Novel Solid Phases by Self-Assembling of Nanoclusters

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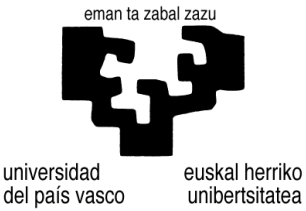
Donostia International Physics Center (DIPC) PK 1072, 20080 Donostia (Basque Country)

October 8, 2014



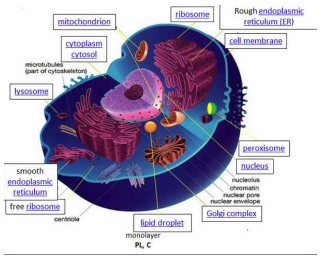
Outline

1. Introduction

Organic vs Inorganic

Organic

- Composition: C and some few other atoms



- Origin: mostly animal, vegetal and... **Synthesis**
- Relatively fast reaction rates $\Rightarrow$ kinetic control $\Rightarrow$ Metastable products allowed.

Inorganic

- Composition: Made of most elements

- Origin: mostly mineral. **Few sinthesized.**
- Slow reaction rates $\Rightarrow$ thermodynamic control $\Rightarrow$ Thermodynamic products.

Organic vs Inorganic

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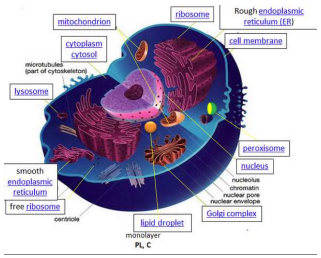

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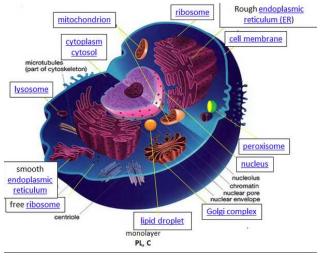

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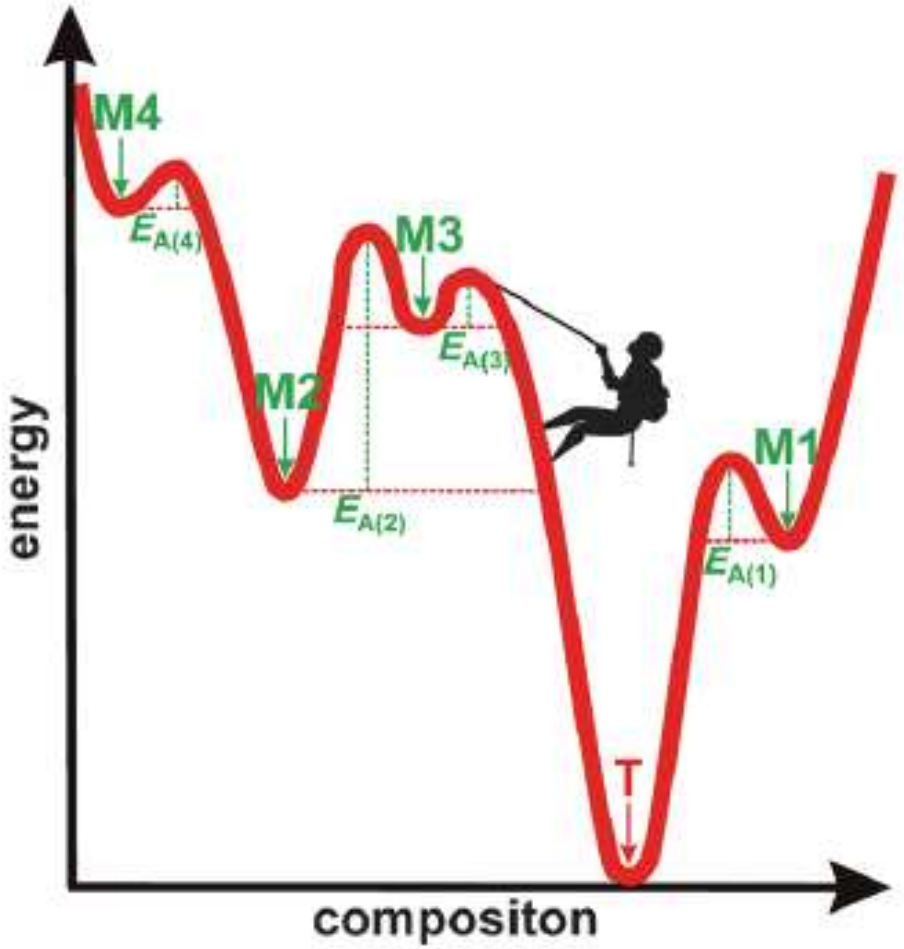

Inorganic solids

- Thermodynamic products: One or few polymorphs.
- Climb to higher metastable polymorphs possible?
- Probably new experimental strategies needed.
- Computational Chemistry: Predictive Tool.

C. Feldmann "Metastable Solids—Terra Incognita Awaiting Discovery" Angew. Chem. Int. Ed. 52, 7610-7611, 2013

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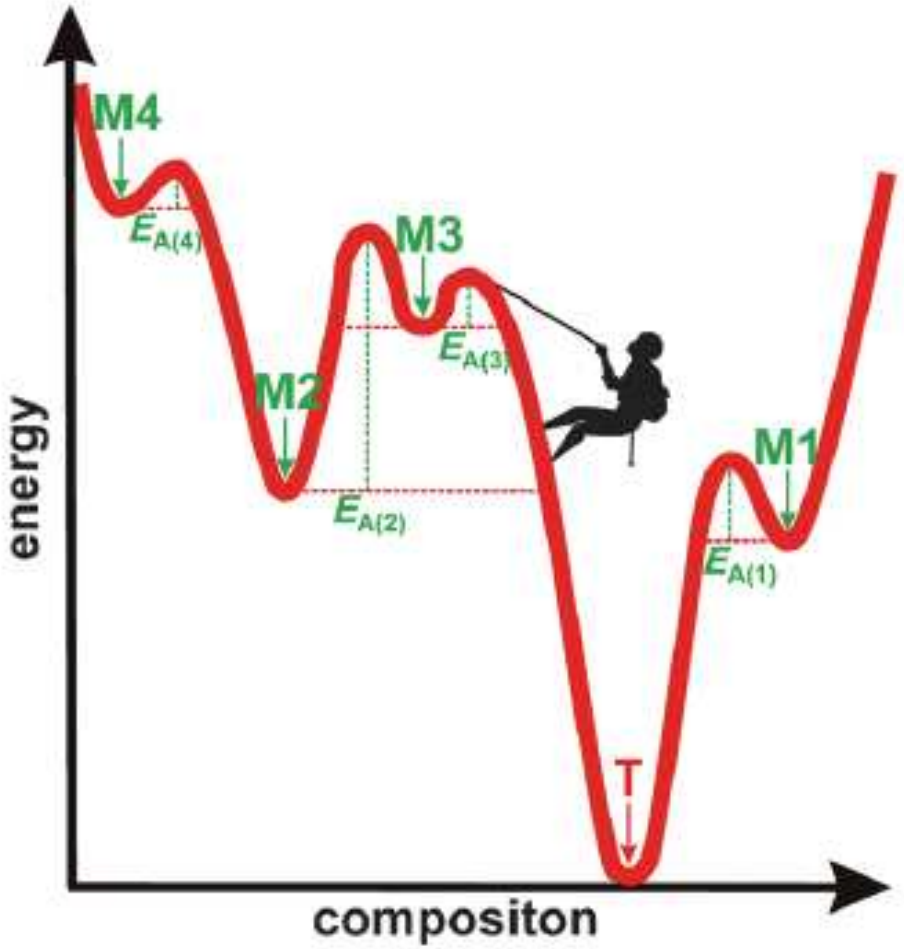

