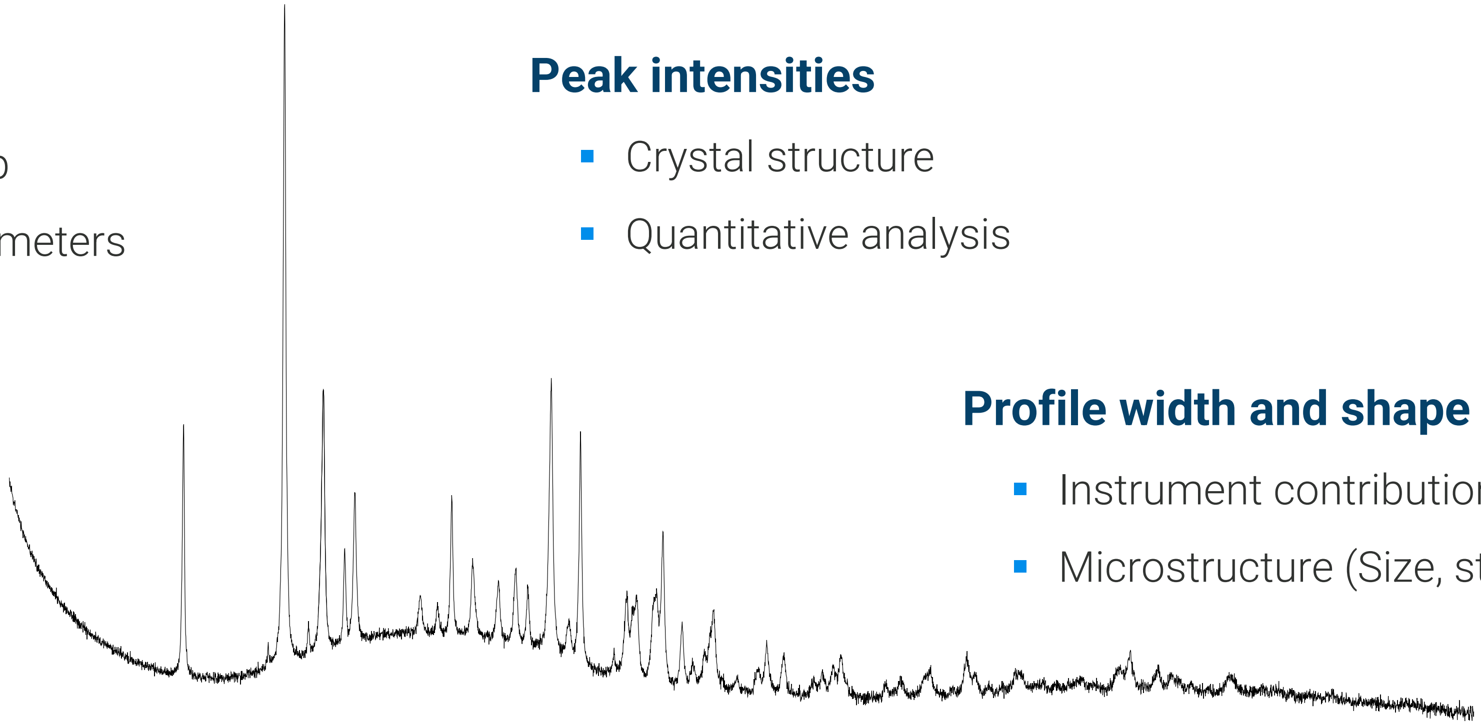
SINGLE LINE SUBTITLE WITH A MAXIMUM OF APPROX. 90 CHARACTERS

Introduction to Pair Distribution Function Analysis

Intro to PDF Analysis
Outline

Not on the agenda:
Math

Information in Diffraction Patterns



Peak positions

- Space group
- Lattice parameters

Peak intensities

- Crystal structure
- Quantitative analysis

Profile width and shape

- Instrument contributions
- Microstructure (Size, strain, stacking faults, ...)

Background

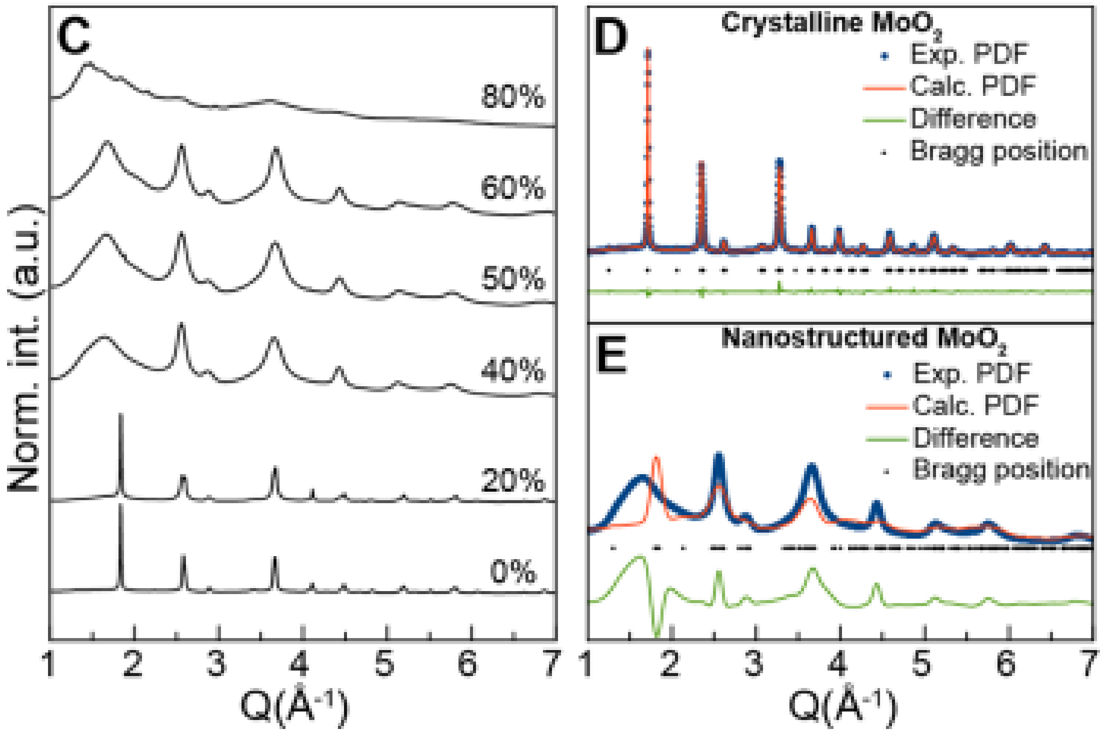
- Scattering from sample environment (air, sample holder, ...)
- Local order / disorder
- Amorphous phase amounts, "degree of crystallinity"

Why use PDF?
Nanosizing of MoO_2

- MoO_2 prepared using different amounts of oleylamine
- Larger amounts of oleylamine produces smaller particles
- However, the structure looks quite different from the bulk material

- Nanostructured MoO_2 cannot be evaluated using traditional Rietveld analysis!

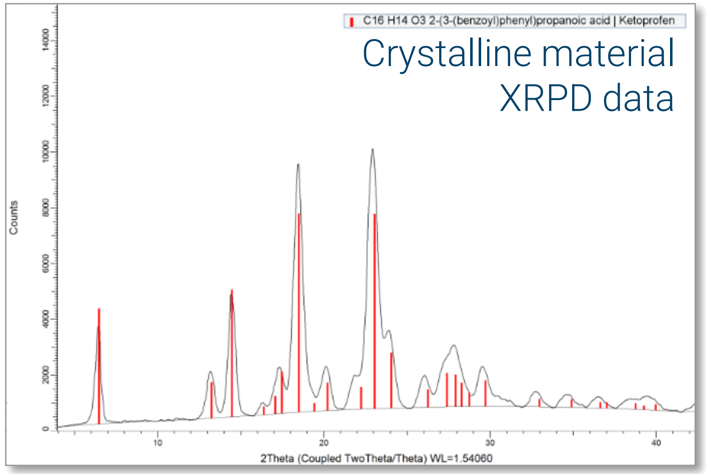
Oleylamine/ethanol ratio



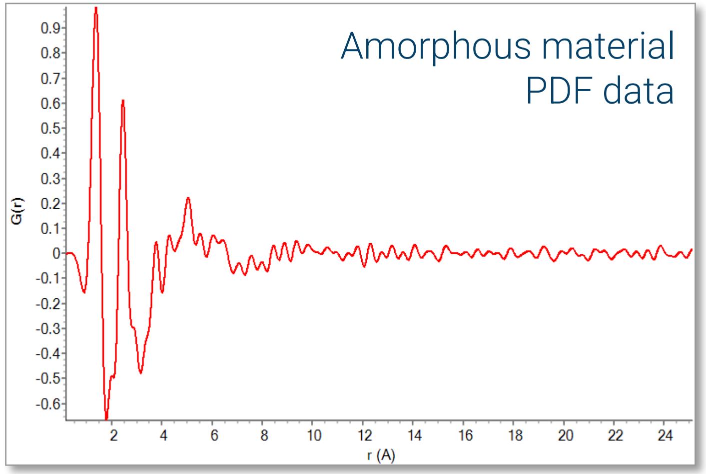
T. L. Christiansen et al., *ACS Nano*, 2019, 8725-8735

Why use PDF?

