

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

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GTT-Technologies



# Outline

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



# Thermodynamic database content

- $\Delta H^{298}$
- $S^{298}$
- $C_p(T)$       **$G(T)$**
- $\mu$
- $T_C$

Energy: Joules Pressure: atm Al

File Edit Units View Tools ViewData Help

Formula: Al

S1 properties

Heat of form. + Entropy Heat + Temperature of transf.

Form. of S1

$\Delta H^{298}$ (Joules)	$S^{298}$ (J/(mol K))
0	28.2999967235571

Phase Name: fcc\_Al Reference no.: 501 Density g/cc: 2.69822

Extended properties (optional)

Birch-Murnaghan

Therm. expans. (/K)	Compressibility (/bar)	Bulk mod. deriv.
3.4329E-5		
7.6228E-8 T		(T-T0)ln(T/T0)
0.00358254 /T		T^2
0.00857216 /T^2		T^3

Magnetic Moment (D) Temperature: Curie (selected) Neel K

P factor: 0.28 (selected) 0.40

FactSage 7.1 C:\FACTSAGE71\FACTDATA\FTLITE60BASE.CDB (v7.10) 1410 compounds read-only



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  - $\mu$
  - $T_C$
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- $\rho$
  - $\alpha(T)$       **$G(T,p)$**
  - $\kappa(T)$
  - $B'(T)$

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---

- $L(T)$      **G(T,p,X<sub>i</sub>)**

FactSage 7.1: Solution

File Edit Units Options Tools Help

Function Name: FNMnsoln.LIQU.Xss(Fe:Mn)

Solutions (7)

- LIQU (7-1) (RKMP)
  - SubLattice
    - A (3)
  - End Members (3)
    - (0) Fe
    - (1) Mn
    - (2) Nd
  - Mixables (0)
  - Interactions (8)
    - (0) Fe:Mn
    - (1) Fe:Mn
    - (2) Fe:Nd
    - (3) Fe:Nd
    - (4) Fe:Nd
    - (5) Mn:Nd
    - (6) Mn:Nd
    - (7) Mn:Nd
- FCC (12-2) (SUBL)

$g^E$  Binary term

$${}^iL_{AB}X_A X_B (X_A - X_B)^i$$

$i \geq 0$

( $X = \text{site fraction}$ )

A: Fe  
B: Mn

$i$   J/mol

${}^iL_{AB}$

C:\FactSage71\FACTDATA\Hitachi\NdFeMn\FNMnsoln.sln



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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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- Ideal: **Experimental error bars can be evaluated to fit the thermodynamic properties to all measurements**
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  - Real: **Thermodynamic properties are fitted to all available measurements**
- 2<sup>nd</sup> step: Consistency checks of binary and ternary systems!**



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# Database development based on ab initio

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→ [materialsproject.org](http://materialsproject.org), [oqmd.org](http://oqmd.org), [aflowlib.org](http://aflowlib.org), [nomad-coe.eu](http://nomad-coe.eu)



