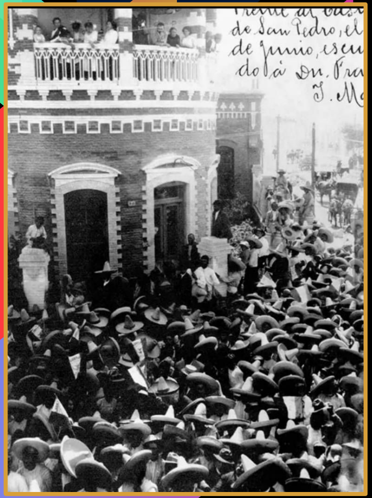
La **superconductividad** a temperatura ambiente bajo presión en sistemas de hidrógeno, ¿es una realidad u otra aserción falsa?



José A. Flores-Livas

Sapienza, University of Rome and RIKEN, Tokyo

20.11.2021, online talk. BAUP-UNAM?

Contenido

1 Introducción a los métodos computacionales para la predicción de cristales ~30 m

2 Efectos cuánticos en sistemas de hidruro a alta presión (Química exótica) ~10 m

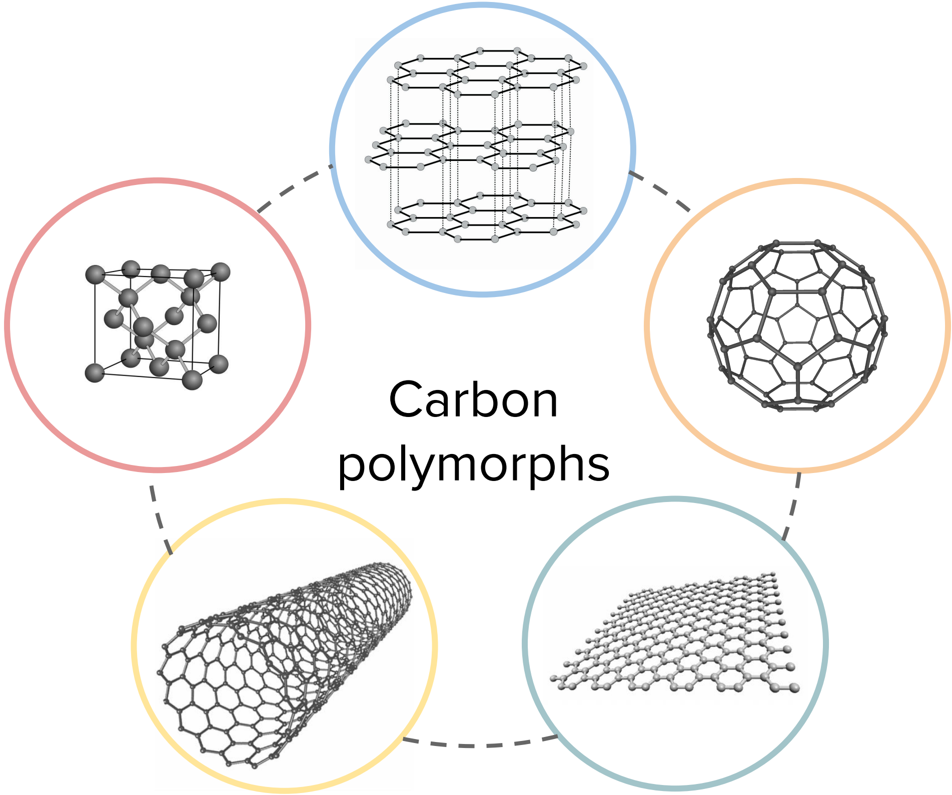
3 Superconductividad a temperatura ambiente en el CSH? < 10 m

Tabla de contenido:

Is it Possible to Predict the Crystal Structure of a Substance ?

“One of the continuing scandals in the physical sciences is that it remains impossible to predict the structure of even the simplest crystalline solids from a knowledge of their composition.” *John Maddox,* ***Nature*** *1988*

Some substances have more than one crystal structure !

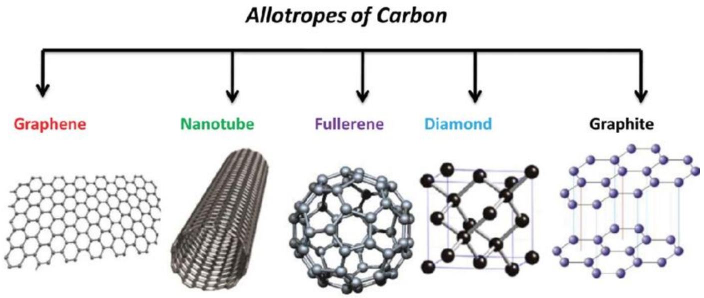


Carbon
polymorphs

Polymorphism

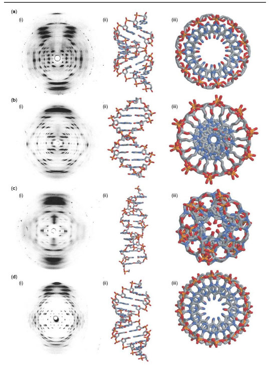
Arrangement of atoms in

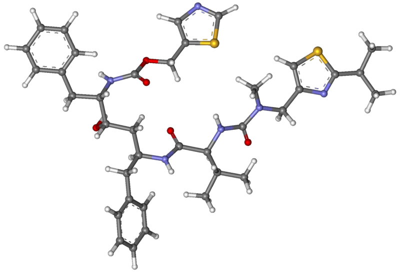
Materials Science

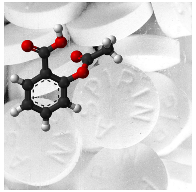


Other Sciences

Polymorphism is important in pharmaceutical industry, drugs, organic and inorganic compounds, viruses, of course DNA.







Ritonavir (HIV/AIDS) case: form I during development but once in market form II was found more stable. Loses of millions US dollars.

Why we want to know the structure or predict it?

The arrangement of atoms is the most important piece of information about a material.

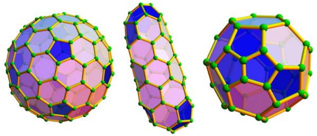
From the structure one can derive models as well, obtain observables (physical properties) of molecules, crystals, etc, using quantum-mechanical methods.

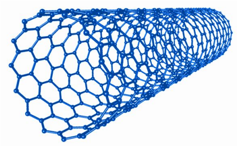
Fundamental tool widely use

- ➔ To interpret experimental data of poor quality.
- ➔ To study materials under thermodynamic conditions beyond experimental limits.
- ➔ As a driving force for materials design: artificial intelligence, neural networks and machine learning.

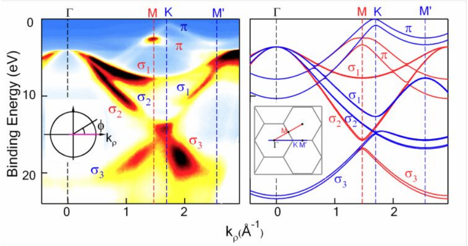
Structure related properties

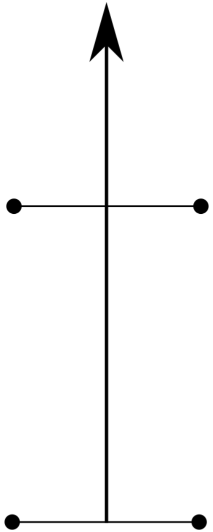
Material's properties are linked to atomic structure



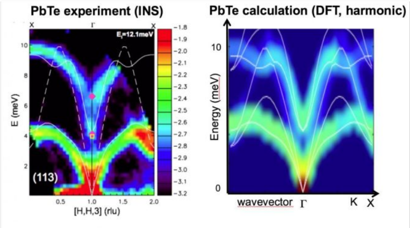


Strongly correlated electrons



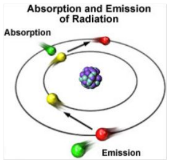


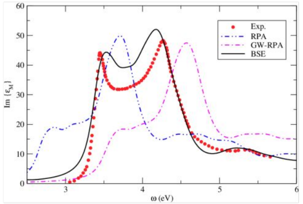
Vibrations and e-p coupling



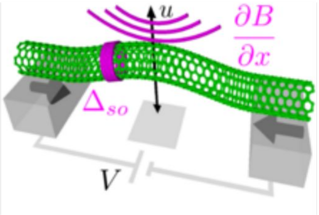
Delaire *et al.*, Nature Materials 2011

Electronic excitations





Transport and e-dynamics



The global minimum: Minimizing a target function

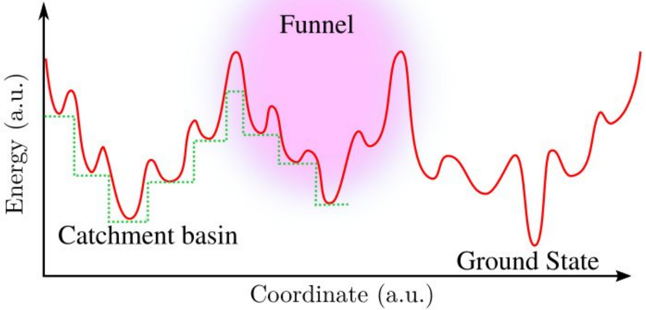
- ➔ Structure prediction ↔ global optimization of Gibbs free energy.

$$G = E + P\cdot\Omega - TS$$

- ➔ It is a *3N -dim* potential energy or *3N + 9-dim* enthalpy surface

$$H = E(\mathbf{R}_1, \ldots \mathbf{R}_N, h) + P \cdot \Omega(h), h = \mathbf{a}, \mathbf{b}, \mathbf{c}$$

- ➔ Stable configurations are minima on the potential energy surface: $\frac{\partial E}{\partial \mathbf{R}_i^{\gamma}} = 0$
- ➔ Structures are minima on a surface (enthalpy) with real $\omega(\vec{q})$

