Friedrich-Alexander-Universität
Naturwissenschaftliche Fakultät

DISCUS Workshop
Pair Distribution Function PDF

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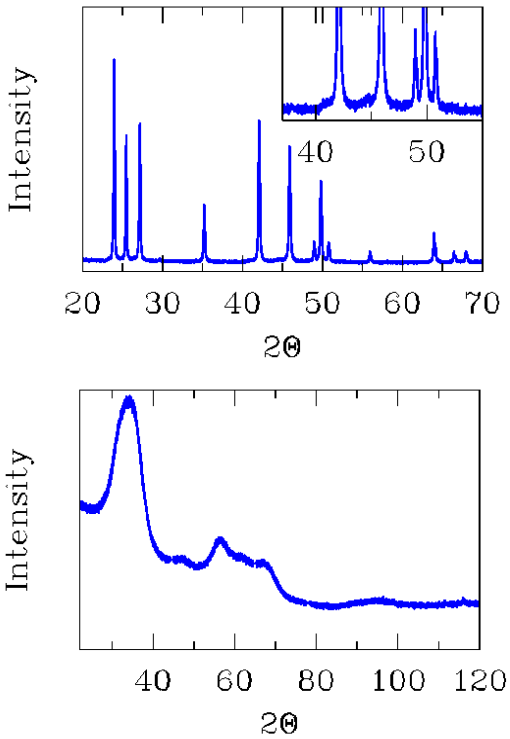
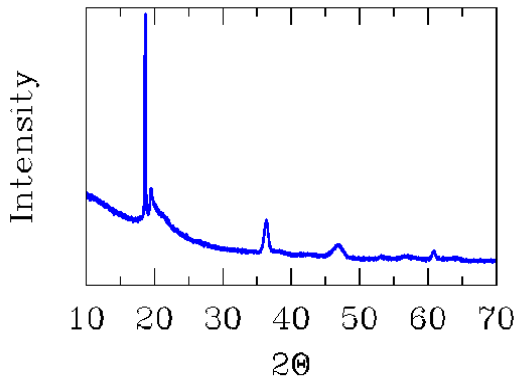
Pair Distribution Function

