Ab-initio prediction of novel phases of transition metal oxides

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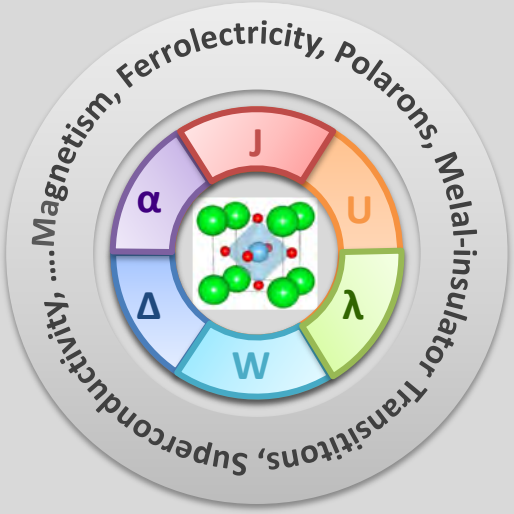
Dipartimento di Fisica,

Sapienza Universita' di Roma, Italy

Spice Workshop, Novel Electronic and Magnetic Phases in Correlated Spin-Orbit Coupled Oxides, **Mainz, 15 Nov. 2019**

Novel Transition Metal Oxides:



Tomorrow's electronics: novel materials with improved functionalities.

Transition metal oxides: several emerging behaviors due to the interplay of competing energy scales: electrons (U,J,SOC), lattice (λ), …

Can *ab-initio* calculations help guide experiment?

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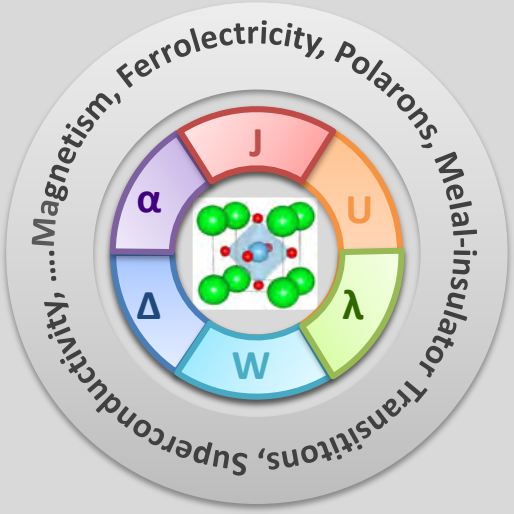

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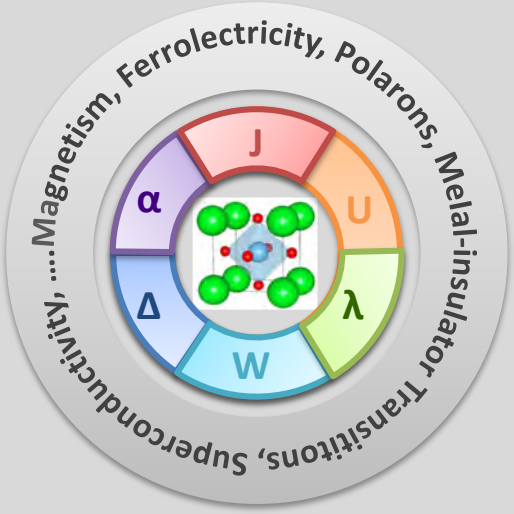

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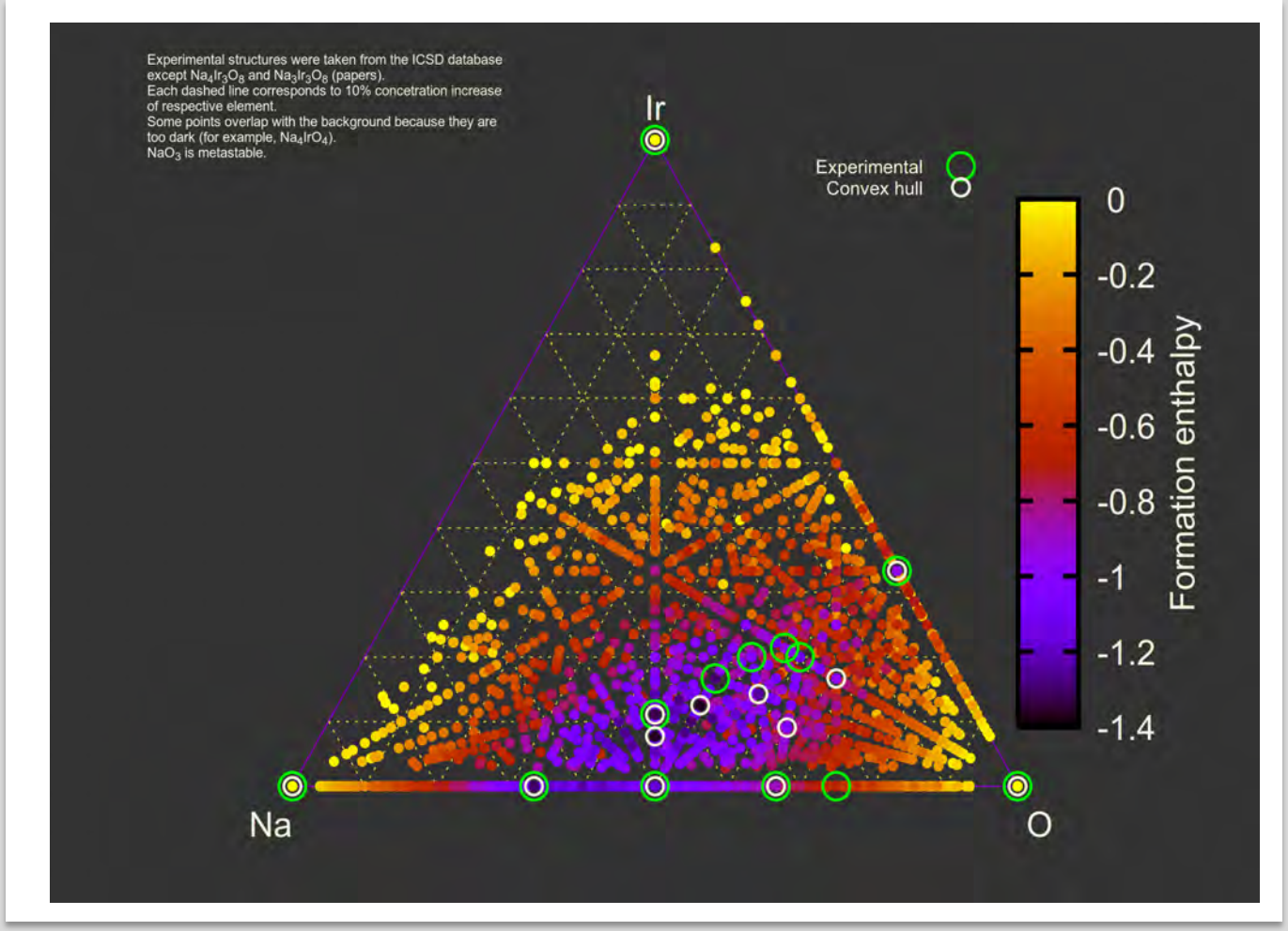
Novel TMO: Material Prediction

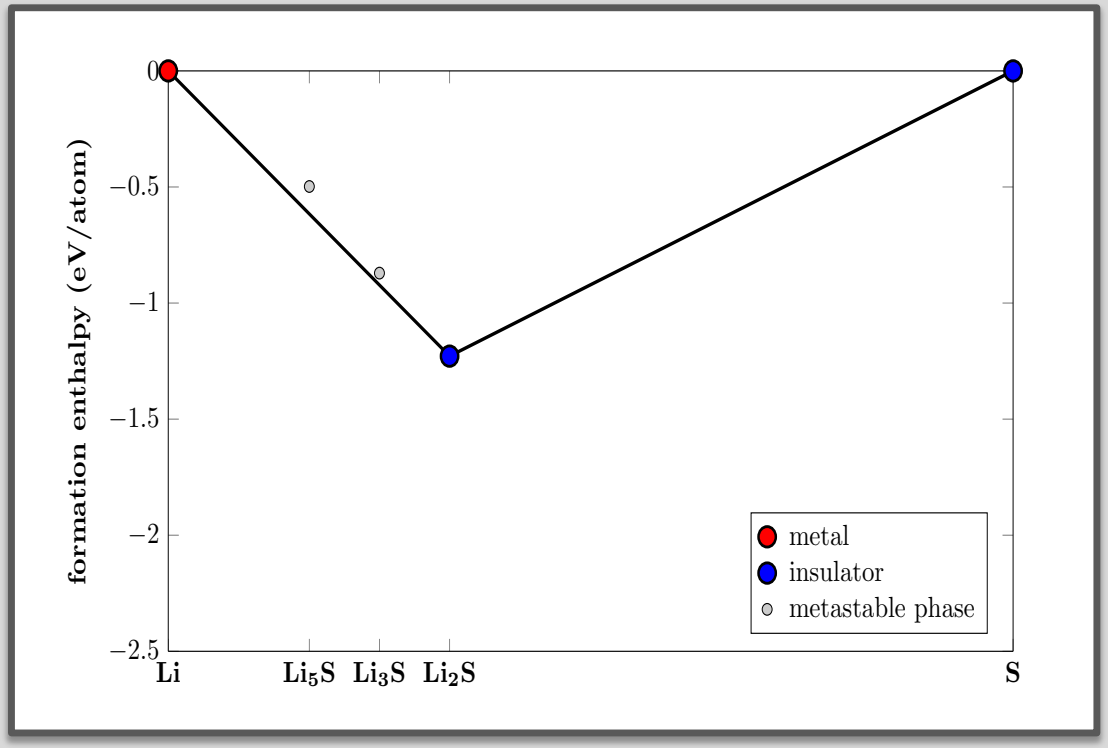


Methods for **crystal structure prediction** and **thermodynamics** can be used to predict phase diagrams and locate suitable ranges of composition, pressure and doping and identifying promising structures and functionalities…

Predicting phase diagrams… how does it work?