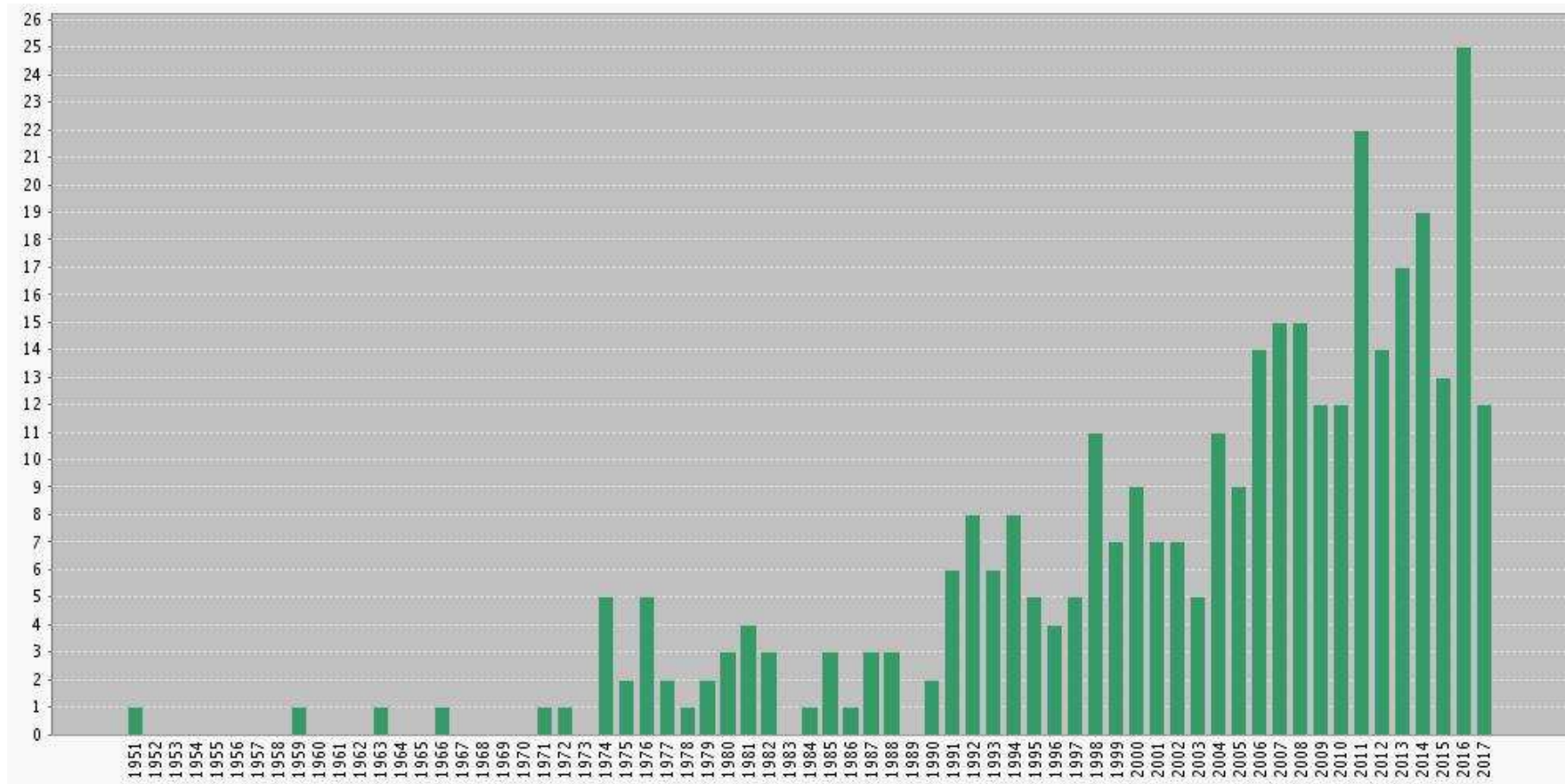
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# Challenge: $\Delta H_{f,\text{experiment}} \leftrightarrow \Delta H_{f,\text{ab initio}}$

Publications including “lattice stability”

