Analyse structurale par la fonction de distribution de paires.

Pierre BORDET
Institut Néel,
CNRS-UJF Grenoble
pierre.bordet@grenoble.cnrs.fr

ЯECIPROCS

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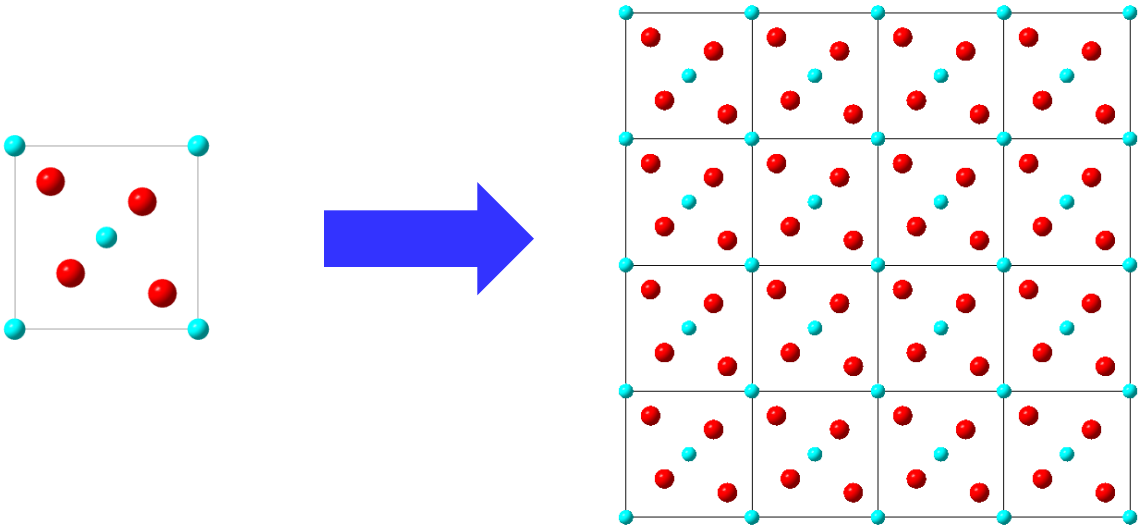
La cristallographe étudie et «utilise » les cristaux pour comprendre la structure des matériaux



Les cristaux sont périodiques et symétriques
c'est pourquoi la diffraction (RX, etc…) est si efficace pour les étudier

On sait (en général) déterminer la structure d'un monocristal

Or, tous les matériaux ne sont pas naturellement monocristallins

On veut connaitre leur structure

=> **idée 1** = en faire des monocristaux
(ex : chimie du solide, petites molécules, bio structurale…)

Mais,

ça ne marche pas toujours,
on veut connaitre la structure du matériau « réel » (désordre, poudre, nano…)
on veut l'étudier « in situ » , «in operando », etc…

=> **idée 2** = méthodes d'étude structurale de matériaux non monocristallins
=> poudres, amorphes, désordre, multiphases…..

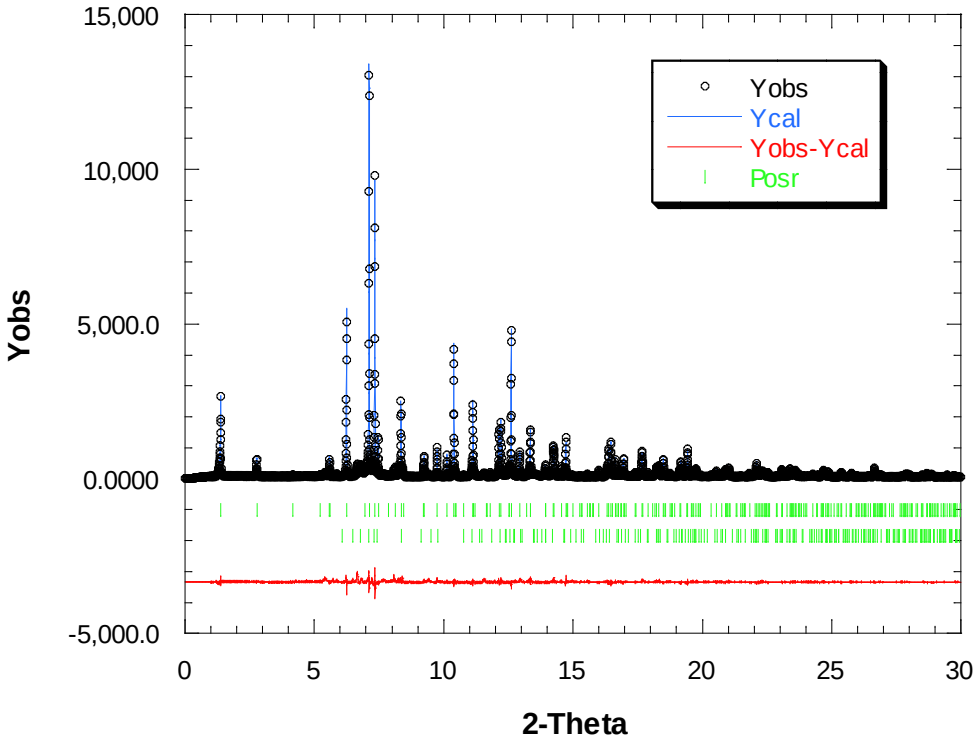
Diffraction, spectroscopies (IR, Raman, RMN), microscopie électronique , SAXS, EXAFS…

Analyse de la diffusion totale par la fonction de distribution de paires

Diffraction de poudres : méthode de Rietveld

$$yci = ybi + \sum_{\Phi=1}^{N} S_{\Phi} \sum_{k=k1}^{k2} j_{\Phi k} . Lp_{\Phi k} . O_{\Phi k} . M . \left| F_{\Phi k} \right|^2 . \Omega_{i\Phi k}$$

$$F_{hkl} = \sum_{j \subset cell} f_j T_j \exp(2i\pi(hx_j + ky_j + lz_j))$$



On ne s'intéresse qu'aux pics de Bragg = aspect cristallin ordonné.

Tous ce qui est non-cristallin :

« bruit de fond »

« diffusion diffuse »

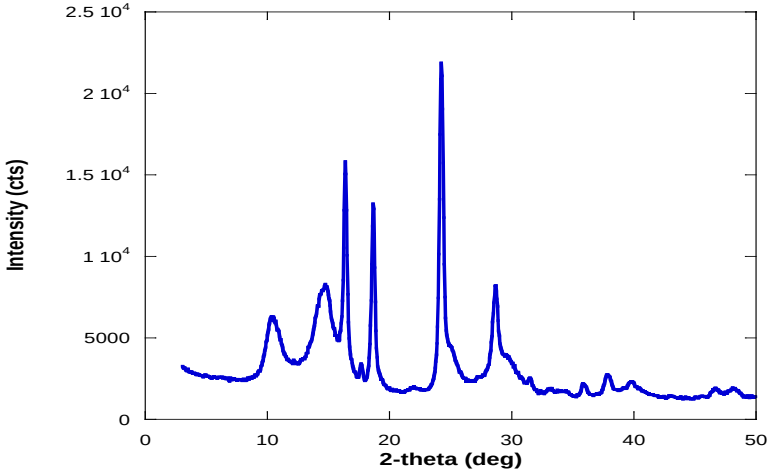
Pour étudier le matériau réel :

modéliser la diffusion totale

Expériences de diffraction avec un “mauvais” cristal ??

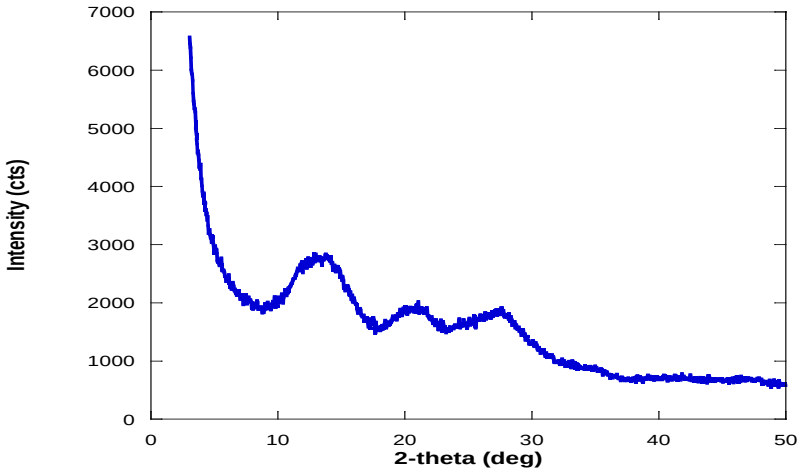
Cristal ordonné + désordre partiel

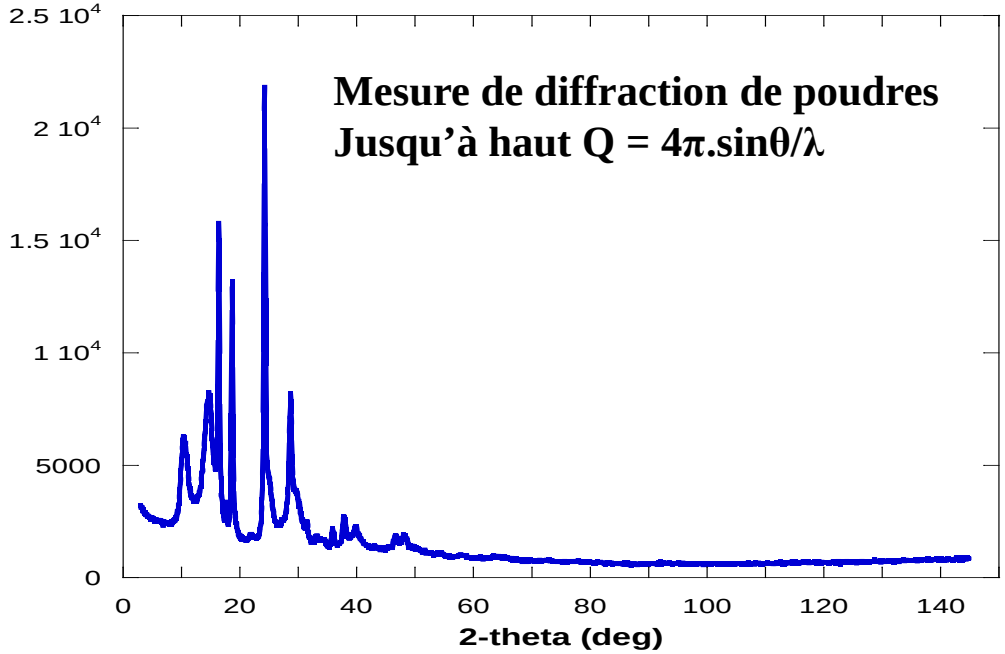
espace direct:
on peut définir une structure
moyenne ≠ structure locale (=>désordre)
espace réciproque :
présence de pics de Bragg + fond diffus



Domaines nano-cristallins

espace direct:
structure bien définie dans des
domaines très petits (qq nm) ≠ amorphe
espace réciproque:
pics de Bragg larges ou absents, selon
la taille des domaines

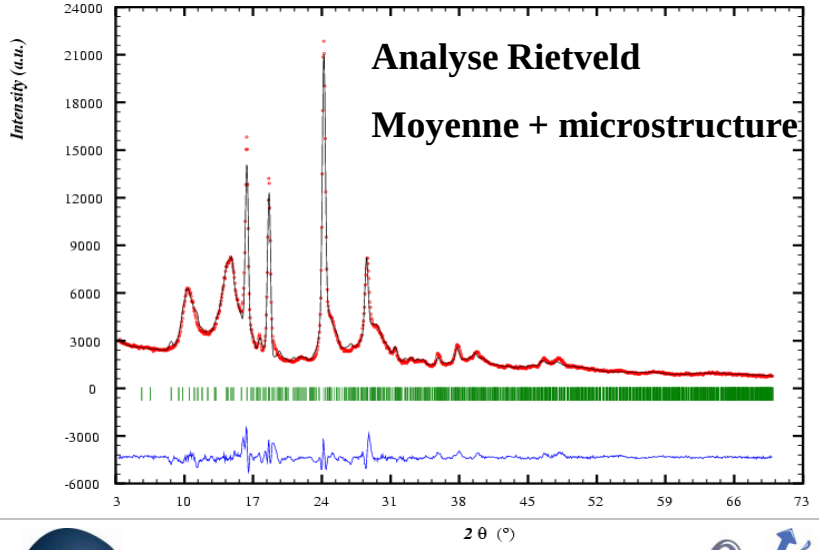


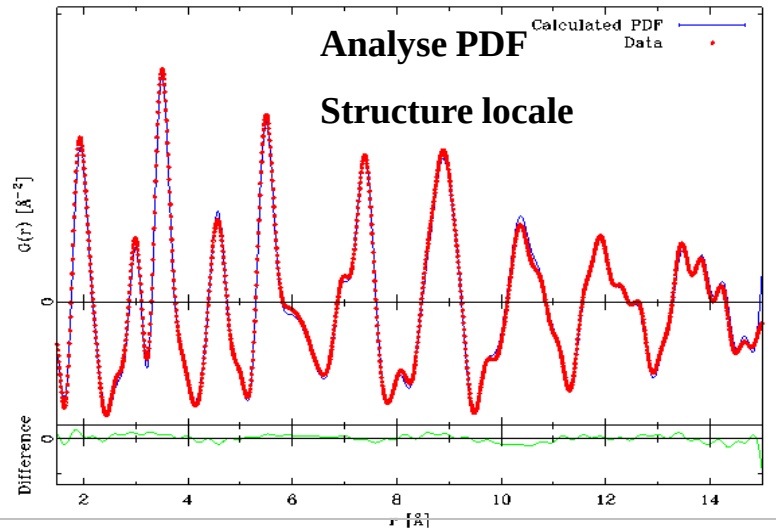


Espace Réciproque

Espace direct

Diffusion Totale





Intensité diffusée = section efficace différentielle élastique (échantillon quelconque)

$$\frac{d\sigma}{d\Omega} = I(\vec{Q}) = \left\langle A(\vec{Q})A^*(\vec{Q}) \right\rangle = \sum_{j=1}^{N}\sum_{k=1}^{N} f_j f_k^* \left\langle e^{i\vec{Q}.(\vec{r}_j - \vec{r}_k)} \right\rangle$$

< > : moyenne temporelle,
Q : vecteur diffusion
f : facteur de diffusion

Si on peut définir une structure moyenne (r=R+u)

$$I(\vec{Q}) = I_B(\vec{Q}) + I_D(\vec{Q})$$

$$I_B(\vec{Q}) = \sum_j \sum_k f_j f_k^* e^{i\vec{Q}.(\vec{R}_j - \vec{R}_k)} \left\langle e^{iQu_j} \right\rangle \left\langle e^{-iQu_k} \right\rangle$$

$$I_D(\vec{Q}) = \sum_j \sum_k f_j f_k^* e^{i\vec{Q}.(\vec{R}_j - \vec{R}_k)} \left(\left\langle e^{iQ(u_j - u_k)} \right\rangle - \left\langle e^{iQu_j} \right\rangle \left\langle e^{-iQu_k} \right\rangle \right),$$

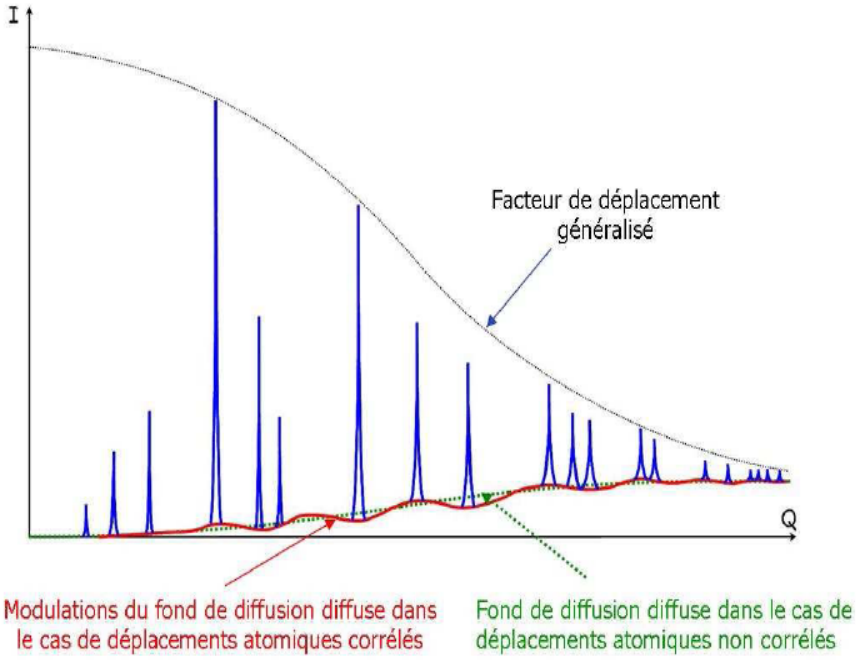
avec

$$\begin{cases} I_B(\vec{Q}) = (2\pi)^3 \frac{N_m}{V_m} \sum_{h\,k\,l} |F_{hkl}(Q)|^2 \, \delta\left(\vec{Q} - \overrightarrow{G_{hkl}}\right) \\ F_{hkl}(Q) = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)} \left\langle e^{iQu_j} \right\rangle \end{cases}$$

Bragg

$$I_D(\vec{Q}) = \sum_j |f_j|^2 \left(1 - \left\langle e^{iQu_j} \right\rangle \left\langle e^{-iQu_j} \right\rangle\right)$$

$$+ \sum_j \sum_{k \neq j} f_j f_k^* e^{i\vec{Q}.(\vec{R}_j - \vec{R}_k)} \left(\left\langle e^{iQ(u_j - u_k)} \right\rangle - \left\langle e^{iQu_j} \right\rangle \left\langle e^{-iQu_k} \right\rangle \right)$$



$$I(Q) = \vec{A}.\vec{A}^* = \sum_{j,k=1}^{N} f_j f_k^* e^{i\vec{Q}(\vec{r_j}-\vec{r_k})}$$

Diffusion : cinématique, statique

$$I(Q) = N.\sum_j |f_j|^2 + \sum_{j\neq k} f_j f_k^* \frac{\sin(Q.r_{jk})}{Q.r_{jk}}$$

Intégration isotrope (poudre, liquide…):
autodiffusion +fonction d'interférence=formule de Debye

$$S(Q) - 1 = \frac{I(Q)}{N(\Sigma_j f_j)^2} - \frac{(\Sigma_j |f_j|^2)}{(\Sigma_j f_j)^2} = \frac{1}{N}\sum_{j\neq k} \frac{f_j f_k^*}{(\Sigma_j f_j)^2} \frac{\sin(Q.r_{jk})}{Q.r_{jk}}$$

S(Q) : fonction de structure de diffusion statique totale

$$S(Q) - 1 = \rho_0 \int_0^\infty \sum_{j\neq k} \frac{f_j f_k^*}{(\Sigma_j f_j)^2} \delta(r - r_{jk}) \frac{\sin(Q.r)}{Q.r} 4\pi r^2 dr$$

$$S(Q) - 1 = \int_0^\infty 4\pi r \rho_0 \sum_{j\neq k} \frac{f_j f_k^*}{(\Sigma_j f_j)^2} \delta(r - r_{jk}) \frac{\sin(Q.r)}{Q} dr$$

$$S(Q) - 1 = \int_0^\infty 4\pi r \rho_0 (g(r) - 1) \frac{\sin(Q.r)}{Q} dr \qquad g(r) = \sum_{j\neq k=1}^{N} \frac{f_j f_k^*}{(\Sigma_j f_j)^2}$$

g(r): fonction de distribution de paires

$$S(Q) - 1 = \int_0^\infty G(r) \frac{\sin(Q.r)}{Q} dr \qquad G(r) = 4\pi r \rho_0 (g(r) - 1) = 4\pi r(\rho(r) - \rho_0)$$

$\rho(r)=\rho_0.g(r)$: densité de paires
ρ_0 : densité numérique

$$G(r) = \frac{1}{r} \sum_{j\neq k=1} \frac{f_j f_k^*}{(\Sigma_j f_j)^2} . \delta(r - r_{jk}) - 4\pi\rho_0$$

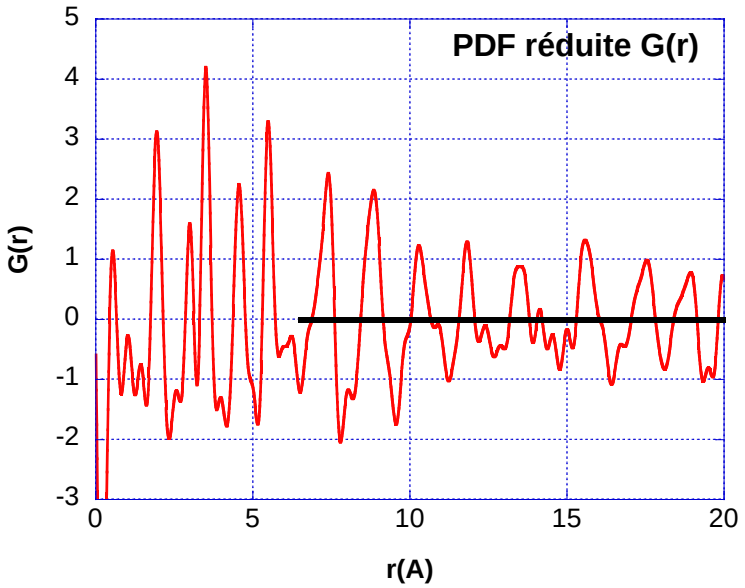
G(r): fonction de distribution de paires réduite

$$G(r) = 4\pi r(\rho(r) - \rho_0) = \frac{2}{\pi} \int_0^\infty Q.(S(Q) - 1).\sin(Qr).dQ$$

$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi}\int_0^\infty Q[S(Q) - 1]\sin(Qr)dQ,$$

G(r) : fonction de distribution de paires réduite = *TF {F(Q)=Q.[S(Q)-1]}*

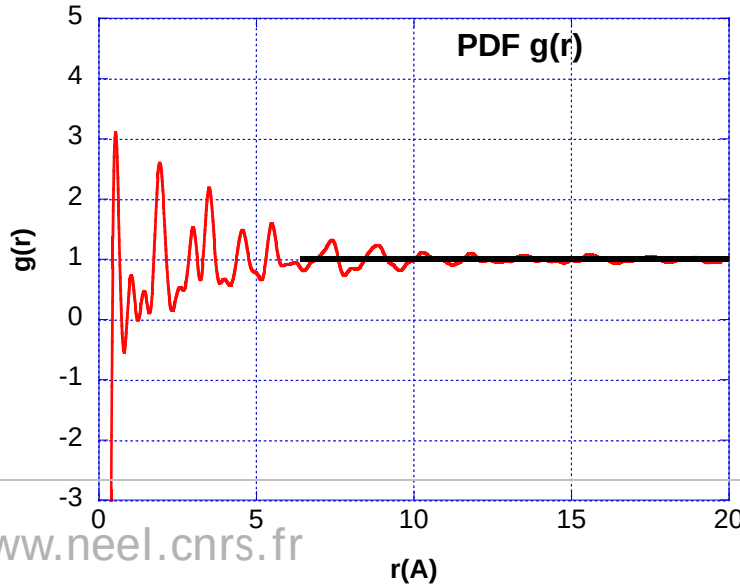
→ *0 qd r→∞ ; amplitude indépdt de r, e.s.d.constant avec r*



$$G(r) = 4\pi r \rho_0 (g(r) - 1) \qquad g(r) = 1 + G(r)/4\pi r \rho_0$$

g(r) : fonction de distribution de paires = *TF {S(Q)}*

→ *1 qd r→∞ ; amplifie bas r, e.s.d.croît avec r*

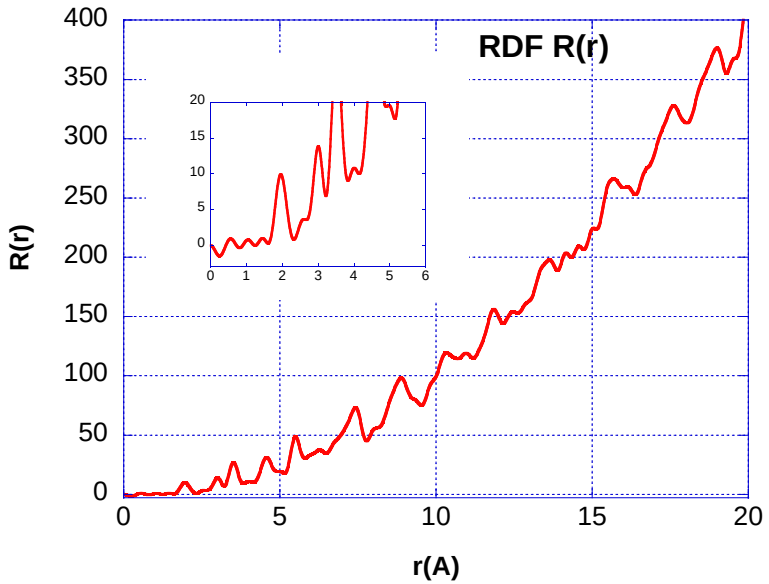


$$R(r) = 4\pi r^2 \rho_0 g(r)$$

R(r) : fonction de distribution radiale

Croît comme r^2

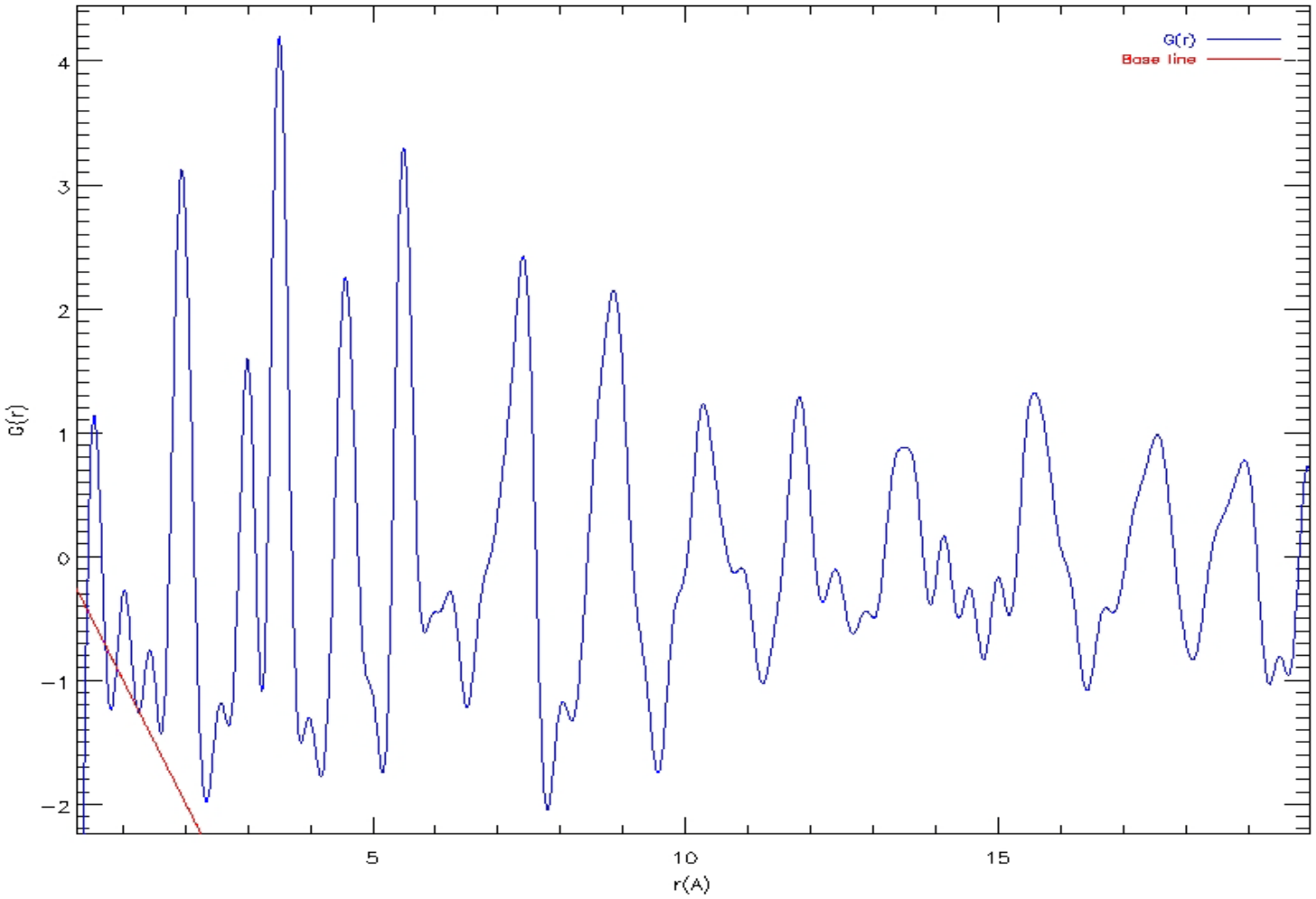
$$Nc = \int_{r1}^{r2} R(r)dr$$



$$G(r) = 4\pi r(\rho(r) - \rho_0) = \frac{2}{\pi}\int_0^{\infty} Q.(S(Q) - 1).\sin(Qr).dQ$$

$$G(r) = \frac{1}{r}\sum_{j \neq k} \frac{f_j f_k^*}{(\Sigma_j f_j)^2}.\delta(r - r_{jk}) - 4\pi\rho_0$$

(unité: Å^{-2})



Largeurs des pics de la PDF

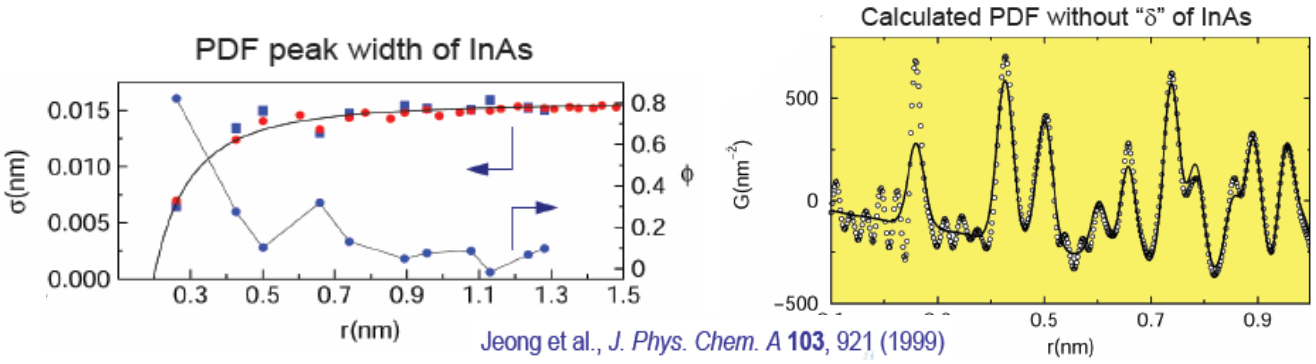
Reflètent la distribution des distances interatomiques dans le matériau

≠ diffraction !!

