Three-dimensional pair distribution functions: 3D-ΔPDF

An Introduction

Ella Mara Schmidt, Crystallography & Geomaterials Research, Faculty of Geosciences, University of Bremen, Germany.

Mainz, December 8, 2022

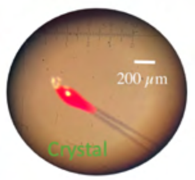
Crystalline Materials

"A material is a crystal if it has essentially a sharp diffraction pattern. The word essentially means that most of the intensity of the diffraction is concentrated in relatively sharp Bragg peaks, besides the always present diffuse scattering." [1]

[1] IUCr. Report of the Executive Committee for 1991. *Acta Cryst.* **A48**, 922-946 (1992).

Crystalline Materials

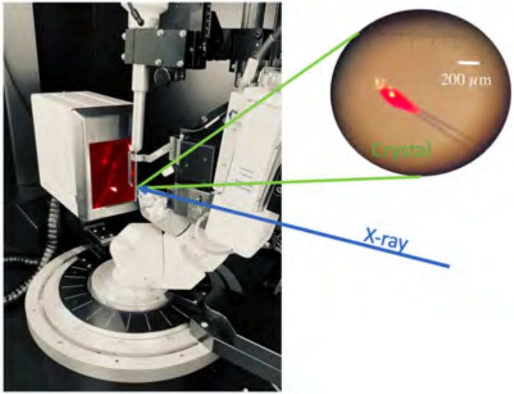
"A material is a crystal if it has essentially a sharp diffraction pattern. The word essentially means that most of the intensity of the diffraction is concentrated in relatively sharp Bragg peaks, besides the always present diffuse scattering." [1]



[1] IUCr. Report of the Executive Committee for 1991. *Acta Cryst.* **A48**, 922-946 (1992).

Crystalline Materials

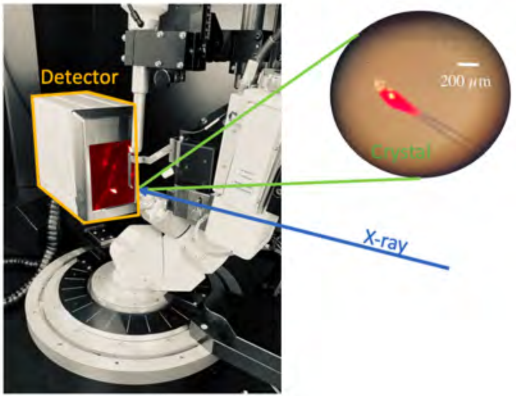
“A material is a crystal if it has essentially a sharp diffraction pattern. The word essentially means that most of the intensity of the diffraction is concentrated in relatively sharp Bragg peaks, besides the always present diffuse scattering.” [1]



[1] IUCr. Report of the Executive Committee for 1991. *Acta Cryst.* **A48**, 922-946 (1992).

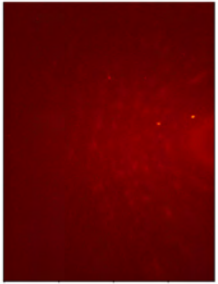
Crystalline Materials

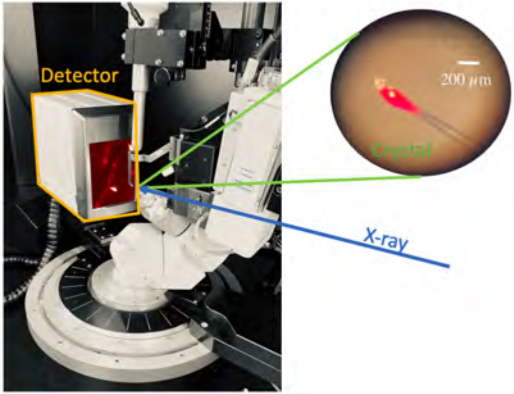
"A material is a crystal if it has essentially a sharp diffraction pattern. The word essentially means that most of the intensity of the diffraction is concentrated in relatively sharp Bragg peaks, besides the always present diffuse scattering." [1]



[1] IUCr. Report of the Executive Committee for 1991. *Acta Cryst.* **A48**, 922-946 (1992).

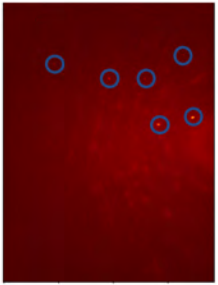
Crystalline Materials

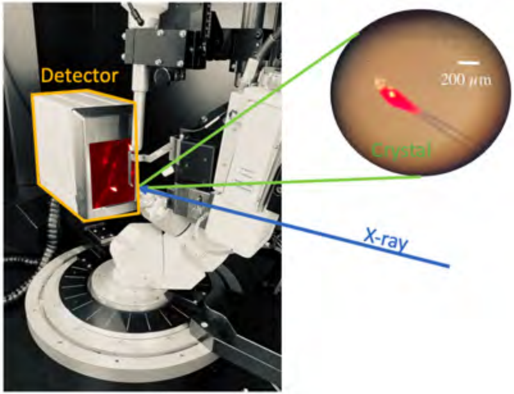




[1] IUCr. Report of the Executive Committee for 1991. *Acta Cryst.* **A48**, 922-946 (1992).

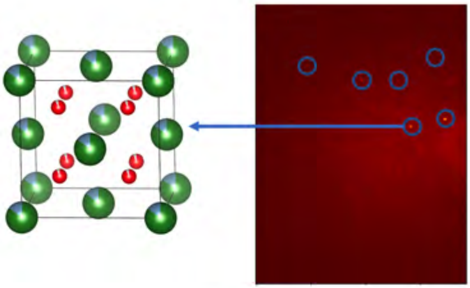
Crystalline Materials

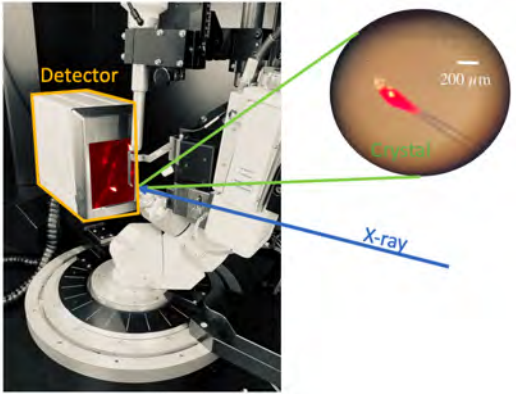




[1] IUCr. Report of the Executive Committee for 1991. *Acta Cryst.* **A48**, 922-946 (1992).

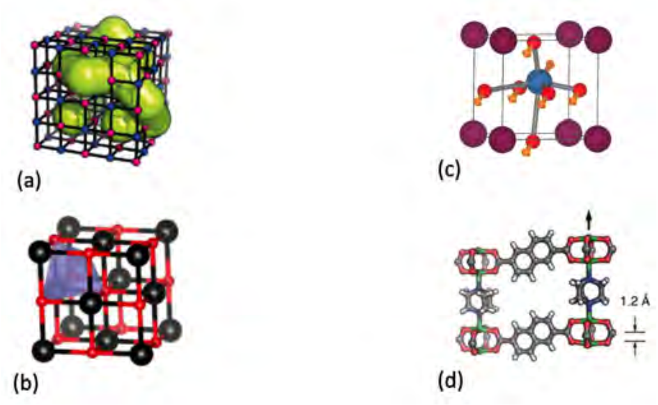
Crystalline Materials





[1] IUCr. Report of the Executive Committee for 1991. *Acta Cryst.* **A48**, 922-946 (1992).

