BENEATH THE SURFACE: X-RAY ANALYSES OF BATTERY MATERIALS AND STRUCTURES

A Battery Webinar Series by Rigaku

Pair Distribution Function (PDF) Analysis for Everyday Battery Analysis

February 21, 2024 at 1:00 PM

- *You will be muted during the webinar.*
- *You can ask questions using the Q&A tool.*
- *You should hear music if your sound is working.*

BENEATH THE SURFACE: X-RAY ANALYSES OF BATTERY MATERIALS AND STRUCTURES

A Battery Webinar Series by Rigaku

Pair Distribution Function (PDF) Analysis for Everyday Battery Analysis

February 21, 2024 at 1:00 PM

We are starting now…

Presenter: **Simon Bates** | VP Science and Technology

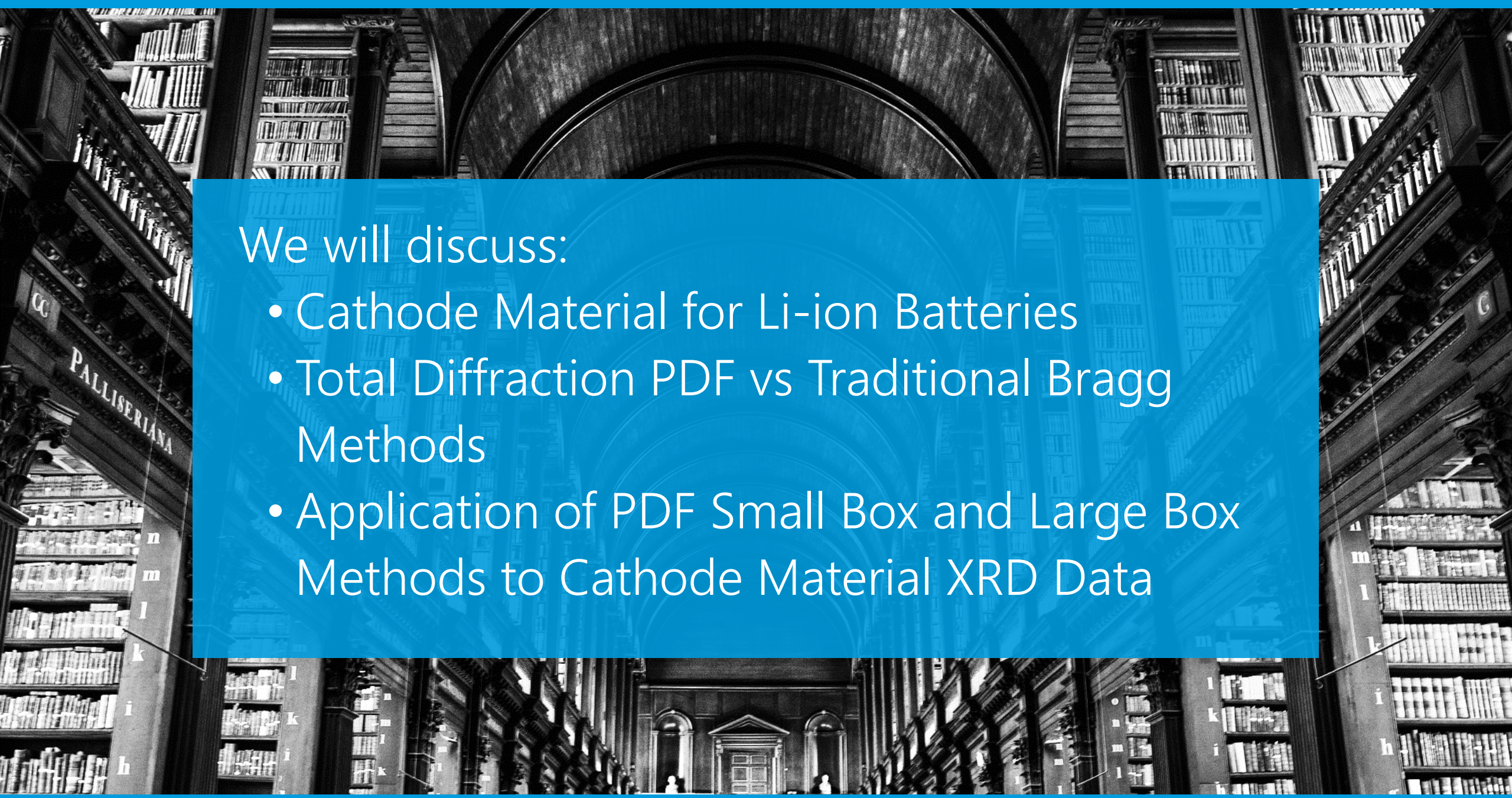
Co-presenter: **Tom Concolino**| National XRD Sales Manager

Host: **Aya Takase** | Head of Global Marketing

You can ask questions following the presentation.

Recording will be available tomorrow.

PAIR DISTRIBUTION FUNCTION (PDF) ANALYSIS FOR EVERYDAY BATTERY ANALYSIS



We will discuss:

- Cathode Material for Li-ion Batteries
- Total Diffraction PDF vs Traditional Bragg Methods
- Application of PDF Small Box and Large Box Methods to Cathode Material XRD Data

WHY IS THIS TOPIC IMPORTANT?

Aging and degradation of cathode material.

Total Diffraction and PDF analysis returns a detailed atomistic level model of the impact of repeated charge / discharge.

Allows fine tuning of composition / doping / coating to optimize cathode longevity.

Applicable to anode material and solid-state electrolyte.

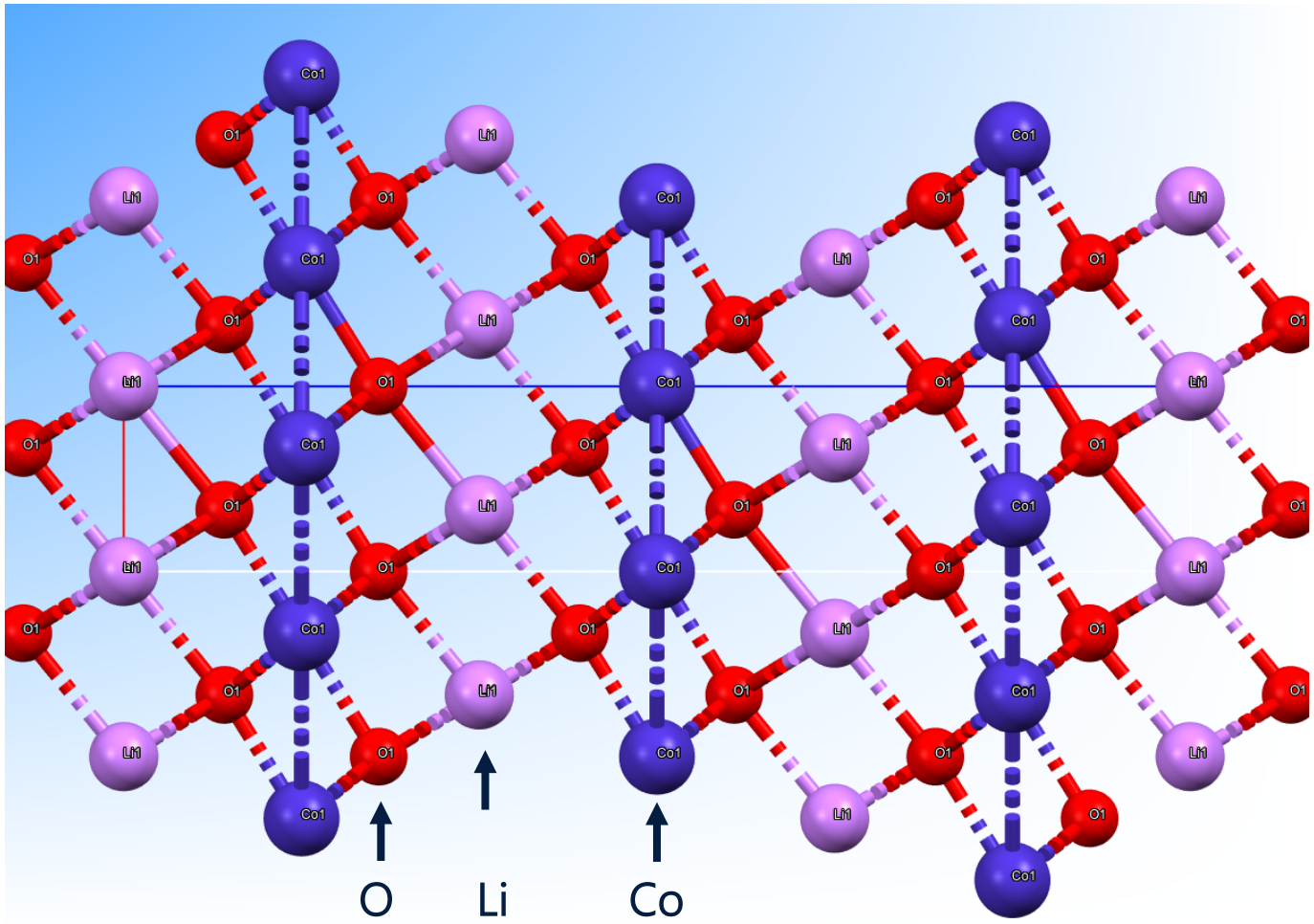
Li-ion Cathode Analogue Li Co O2

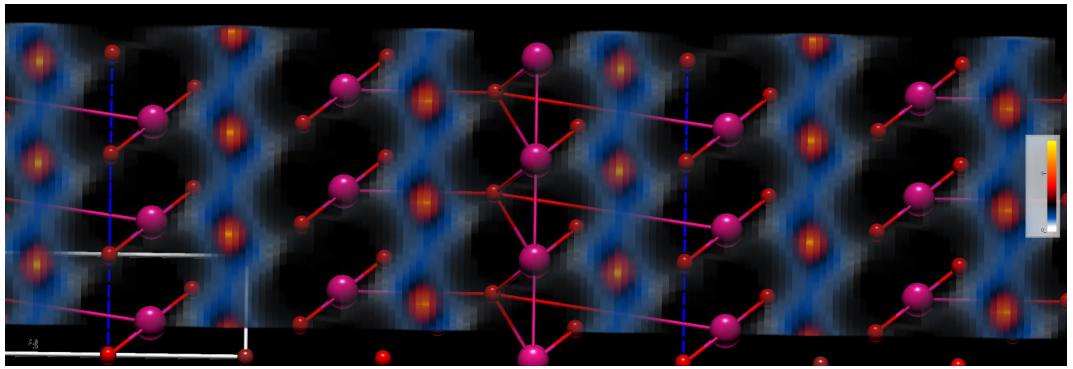
Li Co O2 - analogue

Trigonal R-3m

a=*b* ~ 2.817 Å
c ~ 14.05 Å, gamma = 120 º2θ

Co forms rigid two-dimension sheet framework
O bonded top and bottom of Co sheets
Li relative mobile to travel between sheets





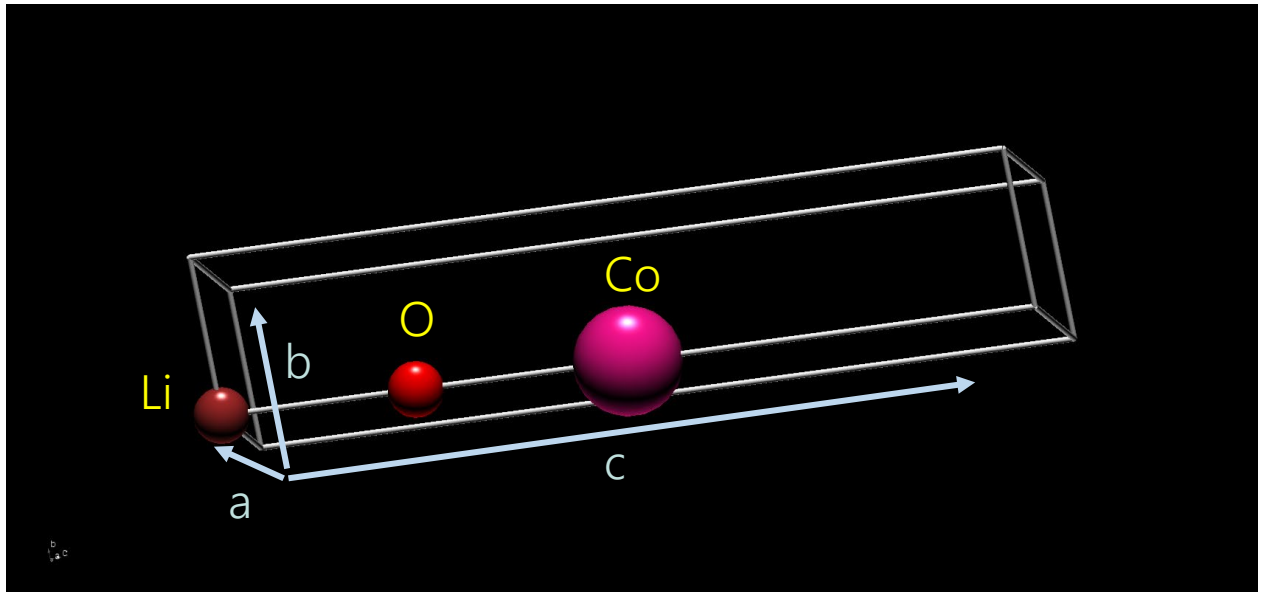
Li ion BVS

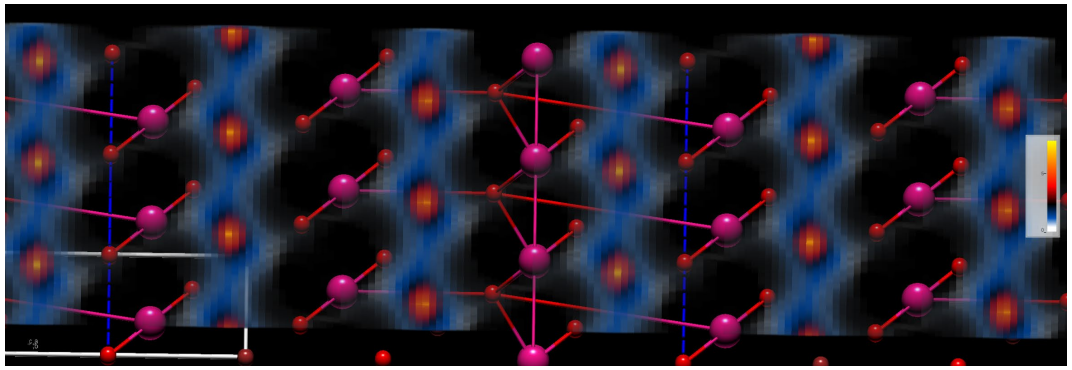
Li Co O2 - analogue

Crystal structure represented by just 3 atoms in asymmetric unit.

Positions governed by symmetry constraints. Only O is free to move (along c-axis).

Disordered modeled by occupation numbers and thermal parameters.





Li ion BVS

Idealistic and overly constrained model of average order.

