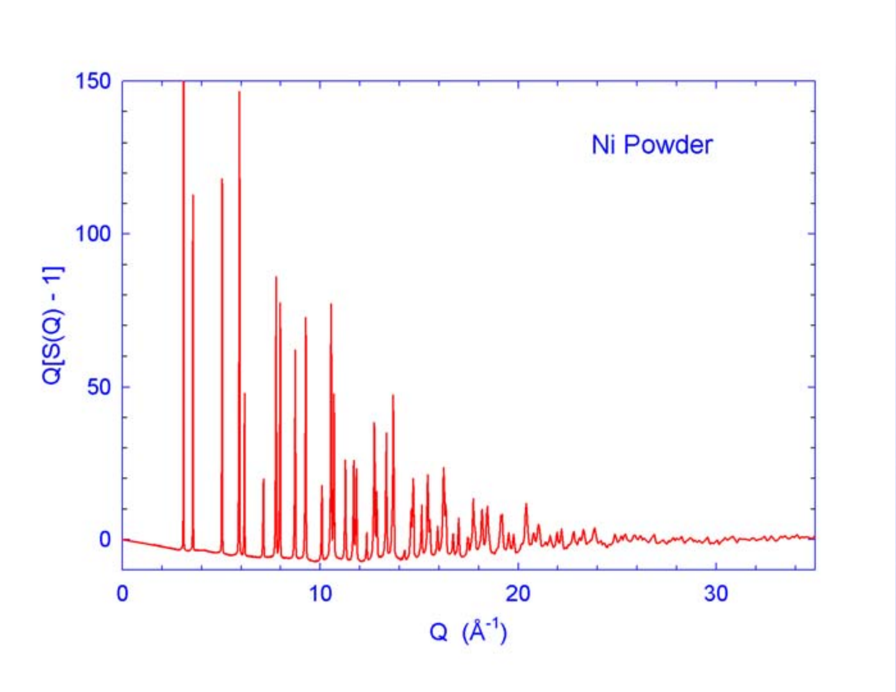
X-ray or neutron scattering intensity is Fourier-transformed to give distribution of inter-atomic distances in a real space.

$$\rho(r) = \rho_0 + \frac{1}{2\pi^2 r}\int_0^\infty [S(Q)-1]\sin(Qr)Q\,dq$$

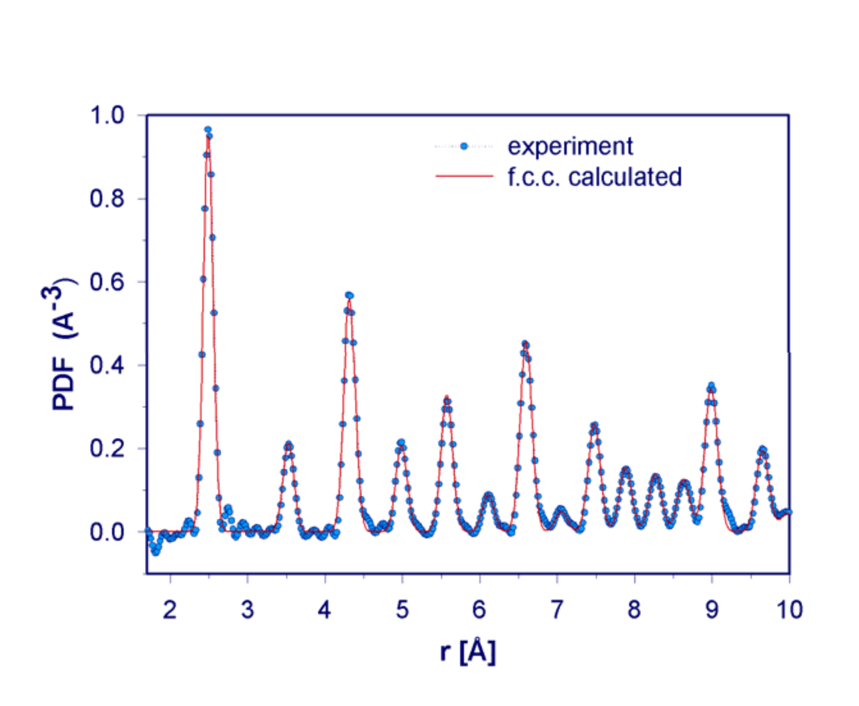
$Q=4\pi \sin\Theta/\lambda$, $S(Q)$ structure function (normalized diffraction intensity).

