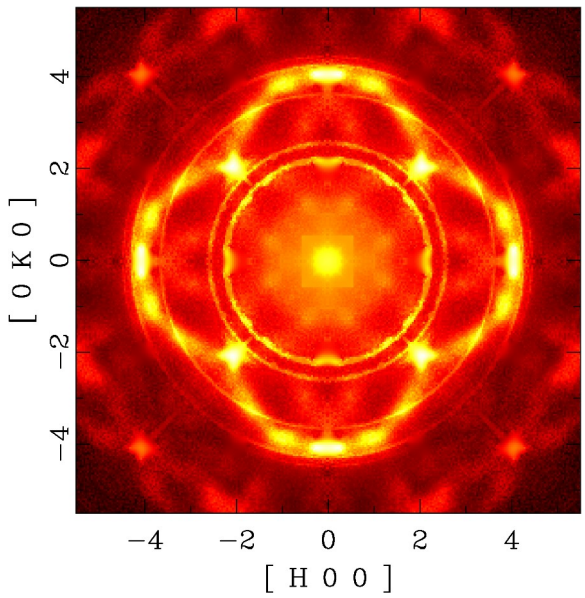
Friedrich-Alexander-Universität
Naturwissenschaftliche Fakultät

Analyzing Single Crystal Diffuse Scattering

Reinhard B. Neder
Crystallography and Structural Physics
Friedrich-Alexander-Universität Erlangen-Nürnberg

reinhard.neder@fau.de

Diffuse Scattering



$(Zr,Ca)O_{2-x}$ @ Corelli

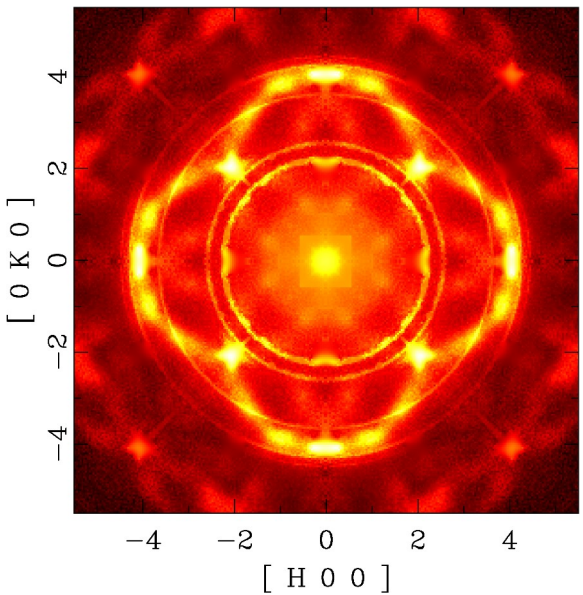
Broad diffraction signal off the Bragg reflections

Perfect, periodic crystal
Bragg reflections only

Any deviation from perfect periodicity
diffuse scattering

Diffuse Scattering

Any deviation from perfect periodicity diffuse scattering



$(Zr,Ca)O_{2-x}$ @ Corelli

Static deviations

- Distribution of atoms/molecules
- Deviations from average position

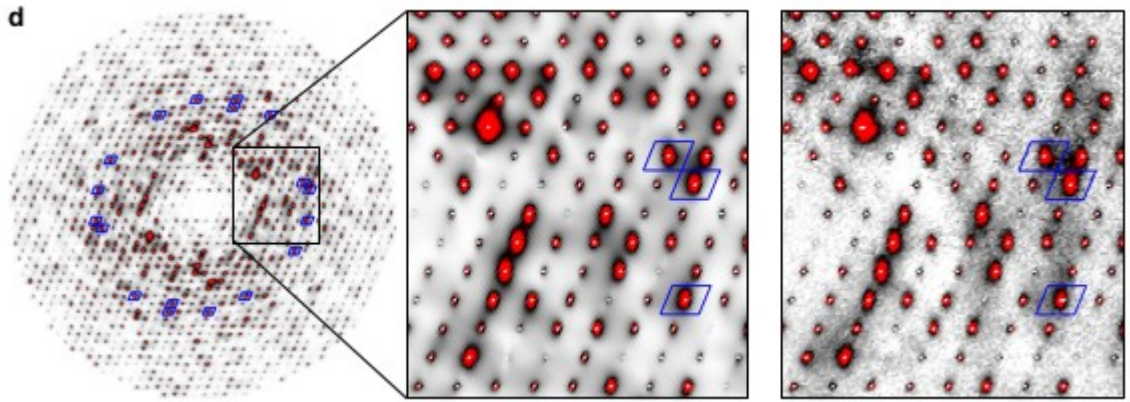
Diffuse Scattering

Any deviation from perfect periodicity
diffuse scattering

Dynamic deviations

Correlated atoms/molecule motion

Lysozyme



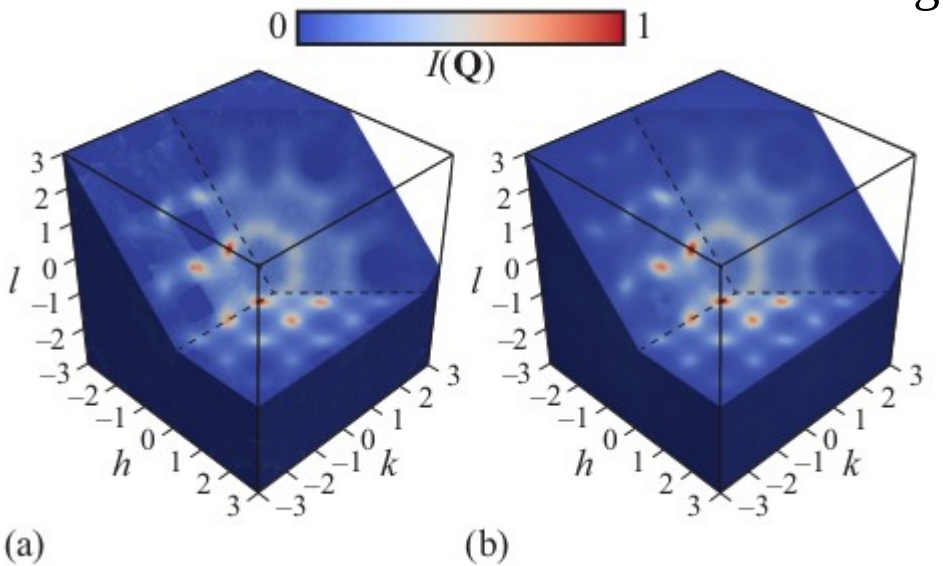
Phonons

Meisburger et al. Nature Comm. (2020) **11** 1271

Diffuse Scattering

Any deviation from perfect periodicity diffuse scattering

MnO



Excitation deviations

Magnetic disorder

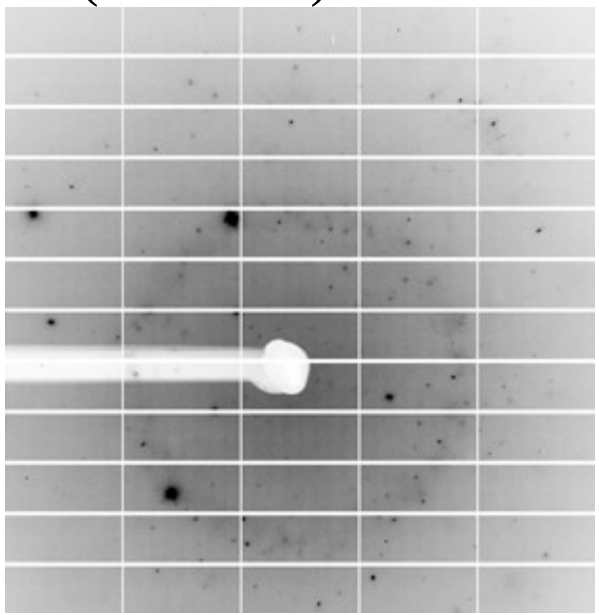
Static distribution
Dynamic distribution

Paddison et al. Phys. Rev. B. (2018) **97** 014429

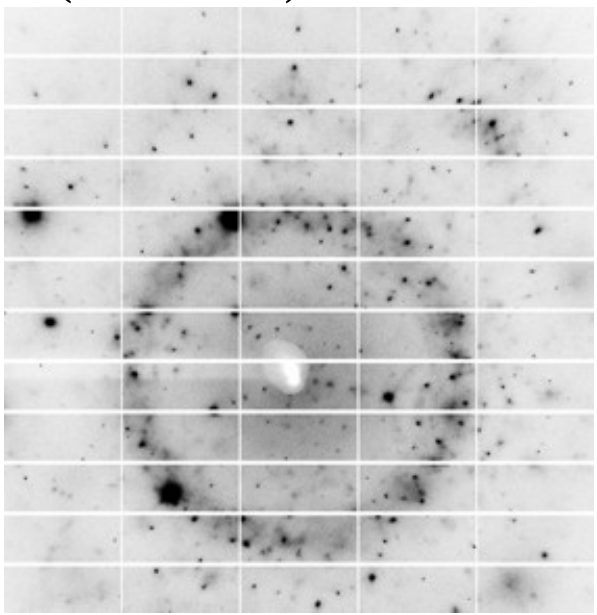
Pixel counting energy discrimination detectors

Copper Fluorescence 8.05 keV

E(primary) : 16 keV
E(threshold) : 8 keV



E(primary) : 16 keV
E(threshold) : 10 keV

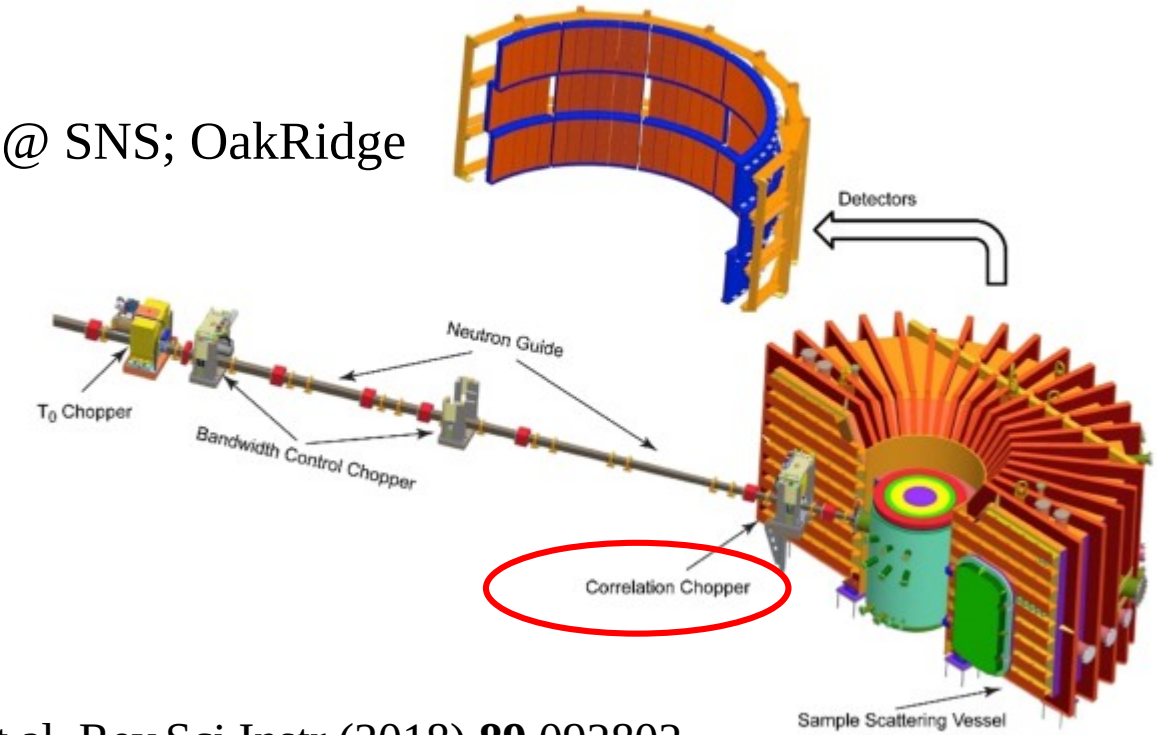


Pilatus @ Swiss Light Source, Sample: *i*-AlCuFe

Th. Weber, personal communication

Cross correlation for energy discrimination

Corelli @ SNS; OakRidge



Effective selection of
Elastic diffuse scattering

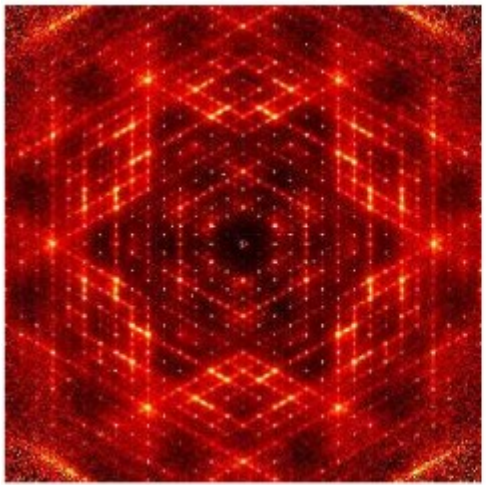
Random chopper windows
Asynchronous rotation

