

# Structure / Phase Search with DFT

Marie-Liesse Doublet

INSTITUT CHARLES GERHARDT, CNRS - Université Montpellier  
RS<sub>2</sub>E Réseau Stockage Electrochimique de l'Energie

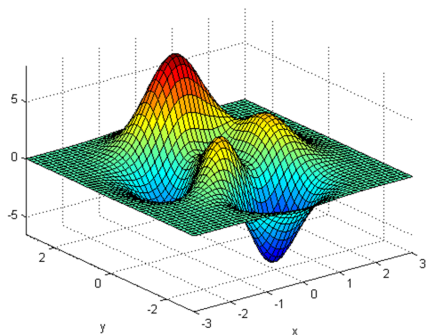
Marie-Liesse.Doublet@umontpellier.fr

February 6, 2018

# Take-Home Message 1

30 years ago, John Maddox declared that our inability to predict new crystal structure from its chemical composition is a “scandal in the physical sciences” ...[Nature 335 (1988), p. 201]

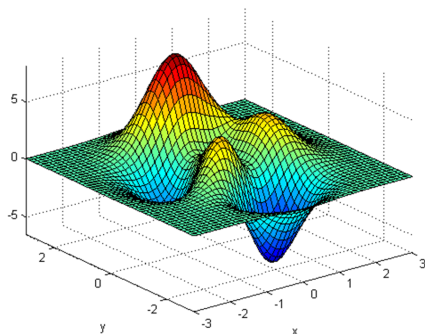
... who knows the Potential Energy Surface (PES) of a material ?



# Take-Home Message 1

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... who knows the Potential Energy Surface (PES) of a material ?



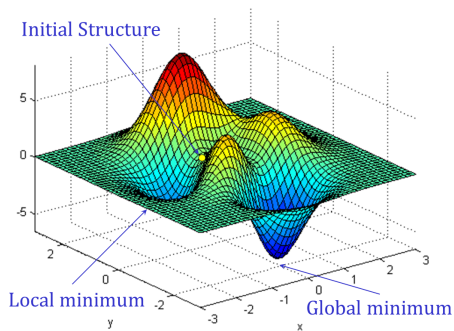
... no one !

# Exploration of the PES

- Structural relaxations in periodic DFT codes

$$\hat{H}(r_i, R_\alpha) \equiv \hat{H}_{R_\alpha}^{el}(r_i) \quad \text{Choice of the DFT XC functional}$$

$$E_{GS}^{DFT}[\rho] \longrightarrow \frac{\partial E}{\partial R_\alpha} \quad \text{Hellmann-Feynman forces}$$

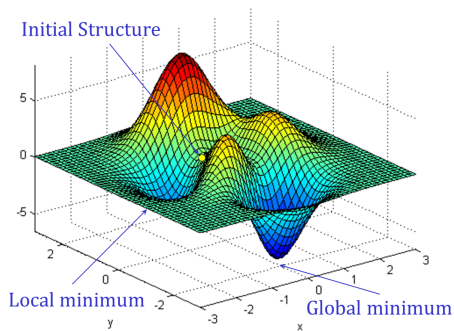


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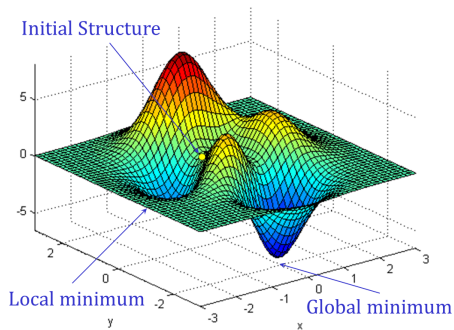
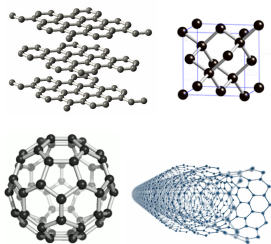
LOCAL energy minimization procedures !

# Exploration of the PES

- Structural relaxations in periodic DFT codes

Constrained simulation boxes → Impact on Polymorphism

Fully ordered structures → No statistical distribution



# Exploration of the PES

- Sampling Methods → Global minimization procedures

- Stochastic algorithms

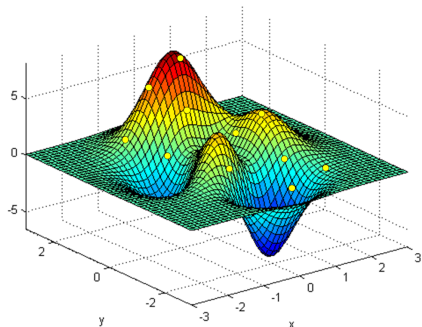
- Simulated annealing (Thermostat)  
Random displacements / perm.