Used for the study of glasses and liquids. Limitation in Q has been a problem, but solved by synchrotron radiation.

Local Structure by Atomic Pair-Density Function (PDF)



⇒ *FT*

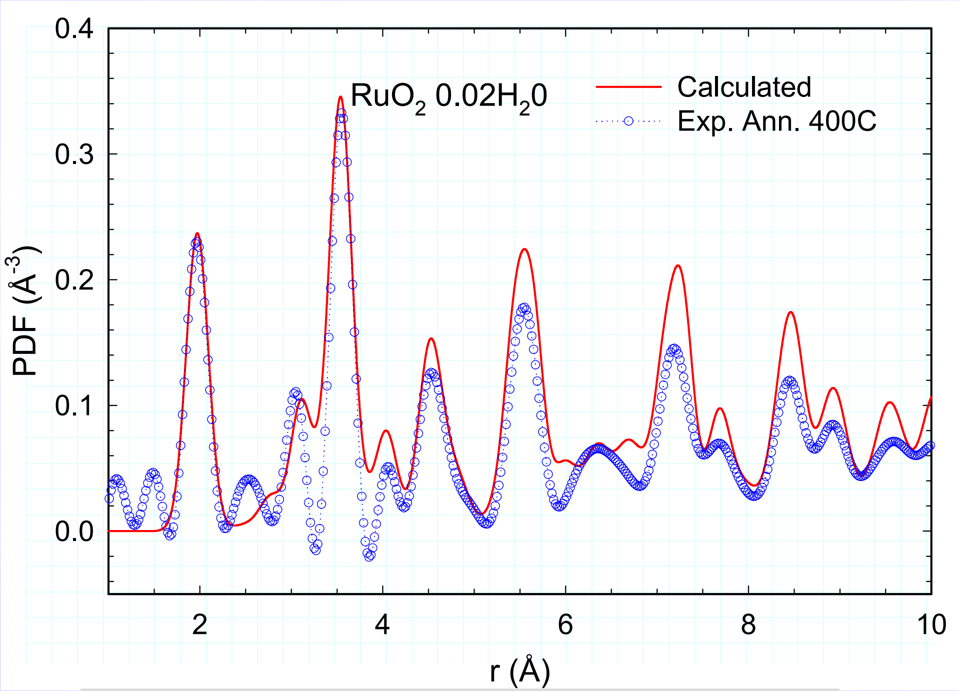


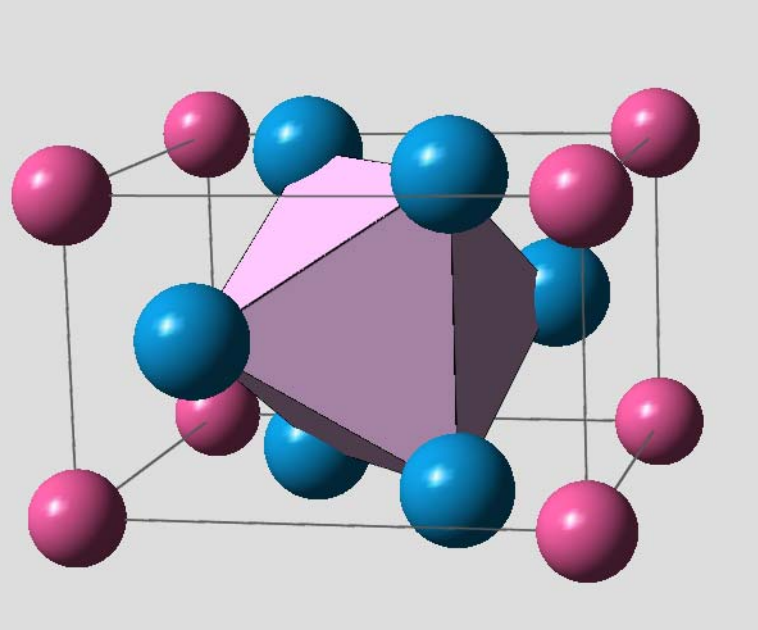
- ***Distribution of distances between atoms, can describe local structural deviations.***
- ***"Underneath the Bragg Peaks", T. Egami and S. J. L. Billinge (Pergamon Press, Oxford, 2003).***

