Diffuse scattering and PDF analysis

(found in the background of Bragg peaks)

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Acknowledgements

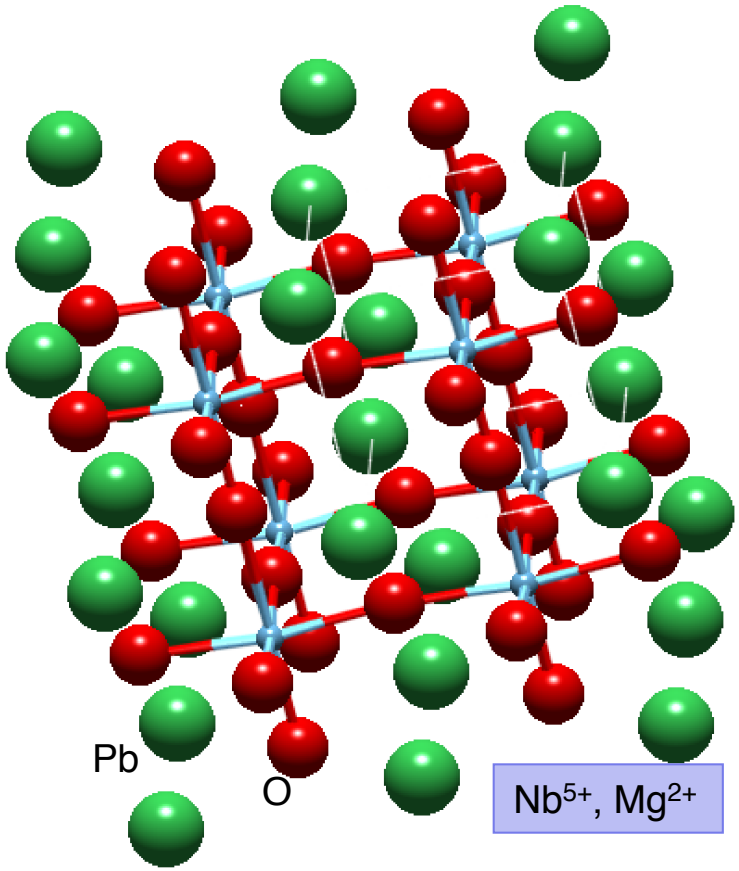
Institute of Physics AS CR, Prague:

Marek Pasciak
Petr Ondrejkovic
Martin Kempa
Jirka Hlinka

.... and many others:

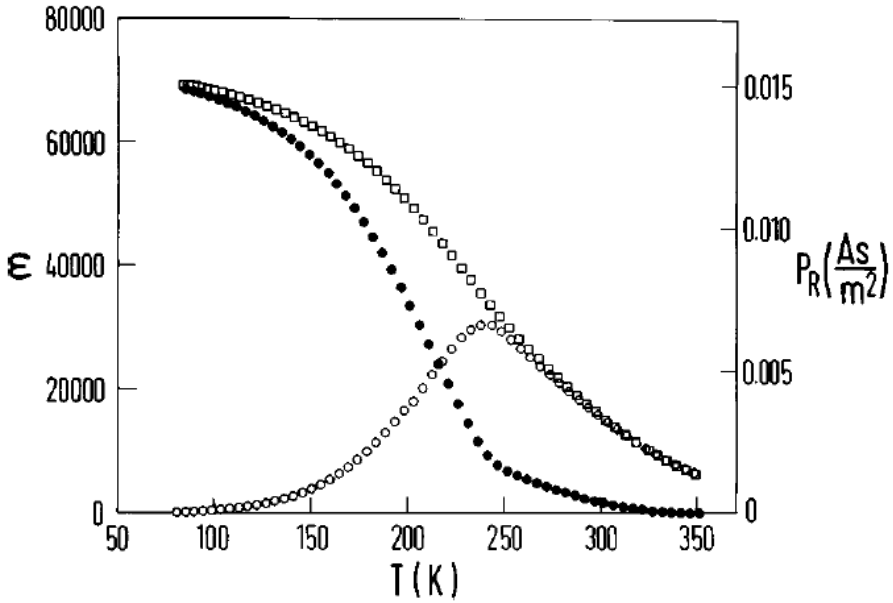
Henry Fischer (ILL)
Takeshi Egami (ORNL/U_Tennessee)
Sergei Vakhrushev (St. Petersburg)
...

Relaxor ferroelectrics



- PMN ($PbMg_{1/3}Nb_{2/3}O_3$)
- PZN ($PbZn_{1/3}Nb_{2/3}O_3$
- PZN-8% $PbTiO_3$

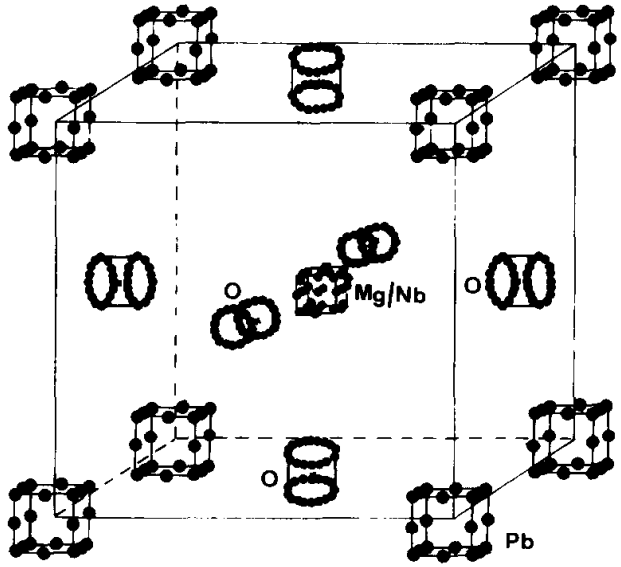
- "ferroelectrics with a diffuse phase transition"
- giant dielectric permitivity
- strong piezoelectricity



Relaxor ferroelectrics

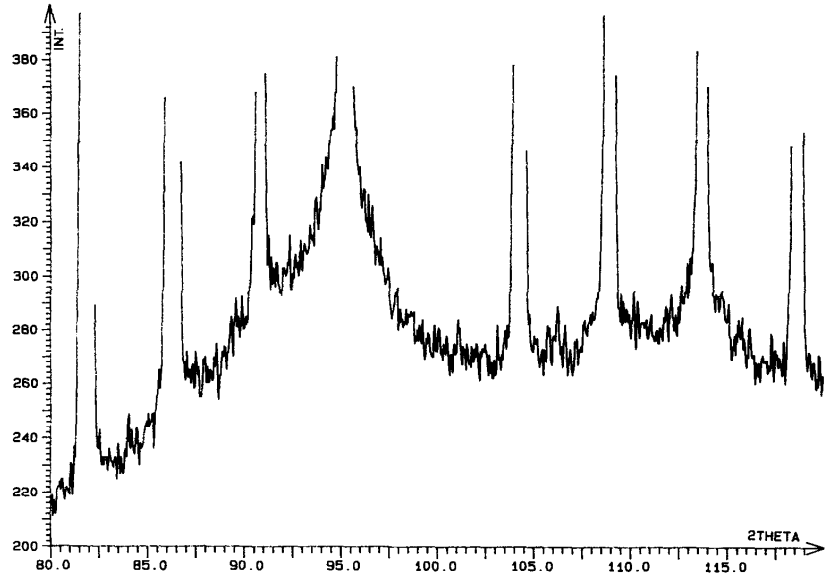
PMN

$(PbMg_{1/3}Nb_{2/3}O_3)$



- joint X-ray & neutron Rietveld refinement
- good Bragg agreement
- poor profile agreement

Bonneau et al., JSSC 91, 350 (1991)



T(K):	307	400	500	600	700	800
Cell parameter						
a (Å)	4.0500(2)	4.0512(1)	4.0533(2)	4.0570(3)	4.0614(3)	4.0660(4)
Atomic shifts (Å)						
X_{Pb} (Å)	0.337(2)	0.324(2)	0.316(2)	0.310(2)	0.306(2)	0.290(3)
X_{Nb}	0.130(4)	0.137(4)	0.132(4)	0.140(4)	0.135(5)	0.147(4)
$X_{O\parallel}$[a]	0.190(3)	0.196(3)	0.200(3)	0.206(3)	0.211(2)	0.194(2)
$X_{O\perp}$	0.073(4)	0.066(4)	0.064(5)	0.060(6)	0.058(6)	0.053(6)
Isotropic thermal parameters (Å^2) (not refined)						
B_{Pb}	0.68	0.94	1.20	1.47	1.79	2.40
$B_{Mg/Nb}$	0.32	0.39	0.53	0.59	0.76	0.79
B_O	0.49	0.58	0.71	0.82	1.00	1.50
Reliability factors (%)						
R_p[b]	6.12	5.65	5.76	5.88	5.64	5.58
R_{wp}[c]	9.64	9.30	9.32	9.35	8.98	8.97
R_B[d]	2.65	2.47	2.55	2.52	2.57	2.83
R_{exp}[e]	4.14	4.16	4.17	4.19	4.22	4.24

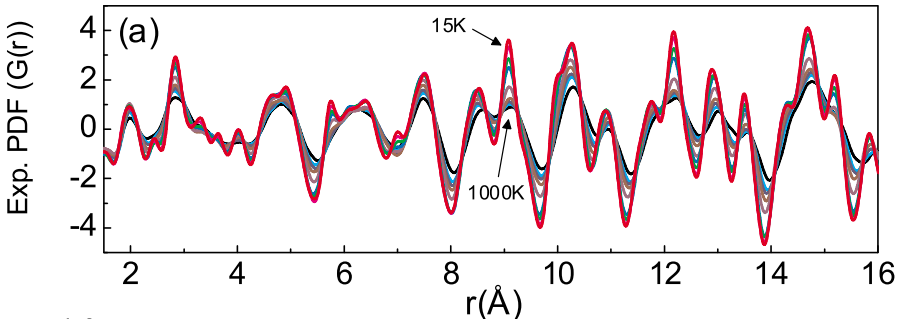
Polar nanoregions

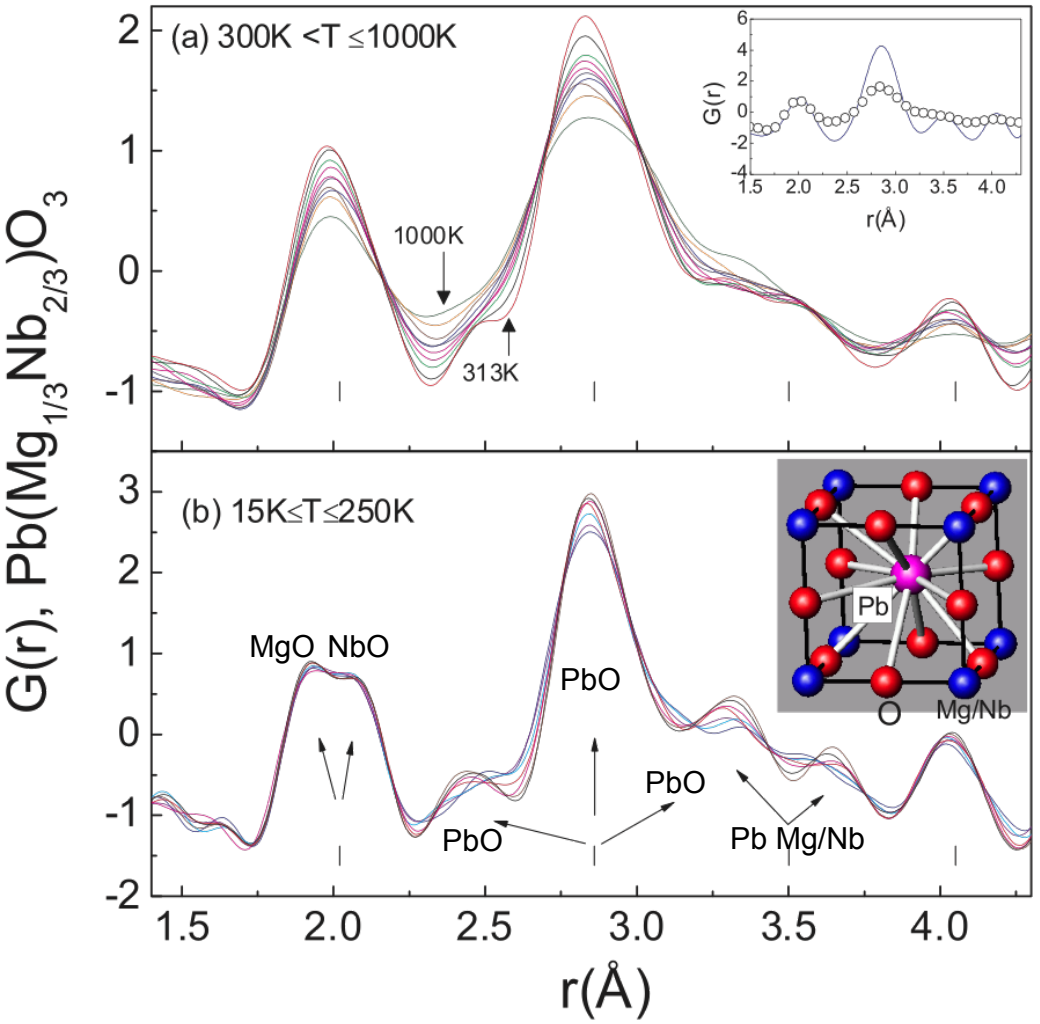
PMN

$(PbMg_{1/3}Nb_{2/3}O_3)$

TOF neutron scattering
NPDF (LANSCE)

$T > 300$ K $\quad Q_{max} = 25$ Å^{-1}
$T < 300$ K $\quad Q_{max} = 30$ Å^{-1}





Jeong et al., PRL 94, 147602 (2005)

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1. Introduction (motivation)
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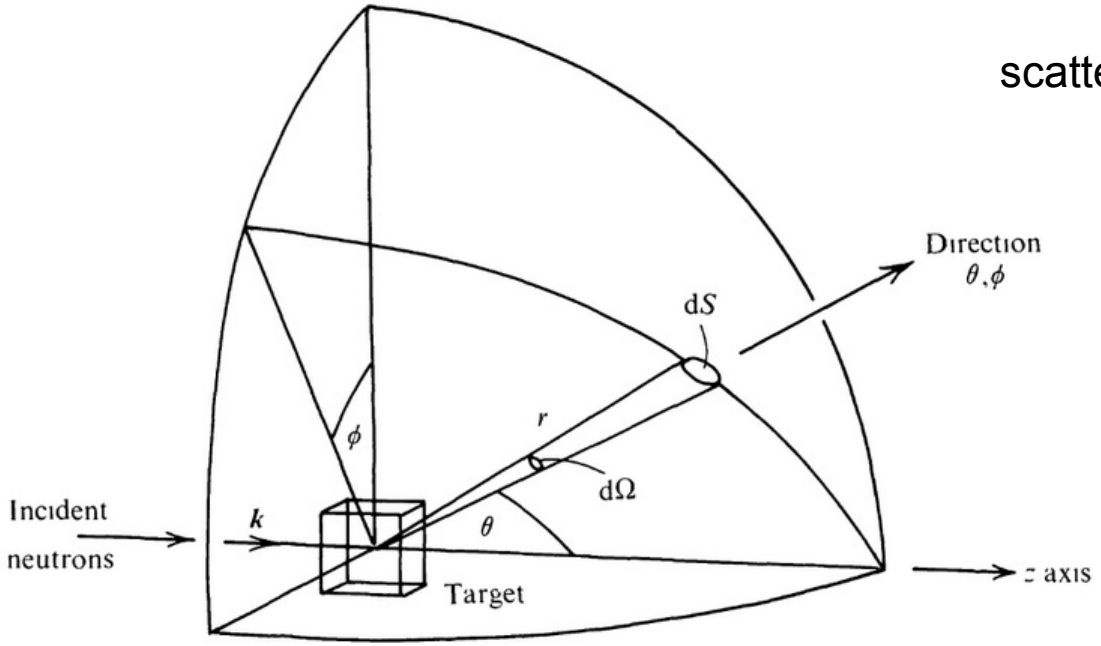
Scattering by a single nucleus



scattered flux through dS:

$$v\left|\psi_{sc}\right|^2 \mathrm{d}S = v\frac{b^2}{r^2}\mathrm{d}S = vb^2\,\mathrm{d}\Omega$$

differential cross-section:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{v\,b^2\,\mathrm{d}\Omega}{\Phi\,\mathrm{d}\Omega} = b^2$$

total cross-section:

$$\sigma_{tot} = \int_{4\pi}\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\mathrm{d}\Omega = 4\pi b^2$$

incident flux:

$$\Phi = v\left|\psi_{inc}\right|^2 = v$$

neutron velocity $v = \dfrac{\hbar k}{m}$

Neutron coherent inelastic scattering

nuclear cross section

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}E}\right)_{coh} = \frac{k_f}{k_0}\frac{1}{2\pi\hbar}\sum_{j,j'}\int_{-\infty}^{\infty} b_j b_{j'} \left\langle \exp\left[-i\vec{Q}\vec{R}_{j'}(0)\right]\exp\left[i\vec{Q}\vec{R}_j(t)\right]\right\rangle \exp(-i\omega t)\,\mathrm{d}t$$

$$\omega = E/\hbar$$

magnetic cross section

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}E}\right) = \frac{1}{2\pi\hbar}\left(\frac{\gamma r_0}{2\mu_B}\right)^2 \frac{k_f}{k_0}$$
$$\sum_{\alpha\beta}\left(\delta_{\alpha\beta} - \hat{Q}_\alpha\hat{Q}_\beta\right)\int\left\langle M_\alpha\left(-\vec{Q},0\right)M_\beta\left(\vec{Q},t\right)\right\rangle \exp(i\omega t)\,\mathrm{d}t$$

These are the most general expressions!
They may serve as basis for numerical simmulations.

