Ab Initio Computation of Free Energies

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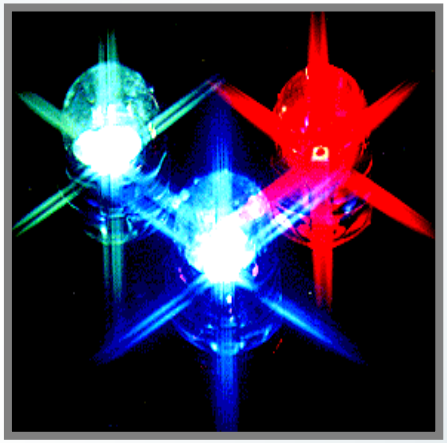
Structural Materials

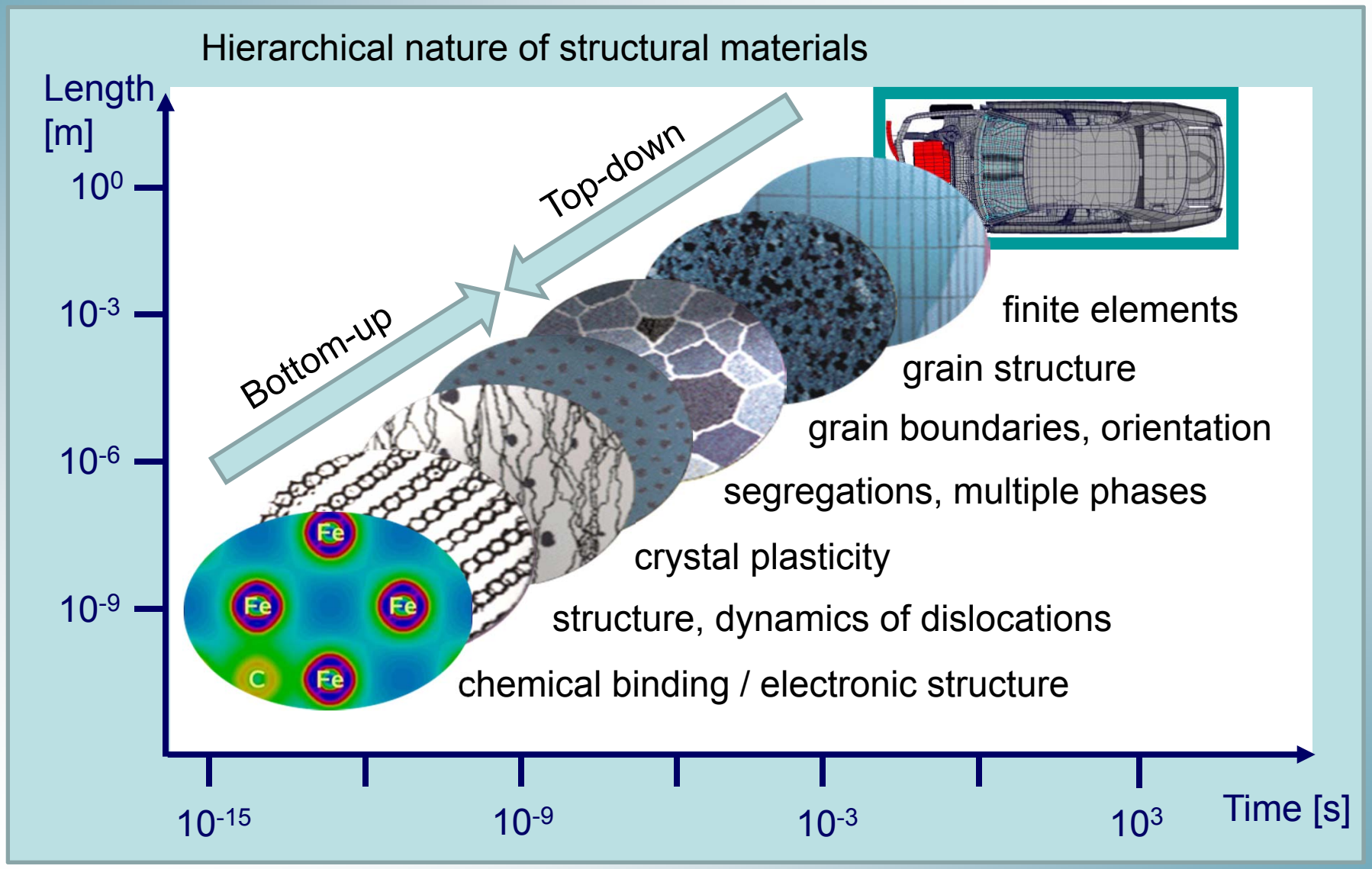


Optoelectronics

Corrosion

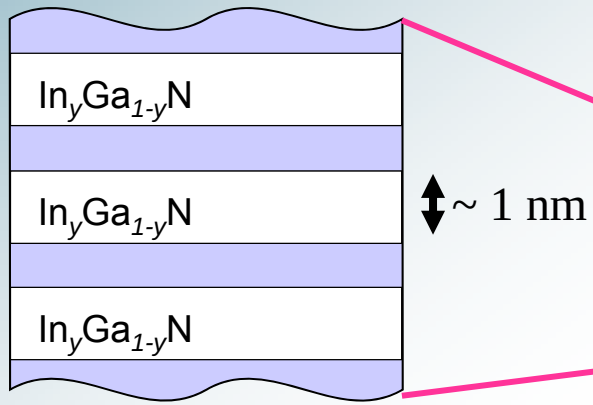
Bio-inspired materials

Challenges in Materials Modeling

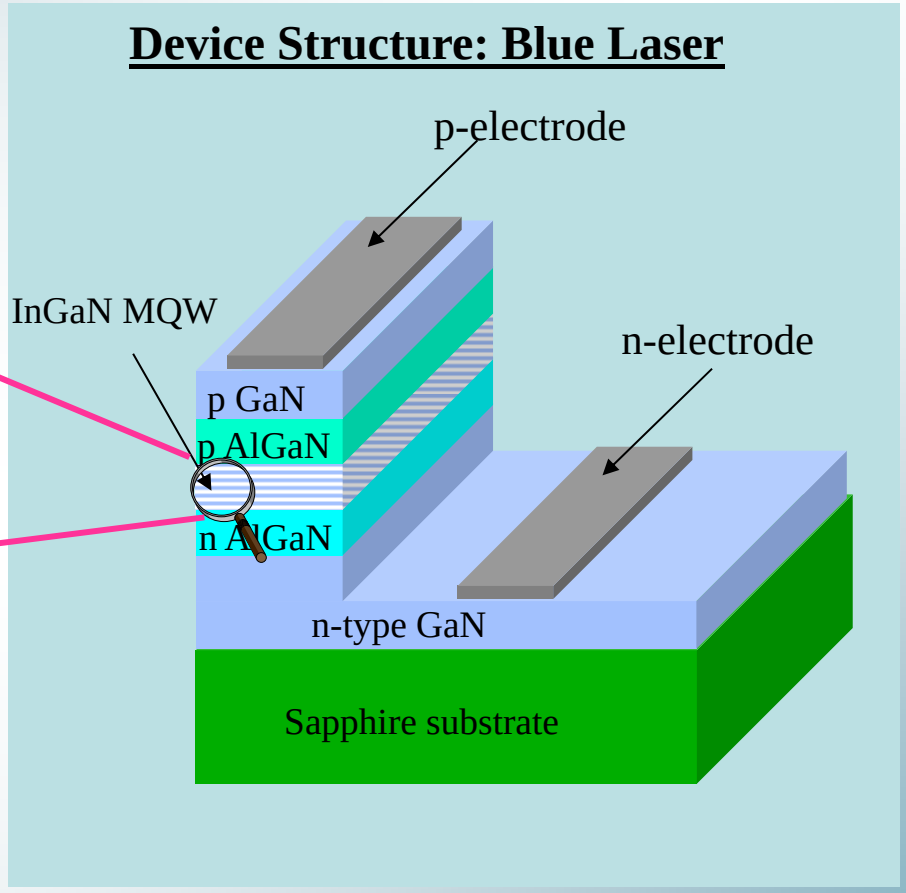