DESIGNING MATERIALS *AB-INITIO*…

Predicting Phase Diagrams:
Convex hull construction



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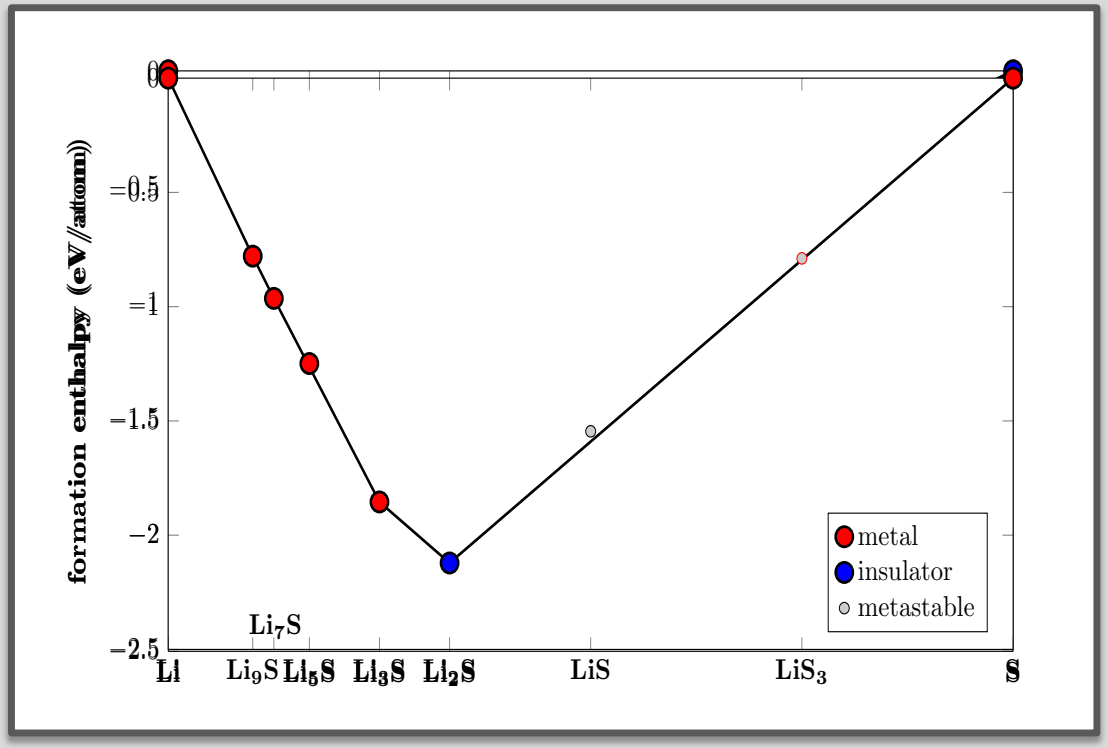
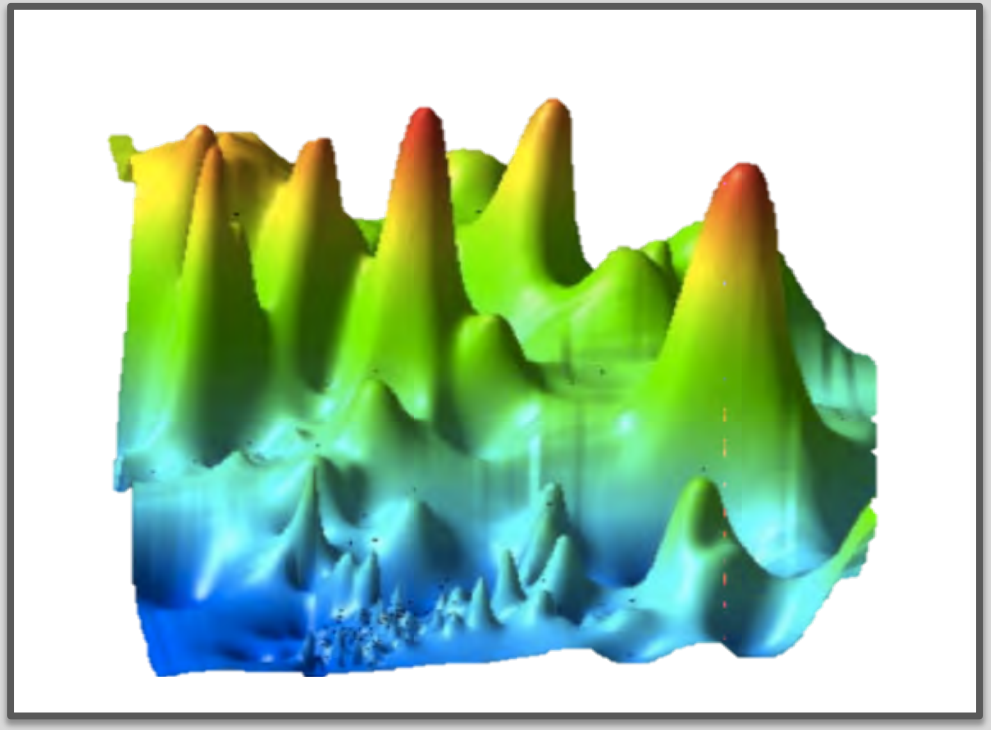


For a **given pressure** the stable stoichiometries lie on the **convex hull**.

High pressures often stabilize new stoichoimetries not seen at ambient pressure:
how to predict the crystal structures of these new phases?

Predicting Phase Diagrams:
Finding unknown structures

For a **given pressure** and **stoichoimetry**, the most stable crystal structure is the **global minimum** of the **energy** (enthalpy) **landscape**.



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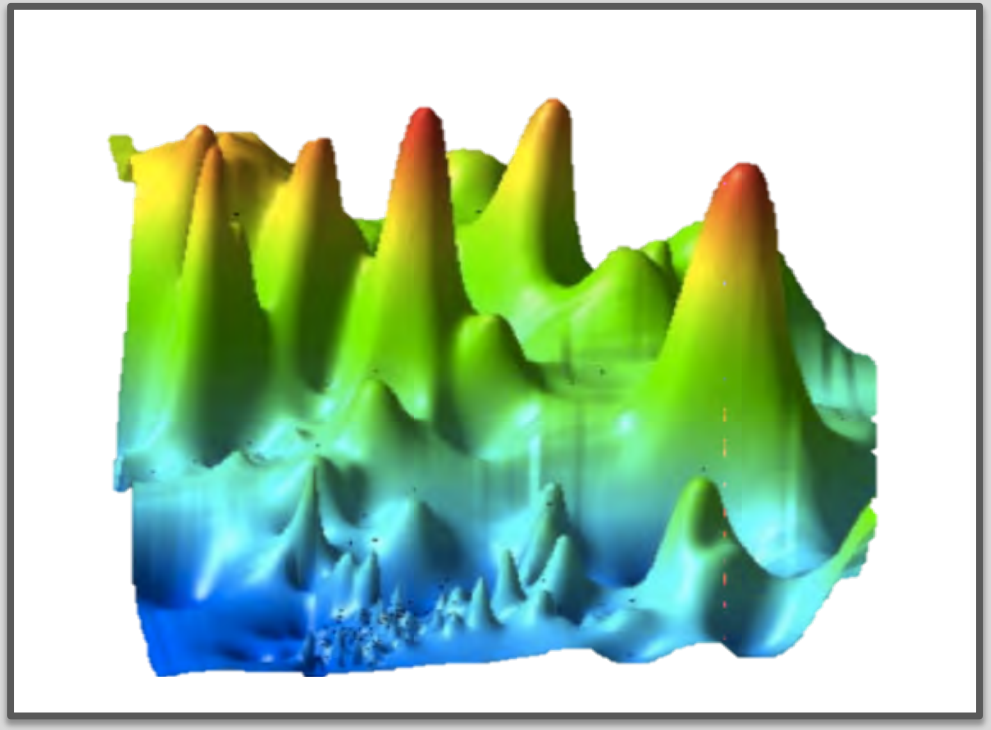

- **Why is it so complicated?**

For $V=10^3$ Å^3, $\delta=0.5$ Å, $N=10$,

$C = 1.6\ 10^{12}$ configurations!!!!!