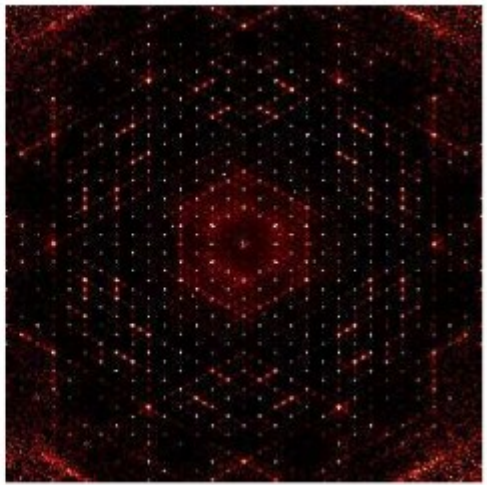
Coates et al. Rev.Sci.Instr (2018) **89** 092802

Ye, .., Rosenkranz J.Appl.Cryst (2018), **51**, 315

Cross correlation for energy discrimination

Benzil Corelli @ SNS; OakRidge





Elastic + Inelastic
100K

Elastic
100K

Effective selection of
Elastic diffuse scattering

Random chopper windows
Asynchronous rotation

Allows excellent distinction between dynamic and static diffuse scattering

Welberry & Whitfield QuntBeamSci (2018), **2**, 2

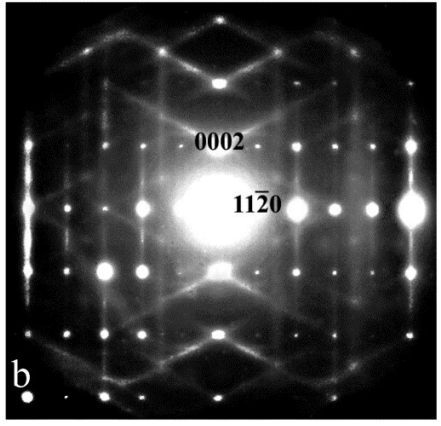
Ye, .., Rosenkranz J.Appl.Cryst (2018), **51**, 315

diffuse electron diffraction

Conventional technique

Pattern taken as oriented zone axis
Dominated by dynamic scattering effects

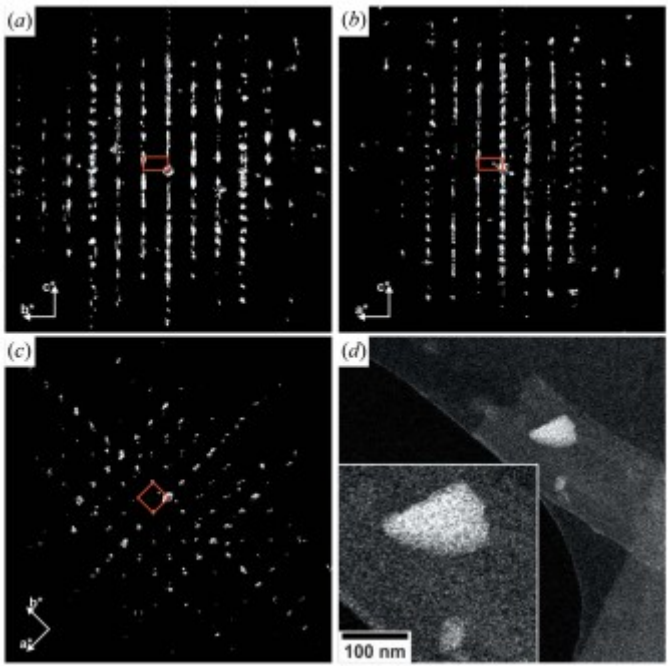
AlPO-#5



Withers et al. Sol.StateSci (2003) **5**, 427

Quantitative diffuse electron diffraction

Zeolite beta



Reconstructed reciprocal layers

Sample is rotated around “random” axis

Automated electron diffraction tomography
U. Kolb et al. Ultramicroscopy (2007), **107**, 507

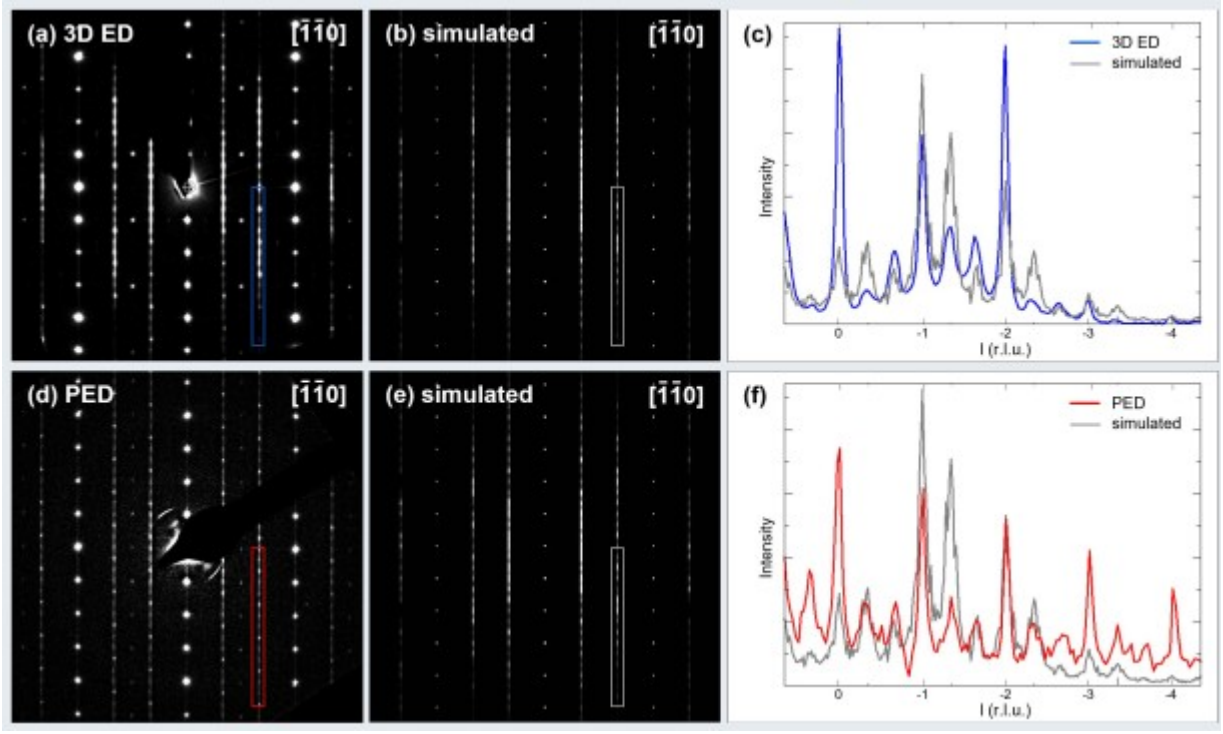
Rotation electron diffraction
Zhang et al. Z. Krist. (2010), **225**, 94.

Minimizes dynamic diffraction effects

Krysiak, .., Neder, Kolb, Acta Cryst. A (2018), **74**, 93

Quantitative diffuse electron diffraction

Li Ni Mn Co O



3D ED
Sample is rotated around "random" axis

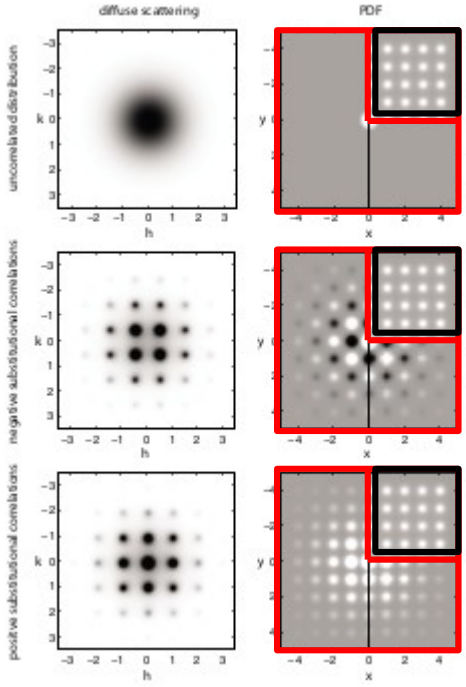
Minimizes dynamic diffraction effects

Conventional zone axis Electron diffraction

Poppe, Vandermeulbroucke, Neder, Hadermann, IUCrJ (2022), **9**, 695

Quantitative 3D-Δ- PDF

Weber & Simonov Z. Krist (2012), **227**, 238



No correlations

Negative correlations

Positive correlations

Fourier transform of Bragg intensity only

Patterson function

Interatomic vectors in SINGLE averaged unit cell, periodic

Fourier transform of total scattering ; Bragg + diffuse

3D-PDF;

Interatomic vectors in actual crystal as in Powder-PDF (RDF, ...)

Fourier transform of Diffuse scattering only

Total scattering – Bragg intensities

3D-Δ- PDF

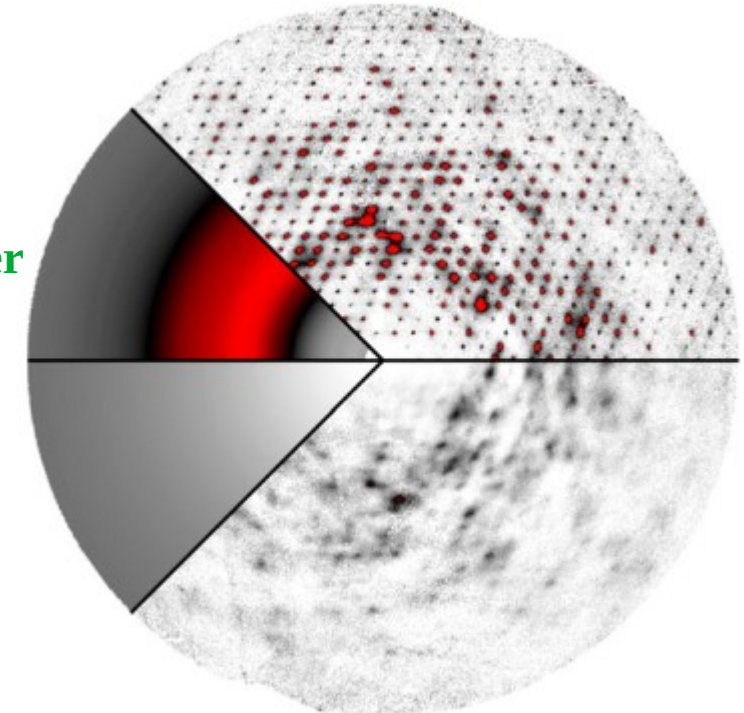
Difference: PDF - Patterson

Diffuse scattering by macromolecules

Broad isotropic ring

Predominantly water
Some SRO

Compton scattering



Intense halos
around Bragg

Phonon scattering !

