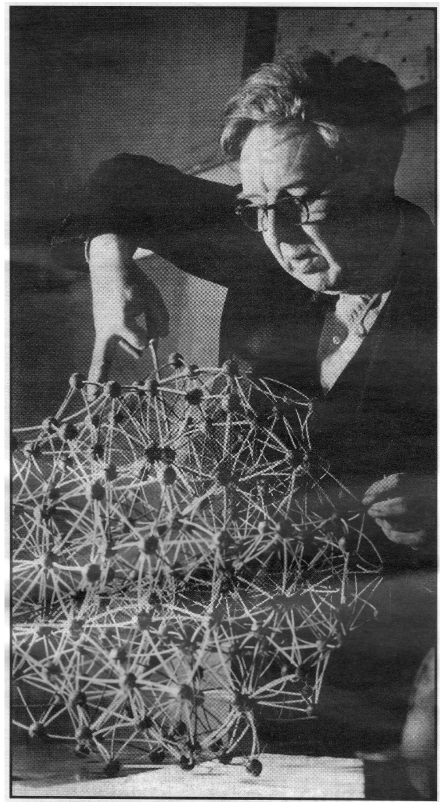
Tracing the pathway to vitrification of a liquid metal in levitation

Authors

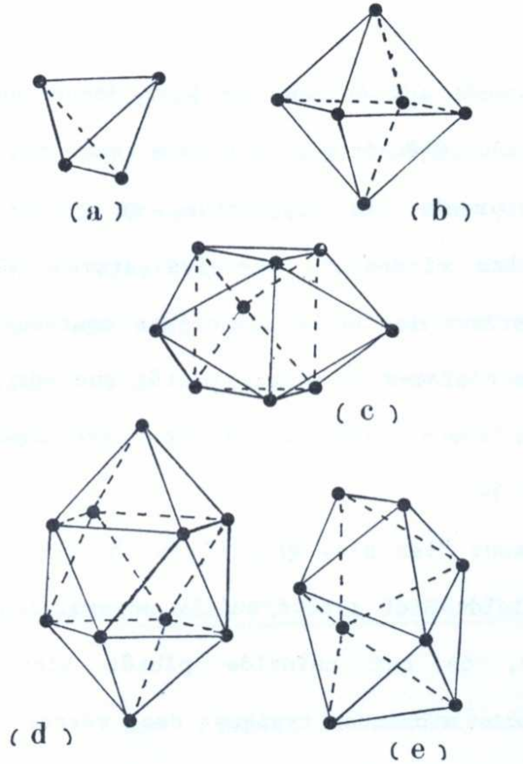
K. Georgarakis[2,1], G. E. Evangelakis[3], L. Hennet[4], J. Antonowicz[5], V. Honkimaki[6], MW Chen[2]

A. R. Yavari[1]

[1]*Euronano SIMaP, Institut National Polytechnique de Grenoble, France*
[2]*WPI Advanced Institute for Materials Research, Tohoku University, Japan*
[3]*University of Ioannina,Greece*
[4]*University of Orleans, France*
[5]*Warsaw University of Technology, Poland*
[6]*European Synchrotron Radiation Facility, Grenoble, France*

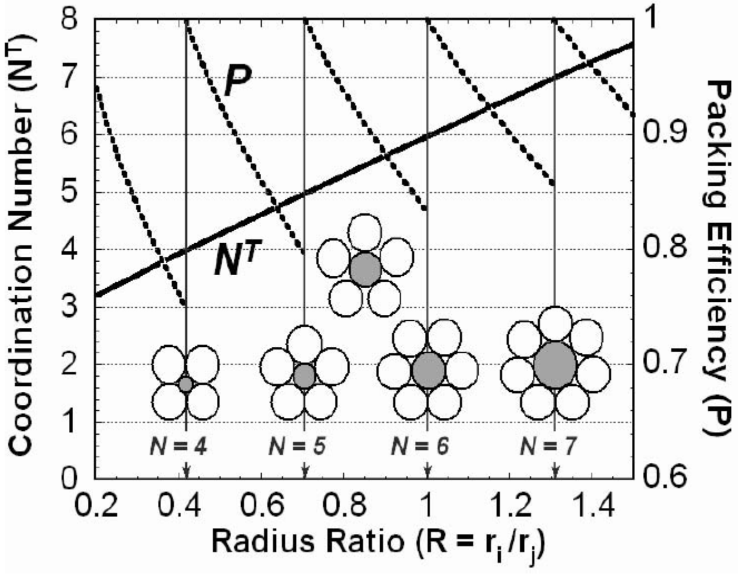


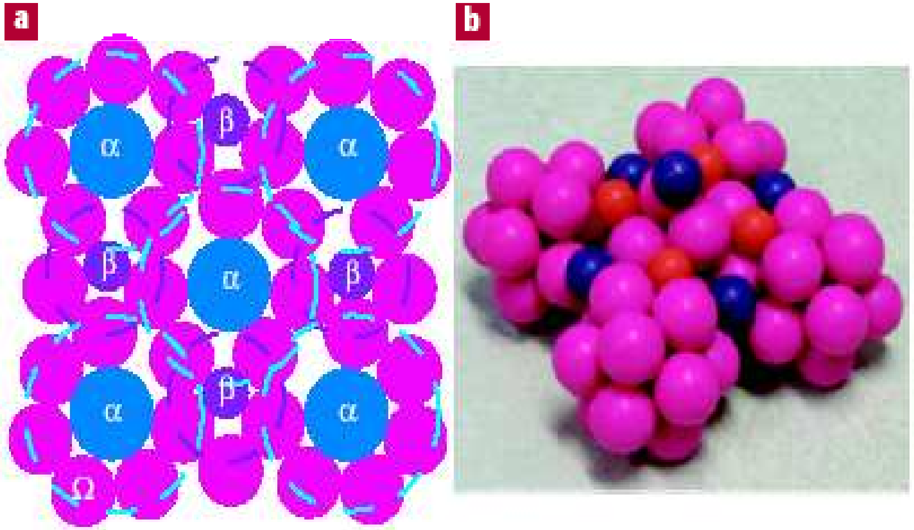
Bernal: with his first ball-and-spoke model of liquid structure

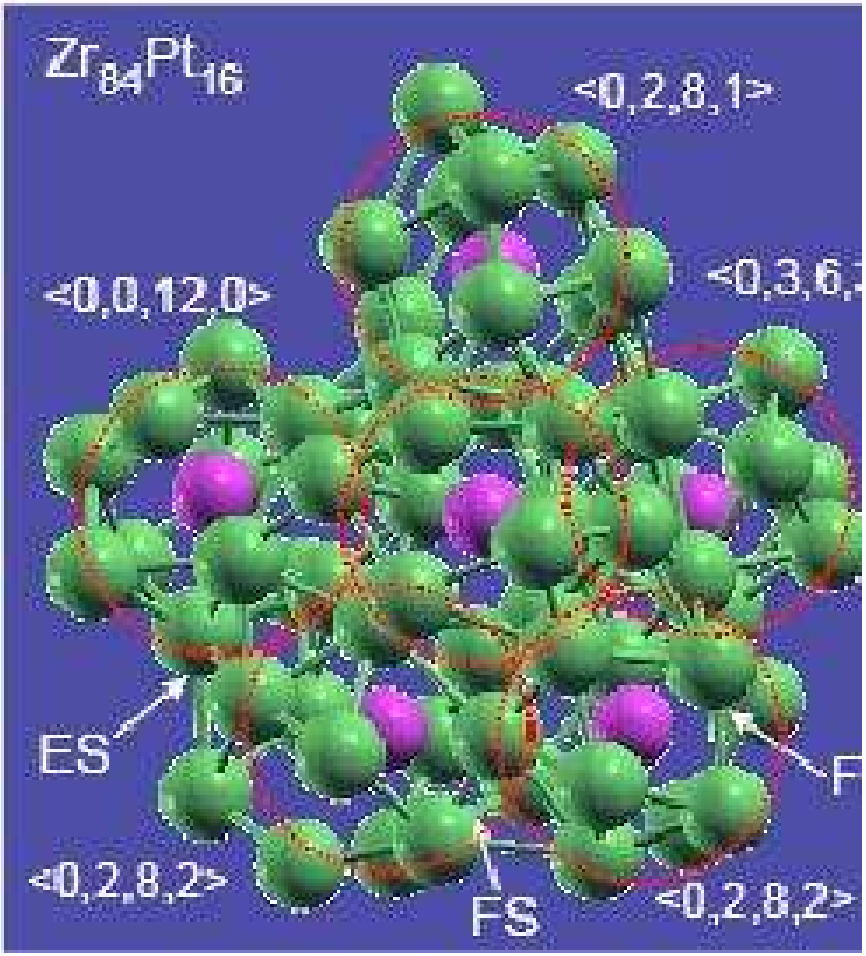


John Desmond Bernal - 1901-1971
The dense random packing DRP model for the structure of liquids.
DRP of A atoms gives a packing fraction of about 66.4% as compared to 74% for fcc and hcp packing or a difference of 11.4%.

from *The Times Higher Education Suppl*. 3 Feb. 2006







-D. Miracle, Nature Materials 2004

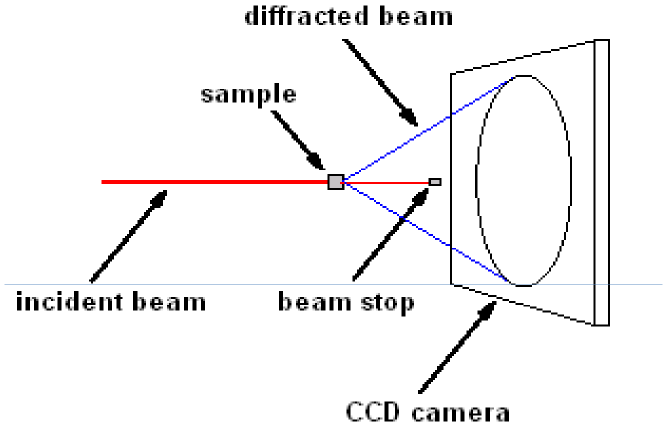
- Yavari, Nature Materials 2005

- Sheng et al, Nature 2006

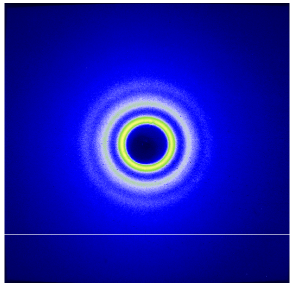
- Yavari, Nature 2006

❑ European Sychrotron Radiation Facility (ESRF)

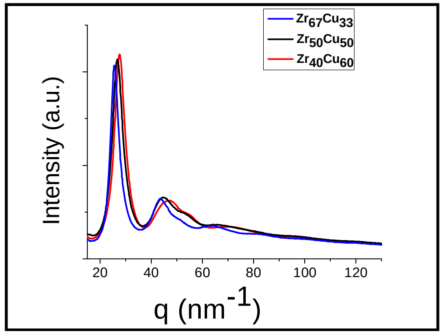
- ➢X-ray diffraction in transmision
- ➢High Energy monochromatic Radiation



Integration of the 2D transmission diffraction pattern

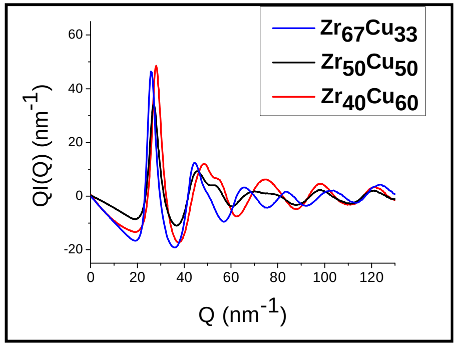


2D CCD camera image



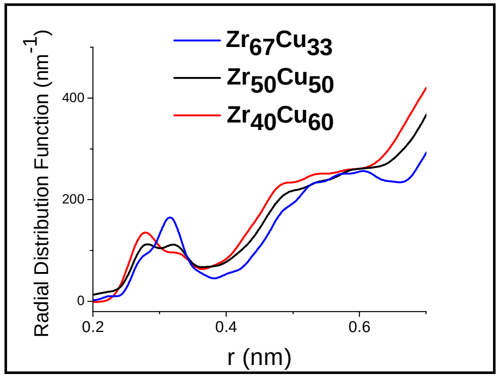
Integrated spectra

Interference Function



q.I(q)