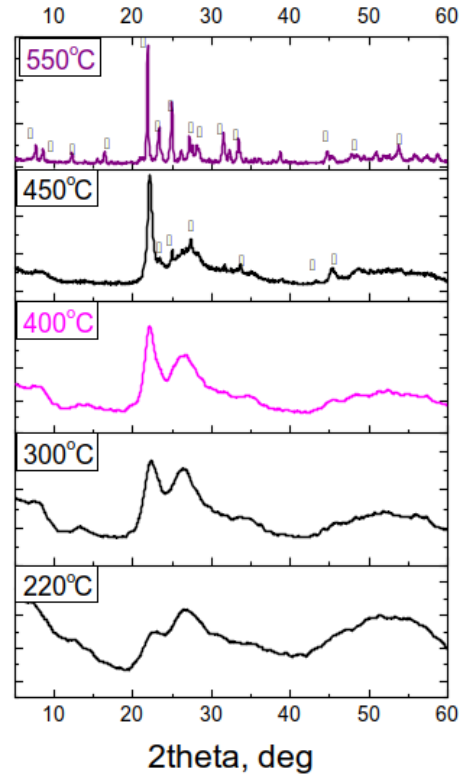
Crystalline material



Nano crystalline ZnO



Massive stacking faults
H_2TiO_3



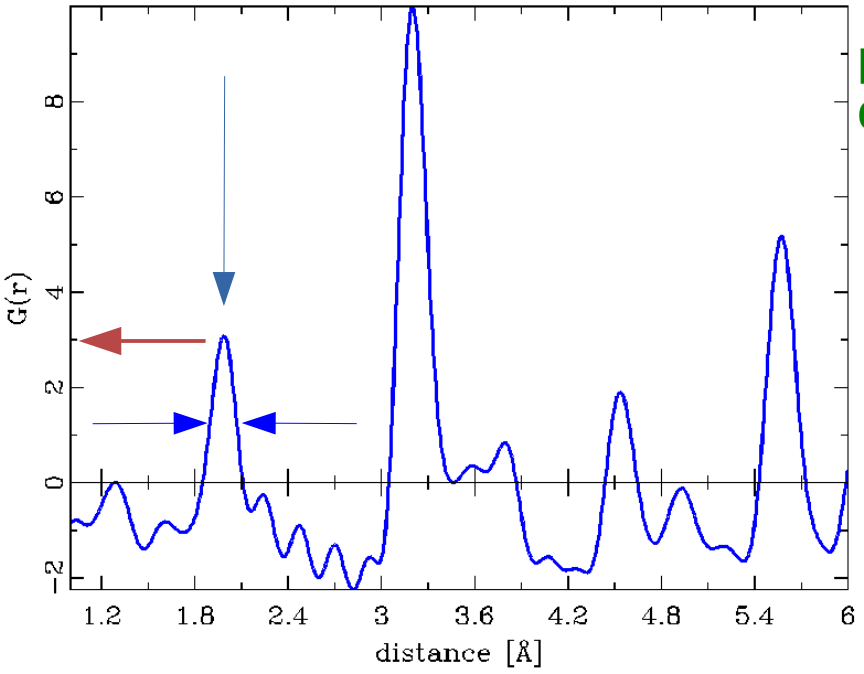
Mo-V-Nb Oxide
Steps during synthesis

Pair Distribution Function

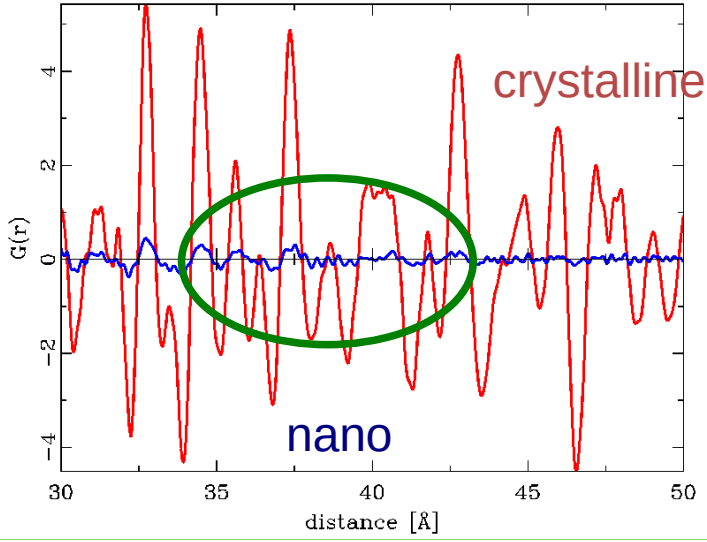
direct measure of
Interatomic distance

number of neighbors

bond length distribution



particle diameter
defects



A pattern in direct space,

essentially a histogram
of interatomic distances,

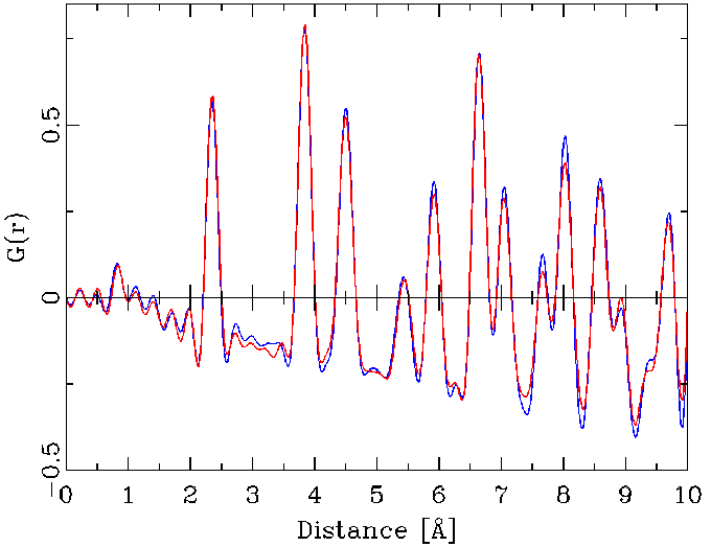
directly converted from
powder diffraction pattern

