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## Neutron and X-Ray Diffraction of Glass

Laurent Cormier

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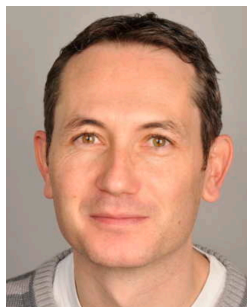
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# Neutron and x-ray diffraction

*Laurent Cormier*

## Author portrait Laurent CORMIER



Laurent Cormier obtained his PhD from the University Pierre and Marie Curie – Paris 6 (France) in 1997 and worked at the Cavendish Laboratory, Cambridge University (UK). He enters at CNRS in 1999. His research focuses on understanding the glass structure at short and medium range order in relation with transport, nucleation and crystallization properties, using experimental and modelling techniques. He received the Gottardi prize by the ICG.

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## **Abstract**

A basic characterization of amorphous materials is usually obtained using diffraction measurements. Indeed, amorphicity is revealed by the absence of sharp Bragg peaks in the angular diffraction pattern, signaling the lack of long-range order and periodicity. However, diffraction patterns obtained by scattering from x-rays, electrons or neutrons contain much more structural information, often overlooked, about the atomic organization of disordered materials. x-ray and neutron diffraction are pioneering tools to get information on the atomic arrangements of non-crystalline materials and, still the earlier x-ray diffraction investigations [1][2][3], are still routinely used structural experimental techniques.

The success of diffraction methods is partly due to the fact that they give the most direct access to the atomic structure; in particular interatomic distances and coordination numbers, and diffraction data can be easily compared to simulations, which is widely used to validate interatomic potentials in Molecular Dynamics. Another advantage of this technique is to probe both the short and intermediate range order, being very sensitive to the nature and extent of disorder in glasses and liquids and an essential probe to understand the structural differences between glasses and their crystalline counterparts. Finally, various environments have been developed allowing high temperature and/or high pressure measurements to be carried out.

## **1. Diffraction by non-crystalline materials**

### **1.1 Scattering of neutrons and x-ray**

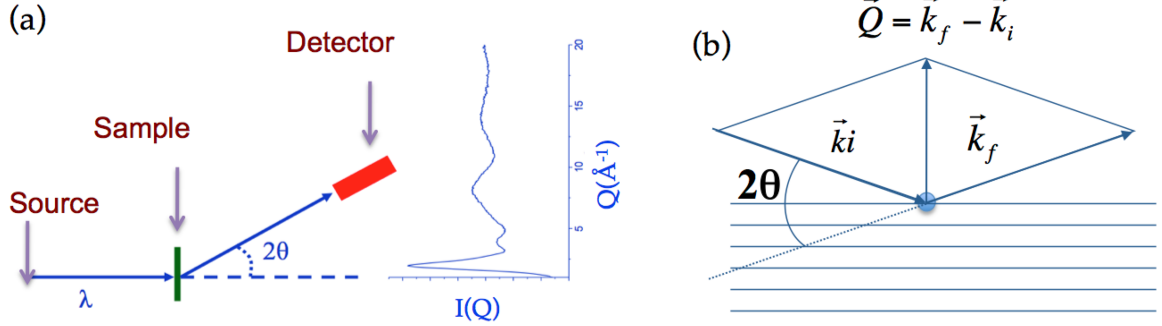
The fundamental aspects of the scattering processes have been completely described elsewhere [4][5][6][7] and we will propose only a brief outline of the theory.

In a conventional diffraction experiments (figure 1.a), the quantity measured by the detector into the small solid angle  $d\Omega$  at the scattering angle  $2\theta$  is the *differential cross section*  $d\sigma/d\Omega$  (in barns/steradian), defined as:

$$\frac{1}{N} \frac{d\sigma}{d\Omega} = \frac{\text{number of quanta of wavelength } \lambda \text{ scattered per unit time into } d\Omega}{N\Phi(\lambda)d\Omega} = I(Q) \quad (1)$$

with  $N$  the number of scattering units in the sample and  $\Phi(\lambda)$  the incident flux of quanta at wavelength  $\lambda$ .  $Q$  (in  $\text{\AA}^{-1}$ ) is the magnitude of the *scattering vector* (figure 1.b) for an elastic scattering, *i.e.*  $k_i = k_f$  (or in the static approximation,  $k_i \approx k_f$ , see below):

$$Q = \frac{4\pi \sin \theta}{\lambda} \quad (2).$$



**Figure 1:** (a) Conventional setup for a diffraction experiment. A monochromator can be placed between the source and sample, which is the case for synchrotrons or steady state reactors. To obtain true elastic scattering, a monochromator should also be placed between the sample and the detector. (b) Scattering from a single atom by an incoming radiation with wavevector  $\vec{k}_i$  of magnitude  $2\pi/\lambda$ , and a scattered wavevector  $\vec{k}_f$ .

The differential cross-section may be separated as a 'distinct' term and a 'self' term [8]:

$$I(Q) = F(Q) + \sum_{\alpha} c_{\alpha} \overline{b_{\alpha}^2} \quad (3)$$

with  $F(Q)$  the *total interference function*,  $c_{\alpha}$  and  $b_{\alpha}$  are the atomic concentration and scattering length of the chemical species  $\alpha$ , respectively. The *neutron scattering length*,  $b$ , measured the strength of the interaction between the neutron and the nucleus, can be positive or negative and is expressed in fm ( $10^{-15}$  m). All the structural information is contained in the interference function that is simply related to a *structure factor*  $S(Q)$  by the relation:

$$S(Q) = \frac{F(Q)}{\left(\sum_{\alpha} c_{\alpha} b_{\alpha}\right)^2} + 1 = \frac{F(Q)}{\overline{b}^2} + 1 \quad (4)$$

with  $S(Q \rightarrow \infty) = 1$  and  $S(Q) \geq 0$ .

The Fourier transform of the structure factor gives a *pair distribution (correlation) function*,  $g(r)$ , describing interatomic interactions in real space [5]:

$$g(r) - 1 = \frac{1}{2\pi^2 r \rho_0} \int_0^{\infty} Q(S(Q) - 1) \sin(Qr) dQ \quad (5)$$

where  $r$  is the interatomic distance,  $\rho_0$  (atoms  $\text{\AA}^{-3}$ ) is the *atomic number density* expressed as a function of the macroscopic density,  $d$  ( $\text{g cm}^{-3}$ ):



$$\rho_0 = \frac{N_A d}{A 10^{24}} \quad (6)$$

$N_A$  being the Avogadro number and  $A$  the atomic weight of the sample.

## 1.2 The static approximation

In a diffraction experiment, the x-ray or neutron is usually detected without a monochromator being placed between the sample and the detector. In such a case, the experiment is not exactly elastic (as it would be if  $k_i = k_f$  in figure 1.b) and energy exchange could occur within the sample due to interactions of neutrons or x-ray photons with thermal vibrations. The static approximation consider that such energy transfers is negligible compared to the incident energy ( $k_i \approx k_f$ ). This approximation works well for x-ray diffraction due to the energy of the incident photon but is not a valid assumption for neutron diffraction so that, in practice, inelasticity corrections have to be taken into account [9][8]. This approximation allows a decoupling between structural and dynamical information [5].

The static approximation considers that the energy exchange  $\hbar\omega$  is small compared to the incident energy  $E_0$ . The  $\hbar\omega$  energy corresponds a characteristic time,  $\tau$ , so that the condition  $\hbar\omega \ll E_0$  corresponds to the condition  $\tau \ll t_0$ , with  $t_0$  the time characteristic for vibrations or relaxations [6]. It implies that the time taken by the neutron (or x-ray photon) to pass from one atom to the next is small compared to an atomic motion. Therefore, a scattering event probes only the static structure of the specimen giving an instantaneous 'snapshot' of the structure. A neutron or x-ray elastic diffraction measurement consists in time-averaging snapshots taken by each incident neutron or x-ray photon.

## 1.3 The Faber-Ziman formalism

For polyatomic materials, the total structure factor is a weighted sum of all *partial structure factors*  $S_{\alpha\beta}(Q)$  in the Faber-Ziman formalism [10]:

$$S(Q) = \sum_{\alpha,\beta} W_{\alpha\beta} S_{\alpha\beta}(Q) \quad (7)$$

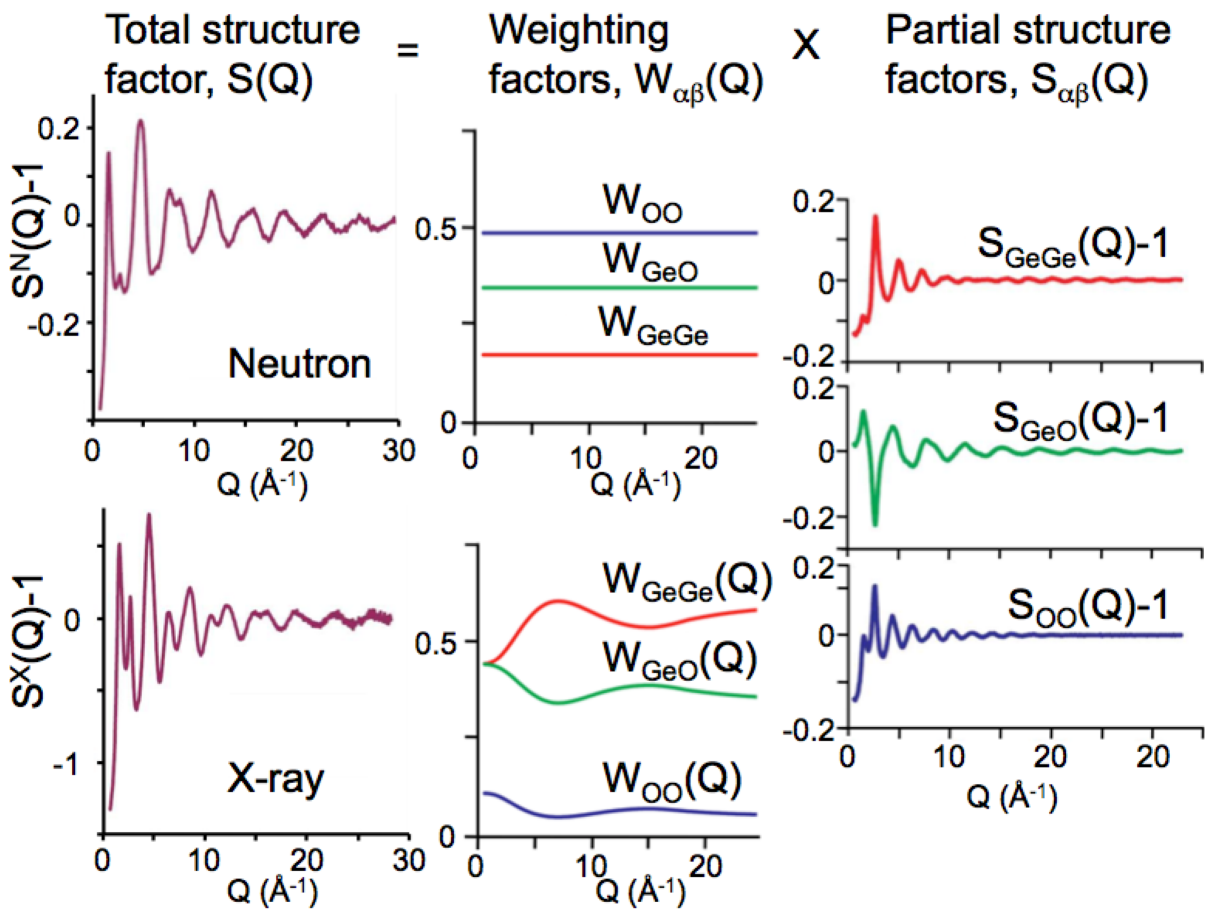
where  $W_{\alpha\beta}$  are the weighting factors and  $S_{\alpha\beta}(Q \rightarrow \infty) = 1$ . The partial structure factors are identical for x-ray and neutron since they only depend on the structure. On the contrary, the weighting factors are independent of the structure but are different when considering diffraction by x-ray photons or neutrons. As a result, the total structure factors,  $S(Q)$ , have significant differences in peak positions and intensities between the two diffraction methods (figure 2).

At this point, it is necessary to distinguish the diffraction process between x-ray and neutron. For x-rays, the quantity equivalent to the neutron scattering length is the *atomic form factor*,  $f(Q,E)$ , which is dependent on both the energy of the incident photon and  $Q$ .  $f(Q,E)$  correspond to the scattering by the electron cloud (while the neutron scattering length  $b$  indicates scattering by the nucleus) and its amplitude increases with atomic number  $Z$  (while  $b$  can be considered usually as a constant).  $b$  and  $f$  are tabulated in references [11][12][13][14]. Due to the  $Q$ -dependence of the form factors, the expression for the weighting factors is slightly different:

$$W_{\alpha\beta}^{neutron} = \frac{c_{\alpha}c_{\beta}b_{\alpha}b_{\beta}(2 - \delta_{\alpha\beta})}{\left(\sum_{\alpha}c_{\alpha}b_{\alpha}\right)^2} \tag{8}$$

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

where the Kronecker delta ( $\delta_{\alpha\beta}$ ) takes into account that  $S_{\alpha\beta}(Q) = S_{\beta\alpha}(Q)$ .



**Figure 2:** (right) For  $\text{GeO}_2$  glass, the three partial functions  $S_{\alpha\beta}(Q)$  contain the structural information. (middle) Each partial structure factor can be multiplied by their respective neutron weighting factors (top) which are constant or by their respective x-ray weighting factors (bottom) which are  $Q$  dependent. (left) The sum of all  $S_{\alpha\beta}(Q)$  multiplied by their weighting factors give the total structure factor for neutron (top) or x-ray (bottom). Due to the different weighting factors, the total structure factors are different, though the structural information (contained in the  $S_{\alpha\beta}(Q)$  functions) is the same. The figure is adapted from [15].

In the case of the neutron, the Fourier transform in equation (5) is straightforward while, for x-rays, it is the Fourier transform of a product of two functions that gives in real space the convolution of the Fourier transforms of each function:

$$\begin{aligned} g^{neutron}(r) &= \sum_{\alpha,\beta} W_{\alpha\beta}^{neutron} g_{\alpha\beta}(r) \\ g^{X-ray}(r) &= FT\left(W_{\alpha\beta}^{X-ray}\right) \otimes g_{\alpha\beta}(r) \end{aligned} \quad (9).$$

where  $\otimes$  is the convolution sign between two functions. To avoid the complex definition of  $g^{X-ray}(r)$ , the weighting factors can be simplified:

$$W_{\alpha\beta}^{X-ray} = \frac{c_{\alpha}c_{\beta}K_{\alpha}K_{\beta}(2-\delta_{\alpha\beta})}{(\sum_{\alpha}c_{\alpha}K_{\alpha})^2} \quad (10)$$

with  $K_{\alpha}$  the effective number of electrons for species  $\alpha$ . With this simplification, the weighting factor is a constant and the pair distribution function has a simpler formulation  $g^{X-ray}(r) = \sum_{\alpha,\beta} W_{\alpha\beta}^{X-ray} g_{\alpha\beta}(r)$ .

The *partial pair distribution function*,  $g_{\alpha\beta}(r)$ , gives the probability of finding an atom of type  $\beta$  at distance  $r$  from an atom of type  $\alpha$  taken at the origin (average distribution of atoms  $\beta$  around an atom  $\alpha$  at the origin) and vice-versa since  $g_{\alpha\beta}(r) = g_{\beta\alpha}(r)$ .

For a system with  $n$  components, there are  $n(n+1)/2$  independent partial structure factors (or partial pair distribution functions, PPDFs). A detailed understanding of the structure requires the complete determination of the set of partial structure factors (or PPDFs) that describe the environment of each atomic species.

#### 1.4 The Bathia-Thornton formalism

An alternative formalism for the partial structure factors has been proposed by Bhatia and Thornton for a binary system based on the local density and concentration [16]. These partial functions correspond to the density fluctuations (topological contribution),  $S_{NN}(Q)$ , the concentration fluctuations (chemical contribution),  $S_{CC}(Q)$ , and the correlations between the two,  $S_{NC}(Q)$ :

$$S(Q) = S_{NN}(Q) + 2 \frac{\Delta b}{\langle b \rangle} S_{NC}(Q) + \left( \frac{\Delta b}{\langle b \rangle} \right)^2 S_{CC}(Q) \quad (11)$$

where  $\langle b \rangle = c_\alpha b_\alpha + c_\beta b_\beta$  and  $\Delta b = |b_\alpha - b_\beta|$ .

These functions are related to the Faber-Ziman partial ones by simple linear combinations, but they emphasize different aspects of the atomic structure as they separate information on the topological order ( $S_{NN}(Q)$ ) from information on the chemical order ( $S_{CC}(Q)$ ):

$$\begin{aligned} S_{NN}(Q) &= c_\alpha^2 S_{\alpha\alpha}(Q) + 2c_\alpha c_\beta S_{\alpha\beta}(Q) + c_\beta^2 S_{\beta\beta}(Q) \\ S_{NC}(Q) &= c_\alpha c_\beta \left[ c_\alpha S_{\alpha\alpha}(Q) - (c_\alpha - c_\beta) S_{\alpha\beta}(Q) - c_\beta S_{\beta\beta}(Q) \right] \\ S_{CC}(Q) &= c_\alpha c_\beta \left[ c_\alpha c_\beta \left\{ S_{\alpha\alpha}(Q) + S_{\beta\beta}(Q) - 2S_{\alpha\beta}(Q) \right\} + 1 \right] \end{aligned} \quad (12).$$

Their use is limited, as restricted to binary materials, but several examples can be founded in Salmon's works [17][18][19].

### 1.5 The Debye equation

For a set of  $N$  identical atoms in an isotropic specimen, Debye has shown that the structure factor can be simplified as [20]:

$$S(Q) = 1 + \frac{1}{N} \sum_{\alpha=1}^N \sum_{\beta \neq \alpha}^N \frac{\sin Q r_{\alpha\beta}}{Q r_{\alpha\beta}} \quad (13).$$

Each characteristic interatomic distance  $r_{\alpha\beta}$  in the sample corresponds in  $S(Q)$  to a damped sine wave of period  $\Delta Q = 2\pi / r_{\alpha\beta}$ . Long period fluctuations in Q-space give rise to short range distances and vice-versa [21].

### 1.6 Real space functions

Different functions (figure 3) can be used in real space which are all related to the pair distribution function  $g(r)$ , describing the local fluctuations in density around the unit:

$$g(r) = \frac{\rho(r)}{\rho_0} \quad (14)$$

where  $\rho(r)$  is the  $r$ -dependent atomic density ( $g(r \rightarrow \infty) = 1$  and  $g(r \rightarrow 0) = 0$ ), defining the number of atoms within a sphere or radius  $r$  [21]. For a polyatomic specimen, the partial pair distribution function  $g_{\alpha\beta}(r)$  is the number of atoms of type  $\beta$  between distances  $r$  and  $r + dr$  from an atom  $\alpha$ :

$$g_{\alpha\beta}(r) = \frac{n_{\alpha\beta}(r)}{c_{\beta}\rho_0 4\pi r^2 dr} \quad (15).$$

Another commonly used function is the *differential (or reduced) correlation function*  $D(r)$  ( $D(r \rightarrow \infty) = 0$ ):

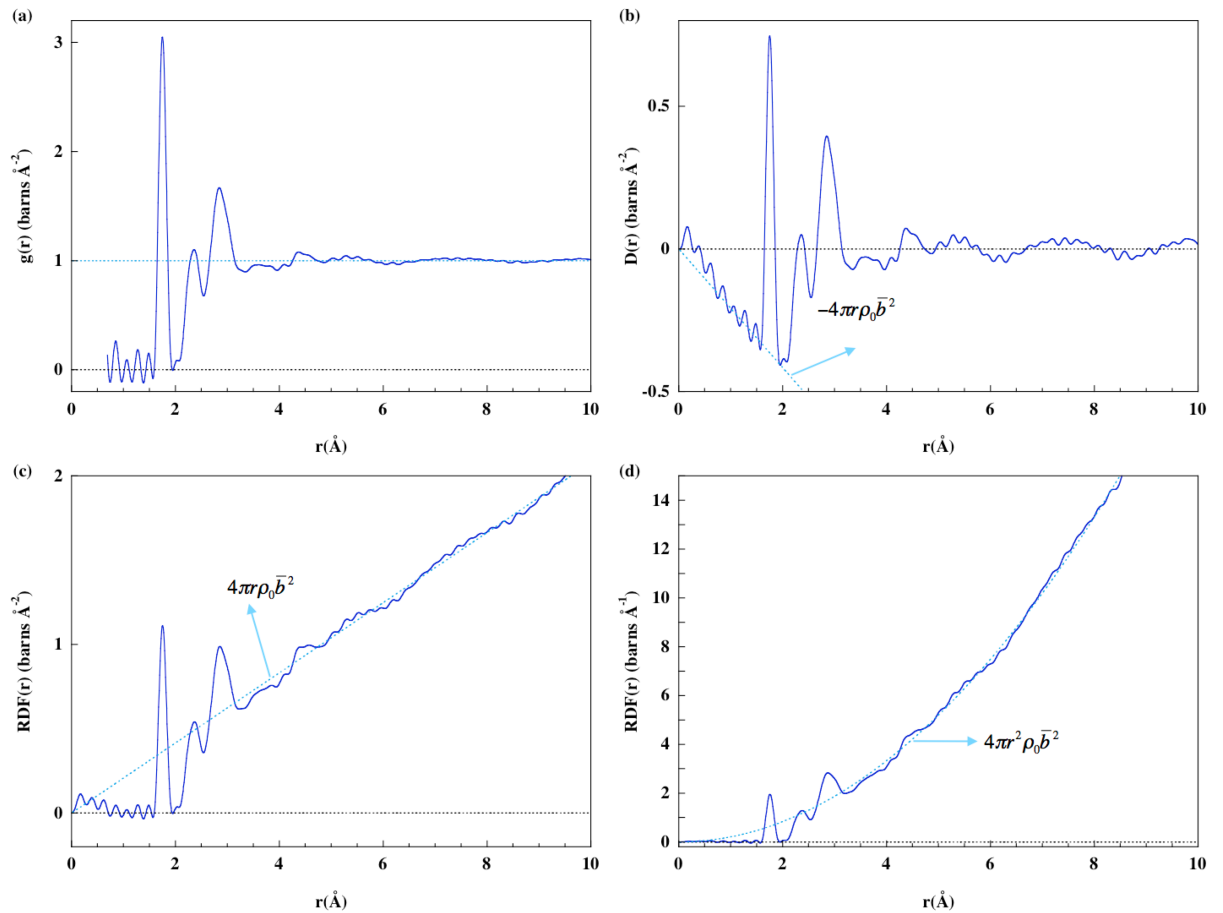
$$D(r) = 4\pi r \bar{b}^2 \rho_0 [g(r) - 1] \quad (16).$$

In this function, only deviations from the average atomic density  $\rho_0$  are considered.

The (total) *radial distribution function*  $RDF(r)$  or the *total distribution function*  $T(r)$  are also used:

$$\begin{aligned} RDF(r) &= 4\pi r^2 \bar{b}^2 \rho_0 g(r) \\ T(r) &= RDF(r)/r = 4\pi r \bar{b}^2 \rho_0 g(r) \end{aligned} \quad (17).$$

An excellent account of these different definitions is given by Keen [22].



**Figure 3:** Relation between the different real space functions (see text) for a 61CaO-39Al<sub>2</sub>O<sub>3</sub> glass [23]: (a) the pair distribution function,  $g(r)$ ; (b) the differential correlation function  $D(r)$ ; (c) the total distribution function  $T(r)$ ; (d) the radial distribution function  $RDF(r)$ .

## 1.7 Fourier transformation

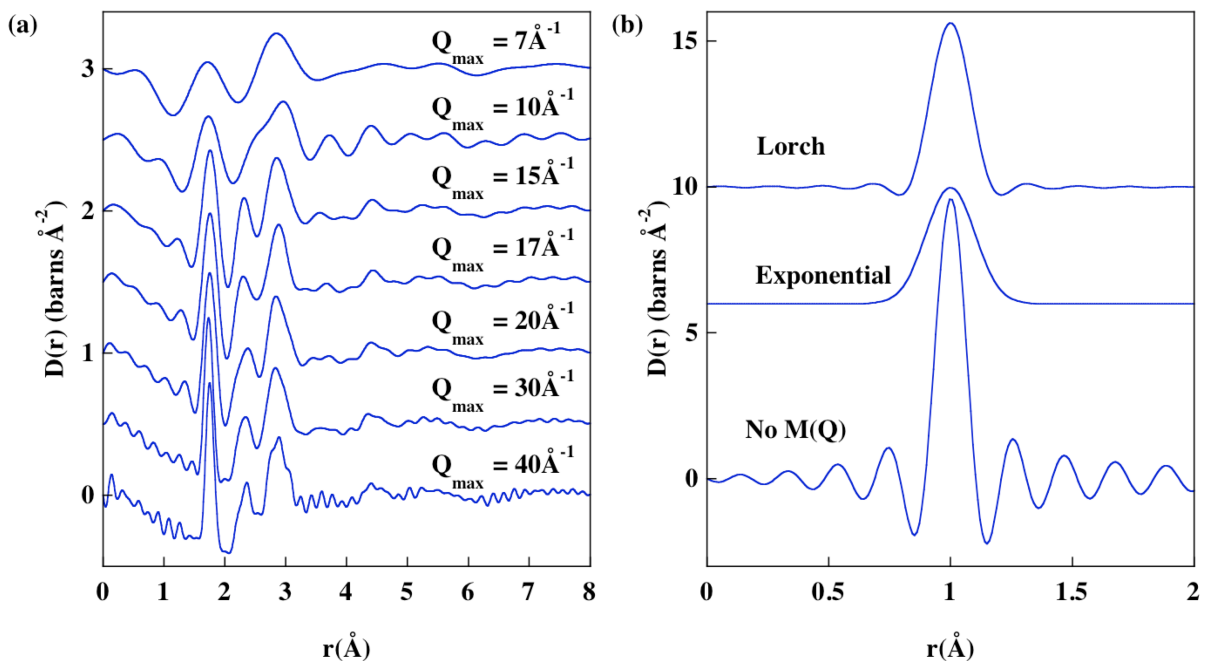
### 1.7.1 Effect of Q range

As shown in figure 4.a, access to high-Q values (*i.e.* high  $Q_{max}$ ) is required to achieve high real space resolution. With a small  $Q_{max}$  value, the dramatic peak broadening results in an overlapping of atom-atom contributions. A high  $Q_{max}$  value allows us to resolve two close interatomic distances.

