Total neutron scattering to obtain a 'complete' structural finger print of nanoparticles

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Outline

- **Introduction**
- **Total scattering**
  - **Bragg- and Diffuse scattering**
  - **The atomic Pair Distribution Function (PDF)**
- **The instrument NPDF**
- **Applications or work in progress ..**
  - ***Domain structures***
  - ***Nano-crystalline*: Gold nanoparticles**
- **Summary and outlook**

Bragg's world: Structure of crystals

The Nobel Prize in Physics 1915

"for their services in the analysis of crystal structure by means of X-rays"

Sir William Henry Bragg

1/2 of the prize

United Kingdom

London University
London, United Kingdom

b. 1862
d. 1942

William Lawrence Bragg

1/2 of the prize

United Kingdom

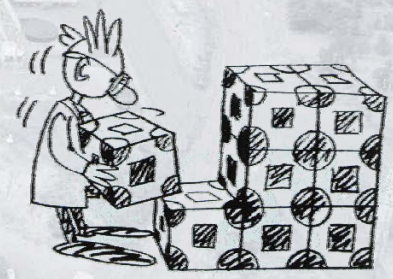
Victoria University
Manchester, United Kingdom

b. 1890
(in Adelaide, Australia)
d. 1971

Bragg's law

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

- **Assumes periodicity**
- **Average structure from Bragg peak positions and intensities**

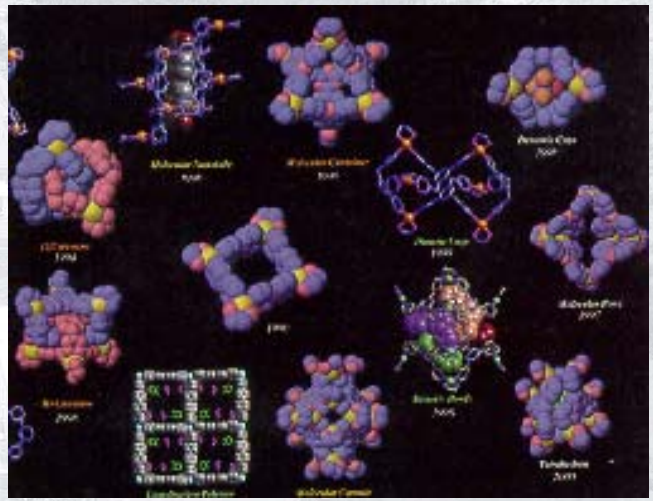


unit cell

The repeating unit of a crystal.

The challenge of *real* materials: Knowing the local structure

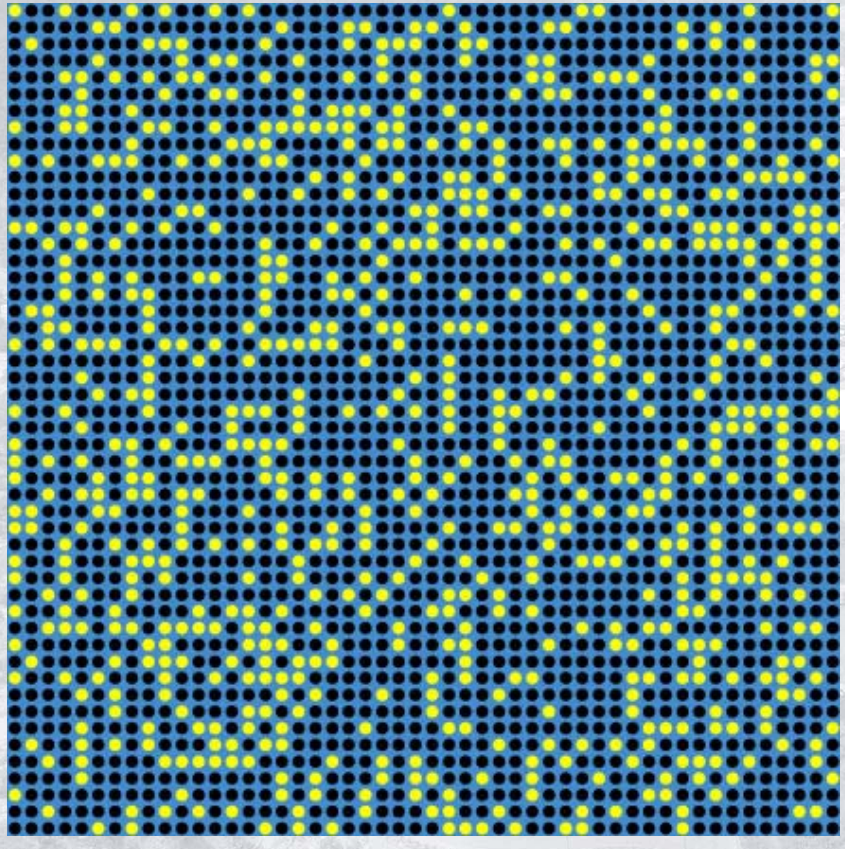
- **Traditional crystallographic approach to structure determination is insufficient or fails for**
  - **Non crystalline materials**
  - **Disordered materials: The interesting properties are often governed by the defects or local structure !**
  - **Nanostructures: Well defined local structure, but long-range order limited to few nanometers (-> badly defined Bragg peaks)**
- **A new approach to determine local and nano-scale structures is needed.**

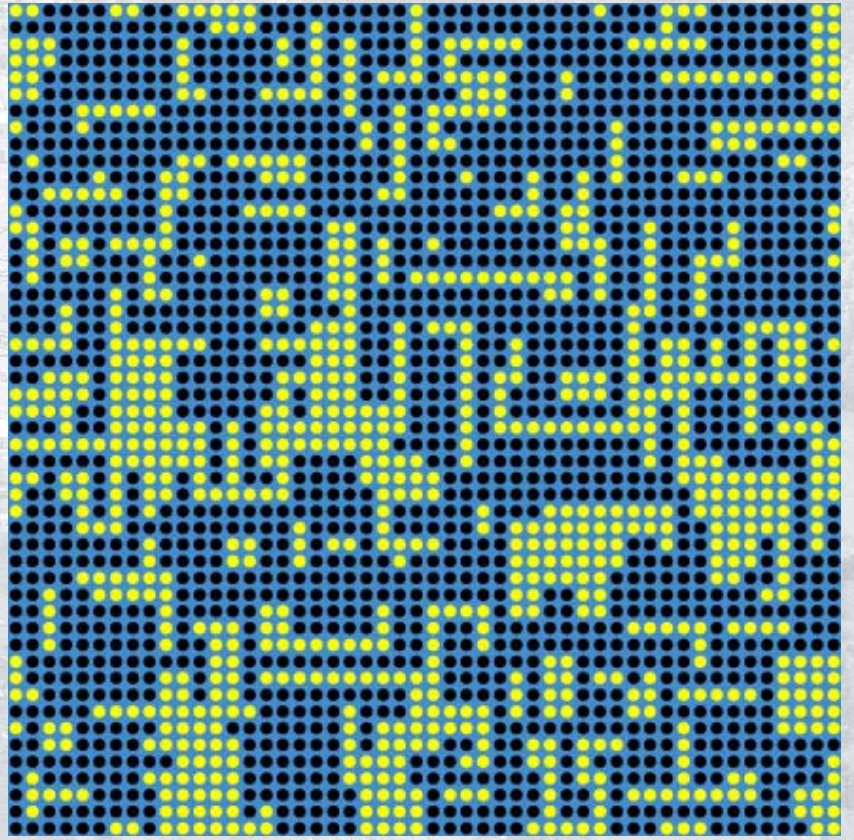


Nanostructures: *Science (290) 2000*

***PDF* opens the door ..**

Total scattering ?

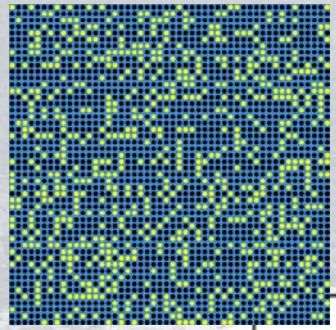




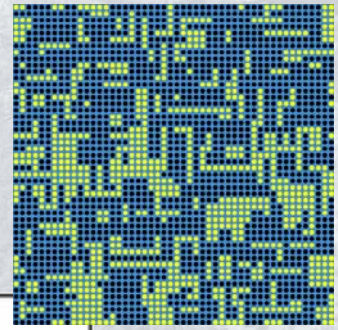
Cross section of 50x50x50 u.c. model crystal consisting of 70% black atoms and 30% *vacancies* !

