

Mesures des propriétés structurales des liquides fondus

Diffraction des rayons X et des neutrons

Louis HENNET

CNRS (ICMN / CEMHTI)
45071 Orléans cedex 02



Louis.hennet@cnrs-orleans.fr

Thomas SCHENK

Université de Lorraine (IJL)
54000 Nancy



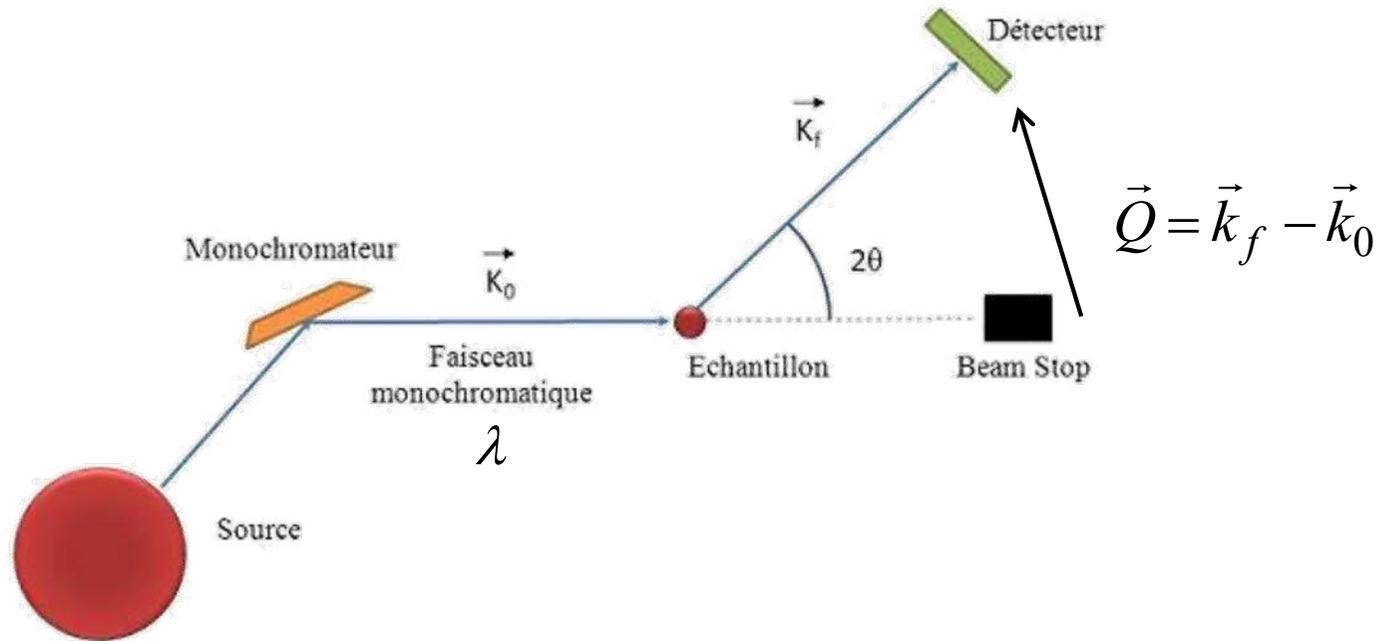
thomas.schenk@univ-lorraine.fr



Plan

- **I - Diffraction des rayons X et des neutrons**
- **II - Systèmes de chauffage**
- **III – Quelques exemples**

Principe d'une expérience de diffraction de rayons X ou de neutrons



Diffraction = processus élastique : $\|\vec{k}_f\| = \|\vec{k}_0\| = \frac{2\pi}{\lambda}$

$$Q = \|\vec{Q}\| = 2\|\vec{k}_f\| \sin \theta = \frac{4\pi \sin \theta}{\lambda}$$

$$I(Q) = \Phi \frac{d\sigma}{d\Omega}(Q) d\Omega$$

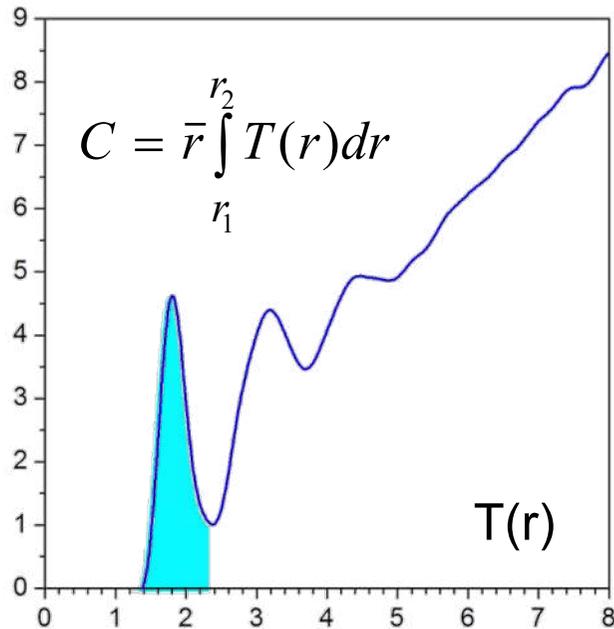
Diffraction des rayons X et des neutrons

Les informations structurales sont contenues dans la fonction de distribution de paires : **$g(r)$**

$g(r)$ est la probabilité de trouver un atome à une distance r d'un autre pris comme origine.

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

$$T(r) = 4\pi r \rho_0 g(r) = RDF(r) / r$$

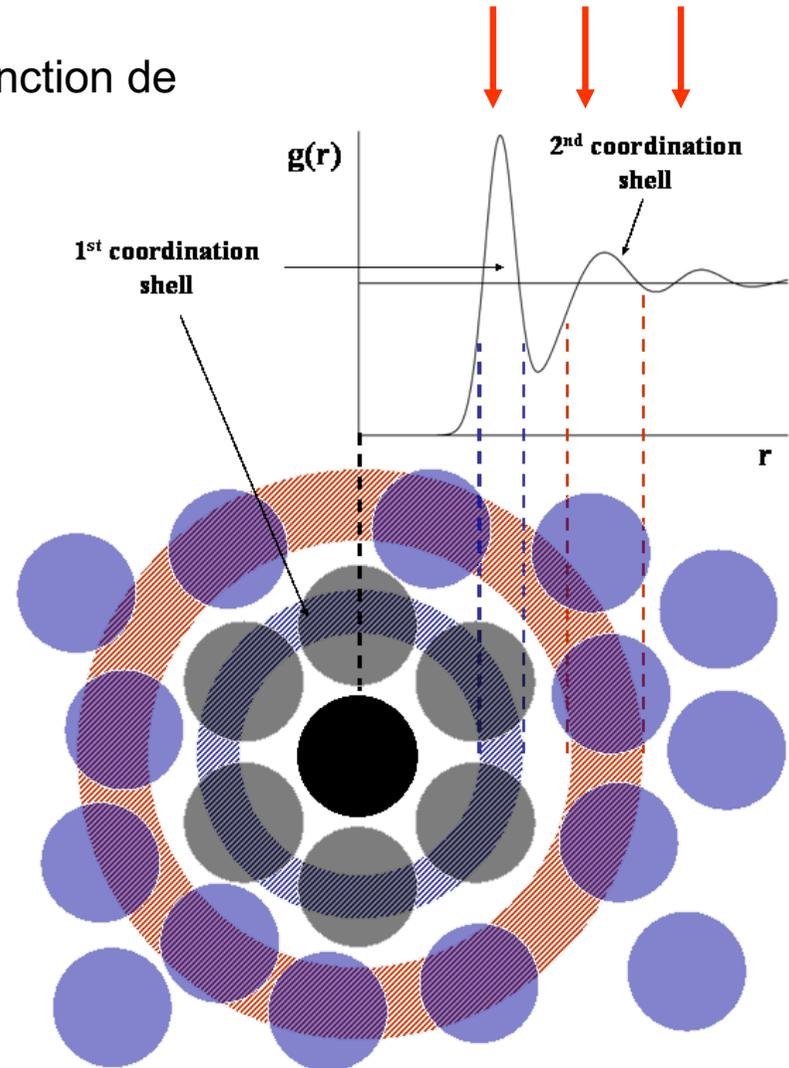


Coordinnances r (Å)

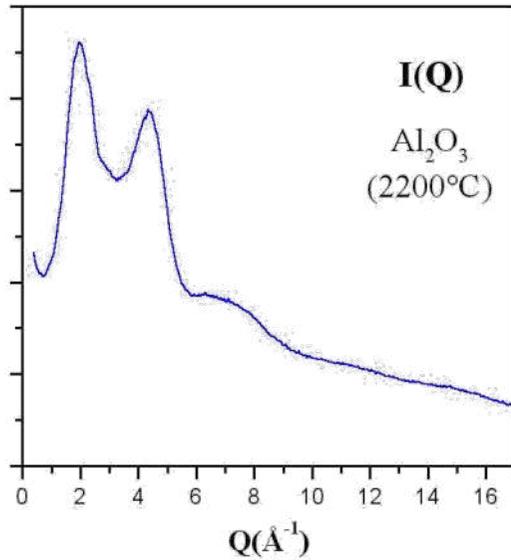
$$g(r) = \sum_i \sum_j W_{ij}(0) g_{ij}(r)$$

Besoin de résolution

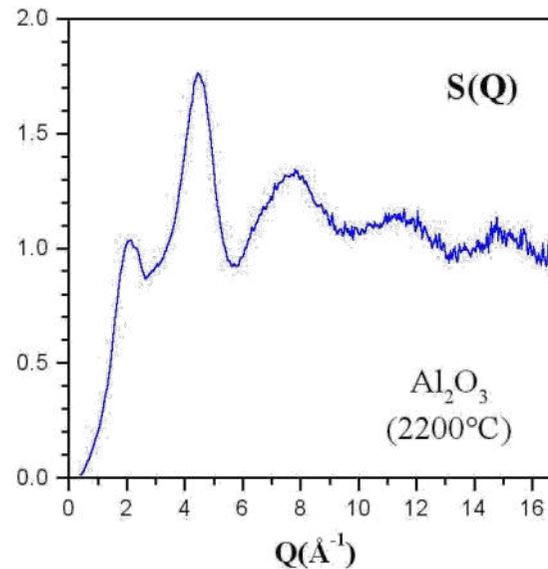
Distances



Formalisme pour les rayons X (id pour les neutrons)



$$I(Q) = I_{air}(Q) + I_{coh}(Q) + I_{compt}(Q) + I_{mult}(Q)$$



$$S(Q) = \frac{\left(I_{coh}(Q) - \langle |f(Q)|^2 \rangle \right)}{\langle f(Q) \rangle^2} + 1$$

$$\langle |f(Q)|^2 \rangle = \sum_i c_i |f_i|^2 \quad \langle f(Q) \rangle^2 = \left| \sum_i c_i f_i \right|^2$$