- Genetic algorithm

- Crystallographic populations  
Darwin principle

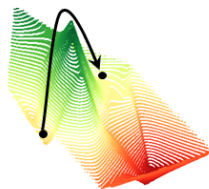
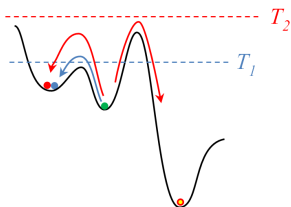
- Bayesian algorithm

- Occurrence probability  
Neuronal networks



Growing interest in the past 15 years (high-throughput calculations)

- How to get around energy barriers of PES?



- Use temperature + quenching
- Less and less used in condensed matter
- Random atomic distributions / permutations
- More and more used in condensed matter

The more you check, the more confident you are on the results ... no limits !  
You can afford "coarse" calculations to screen / identify more interesting areas



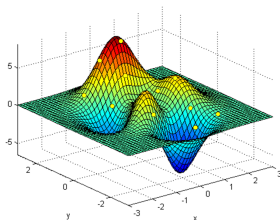
## Material Project

G. Ceder - MIT

(2006)



BAYESIAN ALGORITHM  
Probabilistic  
Neuronal networks



## USPEX

A. Oganov - NYU

(2006)



GENETIC ALGORITHM  
Evolutionary  
Darwin principle

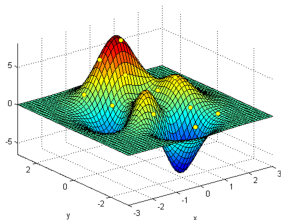
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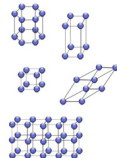
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BAYESIAN ALGORITHM  
Probabilistic  
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Corindon  $Al_2O_3$   
Hematite  $Fe_2O_3$   
Eskolaite  $Cr_2O_3$   
Karelianite  $V_2O_3$   
Tistarite  $Ti_2O_3$



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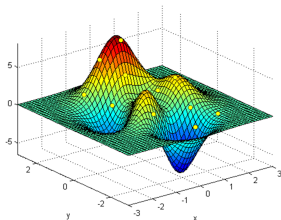
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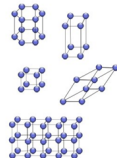
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Structure populations injected in periodic codes to perform Local Energy Minimizations

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(2006)



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### Performances

✓	PES sampling	✓
✓	Numerical cost	✓
✓	Exotic structures	✓

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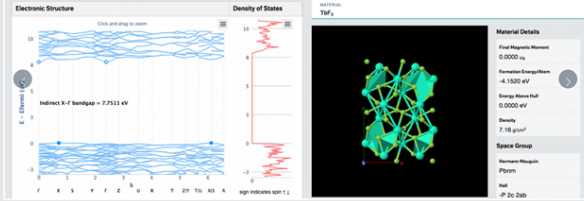
# The Material Project Initiative (MIT / Berkeley)



## The Materials Project

Harnessing the power of supercomputing and state of the art electronic structure methods, the Materials Project provides open web-based access to computed information on known and predicted materials as well as powerful analysis tools to inspire and design novel materials.

[Learn more](#)  [Tutorials](#) [Sign in or Register](#) to start using



**Electronic Structure**

Click and drag to zoom

Indirect X-F bandgap = 7.7511 eV

**Density of States**

sign indicates spin ↑ ↓

**CRYSTAL**  
**TiF<sub>6</sub>**

**Material Details**

- Final Magnetic Moment: 0.0000  $\mu_B$
- Formation Energy/Atom: -4.1520 eV
- Energy Above Hull: 0.0000 eV
- Density: 7.18 g/cm<sup>3</sup>
- Space Group: R-3m
- Hermann Mauguin: P6mm
- Hall: -P 6c 2ab

**EXPLORE MATERIALS**  
Search for materials information by chemistry, composition,

**EXPLORE BATTERIES**  
Find candidate materials for lithium batteries. Get voltage

**VISUALIZE STABILITY**  
Generate phase and pourbaix diagrams to find stable phases and

**INVENT STRUCTURES**  
Design new compounds with our structure editor and substitution

**CALCULATE**  
Calculate the enthalpy of 10,000+ reactions and compare with

Huge open source database - Just play with it !

# The Material Project Initiative (MIT / Berkeley)

The screenshot displays the Materials Project website interface. At the top, there is a navigation bar with "Home", "About", and "Apps" links. Below this is a dark header with a row of circular icons representing various tools and data sources. A tagline reads: "Use data-mined knowledge of experimental crystal data to generate potential new compounds (currently ionic systems only)".

The main content area features a periodic table of elements. A dark sidebar menu is open, titled "Structure Predictor". The menu is organized into several sections:

- Explore Materials**
  - by Elements
  - by Formula
  - by IDs
  - by mpquery
  - by Structure
- Explore Batteries**
  - by Elements
  - by Formula
  - by Material IDs
  - by Battery IDs
- Crystal Toolkit**
  - by Material IDs
  - by Battery IDs
- Structure Predictor**
  - Phase Diagram
  - Pourbaix Diagram
  - Calculate Reaction
  - Thermo
  - Compare Elements
  - Nanoporous Explorer
- Explore Molecules**
  - by Elements
  - by Formula
  - by Inchi
  - RFB Dashboard

At the bottom of the page, there are links for "About", "Forum", "Citing", "Terms of Use", and "API". A footer note states: "Powered by pymatgen, custodian and fireworks".

