Analysis of Local Structure by Atomic Pair Distribution Function

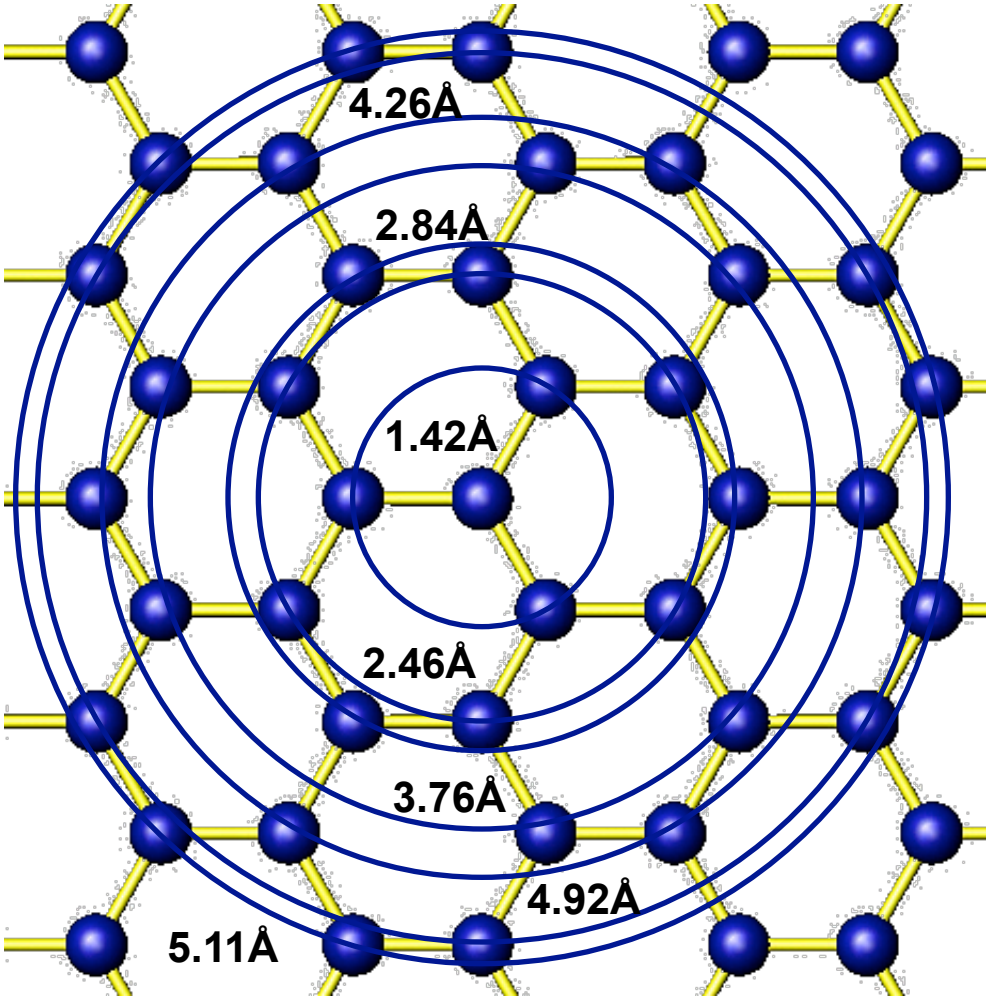
Elena Willinger

Lecture series: Modern Methods in Heterogeneous Catalysis Research

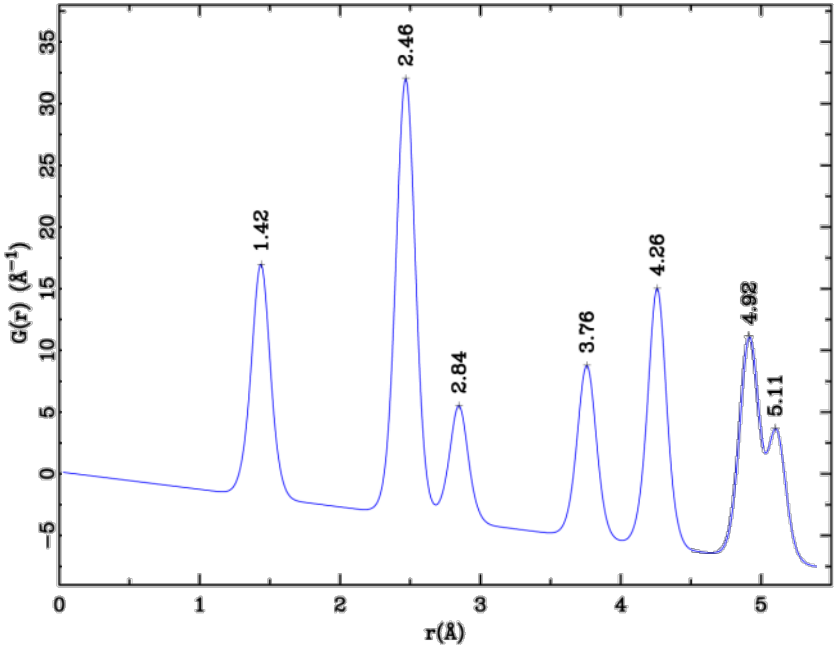
Outline

- What for do we need PDF?
- Scattering intensity
- Mathematical basis of the PDF
- Direct structural information from PDF
- PDF experiments: X-rays, neutrons, electrons
- Catalysis related examples

What is a PDF?



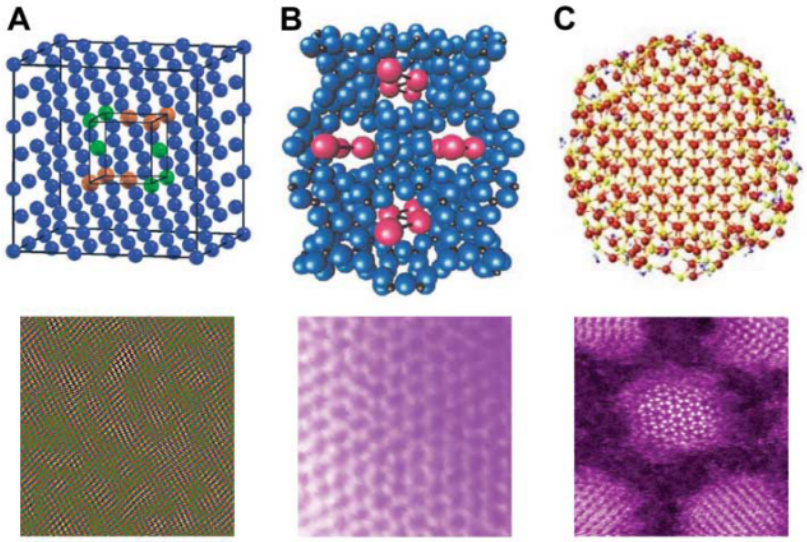
Pair distribution function (PDF) gives the probability of finding an atom at a distance "r" from a given atom.



What for do we need PDF

The challenge : 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 (-> poorly defined Bragg peaks)
- A new approach to determine local and nano-scale structures is needed.

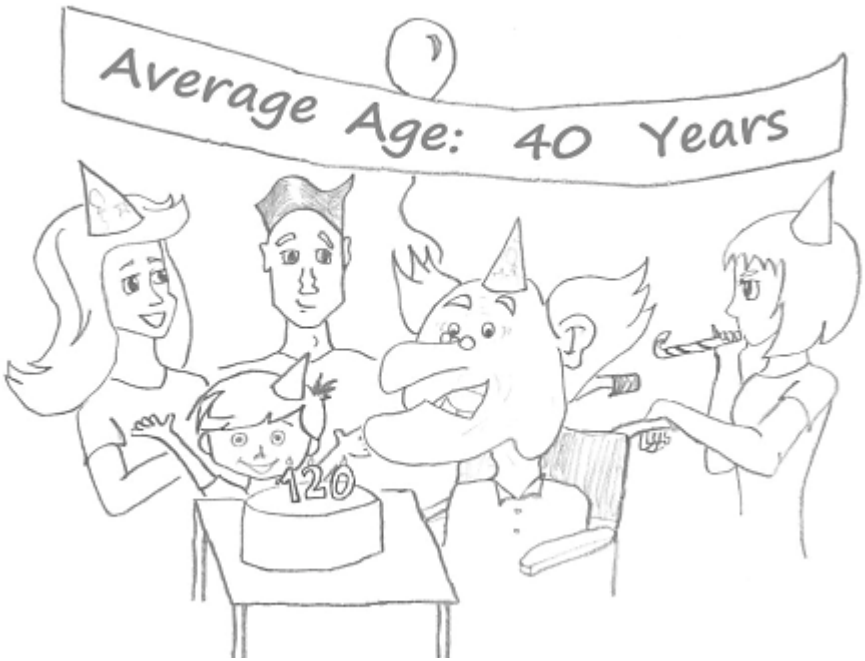


S.J.L. Billinge and I. Levin, **The Problem with Determining Atomic Structure at the Nanoscale**, *Science* **316**, 561 (2007).

What for do we need PDF

Conventional XRD analysis of Bragg intensities yields the **average** structure of materials which can be deceiving !

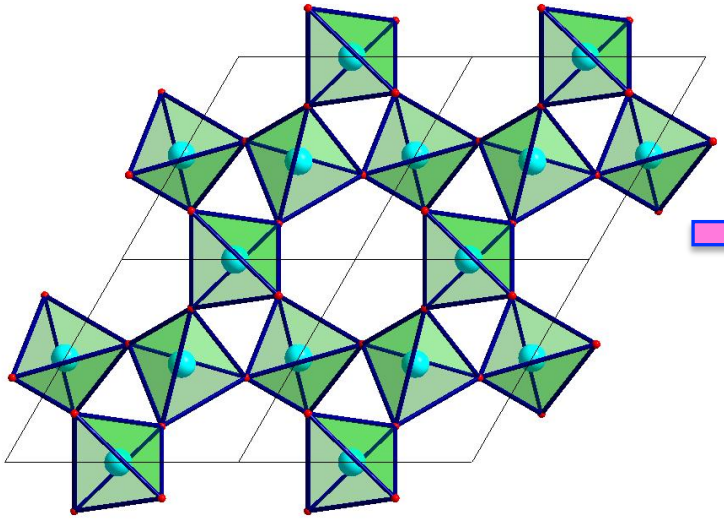
Considering going to a party where all you know is the average age is 40..



What for do we need a PDF?

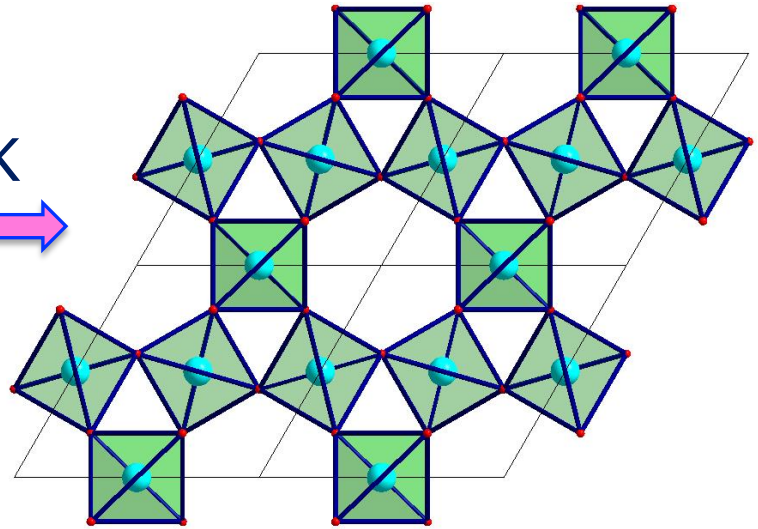
What exactly is meant by the difference between the local structure and the average crystallographic structure?

SiO_2 (α-quartz)

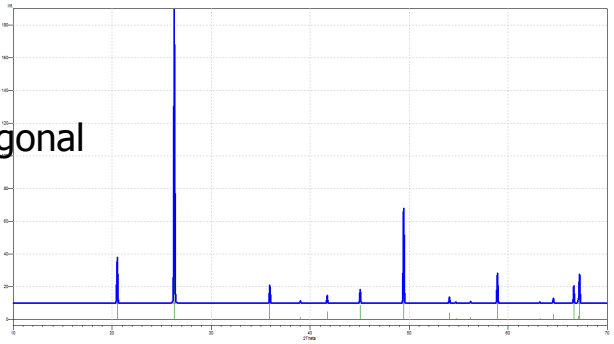


846 K

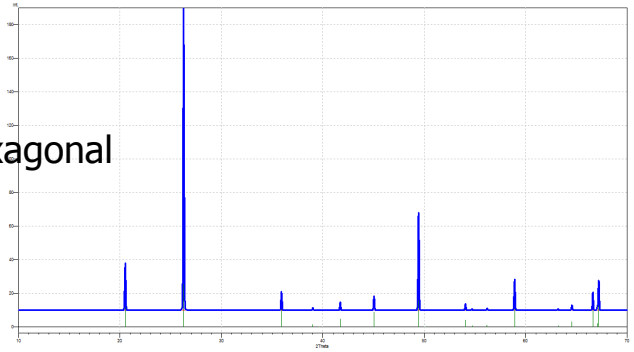
SiO_2 (β-quartz)



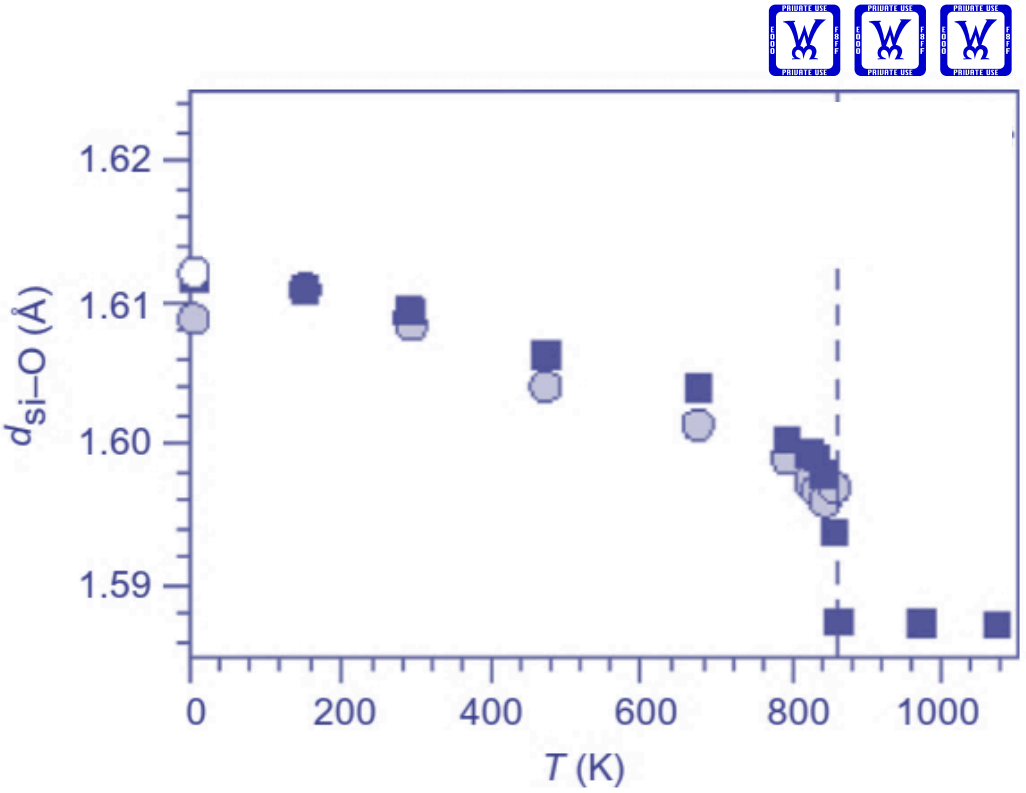
α-quartz
P $3_2$2 (154) - trigonal
a=4.9841(12) Å
c=5.4500(17) Å
V=117.25(5) Å^3

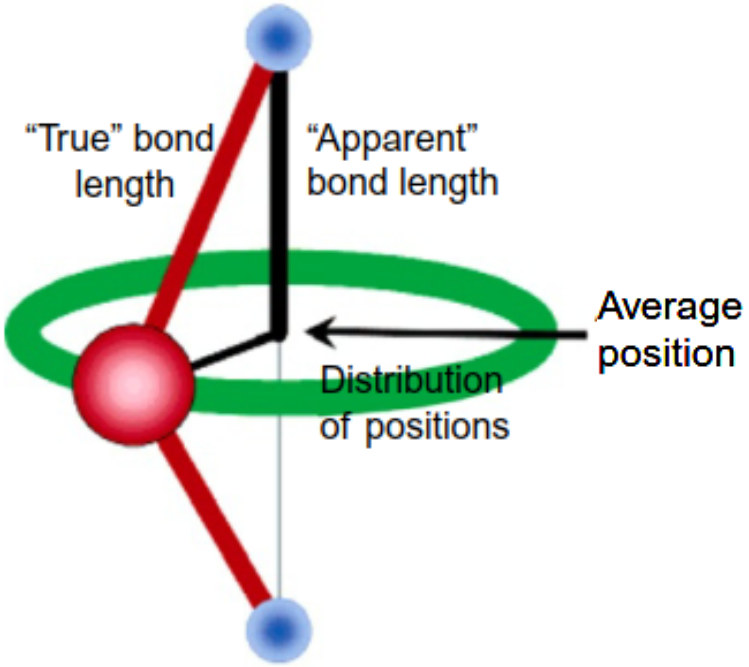


β-quartz
P $6_4$22 (181) - hexagonal
a=4.9965(1) Å
c=5.4543(1) Å
V=117.92(0) Å^3



What for do we need a PDF?



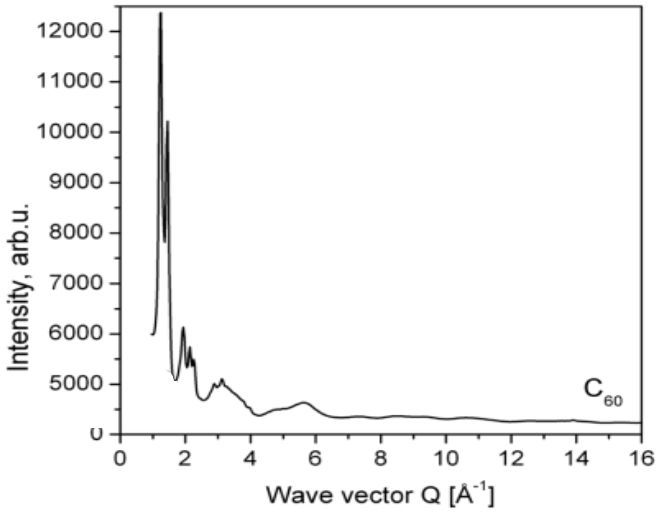


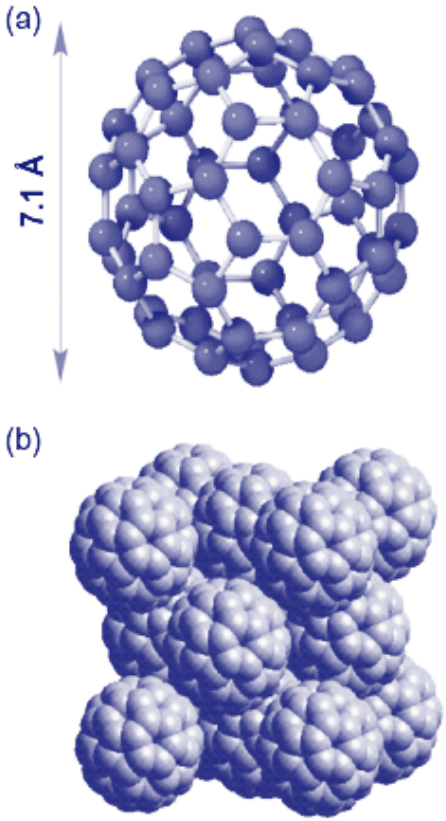
Neutron powder diffraction data

T. Egami & S. Billinge "Underneath the Bragg Peaks"

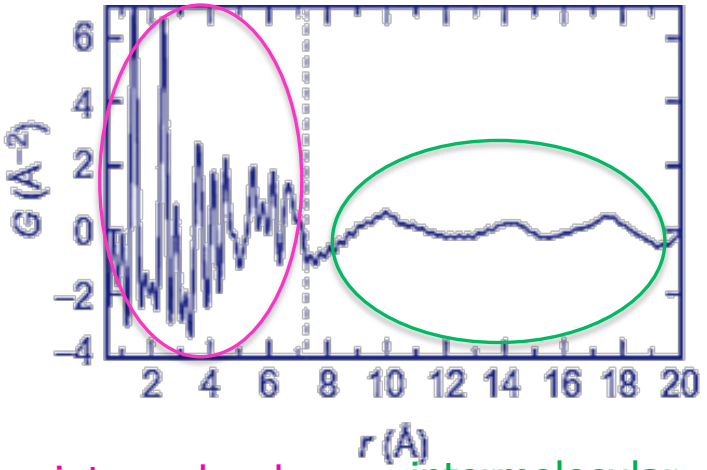
What for do we need a PDF?

XRD pattern





X-ray PDF



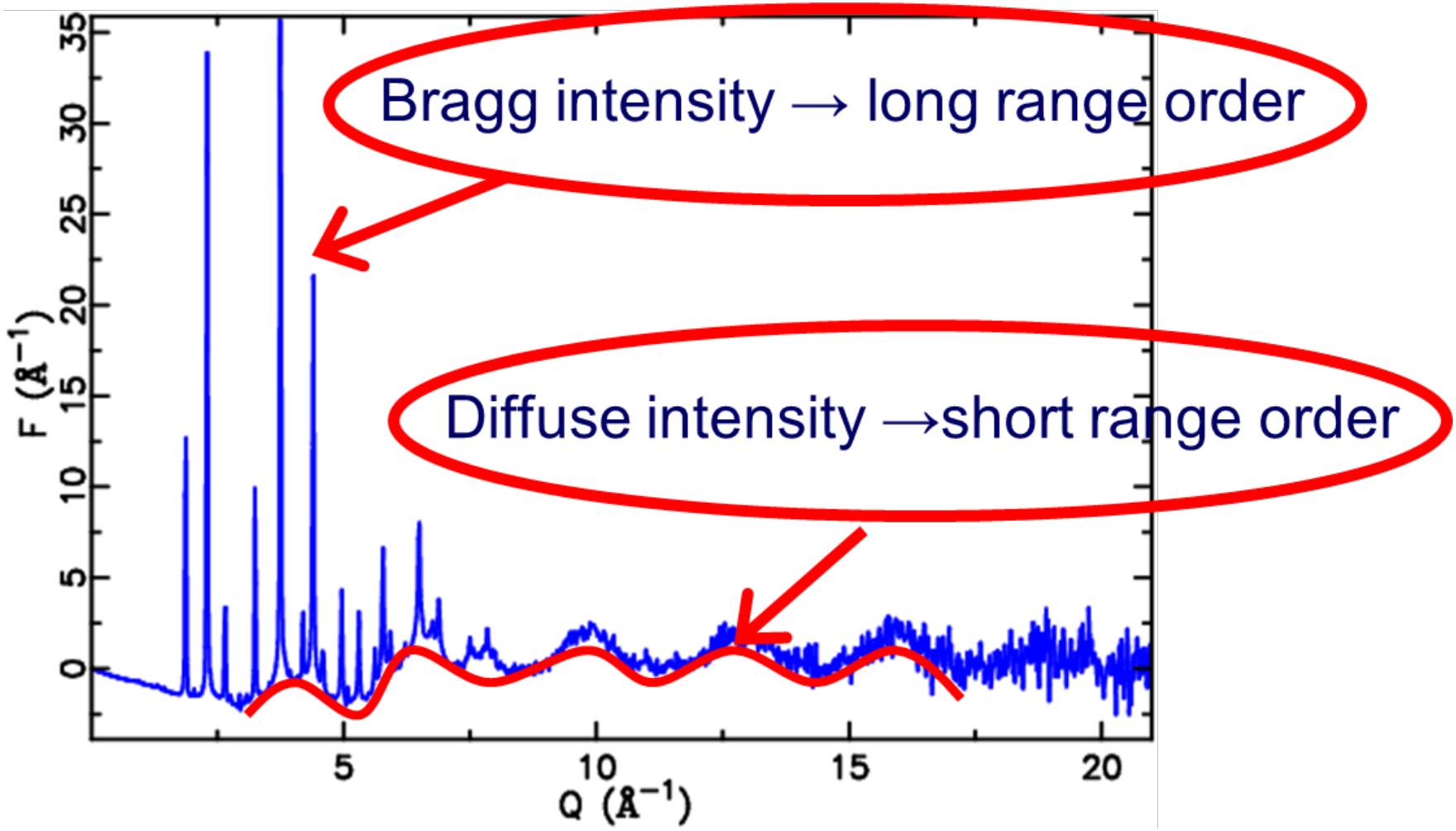
intramolecular correlations

intermolecular correlations

T. Egami & S. Billinge "Underneath the Bragg Peaks"

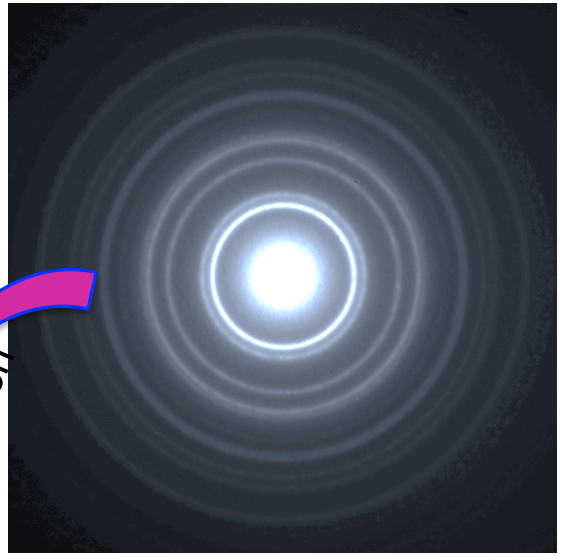
Pair Distribution Function from total scattering experiments