$$f_i = f_i^0(Q) + f_i'(E) + if_i''(E)$$

Résolution dans l'espace réel : $R = \frac{2\pi}{Q_{max}}$

$$Q = \frac{4\pi \sin \theta}{\lambda}$$

Maximisation de Q_{max} : Angles de diffraction larges
Longueurs d'onde courtes

2θ (°)	E(keV) / λ(Å)	Qmax (Å ⁻¹)
140	21 / 0.590	20.0
23	100 / 0.124	20.2

Les fours classiques

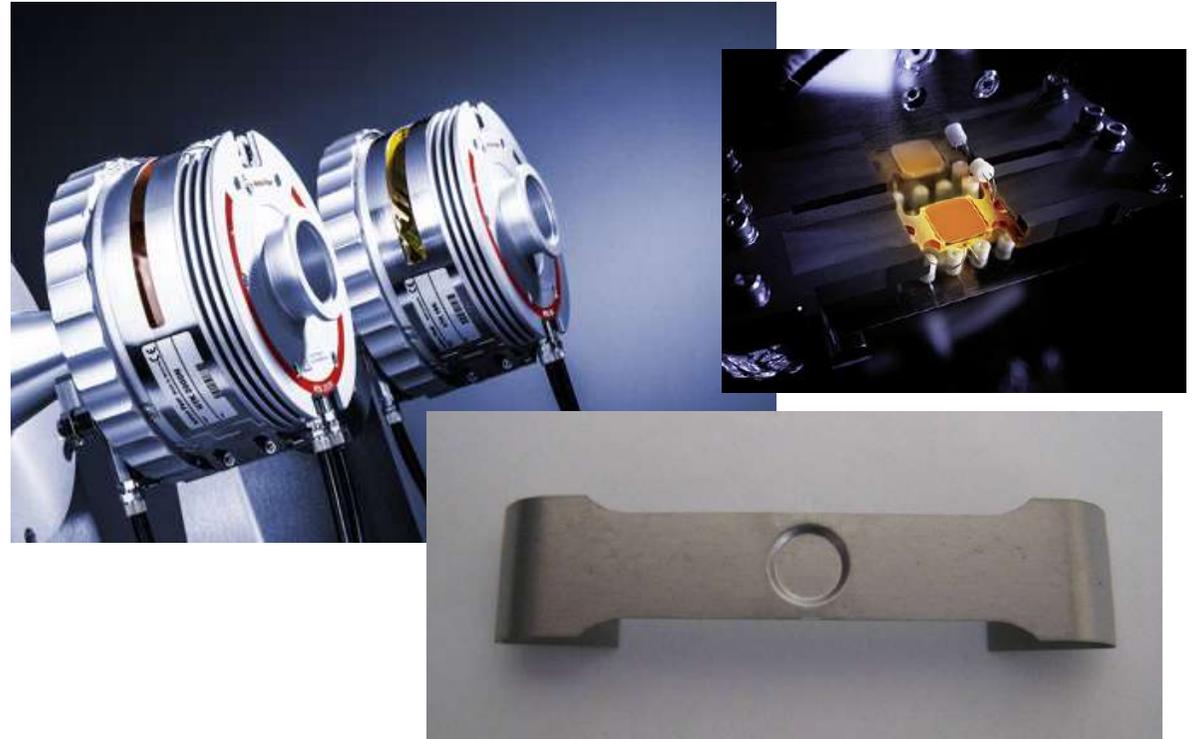
Fours pour la diffraction des rayons X

Bulher



Sous vide : (ruban de tungstène)
T max : 2300 °C
Sous air : (ruban de platine)
T max : 1600 °C

Anton Paar



Ruban avec réservoir

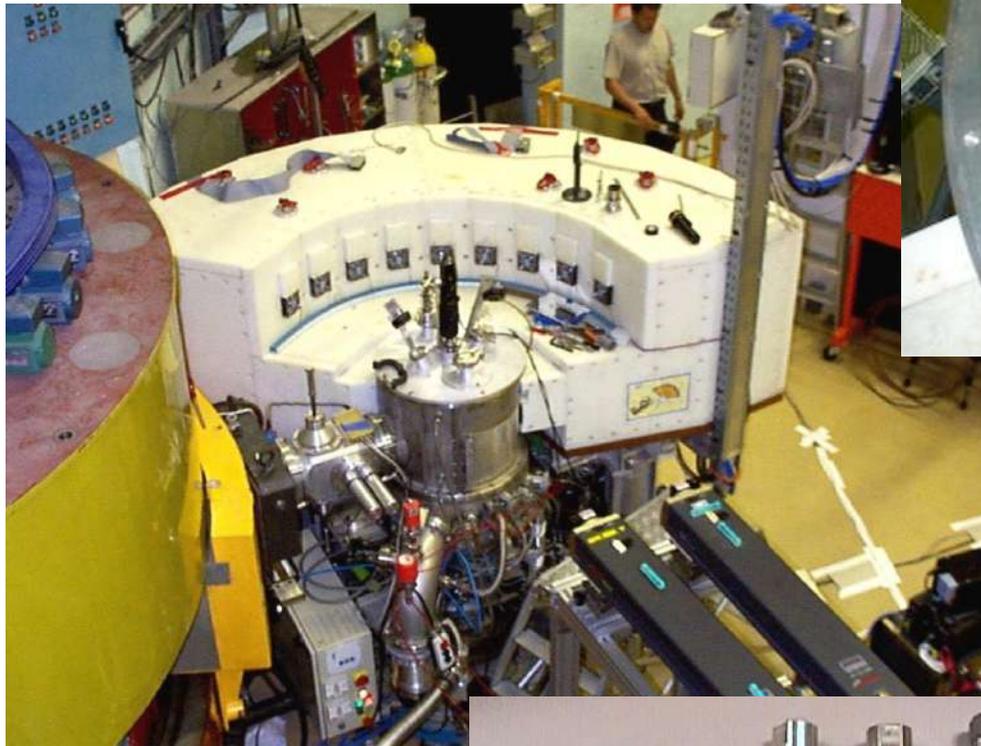


T max : 1500 °C

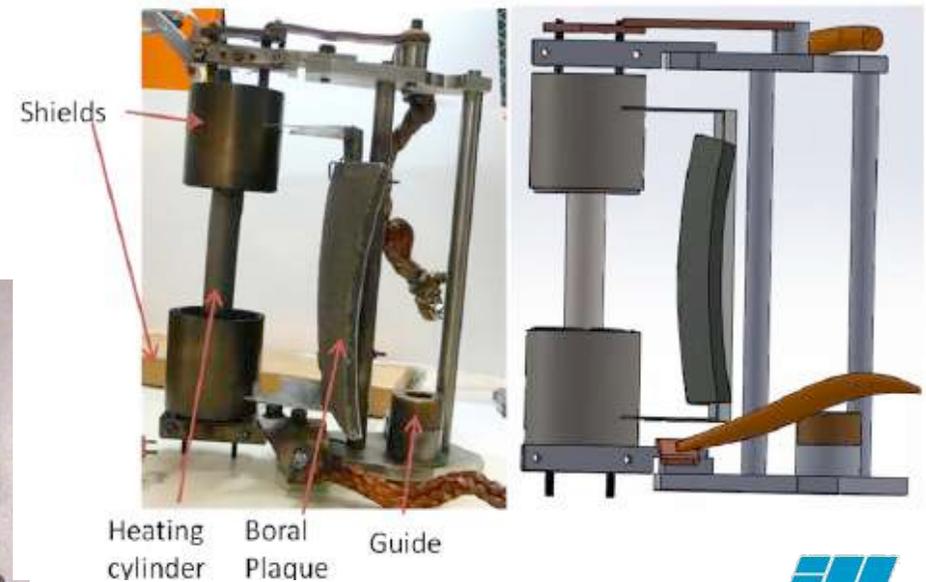
Cellule Linkam®

- Limitation en température (sous air)
- Mesures en réflexion
- Difficile à utiliser sur les grands instruments pour étudier les liquides

Fours pour la diffraction des neutrons



D4C (ILL)



T max : ~1200°C

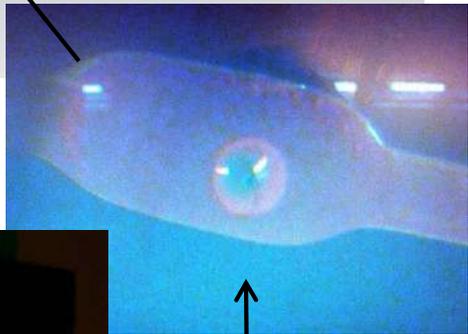
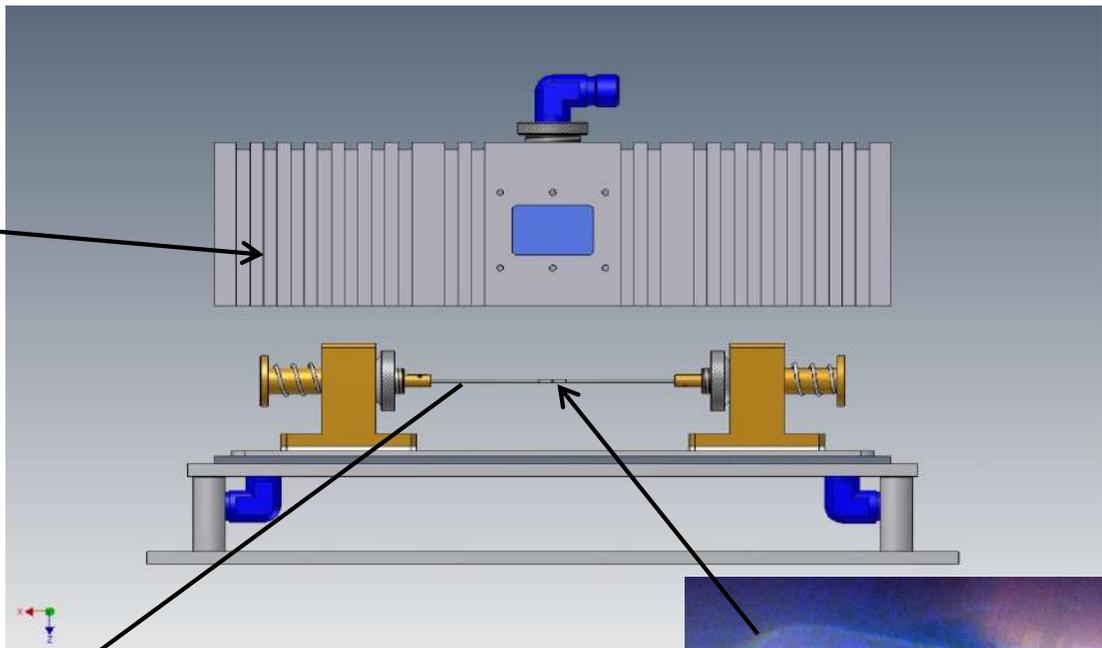
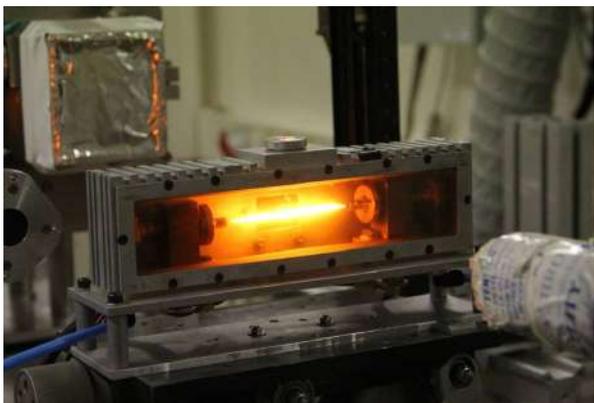


Cellules en vanadium

Le fil chauffant

Développement : D. Neuville (IPGP)

Couvercle étanche
(Atmosphère contrôlée)

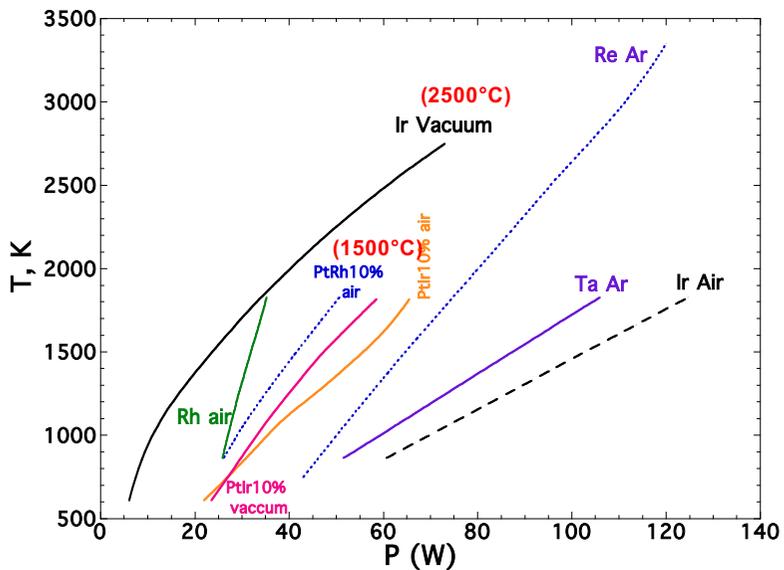


Echantillon



Combinaison facile avec les spectroscopies vibrationnelles

- Raman (IPGP)
- Brillouin (Montpellier)
- Infra-Rouge (SOLEIL)



