UNIVERSITY
OF IOANNINA

ΠΑΝΕΠΙΣΤΗΜΙΟ ΙΩΑΝΝΙΝΩΝ • ΤΜΗΜΑ ΦΥΣΙΚΗΣ
ΕΚ ΠΑΝΤΩΝ ΕΝ ΚΑΙ ΕΞ ΕΝΟΣ ΤΑ ΠΑΝΤΑ
ΗΡΑΚΛΕΙΤΟΣ
• 1970 •

Υπολογιστική Επιστήμη Στερεάς Κατάστασης – Ανάπτυξη και Χαρακτηρισμός Λεπτών Υμενίων

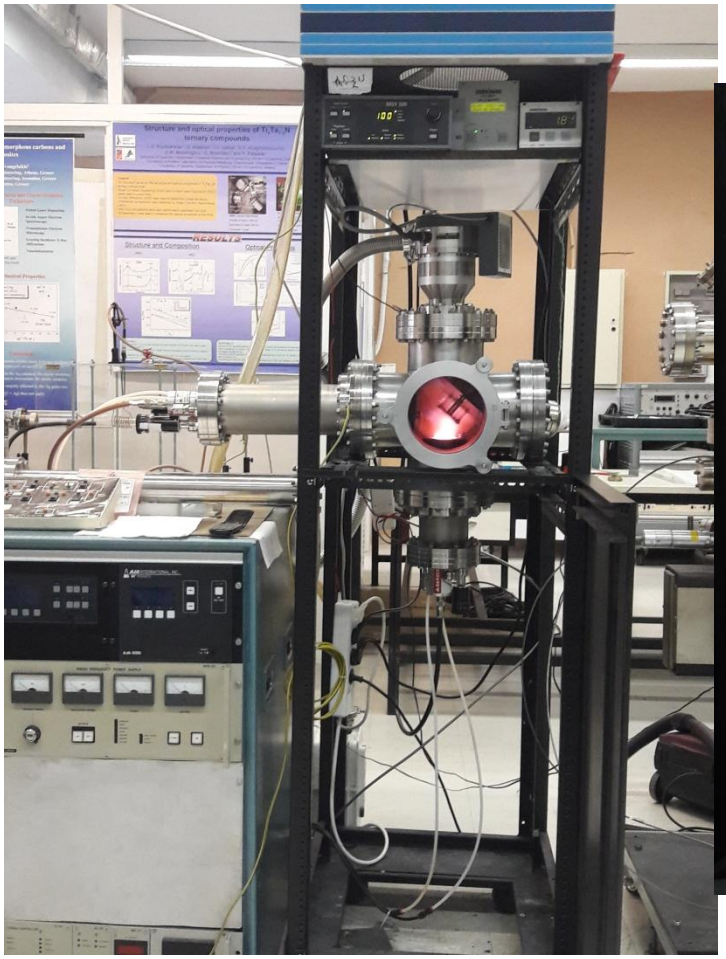
Γ. Ευαγγελάκης **(gevagel@uoi.gr)**

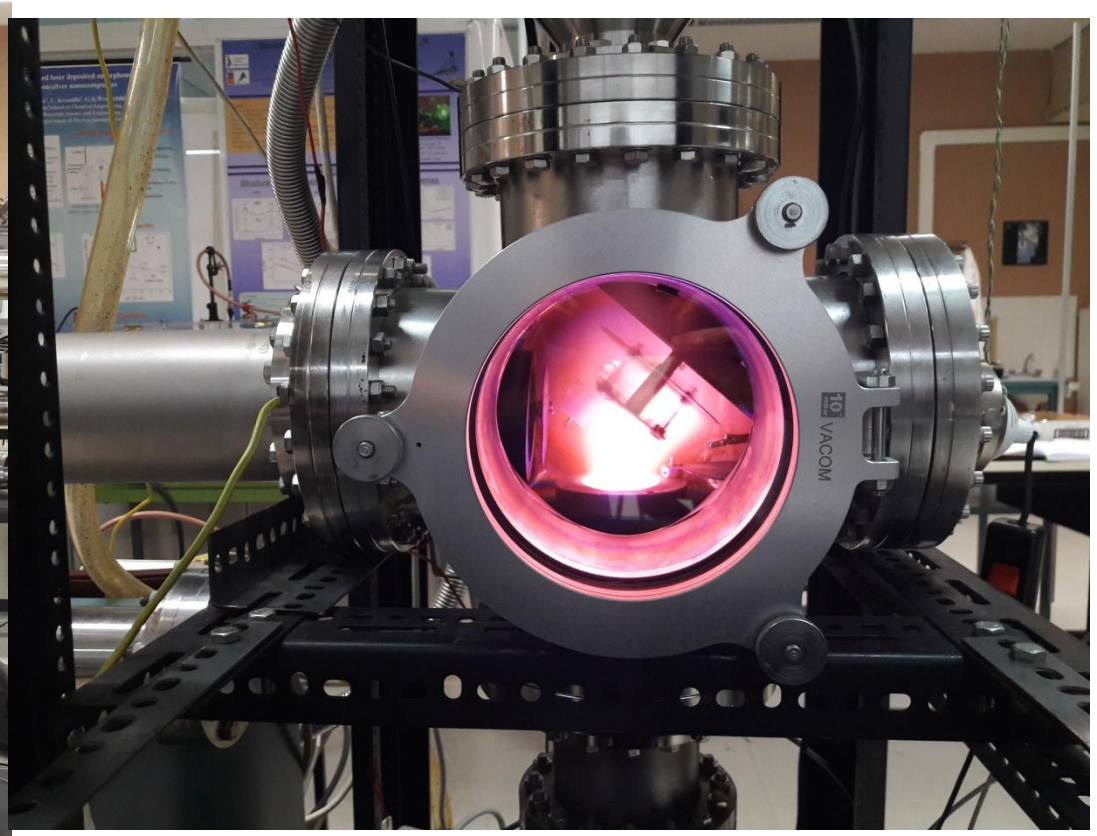
ΙΝΣΤΙΤΟΥΤΟ
ΕΠΙΣΤΗΜΗΣ ΥΛΙΚΩΝ
ΚΑΙ ΥΠΟΛΟΓΙΣΜΩΝ

Available experimental facilities

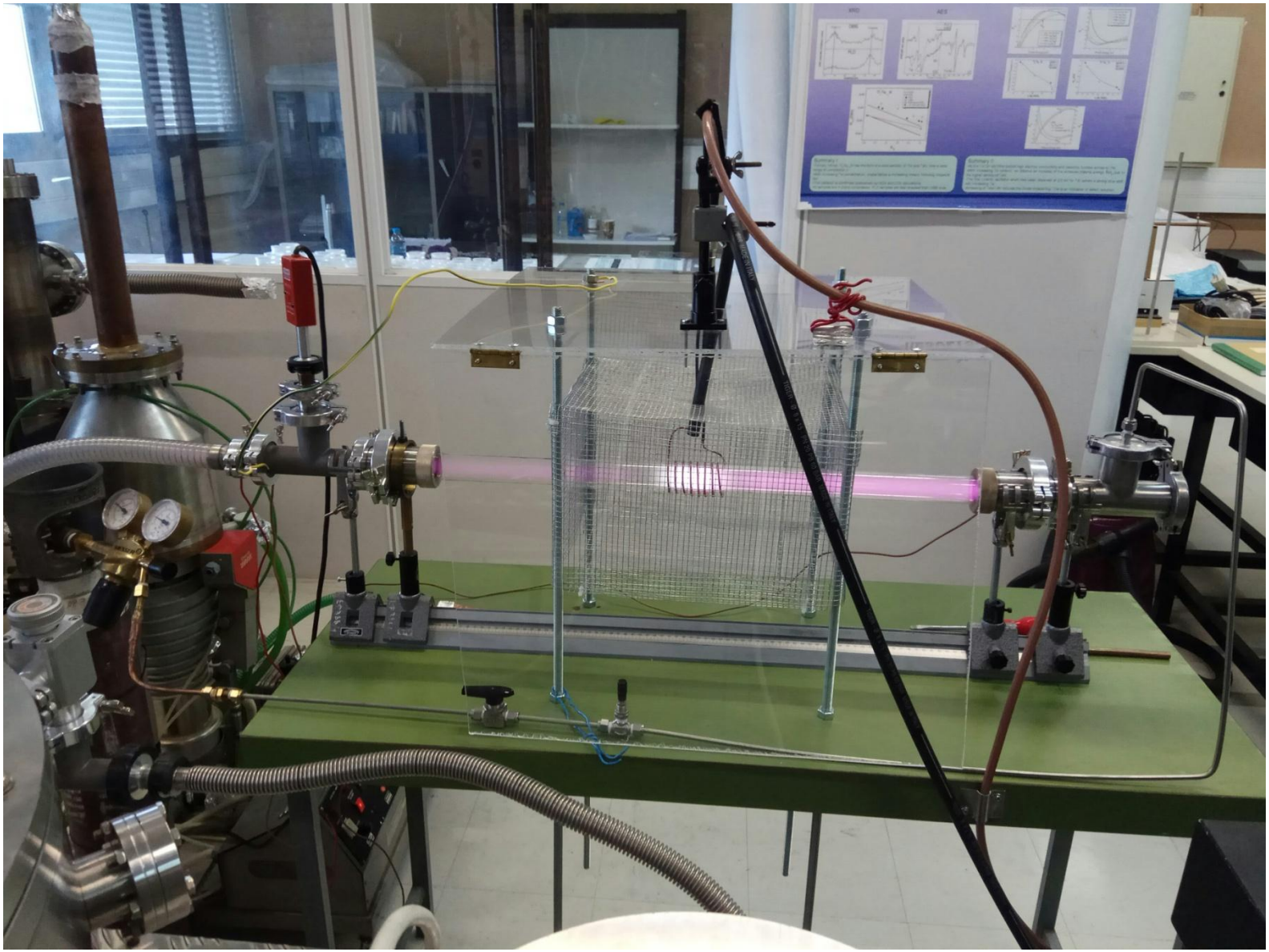
Pulsed Laser Deposition (PLD)

Dual Unbalanced confocal Magnetron Sputtering





Oxygen or Nitrogen Plasma Treatment

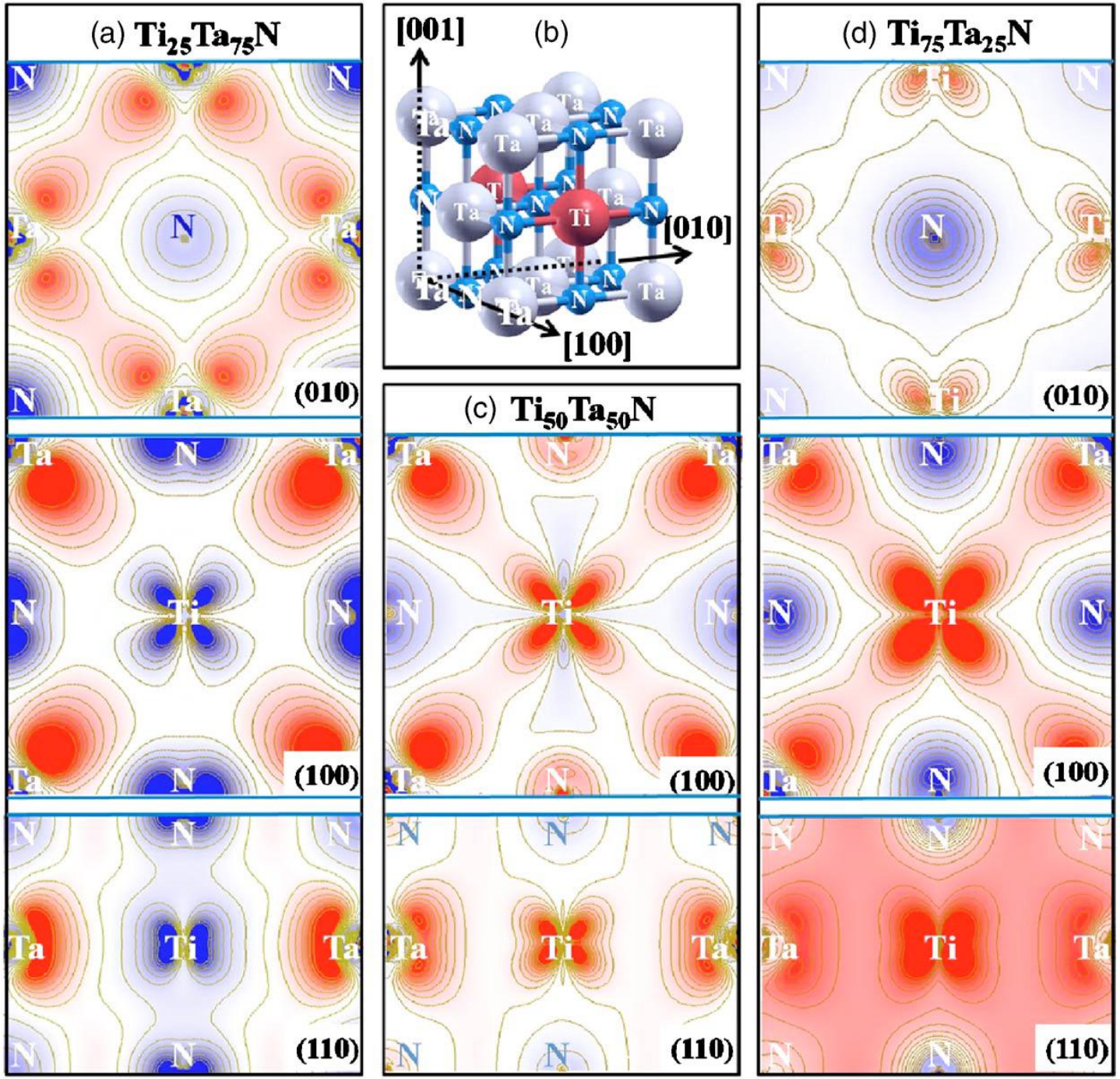


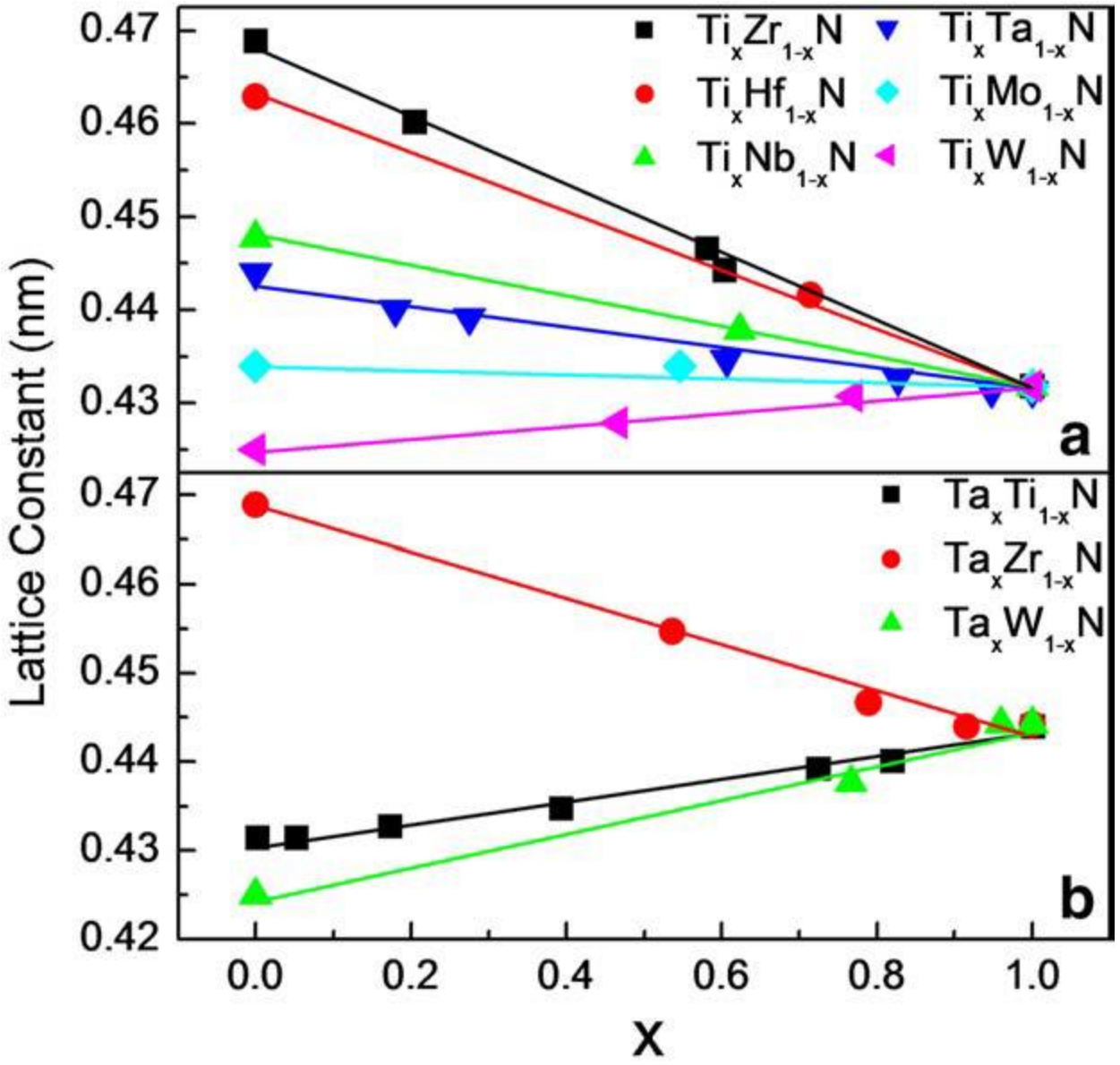
X-Ray Photoelectron Spectroscopy (XPS) High Resolution Electron Energy Loss Spectroscopy (HREELS)