Fourier Transformation



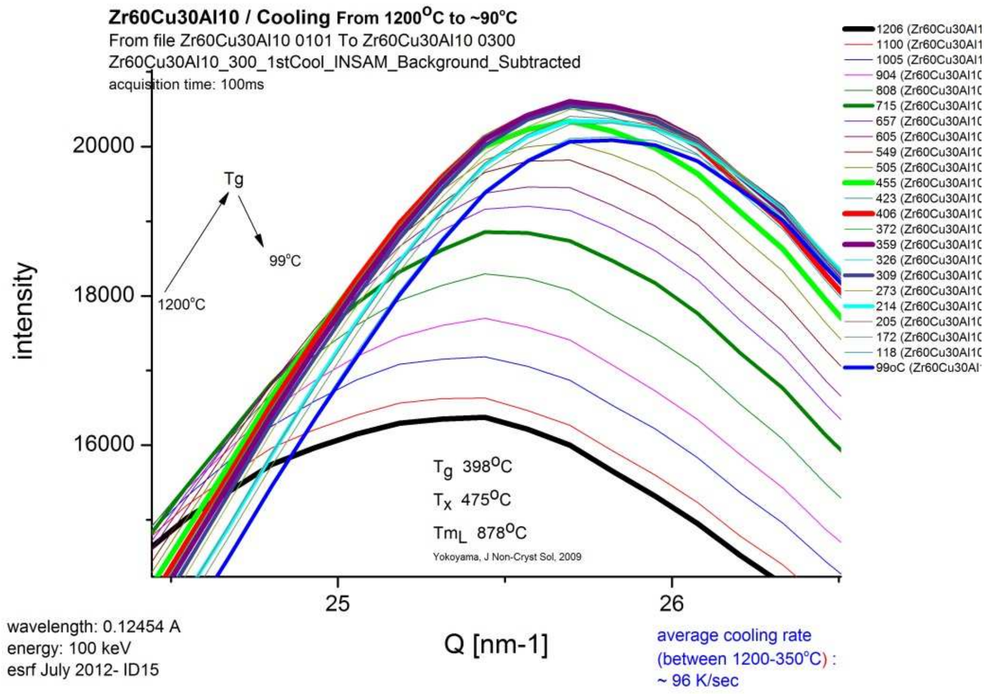
Radial Distribution Function and $G(r) = 4\pi r\,(\rho(r)-\rho_o) = 4\pi\rho_o r\,(g(r)-1)$

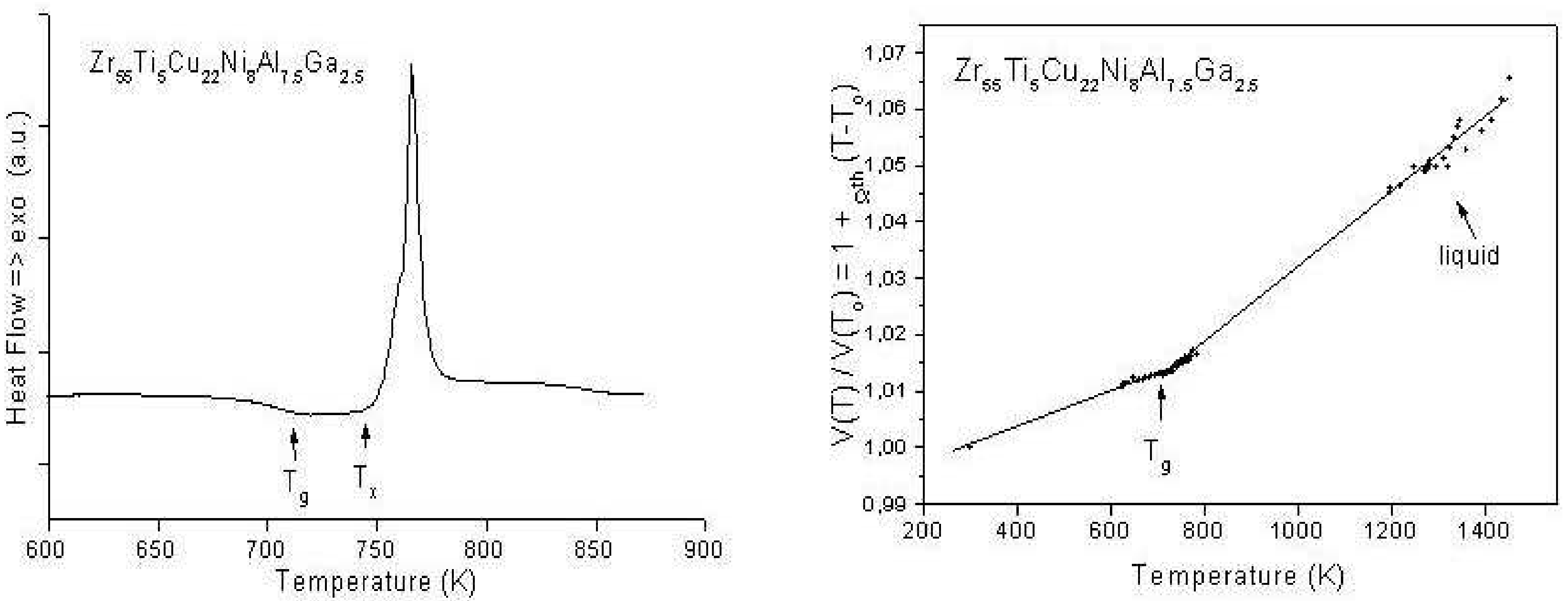
The variation with temperature, of wave-vector Q_{max} or angular position of the diffracted intensity I(Q) below Tg can be treated somewhat as that of a crystal Bragg peak with the volume expansion of glassy structure represented by:

$$\{Q_{max}\ (T_o)\ /\ Q_{max}\ (T)\}^3 = \{V(T)\ /\ V(T_o)\} = \{1 + \alpha_{th}\ (T - T_o)\}$$

α_{th} , the volume coefficient of thermal expansion below T_g can thus be obtained from the temperature slope or derivative of of $\{V(T) / V(T_o)\}$.

Yavari et al Acta Met 2005





$Zr_{55}Ti_5Cu_{22}Ni_8Al_{7.5}Ga_{2.5}$ bulk metallic glass,

a) left: isentropic Tg determined calorimetry;

b) right: isochoric Tg determined from diffraction data.

ELSEVIER

Journal of Non-Crystalline Solids

Volume 247, Issues 1–3, 2 June 1999, Pages 31–34

In situ crystallization of $Zr_{55}Cu_{30}Al_{10}Ni_5$ bulk glass forming from the glassy and undercooled liquid states using synchrotron radiation

A.R. Yavari[a], A. Le Moulec[a], W.J. Botta F[b], A. Inoue[c], P. Rejmankova[d], A. Kvick[d]

[a] Euronano, LTPCM-CNRS umr 5614, Institut National Polytechnique de Grenoble, BP 75, D.U., 38402 St-Martin-d'Hères, France

[b] Department of Engineering Materials, Federal University of São Carlos, 13565-905 São Carlos, SP, Brazil

[c] Institute for Materials Research, Tohoku University, Sendai, Japan

[d] Diffraction Group, European Synchrotron Radiation Facilities, BP 220, Grenoble, France

---

ELSEVIER

Materials Science and Engineering A304–306 (2001) 34–38

MATERIALS SCIENCE & ENGINEERING A

www.elsevier.com/locate/msea

Metastable phases in Zr-based bulk glass-forming alloys detected using a synchrotron beam in transmission

A.R. Yavari[a,*], A. Le Moulec[a], A. Inoue[b], Walter J. Botta F.[c], G. Vaughan[d], A. Kvick[d]

[a] *LTPCM (CNRS umr 5614), Institut National Polytechnique de Grenoble, BP 75, 1130 rue de la Piscine, 38402 St-Martin-d'Héres Campus, Grenoble, France*

[b] *Inoue Superliquid Glass Project, Tohoku University, Sendai, Japan*

[c] *Department de Engenharia de Materiais, Universidade Federal de Sao Carlos, Sao Carlos, SP, Brazil*

[d] *European Synchrotron Radiation Facilities ESRF, 38042 Grenoble, France*

ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Acta Materialia 53 (2005) 1611–1619

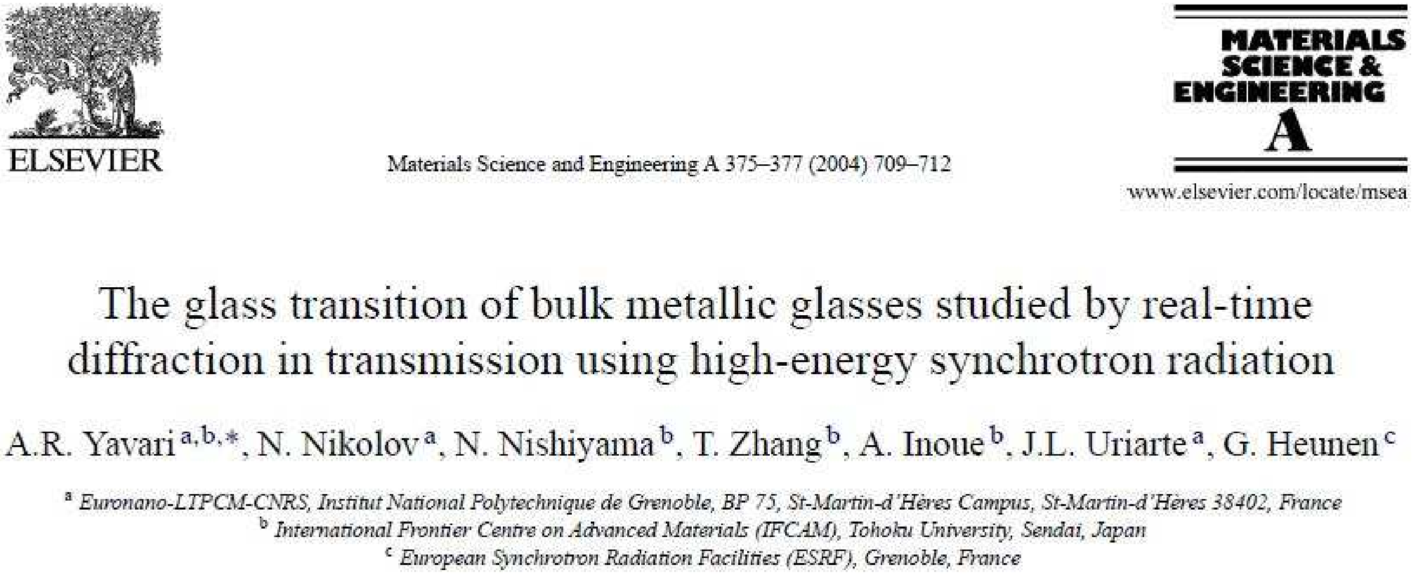
Acta MATERIALIA

www.actamat-journals.com

Excess free volume in metallic glasses measured by X-ray diffraction

Alain Reza Yavari [a,*], Alain Le Moulec [a], Akihisa Inoue [b], Nobuyuki Nishiyama [b], Nicoleta Lupu [a,b], Eiichiro Matsubara [b], Walter José Botta [a,1], Gavin Vaughan [c], Marco Di Michiel [c], Åke Kvick [c]

[a] *Euronano, LTPCM-CNRS, Institut National Polytechnique de Grenoble, 1130 rue de la Piscine, BP 75, 38402 St-Martin-d'Hères Campus, France*
[b] *Institute for Materials Research, Tohoku University, 980-8577 Sendai, Japan*
[c] *European Synchrotron Radiation Facilities (ESRF), 38042 Grenoble, France*



ELSEVIER

Materials Science and Engineering A 375–377 (2004) 709–712

MATERIALS SCIENCE & ENGINEERING A

www.elsevier.com/locate/msea

The glass transition of bulk metallic glasses studied by real-time diffraction in transmission using high-energy synchrotron radiation

A.R. Yavari [a,b,*], N. Nikolov [a], N. Nishiyama [b], T. Zhang [b], A. Inoue [b], J.L. Uriarte [a], G. Heunen [c]

[a] *Euronano-LTPCM-CNRS, Institut National Polytechnique de Grenoble, BP 75, St-Martin-d'Hères Campus, St-Martin-d'Hères 38402, France*
[b] *International Frontier Centre on Advanced Materials (IFCAM), Tohoku University, Sendai, Japan*
[c] *European Synchrotron Radiation Facilities (ESRF), Grenoble, France*

Journal of Alloys and Compounds 388 (2005) L1–L3

Journal of
ALLOYS
AND COMPOUNDS

www.elsevier.com/locate/jallcom

Letter

Glass transition T_g, thermal expansion, and quenched-in free volume ΔV_f in pyrex glass measured by time-resolved X-ray diffraction

K. Ota[a,b], W.J. Botta[a,c], G. Vaughan[d], A.R. Yavari[a,*]

[a] Euronano-LTPCM-CNRS, Institut National Polytechnique de Grenoble, Laboratoire de thermodynamique, Domaine Universitaire BP75, 38402 St-Martin-d'Hères Campus, France
[b] Graduate School of Energy Science, Kyoto University, 606-8501 Kyoto, Japan
[c] Departamento de Engenharia de Materiais, Universidade Federal de São Carlos, CP 676, CEP 13565-905, São Carlos, São Paulo, Brazil
[d] European Synchrotron Radiation Facilities (ESRF), 38042 Grenoble, France