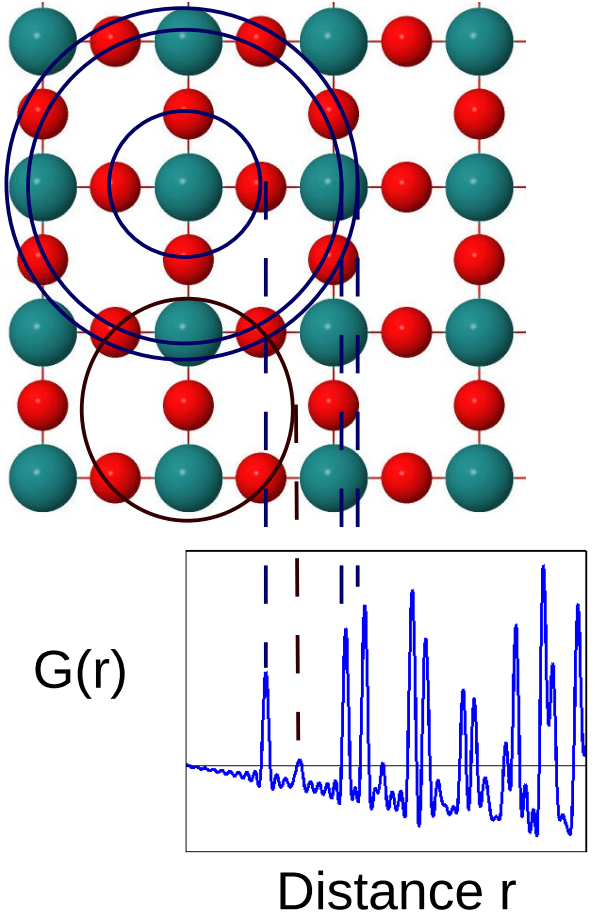
Pair Distribution Function

Pair Distribution Function

Measure of all interatomic distances

- At what distance
- How many neighbors
- How well is distance defined





Pair Distribution Function

Intensity: $I(\vec{h}) = F(\vec{h}) \cdot F^*(\vec{h})$

$$\mathcal{F}[I(\vec{h})] = \mathcal{F}[F(\vec{h}) \cdot F^*(\vec{h})]$$

$$= \mathcal{F}[F(\vec{h})] \circ \mathcal{F}[F^*(\vec{h})]$$

$$= \rho(\vec{r}) \circ \rho^*(-\vec{r})$$

$$= \rho(\vec{r}) \circ \rho(-\vec{r}) = P(\vec{u})$$

$$= \textit{Autocorrelation function } P(\vec{u})$$

Intensity is product of Structure factor and conj. complex

Fourier transform to go back to direct space

Convolution of individual Fourier transforms

Back to electron densities real valued function of r

Auto correlation function: peaks at

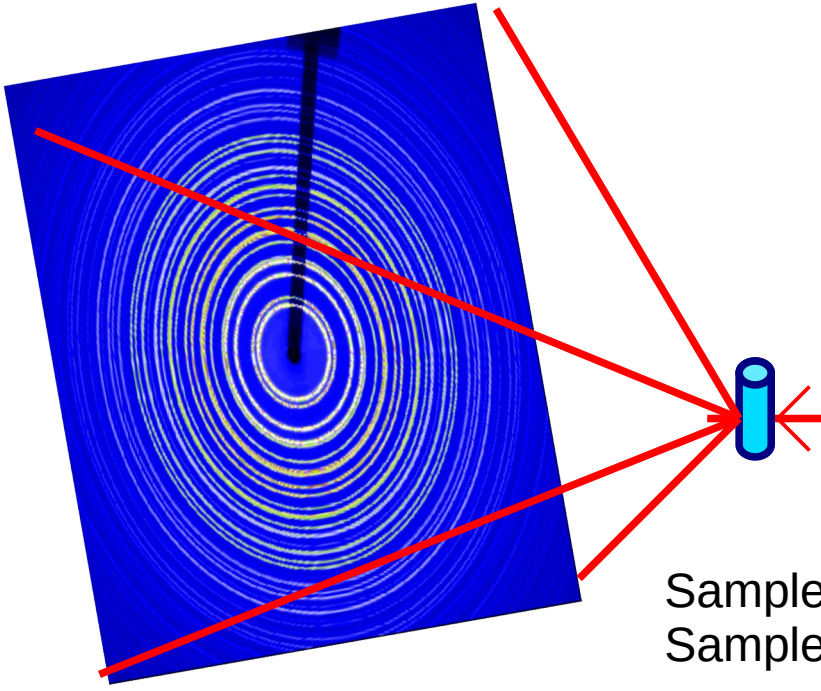
$$P(\vec{u}) \quad if \quad \rho(\vec{r}) * \rho(\vec{r}+\vec{u}) \gg 0$$

Vectors u that correspond to interatomic vectors

Powder	Pair distribution function	PDF	G(r) , g(r)
	radial distribution function	RDF	RDF(r)
Single crystal	3D-PDF / 3D-Δ-PDF		

Pair Distribution Function

Synchrotron Radiation from hard Xray source E ~ 60 to 100keV



Advanced Photon Source, USA

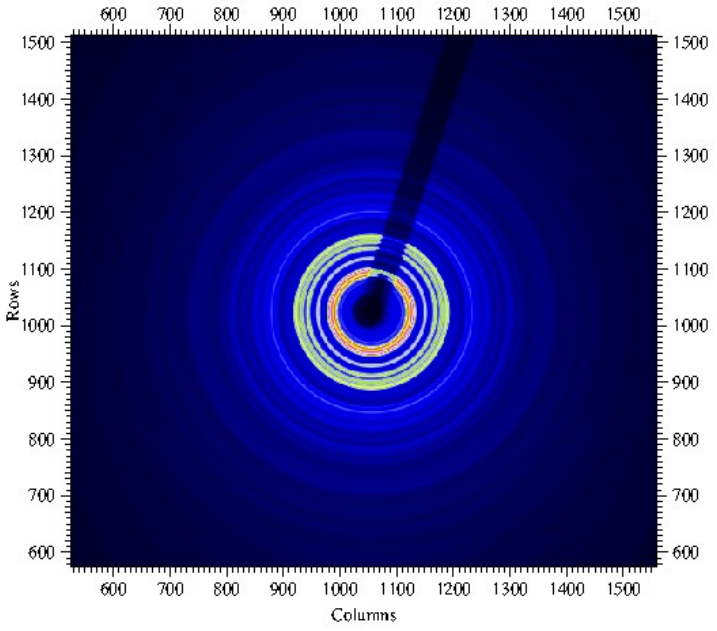
Sample,
Sample environment (T, p, ...)

Beam line 11-IDB

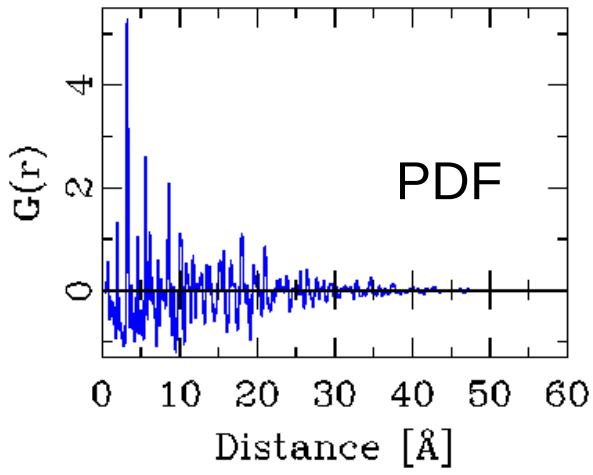
Counting time 1/16 s to 30 sec !!!

