

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

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

Energy: Joules Pressure: atm Al

File Edit Units View Tools ViewData Help

Formula: Al

FTliteBASE

- Al
 - S1
 - Cp 700
 - Cp 933
 - Cp 3900
 - S2
 - S3
 - S4
 - S5
 - S6
 - S7
 - S8
 - S9
 - L1
- FTmiscBASE
- FTOxCNBASE
- FToxidBASE
- FTpulpBASE
- FTsaltBASE

S1 properties

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

Form. of S1

ΔH^{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 K Neel K

P factor: 0.28 0.40

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



Thermodynamic database content

- ΔH^{298}
 - S^{298}
 - $C_p(T)$ **G(T)**
 - μ
 - T_C
-
- ρ
 - $\alpha(T)$ **G(T,p)**
 - $\kappa(T)$
 - $B'(T)$

The screenshot shows the FactSage 7.1 software interface. The main window displays the thermodynamic data for Aluminum (Al) in the fcc phase. The data is organized into several sections:

- Form. of S1:** ΔH^{298} (Joules) = 0, S^{298} (J/(mol K)) = 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		
0.00857216 /T^2		
 - Magnetic Moment (D):** [Empty field]
 - Temperature:** Curie (selected), Neel, [Empty field] K
 - P factor:** 0.28 (selected), 0.40

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



Thermodynamic database content

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- $\kappa(T)$
- $B'(T)$

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

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.

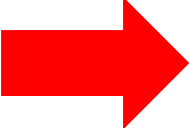


Database development based on experiment

- Ideal: **Experimental error bars can be evaluated to fit the thermodynamic properties to all measurements**
 - binary phase diagram
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- Real: **Thermodynamic properties are fitted to all available measurements**



Database development based on experiment

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 - binary phase diagram
 - enthalpies of (trans-)formation of the compounds
 - enthalpies of mixing and constituent activities of solutions as $f(T)$
 - heat capacities
 - crystal structures  **2nd step: Consistency checks of binary and ternary systems!**
 - density as $f(T)$
 - elastic properties
- Real: **Thermodynamic properties are fitted to all available measurements**



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Database development based on ab initio

- Ideal: The following properties are calculated:
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 - enthalpies of mixing of solutions as $f(T)$
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 - crystal structures, especially for complex solutions
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 - elastic properties as $f(T)$
- Real: Most of these properties can be used!



Database development based on ab initio

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- Real: Most of these properties can be used!

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



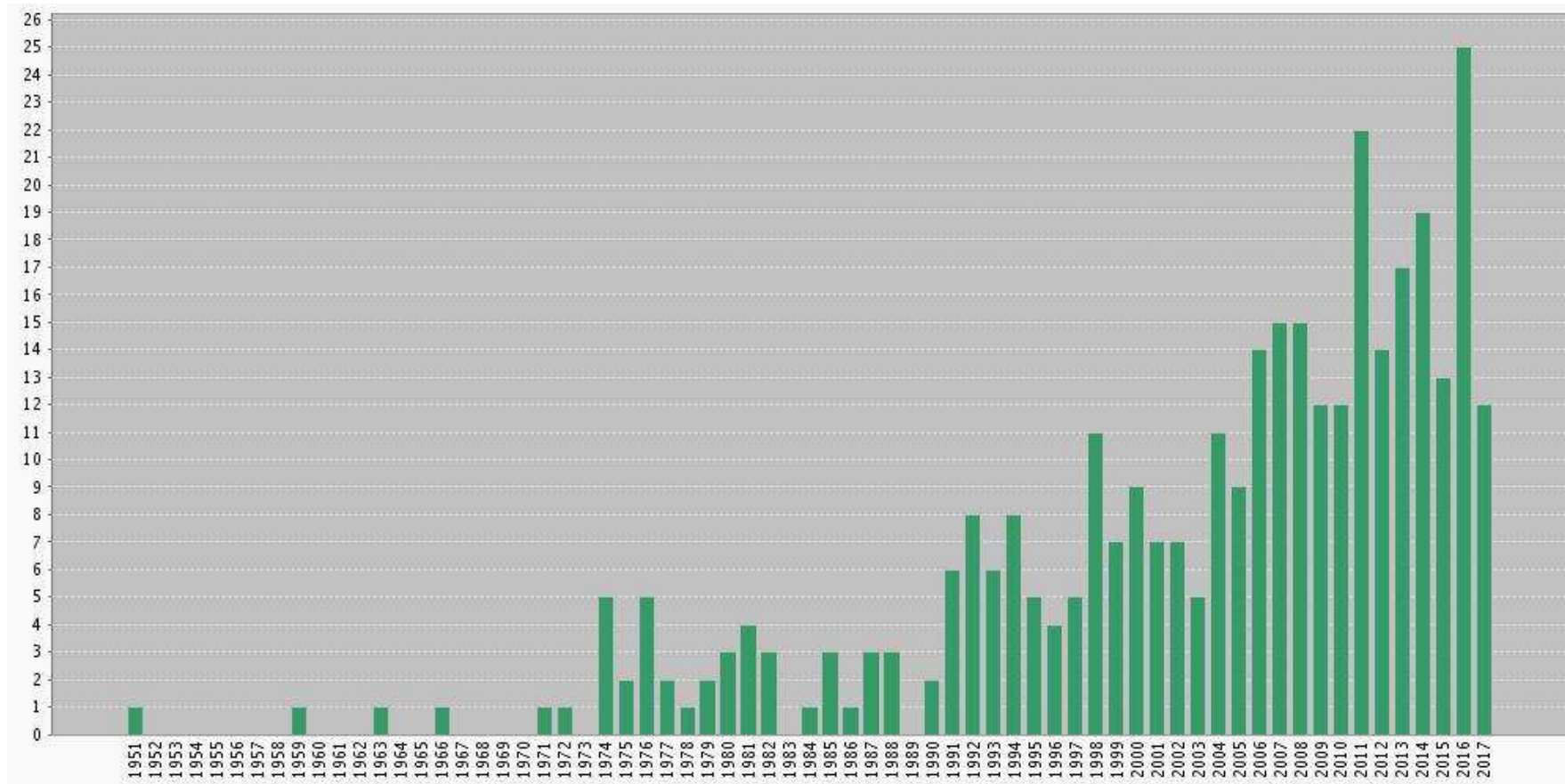
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Challenge: $\Delta H_{f, \text{experiment}} \leftrightarrow \Delta H_{f, \text{ab initio}}$

