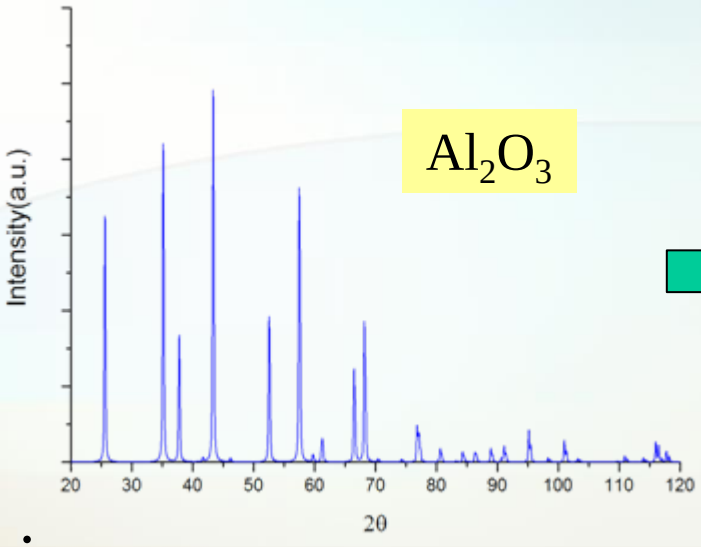
Some results. Outline

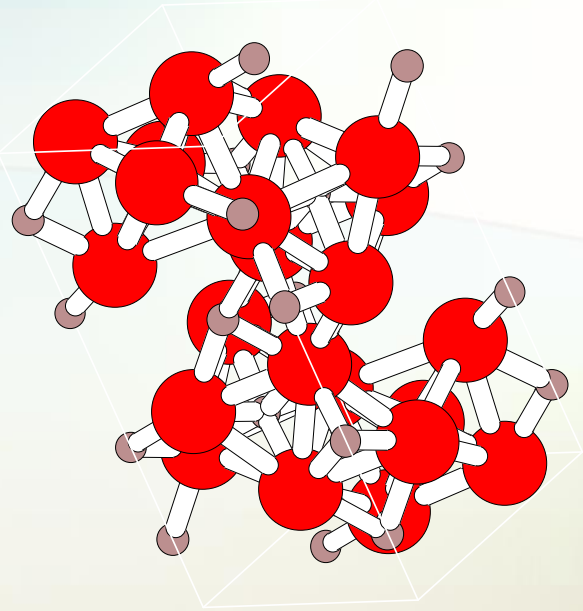
- X-ray experiments
  - ID11 (ESRF)
    - ✓ liquid Si
    - ✓ $(Y_20_3)_x$-$(Al_20_3)_{1-x}$ system
  - ID15 (ESRF)
    - ✓ Al-based alloys
  - ID16 (ESRF)
    - ✓ liquid $(Mg0)_x$-$(Al_20_3)_{1-x}$
- Neutron experiments
  - D4 (ILL)
    - ✓ YAG ($Y_3Al_5O_{12}$)
  - D22 (ILL)
    - ✓ liquid Al-Fe
- Future directions

Structure of liquids

Solid :



Al_2O_3



Liquid :

The structural information is limited to the description of the mean arrangement of the atoms around each atomic species and particularly :

- ✓Interatomic distances
- ✓coordination numbers

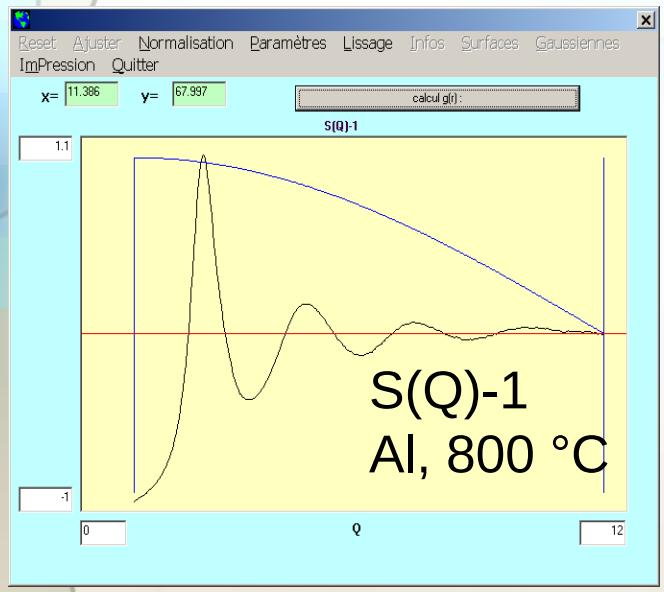
This information is extracted from the pair correlation function g(r)

Data treatment

A diffraction measurement gives: *I(Q)*

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

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

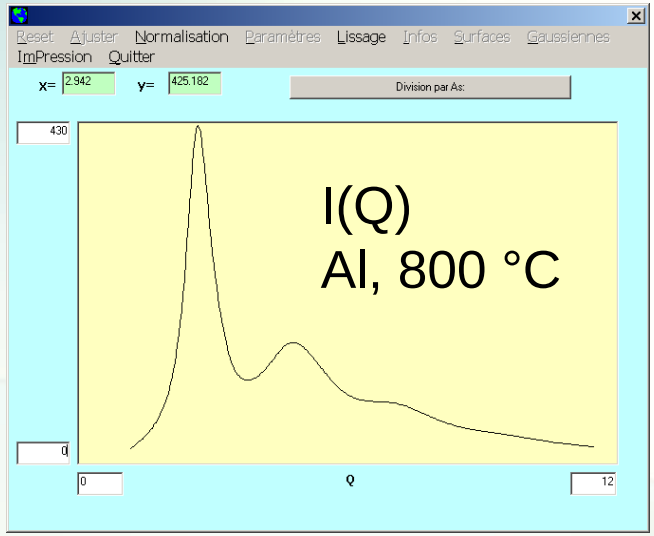


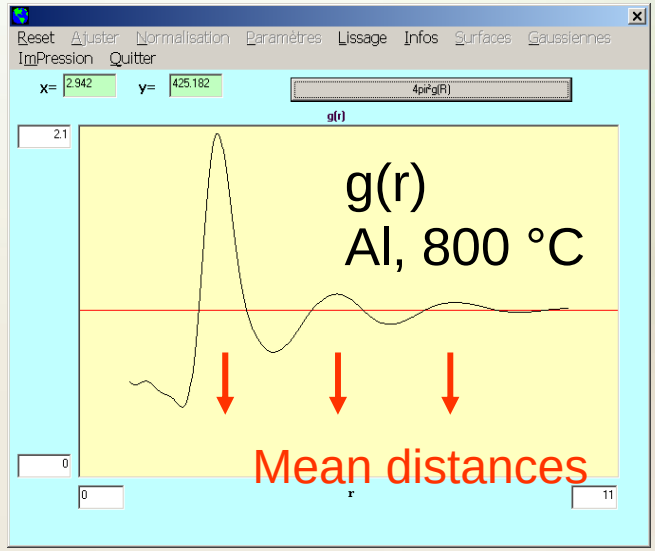
$$S(Q) = \frac{\left(I_{coh}(Q) - \left\langle |f(Q)|^2 \right\rangle\right)}{\left|\langle f(Q) \rangle\right|^2} + 1$$