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Scattering functions

scattered amplitude

$$\psi(\vec{Q}) = \sum_i b_i \exp(-i\vec{Q}\vec{r}_i)$$

scattering length density

$$\rho(\vec{r}) = \sum_i b_i \delta(\vec{r} - \vec{r}_i)$$

scattered intensity

$$I(\vec{Q}) = |\psi(\vec{Q})|^2 = \sum_{ij} b_i b_j \exp\left[-i\vec{Q}(\vec{r}_i - \vec{r}_j)\right]$$

density-density correlation

$$C(\vec{r}) = \langle \rho(\vec{r}_i)\rho(\vec{r} + \vec{r}_i) \rangle_i = \frac{1}{N} \sum_{ij} b_i b_j \delta(\vec{r} - \vec{r}_{ij})$$

spherical average (powder, liquid)

$$I(Q) = \sum_{ij} b_i b_j \frac{\sin Qr_{ij}}{Qr_{ij}}$$

$$N_r(r) = \langle C(\vec{r})\Delta r \rangle_{angle}$$

scattering function, structure factor, ...

$$S(Q) = \frac{I(Q)}{\sum_i b_i^2} = 1 + \frac{2}{\sum_i b_i^2} \sum_{i<j} b_i b_j \frac{\sin Qr_{ij}}{Qr_{ij}}$$

pair distribution function (PDF)

$$g(r) = \frac{N_r(r)}{4\pi N r^2 \Delta r \rho_0} = \frac{1}{2\pi N r^2 \rho_0} \sum_{i<j} b_i b_j \delta(r - r_{ij})$$

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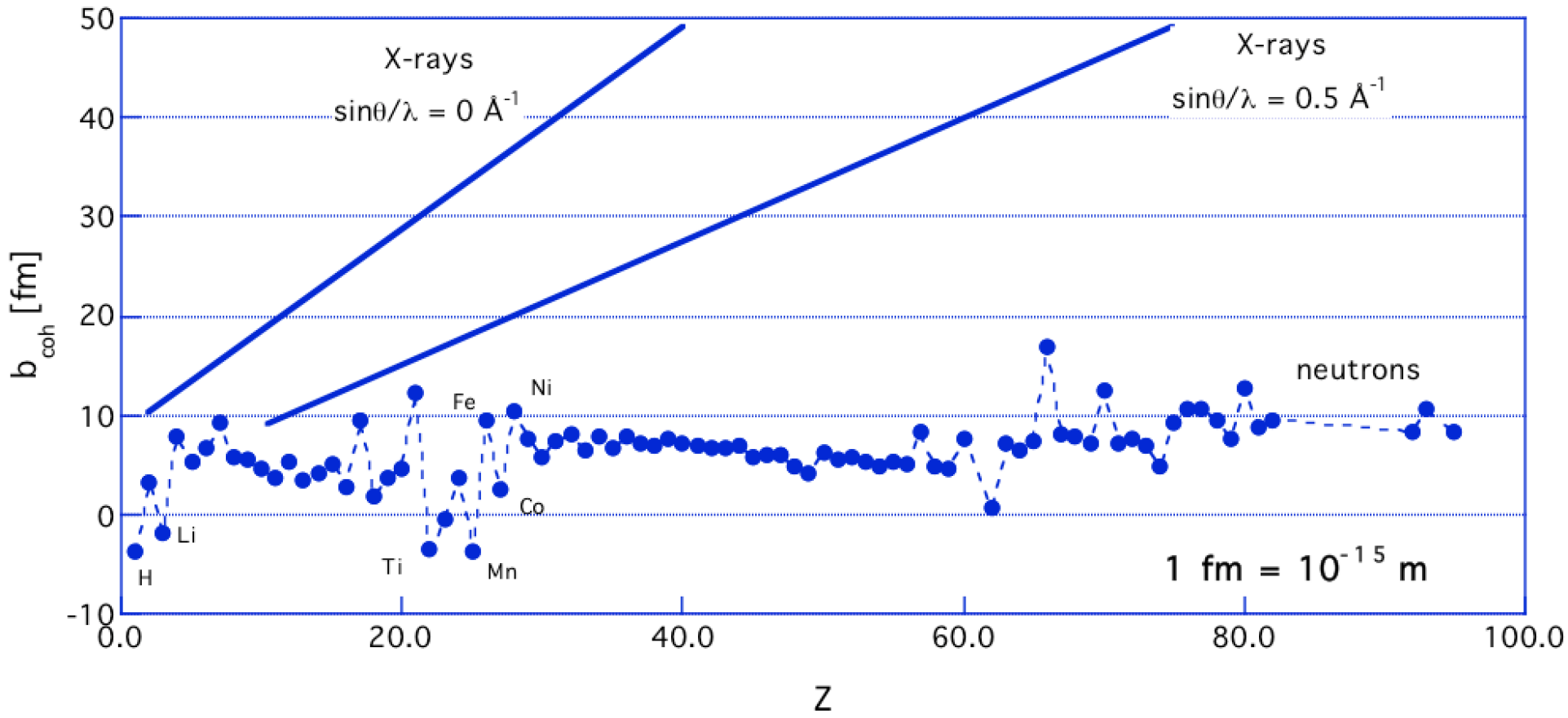
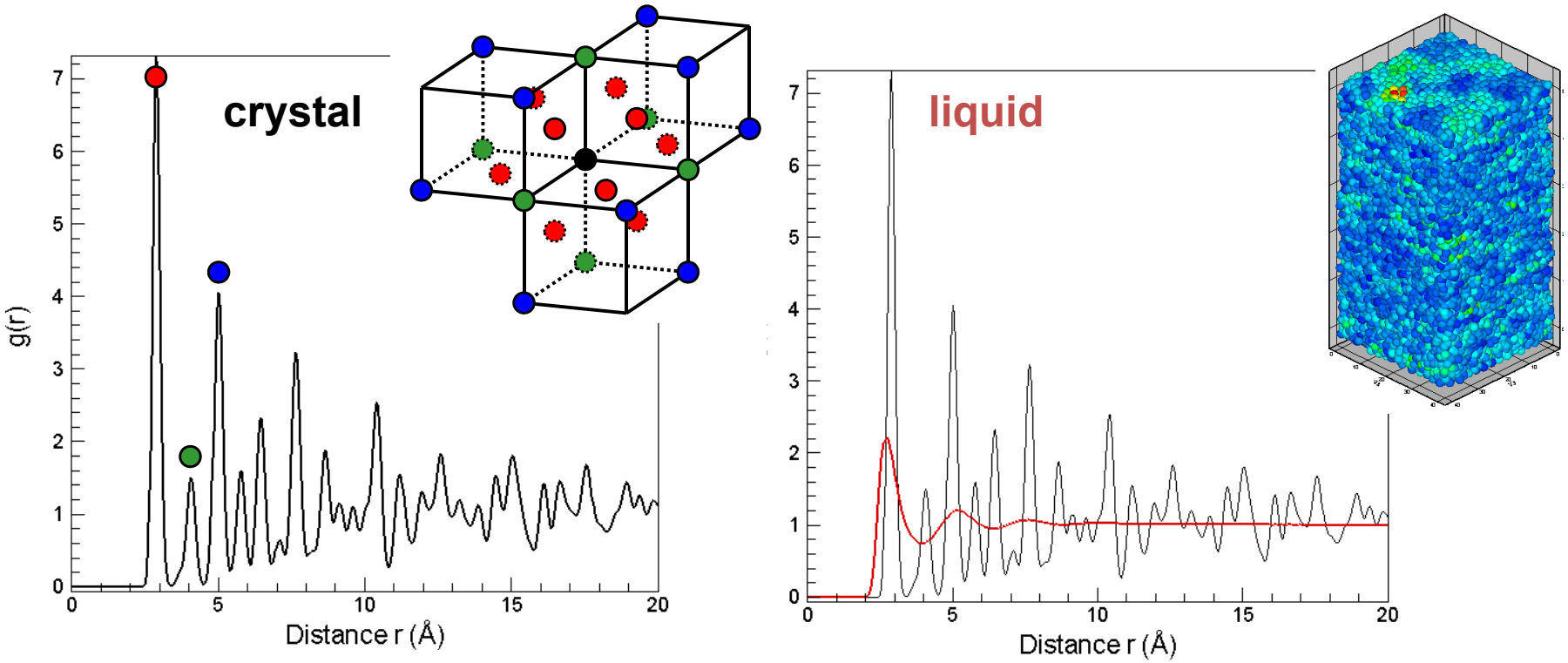
Neutrons *vs.* Xrays



PDF: crystal *vs.* liquid

$$g(r) = 1 + \frac{1}{2\pi N r^2 \rho_0} \sum_{i<j} b_i b_j \, \delta\left(r - r_{ij}\right)$$



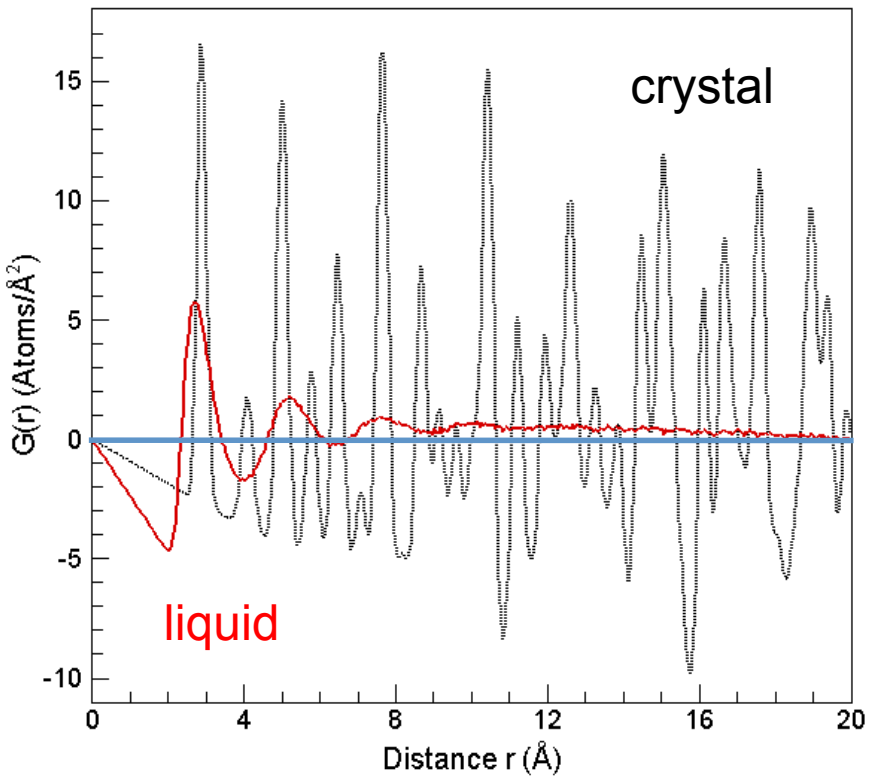
Au (gold) model calculation

courtesy L. Zhigilei, Virginia State university

PDF family

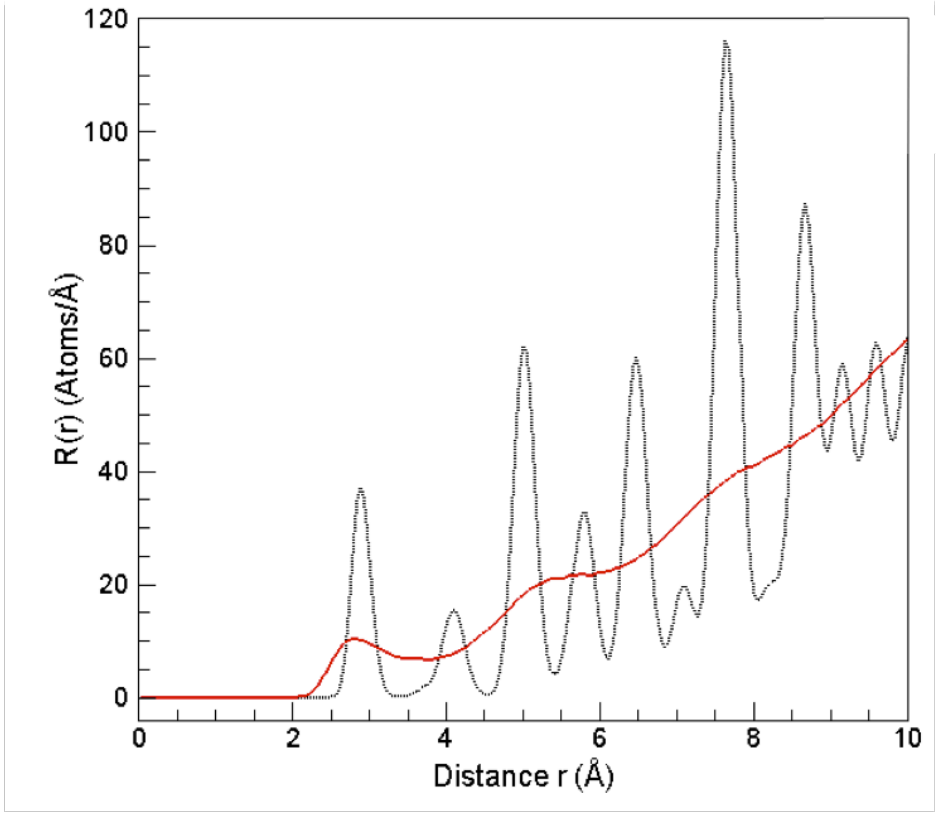
G(r) reduced pair distribution function

$$G(r) = 4\pi r^2 \rho_0 \left[g(r) - 1 \right]$$



R(r) radial distribution function

$$R(r) = 4\pi r^2 \rho_0 \, g(r)$$



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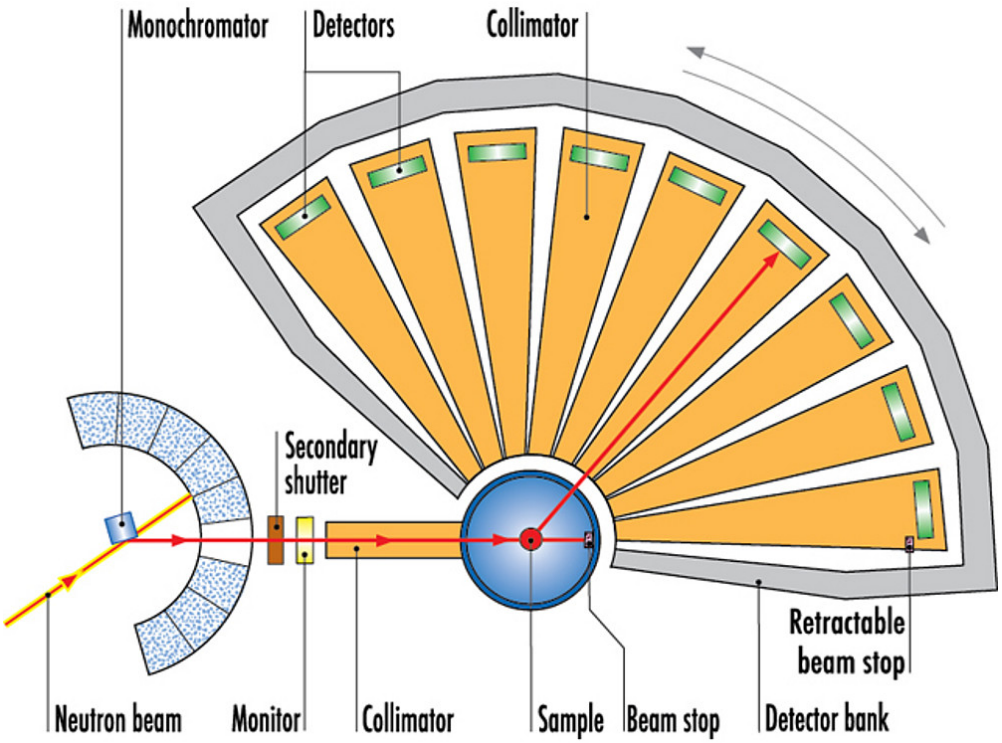
Experimental

