Structure Refinements of II-VI Semiconductor Nanoparticles based on PDF Measurements

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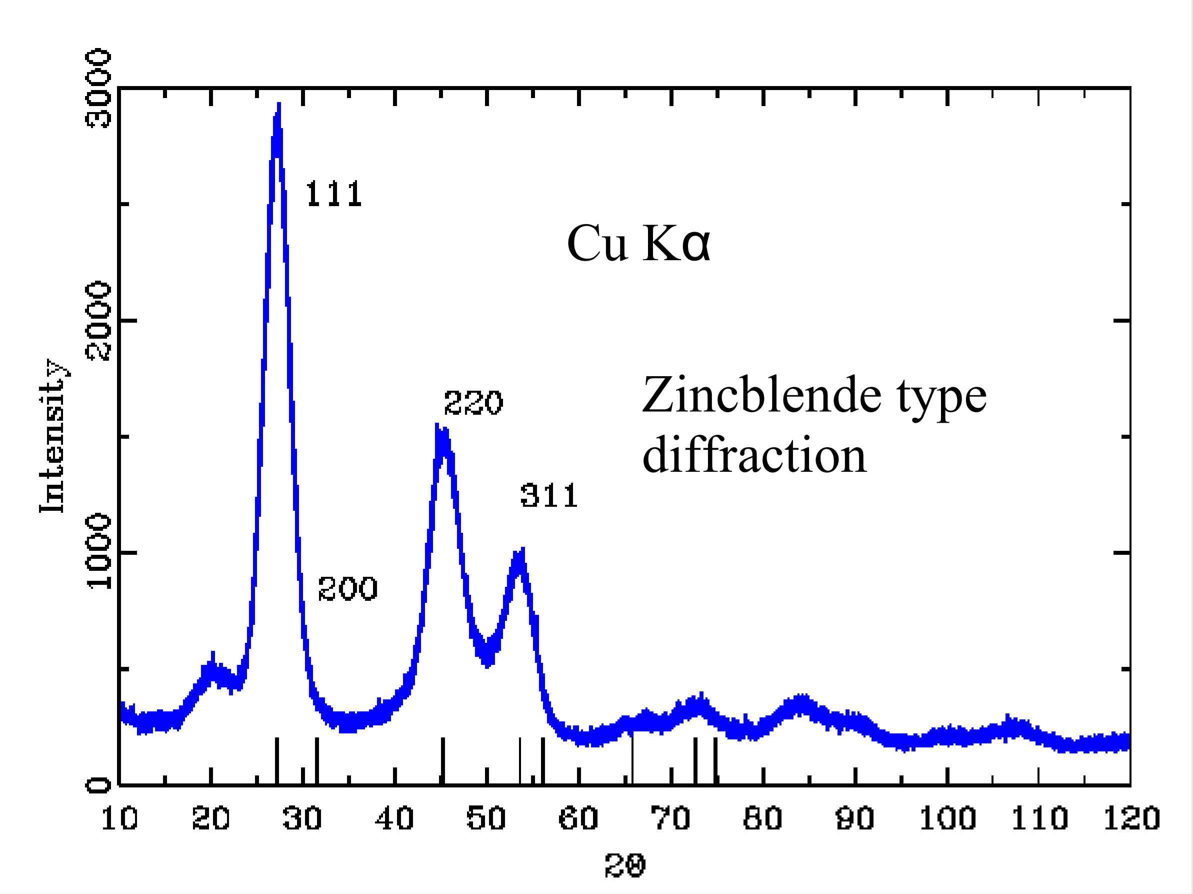
ZnSe Nanoparticles

Synthesis: Se in Trioctylphosphine + $ZnEt_2$
into Hexadecylamin at 310 C

$FWHM_{111}$=3.3

Size ~ 26 Å



Norris, D.J., Yao, N., Charnock, F.T. & Kennedy, T.A. (2001). *Nano Lett*. **1**, 3-6.

ZnSe Nanoparticles

Rietveld Refinement: Zincblende Structure

a =4.00 Å

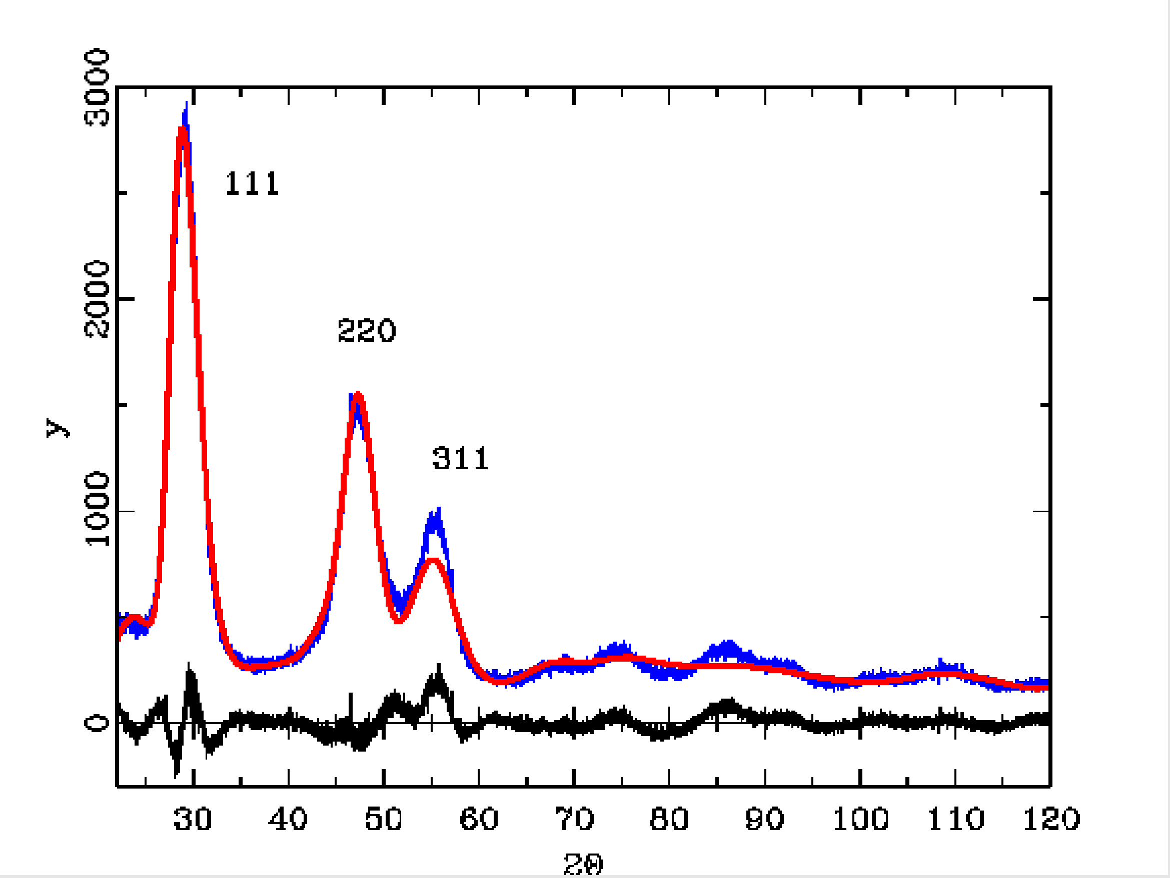
Zn-Se = 2.45 Å

$FWHM_{111}$=3.3

Size ~ 26 Å

R_{wp} =14%

no fit at 311, high order hkl
disordered material



ZnSe Nanoparticles Fitting by Debye

Debye formula :

$$< | F(h) |^2 > = \Sigma_j f_j^2 + \Sigma_i \Sigma_{j,j \neq i} f_i f_j \sin(2\pi h r_{ij}) / (2\pi h r_{ij})$$

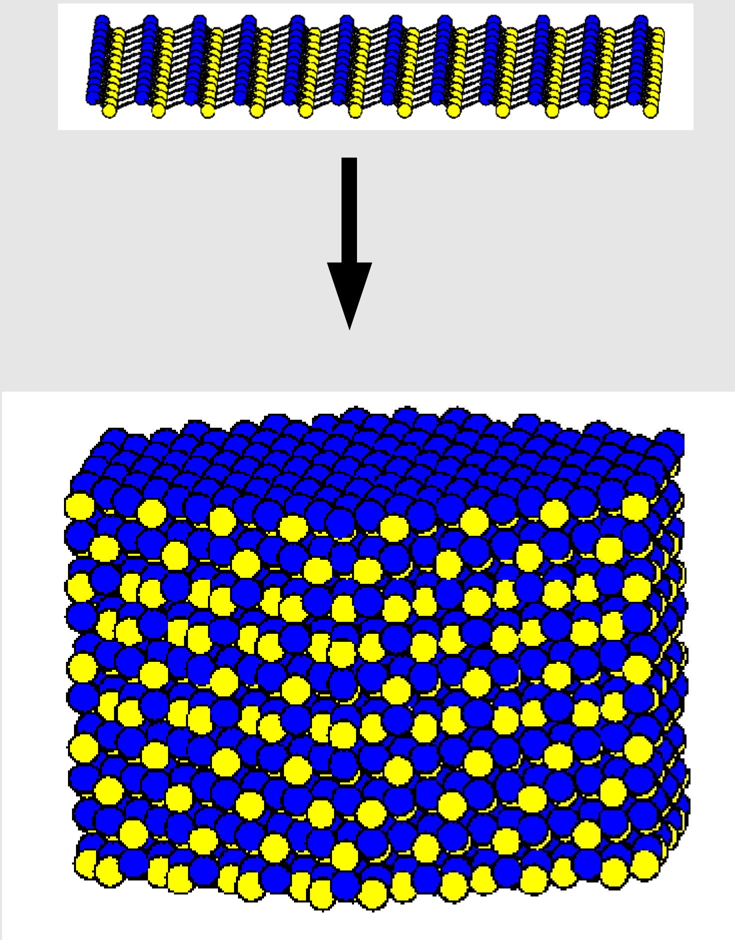
Sum over all atom pairs

→ no restrictions on sample structure

open to finite particle with any shape

defects like stacking faults etc.

creating ZnSe Nanoparticles



{110} and {001}

create a large single Wurtzite layer A/B

Stack along c (with faults)

Cut to proper size

Calculate powder pattern

Repeat and average

Repeat with new set of parameter

using a Differential Evolutionary Scheme

Price, Storn & Lampinen: Differential Evolution, (2006) Springer

ZnSe Nanoparticles

Debye Refinement: Stacking of layers, almost Zincblende structure

a = 3.997 Å

c = 6.501 Å

Zn-Se = 2.39 Å

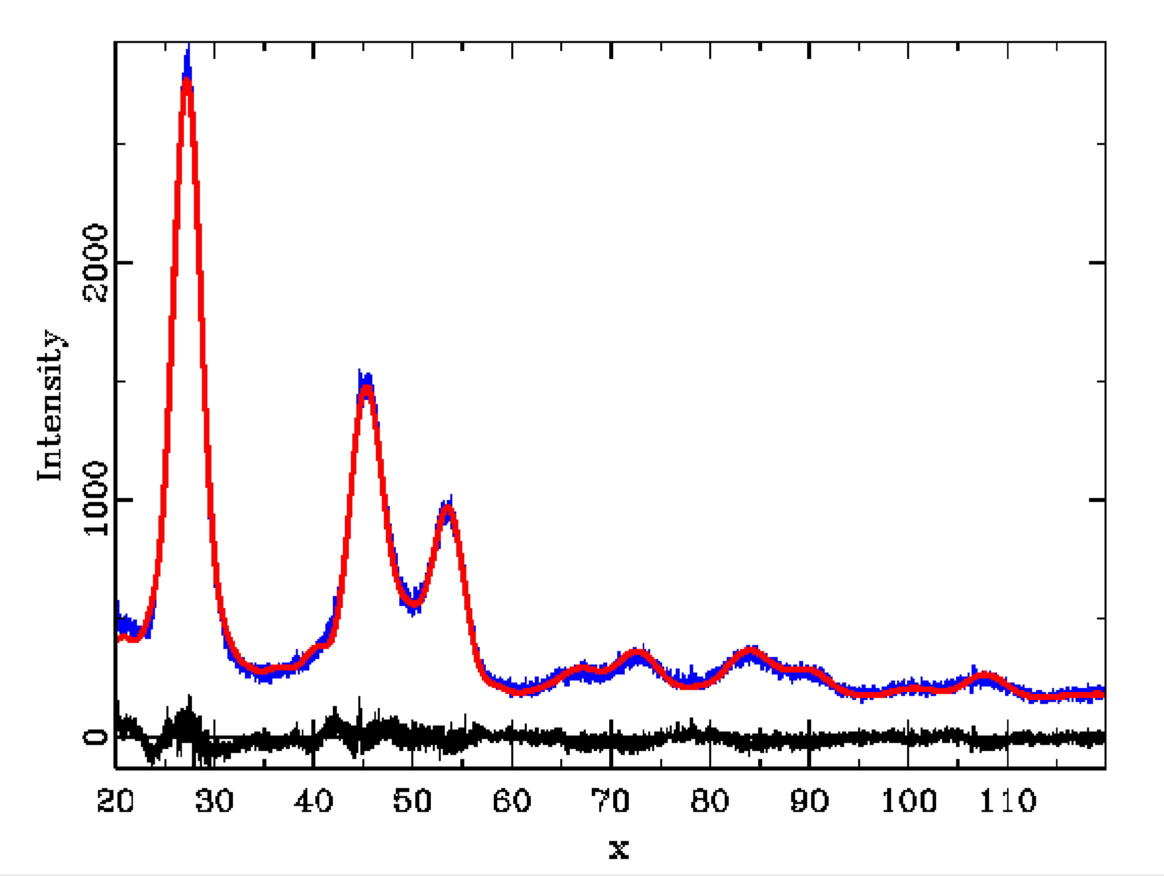
Zn-Se = 2.46 Å

size a-b = 26(2) Å

size c = 32(2) Å

30% stacking fault probability

R_{wp} =5%



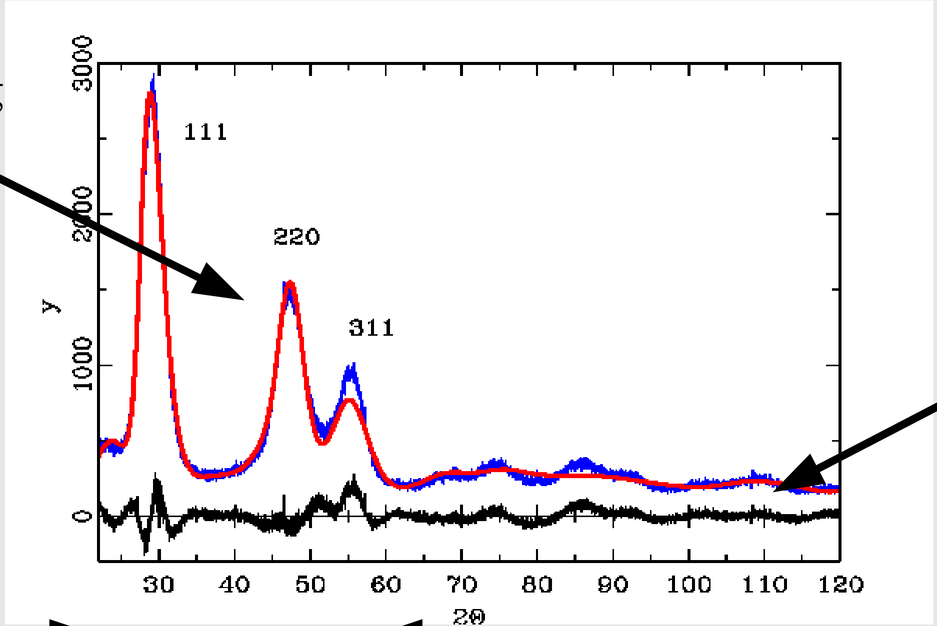
Powder Diffraction

Powder diffraction pattern of a nanoparticle ZnSe

broad overlapping *Bragg* reflections

small particle size

Bragg reflections widened artificially



Rietveld Refinement

large background compared to Bragg reflections at higher 2Θ

defects,
organic ligands
sample environment

Accurate Background estimation very difficult

very limited 2Θ range with significant reflections

small particle size
defects

high uncertainties of structural parameters

limited information content,
high correlation between parameters
defects and size not well treated

PDF

Pair Distribution Function

essentially a Fourier transformation of the full powder diffraction pattern

→ Information about ordered and disordered structure

→ Information in direct space

old technique	B.E. Warren X-ray Diffraction (1969)
does not require Bragg reflections	
old applications	glasses and liquids
modern applications	crystalline materials T. Egami and S.J.L. Billinge Underneath the Bragg Peaks Pergamonn (2003) S.J.L. Billinge and M.F. Thorpe (Eds.) Local Structure from Diffraction Plenum (1998)

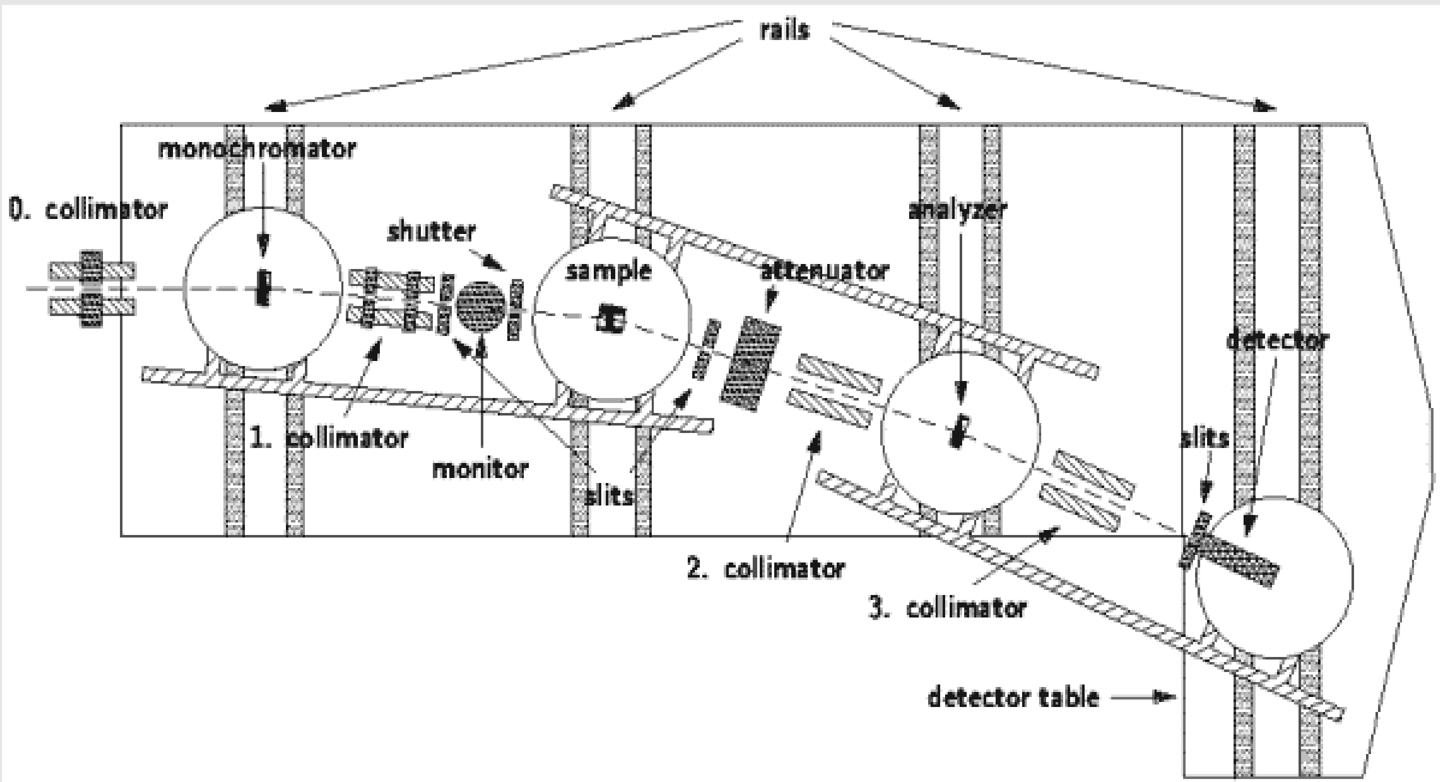
requires modern synchrotron or neutron sources

laboratory: silver or tungsten sources

PDF Data Collection

collect powder pattern to high 2Θ with high energy X-ray radiation

BW5 HASYLAB, DESY, Germany



$\lambda = 0.088$Å
$E = 140$ keV

$2\Theta_{max} = 35°$

$T = 15$ K

$$h_{max} = \left(\frac{٢\sin(\Theta)}{\lambda}\right)_{max} = ٧.٥\ \mathring{A}^{-١}$$

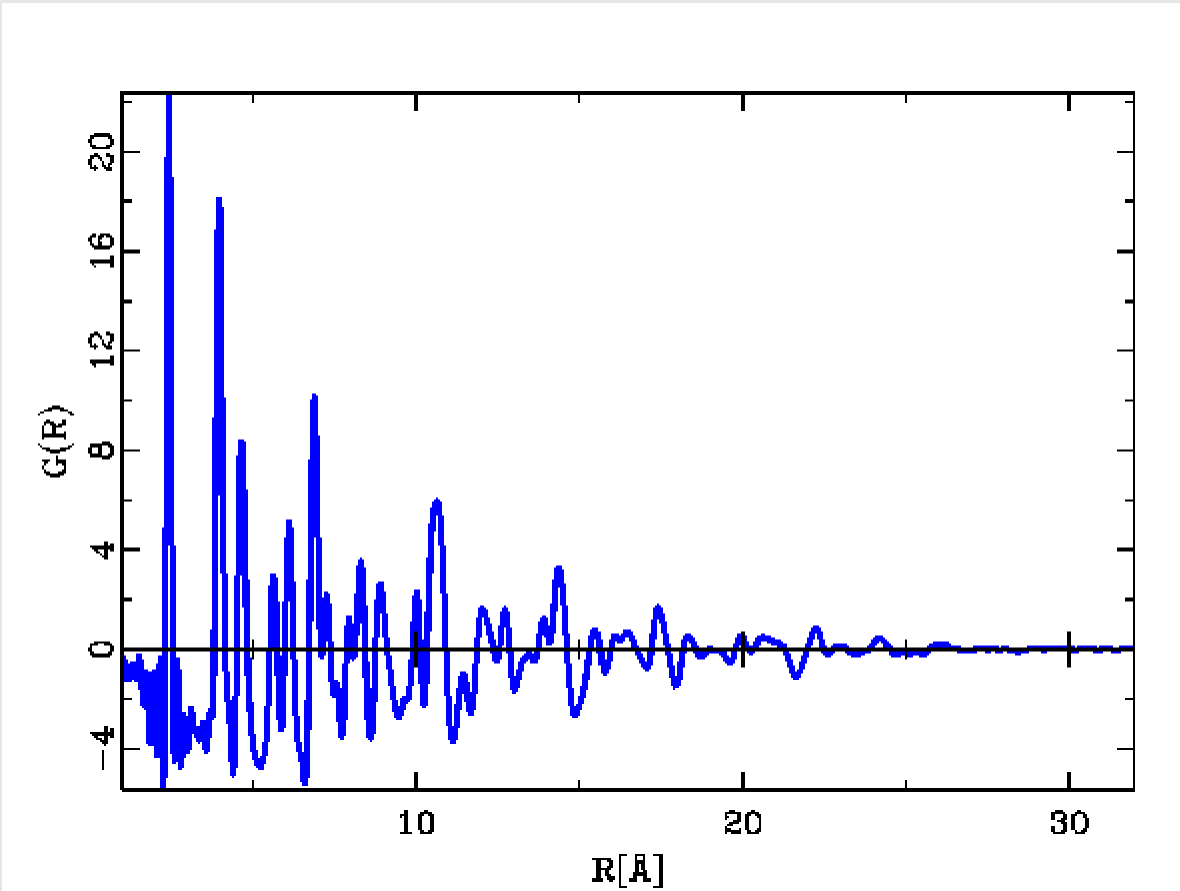
$$Q_{max} = ٢\pi\left(\frac{٢\sin(\Theta)}{\lambda}\right)_{max} = ٤٧\ \mathring{A}^{-١}$$

alternatively
neutron diffraction

www-hasylab.desy.de

http://lansce.lanl.gov/lujan/instruments/NPDF/index.html

ZnSe experimental PDF



Data collection at BW5, HASYLAB, Germany

$\lambda = 0.1036Å$
E = 120 keV

T = 15 K

capillary, 2.5 mm diameter

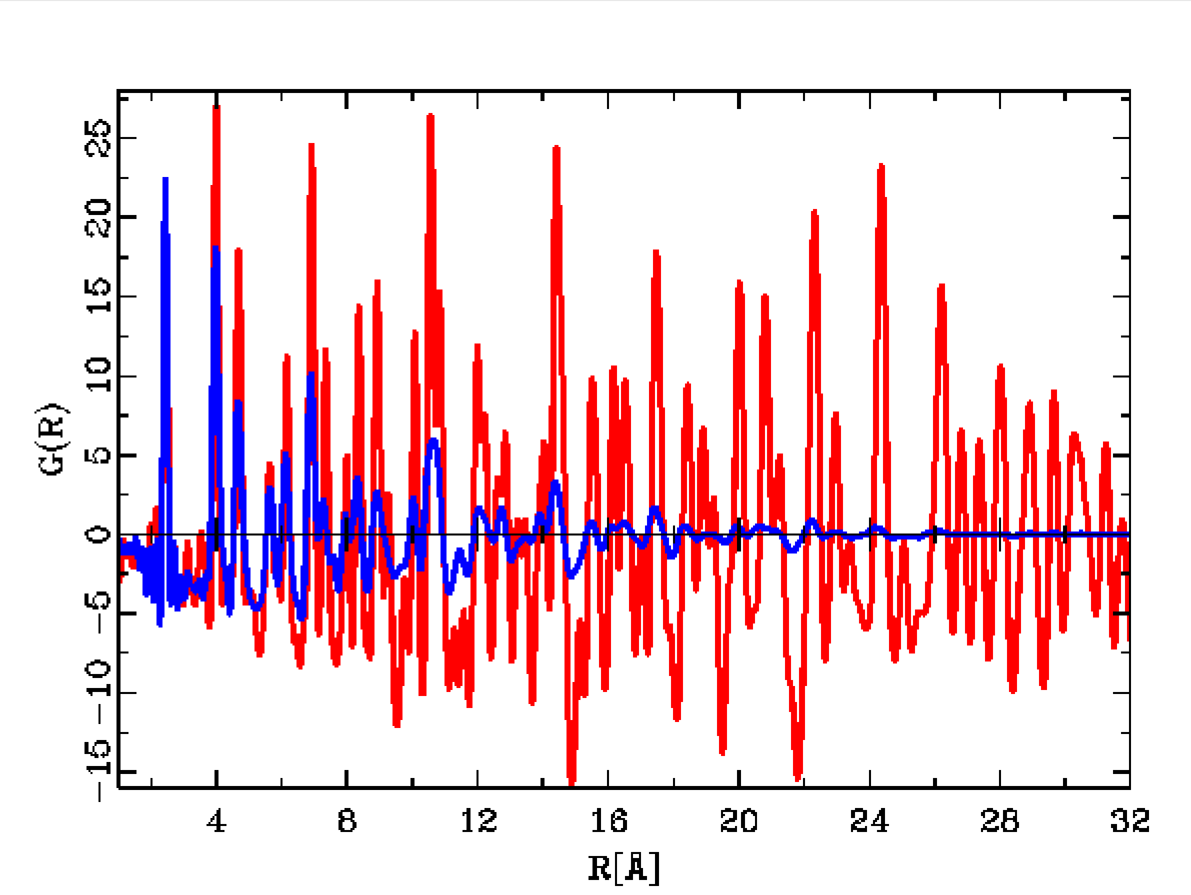
$2\Theta_{max} = 32°$

$$Q_{max} = ٢\pi\left(\frac{٢\sin(\Theta)}{\lambda}\right)_{max} = ٣٠.٨٥\,\mathring{A}^{-١}$$

Data treatment as in Korsounski et al., J. Appl. Cryst. **36**, 1389 (2003)

Neder et al. phys. stat. sol. (c) **4**, 3221 (2007)

