X-ray Diffraction

- Basic aspects of x-ray crystallography and powder diffraction

- Diffraction from nanocrystalline materials

Paolo.Scardi@unitn.it
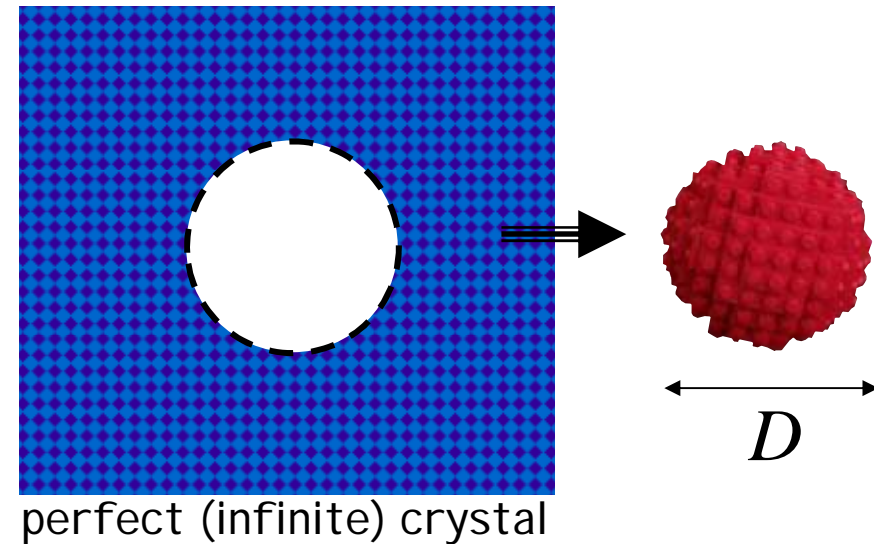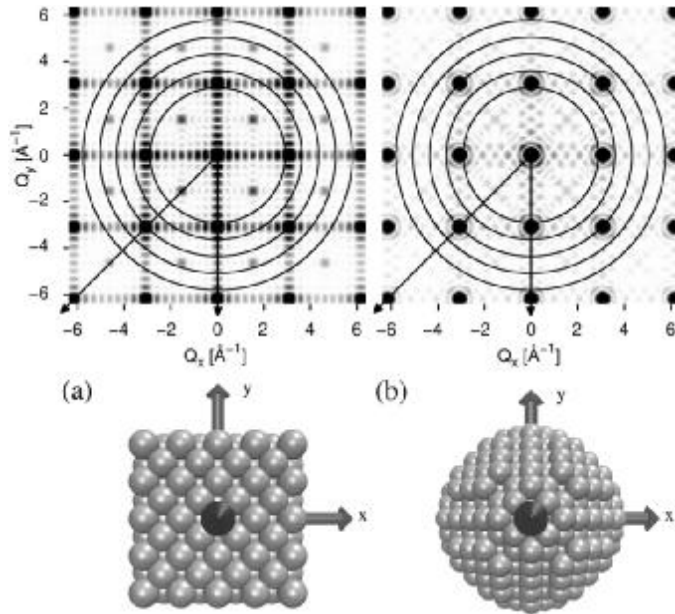
FROM SINGLE CRYSTAL TO POWDER DIFFRACTION

1. Traditional reciprocal space approach : sum & average

perfect (infinite) crystal

$$I_{sc}(\underline{s}) \propto \sum_m \sum_n f_m f_n^* e^{2pi(\underline{S}\cdot\underline{r}_{mn})}$$

$$I_{PD}(s) \propto \frac{\int I_{sc}(\underline{s})d\Omega}{4ps^2} = |F|^2 \left\{ I^{IP}(s) \otimes I^S(s) \otimes I^D(s) \otimes I^F(s) \otimes I^{APB}(s) \otimes I^C(s) \otimes I^{GRS}(s)... \right\}$$
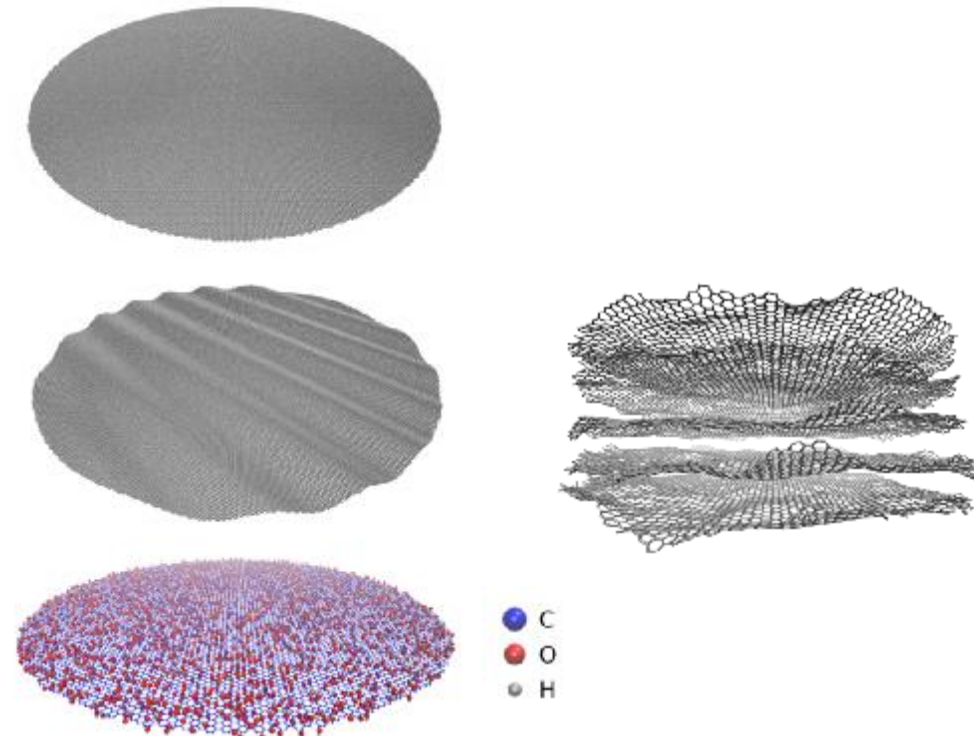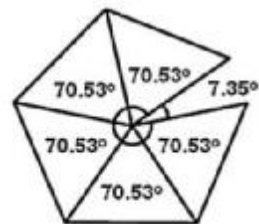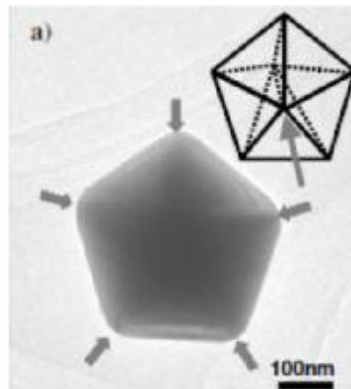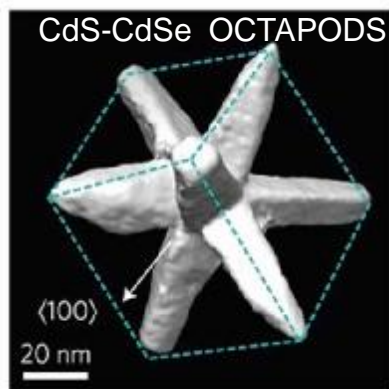
DIFFRACTION FROM NANOCRYSTALLINE MATERIALS

L real nanocrystals are complex objects

non-crystallographic (e.g. multiply twinned) nanoparticles, 2D and highly disordered layer systems:

Ø translational symmetry: not verified

Ø large strain / misfit – complex local atomic arrangement
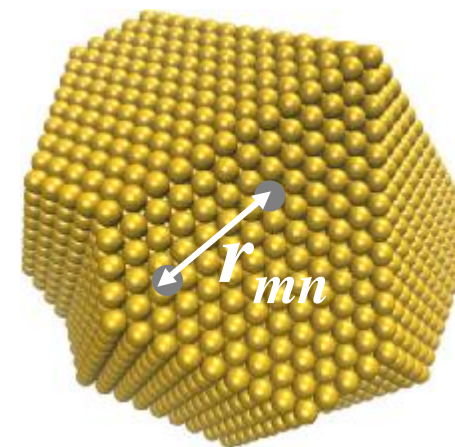
P. Scardi – Diffraction from nanocrystalline materials

