



Unveiling local magnetic correlations: the development of magnetic pair distribution function at CSNS

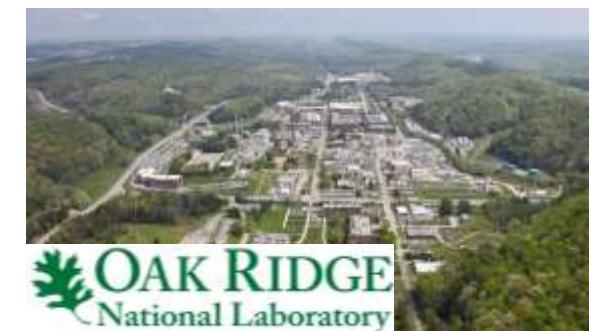
Long Yang (杨龙)
Tongji University



About me



- 2011-2015 Fudan University B.S.
- 2015-2016 Columbia University M.S.
- 2017-2021 Columbia University Ph.D.
- 2017-2020 Oak Ridge National Lab Joint Ph.D.
- 2021-2022 UCLA Postdoc
- 2022-Now Tongji University Assistant Professor





Acknowledgements



Simon Billinge
Columbia Univ.



Matthew Tucker
ORNL



Benjamin Frandsen
Brigham Young Univ.



Wen Yin
CSNS



<https://yanglonggroup.com>



CSNS, Dongguan, China



SNS, ORNL, USA

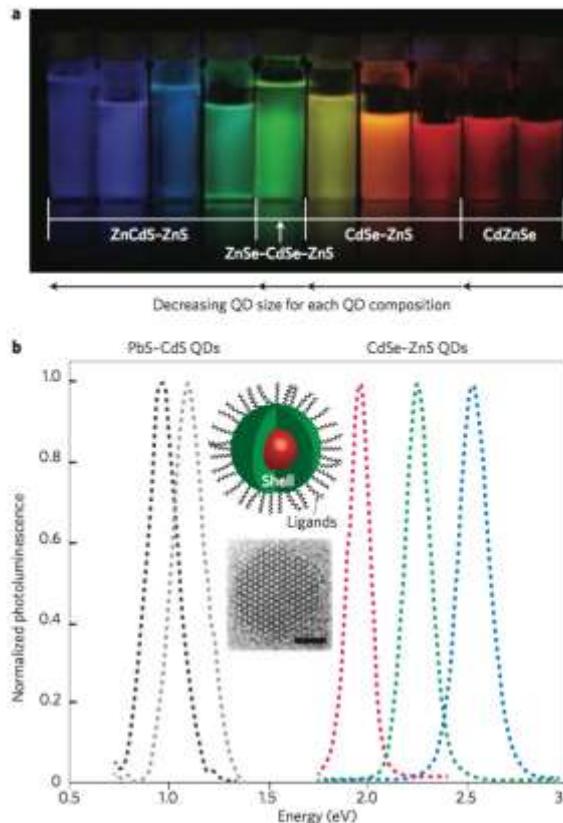
Collaborators:

- **Juping Xu (CSNS)**
- **Yanzhong Pei (Tongji Univ.)**
- **He Lin (SSRF)**
- **Emil Bozin (BNL)**
- **Yuanpeng Zhang (SNS)**
- **Matthew Krogstad (ANL)**
- ...



Structure-Property

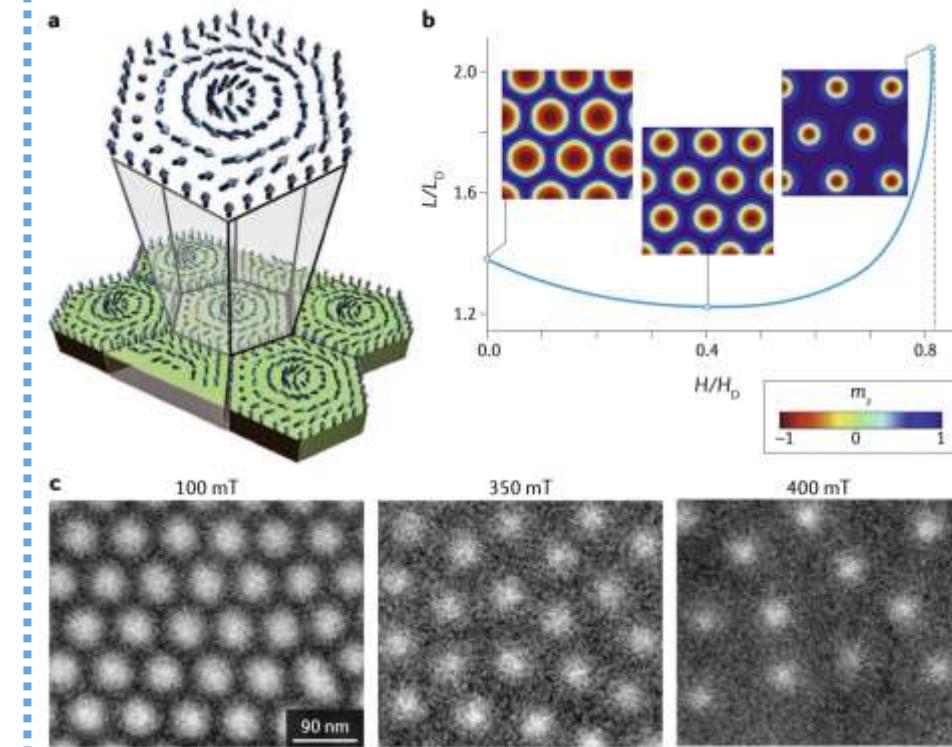
Atomic Structure



Tunable optical properties
in quantum dots

Y. Shirasaki, et al. *Nat. Photonics* 2013, 7, 1.

Magnetic Structure



Magnetic skyrmions for
spintronic applications

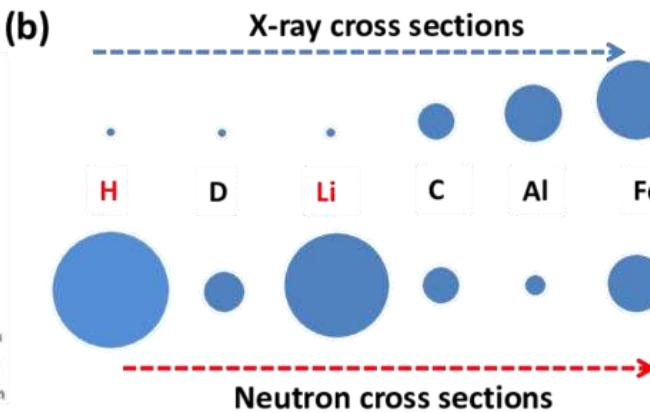
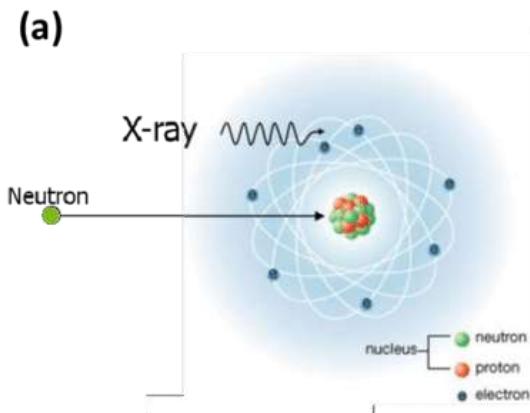
A. Bogdanov and C. Panagopoulos. *Nat. Rev. Phys.* 2020, 2, 9.



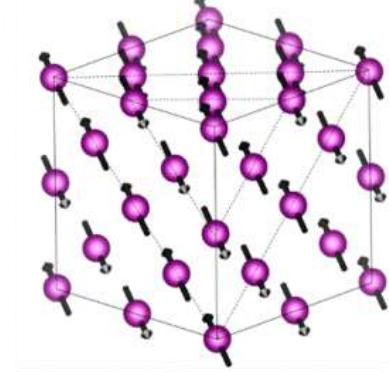
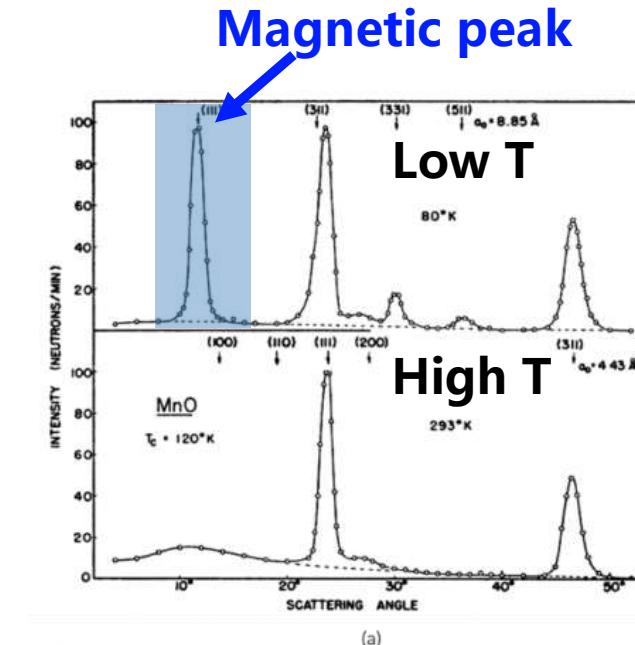
Neutron diffraction



Complementray to x-rays

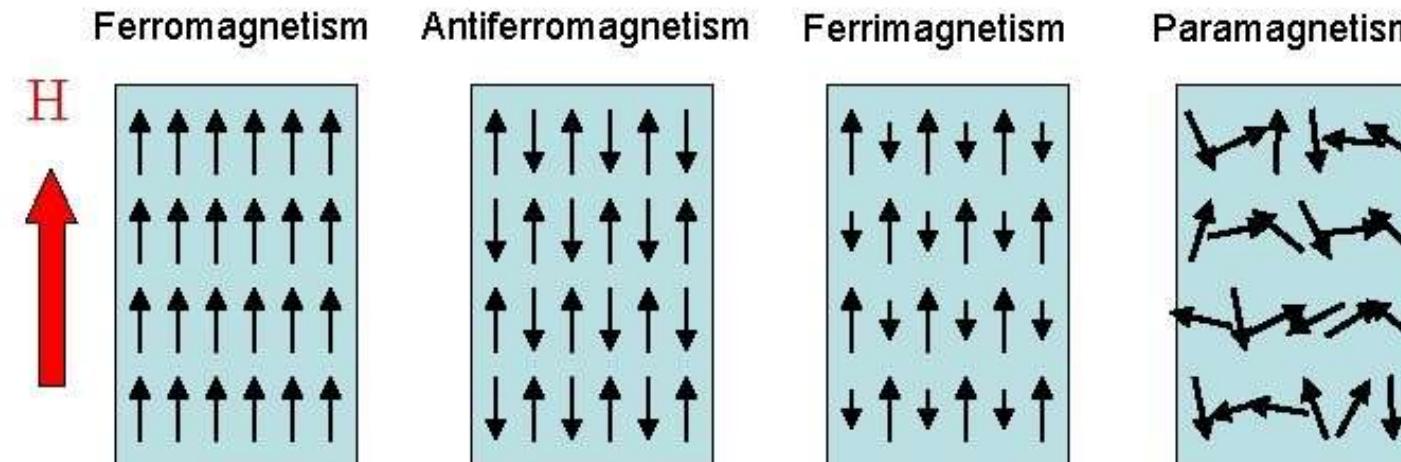
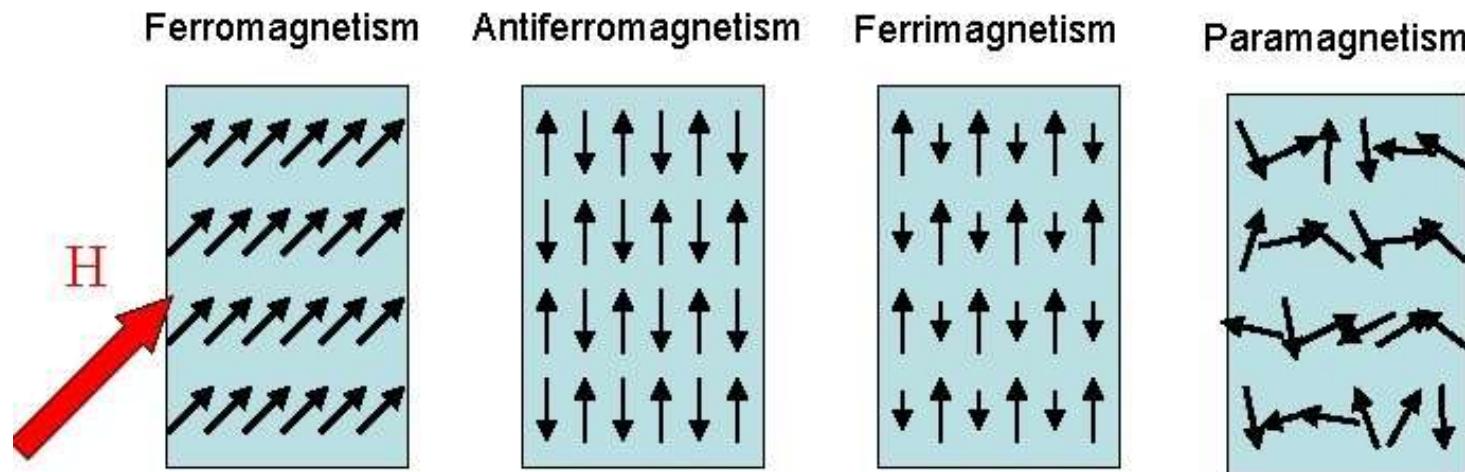


Revealing magnetic structures



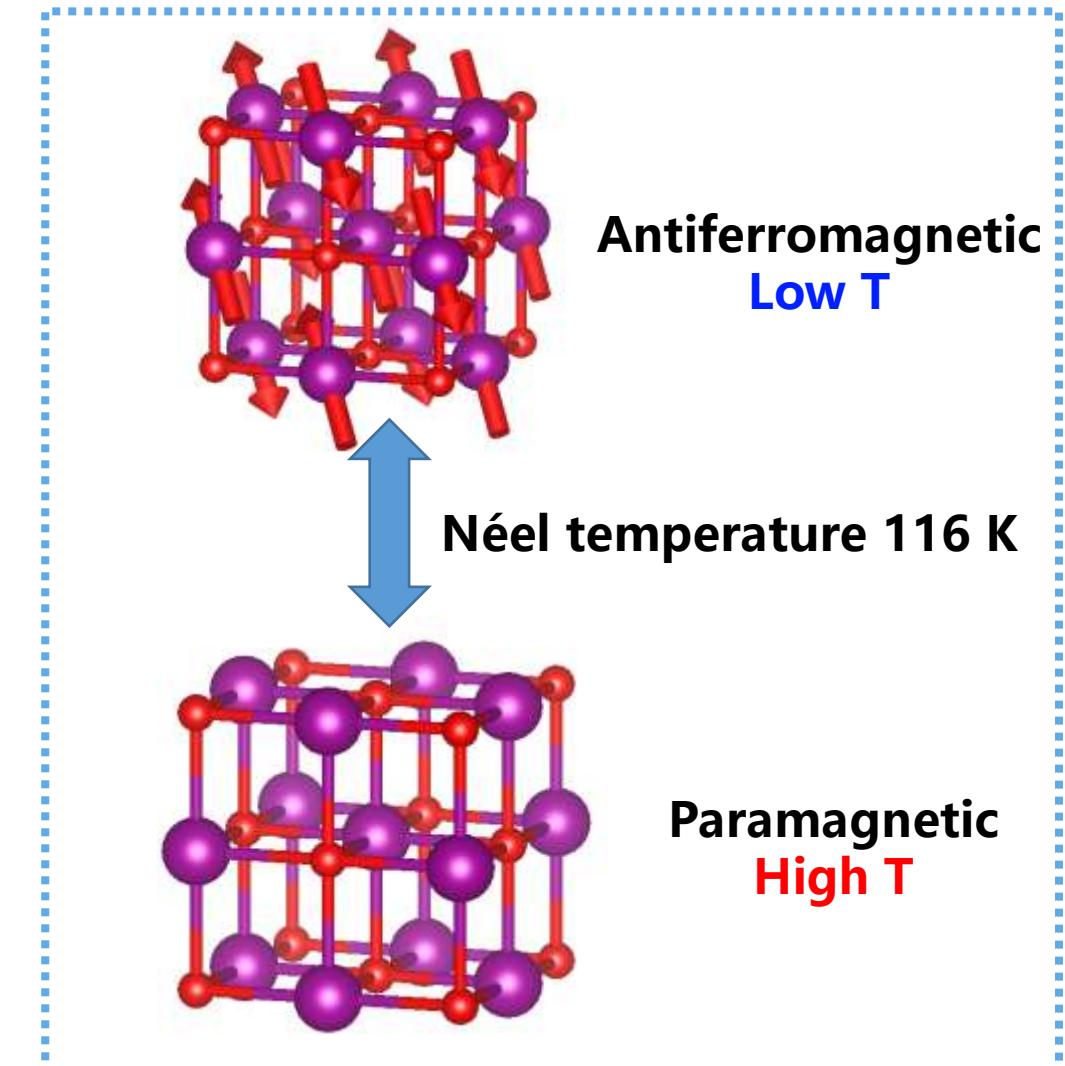
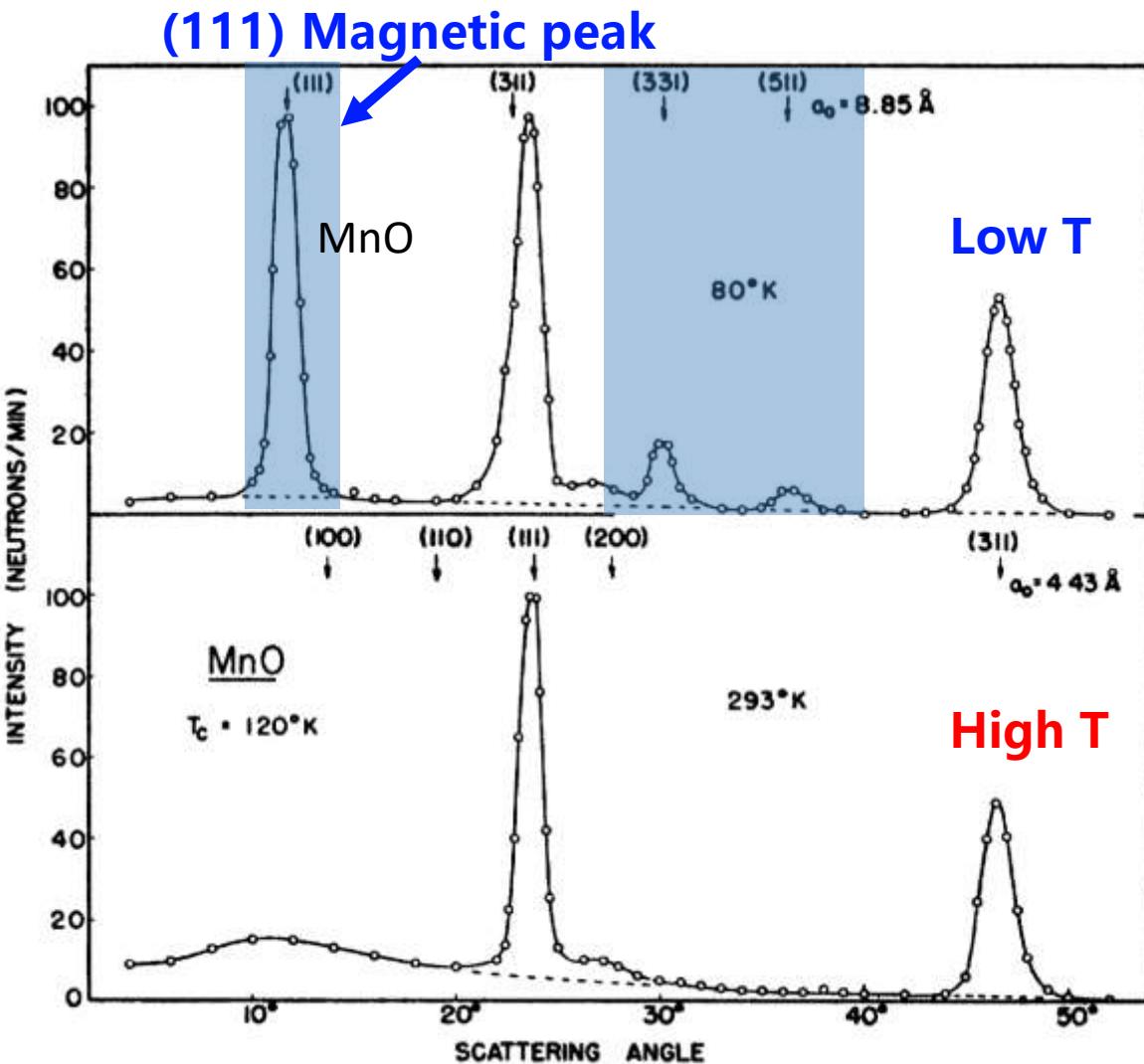


Magnetic structures





MnO

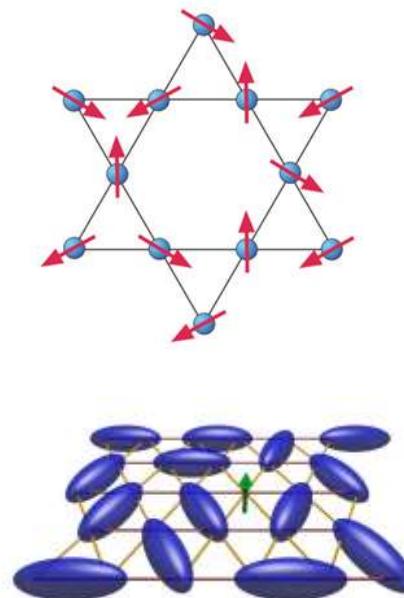




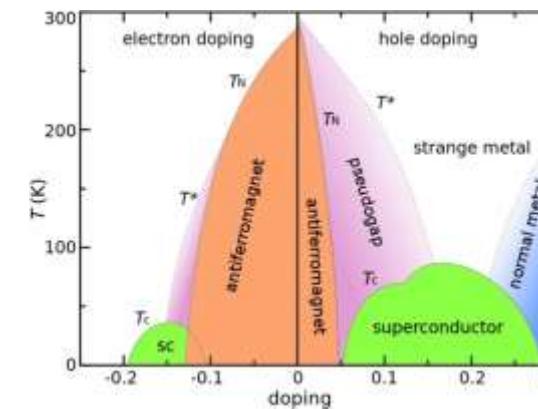
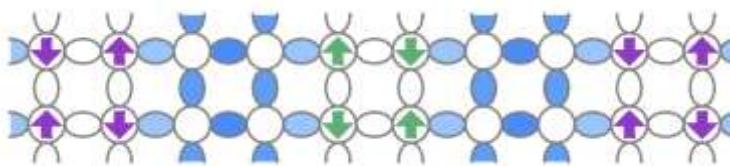
Local magnetic structure

- The short-range local magnetic correlations are important for understanding exotic properties in advanced condensed matters.