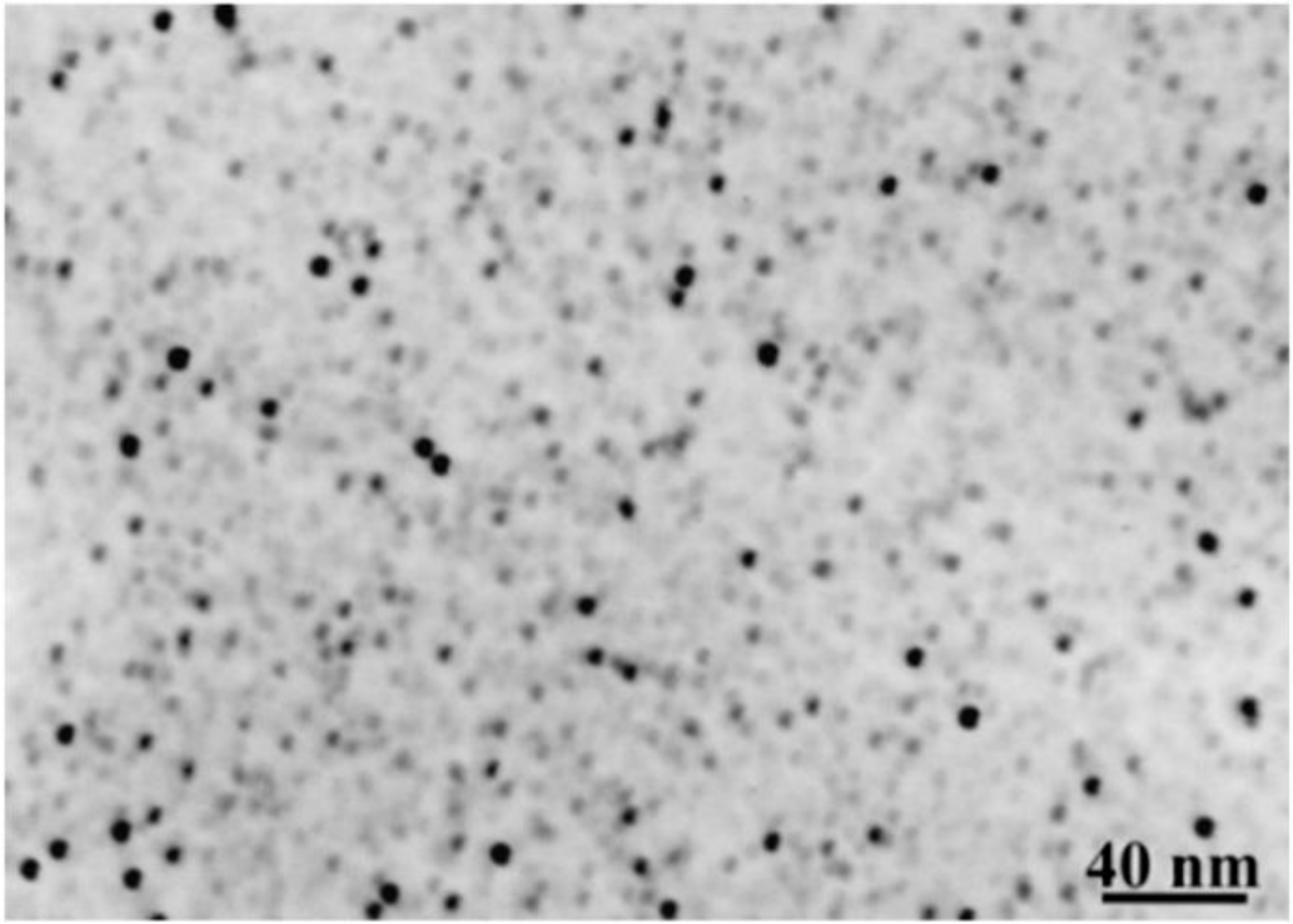
X-Ray Photoelectron Spectroscopy (XPS)
High Resolution Electron Energy Loss Spectroscopy (HREELS)

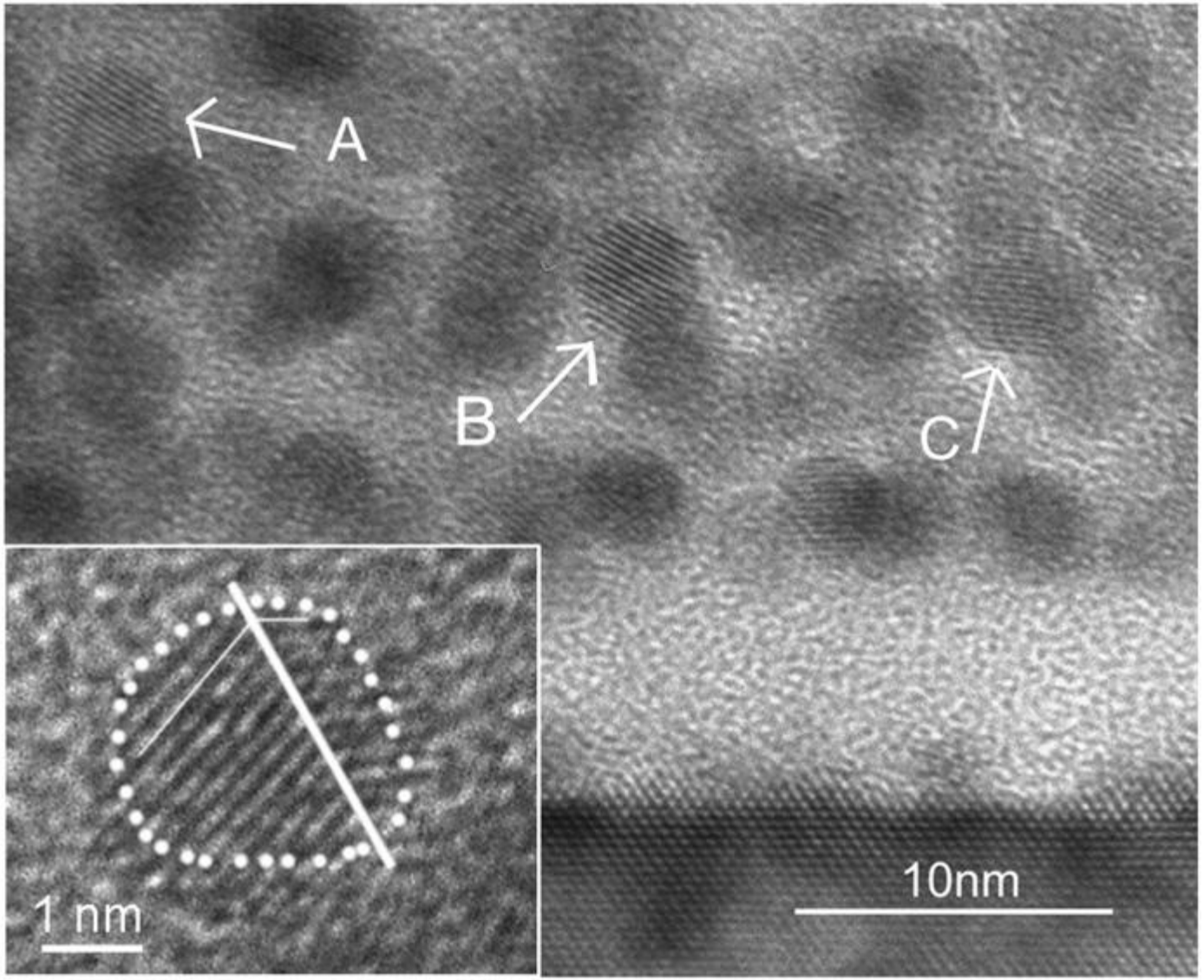
Combination of modeling with experiments; Some successful examples for particular applications

- Conducting metal nitrides
- Diamond-like carbon with Ag nanoparticles inclusions
- AlN with Ag nanoparticles' inclusions
- Metallic Glasses in thin film form for surface functionalization


(a) Ti25Ta75N
(010)
(100)
(110)
[001]
(b)
[010]
[100]
(c) Ti50Ta50N
(010)
(100)
(110)
(d) Ti75Ta25N
(010)
(100)
(110)


Lattice Constant (nm)
0.47
0.46
0.45
0.44
0.43
0.42
0.0
0.2
0.4
0.6
0.8
1.0
X
Ti$_x$Zr$_{1-x}$N
Ti$_x$Hf$_{1-x}$N
Ti$_x$Nb$_{1-x}$N
Ti$_x$Ta$_{1-x}$N
Ti$_x$Mo$_{1-x}$N
Ti$_x$W$_{1-x}$N
a
Ta$_x$Ti$_{1-x}$N
Ta$_x$Zr$_{1-x}$N
Ta$_x$W$_{1-x}$N
b


40 nm

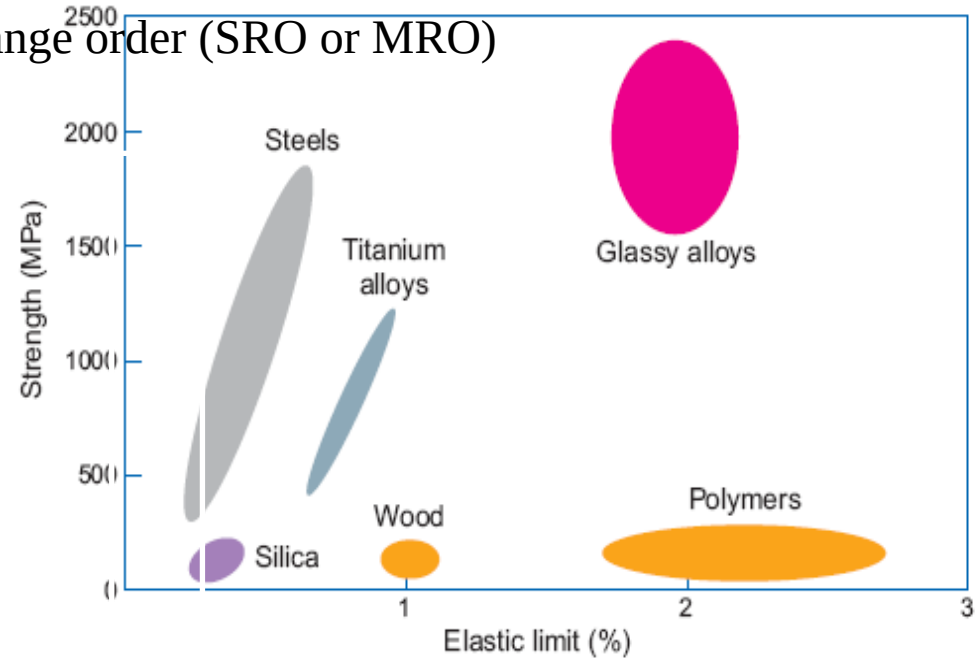

A
B
C
1 nm
10nm

Metallic Glasses (MGs) are amorphous materials characterized by:

- Lack of structural periodicity, Lack of long-range order (LRO)
- No lattice defects, grain boundaries, slip planes, stacking faults
- However, they exhibit short or medium range order (SRO or MRO)

Properties

- ✓ High yield strength 1.5-2.5 GPa
- ✓ High hardness
- ✓ Fracture toughness
- ✓ Wear and corrosion resistance
- ✓ High elastic limit
- ✓ High formability



A. Inoue et al.Mater. Trans., JIM 31, 425_1990

Applications

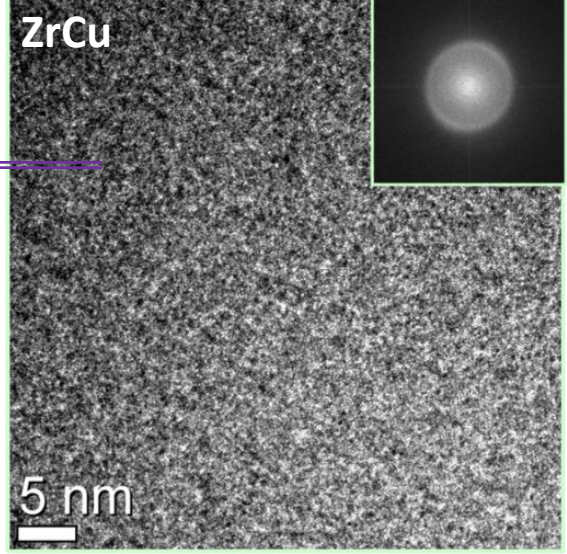
- ✓ Micromechanical devices (MEMS)
- ✓ Springs
- ✓ Medical instrumentation
- ✓ Coatings for self-phones
- ✓ Sports equipment

Drawbacks

- ✓ Small sized samples
- ✓ Low ductility (Brittle at RT)
- ✓ Catastrophic failure above yielding point
- ✓ High cost