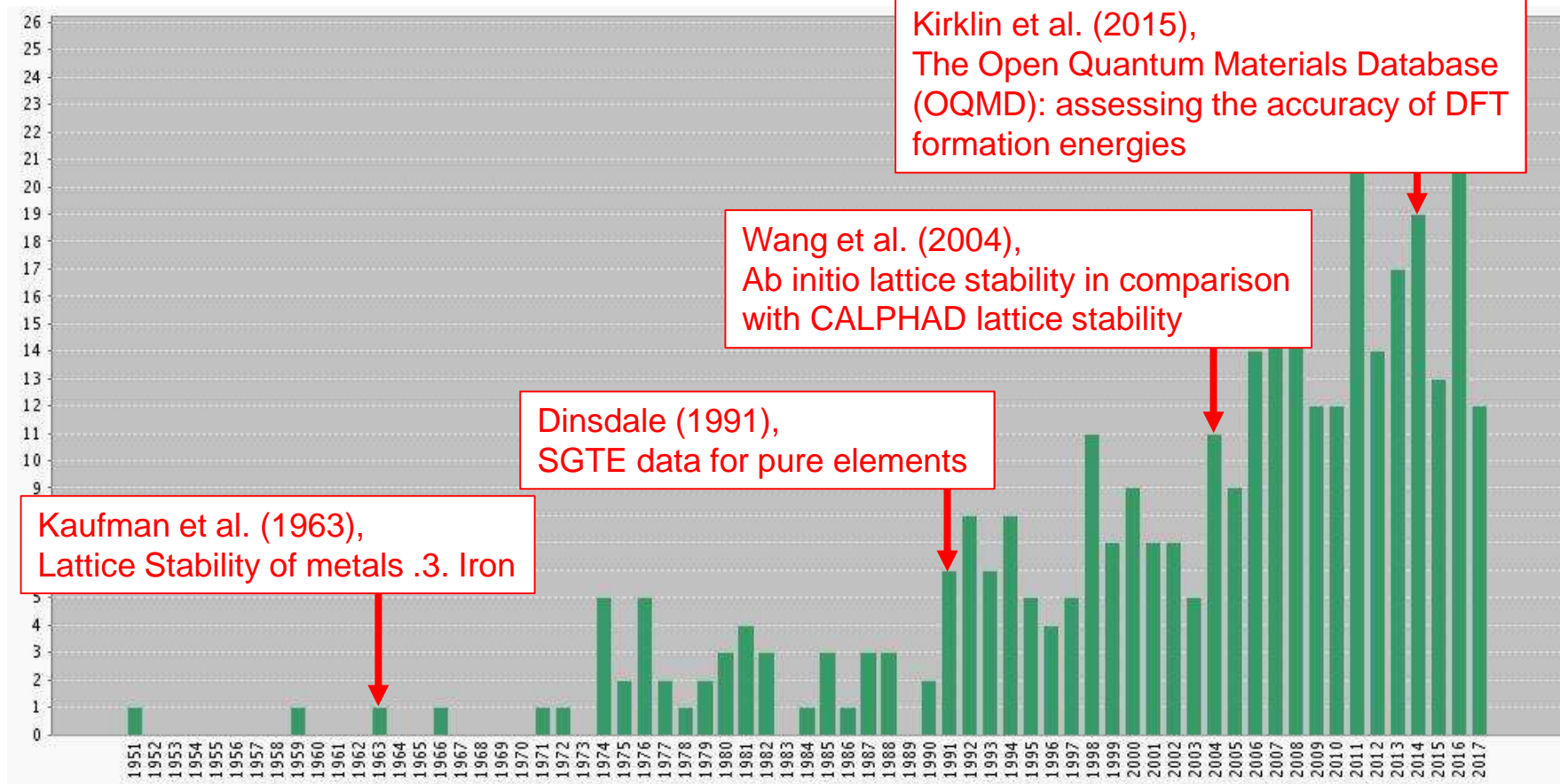


webofknowledge.com



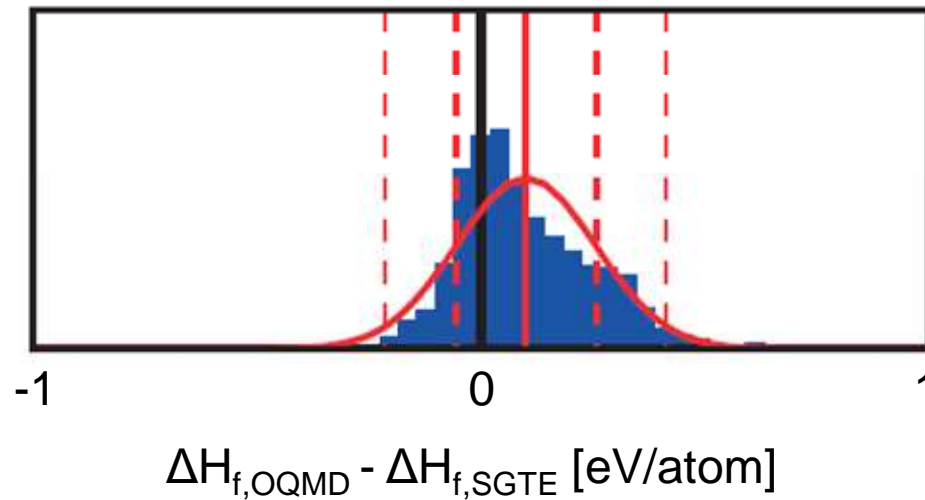
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Raw data:



Mean average error is  $\sim 13$  kJ/mol atoms

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

(1 eV/atom  $\approx$  100 kJ/mol atoms)

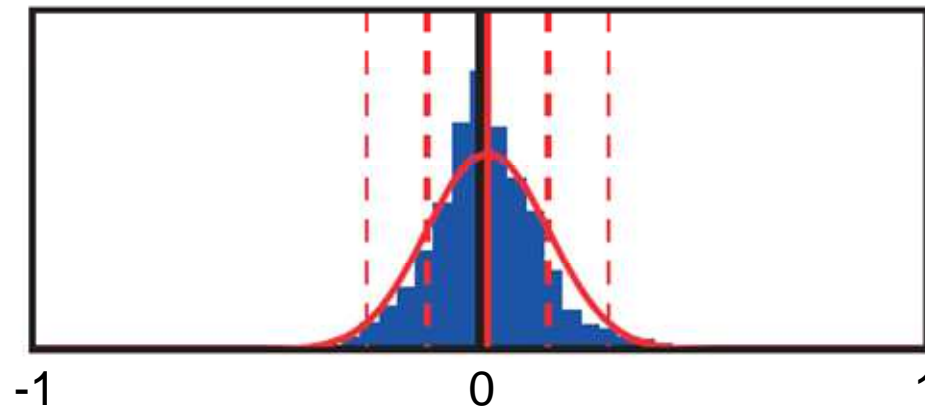




# Challenge: $\Delta H_{f,\text{experiment}} \leftrightarrow \Delta H_{f,\text{ab initio}}$

**WHY?**

Linear correction for elements:



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

Mean average error is ~9 kJ/mol atoms

Kirklin et al. (2015),  
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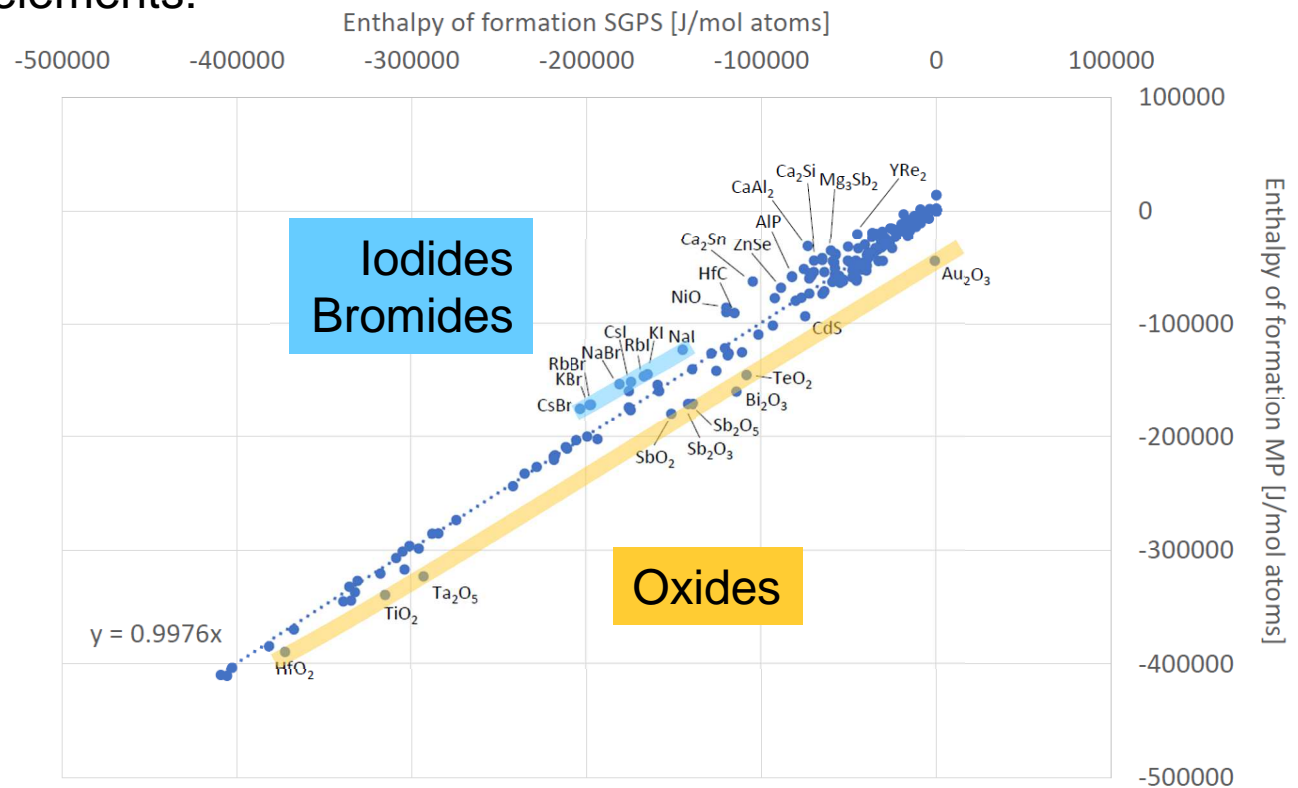
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# Challenge: $\Delta H_{f,\text{experiment}} \leftrightarrow \Delta H_{f,\text{ab initio}}$

**WHY?**

Linear correction for elements:



# Challenge: “High” temperatures

The screenshot shows the FactSage 7.1 interface. The left pane displays a tree view of data bases, with 'Al' selected under 'FTliteBASE'. The right pane shows the 'Cp expression for S1' with the following parameters:

- $\Delta H_{298}$ : 0 J/mol
- $S_{298}$ : 28.2999967235571 J/(mol K)
- Temperature range: from 298.150 K to 700.000 K

The Cp(T) expression is shown as a polynomial:

Term	Value	Temperature Exponent (T^)
$C_p(T)$	24.3671976	0.00
	0.003769324	1.00
	-148184	-2.00
	5.265984E-6	2.00

The status bar at the bottom indicates 'FactSage 7.1' and the file path 'C:\FACTSAGE71\FACTDATA\FTLITE60BASE.CDB (v7.10) 1410 compounds read-only'.



# Challenge: “High“ temperatures

Ab initio calculations are mostly done at 0K.