Tmax en fonction du type de fil et de la puissance appliquée

La lévitation

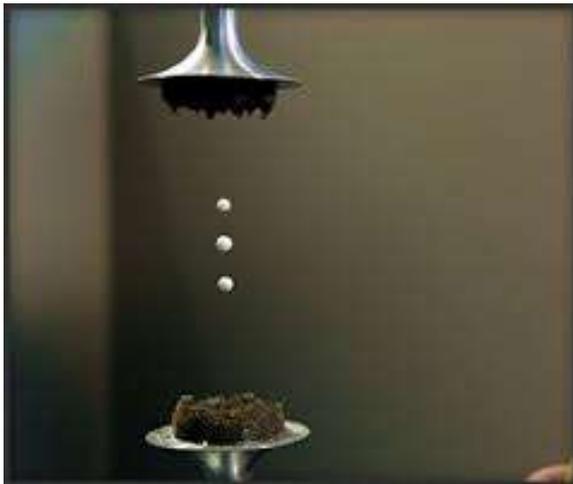
Aperçu des différentes méthodes

Lévitation électromagnétique*



Conducteurs électriques
Chauffage par induction

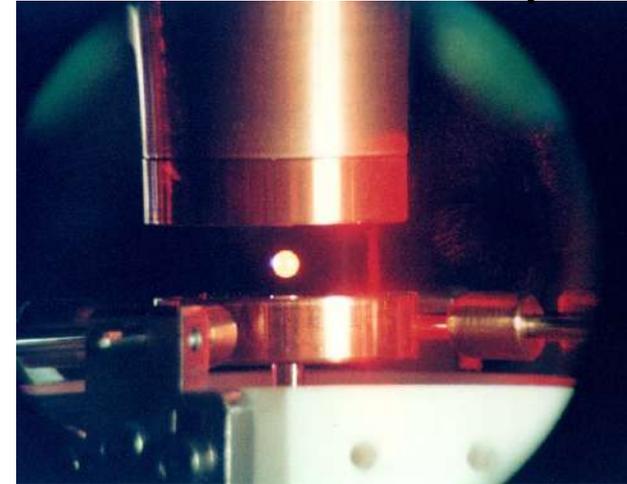
Lévitation acoustique



Initialement pour les liquides
en solution (max 200°C).
Maintenant adaptée pour les
hautes températures.

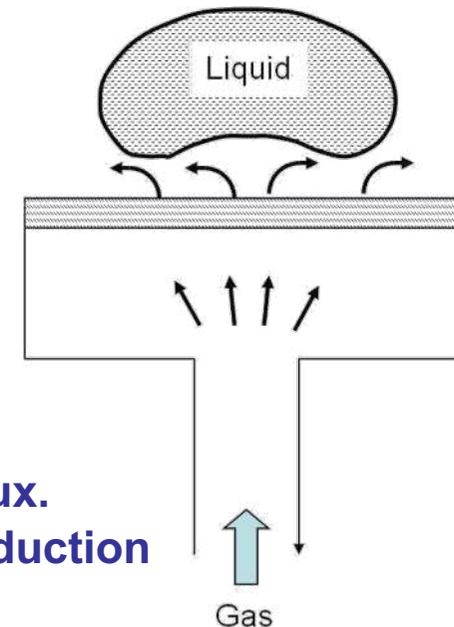
Tous les matériaux.
Chauffage par induction

Lévitation électrostatique*



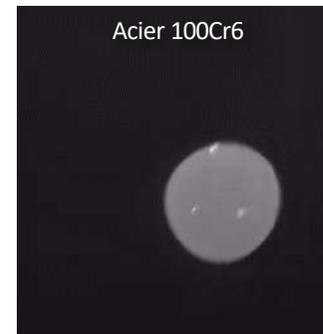
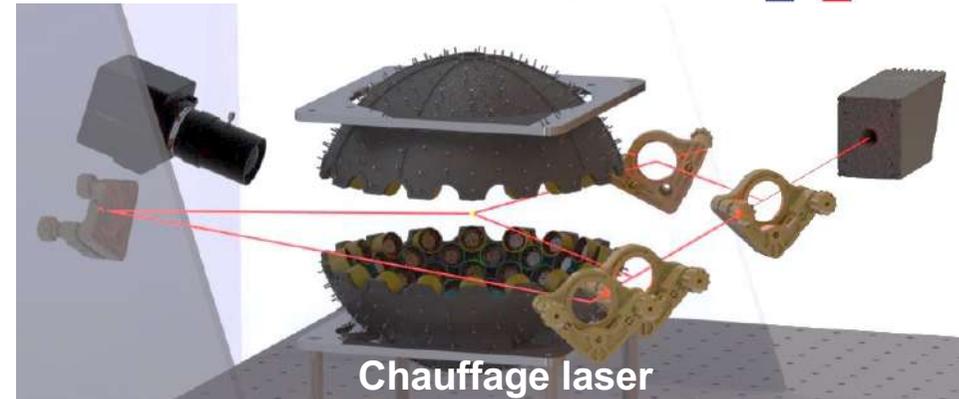
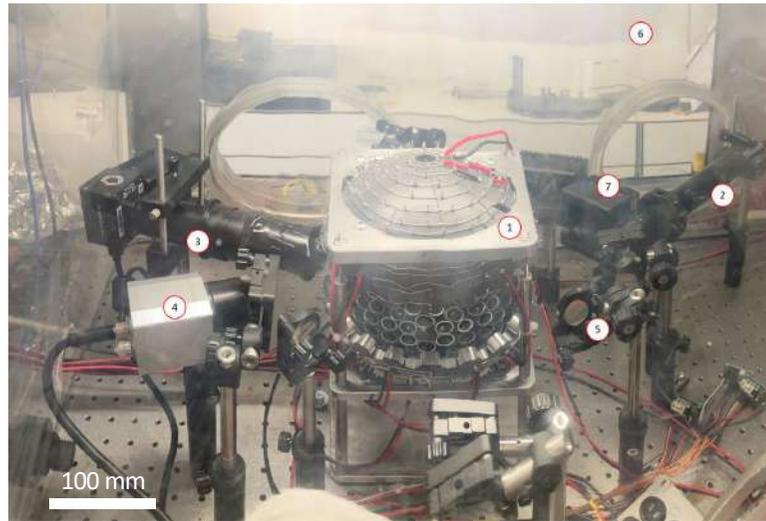
Matériaux pouvant être chargés
électriquement
Chauffage par lasers (CO₂, YAG)

Lévitation aérodynamique (sur film de gaz)

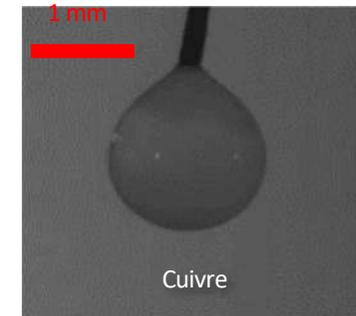


Lévitacion acoustique

Sources : Hervé Strozyk, Jonathan Martens, Thibault Quatravaux (IJL)



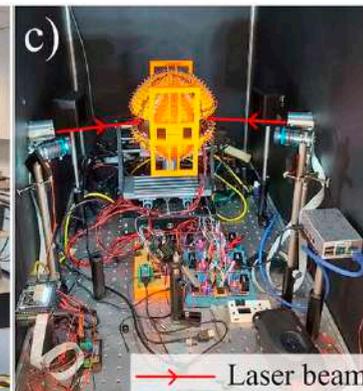
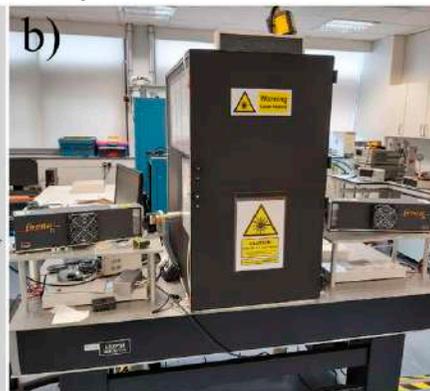
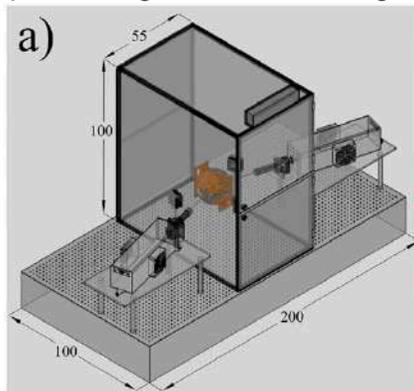
Lévitacion totale



Semi-lévitacion
Production d'échantillons
in situ à partir d'un fil

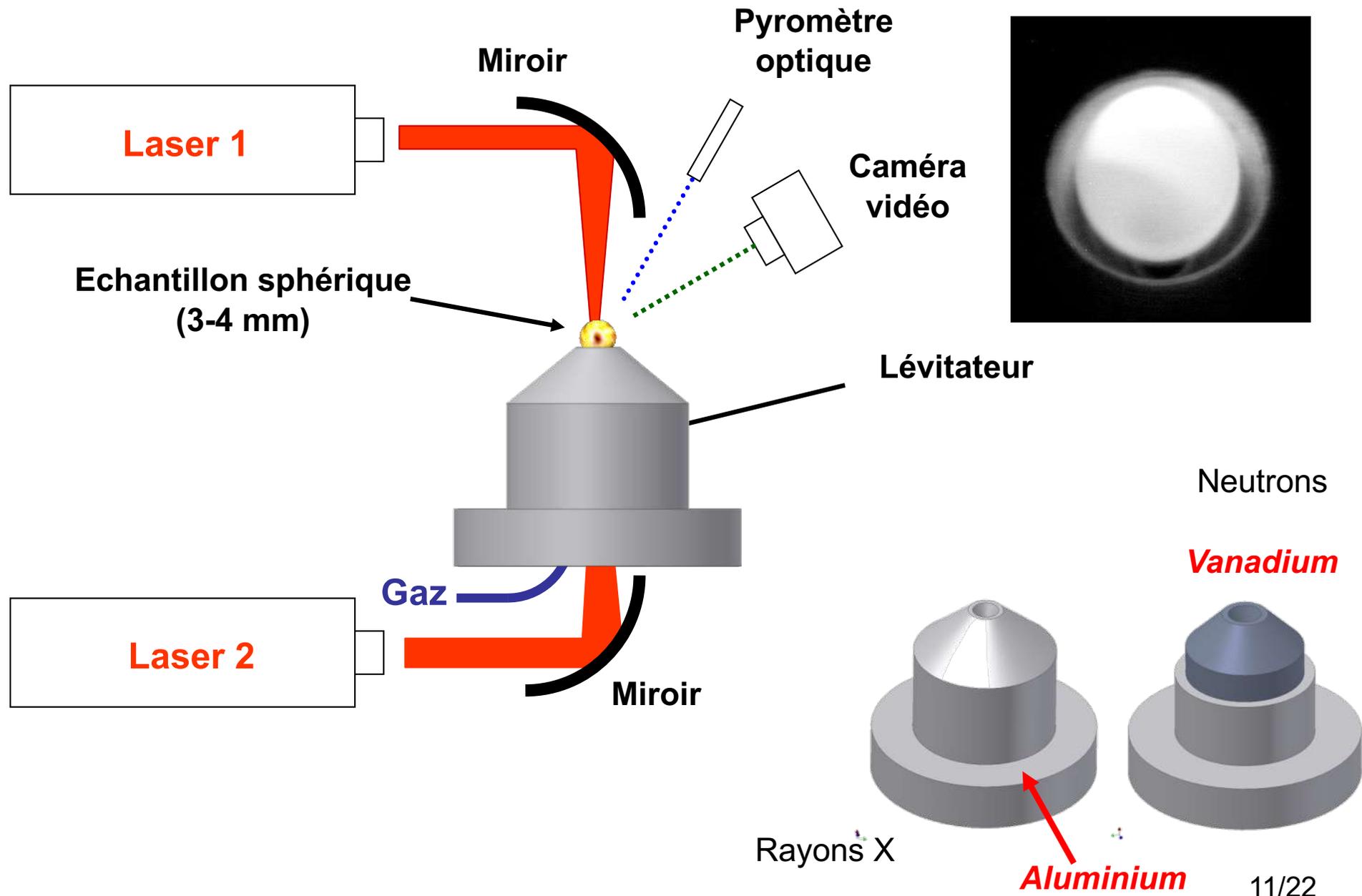


J.W.E Drewitt et al. Rev. Sci. Instrum. 95 103903 (2024)
MightyLev: An acoustic levitator for high-temperature containerless processing of medium- to high-density materials



