# Computational Materials Science: Where Theory Meets Experiments

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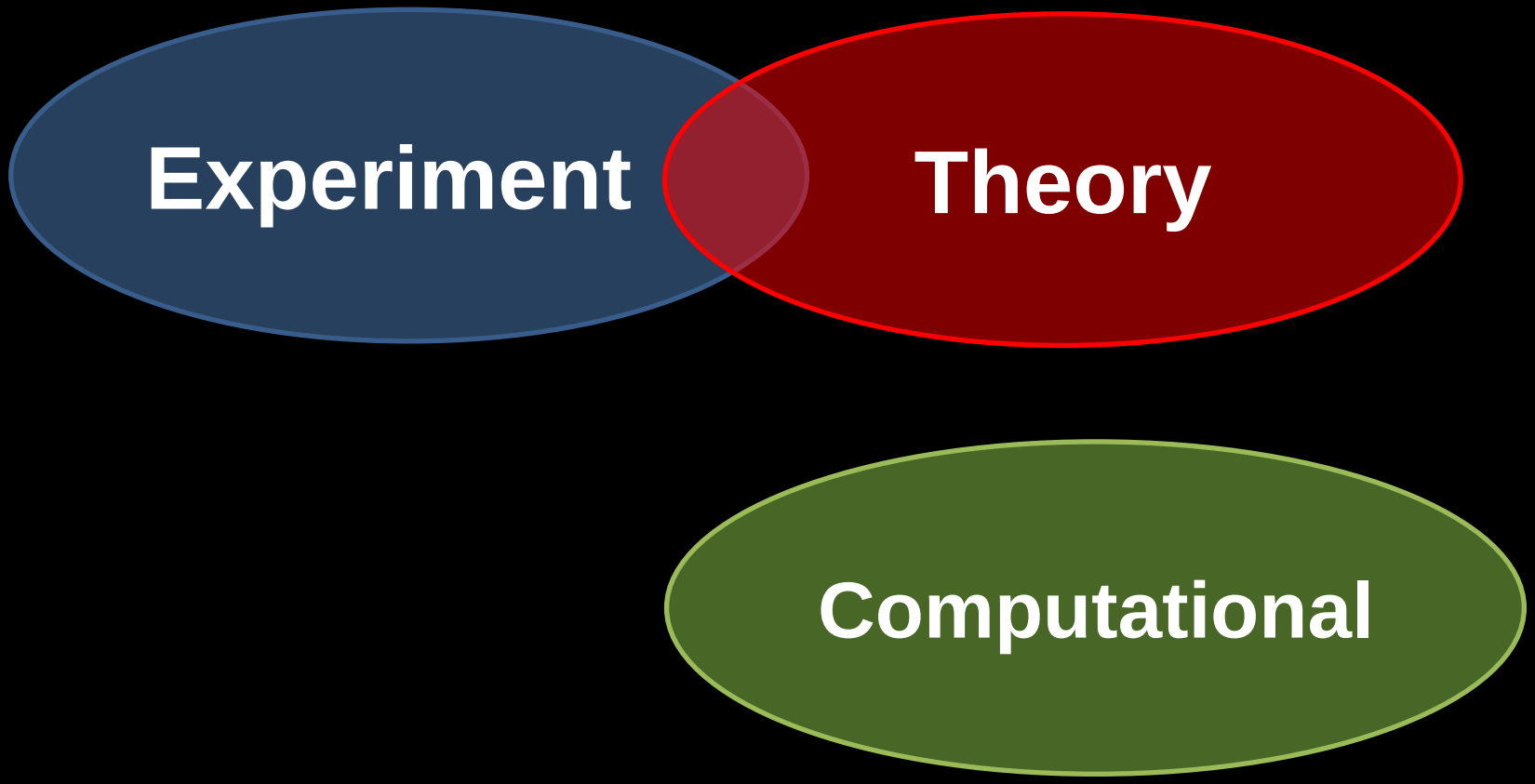
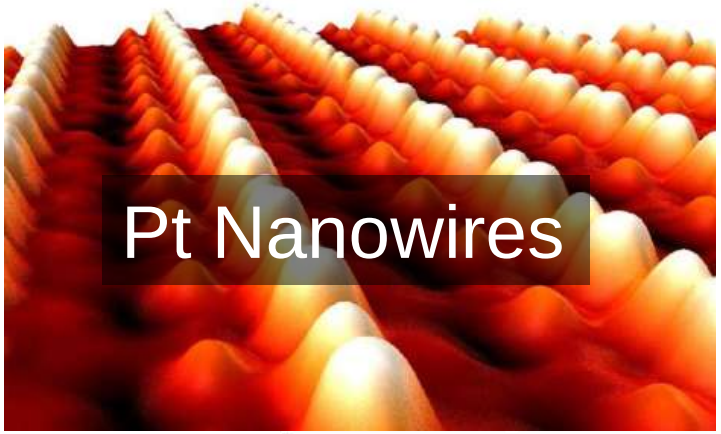
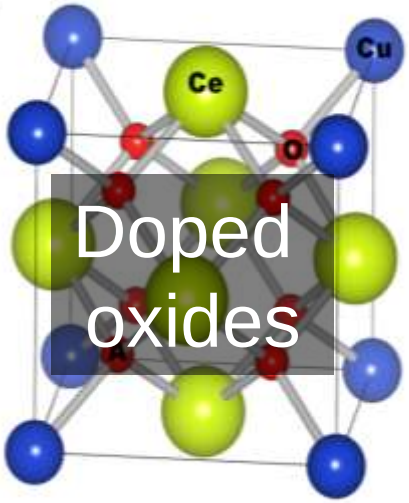
39th ICACC
Daytona Beach, January 27th,2015