The Q-range accessible experimentally is determined by equation (2). The values of  $\theta$  are restricted to  $2\theta = \pi$  in a scattering measurement. The possibility to increase the Q-range is thus achieved essentially by using high incident energy (short incident wavelength  $\lambda$ ) either from synchrotron sources for x-rays or from spallation sources for neutrons.

An example is provided by Petkov *et al.* that used high energy x-ray diffraction (HE-XRD) with  $Q_{max} = 40 \text{ \AA}^{-1}$  in aluminosilicate glasses [24]. The Si-O and Al-O distances, only separated by  $0.15 \text{ \AA}$ , can be clearly differentiated. Using a neutron spallation source, similar  $Q_{max}$  values can be reached. With such diffraction experiment, the two P-O distances existing within a  $\text{PO}_4$  tetrahedra can be resolved [25]. The two P-O components at  $1.43 \text{ \AA}$  and  $1.58 \text{ \AA}$  correspond to the terminal and to the bridging oxygen atoms, respectively.

Finally, we should note that increasing the upper-Q limit increases the noise in real space so that sufficient counting statistics at large-Q values is needed, which increases the time for measurement.



**Figure 4:** (a) Example showing how the  $Q_{max}$  limit in the Fourier transform of the structure factor affects the resolution in real space for a  $61CaO-39Al_2O_3$  glass [23]. (b) Influence of the data truncation without modification function and with two modification functions (exponential and Lorch).

### 1.7.2 Effect of truncation

The data accessible in diffraction experiments are limited in  $Q$ :  $Q_{min} \leq Q \leq Q_{max}$ . The  $Q_{min}$  limit does not affect the Fourier transform since low values can be access experimentally and since the structure factor is multiplied by  $Q$  in the Fourier-sine transform. However, the fact that the Fourier transform cannot be integrated to infinite  $Q$  results in the appearance of peak broadening and parasitic lobes around the peaks in  $D(r)$ , particularly at low  $r$  values. This truncation of the upper- $Q$  limit is equivalent to multiplying the interference function  $F(Q) = Q(S(Q) - 1)$  by a modified  $M(Q)$  function:

$$D(r) = \frac{2}{\pi} \int_0^{\infty} M(Q)F(Q)\sin(rQ)dQ \quad (18)$$

$$\text{with } M(Q) \begin{cases} = 1 & \text{when } Q \leq Q_{max} \\ = 0 & \text{when } Q > Q_{max} \end{cases} .$$

The introduction of  $M(Q)$  is equivalent to a convolution of the correlation function with a peak shape function,  $P(r)$ , which is the cosine transform of  $M(Q)$  [26]:

$$D(r) = \int_0^{\infty} D(r)P(r-u)du \quad (19)$$

$$\text{with } P(r) = \frac{2}{\pi} \int_0^{\infty} M(Q)\cos(rQ)dQ .$$

If  $M(Q)$  is a step function,  $P(r)$  is a SINC function, giving important termination ripples. The effect of truncation can be partly suppressed by using different  $M(Q)$  functions damping the data cut-off at  $Q_{max}$ . This effect is illustrated in figure 4.b.

The primary modification function is a Lorch function [27]:

$$M(Q) \begin{cases} = \frac{\sin(\Delta r Q)}{\Delta r Q} & \text{when } Q \leq Q_{max} \\ = 0 & \text{when } Q > Q_{max} \end{cases} \quad (20)$$

with  $\Delta r = \pi / Q_{max}$ , corresponding to a resolution length in real space.

These smoothly decaying functions reduce unphysical oscillations, but at the expense of further broadening of the peaks in  $D(r)$ . More sophisticated functions using  $r$ -dependent real space broadening were recently proposed in order to minimize the broadening near the first peak [28][29].

The  $Q$  resolution of the instrument adds another exponential dampening effect to the real space information [30]. This has no effect at short  $r$  distance but prevent extraction of pair correlation information beyond  $\sim 50 \text{ \AA}$  [31]. For glasses and liquids, structural fluctuations are not discernible at large  $r$  (isotropic medium) and the atomic density  $\rho(r)$  tends to  $\rho_0$  at large  $r$  so that integration can be truncated safely at  $r \geq 2 \text{ nm}$ .

## 1.8 Data processing

The purpose of a diffraction experiment is to measure  $I(Q)$  and makes all the necessary corrections to extract  $S(Q)$ . The data treatment has been described in numerous papers for neutron [4][32][7] or x-rays [7][4][28][33]. Absolute intensities can be determined for neutrons thanks to the measurement of standard references with known scattering cross-section, such as vanadium. However, for materials with a high inelasticity or major absorption corrections (for example, Li or H), care is necessary in the analysis of neutron diffraction data. The normalization is not straightforward for x-rays and can lead to uncertainties in the determination of the coordination numbers. All sources have adequate codes to correct the data and we could cite mainly *GUDRUN* for neutron spallation sources [34], *CORRECT* for steady-state neutron reactors [35], *GUDRUNX* [28] or *PDFgetX3* [36] for x-ray sources.

Once  $S(Q)$  is correctly obtained, the Fourier transformation allows us to obtain real space information.

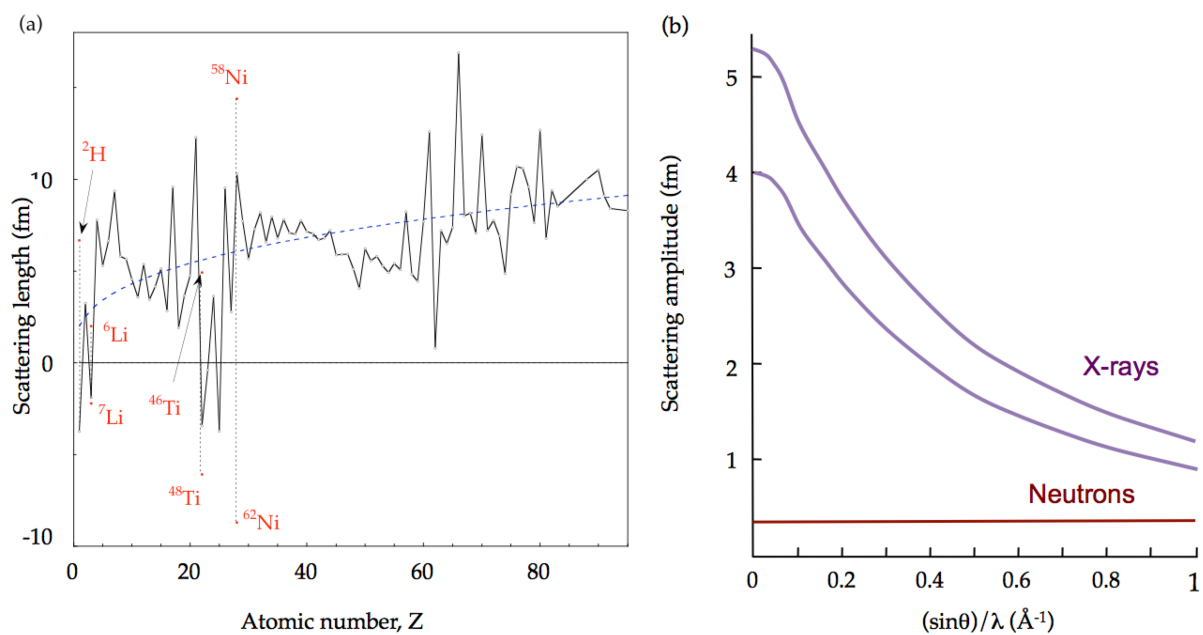
## 2. Complementarity of Neutron and x-ray

Neutron and x-ray diffraction techniques are often associated to provide additional information on the structure of disordered materials (Table 1). These two methods allow access to wide  $Q$ -range domains and thus offer a good resolution of bond lengths and numbers of first neighbors. Neutron diffraction has significant differences with x-ray diffraction [7]. While an x-ray photon is scattered by the atomic electron density, the uncharged neutron interacts directly with the (small) atomic nucleus. As a result, neutrons can be used to study the structural position of light elements such as H or Li and are thus well suited to study aqueous solutions, glassy ices or glass electrolytes for solid-state batteries. Conversely x-ray diffraction is sensitive to high- $Z$  elements. These two techniques are thus complementary because they are sensitive to different elements (figure 2).

Neutron scattering lengths exhibit a non-monotonous evolution as a function of the atomic number,  $Z$ , and are  $Q$ -independent, while x-ray atomic form factors directly depend on  $Z$  and decrease to zero at large- $Q$  values (figure 5). This will limit  $Q_{max}$  values that are obtainable, particularly for



samples containing low Z-elements. Neutron interaction with a given atom nucleus varies not straightforwardly with Z, as it does in the case for x-ray, but may be very different between two neighboring elements and even between isotopes of the same element. This last property is at the basis of the isotopic substitution method (part 4.1). For x-rays, the possibility that the atomic form factor varies close to the absorption edge of a specific element allowed the development of the anomalous scattering method (part 4.2).



**Figure 5:** (a) Erratic evolution of neutron scattering lengths as a function of the atomic number, Z (solid curve), with the slowly increasing potential scattering (dashed curve). (b) Evolution of the x-ray and neutron scattering amplitudes as a function of  $\sin(\theta)/\lambda$ .

The coupling of the two diffraction methods was widely used to study borate or phosphate glasses with high ionic conduction. The glassy borate or phosphate networks could be studied more specifically with the neutron diffraction results, while the organization of the elements responsible for the ionic conduction (alkali oxides or salts) can be investigated by x-ray diffraction [25][37][38][39][40][41].

**Table 1.** Comparison of neutron and x-ray diffraction

x-ray	Neutron
Interaction with electronic cloud	Interaction with the nucleus

$f(Q,E)$ atomic form factor	$b$ neutron scattering length
strong variation of scattered intensity with $\theta$	constant, independent of $\theta$
information on high-Z elements	not a monotonous function of Z
weak scattering for low-Z elements	light elements are visible (H, Li, N, O, etc)
weak contrast for elements with close Z	possibility to distinguish elements with close Z
$f$ varies with the energy $\Rightarrow$ anomalous scattering	$b$ can vary at some energies for some elements $\Rightarrow$ anomalous scattering limited
	$b$ varies among isotopes of the same element $\Rightarrow$ isotopic substitution
Small samples	Large samples
Radiation can cause damage	Radiation can cause activation
No magnetic information	Magnetic information is possible

### 3. Determination of the structural parameters

Structural information is easier to visualize and extract in real space (figure 6). The peak position gives directly the average interatomic bond length,  $r_{\alpha\beta}$ , between an atom  $\alpha$  taken at the origin and an atom  $\beta$  at the distance  $r_{\alpha\beta}$ . Provided that there is limited overlap with other interatomic contributions, a great precision can be achieved: the Si-O bond length has been determined at  $1.605 \pm 0.003 \text{ \AA}$  using neutron diffraction [42].

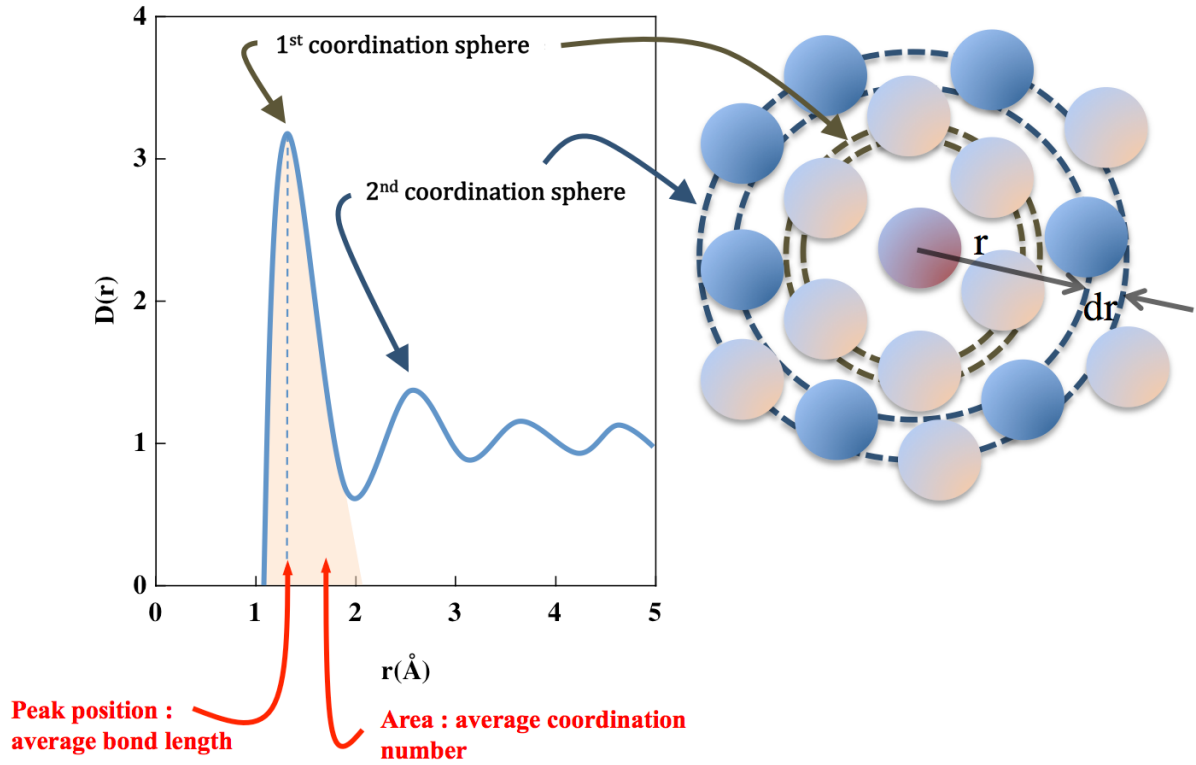
The coordination number,  $N_{\alpha\beta}$ , defines the average number of neighbors  $\beta$  around an atom  $\alpha$ , and it can be calculated by integrating the area under the  $\alpha$ - $\beta$  peak:

$$N_{\alpha\beta} = 4\pi\rho_0 c_{\beta} \int_{r_1}^{r_2} g_{\alpha\beta}(r) r^2 dr \quad (21)$$

where the integration limits ( $r_1$ - $r_2$ ) define the coordination shell. These limits are not always well-defined, in particular in case of partial overlap with another contribution, which affect the accuracy.

The width of the peak  $\sigma_{\alpha\beta}$  gives a measure of the distribution of interatomic distances due to both static structural and thermal disorder. However, the determination of  $\sigma_{\alpha\beta}$  is not direct since a peak

broadening results from the limited- $Q$  integration of the structure factor giving the correlation function.



**Figure 6:** Correlation function and real space information.

$N_{\alpha\beta}$  and  $\sigma_{\alpha\beta}$  factors are closely correlated and subject to more uncertainties. The coordination number is the least accurate parameter because it varies strongly with the slope at the origin or the  $Q$ -range, and the accuracy decreases in case of overlapping peaks. The ability to use different functions (total or partial), that must give the same information, can provide guidance on the accuracy of the values.

These three parameters are often obtained by performing a Gaussian fit of the peak, allowing  $r_{\alpha\beta}$ ,  $N_{\alpha\beta}$  and  $\sigma_{\alpha\beta}$  to vary.

$$g_{\alpha\beta}(r) = \frac{W_{\alpha\beta} N_{\alpha\beta}}{c_{\beta} r \sqrt{2\pi\sigma_{\alpha\beta}^2}} \exp\left(-\frac{(r - r_{\alpha\beta})^2}{2\sigma_{\alpha\beta}^2}\right) \quad (22).$$

The weighting factors  $W_{\alpha\beta}$  are calculated from tabulation of  $b$  and  $f$  [11][12][13][14] and the atomic fraction,  $c$ , is provided by the chemical analysis of the samples.

The  $D(r)$  and  $T(r)$  functions should be preferred as the finite  $Q_{max}$  results in a symmetric peak broadening for these functions [43]. To take into account the  $Q_{max}$  truncation, Gaussian functions have to be convoluted by a resolution function in real space given by the Fourier transform of the Lorch function [44].

#### 4. Difference methods

The  $D(r)$  function is informative but dominated by the correlations having large weighting factors, *e.g.* usually Si-O, O-O and Si-Si in silicate glasses for neutron diffraction measurements. On the other hand, above 3 Å, the various contributions are superimposed, the contributions with small weighting factors being overlapped by those having large weighting factors. It becomes extremely difficult above 3 Å to deconvolute the various contributions for a multicomponent material. The use of structural models can offer an interpretation of  $D(r)$  but this is of course not unequivocal.

For a system with  $n$ -component, there are  $n(n+1)/2$  partial structure factors (or PPDFs) that one wants to retrieve to describe the structure. The detailed understanding of the atomic structure requires the complete determination of the set of partial structure factors, which means that  $n(n+1)/2$  distinct experiments are required. In simple systems, this can be obtained by applying different contrast variation methods. For multicomponent glasses or liquids, these techniques allow the extraction of structural information for one specific element that is otherwise buried beneath other contributions with strong weighting factors.

The only element in  $S(Q)$  that is not structure or composition dependent is the neutron scattering length,  $b$ , or the atomic form factor,  $f(Q,E)$ .  $b$  can vary significantly in amplitude or sign from one element to another or between isotopes of the same element. The first property is used in isomorphic substitutions (exchange of elements playing an identical role in the structure [45]) while the second led to a more rigorous method of contrast, that of isotopic substitution.  $f$  can change close to the absorption edge characteristic of a given element due to anomalous dispersion. The contrast variation is thus the possibility to modify the scattering power ( $b$  or  $f$ ) of a specific element to extract the partial functions associated to this element. The higher the contrast variation, the higher the reliability of the results.

##### 4.1 Neutron diffraction with isotopic substitution (NDIS)

The isotopic substitution method was used for the first time by Enderby to retrieve the three partial structure factors of liquid Cu-Sn alloy [46]. This technique is based on the measurement of the neutron

diffraction (ND) by two samples, prepared rigorously identically (thus assuming the same structure, *i.e.* same  $c_\alpha$ ,  $c_\beta$  and  $g_{\alpha\beta}(r)$ ) but with different isotopic concentrations for one species, here called  $M$ . One can measure two total structure factors from these two samples, where only the weight of the partial structure factors involving  $M$  can vary:

$$\begin{aligned} S(Q) &= \sum_{\alpha, \beta \neq M} c_\alpha c_\beta b_\alpha b_\beta (S_{\alpha\beta}(Q) - 1) + \sum_{\alpha \neq M} c_\alpha c_M b_\alpha b_M (S_{\alpha M}(Q) - 1) + c_M^2 b_M^2 (S_{MM}(Q) - 1) \\ S'(Q) &= \sum_{\alpha, \beta \neq M} c_\alpha c_\beta b_\alpha b_\beta (S_{\alpha\beta}(Q) - 1) + \sum_{\alpha \neq M} c_\alpha c_M b_\alpha b'_M (S_{\alpha M}(Q) - 1) + c_M^2 b_M'^2 (S_{MM}(Q) - 1) \end{aligned} \quad (23).$$

The difference technique consists to subtract these two quantities and therefore to eliminate all terms not involving  $M$  since they are identical. The subtraction gives the first difference function,  $\Delta_M(Q)$ , which is the sum of the partial structure factors centered on the element  $M$ . After Fourier transformation, the  $M$ -centered pair correlation function is obtained:

$$\begin{aligned} G_{M\alpha}(r) &= \frac{2}{\pi} \int \Delta_M(Q) Q \sin(Q) dQ \\ &= 2 \sum_{\alpha \neq M} c_\alpha c_M b_\alpha (b_M - b'_M) g_{M\alpha}(r) + c_M^2 (b_M^2 - b_M'^2) g_{MM}(r) \end{aligned} \quad (24).$$

We have thus a chemically selective probe. The resulting function is analogous to the difference calculated by anomalous x-ray diffraction (part 4.2) or to the Fourier transformation of the EXAFS signal obtained by x-ray absorption spectroscopy.

Additionally, it is possible to measure three samples and thus to obtain two first differences,  $\Delta_M(Q)$  and  $\Delta'_M(Q)$ :

$$\begin{aligned} \Delta_M(Q) &= 2 \sum_{\alpha \neq M} c_\alpha c_M b_\alpha (b_M - b'_M) (S_{M\alpha}(Q) - 1) + c_M^2 (b_M^2 - b_M'^2) (S_{MM}(Q) - 1) \\ \Delta'_M(Q) &= 2 \sum_{\alpha \neq M} c_\alpha c_M b_\alpha (b'_M - b''_M) (S_{M\alpha}(Q) - 1) + c_M^2 (b_M'^2 - b_M''^2) (S_{MM}(Q) - 1) \end{aligned} \quad (25).$$

The weighting factors depend on the difference of the scattering lengths of  $M$  for the terms  $M$ - $\alpha$  ( $\alpha \neq M$ ) while the term  $M$ - $M$  depends on the difference of the square of the scattering lengths. Therefore, a judicious choice of the isotopic composition of the three glasses allows us to equalize the quantity  $\Delta b = b_M - b'_M$  and  $\Delta' b = b'_M - b''_M$ . This condition is easily obtained:

$$b' = \frac{b + b''}{2} \quad (26).$$

The subtraction of these two functions in equation (25) gives the second difference function,  $\Delta(\Delta_M)(Q)$ , in which only the  $M$ - $M$  correlation is present:

$$\Delta(\Delta_M)(Q) = \frac{1}{2} c_M^2 (b_M - b_M'')^2 (S_{MM}(Q) - 1) \quad (27).$$

This function is of course related to a pair correlation function that directly describes the distribution of the element  $M$  within the structure:

$$\begin{aligned} G_{MM}(r) &= \frac{2}{\pi} \int \Delta(\Delta_M)(Q) Q \sin(rQ) dQ \\ &= c_M^2 \frac{(b_M - b_M'')^2}{2} g_{MM}(r) \end{aligned} \quad (28).$$

The limits of NDIS are firstly the small number of elements with isotopes that are suitable. x-rays (with anomalous diffraction) allow access to more elements but they cannot probe light ones such as hydrogen or lithium. These isotopes should be stable and must not be too absorbent. It is necessary that the difference between the scattering lengths of isotopes is large enough, typically  $\Delta b > 3$  fm, to get a first and a second difference. A lower  $\Delta b$  may give access only to a first difference, especially for atomic concentrations lesser than 3 at%. A recent study has demonstrated that oxygen isotope substitution method can be carried out using  $O^{16}$  and  $O^{18}$  isotopes with a  $\Delta b$  of only 0.142 fm [47]. In their experiments, they found a 0.5% difference between the O-H and O-D bond lengths in water, supporting a competing quantum effects model.

Many errors can seriously limit the accuracy (and even correctness) of the difference functions. This method, in contrast to anomalous x-ray diffraction, uses several specimens synthesized under the same conditions and assumed that they have the same structure. Each sample should be identical with the exception of the isotopic composition of  $M$ . This means that the concentration of each element must be perfectly known. The isotopic ratios of  $M$  must also be determined to be able to properly assess  $b_M$  for each sample (although the scattering lengths are not always known precisely). Errors can therefore quickly accumulate and seriously contaminate the second difference, making its extraction delicate.

The first difference has the advantage of reducing the problems associated with systematic errors: corrections of inelasticity and multiple-scattering are largely eliminated in the subtraction. However, we must be aware that those terms reappear in the second difference.

For a binary system, the treatment can be summarized in matrix form:

$$\begin{aligned} \begin{bmatrix} S_1(Q) \\ S_2(Q) \\ S_3(Q) \end{bmatrix} &= \begin{bmatrix} c_\alpha^2 b_\alpha^2 & c_M^2 b_M^2 & 2c_\alpha c_M b_\alpha b_M \\ c_\alpha^2 b_\alpha^2 & c_M^2 b_M'^2 & 2c_\alpha c_M b_\alpha b_M' \\ c_\alpha^2 b_\alpha^2 & c_M^2 b_M''^2 & 2c_\alpha c_M b_\alpha b_M'' \end{bmatrix} \begin{bmatrix} S_{\alpha\alpha}(Q) \\ S_{\alpha\beta}(Q) \\ S_{\beta\beta}(Q) \end{bmatrix} \\ [S(Q)] &= [A][X(Q)] \end{aligned} \quad (29)$$

with  $S_1(Q)$ ,  $S_2(Q)$  and  $S_3(Q)$  the three distinct measurements and changing the isotopic state of the element  $M$ . The formal solution consists in obtaining the partial functions by matrix inversion:

$$[X(Q)] = [A]^{-1}[S(Q)] \quad (30).$$

A few elements (H, Li, Ti, Ni, Cr, Dy) have isotopes with both positive and negative scattering lengths, so that an isotopic mixture can be prepared with a null average scattering length. For a binary system having an element with a zero scattering length, the partial structure factor for the other element is directly measured in a single experiment. This null isotopic substitution technique has been used in several cases: for Dy and Ni in a  $Dy_7Ni_3$  metallic glass allowing the separation of all partial functions [48] or in liquid  $NiSe_2$  to isolate the Se-Se partial structure factor [49].

