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Structural, elastic, vibrational and electronic properties of amorphous Al_2O_3 from *ab initio* calculations

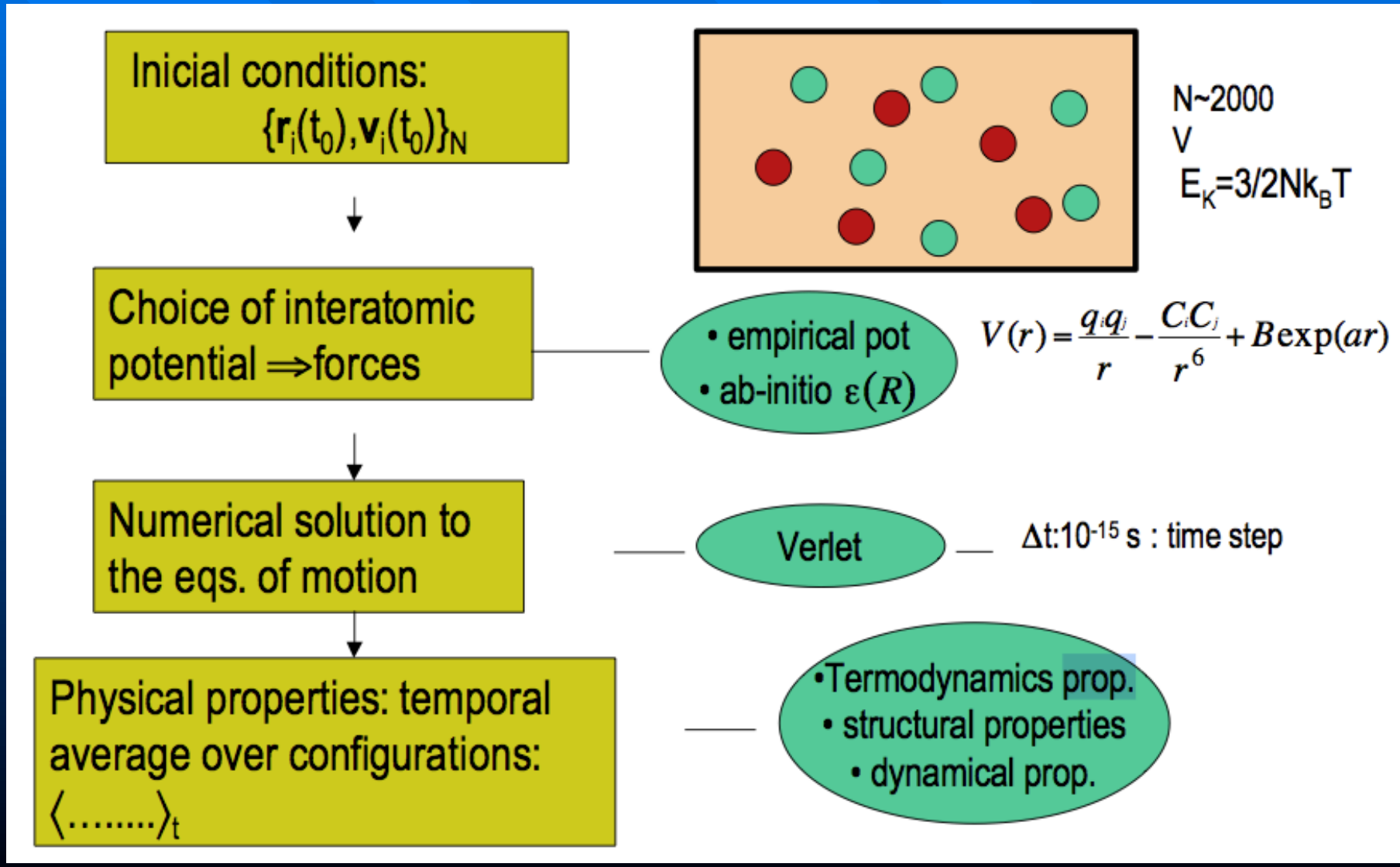
Gonzalo Gutiérrez and Sergio Davis

Department of Physics, Faculty of Sciences

Universidad de Chile, Chile.

www.gnm.cl

Molecular Dynamics simulations



Basic diagnostics

- Pair distribution function
- Angular distribution
- Coordination numbers

- Vibrational density of states *D(w)*

$$Z_{\alpha(\beta)}(t) = \left\langle \sum_{i=1}^{N} m_{i\alpha} \vec{v}_{i\alpha}(0) \cdot \vec{v}_{i\alpha}(t) \right\rangle$$

VACF

$$\mathcal{D}_{\alpha(\beta)}(\omega) = \frac{1}{\sqrt{2\pi}} \int \frac{Z_{\alpha(\beta)}(t)}{Z_{\alpha(\beta)}(0)} \exp(-i\omega t)\, dt$$

- Direct visualization

Al_2O_3

Ceramic material with several technological applications

due to high melting point (2327 K),
extreme hardness (Moh 9) y
low electrical conductivity

