Accelerating Materials Discovery with High-Throughput DFT: The Open Quantum Materials Database (OQMD)

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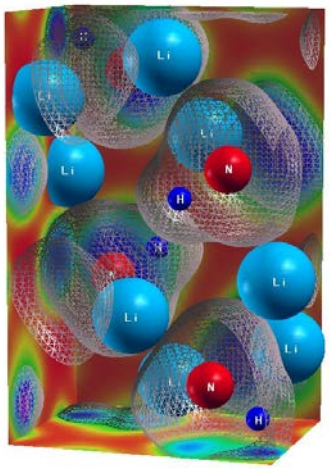
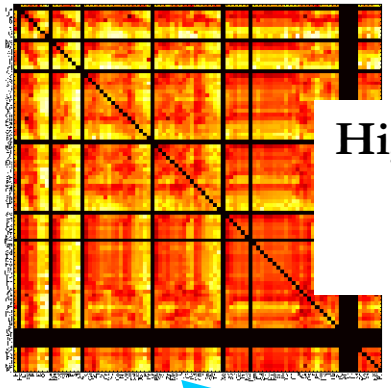
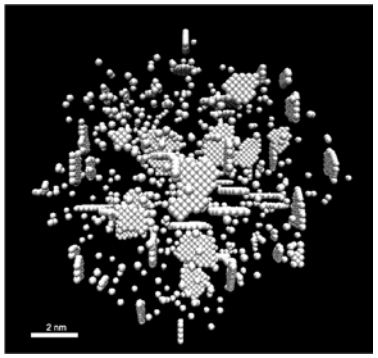
Computational Materials Science: Materials for Alternative Energies and Sustainability



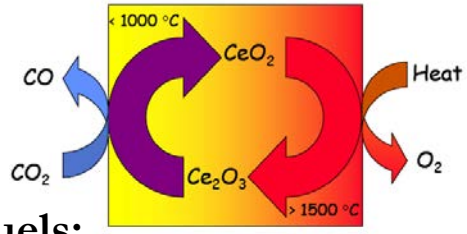


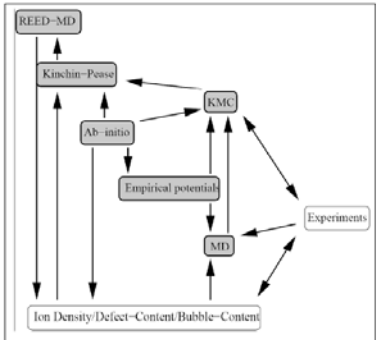
High-Throughput /Machine Learning



Hydrogen Storage

Light-Weight Structural Materials

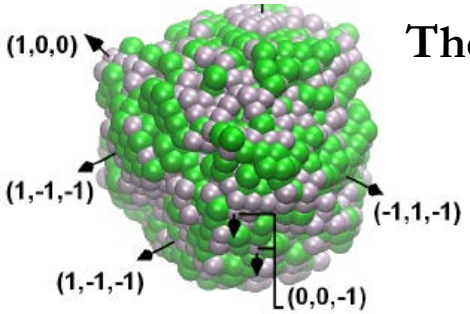




Nuclear Energy Materials

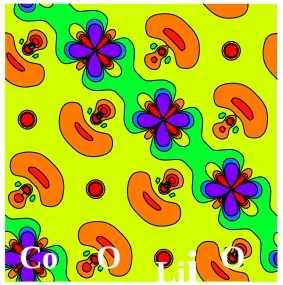
$H\Psi = E\Psi$

Solar Fuels: Thermochemical Production of H_2

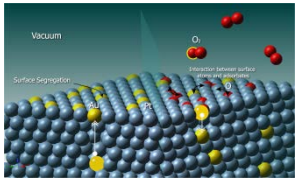


Thermoelectrics

Energy Storage / Batteries



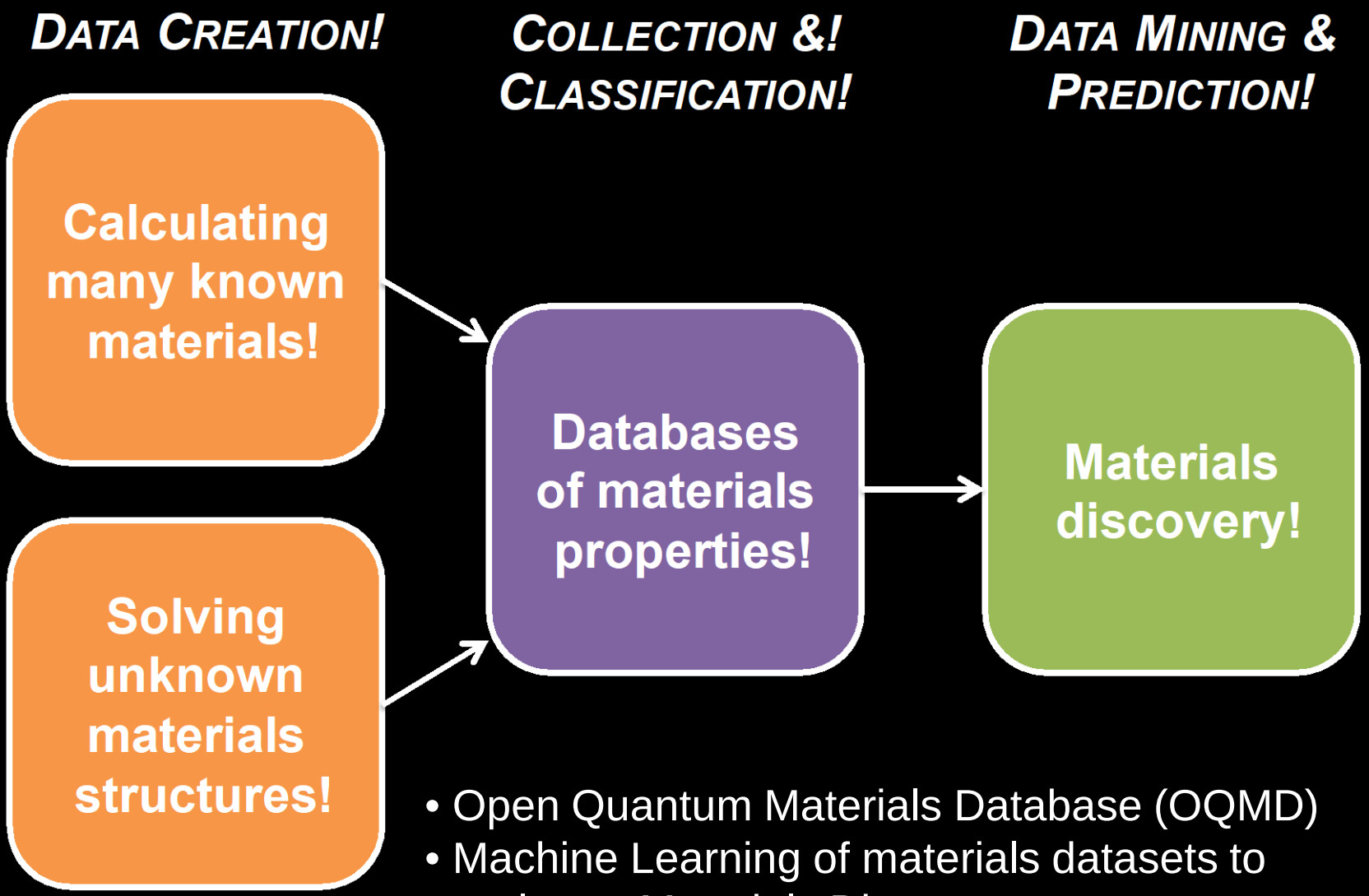
Catalysis / Metal Surfaces



For many energy-related problems: *We need new materials*

- H_2 Storage
  - High volumetric/gravimetric density of H_2, thermodynamically-reversible, fast kinetics
- Thermoelectrics
  - High figure of merit: ZT~3, earth-abundant
- Water Splitting Redox Cycles
  - Redox cycles with favorable thermodynamics (to split H_2O or CO_2); fast kinetics
- Cheap, safe, …

How to use data to accelerate discovery of new materials?

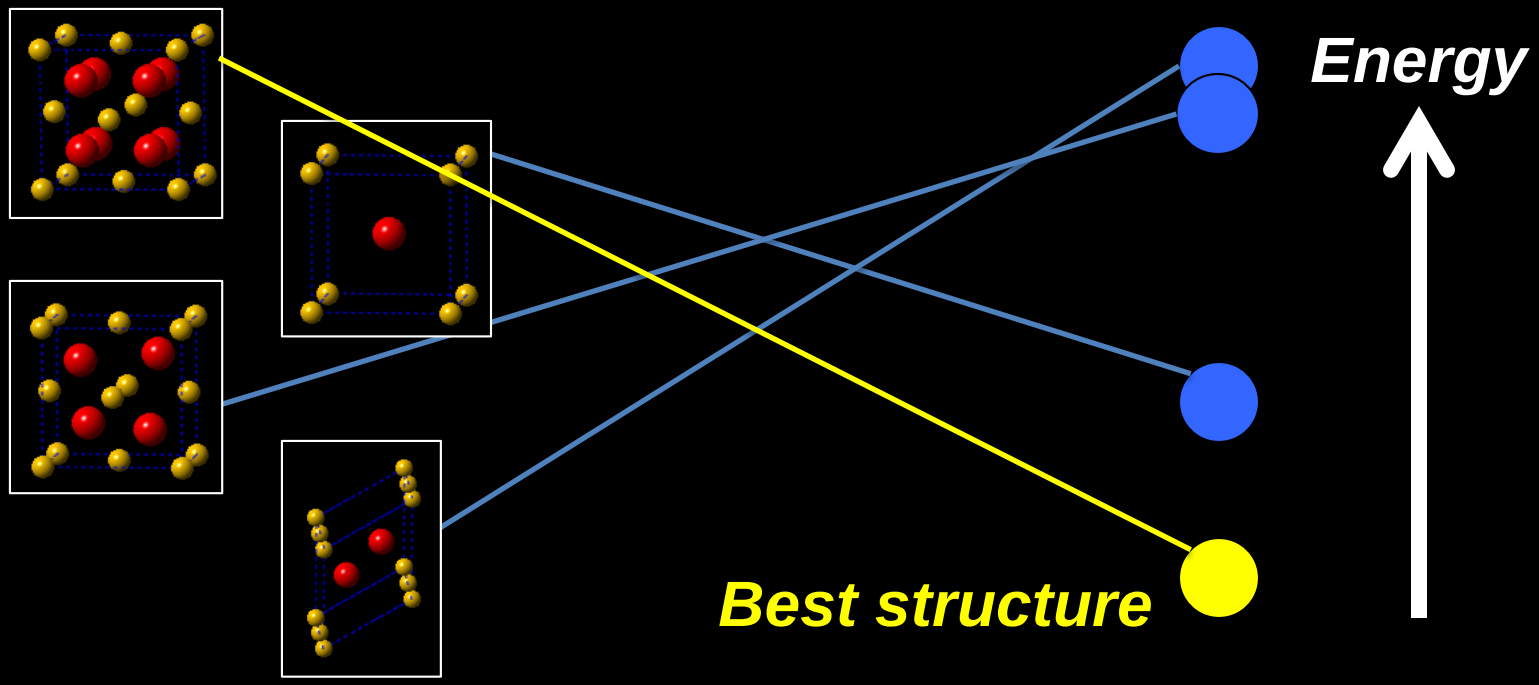


- Open Quantum Materials Database (OQMD)
- Machine Learning of materials datasets to accelerate Materials Discovery

Crystal Structure Example

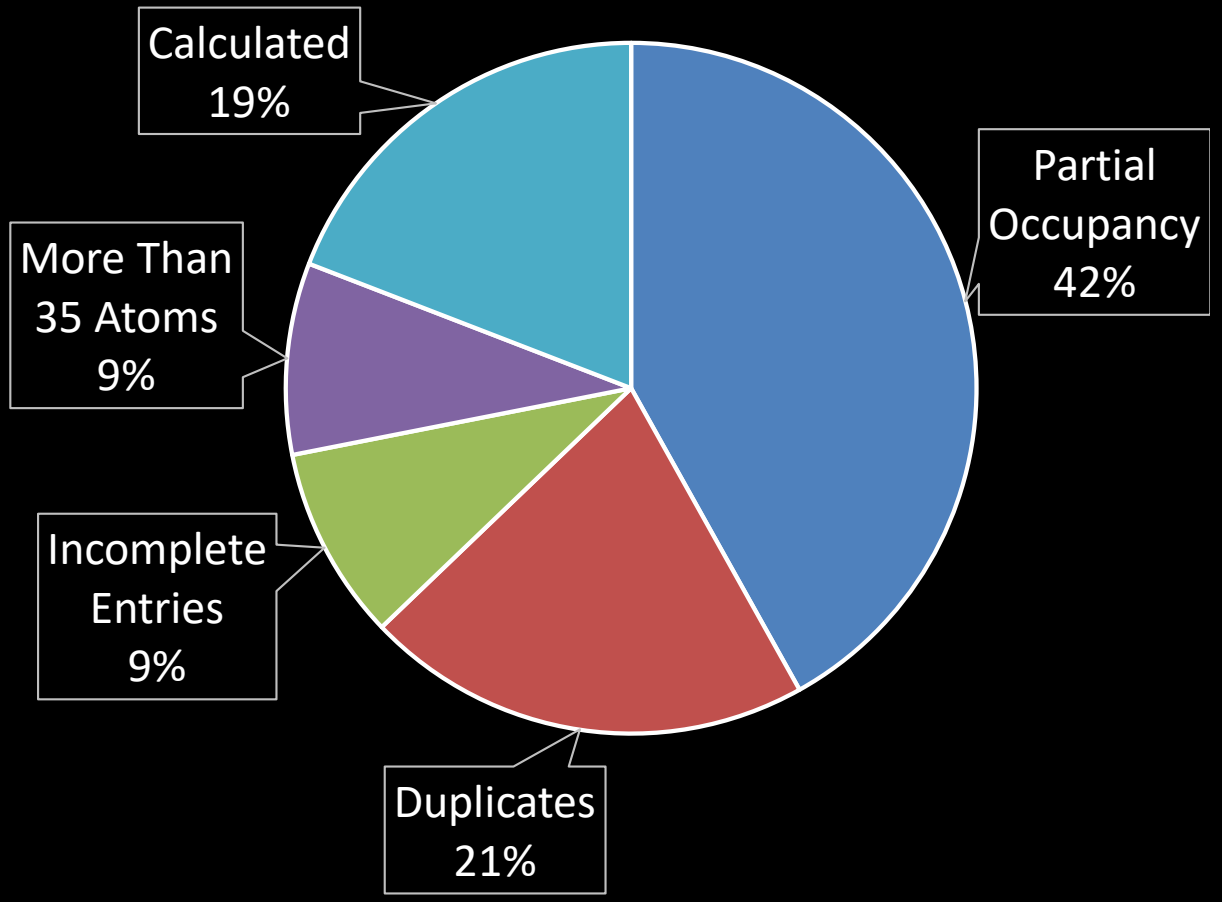
Atomic Coordinates
(r_1, r_2, … r_n)