- **Powder X-ray diffraction** (PXRD) analysis relies on information in the Bragg peaks:
  - Limited to crystalline materials
  - Less useful for small nanoparticles
  - Not useful for glasses and liquids
  - Provides average structure information



- **Pair Distribution Function analysis** makes use of total scattering data (Bragg peaks and diffuse scattering)
  - Useful for crystalline, nano-crystalline materials as well as liquids and glasses
  - Can provide insights where classic diffraction techniques can't
  - Provides local structure information

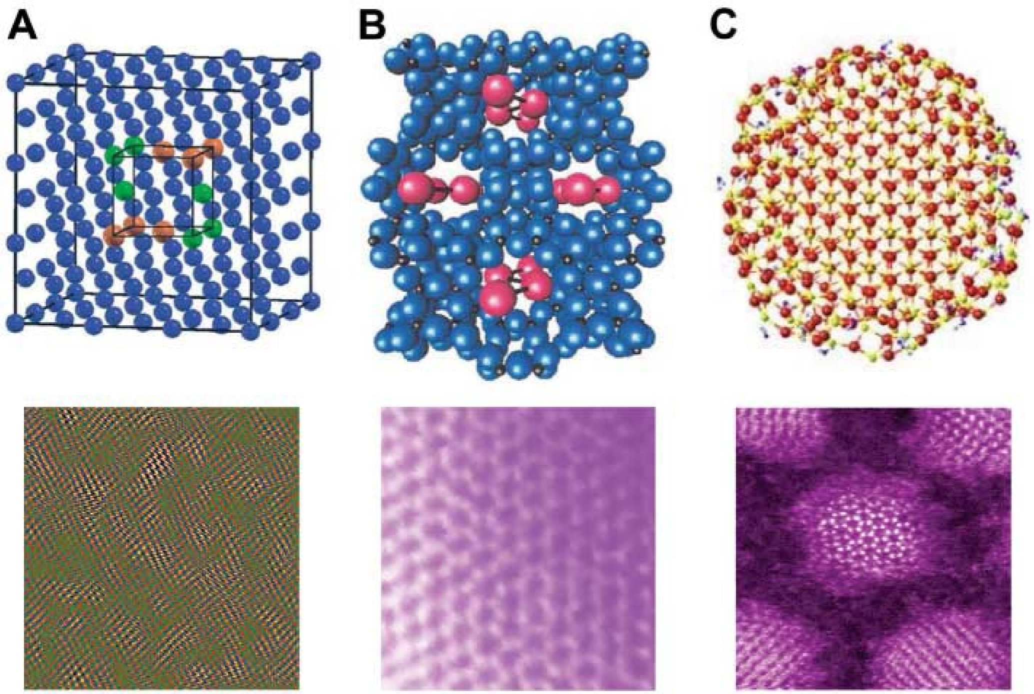


Crystalline materials
- “Unexpected” structure or properties

Disordered materials
- Physical properties are often dictated by defects or domains of local structure

Nanomaterials
- Long-range order limited to a few nanometers
- Poorly defined Bragg peaks

Non-crystalline materials
- Amorphous materials and polymers

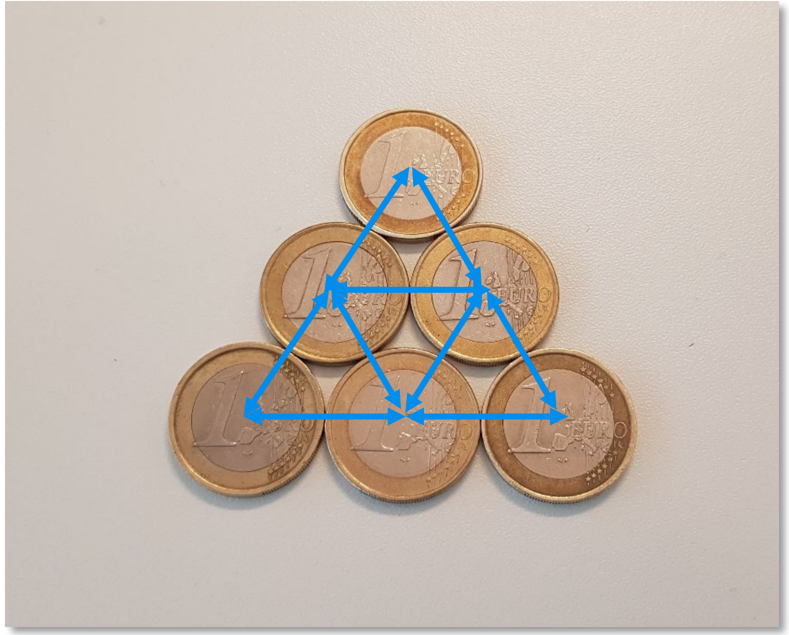


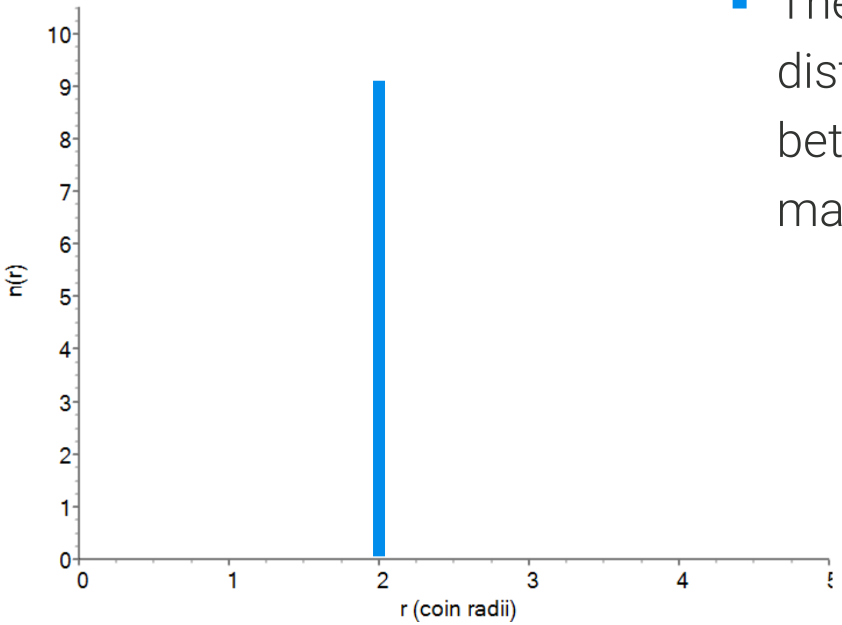
S.J.L. Billinge and I. Levin, The problem with Determining Atomic Structure at the Nanoscale, Science 316, 561 (2007)

INTRODUCTION TO PAIR DISTRIBUTION FUNCTION ANALYSIS

What is a PDF?

What is a PDF?

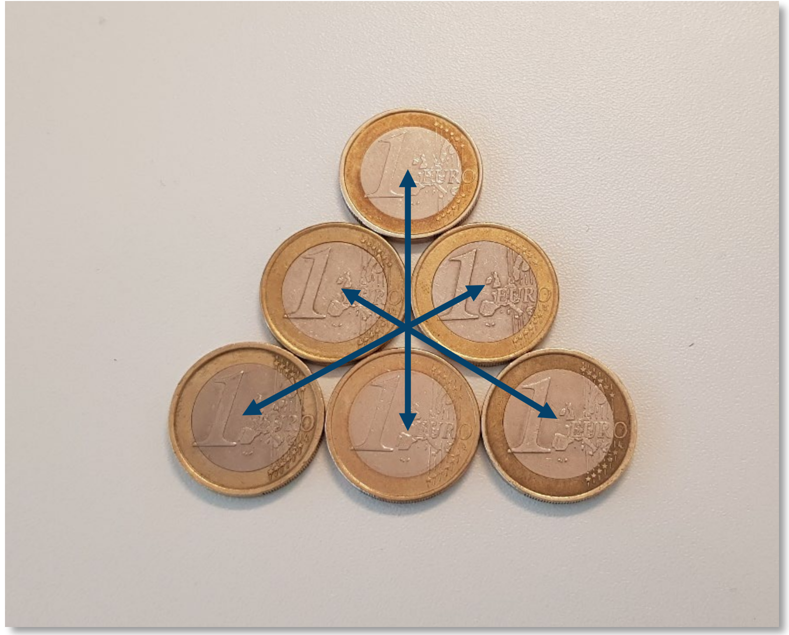


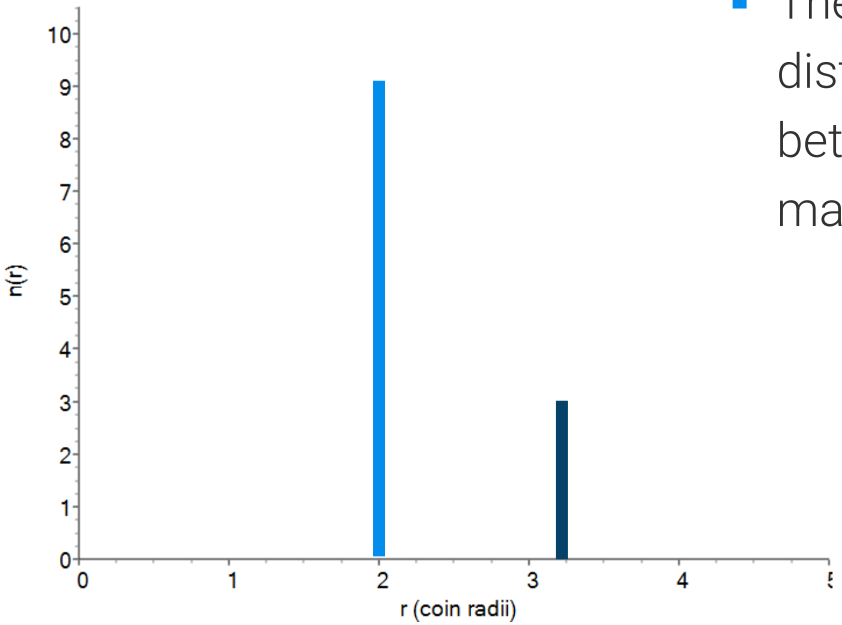


- The PDF shows the frequency distribution of distances between pairs of scatterers in a material

The PDF is a real space function: it tells us ***directly*** *where the coins are in relation to each other*

What is a PDF?

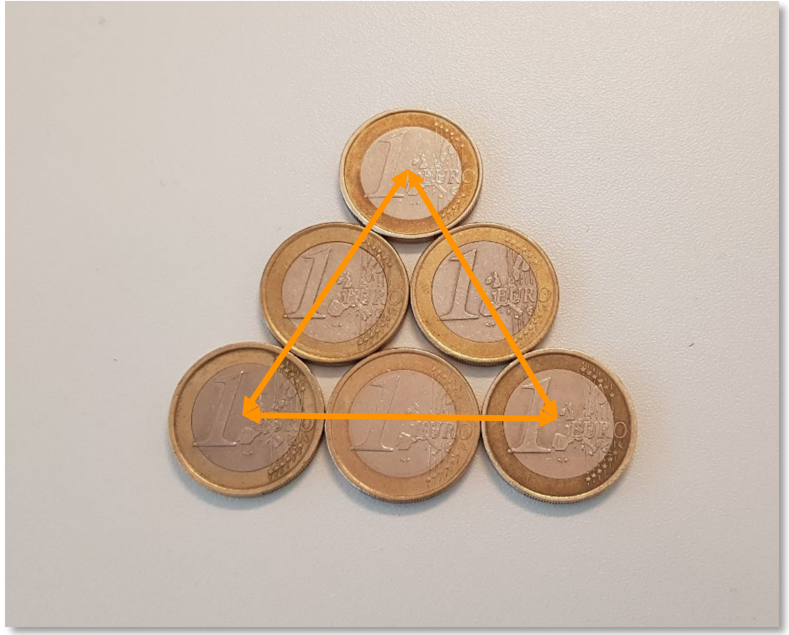


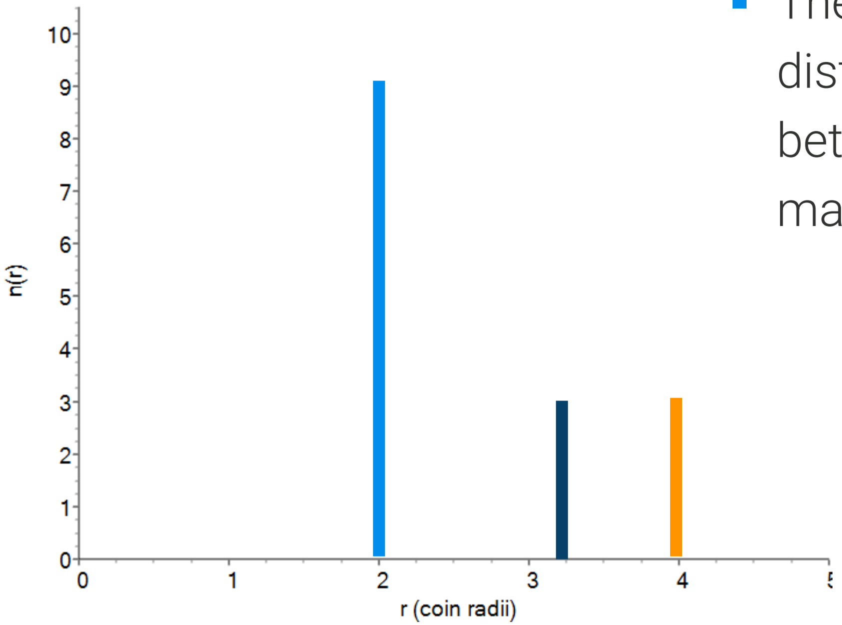


- The PDF shows the frequency distribution of distances between pairs of scatterers in a material

The PDF is a real space function: it tells us ***directly*** *where the coins are in relation to each other*

What is a PDF?