Structural phase transitions

liquid → γ → δ, θ→ α-alumina

amorphous (a.o) → γ → θ→ α-alumina

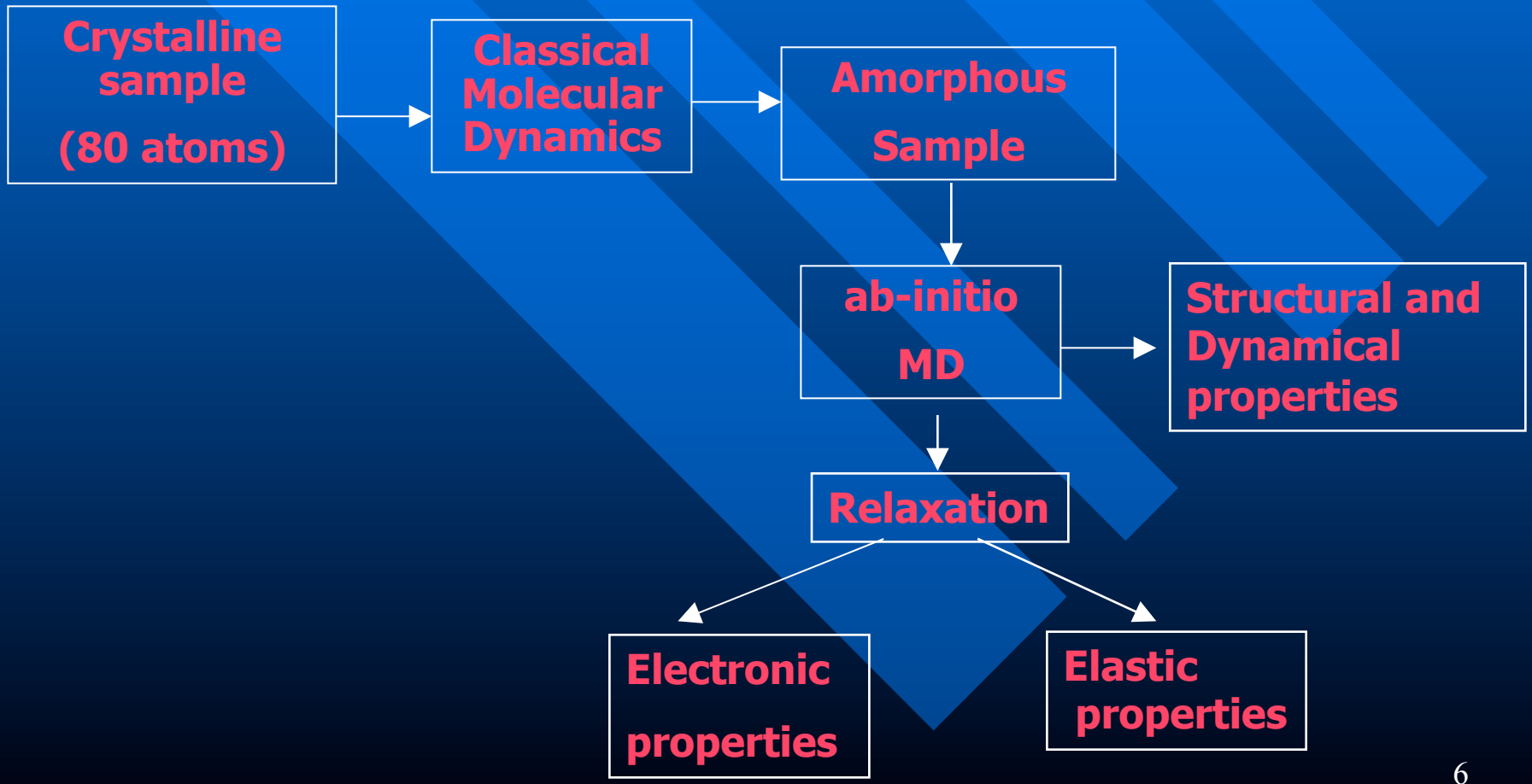
Amorphous Al_2O_3

- Al_2O_3-SiO_2 glass is one of the the most important systems in ceramics science
- Many technological applications: catalisis, dielectric, optical devices, microlectronics and thin films devices
- It is present in the surface of aluminum in contact to air (oxidation and passivation phenomena)
- Most alumina thin films are amorphous:

  they are composed by porous amorphous alumina, but its atomic properties are not well understood so far

Procedure

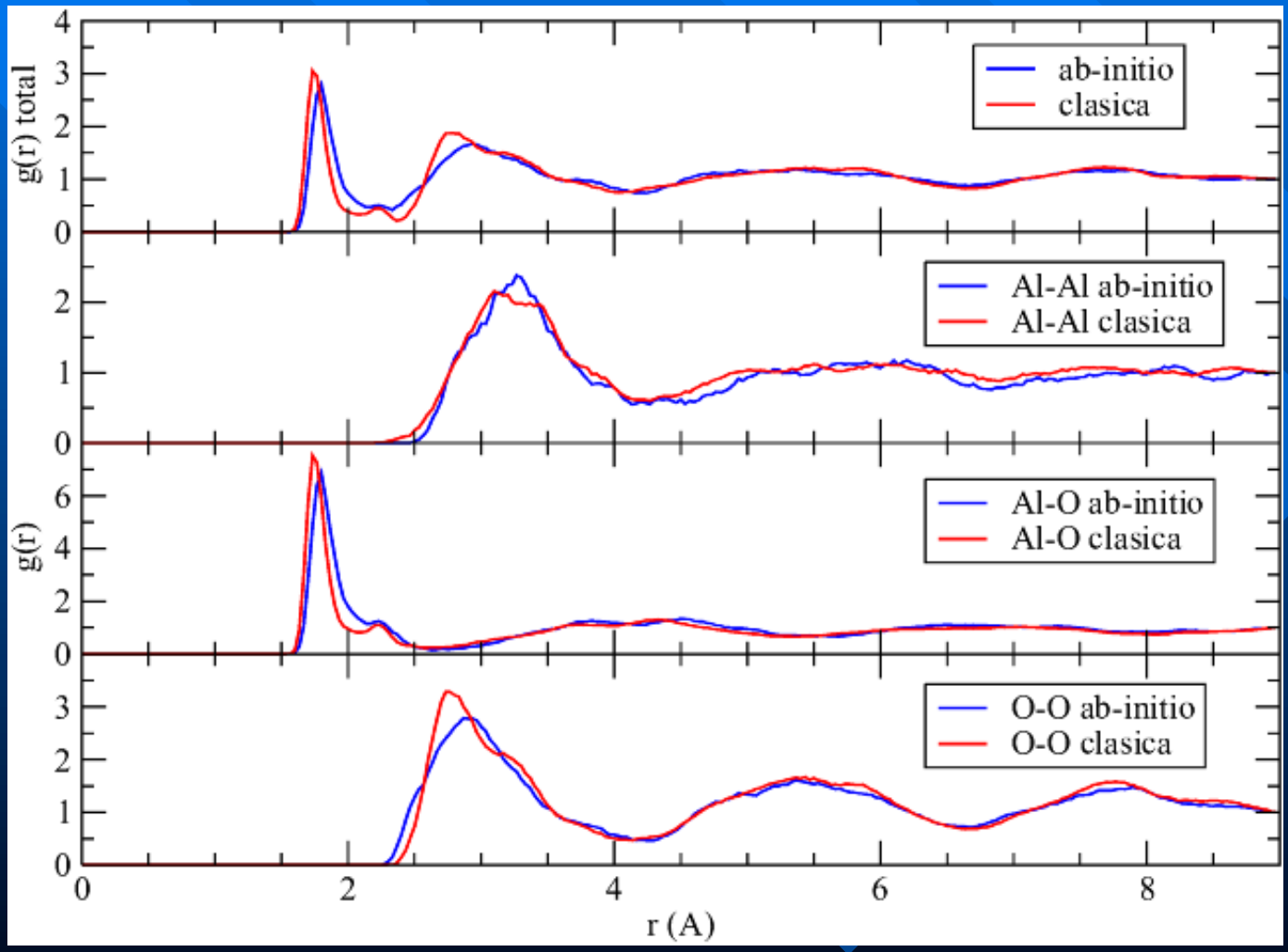
- Combined use of classical an *ab initio* Molecular Dynamics:



Computational details

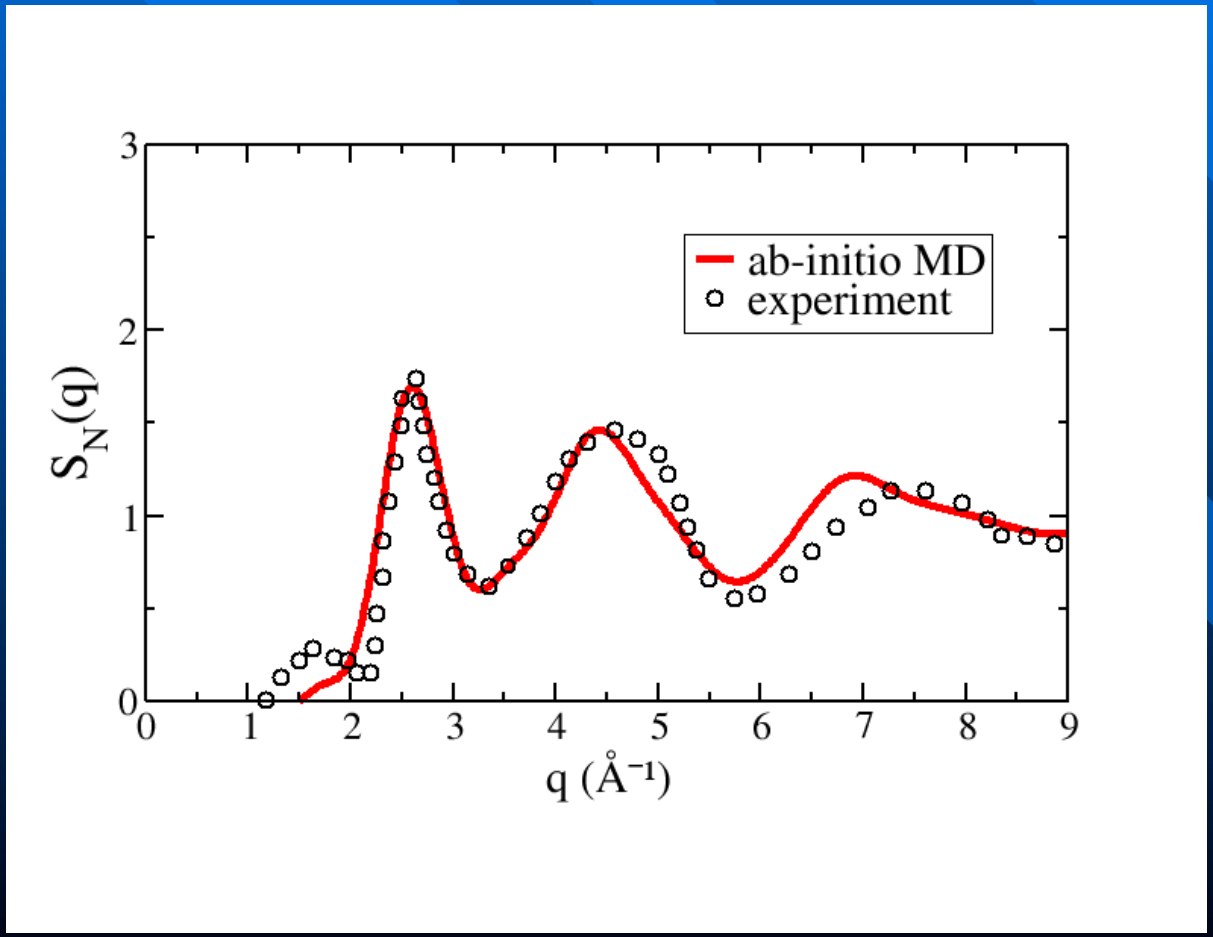
- *ab initio* MD by using VASP (Vienna Ab Initio Simulation Package)
- Density Functional Theory with LDA (local density approximation)
- Ultrasoft pseudopotentials
- Energy cutoff E_{cut} = 296,77 eV (21,81 Ry)
- Only gamma point, Γ = (0,0,0)
- Time step of 3 fs for atomic motion

Pair distribution function



Classical MD: G. G, B. Johansson, PRB 65,104202, (2002); GG et al J. Mat. Sci. 45, 5124 (2010)

Neutron static structure factor: experiments and simulation



Exp.:
P. Lamparter,
R. Kniep,

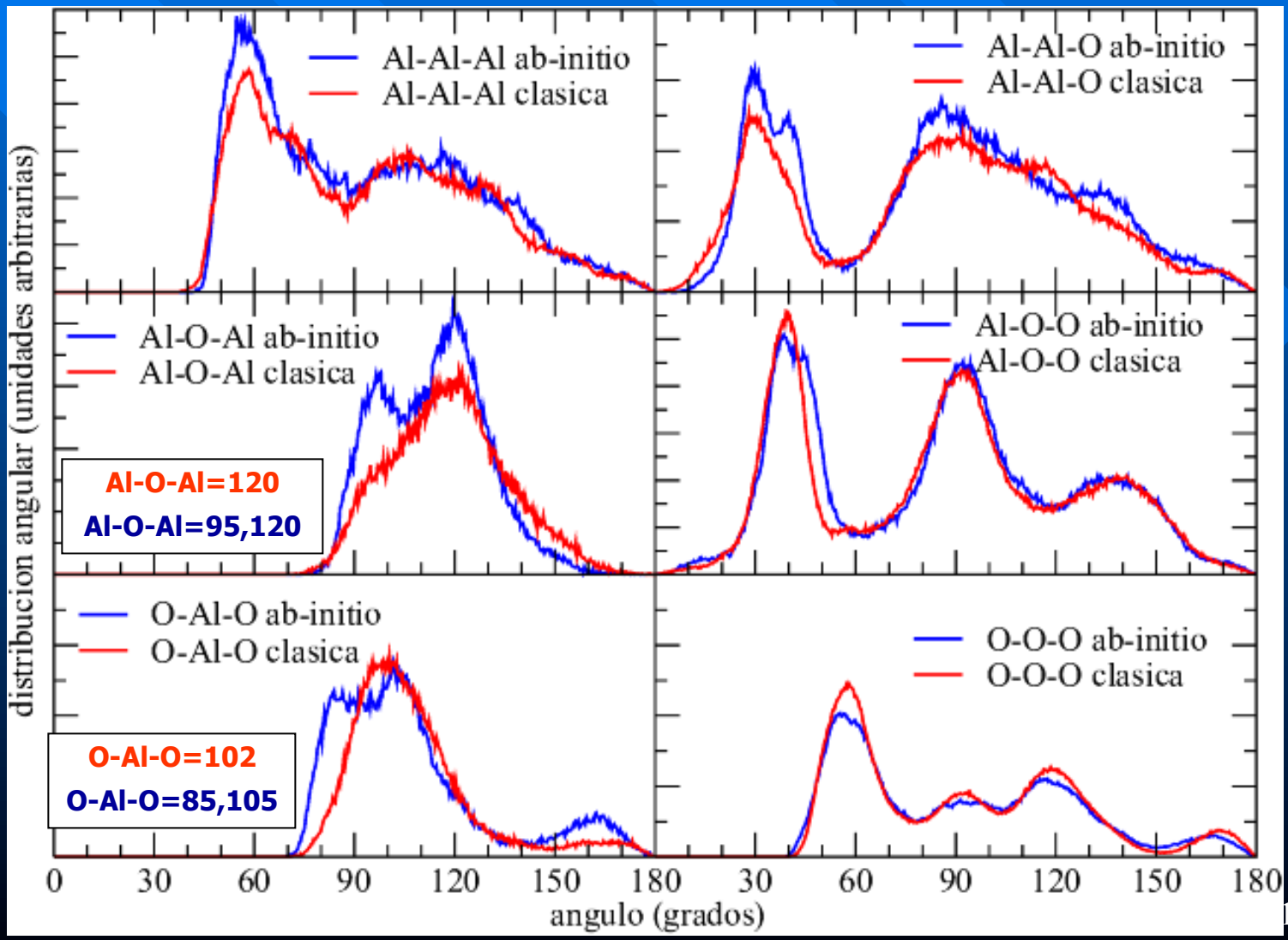
Physics B **234**, 405 (1997)

