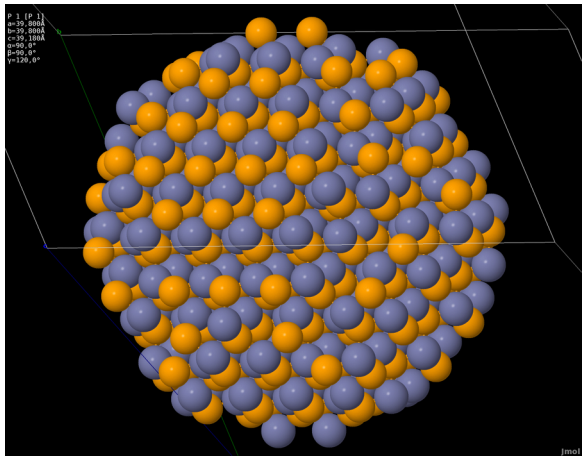
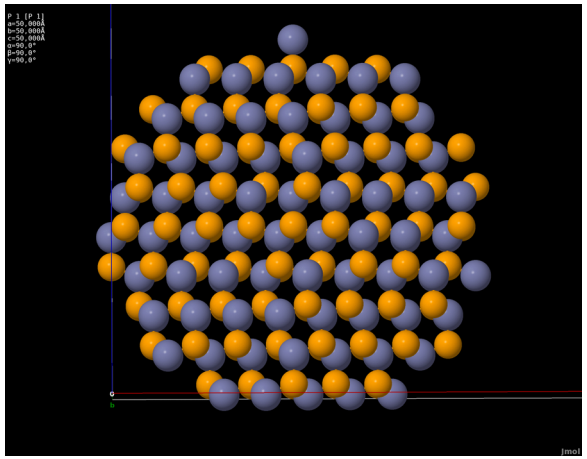


tutorial session VIII

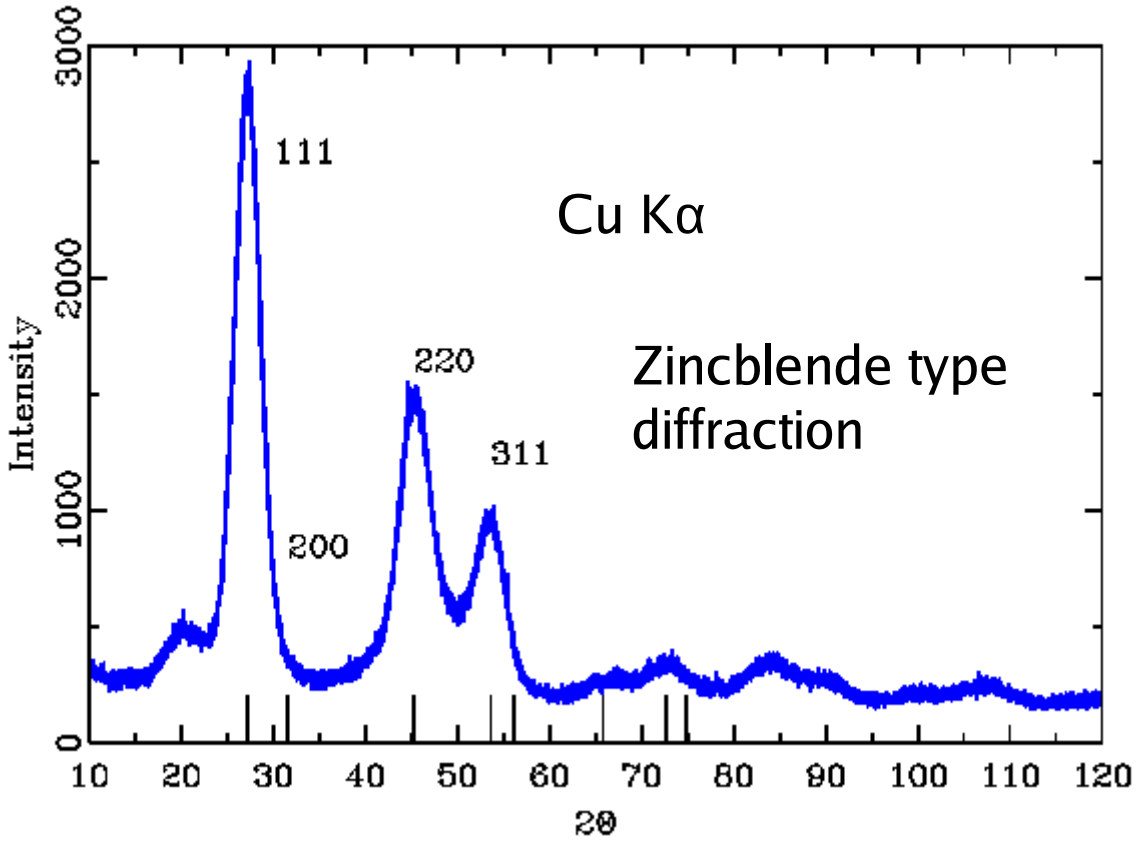
Nanoparticles



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.