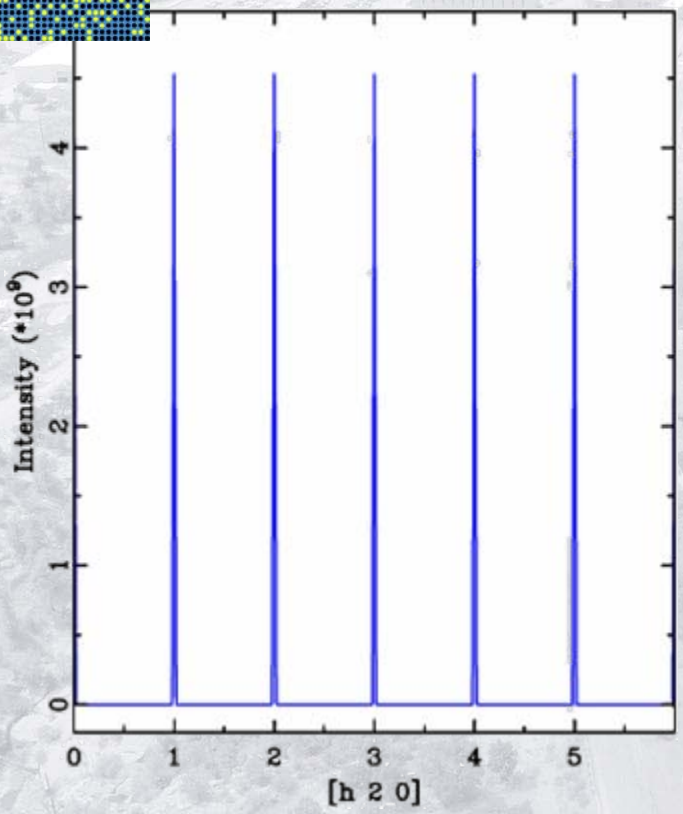
Properties might depend on vacancy ordering !!

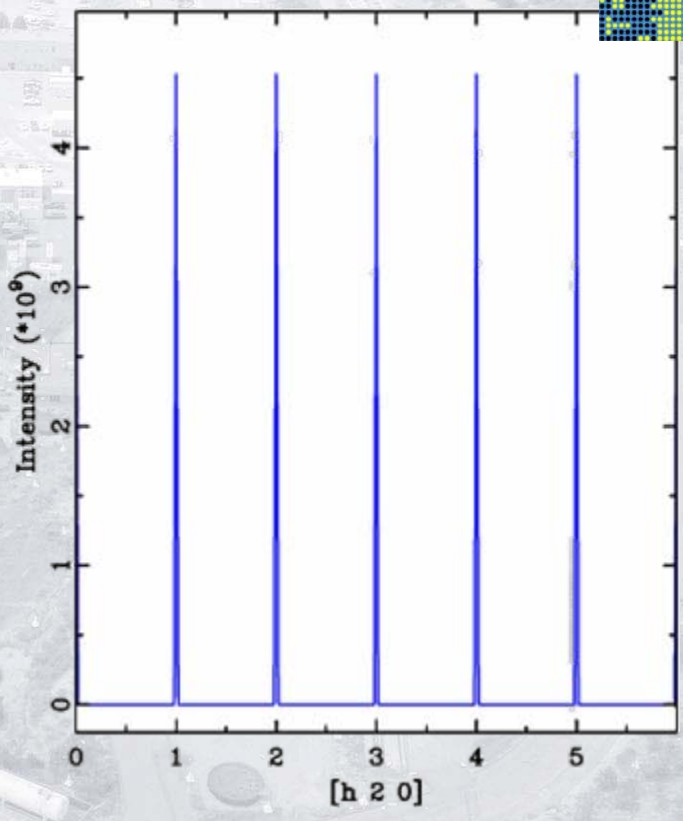
Bragg peaks are blind ..



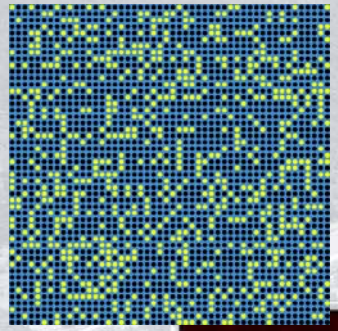
Bragg scattering: Information about the *average* structure, *e.g.* average positions, displacement parameters and occupancies.



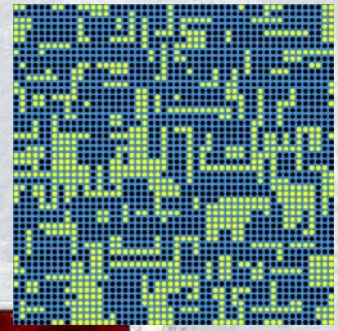


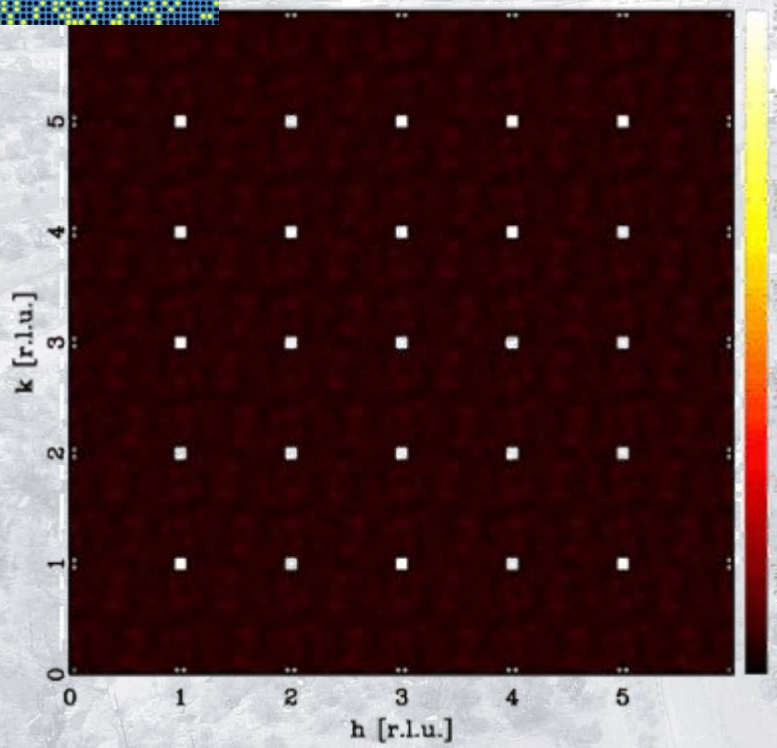


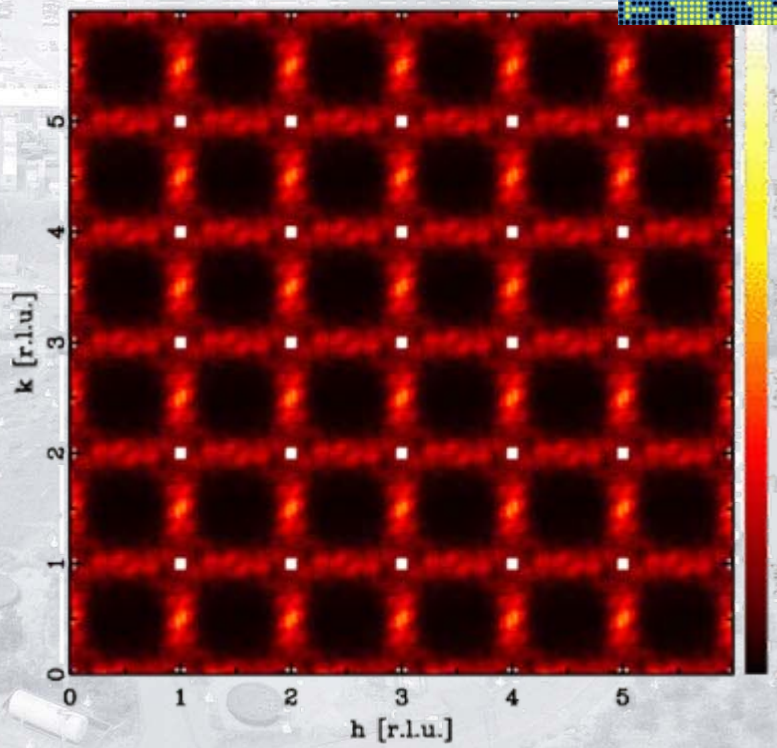
Diffuse scattering to the rescue ..



