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Local Atomic Structure and Elastic Properties of Amorphous Steels

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Metallic glasses

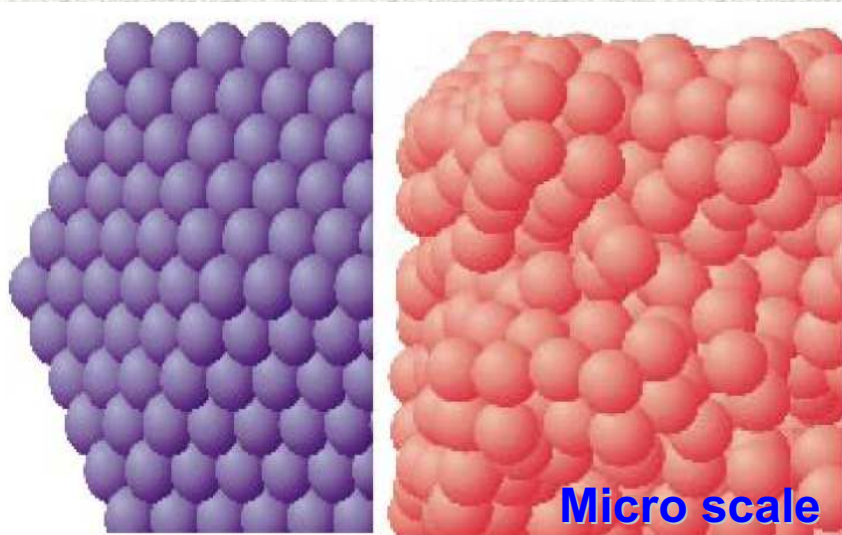
An amorphous metal is a metallic material (usually an alloy rather than a pure metal) with a disordered atomic structure. In contrast to most metals, which are crystalline and therefore have a highly ordered arrangement of atoms, amorphous alloys are non-crystalline. Materials in which such a disordered structure is produced directly from the liquid state during cooling are called "glasses", and so amorphous metals are commonly referred to as "metallic glasses" or "glassy metals".

(Wikipedia)



For the first time metallic glasses were prepared in 50th - 60th of the last century. However, all of them were based on noble metals and, correspondingly, they were very expensive.

Crystals vs. Glasses



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Liquids, upon cooling, tend to crystallize. This means that atoms weakly bound in the liquid in a random-like manner and arrange themselves into well defined, periodic positions.

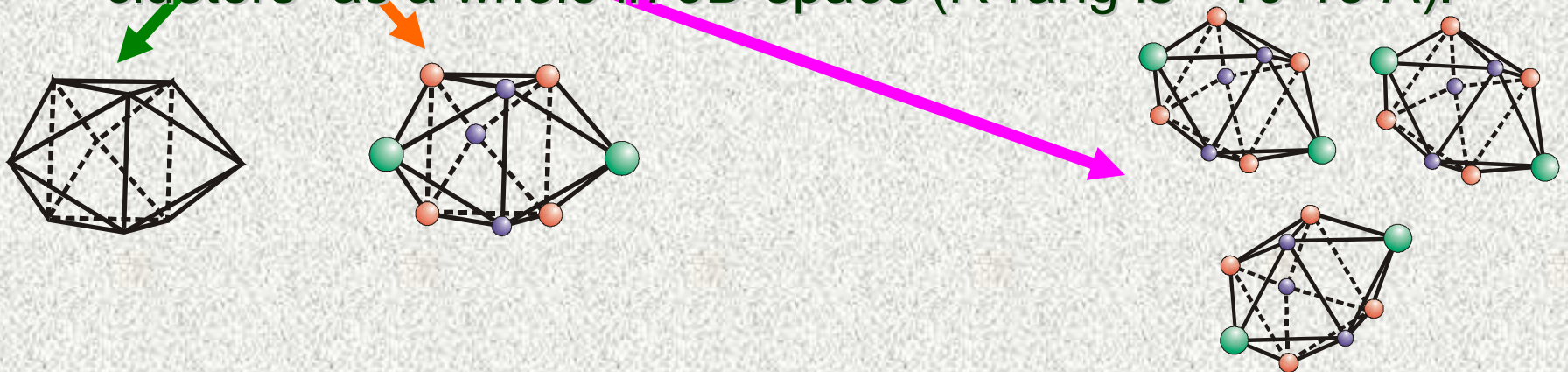
In order crystallization process was effective:

1. The liquid needs to be **sufficiently fluid (low viscosity)** to allow the atoms to rearrange themselves effectively during cooling through the melting point.
2. **The cooling rate needs to be sufficiently slow** that the basic atomic units or molecules have enough time to re-arrange themselves.

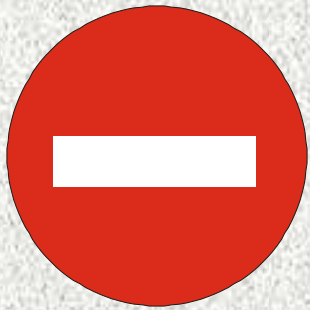
But! If due to some reasons both liquid viscosity and cooling rate are high enough, instead of crystal a glassy state may form after quenching.

Local & Medium range ordering

- There are two types of ordering in glasses:
 1. **Local** and 2. **Medium**.
- **Local order** means atomic ordering in the R-range of first coordination spheres (less than ~ 5 Å). Local ordering includes **topological** ordering (geometry of “clusters”) and **chemical** ordering (order in arrangement of chemically different atoms).
- **Medium range ordering** means mutual arrangement of “clusters” as a whole in 3D-space (R-rang is $\sim 10-15$ Å).



Bad and good pretenders to form a glassy state



- Solids **with simple structures** and non-directional bonds, e.g. metals, have very low viscosity fluids above the melting point and **easily crystallize upon cooling.**

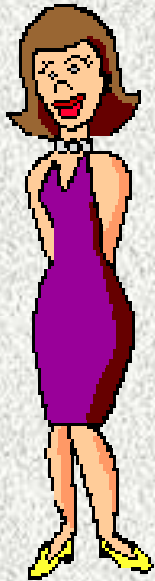


- Solids **with complex structures** and strong, highly directional (covalent) bonds, e.g. silicates, polymers, have high viscosity fluids and **tend to form amorphous or glassy solids.**



Glass forming ability: how to improve?

