Avoiding the Warren, Krutter and Morningstar approximation* in PDF analysis

Olivier MASSON, Philippe THOMAS
IRCER, UMR 7315 CNRS-Université de Limoges

ADD 2019 Conference
Grenoble
17-22 March 2019

* B. E. Warren, H. Krutter and O. Morningstar, J. Am. Ceram. Soc. **19** (1936), 202

Outline of the talk

- The Warren, Krutter and Morningstar (WKM) approximation
- How to easily avoid the WKM approximation using a simple expression
- The effect of the WKM approximation on the PDF peak shape and the refined structural parameters
- An example of PDF analysis without the WKM approximation: the local structure of apatite-type lanthanum silicates ($La_{9.50}(SiO_4)_6O_{2.25}$)

The PDF of multi-component systems

(Total) PDF → $G(r) = \sum_{\alpha,\beta} \gamma_{\alpha\beta}\, G_{\alpha\beta}(r)$ ← partial PDFs

Normalized Faber-Ziman coefficients* ($\sum_{\alpha,\beta} \gamma_{\alpha\beta} = 1$)

Atom fraction, Neutron scattering length

Neutron TS: $\gamma_{\alpha\beta} = \dfrac{c_\alpha c_\beta b_\alpha b_\beta}{\langle b \rangle^2}$ are constant terms and the decomposition of G(r) is exact

Atomic scattering factor

X-ray TS: $\gamma_{\alpha\beta} = \dfrac{c_\alpha c_\beta f_\alpha(Q) f_\beta(Q)}{\langle f(Q) \rangle^2} = \gamma_{\alpha\beta}(Q) \cong \gamma_{\alpha\beta}^{eff}$

WKM approximation

In practice:

$\gamma_{\alpha\beta}^{eff}$ is often set equal to $\gamma_{\alpha\beta}(0)$

$G(r) \cong \sum_{\alpha,\beta} \gamma_{\alpha\beta}(0)\, G_{\alpha\beta}(r)$

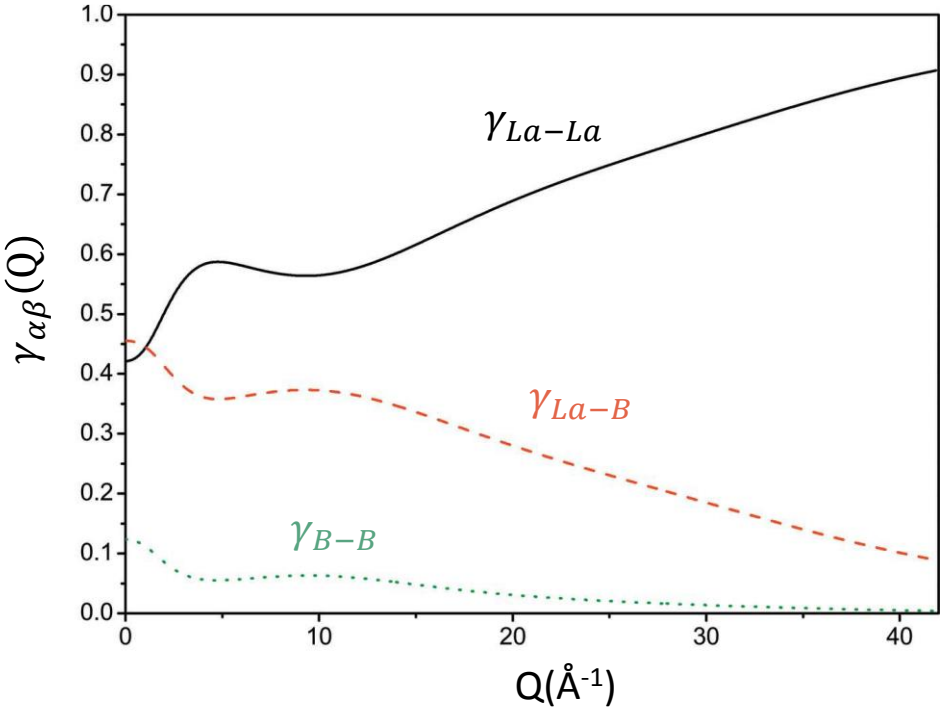
* T. E. Faber and J. M Ziman, Phil. Mag. **11** (1965), 153

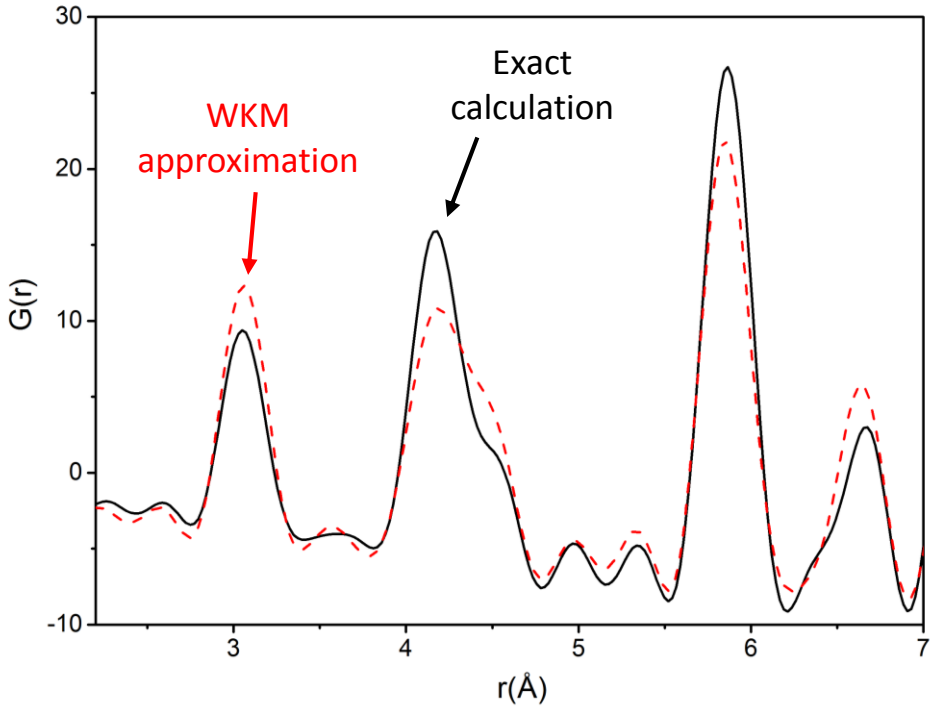
T. Egami and S. J. L. Billinge Underneath the Bragg Peaks, Pergamon Materials Series (2012)

The drawbacks of the WKM approximation:

- It is not defined in a unique way,
- Its accuracy is unknown,
- it can introduce significant errors in the calculation of G(r) for materials combining both heavy and light elements (which is common in practice)