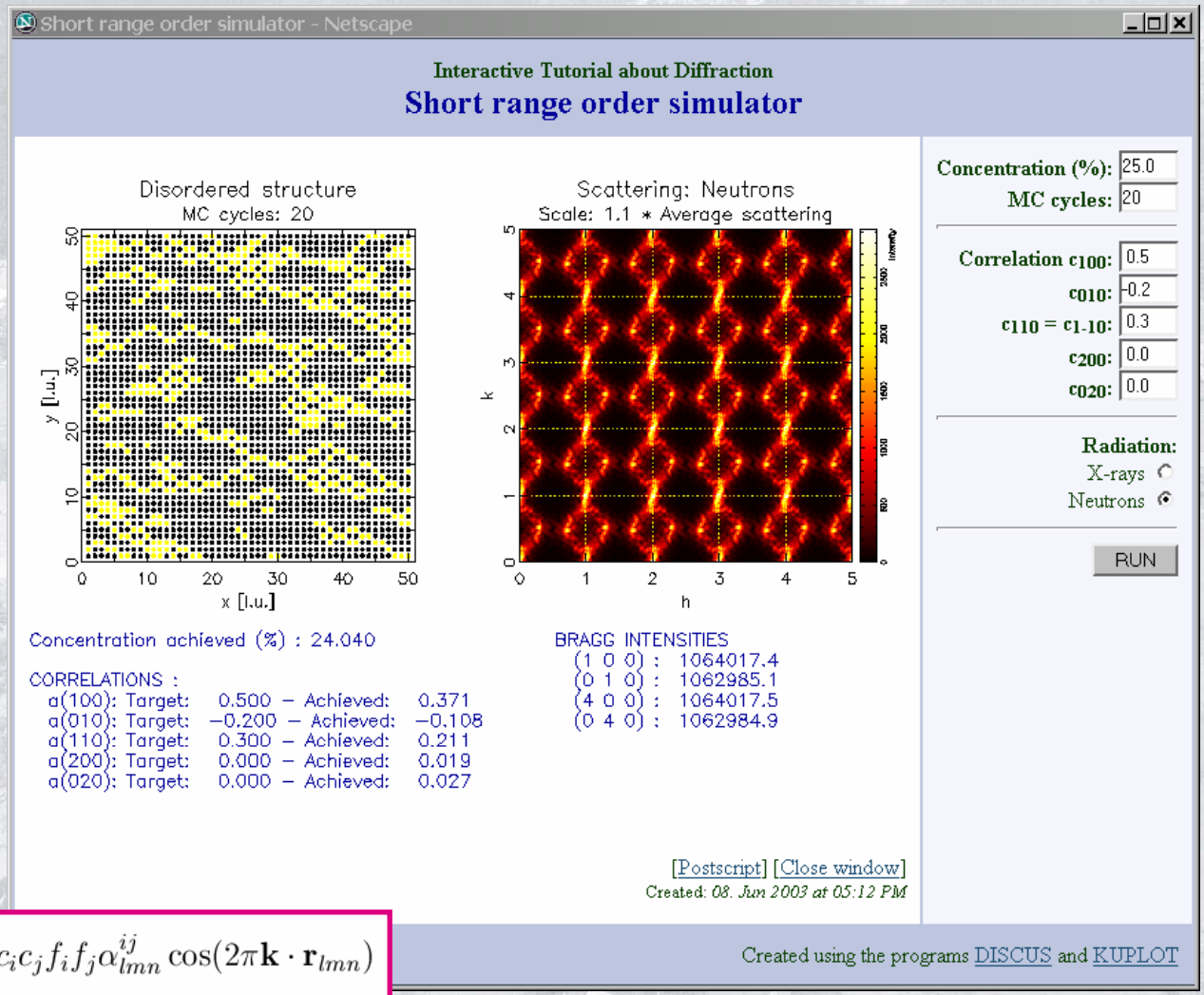
Diffuse scattering: Information about *two-body correlations*, *i.e.* chemical short-range order or local distortions.