+ corrections :

$$\sigma_{ij} = \sigma'_{ij}\sqrt{1 - \frac{\delta_1}{r_{ij}} - \frac{\delta_2}{r_{ij}^2} + Q_{broad}^2 r_{ij}^2}$$

δ_1, δ_2 effets de corrélations de déplacements (HT, BT)



Jeong et al., *J. Phys. Chem. A* **103**, 921 (1999)

Q_{broad} : élargissement du à la résolution en Q

Q_{damp} : diminution gaussienne de la hauteur des pics de la PDF due à la résolution en Q (FWHM)

$$B(r) = e^{-\frac{(rQ_{damp})^2}{2}}$$

Debye-Waller : Déplacement relatif ≠ DW cristallographique

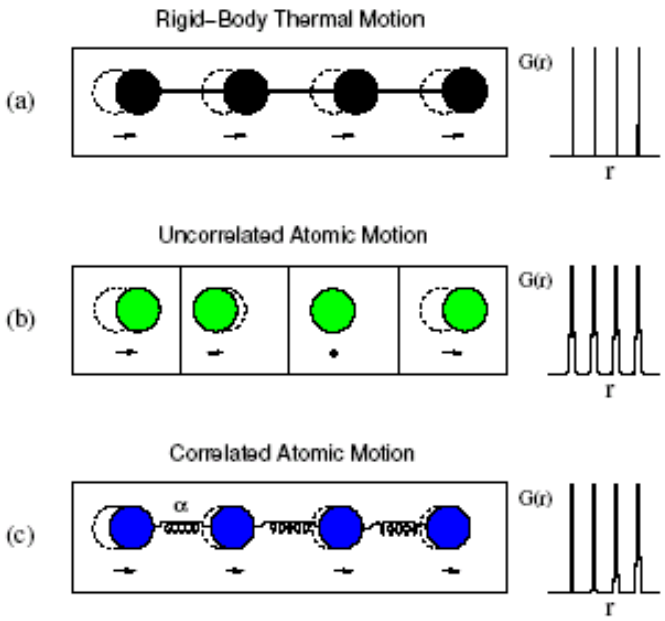
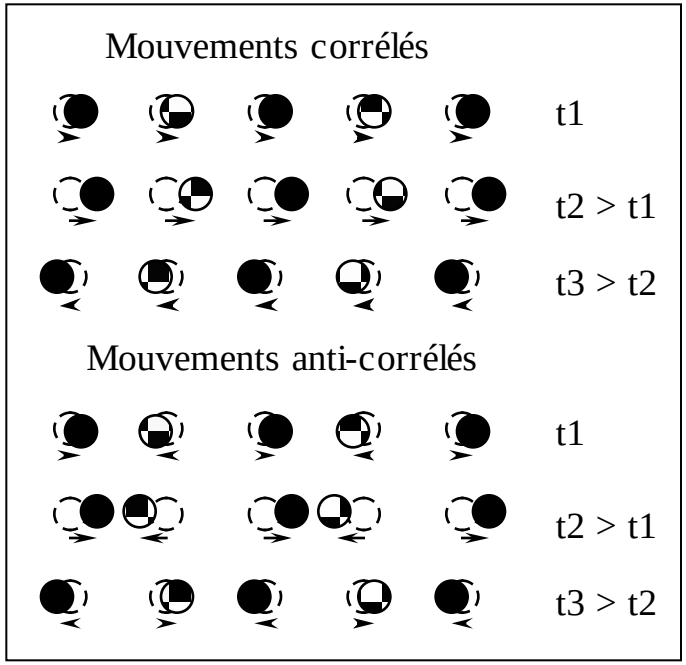


FIG. 1: Schematic diagram showing an instantaneous snapshot of atomic positions in (a) rigid-body model (b) Einstein model (c) Debye model. In (a) and (b) all PDF peaks have the same width independent of atom separation. In (c) the PDF peak width increases up to the root mean-square displacement as the atomic separation increases. α is a spring constant.

Comparer les 2 informe sur les corrélations de déplacement

$$\underbrace{\sigma^2_{ab}}_{PDF} = \underbrace{\sigma^2_{a}}_{Diffrac.} + \sigma^2_{b} - 2\sigma^2_{a}\sigma^2_{b}.\rho$$

ρ = +1 ⇨ corrélation positive
ρ = 0 ⇨ non corrélé
ρ< 0 ⇨ anti-corrélé



A quoi ça peut bien servir ???

Utilisation de la pdf dans l'étude de composés partiellement ordonné et de poudres nanocristallines

Experimentalement, à partir d'un diffractogramme de poudres:

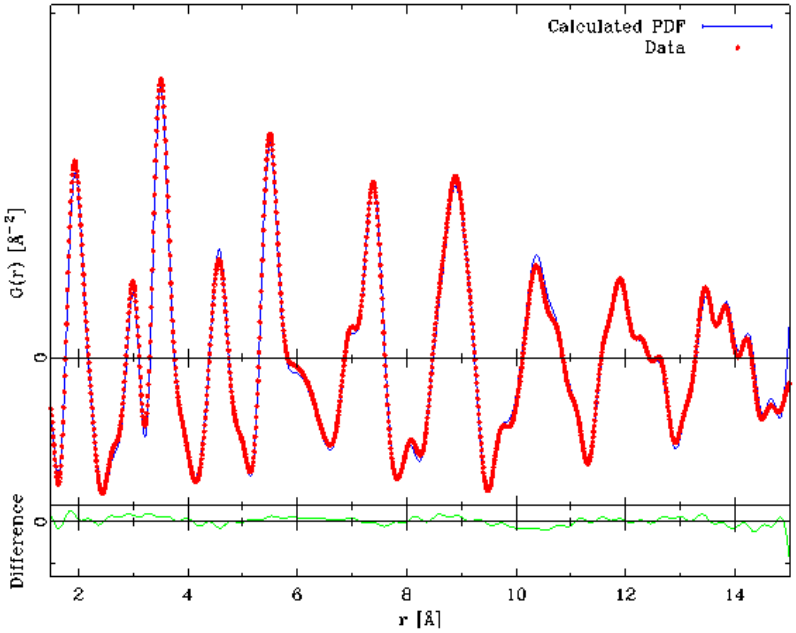
$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi}\int_0^{\infty} Q[S(Q) - 1]\sin(Qr)dQ$$

r = distance interatomique

$\rho(r)$ = densité de paires, ρ_0 : densité numérique moyenne

$S(Q)$=intensité diffusée cohérente normalisée,

$Q=4\pi\sin(\theta)/\lambda$



A partir d'un modèle de structure:

$$G_{calc}(r) = \frac{1}{r}\sum_i\sum_j\left[\frac{b_i b_j}{\langle b\rangle^2}\delta(r - r_{ij})\right] - 4\pi r\rho_0,$$

r_{ij} = distance interatomique

b_i : pouvoir diffusant

=>« **Rietveld »** dans l'espace direct (PDFFIT *Proffen et al.,. Appl. Cryst.,1999)*

=> **RMC sur PDF** (DISCUS, *Proffen et al.,. Appl. Cryst.,1997*)

ou S(Q) (RMCPow, *Mellergard et al., Acta Cryst. A 1999*)

ou les deux (RMCProfile, *Keen et al., JPCM 2005)*

Proffen, S. J. L. Billinge, T. Egami and D. Louca, Z. Kristallogr. 218 (2003) 132–143

Intérêts de l'analyse pdf :

Complémentaire de l'analyse cristallographique classique:

independant de Bragg, utilisation de la diffusion cohérente totale
études structurales locales(amorphes, ordre partiel, nano-grains…)

Exemple :

PDF du C60 (diffraction des neutrons sur poudre).

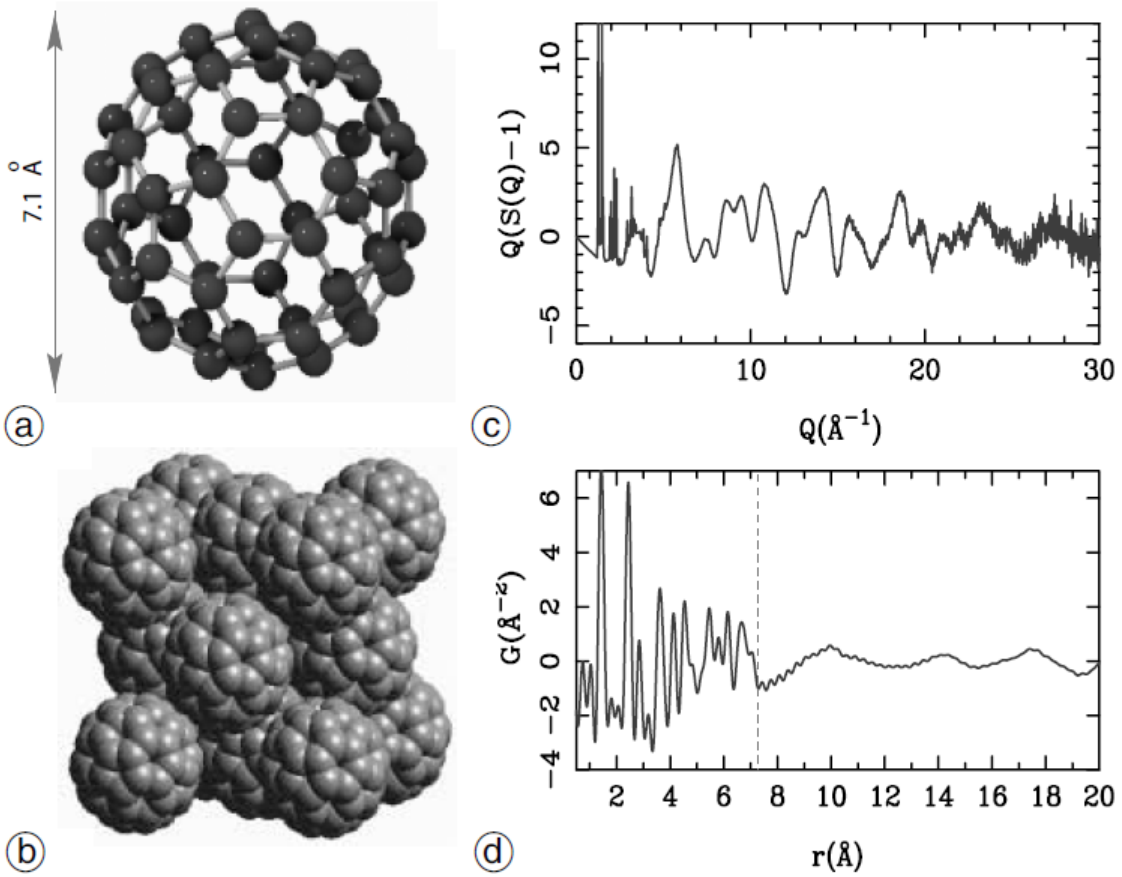
infos :

Distances C-C

Diametre des molécules

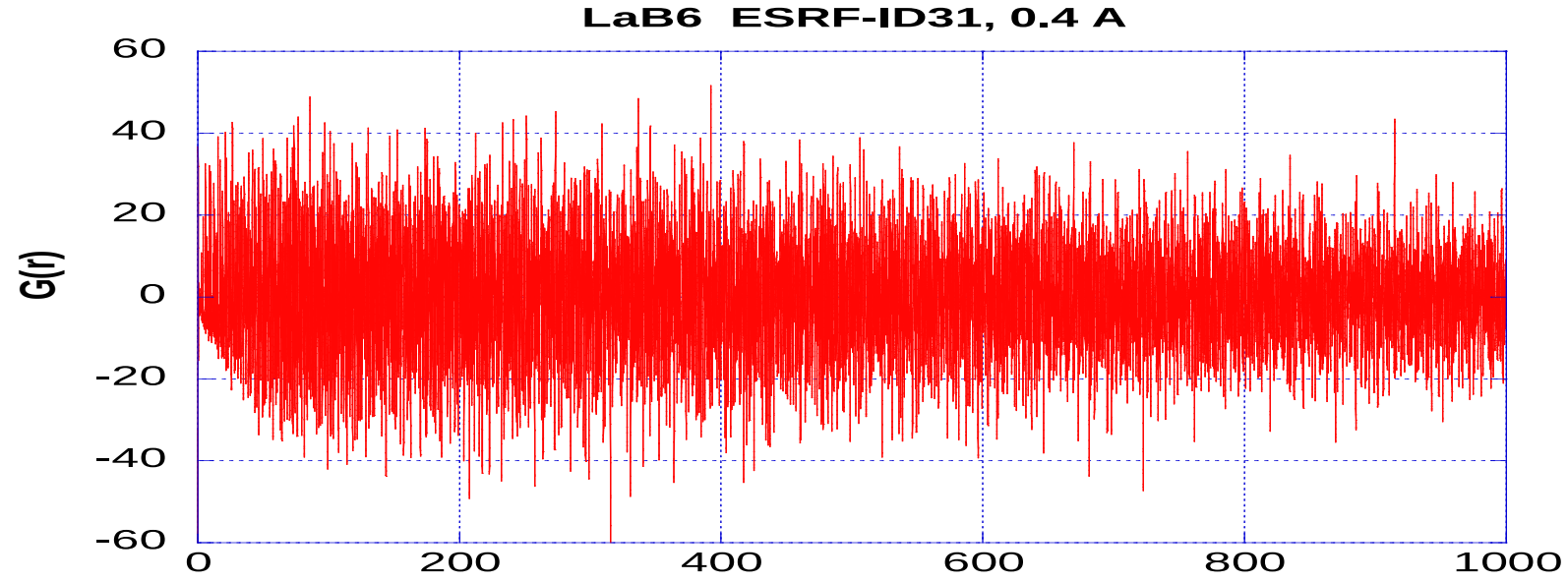
Arrangement cristallin

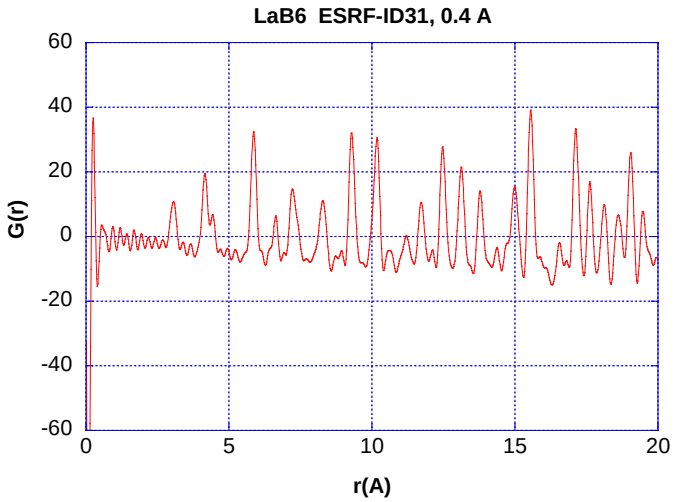
Les molécules tournent incohérentes

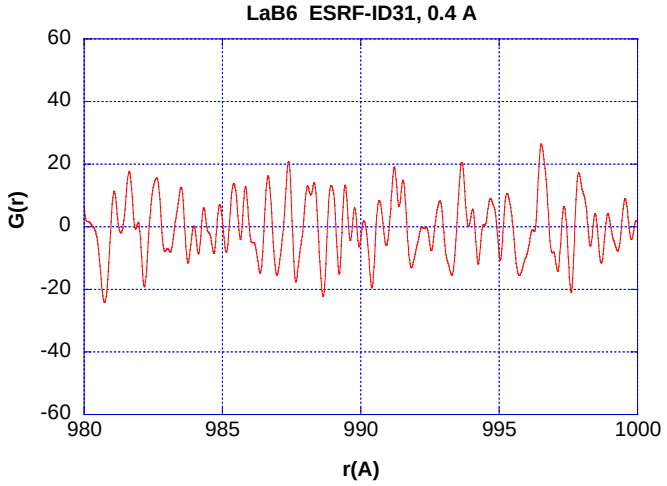


Th. Proffen, S. J. L. Billinge, T. Egami and D. Louca, Z. Kristallogr. 218 (2003) 132–143

PDF = analyse structurale ***multi-échelle***







Nécessite une très haute résolution spatiale

Etudes structurales de matériaux nano-cristallins

$RuO_2.xH_2O$

Différentes températures de recuit
=>différents contenus en eau et cristallinité

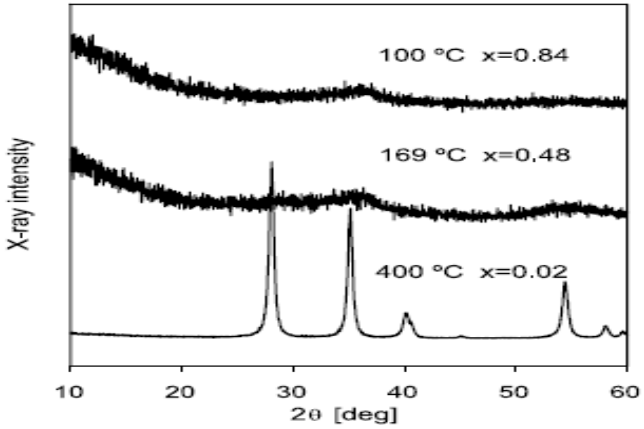
Dérivée de la PDF

=> limite des domaines cohérents

XPD

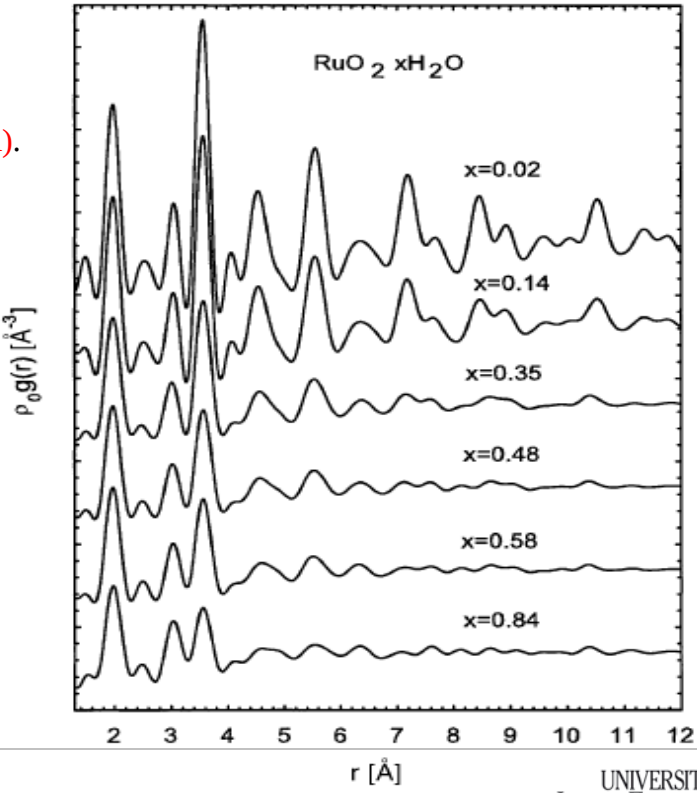
(lab)

CuKα



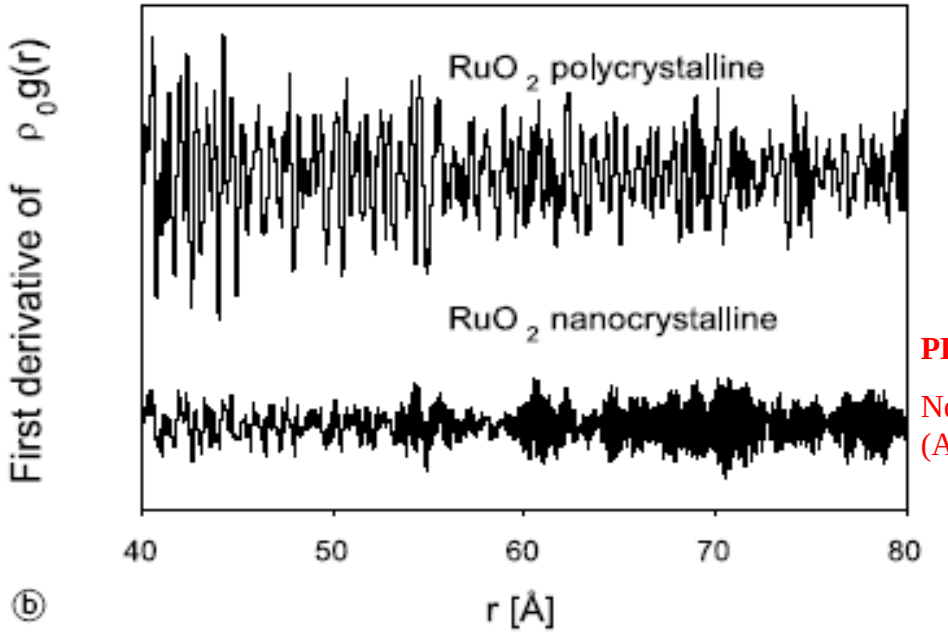
PDF

XPD (X7A).



PDF

Neutron (Argonne)



W. Dmowski and K. E. Swider-Lyons, Z. Kristallogr. 219 (2004) 136–142

Comment la mesurer ??

C’est (presque) une mesure de diffraction de poudres classique

Mais nécessité de mesures à hauts Q et fortes statistiques

=>Utilisation des grands instruments

Neutrons

facteur de diffusion constant (b) => signal à très hauts Q

contraste entre éléments (O, Z voisins, isotopes…)

réacteurs à hauts flux, ex : ILL-D4, λ=0.7,0.5,0.35Å =>Qmax ≈ 33Å^{-1},

sources à spallation, ex : ISIS-GEM, LANL-NPDF (dédiée), Qmax > 45Å^{-1}

Synchrotrons rayons X

signal décroit avec *f(2θ)*

très hauts flux jusqu’à très hautes énergies (≈100keV)

faisceau parallèle + crystal analyseur-> élimine les contributions élastiques

détecteurs 2D: expériences in-situ, résolues en temps

Instruments de laboratoire

Diffracto de poudres de labo optimisé pour hauts Q et statistique

λMoKα (0.71Å) => Qmax≈ 17Å^{-1}

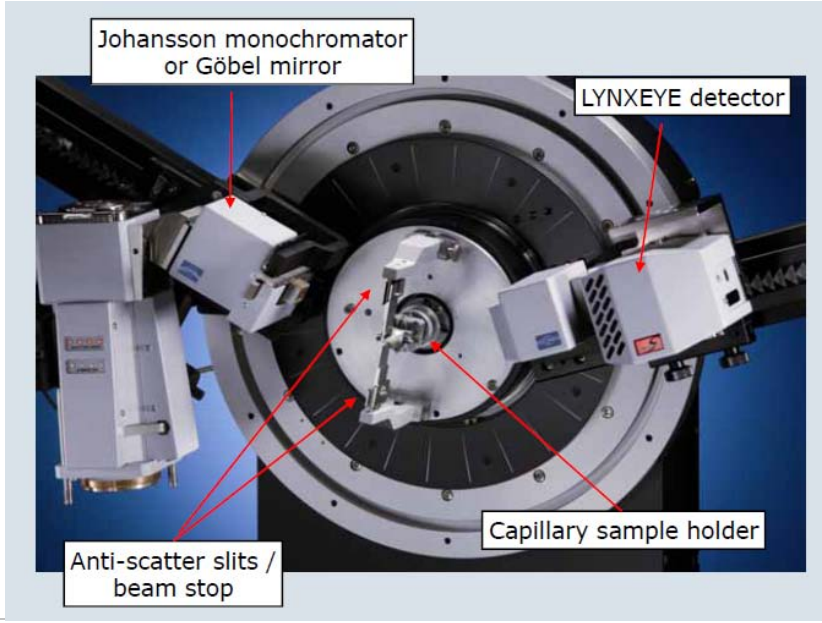
λAgKα (0.56Å) => Qmax≈ 22Å^{-1}

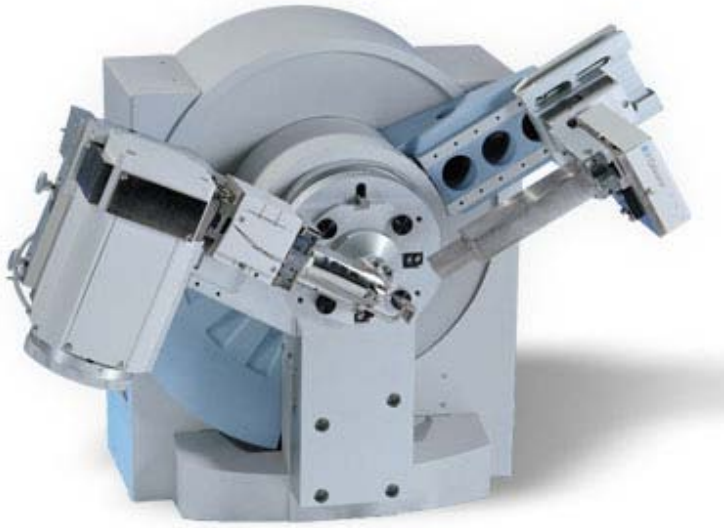
Monochromatisation modérée

(e.g. filtre - graphite primaire - multicouches)

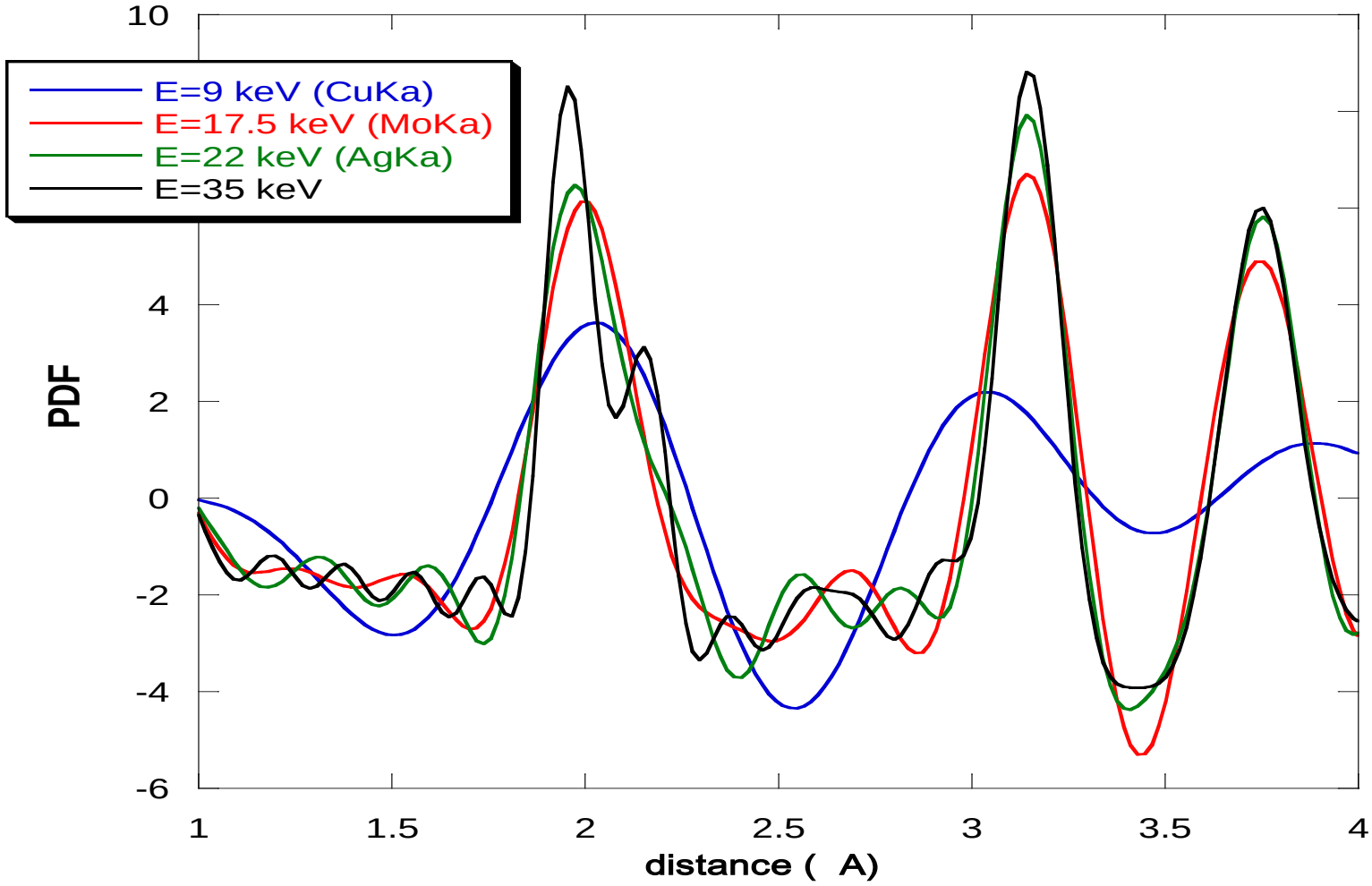
PSD ***(haute énergie !!)***

Debye-Scherrer ou Bragg-Brentano





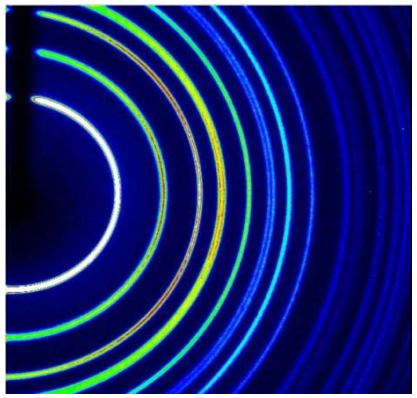
Effet de Q_{max}



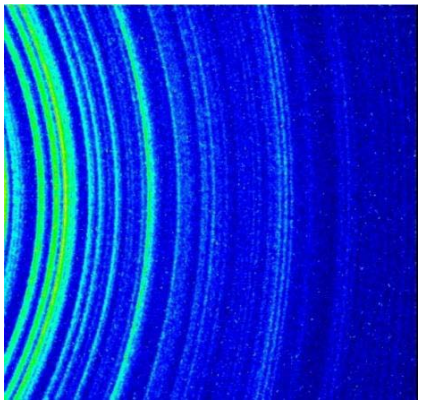
Utilisation d'une camera ApexII et d'une microsource Ag-IμS pour la mesure de la PDF