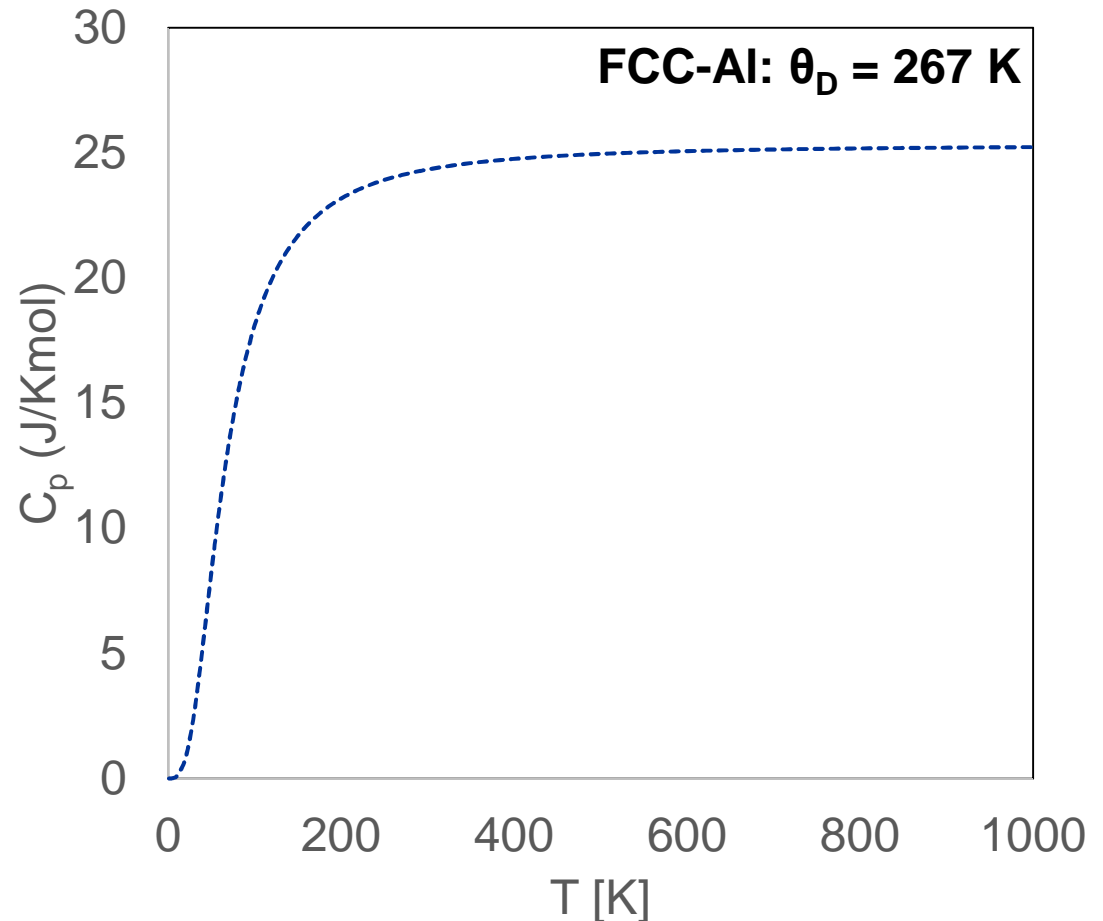
How to extrapolate to room temperature and above?

→ Einstein model

→ Debye model

→ **X**  $C_p = \text{const}$  **X**

→ Other models for  $T > \theta_D$  are computationally expensive!