# The Material Project Initiative (MIT / Berkeley)

Open data online knowledge of experimental phase data to generate personalized new knowledge to be verified online.

Phase Diagram: VOFN

Enter between 2 and 4 different elements/formulae

V + O + F + N

Open Element: V, O, F, N

const  $\mu$

**Compounds**

Stable (25)	Unstable (474)
V <sub>2</sub> O <sub>3</sub>	-2.534 mp-25787
V <sub>2</sub> O <sub>3</sub> F	-2.674 mp-774138
V <sub>2</sub> O <sub>5</sub>	-2.305 mp-25620
V <sub>2</sub> O <sub>5</sub> F <sub>3</sub>	-3.054 mp-779256
V <sub>2</sub> O <sub>5</sub>	-2.524 mp-622497
V <sub>3</sub> O <sub>7</sub>	-2.375 mp-622540
V <sub>4</sub> (OF <sub>3</sub> ) <sub>3</sub>	-2.967 mp-775103
V <sub>4</sub> O <sub>5</sub> F <sub>7</sub>	-2.777 mp-849700
VF <sub>2</sub>	-3.004 mp-555934
VF <sub>3</sub>	-3.228 mp-555931
VF <sub>4</sub>	-3.022 mp-554799
VF <sub>5</sub>	-2.827 mp-558797
VN	-1.355 mp-1018027

NATURAL: VOF<sub>2</sub> ID: mp-565784 DOI: 10.17188/1273163

Material Details

Final Magnetic Moment: 0.000  $\mu_B$

Magnetic Ordering: Non-magnetic

Formation Energy / Atom: -2.753 eV

Energy Above Hull / Atom: 0.000 eV

Density: 2.89  $g/cm^3$

Decomposes To: Stable

Band Gap: 3.655 eV

Space Group: P2<sub>1</sub>/c [14]

Hermann Mauguin: P2<sub>1</sub>/c [14]

Hall: -P 2yc

Point Group: 2/m

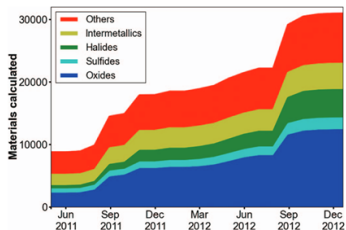
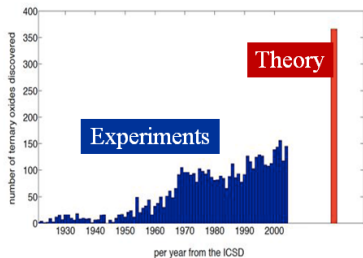
Crystal System: monoclinic

Density of States

Band Structure

Warning! Semi-local DFT tends to severely underestimate bandgaps. Please see the site for more info.

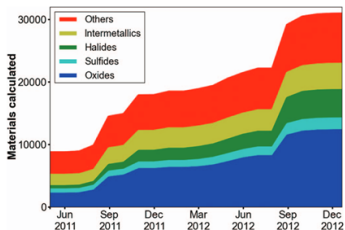
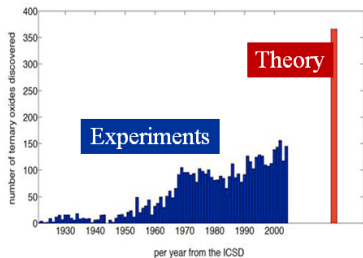
# Combinatorial Approaches (Bayesian or Genetic)



Very powerful to discover new structures but ...



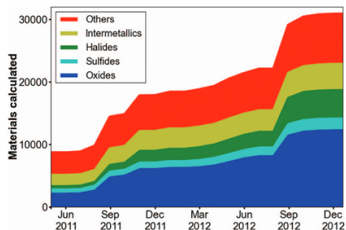
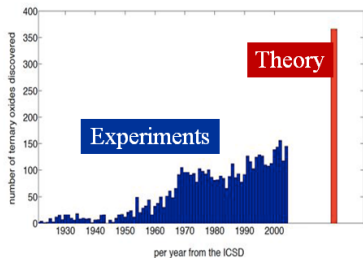
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- Perfectly ordered phases
- What about interpretations ?

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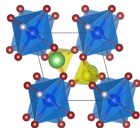
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- Perfectly ordered phases
- What about interpretations ?

... how many of them will be synthesized?  
... how many of them will have the targeted properties?