---

Available online at www.sciencedirect.com

ScienceDirect

Journal of Non-Crystalline Solids 354 (2008) 325–327

JOURNAL OF
NON-CRYSTALLINE SOLIDS

www.elsevier.com/locate/jnoncrysol

Glass transition, thermal expansion and relaxation in B_2O_3 glass measured by time-resolved X-ray diffraction

W.J. Botta [a,*], K. Ota [b], K. Hajlaoui [b], G. Vaughan [c], A.R. Yavari [b]

[a] Federal University of São Carlos, Department of Materials Engineering, P.O. Box 676, 13.565-905 São Carlos, SP, Brazil
[b] Euronano-LTPCM-CNRS, Institut National Polytechnique de Grenoble, BP75, 38402 St-Martin-d'Hères Campus, France
[c] European Synchrotron Radiation Facilities (ESRF), 38042 Grenoble, France

APPLIED PHYSICS LETTERS **94**, 191912 (2009)

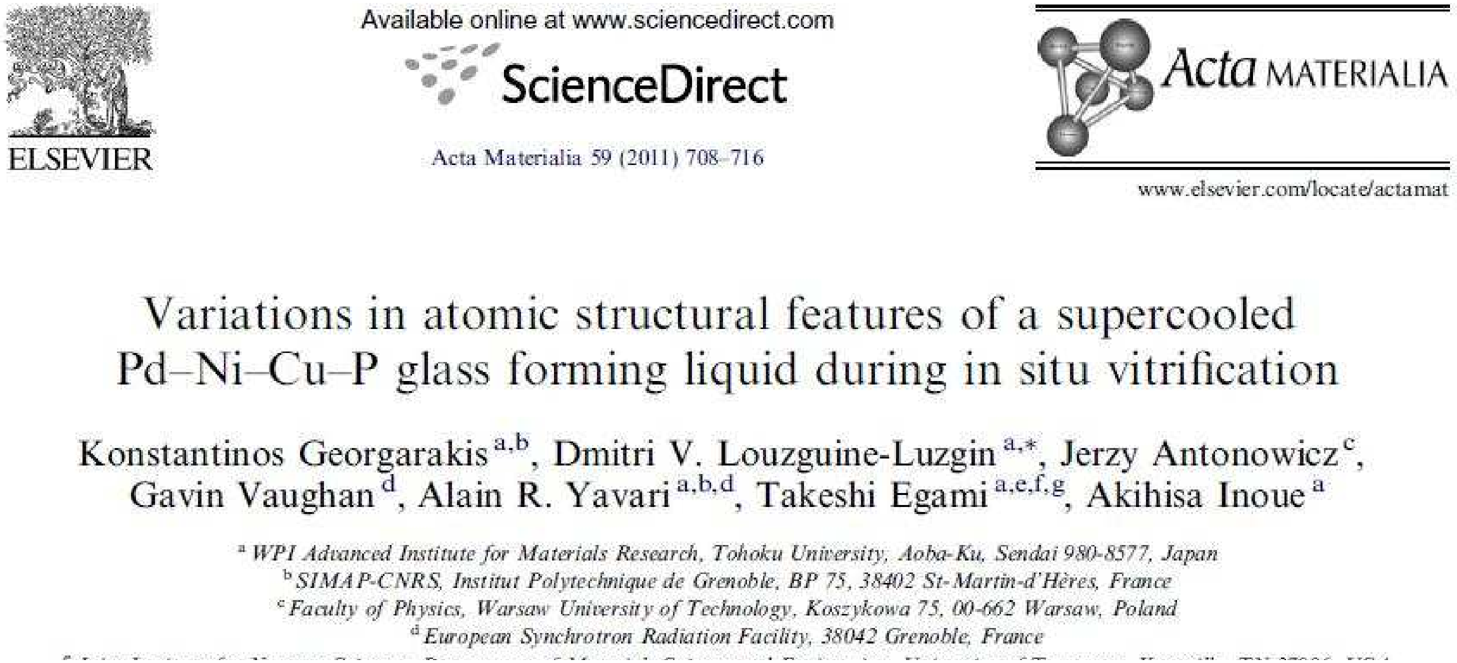
Atomic structure of Zr–Cu glassy alloys and detection of deviations from ideal solution behavior with Al addition by x-ray diffraction using synchrotron light in transmission

K. Georgarakis,[1,2] A. R. Yavari,[2,1,3,a)] D. V. Louzguine-Luzgin,[1] J. Antonowicz,[4]
M. Stoica,[5] Y. Li,[2] M. Satta,[2] A. LeMoulec,[2] G. Vaughan,[3] and A. Inoue[1]
[1]*WPI-AIMR, Tohoku University, Aoba-Ku, Sendai 980-8577, Japan*
[2]*Euronano-SIMaP-CNRS, INP Grenoble, St-Martin-d'Hères 38402, France*
[3]*European Synchrotron Radiation Facility (ESRF), Grenoble 38042, France*
[4]*Faculty of Physics, Warsaw University of Technology, Warsaw 00-662, Poland*
[5]*IFW Dresden, Institute for Complex Materials, Dresden D-01171, Germany*

JOURNAL OF APPLIED PHYSICS **108**, 023514 (2010)

On the atomic structure of Zr–Ni and Zr–Ni–Al metallic glasses

K. Georgarakis,[1,2,a)] A. R. Yavari,[2,1,3] M. Aljerf,[2] D. V. Louzguine-Luzgin,[1] M. Stoica,[4]
G. Vaughan,[3] and A. Inoue[1]
[1]*WPI Advanced Institute for Materials Research, Tohoku University, Aoba-Ku, Sendai 980-8577, Japan*
[2]*Euronano SIMaP-CNRS, Institut National Polytechnique de Grenoble, St-Martin-d'Hères 38402, France*
[3]*European Synchrotron Radiation Facility, 6 rue Jules Horowitz, 38042 Grenoble, France*
[4]*IFW Dresden, Institute for Complex Materials, P. O. Box 270116, D–01171 Dresden, Germany*



Available online at www.sciencedirect.com
ScienceDirect
Acta Materialia 59 (2011) 708–716
ELSEVIER
Acta MATERIALIA
www.elsevier.com/locate/actamat

Variations in atomic structural features of a supercooled Pd–Ni–Cu–P glass forming liquid during in situ vitrification

Konstantinos Georgarakis [a,b], Dmitri V. Louzguine-Luzgin [a,*], Jerzy Antonowicz [c], Gavin Vaughan [d], Alain R. Yavari [a,b,d], Takeshi Egami [a,e,f,g], Akihisa Inoue [a]

[a] *WPI Advanced Institute for Materials Research, Tohoku University, Aoba-Ku, Sendai 980-8577, Japan*
[b] *SIMAP-CNRS, Institut Polytechnique de Grenoble, BP 75, 38402 St-Martin-d'Hères, France*
[c] *Faculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland*
[d] *European Synchrotron Radiation Facility, 38042 Grenoble, France*

JOURNAL OF APPLIED PHYSICS **110**, 043519 (2011)

Structural basis for supercooled liquid fragility established by synchrotron-radiation method and computer simulation

D. V. Louzguine-Luzgin,[1,a)] R. Belosludov,[2] A. R. Yavari,[1,3,4] K. Georgarakis,[1,3]
G. Vaughan,[4] Y. Kawazoe,[2] T. Egami,[5,6,1] and A. Inoue[1]
[1]*WPI Advanced Institute for Materials Research, Tohoku University, Aoba-Ku, Sendai 980-8577, Japan*
[2]*Institute for Materials Research, Tohoku University, Aoba-Ku, Sendai 980-8577, Japan*
[3]*SIMAP-LTPCM, Institut National Polytechnique de Grenoble, St-Martin-d'Hères Campus, Grenoble, BP 75, 38402, France*
[4]*European Synchrotron Radiation Facility, 38042, Grenoble, France*
[5]*Joint Institute for Neutron Sciences, Department of Materials Science and Engineering and Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996, USA*
[6]*Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

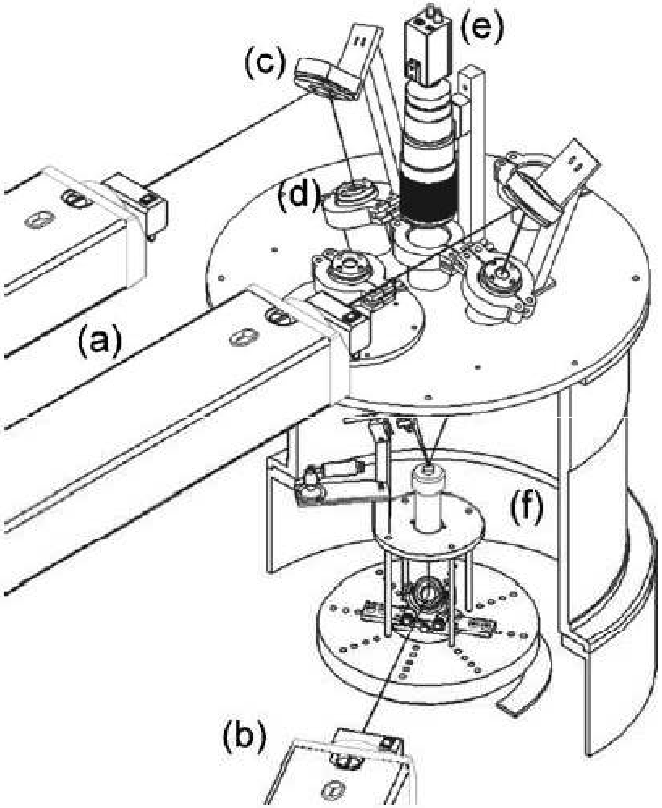
PRL **109**, 085501 (2012) PHYSICAL REVIEW LETTERS week ending 24 AUGUST 2012

Crystallization during Bending of a Pd-Based Metallic Glass Detected by X-Ray Microscopy

Alain Reza Yavari,[1,2,*] Konstantinos Georgarakis,[2,1] Jerzy Antonowicz,[3] Mihai Stoica,[4] Nobuyuki Nishiyama,[2]
Gavin Vaughan,[5] Mingwei Chen,[2] and Michel Pons[1]
[1]*Euronano SIMaP-CNRS, Institut Polytechnique de Grenoble INPG, 38402, France*
[2]*WPI AIMR Tohoku University, Japan*
[3]*Faculty of Physics, Warsaw University of Technology, Poland*
[4]*Institute for Complex Materials, IFW Dresden, Germany*
[5]*European Synchrotron Radiation Facility ESRF, Grenoble, France*

(Received 17 April 2012; published 21 August 2012)

container-less solidification: aerodynamic levitation



Schematic view of the experimental arrangement: laser heads (a,b), spherical mirrors (c), NaCl windows, (d) video camera (e), and levitation device (f).

REVIEW OF SCIENTIFIC INSTRUMENTS 77, 053903 (2006)

Levitation apparatus for neutron diffraction investigations on high temperature liquids

Louis Hennet,[a] Irina Pozdnyakova, and Aleksei Bytchkov
CNRS-CRMHT, 1d avenue de la Recherche Scientifique, 45071 Orléans Cedex 2, France