# Challenge: Liquid and gas phases

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



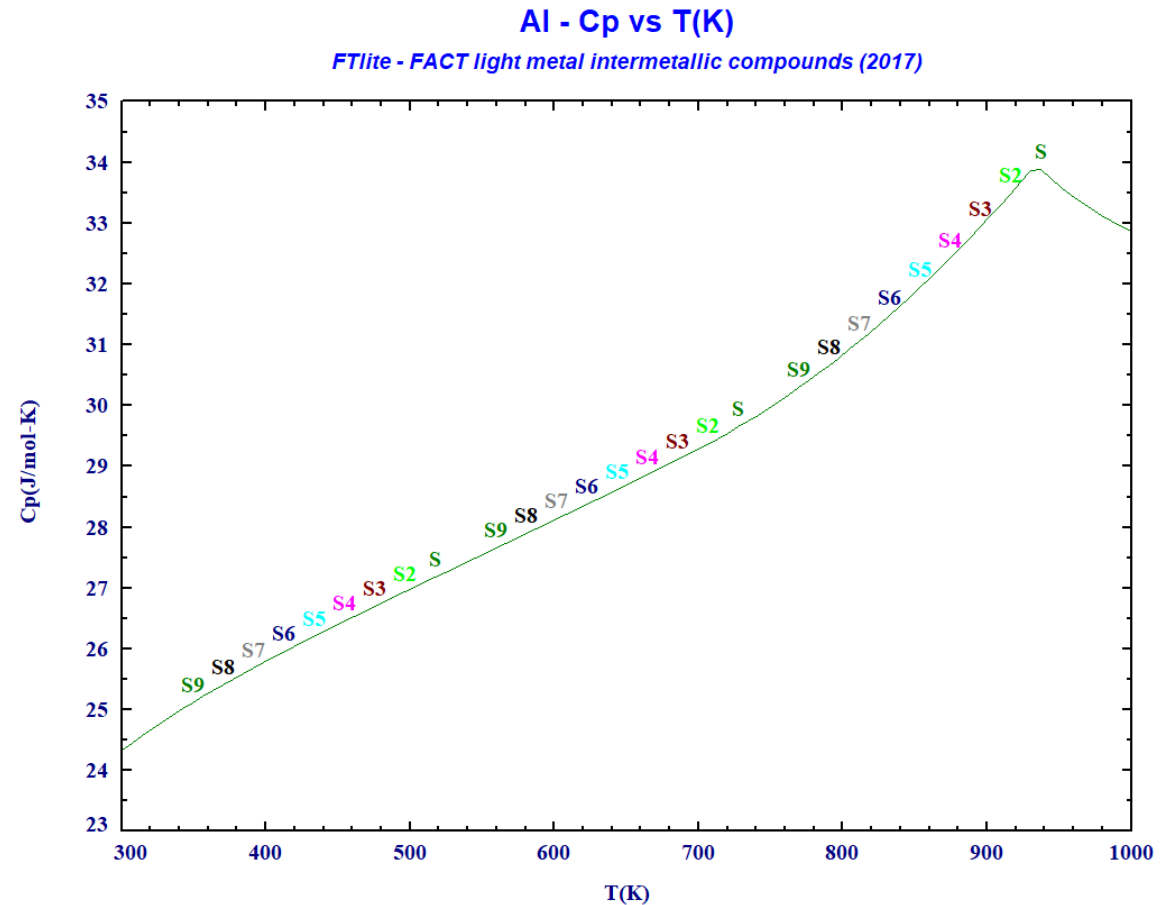
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# Opportunities: Unstable allotropes

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

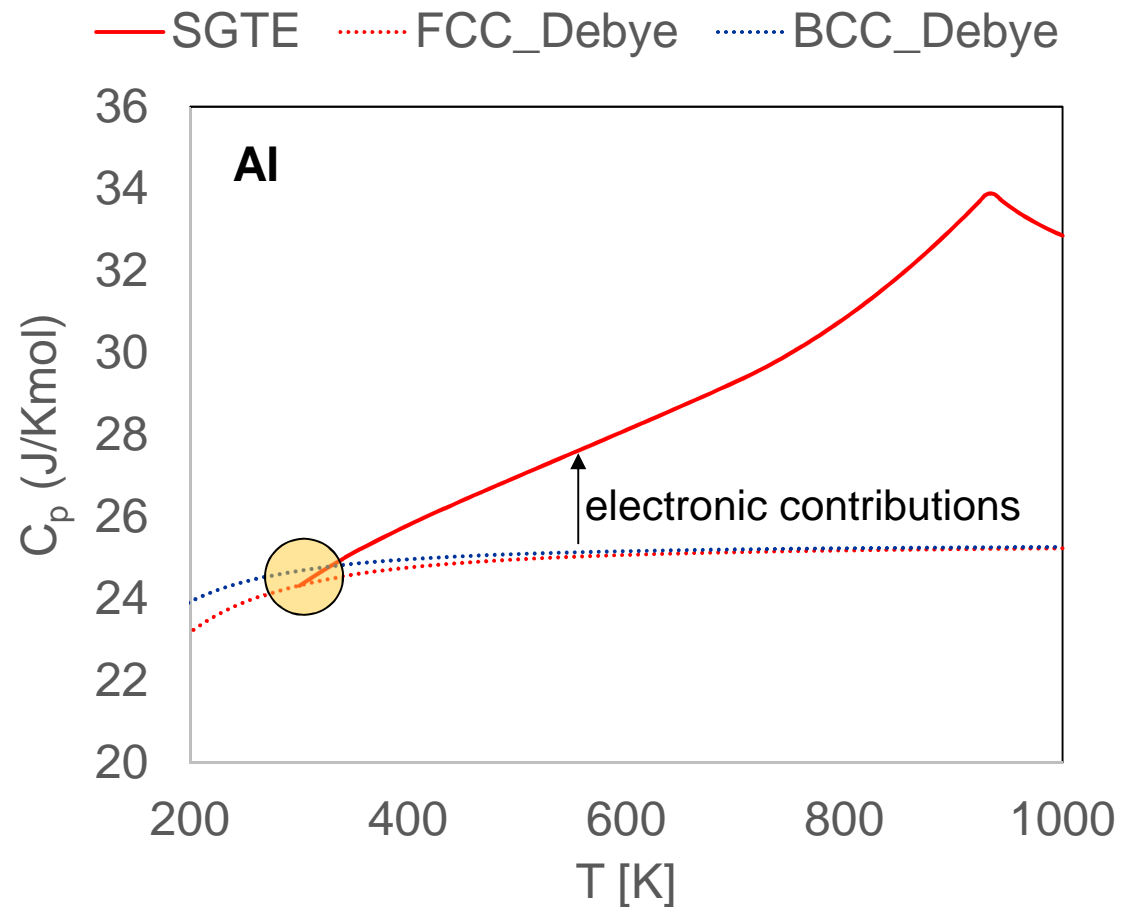


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There is an excellent agreement of  $C_{p,\text{FCC-Al}}$  between SGTE and ab initio calculations at 298 K  $\approx \theta_D$  (=267K).

