Neutron and X-ray diffraction

Laurent Cormier

Institut de Minéralogie, Physique des Matériaux et Cosmochimie
Université Pierre et Marie Curie – CNRS
Paris, France
cormier@impmc.upmc.fr

Cargese School

First structural studies by X-ray diffraction

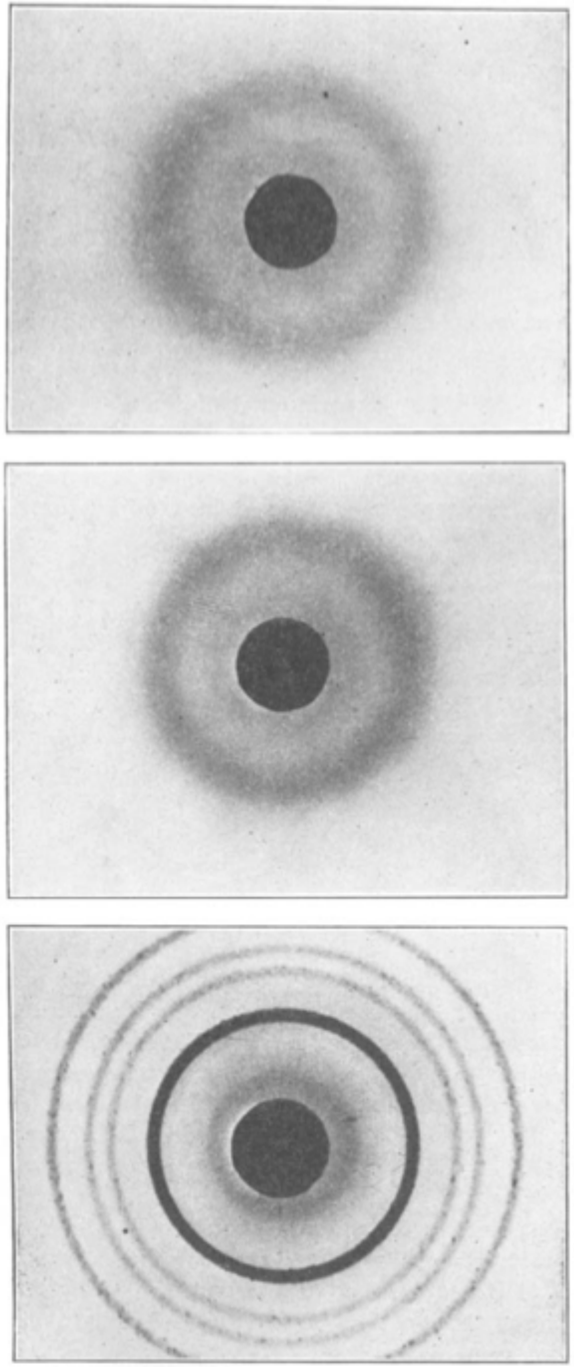


Fig. 2.—X-ray diffraction pattern: (*top*) Pyrex-brand resistance glass; (*center*) vitreous silica; (*bottom*) cristobalite.

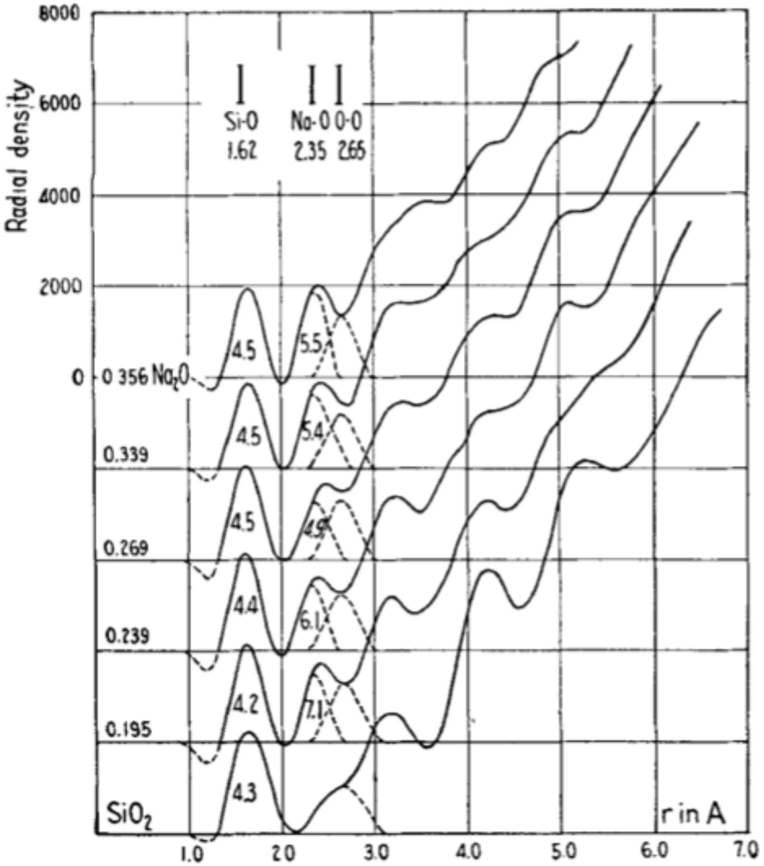


Fig. 3.—Radial distribution curves for soda-silica glass.

Warren, B.E., 1934. The diffraction of X-rays in glass. Phys. Rev. B, 45, 657-661.

Warren, B.E., 1934. X-ray determination of the structure of glass. J. Am. Ceram. Soc., 17, 249-254.

Warren, B.E., Biscoe, J., 1938. Fourier analysis of X-ray patterns of soda-silica glass. J. Am. Ceram. Soc., 21, 259-265.

Structural model for covalent glasses

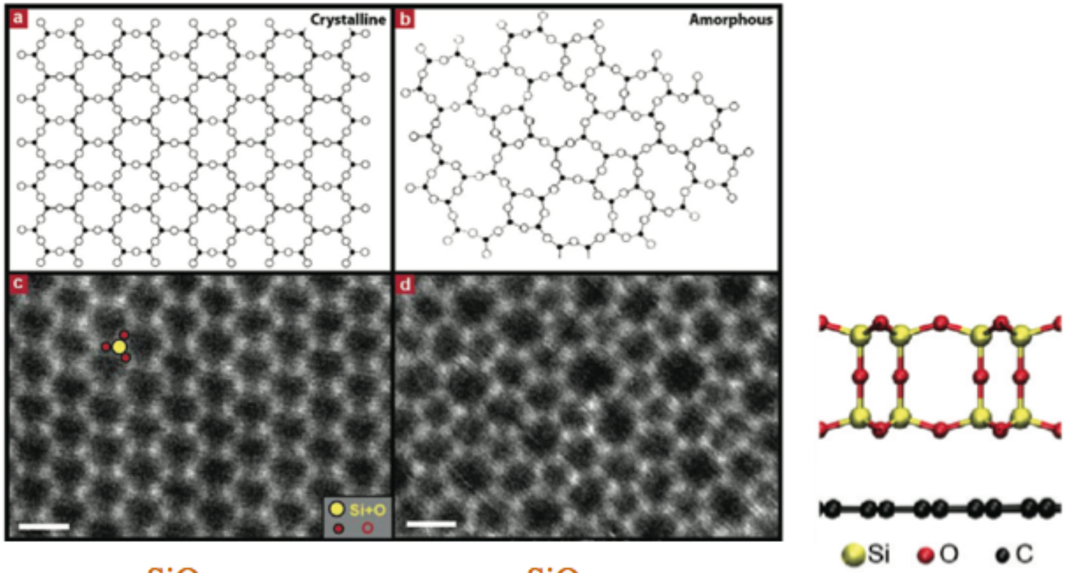
Zachariasen model (1932)

Continuous random network

Rules for glass formation

1. No O atoms bonded to more than 2 cations
2. Coordination cation is small (3,4)
3. O polyhedra are corner-shared (no edge- or face-sharing)
4. To obtain 3D network, at least 3 corners must be shared

Zachariasen, J. Am. Ceram. Soc., 54(1932)3841



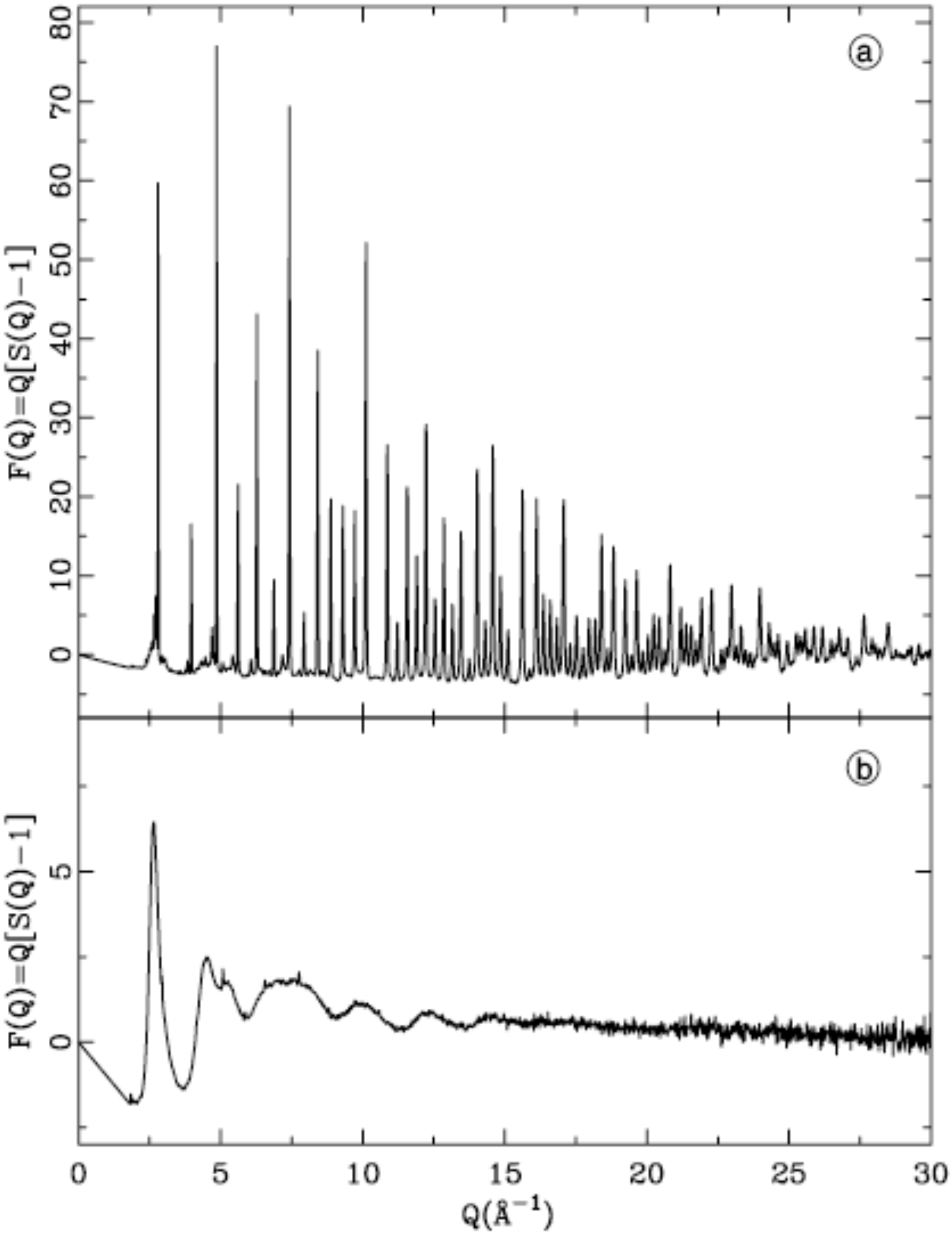
c-SiO_2 a-SiO_2

STEM images

Huang et al., Nano Lett. 12 (2012)1081

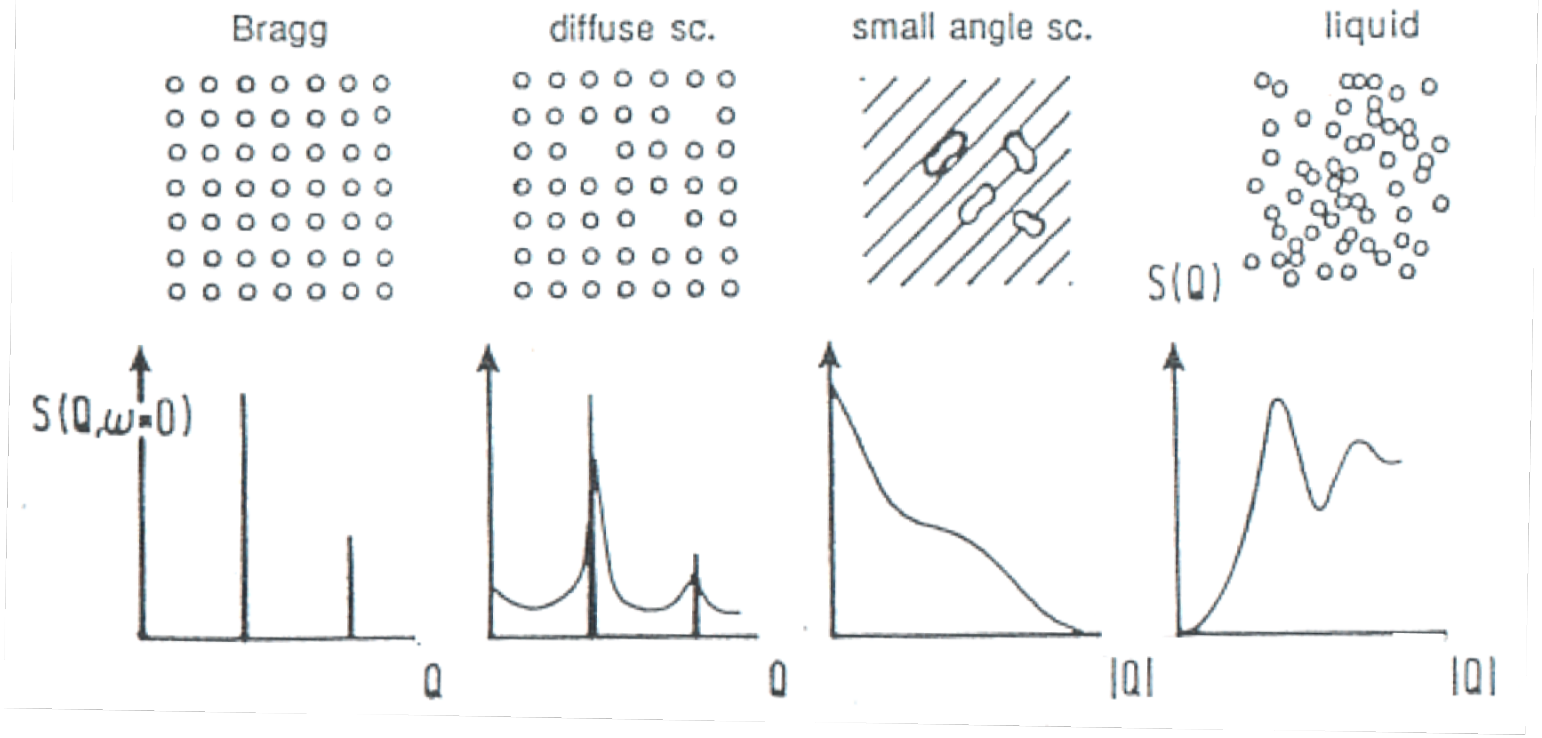
Bragg peaks and amorphous signal

Note the difference in intensity



Diffraction

Diffraction	Diffuse scattering	Small angle scattering	Scattering
Diffraction	**Diffusion diffuse**	**Diffusion aux petits angles**	**Diffusion diffraction**
crystals	disorder in crystals	> 1nm	< 1nm glass - liquid

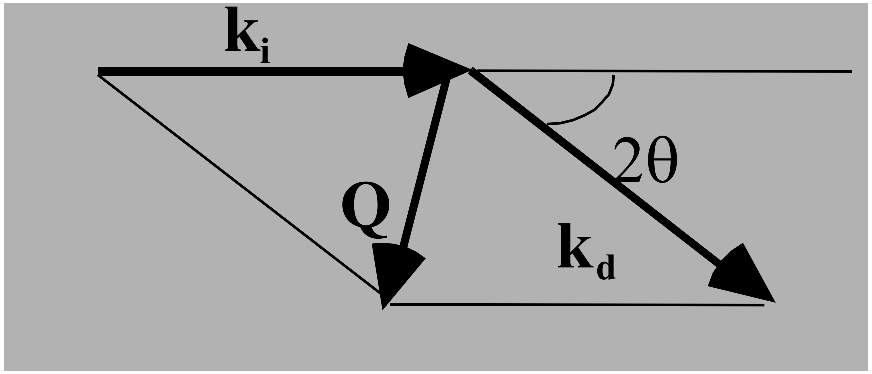


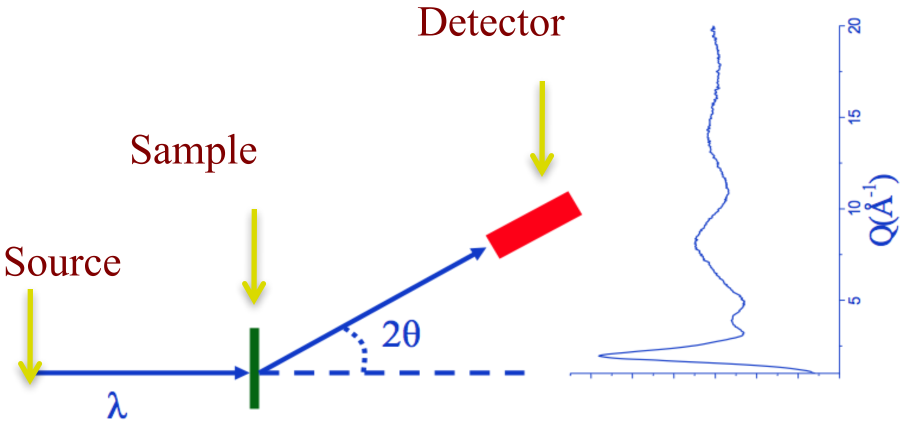
Diffraction

Or simply use the term

PDF (Partial distribution function)

A diffraction experiment





Modulus scattering vector $k_i = 2\pi/\lambda$

Scattering vector $\mathbf{Q} = \mathbf{k}_d - \mathbf{k}_i$

λ: wavelenth of the incident particule

2θ : diffraction angle

Elastic diffusion $k_i = 2\pi/\lambda = k_d = k$

$$Q = 2k\sin\theta$$

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

⚠ Q sometimes noted k (mainly for X-ray)