There are some empirical rules
which could help to enhance GFA (A. Inoue & Co):



- **Three or more different chemical components in final compound** – *as much as possible different types of chemical bonds=increased relaxation time.*
- **Big difference in atomic radii between different elements** – *suppressed diffusion.*
- **High negative enthalpy of mixing** – *atoms should want to “live” together.*

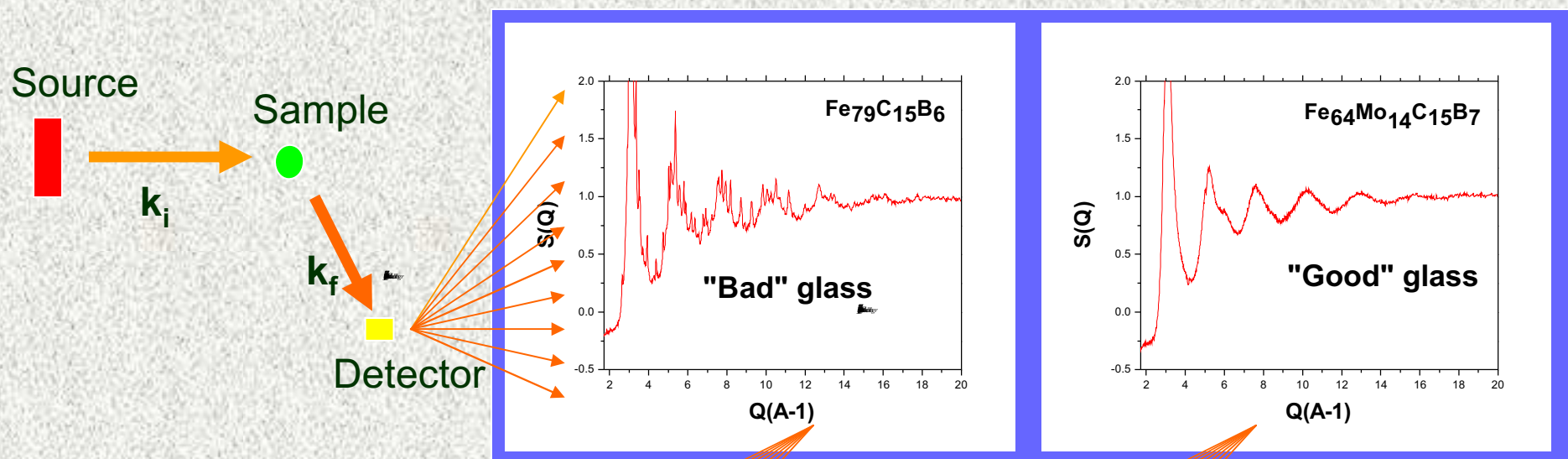
If it is so complex, why do we study metallic glasses?

Because physical properties of MG due to spatial homogeneity of atomic structure and absence of typical crystal-like defects (dislocations, grain boundaries etc.) are unique:

- high electrical conductivity (but lower in 3-5 times in comparison with crystalline alloys);
- high strength (usually in 3-10 times higher than the best steels) with sometimes high ductility;
- high corrosion resistance;
- sometimes MG is a good catalyst (I don't know why);
- soft ferromagnetism;

Methods-Experimental

Neutron/X-ray diffraction via Pair Distribution function (PDF) analysis: PDF gives a distribution of interatomic distances in a sample under study.



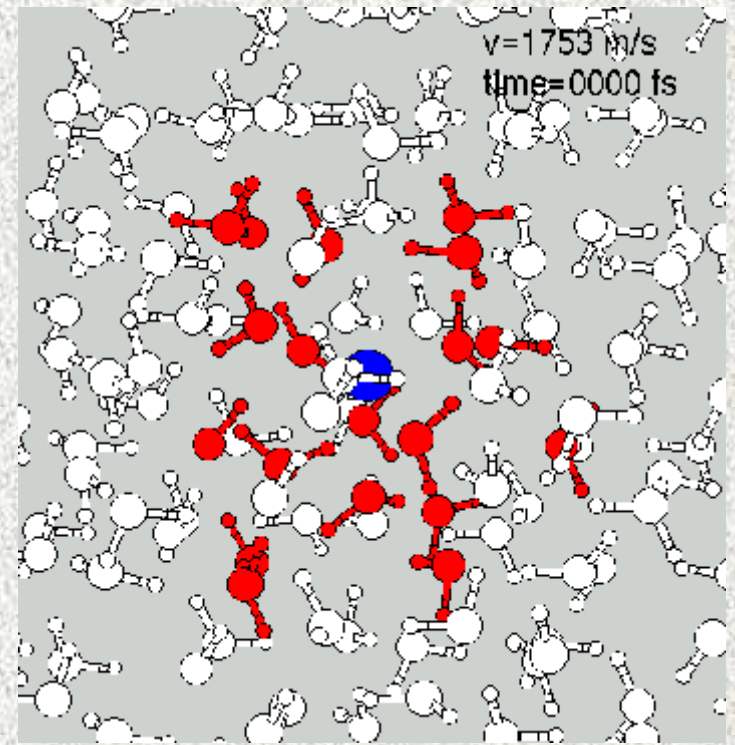
PDF analysis = Fourier analysis of the total scattering (Bragg scattering + diffuse scattering):

$$\rho_{Exp}(r) = \frac{2}{4\pi^2 r} \int_0^{\infty} Q[S^{FZ}(Q) - 1] \sin(Qr) dQ - \rho_0$$

NPDF (LANSCE) and SEPD (ANL) were used for neutron diffraction experiments

Methods-Theoretical

Molecular Dynamics (MD)
is a kind of microscope which allows
one to track evolution of a system in time
at different environment (temperature,
pressure etc.) by solving classical
(Newtonian) equations of motion.



(C) B. J. Alder,
T. E. Wainwright.
J. Chem. Phys. **31 (2):**
459 (1959).

Initial Settings: $\{\vec{x}_i, \vec{v}_i\}$

$$E^k = \frac{3}{2}kT = \sum_{i=1}^N \frac{m_i v_i^2}{2}$$

Atomic Forces

$$\vec{F}_i = -\frac{\partial U}{\partial \vec{r}_i}, \quad U = \sum_{i \neq j} U_{ij}$$

Equations of Motion

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{F}_i \quad \text{or} \quad \left\{ \frac{d\vec{v}_i}{dt} = \frac{\vec{F}_i}{m_i} \text{ and } \frac{d\vec{r}_i}{dt} = \vec{v}_i \right\}$$

New set of $\{\vec{x}_i, \vec{v}_i\}$

New Cycle

What can we do by using these techniques?