Property *P*:
Total Energy



Known “Library” of Materials Structures – The ICSD

- Partnership with the International Crystal Structure Database (ICSD)
- Collection of +161,000 experimentally recorded structures
- Of these, ~45,000 have been calculated in the OQMD
- Remainder uncalculated for one of several reasons

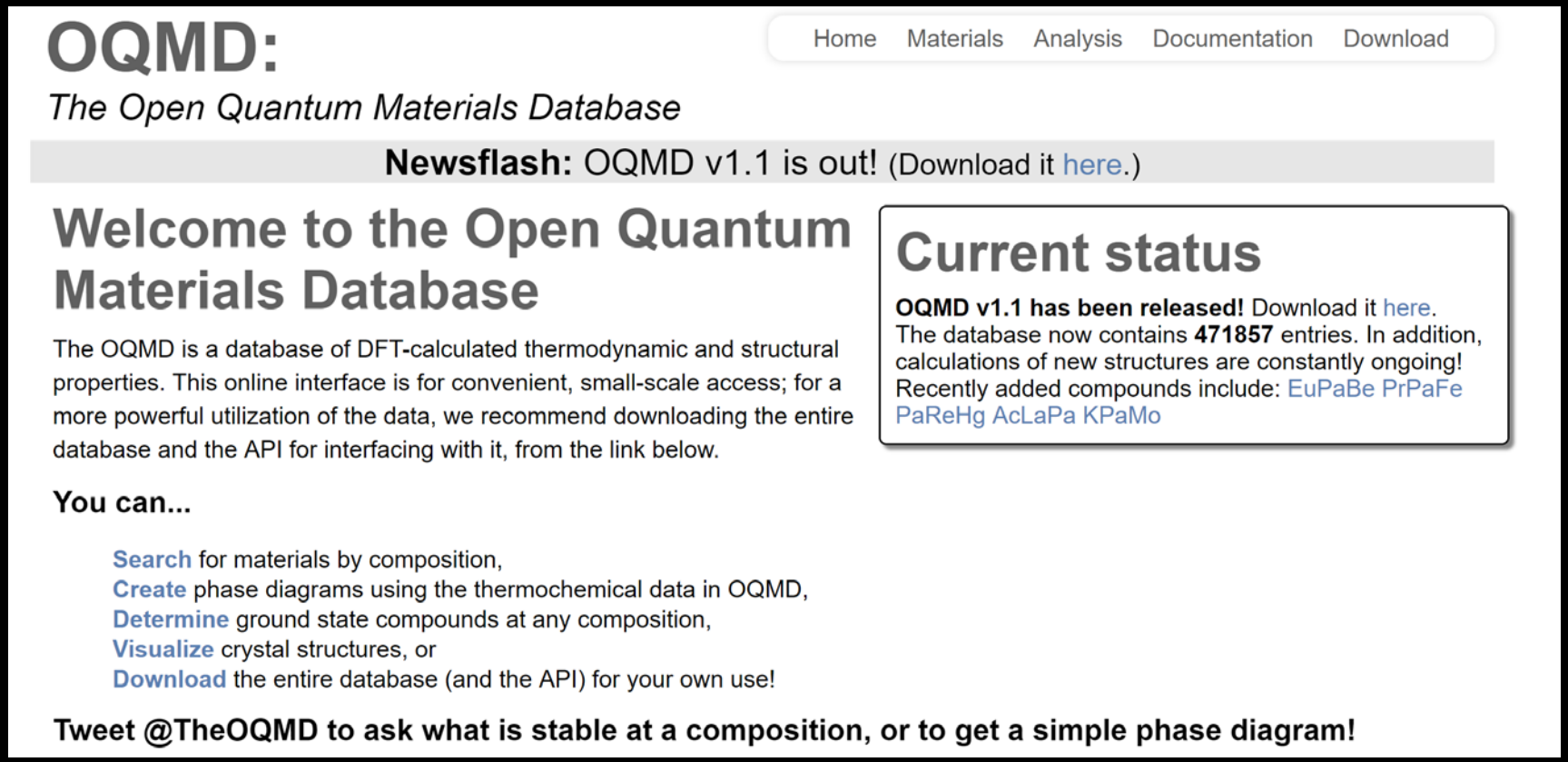


The Open Quantum Materials Database (OQMD)

- **Open** – An online (oqmd.org), freely available database…
- **Quantum** – … of self-consistently DFT-calculated properties…
- **Materials** – … for >45,000 experimentally observed and >500,000 hypothetical structures (decorations of commonly occuring crystal structures)…
- **Database** – … built on a standard and extensible database framework.

Saal, Kirklin, Aykol, Meredig, and Wolverton "*Materials Design and Discovery with High-Throughput Density Functional Theory: The Open Quantum Materials Database (OQMD)*", JOM **65**, 1501 (2013)

oqmd.org



OQMD:

The Open Quantum Materials Database

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Newsflash: OQMD v1.1 is out! (Download it here.)

Welcome to the Open Quantum Materials Database

The OQMD is a database of DFT-calculated thermodynamic and structural properties. This online interface is for convenient, small-scale access; for a more powerful utilization of the data, we recommend downloading the entire database and the API for interfacing with it, from the link below.

Current status

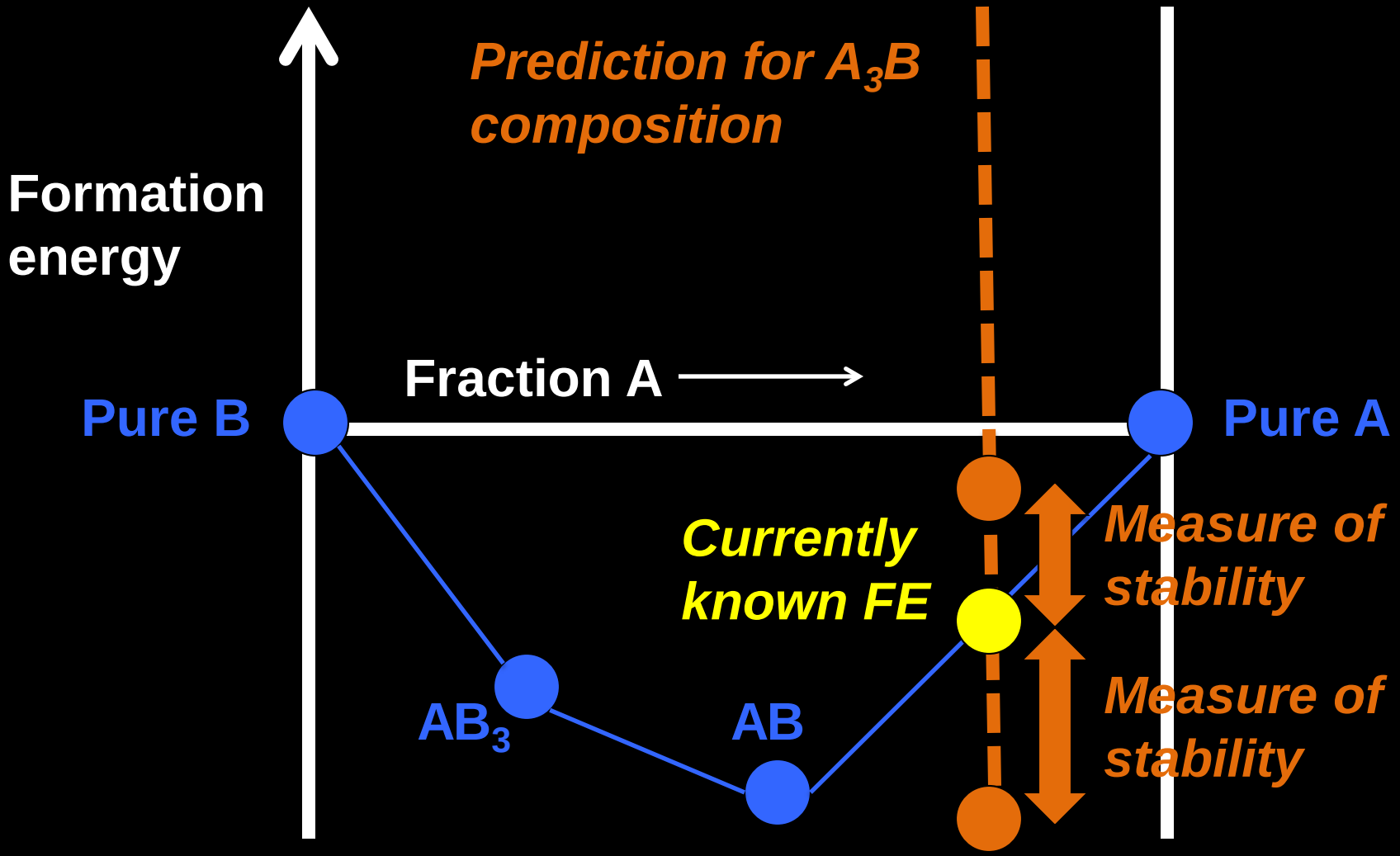
OQMD v1.1 has been released! Download it here.
The database now contains **471857** entries. In addition, calculations of new structures are constantly ongoing!
Recently added compounds include: EuPaBe PrPaFe PaReHg AcLaPa KPaMo

You can...

Search for materials by composition,
Create phase diagrams using the thermochemical data in OQMD,
Determine ground state compounds at any composition,
Visualize crystal structures, or
Download the entire database (and the API) for your own use!

Tweet @TheOQMD to ask what is stable at a composition, or to get a simple phase diagram!

Formation Energy→Stability



convex hull: how to calculate it?

- a highly non-trivial optimization problem for **d**>2! ("simple" tool)
- example: the **quickhull algorithm**

pseudocode for $\mathbf{R^2}$:

1. find two extrema (*a*, *b*) by maximizing any coordinate
2. choose point *c* that is farthest from *a*-*b* in the orthogonal direction [O(n)], and delete all points within Δ(*a*-*b*-*c*) [O(n)]
3. repeat 1., 2. with (*a*, *c*), (*b*, *c*)

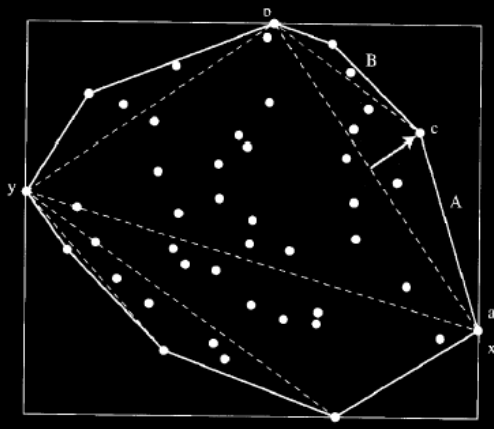


FIGURE 3.3 QuickHull discards the points in $\triangle abc$ (shaded) and recurses on A and B. Here $A = \emptyset$ and $|B| = 2$.

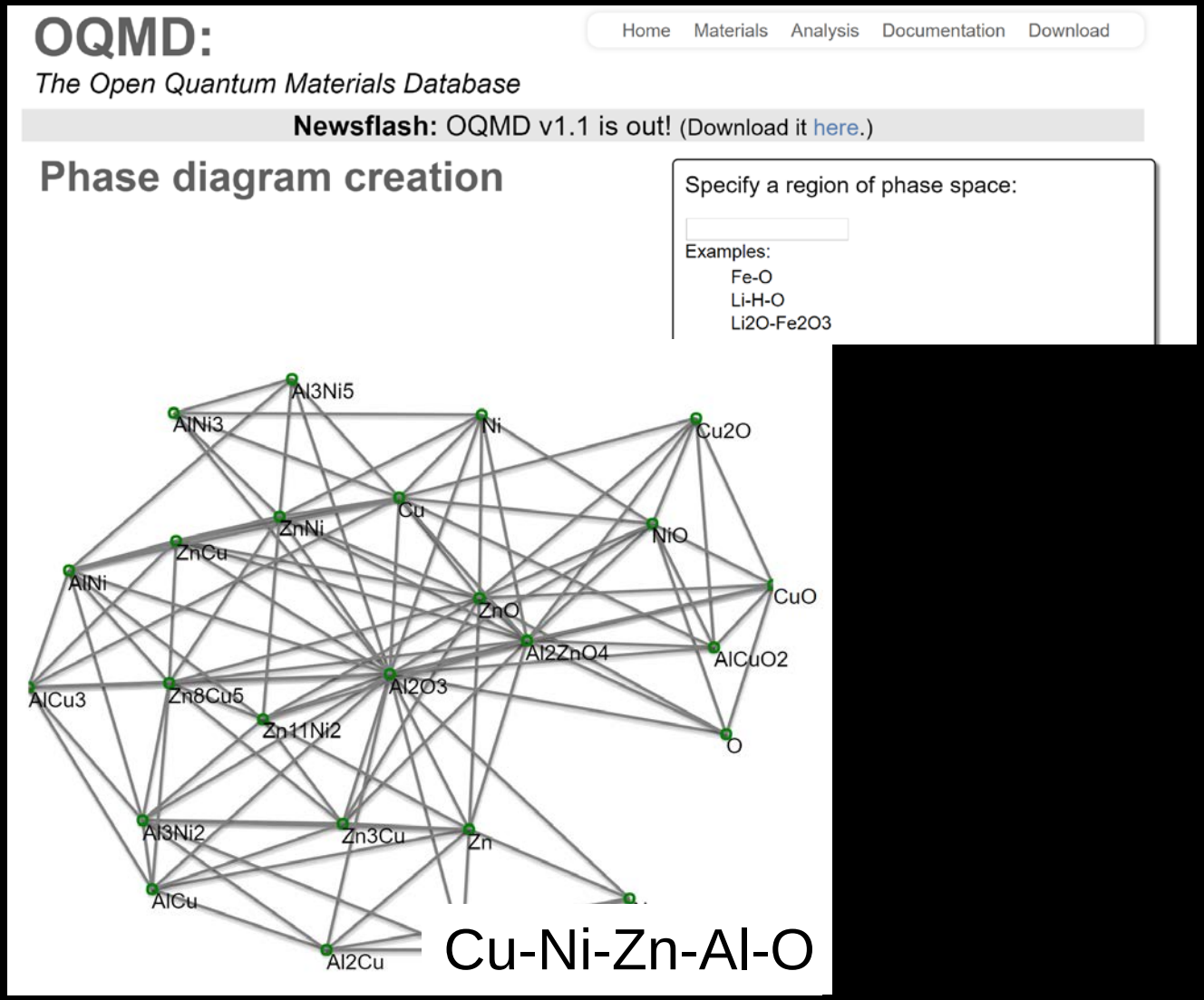
* For phase diagrams, of course, we already know at least 2 extrema, and we care about only one half of the convex hull.

oqmd.org

Phase Diagrams (T=0K)