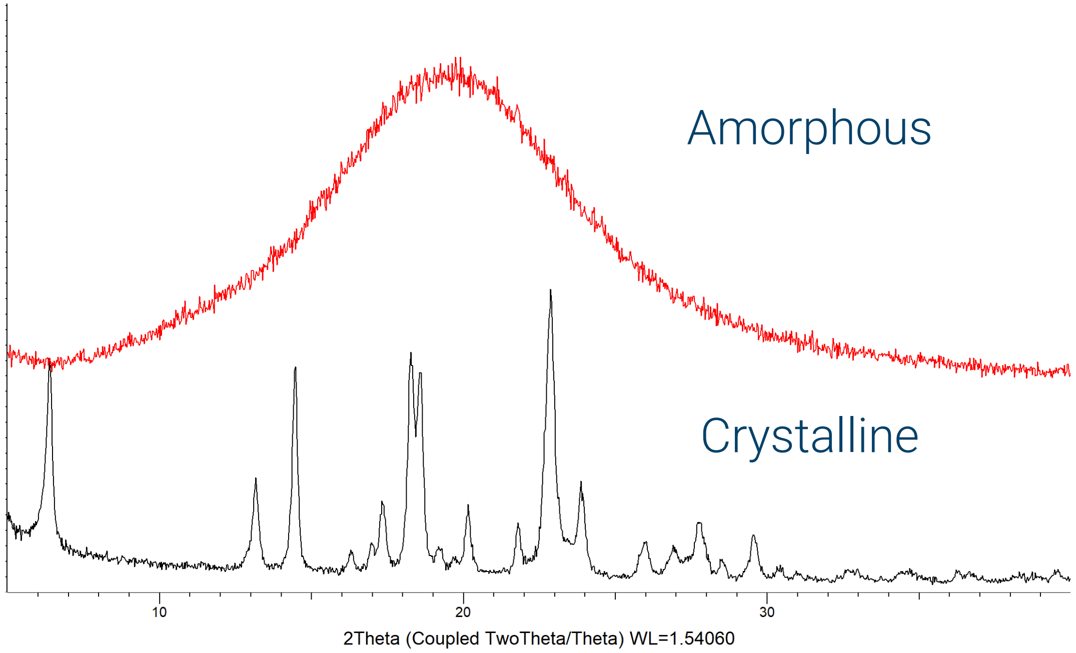


- The PDF shows the frequency distribution of distances between pairs of scatterers in a material

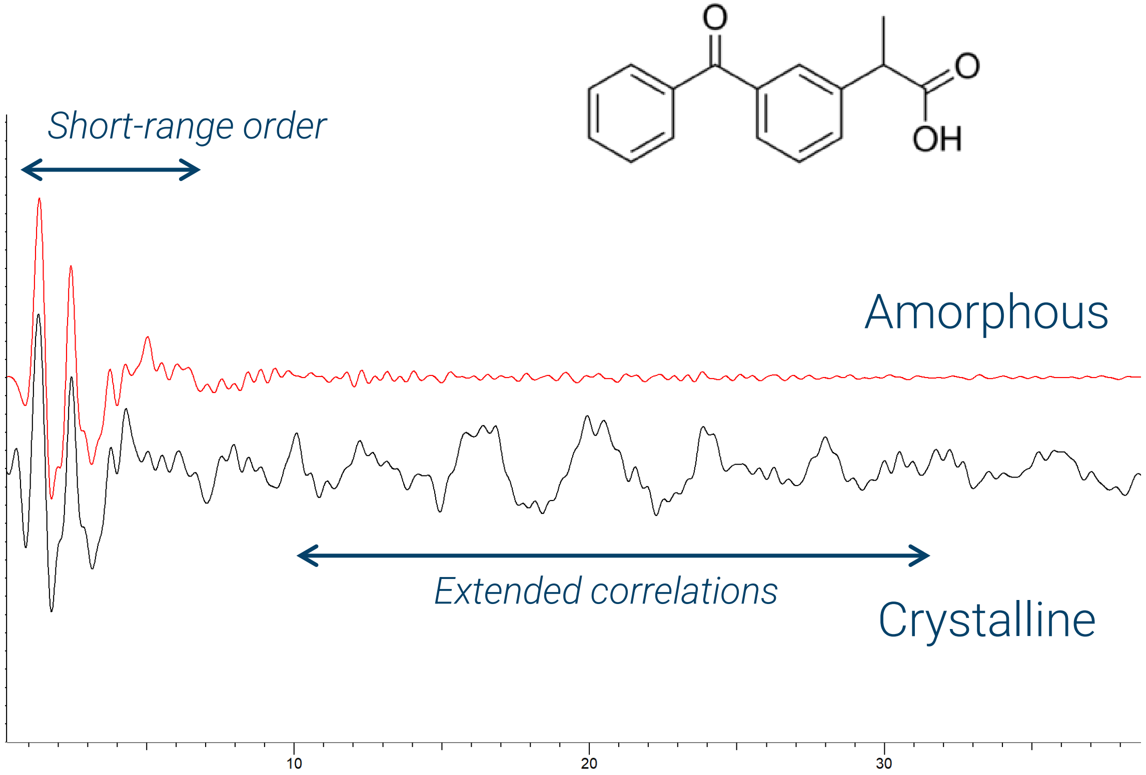
*The PDF is a real space function: it tells us **directly** where the coins are in relation to each other*

What is a PDF?

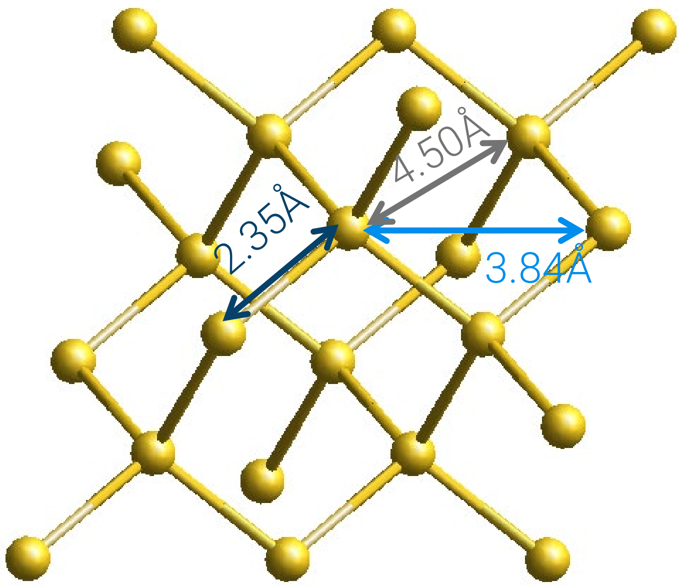
- Diffraction

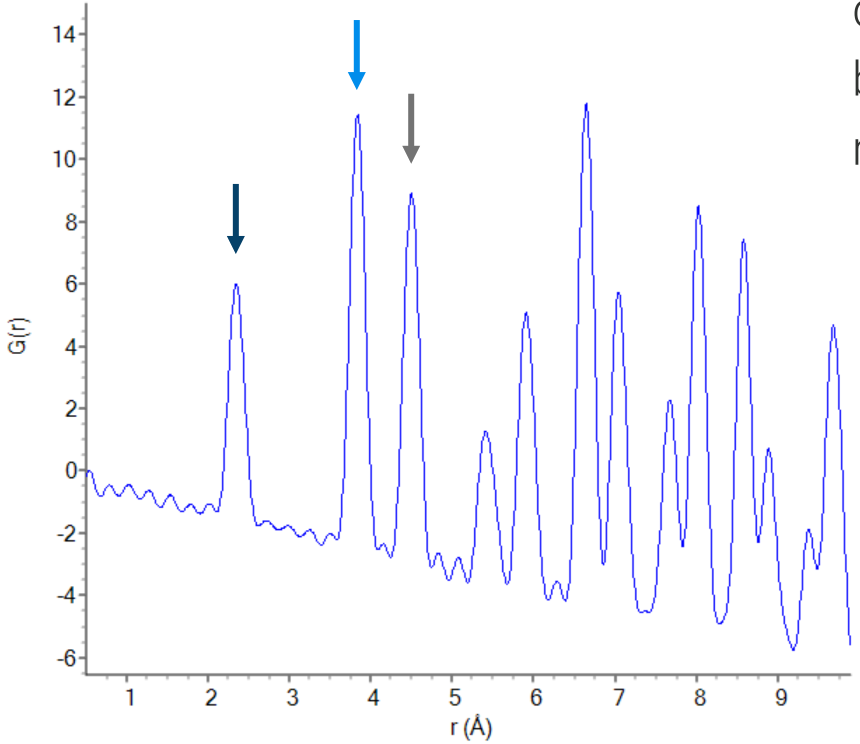


- Pair Distribution Function



What is a PDF?