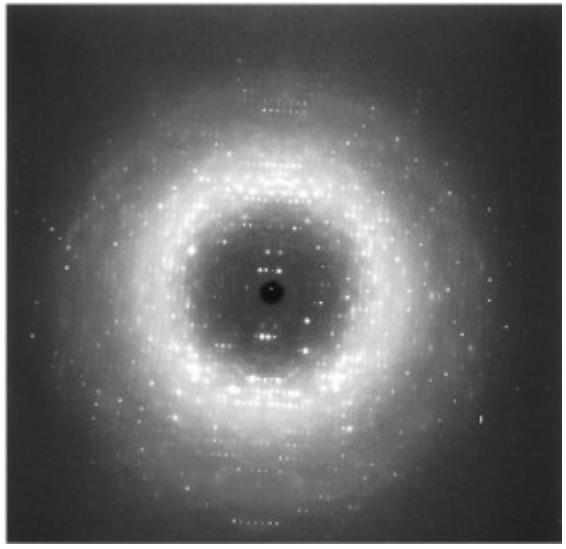
Structured
diffuse scattering

Local dynamic disorder

Lysozyme; 3D reconstruction

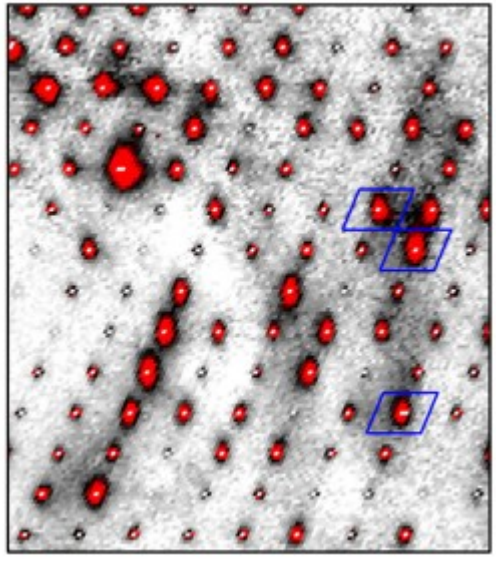
Meisburger, Case, Ando Nature Comm. (2020) **11**, 1271

Diffuse scattering by macromolecules; Interpretation

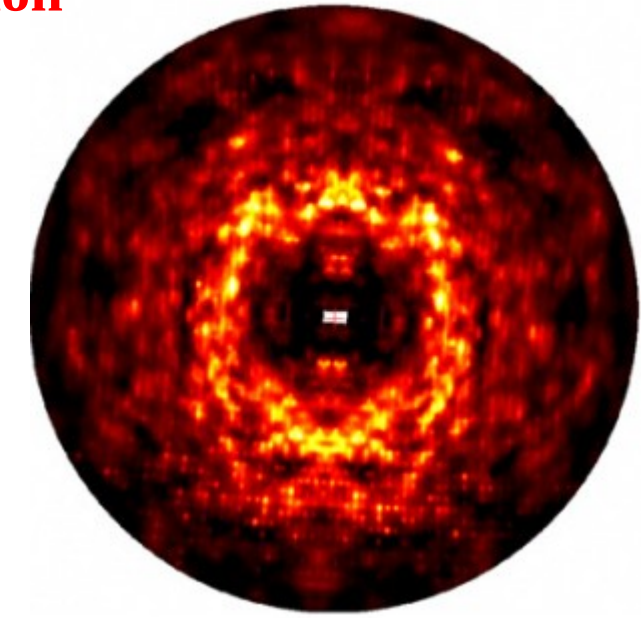


Wall et al. PNAS (1997) **94**, 6180

Wall et al.
CurOpStrBio (2018) **50**, 109



Meisburger, Case, Ando
Nature Comm. (2020) **11**, 1271



Wych et al.
Struc.Dyn. (2019) **6**, 064704

Diffuse scattering by macromolecules; Interpretation

Molecular dynamics simulations

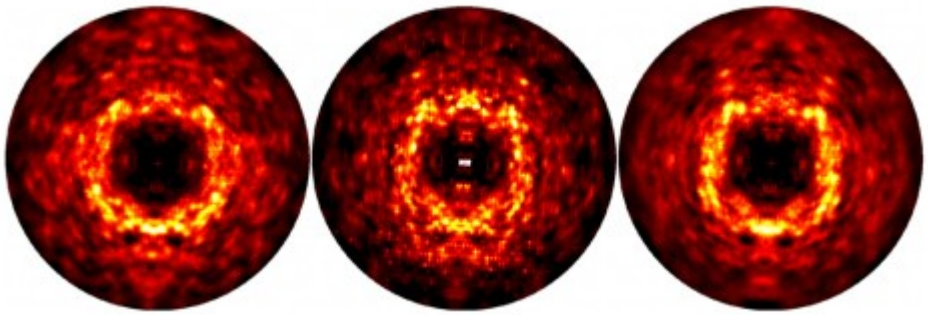
Displacement samples over microseconds!

Diffuse scattering calculated from
small super cell;
sampled n times:

$$D(hkl) = \langle |F_n(hkl)|^2 \rangle_n - |\langle F_n(hkl) \rangle_n|^2$$

Wall IUCrJ (2018) **5**, 172

Calculated Experiment Calculated



Staphylococcal nuclease
Wych et al.
Struc.Dyn. (2019) **6**, 064704

Flexibility within a molecule

Wall et al.
CurOpStrBio (2018) **50**, 109

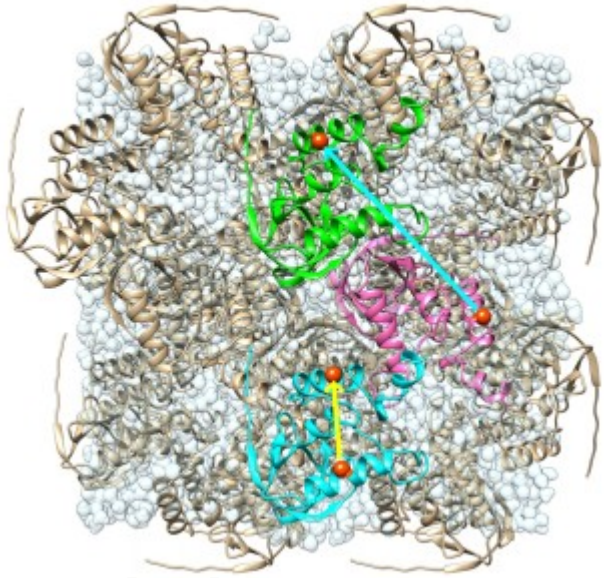
Meisburger, Case, Ando
Nature Comm. (2020) **11**, 1271

Wych et al.
Struc.Dyn. (2019) **6**, 064704

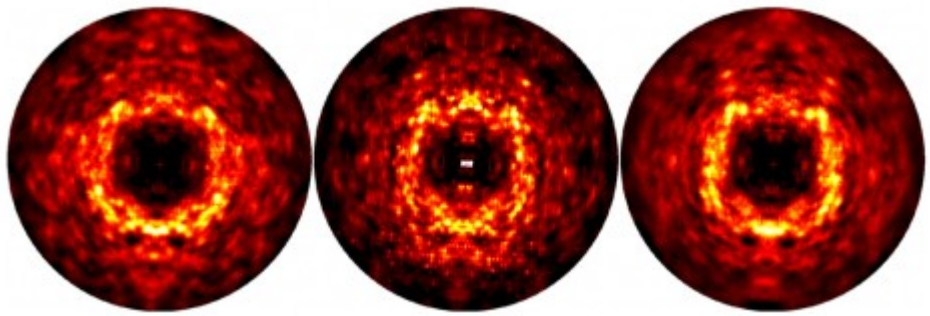
Diffuse scattering by macromolecules; Interpretation

Molecular dynamics simulations

32 proteins
in 2 x 2 x 2
super cell



Calculated Experiment Calculated



Staphylococcal nuclease
Wych et al.
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Flexibility within a molecule

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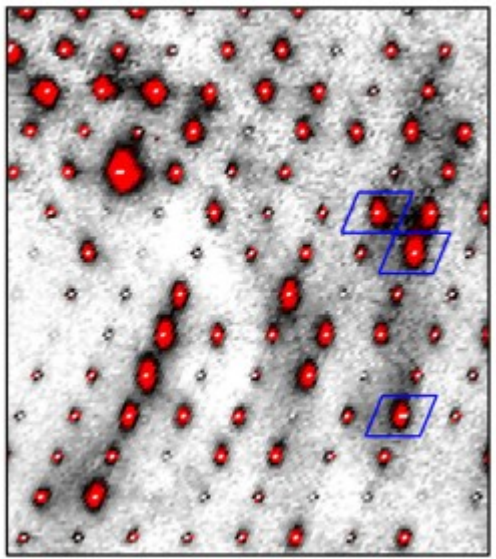
Meisburger, Case, Ando
Nature Comm. (2020) **11**, 1271

Wych et al.
Struc.Dyn. (2019) **6**, 064704

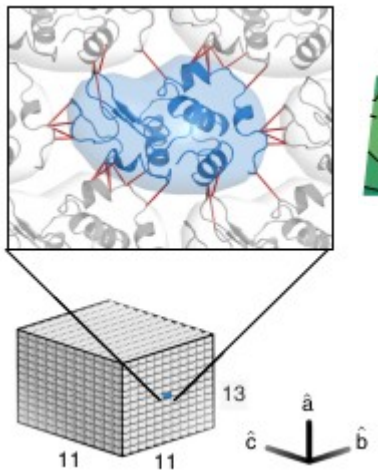
Diffuse scattering by macromolecules; Interpretation

Lattice dynamics !



$$I(q) \propto \frac{1}{|q|^2}$$

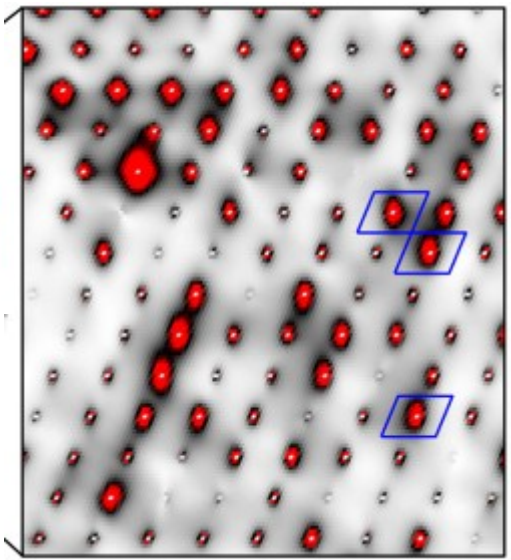
Rigid molecules in 13 x 11 x 11 super cell