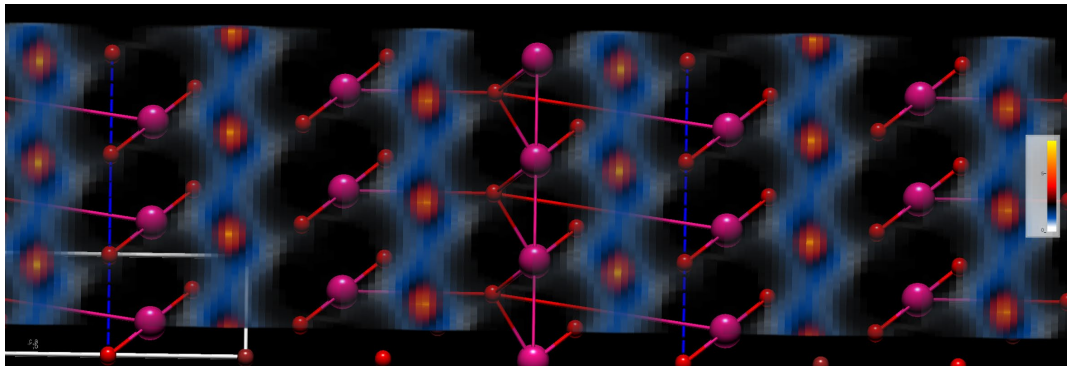
→ Bragg Peaks

Li Co O2 - analogue

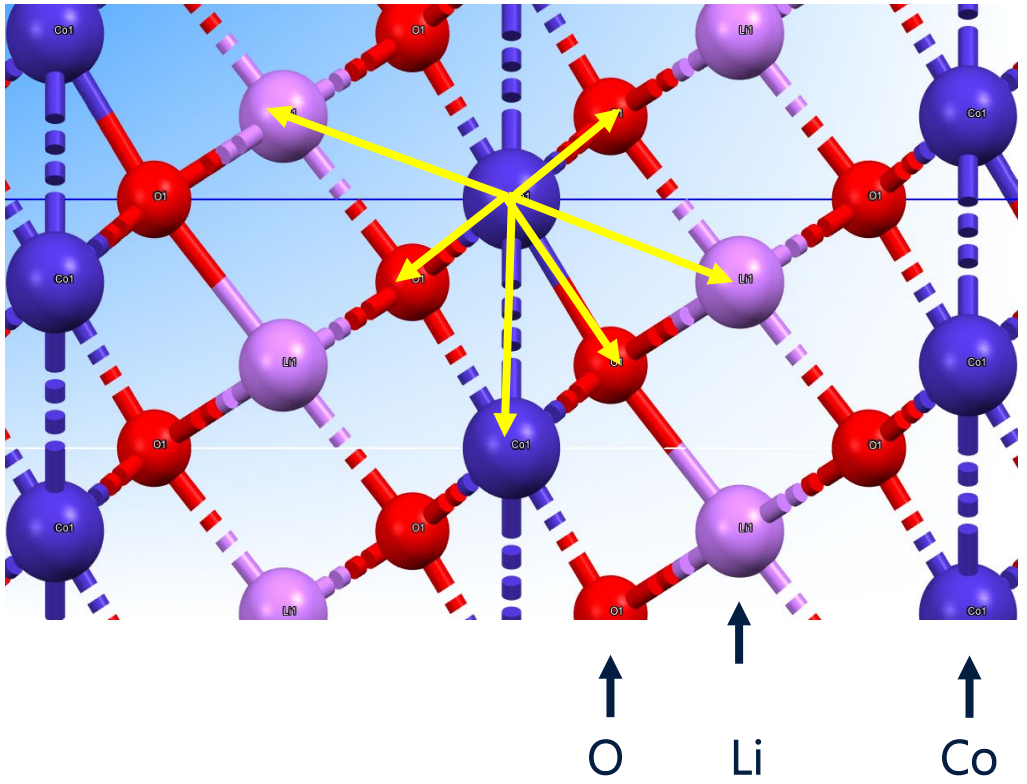
PDF represents atom-atom pair relationships

Local order / disorder independent of symmetry.

Individual atomic relationships can be investigated (Li – Li).

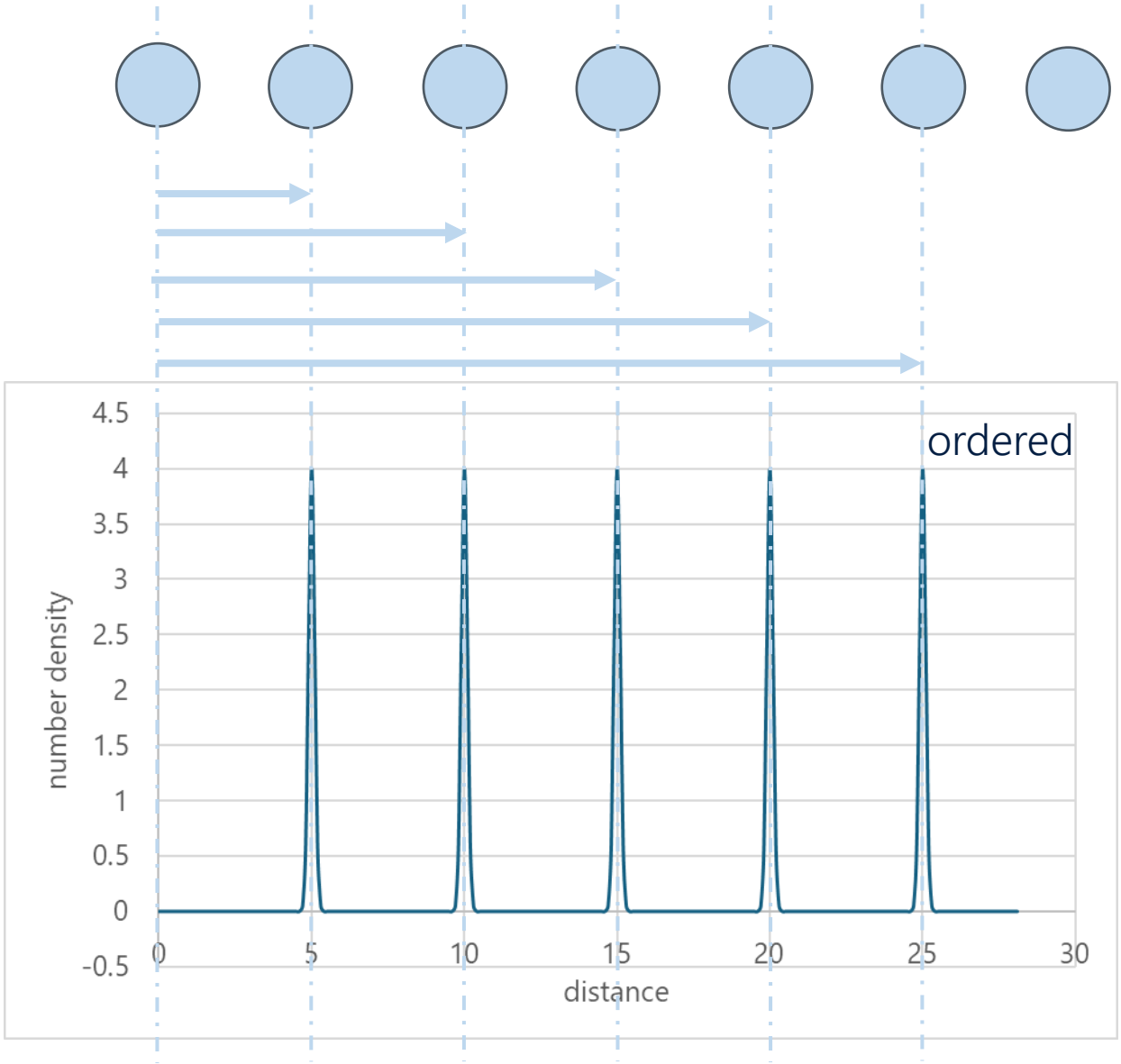


Li ion BVS

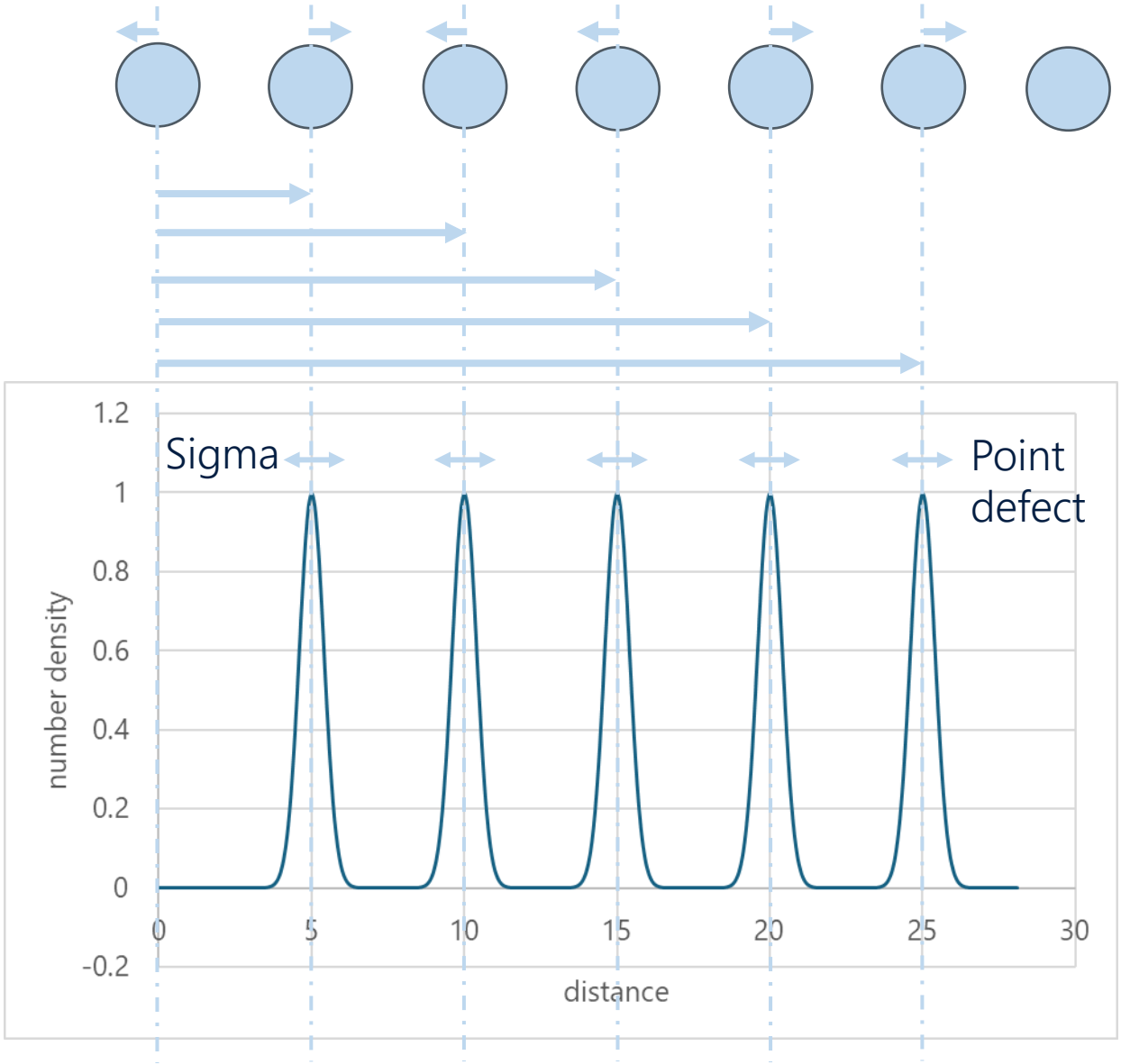


Realistic and complex representation of local order / disorder.

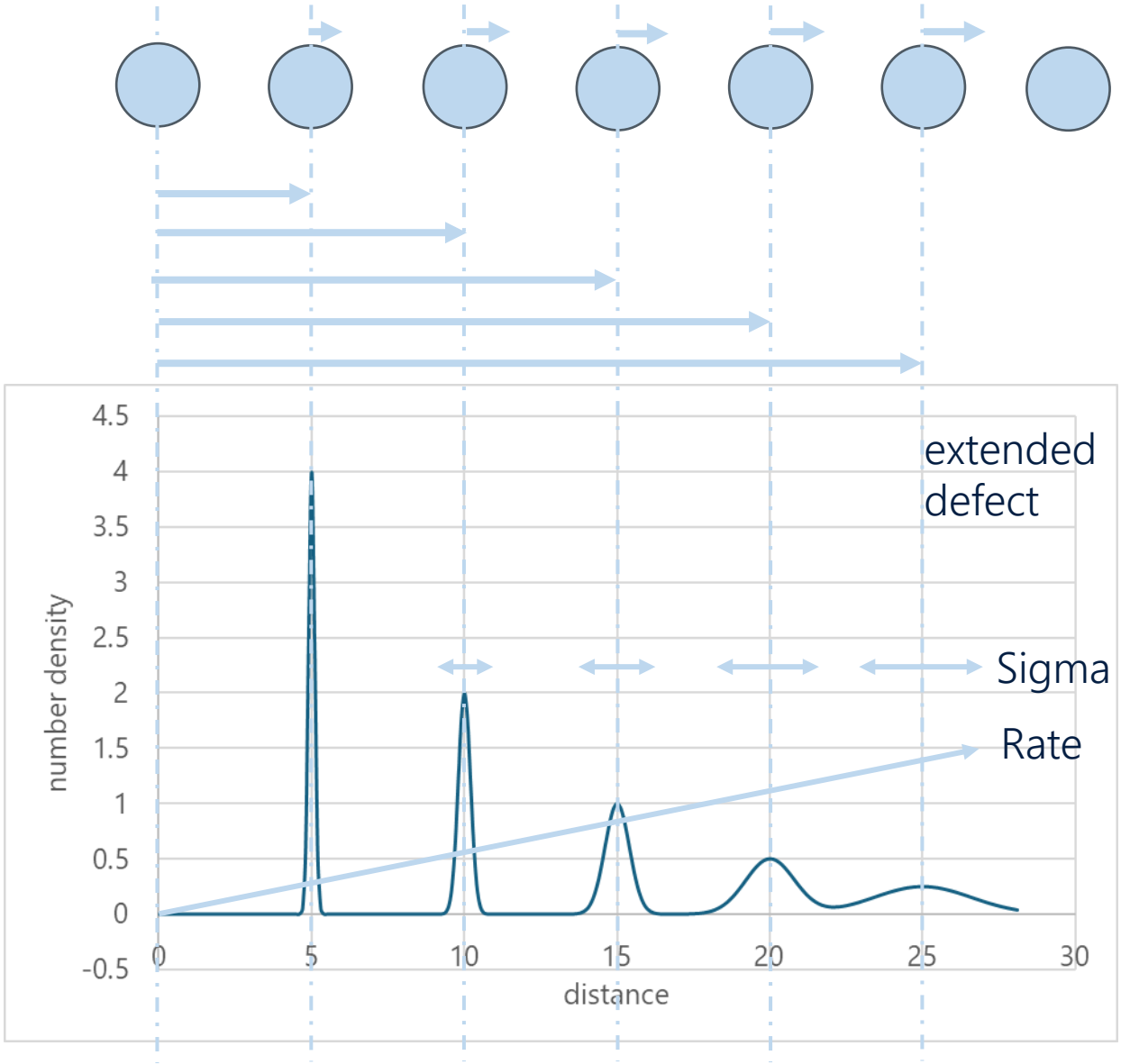
→ Diffuse scattering + Peaks



Radial Distribution function – the origin of the PDF – the impact of disorder.

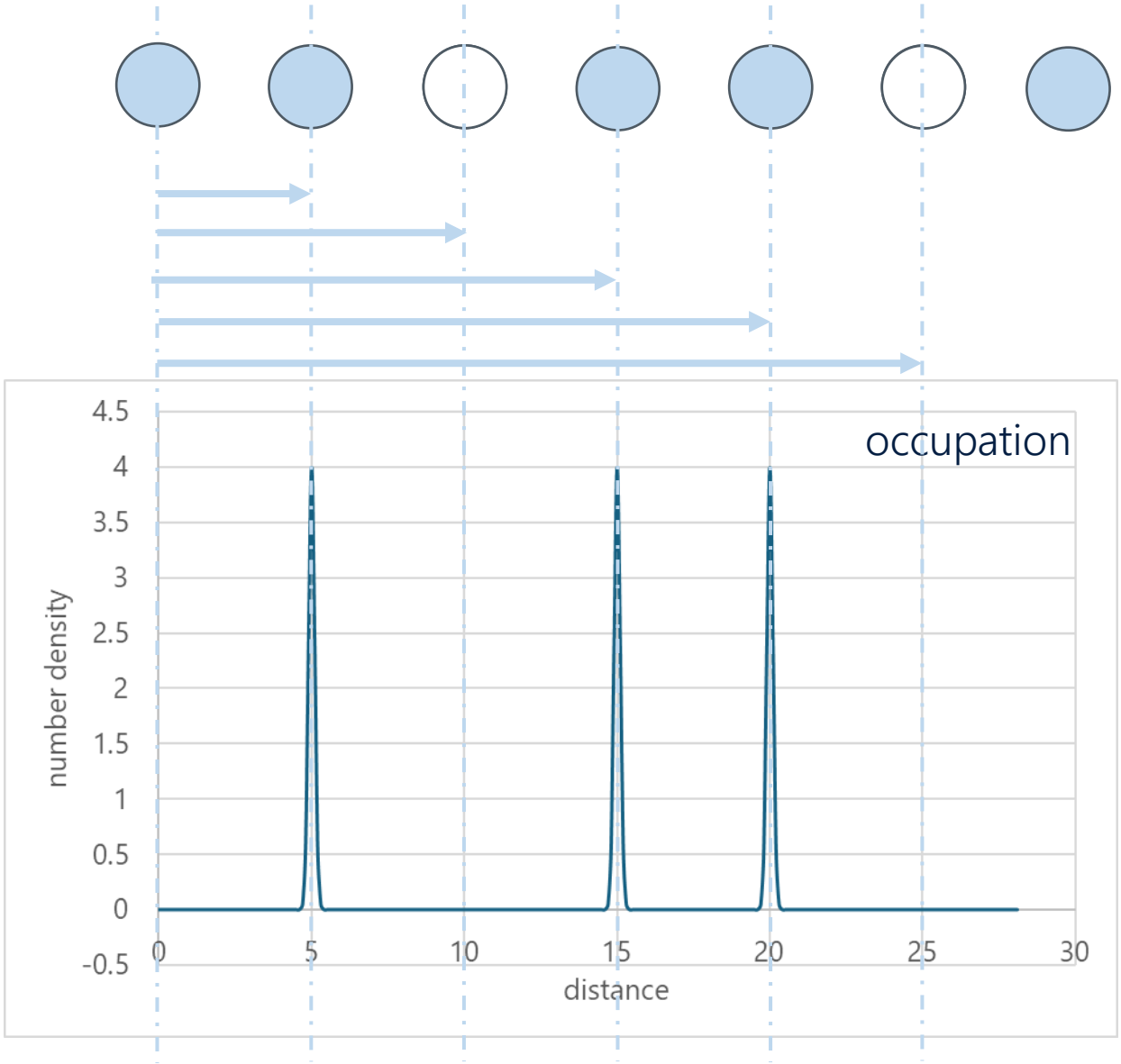


Radial Distribution function – the origin of the PDF – the impact of disorder.