State of the art

CuZr



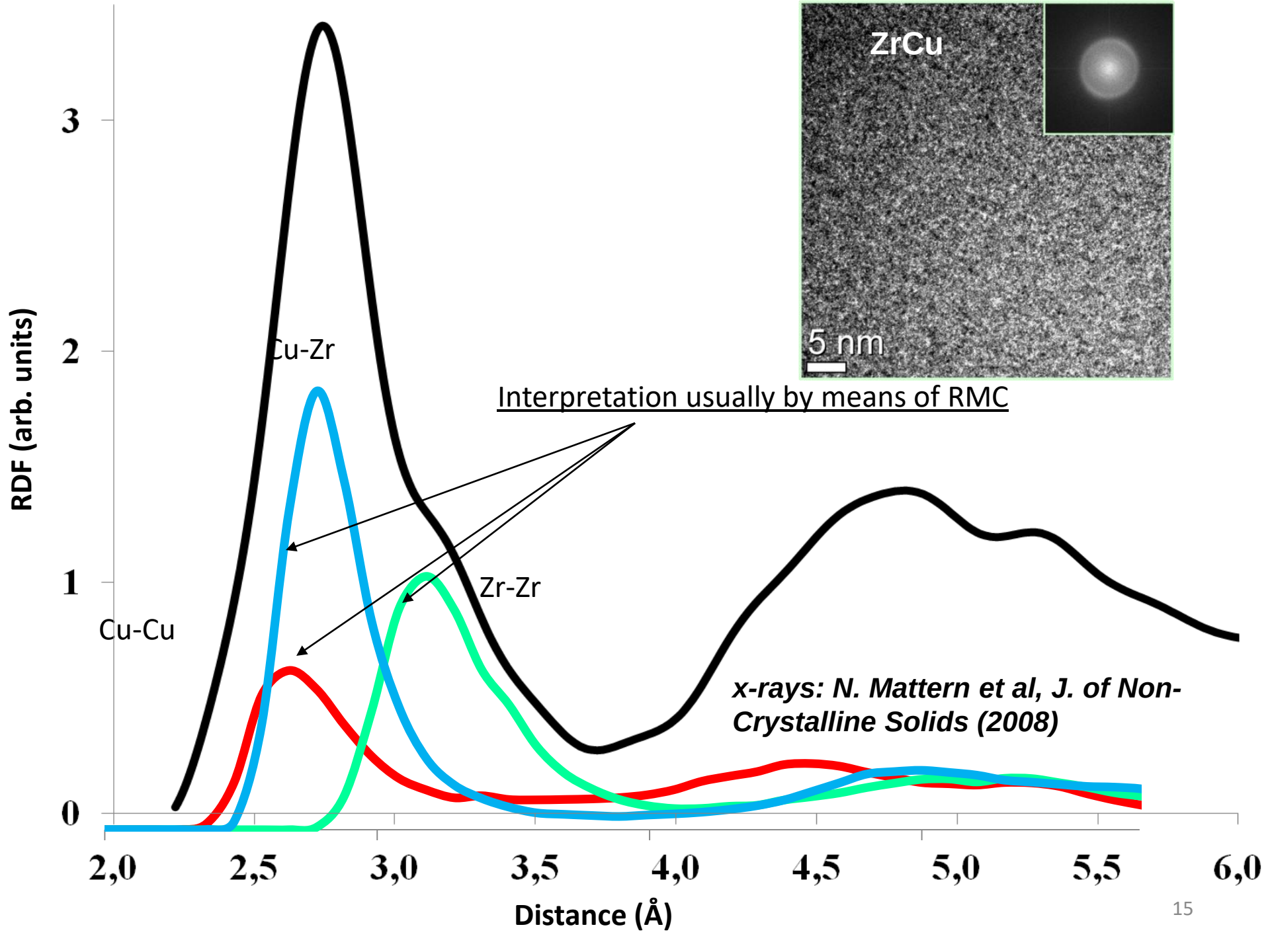
The mechanical properties of Metallic glasses (MG)
Are closely related with their structure-mictrostructure.

Focusing on the CuZr MG recent studies have demonstrated their structure consists of Icosahedral -like (ICO) small clusters (touching or interpenetrating)

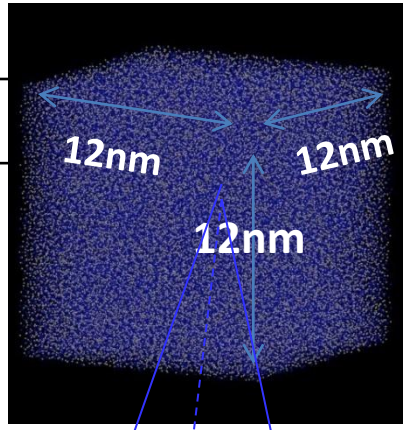
Furthermore, there are important studies aiming in revealing the ways that these clusters may be inter-connected

Nevertheless: it is still unclear whether there is a fundamental structural unit that describes the SRO and how from the SRO we can obtain the medium MRO

1. F. Spaepen, Nature (London), 408, 781 (2000)
2. Y.Q. Cheng, A.J. Cao, H.W. Sheng, E. Ma, Acta Mater. 56, 5263 (2008)
3. X.D. Wang, S. Yin, Q.P. Cao, J.Z. Jiang, Appl. Phys. Lett., 92, 011902 (2008)
4. Ch.E. Lekka, A. Ibenskas, A.R. Yavari, G.A. Evangelakis, Appl. Phys. Lett., 91, 214103 (2007)
5. M. Wakeda, Y. Shibutani, S. Ogata and J. Park, *Intermetallics* 15 (2007), p. 139
6. R.S.Liu,H.R.Liu,K.J.Dong,Z.Y.Hou,Z.A.Tian,P.Peng,A.B.Yu, J. Non-Cryst. Solids 355, 541 (2009)
7. M. Matsuura, M. Sakurai, W. Zhang, A. Inoue, Mat. Sci. Forum, 539-543, 1959 (2007)
8. D.B. Miracle, E.A. Lord, S. Ranganathan, Mat. Trans. 47, 1737 (2006)
9. X.D.Wang,Q.K.Jiang,Q.P.Cao,J.Bednarcik, H. Franz, J.Z. Jiang, J. Appl. Phys. 104, 093519 (2008)


ZrCu
5 nm
Interpretation usually by means of RMC
Cu-Zr
Zr-Zr
Cu-Cu
x-rays: N. Mattern et al, J. of Non-Crystalline Solids (2008)
RDF (arb. units)
Distance (Å)
0
1
2
3
2,0
2,5
3,0
3,5
4,0
4,5
5,0
5,5
6,0

Computational details



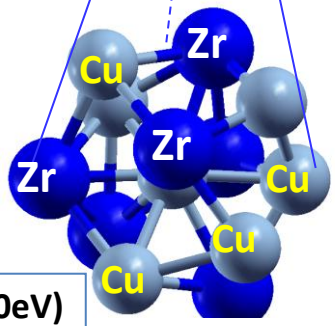
Large-scale molecular dynamics simulations:

based on Semi-Empirical potential model in analogy to the TB-SMA scheme

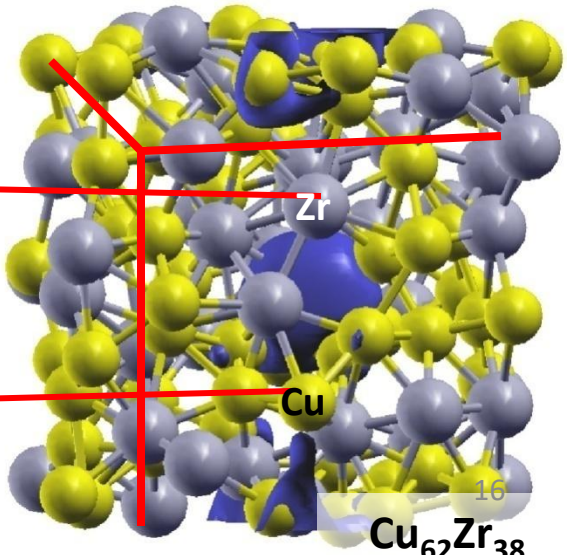
- Systems: Cu_xZr_{1-x} (80<x<20) (128000 atoms)
- the systems were melted at 2000K and subsequently cooled down "*slowly*" to room temperature

Density functional theory calculations: bonding characteristics

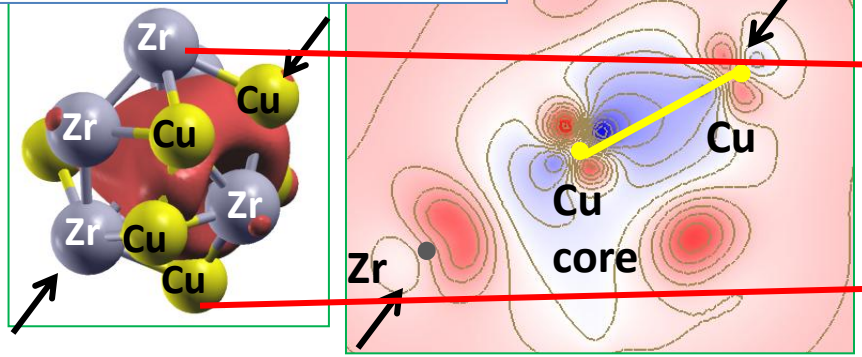
- CuZr pure and influenced by **Al or Nb minor additions**:
  - **Tiny** clusters Cu_8Zr_5, Cu_8Zr_4Al, Cu_8Zr_4Nb, …
  - **Superclusters** like $Cu_{13}Zr_{10}$, $Cu_{13}Zr_9Al$, $Cu_{12}Zr_9Al_2$,…
  - "**Bulk**" system $Cu_{60}Zr_{40}$, CuZr**Al**, CuZr**Nb**



e^- state (-6.0eV)



Lowest valence e^- state (-6.0eV)

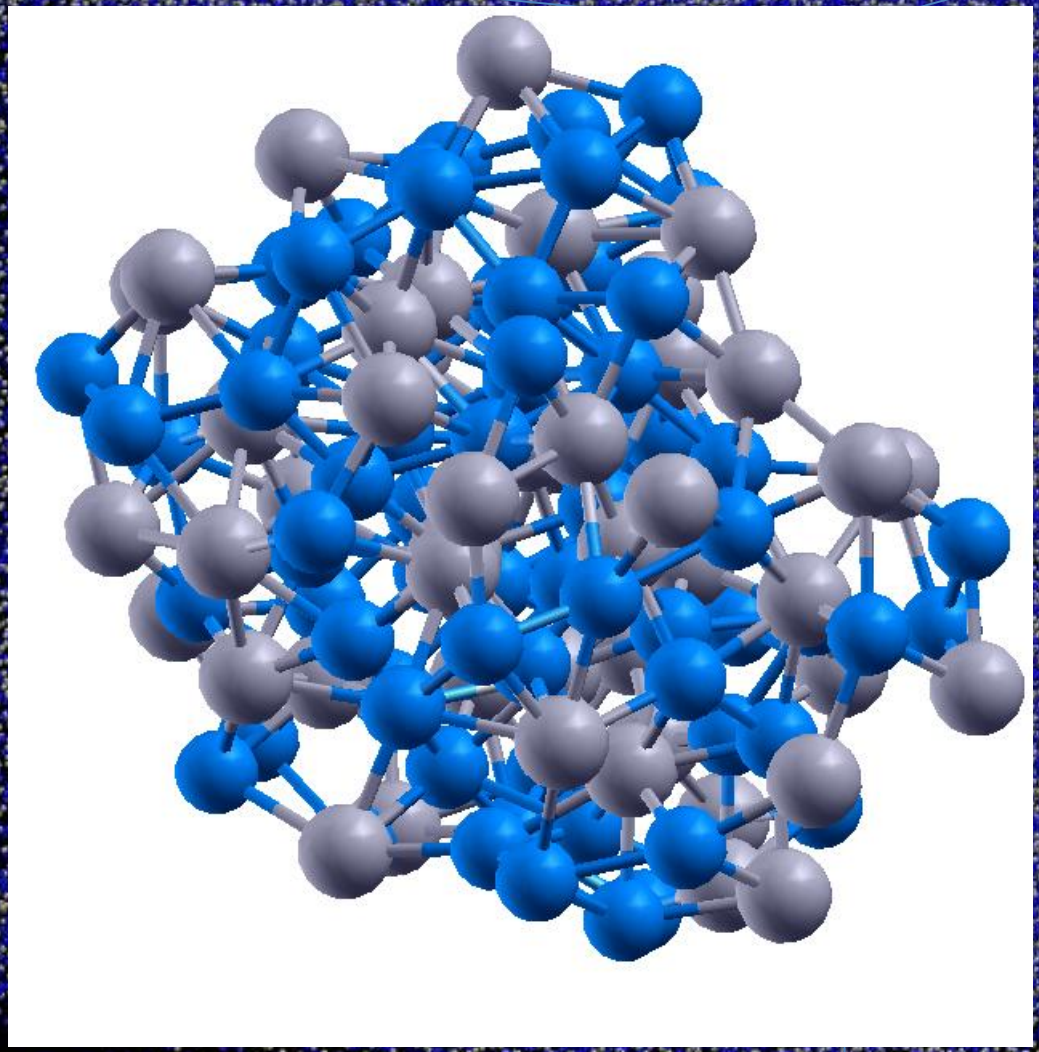


G.A. Almyras, Ch.E. Lekka, N. Mattern, G.A. Evangelakis, Scripta Mater.62, 33 (2010).
Ch.E. Lekka, G.A. Evangelakis, Scripta Mater, 61 974 (2009).

$Cu_{62}Zr_{38}$

Standard Molecular dynamics simulations

Free surface



$Cu_{50}Zr_{50}$

Approach

"Building an MG by Sticking balls and clusters"

Let's consider the case of $Cu_{50}Zr_{50}$

Common Neighbor Analysis revealed the presence of Cu_6Zr_7 ICO Cu-centered 13 atom clusters (~33%) and Cu_7Zr_8 Rhombic-like Zr-centered 15 atom clusters (~50%)

These cluster compositions correspond to concentrations of 46% in Cu

It does NOT correspond to the system's stoichiometry!

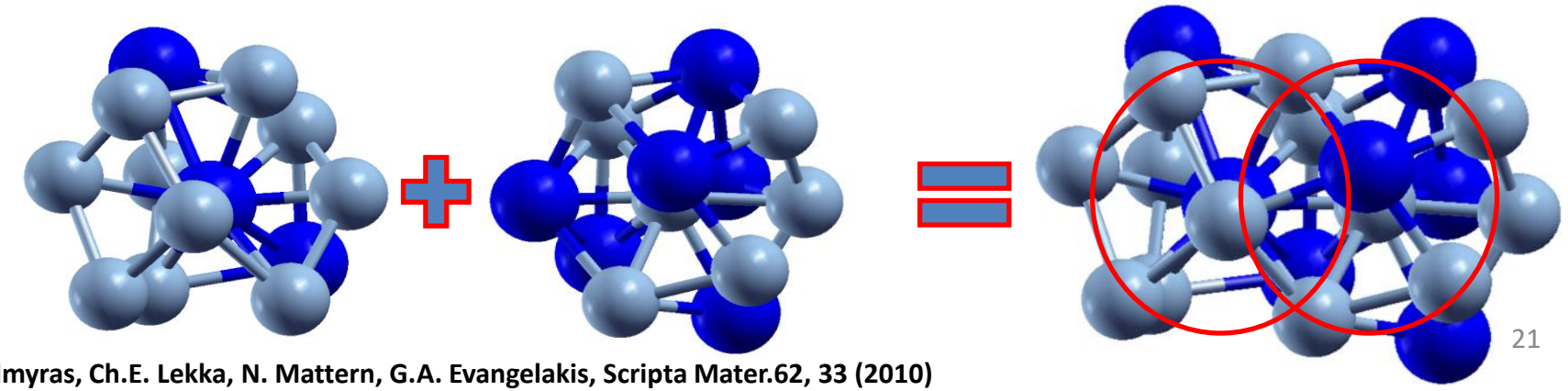
Therefore, the clusters MUST be CONNECTED in order to share atoms and result in the CORRECT stoichiometry

OUR APROACH*

We noticed that
the clusters' compositions ≠ *systems' stoichiometries !*
e.g. $Cu_8Zr_5 \rightarrow Cu_{61.5}Zr_{38.5}$ ≠ $Cu_{65}Zr_{35}$

Taking into account that the MG is locally homogeneous, one would expect that if there was a building unit it should reproduce the systems' compositions

Therefore, the clusters MUST be interconnected to form SuperClusters (SC), so that the resulting SCs would reproduce the system's compositions, e.g. by sharing common atoms .