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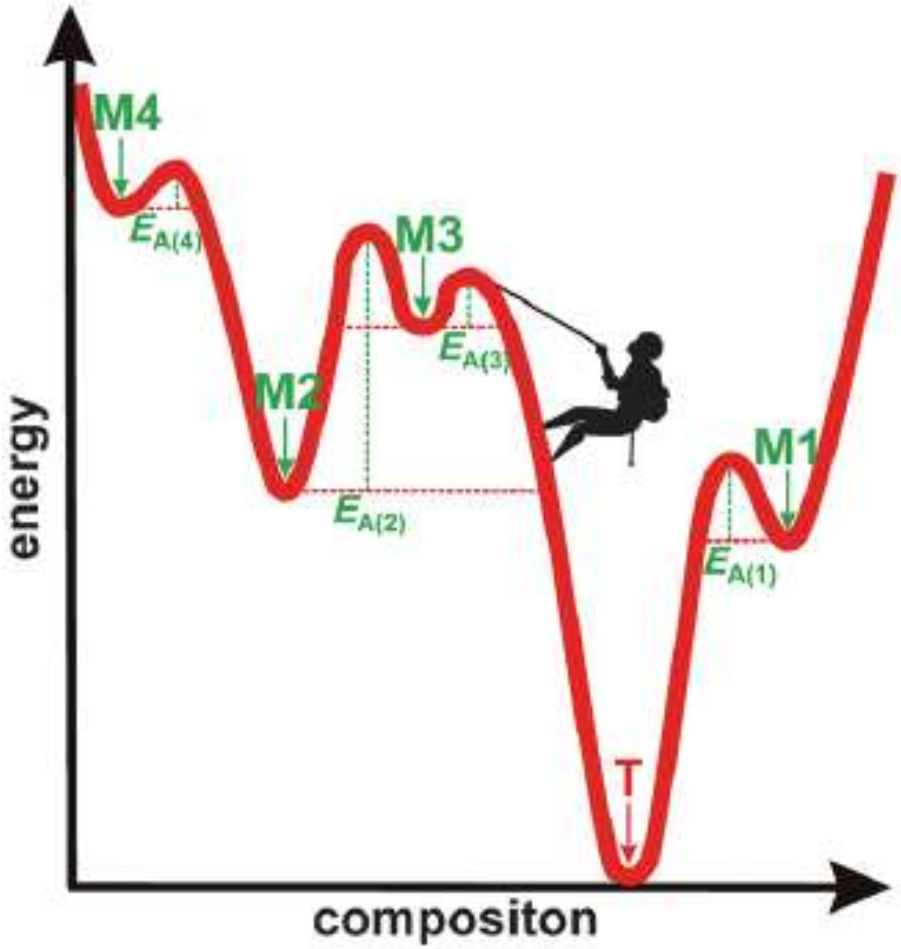

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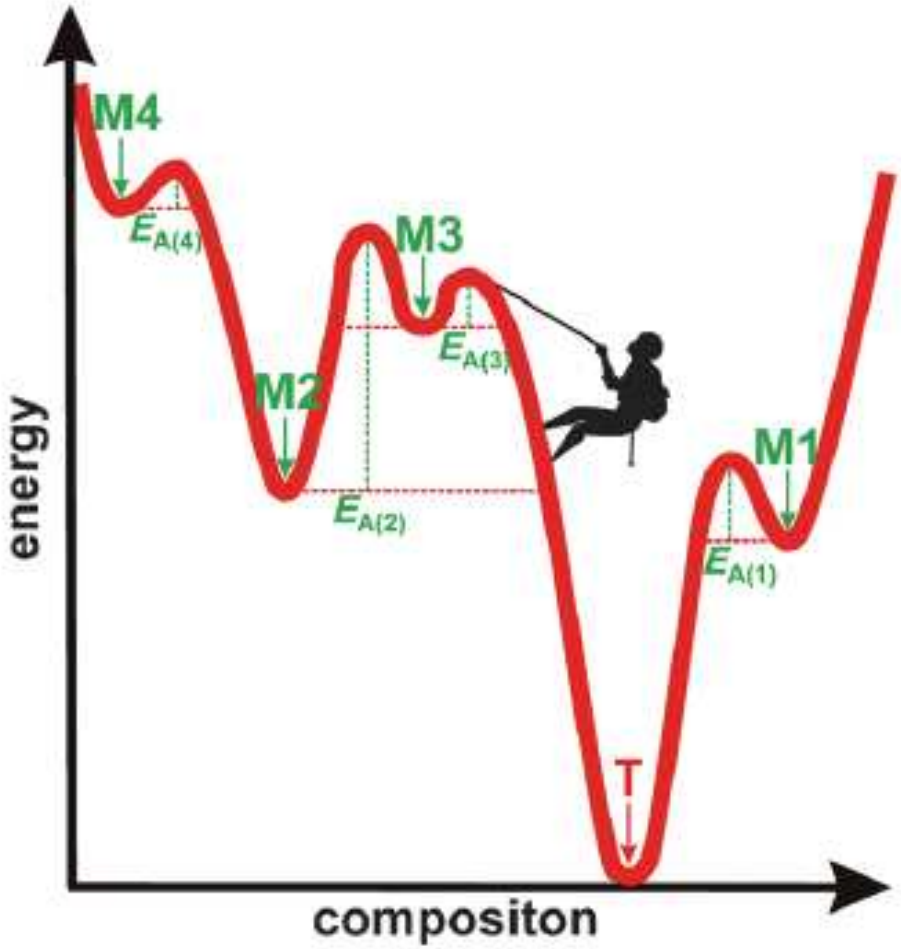

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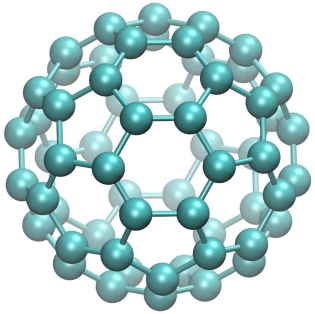
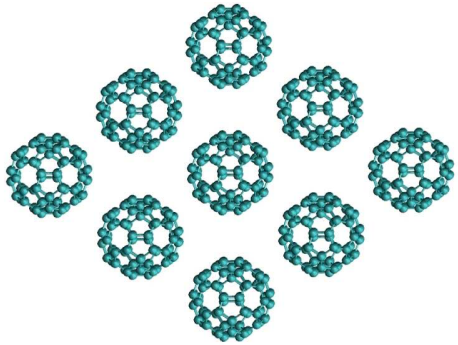
Nanoclusters as Building Blocks