Rietveld Refinement: Zincblende Structure

a =4.00 Å

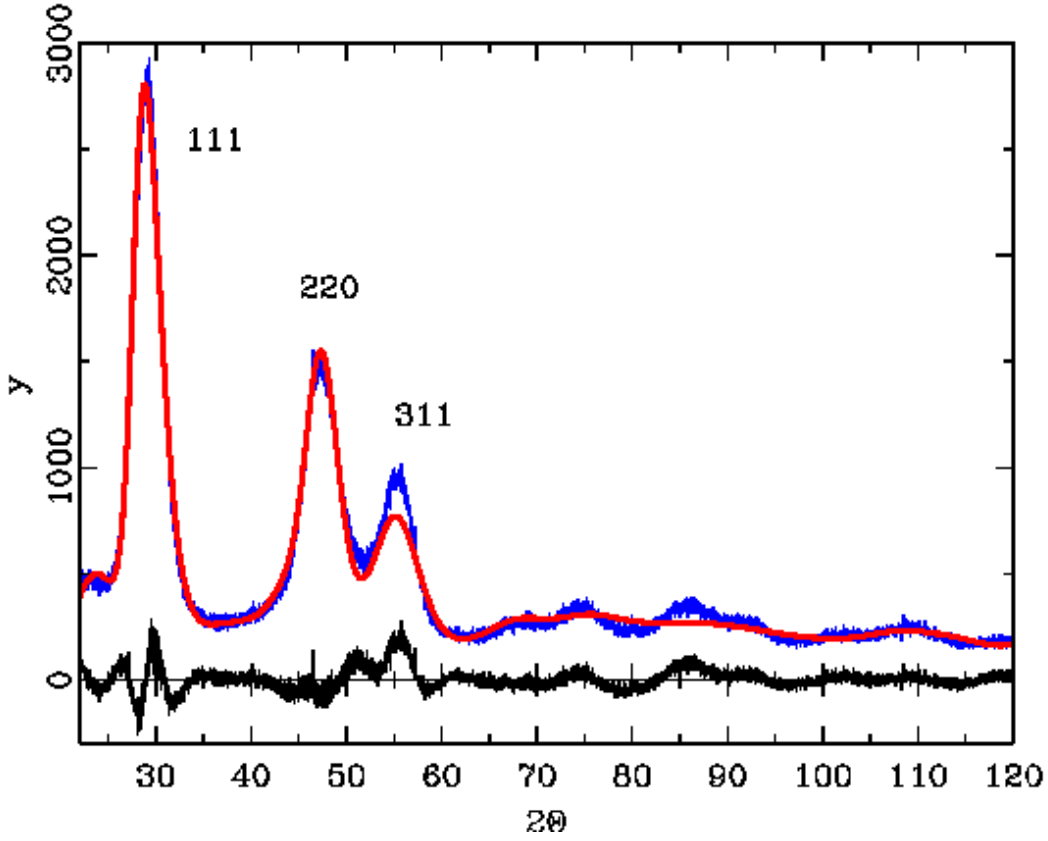
Zn-Se = 2.45 Å

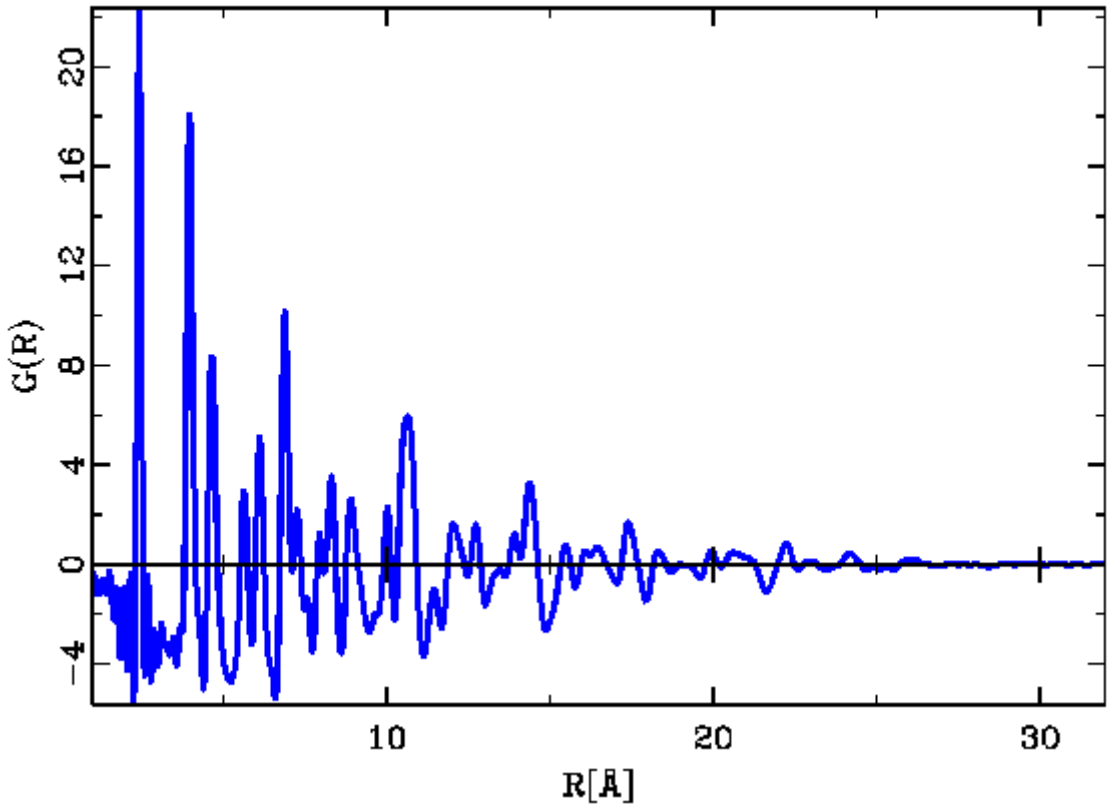
$FWHM_{111}$=3.3

Size ~ 26 Å

R_{wp} =14%

no fit at 311, high order hkl
disordered material





Data collection at BW5, HASYLAB, Germany

$\lambda = 0.1036 Å$

$E = 120$ keV

T = 15 K

capillary, 2.5 mm diameter

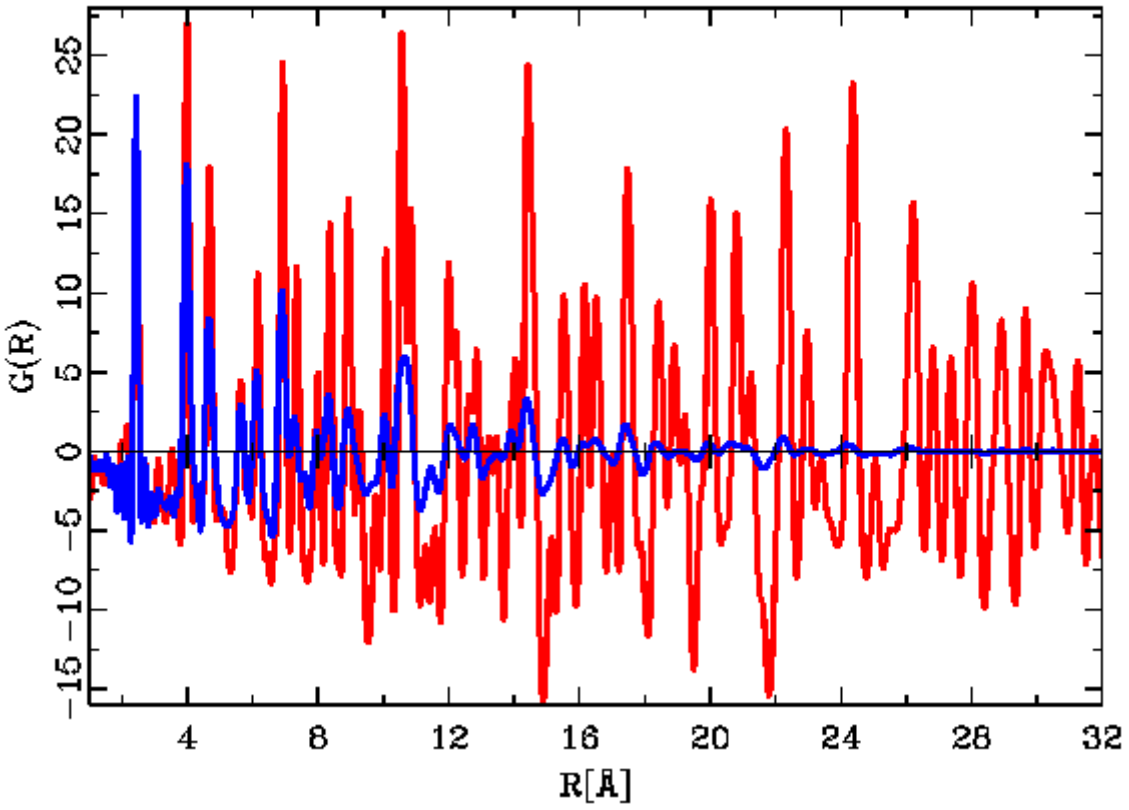
$2\Theta_{max} = 32°$

$$Q_{max} = 2\pi \left(\frac{2\sin(\Theta)}{\lambda} \right)_{max} = 30.85 \, \mathring{A}^{-1}$$

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

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

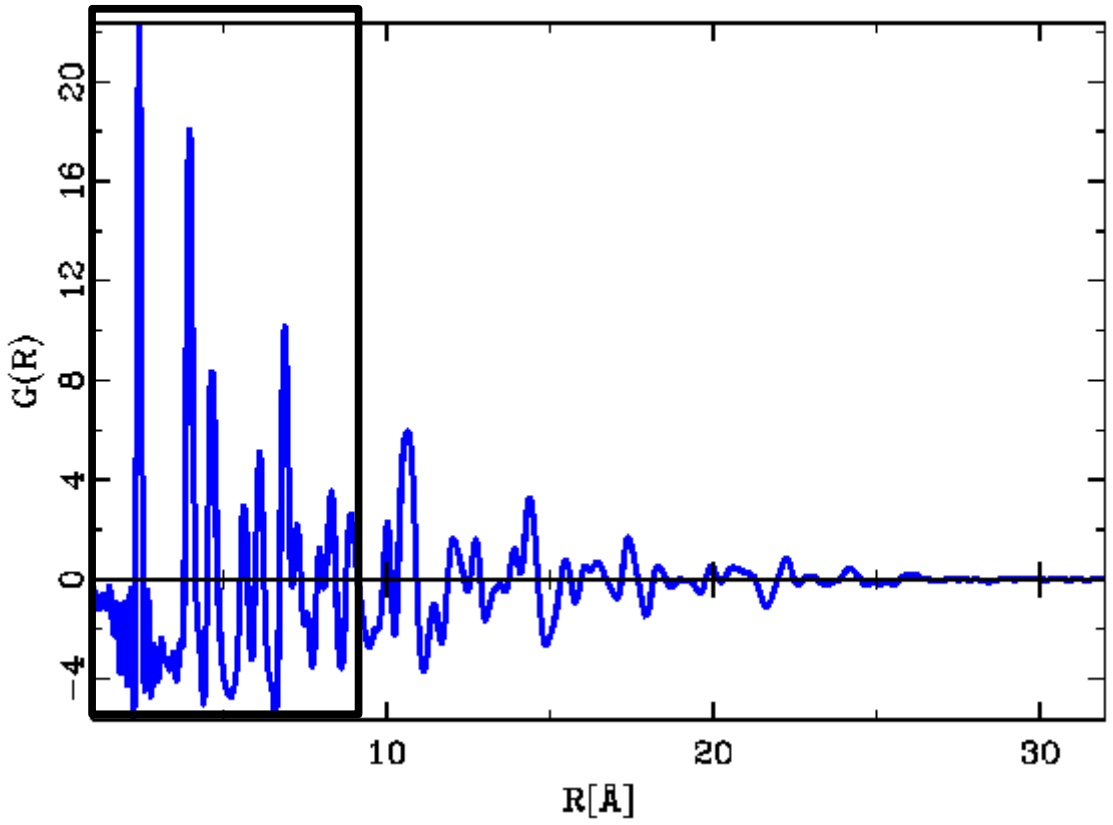
ZnSe experimental PDF; comparison to crystal