D4 (ILL)



λ = 0.5 Å Q ≈ 0.3 – 24 Å^{-1}
typical acquisition time ≈ 3h

excellent stability indispensable!

observed intensity

$$I(Q) \approx S(Q)$$

extracting g(r)

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho_0} \int_0^\infty Q\left[S(Q) - 1\right] \sin(Qr)\, dr$$

- qualitative discussions

modelling S(Q)

$$S(Q) = 1 + 4\pi\rho_0 \int_0^\infty g(r) \frac{\sin Qr}{Qr} r^2 dr$$

- reverse MC
- DFT/molecular dynamics

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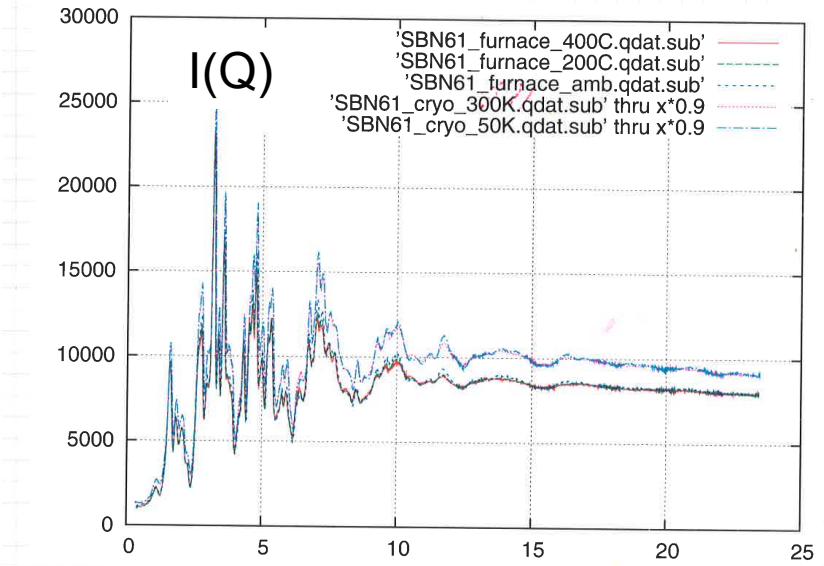
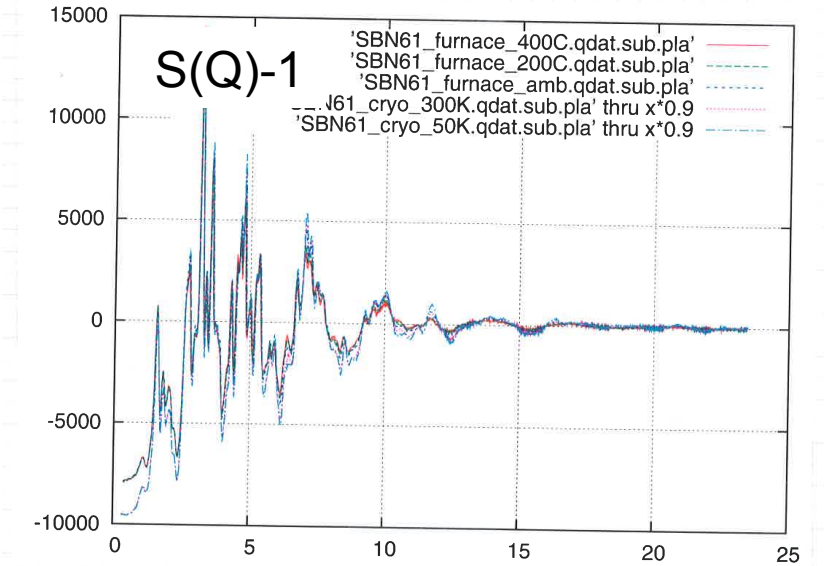
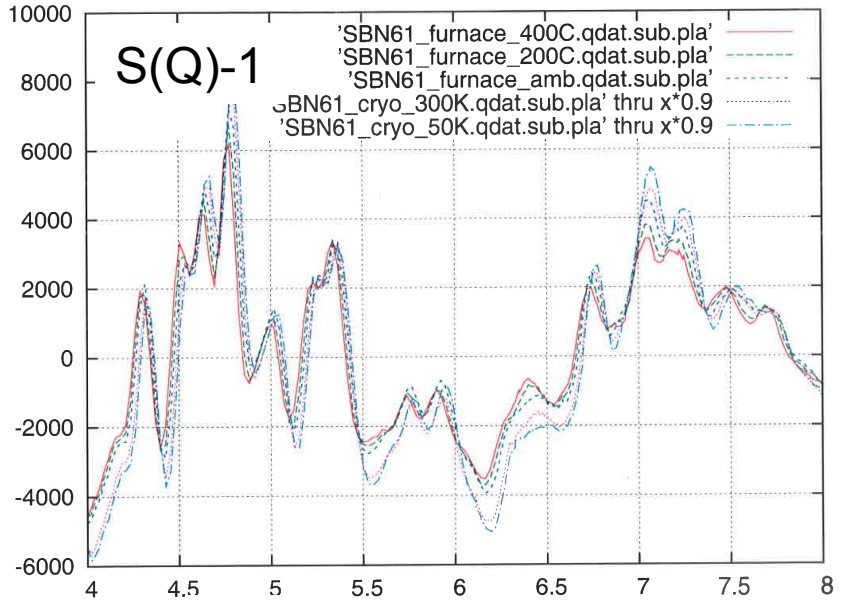
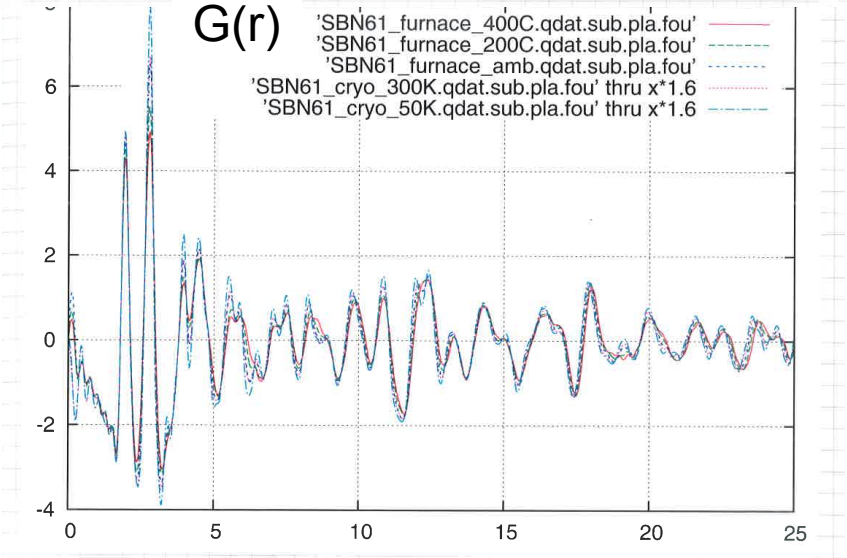
Experimental









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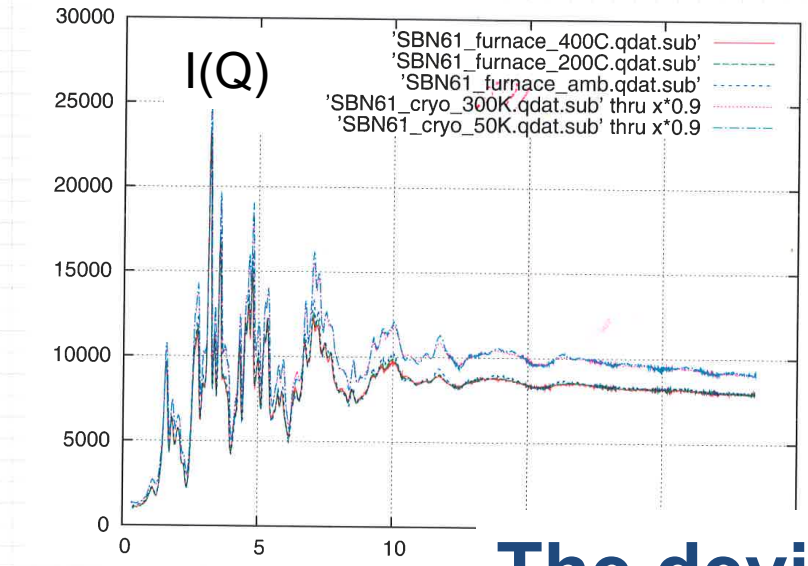
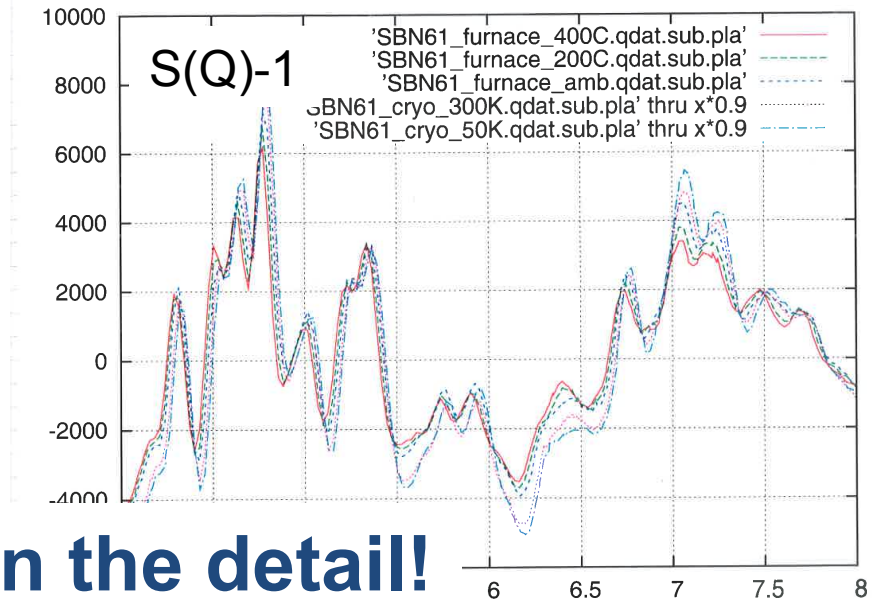
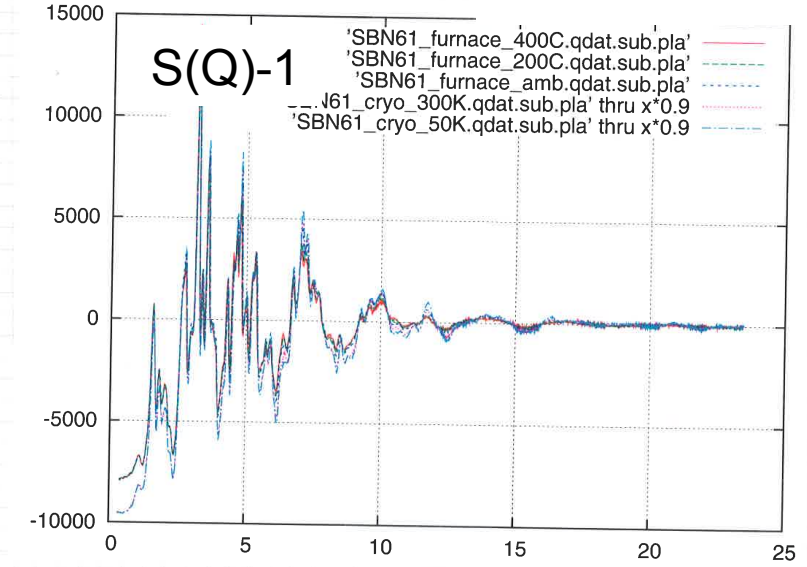
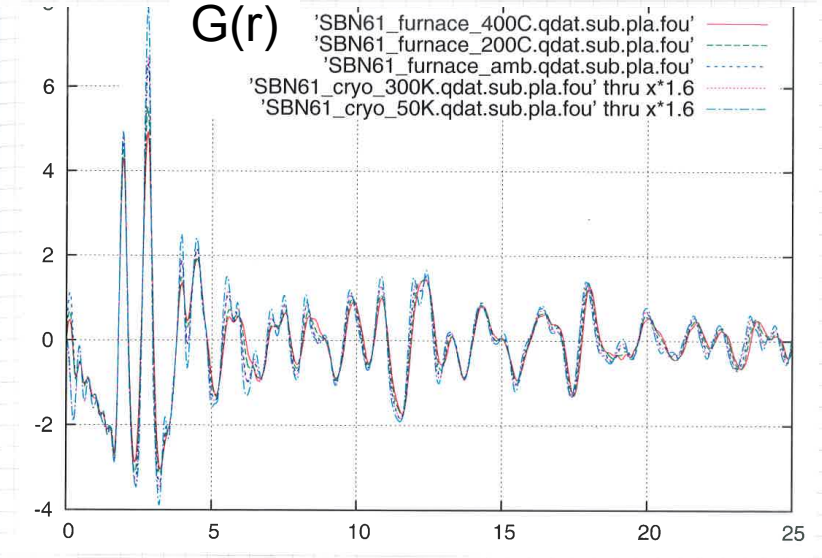
Experimental