Radial Distribution function – the origin of the PDF – the impact of disorder.

Rate = 0 → highly ordered crystalline
Rate = 1 → Complete disorder (Amorphous)



Radial Distribution function – the origin of the PDF – the impact of atom occupation.

POLLING QUESTION #1

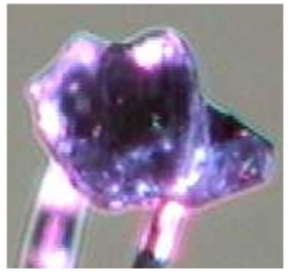
Microsoft Stock

Pair Distribution Function (PDF) Analysis

MEASUREMENT CONSIDERATIONS

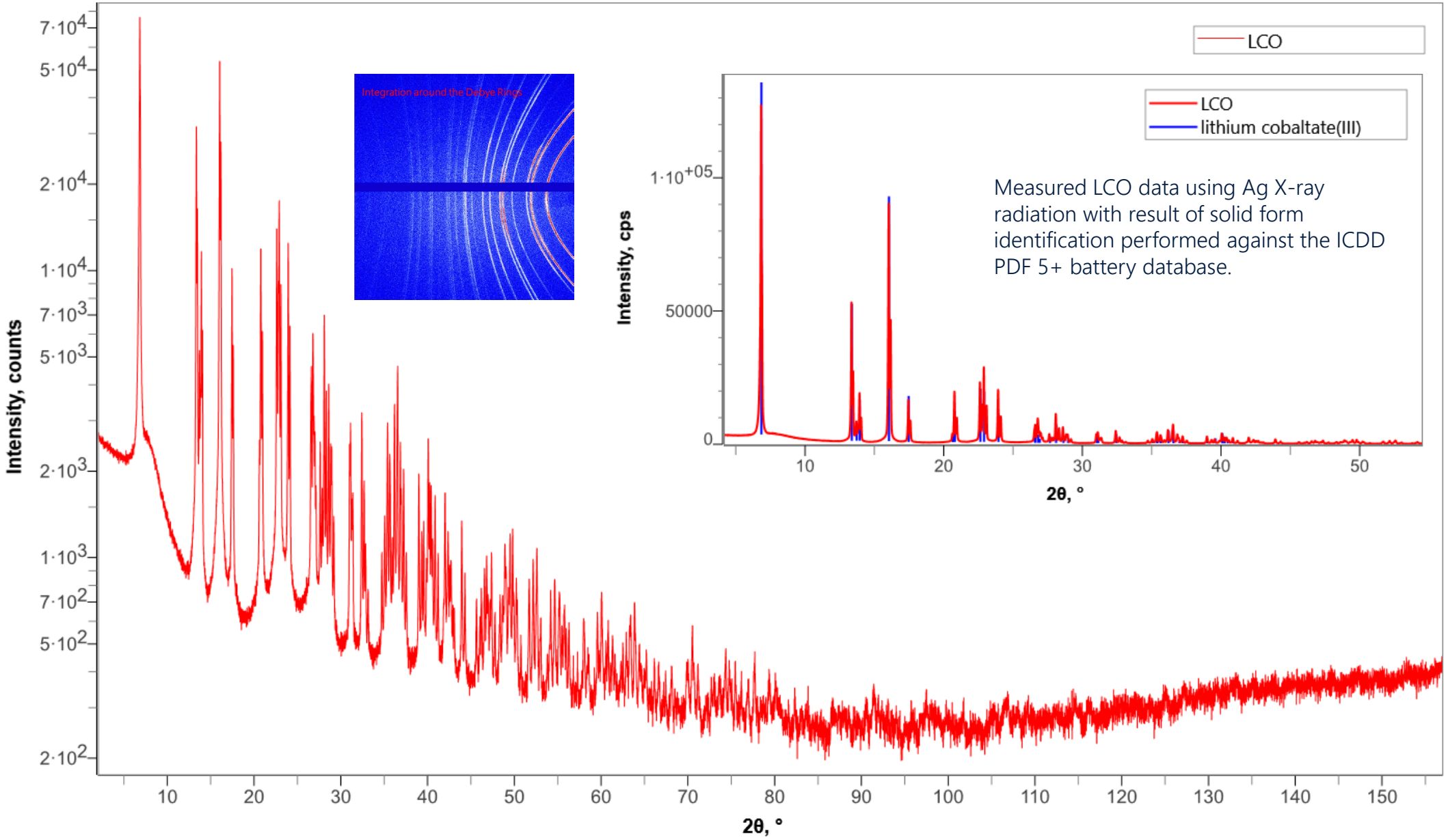
- Total Diffraction
- Isotropic
- Minimize Sample Corrections
- High Q
- High Q (noise)
- Validate to Ni