- binary
- ternary
- quaternary
- higher

Search by composition

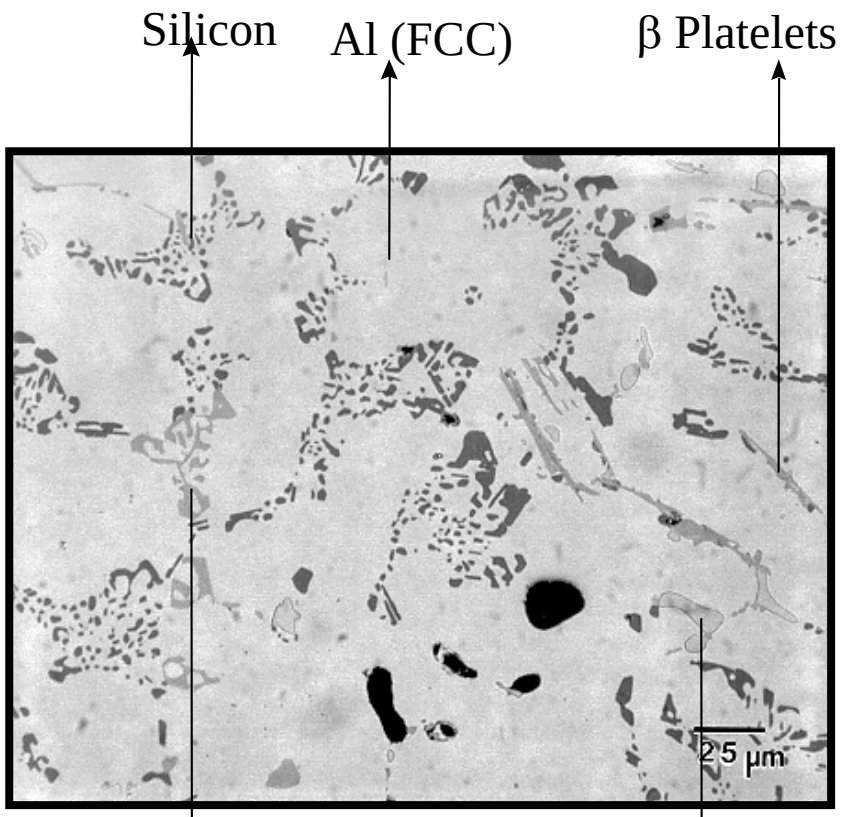


Example 1: Complex Industrial Cast Al alloy

“319 Al”

$Al_{88.08}Si_{7.43}Cu_{3.33}Mg_{0.22}Fe_{0.38}Mn_{0.24}Zn_{0.13}Ti_{0.12}Ni_{0.01}Cr_{0.03}Sr_{0.03}$

Solidification Microstructure (Aluminum 319)



1. **Al-rich (fcc) solid solution + Precipitates: Al-Cu GP zones, θ', S, Q)**
2. **Eutectic Silicon**
3. **Al_2Cu – θ phase**
4. **Script – $Al_{15}(MnFe)_3Si_2$**
5. **β platelets or βFeSi plates (Al_5FeSi)**
6. **Q-phase ($Al_3Cu_2Mg_9Si_7$)**

Credit: Ford Research Lab, VAC Team

What is ground state of the following composition (Al319)?

$Al_{88}Si_7Cu_{1.6}Mg_{0.22}Fe_{0.2}Mn_{0.13}$

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Relative phase compositions

0.0244 Mg9Al3Cu2Si7 + 6.43 Si + 1.55 Al2Cu + 0.2 Al3FeSi2 + 0.13 MnAl12 + 22.7 Al

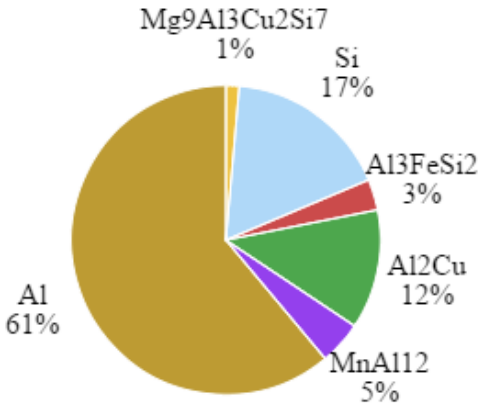
ΔH = -0.037 eV/atom

Search for a composition or region

Al28.08Si7Cu1.6Mg0 submit

Examples:

Al2O3
LiFeO2
Cu2MnAl



Stable phases:

Name	Spacegroup	Formation Energy	Amount
Mg9Al3Cu2Si7	Pm	-0.154	0.02
Si	Fd-3m	-0.000	6.43
Al2Cu	Fm-3m	-0.175	1.55
Al3FeSi2	Pbcn	-0.256	0.20
MnAl12	Im-3	-0.098	0.13
Al	R-3m	0	22.74

Note: Al content was decreased for graphical clarity of pie chart

What is ground state of the following composition (Al319)?

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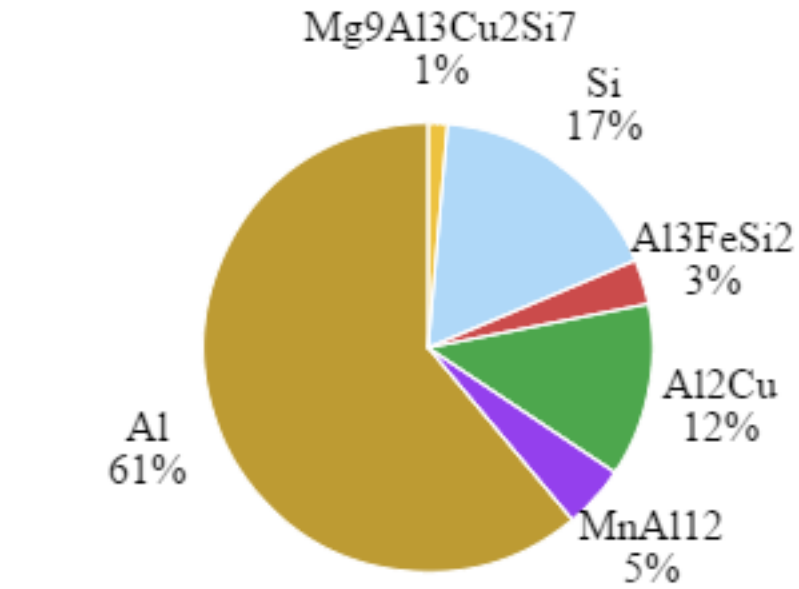

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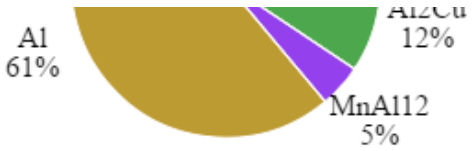

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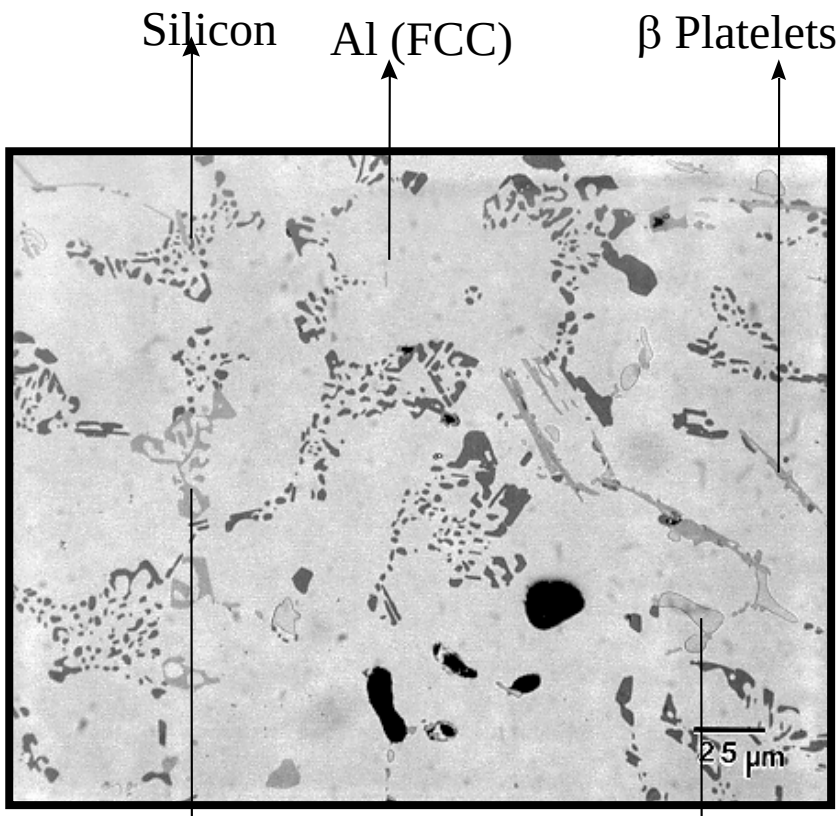

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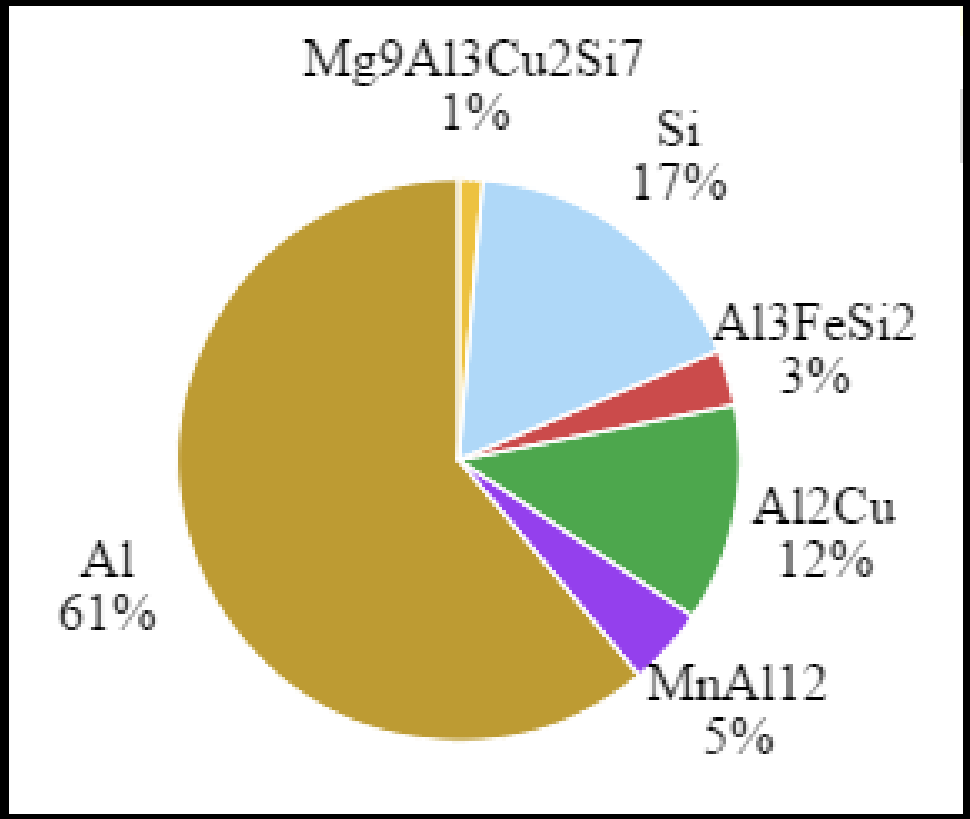
Solidification Microstructure (Aluminum 319)

OQMD Convex Hull Calculation:



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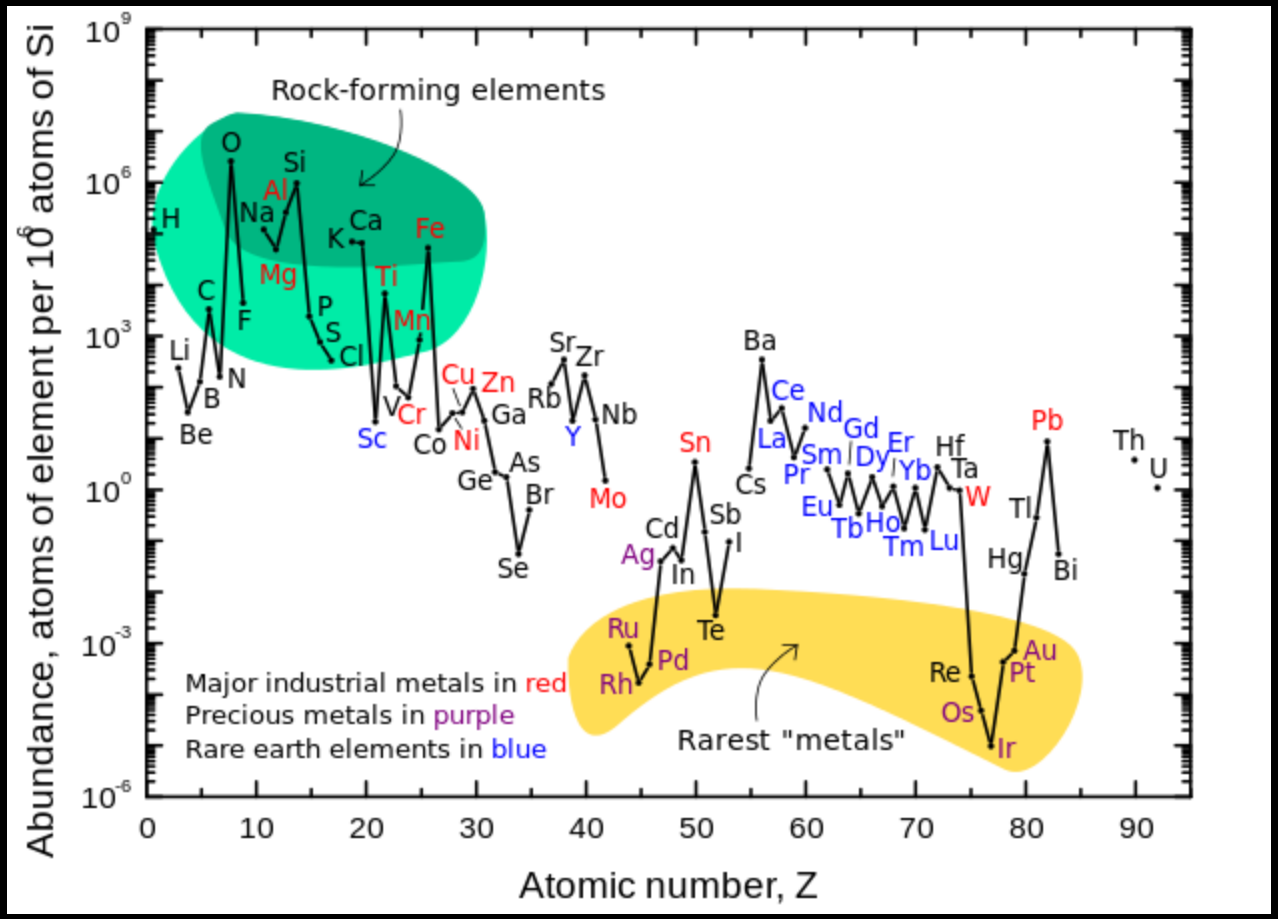
Note: Al content was decreased for graphical clarity of pie chart

Example 2: **What is the phase diagram of the earth? For the composition of the earth, what is the stable collection of phases?**

$O_{506}Si_{180}Al_{54}Fe_{15}Ca_{13}K_{10}Na_{25}Mg_{16}$

Chemical composition of the earth's crust

Source: Wikipedia



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OQMD:

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Home Materials Computing Analysis Documentation Download