*G.A. Almyras, Ch.E. Lekka, N. Mattern, G.A. Evangelakis, Scripta Mater.62, 33 (2010)

*OUR APROACH**

If we denote by N_{cu} and N_{Zr} the Cu and Zr content of a specific cluster that is dominant in a particular stoichiometry, e.g. 8 and 5 for the ICO cluster of the $Cu_{65}Zr_{35}$ case, by Com_{Cu} and Com_{Zr} the Cu and Zr common atoms of the SC, and by Tot_{Cu} and Tot_{Zr} the total number of Cu and Zr atoms in the SC, we can write the following simple relations:

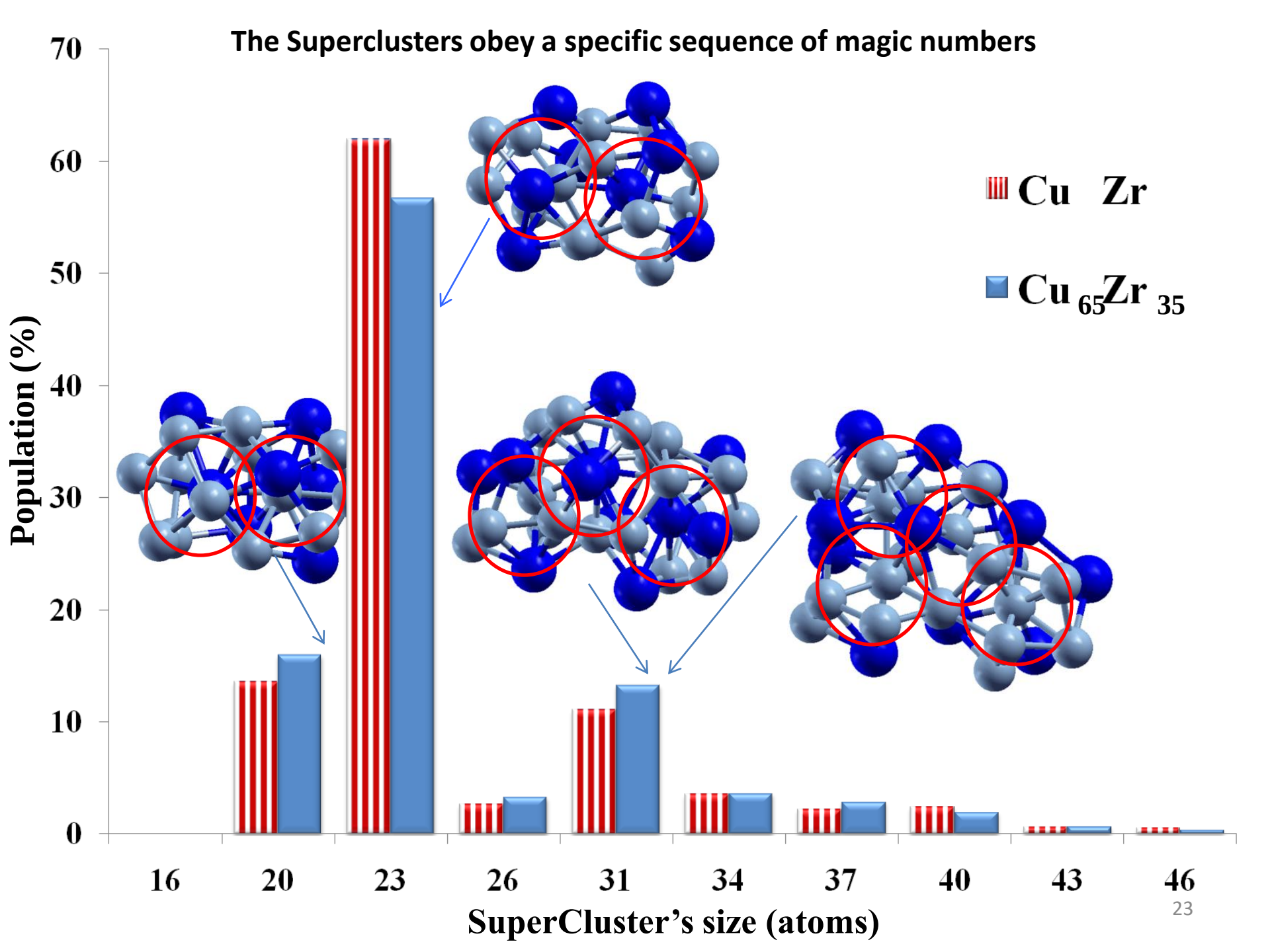
$$Com_{Cu}=Tot_{Cu}-N_{cu}/N_{Zr}(Tot_{Zr}-Com_{Zr})$$

So the number of atoms in the resulting SC, N_{SC}, will be given by:

$$N_{SC}=(Tot_{Cu}-Com_{Cu})+(Tot_{Zr}-Com_{Zr})$$

Consequently, among all poly-icosahedral SCs with magic numbers that could be obtained from the interconnections of simple clusters, the above relations provide the appropriate selection of those SCs that reproduce the system's composition.

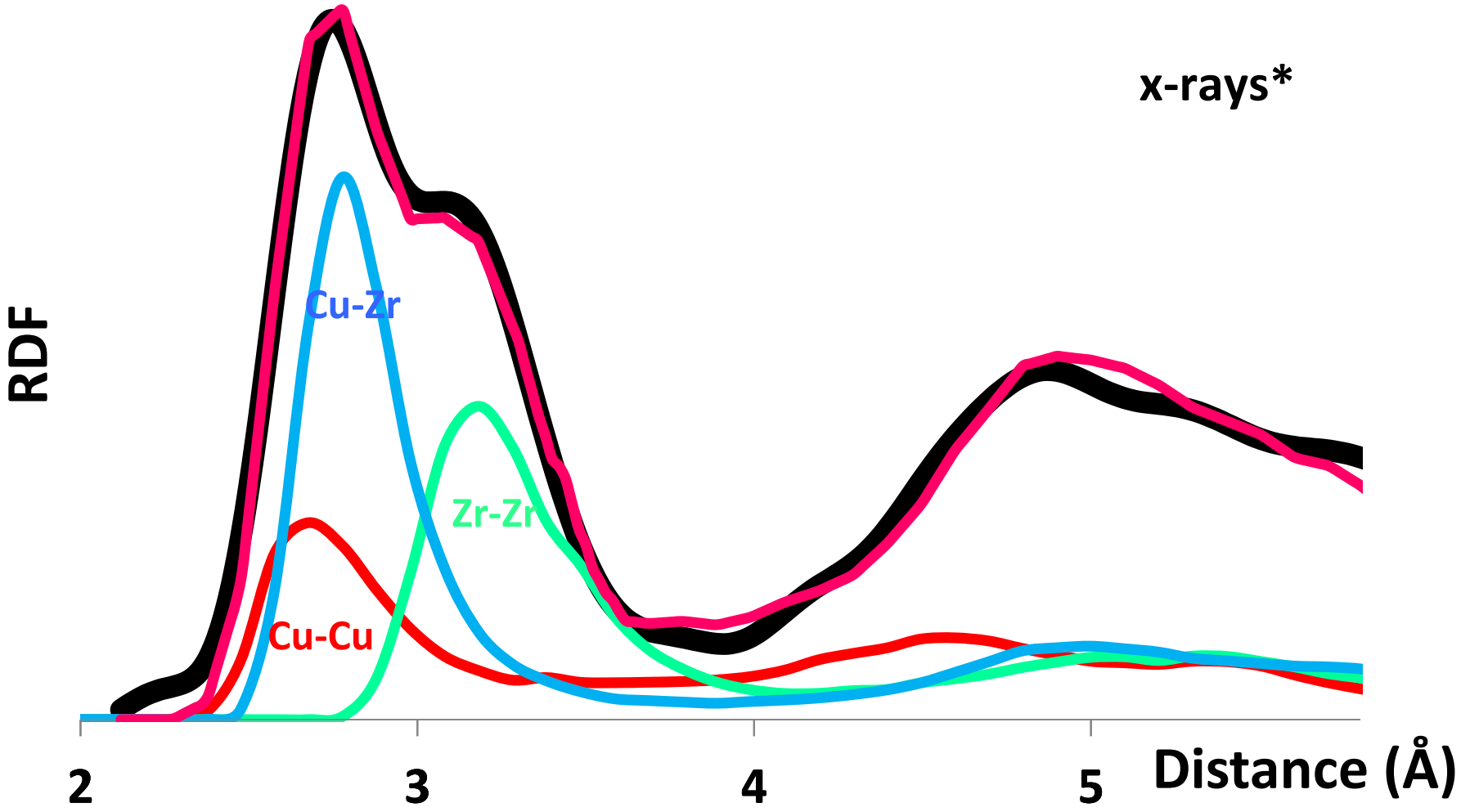
*G.A. Almyras, Ch.E. Lekka, N. Mattern, G.A. Evangelakis, Scripta Mater. 62, 33 (2010)


The Superclusters obey a specific sequence of magic numbers
Population (%)
70
60
50
40
30
20
10
0
Cu Zr
Cu 65Zr 35
16
20
23
26
31
34
37
40
43
46
SuperCluster's size (atoms)

Clusters and their verification (XRD + EXAFS)

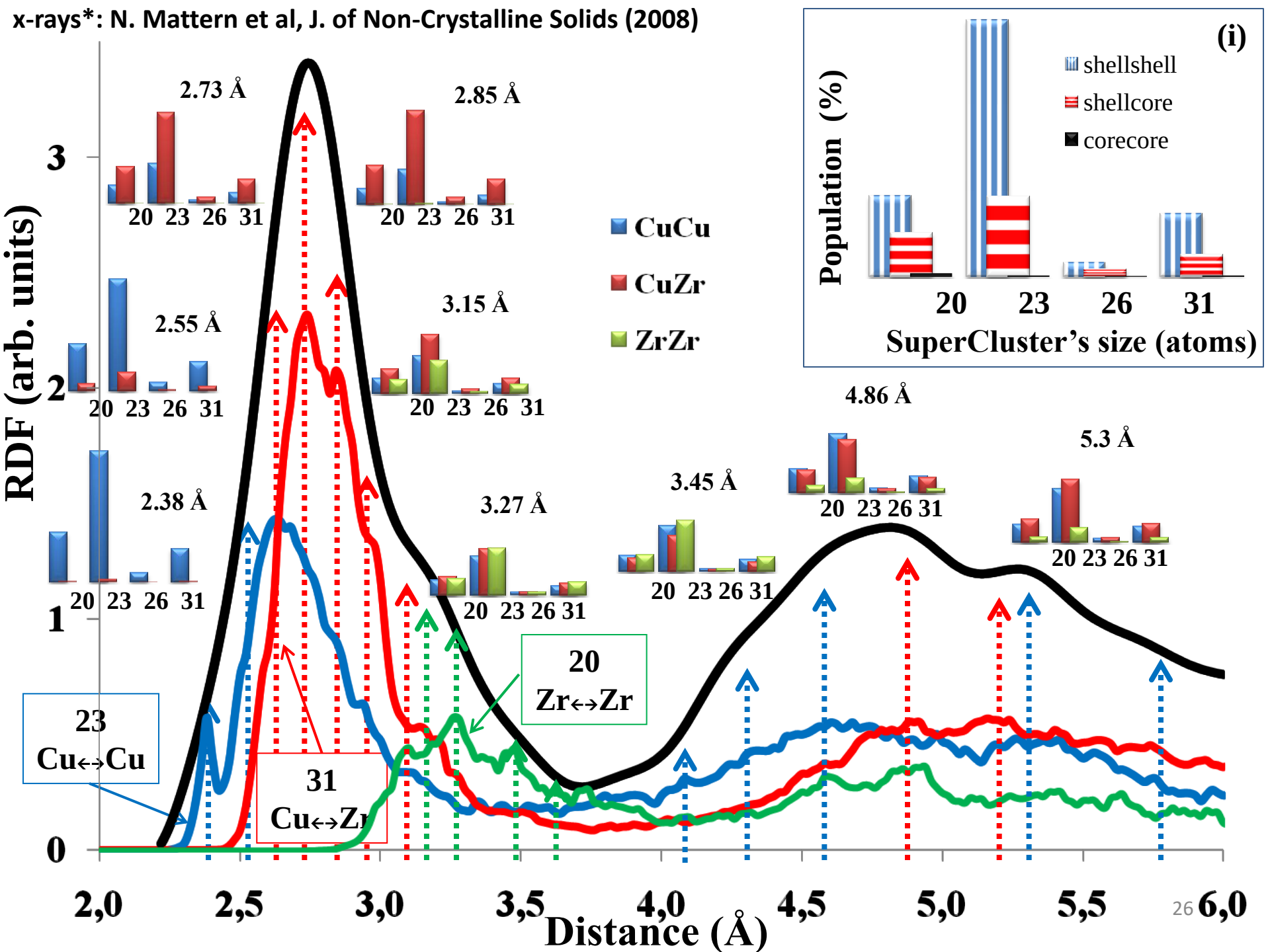
Radial distribution function of $Cu_{50}Zr_{50}$

Cu-Zr centered clusters – common atoms → system 's composition

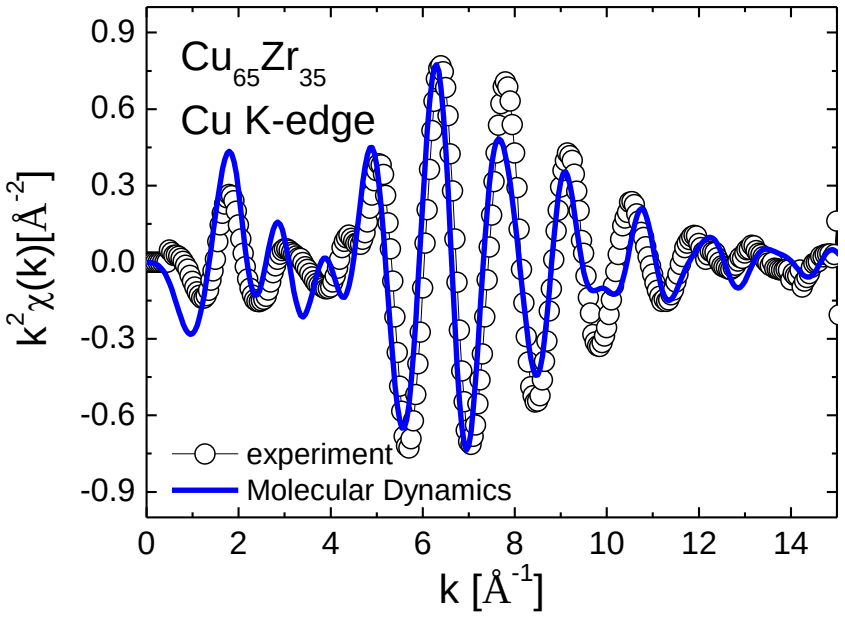


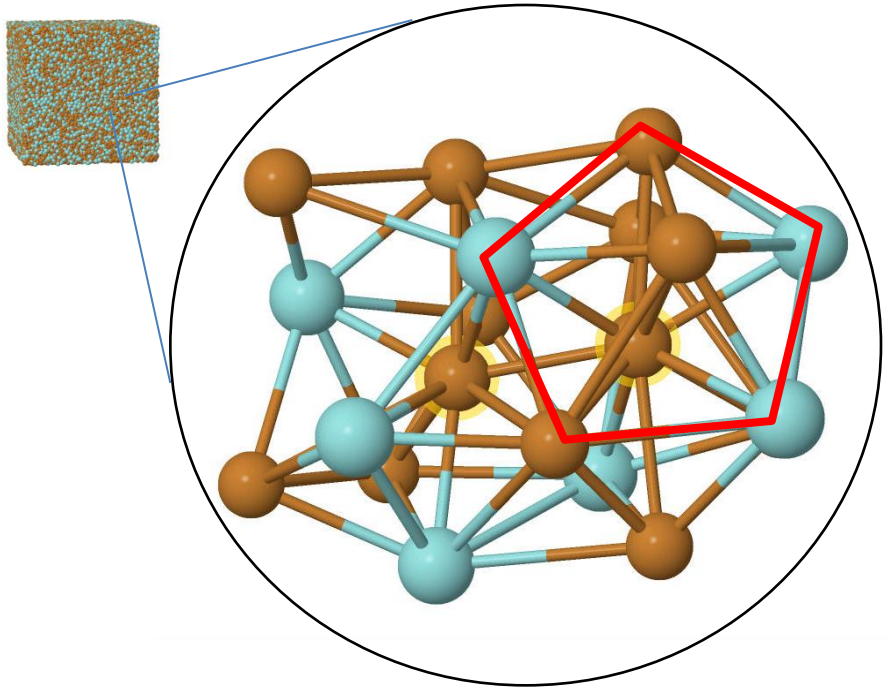
x-rays*: N. Mattern et al, J. of Non-Crystalline Solids 354 (10-11), 1054

x-rays*: N. Mattern et al, J. of Non-Crystalline Solids (2008)