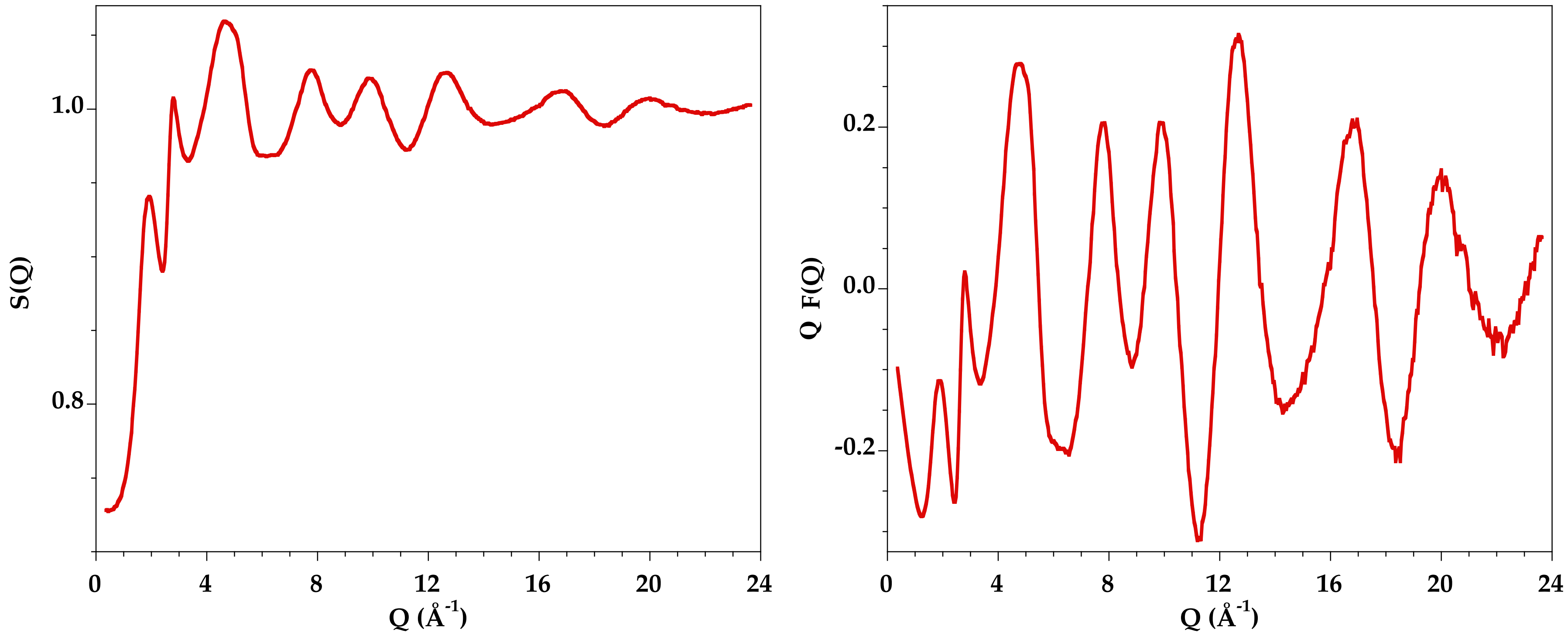
Fonctions in Q-space

S(Q) Structure factor

$F(Q)/\langle b\rangle^2 = S(Q)-1$ Interference function

$$S(Q \rightarrow \infty) \rightarrow 1 \qquad S(Q) \geq 0$$

$$F(Q \rightarrow \infty) \rightarrow 0$$



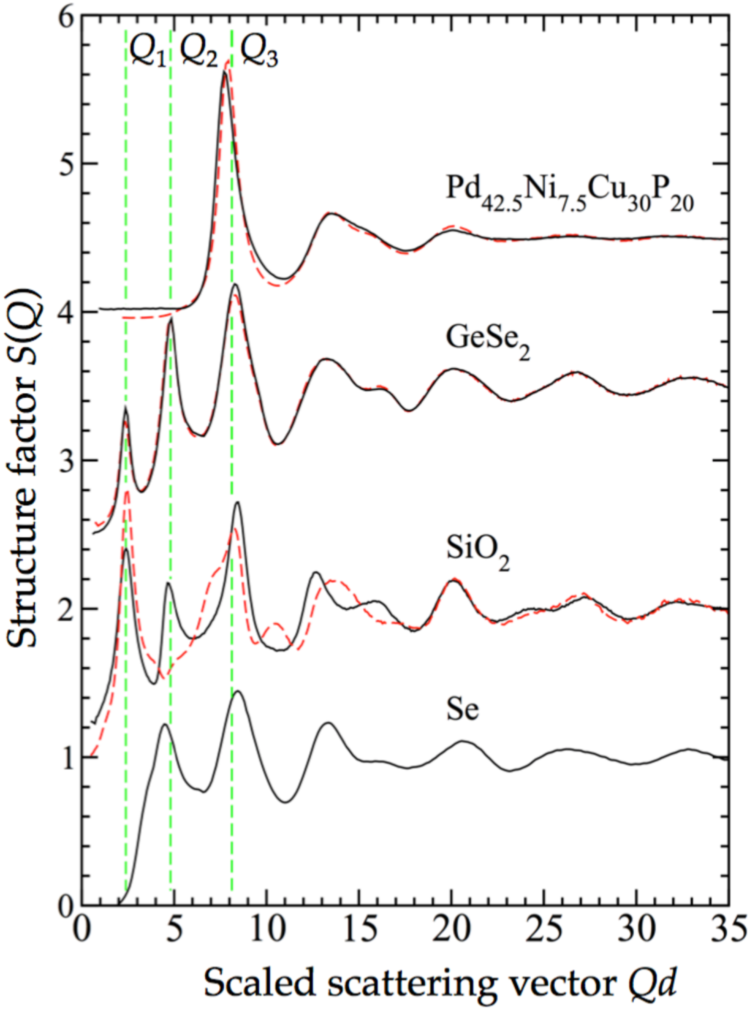
D.A. Keen, *A comparison of various commonly used correlation functions for describing total scattering,* **J. Appl. Cryst. 34 172-177 (2001).**

Low-Q features

$Q_1.d \simeq 2\text{-}3$ => arrangements of network-forming motifs on an intermediate range (first sharp diffraction peak)

$Q_2.d \simeq 4.6\text{-}4.9$ => size of the local network-forming motifs

$Q_3.d \simeq 7.7\text{-}8.9$ => nearest-neighbour separation



Zeidler & SalmonPhys. Rev. B 93 (1016) 214204

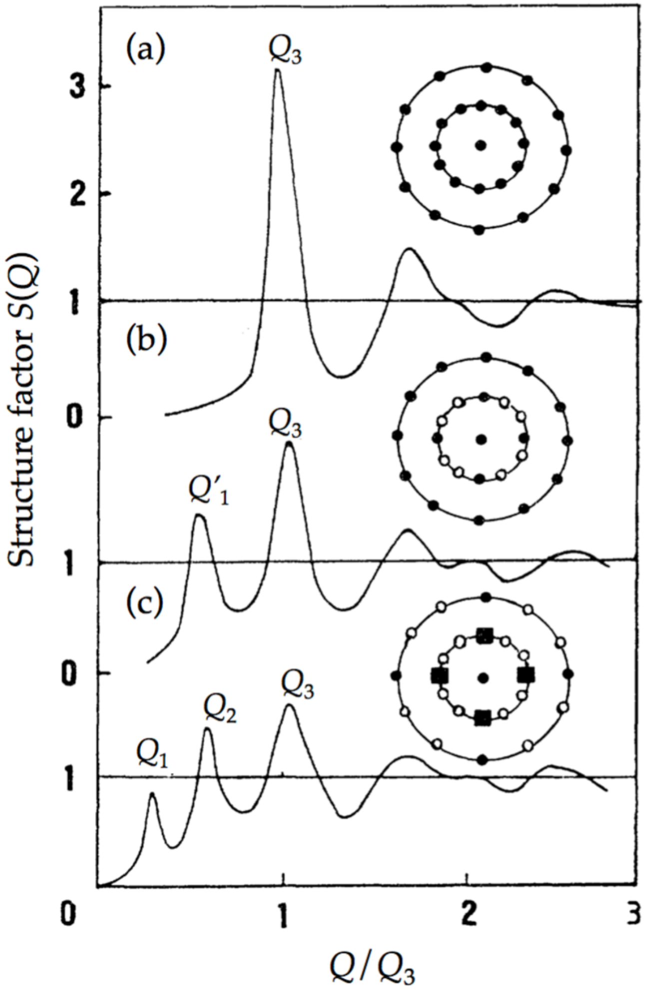
Note : some low-Q features are not present for some classes of glasses (*e.g.* Q_1 and Q_2 are absent in metallic glasses) or are not observable for some diffraction methods (*e.g.* Q_2 is present in neutron diffraction data for SiO_2 but absent in the X-ray diffraction data).

Low-Q features

$Q_1.d \simeq 2\text{-}3$ => arrangements of network-forming motifs on an intermediate range (first sharp diffraction peak)

$Q_2.d \simeq 4.6\text{-}4.9$ => size of the local network-forming motifs

$Q_3.d \simeq 7.7\text{-}8.9$ => nearest-neighbour separation



A dense random packing structure (typical to metallic glasses)

a tetravalent structure (e.g. a-Si)

a 4:2 structure (e.g., a- GeSe2)

Filled circles in (b) and (c) are four-coordinated atoms, filled squares are two-coordinated atoms, and open circles are voids

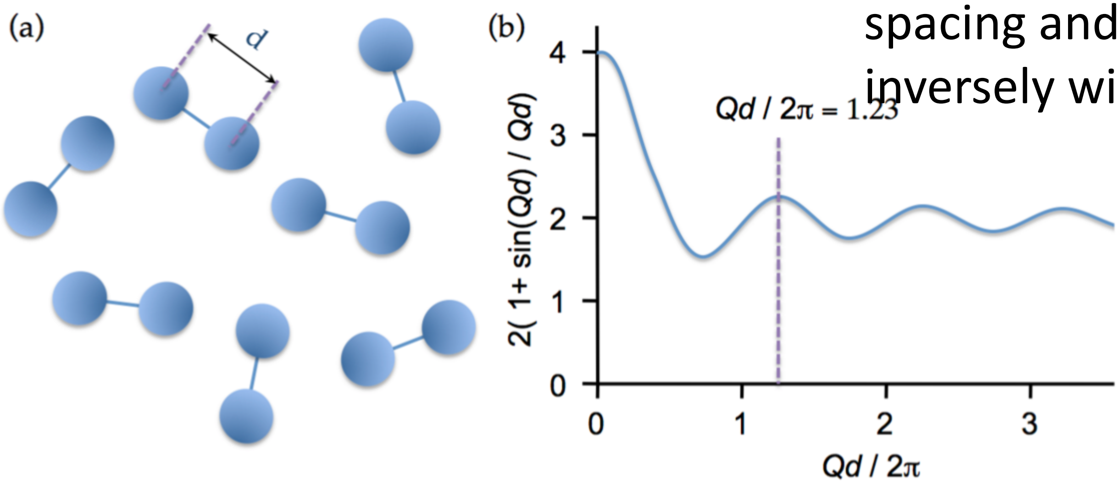
Dixmier J. Phys. I 2 (1992) 1011

Low-Q features

Correlations between, Q3 and the reduced volume

Ehrenfest relation $Q = \frac{4\pi \sin\theta_m}{\lambda} = 1.23\left(\frac{2\pi}{d}\right)$

The position of this peak is associated with the principal diffraction peak ($Q3$). As a consequence, the position $Q3$ is inversely proportional to the mean atomic spacing and the third power of $Q3$ scales inversely with the volume

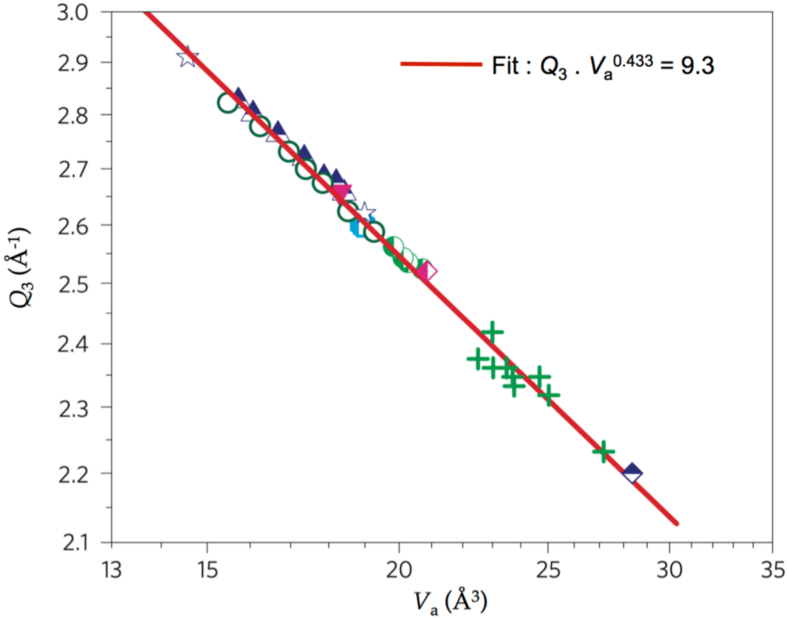


Low-Q features

Correlations between, Q^3 and the reduced volume

$Q^3.V_a^{0.433} = 9.3 \pm 0.2$

power law relationship between the reverse of the principal peak position, $2\pi/Q^3$, and the glass volume $Va = \rho_0 / (N_A M)$

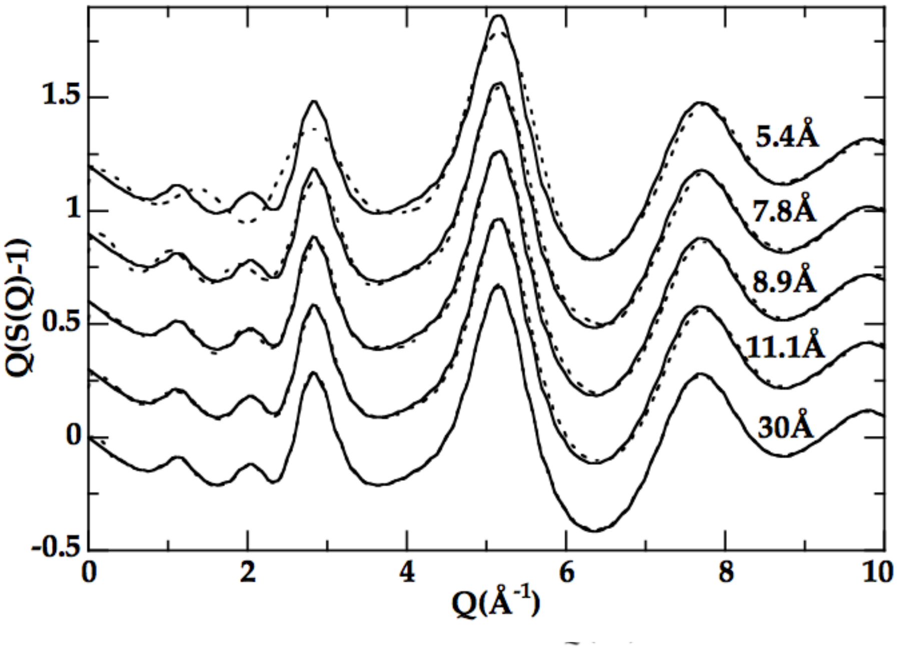


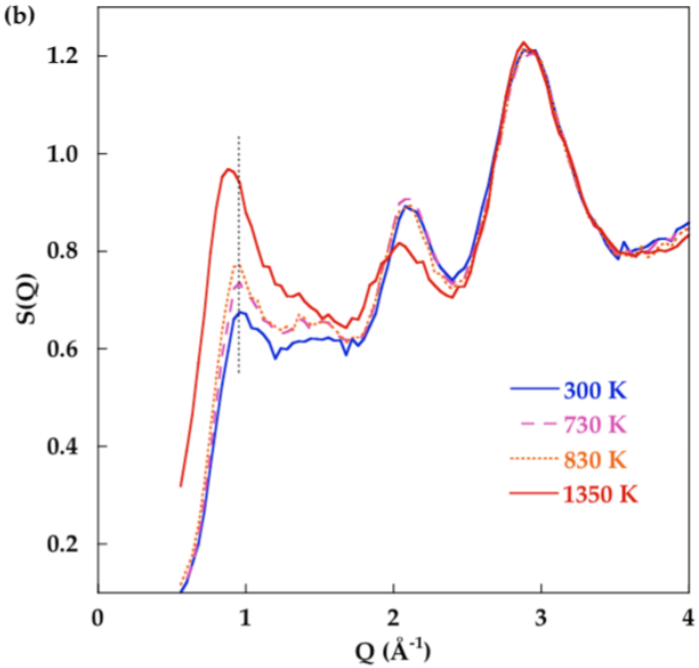
Ma et al., Nat. Mater. 8 (2009) 30

convenient to understand the relative volume (density) change with pressure

Low-Q features – First sharp diffraction peak Q_1

- Important and sometimes anomalous changes with composition, temperature or pressure
- Associated with the presence of medium range order $Q_1 \sim 2\pi/d$
- Not associated with precise features in *r*

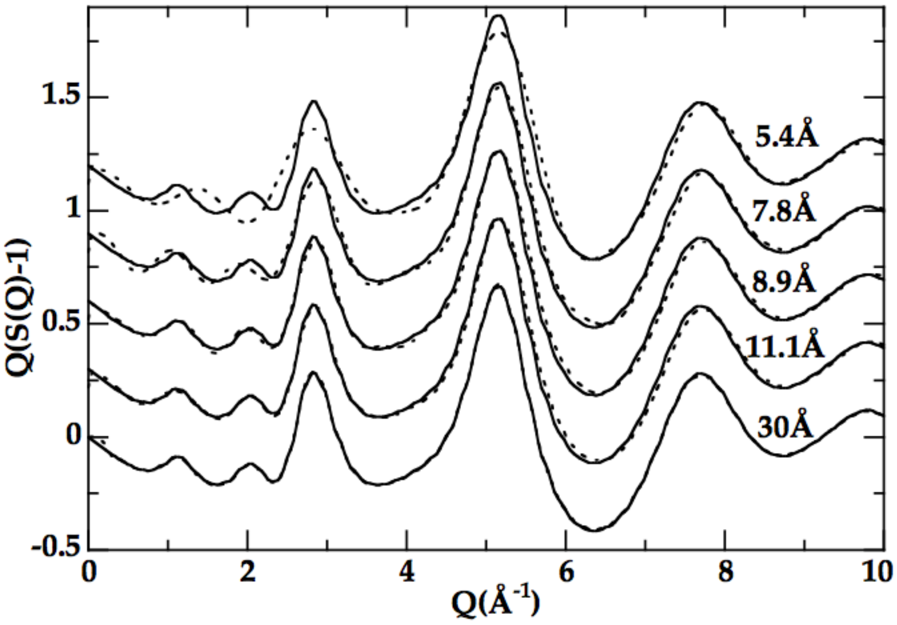


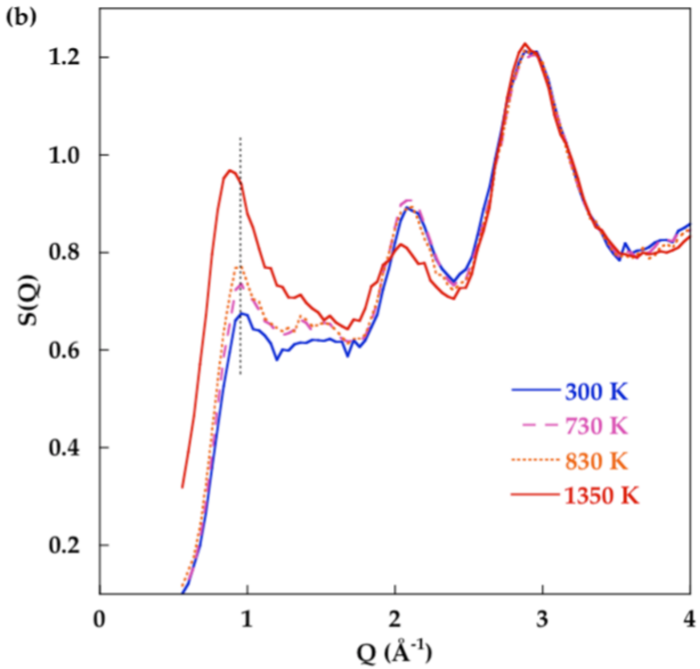


Low-Q features

Various interpretation

- Quasi-crystalline organization, quasi-Bragg peak or quasi-periodic arrangement
- Correlations between clusters and voids





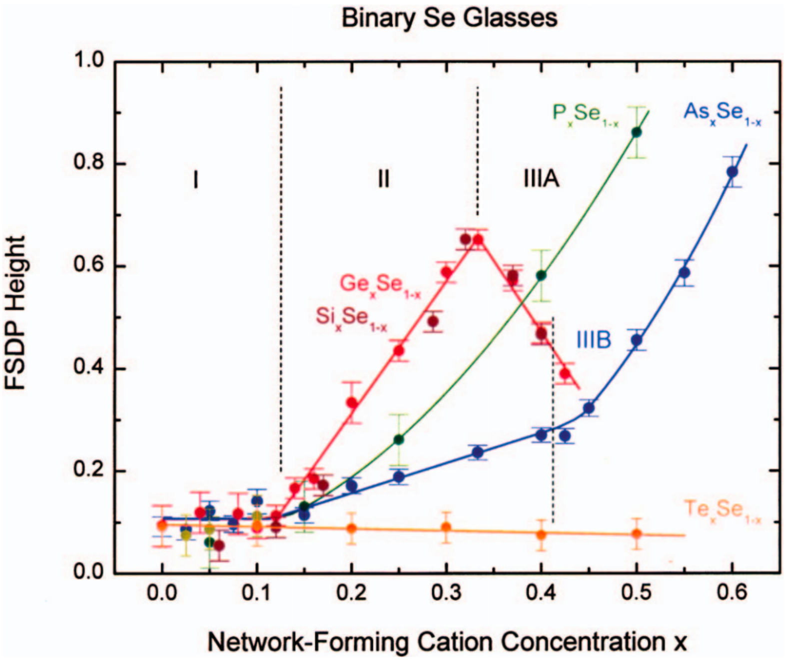
Low-Q features

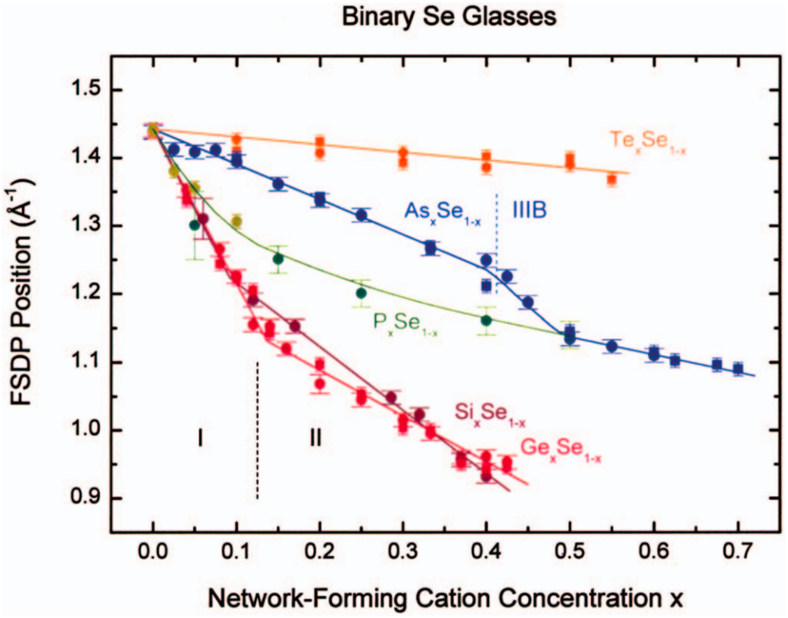
group-IV (GexSe1−x, SixSe1−x) and group-V (AsxSe1−x, PxSe1−x alloys) => strong variation in position and intensity