# Example 1

- The *tavorite*  $\text{LiFeSO}_4\text{F}$  electrode

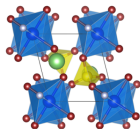


<i>Tavorite Structure</i>	V (volt)
$\text{FeSO}_4\text{F} + \text{Li} \rightarrow \text{LiFeSO}_4\text{F}$	3.6
$\text{AgSO}_4\text{F} + \text{Li} \rightarrow \text{LiAgSO}_4\text{F}$	4.98
$\text{CoSO}_4\text{F} + \text{Li} \rightarrow \text{LiCoSO}_4\text{F}$	4.93
$\text{CrSO}_4\text{F} + \text{Li} \rightarrow \text{LiCrSO}_4\text{F}$	2.95
$\text{CuSO}_4\text{F} + \text{Li} \rightarrow \text{LiCuSO}_4\text{F}$	5.09
$\text{MnSO}_4\text{F} + \text{Li} \rightarrow \text{LiMnSO}_4\text{F}$	4.27
$\text{NiSO}_4\text{F} + \text{Li} \rightarrow \text{LiNiSO}_4\text{F}$	5.35
...	...

Mueller et al. Chem. Mater. 23 (2011) 3854

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<i>Tavorite Structure</i>	V (volt)	Experimental Structures
$\text{FeSO}_4\text{F} + \text{Li} \rightarrow \text{LiFeSO}_4\text{F}$	3.6	EXP
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...	...	...

Poor or no electrochemical activity

Mueller et al. Chem. Mater. 23 (2011) 3854

Computational (high-throughput) Approaches can be very powerful but need to be combined with Conceptual Approaches to perform better

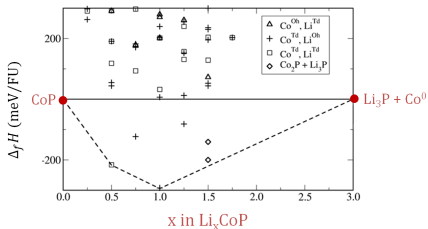
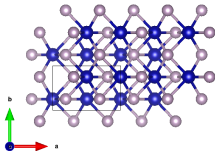
Mix Algorithms & Computations  
with Concepts & Chemical Knowledge

# Mixing Algorithms with Chemical Knowledge

Electrochemical Reaction :  $\text{CoP} + 3\text{Li} \rightleftharpoons \text{Co}^0 + \text{Li}_3\text{P}$

- 1 Use what you know about metal environment, chemical bonding, crystallography to built hypothetical but realistic initial populations
- 2 Use stochastic procedures to make random displacements and/or permutations
- 3 Compute "Phase Stability Diagrams"

$$\Delta_f H(x) = E_{\text{Li}_x\text{CoP}}^{\text{DFT}} - \left\{ \frac{x}{3} \left( E_{\text{Co}^0}^{\text{DFT}} + E_{\text{Li}_3\text{P}}^{\text{DFT}} \right) + \frac{2x}{3} E_{\text{CoP}}^{\text{DFT}} \right\}$$

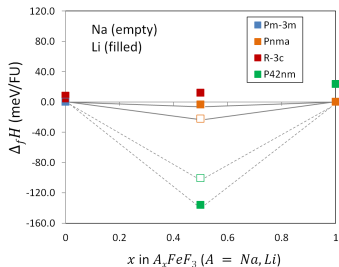


Check the dynamic stability with phonons or experiments

# Mixing Computations with Crystal Structures Analysis

(2006) Electrochemical Reaction :  $FeF_3(R\bar{3}c) + 0.5Li \rightarrow Li_{0.5}FeF_3(P4_2nm)$

(2017) New Mechanism :  $NaFeF_3 - 1Na \rightarrow FeF_3(Pm\bar{3}m)$        $FeF_3 + Li(Na) \rightleftharpoons Li(Na)FeF_3$

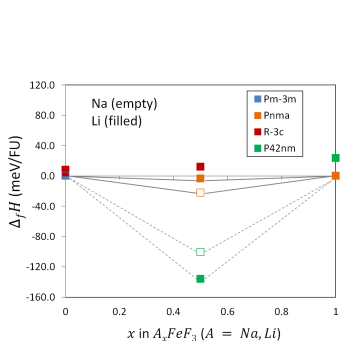


**Kinetic vs. Thermodynamic control**

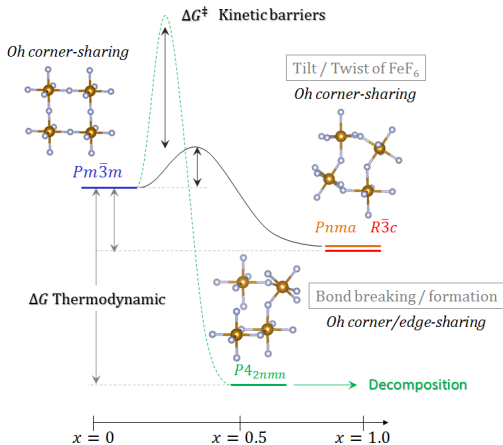
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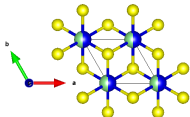


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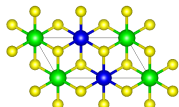
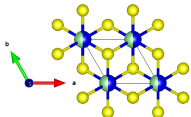




- How to account for fractional site occupations with PERIODIC DFT CALCULATIONS?