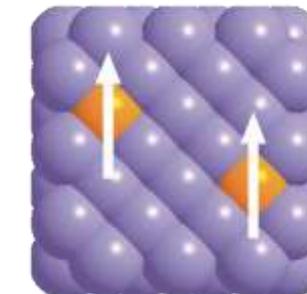
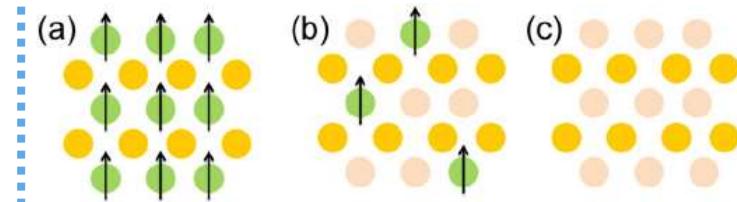
Spin fluctuations in frustrated magnetism



Spinstripe correlations in cuprate superconductors



Spin order in diluted magnetic semiconductors

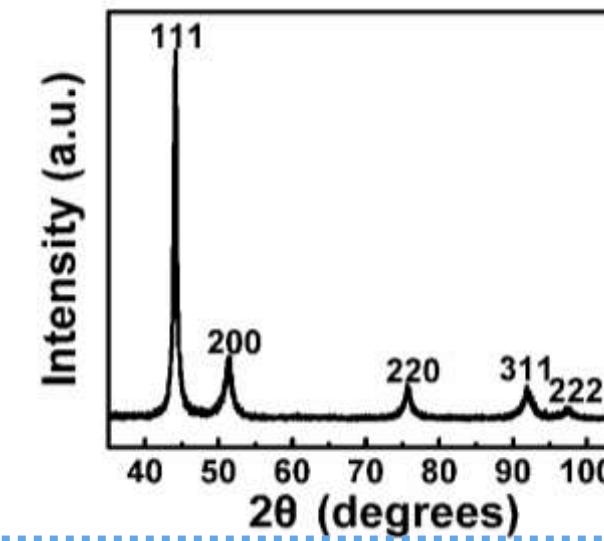
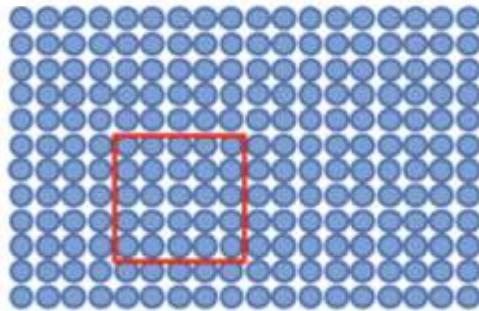




Local structure probe

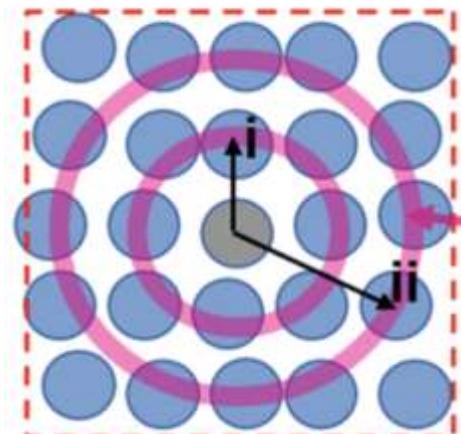
Conventional diffraction

Global structure

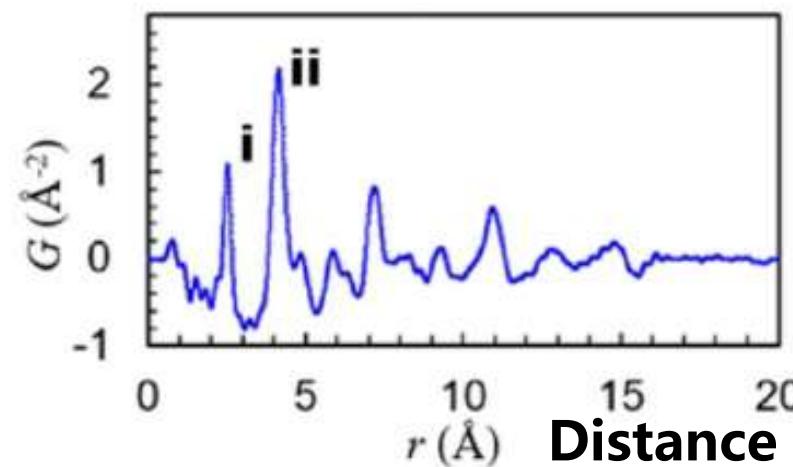


Pair distribution function

Local structure



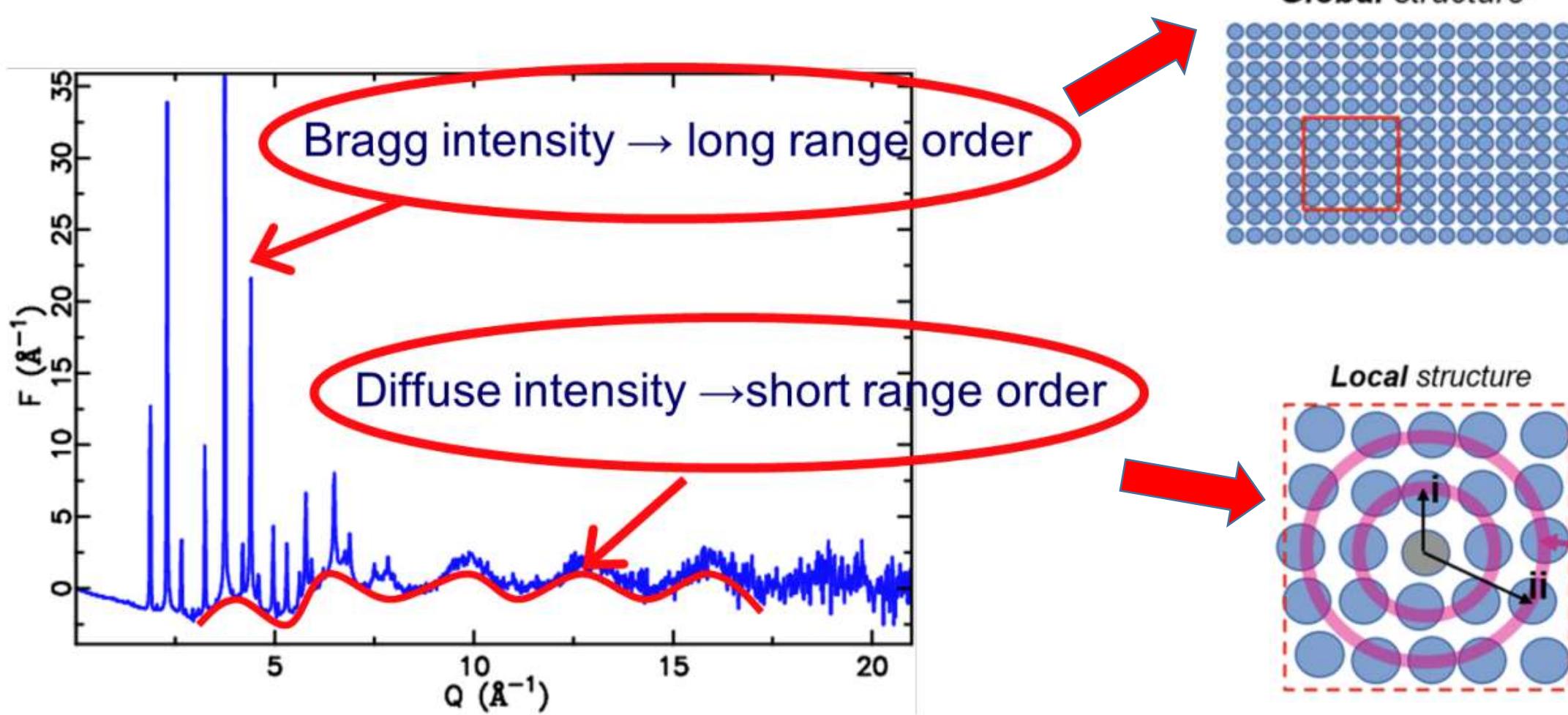
Probability





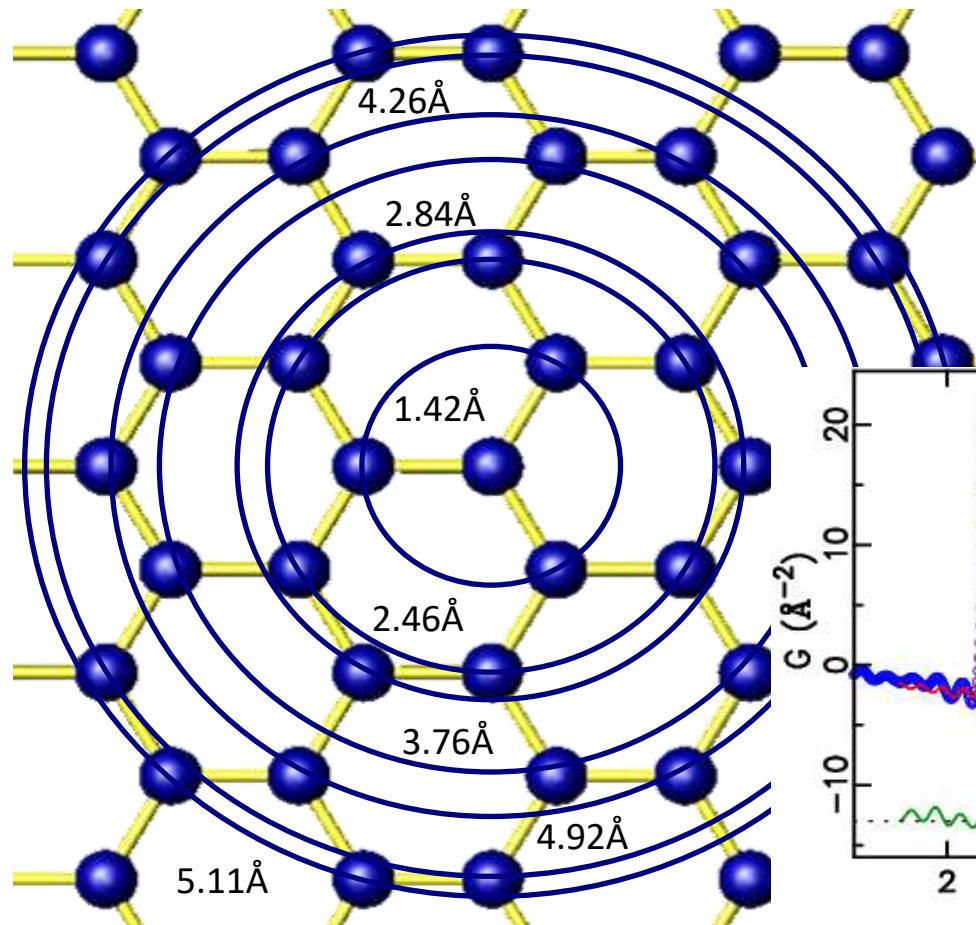
Local structure probe

- Total scattering technique

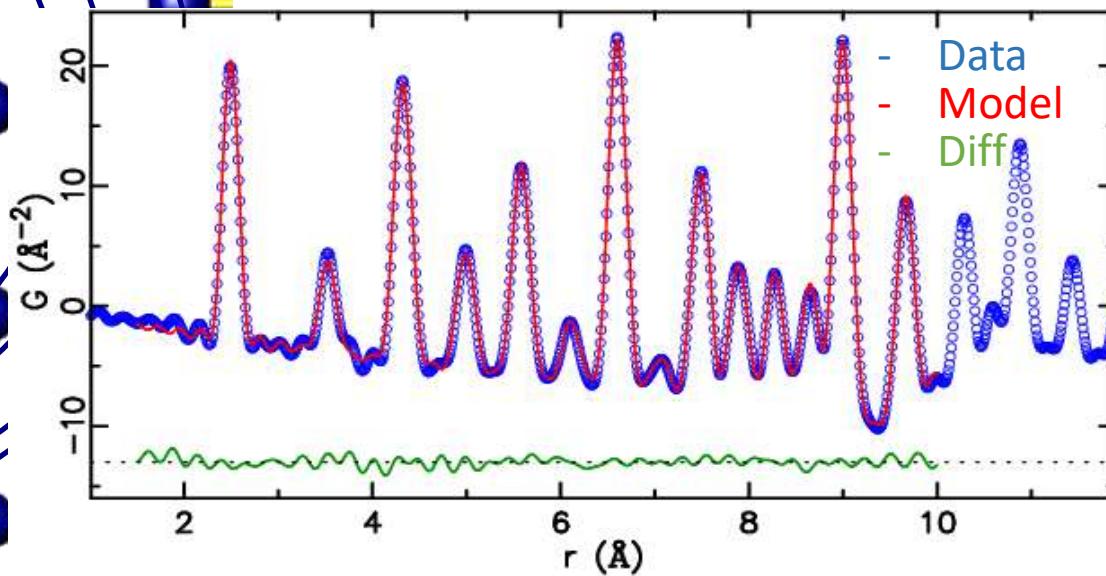




Pair Distribution Function (PDF)



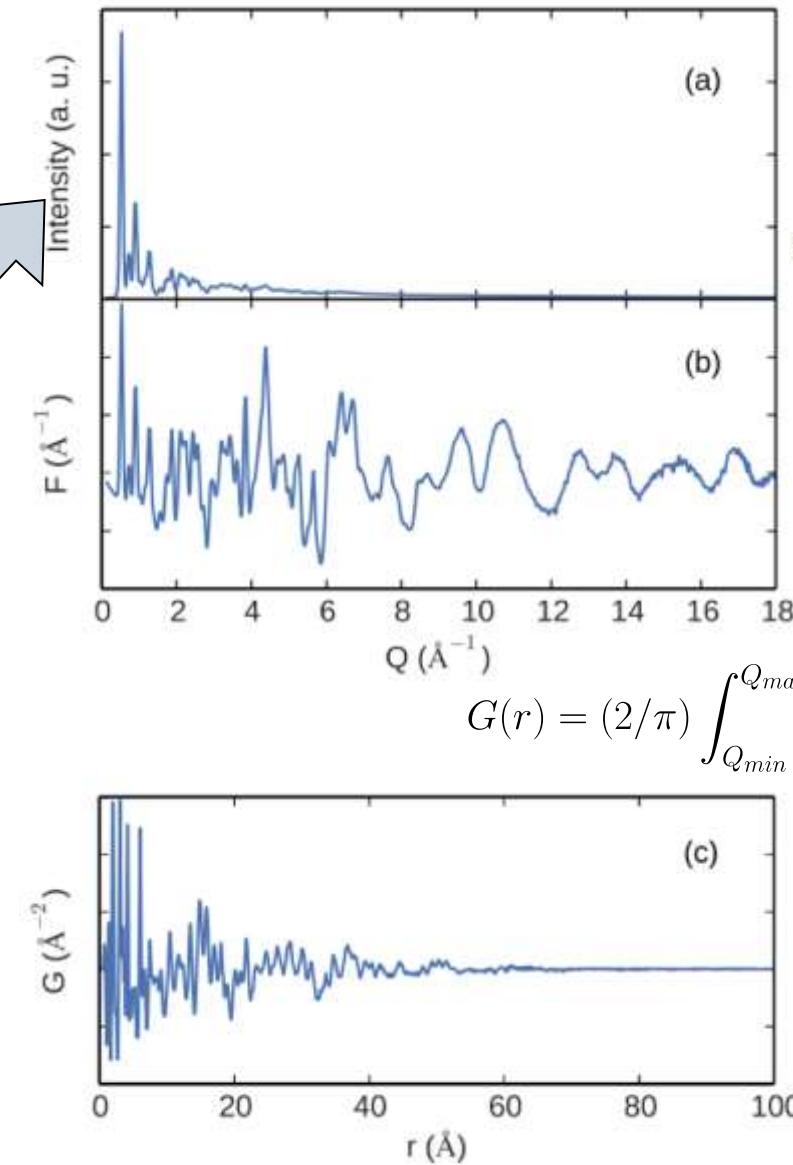
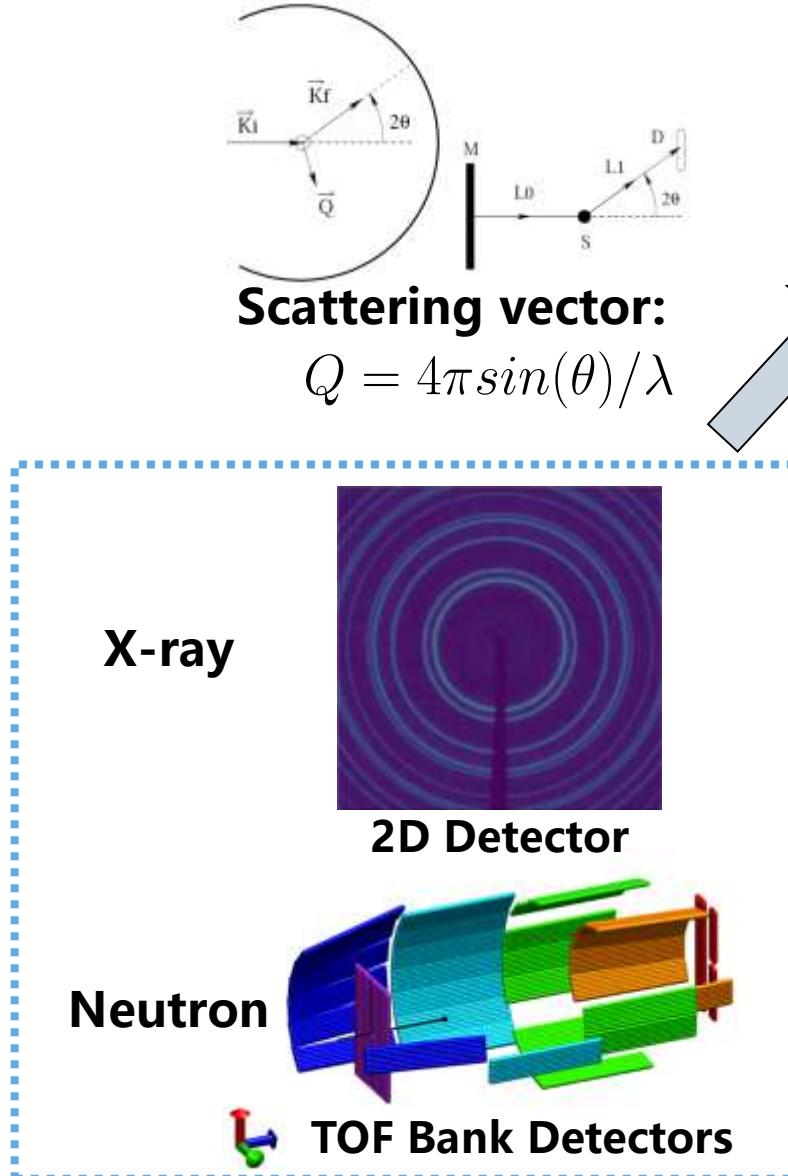
- Local structure probe.
- PDF gives the probability of finding an atom at a distance “r” from a given atom.
- Neutron, x-ray, electron.....



Sub-nanometer resolution



1D-PDF data processing



Integrated 1D data

$$S(Q)-1 = \frac{I(Q)}{N \langle f \rangle^2} - \frac{\langle f^2 \rangle}{\langle f \rangle^2}$$
$$F(Q) = Q[S(Q)-1]$$

Structure function

$$G(r) = (2/\pi) \int_{Q_{min}}^{Q_{max}} F(Q) \sin(Qr) dQ$$

PDF

PDFgetN, PDFgetX



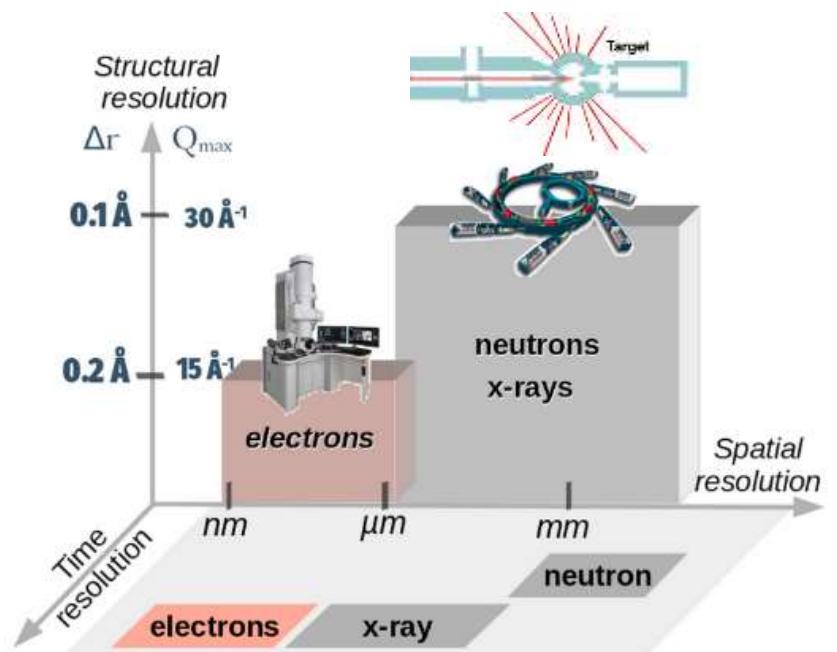
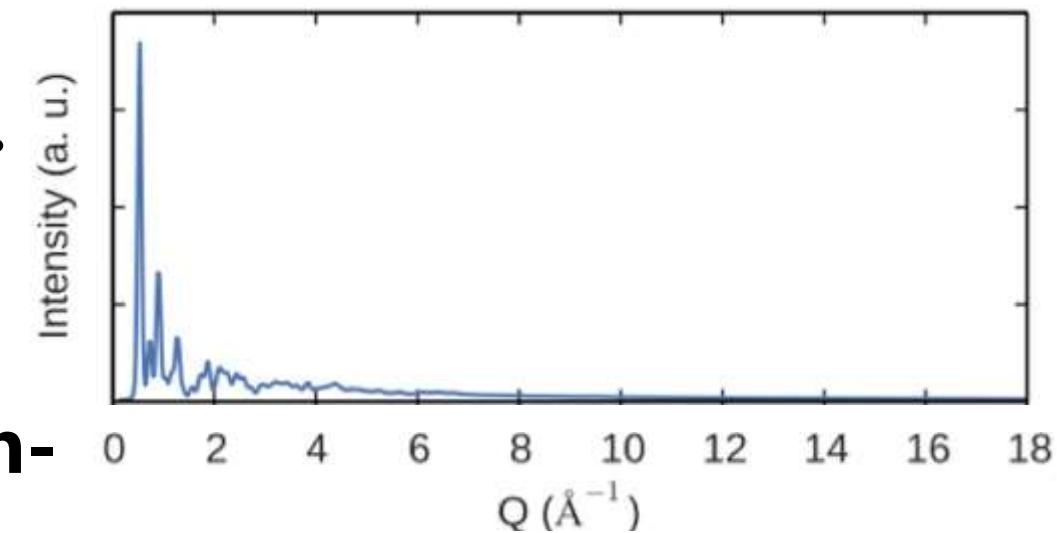
Why do we need spallation neutron source?

- Low-Q: mostly Bragg peaks.
- High-Q: weak diffuse scattering.

$$Q = \frac{4\pi \sin \theta}{\lambda}$$

- We need short-wavelength (high-energy), to get large Q_{\max} .
- To improve real space resolution Δr .

$$\Delta r \sim \frac{\pi}{Q_{\max}}$$

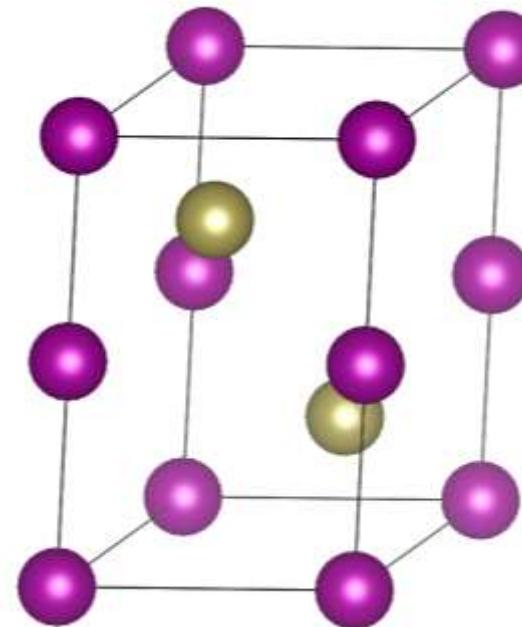




Local structure probe

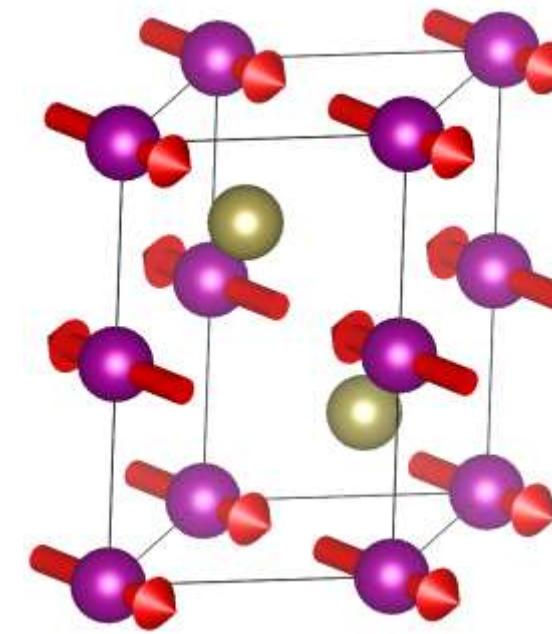
- In a neutron total scattering experiment, we can obtain both!