Publications including “lattice stability”

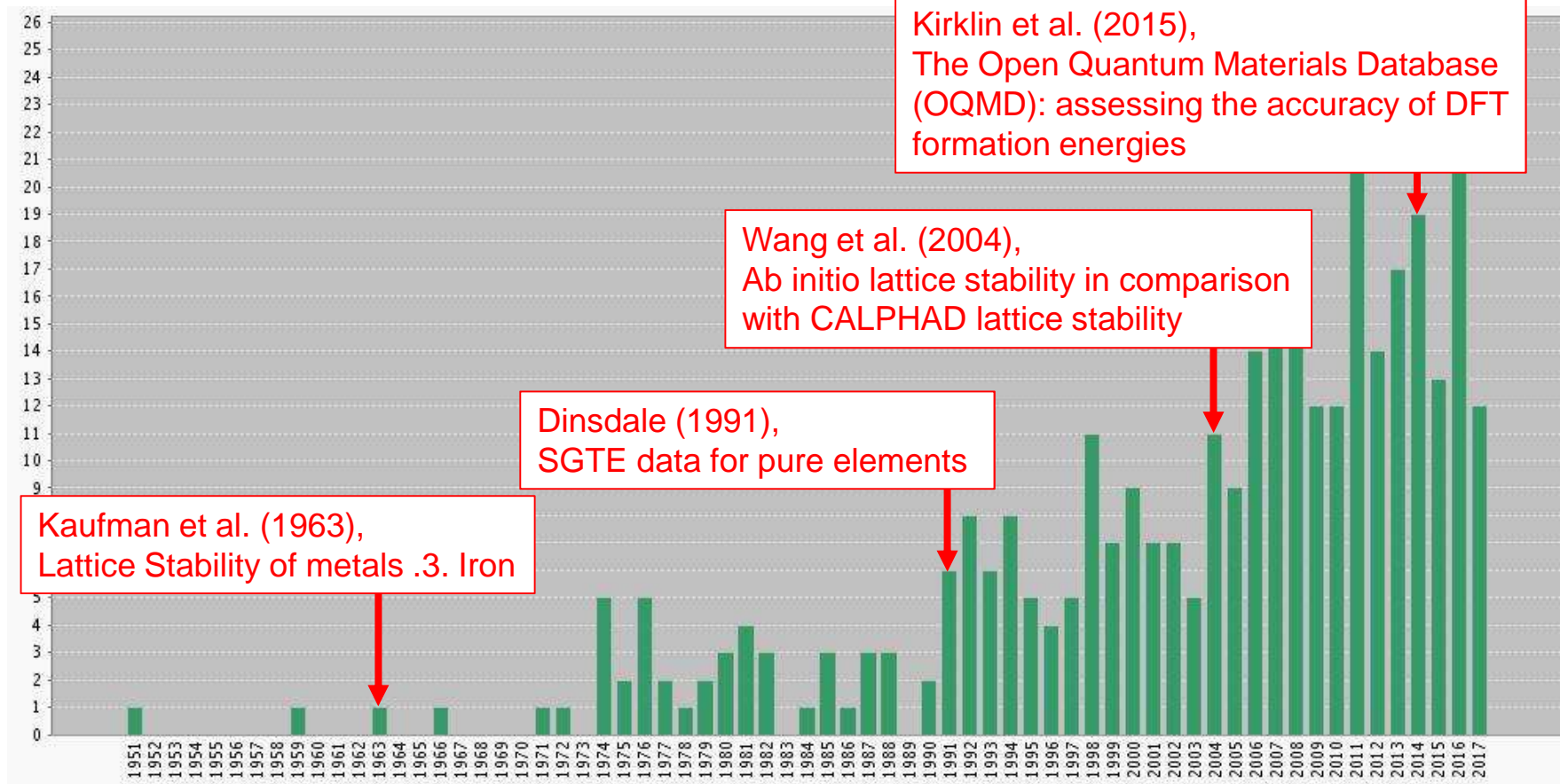


webofknowledge.com



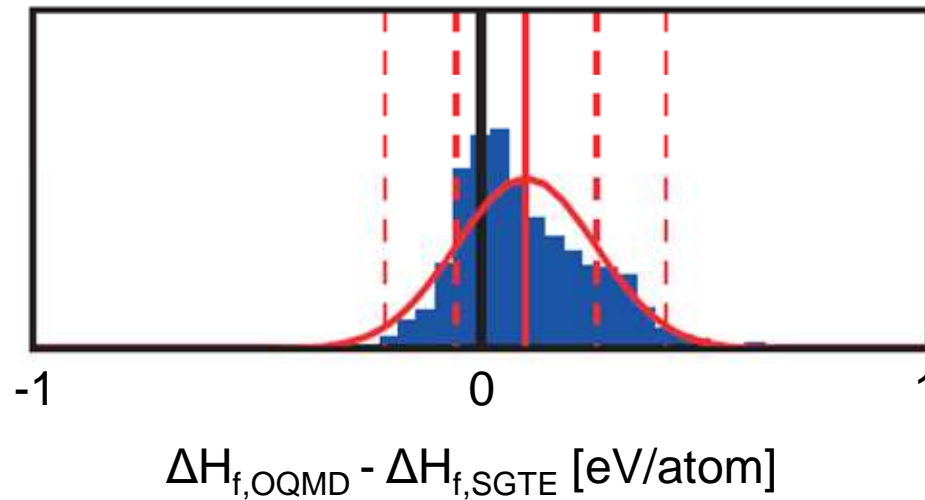
Challenge: $\Delta H_{f,\text{experiment}} \leftrightarrow \Delta H_{f,\text{ab initio}}$

Publications including “lattice stability”



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