Relative phase compositions

8 MgFeSiO4 + 9 CaAl2Si2O8 + 25 NaAlSi3O8 + 4 CaMgSi2O6 + 39.7 SiO2 + 10 KAlSi3O8 + 3.5 MgFe2O4 + 0.25 Mg2Al4Si5O18

ΔH = -3.046 eV/atom

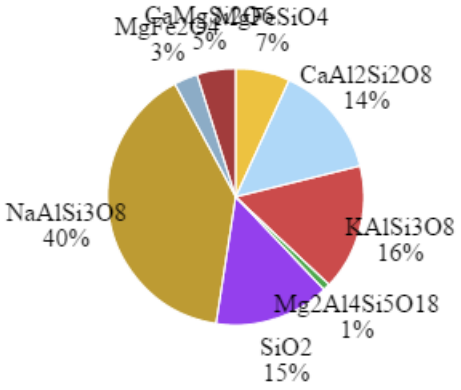
Search for a composition or region

O506Si180Al54Fe15(submit

Examples:

Al2O3
LiFeO2
Cu2MnAl

Stable phases:



Name	Spacegroup	Formation Energy	Amount
MgFeSiO4	Pnma	-2.685	8.00
CaAl2Si2O8	P21	-3.264	9.00
KAlSi3O8	P-1	-3.079	10.00
CaMgSi2O6	C2/c	-3.195	4.00
SiO2	I-42d	-3.078	39.75
NaAlSi3O8	P-1	-3.057	25.00
MgFe2O4	Fd-3m	-2.085	3.50
Mg2Al4Si5O18	Cccm	-3.170	0.25

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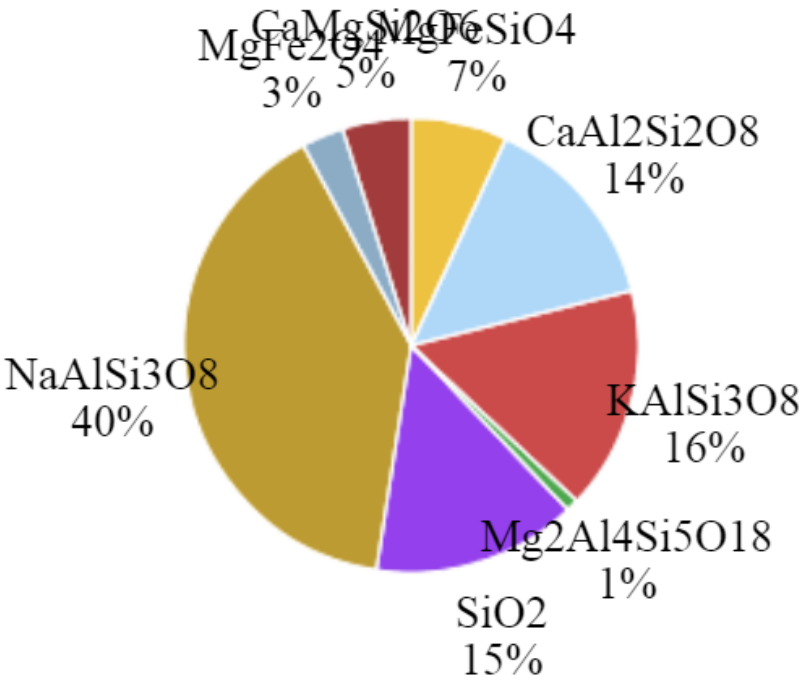

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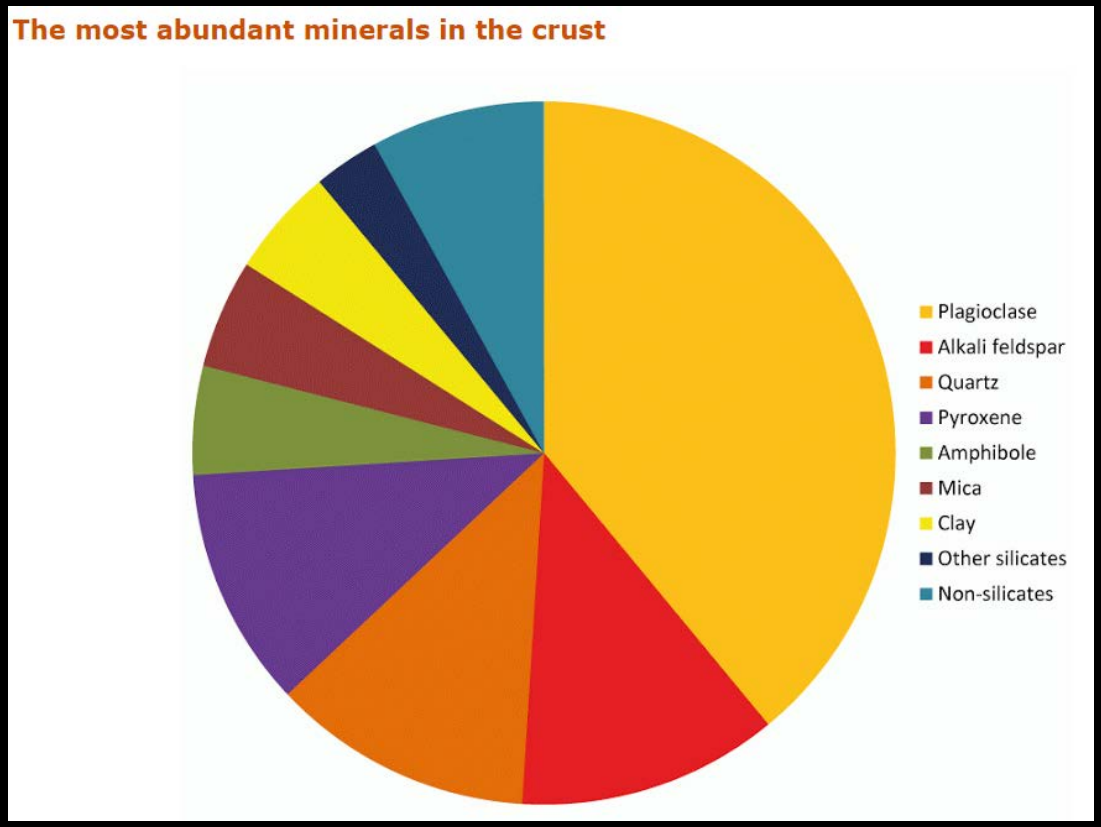
What minerals are actually in the earth's crust?

"More than 90% on the crust is composed of silicate minerals. Most abundant silicates are feldspars (plagioclase (39%) and alkali feldspar (12%)). Other common silicate minerals are quartz (12%) pyroxenes (11%), amphiboles (5%)... " Source: sandatlas.com



Plagioclase:
$NaAlSi_3O_8$ to $CaAl_2Si_2O_8$
Alkali Feldspar:
$KAlSi_3O_8$
Quartz:
SiO_2
Pyroxene:
$CaMgSi_2O_6$

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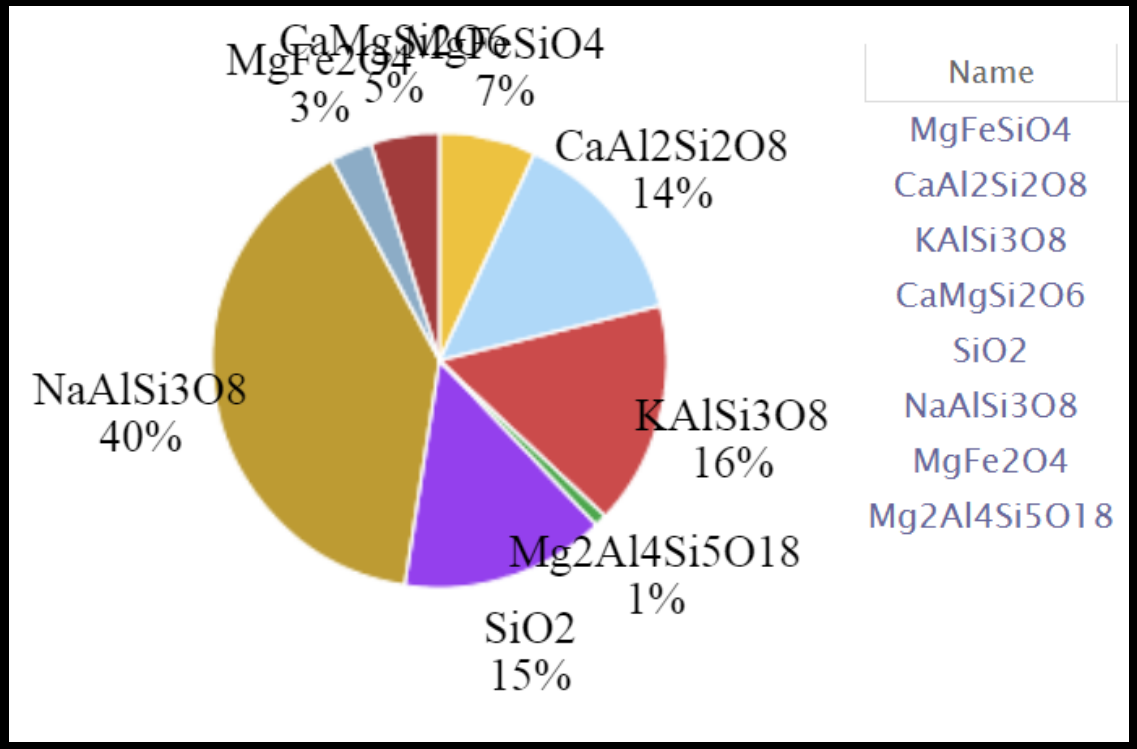

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Example 3: **The Phase Diagram of Everything**

What if we extend this idea to compute the ground state convex hull of the ~100-component phase diagram (for all elements in the periodic table)?

There is only one such phase diagram, and all other diagrams are merely sections of this “phase diagram of everything”

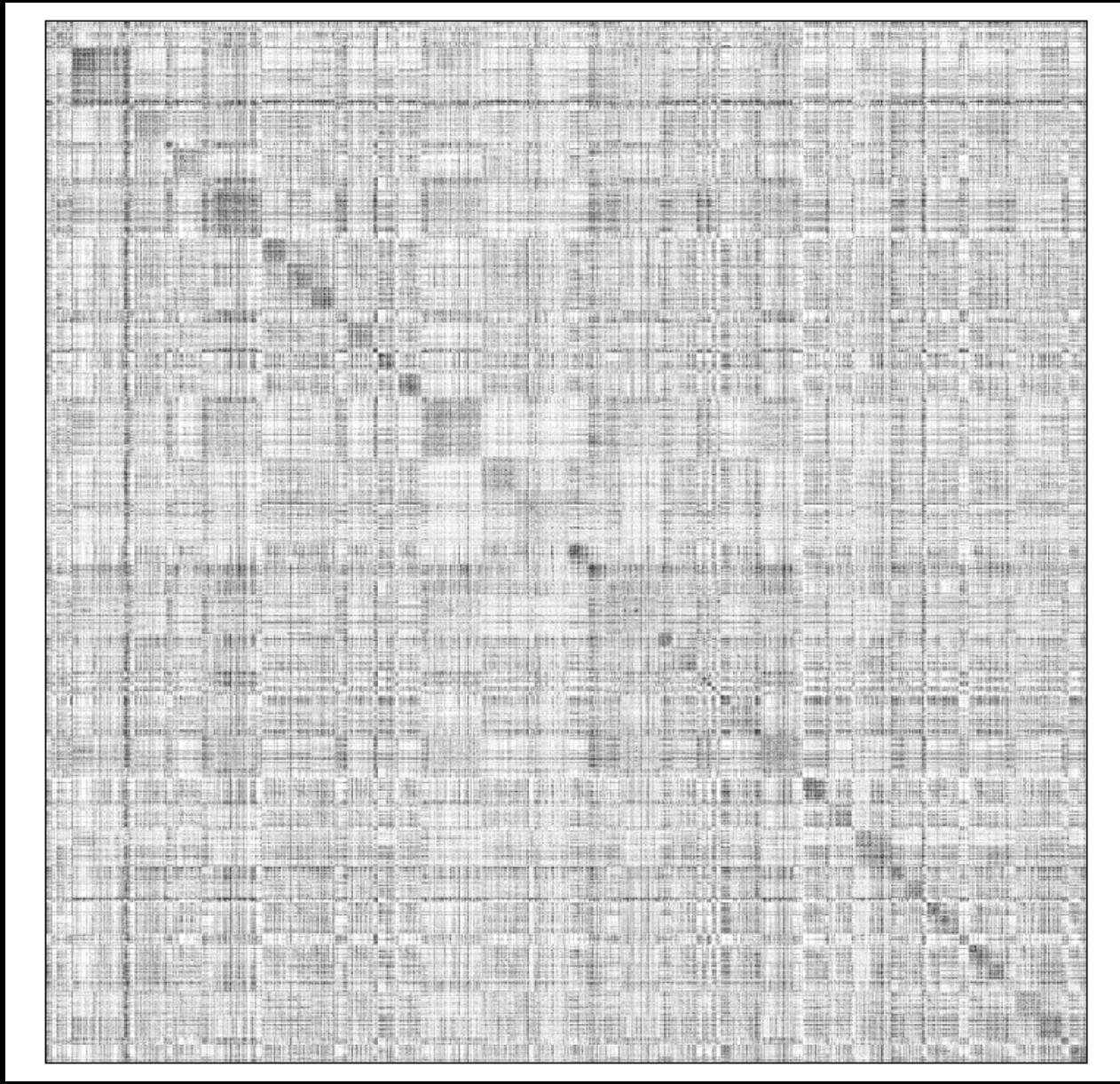
Using OQMD, we have computed this phase diagram. However, the question is, how to represent it?