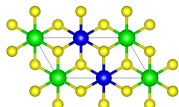
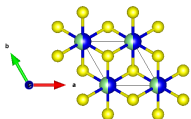


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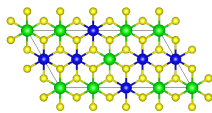
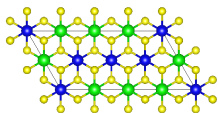


$2 \times 1 \times 1$  supercell

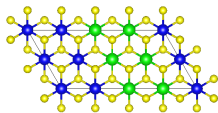
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$2 \times 1 \times 1$  supercell



$2 \times 2 \times 1$  supercells

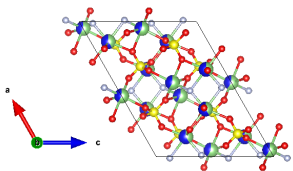


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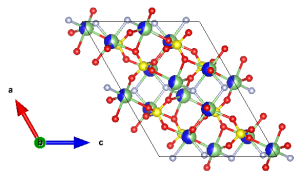
- Use Lattice Model to build Cluster Expansion of Energy

$$E(\sigma) = E_0 + \sum_i V_i \sigma_i + \sum_{\langle i,j \rangle} V_{i,j} \sigma_{i,j} + \dots$$

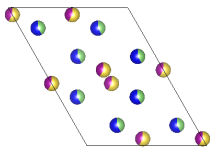
## 2) Sometimes cheaper to look at Local Chemical Bonds



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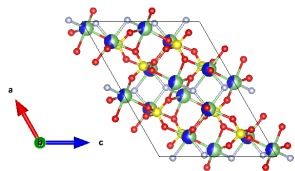
$LiFe^{2+}SO_4F$



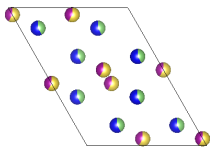
4900 configurations !

2  $\neq$  sites M1 and M2

## 2) Sometimes cheaper to look at Local Chemical Bonds



$\text{LiFe}^{2+}\text{SO}_4\text{F}$



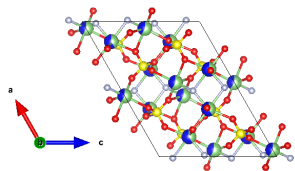
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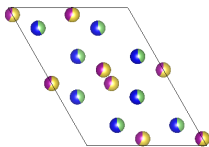
$\text{Fe}^{2+} - \text{Fe}^{2+}$

- corner-sharing ( $d=3.6\text{\AA}$ )
- edge-sharing ( $d=3.1\text{\AA}$ )

## 2) Sometimes cheaper to look at Local Chemical Bonds



$\text{LiFe}^{2+}\text{SO}_4\text{F}$

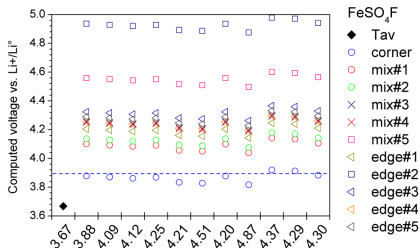


4900 configurations !

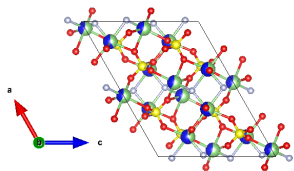
$2 \neq$  sites **M1** and **M2**

$\text{Fe}^{2+} - \text{Fe}^{2+}$

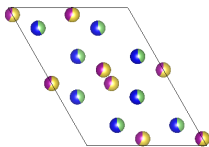
- corner-sharing ( $d=3.6\text{\AA}$ )
- edge-sharing ( $d=3.1\text{\AA}$ )



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$\text{LiFe}^{2+}\text{SO}_4\text{F}$

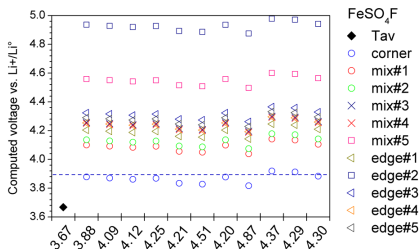


4900 configurations !