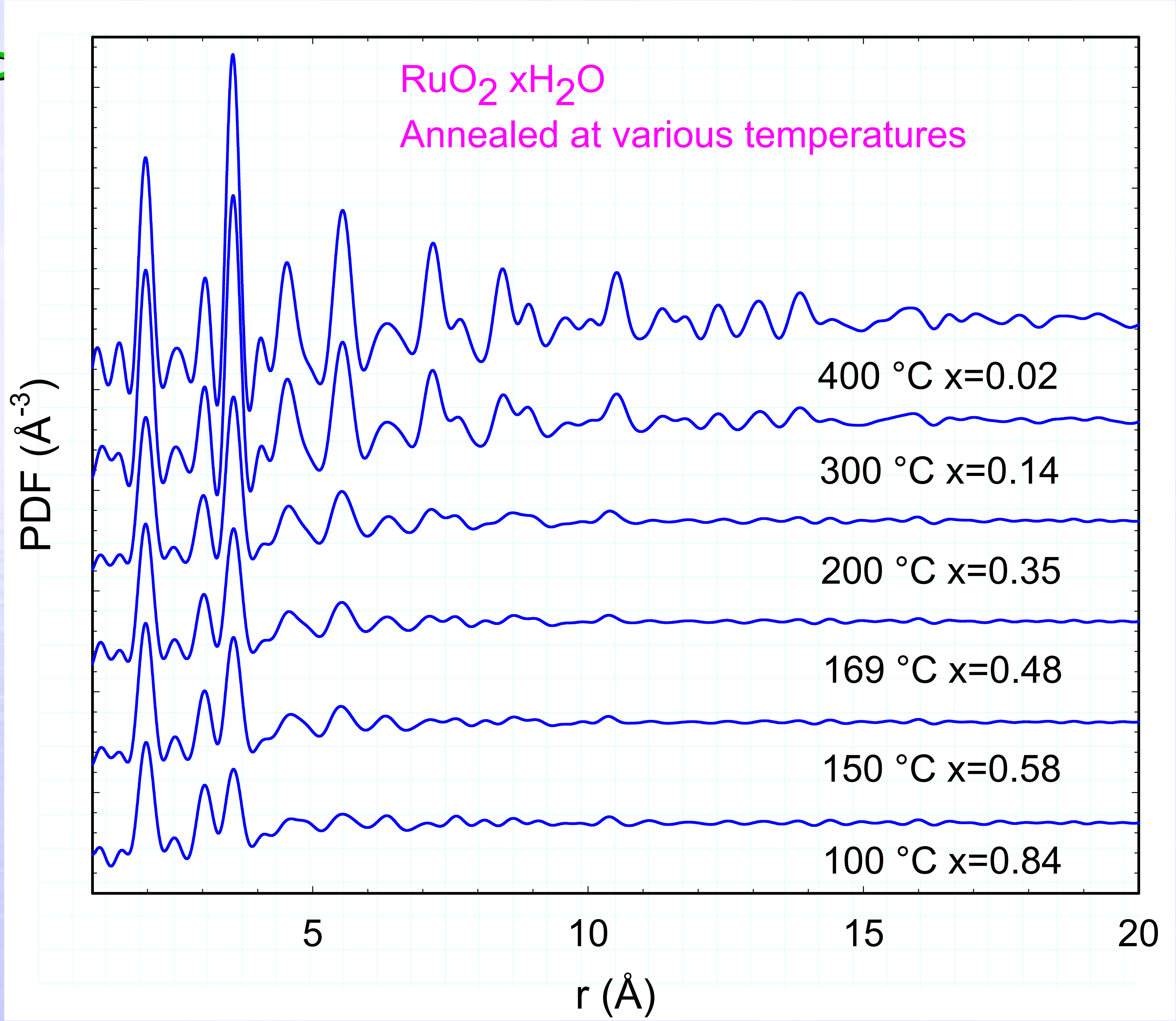
Nano-Particles used regularly by chemical industry;

RuO_xH_y ($RuO_2 \cdot xH_2O$)

- Anode for Direct Methanol Fuel Cell
- Nano-particles with addition of water.