Atomic PDF



Local atomic structure

Magnetic PDF



Local magnetic structure



mPDF theory

The orientationally averaged magnetic scattering (Blech and Averbach. Physics, 1964):

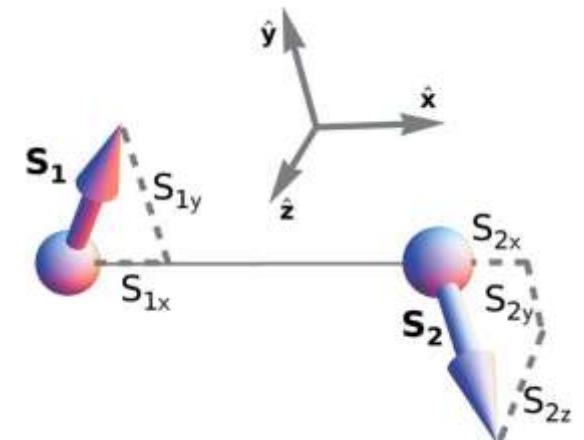
$$\frac{d\sigma}{d\Omega} = \frac{2}{3} NS(S+1)(\gamma r_0)^2 f^2 + (\gamma r_0)^2 f^2 \times \sum_{i \neq j} \left\{ A_{ij} \frac{\sin \kappa r_{ij}}{\kappa r_{ij}} + B_{ij} \left[\frac{\sin \kappa r_{ij}}{(\kappa r_{ij})^3} - \frac{\cos \kappa r_{ij}}{(\kappa r_{ij})^2} \right] \right\}$$

Self-scattering ($i=j$)

$$A_{ij} = \langle S_i^y S_j^y \rangle \quad B_{ij} = 2\langle S_i^x S_j^x \rangle - \langle S_i^y S_j^y \rangle$$

$$S(\kappa) = \frac{d\sigma/d\Omega}{\frac{2}{3} N S(S+1)(\gamma r_0)^2 f^2} = 1 + \frac{1}{N} \frac{3}{2S(S+1)}$$

$$\times \sum_{i \neq j} \left\{ A_{ij} \frac{\sin \kappa r_{ij}}{\kappa r_{ij}} + B_{ij} \left[\frac{\sin \kappa r_{ij}}{(\kappa r_{ij})^3} - \frac{\cos \kappa r_{ij}}{(\kappa r_{ij})^2} \right] \right\}$$



$$\hat{\mathbf{x}} = \frac{\mathbf{r}_j - \mathbf{r}_i}{|\mathbf{r}_j - \mathbf{r}_i|} \text{ and } \hat{\mathbf{y}} = \frac{\mathbf{S}_i - \hat{\mathbf{x}}(\mathbf{S}_i \cdot \hat{\mathbf{x}})}{|\mathbf{S}_i - \hat{\mathbf{x}}(\mathbf{S}_i \cdot \hat{\mathbf{x}})|}$$



mPDF theory

- Reduced structure function $F(\kappa) = \kappa[S(\kappa) - 1]$

$$F(\kappa) = \frac{1}{N} \frac{3}{2S(S+1)} \times \sum_{i \neq j} \left[A_{ij} \frac{\sin \kappa r_{ij}}{r_{ij}} + B_{ij} \left(\frac{\sin \kappa r_{ij}}{\kappa^2 r_{ij}^3} - \frac{\cos \kappa r_{ij}}{\kappa r_{ij}^2} \right) \right]$$

- mPDF via Fourier transform

$$f(r) = \frac{2}{\pi} \int_0^\infty d\kappa F(\kappa) \sin \kappa r$$

mPDF contains both **spatial** and **orientational** magnetic correlations.

$$= \frac{1}{N} \frac{3}{2S(S+1)} \sum_{i \neq j} \left\{ \frac{A_{ij}}{r} \delta(r - r_{ij}) + B_{ij} \frac{r}{r_{ij}^3} [1 - \Theta(r - r_{ij})] \right\}$$

- Atomic PDF

$$f_{\text{atPDF}}(r) = (1/rN) \sum_{i \neq j} \delta(r - r_{ij})$$



mPDF theory

$$f(r) = \frac{2}{\pi} \int_0^\infty Q \left[\frac{I_m}{\frac{2}{3} N_s S(S+1)(\gamma r_0)^2 f_m^2(Q)} - 1 \right] \sin Qr \, dQ \quad (1) \quad \xleftarrow{\text{Experimental mPDF}}$$

$$= \frac{1}{N_s} \frac{3}{2S(S+1)} \sum_{i \neq j} \left[\frac{A_{ij}}{r} \delta(r - r_{ij}) + B_{ij} \frac{r}{r_{ij}^3} \Theta(r_{ij} - r) \right], \quad (2) \quad \xleftarrow{\text{Simulated mPDF}}$$

- $f_m(Q)$ is the magnetic form factor

X-ray $F_{hkl} = \sum f_j \exp(2\pi i(hx + ky + lz)) e^{-2W}$

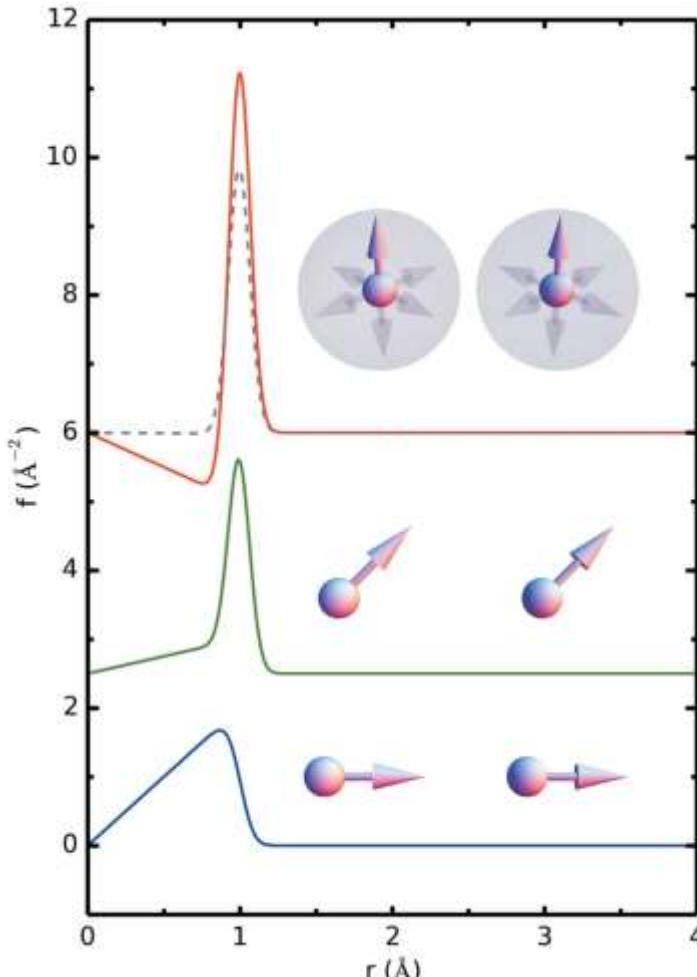
Neutron $F_{hkl} = \sum b_j \exp(2\pi i(hx + ky + lz)) e^{-2W}$

Magnetic $F_{hkl} = \sum q_j f_{Mj} \exp(2\pi i(hx + ky + lz)) e^{-2W}$



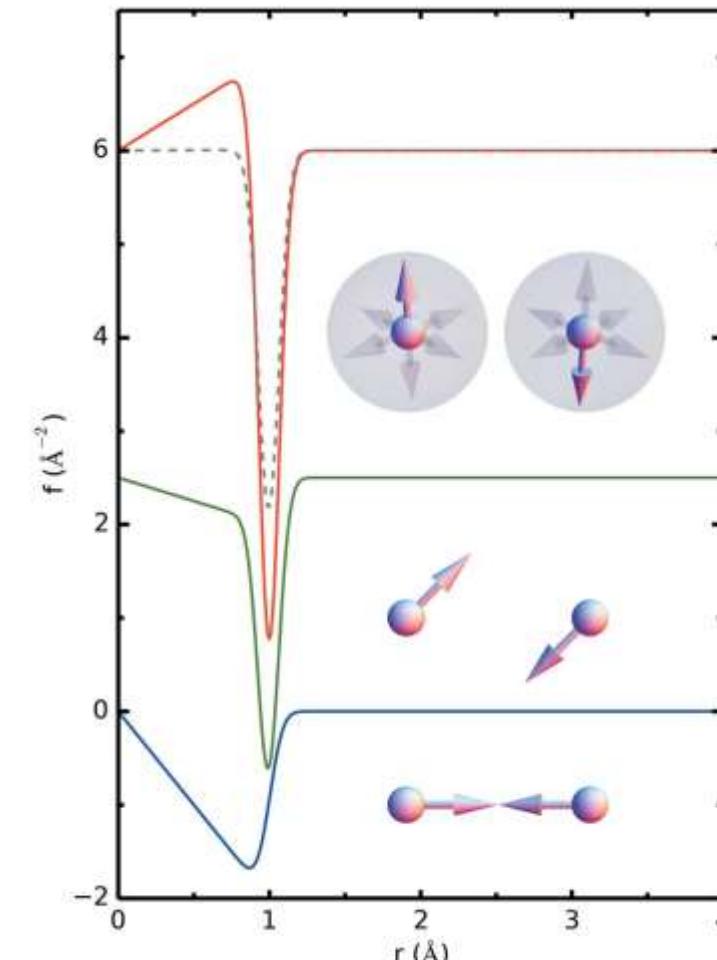
mPDF

Ferromagnetic



Positive peak

Antiferromagnetic

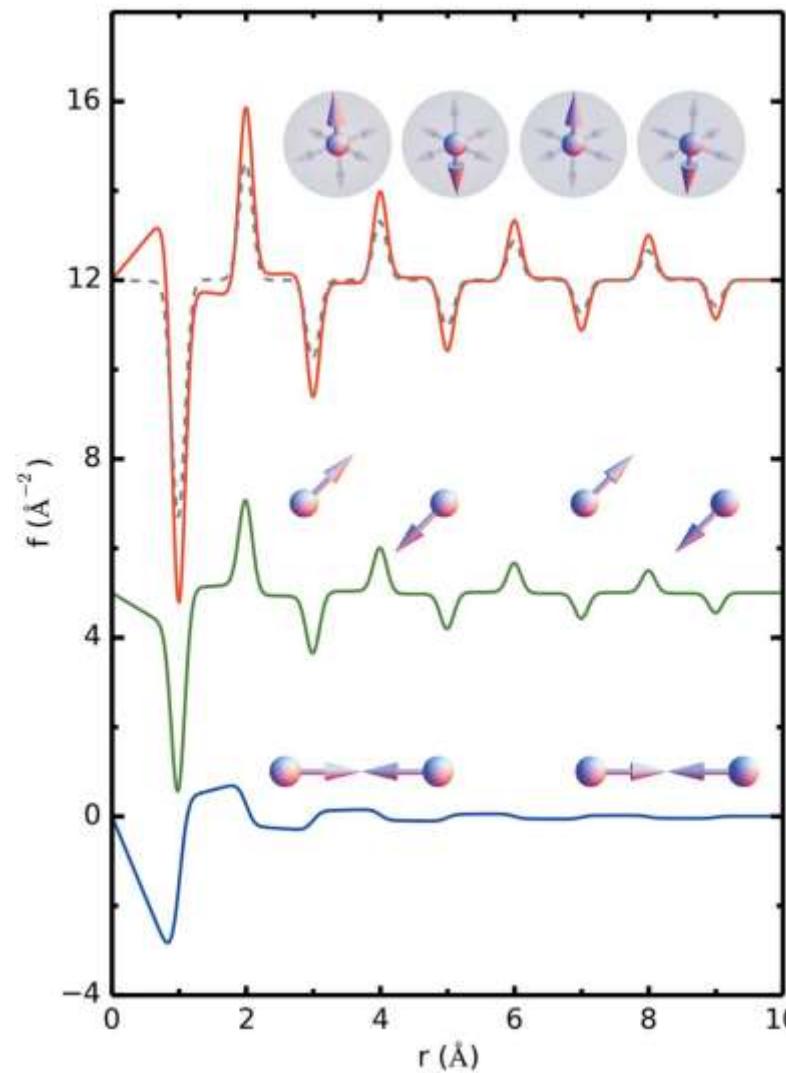


Negative peak

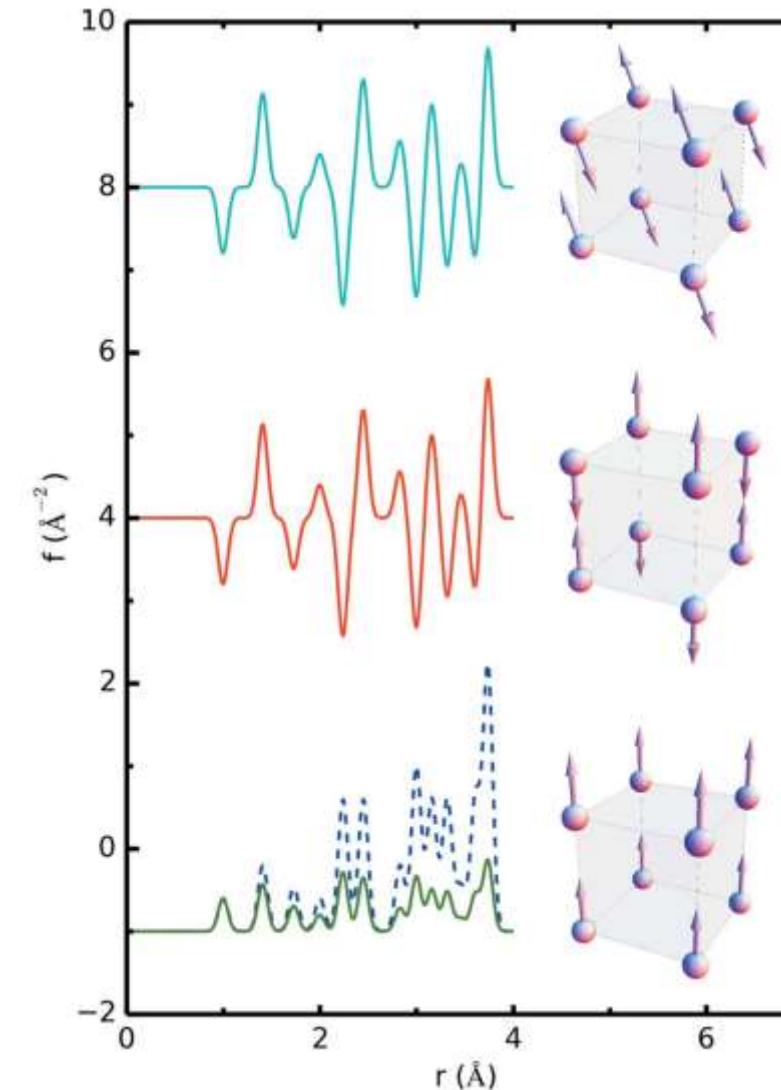


mPDF

1D structure



3D structure



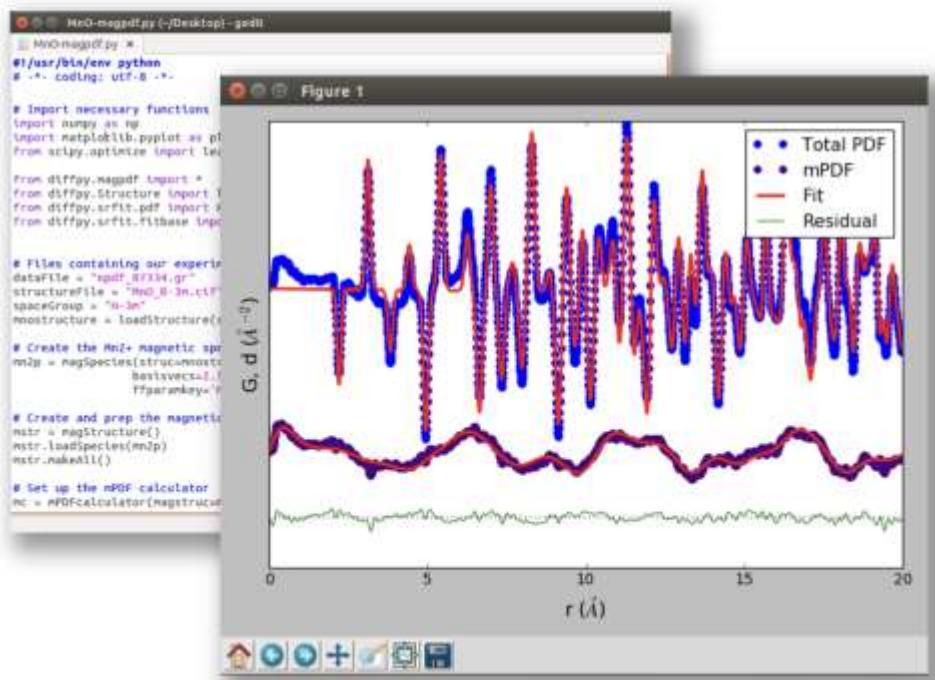


DiffPy.mPDF

DiffPy Community Publications Products

mpdf

The diffpy.mpdf package provides a convenient method for computing the magnetic PDF (mPDF) from magnetic structures and performing fits to neutron total scattering data. The mPDF is calculated by an MPDFcalculator object, which extracts the spin positions and spin vectors from a MagStructure object that the MPDFcalculator takes as input. The MagStructure object in turn can contain multiple MagSpecies objects, which generate magnetic configurations based on a diffpy.structure object and a set of propagation vectors and basis vectors provided by the user. Alternatively, the user can manually define a magnetic unit cell that will be used to generate the magnetic structure, or the magnetic structure can be defined simply as lists of spin positions and spin vectors provided by the user.



```
02_mPDF_simpleFit.py
```

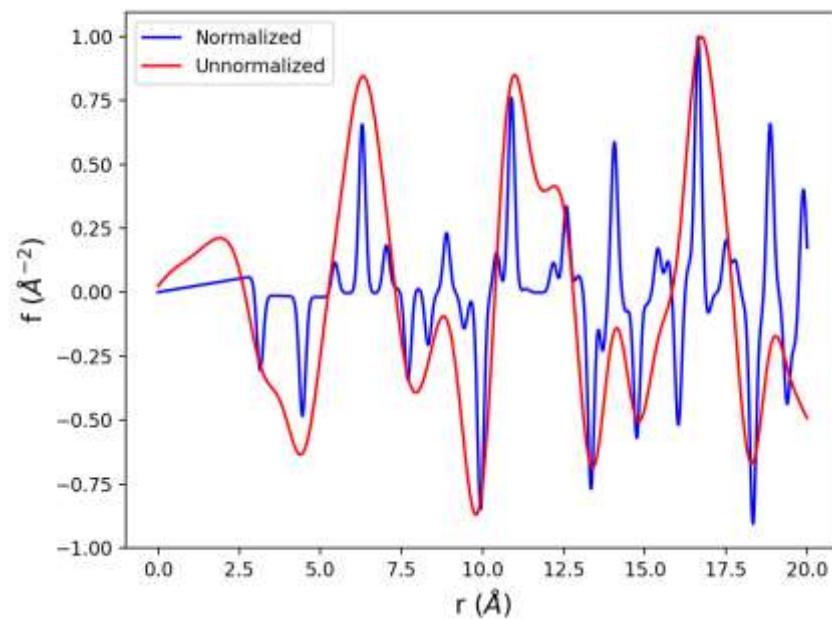
```
1 #!/usr/bin/env python
2
3 import numpy as np
4 import matplotlib.pyplot as plt
5 from diffpy.mpdf import *
6 from diffpy.structure import loadStructure
7 from diffpy.srfit.fitbase import Profile, FitContribution
8 from diffpy.srfit.fitbase import FitRecipe, FitResults
9
10
11 # read in the mcif
12 mcif = '1.31_MnO.mcif'
13 mstr = create_from_mcif(mcif, ffparamkey='Mn2')
14
15 # adjust the unit cell parameters to agree with the results of the
16 a_fit = 4.44864 # fill in the value from the fit
17 alpha_fit = 90.2175 # fill in the value from the fit
18 mstr.struc.lattice.a = 2*a_fit # multiply by two because the magnet
19 mstr.struc.lattice.b = 2*a_fit
20 mstr.struc.lattice.c = 2*a_fit
21 mstr.struc.lattice.alpha = alpha_fit
22 mstr.struc.lattice.beta = alpha_fit
23 mstr.struc.lattice.gamma = alpha_fit
24
25 mstr.makeAll()
26
27
28 fit_file = 'LY4T20_RUN19625_Gr.fgr'
29 r, gcalc, _, _, gdiff = np.loadtxt(fit_file, skiprows=12).T
30 gobs = gcalc + gdiff
31
32 qmag = 1.0*gdiff # we set the experimental mPDF to the fit residual
```