Interatomic distances and coordination numbers

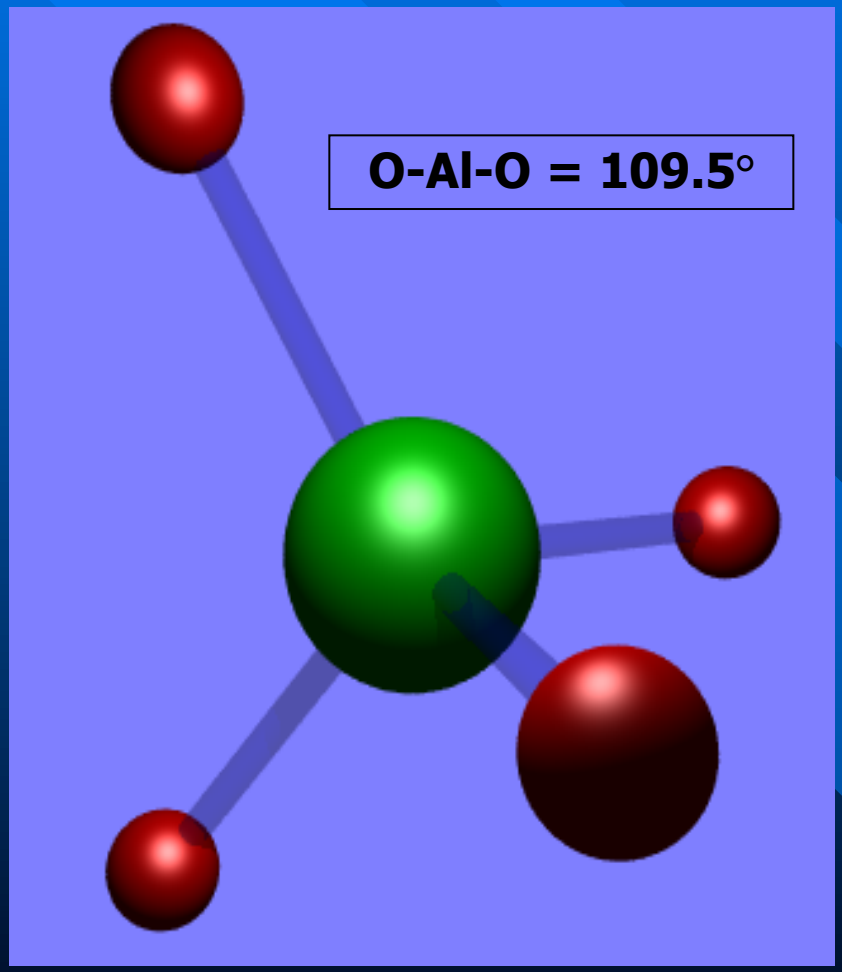
Results	R_{Al-Al} (Ă)	R_{Al-O} (Ă)	R_{O-O} (Ă)
Lamparter y Kniep	3,2 ± 0,55	1,8 ± 0,21	2,8 ± 0,58
Cassical MD	3,24	1,74	2,77
ab initio MD	3,27	1,80	2,91

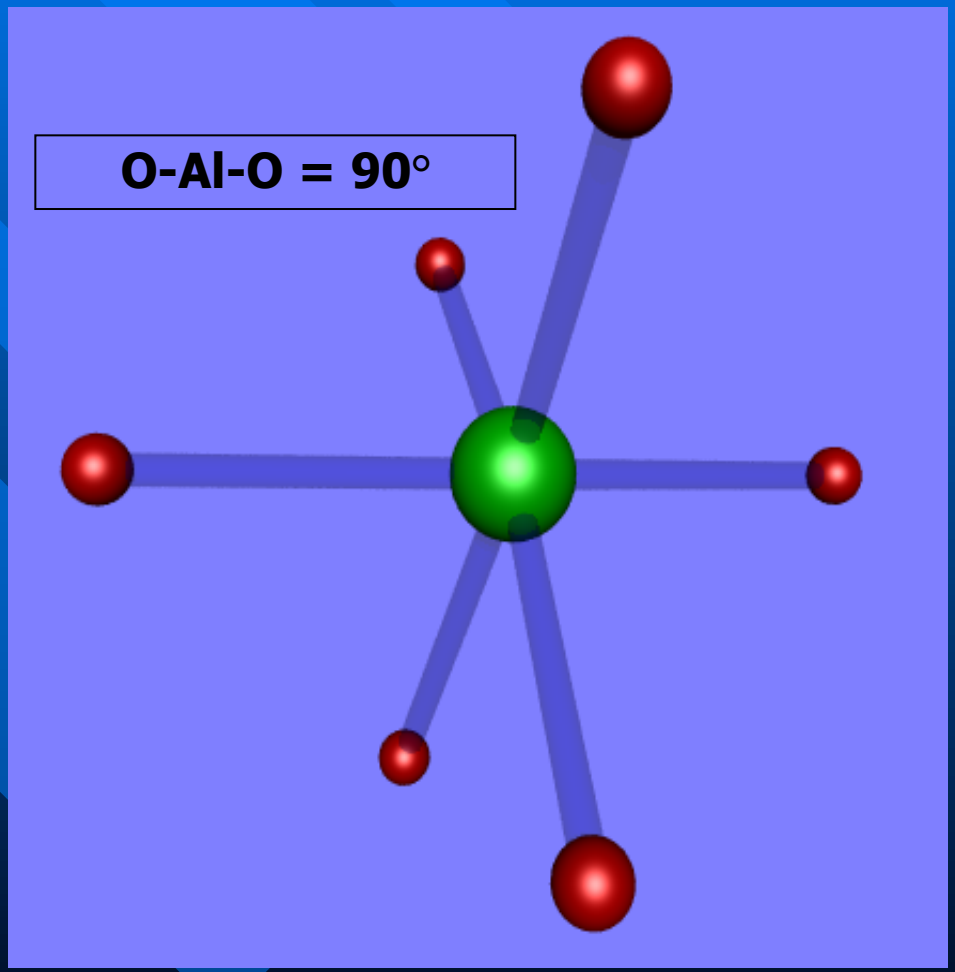
Results	n_{Al-Al}	n_{Al-O}	n_{O-Al}	n_{O-O}
Classical MD	9,1	3,97	2,65	16,85
ab initio MD	8,9	4,49	2,99	16,46