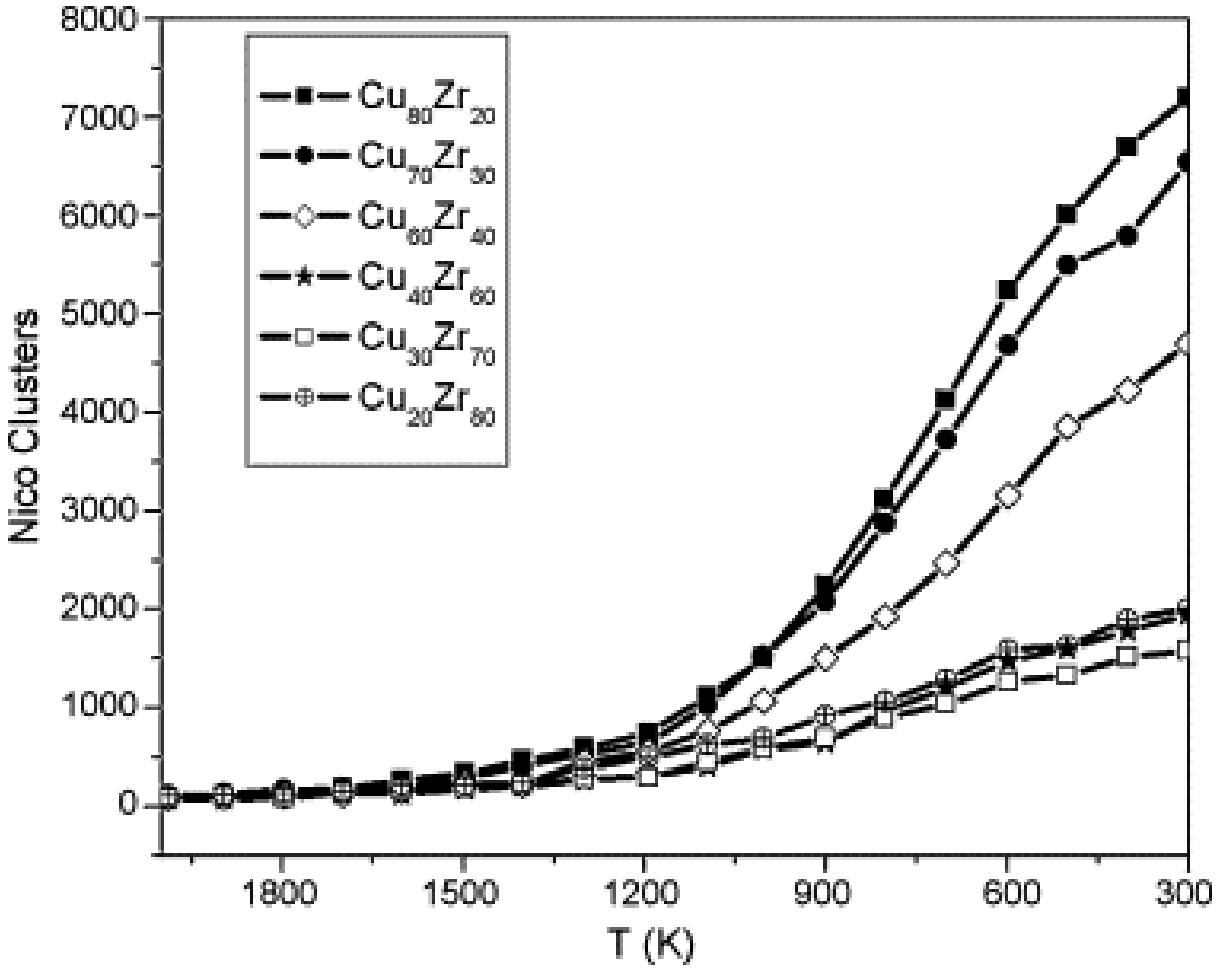
Molecular dynamics simulations and EXAFS



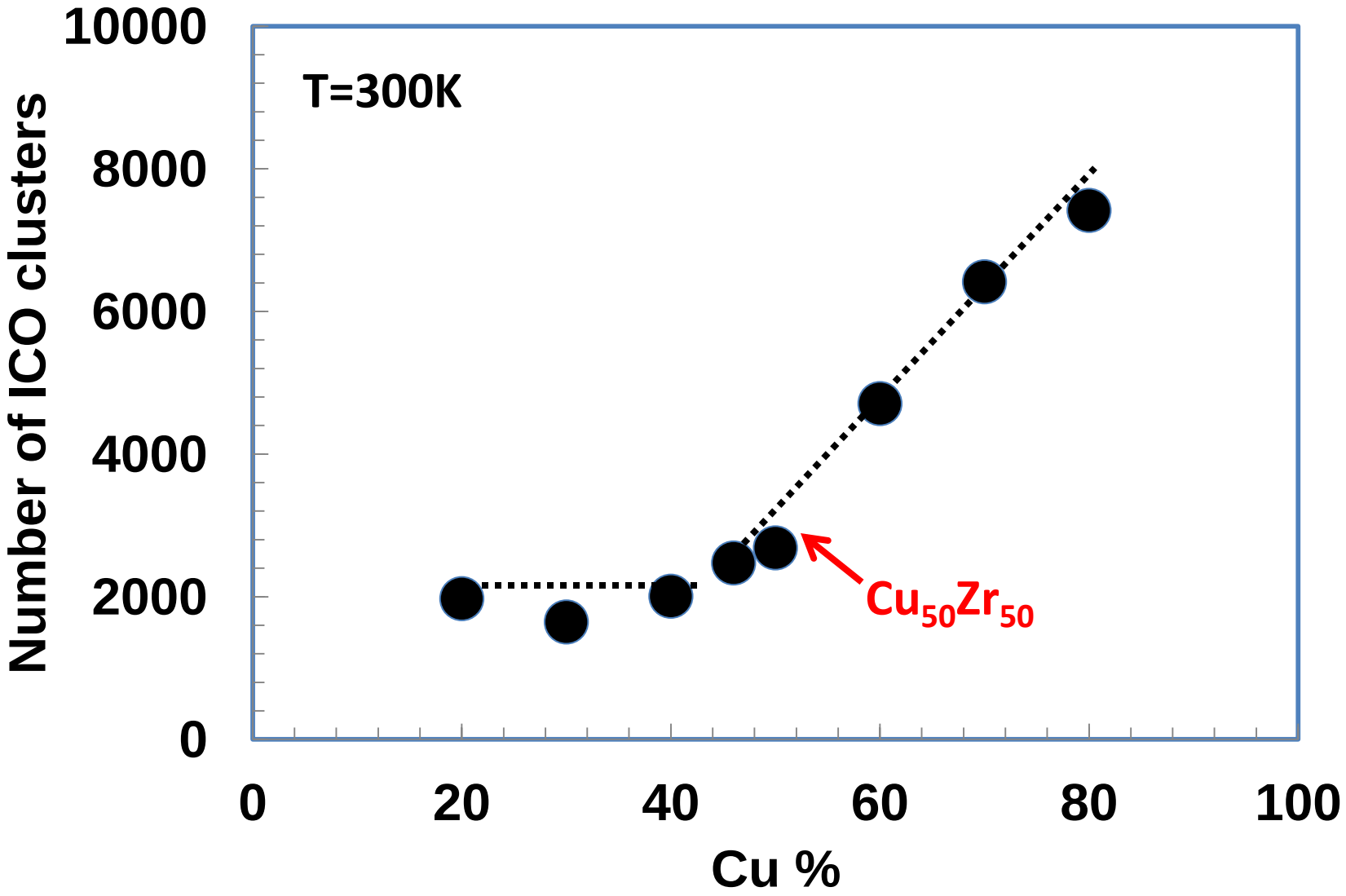


- MD simulations are in excellent agreement with the experimental EXAFS spectra.
- Atomic structure of Cu-Zr binary glasses consists of interpenetrating icoshedral-like clusters involving five-fold symmetry.

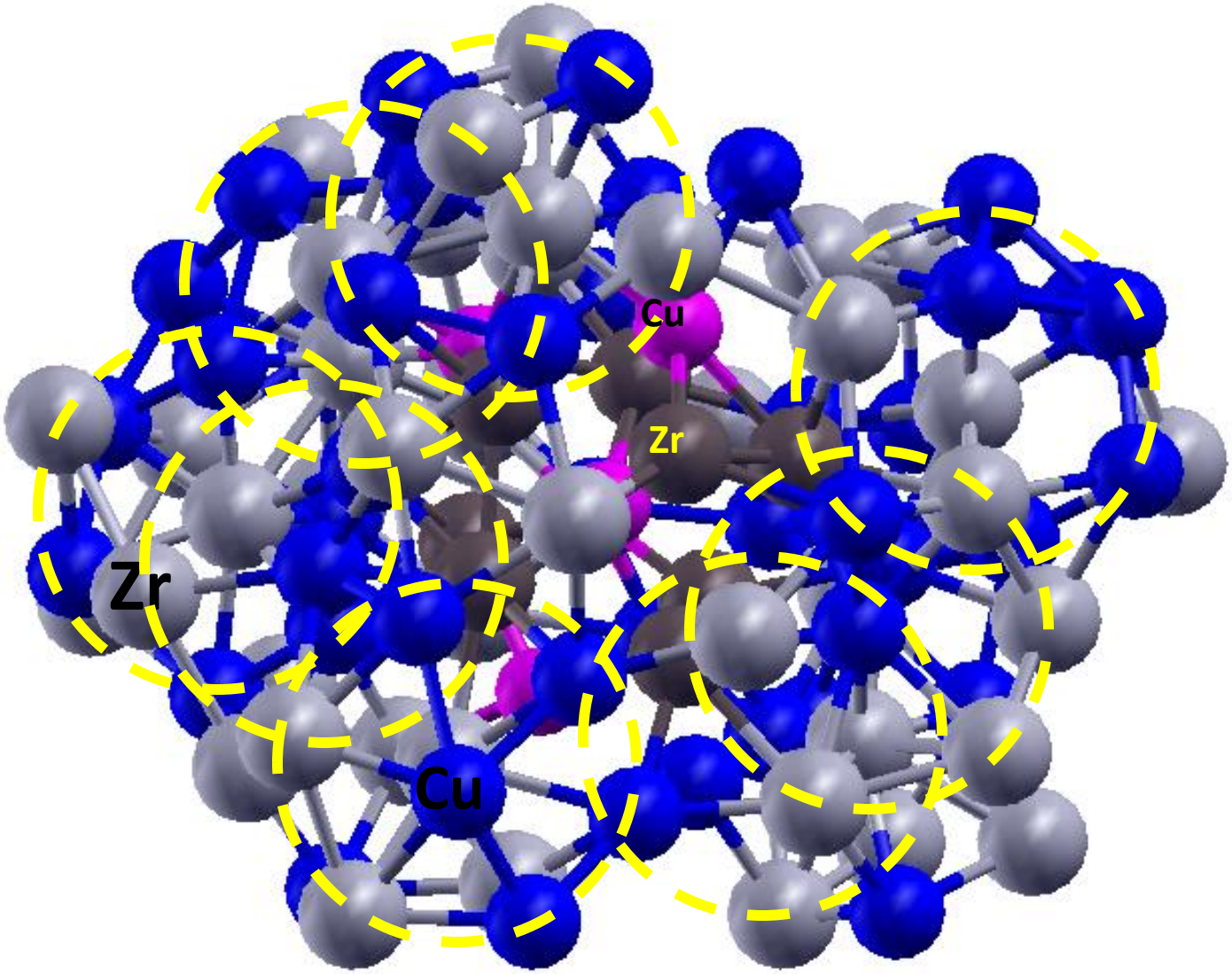
J. Antonowicz, A. Pietnoczka, T. Drobiazg, G.A. Almyras, D.G. Papageorgiou, G.A. Evangelakis, *Phil. Mag.* **92** (2012) 1865


Nico Clusters
T (K)
8000
7000
6000
5000
4000
3000
2000
1000
0
1800
1500
1200
900
600
300
Cu80Zr20
Cu70Zr30
Cu60Zr40
Cu40Zr60
Cu30Zr70
Cu20Zr80

Cu concentration dependence of the number of icosahedral clusters



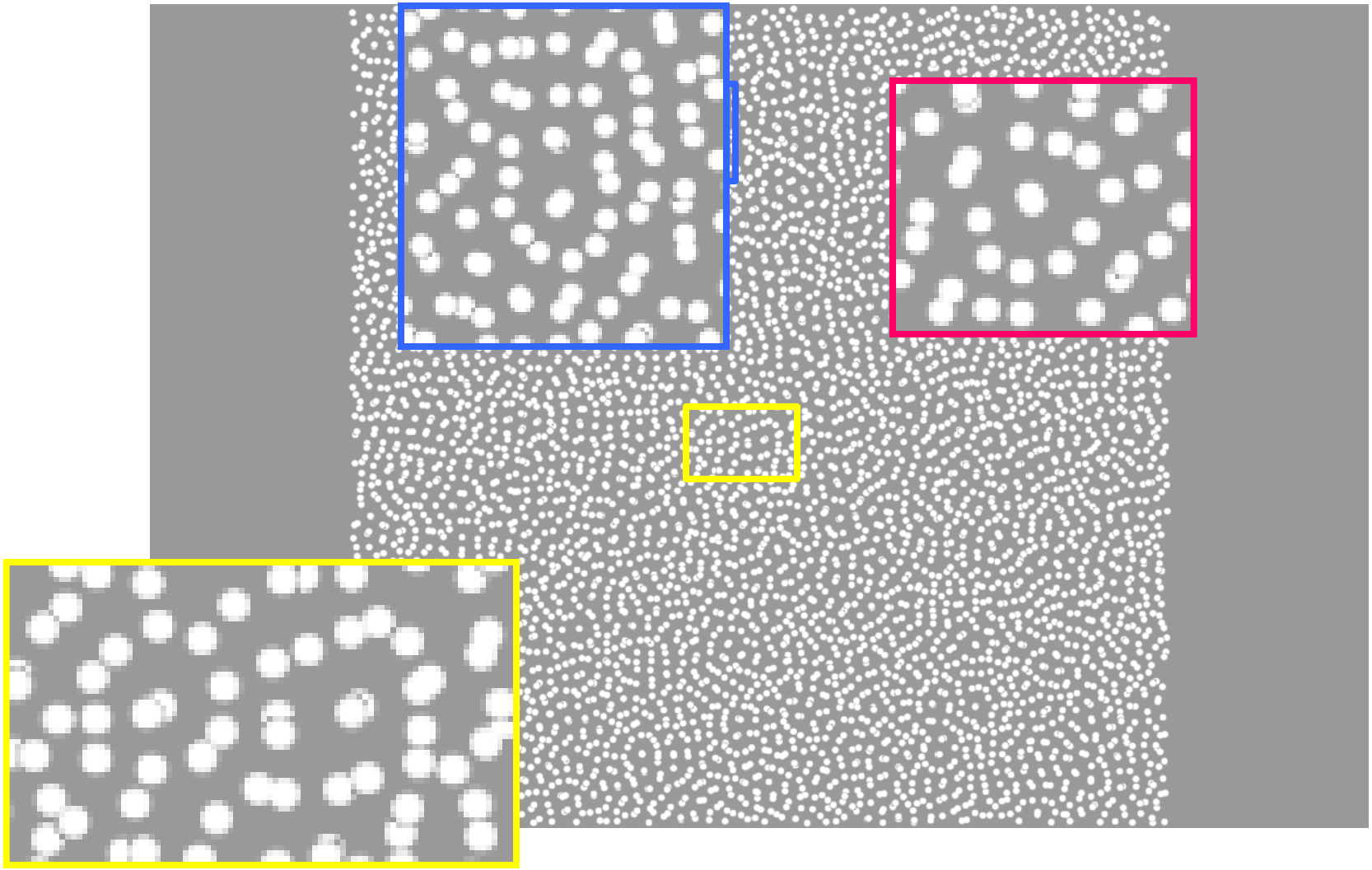
NOW ➔ Search all possible clusters (based on coordination numbers - including those with no geometrical identification)