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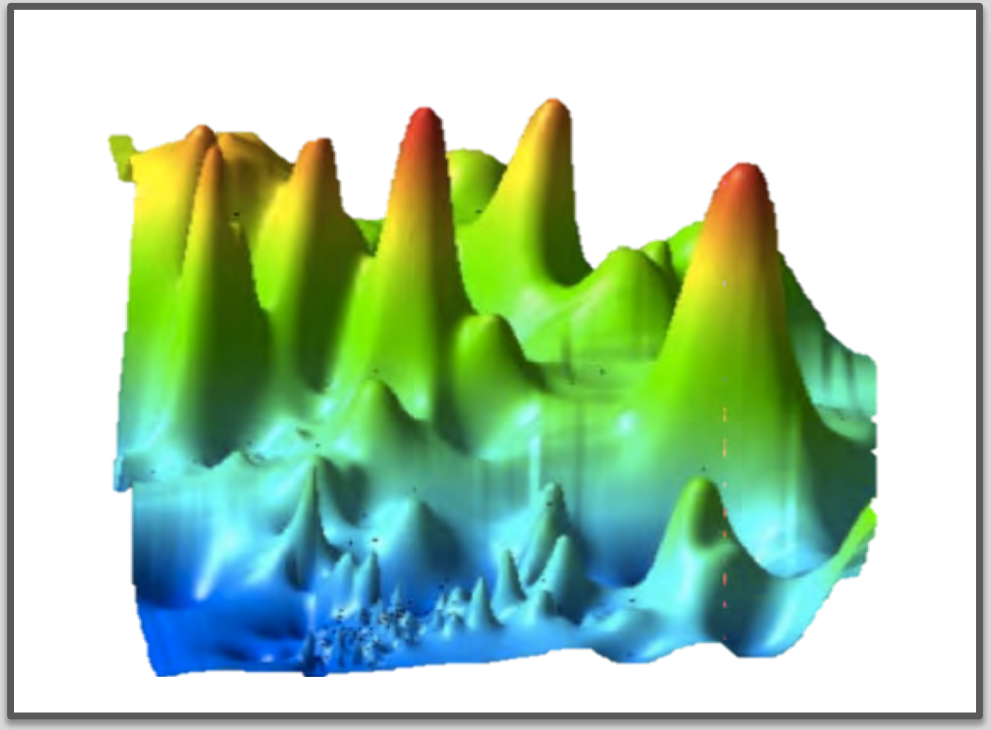

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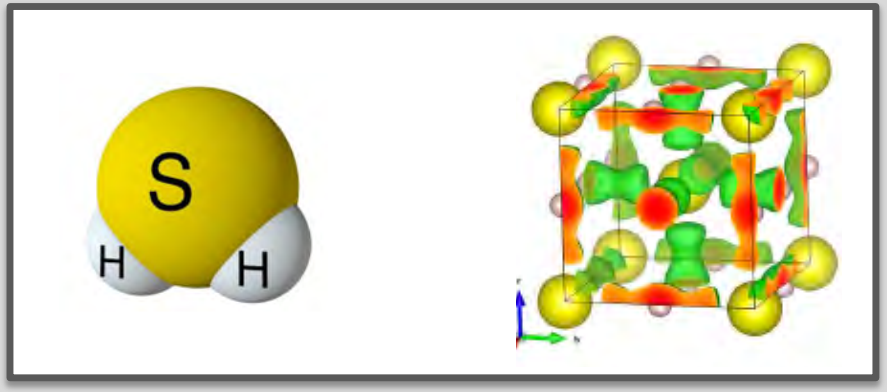
Practically impossible to scan the whole phase space!!!!

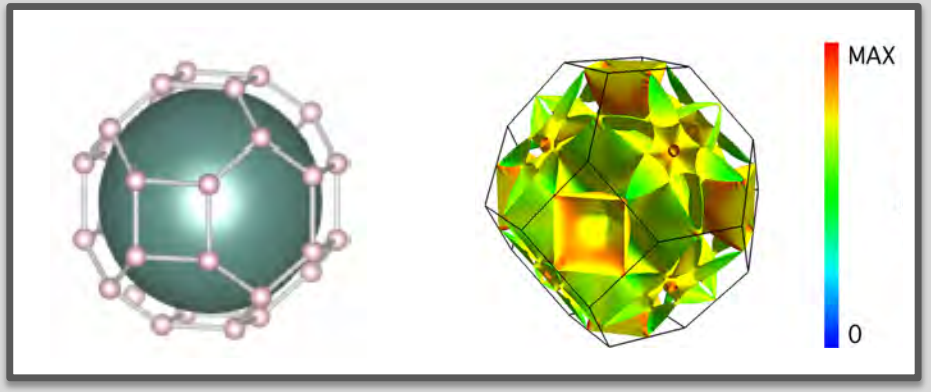
Predicting Phase Diagrams:
Crystal structure prediction

Several **efficient** methods implemented to explore the energy surface: (ab-initio random search, minima hopping, metadynamics, evolutionary algorithms) – *see Woodley & Catlow, Nat. Mat. 2008.*

Example: Near Room-Temperature Superconductivity in high-P Hydrides



SH_3, A. P. Drozdov et al., Nature 2015 (prediction Duan et al, Sci Rep. 2014).



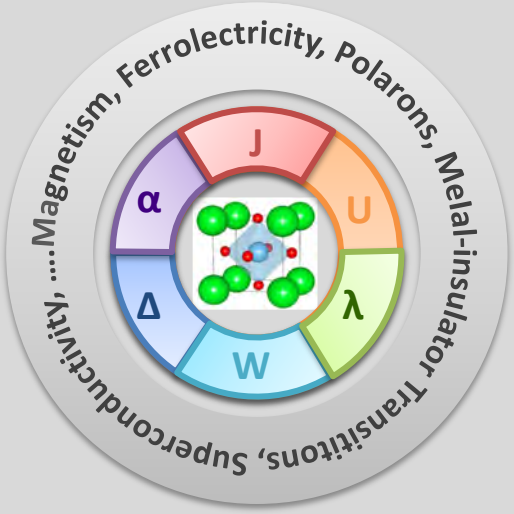
LaH_{10}, A. P. Drozdov et al., Nature 2019 (prediction F. Peng et al., PRL 2017).

A Perspective on Conventional High-Temperature Superconductors at High Pressure: Methods and Materials, J.A. Flores-Livas, L. Boeri, A. Sanna, G. Profeta, R. Arita, M. Eremets, Rep. Progr. Phys. 2019

How well does it work for (***transition metal) oxides***?

DESIGNING MATERIALS *AB-INITIO*…

Novel Transition Metal Oxides:



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- **Can *ab-initio* calculations help guide experiment?**
  - *Ab-initio* **material prediction**, what does it mean?
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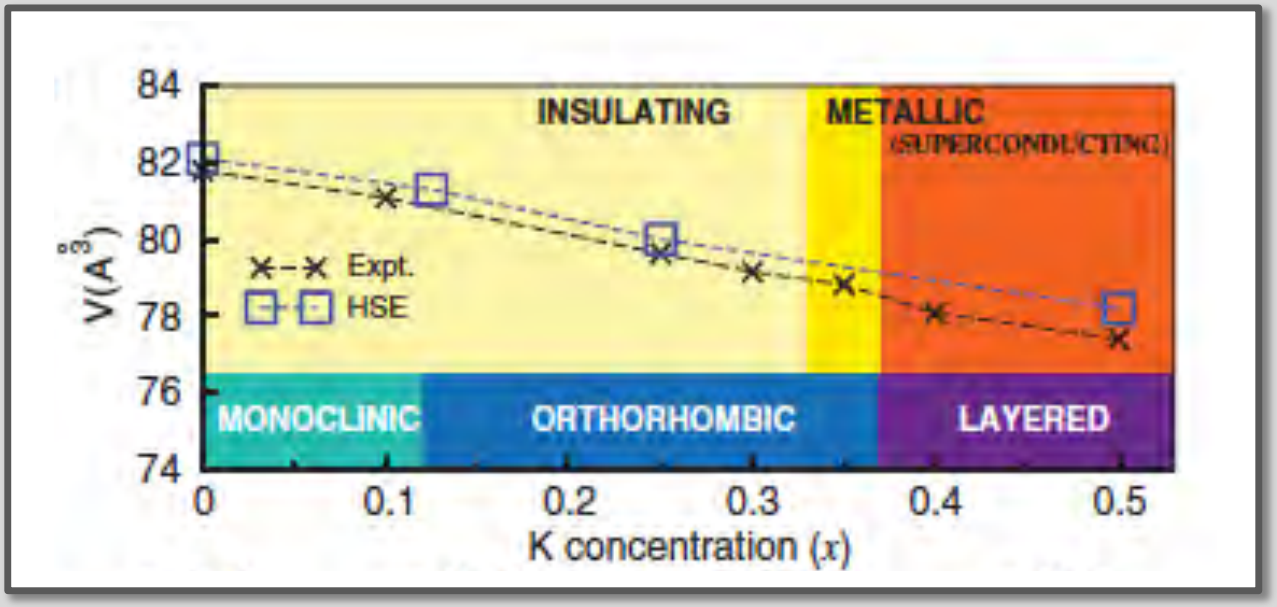

- **Undoped: 3D CDW** distortion of the perovskite structure (breathing + tilting) due to Bi3+/Bi5+ charge disproportionation; insulating ($\Delta \approx$ **1 eV**)
- **Doping** (K/Pb) **suppresses CDW** and induces **superconductivity**, T_c < 30 K (*Cava et al.*, Nature 1988; *Hinks et al.*, Nature 1988).