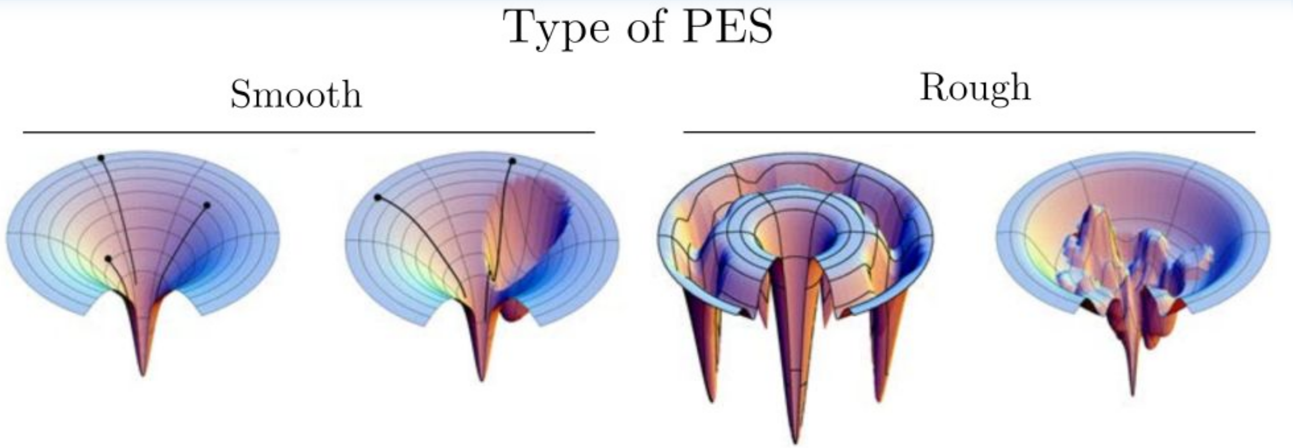


Energy landscapes

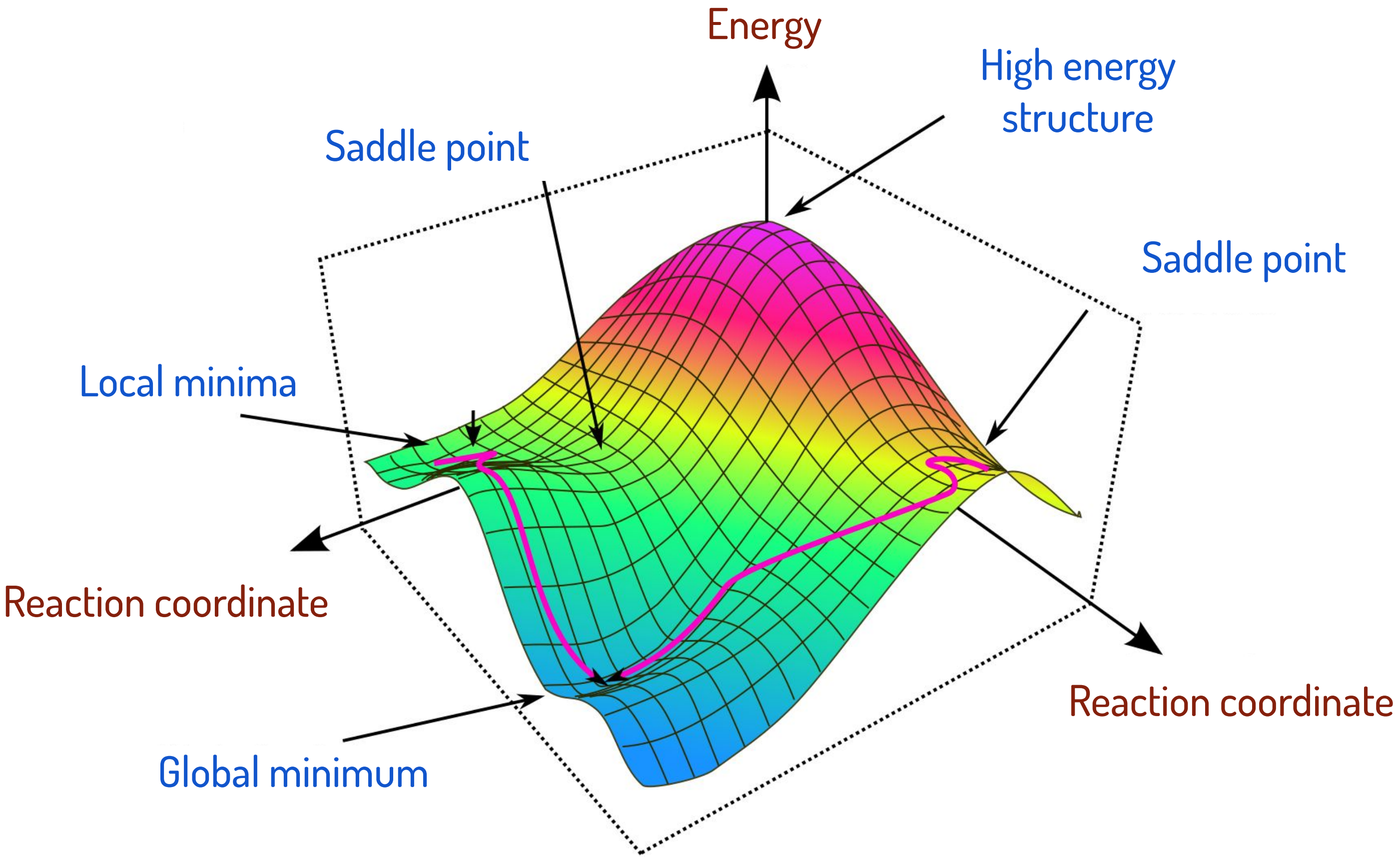
What is the Potential Energy Surface? (PES)

A potential energy surface is a mathematical function that gives the energy of a system as a function of its geometry.

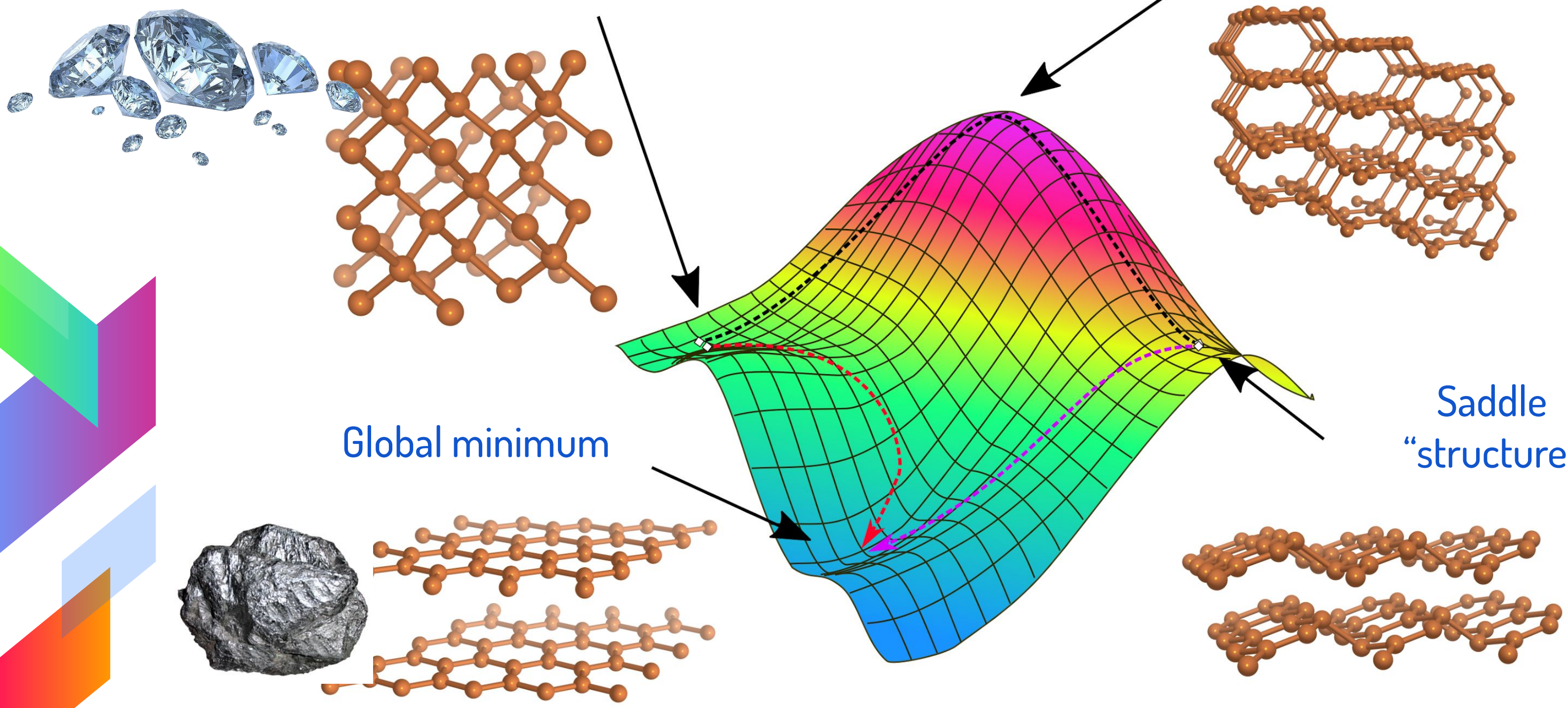
- Energy landscape depends on chemical space
- Accessible for molecular and crystals systems
- Energy evaluated using force-fields, tight-binding, DFT and ML



Potential energy surface



Potential energy surface



Local minima

High energy
structure

Global minimum

Saddle
“structure”

Q: How hard is this problem?

For instance the right stoichiometry is a NP problem

In practice, only a finite number of stoichiometries can be searched, and only a finite number of structures with a particular stoichiometry can be calculated, whereas both the number of stoichiometries and number of structures are in *principle* infinite!

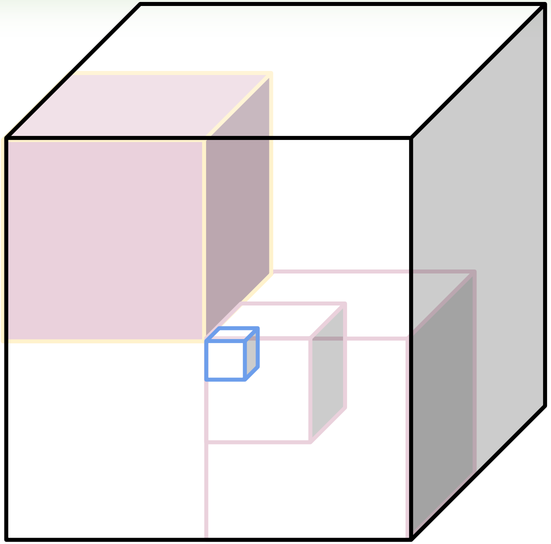
- ➔ NP refers to non-deterministic polynomial-time problem.
- ➔ http://mathworld.wolfram.com/NP-Problem.html
- ➔ If a problem is known to be NP, and a solution to the problem is somehow known, then demonstrating the correctness of the solution can always be reduced to a single P (polynomial time) verification. If P and NP are not equivalent, then the solution of NP-problems requires (in the worst case) an exhaustive search.

- ➔ Millennium Problems: P vs NP Problem

Q: Do you want to help to solve this problem?

Number of minima: exponential growth with N-atoms

- In simple arguments: suppose that an extensive system of **N** atoms can be divided into **M** equivalent subsystems, each of **N/M** atoms
- If these subsystems are **large enough**, these will also **have independent stable configurations**
- The total number of **locally stable configurations** of the system (n_s) therefore satisfies:



$$n_s(N) = n_s^M(N/M)$$

The solution to the Eq. is

$$n_s(N) = e^{\beta N}$$

Q: is it like this?

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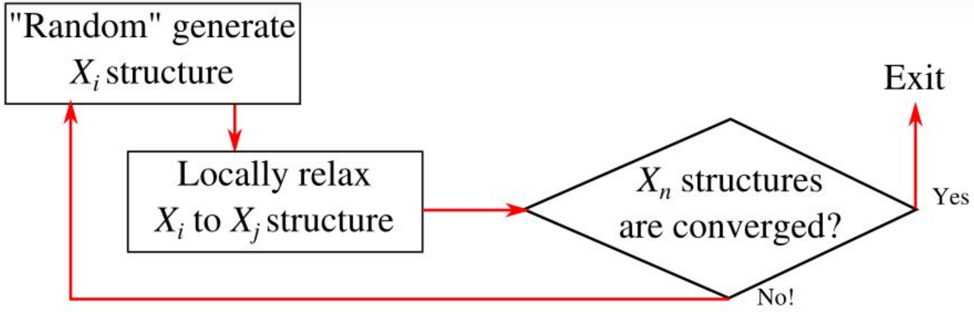
IV) *Perspectivas y discusion*

Random Search

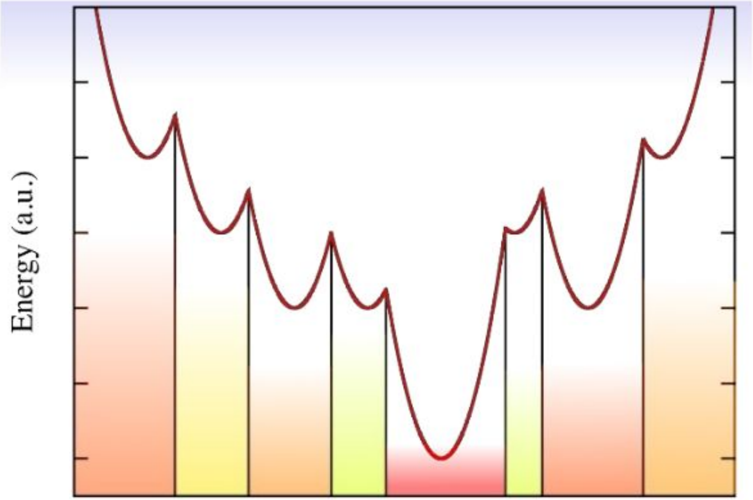
➔ It is simple, easy to implement, surprisingly successful: robust.



But, how random is random?

- ➔ Implement penalty radii
- ➔ Insight from chemical composition
- ➔ Constrain or exploit symmetry
- ➔ Despite all this, it is a "Shake and bake" method and is *not suitable for many atoms*
- ➔ Not suitable for glassy systems. No thermodynamics are really known

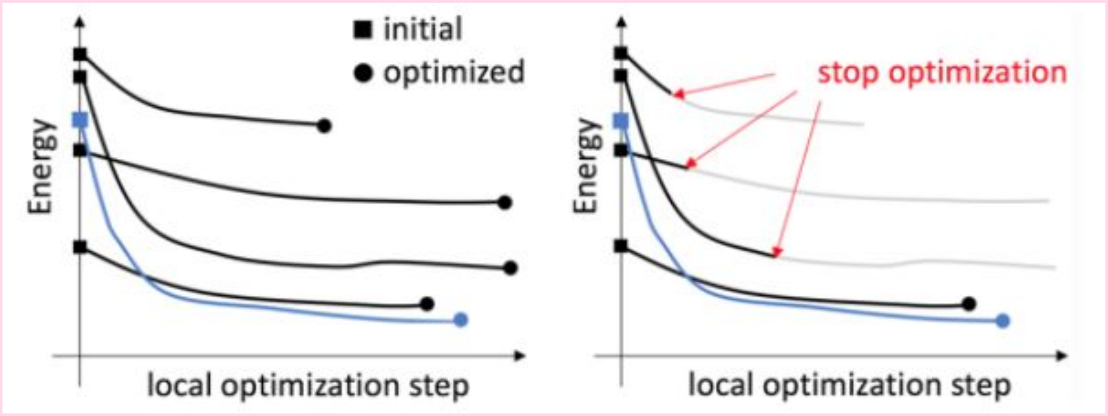
Random search: AIRSS



- ➔ Width of catchment basins correlates well with well(s) energy.
- ➔ Successful implementation: Ab initio Random Structure Searching (AIRSS).*

* Pickard and Needs, PSI-k Highlight **100**, (2010).