ZnSe: Comparison to crystalline ZnSe

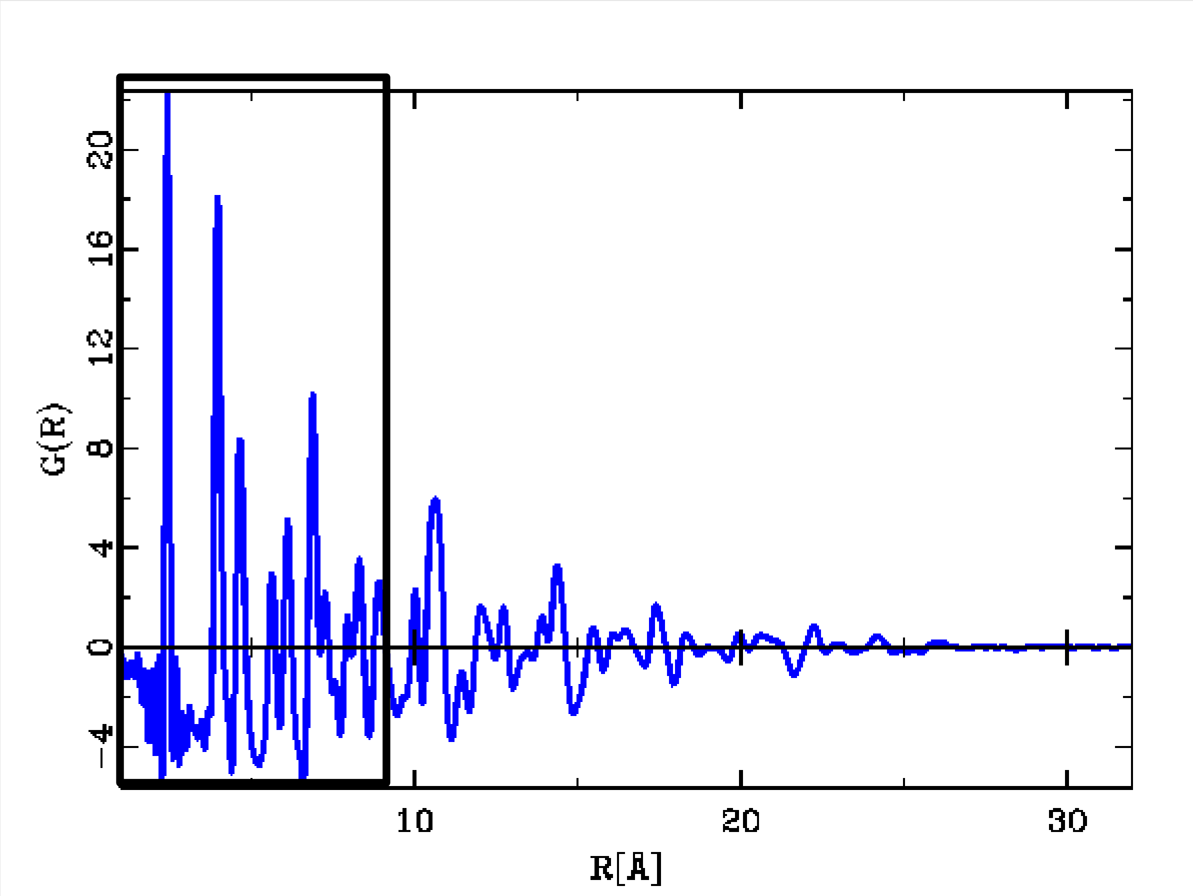


crystalline ZnSe

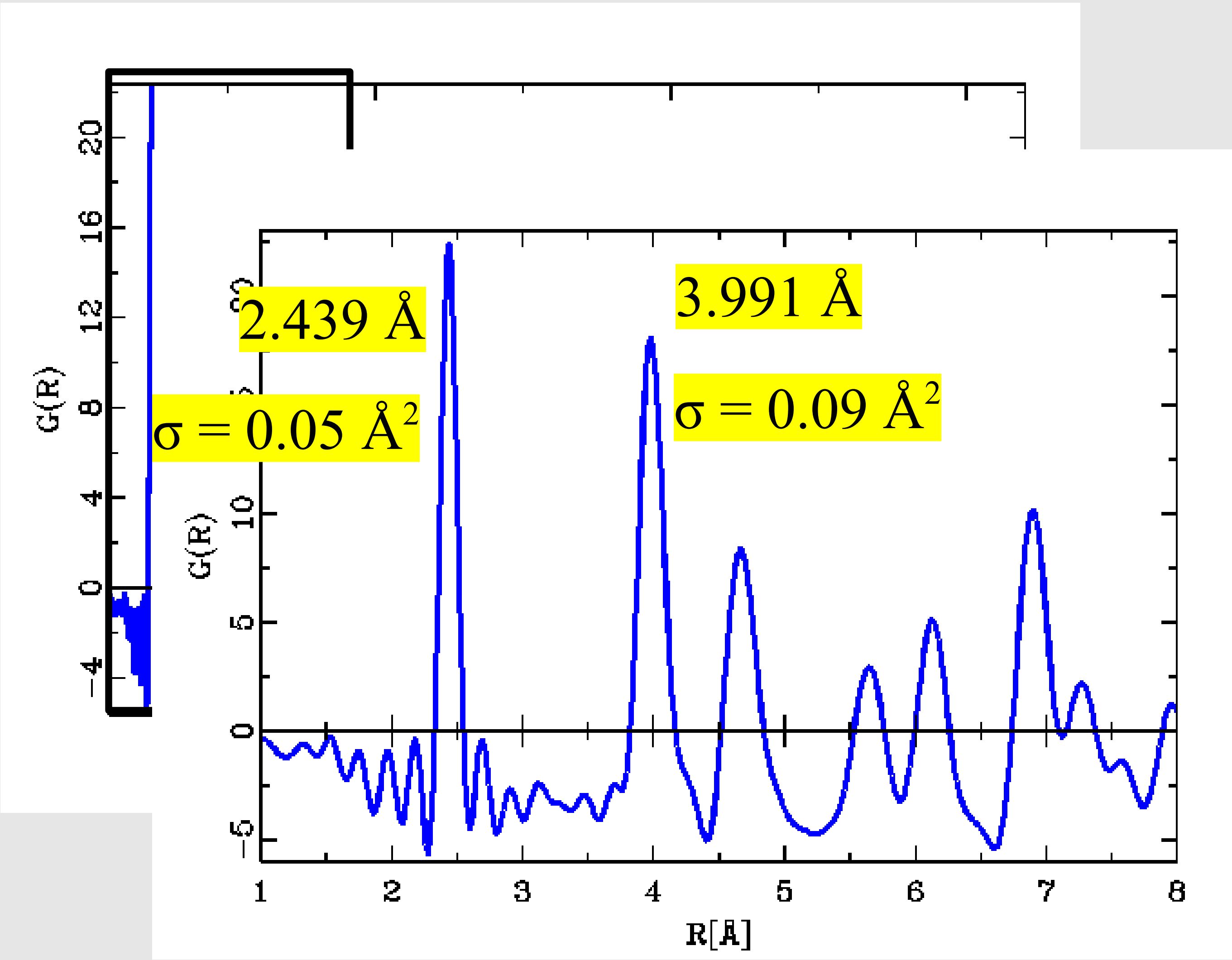
nanocrystalline ZnSe

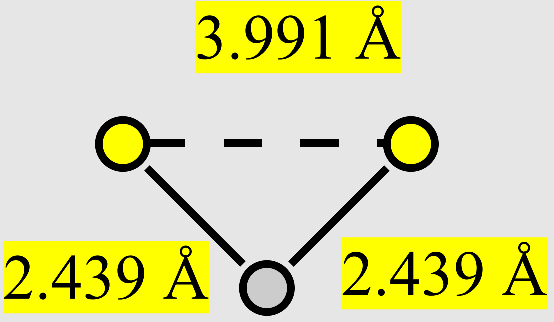
identical experimental conditions for both samples

ZnSe experimental PDF



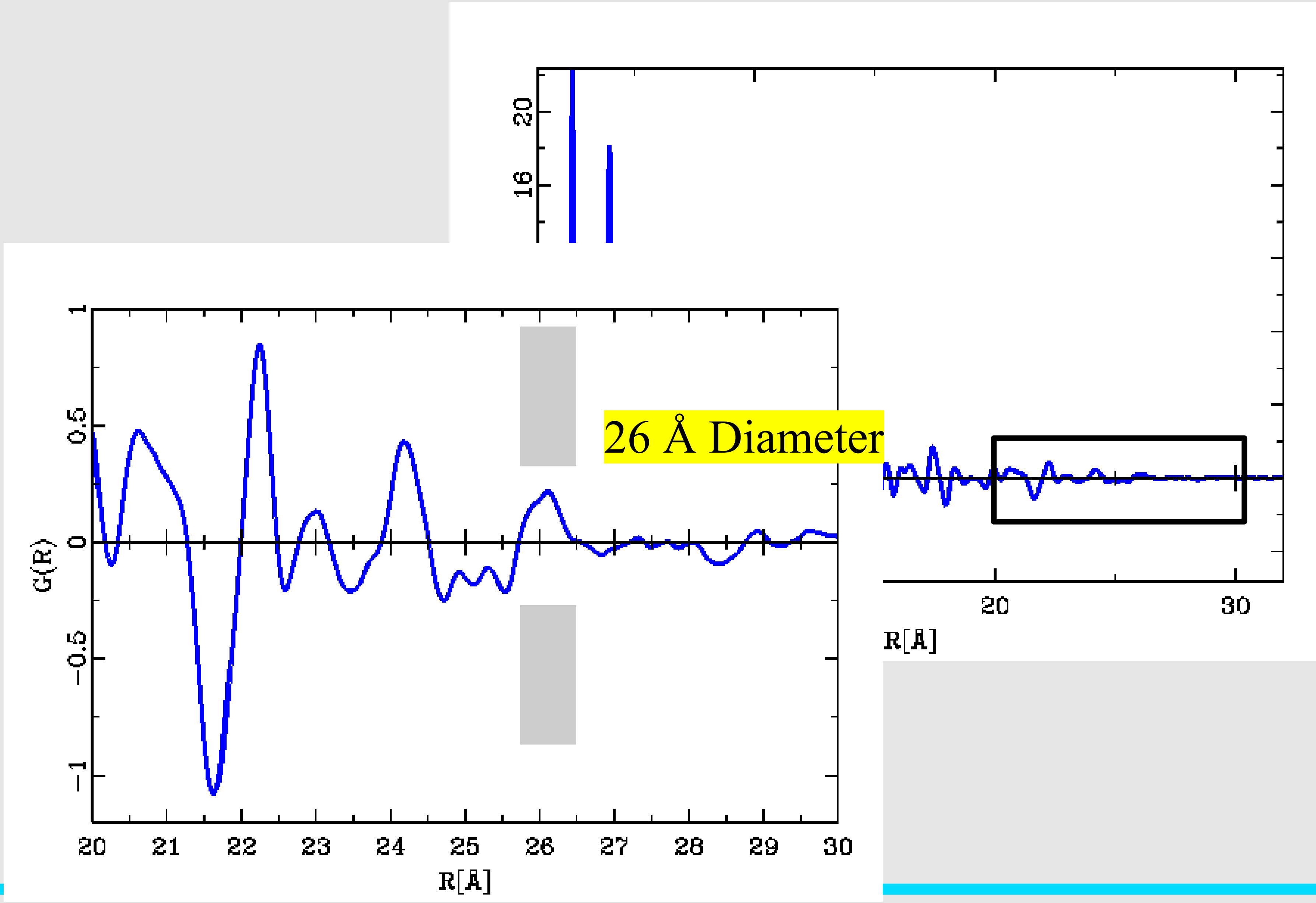
ZnSe experimental PDF





tetrahedral structure bond angle 109.8

ZnSe Nanoparticles



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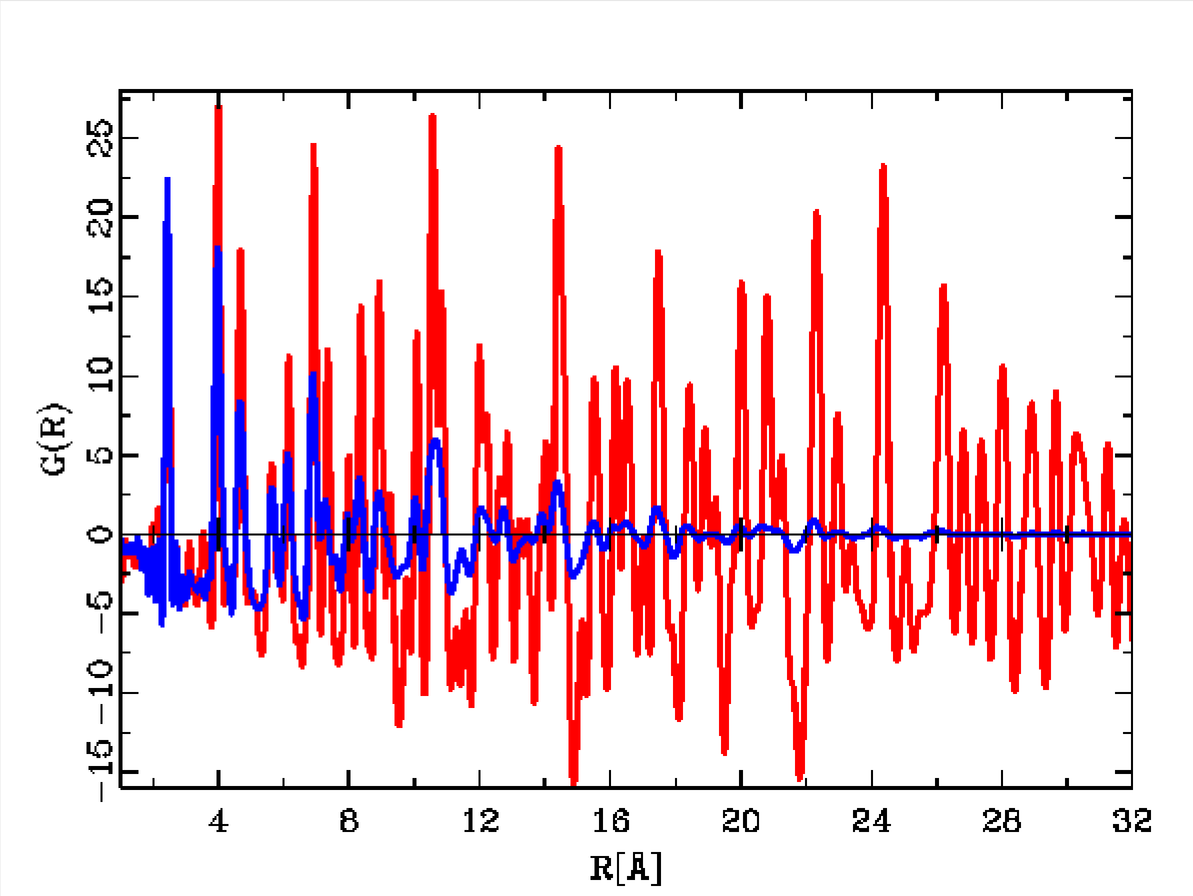
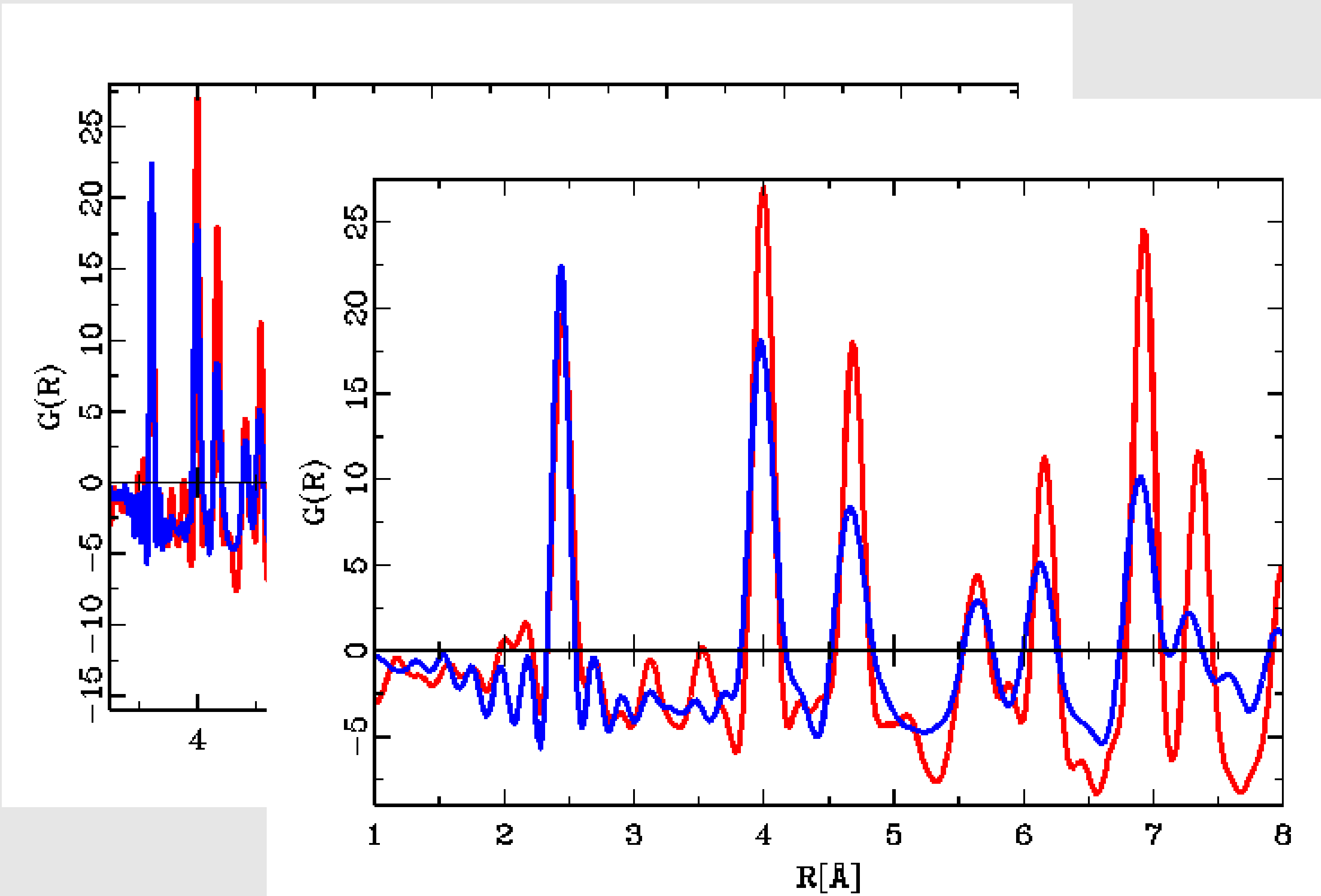


crystalline ZnSe

nanocrystalline ZnSe

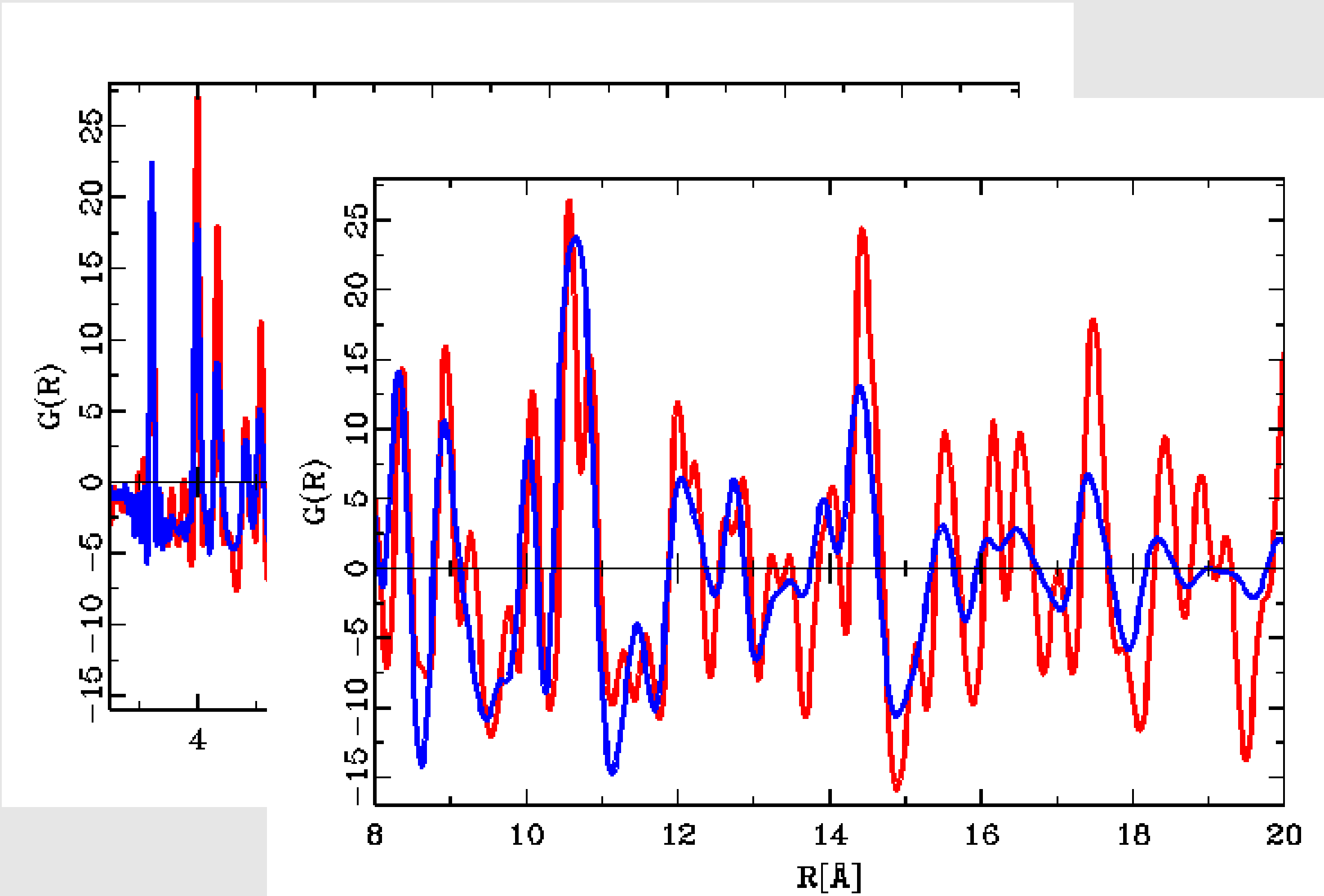
ZnSe: Comparison to crystalline ZnSe



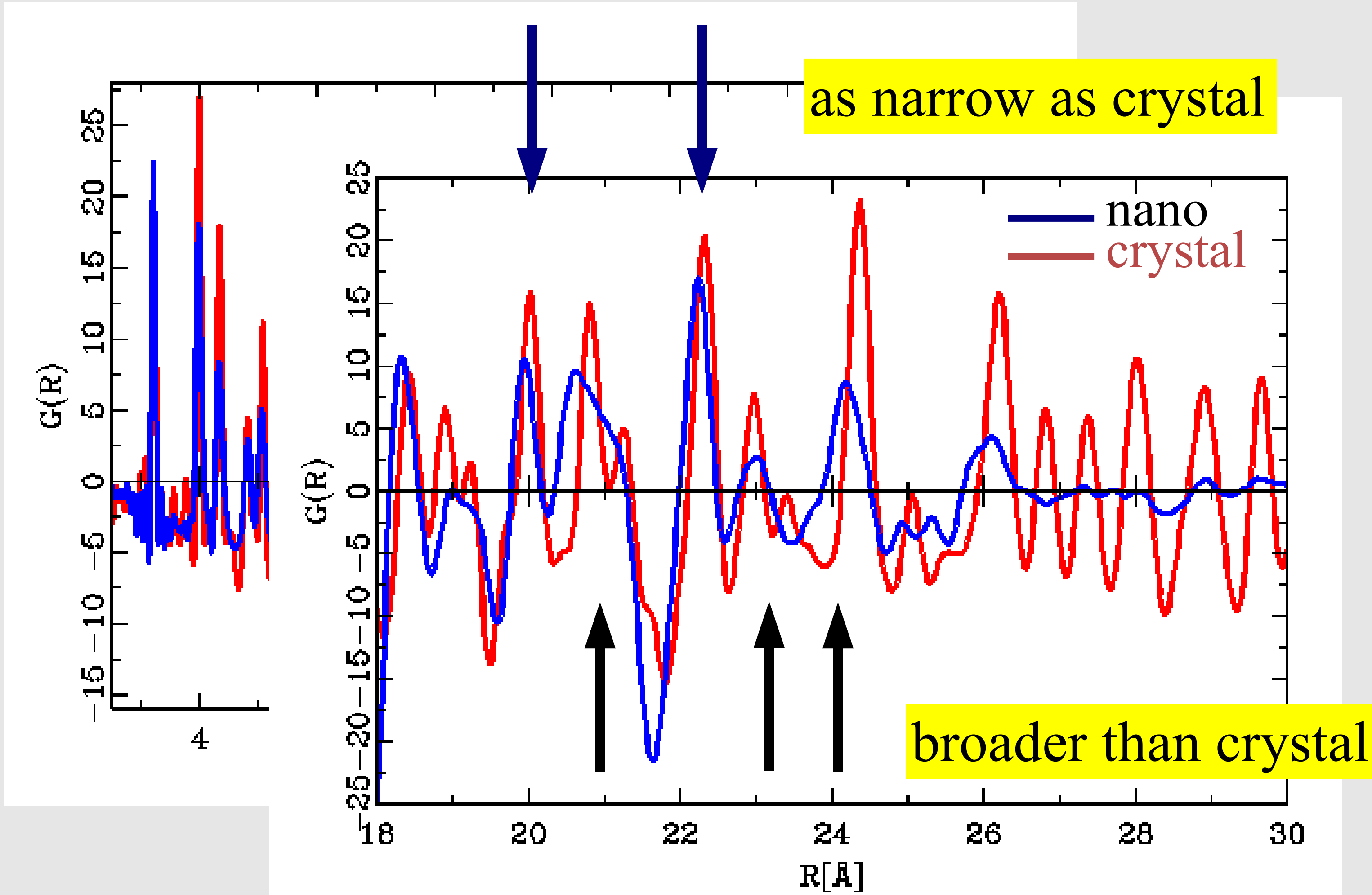
2.439 Å $\sigma = 0.05$ Å^2 3.991 Å $\sigma = 0.09$ Å^2

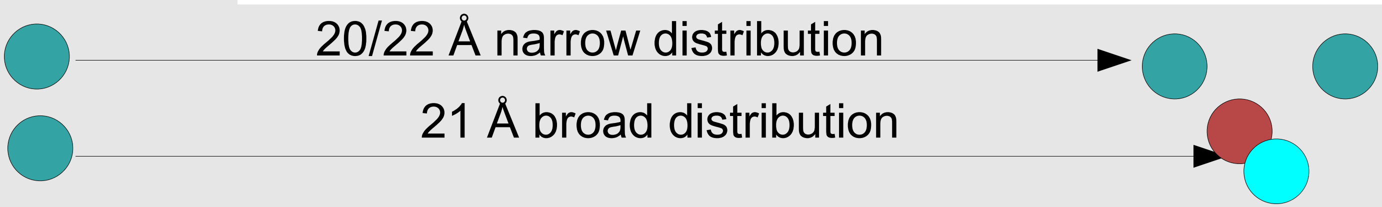
2.450 Å $\sigma = 0.05$ Å^2 3.999 Å $\sigma = 0.06$ Å^2