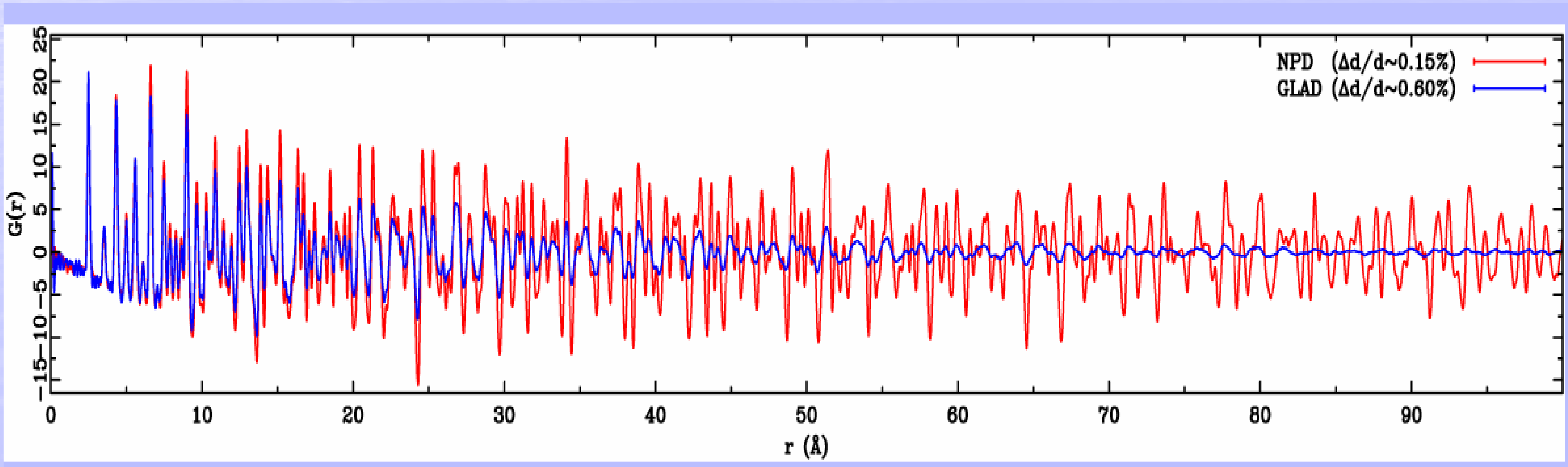




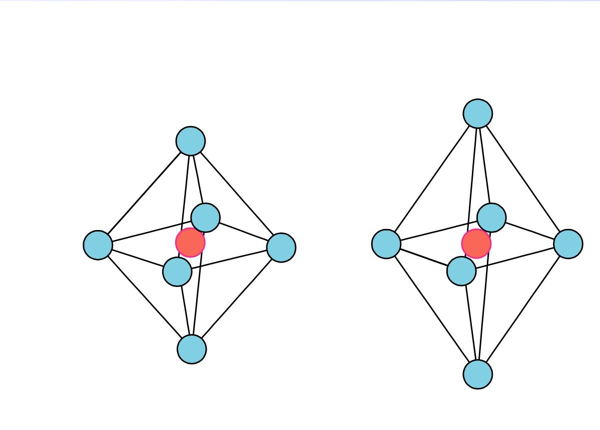
RuO2 xH2O
Annealed at various temperatures
400 °C x=0.02
300 °C x=0.14
200 °C x=0.35
169 °C x=0.48
150 °C x=0.58
100 °C x=0.84
PDF (Å-3)
5
10
15
20
r (Å)