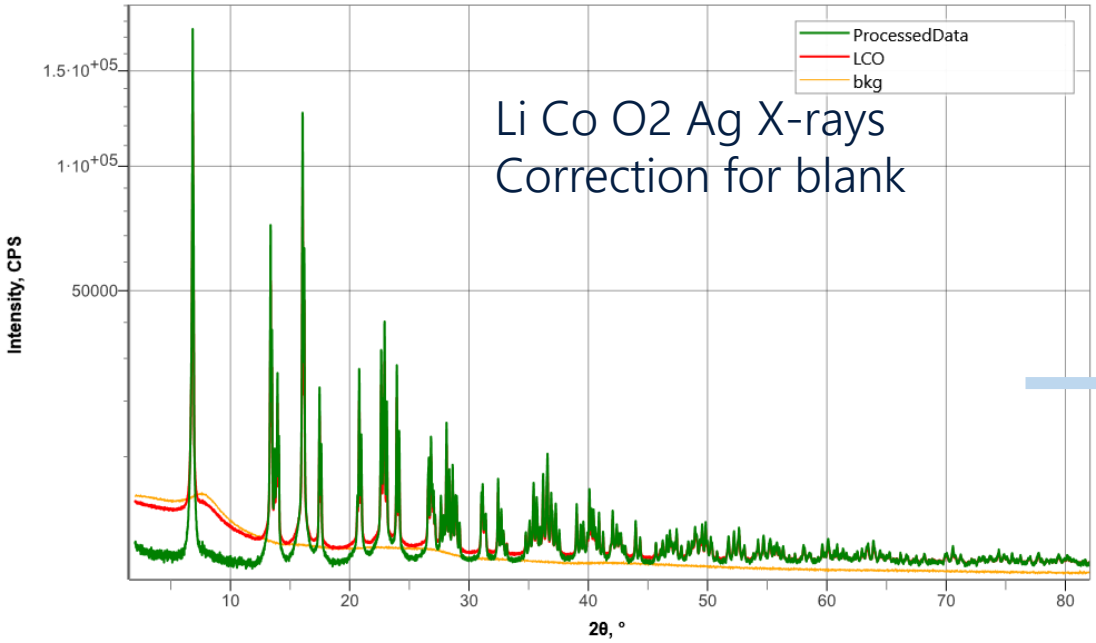
SmartLab 9kW horizontal capillary

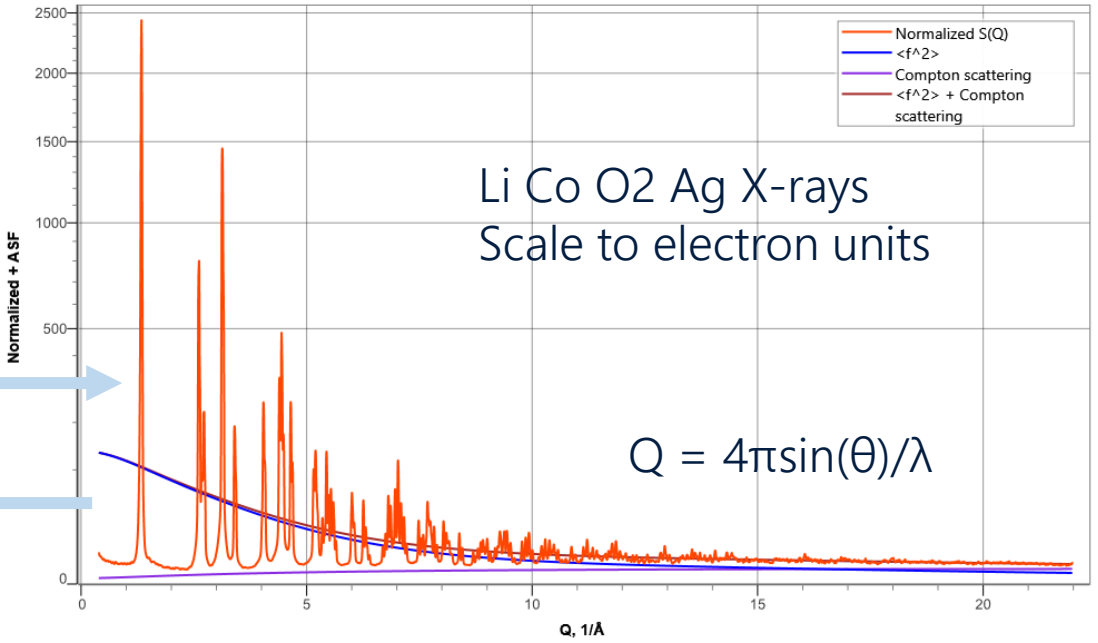


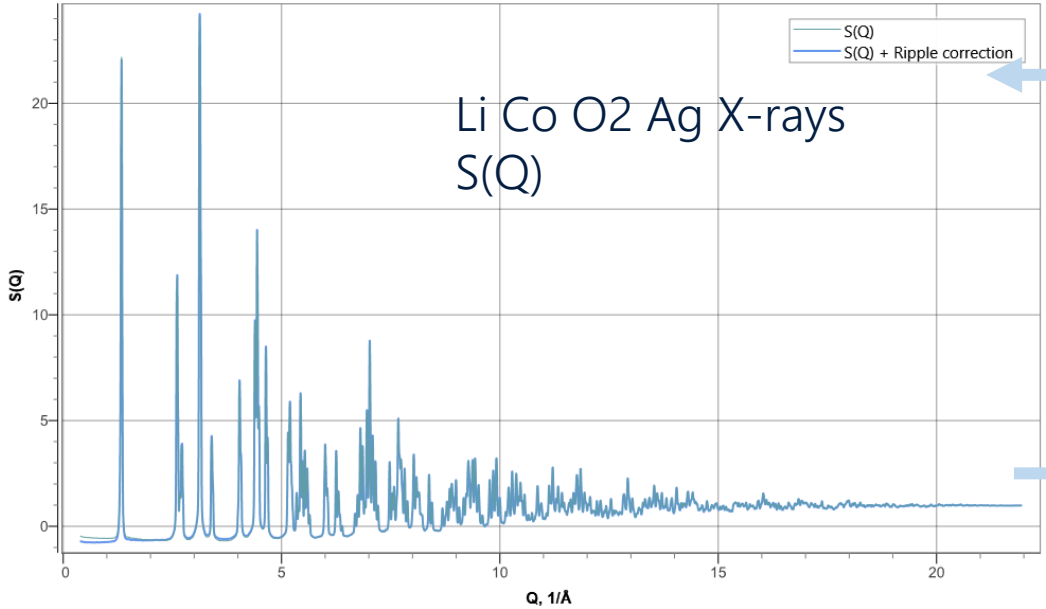
Synergy S micro-diffraction

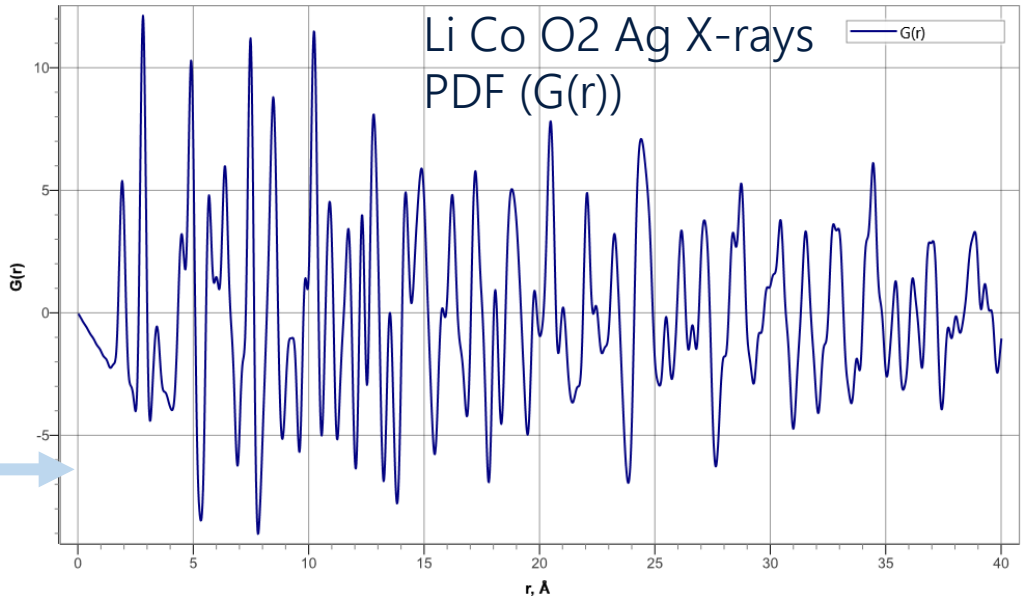
Li Co O2

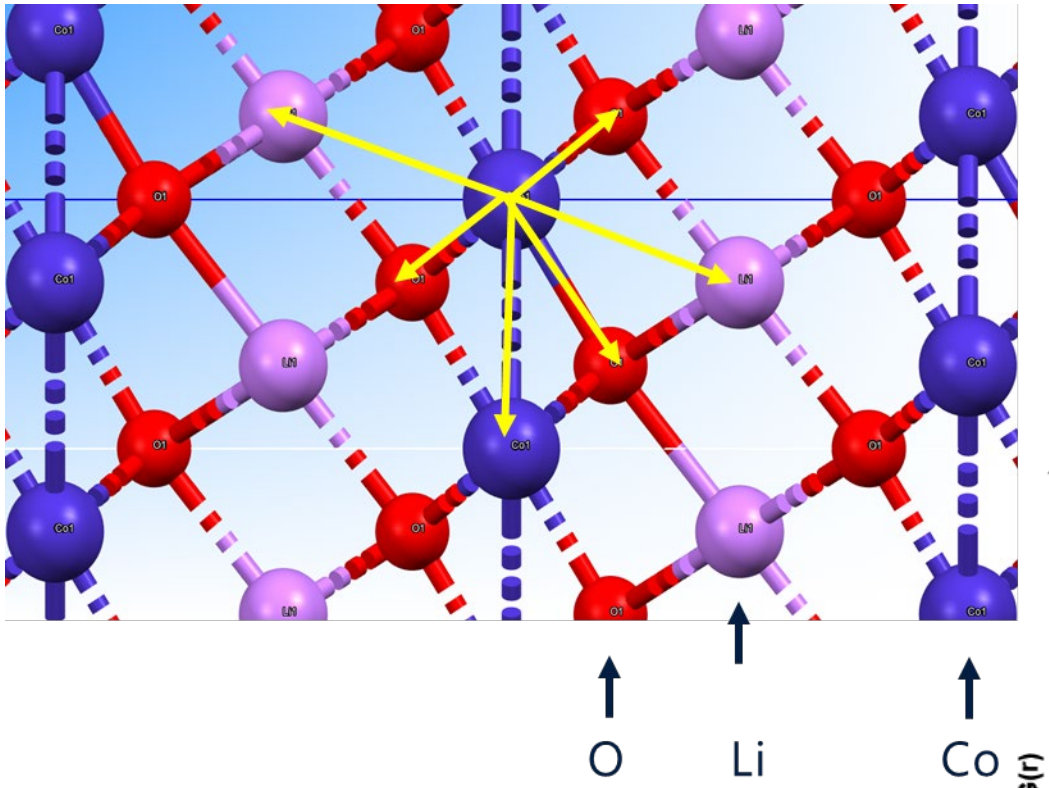


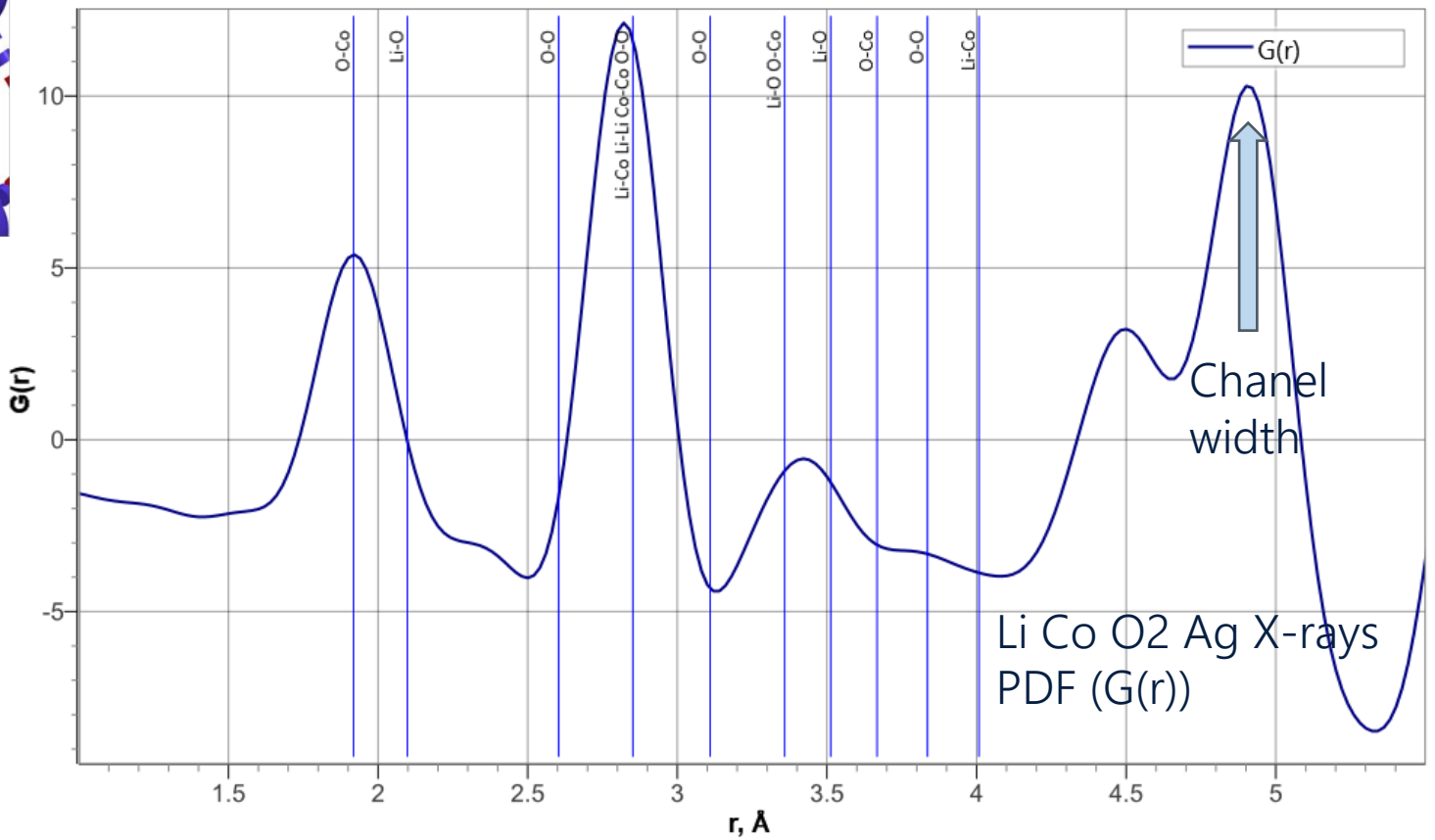






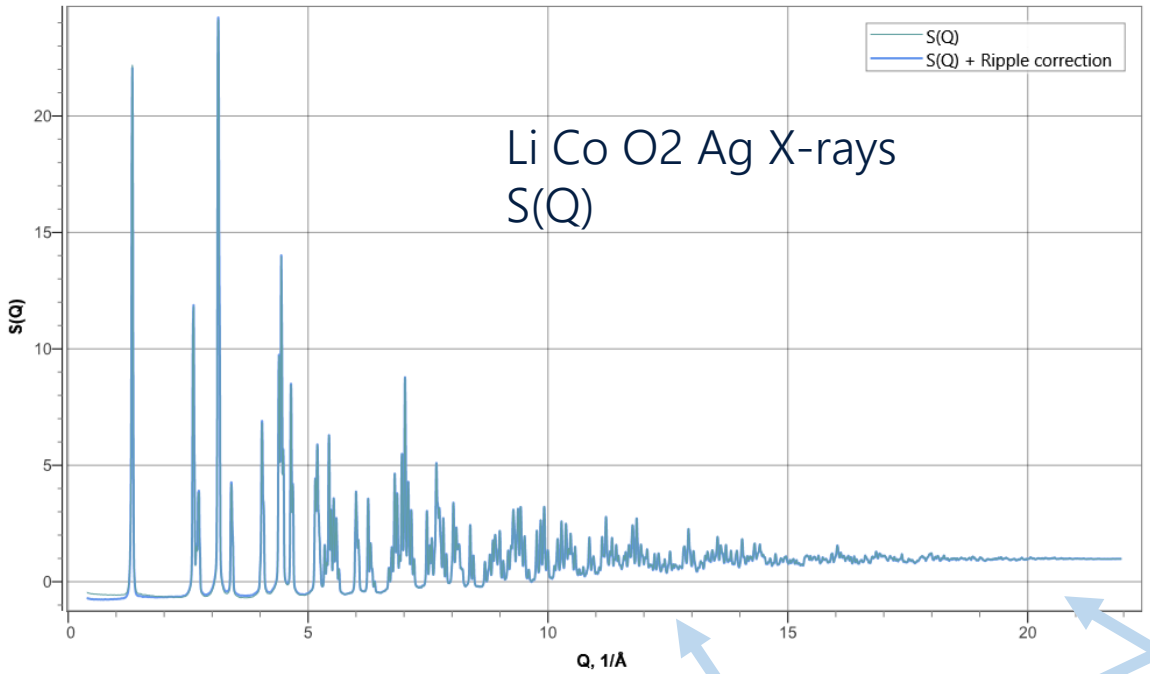


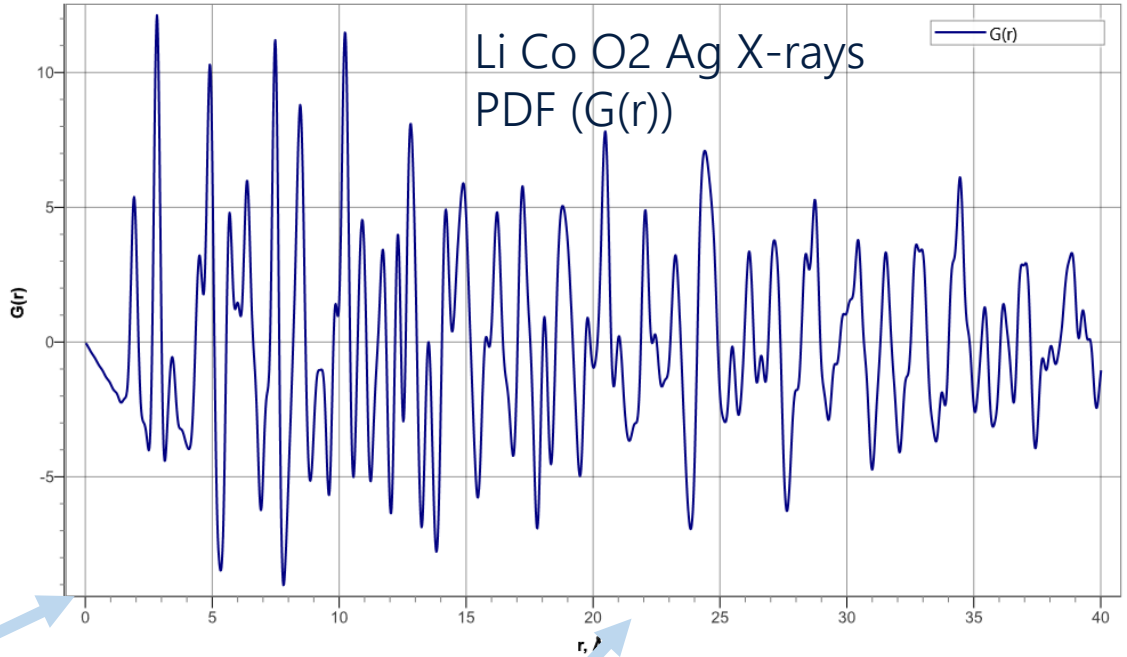


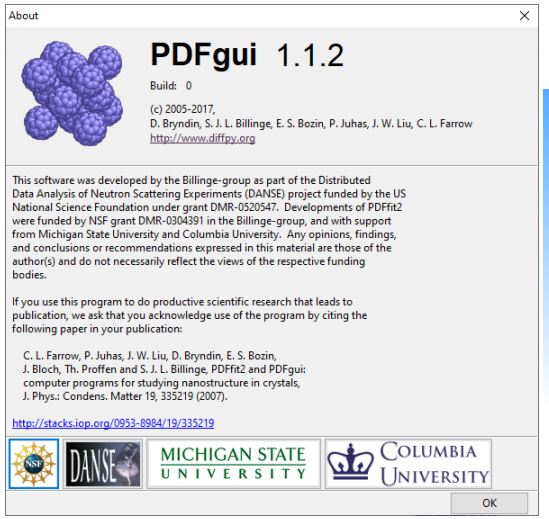


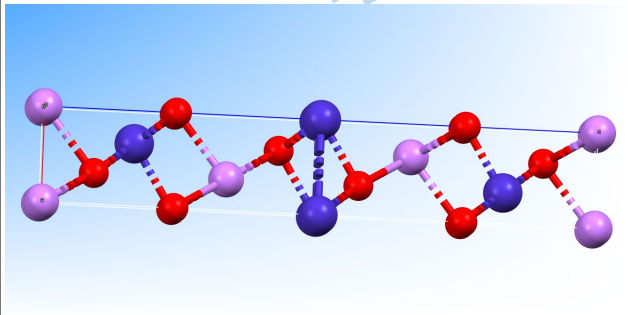
Realistic and complex representation of local order / disorder.

Channel width between the 2D cobalt sheets can be directly determined form observed PDF peak positions of Co – Co interactions.

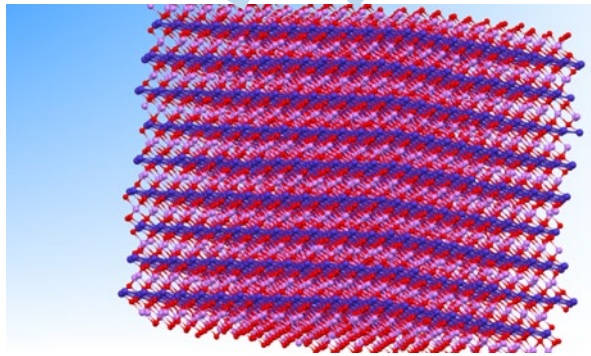








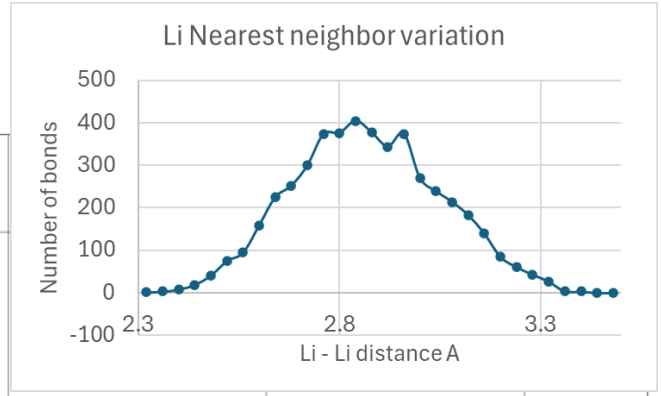
Small Box Model



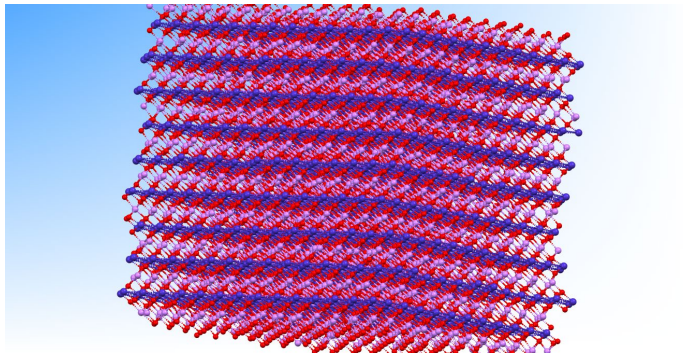
Big Box Model

Reverse Monte Carlo modeling Rigaku SmartLab Studio II (V5)