ZnSe Nanoparticles



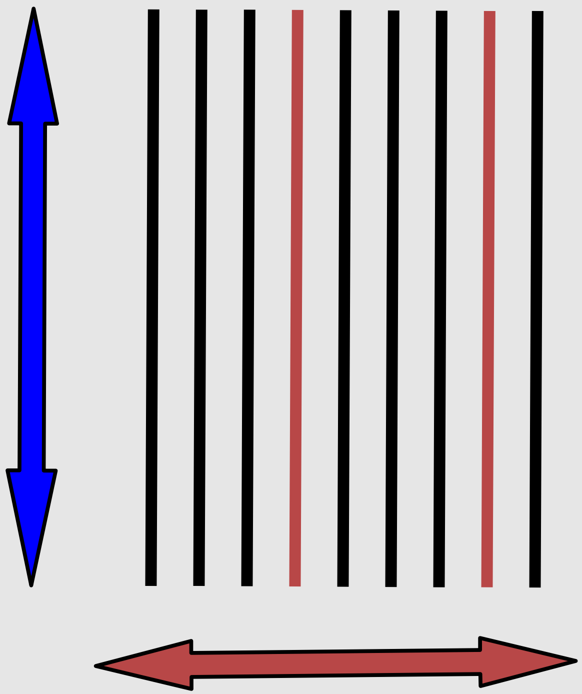
ZnSe Nanoparticles





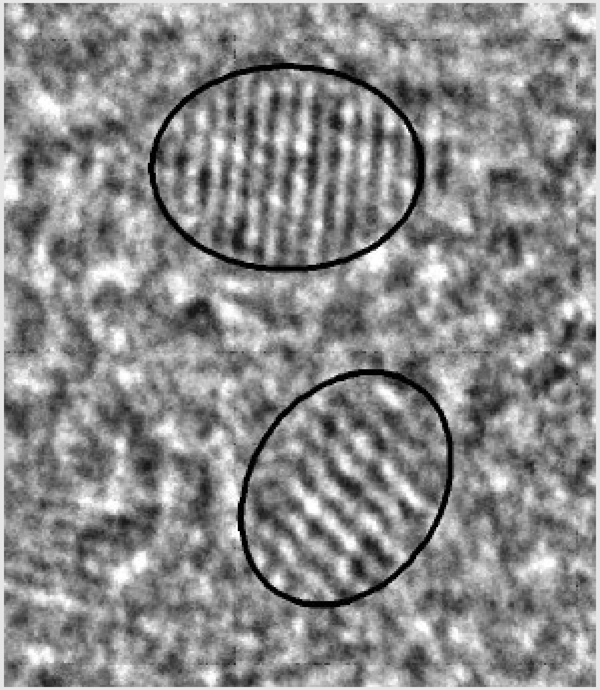
ZnSe Nanoparticles

structural coherence



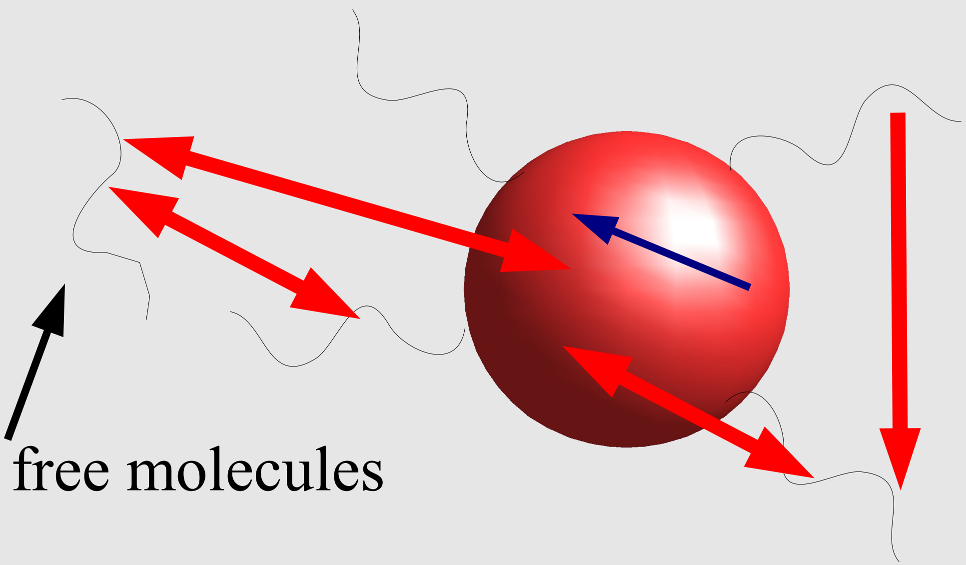
loss of coherence due to stacking faults

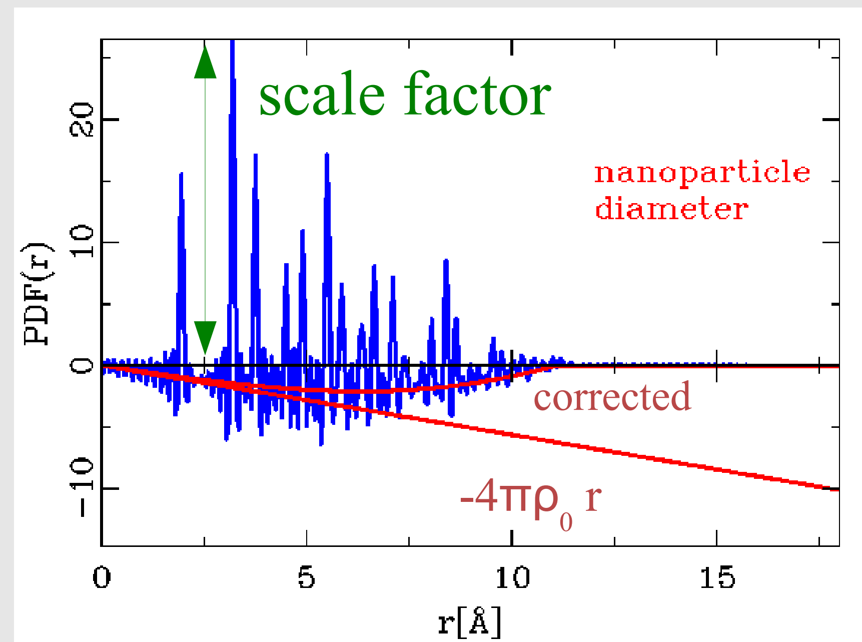
~8 to 10 monolayers
= 4 to 5 unit cells along c
= 24 to 30 Å



Calculation of the PDF for nanoparticles

Nanoparticle with core and stabilizing molecules





Vectors within core defined by model structure

ill defined vectors, not part of the structural model

volume ratio, inaccurate chemical analysis, not part of model

Algorithms for PDF Simulation of Nanoparticles

Simulate a crystal of N*M*O cells

calculated PDF with periodic boundary conditions
multiply PDF by suitable shape function

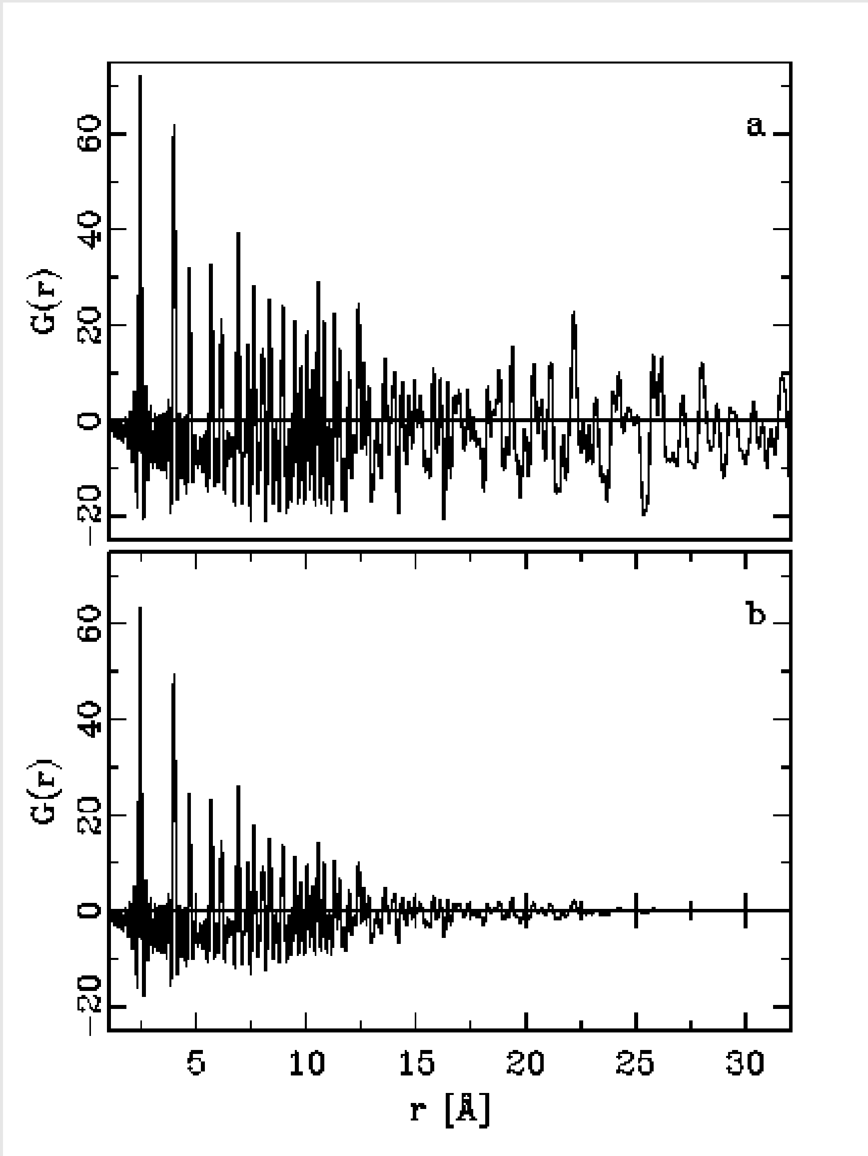
Howell et al., Phys. Rev. B **73**, 094107 (2006)
Kodama et al., Acta. Cryst. A **62**, 444 (2006)

Simulate a finite nanoparticle

calculate PDF from finite model
correct shape of $-4 \pi \rho_0 r$ line

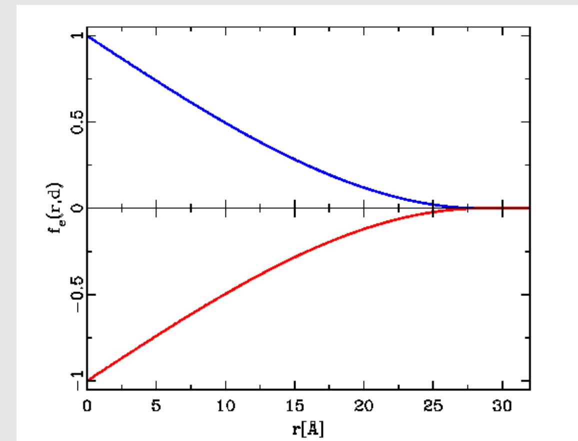
Neder et al. J. Phys.: Condens. Matter **17**, S125 (2005)
Neder et al. phys. stat sol. (c),**4**, 3221 (2007)

PDF Simulation of Nanoparticles; envelope function



PDF of periodic ZnSe

q_{max}, q_{alpha}, etc. taken from fit to crystalline sample



as above, PDF multiplied by envelope function for a sphere

$$PDF_{nano} = PDF_{crystal} * f_e(r,d)$$

$$f_e(r,d) = 1 – 3/2\ r/d + ½\ (r/d)^3$$

defects can be treated

limited to basic shapes

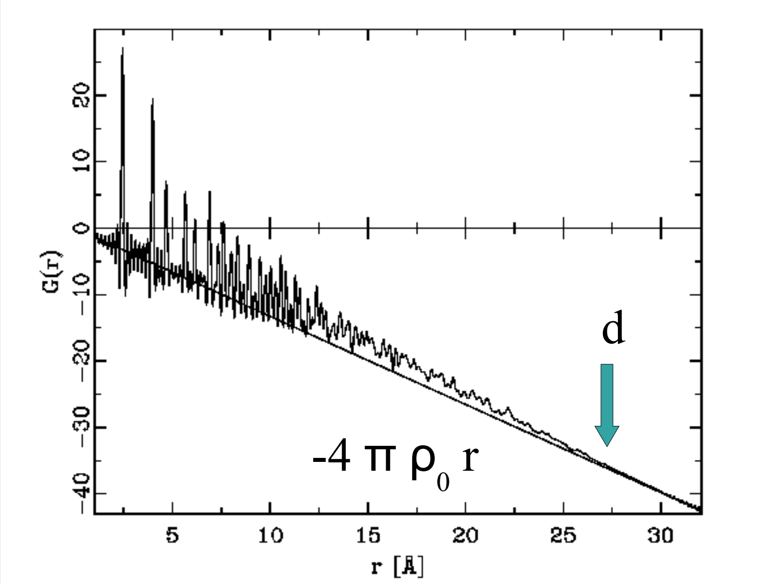
treats two different effects!

- finite particle size
- change of average number density

Howell et al., Phys. Rev. B **73**, 094107 (2006); Kodama et al., Acta. Cryst. A **62**, 444 (2006)

PDF Simulation of Nanoparticles; finite particle

Simulation of a single finite sized ZnSe particle



PDF calculated without
periodic boundary conditions

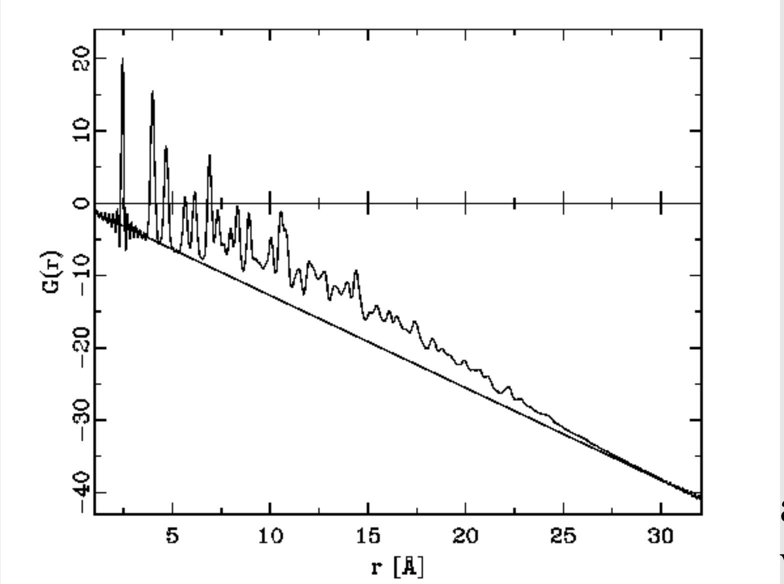
q_{max}, q_{alpha}, etc. taken from fit to
crystalline sample

open to any shape
here elliptical shape!

defects can be treated

defects in a single simulation are **NOT**
a true represenation for whole sample

requires assembly average
assemly average may include:
defect distribution
size/shape distribution



average PDF of 20 individual particles
with stacking fault

Neder et al. phys. stat. sol. (c) **4**, 3221 (2007)

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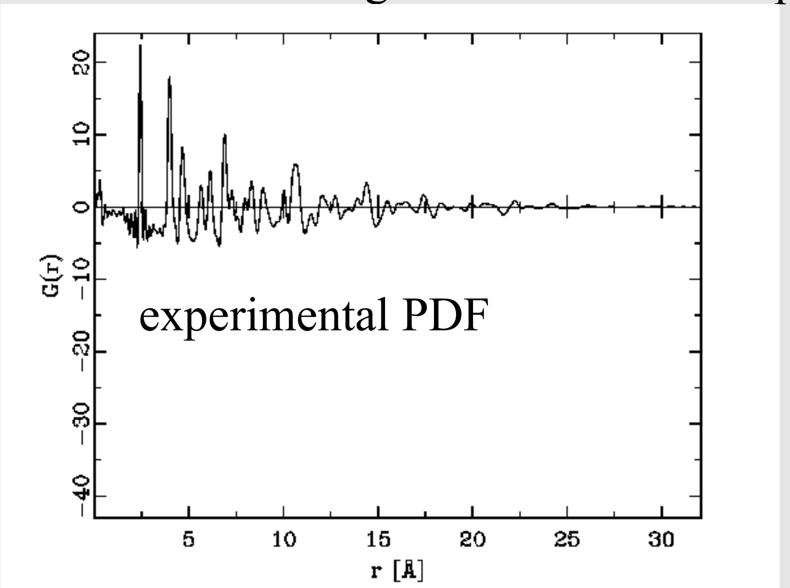

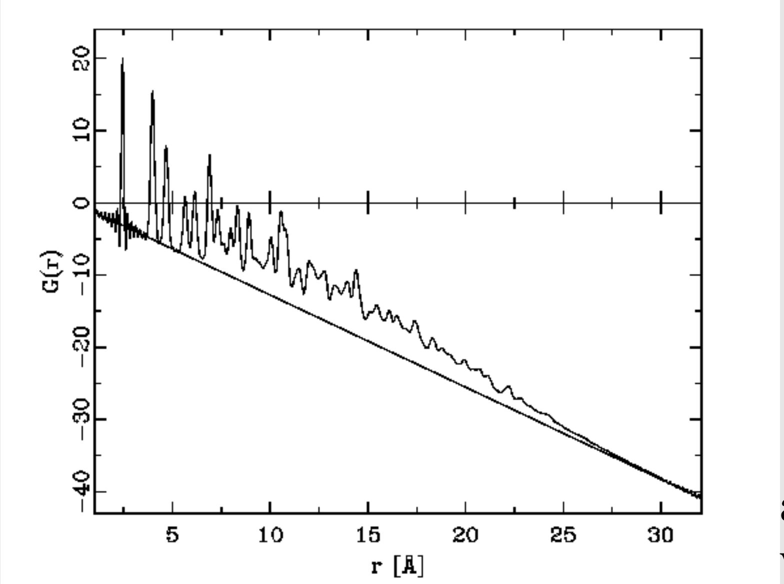

average PDF of 20 individual particles
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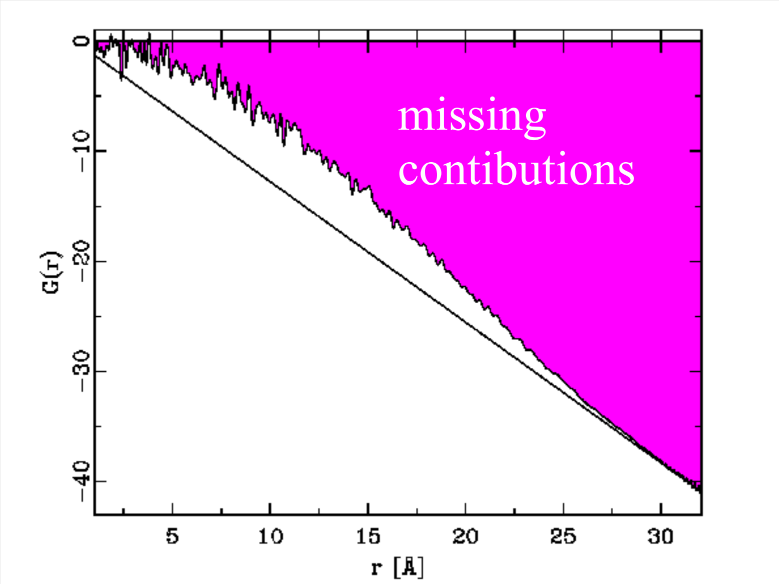
Difference calc - exp:



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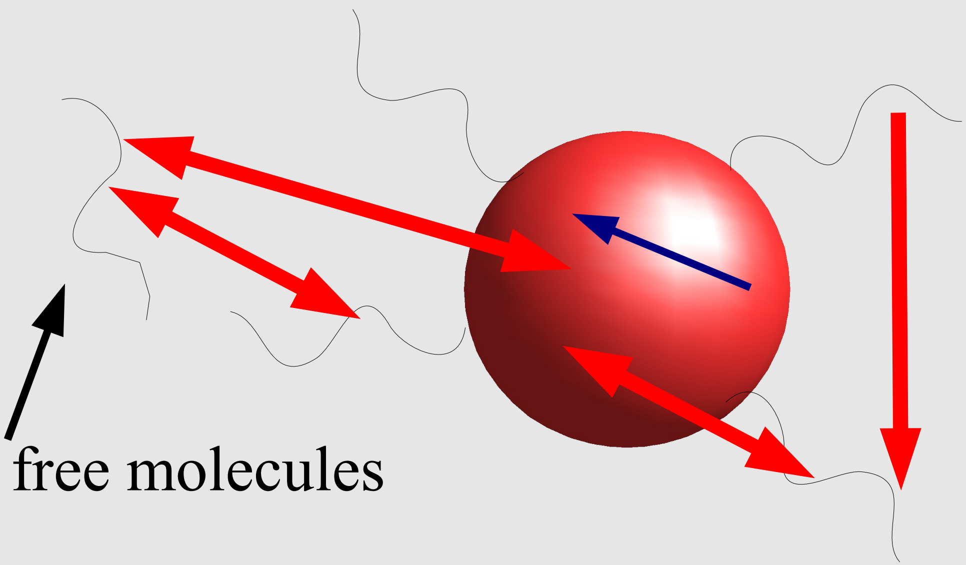
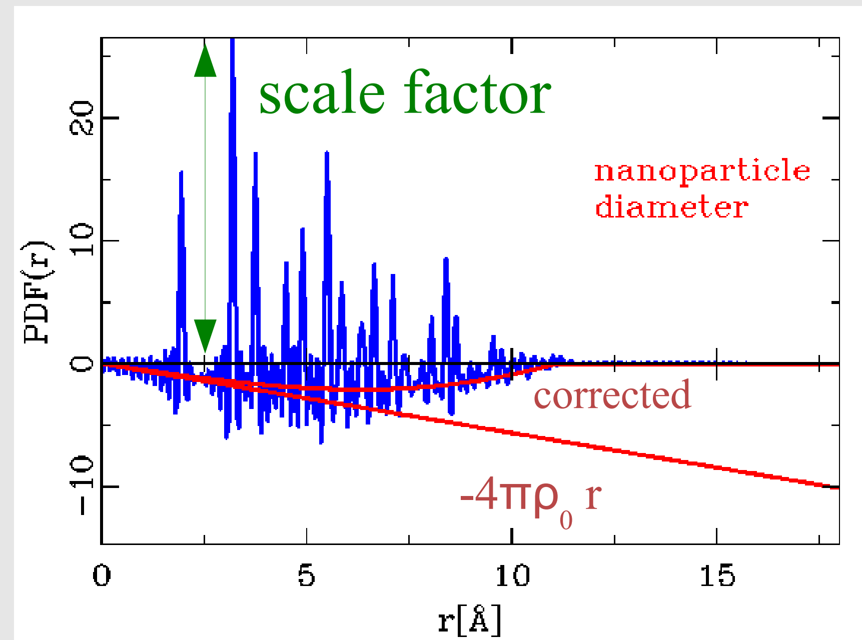
Calculation of the PDF for nanoparticles

Nanoparticle with core and stabilizing molecules





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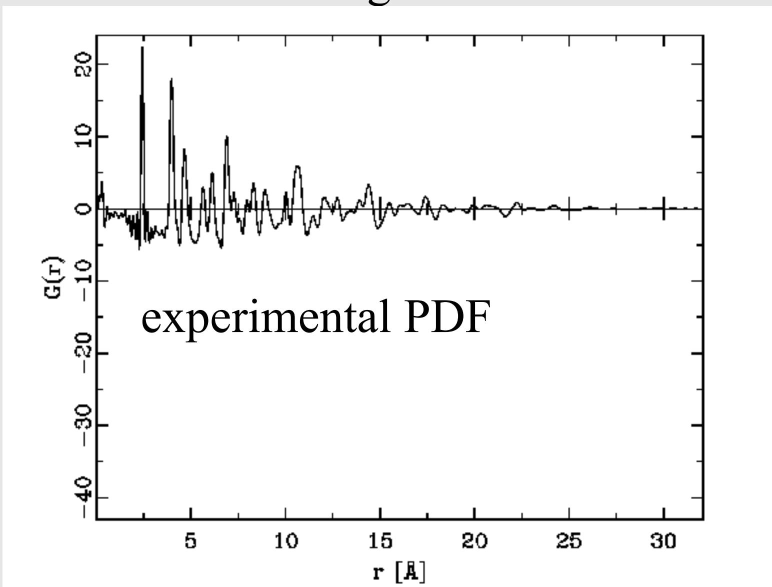
PDF Simulation of Nanoparticles; finite particle

Simulation of a single finite sized ZnSe particle



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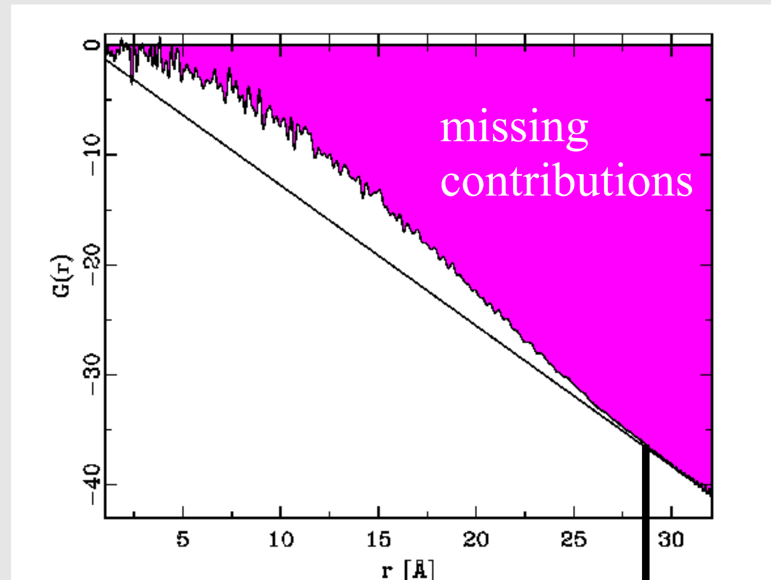
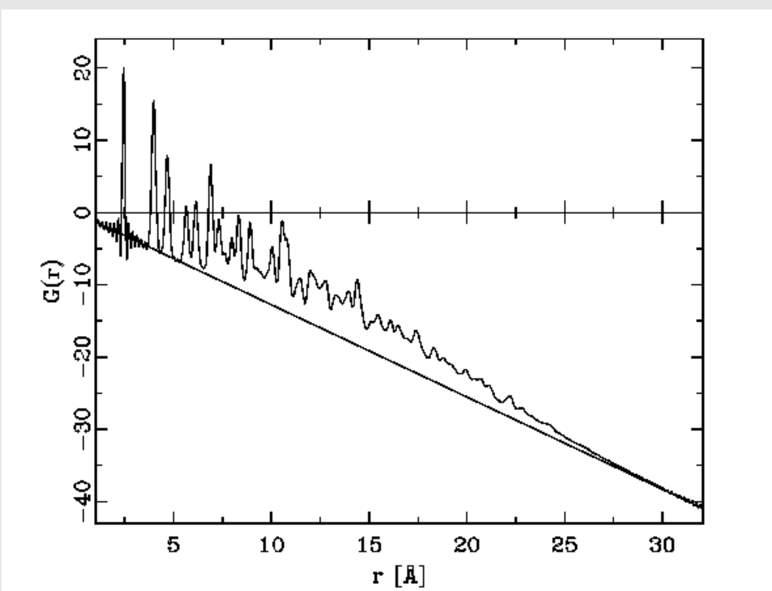




r < d:
vectors within model

r > d:
no vectors in model
G(r) = 0 instead of
$-4 \pi \rho_0 r$

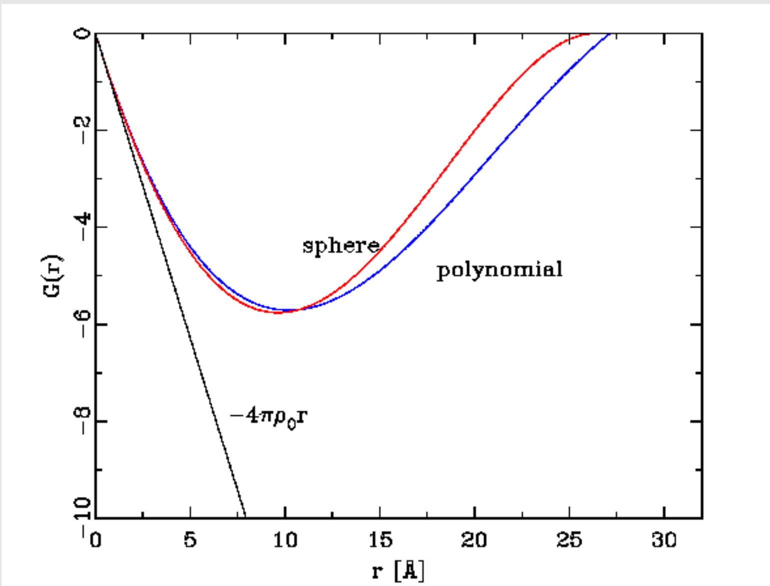
$G(r)_{total}$ is:

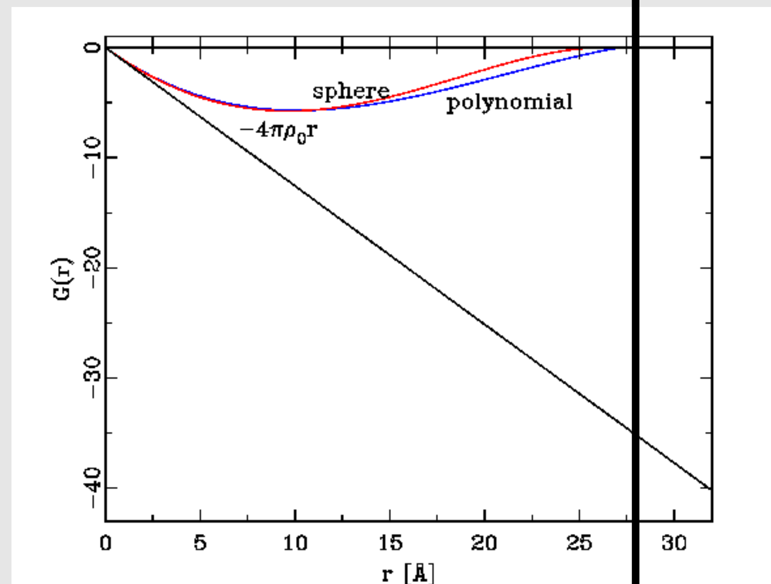
$-4 \pi \rho_0 r + p_0 + p_1 r + p_2 r^2 + p_3 r^3 + G(r)_{model}$

average PDF of 20 individual particles
with stacking fault

PDF Simulation of Nanoparticles; finite particle

Simulation of a single finite sized ZnSe particle





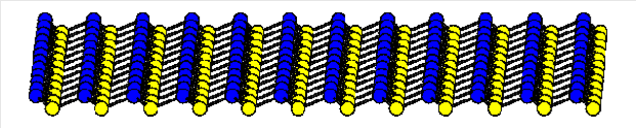
r < d:
vectors in model:
$G(r) = G(r)_{model}$ + *background* contribution

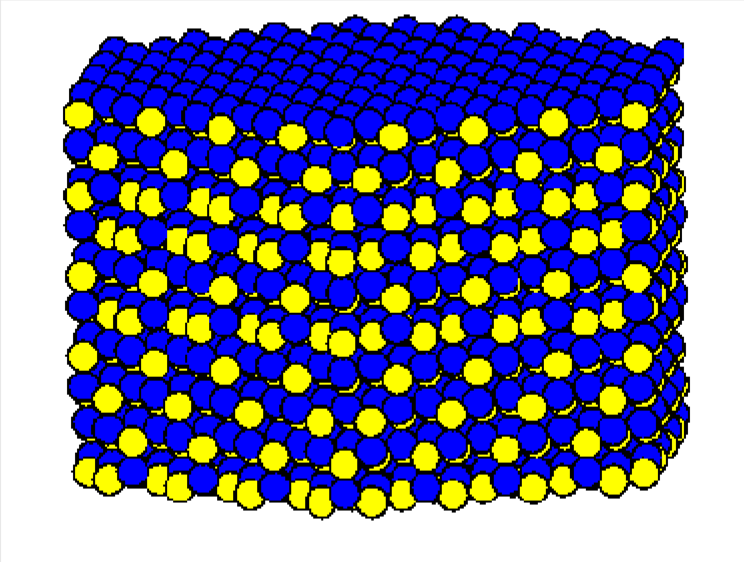
$-4\pi\rho_0 r + p_0 + p_1 r + p_2 r^2 + p_3 r^3$

r > d:
no vectors in model:
G(r) = 0

sphere:
$-4\pi\rho_0 r * f_e(r,d) = -4\pi\rho_0 r * [1 - 3/2\, r/d + ½ (r/d)^3]$

creating ZnSe Nanoparticles





{110} and {001}

create a large single Wurtzite layer A/B

Stack along c (with faults)

Cut to proper size

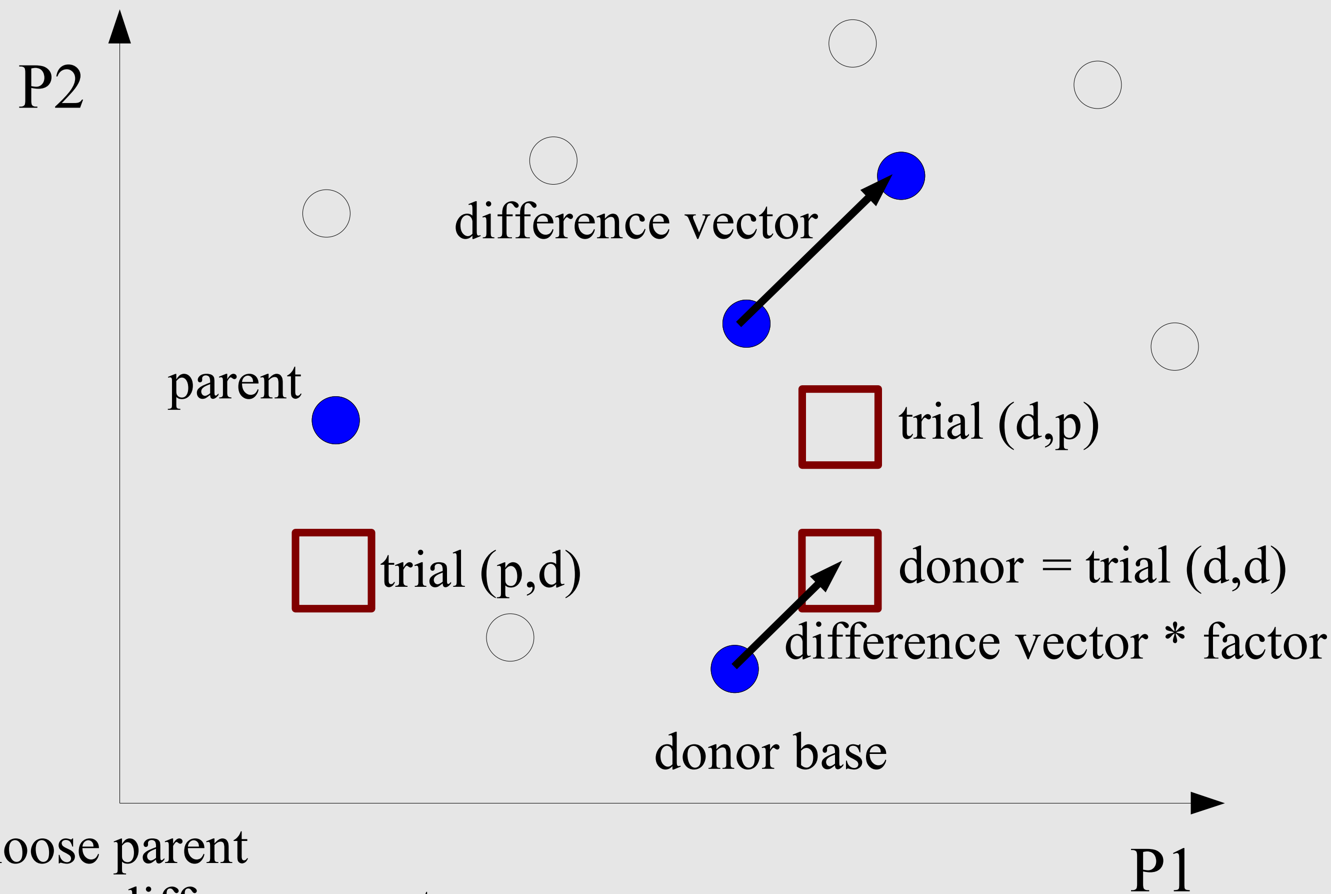
Calculate PDF / powder pattern

Repeat and average

Repeat with new set of parameter

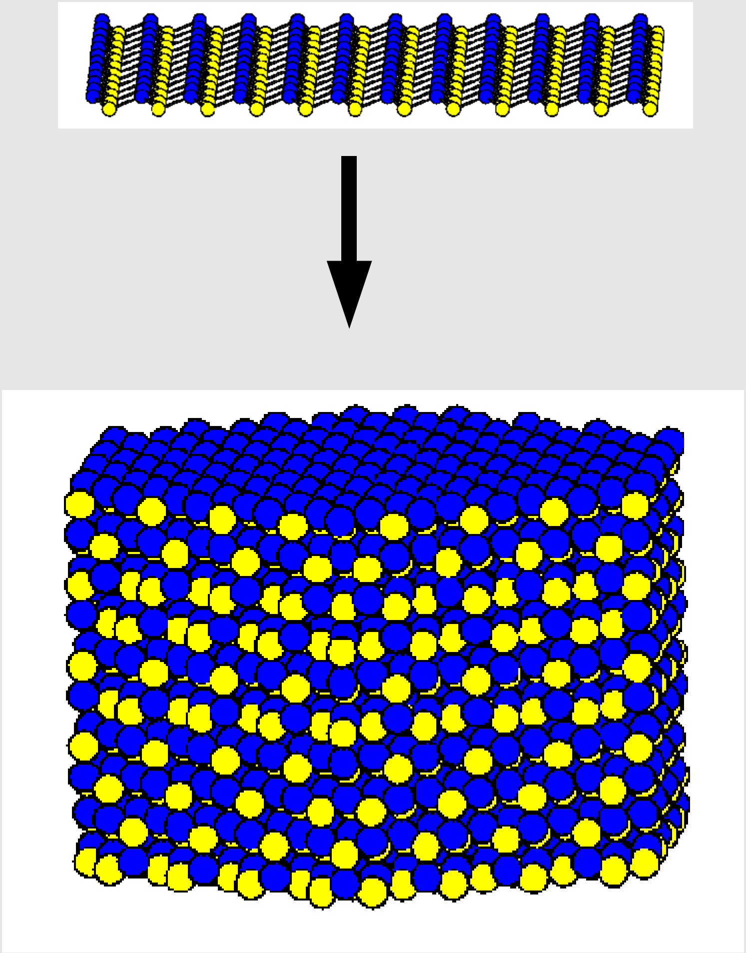
using a Differential Evolutionary Scheme

Differential Evolution



choose parent
choose difference vector
add to donor base to get donor
cross-over between parent and donor
compute cost function, keep better of parent/trial

creating ZnO Nanoparticles



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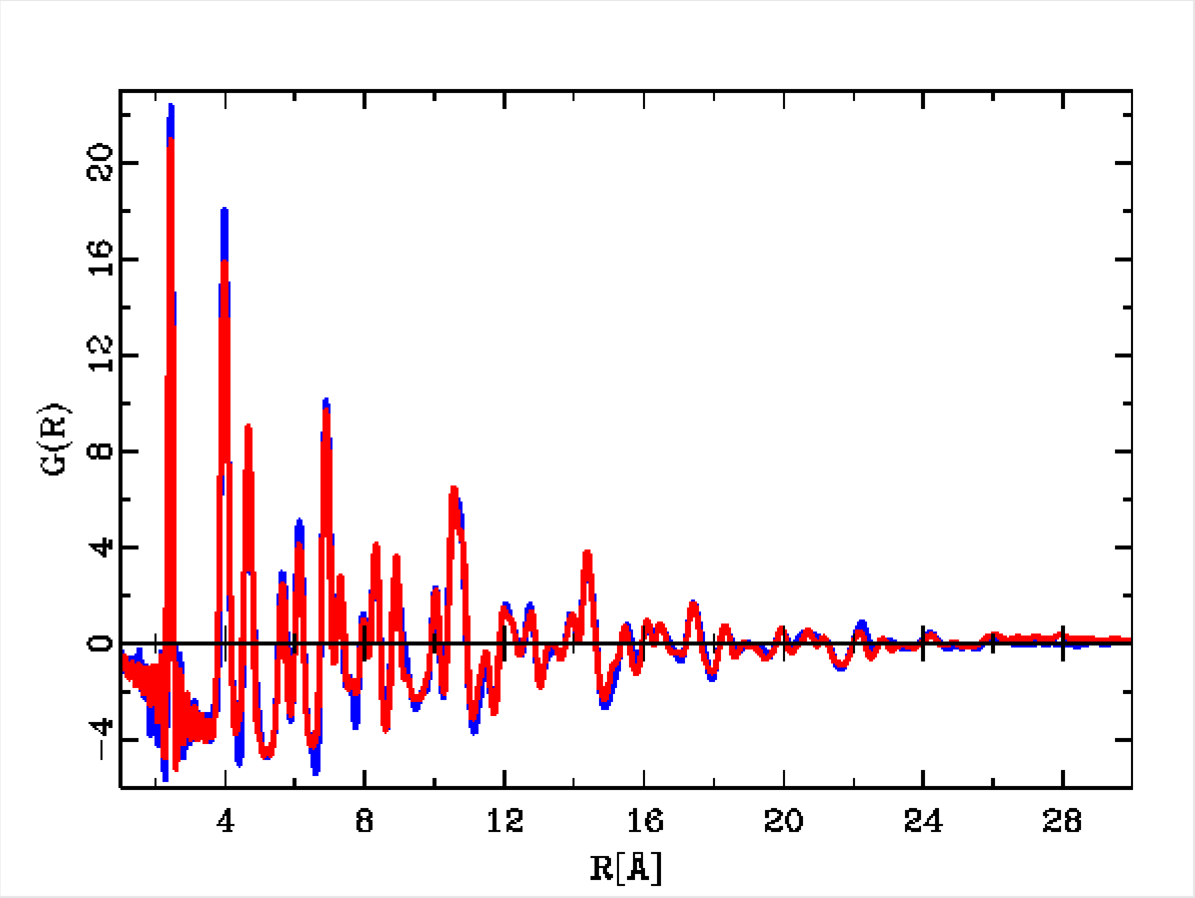
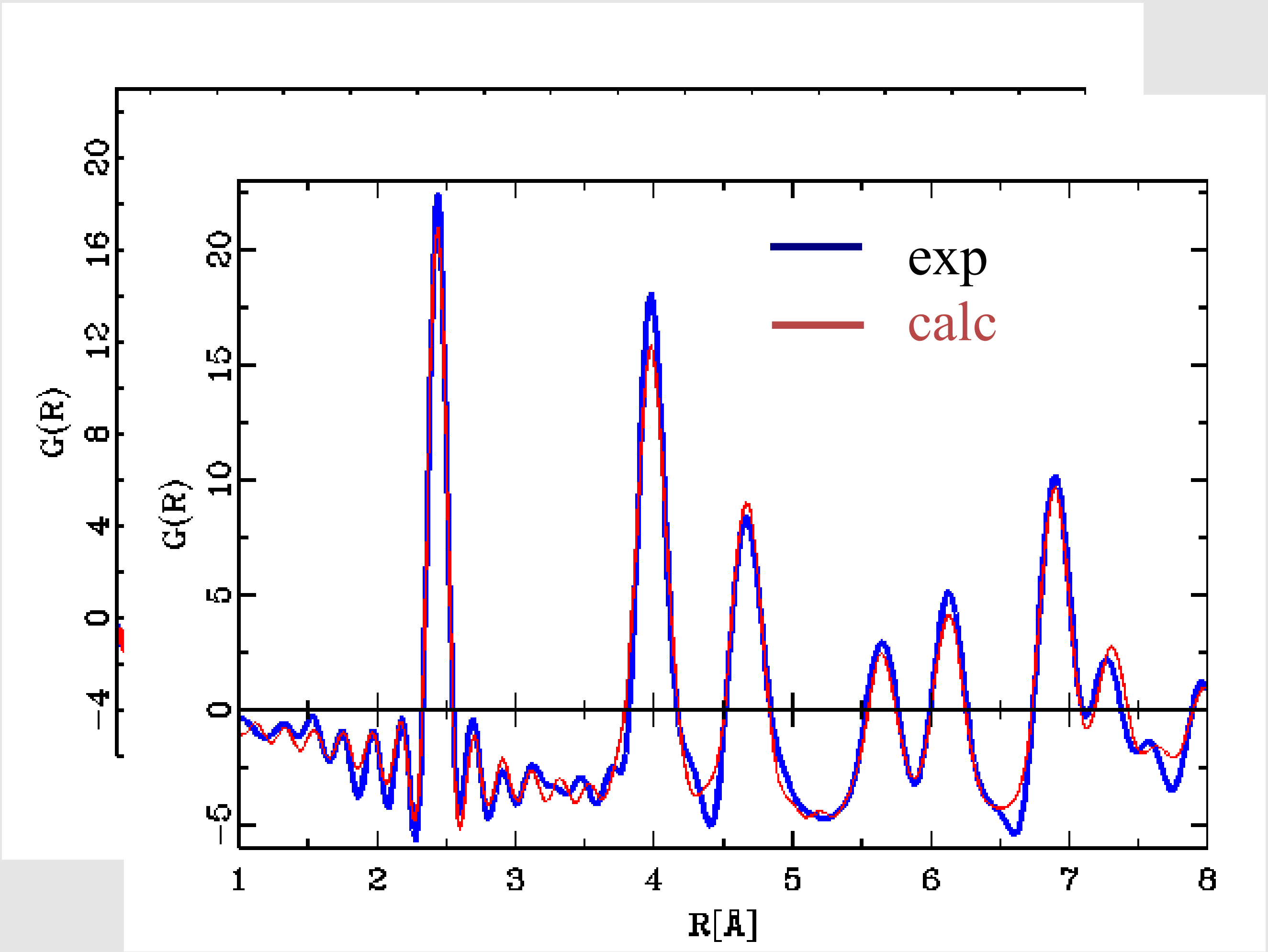
ZnSe Nanoparticles



ZnSe Nanoparticles



a 3.987 Å
c 6.493 Å

ideal tetrahedron
Zn-Se = 2.45(1) Å

size a-b= 24(2) Å
size c = 31(2) Å

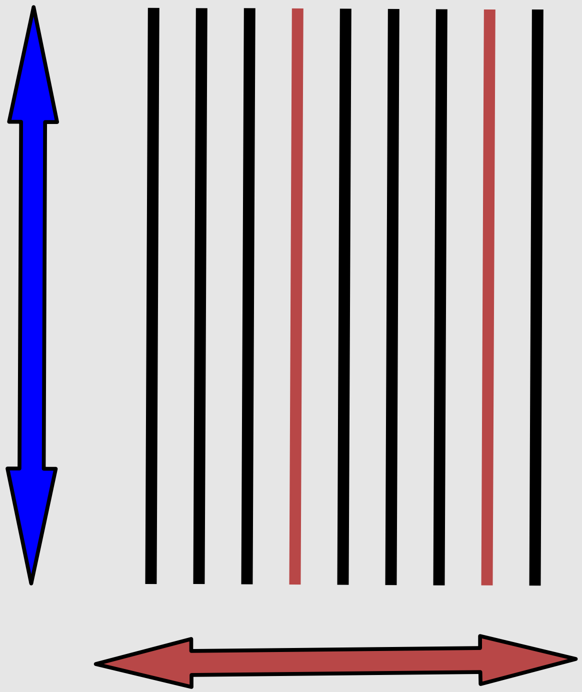
ratio d_c/d_{ab} = 1.2
elliptical shape

Stacking fault:
0.7

No distinction: prismatic vs spherical crystal

ZnSe Nanoparticles

structural coherence



loss of coherence due
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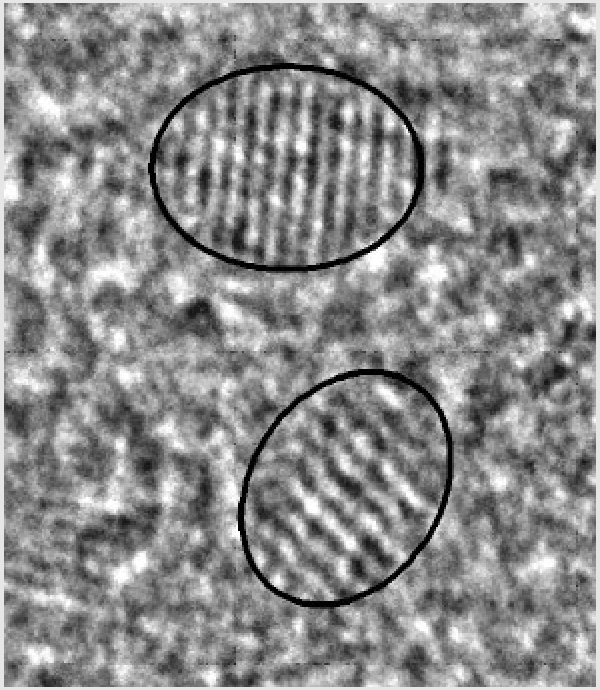
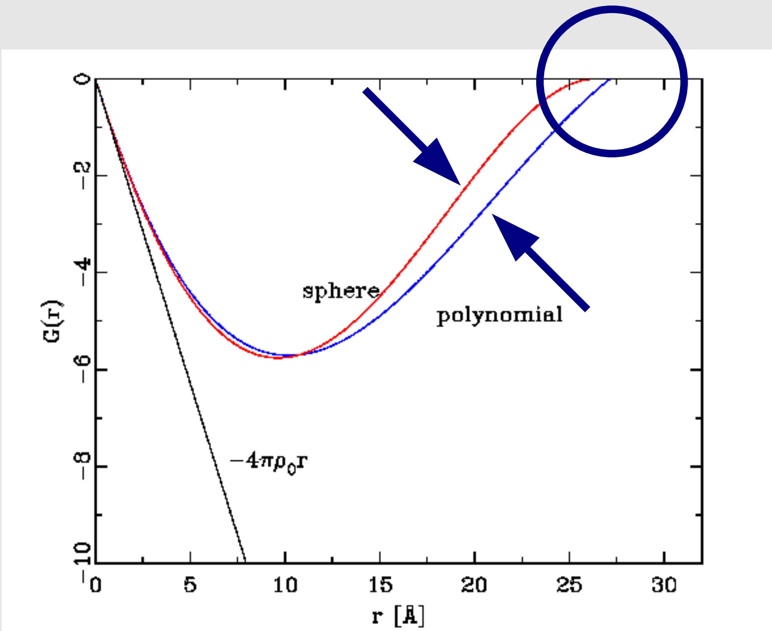
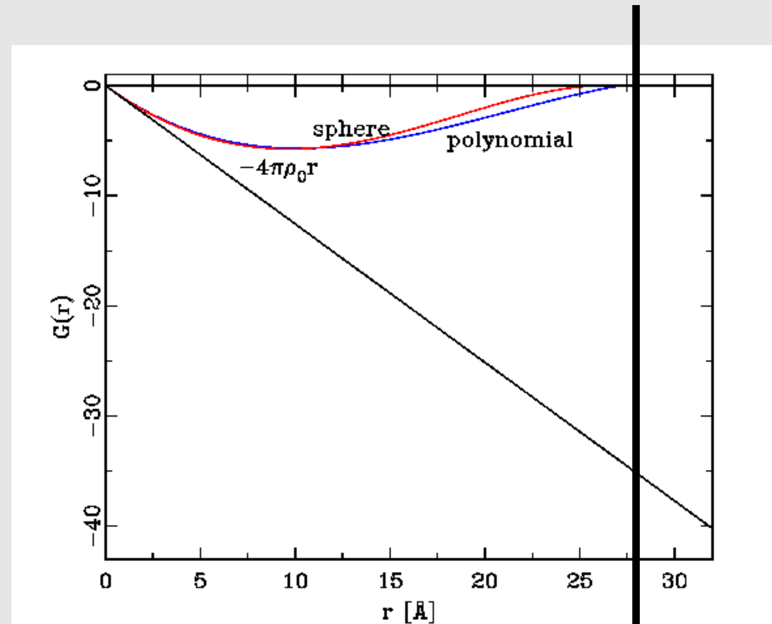
~8 to 10 monolayers
= 4 to 5 unit cells along c
= 24 to 30 Å



PDF Simulation of Nanoparticles; finite particle

Simulation of a single finite sized ZnSe particle





r < d:
vectors in model:
G(r) = G(r)$_{model}$ + *background* contribution

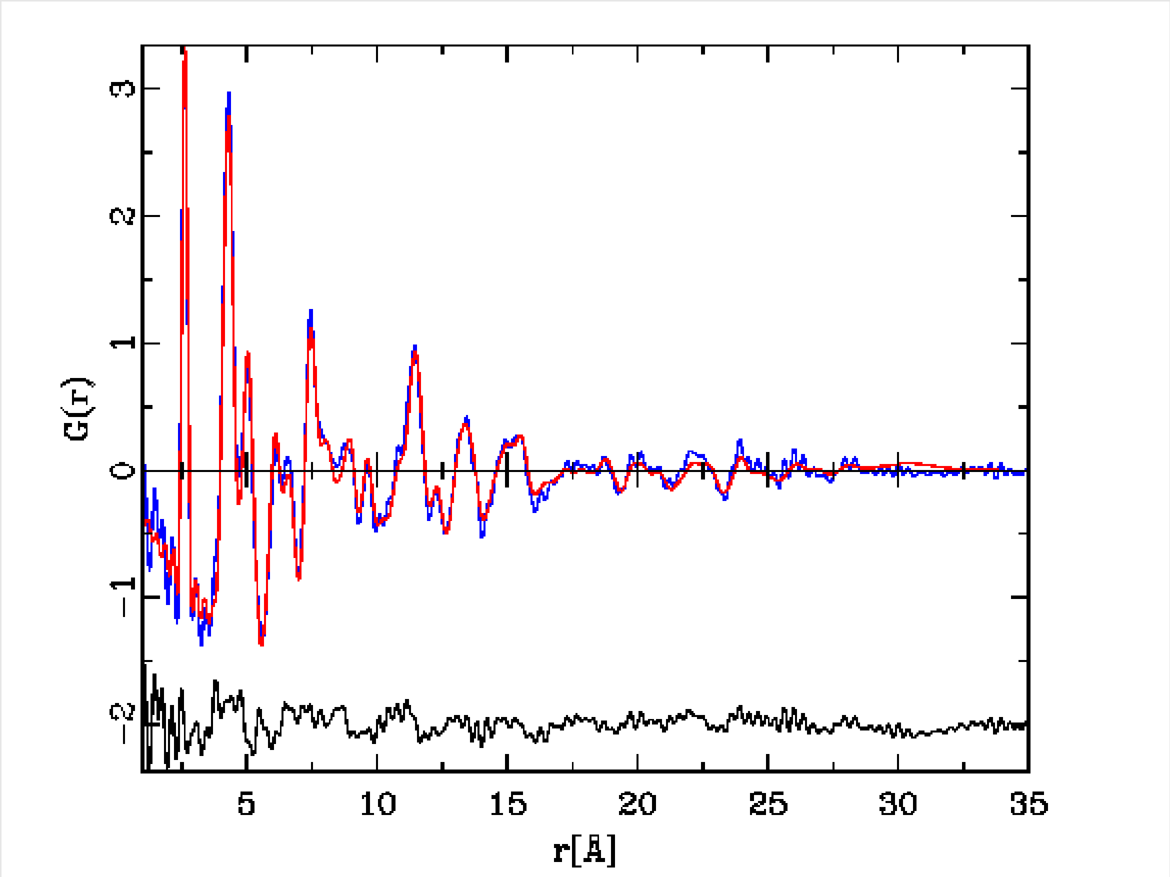
$-4\pi\rho_0 r + p_0 + p_1 r + p_2 r^2 + p_3 r^3$

r > d:
no vectors in model:
G(r) = 0

sphere:
$-4\pi\rho_0 r * f_e(r,\mathbf{d}) = -4\pi\rho_0 r * [\,1 - 3/2\, r/\mathbf{d} + ½\,(r/\mathbf{d})^3]$

d = 1/3 (2*24 + 31) Å

CdSe Nanoparticles (Billinge)



a 4.303 Å
c 6.997 Å

non ideal tetrahedron
z(Zn) = 0.382 Å
B iso = 2.3!
size a-b= 35(2) Å
size c = 32(2) Å

ratio d_c/d_{ab} = 0.9
almost spherical shape

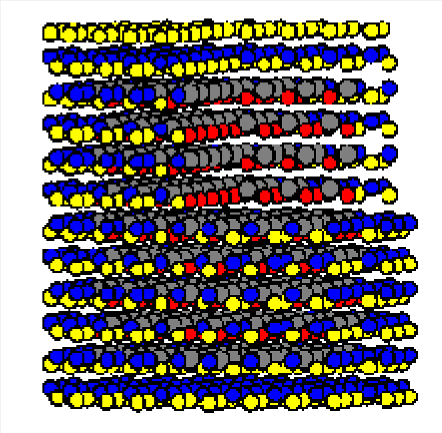
Stacking fault:
0.28

density = 0.024
first peak width = 0.56

scale = 0.85

δ = 0.00028
γ = 0.08
Q_{max} = 19 $Å^{-1}$

CdSe/ZnS Core/Shell particles

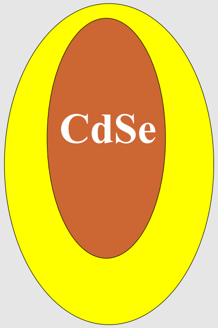


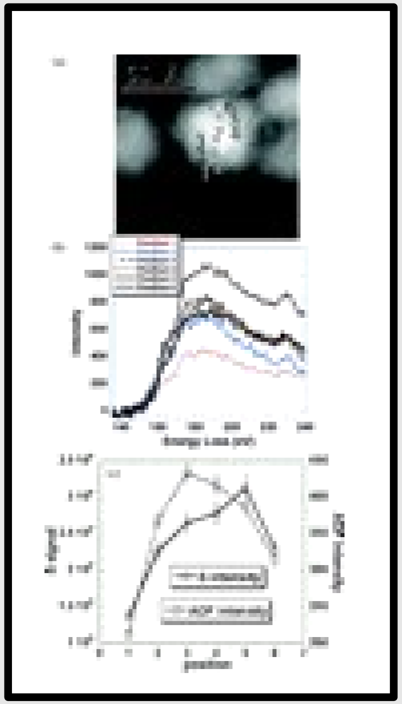
Core: CdSe ~3.2 nm Ø
Shell: ZnS ~1 layer
Stabilizer: TOPO

Band gap ZnS > CdSe
efficient luminosity
quantum confinement

Structure of Core / Shell ?