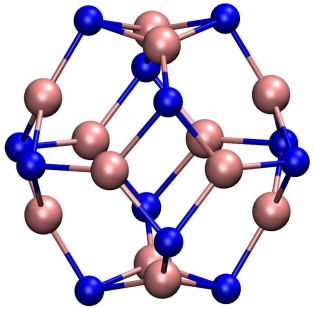


C_{60}

$\rightarrow$

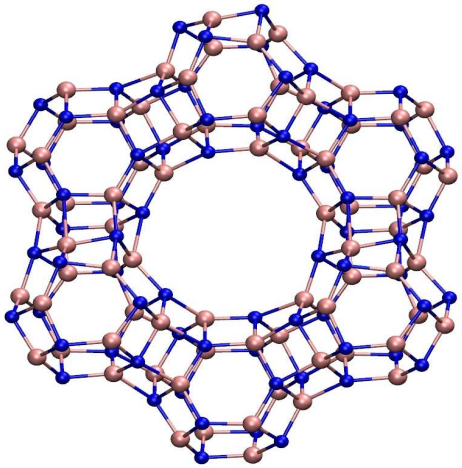


Fullerite



$(BN)_{12}$

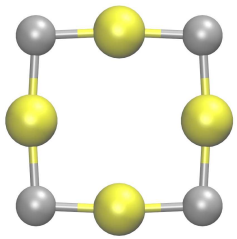
$\rightarrow$



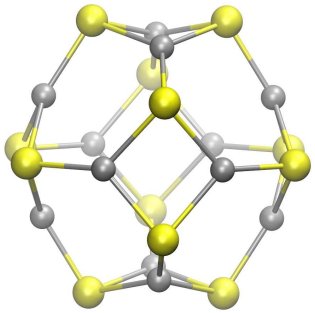
E-BN or FAU $(BN)_{12}$

II-VI Nanoclusters

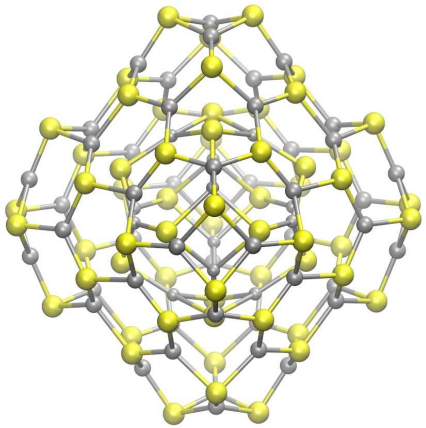
- Interesting semiconductor properties
- Synthesis: Colloidal Chemistry. Laser Ablation.



Ring-Like

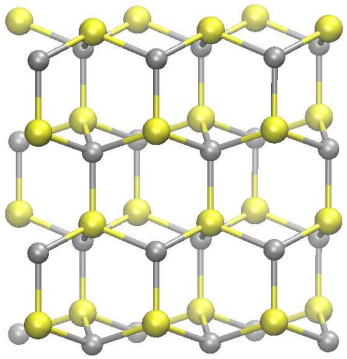


Spheroids



Onion-like

...



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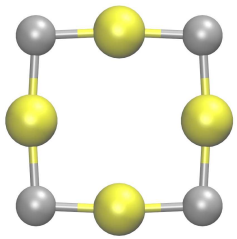

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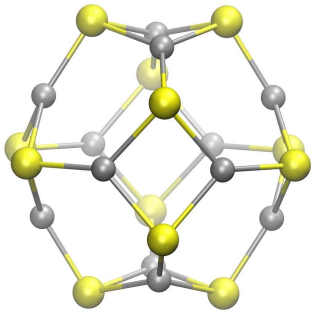

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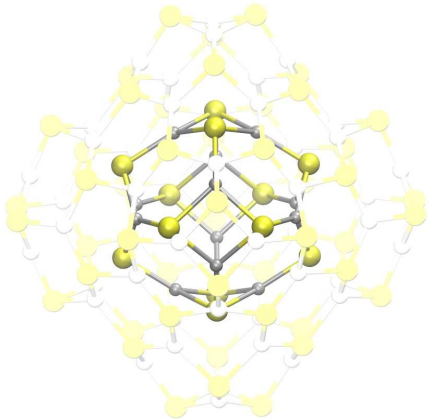

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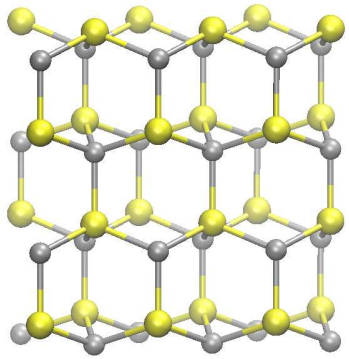

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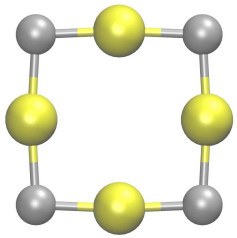

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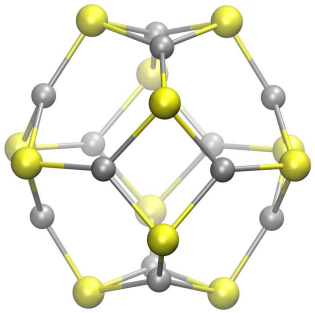

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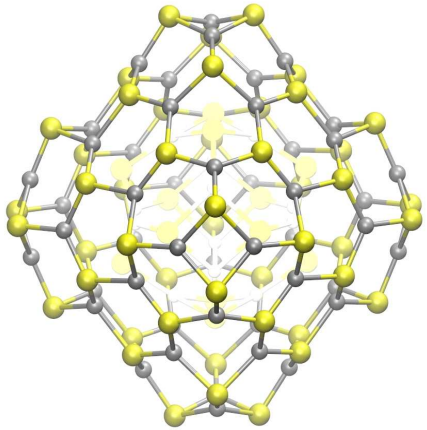

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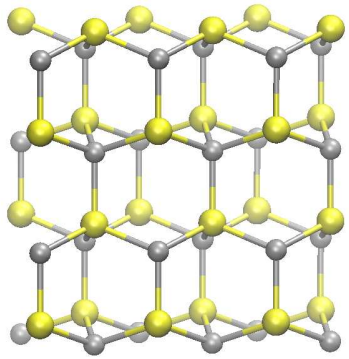

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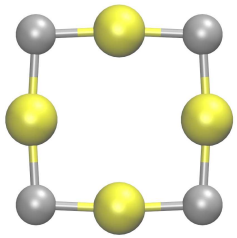

