Thermodynamic database development based on ab initio calculations: challenges and opportunities

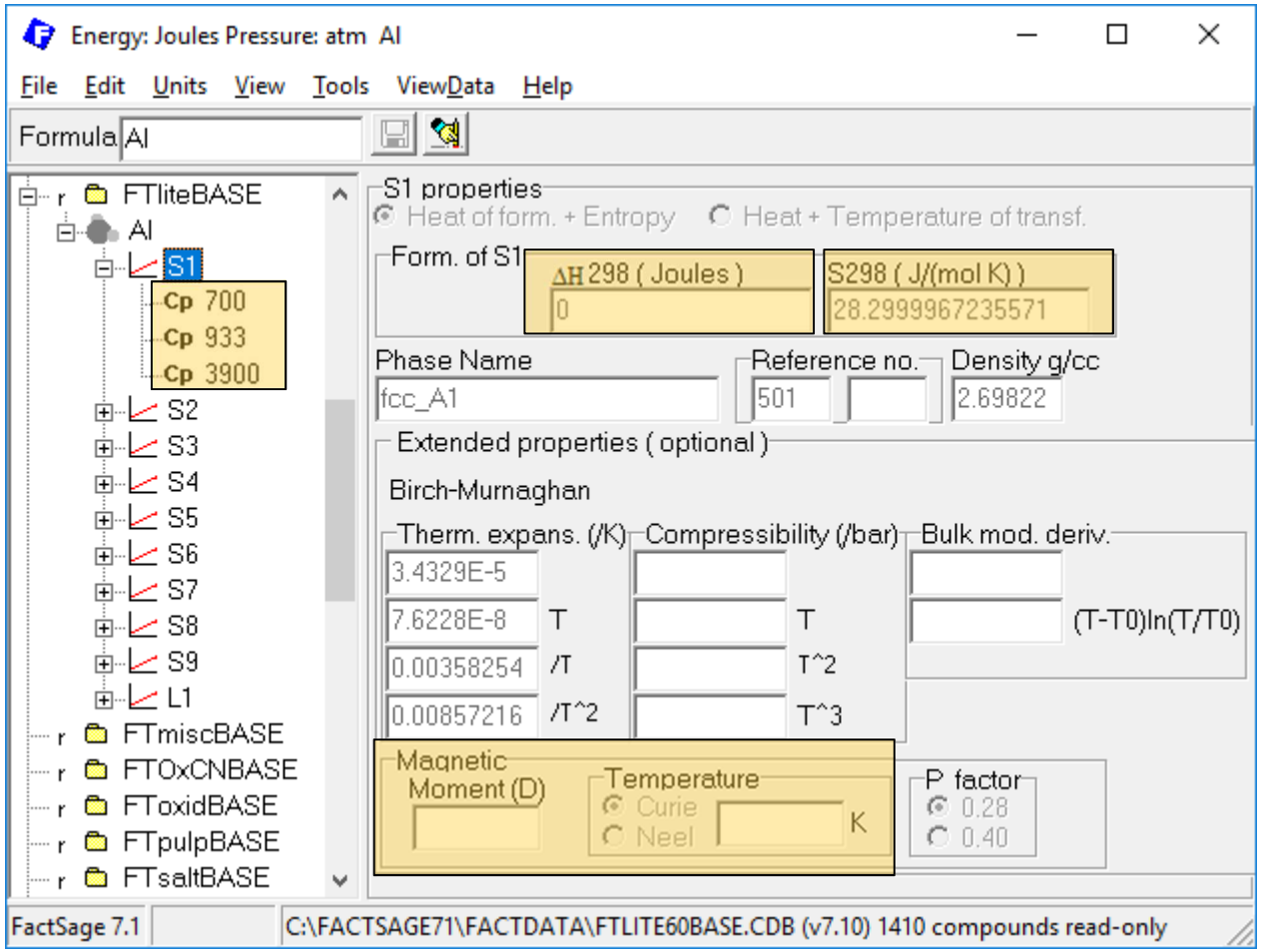
M. to Baben, C. Kattuputhur, K. Hack,
GTT-Technologies

Outline

- Thermodynamic database content
- Database development
  - Based on experiments
  - Based on ab initio
- Challenges
- Opportunities

Thermodynamic database content

- ΔH^{298}
- S^{298}
- $C_p(T)$ **G(T)**
- μ
- T_C



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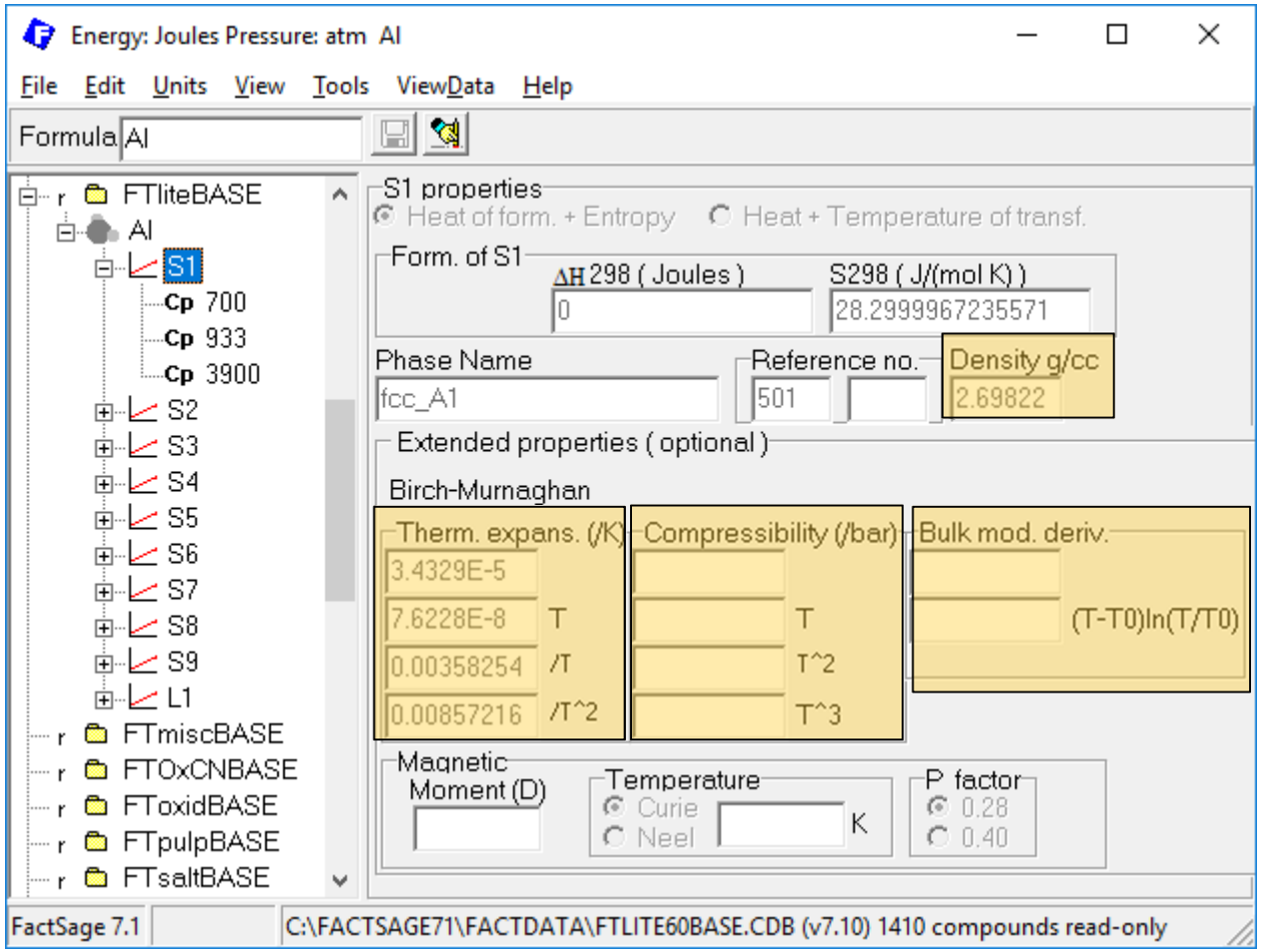