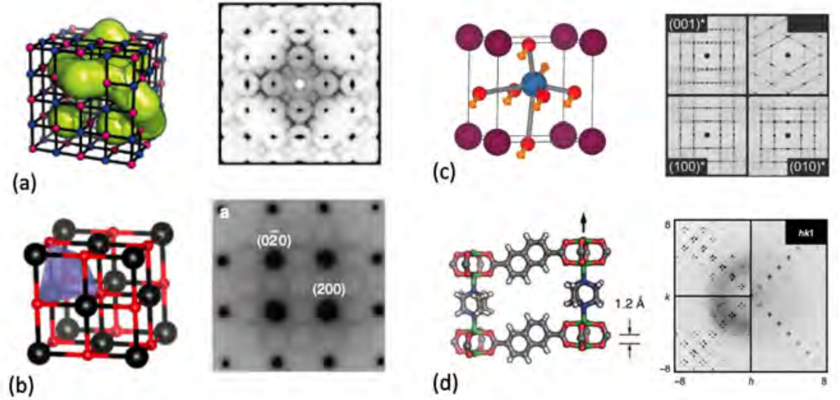
Correlated Disorder in Functional Materials



(a) Prussian blue analogues [2]
(b) Rocksalt cathode materials [3]
(c) Relaxor ferroelectrics [4]
(d) Metal-organic frameworks [5]

[2] Simonov, A. *et al.* *Nature*. **578**, 256-260 (2020).
[3] Ji, H., *et al.* *Nat. Commun.* **10**, 592 (2019).
[4] Senn, M. S. *et al.* *Phys. Rev. Lett.* **116**, 207602 (2016).
[5] Ehrling, S., *et al.* Nat. Chem. **13**, 568–574 (2021).

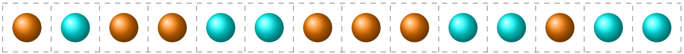
Correlated Disorder in Functional Materials

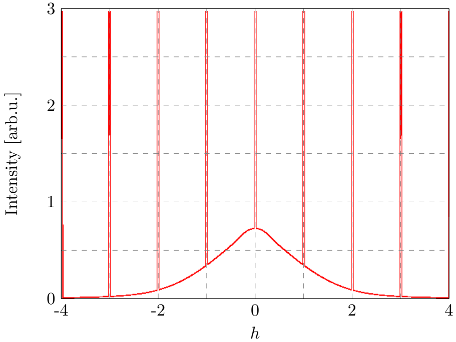


(a) Prussian blue analogues [2]
(b) Rocksalt cathode materials [3]
(c) Relaxor ferroelectrics [4]
(d) Metal-organic frameworks [5]

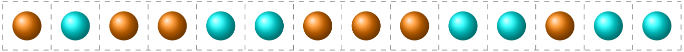
[2] Simonov, A. *et al. Nature*. **578**, 256-260 (2020).
[3] Ji, H., *et al. Nat. Commun.* **10**, 592 (2019).
[4] Senn, M. S. *et al. Phys. Rev. Lett.* **116**, 207602 (2016).
[5] Ehrling, S., *et al.* Nat. Chem. **13**, 568–574 (2021).

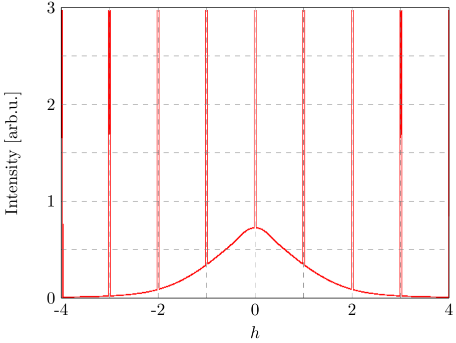
Understanding diffuse scattering





Understanding diffuse scattering

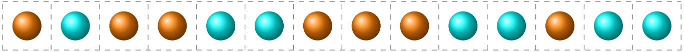


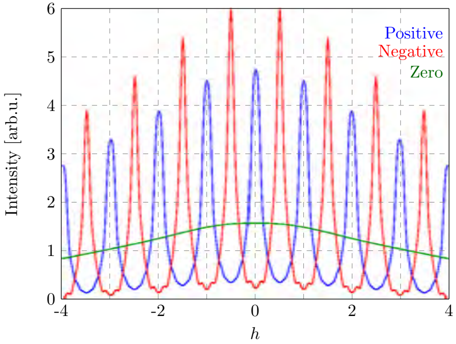


→ Bragg data analysis still yields an average unit cell

→ Information about local order is only encoded in the diffuse scattering

Substitutional disorder



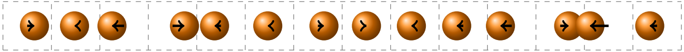


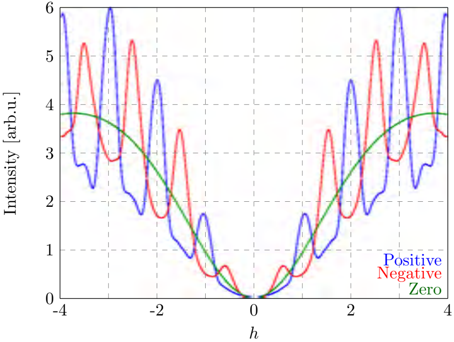
Warren-Cowley short-range order parameter

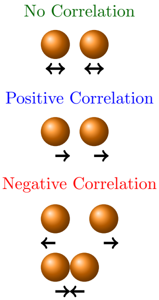
$$\alpha_{\vec{v}} = 1 - \frac{p_{\vec{v}}^{AB}}{m_A m_B}$$

$$\begin{cases} > 0 & \text{Positive correlation} \\ = 0 & \text{No correlation} \\ < 0 & \text{Negative correlation} \end{cases}$$

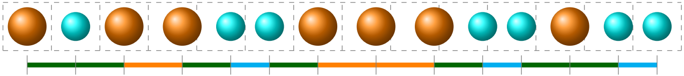
Displacement disorder

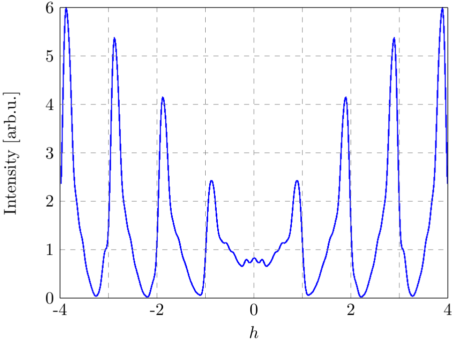


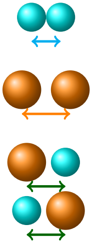




Atomic size effect







Diffuse Scattering Analysis

Aim: Determine correlations between disordered components quantitatively and understand local atomic arrangements

Available tools:

[6] Welberrry, T.R. & Weber, T. (2016). *Crystallogr. Rev.* **22**, 2–78.
[7] Schmidt, E.M & Neder, R.B. (2017). *Acta Cryst.*,**A73**, 231-237.
[8] Neder, R. B. & Proffen, T. (2008) *Diffuse Scattering and Defect Structure Simulations*. Oxford University Press.
[9] Proffen, T. & Welberry, T. R. (1997) *Acta Cryst.* **A53**, 202-216.
[10] Schmidt, E. M. *et al.* (2022) *IUCrJ.*, **9**, 21-30.
[11] Simonov, A., *et al.* (2014) *J. Appl. Cryst.*, **47**, 1146-1152.