NFC : network-forming cations

chainlike group-VI alloy TexSe1−x => no dramatic evolution

Bychkov et al., Phys. Rev. B 72 (2005) 172107





random distribution
of the NFC-related
structural units

network formation
by NFC-related
structural units

homopolar NFC-NFC bonds
Ge and Si no longer NFC but depolymerize the network

Faber-Ziman formalism

Partial structure factor

Partial pair distribution function (PPDF)

$$F(Q) = \sum_{\alpha,\beta\geq\alpha} (2-\delta_{\alpha\beta}) c_\alpha c_\beta c_\alpha b_\beta \left[4\pi\rho_0 \int r2(g_{\alpha\beta}(r)-1) \frac{sinQr}{Qr} dr \right]$$

Atomic fraction of component α

Neutron scattering length or X-ray form factor f(Q)

System of *n* chemical species

***n* (*n*+1)/2** independent PPDF $g_{\alpha\beta}(r)$

$\rho 0$ (atome $Å^{-3}$) is the average atomic density which can be obtained from the macroscopic density d(g cm^{-3}) :

$$\rho_0 = \frac{Nd}{A\times10^{24}}$$

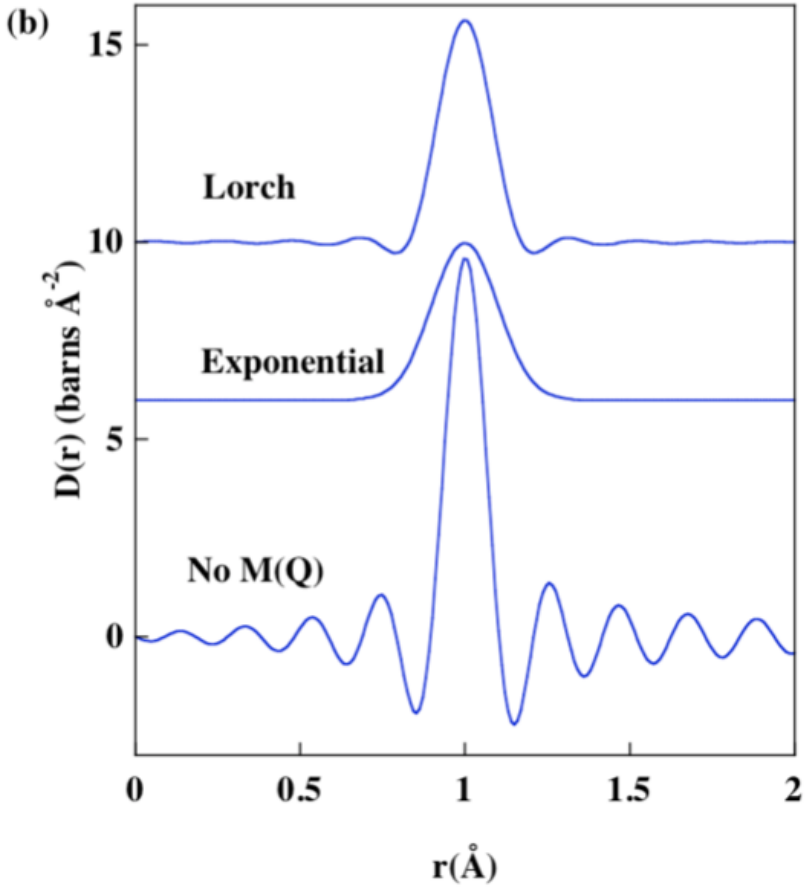
A = Atomic mass of the sample

Fourier transform

$$G(r) = \frac{2}{p}\int_0^{Q_{\max}} Q\left(S(Q)-1\right)M(Q)\sin\left(rQ\right)dQ$$

M(Q) : modification function

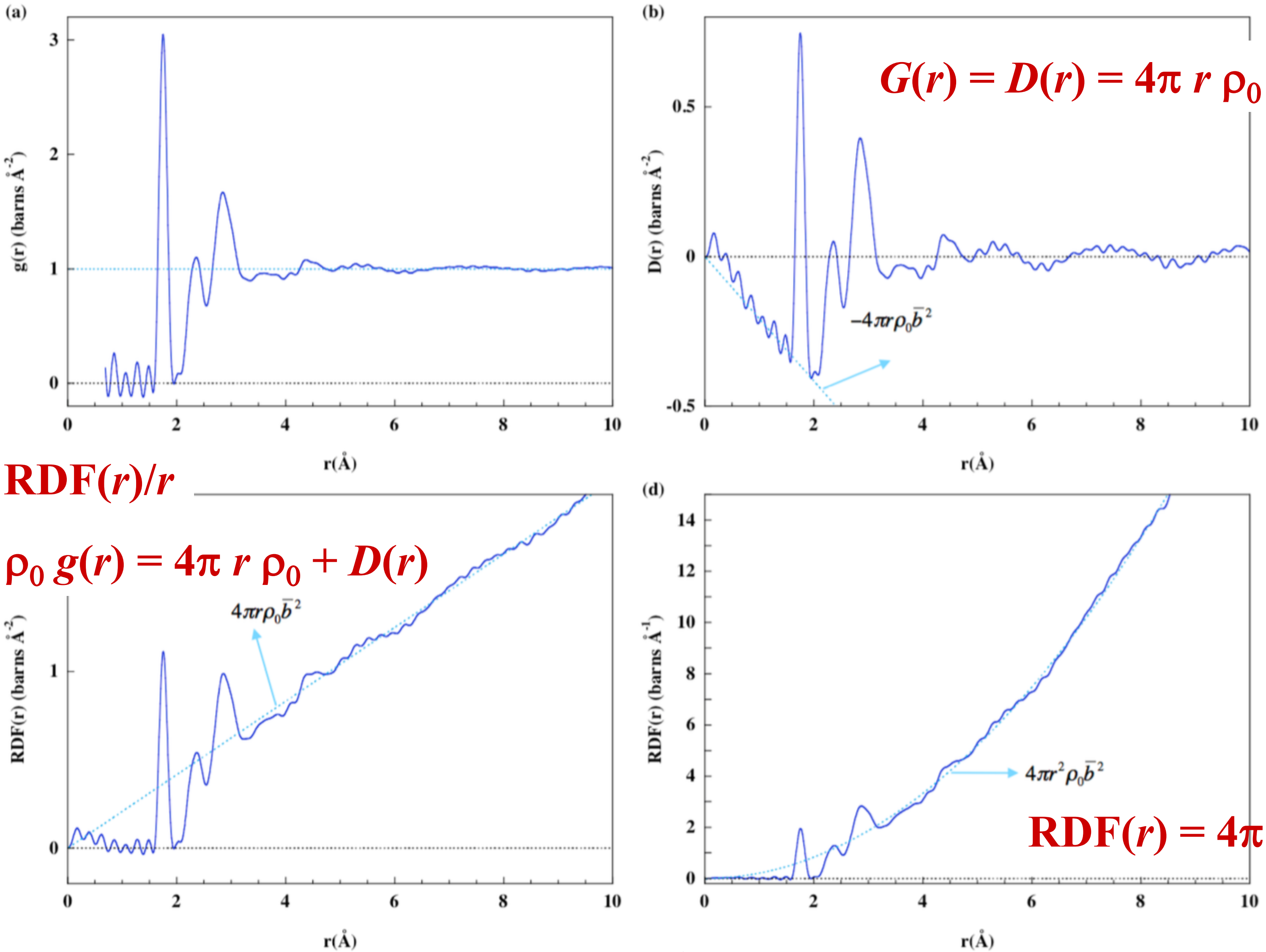
⇒ limit effect of truncation of the data



Fonctions dans l’espace réel

✓Pair distribution function $g(r)$

✓Pair correlation function $G(r)$ or differential correlation function $D(r)$



$$G(r) = D(r) = 4\pi\, r\, \rho_0\, [g(r) - 1]$$

$$T(r) = \mathrm{RDF}(r)/r$$

$$= 4\pi\, r\, \rho_0\, g(r) = 4\pi\, r\, \rho_0 + D(r)$$

$$\mathrm{RDF}(r) = 4\pi\, r^2\, \rho_0\, g(r)$$

✓Total distribution function T(r)

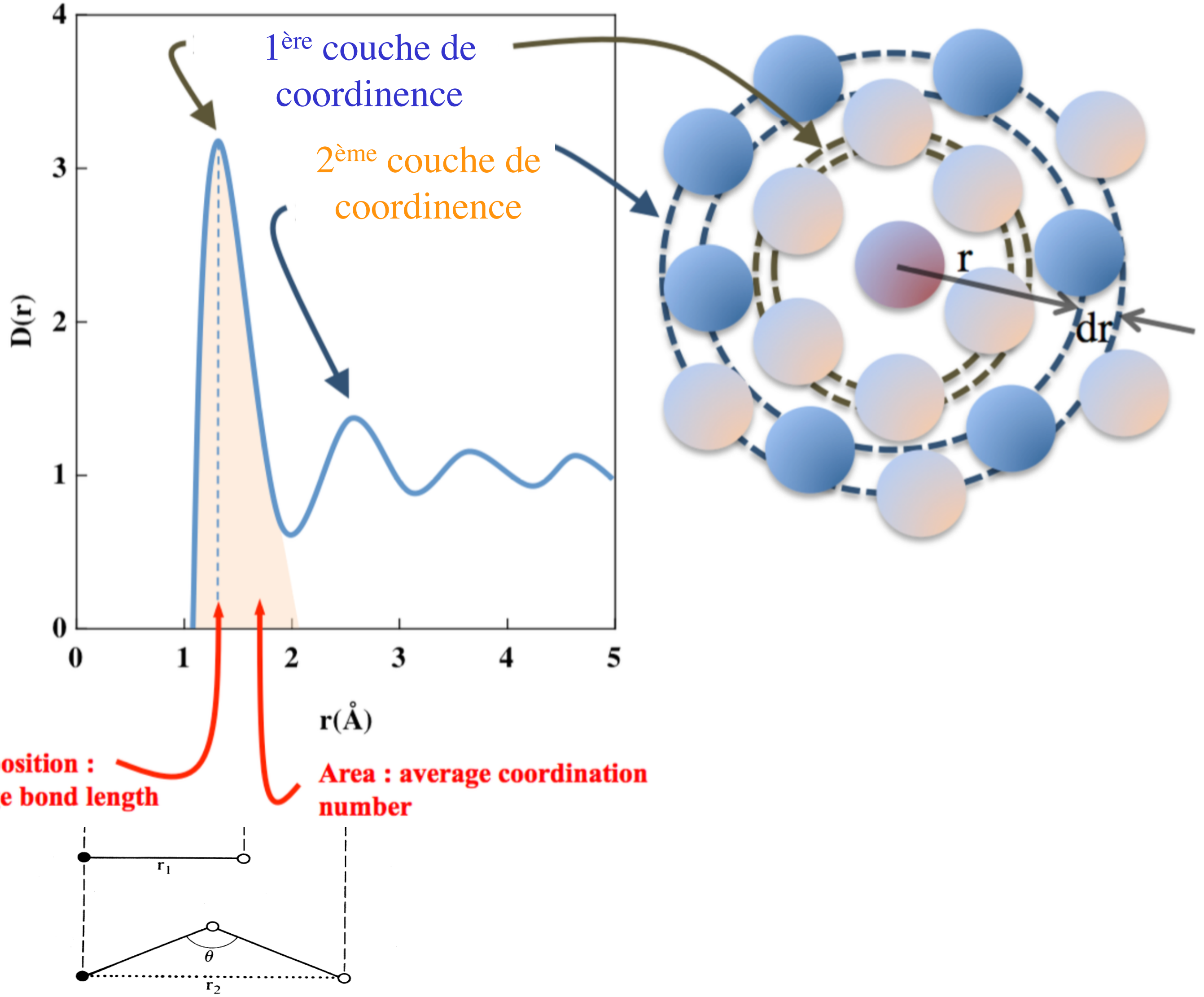
✓Radial distribution function RDF(r)

Information from the correlation function

✓ Peak position
➪Distances and angles between atoms

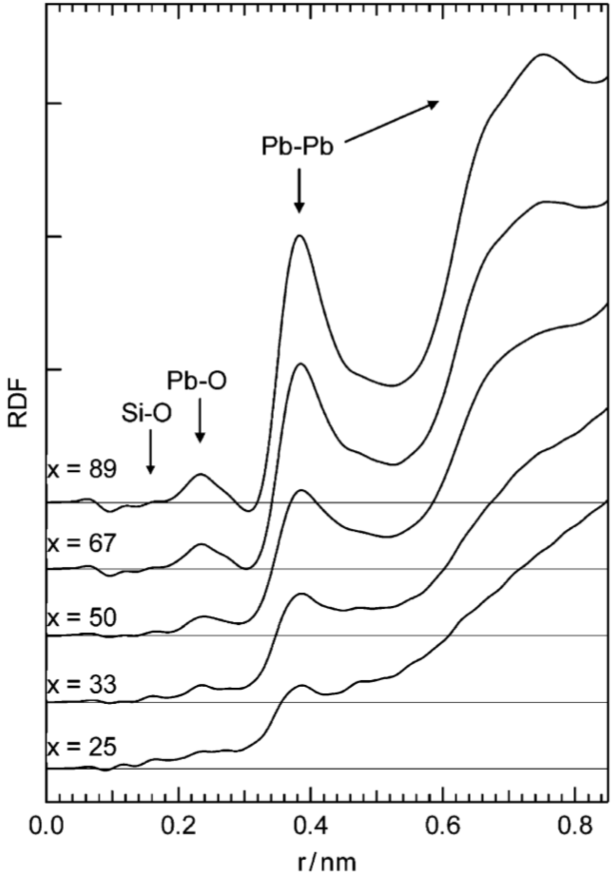
✓ Peak area
➪Coordination number

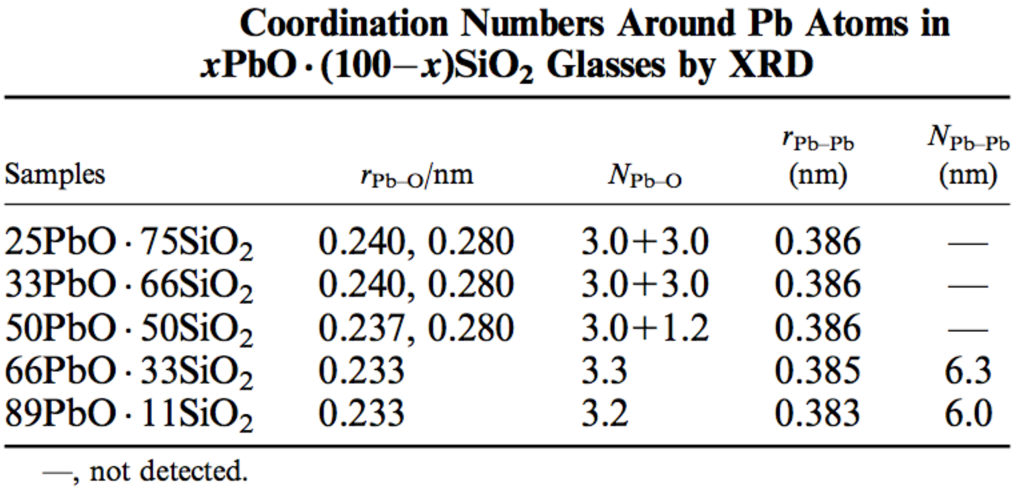
✓ Full width half maximum
➪Disorder



Unidimensional representation of a 3D structure

Lead silicate glasses

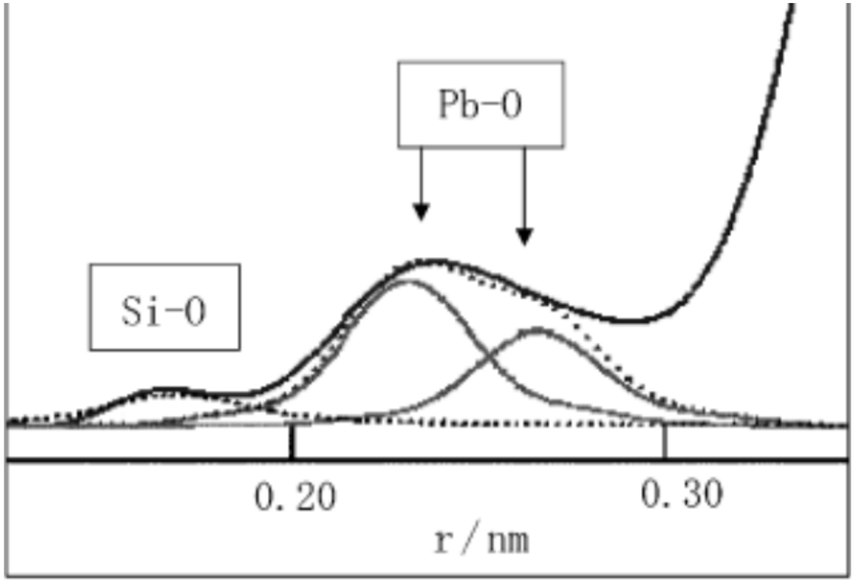




Coordination Numbers Around Pb Atoms in xPbO · (100−x)SiO_2 Glasses by XRD

Samples	r_{Pb-O}/nm	N_{Pb-O}	r_{Pb-Pb} (nm)	N_{Pb-Pb} (nm)
25PbO · 75SiO_2	0.240, 0.280	3.0+3.0	0.386	—
33PbO · 66SiO_2	0.240, 0.280	3.0+3.0	0.386	—
50PbO · 50SiO_2	0.237, 0.280	3.0+1.2	0.386	—
66PbO · 33SiO_2	0.233	3.3	0.385	6.3
89PbO · 11SiO_2	0.233	3.2	0.383	6.0

—, not detected.

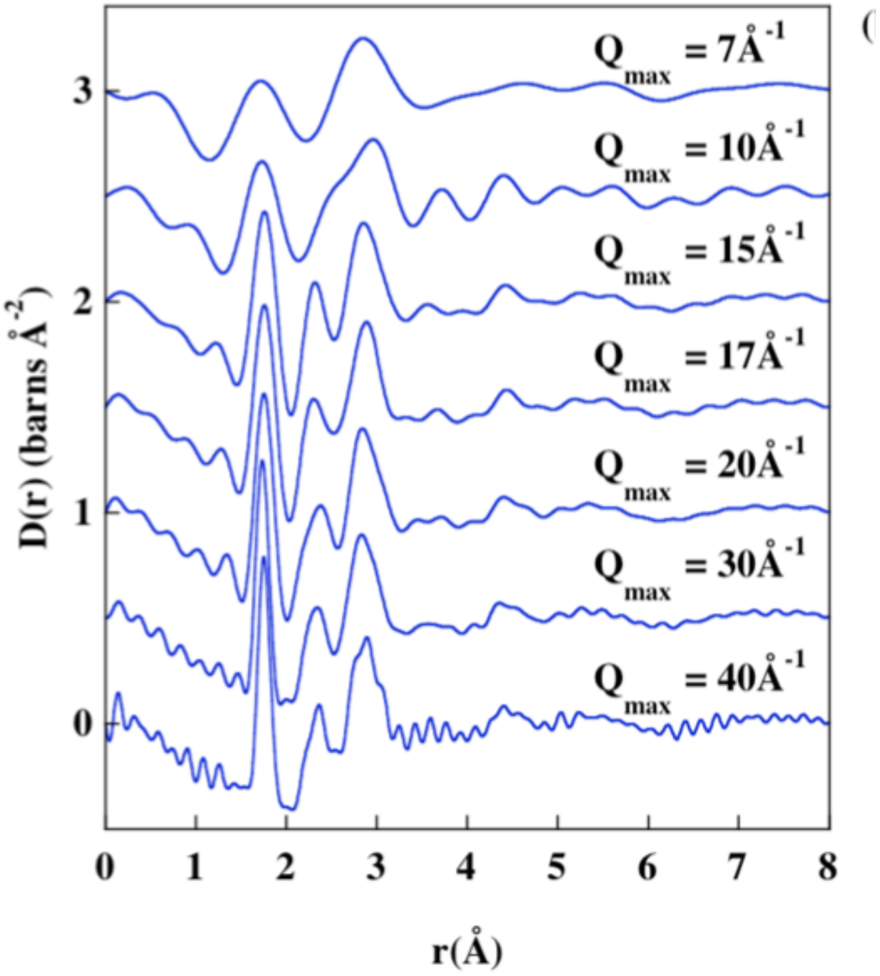


Kohara (2010) PbO_4 tetrahedra are in majority, although PbO_3 and PbO_5
Takahashi (2005) PbO_3+$_3$ unit is dominant

Kohara et al., Phys. Rev. B 82 (2010) 134209
Takahashi et al., J. Am. Ceram. Soc., 88 (2005) 1591