Lévitration aérodynamique (en buse conique)

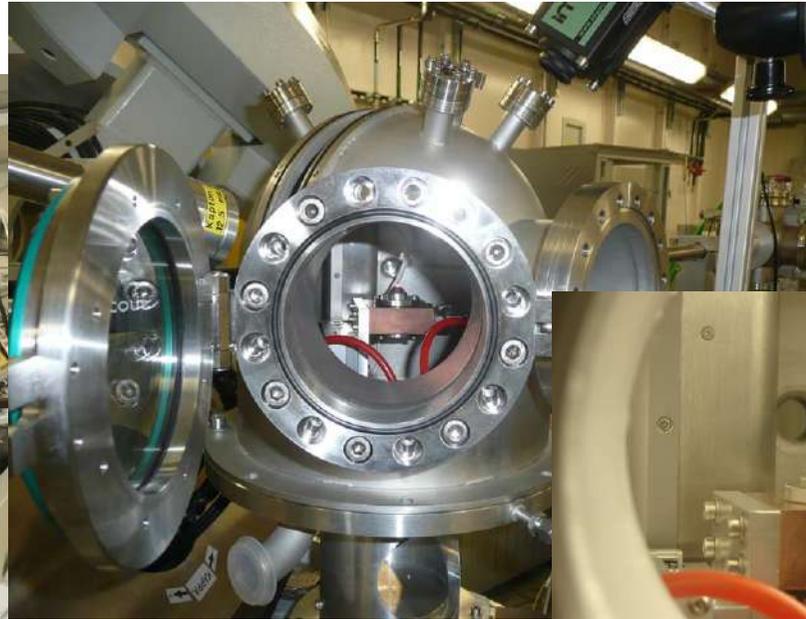
Chauffage par laser CO₂



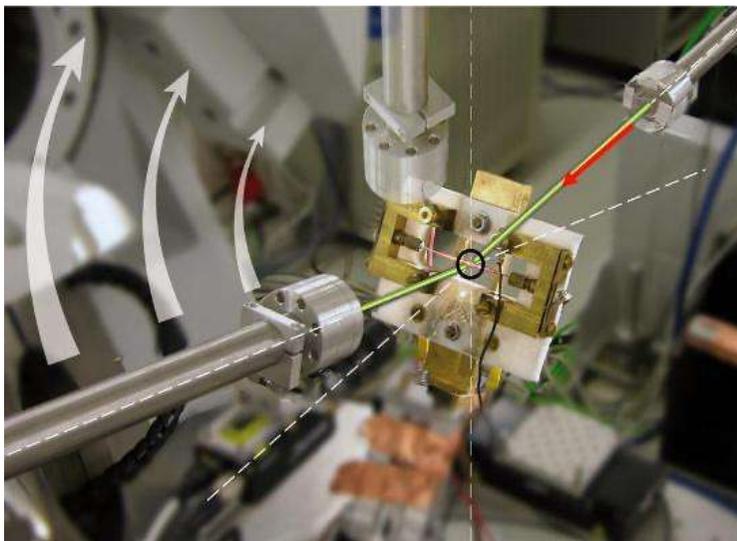
Ligne Diffabs



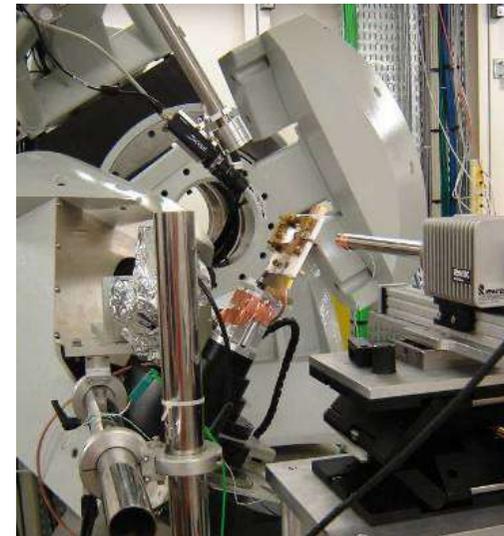
Lévitration (CEMHTI)

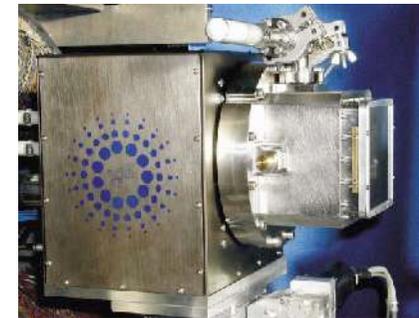
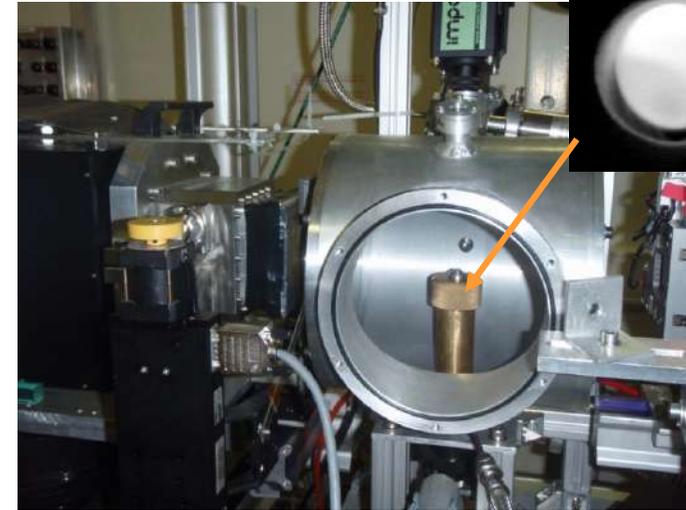
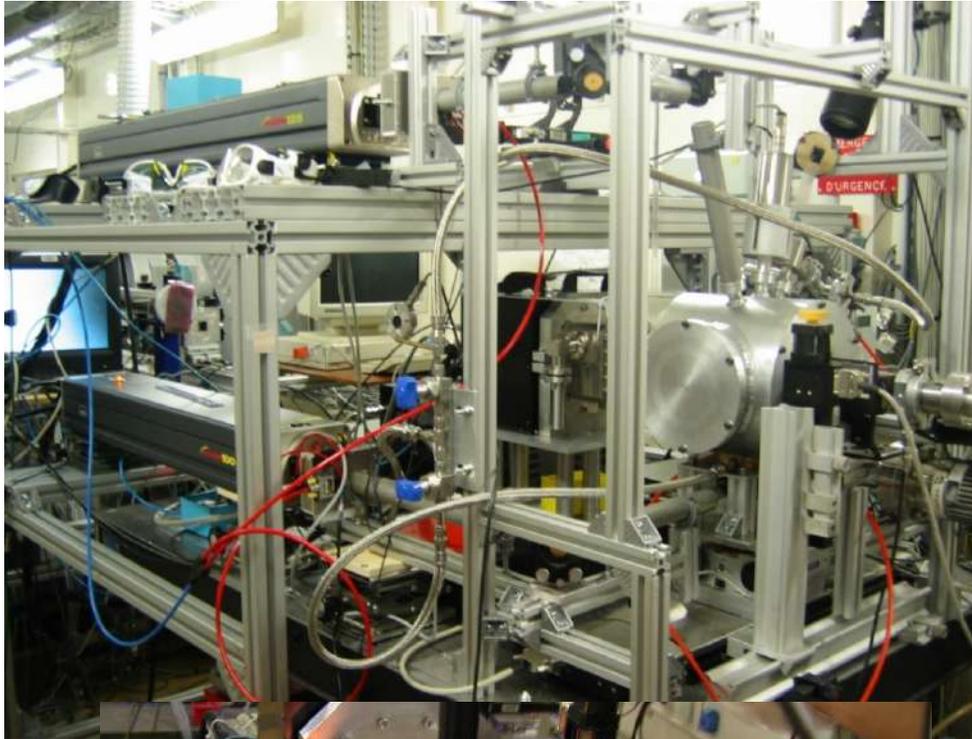


Four à fil (IPGP)



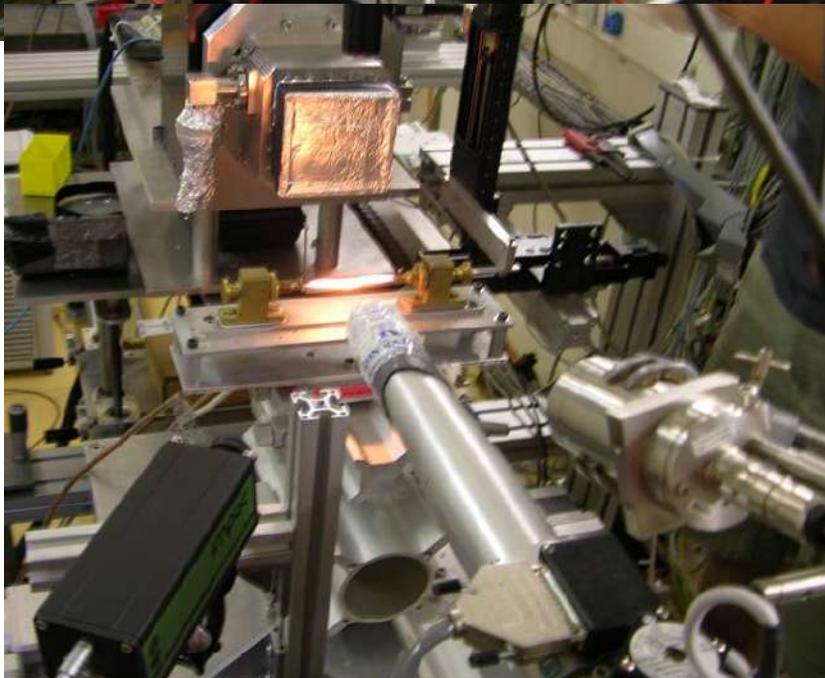
Dans les 2 cas :
Possibilité de couplage Absorption/Diffraction
(En fonction du seuil d'absorption)





FRELON (Fast REadout LOW Noise)

Four à fil
(IPGP)



2 configurations :

Diffraction classique

2 Distances : 150 & 400mm

Gamme en Q : 0.3-35 Å⁻¹ (100keV)