Effect of local anisotropy

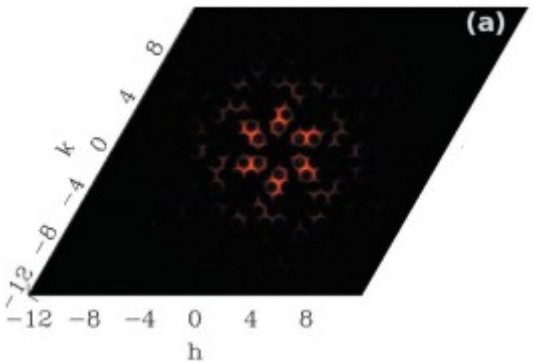
1 12 13

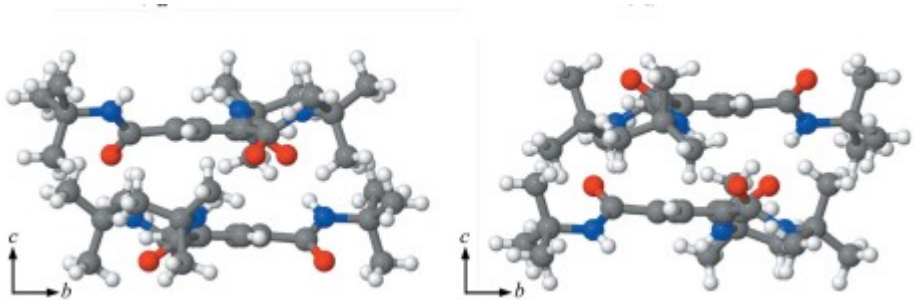
Calculated



Meisburger, Case, Ando
Nature Comm. (2020) **11**, 1271

Diffuse scattering by molecules; Interpretation





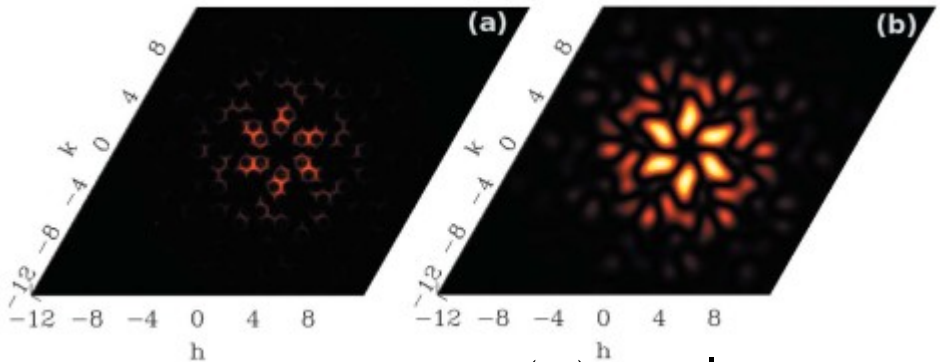
Simonov et al. J.Appl.Cryst (2014) **47**, 2011

tris-tert-butyl-1,3,5-benzene tricarboxamide

Diffuse scattering by molecules in two orientations

$$I(q) \propto |F_{mol}|^2$$

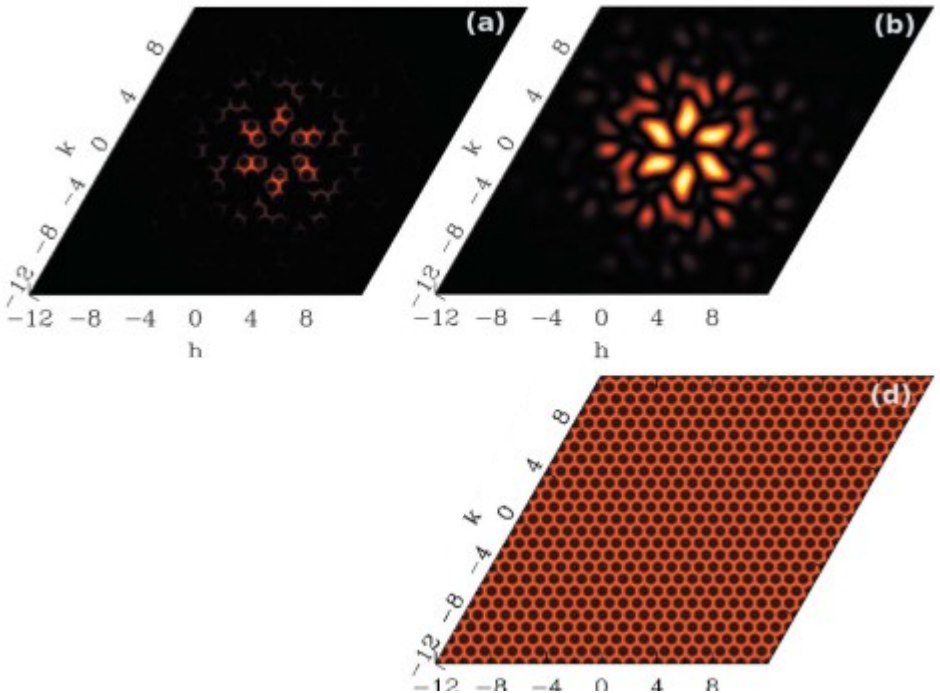
Diffuse scattering by molecules; Interpretation



Diffraction pattern of molecular form factor difference squared

$$I(q) \propto \left| F_{mol,u} - F_{mol,d} \right|^2$$

Diffuse scattering by molecules; Interpretation



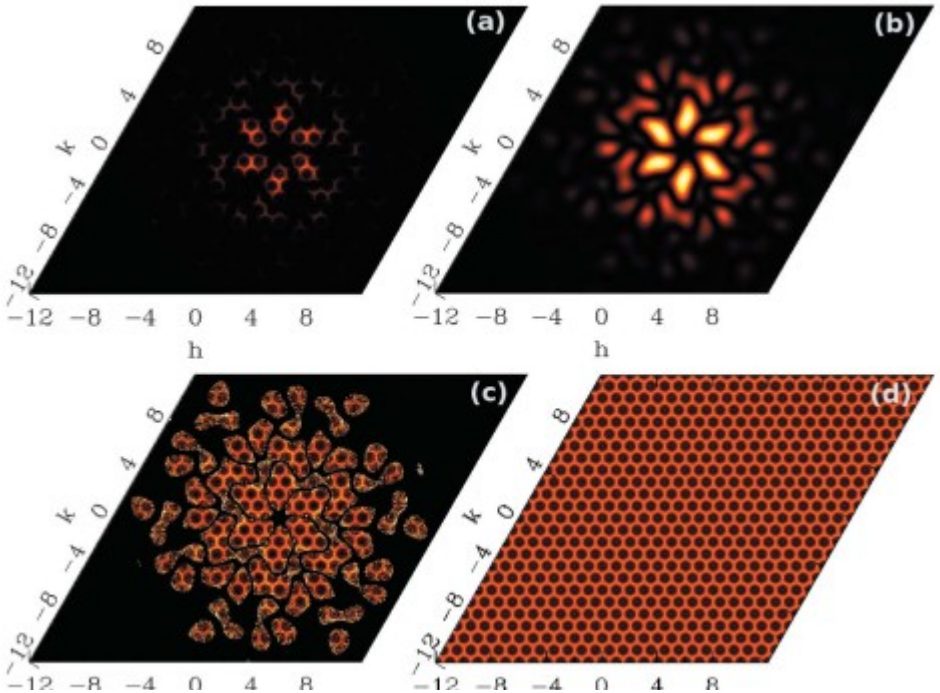
Diffraction pattern of molecular form factor difference squared

$$I(q) \propto \left| F_{mol,u} - F_{mol,d} \right|^2$$

SRO * | $F_{mol,u}$-F_{mol_d} |^2 = Experiment
d) * b) = a)

Intensity of point scatterer with negative first neighbor correlation

Diffuse scattering by molecules; Interpretation



Intensity after division by b)

Intensity of point scatterer with negative first neighbor correlation

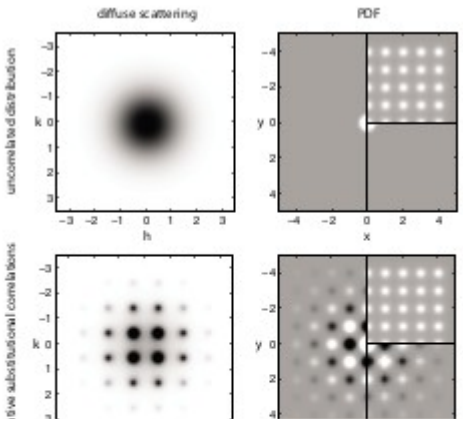
Diffraction pattern of molecular form factor difference squared

$$I(q) \propto \left| F_{mol,u} - F_{mol,d} \right|^2$$

Experiment / $|F_{mol,u}-F_{mol\_d}|^2$ = SRO
a) / b) = c) ≈ d)

Division provides more unambiguous interpretation

Quantitative 3D-Δ- PDF



Initial workflow

Fine slicing in reciprocal space
ideally at several axes

3D-reconstruction of reciprocal space
Scaling; Detector artifacts; Outlier rejection;
Symmetrization;
Bragg reflection removal

Original 3D PDF punch and fill	Kobas et al. Phys.Rev.B (2005), **71**, 224205
Uncertainties ; punch and fill	Simonov et al. J. Appl. Cryst. (2014), **47**, 2011
KAREN; Outlier rejections	Weng et al. J. Appl. Cryst. (2020), **53**, 159
Full workflow	Koch et al. Acta. Cryst. A (2021), **77**, 611

Weber & Simonov Z. Krist (2012), **227**, 238

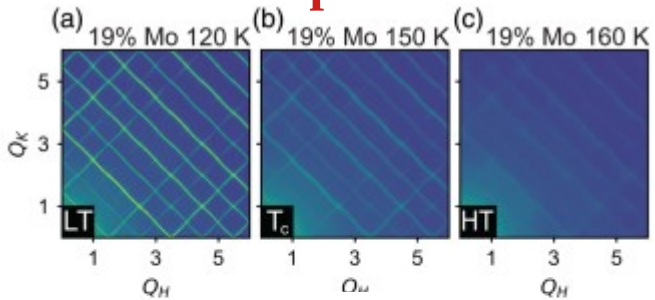
Interpretation; Model building

Quantitative 3D-Δ- PDF

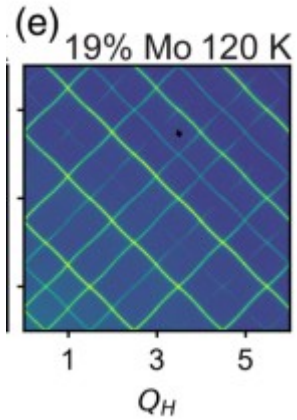
Local order in metal doped $Mo_xV_{1-x}O_2$

Temperature

L = 0.5



L = 1.5



Rutile type structure

Sharp rods parallel <110>*

2D-"defects" with
long range order along <1$\bar{1}$0>

No rod at origin
projected structure is periodic
at l = half-integer layers

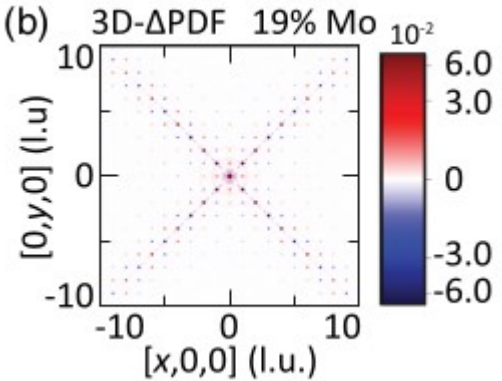
Doubling of unit cell along c

Mild off-axis curvature **??**

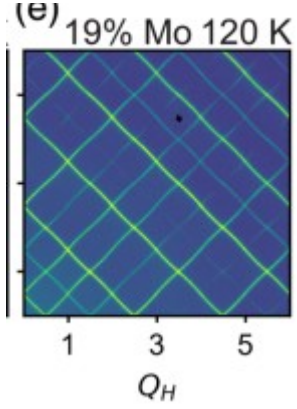
Interpretation; Model building

Quantitative 3D-Δ- PDF

xy0



L = 1.5



Local order in metal doped VO_2

Rutile type structure

Sharp rods parallel <110>

2D-"defects" with long range order along <1$\bar{1}$0>

at l = half-integer layers

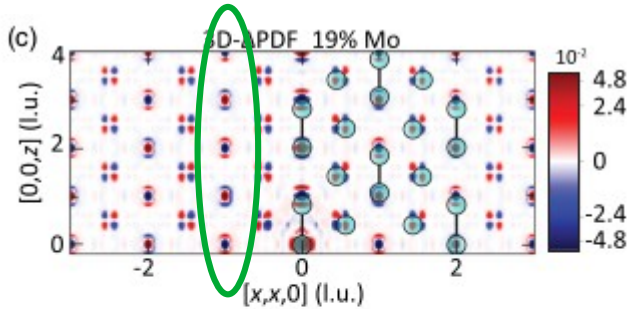
Doubling of unit cell along c

Mild off-axis curvature **??**

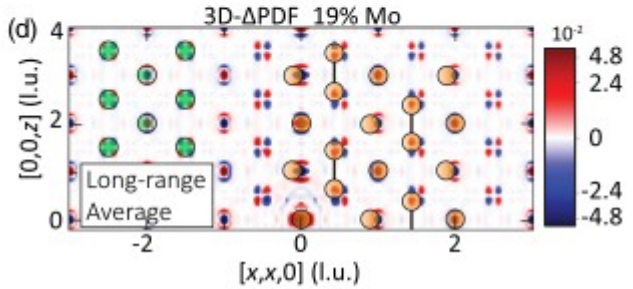
Interpretation; Model building

Quantitative 3D-Δ- PDF

XXZ



XXZ



Local order in metal doped VO_2

Rutile type structure

Sequence of short / normal / long distances along [001]