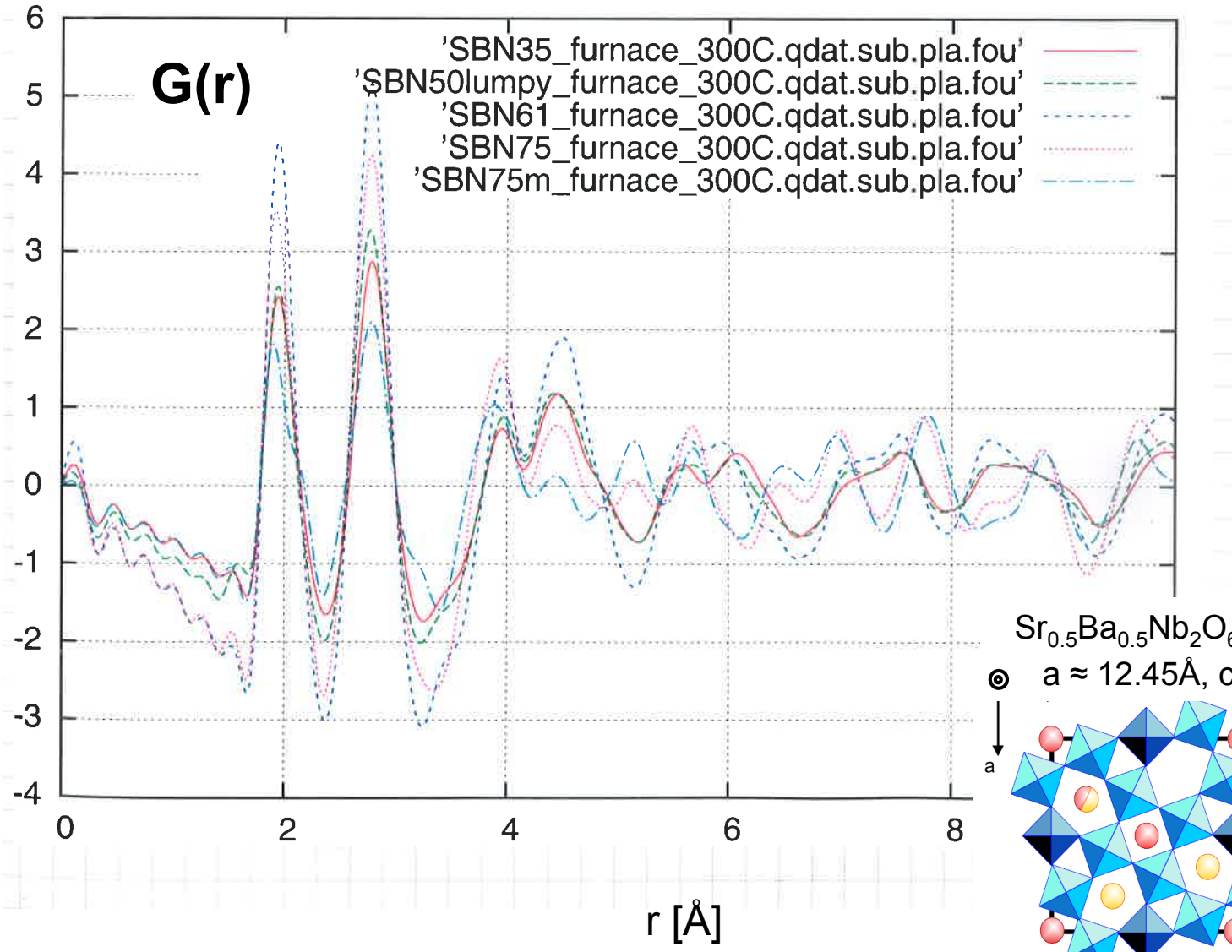


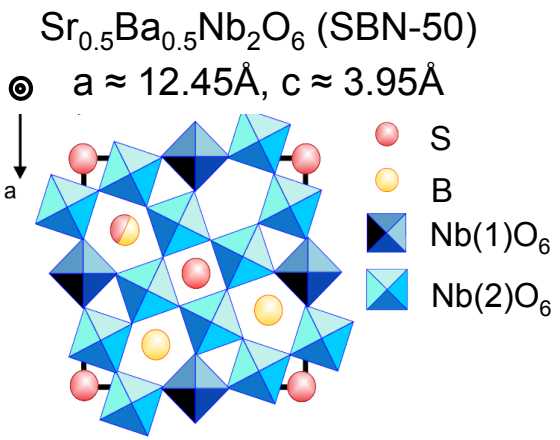
The devil is in the detail!





Experimental





tetragonal tungsten bronze

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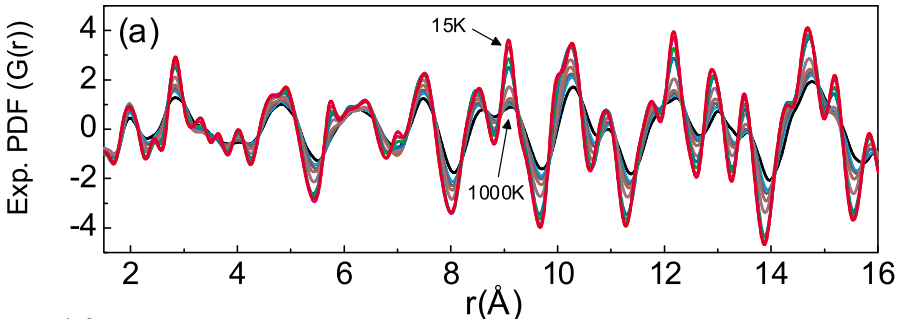
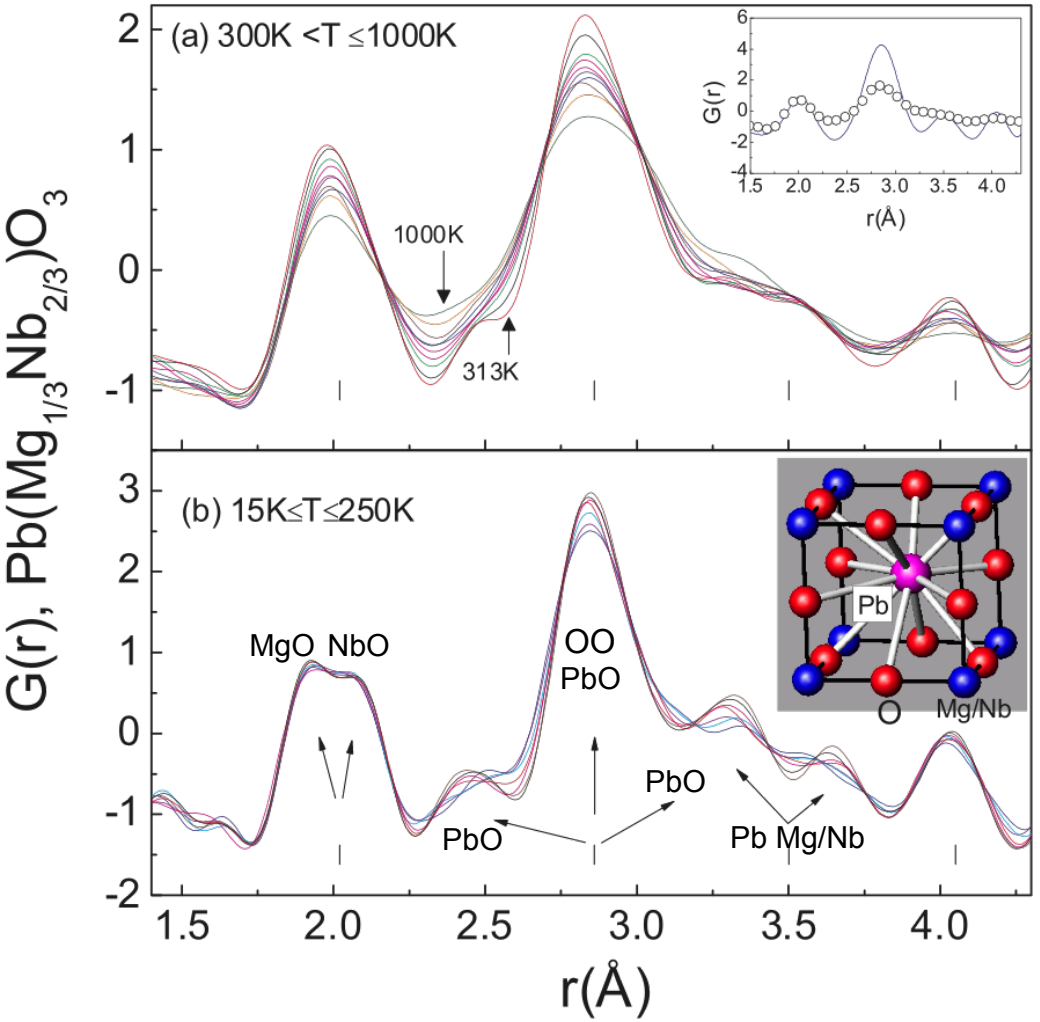
Polar nanoregions

PMN

TOF neutron scattering
NPDF (LANSCE)

T > 300 K Q_{max} = 25 Å^{-1}
T < 300 K Q_{max} = 30 Å^{-1}

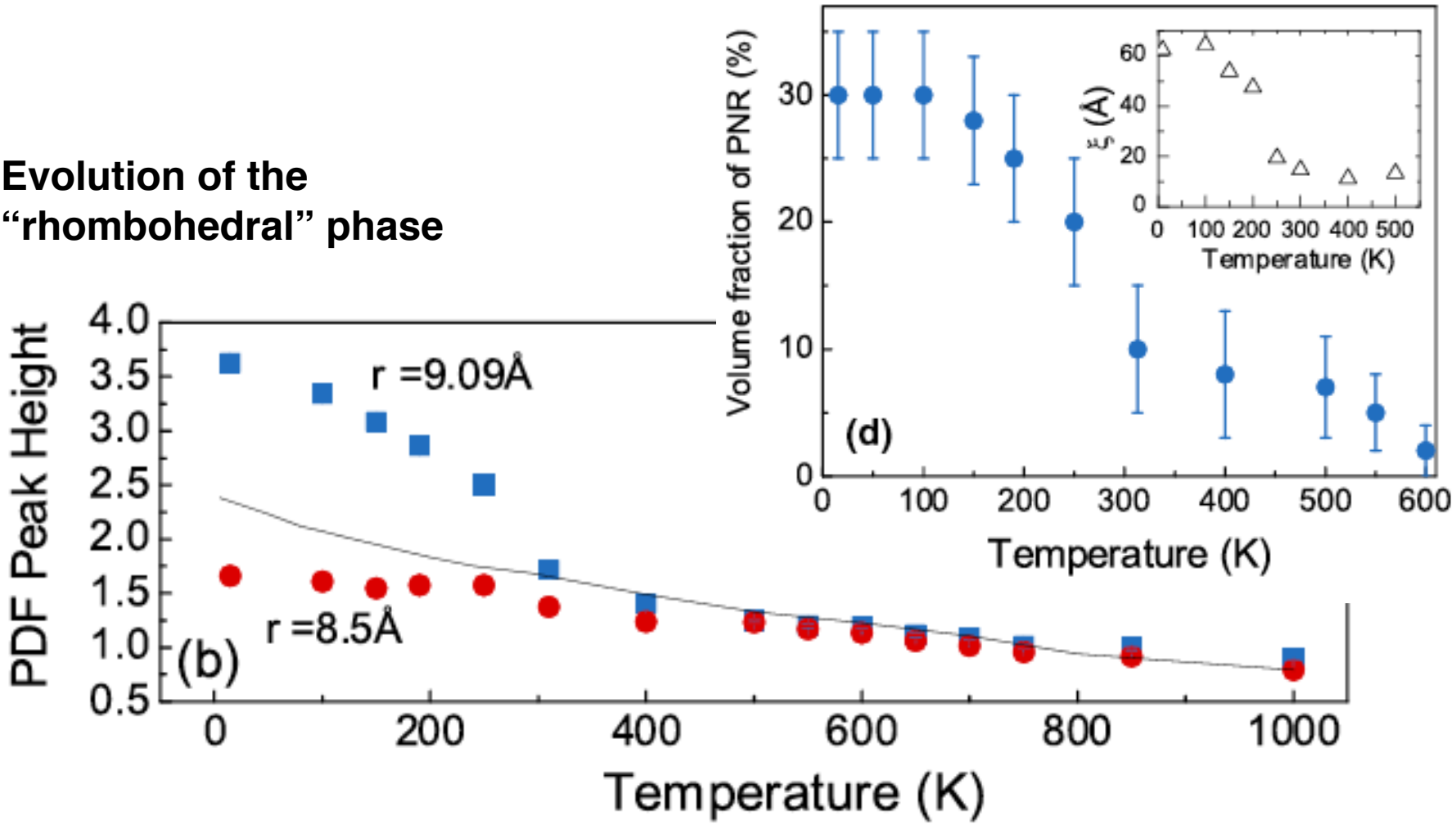




Jeong et al., PRL 94, 147602 (2005)

Polar nanoregions

Evolution of the "rhombohedral" phase



Egami et al., PRL 94, 147602 (2005)

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reverse MonteCarlo

RMC principles

1. generate a supercell with periodic boundary conditions, adequate structure, chemical composition & density
2. calculate its PDFs (referred to as “old” later on)
3. do FT to obtain the partial and total structure factors S(Q) or S(Q,w)
4. get χ^2 between the total structure factor and experimental data
5. make a random change in the model (constraints!)
6. recalculate S(Q) and χ^2
7. accept modification if $\chi^2_{new} < \chi^2_{old}$, otherwise only with some weight, eg. $\exp[-(\chi^2_{new} - \chi^2_{old})]$
8. repeat from point 5 again until χ^2_{new} matches χ^2_{old}

R.L. McGreevy, J.Phys.: Condens. Matter 13 (2001) 201

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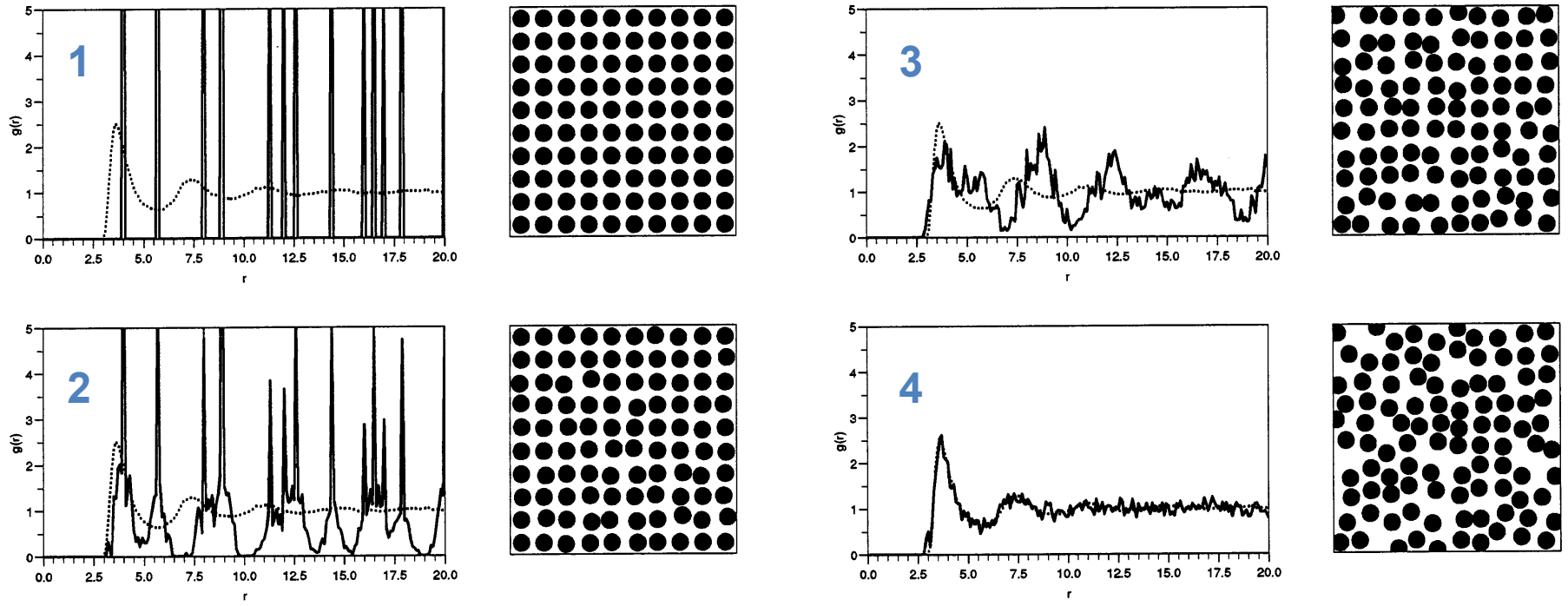
RMC principles



evolution of an RMC model of g(r)