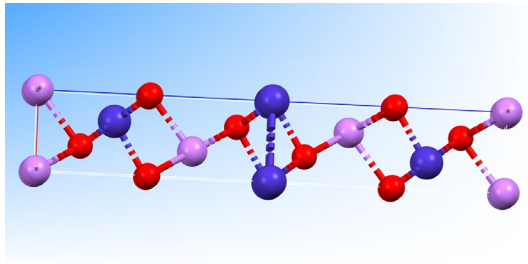
RMC Li Co O2

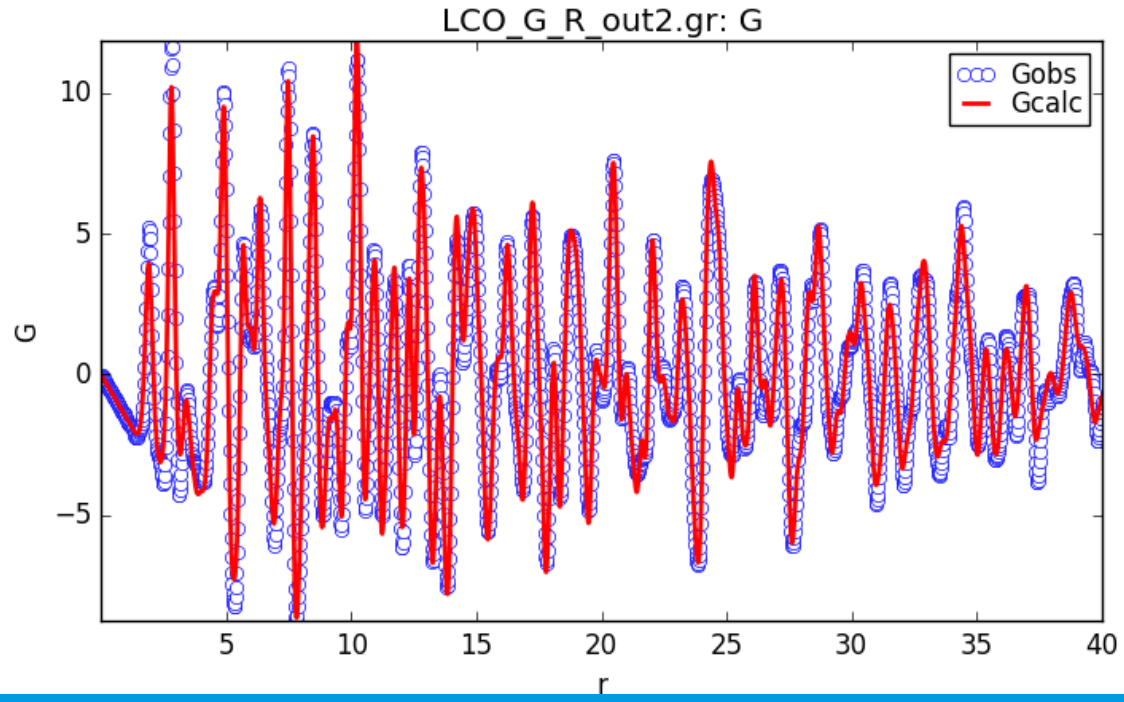


R factor ~ 8.6%
Fit to S(Q)
Li – Li 2.8194Å
Sigma 0.11Å

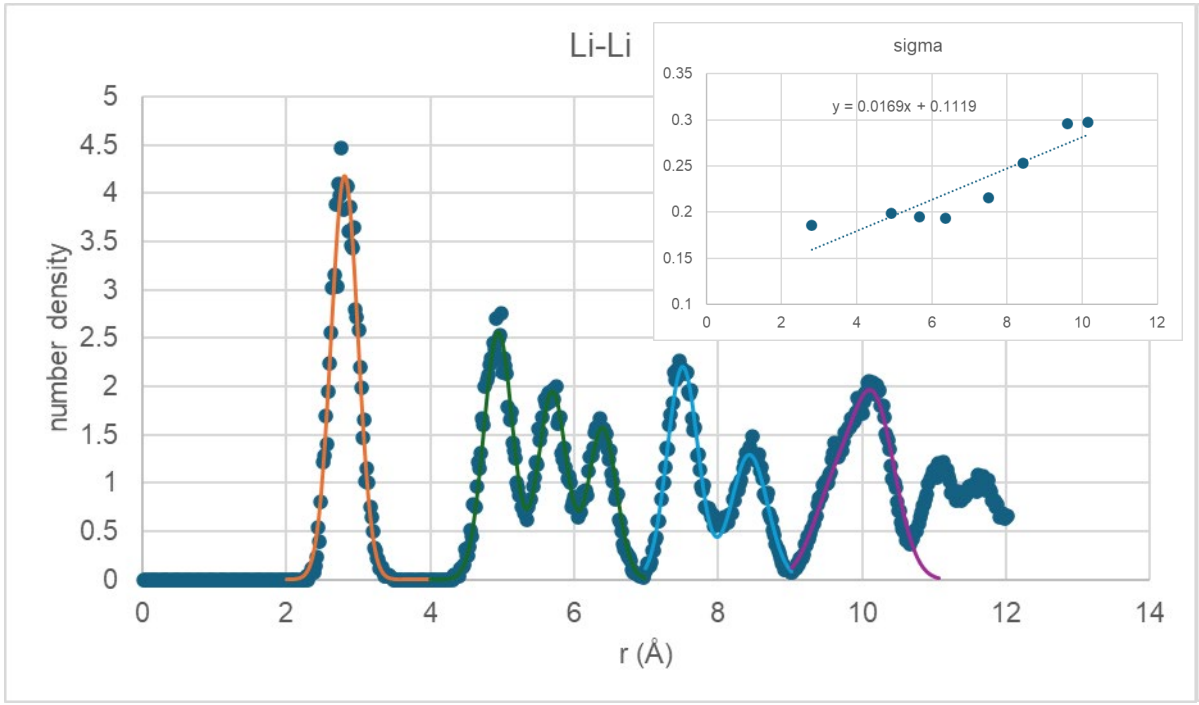


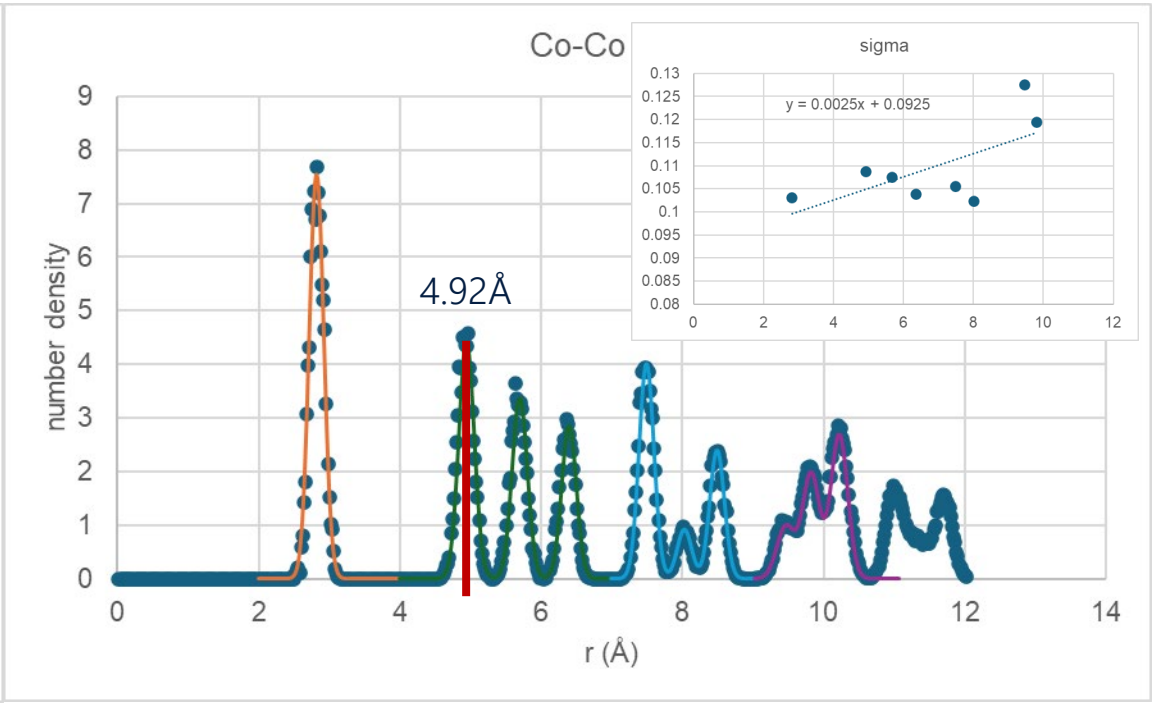
PDF GUI isotropic thermal parameters for LCO
Sigma ~ 0.11Å for Lithium - occ: 0.88
Sigma ~ 0.072Å for Co
unit cell parameters a=b=2.8191Å, c=14.0679Å
R factor ~ 16%





Solution	Li – Li (Å)	Li σ (Å)	Disorder rate	Co σ (Å)	Disorder rate
Single Crystal	2.82	0.079		0.055	
Small Box	2.82	0.11		0.07	
Big Box	2.82	0.11	0.017	0.09	0.0025