Raw data:



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

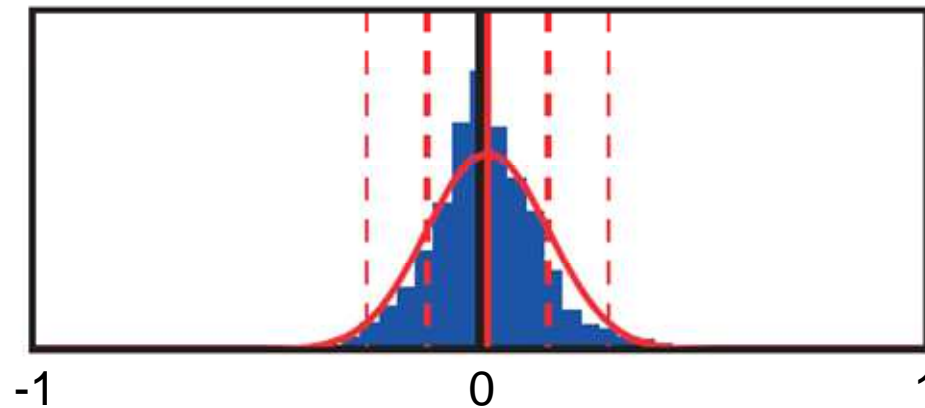
(1 eV/atom \approx 100 kJ/mol atoms)



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),
The Open Quantum Materials Database
(OQMD): assessing the accuracy of DFT
formation energies