R.L. McGreevy, J.Phys.: Condens. Matter 13 (2001) 201

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RMC implementation

RMCPA, RMCPOW, RMCSPIN
R.L. McGreevy, J. Phys.: Condens. Matter 13 (2001) R877

RMCProfile
Tucker, M. G.; Dove, M. T.; Keen, D. A. Application of the Reverse Monte Carlo method to Crystalline Materials.
J. Appl. Crystallogr., 34 (2001) 630

RMCProfile+
Eremenko, M.; Krayzman, V.; Gagin, A.; Levin, I. Advancing reverse Monte Carlo structure refinements to the nanoscale.
J. Appl. Crystallogr., 50 (2017) 1561

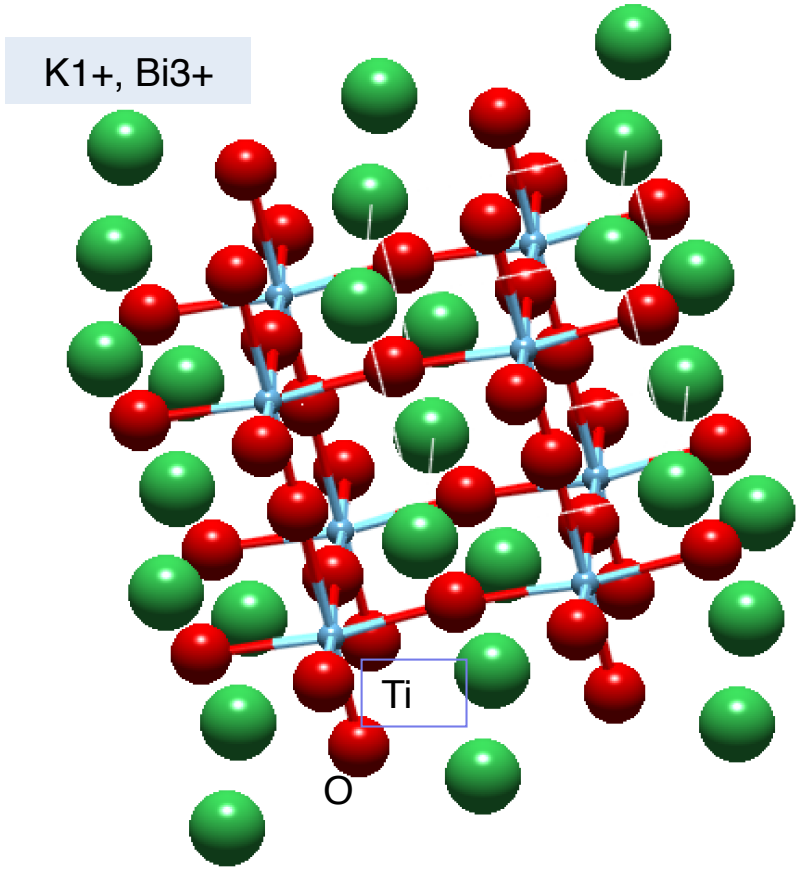
http://www.rmcprofile.org

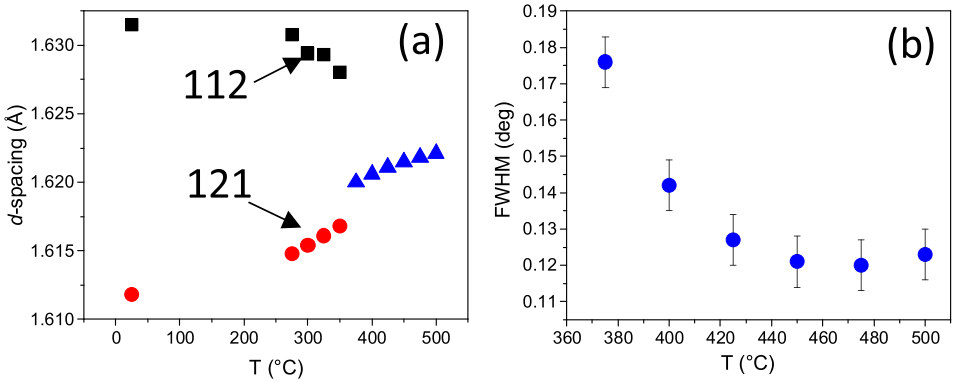
Materials Measurement Science Division,
National Institute of Standards and Technology,
Gaithersburg, MD, USA

Th. Proffen, J.Phys.: Condens. Matter 13 (2001) 201

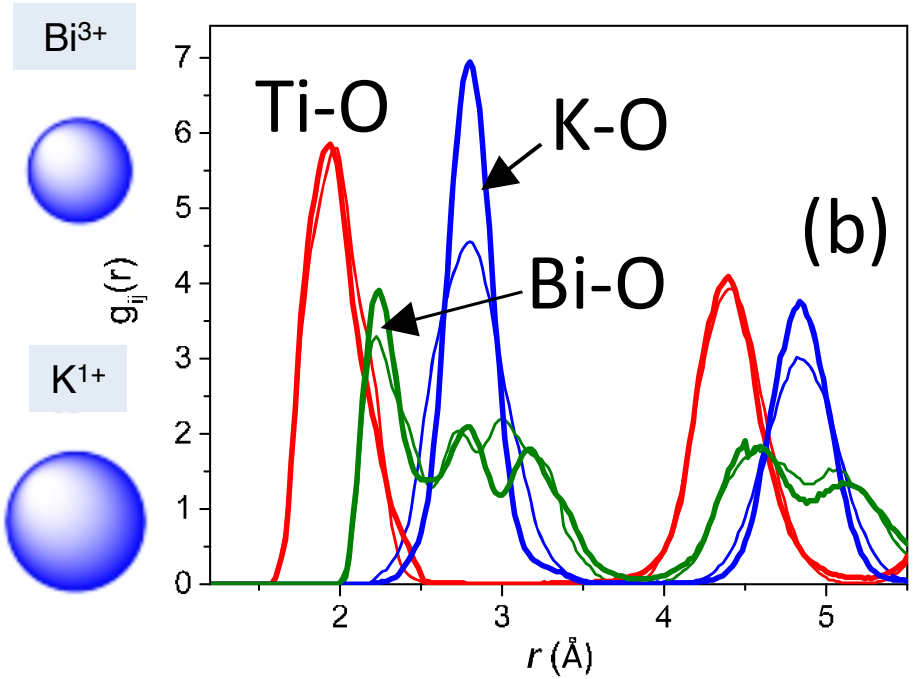
$K_{0.5}Bi_{0.5}TiO_3$

relaxor with A-site disorder



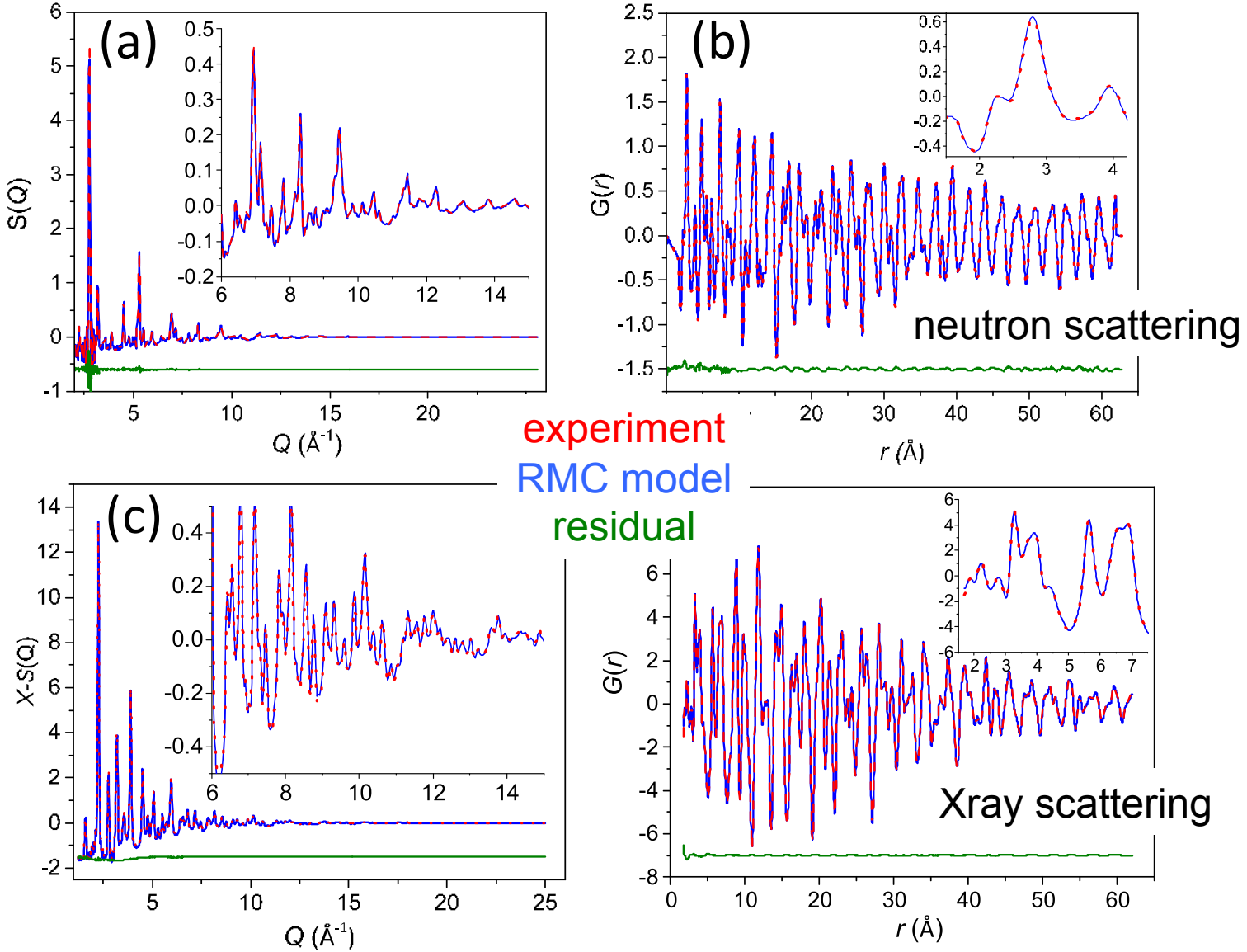


tetragonal below 360 ºC



I. Levin et al., Chem. Matter 31 (2019) 2450

$K_{0.5}Bi_{0.5}TiO_3$



simultaneous RMC refinement

I. Levin et al., Chem. Matter 31 (2019) 2450

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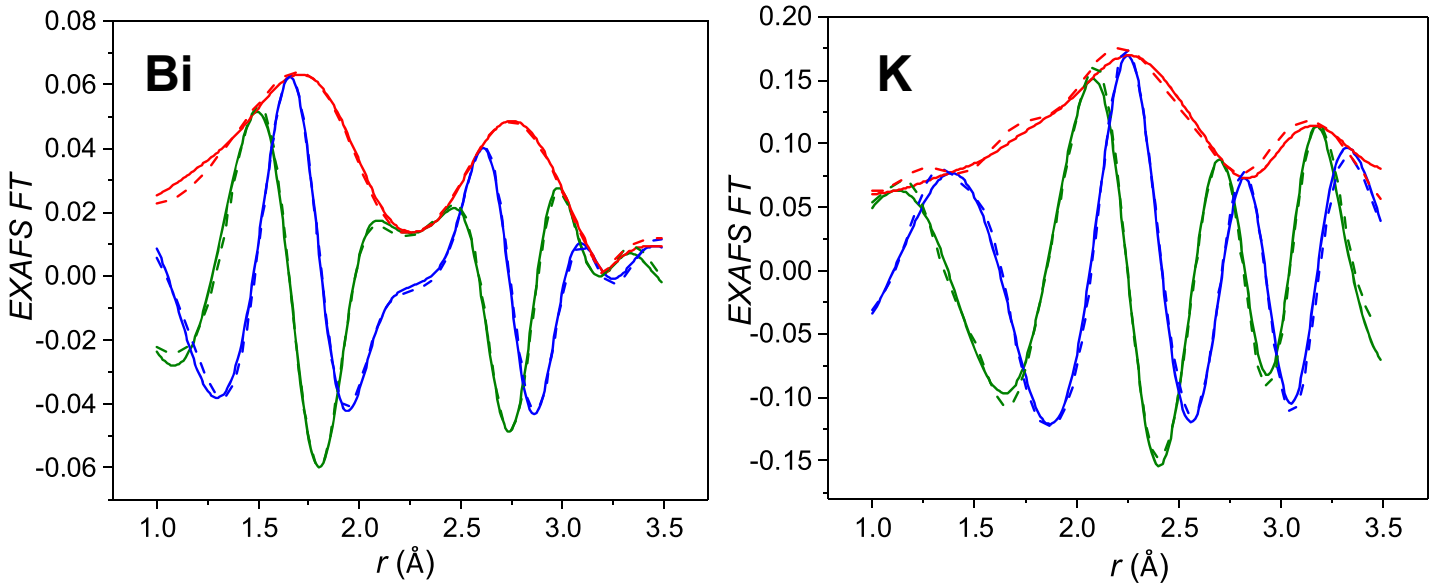
$K_{0.5}Bi_{0.5}TiO_3$



simultaneous RMC refinement

expt. dashed
calc. solid

magnitude
real part
imaginary part

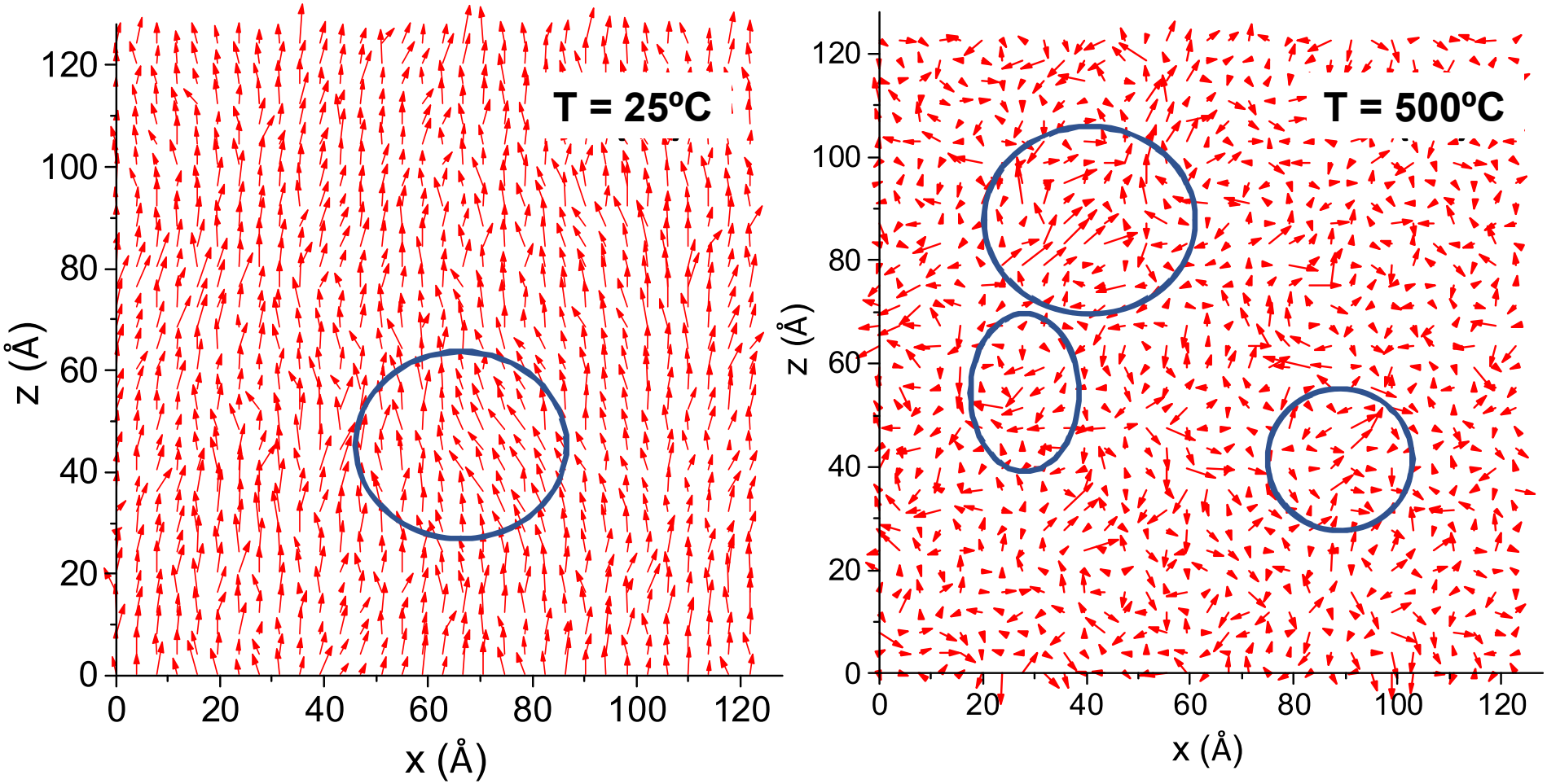
EXAFS
FT ≈ 3 - 11 Å^{-1}

*"The presence of **at least some discrepancies** between the experimental and calculated signals is expected given the inevitable systematic errors in each dataset plus those introduced by the assumptions (e.g., data weighing) involved in data fitting."*