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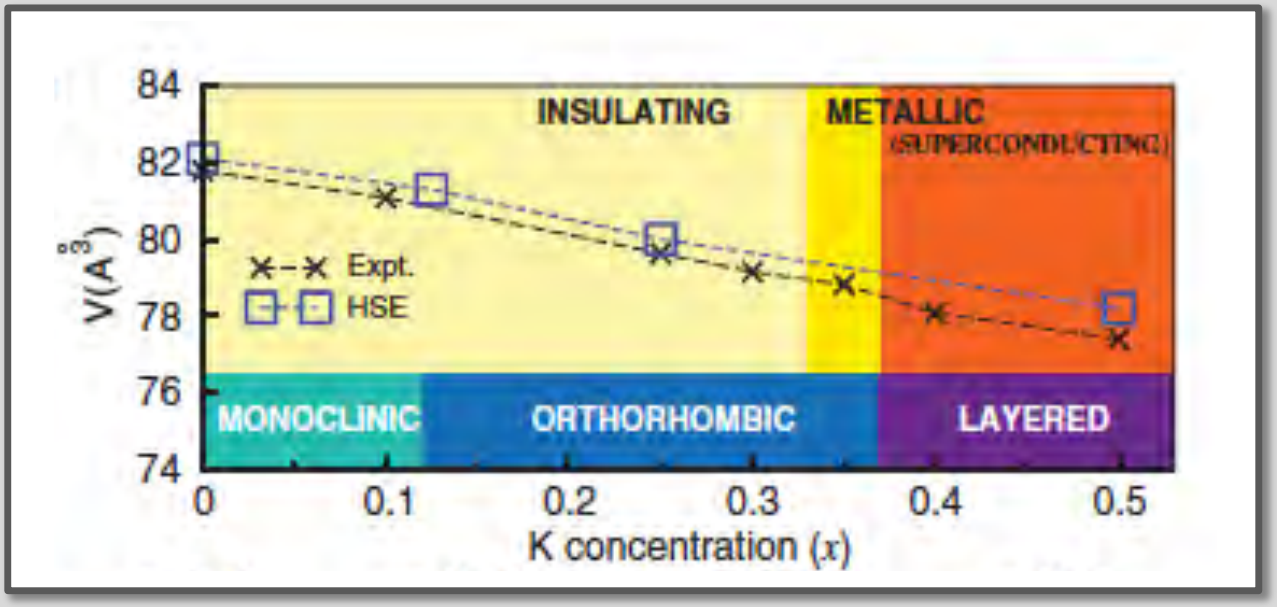

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- **DFT** reproduces CDW distortion, but not the insulating state (O.K.Andersen/s group, 1988-91) (needs LDA+U or hybrids); hybrid functionals (HSE) reproduce CDW and its suppression upon doping (*C. Franchini, G. Kresse, and R. Podloucky, PRL 2009.*).
- **TH:** Origin of **superconductivity**: negative U? Phonons? (*Meregalli & Savrasov, PRB 1998; Bazhirov, Louie, Cohen, PRB 2013);* Phonons+ U ?(*Yin, Haule Kotliar, PRX 2013).*

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What happens with pressure?

Will pressure suppress the CDW distortion and induce superconductivity?

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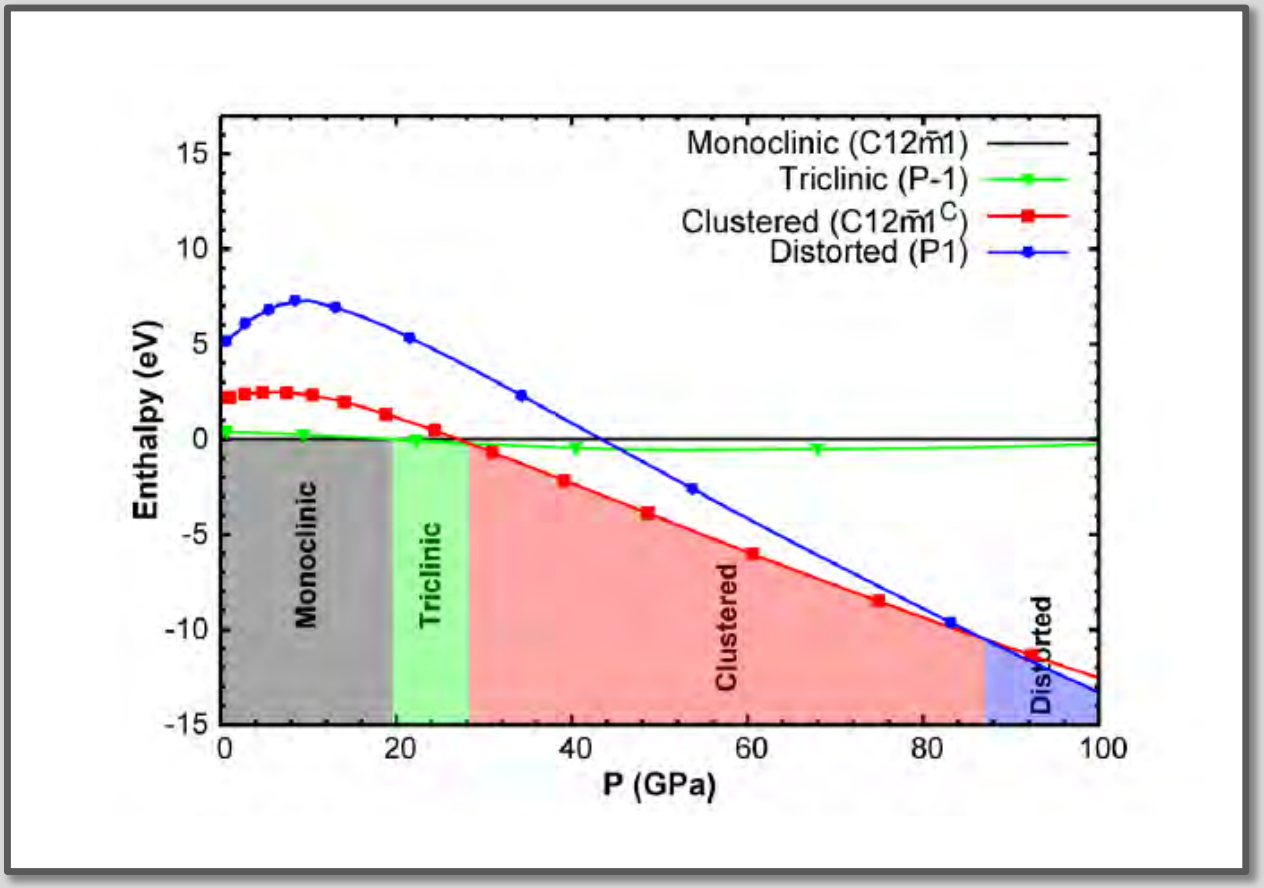
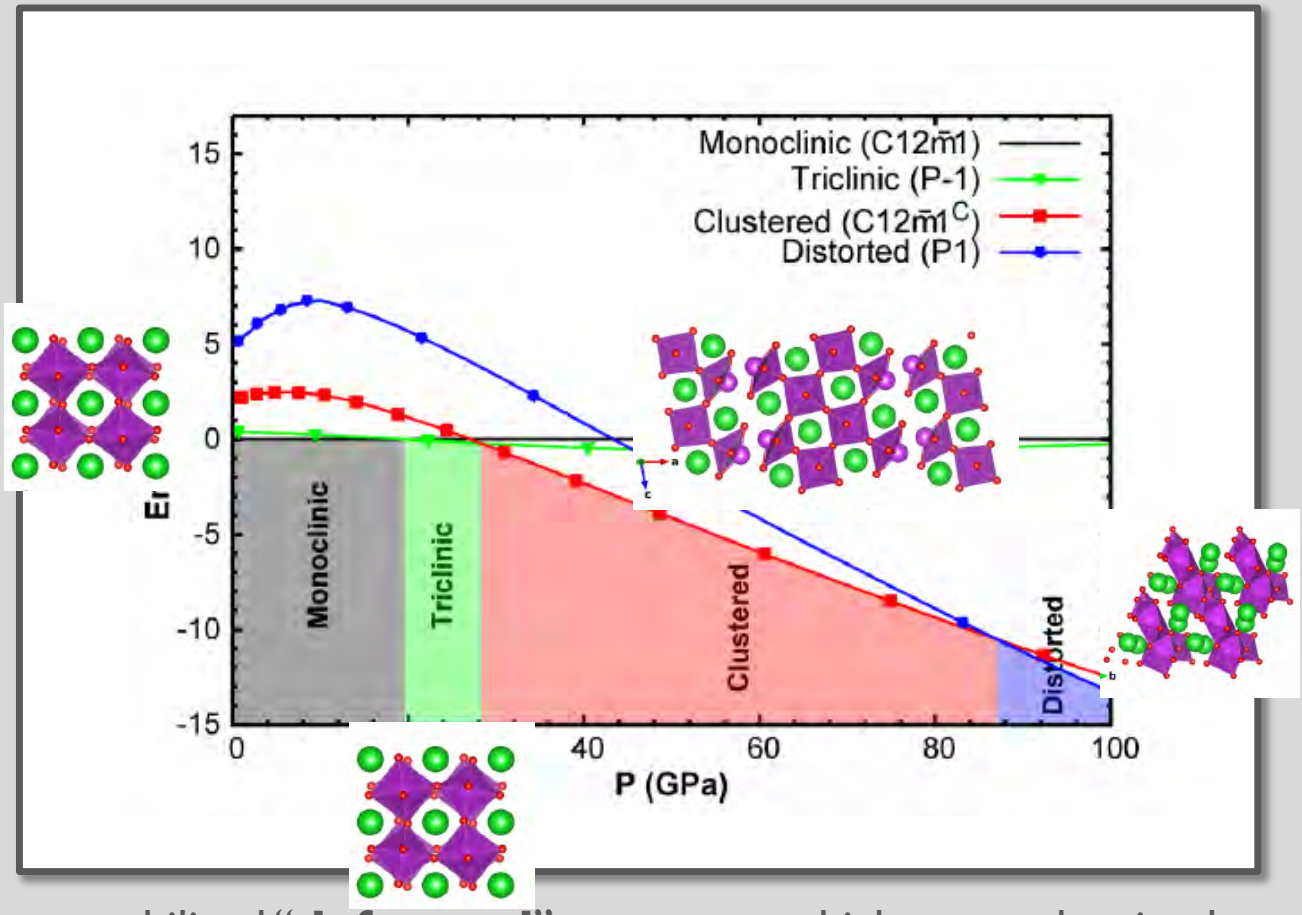