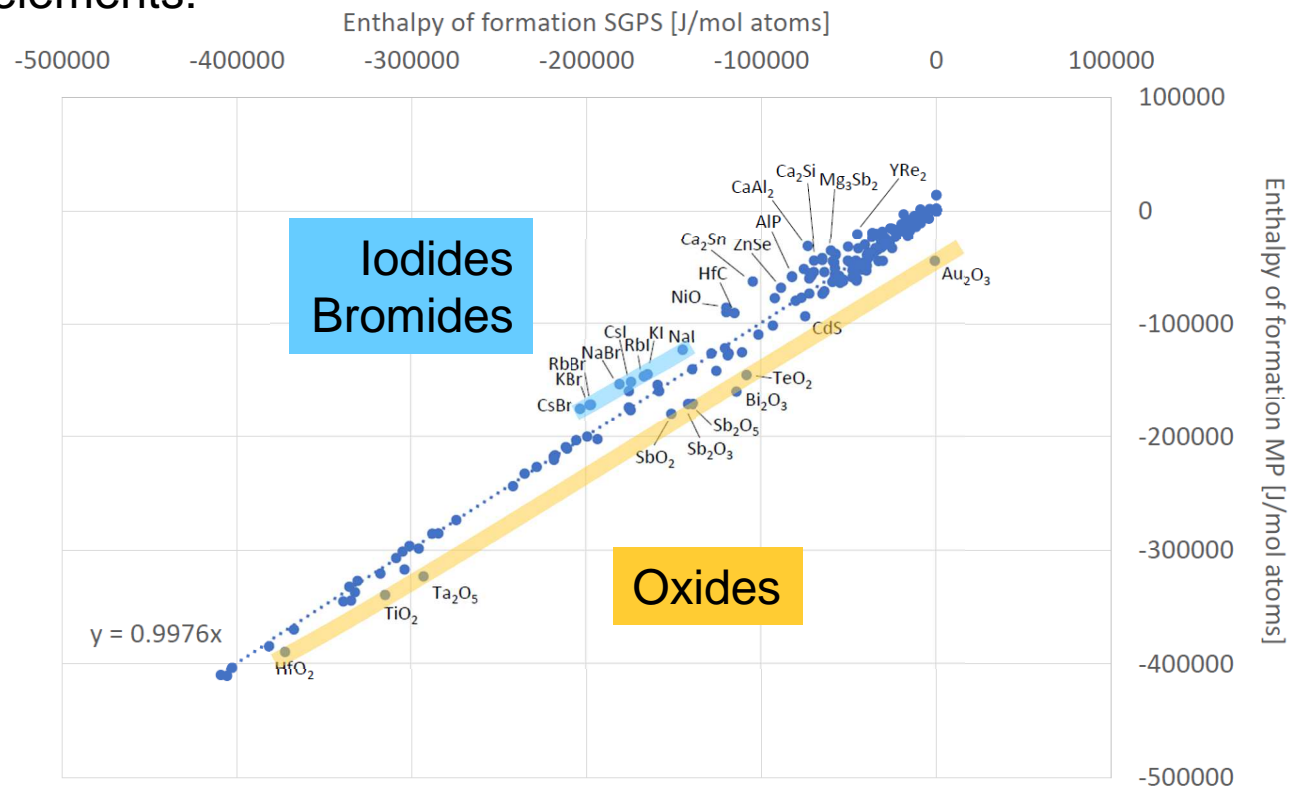
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Challenge: $\Delta H_{f, \text{experiment}} \leftrightarrow \Delta H_{f, \text{ab initio}}$

WHY?

Linear correction for elements:



Challenge: “High” temperatures

Energy: Joules Pressure: atm Al

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Formula: Al

FScoppBASE
 FSleadBASE
 FSstelBASE
 FSupsiBASE
 FTdemoBASE
 FTfritzBASE
 FTHallBASE
 FTHeigBASE
 FTliteBASE
 Al
 S1
 Cp 700
 Cp 933
 Cp 3900
 S2
 S3
 S4
 S5
 S6
 S7

Cp expression for S1
 ΔH_{298} : 0 J/mol
 S_{298} : 28.2999967235571 J/(mol K)
 from 298.150 K to 700.000 K

Cp
H
S
G Edit

Cp(T) =	24.3671976	T ^{0.00}
	0.003769324	T ^{1.00}
	-148184	T ^{-2.00}
	5.265984E-6	T ^{2.00}
		T
		T
		T
		T

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



Challenge: “High“ temperatures

Ab initio calculations are mostly done at 0K.