Optoelectronic Devices

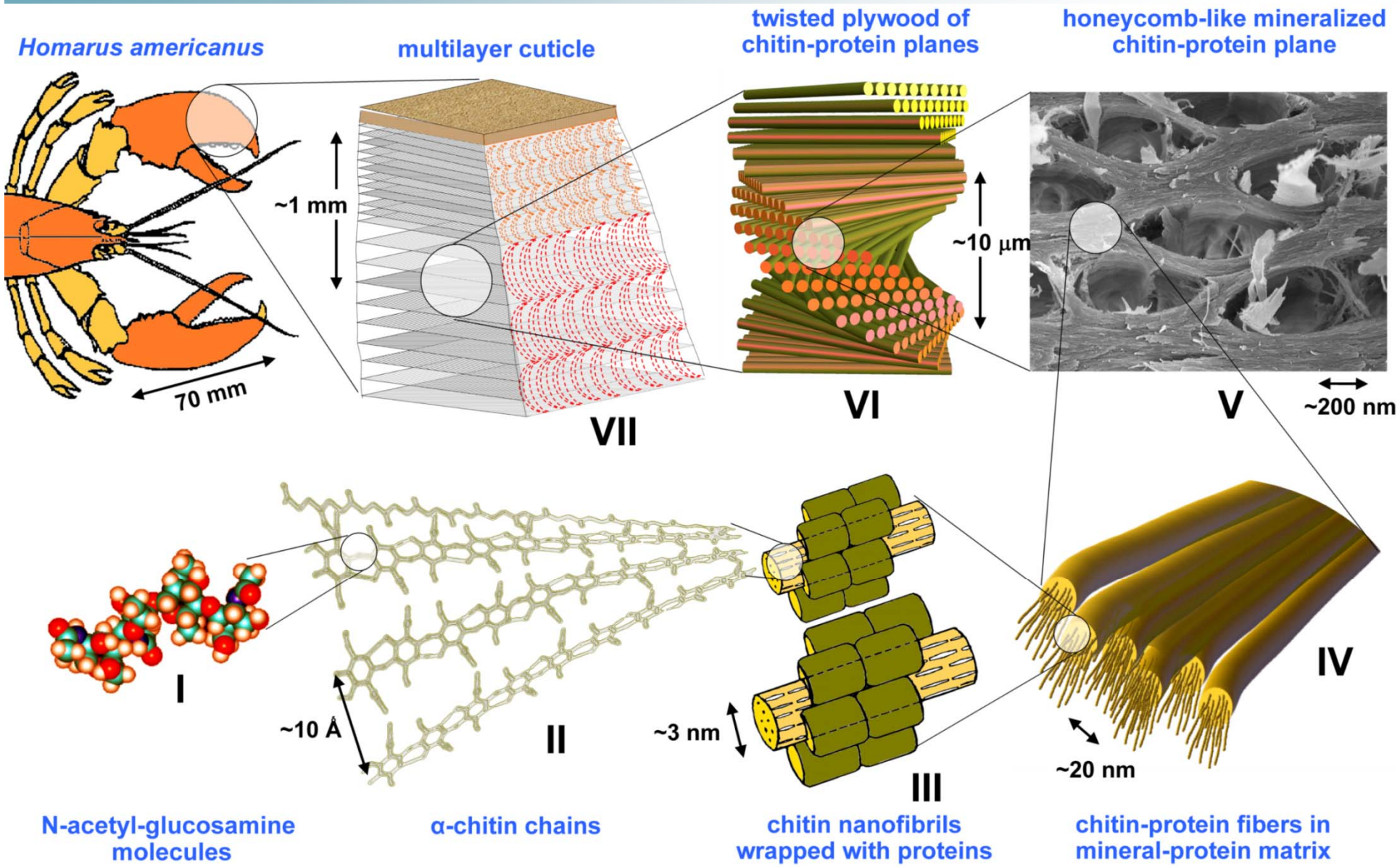
Structural design of the active region



⇨ quantum well structure



Challenges in Materials Modeling



Aim

Development of accurate and reliable simulation tools for materials design

Are QM-based bottom-up methods able to address complexity and high temperature properties of modern materials?