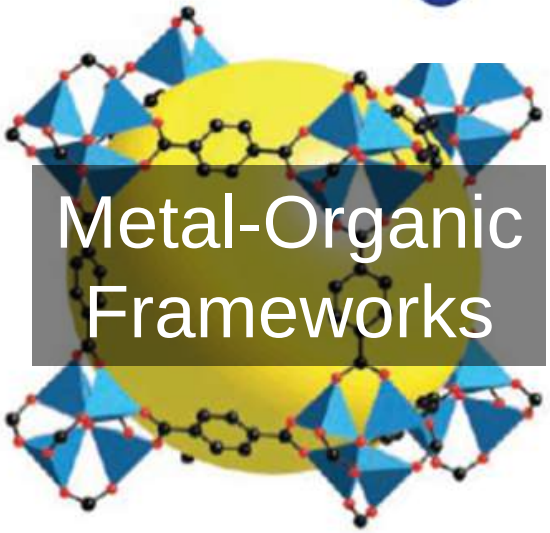
# Materials Science



# Computational ↔ Experiment: 3 Examples



# Properties for Comparison

**Energy**

Absolute and strict wrt model ➘ easy in calculations

**Lattice**

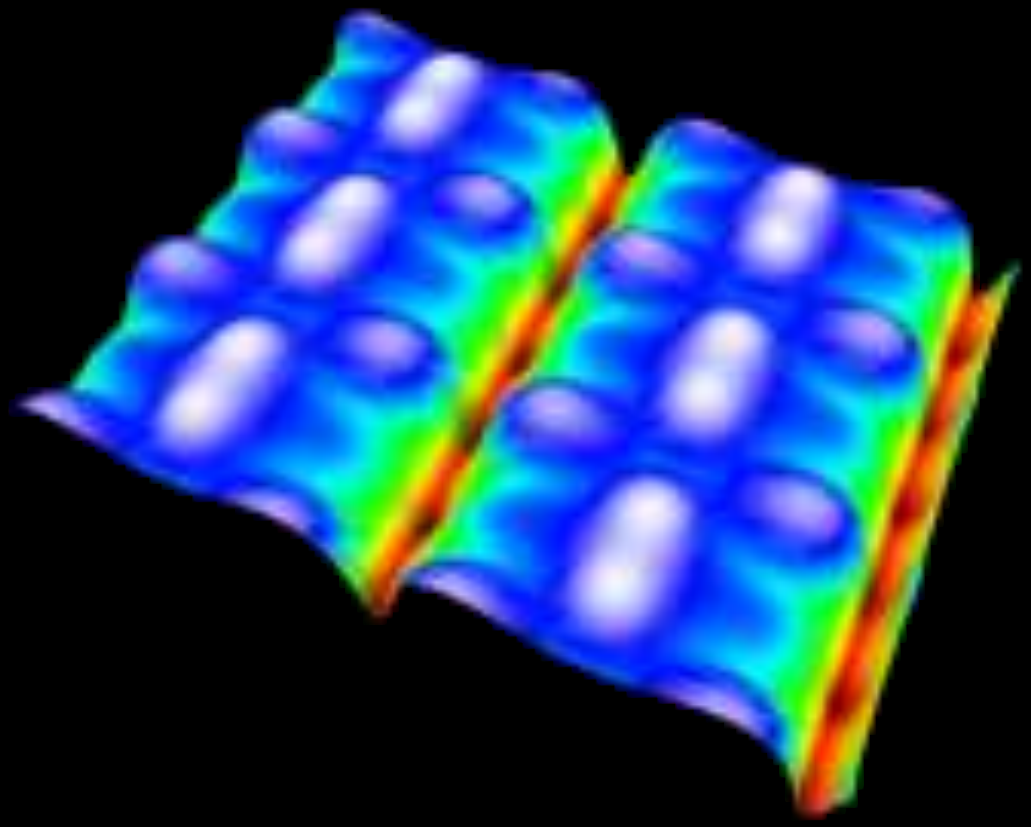
**Bulk Modulus**

**XRD**

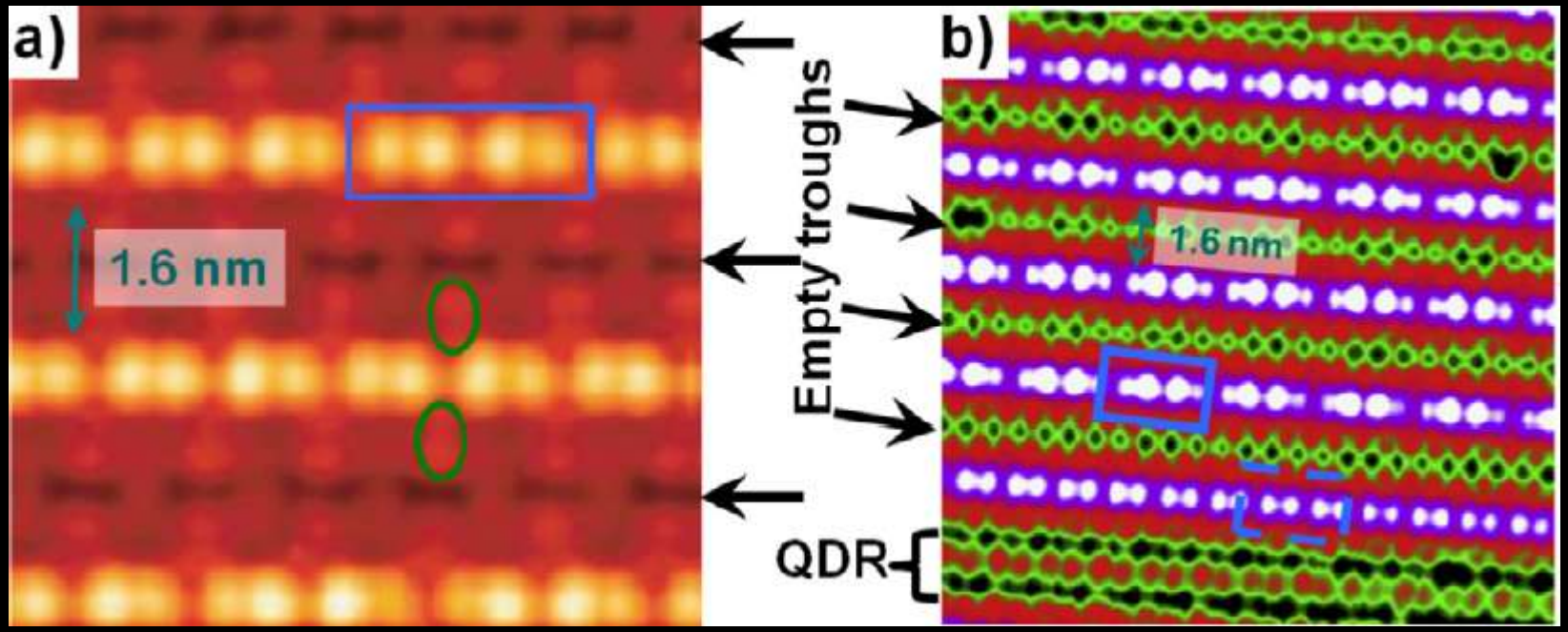
Post processing to get to model ➘ easy in experiment

**STM**

# Nanowires



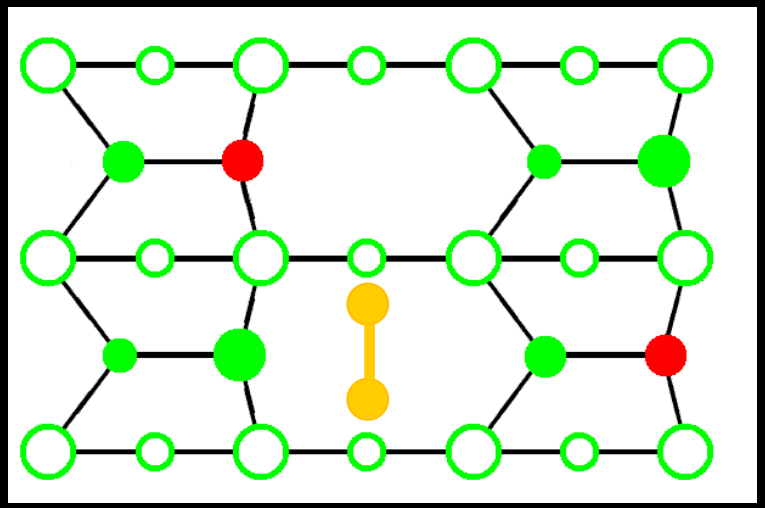
# Nanowires: Experiment



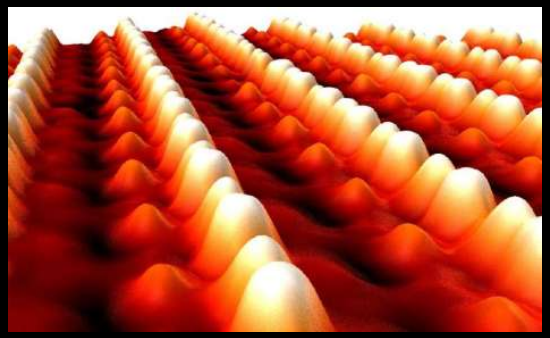


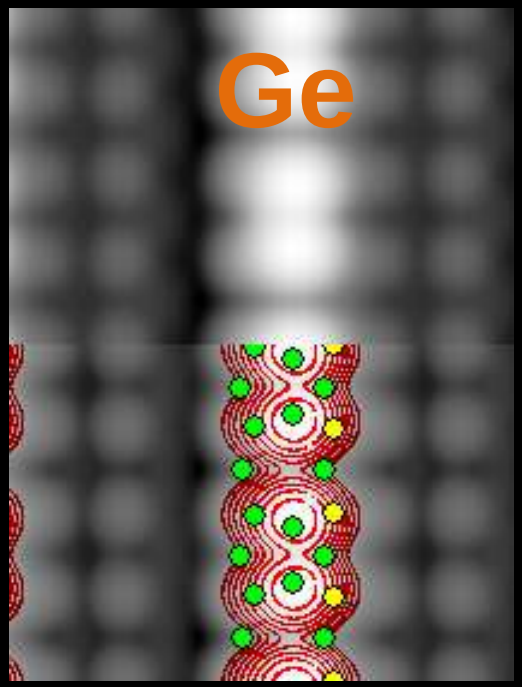
Gurlu O. *et al.*, Appl. Phys. Lett. 83, 4610 (2003)
Oncel N. *et al.*, Phys. Rev. Lett. 95, 116801 (2005)
Schafer J. *et al.*, Phys. Rev. B 74, 041404 (2006)
Mochizuki I. *et al.*, Phys. Rev. B 85, 245438 (2012)
Heimbuch R. *et al.*, J. Phys.: Condes. Matter 25, 014014 (2013)

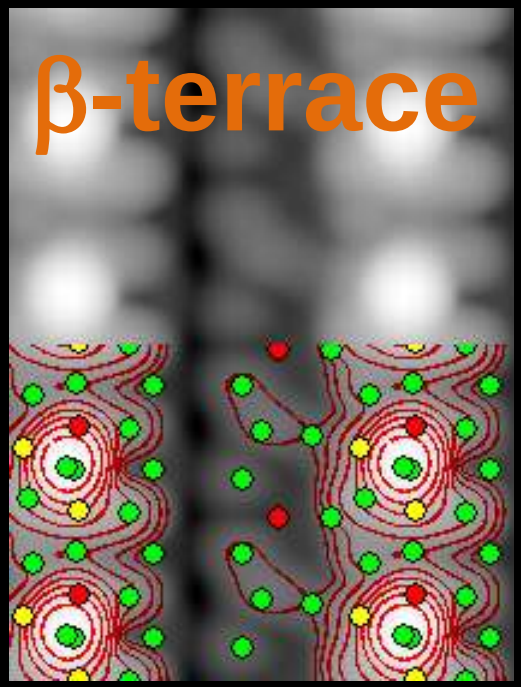
# Nanowires: Computational



- Pt atoms
- Ge atoms
- Pt dimer

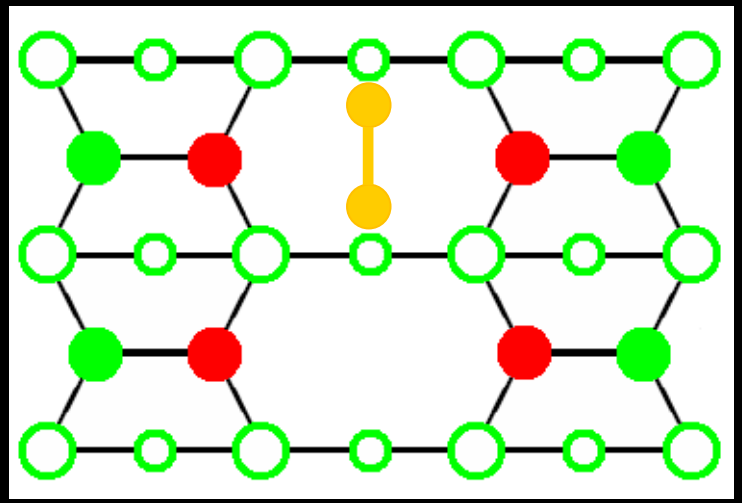




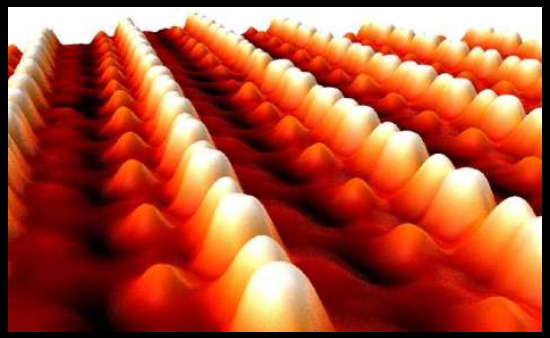




Phys. Rev B 77, 241308(R) (2008)
Phys. Rev B 81, 085410 (2010)