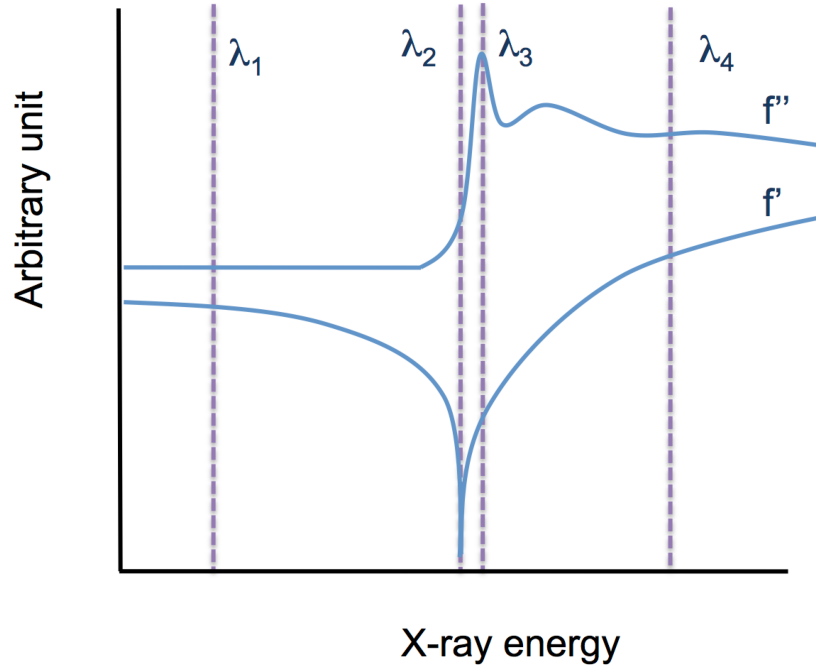
## 4.2 Anomalous x-ray diffraction (AXRD)

x-ray diffraction (XRD) is widely used as a complementary technique to neutron diffraction (part 2) and can also allow the determination of partial functions through a difference method. The structure factor determined by XRD is the sum of all the partial structure factors as shown in equation (7) but, contrary to  $b$ , the atomic form factors  $f$  depend upon  $Q$  and the incident energy,  $E$ . It is possible to change  $f(Q,E)$  at the absorption edge energy,  $E_{edge}$ , of a specific element, leading to the technique of anomalous x-ray diffraction [50][51].

The atomic form factor has a complex nature:

$$f(Q,E) = f_0(Q) + f'(E) + if''(E) \quad (31).$$

$f_0(Q)$  is the usual energy-independent term that controls the  $Q$ -dependence.  $f'(E)$  and  $f''(E)$  are the real and imaginary parts corresponding to the anomalous term. Near an absorption edge, they change drastically giving different scattering.



**Figure 7:** Variation of  $f'$  and  $f''$  near an absorption edge energy  $E_{edge}$  ( $\lambda_2$ ,  $\lambda_3$ ). AXRD usually considers two experiments at the edge ( $\lambda_2$  or  $\lambda_3$ ) and far below the edge ( $\lambda_1$ ) where  $f'$  and  $f''$  are almost constant, rather than above the edge ( $\lambda_4$ ) due to oscillations in  $f''$ .

In an AXRD experiment, the scattering intensities for a same sample are measured at two different energies (figure 7), one close to the absorption edge  $E_{edge}$  (where the variation of  $f$  is the highest) and another one several hundred eV below  $E_{edge}$  (to avoid problems of absorption and fluorescence above  $E_{edge}$ ). The subtraction of the two measured intensities gives a first difference function:

$$\Delta_M(Q) = \sum_{\substack{\alpha \\ \alpha \neq M}} DW_{\alpha M} (S_{\alpha M}(Q) - 1) \quad (32)$$

with  $DW_{\alpha M}(Q)$  the differential weighting factor for the pair  $\alpha$ -M:

$$DW_{\alpha M} = \frac{c_\alpha c_M D(f_M f_\alpha^* + f_M^* f_\alpha)}{D(|\langle f \rangle|^2)} \quad (33).$$

The difference function limits information to the environment around the specific element, M, but this limitation is not a handicap because it allows us to isolate a signal which is overlapped in the total distribution function by stronger correlations. Though AXRD can be obtained at three different energies allowing the extraction of a second difference function, the contrast to retrieve a partial function  $M$ - $M$  is low and this method has been little used. An example is the study of the distribution of Ba in silicate glasses [52]. Anomalous diffraction can also be obtained for certain energies using neutrons [53], but this is restricted to a limited number of elements (e.g. Sm).



An advantage of AXRD is that a large number of elements are available, especially considering the possibility of using K or L absorption edges for low- and high-Z elements, respectively. The major limitation concerns the accessible  $Q$  range that is limited by the choice of the absorption edge energy,  $E_{edge} = hc / \lambda_{edge}$ . Given this wavelength  $\lambda_{edge}$ , a maximum momentum transfer of  $Q_{max} = 4\pi \sin\theta_{max} / \lambda_{edge}$  can be obtained. In practice, a minimum  $E_{edge}$  of 10 eV is necessary, to get a  $Q_{max} \sim 10 \text{ \AA}^{-1}$ . Therefore, AXRD is suited for elements of  $Z \geq 26$  (iron K-edge absorption).

As an example, this technique has been applied to  $\text{Ge}_x\text{Se}_{1-x}$  glasses at energies close to the Ge and Se K-edges absorption. The partial functions show a gradual change with  $x$  but intermediate-range structure probed by pre-peak position in the  $S_{\text{SeSe}}(Q)$  partial structure factor indicates that the stiffness transition at  $x = 0.20$  can be observed [54].

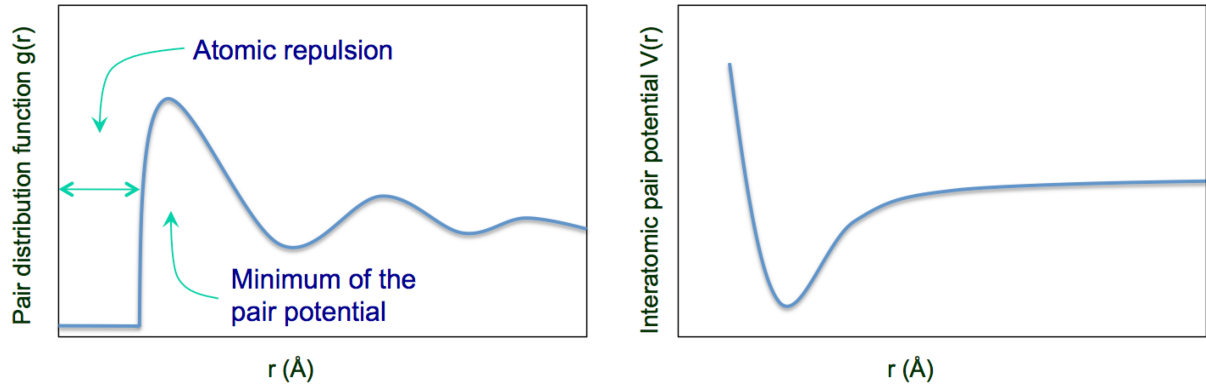
### 4.3 Coupling x-ray and neutron diffraction

One possibility of determining the difference function is by combining neutron and x-ray data, which can be realized on the same sample [4]. A first order difference function can be obtained, though the sources of errors are important due to different experimental set-ups and resolutions and due to the  $Q$ -dependence of the form factors.

## 5. RMC and related methods

Despite the development of experimental techniques, our representation of the glass structure remains partial. The use of simulations can help to better constrain structural models. Since correlation functions are one-dimensional, the construction of three-dimensional structural models can be used to describe the isotropic 3-D arrangements characteristic of glass structure. Different modeling techniques associated with fitting of the experimental diffraction data have been developed, in particular Reverse Monte Carlo (RMC) and Empirical Potential Structure Refinement (EPSR). There are analogs for disordered materials to the Rietveld refinement methods for crystalline powder patterns.

An analogy can be pointed out between the  $g(r)$  and the pair potential  $V(r)$  (figure 8). The low- $r$  part represents the repulsion of two neighboring atoms defining the distance of closest approach between atoms. This mimics the coulombic repulsive term in  $V(r)$  that hinders the particles from colliding. The peak position and width between two neighboring atoms in  $g(r)$  mimics the form of the pair potential (energy position and depth of the potential well), *i.e.* the attractive term of the potential.



**Figure 8:** Analogy between the pair distribution function and the interatomic pair potential (see text).

Molecular dynamics and Monte Carlo techniques have been more widely used. Molecular Dynamics (MD) allows tracking the movements of a set of atoms interacting within a given potential force field as a function of time and also of the temperature/pressure. Information on the liquid dynamics behavior at the glass transition temperature or on the glass structure can be obtained. This method has been applied to a large number of oxide glasses [55][56]. However, for reasons of computational time, quenching rates are significantly higher than those obtained experimentally [57]. In addition, the determination of potential correctly representing the atomic interactions is difficult. As an alternative to this approach, the Monte Carlo method use potentials and move randomly atoms to minimize the energy of the system [58].

These models can be compared to experimental data to test the validity of simulations over different length scales or to improve the pair potentials. The evaluation of the (dis)agreement between simulation and experiment should require a factor of goodness of fit, such as the one proposed by Wright [59]:

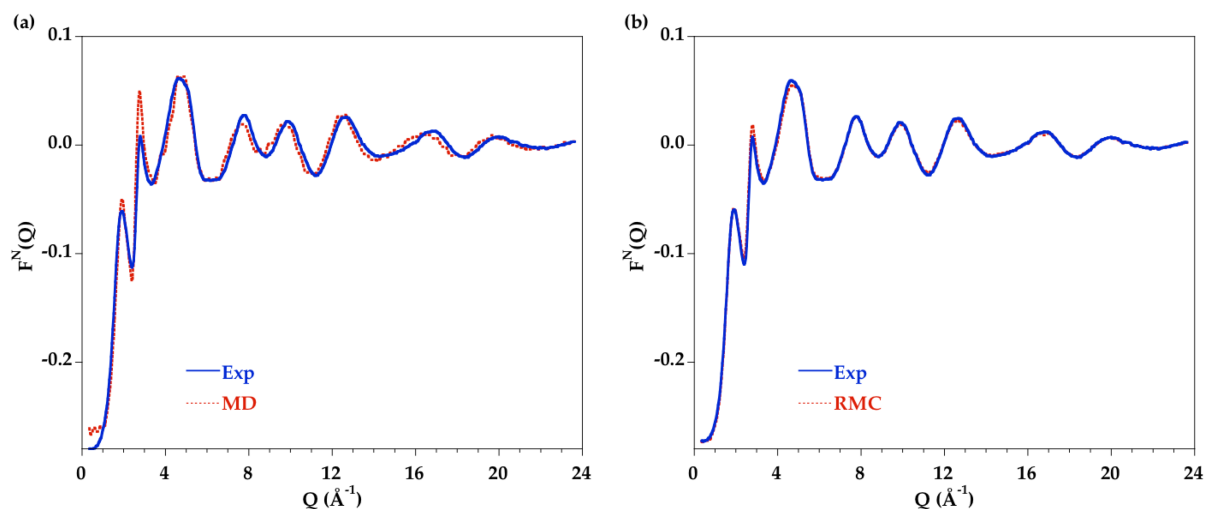
$$R_{\chi} \left( \frac{\sum_i [T_{\text{exp}}(r_i) - T_{\text{sim}}(r_i)]^2}{\sum_i T_{\text{exp}}^2(r_i)} \right)^{1/2} \quad (34).$$

with  $T_{\text{exp}}$  and  $T_{\text{sim}}$  the experimental and simulation total distribution functions

If the agreement is not satisfactory, other techniques can be used for elucidating the detailed atomic structure based on fitting the experimental diffraction data (and possibly additional structural information). The Reverse Monte Carlo (RMC) method involves iteratively moving a set of atoms randomly to reproduce the experimental data, without recourse to interatomic potentials [60][61][61]. After each random move, the difference between experiment and model is calculated and, if the move improves the agreement, the atomic displacement is accepted, otherwise the structure change is

allowed with some probability to avoid local minima. This procedure is repeated until a satisfactory refinement of the experimental data is achieved. Additional constraints such as the density, known coordination numbers, etc, can greatly improve the final RMC model. RMC allows the generation of atomistic models in quantitative agreement with diffraction data and structural information extracted from these models can improve our understanding of the glass structure.

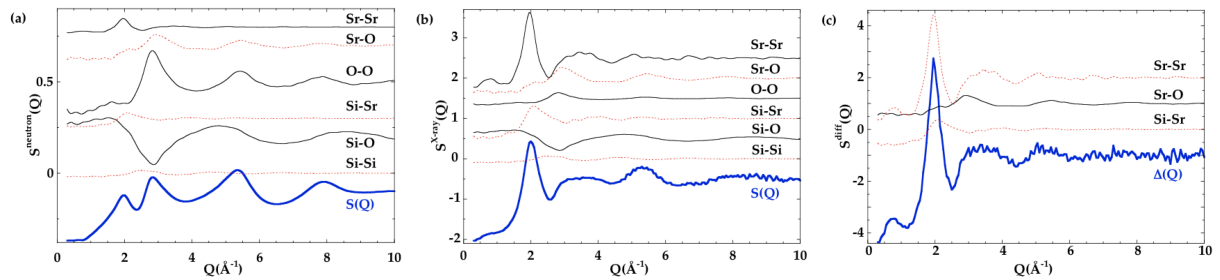
The initial model is a key parameter in RMC modeling. Large atomic boxes are required, containing several thousands of atoms. Random configurations are usually chosen but, after RMC fitting, such structures yield models with important and unrealistic entropic energies. Indeed, RMC is a maximum entropy approach giving the most disordered structure that is in accord with the experimental data. MD simulations offer more realistic starting models if interatomic potentials are available [62]. Even with the best current MD simulations, differences in peak positions and intensities exist with the experimental data. We present in figure 9.a a comparison between neutron data and MD simulations obtained on a  $\text{MgSiO}_3$  glass with pair interaction potentials [63], showing small discrepancies in the structure factors between experiments and MD. These models can therefore be adjusted by using the RMC method to obtain atomistic structures in agreement with the experimental data (figure 9.b).



**Figure 9:** (a) Comparison between neutron structure factors obtained experimentally (solid line) and by MD simulations for a  $\text{MgSiO}_3$  glass. (b) Comparison between neutron structure factors obtained experimentally (solid line) and after running RMC starting with the MD simulations.

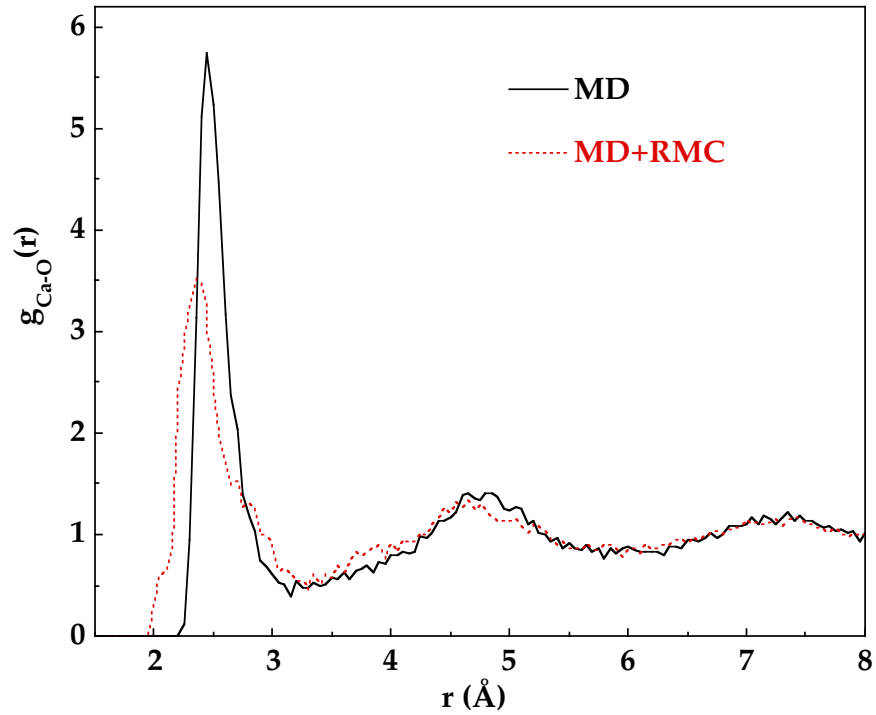
Several software packages can be used to realize this RMC fitting process: *RMC++* [64], *RMC\_POT* [65] or *RMCProfile* [66], all available at <http://www.wisis2.isis.rl.ac.uk/rmc/>. Some of these programs now incorporate an extensive use of interatomic potential functions.

The coupling between experiments and RMC allows a better interpretation of the experimental data obtained on multicomponent glasses, since different partial structure factors or partial pair distribution can be extracted. Figure 10 shows the results obtained on a  $\text{SrSiO}_3$  glass by refining simultaneously ND (figure 10.a) and AXRD at the Sr K-edge (figure 10.b), allowing to obtain a first difference function centered on Sr (figure 10.c). This example shows the interest of coupling the two diffraction techniques due to different weighting factors: ND is most sensitive to the pairs associated with the silicate network and XRD will be heavily weighted by the pairs associated with strontium. This study allowed understanding the arrangements of the Sr cations in glasses and the similarities with crystals of equivalent composition [41]. The analysis of correlation functions reveals that strontium has a different environment and a different distribution within the structure if it acts as modifier or charge compensator.



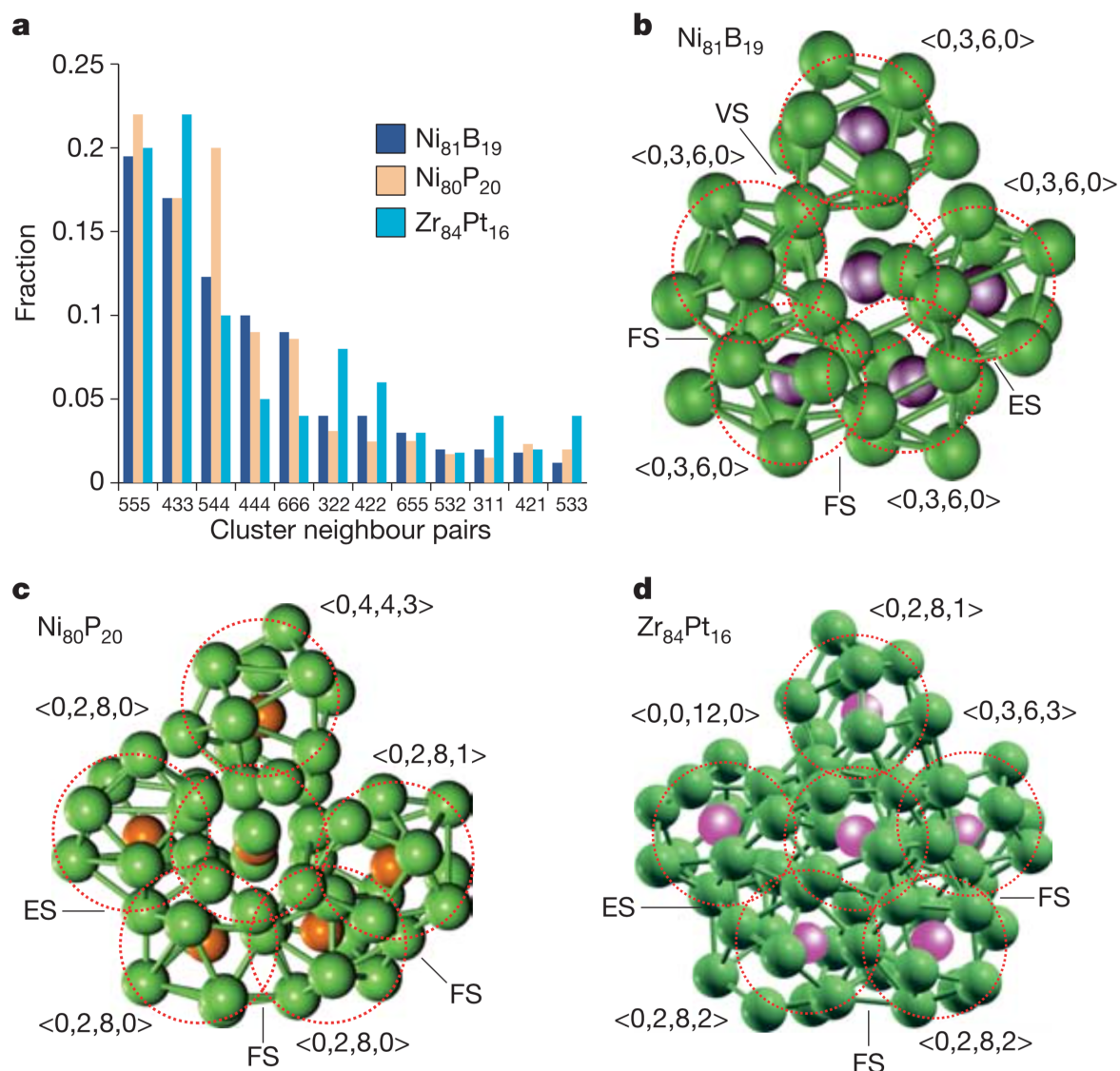
**Figure 10:** Total structure factors obtained by (a) neutron diffraction, (b) x-ray diffraction and (c) structure factor of first difference determined by anomalous x-ray diffraction at the Sr K-edge for a  $\text{SrSiO}_3$  glass, compared with the weighted partial structure factors determined by RMC modeling.

A RMC development is to improve interatomic pair potentials used in classical MD simulations. Indeed, by calculating partial pairs distributions before and after the RMC procedure, it is possible to determine the pairs that have varied the most and require an optimization of their potential parameters. Figure 11 compares the Ca-O pair before and after the RMC adjustment, which highlights the need for a lower Ca-O bond length to achieve a good agreement with the experimental data. This type of approach allowed the modification of the Ca-O pair potential [67].



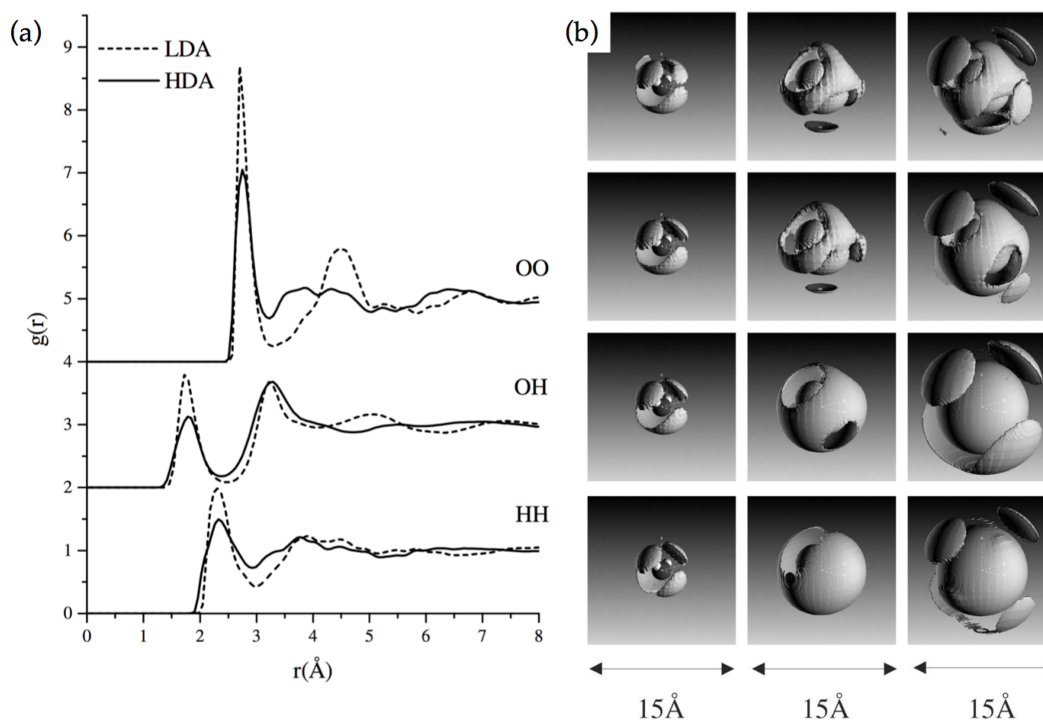
**Figure 11:** The Ca-O pair distribution function calculated by molecular dynamics (full curve) and adjusted by RMC (dotted curve) for a 61CaO-39Al<sub>2</sub>O<sub>3</sub> glass. There is a displacement of the first peak at 2.44 Å in the MD model to 2.35 Å after RMC. The figure is adapted from [68].

Much of our existing knowledge about the atomic structure of metallic glasses is based on RMC and diffraction measurements (as well as MD simulations) [69][70][71]. Efficient atomic packing is a fundamental principle underlying the formation and stability in such systems. RMC structural models for binary nickel-based and zirconium-based metallic glasses were obtained [70], enabling knowledge of the three-dimensional positioning of the atoms. The short-range order (SRO) is characterized by solute-centered clusters (various polyhedra of around 9 to 13 atoms) each of which is made up of a solute atom surrounded by a majority of solvent atoms. The intermediate range order (IRO) is constructed by packing of these polyhedral clusters with appreciable icosahedral medium-range order (figure 12), regardless of the short-range order within the clusters. Icosahedral order has a fivefold rotational symmetry that is incompatible with translational symmetry and favor glass forming ability.