<https://www.diffpy.org/products/mPDF.html>

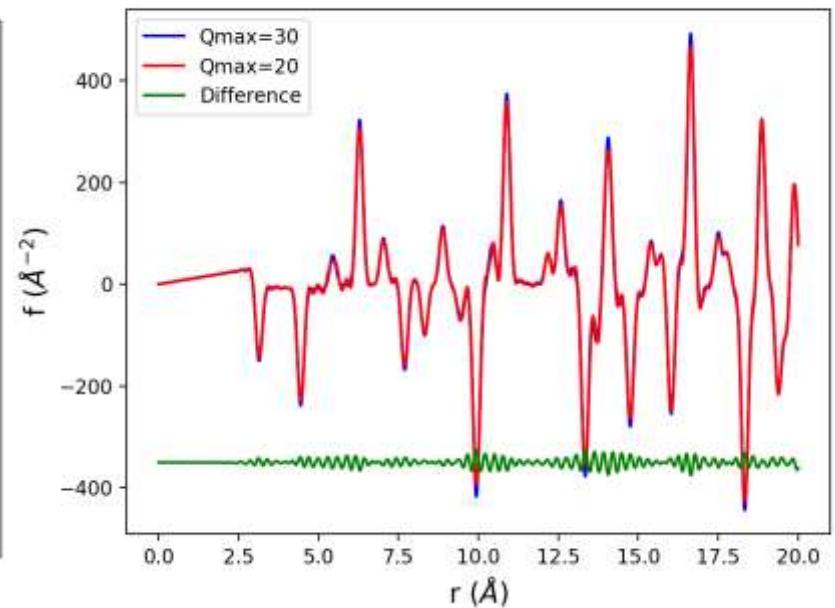


DiffPy.mPDF

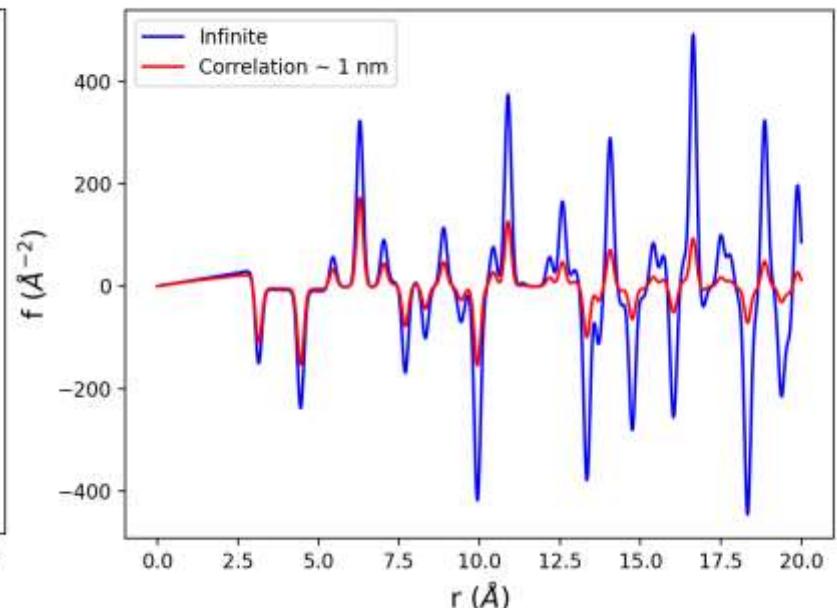
Normalized v.s. Unnormalized



Q_{\max} effect



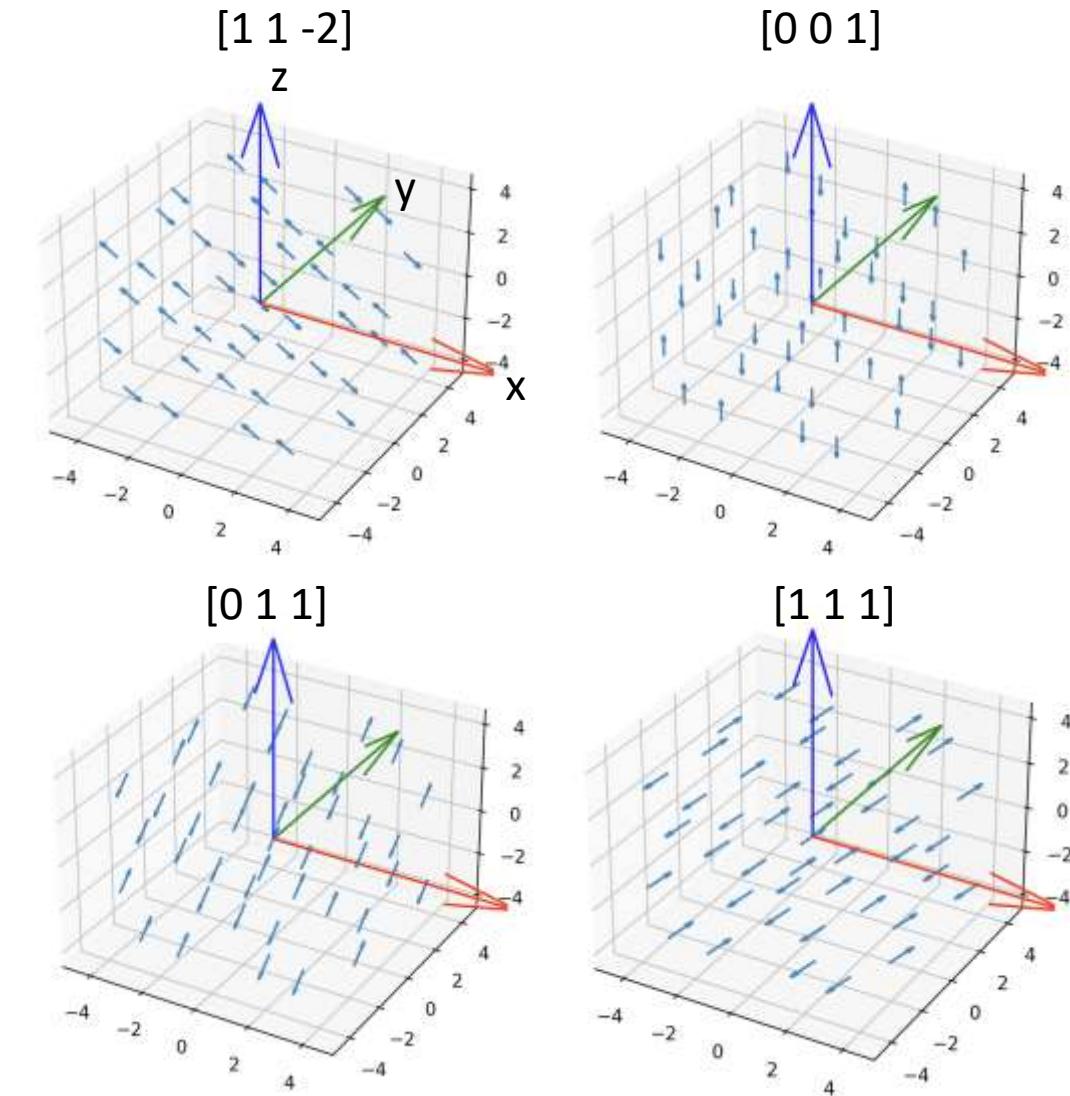
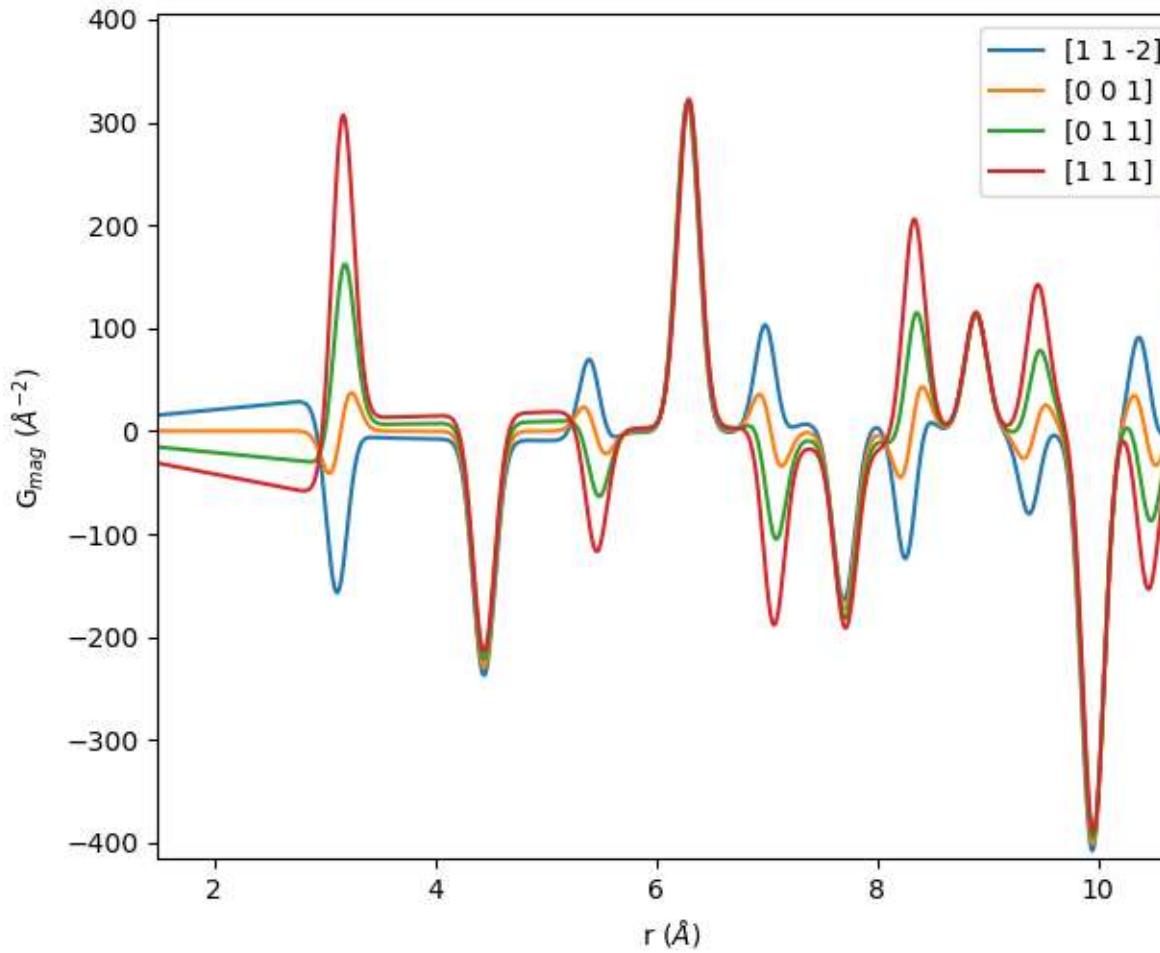
Finite correlation length





DiffPy.mPDF

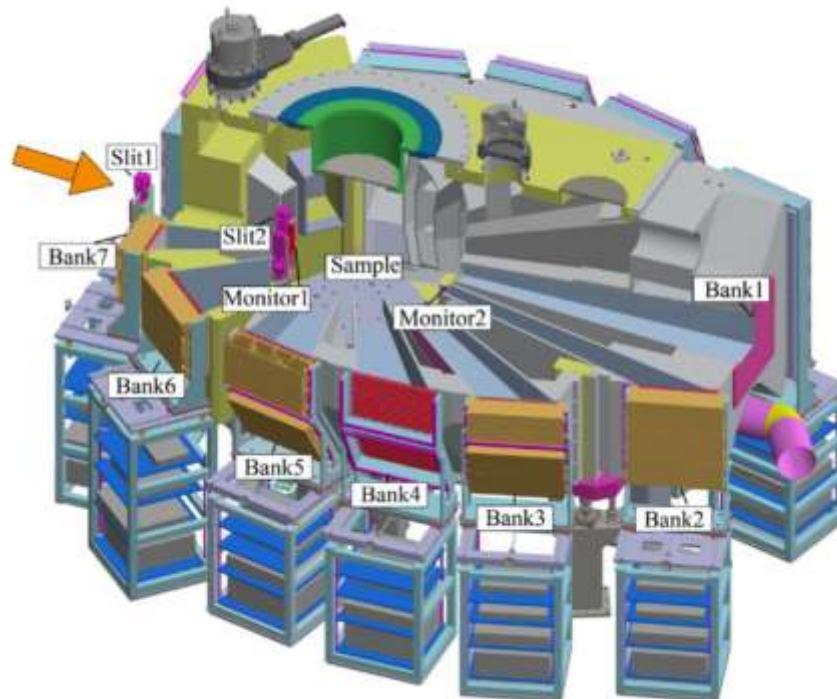
Different spin directions





Multi-physics instrument, CSNS

- The first total scattering neutron diffractometer in China.



Nuclear Inst. and Methods in Physics Research, A 1013 (2021) 165642



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Nuclear Inst. and Methods in Physics Research, A

journal homepage: www.elsevier.com/locate/nima



Multi-physics instrument: Total scattering neutron time-of-flight diffractometer at China Spallation Neutron Source

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^a Institute of High Energy Physics, Chinese Academy of Sciences (CAS), Beijing 100049, China

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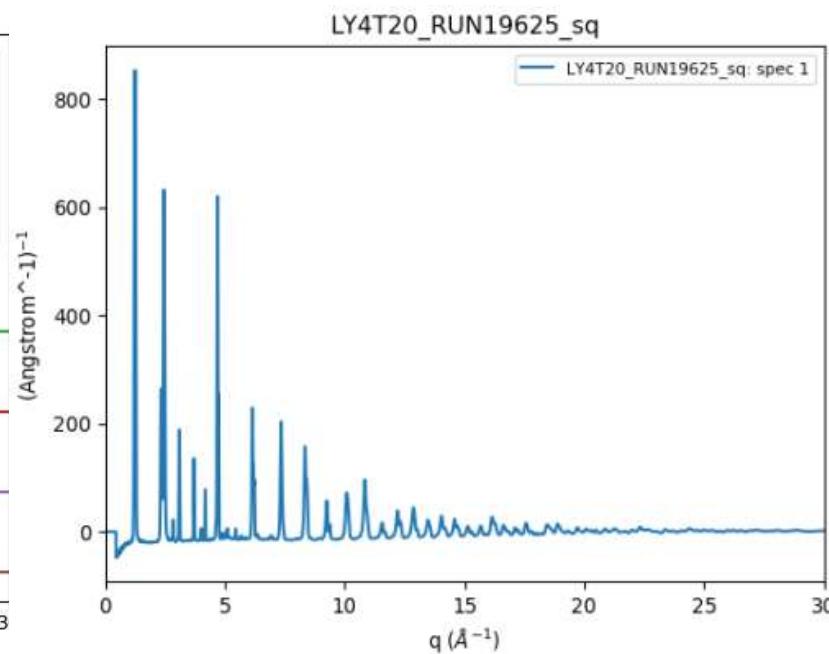
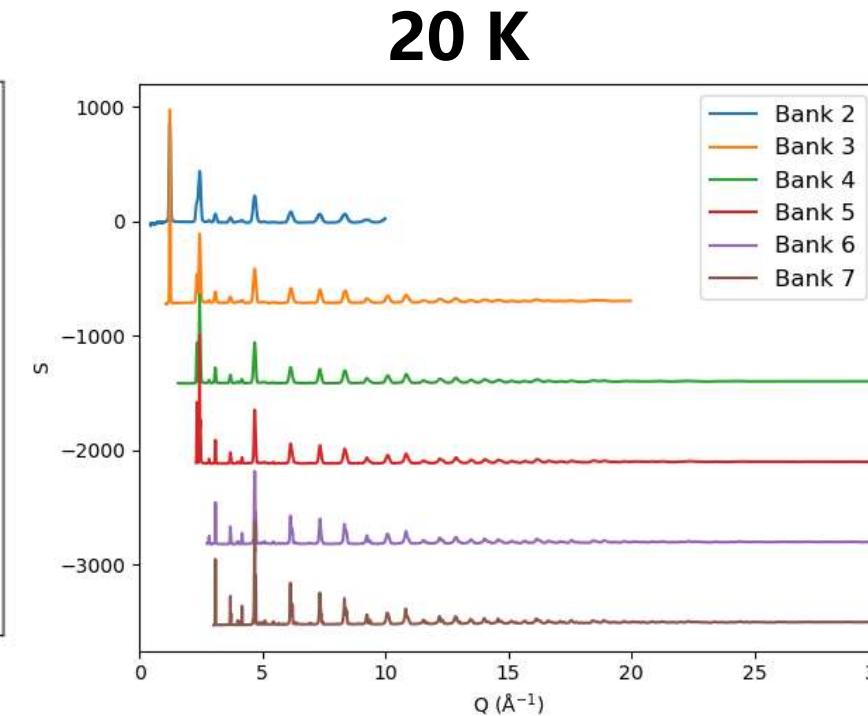
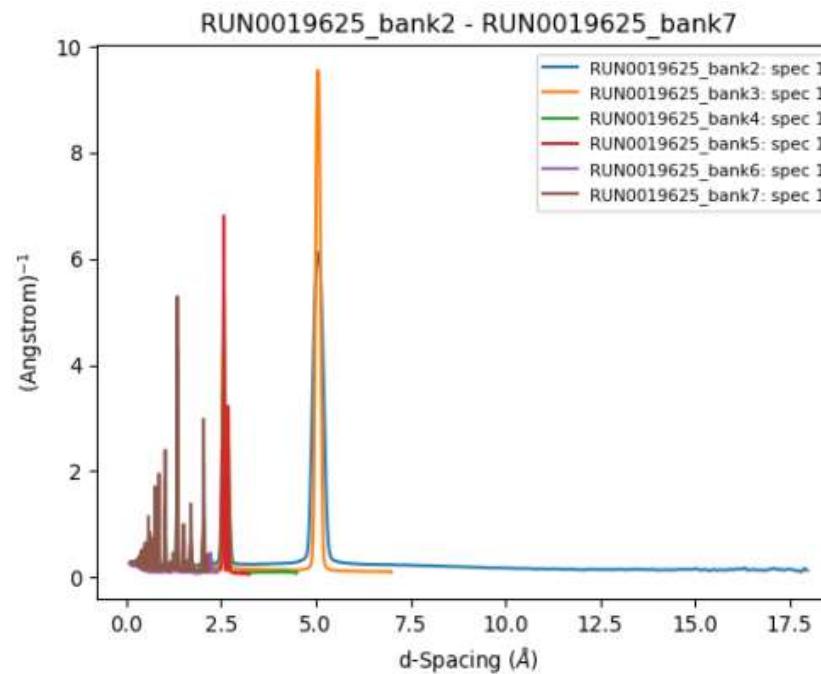
^d Department of Physics and Materials Science, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong, China

Table 1
Parameters of the MPI detector array.

Detector bank No.	Secondary flight path L ₂ (m)	Scattering angle 2θ (Degree)	³ He tube style	Number of ³ He tubes/module ^a	Number of ³ He tubes/module ^b	Calculated dQ/Q @~1 Å	Estimated Q range (Å ⁻¹)
Bank01	2.82	2.9–5.04	0.5 m×1/2 inch	—	20/1	—	0.1–2.7
Bank02	2.319–2.711	12.54–17.62	Type-1:20 atm, 0.5 m×1 inch	—	96/12	6%	0.45–9
Bank03	1.772–2.065	31.42–25	32/4	96/12	2.1%	1.1–22	
Bank04	1.351–1.599	51.25–67.32	48/6	112/14	1.3%	1.8–34	
Bank05	1..131–1.220	81.55–105.18	72/9	112/14	0.8%	2.7–49	
Bank06	1.166–1.191	121.80–145.51	32/4	64/8	0.55%	3.6–59	
Bank07	1.232–1.314	157.47–170.00	Type-2: 20 atm, 0.3 m×1 inch	64/8	64/8	0.39%	4.1–62



MnO data



Experiment setup

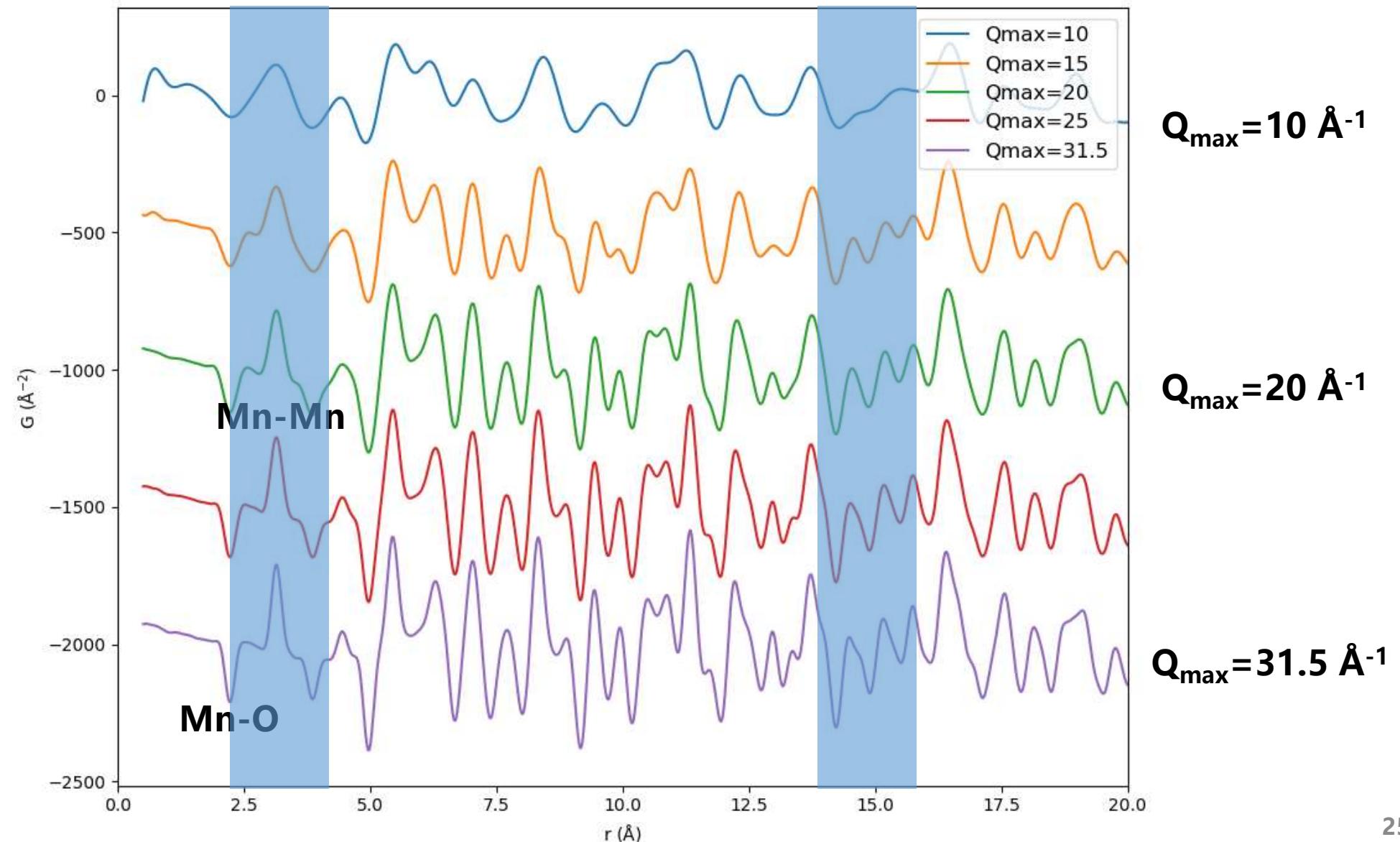
- Sample Environment: CCR06
- Sample holder: 9mm vanadium can
- Sample install: He glovebox
- Sealed ring: In
- Neutron wavelength: 0.1-4.5 Å

Data collected at March 2023 @ MPI

Courtesy of Juping Xu (CSNS)



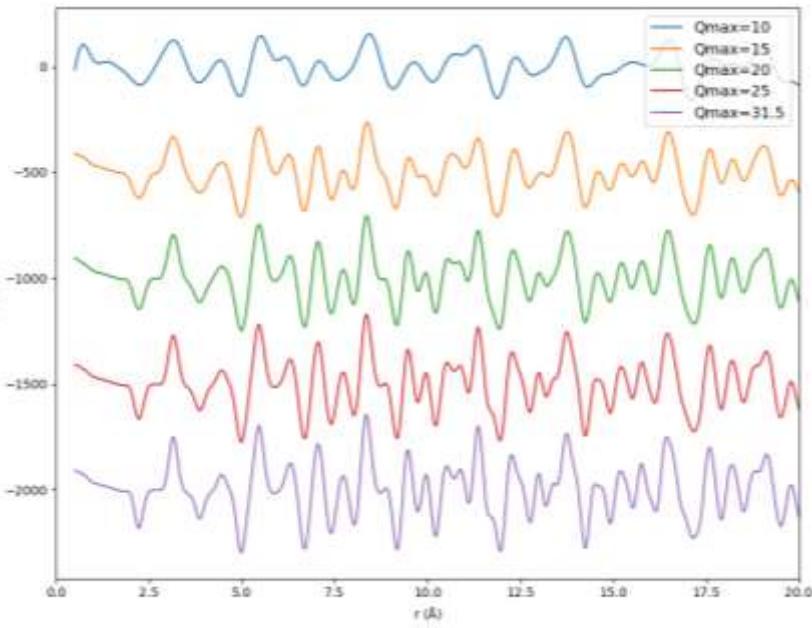
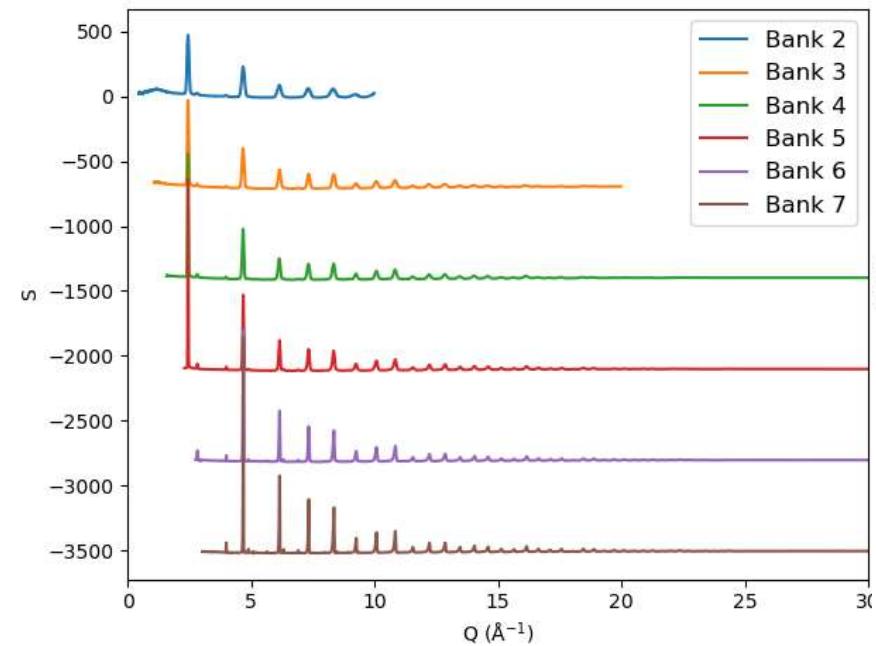
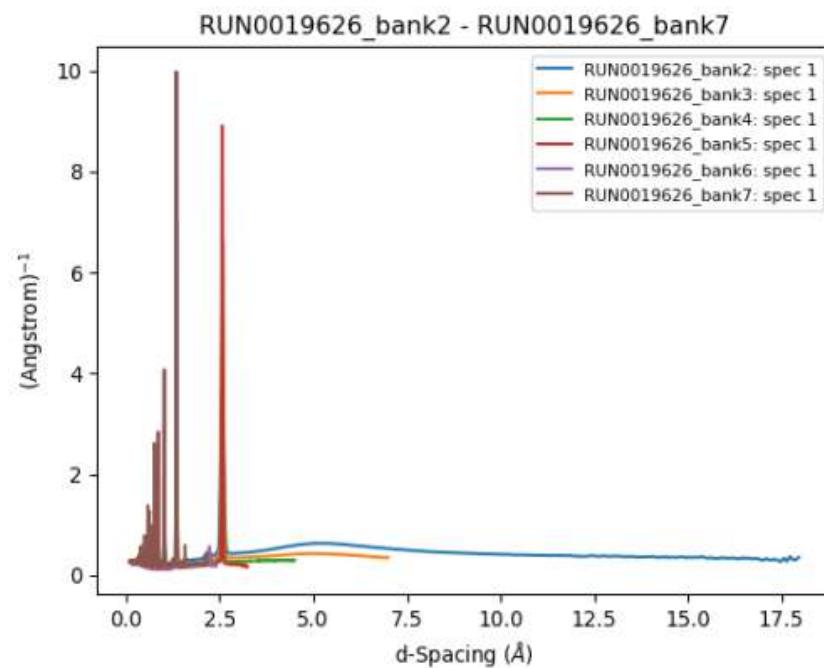
PDF