Fourier transform

$$G(r) = \frac{2}{p}\int_0^{Q_{\max}} Q(S(Q)-1)M(Q)\sin(rQ)\,dQ$$

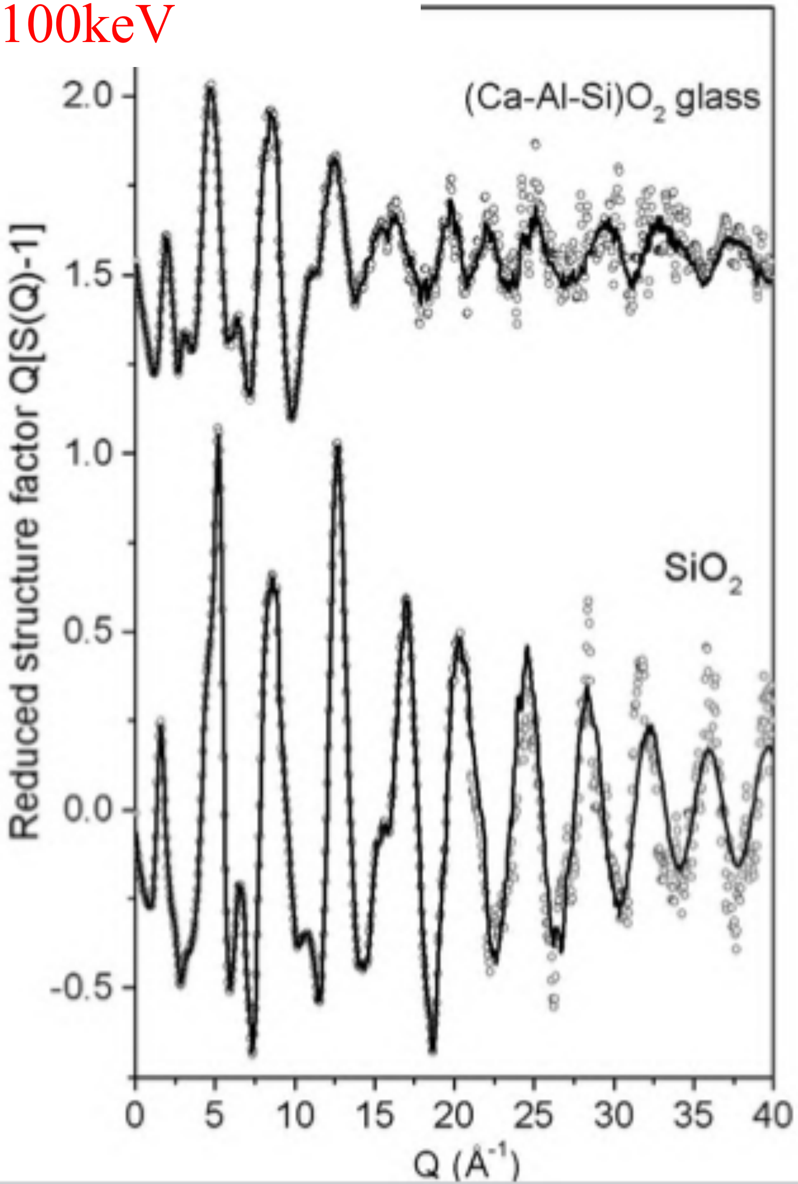


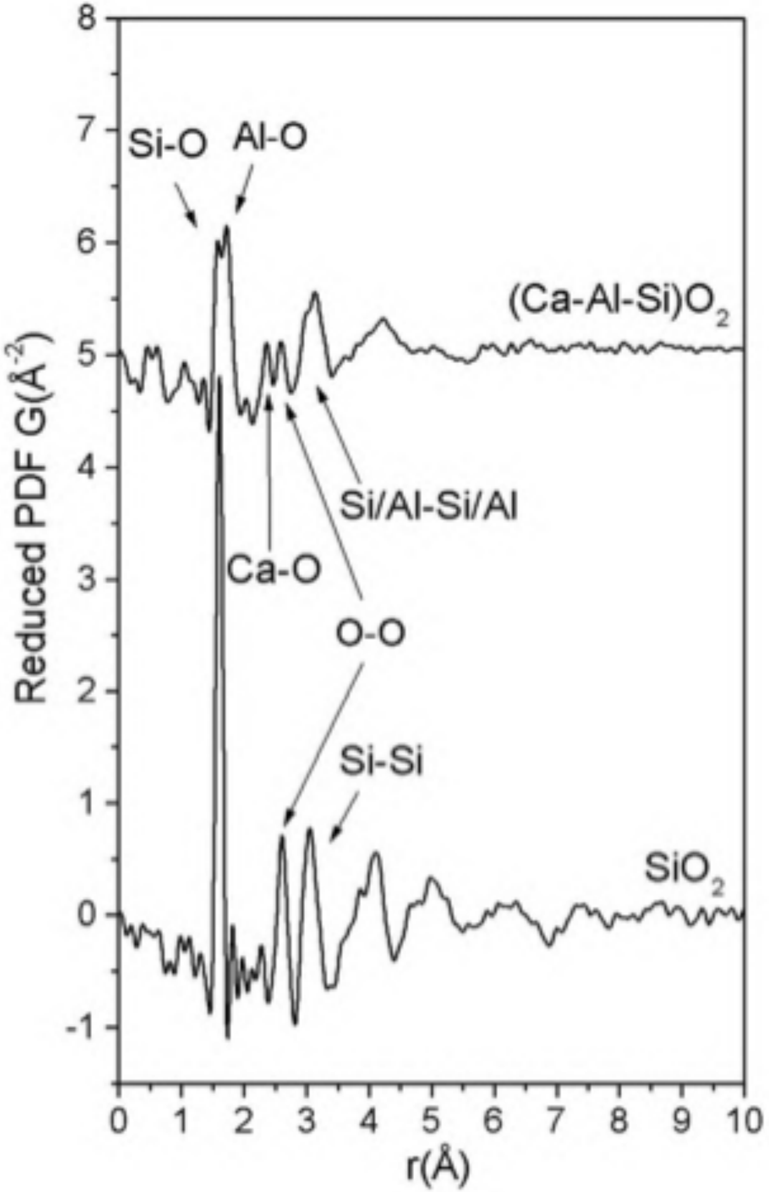
High resolution diffraction

Use of high energy
X-rays
E=100keV

Distance Si-O=1.62 Å

Distance Al-O=1.75 Å

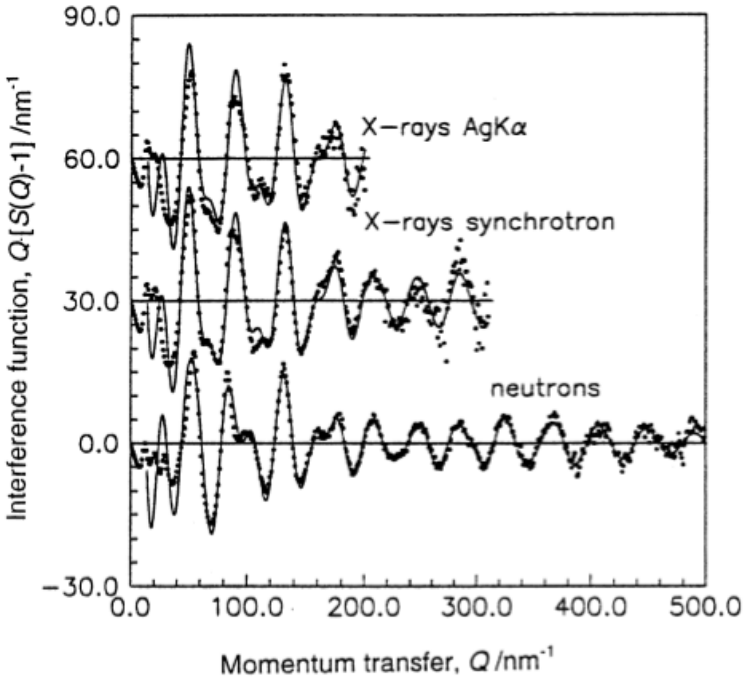


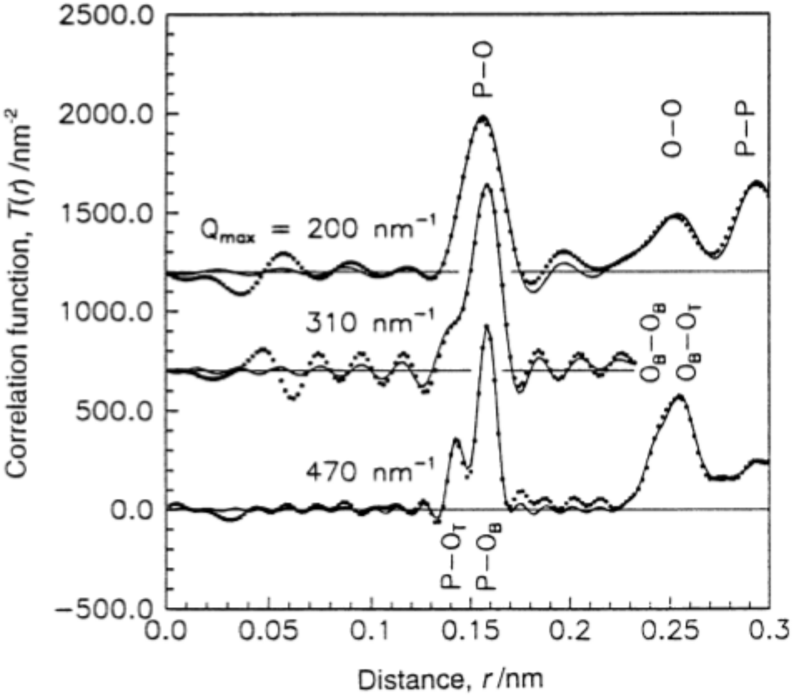


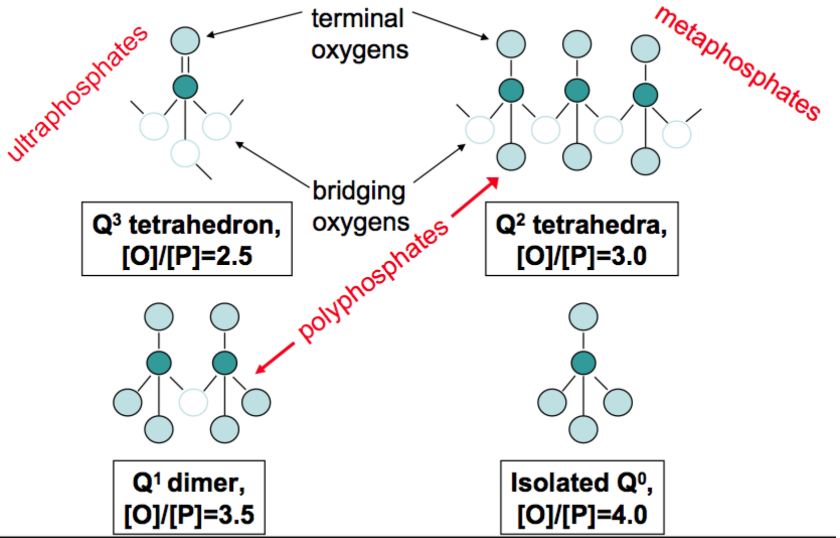
High resolution diffraction

Vitreous P_2O_5 $P\ 2s^22p^3$

Possibility to distinguish O linked with P
O_T: terminal oxygen = end of chain
O_B: bridging oxygen





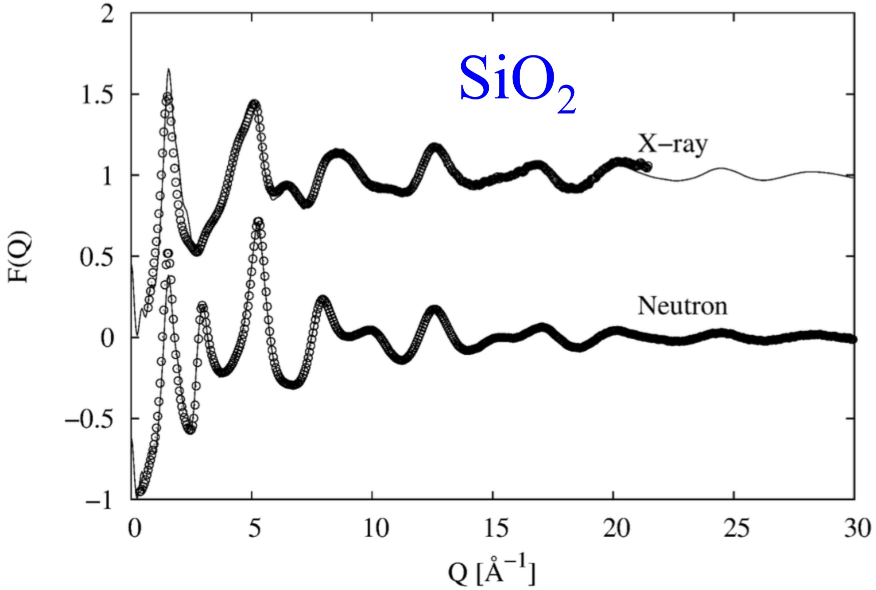


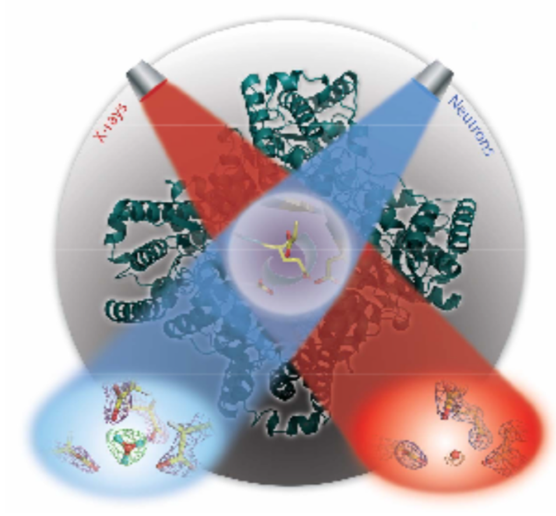
Hoppe et al., Sol. St. Comm., 115(2000)559

Better to use neutron or X-rays?

Use both !

They are complementary





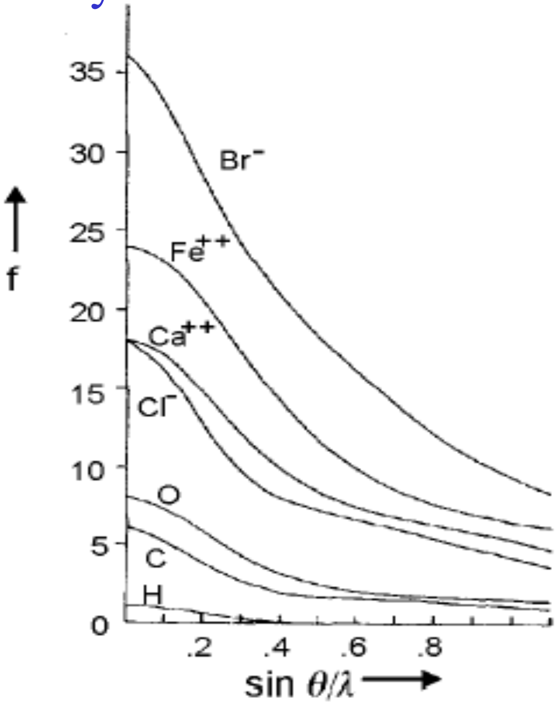
Comparison between neutron and X-ray diffraction

X-ray

Interaction with electronic cloud

f(Q) form factor

✓Strong variation of scattered intensity with θ



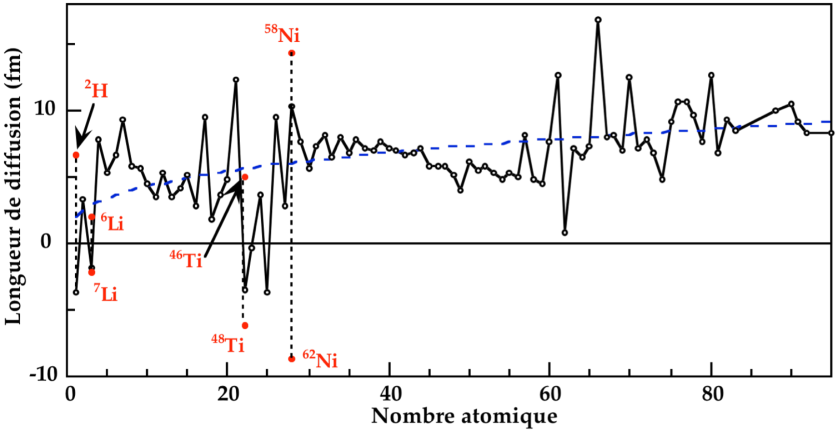
θ = 0, I = Z

Neutrons

Interaction with the nucleus

b neutron scattering length

✓ b not a monotonous function of Z



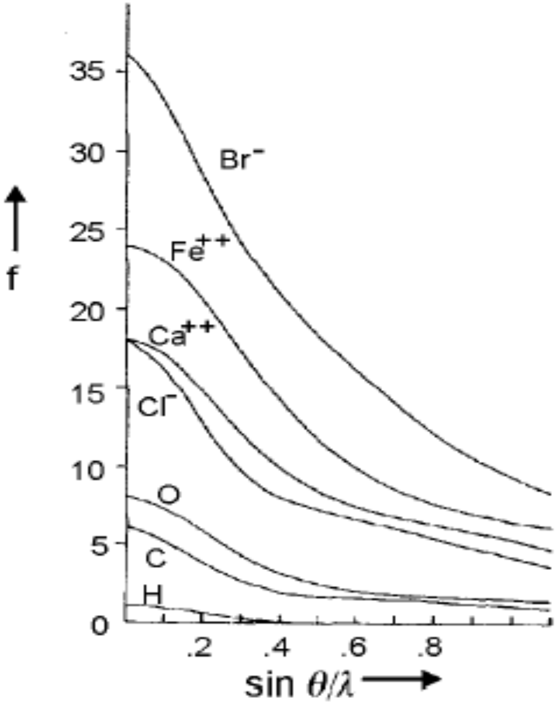
Comparison between neutron and X-ray diffraction

X-ray

f(Q) form factor

✓ information on high Z elements

✓ weak contrast for elements with close Z



$\theta = 0, I = Z$

Neutrons

b neutron scattering length

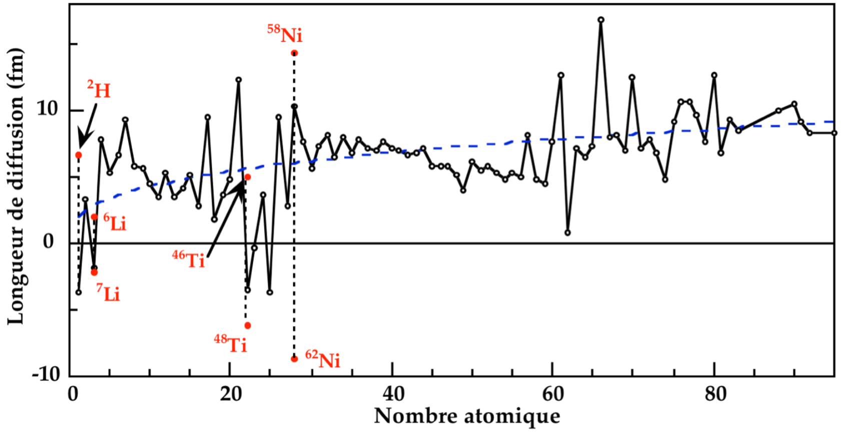
✓ b independent of Q = constant

⇒ light elements are visible (H, Li, N, O, etc)

⇒ possibility to distinguish elements with close Z

✓b vary among isotopes of the same elment

⇒ isotopic substitution (Ex: H/D)



Comparaison entre diffraction des neutrons et rayons X

Facteur de structure S(Q) : somme des **facteurs de structure partiels, $S_{\alpha\beta}(Q)$:**

$$S(Q)=\sum_{\alpha,\beta} W_{\alpha\beta}(Q)S_{\alpha\beta}(Q)$$

Facteurs pondérants

RX

$$W_{\alpha\beta}(Q)=c_\alpha c_\beta f_\alpha(Q,E)f_\beta(Q,E)\left(2-\delta_{\alpha\beta}\right)$$

Neutrons

$$W_{\alpha\beta}(Q)=c_\alpha c_\beta b_\alpha b_\beta\left(2-\delta_{\alpha\beta}\right)$$

Fonction de corrélation

RX

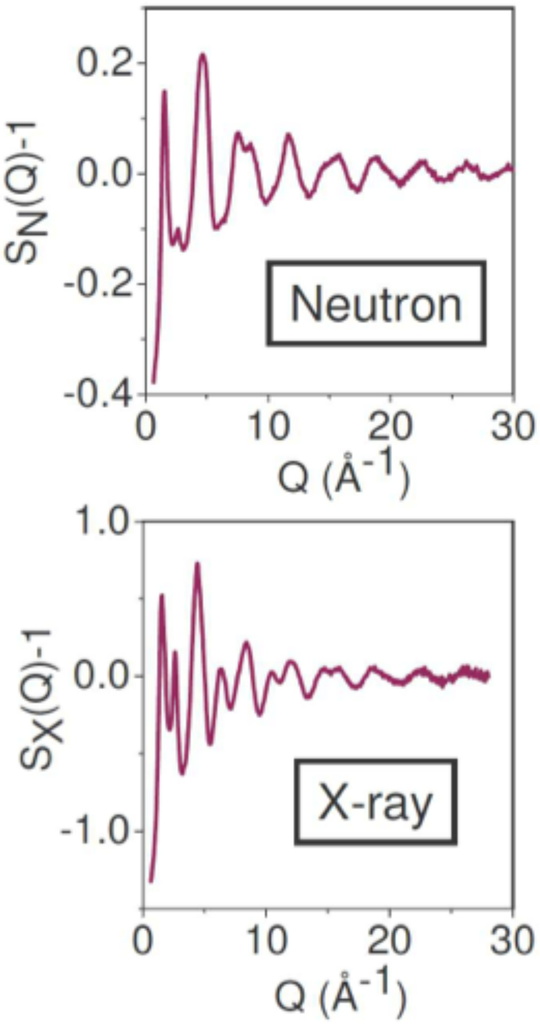
$$G(r)=\sum_{\alpha,\beta\geq\alpha} TF\left(W_{\alpha\beta}\right)\otimes g_{\alpha\beta}(r)$$