Questions:

Is the accuracy at the most fundamental level sufficiently accurate? (How “robust” are today's available ab initio techniques?)

Can such an approach be used on present day computers? (“smart” statistical approaches to sample huge configuration space)

Can we estimate error bars through all scales?

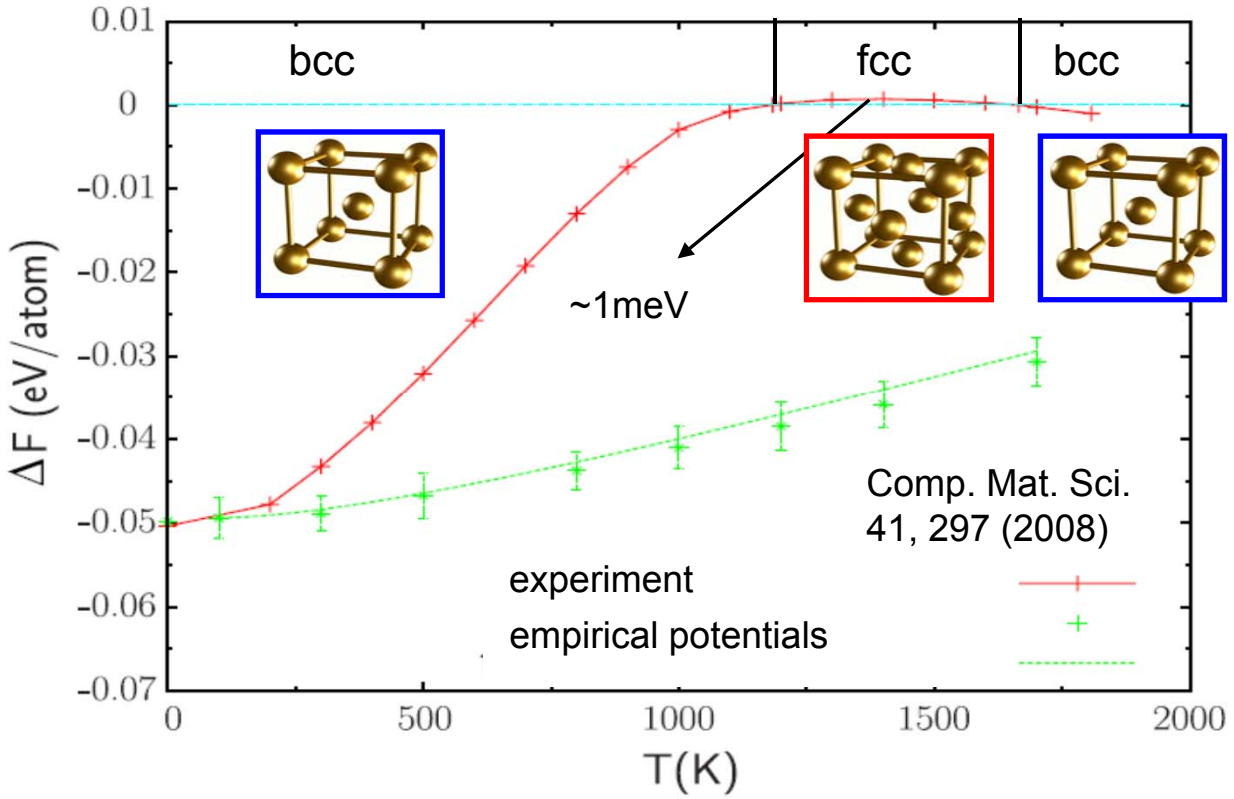
Key quantity:

Free energy: Materials properties at finite temperatures

Solid-Solid Phase Transitions

Key quantity: Free energy

Free energy difference between bcc and fcc iron



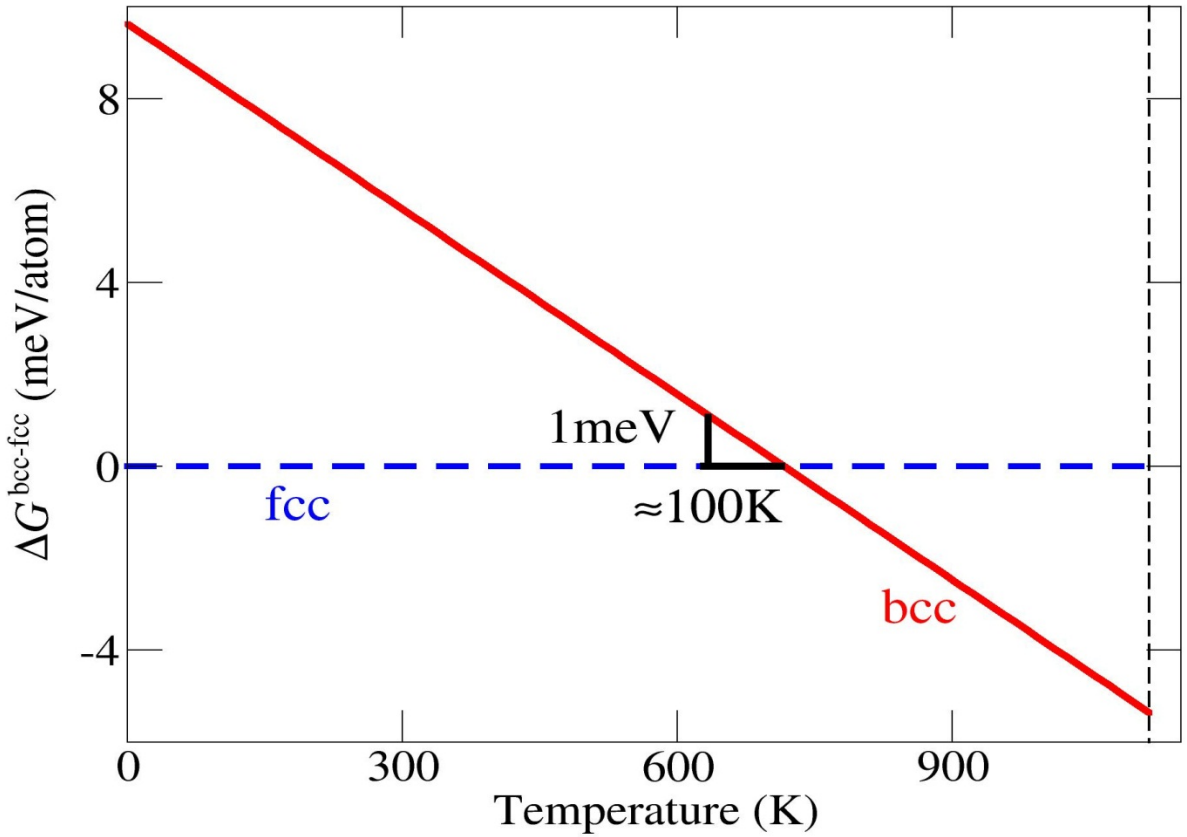
Energy resolution better 1 meV!

→ Can we achieve such accuracy with present day DFT functionals?

→ Can we "afford" statistical averages with such an accuracy?

Free energies: What accuracy is needed?

Free energy difference between bcc and fcc calcium



Target:

Numerical precision <1meV

→ remaining error purely due to xc-functional

DFT has been originally developed as a ground state (T=0K) theory

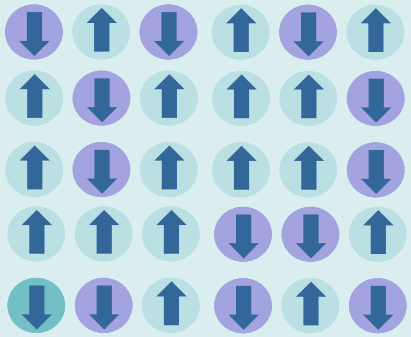
→ How to extend it to finite temperatures?

Ab initio computed Free energies

Approach (schematic):

Energy for any configuration/phase can be computed:

$$E_{tot}\left(\left\{\vec{R}_I, Z_I, \vec{\sigma}_I, f_i, \ldots\right\}\right)$$



→ applicable to any system: bulk, surface, nano, …

All possible excitation mechanisms can be described:

→ vibrational, magnetic, electronic, chemical, …

Statistical averages provide thermodynamic quantities:

$$Z(V,T,x) = \left\langle e^{-E^{BOS}\left(\left\{\vec{R}_I, Z_I, \sigma_I, f_i, \ldots\right\}_V\right)/k_B T} \right\rangle_{V,T,x}$$

Knowledge of partition function allows to derive any thermodynamic quantity!

Ab initio Thermodynamics

➡ Key: Calculate partition function

10^7 configurations

a few hours

$$Z(\hat{A},T) = \sum_{\{\vec{R}_I\}_{\hat{A}}} e^{-E^{BOS}\left(\{\vec{R}_I, Z_I\}_{\hat{A}}\right)/k_B T}$$