KappaCCD + camera ApexII, *evalCCD*

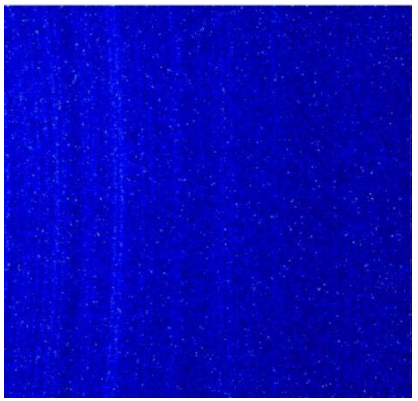
θ=0



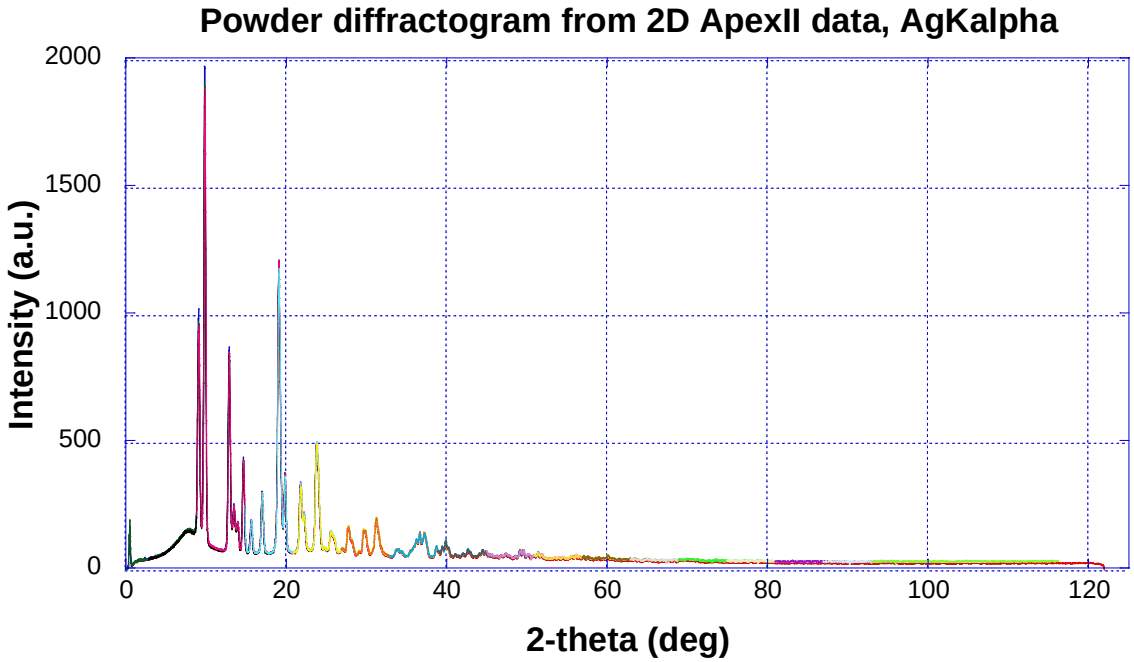
θ=9



θ=25

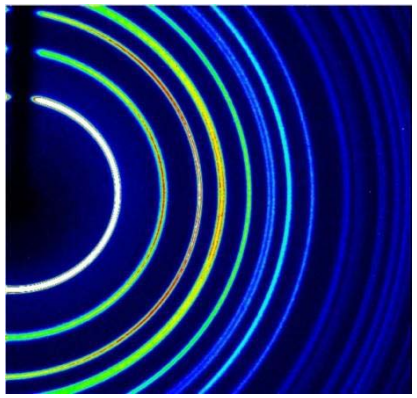


θ=41

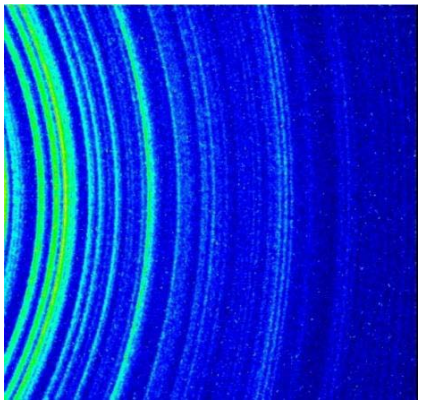


36 images mesurées tous les 3 , 5min/image

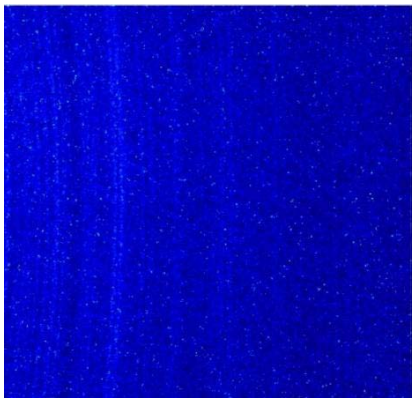
θ=0



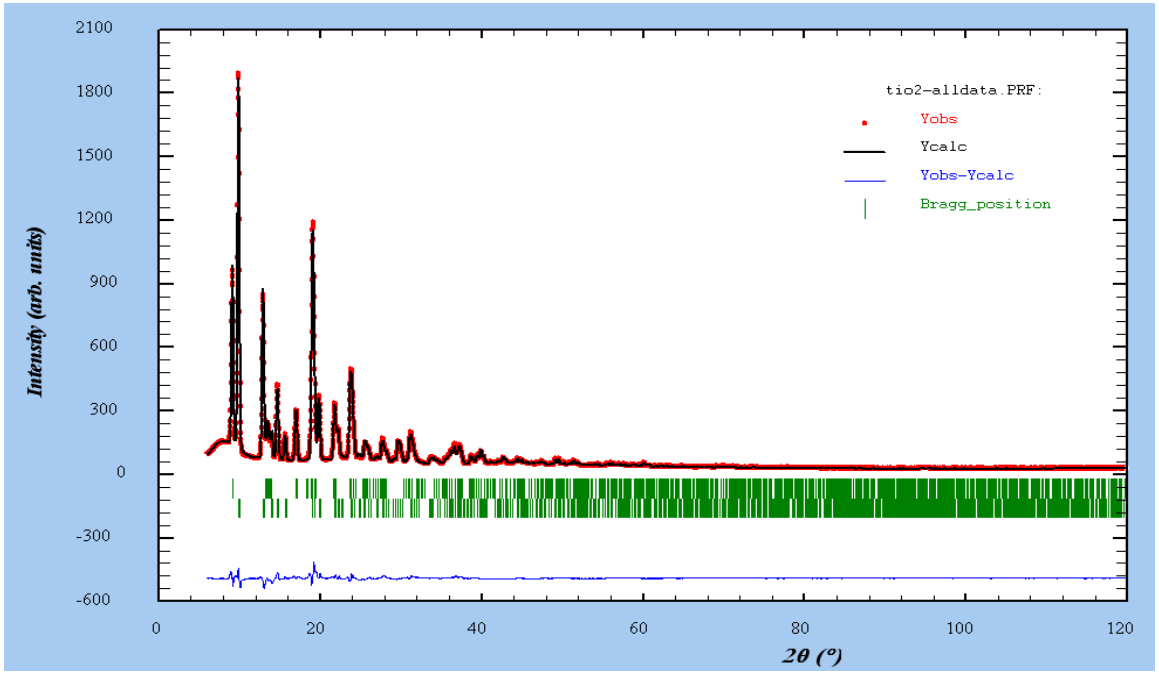
θ=9



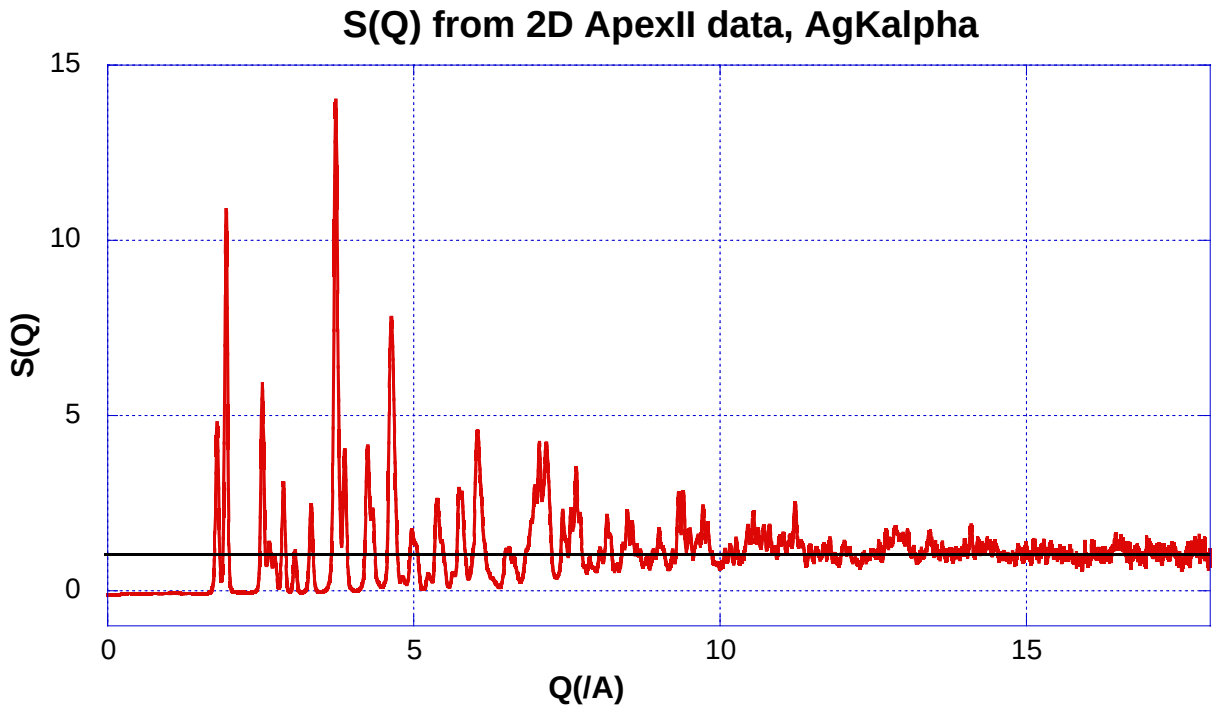
θ=25



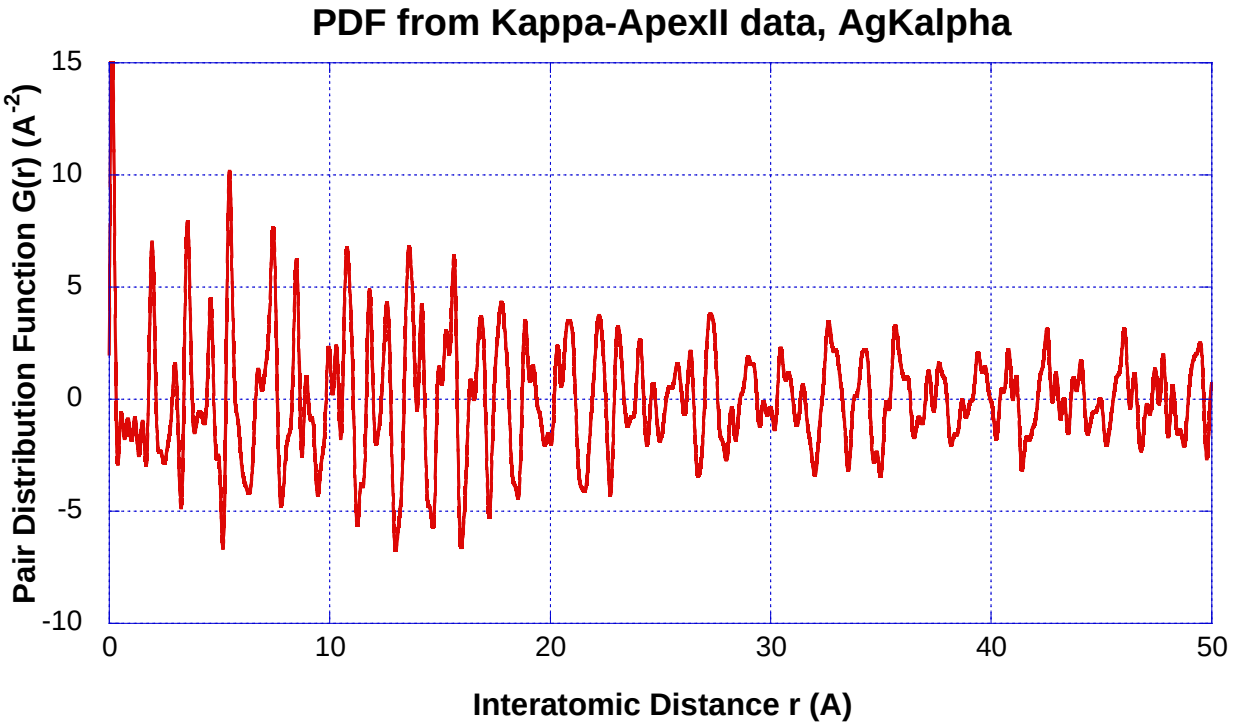
θ=41


tio2-alldata.PRF:
Yobs
Ycalc
Yobs-Ycalc
Bragg_position
Intensity (arb. units)
2θ (°)
2100
1800
1500
1200
900
600
300
0
-300
-600
0
20
40
60
80
100
120

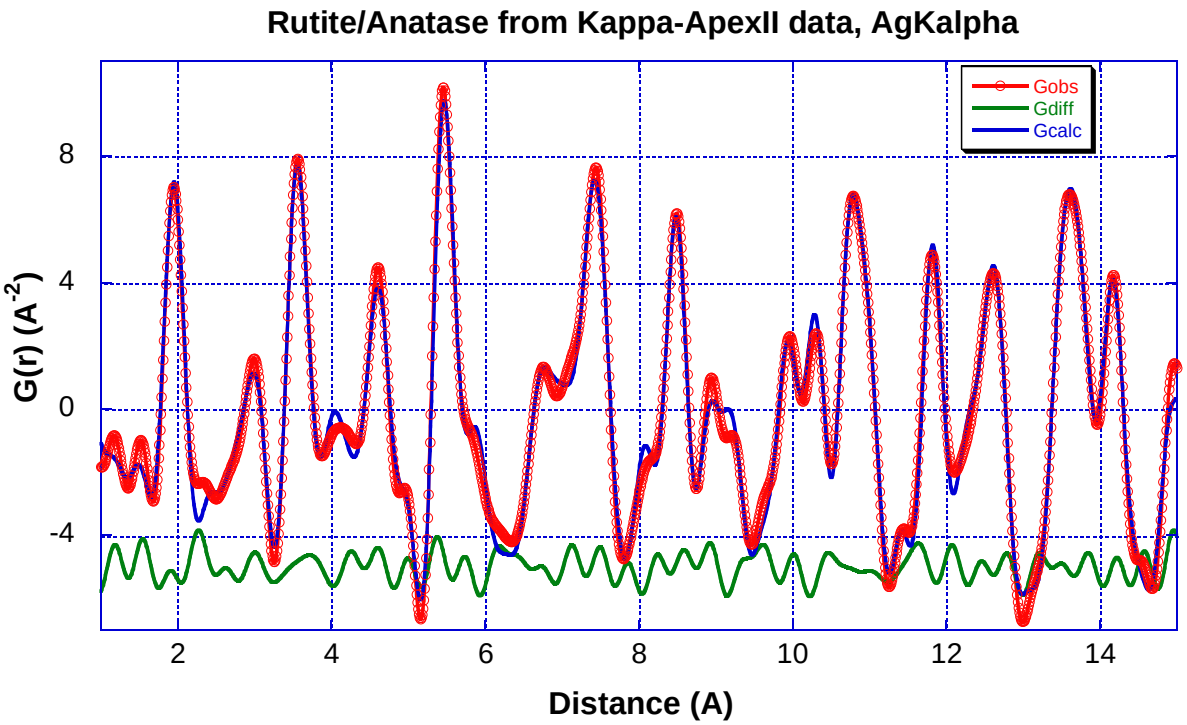
Fit de la PDF, mélange TiO_2 Rutile + Anatase



Fit de la PDF, mélange TiO_2 Rutile + Anatase



Fit de la PDF, mélange TiO_2 Rutile + Anatase



Comment traiter le diagramme pour en extraire la PDF ??

Obtenir la PDF expérimentale (cas des rayons X B.B.)

$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi}\int_0^{\infty} Q[S(Q) - 1]\sin(Qr)dQ,$$

I(Q)

X'pert

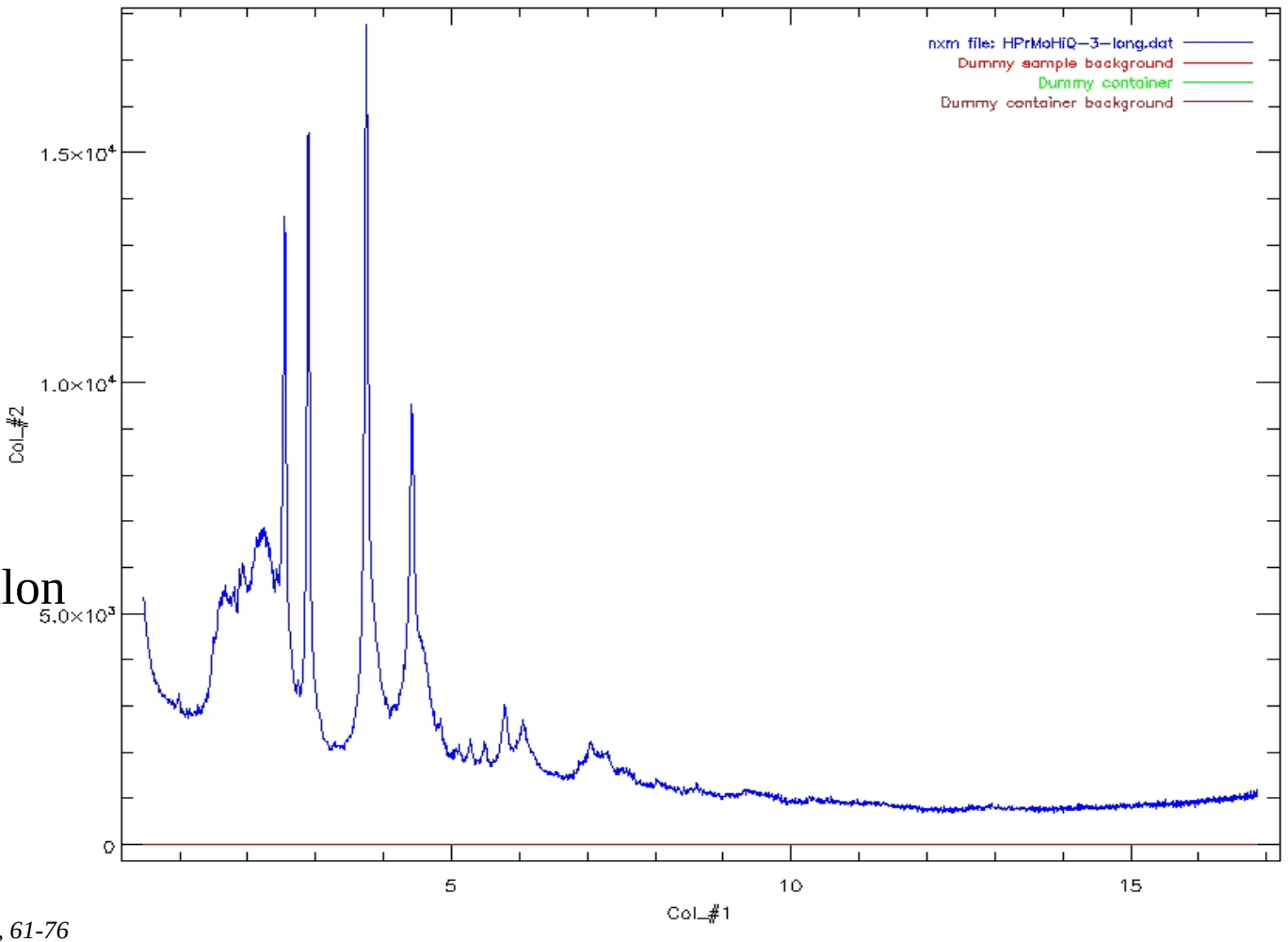
Bragg-Brentano

X'celerator

λMoKα

Miroir Göbel

Pas de porte échantillon



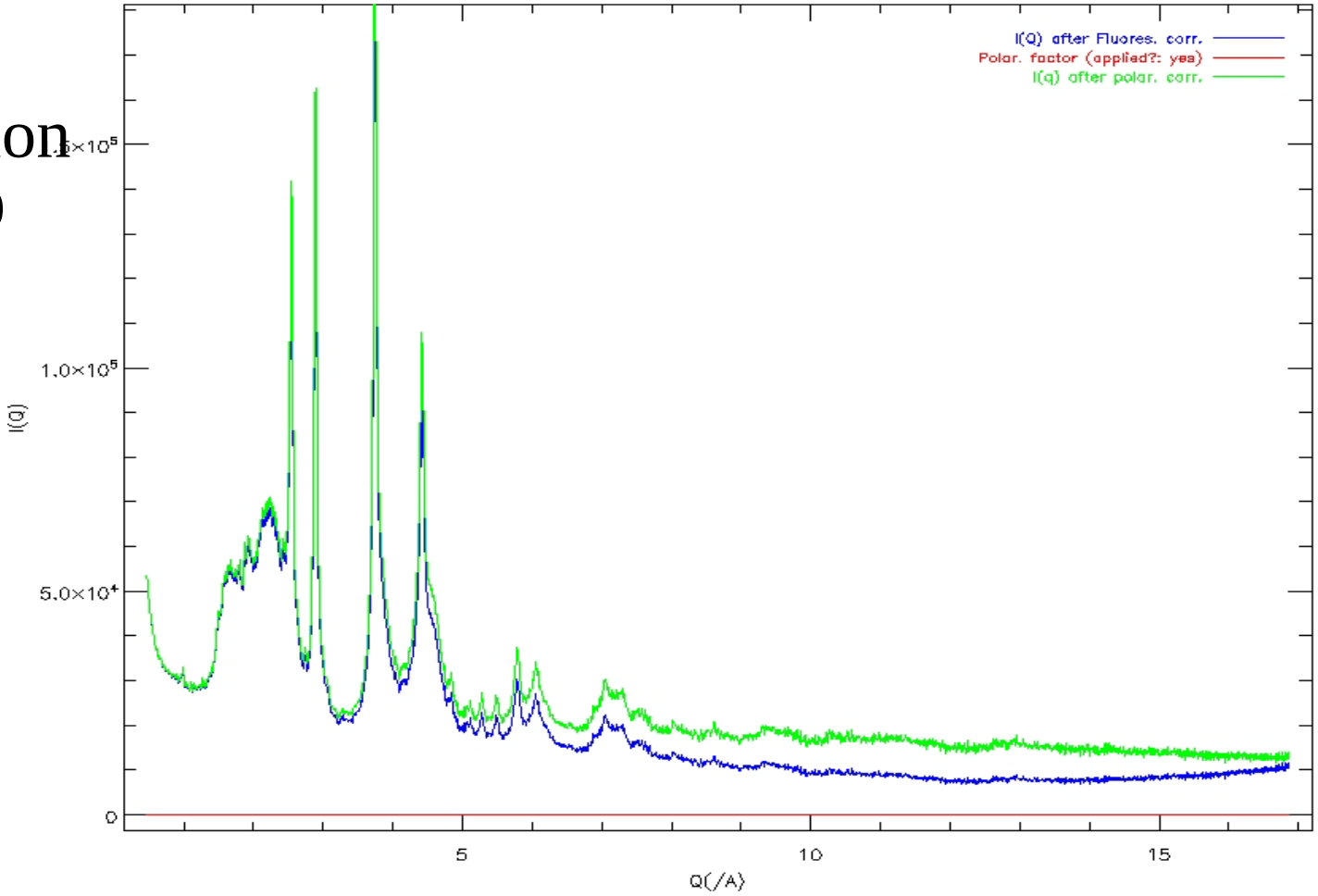
B.J. Thijsse, J. Appl. Cryst. (1984). 17, 61-76

Obtenir la PDF expérimentale (cas des rayons X B.B.)

$$P = (1 + x\,\cos^2 2\theta)/(1 + y)$$

$x = \cos^2 2\alpha_c$ ou $\cos 2\alpha_c$ Mono. mosaic ou parfait; primaire : *x=y*; diffracté, *y=1*

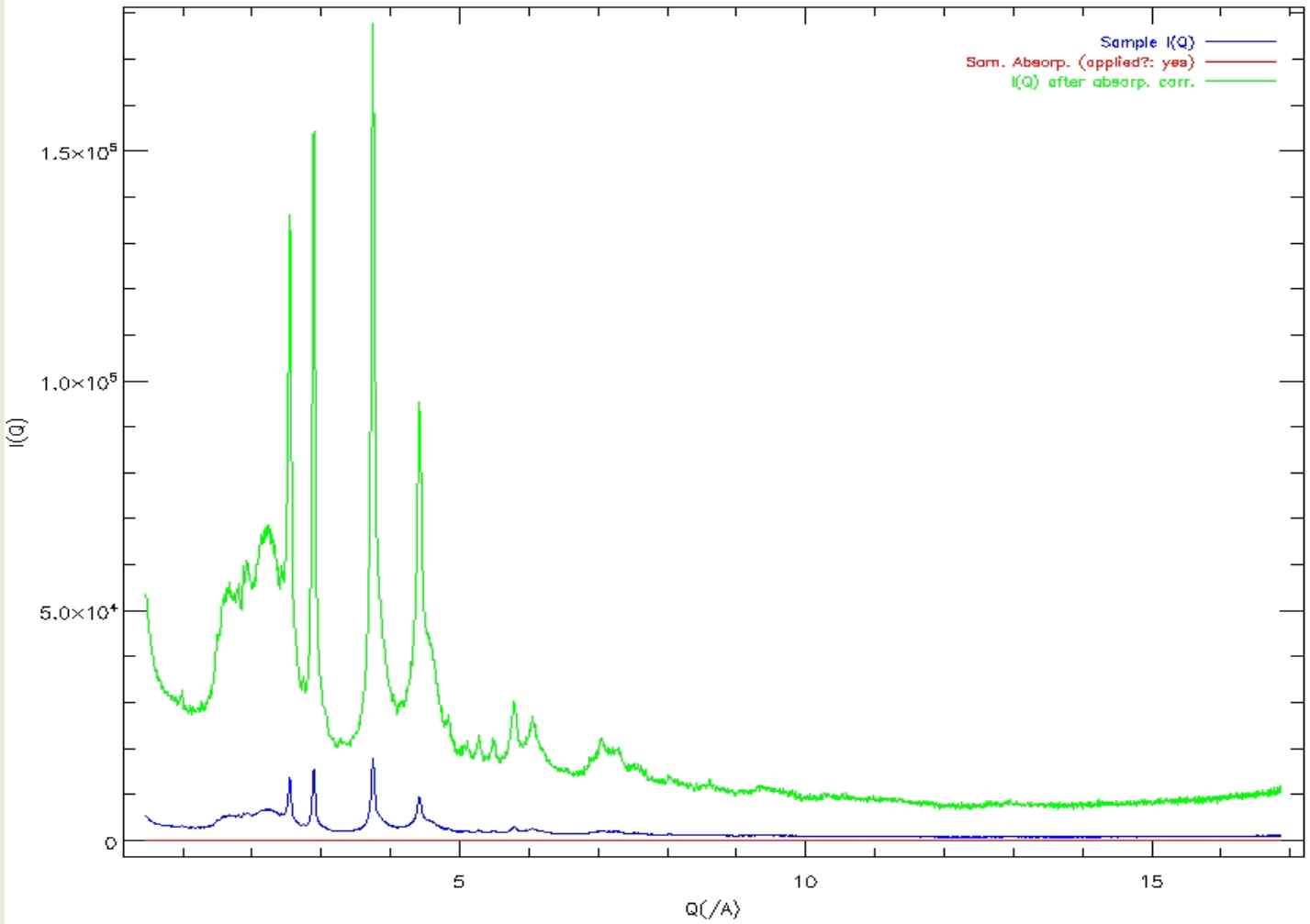
Polarisation
(pas Lorentz)



Obtenir la PDF expérimentale (cas des rayons X B.B.)

$$A_{refl} = [1 - \exp(-2\mu\, t/\sin\theta]/2\mu$$

Absorption



Obtenir la PDF expérimentale (cas des rayons X B.B.)

Compton

$$I_a^{\text{incoh}}(Q) = \left(\frac{\lambda}{\lambda'}\right)^2 \sum_{j=1}^{n} c_j Z_j \frac{(b_j Q)^{a_j}}{1+(b_j Q)^{a_j}} \qquad (A2)$$

with n the number of atomic species, Z_j the atomic number of species j, and a_j and b_j semi-empirical expressions given by

$$a_j = 2{\cdot}6917\, Z_j^{-1} + 1{\cdot}2450 \qquad (A3)$$

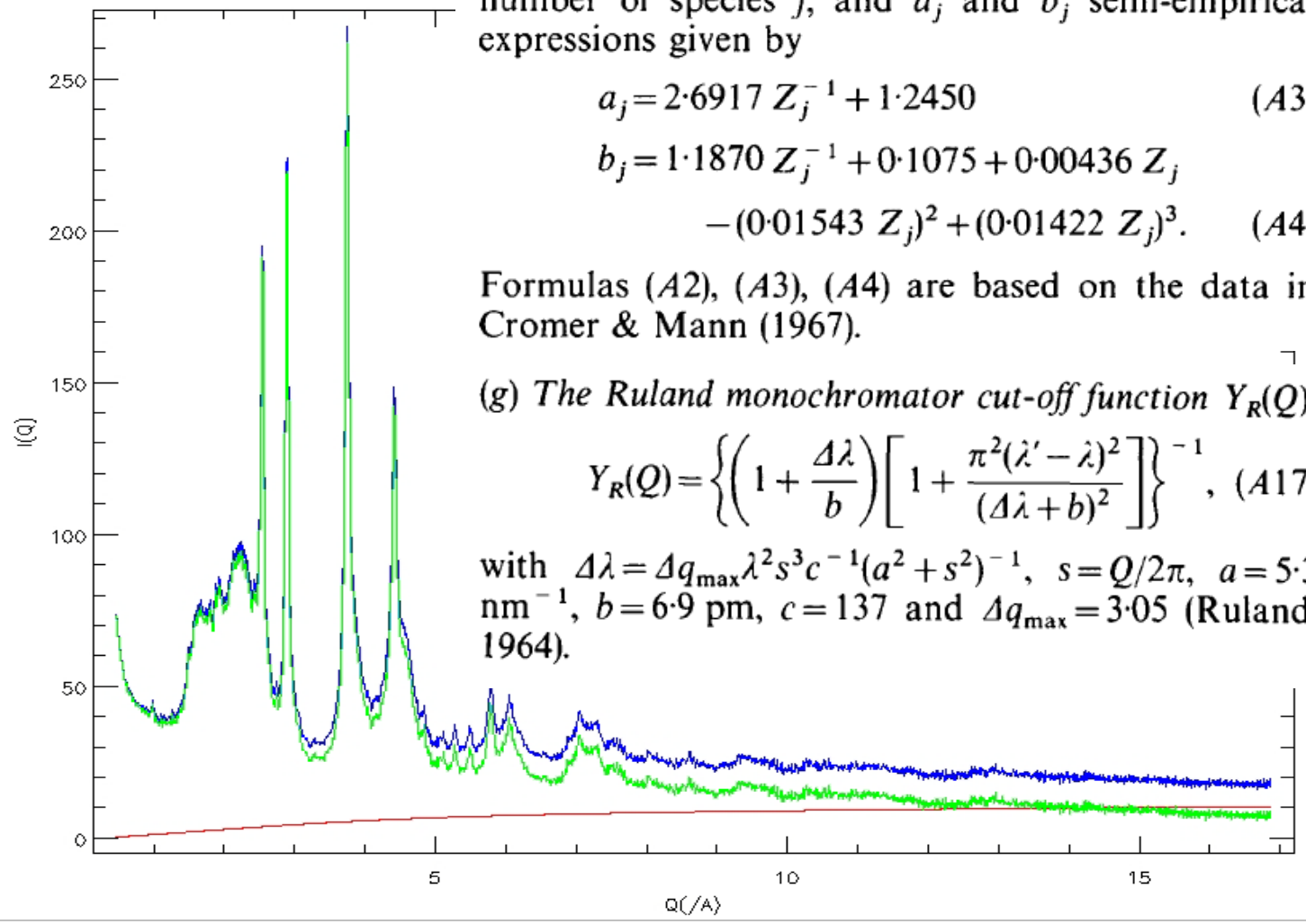
$$b_j = 1{\cdot}1870\, Z_j^{-1} + 0{\cdot}1075 + 0{\cdot}00436\, Z_j - (0{\cdot}01543\, Z_j)^2 + (0{\cdot}01422\, Z_j)^3. \qquad (A4)$$

Formulas (A2), (A3), (A4) are based on the data in Cromer & Mann (1967).

(g) *The Ruland monochromator cut-off function* $Y_R(Q)$

$$Y_R(Q) = \left\{\left(1+\frac{\Delta\lambda}{b}\right)\left[1+\frac{\pi^2(\lambda'-\lambda)^2}{(\Delta\lambda+b)^2}\right]\right\}^{-1}, \qquad (A17)$$

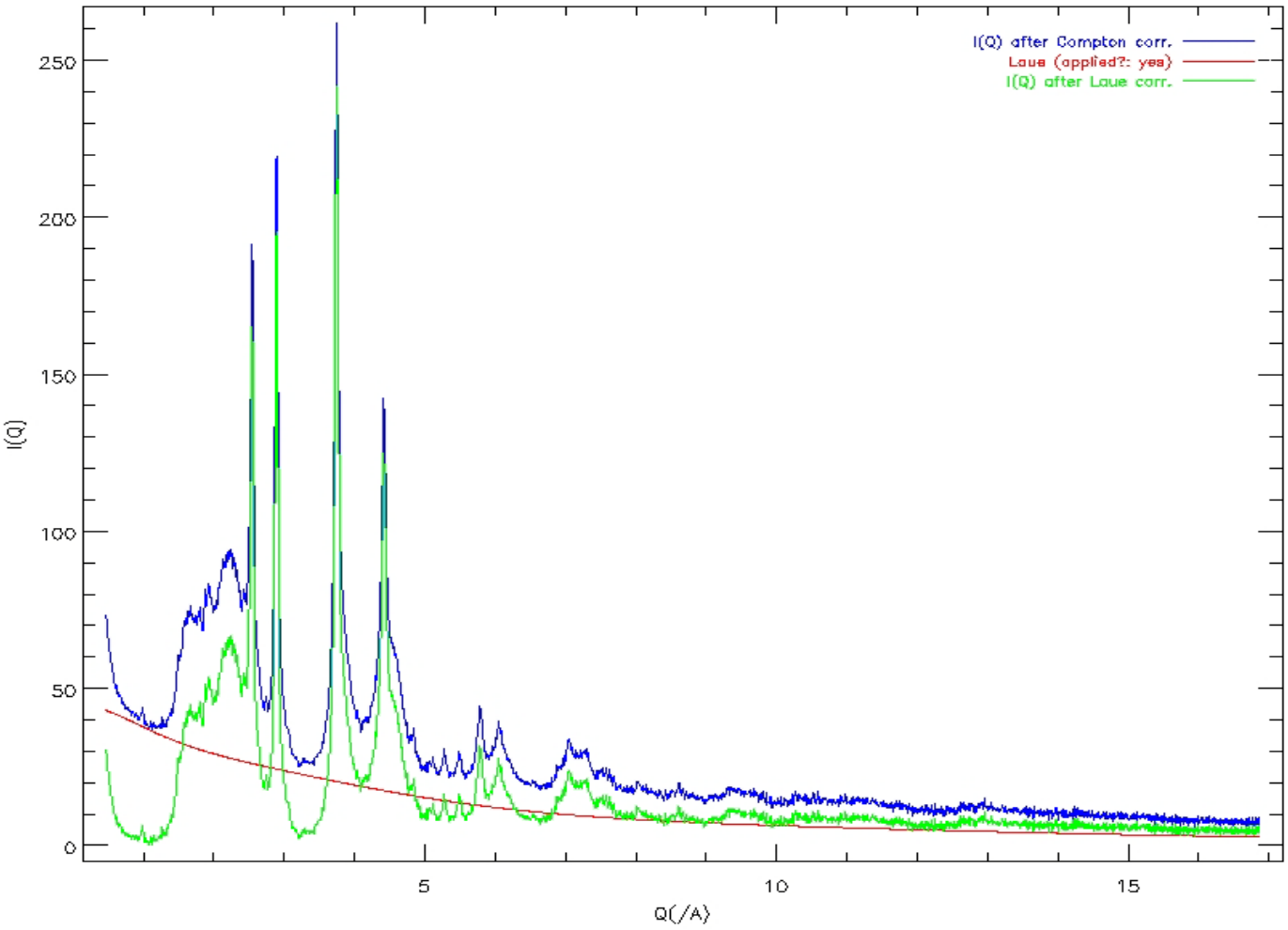
with $\Delta\lambda = \Delta q_{\max}\lambda^2 s^3 c^{-1}(a^2+s^2)^{-1}$, $s = Q/2\pi$, $a = 5{\cdot}3$ nm^{-1}, $b = 6{\cdot}9$ pm, $c = 137$ and $\Delta q_{\max} = 3{\cdot}05$ (Ruland, 1964).