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





# Opportunities: Unstable allotropes

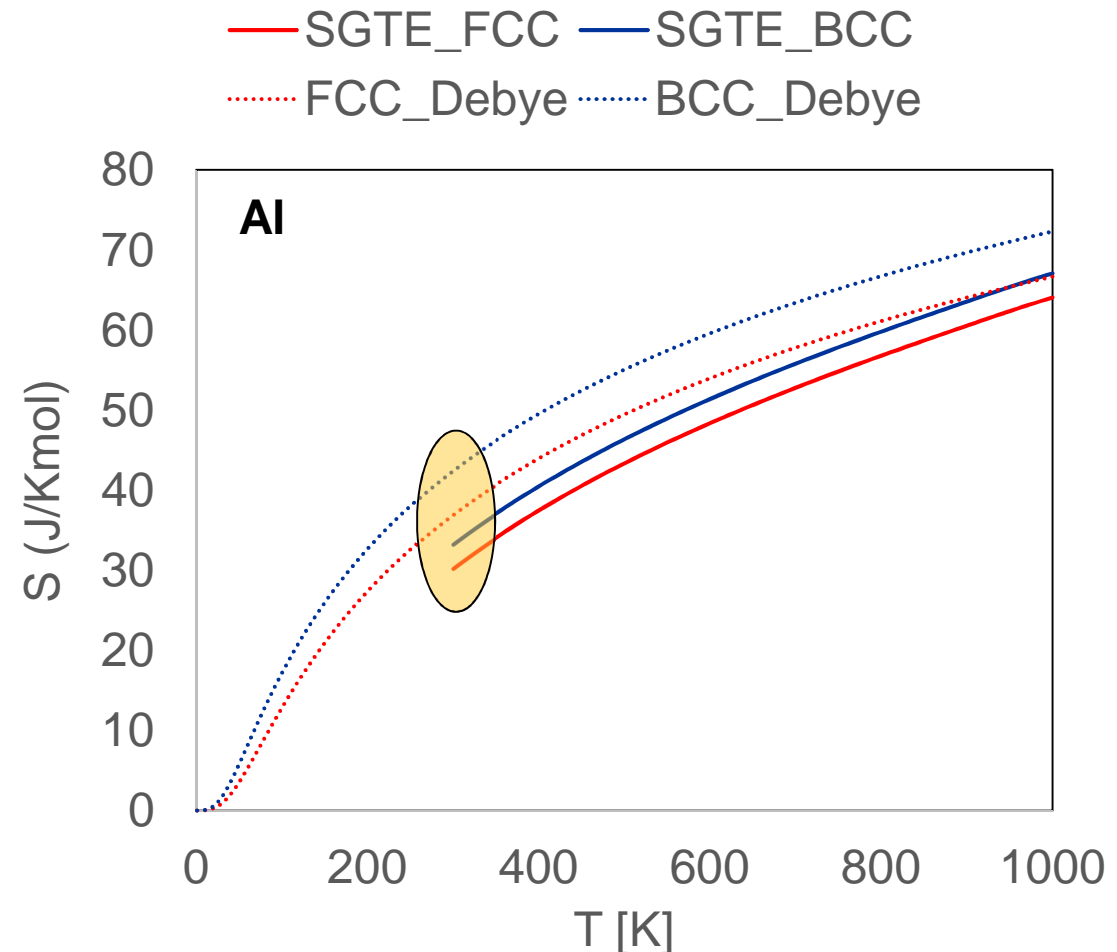
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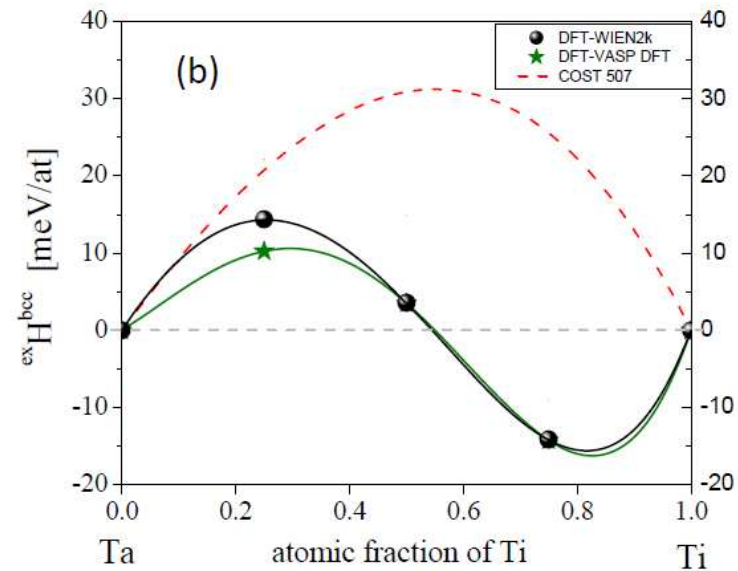
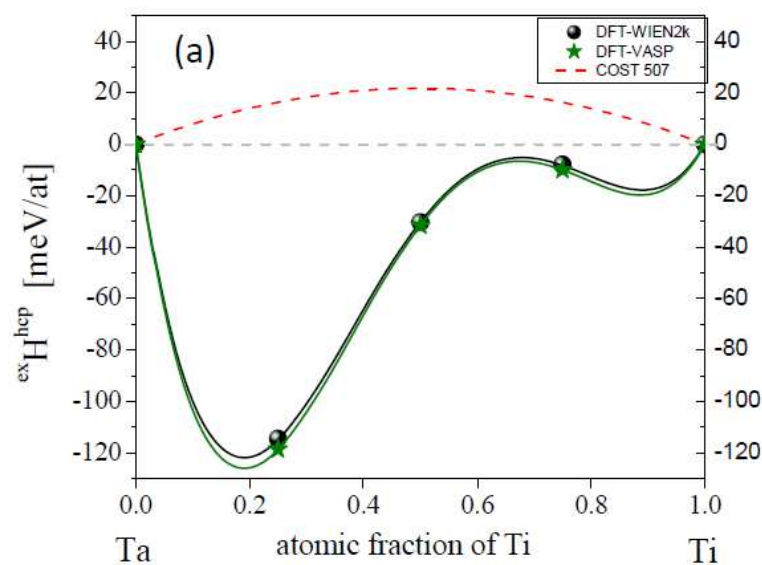
There is a disagreement of  $S_{FCC-Al}$  between SGTE and ab initio calculations at  $298\text{ K}$ .