**Figure 12:** (a) Cluster neighbor analysis showing that the local clusters (solute-centered polyhedra) exhibit icosahedral order. (b), (c) and (d) Typical packing of clusters showing fivefold symmetry detailed for  $\text{Ni}_{81}\text{B}_{19}$ ,  $\text{Ni}_{80}\text{P}_{20}$  and  $\text{Zr}_{84}\text{Pt}_{16}$  metallic glasses, respectively. FS, ES and VS stand for face-sharing, edge-sharing and vertex-sharing, respectively. Reprinted by permission from Macmillan Publishers Ltd: Nature ([70]), copyright (2006).

Another method based on the refinement of diffraction data is Empirical Potential Structural Refinement (EPSR) modeling [72]. This tool uses realistic intra- and inter-molecular potentials that constrain the atomic positions in the simulation box. An empirical potential is introduced as a perturbation to the arbitrary potential functions, generated from the difference between measured and calculated structure factors or radial distribution functions. A Monte Carlo refinement of this empirical potential is successively obtained as the atoms or molecules are move, enabling the best possible agreement with the experimental data. As for RMC, a 3D atomic model is obtained, consistent with the measured diffraction data. This method has been particularly developed for molecular systems, such as water (figure 13).

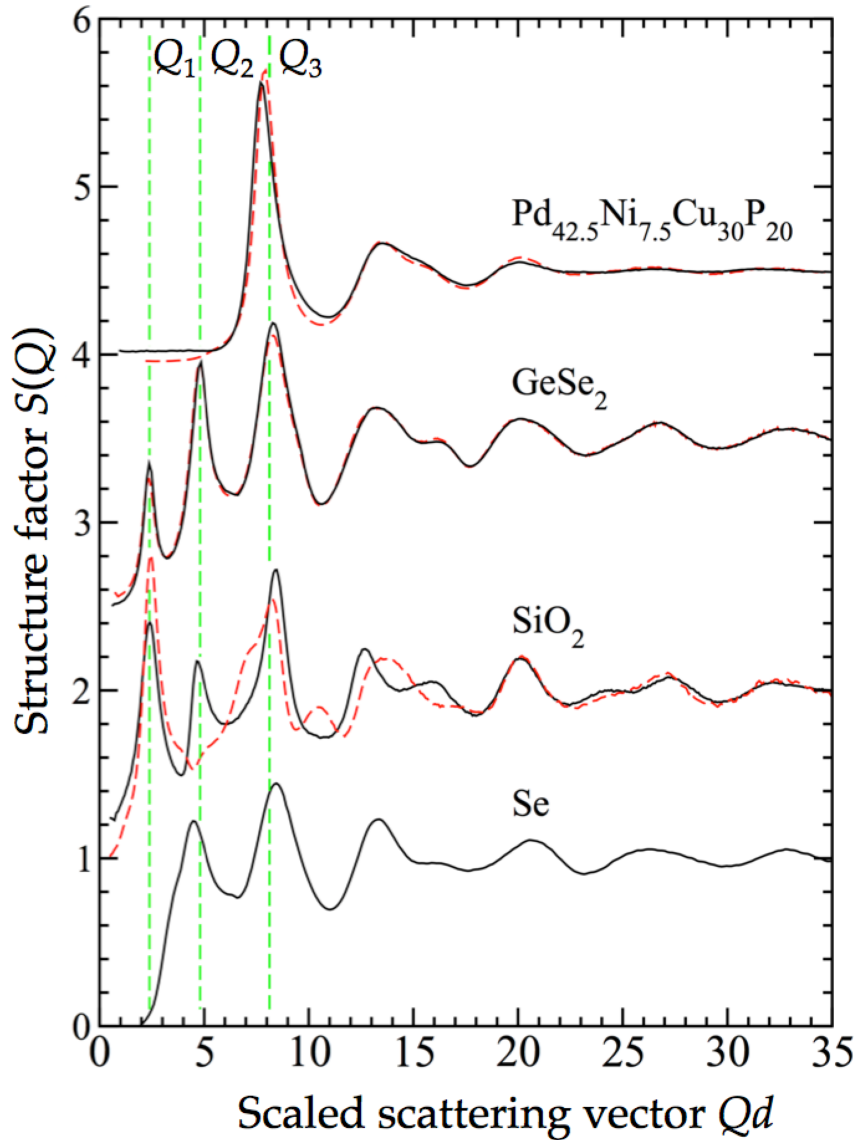


**Figure 13:** (a) Inter-molecular PPDFs of high-density (HDA) and low-density (LDA) amorphous water (see section 7.4.1) at 80 K. (b) Three dimensional arrangement of the oxygen atoms around a water molecule (spatial distribution function) showing the first, second and third O neighbors (from left to right) for crystalline ice at 220 K, LDA at 80 K, liquid water at 298 K [24], and HDA at 80 K. Reprinted with permission from [73]. Copyright (2002) by the American Physical Society.

## 6. Case studies of glass investigation by neutron and x-ray diffraction

### 6.1 The low-Q features

In the structure factors, it is often useful to consider the domain at low- $Q$  values. For simple glasses, three peaks  $Q_1$ ,  $Q_2$  and  $Q_3$  are characteristic features that scale roughly with the interatomic distance  $d$  (figure 14):  $Q_1.d \simeq 2-3$ ,  $Q_2.d \simeq 4.6-4.9$ ,  $Q_3.d \simeq 7.7-8.9$  [74]. At these peak positions correspond ordering at different length scales: nearest-neighbor separation for  $Q_3$ , size of the local network-forming motifs for  $Q_2$  and arrangements of these motifs on an intermediate range for  $Q_1$ . Note that 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  $\text{SiO}_2$  but absent in the x-ray diffraction data).



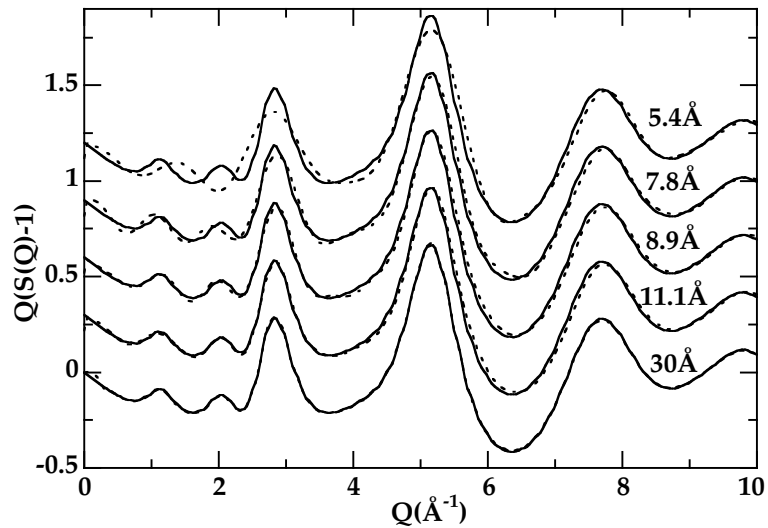
**Figure 14:** Typical structure factors obtained by neutron diffraction (solid curves) or x-ray diffraction (broken curves) for various glasses as a function of the scaled scattering vector  $Qd$ . The figure is adapted from [74].

The low- $Q$  region is usually dominated by the peak  $Q_1$ , referred to as "First Sharp Diffraction Peak" (FSDP), but several peaks or shoulders can coexist in chemically complex glasses. The features at low- $Q$  values have attracted considerable attention as they are a characteristic of topological organization at the IRO (figure 15). If the low- $Q$  feature at position  $Q_1$  is isolated and Fourier transformed, it gives in  $r$ -space a decaying sine function with periodicity  $2\pi / Q_1$ . The correlation length in real space of the decaying oscillations corresponds to the full half width maximum (FHWM) of the  $Q_1$  peak,  $2\pi / \text{FHWM}$ , giving typical values of 15-25 Å [75].

This feature is seen in a wide range of disordered systems, persisting even into the liquid state. Its intensity is highly sensitive to disorder (e.g., in neutron bombarded  $\text{SiO}_2$ , the peak becomes weaker)



and exhibits anomalous behavior with pressure [76][77][78][79], temperature [80][81][82][83], pressure/temperature [84][85][86] and composition [87][88][89][90][91][92]. For instance, the peak intensity decreases with  $P$  and increases with  $T$  unlike the normal behavior of the other peaks. This anomalous  $T$ -dependence suggests a similar origin with the anomalous low-frequency, low- $T$  vibrational properties. Relationships with system dynamics or fragility have been suggested [93].



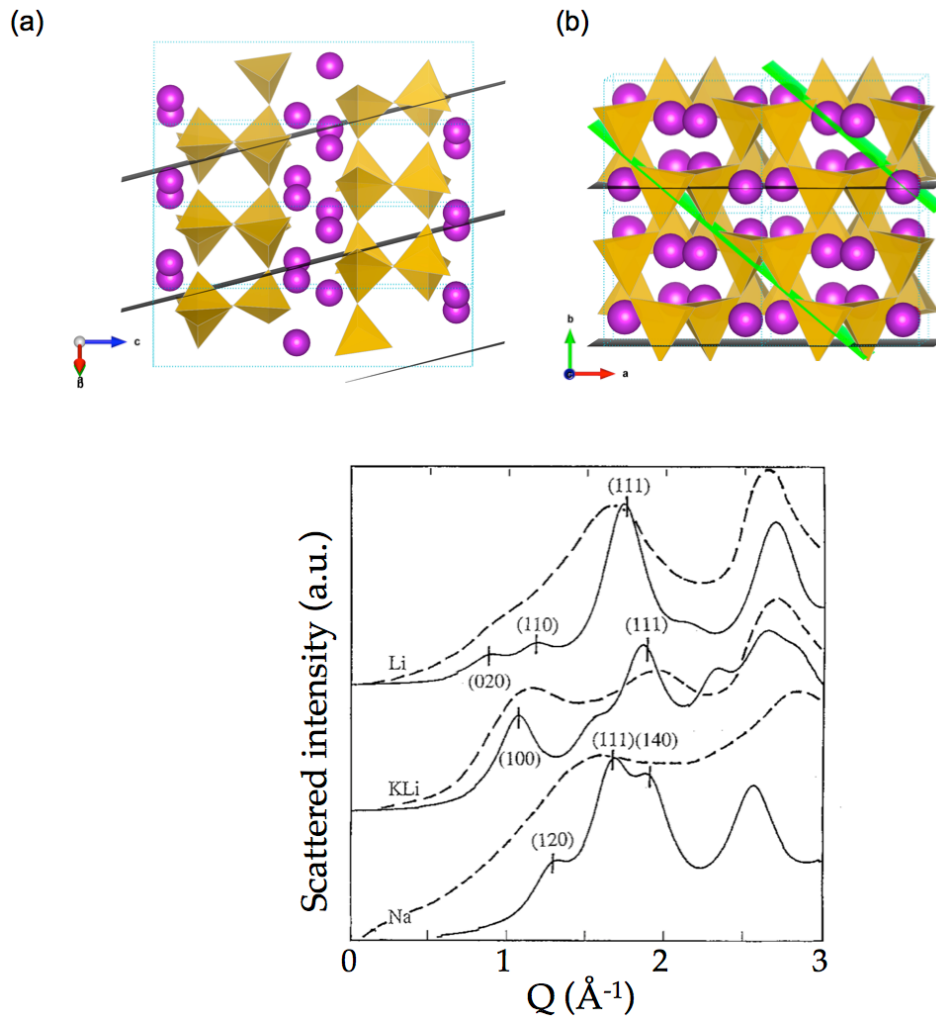
**Figure 15:** Interference function,  $Q(S(Q)-1)$  of a  $K_2TiSi_2O_7$  glass obtained by Fourier transformation of  $D(r)$  truncated at different values of  $r$  (dashed curves), chosen as even nodes of  $D(r)$ . The experimental interference function (solid curve) is shown as comparison. A value of  $r = 8.9 \text{ \AA}$  is necessary to fully reproduce the peaks, particularly the one at  $\sim 1.12 \text{ \AA}^{-1}$ .

Whether included or not in the Fourier transformation, the low- $Q$  feature is not related to a well-localized real-space feature in the correlation function, indicating that it corresponds to subtle organization at intermediate range. Difference function indicates that the main contribution usually comes from cation-cation correlation in the materials [80][94][50][95] though other authors suggest that the low- $Q$  features appear primarily from density fluctuations and not concentration fluctuations [96].

Although essential to the understanding of IRO, the origin of the peaks present in this region remains controversial [97][98][99][100]. Several general explanations have been proposed for the universal origin of this peak.

### 6.1.1 Quasi-crystalline organization, quasi-Bragg peak or quasi-periodic arrangement

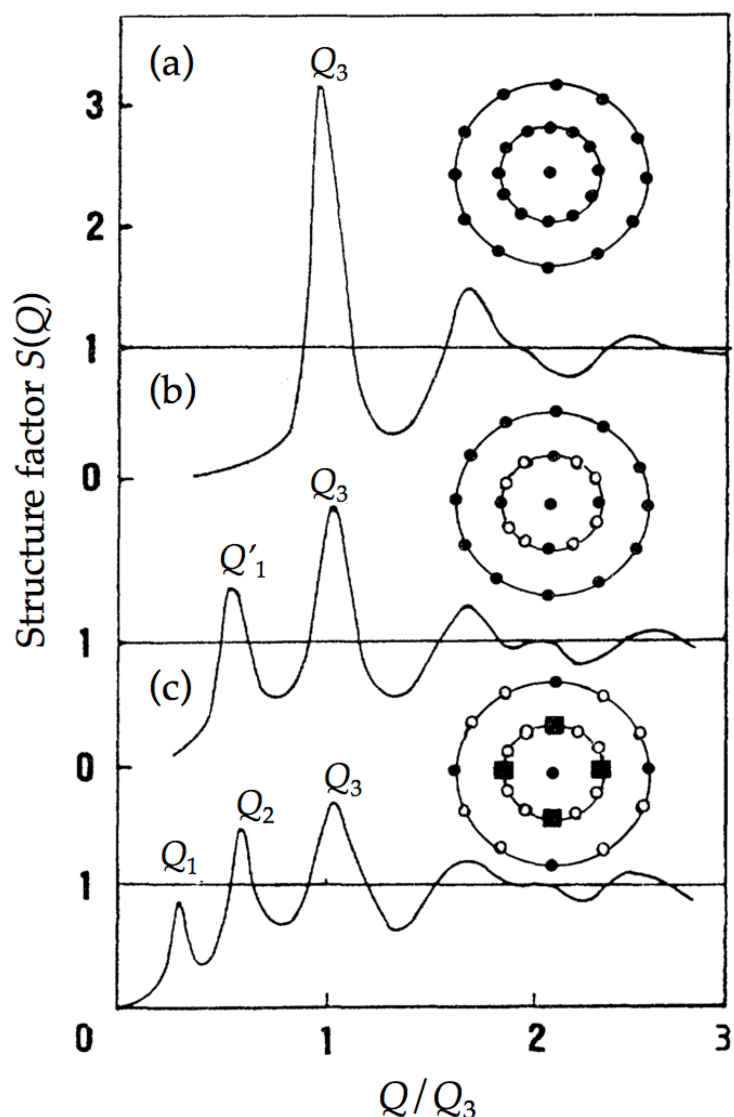
The position of these low- $Q$  features in glasses, melts and simple liquids often appears at similar scattering vectors than strong Bragg peaks in compositionally equivalent crystals, suggesting a general correspondence. It was proposed that these peaks result from a broadening of the Bragg reflections corresponding to periodic anisotropic spacing of limited coherence length in real space [99][101][102][103], as structures in layers existing in chalcogenide glasses [81][82][77]. Liquids can also present these structures with intensities sometimes greater than in glasses. As it seems improbable that the liquid is more organized than the glass, the stronger intensity seems an indication that the layer models do not work [98]. However this intensity increase is not inevitably related with a more ordered structure [101][102][103]. It was suggested that, with the temperature increase, a relaxation of the constraints of the arrangements provokes an increase of the intra-layer correlations [81][82]. It was also considered that in glasses such as  $\text{SiO}_2$ , layer structure is improbable. Gaskell and Wallis [100] used various models developed for silica glass to show that they contain planar corrugated sheet structures associated with reasonably well-defined interplanar spacings similar to  $\{111\}$  planes of  $\beta$ -cristobalite. They interpret these quasi-Bragg planes as the origin of the low- $Q$  peak in  $\text{SiO}_2$  glass. Since, in most glasses, the low- $Q$  peak position corresponds closely to the position of a strong diffraction peak (often the lowest  $Q$  feature) of a corresponding crystalline phase, these similarities suggest a general explanation: the remaining of quasi-Bragg planes (distorted, imperfect and not necessarily “plane”) in the glasses similar to those presents in the related crystalline phases (figure 16). This model does not imply a layer glass structure and has connections with the Elliott’s model of interferences between the network and voids [104]. On the other hand, this model received the support of modeling [105] and is connected with liquid models [106][107]. Although not indicating a microcrystallite model, this interpretation emphasizes the important similarities between glasses and crystals in the organization at intermediate distances, which is also seen in the analysis of the first difference functions (see sections 6.4 & 6.5).



**Figure 16:** (a) The structure of  $c\text{-Li}_2\text{Si}_2\text{O}_5$  showing planes parallel to (111) in  $c\text{-Li}_2\text{Si}_2\text{O}_5$  which are associated with the strong peak at  $1.7\text{-}1.8 \text{ \AA}^{-1}$  in (c), and can be associated with a similar feature in the corresponding glasses. (b) Projection of the structure along [100] showing corrugated planes of  $\text{Si}_2\text{O}_5$  units. Planes parallel to (020) (horizontal, black) and (110) (inclined, green) are shown and are associated with the weak features at  $\sim 1 \text{ \AA}^{-1}$  in (c). (c) Experimental neutron diffraction data (dashed curves) for disilicate glasses containing Li, K/Li and Na compared with simulated neutron diffraction calculated from the crystal structures (solid curves). The disorder is simulated by considering crystallites with 2 nm in size (not meaning a microcrystallite model). The figure is adapted from [108].

### 6.1.2 Correlations between clusters and voids

Price and Moss [97] have suggested an explanation based on the packing of the basic structural or molecular units, which are observed in some tetrahedral molecular compounds [109]. One problem is that these clusters are ill-defined and the structure between these clusters is not specified. For liquids like  $\text{CCl}_4$ , the diffracted intensity is a sum of inter- and intra-molecular terms. The low- $Q$  peak appears as a combination of a strongly  $Q$ -dependent intermolecular term (decreasing with  $Q$ ) and the wing of the first “normal” diffraction peak (increasing with  $Q$ ).



**Figure 17:** Structure factors calculated for different models and normalized in  $Q$  to the position of the principal peak  $Q_3$  determined by the nearest-neighbor distance. (a) A dense random packing structure (typical to metallic glasses), (b) a tetravalent structure (e.g.,  $\alpha$ -Si), and (c) a 4:2 structure (e.g.,  $\alpha$ -GeSe<sub>2</sub>).  $Q_1$  and  $Q'_1$  correspond to FSDP and  $Q_2$  to a second sharp diffraction peak with the same origin but different length scales. Filled circles in (b) and (c) are four-coordinated atoms, filled squares are two-coordinated atoms, and open circles are voids. The figure is adapted from [110][111].

Dixmier and Blétry [110][112][110] emphasized the role of holes for tetravalent vitreous structures which has been used by Elliott for a broader interpretation [98][113]. Elliott considers that these low- $Q$  features derive from the chemical organization at short distance of the interstitial voids around cation-centered clusters which can be for example the  $\text{SiO}_4$  tetrahedra in silicates (figure 17). It was shown that the lowest- $Q$  and most intense peak originates from a rapidly decaying inter-cluster structure factor, *i.e.* simply an artifact resulting from the addition of a rapidly decreasing intra-

molecular form factor and the increasing inter-cluster structure factor at small  $Q$  [98]. It can be noted that, in the correlation functions, low atomic occupation zones around 5 Å are present [114]. The behavior in pressure, temperature and composition can be qualitatively explained by this model. For instance, the empty space within the structure reduces in volume as pressure is applied [113][115].

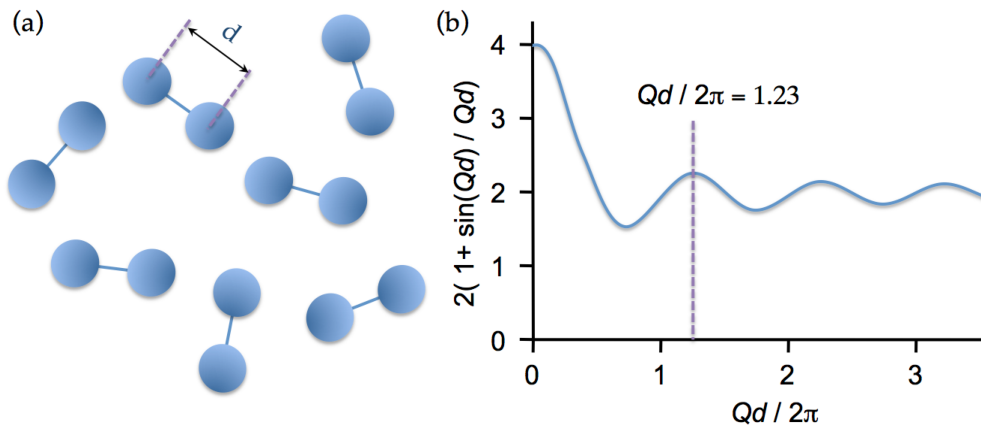
### 6.1.3 Correlations between, $Q_1$ and the reduced volume

Simplifying the Debye formula in equation (13) for a diatomic gas composed of two atoms of scattering power  $b$ , at a distance  $d$  from each other (figure 18.a), we obtain [116]:

$$S(Q) \propto \sum_{\alpha\beta} b_\alpha b_\beta \frac{\sin Qr_{\alpha\beta}}{Qr_{\alpha\beta}} = 2b^2 \left( 1 + \frac{\sin Qd}{Qd} \right) \quad (35).$$

For  $Q = 0$ , the intensity is equal to  $4b^2$  and after several oscillations tends to  $2b^2$ , i.e. the sum of the intensities diffracted by the two atoms of the molecule (figure 18.b). The function presents a succession of maxima and the first and highest diffraction maximum is obtained by setting the derivative of equation (35) with respect to  $(Q.d)$  to zero, which gives the Ehrenfest relation [117][116]:

$$Q = \frac{4\pi \sin \theta_m}{\lambda} = 1.23 \left( \frac{2\pi}{d} \right) \quad (36).$$



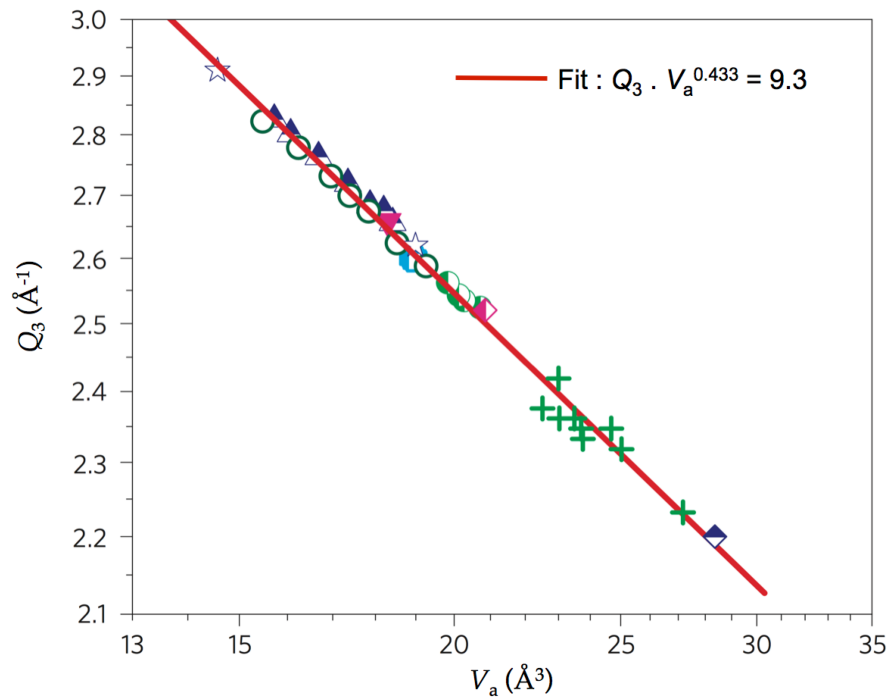
**Figure 18:** (a) Representation of a gas composed of a diatomic molecule with an interatomic distance  $d$ . (b) The scattering power per molecule of a diatomic gas showing successive maxima.

The position of this peak is associated with the principal diffraction peak ( $Q_3$ ). As a consequence, the position  $Q_3$  is inversely proportional to the mean atomic spacing and the third power of  $Q_3$  scales inversely with the volume. In metallic glasses, it was used to determine the thermal expansion

coefficient by following the variation of  $Q_3$  with temperature [118]. A power law relationship is proposed between the reverse of the principal peak position,  $2\pi/Q_3$ , and the glass volume  $V_a = \rho_0 / (N_A M)$  for various metallic glasses [119]. The following relationship corresponds to the plot in figure 19:

$$Q_3 \cdot V_a^{0.433} = 9.3 \pm 0.2 \quad (37).$$

The power of 0.433 is significantly different to  $1/3$  that would be expected for crystals and this has been interpreted as indicative of a fractal network with a fractal dimensionality of  $(0.433)^{-1} = 2.31$  [119]. This correlation is convenient to understand the relative volume (density) change with pressure (see section 7.4.5).