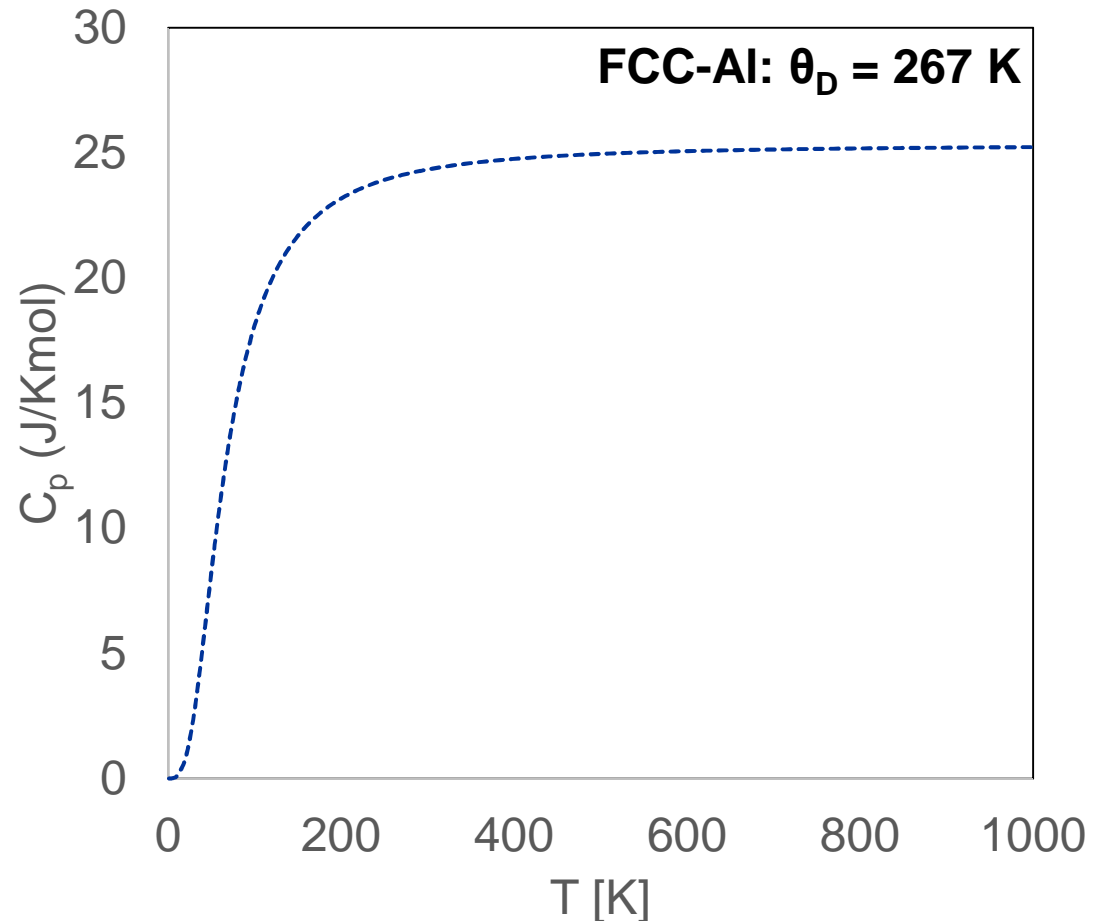
How to extrapolate to room temperature and above?

→ 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...



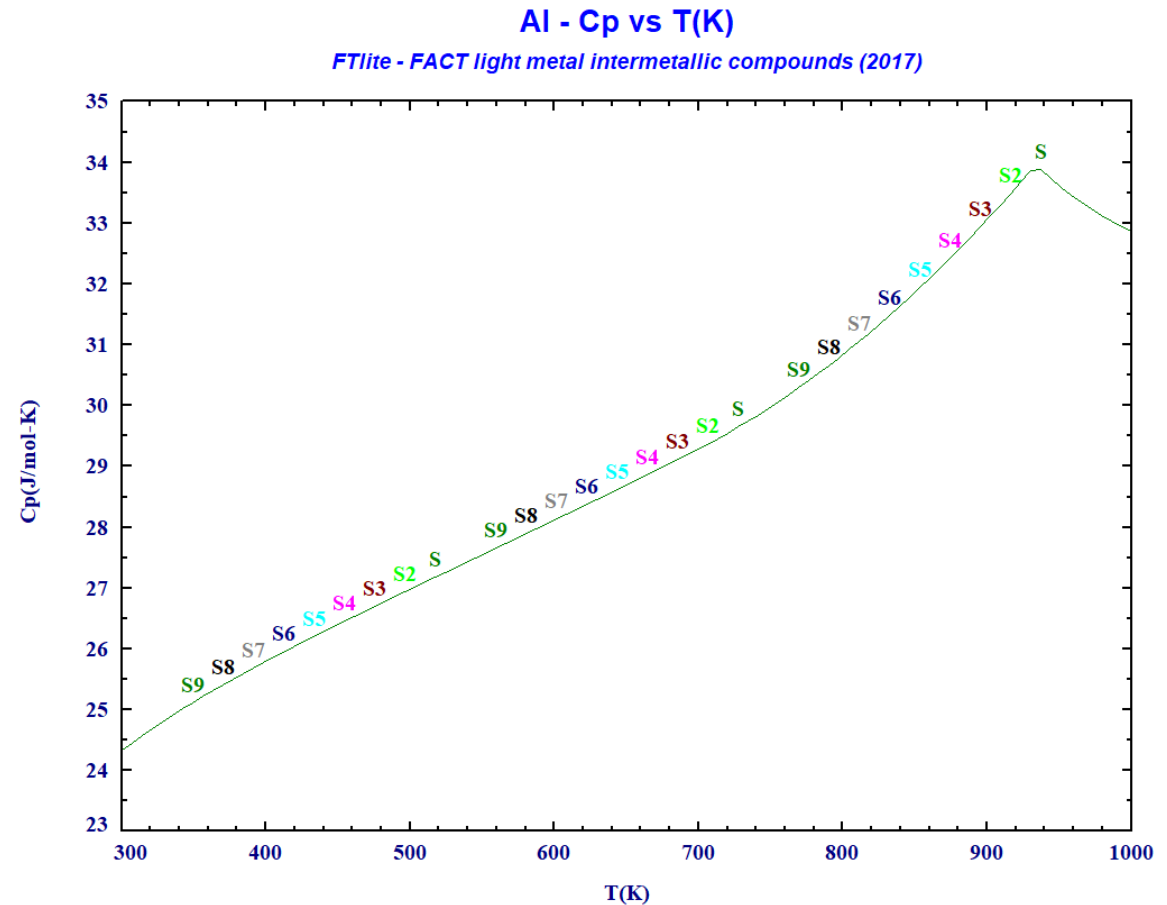
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Opportunities: Unstable allotropes