Fine-grained optimization method

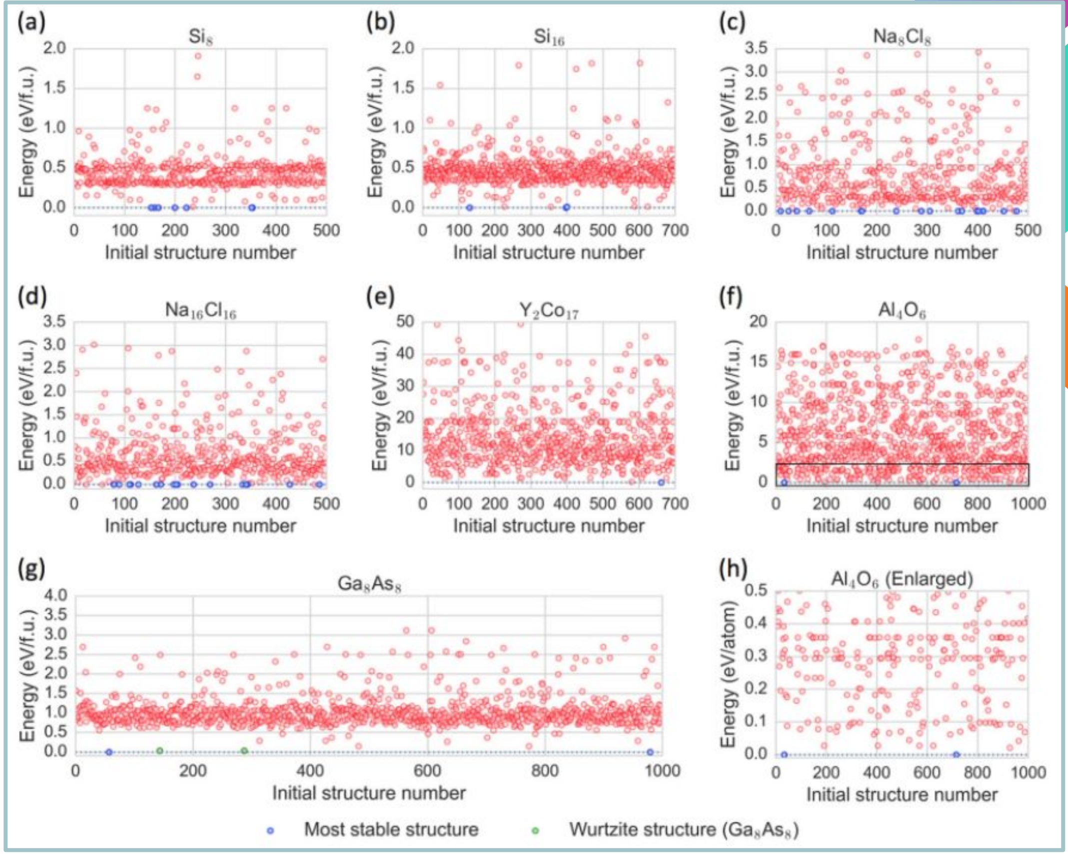


- ➔ CSP by applying relaxation schemes to randomly generated (CrySPY)
- ➔ Local optimization controlled by LAQA, and sLAQA (Look Ahead based on Quadratic Approximation)
- ➔ Foresee the energies of selected structure by scoring: i.e Norm on forces, etc.
- ➔ "From a sufficient number of structures, at least some are expected to be close or to relax to the most stable ones"

See Terayama, Yamashita, Oguchi and Tsuda, npj Comu. Mat (2018)

Locally optimized total energies (from random structures)

- It is possible to find the most stable structures, but
- It is a stochastic approach that could be very expensive if a ‘smart’ optimizer is not used
- Not suitable for glassy systems.
- No thermodynamics are really known



See Terayama, Yamashita, Oguchi and Tsuda, npj Comu. Mat (2018)

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Thermodynamic methods

- Method to generate a Boltzmann distribution.
- Probability of finding configuration *X* is proportional to $e^{\frac{-E(X)}{KT}}$
- At sufficiently low *T*, the ground state will be the dominant configuration.
- Works well for single-funnel energy landscapes.

Simulated annealing

➔ Mimics the process to reduce defects in solids: higher barriers can be crossed at high temperature.

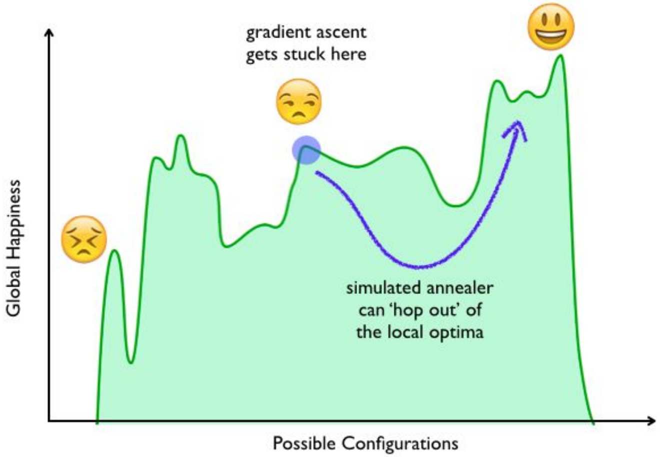
➔ System is propagated by molecular dynamics at high T.

➔ Controlled cooling: crystallization to the ground state according to the Boltzmann distribution.

➔ Guaranteed to find the global minimum if thermodynamic equilibrium is reached.

Simulated annealing

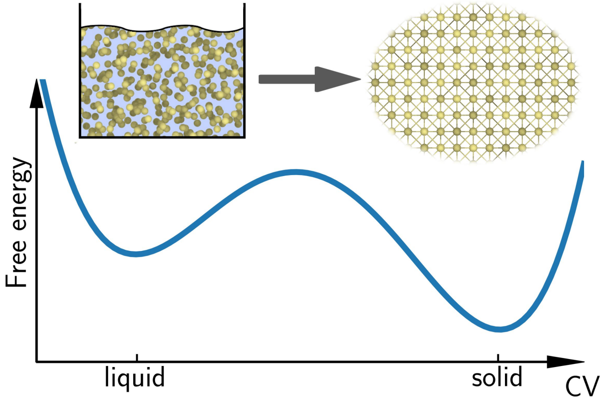
```
initialize $E_{kin}^{ref}$ and $E_{kin}^{final} \approx 0$, random velocities of atoms $E_{kin}^{ref}$
while $E_{kin}^{ref} > E_{kin}^{final}$ do
    $E_{kin}^{ref} = E_{kin}^{ref} \times 0.99999$
    Perform MD step and update $E_{kin}$
    if $E_{kin} > E_{kin}^{ref}$ then
        reduce velocities by 0.99
    else
        increase velocities by 1.01
    end if
end while
```



- ➔ In practice rather slow, depending on the annealing schedule.
- ➔ Often gets stuck in a funnel or local minimum.

See Kirkpatrick et al. Science 220 (4598) (1983)

Metadynamics



- ➔ Metadynamics is performed in the space defined by collective variables S.
- ➔ The dynamics is driven by the free energy and is biased by a history-dependent potential constructed as a sum of Gaussians centered along the trajectory of S.
- ➔ Not useful for crystal discover.
- ➔ But this approach can compute the free energy, exploring reaction pathways and accelerating rare events.

See Laio & Parrinello, 2002; and its variants

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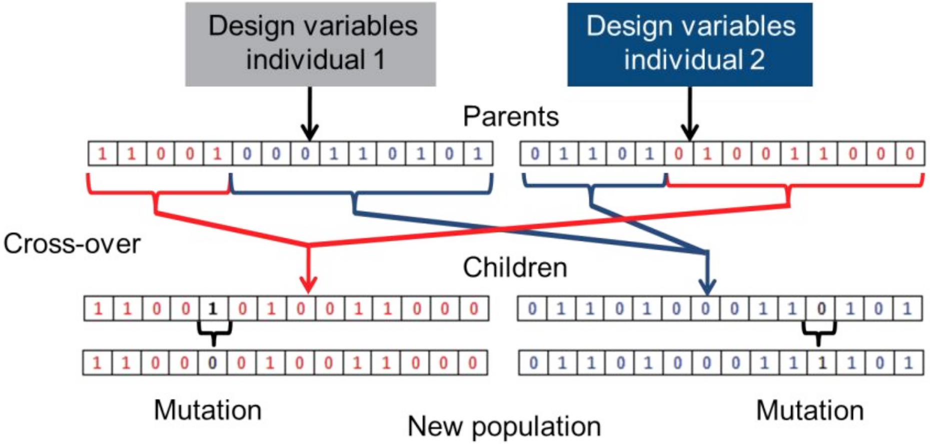
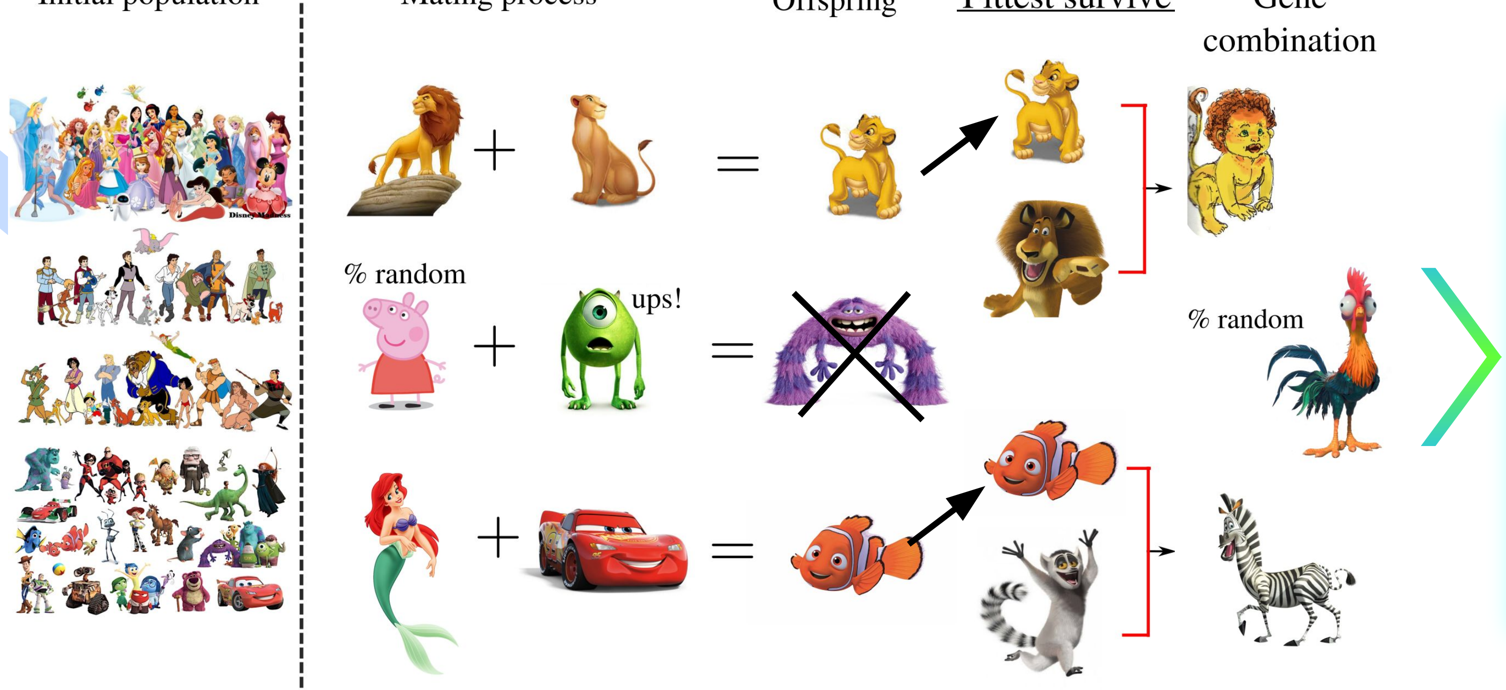
Genetic *evolutionary* based algorithms

- Mimic a Darwinistic evolution.
- Population of individuals (solutions X_i) with genes, represented by binary strings.
- Genetic operations: Gene crossing, mutation, selection, mating, recombine, etc.
- Survival of the fittest, bad solutions are eliminated: Peppa pig !
- Iterate and keep population healthy: **low energy and high gene diversity.**



Genetic algorithms:

"Quantum Darwinism"



Initial population

Mating process

% random

ups!