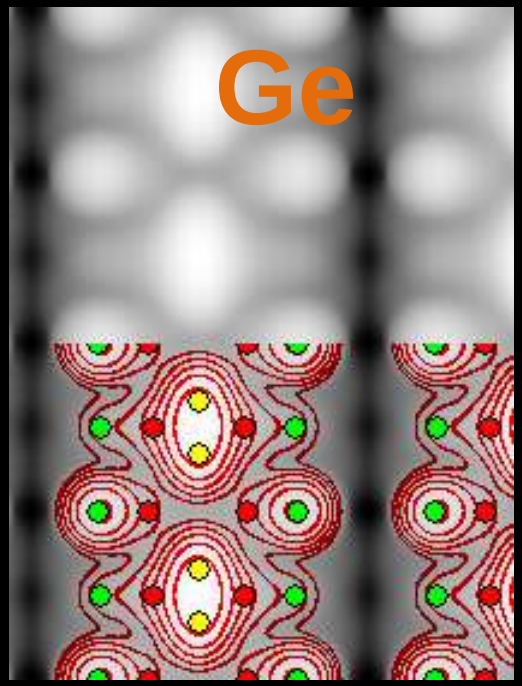
# Nanowires: Computational

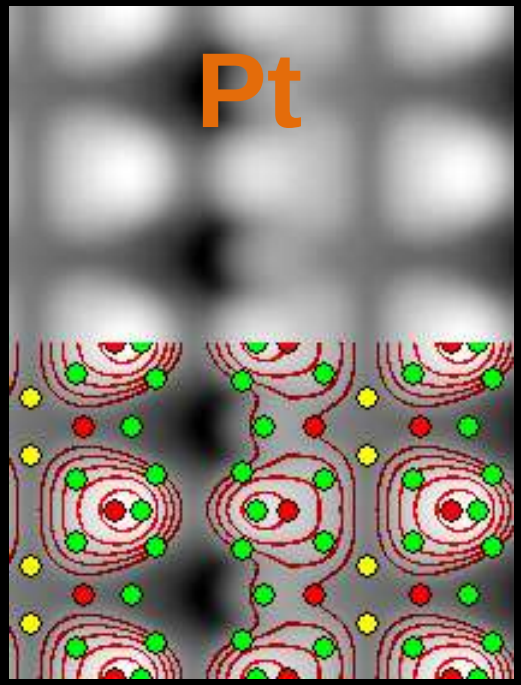


- Pt atoms
- Ge atoms
- Pt/Ge dimer



| | $E_f$ NW-chain (meV/atom) |
|---|---|
| Ge NW | -379 |
| Pt NW | -738 |

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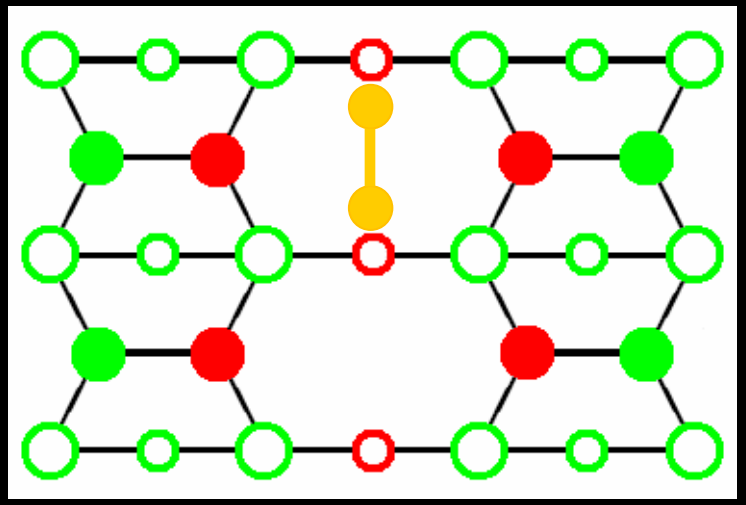
# Nanowires: Computational



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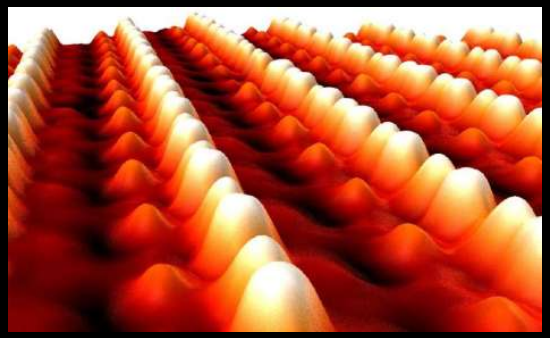
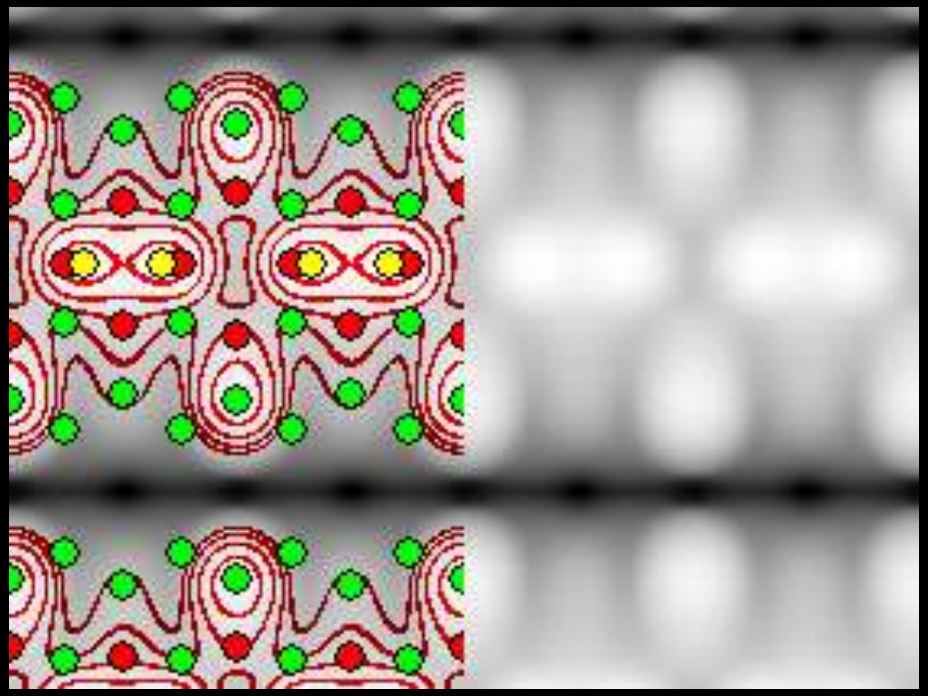
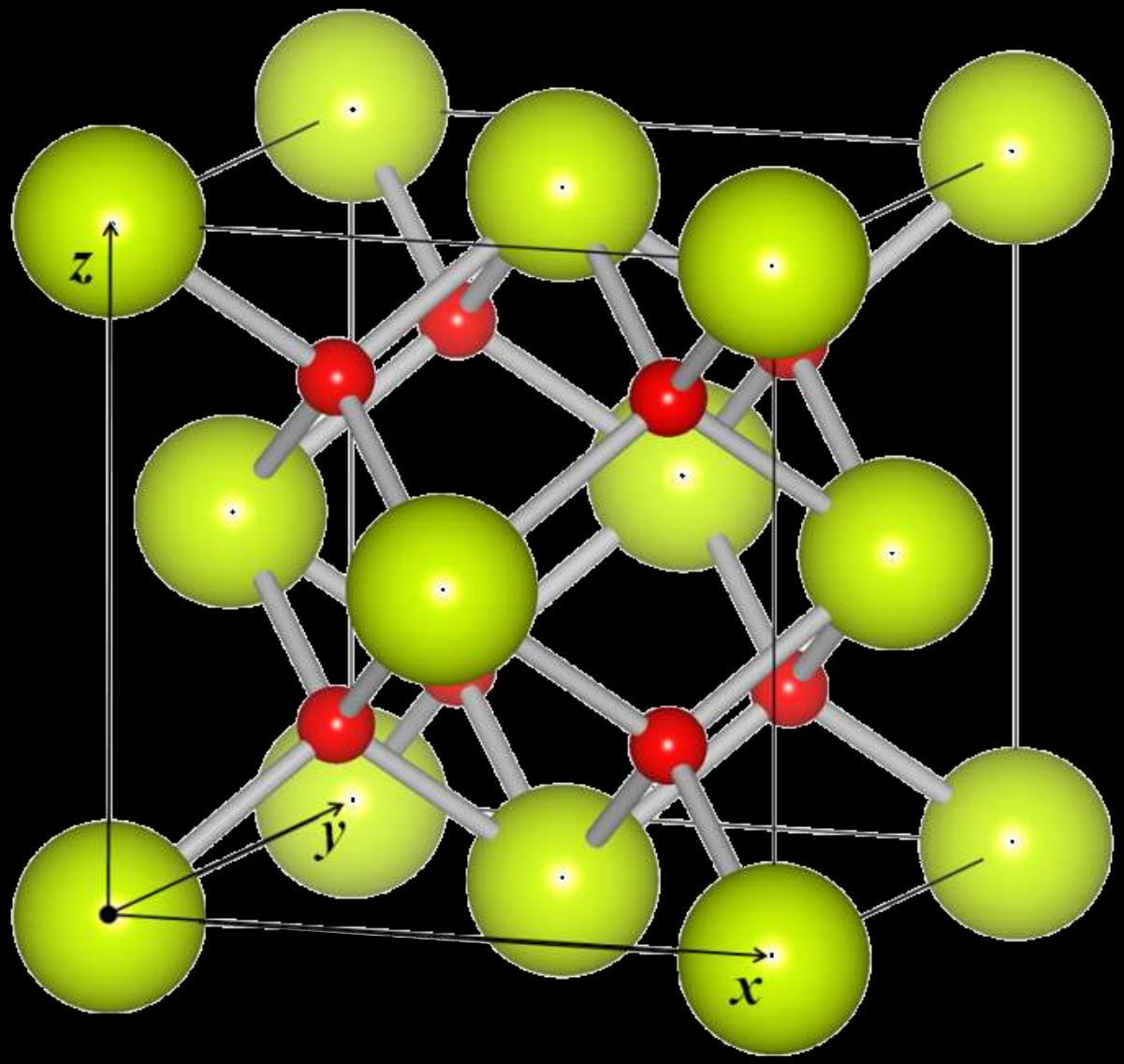