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

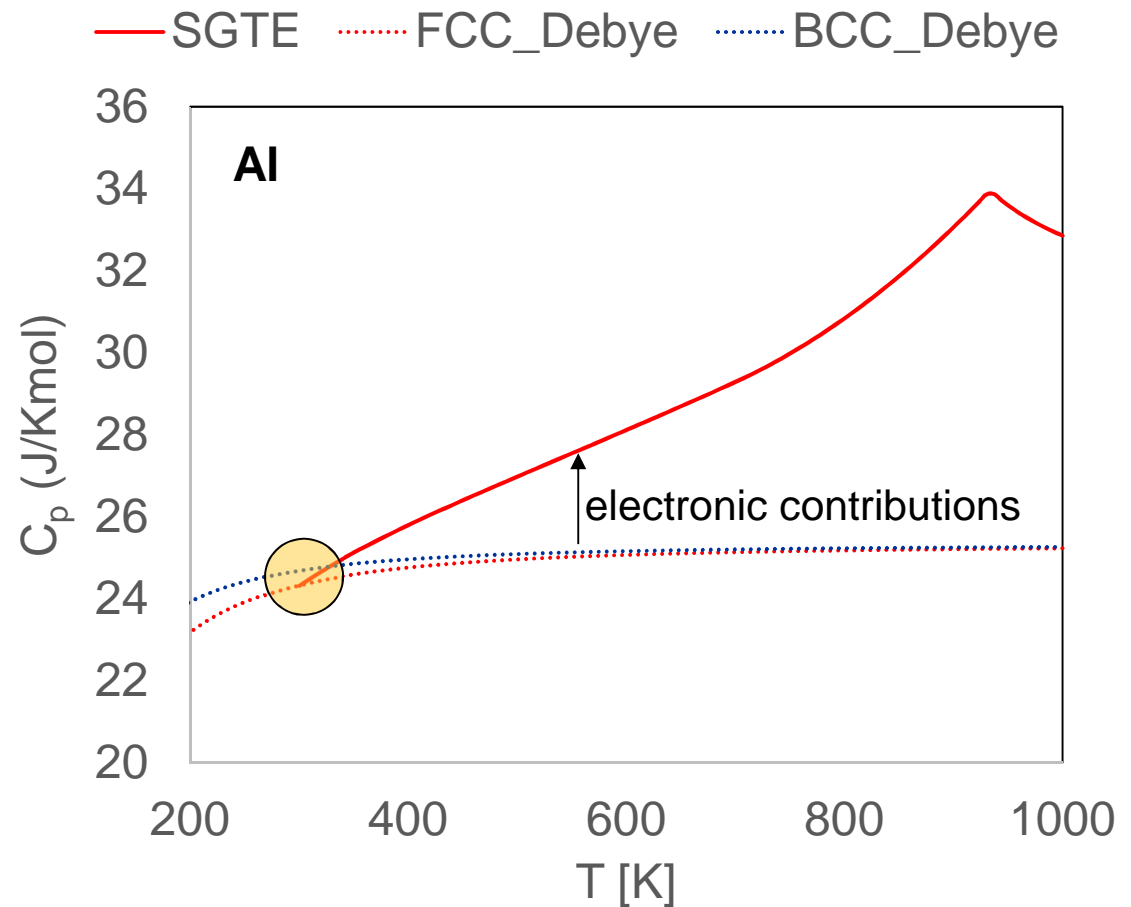


Opportunities: Unstable allotropes

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

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