**Figure 19:** Power law scaling of the peak  $Q_3$  as a function of the atomic volume  $V_a$ . Both axis are in a logarithmic scale. The symbols represent the experimental points for various metallic glasses. The figure is adapted from [119].

## 6.2 The polymeric network

Neutron diffraction is one of the most widely used methods to study the glass structure. In particular, the quantitative structural information on network formers and on the polymeric network can be obtained through the total correlation functions, in which the pairs associated with the glassy matrix are dominant. Pure silica and boron glasses have been widely studied by this method [42][120][121].

In phosphate glasses, it was possible to separate the contributions between the bridging oxygen anions and non-bridging oxygen anions around a phosphorus atom [25]. Such data provide constraints on the polymerization of the chains of  $\text{PO}_4$  tetrahedra according to modifier oxide contents. Coupling ND and XRD with RMC allowed building structural models. These models showed for example that two alkalis present in glasses were distributed homogeneously [37]. The addition of salts in these glasses (for instance AgI [122]) leads to the expansion of the network, which promotes the formation of paths for ionic diffusion.

In borate glasses, large- $Q$  values enable discrimination of two distances corresponding to three-fold coordinated boron ( $\text{BO}_3$ ) boron and four-fold coordinated boron ( $\text{BO}_4$ ) [39]. The  $\text{BO}_3/\text{BO}_4$  ratio can be tracked according to the composition and excellent agreement is obtained with RMC experiments. Various studies have been conducted on borate or phosphate ionic glasses combining often ND, XRD and RMC modeling. It has been shown that IRO of the borate network decreases with an increase in doping salt concentration, and that the borate network forms a chain structure with AgI salt ions cross-linking these chains, while (Li, Na)(Cl,Br) salt ions enter the structural free volume and dilates the borate network [40].

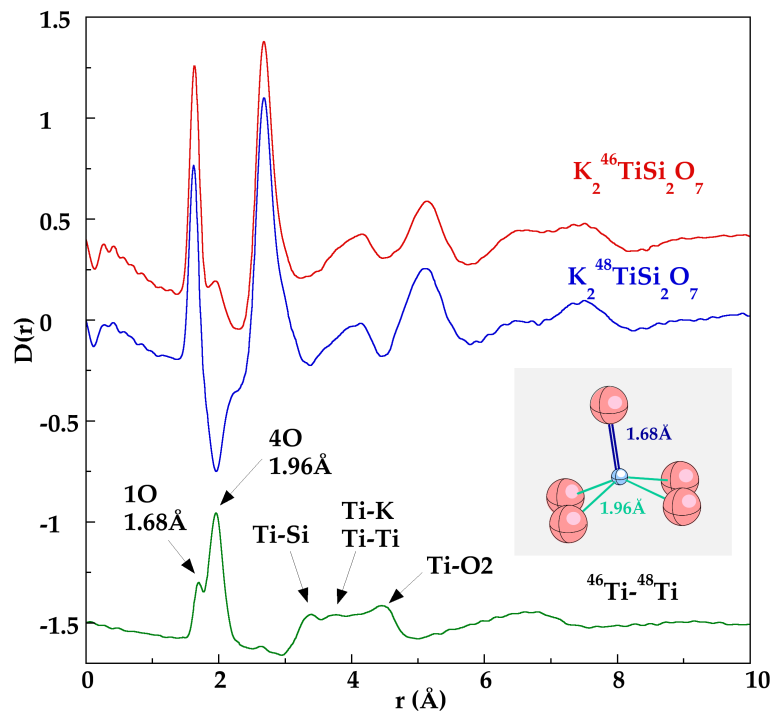
NDIS was also used to extract the different PPDFs in the glassy network. In particular, in a  $\text{GeSe}_2$  glass [94] [123], all pairs have been determined. The basic structural units are  $\text{GeSe}_4$  tetrahedra arranged with both edge- and corner-sharing. The chemical order existing in oxide glasses is broken as homo-nuclear (homopolar) bonds have been evidenced by NDIS. Ion conductive chalcogenide glasses have been also extensively studied by this method to determine the interaction between the network and the added salts [124][125][126][127].

### 6.3 Cation sites in glasses

AXRD and NDIS are chemically selective methods, similar to EXAFS, but they have the advantage of being able to probe the structure with better accuracy [128] and larger distances (typically 10 Å). The use of materials isotopically substituted gives similar information to AXRD but for different elements, with a better experimental counting statistics and the ability to directly extract the cation-cation distances and coordination numbers.

The interest of the first difference function (see section 4.1) can be understood in figure 20 that shows the correlation functions determined in a complete study on a  $\text{K}_2\text{TiSi}_2\text{O}_7$  glass with isotopic substitution of Ti [129]. In the first difference function,  $G_{\text{TiO}}(r)$ , we observe that Si-O and O-O correlations, having important weights, are eliminated. It appears then that the first layer of oxygen neighbors surrounding Ti can be deconvoluted into two distinct Ti-O distances at 1.68 and 1.96 Å,

which allows the unambiguous determination of the Ti site as a square-based pyramid. Contrary to EXAFS that shows a single distribution [130], the NDIS method is able to solve the two Ti-O distances, thanks to the wide available  $Q$ -range that gives a better real space resolution.



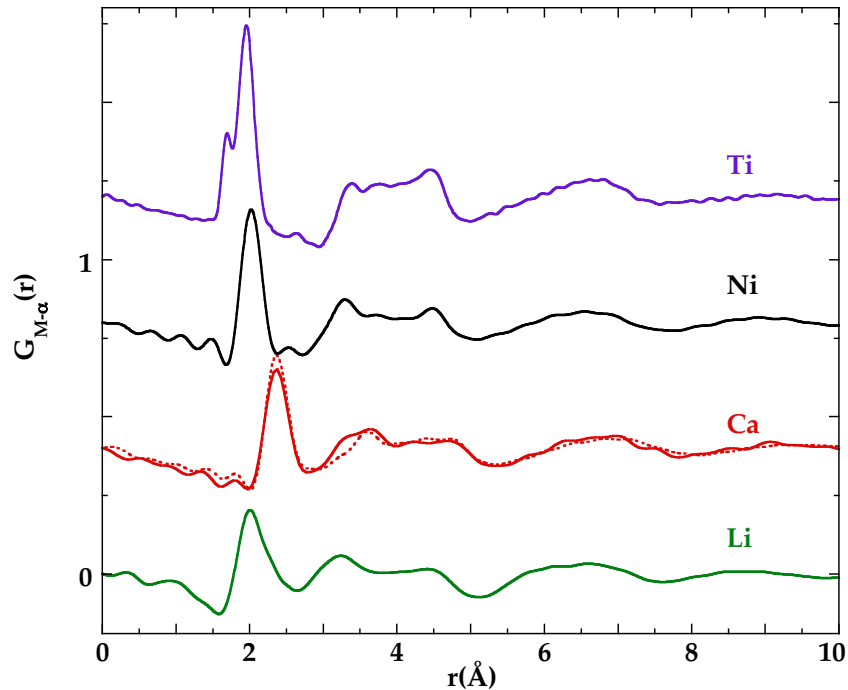
**Figure 20:** Differential correlation functions obtained for a  $K_2TiSi_2O_7$  glass containing  $^{46}Ti$  isotopes (top curve) and  $^{48}Ti$  isotopes (middle curve) compared with the first difference functions ( $^{46}Ti$ - $^{48}Ti$ , lower curve) for Ti. Insert shows the  $TiO_5$  site. The figure is adapted from [129].

Some examples of first difference functions obtained by NDIS for cations in silicate and aluminosilicate glasses are presented in figure 21 [131]. Important similarities exist in these functions, regardless of the cation concentration (*e.g.*, 5.9 at.% for Ni in  $Ca_2NiSi_3O_9$  [132] vs 14.3 at.% for Li in  $LiAlSiO_4$  [133]) or the glassy matrix (*e.g.*, Li in a silicate,  $Li_2Si_2O_5$  [134] or an aluminosilicate,  $LiAlSiO_4$ ). Structural oscillations are discernible up to 10 Å in  $G_{M\alpha}(r)$ , functions, which indicates a cationic arrangement very well defined at medium range distances.

All  $G_{M\alpha}(r)$  functions have a first sharp peak that results from the first shell of oxygen neighbors, indicating very well defined cationic sites in glasses. These sites present cation-oxygen distances and coordination numbers that may be similar to those observed in compositionally equivalent crystals, often with a low coordination number and a small radial disorder (Li at the center of a tetrahedral sites, Ti at the center of a pyramidal site). However, cations with higher field strength have lower coordination numbers in glasses compared to crystals. This is the case of  $Ca^{2+}$  (coordination number 8



in the  $\text{CaNiSi}_2\text{O}_6$  crystal and coordination number 6 in the  $\text{Ca}_2\text{NiSi}_3\text{O}_9$  glass) and  $\text{Ni}^{2+}$  (coordination number 6 in the  $\text{CaNiSi}_2\text{O}_6$  crystal and coordination number 5 in the  $\text{Ca}_2\text{NiSi}_3\text{O}_9$  glass).



**Figure 21:** Comparison of first difference functions,  $G_{M-\alpha}(r)$  for Ti in  $\text{K}_2\text{TiSi}_2\text{O}_7$ , Ni and Ca in  $\text{Ca}_2\text{NiSi}_3\text{O}_9$  (solid curve) and Ca in  $\text{CaSiO}_3$  (dashed curve), Li in  $\text{LiAlSiO}_4$  (from top to bottom). The figure is adapted from [131].

The effects of radial disorder can also be quantified by NDIS. The main cation-oxygen correlations show standard deviations which are similar for all glasses,  $\sim 0.1 \text{ \AA}$ . Very well resolved site geometries are found by using extended  $Q$ -ranges. Good contrast of Ti isotopes allowed the deconvolution of two Ti-O distances separated by  $0.3 \text{ \AA}$  in  $\text{K}_2\text{TiSi}_2\text{O}_7$  glass [129]. Site distortions were also assessed in the case of Li [133] [134][135]. Lithium is always four-fold coordinated in the oxide glasses, but differences are observed. The local environment around Li in aluminosilicate glasses is strongly distorted (3 O at  $2.02 \text{ \AA}$  and 1 O at  $2.32 \text{ \AA}$ ) with a stronger distortion and a larger average distance than for silicates. RMC modeling showed that the  $\text{LiO}_4$  tetrahedra share edges with the  $\text{AlO}_4$  tetrahedra in the  $\text{LiAlSiO}_4$  glass, which involves short distances (Si, Al)- Li ( $\sim 2.6$ - $2.7 \text{ \AA}$ ) and long Li-O distances. These distances and the Li site distortion in  $\text{LiAlSiO}_4$  are related to the role of Li as charge compensator in aluminosilicates, unlike a network modifying role in silicates where  $\text{LiO}_4$  and  $\text{SiO}_4$  tetrahedra are sharing corners. These data replicate those observed in compositionally close crystals and show that the local geometry of the Li site reflects important differences in the structural organization at longer distance. Asymmetric

distribution also exists for Ca and Ni: the  $G_{M\alpha}(r)$  function presents a broad contribution at large- $r$  values, though an exact determination is difficult.

#### 6.4 Cationic arrangement at medium range distances

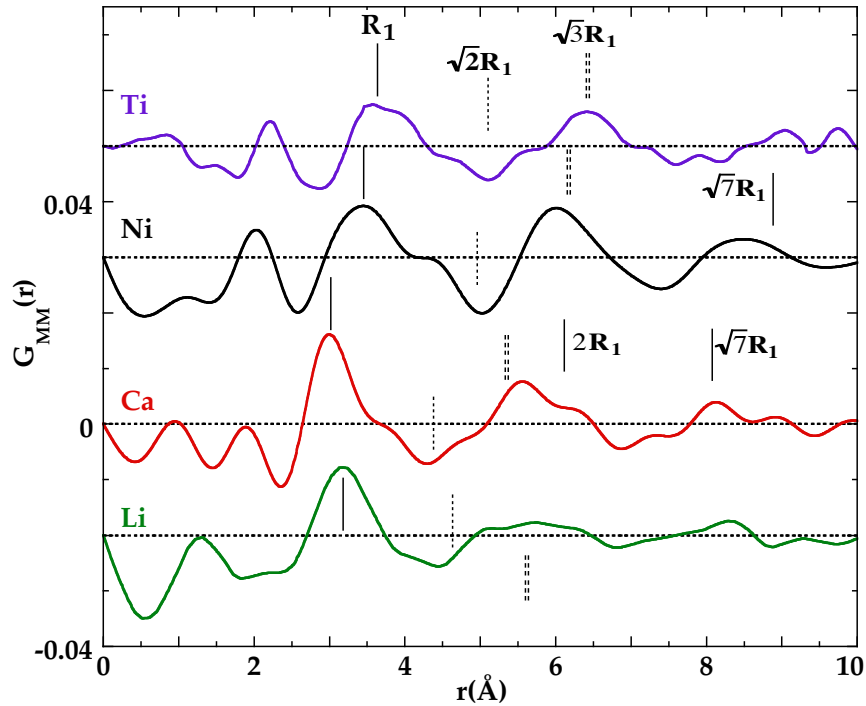
Between 3 and 5 Å, all  $G_{M\alpha}(r)$  functions present several contributions related to second and further neighbors (figure 21). These peaks are close to those observed in compositionally equivalent crystals, which indicate that the glass structure retains some structural features of crystals. However, the presence of contributions beyond 5 Å in crystals is contrary to a model of microcrystallites [136]. Contrary to crystals, there is a structural deficit around 5-6 Å for all the studied cations. Difference functions obtained by AXRD exhibit the same lack of correlations (*e.g.* for Sr in silicate glasses [137]).

Beyond 5 Å, large contributions centered at 7 and 9 Å are observed and are not comparable to the distances in crystals. The distance at 5 Å can therefore be regarded as the size limit of the structural organizations that are similar in crystals and glasses. However, a large order persists beyond 5 Å as can be found by calculating a second difference by NDIS or by MD calculations .

#### 6.5 Non-homogeneous distribution of cations

Second-order difference functions (see section 4.1) have been obtained for Ti [129], Ni [132], Ca [138] and Li [134] in silicate glasses [139]. These functions reflect the distribution of cations in the glassy network and reveal significant similarities. Figure 22 shows the well-defined  $M$ - $M$  correlation functions.

The presence of a first short cations-cation distance indicates a non homogenous distribution of these elements in the glass structure as a homogeneous distribution consisting of a compact arrangement of spheres would give a first cation-cation distance at  $\sim 6$  Å ( $R_{MM} = (6 \times 0.63 / \pi \rho_0 c_M)^{1/3}$ ). In  $\text{CaSiO}_3$  glass, it was concluded that nearest neighbor Ca–Ca distances can be associated with edge-sharing six-fold coordinated Ca–O polyhedra [138]. In  $\text{Ca}_2\text{NiSi}_3\text{O}_9$  glass, edge-sharing linkages are proposed between trigonal bipyramids for  $\text{NiO}_5$  sites [132]. On the other hand, the nearest neighbor Ti-Ti distance indicates corner-sharing polyhedra, charge compensated by adjacent alkalis in  $\text{K}_2\text{TiSi}_2\text{O}_7$  glass [129].



**Figure 22:** Cation-cation distribution,  $G_{MM}(r)$ , in glasses obtained by Fourier transformation of the second difference functions for Ti in  $K_2TiSi_2O_7$ , Ni and Ca in  $Ca_2NiSi_3O_9$  Ca, and Li in  $LiAlSiO_4$  (From top to bottom). The figure is adapted from [139].

The region extending up to 9-10 Å indicates a significant IRO. For all studied cations, if  $R_1$  is the first  $M-M$  distance, the second one appears close to  $\sqrt{3}R_1$  and the third close to  $\sqrt{7}R_1$ . In addition, the distance at  $\sqrt{2}R_1$ , which is characteristic of a tri-dimensional arrangement of polyhedra, is absent. These information reflect a cationic structural organization that has a strong bi-dimensional character in these glasses [138] and deviate from the completely random cationic arrangement as historically suggested by Warren [140]. Diffraction studies reveal a more ordered glass structure and the second difference function is the more convincing experimental evidence for clustering and percolation domains in silicate glass structure [141], consistent with the Modified Random Network model proposed by Greaves [142].

Similar  $M-M$  distances were observed by XRD in borate or silicate glasses containing heavy elements since the  $M-M$  pair dominates the experimental structure factors. These studies show correlations near 4.7 Å and 10 Å due to cation-cation pairs in silicate and borate glasses [143][144][145][146][147][148], on a very wide range of composition (3-65 mol% non-network former oxides). A study by AXRD at the Sr K-edge in silicate glasses has also shown Sr-Sr distances at 7 Å [137]. These heterogeneous structures are strengthened by numerical calculation such as MD [149] or RMC [150][151], which are able to reproduce cation-rich regions.

## 7. *In situ* high temperature / high pressure diffraction

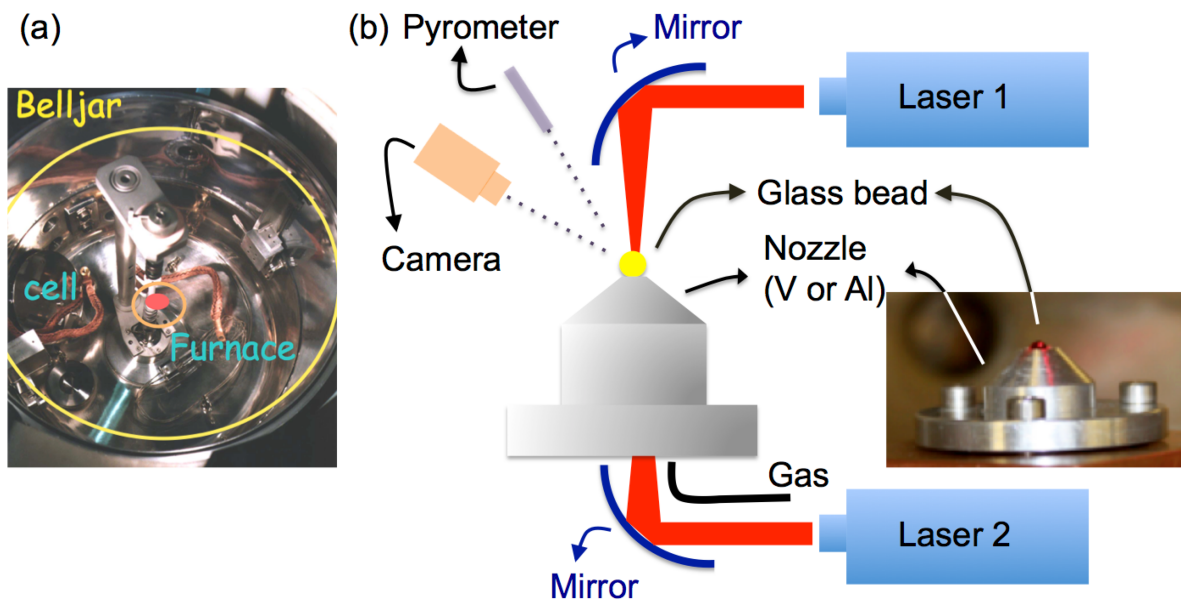
Direct studies of the structure of glasses at high temperature and high pressure address important fundamental questions and are of great interest in different domains of research such as material science or geophysics.

Structural changes induced by temperature can govern important properties or phenomena: the glass transition occurs in the supercooled liquids and experimental and simulation studies are now consistent with subtle structural reorganization at intermediate range; nucleation/crystallization are events occurring into the supercooled state and *in situ* experiments can be useful to probe transient phases; glasses were studied as analogs for melts or liquids in industrial furnaces or for natural magmas, but significant structural differences can exist between glass and melt and a detailed understanding of such differences is important to understand the behavior and properties at high temperature. Since the first extensive diffraction studies of liquids by Waseda [152][153], important experimental developments have been obtained allowing investigation of very high temperature and increasing the accuracy of diffraction data.

The structure of liquid and amorphous materials at high pressure is crucial for geophysicist, interested in silicate melts relevant to earth and planetary sciences, but also to material scientists, wishing to obtain new materials having novel properties. *In situ* investigation is mandatory because pressure-induced modifications, such as coordination changes, are usually reversible.

### 7.1 High temperature experimental techniques

In a ND experiment, vanadium can be used as a resistive element since this material has mainly an incoherent scattering and gives negligible Bragg peaks. Using several sheets of vanadium as shielding, temperatures up to  $\sim 1200^\circ\text{C}$  can be reached, just before softening of vanadium (figure 23.a). The advantage of such a furnace is that large sample volume can be used and measurements are carried out in high vacuum, minimizing statistical noise. Samples are contained in silica tube containers (e.g., for chalcogenide glasses) or in vanadium cells (e.g., for oxide glasses). Some commercial heating devices are available also in synchrotrons, providing controlled atmospheres. However, these furnaces give access to a limited range of temperature ( $<1500^\circ\text{C}$  at best), which prevents the investigation of refractory materials or liquids melting at very high temperatures.



**Figure 23:** (a) Picture of a vanadium furnace positioned inside the belljar of the 7C2 diffractometer at LLB (Saclay, France). (b) Schematic representation of an aerodynamic levitation setup used for diffraction experiments on a neutron source or a synchrotron. The glass sphere is levitated by a gas jet and heated using two lasers (from top and bottom to reduce thermal gradient) in a neutron source or a synchrotron.

In large facilities (neutron sources or synchrotrons), levitation techniques became widely available during the past twenty years. Various experimental set-up to levitate a sample have been developed and were reviewed by Henet [154]: electromagnetic levitation (EML) [155], electrostatic levitation [156], acoustic levitation [157] and gas flow either as gas film levitation [158] or aerodynamic levitation [159][160]. They are containerless methods useful to avoid heterogeneous nucleation from the cell walls or contamination between the sample and the container. The technique is also useful to extend the glass domain and explores the structure of glass compositions that are not quenchable in crucibles. The aerodynamic levitation (CNL, conical nozzle levitation) is the most popular tool [161] and consists in the levitation by a gas jet (usually argon) of a glass bead placed on a levitator composed of a water cooled conical nozzle (figure 23.b). Using a CO<sub>2</sub> or YAG laser heating, temperatures up to 3000 °C can be reached. Since nucleation is hindered due to the lack of interfaces with a container, supercooled liquids can be investigated few hundred degrees below the melting point. The sample bead is small (few mm in diameter) and only partially interacting with the incoming radiation, so a very low experimental and stable background is required. Using neutron sources, measurement times are typically several hours, requiring a good stability of the bead in the gas jet. Using synchrotrons, time resolved experiments are possible since diffractograms are acquired in a few ms with good counting statistics. A major drawback is the volatilization that can occur and experimenters must be attentive that the evaporation rate remains extremely low for the time scale of the experiment.

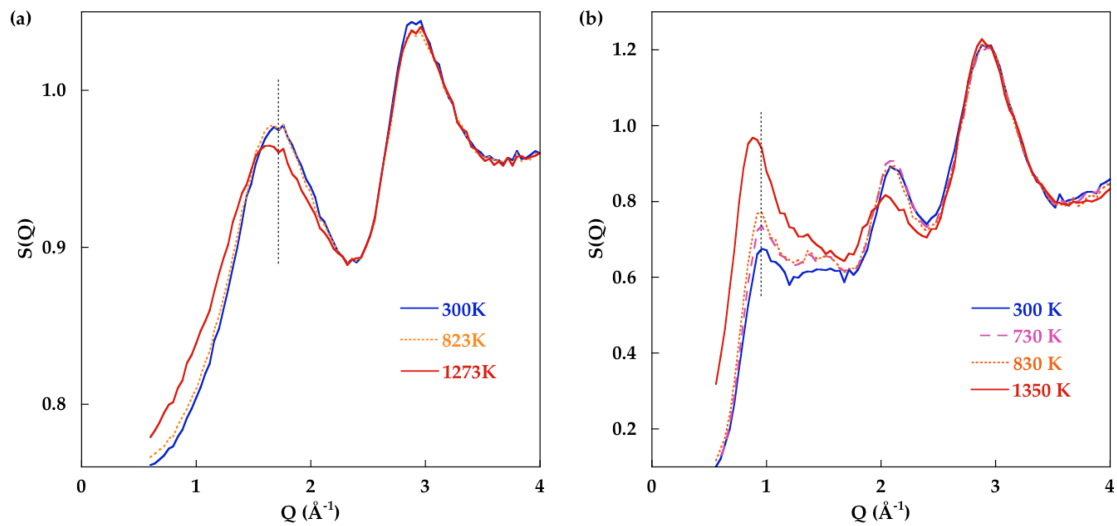
## 7.2 Case studies of temperature-induced modifications

### 7.2.1 Temperature evolution of the low- $Q$ features

The FSDP (see section 6.1) in silica decreases in amplitude up to 1036 °C as expected [162][163] and as observed for the other peaks, with a normal Debye-Waller behavior. This is in contrast to the anomalous temperature dependence of the FSDP in oxide and chalcogenide glasses [98]. This normal behavior for silica is associated with the nearly zero thermal expansion coefficient and the dominant effect of thermal vibrations.

The position of the FSDP sometimes shifts to lower- $Q$  values with increasing temperature as shown in figure 24a for a 15Na<sub>2</sub>O-10CaO-75SiO<sub>2</sub> glass (window glass composition) where the  $Q_1$  peak position is shifted from 1.72 Å<sup>-1</sup> in the glass to ~1.62 Å<sup>-1</sup> in the liquid at 1000 °C [164]. But this does not necessarily imply an important change at intermediate range. Indeed, thermal expansion (decrease of the density) has a similar effect, since the third power of  $Q_1$  scales inversely with the volume (see section 6.1.3).