Neutrons

$$G(r)=\sum_{\alpha,\beta\geq\alpha} W_{\alpha\beta}g_{\alpha\beta}(r)$$

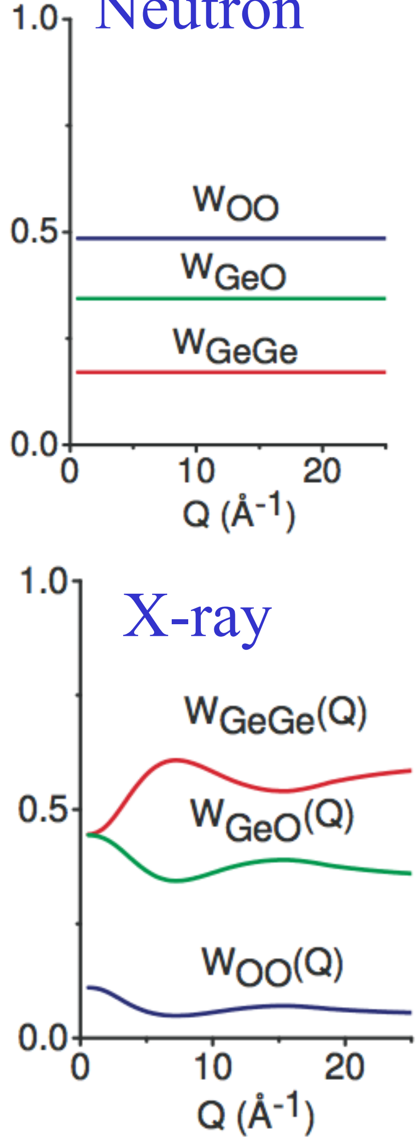
Fonctions de distribution de paires partielles : $g_{\alpha\beta}(r)$

Total Structure Factor, S(Q) = Weighting factors, $W_{\alpha\beta}(Q)$ X Partial Structure Factors, $S_{\alpha\beta(}Q)$



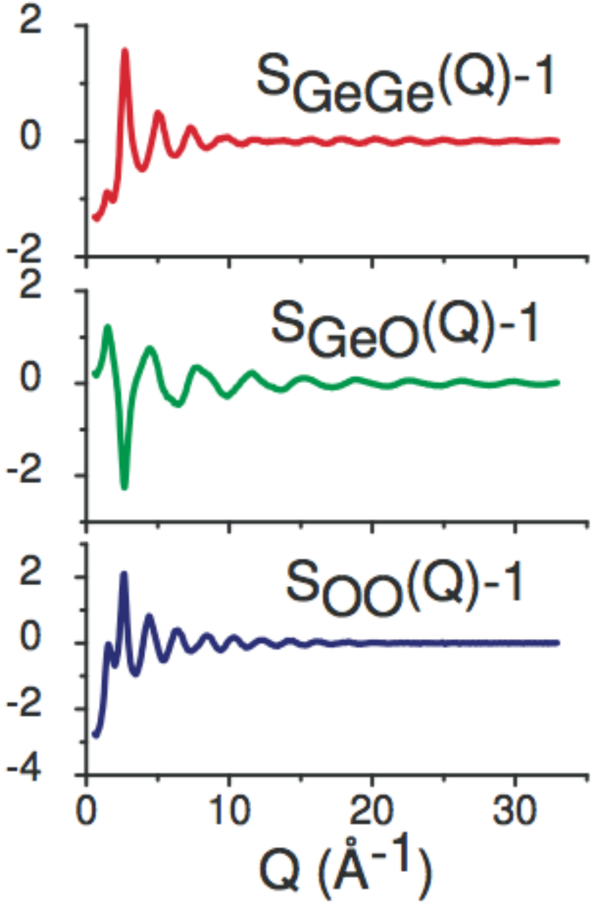
$c_a c_b b_a b_b$

Neutron



X-ray

GeO_2



From Benmore

GeO_2 glass

Neutron diffraction for silica glass: radial distribution function

Polyatomic solid

Q(S(Q)-1)

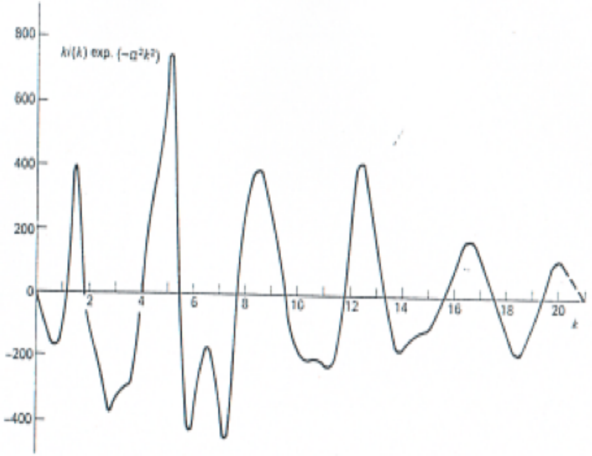
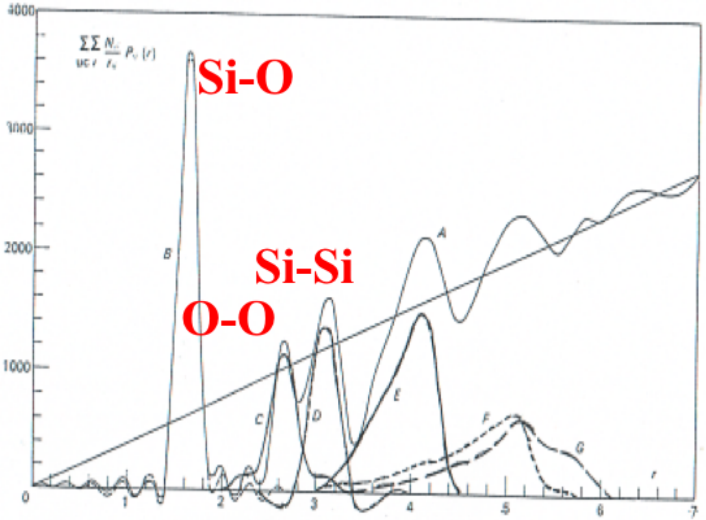


Fig. 3. The experimental $ki(k)\exp(-\alpha^2k^2)$ for SiO_2, with $\alpha=0{\cdot}056$ and $g(k)=f_e$.

Glass SiO_2

Correlation function



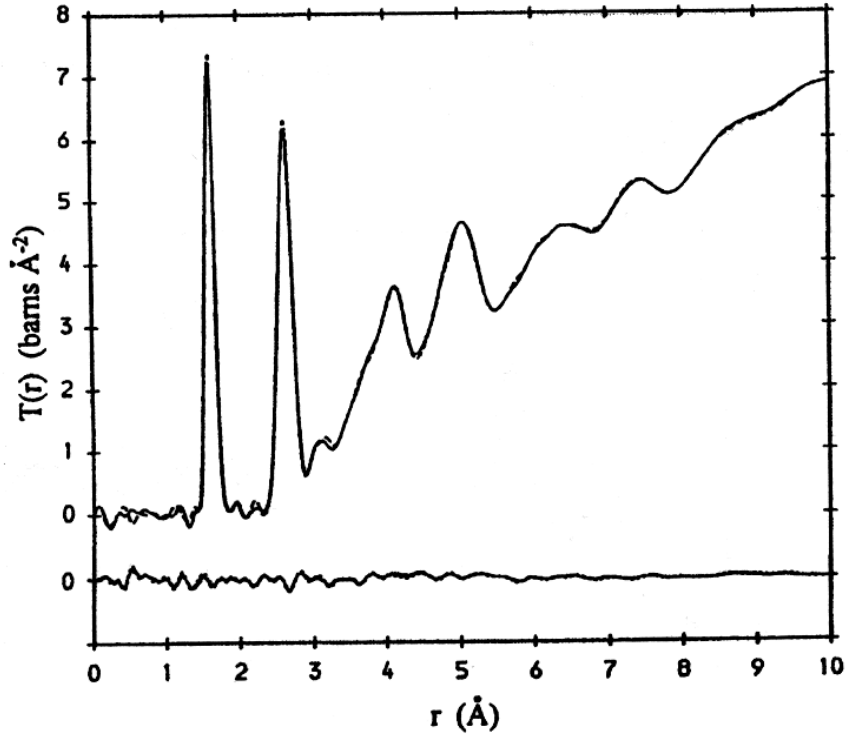
Overlapping of PPDF $G_{\alpha\beta}(r)$

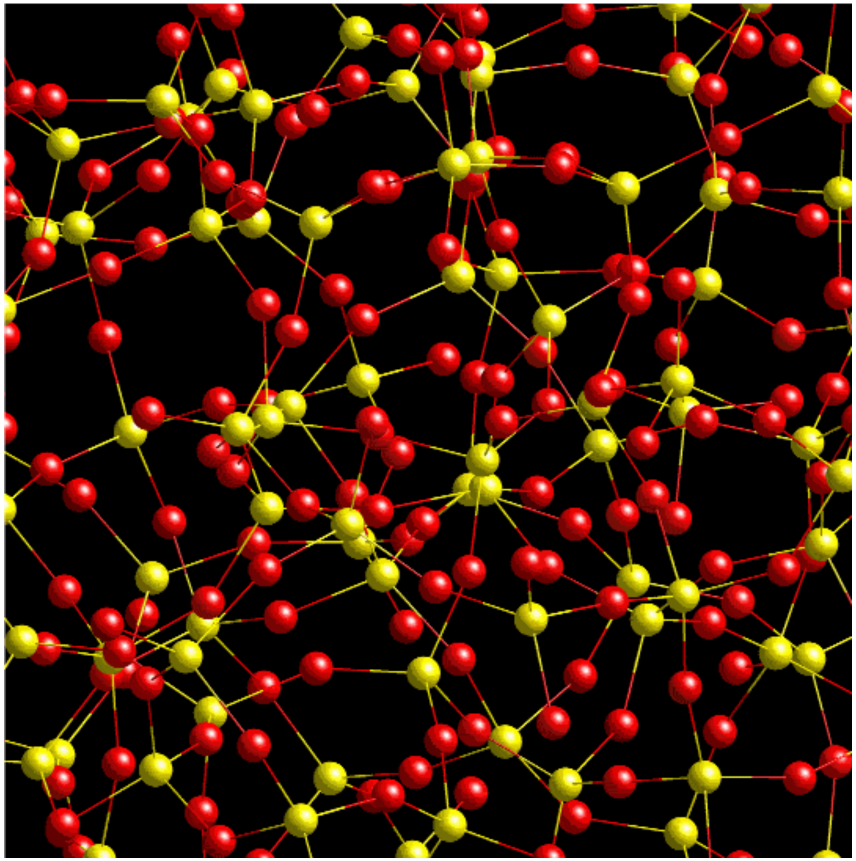
Fig. 4. The pair function distribution curves for SiO_2. A is the measured curve. The computed contributions are given by: B, Si–O; C, O–O; D, Si–Si; E, Si–2nd O; F, O–2nd O; G, Si–2nd Si.

R. L. Mozzi, Warren, B.E., J. Appl. Cryst. 2, 164 (1969)

Extract information from diffraction data: numerical modelling

Classical Molecular Dynamics
Ab inito Molecular Dynamics
RMC and EPSR (Monte Carlo methods)

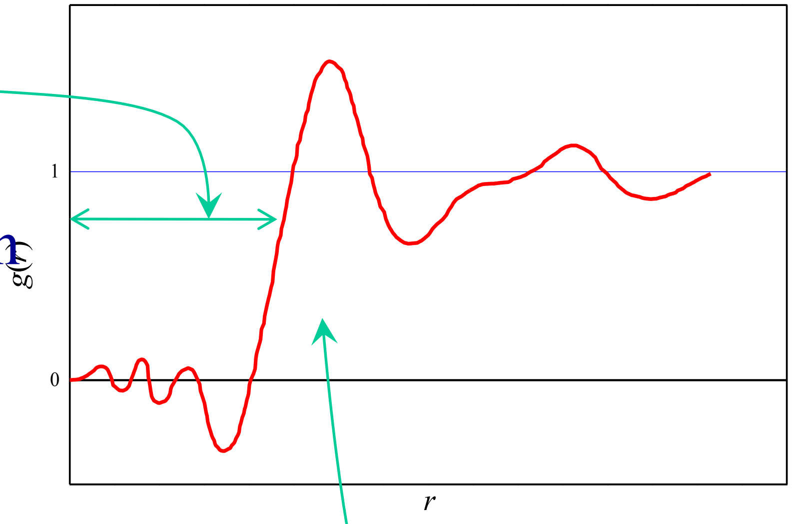




Pair distribution function *g*(*r*)

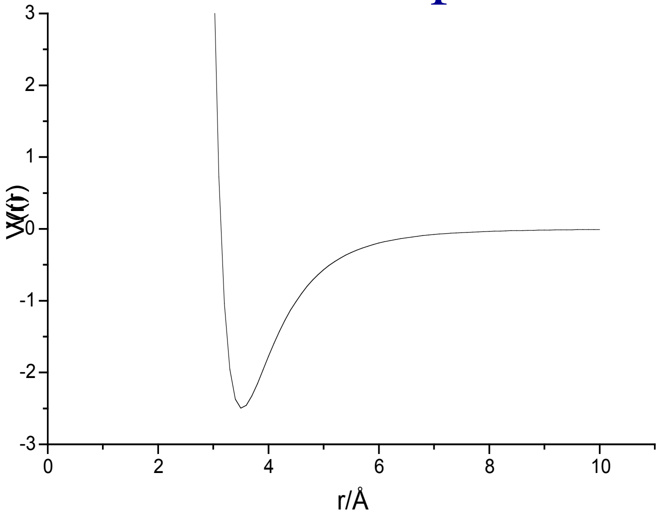
Measures the probability that two atoms are separated by a distance *r*

Atomic repulsion



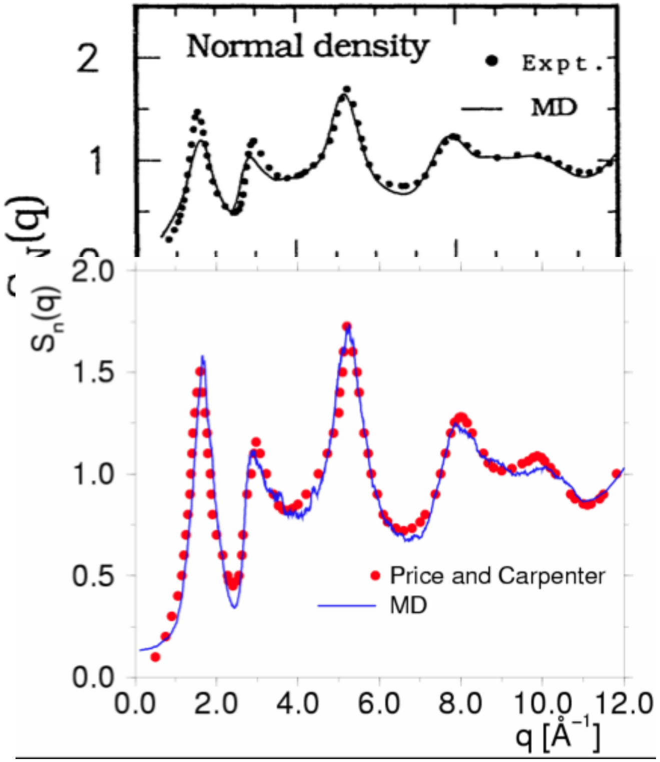
Minimum of the pair potential

Interatomic potential



- ✓ Structural test of the MD models
- ✓ Improvement of potentials

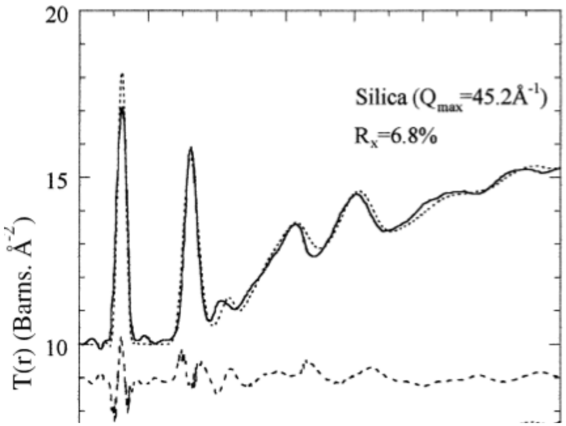
Comparison experiment / simulation

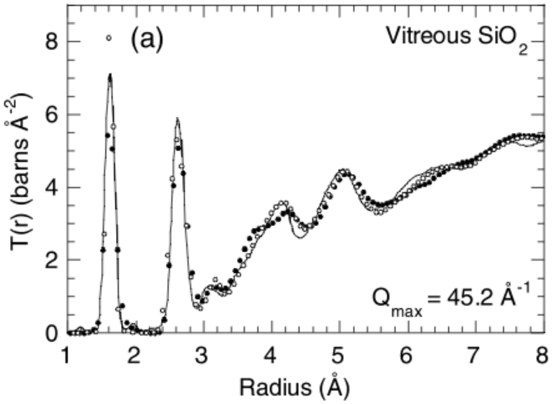


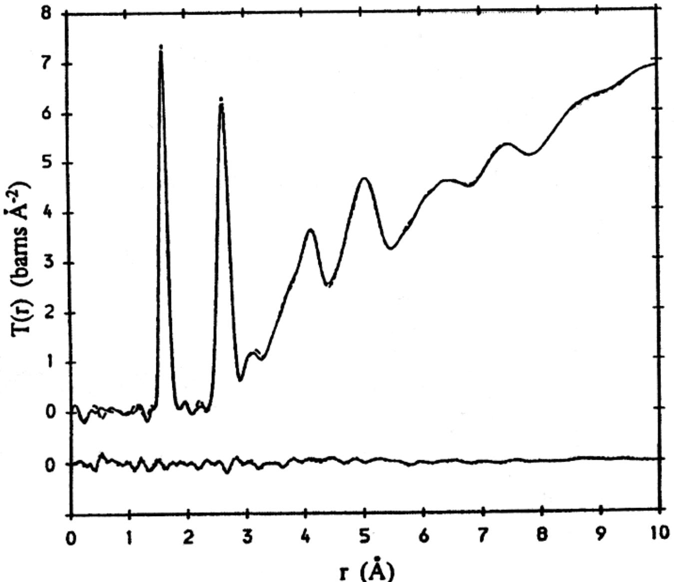
Always good agreement in publication !

$$R_c = \left(\frac{\sum_i \left[T_{\exp}(r_i) - T_{sim}(r_i) \right]^2}{\sum_i T_{\exp}^2 (r_i)} \right)^{1/2}$$

Wright, J. Non-Cryst. Solids, 159 (1993)264



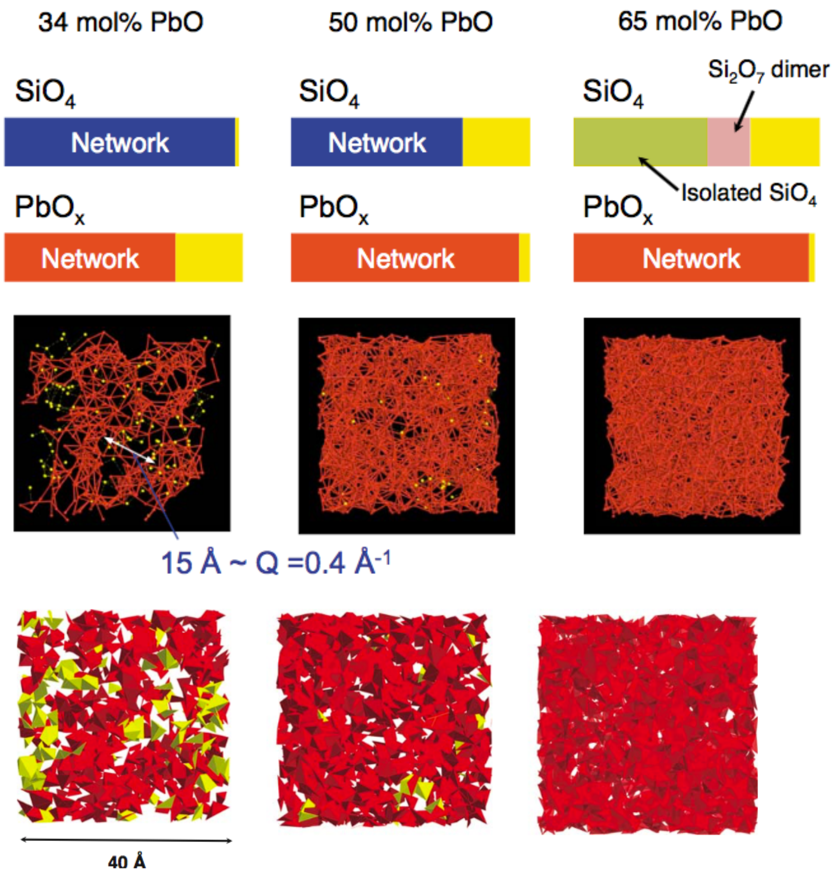




Lead silicate glasses

RMC modeling => quantitative fit of the experimental data

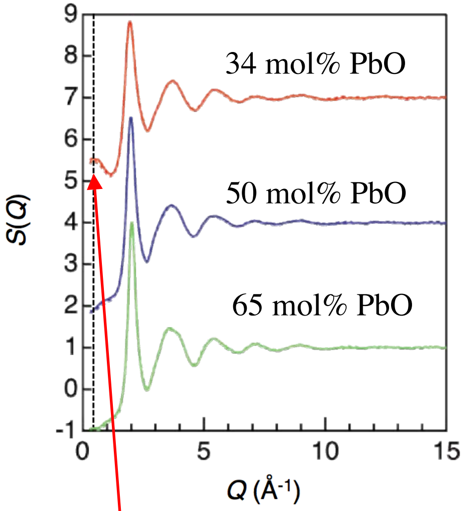
34mol% PbO : large fraction of PbO*x* polyhedra do not participate in network formation non-network PbO*x* unit (isolated short chains or complex units) = yellow points