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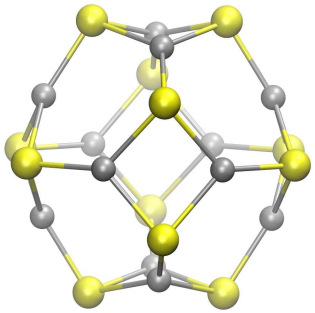

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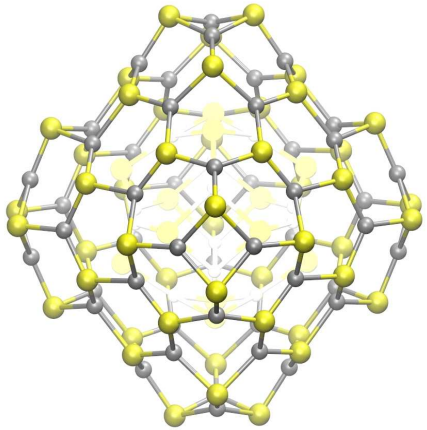

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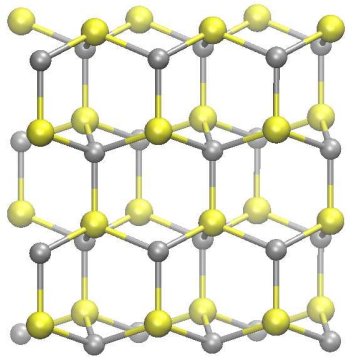

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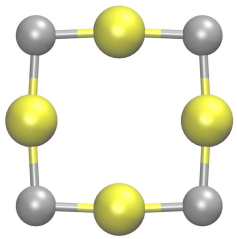

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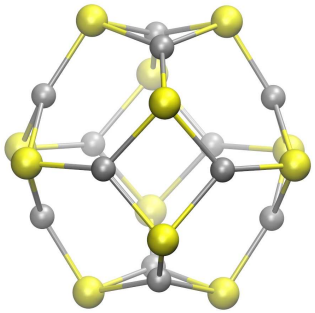

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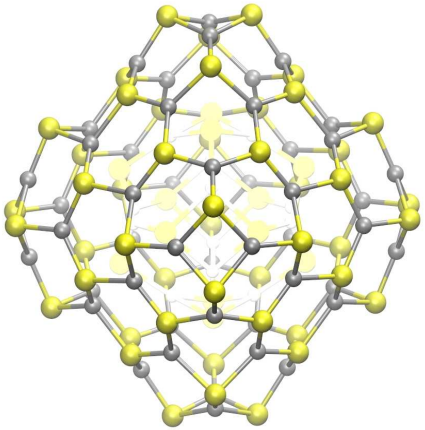

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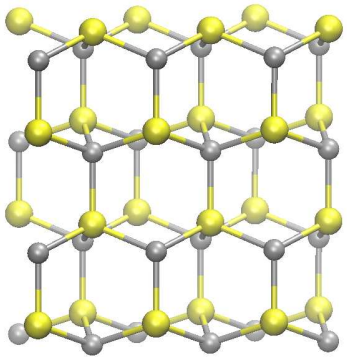

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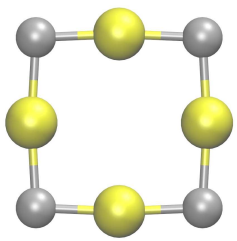

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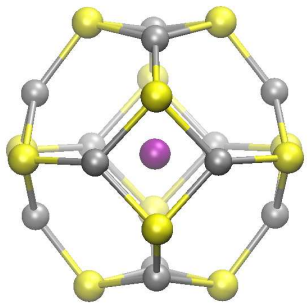

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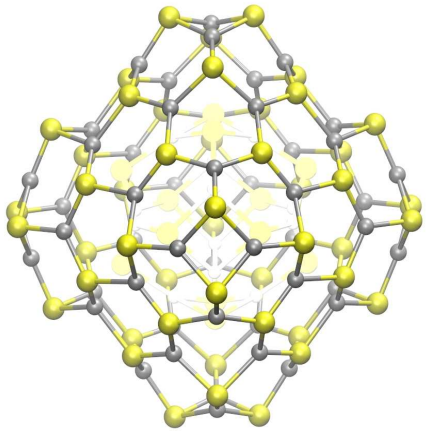

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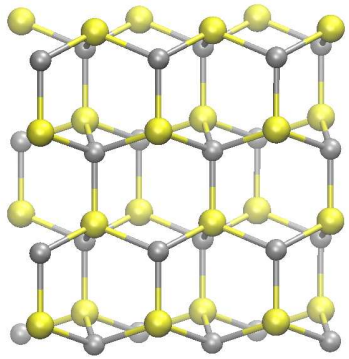


Bulk-like

Aim

Two-fold:

- Characterization of bare and endohedrally doped nanoclusters
  - E. Jimenez-Izal et. al. J. Phys. Chem. C, 115, 7829 (2011)
- Study their interactions
  - Dimers
  - Solids
    - Assembly of $(CdS)_{12}$ and $(CdS)_{16}$ bare nanoclusters
    - Assembly of $K@(CdS)_i$-$X@(CdS)_i$ nanoclusters, i= 12, 16, X= Cl, Br
  - E. Jimenez-Izal et. al., Phys. Chem. Chem. Phys. 14, 9676 (2012).

2. Methods

Methods

Gas phase calculations:

- Gaussian Software
- Gradient corrected hybrid B3LYP functional
- 6-311+G(d) for monovalent and divalent atoms
- Fully relativistic multielectron fit pseudopotentials by Dolg et al. for dopant TM and TZP quality basis set including diffuse orbitals
- SKBJ(d) core potentials and DZP basis set for nanoparticle atoms

Methods

Quantum molecular dynamic simulations and solid state calculations:

- SIESTA Software
- rPBE, DZP basis set, norm-conserving pseudopotentials

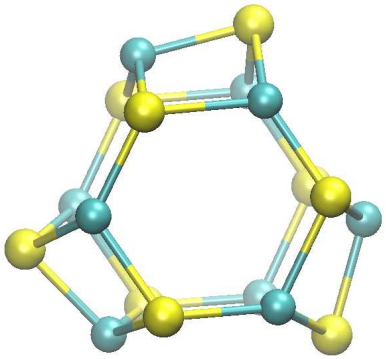
1. QMD simulations
   - Born-Oppenheimer MD simulations
   - Simulations as long as 6 ps; time-step of 1 fs
   - 298 K controlled by means of Nose thermostat
2. Solid state calculations
   - Intra- and inter-cell parameters optimized
   - 27 K points

Matxain et al. *J. Phys. Chem. C* **111**, 13354 (2007)

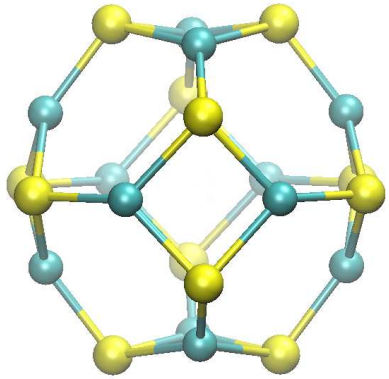
Matxain et al. *Chem. Eur. J.* **15**, 5138 (2009)