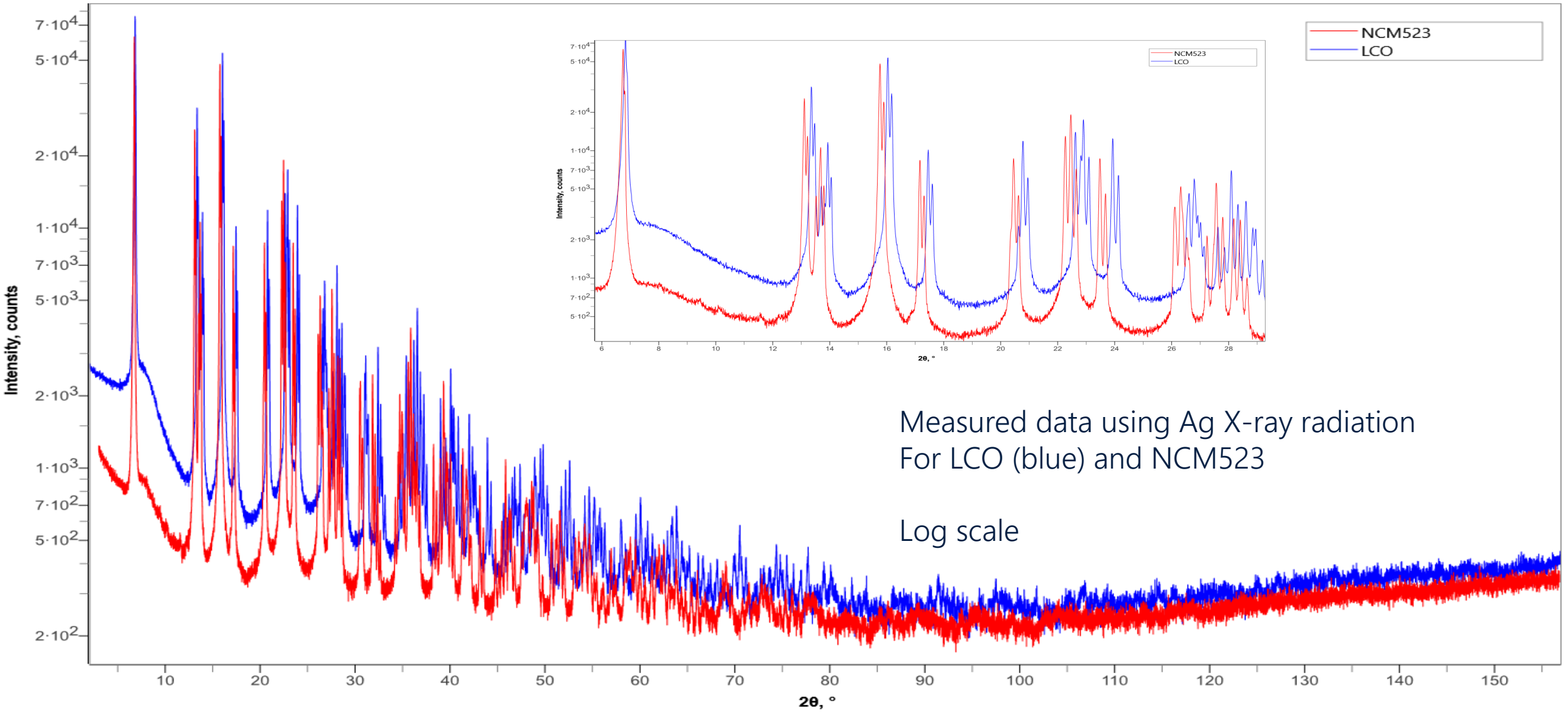


Big Box RMC atom-atom distance by atom type

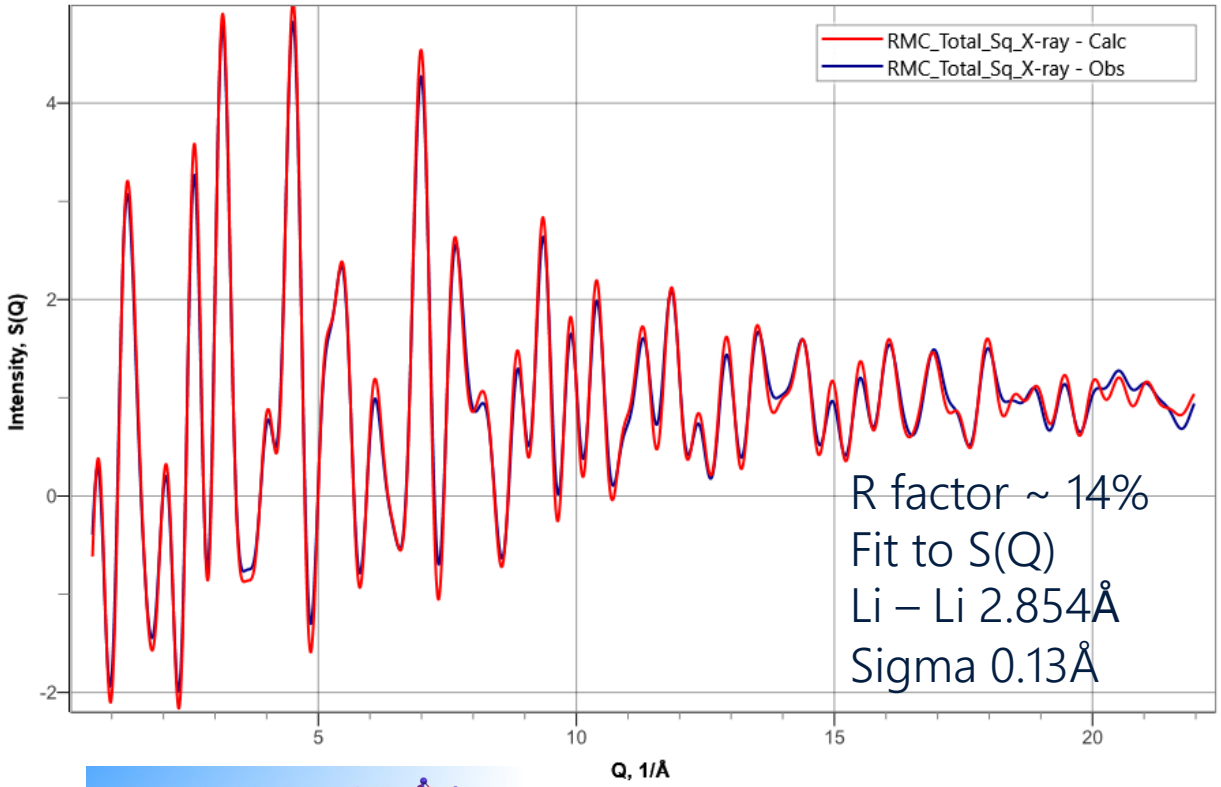
POLLING QUESTION #2

Microsoft Stock

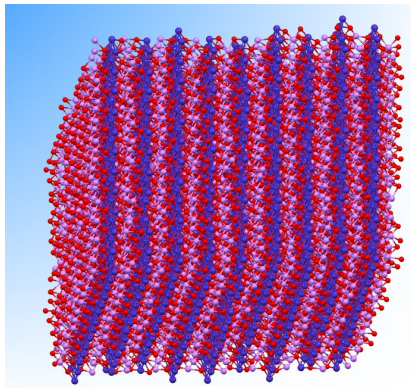
Li-ion Cathode NMC532



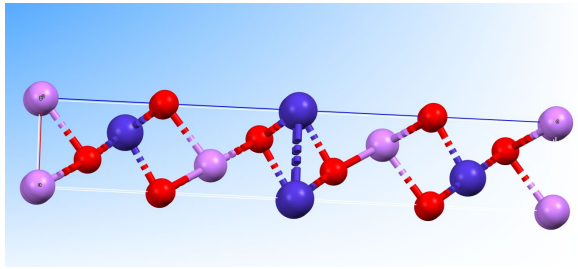
RMC Li NCM523 O2

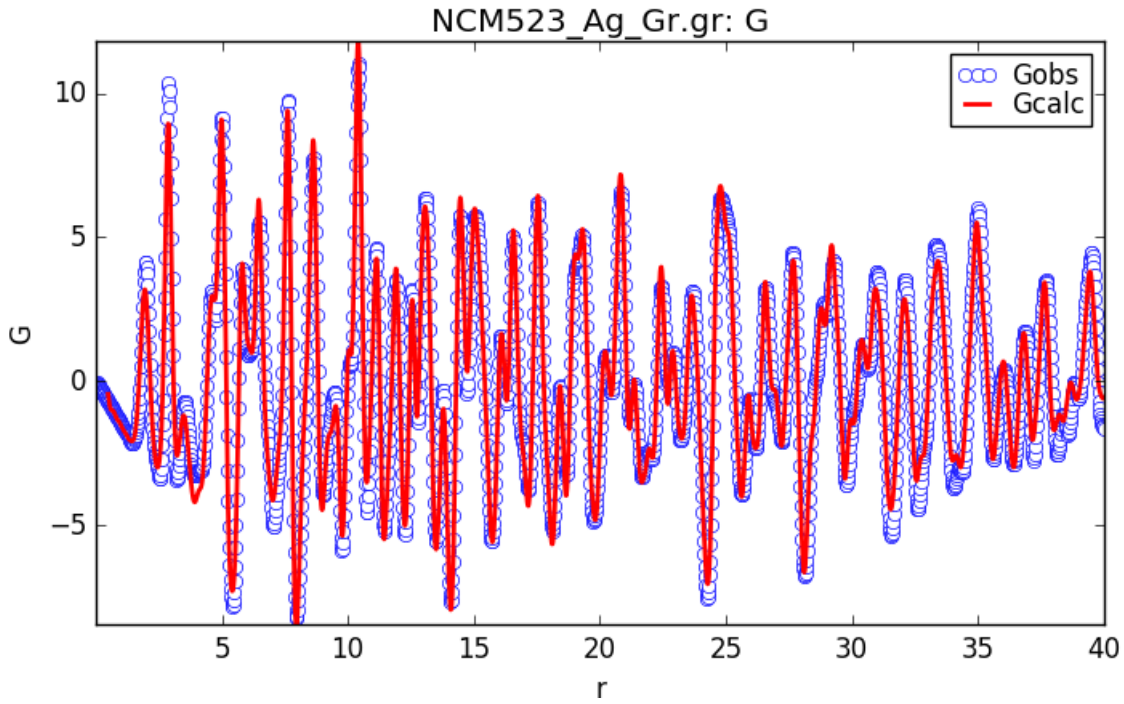


R factor ~ 14%
Fit to S(Q)
Li – Li 2.854Å
Sigma 0.13Å



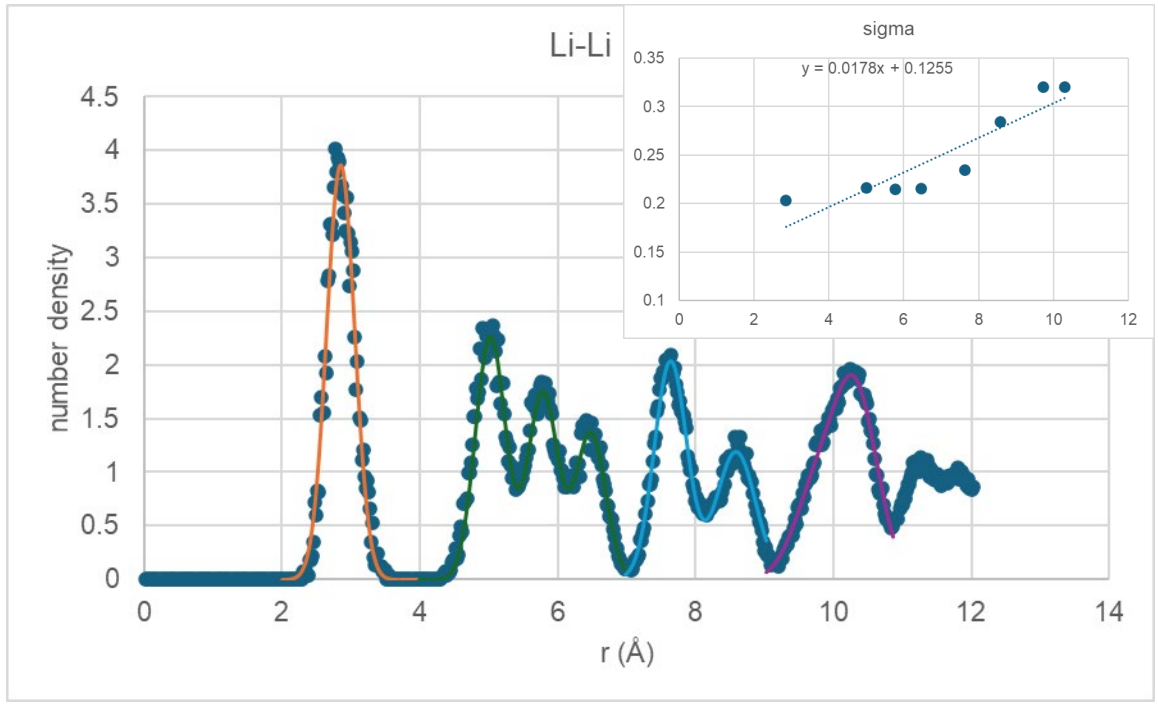
PDF GUI isotropic thermal parameters for Li NCM O2
Sigma ~ 0.10Å for Lithium - occ: 1.02
Sigma ~ 0.09Å for Co (O occ ~ 0.85)
unit cell parameters a=b=2.8743Å c=14.251Å
R factor ~ 15%

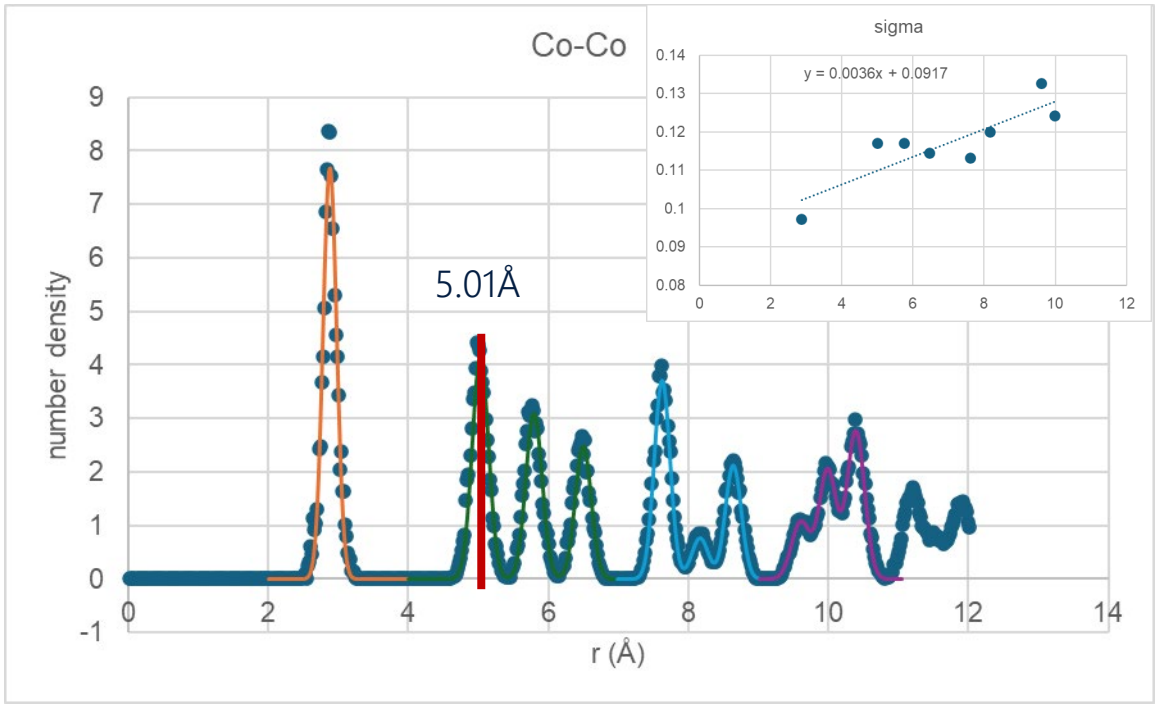




Li NCM523 O2

Solution	Li – Li (Å)	Li σ (Å)	Disorder rate	Co σ (Å)	Disorder rate
Single Crystal	2.86	0.08		0.08	
Small Box	2.874	0.11		0.09	
Big Box	2.854	0.13	0.018	0.09	0.0036



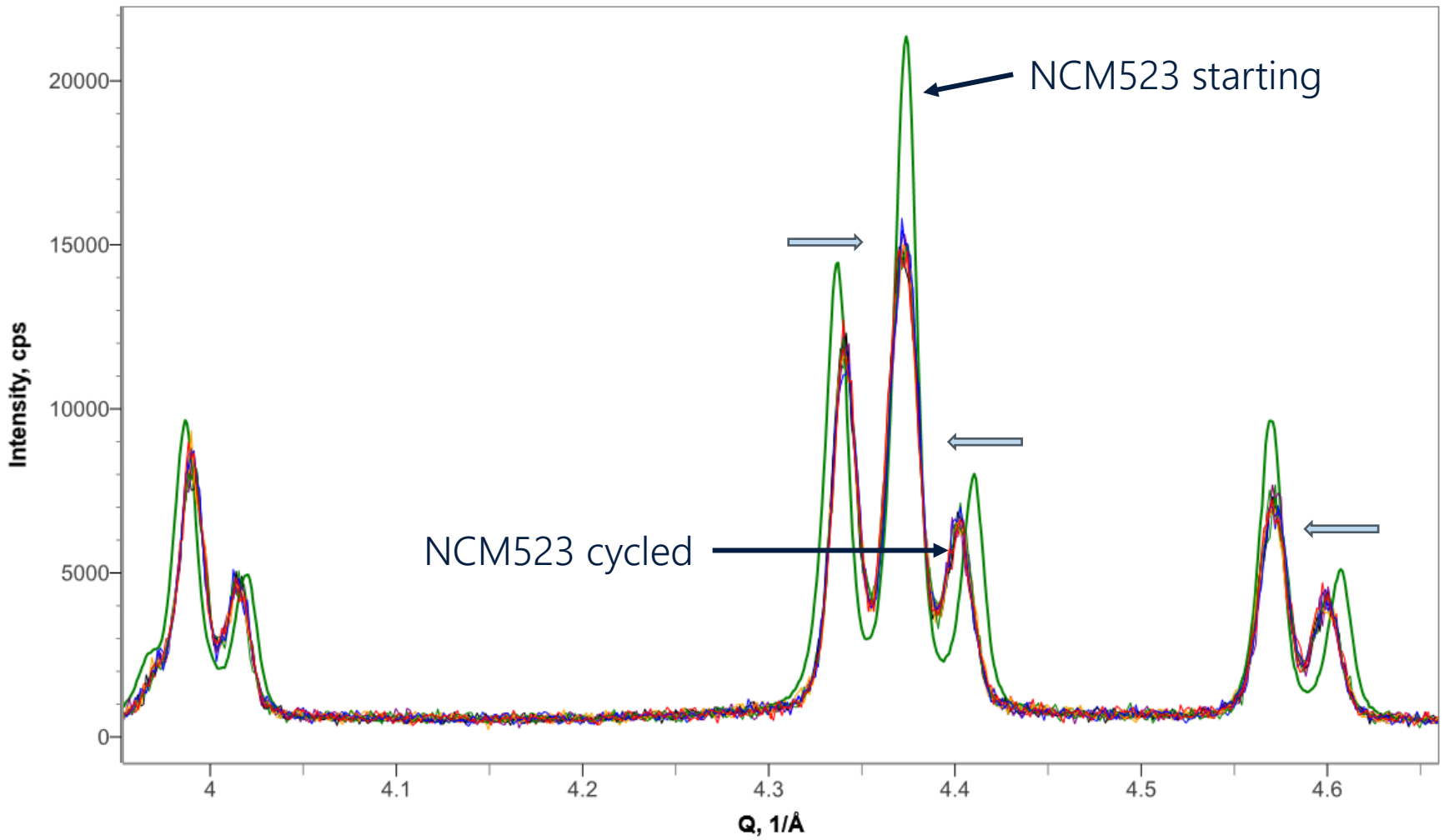


Big Box RMC atom-atom distance by atom type

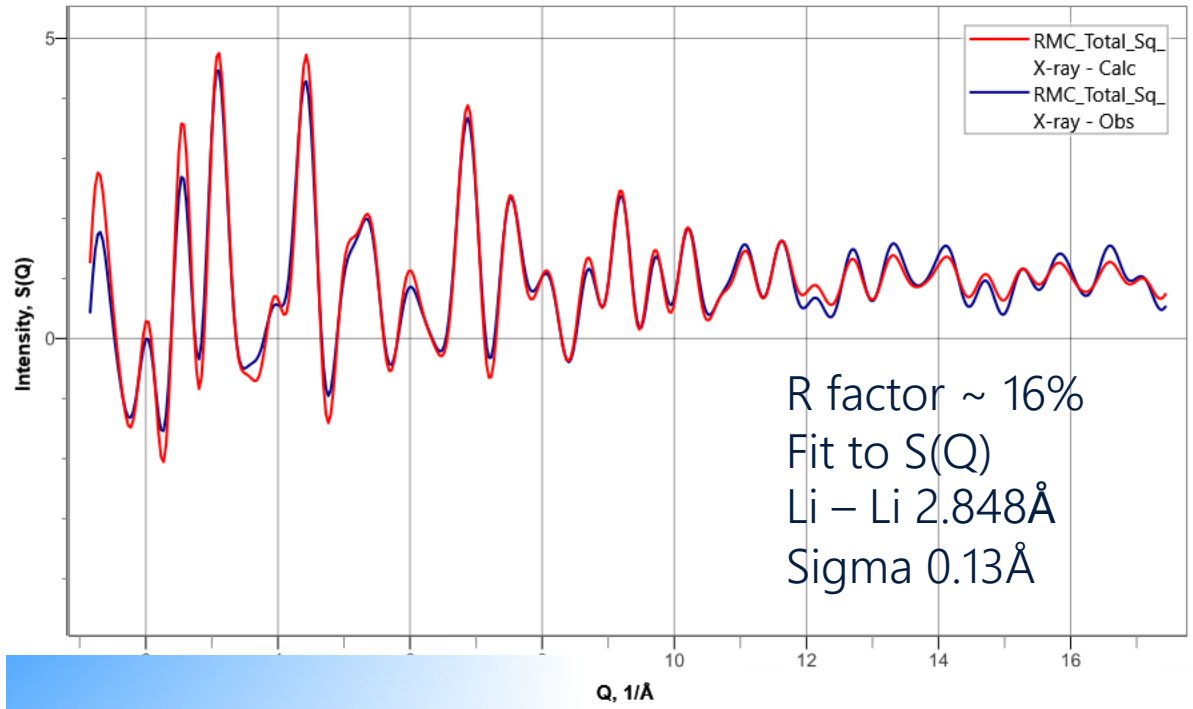
Li-ion Cathode NMC532 Cycled

Cycled material

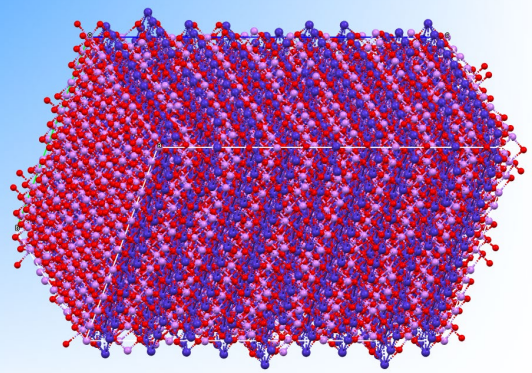
Initial NCM523 (measured with silver radiation compared with cycled NCM523 (measured with Mo)