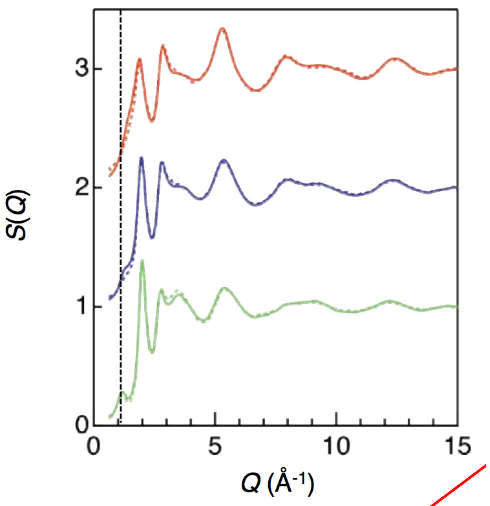
Kohara et al., Phys. Rev. B 82 (2010) 134209

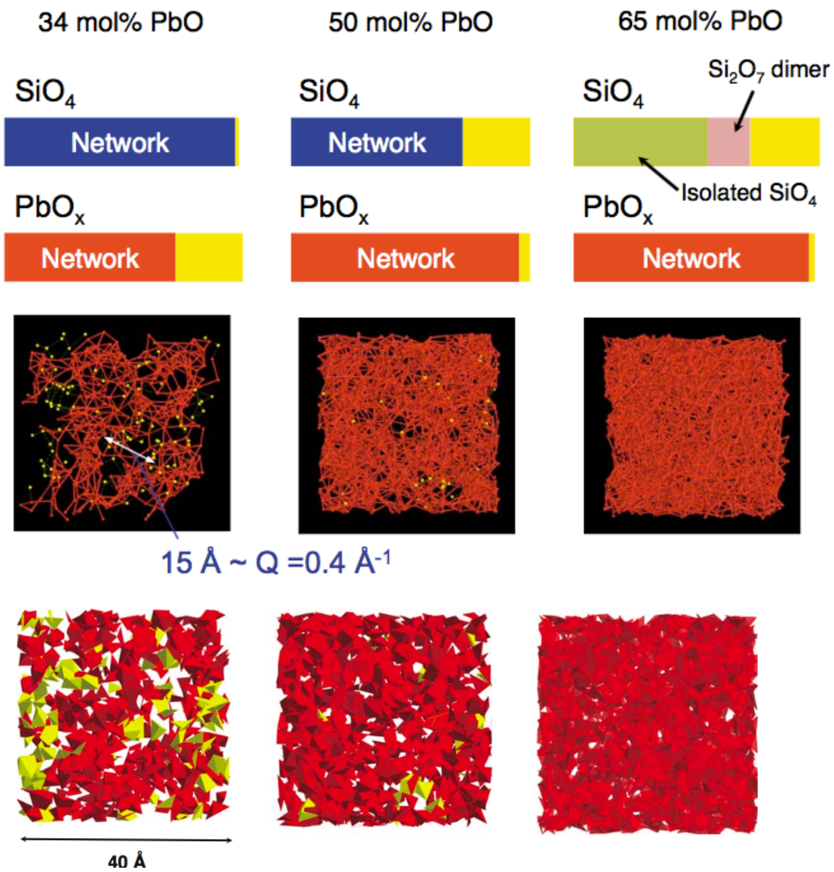
Lead silicate glasses

X-ray



Neutron





inhomogeneous lead distribution
Peak at $Q_P=0.4$ Å^{-1} =>
distance $2p/Q_p$~15 Å

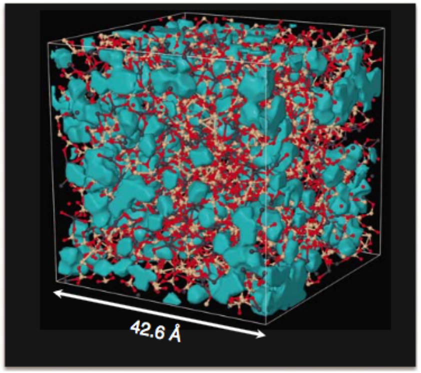
34mol% PbO : large fraction of PbO*x* polyhedra do not participate in network formation non-network PbO*x* unit (isolated short chains or complex units) = yellow points

Kohara et al., Phys. Rev. B 82 (2010) 134209

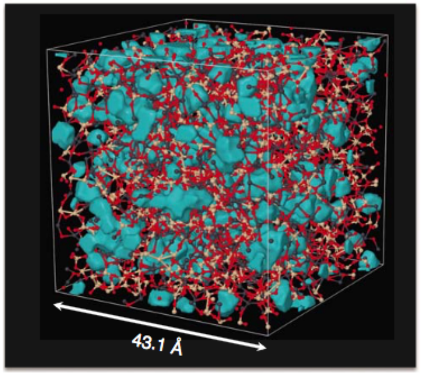
Lead silicate glasses : a binary network-former glass

Cyan= voids

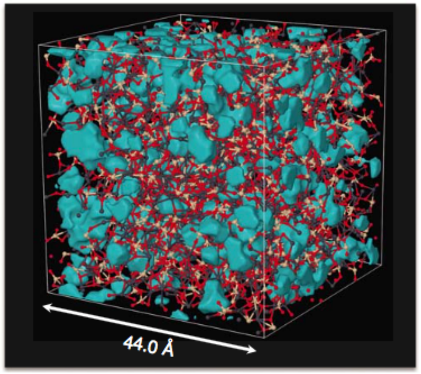
34 mol% PbO



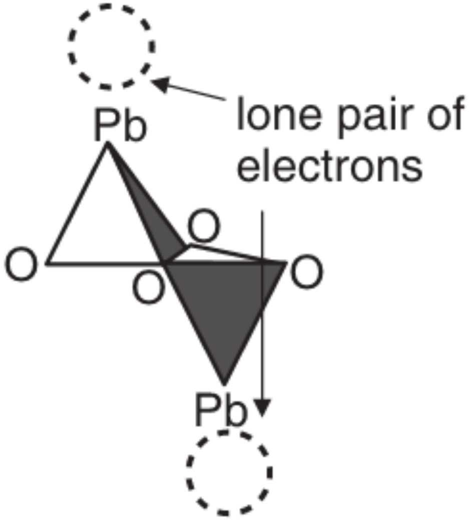
50 mol% PbO



65 mol% PbO



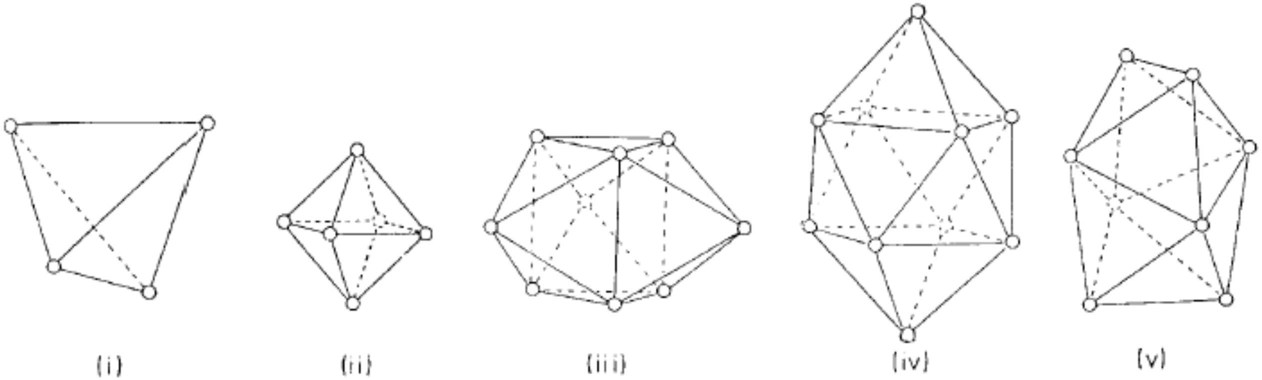
PbO-SiO$_2$ glass as a "binary network-former glass" with large amounts of free volume (voids)



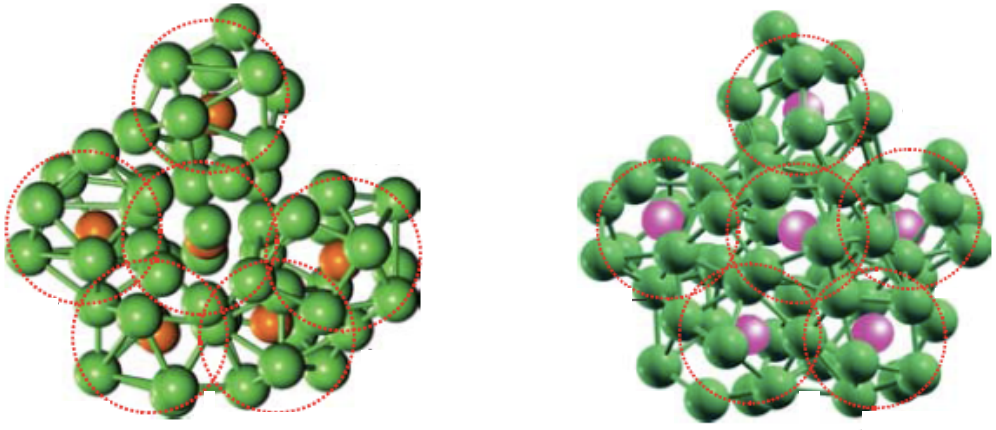
Kohara et al., Phys. Rev. B 82 (2010) 134209

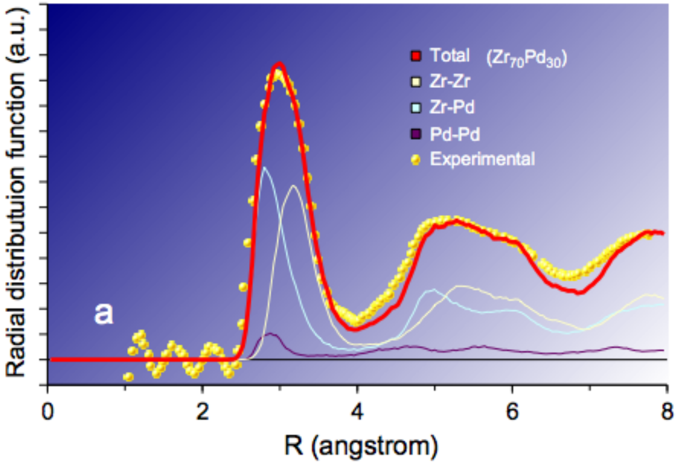
A new order for metallic glasses

Random sphere packing with canonical polyhedra



Also medium range order (with 5-fold symmetry)
X-ray diffraction + RMC modeling





Sheng et al., Nature, 439(2006)419

Extract information from diffraction data: experimental contrast methods

System of *n* chemical species

Number of independent $S_{\alpha\beta}(Q)$: n(n+1)/2

$$F(Q) = \sum_{a,b} c_a c_b b_a b_b \left[S_{ab}(Q) - 1 \right]$$

We need N= n(n+1)/2 different experiments !

Difference method

Neutron: isotopic substitution

X-ray: anmalous diffraction

Isotopic substitution (neutron diffraction)

First difference method

M = substituted element

$$F_{\exp 1}(Q) = \sum_{a} c_a b_a^2 + \sum_{a,b \neq M} c_a c_b b_a b_b \left(S_{ab}(Q) - 1\right) + \sum_{M,a} c_a c_M b_a b_{M1} \left(S_{Ma}(Q) - 1\right)$$

Sample 1

$$F_{\exp 2}(Q) = \sum_{a} c_a b_a^2 + \sum_{a,b \neq M} c_a c_b b_a b_b \left(S_{ab}(Q) - 1\right) + \sum_{M,a} c_a c_M b_a b_{M2} \left(S_{Ma}(Q) - 1\right)$$

Sample 2

Cormier et al., Chem. Geol. 174(2001)349

Isotopic substitution (neutron diffraction)

First difference method

M = substituted element

$$F_{\exp 1}(Q) = \sum_{a} c_a b_a^2 + \xcancel{\sum_{a,b\neq M} c_a c_b b_a b_b\left(S_{ab}(Q)-1\right)} + \sum_{M,a} c_a c_M b_a b_{M1}\left(S_{Ma}(Q)-1\right)$$

Sample 1

$$F_{\exp 2}(Q) = \sum_{a} c_a b_a^2 + \xcancel{\sum_{a,b\neq M} c_a c_b b_a b_b\left(S_{ab}(Q)-1\right)} + \sum_{M,a} c_a c_M b_a b_{M2}\left(S_{Ma}(Q)-1\right)$$

Sample 2

$$\Delta F(Q) = F_{\exp 1}(Q) - F_{\exp 2}(Q)$$

$$\rightarrow \quad \boxed{\Delta F(Q) = \sum_{a\neq M} A\left(S_{Ma}(Q)-1\right) + B\left(S_{MM}(Q)-1\right)}$$

with $A = 2c_a c_M b_a\left(b_{M1} - b_{M2}\right)$ $B = c_M^2\left(b_{M1}^2 - b_{M2}^2\right)$

For a binary system with species α,β :

$$\underbrace{\bar{b}^2\left[S(Q)-1\right]}_{\boldsymbol{F(Q)}} = \sum_{a,b} c_a c_b b_a b_b \left[S_{ab}(Q)-1\right]$$

Matrix

$$\begin{pmatrix} F_{\exp 1}(Q) \\ F_{\exp 2}(Q) \\ F_{\exp 3}(Q) \end{pmatrix} = \begin{pmatrix} c_a^2 b_{a1}^2 & c_b^2 b_{b1}^2 & c_a c_b b_{a1} b_{b1} \\ c_a^2 b_{a2}^2 & c_b^2 b_{b2}^2 & c_a c_b b_{a2} b_{b2} \\ c_a^2 b_{a3}^2 & c_b^2 b_{b3}^2 & c_a c_b b_{a3} b_{b3} \end{pmatrix} \begin{pmatrix} F_{aa}(Q) \\ F_{bb}(Q) \\ F_{ab}(Q) \end{pmatrix} = \begin{pmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{pmatrix} \begin{pmatrix} F_{aa}(Q) \\ F_{bb}(Q) \\ F_{ab}(Q) \end{pmatrix}$$

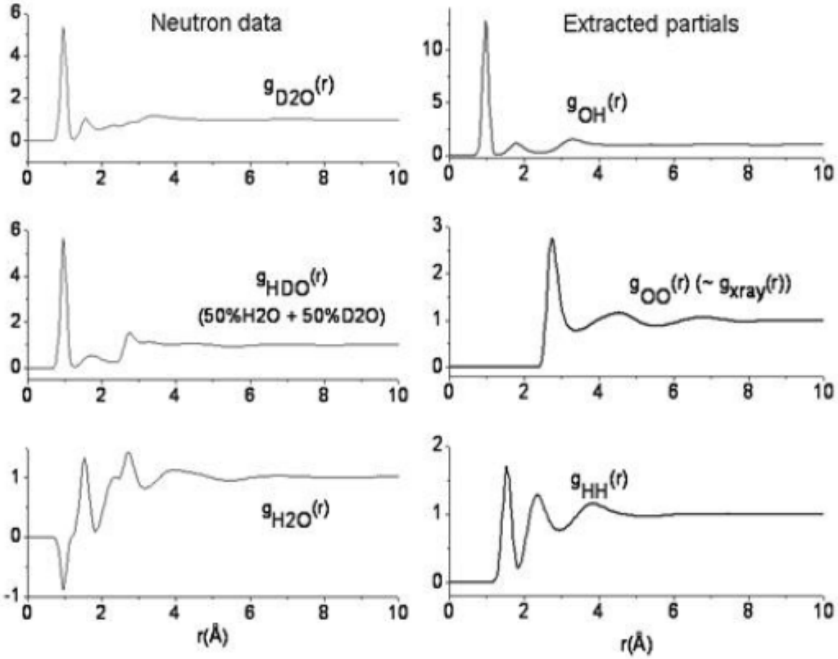
Fixed composition: constant c_α , c_β

Isotopes with a good contrast
$b_{\alpha i}$: scattering length for isotope i of species α

Matrix inversion allows the determination of partial structure factors $S_{ab}(Q)$:

$$\left[F_{\exp}(Q)\right] = [A]\left[F_{ab}(Q)\right]$$

$$\left[F_{ab}(Q)\right] = [A]^{-1}\left[F_{\exp}(Q)\right]$$

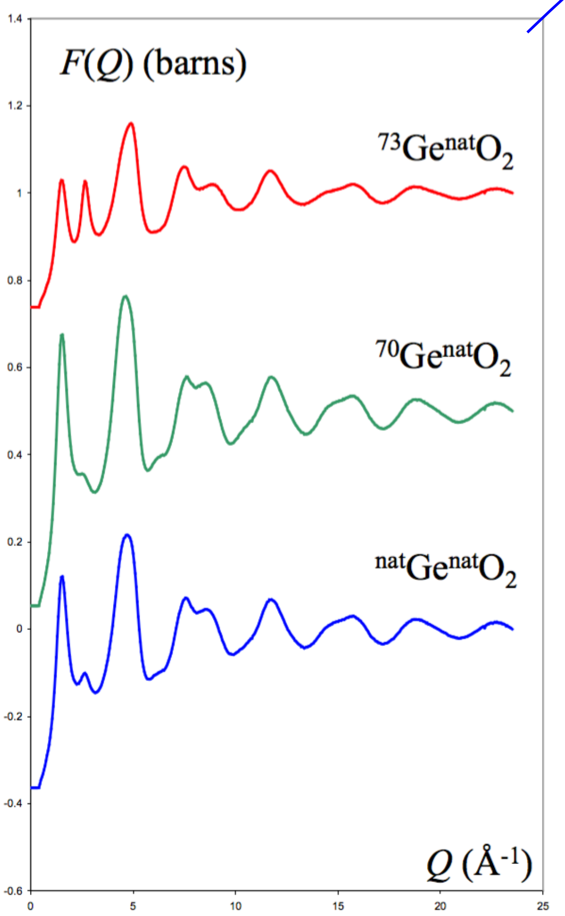


Possibility to do isomorphic substitution:
Two different chemical species with similar radius (same place within the structure ?) but different b

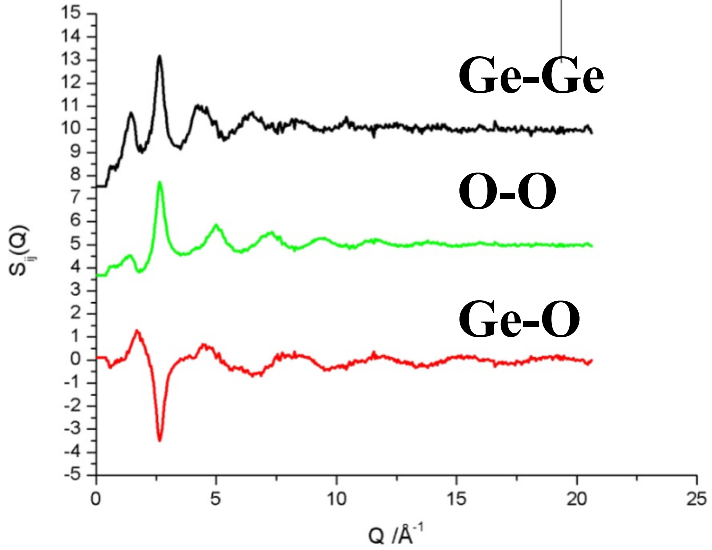
Isotopic substitution (neutron diffraction)

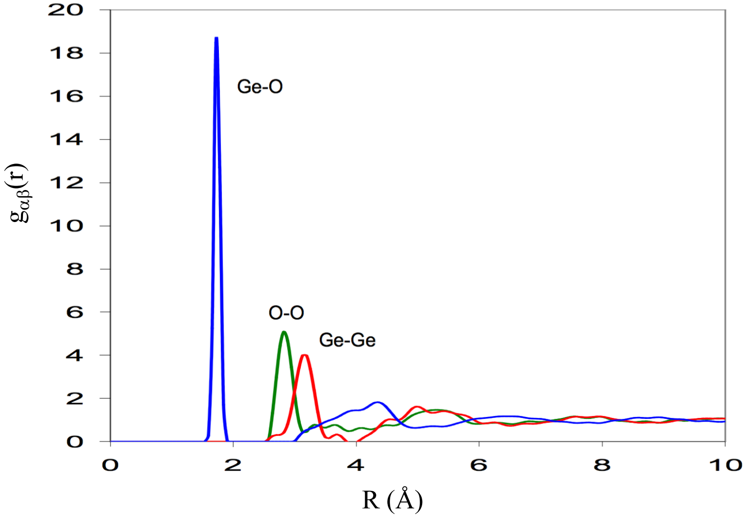
3 different samples

3 different partial functions isolated



GeO_2 glass



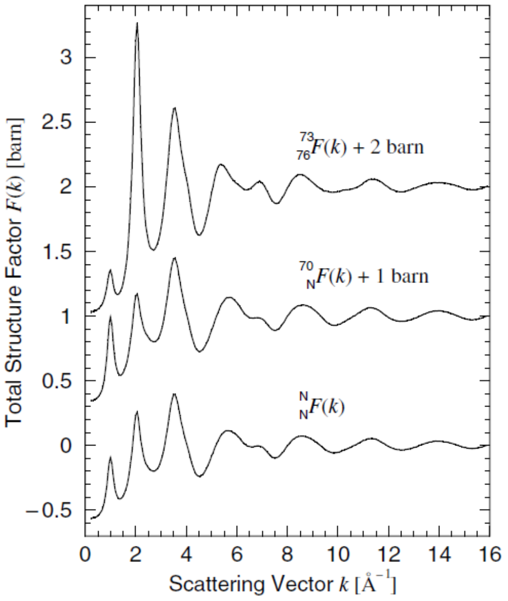


From Salmon et al.