Offspring

Fittest survive

Gene combination

% random

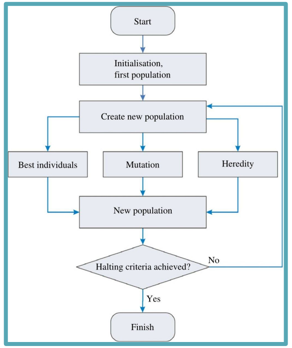
% random

Painful process

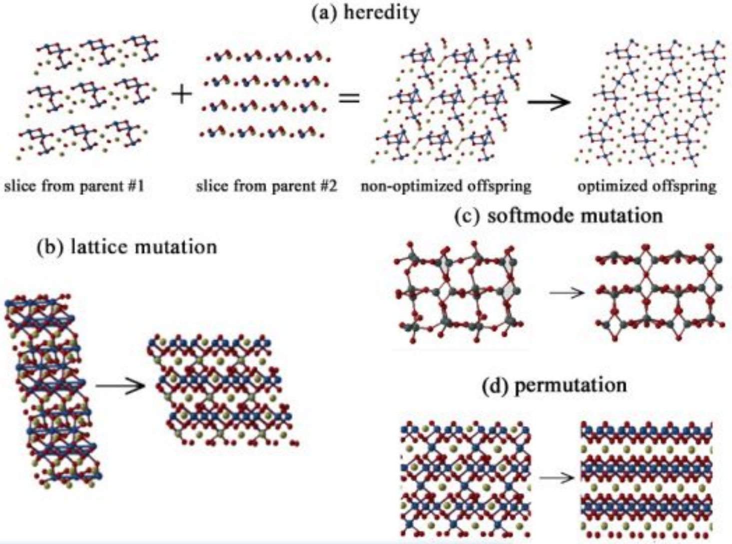
of generations:

Evolution

Genetic *evolutionary* based algorithms



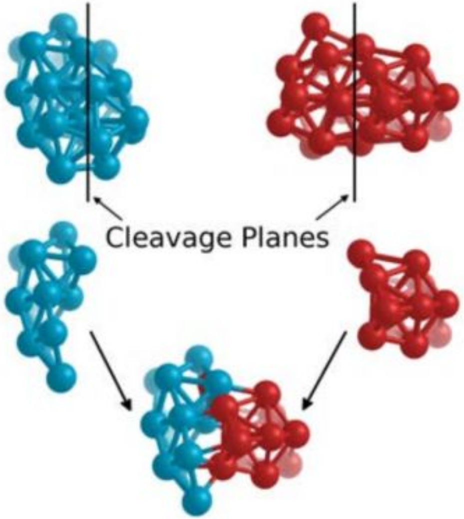
- ➔ Unnatural to map continuous atomic coordinates to binary strings.
- ➔ Modern GAs operate directly on atomic coordinates.
- ➔ Various methods to perform crossover in structures.
- ➔ GA implementations: **USPEX, XtalOpt, GASP, firefly, Abinit,** etc.


(a) heredity

(b) lattice mutation

(c) softmode mutation

(d) permutation



See Glass, Oganov and variants

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Minima Hopping Method (MHM)

Approach of the method

Use walker to explore the *(3N – 3) + 6–dim* enthalpy surface by visiting local minima efficiently, hopping from one minimum to the next.*

Strategy of the walker

- ➔ Perform hops that lead to low energy structures.
- ➔ Avoid revisiting local minima.
- ➔ Allow crossing already explored regions on PES.
- ➔ How to hop: random displacements, single ended saddle point, etc.
- ➔ Constant energy Molecular Dynamics is more efficient!

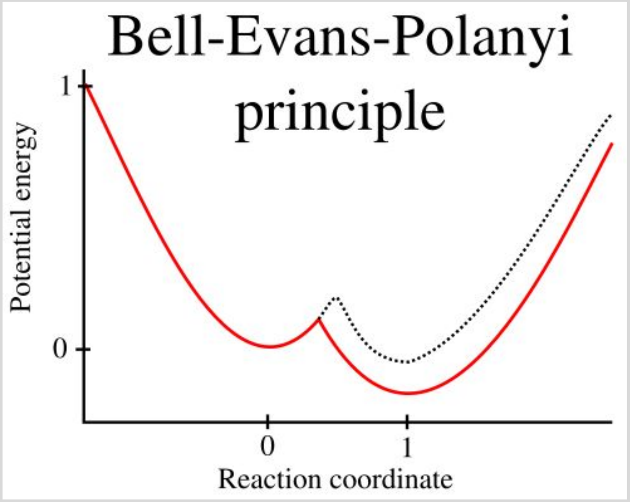
* MHM: Goedecker Journal of Chemical Physics, **120**, 9911, 2004

Optimal moves

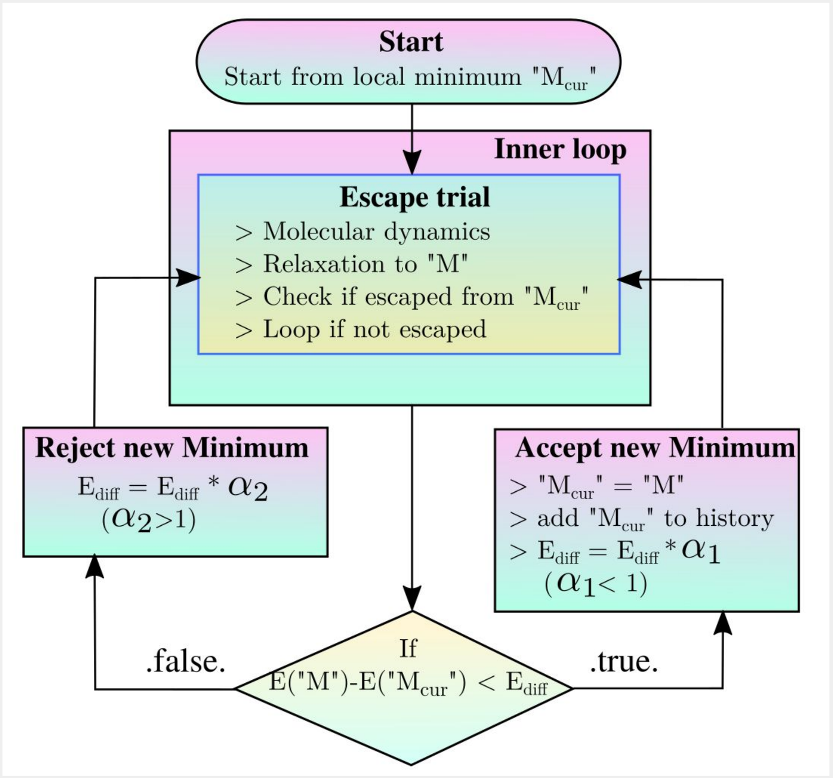
-- The difference in activation energy between two reactions of the same family is proportional to the difference of their enthalpy of reaction --

"Exothermic reactions have a low activation energy"

- Reactant and product are neighboring minima and chemical reactions are transitions of barriers connecting them.
- Energy conservation limits surmountable barrier height by E_{kin}.
- Low E_{kin} in MD for hops into low neighboring minima !



The algorithm



See: Amsler, Goedecker and Flores work

Inner loop

- Perform MD escape trials followed by local geometry relaxation.
- E_{kin} continuously adjusted

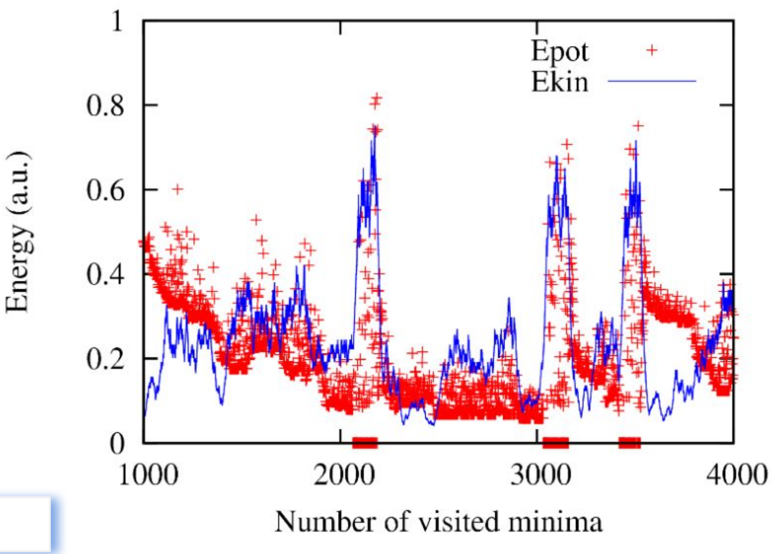
Outer loop

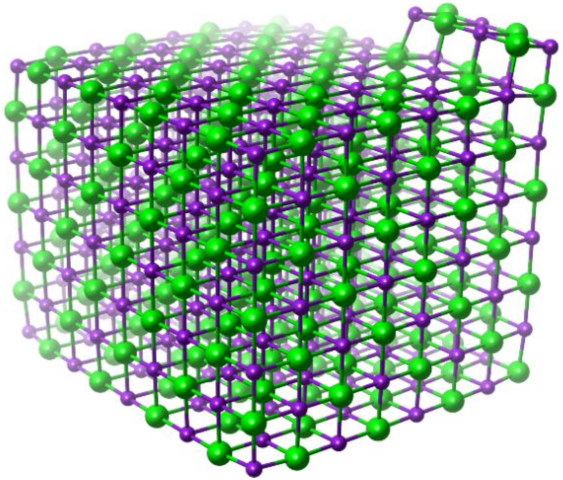
- ➔ Accepting or rejecting.
- ➔ Preference for lower energy, E_{diff}
- ➔ Dynamic E_{diff} 50% accepted. Eventually accept high energy structures.
- ➔ Feedback on E_{kin} based on history

Example of the feedback mechanism

Minima hopping for a 512 atom NaCl cluster

- Global minimum: 8 by 8 by 8 cube
- Wrong funnel: 7 by 8 by 9 (=504) cuboid with defects

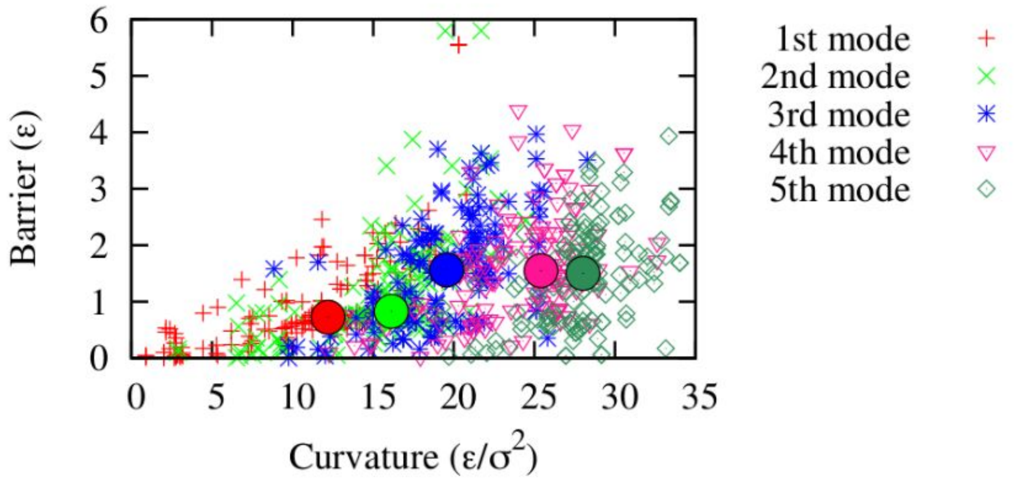




See: Amsler work

Optimizing the Moves

- Efficiency depends highly on the moves.
- Optimized initial velocity of MD trajectory is crucial.
- Soft modes lead to low barriers -Softening-



Curvatures of eigenmodes of local minima correlate with corresponding energy barrier heights. Align initial MD velocity vectors along soft modes!