Temps de comptage : 1min

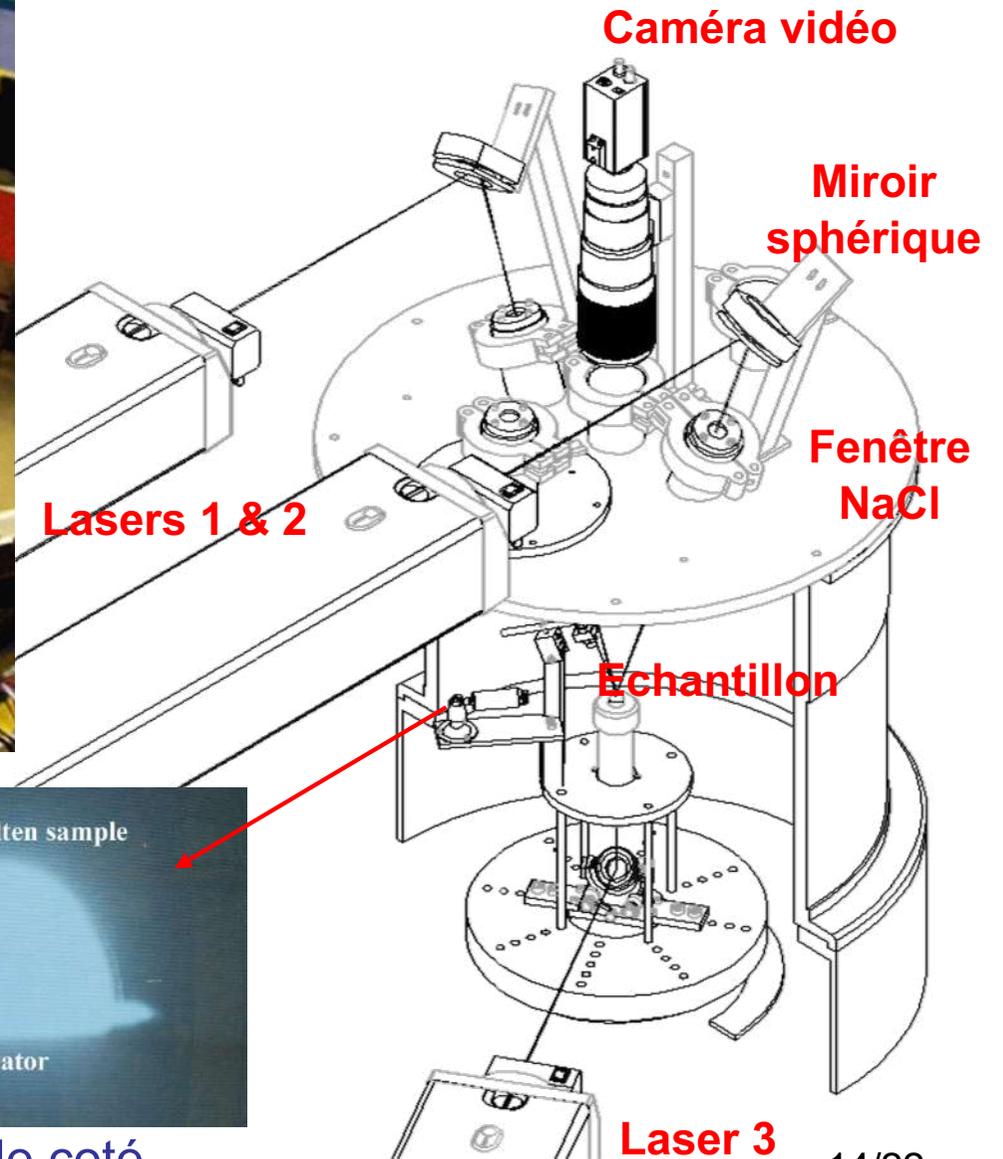
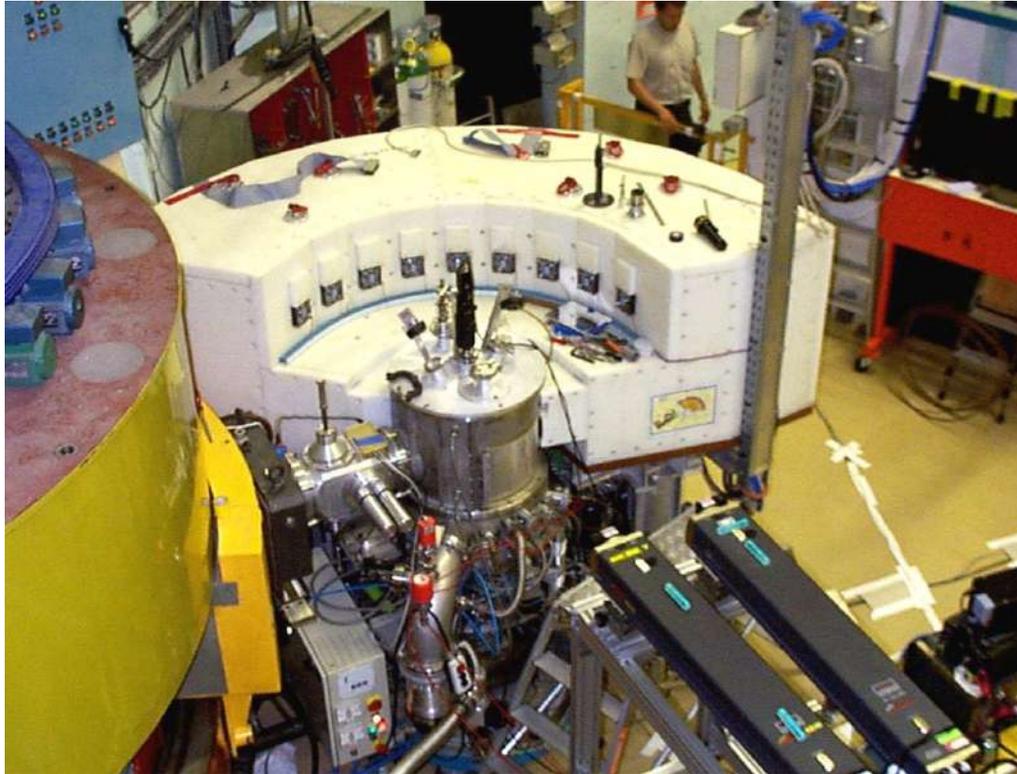
Diffraction rapide

1 Distance : 200mm

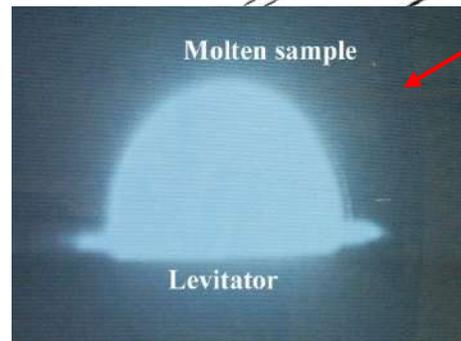
Gamme en Q 0.6-25 Å⁻¹ (100keV)

Temps de comptage : 30 ms

Lévitacion - Diffractomètre D4C @ ILL



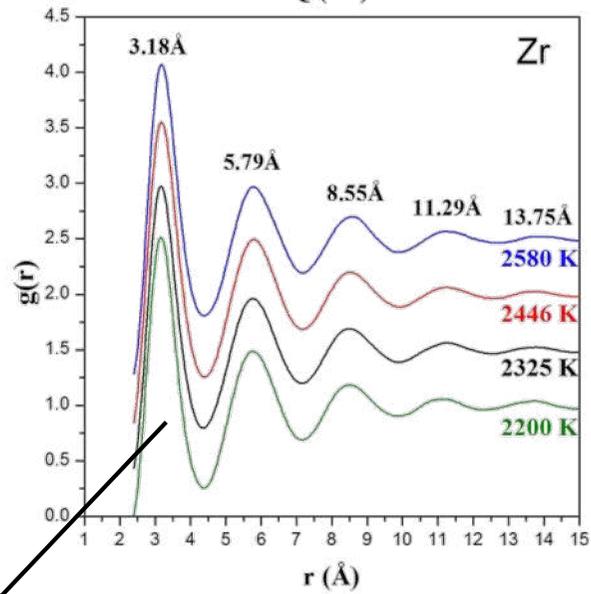
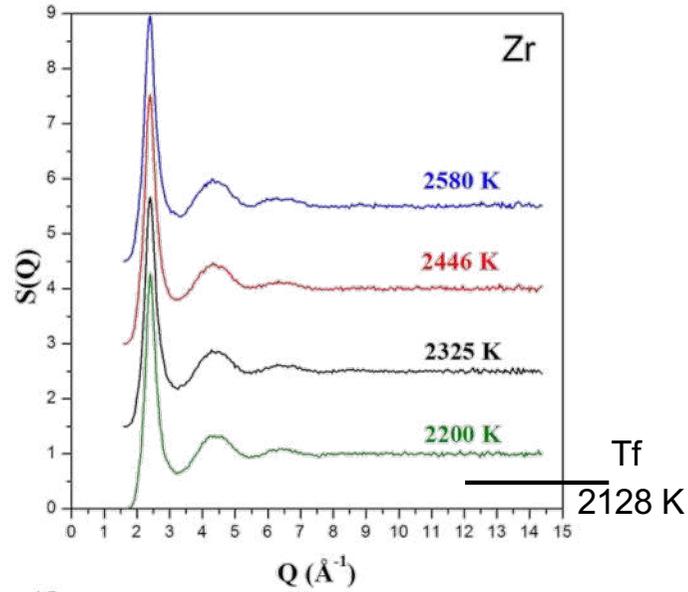
Temps de comptage
typique : 1 à 3 h



Vue de coté

Exemples

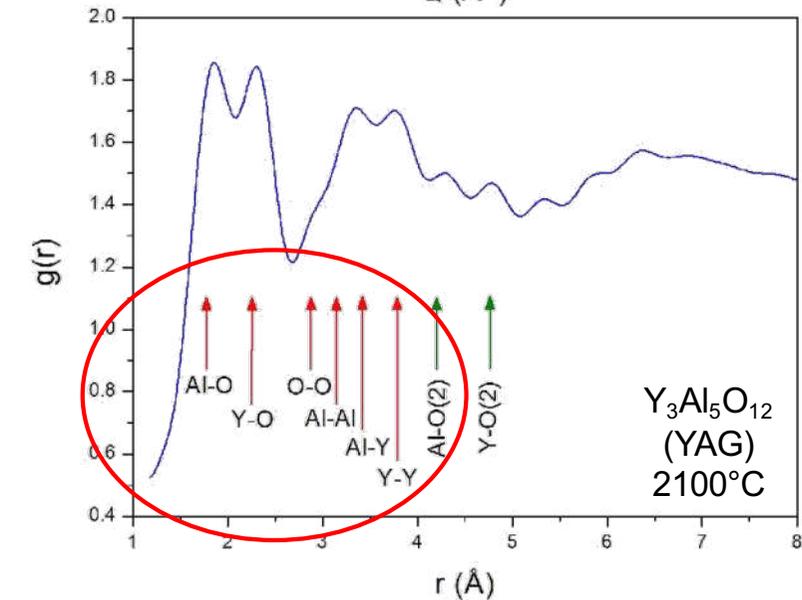
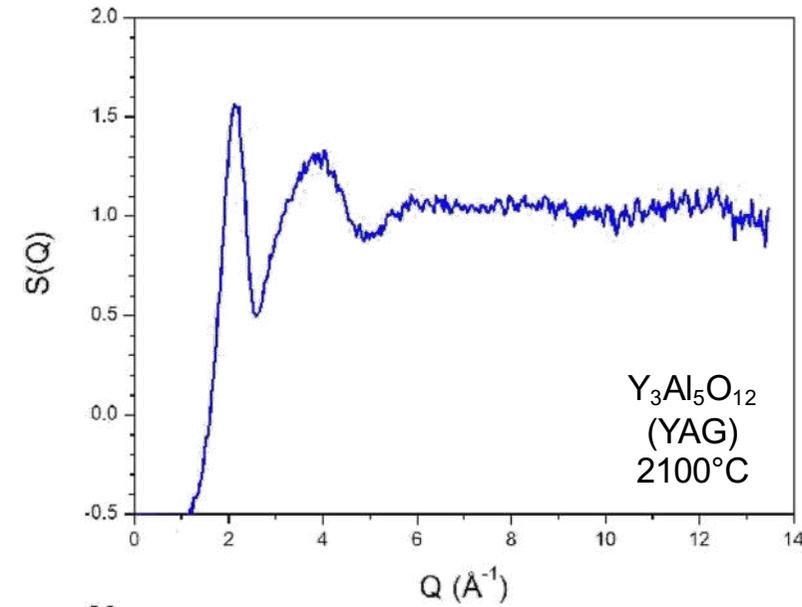
1 élément