PDF from total scattering experiments (X-ray, neutron or electron sources)



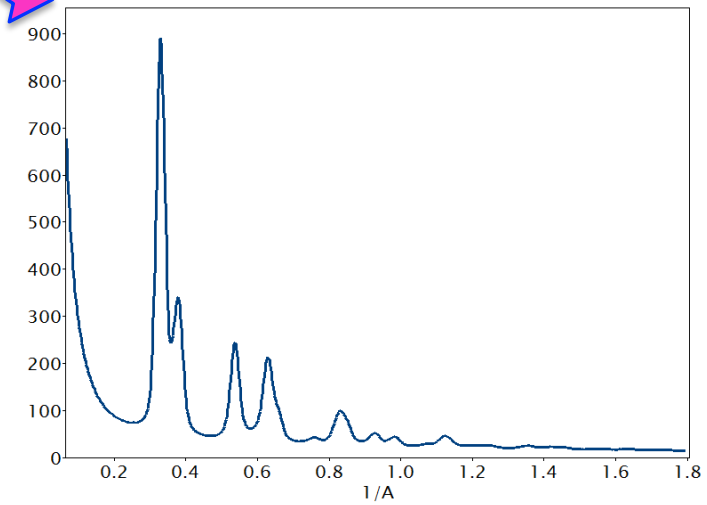
Pair Distribution Function from total scattering experiments

2D diffraction pattern

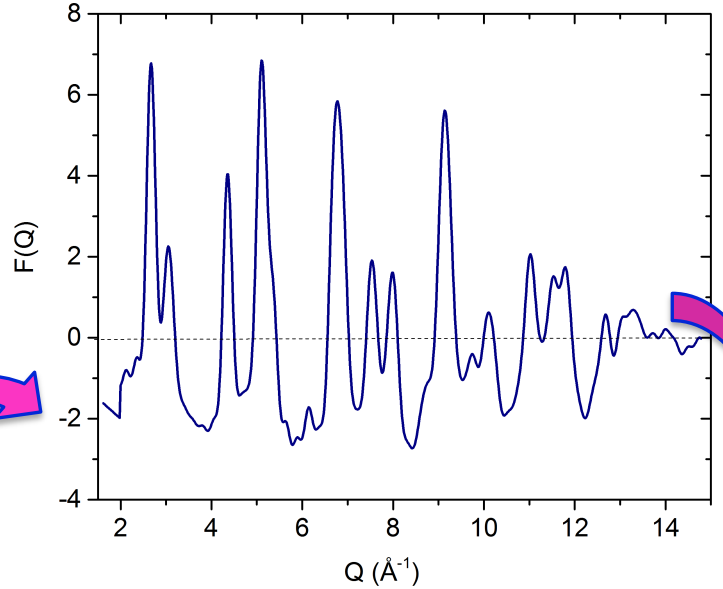


Azimuthal integration

Intensity profile of the 2D diffraction pattern

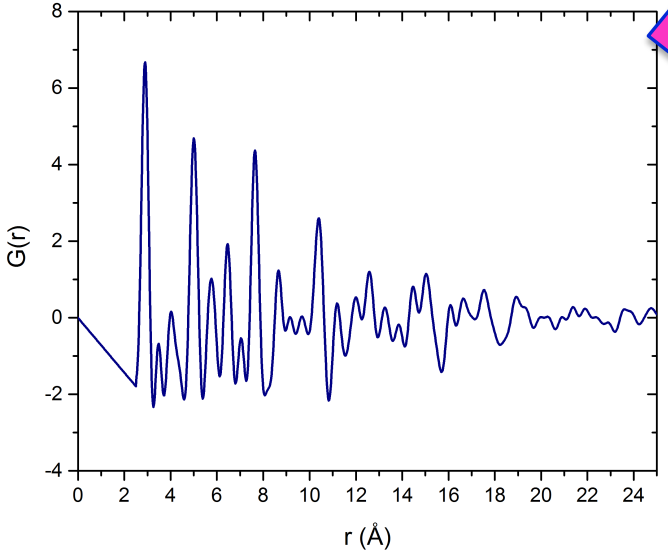


Reduced structure function



Fourier transform

Reduced PDF



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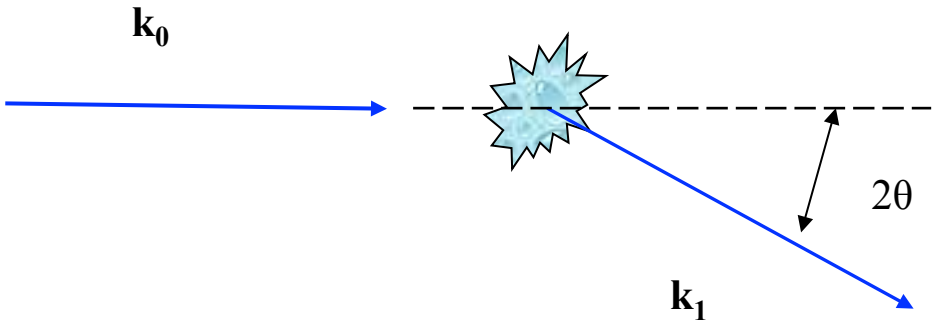
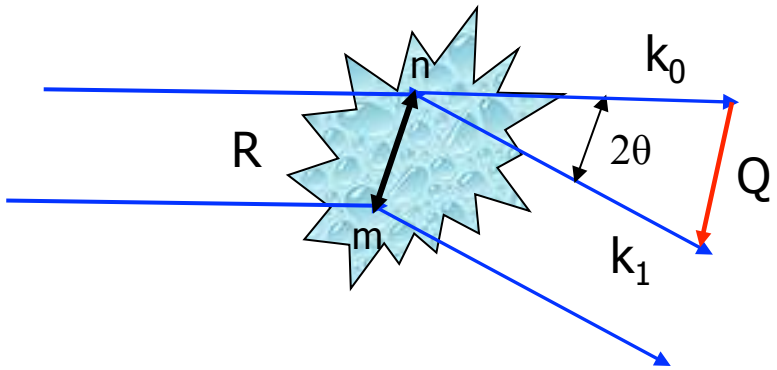
X-ray scattering physics

Plane wave approximation → the source and detector are far away from the object
the object is small



Elastic - no energy loss
coherent - no random phase shift
scattering

X-ray scattering physics



$Q = 2|k|\sin\theta$ scattering vector

$\Delta\varphi = \mathbf{Q}\bullet\mathbf{R}$ phase shift

Scattering intensity

$$I(\mathbf{Q}) = \Sigma A_m e^{-i(\mathbf{Q}\cdot\mathbf{R}_m)} \bullet \Sigma A_n e^{i(\mathbf{Q}\cdot\mathbf{R}_n)} = \Sigma\Sigma A_m A_n e^{-i(\mathbf{Q}\cdot(\mathbf{R}_m - \mathbf{R}_n))}$$

$\{\mathbf{R}_m - \mathbf{R}_n\}$ – Object property (unique set)

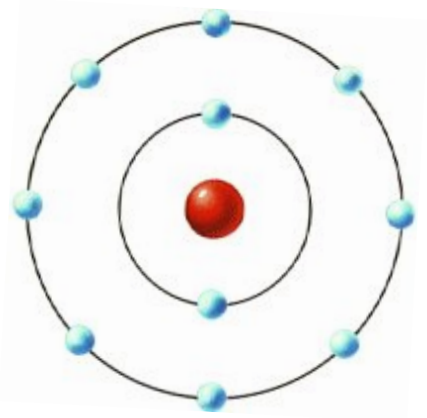
X-ray scattering physics

Atomic scattering amplitude E(Q)

E(Q) is the sum of all the electrons scattering amplitudes

$$A_{at}(Q) = \sum_{j=0}^{Z-1} A_e(Q) e^{-i(Qr)}$$

Atomic scattering factor f(Q)



$$f(Q) = A_{at}(Q) / A_e(Q)$$

$$f(Q) = \sum_{j=0}^{Z-1} e^{-i(Qrj)}$$

$Q=0, f(Q)=Z$

$$f_e(Q) = \frac{2}{a_0}\left[\frac{Z - f_X(Q)}{Q^2}\right]$$

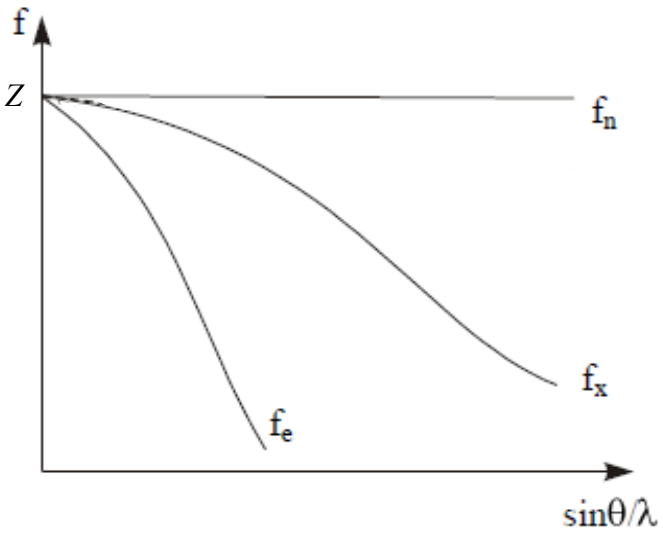
Bohr radius $a_0 \approx 0.5292$ Å

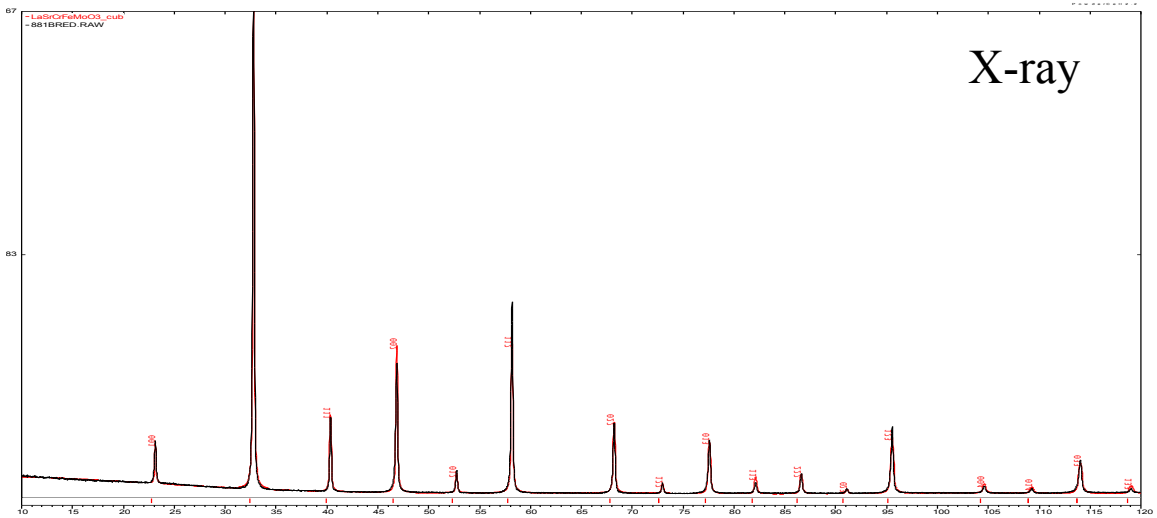
$r_j=0$, $f(Q)=Z$ *and doesn't depend on Q*

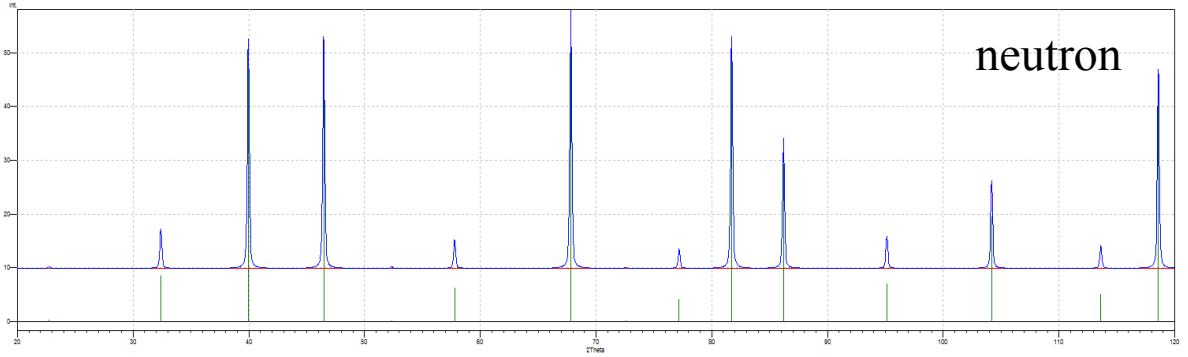
↓

Since electrons are not concentrated in one point *f(Q)* depends on Q = $4\pi\sin\theta/\lambda$

Atomic scattering factor







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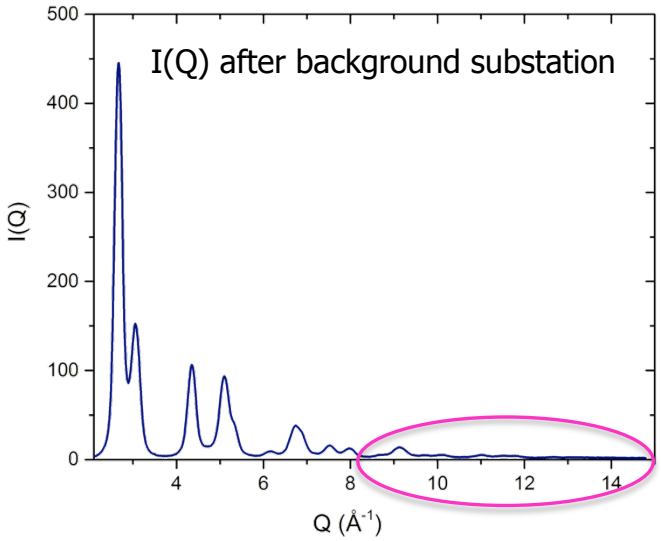
Mathematical basis of the PDF

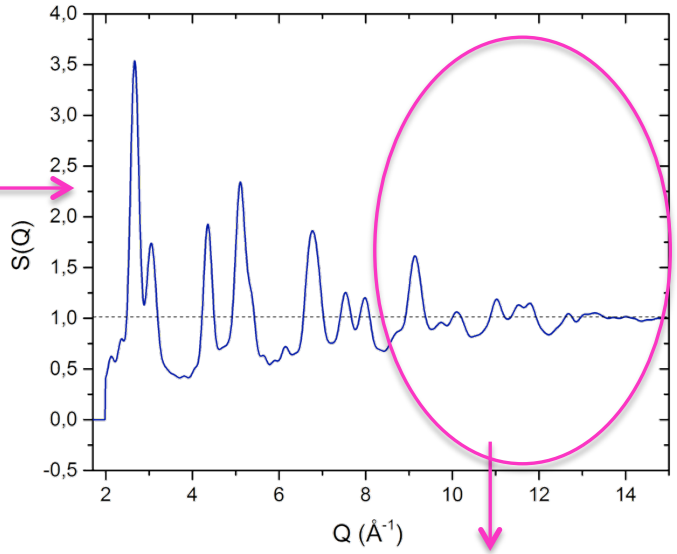
Debye's scattering intensity

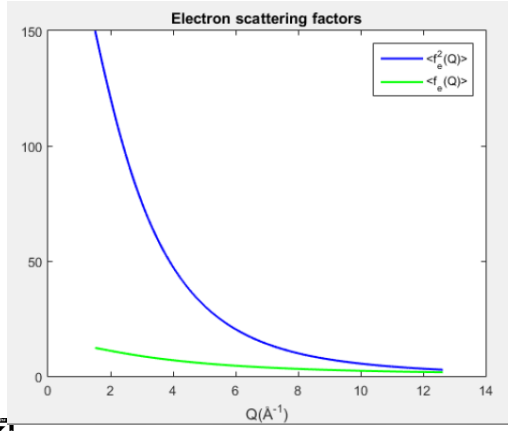
$$I(Q) = \sum_{j,k}^{N} f_j(Q) f_k(Q) \frac{\sin(Qr_{jk})}{Qr_{jk}}$$



Total scattering structure function

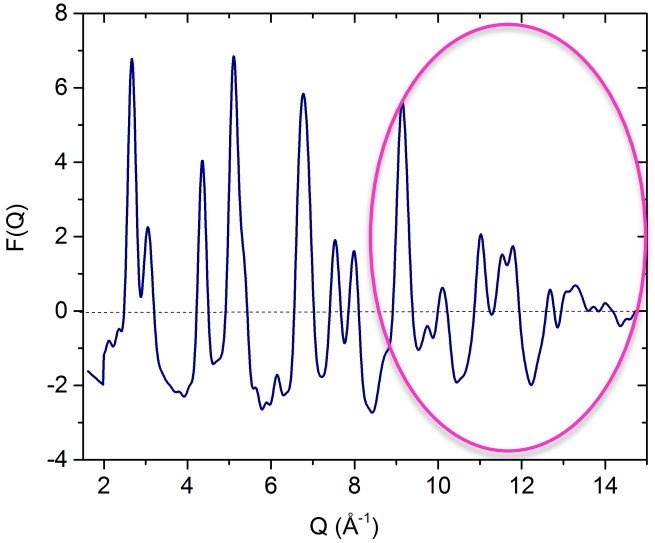
$$S(Q) = 1 + \frac{I(Q) - \langle f^2(Q) \rangle_{composition}}{\langle f(Q) \rangle^2_{composition}}$$

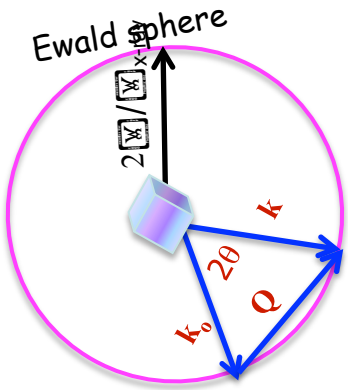




Reduced total scattering structure function

$$F(Q) = Q[S(Q) - 1]$$





$Q = 2|k|\sin\theta$

$k = 2\pi/\lambda$

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

$Q = 2\pi/d$

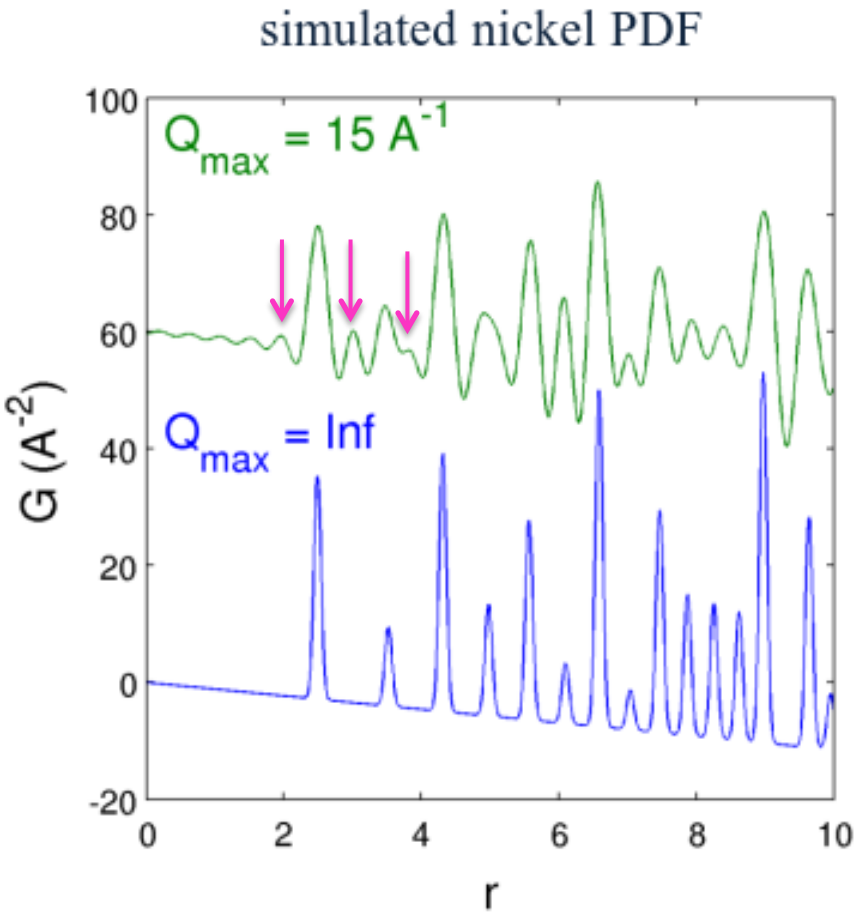
Mathematical basis of the PDF

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

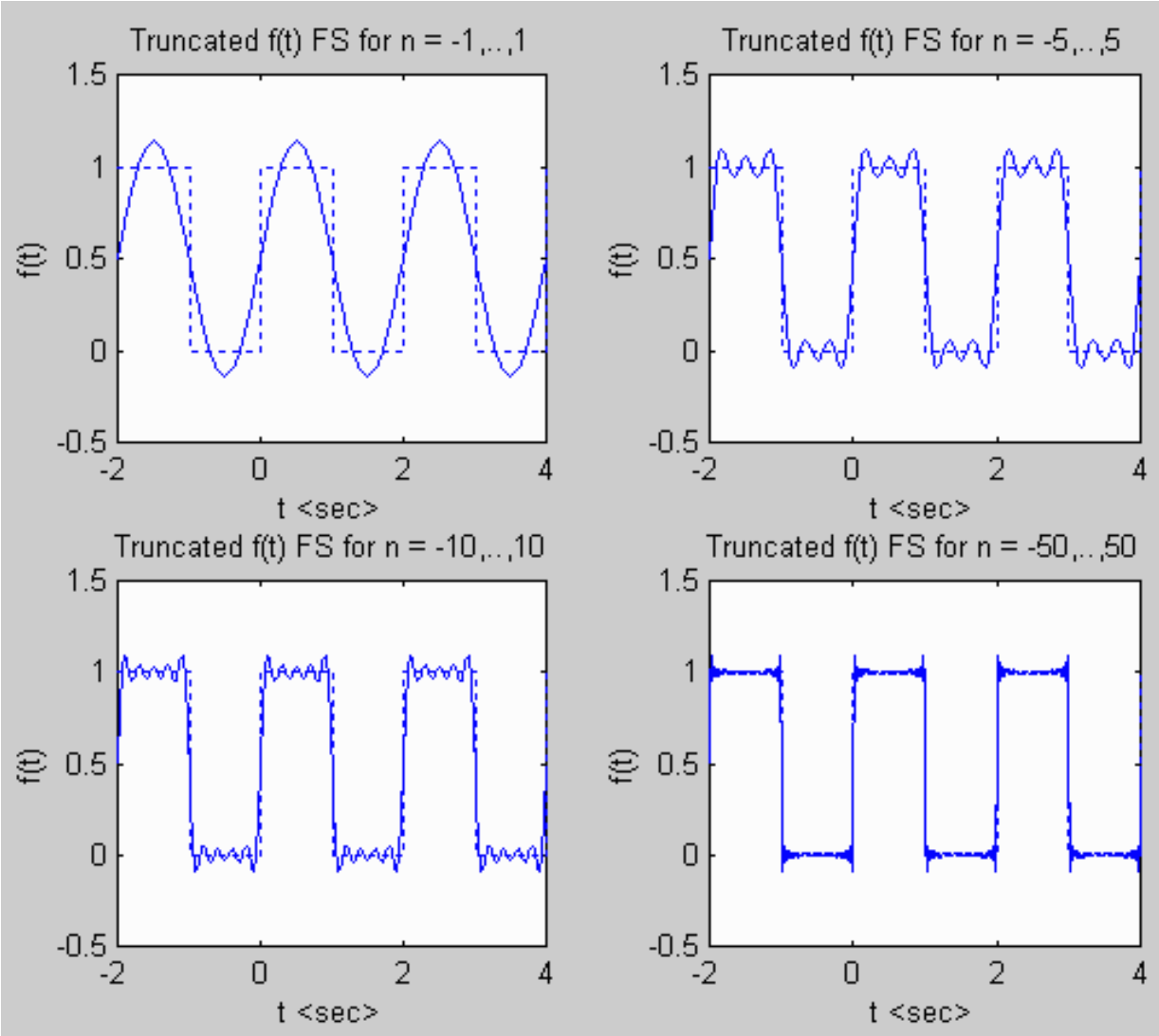
In practice, Q_{min} and Q_{max} are limited