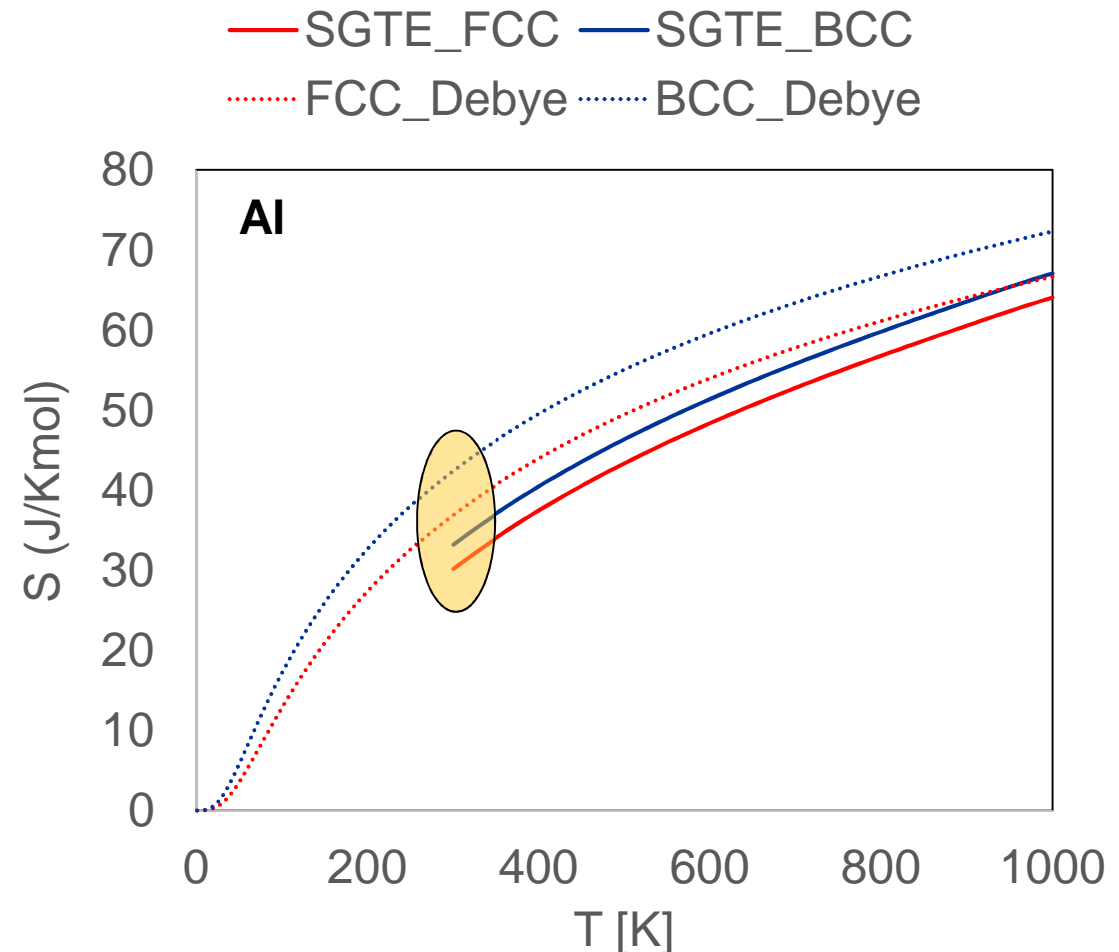
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There is an excellent agreement of $C_{p,FCC-Al}$ between SGTE and ab initio calculations at $298\text{ K} \approx \theta_D (=267\text{K})$.