Requirement for Successful PDF Study

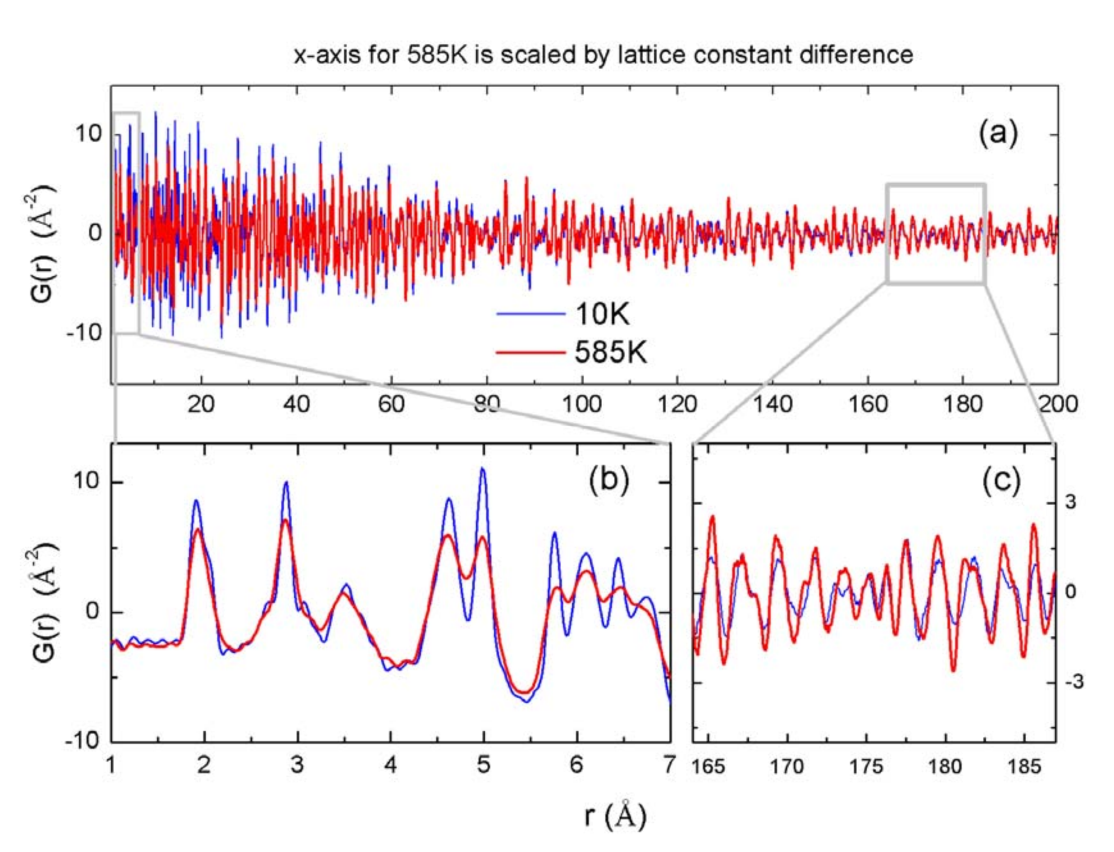
- Wide range of *Q*: $Q_{max} > 35$ Å^{-1} or more
- High intensity: Total count 10^7 or more
- High *Q*-resolution: $\Delta Q/Q < 10^{-3}$
- Pulsed neutron, or high-energy X-ray diffraction
  - Incident energy > 100 keV
  - Use of an image plate