Q_{max}= 30-50 Å^{-1} (X-ray Synchrotron)
Q_{max}= 10-23 Å^{-1} (electrons)

$$G(r) = \left(\frac{2}{\pi}\right)\int_{Q_{min}}^{Q_{max}} F(Q)\sin(Qr)\mathrm{d}Q$$

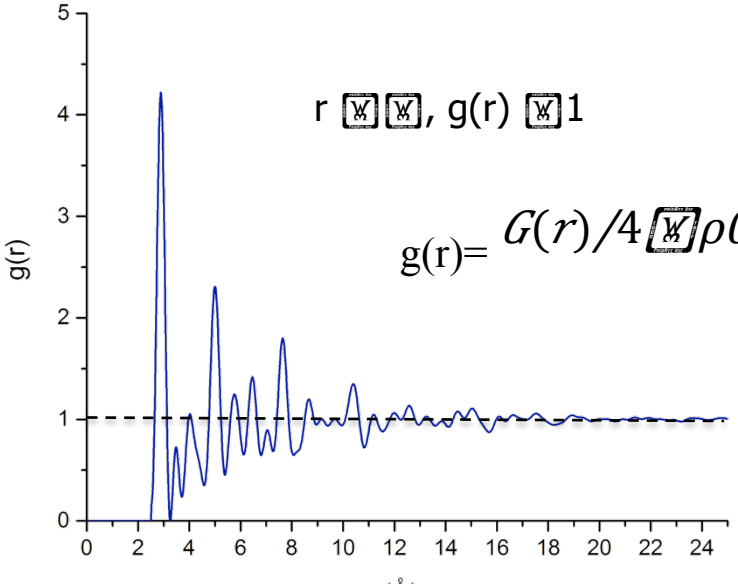


Truncation of Fourier series



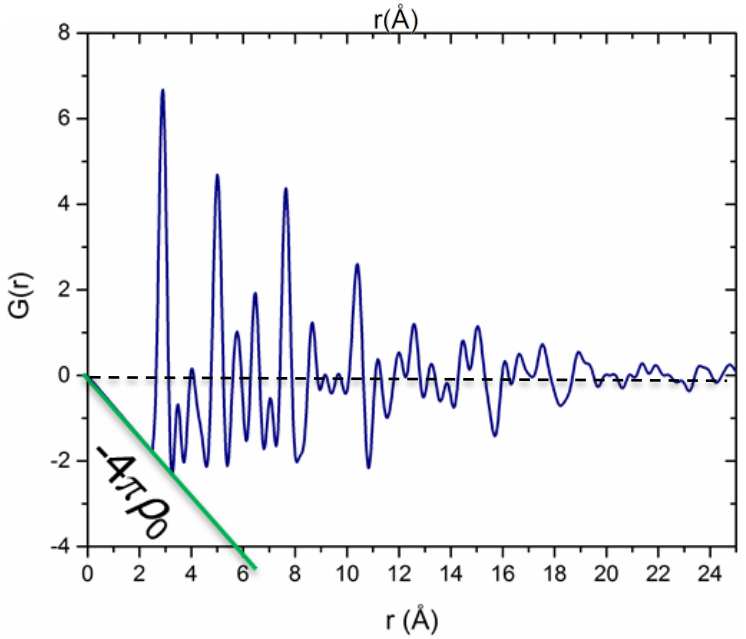
Mathematical basis of the PDF

Pair correlation functions and relationship between them



r □□, g(r) □1

g(r)= $G(r)/4\square\rho 0r$



pair density function: □□r□ = □0g□r□

the average number density of the material

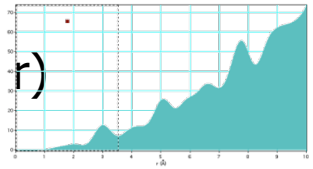
G(r)=4□r(□(r)-□0)= 4□ r□0(g(r)-1

Pair density function

reduced PDF

PDF

R(r)=4□ r2□ r)



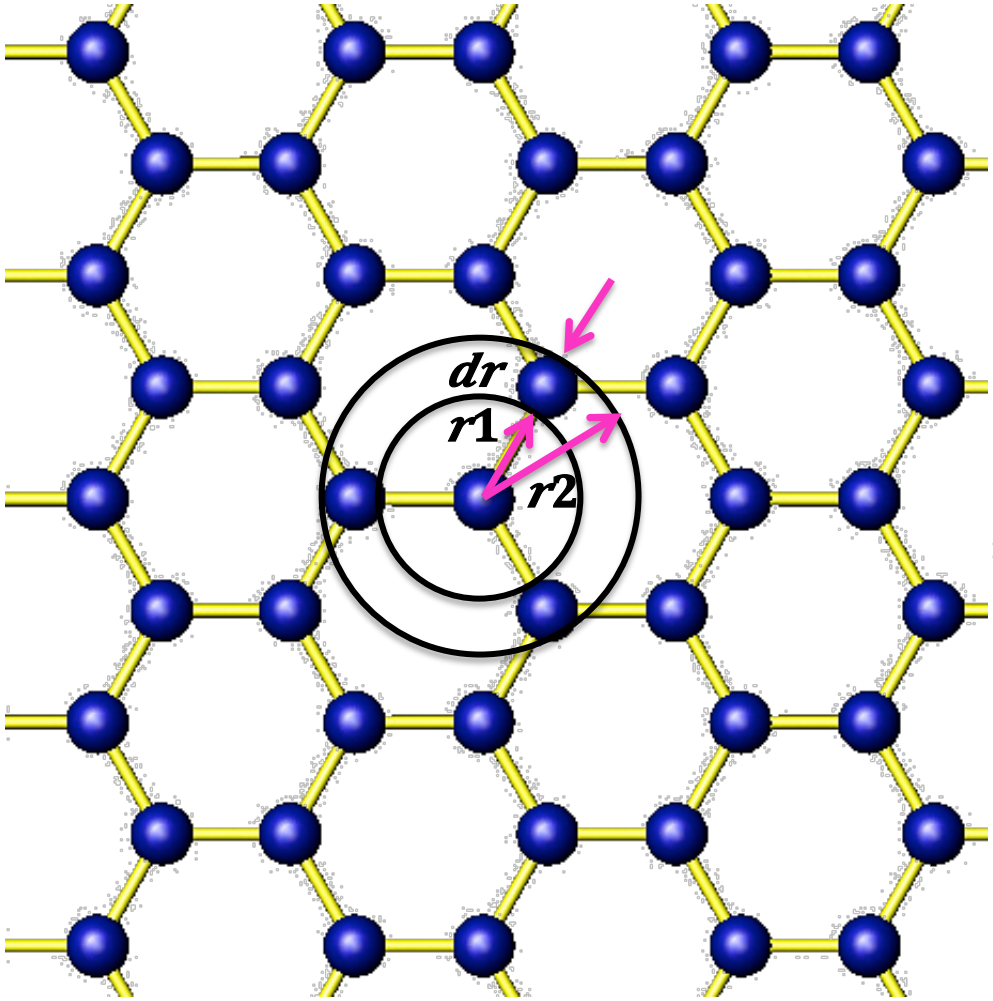
Radial distribution function

G(r)= R(r)/r-4□ r□0

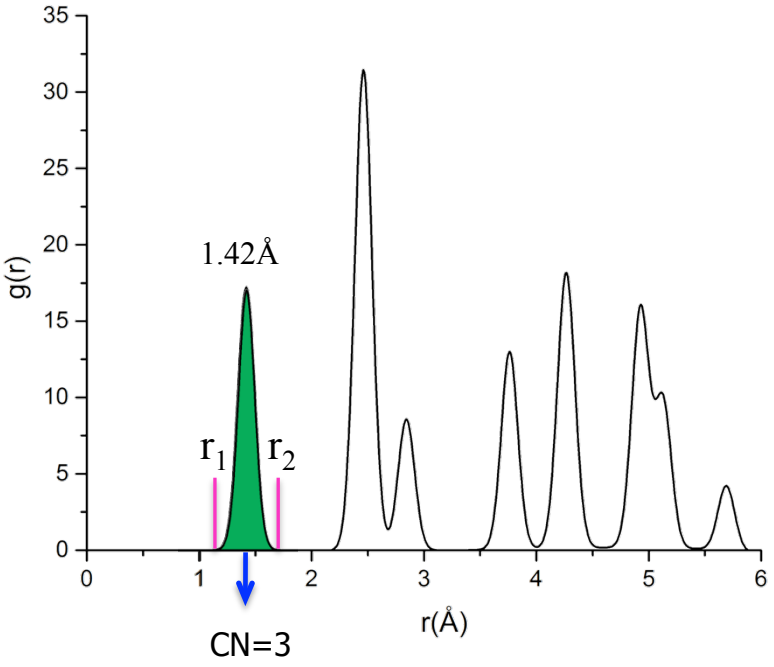
$N_c = \int_{r1}^{r2} R(r)dr$ the number of neighbors

Mathematical basis of the PDF

$$N_{Coord} = \int_{r_1}^{r_2} R(r)dr = \int_{r_1}^{r_2} 4\pi\rho_0 r^2 g(r)dr$$ → the number of neighbors



$R(r)dr$ is a number of atoms in an annulus of thickness dr at a distance r from another atom



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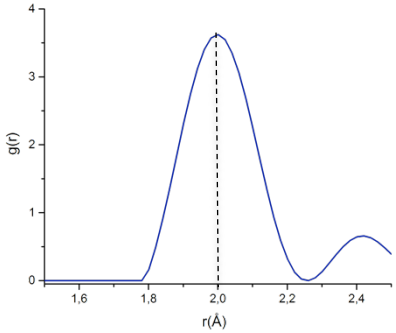
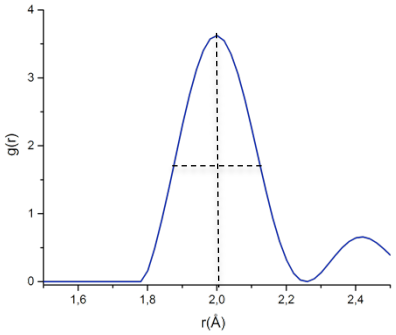
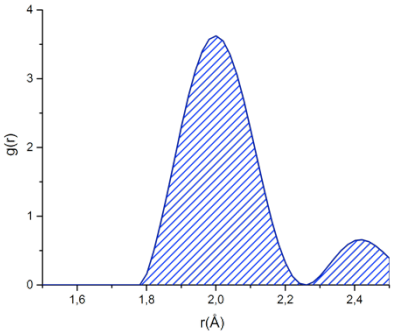
Direct information from the PDF

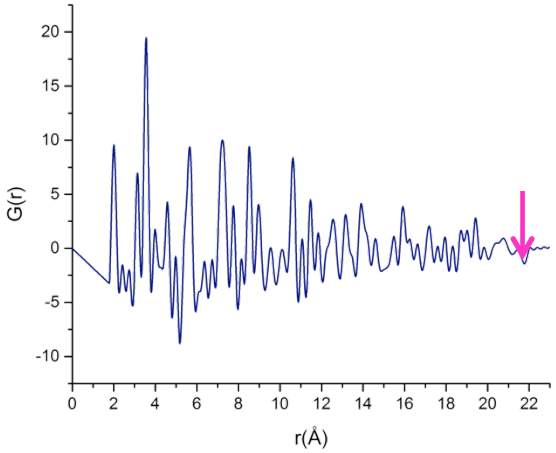
PDF contains the following structural/ configurational information:

- Average interatomic distances → PDF peak position
- A structural disorder → PDF peak width (FWHM)
- Average coordination properties → Integral intensity of PDF peaks
- Particle size effect → PDF peak cut-off



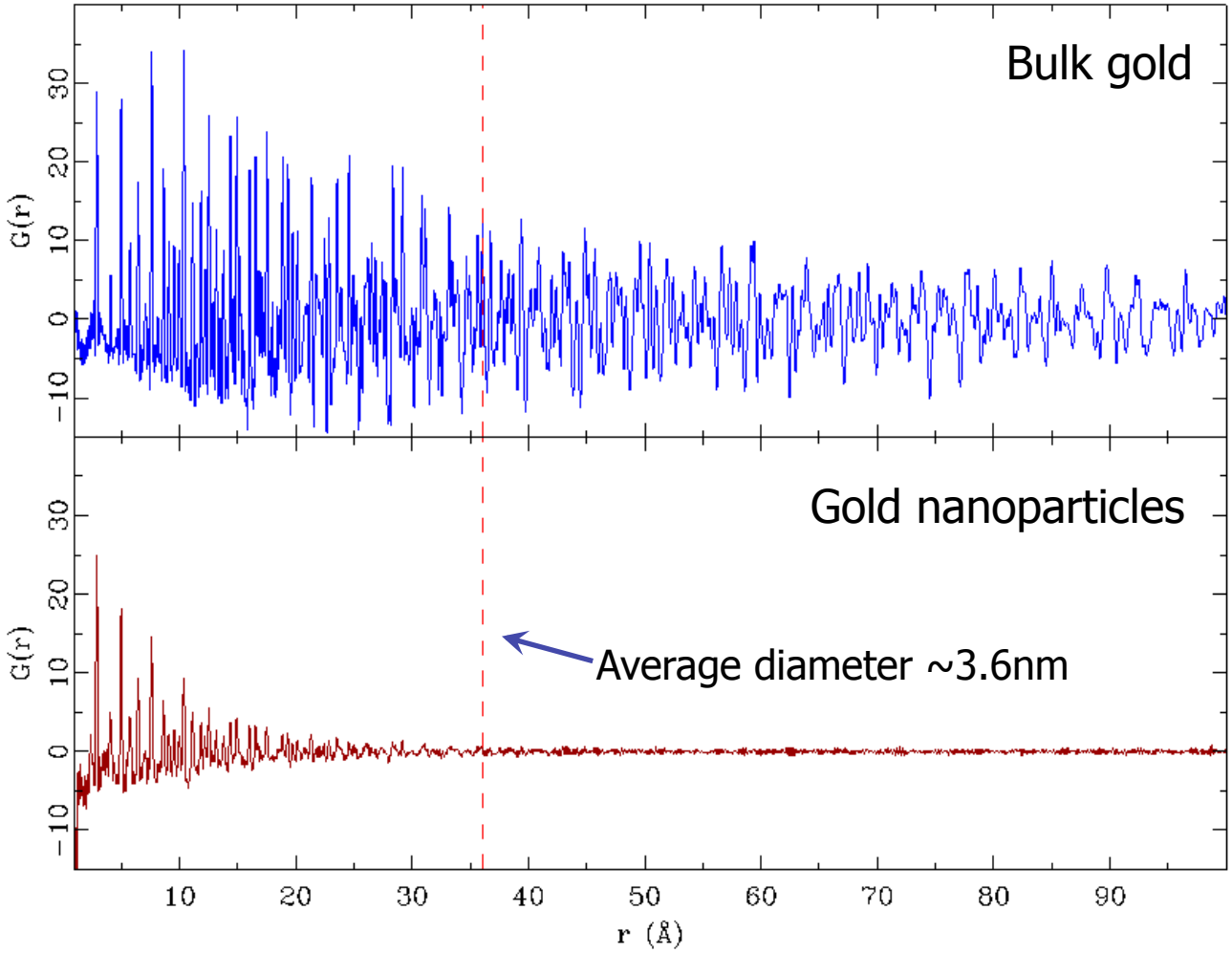






Direct information from the PDF

- PDF peak cut-off



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).

Direct information from the PDF

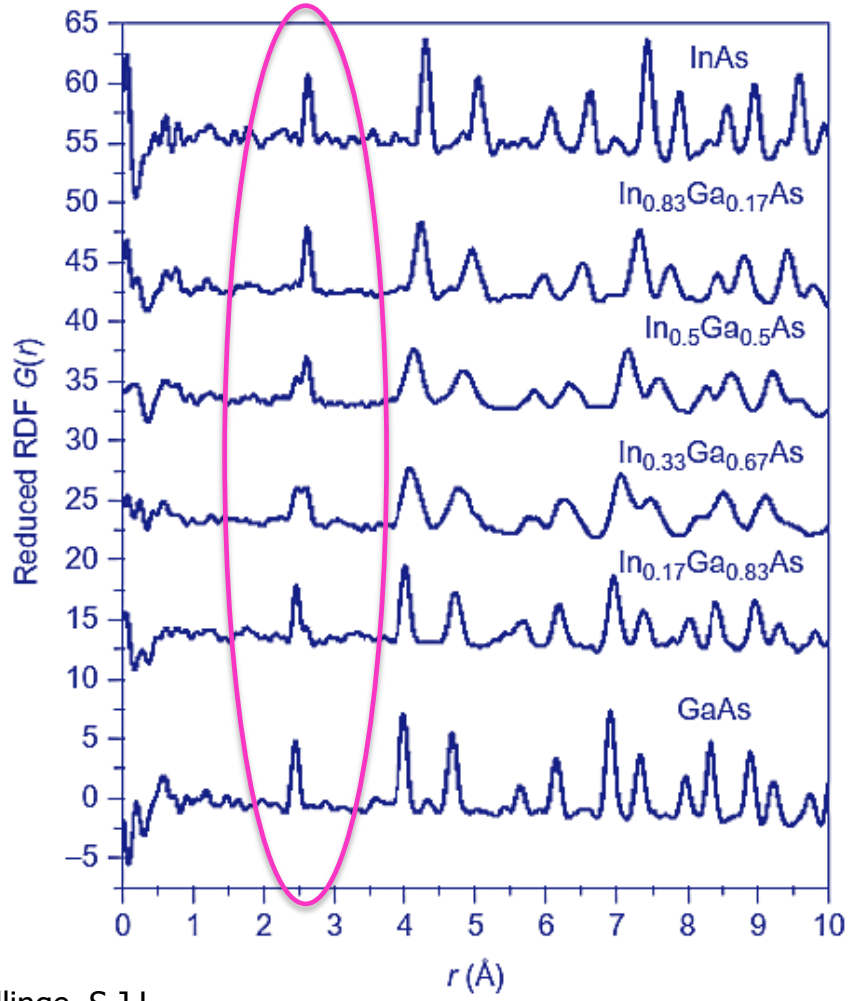
- The PDF peak position yields bond length directly

$In_{1-x}Ga_xAs$

In-As
Ga-As
bond length differs by ~0.14 Å

The lattice constant changes linearly with x, following Vegard's low

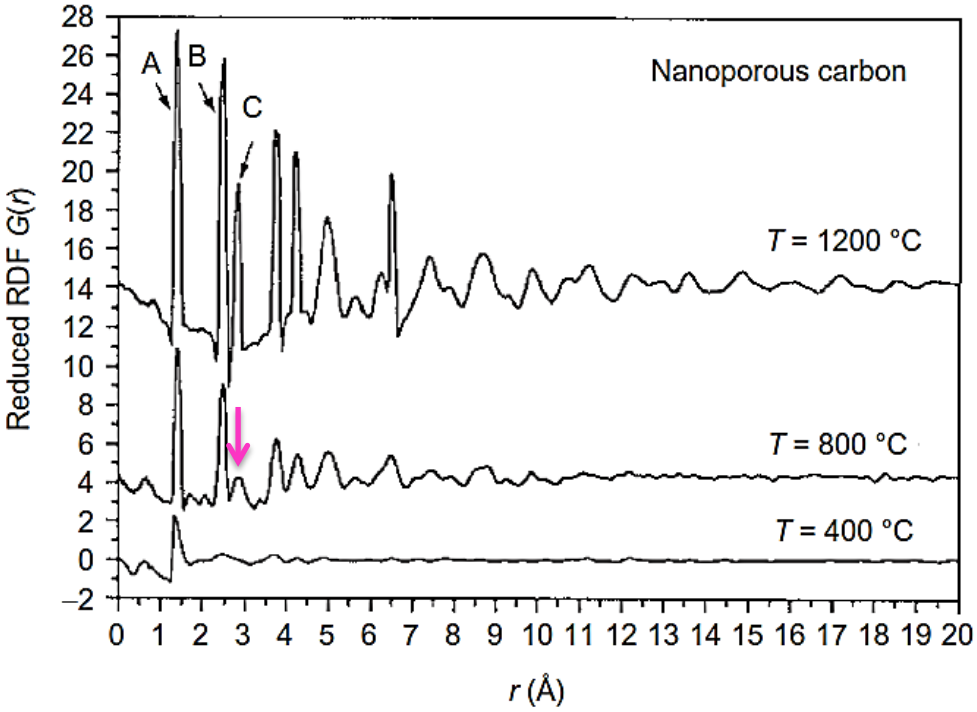
The crystallographic (Ga,In)-As distance represents only the average distance between the atoms at the (Ga,In) and As sites and corresponds to neither the actual Ga-As nor In-As distances.

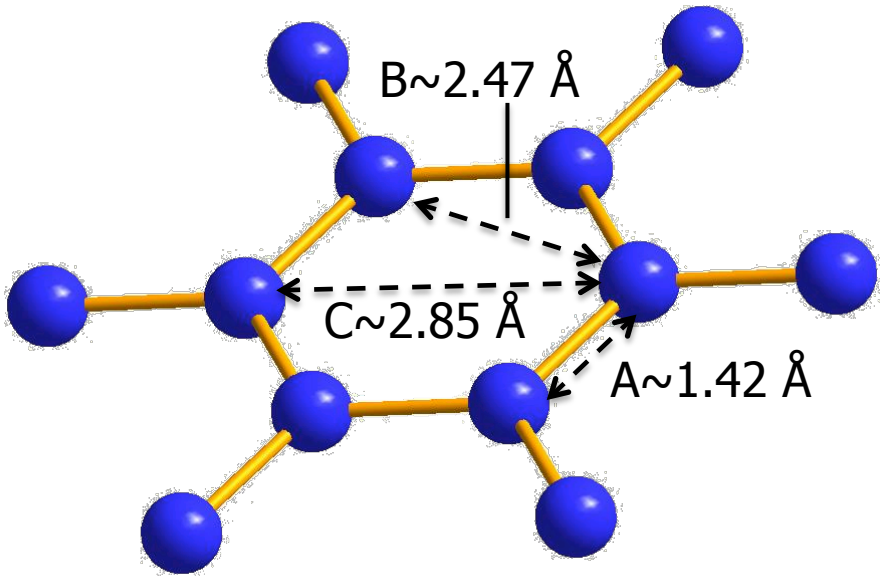


Petkov, V., Jeong, I.-K., Chung, J.S., Thorpe, M.F., Kycia, S. & Billinge, S.J.L. (1999) Phys. Rev.Lett., 83, 4089.