2. Direct (real) space approach : average & sum

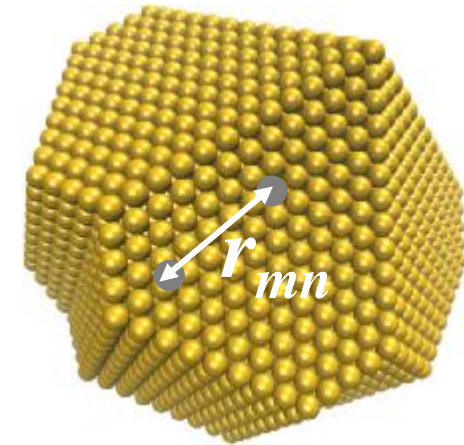$$I_{PD}(s) = \frac{|f|^2 \int \sum_m \sum_n e^{2pi(\underline{s} \cdot \underline{r}_{mn})} d\Omega}{4p\,s^2}$$

DIFFRACTION FROM NANOCRYSTALLINE MATERIALS

2. Direct (real) space approach : average & sum

$$I_{PD}(s) = \frac{|f|^2 \sum_m \sum_n \int e^{2pi(\underline{s} \cdot \underline{r}_{mn})} d\Omega}{4ps^2}$$

$$\left\langle e^{2pi(\underline{s} \cdot \underline{r}_{mn})} \right\rangle = \frac{1}{4pr_{mn}^2} \int_0^p e^{2pisr_{mn}\cos f} 2pr_{mn}^2 \sin f \, df = \frac{\sin(2psr_{mn})}{2psr_{mn}}$$
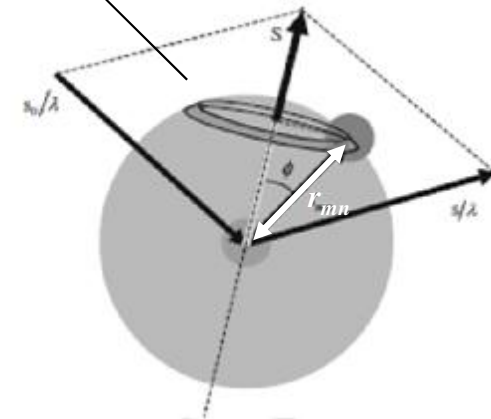
$$I_{PD}(s) = |f|^2 \sum_m \sum_n \frac{\sin(2psr_{mn})}{2psr_{mn}}$$

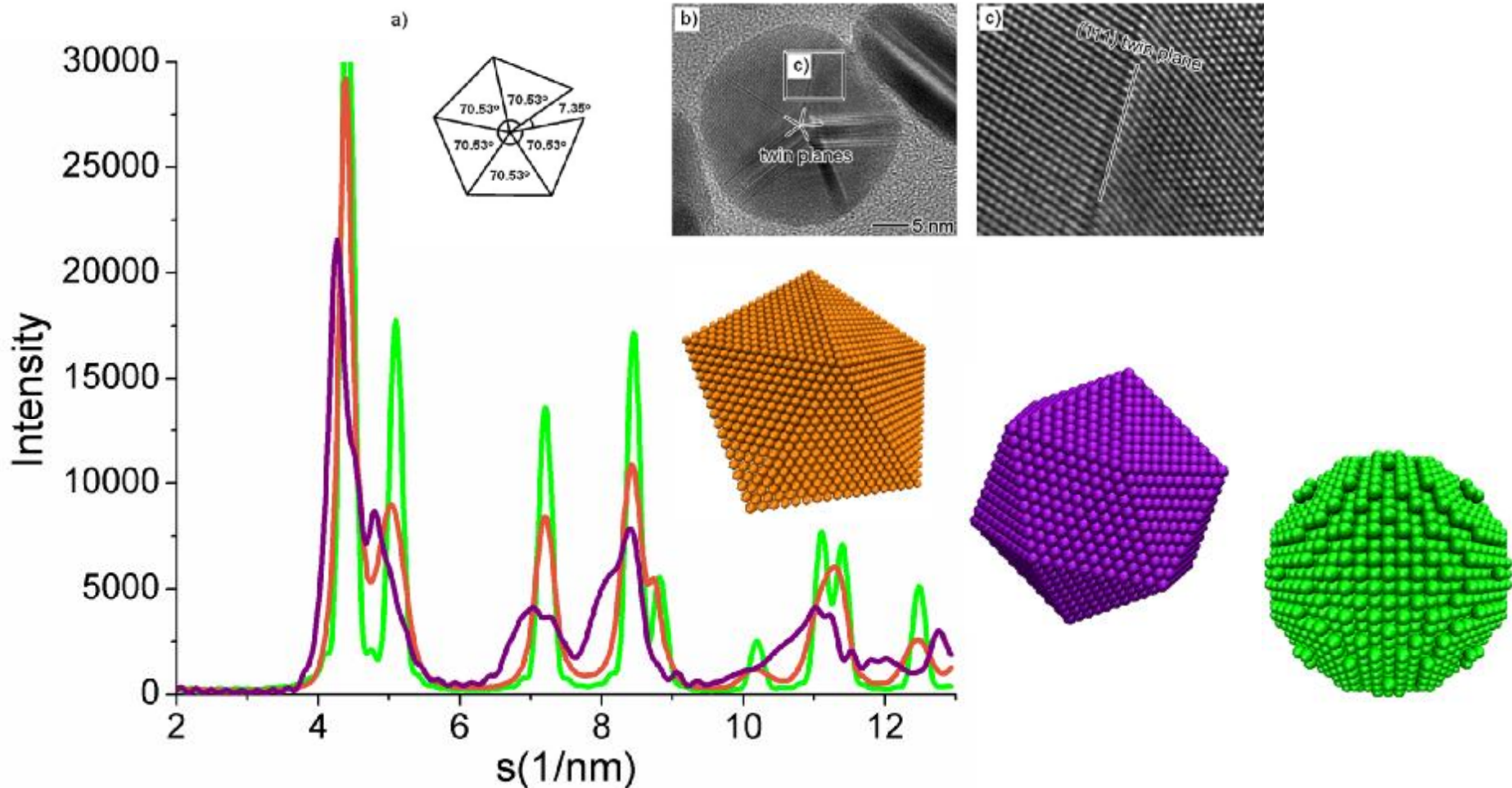Debye Scattering Equation (DSE)

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$$I_{PD}(s) = |f|^2 \sum_m \sum_n \frac{\sin(2p\,sr_{mn})}{2p\,sr_{mn}}$$

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$$I_{PD}(s) = |f|^2 \sum_m \sum_n \frac{\sin(2p\, sr_{mn})}{2p\, sr_{mn}}$$

Figure 7
Powder patterns for graphene disks of diameter $D = 500$ Å. Regular, flat graphene (bottom), undulate graphene (middle) and graphene with a random roughness (top). See text for details.

L. Gelisio et al., J. Appl. Cryst. 43 (2014) 647

Debye Scattering Equation (DSE)

$$I_{PD}(s) = |f|^2 \sum_m \sum_n \frac{\sin(2p\,sr_{mn})}{2p\,sr_{mn}}$$

L. Gelisio, PhD Thesis, Univ. of Trento, 2014

— swCN(10,5) L = 25 nm

Carbon nanotubes

Debye Scattering Equation (DSE)