CN~12

Diffraction des rayons X

Plusieurs éléments

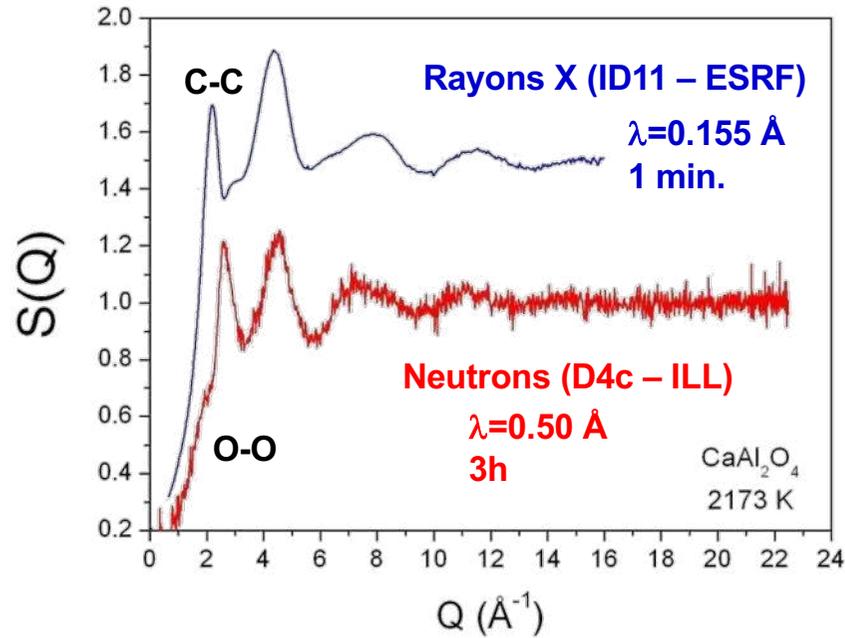


Superposition des partiels pour chaque paires
6 partiels $[n(n+1)/2]$

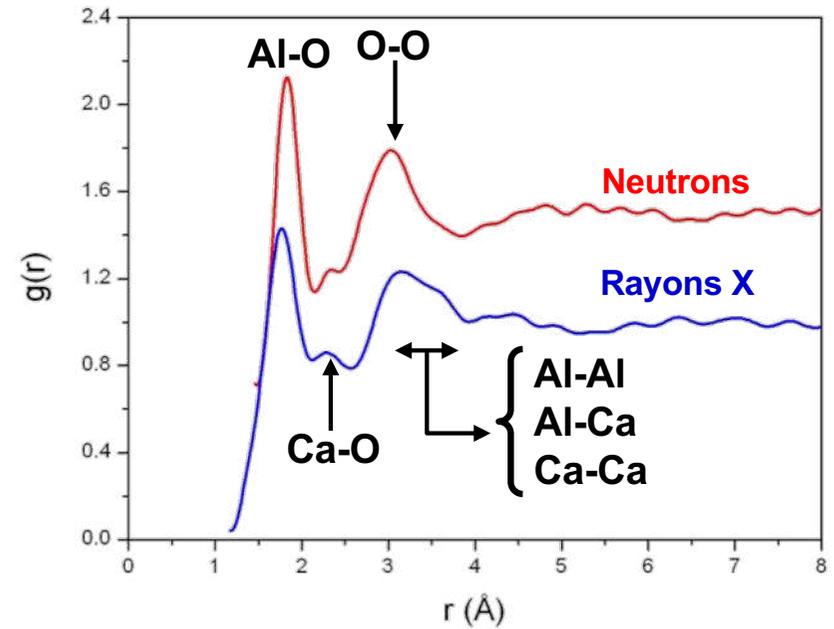
→ **L'interprétation est plus difficile**

Exemples : CaAl_2O_4

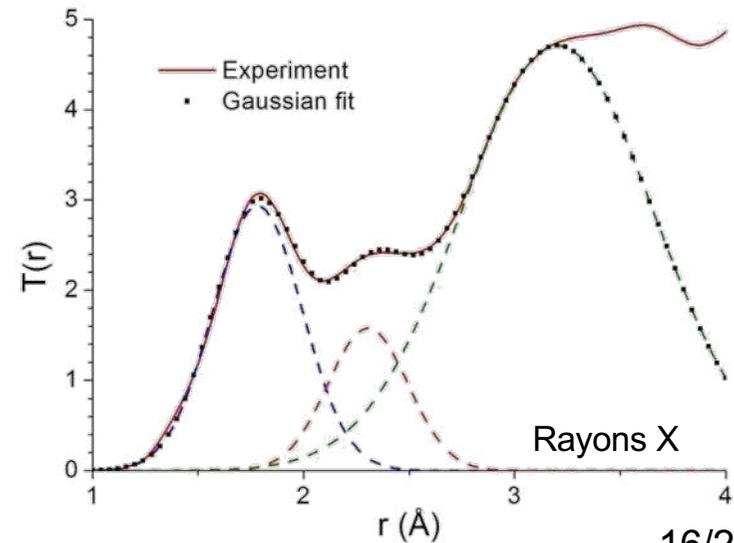
Facteurs de structure



Fonction de distribution de paires



Fonction de corrélation totale



	$r_{\text{Al-O}}$	$C_{\text{Al-O}}$	$r_{\text{Ca-O}}$	$C_{\text{Ca-O}}$
X-rays	1.81 Å	4.5	2.32 Å	4.5-5.5
Neutrons	1.78 Å	4.3	2.30 Å	3.9-5.3

Simulations

Dynamique moléculaire

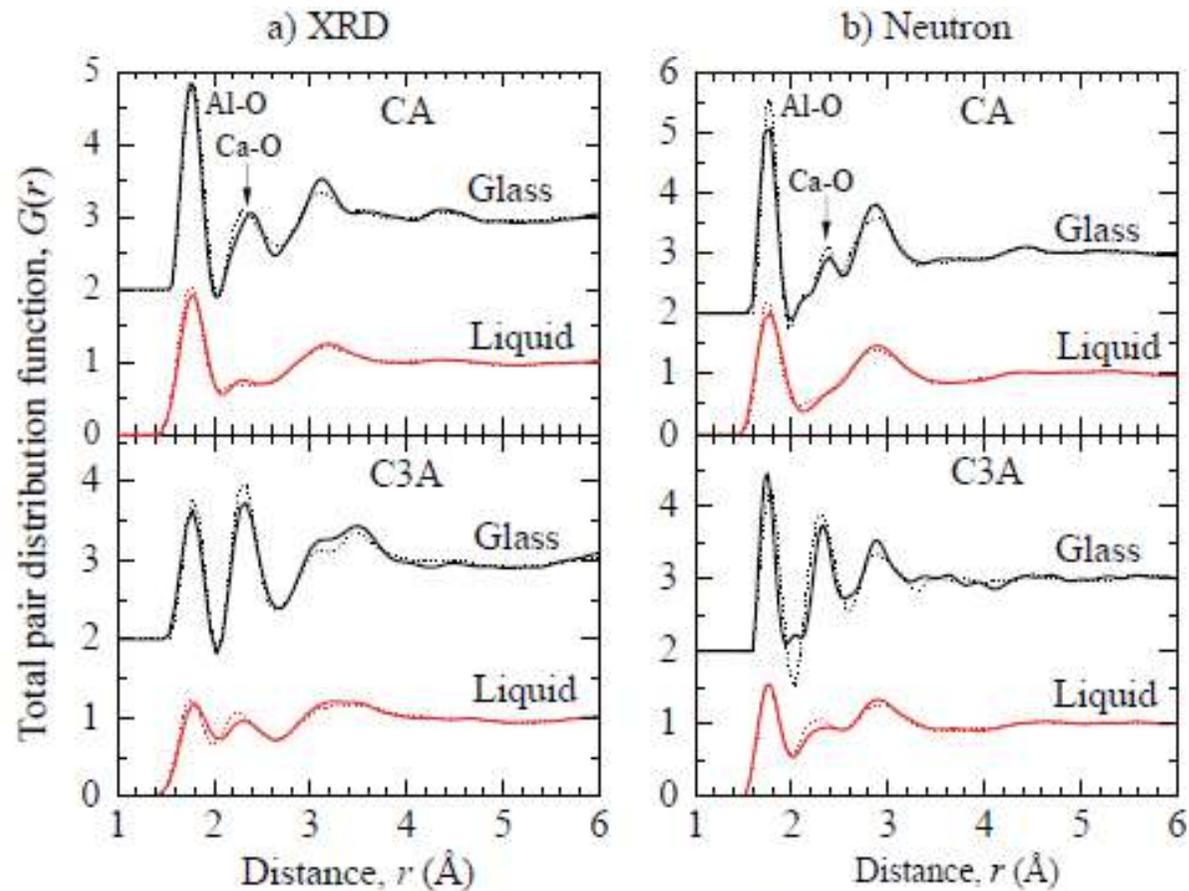
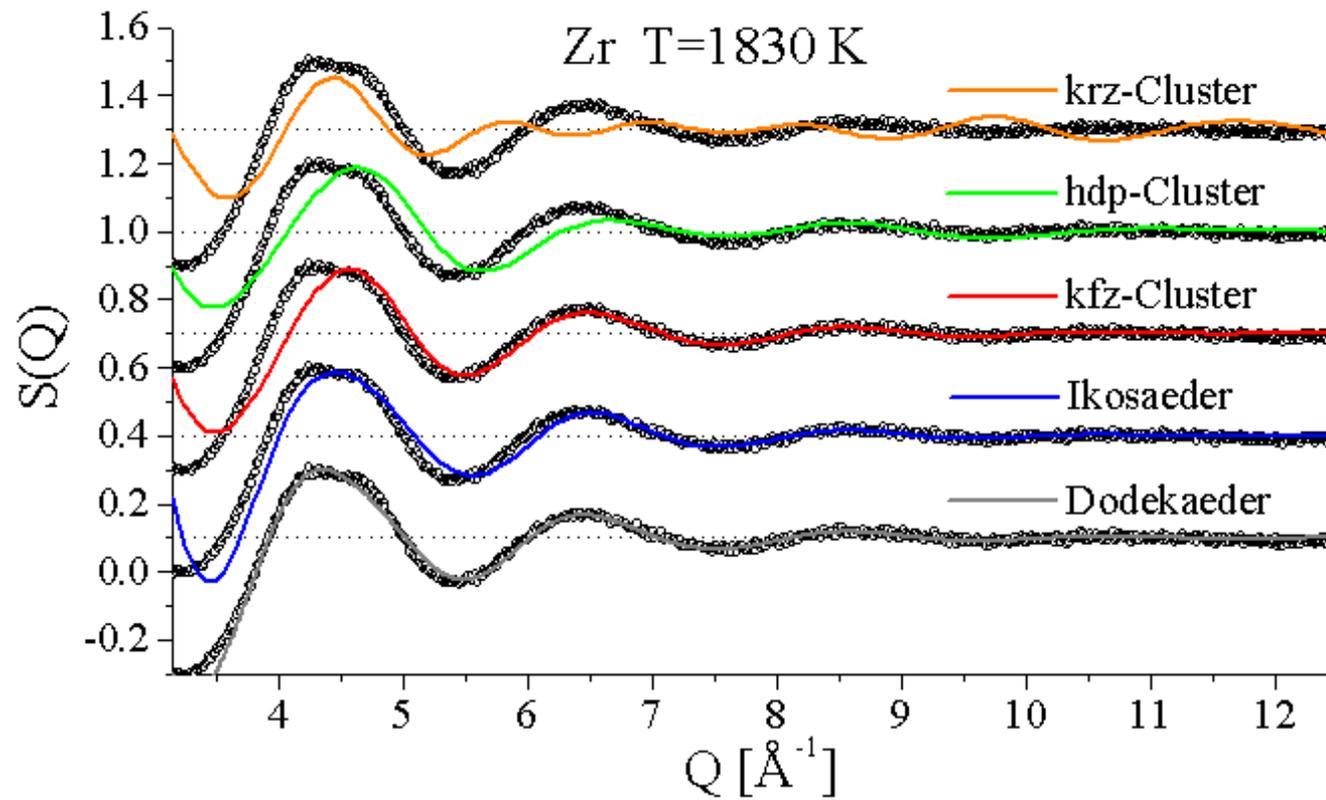


Figure 15. Total pair distribution functions $G(r)$ from **a)** x-ray and **b)** neutron diffraction of CA and C3A glasses (solid black curves) and liquids (solid red curves) together with the corresponding functions computed directly from MD simulations (dotted curves) (data from Drewitt et al. 2011, 2012, 2017, 2019).