Exemple: the case of LaB_6





The PDF is a linear combination of “modified” partial PDFs

$$G(r) = \sum_{\alpha,\beta} a_{\alpha\beta}\, G^X_{\alpha\beta}(r) \quad \text{with} \quad G^X_{\alpha\beta}(r) = G_{\alpha\beta}(r) + \sum_{k=1}^{+\infty} w_{\alpha\beta}(r_k)\left[G_{\alpha\beta}(r-r_k) + G_{\alpha\beta}(r+r_k)\right]$$

$$\begin{cases} a_{\alpha\beta} = \dfrac{1}{Q_{max}} \displaystyle\int_0^{Q_{max}} \gamma_{\alpha\beta}(Q)dQ & \text{with} \quad \displaystyle\sum_{\alpha,\beta} a_{\alpha\beta} = 1 \\ w_{\alpha\beta}(r_k) = \dfrac{\int_0^{Q_{max}} \gamma_{\alpha\beta}(Q)\cos(Qr_k)\,dQ}{a_{\alpha\beta}\, Q_{max}} & \text{with} \quad r_k = \dfrac{\pi}{Q_{max}}k \end{cases}$$

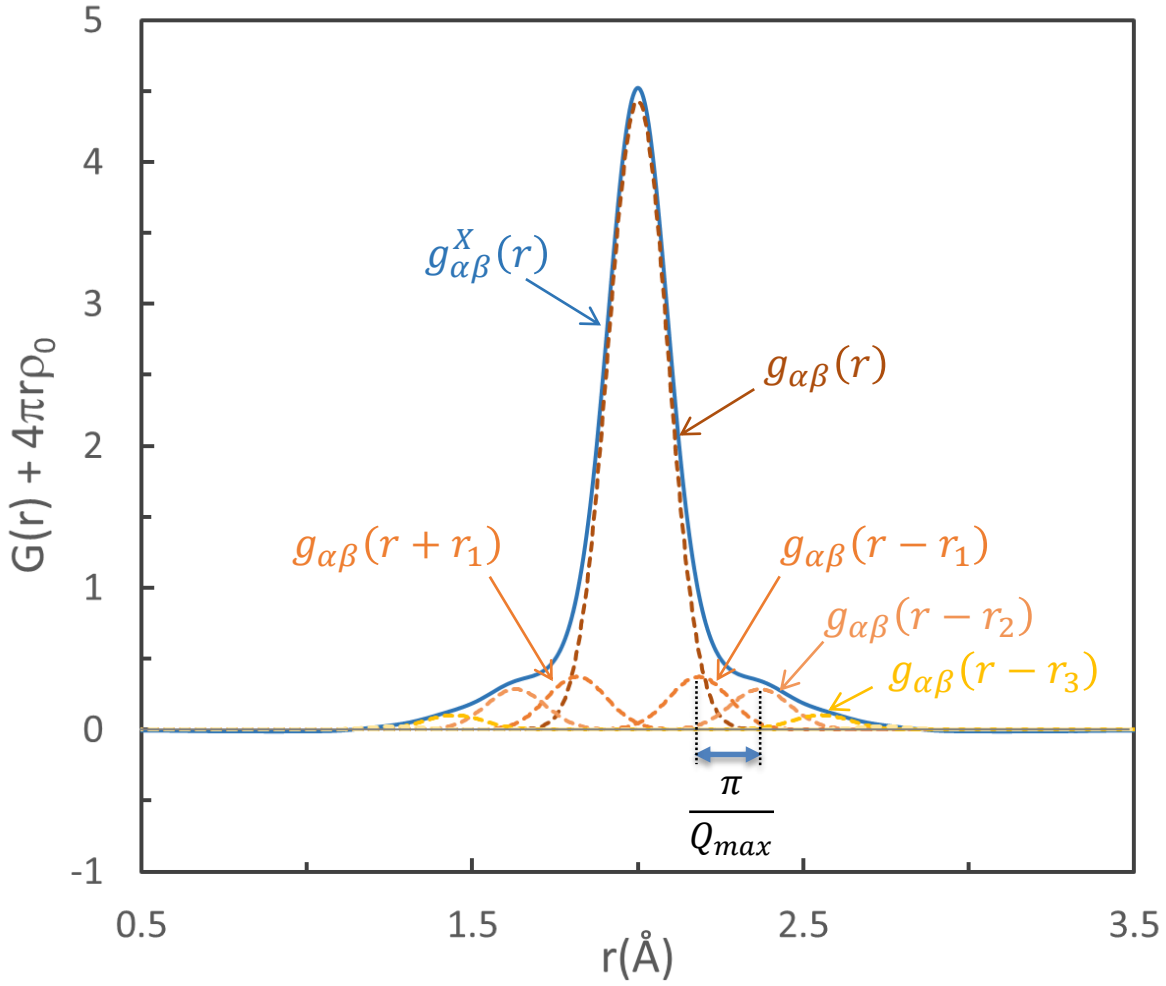
very few terms (N < 10) are necessary to calculate G(r) with great accuracy

In practice : $$G^X_{\alpha\beta}(r) = G_{\alpha\beta}(r) + \sum_{k=1}^{N} w_{\alpha\beta}(r_k)\left[G_{\alpha\beta}(r-r_k) + G_{\alpha\beta}(r+r_k)\right]$$