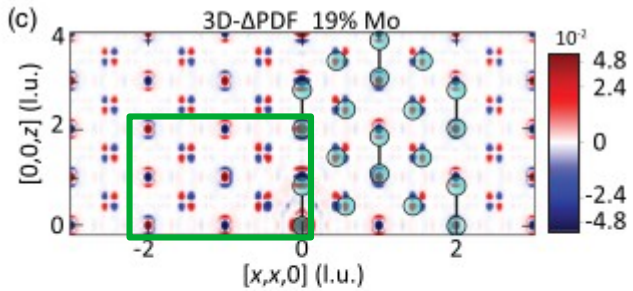
Dimerization of Metal-Metal pairs along [001]

19%: Correlations along <110> and [00l] !

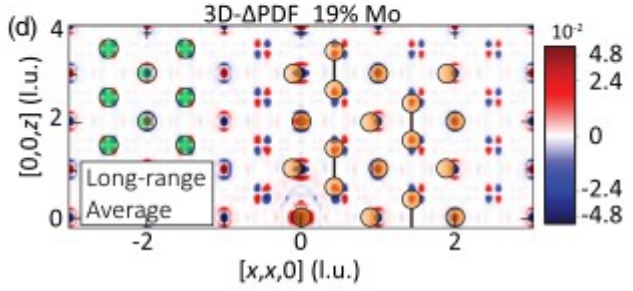
Interpretation; Model building

Quantitative 3D-Δ- PDF

XXZ



XXZ



Local order in metal doped VO_2

Rutile type structure

Sequence of short / normal / long distances along [001]

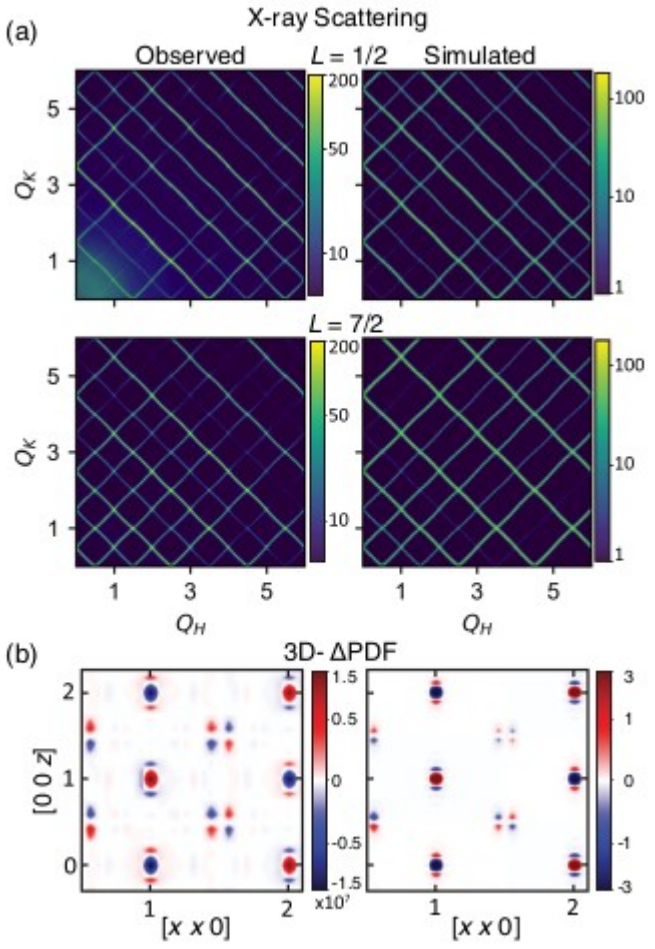
Dimerization of Metal-Metal pairs along [001]

Doubling of unit cell

Alternation of Dimers and shifts

19%: Correlations along <110> and [00l] !

Interpretation; Model building

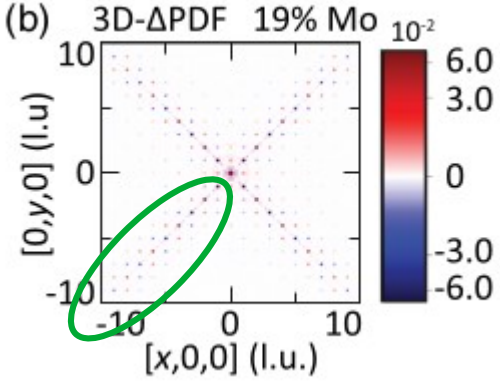


Local order in metal doped VO_2

Rutile type structure

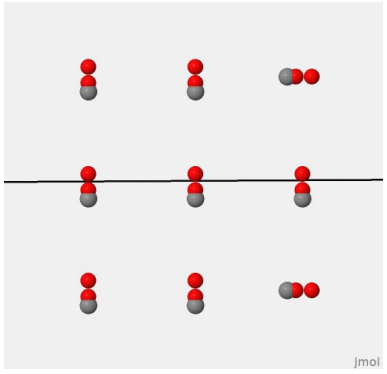
Diffuse scattering calculated from atomistic model in DISCUS program

Off-axis curvature is caused by
Width of [110] streak in 3D- Δ -PDF



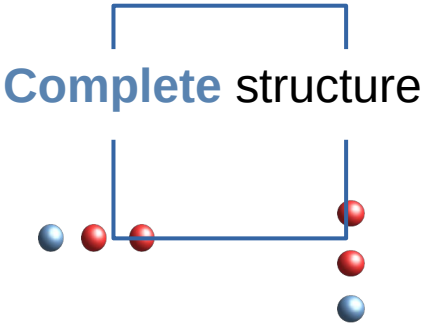
Interpretation; Molecular structures

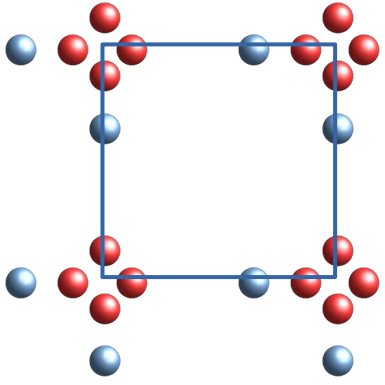
Linear C-O-O molecule in two orientations



Complete structure

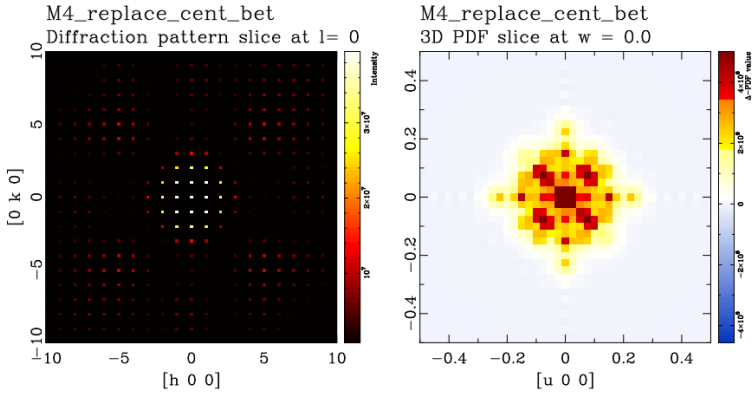
no correlation between molecules





Average structure

Interpretation; Molecular structures

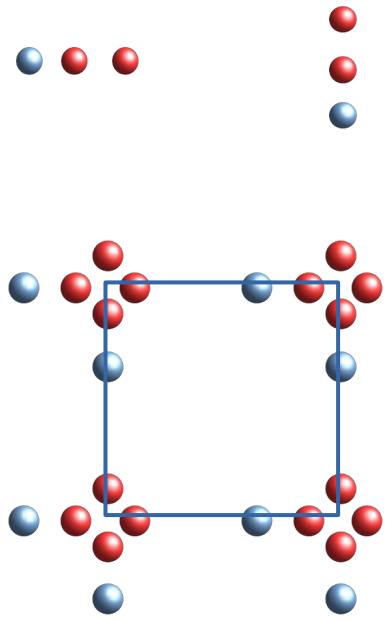


Patterson

Average structure Patterson

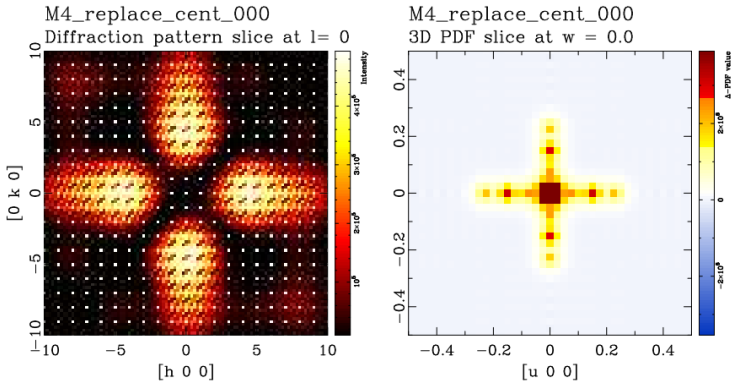
Positive peaks
interatomic vectors in **average** structure