Joe Poon



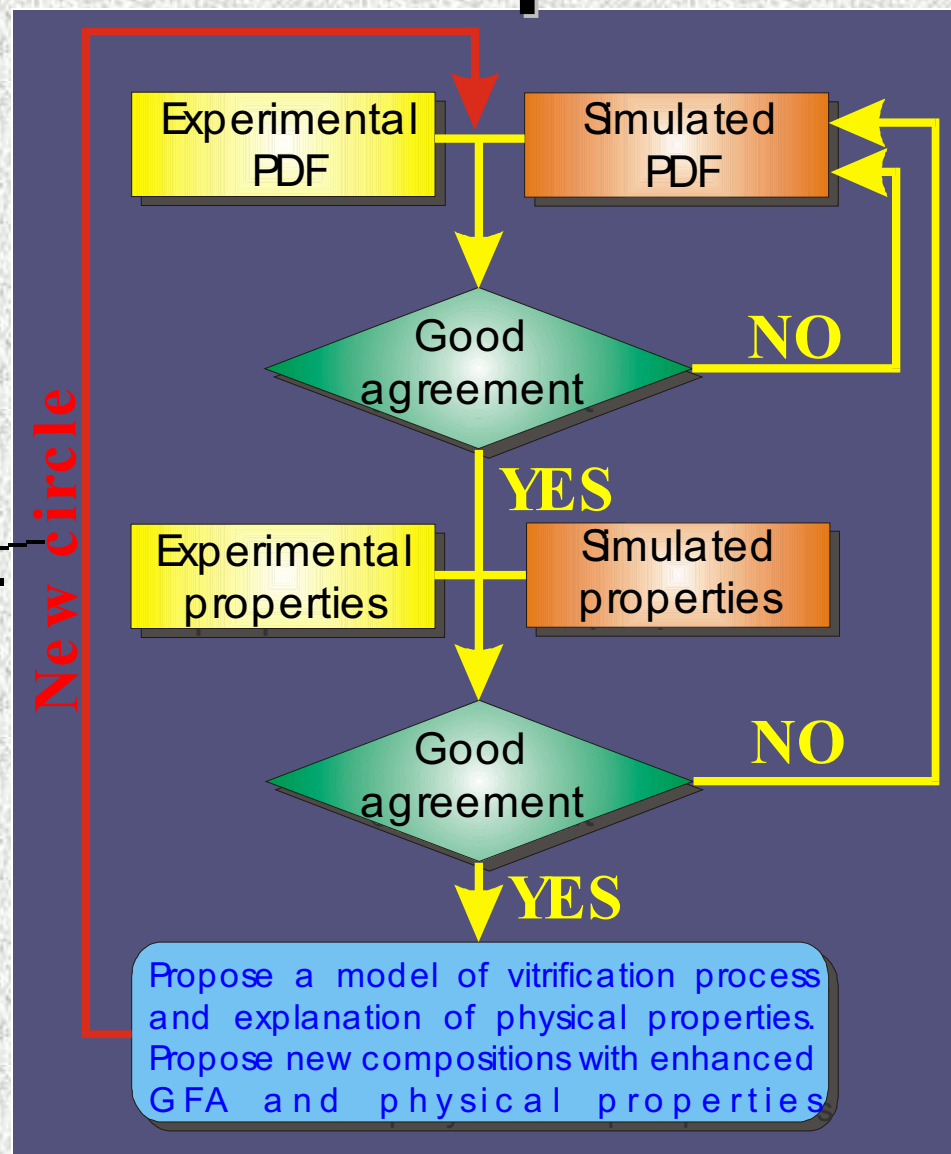
Mike Widom



Despina Louca



Slava Kazimirov



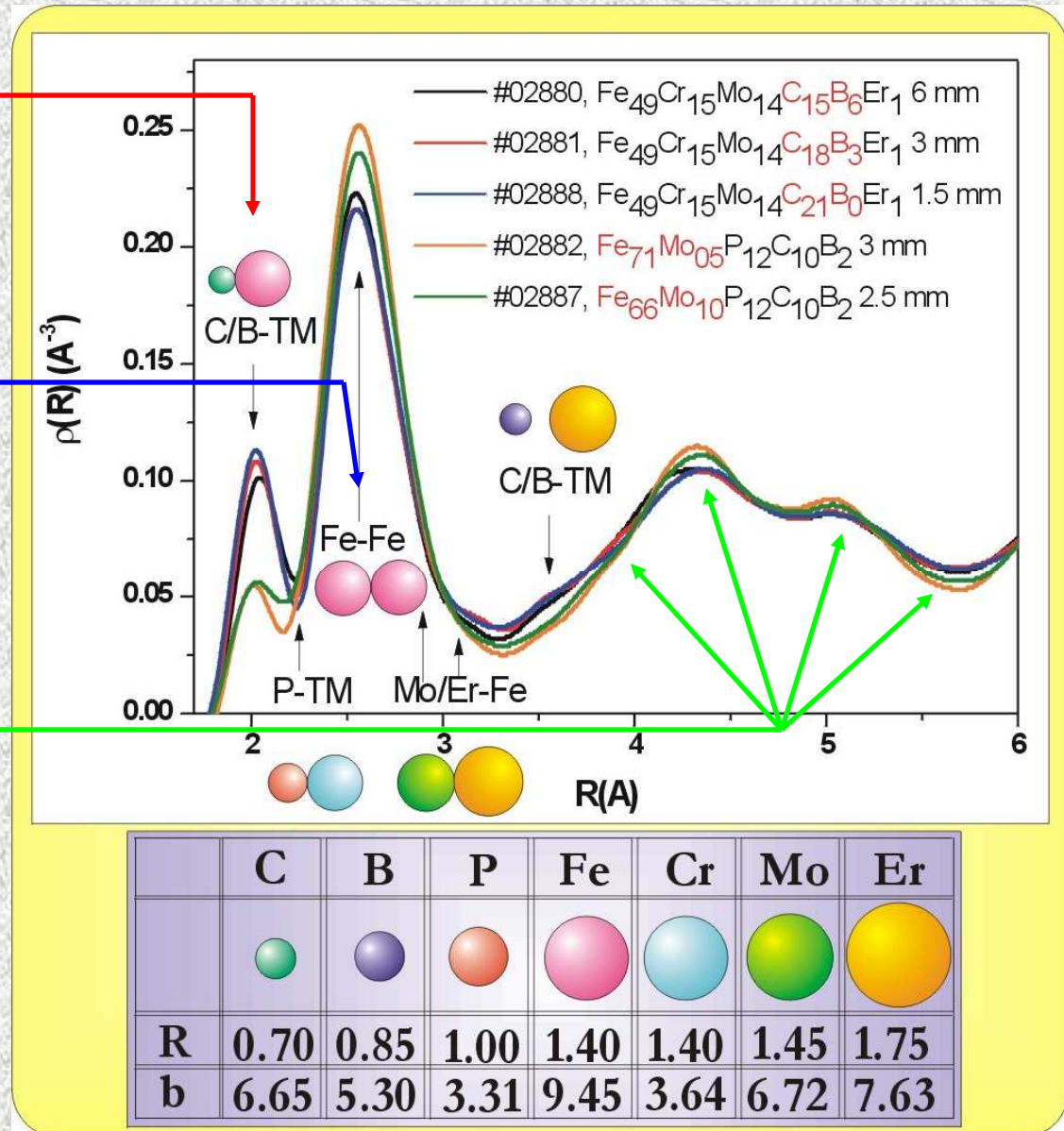
Typical experimental PDFs

Low R peak corresponds to correlations with the lowest interatomic distances: C/B-TM:

$$\rho_{Model}(r) = \frac{1}{4\pi N r^2} \sum_i \sum_j \frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij})$$

The highest peak mostly corresponds to Fe-Fe correlations due to high Fe content and the highest coherent length of Fe.

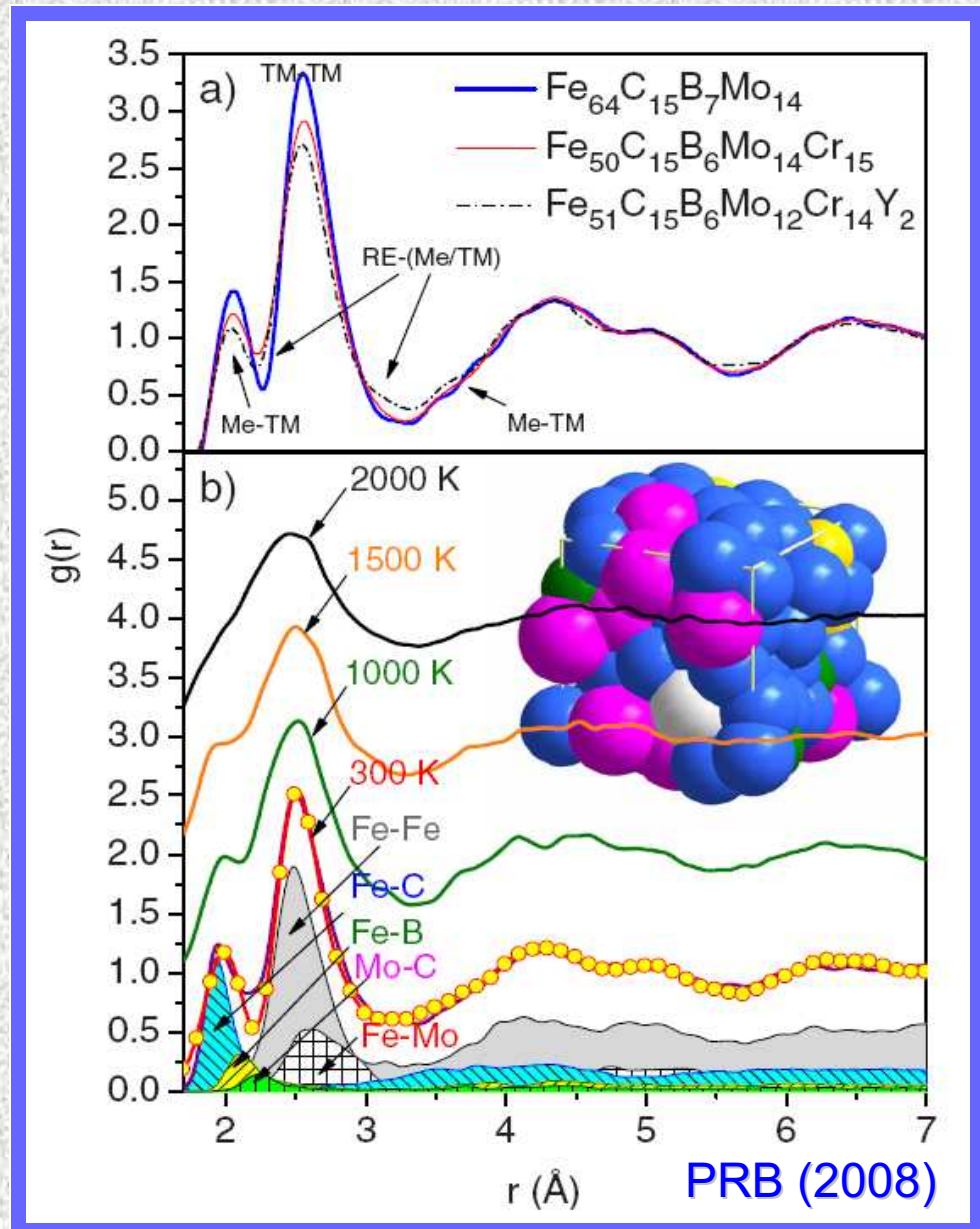
The next coordination sphere accumulate a number of different contributions due to what peaks become less resolved.



Ab initio models of the glasses

The experimental and the simulated PDFs are in a good agreement. Thus, the structural model describe real structure correctly. This means, that chosen theoretical approaches are applicable with respect to this class of materials.

By using obtained structural models we can extract information about local atomic structure and simulate some physical properties for the concrete chemical composition.