Masson, O., Thomas, P., *J. Appl. Cryst.* 2013, *46 (2), 461-465.*

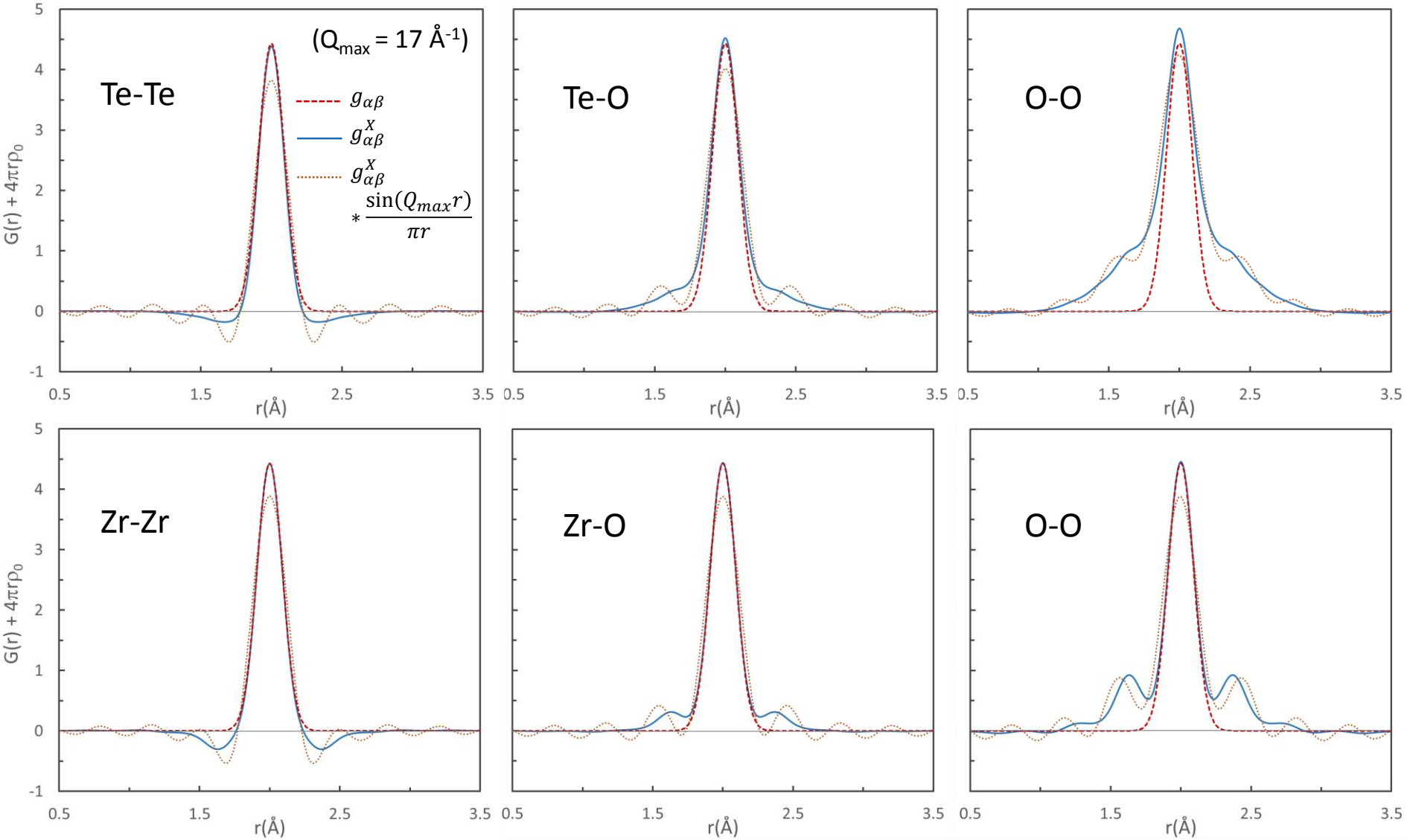
The shape of PDF peaks

A single PDF peak : $g(r) \propto g^X_{\alpha\beta}(r) = g_{\alpha\beta}(r) + \sum_{k=1}^{N} w_{\alpha\beta}(r_k)\left[g_{\alpha\beta}(r-r_k) + g_{\alpha\beta}(r+r_k)\right]$

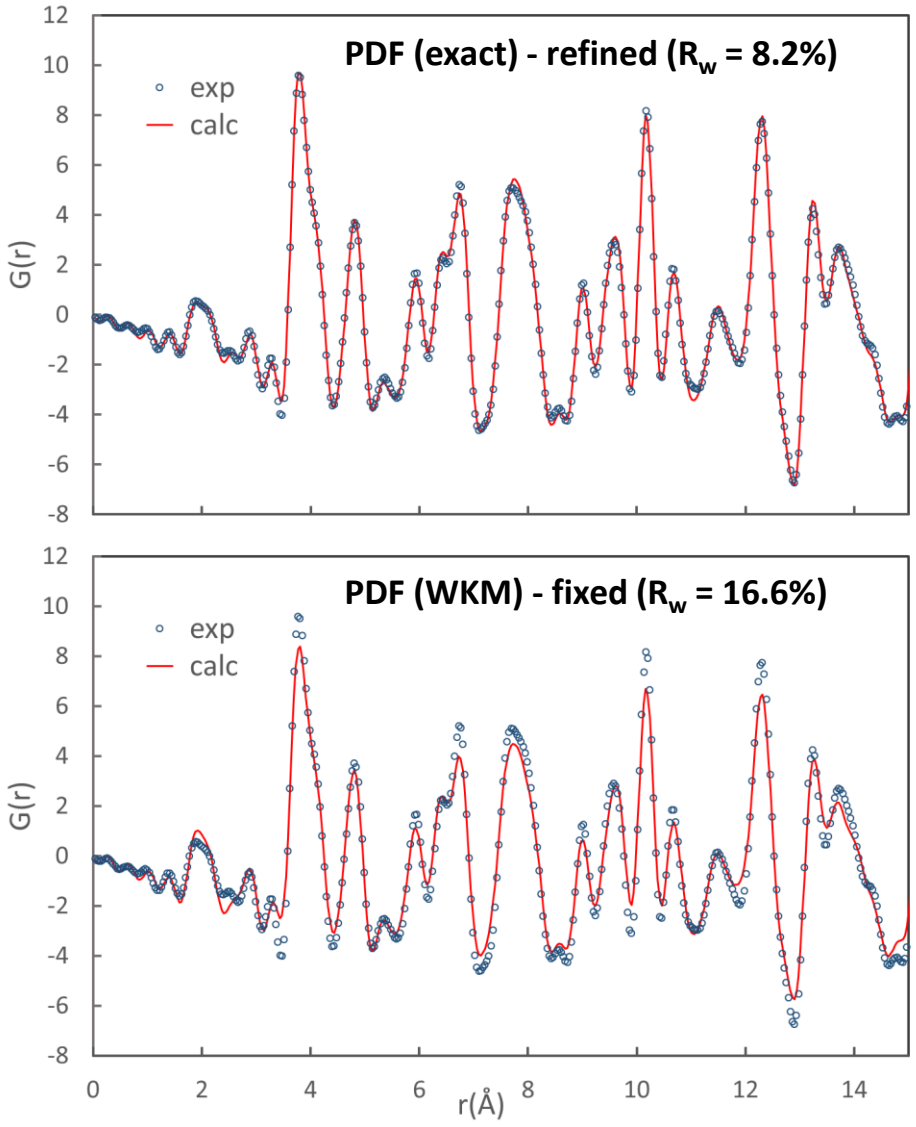


k	$w_{\alpha\beta}(r_k)$
1	0.0842
2	0.0645
3	0.0232
4	0.0050
5	-0.0021
6	-0.0022
7	-0.0019
8	-0.0009
9	-0.0007
10	-0.0002

Some examples of peak shape (TeO_2, ZrO_2)