3. Results and Discussion

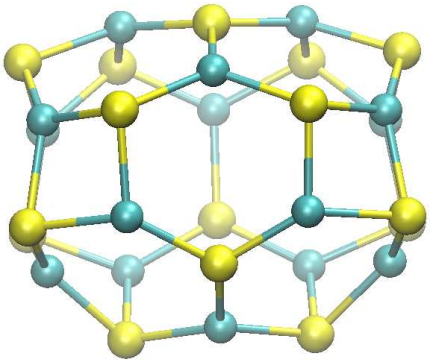
Bare Nanoclusters



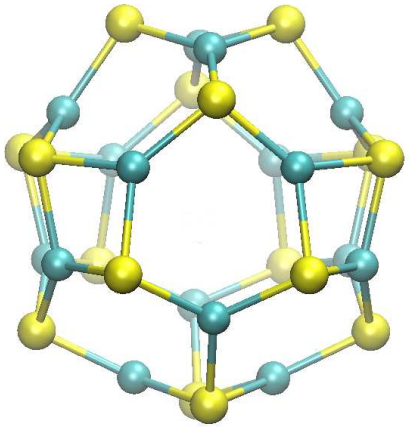
$(CdS)_9$



$(CdS)_{12}$



$(CdS)_{15}$



$(CdS)_{16}$

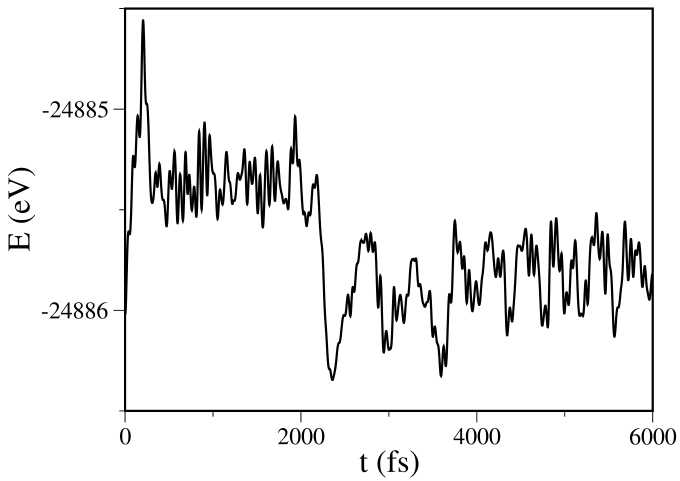
Matxain et al. *J. Phys. Chem. A* **108**, 10502 (2004)

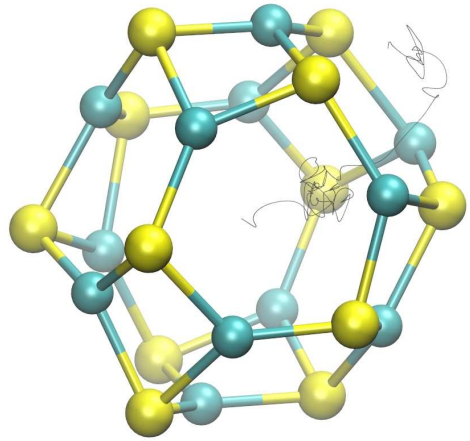
Endohedrally Doped Nanoclusters

- Endohedrally doped $(CdS)_i$ nanoclusters with **monovalent atoms**, i=9, 12, 15, 16.
  - $(Y@(CdS)_i)^{0,+1}$, Y= Na, K
  - $(X@(CdS)_i)^{0,-1}$, X= Cl, Br
- All structures local minima of the PES
- But, according to QMD calculations...

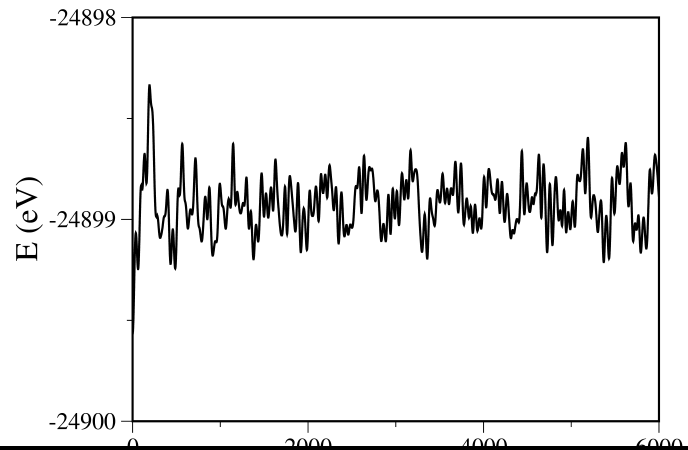
Dynamical behavior

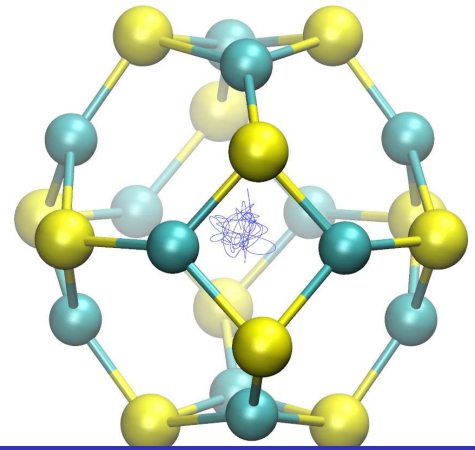
- $Na@(CdS)_{12}$: representative of all Na doped structures