I. Levin et al., Chem. Matter 31 (2019) 2450

$K_{0.5}Bi_{0.5}TiO_3$

Bi displacements



encircled areas of displacement correlations ≈ "**nanodomains**"

I. Levin et al., Chem. Matter 31 (2019) 2450

PMN revisited (2019)

nature COMMUNICATIONS

ARTICLE

https://doi.org/10.1038/s41467-019-10665-4 OPEN

Local atomic order and hierarchical polar nanoregions in a classical relaxor ferroelectric

M. Eremenko[1], V. Krayzman[1], A. Bosak[2], H.Y. Playford[3], K.W. Chapman[4], J.C. Woicik[1], B. Ravel[1] & I. Levin[1]

Experimental data

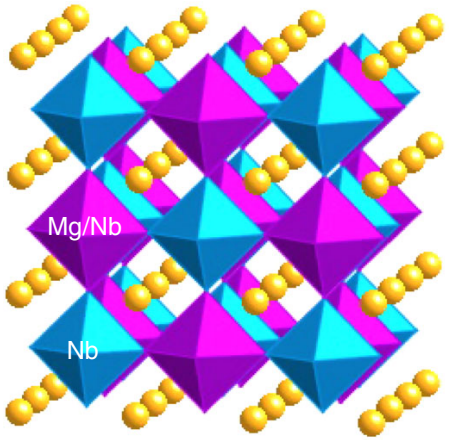
- neutron total scattering - powder, POLARIS (ISIS)
- SR total scattering – powder, 11-ID-B (APS)
- SR diffuse scattering - single crystal, ID29 (ESRF)
- EXAFS – Pb-L_3 & Nb-K edges, BL06 (NSLS-II)
- electron microscopy – SEM & TEM (300kV)

Analysis & modelling

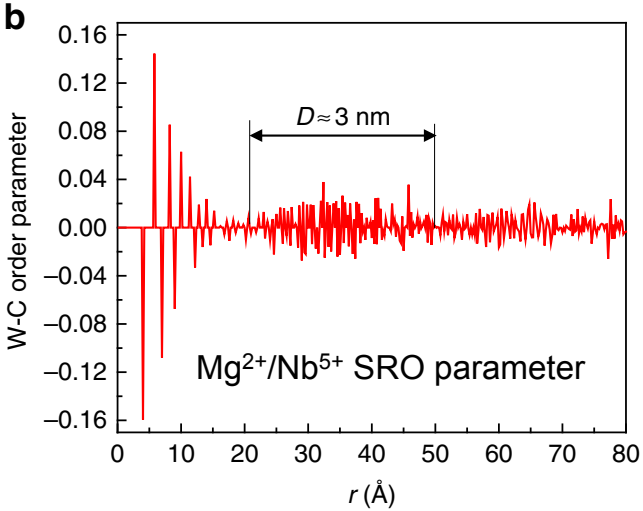
- standard data reduction software
- joint reverse MC structure refinement
- supercell 40x40x40 cells (320 000 atoms)
- RMCProfile software (dev version)
- extensive use of GPU computing

PMN revisited (2019)

fcc 1:1
Mg^{2+}/Nb^{5+}
clusters



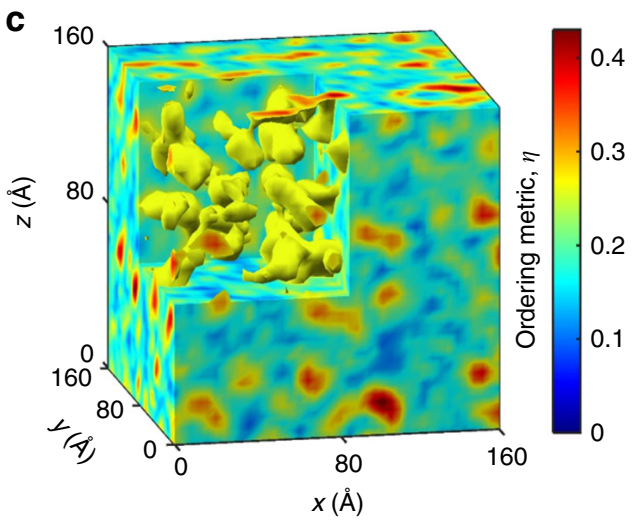
chemical Mg^{2+}/Nb^{5+} short-range order

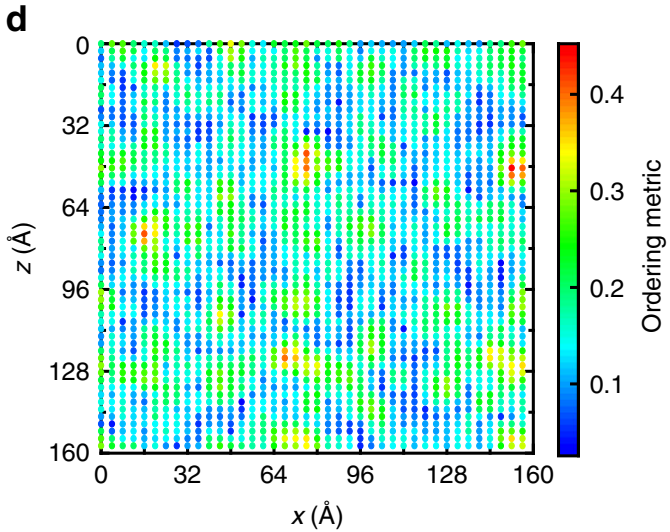


simple model:
sphere (R) of 1:1 (Mg^{2+} : Nb^{5+}) composition
covered by a $PbNbO_3$ shell (d)
having volumes 2:1

d/R = 0.145 ≈ 1/7

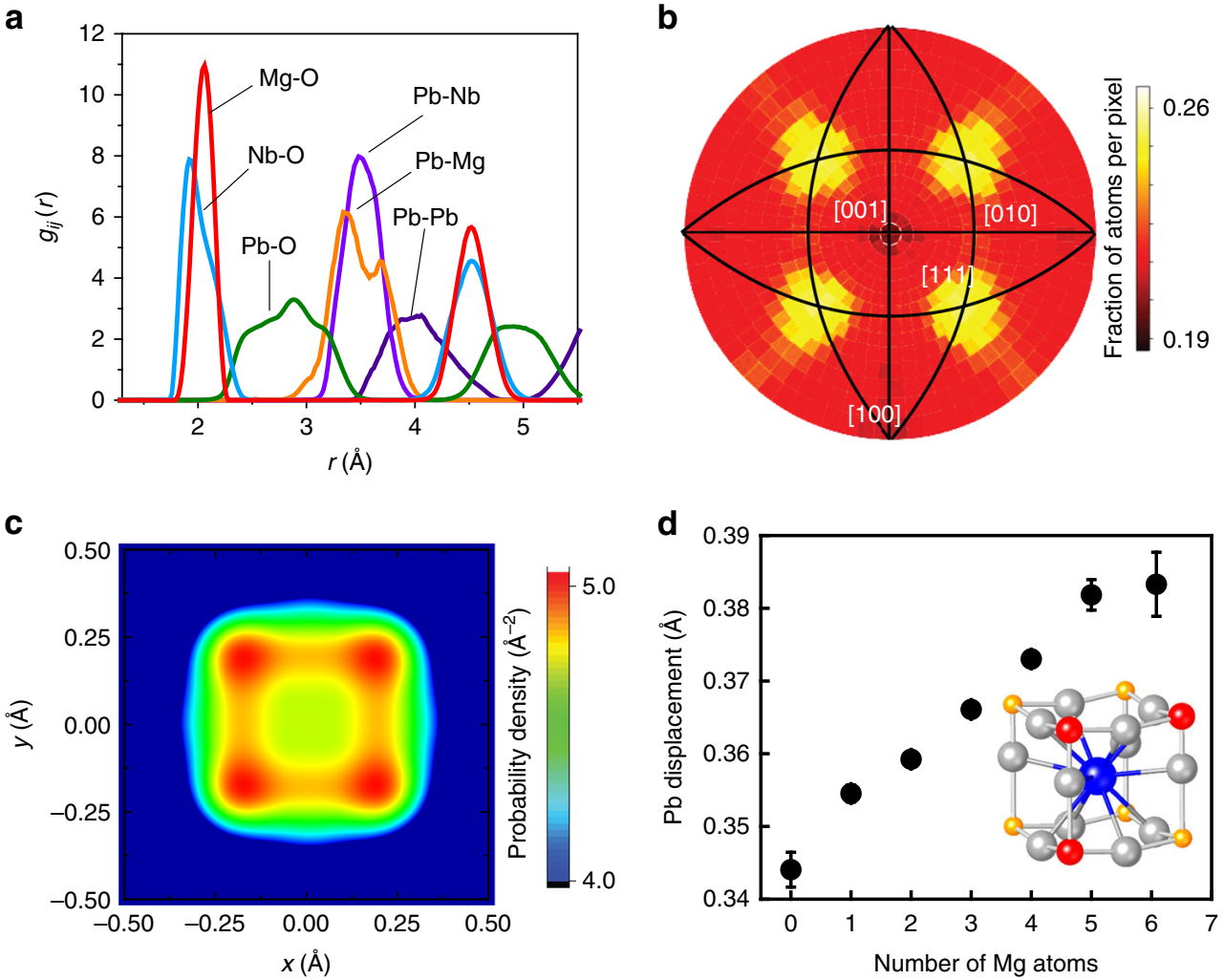
not much scope for true Nb^{5+} matrix with electric fields





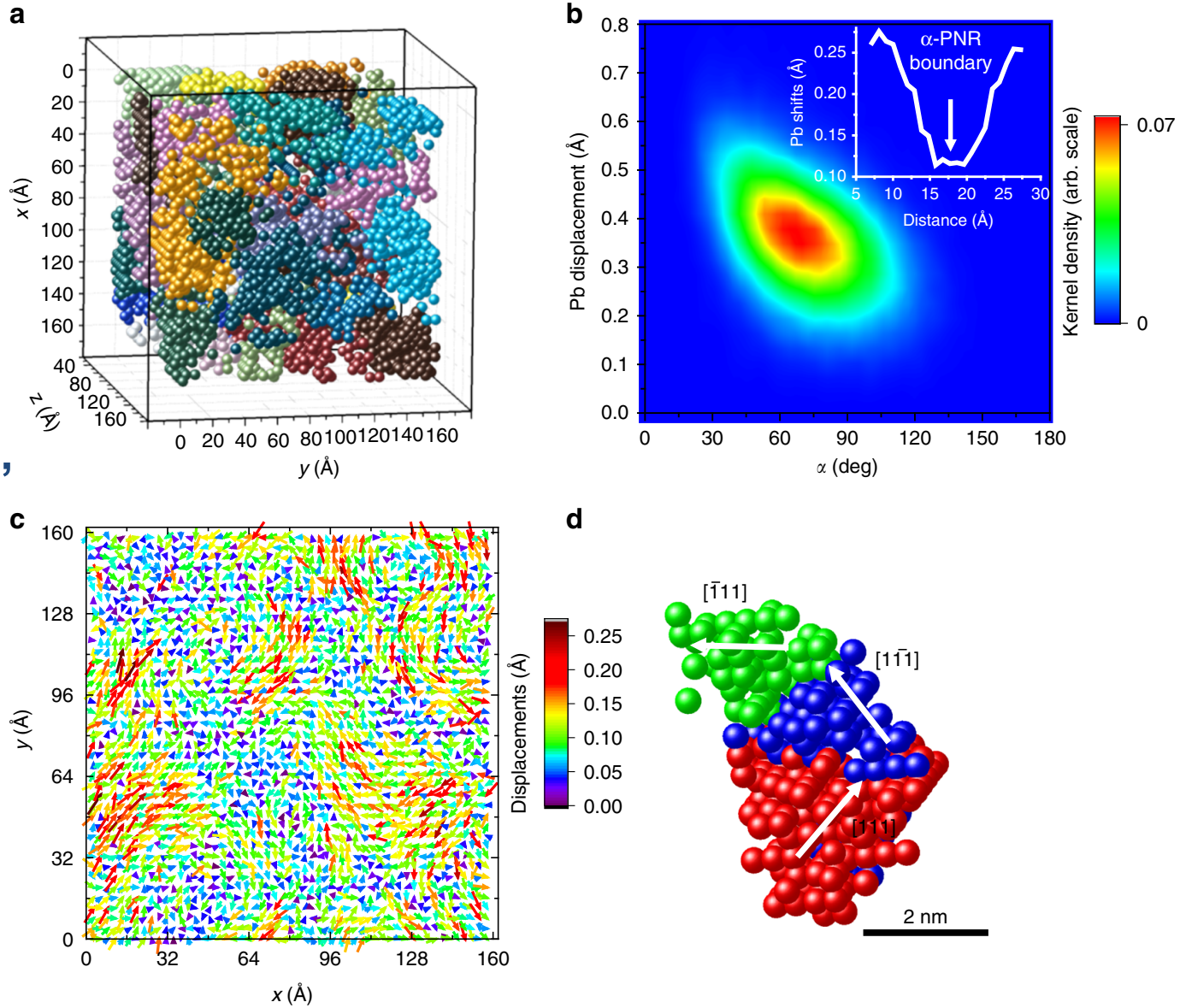
PMN revisited (2019)

Pb displacements



PMN revisited (2019)

“polar nanodomains”



NEUTRONS FOR SOCIETY

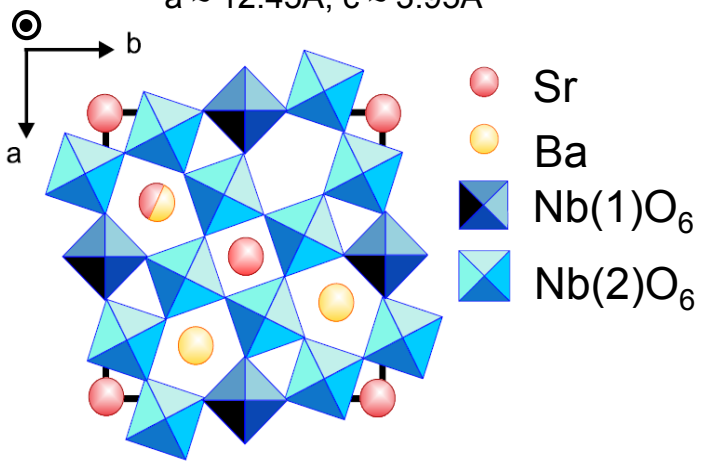
Talk outline

1. Introduction (motivation)
2. Elements of scattering theory
3. Experimental aspects
4. **Interpretation**
   - intuitive (qualitative) analysis
   - reverse MC structure reconstruction
   - **molecular dynamics simulation**
5. Concluding remarks