Structure refinement of α-TeO_2: PDF versus Rietveld

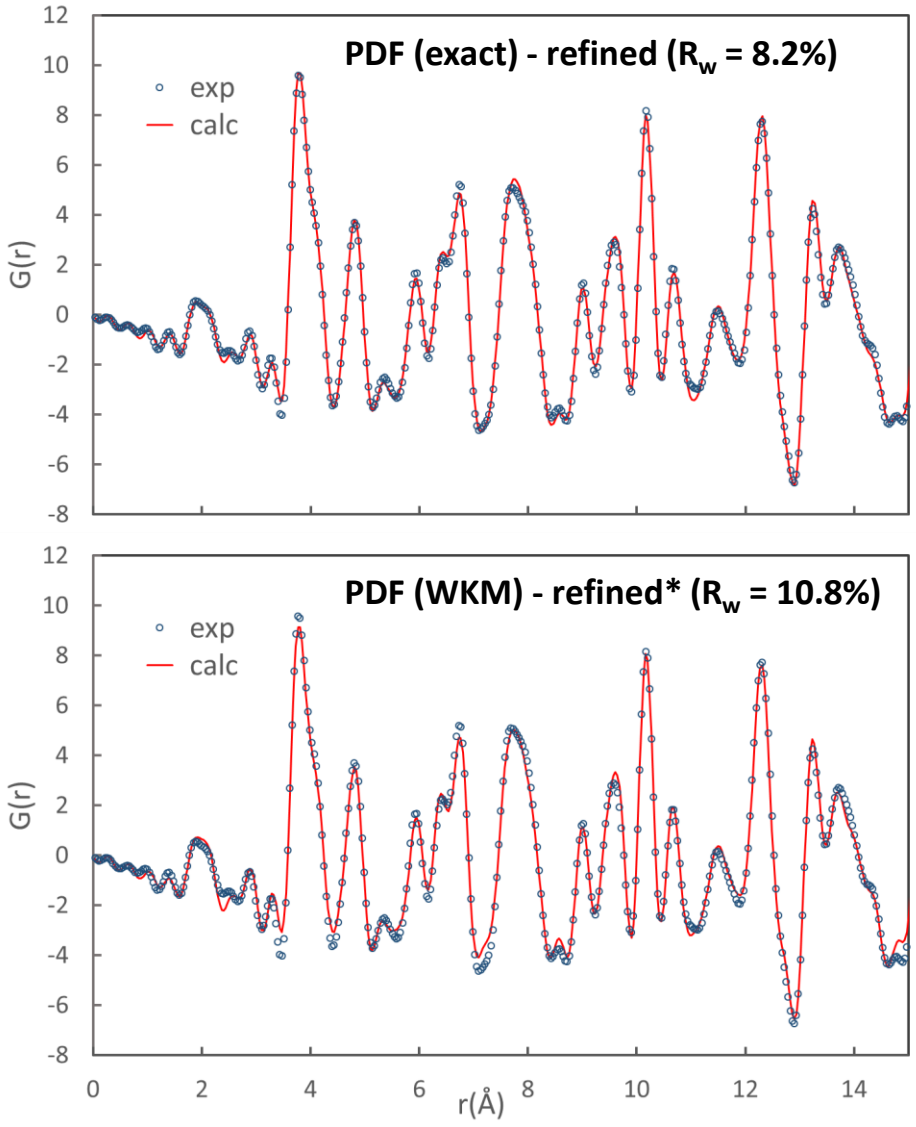


SG: $P4_12_12$ with Te (4a) and O (8b)

PDF (Q_{max} = 17 Å^{-1}), Rietveld (Cu$K\alpha_1$)

	PDF (exact)	PDF (WKM)	Rietveld
a (Å)	4.818		4.808
c (Å)	7.621		7.612
x_{Te}	0.0271		0.0268
x_O	0.1375		0.1386
y_O	0.2590		0.2576
z_O	0.1877		0.1862
U_{iso}(Te) /Å²	0.0071		0.0075
U_{iso}(O) /Å²	0.0128		0.0122

Structure refinement of α-TeO_2: PDF versus Rietveld



SG: $P4_12_12$ with Te (4a) and O (8b)

PDF (Q_{max} = 17 Å^{-1}), Rietveld (Cu$K\alpha_1$)

	PDF (exact)	PDF (WKM)	Rietveld
a (Å)	4.818	4.816	4.808
c (Å)	7.621	7.624	7.612
x_{Te}	0.0271	0.0262	0.0268
x_O	0.1375	0.1390	0.1386
y_O	0.2590	0.2593	0.2576
z_O	0.1877	0.1868	0.1862
U_{iso}(Te) /Å²	0.0071	0.0049	0.0075
U_{iso}(O) /Å²	0.0128	0.0224	0.0122

*PDFgui:
C. L. Farrow et al., *J. Phys.: Condens. Mat.* **19** (2007), 335219

The local structure of apatite-type lanthanum silicates ($La_{9.50}(SiO_4)_6O_{2.25}$): localization of interstitial oxide ions within the conduction channels

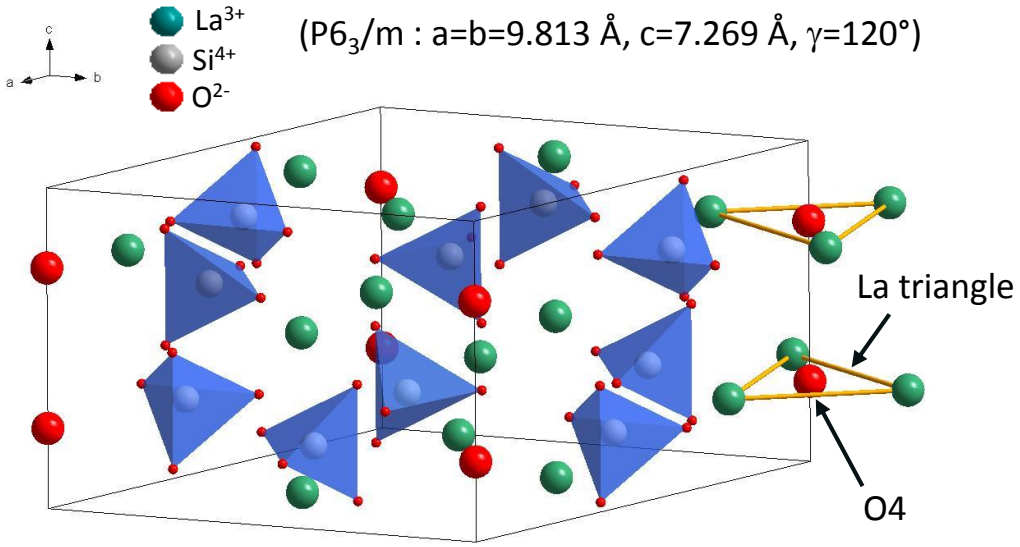
… using precise PDF computation from structure models obtained from DFT (Density Functional Theory) calculations

O. Masson, A. Berghout et al., *Sci. Technol. Adv. Mater., 2017, 18, 644-653*

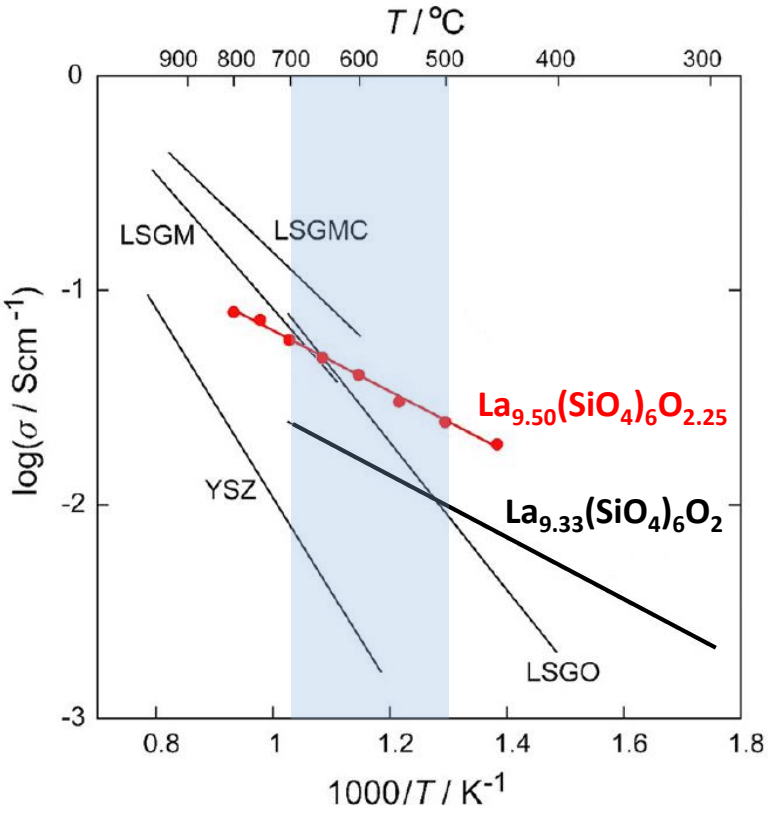
Apatite-type lanthanum silicates

$La_{9.33}\square_{0.67}(SiO_4)_6O_2$ (reference compound)