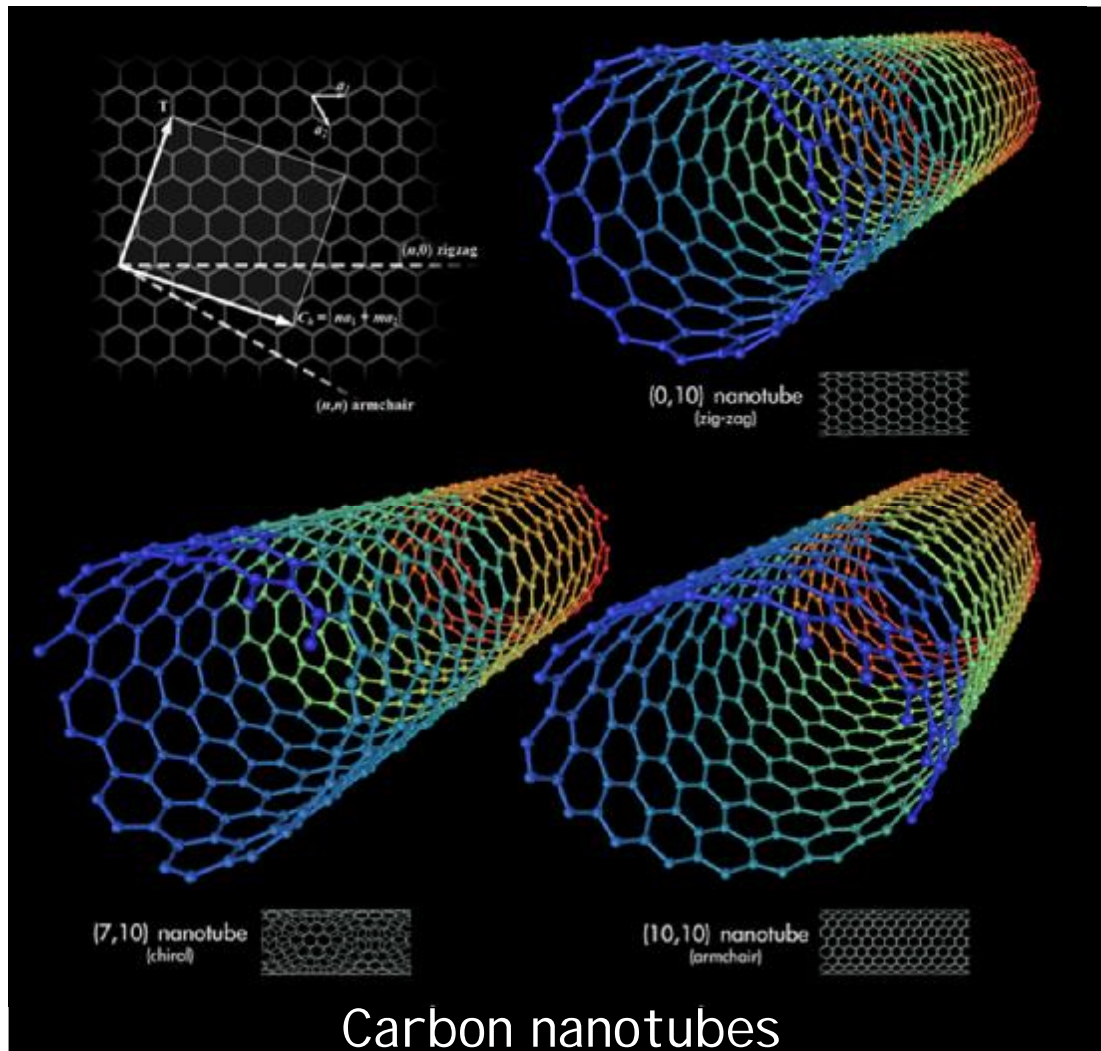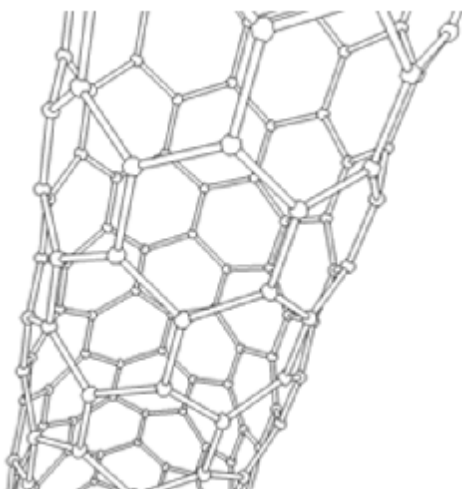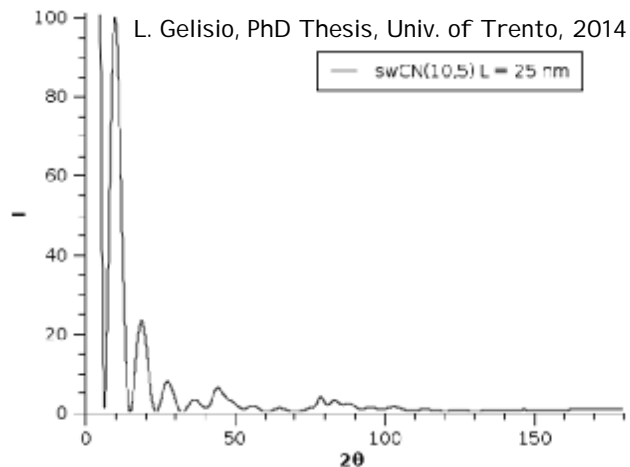$$I_{PD}(s) = |f|^2 \sum_m \sum_n \frac{\sin(2\pi s r_{mn})}{2\pi s r_{mn}} \equiv |f|^2 \sum_{mn} B_{mn} \frac{\sin(2\pi s r_{mn})}{2\pi s r_{mn}}$$

Atomic distance histogram (B_{mn}) for a cubic crystal with 8x8x8 sc unit cells (a) and corresponding powder pattern according to $I_{PD}(s)$, with f=1, unit cell parameter, a_0=0.361 nm (b).
P. Scardi & L. Gelisio, "Diffraction from nanocrystalline materials", Chapter XVIII in Synchrotron Radiation, ed. S. Mobilio et al. Springer 2015.

In the coming months, look for a special issue of Acta Crystallographyca A, edited by Billinge, Cervellino, Neder & Scardi
Total Scattering methods – the 100 Years of the Debye Scattering Equation (DSE2015 conference, Cavalese (I) June 2015)

Zernike & Prins (1927): for amorphous specimens, volume *V*, *N* atoms, the *radial distribution function* (RDF) is:

$$RDF(r) = 4pr^2r(r) \cong 4pr^2r_0 + 8pr\int_0^\infty s\left[\frac{I(s)}{Nf^2} - 1\right]Sin(2psr)ds$$

intensity in absolute units:

$$\left[\frac{I(s)/N - f^2}{f^2}\right] \rightarrow = \left[\frac{(a-d)-c}{c}\right]$$