Complete structure



Average
structure

Interpretation; Molecular structures

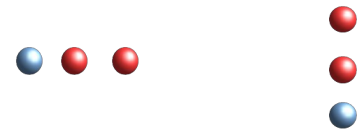


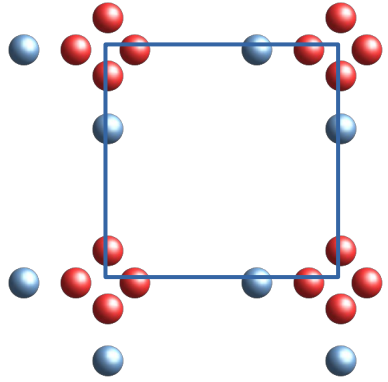
3D PDF

Complete structure Patterson

Positive peaks
interatomic vectors in **actual / complete** structure

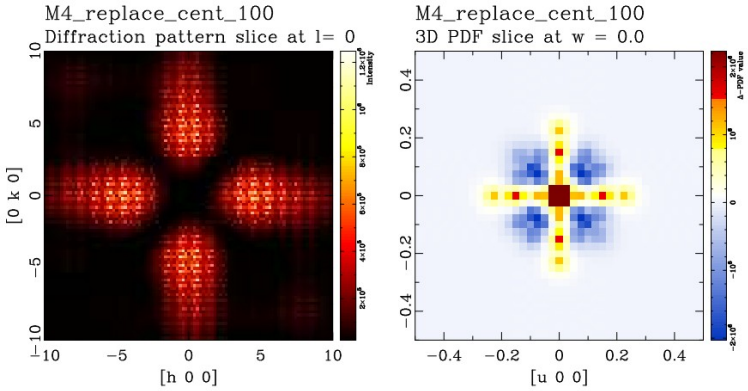
Complete structure





Average structure

Interpretation; Molecular structures



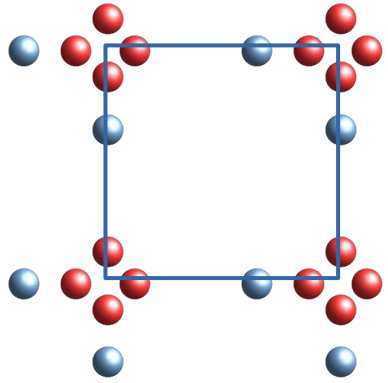
3D - Δ - PDF

„Local“ structure Patterson

Difference: **Complete** – **Average**

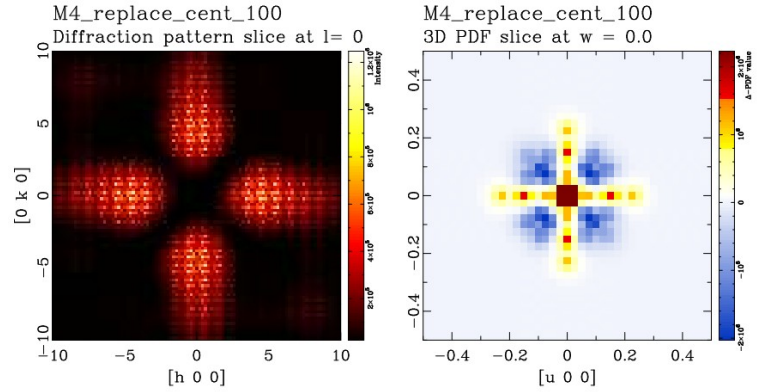
Positive and **Negative** peaks
Deviations of **local** from **average** structure

Complete structure

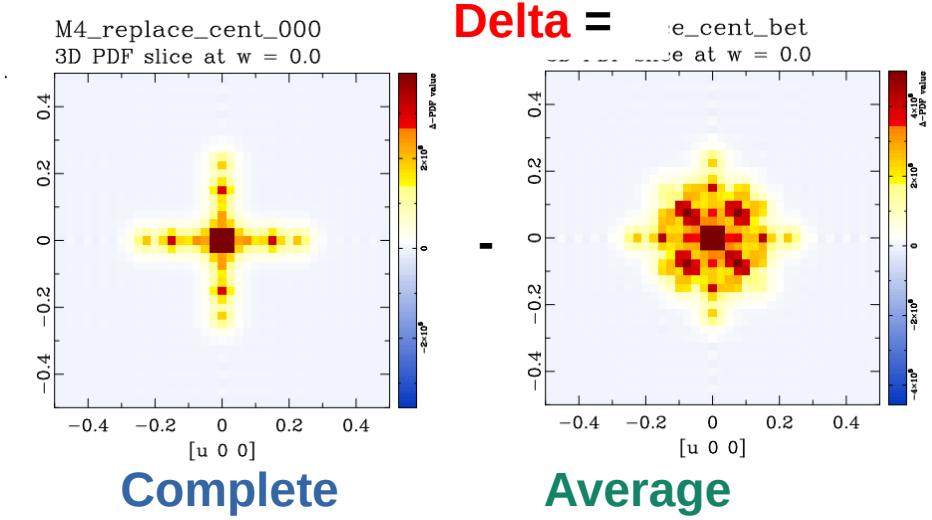


Average structure

Interpretation; Molecular structures

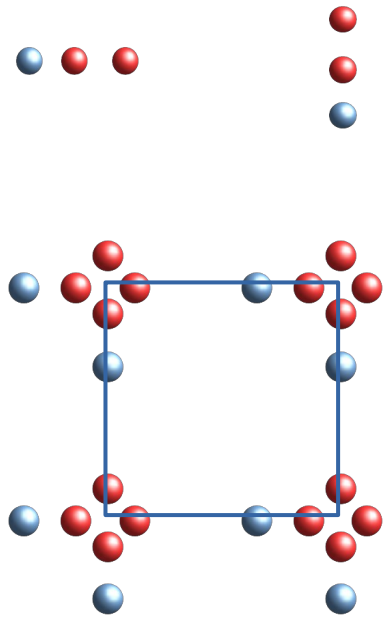


Delta =



Complete **Average**

Complete structure



Average structure

Interpretation; Molecular structures

Patterson

3-D inverse Fourier transform of the **Bragg** scattering

Interatomic vectors periodic

average structure

$$P(\boldsymbol{u}) = F^{-1} I(\boldsymbol{hkl})$$

$$P(\boldsymbol{u}) = F^{-1}\left[F^{*}(\boldsymbol{hkl})\cdot F(\boldsymbol{hkl})\right] = \rho(\boldsymbol{r}) \otimes \rho(-\boldsymbol{r})$$

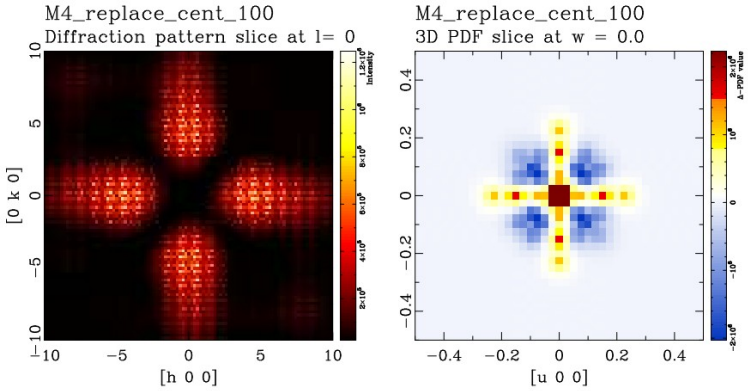
$$P(\boldsymbol{u}) = F^{-1}\left[F^{*}(\boldsymbol{hkl})\cdot E(\boldsymbol{hkl})\right]$$ Sharpened **Patterson**

$$P(\boldsymbol{u}) = F^{-1}\left[E^{*}(\boldsymbol{hkl})\cdot E(\boldsymbol{hkl})\right]$$ Super sharpened **Patterson**

$$PDF(\boldsymbol{u}) = F^{-1}\frac{I(\boldsymbol{Q})}{\langle f^{2}\rangle}$$ Super sharpened **3D PDF**

$$E(\boldsymbol{hkl}) = \frac{F(\boldsymbol{hkl})}{\sqrt{\langle I(\boldsymbol{hkl})\rangle_{\Delta\Theta}}}$$

Interpretation; Molecular structures



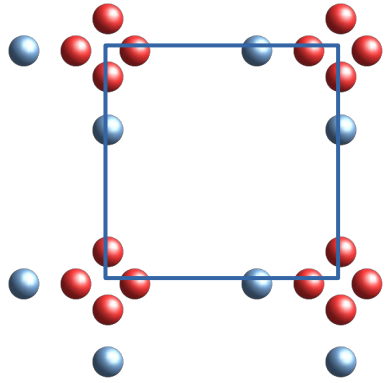
3D - Δ - PDF

„Local“ structure Patterson

Difference: **Complete** – **Average**

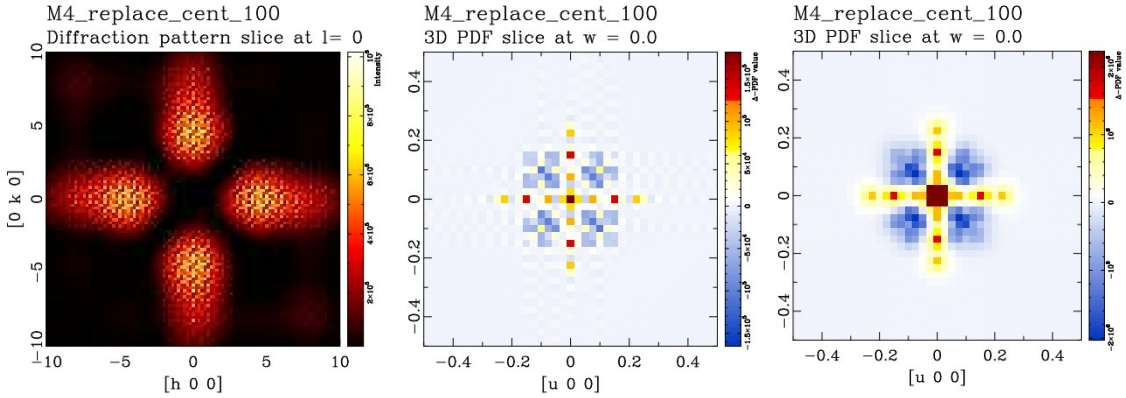
Positive and **Negative** peaks
Deviations of **local** from **average** structure

Complete structure



Average structure

Interpretation; Molecular structures



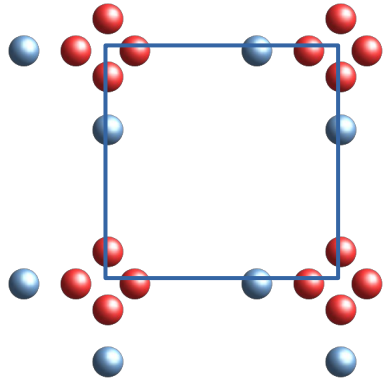
3D - Δ - PDF

„Local“ structure Patterson

Difference: **Complete** – **Average**

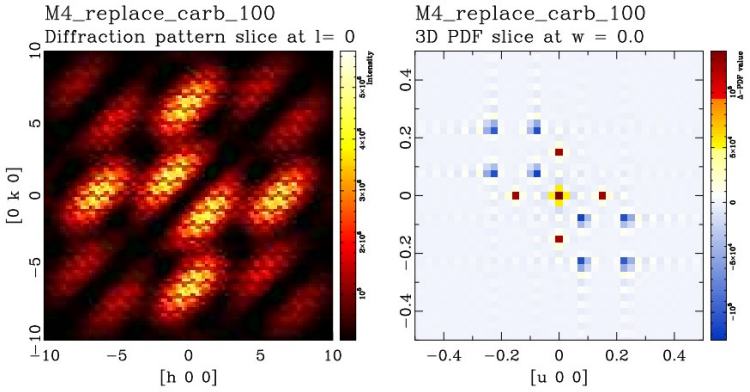
Positive and **Negative** peaks
Deviations of **local** from **average** structure

Complete structure



Average structure

Interpretation; Molecular structures



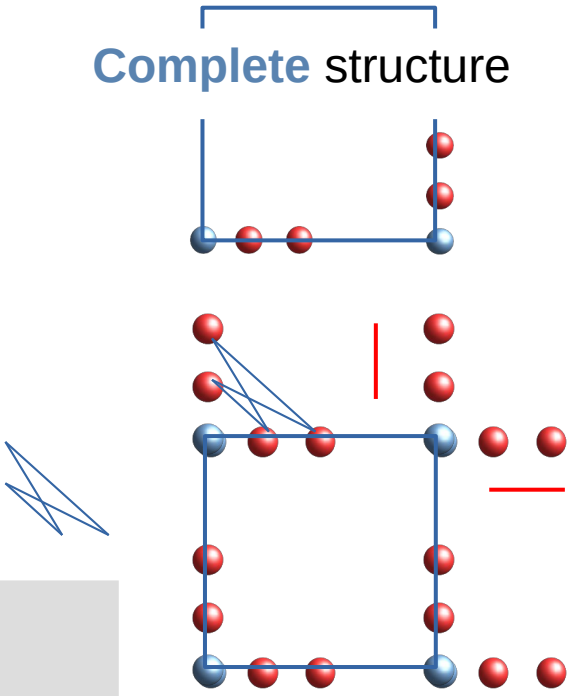
3D - Δ - PDF

„Local“ structure Patterson

Difference: **Complete** - **Average**

No C..O vectors
in **3D -Δ- PDF**

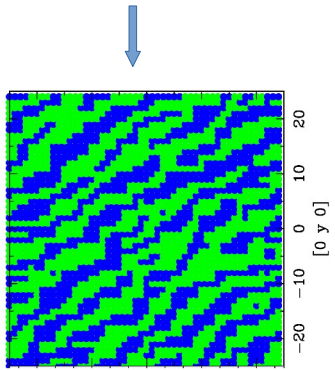
No positive /negative
Although **disordered**!