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

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

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





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

Positions ⟶ **Interatomic distances**

Areas ⟶ **Coordination numbers**

Multicomponent materials: $g(r) = \sum_{i,j} W_{ij} g_{ij}(r)$

Experiments at ESRF - 1

ID 11 Beamline, February 2007

High energy x-ray diffraction

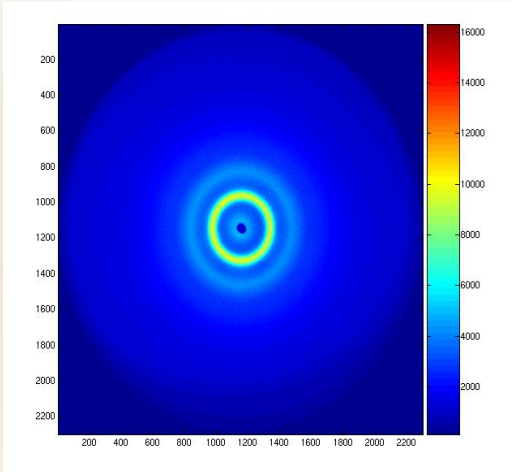
⇒ large Q-range for small 2θ

Data acquisition

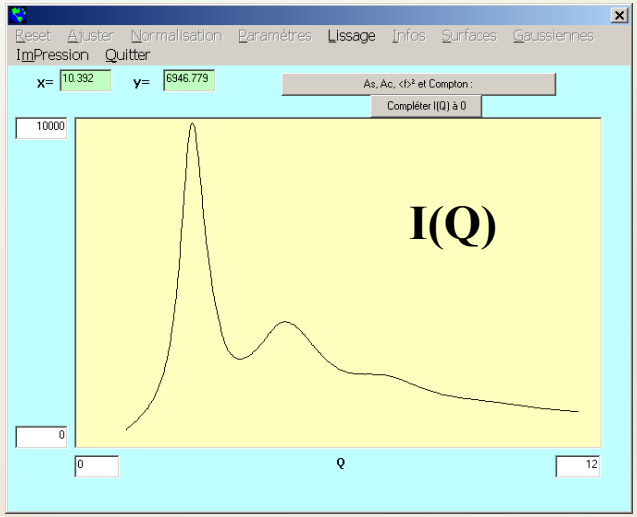
⇒ high resolution

⇒ short acquisition time

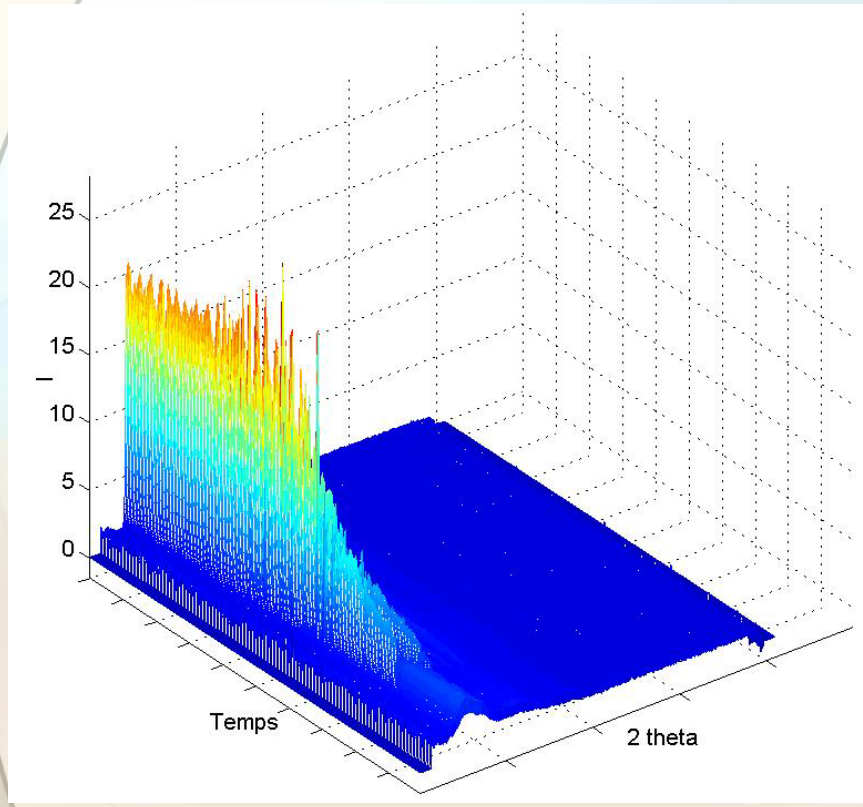
X-ray energy: 79.9 keV
X-ray detector: camera FRELON (minimum acquisition time10 μsec)
Q-range: 0.8 – 19.5 Å^{-1}



Integration:
Fit2D



Objective:
Studies of structure changes in real time



Crystallization of Si

Measurement time:
50 μsec – TR
60 sec – static

Samples:

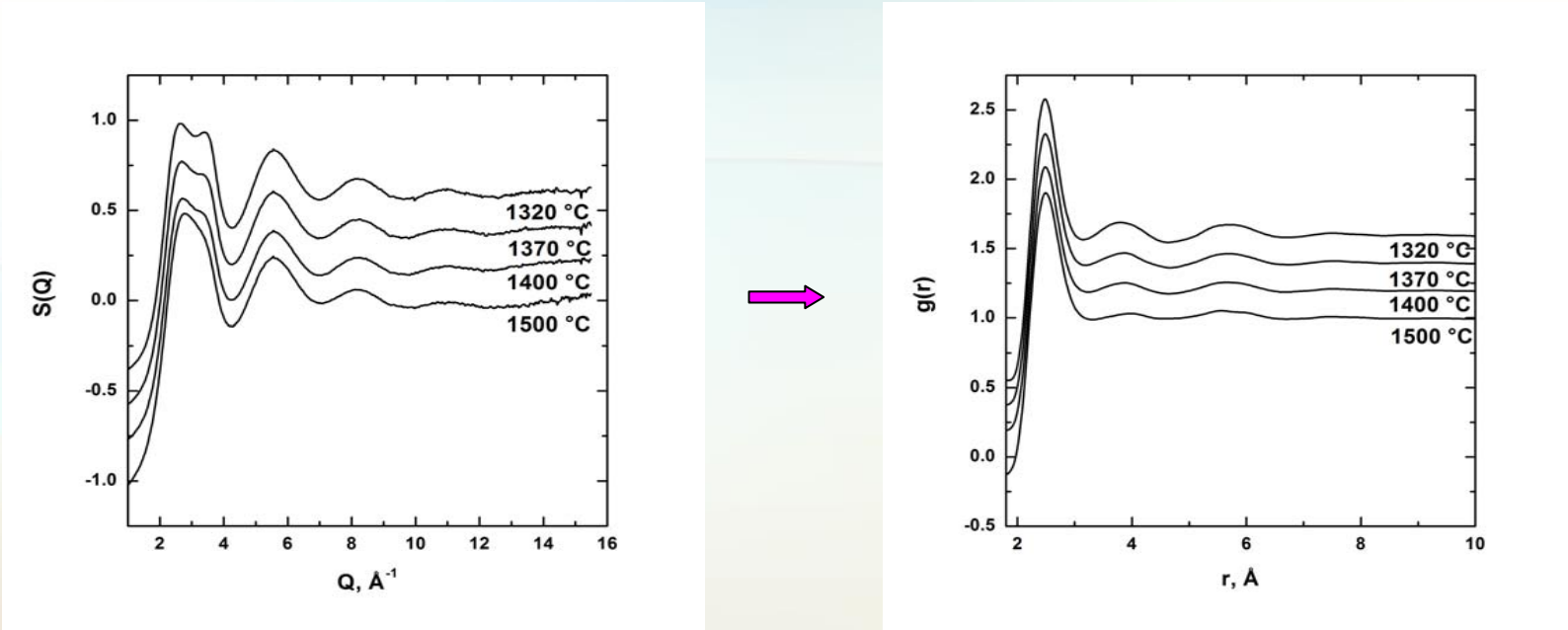
- ***liquid $(CaO)_x$-$(Al_2O_3)_{1-x}$ system***
- ***liquid $(MgO)_x$-$(Al_2O_3)_{1-x}$ system***
- ***liquid $(Y_20_3)_x$-$(Al_20_3)_{1-x}$ system***

(liquid-liquid transition)

- ***liquid Si_xGe_{1-x} system***
- ***liquid $(SiO_2)_x$-$(Al_2O_3)_{1-x}$ system***
- ***$Ca_2Nb_2O_7$***

Preliminary data

Liquid Si



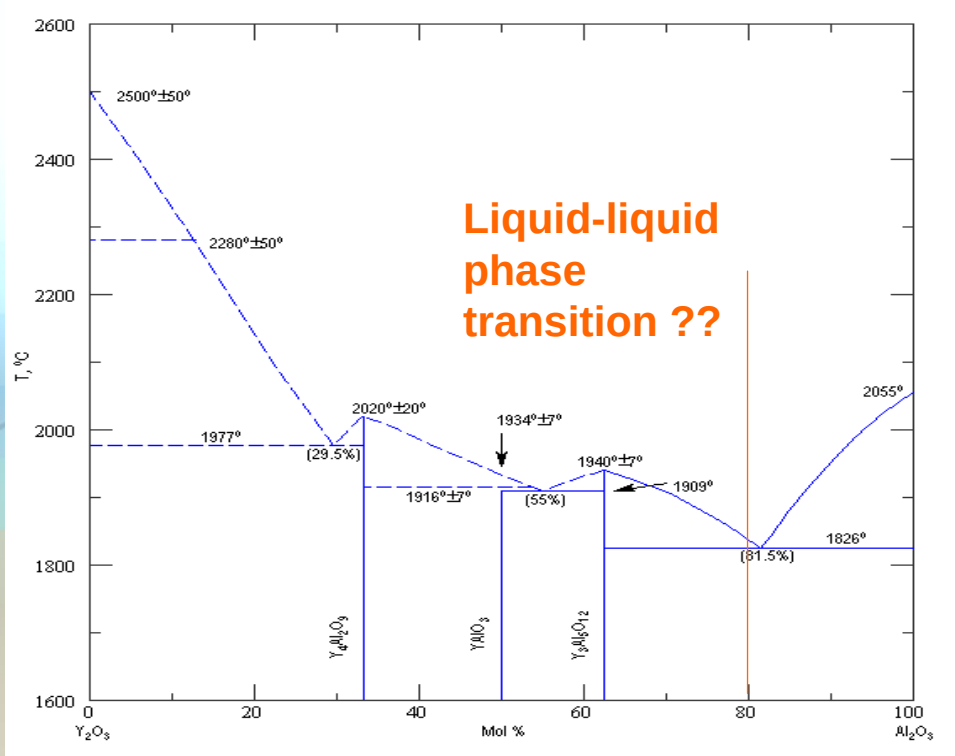
Distances are in accordance with the previous studies (r_1~2.5 Å)