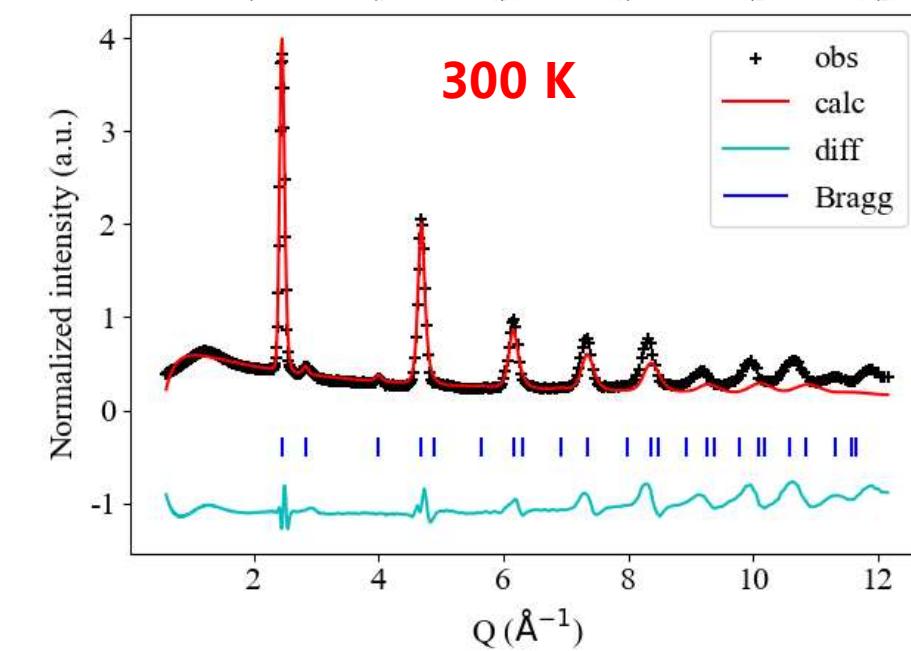
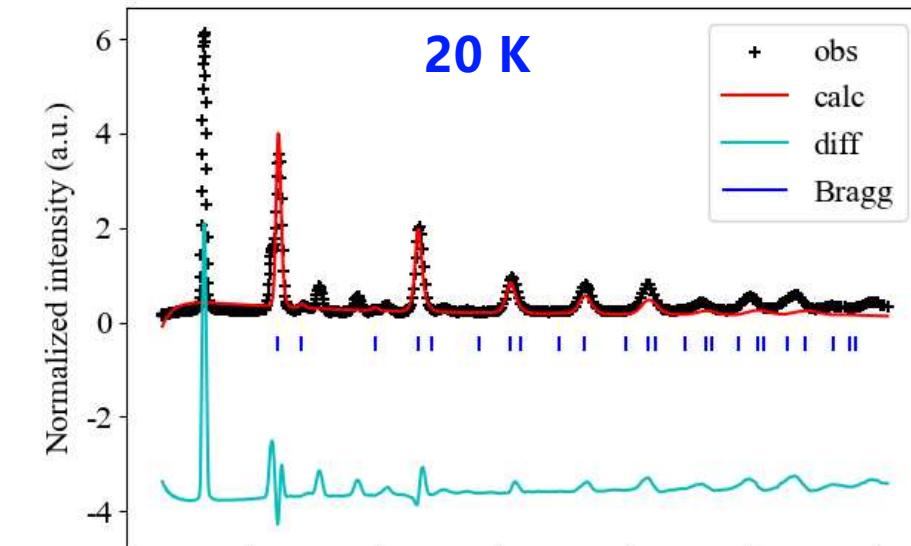
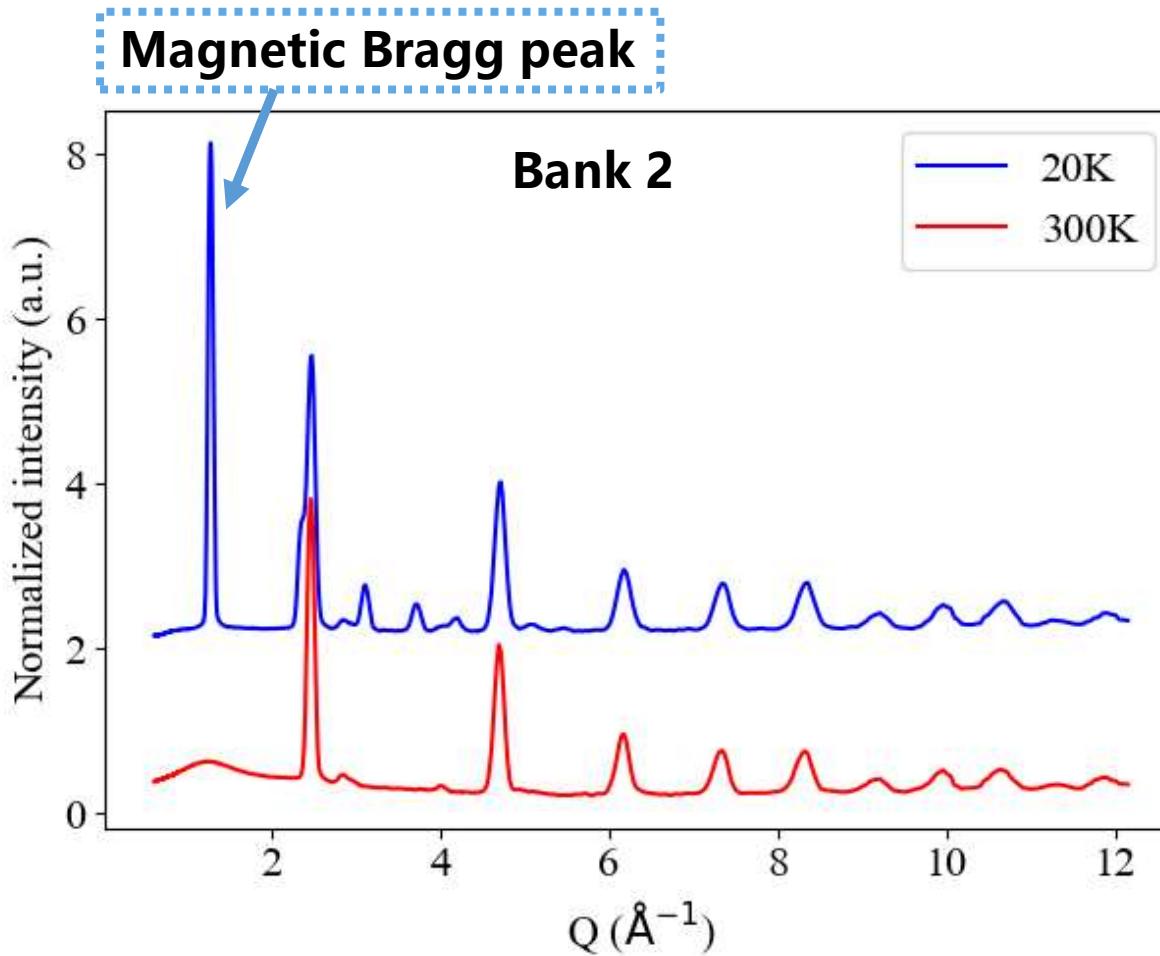
MnO data

300 K



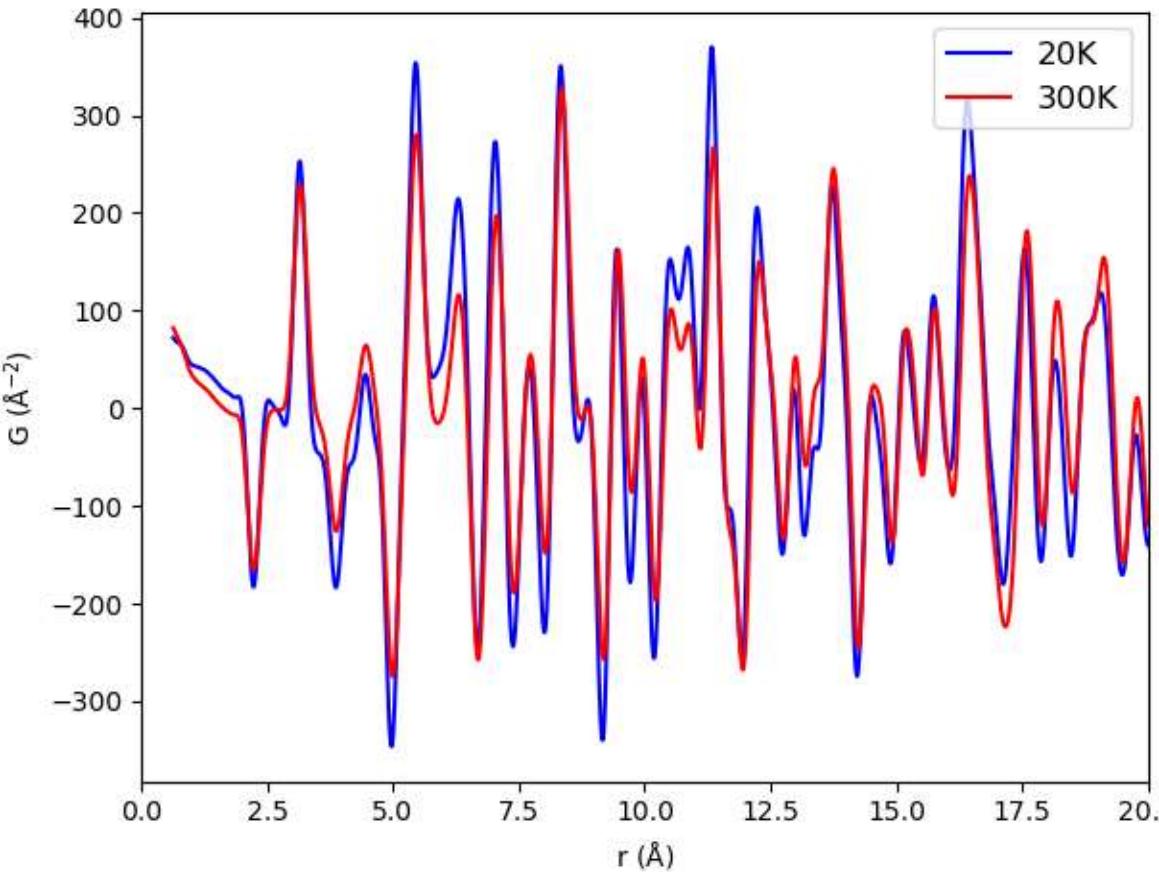


Reciprocal space data analysis

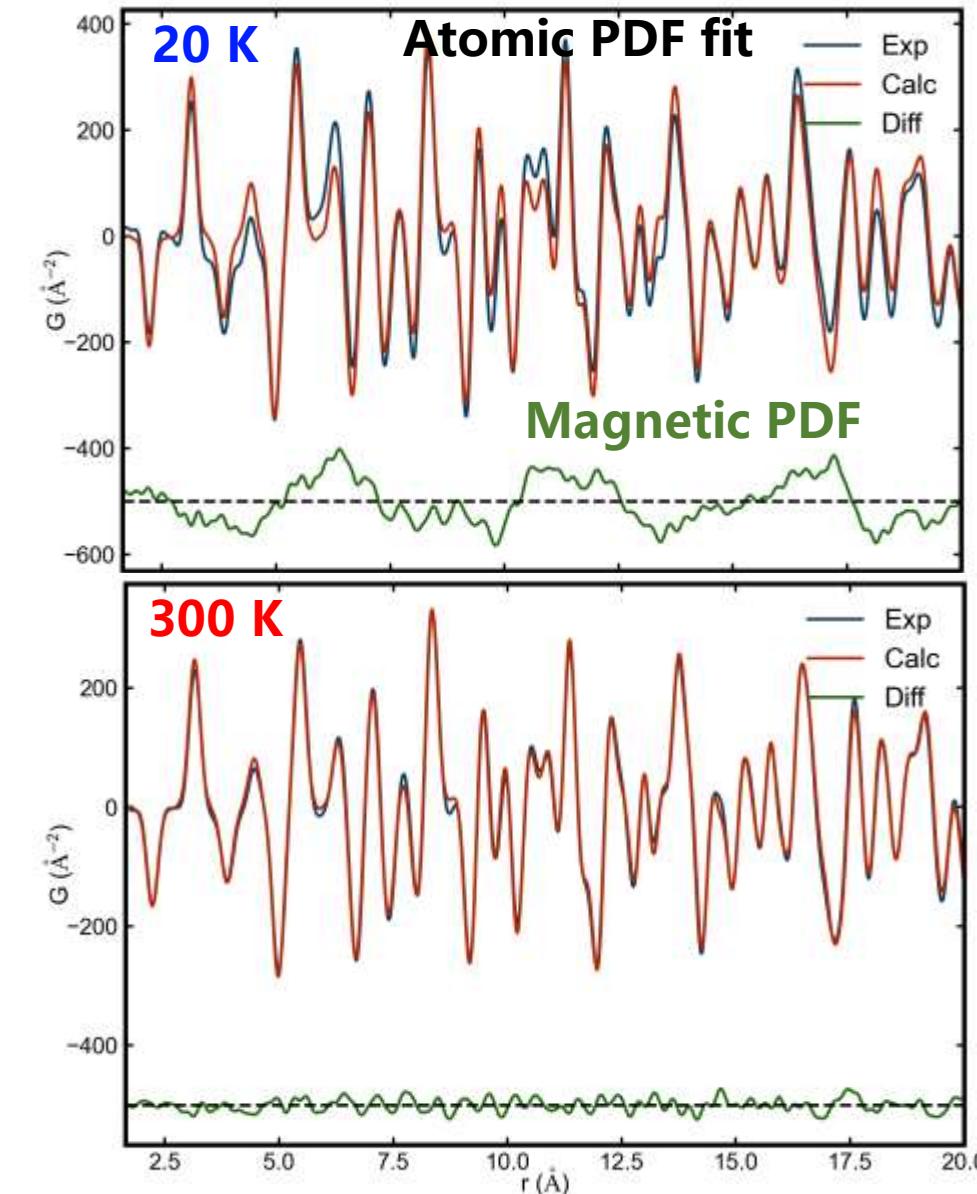




Real space atomic PDF data analysis

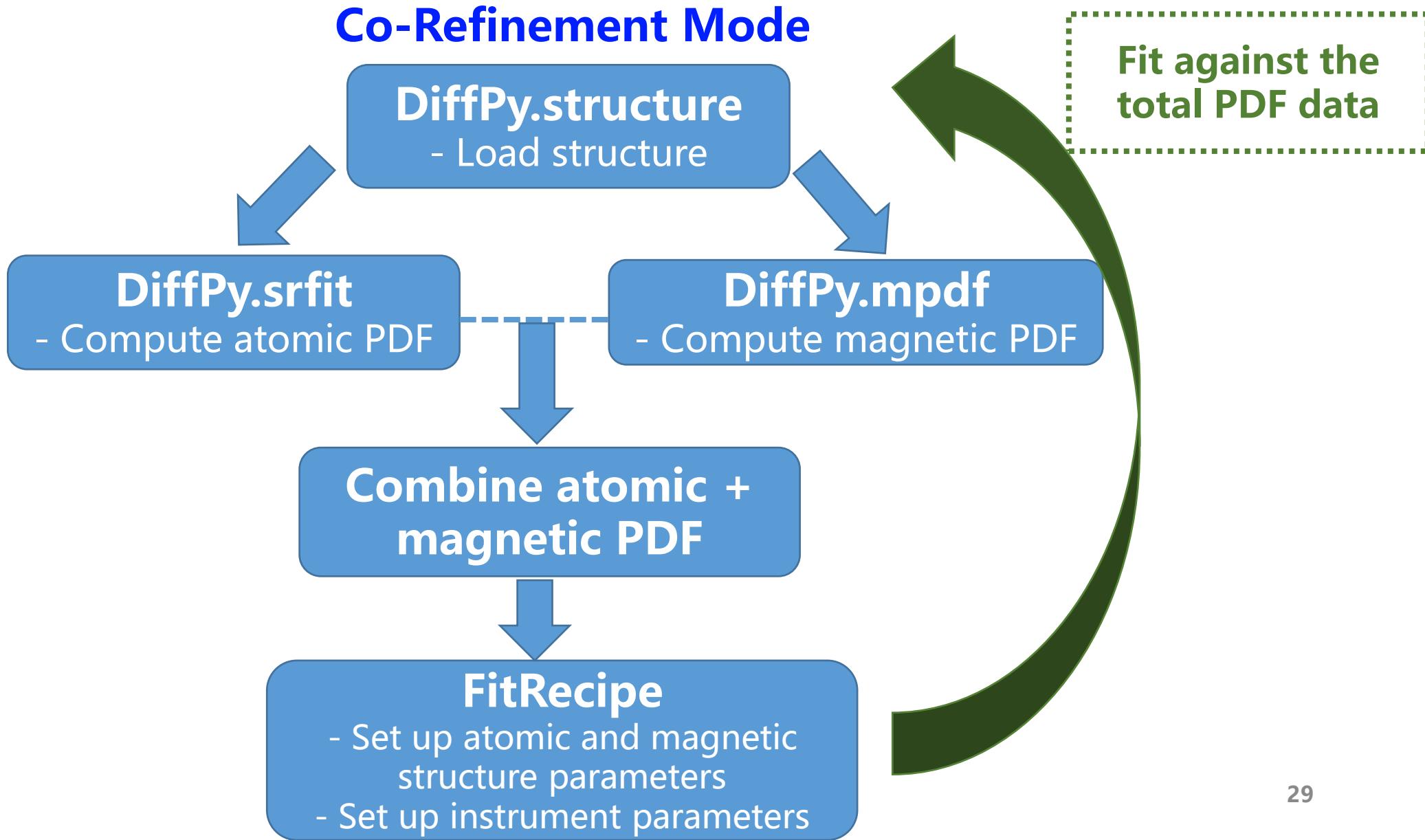


- After fitting atomic structure, the magnetic signals left are prominent.