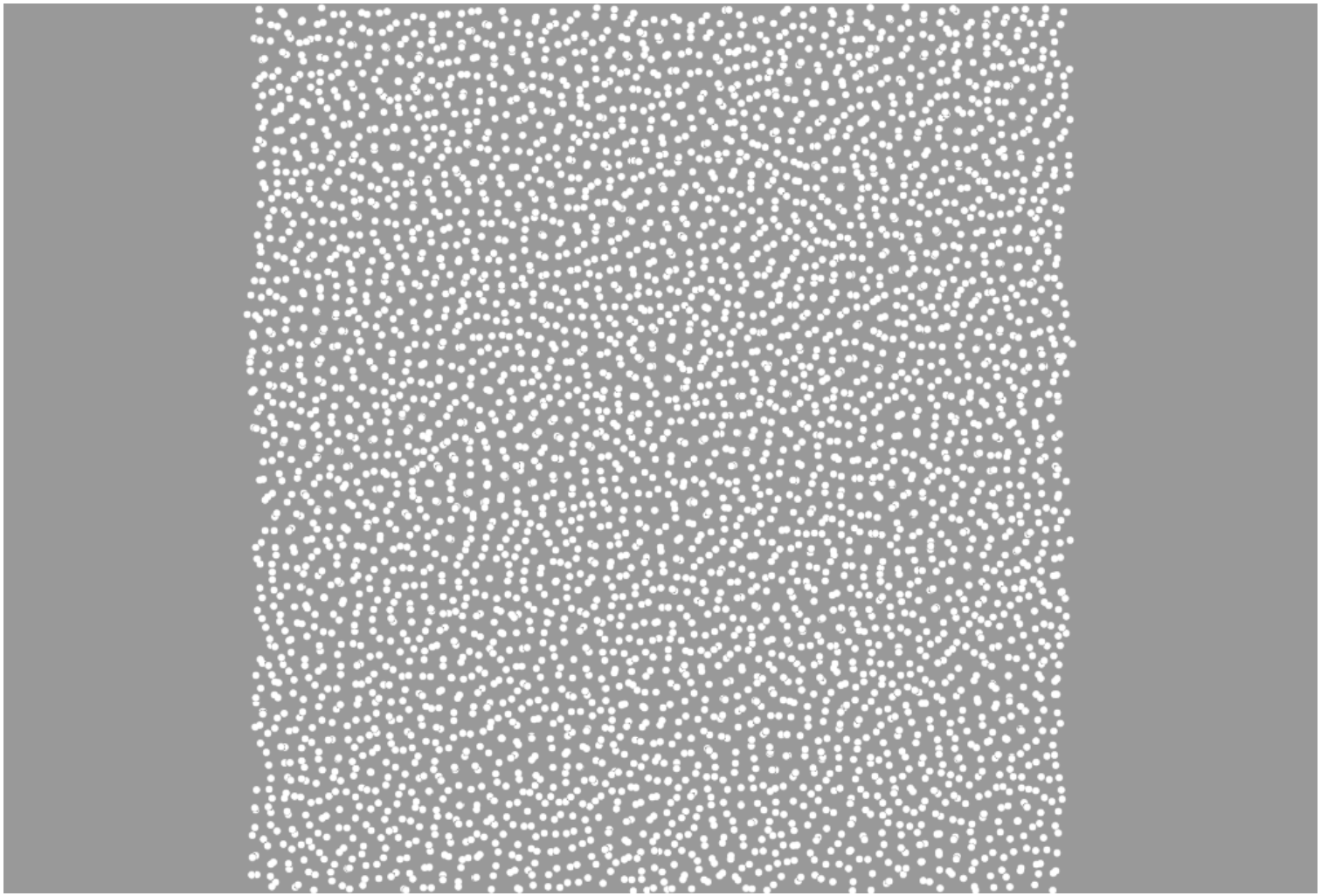
Tensile Deformation and ICOs

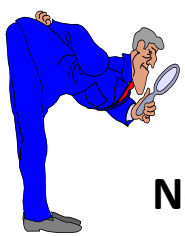
Close view of a thin slice at **equilibrium**

$Cu_{46}Zr_{54}$



After tensile deformation 24%

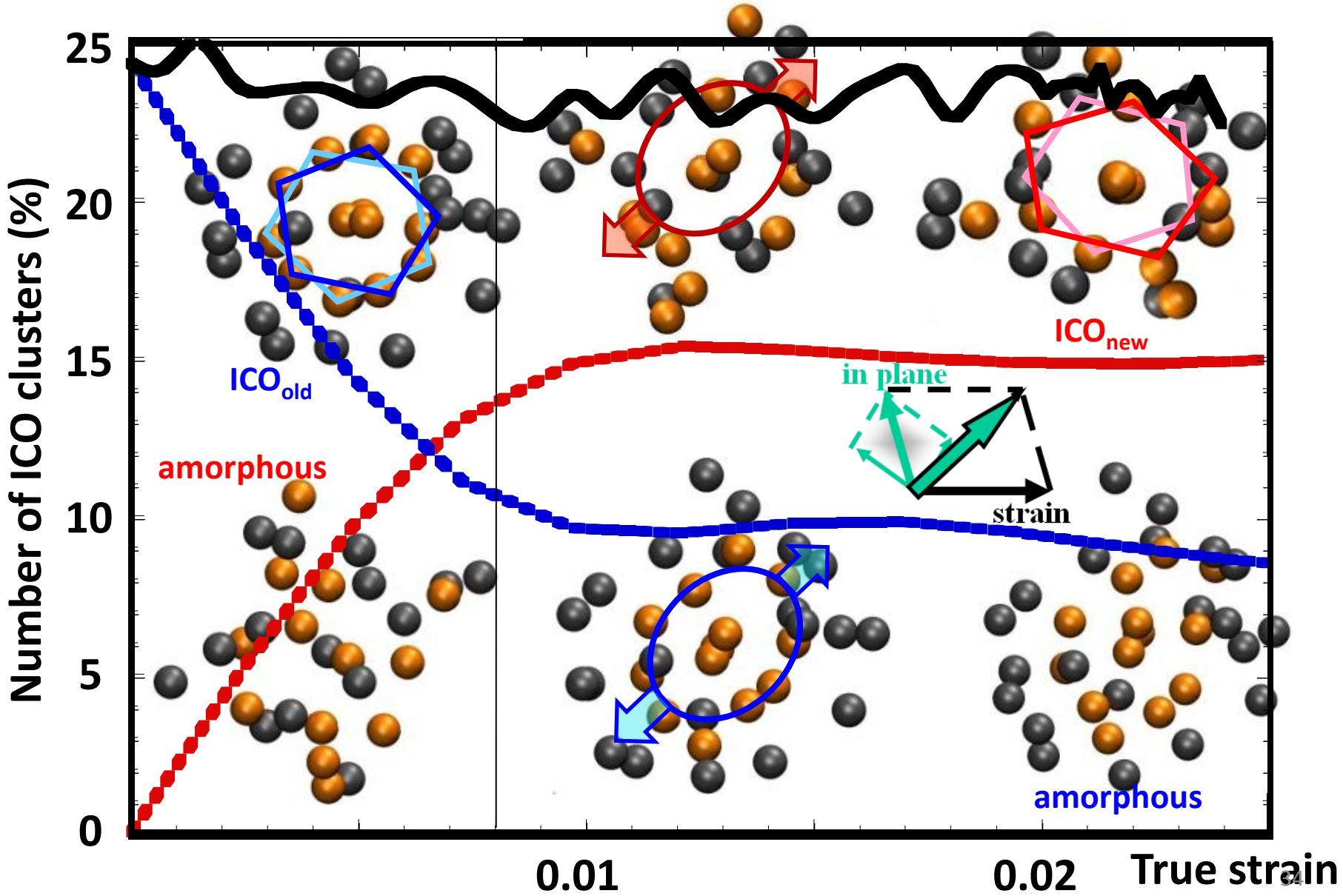




No visible change…

Up to Yielding

Destruction (old-ICO) and Recreation (new-ICO) clusters upon tensile deformation



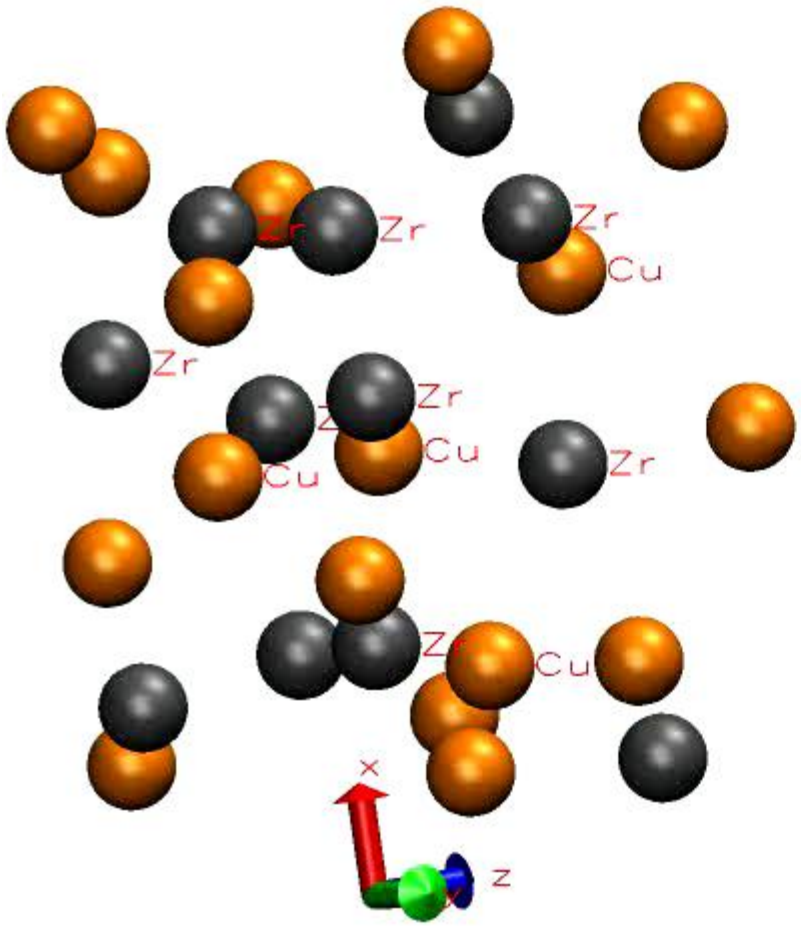
Ch.E.Lekka, A. Ibenskas, A.R.Yavari, G.A. Evangelakis, APL 91 (2007) 214103

Up to Yielding

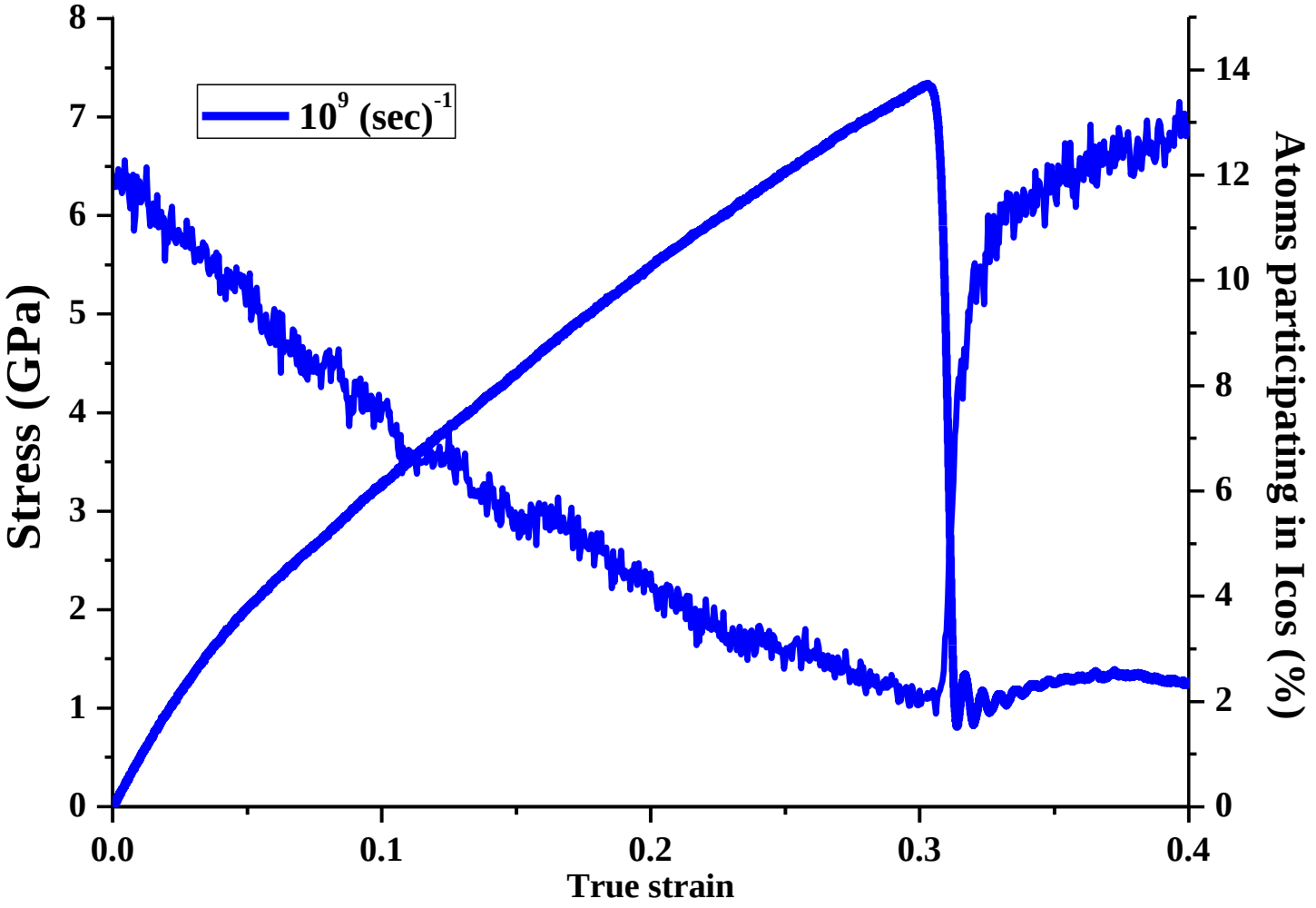
$Cu_{46}Zr_{54}$

Creation AND destruction of an ICO cluster under tensile deformation

Ch.E. Lekka, A. Ibenskas, A.R. Yavari, G.A. Evangelakis, Appl. Phys. Lett., 91, 214103 (2007)