Average
structure

Interpretation

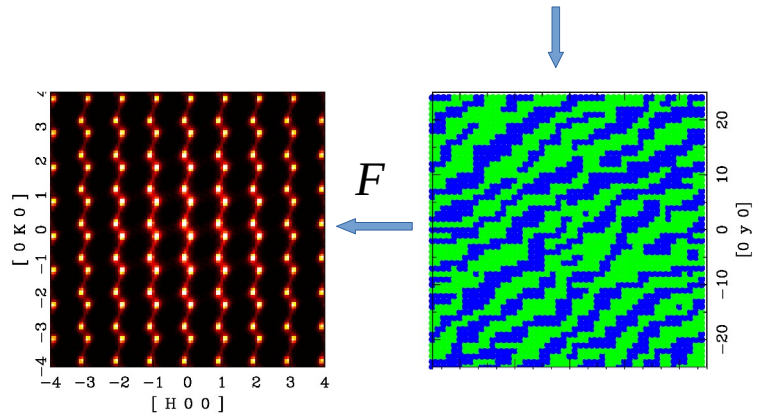
Simulation / refinement
of disordered structural model



DISCUS: www.github.com/tproffen/DiffuseCode

Interpretation

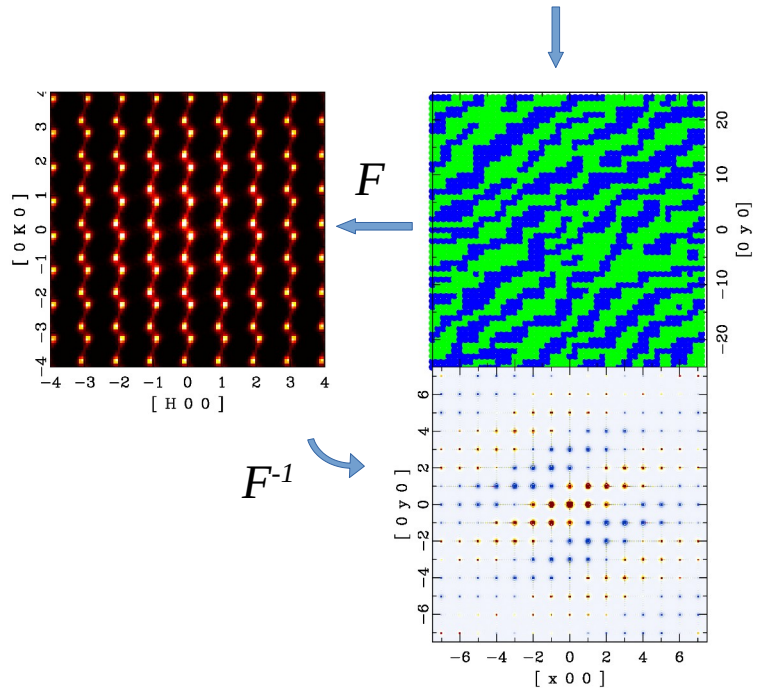
Simulation / refinement
of disordered structural model



DISCUS: www.github.com/tproffen/DiffuseCode

Interpretation

Simulation / refinement
of disordered structural model

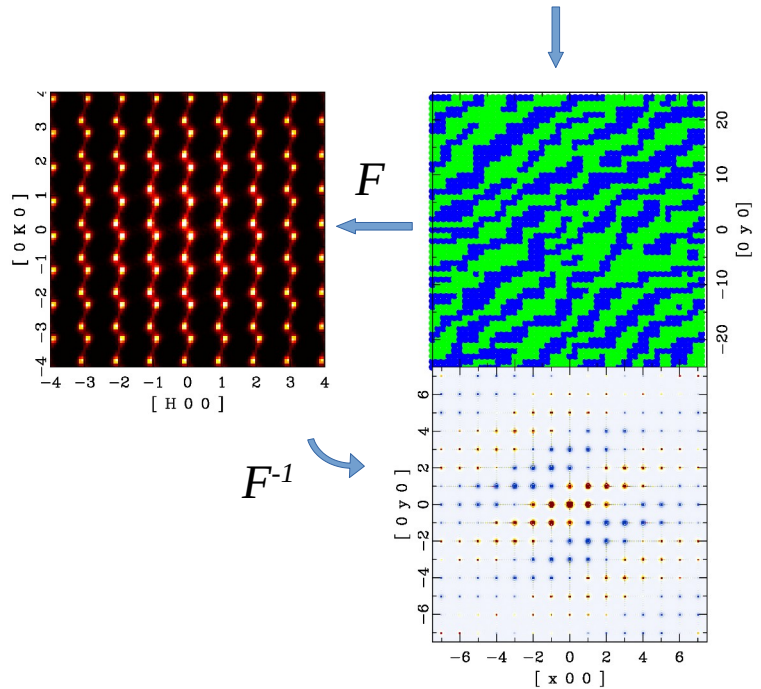


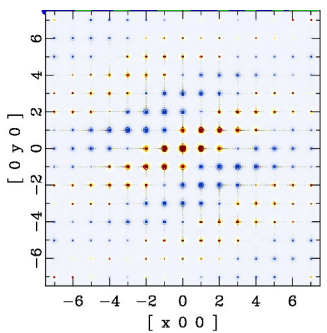
DISCUS: www.github.com/tproffen/DiffuseCode

Interpretation

Simulation / refinement
of disordered structural model

Simulation / refinement
of correlation parameters



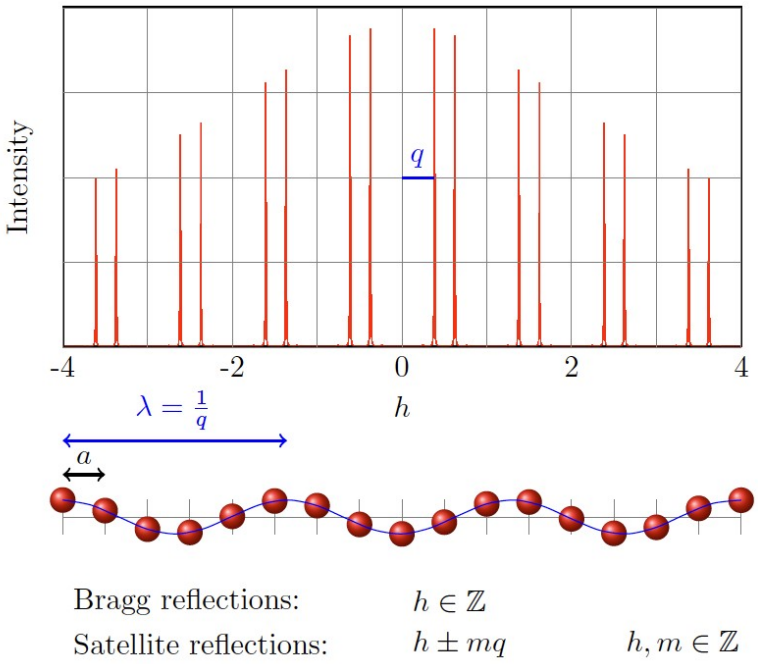


DISCUS: www.github.com/tproffen/DiffuseCode

Yell: www.github.com/YellProgram

Interpretation

Simulation / refinement of disordered structural model



Superspace concept

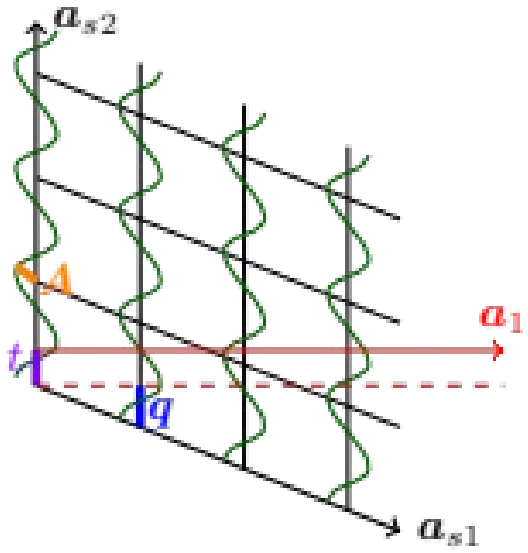
Main Bragg reflections omitted

$$\vec{u}(\vec{a}) = \vec{A}\cos\left(2\pi\left(\vec{q}\,\vec{a} + t\right)\right)$$

Interpretation

Simulation / refinement of disordered structural model

Superspace concept



q **direction** and **periodicity** of modulation function

A modulation function **amplitude**

t initial phase of modulation function

displacement or substitutional modulation function

real space is **cut** through real superspace

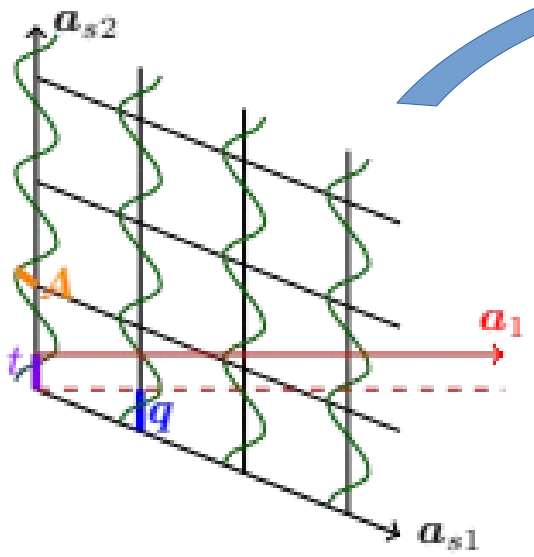
reciprocal space is **projection** of reciprocal superspace