No EXP: High-pressure diagram: ab-initio evolutionary crystal structure prediction *(A. Smolyanyuk, L. Boeri, C. Franchini, PRB 2017)*.

An old puzzle: $BaBiO_3$

What happens with pressure?

Will pressure suppress the CDW distortion and induce superconductivity? **NO!**



High pressures stabilized "**deformed**" structures, which cannot be simply obtained from the perovskite; all high-P structures are **INSULATING**.

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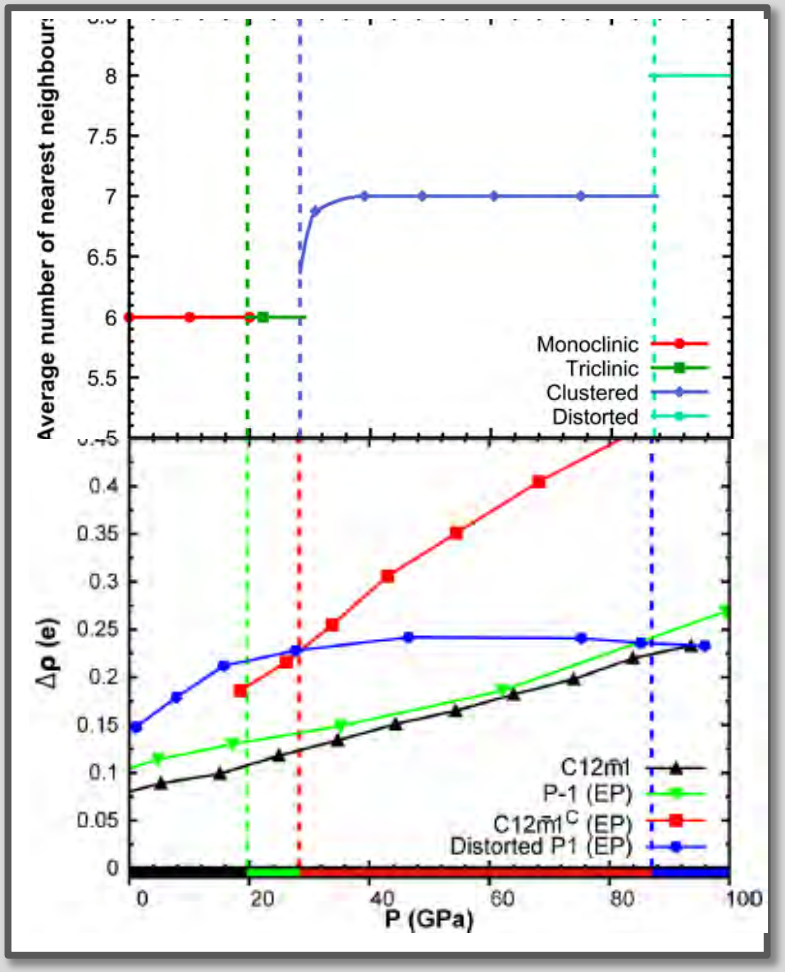
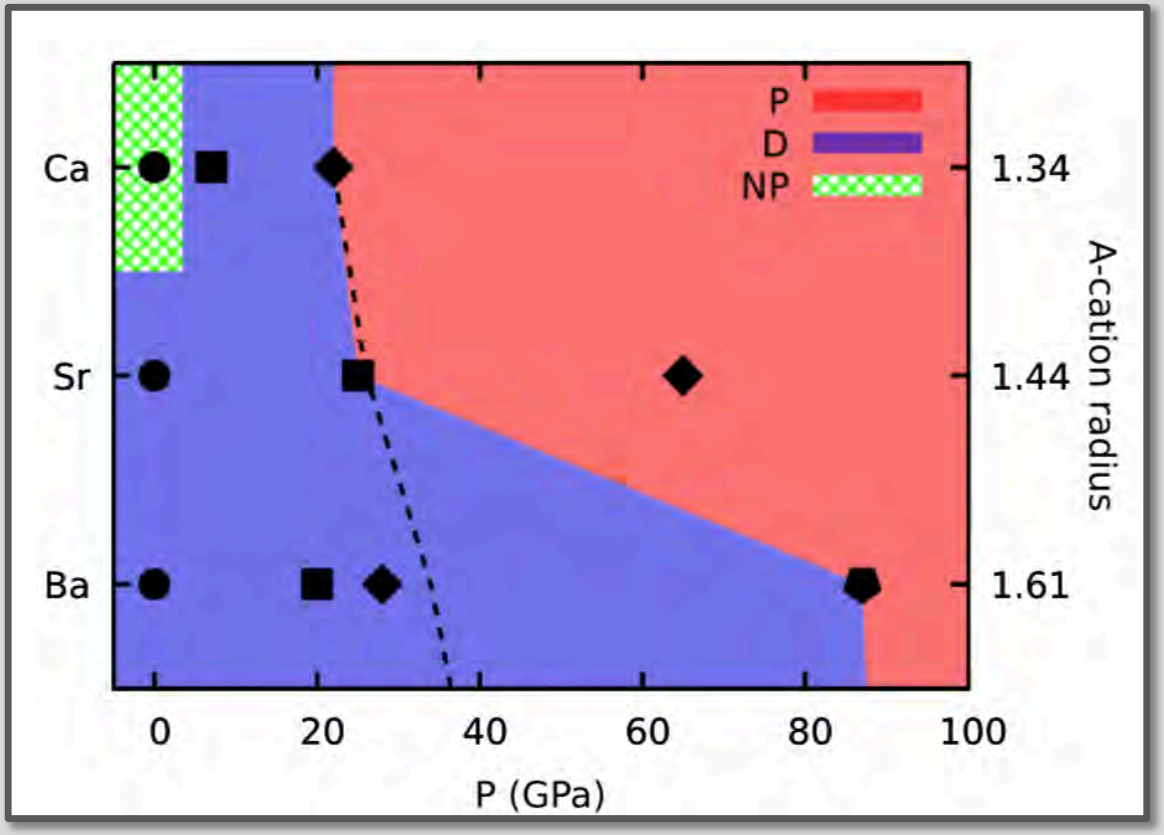


- High pressures stabilized "**deformed**" structures, which **cannot** be simply obtained as a distortion of the **perovskite** (group/subgroup analysis doesn't work).
- All high-P structures are **INSULATING**.
- "**Deformed**" structures contain pairs of inequivalent (Bi3+/Bi5+) bismut atoms -> charge disproportionation.
- **EXP confirmation:** R. Martonak, et al. , PRM **1**, 023601 (2017): Metadynamics + high-pressure resistivity measurements: **$BaBiO_3$ distorts and remains insulating up to 80 Gpa (EXP)!**