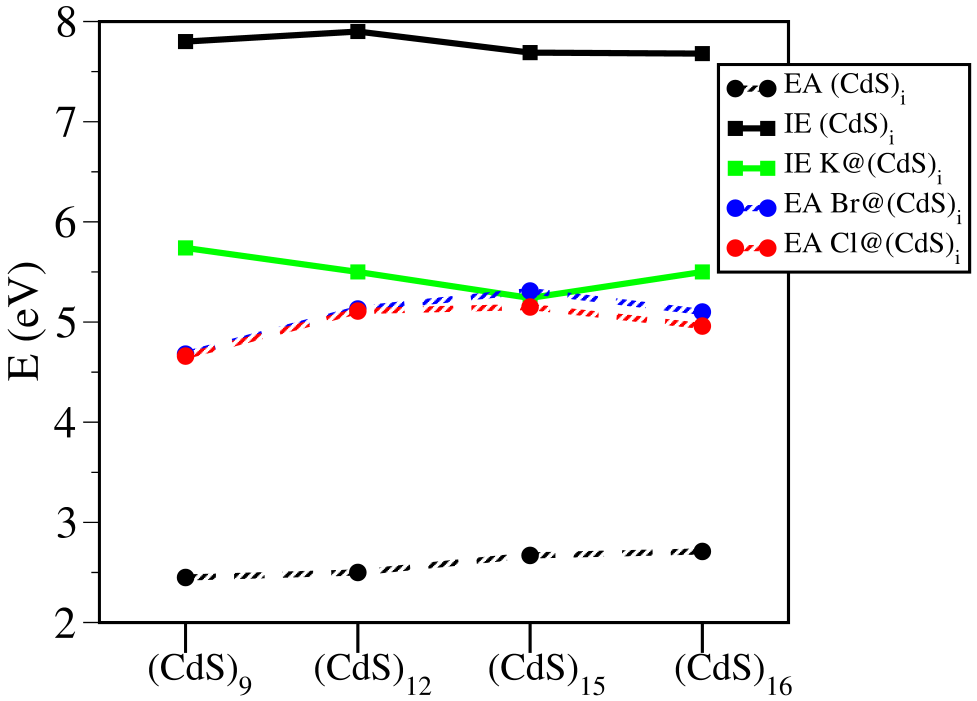


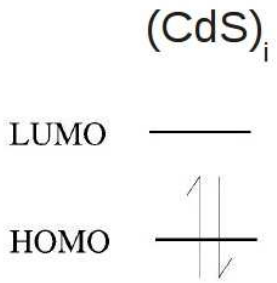
- $K@(CdS)_{12}$: representative of all the rest

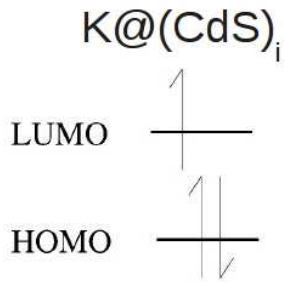


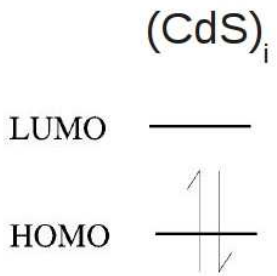


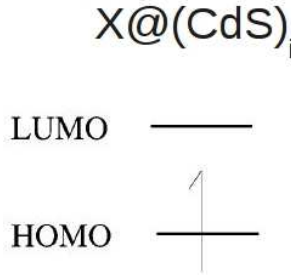
Electronic Properties











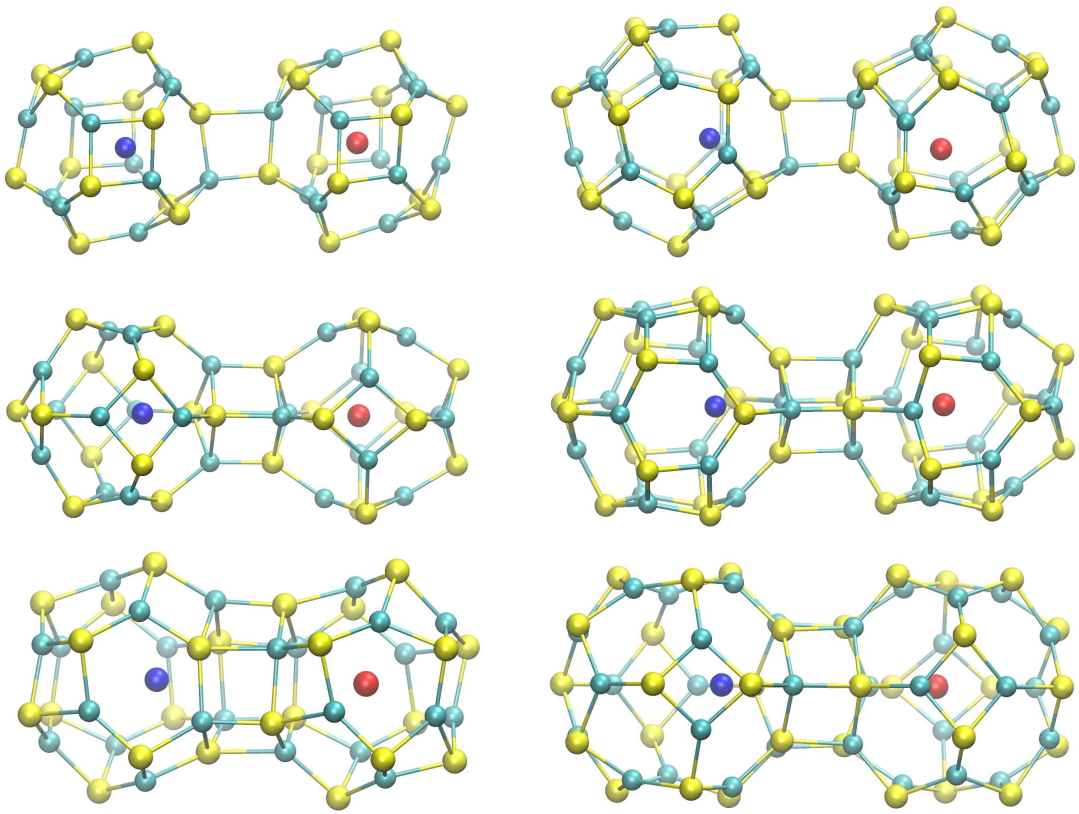
IE K $\sim$ IE K@(CdS)$_i$ $<$ IE (CdS)$_i$