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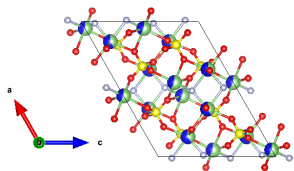


$\text{Fe}^{3+} - \text{Fe}^{3+}$

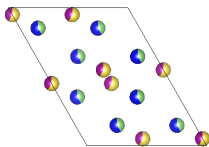
- corner-sharing ( $d=3.6\text{\AA}$ )



## 2) Sometimes cheaper to look at Local Chemical Bonds



$\text{LiFe}^{2+}\text{SO}_4\text{F}$

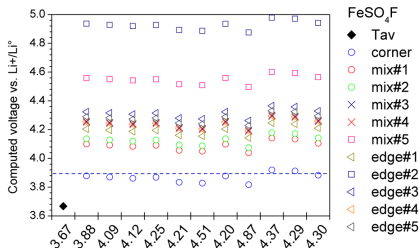


4900 configurations !

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- corner-sharing ( $d=3.6\text{\AA}$ )
- edge-sharing ( $d=3.1\text{\AA}$ )



$\text{Fe}^{3+} - \text{Fe}^{3+}$

- corner-sharing ( $d=3.6\text{\AA}$ )
- ⊕ Still consistent with M1/M2 disorder
- ⊕ Equivalent results whatever  $U_{\text{Fe}}$  (2-6 eV)

## Take-Home Message 3

Sometimes computations are less required than chemical intuitions, basic rules of chemical bonding, electronegativity, polarisability ... to make rational design of new materials

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Most often, the "ideal structure / phase" you are looking for to improve one given target property / application already exists in the crystallographic databases.

## Take-Home Message 3

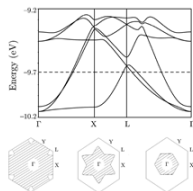
Sometimes computations are less required than chemical intuitions, basic rules of chemical bonding, electronegativity, polarisability ... to make rational design of new materials

Most often, the "ideal structure / phase" you are looking for to improve one given target property / application already exists in the crystallographic databases.

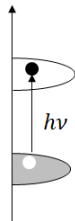
You just don't know where to search it ...

# Tuning a Property through Material Functionalization

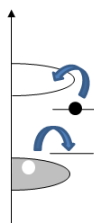
## Transport



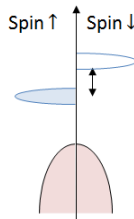
## Optical



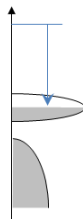
## Doping



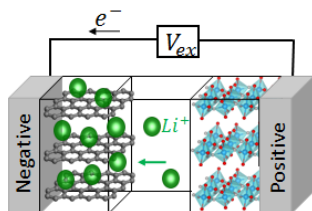
## Magnetism



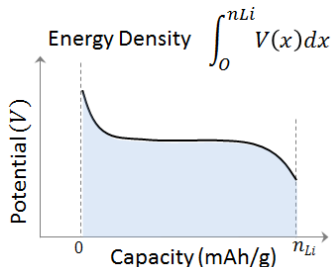
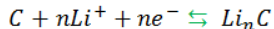
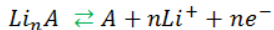
## Redox



# Design of Redox Materials



Discharge / Charge

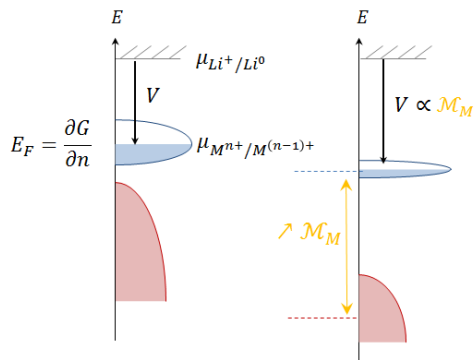


Potential  $V(\text{Volt}) = -\frac{1}{nF} \Delta_r G$

Capacity  $C(\text{mAh/g}) = \frac{\Delta x_{Li} \cdot F}{\mathcal{M}}$

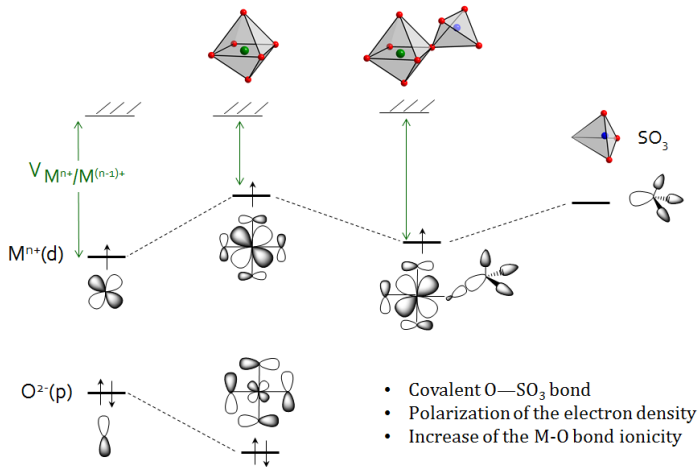
# Design of Redox Materials

- Conceptual Approach to the Potential  
Goodenough (1997)