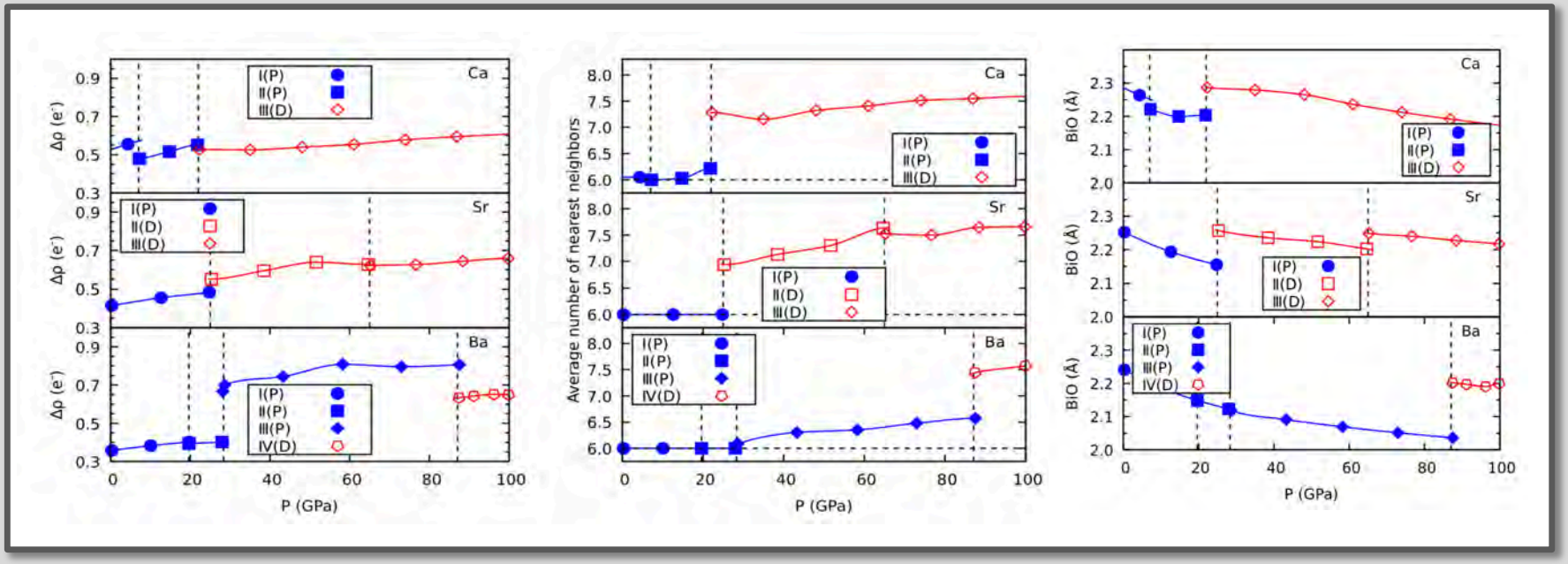
Bismutates @ High Pressures:
General Trends

	1 H Hydrogen 1.008	Atomic Sym Name Weight
2	3 Li Lithium 6.94	4 Be Beryllium 9.0122
3	11 Na Sodium 22.990	12 Mg Magnesium 24.305
4	19 K Potassium 39.098	20 Ca Calcium 40.078
5	37 Rb Rubidium 85.468	38 Sr Strontium 87.62
6	55 Cs Caesium 132.91	56 Ba Barium 137.33
7	87 Fr Francium (223)	88 Ra Radium (226)



- Charge disproportionation, insulating behavior and distorted structures are a common feature of AE bismutates at high pressure!
- **Chemical pressure:** the distorted phase occurs at lower P with smaller cation!

High-P distortions in Bismutates:
Physical origin



- Volume: Deformed structures are more compact than perovskite ones
- Bader charge analysis: Deformed structures preserve charge disproportionation.
- The number of Bi-O bonds increases upon forming distorted structures
- The average Bi-O bond length is larger in deformed structures.

Deformation permits to obtained more packed structures with optimal B—O bond-length!

What Next? Predicting new materials and functionalities…

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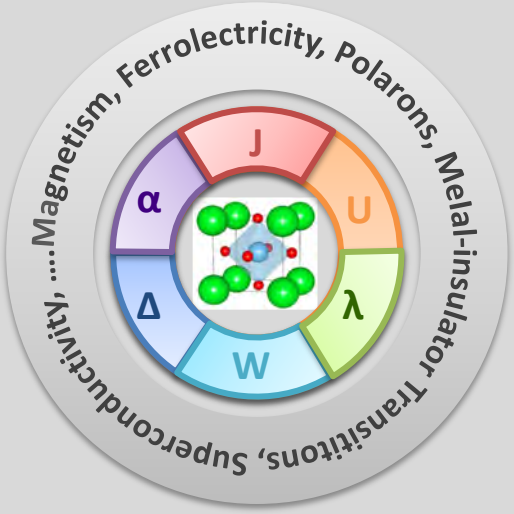

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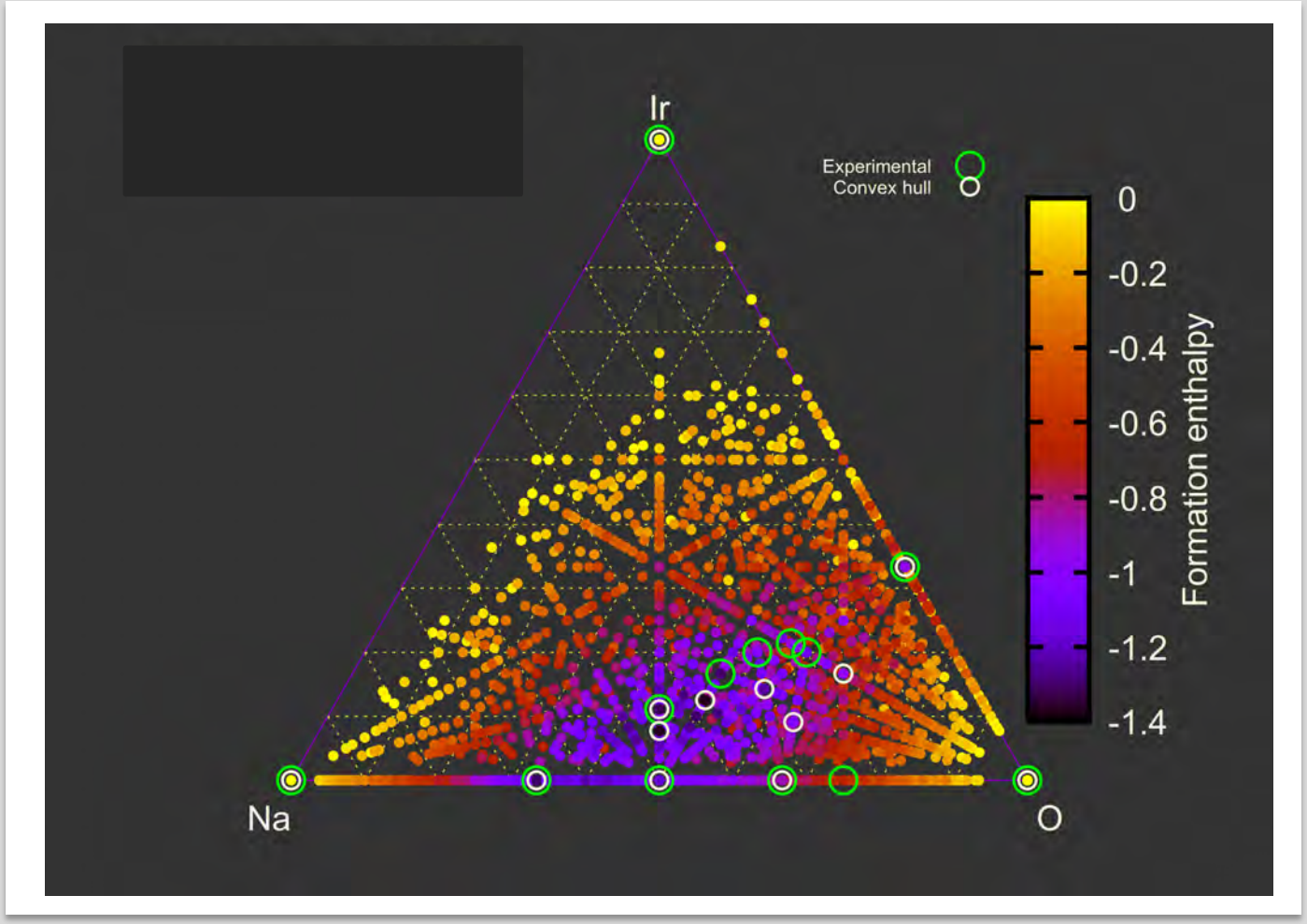
Hunting in the zoo of iridates: *first surprises*