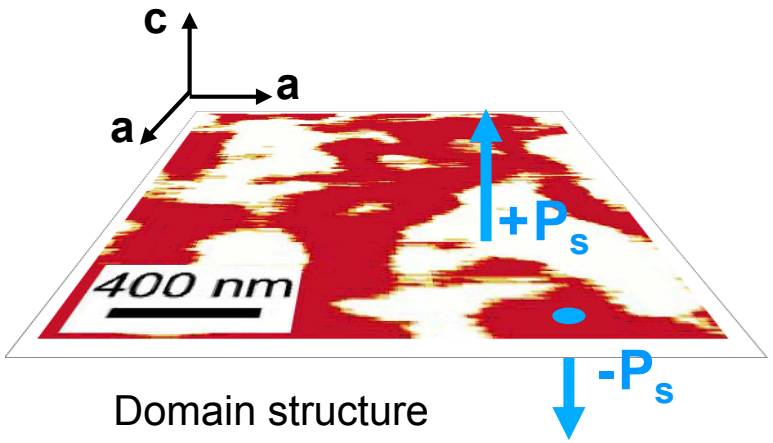
SBN - uniaxial relaxor

$Sr_{0.5}Ba_{0.5}Nb_2O_6$ (SBN-50)

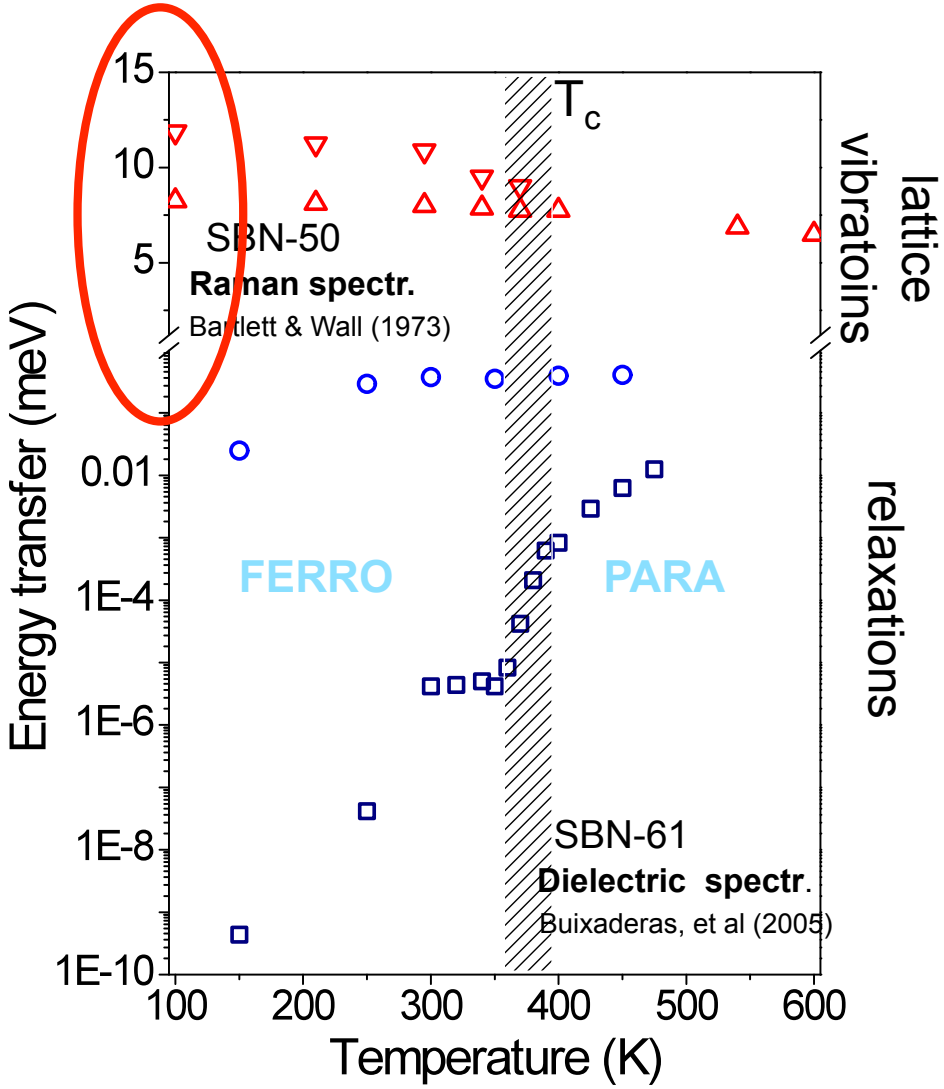
a ≈ 12.45Å, c ≈ 3.95Å



tetragonal tungsten bronze



Domain structure
(T = 300K)



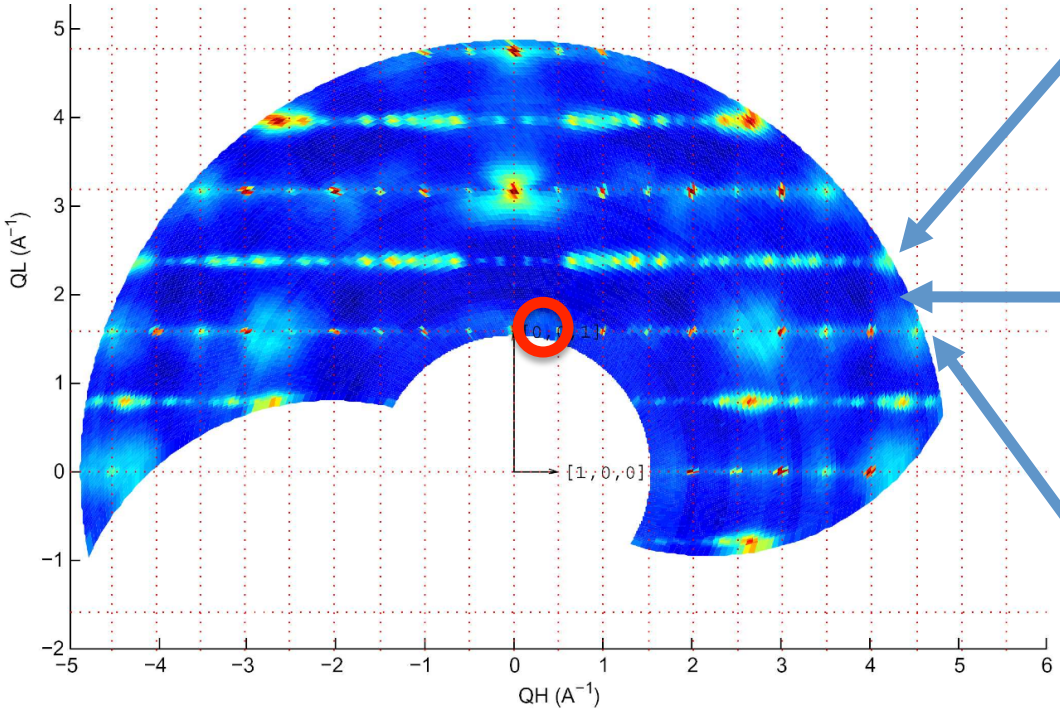
P. Ondrejkovic et al. PRL 113, 167601 (2014)

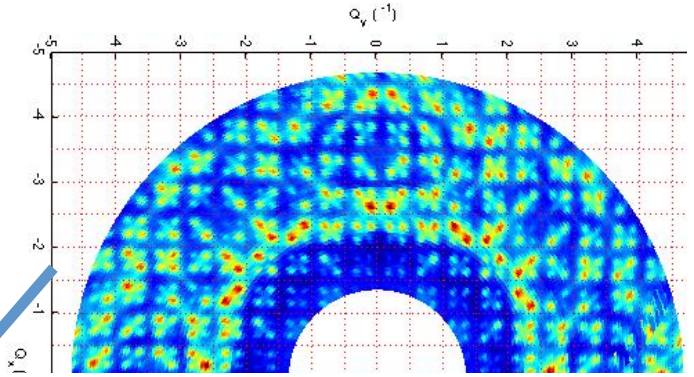
SBN - uniaxial relaxor

SBN-50

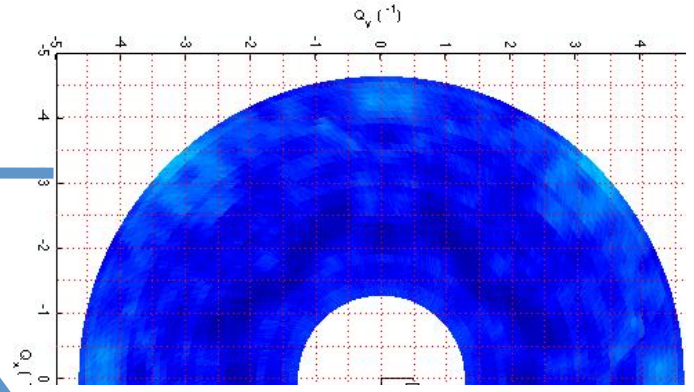
neutron diffuse scattering
(single crystal)

(h 0 l)

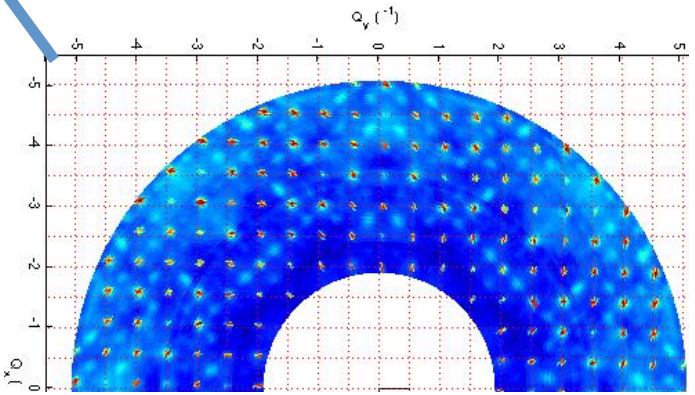




(h k 0.5)



(h k 0.25)



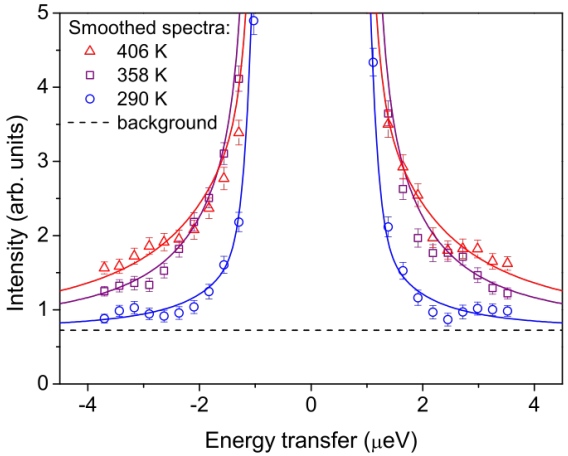
(h k 0)

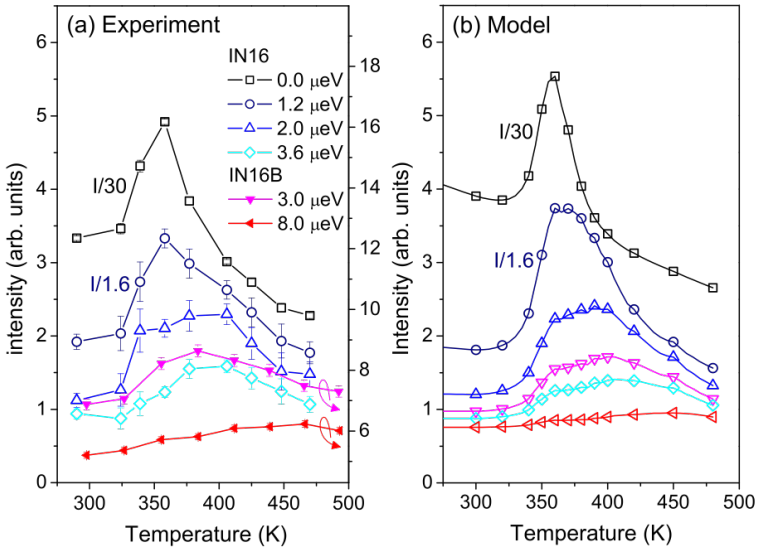
IN20 FC

ΔE = 0 meV, T = 300 K

Relaxation dynamics

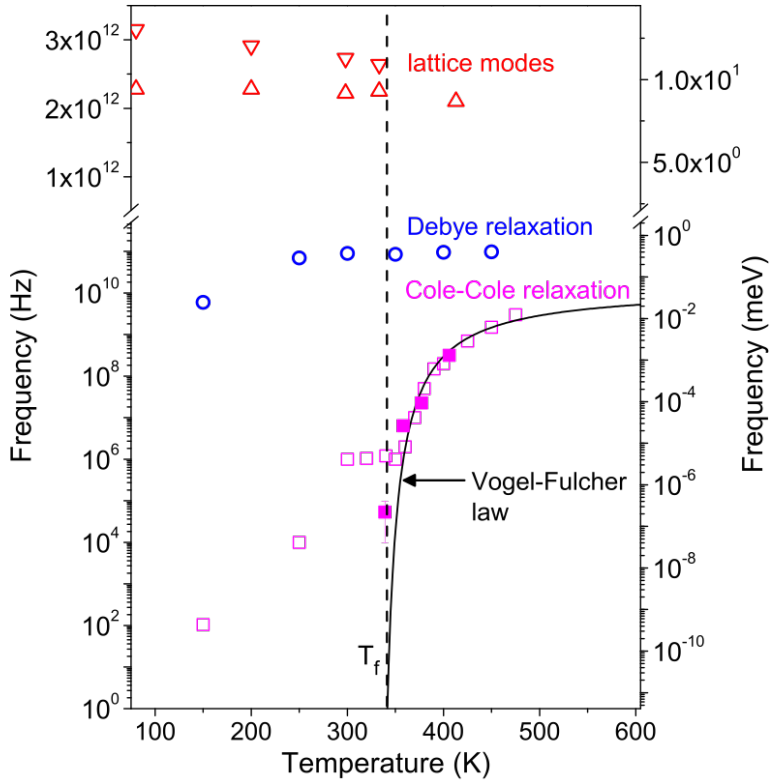
Backscattering (IN16)





$Sr_{.61}Ba_{.39}Nb_2O_6$

(uniaxial relaxor)



non-Arrhenius behaviour

P. Ondrejkovic et al. PRL 113, 167601 (2014)

SBN @ D4

D4

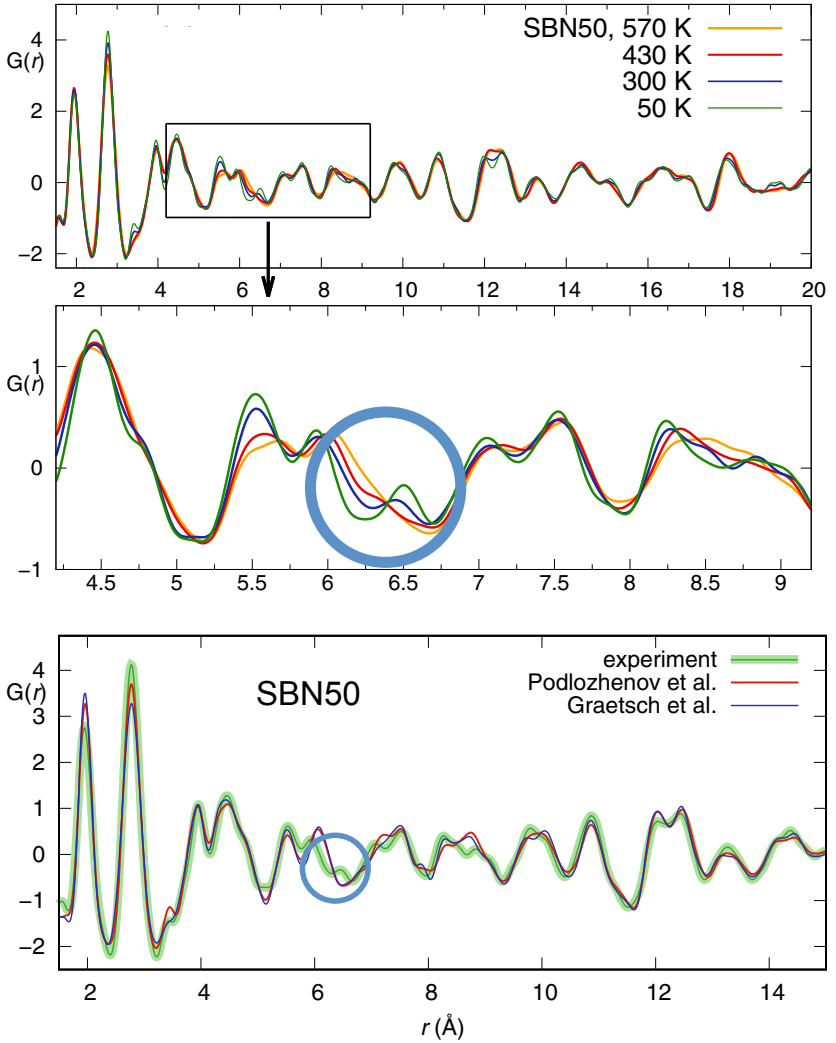
λ = 0.5 Å
Q = 0.3 – 23.5 Å^{-1}

observed G(r)

G(r) detail

$$G(r) = K\frac{2}{\pi}\int_0^{Q\,\max} Q\left[S(Q)-1\right]\sin(Qr)\,dr$$

T = 300K
comparison to reported structures (average *Pb4m* etc.)