# Design of Redox Materials

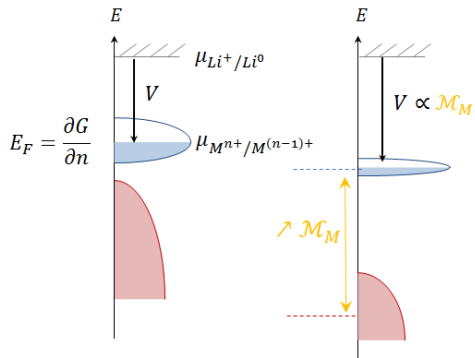
- Conceptual Approach to the Potential Molecular Orbital Picture (local)





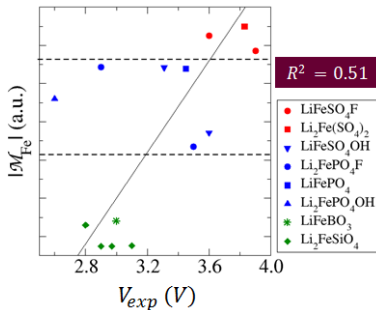
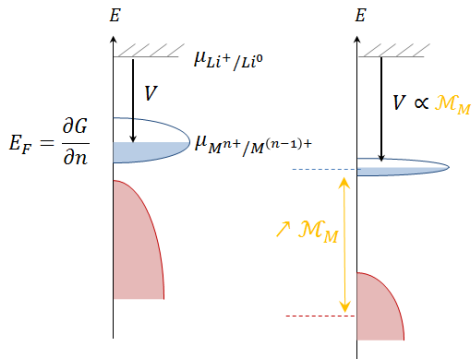
# Design of Redox Materials

- Conceptual Approach to the Potential  
Goodenough (1997)



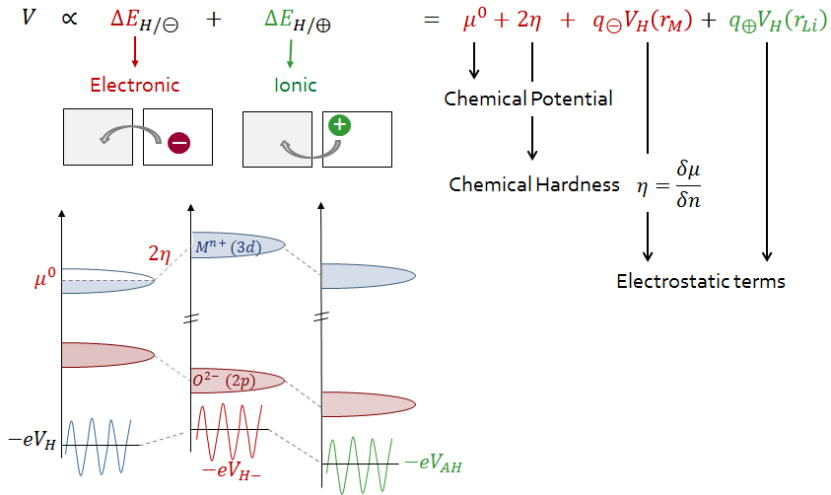
# Design of Redox Materials

- Conceptual Approach to the Potential  
Goodenough (1997)



# Design of Redox Materials


- Conceptual / Perturbative Approach to the Potential



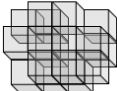
# Design of Redox Materials

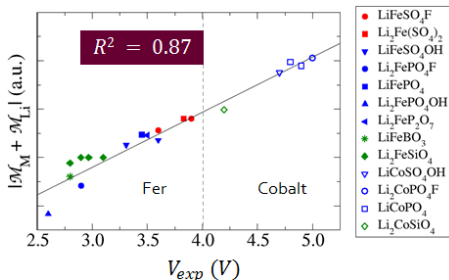
- Conceptual / Perturbative Approach to the Potential

$$V \propto \underbrace{\Delta E_{H/\ominus}}_{\text{Electronic}} + \underbrace{\Delta E_{H/\oplus}}_{\text{Ionic}} = \underbrace{\mu^0 + 2\eta}_{\text{Short-Range}} + \underbrace{q_{\ominus}V_H(r_M) + q_{\oplus}V_H(r_{Li})}_{\text{Long-Range}}$$



M-L



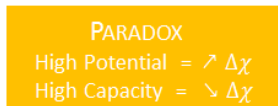
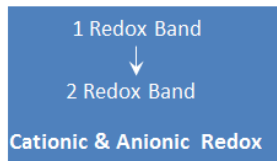
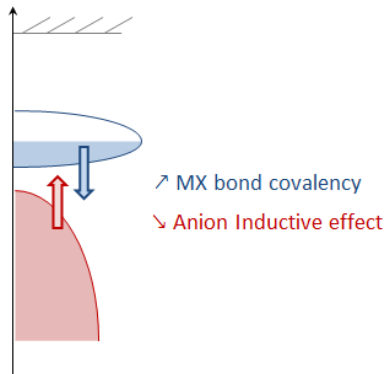


- Works pretty well
- New SR and LR Descriptors
- We know where to search in the database ...