Obtenir la PDF expérimentale (cas des rayons X B.B.)

$$S(Q) = [I_{eu}^{coh} - (\langle f^2 \rangle - \langle f \rangle^2)]/\langle f \rangle^2$$

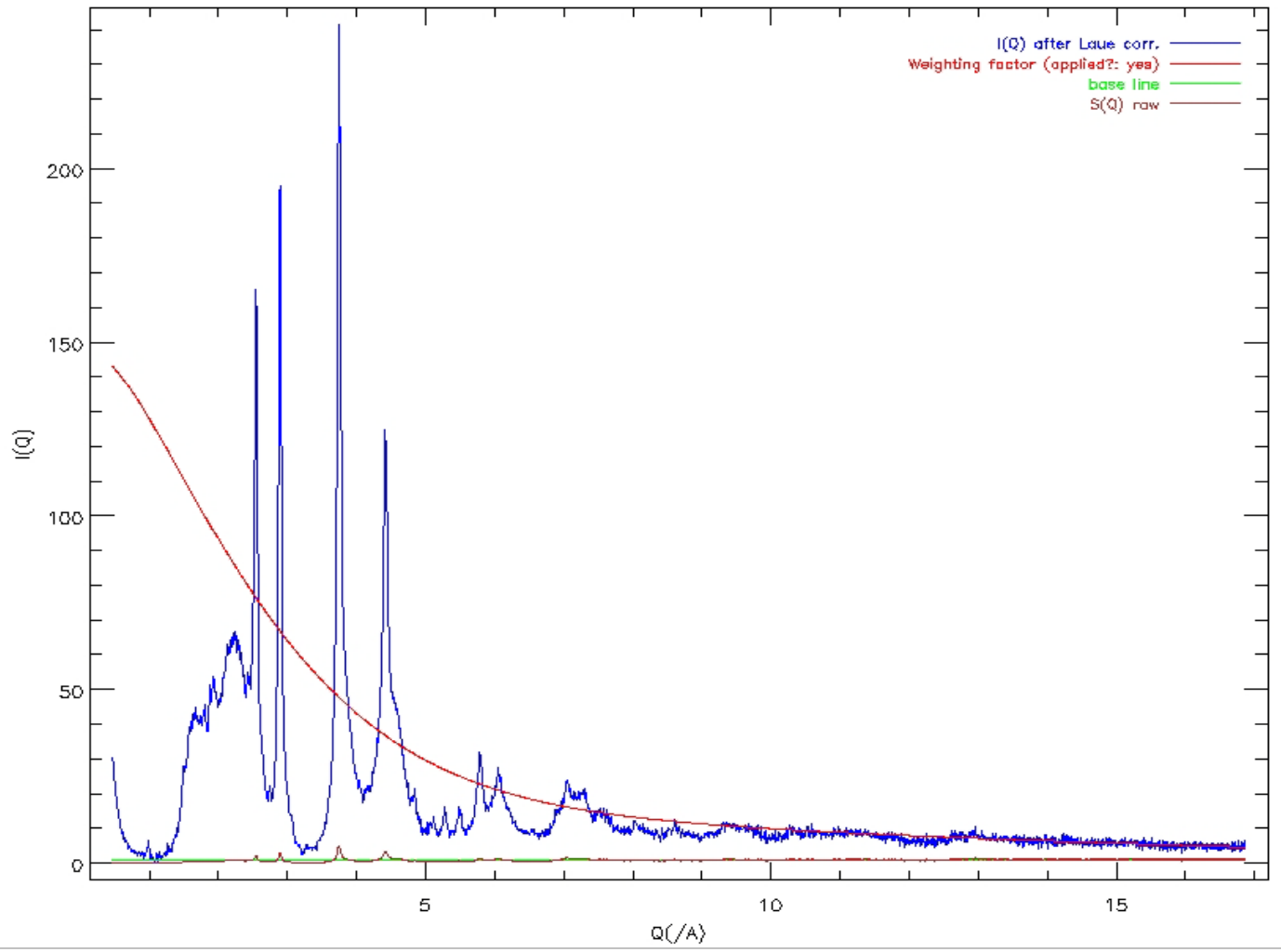
Laue diffuse



Obtenir la PDF expérimentale (cas des rayons X B.B.)

$$S(Q) = [I_{eu}^{coh} - (\langle f^2 \rangle - \langle f \rangle^2)]/\langle f \rangle^2$$

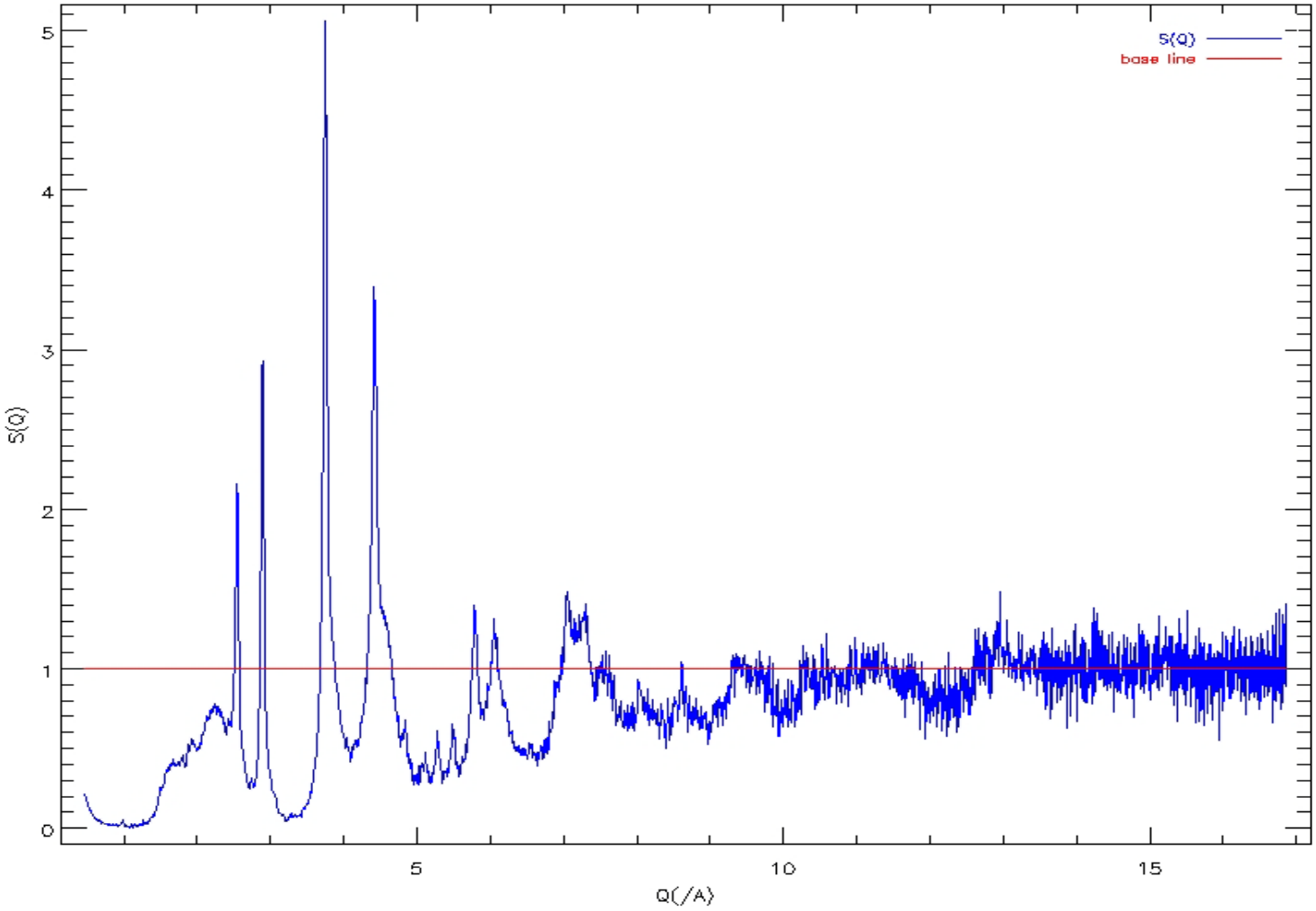
Normalisation
<f>^{2}



Obtenir la PDF expérimentale (cas des rayons X B.B.)

$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi}\int_0^{\infty} Q[S(Q) - 1]\sin(Qr)dQ,$$

S(Q)

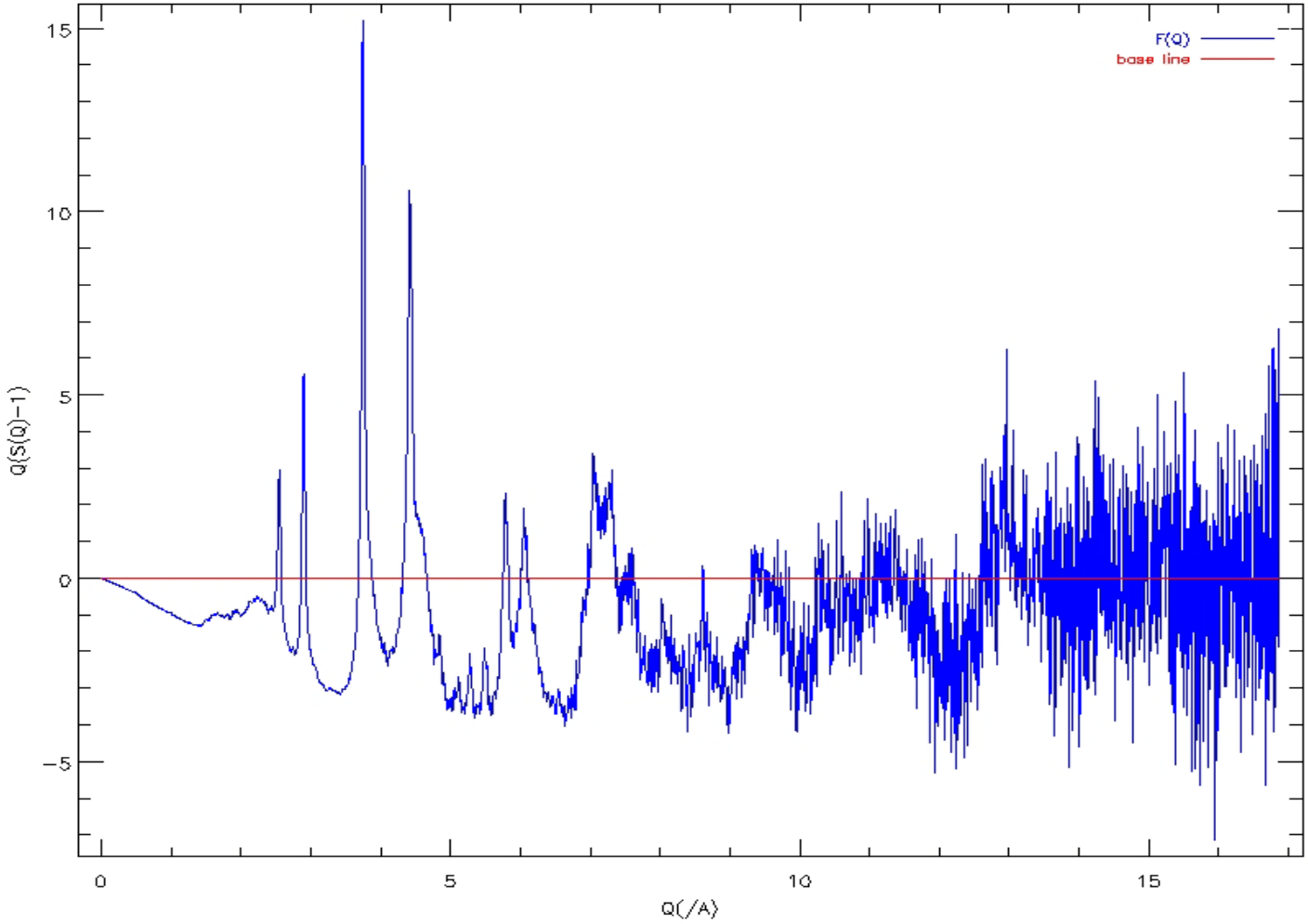


Obtenir la PDF expérimentale (cas des rayons X B.B.)

$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi}\int_0^{\infty} Q[S(Q) - 1]\sin(Qr)dQ,$$

F(Q)

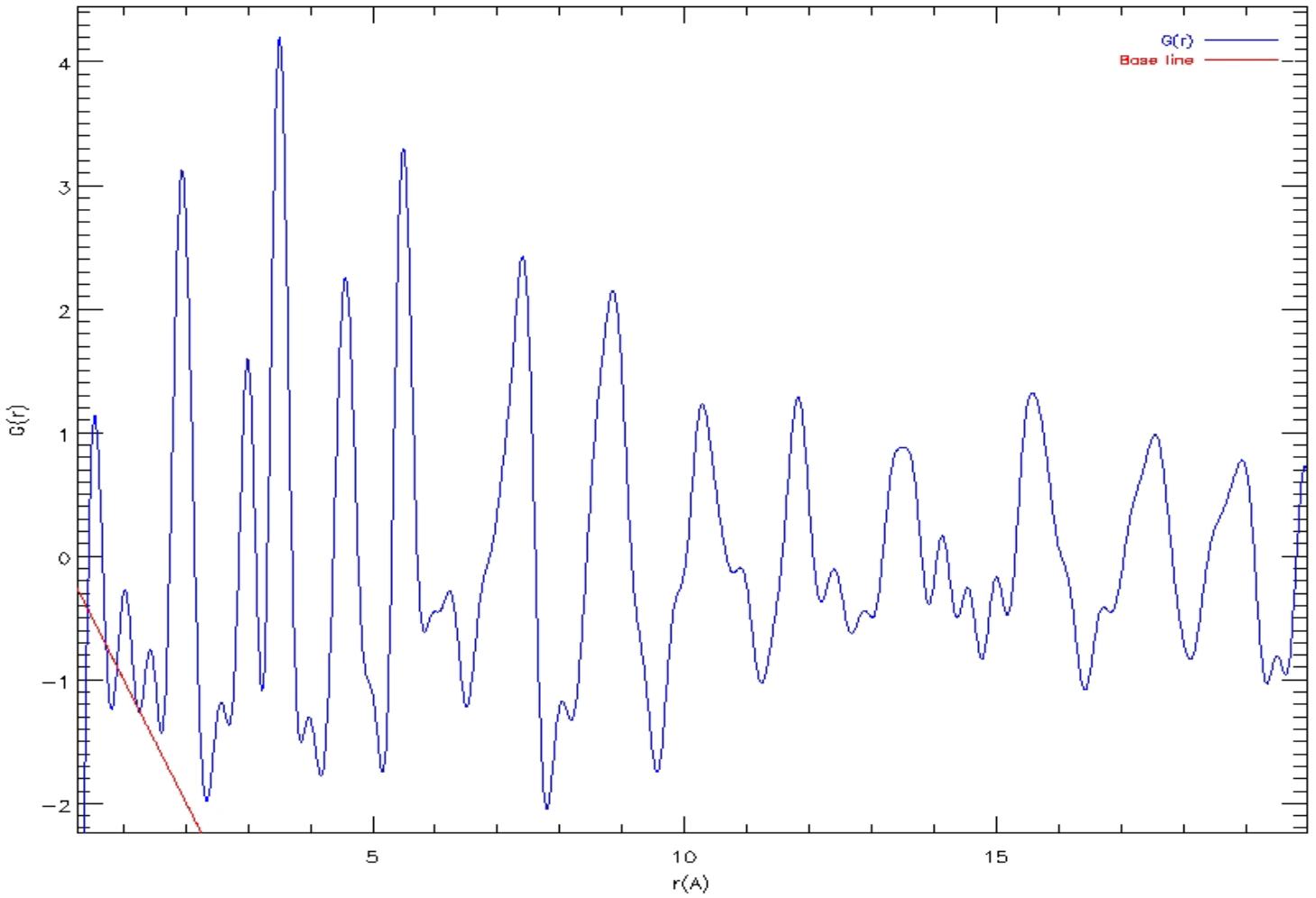
F(Q)=Q(SQ)-1)

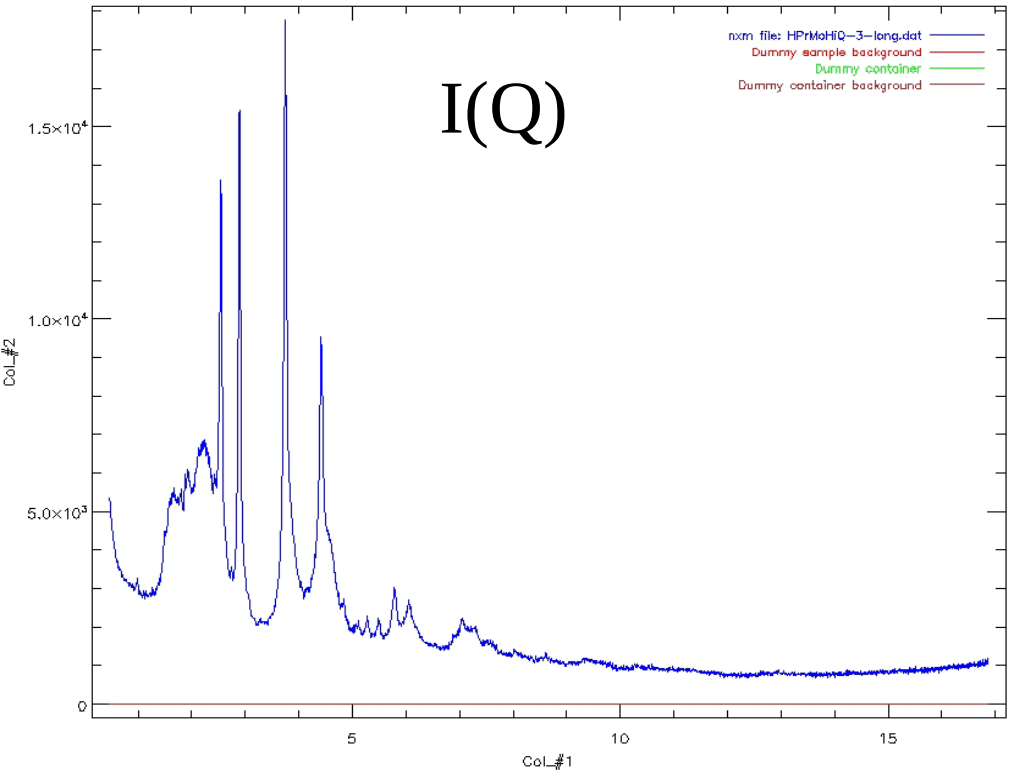


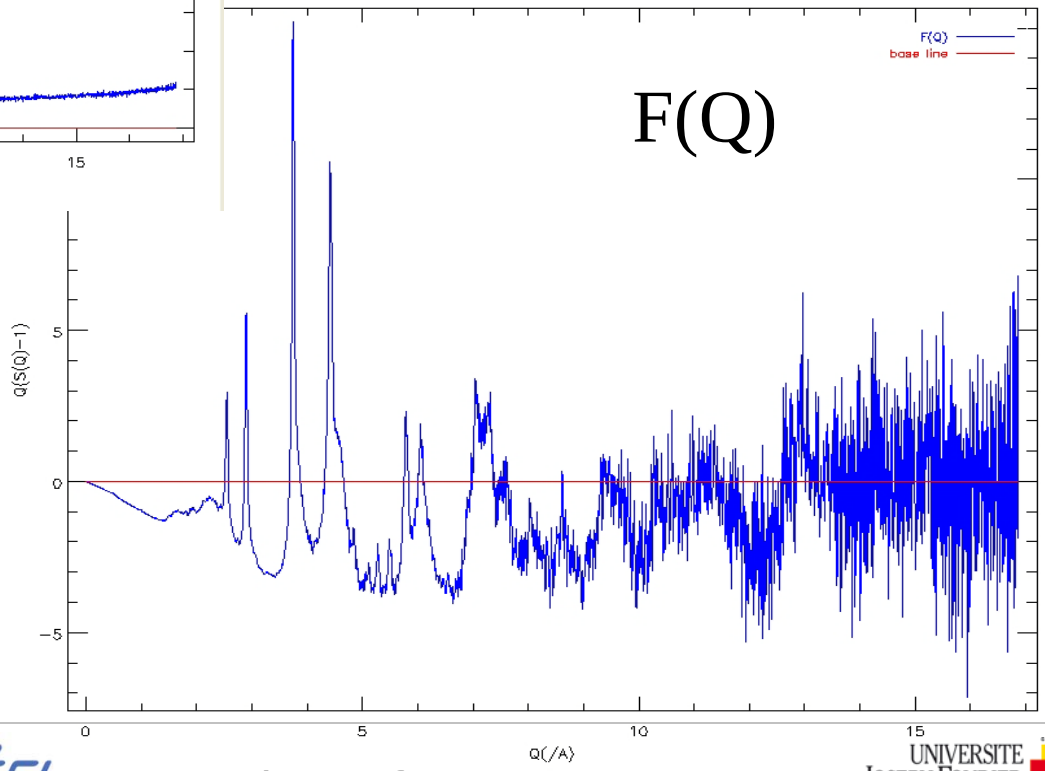
Obtenir la PDF expérimentale (cas des rayons X B.B.)

$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi}\int_0^{\infty} Q[S(Q) - 1]\sin(Qr)dQ,$$

G(r)







Mesurer à hauts Q

Fortes statistiques à hauts Q

Exemples

Exemple : hydroxilian pseudo rutile (HPR)

(I.E. Grey, CSIRO, Melbourne)

XRPD :

Cohérence du réseau O

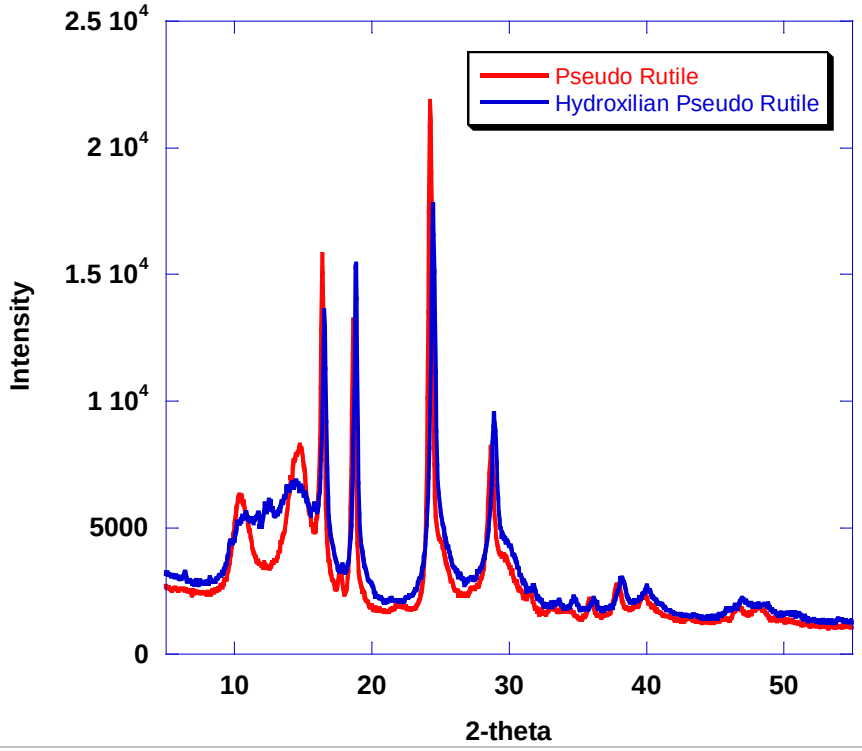
Affinement Rietveld

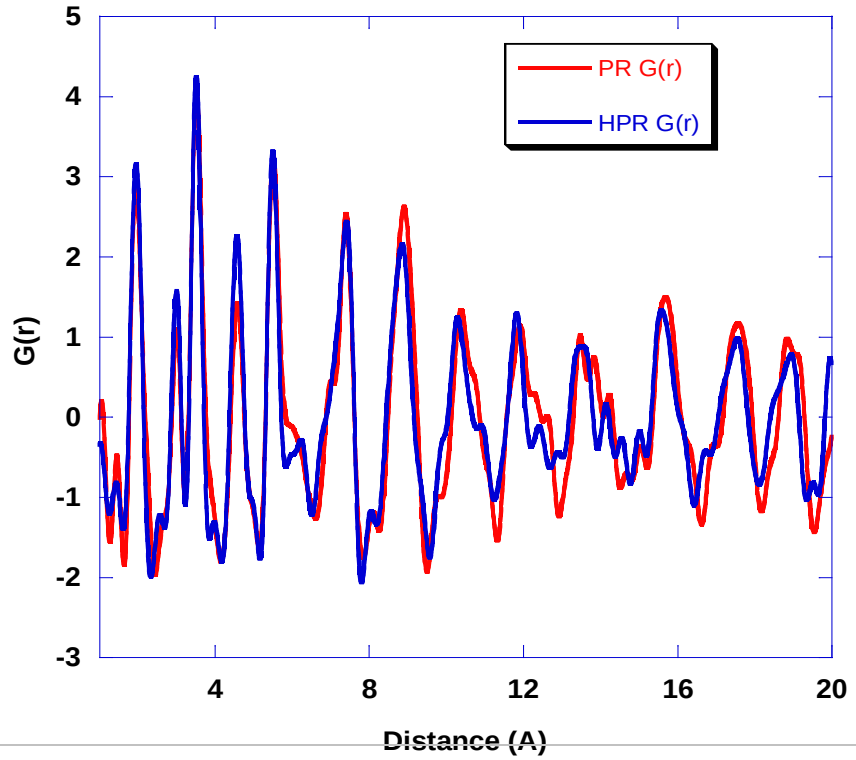
=> Paramètres moyens dans la sous-maille

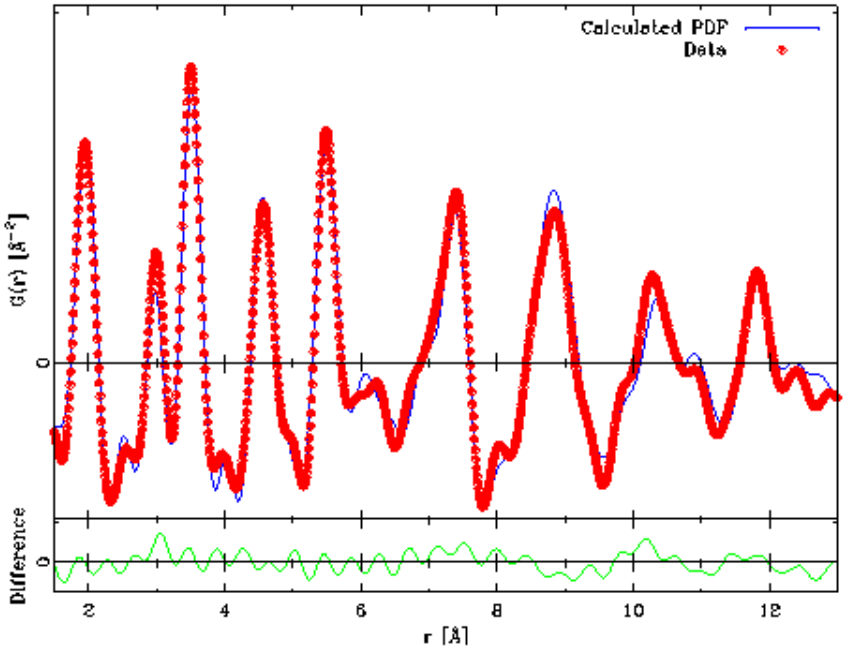
PDF :

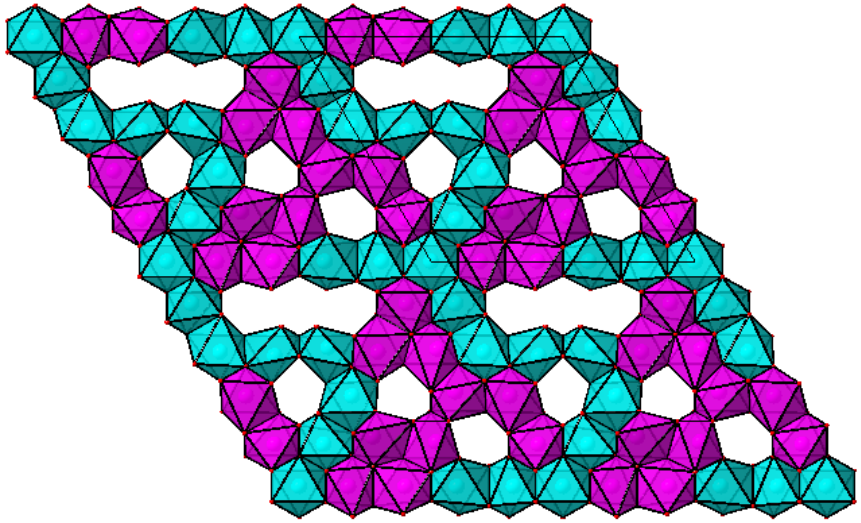
distances bien définies (≠amorphe)

Les 2 structures locales sont similaires

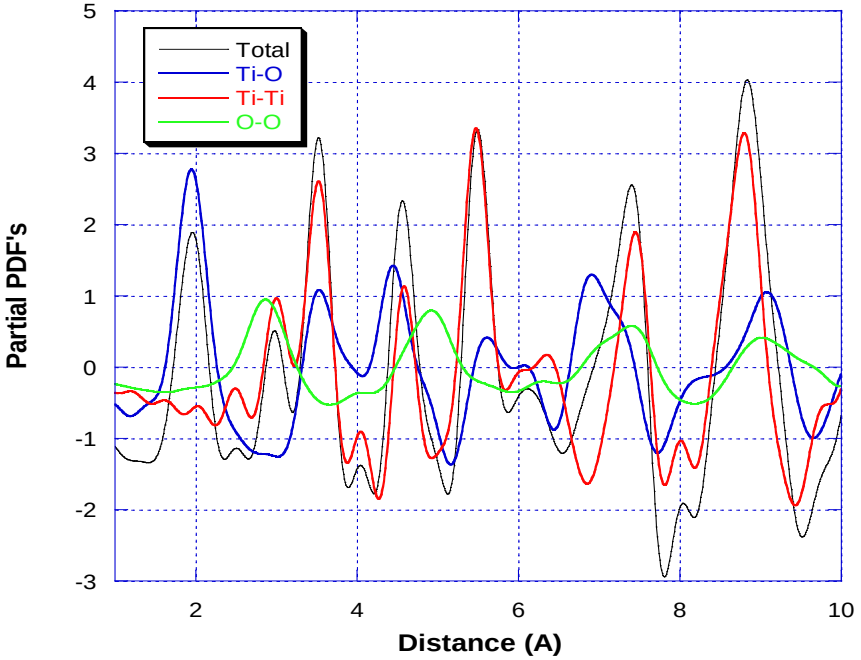








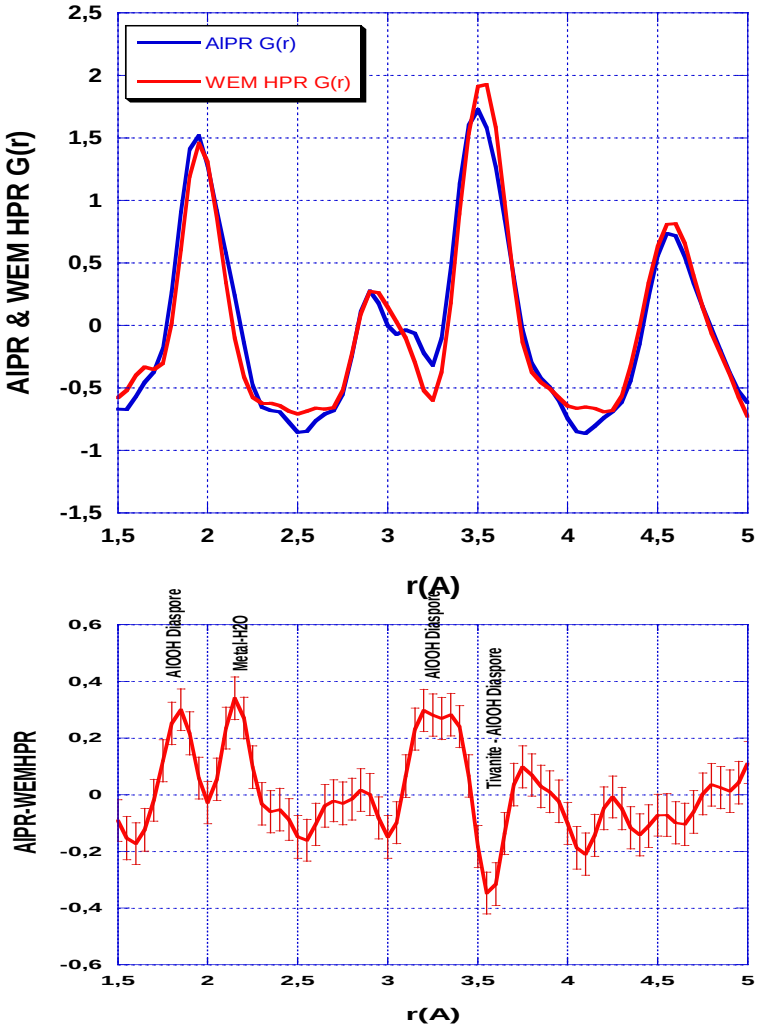
Purple up, cyan down



PdfFit avec contraintes

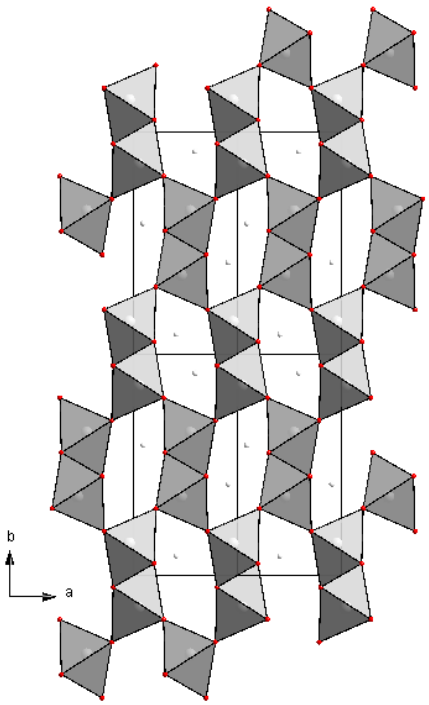
Le modèle de structure locale est valide
On peut extraire la distribution des distances
 => image statistique des distortions locales
Pas de solution unique
(car pas de structure unique)

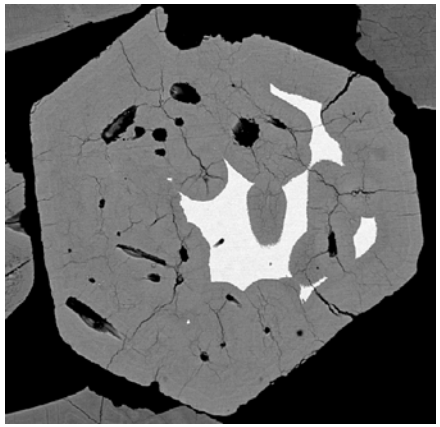
PDF différence entre 2 HPR avec et sans Al



⇒ **AlOOH diaspore**.