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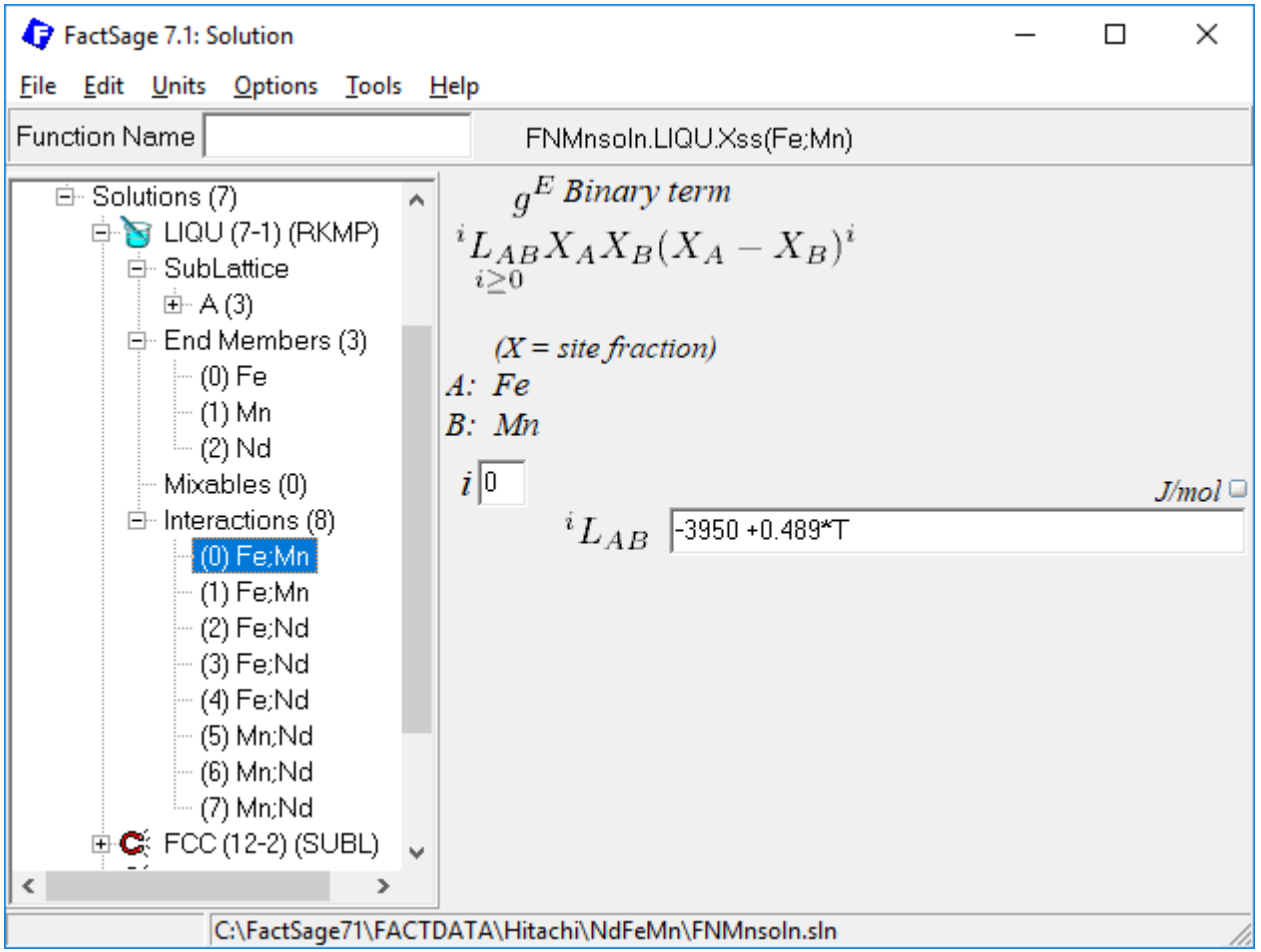
- $L(T)$ **$G(T,p,X_i)$**



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Database development based on experiment

- Ideal: The following properties are measured:
  - binary phase diagram
  - enthalpies of (trans-)formation of the compounds
  - enthalpies of mixing and constituent activities of solutions as f(T)
  - heat capacities of compounds and solutions
  - crystal structures, especially for complex solutions
  - density as f(T)
  - elastic properties as f(T)
- Real: Few of the properties are measured.

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Experimental error bars can be evaluated to fit the thermodynamic properties to all measurements

Thermodynamic properties are fitted to all available measurements

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2nd step: Consistency checks of binary and ternary systems!