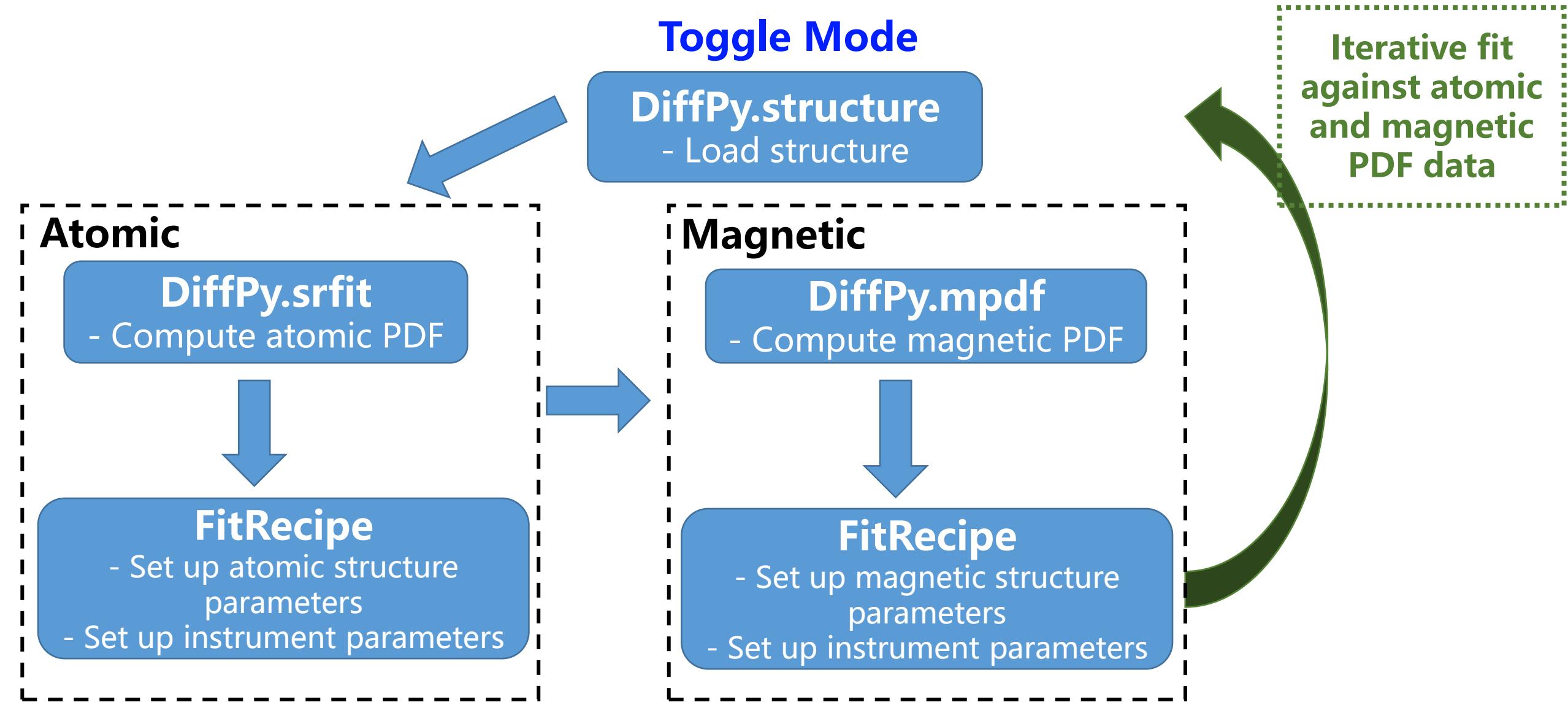


Software framework



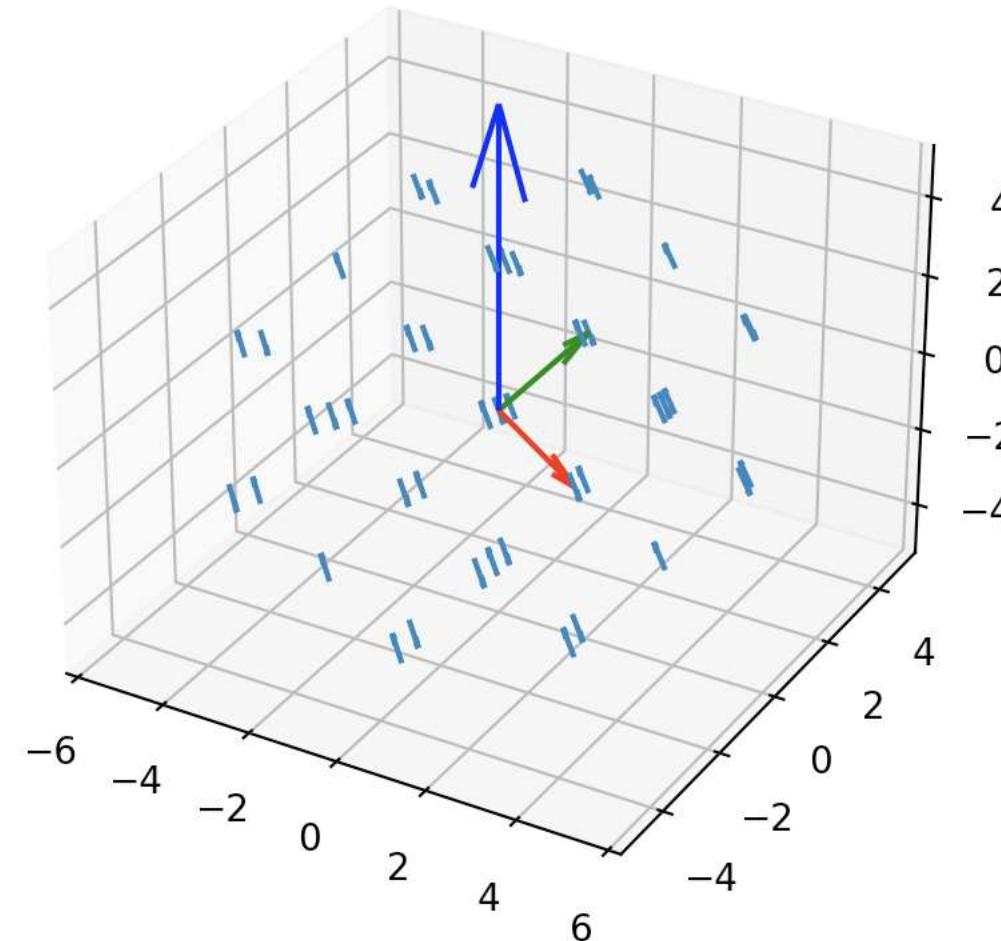


Software framework





Magnetic structure



Set up initial magnetic structure

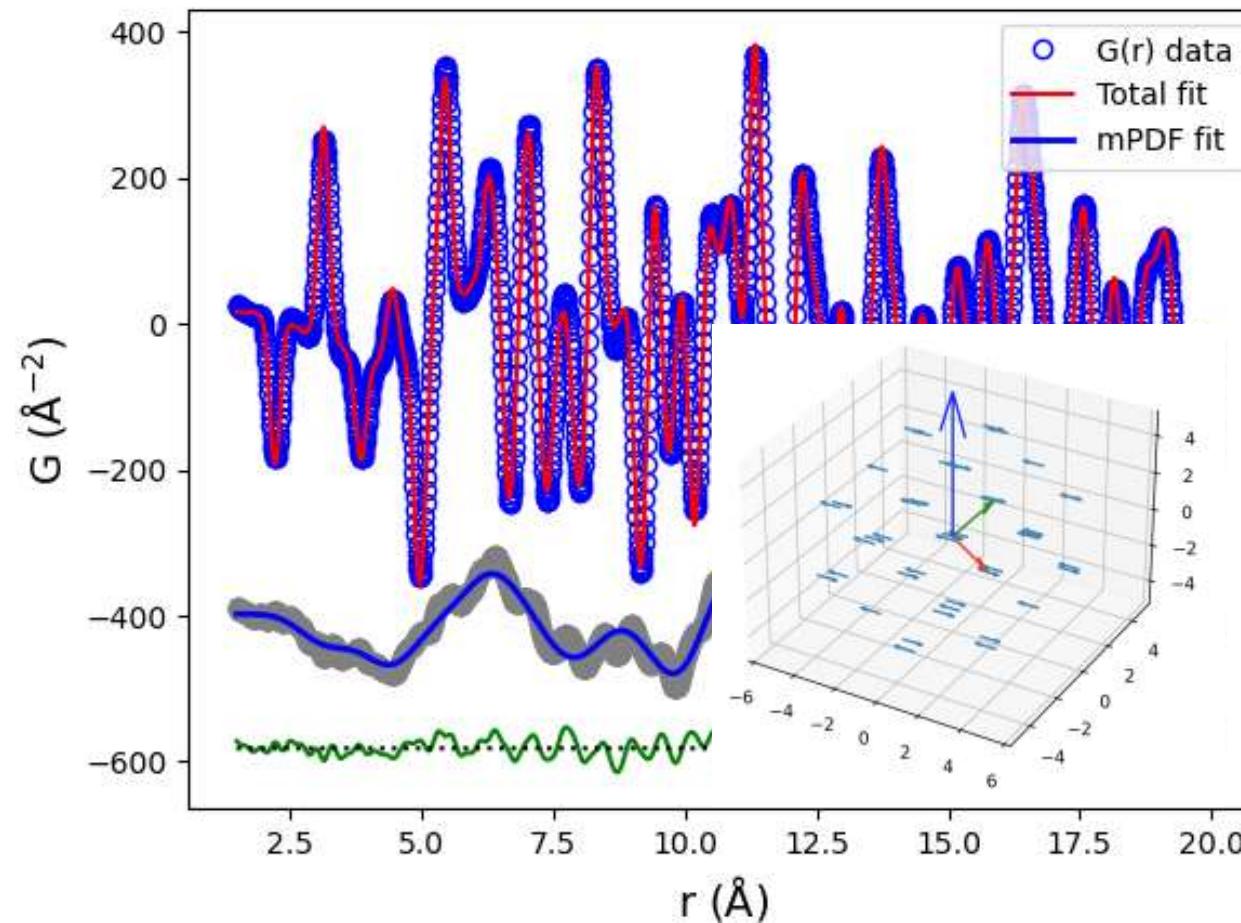
- Magnetic basis vector = [1, -1, 0]
- Magnetic propagation vector = [0, 0, 1.5]



$Q_{\max} = 25 \text{ \AA}^{-1}$

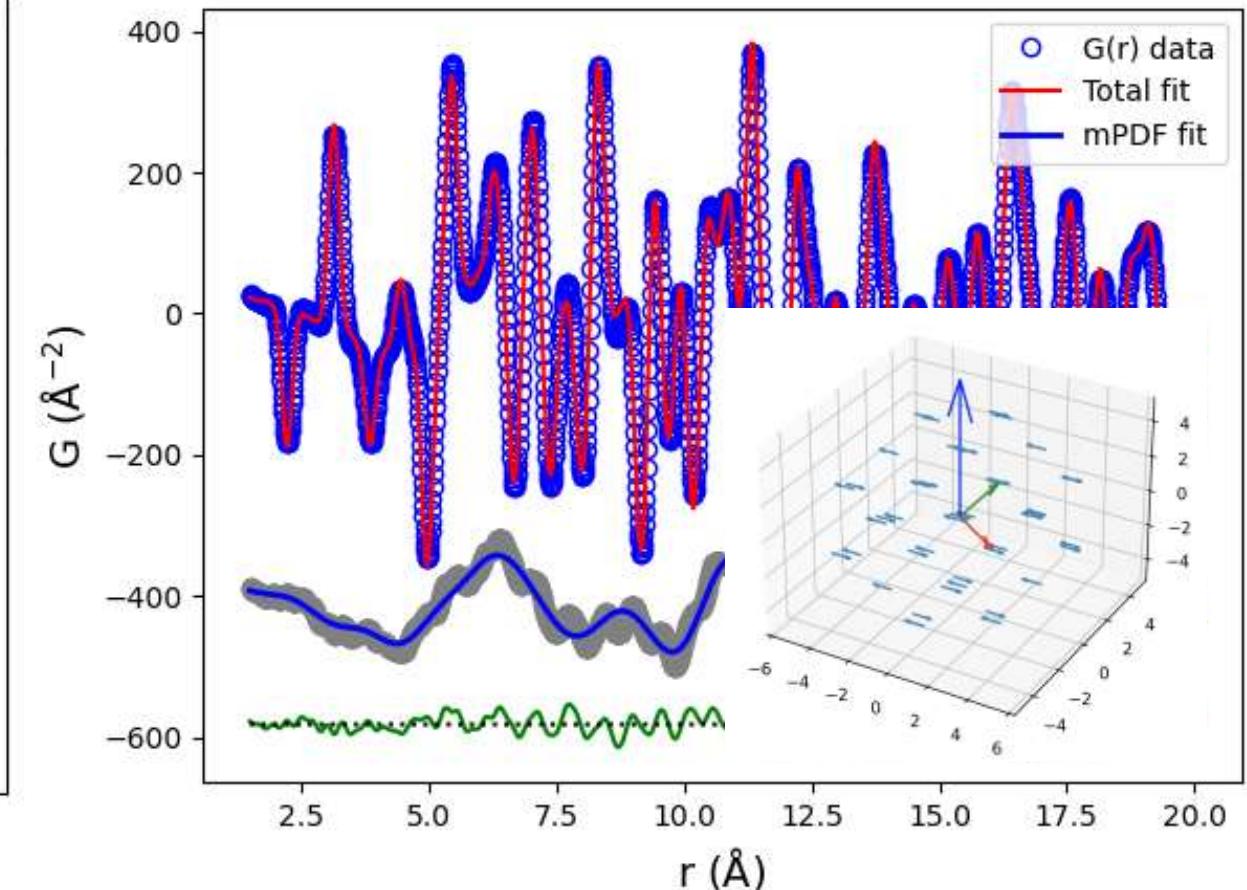
Co-refinement

$R_w = 0.086$



Toggle

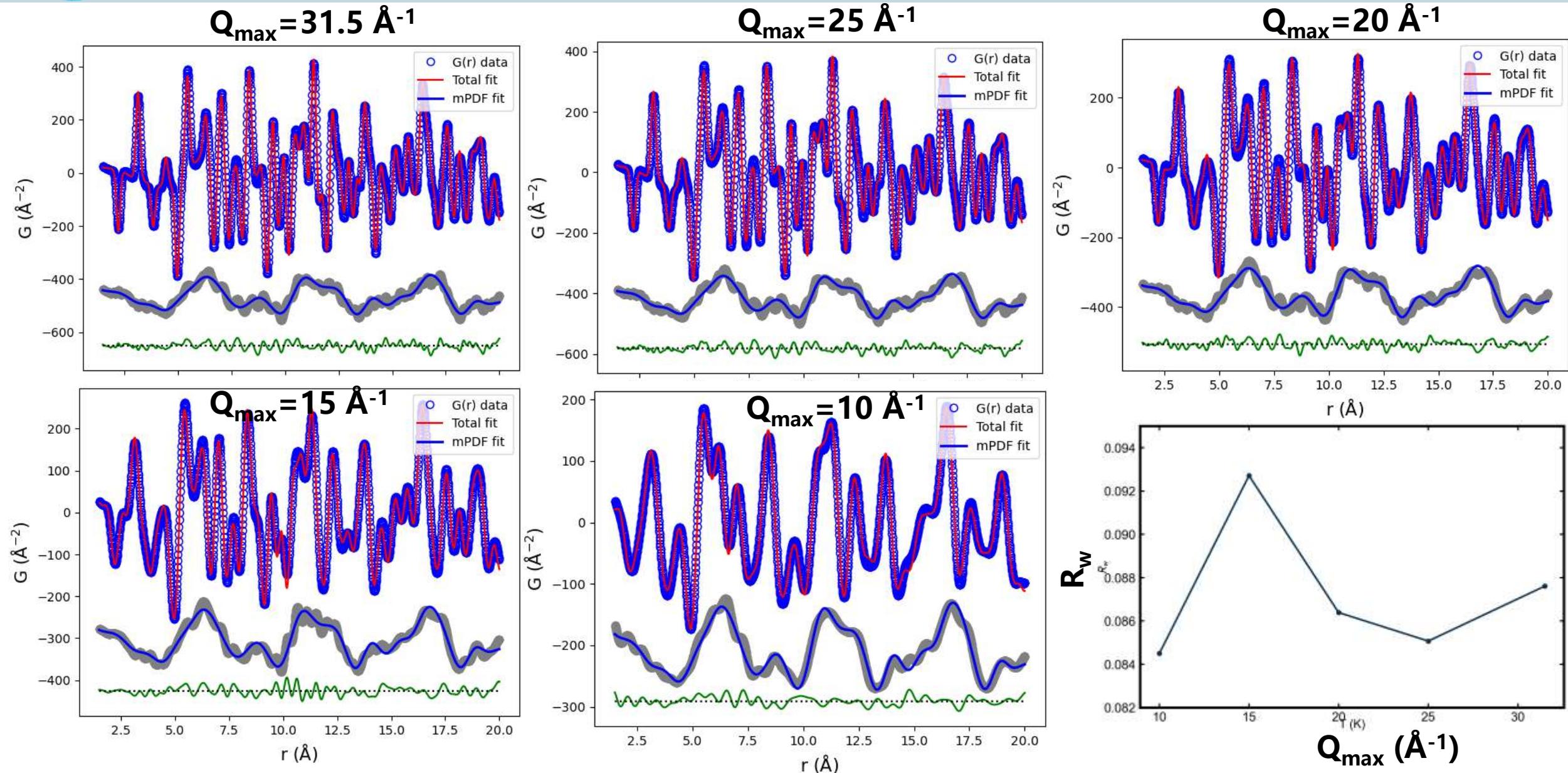
$R_w = 0.085$



- Co-refinement and toggle algorithms perform similarly well.



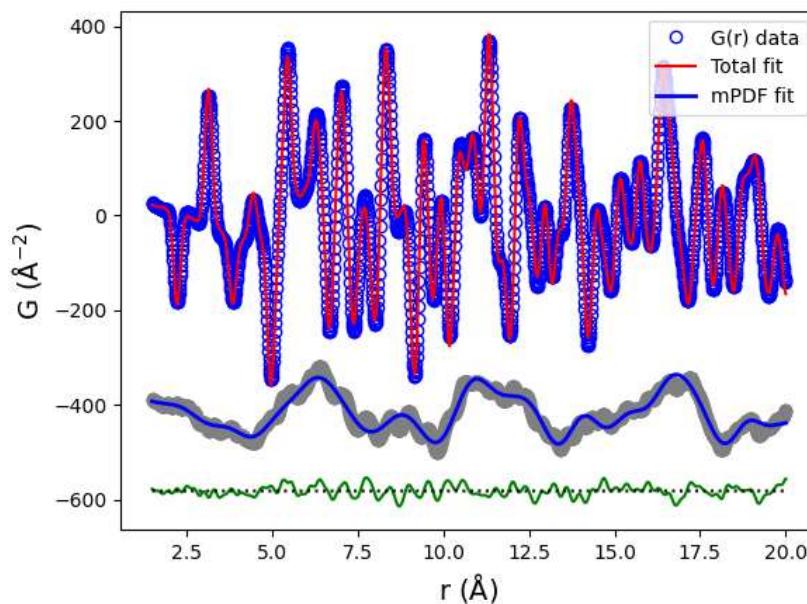
Different Q_{\max}





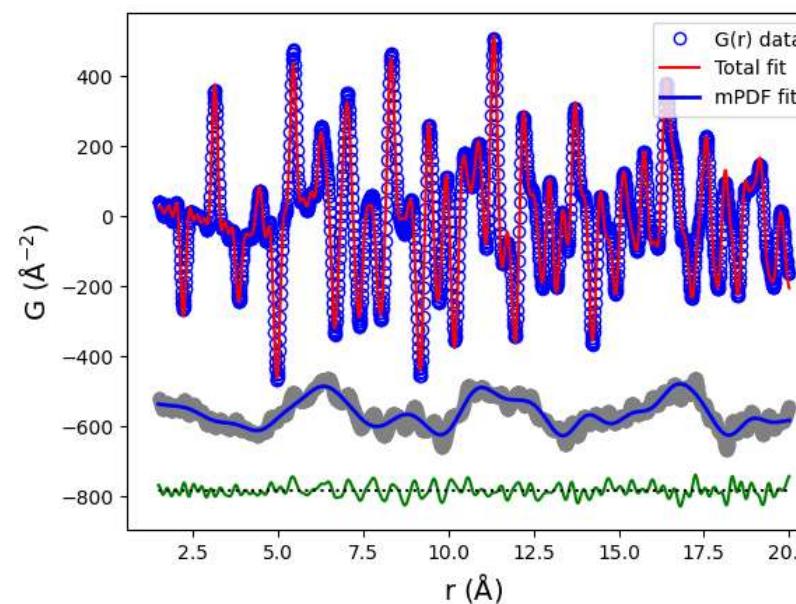
Lorch function

No lorch

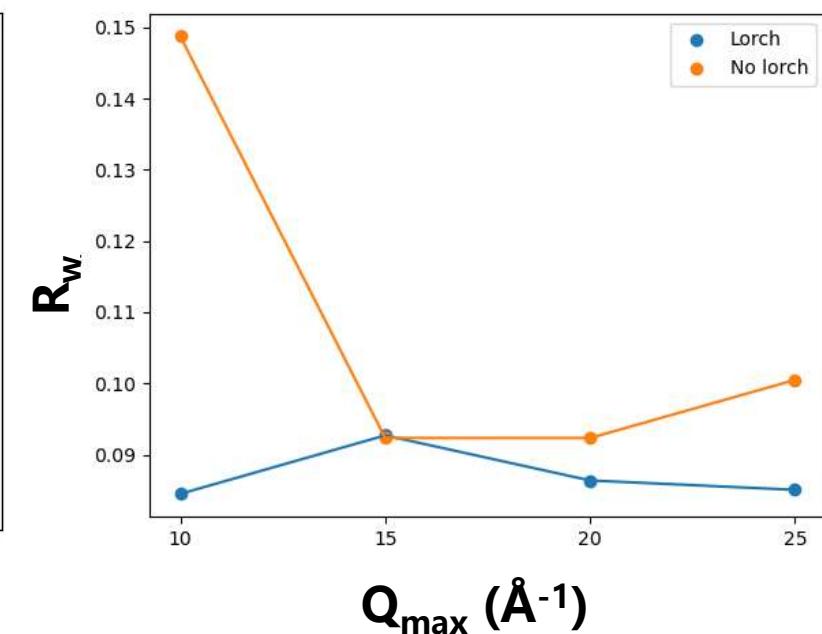


$$Q_{\max} = 25 \text{ \AA}^{-1}$$
$$R_w = 0.100$$

Lorch



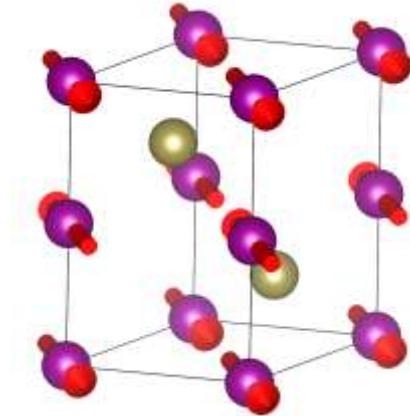
$$Q_{\max} = 25 \text{ \AA}^{-1}$$
$$R_w = 0.085$$





MnTe

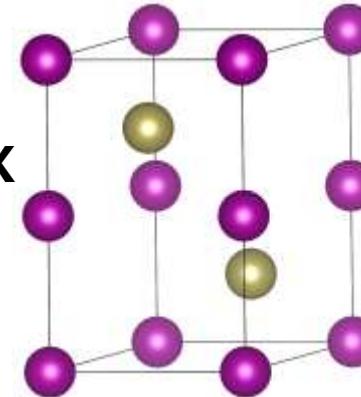
- Short-range antiferromagnetic correlations enhanced thermoelectric material.



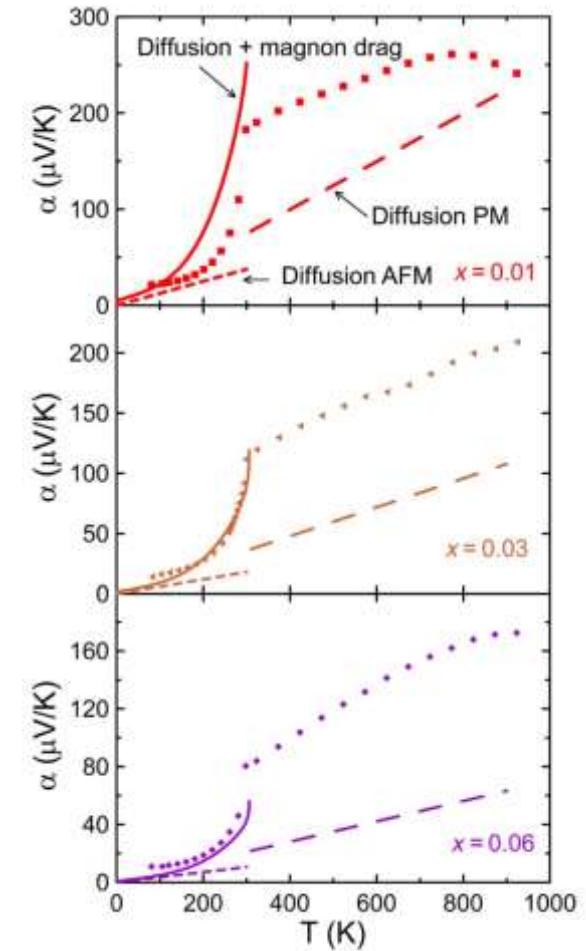
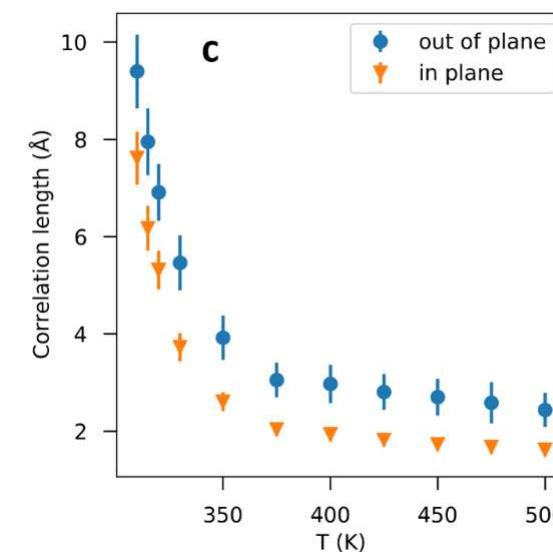
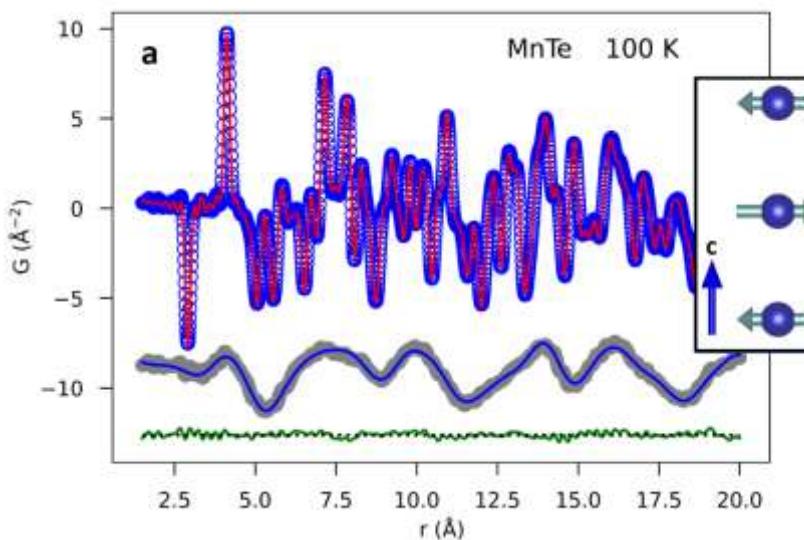
Néel temperature 307 K