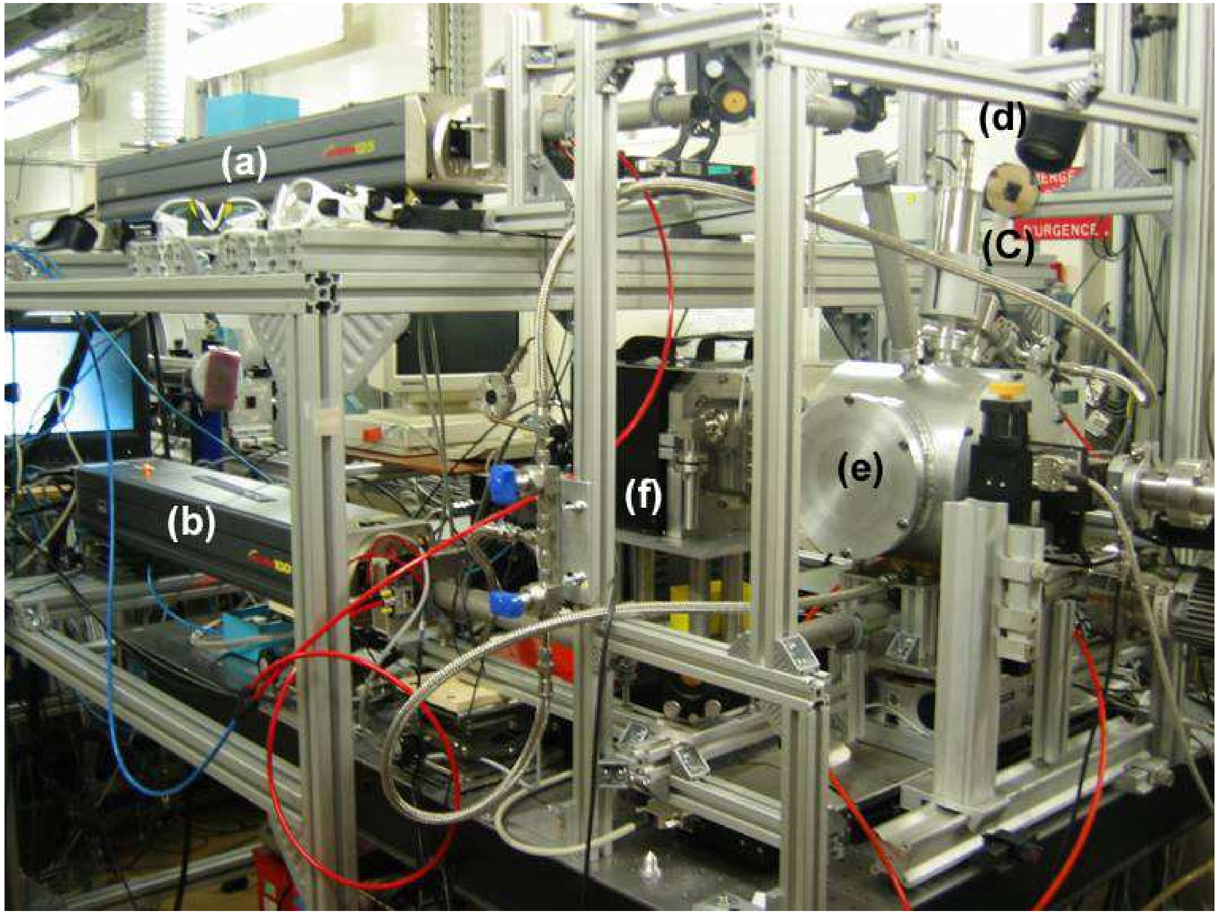
Viviana Cristiglio, Pierre Palleau, Henry E. Fischer, Gabriel J. Cuello, and Mark Johnson
ILL, 6 rue jules Horowitz, BP 156, 38042 Grenoble Cedex 9, France

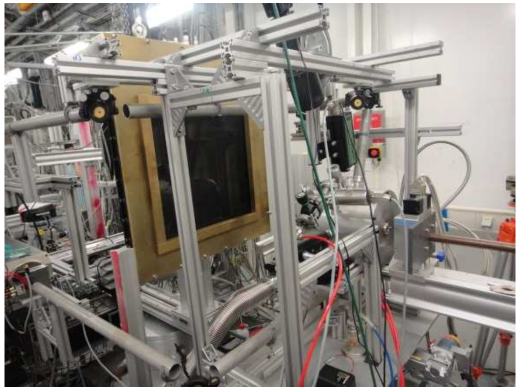
Philippe Melin, Didier Zanghi, Séverine Brassamin,
Jean-François Brun, and David L. Price
CNRS-CRMHT, 1d avenue de la Recherche Scientifique, 45071 Orléans Cedex 2, France

Marie-Louise Saboungi
CRMD, 1b rue de la Férollerie, 45071 Orléans Cedex 2, France

(Received 7 March 2006; accepted 2 April 2006; published online 19 May 2006)

We describe a new high temperature environment based on aerodynamic levitation and laser heating designed for neutron scattering experiments up to 3000 °C. The sample is heated to the desired temperature with three CO_2 lasers from different directions in order to obtain a homogeneous temperature distribution. The apparent temperature of the sample is measured with an optical pyrometer, and two video cameras are employed to monitor the sample behavior during heating. The levitation setup is enclosed in a vacuum-tight chamber, enabling a high degree of gas purity and a reproducible sample environment for structural investigations on both oxide and metallic melts. High-quality neutron diffraction data have been obtained on liquid $Y_3Al_5O_{12}$ and ZrNi alloy for relatively short counting times (1.5 h). © *2006 American Institute of Physics.*

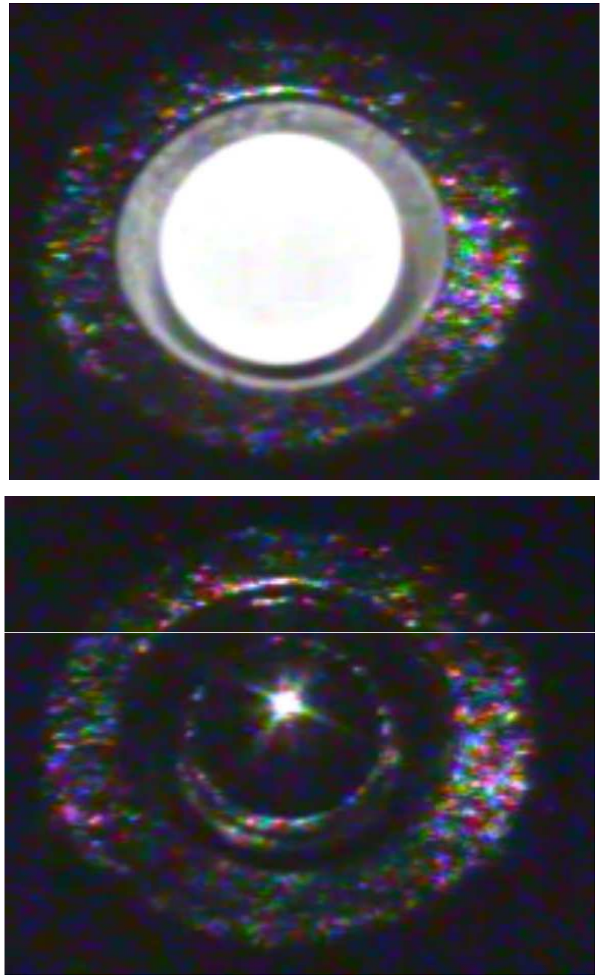




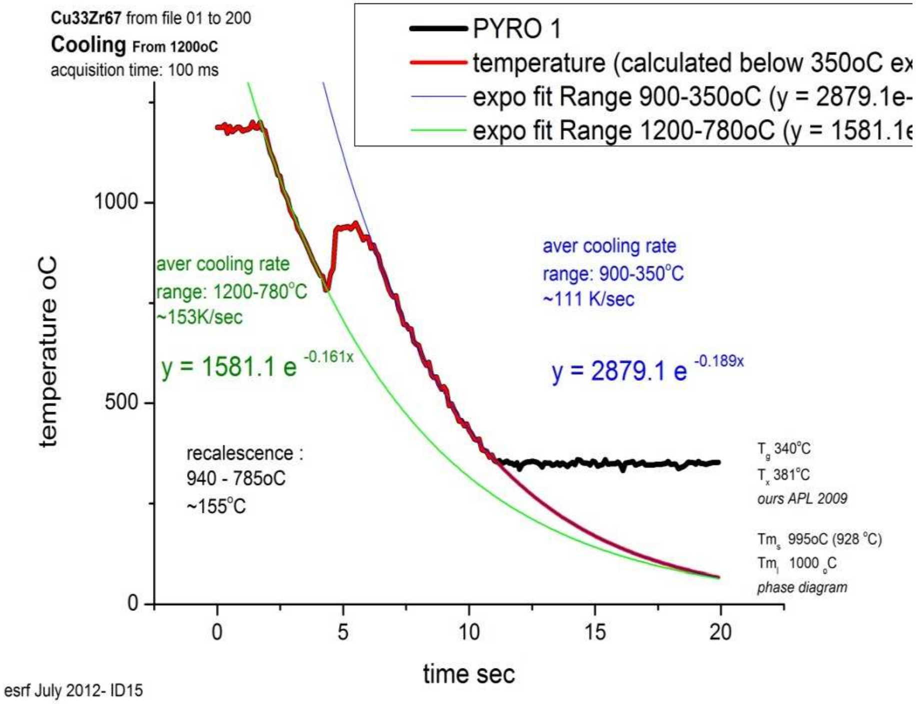
Levitation environment at ID11. Laser heads (a,b), pyrometer (d), video camera (c), levitation chamber (e), Frelon detector (f).