Pair Distribution Function

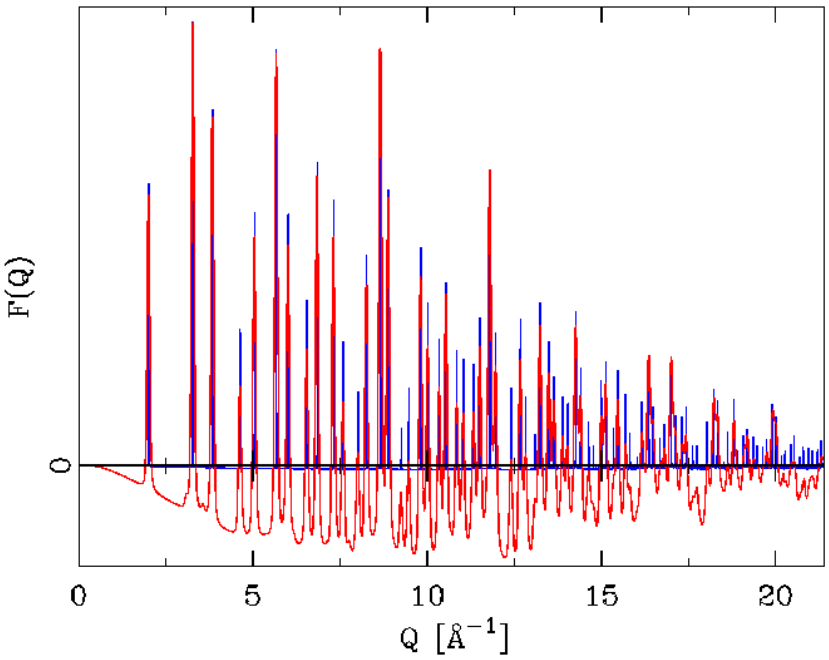
Rapid-aquisition PDF



Integration
Fourier transform



Pair Distribution Function



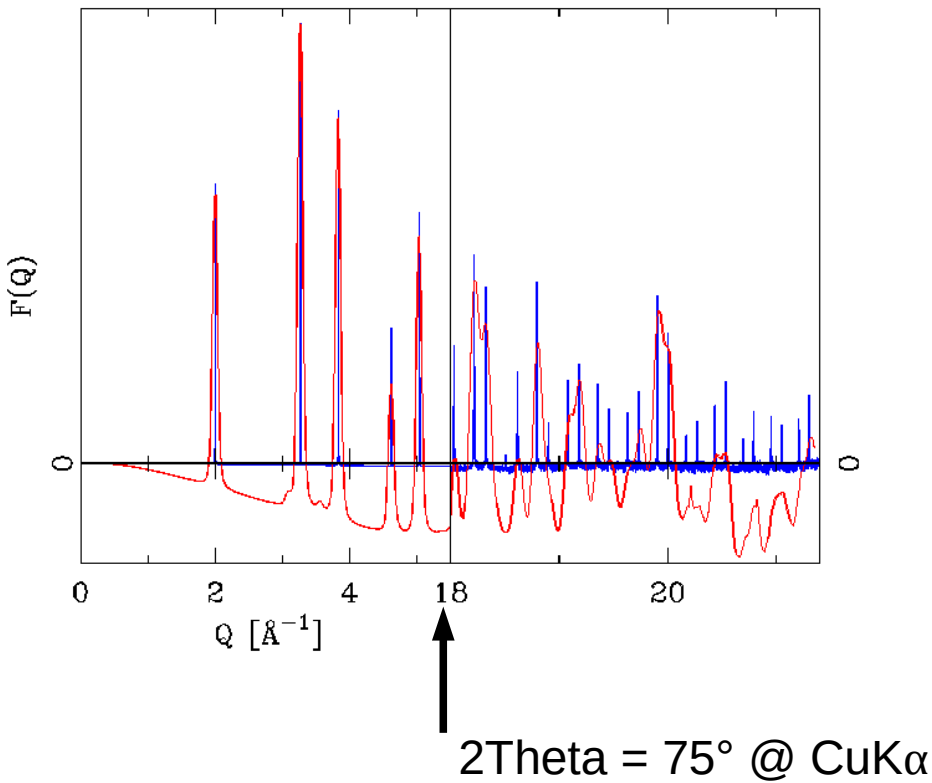
Reduced normalized intensity F(Q)