($P6_3/m$: a=b=9.813 Å, c=7.269 Å, γ=120°)



Unit cell perspective view



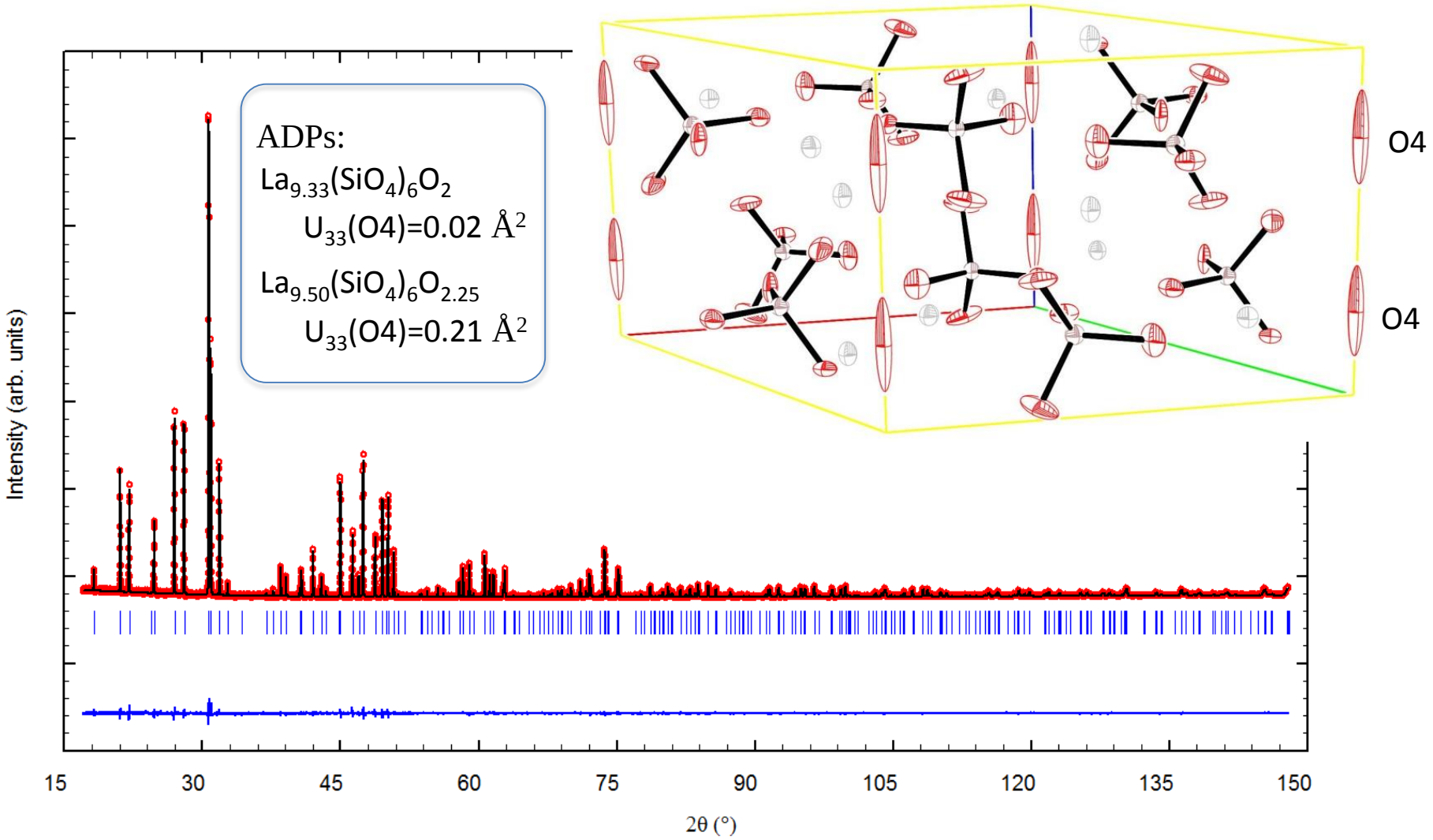
❑ Conductivity can be strongly stimulated by introducing excess oxide-ions in the structure (i.e. x>0 in $La_{9.33+0.67x}(SiO_4)_6O_{2+x}$)

❑ The oxide ion conduction may proceed via an interstitialcy mechanism*

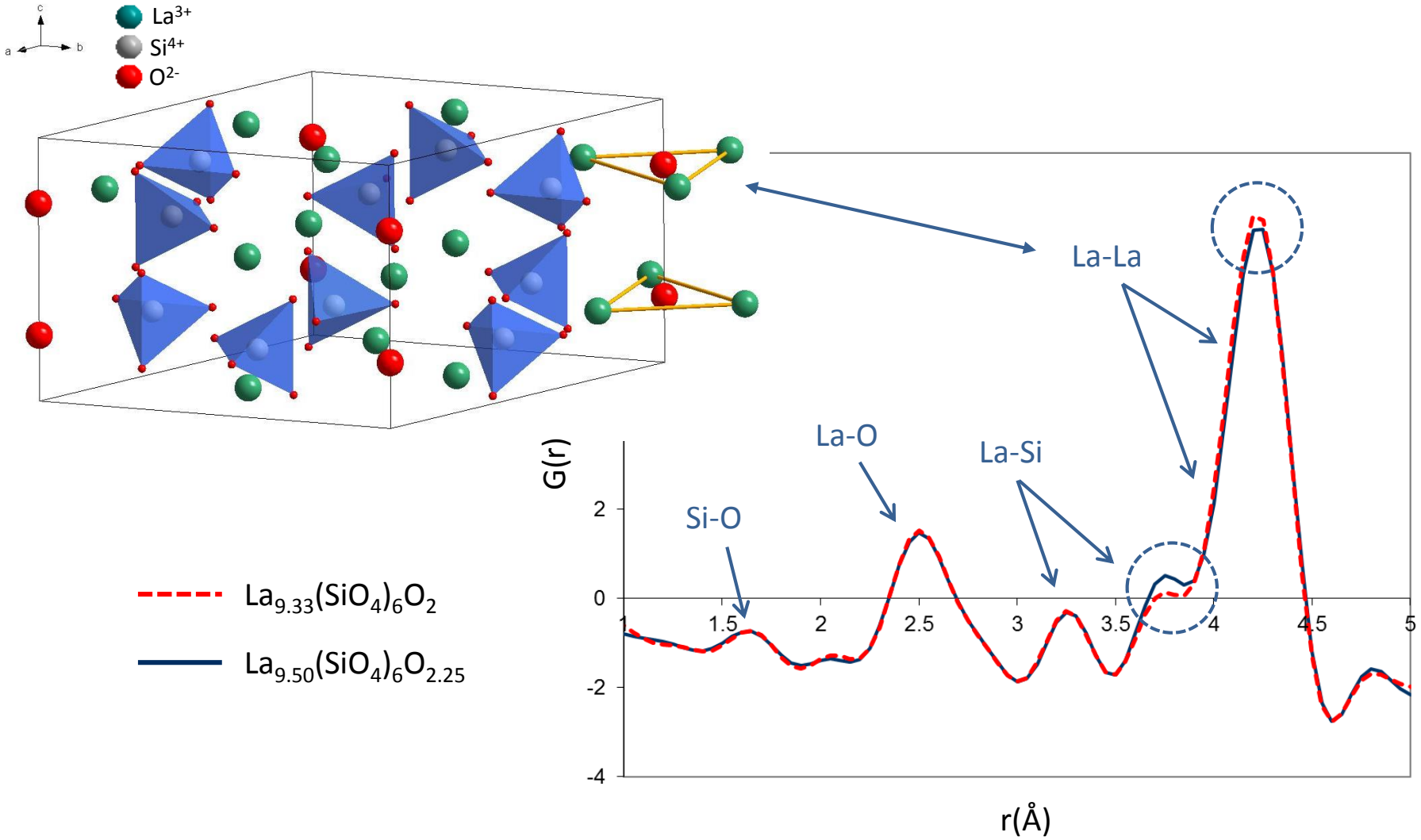
Where are the interstitial/excess oxide ions localized ?