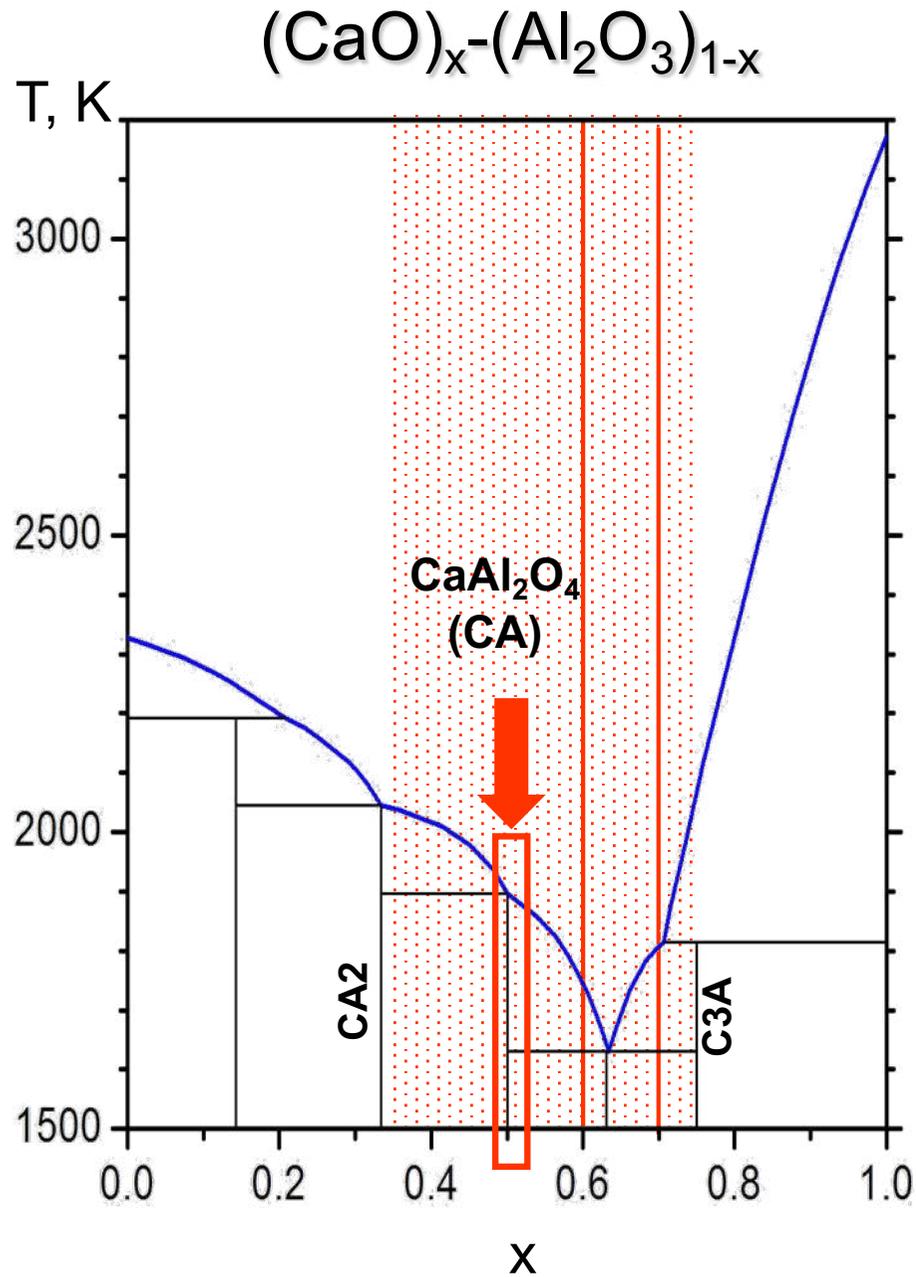
James WE Drewitt, Louis Henet, Daniel R. Neuville. From Short to Medium Range Order in Glasses and Melts by Diffraction and Raman Spectroscopy. *Reviews in Mineralogy and Geochemistry* 87, 55-103 (2022)

Simulations

Simulation de $S(Q)$ pour des clusters simples ("cc, cfc, hcp, icosaédrique et dodécaédrique)

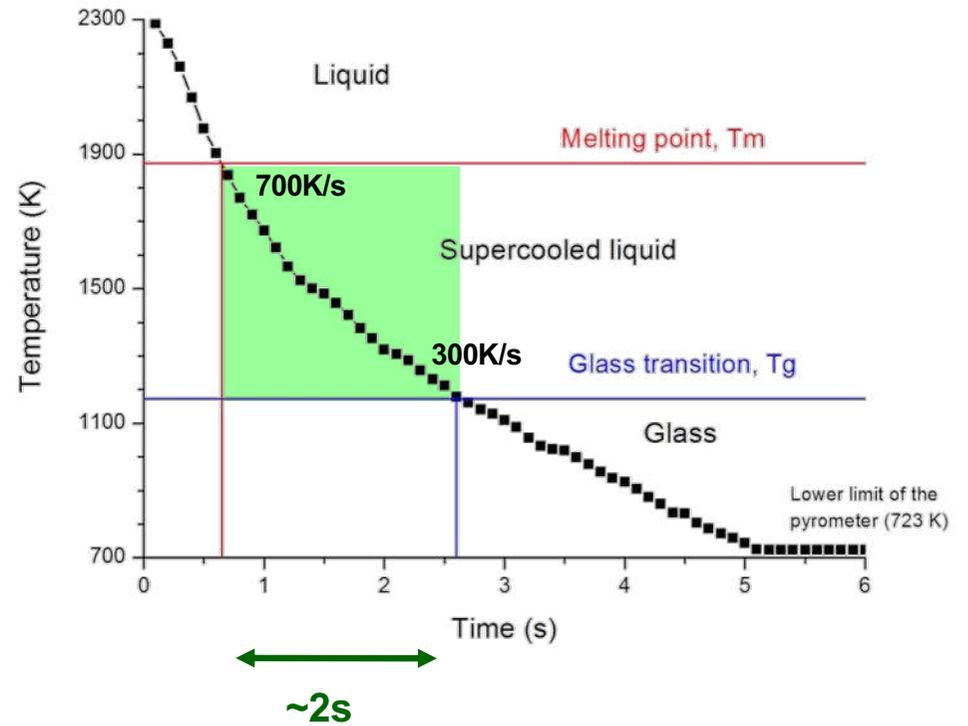


Quelques avantages des technique de lévitation

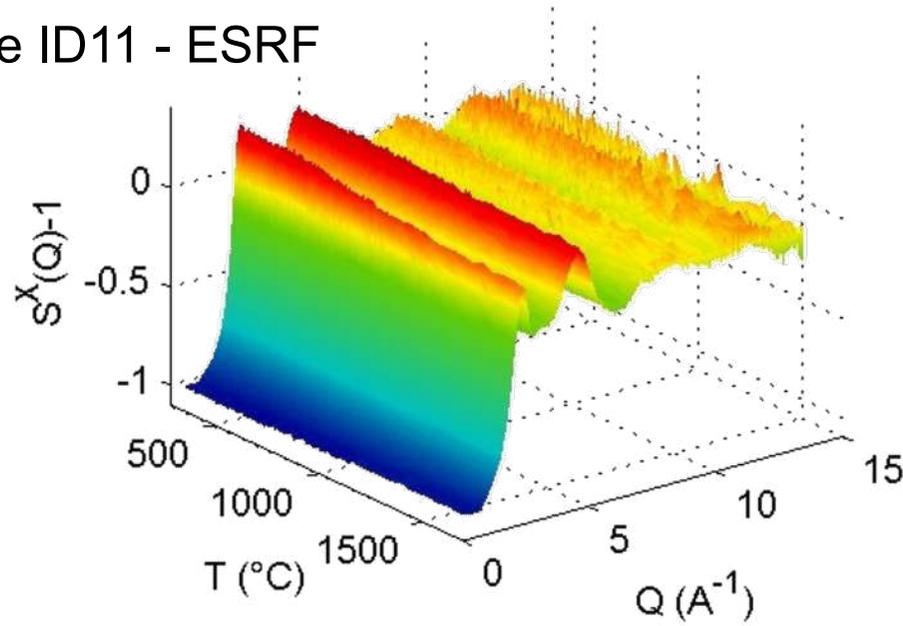


CaAl_2O_4 (CA)
 Tm: 1878 K
 Tg: 1180K

Domaines de vitrification plus larges
 Vitesses de refroidissement rapides



Ligne ID11 - ESRF



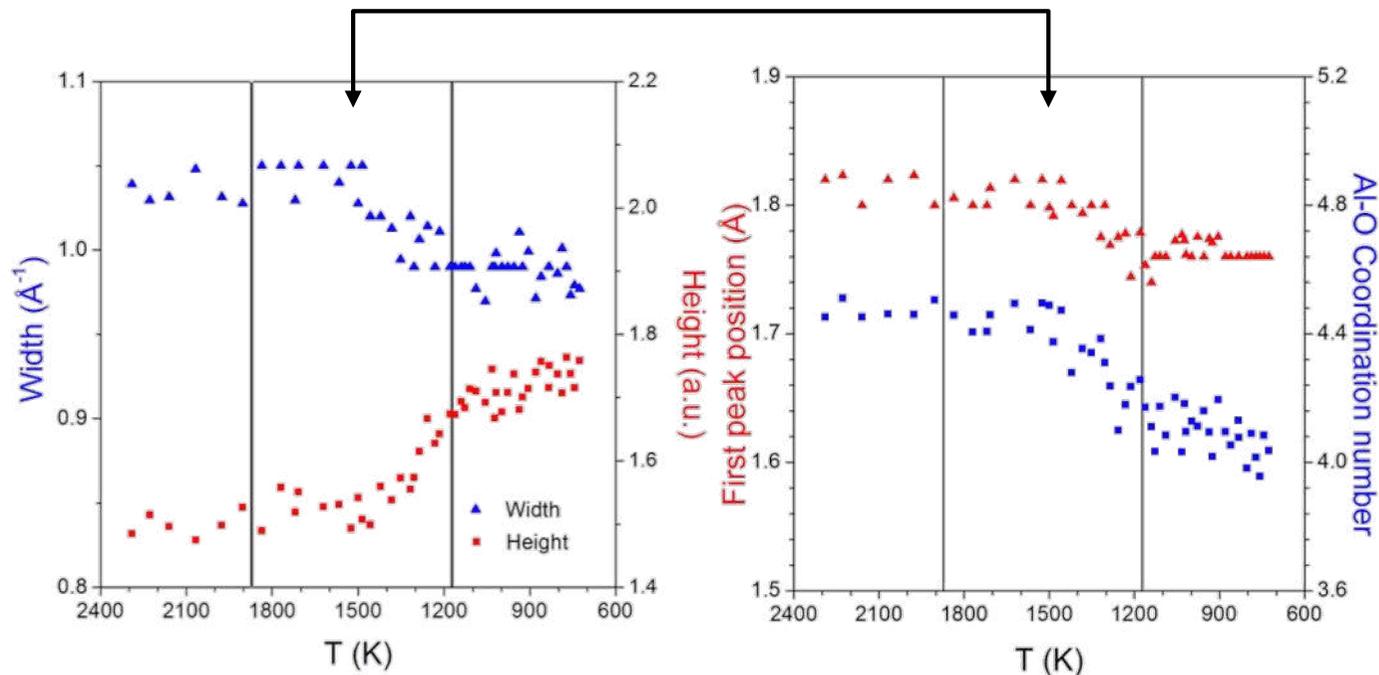
$T_m \searrow T_g \sim 2s$

Mesures rapides :