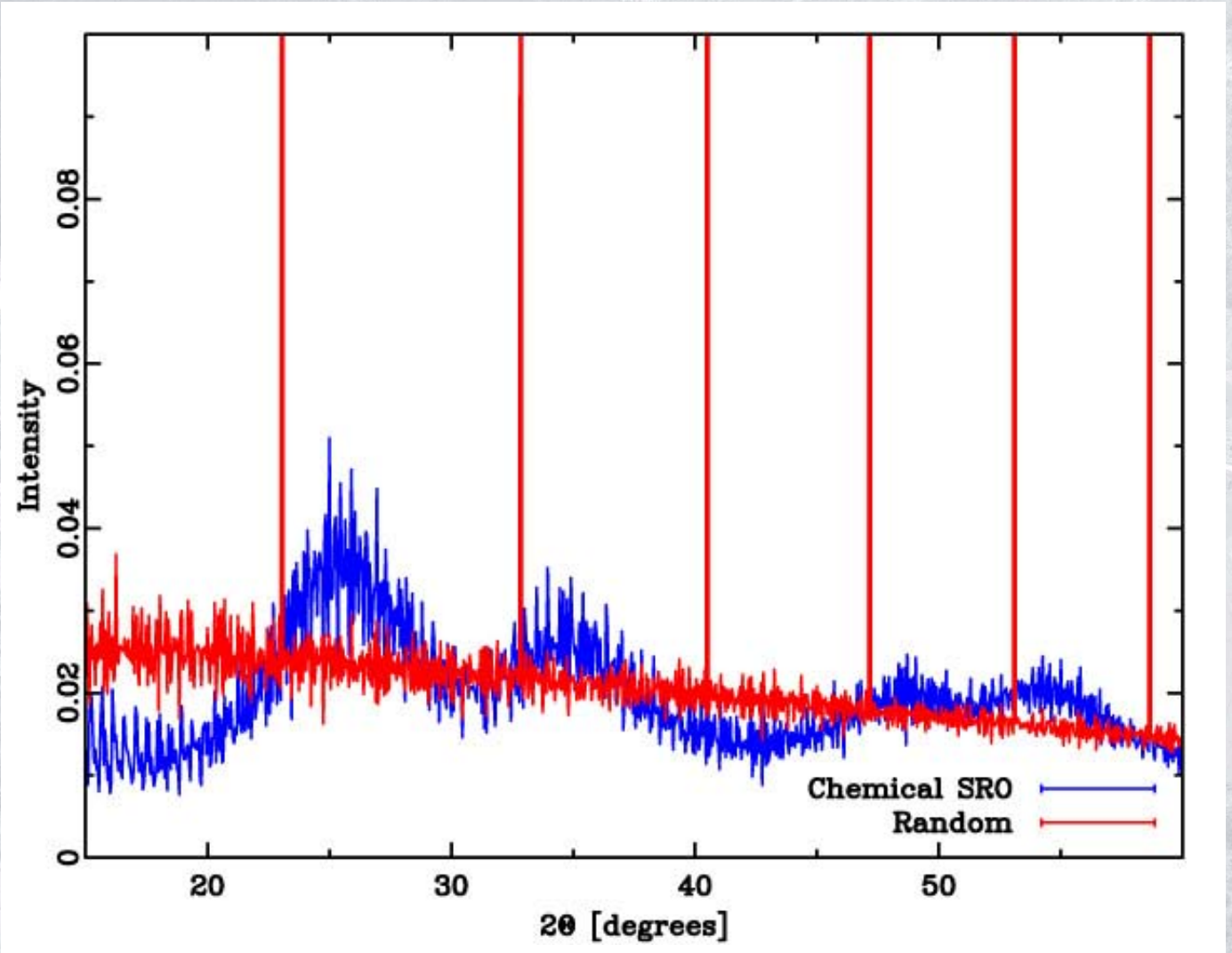


See http://www.totalscattering.org/teaching/

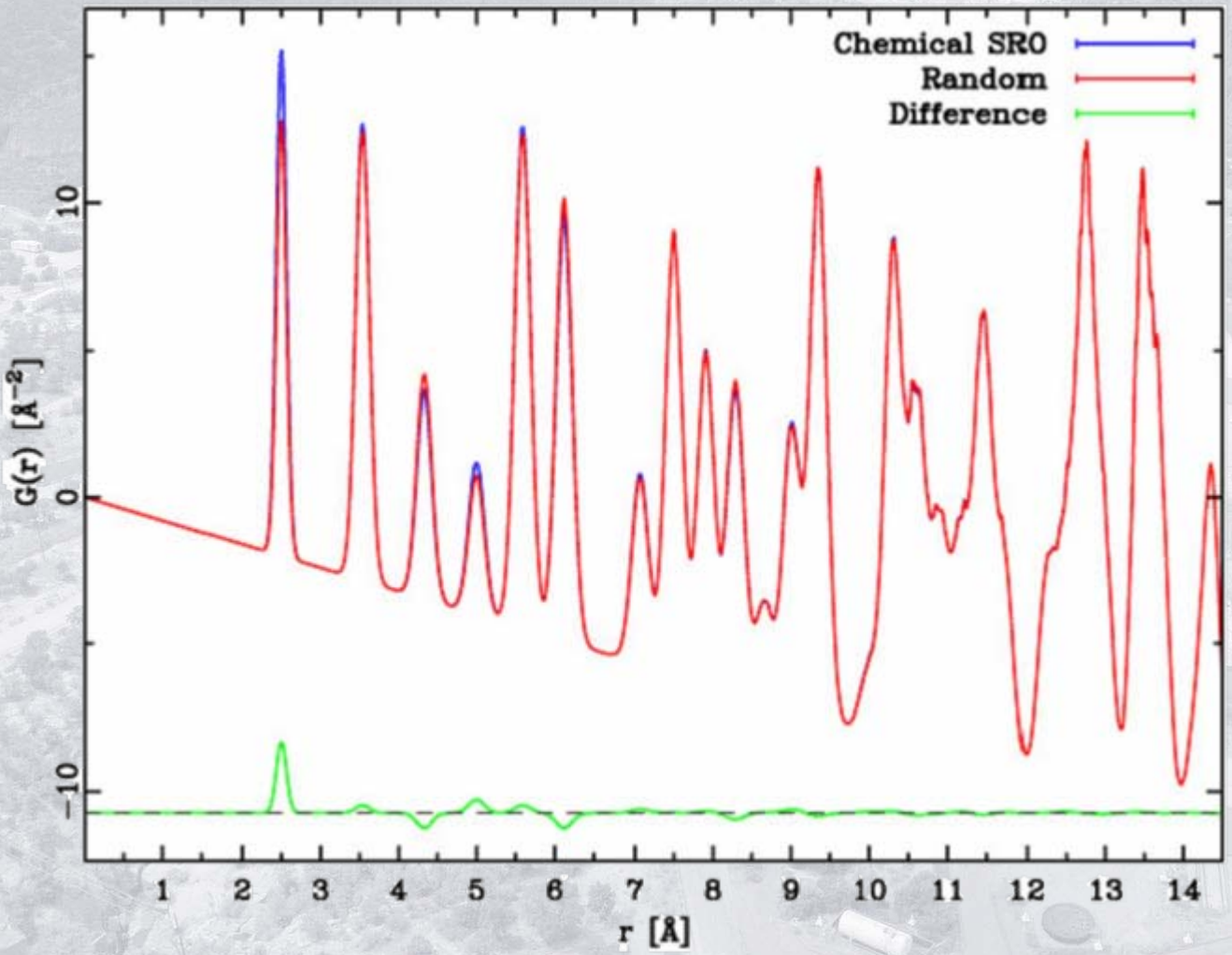


$$I_{\mathrm{sro}} = -\sum_{ij}\sum_{lmn} c_i c_j f_i f_j \alpha_{lmn}^{ij} \cos(2\pi \mathbf{k}\cdot\mathbf{r}_{lmn})$$

How about powder diffraction ?



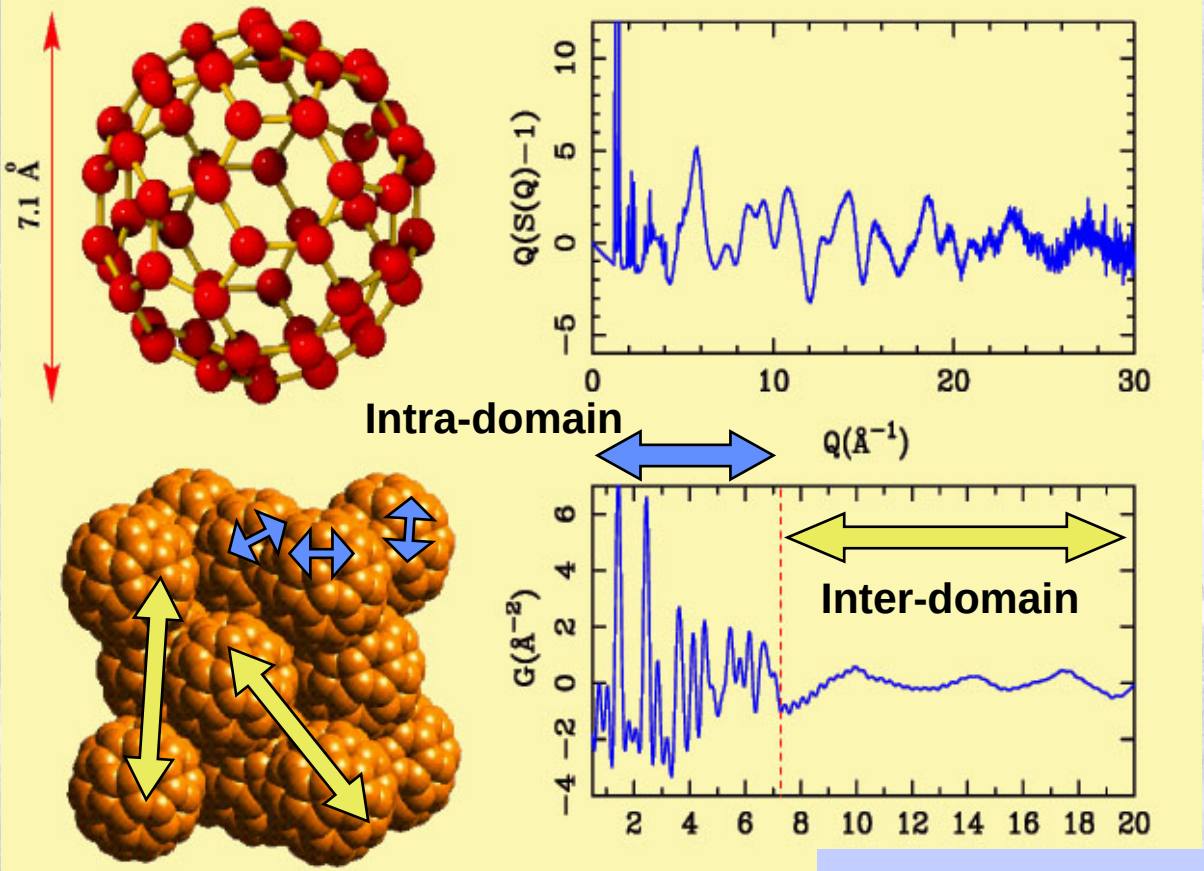
Finally the Pair Distribution Function (PDF)



The PDF is the Fourier transform of the total scattering diffraction pattern !

Proffen, *Z. Krist*, **215**, 661 (2000)

What is a PDF?



Example:
C_{60} - 'Bucky balls'

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

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

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

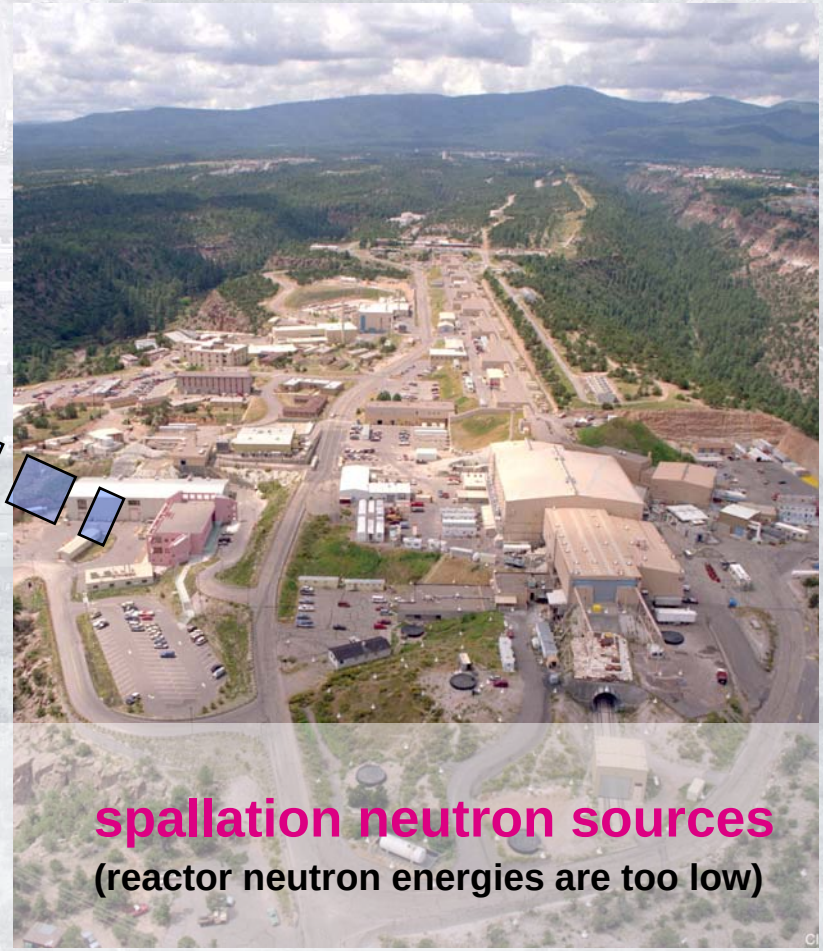
What is required to obtain high quality PDFs ?