Thermodynamic properties are fitted to all available measurements

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→ materialsproject.org, oqmd.org, aflowlib.org, nomad-coe.eu

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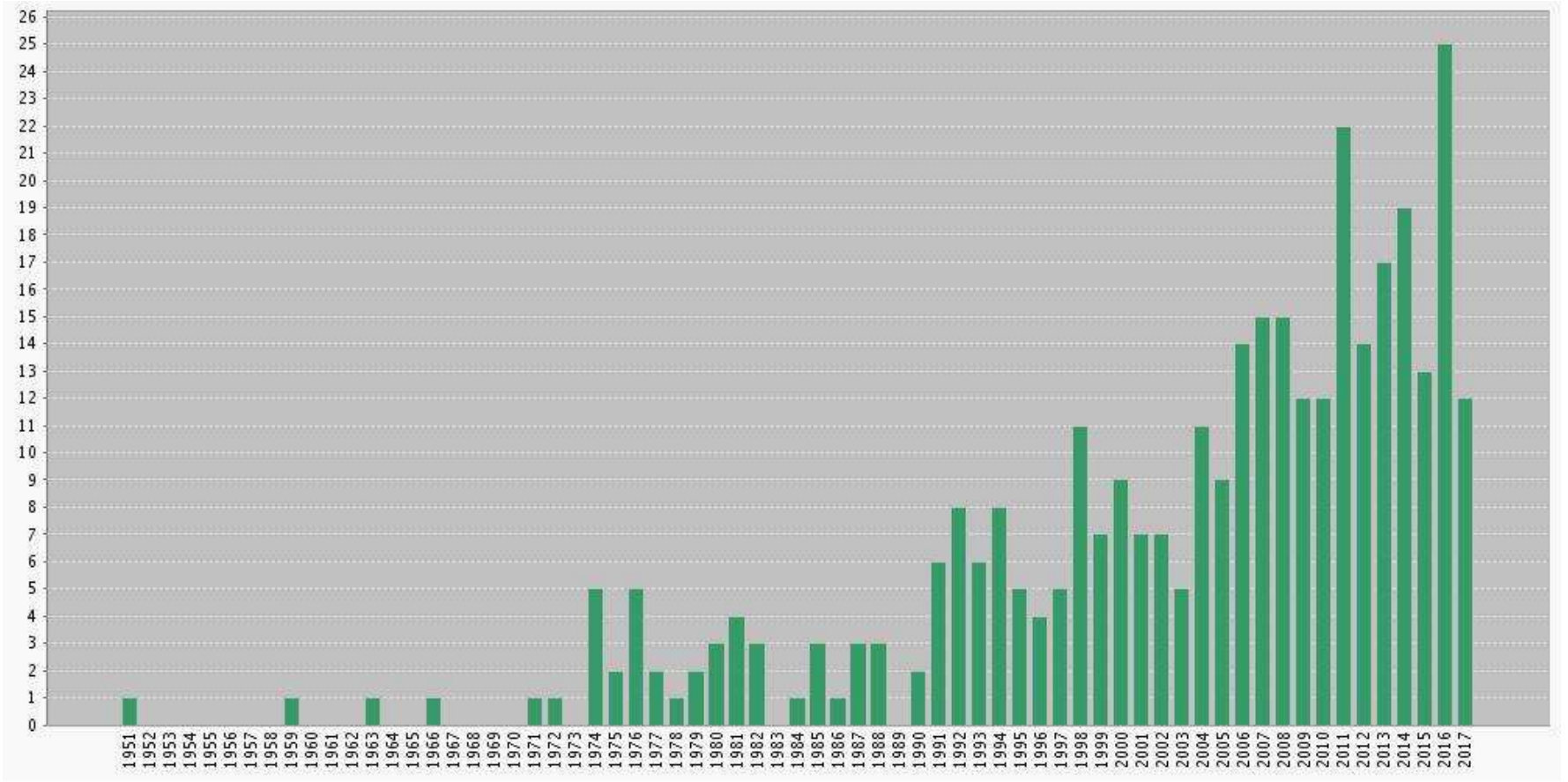
Challenge: $\Delta H_{f,experiment} \leftrightarrow \Delta H_{f,ab\ initio}$

Publications including “lattice stability”



webofknowledge.com

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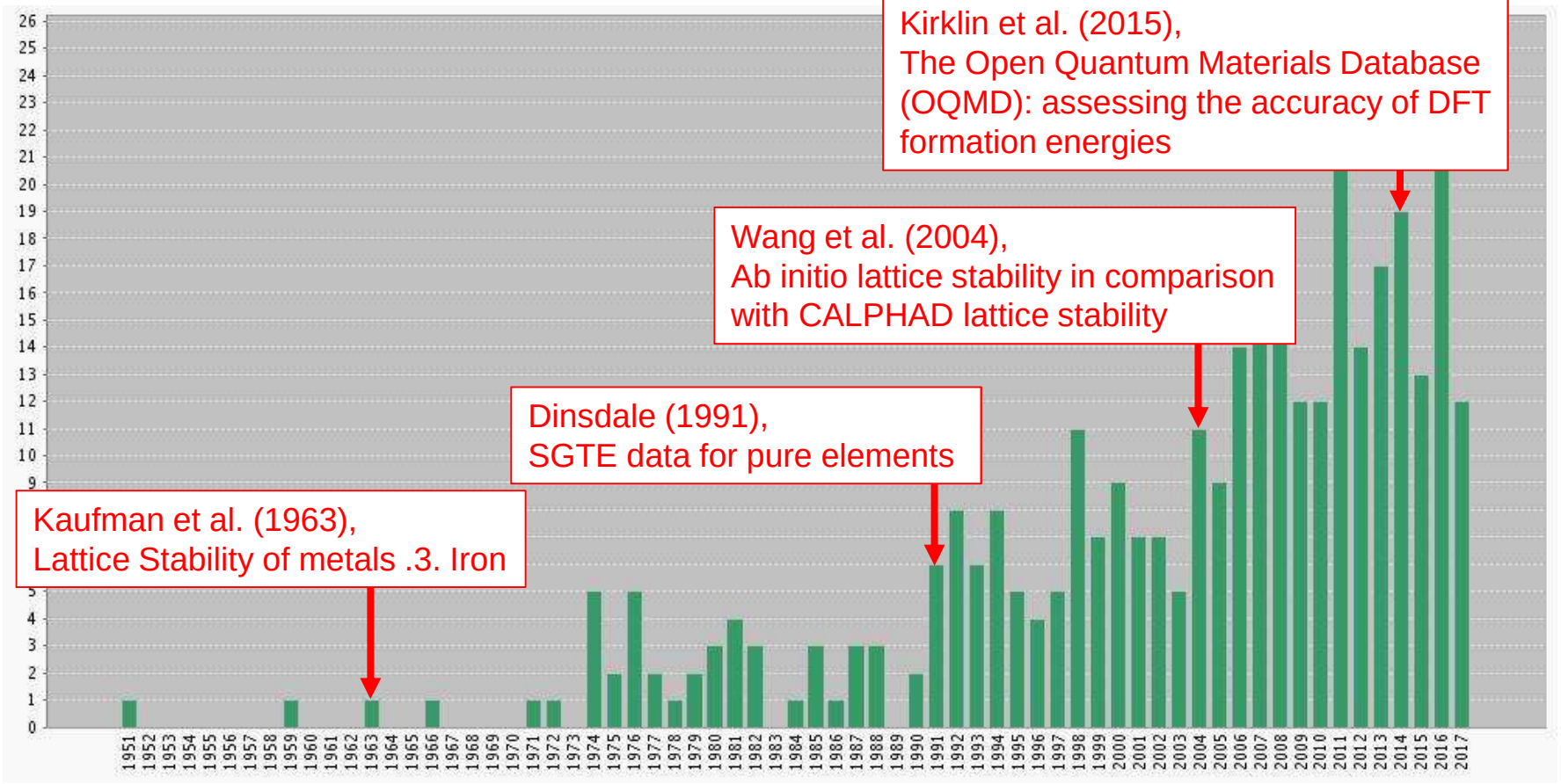