Direct information from the PDF

- The integral intensity of PDF peaks yields the coordination number of the atom-atom correlation

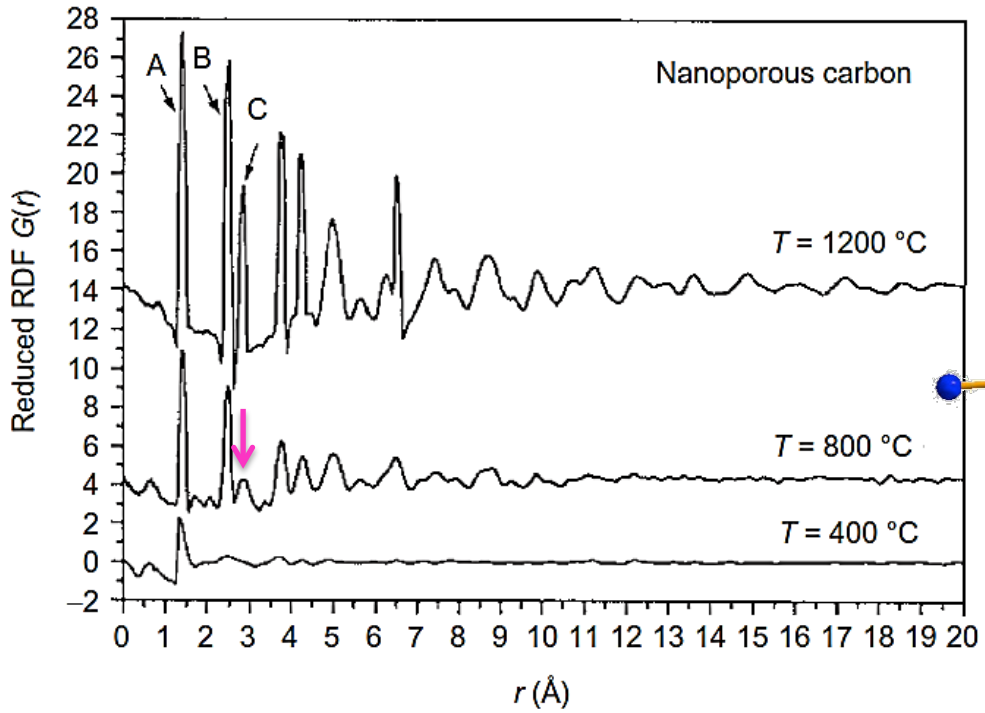


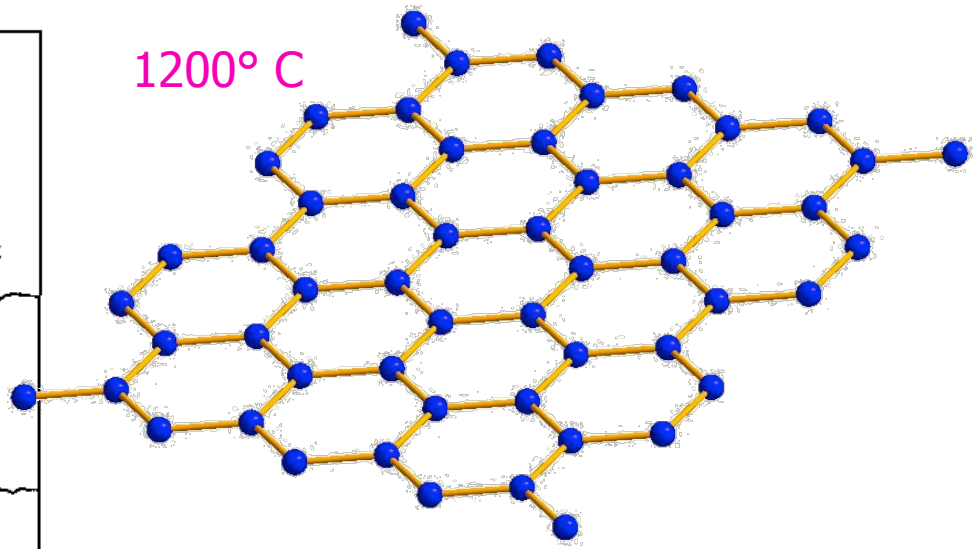


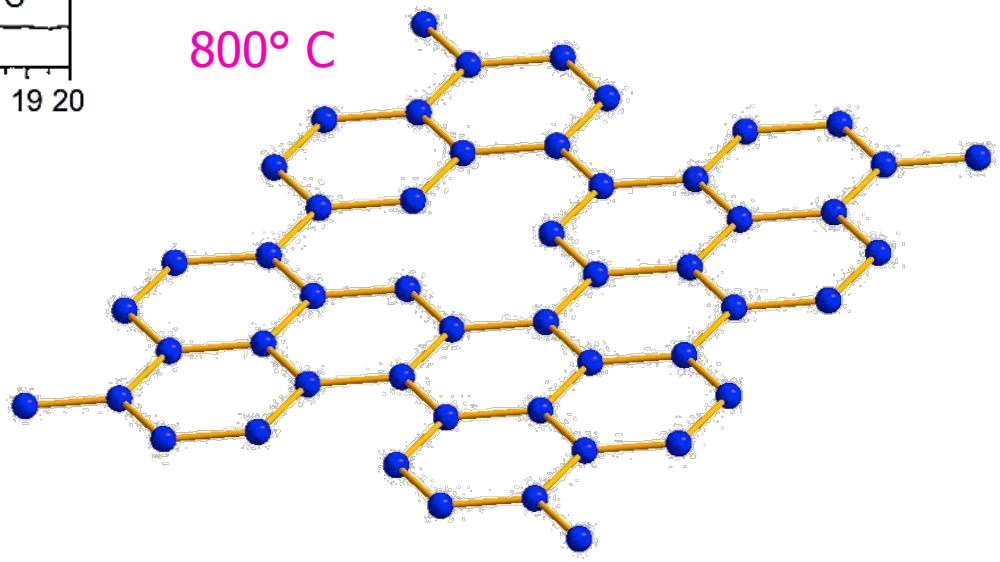
	A (c.n.)
1200° C	3
800° C	2.6
400° C	1.9

Petkov *et al.*, PHILOSOPHICAL MAGAZINE B, 1999, VOL. 79, No. 10, 1519-1530

Direct information from the PDF



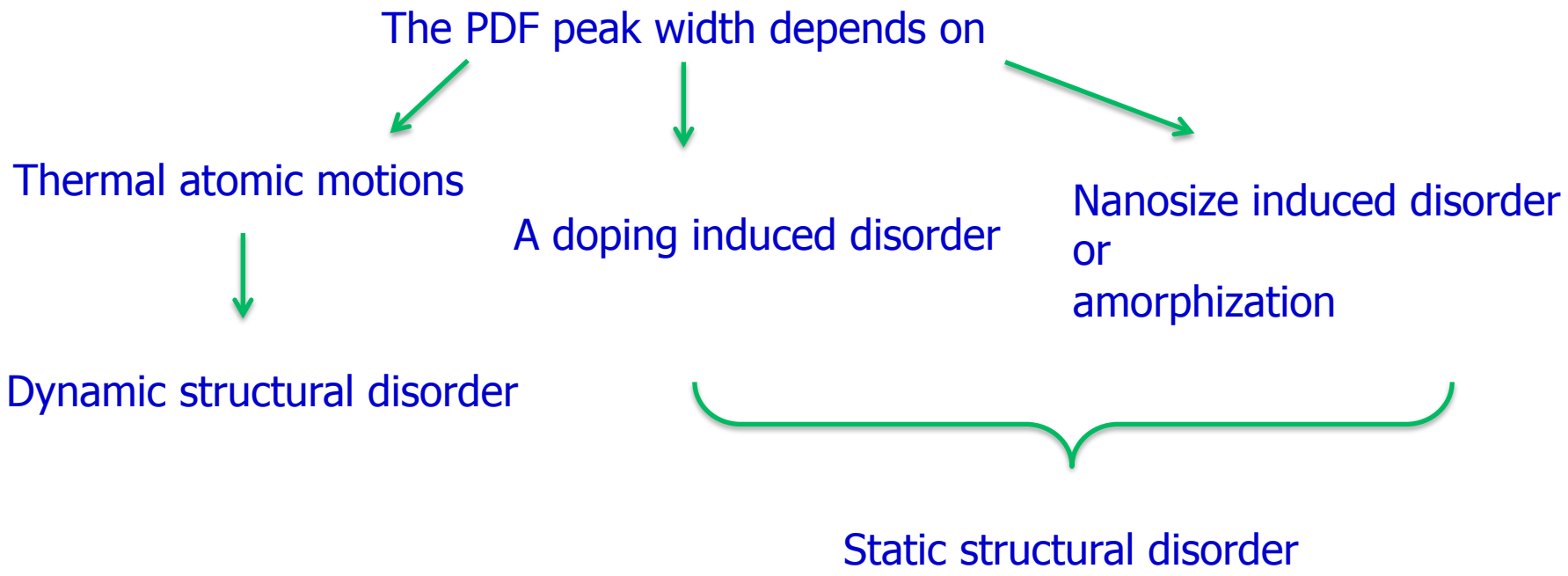




Petkov *et al.*, PHILOSOPHICAL MAGAZINE B, 1999, VOL. 79, No. 10, 1519-1530

Direct information from the PDF

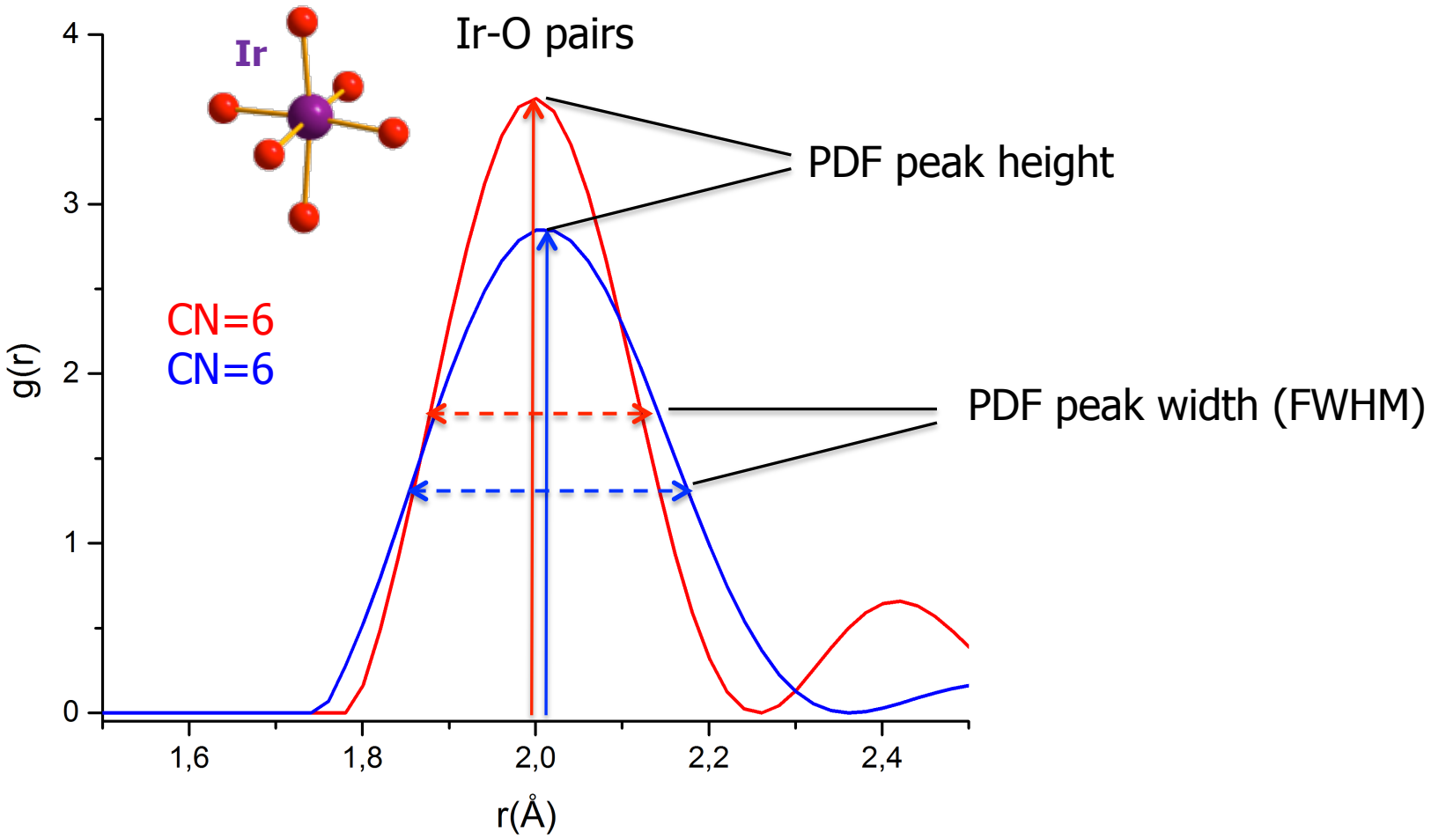
- The PDF peak width reveals information about static and dynamic disorder of atomic pairs



Direct information from the PDF

PDF peak height and PDF peak width are inversely proportional

IrO_2 crystalline phase (Ir^{4+})
IrO_x hydroxide disordered phase (Ir^{4}+Ir^{3+})

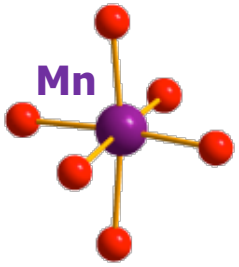


Direct information from the PDF

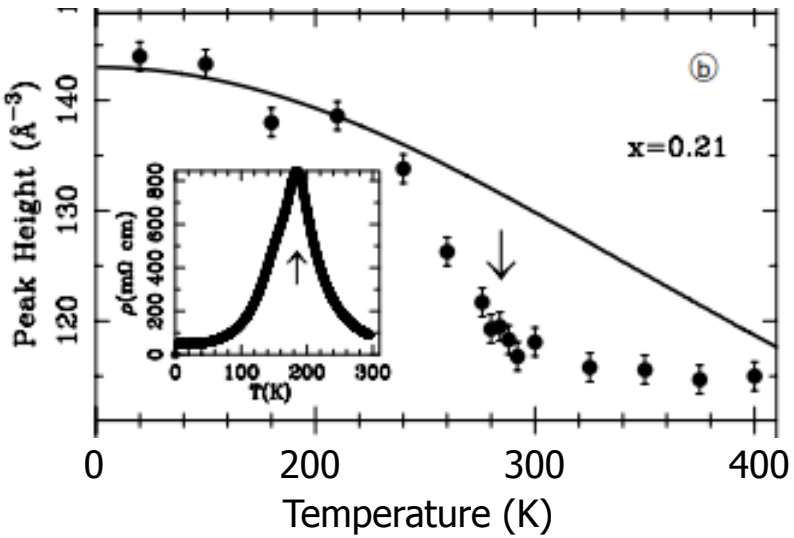
The PDF peak width as a function of doping and temperature

$La_{0.79}Ca_{0.21}MnO_3$

shows a phase transition from insulating paramagnetic phase to a metallic ferromagnetic phase



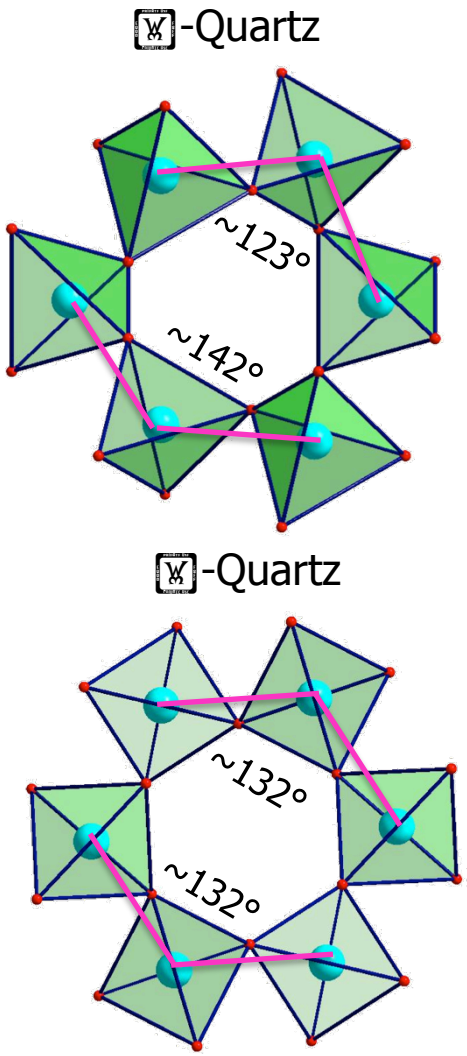
Insulating phase has localized charges: Mn^{3+} and Mn^{4+}
Metallic phase has delocalized charges: $Mn^{(3+x)+}$



Th. Proffen *et al.* Z. Kristallogr. 218 (2003) 132 – 143

Direct information from the PDF

The PDF peak width as a function of temperature



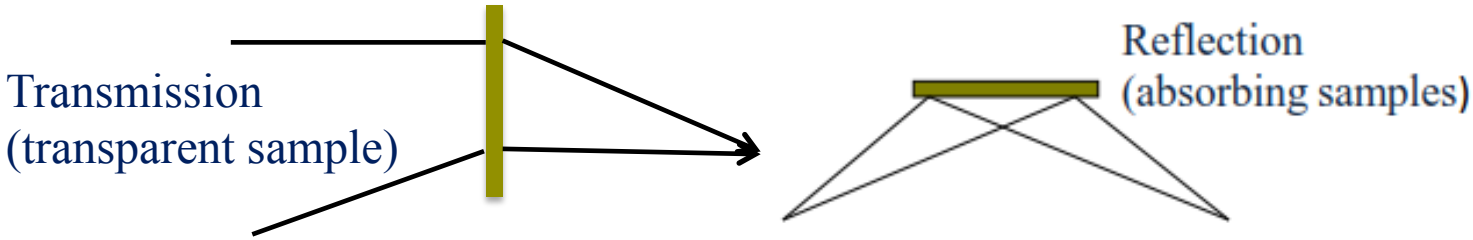
J. Phys.: Condens. Matter 12 (2000) L723–L730

Outline

- What for do we need PDF?
- Scattering intensity
- Mathematical basis of the PDF
- Direct structural information from PDF
- PDF experiments: X-rays, neutrons, electrons
- Catalysis related examples

Where can we measure X-ray PDF?

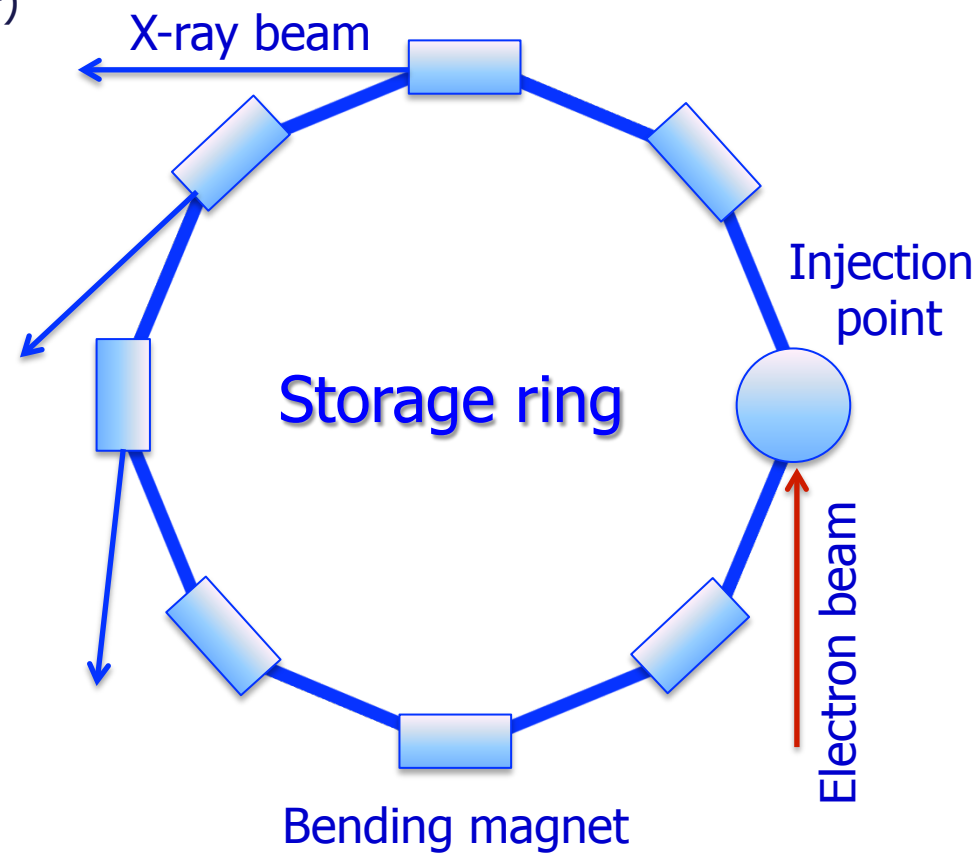
- In house X-ray experiments:
  - Low *r* resolution, slow (and/or poor statistics)
  - *Mo*: $Q_{max} \sim 17 Å^{-1}$, *Ag*: $Q_{max} \sim 20 Å^{-1}$
  - Easy
  - Flat plate transmission or reflection geometry



- Synchrotron experiments:
  - Little precious beamtime, but measurements are quick(er)
  - High *r* resolution using high energy X-rays ($Q_{max} > 60 Å^{-1}$)
  - High intensity (x 10,000 times stronger)
  - Parallel beam optics
  - Generally flat plate or cylindrical transmission geometry

Where can we measure X-ray PDF?

European Synchrotron Radiation Facility (ESRF)
Location: Grenoble (France)



Advantages:

High brightness → small samples
High collimation → high resolution of 2θ
Continuous spread of wavelengths

Disadvantage:

the synchrotron sources are not available on a daily basis

Where can we measure X-ray PDF?

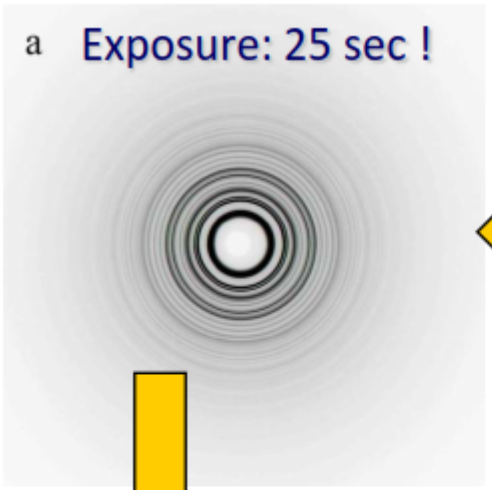
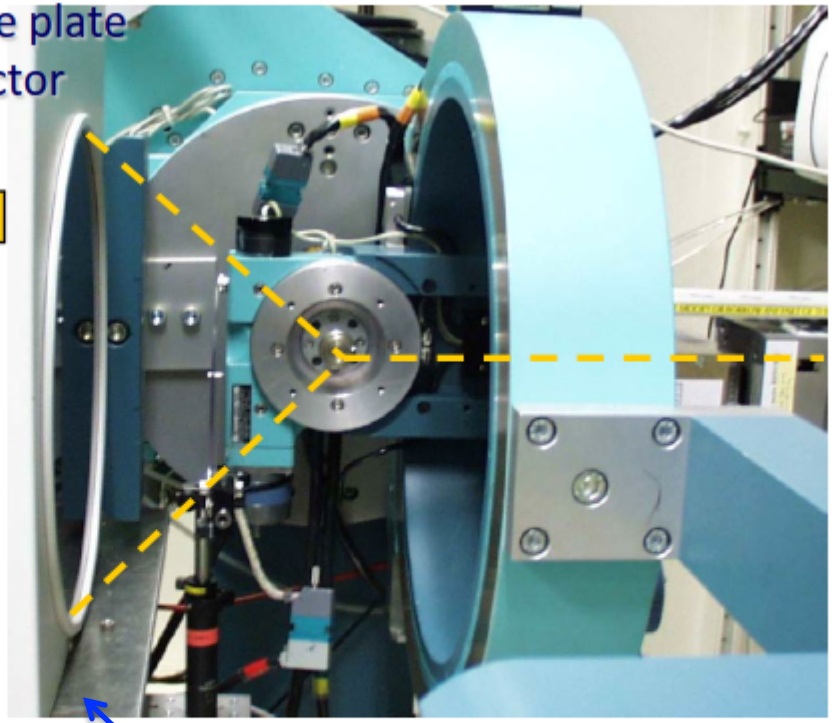
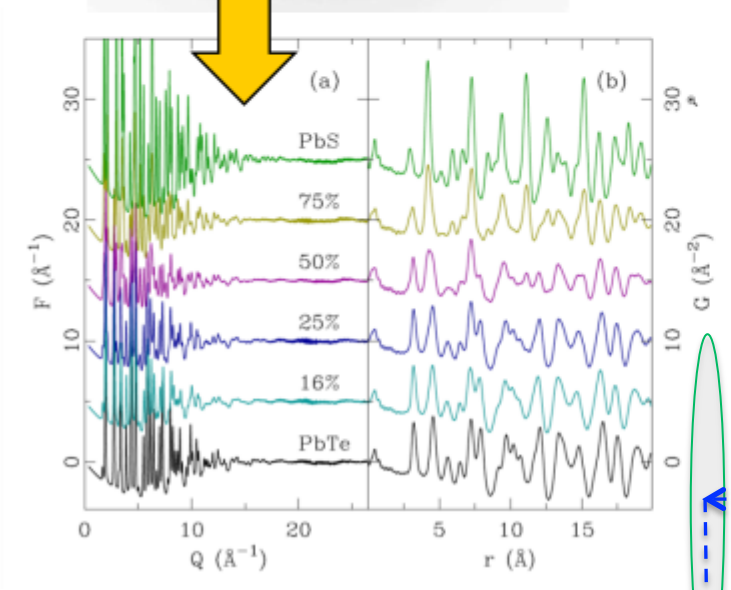
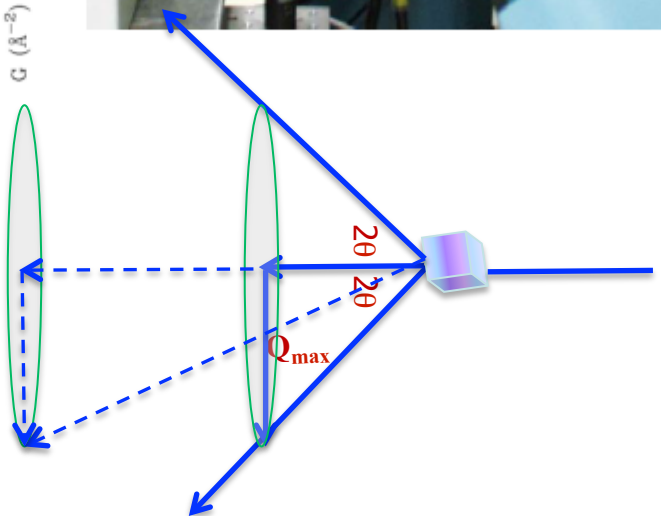


Image plate detector



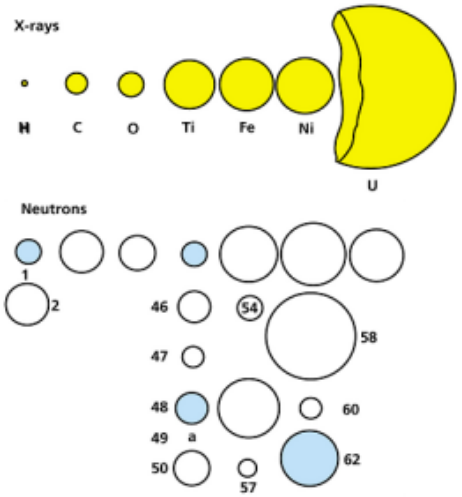




P.J. Chupas, X. Qiu, J.C. Hanson, P.L. Lee, C.P. Grey and S.J.L. Billinge, **Rapid-acquisition pair distribution function (RA-PDF) analysis**, *J. Appl. Cryst.* **36**, 1342-1347 (2003).