The convex hull for the ~21,000 phases that are stable in the OQMD: ~41,000,000 tie-lines

Example 2: **The Phase Diagram of Everything**

One representation:
Adjacency matrix:

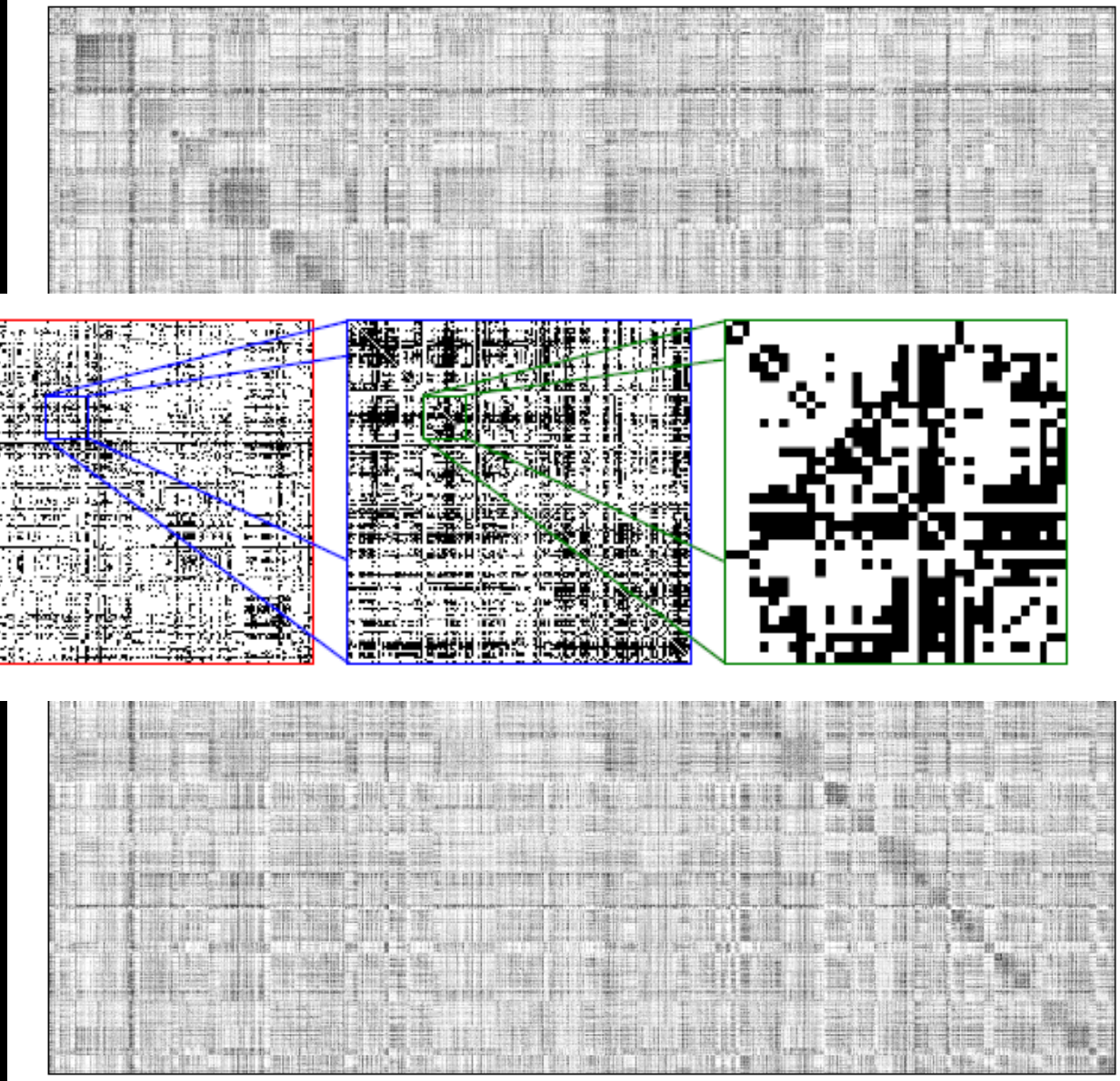
- ~21,000x21,000 matrix of all stable phases.
- Each element is black if a stable tie-line exists between phases, else white.
- Complete adjacency matrix is available at oqmd.org



Example 2: **The Phase Diagram of Everything**

One representation:
Adjacency matrix:

- 19230x19230 n
  p
- E
  b
  li
  p
- Complete adjacency matrix is available at oqmd.org



Network Analysis of Synthesizable Materials Discovery

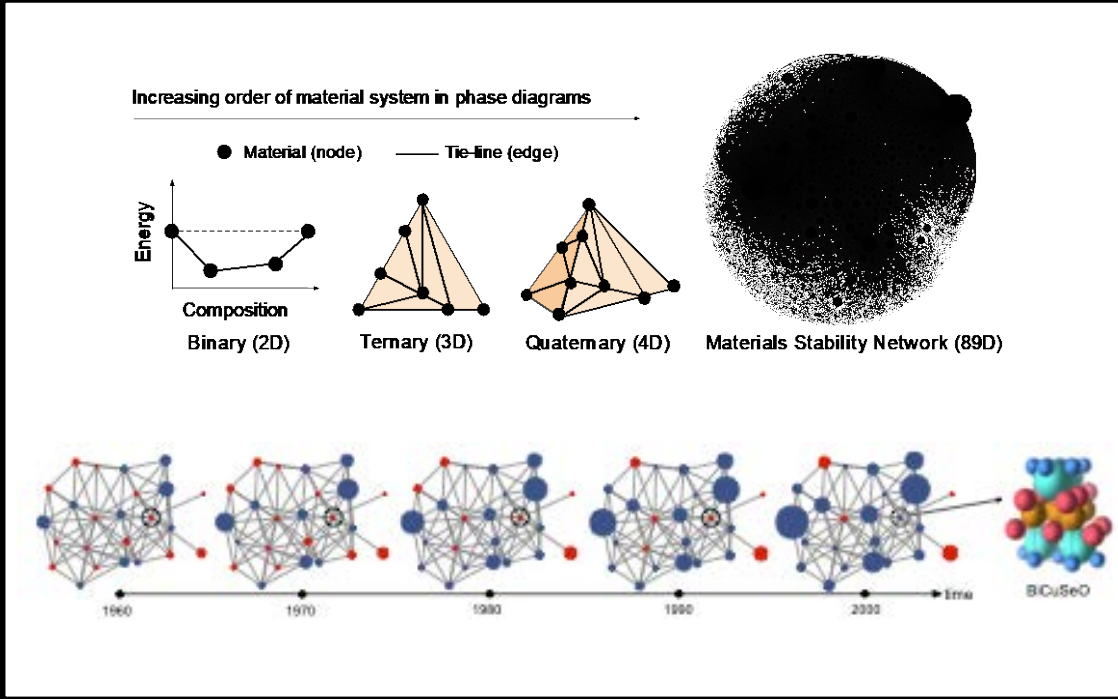
"Phase diagram of everything": network of phases and tie-lines, which connect phases.

Topology of convex hull network allows us to determine "reactivity" or "nobility" of compounds.

Can computationally predicted materials be synthesized?

Construct "materials stability network" from convex hull along with database of experimentally discovered materials (and date of their discovery).

The time-evolution of the underlying network allows us to predict the likelihood that hypothetical, computer-generated materials will be amenable to successful experimental synthesis.



(A) Network representation of materials phase diagrams. The schematic illustrates T=0K phase diagrams or convex hulls 2-dimensions (binary) onwards, and their representation as networks with materials as nodes and tie-lines as edges. (B) Time evolution of the local environment of BiCuSeO in the overall "material stability network". Known materials are shown in blue and those yet to be discovered as shown in red.

Aykol et al., arXiv:1806.05772 (2018); Hegde et al., arXiv:1808.10869 (2018)

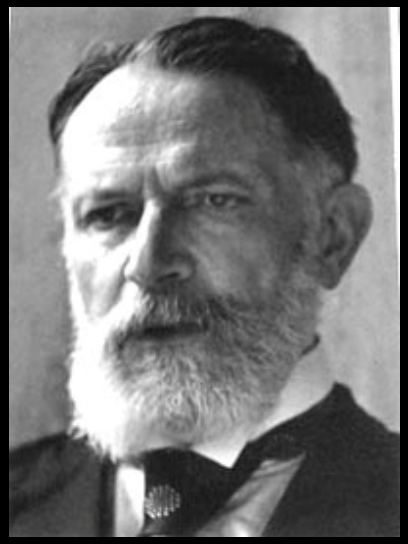
High-Throughput DFT Calculations: OQMD

Can search through database to "screen" materials for various applications

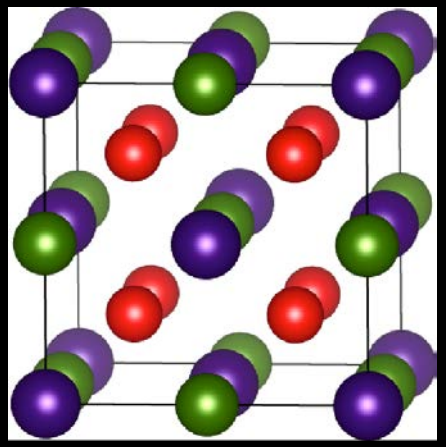
- Heusler phase precipitates
- High strength Mg alloys
- Li-ion battery coatings
- Li-ion battery electrodes
- High-efficiency Thermoelectrics
- Solar Thermochemical Water Splitting Perovskites
- Spintronic Materials

Saal, Kirklin, Aykol, Meredig, and Wolverton "*Materials Design and Discovery with High-Throughput Density Functional Theory: The Open Quantum Mechanical Database (OQMD)*", JOM **65**, 1501 (2013)

(Full) Heusler phase



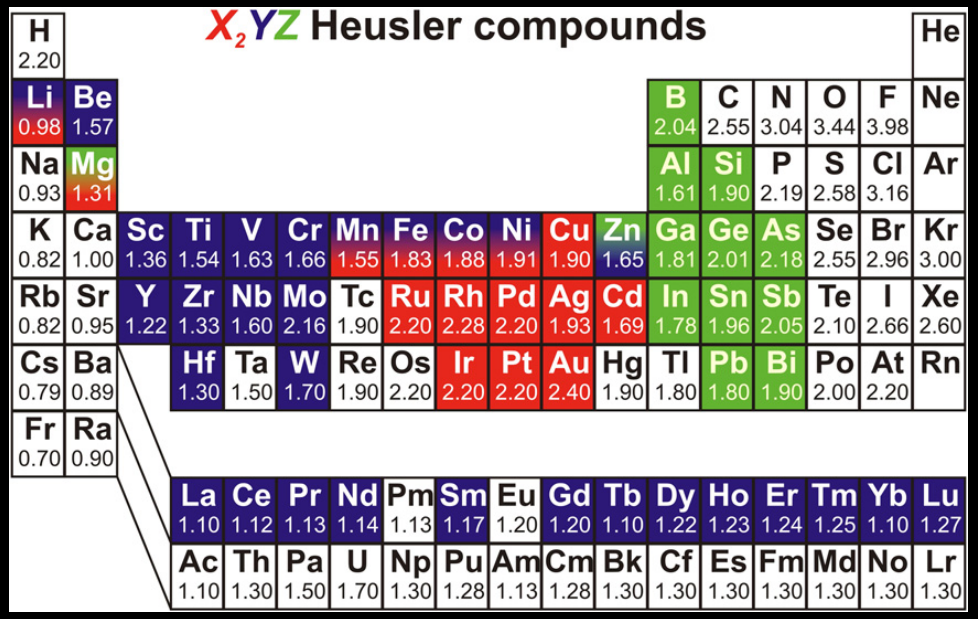
Friedrich Heusler
(1866-1947)



Full Heusler: $\mathbf{X_2YZ}$
Space group: $F_{m\text{-}3m}$
Prototype: Cu_2MnAl

Half-Heusler: **XYZ**
one X sublattice is not occupied

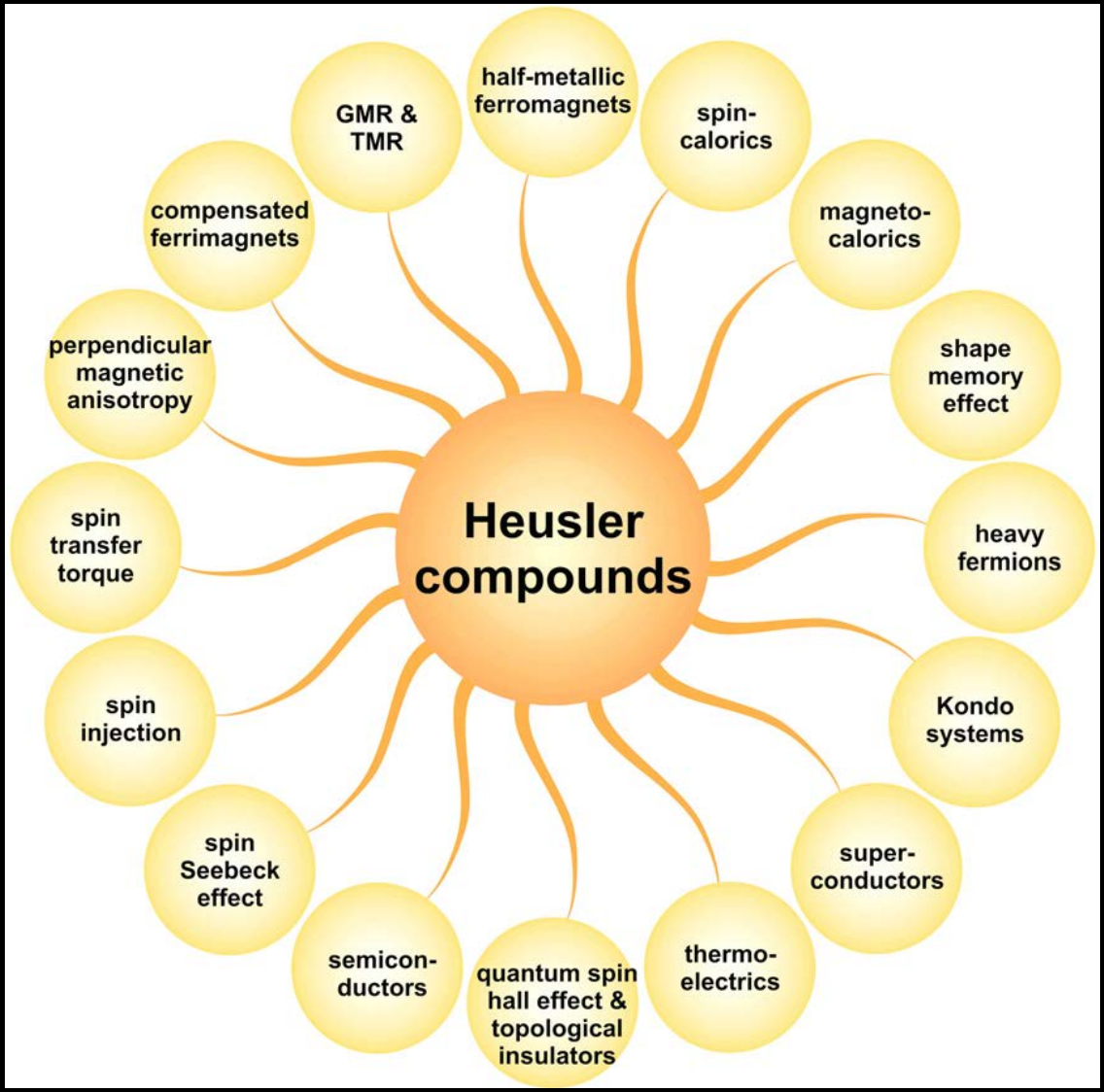
- 281 Full Heuslers in ICSD
- ~180,000 potential X_2YZ compounds
- Are there new Full Heuslers awaiting discovery?
- Gautier et al. predicted 54/synthesized 15 new half-Heusler compounds



Gautier et al., Nature Chem. 7, 308 (2015)

T. Graf, C. Felser, and S. Parkin, Prog. Solid State Chem. 39, 1 (2011)

Properties & Applications



A wide variety of functional applications

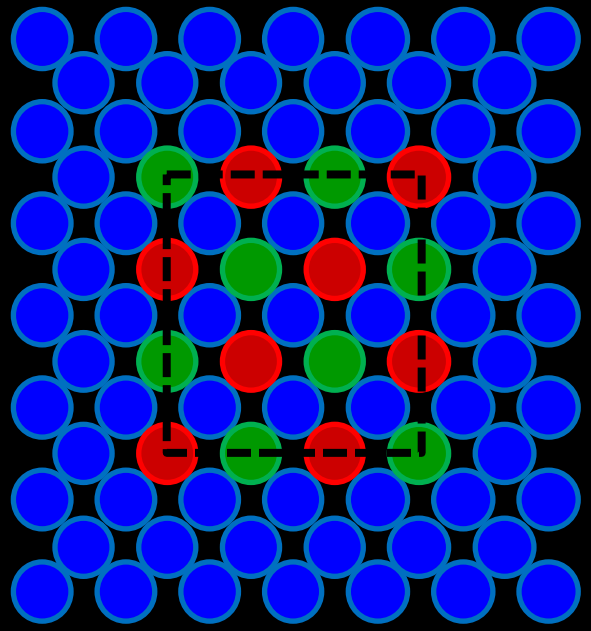
What about structural applications?