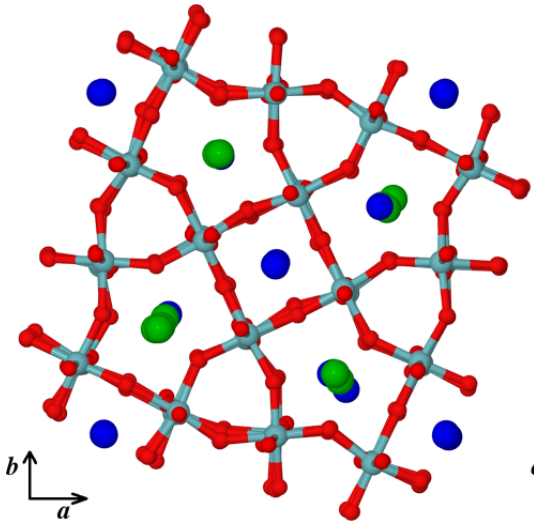


M. Pasciak et al., Phys. Rev. B 99 (2019) 104102

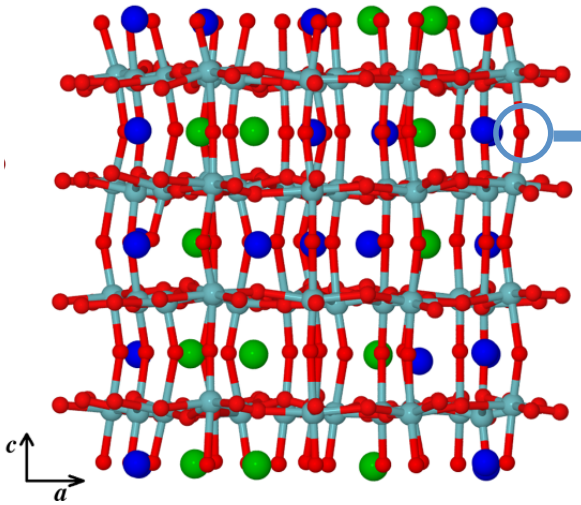
SBN50

ab-initio molecular dynamics

(*SIESTA*, 2x2x8 supercell)



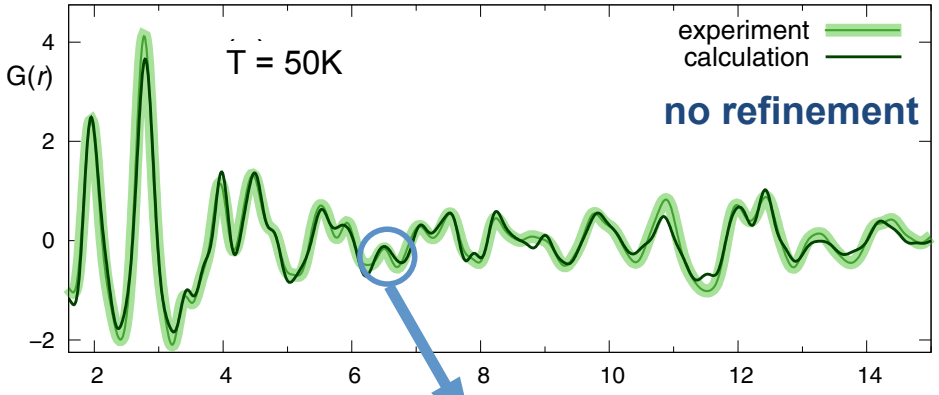
optimized unit cell

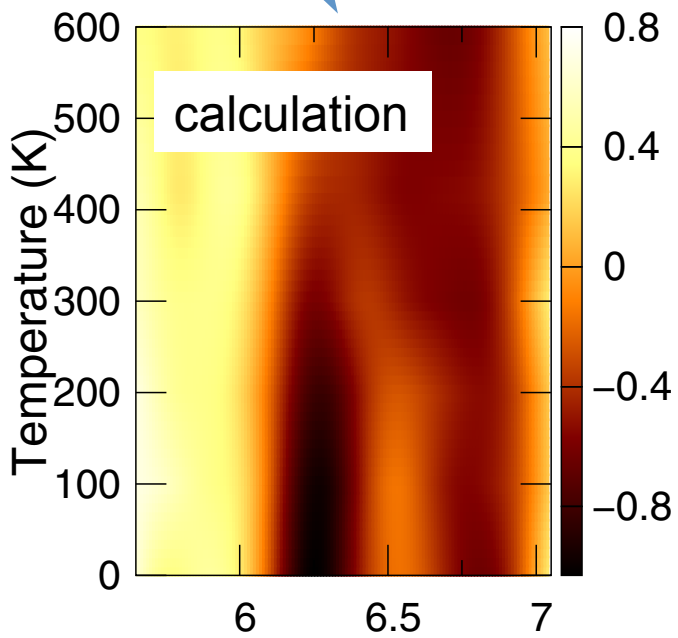


buckling of

apical oxygens

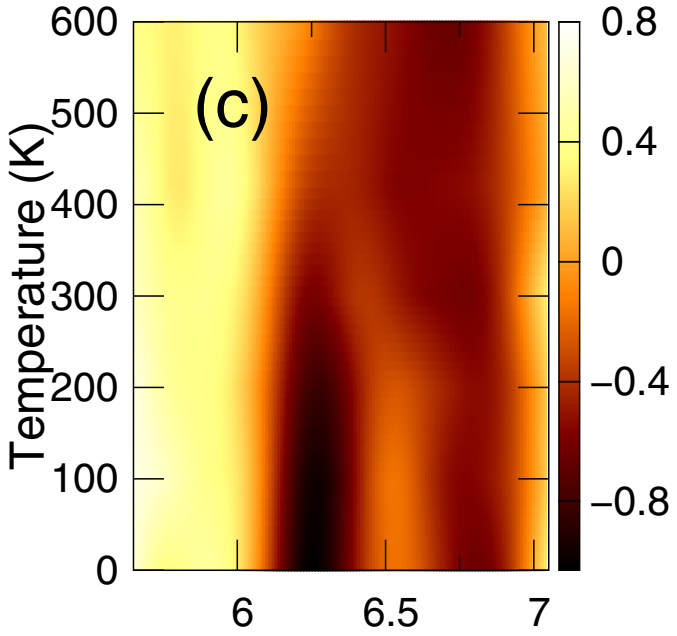
PDF

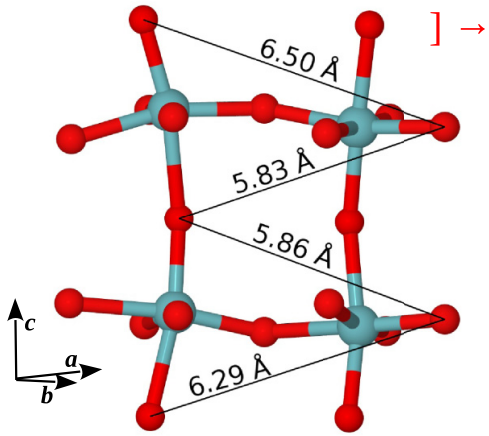




M. Pasciak et al., Phys. Rev. B 99 (2019) 104102

SBN50

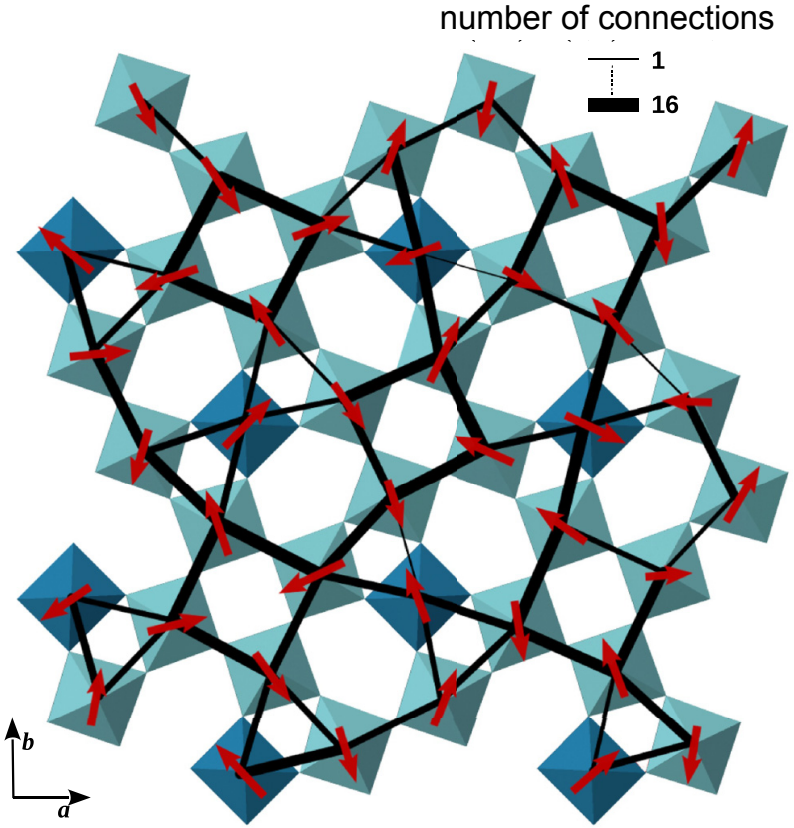




] → apical

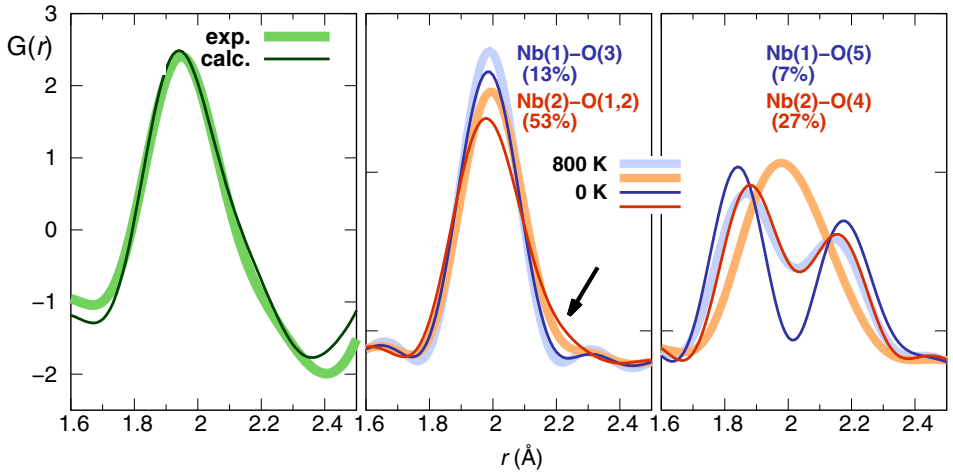
] → equatorial

octahedral tilts

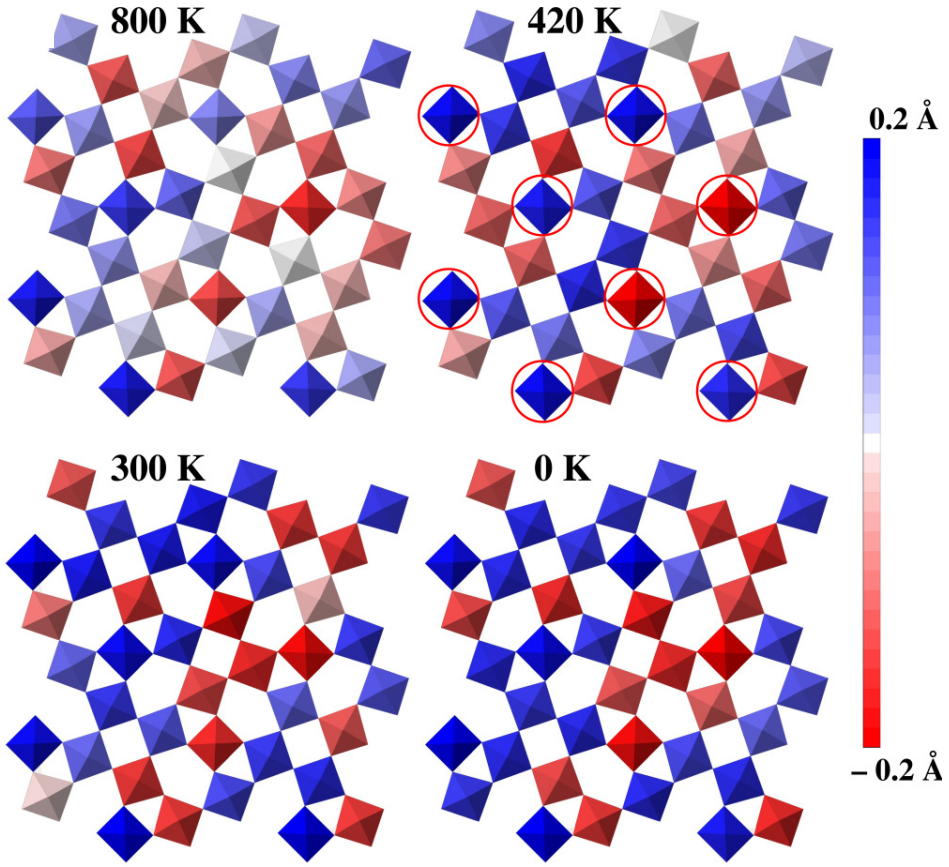


M. Pasciak et al., Phys. Rev. B 99 (2019) 104102

SBN50



Nb displacements
inside octahedra



local polarisation

M. Pasciak et al., Phys. Rev. B 99 (2019) 104102

NEUTRONS FOR SOCIETY

Concluding remarks

- PDF analysis is a powerful tool to characterise ill ordered structures
- simple & intuitive for simple systems
- complex scenarios call for modelling efforts
- recent advances in computing open new avenues

T. Egami and S. J. Billinge
Underneath the Bragg Peaks: Structural Analysis of Complex Materials
Elsevier, New York, 2003

R.B. Neder, T. Proffen
Diffuse scattering and defect structure simmulations
(A cookbook using the program DISCUS)
IUCr & Oxford University Press, 2008