Orbital Frustration in $LiNiO_2$



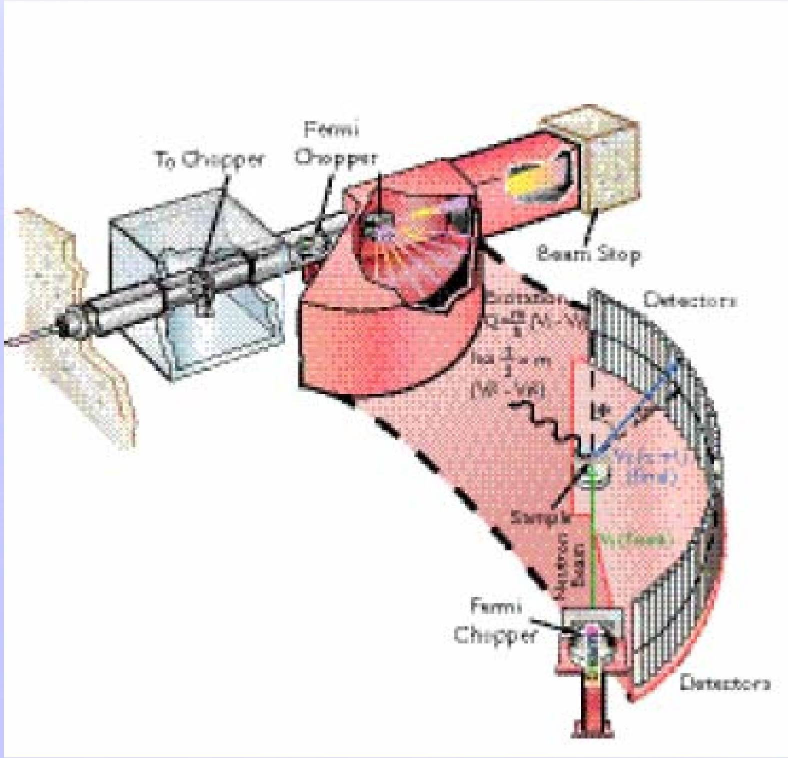
PDF Obtained with the NPDF, LANSCE

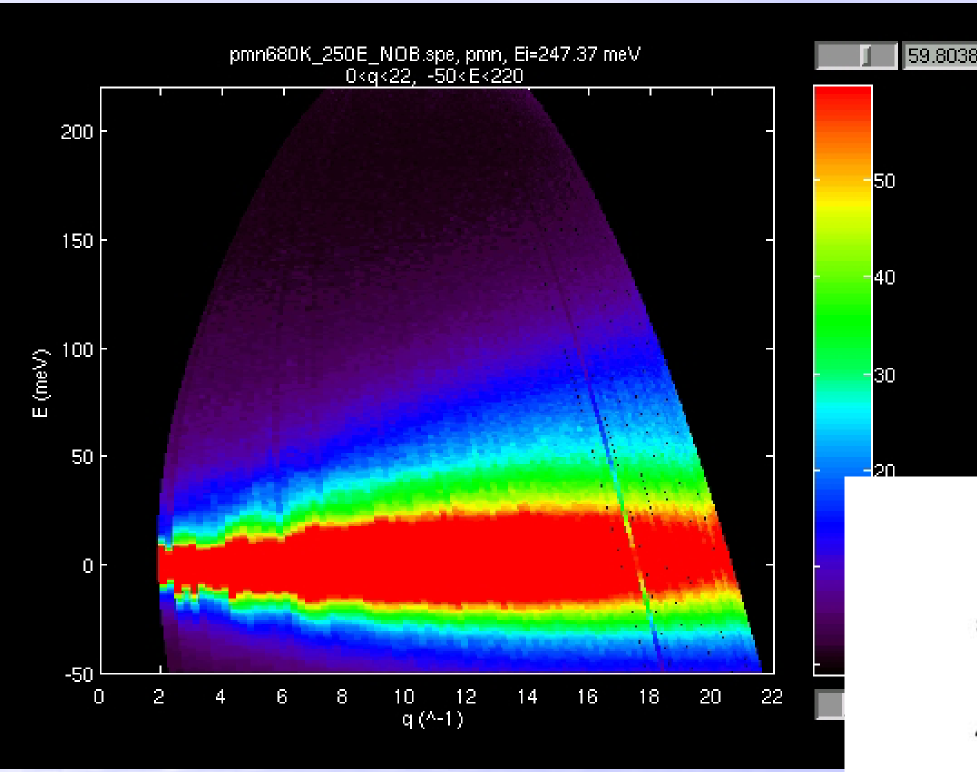


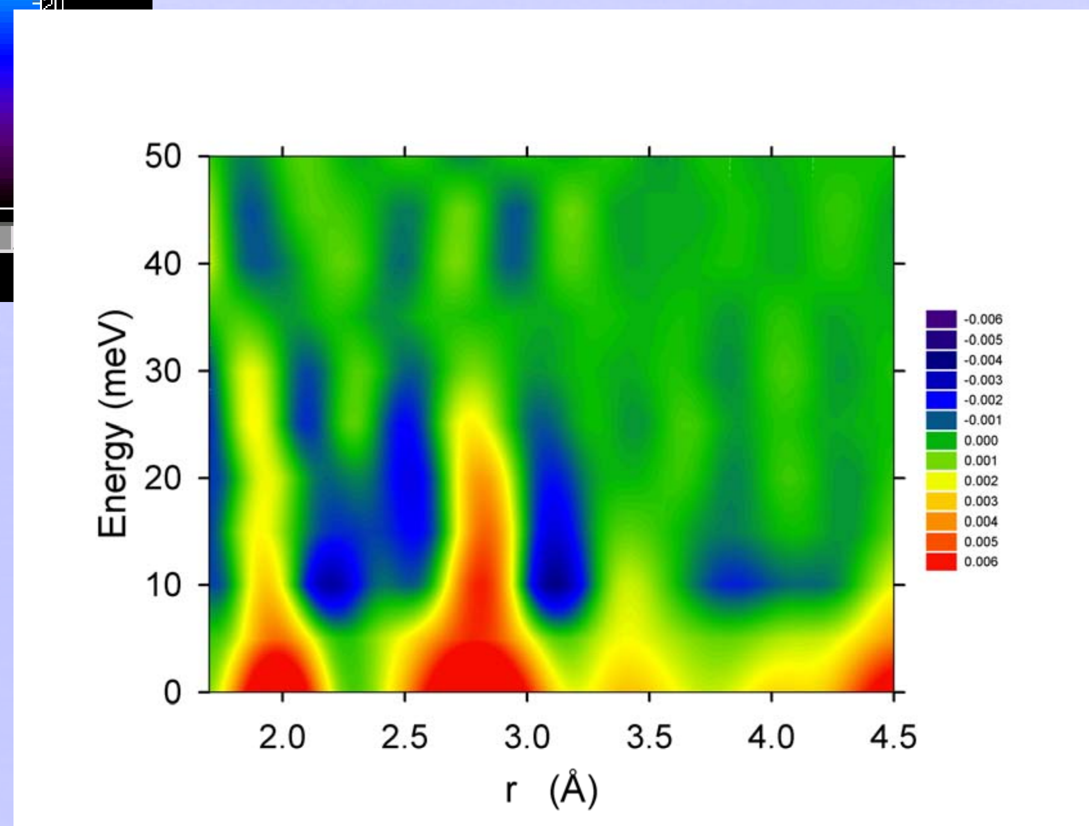
- The first peak of the PDF (Ni-O peak) shows local Jahn-Teller distortion. But there is no long-range JT distortion.
- 3-sublattice structure resolves the local frustration, but nano-scale frustration creates domains.