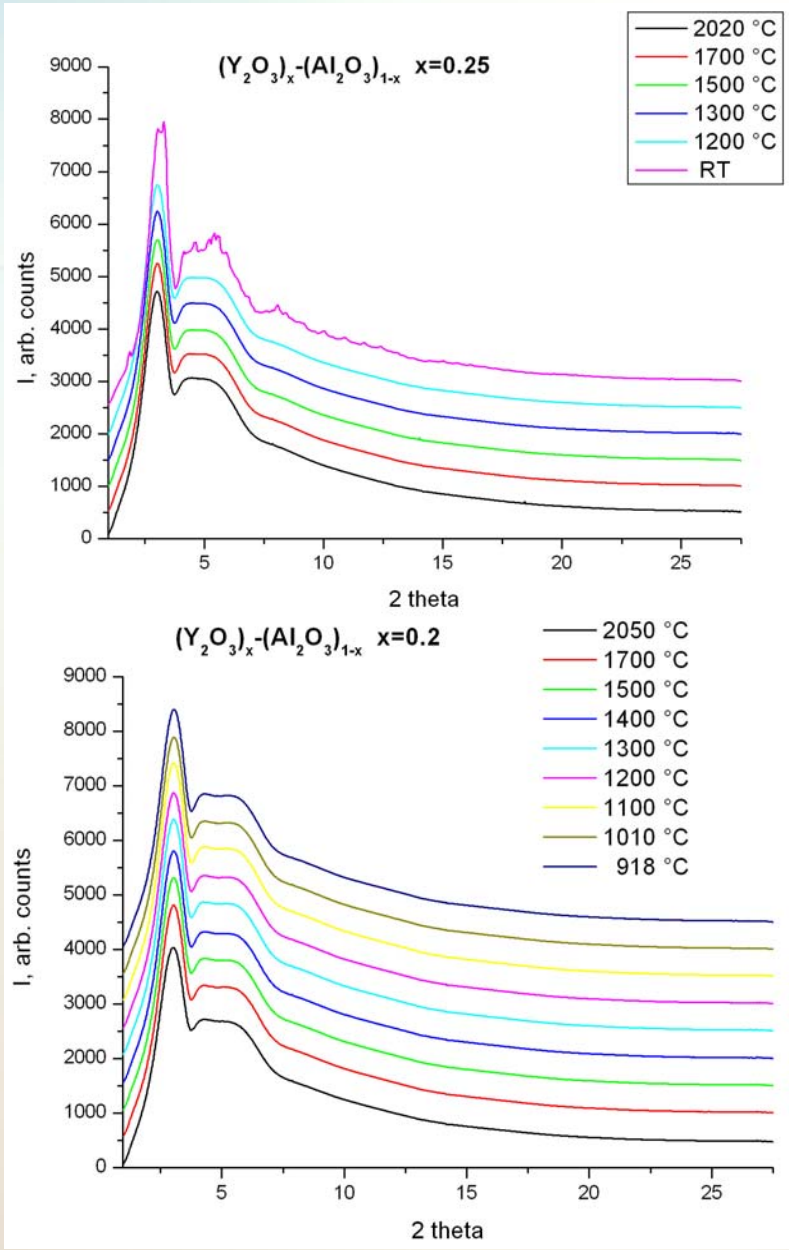
Decrease of the coordination number in the supercooling state is in accordance of the data obtained by Ansell et.al.*

***S. Ansell, S. Krishnan, J.J. Felten, and D.L. Price**

J. Phys.:Cond. Mat. 10, L73 (1998)

$(Y_2O_3)_x$-$(Al_2O_3)_{1-x}$





Strong supercooling.
No obvious structure changes with temperature.
The crystallization seems to be happened at x=0.25 composition.

Experiments at ESRF - 2

ID 15B Beamline, February 2005

X-ray energy: 88.51 keV
X-ray detector: MAR345
(345 mm, pixel size is 150 μm)
Readout time (scan + erase) ~ 1-2 min
Q-range: 0.8 - 14 $Å^{-1}$

Materials:

- Al-Fe (4.22at% and 7.5at%Fe)
- Al-Ti (0.5at% and 1.0at% Ti)
- Al-Cu (17at%Cu-eutectic and 33at%Cu-Al_2Cu
- Al-Ni (2.7at%Ni-eutectic and 25at%Ni-Al_3Ni

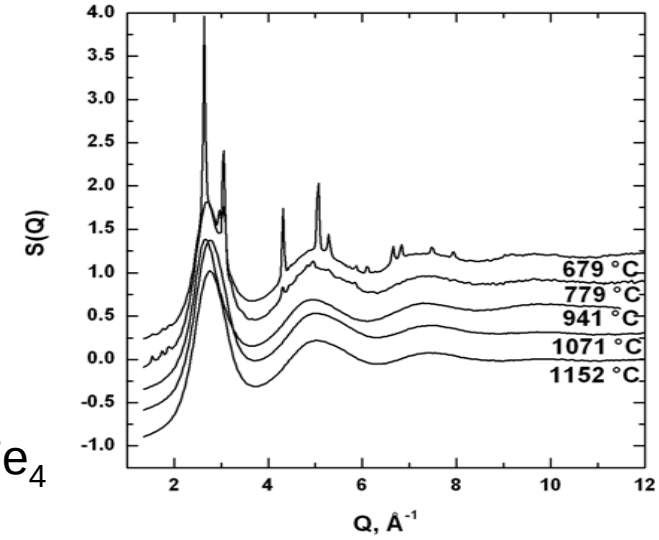
Objectives:

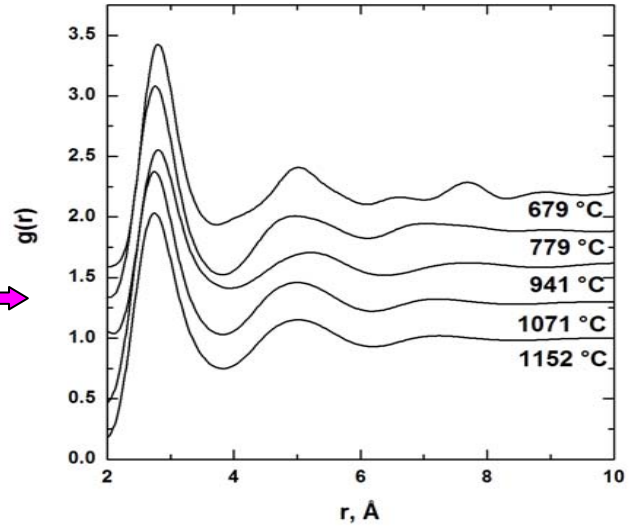
Local structure

- Coordination numbers
- Distances
- Clusters
- Supercooling

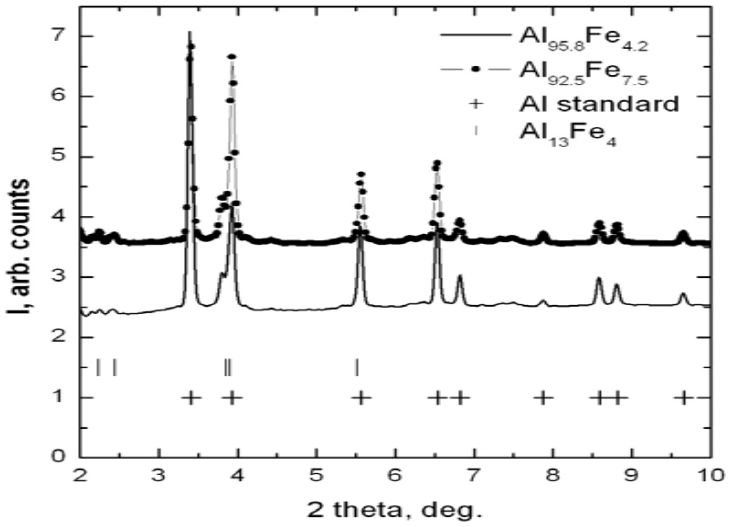
Al-Fe alloys

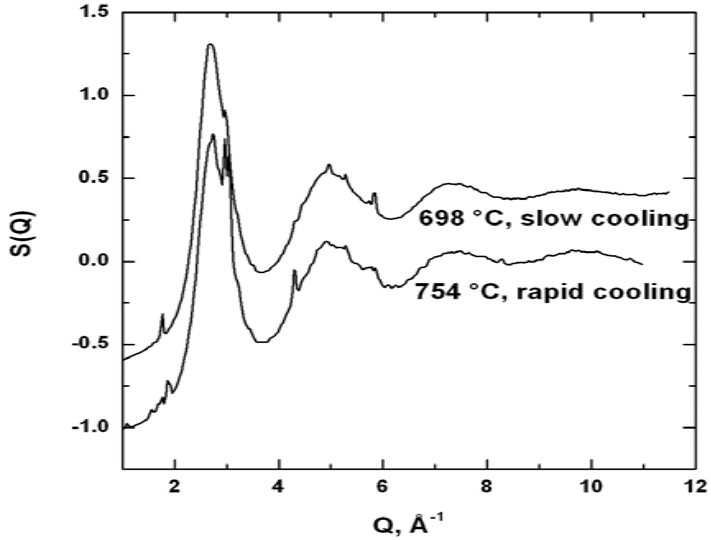
Liquid $Al_{95.8}Fe_{4.2}$ at different temperatures