⇒ Normalement non stable,
mais HPR=template
=> Localisé dans les nanopores des grains.





Exemple : structure locale du TiO_2 nano-cristallin

TiO_2 nano-cristallin pour pile solaires (cellules de Graetzel)

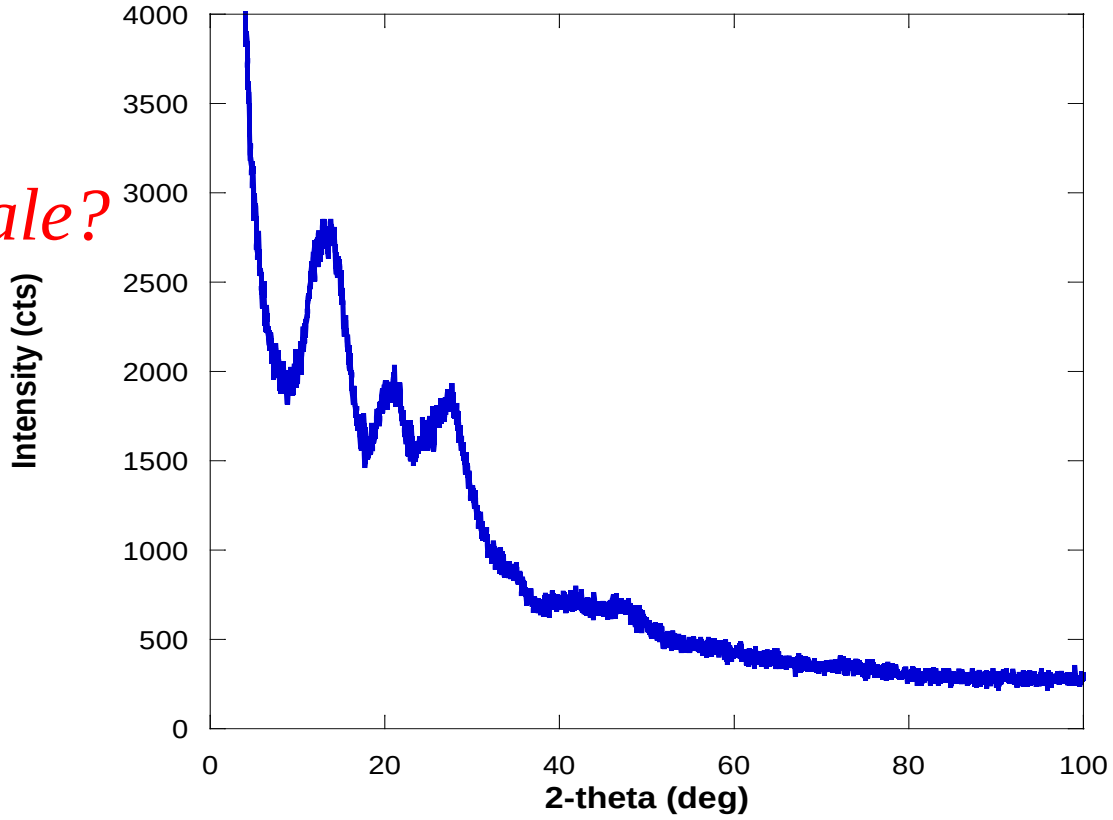
Synthésisé par chimie douce (sol-gel)

recuit => anatase

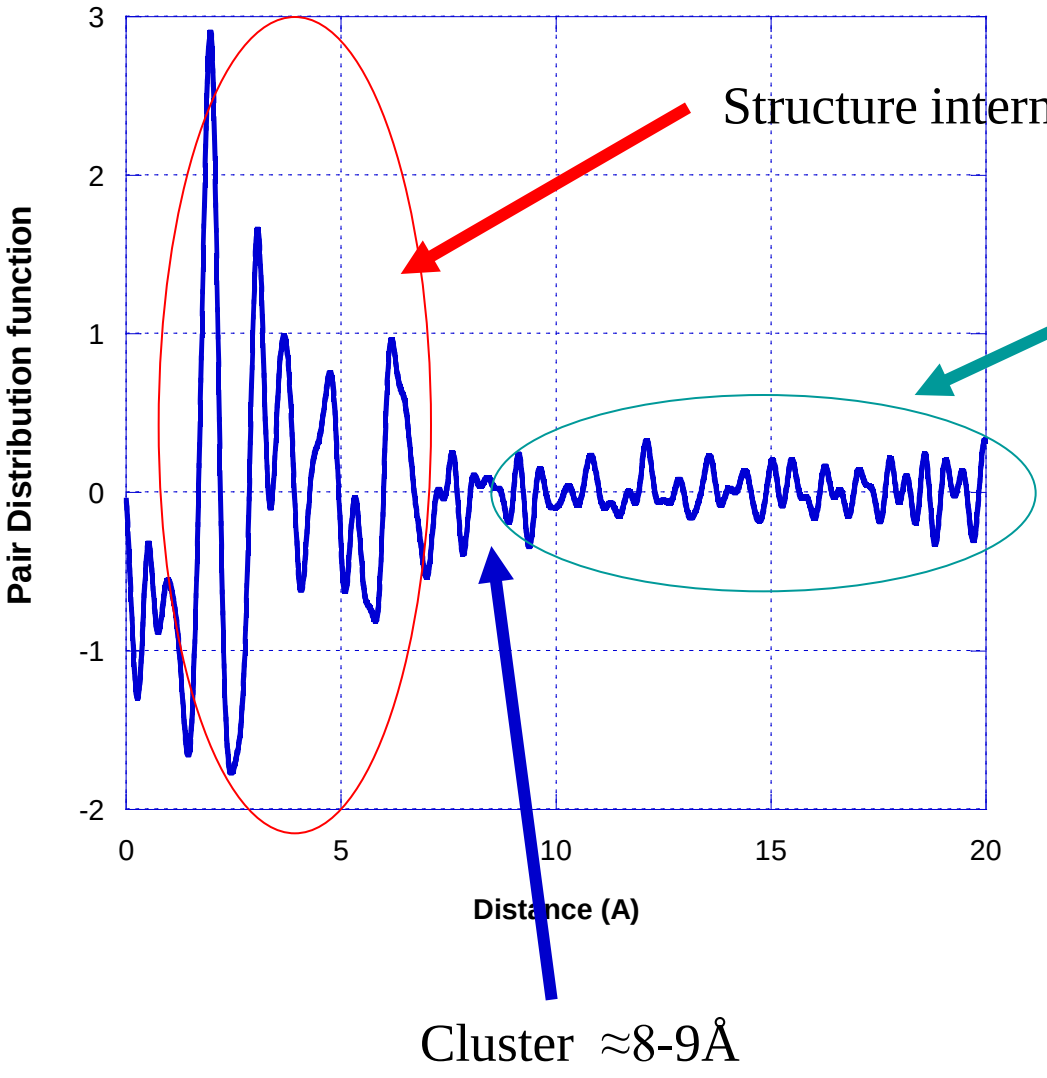
quelle est la structure locale?

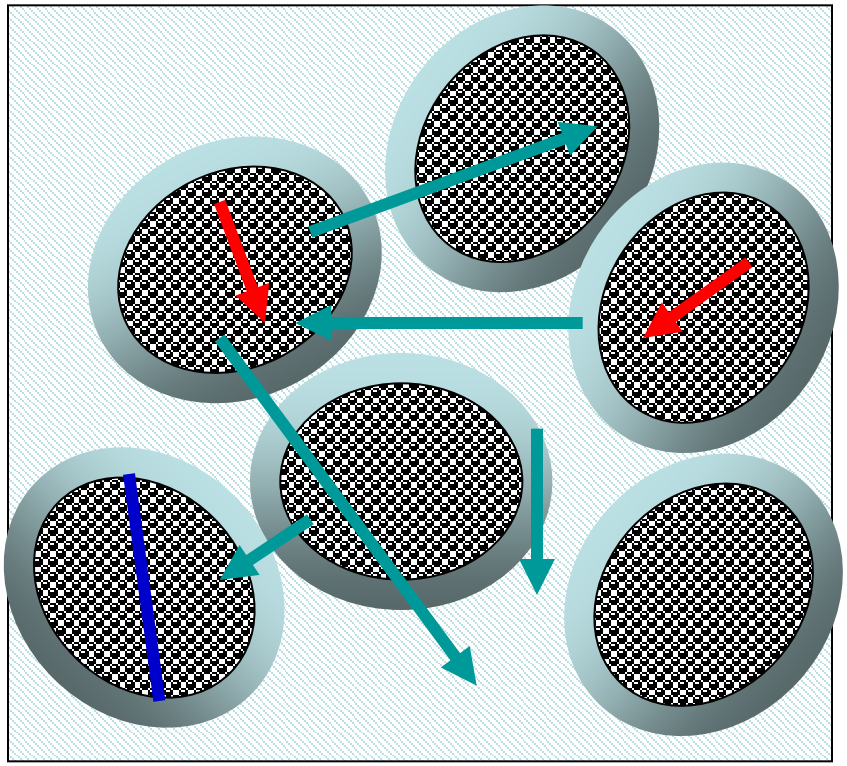
X-ray diffraction de poudres

- Panalytical X'pert diffract.
- Mo graded multilayer optics, λ=0.7107Å
- Bragg-Brentano geometry
- X'celerator detector
- Qmax=16.8Å^{-1}

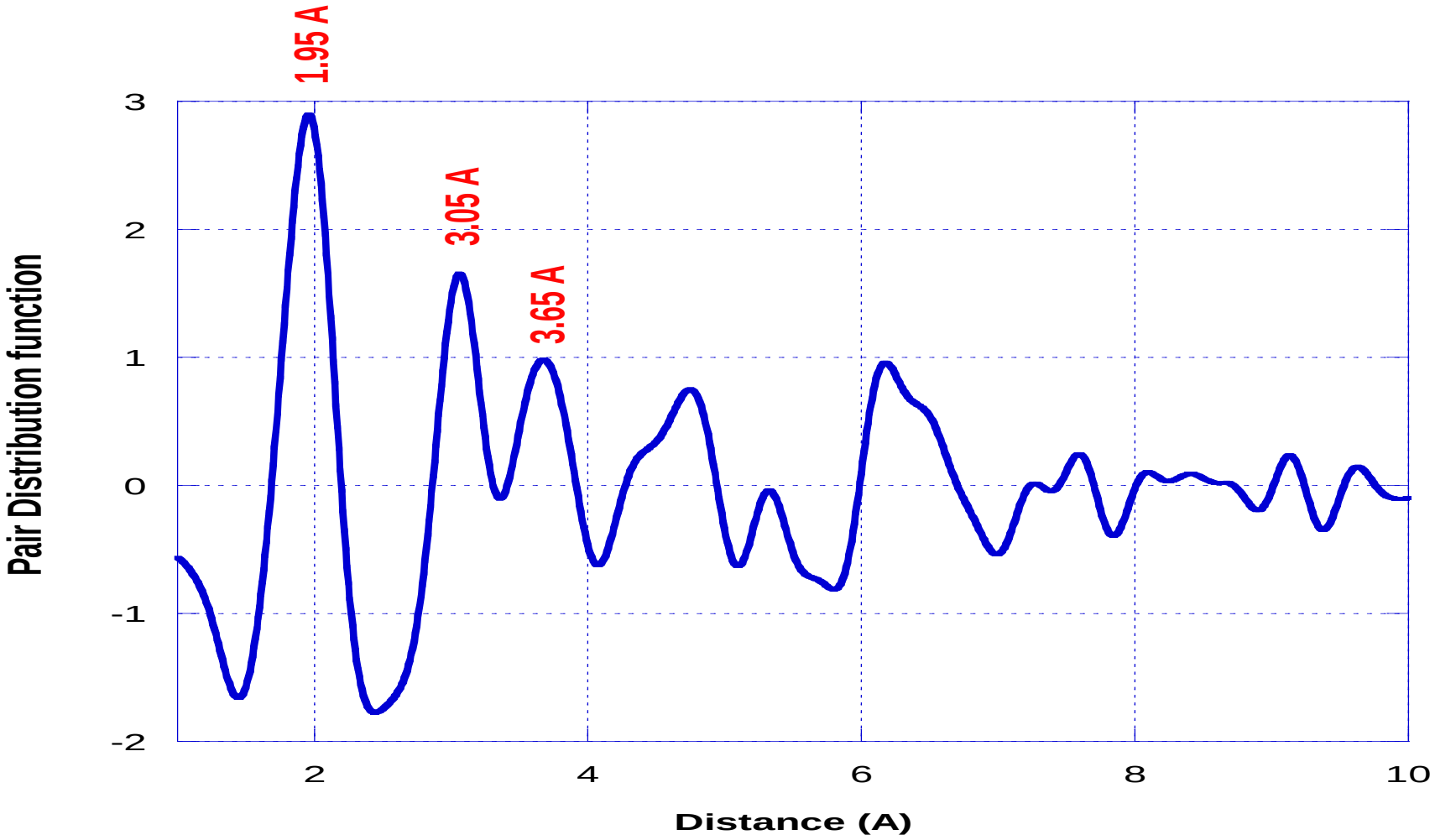


La PDF informe sur la taille des grains et leur structure interne

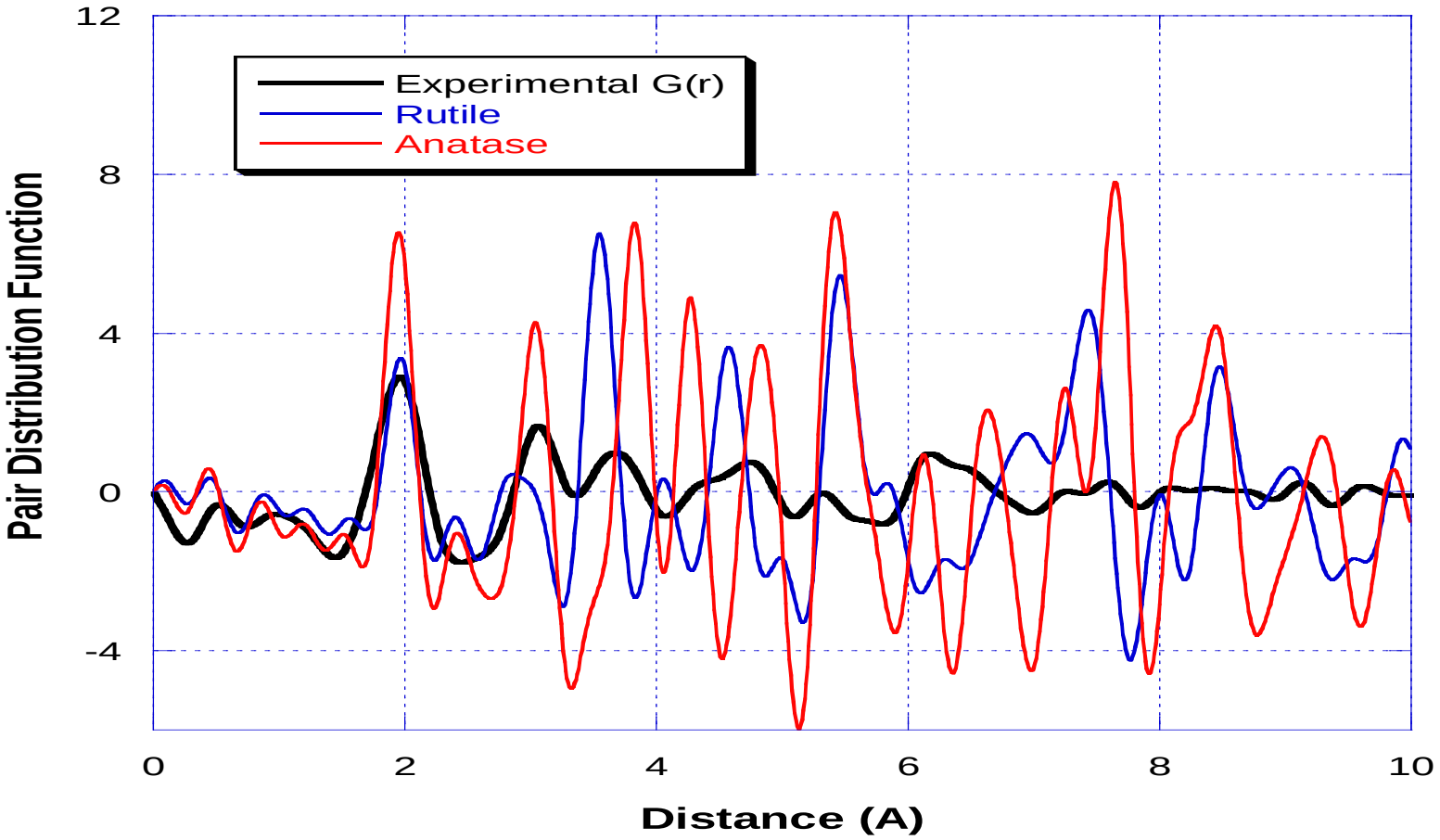


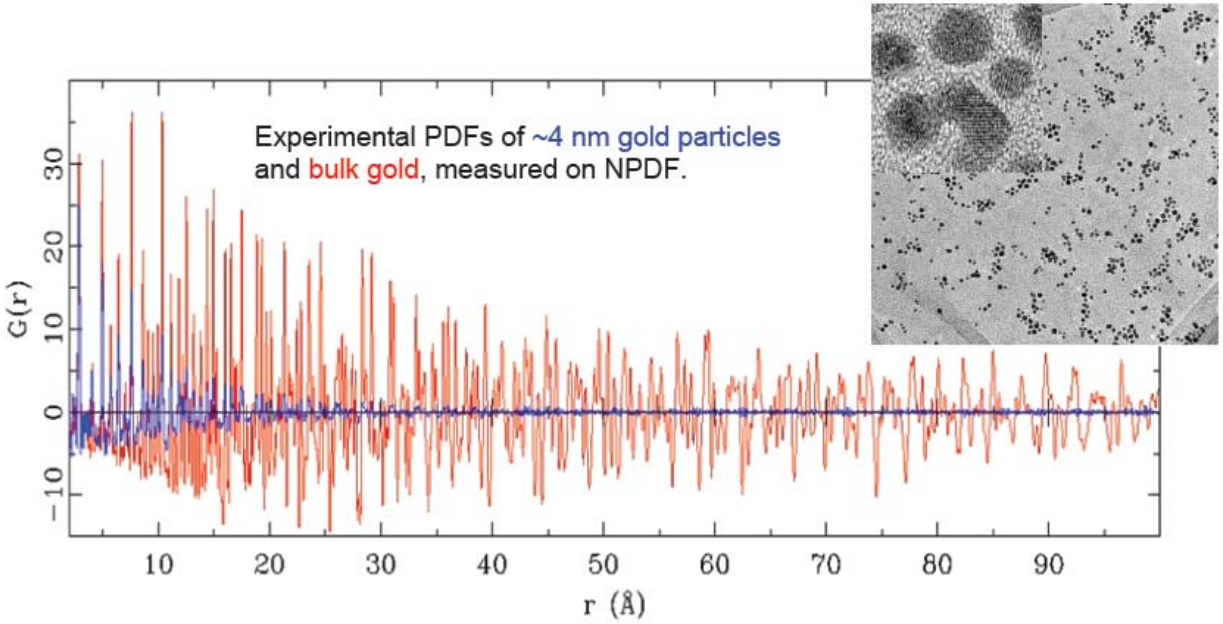


Coordination octahédrique



Localement ≠ rutile, anatase





K.L. Page, Th. Proffen, H. Terrones, M. Terrones, L. Lee, Y. Yang, S. Stemmer, R. Seshadri and A.K. Cheetham, **Direct Observation of the Structure of Gold Nanoparticles by Total Scattering Powder Neutron Diffraction**, *Chem. Phys. Lett.* **393**, 385-388 (2004).

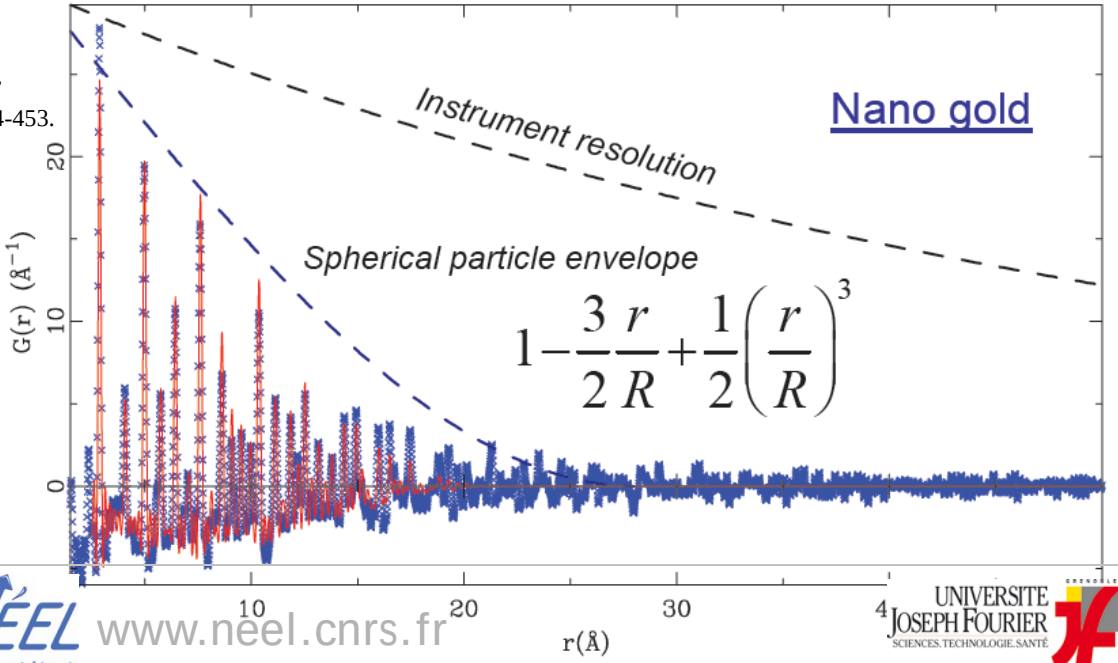
Facteur de forme de la particule:

"Finite Size Effects of Nanoparticles to the Atomic Pair Distribution Functions"
K. Kodama, S. Iikubo, T. Taguchi and S. Shamoto, Acta Cryst. A 62 (2006) 444-453.

$$G(r) \approx f(r) G_{\infty}(r)$$

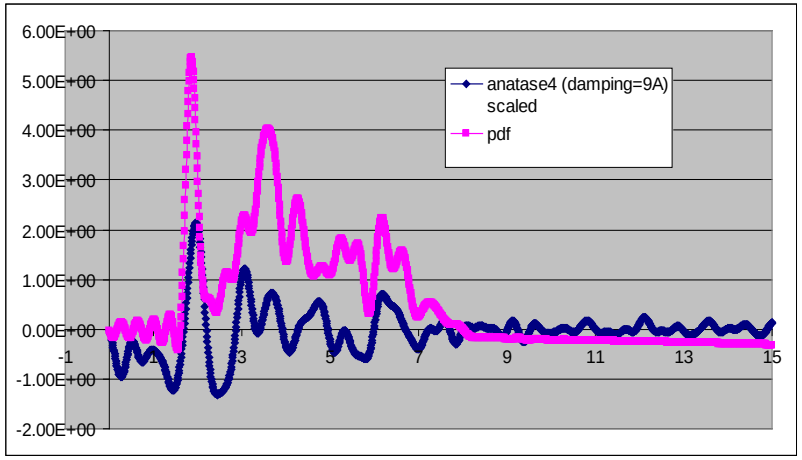
f(r) dépend de la forme (cf *SAS*)

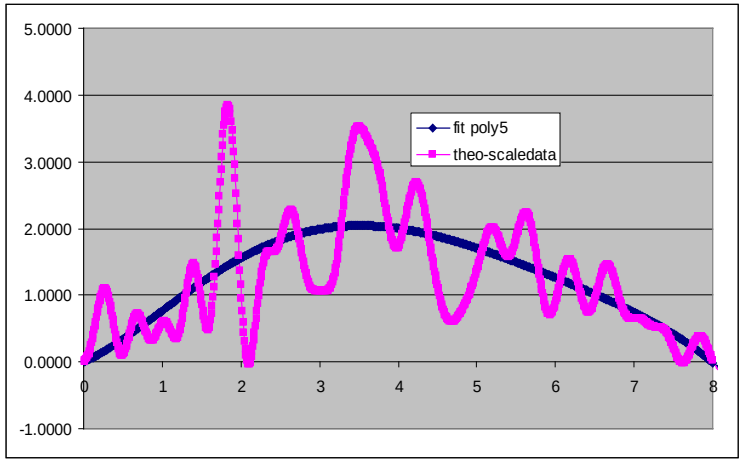
Pour une sphère: *f(r)* = $1 - \frac{3}{2}\frac{r}{R} + \frac{1}{2}\left(\frac{r}{R}\right)^3$



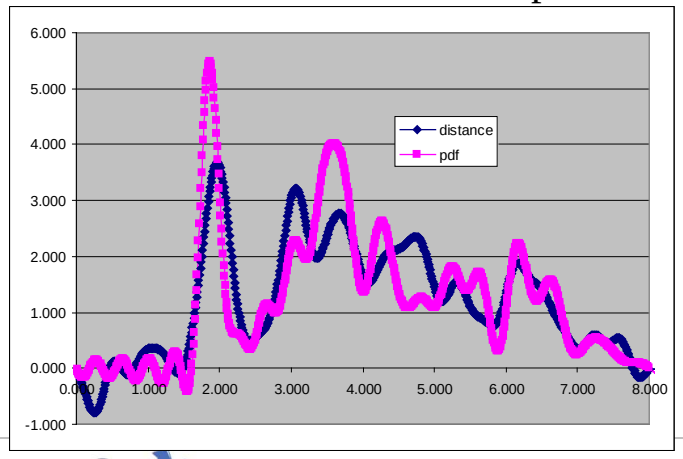
Particules de forme quelconque

La PDF théorique est calculée en plaçant la particule dans une très grande maille pour éviter les contributions inter-particules. Mais la densité moyenne est fausse et non constante.





On calcule la PDF théorique, on soustrait l'expérimentale et on fitte la différence avec un polynome et un facteur d'échelle. La correction est appliquée aux données expérimentales, puis on affine le modèle. On boucle la procédure avec le nouveau modèle.



Modélisation de la structure des clusters

On ne sait pas résoudre ab initio

On produit un modèle raisonable de la structure avec

connaissance cristallo-chimique

modélisation quantique (énergie de configuration)

infos d'autres techniques(e^- microscopie, spectroscopies)

On calcule la pdf et compare à la pdf experimentale

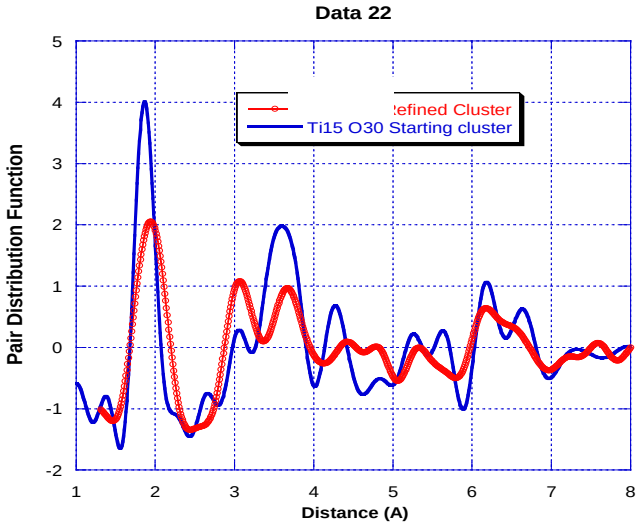
Rejette si trop mauvais

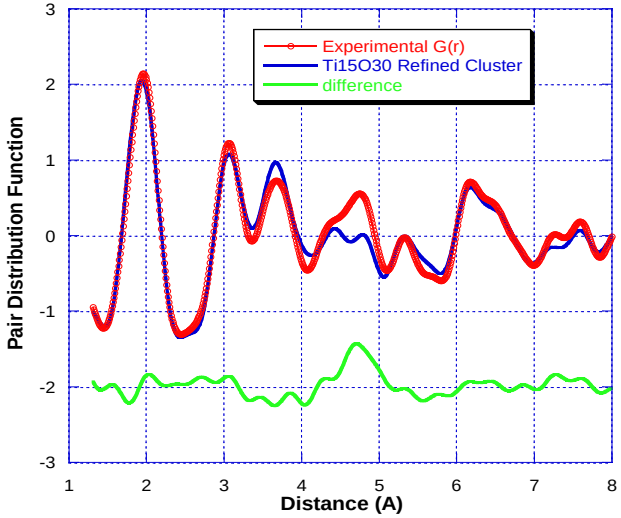
Sinon, affinement dans l'espace direct (PDFFit)

Recalcul de l'énergie de configuration du modèle affiné

….