Local order via Voronoi analysis-I

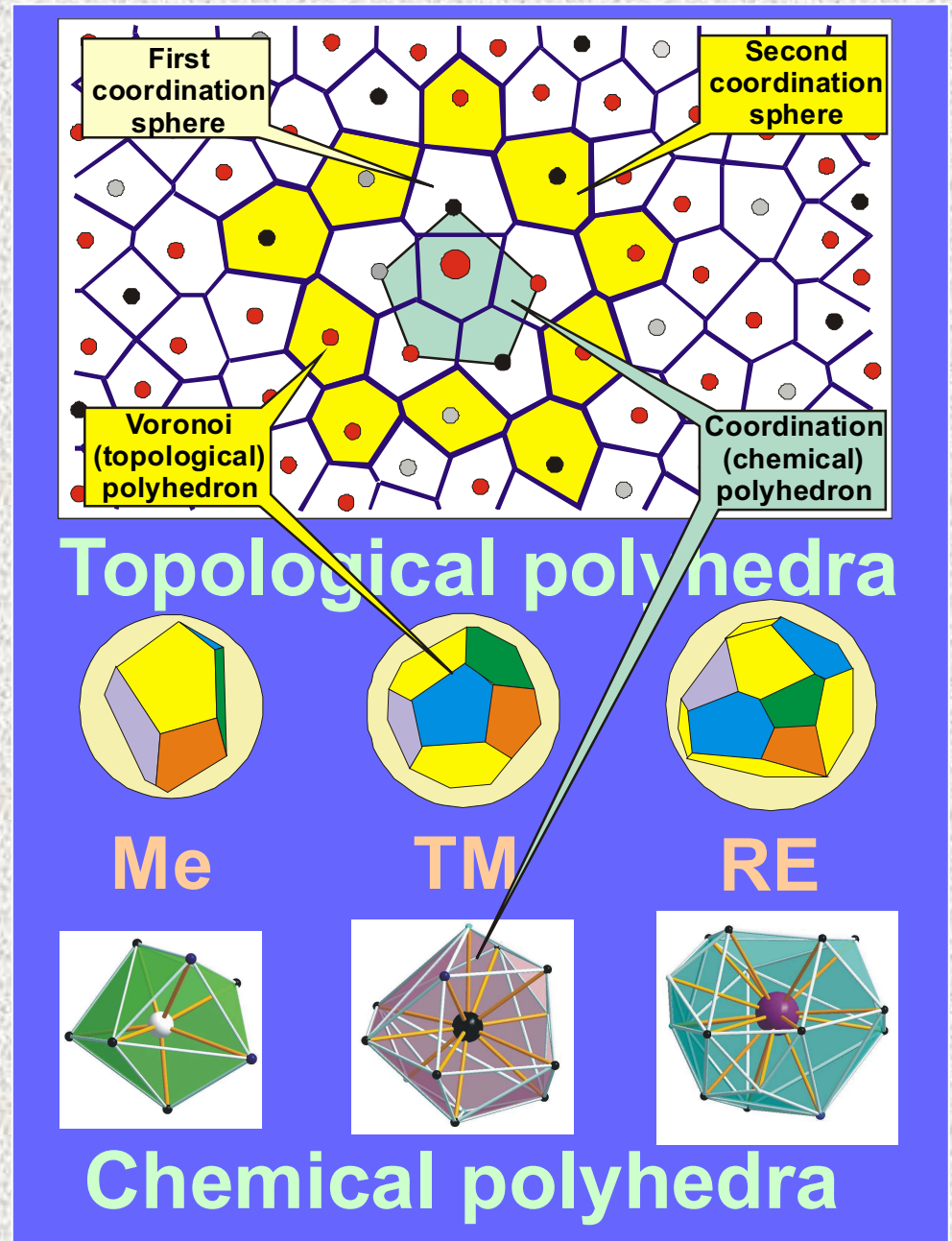
This method allows one to fill space by so-called Voronoi polyhedra.

Characteristic polyhedra around each atom in the structure can be extracted. These polyhedra are similar for chemically different compositions.

They can serve as main building blocks of metallic glasses.

Further analysis allows us to extract information about coordination numbers...

... and local chemical order in a system under study...

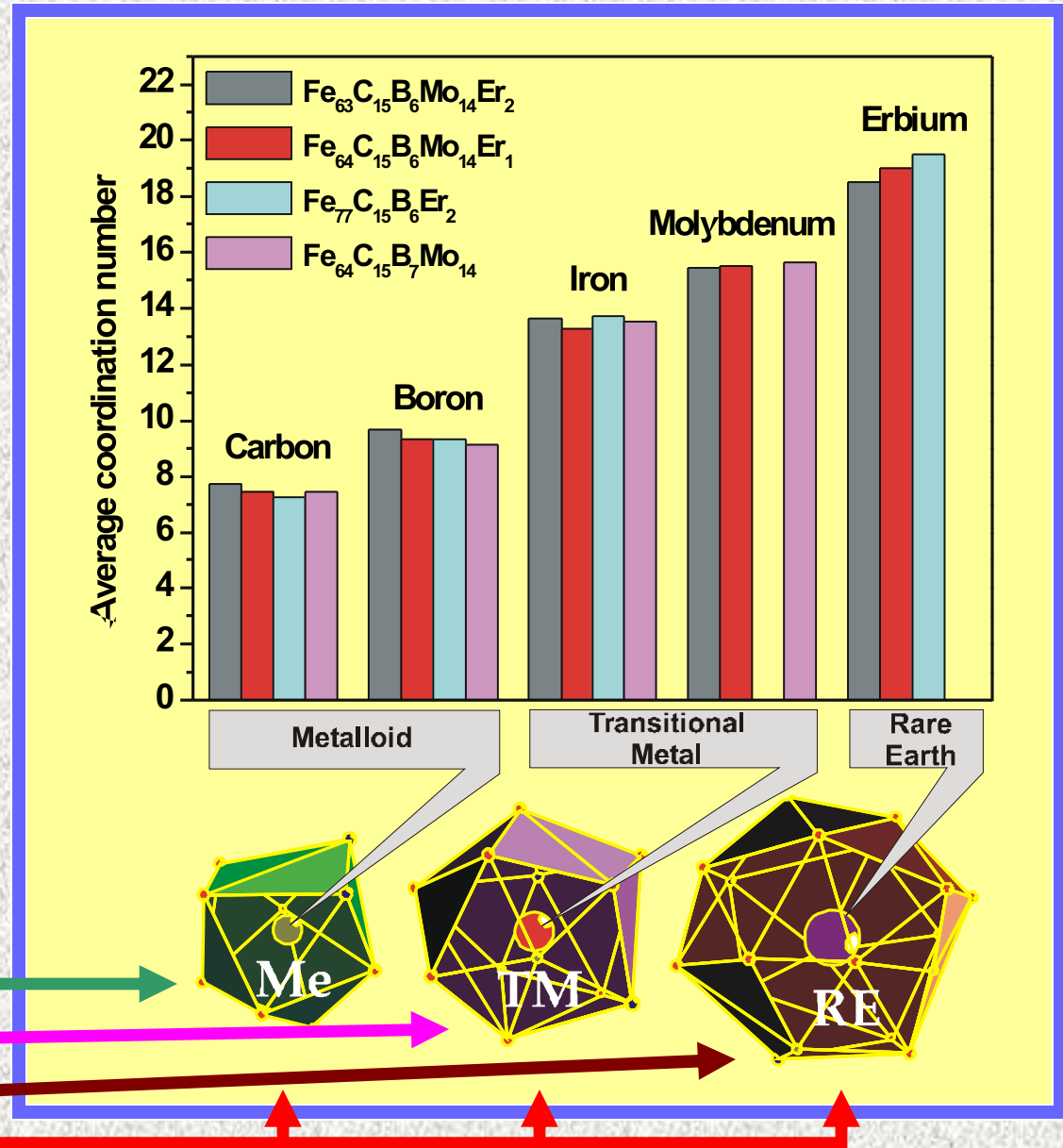


Local order via Voronoi analysis-II

In spite of the difference in chemical compositions, local order is very similar for different glasses.