The FSDP increases in intensity in glasses (*e.g.* As<sub>2</sub>Se<sub>3</sub> up to the glass transition temperature,  $T_g$  [82]) and even persists in the liquid state. This is remarkably evident in alkali silicate melts. In K<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, the first peak at  $Q_1 = 0.97$  Å<sup>-1</sup> in the neutron structure factor presents drastic changes when temperature exceeds  $T_g$  (figure 24.b), with a marked increase in intensity [83]. RMC modeling indicates that this peak has important contributions from the partial functions involving oxygens (mainly BO-BO and Si-BO correlations while BO-NBO and Si-NBO have anti-phase contributions, where BO and NBO are bridging and non-bridging oxygen anions, respectively). This peak is related to the structural organization of the silicate network supporting the concept of cation channels.

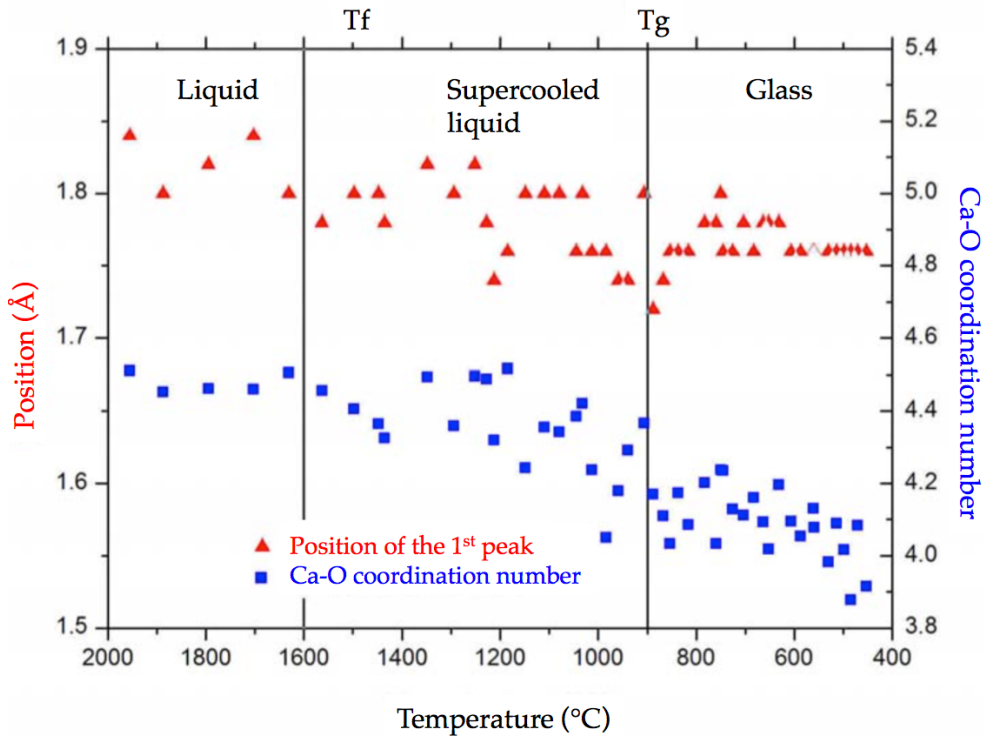


**Figure 24:** (a) Evolution of the low- $Q$  features in the neutron structure factors for a  $15\text{Na}_2\text{O}-10\text{CaO}-75\text{SiO}_2$  glass/melt showing the shift of the first peak towards lower  $Q$  values. The figure is adapted from [164]. (b) Evolution of the low- $Q$  features in the neutron structure factors for a  $\text{K}_2\text{Si}_2\text{O}_5$  glass/melt showing the dramatic increase in the intensity of the first peak. Data were obtained using a Joule vanadium furnace on the 7C2 diffractometer at LLB (Saclay, France). The figure is adapted from [83].

### 7.2.2 Evolution of short range order with temperature

The pioneering diffraction works using levitation were focused on investigation of refractory materials such as  $\text{Al}_2\text{O}_3$  [165][160]. They revealed a decrease of the Al coordination number on melting. However the  $Q$ -range and counting statistics were very limited and the neutron/x-ray diffraction were recently revisited [29], taking advantage of the experimental advances and the development of new detectors. In this new study, they also combined their diffraction data with RMC modeling and they evidenced that  $\text{AlO}_4$  and  $\text{AlO}_5$  units dominate the melt, in an approximate ratio of 2:1. Al-O-Al connections are dominated by corner-sharing but a significant amount of edge-sharing exists ( $\sim 16\%$ ).

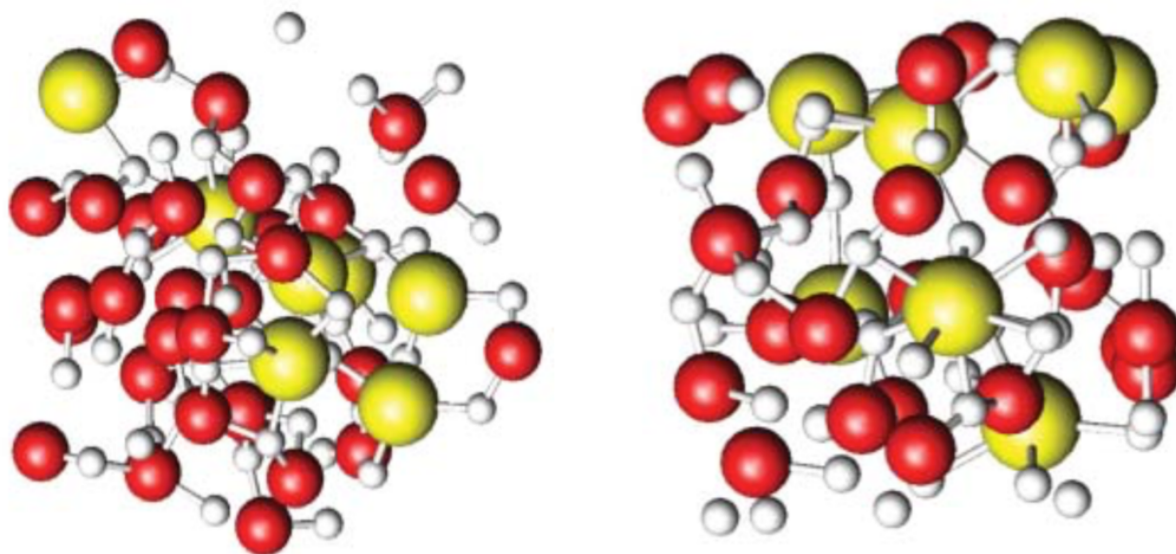
The structure of  $(\text{CaO})_x(\text{Al}_2\text{O}_3)_{1-x}$  glasses and liquids have been widely studied by CNL [166][167][168][169]. Coupled with MD simulations [166][167], ND and XRD measurements indicate that Al is predominantly in tetrahedral position, with  $\sim 20\%$  of fivefold coordinated Al at  $x=0.33$  and fewer  $\text{AlO}_5$  units as the CaO content decreases. Ca is predominantly sixfold coordinated in distorted octahedra but with a broad range of coordination environments (figure 25). Another study agrees with  $\text{AlO}_4$  tetrahedra but found a lower coordination Ca-O number of  $\sim 5$  in the melt [168]. This discrepancy results from different fitting criteria (cut-off distance for instance) and the difficulty in separating the Ca-O pair from the overlap of other contributions. It is also found that the structure for the eutectic liquid (64mol% CaO) does not change significantly with temperature between 1600 °C and 1970 °C.



**Figure 25:** Evolutions of the position of the Al-O peak in the pair distribution functions obtained by neutron and x-ray diffraction and the average Al-O coordination number upon cooling a liquid  $\text{CaAl}_2\text{O}_4$  from 1900 °C. The figure is adapted from [169].

HE-XRD has been used to investigate the liquid-liquid (L-L) transition between two forms of  $\text{Y}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$  glass with low-density (LD) and high-density (HD) [170]. They have associated structural changes with the onset of the L-L transformation that affects the Al and Y environment. The low and high density configurations calculated by MD simulations are shown in figure 26 and these models exhibit changes that match the difference in the experimental diffraction patterns. The main change in structure on liquid-liquid transition is not an Al coordination change but rather an increase in IRO seen as changes in the coordination polyhedra of  $\text{Y}^{3+}$  and in connectivity and arrangement of Al and Y polyhedra [171][172].

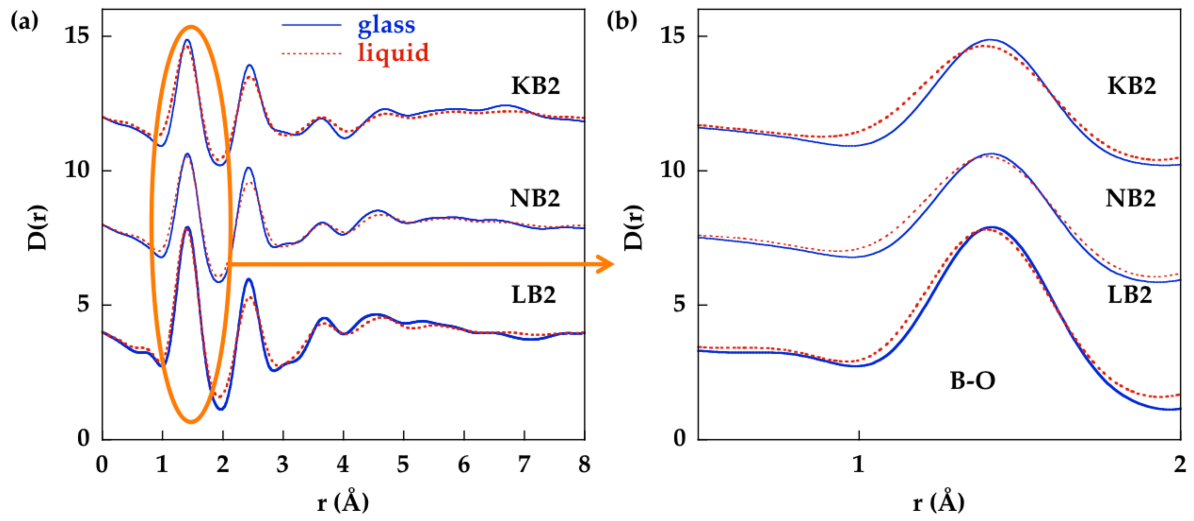




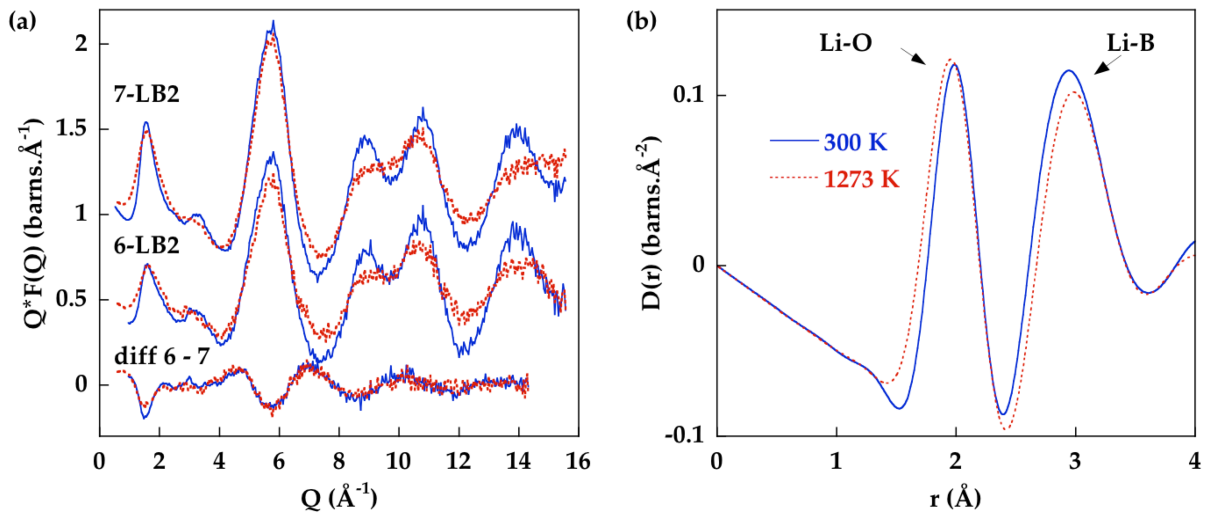
**Figure 26:** Possible configurations for HD (left) and LD (right) glasses quenched from  $Y_2O_3-Al_2O_3$  liquids obtained by RMC modeling of the neutron and x-ray diffraction data. Reprinted from [172], Copyright (2006), with permission from the Royal Society of Chemistry.

AXRD has been rarely used to investigate glass/melt modifications. However, this technique has been combined with CNL to investigate the liquid structure of  $Y_2O_3$  [173]. The Y-O coordination of 6-7 and the Y-Y coordination of  $\sim 12$  imply the preservation of the close packing existing in the high-temperature polymorph. An unusually sharp main diffraction peak suggests a high degree of chemical order.

In alkali borate glasses, boron atoms can be present in triangular or tetrahedral sites. Using high resolution neutron diffraction, a detailed analysis of the first peak in real space reveals two different B-O nearest-neighbor distances at 1.37 Å and 1.47 Å, corresponding to  $BO_3$  and  $BO_4$  units, respectively (Swenson 1995). In pure  $B_2O_3$  melt, the temperature-induced structural evolution has been described, using *in situ* neutron/x-ray diffraction, as a gradual opening of boroxol rings above  $T_g$  [174][121]. The structural changes of the local boron environment have also been quantified by ND in alkali borate glasses (figure 27), showing a partial conversion of  $BO_4$  units present in the glass to  $BO_3$  units in the melt [175][176]. This conversion implies the formation of non-bridging oxygens (NBOs) and the disappearance of bridging oxygens (BOs). Using NDIS ( $^7Li/{}^6Li$  isotopic substitution), the environment around the alkali atoms was also shown to vary (figure 28). The first Li-O distance in the  $D_{Li-\alpha}(r)$  shortens by -0.02 Å in the liquid state, which is due to the shorter Li-NBO distance compared to the Li-BO ones. Therefore, a higher number of NBO is expected in the first coordination sphere of Li in liquids and the Li structural role evolves from charge compensator in the glass, associated with  $BO_4$  units, to modifier in the melt, associated with NBOs [177].

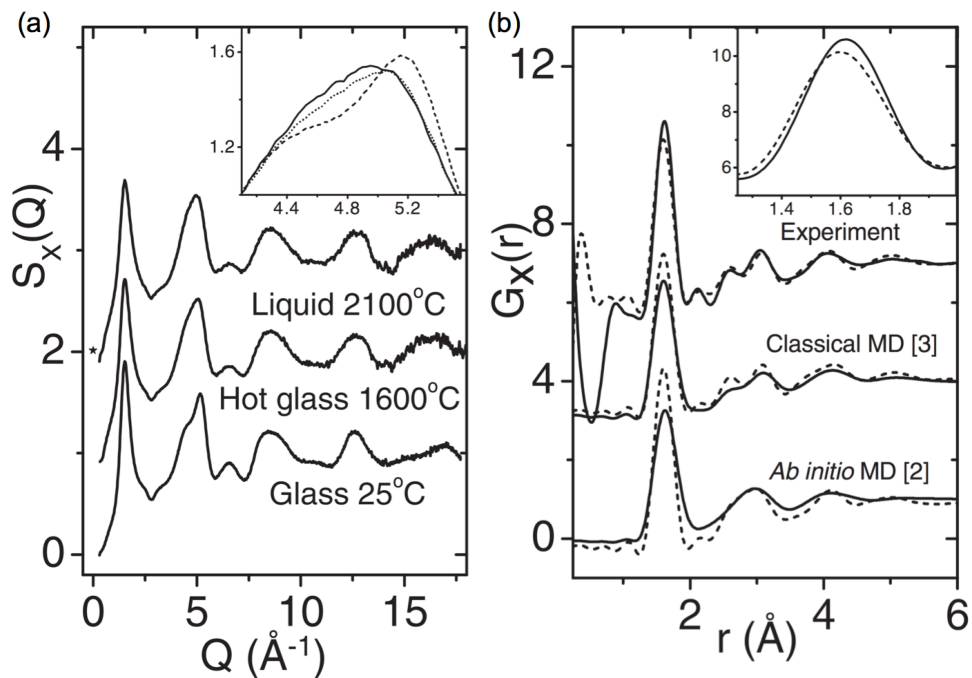


**Figure 27:** (a) Differential correlation functions,  $D(r)$ , for the glass (solid curves) and the liquid (dashed curves) for  $K_2B_4O_7$  (KB2),  $Na_2B_4O_7$  (NB2) and  $Li_2B_4O_7$  (LB2), from top to bottom. (b) Low- $r$  part of the  $D(r)$  functions showing the shift towards low- $r$  values with increasing temperature. The figure is adapted from [175].



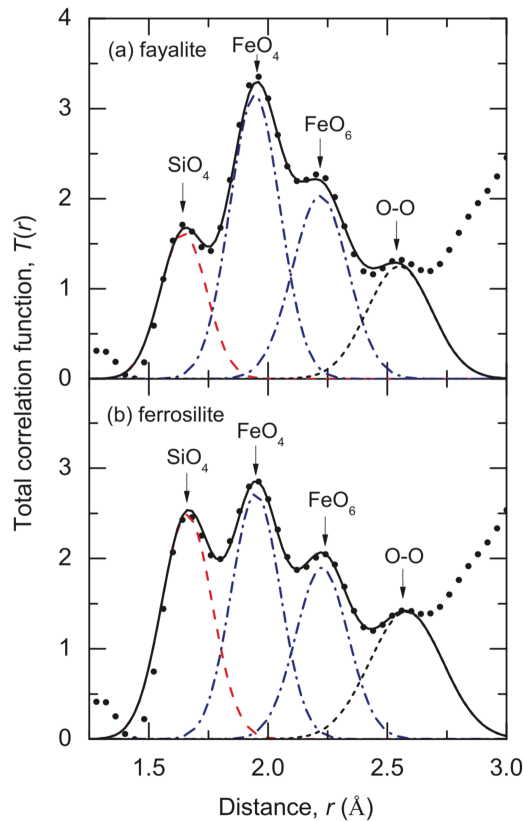
**Figure 28:** (a) Interference functions,  $Q^2F(Q) - 1$ , at 300K (solid curves) and at 1273K (dashed curves) for  $Li_2B_4O_7$  containing 7Li isotopes (7LB2) and 6Li isotopes (6LB2) and first difference function (diff 6 - 7) extracting the Li-centered partial functions. (b) First difference function in real space showing the shift of the first Li-O bond distance towards lower  $r$ -values in the liquid state. The figure is adapted from [177].

In  $SiO_2$ , the temperature has little effect on the  $SiO_4$  tetrahedra that remain the main structural units in silicate melts, with a coefficient of thermal expansion of the Si-O bond estimated by ND at  $(2.2 \pm 0.4) \times 10^{-6} K^{-1}$  [178]. The  $D(r)$  function of silica shows a small decrease of the Si-O-Si mean bond angle and an expansion of the network between 5 and 9 Å (figure 29), but an important IRO persists in the liquid state [179].



**Figure 29:** (a) Experimental x-ray structure factors for  $\text{SiO}_2$ . Insert: second peak emphasizing the main changes between the glass (dotted curve) and the liquid (solid curve). (b) Top curves: experimental x-ray correlation functions for the glass (dashed curve) and the liquid (solid curve). Middle curves: classical MD simulations. Bottom curves: *ab initio* simulations. Insert: Shift in experimental data of the Si-O peak. Reprinted with permission from [179]. Copyright (2007) by the American Physical Society.

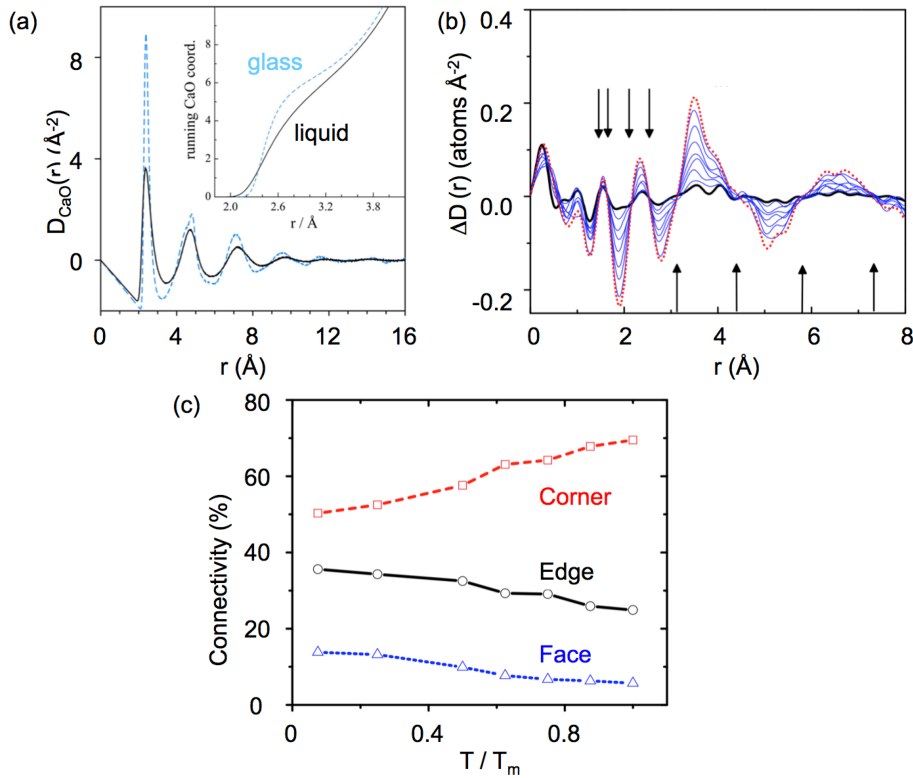
In silicate glasses, substantial changes in cation coordination number are important in order to understand melt properties such as melt/crystal partitioning, transport, ionic conduction ... In the binary  $\text{MgO-SiO}_2$  system, the average Mg-O coordination numbers decrease on cooling from  $\sim 5.2$  in the liquid to 4.5 in the glass, using *in situ* XRD and RMC fitting [180]. This change in structure allows the authors to conclude that the distorted magnesium percolation domains occur in liquids with lower MgO contents compared to glasses. The structure of iron-bearing silicates glasses was measured using HE-XRD combined with laser-heated aerodynamic levitation [181]. The technique is particularly well-suited to investigate such liquids as certain compositions ( $\text{Fe}_2\text{SiO}_4$ ) are not quenchable and their structure can only be studied *in situ*. The Gaussian fit of the correlation function indicates two Fe-O distances at 1.93 Å and 2.20 Å (figure 30), corresponding to  $\text{FeO}_4$  and  $\text{FeO}_6$  polyhedra, respectively. The coexistence of these two states has important implications for the partitioning behavior of iron or transport of magmas.



**Figure 30:** Neutron total distribution functions,  $T(r)$  (black circles), for (a) liquid fayalite  $\text{Fe}_2\text{SiO}_4$  and (b) liquid ferrosilite  $\text{FeSiO}_3$  [181]. The long dashed curve is the Gaussian fit of the Si-O peak. The chained curves are the Gaussian fits of the first and second Fe-O peaks, due to  $\text{FeO}_4$  tetrahedra and  $\text{FeO}_6$  octahedra, respectively. The short dashed curve is the approximate contribution for the O-O pair correlation. The solid curve is the sum of the fitted Gaussians. Reprinted with permission from [181]. Copyright (2013) by the American Physical Society.

### 7.2.3 Evolution of intermediate range order with temperature

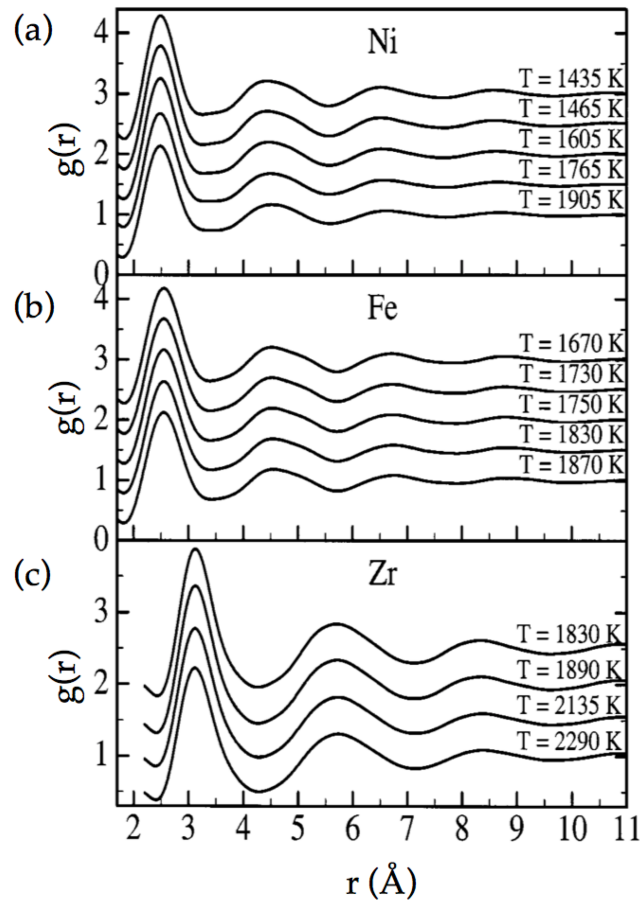
XRD measurements were performed on aerodynamically levitated  $\text{CaSiO}_3$  droplets [182]. When cooled, the presence of isobestic points is observed on the correlation functions (figure 31), reproduced by MD simulations, which are used to characterize the polymerization process. A linear behavior is evidenced in the melt while a rapid growth is observed just above  $T_g$  and near  $1.2T_g$ . The MD simulations show more edge-shared polyhedra and fewer corner-shared polyhedra in the glass model than the liquid one. Local structural information on the Ca environment has been extracted from NDIS experiments using CNL [183]. A decrease of the intensity of the first Ca-O bond peak at  $2.42 \text{ \AA}$  is observed in the liquid compared to the glass, which is attributed to the distortion of polyhedra. There is also a decrease in the average coordination number for Ca or a redistribution of Ca-O bond lengths to longer distances in the melt.