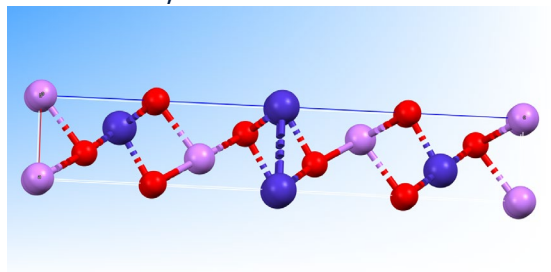
RMC Li NCM523 O2 Cycled

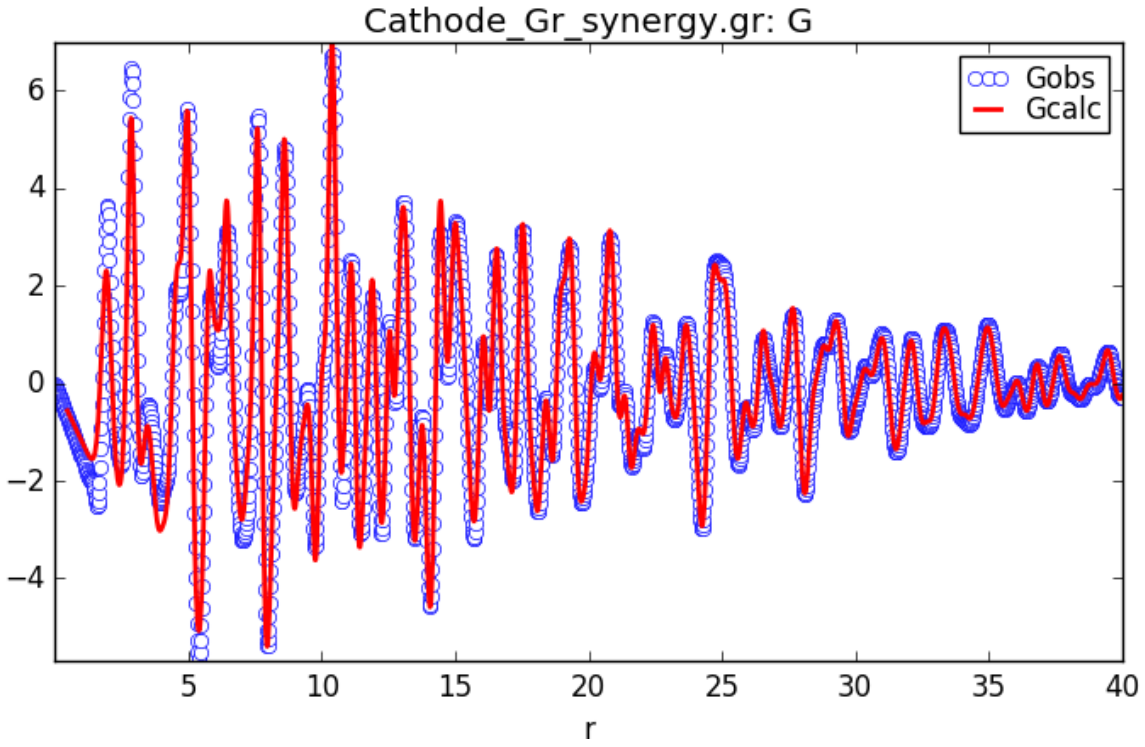


R factor ~ 16%
Fit to S(Q)
Li – Li 2.848Å
Sigma 0.13Å



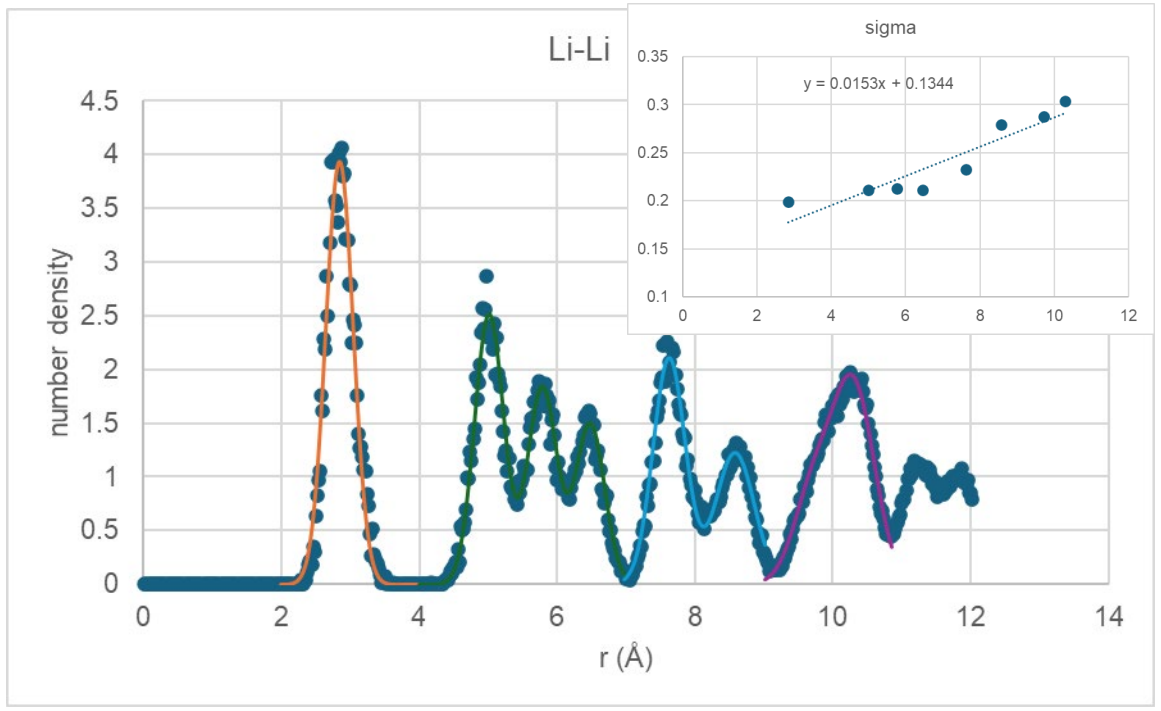
PDF GUI isotropic thermal parameters for NMC 532 Cycled - Synergy
Sigma ~ 0.1Å for Li
Sigma ~ 0.095Å for Co
unit cell parameters a=b=2.8732Å, c=14.228Å
R factor ~ 16%

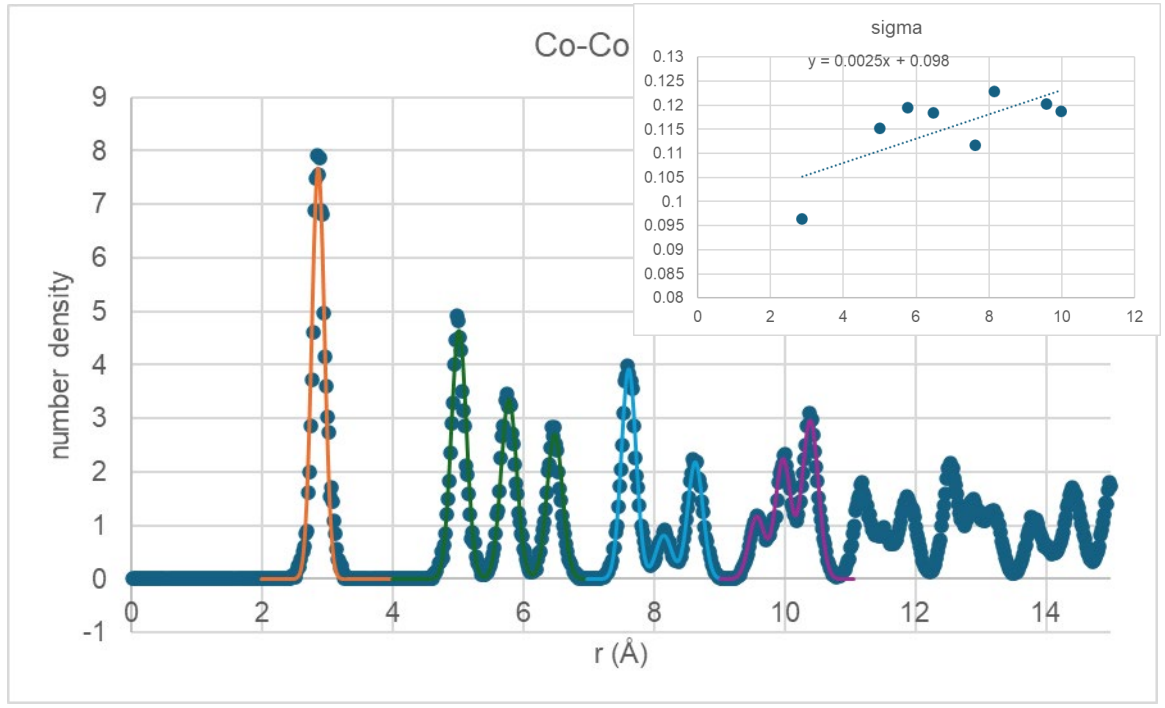




Li NCM523 O2

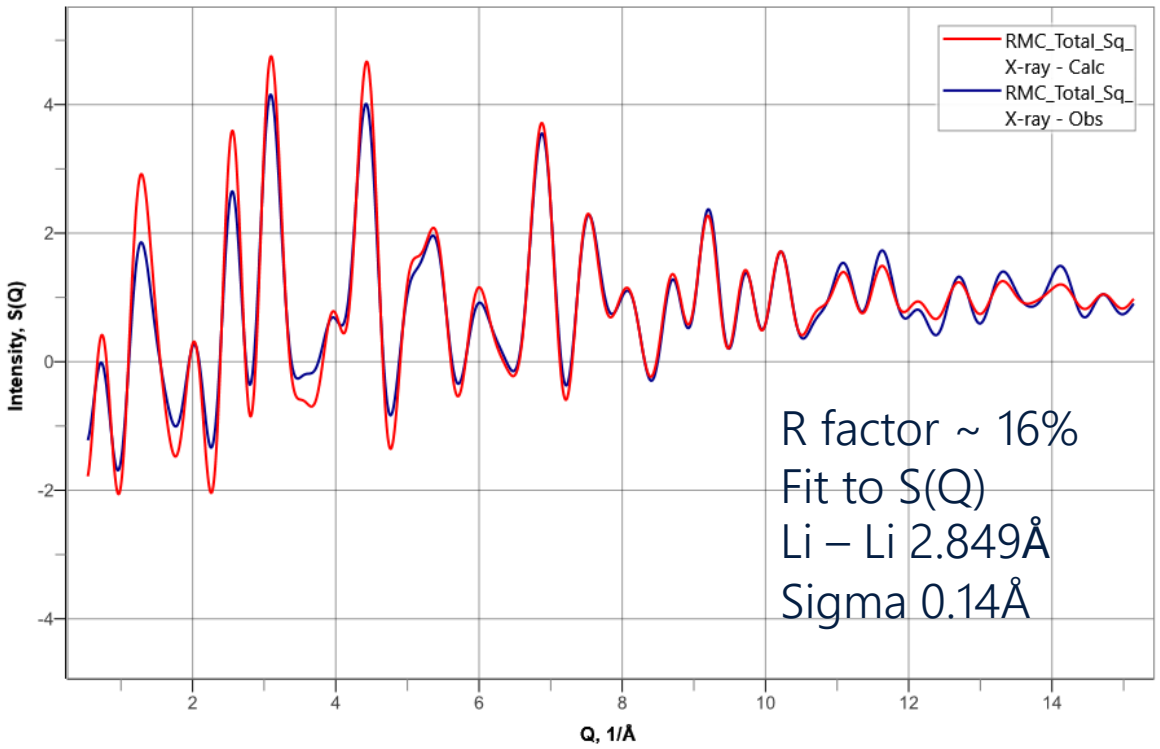
Solution	Li – Li (Å)	Li σ (Å)	Disorder rate	Co σ (Å)	Disorder rate
Single Crystal	2.86	0.08		0.08	
Small Box	2.873	0.11		0.09	
Big Box	2.848	0.13	0.015	0.10	0.0025



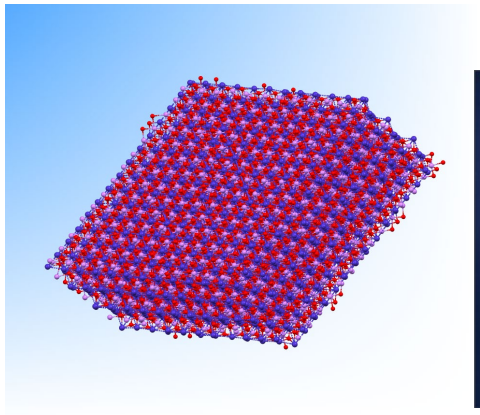


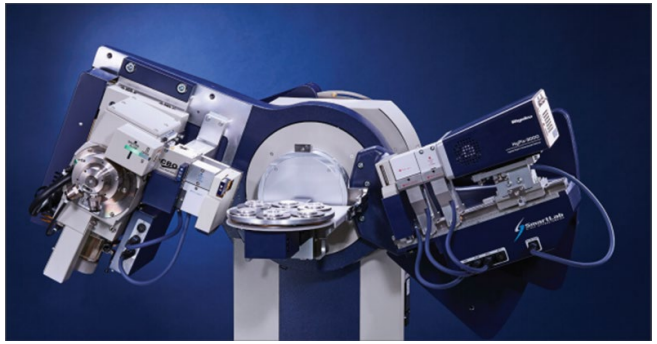
Big Box RMC atom-atom distance by atom type

RMC

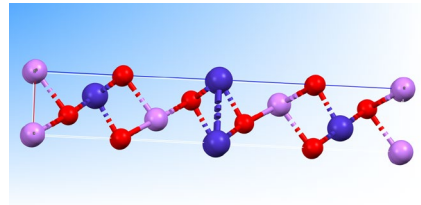


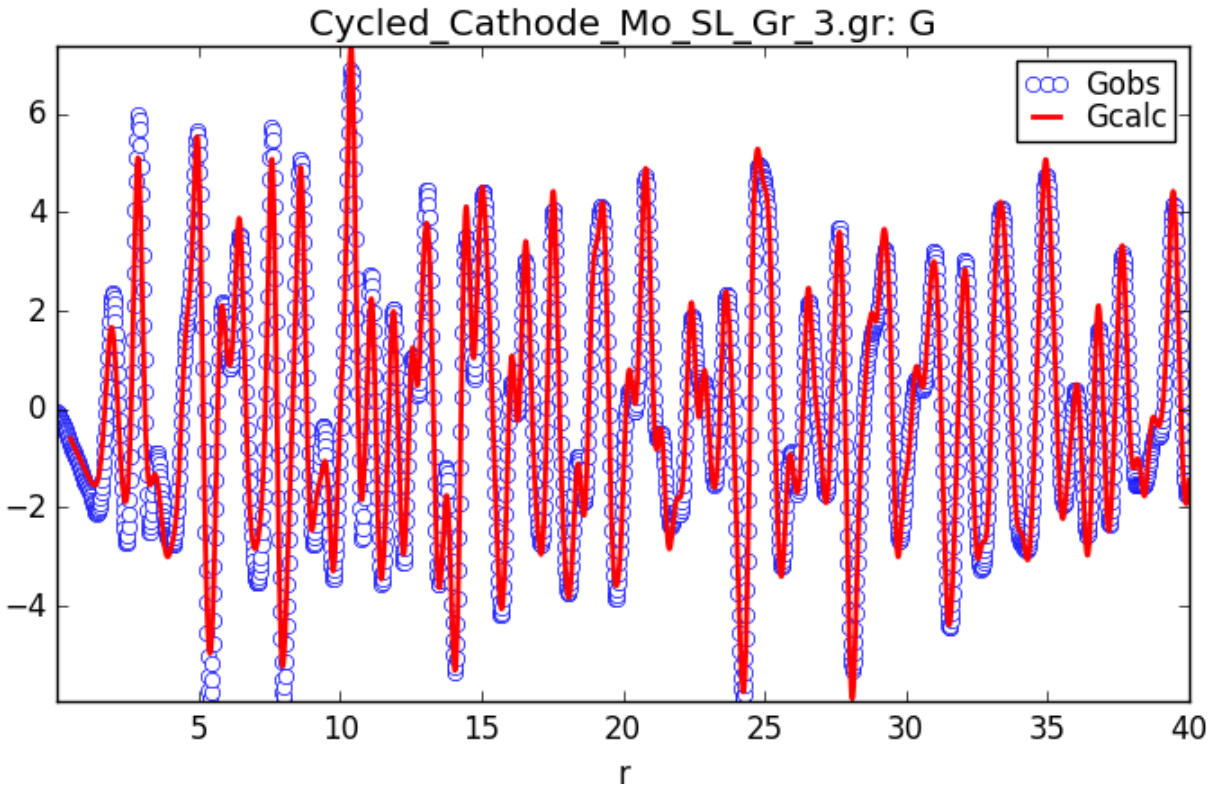
R factor ~ 16%
Fit to S(Q)
Li – Li 2.849Å
Sigma 0.14Å





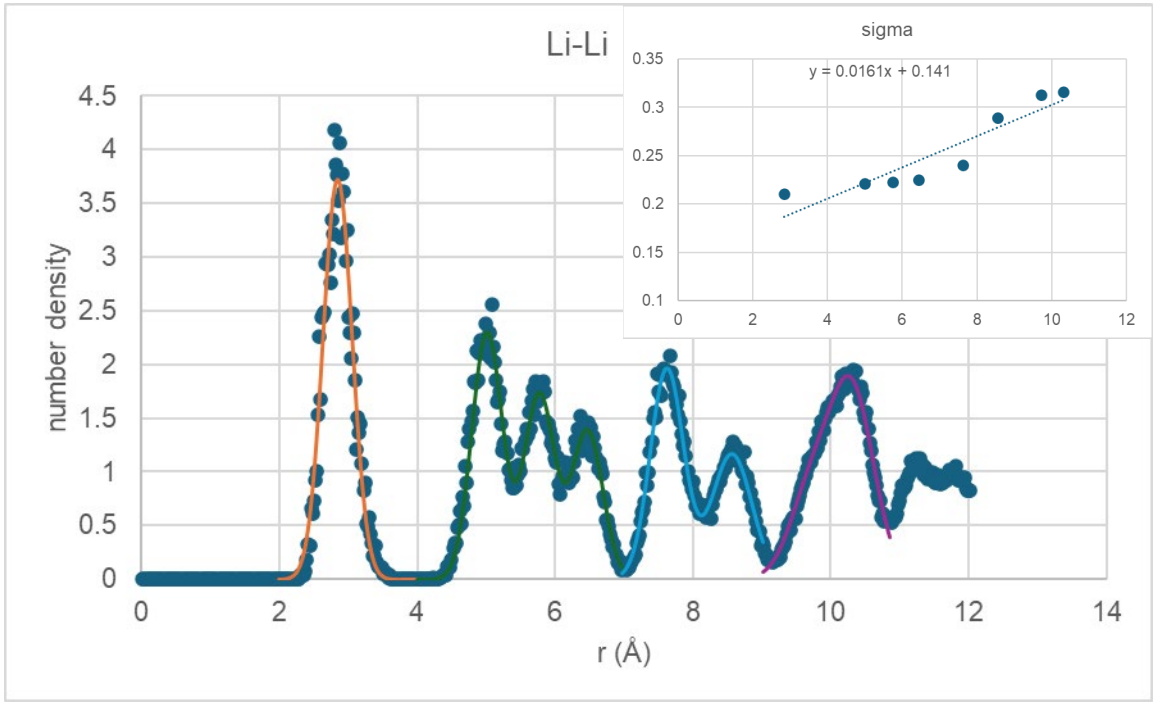
PDF GUI isotropic thermal parameters for NMC 532
Cycled – 9kW
Sigma ~ 0.11Å for Li (occ 1.2)
Sigma ~ 0.11Å for Co
unit cell parameters a=b=2.8714Å, c=14.244Å
R factor ~ 14%