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



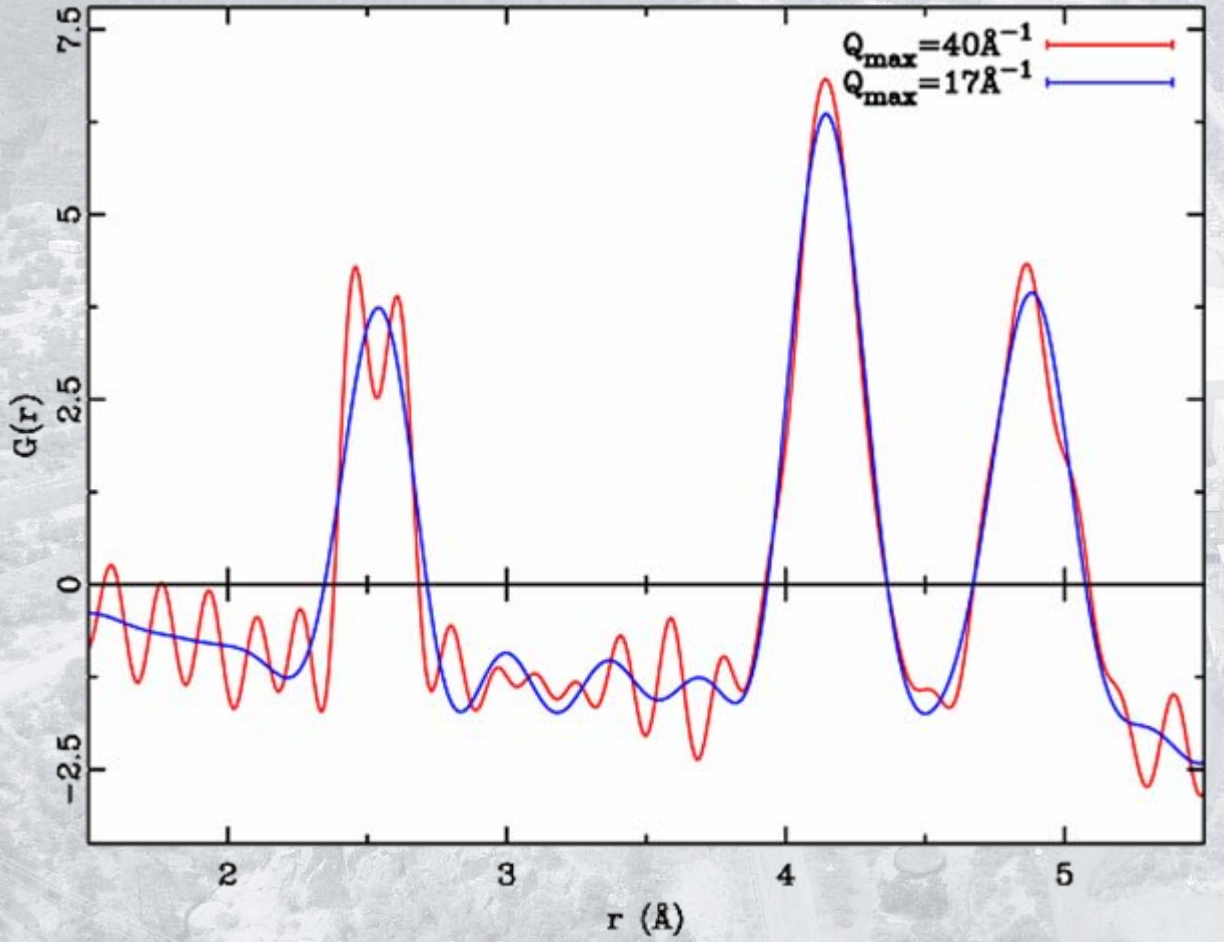
Where ?

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} …



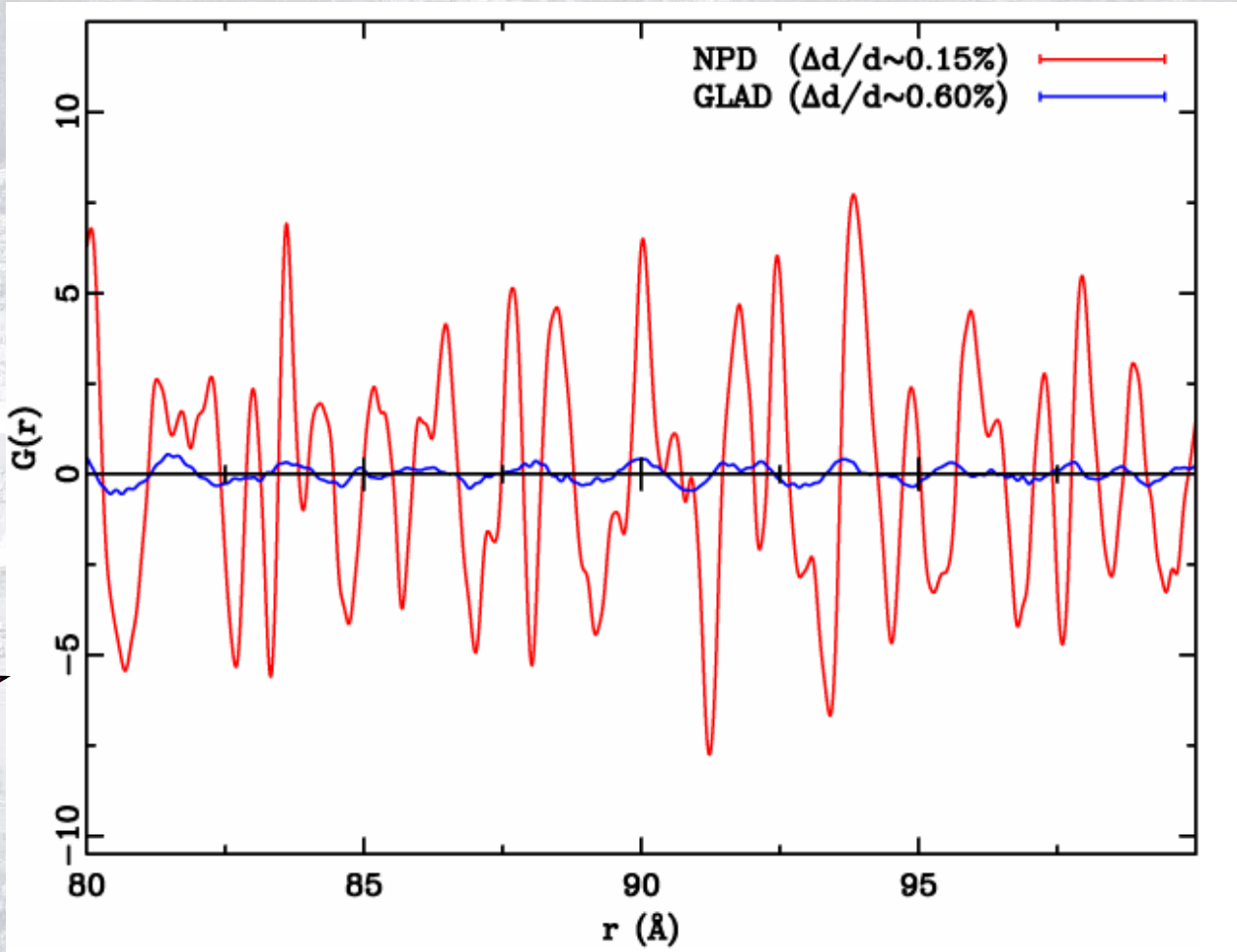
Termination of integral at Q_{max} results in convolution of G(r) with $\sin(Q_{max} r)/r$.

$ZnSe_{0.5}Te_{0.5}$ 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 …

Comparison of measurements of Nickel powder on instruments GLAD at IPNS and NPD at MLNSC.



PDF goes "Nano"

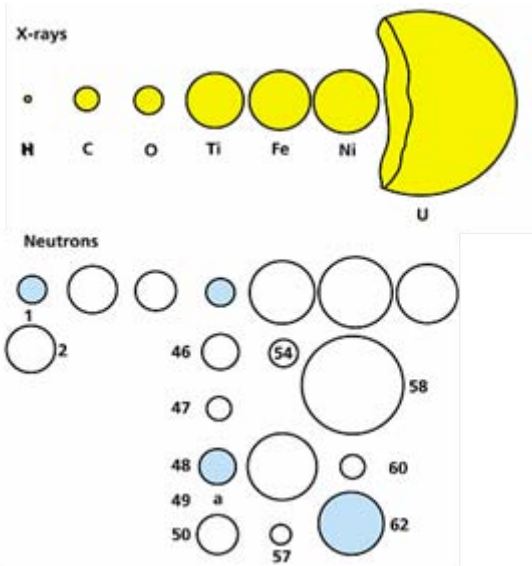
High Q resolution: Large *r* range (PDF dampened by *exp -(rΔQ)²/2)*)

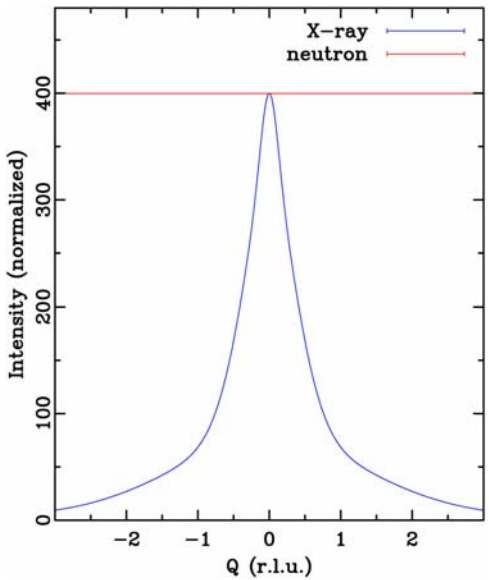
Total neutron scattering

Why use neutrons ?