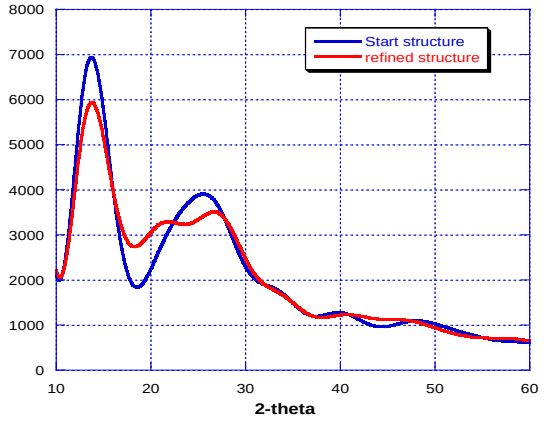
Essai d'affinement PDF dans l'espace direct : $Ti_{15}O_{30}$ cluster (*S. Hamad et al. (2005)*)

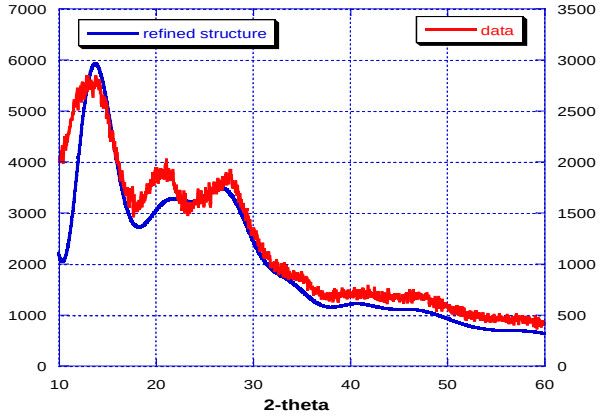




Diffractograme recalculé avec la formule de Debye

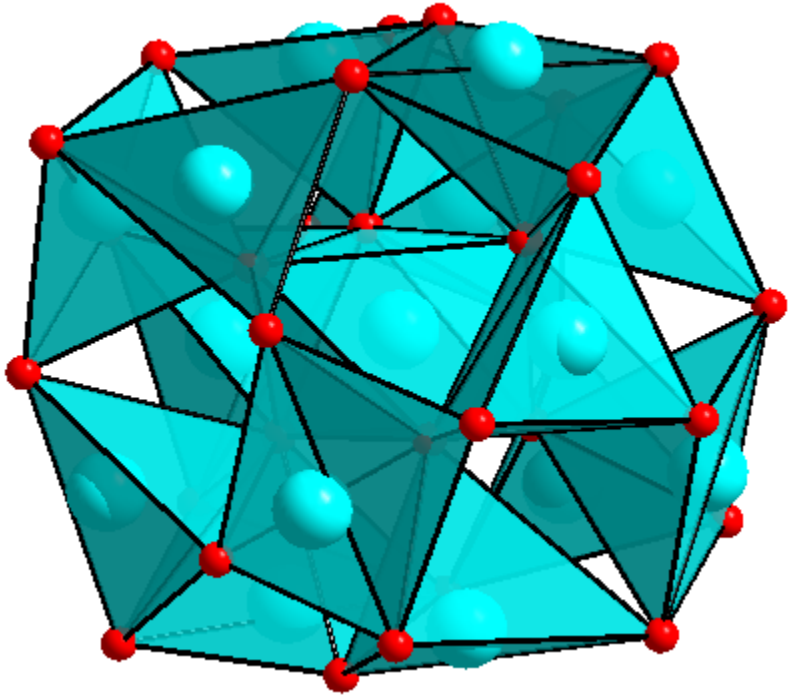
$$I(2\theta) = \sum_{ij} b_i b_j \sin(Qr_{ij}) / Qr_{ij}$$



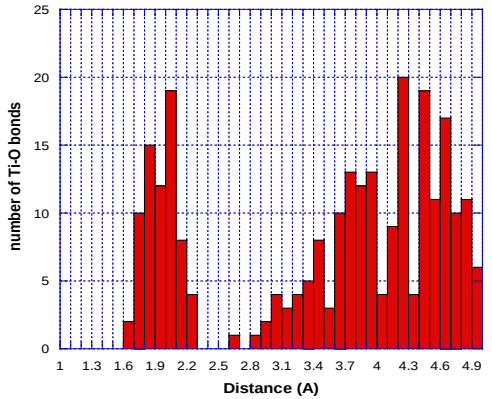


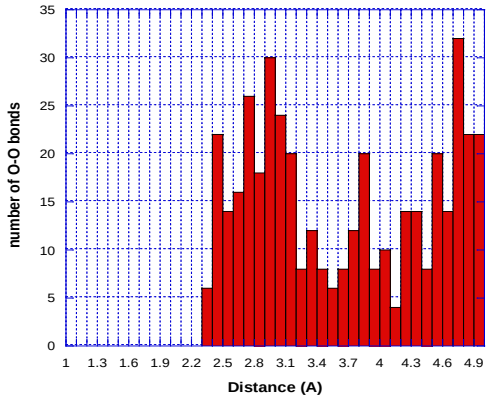
$Ti_{15}O_{30}$

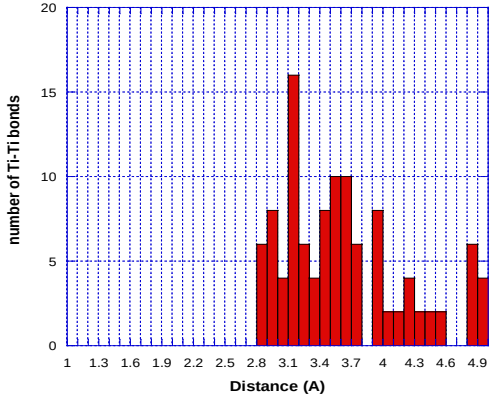
Après affinement PDF



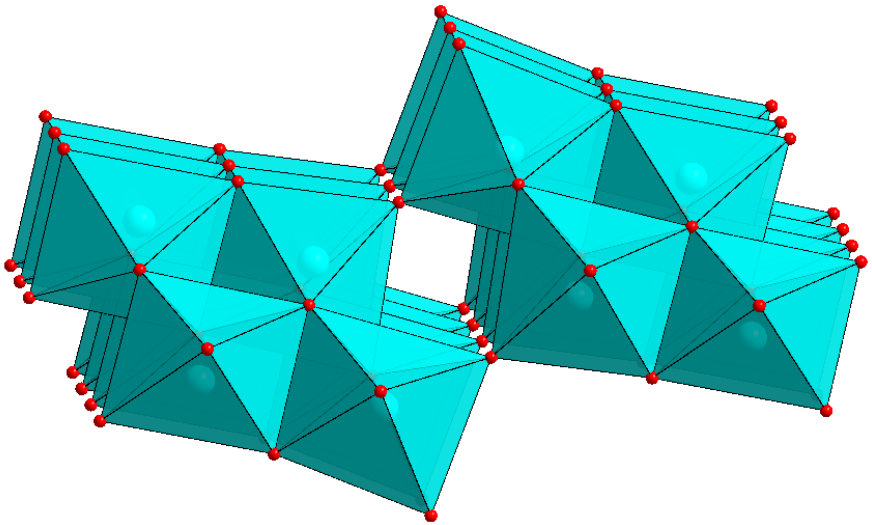
1 Ti 6-coordinated
8 Ti 5-coordinated
6 Ti 4-coordinated

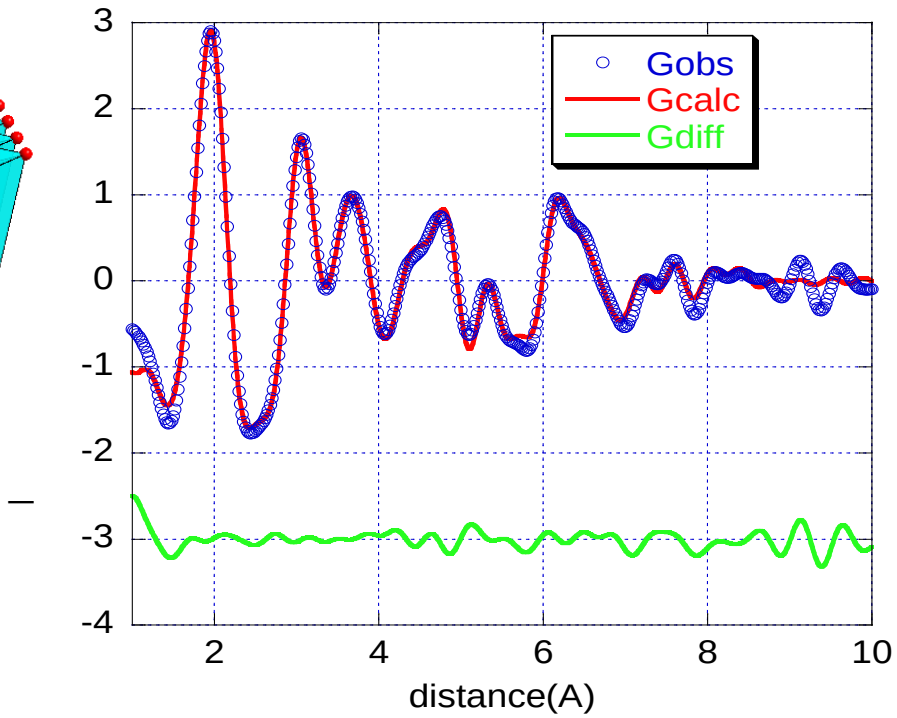


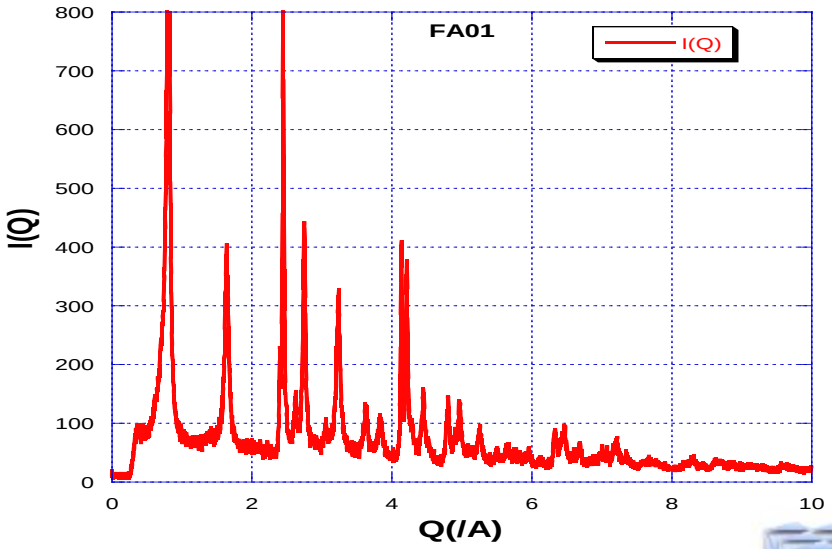


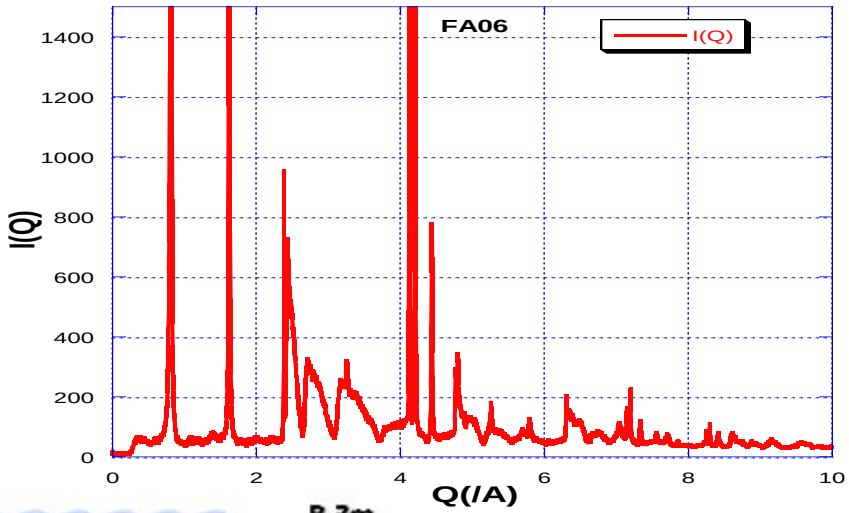


Meilleur modèle ;
Construit à partir de $H_2Ti_3O_7$



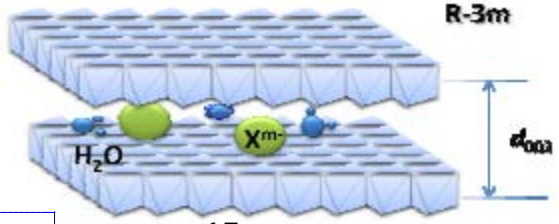


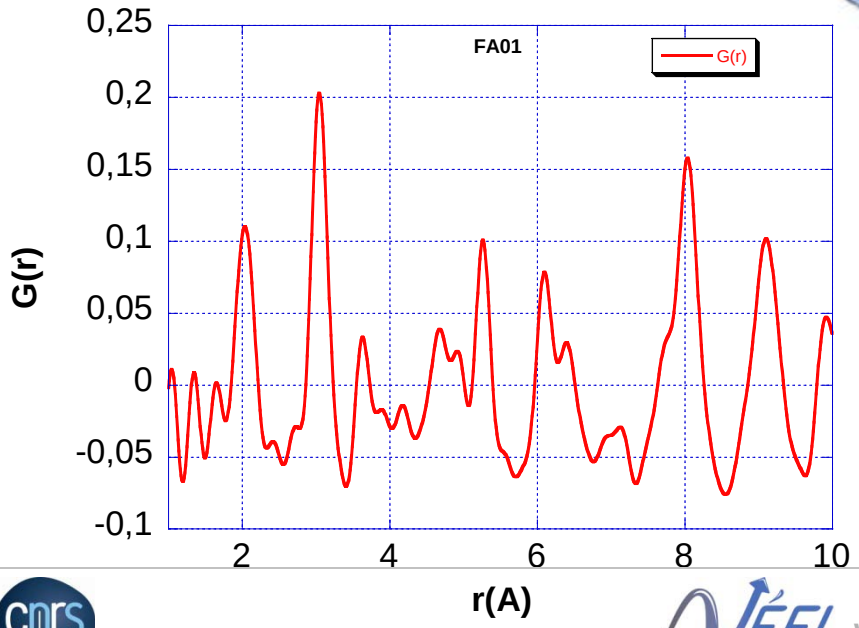


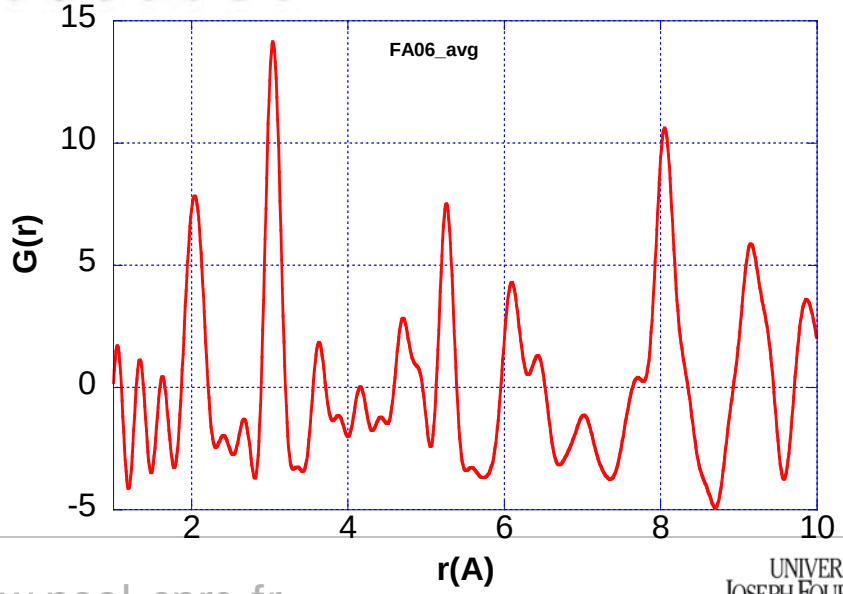


Hydroxides Doubles Lamellaires

Ch. Taviot-Guého, UBP, Clermont-Ferrand



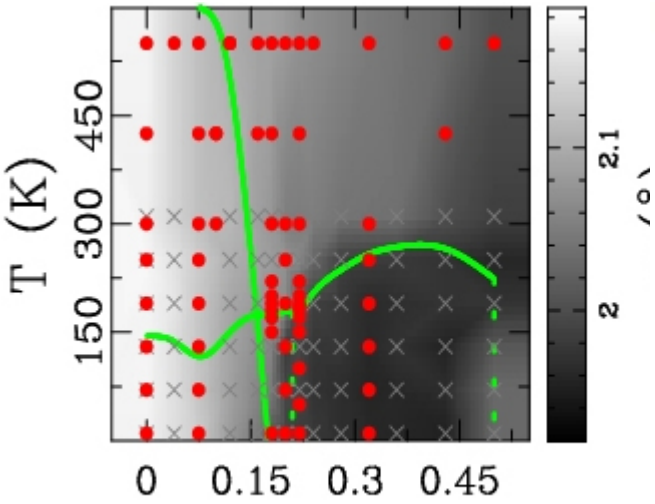


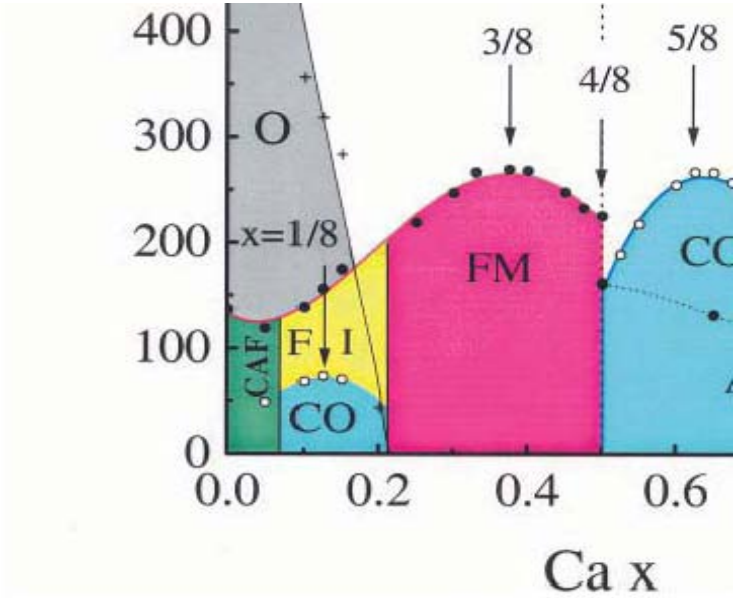


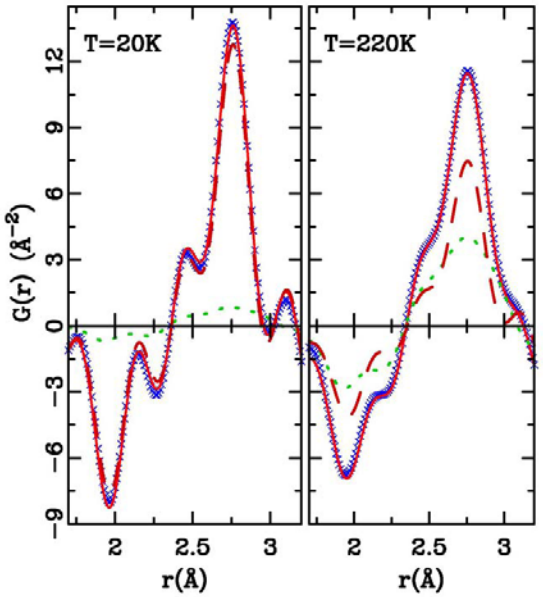
(LaCa)MnO_3 manganites

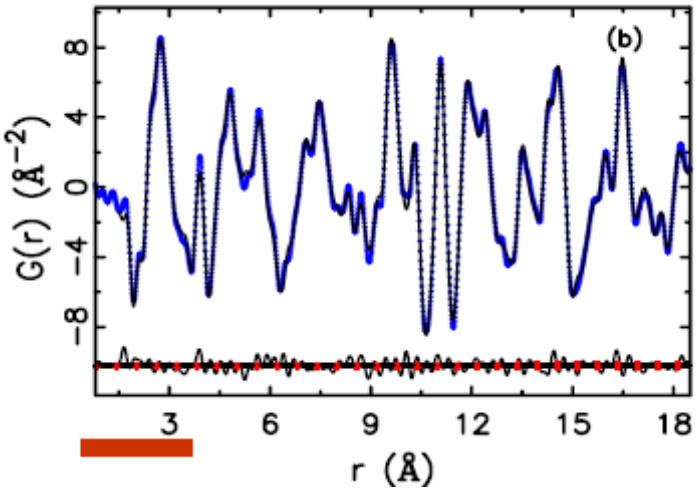
Comparaison des structures locale et moyenne

La distorsion JT persiste dans la phase métallique ?



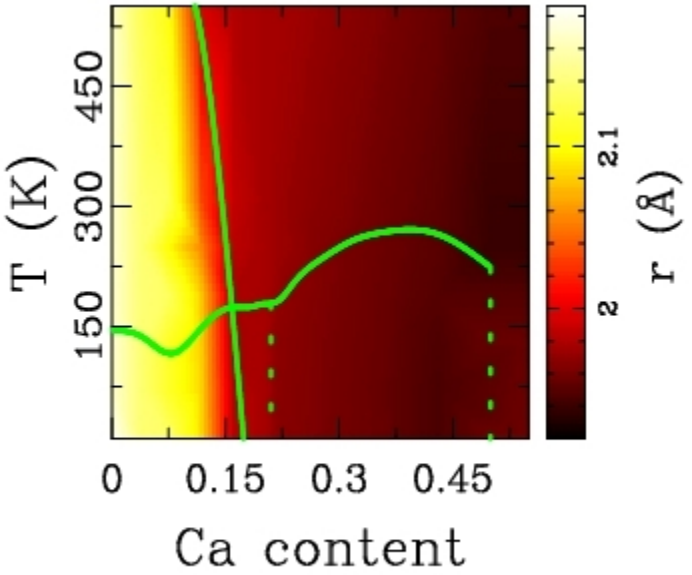




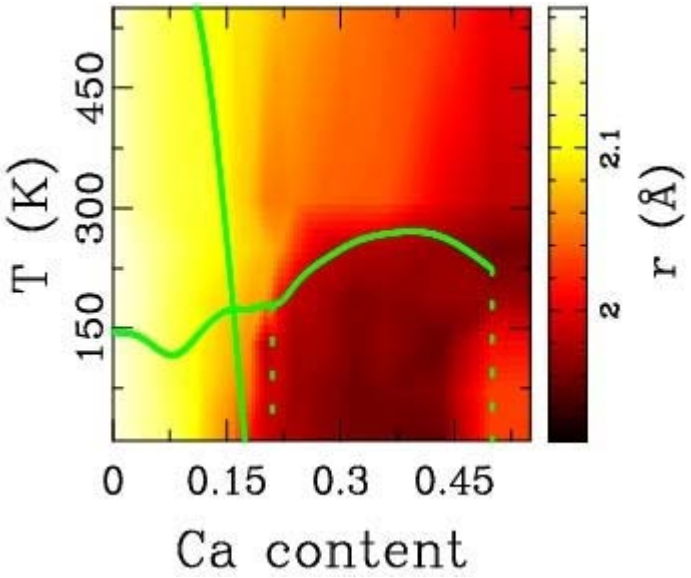


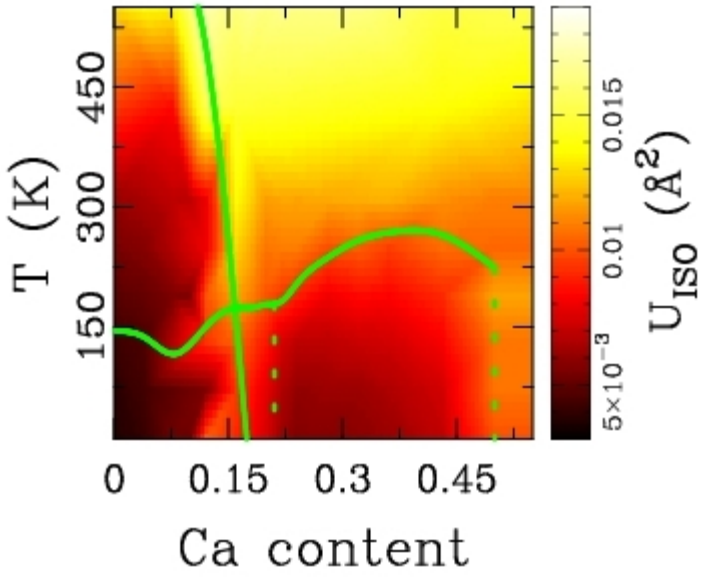
(x,T) results: Rietveld vs PDF (Pbnm)
Longueur de liaison (=distorsion Jahn-Teller)

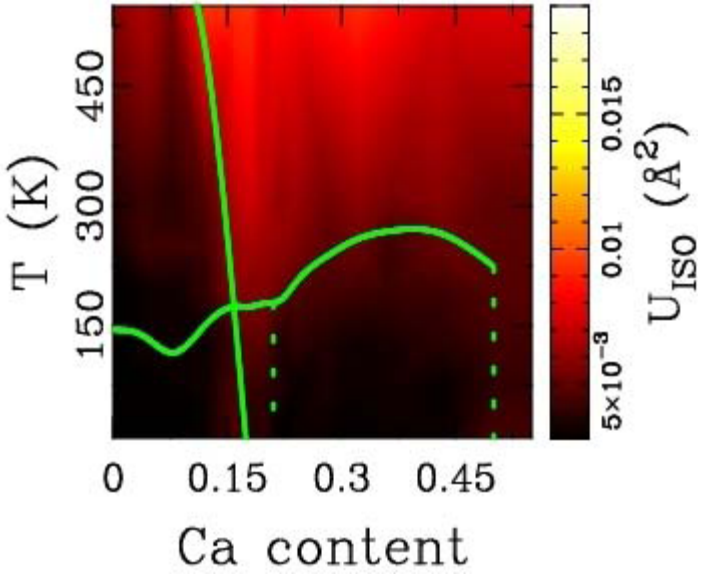
AVERAGE



LOCAL



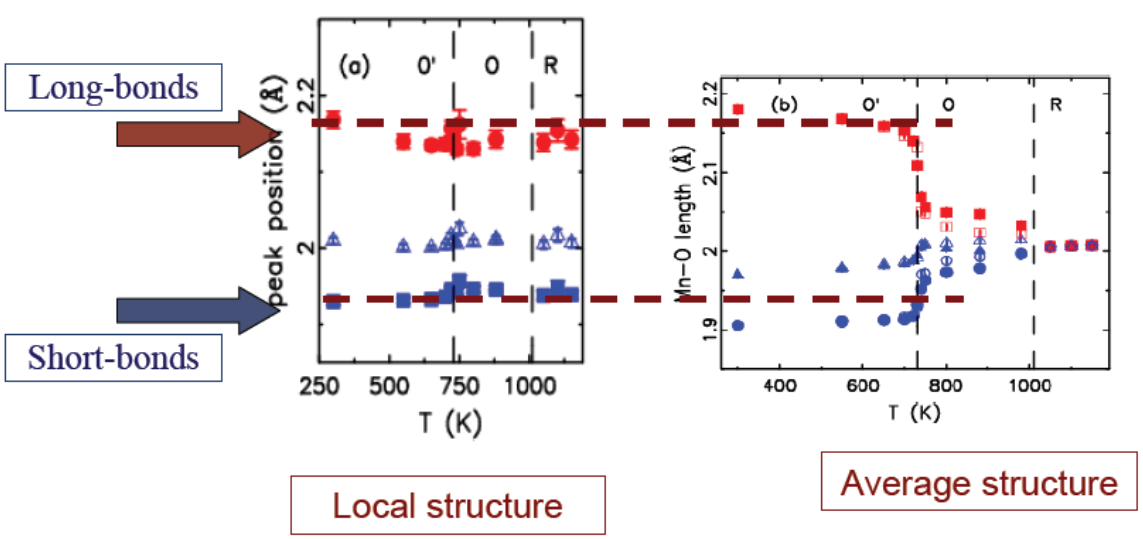




LaMnO3 *vs T*:

Mn-O bonds are constant up to the R phase

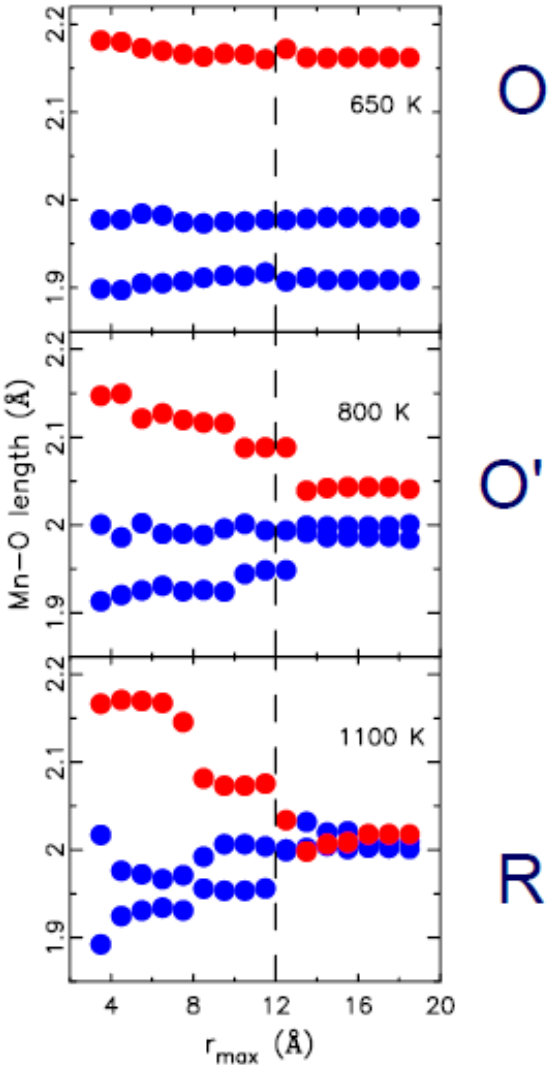
JT distortion persists locally in the ortho and rhombo phases



LaMnO3 *vs r*:

Affis dans des domaines en r variables

Fixe r_{min}, varie r_{max}



O'X. Qiuet al., Phys. Rev. Lett. 94, 177203, (2005)

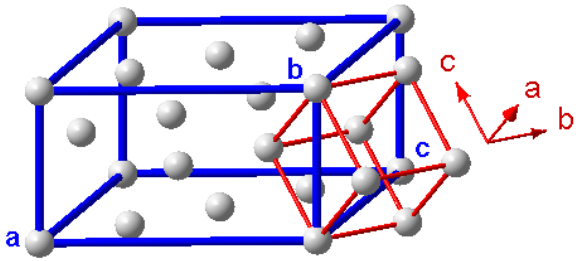
Perovskites multiferroïques : structures de $BiMnO_3$ et $BiCrO_3$

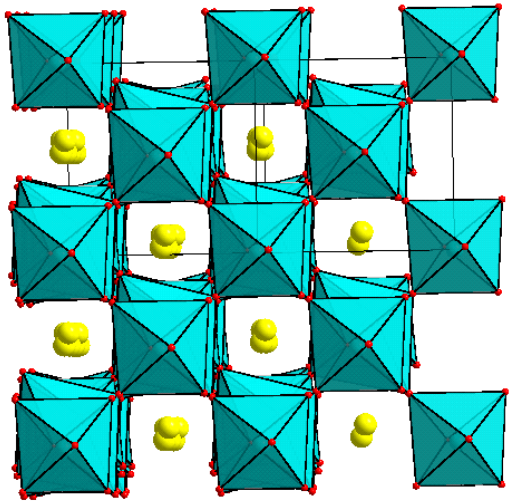
$BiMnO_3$:T("FE")=760K, T(FM)=105K
$BiCrO_3$:T("FE")=430K, T(AFM)=120K

Structure proposée: Pbnm => C121 at 430K

a=9.47Å, b=5.48Å, c=9.59Å, [illegible]

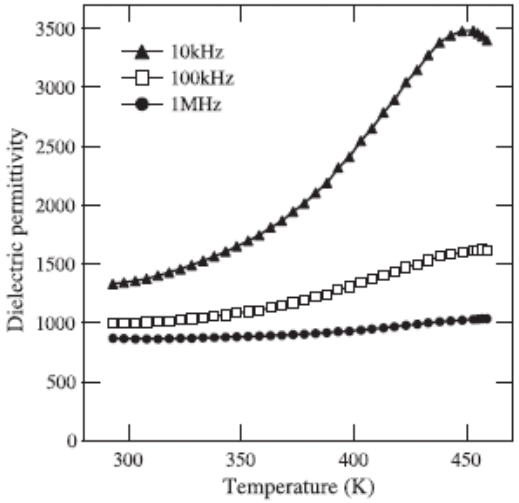
isostructuraux

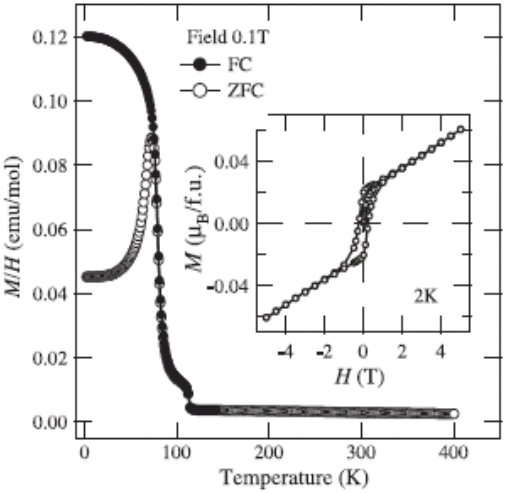




Synthèse HP-HT
TEM, RX, thermo-chimie
RX In situ HP-HT

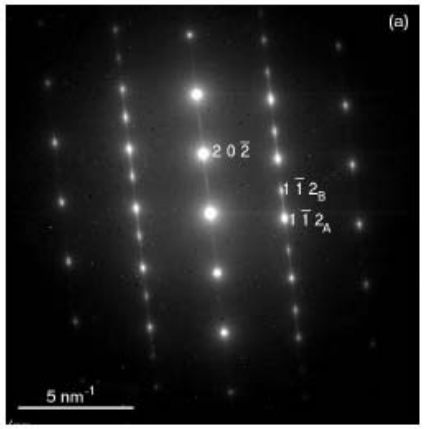
C Darie, P. Toulemonde, C. Goujon,
H. Klein, M. Bacia, P. Bordet
Coll. *ESRF, LMGP…*



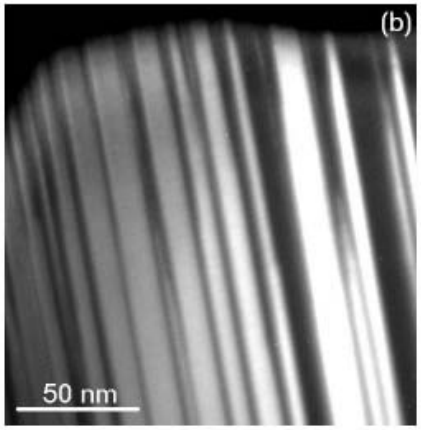


Niitaka et al., Solid State Ionics 172 (2004) 557–559

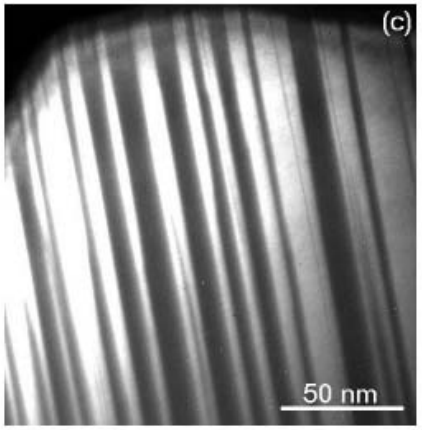
Structure « moyenne » de $BiCrO_3$



(a) Electron diffraction pattern of the [1 3 1] zone axis of monoclinic $BiCrO_3$.