heating

antiferromagnetic



paramagnetic

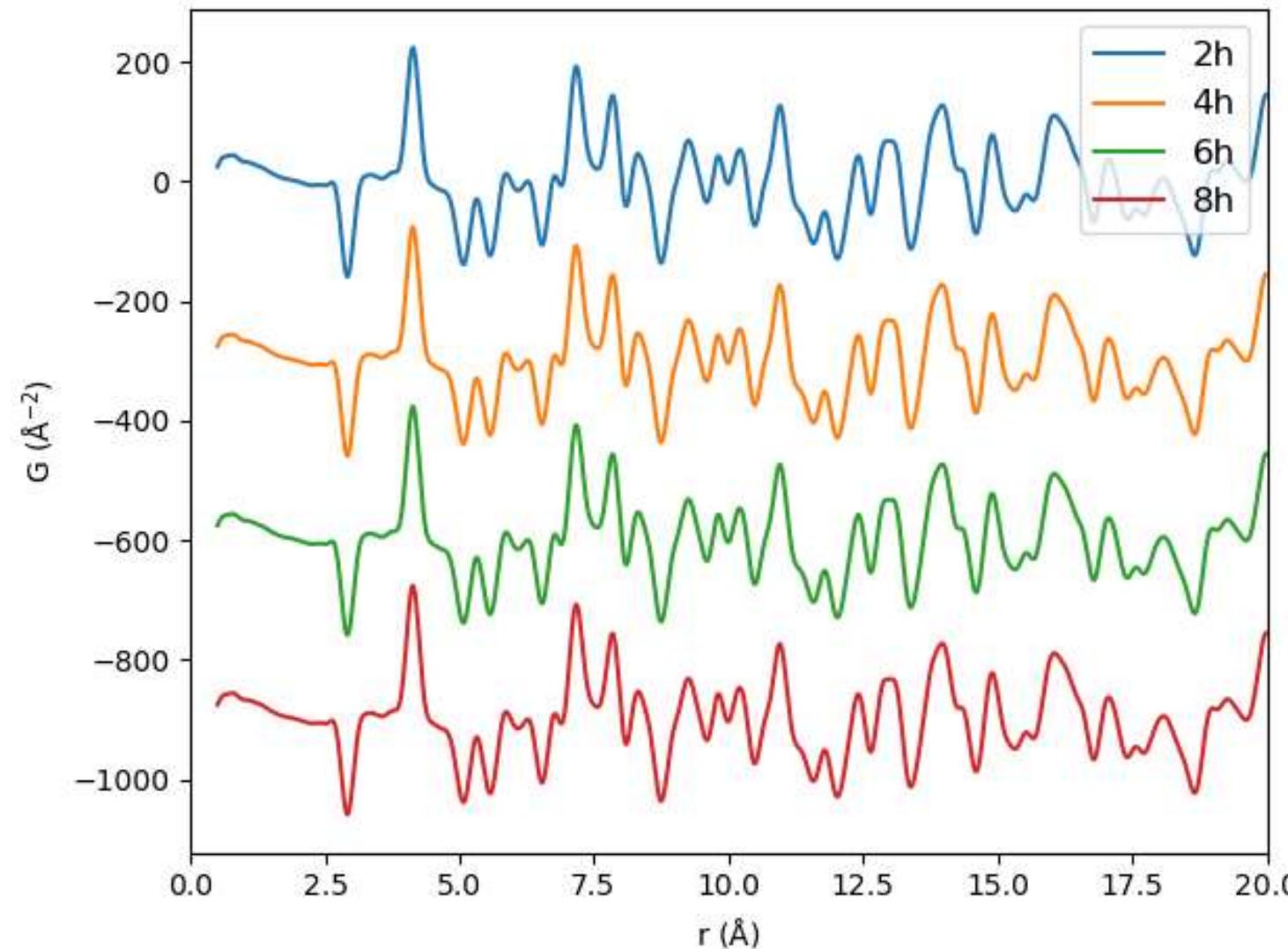


R. Baral, et al., *Matter*, 2022, 5, 6.
Y. Zheng, et al., *Sci. Adv.*, 2019, 5, 9.



Different exposure time

20 K

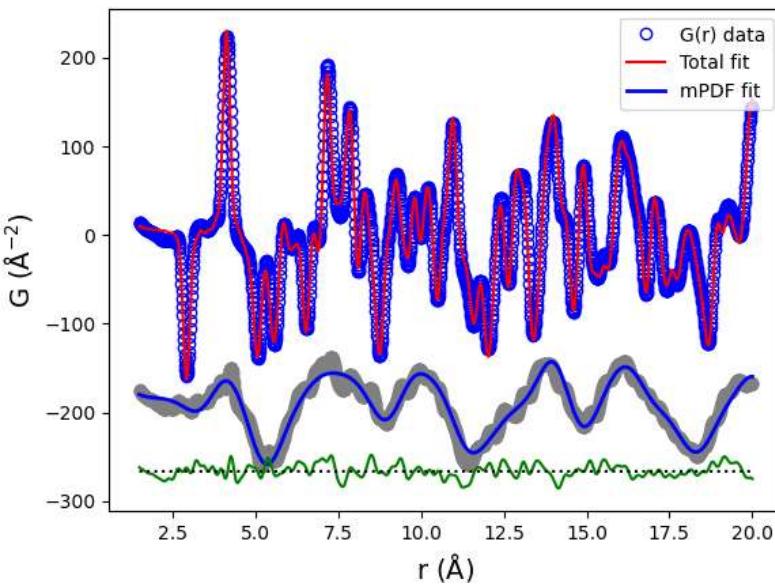


@MPI

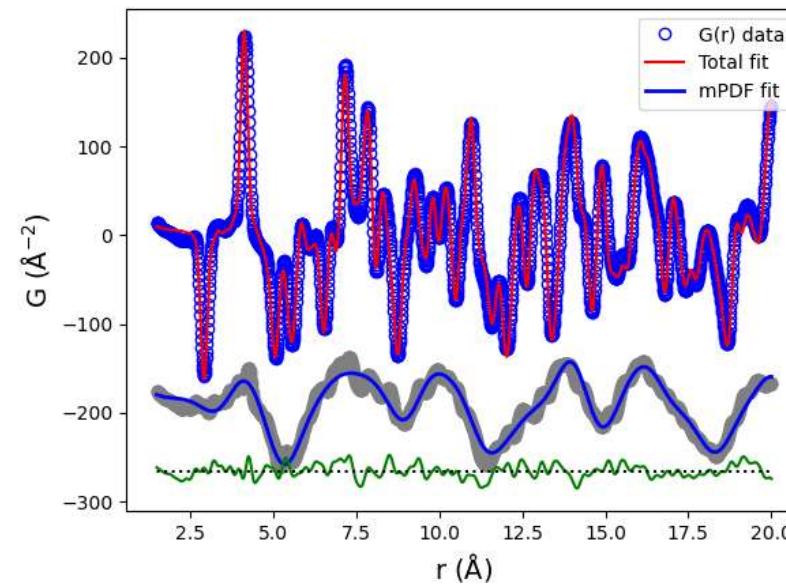


MnTe - different exposure time

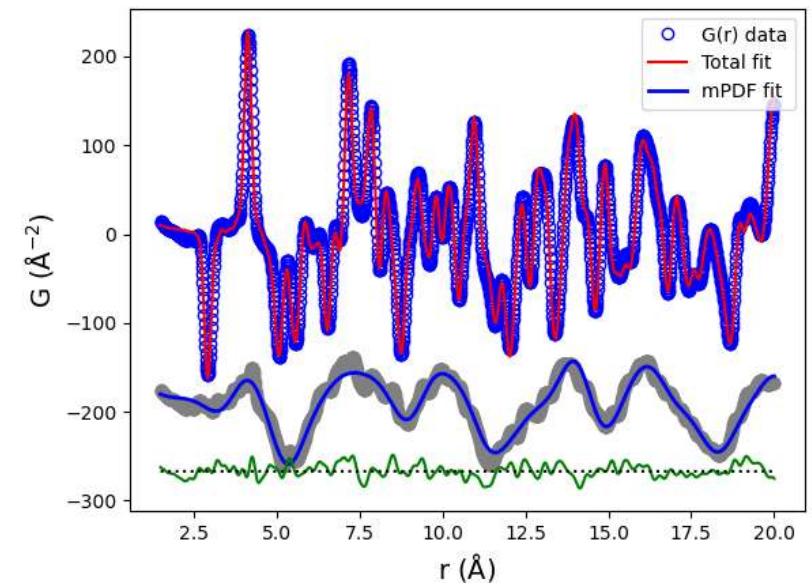
8h
 $R_w = 0.113$



6h
 $R_w = 0.114$



2h
 $R_w = 0.113$





MnTe - different exposure time

20 K	8h	6h	2h
a (Å)	4.138	4.138	4.139
c (Å)	6.682	6.682	6.680
U_{Mn11} (Å ²)	0.0067	0.0068	0.0068
U_{Mn33} (Å ²)	0.0132	0.0132	0.0124
U_{O11} (Å ²)	0.0055	0.0055	0.0055
U_{O33} (Å ²)	0.0068	0.0067	0.0066
Corr. L (Å)	>1000	>1000	>1000
R_w	0.113	0.114	0.113

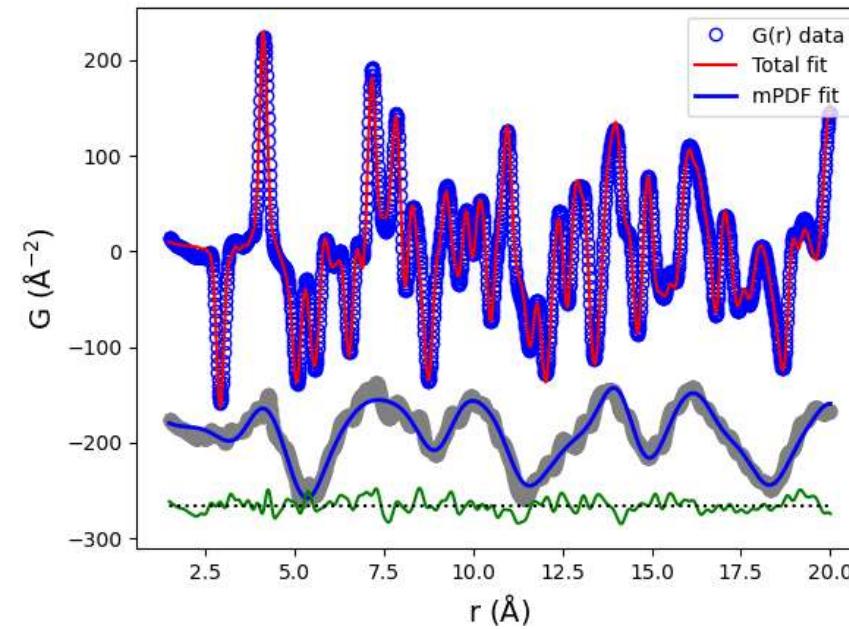
- High-quality mPDF data can be collected in **2 hours** at MPI.



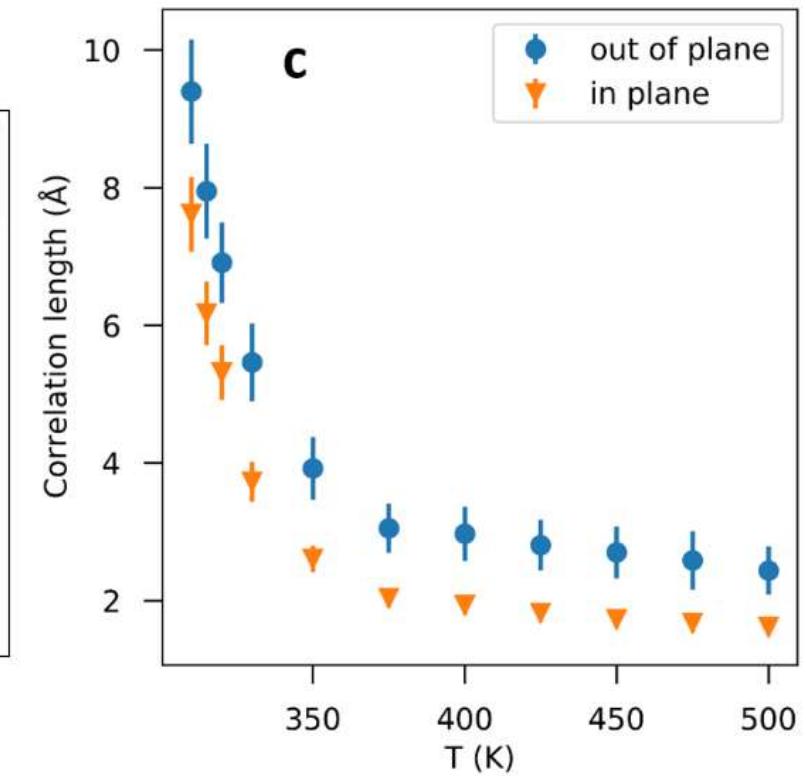
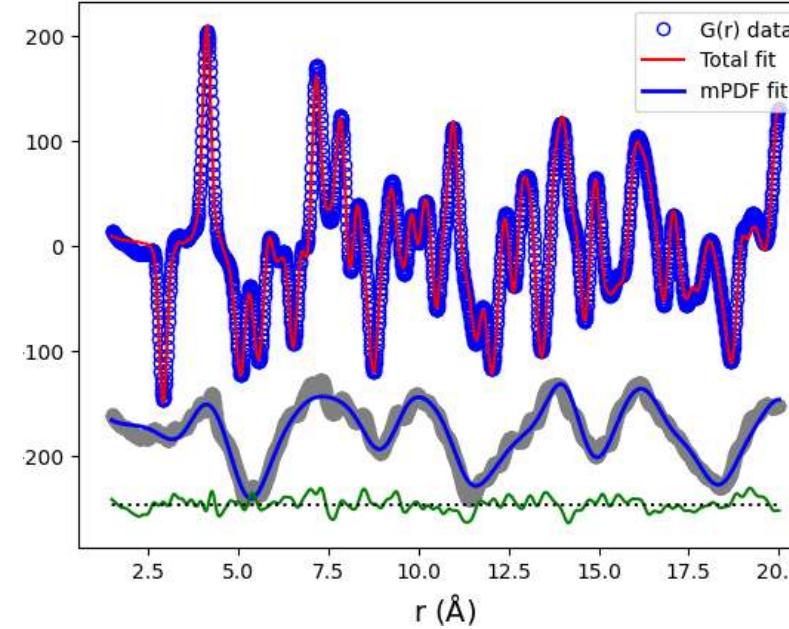
MnTe

Same exposure time

20K



100K



- The short-range antiferromagnetic correlation persists above Néel temperature.



DiffPy



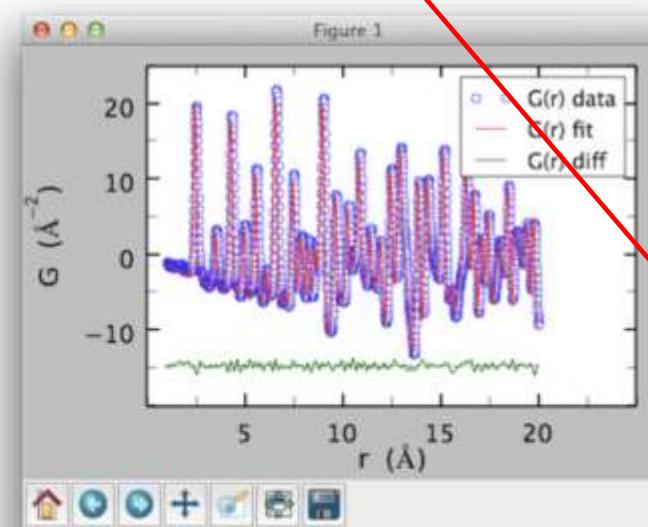
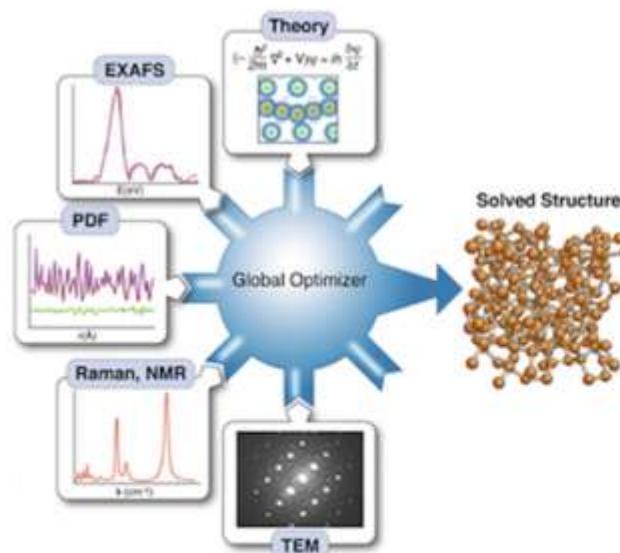
DiffPy-CMI upgrade 3.0 for Python 2 and 3 is now available! (Mar 14, 2019)

[Get DiffPy-CMI](#)

[Credits](#)

DiffPy - Atomic Structure Analysis in Python

A free and open source software project to provide python software for diffraction analysis and the study of the atomic structure of materials.



Products ▾

- DiffPy-CMI
- xPDFsuite
- PDFgetX3, PDFgetN3 and PDFgetS3
- PDFgui
- SrMise
- mPDF
- xINTERPDF
- Python Packages

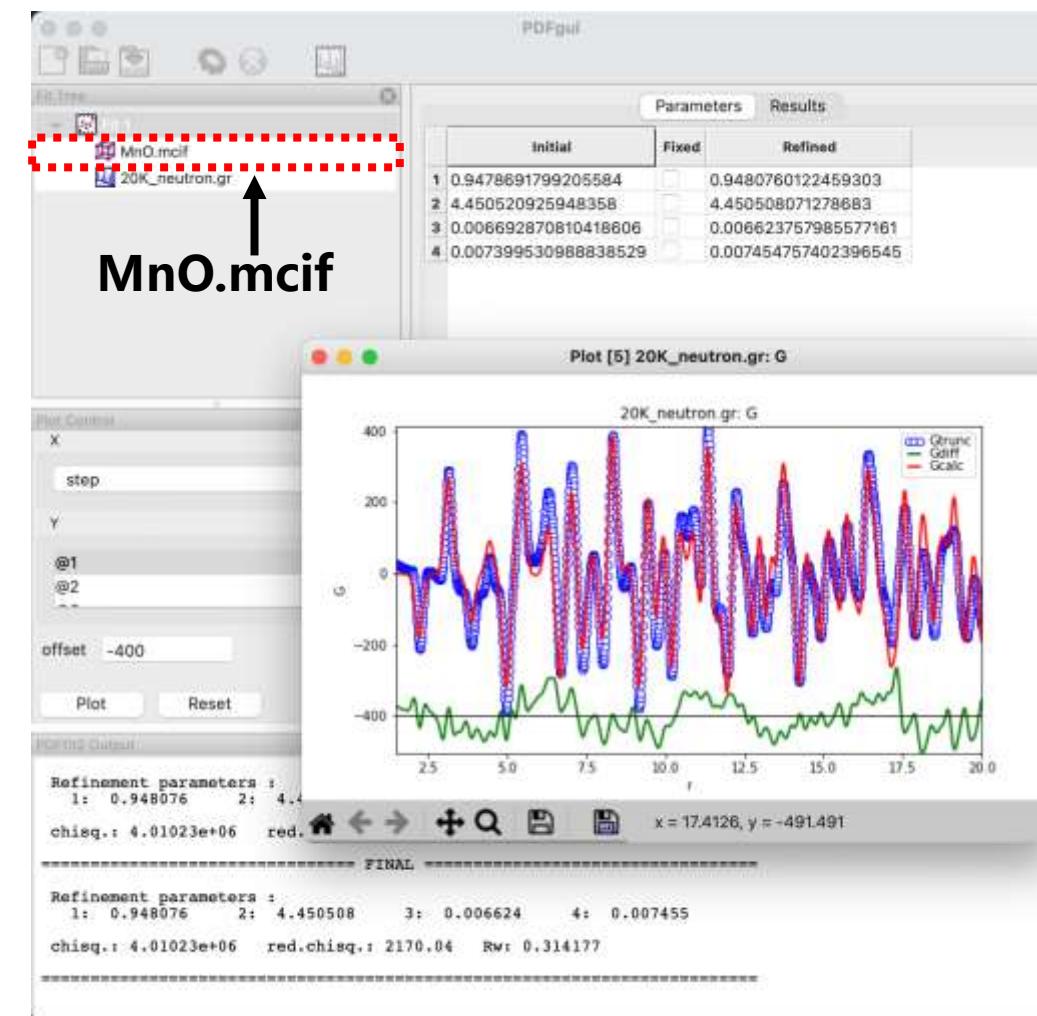
Release of PDFgui 2.0

<https://diffpy.org>



PDFgui 2.X

- Support mPDF refinement
- UI visualize magnetic structure





PDF in the Cloud

The screenshot shows the main interface of the PDF in the Cloud website. At the top, there's a navigation bar with a logo, a search bar containing 'https://pdfitc.org', and a 'Log In' button. Below the header, the title 'PDF IN THE CLOUD' is displayed next to a purple flower icon.

structureMining: Auto search for the best structures from an experimental PDF. Includes a circular visualization of a crystal structure and a 'start' button.

spacegroupMining: Auto search for the best space groups from an experimental PDF. Includes a circular visualization of a space group diagram and a 'start' button.

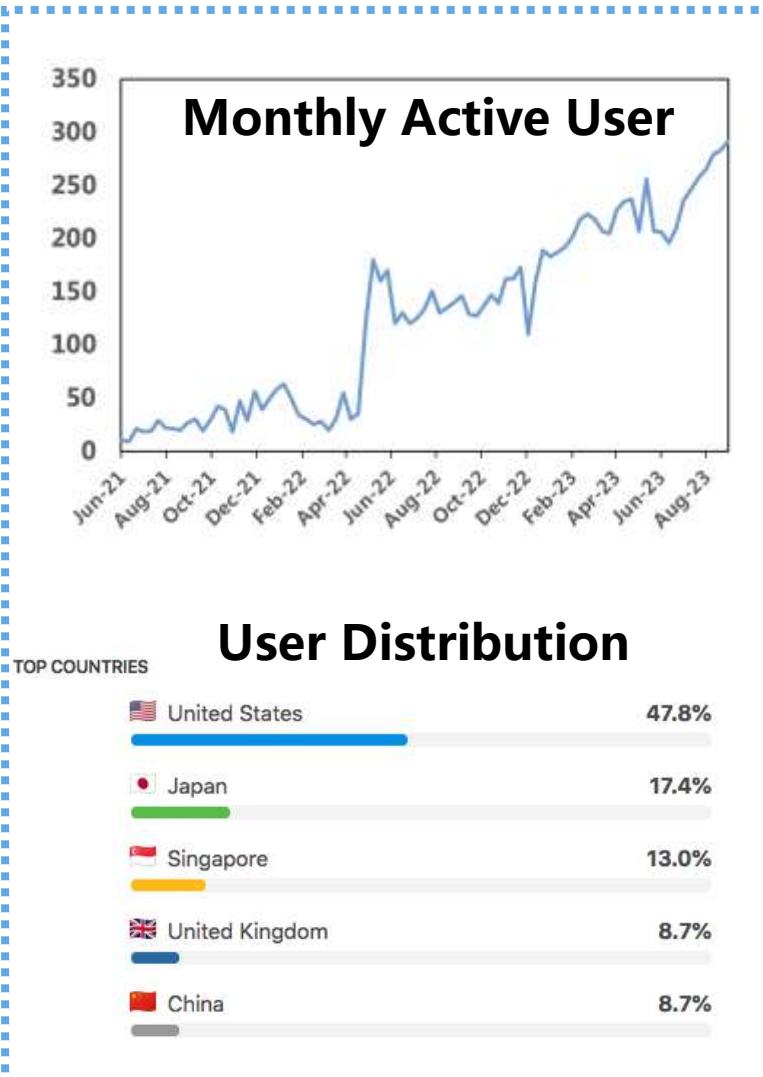
similarityMapping: Calculate the correlation between experimental PDFs. Includes a circular visualization of a heatmap and a 'start' button.

nmfMapping: Disentangle structural phase components and their ratios from sets of PDFs or powder diffraction patterns. Includes a circular visualization of a stacked area chart and a 'start' button.

At the bottom of the page, there's a footer with links: 'About | Contact | Terms of Use | Privacy Policy | Citing'.

<https://pdfitc.org>

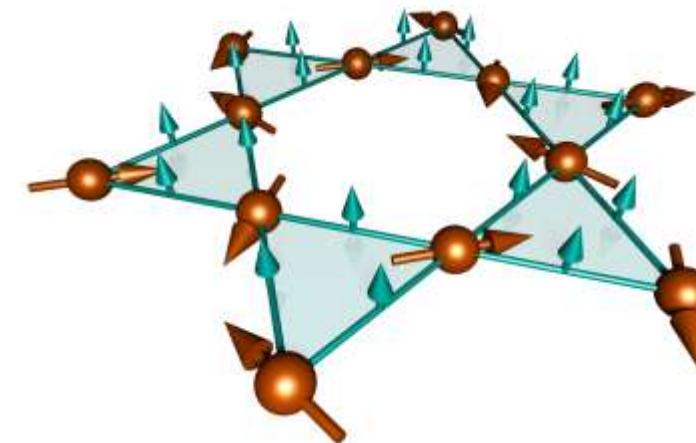
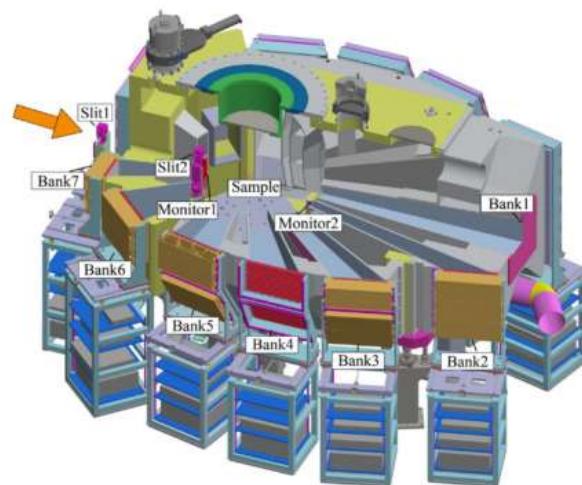
L. Yang, et al. Acta Crystallogr. A (2021) 42





Summary

- The MPI instrument is capable of collecting high quality mPDF data.
- The mPDF may serve as a promising method for exploring local magnetic correlations in complicated condensed matters.



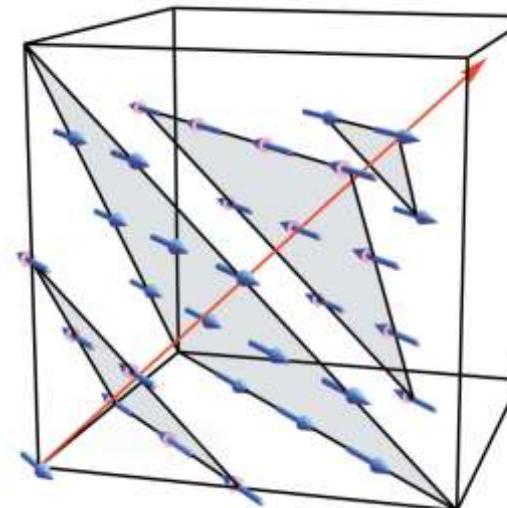
Thank you!