Diffuse Scattering Analysis

Aim: Determine correlations between disordered components quantitatively and understand local atomic arrangements

Available tools:

- Analytical modelling [6,7]

$$I_{Diffuse}(\vec{h}) \propto 2 \sum_{\vec{v} \neq \vec{0}} \Big[\left[p_{\vec{v}}^{AA} |F_A|^2 \cos(2\pi \vec{h}\vec{\delta}_{\vec{v}}^{AA}) + p_{\vec{v}}^{BB} |F_B|^2 \cos(2\pi \vec{h}\vec{\delta}_{\vec{v}}^{BB}) + p_{\vec{v}}^{AB}(F_A F_B^\star + F_B F_A^\star) \cos(2\pi \vec{h}\vec{\delta}_{\vec{v}}^{AB})\right] \cdot \exp(-2\pi^2 \vec{h}\underline{\underline{\sigma}}_{\vec{v}}\vec{h}) - |m_A F_A + m_B F_B|^2 \cos(2\pi \vec{h}\vec{v}) \cdot \exp(-4\pi^2 \vec{h}\underline{\underline{\sigma}}\vec{h}) \Big]$$

$$+ m_A |F_A|^2 + m_B |F_B|^2 - |m_A F_A + m_B F_B|^2 \cdot \exp(-4\pi^2 (\vec{h}\underline{\underline{\sigma}}\vec{h}))$$

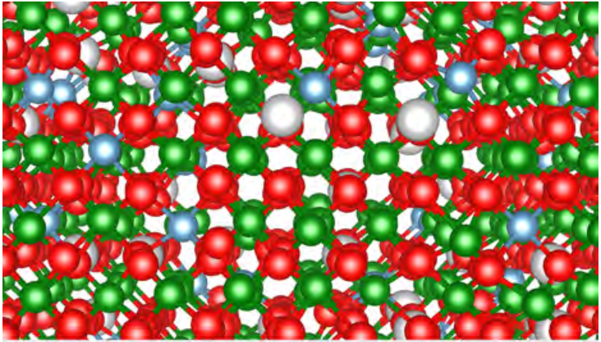
[6] Welberry, T.R. & Weber, T. (2016). *Crystallogr. Rev.* **22**, 2–78.
[7] Schmidt, E.M & Neder, R.B. (2017). *Acta Cryst.*,**A73**, 231-237.
[8] Neder, R. B. & Proffen, T. (2008) *Diffuse Scattering and Defect Structure Simulations.* Oxford University Press.
[9] Proffen, T. & Welberry, T. R. (1997) *Acta Cryst.* **A53**, 202-216.
[10] Schmidt, E. M. *et al.* (2022) *IUCrJ.*, **9**, 21-30.
[11] Simonov, A., *et al.* (2014) *J. Appl. Cryst.*, **47**, 1146-1152.

Diffuse Scattering Analysis

Aim: Determine correlations between disordered components quantitatively and understand local atomic arrangements

Available tools:

- Analytical modelling [6,7]
- Direct Monte Carlo modelling [8]



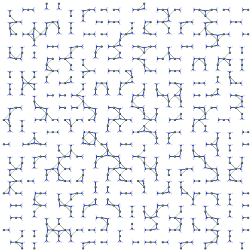
[6] Welberrry, T.R. & Weber, T. (2016). *Crystallogr. Rev.* **22**, 2–78.
[7] Schmidt, E.M & Neder, R.B. (2017). *Acta Cryst.*,**A73**, 231-237.
[8] Neder, R. B. & Proffen, T. (2008) *Diffuse Scattering and Defect Structure Simulations*. Oxford University Press.
[9] Proffen, T. & Welberry, T. R. (1997) *Acta Cryst.* **A53**, 202-216.
[10] Schmidt, E. M. *et al.* (2022) *IUCrJ.*, **9**, 21-30.
[11] Simonov, A., *et al.* (2014) *J. Appl. Cryst.*, **47**, 1146-1152.

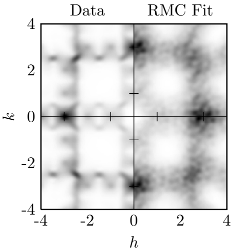
Diffuse Scattering Analysis

Aim: Determine correlations between disordered components quantitatively and understand local atomic arrangements

Available tools:

- Analytical modelling [6,7]
- Direct Monte Carlo modelling [8]
- Reverse Monte Carlo modelling [9]





[6] Welberry, T.R. & Weber, T. (2016). *Crystallogr. Rev.* **22**, 2–78.
[7] Schmidt, E.M & Neder, R.B. (2017). *Acta Cryst.*,**A73**, 231-237.
[8] Neder, R. B. & Proffen, T. (2008) *Diffuse Scattering and Defect Structure Simulations*. Oxford University Press.
[9] Proffen, T. & Welberry, T. R. (1997) *Acta Cryst.* **A53**, 202-216.
[10] Schmidt, E. M. *et al.* (2022) *IUCrJ.*, **9**, 21-30.
[11] Simonov, A., *et al.* (2014) *J. Appl. Cryst.*, **47**, 1146-1152.

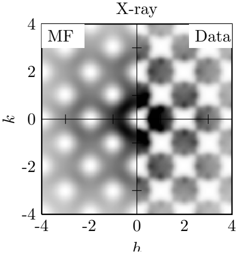
Diffuse Scattering Analysis

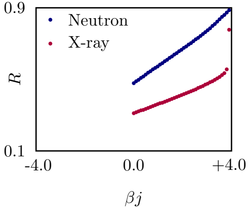
Aim: Determine correlations between disordered components quantitatively and understand local atomic arrangements

$$I(\boldsymbol{q}) \propto \mathrm{Tr}\left\{\underline{\underline{MF}}\left[\underline{\underline{1}} + \beta\underline{\underline{MJ}}(\boldsymbol{q})\right]^{-1}\right\}$$

Available tools:

- Analytical modelling [6,7]
- Direct Monte Carlo modelling [8]
- Reverse Monte Carlo modelling [9]
- Mean field approximations [10]





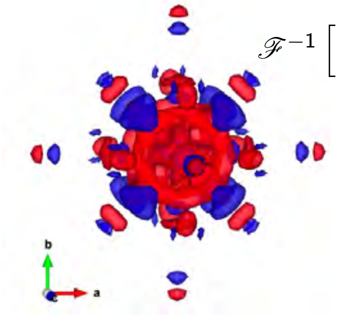
[6] Welberry, T.R. & Weber, T. (2016). *Crystallogr. Rev.* **22**, 2–78.
[7] Schmidt, E.M & Neder, R.B. (2017). *Acta Cryst.*,**A73**, 231-237.
[8] Neder, R. B. & Proffen, T. (2008) *Diffuse Scattering and Defect Structure Simulations*. Oxford University Press.
[9] Proffen, T. & Welberry, T. R. (1997) *Acta Cryst.* **A53**, 202-216.
[10] Schmidt, E. M. *et al.* (2022) *IUCrJ.*, **9**, 21-30.
[11] Simonov, A., *et al.* (2014) *J. Appl. Cryst.*, **47**, 1146-1152.