Local order can be considered in terms of **coordination polyhedra**. Coordination polyhedra can be considered as a main structural units of metallic glasses unlike elementary unit cells is crystals.

Coordination numbers (CN) of different chemical species depend mostly on atomic radii:
 CN(Me)~7-9
 CN(TM)~12-15
 CN(RE)~18-19



Local chemical order

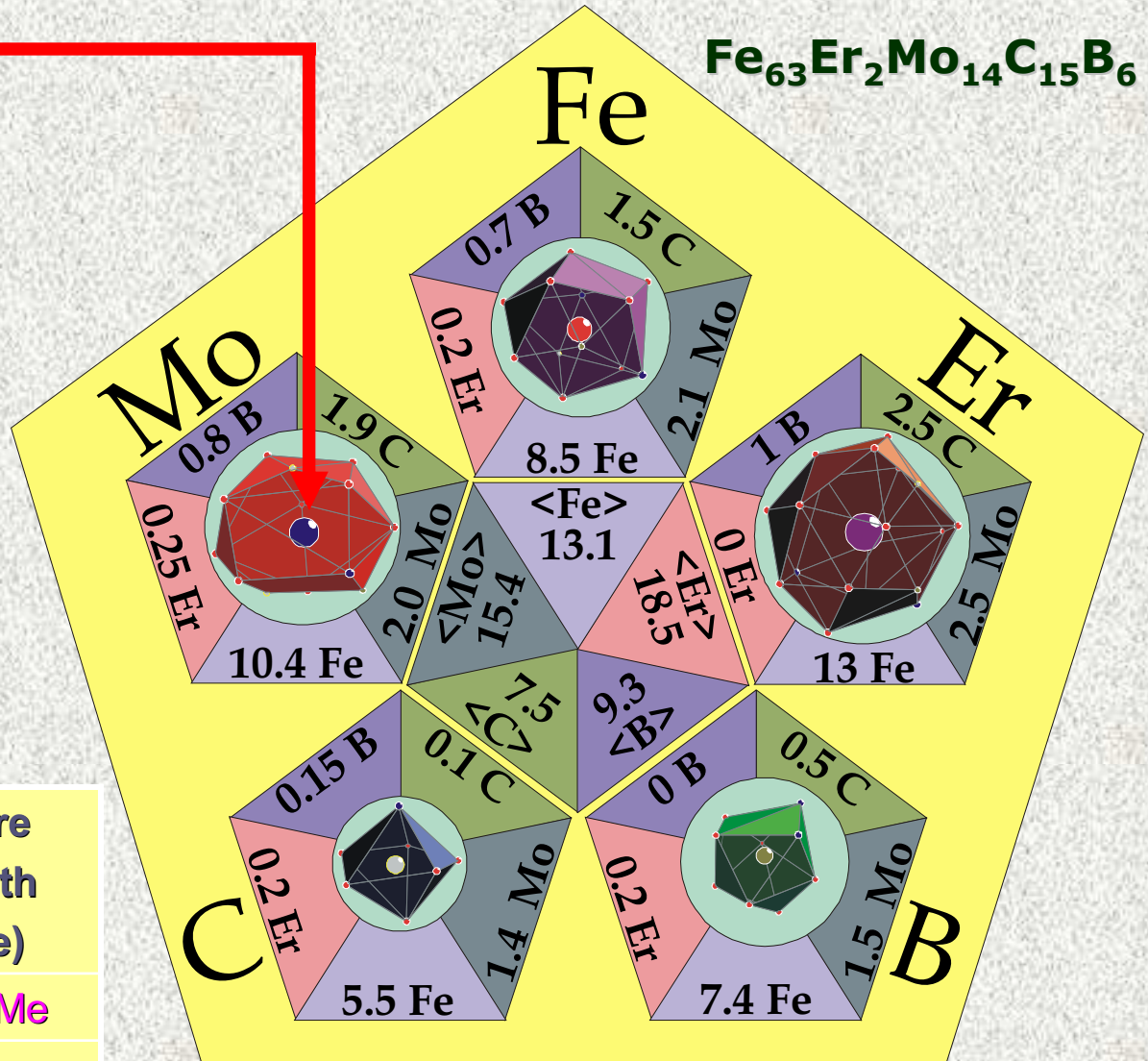
For example,
around **Molybdenum** we can find **ON AVERAGE**

0.8 B
+1.9 C
+10.4 Fe
+2.0 Mo
+0.25 Er

$\langle \text{CN}(\text{Mo}) \rangle \sim 15.4$

Amount of different
atomic species around

Metalloid (Me)	Transition metal (TM)	Rare Earth (Re)
~0 Me	2-3 Me	3-4 Me
7-9 TM	11-13 TM	13-15 TM
0.2 RE	0.2 RE	0 RE