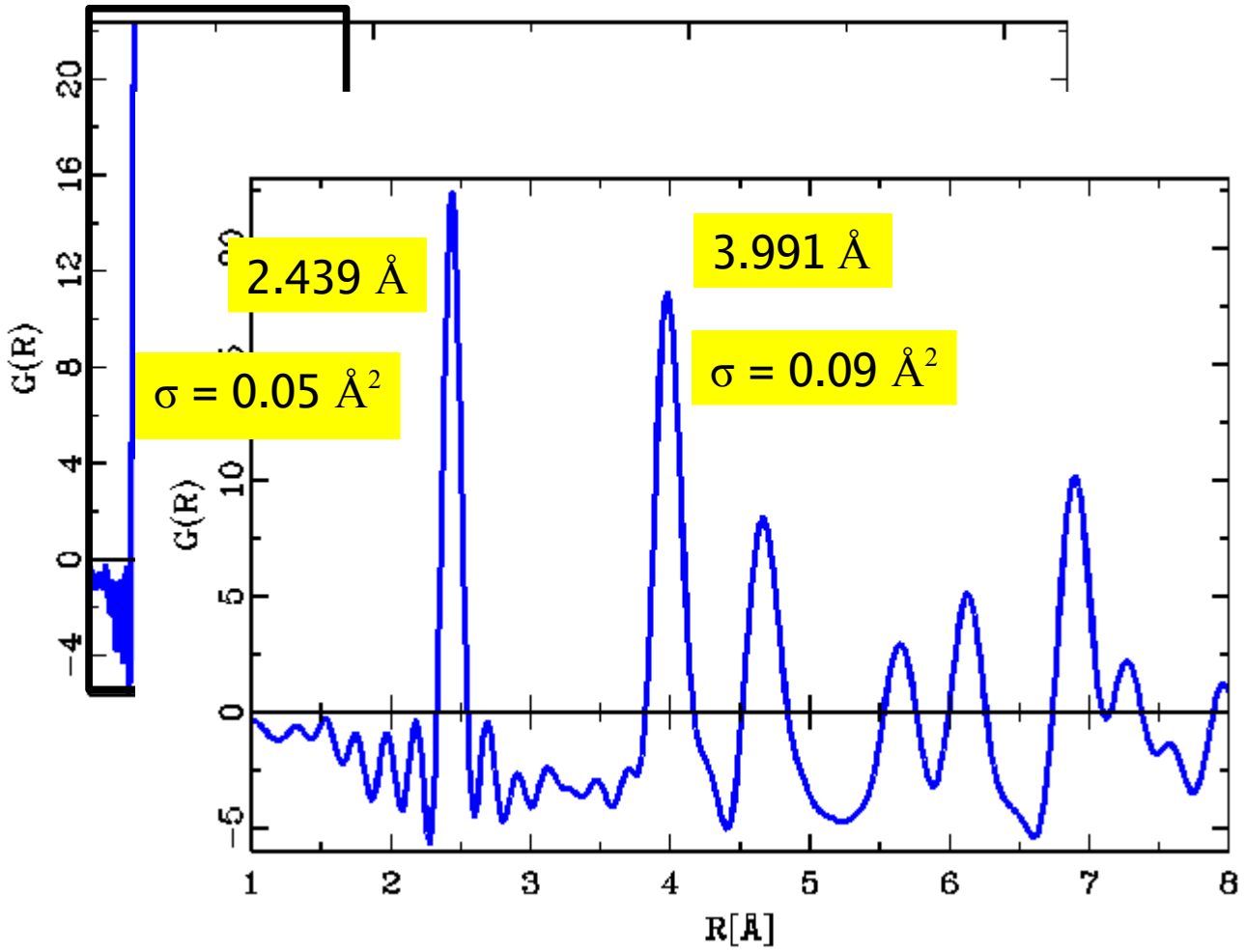


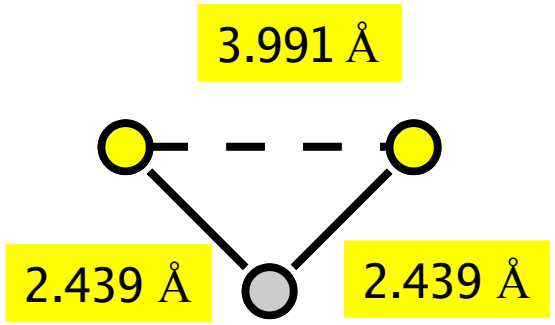
crystalline ZnSe

nanocrystalline ZnSe

identical experimental conditions for both samples

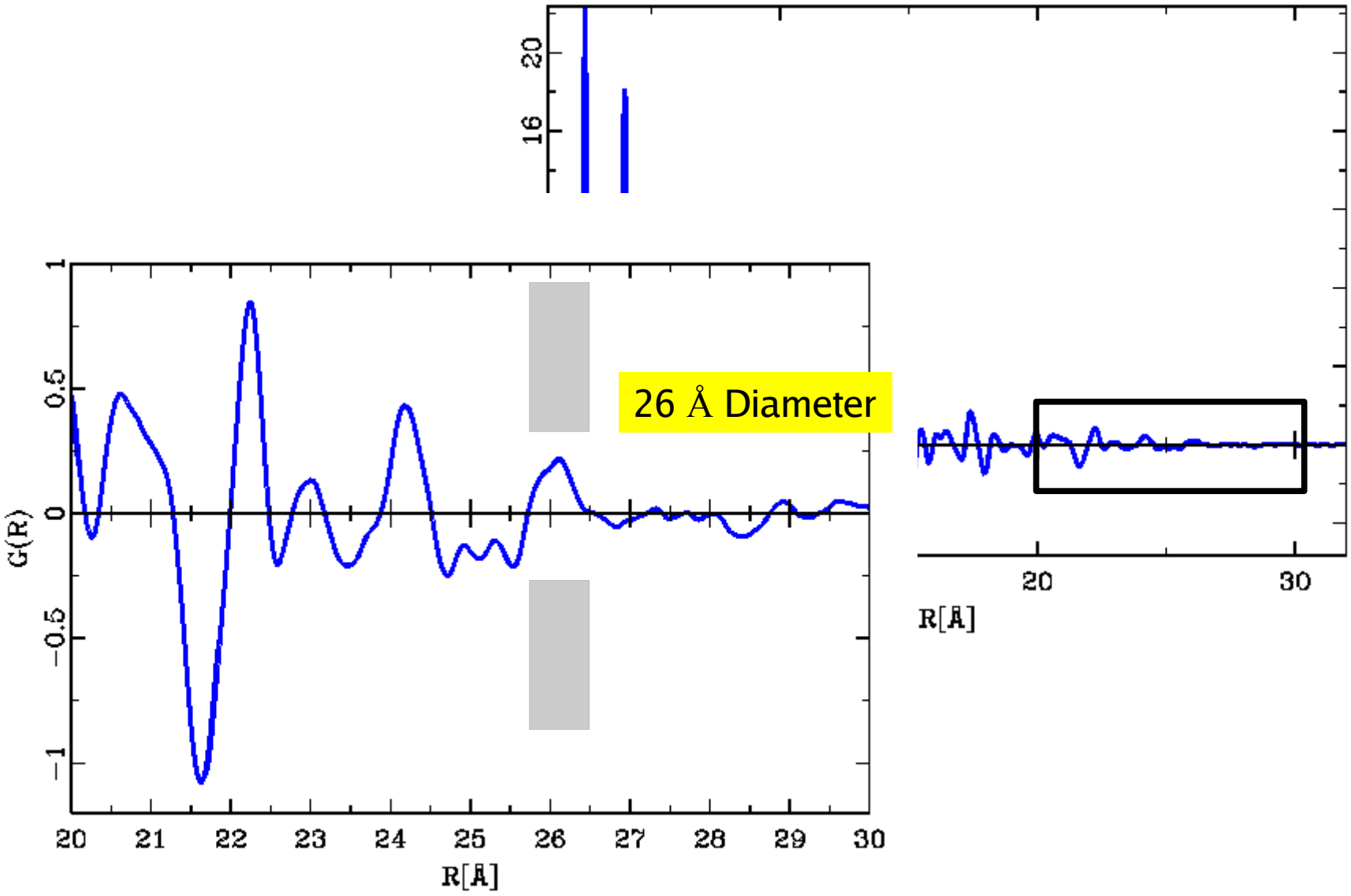

G(R)
20
16
12
8
4
0
−4
10
20
30
R[Å]