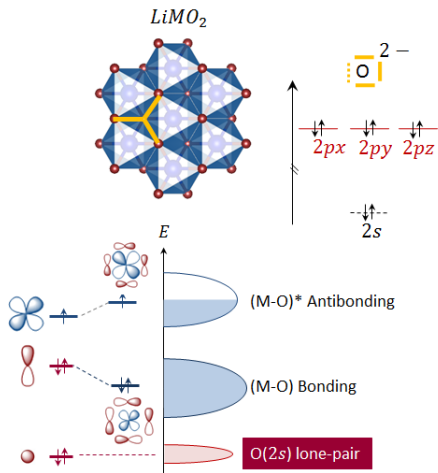
# Design of Redox Materials

- Conceptual Approach to the Capacity

J. Rouxel (1996) "Anion-cation redox competition and the formation of new compounds in highly covalent systems"

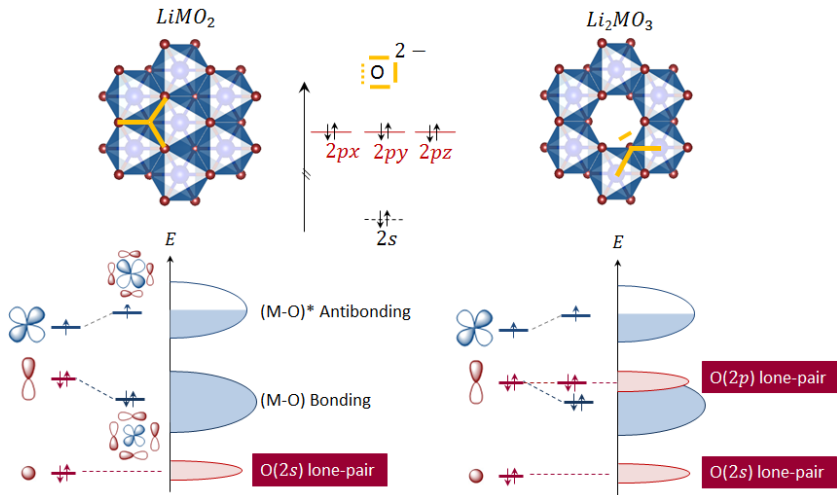


# Design of Redox Materials



know to be instable when removing Li

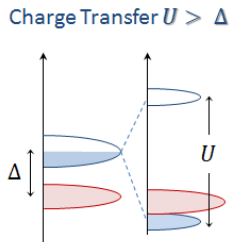
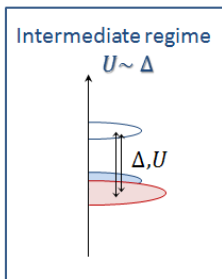
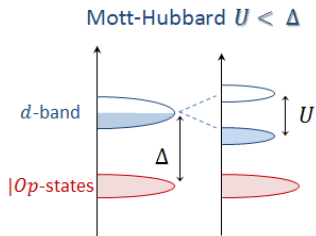
# Design of Redox Materials



Known to be unstable when removing Li

Work much better but not for all TMs

# Design of Redox Materials



M(4d), M(5d) High Energy Density

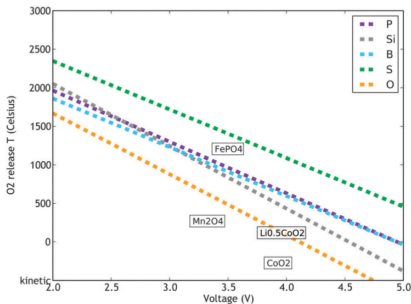
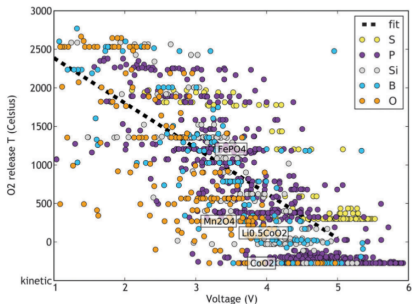
M(3d) Structure Instability

Energy & Envir. Sci. 17, 5942-5953 (2017)



# Design of Redox Materials

- Voltage vs.  $O_2$  release



PCCP 17, 5942-5953 (2015)

Do you really need so many calculations were needed ?

Never forget that low-energy properties of materials are mainly governed / dictated by crystal structures and local chemical bonding !

- Global exploration of PES are very tough procedures that sometimes work, sometimes not. Not necessarily related to DFT weakness when it fails !
- Computational (high-throughput) calculations must be combined with more Conceptual approaches to accelerate the discovery of new materials
- Almost all physical / chemical properties can be rationalized with meaningful descriptors that help guiding experimentalists towards new directions

Never forget that the "ideal structure" of the property you target for the next Nobel Price is most likely already in ICSD ! Think more about meta-stability for breakthrough...