| | $E_f$ NW-chain (meV/atom) |
|---|---|
| Ge NW | -522 |
| Pt NW | 25 |

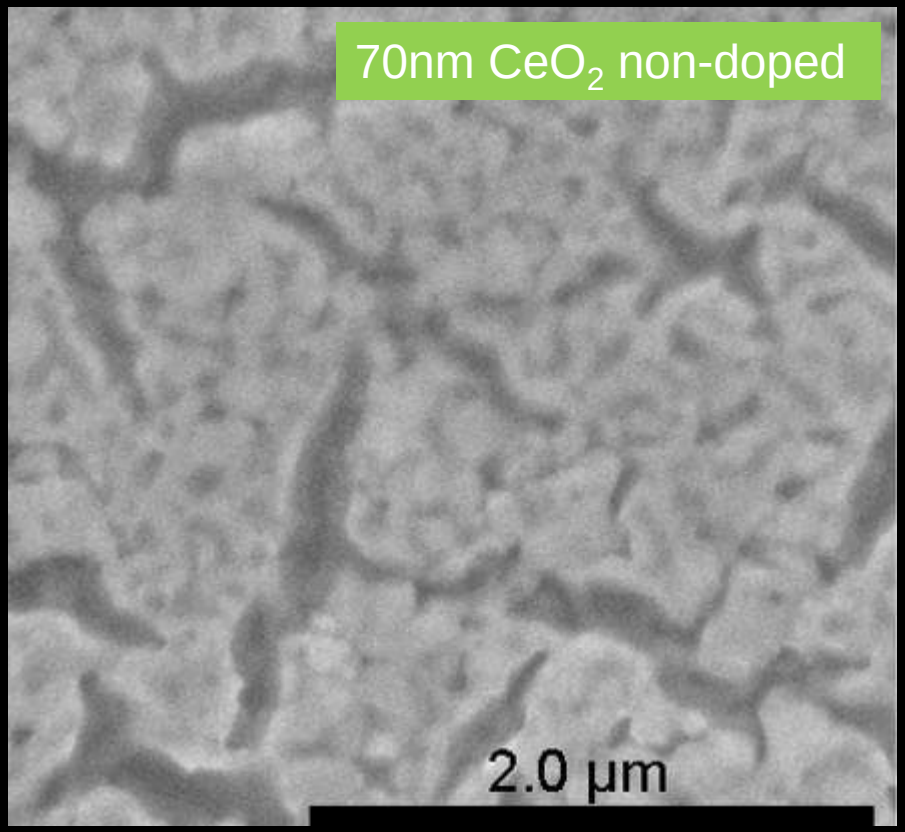


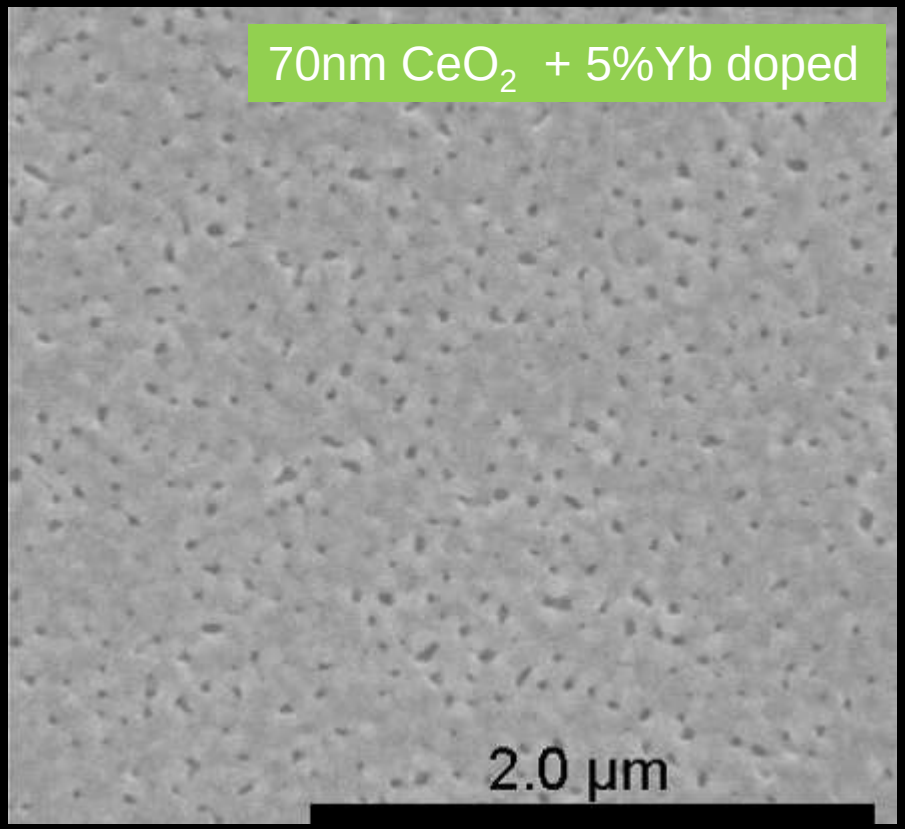
Phys. Rev B 77, 241308(R) (2008)
Phys. Rev B 81, 085410 (2010)
J., Phys.: Condens. Matter 26, 133001 (2014)

# Doped Cerates

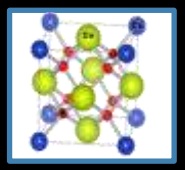


# Doped Cerates for buffer layers




Van de Velde N. *et al.*, Eur. J. Inor. Chem. 2, 233-241 (2010)



# Doped Cerates for buffer layers: +IV

| | $E_f$ (eV) | | | |
|---|---|---|---|---|
| | 25% | 12.5% | 3.704% | 3.125% |
| | LDA | | | |
| $CeO_2$ | -11.484[a] | | | |
| $La_2Zr_2O_7$ | -42.421[a] | | | |
| C | 20.424 | 20.643 | 20.736 | 20.737 |
| Si | 8.288 | 8.078 | 8.050 | 8.052 |
| Ge | 9.404 | 9.134 | 9.110 | 9.105 |
| Sn | 7.061 | 6.866 | 6.851 | 6.851 |
| Pb | 8.963 | 8.757 | 8.742 | 8.745 |
| Ti | 3.168 | 3.254 | 3.248 | 3.233 |
| Zr | 0.530 | 0.555 | 0.548 | 0.543 |
| Hf | 0.105 | 0.139 | 0.131 | 0.128 |

**Reference energy:**
**oxygen vacancy formation energy 4.0 eV @ 1.56%**

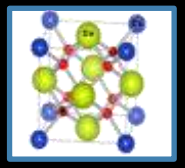
**Large variation wrt dopant element**

**IVa 'unstable'**

**IVb 'stable'**

**Little variation wrt dopant concentration**

J. Am. Ceram. Soc. 97(1), 258-266 (2014)



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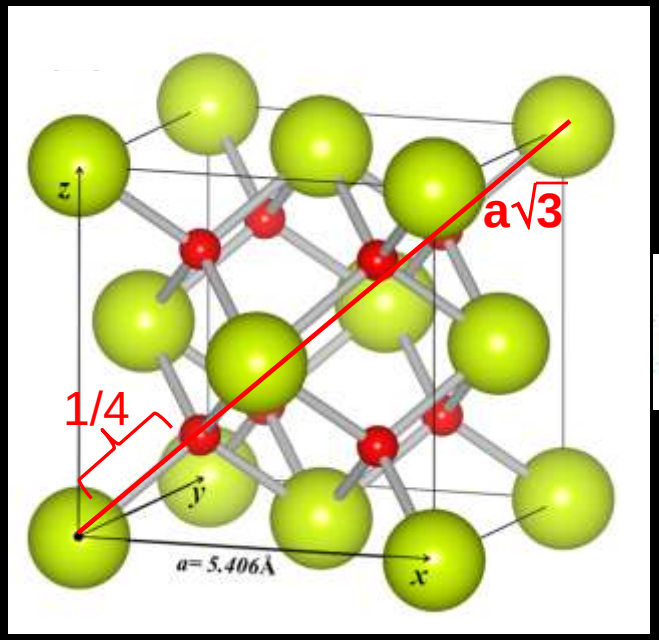



$$R_O + R_{Ce} = a_{CeO_2}\frac{\sqrt{3}}{4}$$

$$R_O + \left((1-x)R_{Ce} + xR_M\right) = a_{Ce_{1-x}M_xO_2}\frac{\sqrt{3}}{4}$$

$$\Rightarrow R_M = \frac{a_{Ce_{1-x}M_xO_2}\frac{\sqrt{3}}{4} - R_O - (1-x)R_{Ce}}{x}$$