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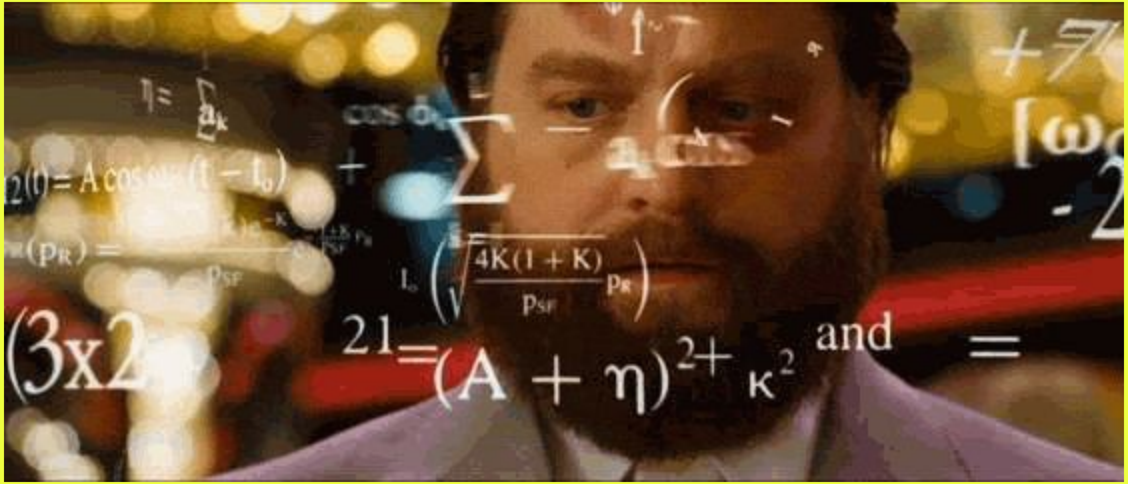
How big is the chemical space?

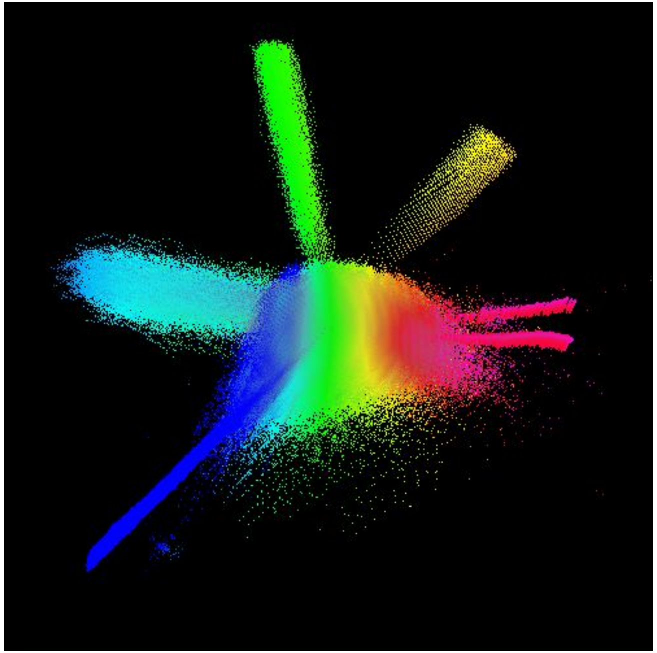


First: molecules and chemical compounds

Cheminformatics refers to the property space spanned by all possible molecules and chemical compounds adhering to a given set of construction principles and boundary conditions

As of July 2009, there were **49,037,297** organic and inorganic substances registered

- ➔ Drug discovery
- ➔ Chemical reaction, etc.



(View of chemical space)
A projection of the 42-dimensional

Materials discovery: The Chemical Space

Find element that “do mix” (miscible)

- Binaries: $\binom{112}{2} \approx 6,000$
- Ternaries: $\binom{112}{3} \approx 200,000$
- Quaternaries: $\binom{112}{4} \approx 6,000,000$

- Find possible stoichiometries (convex hull).
- Find correct crystal structure.
- Non-ambient conditions. (pressure/temperature/strain)

Search space practically impossible !

To accelerate materials discovery:

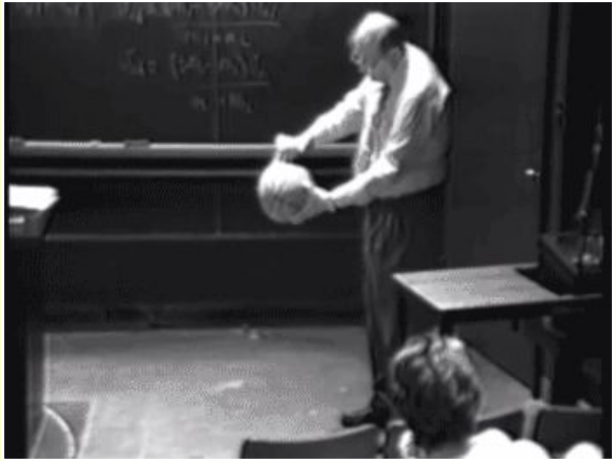
→ High-Throughput, database(s), etc.

→ Select few prototype and substitute sites.

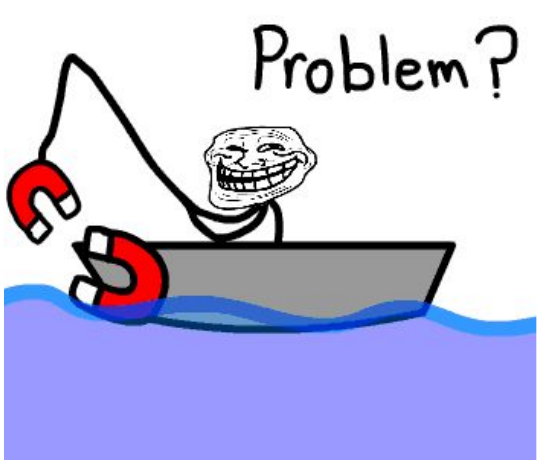
→ Constrain the space search.

How do we approach the problem?

I)



II)



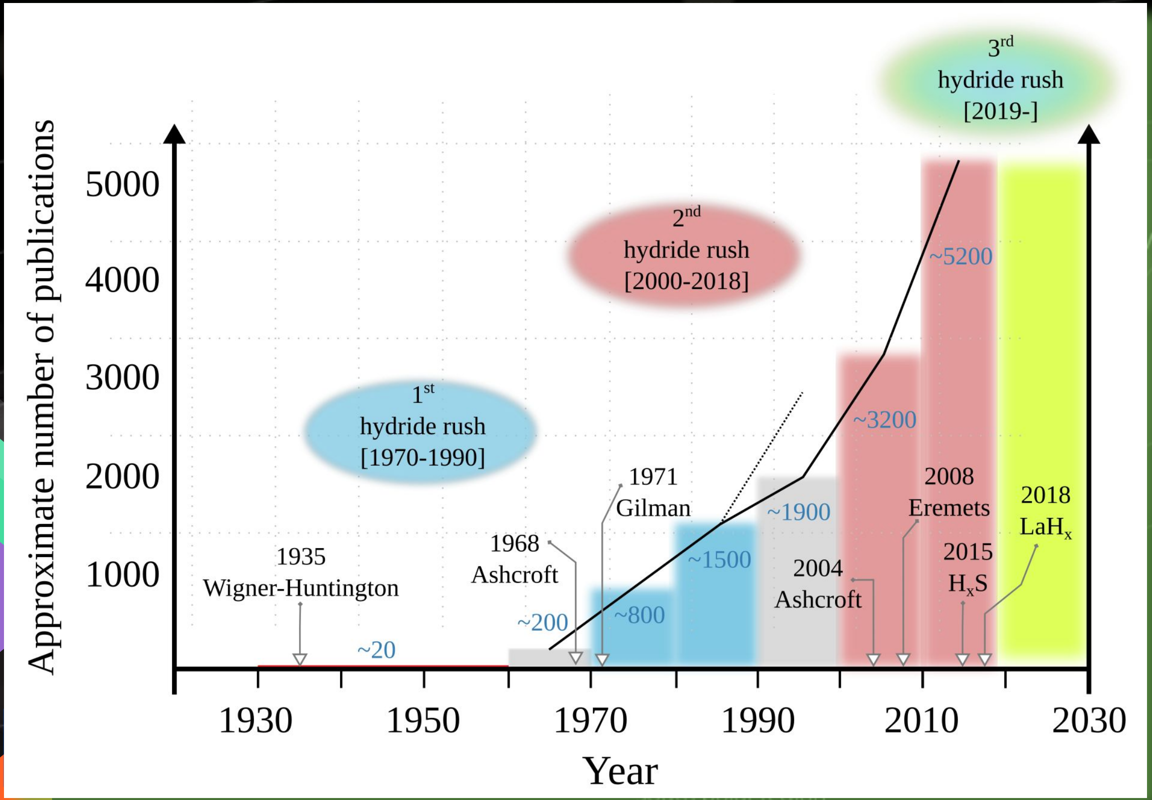
III)

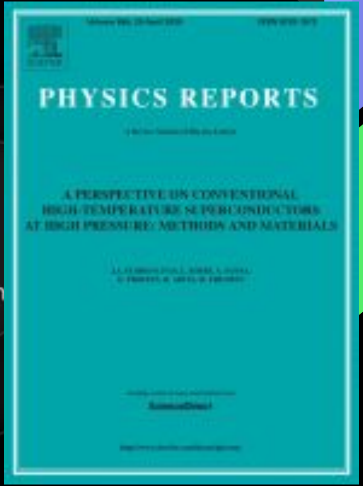
Experimental Science

Computational Science

Tabla de contenido:

Exotic chemistry






Science

REPORTS

Cite as: R. P. Dias *et al.*, *Science* 10.1126/science.aal1579 (2017).

Observation of the Wigner-Huntington transition to metallic hydrogen

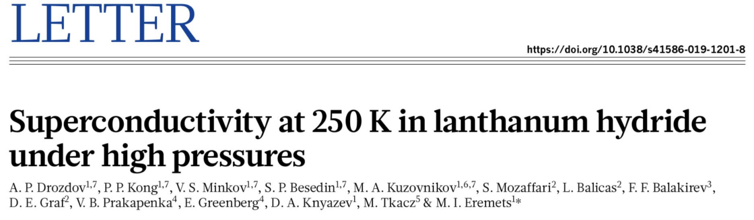
Ranga P. Dias and Isaac F. Silvera*

Lyman Laboratory of Physics, Harvard University, Cambridge, MA 02138, USA.

*Corresponding author. Email: silvera@physics.harvard.edu

Reference: "**A Perspective on Conventional High-Temperature Superconductors at High Pressure: Methods and Materials**" by Jose Flores-Livas et al. (Free access!!!)

Superconductivity at -23 C !