X-rays or neutrons?

Highly complementary, depends on the nature of the problem at hand



Synchrotron X-rays

f – proportional to Z (atomic number)

poor sensitivity to light elements

f – decreases with $Q = 4\pi \sin\theta / \lambda$

sample amount ~ 100 mg

acquisition time:
~5 hours for point detector
~10 seconds for area detector
~0.1 seconds a-Si area detector

Neutrons

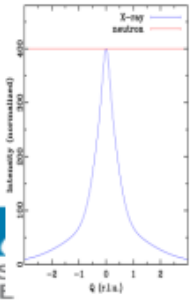
b – fluctuates with Z

sensitive to light elements

b – constant with Q

sample amount ~ 5 – 10 g

acquisition time:
~2-5 hours, possibly longer
(much faster at the latest neutron sources,
e.g., Oak Ridge Laboratory, Tennessee)



Choice could depend also on issues related to the underlying structure, or sample characteristics such as size or absorption

NEUTRONS FOR SCIENCE

BROOKHAVEN NATIONAL LABORATORY

X-rays or electrons?

Pros

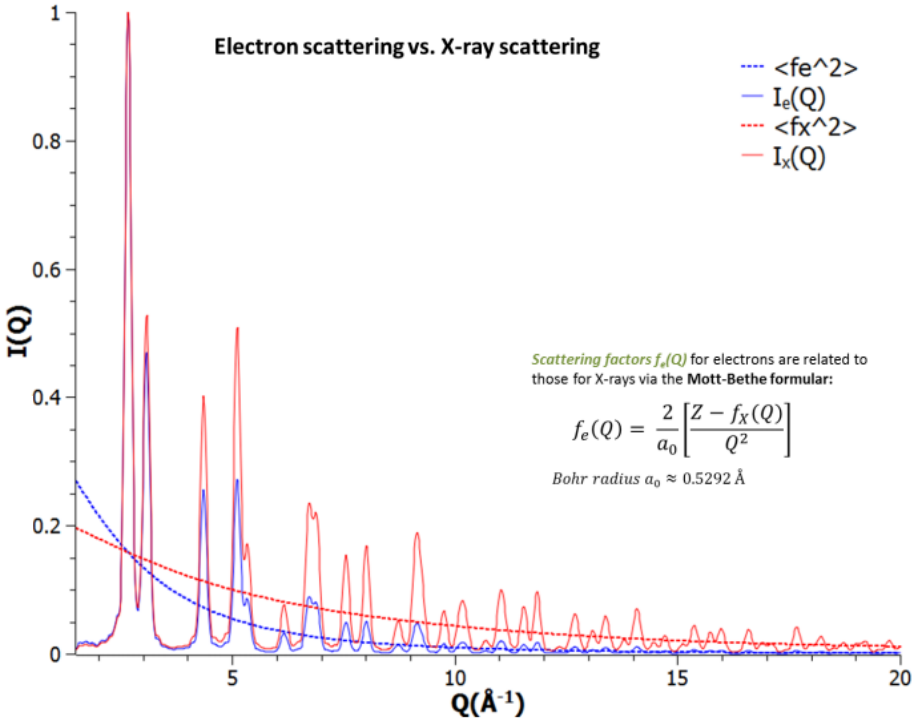
1. A low amount of a sample is needed (fractions of µg).

2. Synchrotron beam time is not needed!!!
TEM operator can easily switch from the image- to diffraction-mode.

3. It is a local method in the TEM.

Cons

1.



2. Electron beam sensitivity of some materials

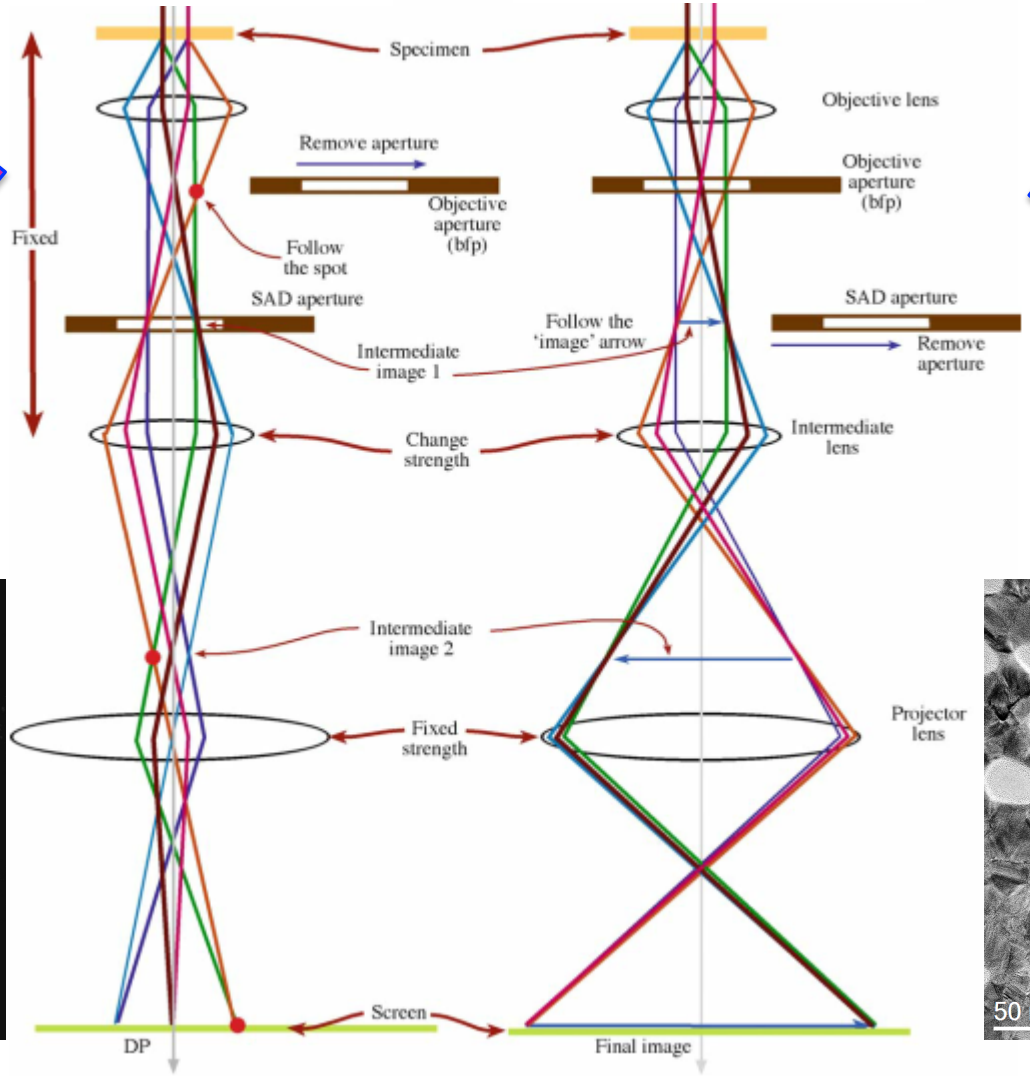
⇩

Electron beam radiation damage is 10 order of magnitude higher than that of X-rays

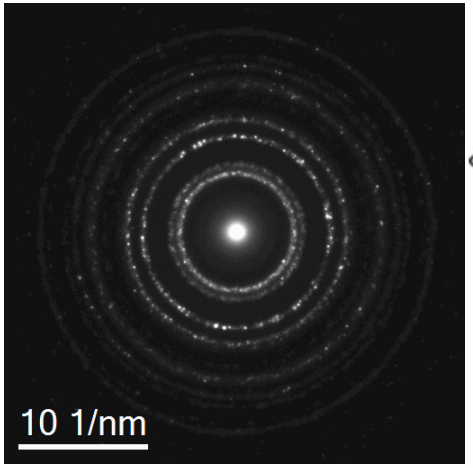
TEM

Diffraction mode

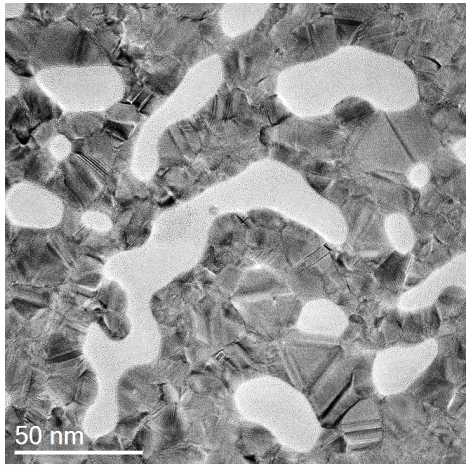
TEM image mode



SAED pattern



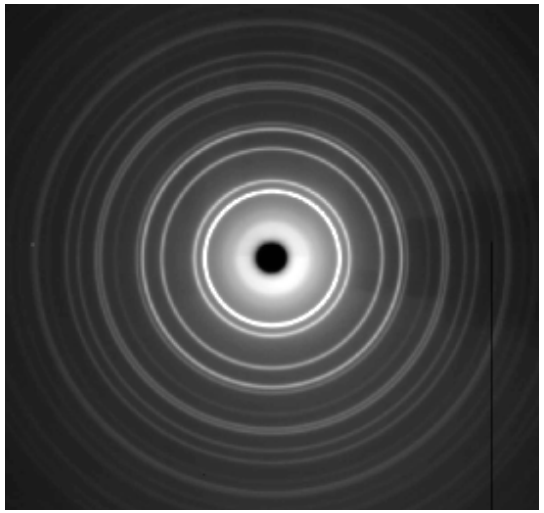
TEM image



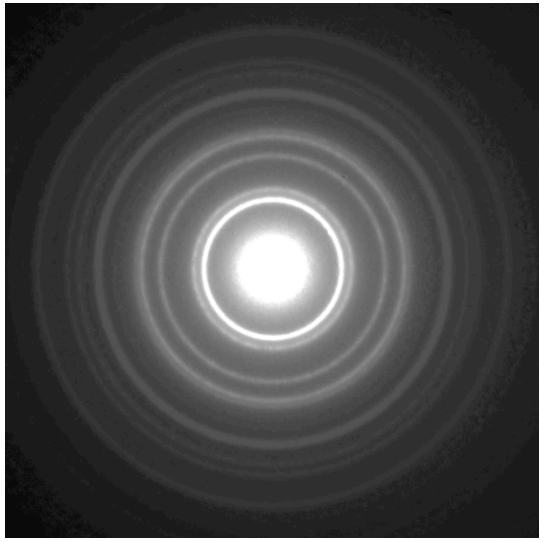
X-rays or electrons?

10 nm Au nanoparticles (Q_{max}=10Å^{-1})

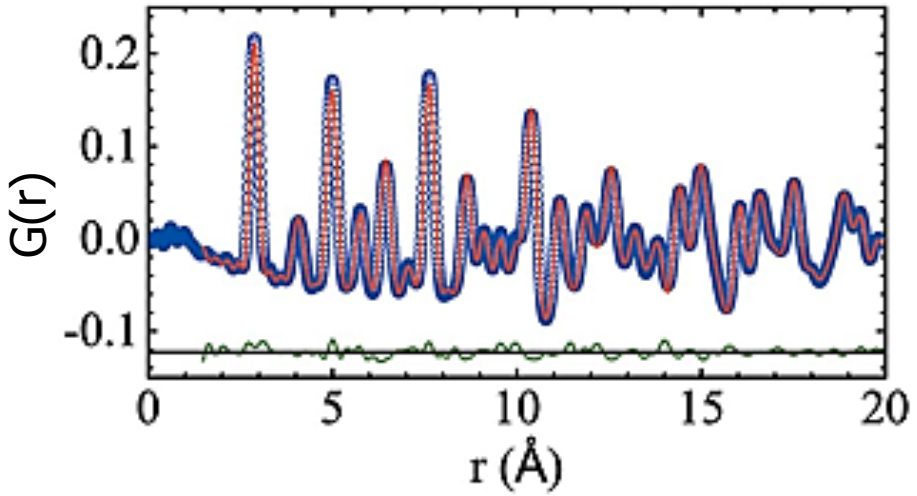
2D XRD pattern



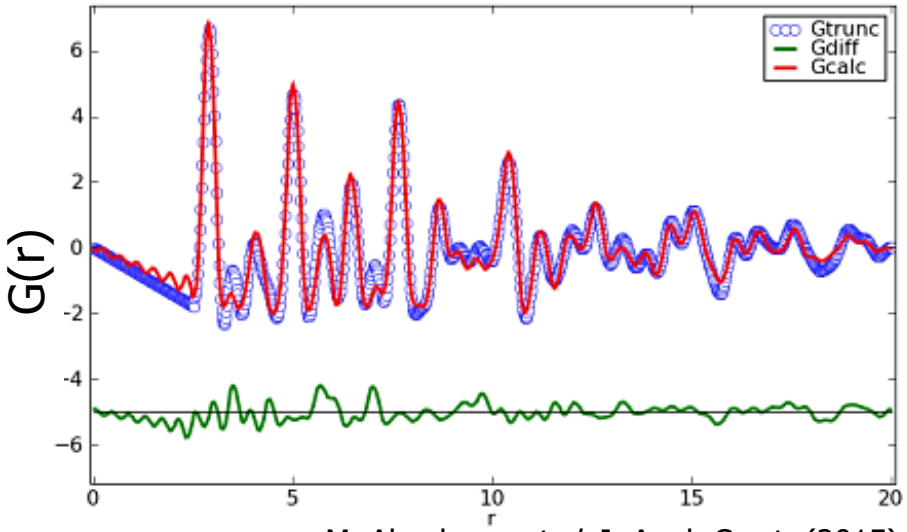
2D ED pattern



X-ray PDF



electron PDF



M. Abeykoon *et al.* J. Appl. Cryst. (2015). 48, 244–251

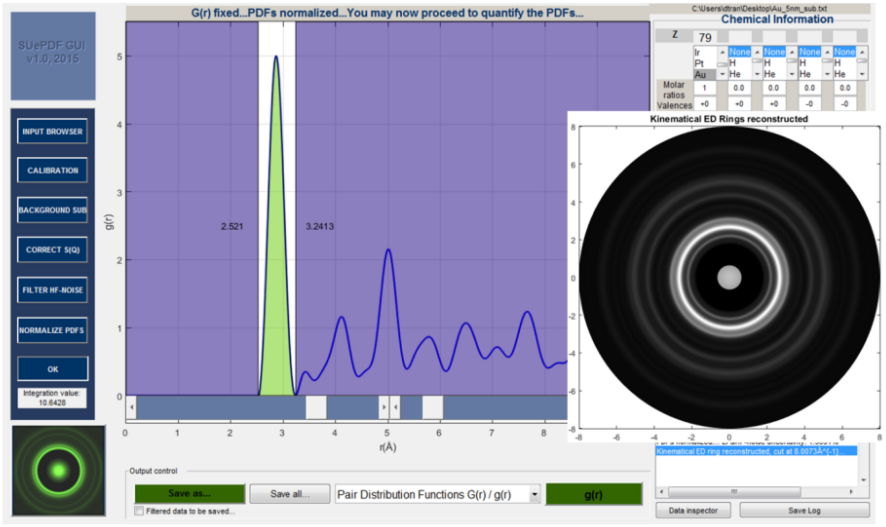
Software for PDF modelling

The Software to abstract PDF from diffraction data

PDFgetX3 for XRD pattern

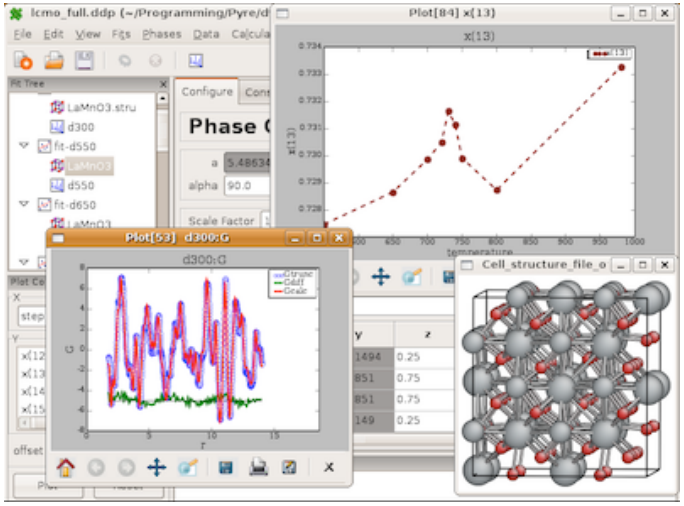
PDFgetN for NPD pattern

SUePDF for electron diffraction pattern



The software to model PDF

PDFgui (a least squares approach)



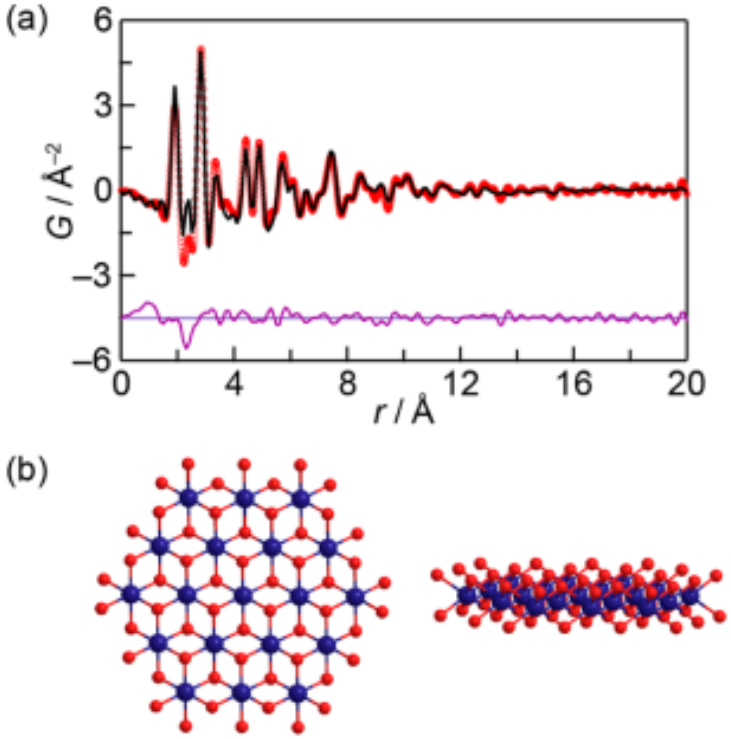
DiffPy-CMI advanced modelling

THE BILLINGE GROUP: COLUMBIA UNIVERSITY
Department of Applied Physics and Applied Mathematics
https://thebillingegroup.com/simon-billinge/

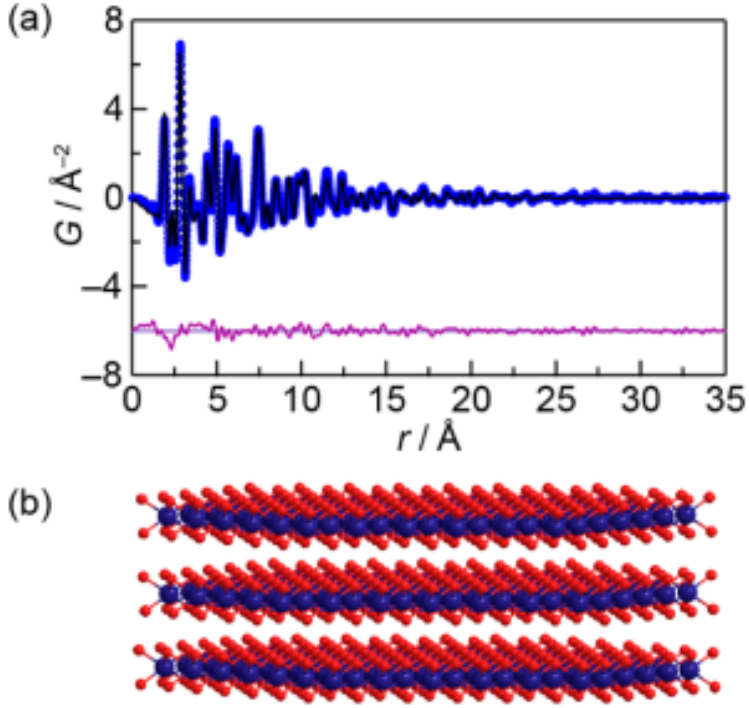
Software for PDF modelling

Advanced modeling for nanoscale materials with SrFit and SrReal using Debye equation

CoPi



CoBi



Christopher L. Farrow *et al*. J. Am. Chem. Soc. 2013, 135, 6403−6406

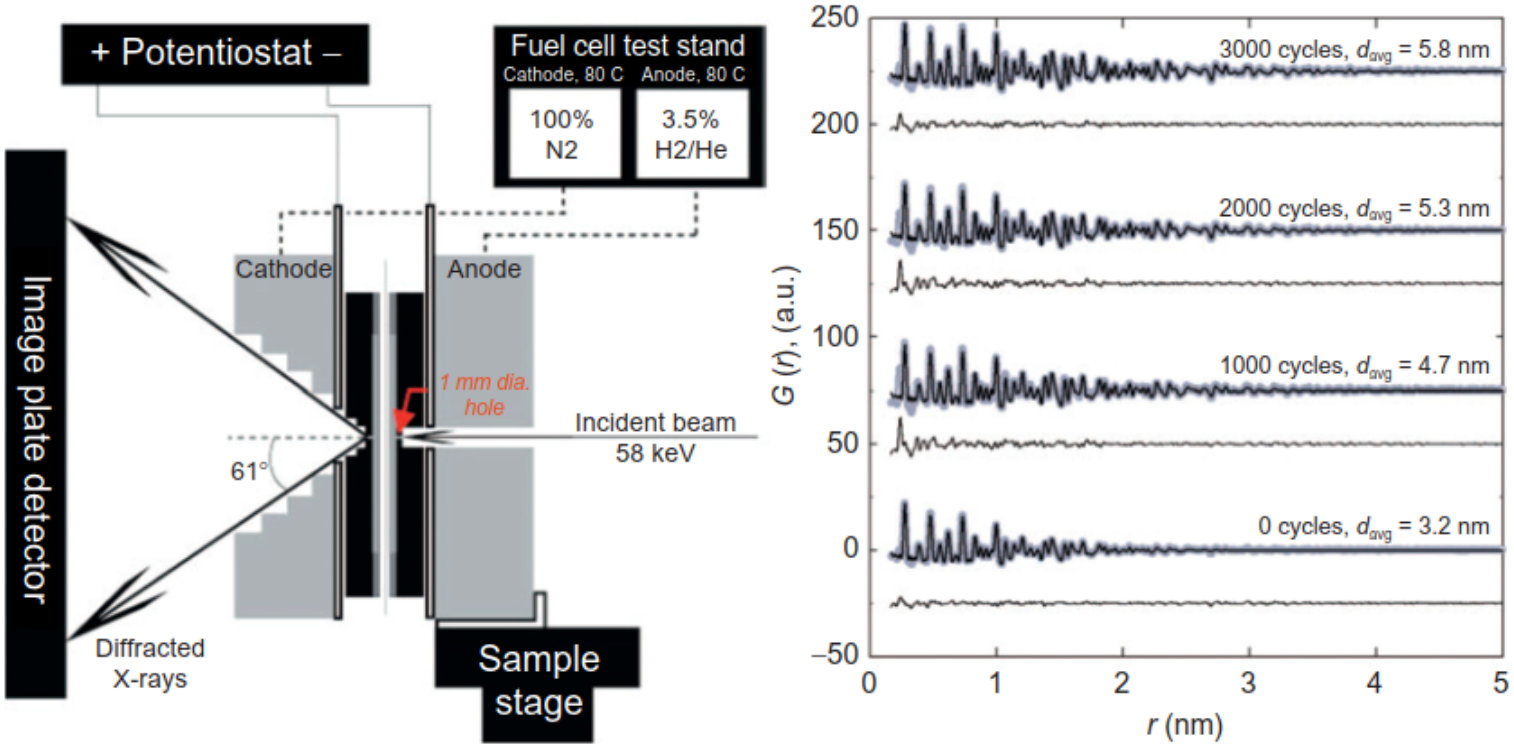
Outline

- What for do we need PDF?
- Scattering intensity
- Mathematical basis of the PDF
- Direct structural information from PDF
- PDF experiments: X-rays, neutrons, electrons
- Catalysis related examples