Iridates Ternary convex hull of stability, *hunting* for promising phases…

A. Smolyanyuk, L. Boeri, unpublished

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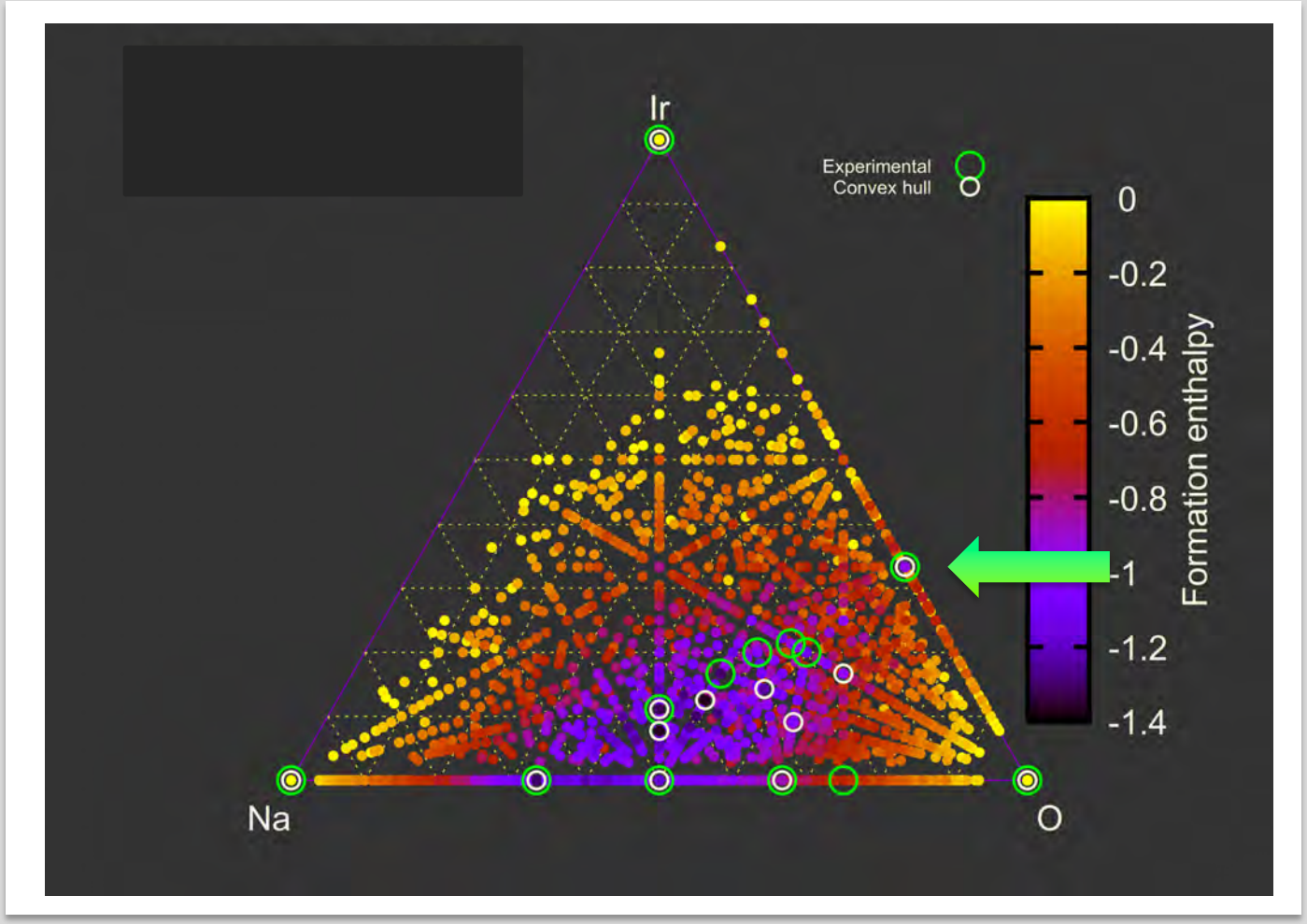

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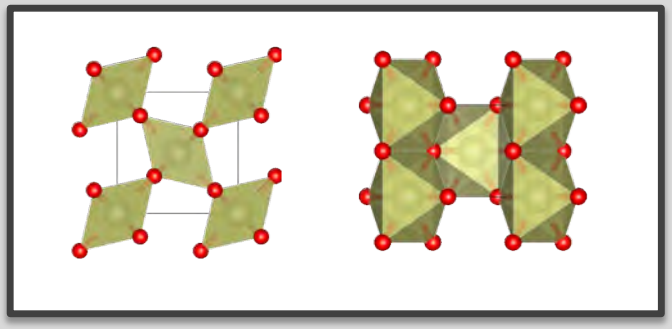
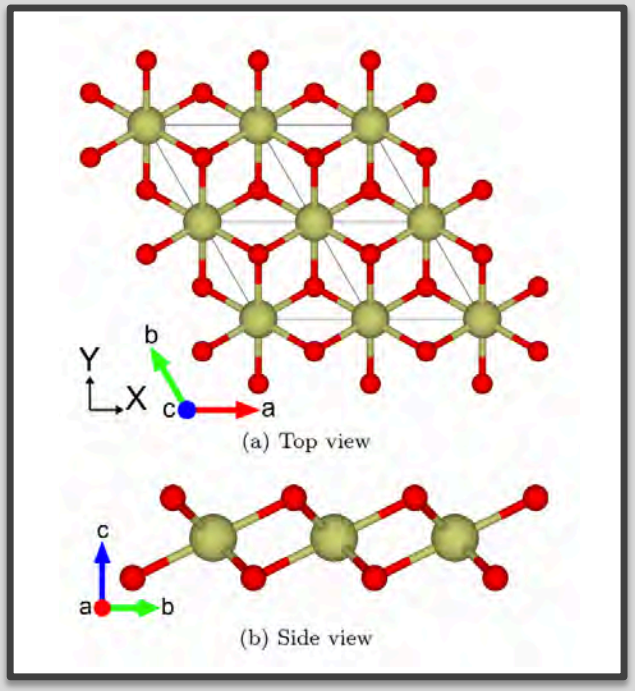
IrO_2



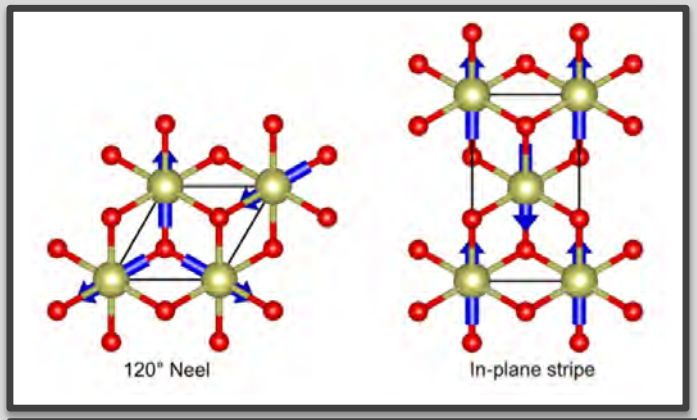
- **IrO_2 bulk: rutile, insulating**

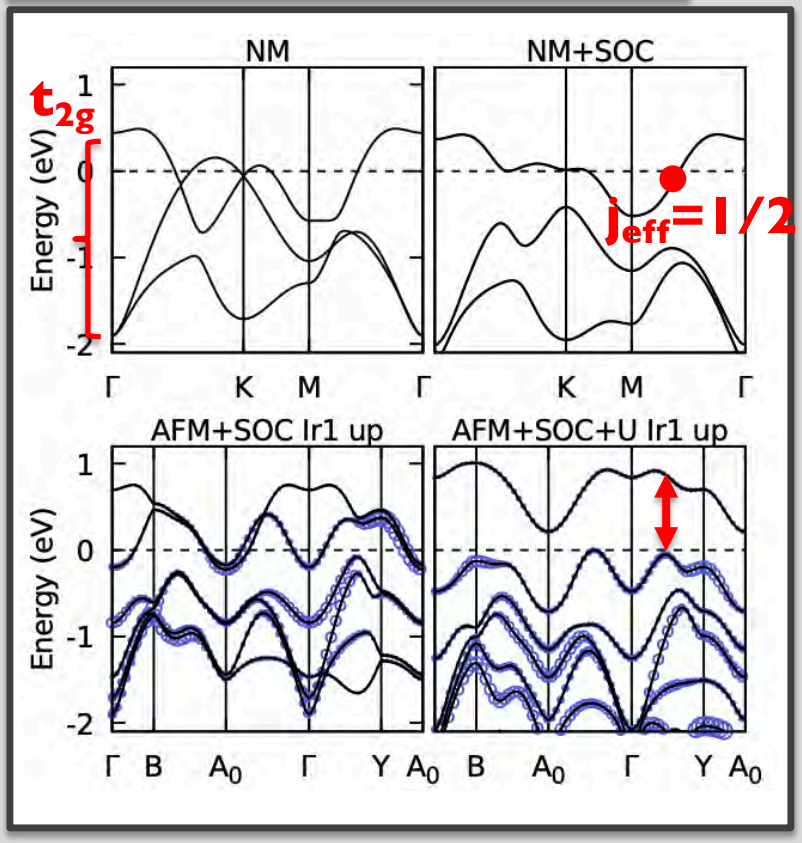


- **IrO_2 2D:** several metastable structures, with **Ir triangular** lattice.
  Formation enthalpy comparable to other 2D materials.
  Wan-der-Waals bound, easily exfoliable.

A. Smolyanyuk, M. Aichhorn, I. Mazin, and L. Boeri, arXiv preprint arXiv:1907.01966 (2019).

2D-IrO_2





- **Magnetism:**
  - Quasi-deg. 120 Neel and in-plane stripe.
  - Strongly anisotropic magnetic interactions.
  - Soft out-of-plane magnetic moment.