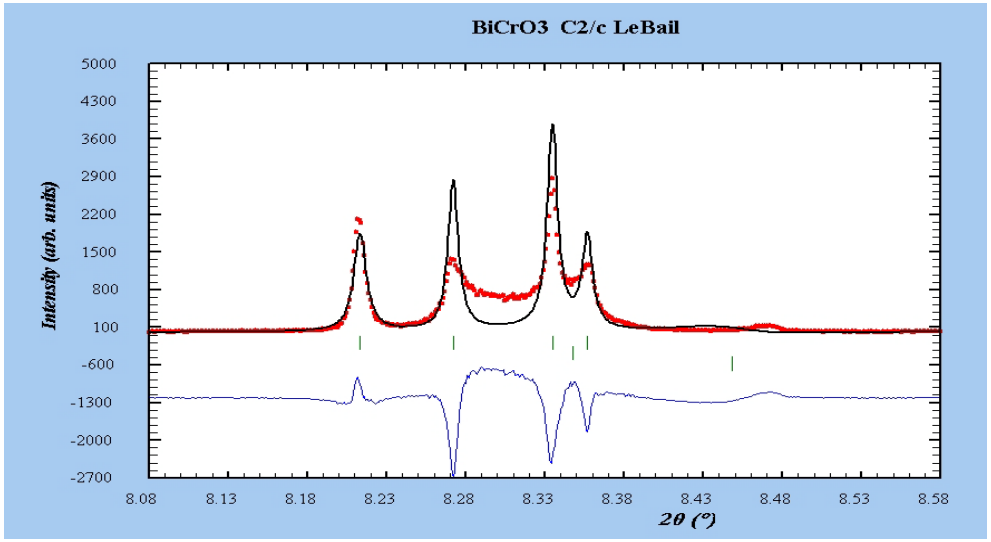


(b) Dark field image of $BiCrO_3$ selecting a spot of family A.



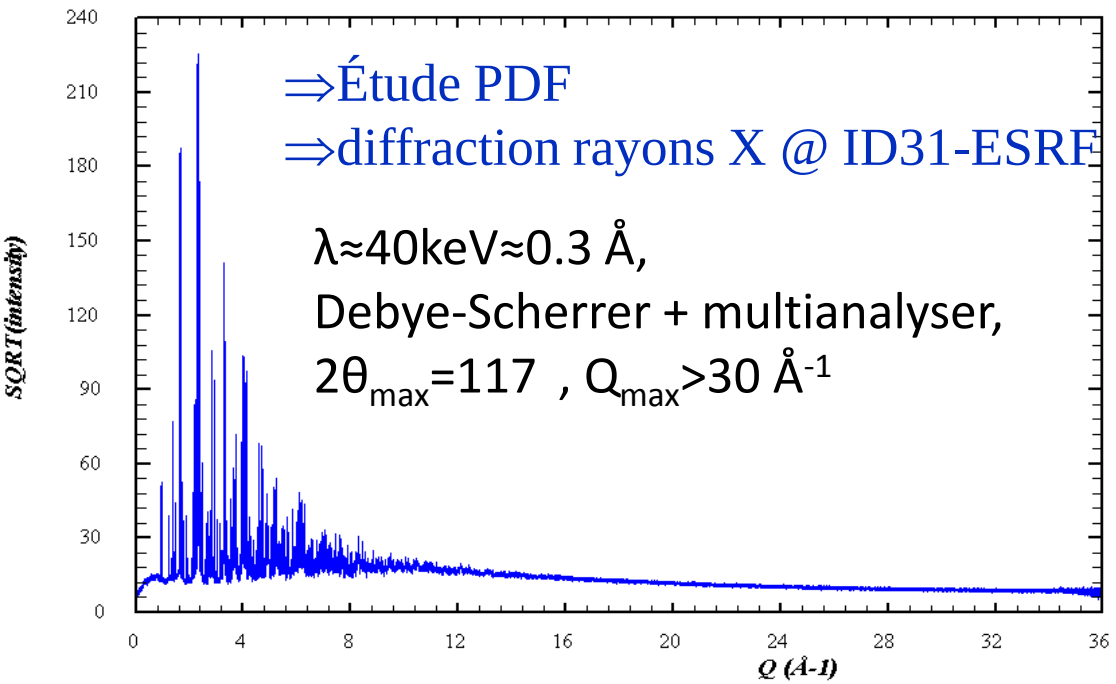
(c) Dark field image of $BiCrO_3$ selecting a spot of family B.

TEM
Macles
Qques nanomètres

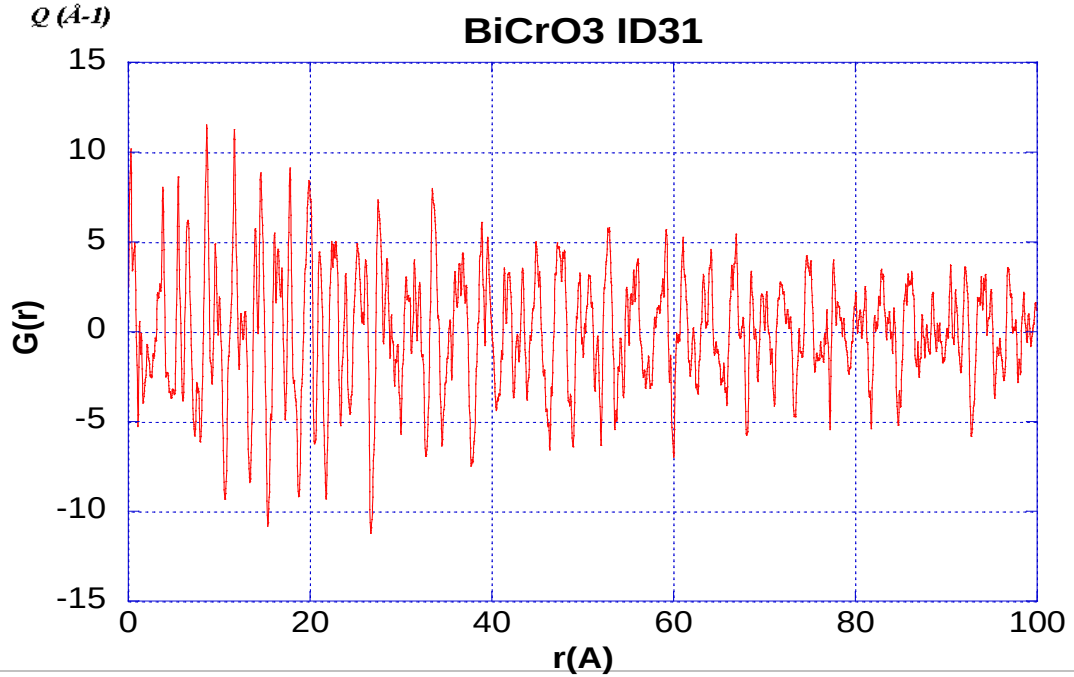


ESRF-ID31
Diffusion diffuse

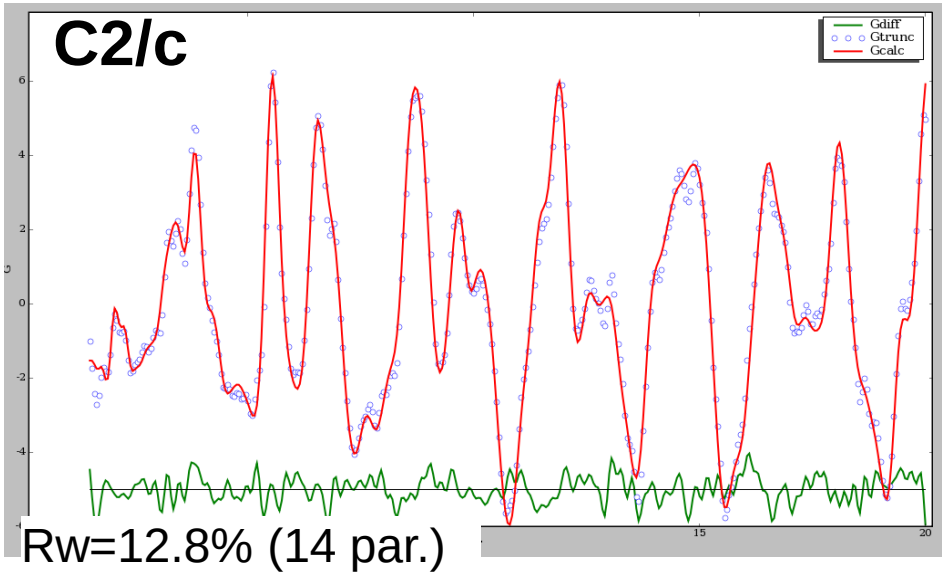
=> Affinements impossibles



Mesure de $BiMnO_3$ et $BiCrO_3$



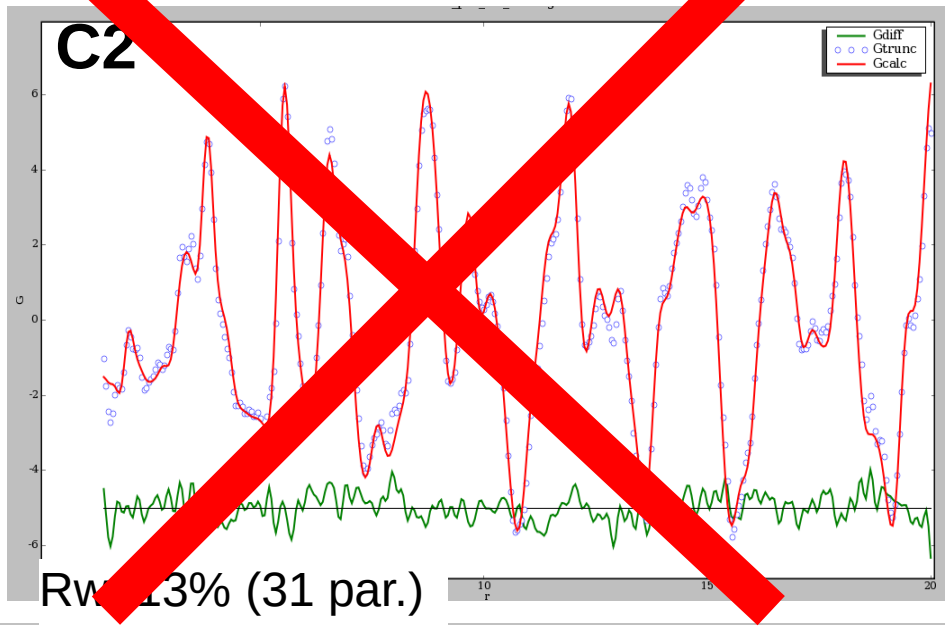
$BiMnO_3$ Affinements de la PDF -> 20Å



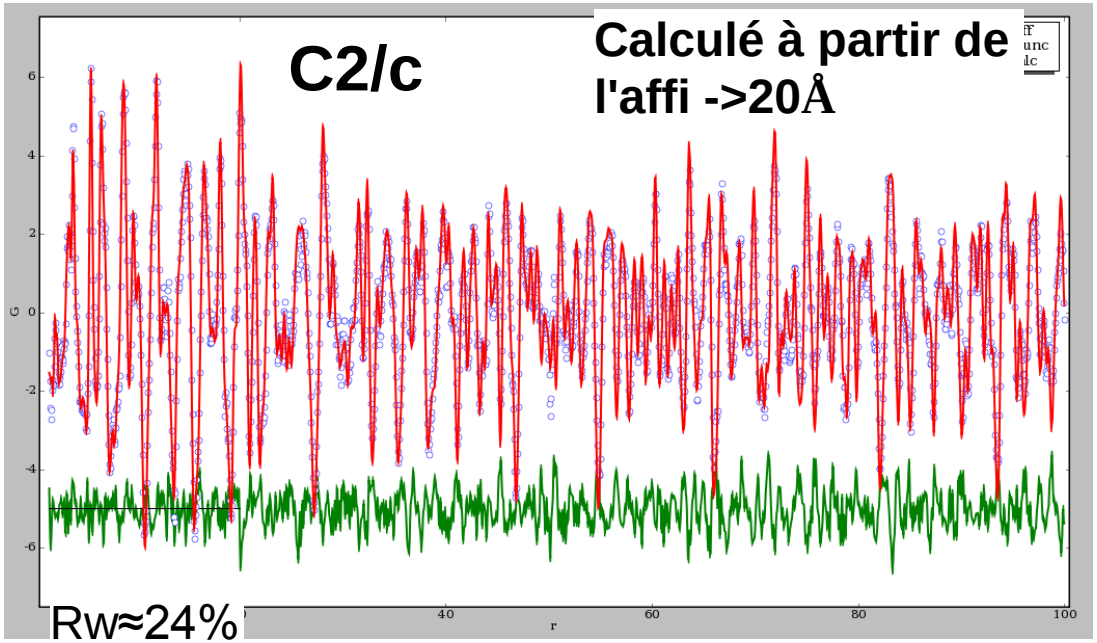
Rw=12.8% (14 par.)

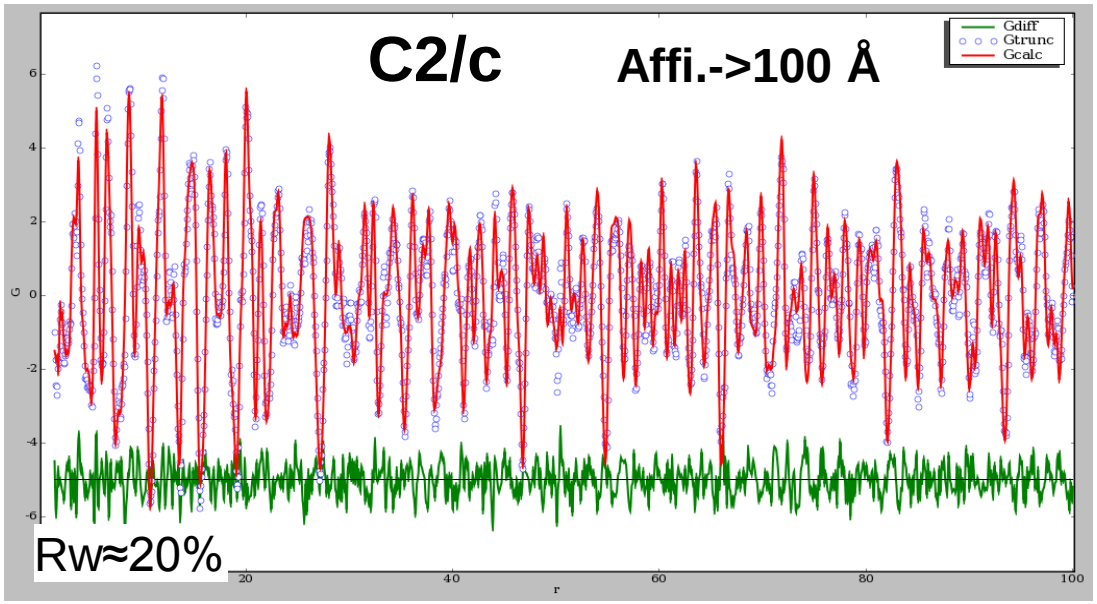
C2/c : Centrosymétrique
(=> pas ferroélectrique)

C2 : Non Centrosymétrique
(=> ferroélectrique)



Rw=13% (31 par.)





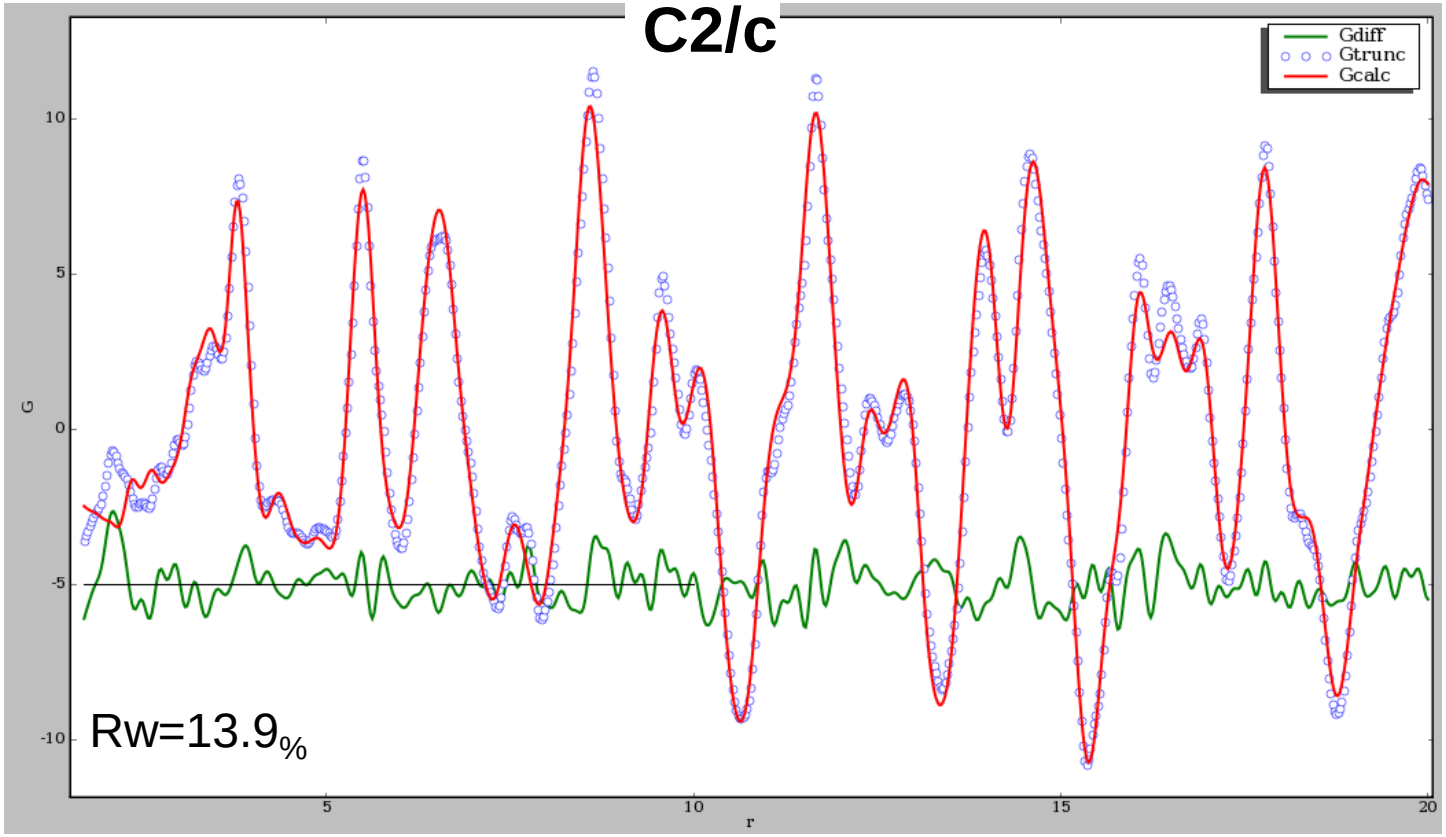
$BiMnO_3$

Structure locale

≈ structure moyenne

pas de désordre

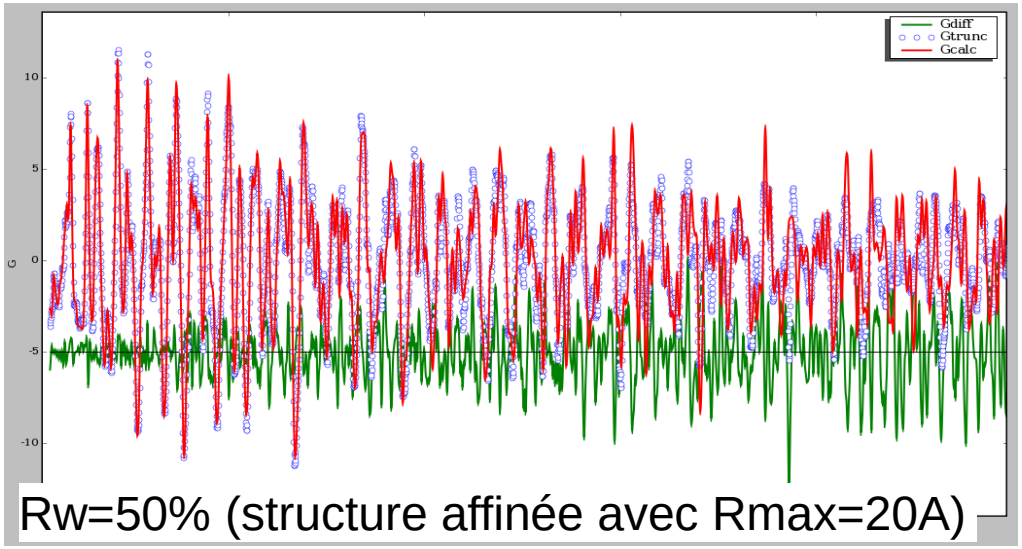
$BiCrO_3$: on a accès à la structure locale malgré les macles



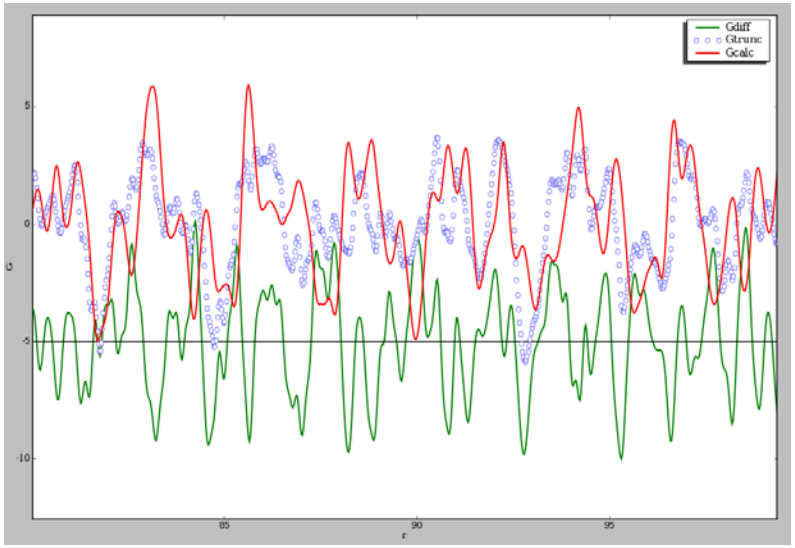
Affinement correct avec C2/c (pas mieux en C2)

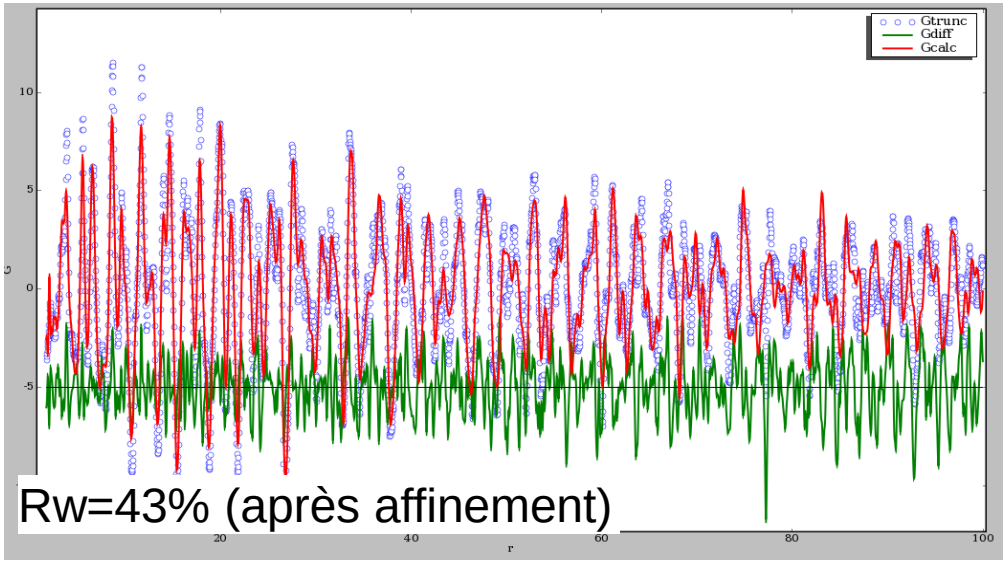
Qualité comparable (un peu moins bonne) que $BiMnO_3$

=> structure locale centrosymétrique



Rw=50% (structure affinée avec Rmax=20A)





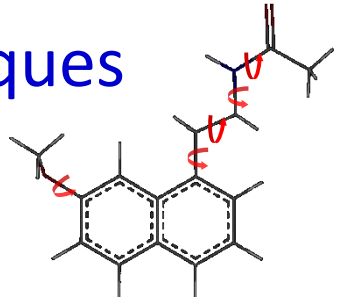
Rw=43% (après affinement)

Structure locale
≠structure moyenne

=> influence des macles

=> étudier la structure
des parois de macles

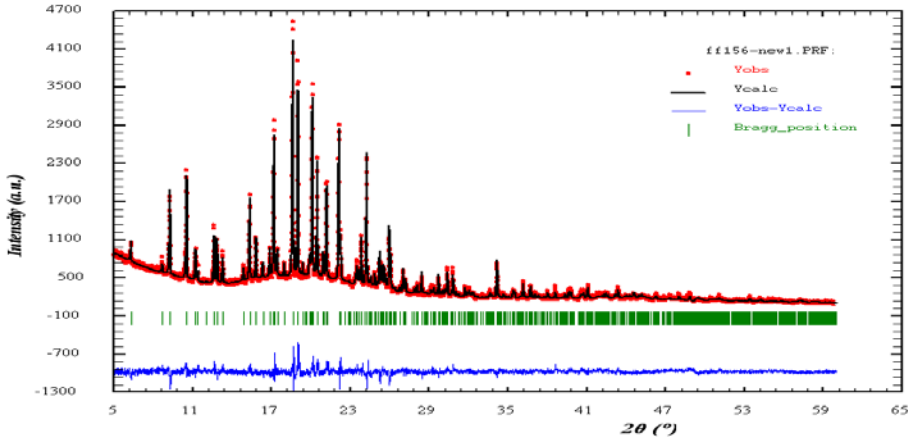
Analyse PDF de matériaux pharmaceutiques

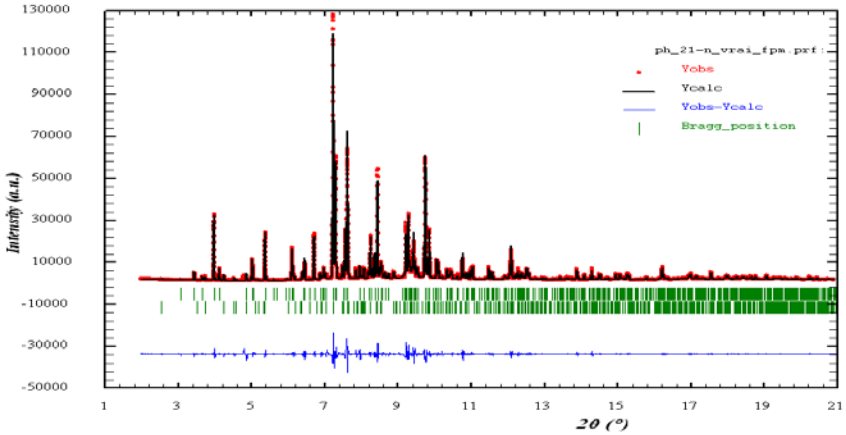


En général plusieurs polymorphes

=>Structure sur poudres, blocs rigides

Polymorphes de l'agomélatine :





Nouvelles méthodes de synthèse

(p. ex. broyage)

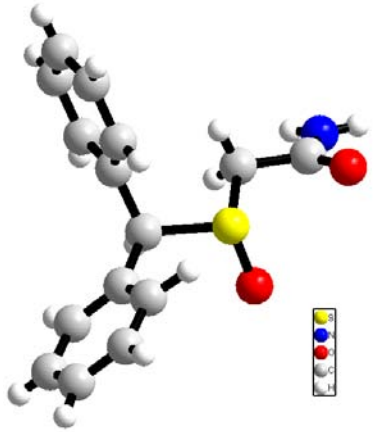
⇒**Nouveaux *polymorphes mal cristallisés***

⇒Propriétés différentes

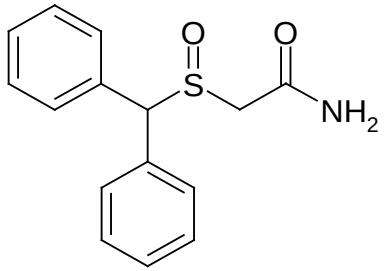
⇒Meilleure solubilité/efficacité

⇒**PDF pour déterminer leur structure :**

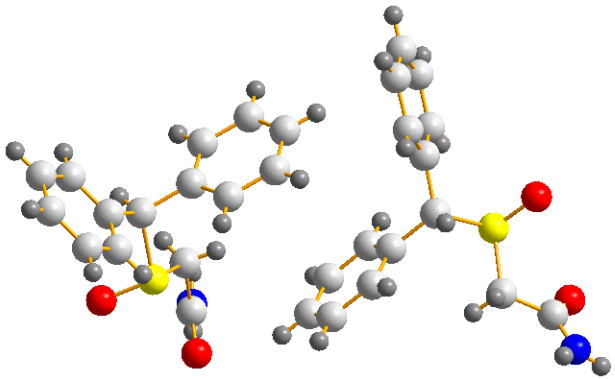
⇒ *ab initio recuit simulé en blocs rigides*

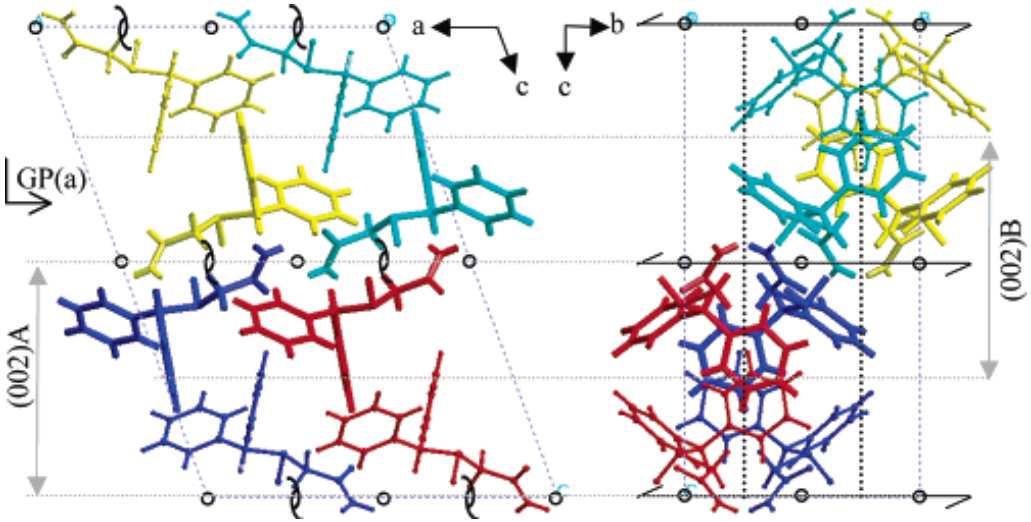


exemple d'étude PDF de composé pharmaceutique: rac-modafinil, *coll. G. Coquerel et al. (univ. Rouen)*