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

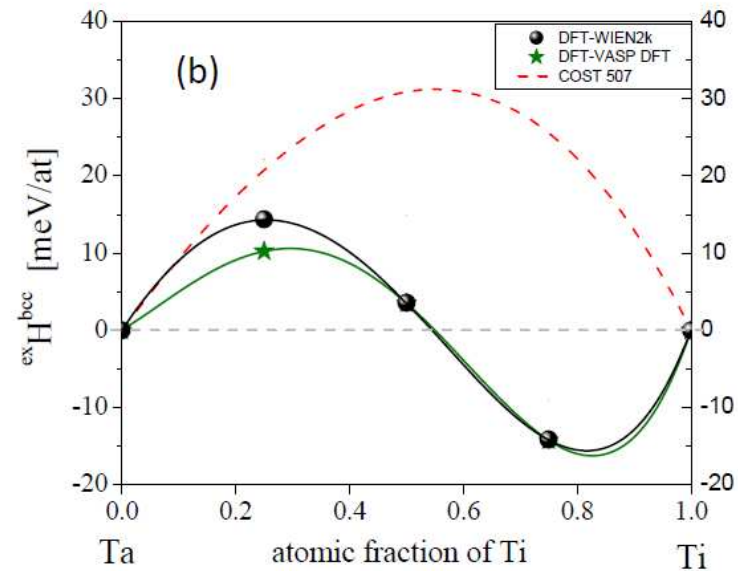
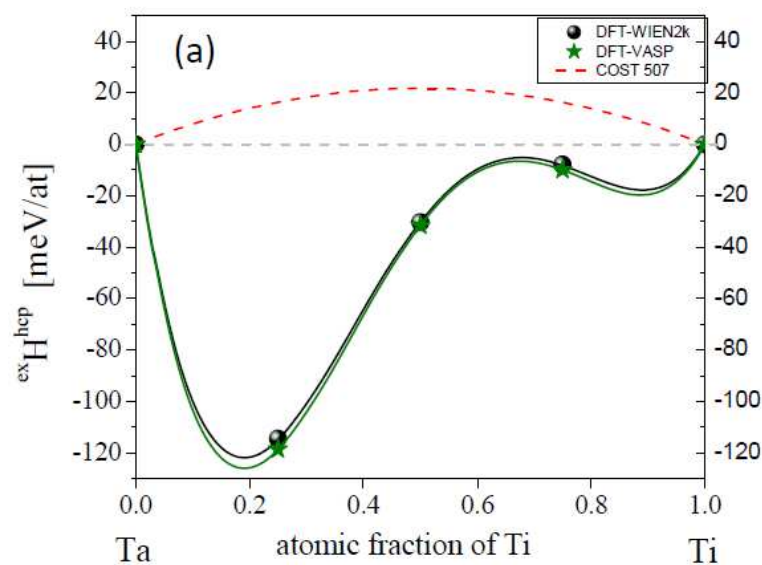
There is a disagreement of S_{FCC-Al} between SGTE and ab initio calculations at 298 K .

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.

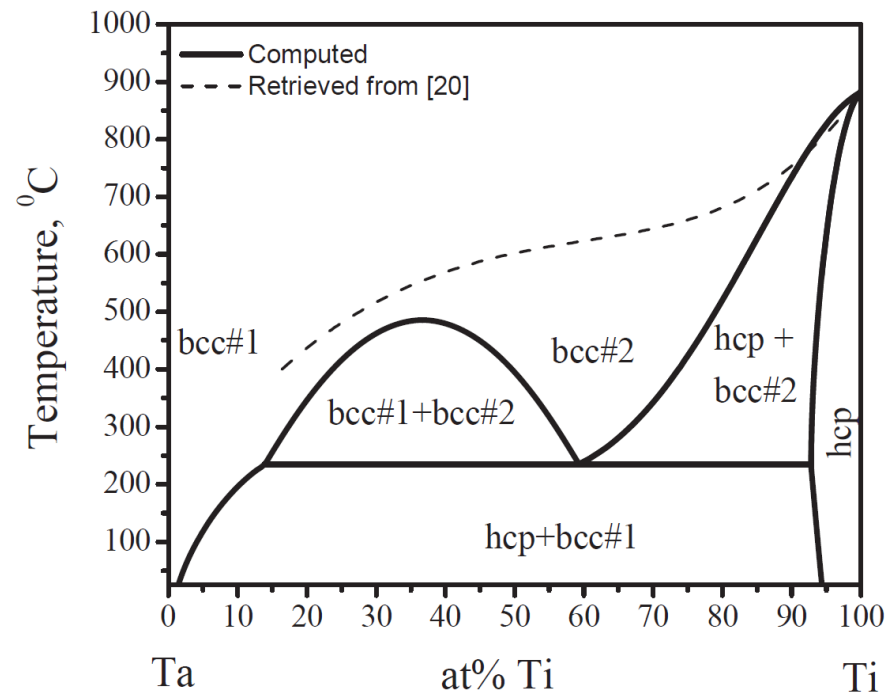


Barzilai, Acta Materialia 120 (2016) 255.



Opportunities: Enthalpies at low T

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



“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



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

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 ΔH_f^{0K})

~70 non-radioactive, non-noble gas elements

→ $70 \cdot 69 = 4830$ binary systems

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



Thank you very much for your attention!