Ab initio thermodynamics: Fundamentals

➡ Key: Calculate partition function

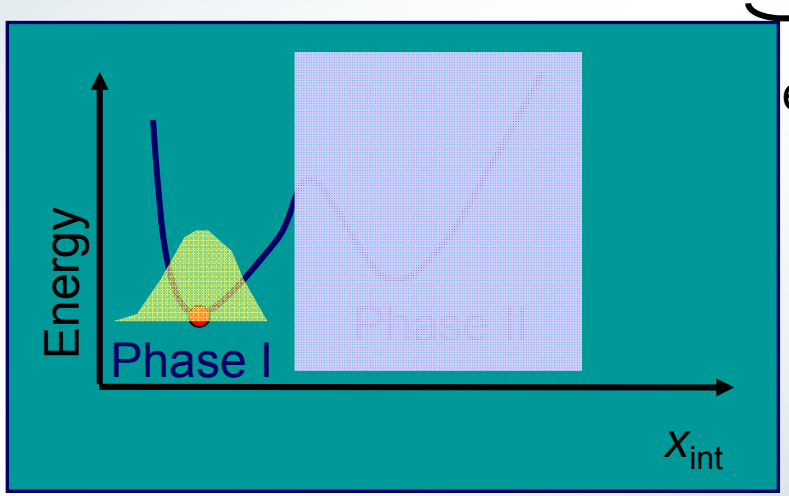
DFT Experiment

$$Z^{vib}(V,T) = \sum_{\{\vec{R}_I\}_V} e^{-E^{BO}\left(\{\vec{R}_I\}_V\right)/k_B T}$$

Reduce ⬇ dimensionality

$$Z^{vib}_{Phase}(V,T) = N_{\deg} e^{-E^{tot}\left(\{\vec{R}_I\}_V^{Phase}\right)/k_B T} \sum_{\{\vec{R}_I\}_V} e^{-E^{vib}\left(\{\vec{R}_I\}_V^{Phase}\right)/k_B T}$$

equil. config.

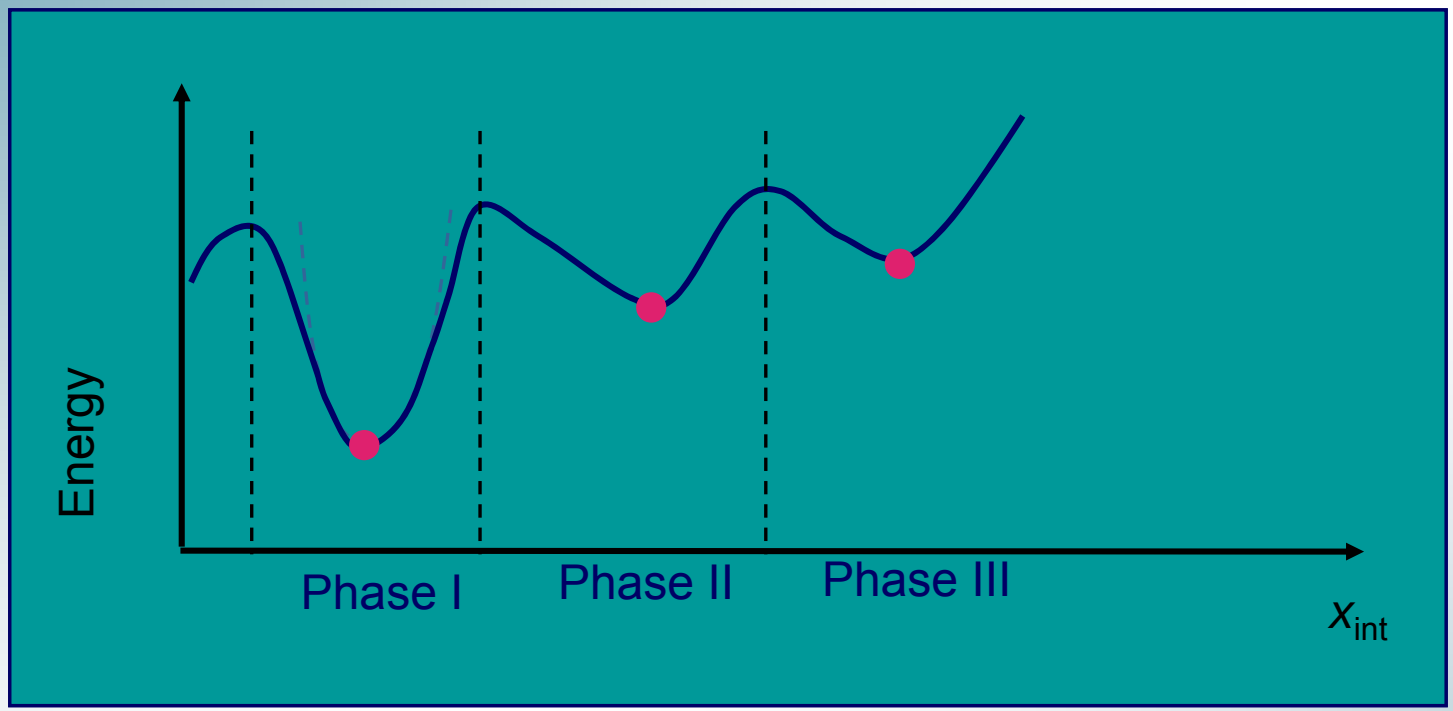


$$D_{I,J} = \frac{\partial E^{tot}\left(\{\vec{R}_I\}_V^{Phase}\right)}{\partial u_I \partial u_J}$$

vibronic config.