2-(diphénylméthyl)sulfinyl)-N-acétamide



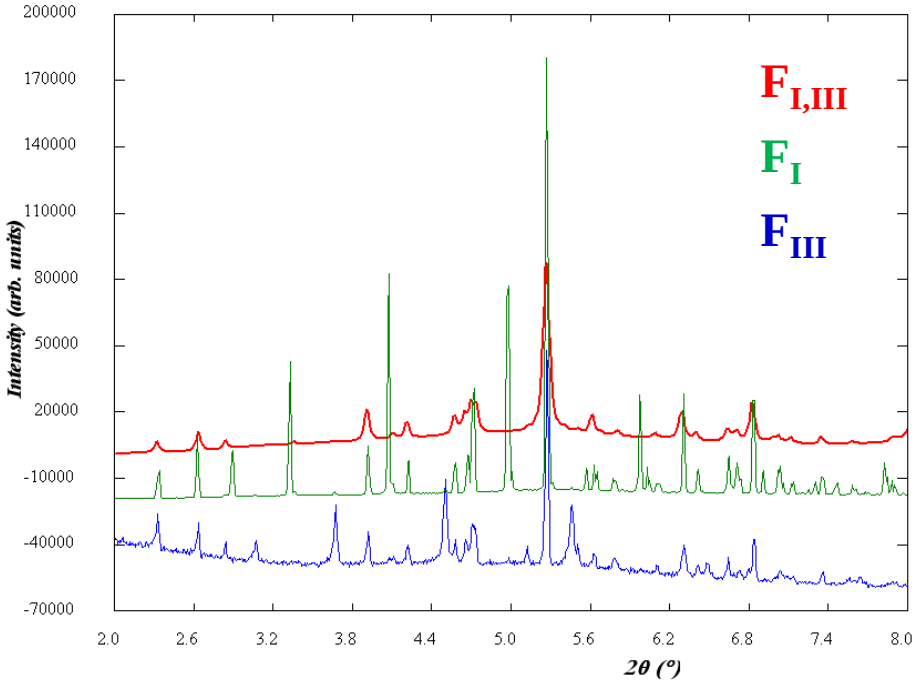


M. Pauchet et al.,
Crystal Growth and Design, 4-6, 1144 (2004)

7 polymorphes

Formes F_I & F_{III} quasi - isoenergétiques
change of (002)A slab stacking along *a*

Forme $F_{I,III}$ obtenue par broyage haute énergie, ou spray drying. Fortement désordonnée
Structure inconnue

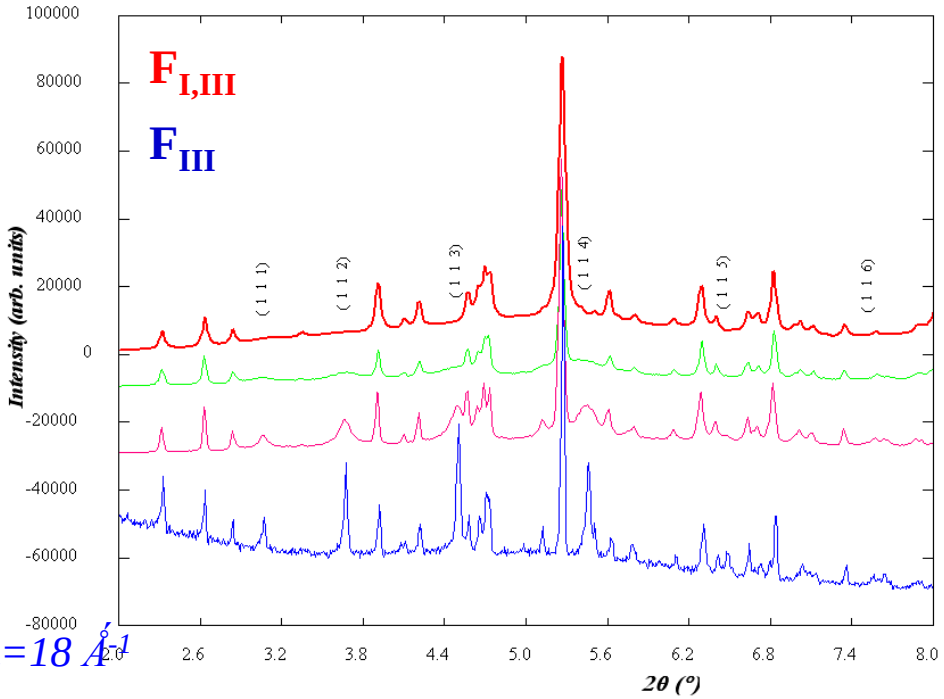


$F_{I,III}$ réflexions communes à F_I & F_{III}

LeBail fits => domaines ~ 5 nm

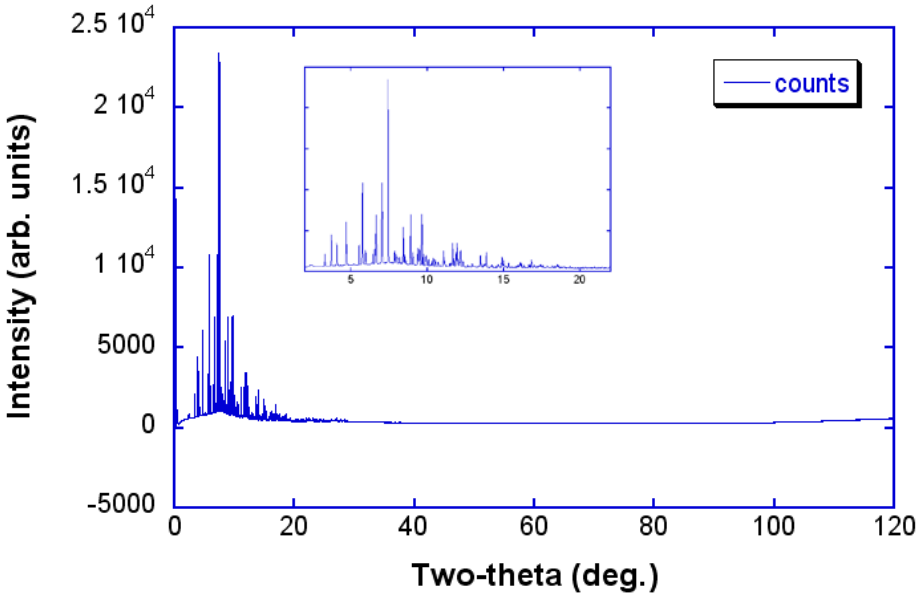
états intermédiaires :
Disparition progressive des (11*l*)

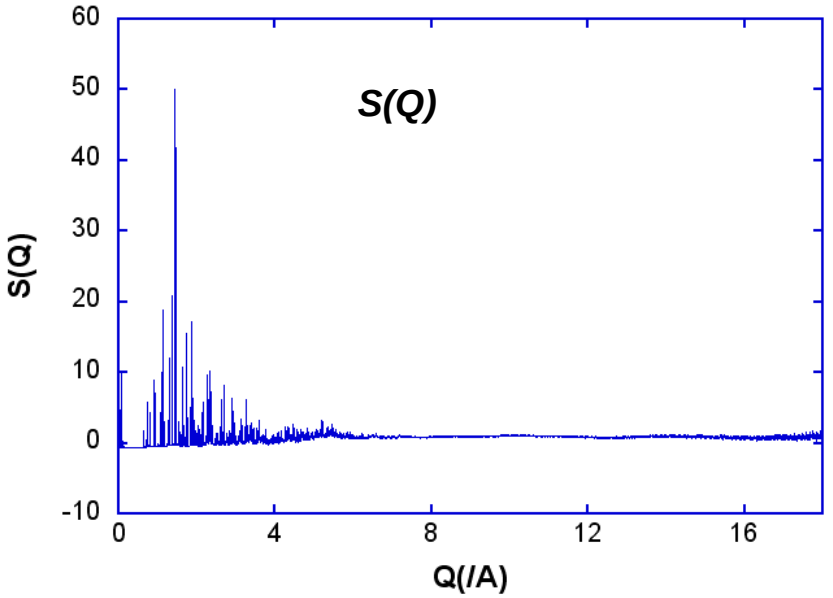
Diffractogrammes de mauvaise qualité
=> structure non résolue



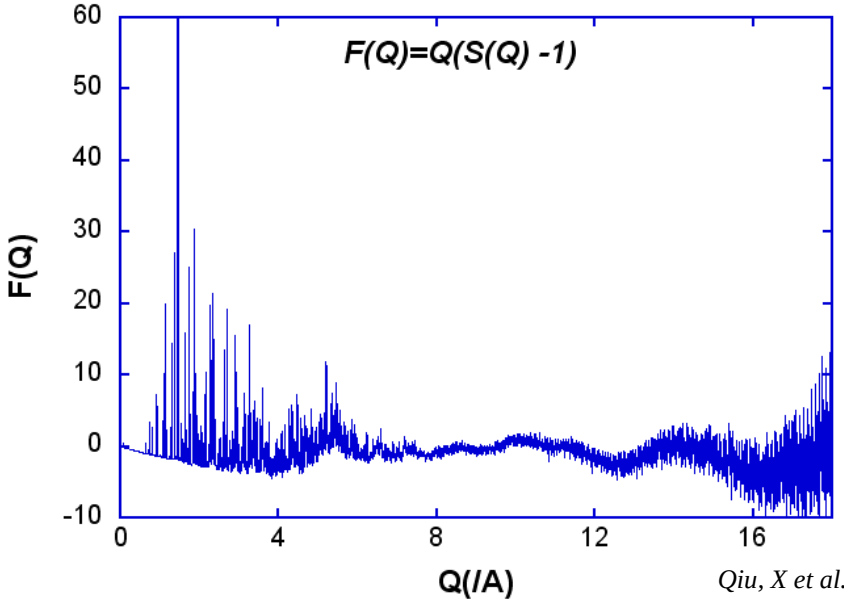
⇒*PDF experiment,*

ESRF CRG-D2AM, Debye-Scherrer,
Pixel detector (XPAD)
λ=0.563 Å, E=22 KeV, $2\theta_{max}$=120 , Q_{max}=18 Å^{-1}



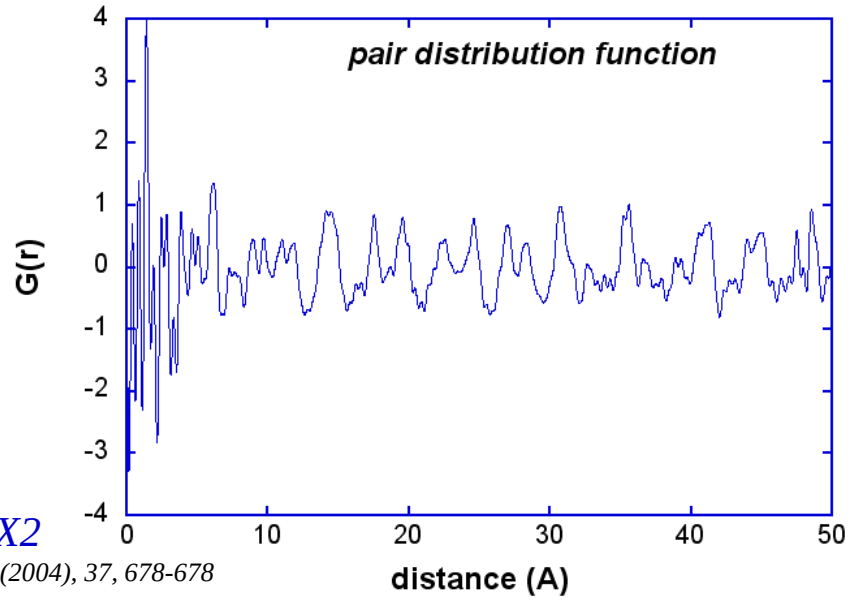


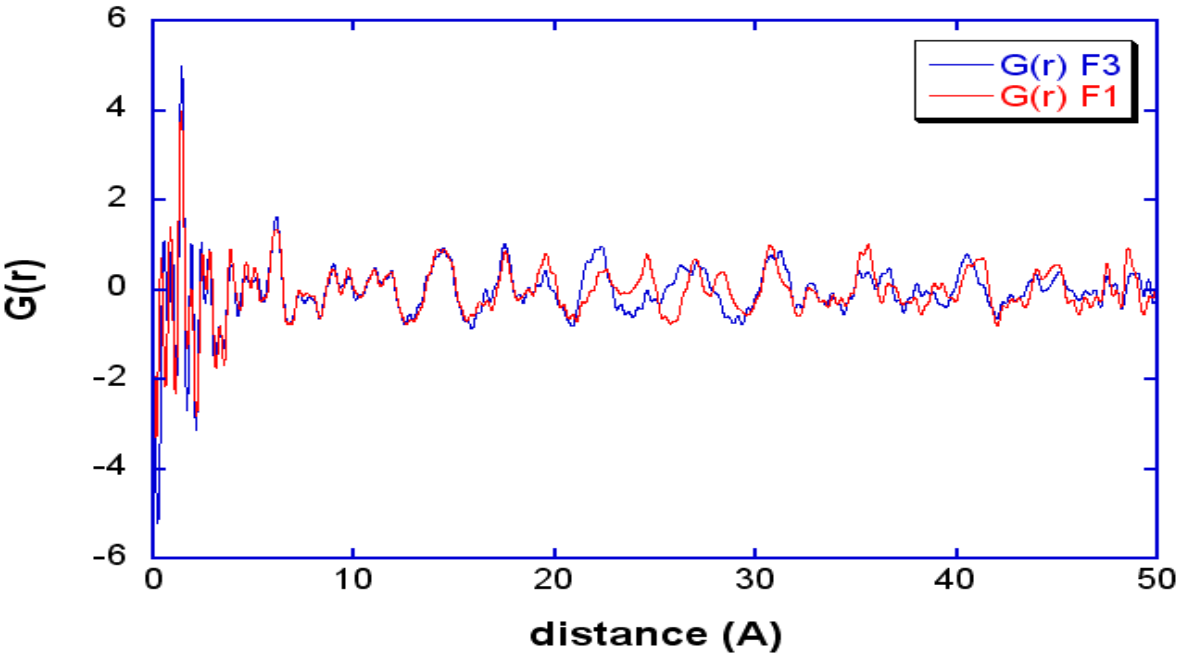
Modafinil, mesure PDF de F_I



PDFGetX2

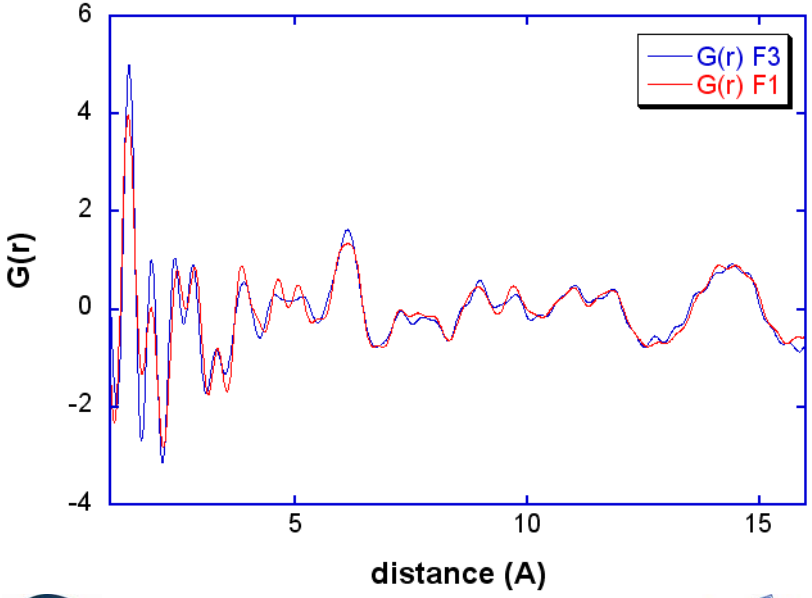
Qiu, X et al., J. Appl. Crystal. (2004), 37, 678-678



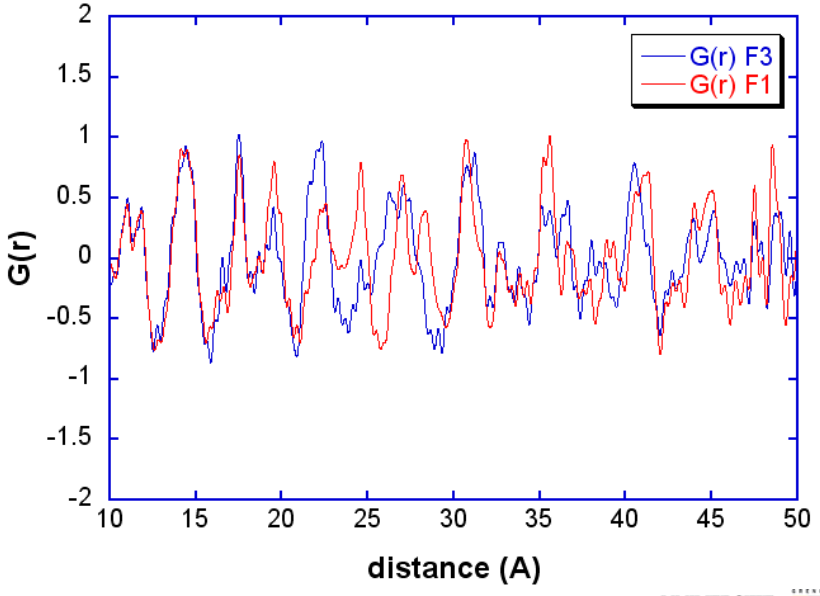


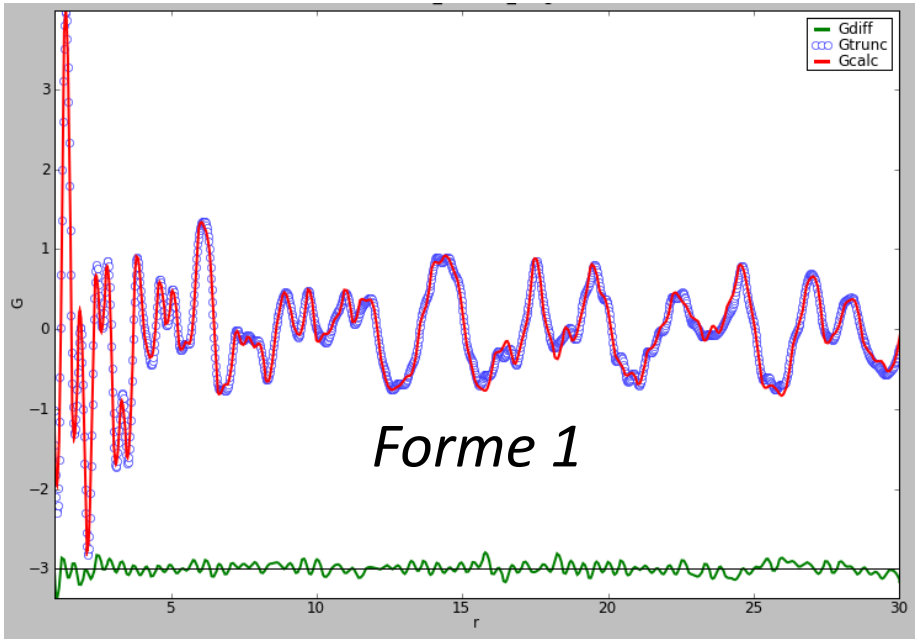
PDF of forms 1 & 3 of modafinil

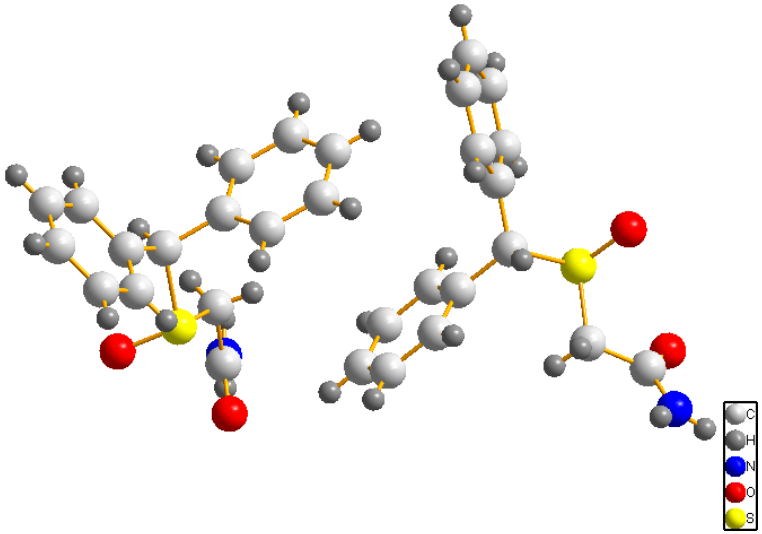
Mêmes molécules



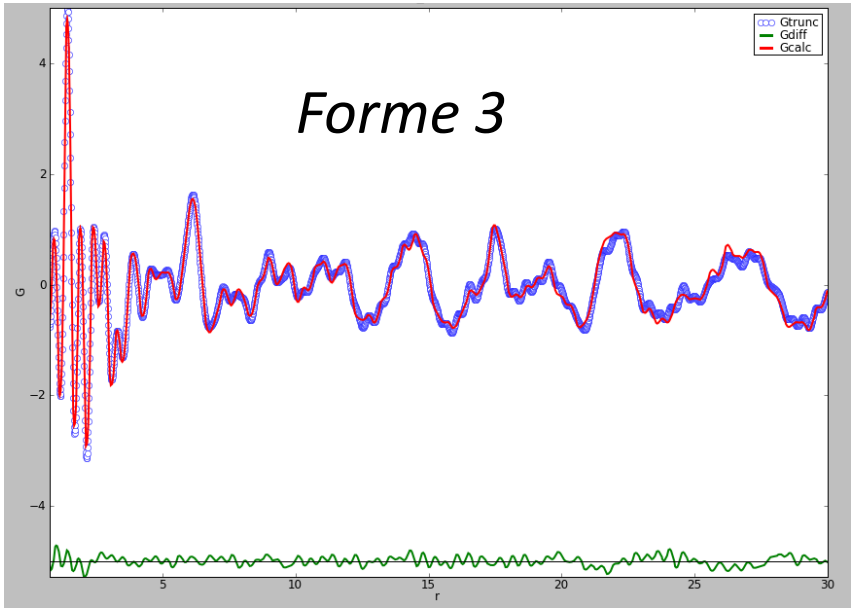
Différents arrangements

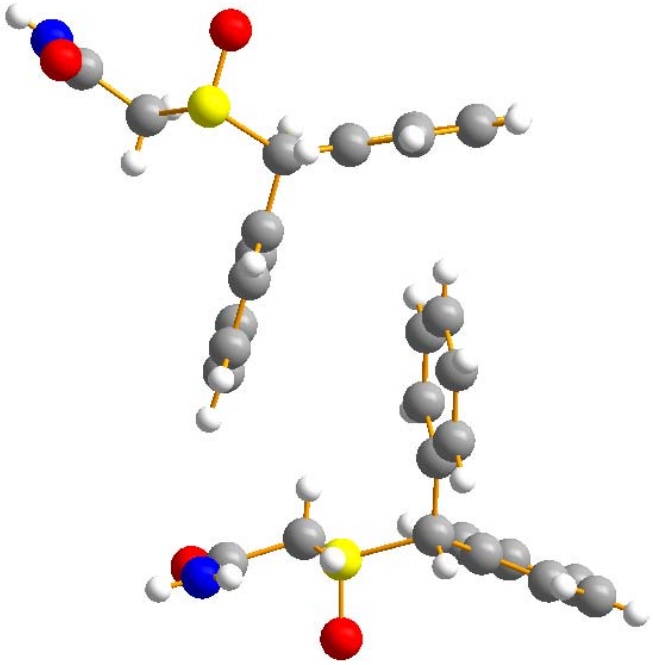




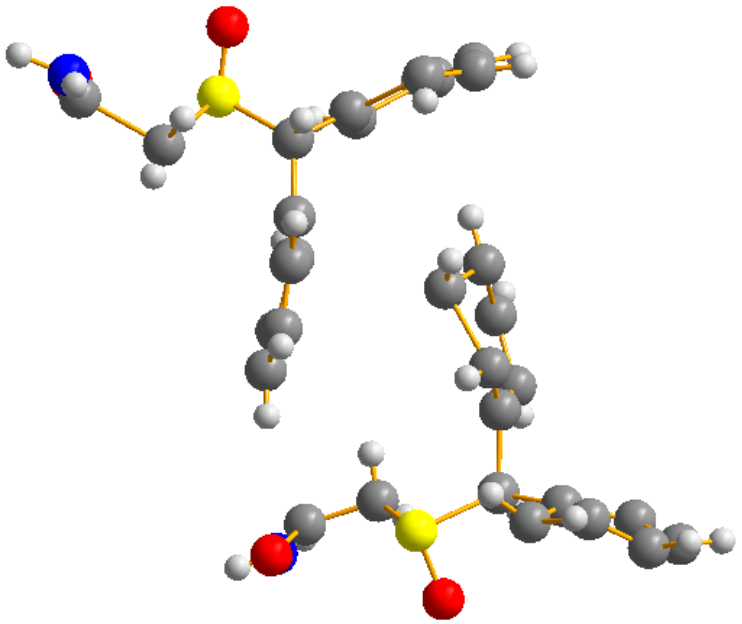


Affinements de la PDF





original



affiné

Faible écart moyen entre les 2 structures,
Trop de paramètres indépendents (115)
Nécessite un traitement en blocs rigides (positions, DW).

“amorphous” materials have a richer “PDF signature”

2 different “amorphous” compounds are hard to differentiate from their powder diffractogram

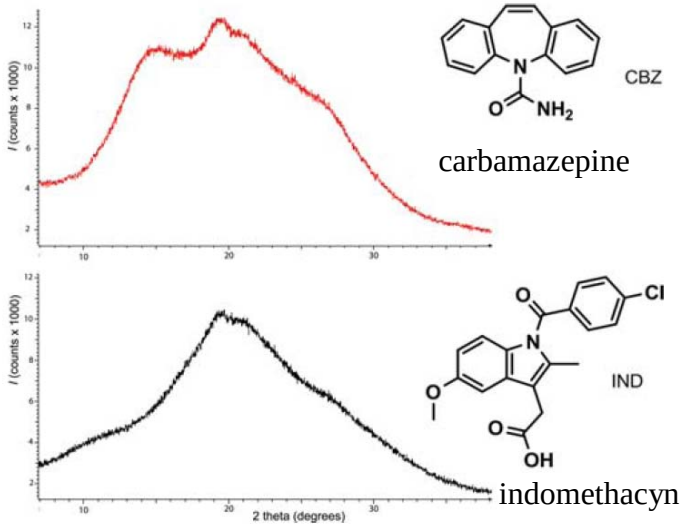


Fig. 1 Molecular structures and laboratory Cu Kα_1 XRPD patterns for X-ray amorphous melt-quenched samples of CBZ (top) and IND (bottom).

An amorphous sample can be identified from its PDF by comparison with a crystalline isomorph

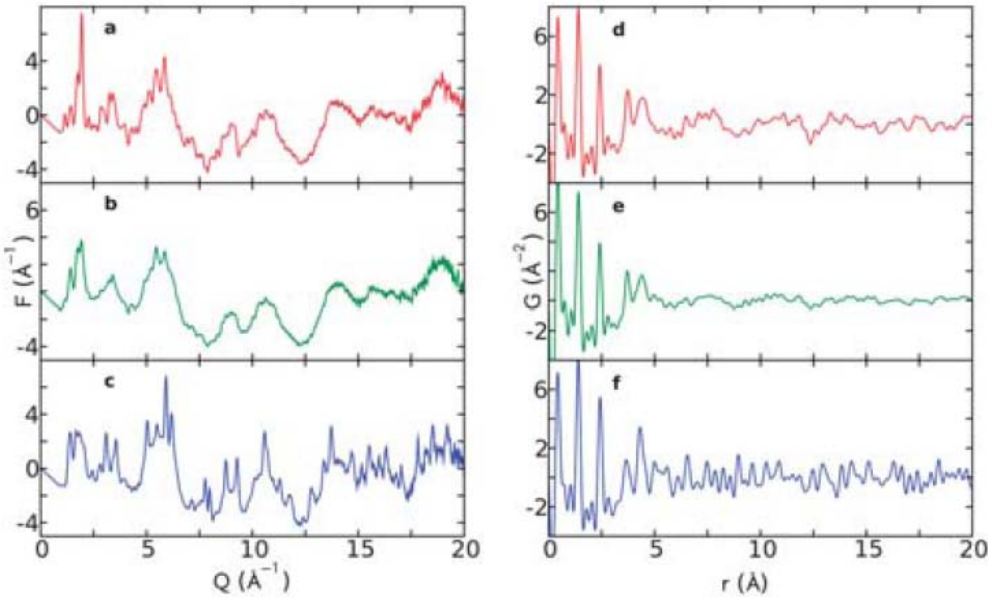


Fig. 2 Total scattering diffraction patterns and TSPDFs of CBZ. Panels (a) and (d) correspond to CBZ III, (b) and (e) to the melt-quenched sample and (c) and (f) to CBZ I; (a), (b), (c) show the total scattering data in the form of $F(Q)$ (see ESI)† whilst (d), (e), (f) are in the form of the TSPDF, $G(r)$.

⇒Identify amorphous/nano compounds from their PDF

Requires λMo or λAg high Q PDF data

Characterisation of amorphous and nanocrystalline molecular materials by total scattering†

Simon J. L. Billinge,*[a,b] Timur Dykhne,[a] Pavol Juhás,[a] Emil Božin,[a,b] Ryan Taylor,[c] Alastair J. Florence[c] and Kenneth Shankland[d]

CrystEngComm, 2010, **12**, 1366–1368

Conclusions

✓La PDF peut être utilisée pour étudier la structure
locale et multi-échelle

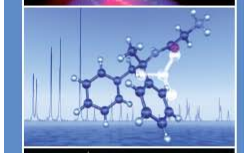
✓Nécessite des données spécifique
haut Q et fortes statistiques

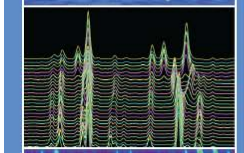
✓Structurelocale ≠ structure moyenne, nano-clusters, désordre

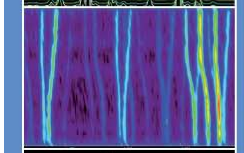
✓Pas de solution unique, pas d'ab initio
=> Savoir proposer un modèle

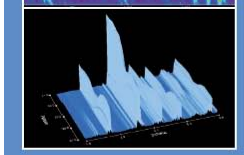
✓Complémentaire des autres méthodes

Merci de votre attention !









EPDIC 13

the European Powder Diffraction conference
Grenoble 28-31 October 2012

The **European Powder Diffraction Conference** (**EPDIC**) is the only European conference completely dedicated to all aspects of the analysis of polycrystalline materials by diffraction methods.

Started in Munich in 1991, **EPDIC**s have rapidly become reference points for all researchers in the field and are now regarded to be ideal places for the presentation and diffusion of new developments in powder diffraction instrumentation, analysis, and applications.

EPDIC conferences are intended to be the place where all powder diffractionists, independently of whether they are more interested in the theoretical advances or in the application of the techniques, can meet and exchange ideas and experiences.

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1- Nano-Imaging with X-rays.
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5- Charge density analysis via powder diffraction
6- Hydrogen storage and energy related materials

12 micro-symposia

1 - Total Scattering studies and Disorder
2 - Ab initio Structure Solution
3 - Powder diffraction for Biological and Molecular Materials
4 - Combined Methods for Structure Investigation and 3-D imaging
5 - Materials for Sustainable Development
6 - Progress in Instrumentation
7 - Texture and residual stress analysis
8 - In Situ, In Operando Studies
9 - Nanomaterials, surfaces and Interfaces
10 - Neutron Structural and Magnetic Scattering
11 - Structure and Properties of Functional Materials
12 - Advances in diffraction Line Profile Analysis.

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Contact :

Pierre Bordet
Institut Néel, CNRS & UJF, Grenoble
Phone : +33 (0)4 76 88 78 07
E-mail : epdic13@grenoble.cnrs.fr

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