T. Graf, C. Felser, and S. Parkin, Prog. Solid State Chem. 39, 1 (2011)

Precipitate strengthening in metals

Motivation

The presence of precipitates in a matrix impedes the motion of dislocations, increasing the yield strength.

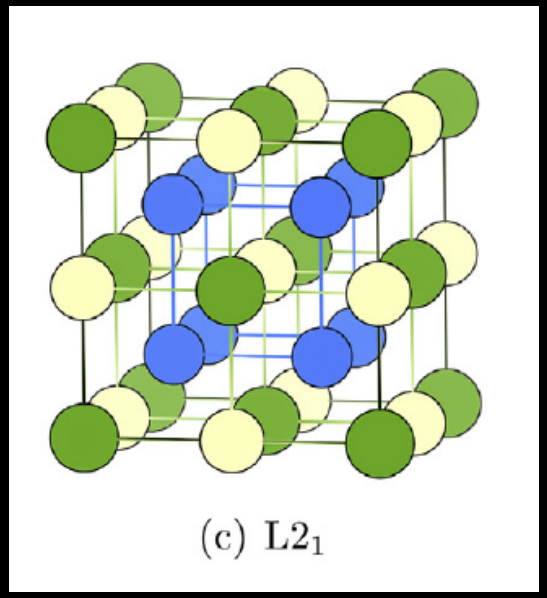


A good precipitate strengthener:

- Is coherent with the lattice
- Is stable or nearly stable
- Is in equilibrium with the host lattice
- Requires only low cost elements (no rare earths, noble metals)
- Many other properties…

Can we search for promising precipitate candidates using high-throughput DFT?

High-throughput search for matrix/precipitate systems



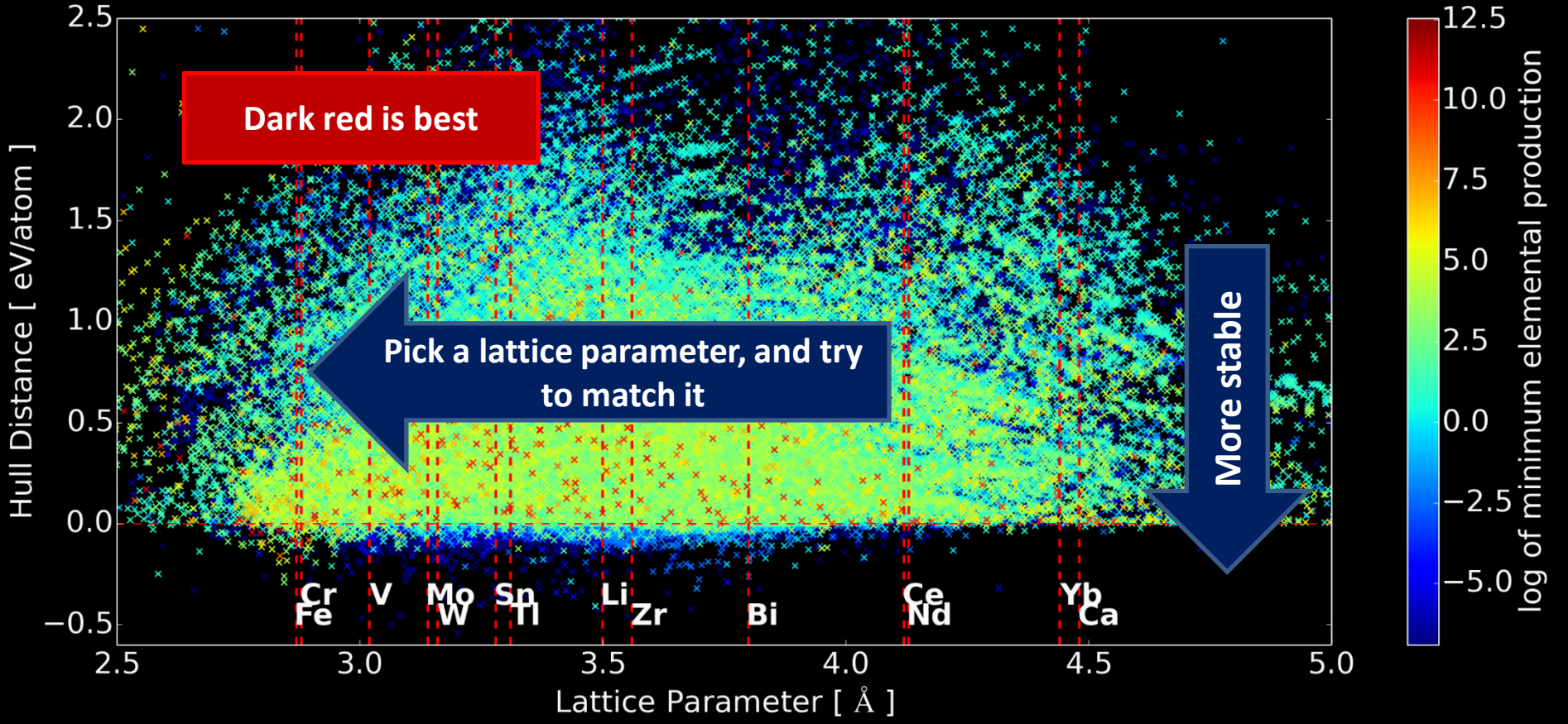
Matrix/precipitate: bcc/Heusler (full)

Can the Heusler structure make a good strengthening precipitate for bcc metals?

Calculate all possible decorations (180,000) and screen for:
1) stability, 2) tie-line with matrix phase, 3) lattice mismatch, and 4) cost

High-throughput search for Heusler X_2YZ precipitate strengtheners in BCC metals

> 180,000 DFT calculations of X_2YZ Heuslers
(essentially for all possible X, Y, Z)

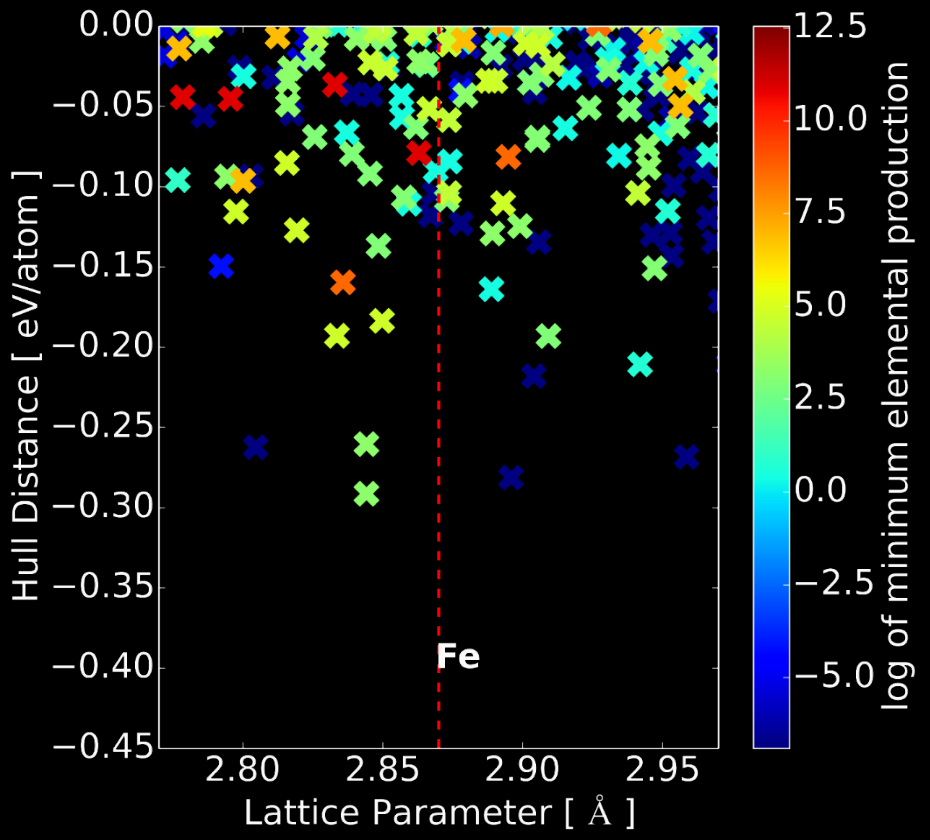


S. Kirklin, J. E. Saal, V. I. Hegde, and C. Wolverton, "High-throughput computational search for strengthening precipitates in alloys" Acta Materialia 102, 125 (2016).

Heusler phase strengthening precipitates in BCC Fe

Objective Function: Weighted average of
(a) lattice mismatch, (b) stability, and (c) elemental production

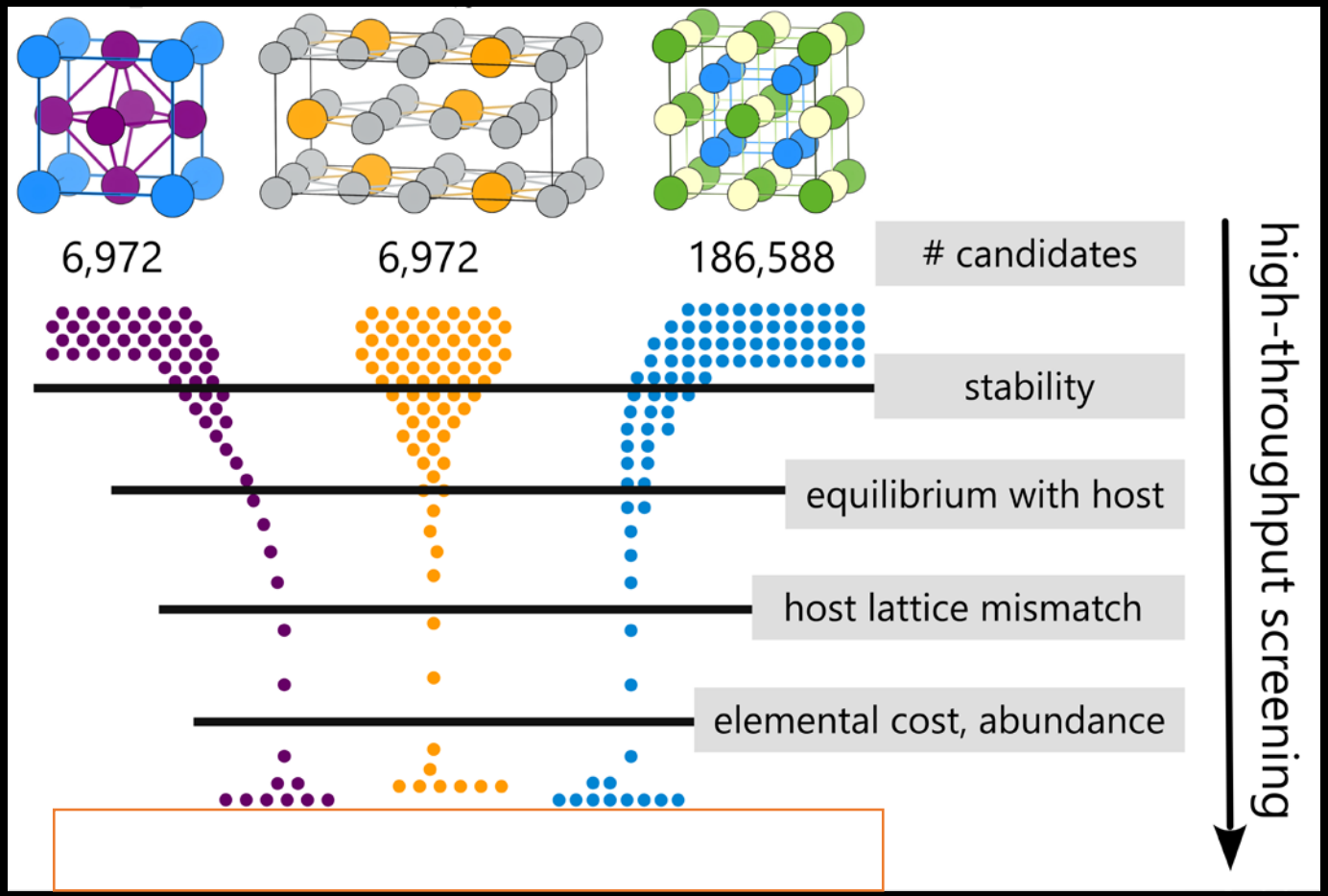
Best Ranked Compositions	
1	Fe_2SiTi
2	Fe_2AlV
3	Co_2GaTi
4	Fe_2AlTa
5	Fe_2AlNb
6	Mn_2SiV
7	Fe_2SiV
8	Fe_2GaV
9	Co_2TiZn
10	Co_2AlTi



Can easily change objective function, or add constraints (e.g., precipitate must contain Cu) to find new candidates

S. Kirklin, J. E. Saal, V. I. Hegde, and C. Wolverton, "High-throughput computational search for strengthening precipitates in alloys" Acta Materialia 102, 125 (2016).

Data-Driven Approaches: High-throughput computational materials screening



Kirklin, S., Saal, J. E., Hegde, V. I., & Wolverton, C. “High-throughput computational search for strengthening precipitates in alloys”, *Acta Materialia*, *102*, 125-135.

What else can we do with this large 180,000 data set of Heusler compounds?