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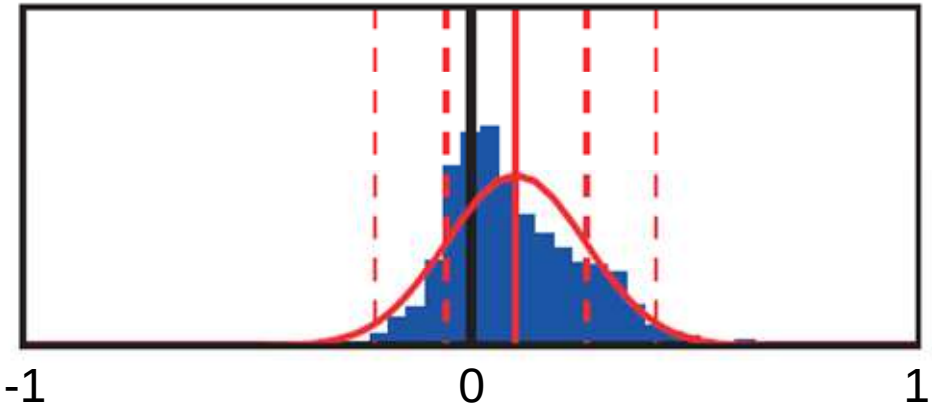
Raw data:



$\Delta H_{f,OQMD} - \Delta H_{f,SGTE}$ [eV/atom]

Mean average error is ~13 kJ/mol atoms

Kirklin et al. (2015),
The Open Quantum Materials Database (OQMD): assessing the accuracy of DFT formation energies

(1 eV/atom ≈ 100 kJ/mol atoms)

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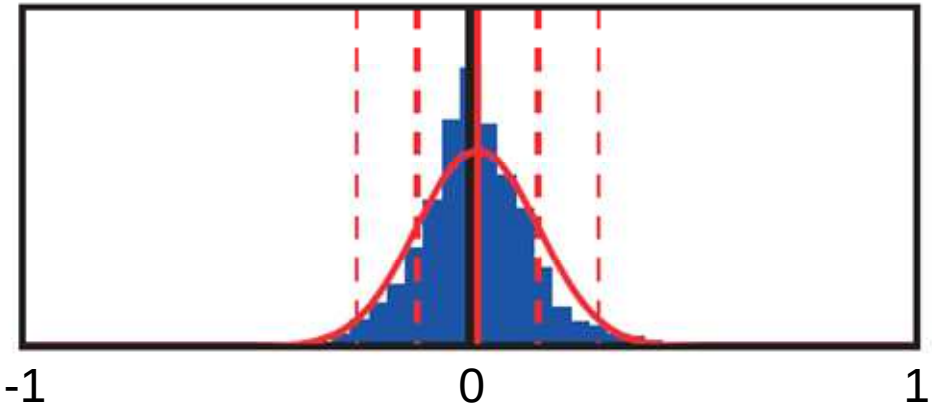
WHY?

Linear correction for elements:



$\Delta H_{f,OQMD} - \Delta H_{f,SGTE}$ [eV/atom]