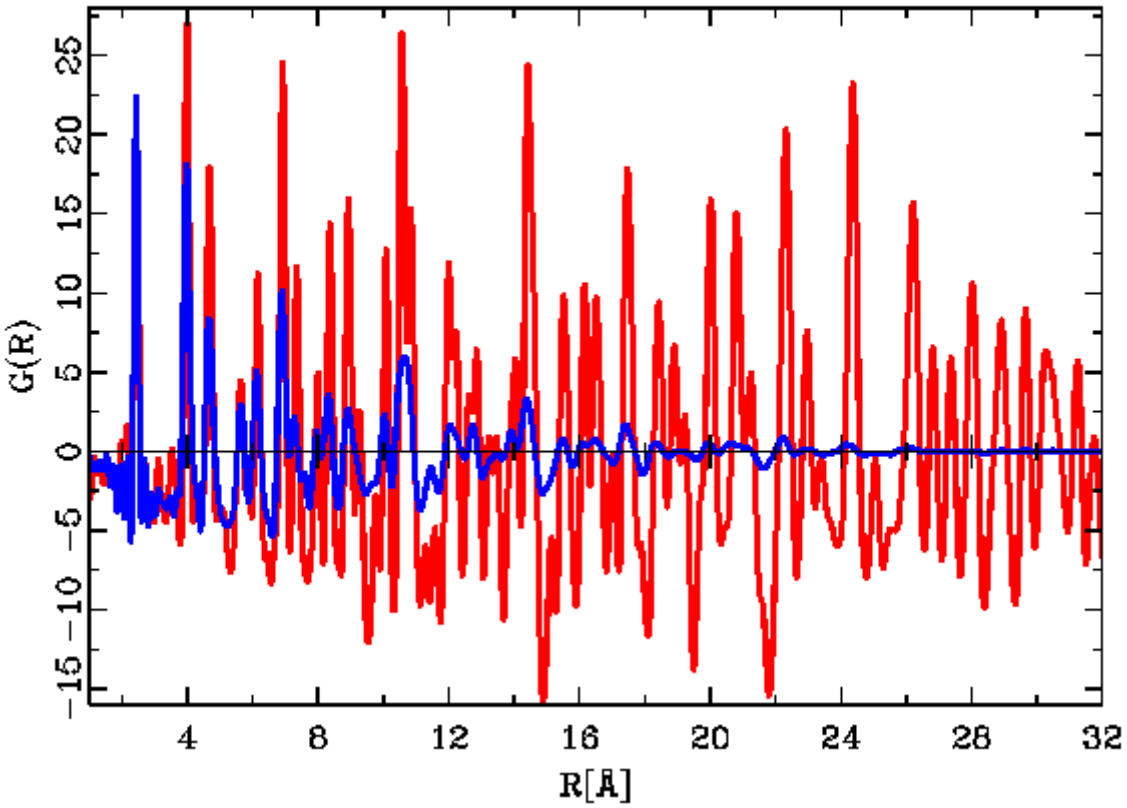




tetrahedral structure

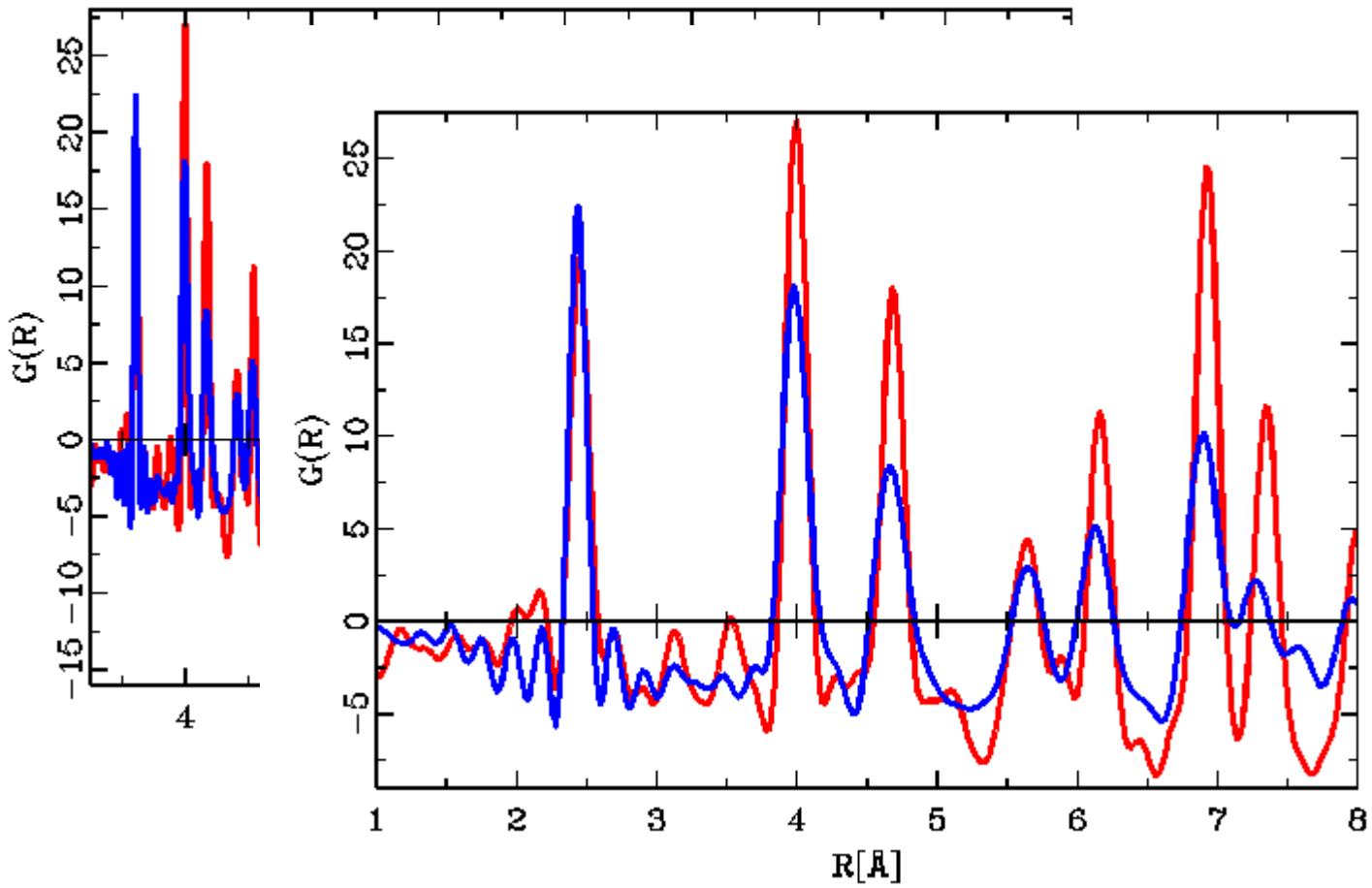
bond angle 109.8


20
16
1
0.5
0
−0.5
−1
G(R)
20
21
22
23
24
25
26
27
28
29
30
R[Å]
26 Å Diameter
20
30
R[Å]