* Béchade, E., Masson et al., Chem. Mater. 2009, 21, 2508-2517

XRD Rietveld refinement of the average structure ($P6_3/m$)



PDF (X-ray TS) of the $La_{9.33}(SiO_4)_6O_2$ and $La_{9.50}(SiO_4)_6O_{2.25}$ samples



Construction of the structure models: methodology

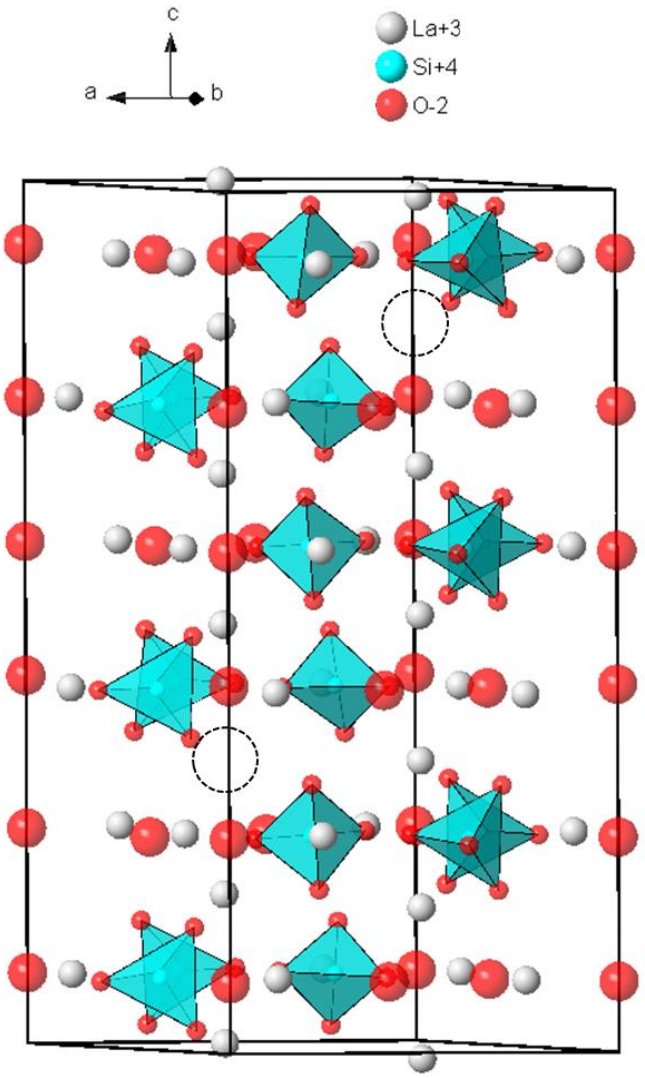
- Construction of supercells:
  - $La_{9.33}(SiO_4)_6O_2$ model : (1x1x3) supercell (124 atoms)
  - $La_{9.50}(SiO_4)_6O_{2.25}$ model : (1x1x4) supercell (167 atoms)
    - with O_i within the conduction channel
    - with O_i at the periphery of the conduction channel

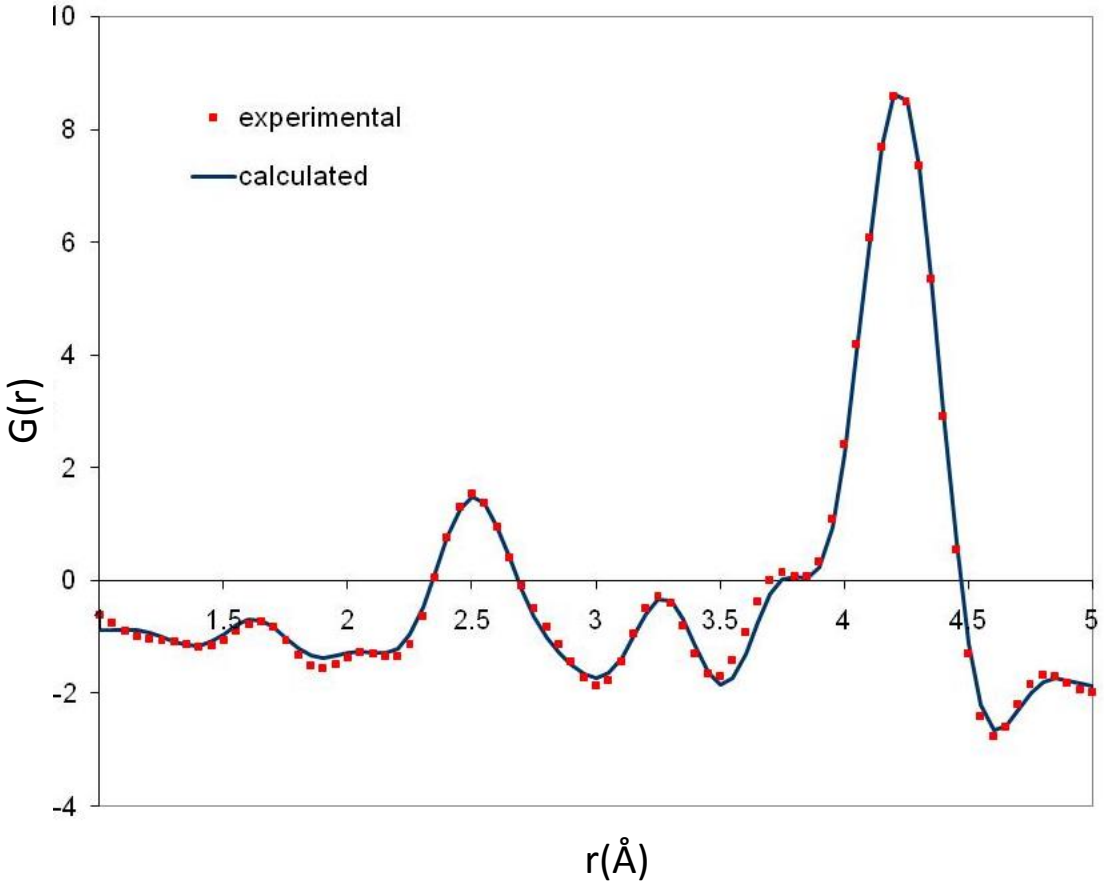
- Structure relaxations based on the Density Functional Theory (DFT):
  - VASP code, plane wave – pseudopotential, GGA PW91 functional
  - The metric of the cells was constrained (a=b, α=β=90°, γ=120°) during the DFT cycles