f^2
$i(M)$ (*Compton*)
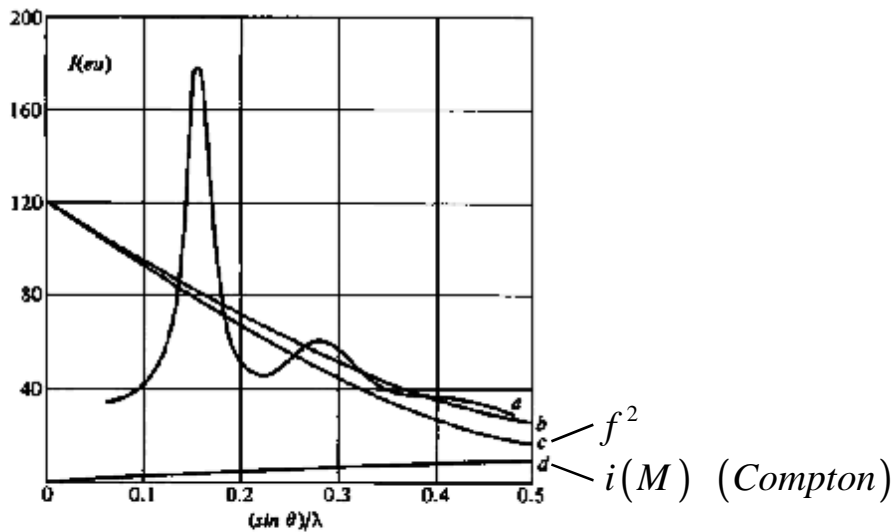
Fig. 10.4 (a) Total intensity curve for liquid sodium in electron units per atom, unmodified plus modified. (b) Total independent scattering per atom. (c) Independent unmodified scattering per atom f^2. (d) Modified scattering per atom $i(M)$.
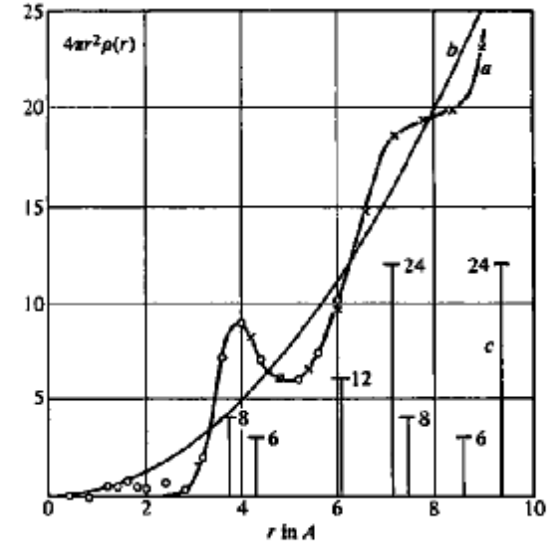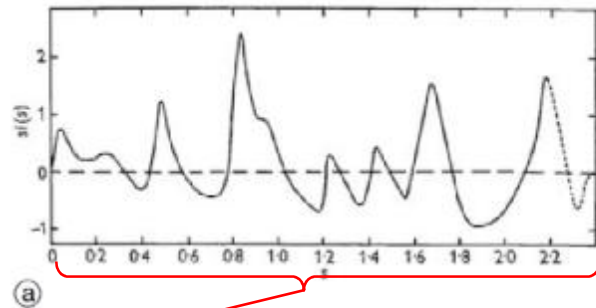
Fig. 10.6 (a) The radial distribution function $4\pi r^2\rho(r)$ for liquid sodium. (b) The average density curve $4\pi r^2\rho_a$. (c) The distribution of neighbors in crystalline sodium.
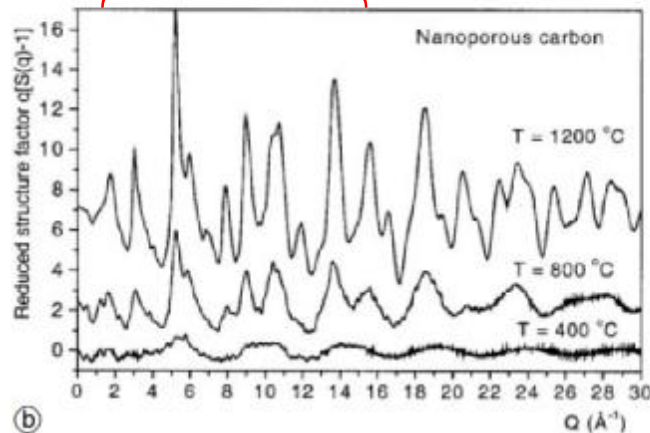
PDF AND SYNCHROTRON RADIATION
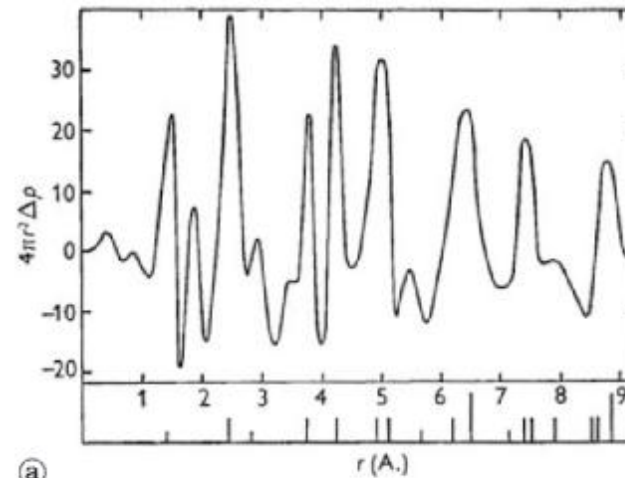
SR is mandatory to improve resolution!

1950

1999

Fig. 1. Comparison of data from disordered carbon from (a) 1950 (Franklin, 1950) and (b) 1999 (Petkov et al., 1999a). This figure shows that both $i(Q) = Q[S(Q) - 1]$ curves are of essentially equal quality but the 1999 data in the lower panel extend over a much greater range of Q. Note the different scales; Q in the 1999 data and s in the 1950 data are related by $Q = 2\pi s$. The Fourier transforms of the data can be compared in Fig. 2.
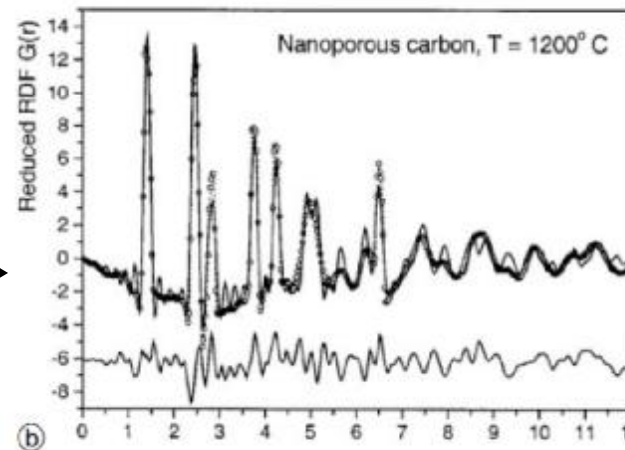
Fig. 2. Comparison of data from disordered carbon from (a) 1950 (Franklin, 1950) and (b) 1999 (Petkov et al., 1999a). The PDFs obtained by Fourier transforming the two data-sets shown in Fig. 1 are shown in the top (1950 data) and bottom (1999 data) panels, respectively. Note that when data are measured over a sufficiently wide range of Q termination ripples, evident as a spurious peak at $r = 2.5$ Å in the 1950 PDF, for example, are not a problem.

à S. J. L. Billinge, Z. Kristallogr. 219 (2004) 117

PAIR DISTRIBUTION FUNCTION (PDF)

$$RDF(r) = 4pr^2 r(r)$$ radial distribution function

$$G(r) = 4pr\left[r(r) - r_0\right]$$ reduced radial distribution function

$$g(r) = r(r)/r_0$$ pair distribution function - PDF

$$= 1 + \frac{2}{r_0 r} \int_0^\infty s\left[S(s) - 1\right] Sin(2psr)\, ds \qquad S(s) = \frac{I(s)}{Nf^2}$$

à S. J. L. Billinge, Z. Kristallogr. 219 (2004) 117

SR is mandatory to improve
resolution!