- **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 ..**

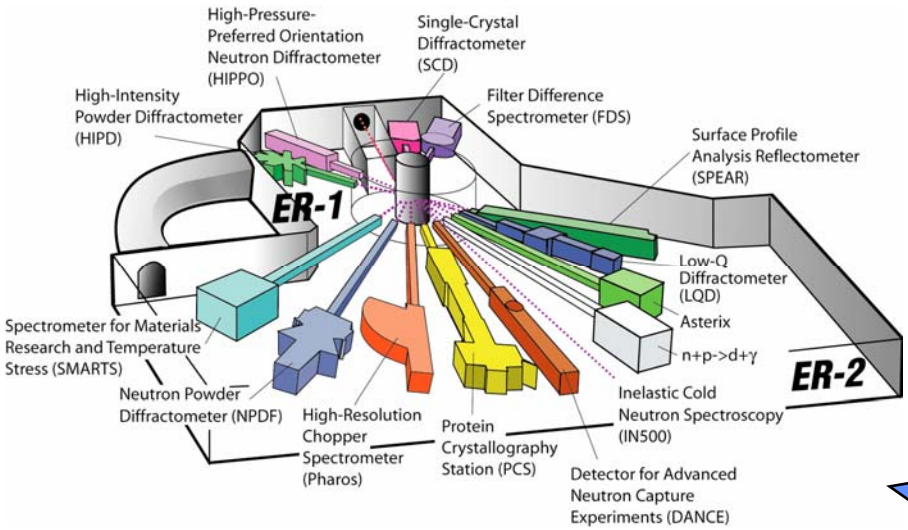
X-ray and neutron scattering Lengths for selected elements.





Scattering from single atom

The instrument NPDF



NPDF
Flightpath 1

Total budget: $1.1 M
PI: Takeshi Egami
Sponsors:

LANSCE Penn STONY BROOK UCSB UNIVERSITY of VIRGINIA MICHIGAN STATE UNIVERSITY

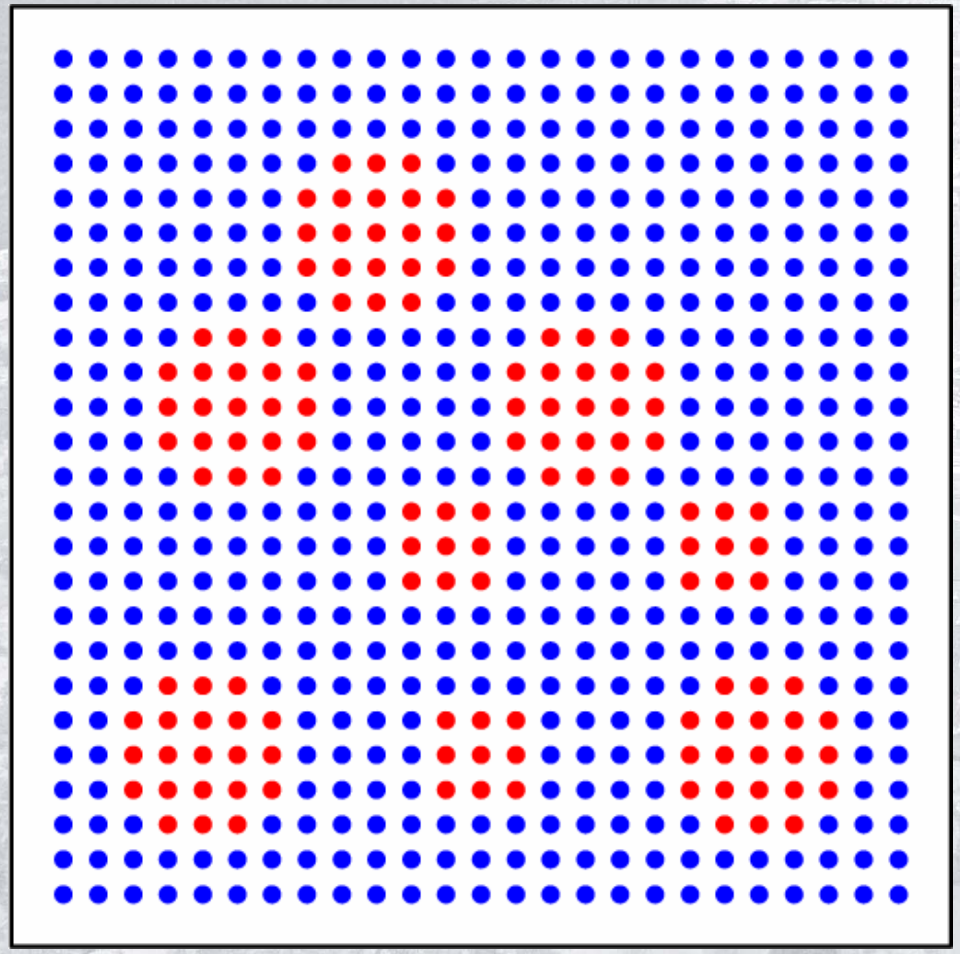
Domain structures

Katharine Page

Thomas Proffen

Facilities: Lujan
Funding: DOE, NASA

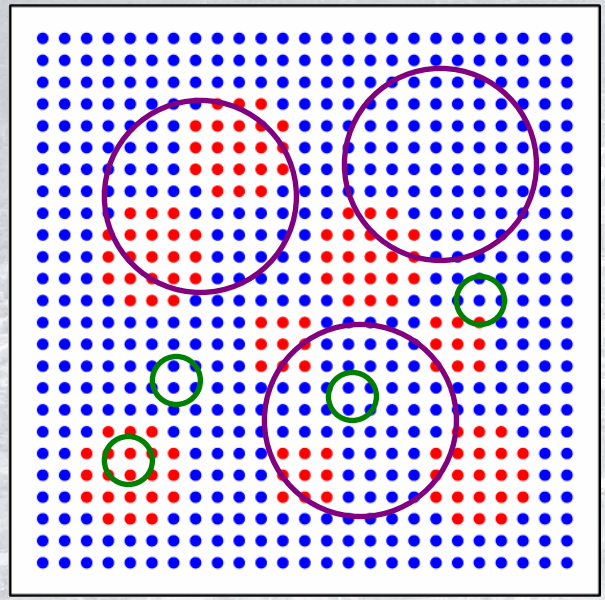
Domain structures : Simulated example



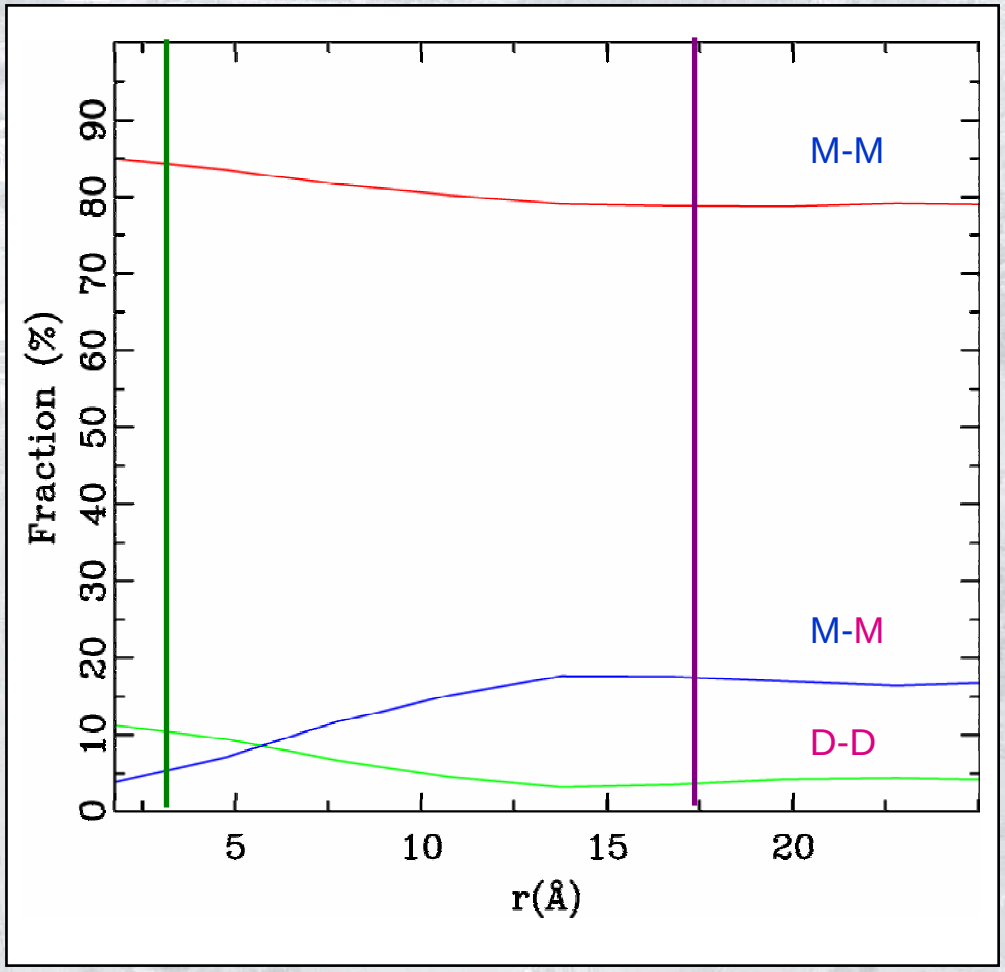
Proffen & Page, *Z. Krist.* (2004), in press

- Simulated structure of 20x20x20 unit cells.
- Matrix (M): blue atoms
- Domains (D): red atoms, spherical shape, d=15Å.
- Simulated using DISCUS.