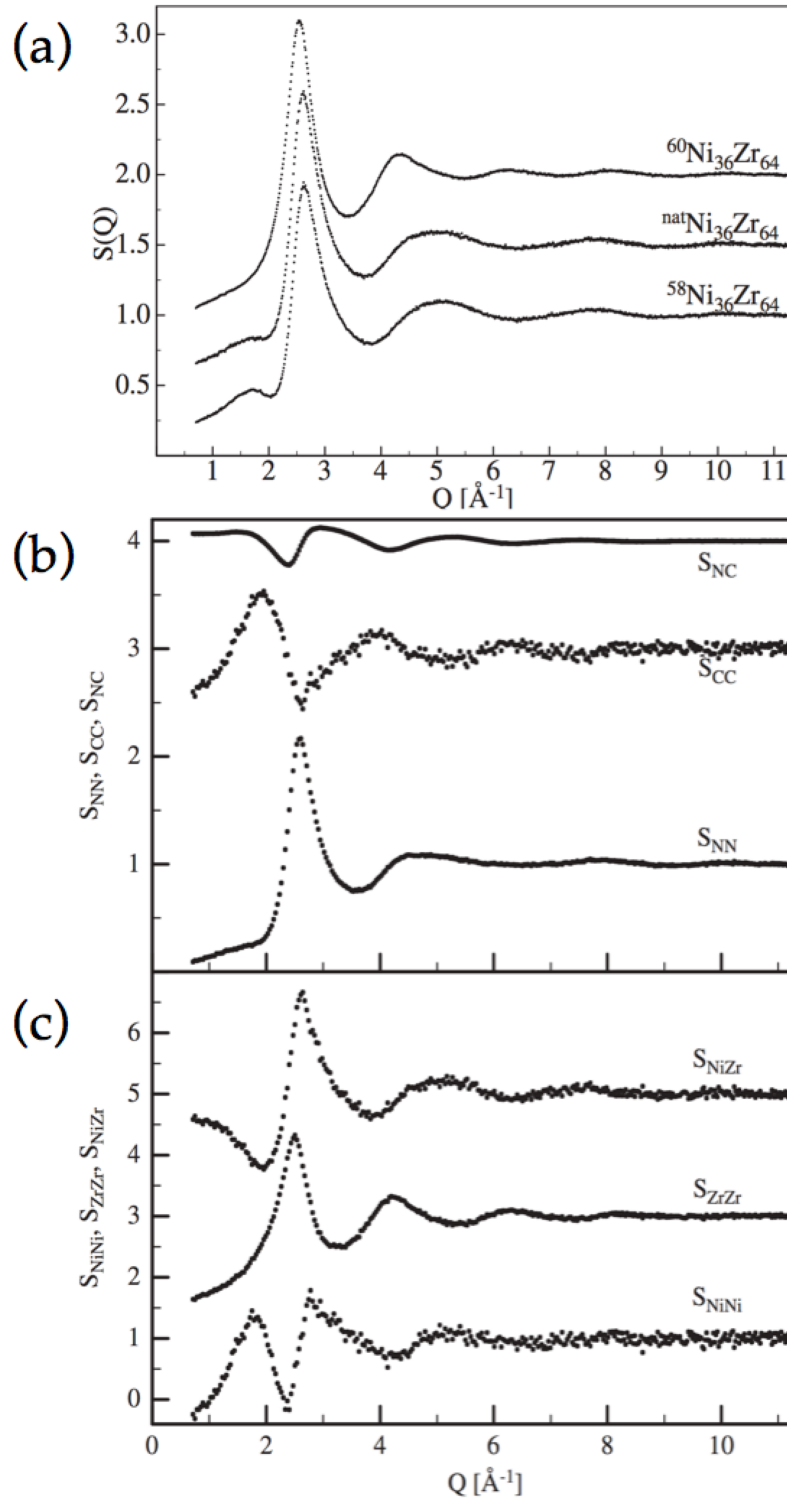
**Figure 31:** (a) NDIS data showing the Ca-O partial distribution function,  $D_{CaO}(r)$  (solid curve), for the liquid  $CaSiO_3$  compared with the MD simulation for the glass (dashed curve) and liquid (solid curve). The insert presents the Ca-O running coordination number determined by MD simulations. Reprinted with permission from [183]. Copyright (2012) American Chemical Society. (b) Difference of the x-ray correlation function,  $\Delta D(r) = D_T(r) - D_0(r)$ , where the highest temperature  $D_0(r)$  at 1900 °C has been subtracted. The isobestic points are marked with arrows. The figure is adapted from [182]. (c) Changes in the connectivity between Ca polyhedra for the liquid/glass MD models of  $CaSiO_3$  as a function of temperature. Reprinted with permission from [182]. Copyright (2010) by the American Physical Society.

The structure of metallic melts have been mainly studied using the EML environment, from the liquid state to a high undercooling [184]. In Ni, Zr and Fe metallic melts (figure 32), icosahedral short range order (ISRO) has been evidenced though larger polytetrahedral aggregates (such as dodecahedra) are prevalent in the liquid state. This ISRO appears as a split peak of the second peak in  $S(Q)$ . It is present already above the melting temperature and becomes more pronounced in the undercooled metastable state. NDIS experiments were carried out on  $Ni_{36}Zr_{64}$  alloys using Ni isotopic substitution (figure 33), which allowed the extraction of all the partial functions [185]. The EML is advantageous in the case of NDIS since large samples can be levitated, improving good counting statistics. These partials indicate a preference of Ni-Zr nearest neighbors suggesting a pronounced chemical SRO. A high nearest-neighbor coordination number of 13.9 is determined. In contrast to most melts of pure metals or of metallic alloys, ISRO was not observed in the  $Ni_{36}Zr_{64}$  melts, which could result from the large difference of the atomic radii ( $R_{Zr} / R_{Ni} = 1.29$ ). The CNL technique was also employed to measure NDIS for NiSi and NiSi<sub>2</sub> alloys [186]. Both alloys exhibit a strong tendency to

hetero-coordination within the first coordination shell. In particular, the tendency to form Si-Si covalent bonds with somewhat greater distances influences the atomic structure of the NiSi melts. The structure of complex metallic alloys has been recently investigated showing the development of the ISRO upon cooling [187][188], with important consequences for glass stability.



**Figure 32:** Neutron diffraction structure factors at different temperatures for (a) Ni melts, (b) Fe melts and (c) Zr melts. The figure is adapted from [184].



**Figure 33:** (a) Neutron diffraction total structure factors for  $^{58}\text{Ni}_{36}\text{Zr}_{64}$ ,  $^{60}\text{Ni}_{36}\text{Zr}_{64}$ , and  $^{\text{nat}}\text{Ni}_{36}\text{Zr}_{64}$  at  $T = 1375$  K. (b) Partial Bathia-Thornton and (c) partial Faber-Ziman structure factors. Reprinted with permission from [185]. Copyright (2009) by the American Physical Society.

Rapid changes in the atomic structure of liquid tellurium has been shown by HE-XRD [189]. The structural evolution allows a better understanding of the density anomaly and the semiconductor-metal (SC-M) transition. Twofold and threefold local coordination coexist with a majority of the

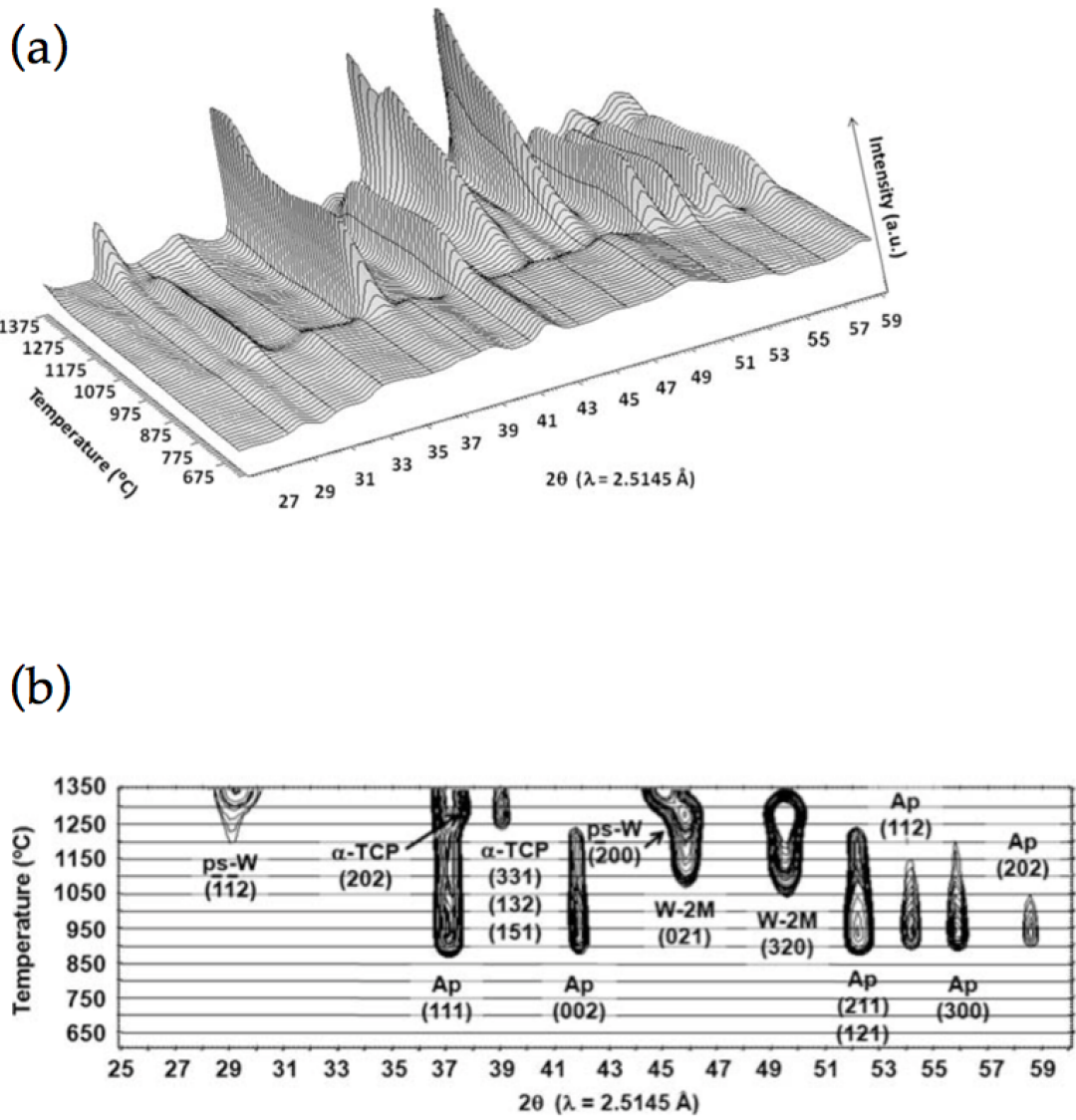
formers which are slightly more present at lower temperature. The density maximum near the melting point reflects the temperature-dependent changes in chain lengths (longer chains at low  $T$ ), ring distribution (larger rings at low  $T$ ) and cavity volumes that are more abundant but with smaller sizes at low  $T$ . Cavities in the interchain regions at low temperatures explain the density minimum. The broadening of bond angle distribution at high temperatures is related to the SC-M transition.

ND and HE-XRD measurements have been carried out on  $\text{TeX}_4$  ( $X=\text{Cl}, \text{Br}$ ) liquids, in which chalcogens have covalent bonds and halide have ionic bonds [190]. Tellurium is present in tetrahedral coordination with Cl or Br. The intense FSDP suggest a pronounced intermediate range structure that consists of  $\text{Te}_2\text{X}_8$  dimers, different to the monomeric gas and the tetrameric solid:  $\text{Te}_4\text{X}_{16}$  (solid)  $\rightarrow$   $\text{Te}_2\text{X}_8$  (liquid)  $\rightarrow$   $\text{TeX}_4$  (gas). A broader composition range of  $\text{Te}_{1-x}\text{Cl}_x$  liquids, outside the glassy domains, has been investigated by ND [191]. Contrary to Cl-rich compositions, the ND structure factors of Te-rich liquid alloys exhibit a weak FSDP due to a chain network structure. As the Cl content increases, the structure progressively evolves from a chain network to a molecular-like behavior, the final member being  $\text{Te}_2\text{Cl}_8$  dimers.

#### **7.2.4 Thermodiffraction**

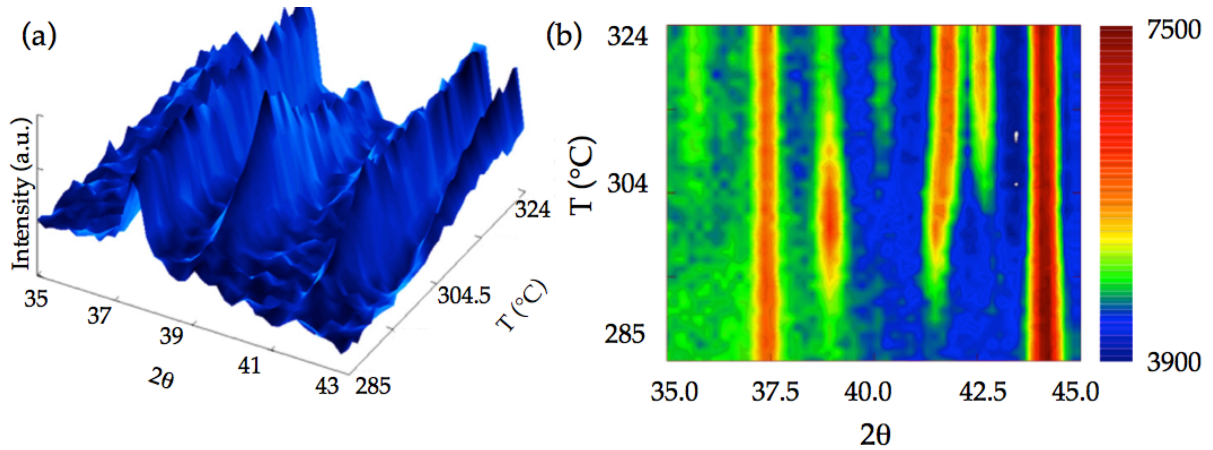
Thermodiffraction is time-resolved diffraction acquisition at high temperatures. Diffractograms can be completed in up to  $80^\circ$  in 2.5 min acquisition times with ND [192] and in few ms with XRD. Such measurements are particularly useful to follow the real-time evolution of non-isothermal nucleation. In a bioactive glass  $\text{CaSiO}_3\text{-Ca}_3(\text{PO}_4)_2$ , the growth and disappearance of the successive phases can be easily visualized on a 2D map (figure 34.b), which is the projection of the 3D thermodiffractograms (figure 34.a). The crystallization sequence with the domains of the different crystalline phases is clearly identified.





**Figure 34:** (a) Evolution with time of non-isothermal crystallization of a  $\text{CaSiO}_3\text{-Ca}_3(\text{PO}_4)_2$  glass showing neutron diffraction data collected from 600 to 1375 °C at 5 °C min<sup>-1</sup>. (b) 2D projection of the thermodiffractograms in (a). The crystallization events (growth or collapse) are directly visualized (Ap, Ca-deficient apatite; W-2M, wollastonite-2M; ps-W, pseudowollastonite;  $\alpha$ -TCP,  $\alpha$ -tricalcium phosphate). Reprinted from [192], Copyright (2009), with permission from Elsevier.

A complex crystallization sequence has been demonstrated by neutron thermodiffraction of the  $\text{Ag}_x(\text{Ge}_{0.25}\text{Se}_{0.75})_{1-x}$  glasses with  $x = 15, 25$  [193]. In agreement with the Ag-Ge-Se phase diagram, the primary crystals are the two stable phases, *i.e.*,  $\text{Ag}_8\text{GeSe}_6$  and  $\text{GeSe}_2$ . However, *in situ* measurements highlight an additional phase ( $\text{Ag}_2\text{GeSe}_3$ ), which is signaled by peaks located at 39° and 50.2° (figure 35). This phase is unstable and decomposes upon further heating, giving a new phase of  $\text{Ag}_{10}\text{Ge}_3\text{Se}_{11}$  composition along with the stable  $\text{GeSe}_2$  phase.

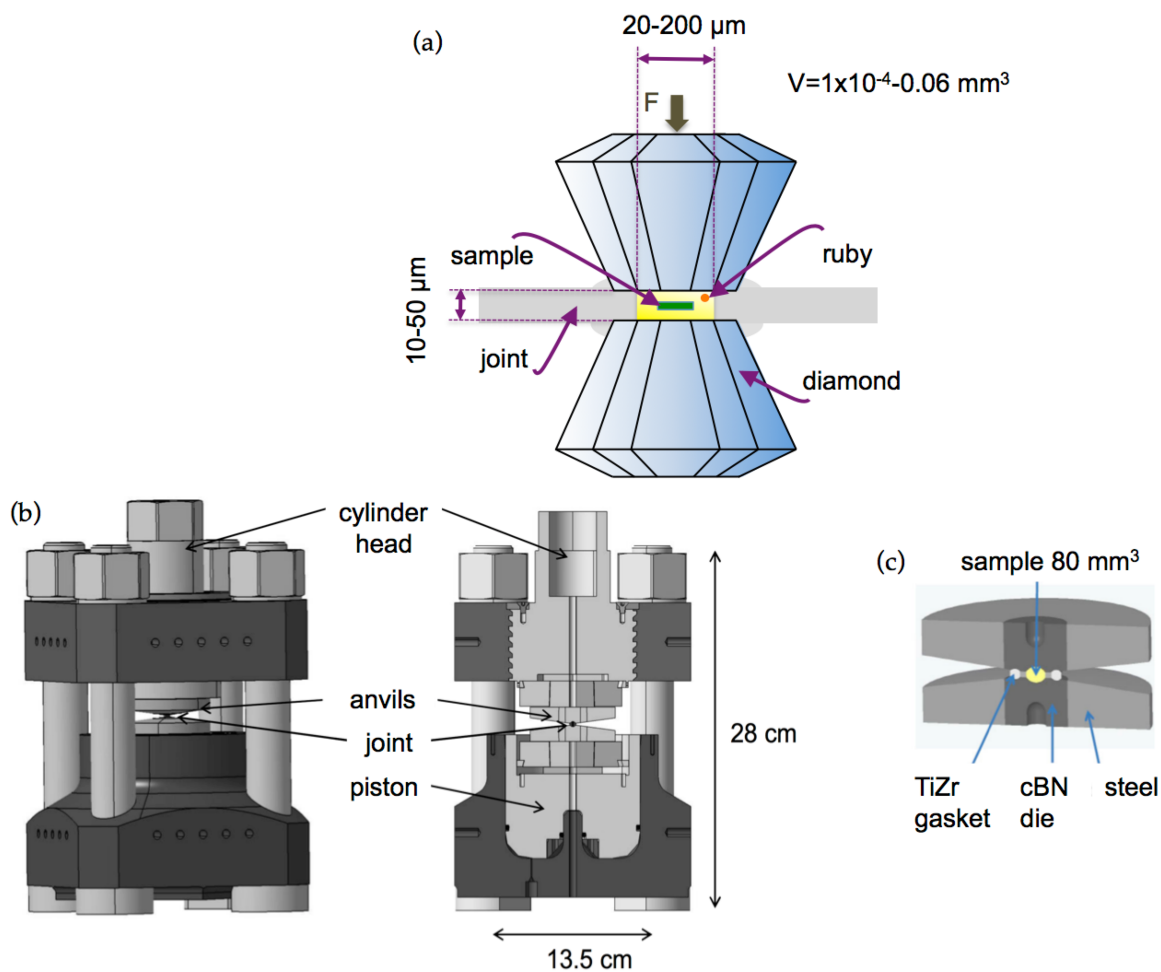


**Figure 35:** (a) Neutron thermodiffractograms for the  $\text{Ag}_{25}\text{Ge}_{18.75}\text{Se}_{56.25}$  glass. Graphs show a peak at  $2\theta \approx 39^\circ$ , characteristic of the intermediate phase  $\text{Ag}_2\text{GeSe}_3$ , whose intensity appears at 285 °C and decreases above 320 °C. (b) 2D projection of the thermodiffractograms on (a) revealing the intermediate phase around 39°. The figure is adapted from [193].

### 7.3 High pressure experimental techniques

Two general pressure cells are most currently used on large facilities: the diamond anvil cell (DAC) [194] and the large volume press [195].

In the DAC (figure 36.a), the sample is squeezed between the flat parallel culets of two opposed diamonds (single crystal, sometimes specially designed) and maintained between the diamond anvils by a hole drilled in a gasket. An inflated gas membrane transmits a mechanical force to the diamond table, pressing the diamonds together and increasing the pressure in the sample chamber. Resistance heating or laser heating can be used to generate high temperature. The advantage of DAC is that diamonds are transparent to x-rays. However, to achieve high pressure, the sample size is very small ( $\sim 50 \mu\text{m}$  thick and  $< 200 \mu\text{m}$  in diameter). Note that “large volume” DAC are currently developed on neutron source (SNPD beamline at Oak Ridge, USA) to investigate disordered materials.



**Figure 36:** (a) Illustration of diamond anvil cell. (b) Illustration of V4 large volume Paris-Edinburg press. On the cutting, the vertical access for the incident beam can be seen. The figure is adapted from [196]. (c) Cross-section of opposed anvils in the PE press. The figure is adapted from [197].

Large volume apparatus (figure 36.b), Paris-Edinburgh (PE) press [198][199]), can be used for ND and XRD to achieve pressure up to 25 GPa. The PE press is composed of multi- or toroidal type anvils and a metal gasket, usually TiZr for ND as this alloy has almost null scattering (figure 36.c). A hydraulic press connected to the piston by a capillary is used to generate the force. A major advantage of PE press is that large sample volume can be compressed compared to DAC:  $\sim 100 \text{ mm}^3$  for WC anvils, with pressure limited to  $\sim 10 \text{ GPa}$ , and  $\sim 35 \text{ mm}^3$  for sintered diamond, achieving pressure up to 25 GPa [200]. As the incident beam passes through the cell assembly and the diffracted beam is usually detected in the gasket plane, the background scattering is important. Moreover, this background is pressure-dependent, resulting from the deformation of the gasket with pressure. The data correction is thus tedious as the background is hard to subtract, especially for weakly scattering samples. Another

limitation also existing for DAC is the angular exit aperture which can restrict the accessible maximum  $Q$ .

## 7.4 Case studies of pressure-induced modifications

A structural modification is usually the response to an applied pressure, modifying the properties of the material. Distinct amorphous states lead to the notion of polyamorphism or amorphous-amorphous (A-A) transition induced by pressure [201]. Considerable research using diffraction methods has been active in this topic in various glass systems, such as ice, oxides, chalcogenide or metallic alloys. The A-A transformation can be the viewable aspect of a liquid-liquid transition which could be present in the supercooled regime [202].

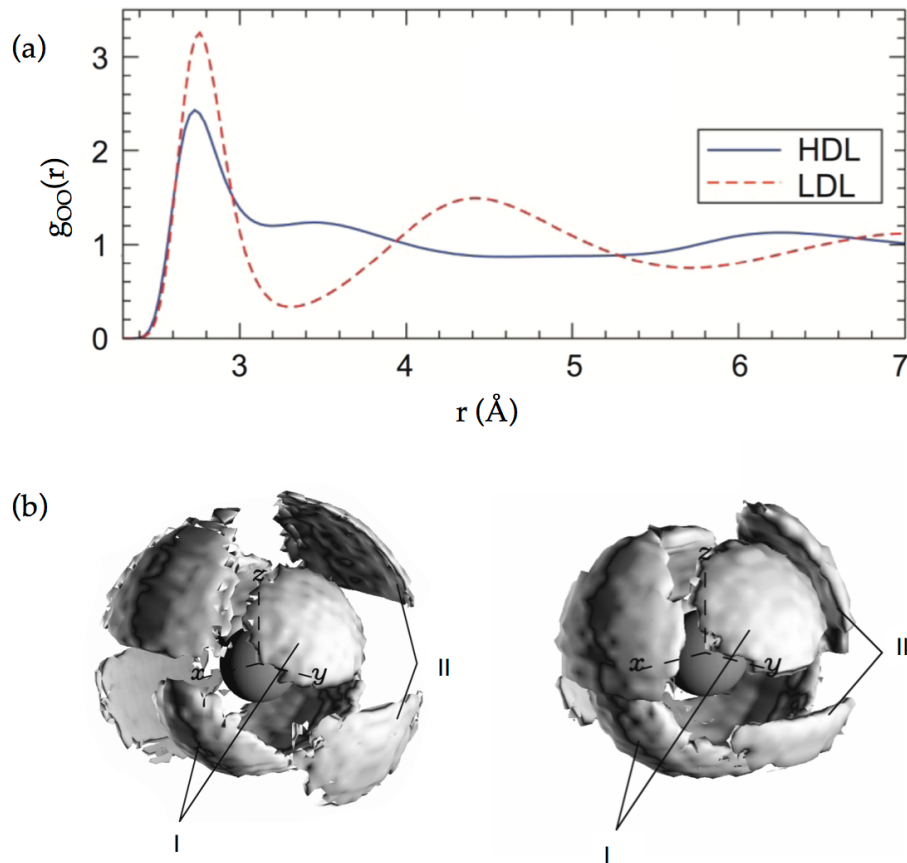
### 7.4.1 Amorphous forms of $H_2O$

The polyamorphism in water has been the subject of numerous *in situ* diffraction studies to investigate the apparent “first order-like” transition between the low density amorphous water (LDA) and the high density amorphous form (HDA). These two amorphous states have both a fully hydrogen-bonded tetrahedral network with HDA having a structure close to that of liquid water at high pressure and LDA a structure close to ice 1h (figure 13) [73]. The different structures are particularly evidenced in the  $g_{OO}(r)$  partial function determined by NDIS and combined with EPSR (figure 37.a) [73]. The O-O coordination number increases from 3.7 in LDA to 5 in HDA indicating an additional fifth interstitial water molecule in HDA in the first neighbor shell, which gives a less ordered HDA structure compared to LDA. The pressure applied to transform LDA to HDA results in the collapse of the second neighbor shell of water molecules that eventually become interstitial, as demonstrated by spatial density functions obtained from EPSR models based on the diffraction data (figure 37.b) [203]. The interpenetrating network of water molecules stabilizes the HDA structure as this state can be recovered to ambient pressure.