PSI high resolution data
Silicon

$Q_{max} = 21. Å^{-1}$
Synchrotron

$Q_{max} = 15. Å^{-1}$
Mo-Kα

$Q_{max} = 7. Å^{-1}$
Cu-Kα

Width of PDF maxima
decreases with increasing
Q_{max}

Reasonable for $Q_{max} > 20 Å^{-1}$

à Courtesy of R. Neder

PDF OF NANOPARTICLE SYSTEMS

Effect of finite size and shape
of the nanoparticle

crystalline ZnSe

nanocrystaline ZnSe

à Courtesy of R. Neder

PDF OF NANOPARTICLE SYSTEMS

Indication of stacking faults
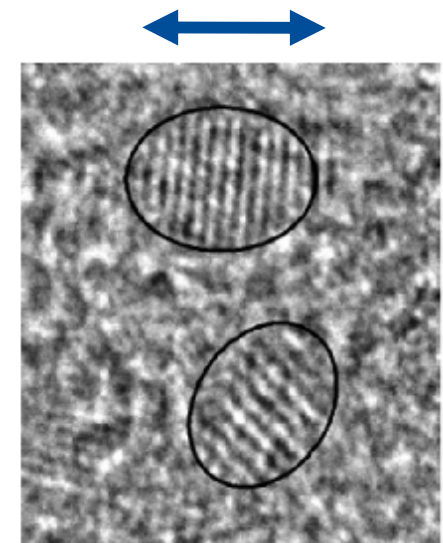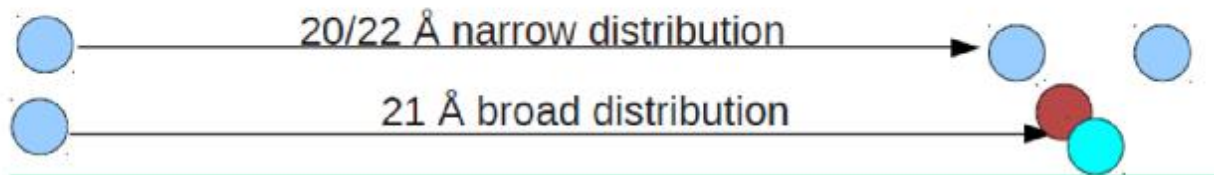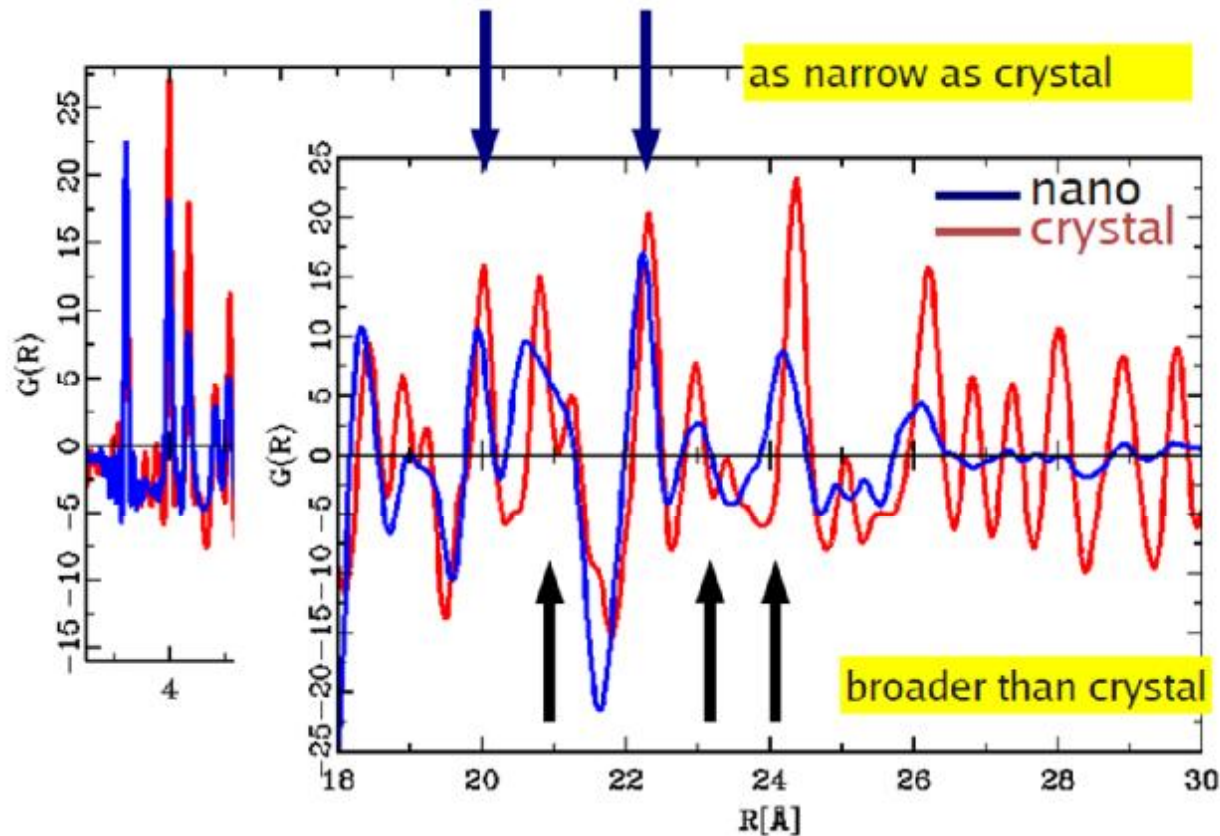
as narrow as crystal

nano
crystal

broader than crystal

20/22 Å narrow distribution

21 Å broad distribution

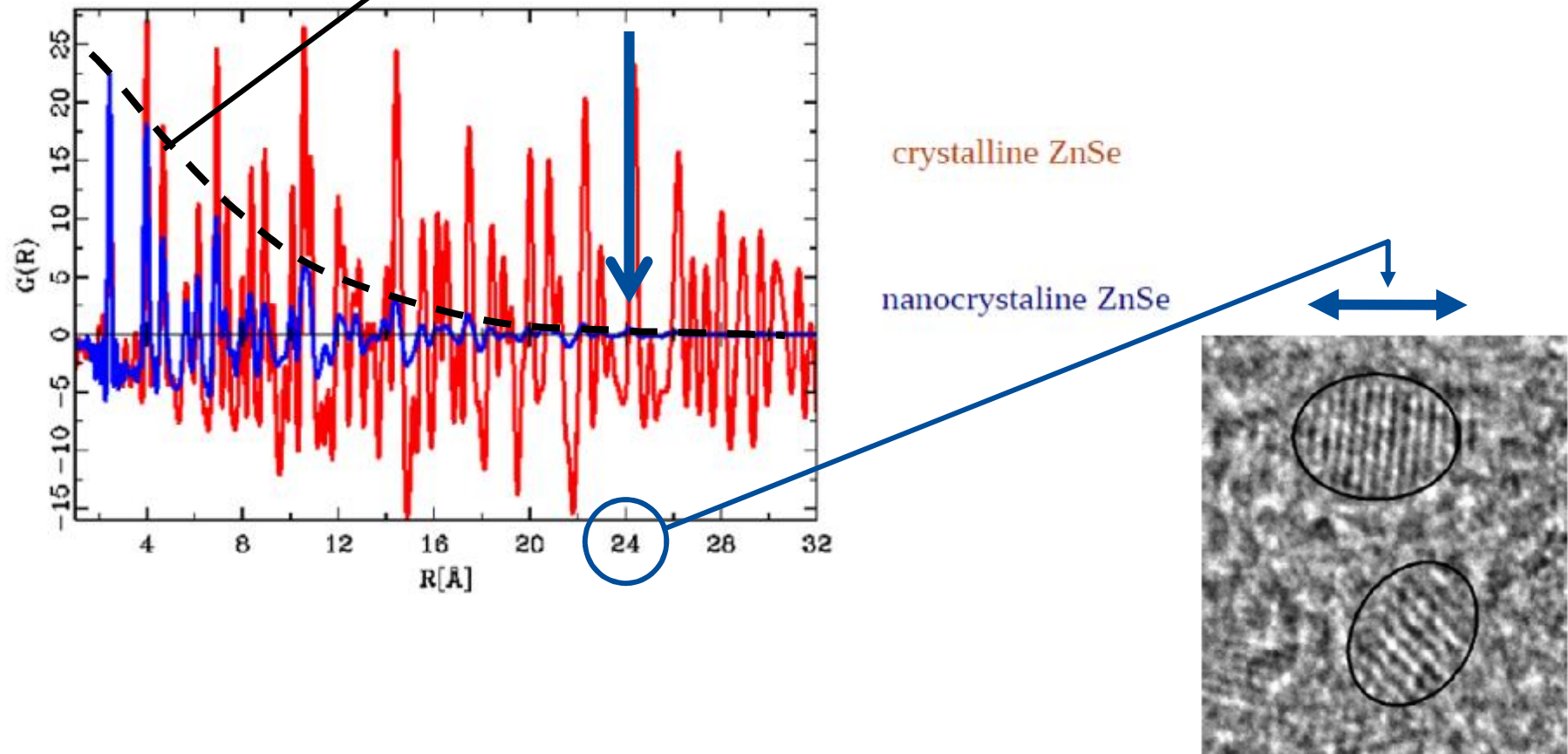à Courtesy of R. Neder

Au nanoparticle + ligand

Au + S-CH2-CH2-(CF2)5-CF3

Gold -Ligand
Au – S 2.42Å

Ligand -
Ligand
C-C 1.5Å
C-F 1.3Å

Au - Au

G(r)

distance [Å]
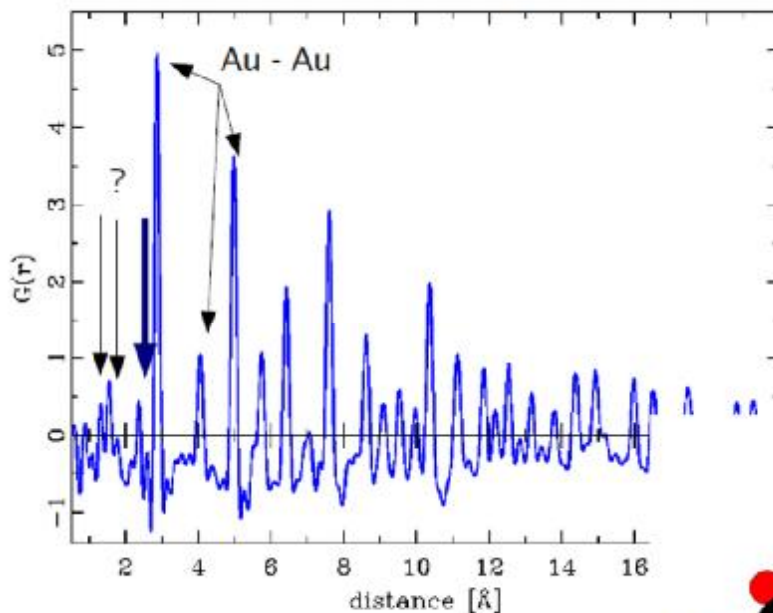
Au
F m 3 m
a 4.064 Å
Au-Au 2.837Å

Number ?
Placement ?
Composition ?