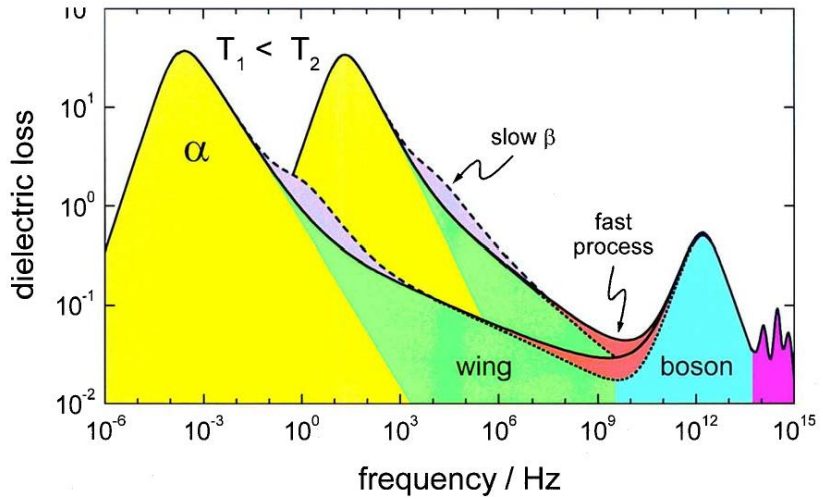


Tensile deformation of $Cu_{50}Zr_{50}$ and ICOs' evolution with strain



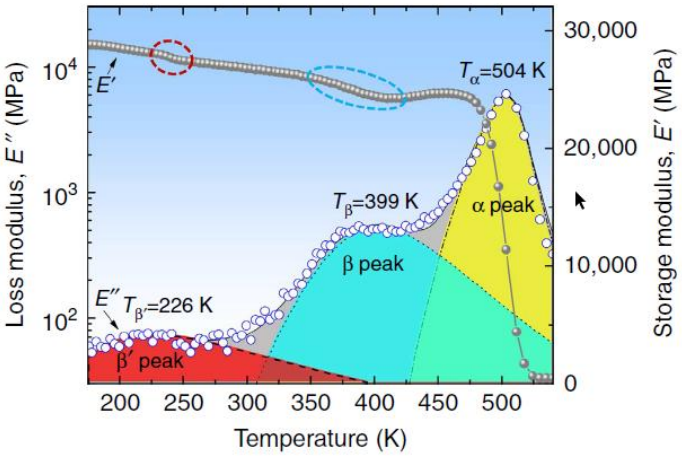
Dynamics of a "QUIESCENT" Glass

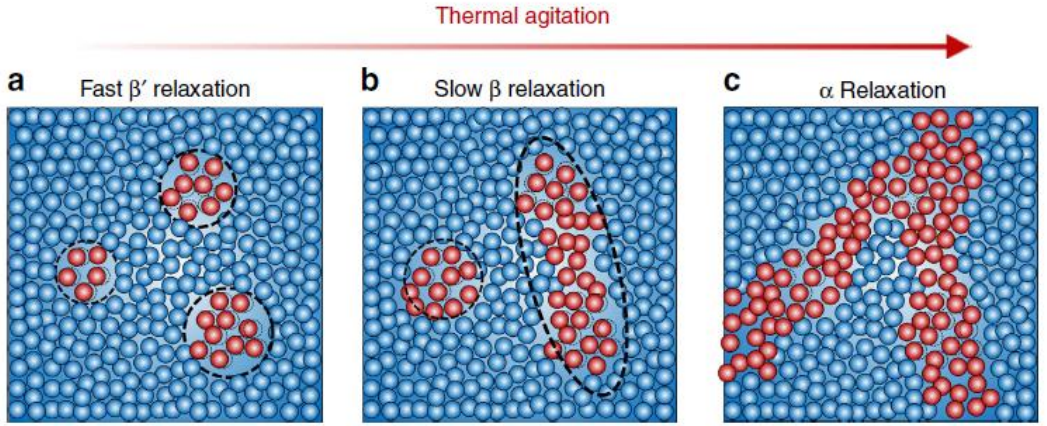
Complex relaxation dynamics:



Schematic view of the frequency dependent dielectric loss in glass-forming materials

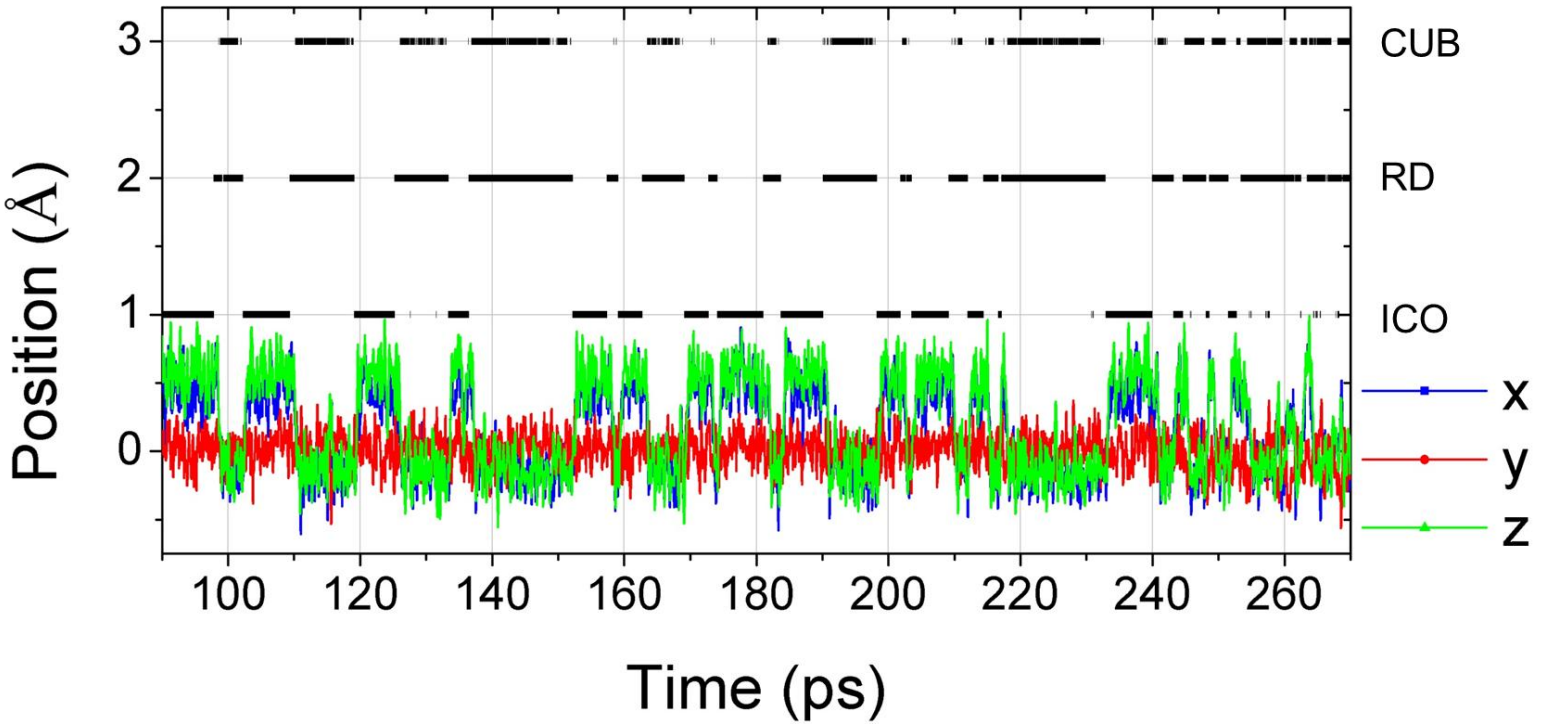
P. Lunkenheimer , U. Schneider , R. Brand & A. Loid.
Contemp. Phys, 41:1, 15-36 (2010)





Q. Wang, S. T. Zhang, Y. Yang, Y. D. Dong, C. T. Liu, and J. Lu.
Nat. Commun. 6, 7876 (2015).

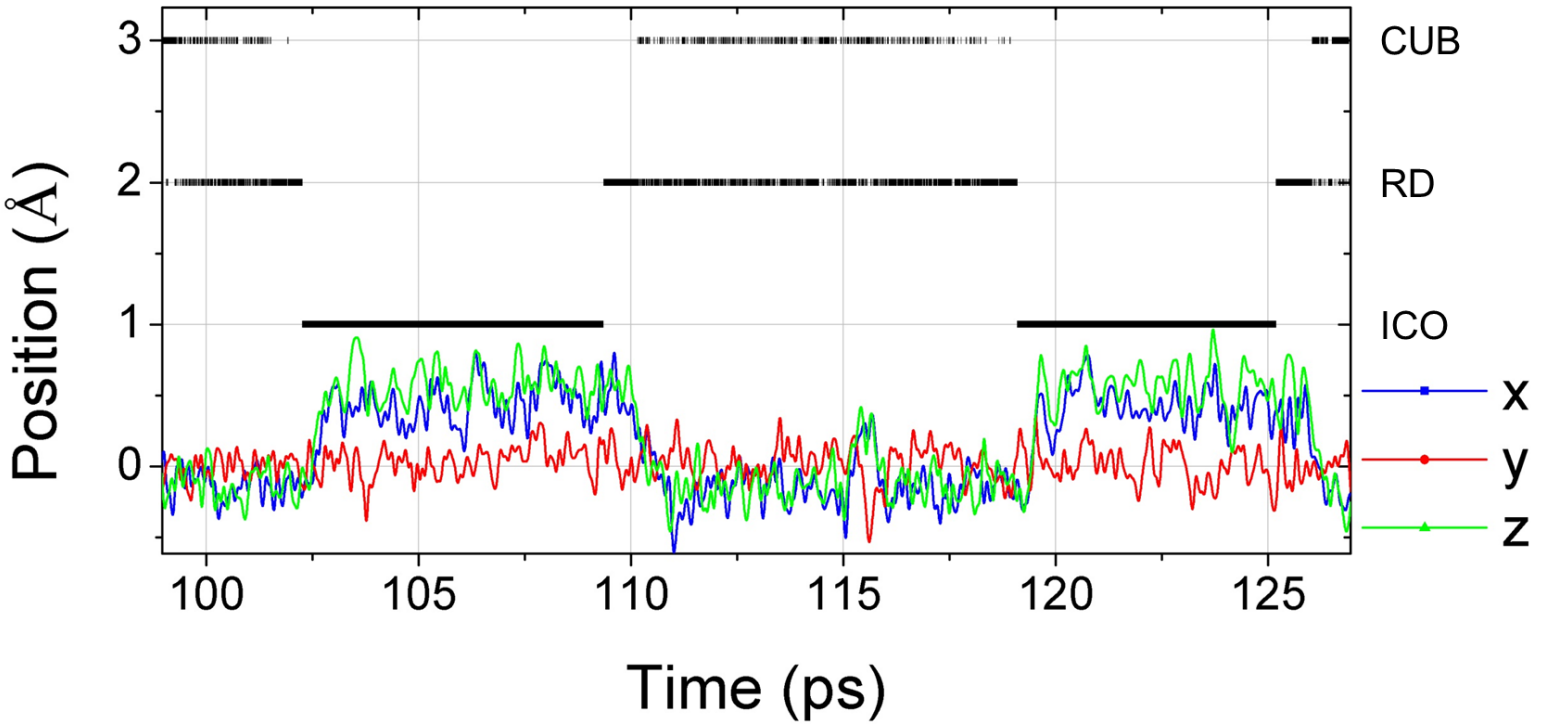
Atoms´ position in time for 300 K:



Representative atoms´ position in time for 300 K and corresponding cluster structure

- **Wide distribution of distances** (from 0.1 to more than 1.5 Å) **and life-times** (from 1.5 to more than 100 ps)
- **Characteristic forwards and backwards movement.** The net mass flow is practically negligible (i.e. **no diffusion** was found at room temperature)

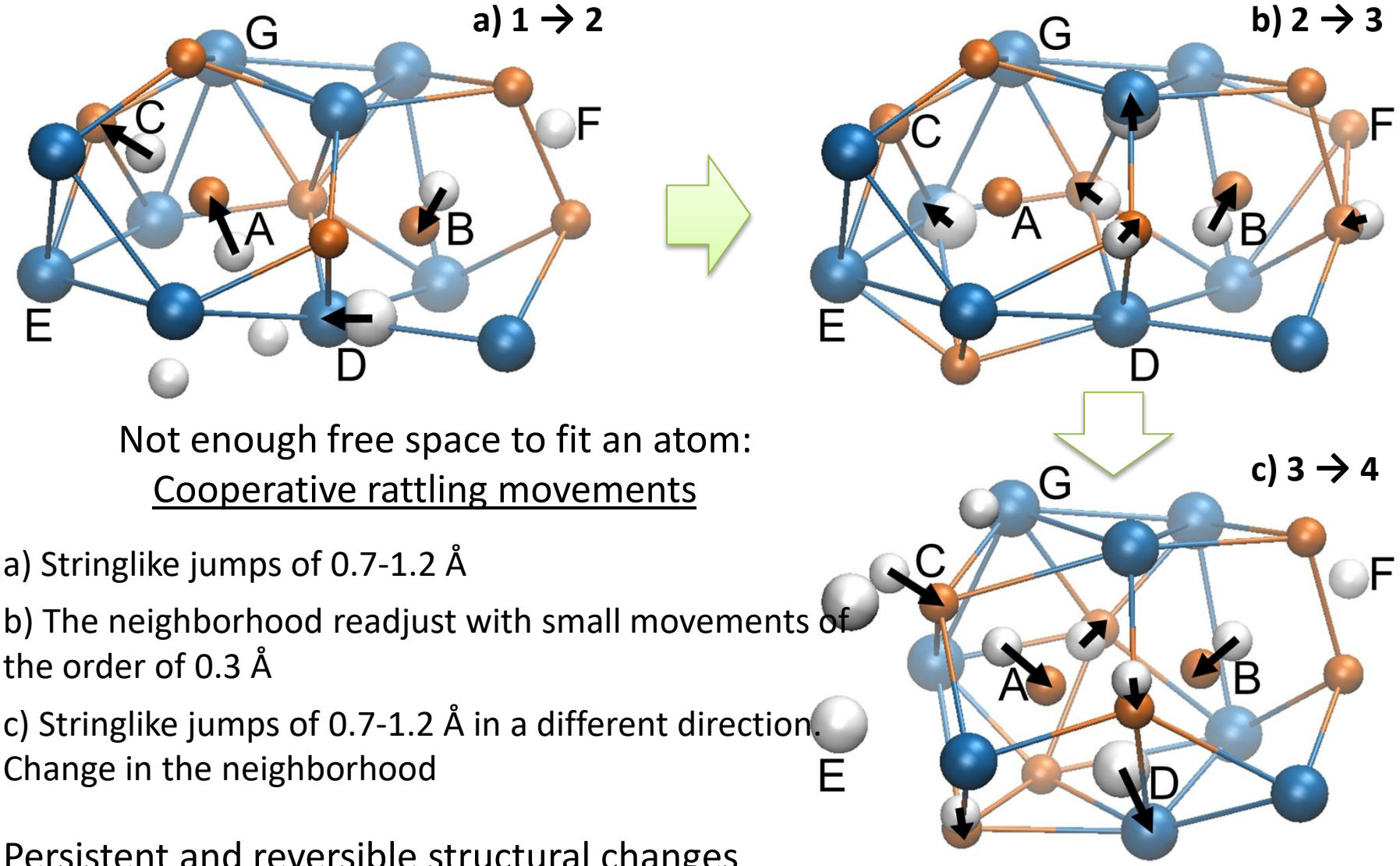
atoms´ position in time for 300 K (zoom):