Domain structures : Pair Distribution Function



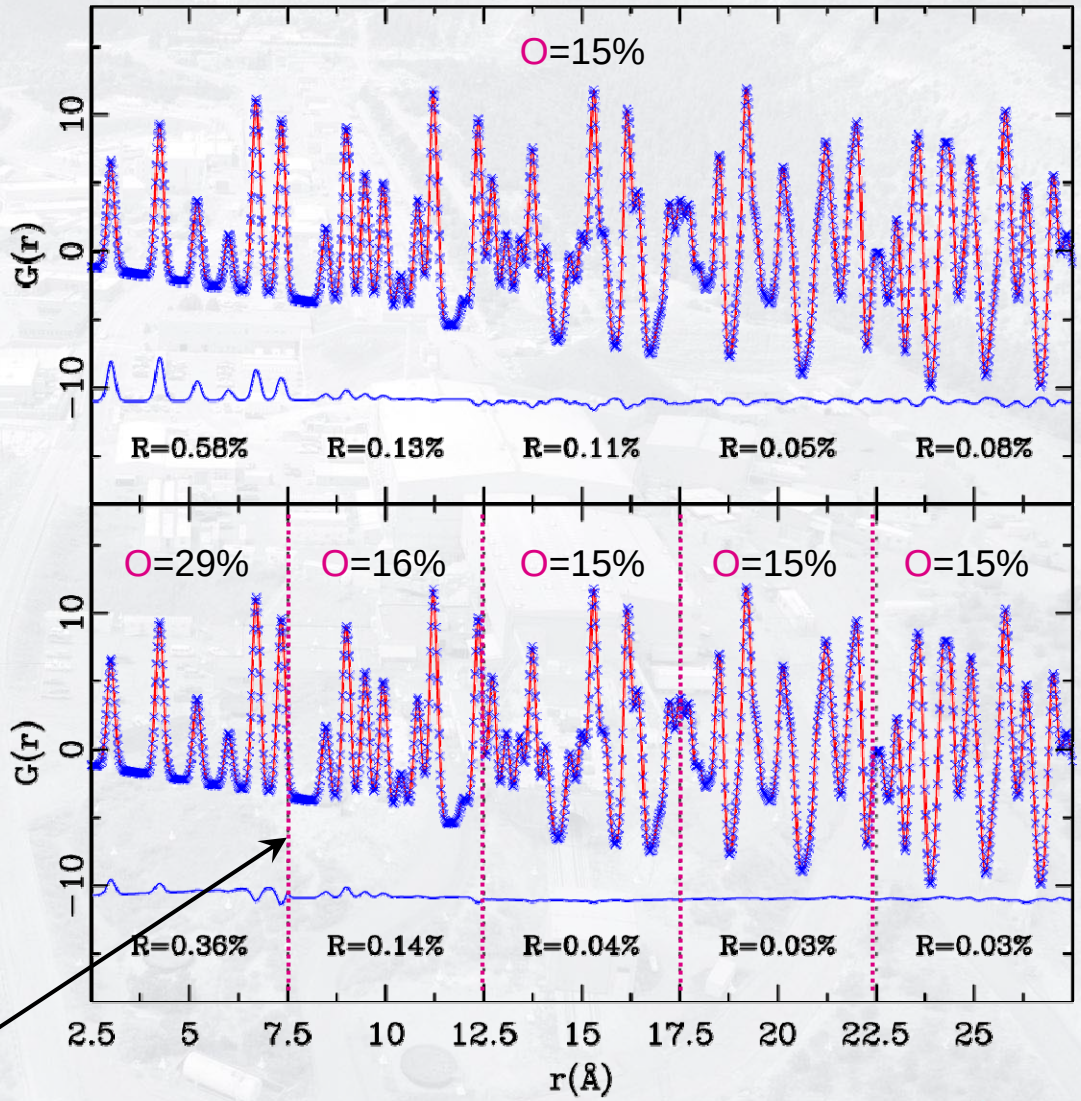
r < Domain size:
Mainly D-D and M-M pairs



Domain structures : R-dependent refinements

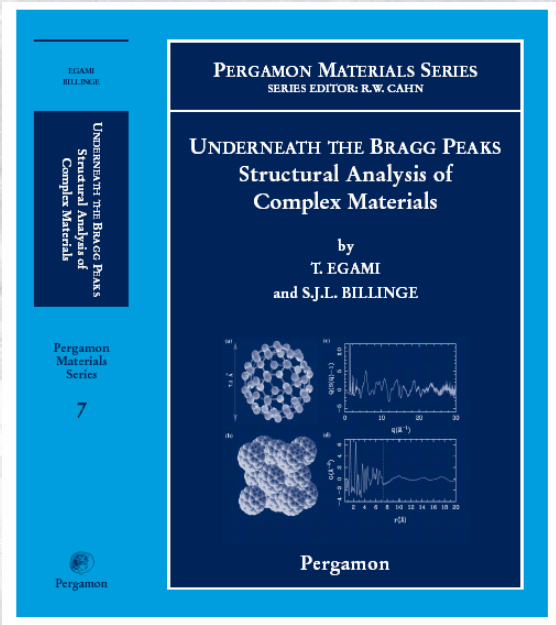
- ***Top***: **Refinement of single-phase model with blue/red fractional occupancies (O).**
- ***Bottom***: **Refinement of same model for 5Å wide sections.**
- **Extensions:**
  - **Multi phase models**
  - **Modeling of boundary**
  - **R-dependent refinable mixing parameters**

Domain radius



Summary and more information

- Analysis of total scattering gives valuable insight in structure ⇔ properties relationship
- High-resolution instruments open the door to medium-range order investigations
- Obtain structural information from disordered crystalline, amorphous of composite materials
- Fast powder measurements allow systematic exploration of local structure as function of *T, x, P*