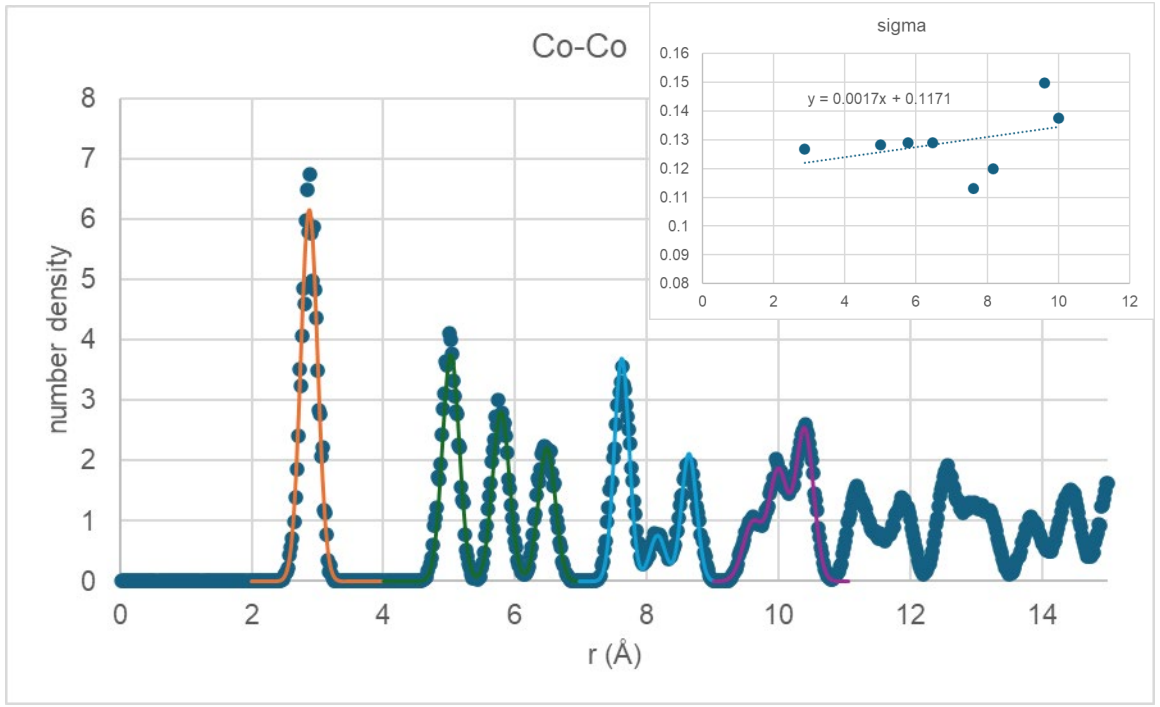




Li NCM523 O2

Solution	Li – Li (Å)	Li σ (Å)	Disorder rate	Co σ (Å)	Disorder rate
Single Crystal	2.86	0.08		0.08	
Small Box	2.871	0.11		0.09	
Big Box	2.849	0.14	0.016	0.12	0.0017





Big Box RMC atom-atom distance by atom type

Li NCM523 O2

Big Box RMC atom-atom distance by atom type

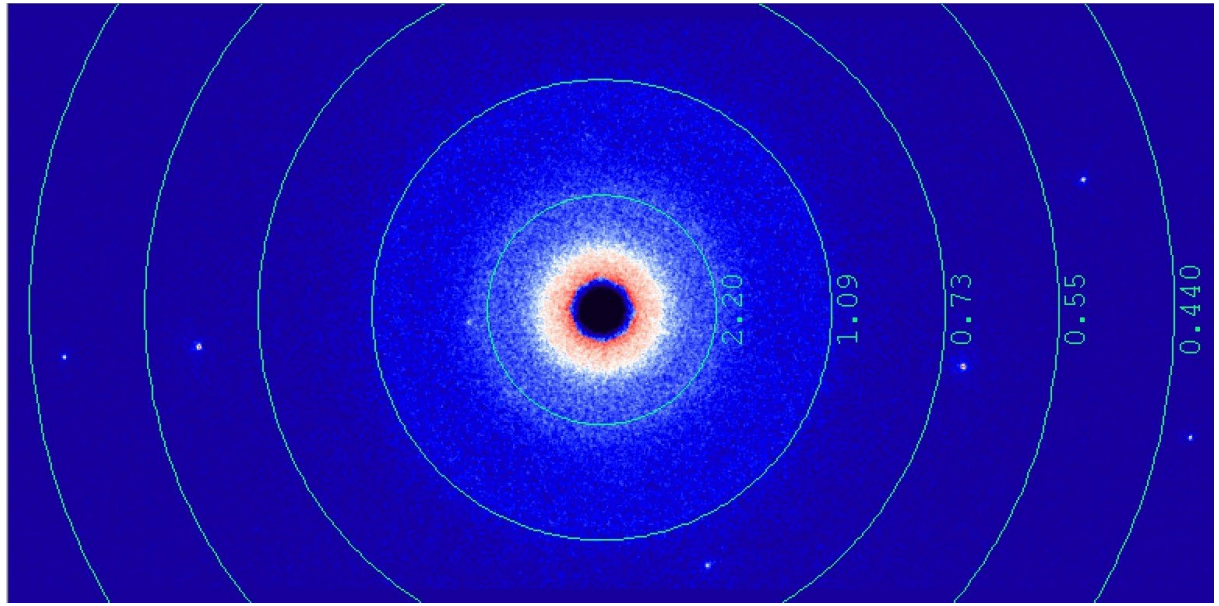
Solution	Li – Li (Å)	Li σ (Å)	Disorder rate	Li Occupation	Co σ (Å)	Disorder rate	R-factor
Li Co O2	2.82	0.11	0.017	0.9	0.09	0.0025	8.6%
Li NMCO2	2.854	0.13	0.018	1.02	0.09	0.0036	14%
Cycled - Synergy	2.848	0.13	0.015	1.4	0.10	0.0025	16%
Cycled - SmartLab	2.849	0.14	0.016	1.3	0.12	0.0017	16%

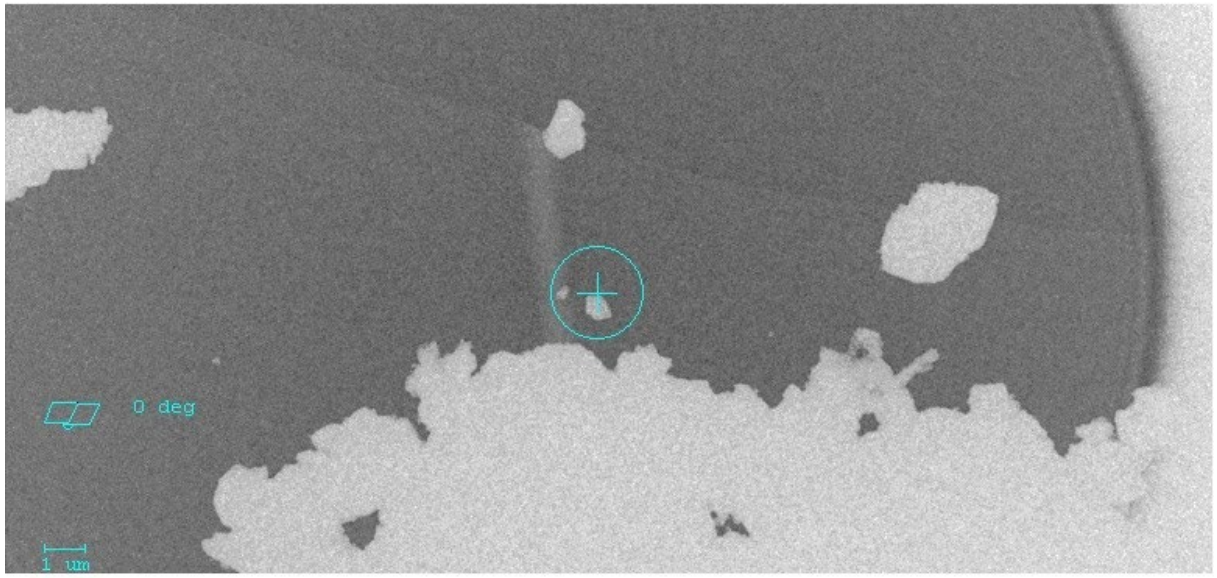
Li occupancy of about 1.4 corresponds to about a 4% Li replacement with Ni – for example.

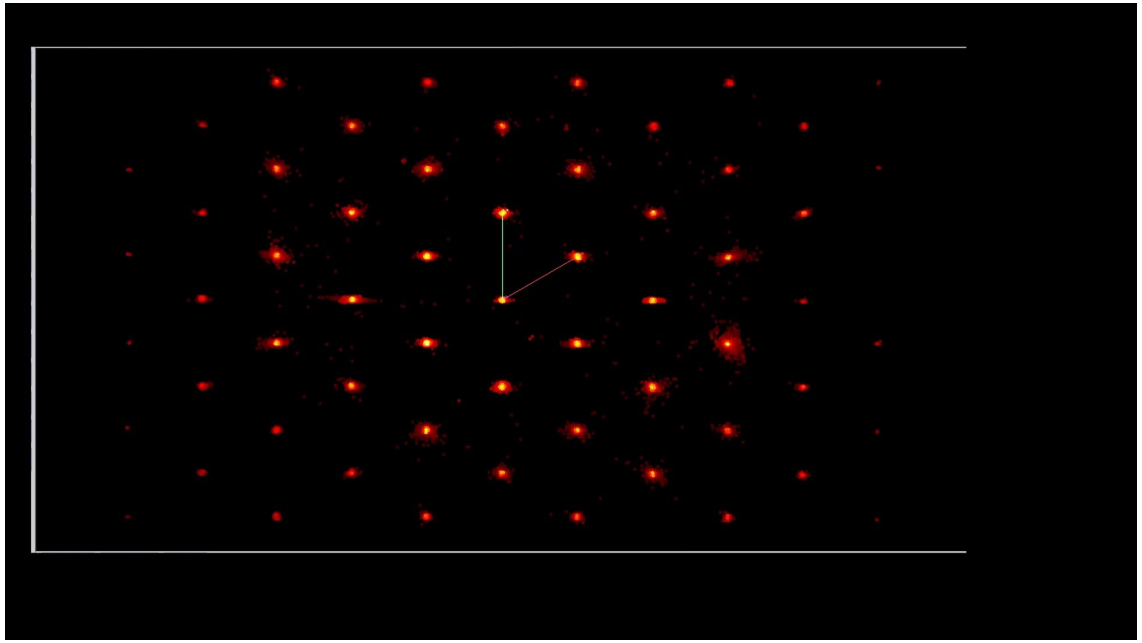
POLLING QUESTION #3

Microsoft Stock

Electron Diffraction Investigation



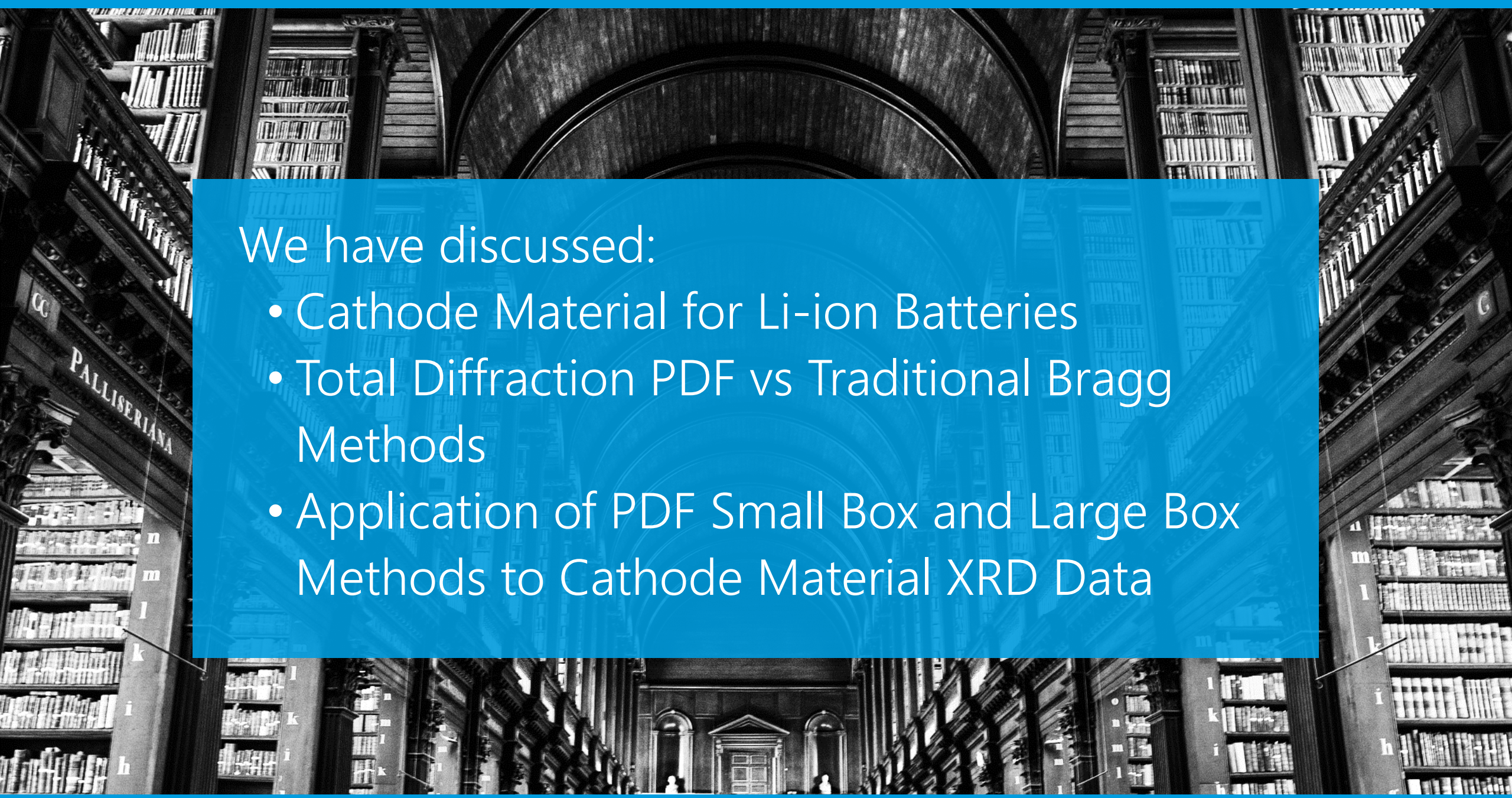




To further investigate the Li occupation numbers, Electron Diffraction performed on individual nanoparticles of cathode material.

Different polymorphs of NCM523 observed: monoclinic and trigonal

Electron Diffraction Crystal structure of NCM523 on nanoparticles taken from a cycled battery.



We have discussed:

- Cathode Material for Li-ion Batteries
- Total Diffraction PDF vs Traditional Bragg Methods
- Application of PDF Small Box and Large Box Methods to Cathode Material XRD Data

Questions & Answers

We'll follow up with your questions.

Recording will be available tomorrow.

Register for the next workshop.

BENEATH THE SURFACE: X-RAY ANALYSES OF BATTERY MATERIALS AND STRUCTURES

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THANK YOU