Hennet L. et al, *J. Non-Cryst. Solids* 354 (2008) 5104

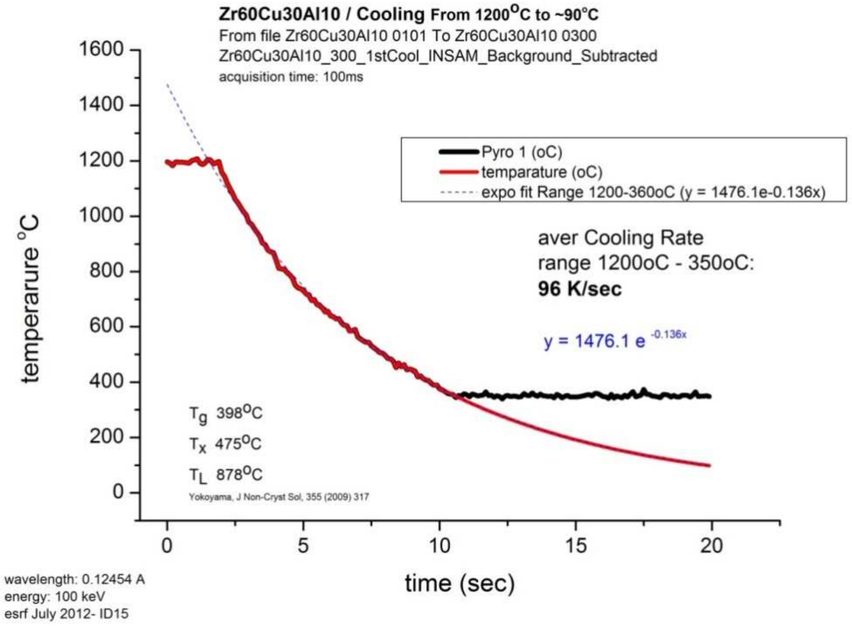

90
100
110



Zr67Cu33



Zr60Cu30Al10

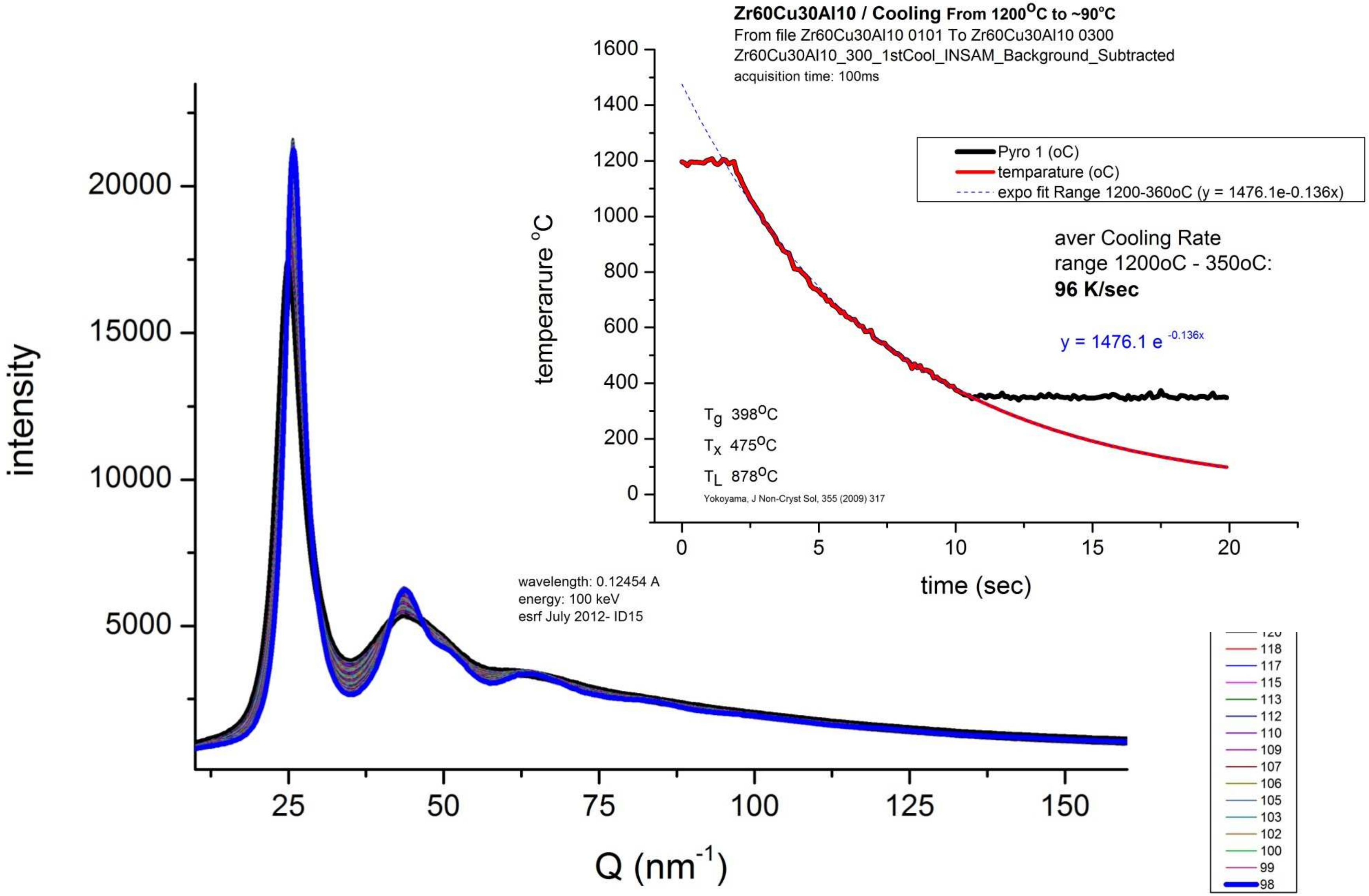


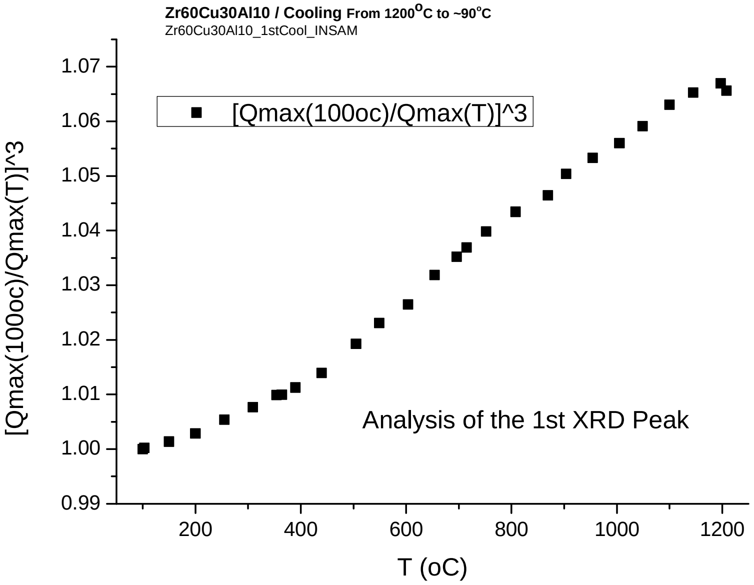
Al addition in Zr-Cu metallic glasses

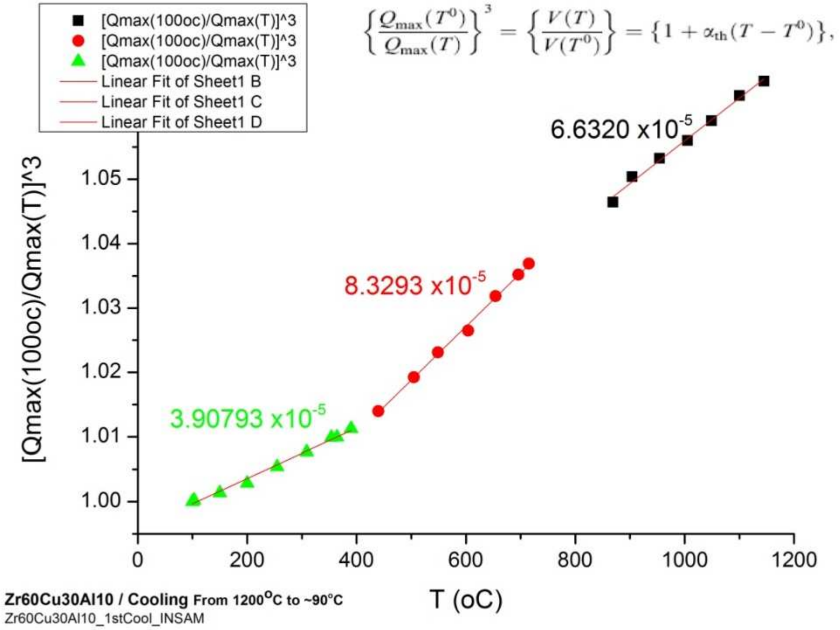
- increase the frequency of icosahederal clusters
- enhance their stability through electronic interactions associated with bond shortening
- leading in sluggish kinetics in the supercooled liquid

➢ **enhance glass forming ability**.

Cooling from the melt

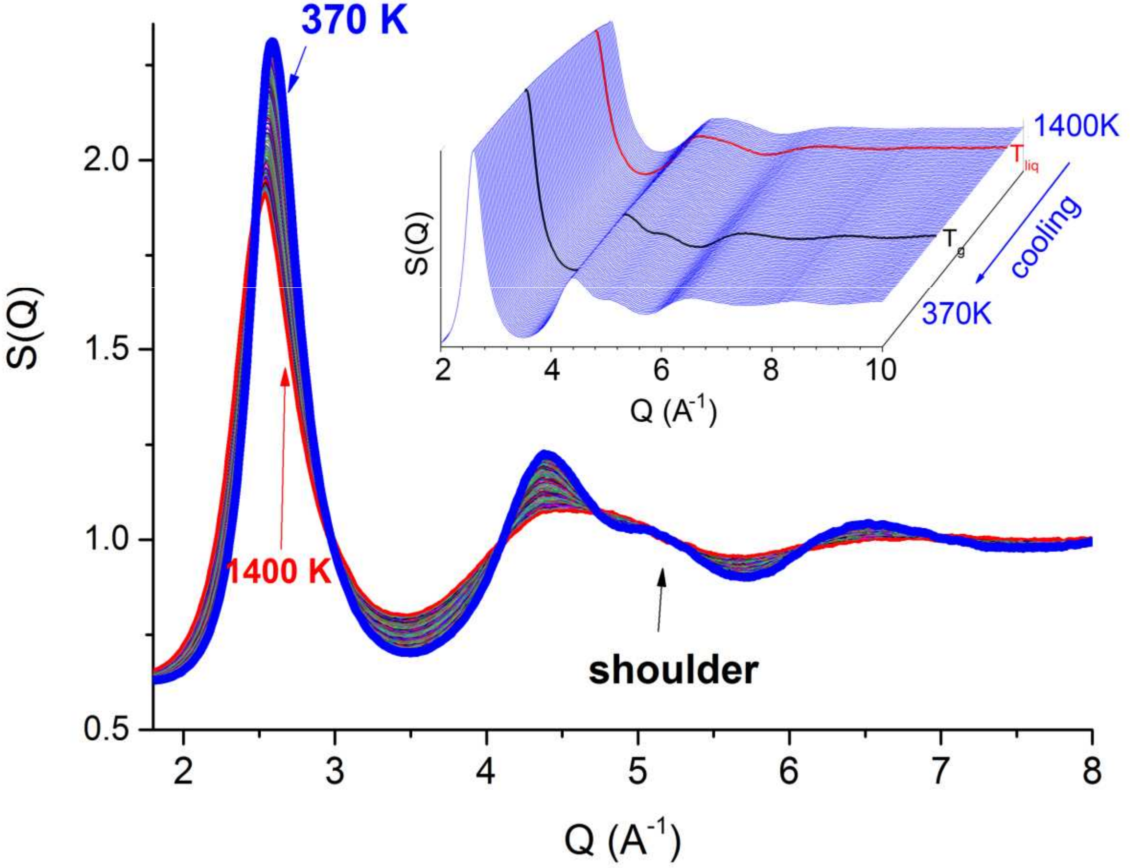




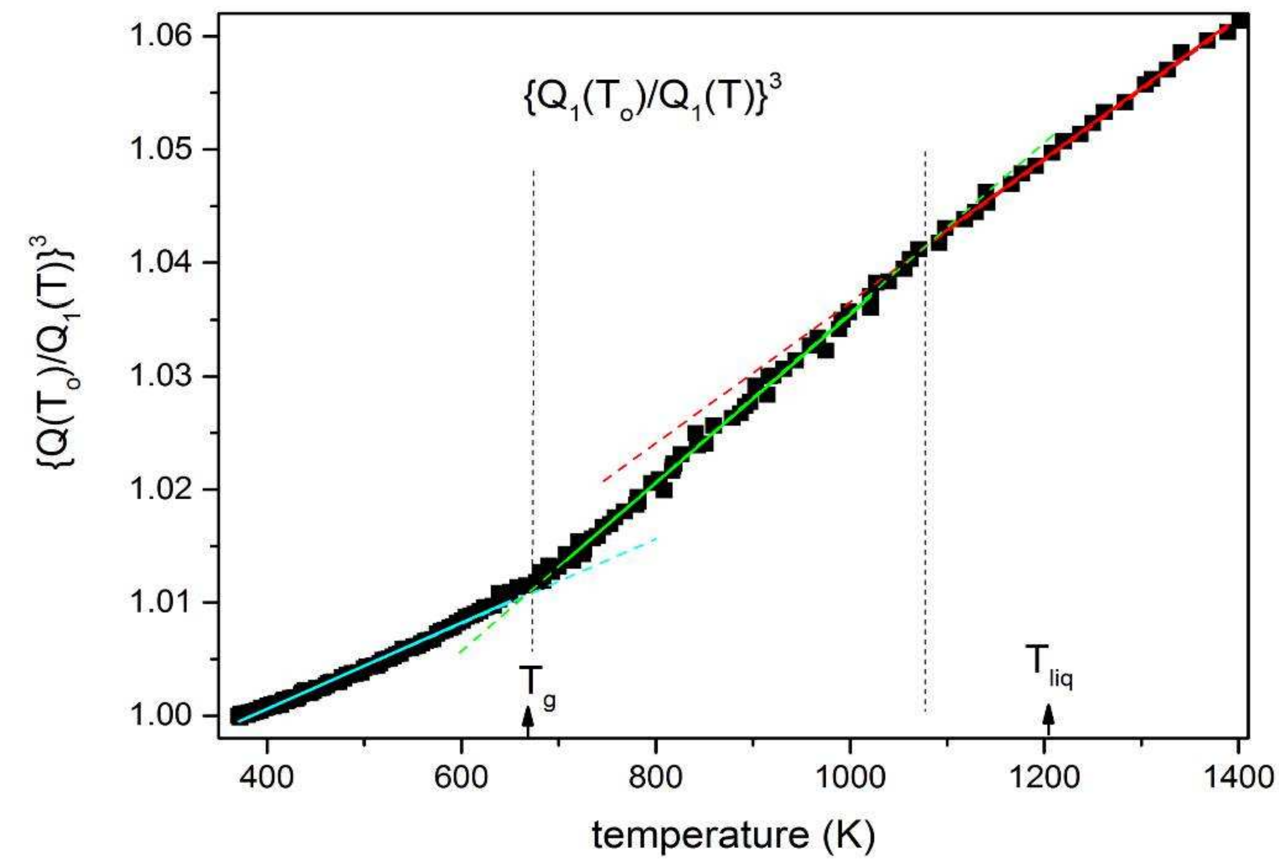


$a_{v\,(liquid)}$: 6.7 x 10^{-5} 1/K [Yokoyama et al, J Non Cryst Sol 2009]
$a_{v\,(glass)}$: 3.15 x 10^{-5} 1/K [C Fan et al, Intermet 2012]