Heusler-based Thermoelectrics

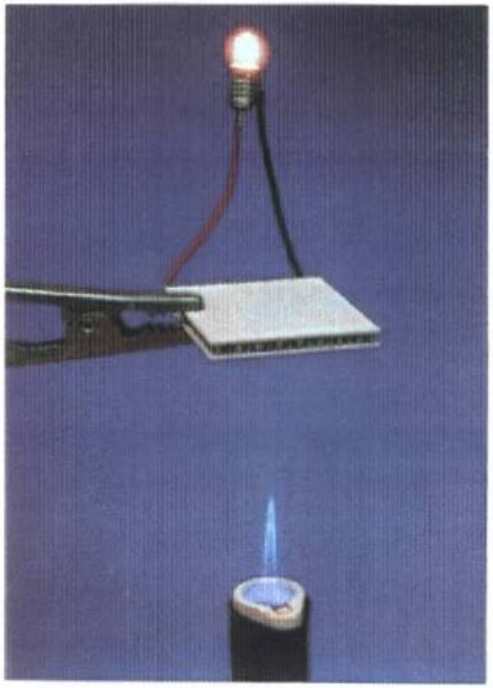
IIa. Full Heusler Thermoelectrics

J. He et al., Phys. Rev. Lett. 117, 046602 (2016).

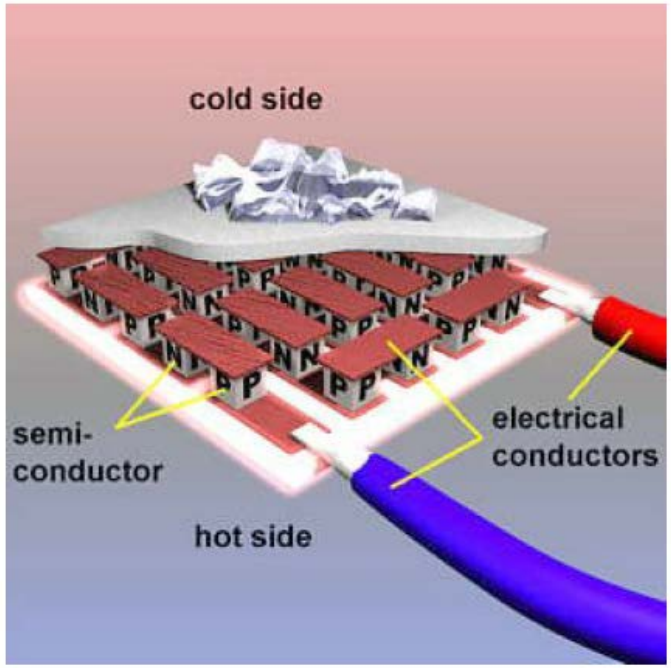
IIb. Nanostructured (Two-phase) Thermoelectrics

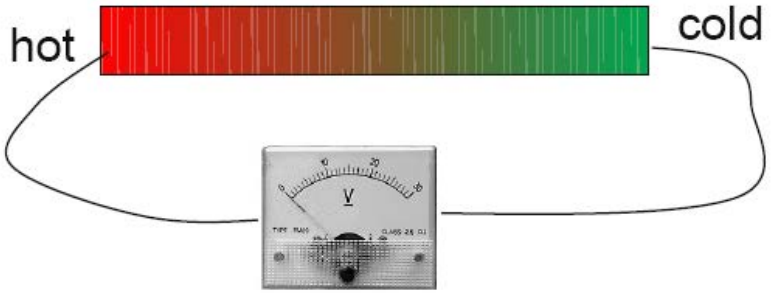
V. Kocevski et al., Chem. Mater. 29, 9386 (2017).

Heat to Energy Directly - Thermoelectrics



Electrical
Power Generation





Thermopower
Seebeck
coefficient

$\alpha = \Delta V/\Delta T$

What properties make a good (efficient) thermoelectric material?

Credit: www.dts-generator.com

Why are Efficient Thermoelectrics Hard to Find?

Contraindicated Properties

- Carrier Concentration (Seebek vs. elec. Cond.)
- Electrical vs. Thermal conductivity

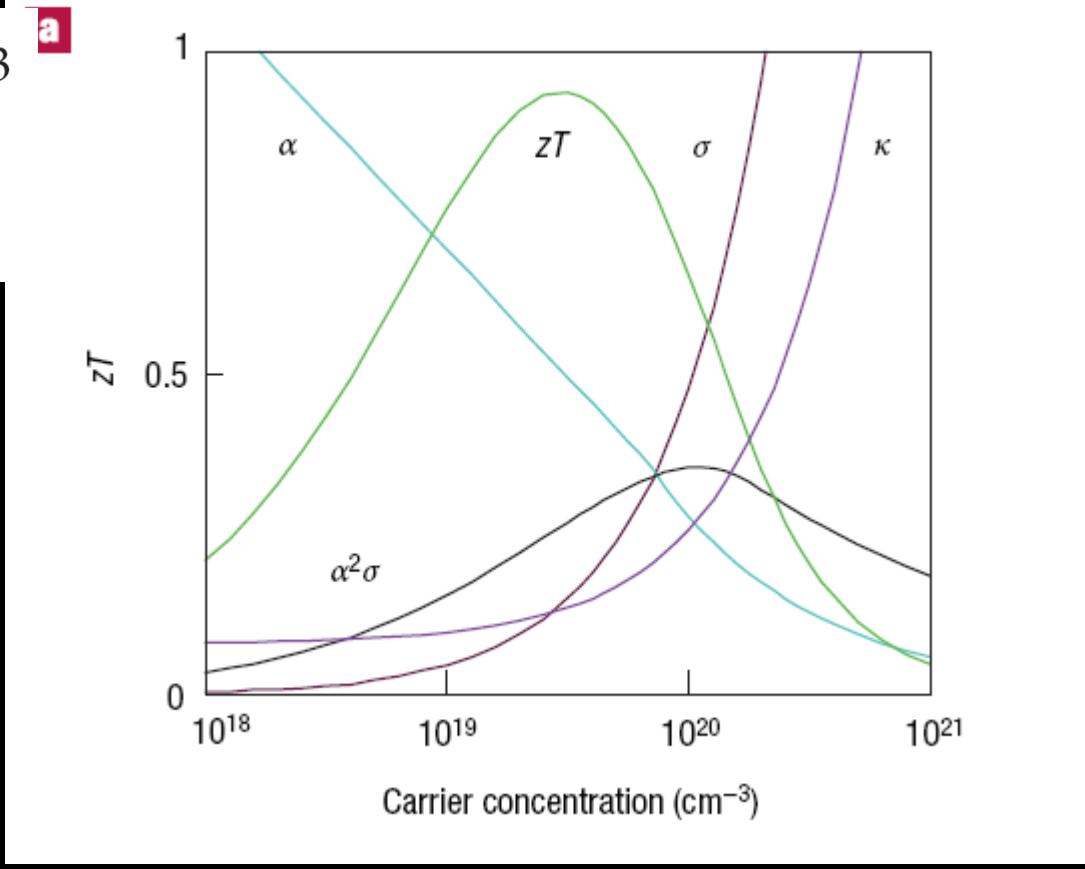
$$ZT = \frac{\alpha^2 \sigma}{\kappa_e + \kappa_l} T$$

$$\alpha = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}$$

$$\sigma = ne\mu$$

$$\kappa = \kappa_e + \kappa_l$$

$$\kappa_e = L\sigma T = ne\mu LT$$

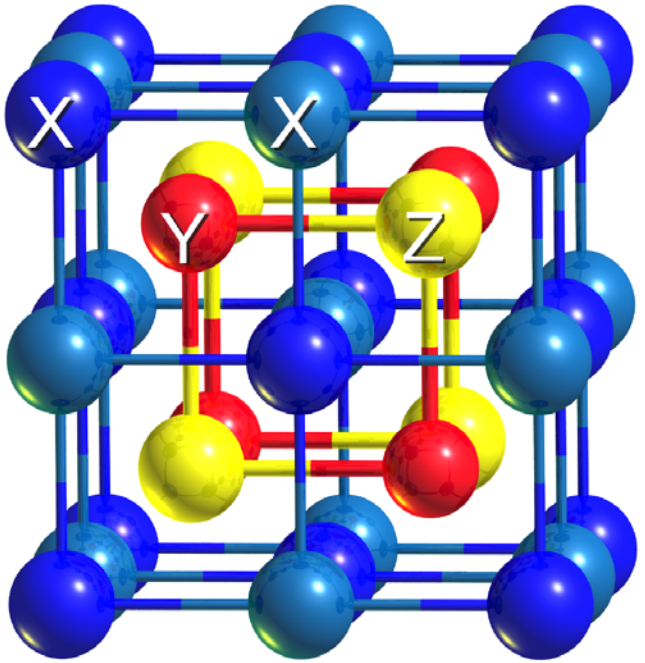


Snyder and Toberer, 2008

Heusler phase Thermoelectrics

- Half (full) Heusler structure $X_{(2)}YZ$
  X in SC or FCC structure (full/half)
  Y and Z in rocksalt structure
- Half and (to a lesser extent) full-Heusler have high thermal stability and promising ZT
- Semiconducting half-Heusler: 18 VE
  XNiSn, XCoSb, X={Ti, Hf, Zr}: n-type with $ZT \approx 1$
  FeYSb, Y={V, Nb}: p-type with $ZT > 1$
- Semiconducting full-Heusler: 8 or 24 VE
  Fe_2VAl: $ZT = 0.13 - 0.2$

$$ZT = \frac{\sigma S^2 T}{\kappa_{el} + \kappa_{lat}}$$



Full (Half) Heusler

Good

High σS^2

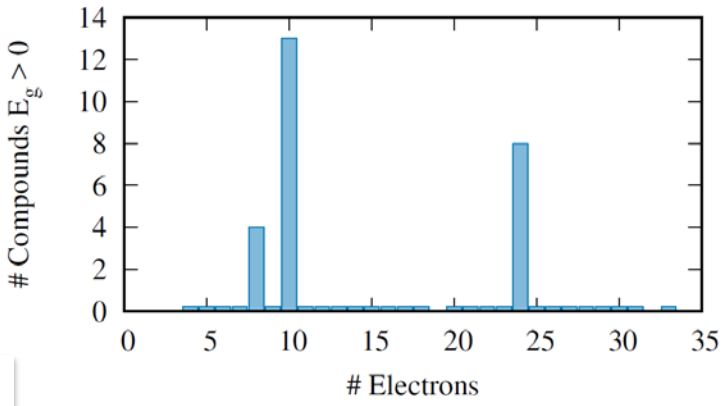
Bad

High κ_{lat}

High-Throughput Screening for Full Heusler Semiconductors

Discovery of New Class of Compounds
“R-Heuslers” (Rattling)

- 281 full Heusler in ICSD
- High-throughput with 53 elements
- In total 74,412 compositions
- 964 stable in OQMD
- Discovery of 10 electron semiconductors:
  - X alkaline earth {Ba, Sr, Ca}
  - Y noble metals {Au, Hg}
  - Z IV and V group {Sn, Pb, As, Sb, Bi}

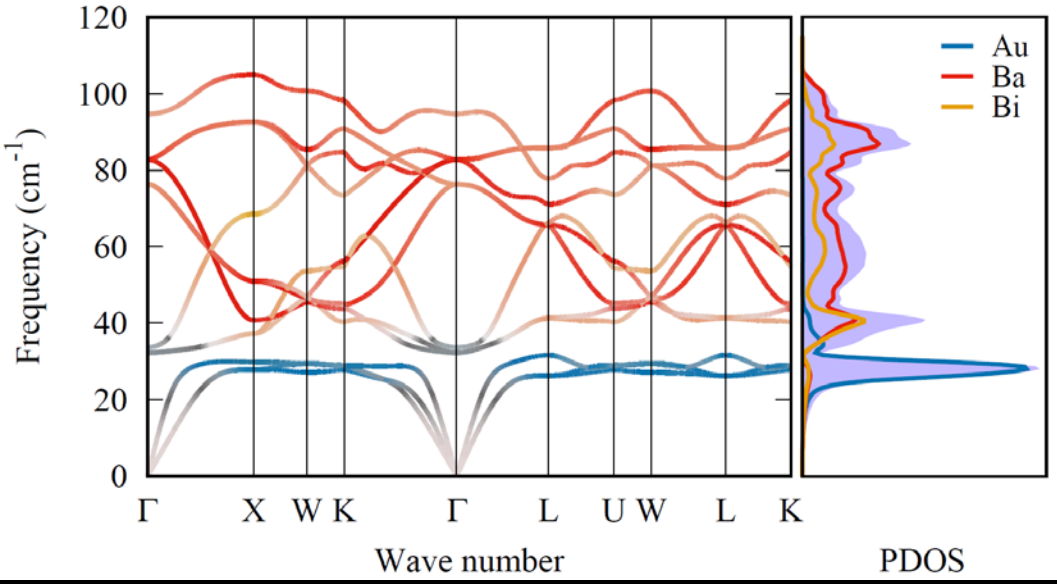


J. He, M. Amsler, et al, Phys. Rev. Lett. 117, 046602 (2016).

Phonons of R-Heuslers

Phonon band structure of Ba_2AuBi

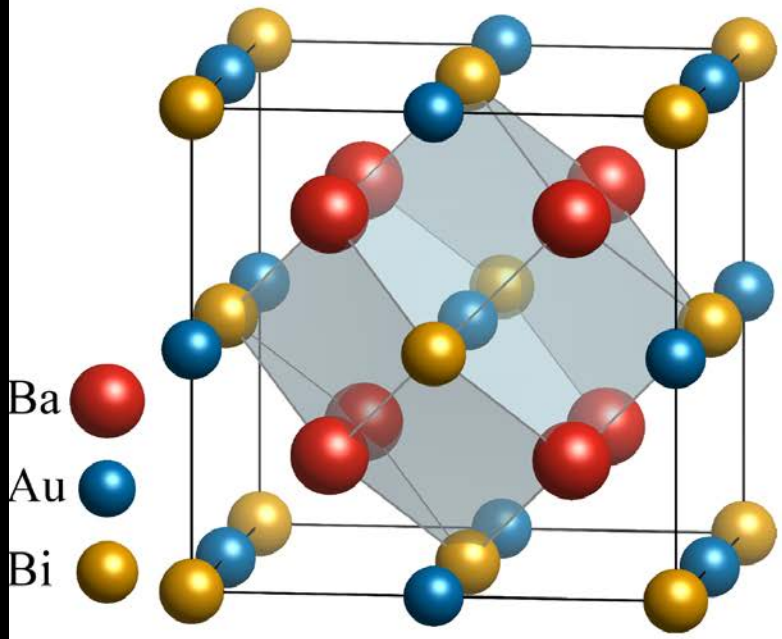
- Overall low phonon energies
- Avoided crossing of the acoustic branches
- Acoustic modes dominated by Au

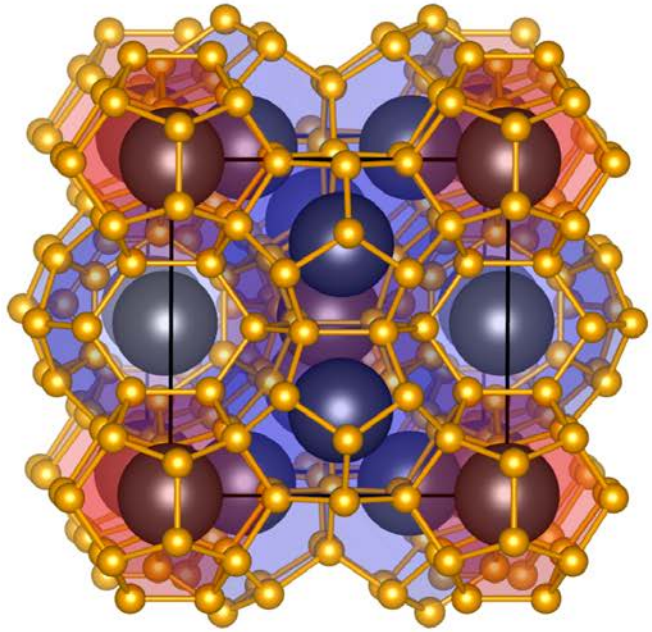


J. He, M. Amsler, et al, Phys. Rev. Lett. 117, 046602 (2016).

R-Heuslers: Rattling in Pseudo-Cages

Au atoms move in the Heusler structure...