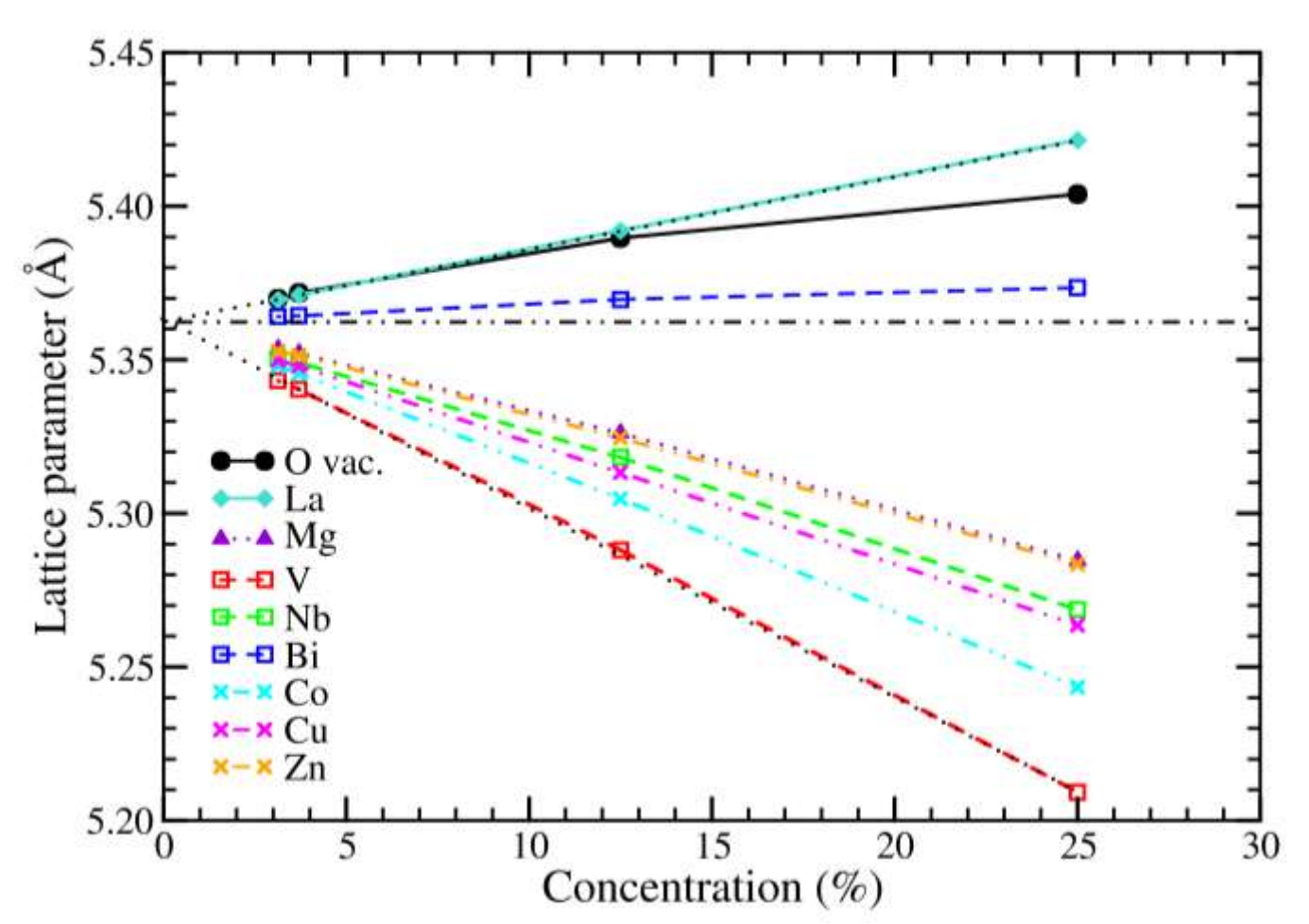
$$\Rightarrow a_{Ce_{1-x}M_xO_2} = a_{CeO_2} + \left(\frac{4}{\sqrt{3}}(R_O + R_M) - a_{CeO_2}\right)x$$

$$y = a + bx$$

**(empirical) Vegard's Law**

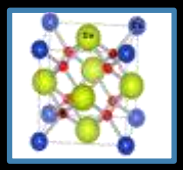
Appl. Surf. Sci. 260, 32-35 (2012)

# Doped Cerates for buffer layers




(empirical) **Vegard's Law**

Appl. Surf. Sci. 260, 32-35 (2012)



# Doped Cerates for buffer layers

$$B = -V\frac{\partial P}{\partial V}$$

| system | $\Delta V_0$ (%) | $B_0$ (GPa) | $B'_0$ (-) |
|---|---|---|---|
| $CeO_2$ | 163.39* | 174.2 | 4.49 |
| $Ce_{0.75}C_{0.25}O_2$ | -3.96 | 125.5 | 4.55 |
| $Ce_{0.75}Si_{0.25}O_2$ | -9.18 | 176.8 | 4.77 |
| $Ce_{0.75}Ge_{0.25}O_2$ | -6.09 | 160.1 | 5.03 |
| $Ce_{0.75}Sn_{0.25}O_2$ | -3.24 | 172.1 | 4.65 |
| $Ce_{0.75}Pb_{0.25}O_2$ | 0.13 | 154.3 | 4.98 |
| $Ce_{0.75}Ti_{0.25}O_2$ | -7.60 | 185.4 | 4.46 |
| $Ce_{0.75}Zr_{0.25}O_2$ | -4.62 | 190.8 | 4.48 |
| $Ce_{0.75}Hf_{0.25}O_2$ | -5.19 | 191.0 | 4.42 |

J. Am. Ceram. Soc. 97(1), 258-266 (2014) & J. Mater. Chem. A 2 13723-13737 (2014)

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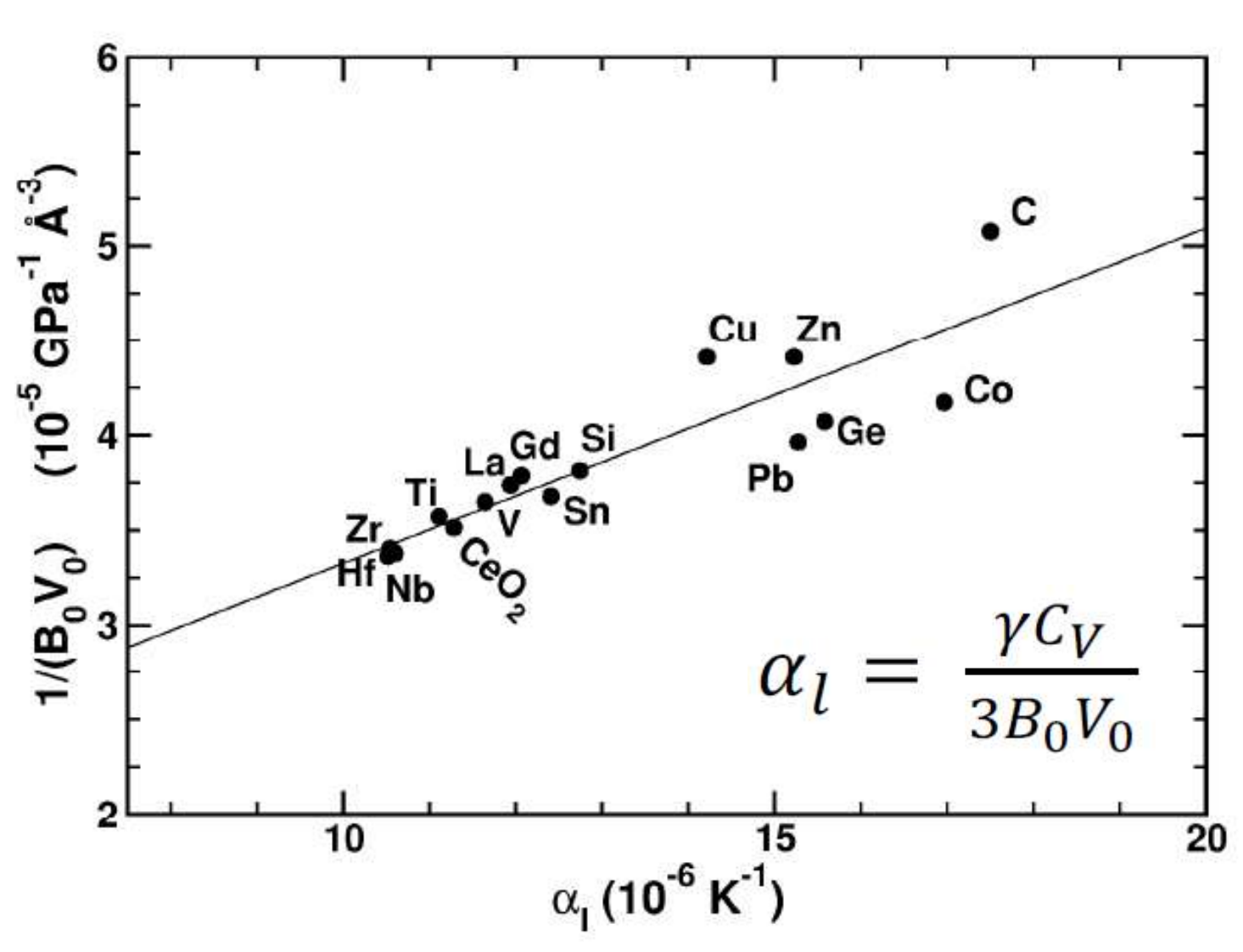
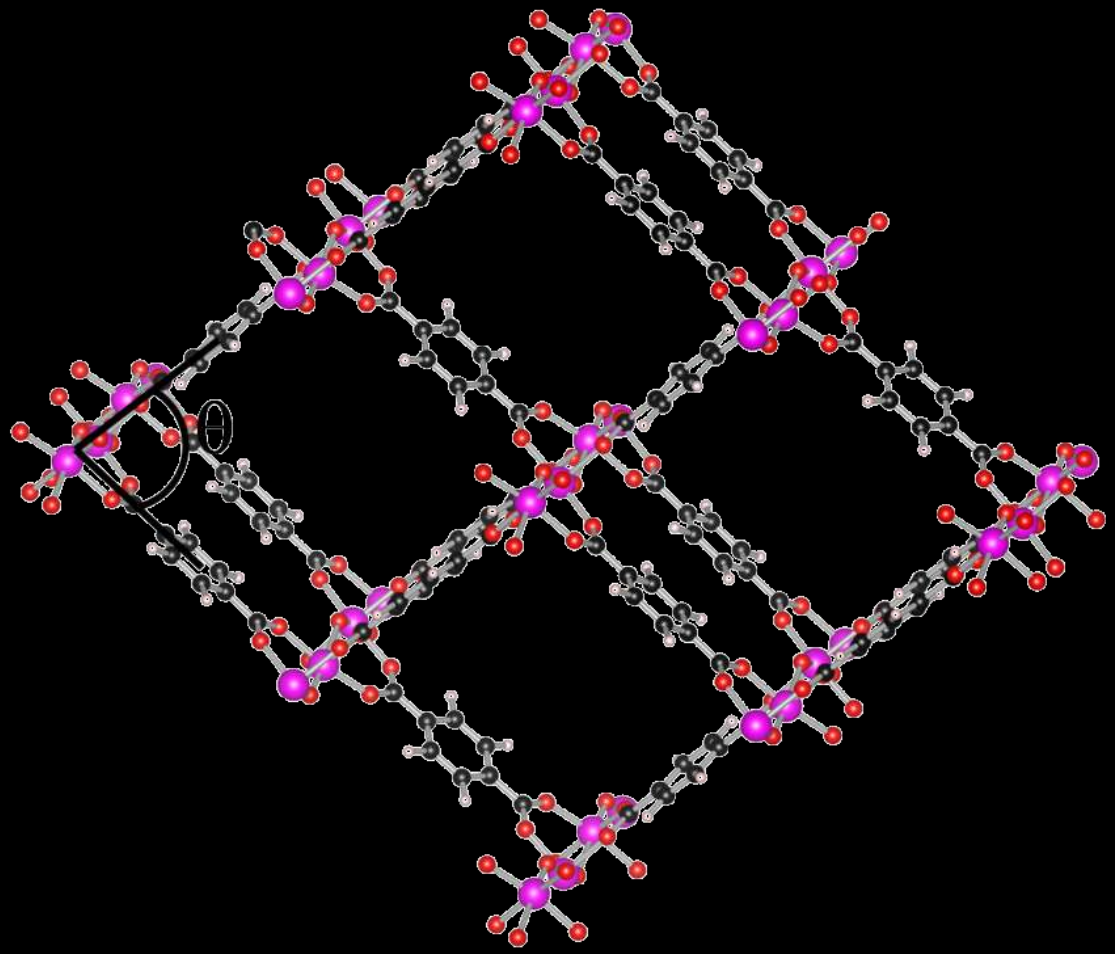
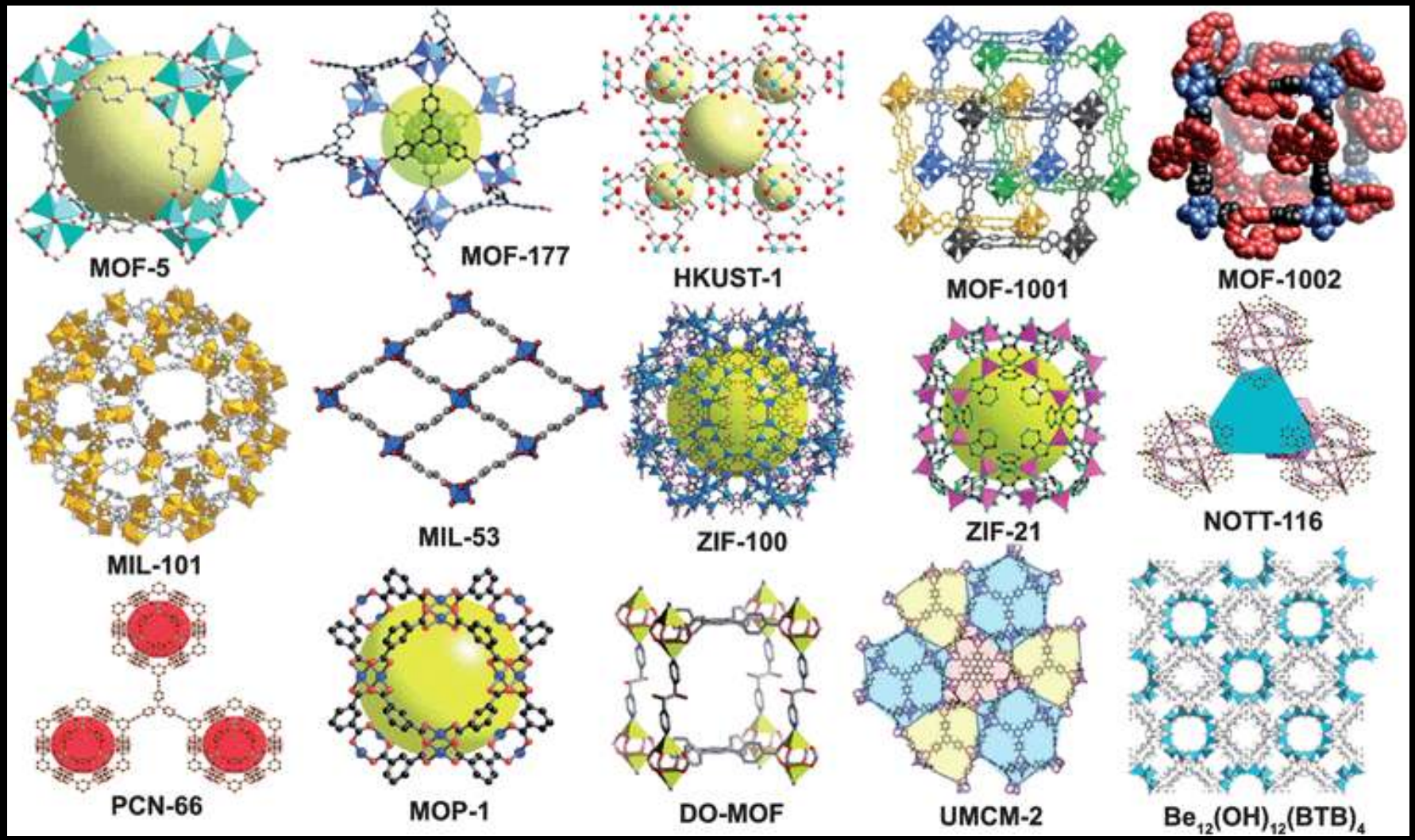