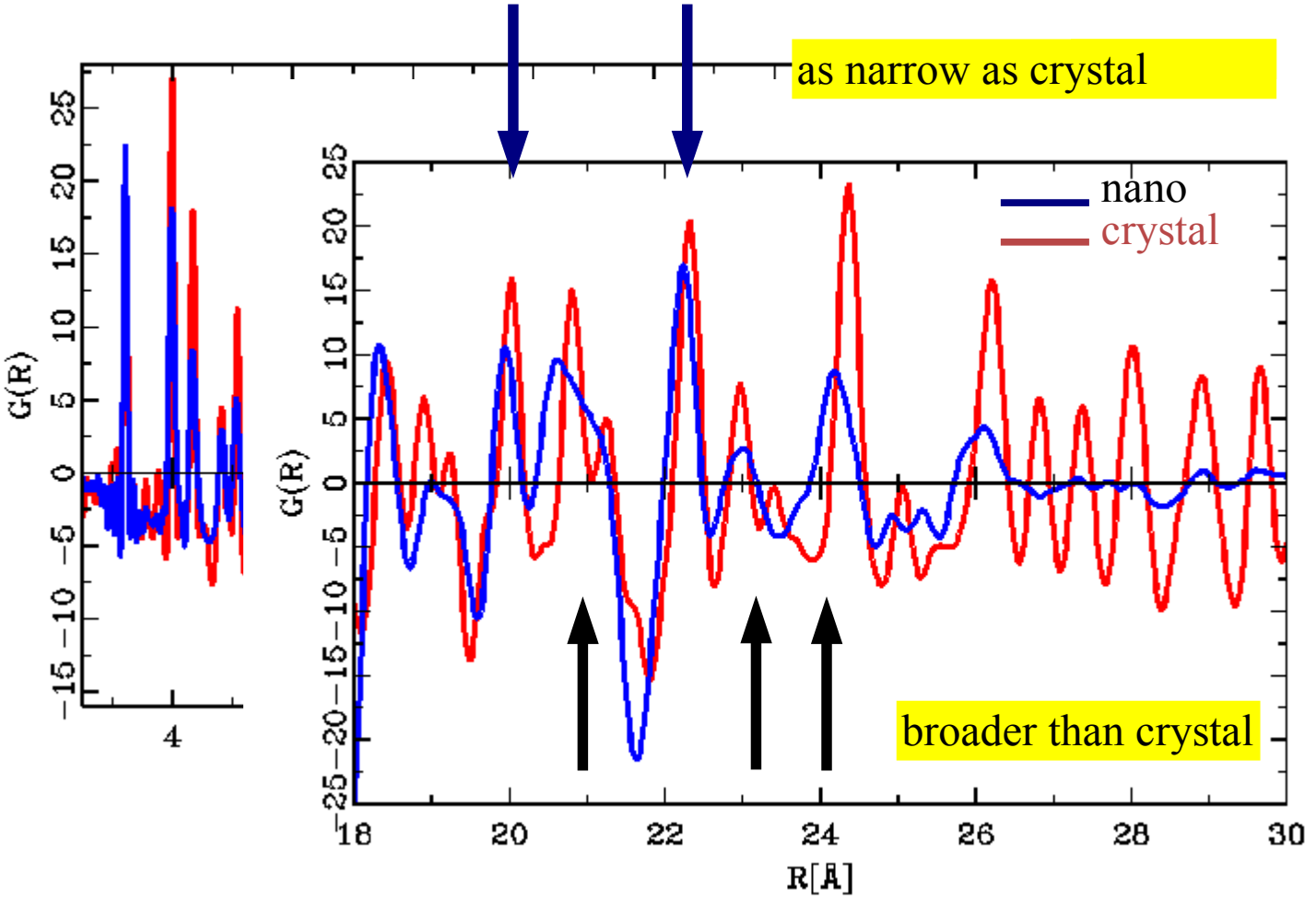
crystalline ZnSe

nanocrystalline ZnSe

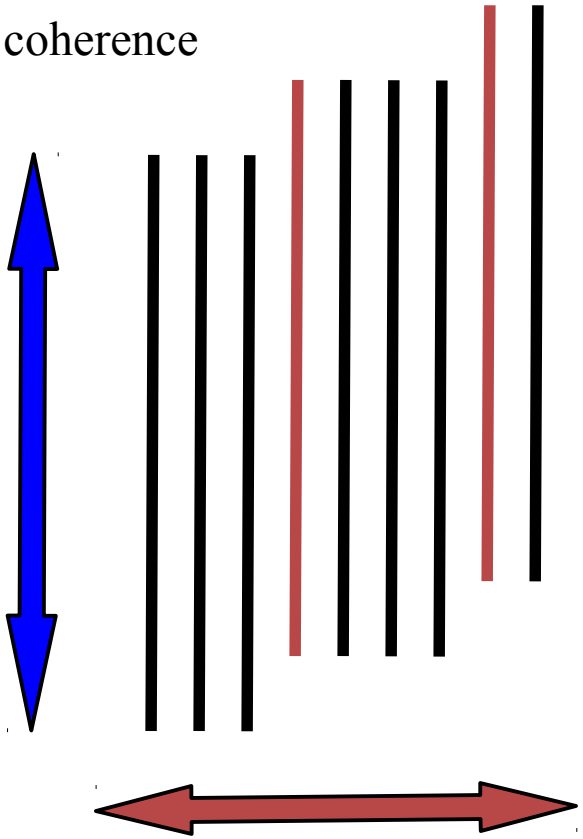


2.439 Å σ = 0.05 Å^2 3.991 Å σ = 0.09 Å^2

2.450 Å σ = 0.05 Å^2 3.999 Å σ = 0.06 Å^2

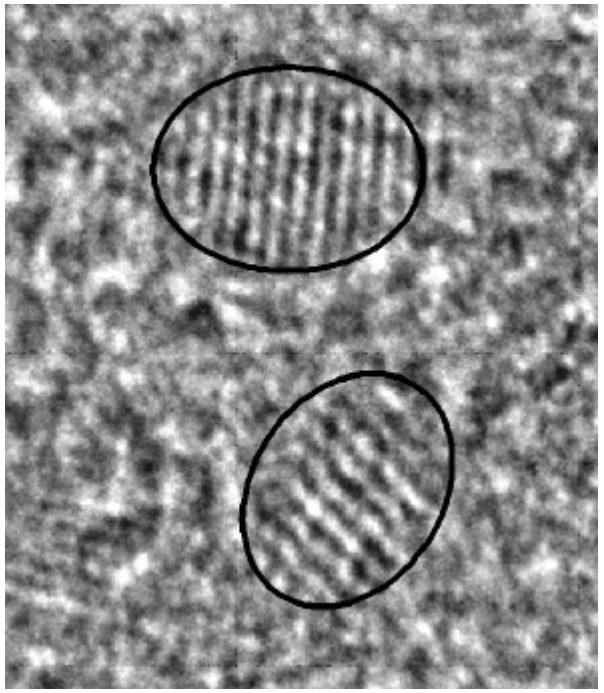

as narrow as crystal
nano
crystal
broader than crystal
G(R)
R[Å]
18
20
22
24
26
28
30
4
20/22 Å narrow distribution
21 Å broad distribution

structural coherence

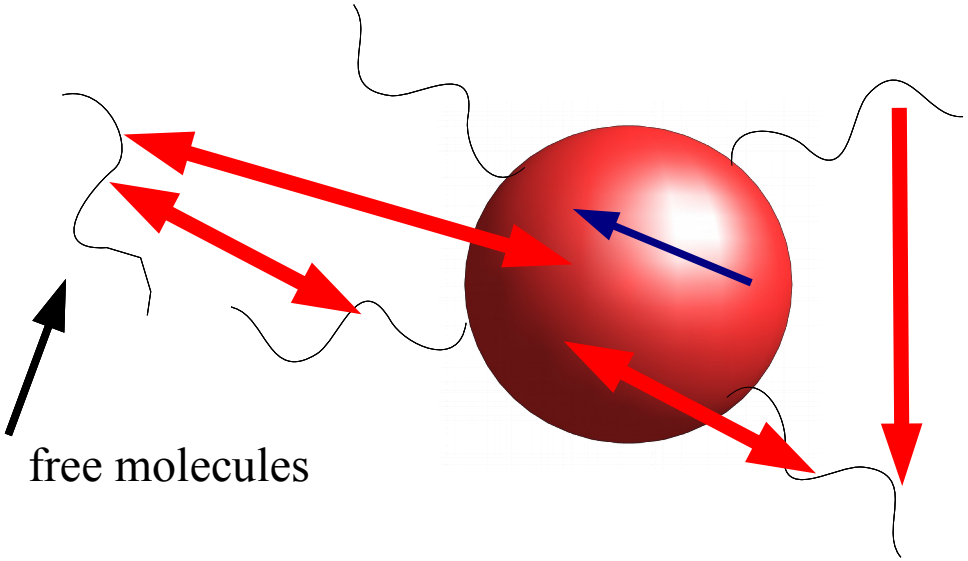


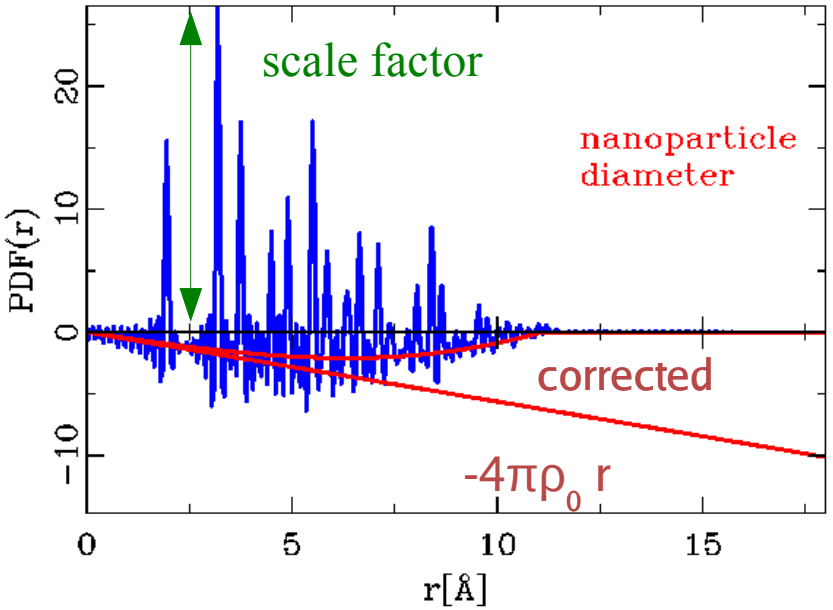
loss of coherence due
to stacking faults