PSI high resolution data
~ 30 min

APS low resolution data
~ 1 min

Reflections well resolved
at PSI up to
and beyond 21.4 Å^{-1}

Pair Distribution Function



PSI high resolution data
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Reflections well resolved
at PSI up to
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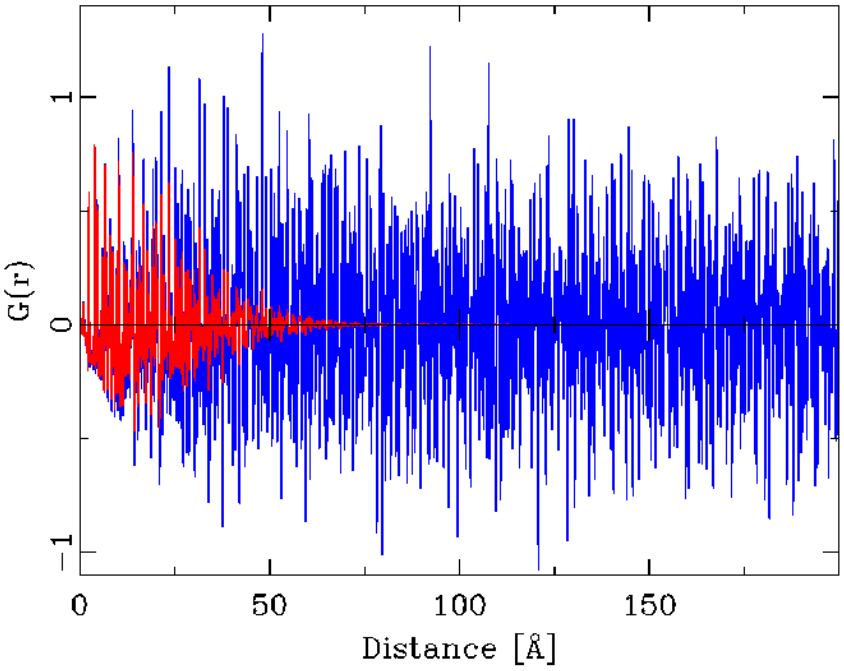
Pair Distribution Function



PSI high resolution data
~ 30 min

APS low resolution data
~ 1 min

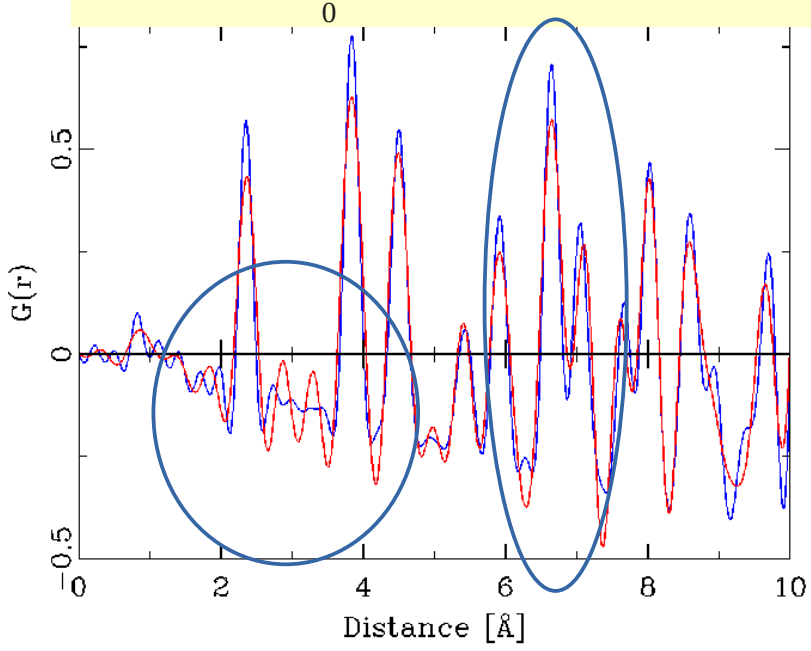
Reflections well resolved
at PSI up to
and beyond 21.4 $Å^{-1}$

PDF peak height influences determination of nanoparticle diameter

High resolution NOT needed for small (<5nm) objects; only good if sample has narrow Bragg

Pair Distribution Function

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



PSI high resolution data
Silicon

Q_{max} = 21. Å^{-1} Synchrotron

Q_{max} = 15. Å^{-1} Mo-Kα

Apparent shift of smaller PDF maxima !?!

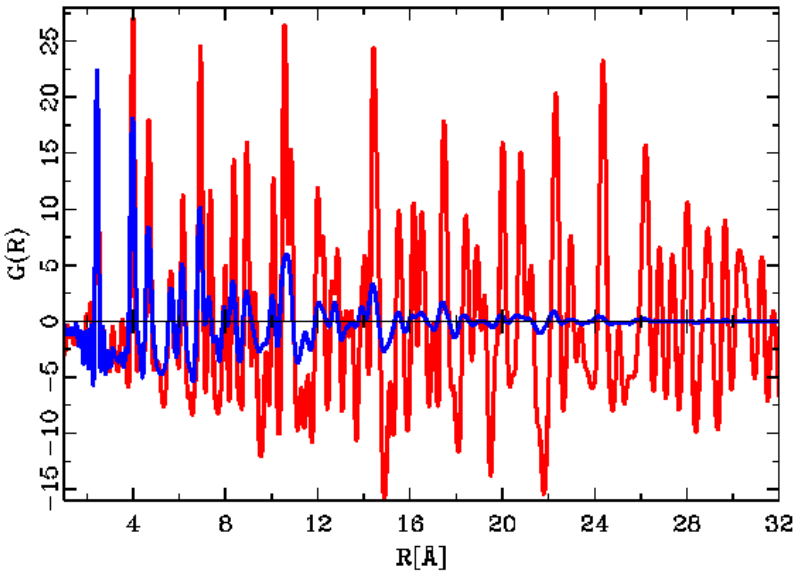
decreases with increasing Q_{max}

Be careful with direct interpretation of peak positions!