- **Electronic Structure:**

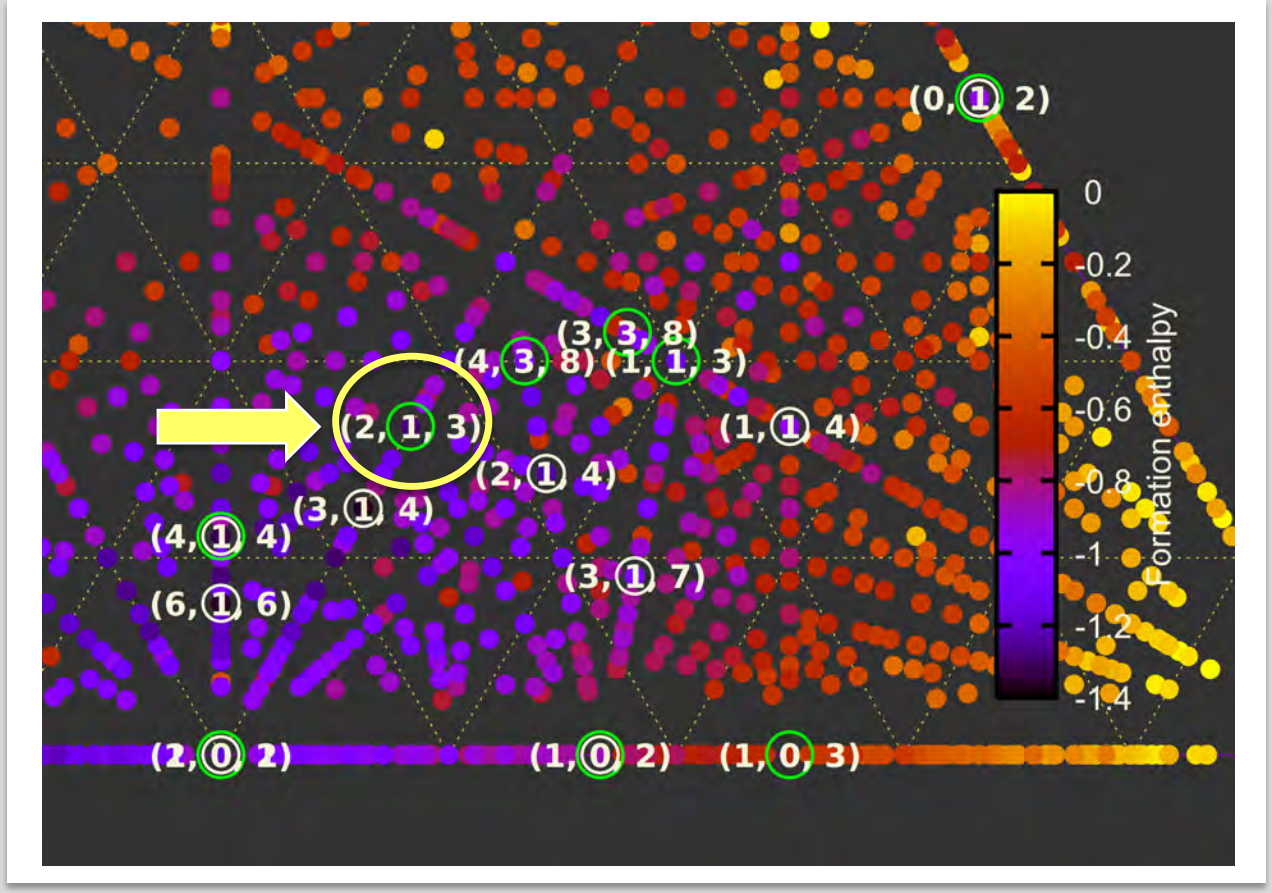
  Magnetism + SOC + U
  = weakly insulating (jeff=1/2 half-filled).
  Lattice Dynamics: Dynamically Stable

2D-IrO_2 synthesizable;
Triangular Ir lattice with non-trivial magnetic properties.

See also R.D. Johnson et al., cond-mat/1908.04584

Novel Quantum and Functional Materials

- Can *ab-initio* calculations help guide experiment in **transition metal oxides**?



Iridates

Ternary convex hull of stability, *hunting* for promising phases… Once promising composition have been identified, we can **zoom in** and **look for promising crystal structures/bonding environments**

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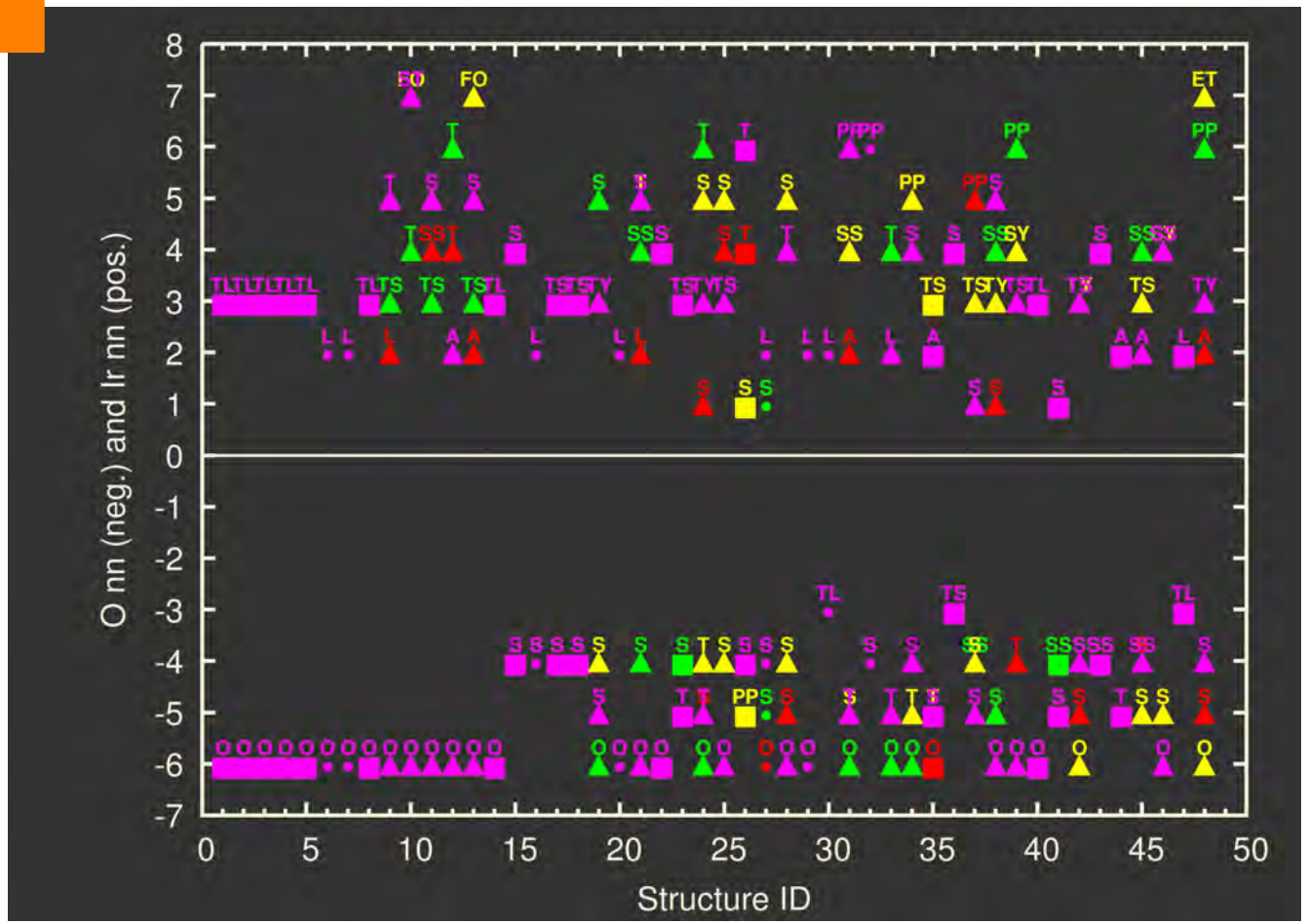
Li_2O_3



A. Smolyanyuk, L. Boeri, unpublished

In summary…

- **Can *ab-initio* calculations help guide experiment to find novel quantum and functional materials (transition metal oxides)?**
  - *Ab-initio* **material prediction**, what does it mean?
  - An old puzzle: $BaBiO_3$

    "Ab initio prediction of the high-pressure phase diagram of $BaBiO_3$", A. Smolyanyuk, Lilia Boeri, and C. Franchini, Phys. Rev. B **96**, 035103 (2017).
  - Bismuthates @ High Pressure: General Trends

    "*Charge Disproportionation in the high-pressure phase diagram of bismuth oxides*", A. Smolyanyuk, C. Franchini, L. Boeri, Phys. Rev. B **98**, 115158 (2018).
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    «Ab-initio prediction of a two-dimensional variant of the iridate IrO_2», A. Smolyanyuk, M. Aichhorn, I.I. Mazin,and L. Boeri, cond-mat/1907.01966.

What next?

Novel ternary phases, high-P phase diagrams, … **New Physics!!**

THANK YOU!!!!!

And thanks to...

M. Aichhorn,
TU Graz

A. Smolyanyuk,
TU Graz

C. Franchini,
Uni Wien
& Bologna

ME!

I.I. Mazin,
George Mason

FWF

Vienna Computational Materials Laboratory
ViCoM