Mean average error is ~9 kJ/mol atoms

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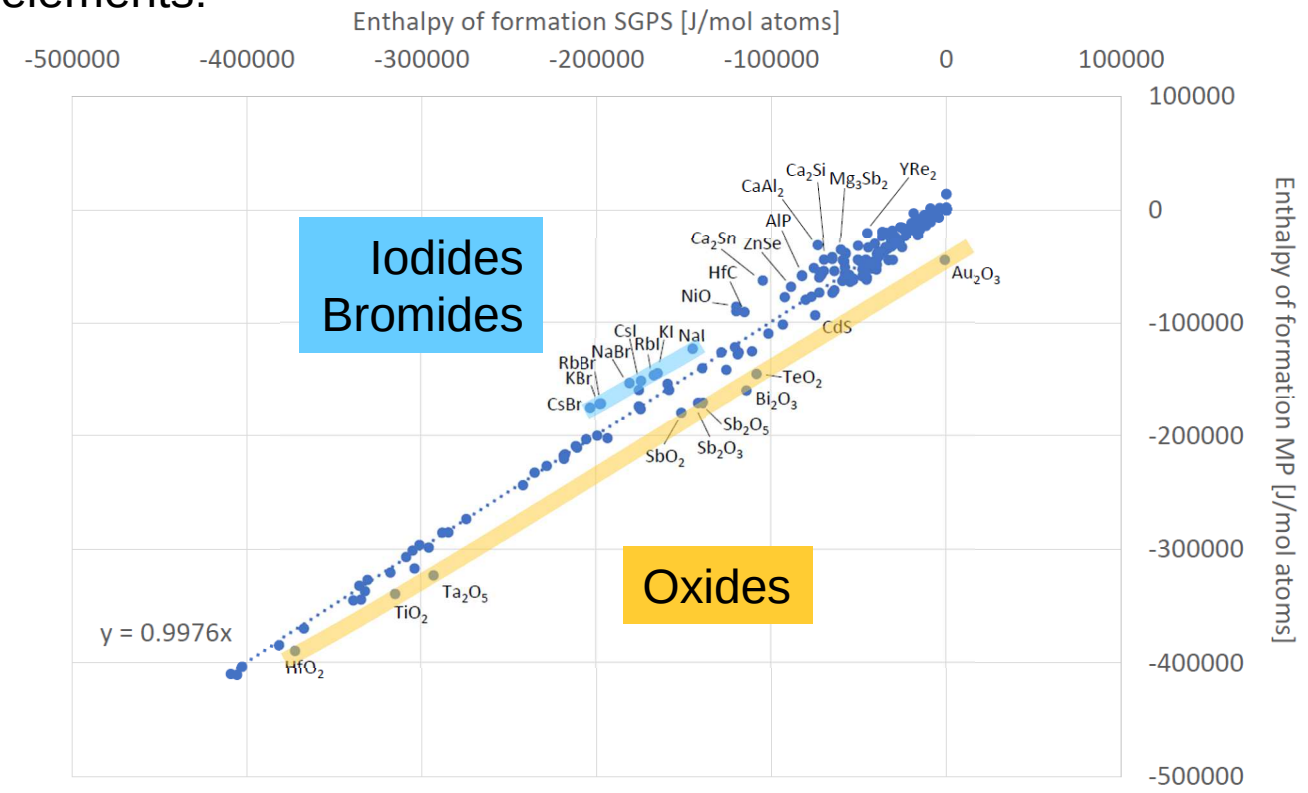
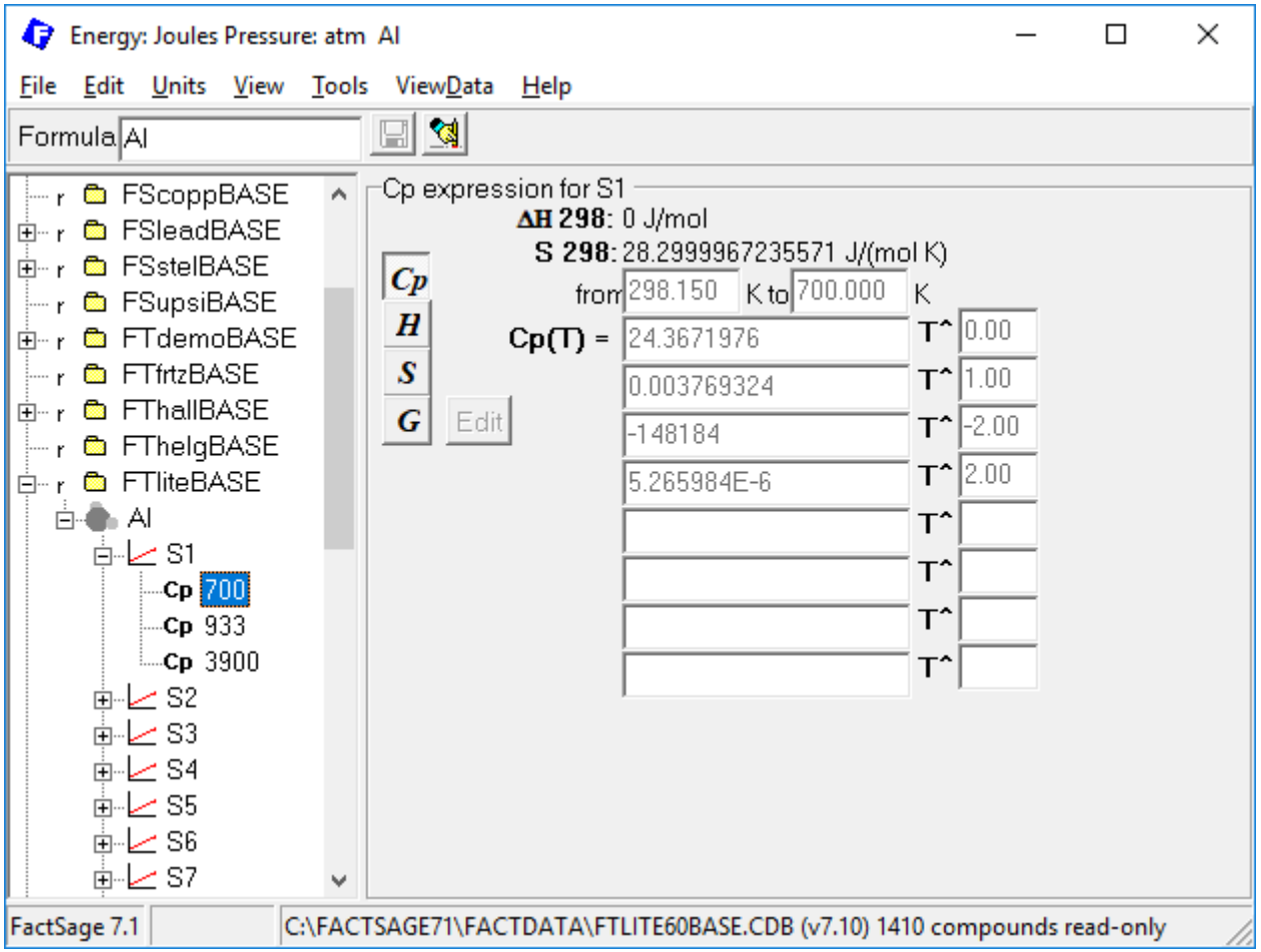


Challenge: “High“ temperatures



Challenge: “High“ temperatures

Ab initio calculations are mostly done at 0K.