Diffuse Scattering Analysis

Aim: Determine correlations between disordered components quantitatively and understand local atomic arrangements

Available tools:

- Analytical modelling [6,7]
- Direct Monte Carlo modelling [8]
- Reverse Monte Carlo modelling [9]
- Mean field approximations [10]
- 3D-pair distribution functions [11]



$$\mathscr{F}^{-1}\left[I_{Diff}\left(\vec{h}\right)\right]$$

[6] Welberry, T.R. & Weber, T. (2016). *Crystallogr. Rev.* **22**, 2–78.
[7] Schmidt, E.M & Neder, R.B. (2017). *Acta Cryst.*,**A73**, 231-237.
[8] Neder, R. B. & Proffen, T. (2008) *Diffuse Scattering and Defect Structure Simulations*. Oxford University Press.
[9] Proffen, T. & Welberry, T. R. (1997) *Acta Cryst.* **A53**, 202-216.
[10] Schmidt, E. M. *et al.* (2022) *IUCrJ.*, **9**, 21-30.
[11] Simonov, A., *et al.* (2014) *J. Appl. Cryst.*, **47**, 1146-1152.

3D-ΔPDF Method

Mathematical definition

PDF: $$\mathscr{F}^{-1}\left[I_{Tot}\left(\vec{h}\right)\right] = \langle\rho\left(\vec{x}\right) * \rho\left(\vec{x}\right)\rangle$$

All interatomic distances

Patterson-Function: $$\mathscr{F}^{-1}\left[I_{Bragg}\left(\vec{h}\right)\right] = \langle\rho\left(\vec{x}\right)\rangle * \langle\rho\left(\vec{x}\right)\rangle$$

Interatomic distances of average structure

[12] Weber, T. and Simonov, A. (2012) *Z. Krist.* **227**, 238-247.

3D-ΔPDF Method

Mathematical definition

PDF: $$\mathscr{F}^{-1}\left[I_{Tot}\left(\vec{h}\right)\right] = \langle\rho\left(\vec{x}\right) * \rho\left(\vec{x}\right)\rangle$$

All interatomic distances

Patterson-Function: $$\mathscr{F}^{-1}\left[I_{Bragg}\left(\vec{h}\right)\right] = \langle\rho\left(\vec{x}\right)\rangle * \langle\rho\left(\vec{x}\right)\rangle$$

Interatomic distances of average structure

3D-ΔPDF: $$\mathscr{F}^{-1}\left[I_{Diff}\left(\vec{h}\right)\right] = \mathscr{F}^{-1}\left[I_{Tot}\left(\vec{h}\right) - I_{Bragg}\left(\vec{h}\right)\right]$$

Difference real vs. average structure [3]

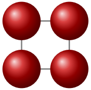
[12] Weber, T. and Simonov, A. (2012) *Z. Krist.* **227**, 238-247.

3D-ΔPDF Signatures

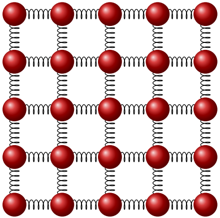
PDF peak width: spread of interatomic distance of neighbouring atoms

Patterson peak width: given by overall atomic displacement parameter

Average structure



Real structure

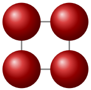


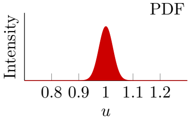
3D-ΔPDF Signatures

PDF peak width: spread of interatomic distance of neighbouring atoms

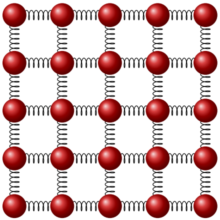
Patterson peak width: given by overall atomic displacement parameter

Average structure





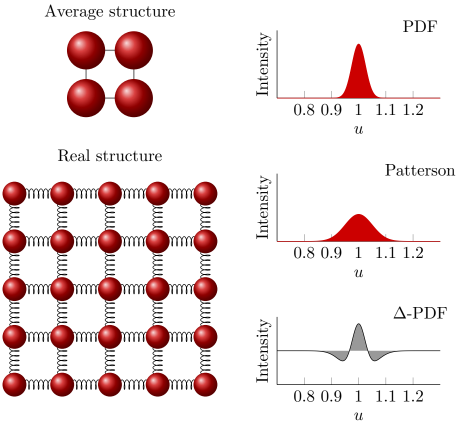
Real structure



3D-ΔPDF Signatures

PDF peak width: spread of interatomic distance of neighbouring atoms

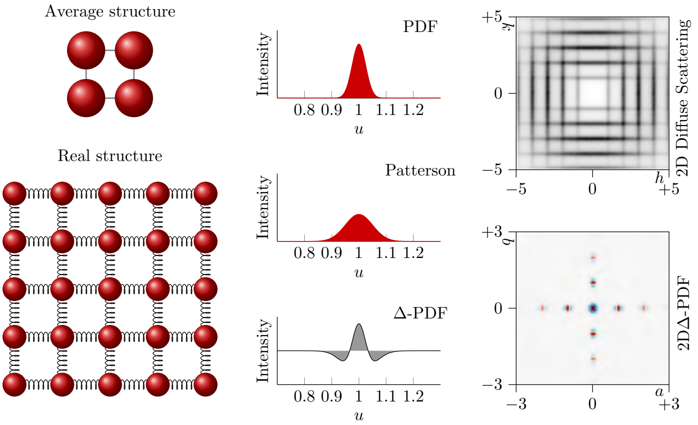
Patterson peak width: given by overall atomic displacement parameter



3D-ΔPDF Signatures

PDF peak width: spread of interatomic distance of neighbouring atoms

Patterson peak width: given by overall atomic displacement parameter



3D-ΔPDF Signatures

PDF peak height:

$$\sum_{AB} \frac{n_{AB}}{n_t} \cdot f_A \cdot f_B$$

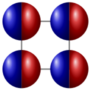
n_{AB}: # of AB pairs
n_t: total # of pairs
f_A: Scattering factor A
f_B: Scattering factor B

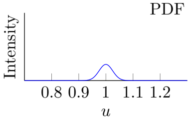
Patterson peak height:

$$(m_A f_A)(m_B f_B)$$

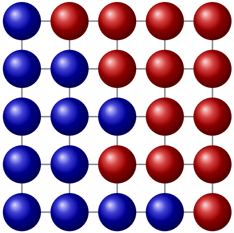
m_A: concentration of A
m_B: concentration of B

Average structure





Real structure



3D-ΔPDF Signatures

PDF peak height:

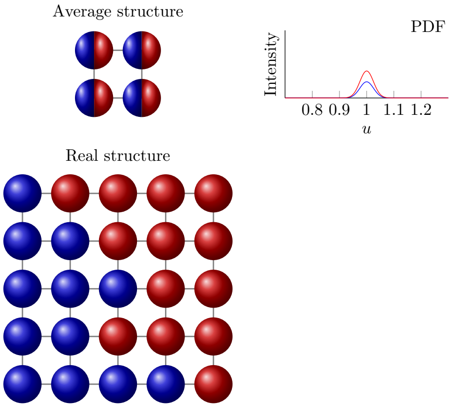
$$\sum_{AB} \frac{n_{AB}}{n_t} \cdot f_A \cdot f_B$$

n_{AB}: # of AB pairs
n_t: total # of pairs
f_A: Scattering factor A
f_B: Scattering factor B

Patterson peak height:

$$(m_A f_A)(m_B f_B)$$

m_A: concentration of A
m_B: concentration of B



3D-ΔPDF Signatures

PDF peak height:

$$\sum_{AB} \frac{n_{AB}}{n_t} \cdot f_A \cdot f_B$$

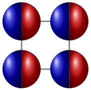
n_{AB}: # of AB pairs
n_t: total # of pairs
f_A: Scattering factor A
f_B: Scattering factor B

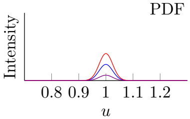
Patterson peak height:

$$(m_A f_A)(m_B f_B)$$

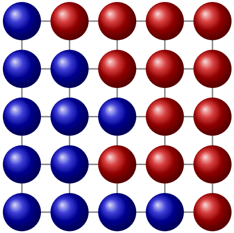
m_A: concentration of A
m_B: concentration of B

Average structure





Real structure



3D-ΔPDF Signatures

PDF peak height:

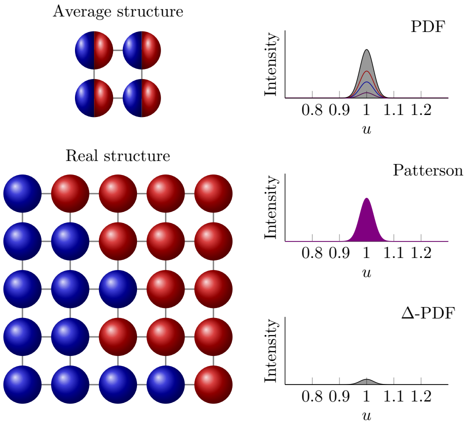
$$\sum_{AB} \frac{n_{AB}}{n_t} \cdot f_A \cdot f_B$$

n_{AB}: # of AB pairs
n_t: total # of pairs
f_A: Scattering factor A
f_B: Scattering factor B

Patterson peak height:

$$(m_A f_A)(m_B f_B)$$

m_A: concentration of A
m_B: concentration of B



3D-ΔPDF Signatures

PDF peak height:

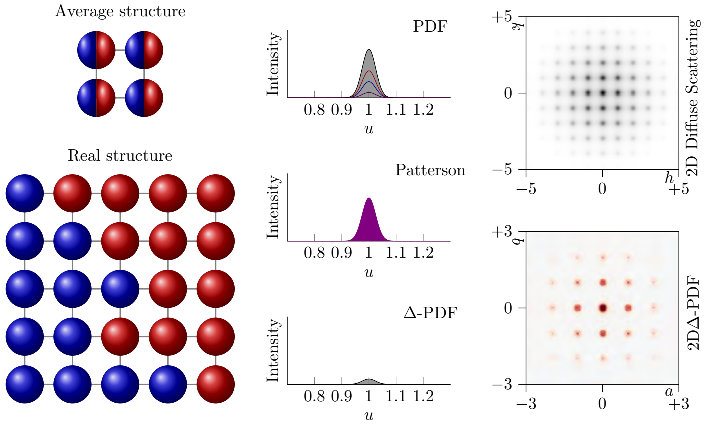
$$\sum_{AB} \frac{n_{AB}}{n_t} \cdot f_A \cdot f_B$$

n_{AB}: # of AB pairs
n_t: total # of pairs
f_A: Scattering factor A
f_B: Scattering factor B

Patterson peak height:

$$(m_A f_A)(m_B f_B)$$

m_A: concentration of A
m_B: concentration of B



3D-ΔPDF Signatures

PDF peak height:

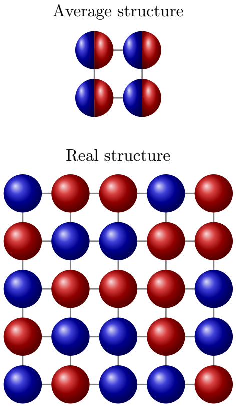
$$\sum_{AB} \frac{n_{AB}}{n_t} \cdot f_A \cdot f_B$$

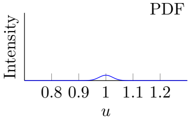
n_{AB}: # of AB pairs
n_t: total # of pairs
f_A: Scattering factor A
f_B: Scattering factor B

Patterson peak height:

$$(m_A f_A)(m_B f_B)$$

m_A: concentration of A
m_B: concentration of B





3D-ΔPDF Signatures

PDF peak height:

$$\sum_{AB} \frac{n_{AB}}{n_t} \cdot f_A \cdot f_B$$

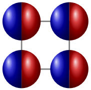
n_{AB}: # of AB pairs
n_t: total # of pairs
f_A: Scattering factor A
f_B: Scattering factor B

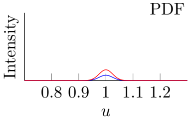
Patterson peak height:

$$(m_A f_A)(m_B f_B)$$

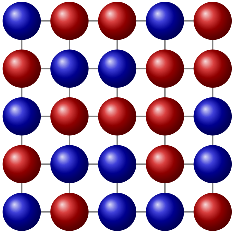
m_A: concentration of A
m_B: concentration of B

Average structure





Real structure



3D-ΔPDF Signatures

PDF peak height:

$$\sum_{AB} \frac{n_{AB}}{n_t} \cdot f_A \cdot f_B$$

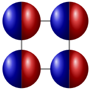
n_{AB}: # of AB pairs
n_t: total # of pairs
f_A: Scattering factor A
f_B: Scattering factor B

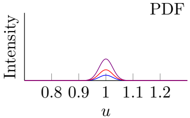
Patterson peak height:

$$(m_A f_A)(m_B f_B)$$

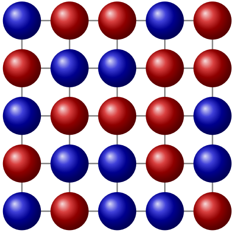
m_A: concentration of A
m_B: concentration of B

Average structure





Real structure



3D-ΔPDF Signatures

PDF peak height:

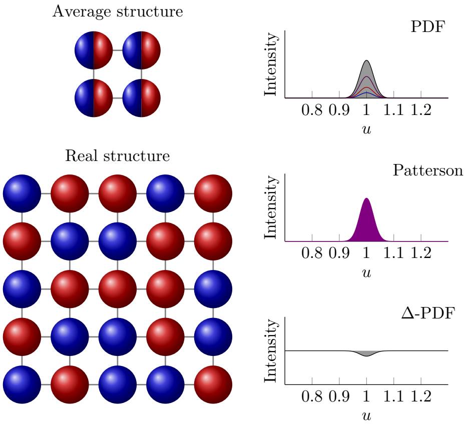
$$\sum_{AB} \frac{n_{AB}}{n_t} \cdot f_A \cdot f_B$$

n_{AB}: # of AB pairs
n_t: total # of pairs
f_A: Scattering factor A
f_B: Scattering factor B