EA (CdS)$_i$ $<$ EA X $<$ EA X@(CdS)$_i$

EA X@(CdS)$_i$ $\sim$ IE K@(CdS)$_i$

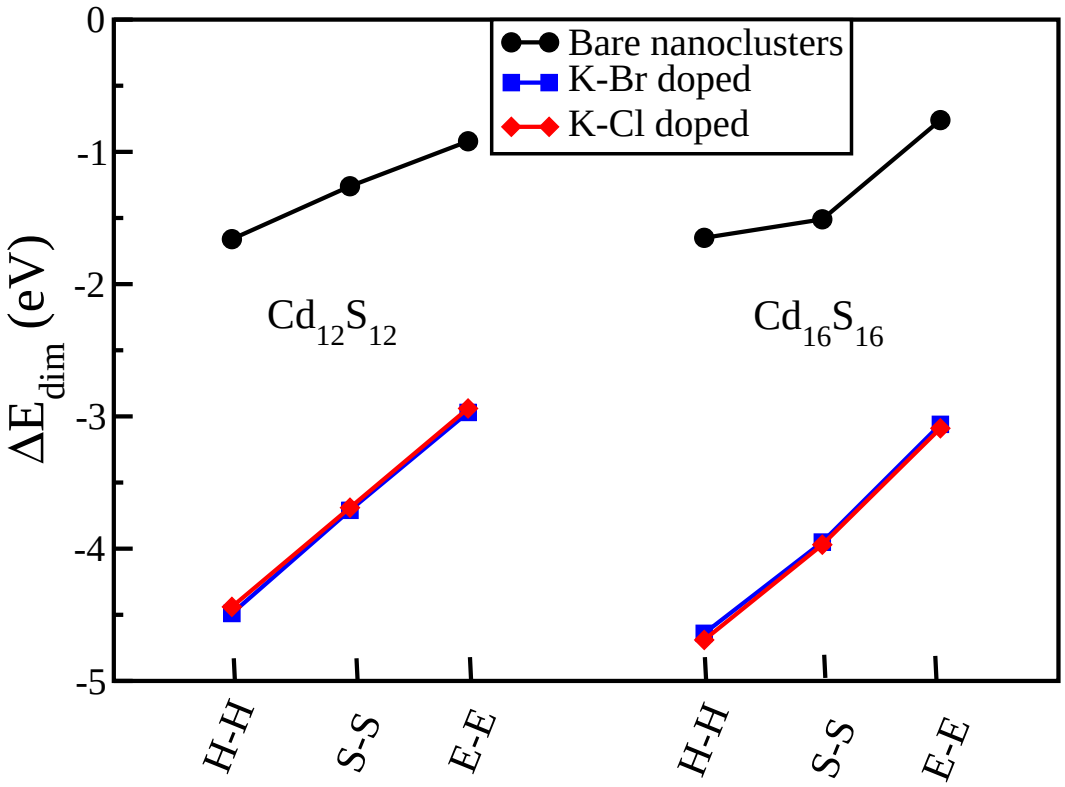
Resulting Structures of Dimers

(K-Br)@((CdS)$_i$)$_2$



Blue = Cd Yellow = S Dark blue = K Red = Br

Dimers

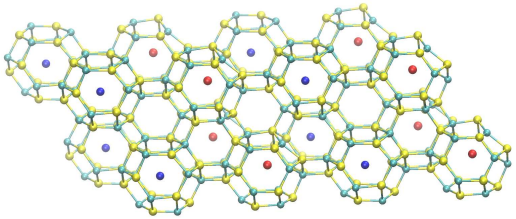


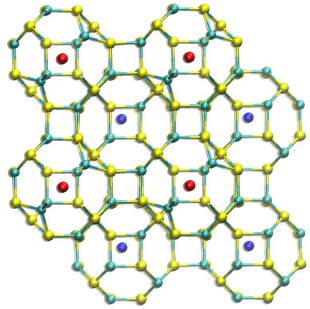
- Number of bonds ↑ ⇒ Stability ↑
- After doping: Stability ↑, $\triangle\varepsilon_{HL}$ ↓
- $q_K \sim$ 0.5 ; $q_X \sim$ -0.8 ⇒ charge transfer

Resulting Structures of Solids

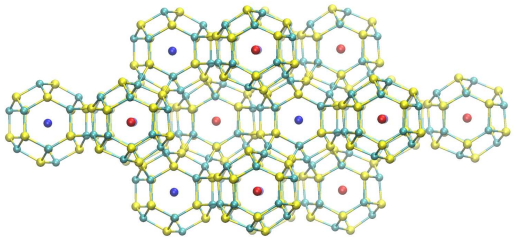
(K-Br)@(CdS)$_i$ i=12 i=16

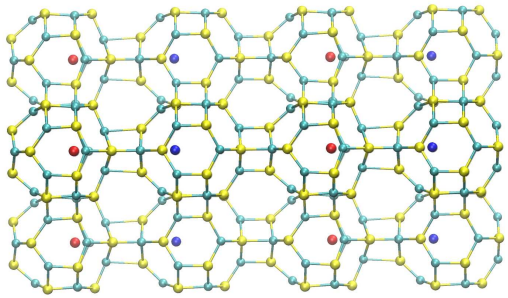
SOD



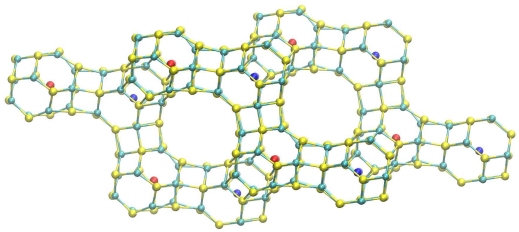


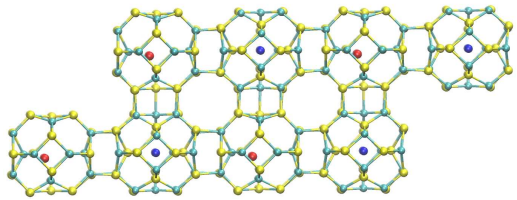
LTA





FAU

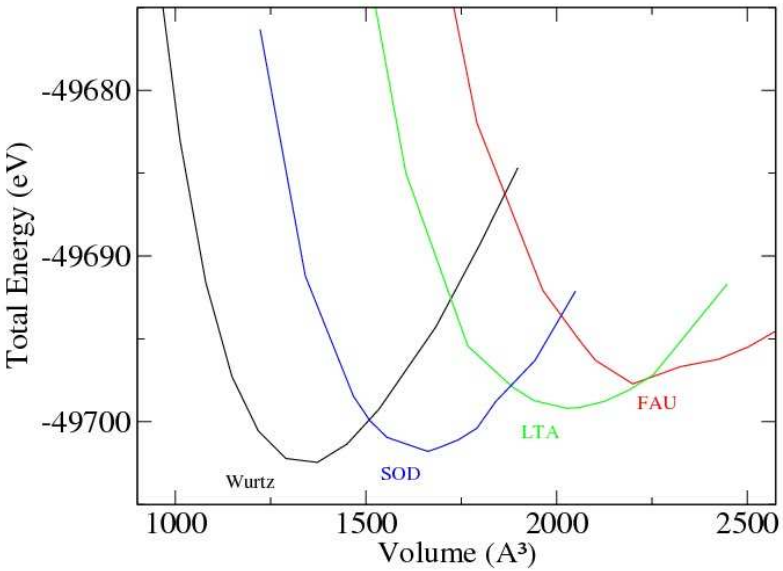




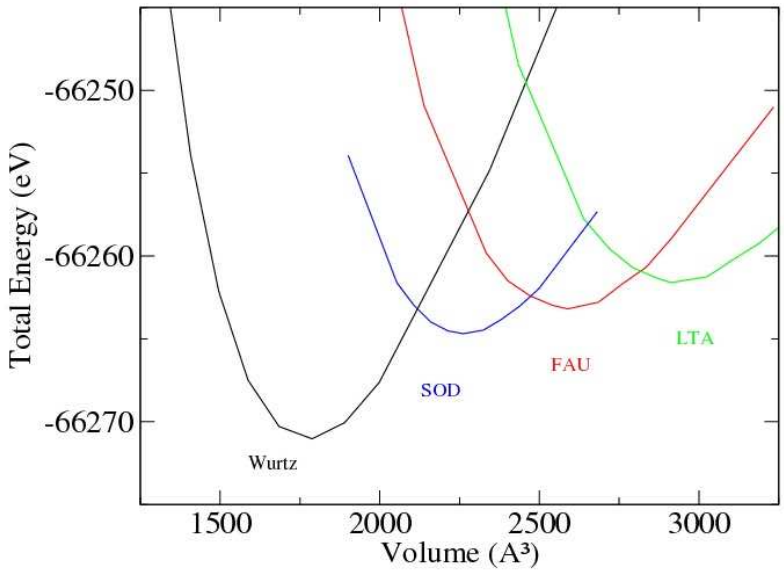
E-E $\rightarrow$SOD S-S $\rightarrow$ LTA H-H $\rightarrow$ FAU