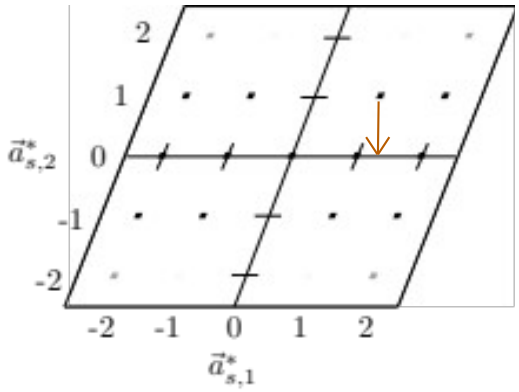
Interpretation

Simulation / refinement
of disordered structural model

Fourier

Superspace concept

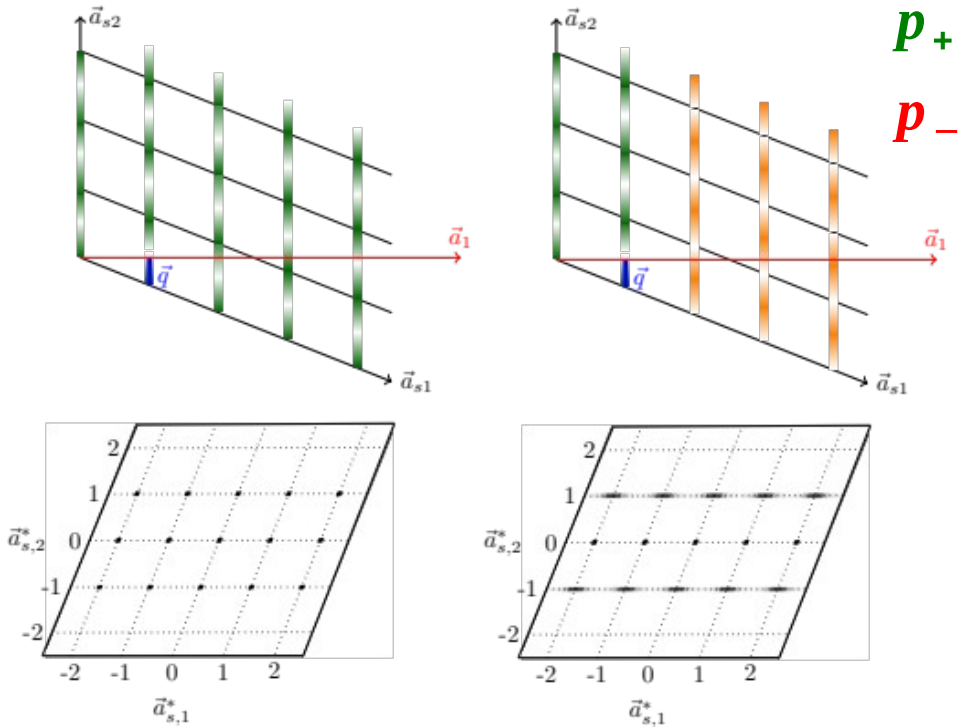




Schmidt & Neder Phy.Rev. B (2019), **100**, 054201

Interpretation

Simulation / refinement of disordered structural model



Superspace concept

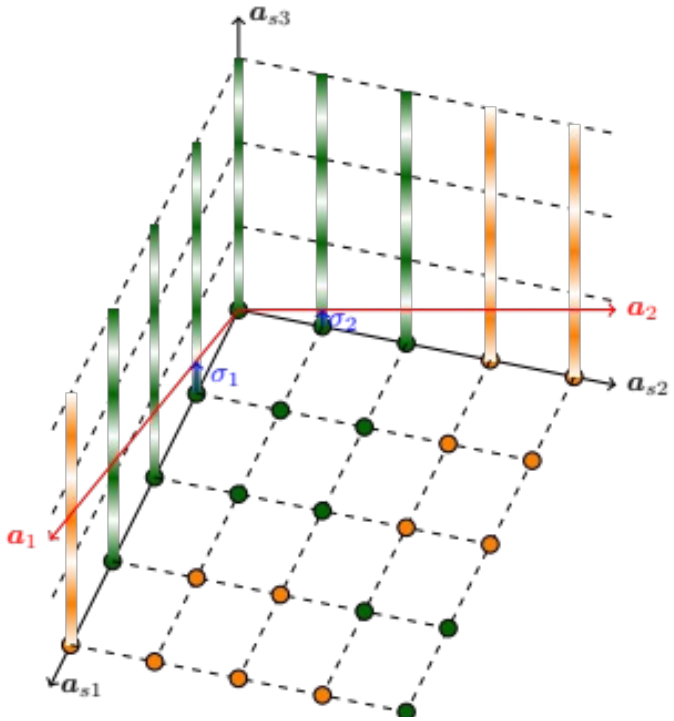
$$p_+(\vec{a}) = p + A\cos(2\pi(\vec{q}\,\vec{a}))$$

$$p_-(\vec{a}) = p - A\cos(2\pi(\vec{q}\,\vec{a}))$$

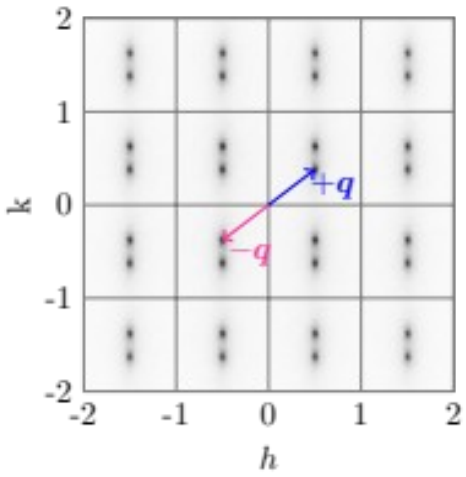
Without long range order in superspace satellites turn into broad maxima

Interpretation

Simulation / refinement
of disordered structural model



Superspace concept



$\vec{q} = (\frac{1}{2}, \frac{1}{\sqrt{7}})$

SRO parameter

$\alpha^S_{(1,0)} = 0.7$

$\alpha^S_{(0,1)} = 0.5$

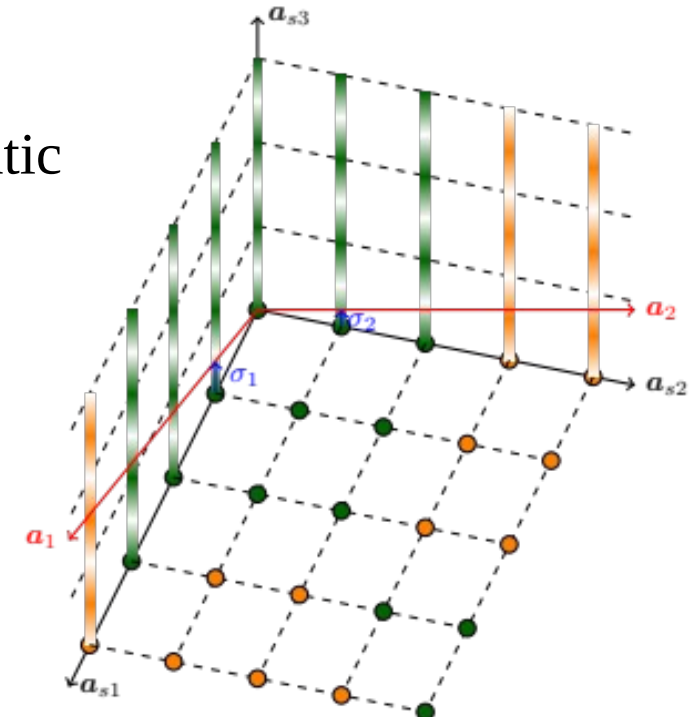
Position , shape, width of diffuse maxima
can arbitrarily be designed,
based on structural model

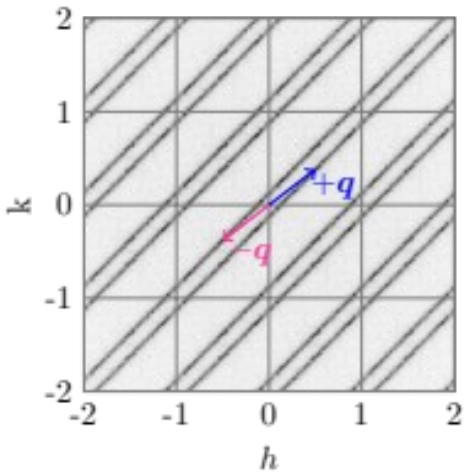
Interpretation

Simulation / refinement of disordered structural model

Superspace concept

static





$\vec{q} = (\frac{1}{2}, \frac{1}{\sqrt{7}})$

SRO parameter

$\alpha^S_{(1,1)} = 0.95$

$\alpha^S_{(\bar{1},1)} = 0.0$

Position , shape, width of diffuse maxima can arbitrarily be designed, based on structural model

Interpretation

Simulation / refinement
of disorder theory

Warren-Cowley
short range order parameter

Weber Z. Krist (2012), 227, 238

Interpretation

Simulation / refinement of disorder theory

Warren-Cowley
short range order parameter

Weber Z. Krist (2012), 227, 238

Mean field theory

Minimize energy for system in different **states** :

States : Spin / Orientation / Type / …

$$H = \frac{1}{2}\sum_j \sum_k \sum_l^s \sum_m^s \mu_j^l \, J_{jk}^{lm} \, \mu_k^m$$

Objects **States**

μ_j^l **1 if Object j** is in **state l**

J_{jk}^{lm} Energy if
Object j is in **state l**
Object k is in **state m**

Interpretation

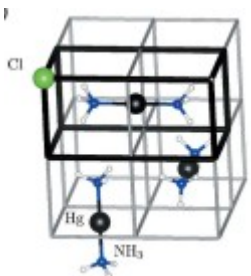
Simulation / refinement of disorder theory

Mean field theory

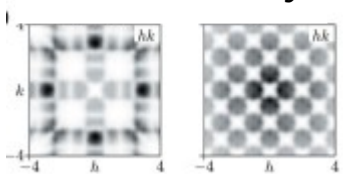
Warren-Cowley
short range order parameter

Weber Z. Krist (2012), 227, 238

$Hg(NH_3)_2Cl_2$



Neutron xray



Objects:
$Hg(NH_3)_2$

States.
[100]; [010]; [001]

States : Spin / Orientation / Type / …

μ_j^l **1 if Object j** is in **state l**

J_{jk}^{lm} Energy if
Object j is in **state l**
Object k is in **state m**

Interpretation

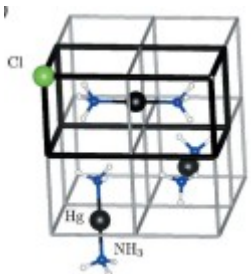
Simulation / refinement of disorder theory

Mean field theory

Warren-Cowley
short range order parameter

Weber Z. Krist (2012), 227, 238

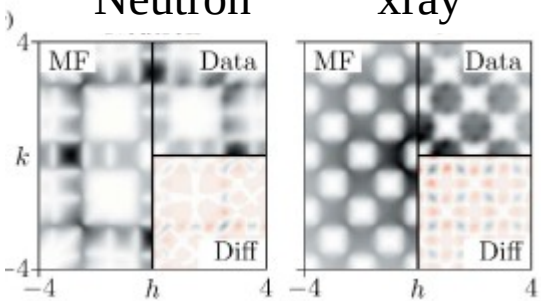
$Hg(NH_3)_2Cl_2$



Objects:
$Hg(NH_3)_2$

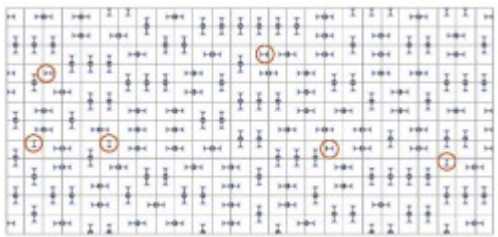
States.
[100]; [010]; [001]

Neutron xray

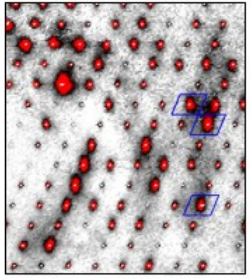


Calculated as result of
Least-squares refinement of **J**

Structure simulated from J



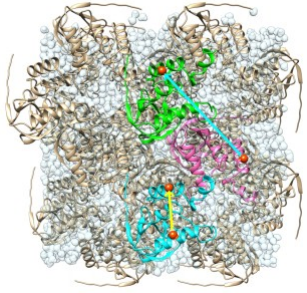
Interpretation



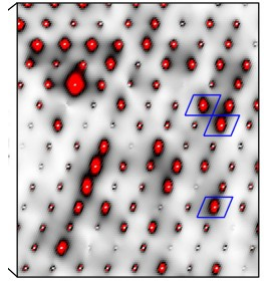
dynamic

Simulation / refinement
force fields / molecular dynamics

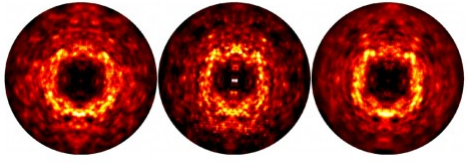
Structure snapshot
at steps in time



Phonon scattering



$$D(hkl) = \langle |F_n(hkl)|^2 \rangle_n - |\langle F_n(hkl) \rangle_n|^2$$



local dynamics

extended dynamics

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U. Kolb, Univ Mainz

R. Poppe, Antwerp
D. Vandermeulebrouke, Antwerp
J. Hadermann, Antwerp

DISCUS: Workshop

Erlangen February 9 - 13
www.icsp.nat.fau.eu/neder-group/discus-home

"A beautiful disorder is an effect of art."

Nicolas Boileau