- Calculation of the corresponding PDF by taking into account:
  - The a and b cell parameters were adjusted to the experimental values
  - A small isotropic displacement parameter was added for each kind of atoms in the model
  - The PDF was calculated precisely, i.e. without the WKM approximation, using the partial PDFs calculated with PDFgui*.

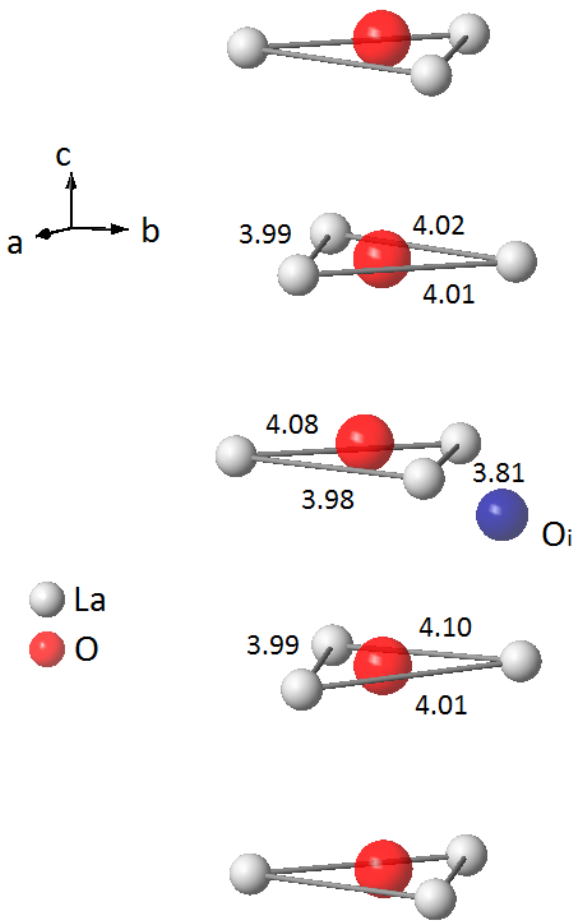
*PDFgui: C. L. Farrow et al., *J. Phys.: Condens. Mat.* **19** (2007), 335219

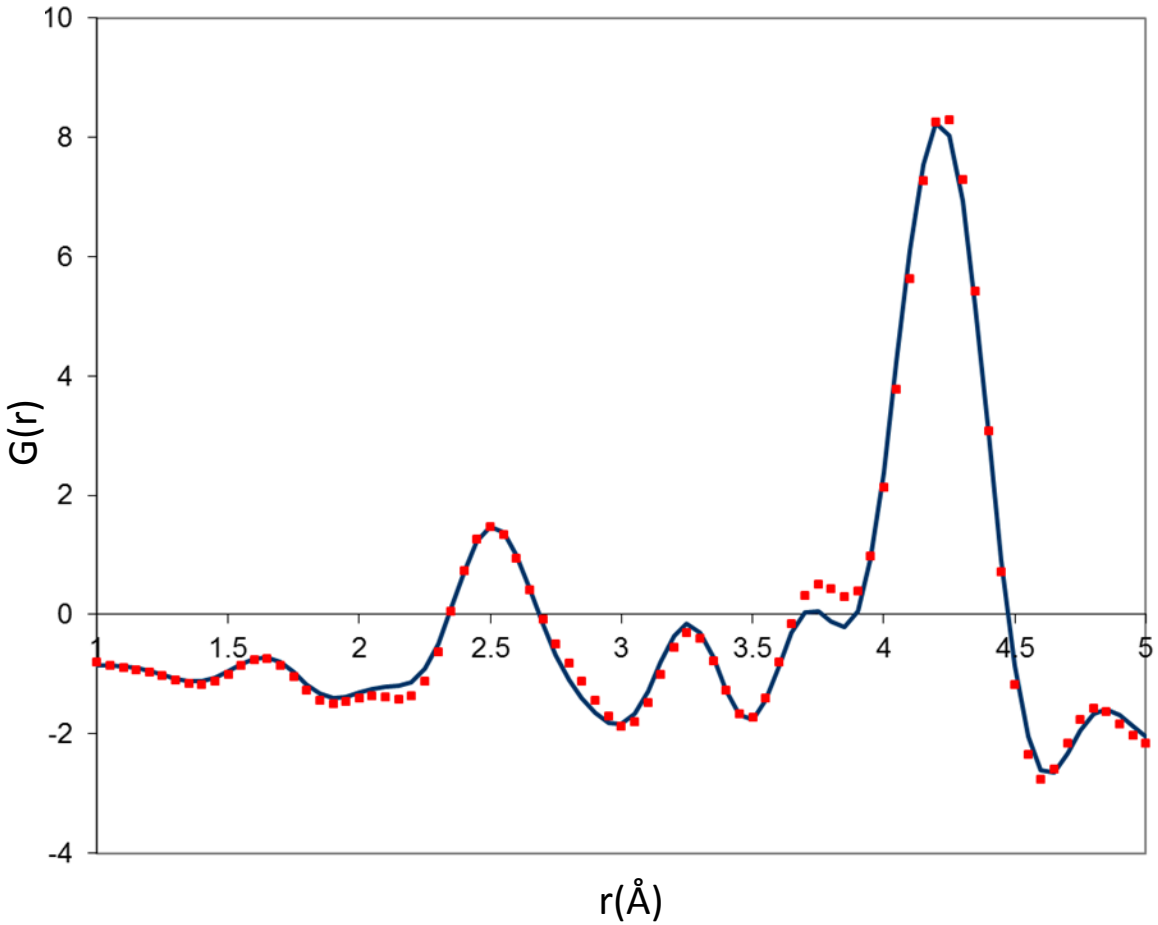
$La_{9.33}(SiO_4)_6O_2$: DFT model / experiment