- The PDF shows the frequency distribution of distances between pairs of scatterers in a material

Information content in the PDF

Peak positions

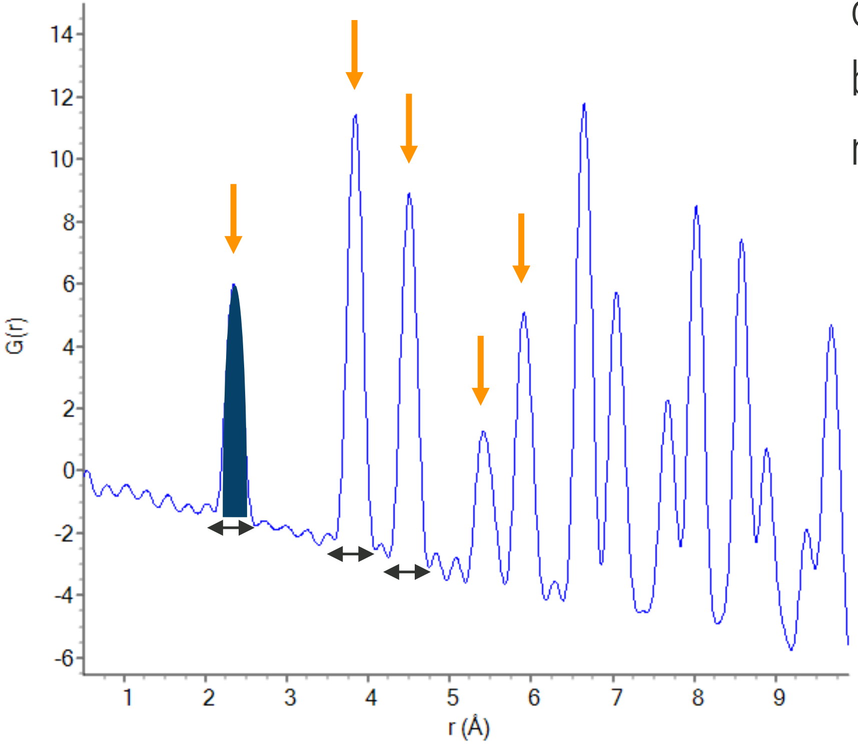
- Bond lengths, interatomic distances

Peak areas

- Coordination number

Peak widths

- Dynamic disorder (ADPs)
- Static disorder



- The PDF shows the frequency distribution of distances between pairs of scatterers in a material

Information content in the PDF

Peak positions

- Bond lengths, interatomic distances

Peak areas

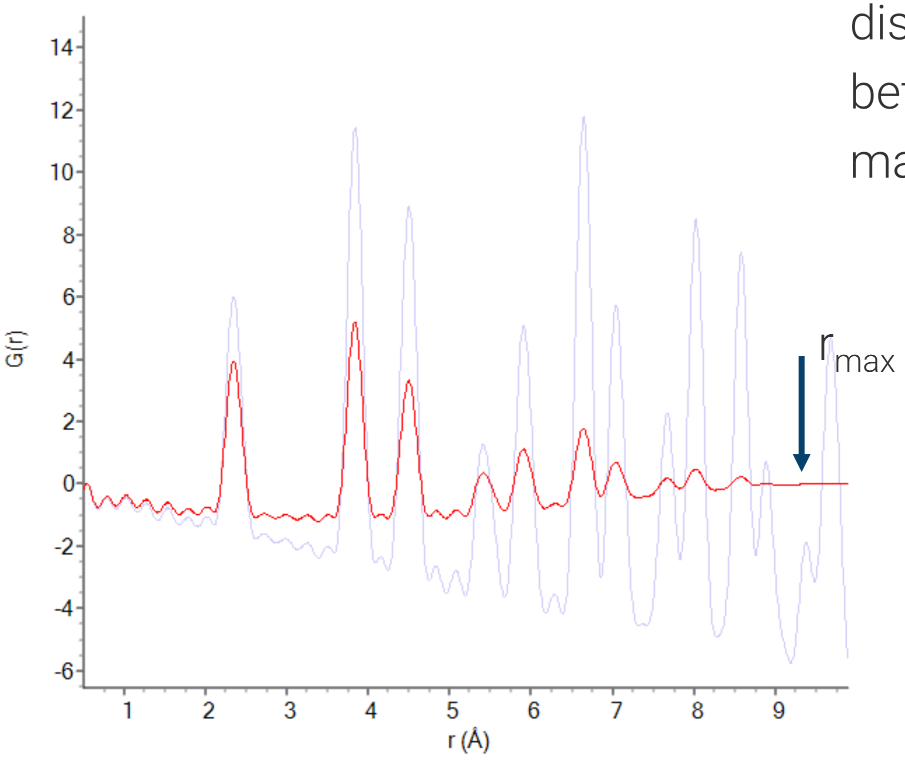
- Coordination number

Peak widths

- Dynamic disorder (ADPs)
- Static disorder

PDF peak damping

- Crystallite size



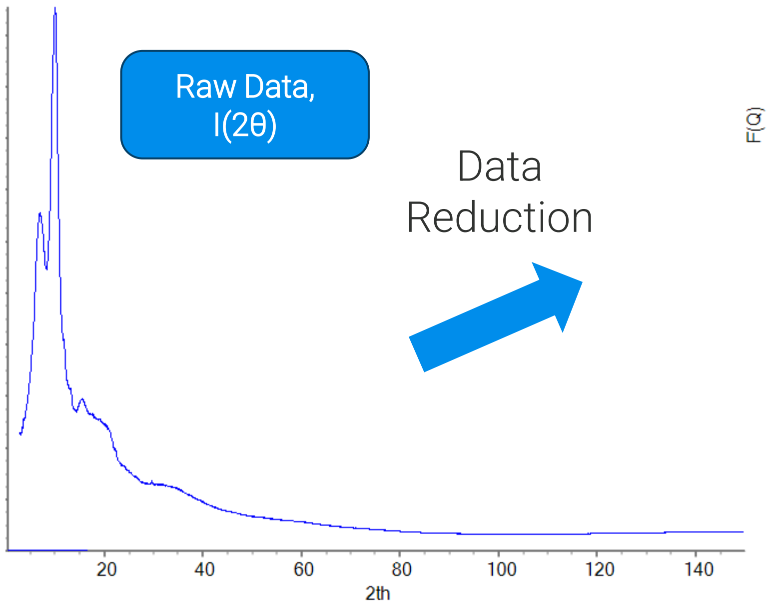
- The PDF shows the frequency distribution of distances between pairs of scatterers in a material

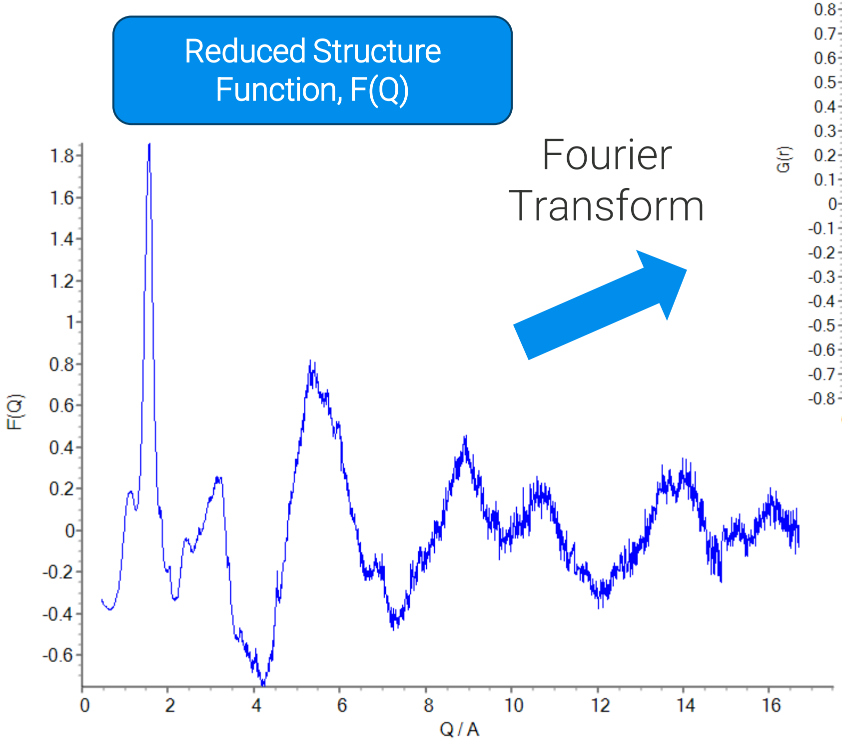
INTRODUCTION TO PAIR DISTRIBUTION FUNCTION ANALYSIS

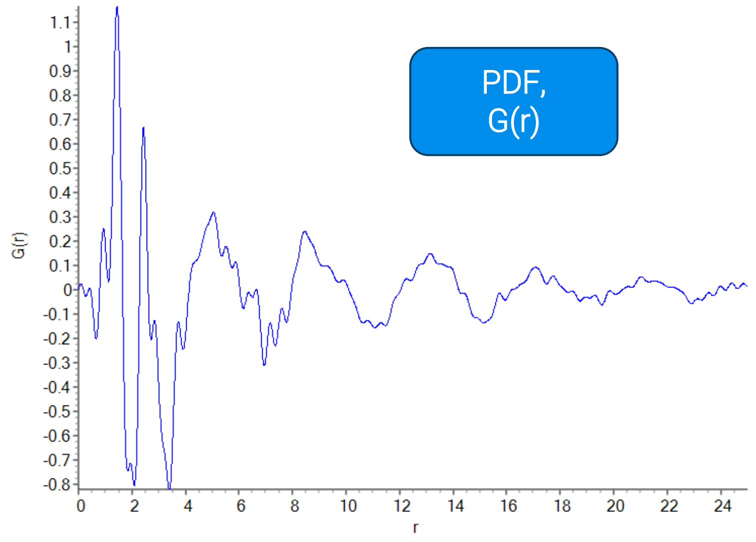
How do I get a PDF?