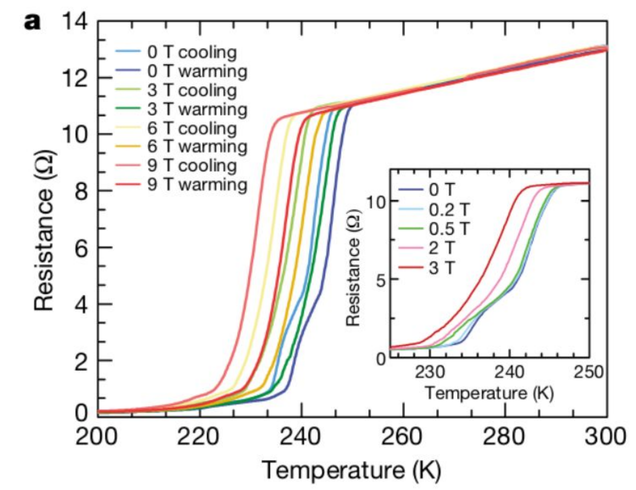


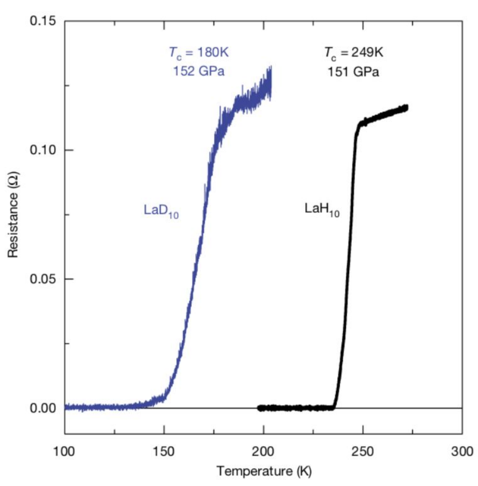
LETTER

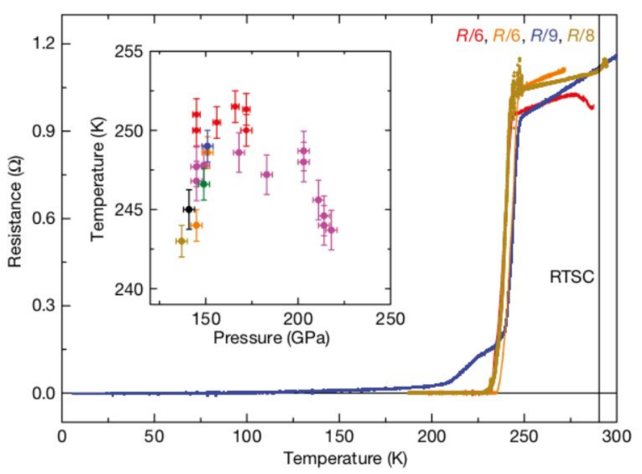
https://doi.org/10.1038/s41586-019-1201-8

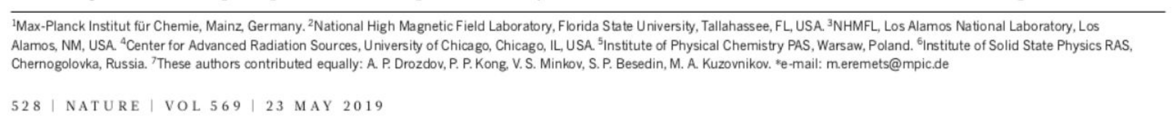
Superconductivity at 250 K in lanthanum hydride under high pressures

A. P. Drozdov[1,7], P. P. Kong[1,7], V. S. Minkov[1,7], S. P. Besedin[1,7], M. A. Kuzovnikov[1,6,7], S. Mozaffari[2], L. Balicas[2], F. F. Balakirev[3], D. E. Graf[2], V. B. Prakapenka[4], E. Greenberg[4], D. A. Knyazev[1], M. Tkacz[5] & M. I. Eremets[1]*









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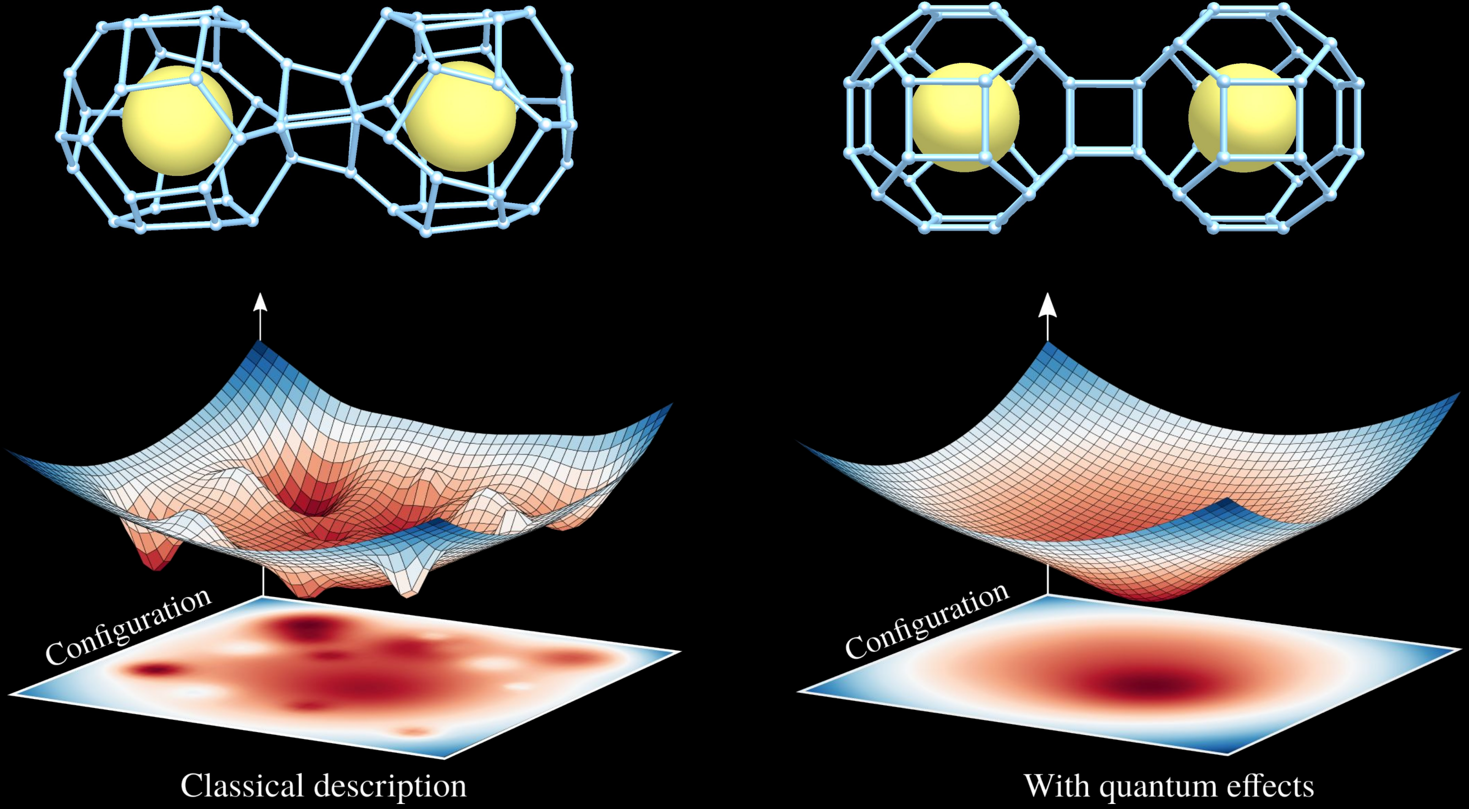
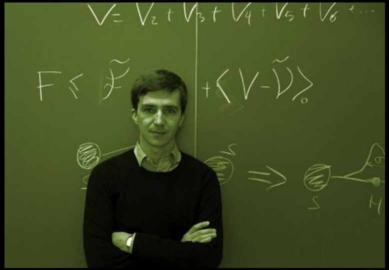
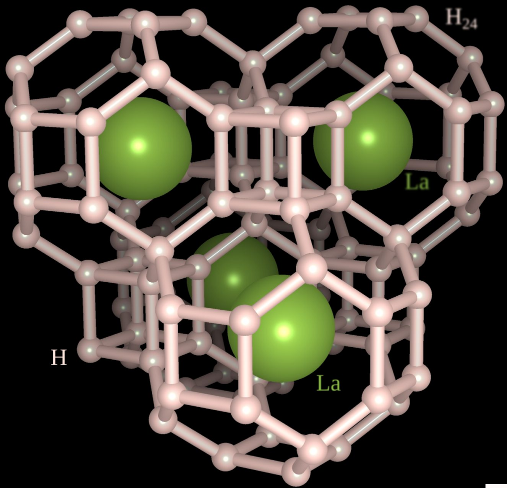
Structure prediction on “Supra” Hydrides: LaH_{10}



Experiments *In silico*: supercomputers



Errea, Belli, Bianco
(Donosti)

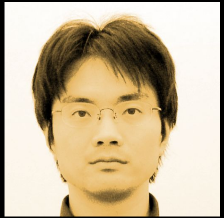


(Mauri, Monacelli) (Roma)

Calandra (Paris)

Sanna (Halle)

Arita (東京)

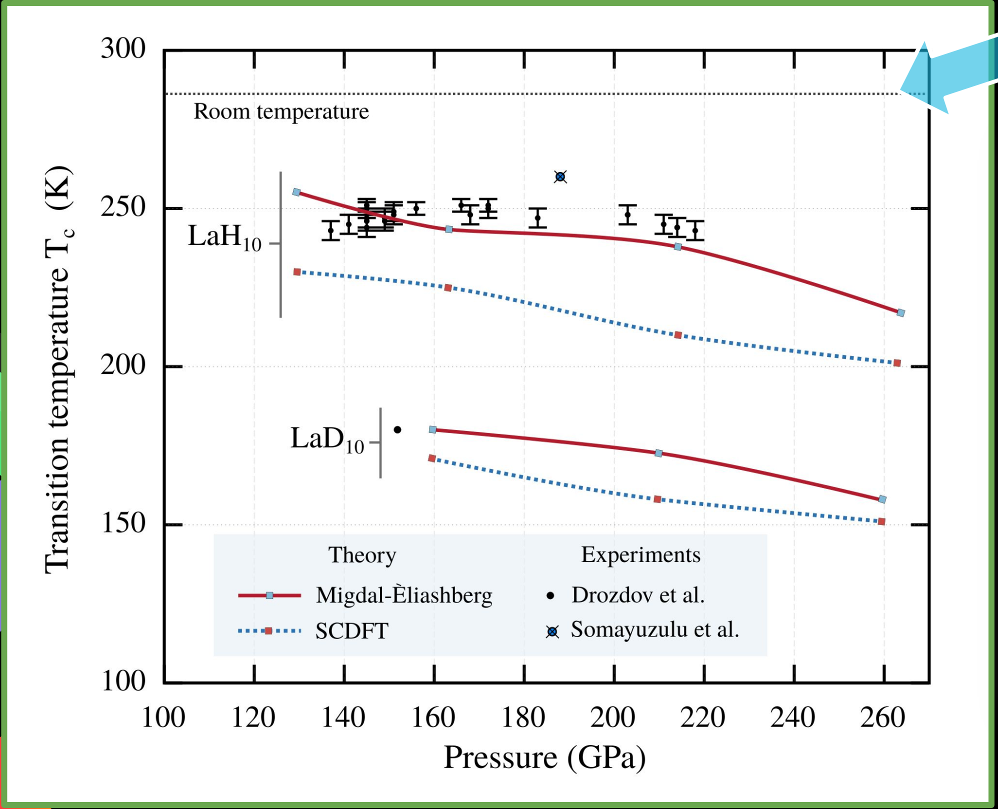


Koretsune (仙台)

Tadano (筑波)

Quantum Crystal Structure in the 250 K Superconducting Lanthanum Hydride.
I. Errea, F. Belli, L. Monacelli, A. Sanna, T. Koretsune, T. Tadano, R. Bianco, M. Calandra, R. Arita, F. Mauri and **J. A. Flores-Livas**. **Nature** 2020.

What is next? Answer: Room temperature!

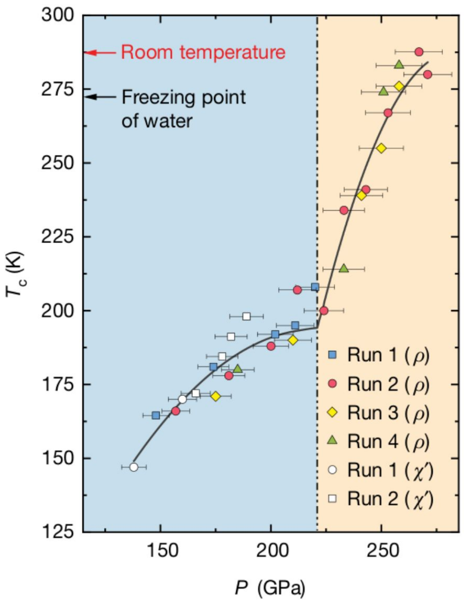


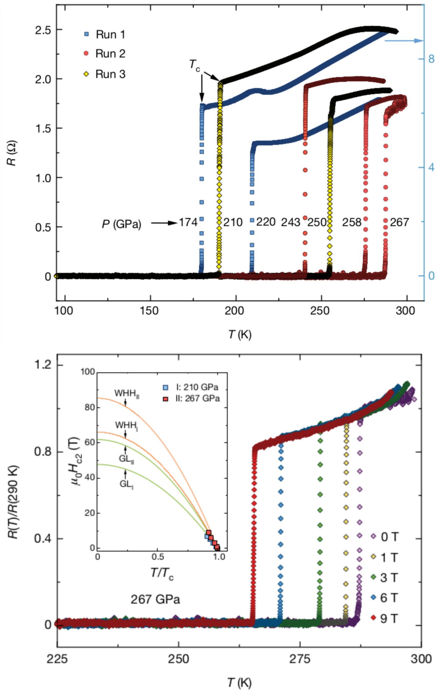
- ➔ How do we reach it?
- ➔ Can we cut by half the pressure? (currently 1.5 mbar)
- ➔ Much more development is necessary <u>computationally</u> and <u>theoretically</u>