Ab initio thermodynamics: Fundamentals

Consider Born-Oppenheimer Surface



Divide high dimensional phase space into well defined regions
→ split up energy in corresponding contributions

$$E^{\mathrm{BOS}}\left(\left\{\vec{R}_I, Z_I\right\}\right) = E_\sigma^{\mathrm{min}} + E_\sigma^{\mathrm{harm}} + E_\sigma^{\mathrm{anharm}}$$

Ab initio Thermodynamics

$$Z(V,T,x) = \left\langle e^{-E^{BOS}\left(\left\{\vec{R}_I, Z_I, \sigma_I, f_i, \ldots\right\}\right)/k_B T} \right\rangle_{V,T,x}$$

$$= \sum_{\left\{\vec{R}_I, Z_I, \sigma_I, f_i, \ldots\right\}} e^{-E^{BOS}\left(\left\{\vec{R}_I, Z_I, \sigma_I, f_i, \ldots\right\}\right)/k_B T} \Bigg|_{V,T,x}$$

Statistical averages over coordinates, magnetic moments, occupations, chemical compositions

Adiabatic approximation

$$= \sum_{\left\{\vec{R}_I\right\}} e^{-E^{BOS}\left(\left\{\vec{R}_I\right\}; \left\{Z_I, \sigma_I, f_i, \ldots\right\}_{fixed}\right)/k_B T} \Bigg|_{V,T,x}$$

Vibrational excitations

$$\times \sum_{\left\{f_i\right\}} e^{-E^{BOS}\left(\left\{f_i\right\}; \left\{\vec{R}_I, Z_I, \sigma_I, \ldots\right\}_{fixed}\right)/k_B T} \Bigg|_{V,T,x}$$

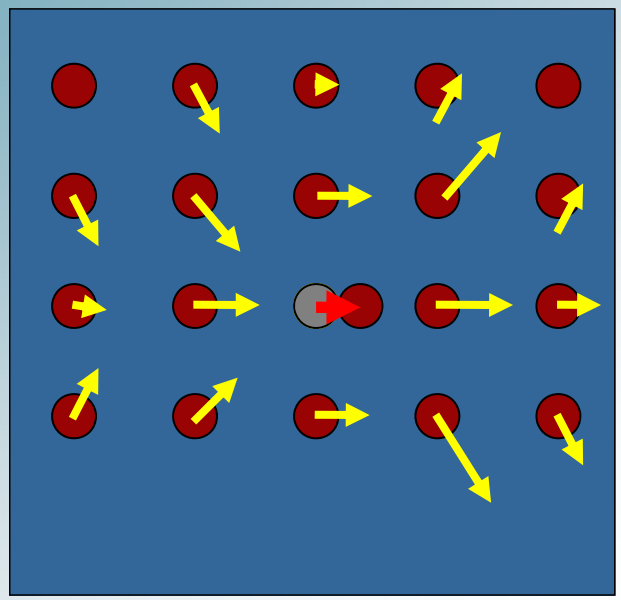
Electronic excitations

+ cross terms

e.g. electron-phonon interactions

Quasiharmonic approximation + electronic excitations

Vibronic excitations



$$\left[T_{ion} + E^{BOS}\left(\underline{\underline{A}}, \tau_1, \ldots, \tau_b\right)\right]\Lambda = E\Lambda$$

$$F_j = -\frac{\partial\, E^{BOS}(\tau_1, \tau_2, \ldots)}{\partial\, \tau_j}$$

Dynamical matrix:

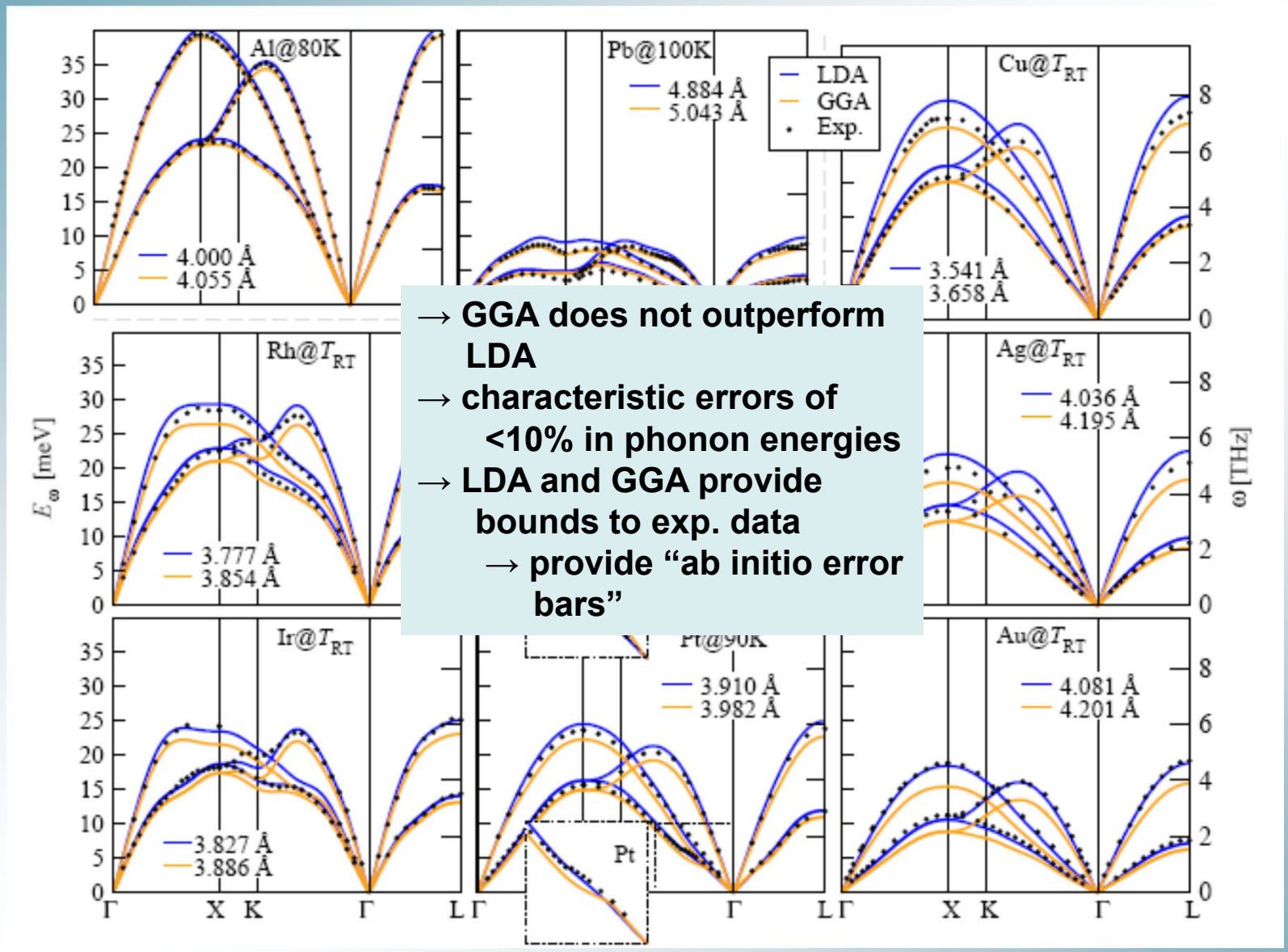
$$D_{ij} = -\frac{\partial\, F_i\,(\tau_1, \tau_2, \ldots)}{\partial\, \tau_j}$$