How do I get a PDF?
3 Main Steps

1. Collect raw data to high Q
2. Remove all non-coherent scattering signal, normalization
3. Fourier transform

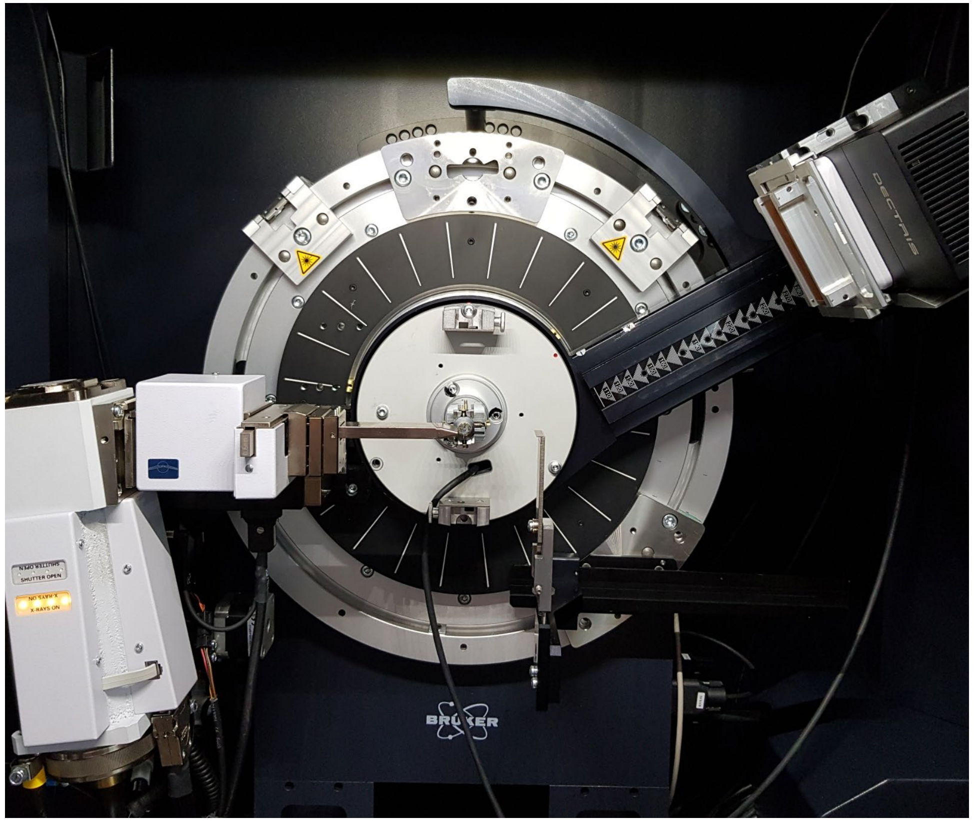






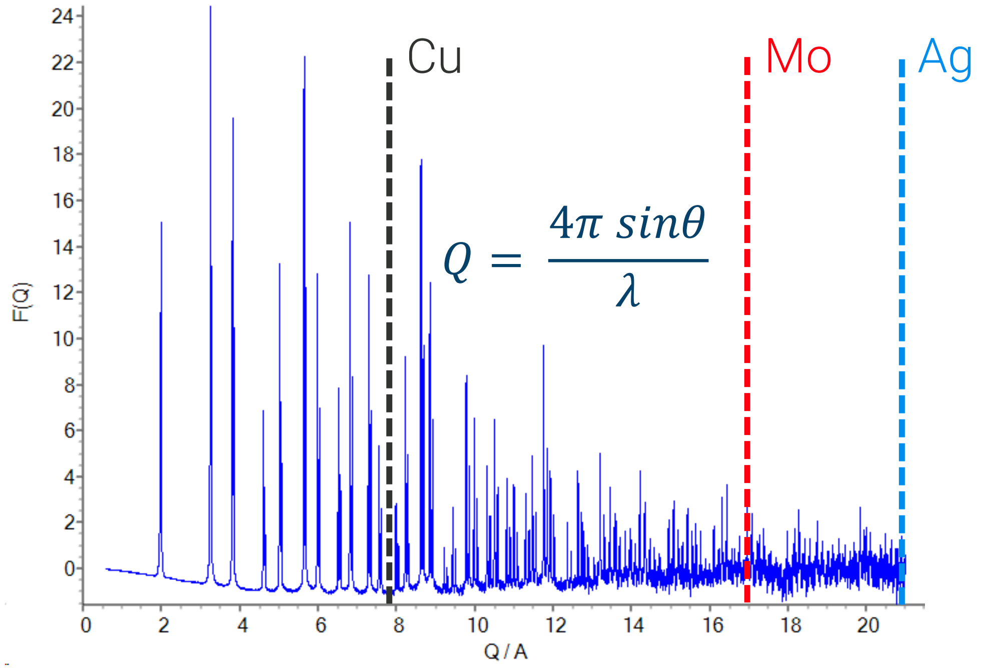
How do I get a PDF?
Data Collection Requirements

- High energy x-rays (Mo or Ag source) to collect data to high Q
- Good counting statistics, especially at high Q
- Low background
- Good angular resolution?



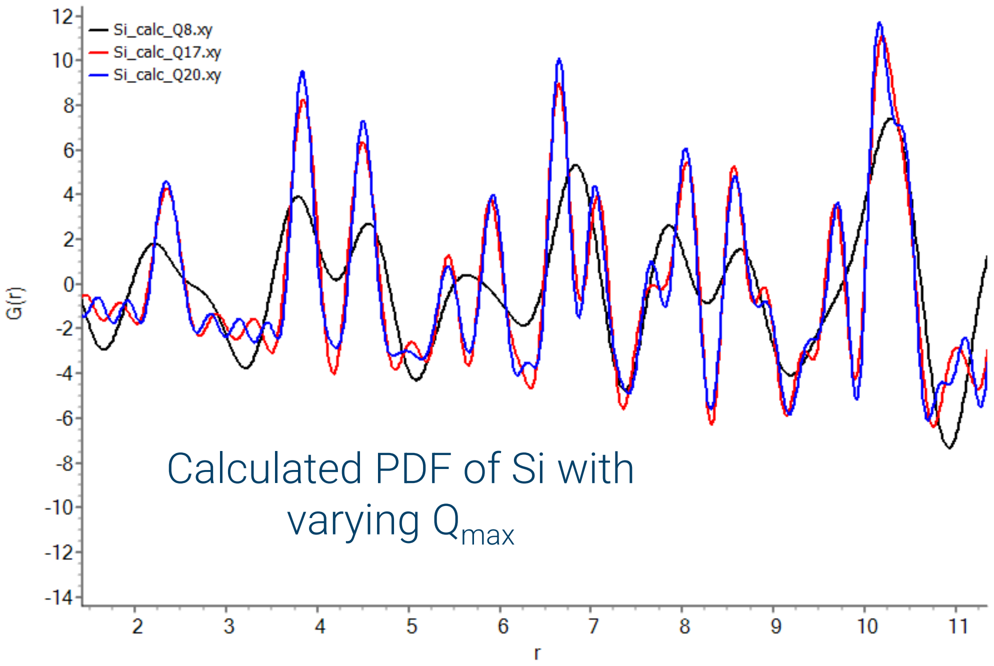
Why high energy X-rays?

Source	$E_{K\alpha1}$	$\lambda_{K\alpha1}$	$2\theta_{max}$	Q_{max}
Cu	8.05 keV	1.541Å	160°	8.0 Å^{-1}
Mo	17.48 keV	0.708Å	160°	17.5 Å^{-1}
Ag	22.16 keV	0.559Å	160°	22.0 Å^{-1}



$$Q = \frac{4\pi \sin\theta}{\lambda}$$

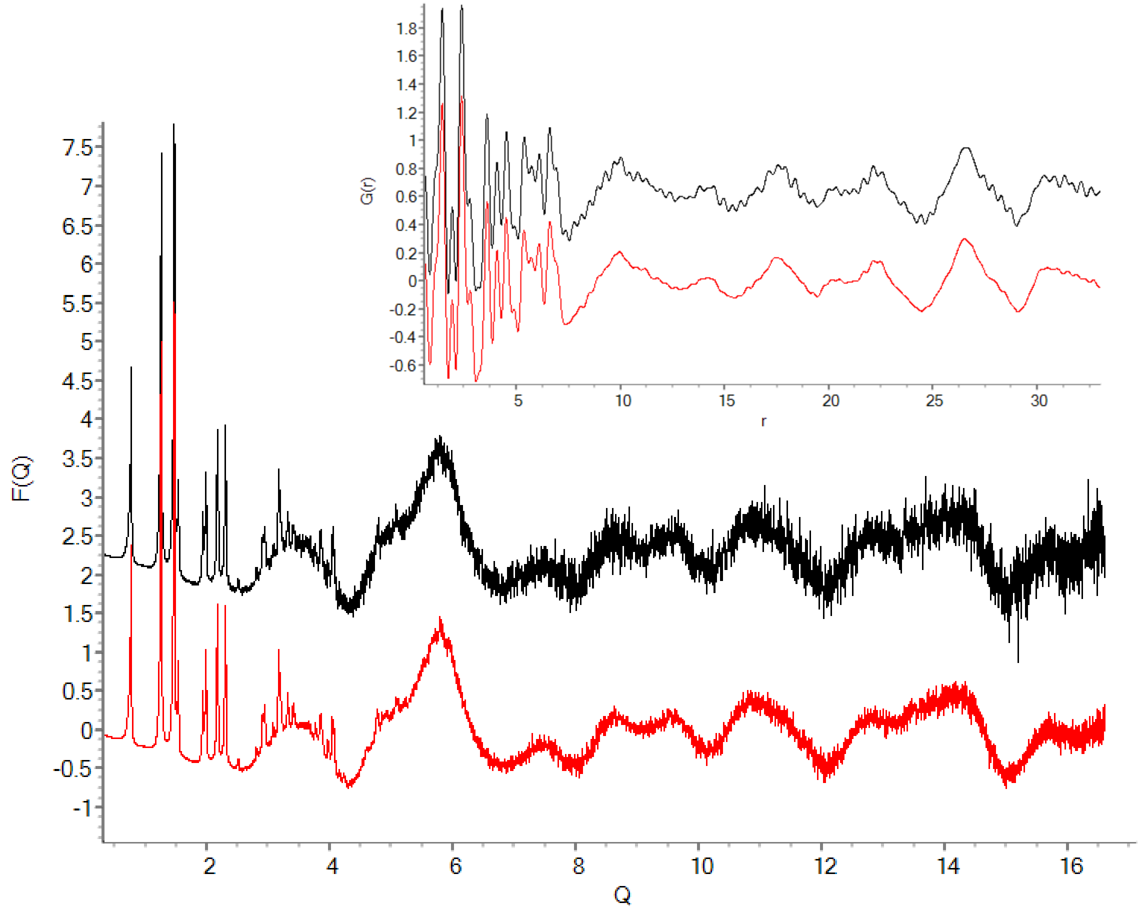
- The **resolution** of the PDF depends strongly on the Q_{max} reached in the experiment!



Calculated PDF of Si with varying Q_{max}

Good counting statistics are important, too

- The large field-of-view for the EIGER2 means more diffracted x-rays are collected and better counting statistics for PDF measurements
- This can be seen in the reduced structure function, F(Q), which is the normalized coherent scattered intensity
- Noise in the F(Q) translates to noise in the PDF
- Data collected in 6 h



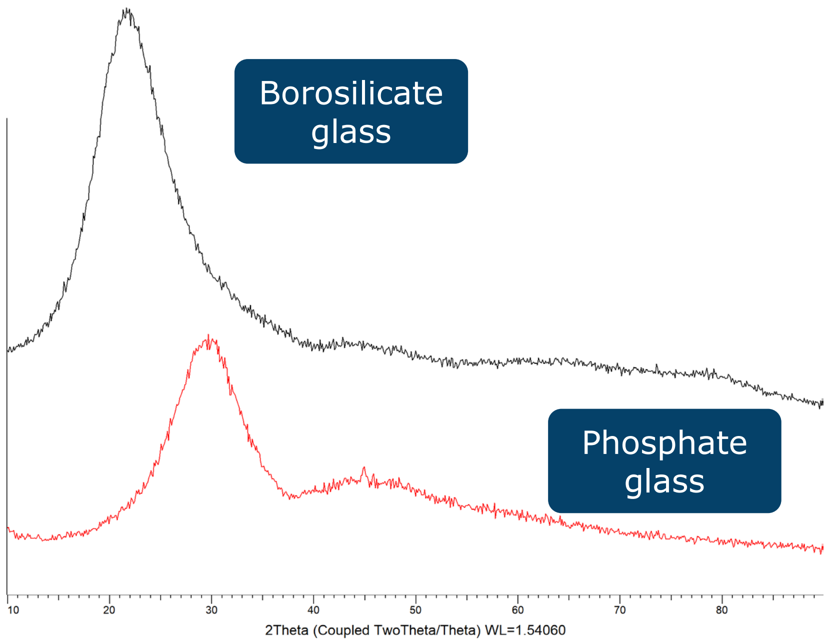
INTRODUCTION TO PAIR DISTRIBUTION FUNCTION ANALYSIS

What can I see in a PDF?