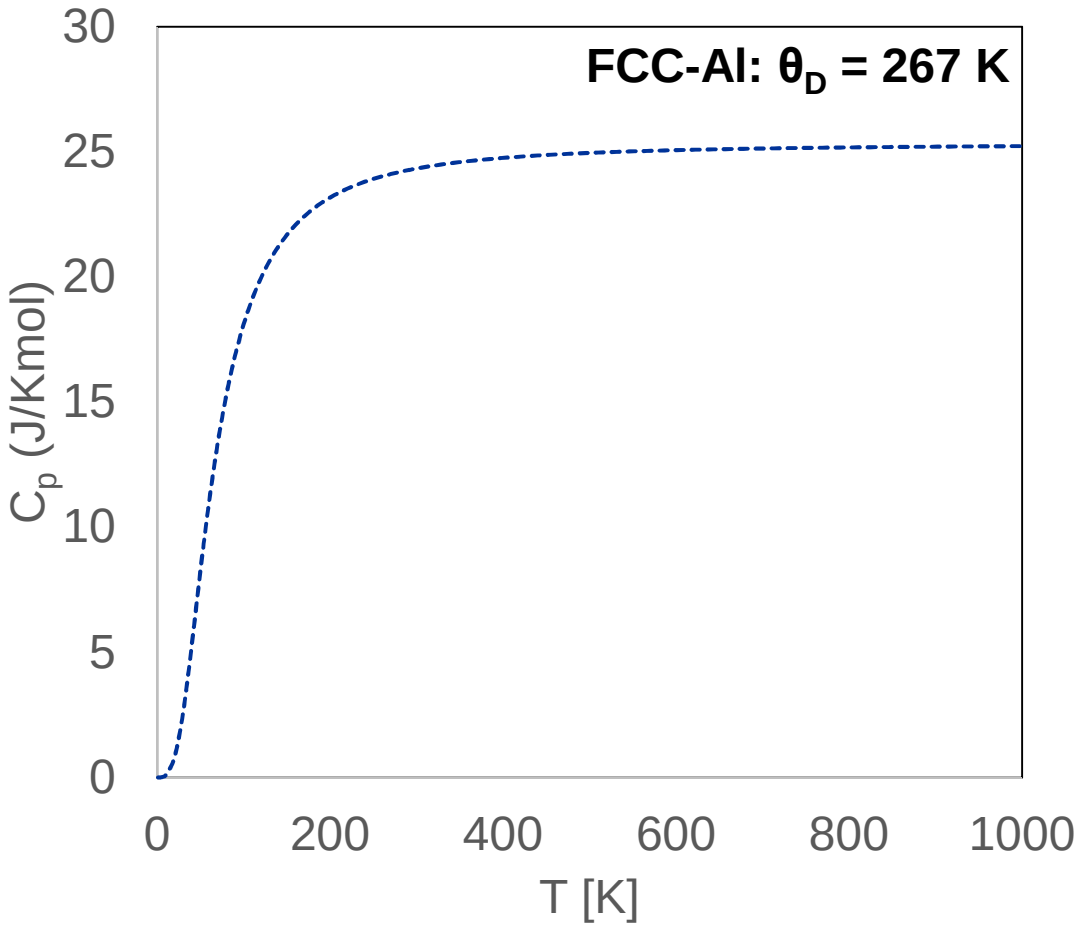
How to extrapolate to room temperature and above?

→ Einstein model

→ Debye model

→ X C_p = const X

→ Other models for T > θ_D are computationally expensive!



Challenge: Liquid and gas phases

- There is currently no high-throughput solution in ab initio calculations…

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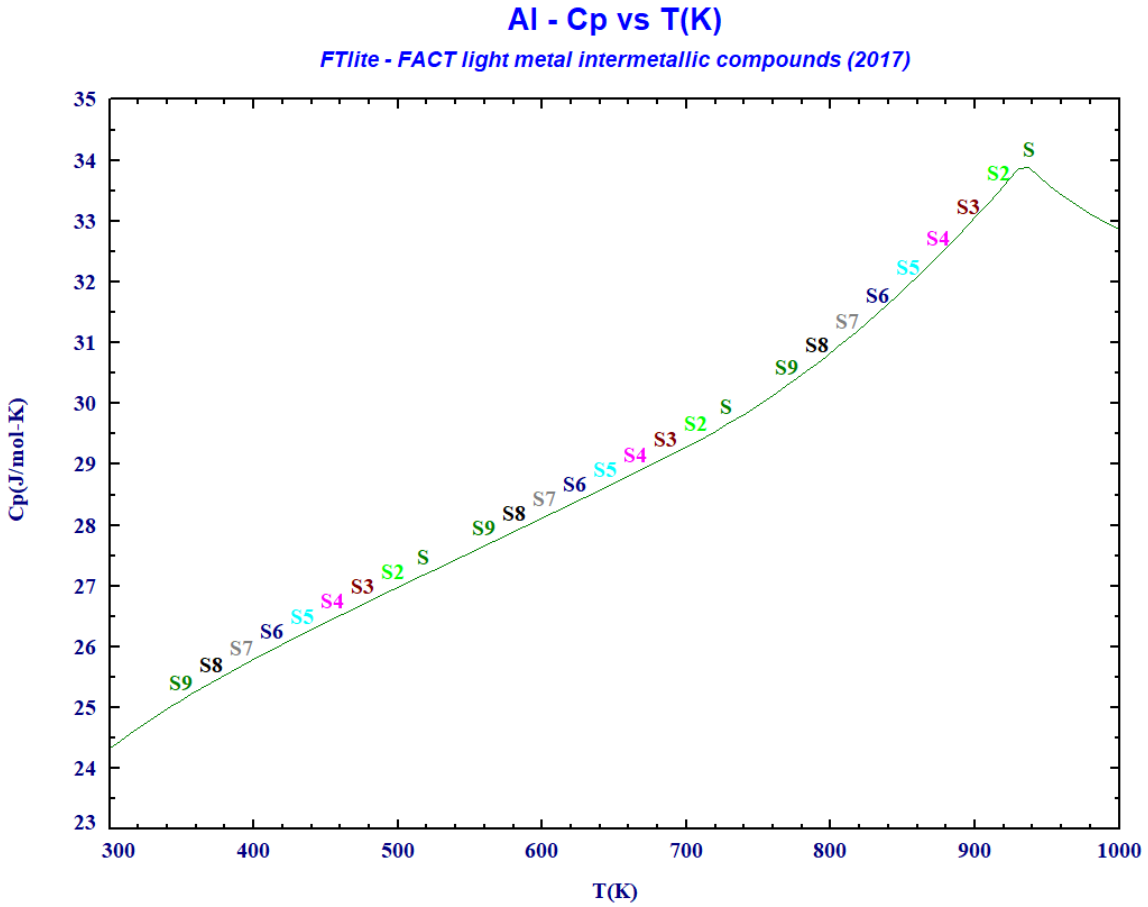
Opportunities: Unstable allotropes

Different allotropes are often modelled with the same $C_p(T)$-function.