Stability

$(CdS)_{12}$

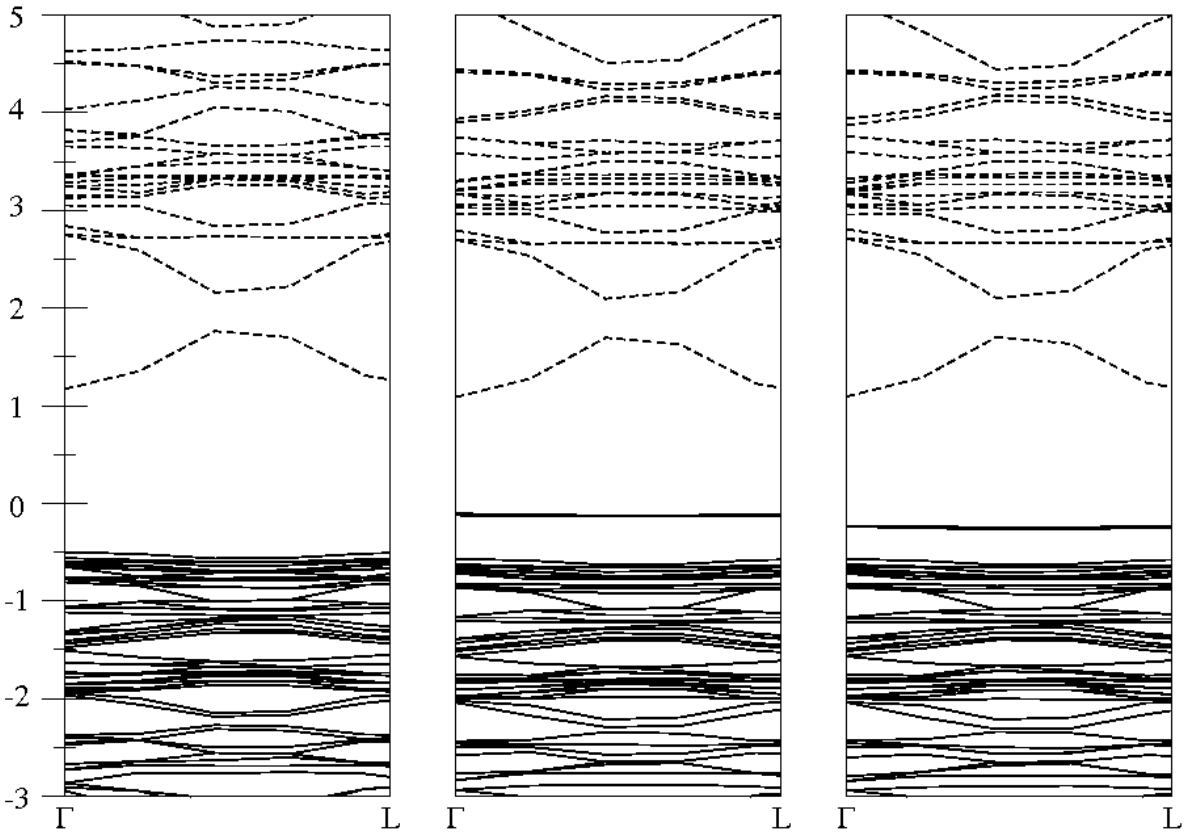


$(CdS)_{16}$



- Compactness ↑ ⇒ Stability ↑
- After doping: Stability ↑

Bands



Left: LTA $(CdS)_{12}$. $\triangle_\Gamma$= 1.66 eV.

Middle: LTA (K-Cl)@$(CdS)_{12}$. $\triangle_\Gamma$= 1.22 eV

Right: LTA (K-Br)@$(CdS)_{12}$. $\triangle_\Gamma$= 1.33 eV

After doping: $\triangle_\Gamma\downarrow$

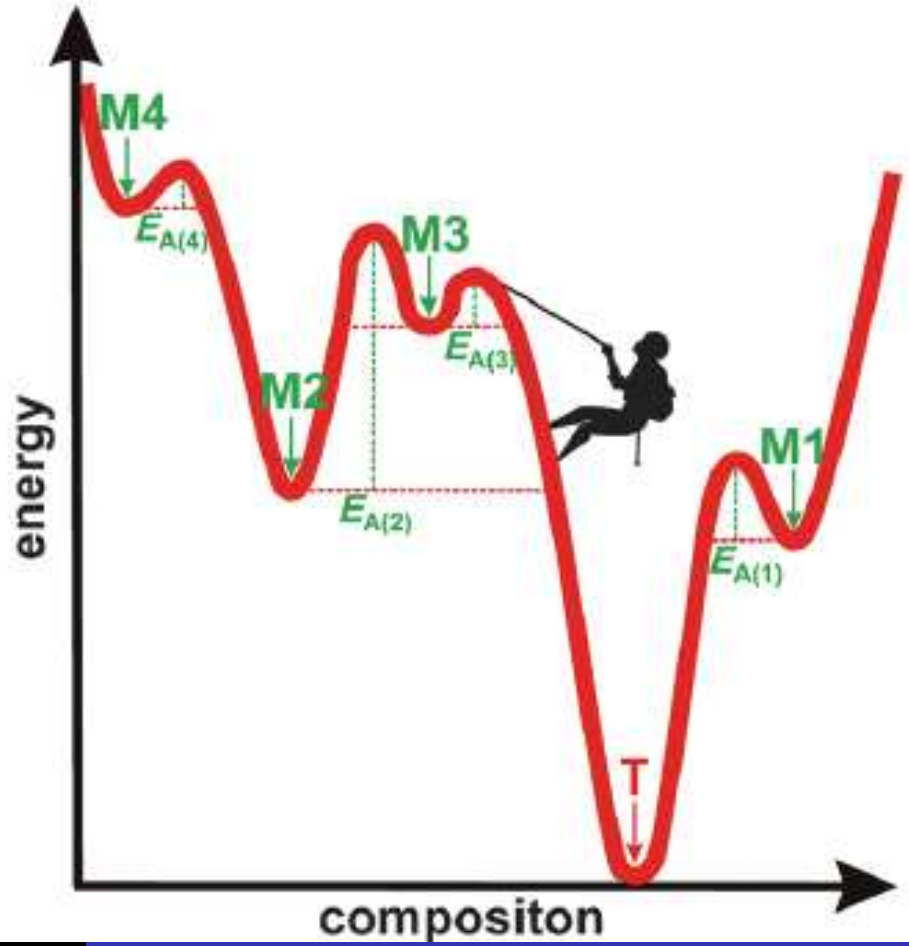
4. Conclusions

Conclusions

- New metastable CdS polymorphs
- Endohedral doping:
  - Increases the stability
  - Decreases the band-gap
- Low-dense, nano-porous materials
- Other materials:
  - II-VI, III-V, NaCl, SiO_2 etc...

Conclusions

Is there plenty of room at the top (of the potential energy surface) ?



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