15 K
NPDF, Los Alamos
Page, et al., Chem. Phys. Lett. **393** (2004) 385-388.

à Courtesy of R. Neder

Au nanoparticle + ligand

Au + S-CH2-CH2-(CF2)5-CF3

**Gold -Ligand
Au – S 2.42Å**

Ligand -
Ligand
C-C 1.5Å
C-F 1.3Å

15 K
NPDF, Los Alamos
K. Page et al. J. Appl. Cryst. (2011)
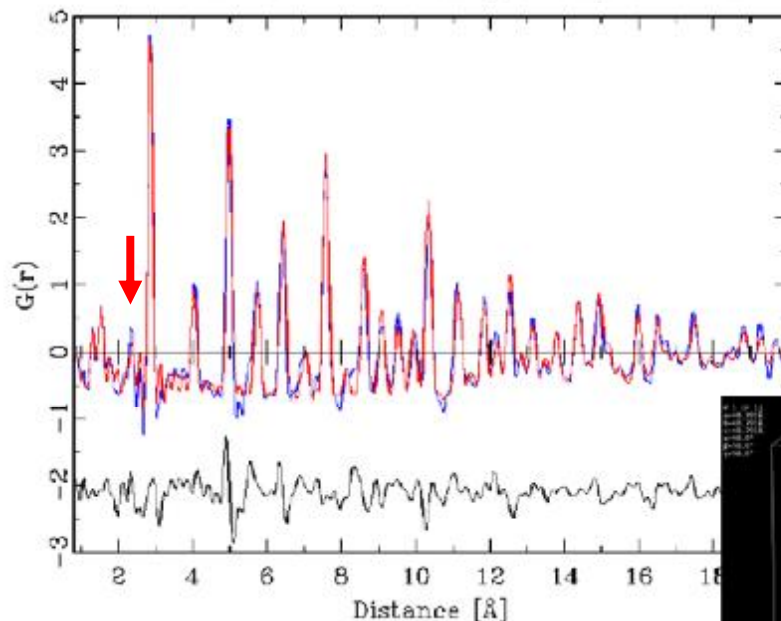
a(Au)	4.0658Å	(1)
Au – Au	2.8750Å	(1)
B(Au)	0.32Å²	(4)
B(Ligand)	0.45Å²	(10)
Diameter	20Å	(2)
N(ligand)	20	(6)
P(Fluorine)	0.65	(15)
Au – S	2.42Å	fixed!
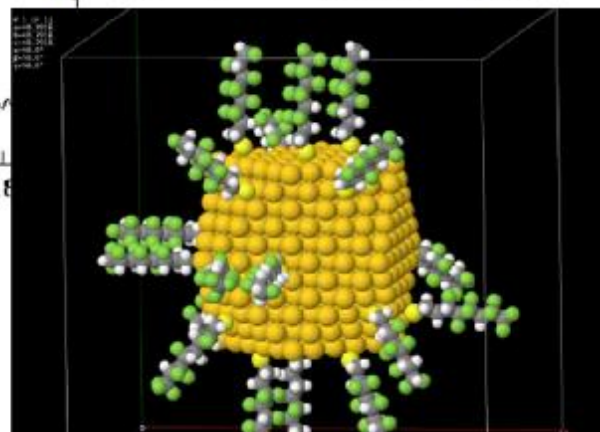
Bottom-up modelling   DISCUS
                         DIFFEV

à Courtesy of R. Neder

TOTAL SCATTERING TECHNIQUES

PDF approach
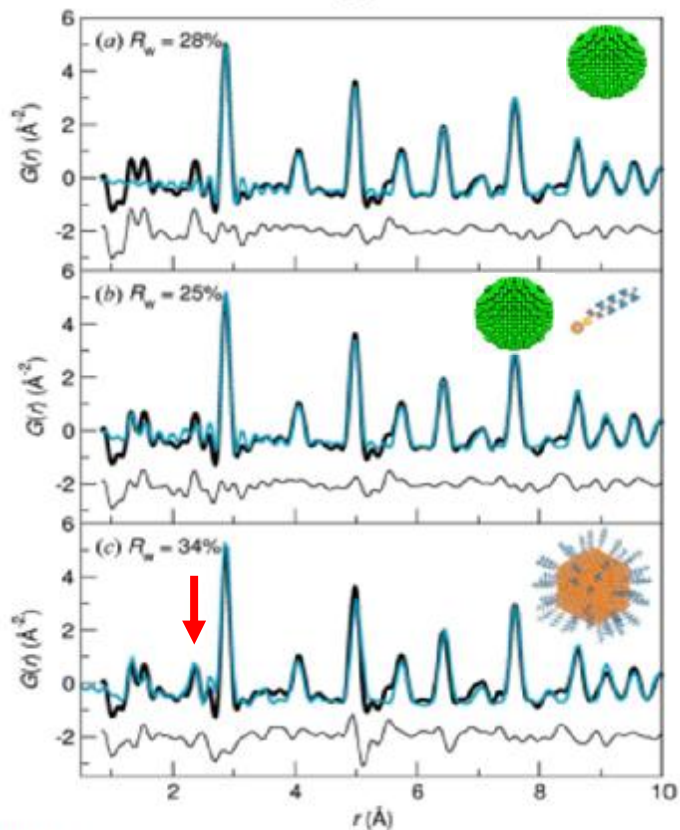
Figure 5
The first 10 Å of three 20 Å fits to 15 K data from Au nanoparticles. Data are shown as circles and fits as lines through the data, and difference curves lie below. (a) Fit from single-phase (f.c.c. Au) refinement using *PDFgui*. (b) Fit from two-phase refinement using *PDFgui*. (c) Fit from finite ligand-capped nanoparticle model using *DIFFEV*.

K. Page et al., J.Appl.Cryst. 44 (2011) 327

Debye Scattering Equation

FIG. 2. (Color online) Experimental x-ray powder pattern for the studied Pd nanocrystals. The inset shows a detail of the (200) peak. Arrows on the latter indicate the interference fringes from the parallel 100 facets of the nanocrystals, which correspond to the analogous features observed in reciprocal space (RS) (above): Powder diffraction integrates information over spheres of growing radius in RS, as schematically represented in the inset of the upper figure.