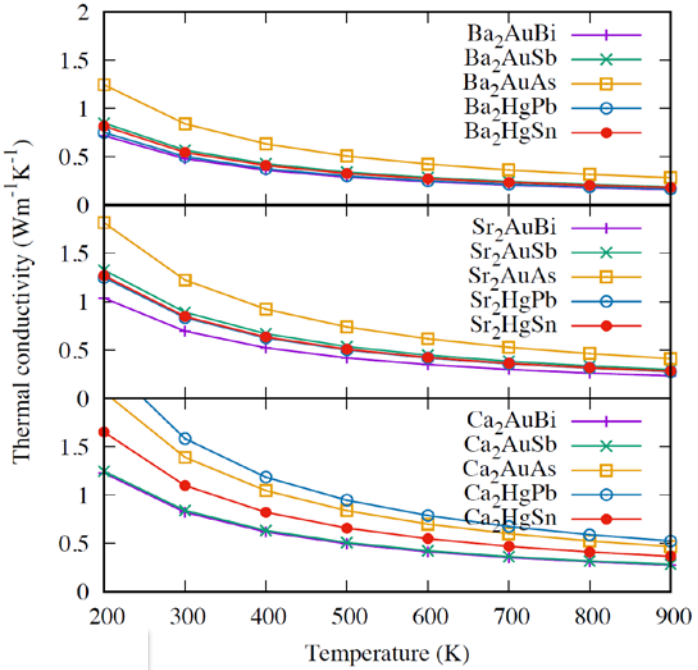


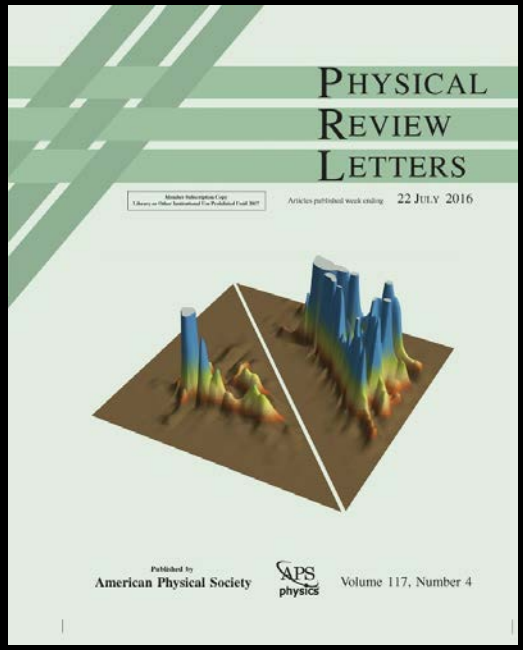
...like guest atoms rattle in host cages of clathrates

J. He, M. Amsler, et al, Phys. Rev. Lett. 117, 046602 (2016).

Lattice Thermal Conductivity of R-Heuslers

- Anharmonic terms give rise to phonon scattering
- 3rd order force constants from Compressive Sensing Lattice Dynamics (CSLD)
- Solved the (linearized) Boltzmann transport equation to get κ_{lat}
- SnSe: $\kappa_{\text{lat}} = 0.47\ \text{Wm}^{-1}\text{K}^{-1}$





CSLD: F. Zhou, W. Nielson, Y. Xia, and V. Ozoliņš, Phys. Rev. Lett. 113, 185501 (2014).

J. He, M. Amsler, et al, Phys. Rev. Lett. 117, 046602 (2016).

Electron Counting to Discover Novel Classes of Functional Heusler Phase Compounds

IIIa. "Three-quarter Heusler": Vacancies stabilize new Heusler structure
N. Naghibolashrafi et al., Phys. Rev. B 93, 104424 (2016).

IIIb. 18e Quaternary Heusler Compoounds
J. G. He et al., Chem. Mater. 30, 4978 (2018).

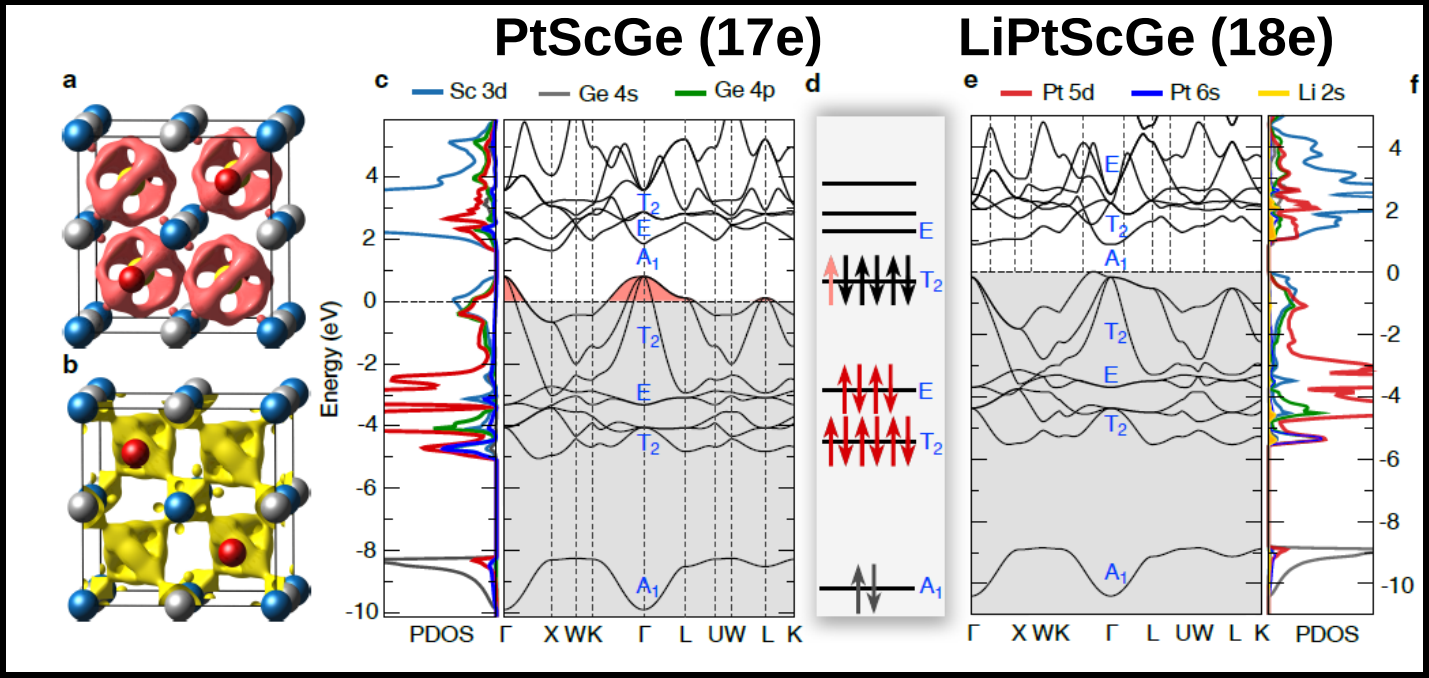
IIIc. Are there any 19e Heusler phases?
S. Anand et al., Energy Env. Sci. 11, 1480 (2018).

IIId. Heuslers for spintronics
J. Ma et al., Phys. Rev. B 95, 024411 (2017).

Designing and discovering a new family of semiconducting quaternary Heusler compounds based on the 18-electron rule

Q. How do we stabilize 17e Heusler compounds?

A. Make them 18e by addition of Li



Discovery of **99 new stable quaternary Heusler compounds**!
(Previously, only 2 known experimentally)
Promising properties for photovoltaics (absorption, effective masses) and thermoelectrics (thermal conductivity, Seebeck)

J. G. He et al., Chem. Mater. 30, 4978 (2018).

Q. How can we stabilize 19e Heusler Compounds?
A. Make them 18e with defects/vacancies

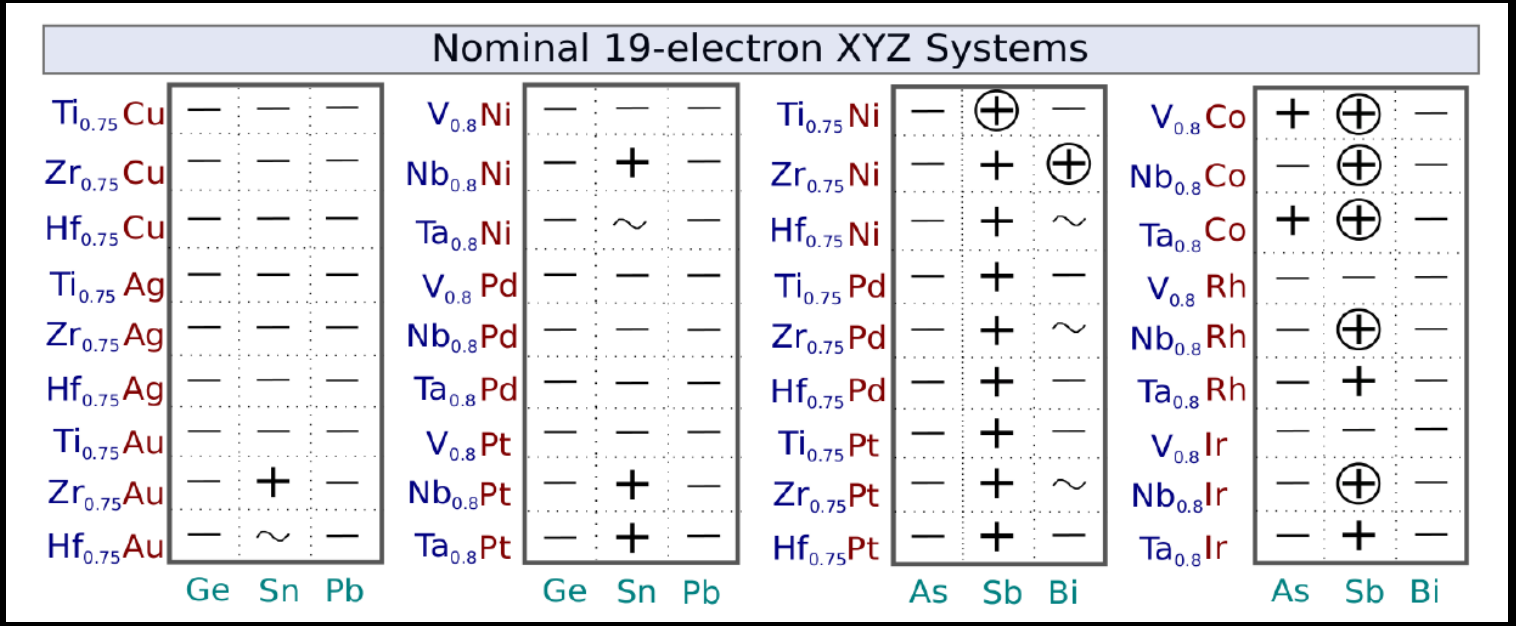
Nearly <u>all</u> 19e compounds are stabilized by changing stoichiometry to 18e

Example:
CoVSb (19e) - unstable
$CoV_{0.8}Sb$(18e) – stable
Off-stoichiometry in this compound is experimentally verified!

Circles: compounds previously reported as 19e

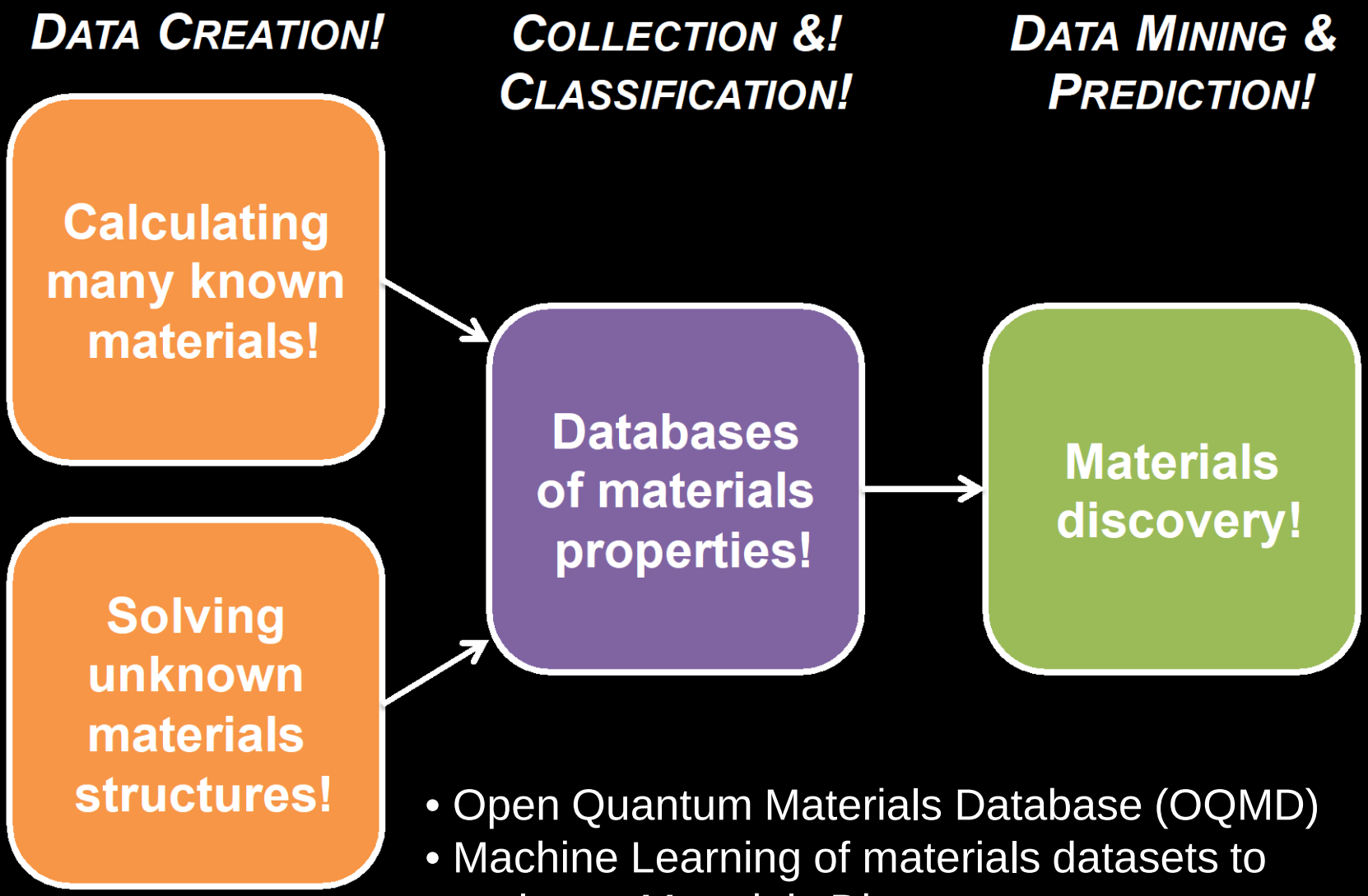
+

Compounds stable at 18e composition



S. Anand et al., Energy Env. Sci. 11, 1480 (2018).
Zeier et al., Chem. Mater. 29, 1210 (2017).

How to discover new materials?



- Open Quantum Materials Database (OQMD)
- Machine Learning of materials datasets to accelerate Materials Discovery