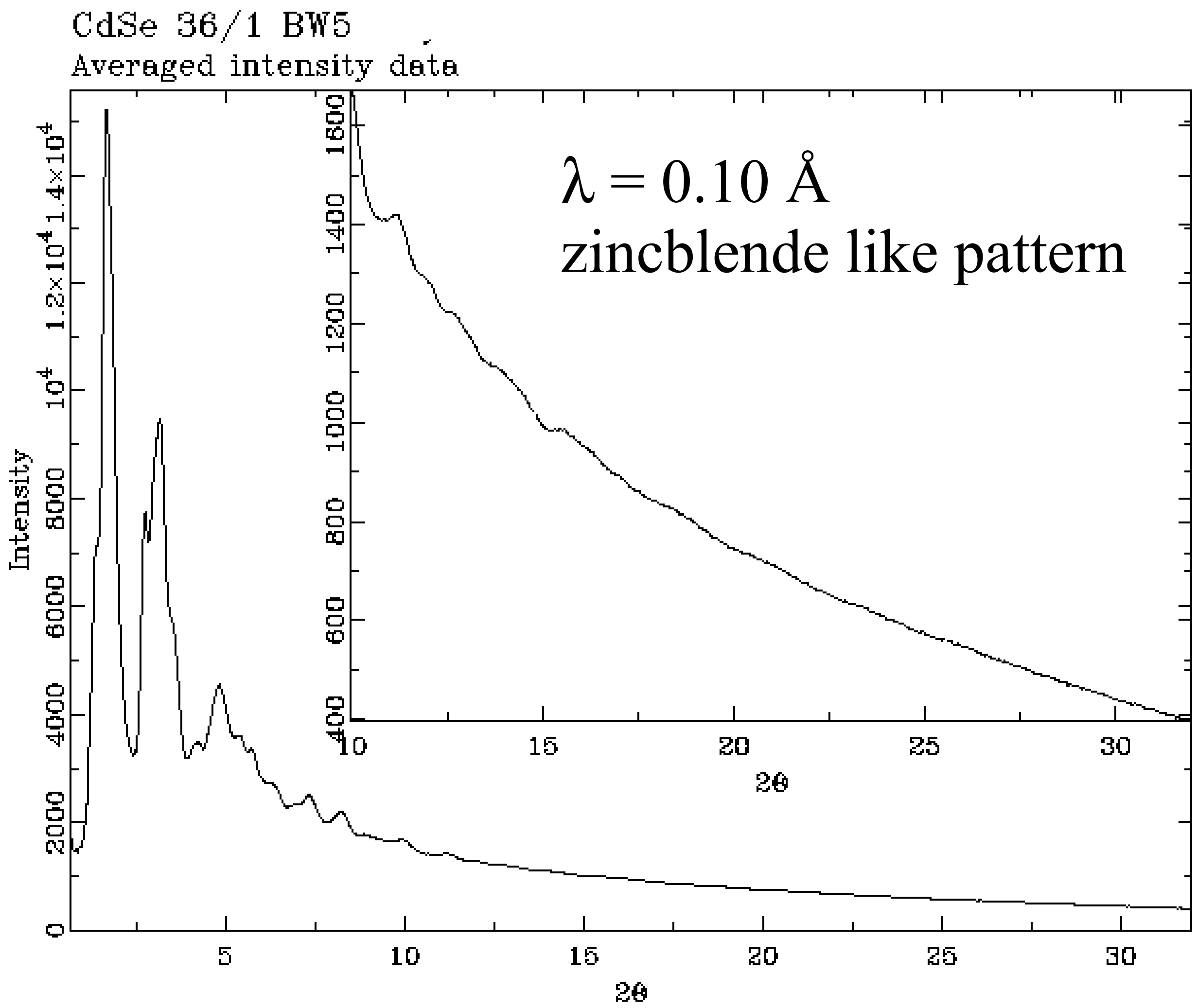
Epitaxial growth ? 11% lattice mismatch!