A third denser amorphous form of water (Very High-Density Amorphous, VHDA) has been discovered and can be differentiated from HDA by its diffraction pattern: its structure factor has a sharp first peak shifted to higher  $Q$  values compared to  $S(Q)$  for HDA. This increase in the IRO is associated with a second interstitial water molecule [204], which is confirmed in the  $g_{OO}(r)$  partial function [205].

As *in situ* studies are possible, neutron diffraction has been also used to follow the LDA  $\rightarrow$  HDA transition using the PE pressure cell [206][207]. The structure factors exhibit a decreasing peak at

1.71  $\text{\AA}^{-1}$  and a growing peak at 2.25  $\text{\AA}^{-1}$ , attributed to LDA and HDA, respectively. During the transition, changes in the position and height of the FSDP and in the position of the interstitial water molecule indicate distinct structural relaxation processes. A continuous series of metastable forms change the IRO during the transition and then structural relaxation in the second coordination shell of the LDA form appears [208][209].



**Figure 37:** (a)  $g_{OO}(r)$  pair distribution functions for HDA and LDA as obtained by EPSR. The figure is adapted from [210]. (b) Three dimensional arrangements of the oxygen atoms around a water molecule (spatial distribution functions) for HDA and LDA. The pronounced lobes render the spatial density functions for the first (I) and second (II) shells of water molecules. showing the collapse of the second O-O shell in HAD (lobes II). Reprinted from [203], Copyright (2000), with permission from the American Physical Society.

#### 7.4.2 Density driven transformation in $B_2O_3$

$B_2O_3$  glass has been investigated by XRD up to 9.5 GPa [211] and by ND up to 17.5 GPa [212]. The position of the first peak in  $S(Q)$  is linearly shifted towards high-Q values upon compression. This change indicates a reorganization of the IRO, interpreted as the break of boroxol rings below 3.5 GPa. Above 3.5 GPa, the real space function shows a change in boron coordination where  $BO_3$  units are converted to  $BO_4$  units. At 11-14 GPa, the decomposition of boroxol rings is achieved as seen in the

disappearance of the third peak in the distribution function and only the local boron conversion to  $\text{BO}_4$  takes place at higher pressure.

### 7.4.3 Polyamorphism in $\text{SiO}_2$ and $\text{GeO}_2$

$\text{SiO}_2$  and  $\text{GeO}_2$  are typical examples of 'strong', tetrahedral network glass-forming systems. The polyamorphism of these glasses correspond to an A-A transition from an open network structure based on corner-linked tetrahedra at low pressure, to a network dominated by  $\text{SiO}_6$  or  $\text{GeO}_6$  octahedra at high pressure.

These glasses were initially studied after decompression from high pressure allowing a permanent densification of the structure to be maintained [213][214][215]. Such permanently densified glasses show mainly structural changes at IRO with a decrease in the A-O and O-O distances (A=Si, Ge) due to rotation of the A-O-A bond angles and distortion of the  $\text{AO}_4$  tetrahedra [213].

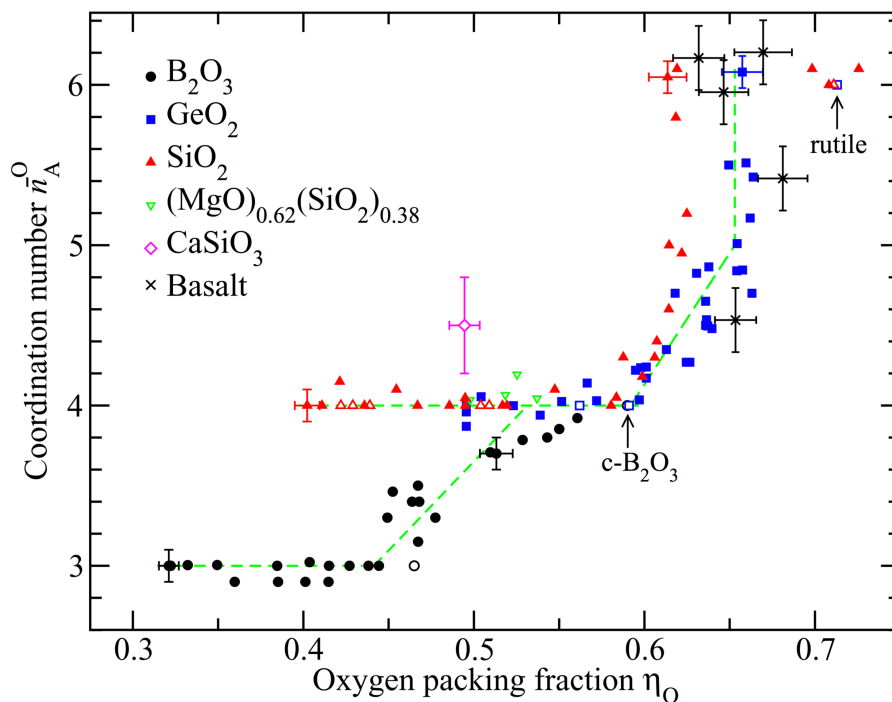
Coordination changes can only be addressed by *in situ* measurements as first demonstrated by x-ray absorption experiments [216]. The first *in situ* diffraction study has been reported using x-rays on  $\text{SiO}_2$  up to 42 GPa and has revealed a gradual increase of the mean coordination number around Si,  $n_{\text{Si}}$ , from four to six above 10 GPa [217]. In the last decade, XRD and ND were widely used to investigate the pressure-induced structural modifications in  $\text{SiO}_2$  (using XRD [218][219][220][221][222] and ND [223]) and  $\text{GeO}_2$  (using XRD [76][224][225][226] and ND [76][227][228] including isotopic substitution of Ge ( $^{\text{nat}}\text{Ge}/^{70}\text{Ge}/^{73}\text{Ge}$ ) [229]).

The structure factors for  $\text{SiO}_2$  and  $\text{GeO}_2$  are modified as the pressure is increased: the FSDP moves to higher-Q values and the principal peak becomes sharper in  $S^M(Q)$  and more discernible in  $S^X(Q)$ . These changes indicate a decrease in IRO through the shrinkage and collapse of the open network structures.

The analysis of the distribution functions allows more information on the local order to be obtained. At low pressure, the tetrahedral structure is preserved and densification proceeds via an increase in the packing of  $\text{AO}_4$  tetrahedra. The  $n_{\text{Si}}$  increases above four at  $P > 10$  GPa while the Si-O bond length does not increase initially but presents the appearance of a shoulder on its high- $r$  side. The domain of coordination change is still debated but occurs mainly in the range 10-40 GPa. The tetrahedral-octahedral change occurs at lower pressure in  $\text{GeO}_2$  by comparison with  $\text{SiO}_2$  [216][230], with a  $n_{\text{Ge}}$  increase when  $P > 5$  GPa [231]. The complete partial functions extracted from NDIS allowed the determination of the pressure dependence of the Ge-O-Ge bond angle [229]. As high coordinated  $\text{AO}_6$  species are formed, the mean coordination number for O,  $n_{\text{O}}$ , also increases.

The transition domain is not necessarily a simple mixture of four- and six-fold coordinated sites and intermediate  $AO_5$  species can coexist. However, the experimental evidence of such  $AO_5$  species has not been unambiguously proven by diffraction methods, though MD simulations consistent with experimental data advocate, for instance, for  $SiO_5$  units over the window  $P \sim 20\text{--}45$  GPa while  $SiO_6$  units dominate when  $P \gtrsim 32$  GPa [231]. Therefore,  $AO_5$  units should play a key role in the mechanism of polyamorphism.

The oxygen-packing fraction  $\eta_o$  has been proposed to rationalize the changes in the coordination number [232][233]. The mean A–O coordination number  $\bar{n}_A^O$  shows an interesting dependence with  $\eta_o$  for a large number of glassy and liquid network-forming materials (figure 38).  $BO_3$  triangles and  $AO_4$  tetrahedra show a plateau of stability ending at  $\eta_o \simeq 0.44$  and at  $\eta_o \simeq 0.59$ , respectively. At higher packing fraction, the conversion to  $BO_4$  or  $AO_6$  takes place. We can also note that  $SiO_2$  and  $GeO_2$  increase coordination at the same  $\eta_o$ . The upper limit of stability for  $AO_4$  tetrahedra corresponds to the packing fraction for a random loose packing (RLP) of hard spheres, *i.e.*  $\eta_{RLP} = 0.55\text{--}0.60$ , and  $\bar{n}_A^O$  increases rapidly as  $\eta_o$  approaches the expected packing fraction for a random close packing (RCP) of hard spheres, *i.e.*  $\eta_{RCP} = 0.64$ . At the latter packing, the transformation to an octahedral network is largely completed. Therefore network-forming motifs govern the topological ordering and can be predicted based on  $\eta_o$  behavior. The evolution of  $Q_1$  position with pressure has a common behavior with  $\eta_o$  [74].



**Figure 38:** Variation of the mean A–O coordination number as function of the oxygen-packing fraction  $\eta_o$  for oxide glasses and liquids under high pressure conditions [231].

#### **7.4.4 Chalcogenide glass GeSe<sub>2</sub>**

GeSe<sub>2</sub> is representative of chalcogenide glass in which the mechanism of pressure-driven network collapse can differ to that in oxide glasses due to the presence of edge-sharing GeSe<sub>4</sub> tetrahedra and homopolar bonds. This glass was investigated by *in situ* XRD [234] and NDIS [235][236]. NDIS is particularly useful since neutron and x-ray diffraction methods give essentially the same information due to similar scattering amplitudes for Ge and Se.

The FSDP is shifted to a larger- $Q$  value upon compression and almost vanishes at 9.3 GPa. The principal peak also moves to a larger- $Q$  value but its height increases, as the pressure dependence for GeO<sub>2</sub>. These changes were interpreted as a loss of the IRO associated with the FSDP and a dominant extended-range ordering associated with the principal peak with increasing pressure, corresponding to the transformation from a 'strong' low-density to a 'fragile' high-density glass [231].

The first average peak in the pair distribution function,  $\bar{r}$ , slightly decreases with increasing density up to  $P \sim 12.8$  GPa, while the average coordination number,  $\bar{n}$ , remains at 2.67. At higher densities,  $\bar{r}$  and  $\bar{n}$  increase to accommodate a larger number of nearest-neighbors. MD simulations indicate that, up to 8.2 GPa, the proportion of corner-sharing tetrahedra increases at the expense of edge-sharing tetrahedra, with a ratio from 1.3 to 1.7. According to MD simulations, homopolar bonds are largely present on the high coordinated Ge and Se atoms and play a key role in the density-driven structural transformations.

The pressure-induced structural modifications are continuous and occur on a broad pressure range, suggesting that densification is not an A-A transition. According to diffraction results, GeSe<sub>2</sub> glass keeps a semi-conducting behavior.

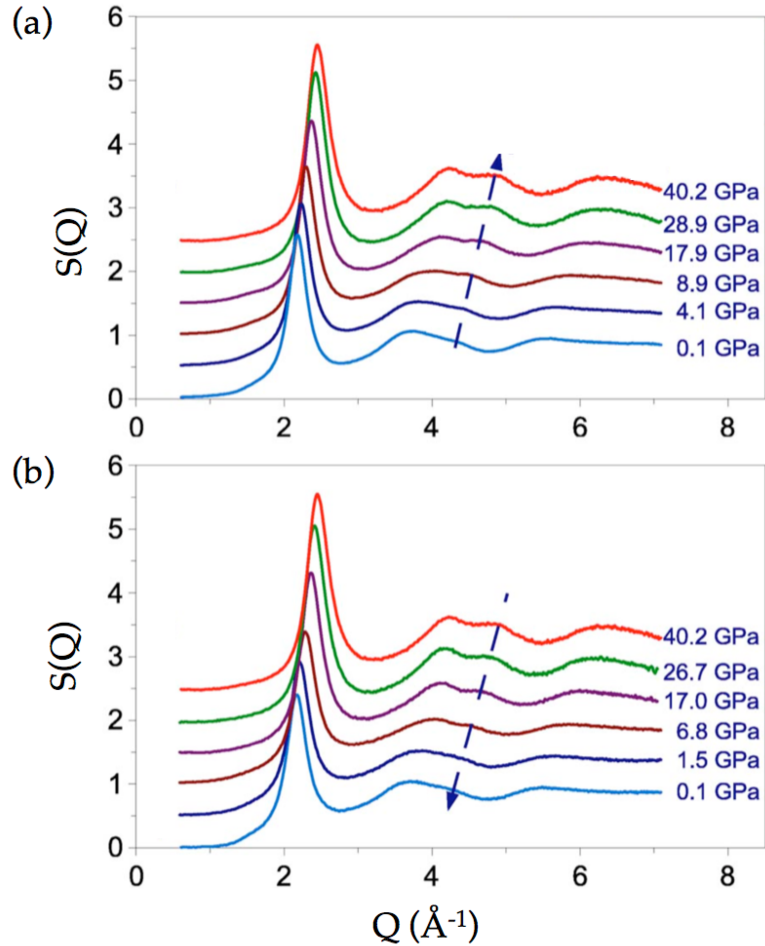
The structure of liquid GeSe<sub>2</sub> has also been studied under pressure [237], showing changes in the IRO, as reflected by changes in the FSDP on a narrow pressure range between 4.1 and 5.1 GPa. These modifications were interpreted as a continuous evolution from a two-dimensional to a three dimensional network.

#### **7.4.5 Polyamorphism in metallic glasses**

The coordination change associated with bond lengthening observed in oxide glasses (part 7.4.2 and 7.4.3) are not expected in non-directional, densely packed metallic glasses (MGs). Indeed, these materials have already a high coordination number (12-14) and are spatially compact. An *in situ* high-pressure XRD study on a La<sub>75</sub>Al<sub>25</sub> MG shows a gradual and completely reversible compression (figure



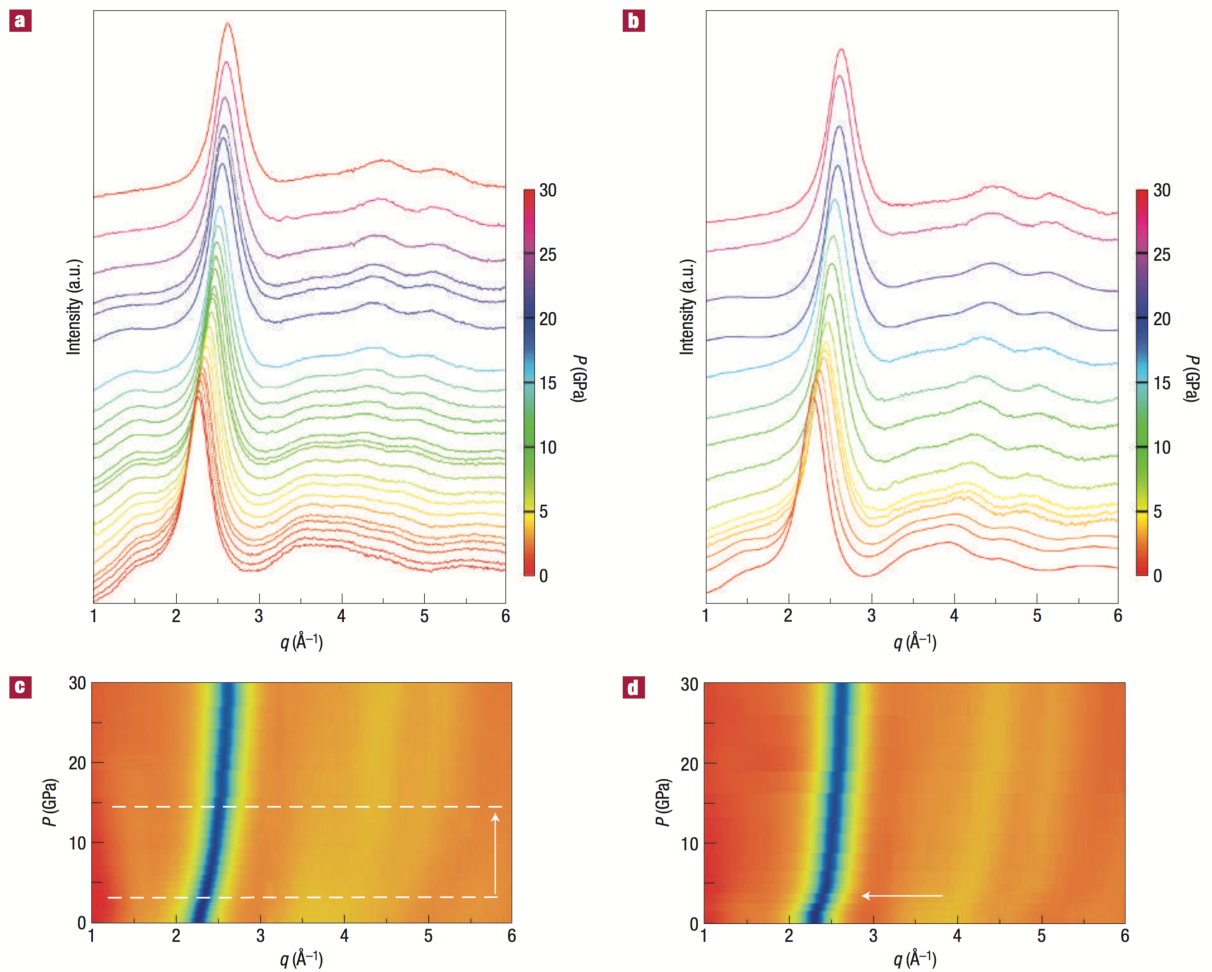
39) [238]. Based on *ab initio* MD simulations and RMC fitting, changes in atomic size ratio and coordination number were identified as a conversion of prism-type coordination to icosahedral short-range order.



**Figure 39:** *x*-ray structure factors for a  $\text{La}_{75}\text{Al}_{25}$  metallic glass at different pressures upon (a) compression and (b) decompression showing the reversibility of the changes. The dashed arrow emphasizes a shoulder that becomes more apparent with increasing pressure. The figure is adapted from [238].

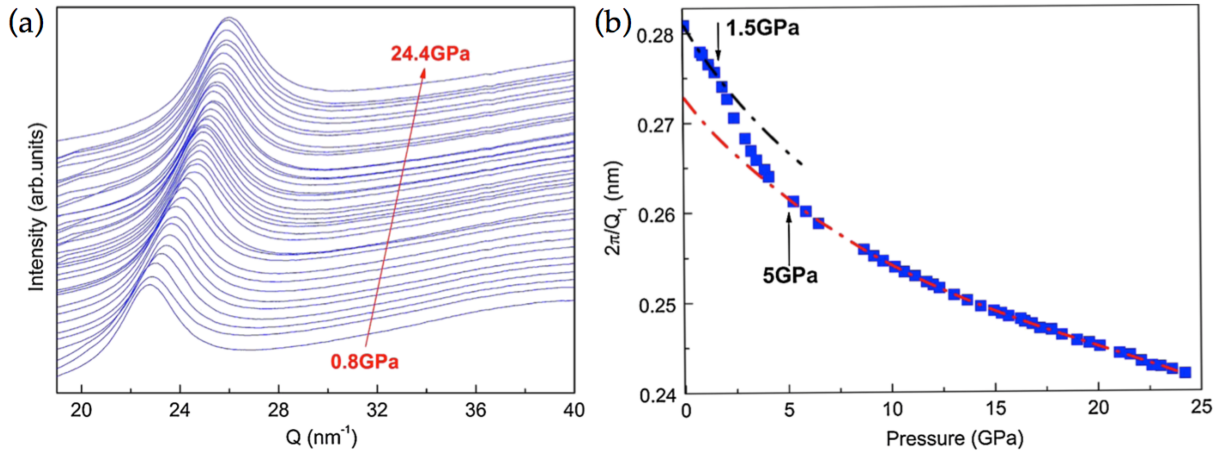
However, evidences of pressure-induced polymorphism were recently reported in various MGs mainly based on Ce-Al alloys ( $\text{Ce}_{32}\text{La}_{32}\text{Al}_{16}\text{Ni}_5\text{Cu}_{15}$  [239],  $\text{Ce}_{55}\text{Al}_{45}$  [240],  $\text{Ce}_{75}\text{Al}_{25}$  [241],  $\text{Ce}_{75}\text{Al}_{23}\text{Si}_2$  [241] and  $\text{Ce}_{70}\text{Al}_{10}\text{Ni}_{10}\text{Cu}_{10}$  [84].), mostly using *in situ* high-pressure XRD measurements carried out on synchrotrons.

The position of the main peak  $Q_3$  in the structure factors tracks with increasing pressure, showing significant shift towards high- $Q$  values in some narrow pressure range (Figure 40). Similar to oxide or chalcogenide glasses, these changes are reversible when the pressure is released with an important hysteresis.



**Figure 40:** Evolution of XRD patterns of a  $Ce_{55}Al_{45}$  metallic glass in a diamond anvil cell upon (a) compression and (b) decompression. (c) The XRD intensity peak gradually shifts to high- $Q$  values during compression in the pressure range 2.0–13.5 GPa. (d) During decompression, the arrow at  $\sim 2$  GPa marks an abrupt shift towards low- $Q$  values. Reprinted by permission from Macmillan Publishers Ltd: Nature [240], copyright (2007).

The inverse position of the main diffraction peak,  $2\pi/Q_3$ , can be estimated using a Voigt line profile after subtracting baseline. As seen previously (part 6.1.3),  $2\pi/Q_3$  can be correlated to the relative volume (density) change as a function of pressure. The plot of  $2\pi/Q_3$  over pressure allows the observation of a clear transition between 1.5 and 5 GPa from a low-density state to a high-density state (figure 41). The transition starts from a LDA at low pressure, and goes through continuous densification ending with a HDA at high pressure. A large density difference is observed between the two polyamorphs. In figure 41, the volume collapse can be estimated with the 1/3 power law function giving about 8.6% volume reduction (2.9% in  $2\pi/Q_3$ ).



**Figure 41:** (a) Evolution of XRD patterns of a  $Ce_{75}Al_{45}$  metallic glass. (b) Inverse  $Q_3$  positions as a function of pressure. The dashed black and red curves correspond to LDA and HDA, respectively. Reprinted with permission from [242]. Copyright (2010) by the American Physical Society.

The suggested mechanism is an increase in Ce-Ce interactions leading to delocalization of some electrons in the 4f shells (from localized state  $4f^1$  to delocalized state  $4f^0$ ) under high pressure [240]. *Ab initio* MD simulations confirm this scenario which causes a splitting of the Ce-Ce nearest neighbor distance with one position having a significant bond shortening. Unlike the structural transition in ordinary amorphous materials [201], MGs exhibit an electronic polyamorphism. This large electronic configuration change has also been observed in other bulk metallic glasses (lanthanide-based MGs [86]) indicating that this mechanism is common. The A-A configuration change is not restricted to MGs having  $f$  electron: in Ca-Al MGs [79], a transfer of  $s$  electrons into  $d$  orbitals under pressure has been proposed to explain the A-A transition.

A liquid-liquid phase transition in the monatomic liquid metal cerium has also been reported using *in situ* high- $P$ /high- $T$  XRD experiments [243]. At a given pressure, a high-density liquid transforms to a low-density liquid with increasing temperature. Again, the origin of this transition is due to delocalization of  $f$  electrons. It was proposed that this transition reflects the liquid-liquid critical point in the Ce phase diagrams.

## 8. Conclusion and perspectives

In this chapter, we have introduced the fundamental concepts of the neutron and x-ray diffraction methods, emphasizing the difference and complementarity of the two techniques, the possibility to extract more structural information using contrast methods (neutron diffraction with isotopic substitution or anomalous diffraction) or the clear contribution of refinement methods (RMC, EPSR) or MD simulations. The synergism between diffraction data and simulation/modeling techniques is

now a routine procedure, beneficial for both tools and improving our current representation of the three-dimensional atomic arrangements in glasses. Oxide, chalcogenide or metallic glasses, among others, have been the subject of a tremendous number of investigation using neutron/x-ray diffraction and we have thus chosen some representative examples to illustrate the invaluable information that can be determined from diffraction data, leading to a deeper understanding of the glass structure in many amorphous systems. The structural response to pressure and temperature is often an experimental challenge, which has been successfully met by diffraction. Results using *in situ* high pressure/temperature set-ups hold great promise for elucidating the structural behavior in glasses, and thus the changes in their physico-chemical properties. Diffraction will continue to provide an excellent choice for future *in situ* high pressure/temperature studies by still pushing the experimental limits.

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