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



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

Simulate a crystal of N*M*O cells

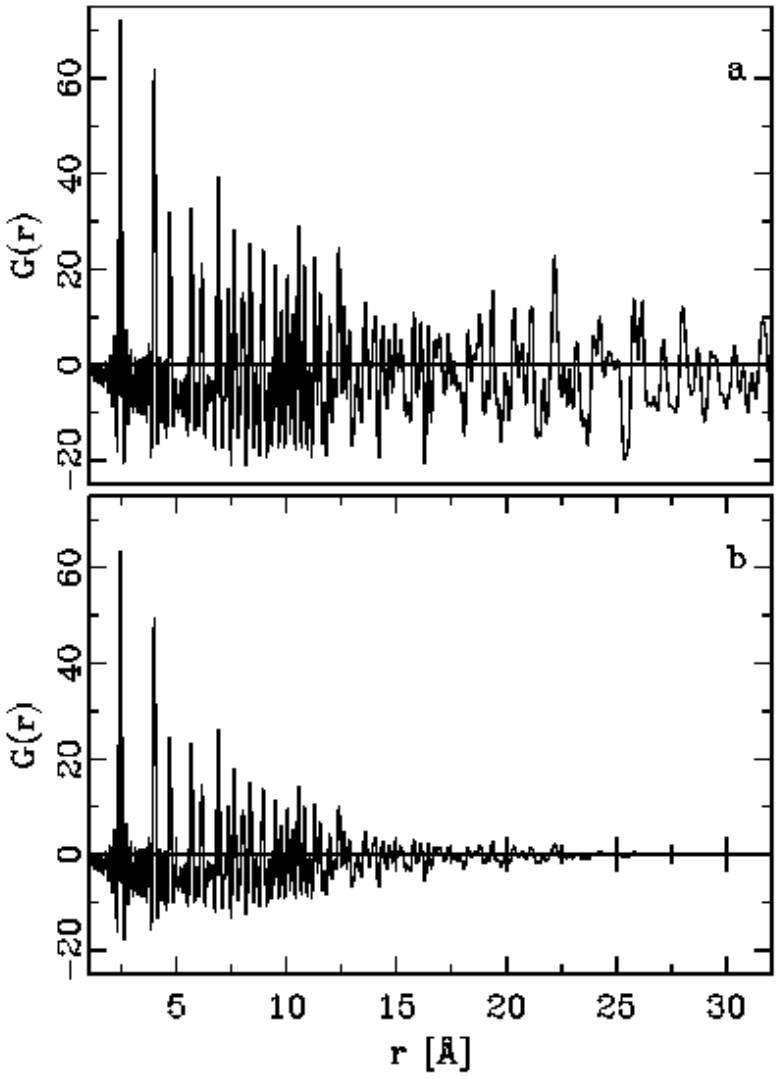
calculated PDF with periodic boundary conditions
multiply PDF by suitable shape function

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

Simulate a finite nanoparticle

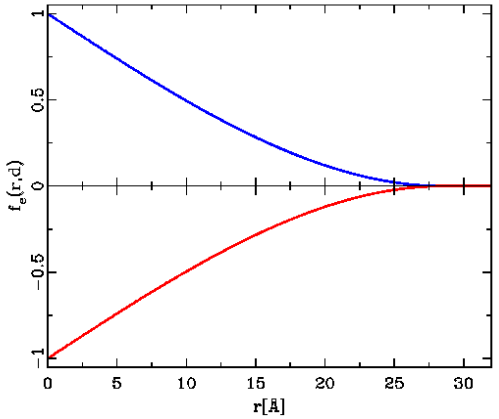
calculate PDF from finite model
correct shape of $-4 \pi \rho_0 r$ line

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



PDF 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

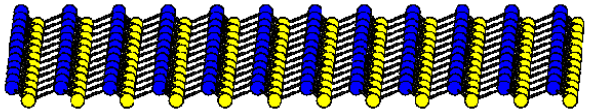
limited to basic shapes

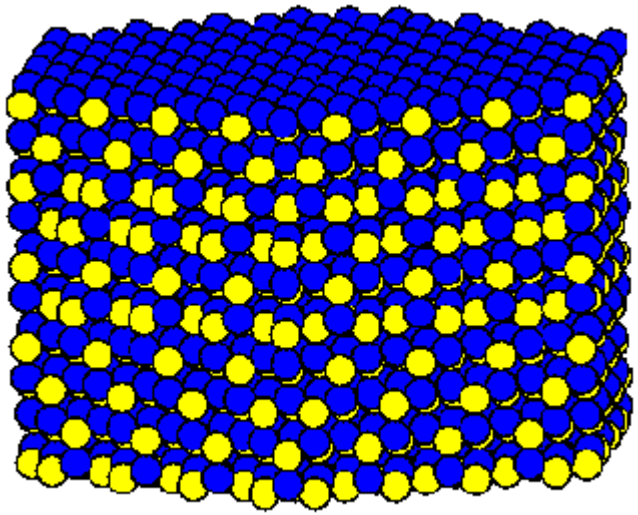
treats two different effects!

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)





{110} and {001}

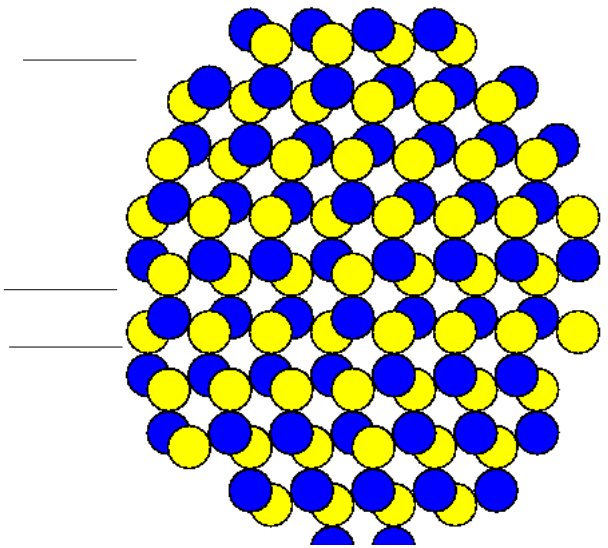
create a large single Wurtzite layer A/B

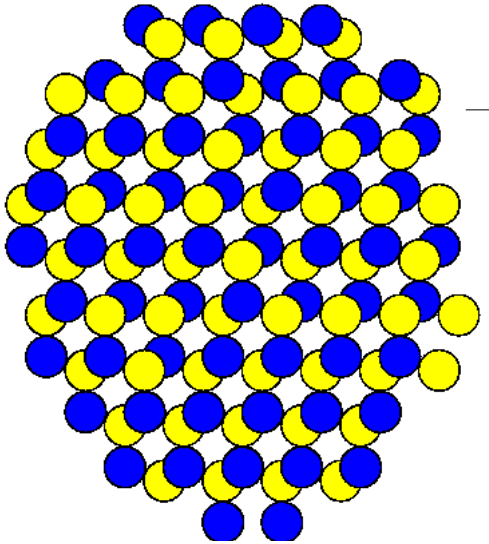
Stack along c (with faults)