- **New:** cristallisation of intermetallic $Al_{13}Fe_4$ at 4.2% Fe

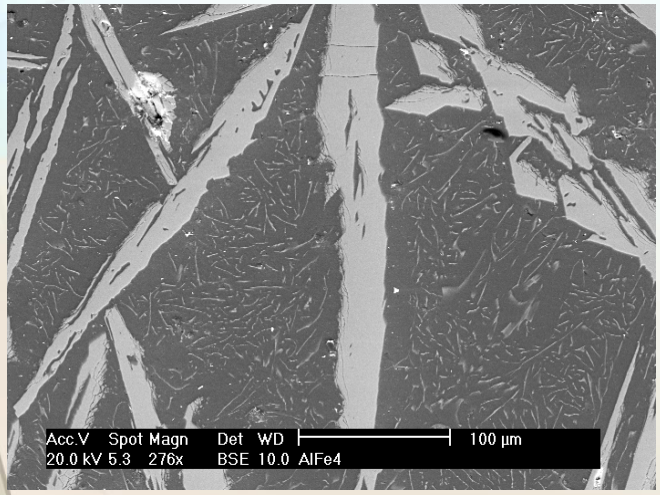




Results

First and second mean interatomic distances nearly temperature-independent

First shell coordination numbers decrease with temperature



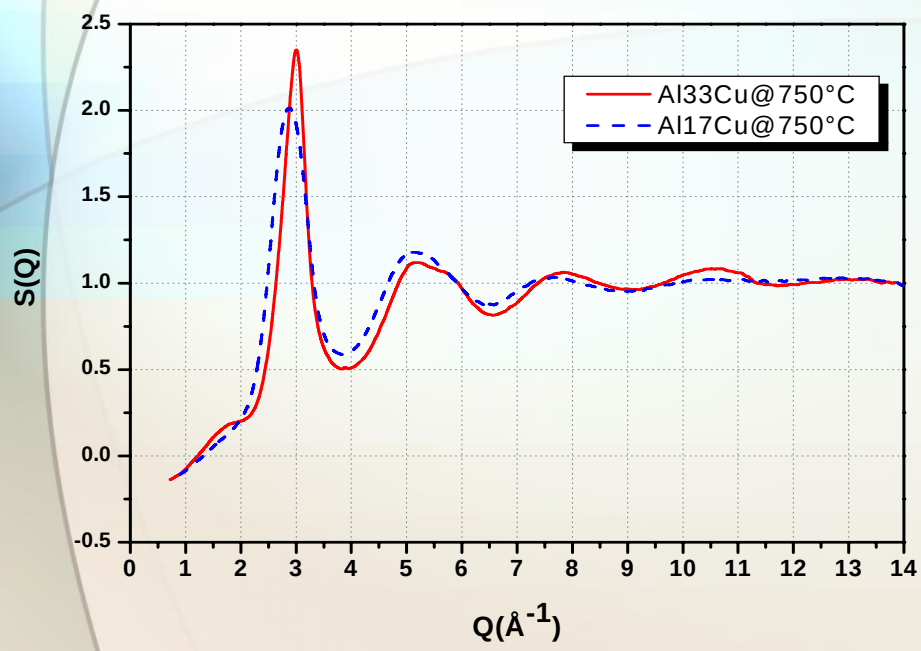
- **Direct observation of the cluster crystallization**
- **Microstructure: needle-like $Al_{13}Fe_4$ clusters in the Al matrix**
- **Two characteristic lenght sizes: ~100 µm and ~10 µm**

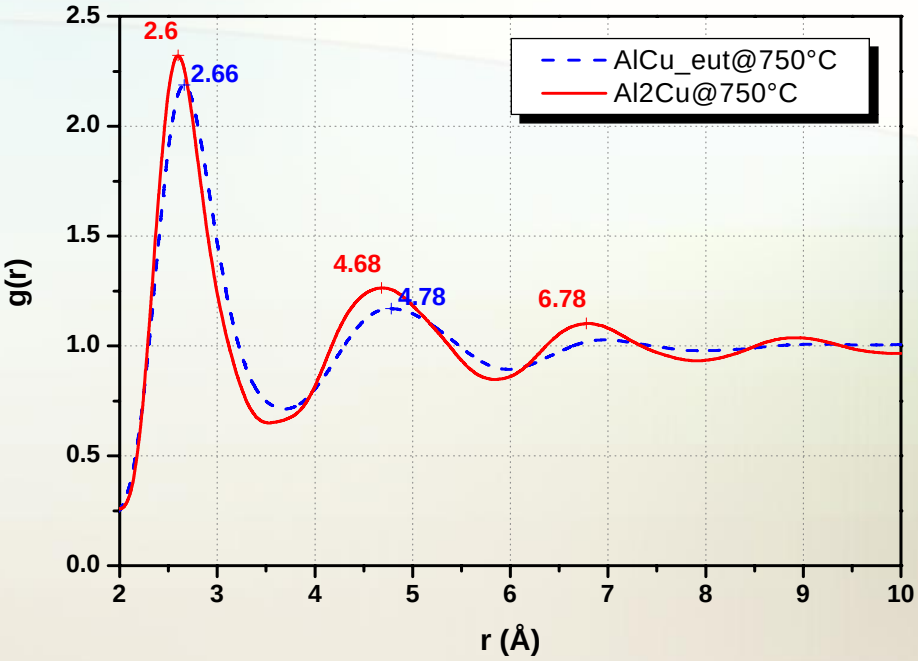
$\Rightarrow$ superior specific strength??

I. Pozdnyakova, L. Hennet, G. Mathiak, J. Brillo, D. Zanghi, J.-F. Brun, S. Brassamin, A. Bytchkov, V. Cristiglio, E. Veron, G. Matzen, G. Geandier, D. Thiaudière, S. C. Moss, I. Egry, D. L. Price
J. Phys.: Condens. Matter 18 (2006) 6469-6480

Al-Cu and Al-Ni alloys

- **Existence of the "pre-peak" in the intermetallic compositions: intermediate-range order, chemical ordering**





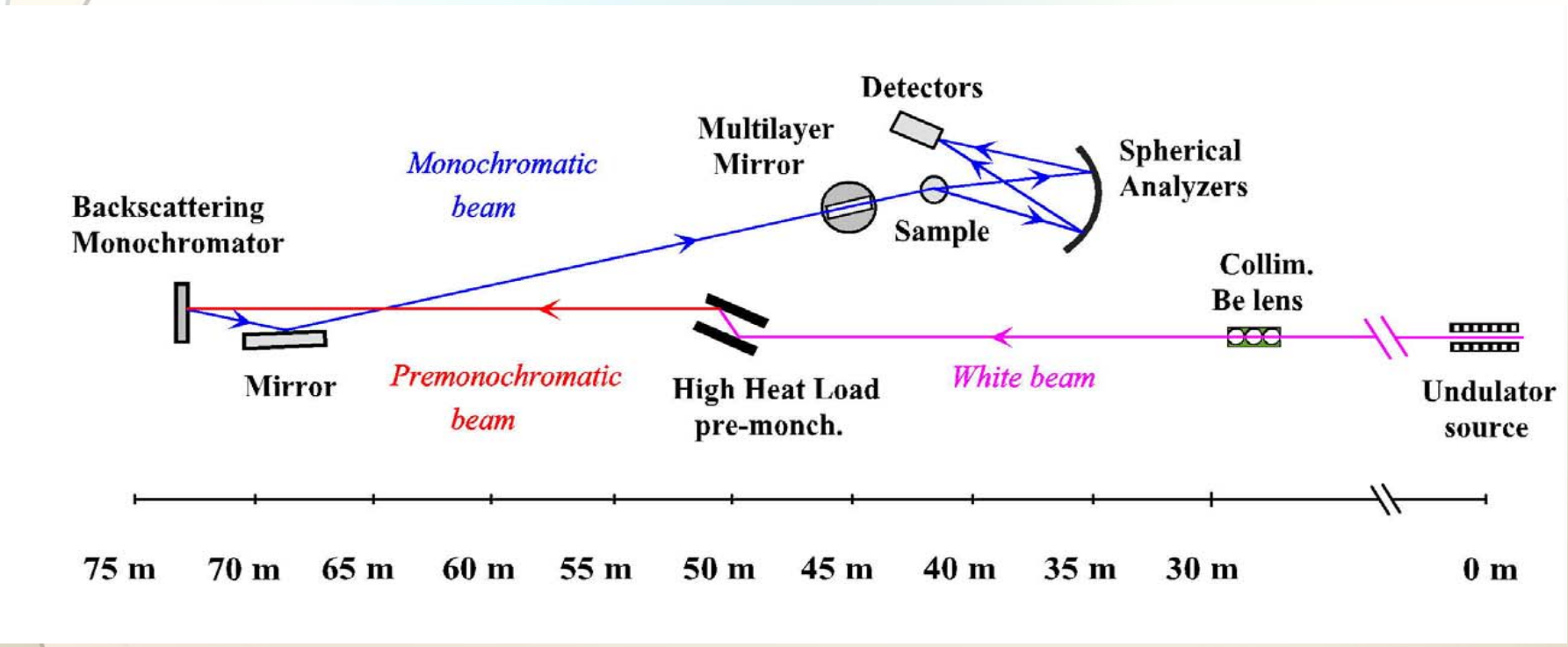
The pre-peak in Al_2Cu was observed for the first time