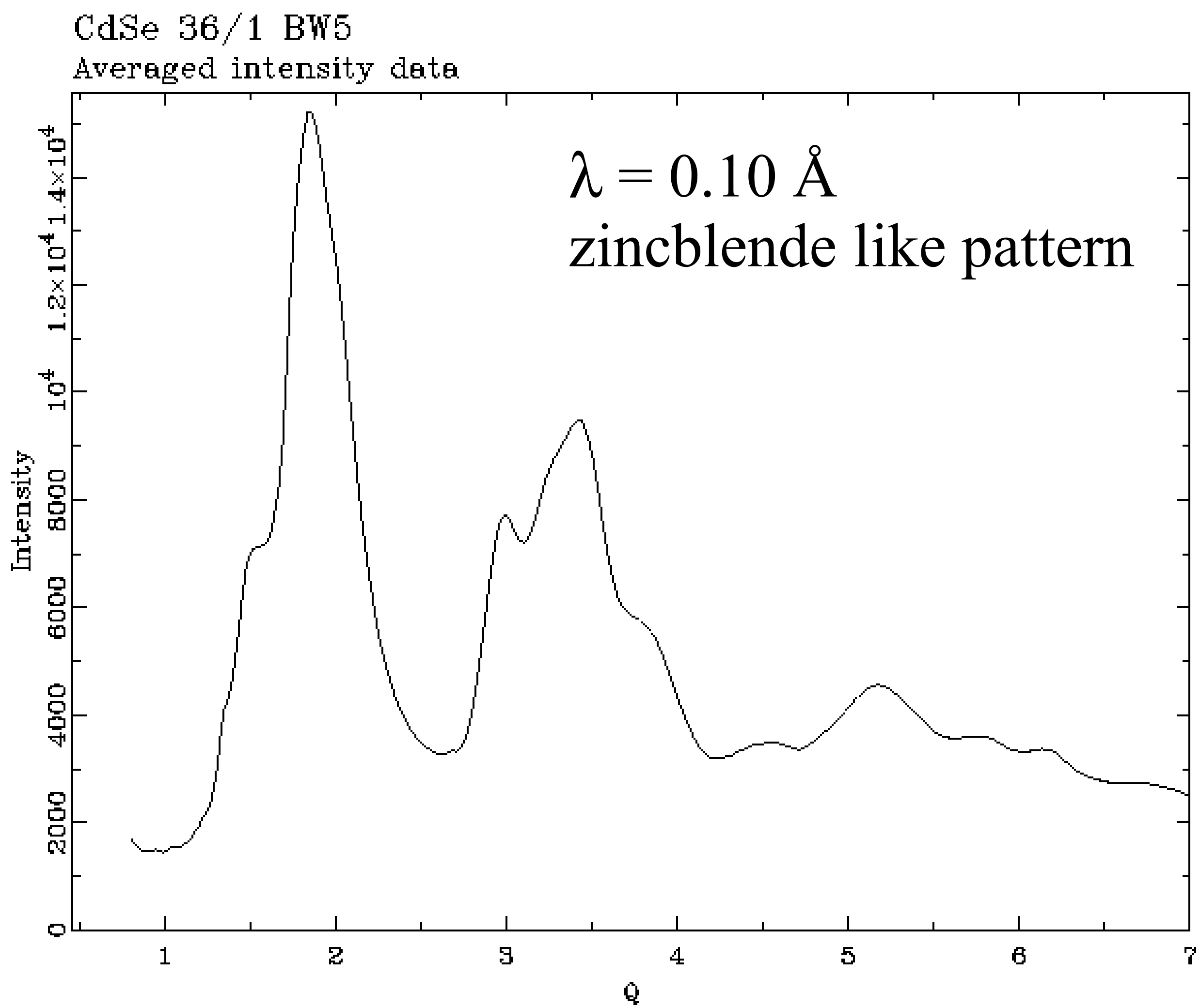


Yu et al. Nano Lett., 5 (4), 565, 2005

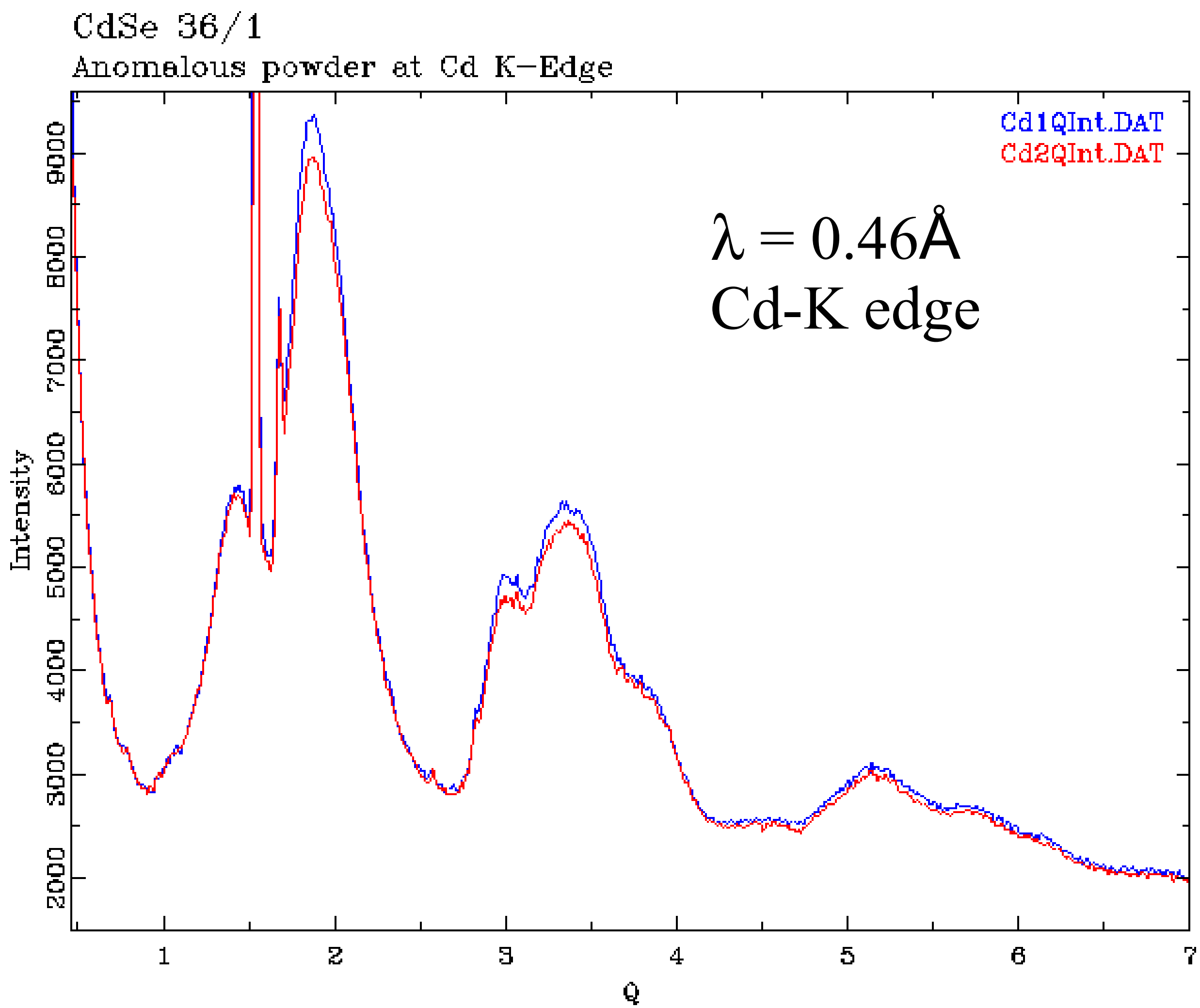
CdSe/ZnS Core/Shell particles



CdSe/ZnS Core/Shell particles

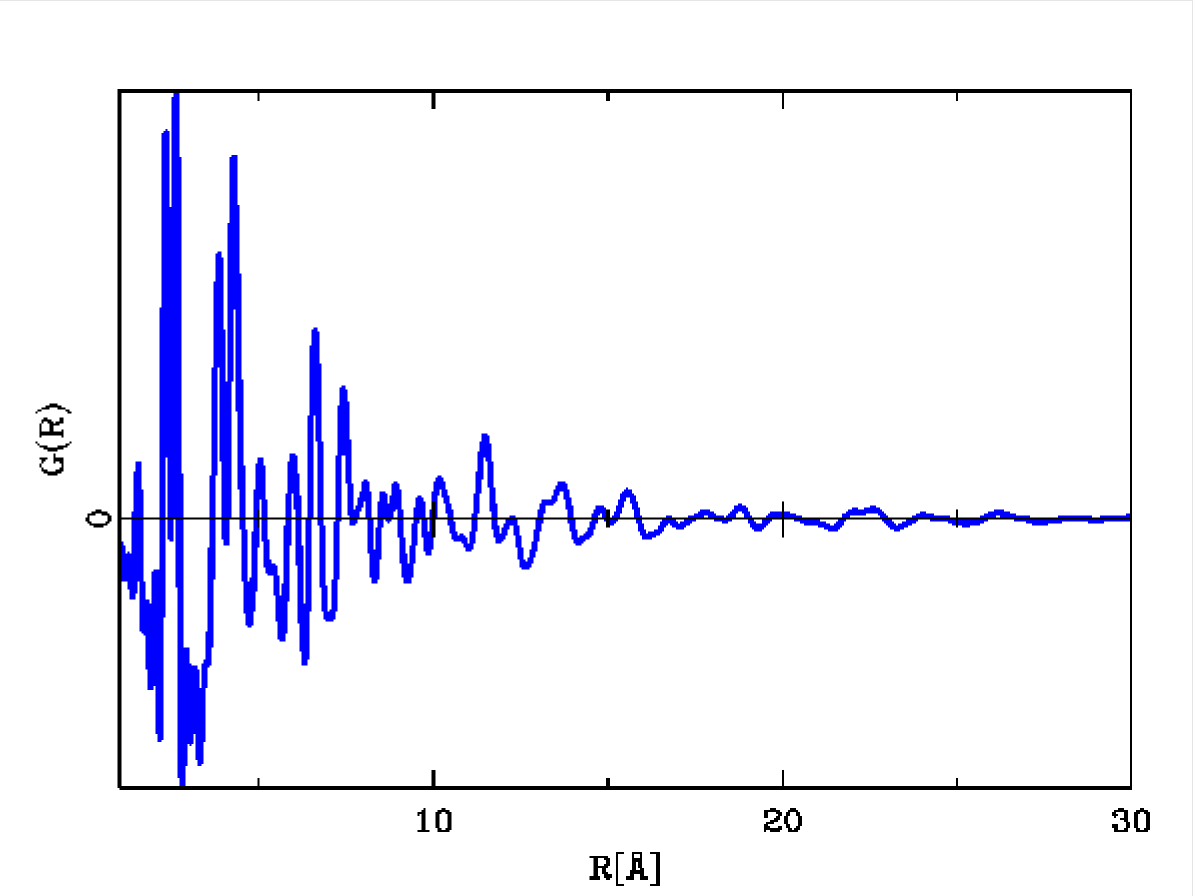


CdSe/ZnS Core/Shell particles

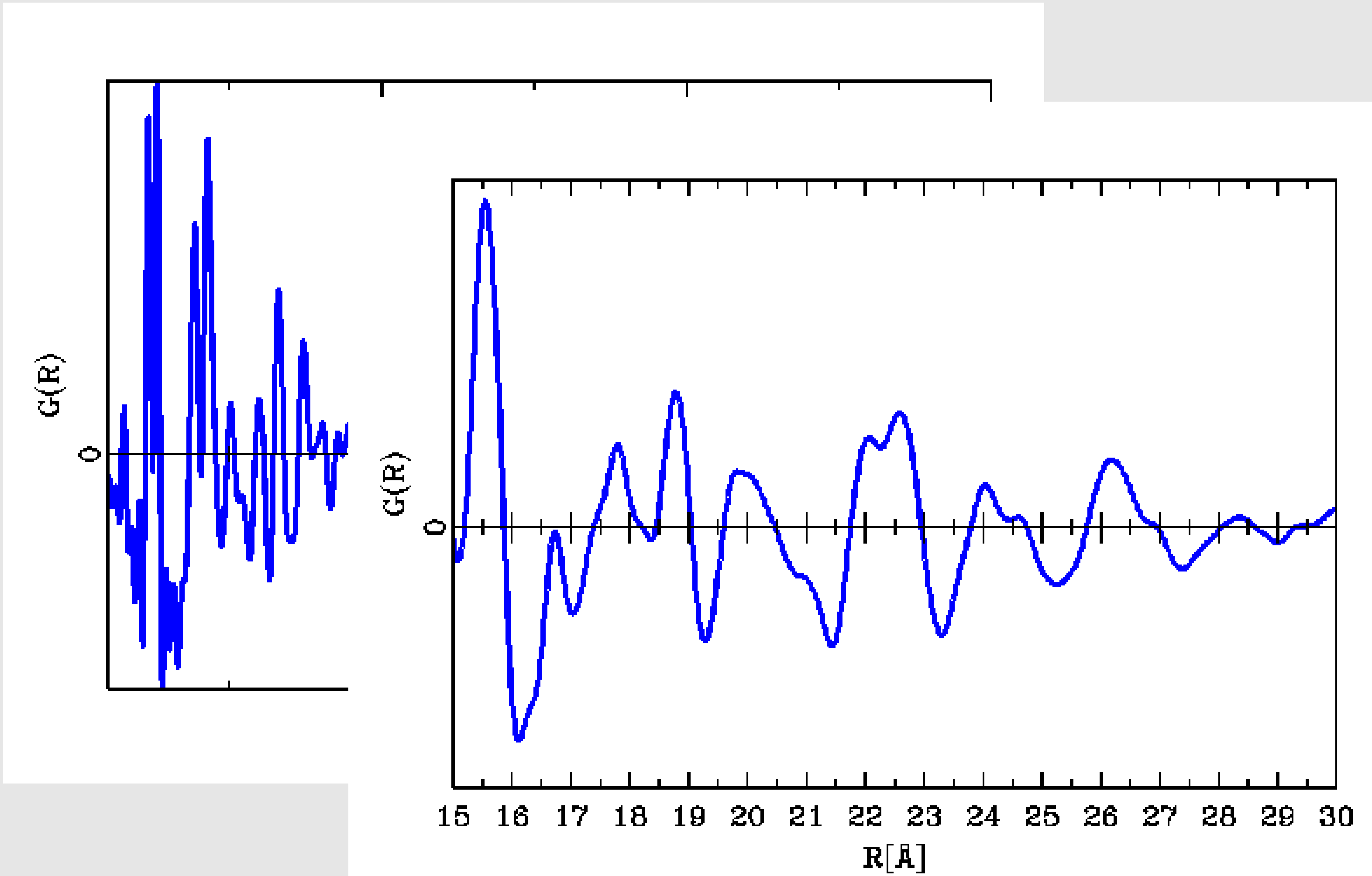


anomalous powder diffraction ==> chemically selective structure info

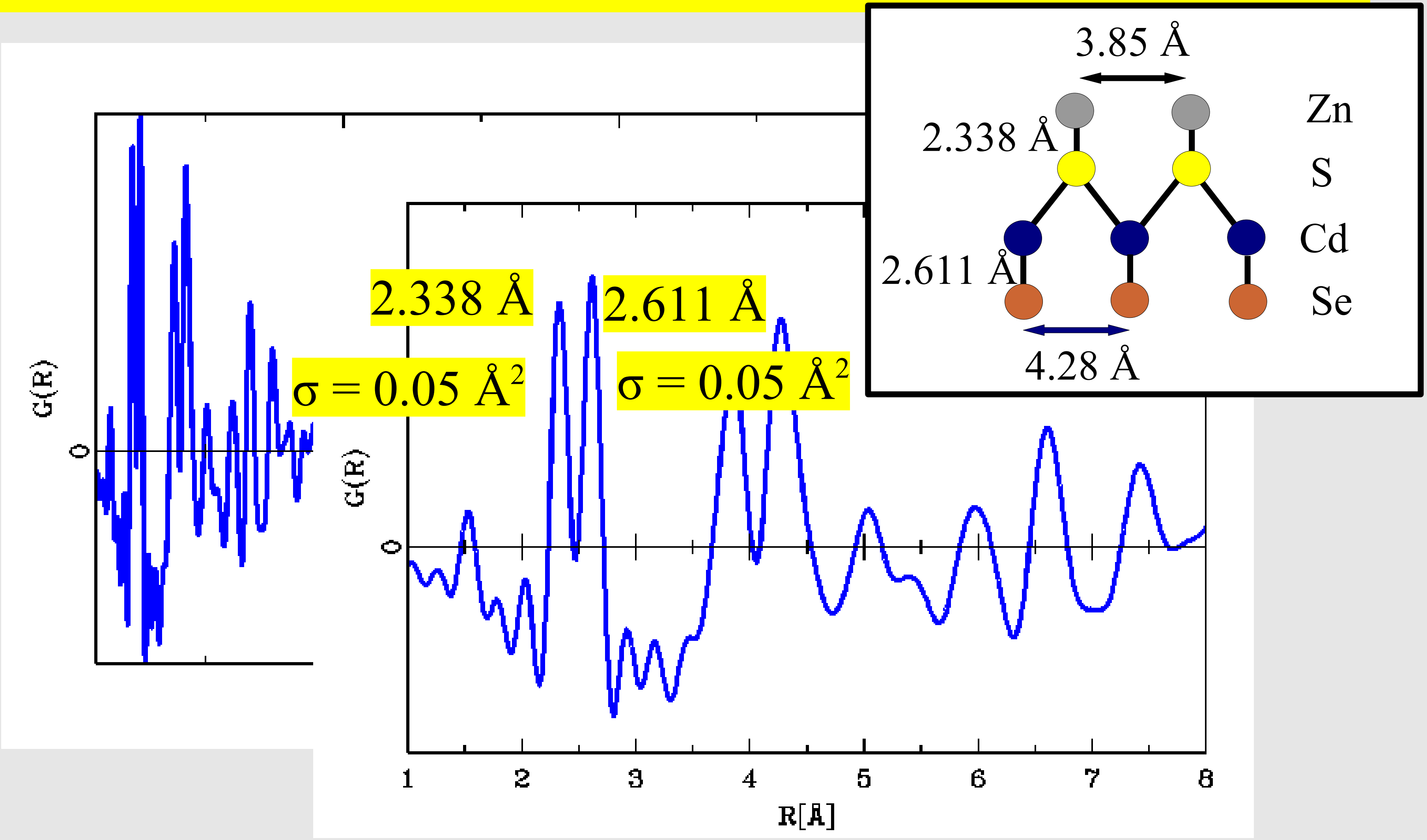
CdSe/ZnS experimental PDF



CdSe/ZnS experimental PDF



CdSe/ZnS experimental PDF

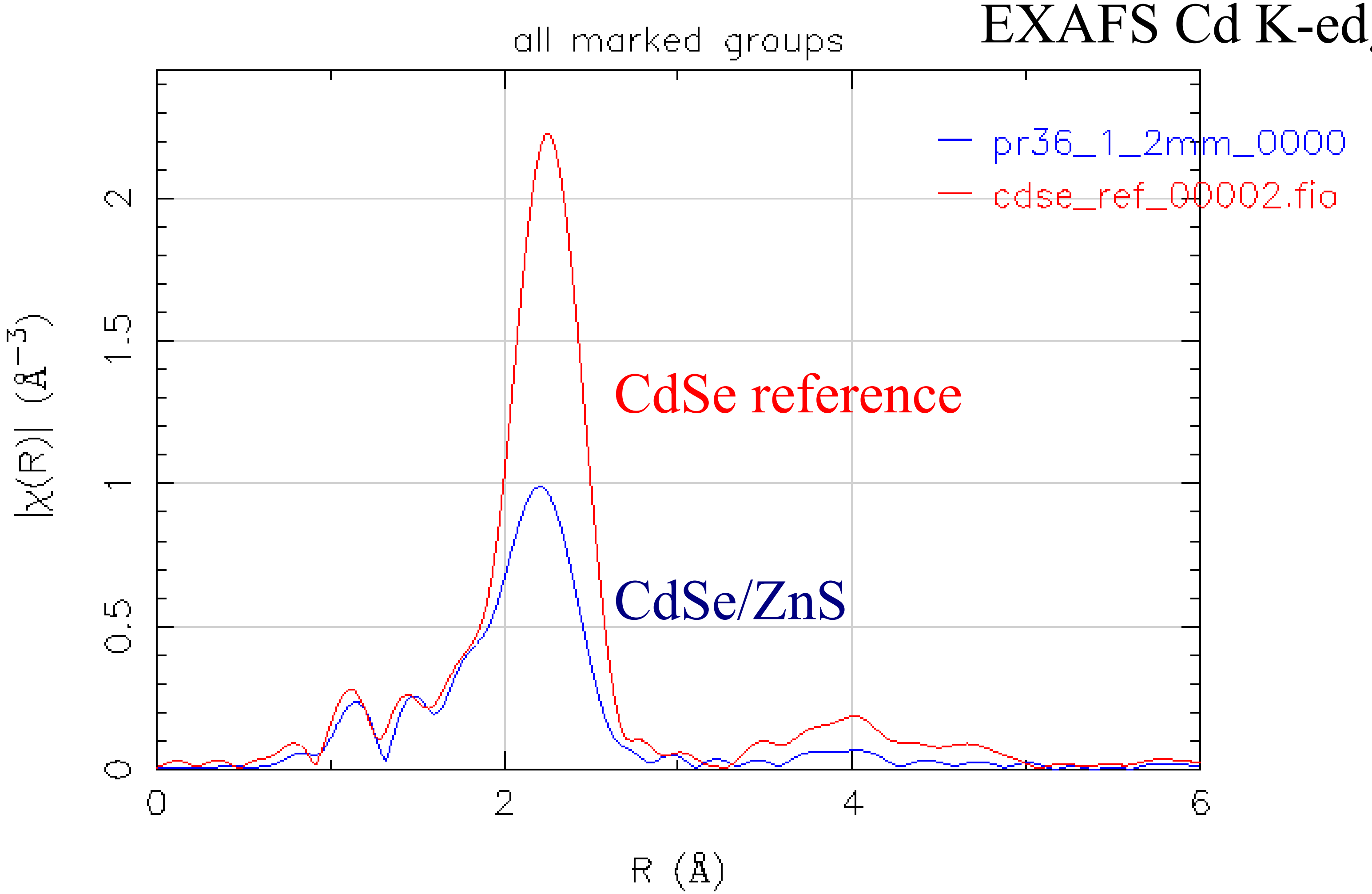


narrow symmetrical first peaks

no indication of interaction

CdSe/ZnS Core/Shell particles

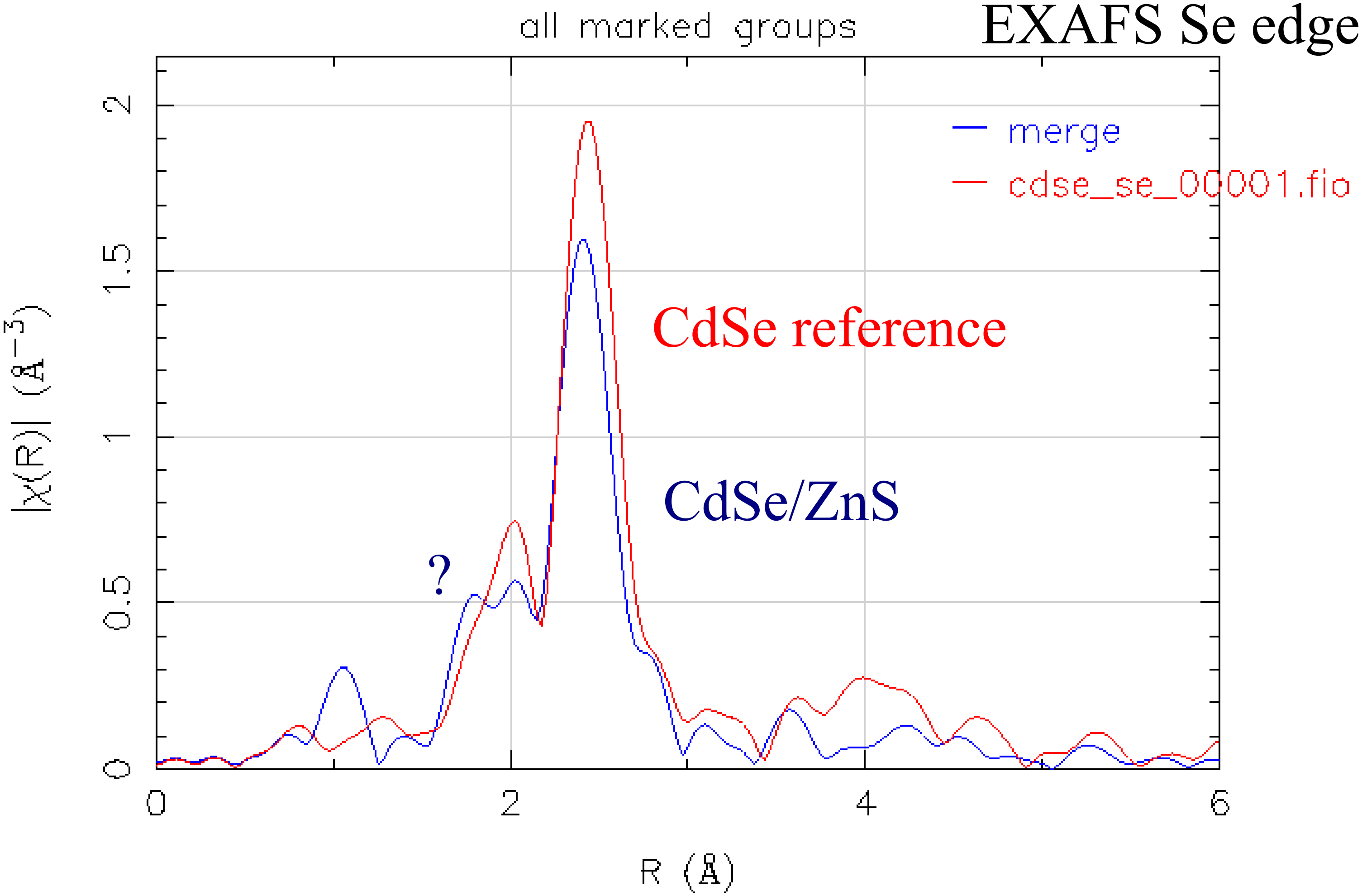
EXAFS Cd K-edge



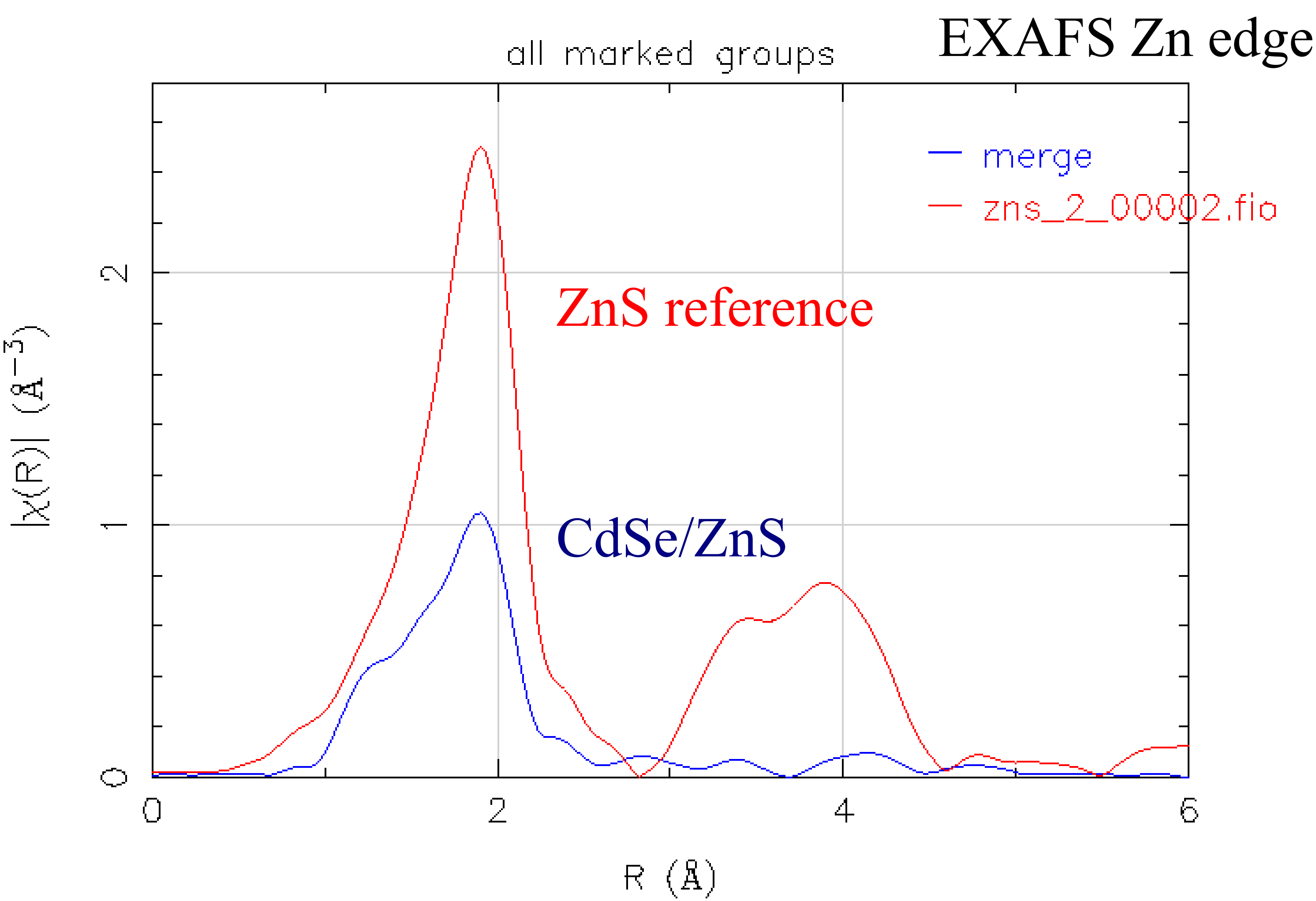
no significant differences   CdSe core like crystalline structure

CdSe/ZnS Core/Shell particles

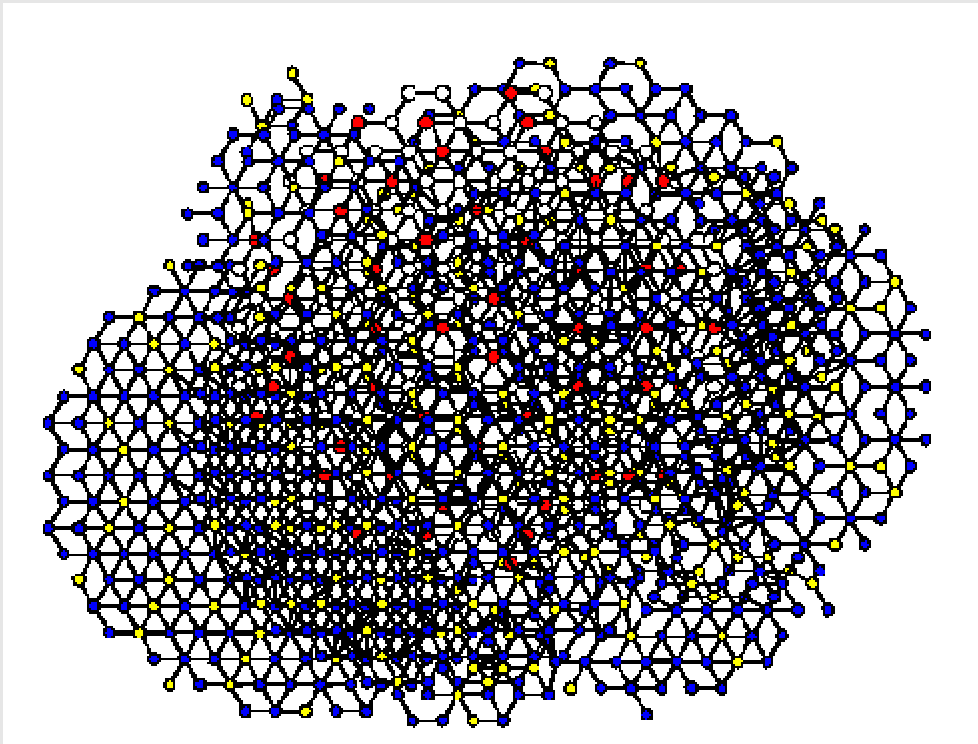
EXAFS Se edge

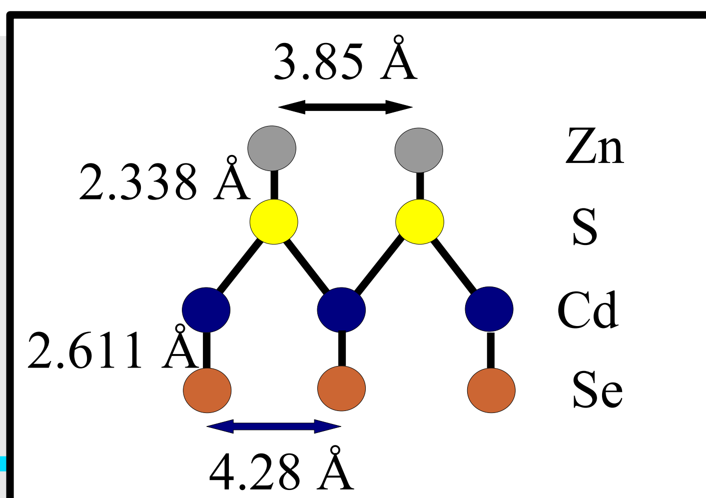


CdSe/ZnS Core/Shell particles



CdSe/ZnS Core/Shell particles





Elliptical CdSe core with stacking faults

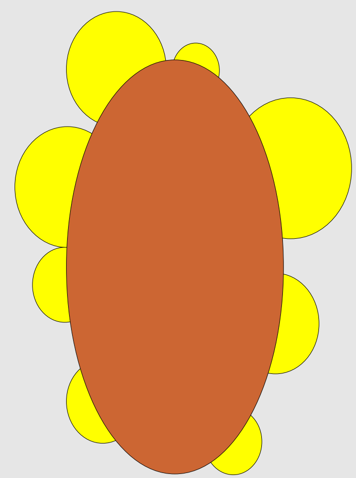
a, c, z, B
Ra, Rc, ρ

ZnS shell consisting of semi spherical subunits with stacking faults size distribution

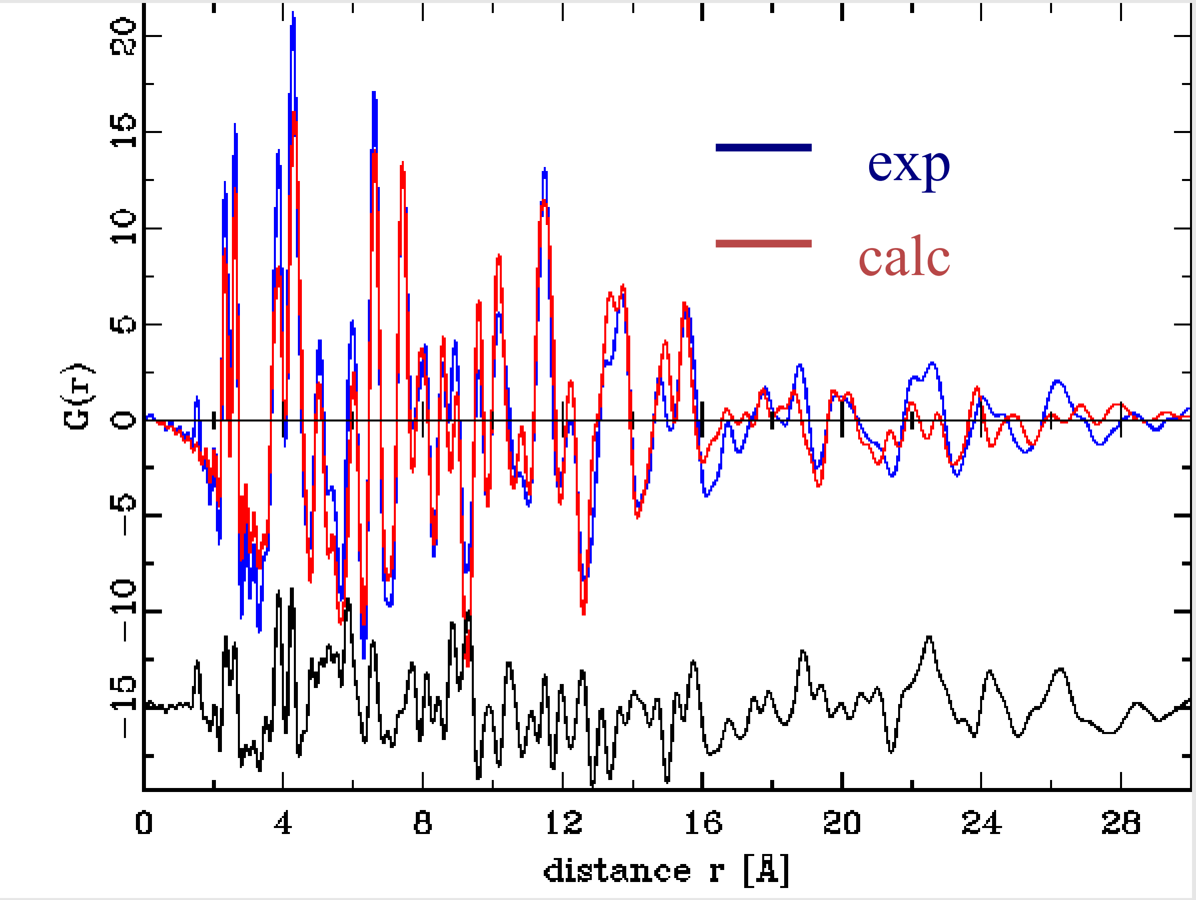
a, c, z, B
Ra, σR, ρ

Shell particles placed randomly at core surface, locally epitaxial

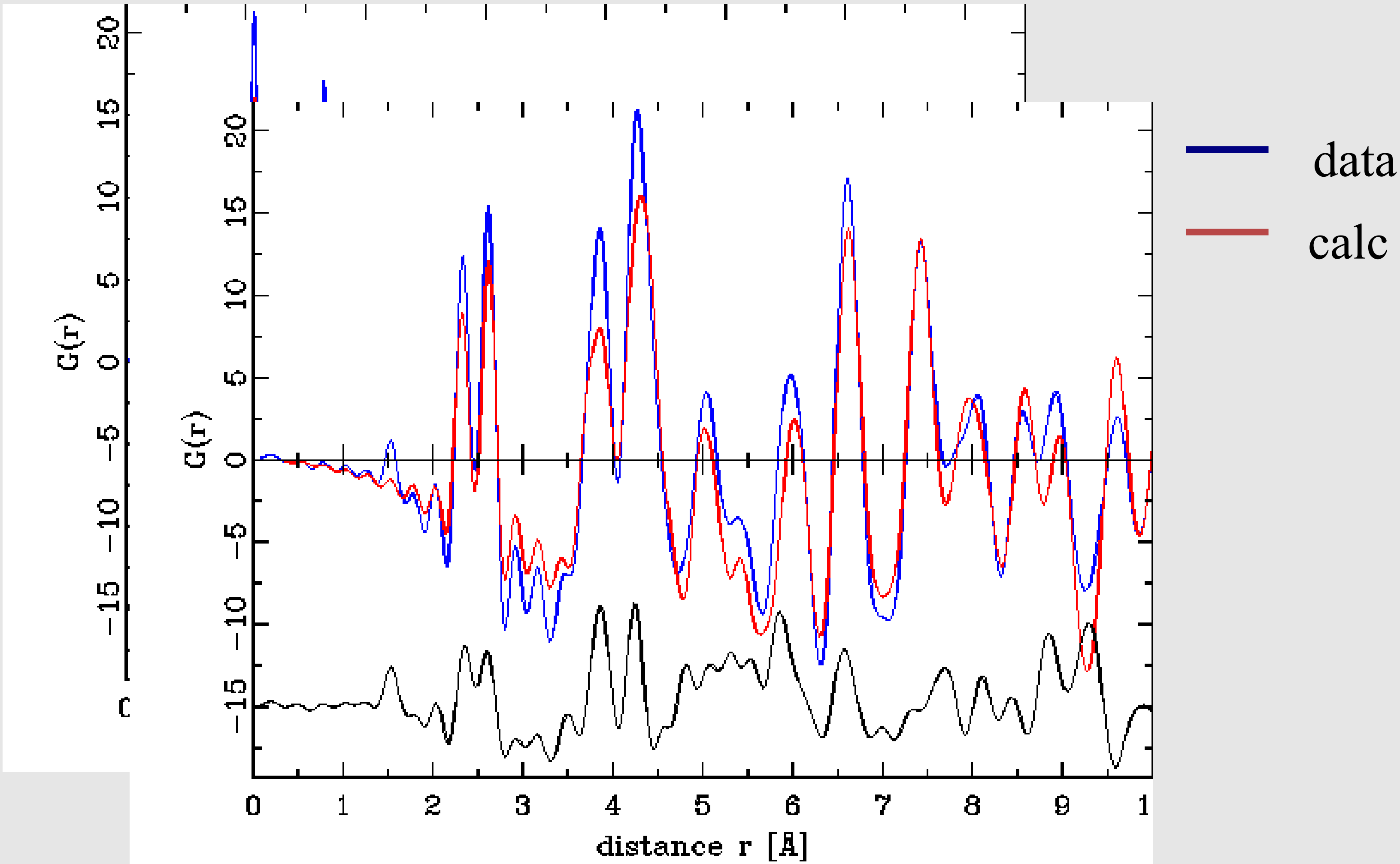
N



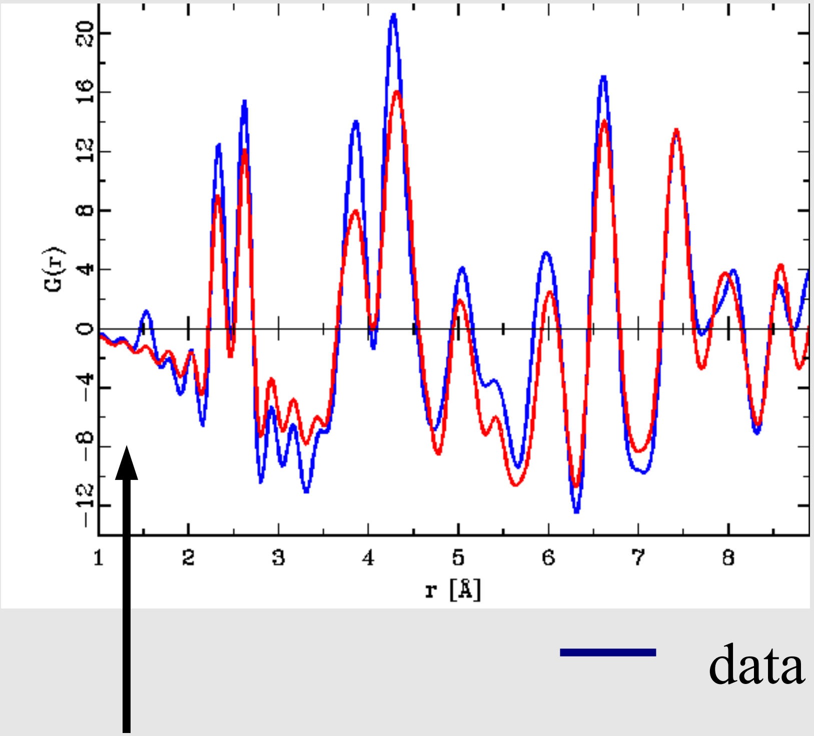
CdSe/ZnS Core/Shell particles



CdSe/ZnS Core/Shell particles



CdSe/ZnS Core/Shell particles



Carbon – Carbon distances

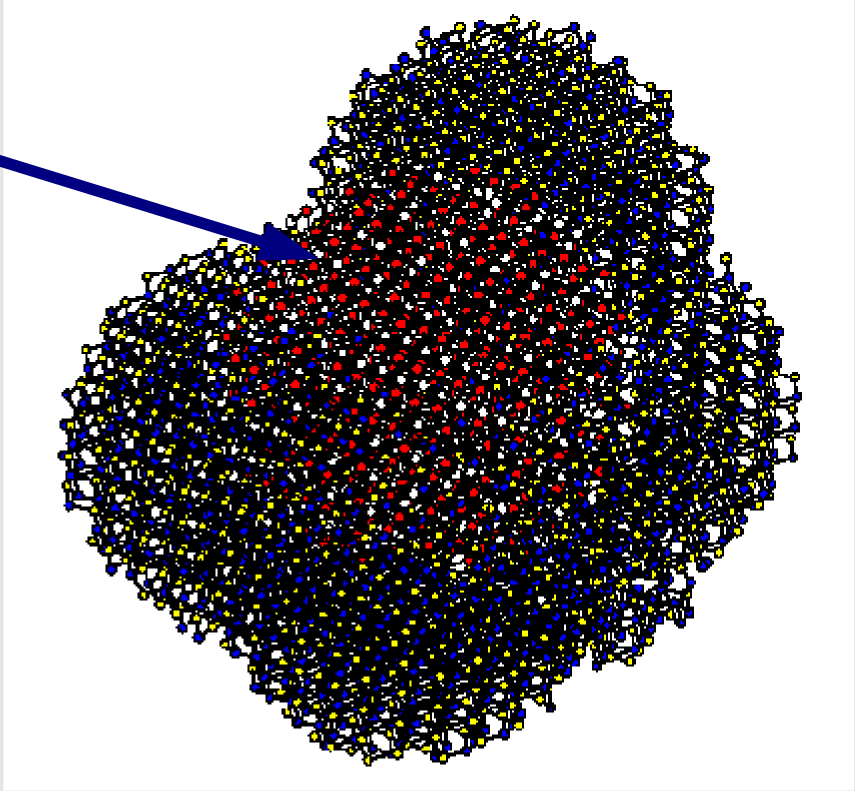
lattice constants as in bulk
core and shell

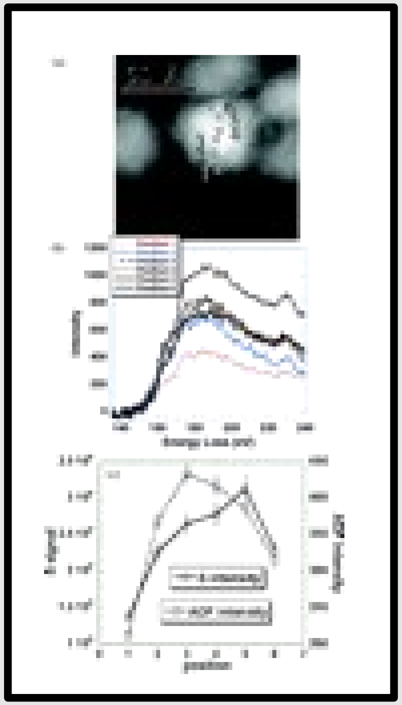
high stacking fault probability
core more wurtzite like 35%
shell highly disorderd 50%