J. Am. Ceram. Soc. 97(1), 258-266 (2014) & J. Mater. Chem. A 2 13723-13737 (2014)

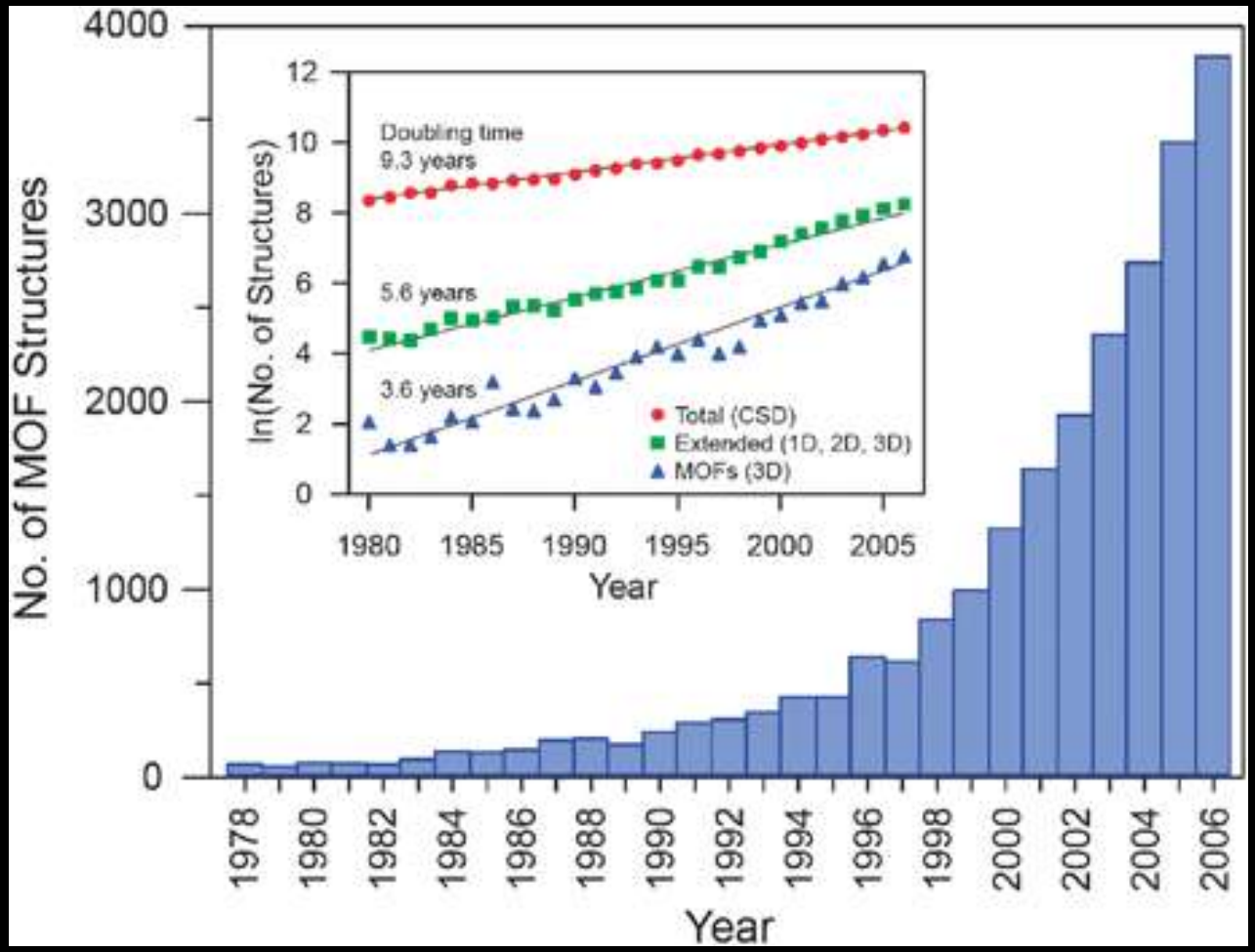
# Metal-Organic Frameworks



# Metal-Organic Frameworks

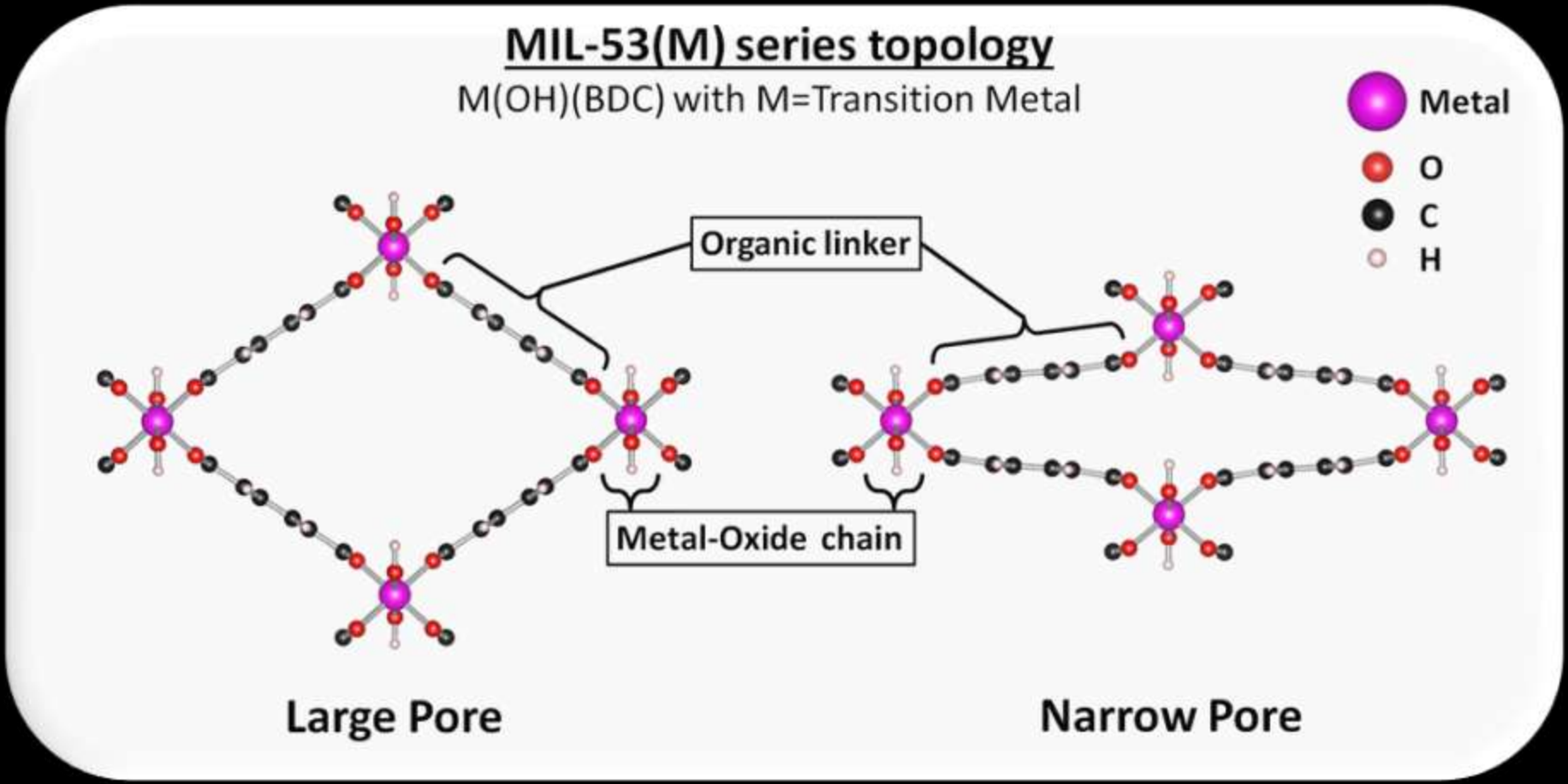


# Metal-Organic Frameworks




*Chem. Soc. Rev.*, 38, 1213-1214(2009)

# MIL- 47($V^{IV}$)

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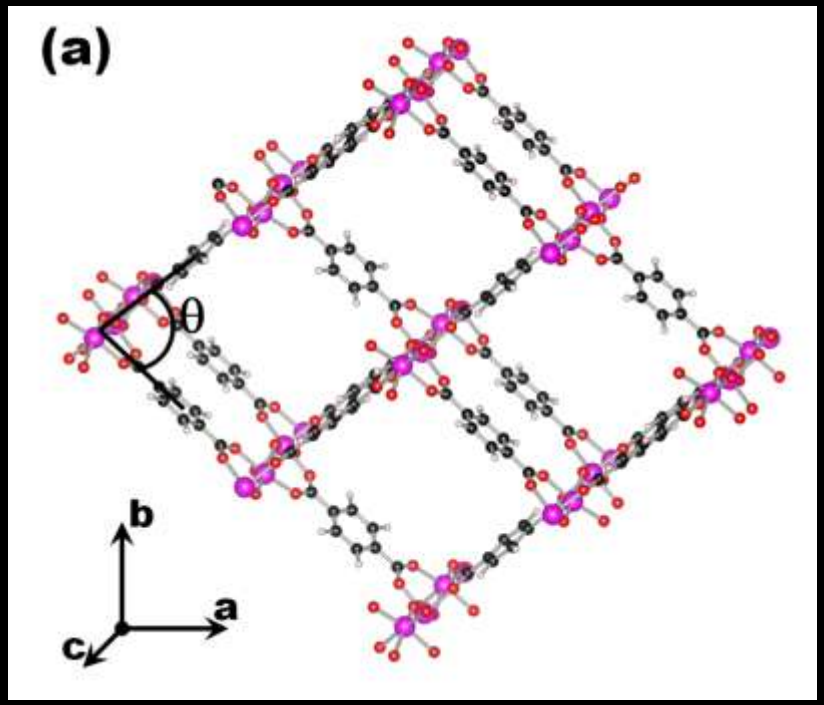