J. Brillo, A. Bytchkov, I. Egry, L. Hennet, G. Mathiak, I. Pozdnyakova, D. L. Price, D. Thiaudiere; D. Zanghi

J. Non-Cryst. Solids, 352, 4008 (2006)

Experiments at ESRF - 3

ID 16 Beamline, April 2005

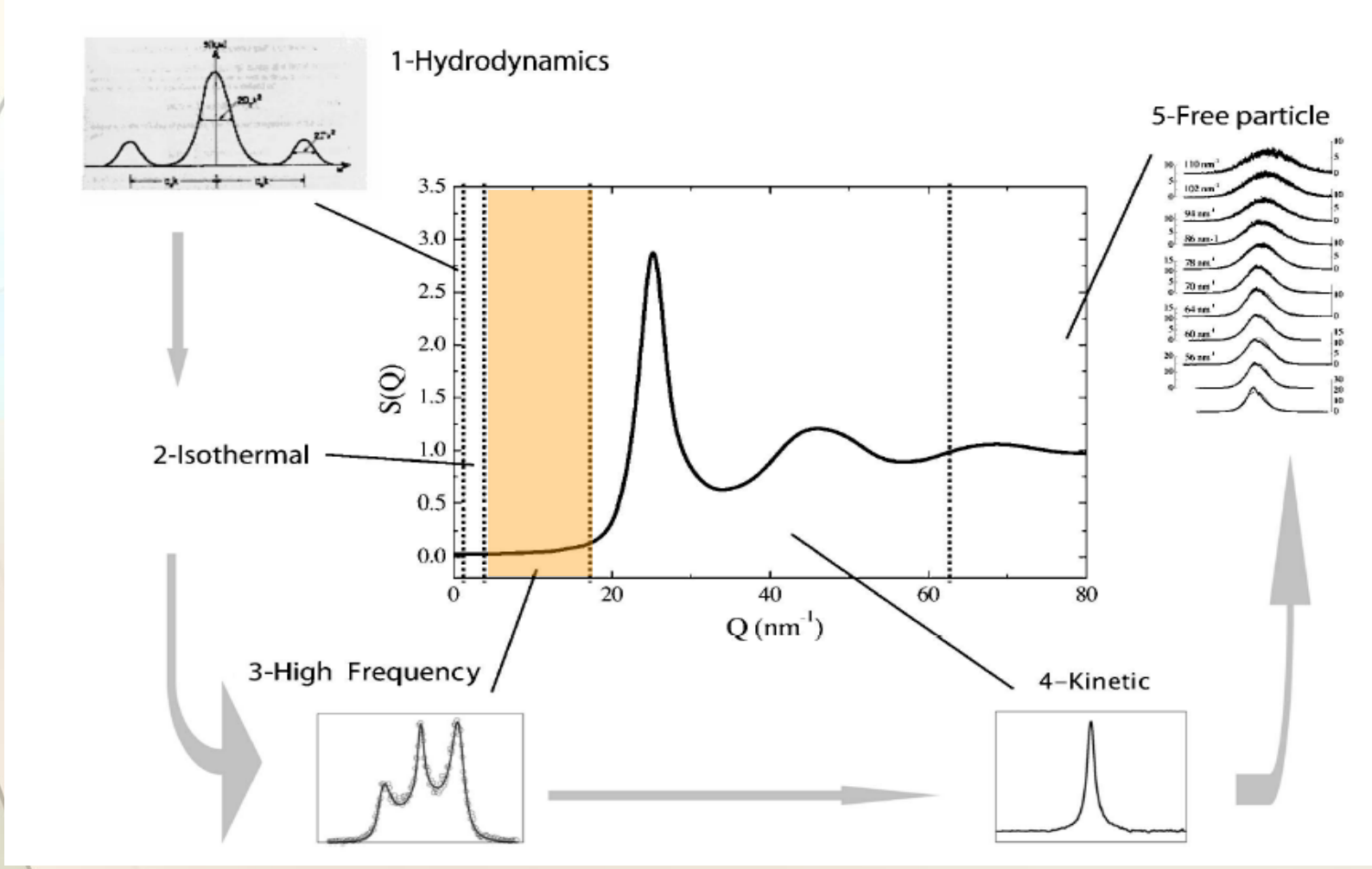


X-ray energy: 21.747 keV (Si (11 11 11) reflection)

Energy resolution: 1.5 meV

Q-range: 1 – 15 nm^{-1}

Dynamics of levitated liquids



T. Scopigno, G. Ruocco, F. Sette, Rev. Mod. Phys. 77, 881 (2005)

Liquid refractory oxides

Objectives:

- **Elastic and transport properties in the liquid state**

  $\Rightarrow$ sound speed

  $\Rightarrow$ melt viscosity

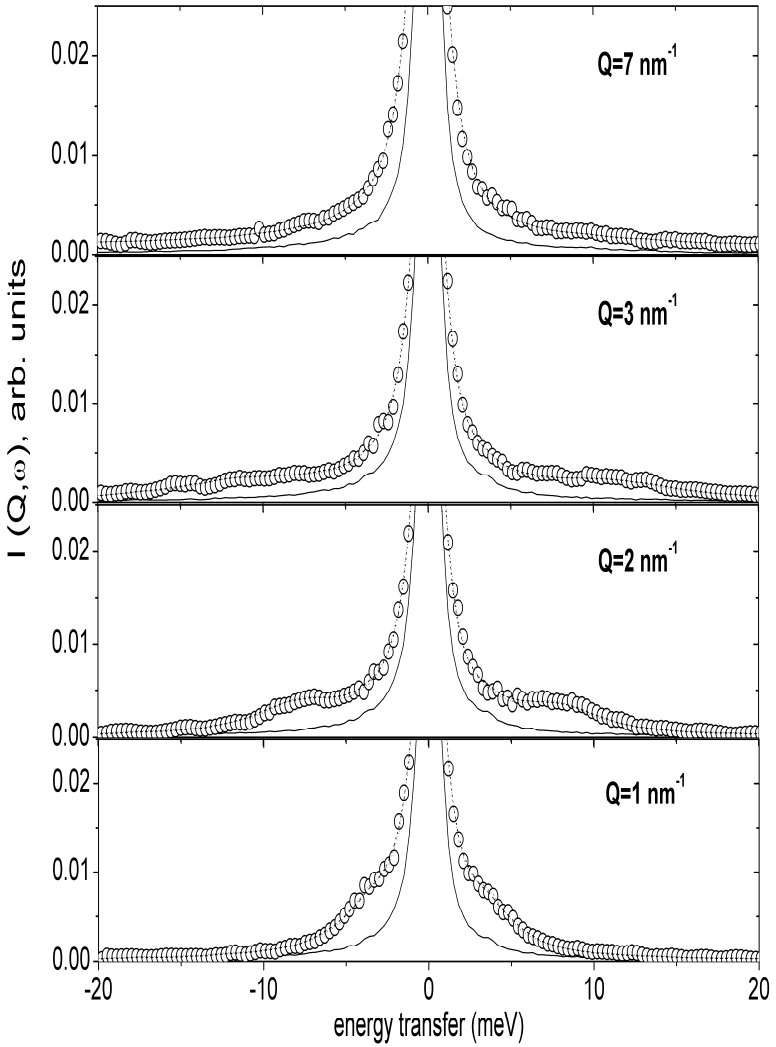
- **Suitability of generalized hydrodynamics for the case of molten oxides**

Materials:

- **$MgAl_2O_4$ (50 mol.% Al_2O_3)**
- **$MgAl_4O_7$ (67 mol.% Al_2O_3)**

Scattered intensity

$MgAl_2O_4$ 2423 K



$$I(Q,\omega) \propto R(\omega) \otimes S(Q,\omega)$$

Generalized Langevin equation

$$m\frac{d\bar{\mathbf{v}}}{dt} = -\int_{-\infty}^{t} m\mathbf{M}(t-s)\bar{\mathbf{v}}(s)ds + \theta(t)$$

M – memory function

$$\mathbf{S(Q,\omega)} = \frac{\mathbf{S(Q)}\pi^{-1}\omega_0^2(Q)\tilde{\mathbf{M}}'(\mathbf{Q},\boldsymbol{\omega})}{\left[\omega^2 - \omega_0^2(Q) + \omega\tilde{\mathbf{M}}''(\mathbf{Q},\boldsymbol{\omega})\right]^2 + \left[\omega\tilde{\mathbf{M}}'(\mathbf{Q},\boldsymbol{\omega})\right]^2}$$

Simplification: S(Q,ω) for one-component system

Data treatment

Memory function: $M(Q,t)=M_{th}(Q,t)+M_L(Q,t)$

Thermal fluctuations — Density fluctuations

$$M_L(Q,t) = 2\Gamma_S(Q)\delta(t) + \Delta^2(Q)e^{-t/\tau(Q)}$$

$$\tilde{M}(Q,\omega) = \frac{\Delta_\alpha{}^2(Q)\tau_\alpha(Q)}{1+i\omega\tau(Q)} + \Gamma_S(Q)$$

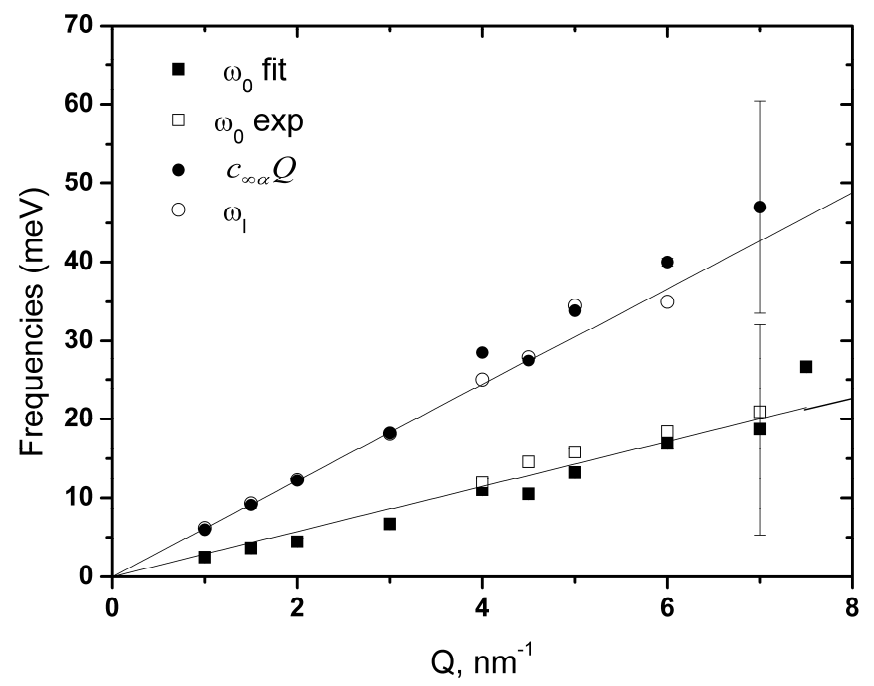
- **Fast process**
- **Slow process: Debye Law (relaxation time: τ / relaxation force Δ)**