Application Example
Glass

Glasses: amorphous materials with no long-range atomic ordering

- Diffraction patterns show only broad features, no Bragg peaks
- What structural information can be extracted?

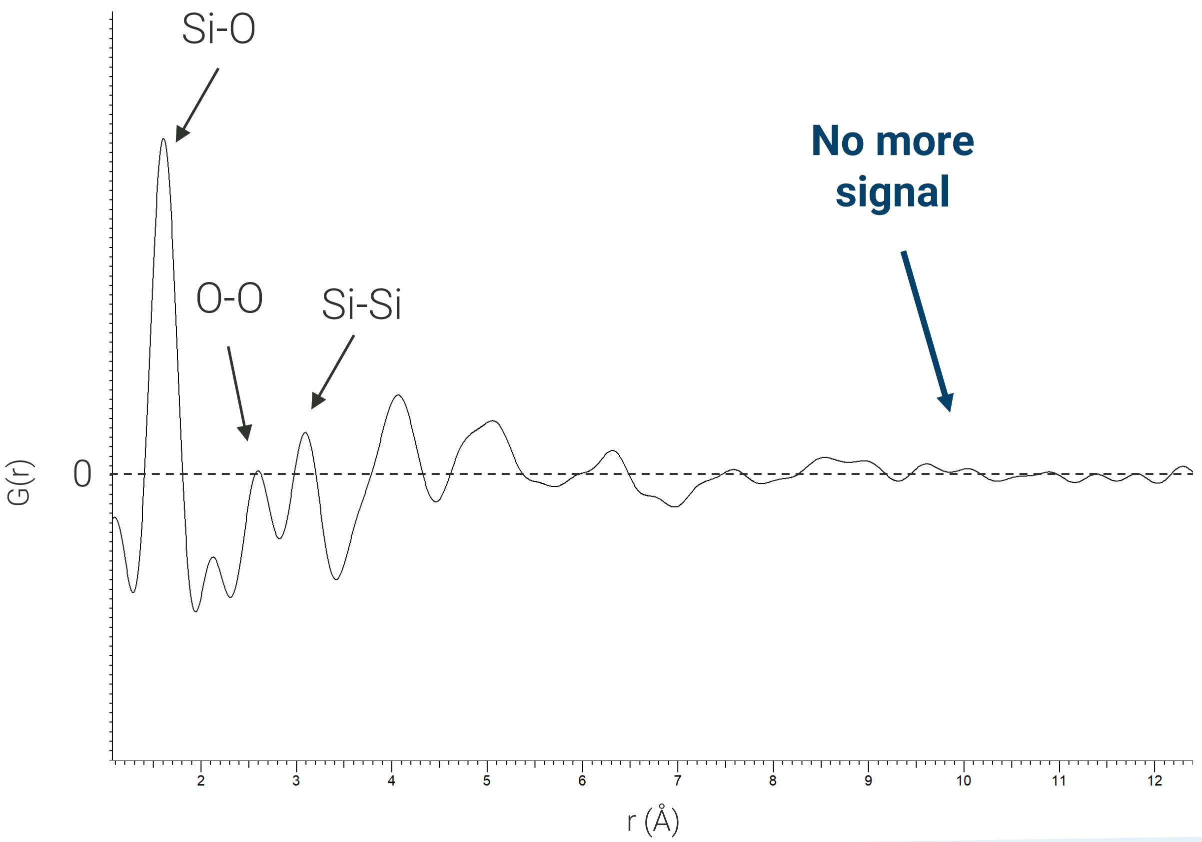


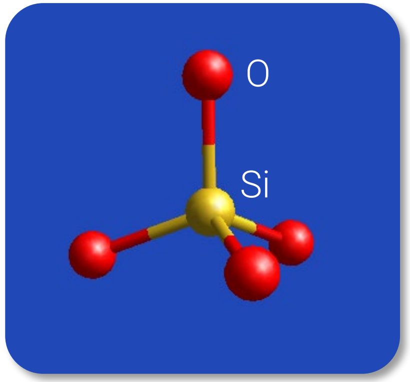
Oxide	(%)
SiO_2	81
B_2O_3	13
Na_2O	3.5
Al_2O_3	2.3
K,Ca	< 1

Oxide	(%)
P_2O_5	30
SrO	20
ZnO	20
CaO	20
Na_2O	10

Application Example
Borosilicate Glass

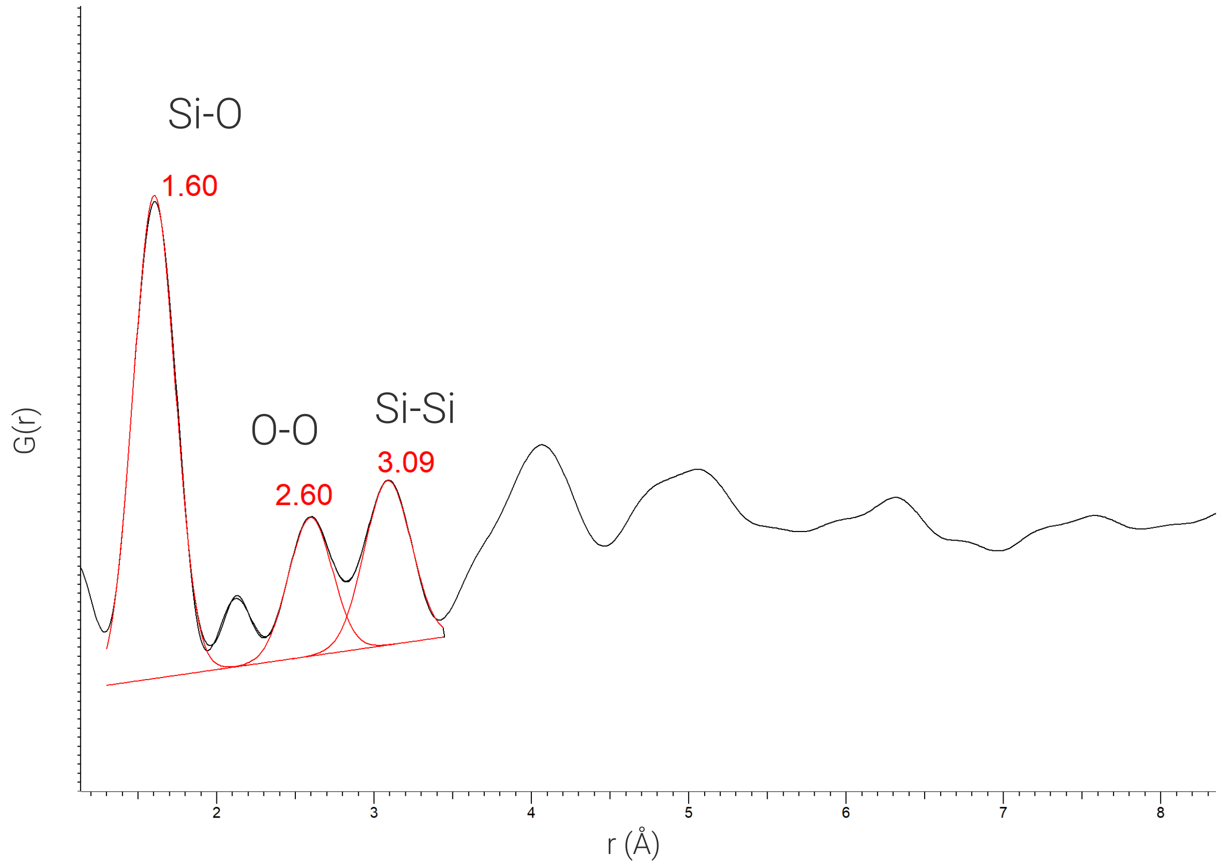
Direct information – what can we see just by looking at the PDF