Patterson peak height:

$$(m_A f_A)(m_B f_B)$$

m_A: concentration of A
m_B: concentration of B



3D-ΔPDF Signatures

PDF peak height:

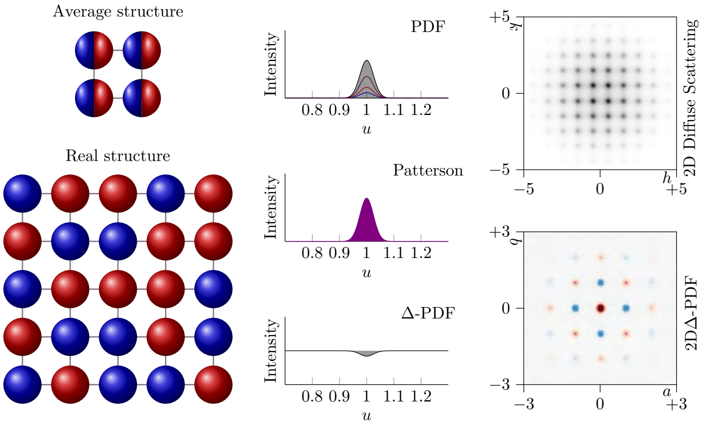
$$\sum_{AB} \frac{n_{AB}}{n_t} \cdot f_A \cdot f_B$$

n_{AB}: # of AB pairs
n_t: total # of pairs
f_A: Scattering factor A
f_B: Scattering factor B

Patterson peak height:

$$(m_A f_A)(m_B f_B)$$

m_A: concentration of A
m_B: concentration of B



3D-ΔPDF Signatures

PDF peak height:

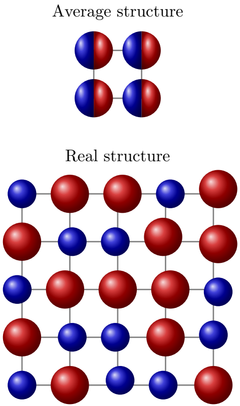
$$\sum_{AB} \frac{n_{AB}}{n_t} \cdot f_A \cdot f_B$$

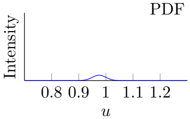
n_{AB}: # of AB pairs
n_t: total # of pairs
f_A: Scattering factor A
f_B: Scattering factor B

Patterson peak height:

$$(m_A f_A)(m_B f_B)$$

m_A: concentration of A
m_B: concentration of B





3D-ΔPDF Signatures

PDF peak height:

$$\sum_{AB} \frac{n_{AB}}{n_t} \cdot f_A \cdot f_B$$

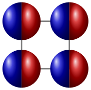
n_{AB}: # of AB pairs
n_t: total # of pairs
f_A: Scattering factor A
f_B: Scattering factor B

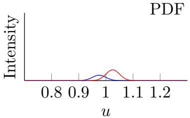
Patterson peak height:

$$(m_A f_A)(m_B f_B)$$

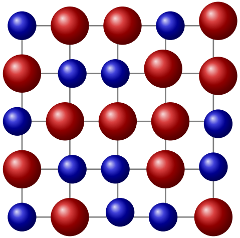
m_A: concentration of A
m_B: concentration of B

Average structure





Real structure



3D-ΔPDF Signatures

PDF peak height:

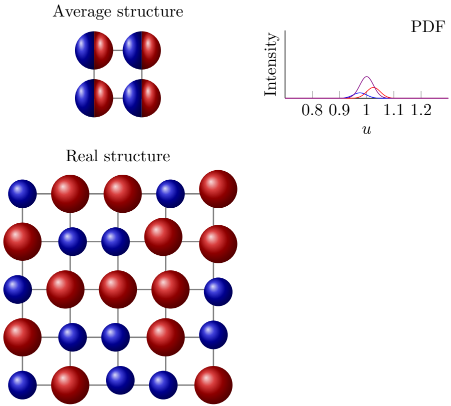
$$\sum_{AB} \frac{n_{AB}}{n_t} \cdot f_A \cdot f_B$$

n_{AB}: # of AB pairs
n_t: total # of pairs
f_A: Scattering factor A
f_B: Scattering factor B

Patterson peak height:

$$(m_A f_A)(m_B f_B)$$

m_A: concentration of A
m_B: concentration of B



3D-ΔPDF Signatures

PDF peak height:

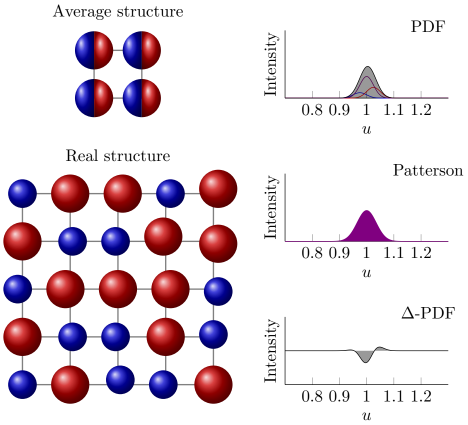
$$\sum_{AB} \frac{n_{AB}}{n_t} \cdot f_A \cdot f_B$$

n_{AB}: # of AB pairs
n_t: total # of pairs
f_A: Scattering factor A
f_B: Scattering factor B

Patterson peak height:

$$(m_A f_A)(m_B f_B)$$

m_A: concentration of A
m_B: concentration of B



3D-ΔPDF Signatures

PDF peak height:

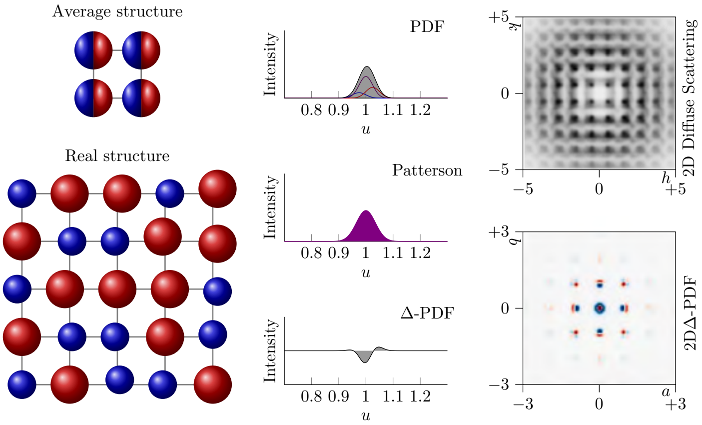
$$\sum_{AB} \frac{n_{AB}}{n_t} \cdot f_A \cdot f_B$$

n_{AB}: # of AB pairs
n_t: total # of pairs
f_A: Scattering factor A
f_B: Scattering factor B