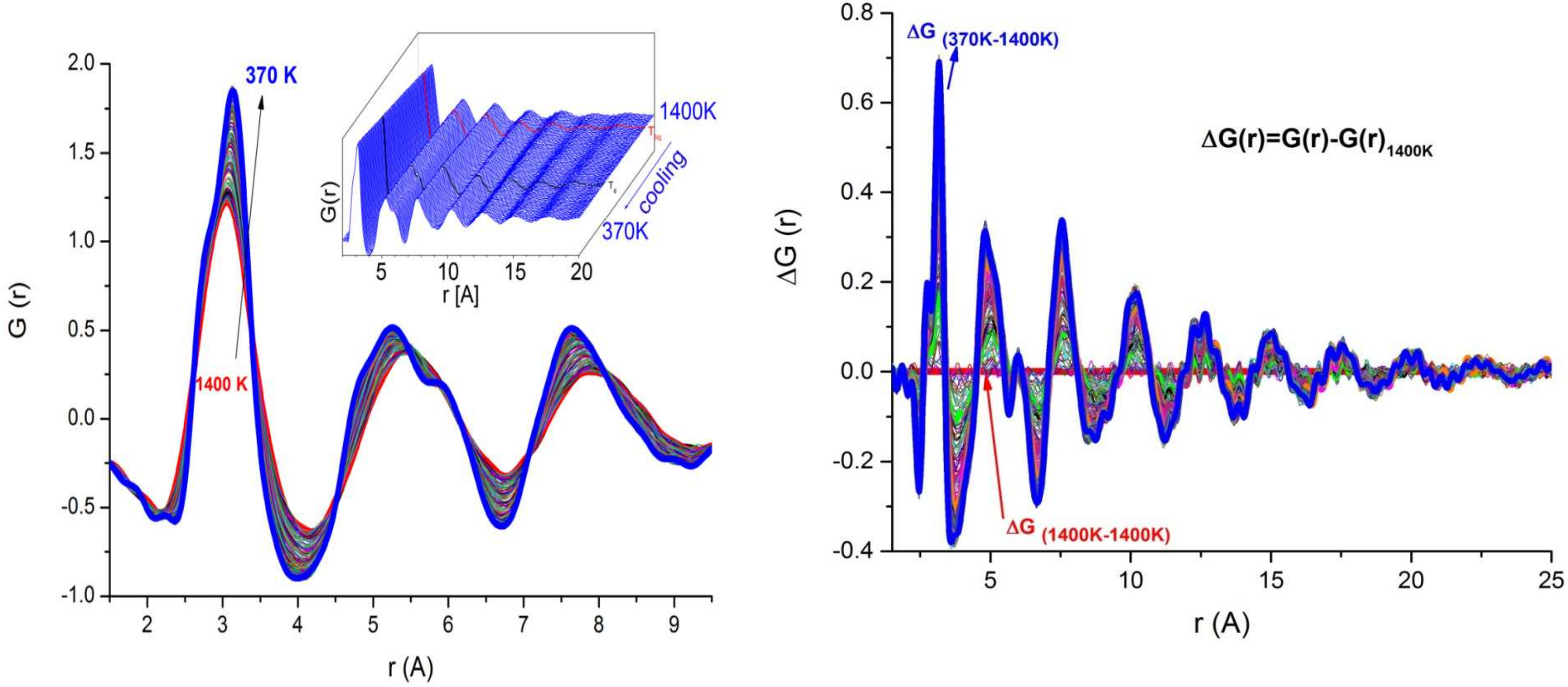
Structure factor S(Q) of $Zr_{60}Cu_{30}Al_{10}$ during cooling from 1400 K to 370 K.



the parameter $(Q_1(T_o)/Q_1(T))^3$ as a function of cooling temperature.



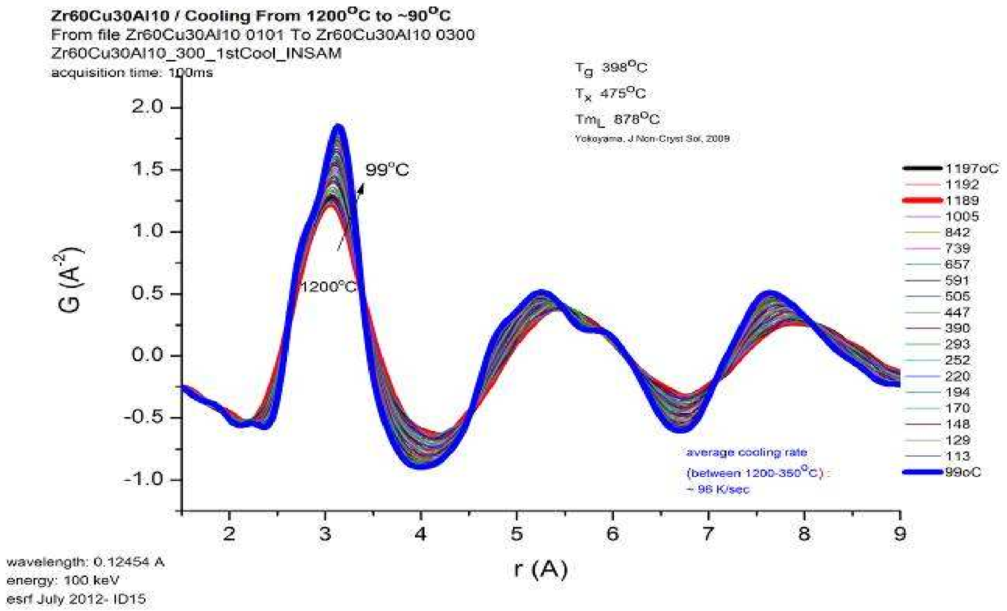
Reduced atomic pair distribution function G(r) of the$Zr_{60}Cu_{30}Al_{10}$liquid during cooling from 1400 to 370K, ΔG(r) functions ($\Delta G(r) = G(r) - G(r)_{1400K}$) showing the growing difference between G(r) at 1400K and those at various temperatures during cooling, close up of the 1st G(r) peak evolution and the ΔG(r)

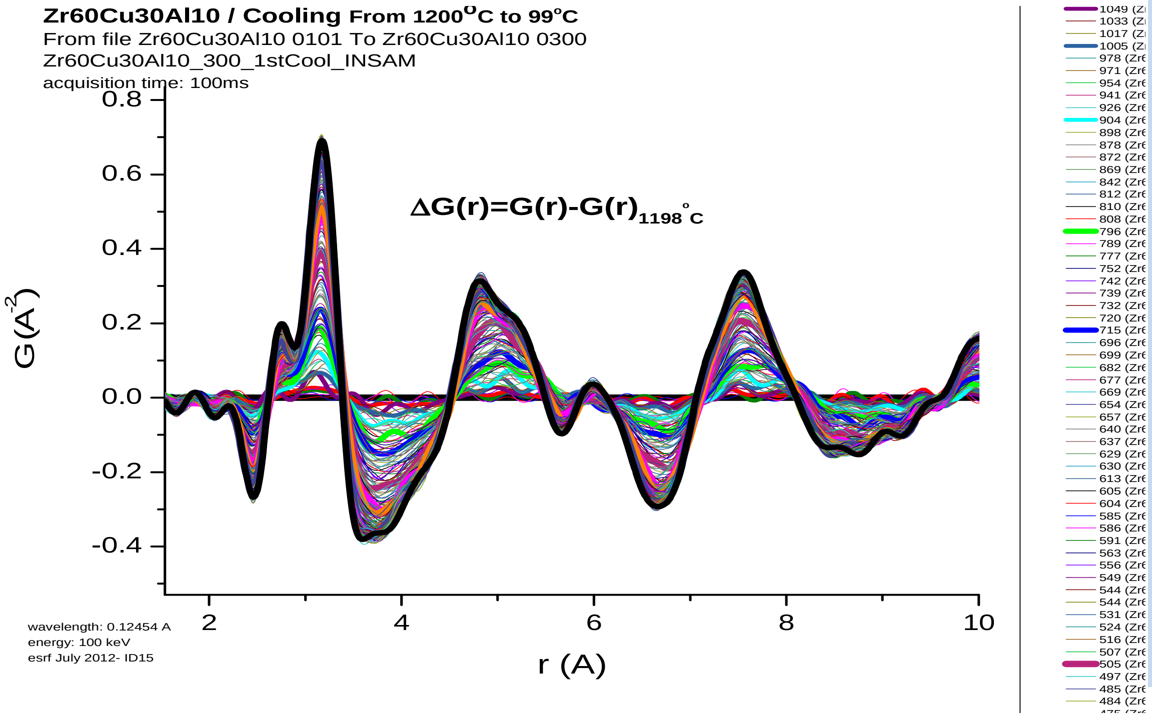


- structural evolution
- from 1200°C to ~100°C

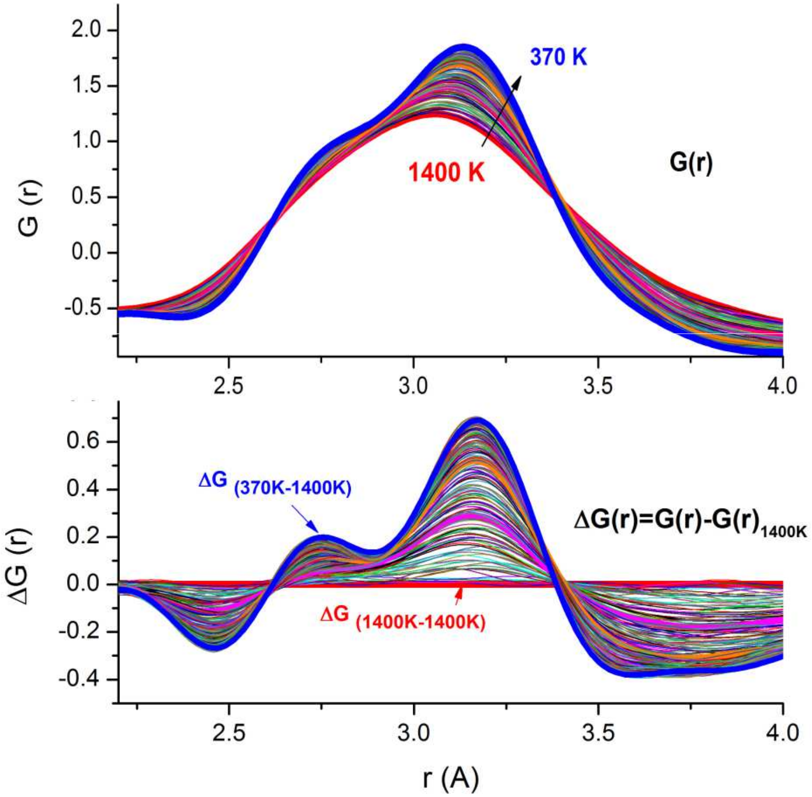
$\Delta Gr = G(r) - G(r)_{1198\ C}$

- Positive values in local maxima
- Negative values in local minima
- More atoms contribute to the SRO and MRO
- Less atoms in the "intermediate distances" ("link atoms")
- Reinforcement of short and medium range order



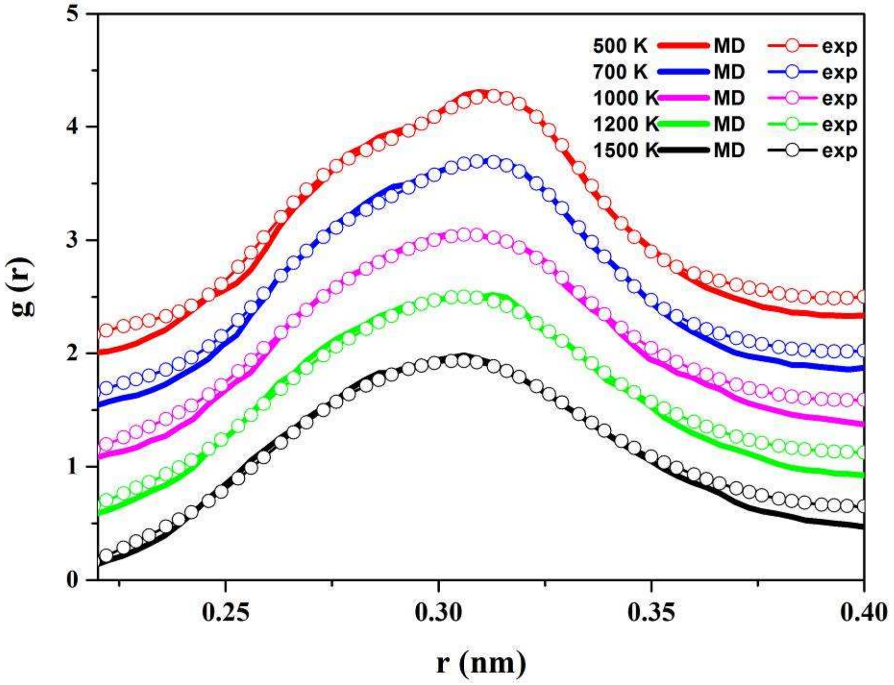


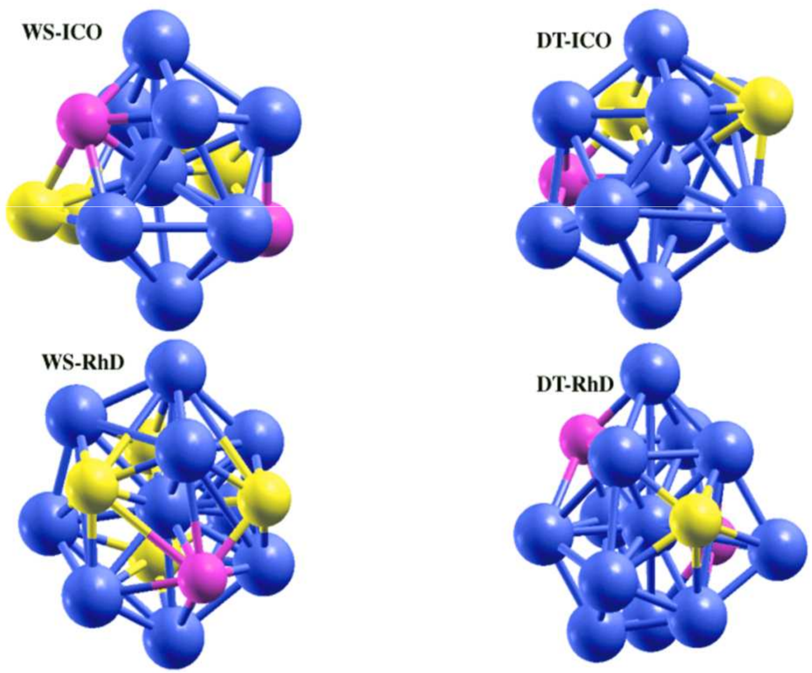
Thermal expansion of the 1st nn atomic shell during cooling