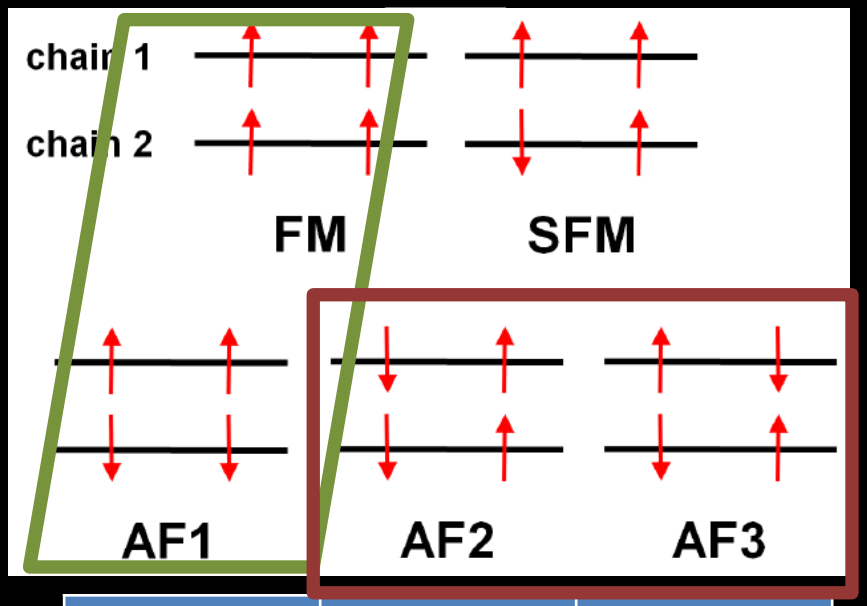
# Spin Configurations vs the World




| | $E_0$ [meV] | $B_0$ [GPa] |
|---|---|---|
| FM | 0 | 5.95 |
| AF1 | -16 | 6.14 |
| SFM | -144 | 7.17 |
| AF2 | -279 | 8.13 |
| AF3 | -278 | 8.12 |

**How to observe in experiment?**

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# MIL-47(V) under pressure

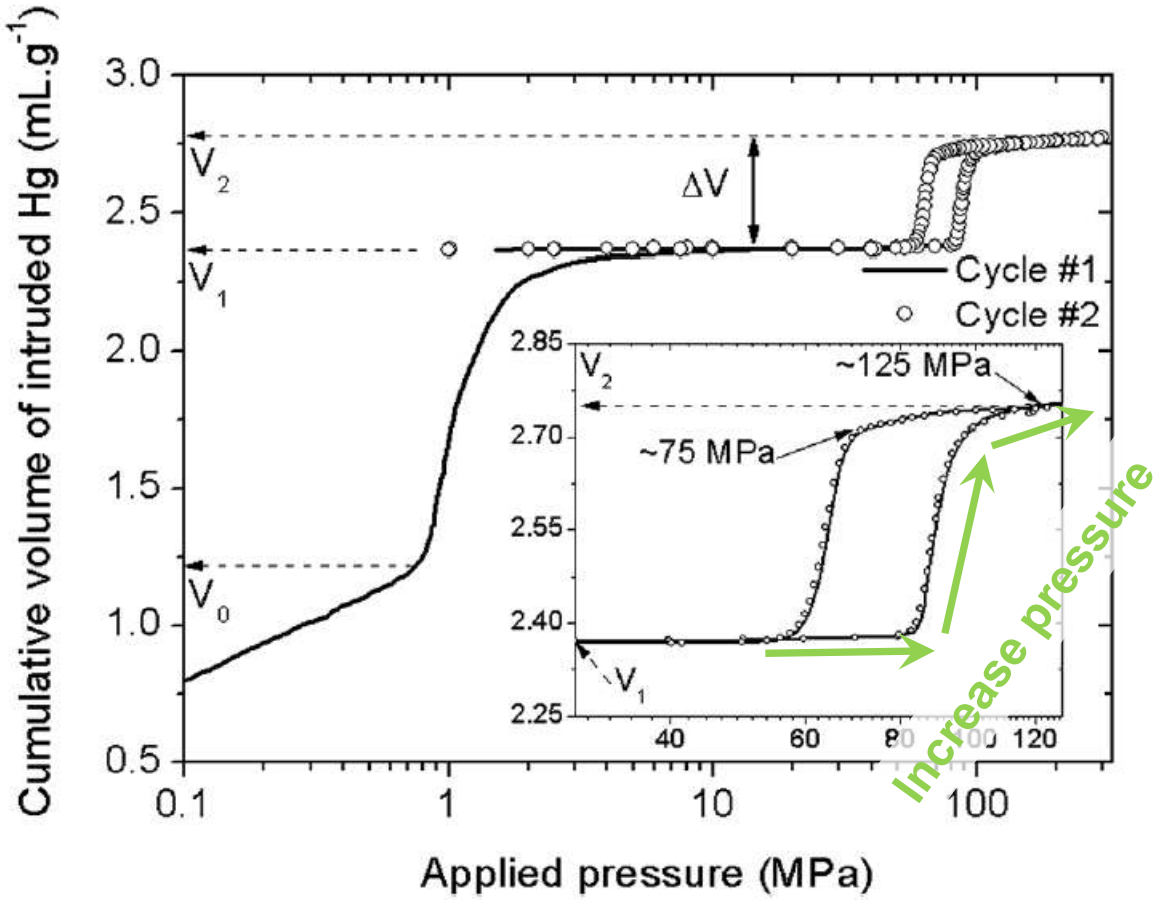
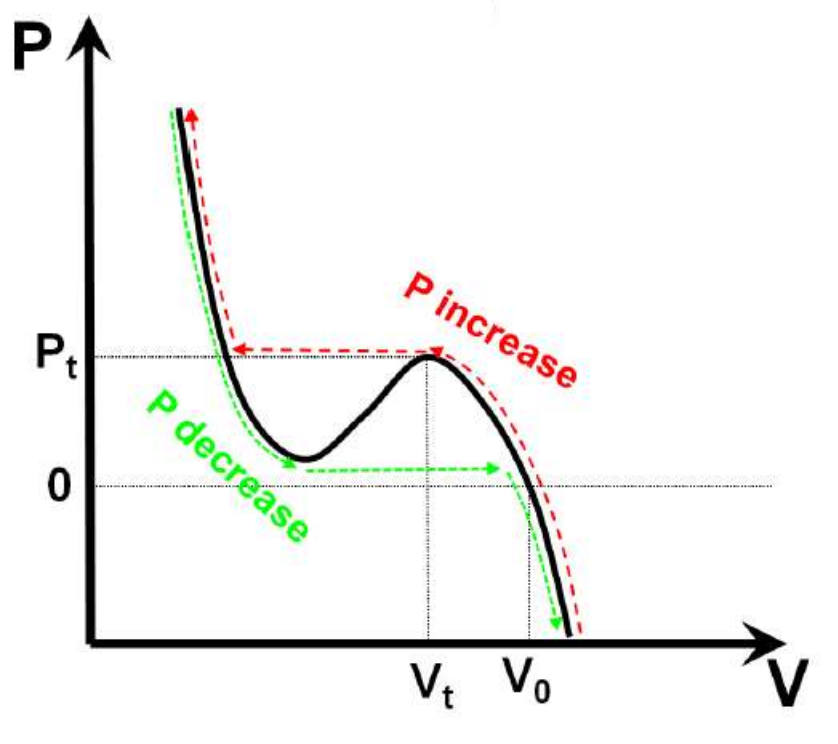