P. Scardi et al., Phys. Rev. B91 (2015) 155414

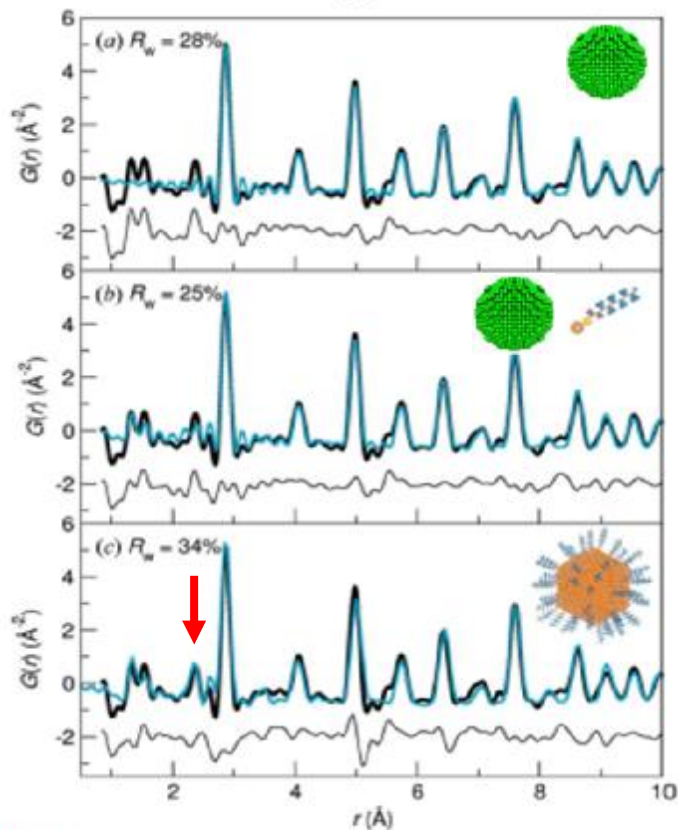## PDF approach

Debye Scattering Equation

Figure 5
The first 10 Å of three 20 Å fits to 15 K data from Au nanoparticles. Data are shown as circles and fits as lines through the data, and difference curves lie below. (*a*) Fit from single-phase (f.c.c. Au) refinement using *PDFgui*. (*b*) Fit from two-phase refinement using *PDFgui*. (*c*) Fit from finite ligand-capped nanoparticle model using *DIFFEV*.
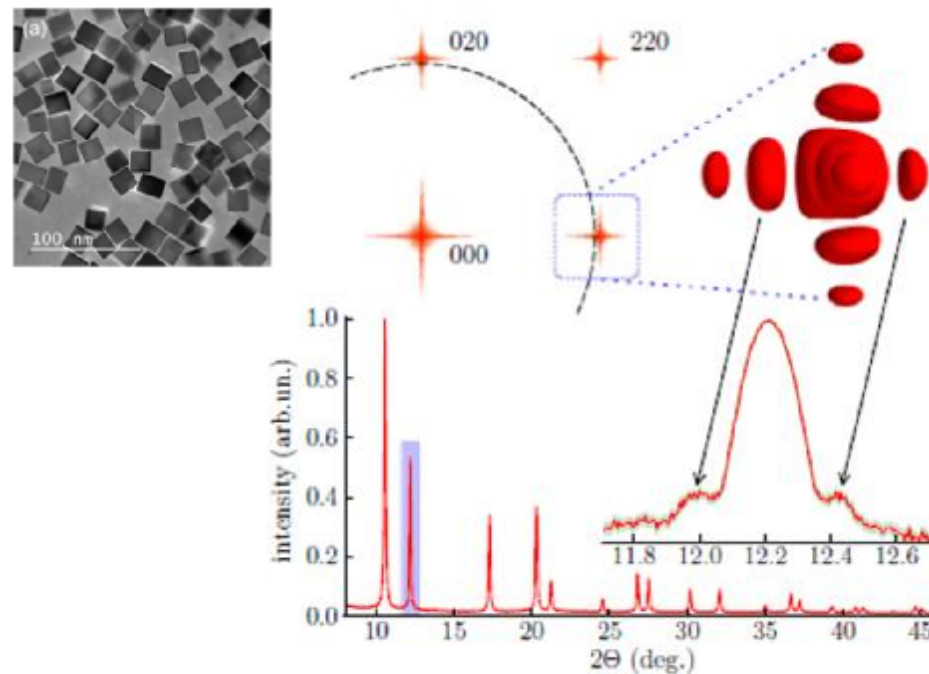
K. Page et al., J.Appl.Cryst. 44 (2011) 327

P. Scardi & L. Gelisio, Nat. Sci. Reports 6, 22221 (2016)

DIFFRACTION FROM NANOCRYSTALLINE MATERIALS

1. Traditional reciprocal space approach : sum & average

$$I_{PD}(s) \propto \frac{\int I_{sc}(\underline{s})d\Omega}{4ps^2} = |F|^2\left\{I^{IP}(s)\otimes I^S(s)\otimes I^D(s)\otimes I^F(s)\otimes I^{APB}(s)\otimes I^C(s)\otimes I^{GRS}(s)...\right\}$$

2. Total Scattering methods

Direct (real) space approach: average & sum
Debye Scattering Equation (DSE)

$$I_{PD}(s) = |f|^2 \sum_m \sum_n \frac{\sin(2ps r_{mn})}{2ps r_{mn}}$$

Pair Distribution Function (PDF)

$$g(r) = \frac{r(r)}{r_0} = 1 + \frac{1}{2p^2 r_0 r}\int_0^\infty Q[S(Q)-1]Sin(Qr)dQ$$

$$I(s) = N|f|^2\left\{1 + \frac{1}{2ps}\int_V 4pr[r(r)-r_0]Sin(2psr)dr\right\}$$

DIFFRACTION FROM NANOCRYSTALLINE MATERIALS

Current research / future trends

à toward an integration between atomistic modelling and diffraction analysis:
real structure of nanoparticle systems

Debye Scattering Equation

$$I_{PD}(s) = |f|^2 \sum_m \sum_n \frac{\sin(2p\,s\,r_{mn})}{2p\,s\,r_{mn}}$$

geometrical
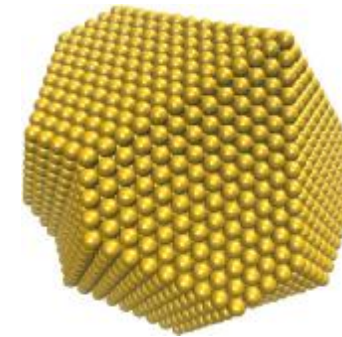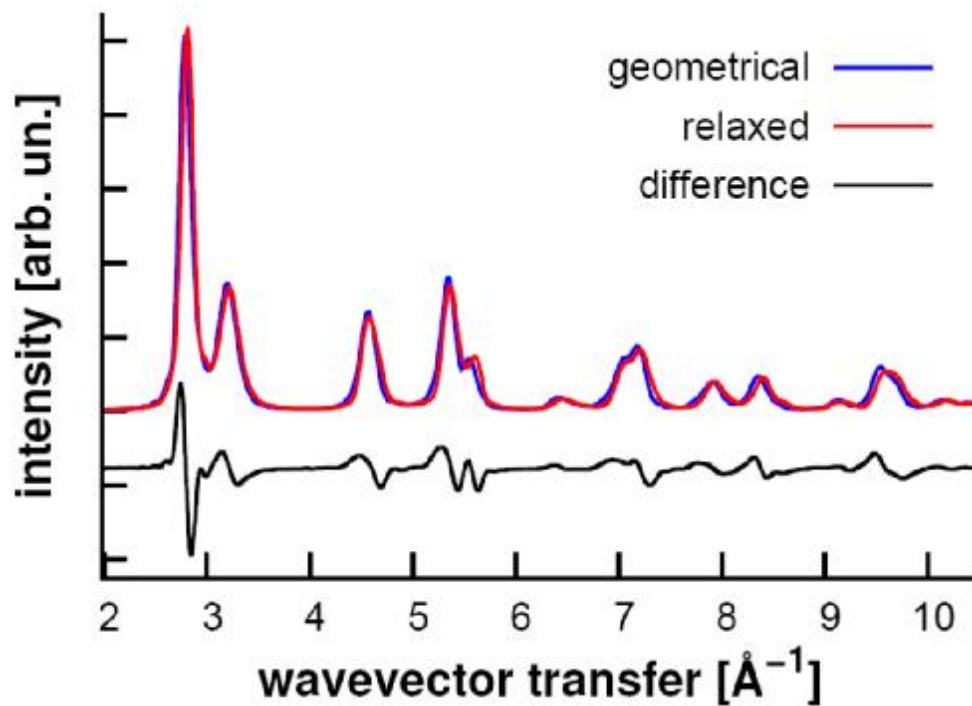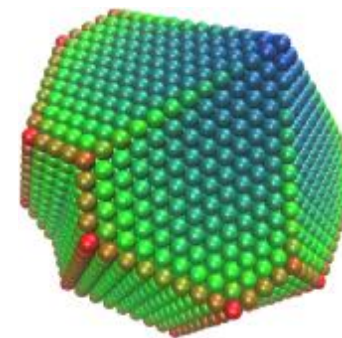

relaxed
(energy minimization)