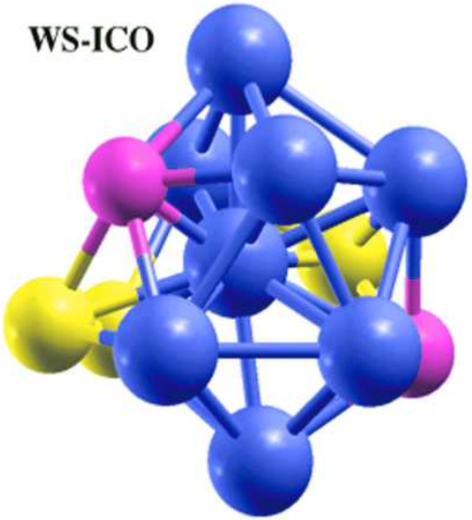
	w_{ij}	r (Å)	ΔH_{mix} (kJ/mol)
Zr-Zr	0.498	3.20	
Cu-Cu	0.066	2.56	
Al-Al	0.001	2.86	
Zr-Cu	0.361	2.88	-23
Zr-Al	0.054	3.03	-44
Cu-Al	0.02	2.71	-1

Total pair distribution functions of the simulated $Zr_{60}Cu_{30}Al_{10}$ alloy at various temperatures in comparison with the experimental data, Representative clusters in $Zr_{60}Cu_{30}Al_{10}$ extracted from an MD configuration at 300K: WS: nearly perfect, DT: Distorted or Truncated.

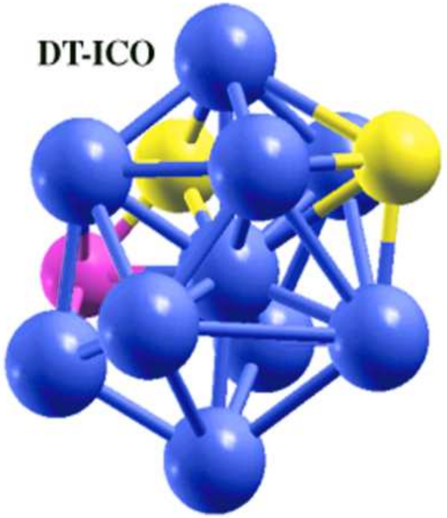




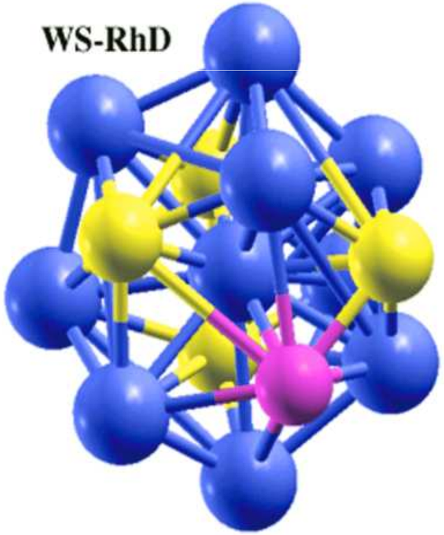
WS-ICO



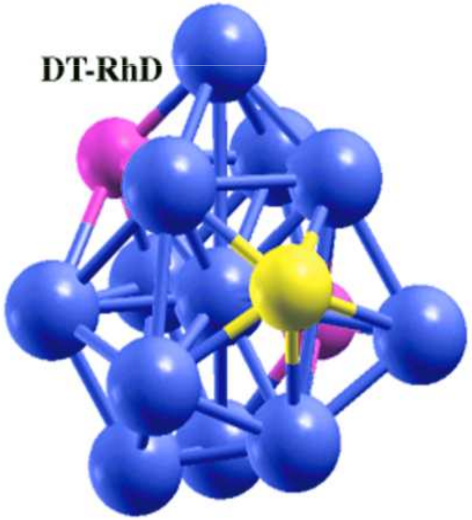
DT-ICO



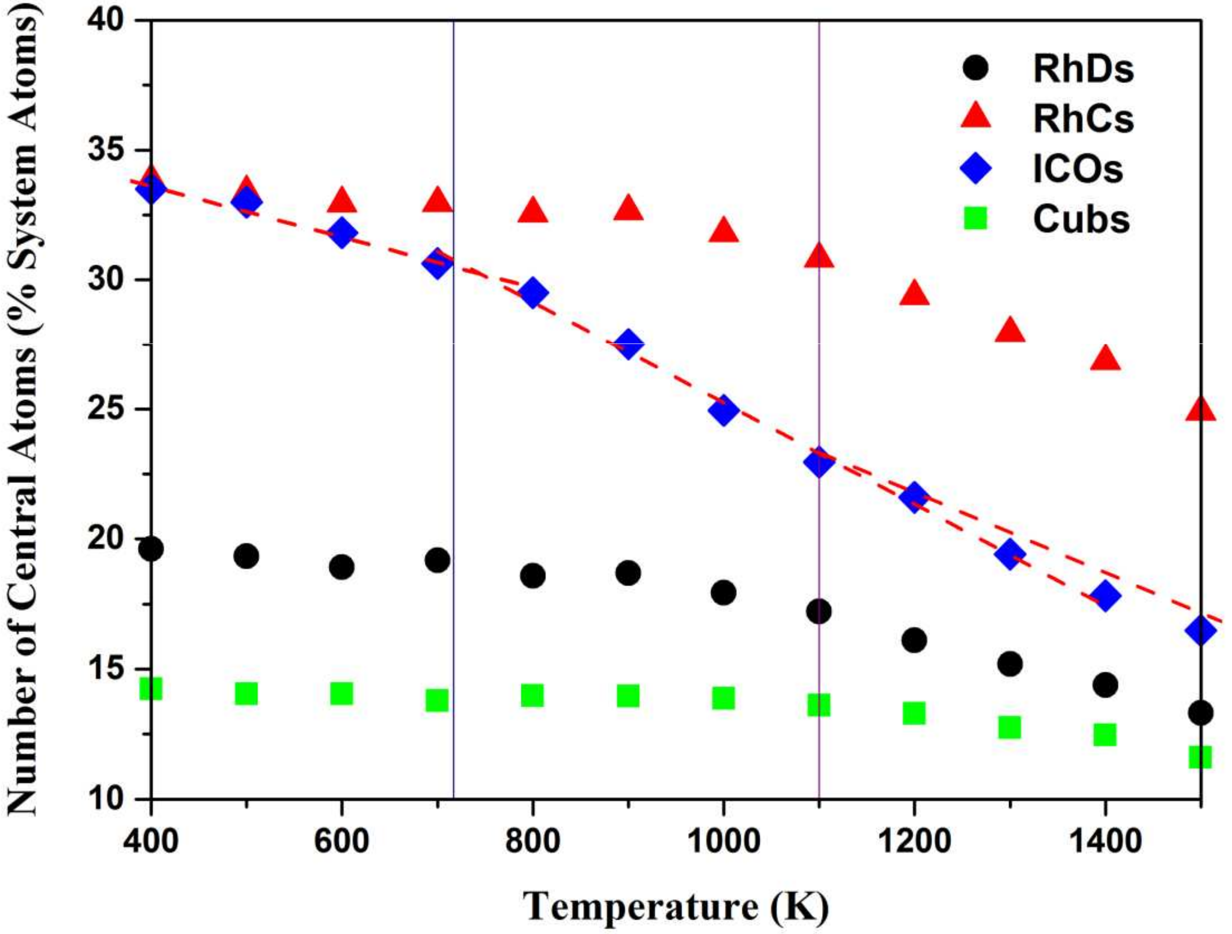
WS-RhD



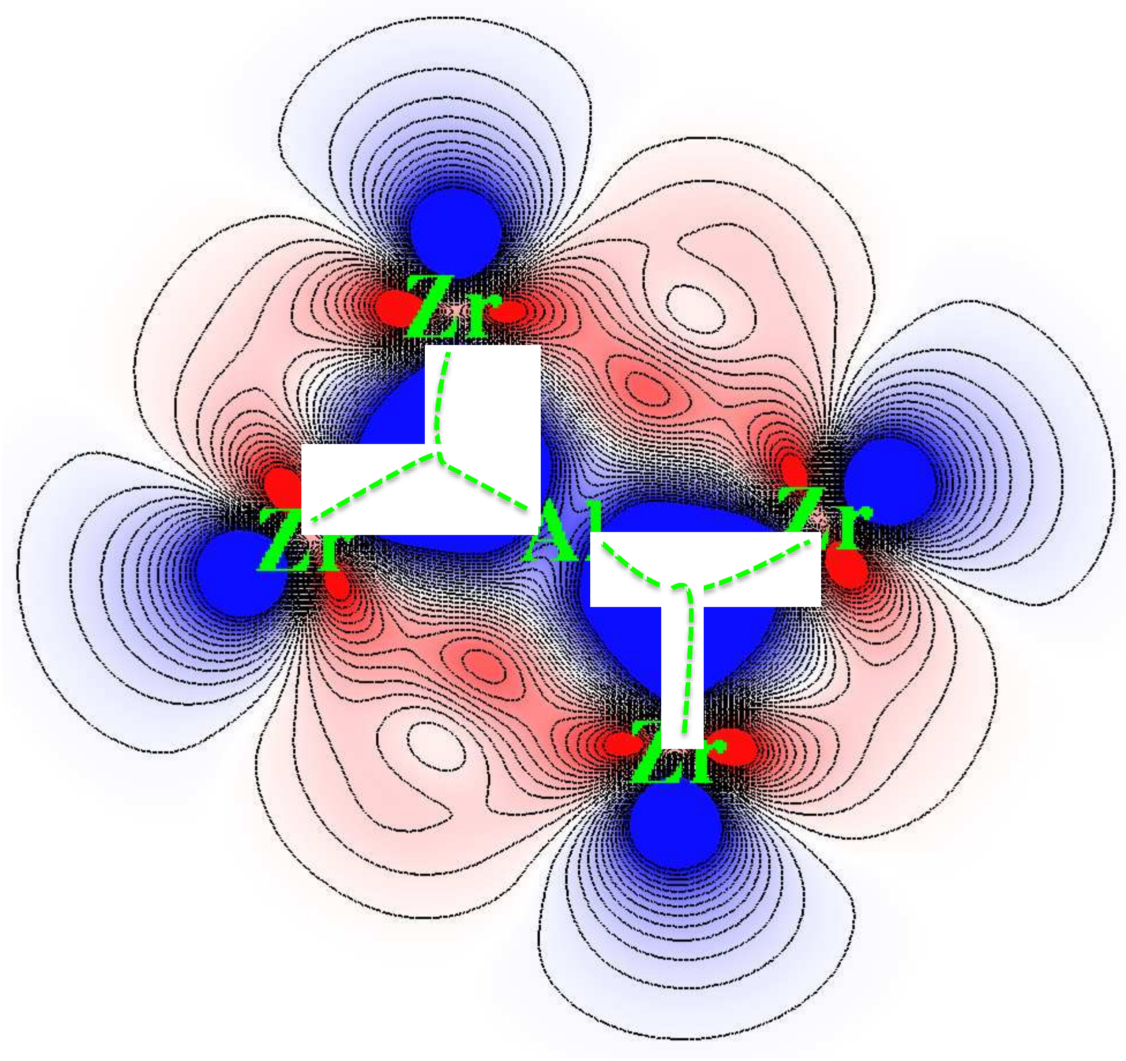
DT-RhD



Populations of the various types of clusters as a function of temperature: Rhombic Dodecahedra (RhD), Icosahedra (ICO) and Cuboctahedra (Cb). RhC denotes the sum of RhD and Cb.