Catalysis related examples

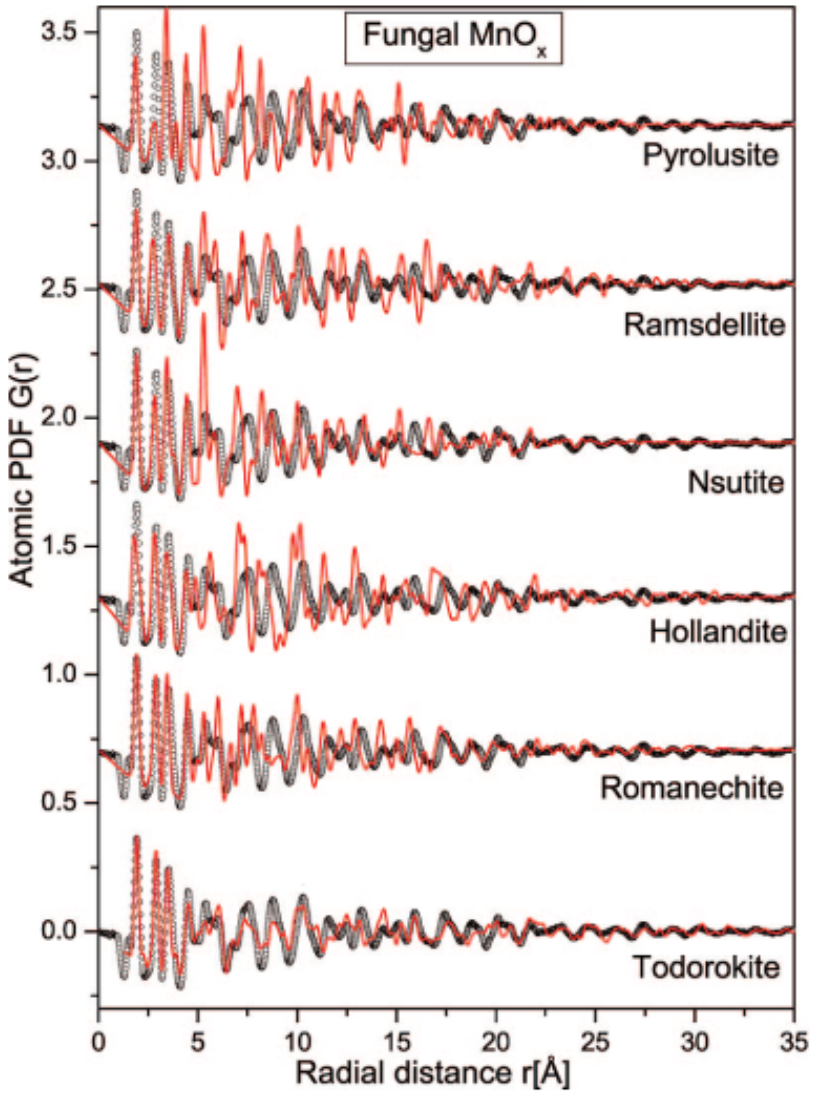
PDF of an Operating Fuel Cell In Operando

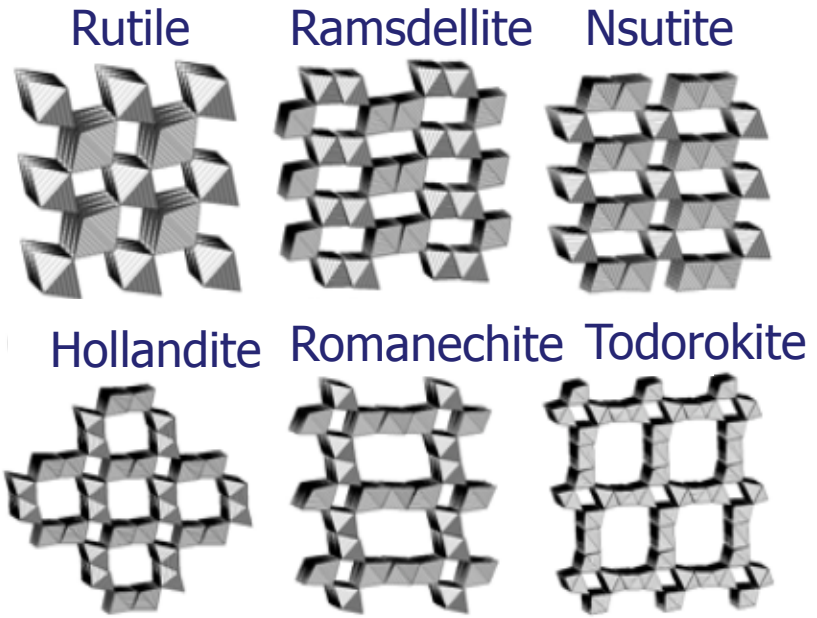
Pt/C catalyst for Data were first measured with this device at 11IDB at APS

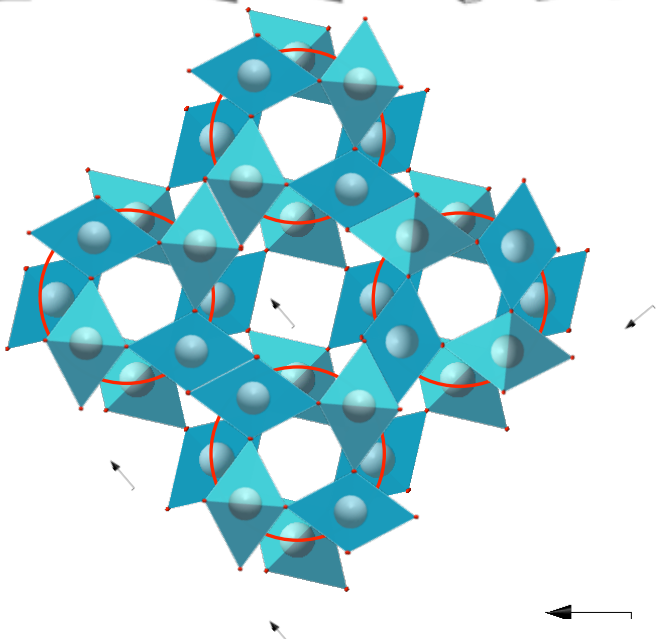


Redmond, E.L., Setzler, B.P., Juhas, P., Billinge, S.J.L. & Fuller, T.F. (2012) Electrochem. Solid State, 15, B72.

Catalysis related examples



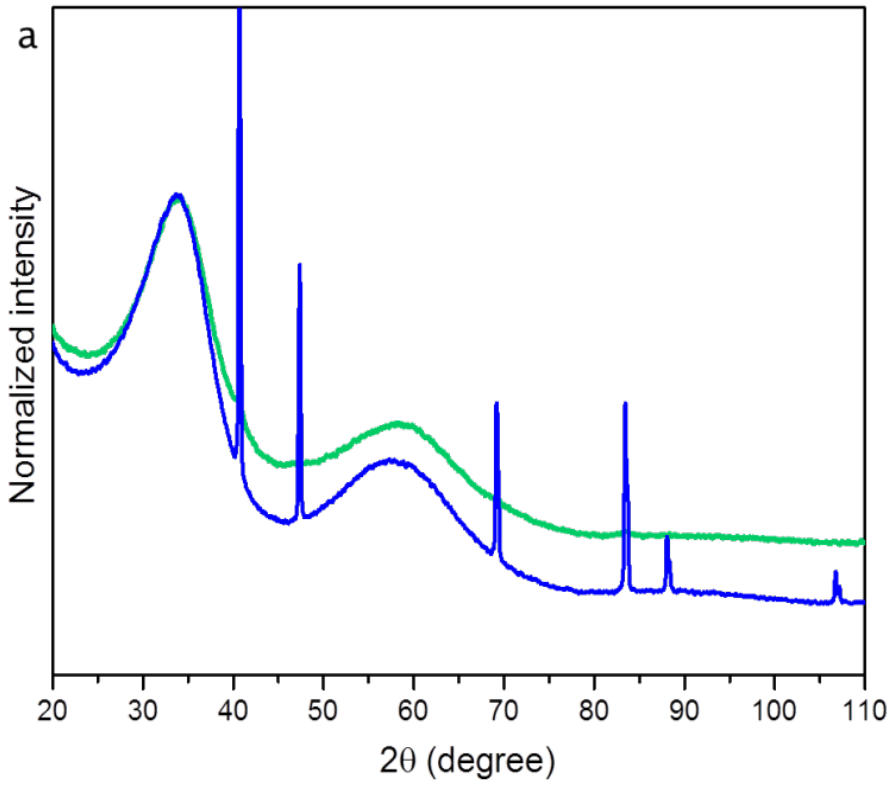




V. Petkov *et al.* ACS Nano **3** 441–445 (2009)

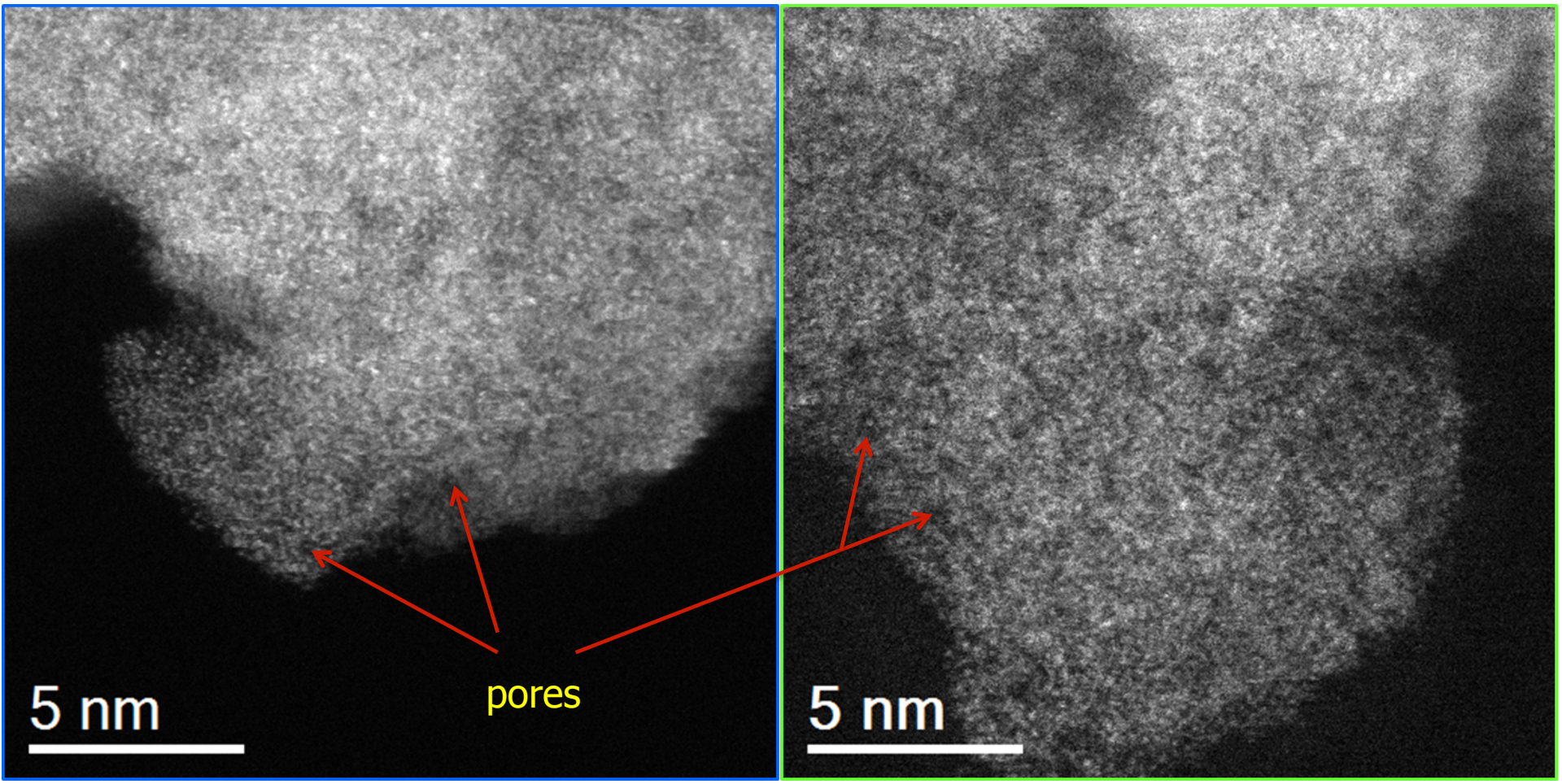
Catalysis related examples

IrOx (FHI-made) shows much higher OER catalytic performance than IrOx (Alfa Aesar)

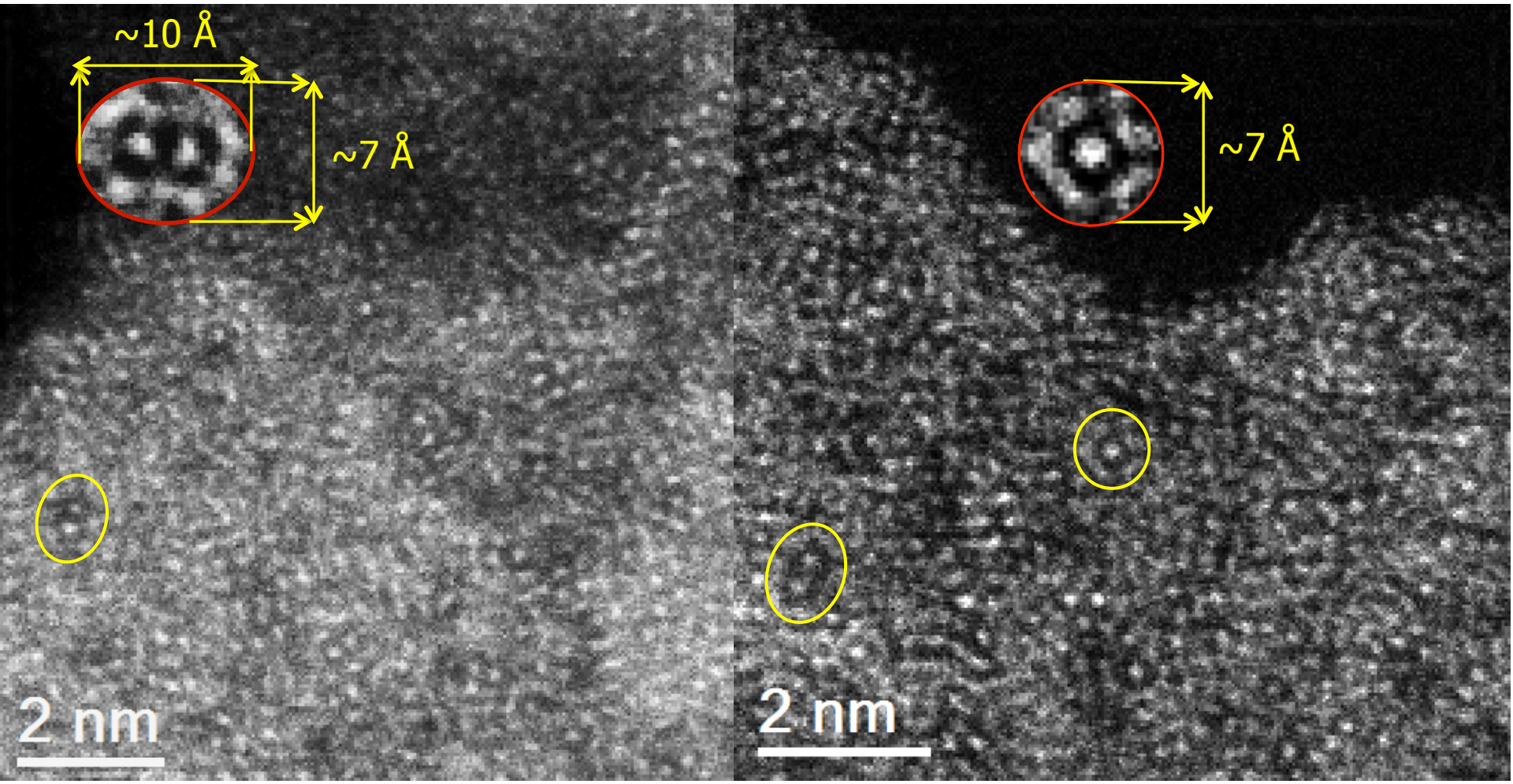


Except for the presence of metal impurities, XRD data does not show essential difference between commercial and FHI-made IrO_x phases

HAADF

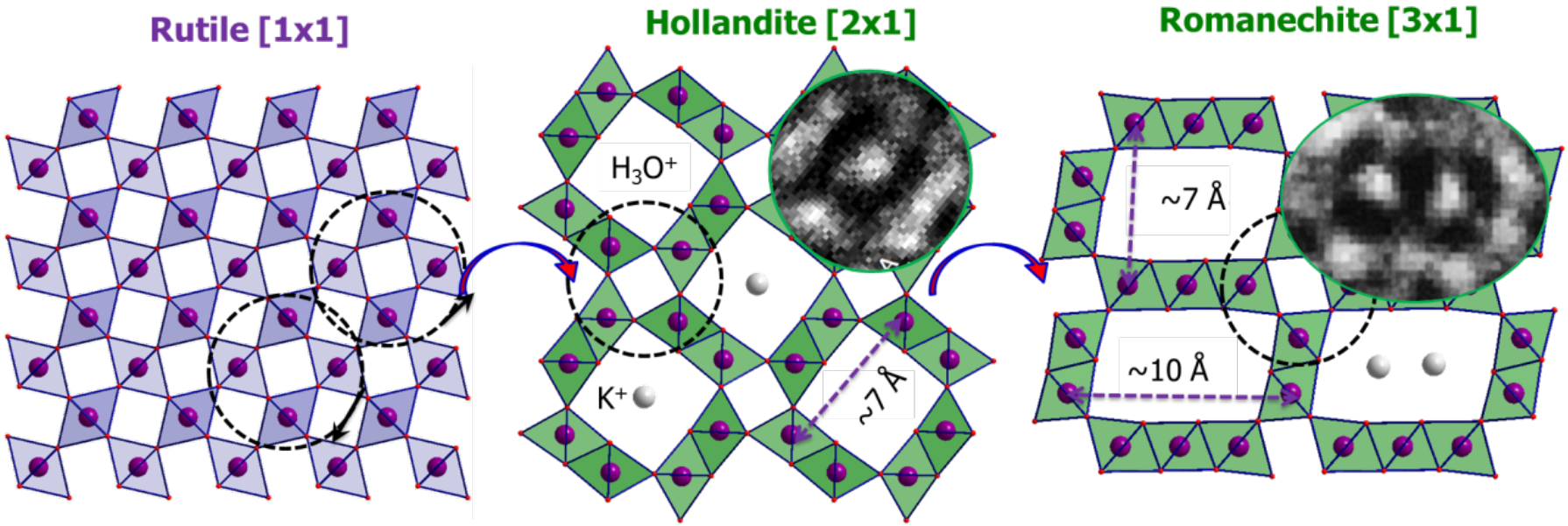


Atomic resolution HAADF



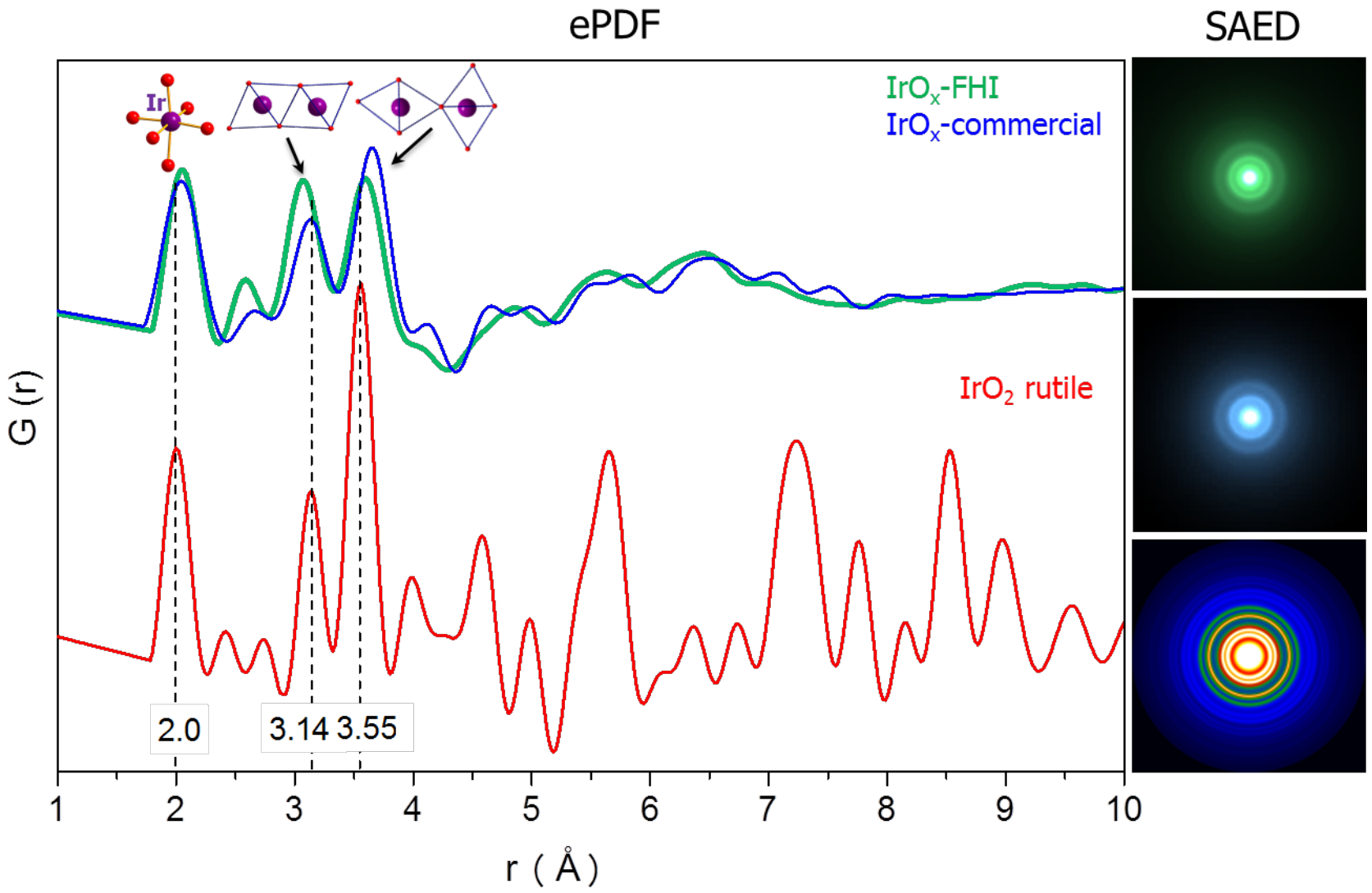
EDX analysis shows O/Ir~2 for both samples
IrO$_x$-FHI shows in addition a trace amount of K