Cut to proper size

Calculate PDF / powder pattern

Repeat and average

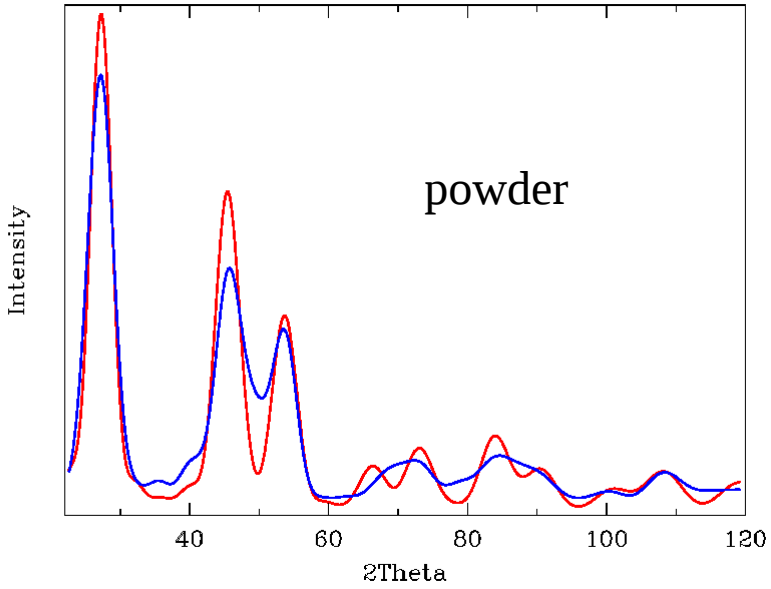


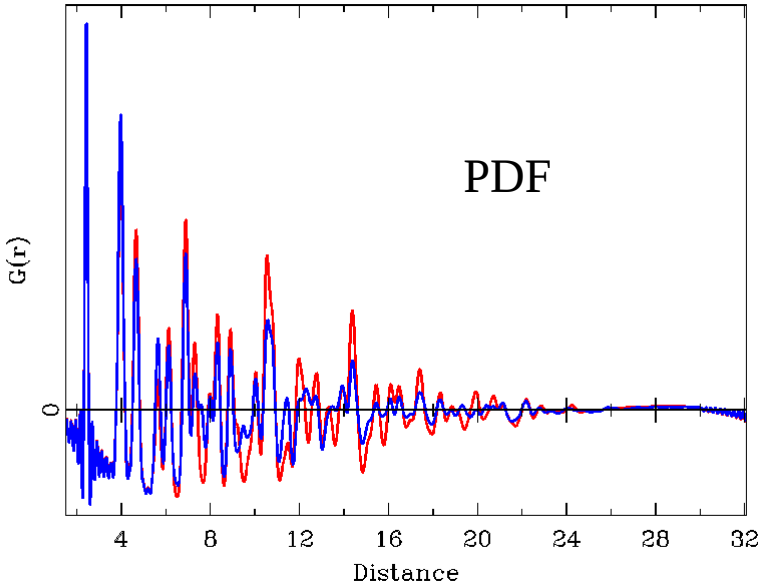


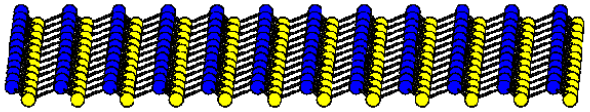
10 layers
simulated with
identical parameters