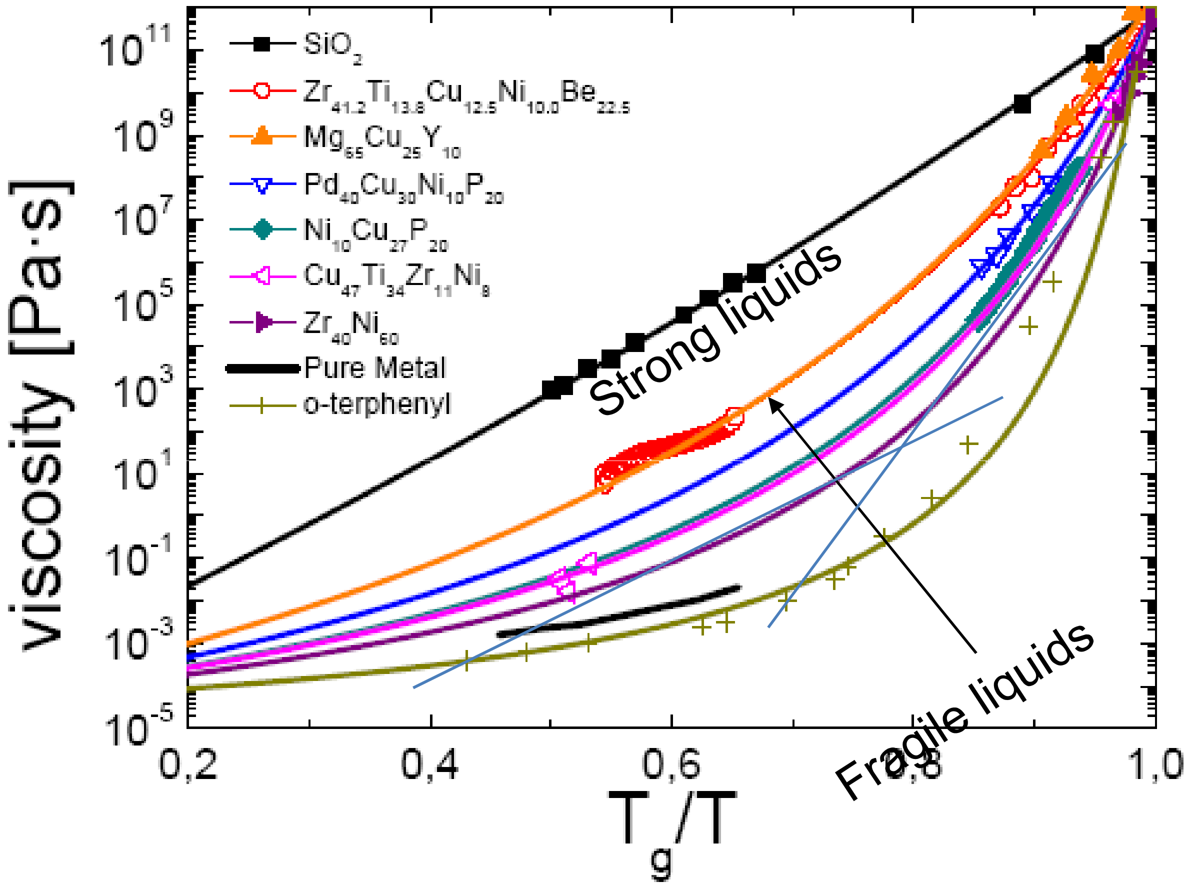


Density function theory calculations of the effect of Al addition to Cu-Zr glass: When aluminium atoms are at the center of the cluster, charge transfer of the Al atoms leads to *pd-d* interactions with the surrounding Zr shell atoms resulting in a densely packed cluster.



Viscosity

D*



Vogel Fulcher Tammann Equation

$$\eta=\eta_0 \exp \left(D^{*}T_0 / T-T_0\right)$$

$$2 < D^{*} < 100$$

R. Busch, J. Schroers and W.H. Wang, MRS Bulletin (2007)

C.A. Angell, J. Physical Chemistry 49, 863 (1988)

Contact info

Web: http://ismanam.org/
euronano@minatec.inpg.fr
Tel: +33 76826766
Fax: +33

Paris, France

situated on the Seine River, in the north of the country, at the heart of the Île-de-France region. Paris, one of the largest population centres in Europe with more than 12 million inhabitants, has the reputation of being the most beautiful and romantic of all cities, brimming with historic associations and remaining vastly influential in the realms of culture, art, fashion, food and design. Dubbed the City of Light (la Ville Lumière) and Capital of Fashion, it is home to the world's finest and most luxurious fashion designers and cosmetics, such as Chanel, Dior, Yves Saint-Laurent, Guerlain, Lancôme, L'Oréal, Clarins, etc. A large part of the city, including the River Seine, is a UNESCO World Heritage Site.

The city has the second highest number of Michelin-restaurants in the world (after Tokyo) and contains numerous iconic landmarks, such as the world's most visited tourist site the Eiffel Tower, the Arc de Triomphe, the Notre-Dame Cathedral, the Louvre Museum, Moulin Rouge, Lido etc, making it the most popular tourist destination in the world with 45 million tourists annually. For centuries, Paris has attracted artists from around the world, arriving in the city to educate themselves and to seek inspiration from its vast pool of artistic resources and galleries. As a result, Paris has acquired a reputation as the "City of Art". Italian artists were a profound influence on the development of art in Paris in the 16th and 17th centuries, particular in sculpture and reliefs.

Paris is a global hub of fashion and has been referred to as the "international capital of style". Paris has a large number of high-end fashion boutiques, and many top designers have their flagship stores in the city, such as Louis Vuitton's store, Christian Dior's 1200 square foot store and

The 22nd International Symposium on Metastable, Amorphous and Nanostructured Materials

ISMANAM 2015

Paris, France
12-17 July 2015

ISMANAM 2015

We are welcoming you to the

International Symposium on Metastable, Amorphous and Nanostructured Materials (ISMANAM 2015) will be held at the Maison de la Mutualité in Paris, France, from 12 to 17 July 2015. The ISMANAM conference series started in 1994, when the 1st Symposium was held in Grenoble (France). The first event was followed by the subsequent symposia organized in Quebec (1995), Rome (1996), Sitges (1997), Wollongong (1998), Dresden (1999), Oxford (2000), Ann Arbor (2001), Seoul (2002), Foz do Iguaçu (2003), Sendai (2004), Paris (2005), Warsaw (2006), Corfu Island (2007), Buenos Aires (2008), Beijing (2009), Zürich (2010), Gijón (2011), Moscow (2012), Turin (2013) and Cancun (2014).

The ISMANAM conference is a multidisciplinary forum which promotes international scientific and technological exchanges on all aspects related to Metastable, Amorphous and Nanostructured Materials.

The conference will cover the following Topics:

- Rapidly quenched alloys
- Nanocrystalline materials and materials with submicrometer-sized grains
- Quasicrystalline materials• Thin films and coatings
- Synthesis techniques and metastable phase formation
- Structure and structure analysis
- Theoretical modeling and computer simulations
- Phase transformations and thermodynamics
- Advanced analytical tools at both the atomic and meso-scale
- All aspects of physical, chemical, and biological properties
- Magnetic properties from the nanoscale to bulk materials
- Mechanical properties at different length scales

Near and long term applications: energy

Organization

Steering Committee

M. Atzmon, USA
M.D. Baró, Spain
W.J. Botta, Brazil
A. Calka, Australia
M. Chen, Japan/China
J. Eckert, Germany
G.A. Evangelakis, Greece
A.L. Greer, UK
K. Kelton, USA
A. Inoue, Japan
T. Kulik, Poland
J. Löffler, Switzerland
N. Lupu, Romania
J. Perepezko, USA
K. Samwer, Germany
R. Schulz, Canada
P. Tiberto, Italy
A.R. Yavari, France (Chair)

National Advisory Committe

E. Blanquet CNRS-INP Grenobl
Y. Champion Paris-Est- UMR 71
J.M. Dubois CNRS-UHP-INPL
K. Georgarakis -INP Grenoble
T. Rouxel, Rennes
M. Pons, CNRS-INP Grenoble
C. Vahlas – ENSIACET
G. Vaughan- ESRF – Grenoble
A.R. Yavari - CNRS-INP Grenobl

Symposium Organizer: Fabienne Fonseca

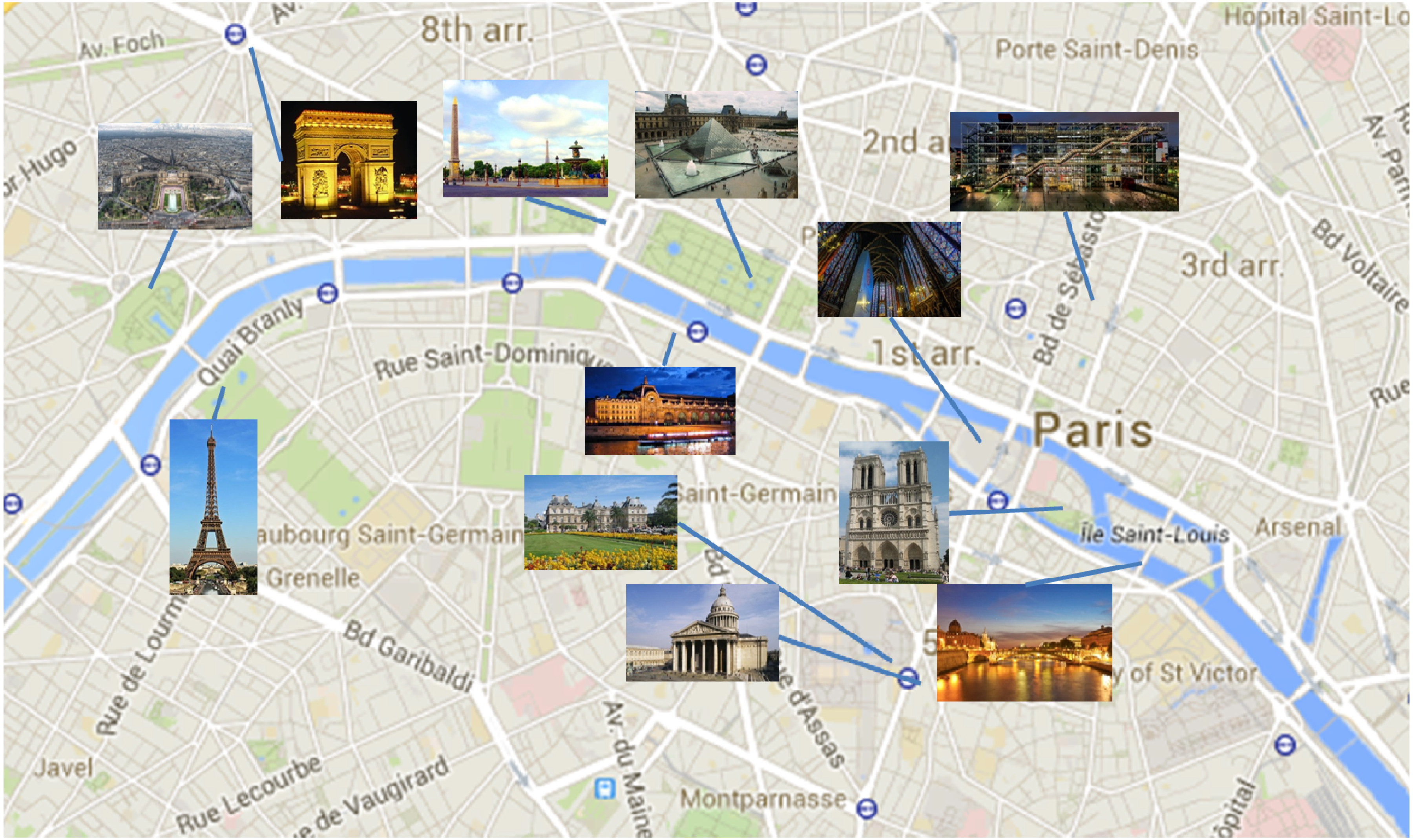
Conference site

The ISMANAM 2015 will be held at Maison de la mutualite. Located on the banks of the Seine in the Latin Quarter, the Maison de la Mutualité is one of the emblems of historic Paris, along with the Notre-Dame Cathedral, the Pantheon, the Sorbonne, the Jardins des Plantes and the Luxembourg Palace.

Address
Maison de la Mutualité
24, rue Saint-Victor. 75005 Paris
www.maisondelamutualite.com

National Committee

E. Blanquet CNRS-INP Grenoble
Y. Champion Paris-Est- UMR 7182
J.M. Dubois CNRS-UHP-INPL
K. Georgarakis -INP Grenoble
T. Rouxel, Rennes
M. Pons, CNRS-INP Grenoble
C. Vahlas – ENSIACET
G. Vaughan- ESRF – Grenoble
A.R. Yavari - CNRS-INP Grenoble


Av. Foch
8th arr.
Porte Saint-Denis
Hôpital Saint-Lo
2nd a
3rd arr.
Bd Voltaire
Av. Parm
Quai Branly
Rue Saint-Dominiq
1st arr.
Bd de Sébasto
Paris
Saint-Germain
Île Saint-Louis
Arsenal
aubourg Saint-Germain
Grenelle
Bd Garibaldi
y of St Victor
Rue de Lourm
Javel
Rue Lecourbe
e de Vaugirard
Av. du Maine
Montparnasse
e d'Assas
Rue

FIN

MERCI DE VOTRE ATTENTION

Thank you for your attention