Angular distribution



Basic building blocks

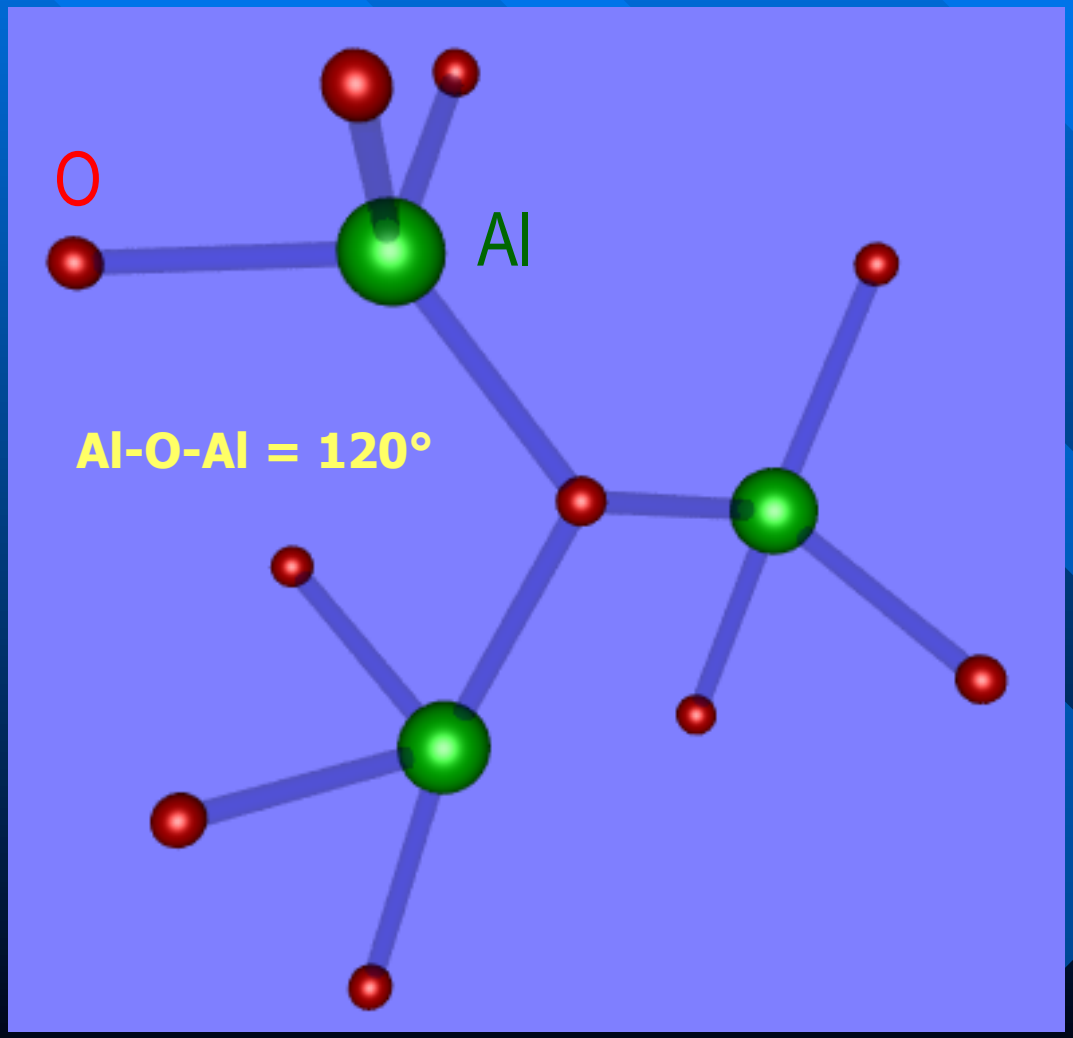


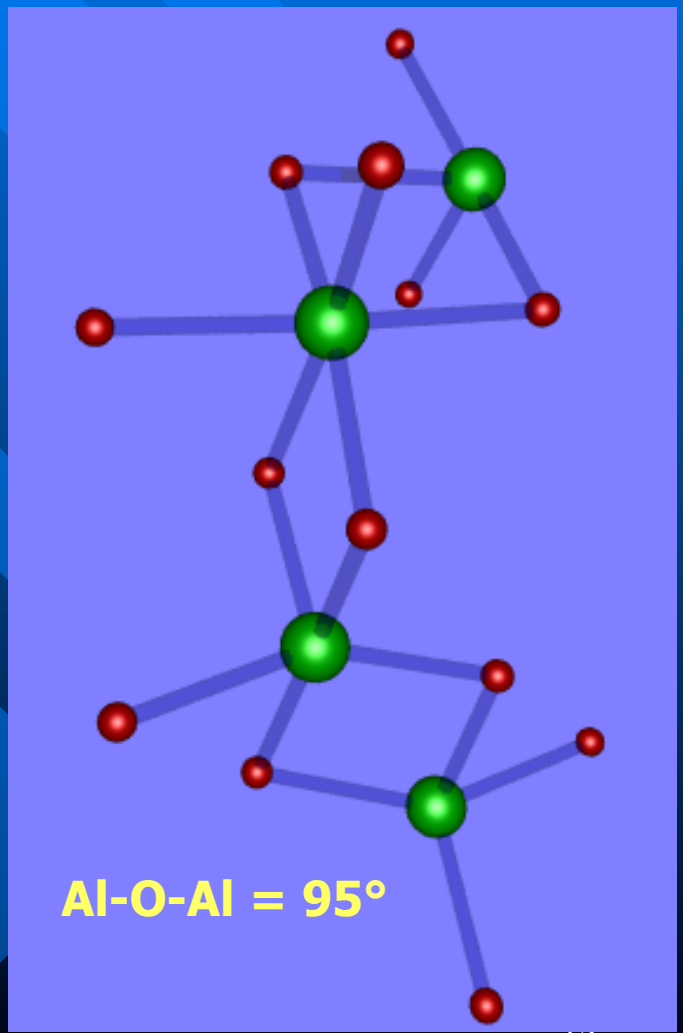


~52 % of AlO_4 terahedron

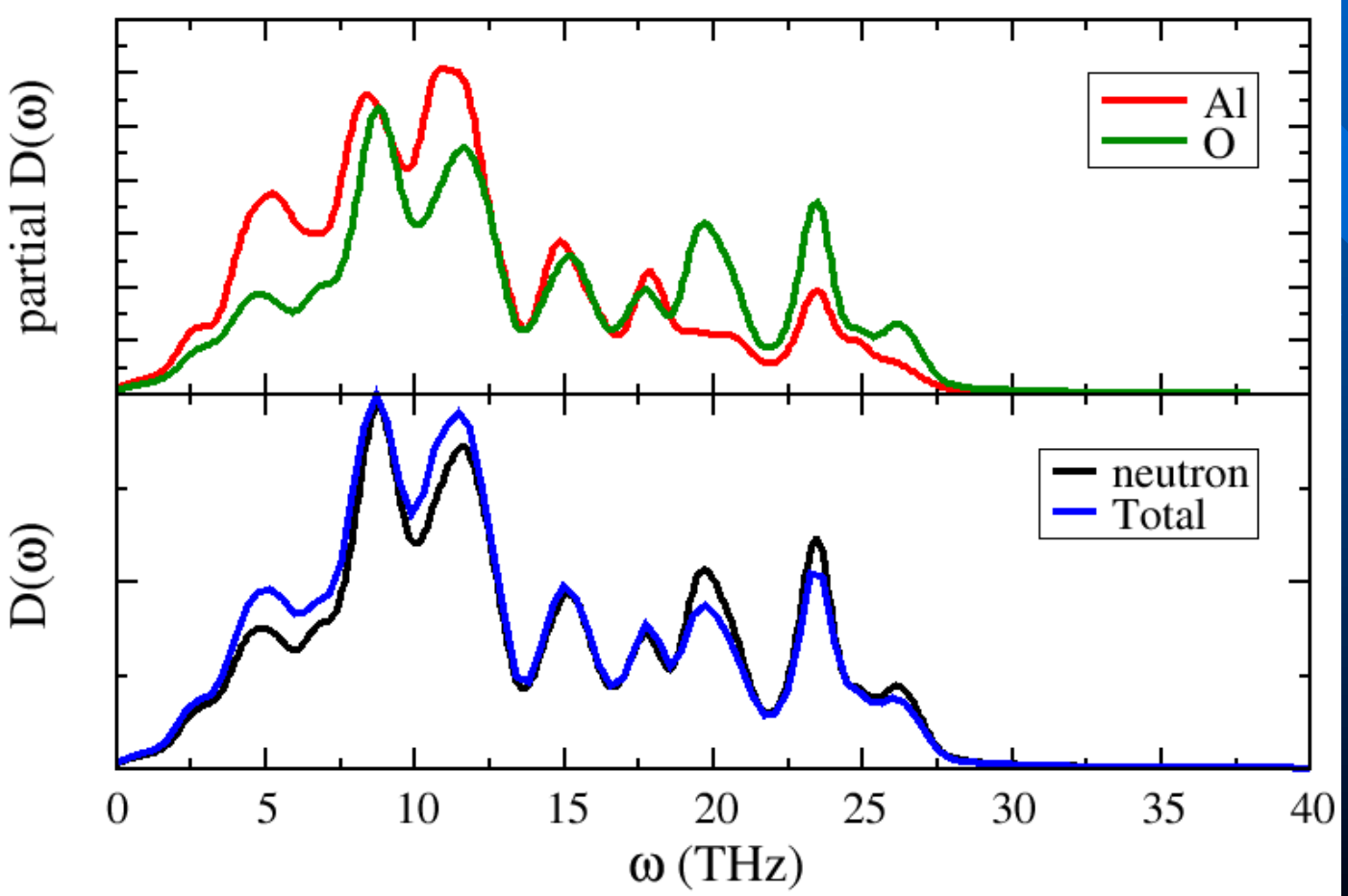
~40 % of AlO_6 octahedron

Connectivity of basic units

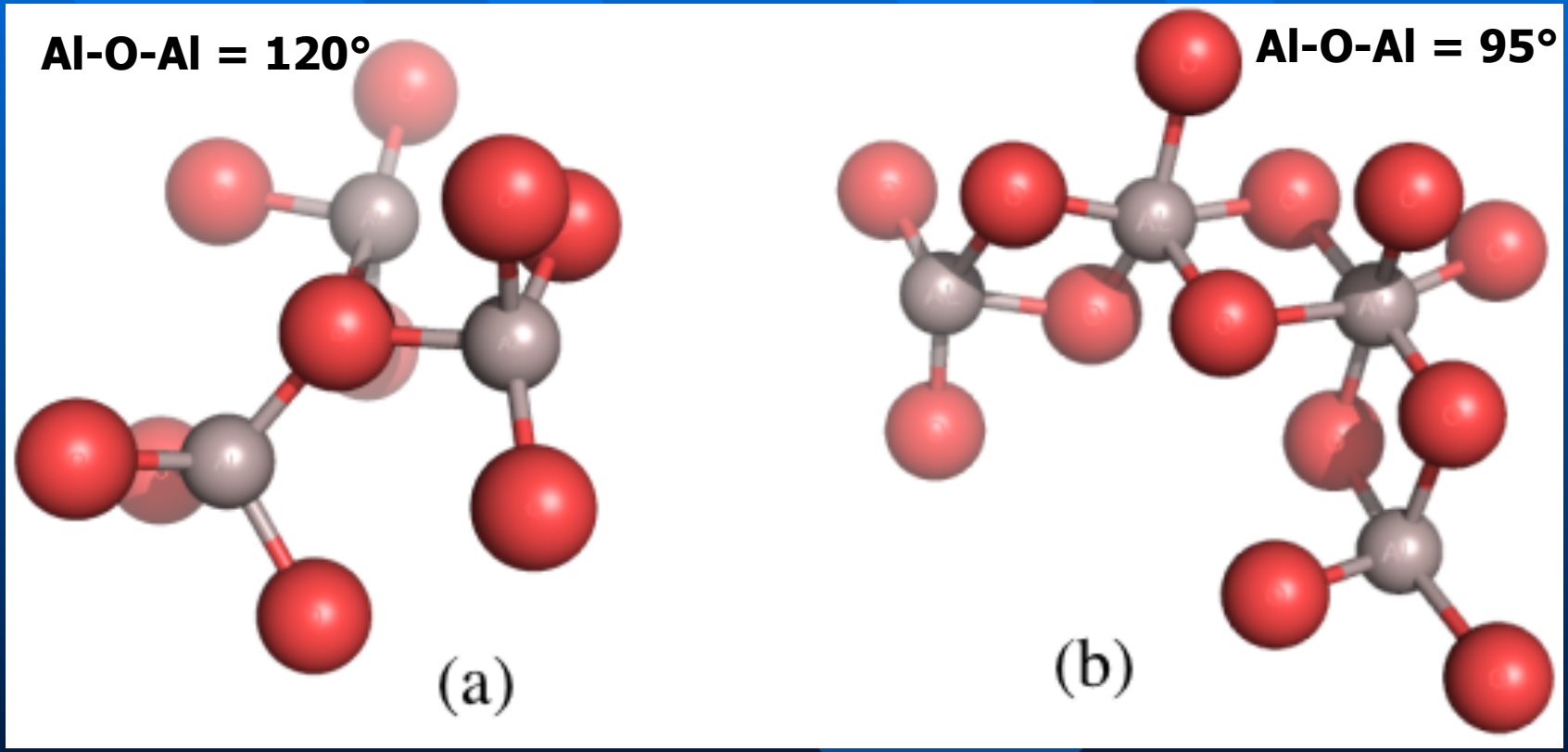




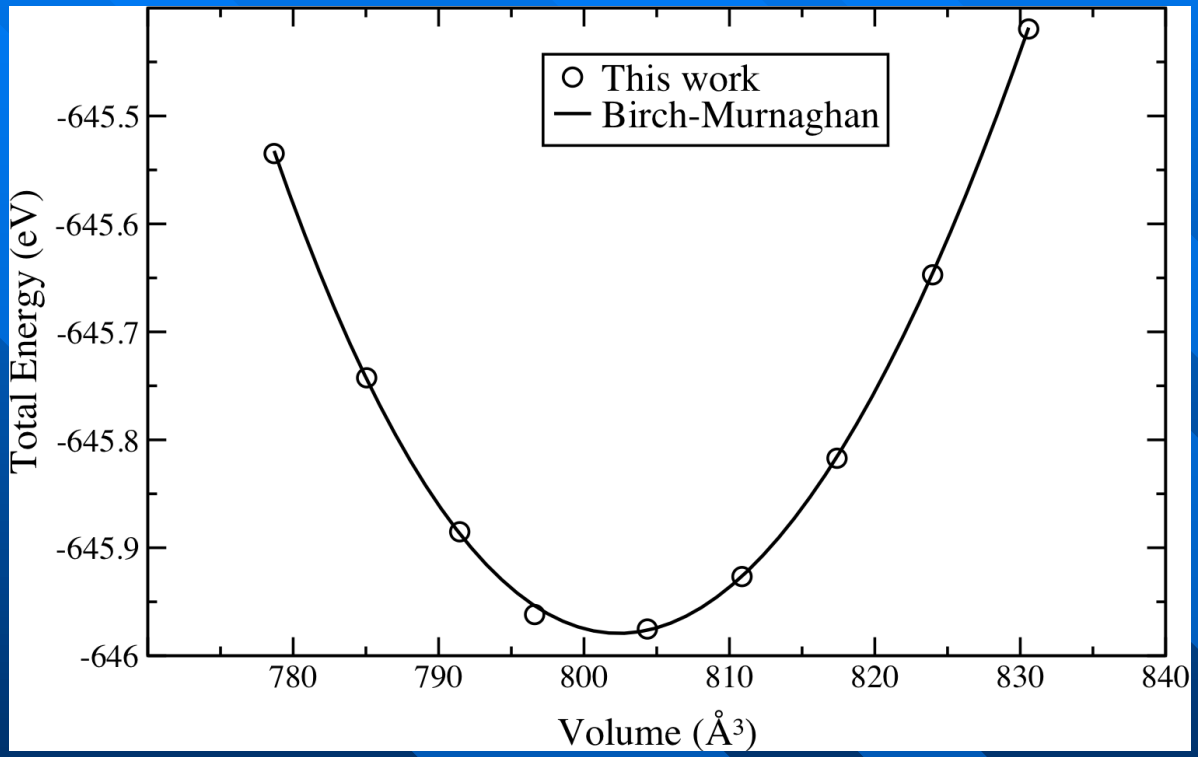
Vibrational density of states



Connectivity between basic units

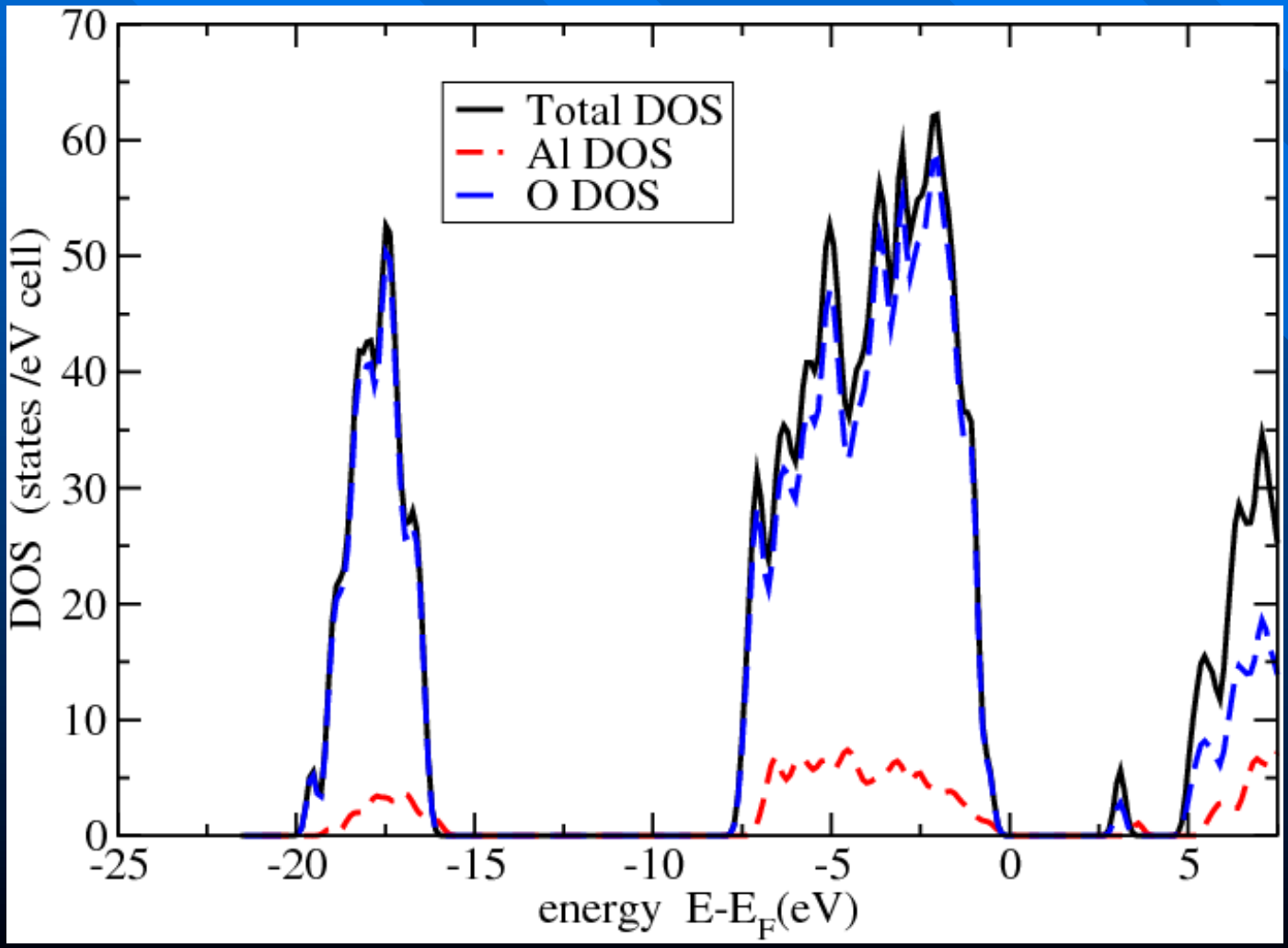


Elastic properties



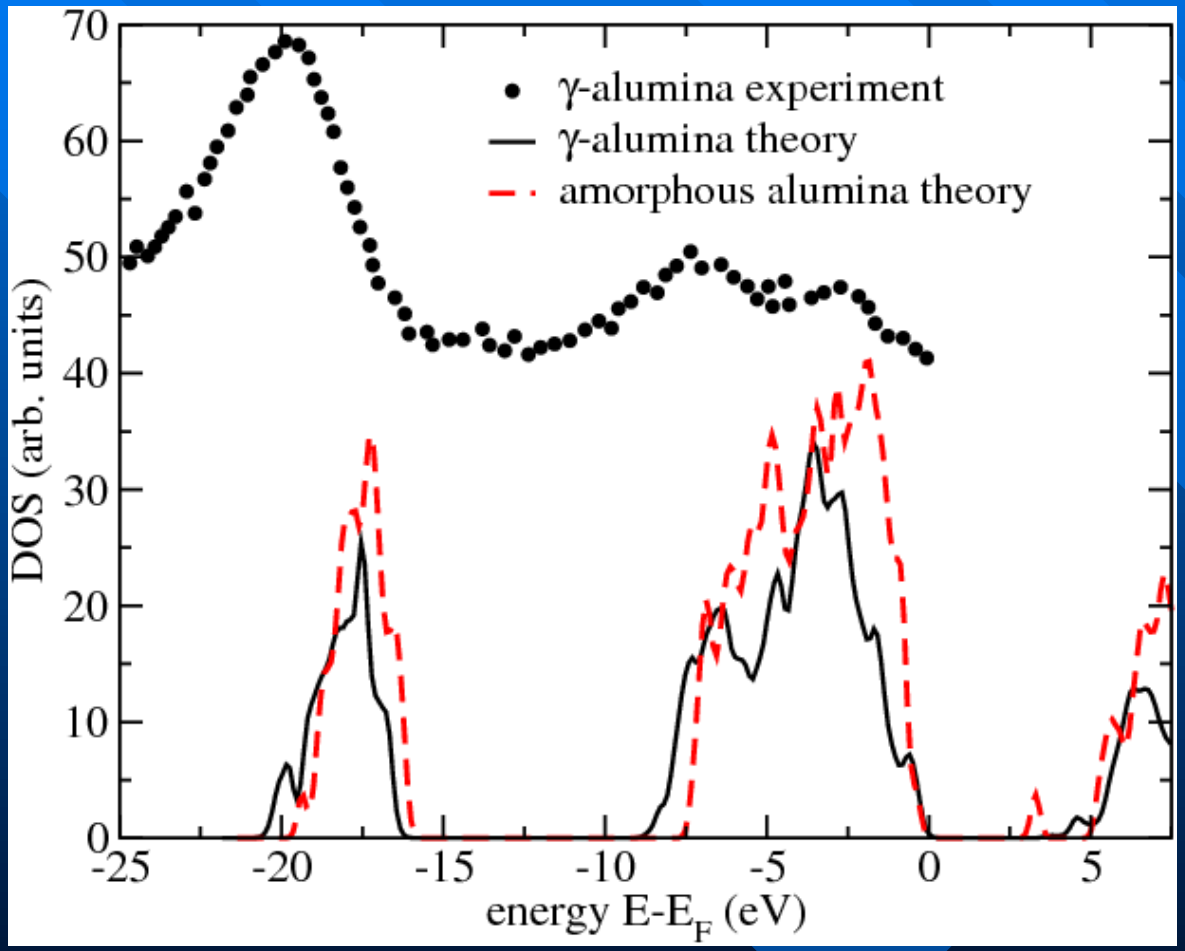
phase	B (GPa)	G (GPa)	E (GPa)	ν
amorph	193.4	141.0	340.3	0.2