Local disorder in Si !?!

Anything that changes with Q_{max} is not real

Pair Distribution Function

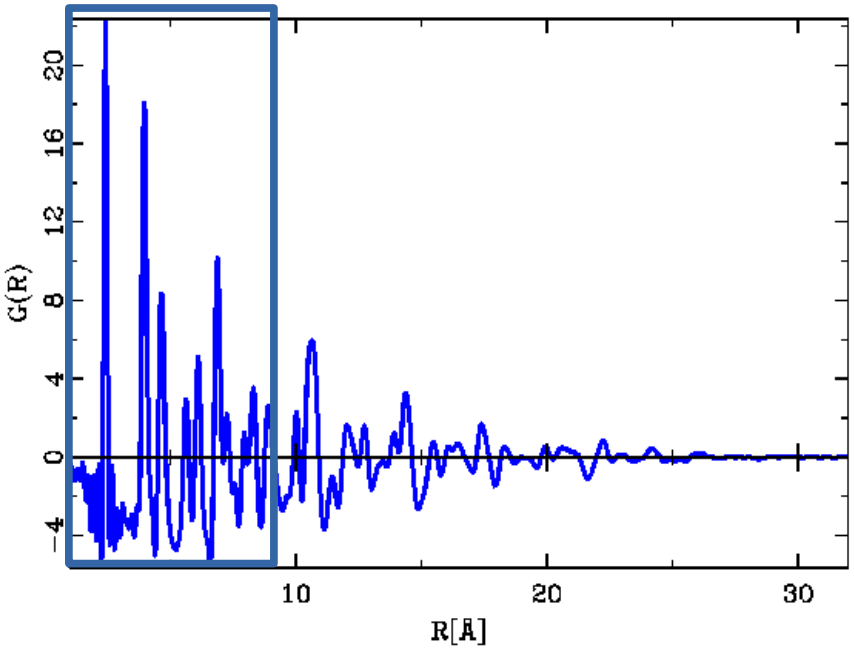


data collected under identical conditions

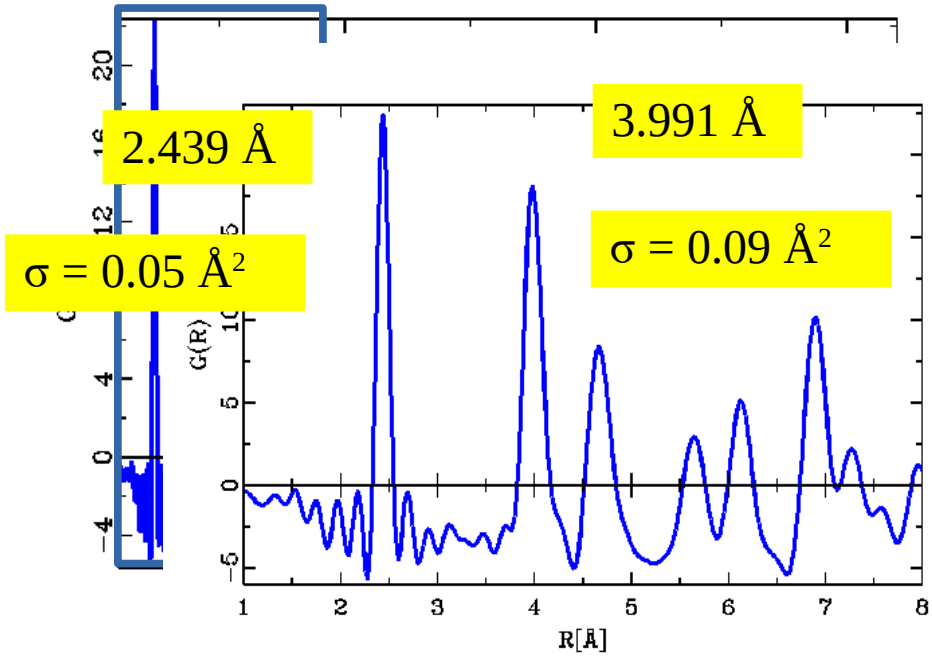
crystalline ZnSe

nanocrystaline ZnSe

Pair Distribution Function

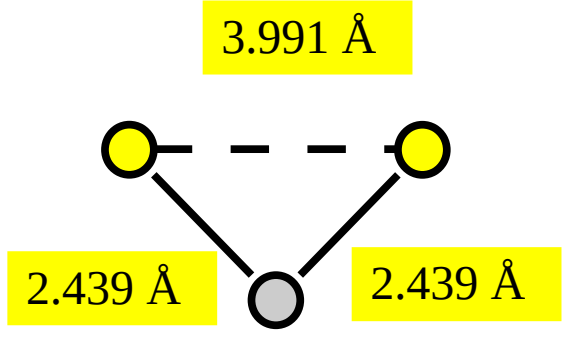


Pair Distribution Function

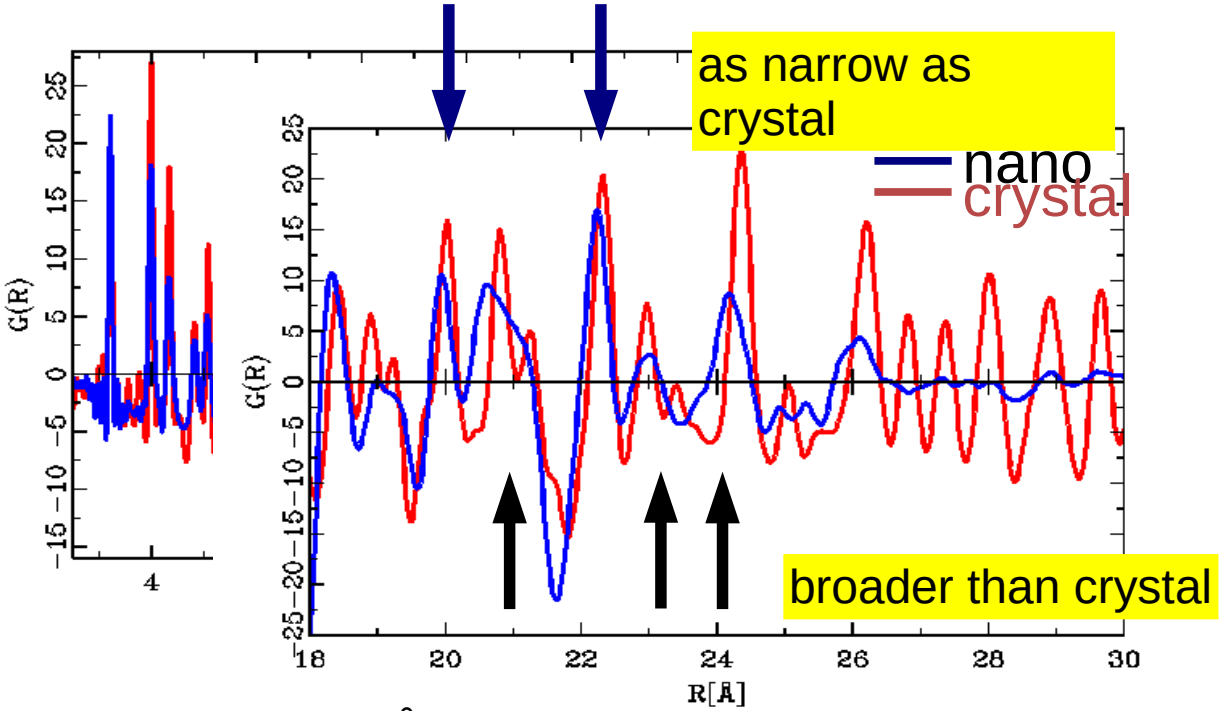


tetrahedral structure

bond angle 109.8

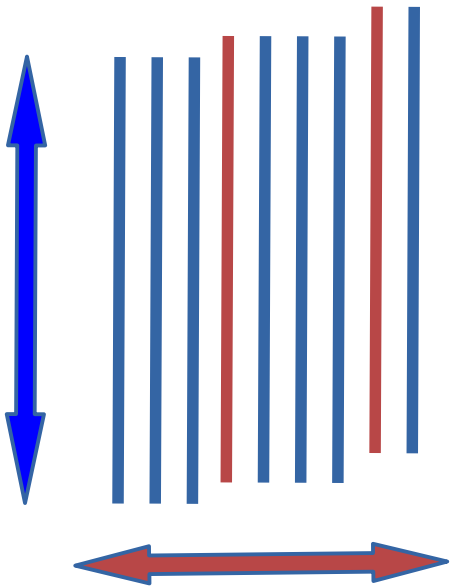


Pair Distribution Function



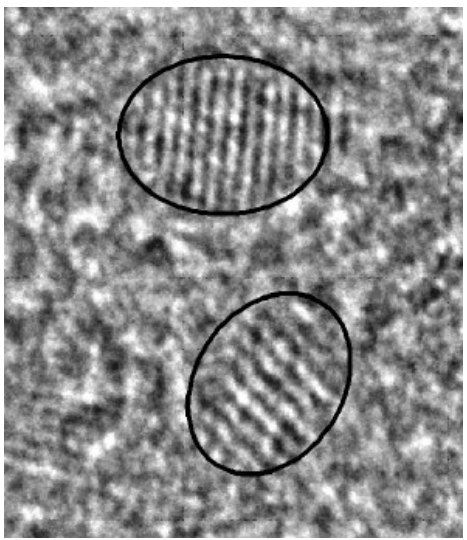
Pair Distribution Function

structural coherence



loss of coherence due
to stacking faults

~8 to 10 monolayers
= 4 to 5 unit cells along c
= 24 to 30 Å



Calculating a Powder diffraction pattern

Rietveld

Complete Integration

Debye-Scattering-Equation

Sum over **a fine 3D-Grid in reciprocal space**

Convolution by profile function

Repeat for all phases

Addition of a background

Calculating a Powder diffraction pattern

Rietveld

Perform a spherical average of Intensity expression

Complete Integration

$$F(hkl) = \sum_{j=1}^{N} f_j e^{2\pi i (h x_j + k y_j + l z_j)}$$

Debye-Scattering-Equation

$$I(hkl) = F(hkl) * F^*(hkl)$$

$$<|F(|\boldsymbol{h}|)|^2> = \sum_i \sum_j f_i f_j \frac{\sin(2\pi|\boldsymbol{h}|\boldsymbol{r_{ij}})}{(2\pi|\boldsymbol{h}|r_{ij})}$$