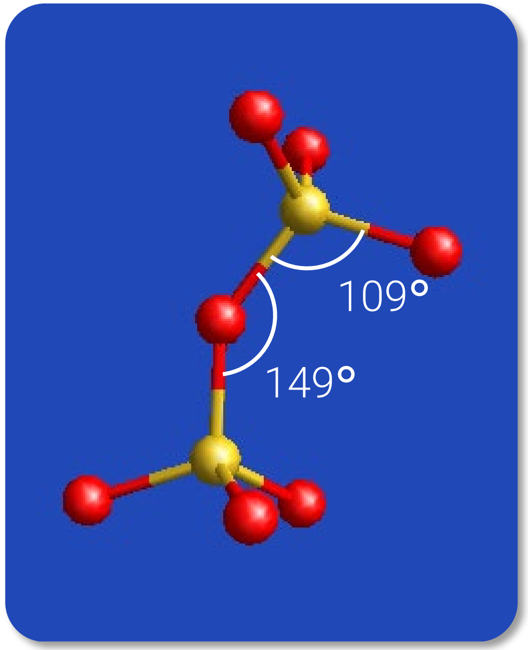




Application Example
Borosilicate Glass

Peak fitting in DIFFRAC.EVA to obtain bond lengths



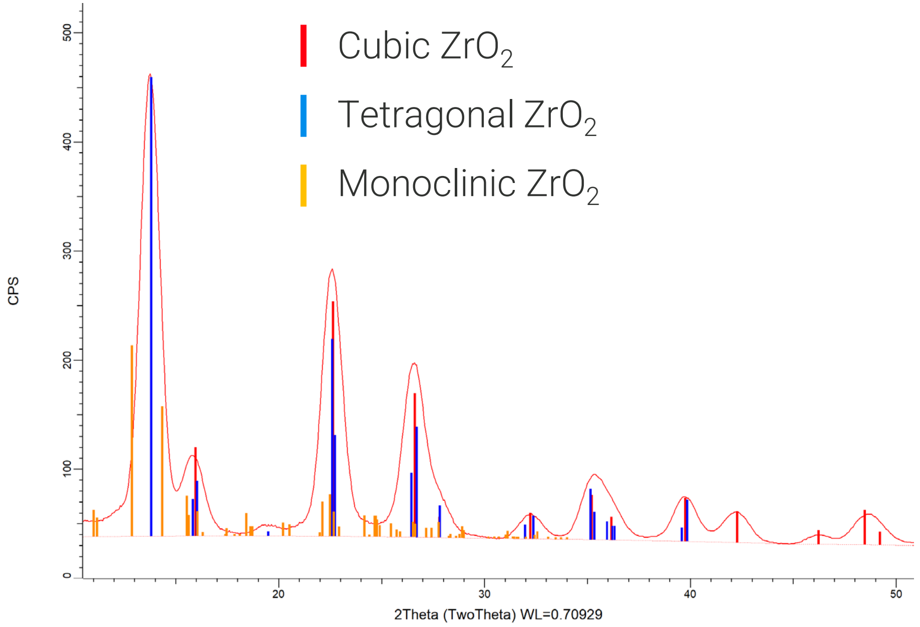


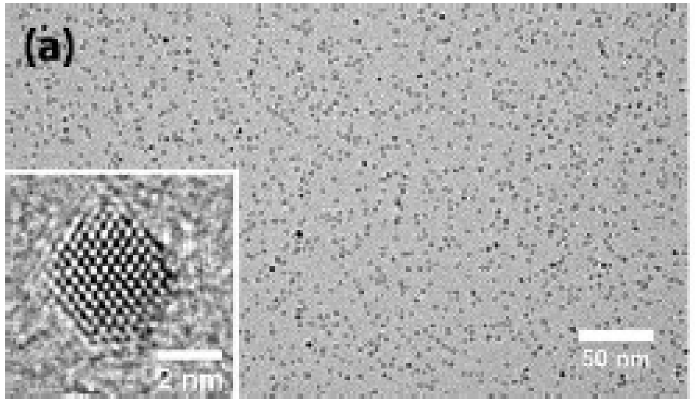
What about nanomaterials? ZrO_2 nanoparticles

- ZrO_2 exists as 3 main polymorphs

  monoclinic → tetragonal → cubic
  1170 °C 2370 °C

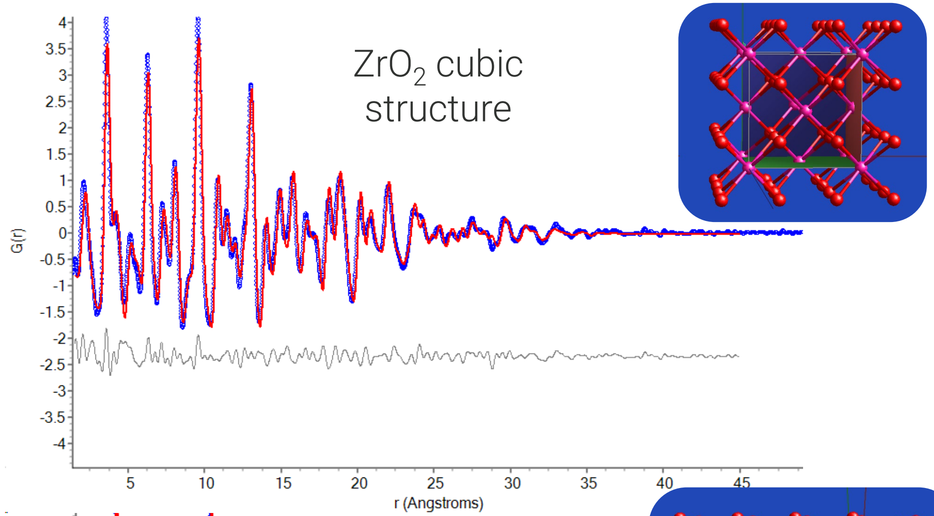
- Each differs in catalytic activity and selectivity

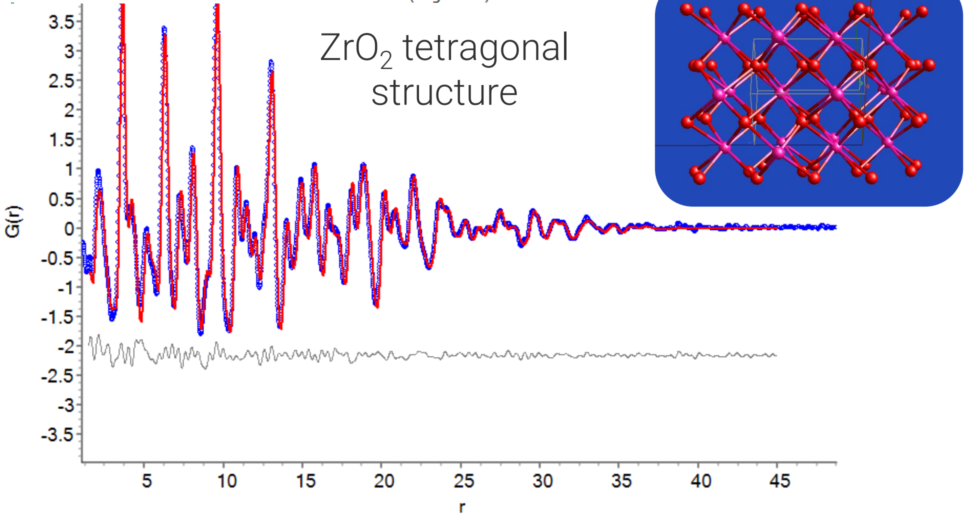




Sample courtesy of Jonathan De Roo, Univ. of Basel
Rijckaert, H. et al., *Materials* **2018,** *11* (7), 1066.

Real-Space Rietveld Refinement ZrO_2 nanoparticles

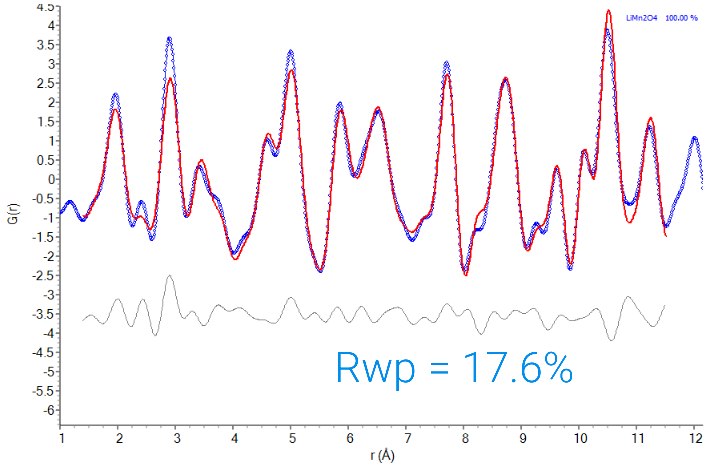




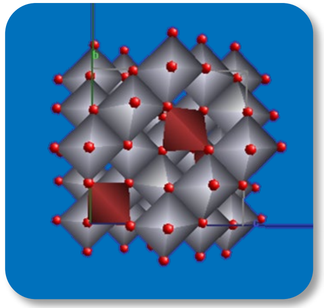
- Comparison of cubic and tetragonal structure models on the PDF data

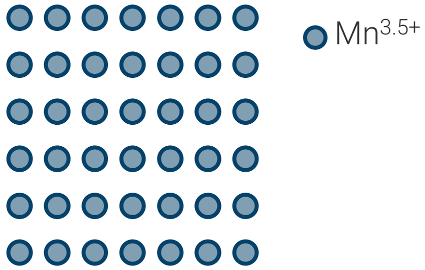
	ZrO_2 (cub)	ZrO_2 (tet)
SG	Fm-3m	$P4_2/nmc$
a (Å)	5.1256(4)	3.6054(2)
c (Å)		5.1925(7)
B_{Zr}	1.03(2)	0.97(1)
B_O	5.64(5)	2.61(4)
dia. (Å)	3.9(1)	4.1(1)
R_{wp} (%)	16.2	11.3

PDF Refinements
Local Structure of $LiMn_2O_4$

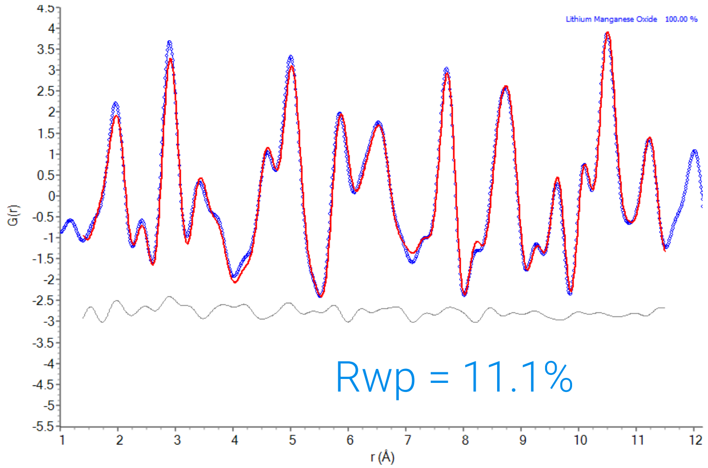


Cubic Fd-3m – disordered $Mn^{3.5+}$

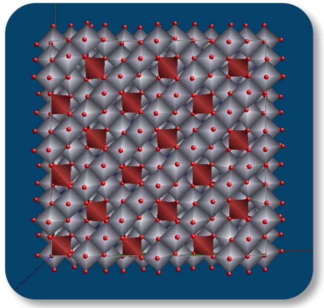


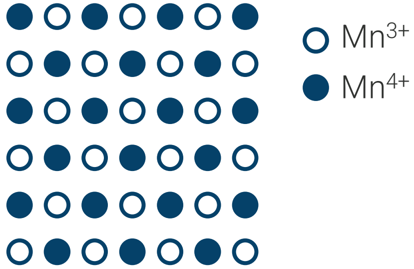


Mn-O bonds: 1.951 Å



Orthorhombic Fddd – ordered Mn^{3+}/ Mn^{4+}



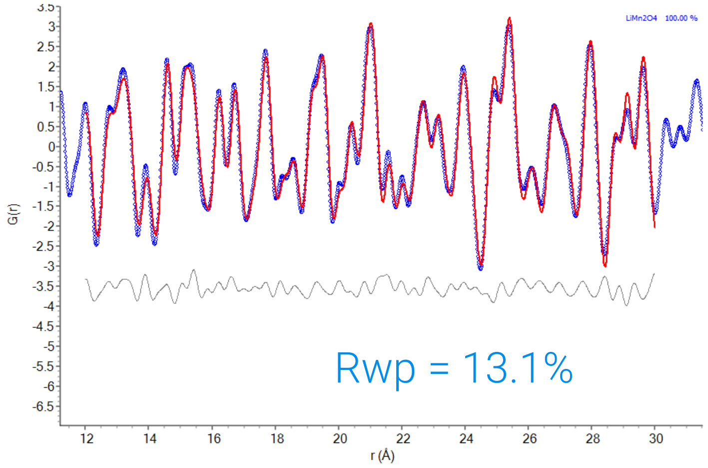


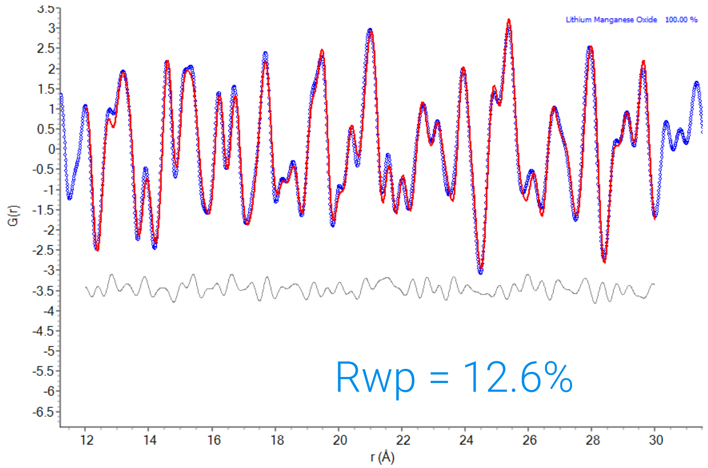
Mn-O bonds: 1.82 – 2.28 Å

- 18 sites vs. 3 sites (cubic)
- Only Mn positions refined
- B_{eq}'s were constrained for each atom type