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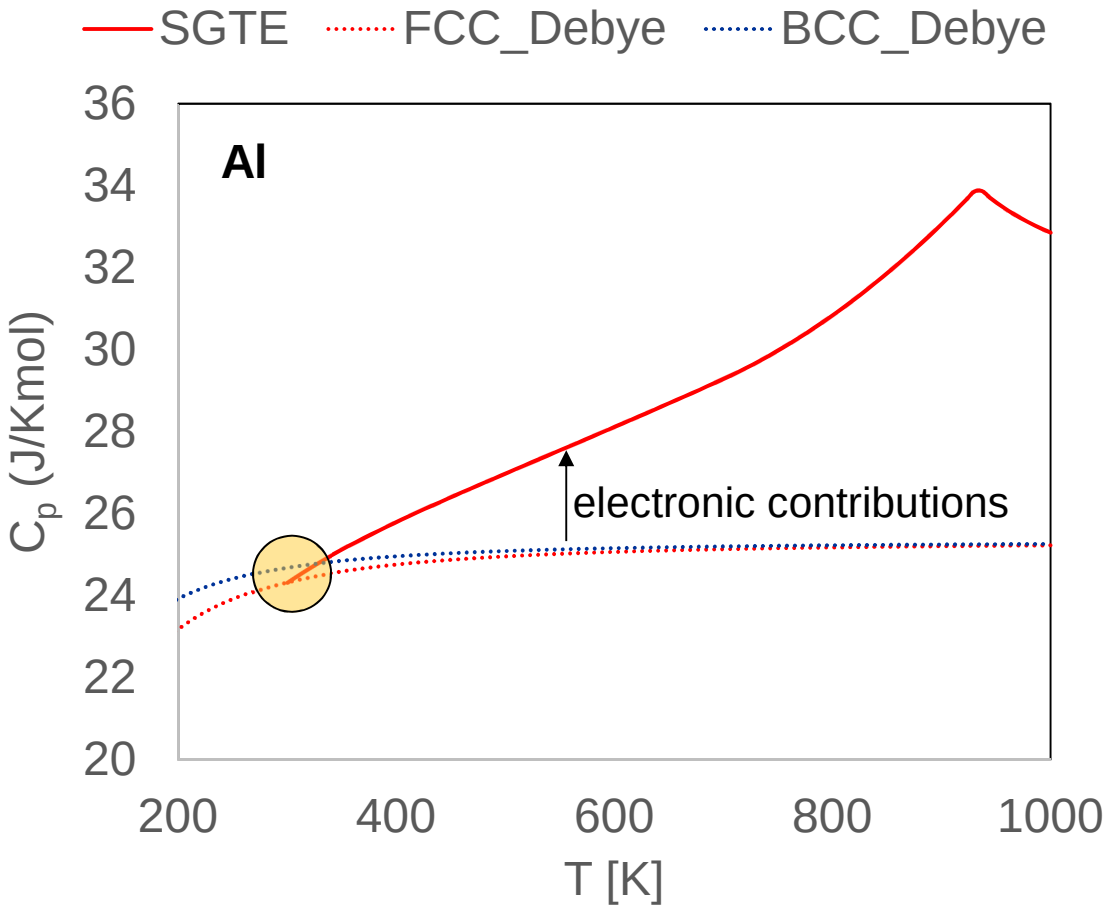
There is an excellent agreement of $C_{p,FCC\text{-}Al}$ between SGTE and ab initio calculations at 298 K ≈ θ_D (=267K).

$C_{p,BCC\text{-}Al}$ should be slightly higher!



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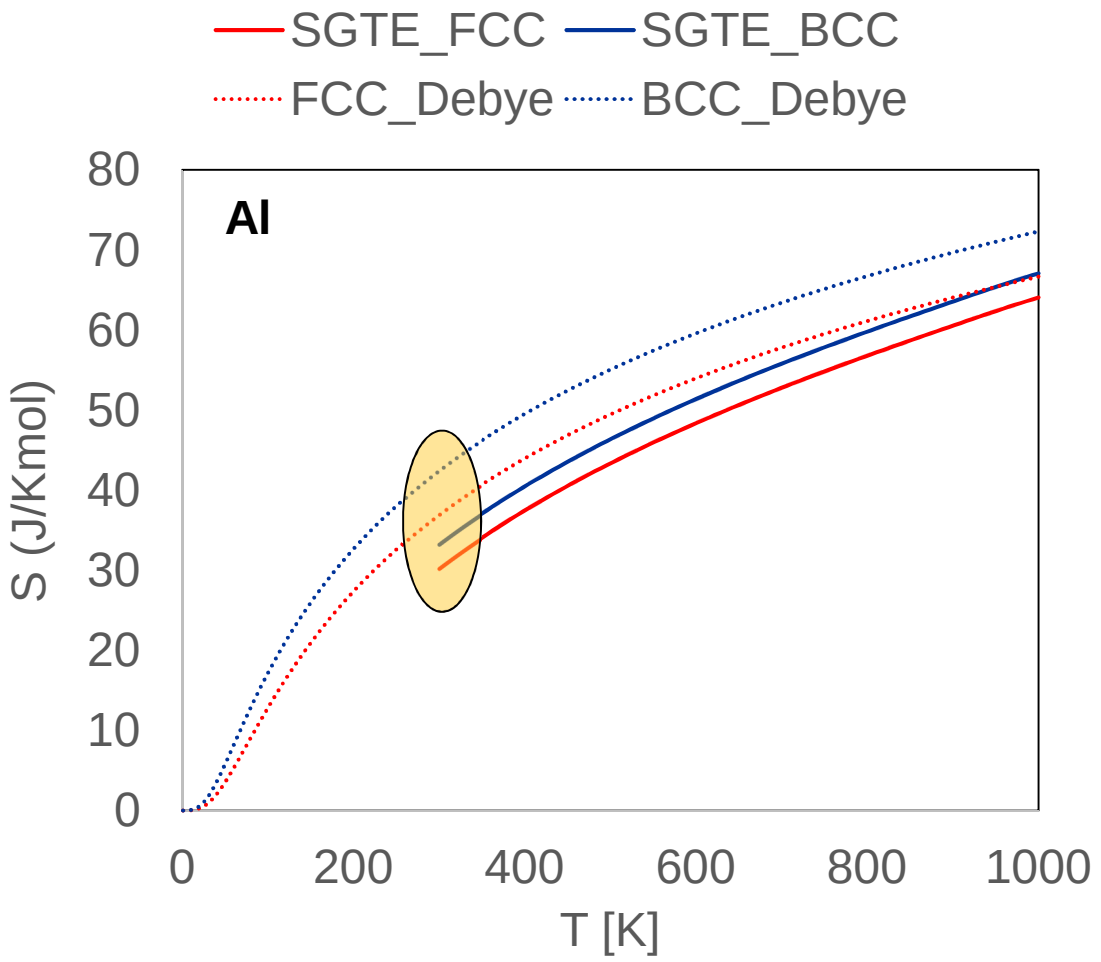
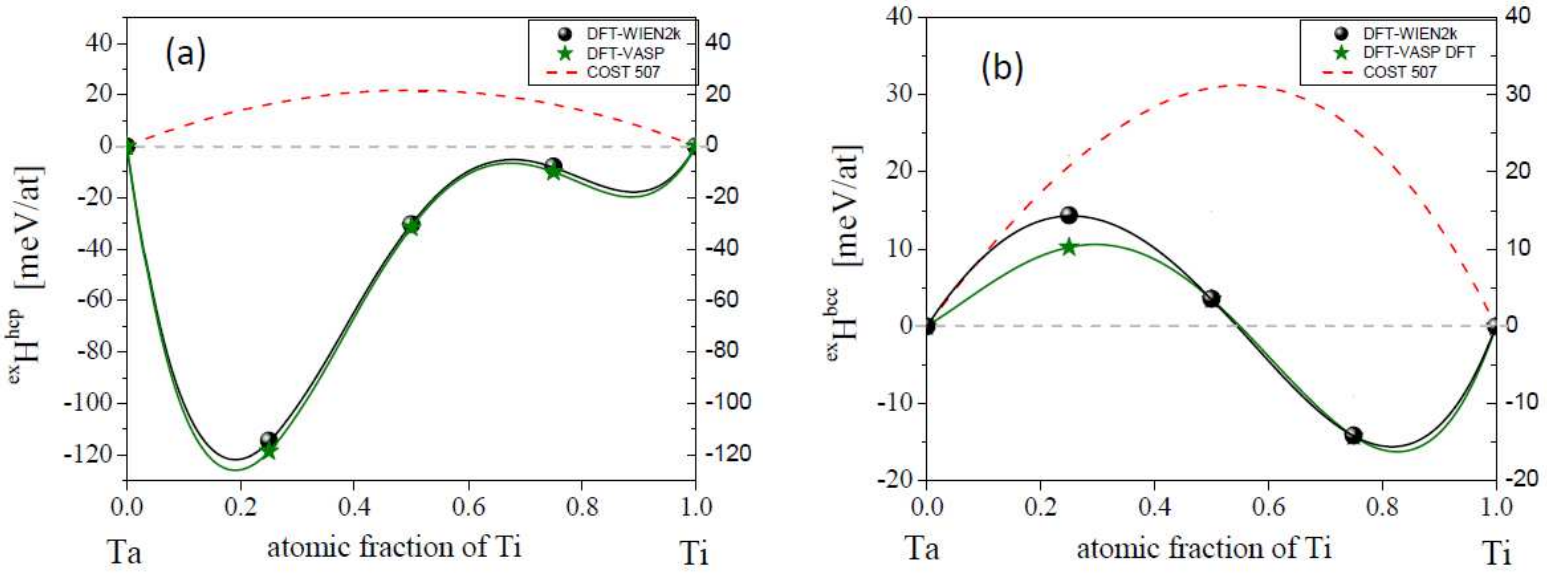
There is a disagreement of S_{FCC-Al} between SGTE and ab initio calculations at 298 K.