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.

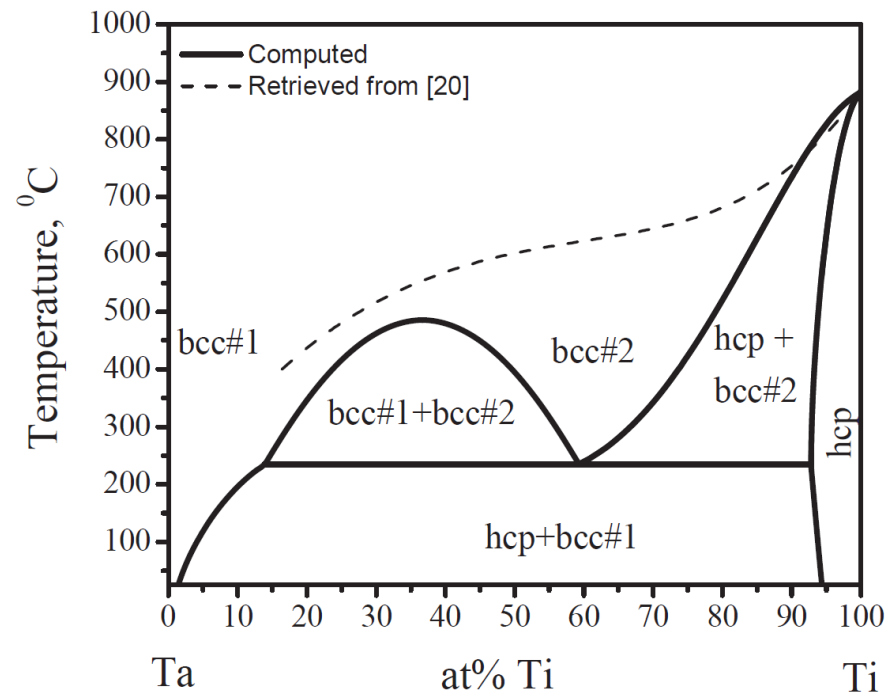


Barzilai, Acta Materialia 120 (2016) 255.



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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	Sn	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

→  $70 \times 69 = 4830$  binary systems

→  $70 \times 69 \times 68 = 328440$  ternary systems



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H	
Li	Be
Na	Mg

B	C	N	O	F	He
Al	Si	P	S	Cl	Ne
					Ar

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  $\Delta H_f^{0K}$ )

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**Thank you very much for your attention!**