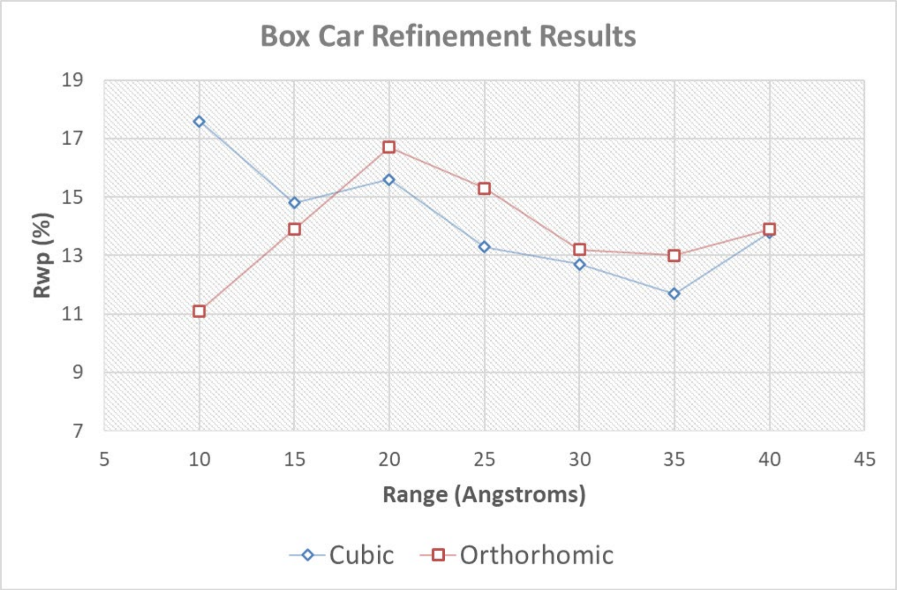
PDF Refinements

Local to Intermediate Structure of $LiMn_2O_4$

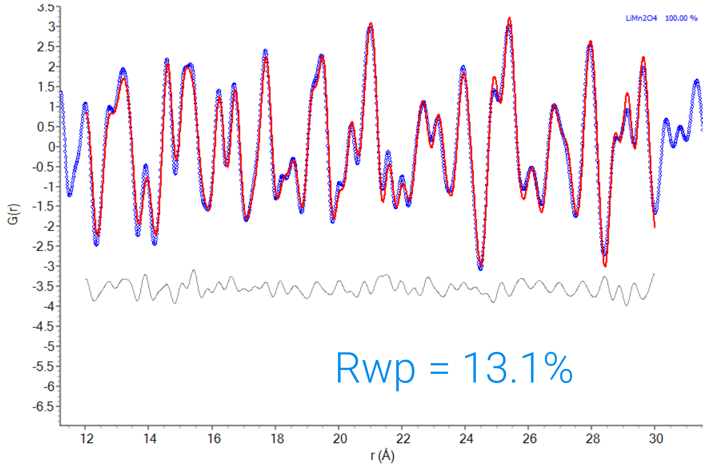




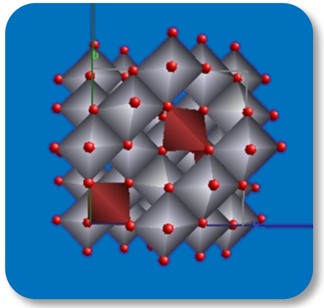
- Fixed length box (10 Å) and performing sequential refinements from low to high r-ranges
- PDF fit to the cubic model gets better at higher r-range
  - Closer to average structure

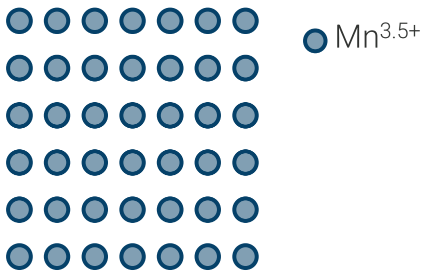


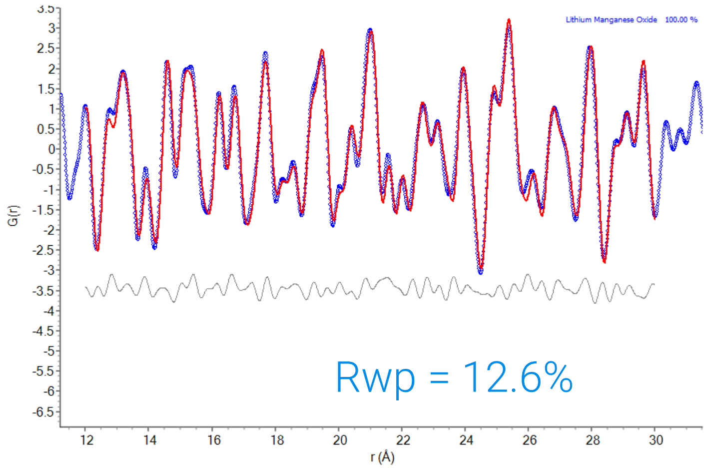
PDF Refinements
Local to Intermediate Structure of $LiMn_2O_4$



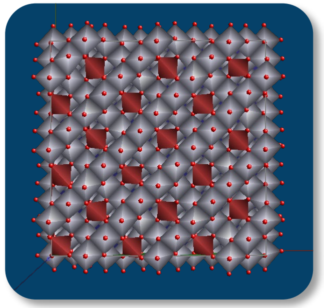
Cubic Fd-3m – disordered $Mn^{3.5+}$ on long range

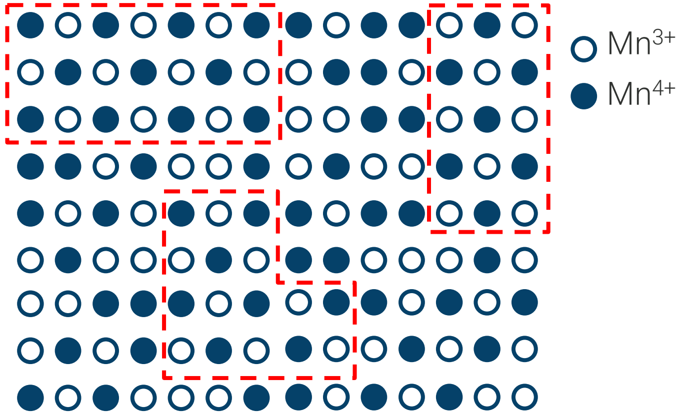






Orthorhombic Fddd - ordered Mn^{3+}/ Mn^{4+} domains





Thank you!

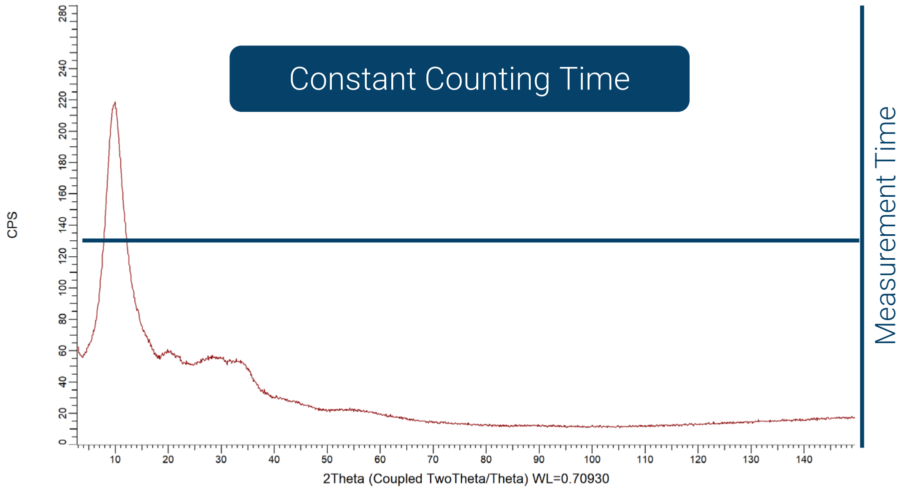
Name
Email or phone number

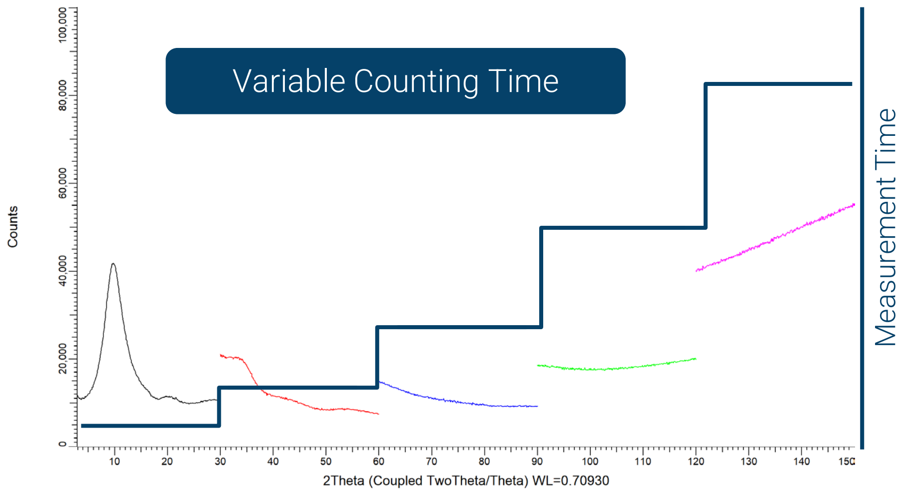
BRUKER

Innovation with Integrity

Data Collection Requirements

How to improve counting statistics as a function of Q?
Variable Counting Time (VCT)





Benefits of Variable Counting Time (VCT)

- Improved counting statistics as function of Q
- More efficient use of measurement time