Patterson peak height:

$$(m_A f_A)(m_B f_B)$$

m_A: concentration of A
m_B: concentration of B



Data processing and reconstruction

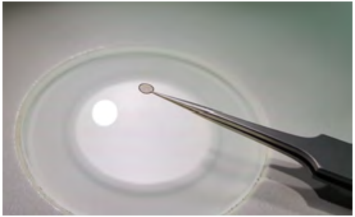
Step 1: Measurement

$\lambda = 0.02508$ Å

0.25° steps

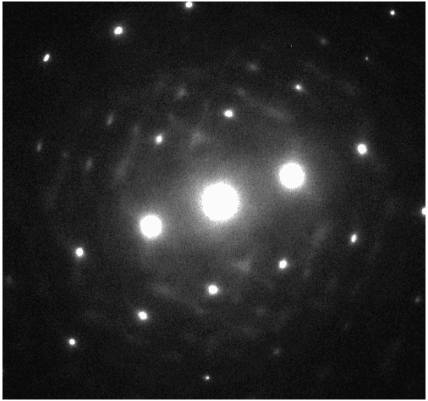
Exposure: 1 s

Microscope: FEI Tecnai G2



Data processing and reconstruction

Step 1: Measurement

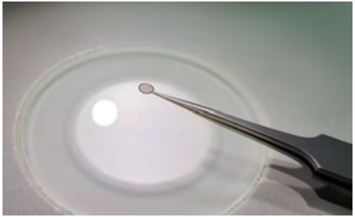


λ= 0.02508 Å

0.25° steps

Exposure: 1 s

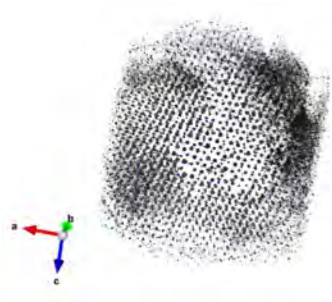
Microscope: FEI Tecnai G2



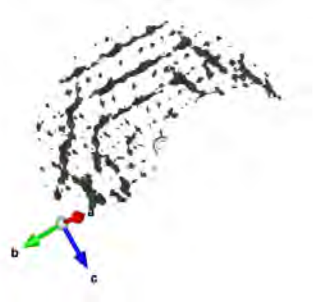
Data processing and reconstruction

Step 1: Measurement: Aim for full reciprocal space coverage

X-ray



Neutron

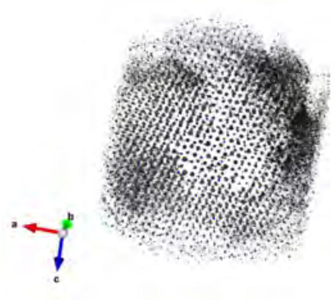


Electron

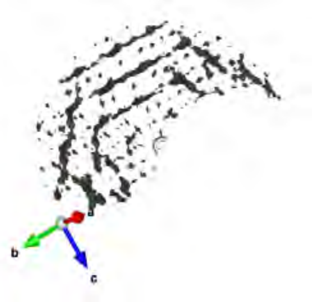
Data processing and reconstruction

Step 1: Measurement: Aim for full reciprocal space coverage

X-ray



Neutron



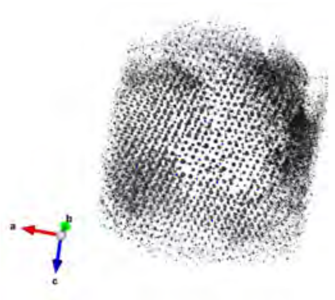
Electron

Data collection times

$\approx$ 2 days | $\approx$ 4 days | $\approx$ 2 min

Data processing and reconstruction

Step 2: 3D-Data reconstruction



Software options:

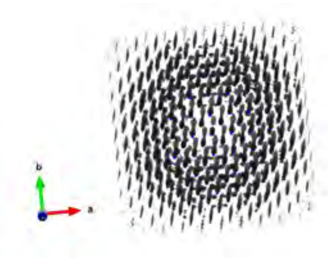
- X-ray data: Meerkat [13], works with orientation matrix from XDS
- Neutron data: Mantid [14]
- 3D-ED data: Pets2 [15], soon eADT
- Customized solutions

[13] https://github.com/aglie/meerkat
[14] https://www.mantidproject.org/
[15] http://pets.fzu.cz/

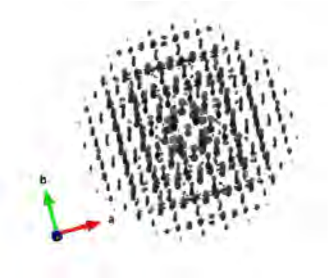
Data processing and reconstruction

Step 3: Symmetry averaging

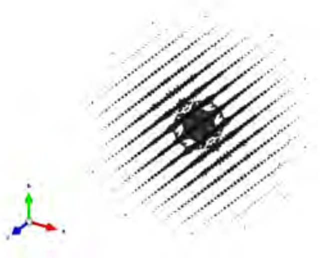
X-ray



Neutron



Electron



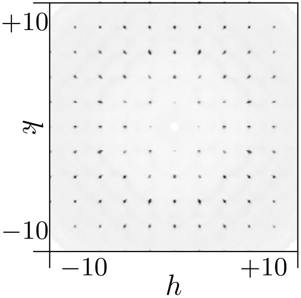
→ Full reciprocal space coverage is needed for the Fourier transform!

Data processing and reconstruction

Step 4: Bragg peak elimination

Normal punch and fill:

- Outlier rejection (KAREN-algorithm [16])
- Punch and fill with average value of surrounding voxels [11]



[16] Weng, J. *et al.* (2020) *J. Appl. Cryst.* **53**, 159-169.
[11] Simonov, A. *et al.* (2014) *J. Appl. Cryst.* **47**, 2011-2018.

Data processing and reconstruction

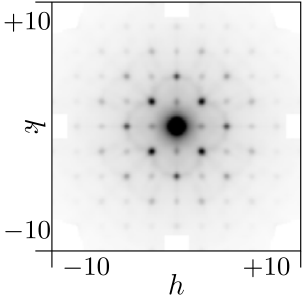
Step 4: Bragg peak elimination

Normal punch and fill:

- Outlier rejection (KAREN-algorithm [16])
- Punch and fill with average value of surrounding voxels [11]

Most of the times needed:

- Punch with larger radius and fill using an interpolation algorithm



[16] Weng, J. *et al.* (2020) *J. Appl. Cryst.* **53**, 159-169.
[11] Simonov, A. *et al.* (2014) *J. Appl. Cryst.* **47**, 2011-2018.

Data processing and reconstruction

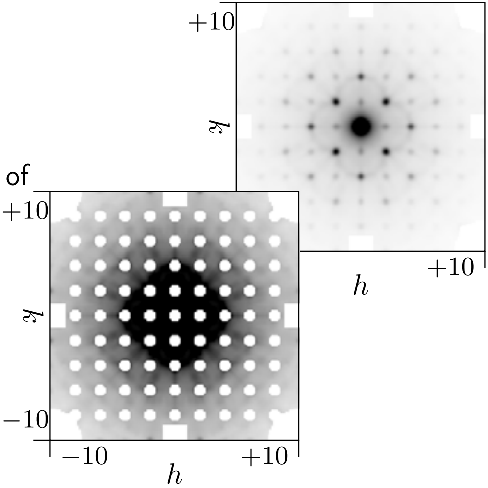
Step 4: Bragg peak elimination

Normal punch and fill:

- Outlier rejection (KAREN-algorithm [16])
- Punch and fill with average value of surrounding voxels [11]

Most of the times needed:

- Punch with larger radius and fill using an interpolation algorithm



[16] Weng, J. *et al.* (2020) *J. Appl. Cryst.* **53**, 159-169.
[11] Simonov, A. *et al.* (2014) *J. Appl. Cryst.* **47**, 2011-2018.