**Fig. 1** Cumulative volume of intruded mercury in a two cycles intrusion–extrusion as a function of the applied pressure obtained for the MIL-47($V^{IV}$) sample.

Yot et al., Chem. Sci. 3, 1100-1104 (2012)

# Spin configurations vs the world

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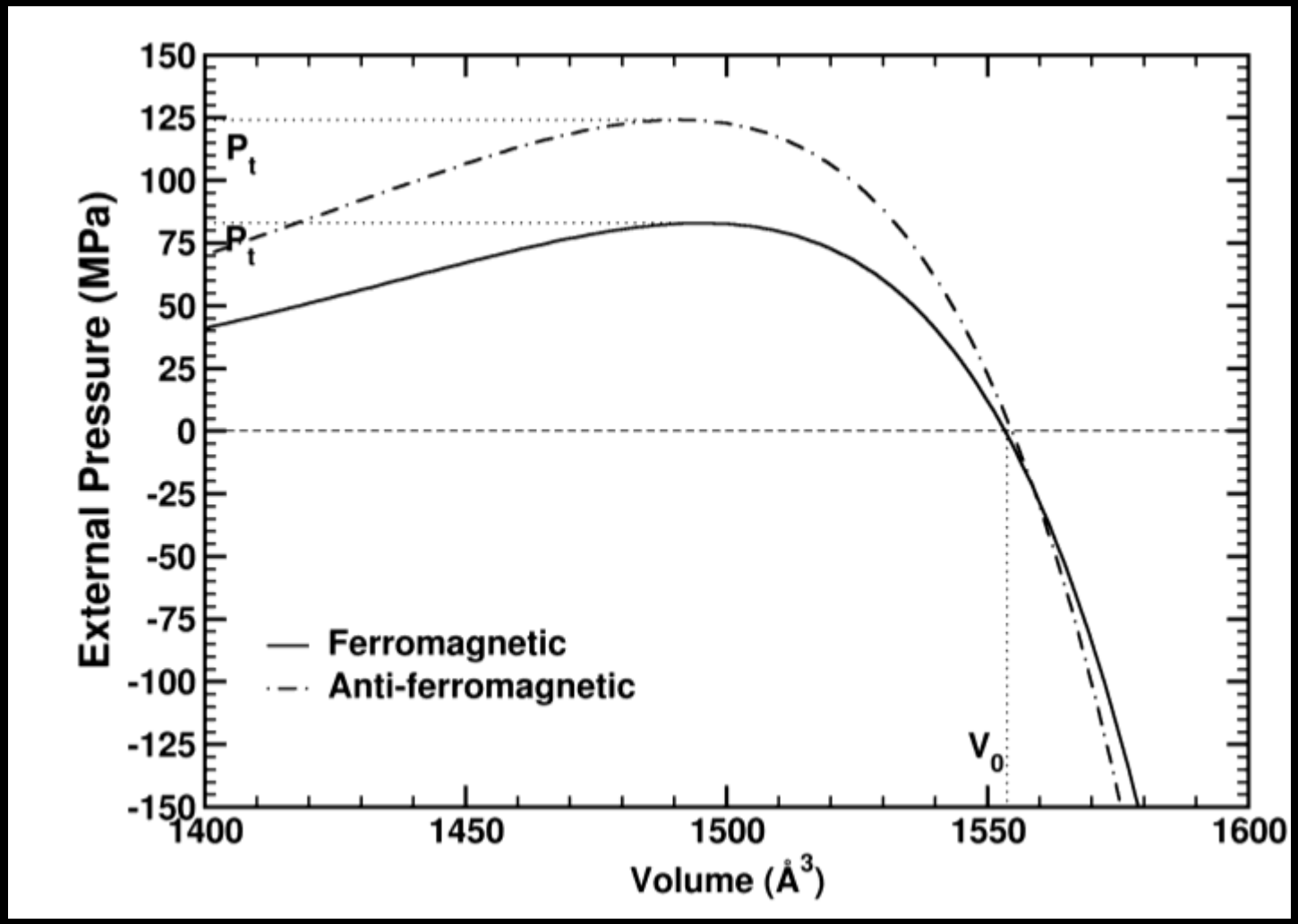


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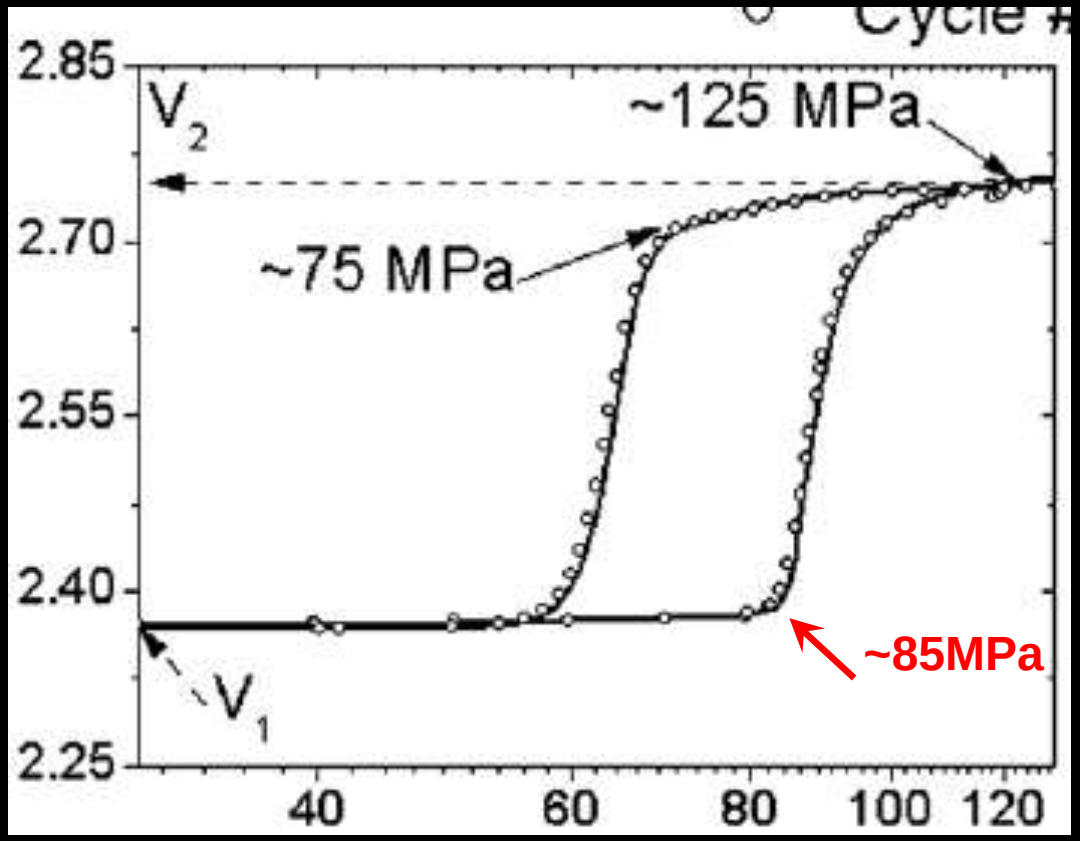


| | $P_t$ [MPa] | $V_t$ [A³] |
|---|---|---|
| FM | 83 | 1495.3 |
| AF1 | 82 | 1498.5 |
| SFM | 102 | 1495.5 |
| AF2 | 124 | 1490.7 |
| AF3 | 124 | 1490.7 |

Yot et al., Chem. Sci. 3, 1100-1104 (2012)

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# Conclusions

- Computational Materials Research provides new opportunities for materials research

- Direct comparison with experiments can provide new fundamental insights.

- Think outside the box to find grounds for comparison

# Acknowledgements


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