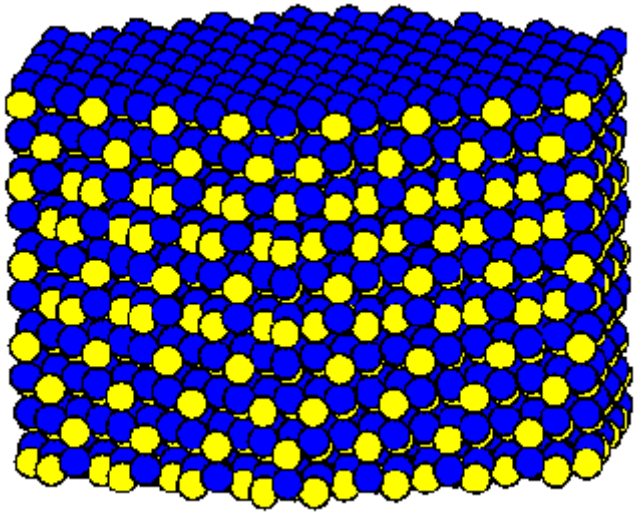
individual location
of stacking faults

each particle is not
representative
==> **need to average**









{110} and {001}

create a large single Wurtzite layer A/B

Stack along c **(with faults)**

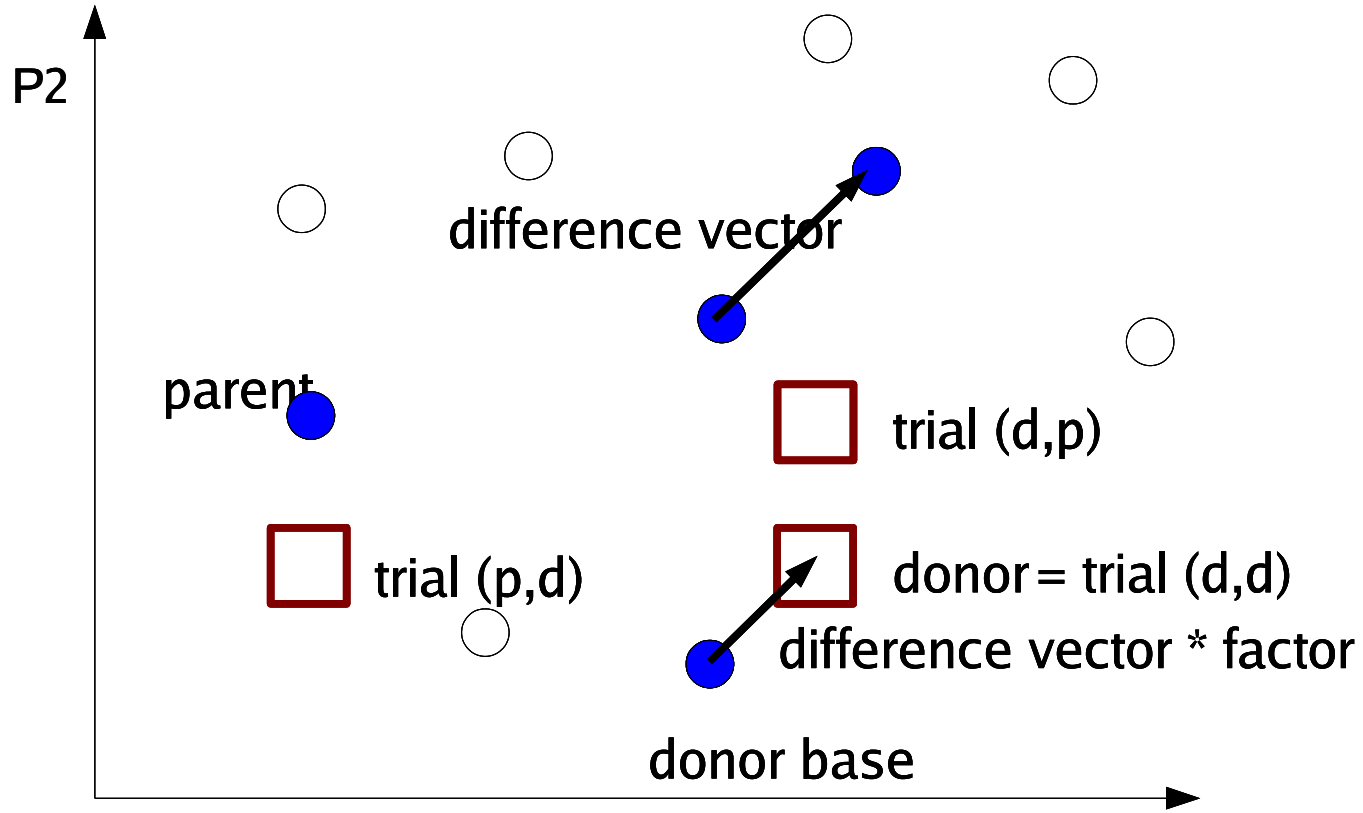
Cut to proper size

Calculate PDF / powder pattern

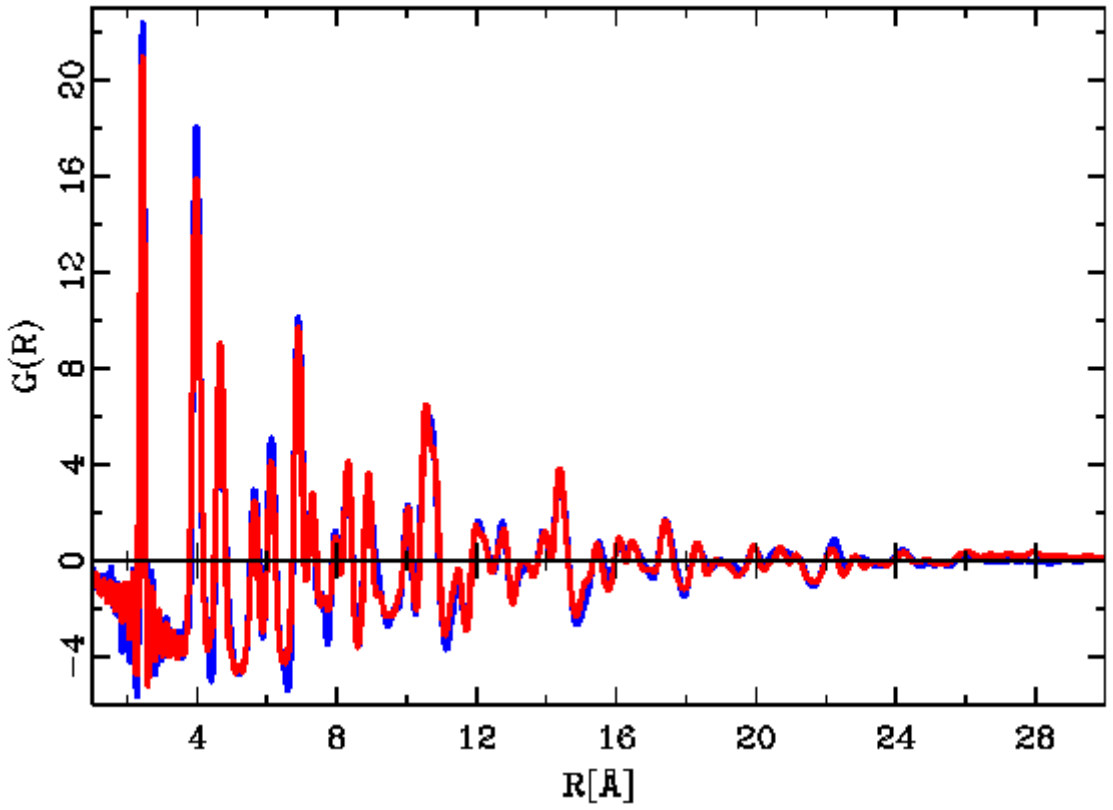
Repeat and **average**

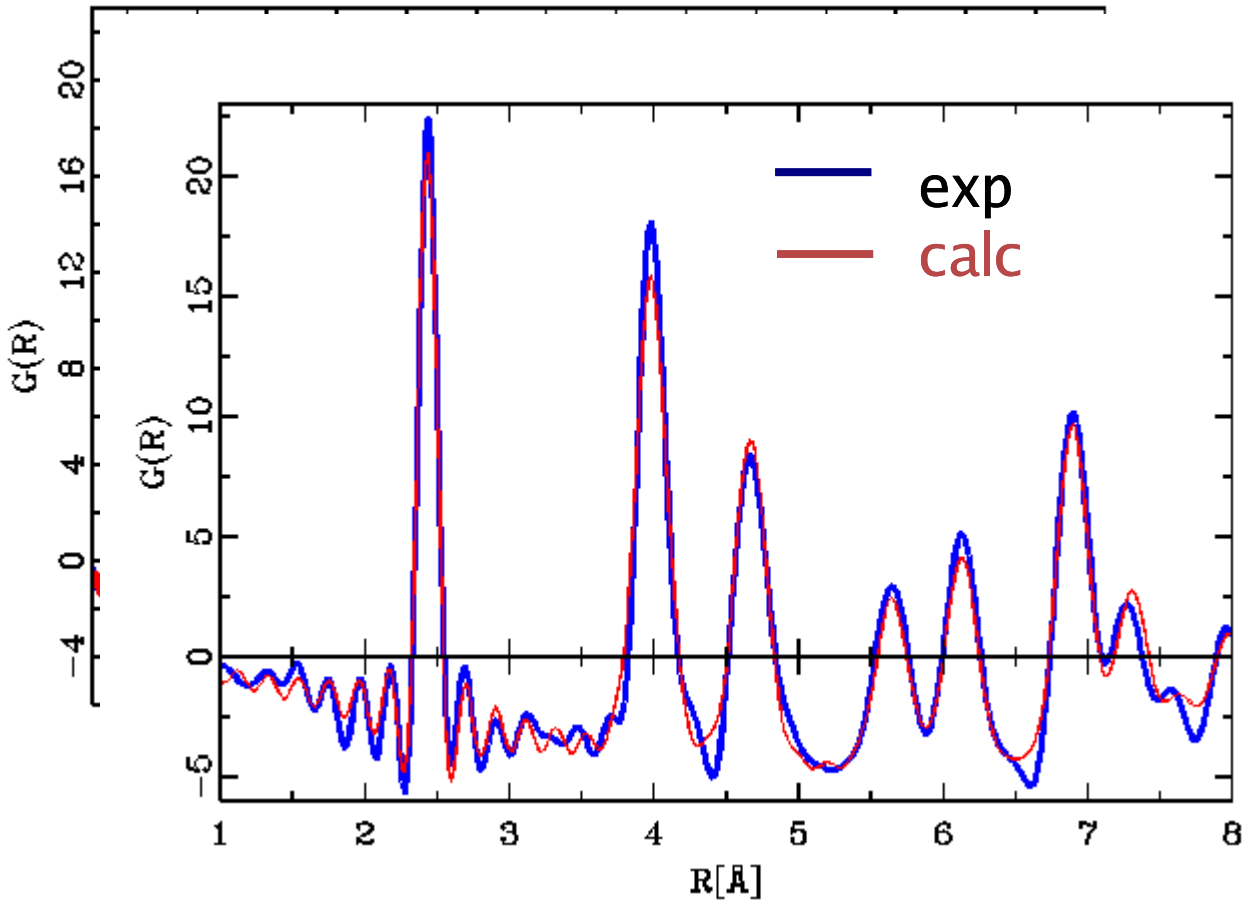
Repeat with new set of parameter

using a Differential Evolutionary Scheme



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


G(R)
20
16
12
8
4
0
−4
4
8
12
16
20
24
28
R[Å]



a 3.987 Å
c 6.493 Å

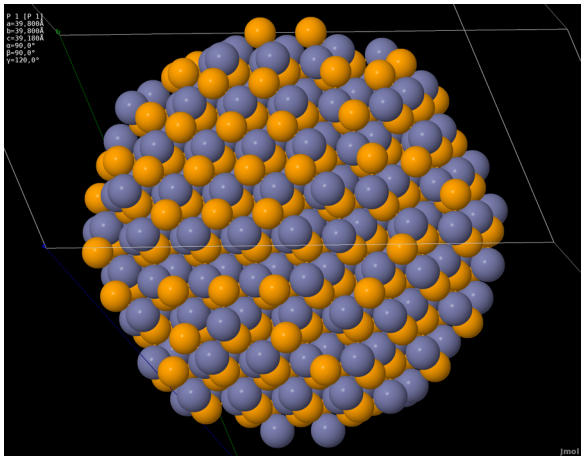
ideal tetrahedron
Zn-Se = 2.45(1) Å

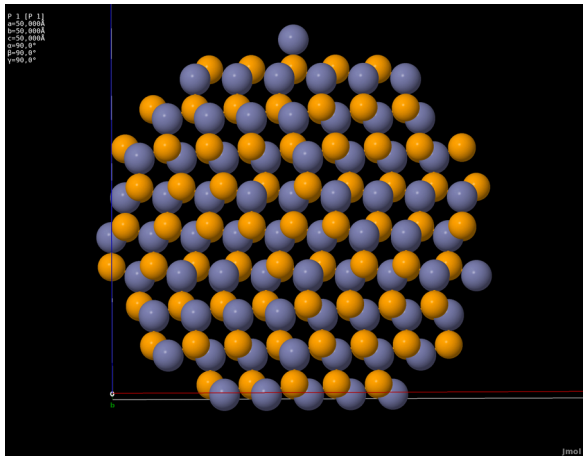
size a-b= 24(2) Å
size c = 31(2) Å

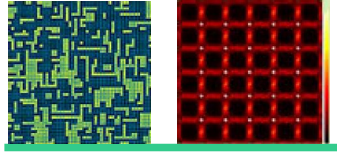
ratio d_c/d_{ab} = 1.2
elliptical shape

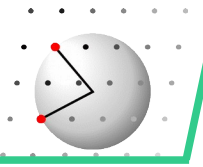
No distinction: prismatic vs spherical crystal

Stacking fault:
0.7







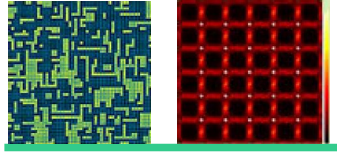


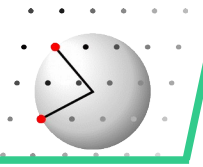
start discus_suite
change to directory Lectures/08.Nanoparticle_example/SIMPLE

run macro nano.mac with different radii as input parameter:

discus> **@nano 10**

start jmol
and plot the nanoparticle
nano.cif





start discus_suite
change to directory Lectures/08.Nanoparticle_example/ELLIPSOID
run macro nano.mac with different radii as input parameter:

discus> **@nano 10, 50**

start jmol
and plot the nanoparticles
PLOT/block_10.0_50.0.cif
PLOT/sheared_10.0_50.0.cif
PLOT/sphere_void_10.0_50.0.cif
PLOT/unsheared_10.0_50.0.cif
PLOT/nano_10.0_50.0.cif

make sure you have three „Terminal“ windows open

change to directory $HOME/08.Nanoparticle_example/ELLIPSOID

start discus and kuplot in the second window

run macro nano.mac with two different radii as input parameter:

discus> @nano 10.0, 20.0

in kuplot run macro knano.mac :

kuplot > @knano 10.0, 20.0

in the third window, start jmol
and plot the nanoparticle nano_10.0_20.0.cif