MnO

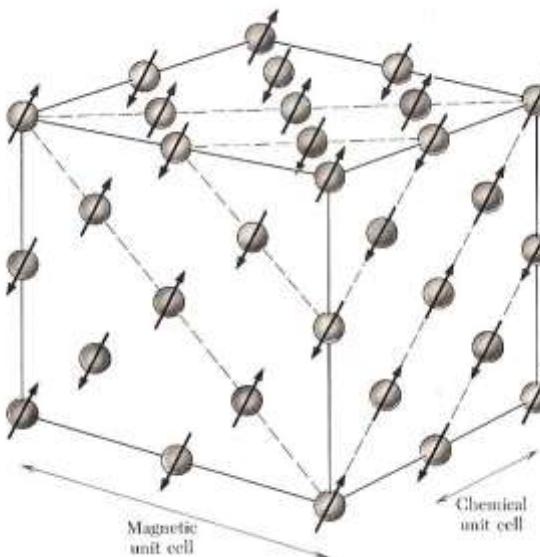
- Early neutron diffraction studies showed that MnO has the cubic rock-salt structure (s.g.: Fm-3m) at high temperature, and rhombohedral phase (s.g.: R-3m) at low temperature. (Shull et al., 1951; Roth, 1958)
- The antiferromagnetic spin arrangement in MnO is compatible only with monoclinic or lower symmetry (Shaked et al., 1988), so the true structural symmetry must be lower than R-3m.





MnO

- In 1949 Clifford Shull and Ernest Wollan showed the magnetic structure of MnO, which leads to the discovery of **antiferromagnetism**.
- The spin alignment axis lies within the (111) plane, and the spin direction reverses between adjacent sheets along the [111] direction.
- Clifford Shull won the Nobel Prize in Physics in 1994.



IUCr NEWSLETTER (2022) VOLUME 30, NUMBER 2

HISTORY OF CRYSTALLOGRAPHY

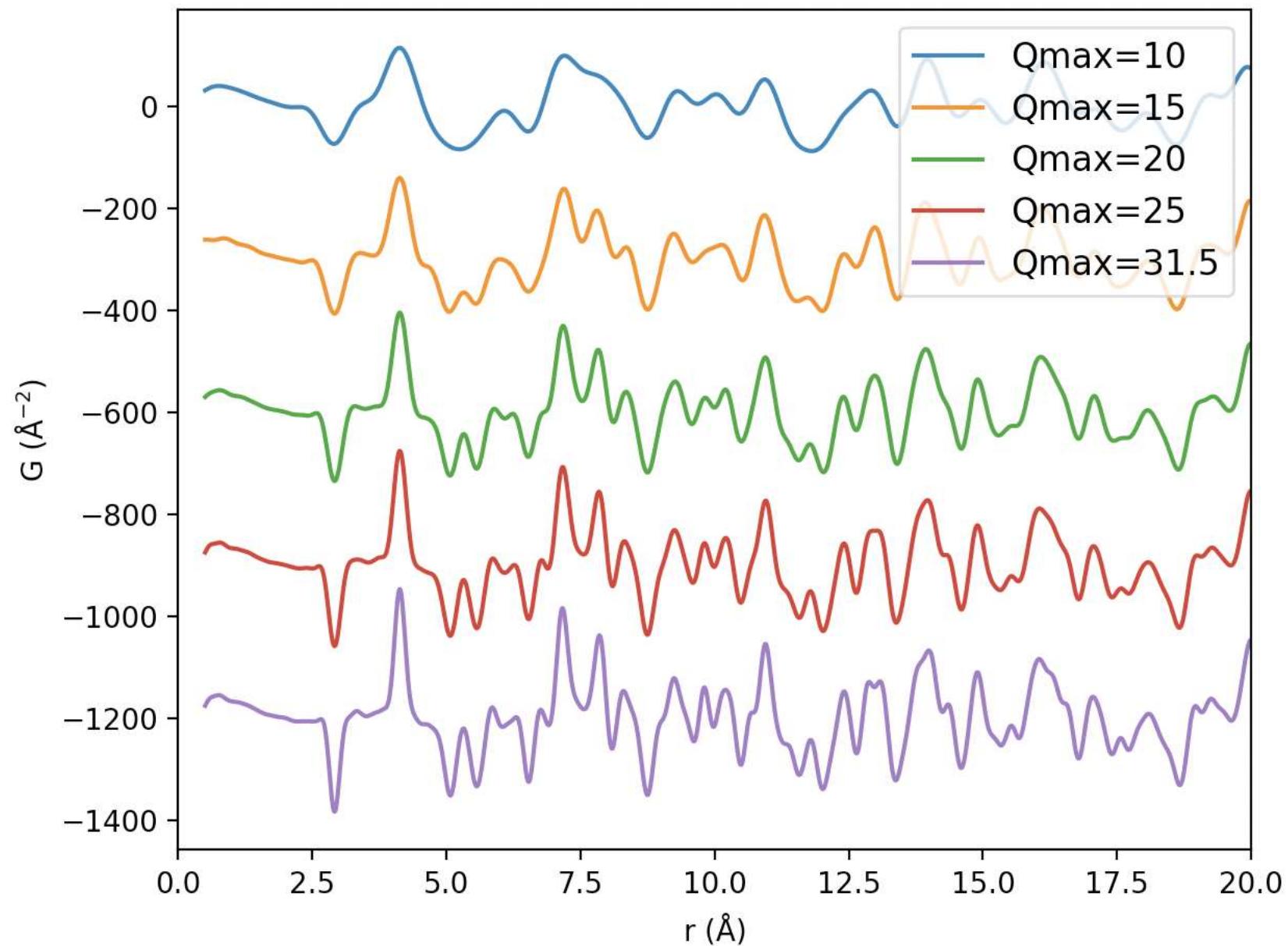
ERNEST O. WOLLAN: AN UNSUNG HERO OF CRYSTALLOGRAPHY

This screenshot shows a news article from the International Union of Crystallography (IUCr) newsletter. The title is "IUCr NEWSLETTER (2022) VOLUME 30, NUMBER 2". Below the title, there is a section titled "HISTORY OF CRYSTALLOGRAPHY" and an article about "ERNEST O. WOLLAN: AN UNSUNG HERO OF CRYSTALLOGRAPHY". The page has a dark header and a colorful image in the background.

courtesy of ORNL



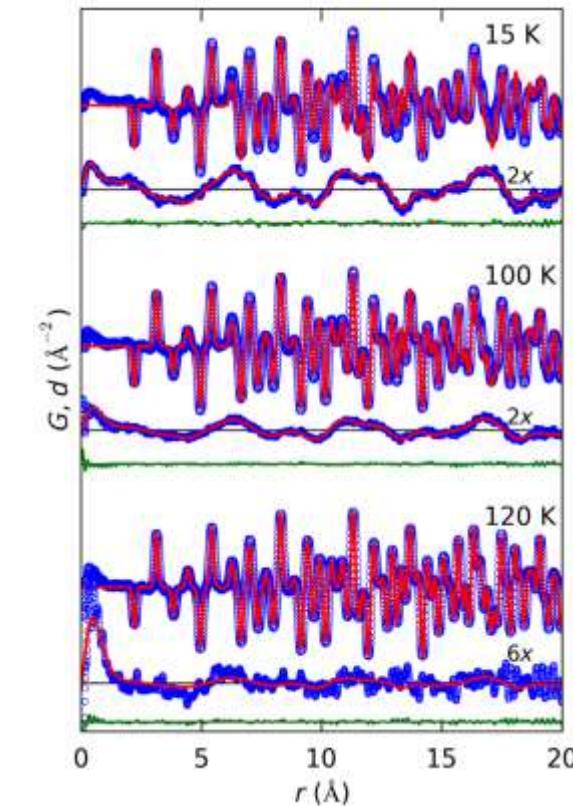
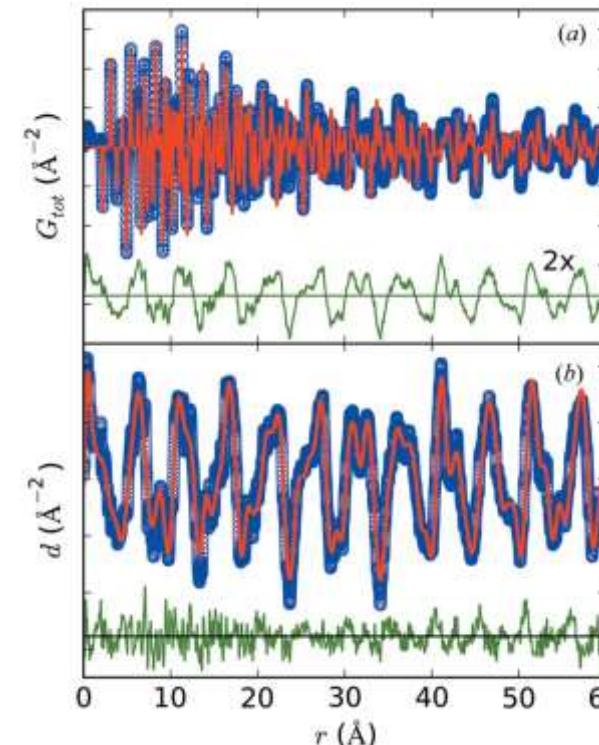
MnTe





Atomic v.s. magnetic PDF

- mPDF is lower in frequency and characteristically broader than the atomic PDF due to the effects of the magnetic form factor.
- mPDF changes more dramatically with temperature.



B. Frandsen, S. J.L. Billinge, *Acta Cryst. A*, 2015, 71, 3.

B. Frandsen, et al., *Phys. Rev. Lett.*, 2016, 116, 19.

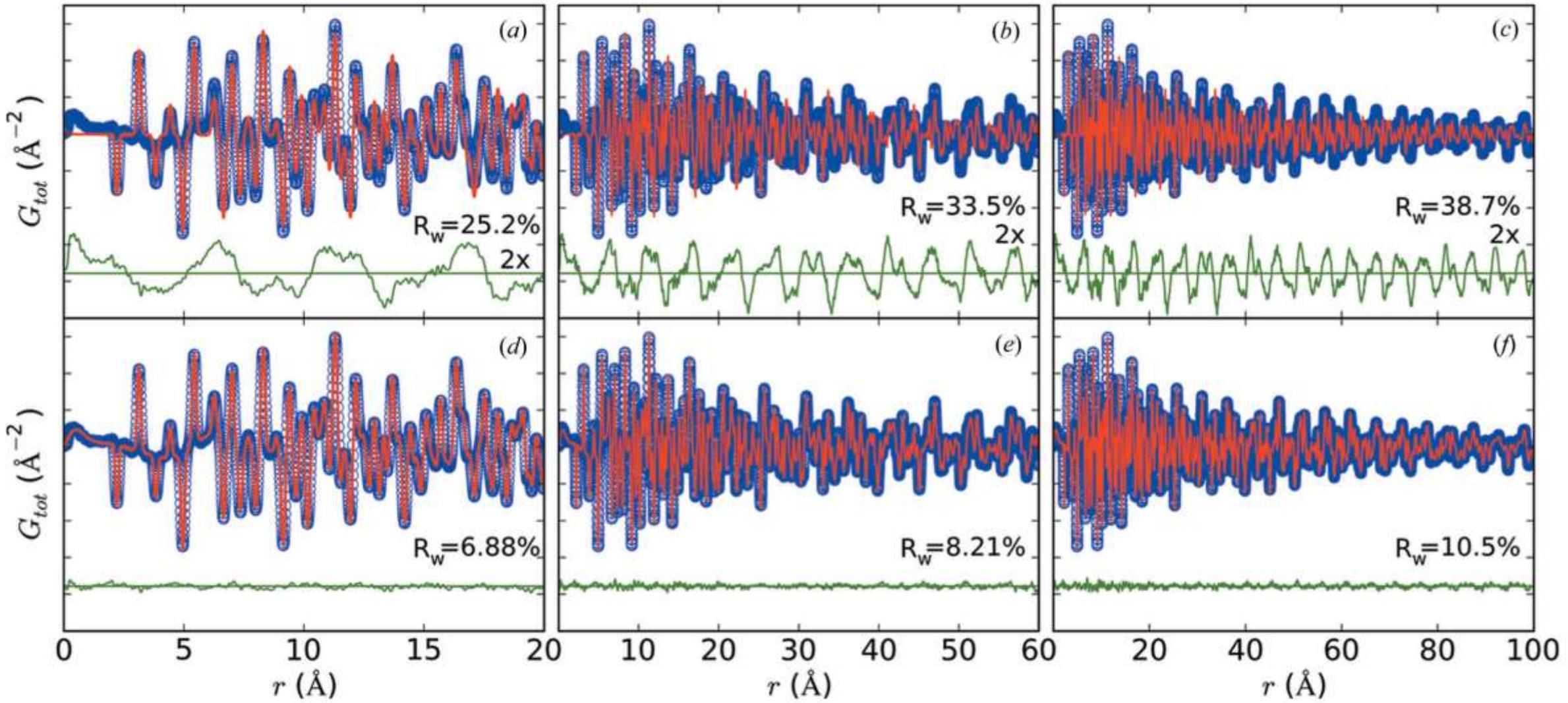
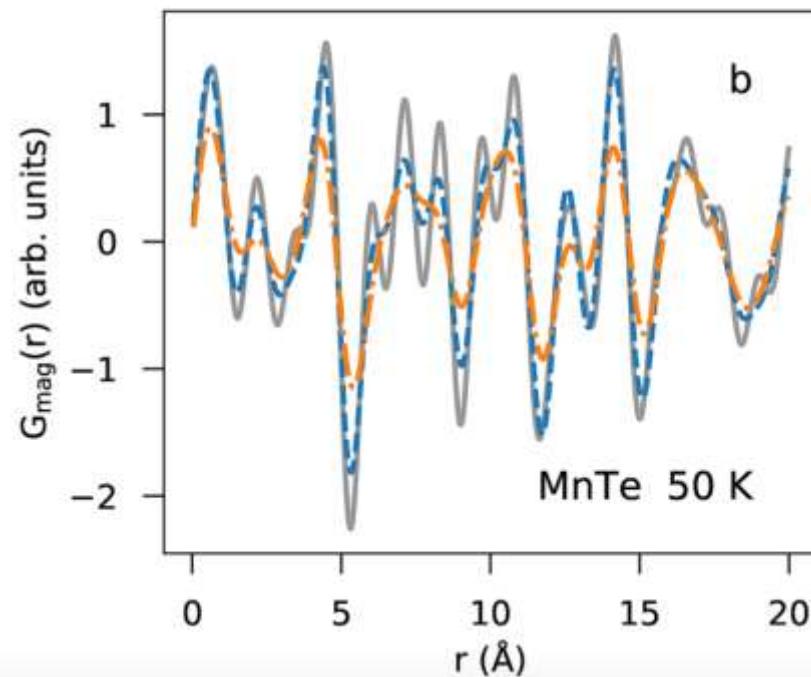


Figure 7

[Save the figure](#)

Atomic and magnetic PDF refinements of the monoclinic model for three fitting ranges. (a)–(c) Refinement results when only the atomic structure is included in the model. The mPDF $d(r)$ is seen in the difference curves, which are multiplied by two for clarity. (d)–(f) Results of co-refinements of the atomic and magnetic PDFs. In all panels, the blue curve is the experimental data, the red curve is the calculated pattern, and the offset green curve is the difference.



step function

$$w_s(Q) = \begin{cases} 1 & \text{if } Q \leq Q_{\max}, \\ 0 & \text{if } Q > Q_{\max}, \end{cases} \quad (6)$$

a modified Fermi-Dirac function

$$W_{\text{FD}}(Q) = \begin{cases} \frac{2}{e^{(Q-Q_{\max})/\Delta} + 1} - 1 & \text{if } Q \leq Q_{\max}, \\ 0 & \text{if } Q > Q_{\max}, \end{cases} \quad (7)$$

and the conventional Lorch function³³

$$w_L(Q) = \begin{cases} \frac{Q_{\max}}{\pi Q} \sin\left(\frac{\pi Q}{Q_{\max}}\right) & \text{if } Q \leq Q_{\max}, \\ 0 & \text{if } Q > Q_{\max}. \end{cases} \quad (8)$$

B. Frandsen, et al., *J Appl. Phys.*, 2022, 132, 22.



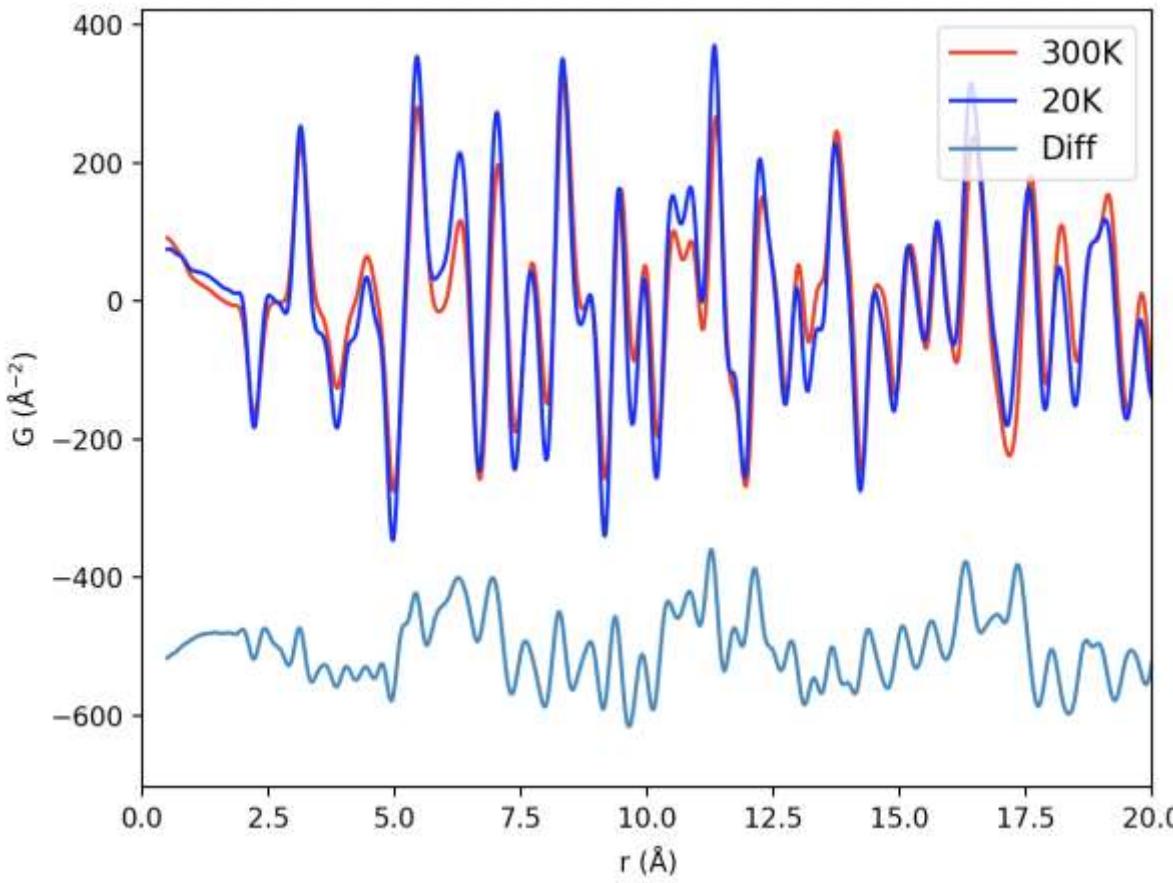
Co-refinement v.s. Toggle

20 K	no mPDF fit	Co-refine mPDF fit	Toggle mPDF fit
a (Å)	3.161	3.161	3.161
c (Å)	7.628	7.619	7.618
U_{Mn11} (Å ²)	0.0050	0.0056	0.0056
U_{Mn33} (Å ²)	0.0044	0.0066	0.0064
U_{O11} (Å ²)	0.0061	0.0060	0.0051
U_{O33} (Å ²)	0.0057	0.0063	0.0066
R_w	0.30	0.086	0.085

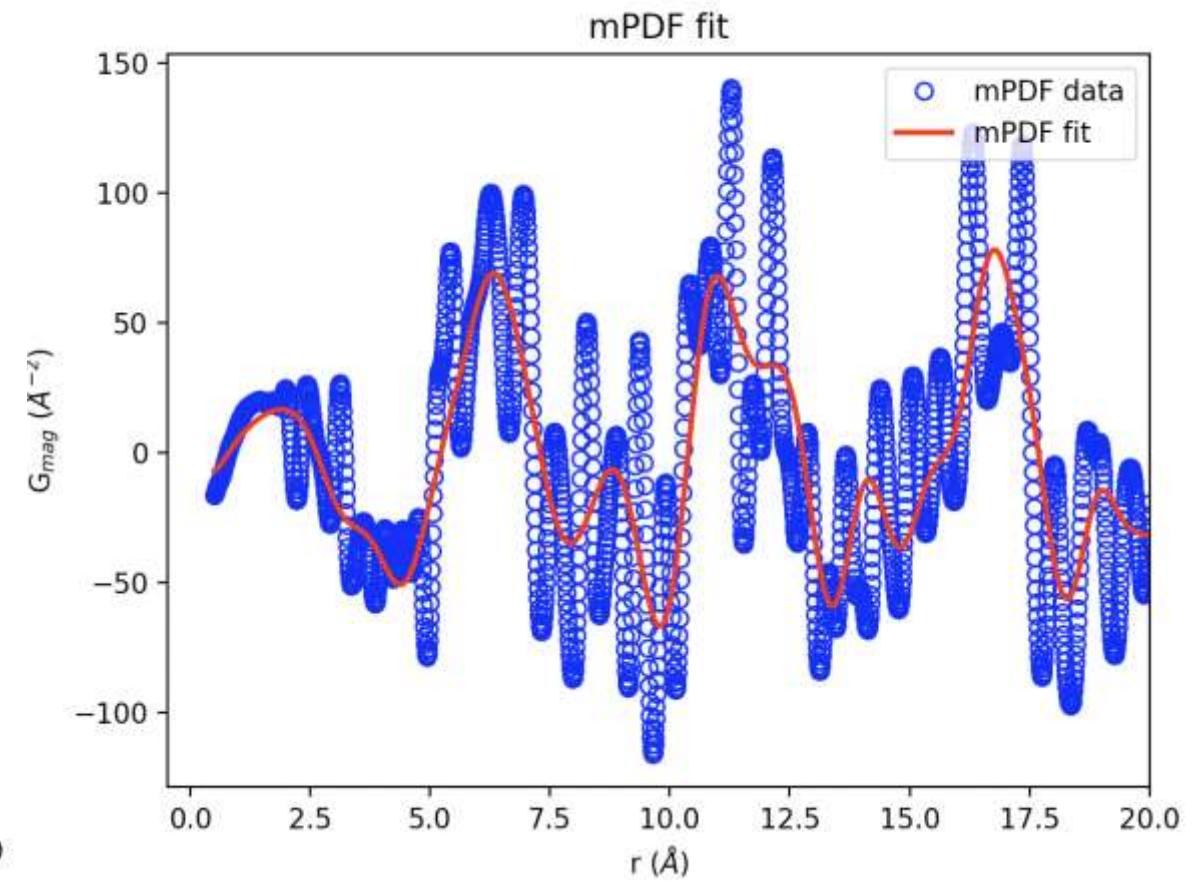
- Co-refinement and toggle algorithms perform similarly well.



MnO 20K-300K



$Q_{\max}=25 \text{\AA}^{-1}$, Use Lorch





mPDF

$$G_{\text{tot}}(r) = \mathcal{F} \left\{ Q \left(\frac{I_n}{N_a \langle b \rangle^2} - \frac{\langle b^2 \rangle}{\langle b \rangle^2} \right) \right\} + \mathcal{F} \left\{ Q \frac{I_m}{N_a \langle b \rangle^2} \right\}$$
$$= G_n(r) + d(r)/N_a \langle b \rangle^2,$$

where $G_n(r)$ is the atomic (nuclear) PDF and $d(r) = \mathcal{F}\{QI_m(Q)\}$ is a quantity that we will call the ‘unnormalized mPDF’, since it does not involve division by the magnetic form factor $f_m(Q)$. A straightforward application of the convolution theorem reveals that

..

$$d(r) = C_1 \times f(r) * S(r) + C_2 \times \frac{dS}{dr},$$

where C_1 and C_2 are constants related by $C_1/C_2 = -1/(2\pi)^{1/2}$ in the fully ordered state, $*$ represents the convolution operation, and $S(r) = \mathcal{F}\{f_m(Q)\} * \mathcal{F}\{f_m(Q)\}$. The quantity $\mathcal{F}\{f_m(Q)\}$ is closely related to the real-space spin density. Roughly speaking, $d(r)$ is equivalent to the proper mPDF $f(r)$ twice broadened by the spin density with an additional peak at low r produced by the derivative term in equation (6). The two