Homopolar bonds in chalcogenide glasses

Example of glassy $GeSe_2$

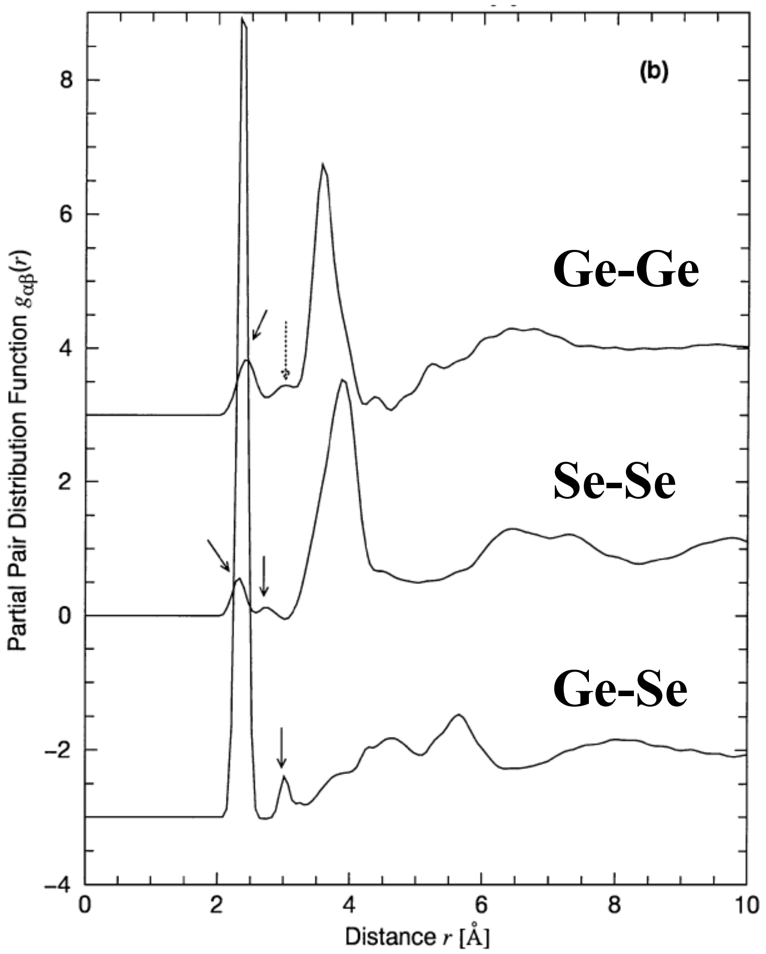
Measure total structure factors for three samples with different isotopic enrichments e.g. $^{N}Ge^{N}Se_2$, $^{70}Ge^{N}Se_2$, $^{73}Ge^{76}Se_2$



Observe:

Ge-Ge and Se-Se homopolar bonds

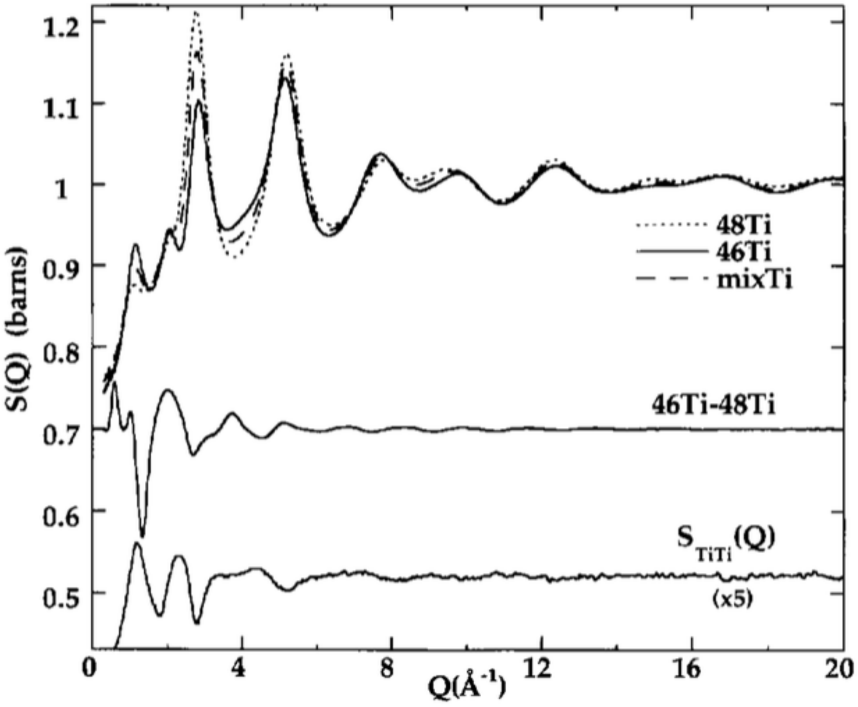
Egde- and corner-sharing $Ge(Se_{1/2})_4$ tetrahedra

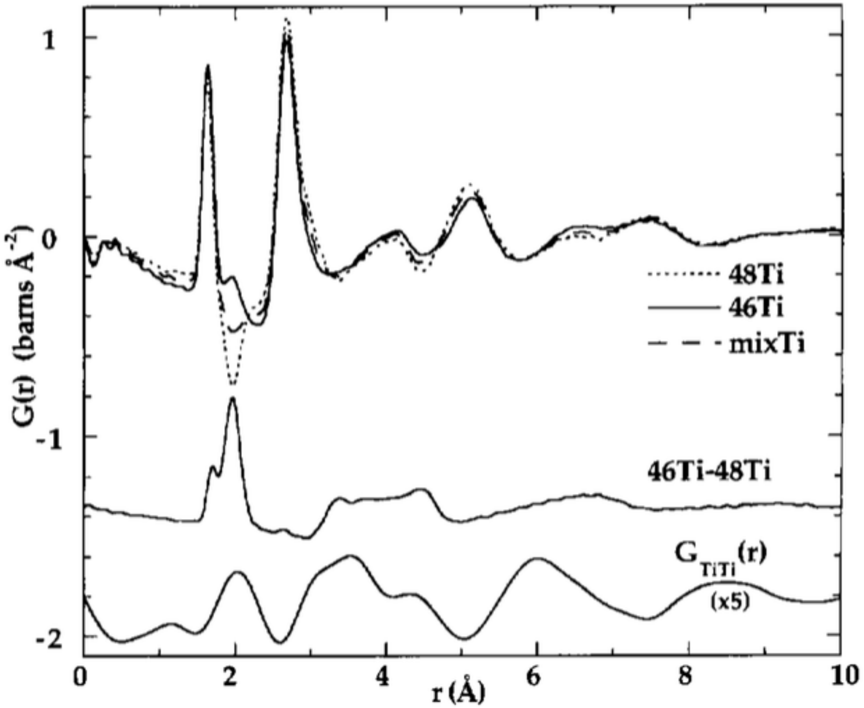


Petri *et al.*, Phys. Rev. Lett.84(2000)2413

Isotopic substitution (neutron diffraction)

Ti : $TiK_2Si_2O_7$ glass

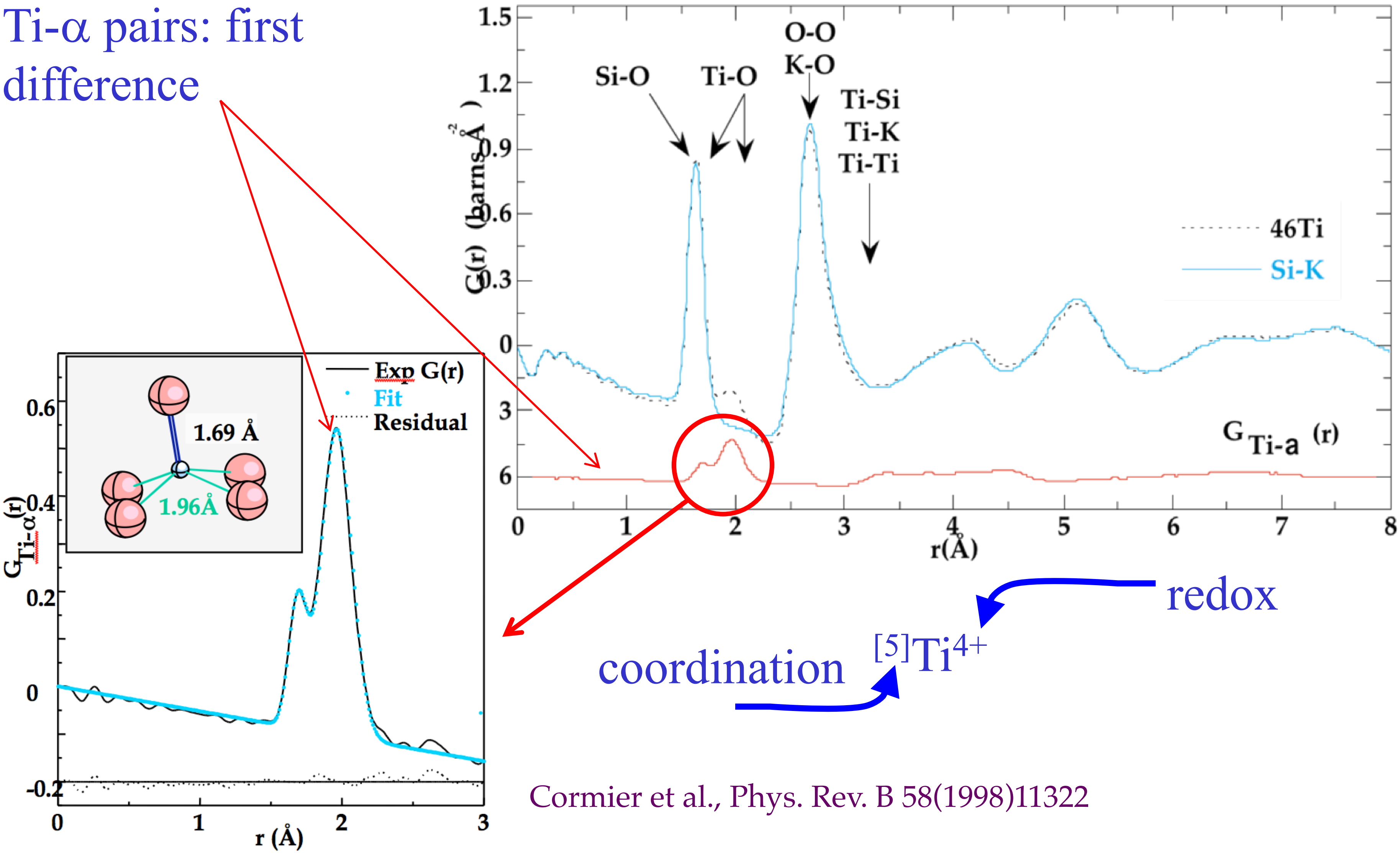




Isotopic substitution (neutron diffraction)

Ti : $TiK_2Si_2O_7$ glass

Ti-α pairs: first difference



redox

coordination $^{[5]}Ti^{4+}$

Cormier et al., Phys. Rev. B 58(1998)11322

Isotopic substitution (neutron diffraction)

Second difference method

M = substituted element

$$\Delta I(Q) = \sum_{a \neq M} 2 c_a c_b b_a \left(b_M - {}^{mix}b_M \right)\left(S_{Ma}(Q) - 1 \right)$$

$$c_M^2 \left(b_M^2 - {}^{mix}b_M^2 \right)\left(S_{MM}(Q) - 1 \right)$$

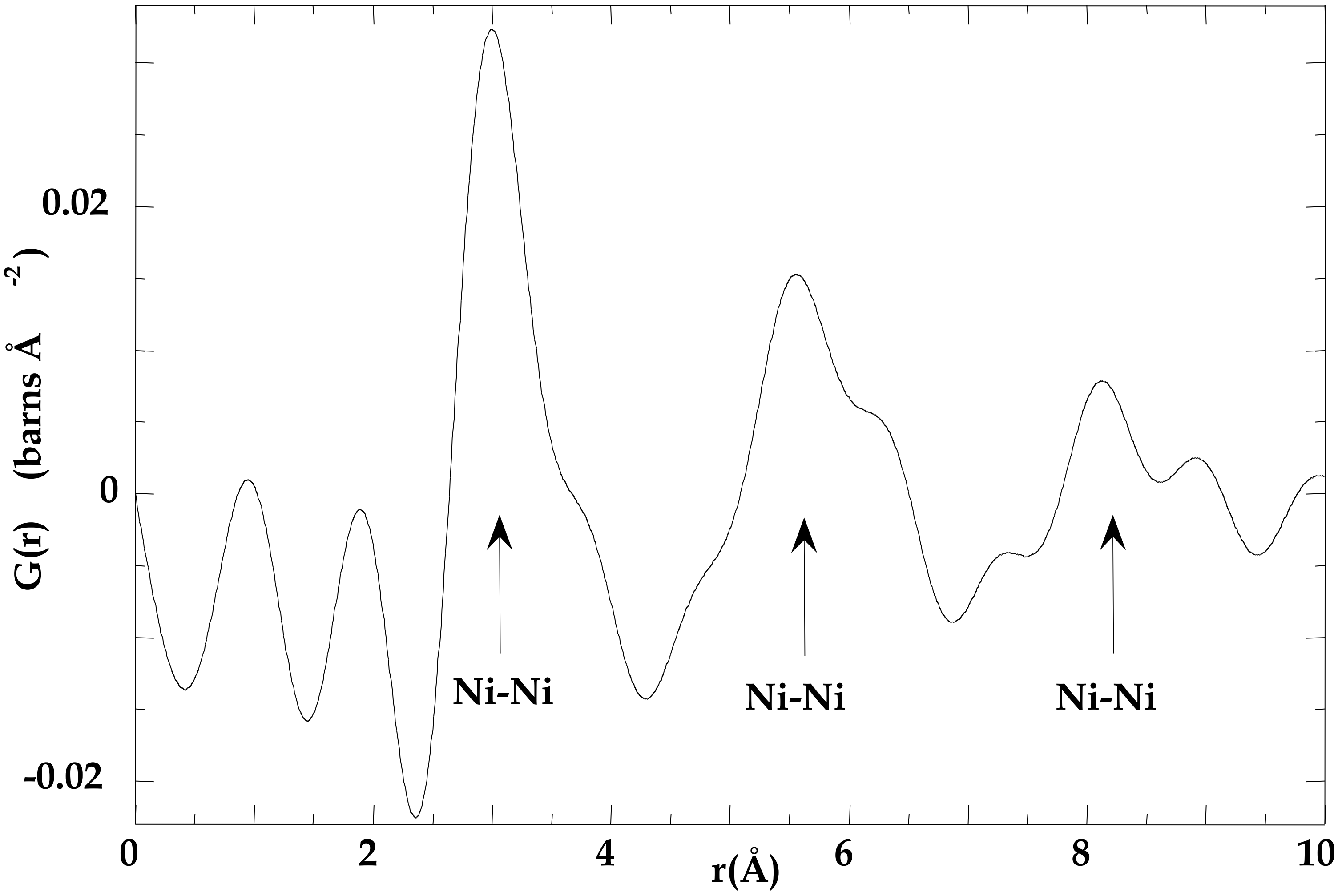
$$\Delta I'(Q) = \sum_{a \neq M} 2 c_a c_b b_a \left({}^{mix}b_M - b'_M \right)\left(S_{Ma}(Q) - 1 \right)$$

$$c_M^2 \left({}^{mix}b_M^2 - b'^2_M \right)\left(S_{MM}(Q) - 1 \right)$$

$$b_M - {}^{mix}b_M = {}^{mix}b_M - b'_M$$

$$\rightarrow \quad 2\Delta\left(\Delta I(Q) \right) = c_M^2 \left[b_M^2 - b'^2_M \right]\left(S_{MM}(Q) - 1 \right)$$

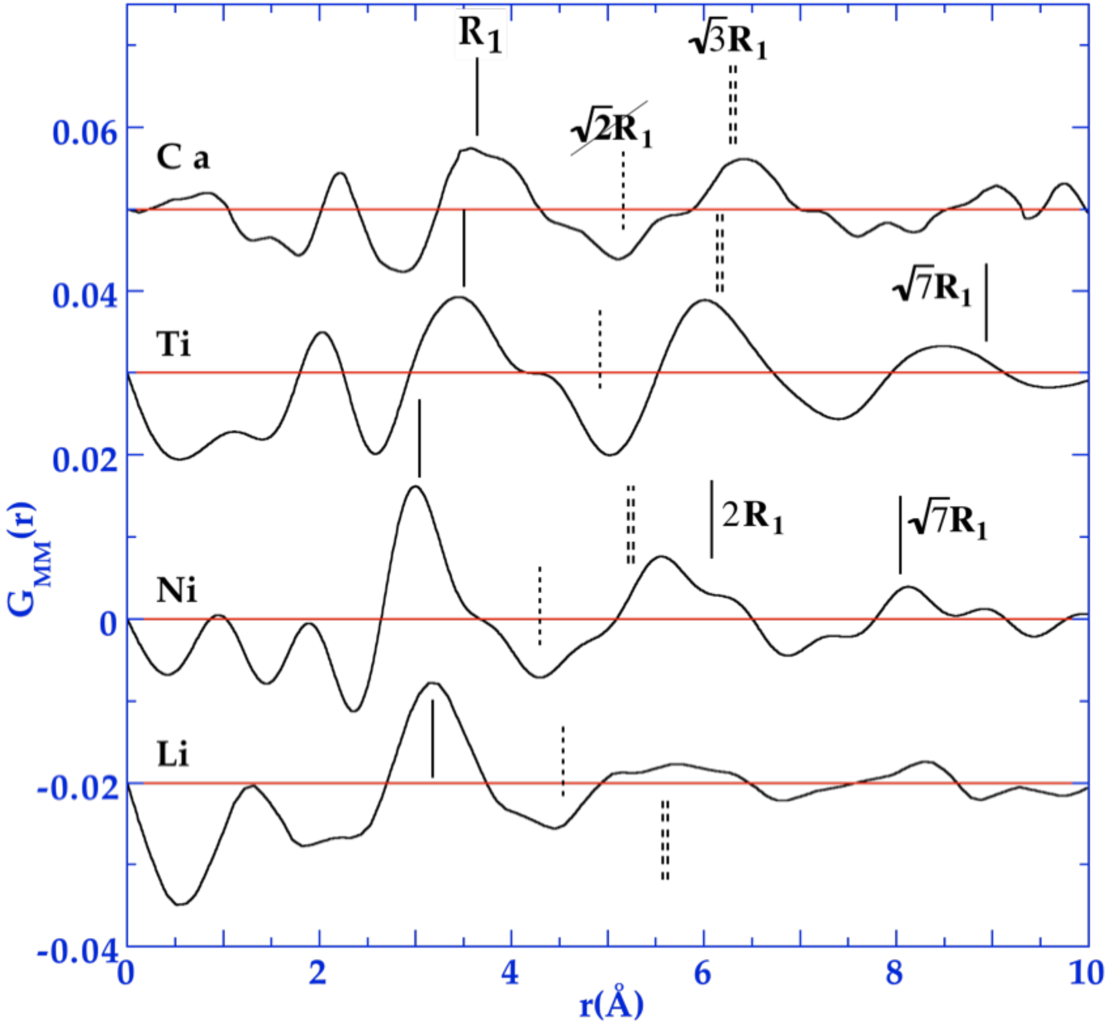
Cormier et al., Chem. Geol. 174, 349 (2001)