37 Å * 39 Å radius core
10 Å thickness shell

no noticeable interaction between
core and shell

CdSe/ZnS Core/Shell particles





Yu et al. Nano Lett., 5 (4), 565, 2005

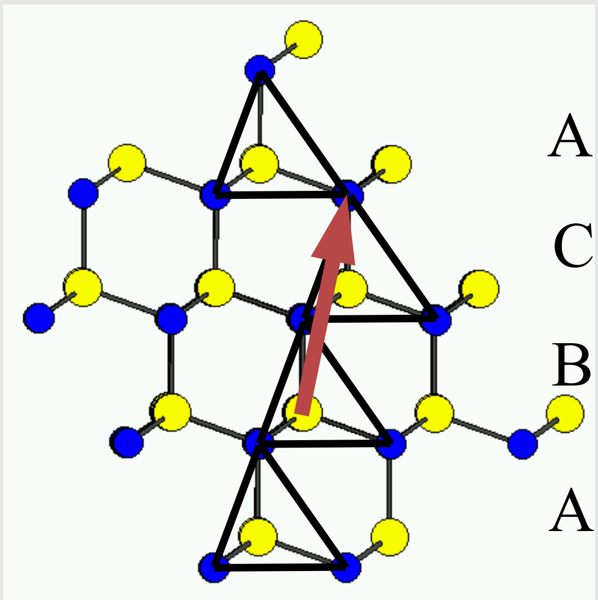
stacking faults in II-VI nanoparticles

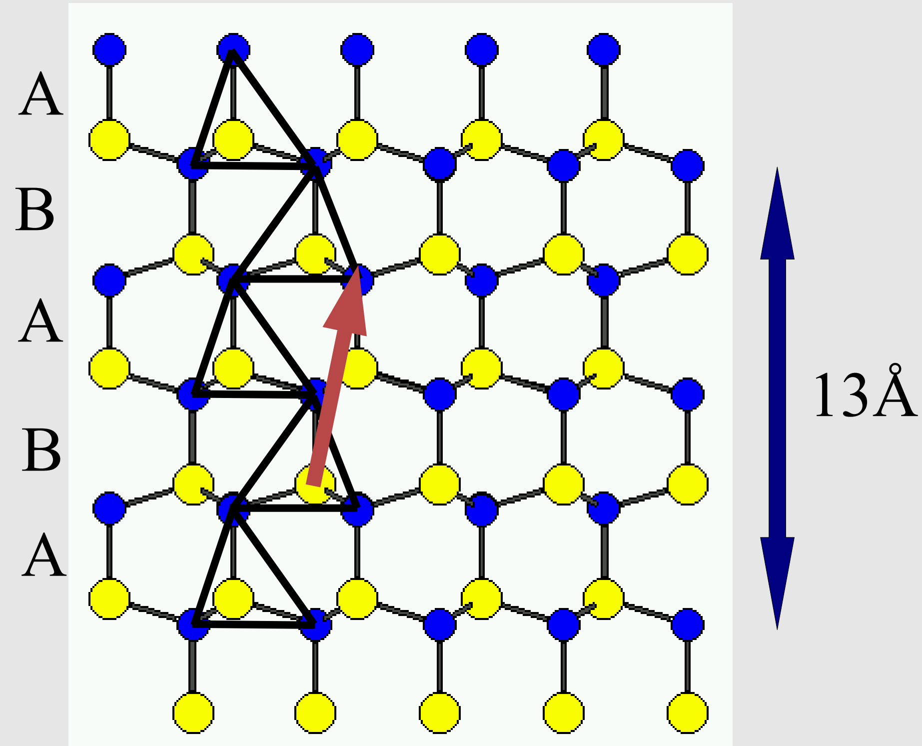
ZnO	Wurtzite	18%
ZnSe	Zincblende	30%

CdSe/ZnS core shell

core	Wurtzite	35%
shell	Zincblende	50%

Stacking Zincblende / Wurtzite





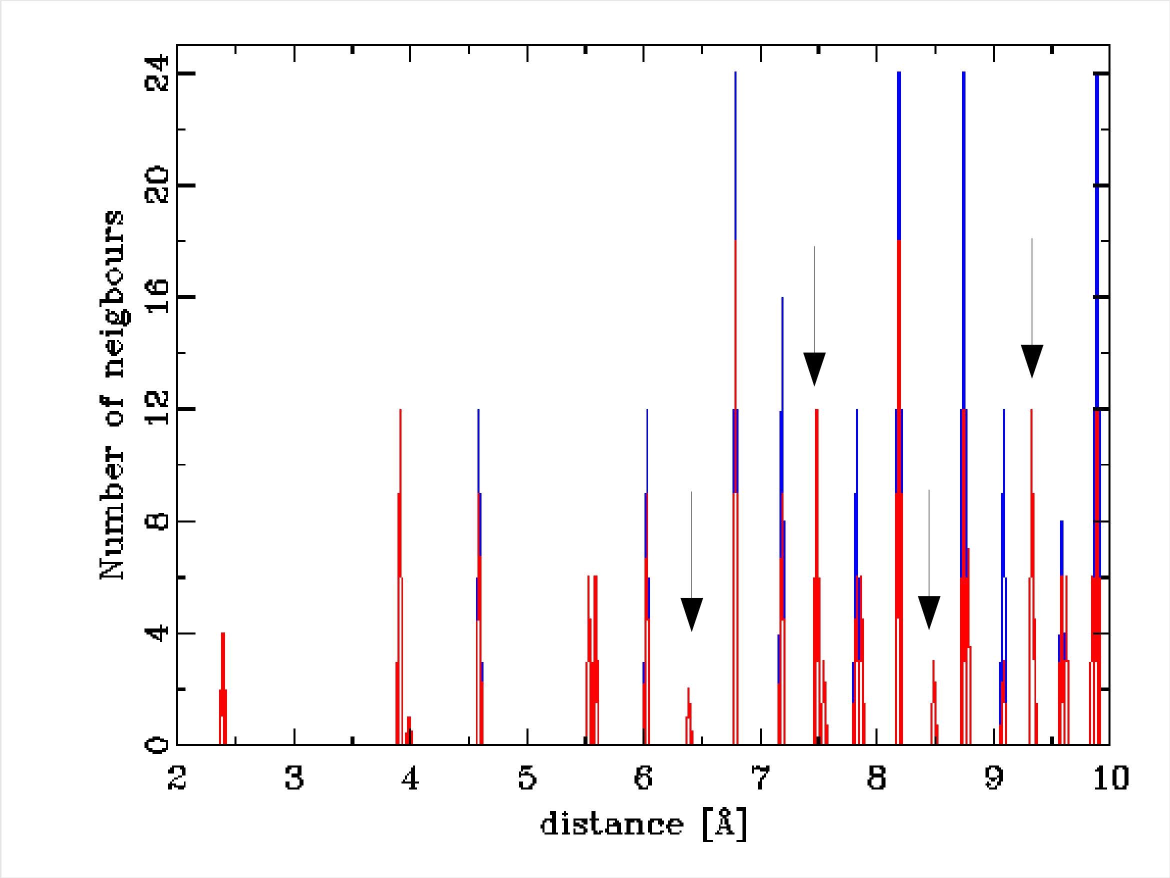
cubic closed packed
stacking of tetrahedra

hexagonal close packed
stacking of tetrahedra

Zincblende

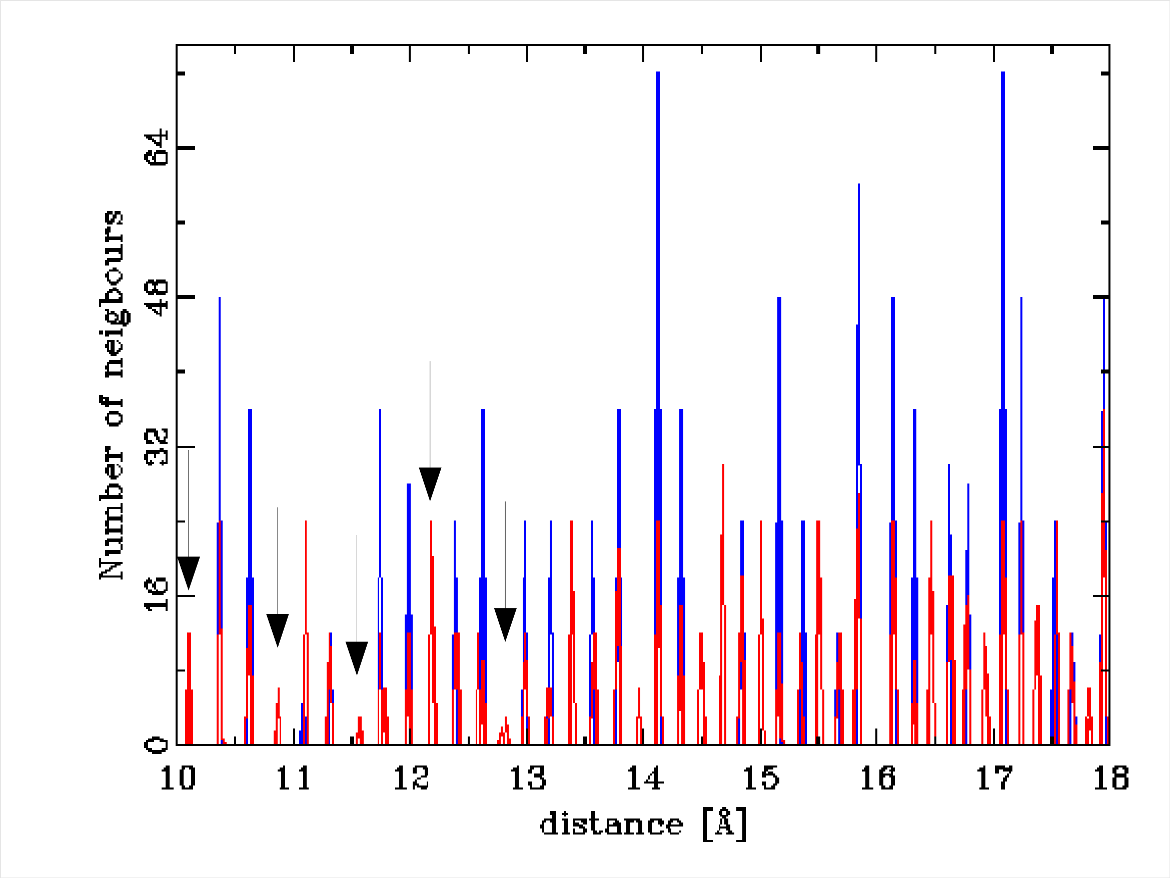
Wurtzite

Stacking Zincblende / Wurtzite



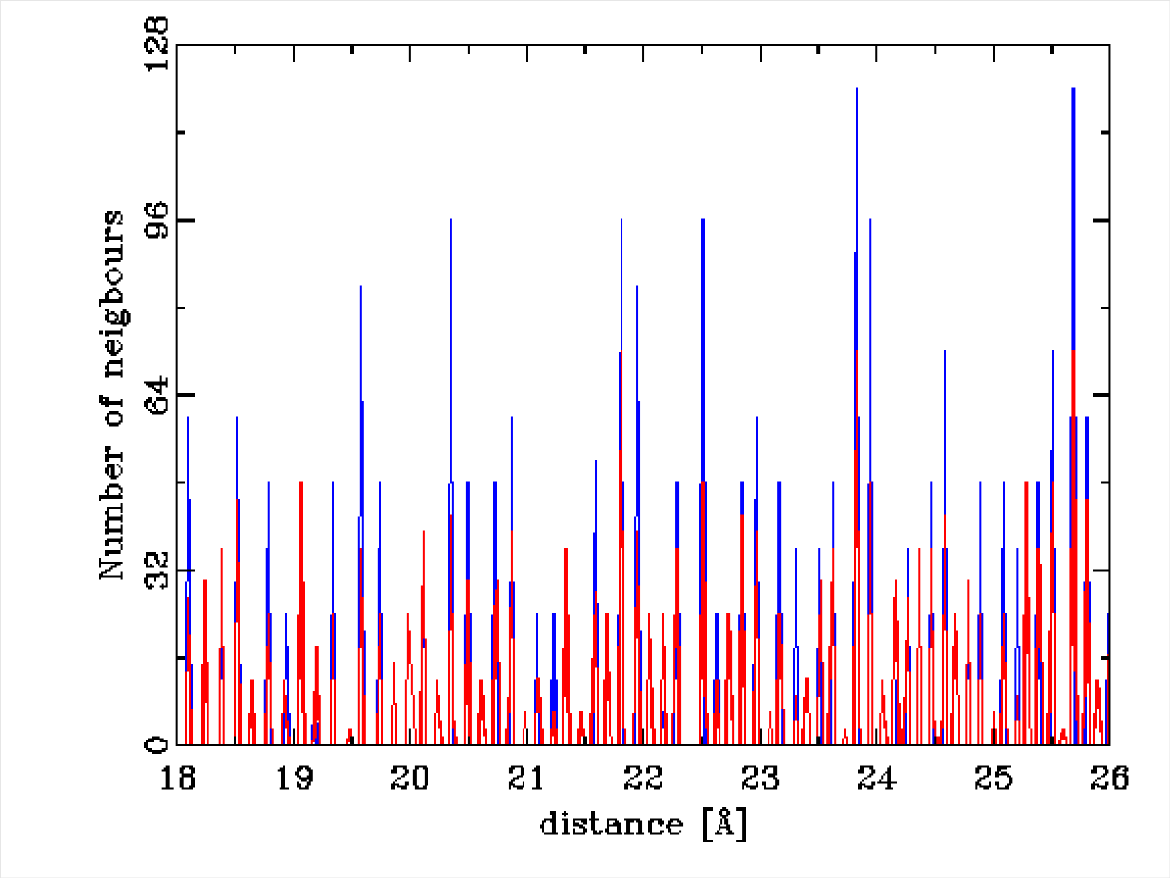
only minor differences in bond lengths

Stacking Zincblende / Wurtzite



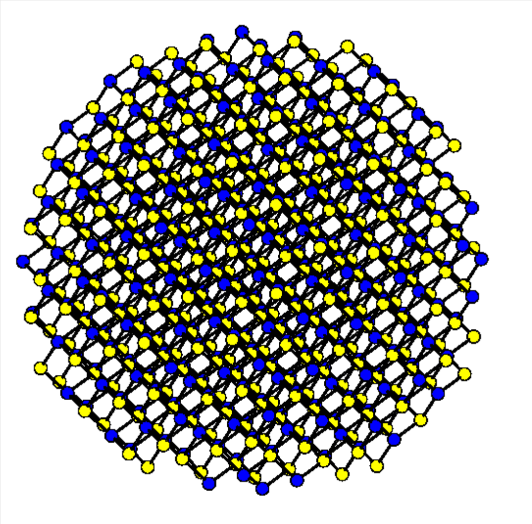
only minor differences in bond lengths
additional different distances in Wurtzite
all Zincblende distances also in Wurtzite!

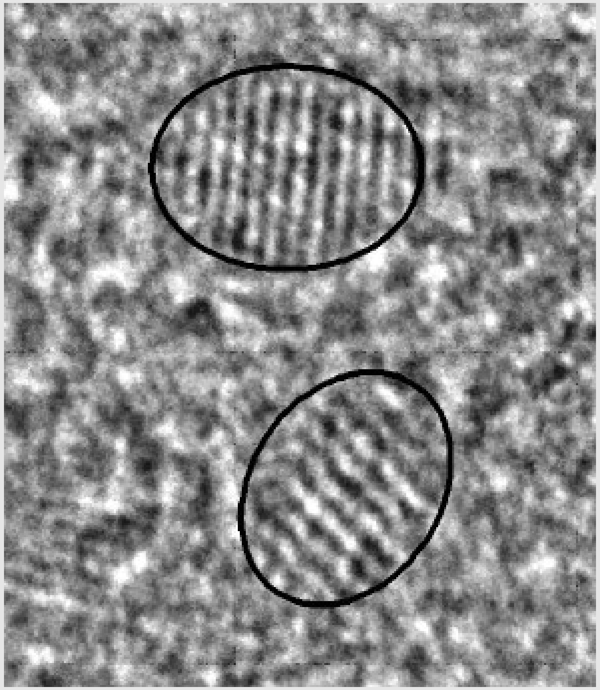
Stacking Zincblende / Wurtzite



only minor differences in bond lengths
additional different distances in Wurtzite
all Zincblende distances also in Wurtzite!

Stacking Zincblende / Wurtzite

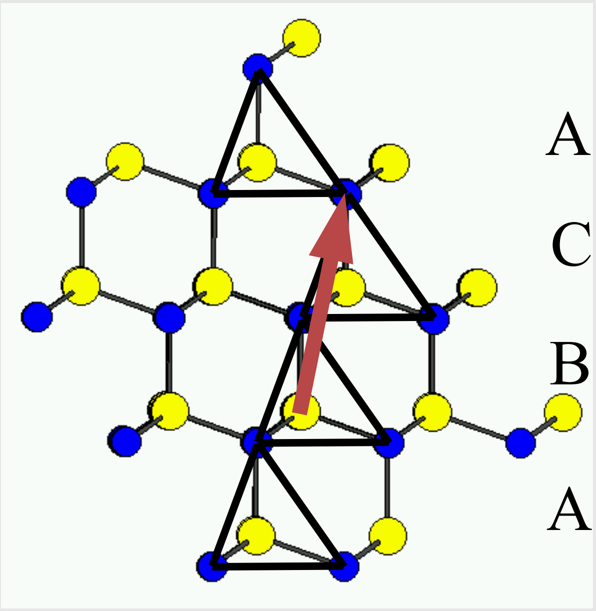




~8 to 10 monolayers
= 4 to 5 unit cells along c
= 24 to 30 Å

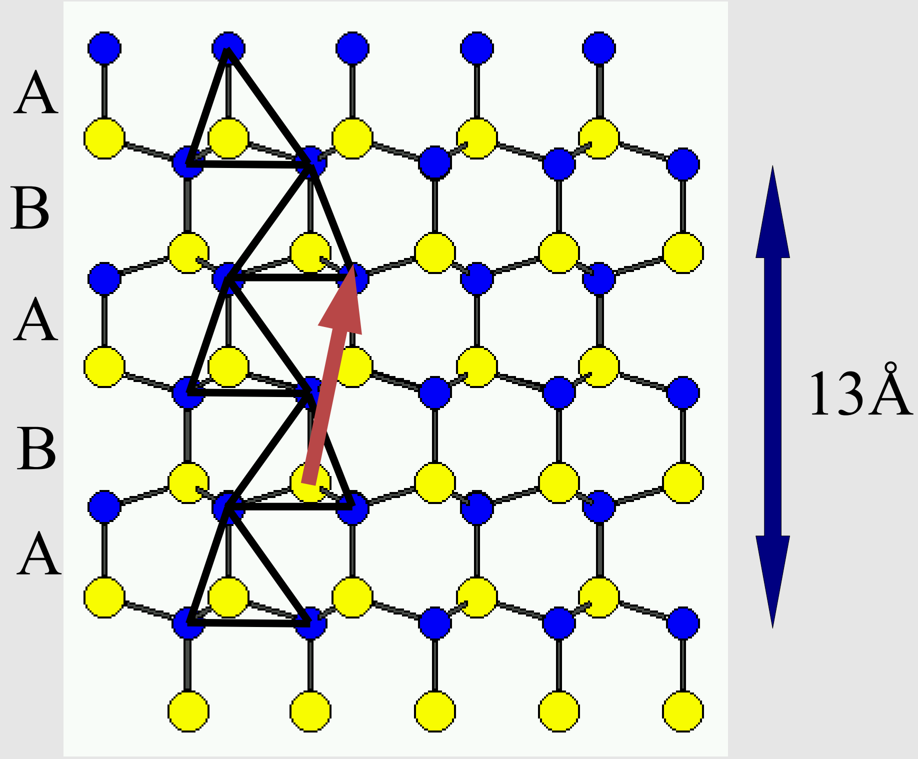
spherical II-VI nanoparticle
30 Å diameter ⇒ 660 atoms
25 Å diameter ⇒ 380 atoms
layered structure layers identical in Wurtzite and Zincblende

Stacking Zincblende / Wurtzite



cubic closed packed
stacking of tetrahedra

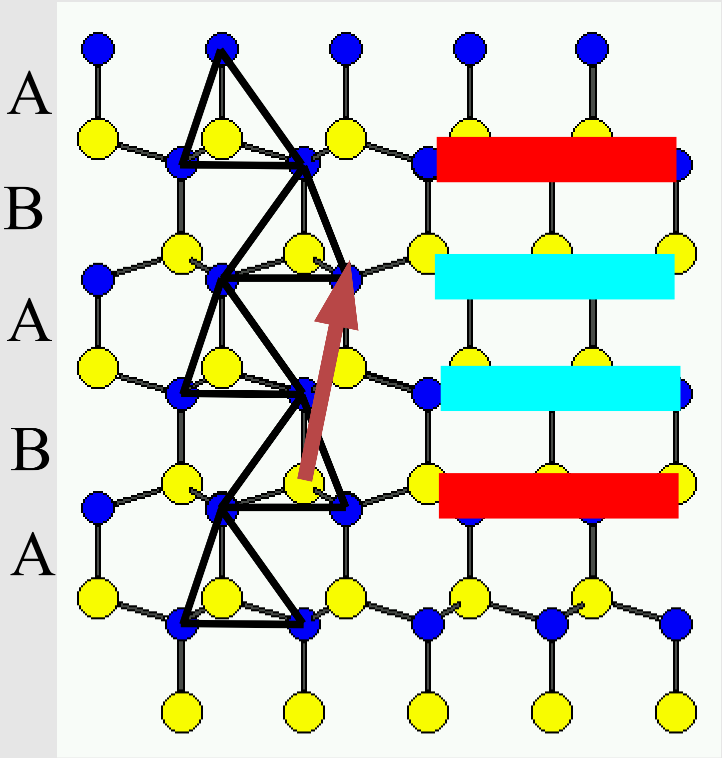
Zincblende

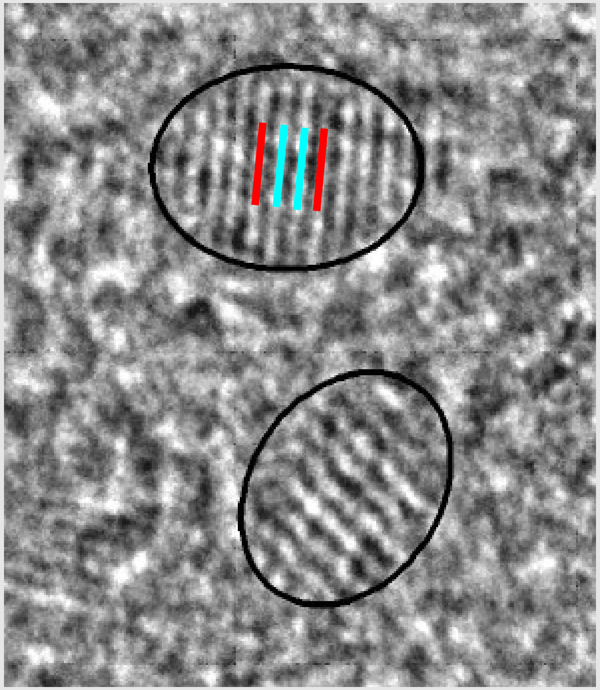


hexagonal close packed
stacking of tetrahedra

Wurtzite

Common building principles





Common structural characteristics:
layered structure layers identical in Wurtzite and Zincblende
⇒ high stacking fault probability

30% probability ≙ 3 to 4 faults

No relaxation of first neighbour distances
Relaxation of second neighbour distance

Acknowledgements

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P. Luczak

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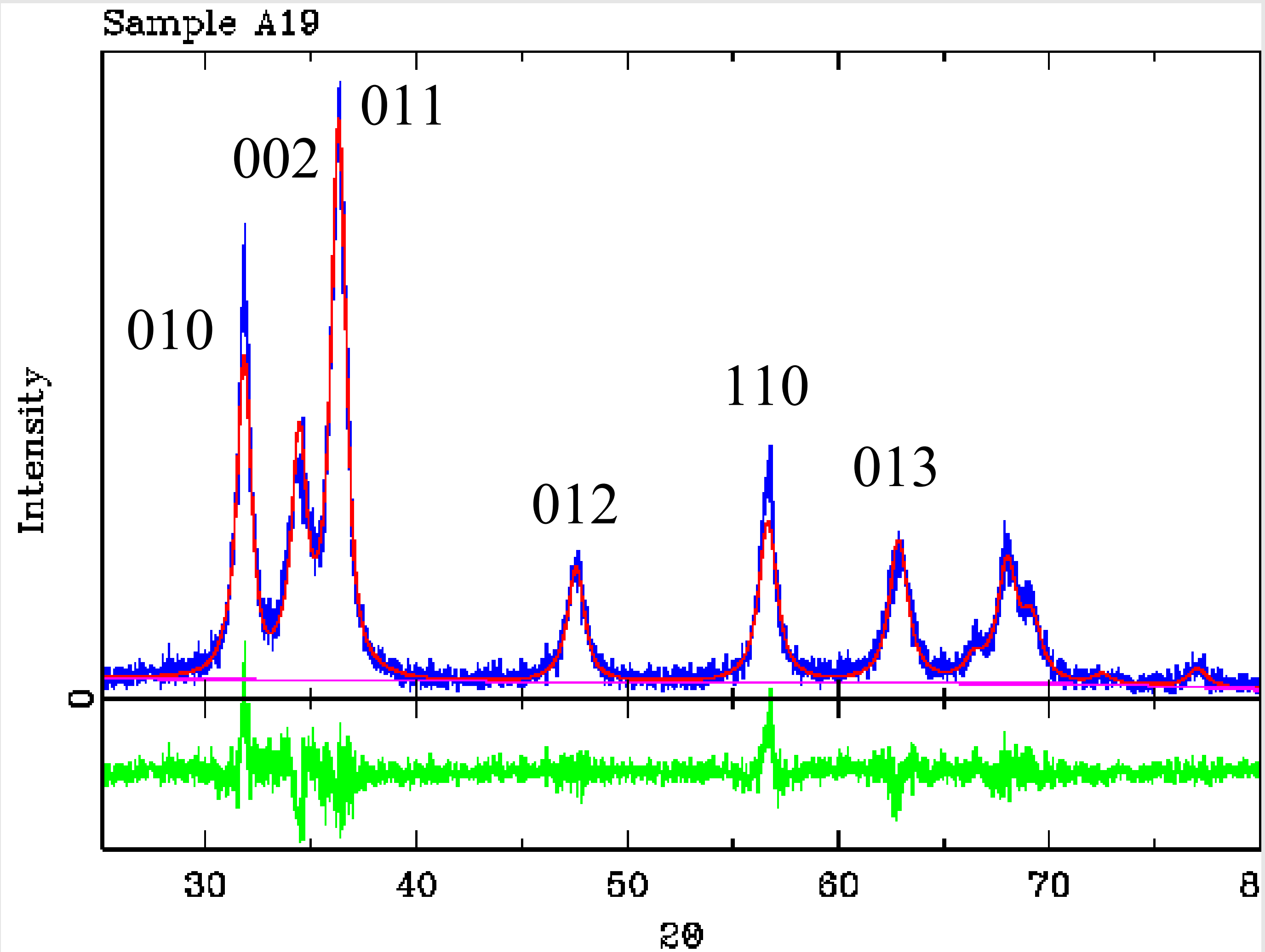
C. Graf
C. Rűhl

German Science Foundation
SFB410 II-VI Semiconductors

ZnO Nanoparticles



Rietveld refinement

Wurtzite

R_{wp} 18 %

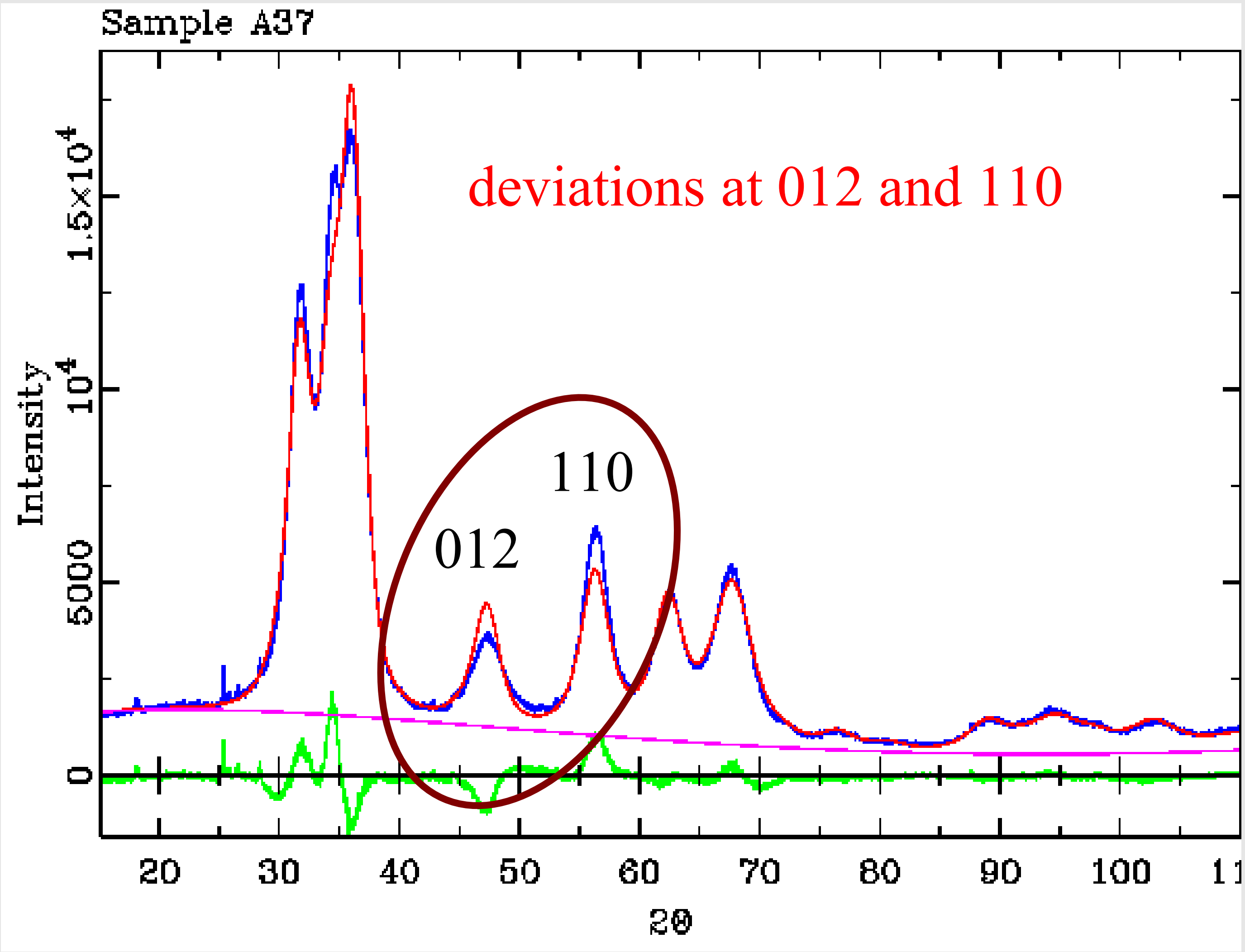
FWHM 60 = 1.0

size 9.5 nm

anisotropic line widths

ZnO Nanoparticles

Rietveld refinement



Wurtzite

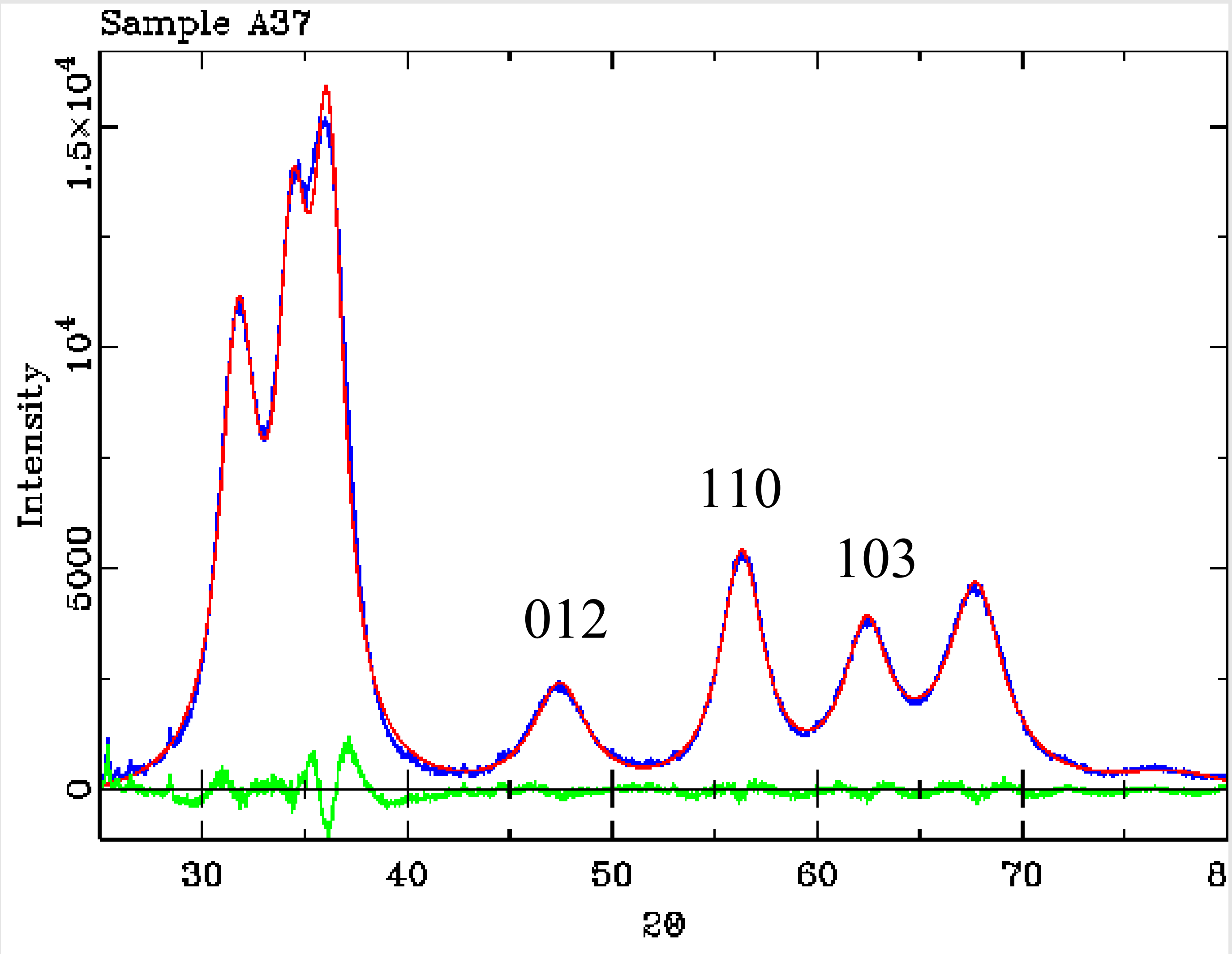
R_{wp} 7 %

FWHM 60 = 3.0

size 3.2 nm

texture
anisotropic shape
stacking faults

ZnO Nanoparticles



Single line fit

hkl	FWHM	Size
110	2.72	3.45
103	2.68	3.60
012	3.75	2.42

texture
anisotropic shape
stacking faults

ZnO Nanoparticles Fitting by Debye

Debye formula :

$$< | F(h) |^2 > = \Sigma_j f_j^2 + \Sigma_i \Sigma_{j,j \neq i} f_i f_j \sin(2\pi h r_{ij}) / (2\pi h r_{ij})$$