Harmonic ansatz for extensions u_i:

$$M_i \ddot{u}_i + \Sigma_j D_{ij} u_j = 0 \;\Leftrightarrow\; \omega^2 u_i = \Sigma_j D_{ij} u_j$$

$$F(T, \underline{\underline{A}}) = E^{BOS} + k_B T \sum_q^{BZ} \sum_i^{3r} \left[\frac{1}{2}\frac{\hbar\omega_i}{k_B T} + \ln\left[1 - \exp\left(\frac{\hbar\omega_i}{k_B T}\right)\right]\right]$$

Vibrational Properties: Phonons



→ GGA does not outperform LDA

→ characteristic errors of <10% in phonon energies

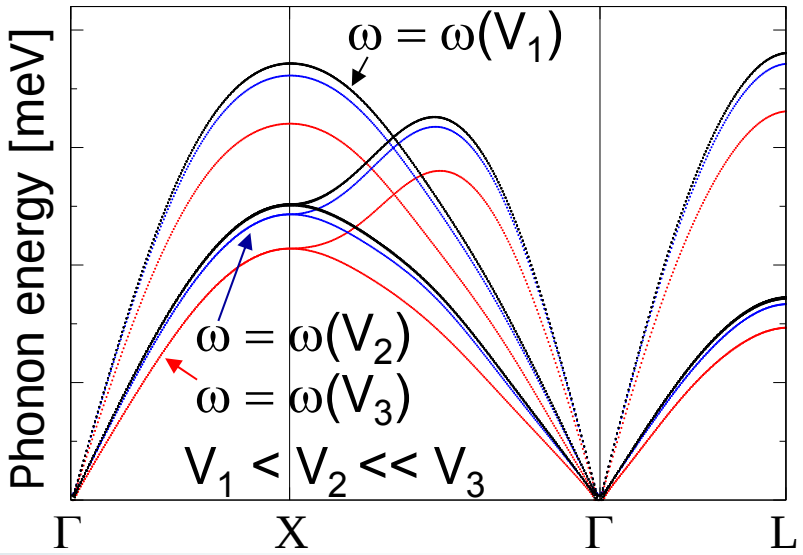
→ LDA and GGA provide bounds to exp. data

→ provide "ab initio error bars"

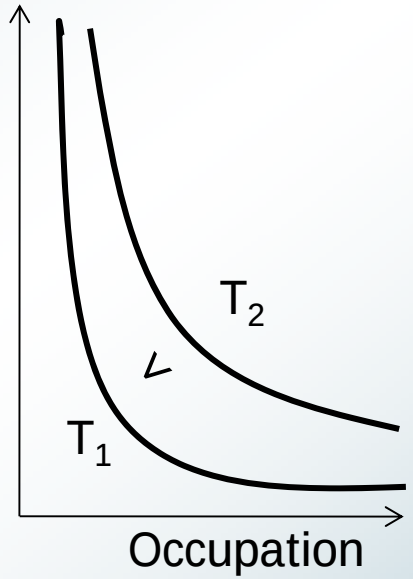
Grabowski, Hickel, JN, PRB 76, 024309 (2007)

Extension to Finite Temperatures

Quasiharmonic approximation



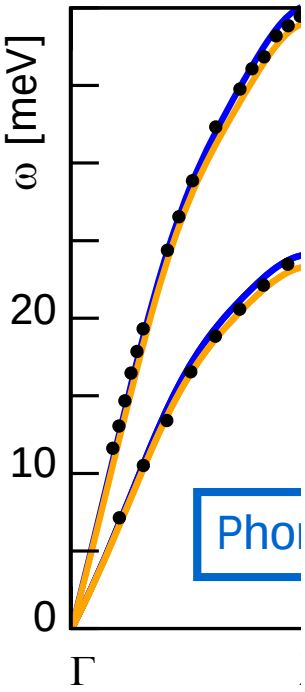
+



Phonons (V) + Bose-Einstein (T) = $F^{vib}(T,V)$

$$F(T,\underline{\underline{A}}) = E^{BOS} + \sum_{q}^{BZ}\sum_{i}^{3r}\left[\frac{1}{2}\hbar\omega_i + k_B T \ln\left[1-\exp\left(-\frac{\hbar\omega_i}{k_B T}\right)\right]\right]$$