Representative atomic position in time for 300 K and corresponding cluster structure

Rattling movements and cluster structures are correlated

Complex cooperative movements:



Not enough free space to fit an atom:
Cooperative rattling movements

a) Stringlike jumps of 0.7-1.2 Å

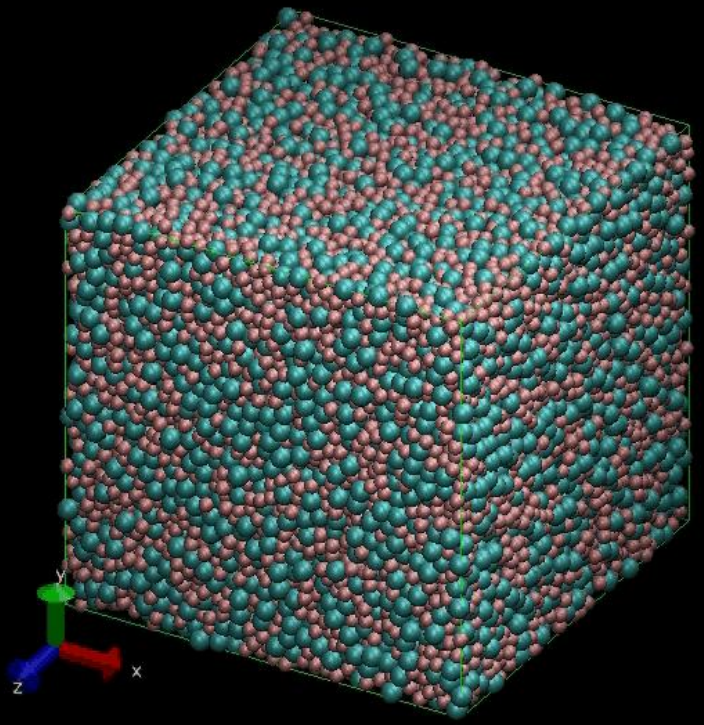
b) The neighborhood readjust with small movements of the order of 0.3 Å

c) Stringlike jumps of 0.7-1.2 Å in a different direction. Change in the neighborhood

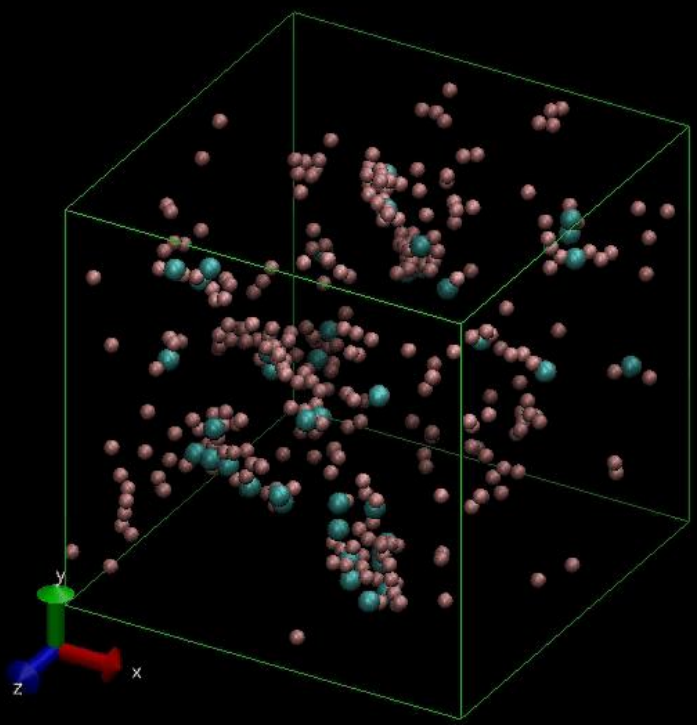
Persistent and reversible structural changes

Locations of the rattling atoms:

System's simulation box

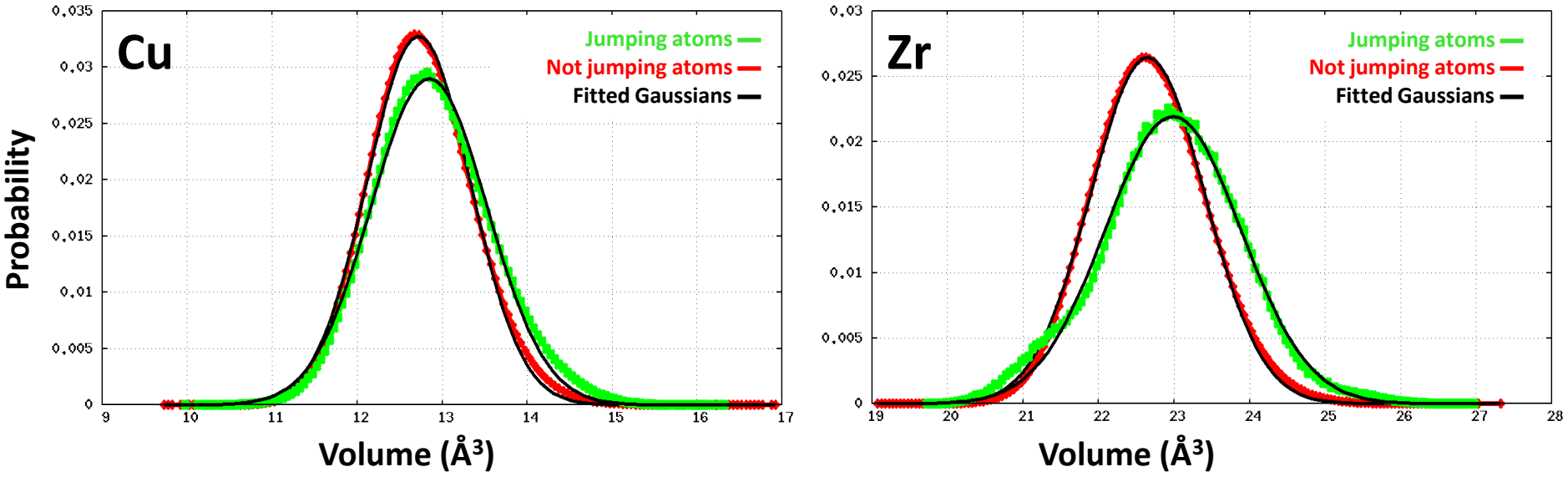


Only rattling atoms
~1% of the system's atoms



Rattling atoms are gathered together in high mobility regions

Atomic Voronoi volume:



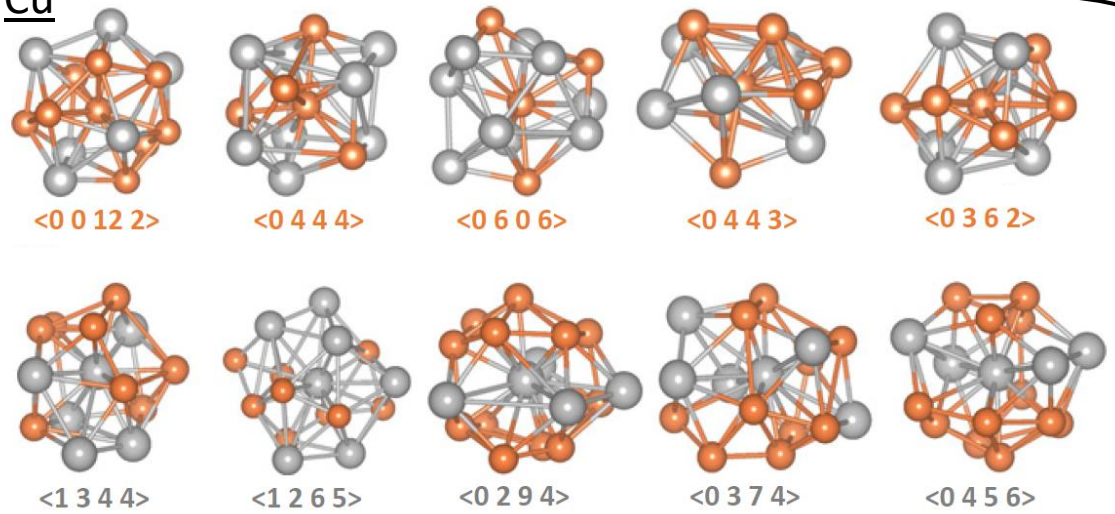
Atomic Voronoi volume of the rattling atoms vs the rest of the atoms in the system

- Distributions' areas normalize to 1
- Cu rattling atoms show an average atomic volume 1% larger than the average atomic volume of the system and a pronounced right-hand tail
- Zr rattling atoms show a 1.5% larger atomic volume over the average atomic volume of the system and the right-hand tail is even more pronounced.

High mobility and loosely packed regions

Rattling atoms, GUMs and STZs:

Cu



Zr

J. Ding, S. Patinet, M.L. Falk, Y.-Q. Cheng, E. Ma.
PNAS 111 (2014) 14052–14056.

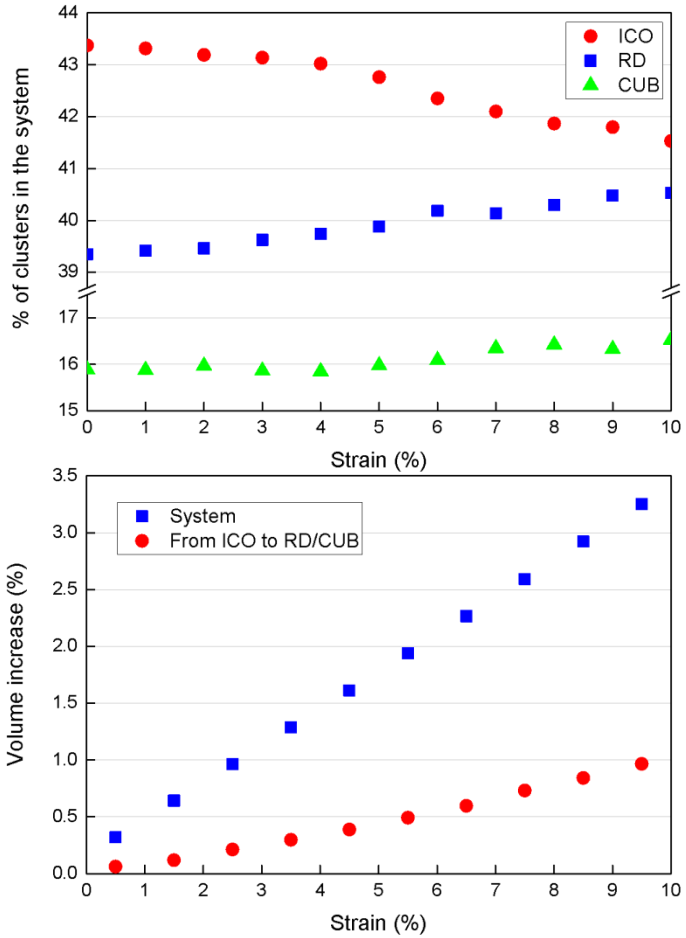
Geometrically Unfavored motifs (GUMs)

Shear Transformation Zones (STZs)

Rattling Atoms

80% of the rattling Cu atoms and 90% of the rattling Zr atoms are centers of GUMs

Tensile strain up to 10%:



Clusters evolution during tensile deformation, normalized with respect to the total number of clusters

- The number of ICO clusters decreases in 1.8% with strain, while the RD clusters increase in 1.2% and the CUB in 0.6%
- Net transformation of ICO to RD and CUB

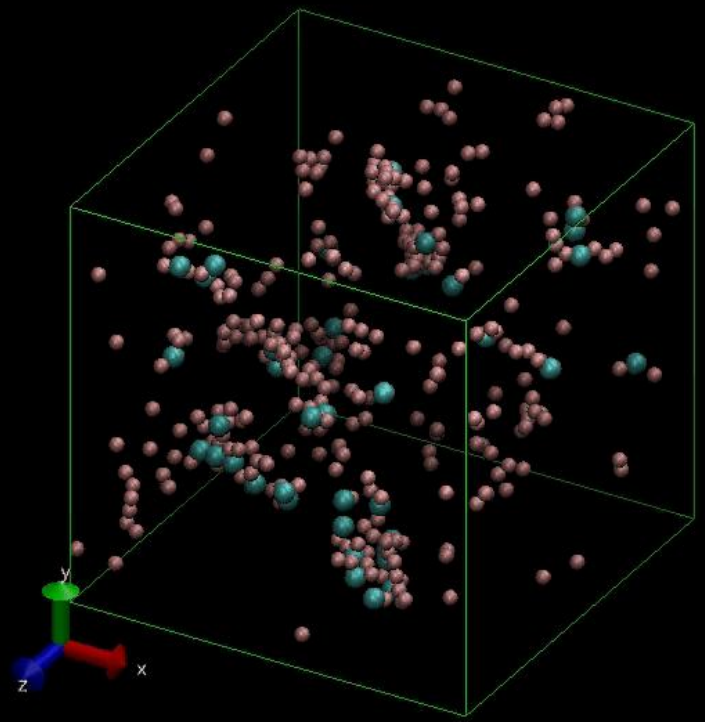
Volume evolution under deformation

- System total volume linearly increases up to 3.3%
- 30% of such volume increase is due to transformations from ICO to RD and CUB

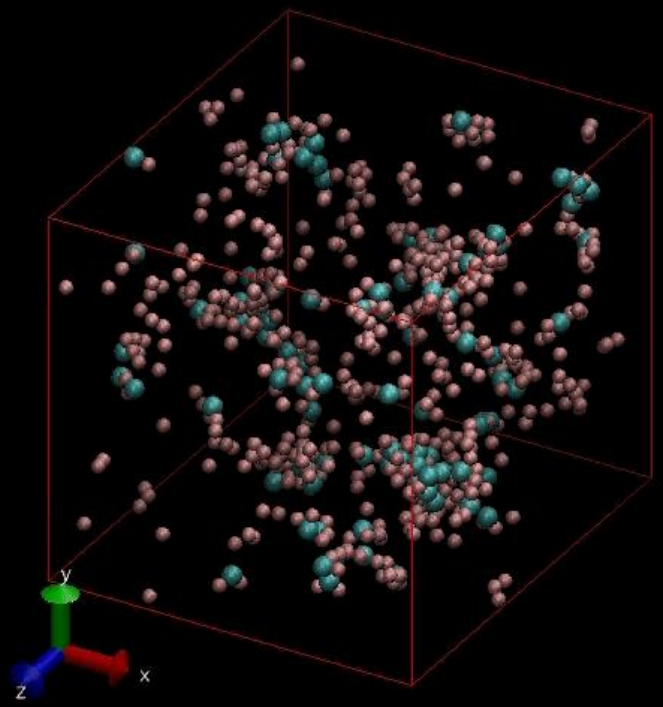
Rattling movements are natural means for the accommodation of the external mechanical solicitation, that takes place through clusters transformations of ICOs to RDs or CUBs.

Location of the rattling atoms under strain:

Rattling atoms at steady state
~1% of the system's atoms



Rattling atoms under strain
~2% of the system's atoms



Loosely packed regions grow when the system is under strain

Conclusions:

- At the steady state 1% of the system's atoms are rattling:
  - Wide distribution of distances and life-times
  - Characteristic forwards and backwards movement (i.e. No diffusion)
  - Rattling atoms are centers of GUMs.
  - Cooperative movements
  - Persistent and reversible structural changes
  - Rattling atoms are gathered together in high mobility and loosely packed regions: Origin of the STZs
- Under strain, the number of rattling atoms doubles:
  - Rattling is the natural means for the accommodation of the external mechanical solicitation, that takes place through clusters transformations of ICOs to RDs or CUBs.
  - Loosely packed regions grow and get connected

Basic atomic mechanism of the fast relaxation processes and link with the STZs as mediators of the plastic flow in MGs