Longitudinal viscosity

$$\eta_l = \frac{\rho\left(\Gamma_S(Q) + \Delta^2(Q)\tau(Q)\right)}{Q^2}$$

Sound speed

$MgAl_2O_4$ 2423 K



Apparent sound speed

$$C_l = \omega_l / Q$$ 9.27 km/s

ω_l - maxima of longitudinal current correlation spectra :

$$J_L(Q,\omega) = \omega^2 / Q^2 S(Q,\omega)$$

Isothermal sound speed

$$C_0 = \omega_0 / Q$$ 4.34 km/s

$$\omega_0^2 = k_B T Q^2 / mS(Q)$$

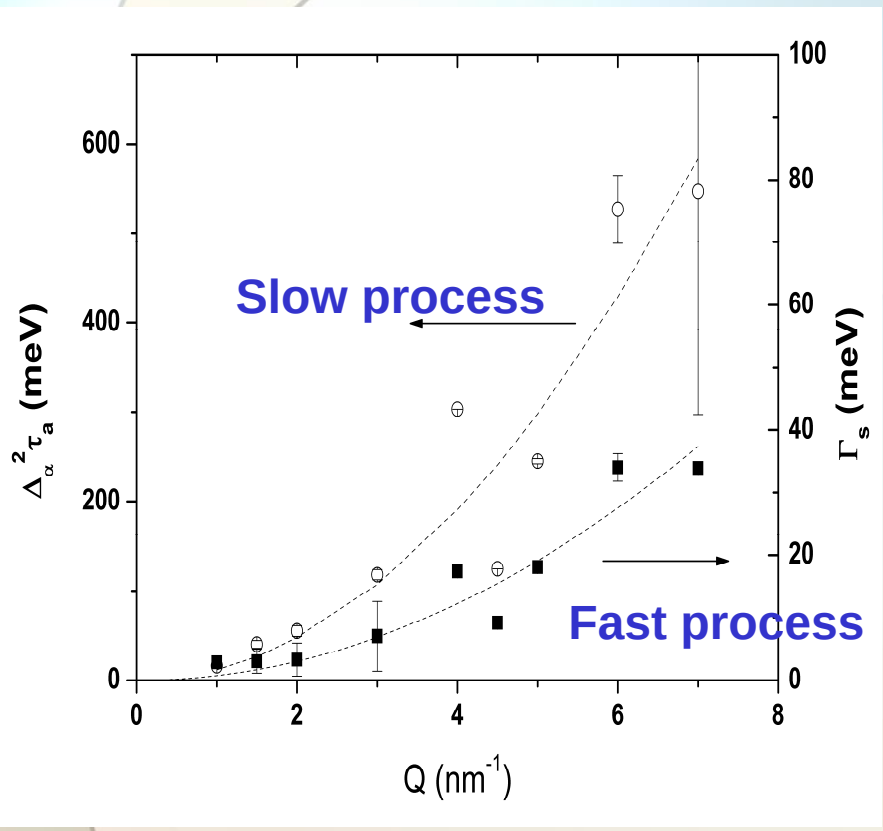
High-frequency sound speed

$$c_{\infty\alpha} = \sqrt{\omega_0^2(Q) + \Delta_\alpha^2(Q)} / Q$$

Apparent sound speed = **high-frequency sound speed**

The transition between C_0 and C_∞ should happen at $Q < 1$ nm^{-1}

Viscosity



$$\eta_l(Q) = \frac{\rho(\Delta_\alpha^2 \tau_\alpha + \Gamma_S)}{Q^2}$$

Sample	η_L, mPa·s		τ, ps
	Exp	MD	
Al_2O_3*	60	45±2	0.5
$MgAl_4O_7$	80±12	51±4	1.15±0.1
$MgAl_2O_4$	60±6	45±2	0.9±0.1

*H. Sinn et. al., Science **299**, 2047 (2003)

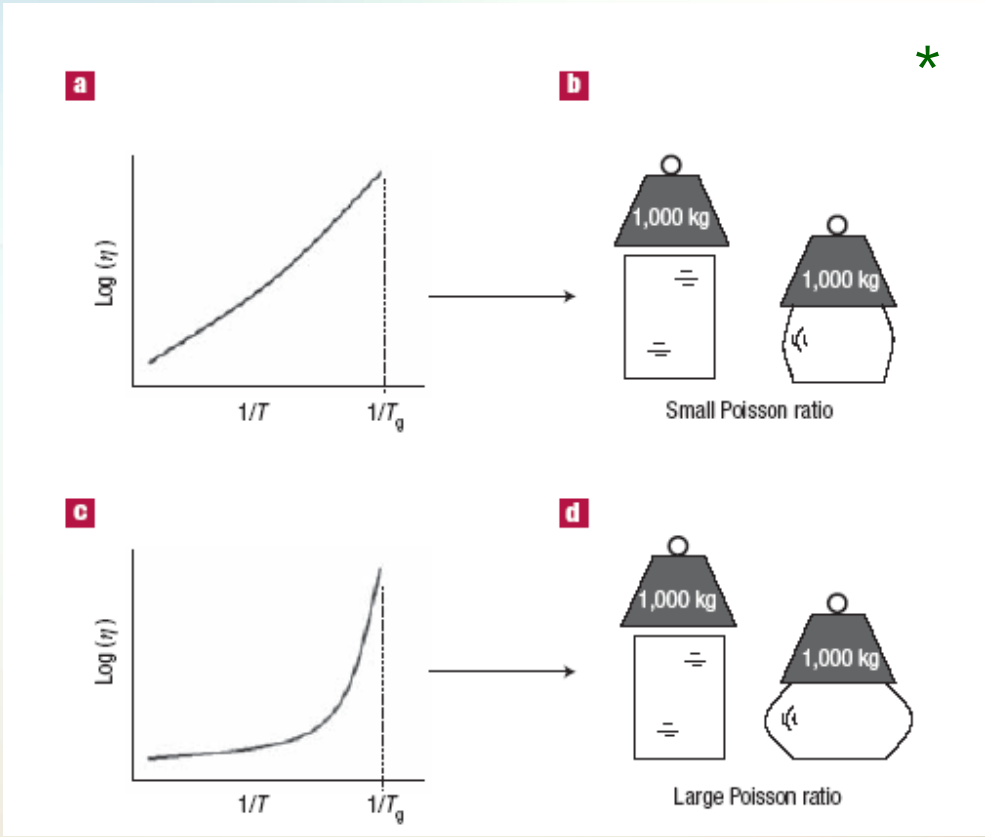
⇒ viscosity maximum at the composition $MgAl_4O_7$??

I.Pozdnyakova, L.Hennet, J.-F.Brun, D.Zanghi, S.Brassamin, V.Cristiglio, D.L.Price, F.Albergamo, A.Bytchkov, S.Jahn, M.-L.Saboungi
J. Chem. Phys. 126 114505-1-4 (2007)

Future directions: “fragile” liquids

New correlations are found:

- Fragility of liquid and Poisson’s ratio of glass#
- **Hypothesis** ⇒ fragility of liquid and short-time properties of liquid*



IS scattering is ONLY technique for studying the elastic response and transport properties SIMULTANEOUSLY

#V. N. Novikov and A. P. Sokolov, Nature 431, 961 (2004)
*J. C. Dyre, Nature Materials 3, 749 (2004)