Crystallographic approach



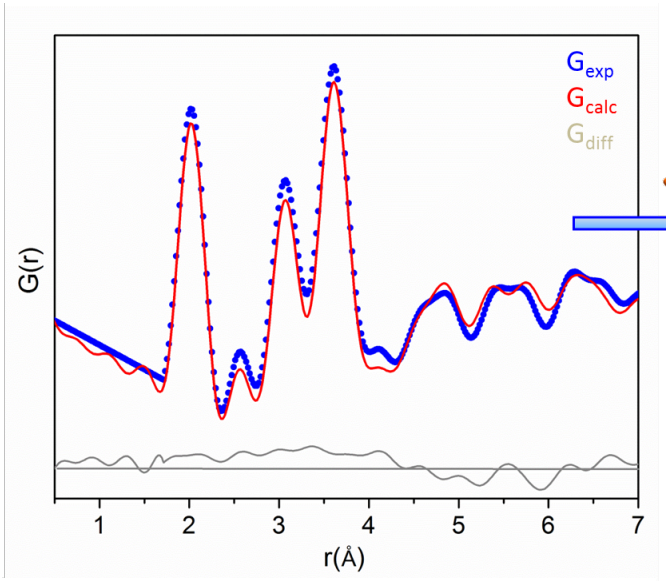
Ir^{4+} $Ir^{4+}Ir^{3+}$ $Ir^{4+}Ir^{3+}$

ePDF analysis

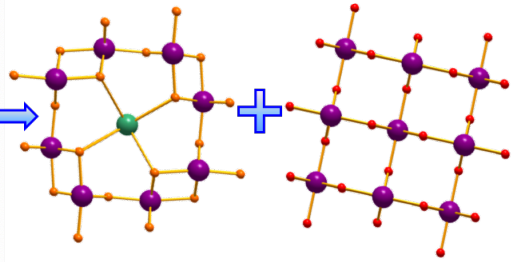


ePDF modeling

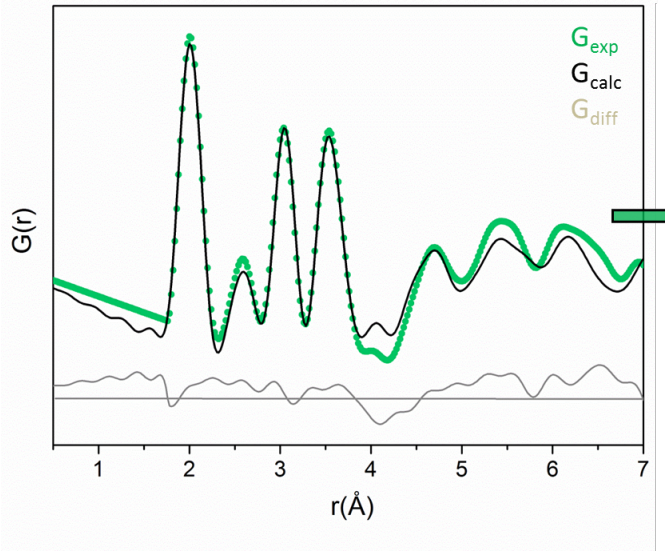
IrO_x-commercial



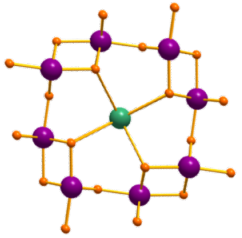
Hollandite + Rutile motifs



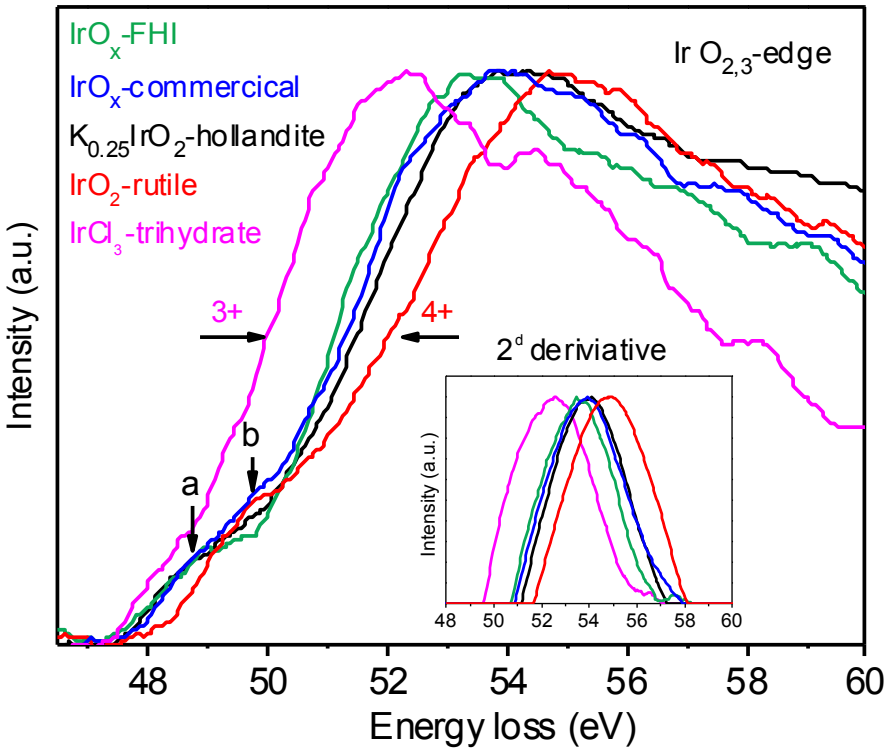
IrO_x-FHI

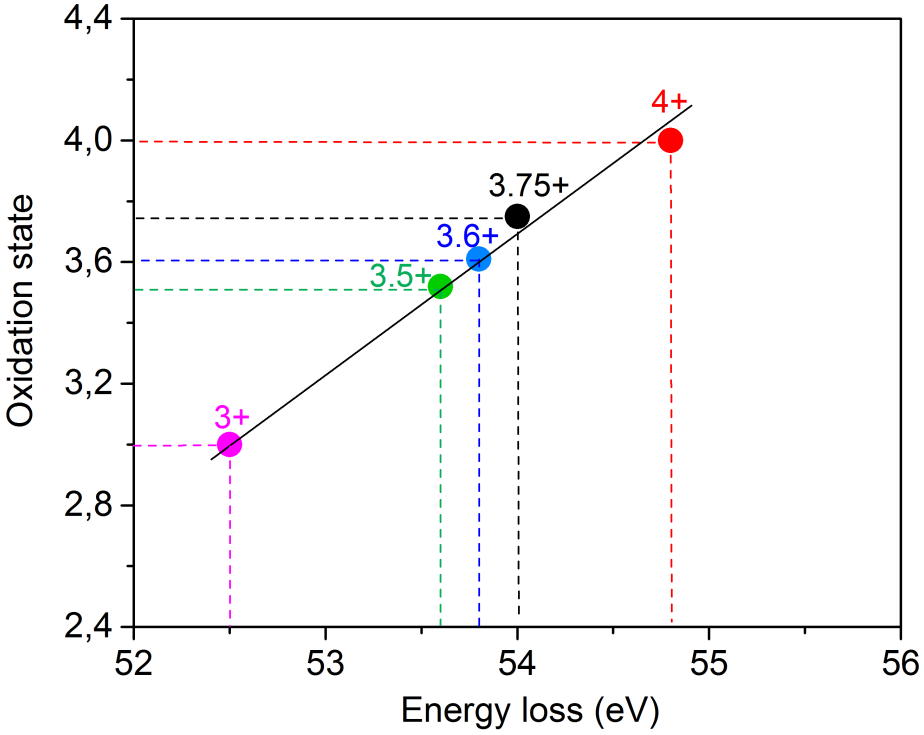


Hollandite motif



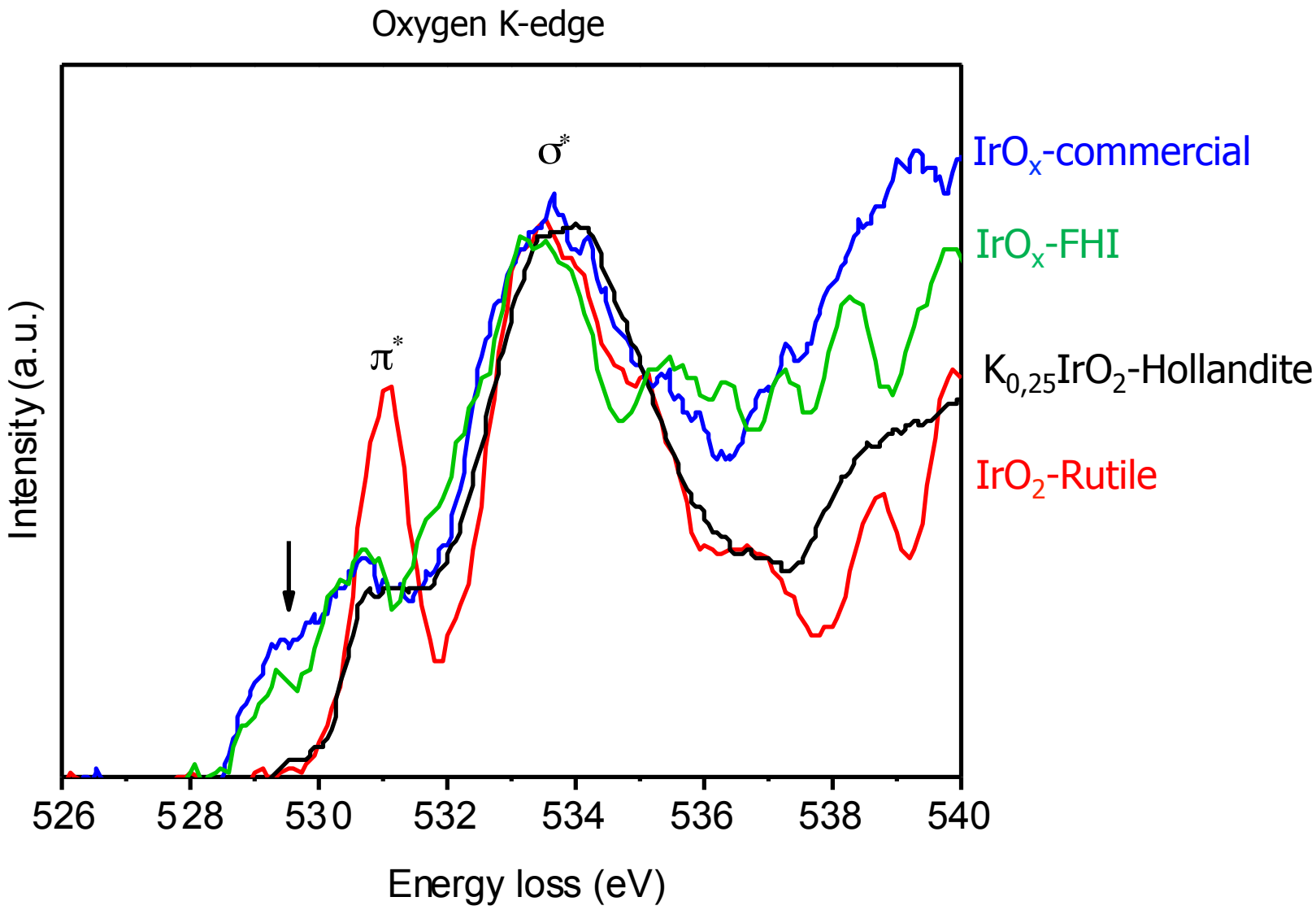
EELS analysis



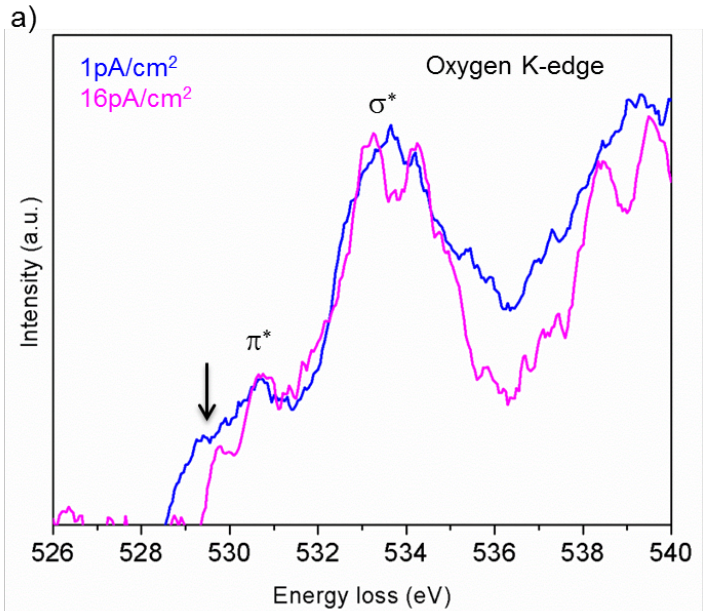


Ir $O_{2,3}$-edge (5p → 5d, 6s electron transitions)

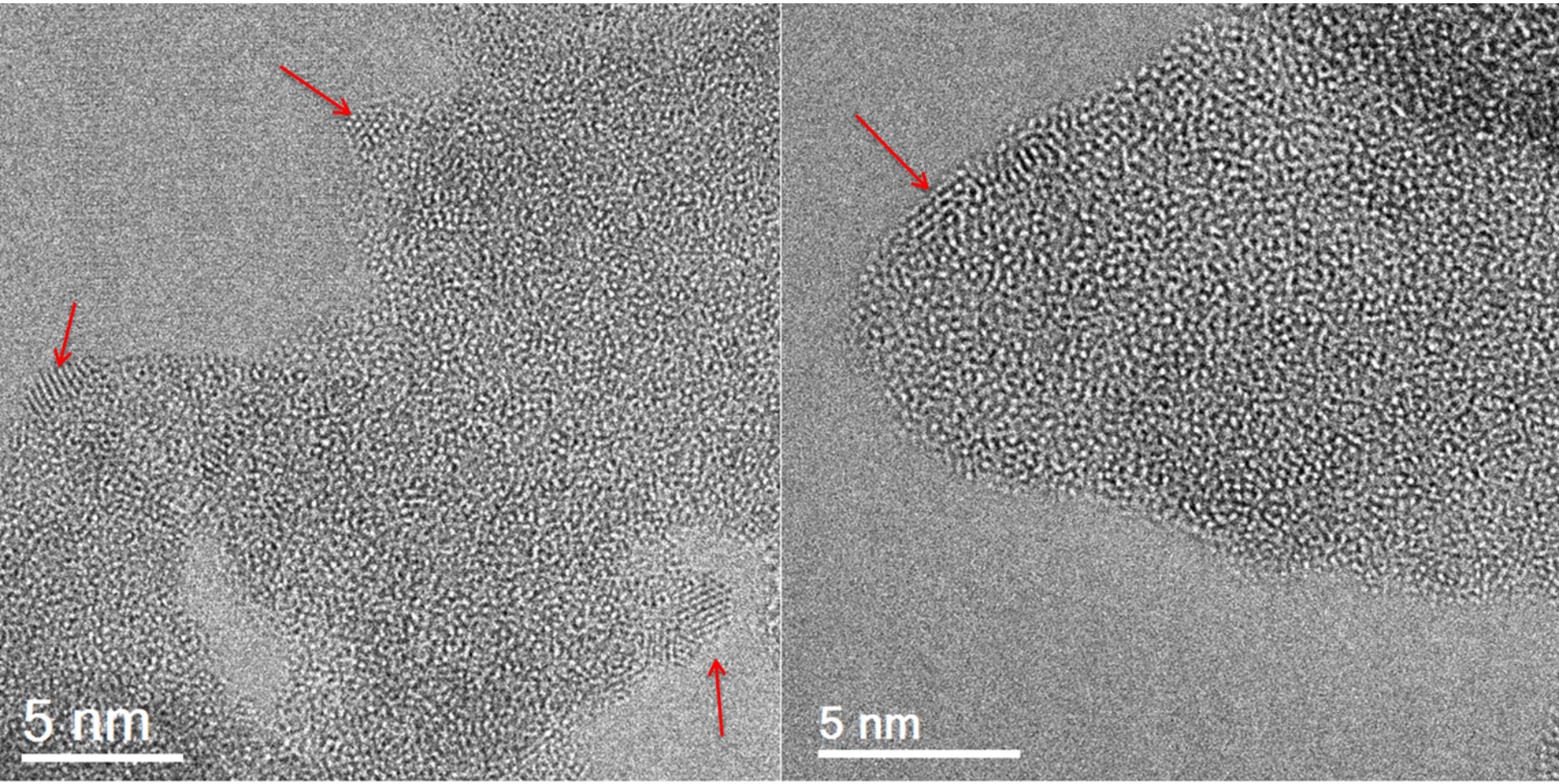
EELS analysis



E-beam effect

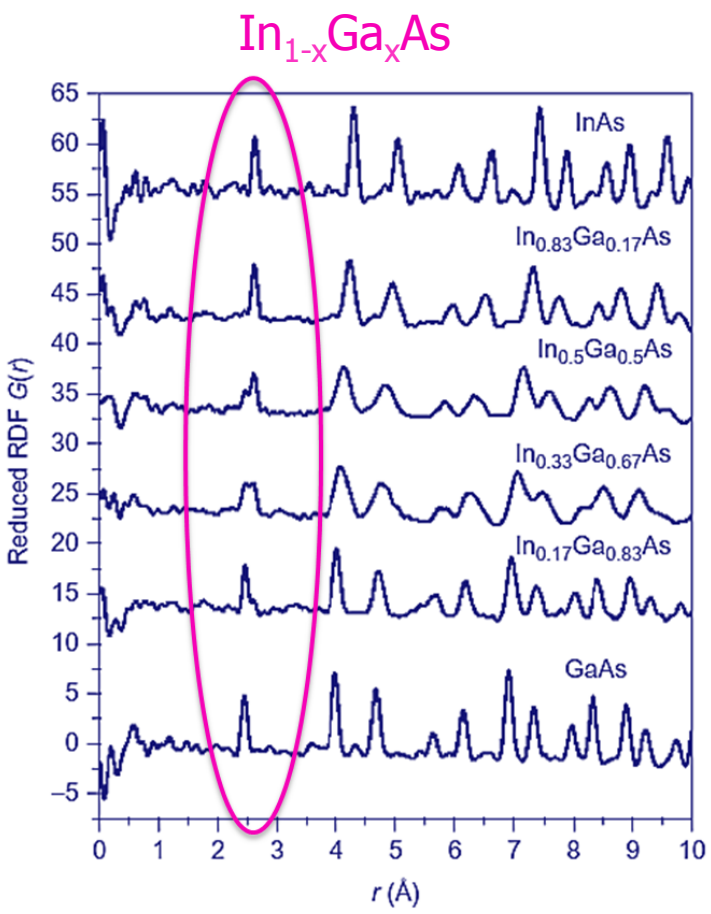


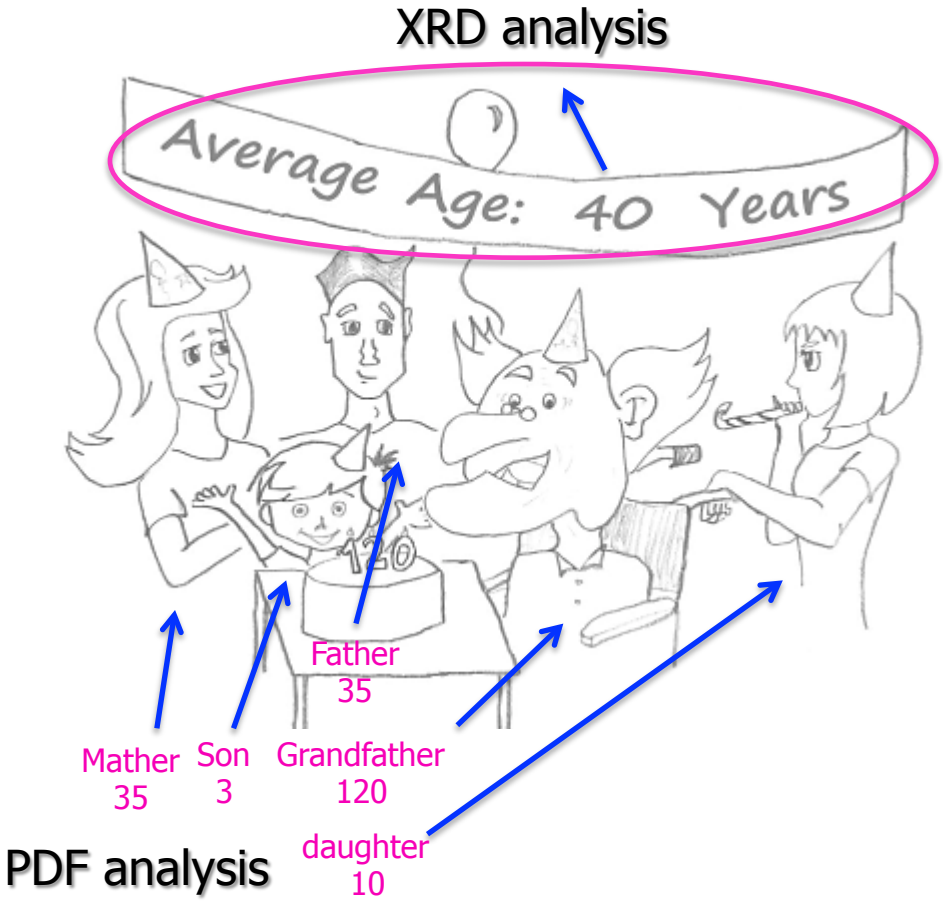
E-beam effect

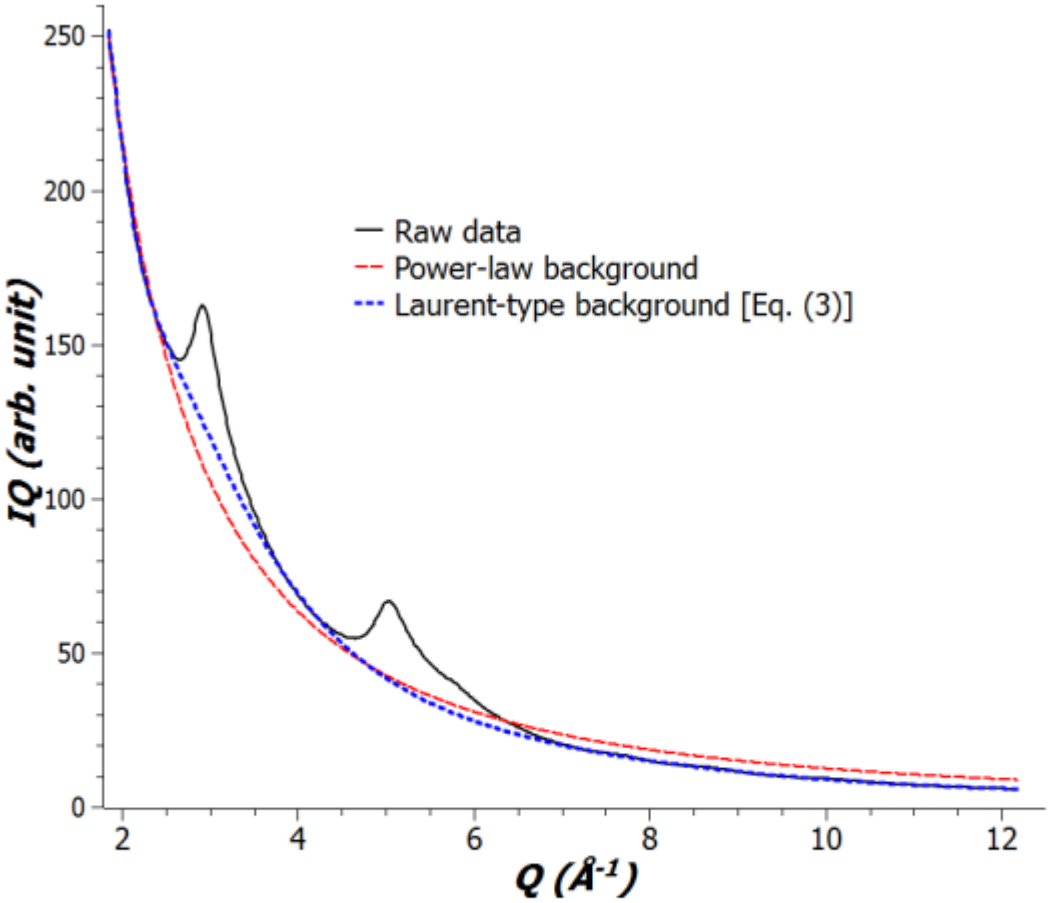


Summary

The PDF allows to reveal the details of the local structure which is not available in the case of conventional structural analysis which deals with the average structure



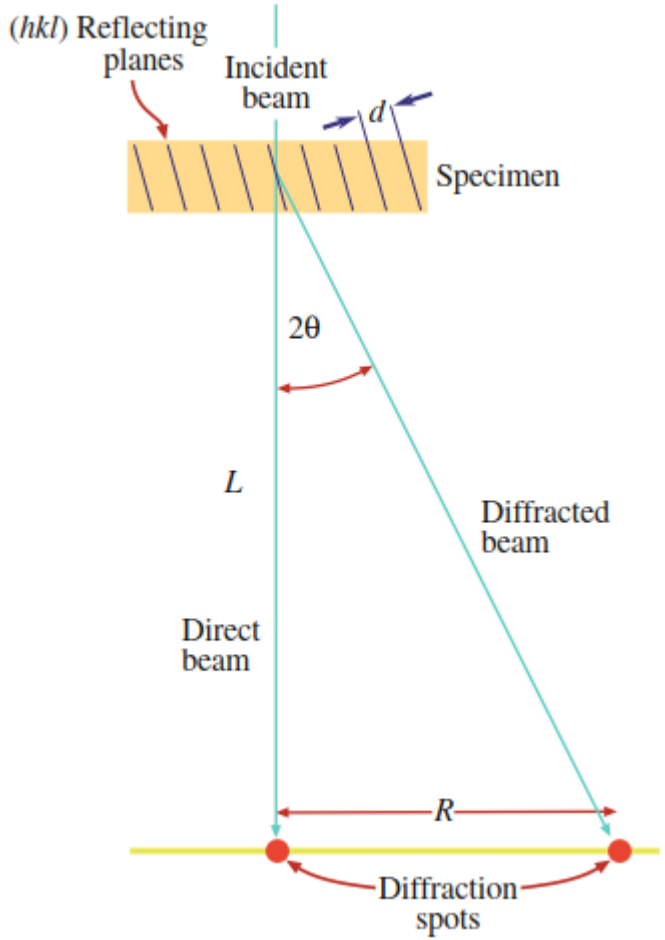




$$B_N(Q) = \sum_{k=1}^{N} \frac{c_k}{Q^k}$$

Figure 1 Background modeling for electron powder diffraction data (solid-black) of nanoporous carbon: power-law model (dash-red) compared with Eq. (4) Laurent-type model (dot-blue) with $N = 7$.