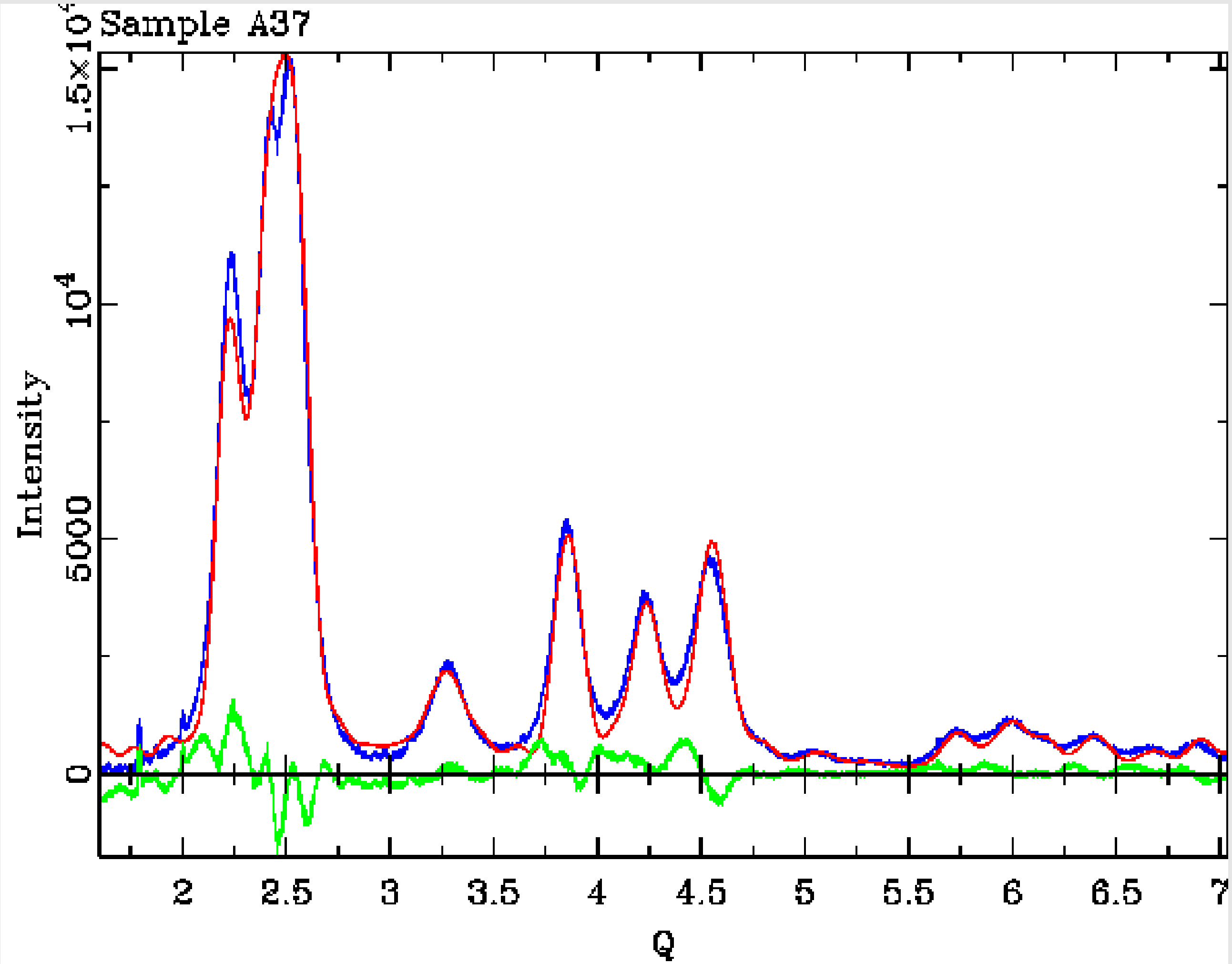
Sum over all atom pairs

→ no restrictions on sample structure

open to finite particle with any shape

defects like stacking faults etc.

ZnO Nanoparticles Fitting by Debye



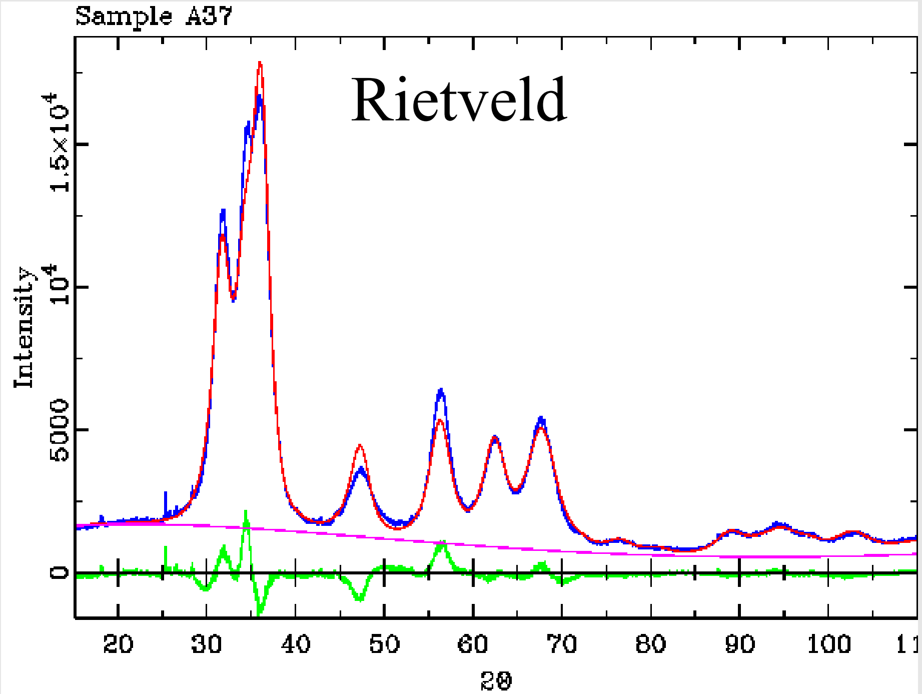
Debye formula

ZnO Wurtzite Structure

a
c
overal U
size in a-b plane
size along c
z(oxygen)
Stacking probability

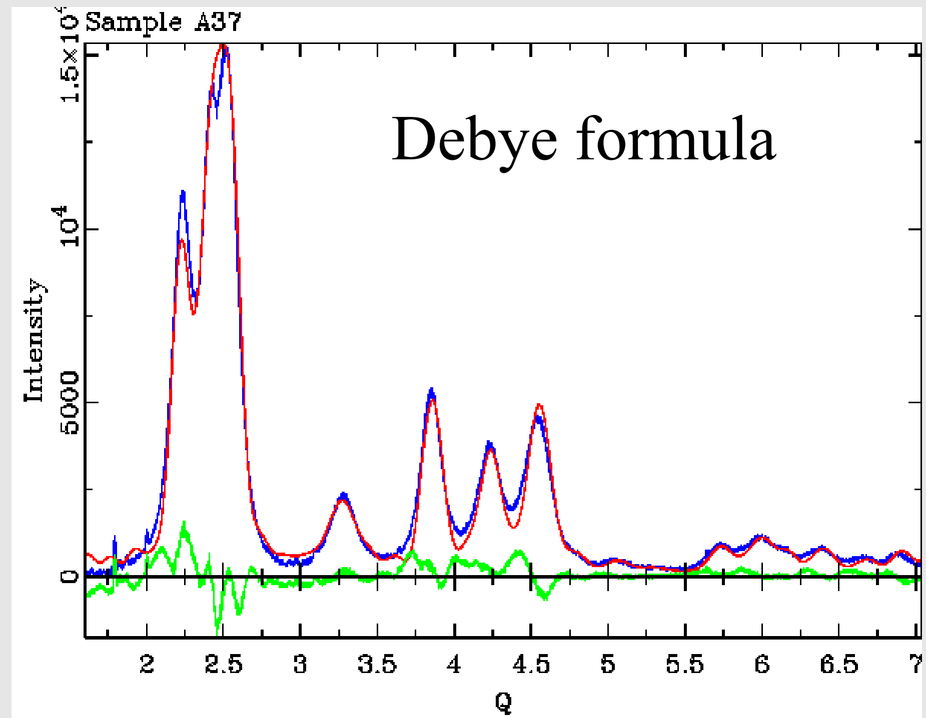
R = 8.8 %

ZnO Nanoparticles

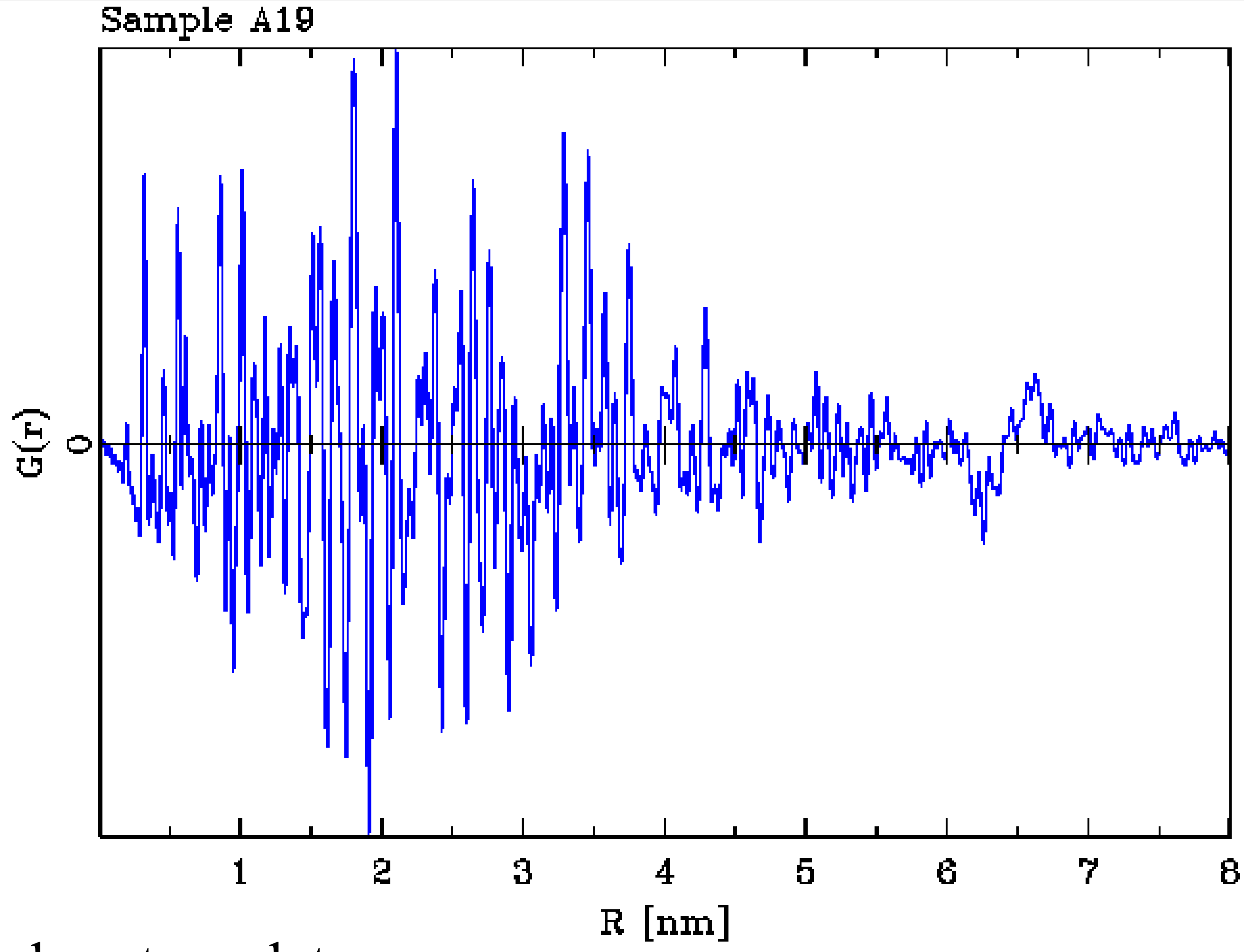


	Rietveld	Debye
a	3.269	3.256
c	5.250	5.224
z(O)	0.3876	0.3861
B	1.1	1.5

	Rietveld	Debye
size	3.2	3.6 / 3.8
prob	---	0.14



ZnO Pair Distribution Function



sharp maxima

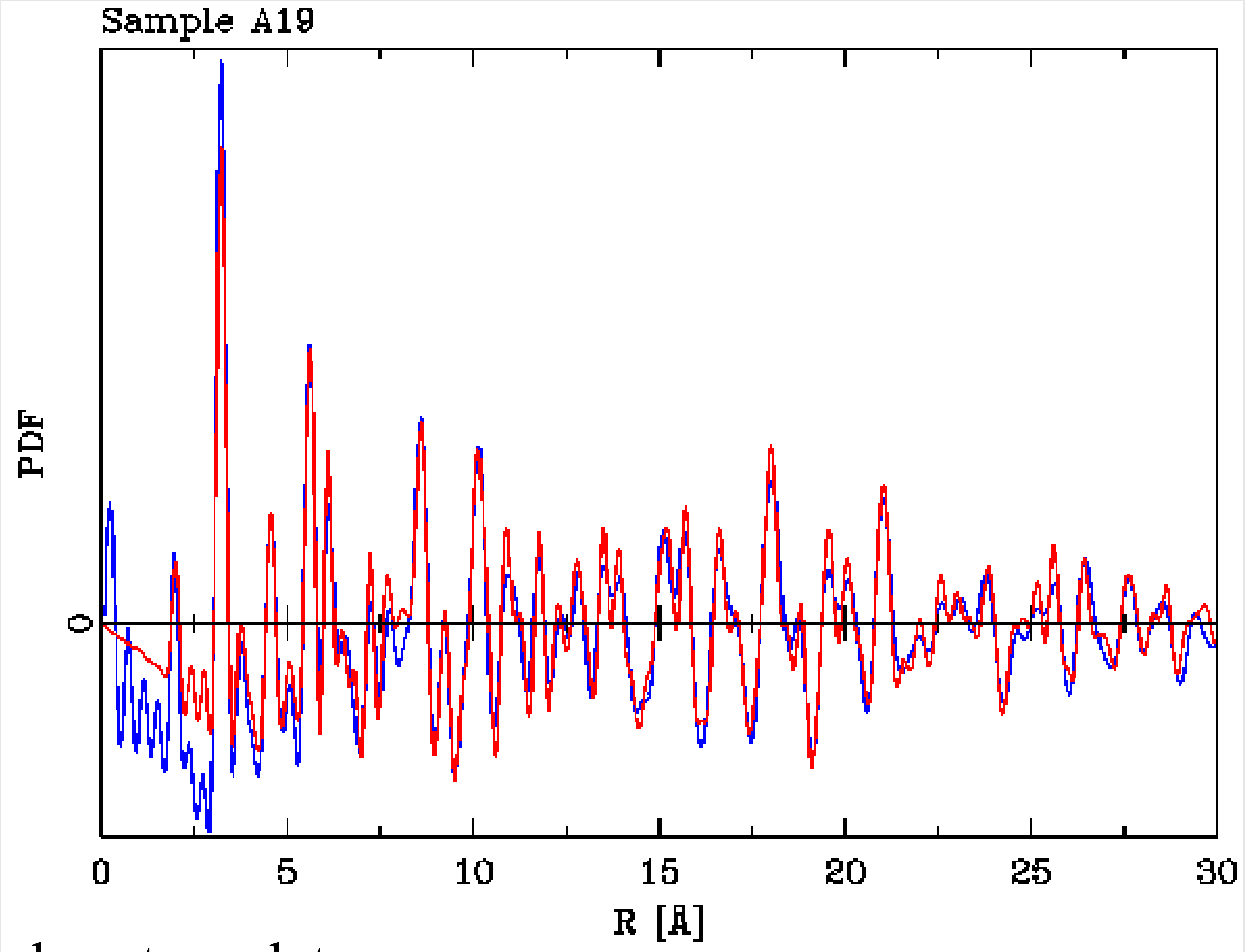
few stacking faults

Size ~ 9.5 nm

laboratory data

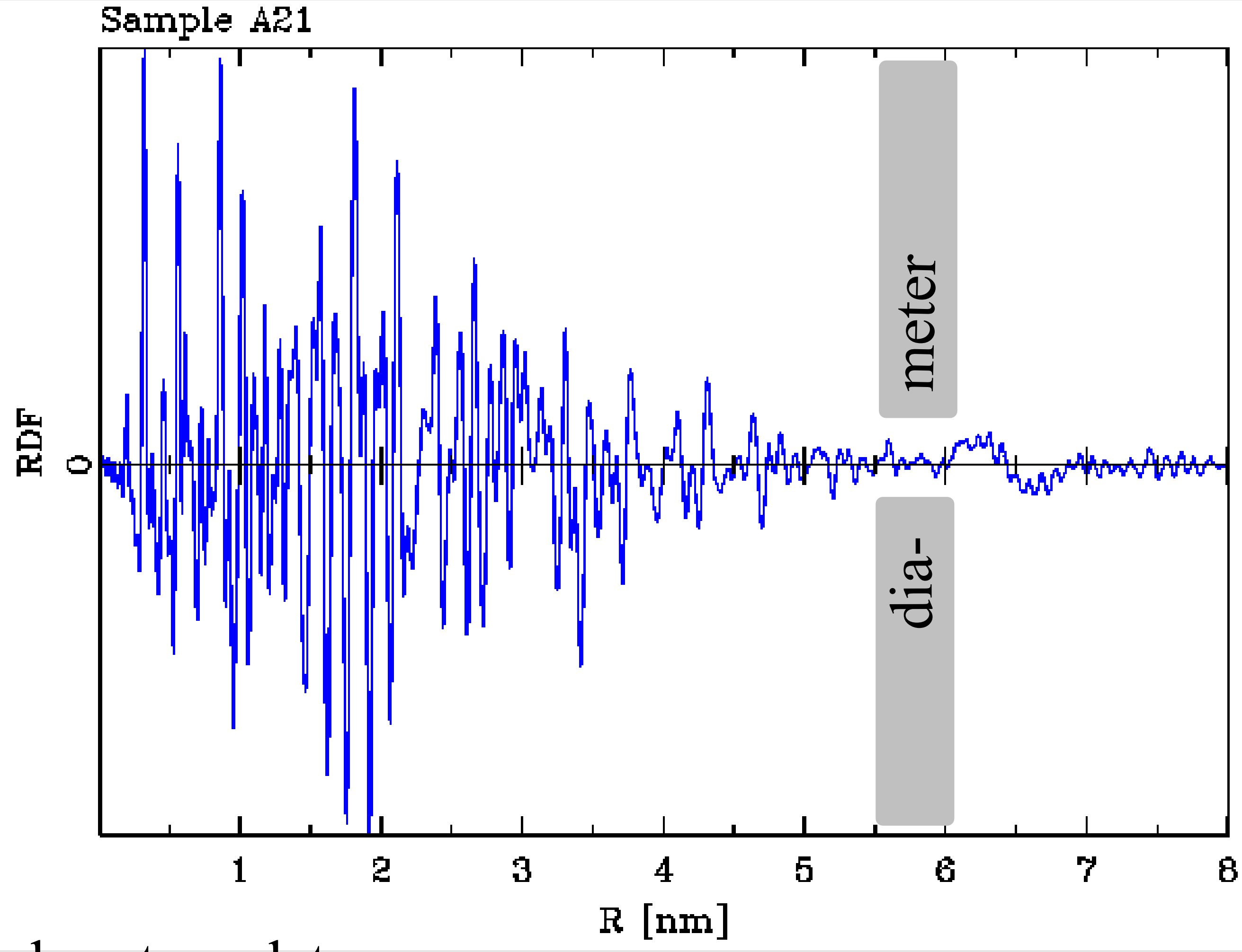
ZnO Pair Distribution Function

simulation based on periodic structure



laboratory data

ZnO Pair Distribution Function



sharp maxima

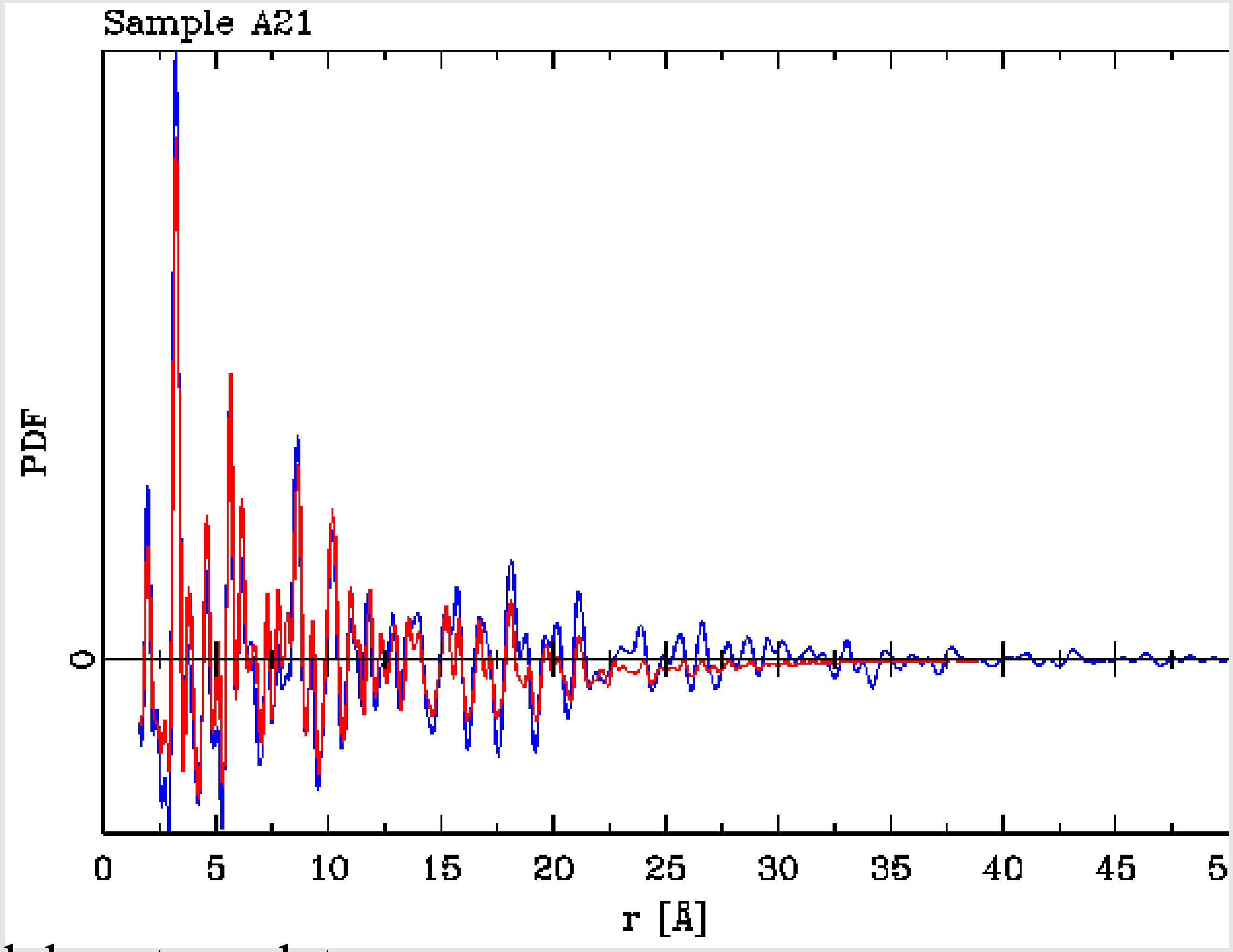
diameter ~ 5.5 nm

single line fit
5.0 nm

Rietveld 3.7 nm

laboratory data

ZnO Pair Distribution Function



laboratory data

prismatic crystals
no stacking faults
a
c
z(O)
B
size

	Rietveld	PDF
a	3.256	3.264
c	5.238	5.250
z(O)	0.3817	0.3836
size	38	63

ZnO Nanoparticles Fitting by Debye

Debye formula :

$$< | F(h) |^2 > = \Sigma_j f_j^2 + \Sigma_i \Sigma_{j,j \neq i} f_i f_j \sin(2\pi h r_{ij}) / (2\pi h r_{ij})$$

$$= N c_J \Sigma_J f_J^2 + 2 \Sigma_I \Sigma_J f_i f_j \Sigma_i \Sigma_{j,j > i} \sin(2\pi h r_{ij}) / (2\pi h r_{ij})$$

ZnO Nanoparticles Fitting by Debye

$$< | F(h) |^2 > = N c_J \Sigma_J f_J^2 + 2 \Sigma_I \Sigma_J f_i f_j \Sigma_i \Sigma_{j, j > i} \sin(2\pi h r_{ij}) / (2\pi h r_{ij})$$

for all atom i
  for all atoms j > i
    compile distance r_{ij} into histogram for type IJ
    compile relative fraction of atoms type I

for all atom pairs IJ
  for all h
    multiply histogram by $\sin(2\pi h r_{ij}) / (2\pi h r_{ij})$ (from lookup table)
    multiply by $2 * f_i f_j$

for all atom type I
  for all h
    add f_i^2 * relative amount