Diffusion

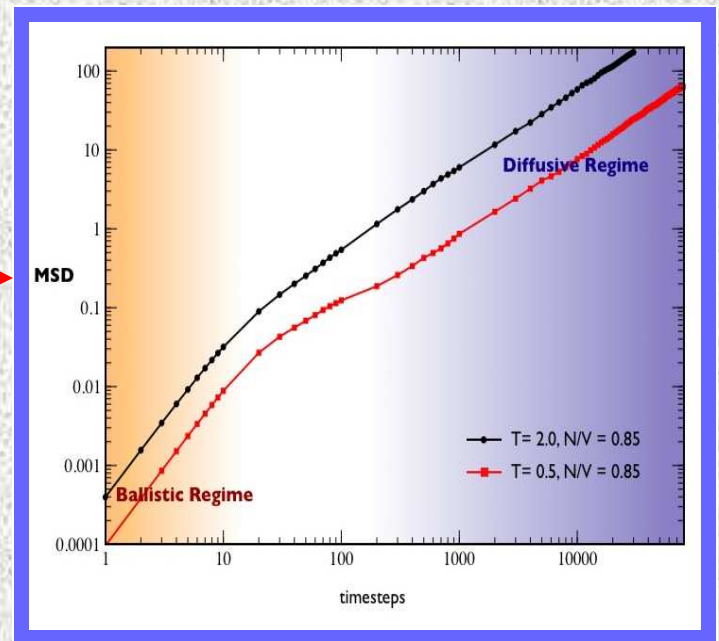
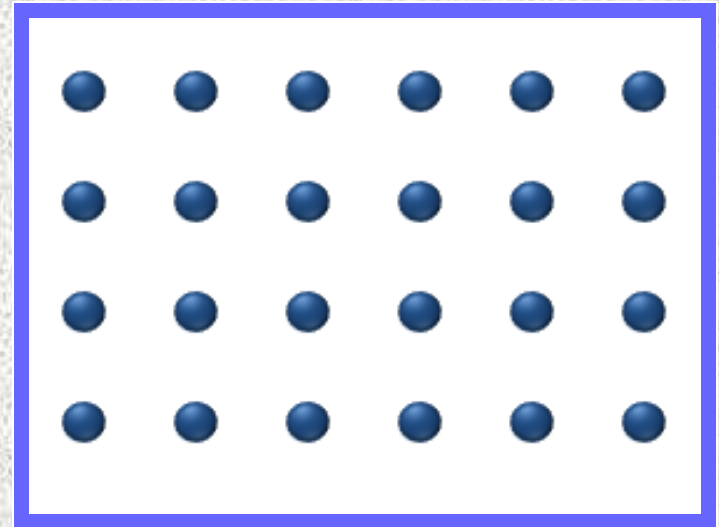
Diffusion is the movement of particles of a substance from an area of high concentration to an area of low concentration, resulting in the equal distribution of the substance (Wikipedia).

In order to estimate diffusion of different atomic species we should track positions of different atoms in time. I.e. we should know **mean square displacements** of atoms as a function of time:

$$\overline{r^2(t,T)} = \frac{1}{N} \sum_{i=1}^N \left(r_i(0,T) - r_i(t,T) \right)^2$$

In this case **diffusion coefficients** of different atomic species can be estimated by the Einstein formula:

$$D = \overline{r^2} / 6t$$

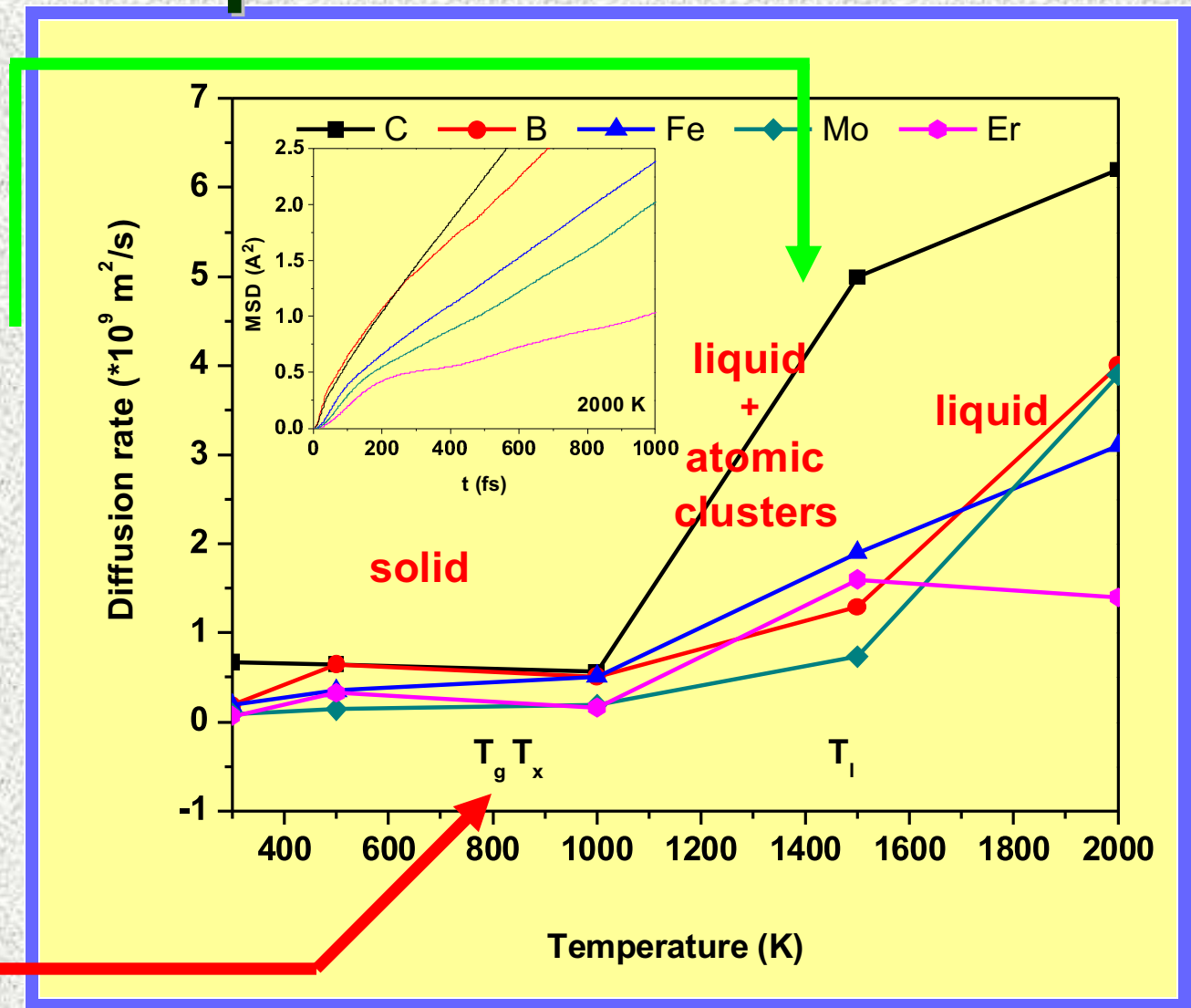


Diffusion of different atomic species

Qualitatively, the small atoms diffuse quickly and large atoms slowly.

At liquidus temperature diffusion rate slows down due to formation of atomic clusters.

Lower glass transition temperature diffusion rate is close to 0 because atoms become frozen and can't move to new position anymore: structure formation is complete.