http://www.totalscattering.org

“Complete” Structure of Gold Nanoparticles

Katharine Page

Thomas Proffen

Ram Seshadri

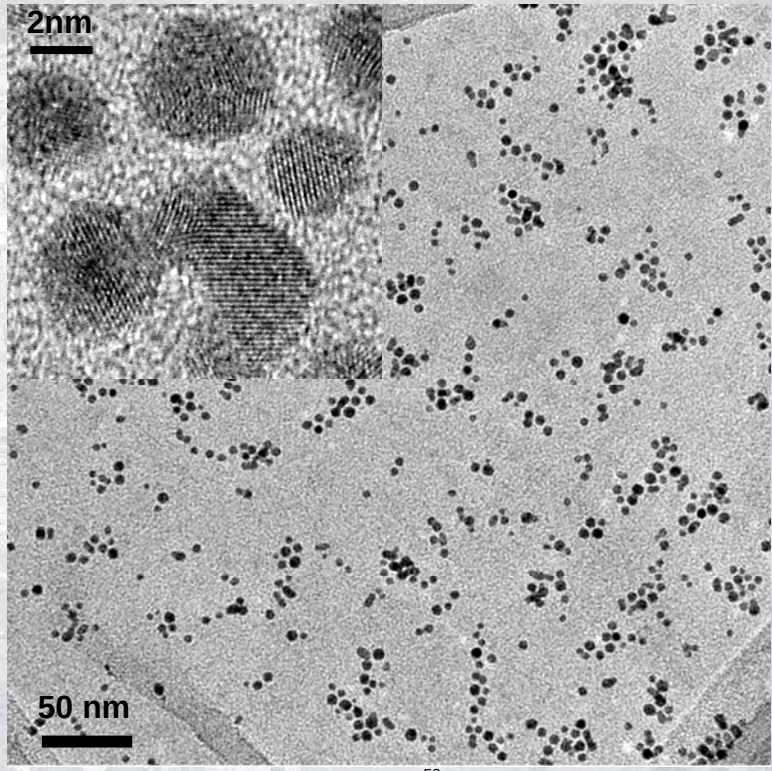
Tony Cheetham

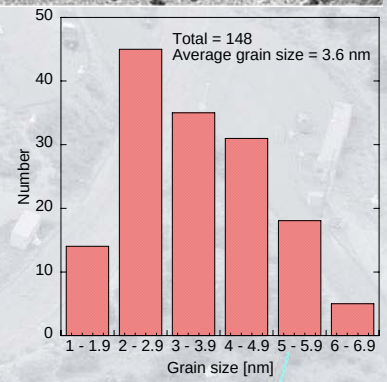
Facilities: Lujan

Funding: DOE, NASA

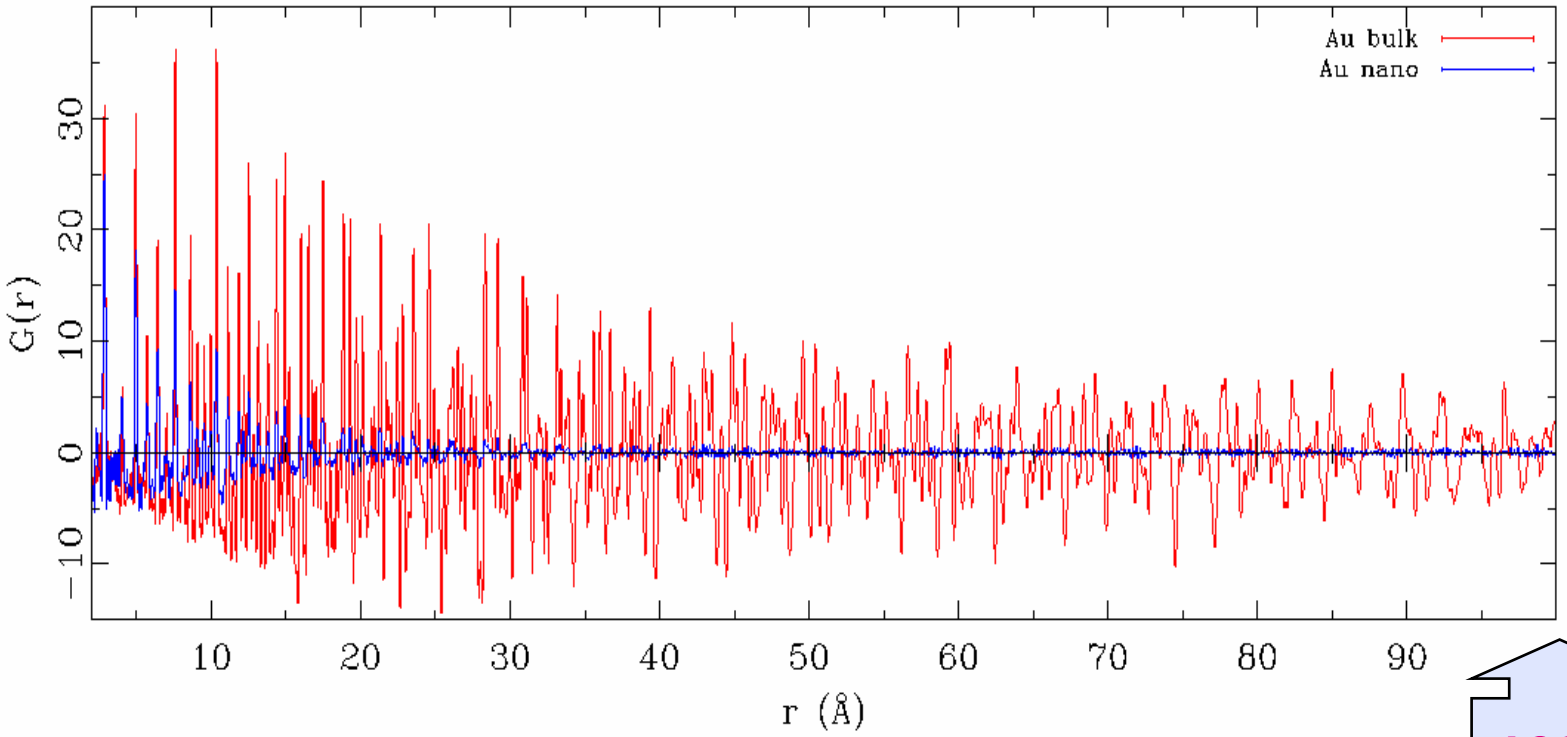
Au nanoparticles : Why PDF ?

- Nanoparticles often show different properties compared to the bulk.
- Difficult to study via Bragg diffraction (broadening of peaks).
- PDF reveals “complete” structural picture – core and surface.
- This study:
  - 5nm monodisperse Au nanoparticles
  - 1.5 grams of material
  - Neutron measurements on NPDF





Au nanoparticles : Nano *vs.* bulk

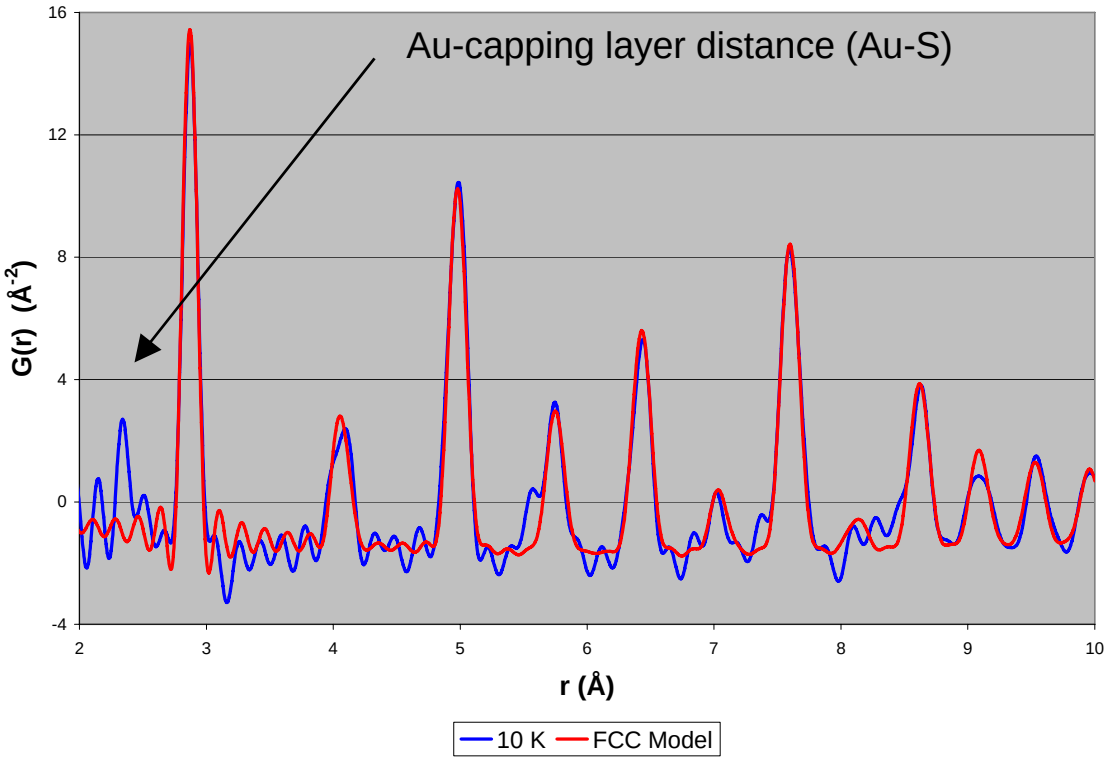


100Å

Experimental PDFs of gold nanoparticles and bulk gold, measured on NPDF.

Au nanoparticles : Structural refinements

- PDF from nano- and bulk gold refined using PDFFIT.
- Nanoparticles show “normal” gold structure.
- No indication of surface relaxations.
- $a_{bulk} < a_{nano}$
- Indication of Au-cap distances



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.* , accepted (2004).

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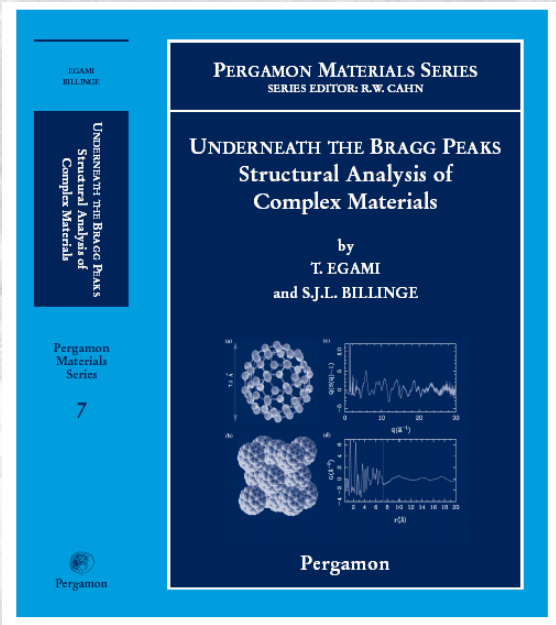

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