Second difference functions for $Ca_2NiSi_3O_9$ =
Ni-Ni distances

Distributionof non-network formers

Second difference functions - cation-cation distribution



Ca : $CaSiO_3$, $CaNiSi_3O_9$

Ti : $TiK_2Si_2O_7$

Ni : $CaNiSi_3O_9$

Li : $Li_2Si_2O_5$

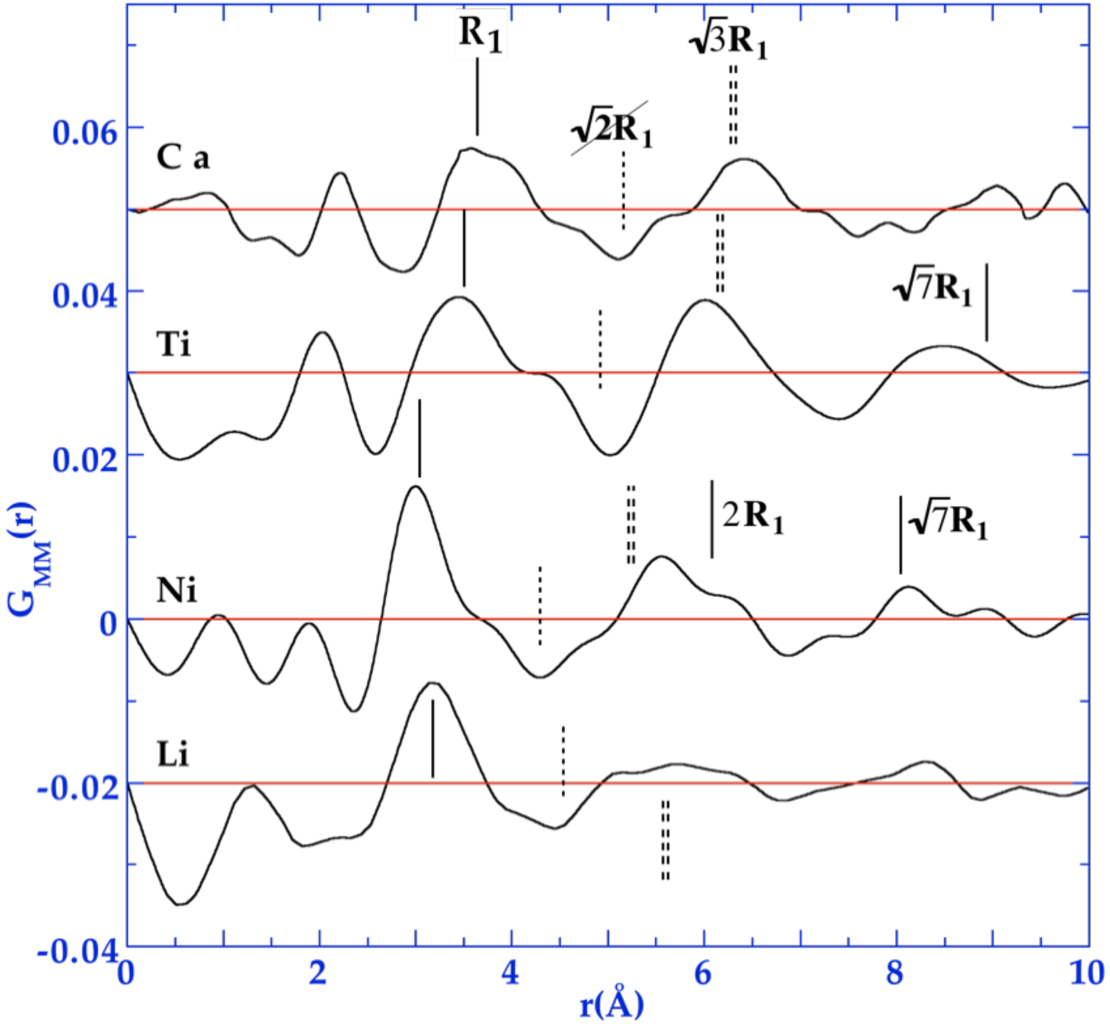
SANDALS at ISIS (UK)

D4 at ILL (Grenoble)

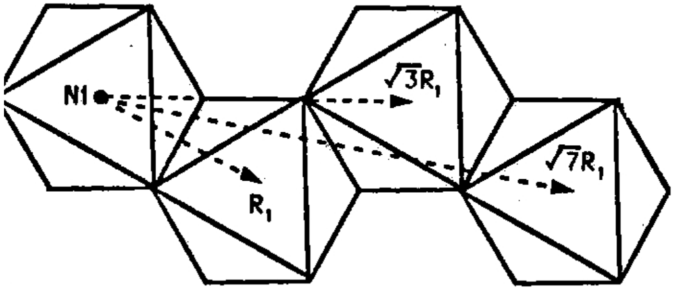
Cormier et al., Chem. Geol., 174 (2001) 349

Distributionof non-network formers

Second difference functions - cation-cation distribution



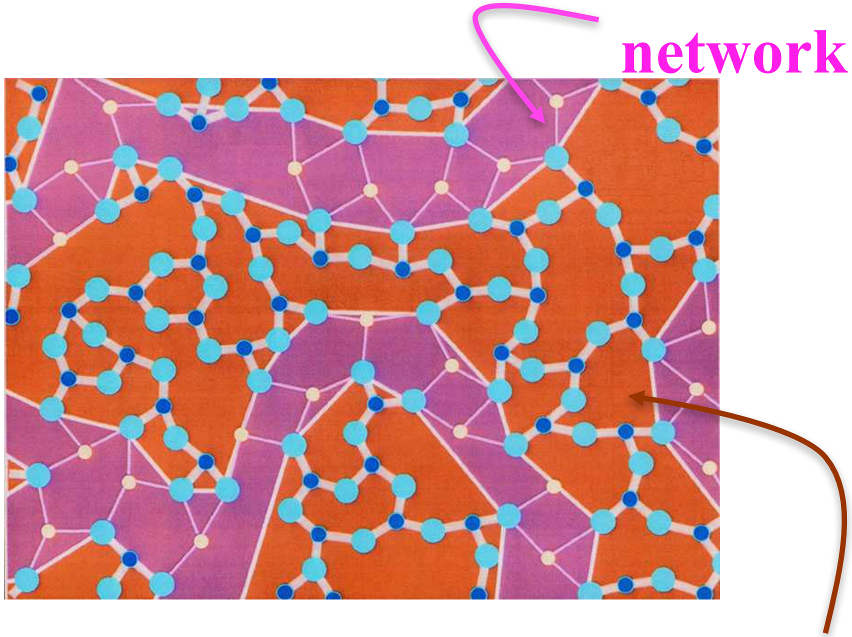
- **R1 short distance**
  Non-homogeneous distribution
- **Second and third neighbours**
  important medium range order
- **Ratio of distances**
  Ordered cationic domains



Cormier et al., Chem. Geol., 174 (2001) 349

Random modified network (Greaves)

Separation regions enriched in network formers and region enriched in network modifiers



Zones enriched with non-network forming cations

Silicate network (or network formers)

Greaves, J. Non-Cryst. Solids 71(1985)203

Anomalous scattering (X-ray diffraction)

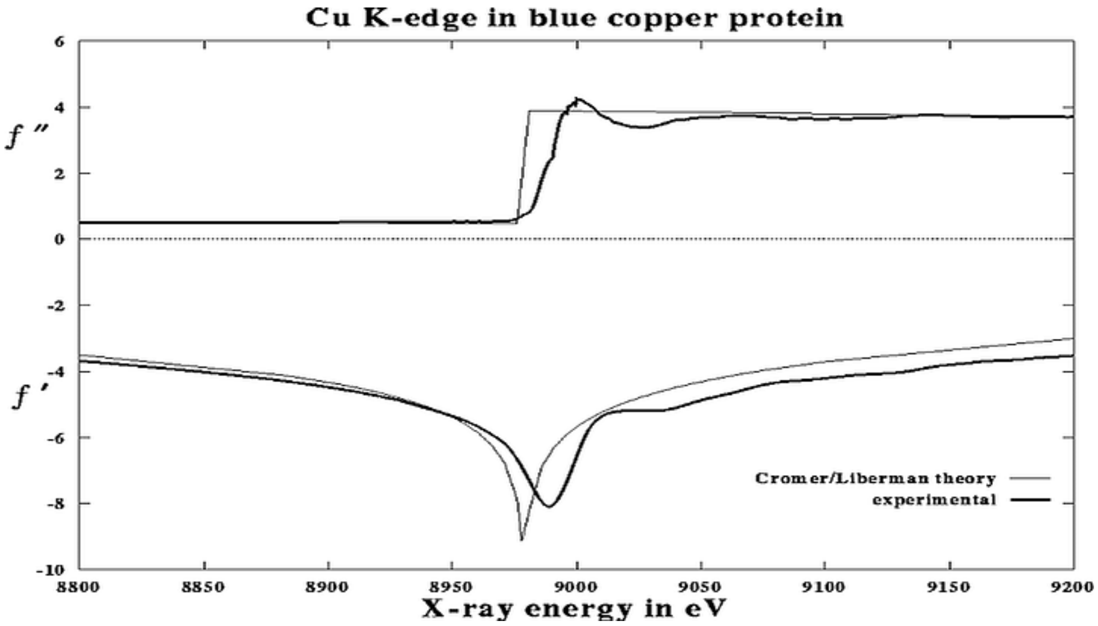
$$S(Q) = \sum_{a,b\geq a} W_{ab}(Q) S_{ab}(Q)$$

$$W_{ab}(Q) = \frac{c_a c_b f_a(Q,E) f_b(Q,E)}{\overline{f(Q,E)}^2}\left(2 - d_{ab}\right)$$

Atomic form factor:

$$f(Q,E) = f_0(Q) + f'(E) + i\ f''(E)$$

f' and f'' strong variation near the absorption edge of a given element

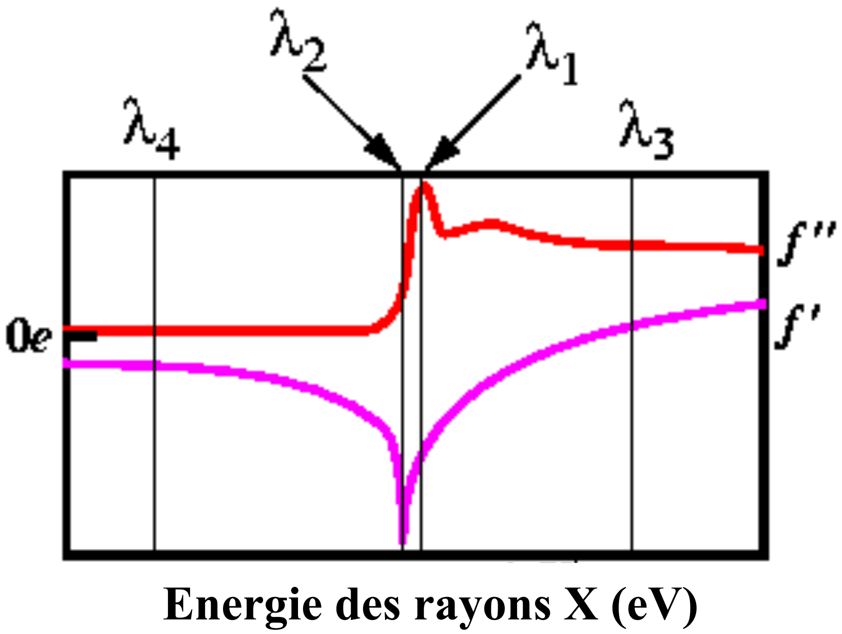

Cu K-edge in blue copper protein

f' and f'' linked by the Kramer-Kronig relation :

$$f'(\omega) = \frac{2}{\pi}\int_0^\infty \frac{\omega' f''(\omega')\partial\omega'}{\omega^2 - \omega'^2}$$

Anomalous scattering (X-ray diffraction)

2 experiments at 2 different energies (different λ):
at the absorption edge (λ1 or λ2)
and far from the edge (λ3)



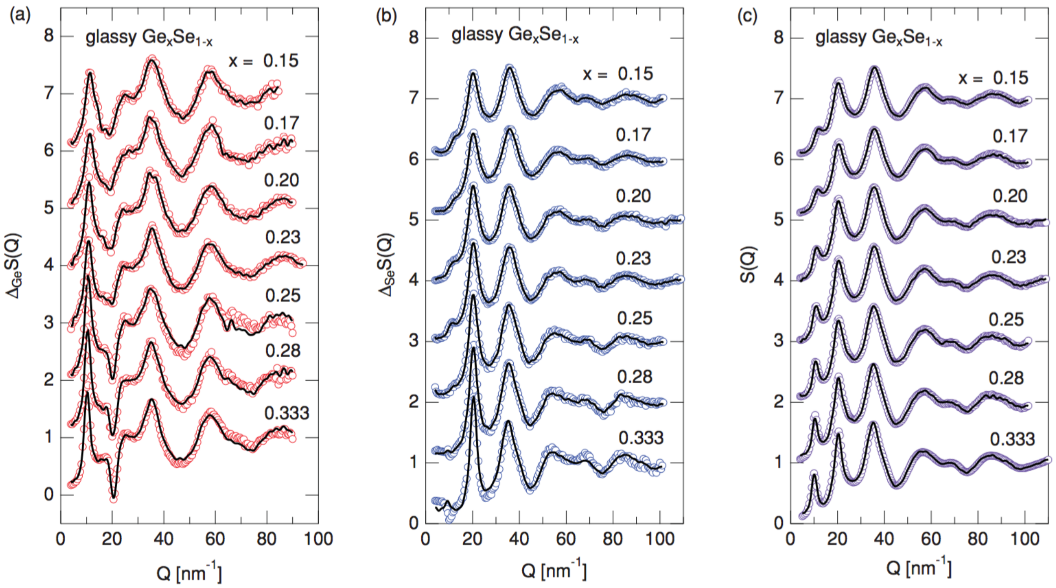
1 sample is needed

⚠ Domain in Q defined by $Q = 4\pi \sin\theta / \lambda$
In practice, only interesting for element above ~Fe otherwise Q-range too small

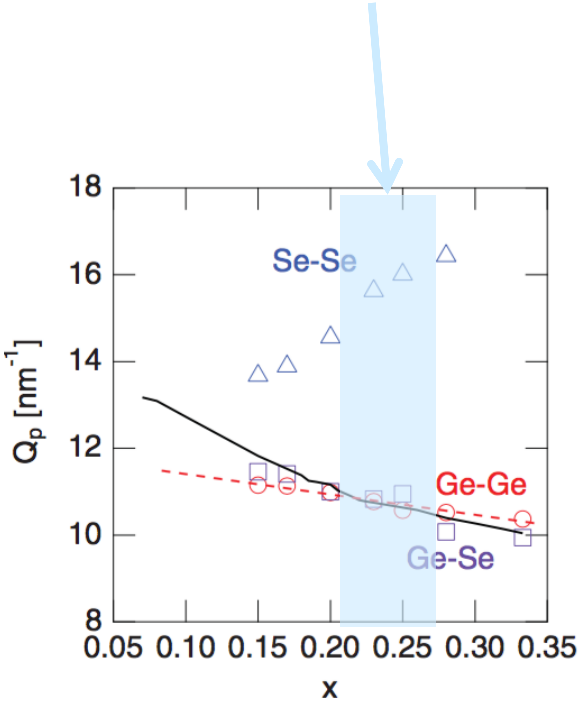
Anomalous scattering (X-ray diffraction)

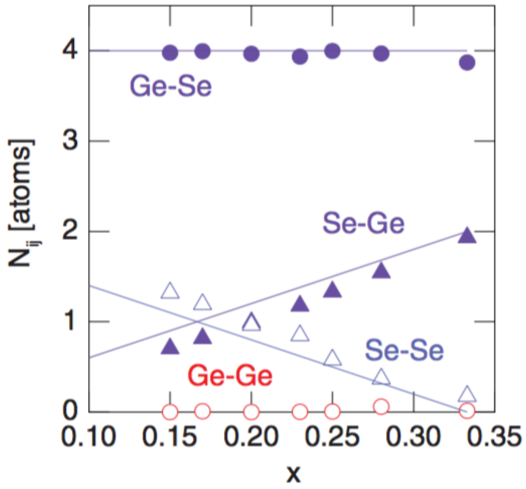
Ge$_x$Se$_{1-x}$

Ge and Se K-edge



Stiffness transition





Short range order

Intermediate range order
More Se6 rings at low x
=>RMC models

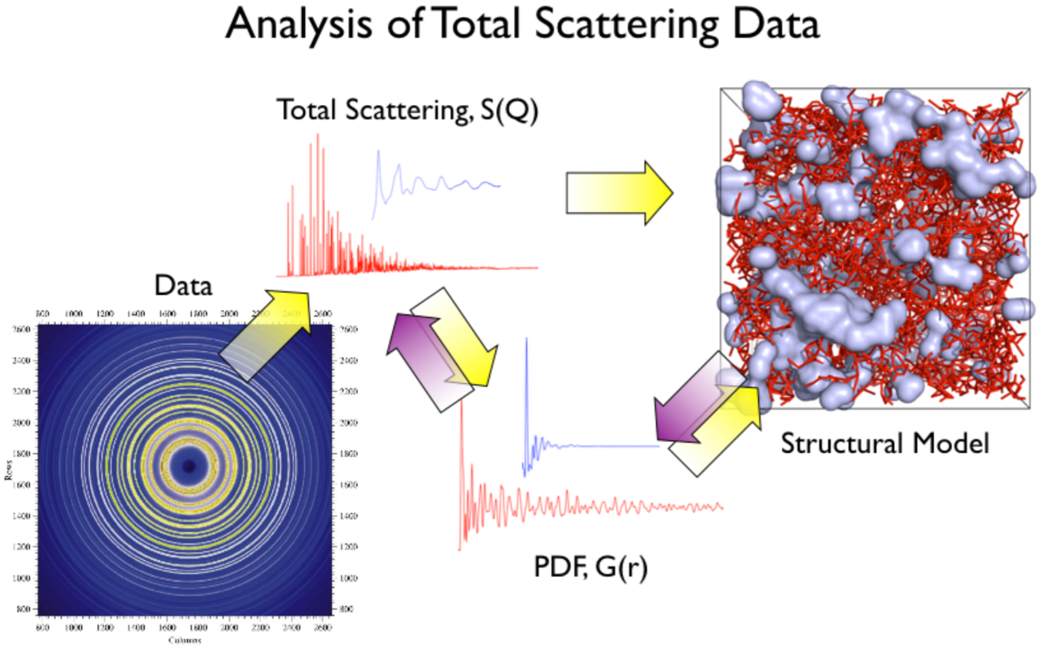
Hosokawa et al., Phys. Rev. B, 84(2011)014201

Summary

Short and medium range order in the same experiments
⇒ structural models can be generated
⇒ or comparison with MD simulations

HP/HT structural transformations

contrast techniques to investigate specific elements



Bibliography

Squires, G. L. *Introduction to the theory of thermal neutron scattering*, Cambridge University Press: Cambridge (1978).

A.C. Wright, *The structure of amorphous solids by x-ray and neutron diffraction*, Advances in Structure Research by Diffraction Methods 5, 1 (1974).

Chieux, P. In *Neutron diffraction*, Dachs, H., Ed., Springer-Verlag: Berlin, (1978).

L. Cormier, *La structure des verres étudiée par diffraction des neutrons*, J. Phys. IV, 111, 187-210 (2003).

H. E. Fischer, A. C. Barnes, P. S. Salmon, *Neutron and x-ray diffraction studies of liquids and glasses*, Reports on Progress in Physics 69, 233-299 (2006).

X-ray diffraction source

Laboratory diffractometer

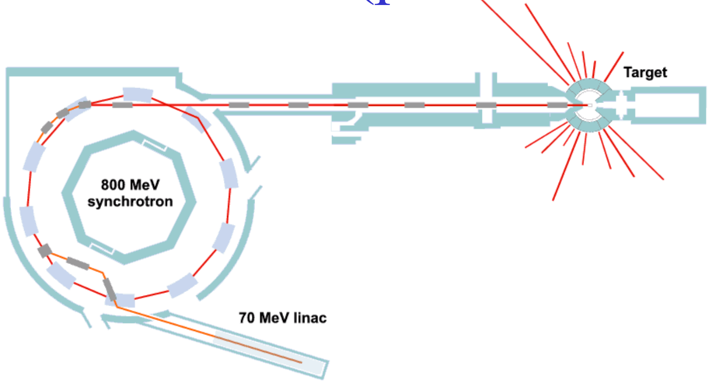
Ex: Empyrean Panalytical
(IMPMC, Paris)
Source: Ag λ=0.56 Å
Q-range: 0.5-21.5 $Å^{-1}$

Synchrotron

Ex: ESRF (Grenoble)
Diffraction, anomalous scattering, temperature, pressure etc …
Q range up to 50 $Å^{-1}$

Neutron diffraction

Spallation source (pulsed source)



Ex: ISIS (UK), ESS (Sweden, 2020?)

Nuclear reactor

Ex: LLB (France), ILL (Grenoble, european source)
7C2 diffractomter at LLB