Dynamic PDF by Inelastic Neutron Scattering

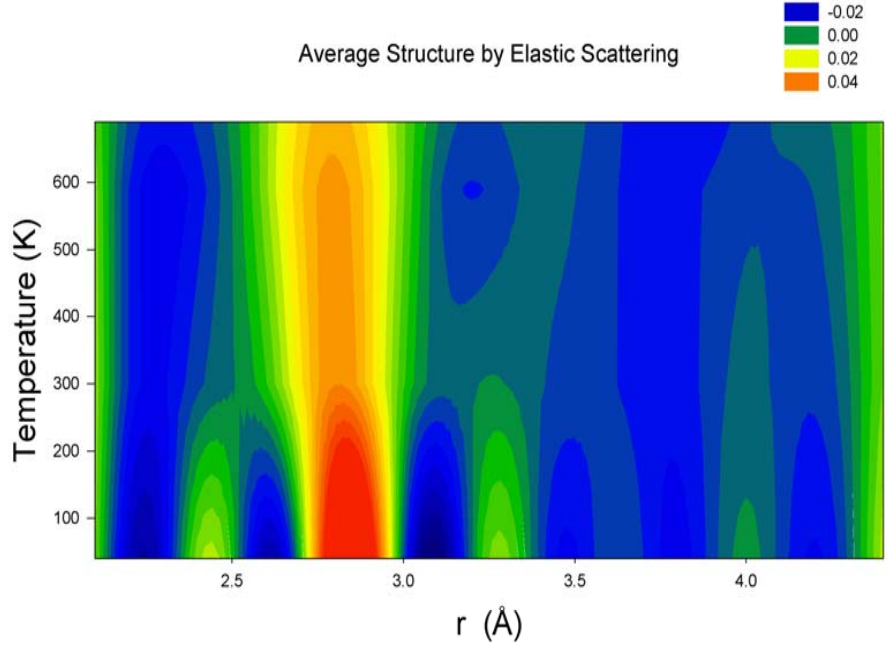
- Inelastic pulsed neutron scattering to obtain dynamic structure factor $S(Q,\omega)$.
- Large range of momentum and energy transfer.
- PHAROS(inelastic chopper spectrometer) of LANSCE, Los Alamos NL.
- Fourier-transform $S(Q,\omega)$ to obtain **dynamic PDF**.
- Relaxor ferroelectric $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN).

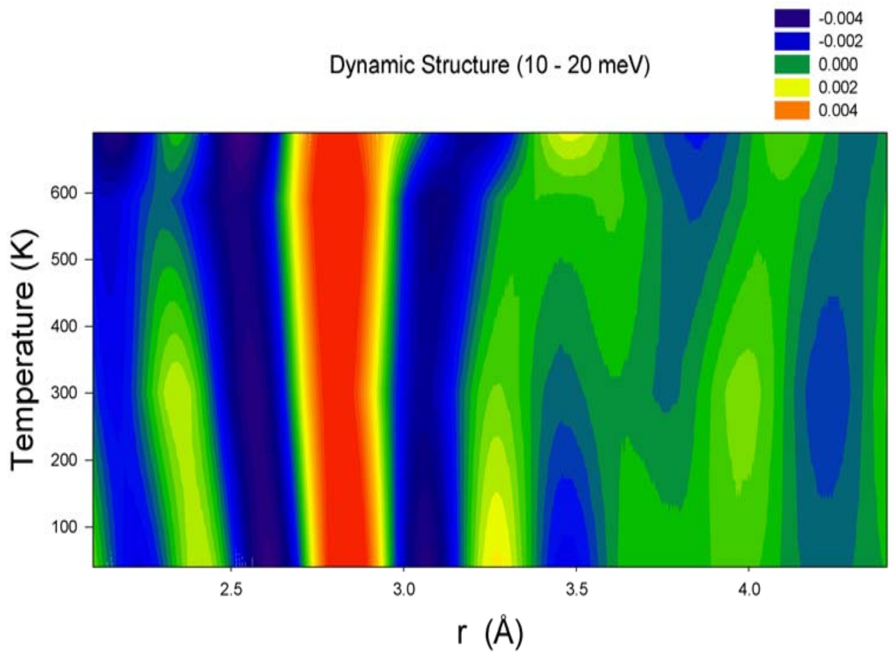






Fourier-transform from Q space to real space





- Static polarization lost at RT.
- Dynamic polarization up to 600 K.

Wish List

- Data quantity as well as quality has been greatly improved due to advances in facilities.
- The PDF method is capable of bridging the gap in structural characterization methods for 0.5 ~ 5 nm.
- The PDF method can now applied on wider range of problems, and is proving to be a powerful technique for study of the **structure and dynamics of nano-materials**.
- To increase the amount of data further a brighter neutron source is required.
  - Marked increase in brightness in the third generation synchrotron source made a large impact.
  - Similar increase in neutron brightness will enable small samples to be studied.