Alpha (Wefers & Misra)	253	164	404	0.23

Electronic density of states



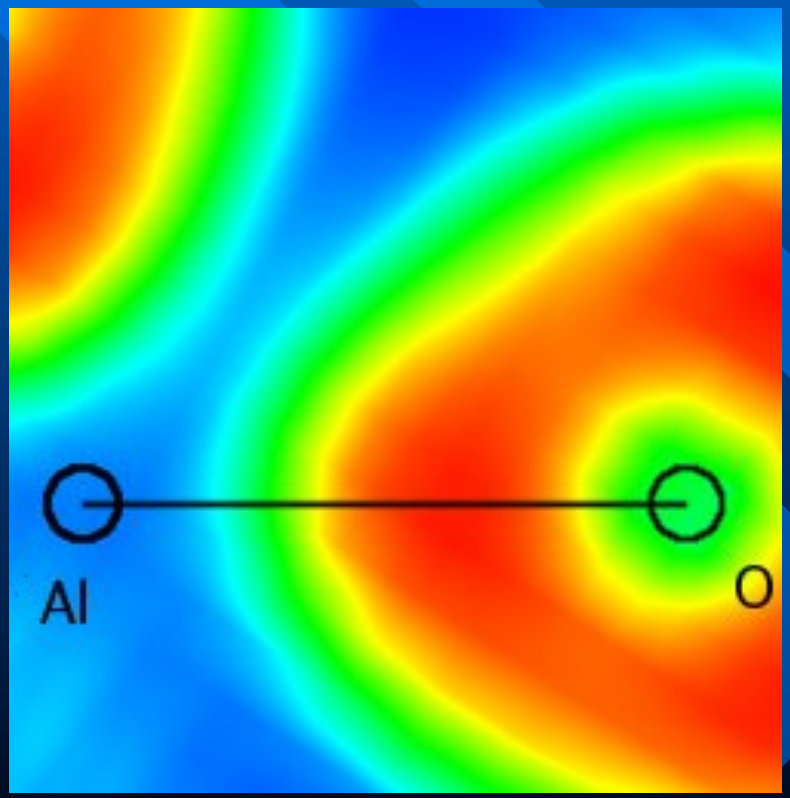
Energy gap
Exp 3.2 eV
Theo. 2.6 eV

Electronic density of states: comparison to γ-alumina



γ-Al_2O_3 Exp: B. Ealet et al. Thin Solid Films **250**, 92 (1994)
Theory: GG, A. Taga. B. Johansson, Phys. Rev. B **65** 012101 (2002)
GG, E. Menéndez, Phys. Rev. B **72** 035116 (2005)

Electron localization function



Charge transfer calculated via Voronoi analysis:
Al ~ 2.89
O ~ -1.92

Different alumina phases