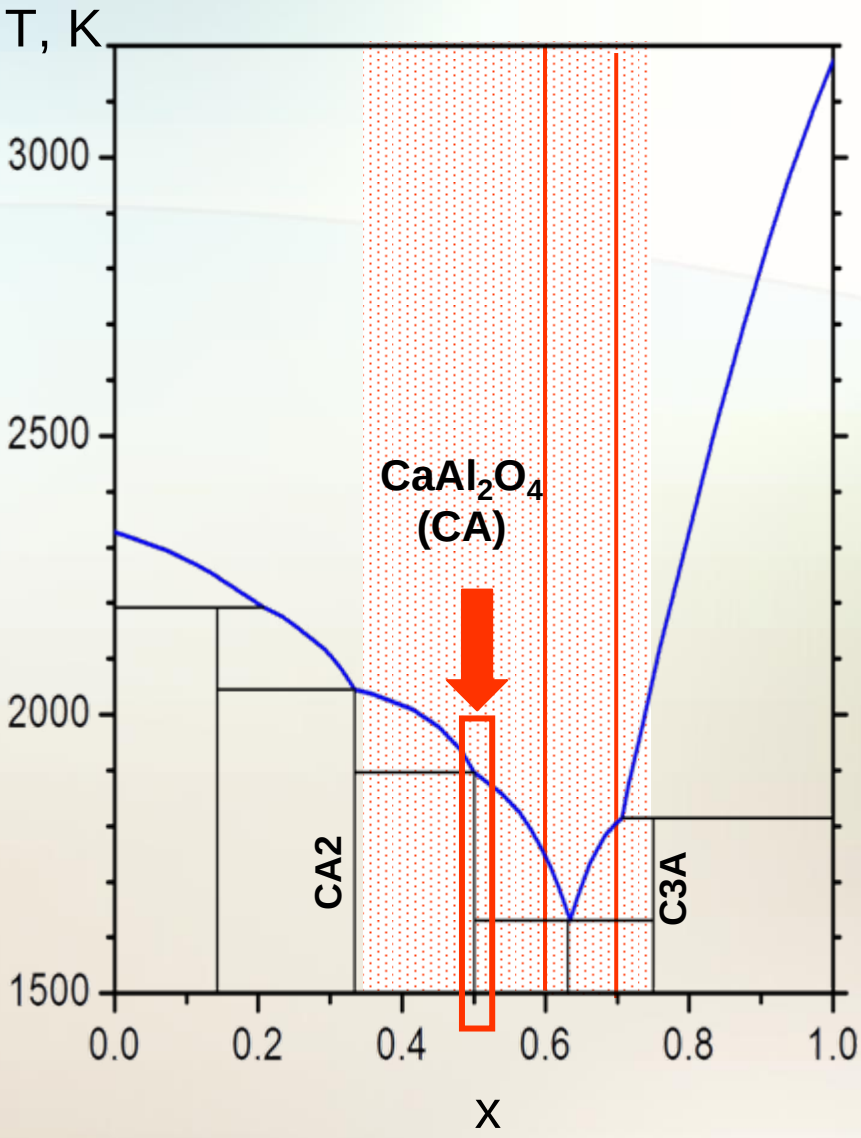
Calcium Aluminate oxides

$(CaO)_x$-$(Al_2O_3)_{1-x}$

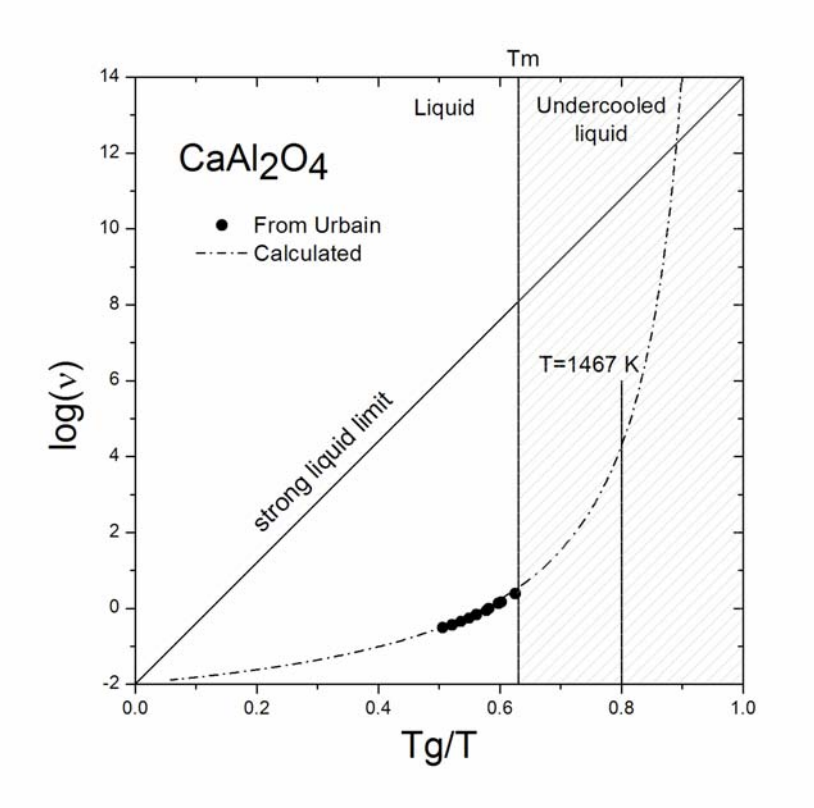
With conventional methods
Narrow vitreous domain: around
x= 0.65

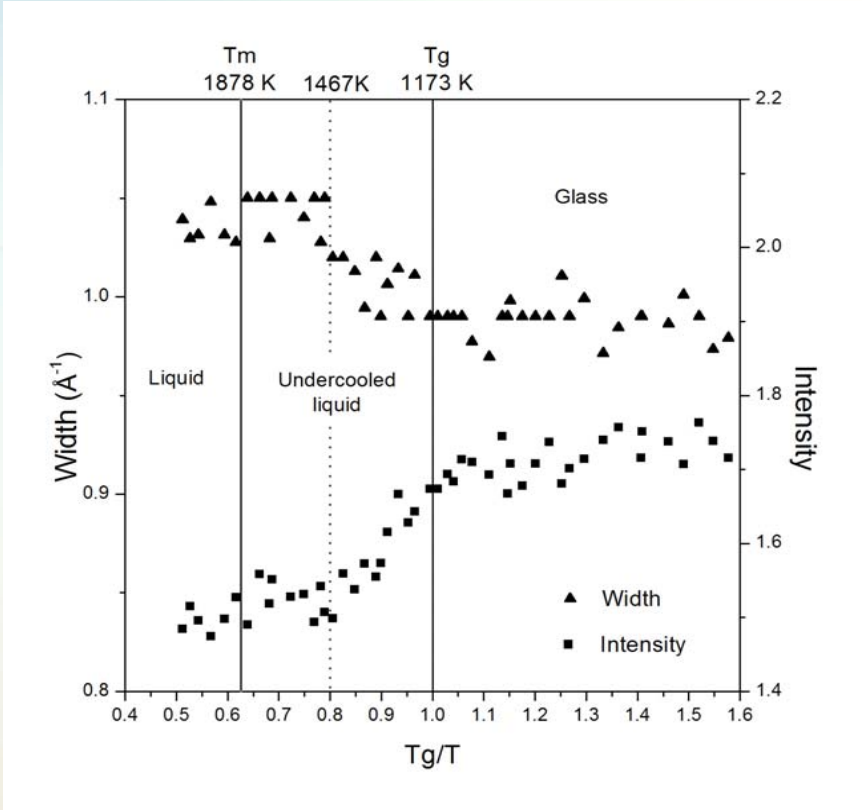
Using levitation techniques
Extension of the vitreous domain to:
0.37<x<0.75

$CaAl_2O_4$ (CA)
(melting point ~ 1873 K)



Calcium Aluminate liquids





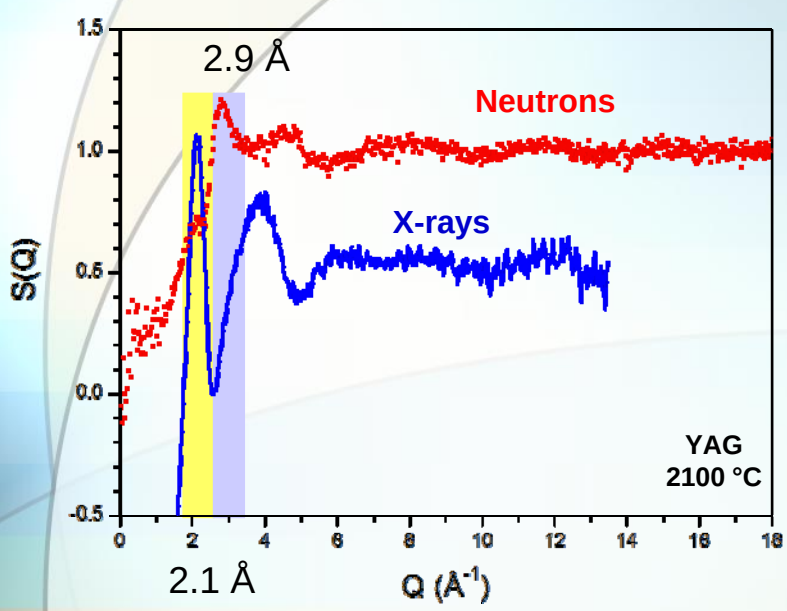
- $CaO\text{-}Al_2O_3$ melts are extremely fragile
- Experimental data on viscosities are incomplete

Width and intensity of the first diffraction peak of the structure factor measured during the cooling of liquid $CaAl_2O_4$

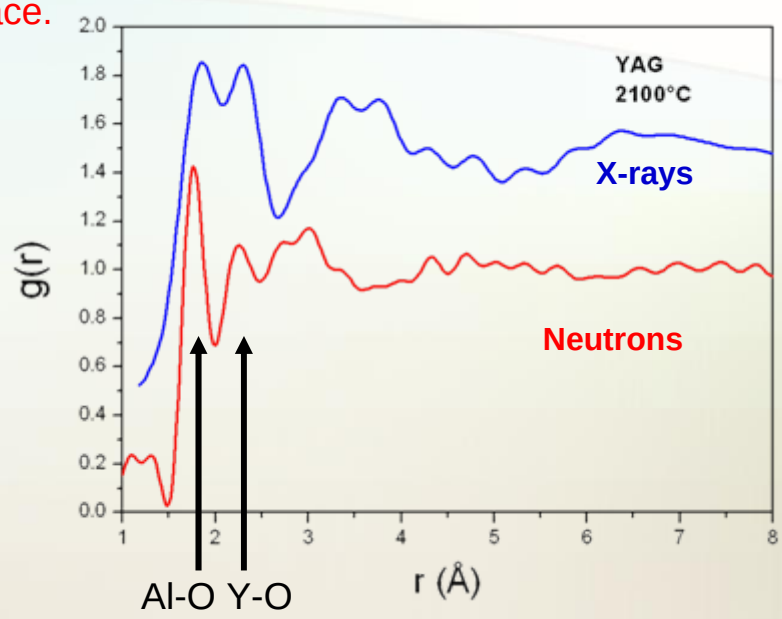
$(Y_2O_3)_x$-$(Al_2O_3)_{1-x}$

X=0.375 YAG ($Y_3Al_5O_{12}$)

(Melting point : 1940 °C)



The larger Q range with neutrons leads to a better resolution in the r-space.



	X-rays	Neutrons
Al-O	**0.175**	**0.198**
Y-O	**0.285**	**0.265**
O-O	**0.129**	**0.400**
Al-Al	**0.060**	**0.024**
Y-Al	**0.193**	**0.066**
Y-Y	**0.158**	**0.045**