DIFFRACTION FROM NANOCRYSTALLINE MATERIALS

Current research / future trends

à   toward an integration between atomistic modelling and diffraction analysis: plastically deformed nanocrystalline systems; grain boundary, line and planar defects
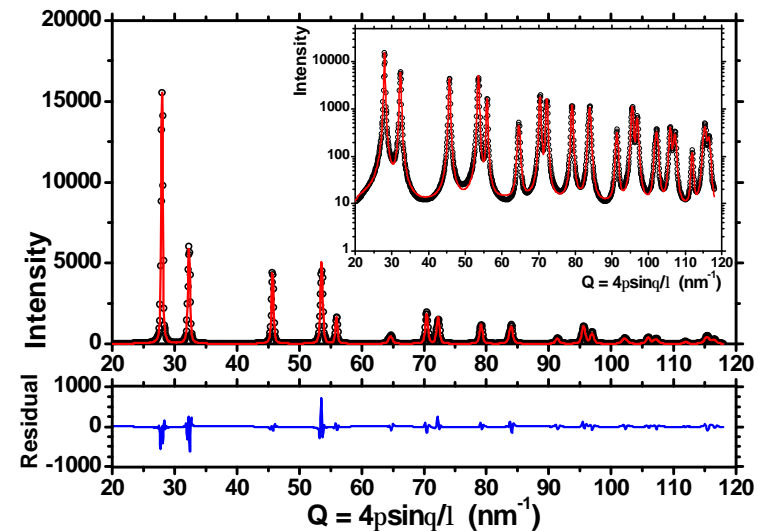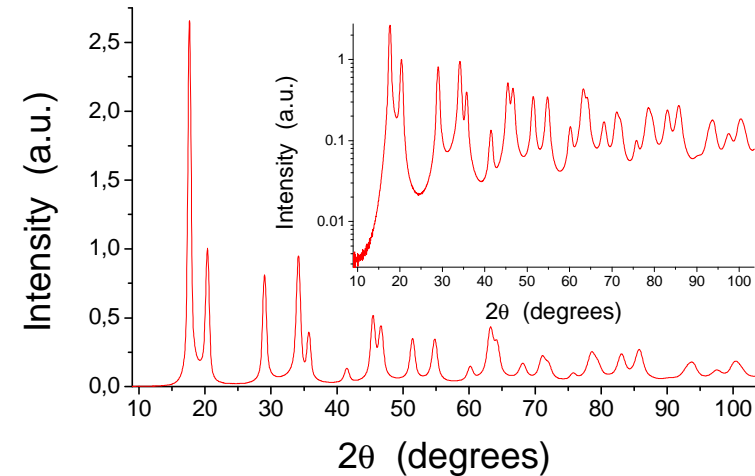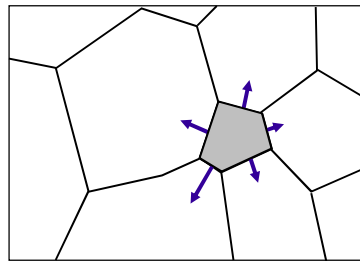
A. Leonardi & P. Scardi, Met. Mat.Trans A (2015). In press

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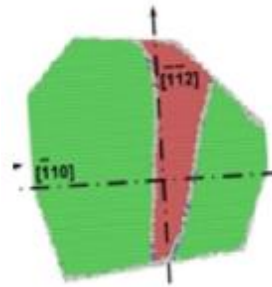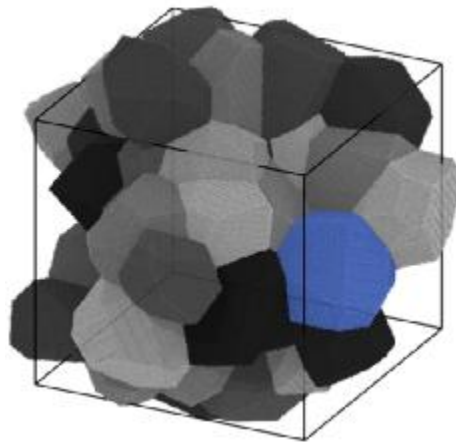H.P. Klug & L.E. Alexander, *X-ray Diffraction procedures*, Wiley, New York, 1974.

B.D. Cullity, *Elements of X-ray Diffraction*, Addison-Wesley, Reading Ma, 1978.
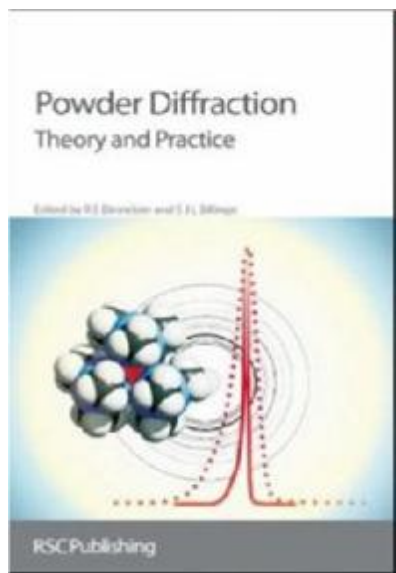
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Springer-Verlag, 2015

State-of-the-art Line Profile Analysis based on Whole Powder Pattern Modelling
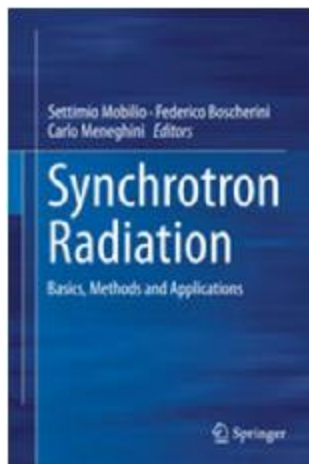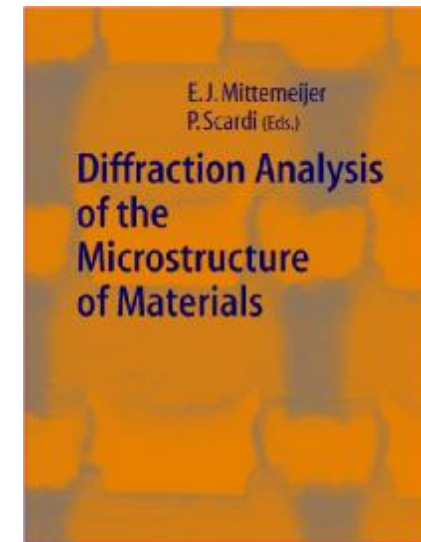
www.nature.com/scientificreports

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OPEN

On the reliability of powder diffraction Line Profile Analysis of plastically deformed nanocrystalline systems

Received: 05 August 2015
Accepted: 06 January 2016
Published: 10 February 2016

Luca Rebuffi[1], Andrea Troian[2], Regina Ciancio[3], Elvio Carlino[3], Amine Amimi[4], Alberto Leonardi[5] & Paolo Scardi[4]

An iron-molybdenum alloy powder was extensively deformed by high energy milling, so to refine the bcc iron domain size to nanometer scale (~10nm) and introduce a strong inhomogeneous strain. Both features contribute to comparable degree to the diffraction peak profile broadening, so that size and strain contributions can be easily separated by exploiting their different dependence on the diffraction angle. To assess the reliability of Line Profile Analysis, results were compared with evidence from other techniques, including scanning and transmission electron microscopy and X-ray small angle scattering. Results confirm the extent of the size broadening effect, whereas molecular dynamics simulations provide insight into the origin of the local atomic, inhomogeneous strain, pointing out the role of dislocations, domain boundaries and interactions among crystalline domains.

doi: 10.1038/srep20712 (2016)

The Debye Scattering Equation for studying static and dynamic disorder in nanocrystals

www.nature.com/scientificreports

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Vibrational Properties of Nanocrystals from the Debye Scattering Equation

Received: 15 November 2015
Accepted: 09 February 2016
Published: 26 February 2016

P. Scardi & L. Gelisio

One hundred years after the original formulation by Petrus J.W. Debije (aka Peter Debye), the Debye Scattering Equation (DSE) is still the most accurate expression to model the diffraction pattern from nanoparticle systems. A major limitation in the original form of the DSE is that it refers to a static domain, so that including thermal disorder usually requires rescaling the equation by a Debye-Waller thermal factor. The last is taken from the traditional diffraction theory developed in Reciprocal Space (RS), which is opposed to the atomistic paradigm of the DSE, usually referred to as Direct Space (DS) approach. Besides being a hybrid of DS and RS expressions, rescaling the DSE by the Debye-Waller factor is an approximation which completely misses the contribution of Temperature Diffuse Scattering (TDS). The present work proposes a solution to include thermal effects coherently with the atomistic approach of the DSE. A deeper insight into the vibrational dynamics of nanostructured materials can be obtained with few changes with respect to the standard formulation of the DSE, providing information on the correlated displacement of vibrating atoms.

doi: 10.1038/srep22221 (2016)

X-ray Diffraction

Paolo.Scardi@unitn.it

per aspera ad astra