TEM



R/L=tan 2□~ □

□□d = 2 sin □~2 □

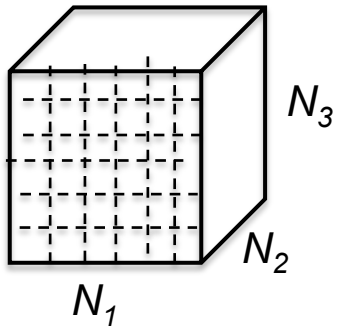
Rd = □L

↓ ↓

constant

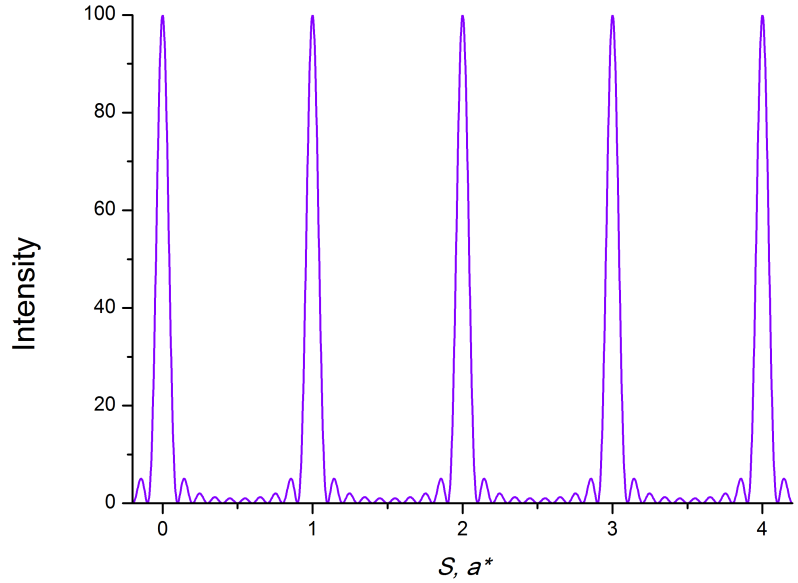
X-ray scattering physics

Finite crystal



$$I \sim \sin^2(N_1\varphi_1)/\sin^2\varphi_1 \cdot \sin^2(N_2\varphi_2)/\sin^2\varphi_2 \cdot \sin$$

$$\varphi_1 = \pi(\boldsymbol{S}\cdot\boldsymbol{a}),\ \varphi_2 = \pi(\boldsymbol{S}\cdot\boldsymbol{b}),\ \varphi_3 = \pi(\boldsymbol{S}\cdot\boldsymbol{c})$$



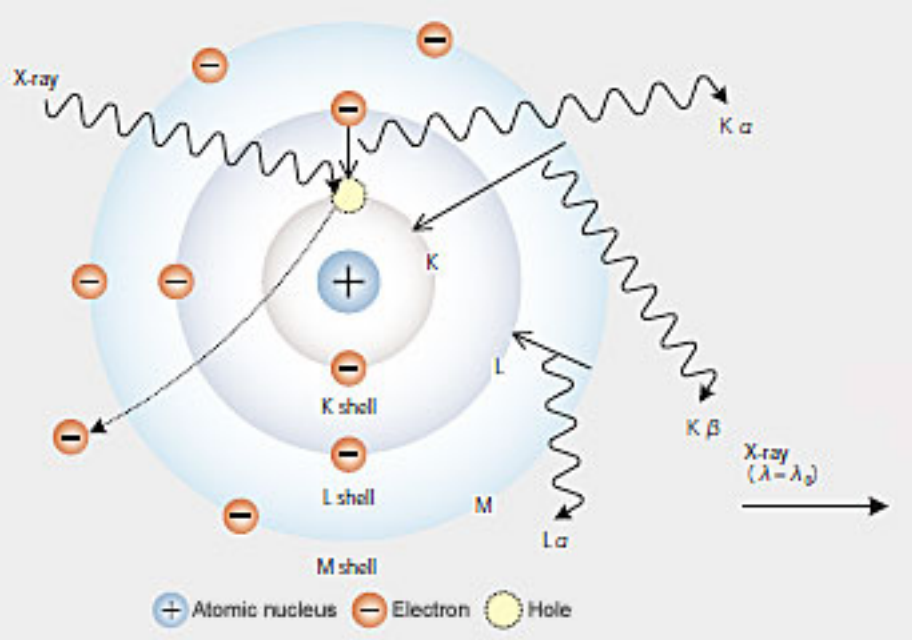
$N_1 = 10$

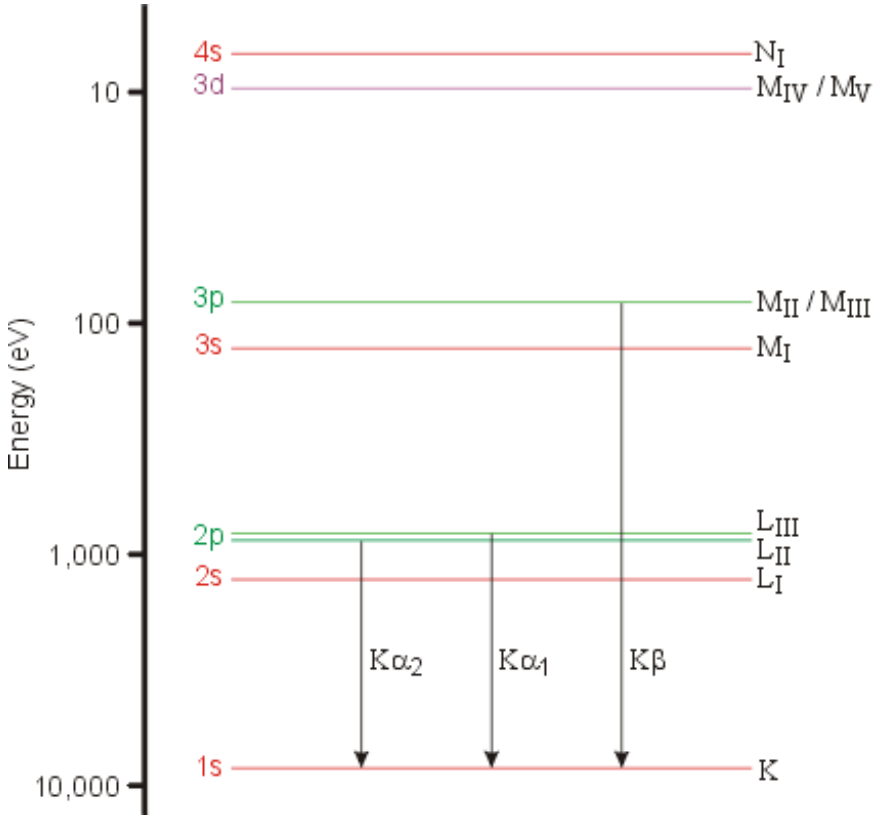
*There are high peaks in I(S) when (**S**· **a***) - integer*

$$N \rightarrow \infty$$

$$I \sim N_1^2 \cdot \delta(\boldsymbol{S}-n\cdot\boldsymbol{a}^*)$$

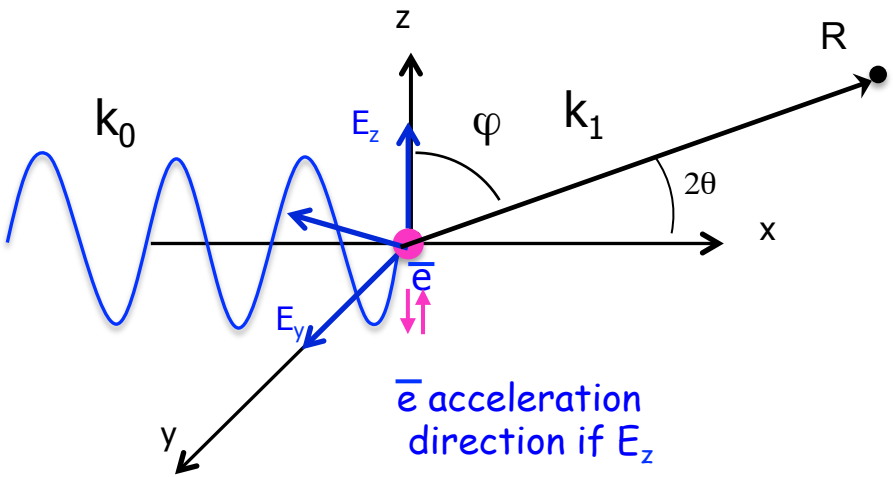
Characteristic X-ray lines



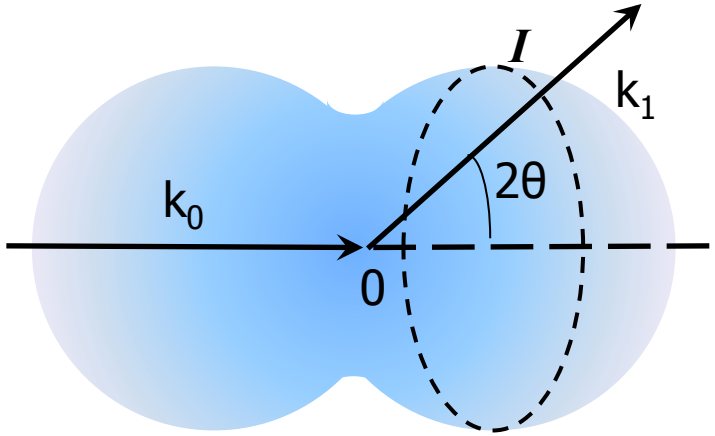


Anode	Kα	Kβ
Cu	1.54184 Å	1.39222 Å
Mo	0.71073 Å	0.63229 Å

Elementary scattering



Scattering intensity distribution

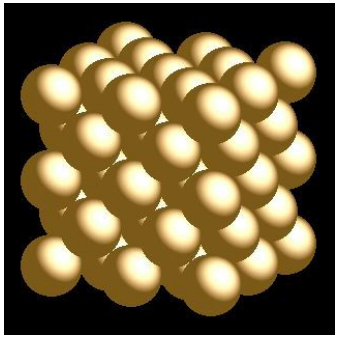


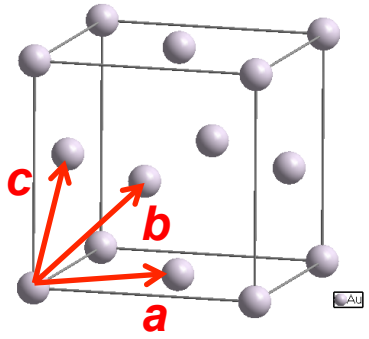
Thomson scattering formula

$$I = I_0 e^4 / r^2 m^2 c^4 \ (1+\cos^2 2\theta/2)$$

X-ray scattering physics

X-ray scattering by crystalline (periodic) ensemble of atoms





$\mathbf{R}_{mnp} = m\mathbf{a} + n\mathbf{b} + p\mathbf{c}$

Periodic arrangement of atoms is given by lattice with the basis vectors ***a,b,c***

Scattering amplitude $A(\mathbf{S}) = A_e \Sigma f_j e^{-i2\pi(\mathbf{S}\cdot\mathbf{R}_j)} = -A_e f \Sigma e^{i2\pi(\mathbf{S}\cdot\mathbf{R}_{mnp})}$

In general $A(\mathbf{S}) \sim 0$ for infinite crystal, i.e. m, n and p $\rightarrow \infty$

But if $(\mathbf{S}\cdot\mathbf{R}_{mnp}) = (\mathbf{S}\cdot\mathbf{a})m + (\mathbf{S}\cdot\mathbf{b})n + (\mathbf{S}\cdot\mathbf{c})p = q$ – integer

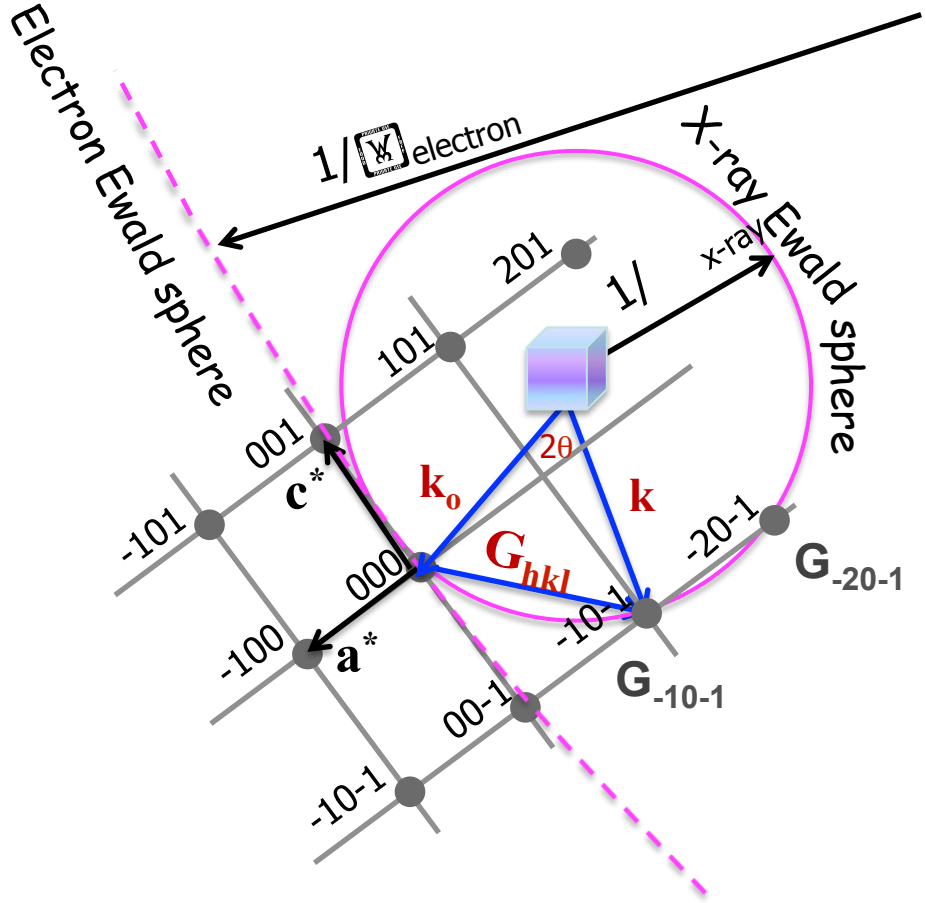
then $e^{i2\pi(\mathbf{S}\cdot\mathbf{R}_{mnp})} = 1$ and $|A(\mathbf{S})| = N A_e f(s)$, N – number of atoms,

There is the only solution: $\mathbf{S} = \{\mathbf{G}_{hkl}\} = \{h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*\}$

with $\mathbf{a}^* = [\mathbf{b}\times\mathbf{c}]/V$, $\mathbf{b}^* = [\mathbf{c}\times\mathbf{a}]/V$, $\mathbf{c}^* = [\mathbf{a}\times\mathbf{b}]/V$, $V = (\mathbf{a}[\mathbf{b}\times\mathbf{c}])$

Ewald construction

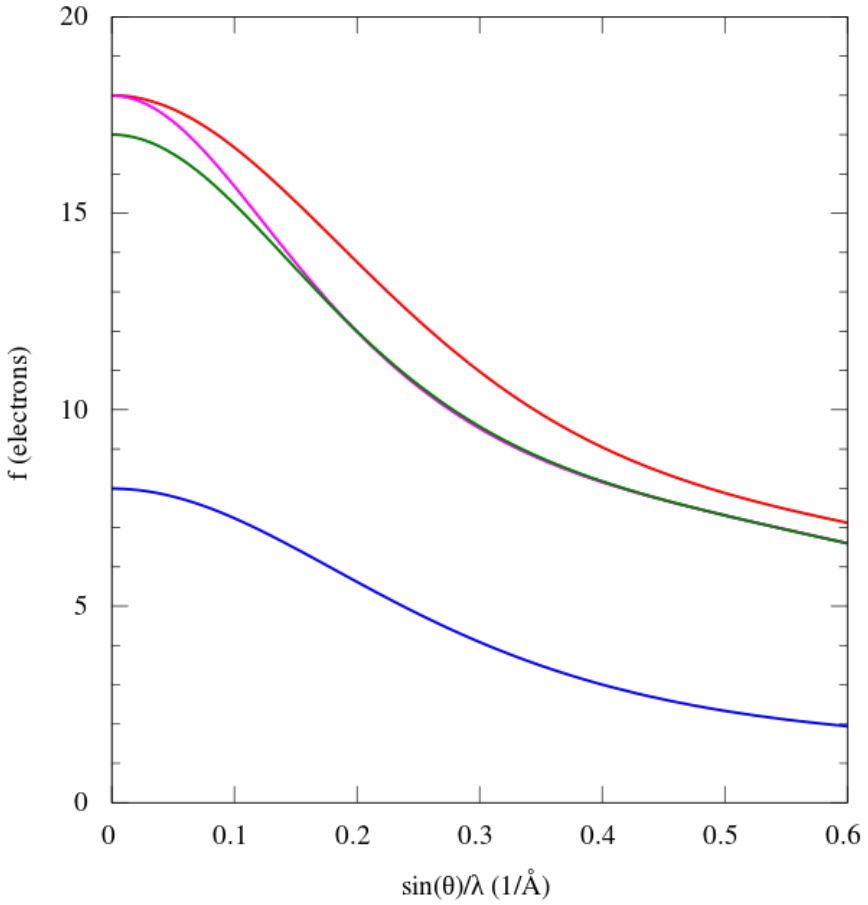
Space of wave vectors - Ewald construction



$$G_{hkl} = ha^* + kb^* + lc^*$$

$$G_{hkl} = 2|k|\sin\theta$$

Atomic scattering factor

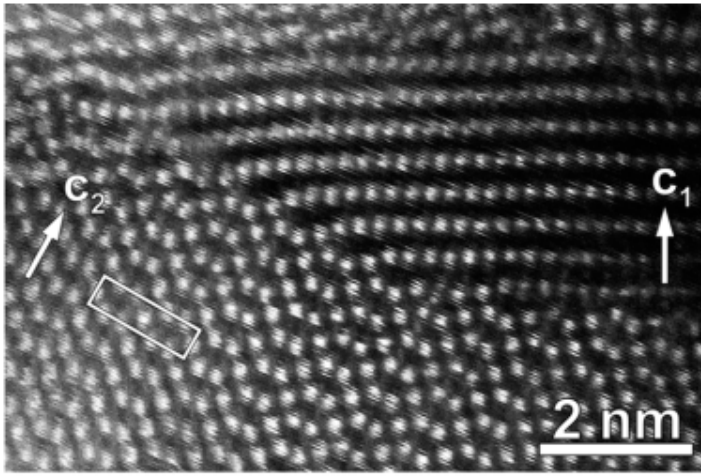


O, z=8, atomic radius =0.66
Cl, z=17, atomic radius=1
Cl-, z=18, radius= 1.81
K, z = 19, atomic radius=2.02
K+ =18, radius= 1.33

X-ray atomic factors of O, Cl , Cl^- and K^+ ; smaller charge distributions have a wider atomic factor.

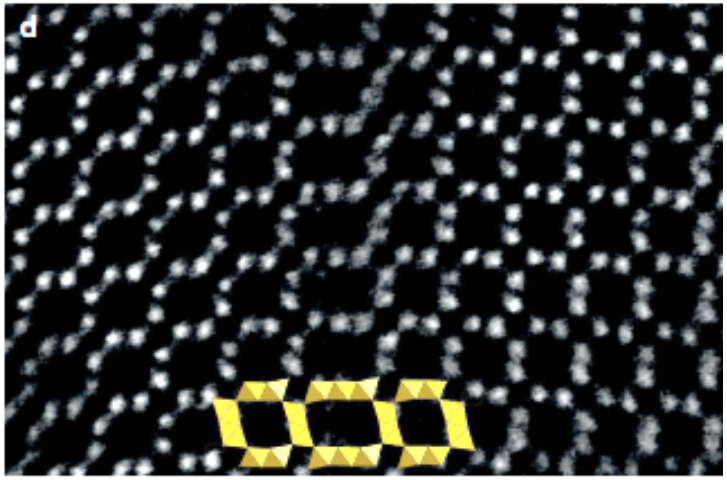
Structural flexibility

HAADF of $LiRhO_2$



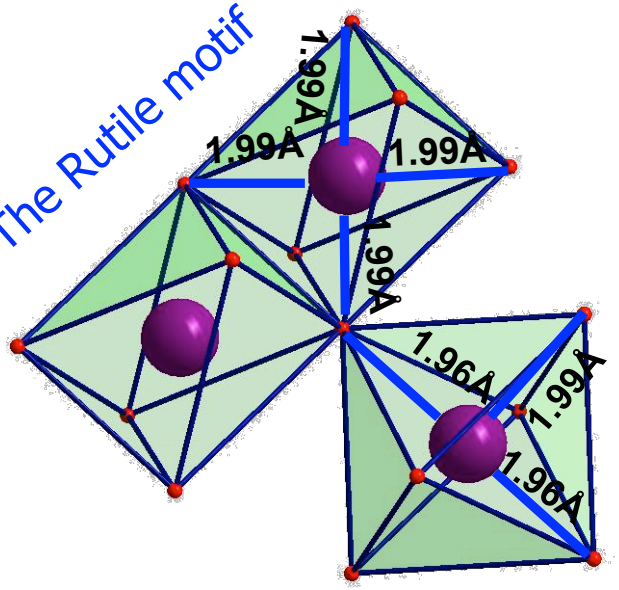
Daria Mikhailova et al., Inorg. Chem. 2016, 55, 7079−7089

HAADF of [W]-MnO_2

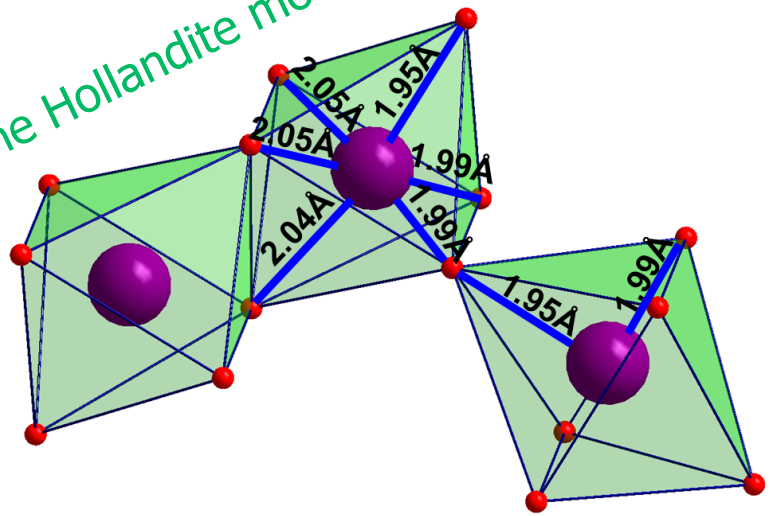


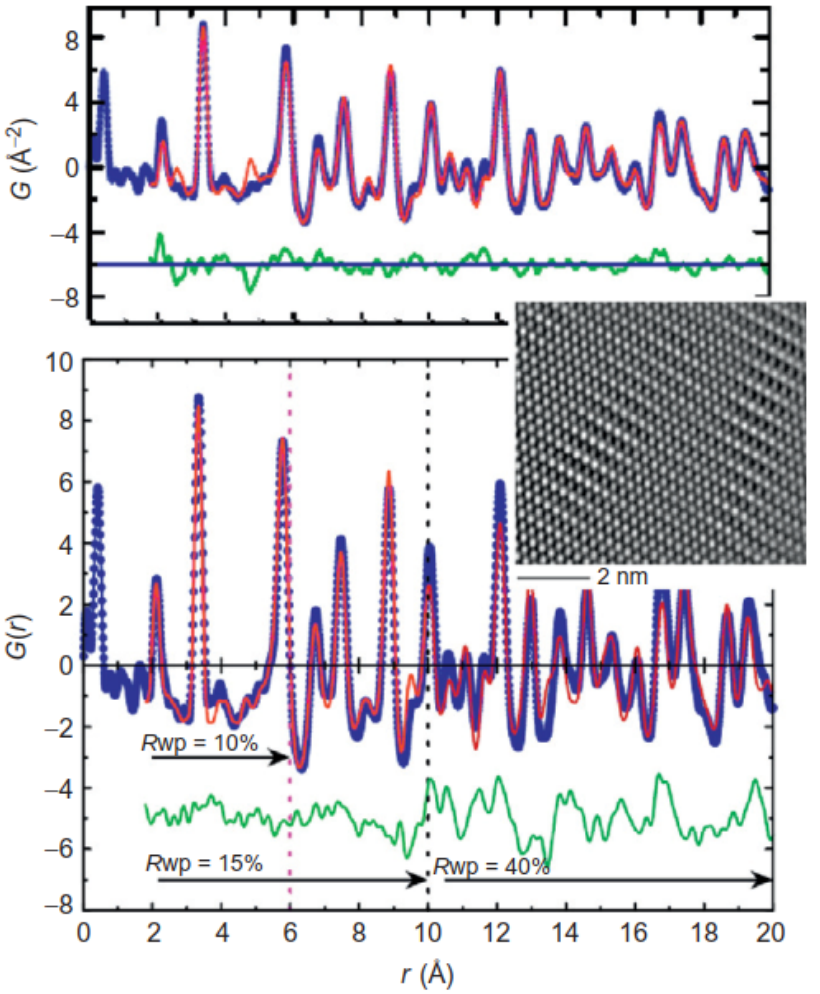
Grangeon et al. Geochem Trans (2015) 16:12

The Rutile motif



The Hollandite motif




G (Å⁻²)
8
4
0
−4
−8
G(r)
10
8
6
4
2
0
−2
−4
−6
−8
2 nm
Rwp = 10%
Rwp = 15%
Rwp = 40%
0
2
4
6
8
10
12
14
16
18
20
r (Å)