0.135

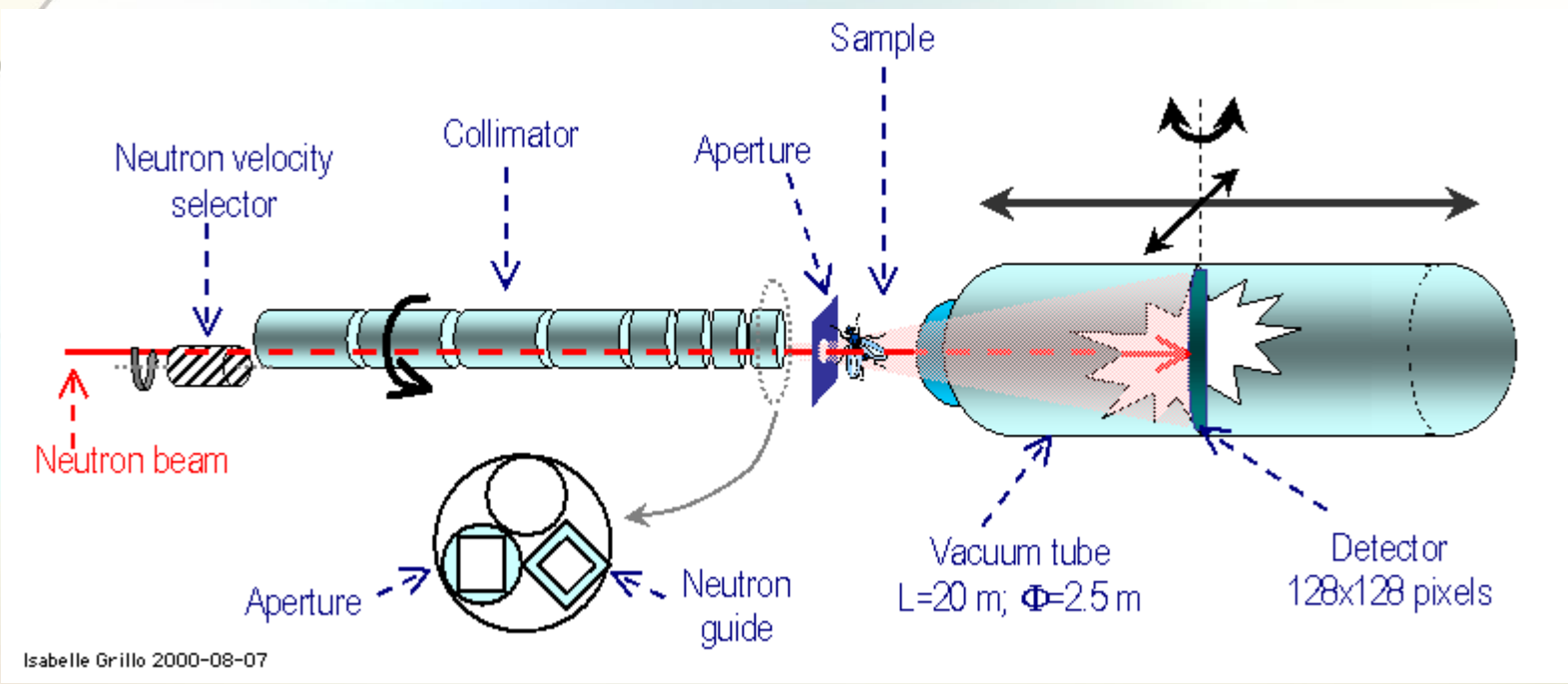
0.411

Weighting factors

	r_{Al-O}	C_{Al-O}	r_{Y-O}	C_{Y-O}
X-rays	1.80 Å	4.2	2.30 Å	6.2
Neutrons	1.78 Å	4.1	2.28 Å	5.6

Good agreement with previous NMR and XRD results

SANS experiment (D22, Oct 06)

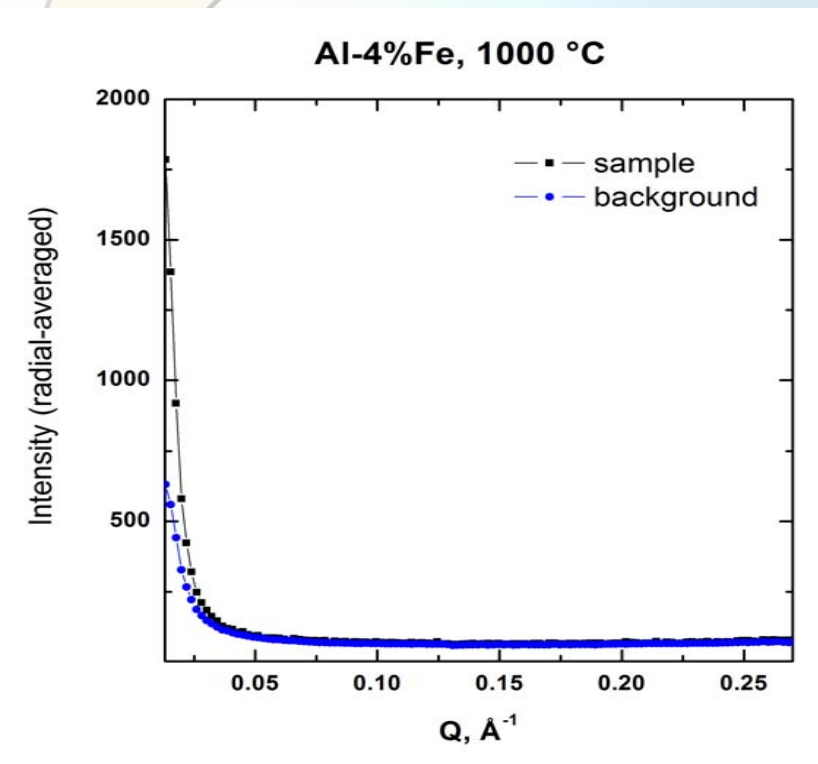


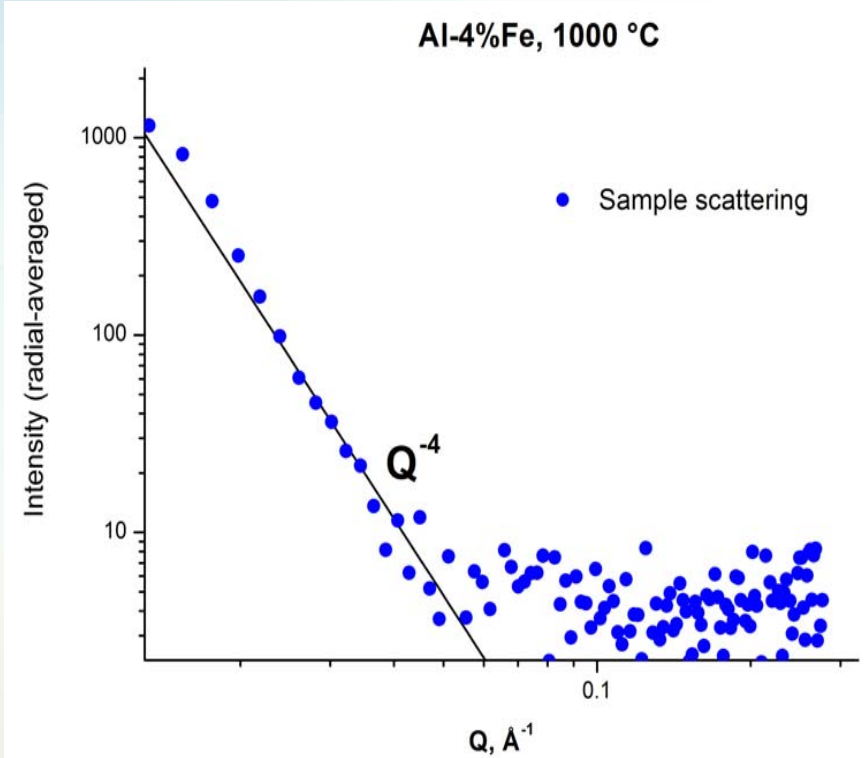
Wavelength: 6 Å
Sample-to-detector distance: 4 m

Samples:

- ***liquid Co-Pd***
- ***liquid Al-4%Fe***
- ***liquid $(Y_2O_3)_x$-$(Al_2O_3)_{1-x}$ (x=0.2; 0.3)***

Few preliminary results

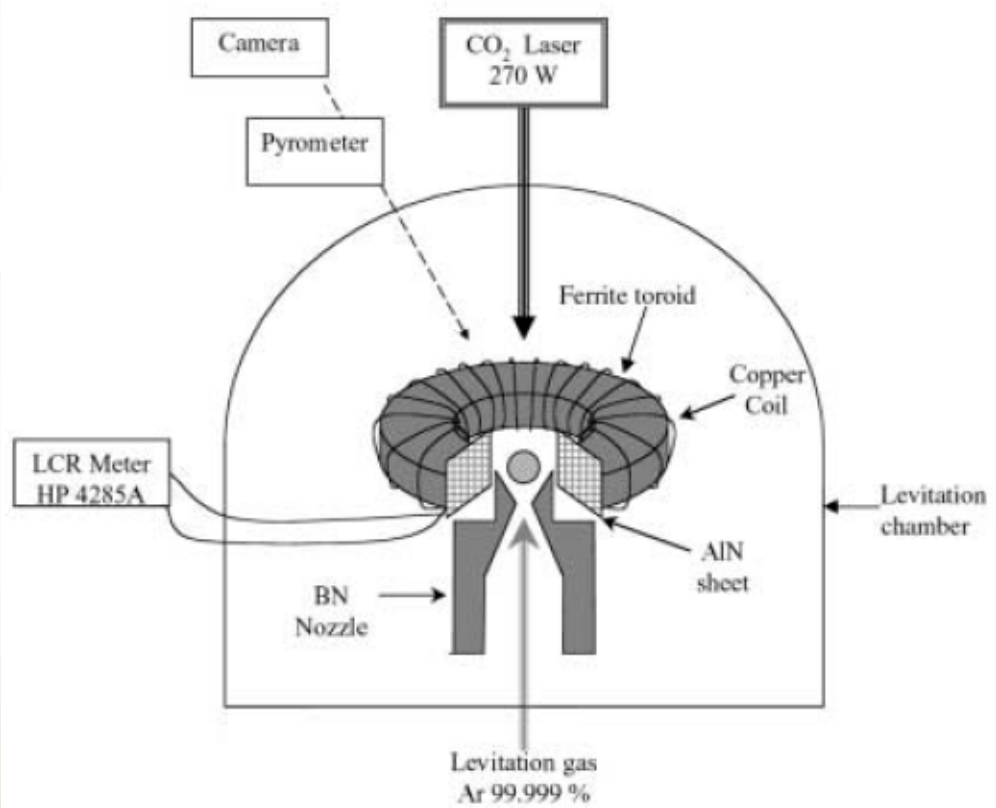




1) Apparently, there is small-angle scattering in the melt well above the liquidus…

2) Scattering domains have sharp boundaries (Porod's Law)

Future directions



Structure + Dynamic + Transport containerless studies