Okawari paper: working on other La-H phases stabilised under specific thermodynamic conditions

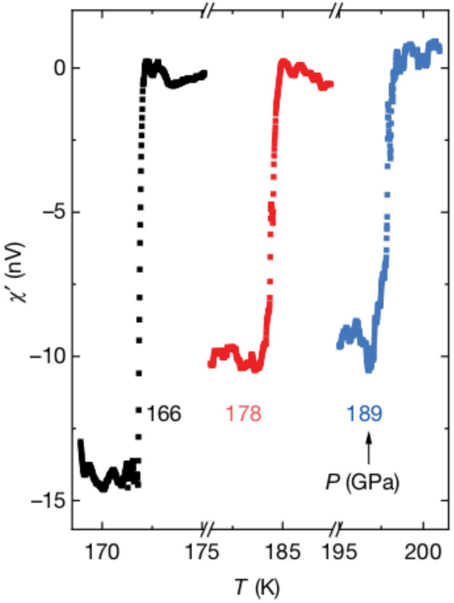
Tabla de contenido:

Evidence for the room temperature superconductor





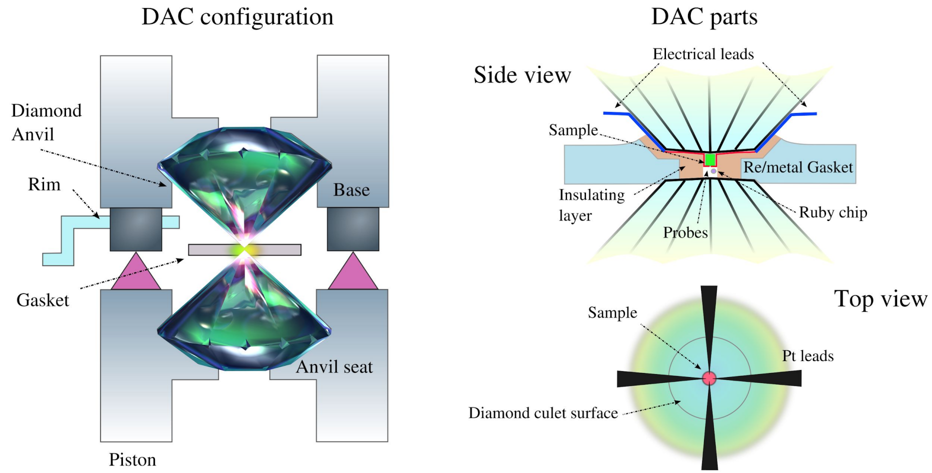
Temperature dependent electrical resistance of the C–S–H system at high pressures. Highest value of Tc is 287.7 ± 1.2 K at 267 ± 10 GPa.



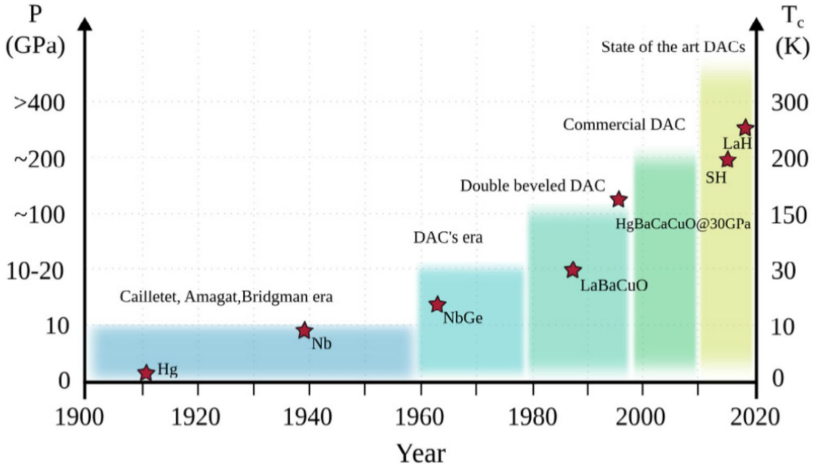
Real part of the a.c. susceptibility in nanovolts versus temperature for the C–S–H system at select pressures from run 2, showing substantial diamagnetic shielding of the superconducting transition for pressures of 160–190 GPa.

Reference: Snider et al. **Nature** Vol. 586 373, October 2020

High pressure, high temperature superconductivity



Left: DAC schematic including anvil seats, gasket and pistons.
Right: detailed design of a DAC for transport measurements under pressure*



Landmarks of pressure and Tc, at parallel, increased along the decades*

Reference: *Flores-Livas, et al. Review article in Phys Reports 856, 1-78 (2020)

Where and How do we start?

Strategy:

1) Analyse the thermodynamic of the system, i.e. crystal structure prediction

2) Associate what is going on in experiments to a theoretical picture, i.e. phase diagram

3) Thermodynamics of channels for doping: **plausibility of doping** to be happening in the system

4) Do account for the RTS? Reproduce the available results: is phonon driven superconductivity? Manufactured results? Novel mechanism?

5) Disentangle the **contradicting arguments** in the literature

6) Check consistency, external feedback, quality control of results: **Spread results**

Has room-temperature superconductivity at high pressure been achieved?

The theoretical/computational evidence presented here shows that there are striking differences

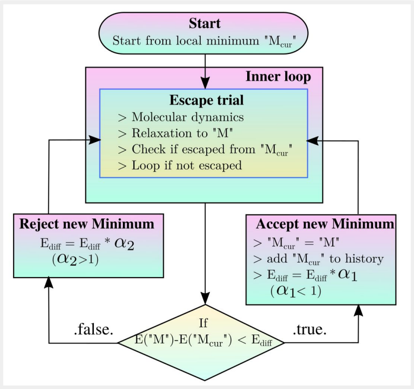
➔ **Thermodynamics**: there is not a single phase competing in enthalpy

➔ **Doping**: Introducing carbon plays against high-Tc: changes the DOS, decouples vibrations

➔ **Superconductivity**: Perhaps the theory's level is insufficient to reconcile the scenario with the present experimental results.

Reference: Flores-Livas, **Nature Vol. 578, April 2020, *"Quantum Crystal Structure in the 250 K Superconducting Lanthanum hydride"*

Theoretical Gibbs triangle



Start
Start from local minimum "M_{cur}"

Inner loop

Escape trial
> Molecular dynamics
> Relaxation to "M"
> Check if escaped from "M_{cur}"
> Loop if not escaped

Reject new Minimum
$E_{diff} = E_{diff} * \alpha_2$
(α_2>1)

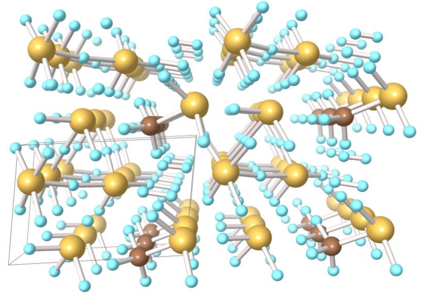
Accept new Minimum
> "M_{cur}" = "M"
> add "M_{cur}" to history
> $E_{diff} = E_{diff} * \alpha_1$
(α_1< 1)

If
E("M")-E("M_{cur}") < E_{diff}

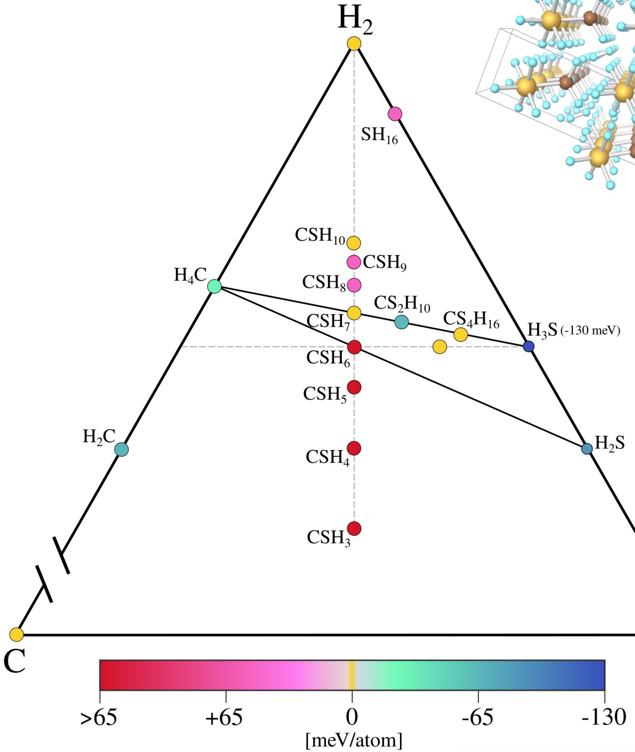
.false.

.true.

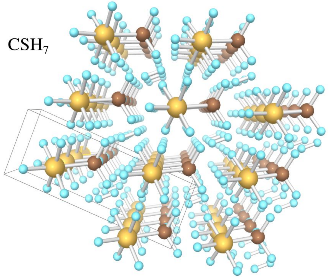
Computational algorithm to search crystals



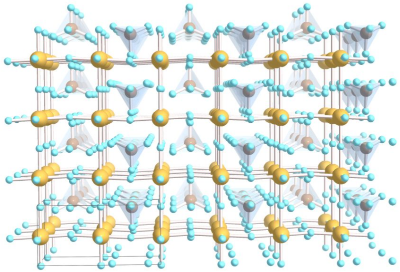
CS_4H_{16}

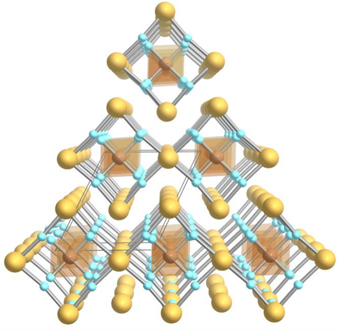


CSH_7



CSH_{10}



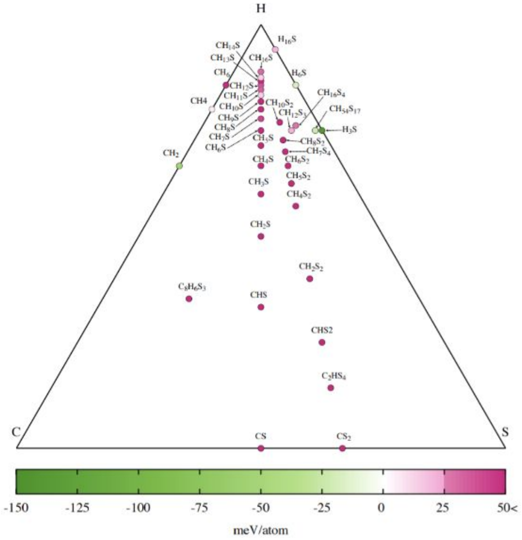


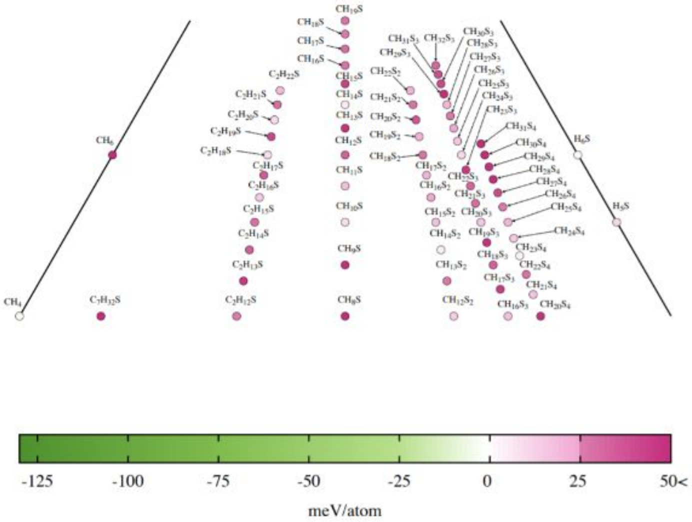
$C_{0.25}S_{0.75}H_3$

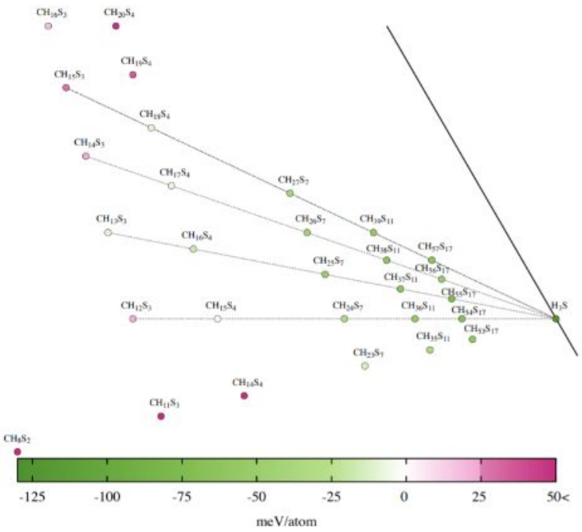
Conclusion: not a single phase is competitive in enthalpy against H_3S