Phase	Density g/cm^3	Al Coordination Number	Bond length Al-O (A)
amorphous[b]	3.17	4(76%), 5 (22%)	1.76
	3.9	4(23%), 5(51%), 6(21%)	1.77
	4.2	4(15%), 5(21%), 6(64%)	1.79
a, ab-initio[d]	3.17	4(50%), 5(42%), 6(5%)	1.81
liquid[a]	3.17	3(13%), 4(66%), 5(20%)	1.76
gamma[c]	3.66	4(37%), 6(63%)	1.94 +/- 0.3
theta	3.65	4(50%), 6(50%)	1.9 +/- 0.3
alpha	3.98	6 (100%)	1.97

a) PRE **61**, 2723 (2000),
b) PRB **65**, 104202 (2002), unpublished (2008)
c) PRB **65**, 012101 (2002), PRB, **72**, 035116 (2005)
d) J. Phys.: Condens. Matter 23, 495401 (2011)

Conclusions

- Using of ab-initio MD appear new features, absent in (simple) empirical interatomic potential
- The building blocks of the system are **AlO_4** and **AlO_6**
- The connectivity of this units is both by the corners (majority) and by the edges (minority)
- The v-DOS present two bands. The low frecuency band is related to the inter-unit vibrations, and the high band to the intra-unit vibrations
- B = 193 GPa, the lower of all polymorph
- The e-DOS is similar to the one of the crystalline γ-Al_2O_3, with a gap of 2.9 eV

Acknowledgments

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