Ab initio calculations can help improving properties that are hard to measure!



Opportunities: Enthalpies at low T

- It is impossible to measure enthalpies at low temperatures due to kinetic constraints.



Barzilai, Acta Materialia 120 (2016) 255.

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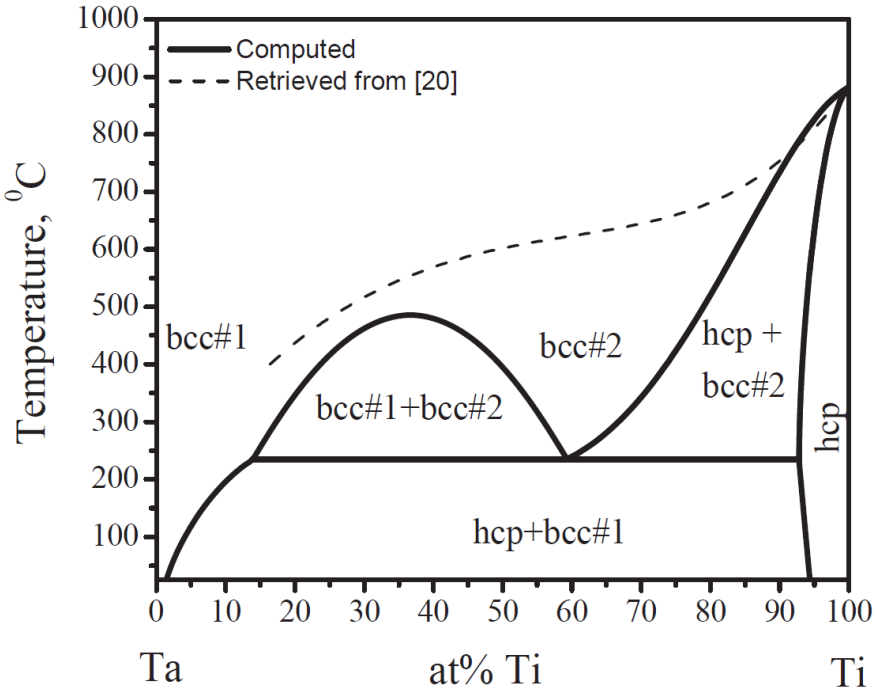

"The predicted critical temperature is very close to the lower limit of the temperature range of currently known experimental phase diagrams."

Barzilai, Acta Materialia 120 (2016) 255.

Opportunities: Navigating Chemical Compound Space

Today: SGTE Solution database contains ~1500 phases.
That allows description of

577 binary systems,
141 ternary systems,
15 higher order systems

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H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sc	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds								

~70 non-radioactive, non-noble gas elements
→*70*69 = 4830 binary systems*
→*70*69*68 = 328440 ternary systems*

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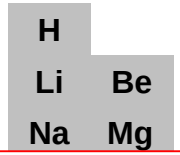

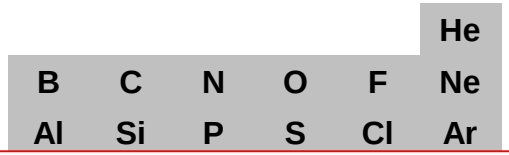

materialsproject.org, oqmd.org, aflowlib.org, nomad-coe.eu
69‘623 + 471‘857 + 1‘672‘887 → 17‘150‘125
compounds (for most of them only ΔH_f^{0K})

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Thank you very much for your attention!