Elastic properties-I

It is known that usually metallic glasses demonstrate a bad ductility. However, some additions could improve ductility of metallic glasses. For example, substitution of C/B by P improve ductility of Fe-TM-(RE)-Me glasses.

We have studied elastic properties of these glasses by simulation of bulk and shear moduli:

$$K = V \left(\frac{d^2 E}{dV^2} \right)_{V_0}$$

$$G = C_{44} = \left(\frac{1}{3} V_0 \right) \left(\frac{d^2 E}{d\varepsilon^2} \right)_{V_0}$$

The results of the simulations are shown in the Table

Compound	$K^{\text{exp}}/K^{\text{th}}$, GPa	$G^{\text{exp}}/\langle G^{\text{th}} \rangle (G_{\text{ab}}, G_{\text{ac}}, G_{\text{bc}})$, GPa
$\text{Fe}_{71}\text{Mo}_5\text{P}_{12}\text{C}_{10}\text{B}_2$?????/ 190	$62.0 \pm 0.7 / \langle 59.2 \rangle (65.3, 50.4, 62.1)$
$\text{Fe}_{66}\text{Mo}_{10}\text{P}_{12}\text{C}_{10}\text{B}_2$	$176 \pm 4 / 187$	$66.1 \pm 0.7 / \langle 65.0 \rangle (62.4, 62.8, 69.9)$
$\text{Fe}_{49}\text{B}_0\text{C}_{21}\text{Mo}_{14}\text{Er}_1\text{Cr}_{15}$?????/213	???????/⟨57.4⟩(68.0, 62.2, 42.1)
$\text{Fe}_{49}\text{B}_3\text{C}_{18}\text{Mo}_{14}\text{Er}_1\text{Cr}_{15}$	$200 \pm 4 / 203$	$80.2 \pm 0.7 / \langle 70.2 \rangle (69.8, 82.4, 58.5)$
$\text{Fe}_{49}\text{B}_6\text{C}_{15}\text{Mo}_{14}\text{Er}_1\text{Cr}_{15}$	$200 \pm 4 / 208$	$81.9 \pm 0.7 / \langle 71.3 \rangle (54.6, 70.0, 88.8)$

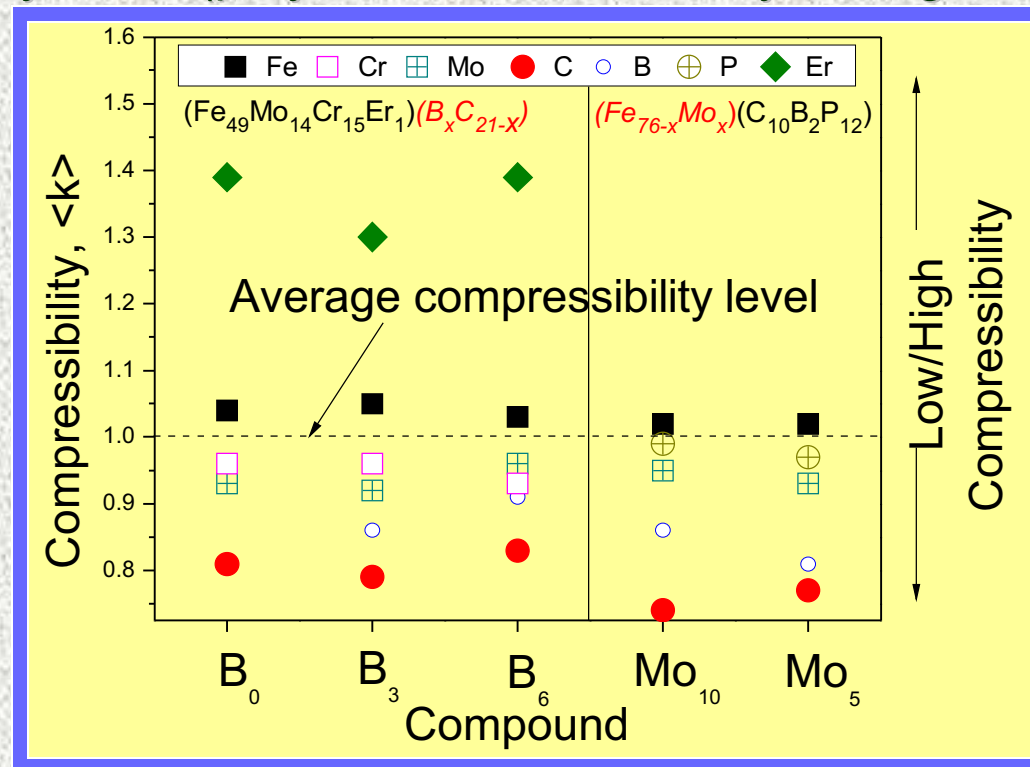
Exp. values of K and G are taken from X.J.Gu et al (2007, 2008)

Elastic properties-II

Let's introduce relative compressibility of polyhedron as

$$k_i = \frac{V_{cell}}{V_i} \frac{dV_i}{dV_{cell}}$$

In homogeneous medium $k=1$. For inhomogeneous medium $k>1$ for “soft” polyhedra (polyhedra with relatively soft bonds) and $k<1$ for “strong” polyhedra (polyhedra with relatively strong bonds).



Conclusion

- Multi-component iron based amorphous alloys with general formula of $TM_xMe_yRE_z$ ($x+y+z=100$ atomic %) were investigated by the neutron diffraction technique and *ab initio* molecular dynamics. Structural models obtained as a result of MD simulation are in a good agreement with experimental data. By using the Voronoi tessellation technique local atomic structure was described in terms of coordination polyhedrons. In spite of differences in chemical compositions of different glasses, some characteristic coordination polyhedrons were constructed. Such polyhedrons should be considered as the main structural units of glasses and are similar for different compositions.
- Simulation of atomic diffusion at different temperatures allowed us to estimate diffusion rates of different atomic elements. It was shown that diffusion rate of different atomic species depended primarily on atomic size. This simulation also allowed us to track the basic stages of the liquid-glass transition and clarify the role of rare earth elements in enhancement of glass forming ability. We believe that this role consists in destabilization of formation of competing crystalline phases (predominantly carbides and borides of transitional metals) and corresponding phase separation.
- Simulation of elastic moduli as a function of chemical composition revealed a close proximity with experimental data and thus confirmed applicability of the obtained structural models and allowed us to make some conclusions about origin of enhanced ductility in some particular alloys.