Convolution by profile function

Repeat for all phases

Addition of a background

Calculating a powder diffraction pattern

Calculating a powder diffraction pattern

Open in Windows Explorer: Lectures2023\
03_Diffraction\

Start DISCUS_SUITE

You should see:

...
User macros in ...
System macros in ...
Start directory ...

suite >

suite > cd Lectures_2023\03_Diffraction

suite > **@complete.mac nickel**

Try: silicon; lab6; kaolinite

POWDER calculate a powder diffraction pattern

Main steps

Radiation:	**xray**;	**neutron**;	**electron**
Wavelength:	**set wvle**;	**set energy**	
Range:	**set tthmin**;	**set tthmax**;	**set dtth**
Algorithm:	**set calc, complete**;	**set calc, debye**	
Profile:	**set profile, pseudo**;	**set profile, off**	
Debye-Waller:	**set temp, use**;	**set temp, ignore**	
LP correction:	**set lpcor, bragg, angle**		

For complete algorithm

Steps in rec.: **set dh**; **set dk**; **set dl**

POWDER calculate a powder diffraction pattern

complete.mac

```
powder
reset      ! Ensure clean start up conditions
neutron                  # Select radiation
set wvle,CU12            # Set the wavelength
set axis,Q               # Perform calculation on equaly spaced Q grid
set calc,complete        # Use complete integration algorithm
```

POWDER calculate a powder diffraction pattern

complete.mac

```
powder
reset      ! Ensure clean start up conditions
neutron                  # Select radiation
set wvle,CU12            # Set the wavelength
set axis,Q               # Perform calculation on equaly spaced Q grid
set calc,complete        # Use complete integration algorithm
#
set dh, 1.0              # Steps in reciprocal space,
set dk, 1.0              # here integer for Bragg only
set dl, 1.0              #
```

POWDER calculate a powder diffraction pattern

complete.mac

```
powder
reset     ! Ensure clean start up conditions
neutron                  # Select radiation
set wvle,CU12            # Set the wavelength
set axis,Q               # Perform calculation on equaly spaced Q grid
set calc,complete        # Use complete integration algorithm
#
set dh, 1.0              # Steps in reciprocal space,
set dk, 1.0              # here integer for Bragg only
set dl, 1.0              #
#
set tthmin, 1.0          # Start/end/step angle in degrees
set tthmax, 90.          # Adapt to experiment
set dtth  , 0.005        # Or: qmin; qmax; dq
```

POWDER calculate a powder diffraction pattern

complete.mac

```
powder
#
set profile, off        # Switch convolution by profile function off
set profile, pseudo     # Use Pseudovoigt (or Pearson VII, or TOF)
set profile, uvw, 0.000, 0.000, 0.005 # Cagliotti u,v,w values
set profile, eta, 0.500   # Mixing parameter 1=Lorenzian 0=Gaussian
set profile, asym, 0.00, 0.00, 0.00, 0.00 #Asymmetry parameters
```

Calculating a powder diffraction pattern

Open in Windows Explorer: Lectures2023\
03_Diffraction\

Start DISCUS_SUITE

You should see:

...
User macros in ...
System macros in ...
Start directory ...

suite >

suite > cd Lectures_2023\03_Diffraction

suite > **@complete.mac nickel**

Modify:

Radiation; Wavelength
2Theta range
Profile parameters

Try: silicon; lab6; kaolinite

Debye Scattering Equation

Double sum over all atom pairs

$$\langle |F(|\boldsymbol{h}|)|^2 \rangle = \sum_i \sum_j f_i f_j \frac{\sin(2\pi|\boldsymbol{h}|\boldsymbol{r_{ij}})}{(2\pi|\boldsymbol{h}|r_{ij})}$$

No constraints on:

periodicity; defects; shape

Calculating a powder diffraction pattern

Open in Windows Explorer: Lectures2023\
03_Diffraction\

Start DISCUS_SUITE

You should see:

...
User macros in ...
System macros in ...
Start directory ...

suite >

suite > **cd Lectures_2023\03_Diffraction**

suite > **@debye.mac 10**

Try: different sizes
WARNING:
TIME = SIZE^6

Calculating a powder diffraction pattern

Open in Windows Explorer: Lectures2023\
03_Diffraction\

Start DISCUS_SUITE

You should see:

...
User macros in ...
System macros in ...
Start directory ...

suite >

suite > **cd Lectures_2023\03_Diffraction**

suite > **@debye.mac 10**

Modify:

Different materials (fixed or as parameter)
Different shapes

Try: different sizes
WARNING:
TIME = SIZE^6