Reference: Wang, Hirayama, Nomoto, Koretsune, Arita, and Flores-Livas, Phys Rev. B 104, 06451 (25/08/2021)

GPU accelerated searches (bigger cells and many more compositions)



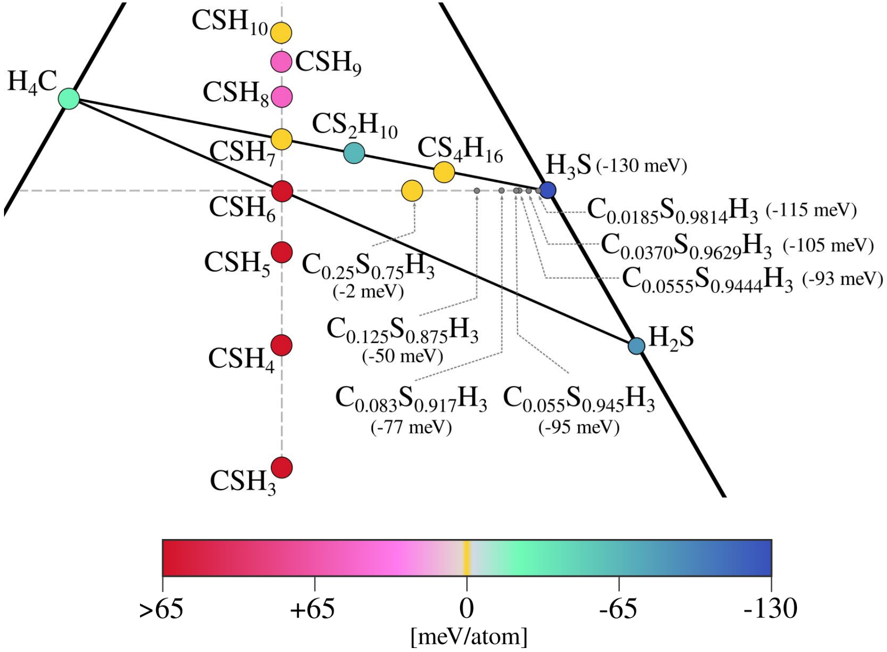




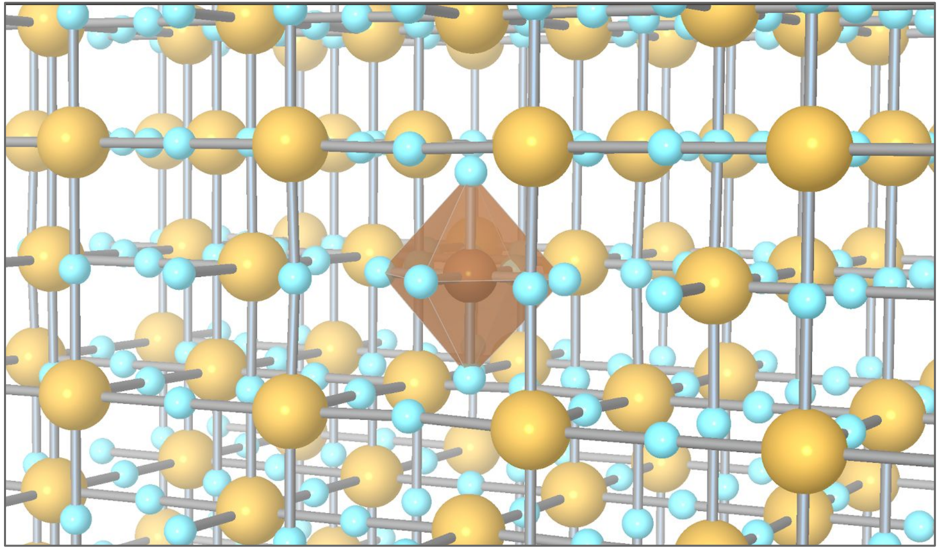
A selection of the 3000 best structures and their density of states is available on this github repository:
https:// github.com/moritzgubler/C-H-S_250GPa.

Reference: Gubler, Flores-Livas, Kozhevnikov and Goedecker, re-submitted yesterday (19/11/2021)

Thermodynamics of the doped phases



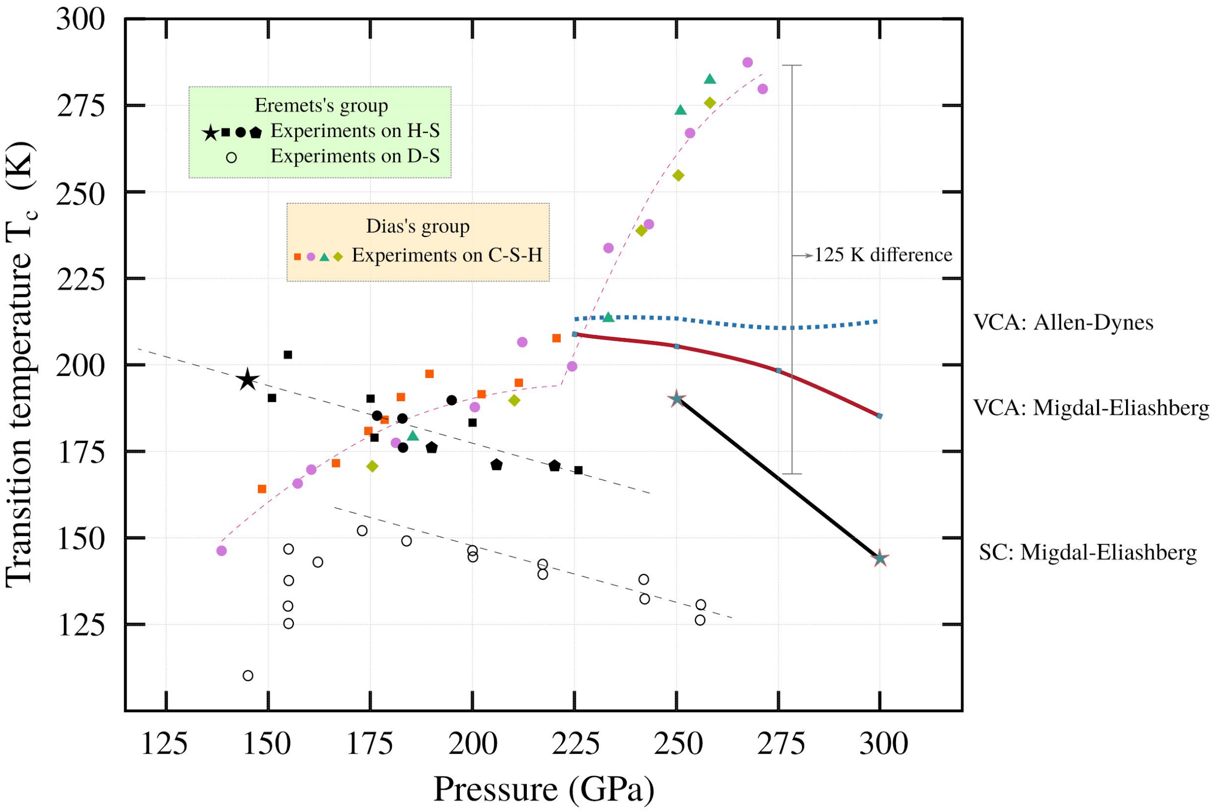
The CHx + H3S case



Conclusion: Doping is competitive but still cost high energy

Reference: **Wang, Hirayama, Nomoto, Koretsune, Arita, and Flores-Livas**, Phys Rev. B 104, 06451 (25/08/2021)

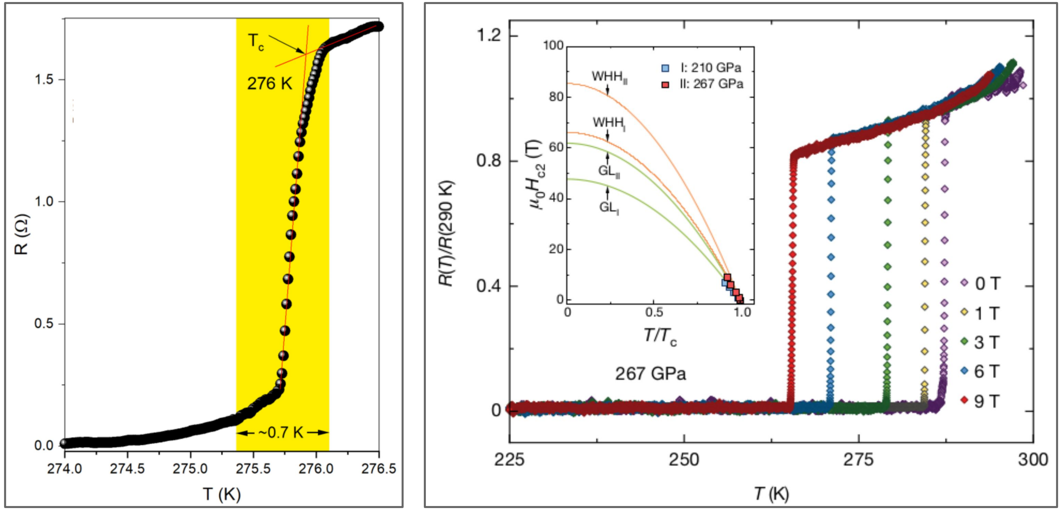
Confront of results: Doped model and Tc estimation



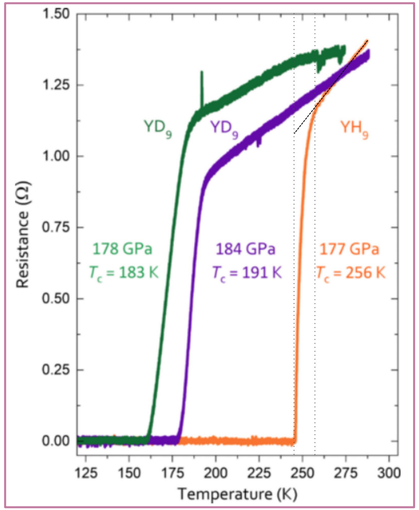
Reference: **Wang, Hirayama, Nomoto, Koretsune, Arita, and Flores-Livas**, Phys Rev. B 104, 06451 (25/08/2021)

If C-S-H is indeed a superconductor, is it an anomalous one?

For a standard type II superconductor an extremely sharp R vs T is anomalous



Snider et al. **Nature** Vol. 586 373, October 2020



Snider et al. **PRL** 126, 117003, 19 March 2021

$$H_{c2}(0) = \frac{\Phi_0}{2\pi\xi(0)^2}$$

$$\lambda(0) = \frac{\Phi_0}{2\sqrt{2}\pi H_c(0)\xi(0)}$$

$$\xi(0) = \frac{\hbar v_F}{\pi\Delta(0)}$$

$$\kappa = \frac{\lambda(0)}{\xi(0)}$$

$$\mathrm{CSH}: \frac{75\ \mathrm{nm}}{2.3\ \mathrm{nm}} = 32 \qquad \mathrm{H_3S}: \frac{164\mathrm{nm}}{2.12\mathrm{nm}} = 77 \qquad \mathrm{LaH_{10}}: \frac{147\mathrm{nm}}{1.69\mathrm{nm}} = 87$$

References:

1. Hirsch and Marsiglio arXiv:2010.10307 [cond-mat].
2. Talantsev, Supercond. Sci. Technol. (2020).
3. Elatresh, Timusk, Phys. Rev. B 102 (2020), 024501.
4. Dogan and Cohen, Physica C: 583 (2021) 1353851

In perspective

C-S-H poses striking anomalies as compared to other systems. What could potentially explain the experimental data?

In the absence of second team reproducing Dias's results possible hypothesis are:

- ➔ **An electronic transition** accompanied by a change of volume (triggered by temperature)**
- ➔ **Metallic-to-semi metallic transition** accompanied by structural transition
- ➔ **Anharmonicity** : stabilising off-enthalpy structures **
- ➔ As for **Doping**: we (or I) can rule out this possibility with a high degree of confidence
- ➔ Novel superconducting mechanism?

Gracias!

ありがとうございます

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