Data processing and reconstruction

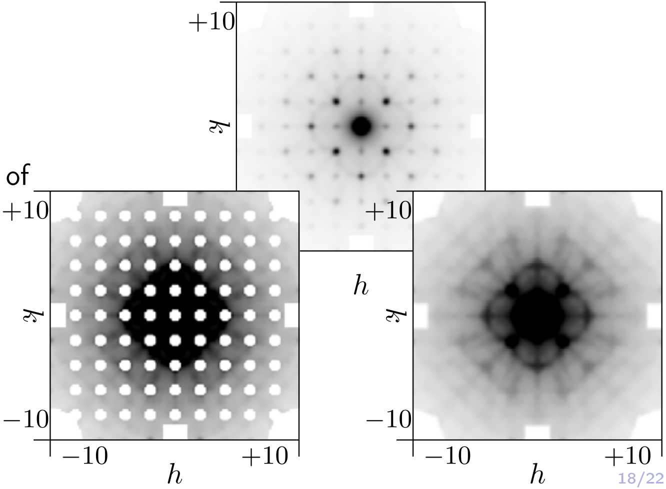
Step 4: Bragg peak elimination

Normal punch and fill:

- Outlier rejection (KAREN-algorithm [16])
- Punch and fill with average value of surrounding voxels [11]

Most of the times needed:

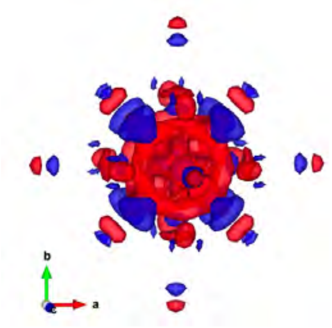
- Punch with larger radius and fill using an interpolation algorithm



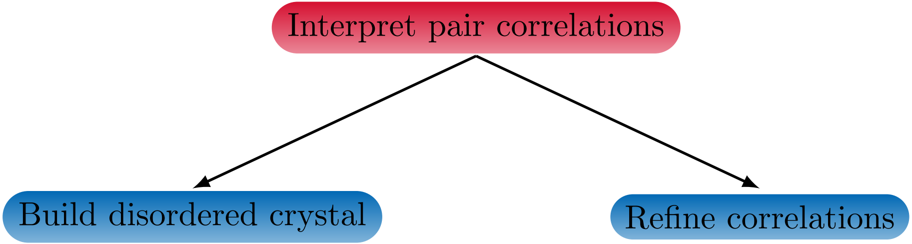
[16] Weng, J. *et al.* (2020) *J. Appl. Cryst.* **53**, 159-169.
[11] Simonov, A. *et al.* (2014) *J. Appl. Cryst.* **47**, 2011-2018.

Data processing and reconstruction

Measure	Measure with maximum reciprocal space coverage Long exposure times are needed
Recon-struct	3D-Reconstruction
Symmetry	Apply symmetry average
Punch and Fill	Eliminate Bragg relections Backgorund subtraction
FFT	Generate the 3D-ΔPDF using a FFT alogrithm

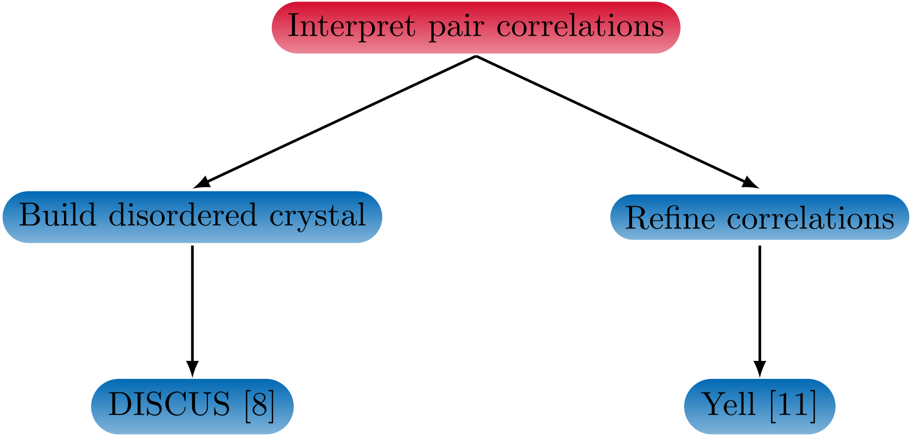


3D-ΔPDF interpretation and modelling



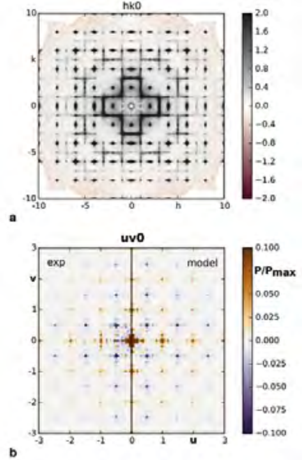
[11] Simonov, A. *et al.* (2014) *J. Appl. Cryst.* **47**, 1146-1152. https://github.com/YellProgram/Yell
[8] Neder, R. B. & Proffen, T. (2008) *Diffuse Scattering and Defect Structure Simulations.* Oxford University Press.

3D-ΔPDF interpretation and modelling

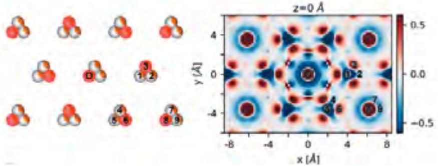


[11] Simonov, A. *et al.* (2014) *J. Appl. Cryst.* **47**, 1146-1152. https://github.com/YellProgram/Yell
[8] Neder, R. B. & Proffen, T. (2008) *Diffuse Scattering and Defect Structure Simulations*. Oxford University Press.

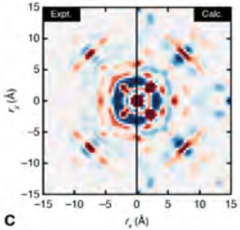
Applications of 3D-ΔPDF



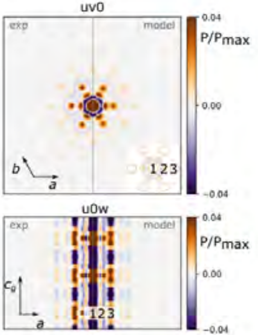
Prussian Blue Analogues [2]



$Cu_{2-x}Se$ [17]



MOFs [18]



Urea inclusion compounds [19]

[2] Simonov, A. *et al.* *Nature*. **578**, 256-260 (2020).
[17] Roth, N. & Iversen, B.B. *Acta Cryst. A* **75**, 465-473.
[18] Meekel, E.G. *et al.* https://arxiv.org/abs/2208.12289
[19] Simonov, A. *et al.* *Phys. Rev. B* **165**, 054206.

Summary

- 3D-ΔPDFs visualize difference pair correlations
- Positive correlations: More scattering density then suggested by the average structure
- Negative correlations: Less scattering density then suggested by the average structure
- Full reciprocal space coverage is needed from measurement
- Good signal to noise ratio and low background are essential
- Large q_{max} is helpful but not as essential as for 1D-PDF