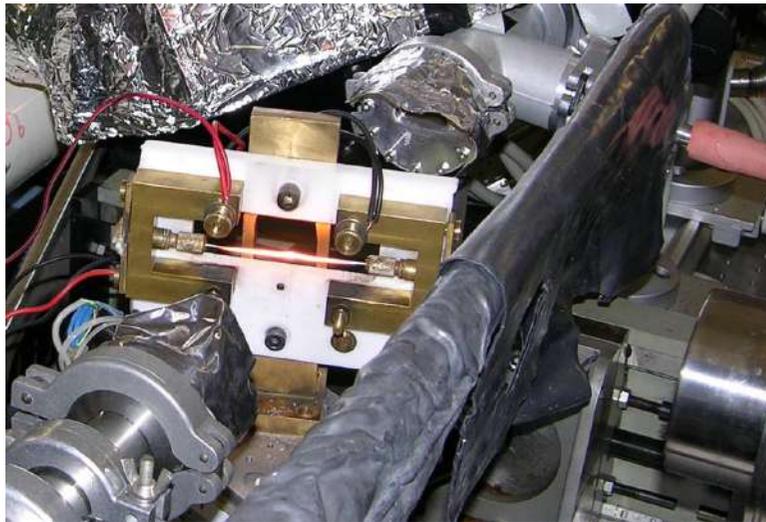
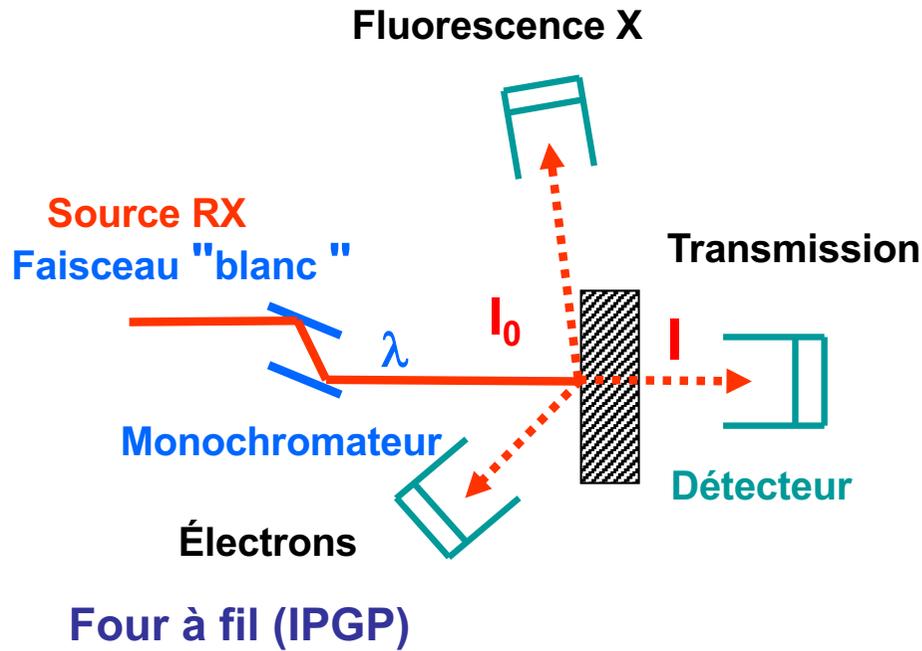
Temps d'acquisition : 50ms

Suivi de l'évolution structurale pendant la formation du verre

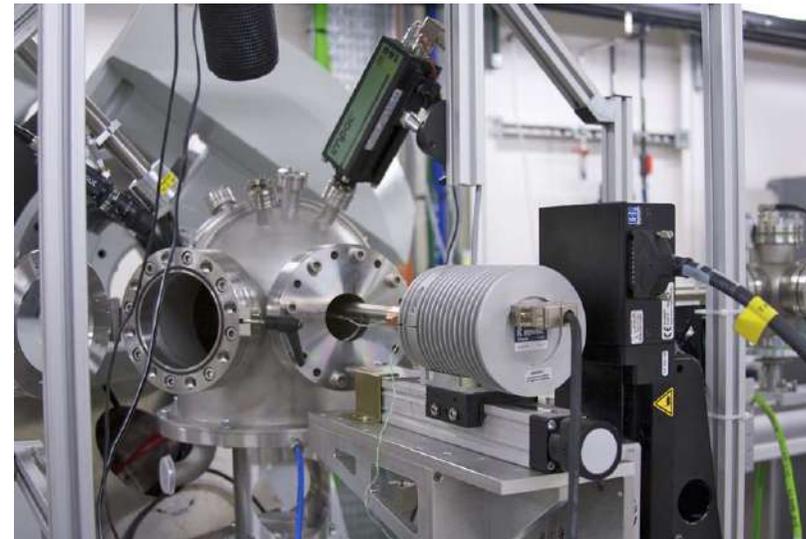
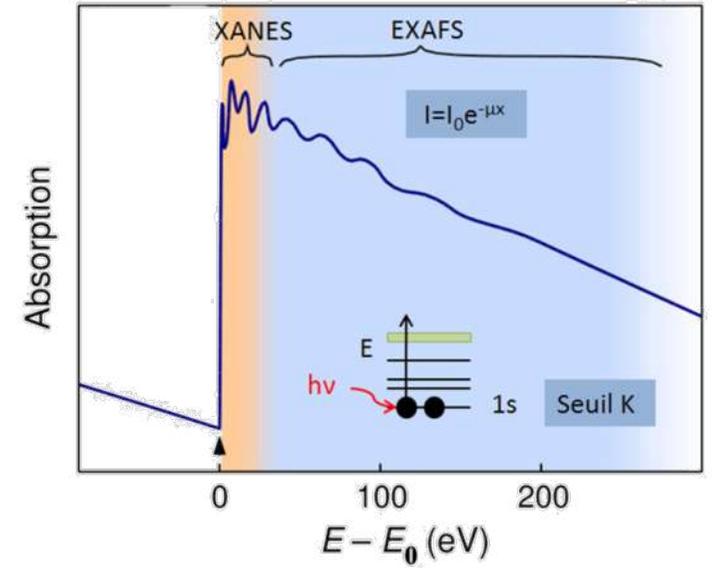
1470 K (1.25T_g)



Absorption des Rayons X



- Transmission et fluorescence
- EXAFS dispersif (suivi temporel)
- Éléments légers



- Uniquement en fluorescence
- Ne convient pas pour les éléments légers

Exemple : XANES

Détermination de l'état d'oxydation (ici Mn et Fe)

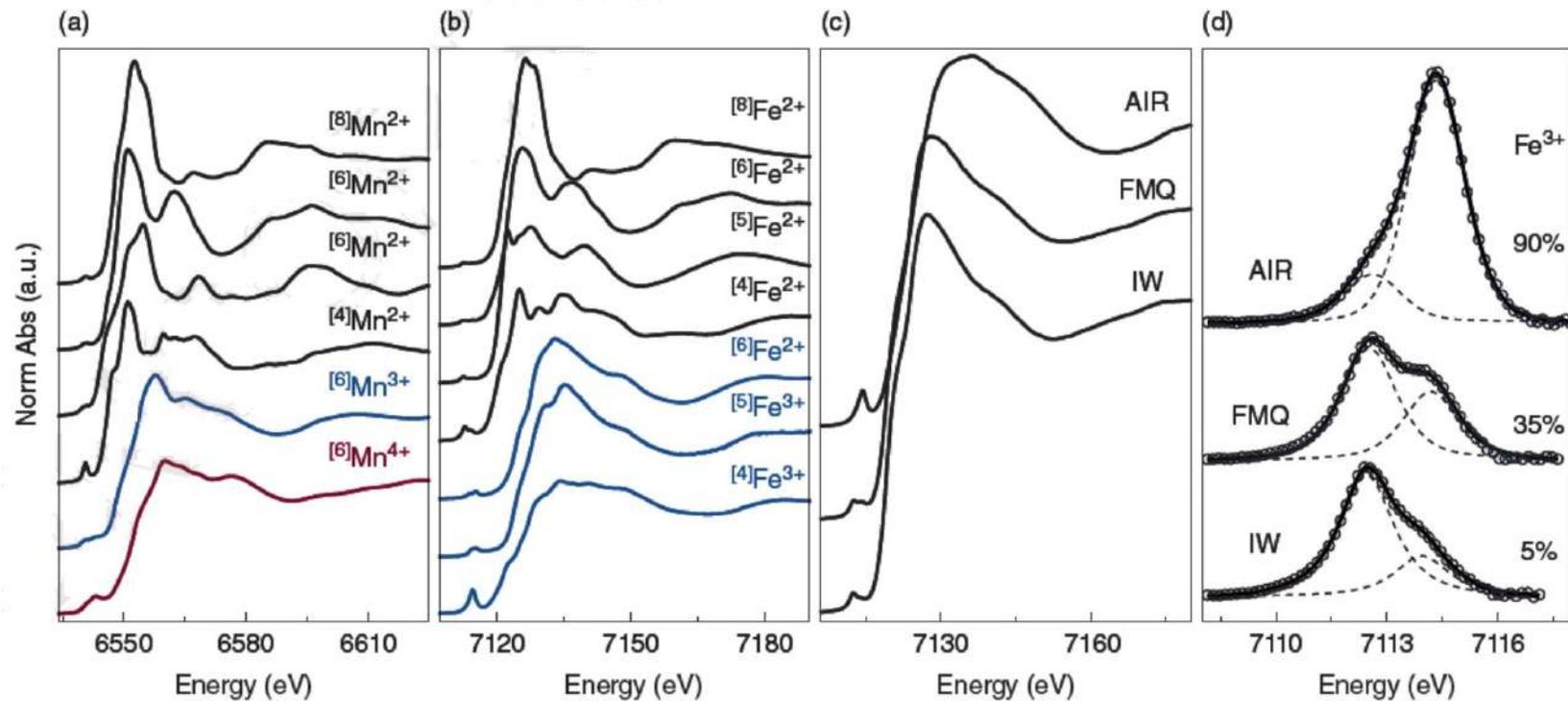


Figure 13.7 K-edge XANES spectra of Mn (a) and Fe (b) crystalline compounds (names listed in Table 13.1). (c) Fe K-edge XANES spectra of silicate glasses equilibrated under different *f*O₂ conditions. (d) background subtracted pre-edge peaks, and their deconvolution; estimated %Fe³⁺ are reported (± 5 %).

Daniel R Neuville, Maria Rita Cicconi, Charles Le Losq. How to Measure the Oxidation State of Multivalent Elements in Minerals, Glasses, and Melts?. *Magma Redox, Geochemistry, Geophysical Monograph 266* (2021)