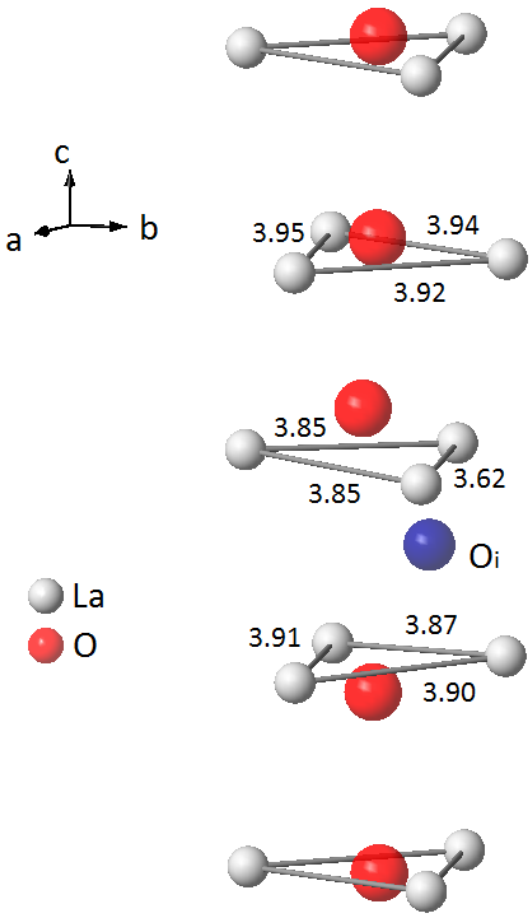


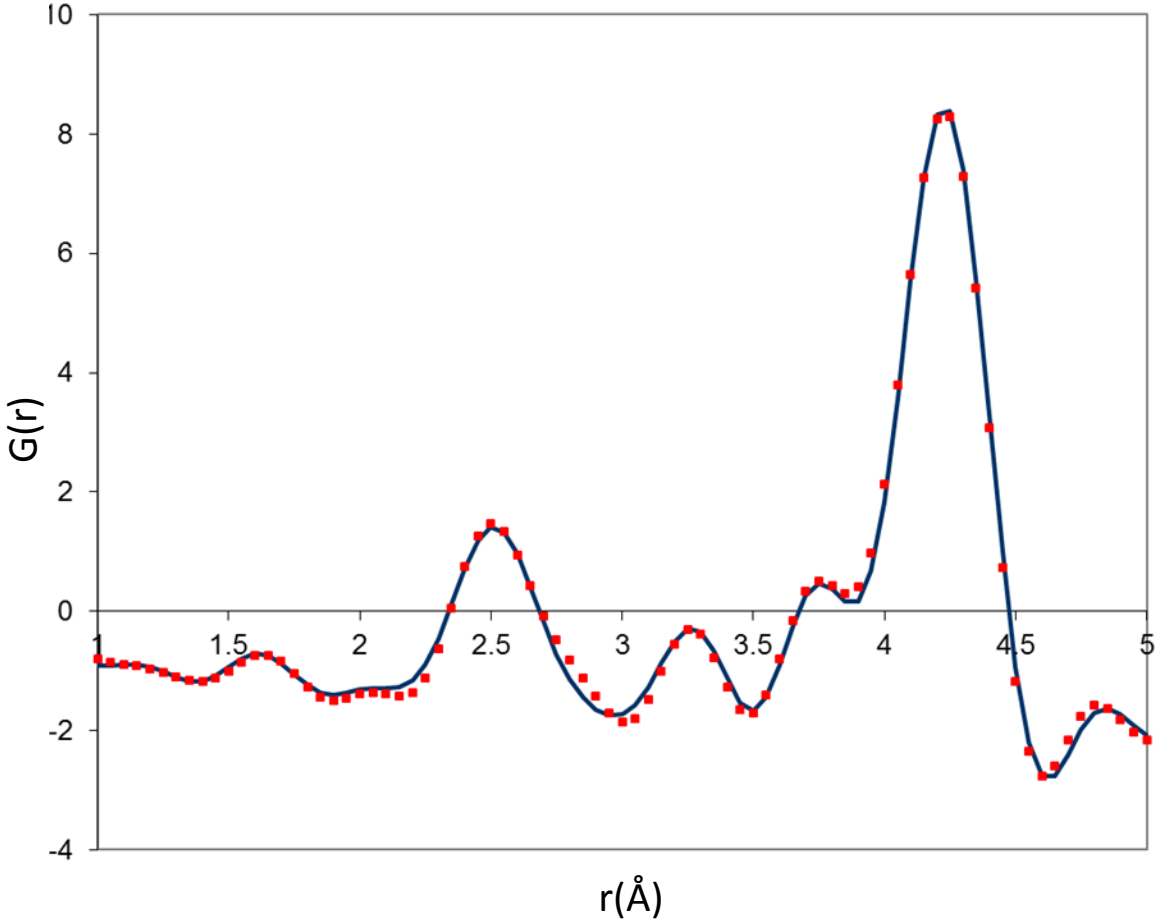
Calculated / experimental for $La_{9.50}(SiO_4)_6O_{2.25}$ DFT model with O_i at the periphery of the conduction channel





Calculated / experimental for $La_{9.50}(SiO_4)_6O_{2.25}$ DFT model with O_i within the conduction channel





$La_{9.50}(SiO_4)_6O_{2.25}$ DFT model – Anisotropic displacement parameters

	U11	U22	U33	U12	U13	U23
La1	0.2	0.2	2.2	0.1	0	0
La2	0.3	0.2	0.8	-0.1	0	0
Si1	0.2	0.2	0.2	0.2	0	0
O1	1.3	1.6	2.1	1.3	0	0
O2	0.3	0.3	1.3	-0.1	0	0
O3	3.9	1.0	0.9	1.5	-1.7	-0.7
O4	0.7	0.7	20.7	0.4	0	0

Calculated ADP (x100 / Å^2) from the DFT model with O_i within the conduction channel

	U11	U22	U33	U12	U13	U23
La1	0.6	0.6	2.3	0.3	0	0
La2	0.6	0.2	0.8	0.1	0	0
Si1	0.2	0.2	0.5	0.1	0	0
O1	1.4	1.7	2.5	1.4	0	0
O2	0.3	0.4	1.4	-0.1	0	0
O3	6.5	4.6	1.6	4.4	-2.9	-2.2
O4	1.0	1.0	3.2	0.5	0	0

Calculated ADP (x100 / Å^2) from the DFT model with O_i at the periphery of the conduction channel

	U11	U22	U33	U12	U13	U23
La1	0.8	0.8	2.5	0.4	0	0
La2	1.0	0.5	0.5	0.2	0	0
Si1	0.8	0.4	0.7	0.6	0	0
O1	2.7	2.8	1.8	2.3	0	0
O2	0.9	0.7	2.0	0.4	0	0
O3	4.8	1.5	1.3	1.7	-1.7	-0.8
O4	0.5	0.5	21.1	0.2	0	0

Experimental ($La_{9.55}(SiO_4)_6O_{2.32}$) ADP (x100 / Å^2) (*)

(*) Leon-Reina, L.; Losilla, E. R.; Martinez-Lara, M.; Bruque, S.; Aranda, M. A. G. J. Mater. Chem. 2004, 14, 1142-1149

Conclusions

- The WKM affects mainly:
  - The PDF peak shape, i.e. the line tails and peak widths
  - The refined ADPs (overestimation for light elements and underestimation for heavy elements)

- With a little effort, the PDF of multicomponent system can be accurately calculated using a linear combination of “modified” partial PDFs

- The PDF analysis is certainly mature enough to avoid the WKM approximation

Thank you for your attention