Example: Bulk (fcc) Alum



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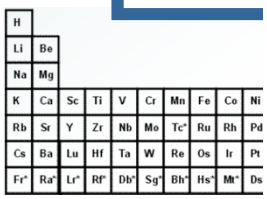
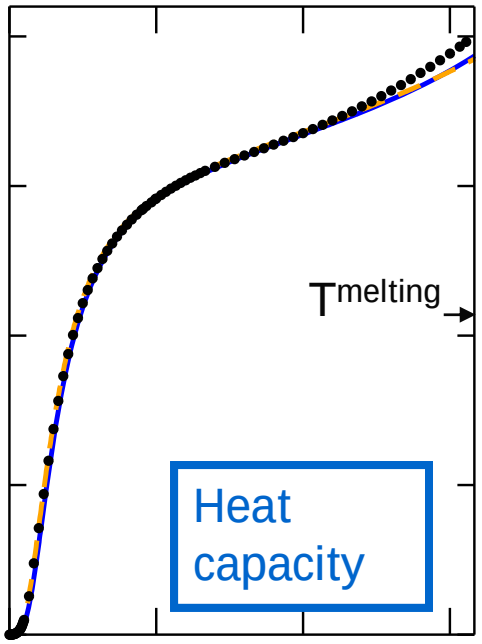
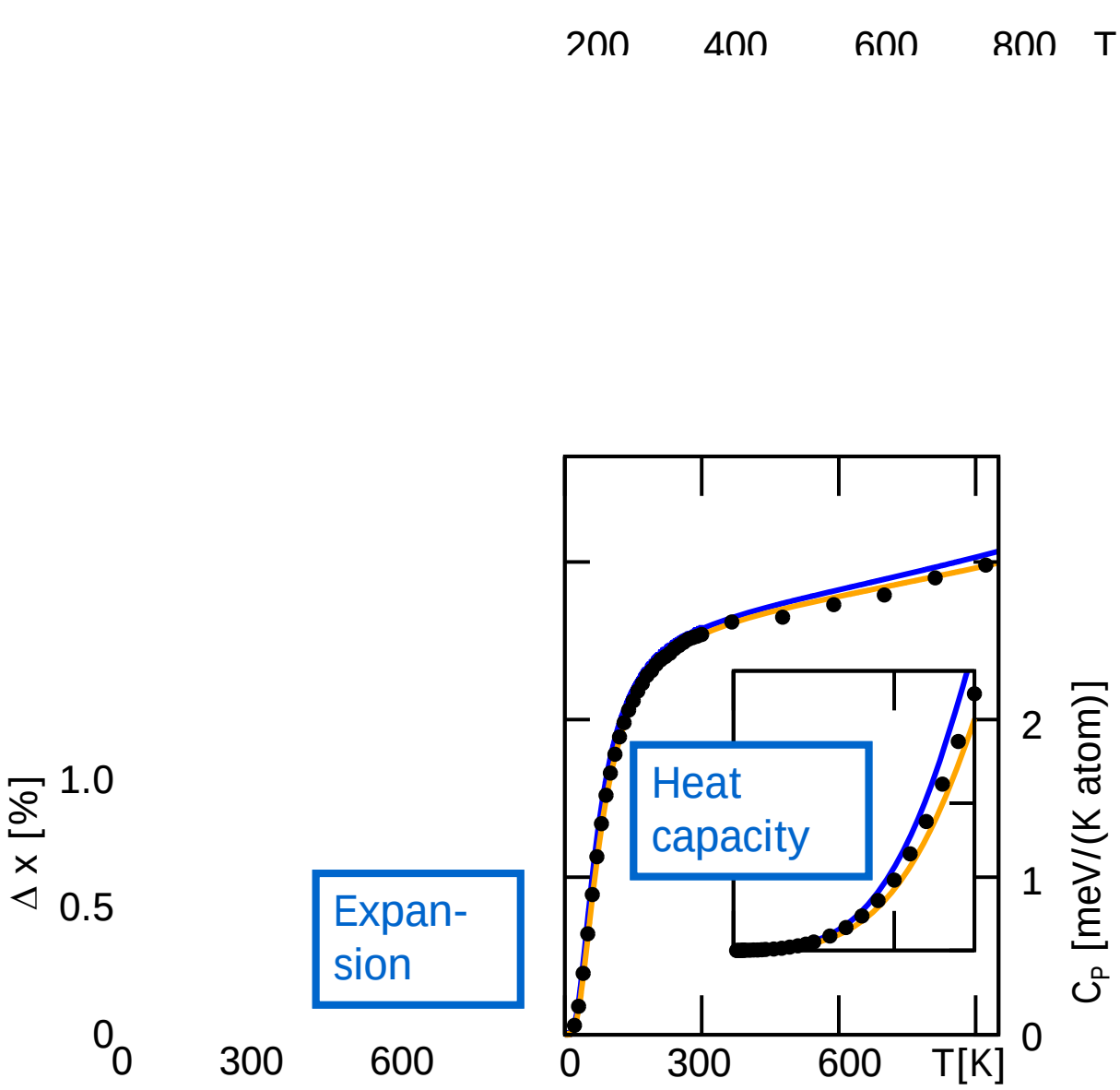
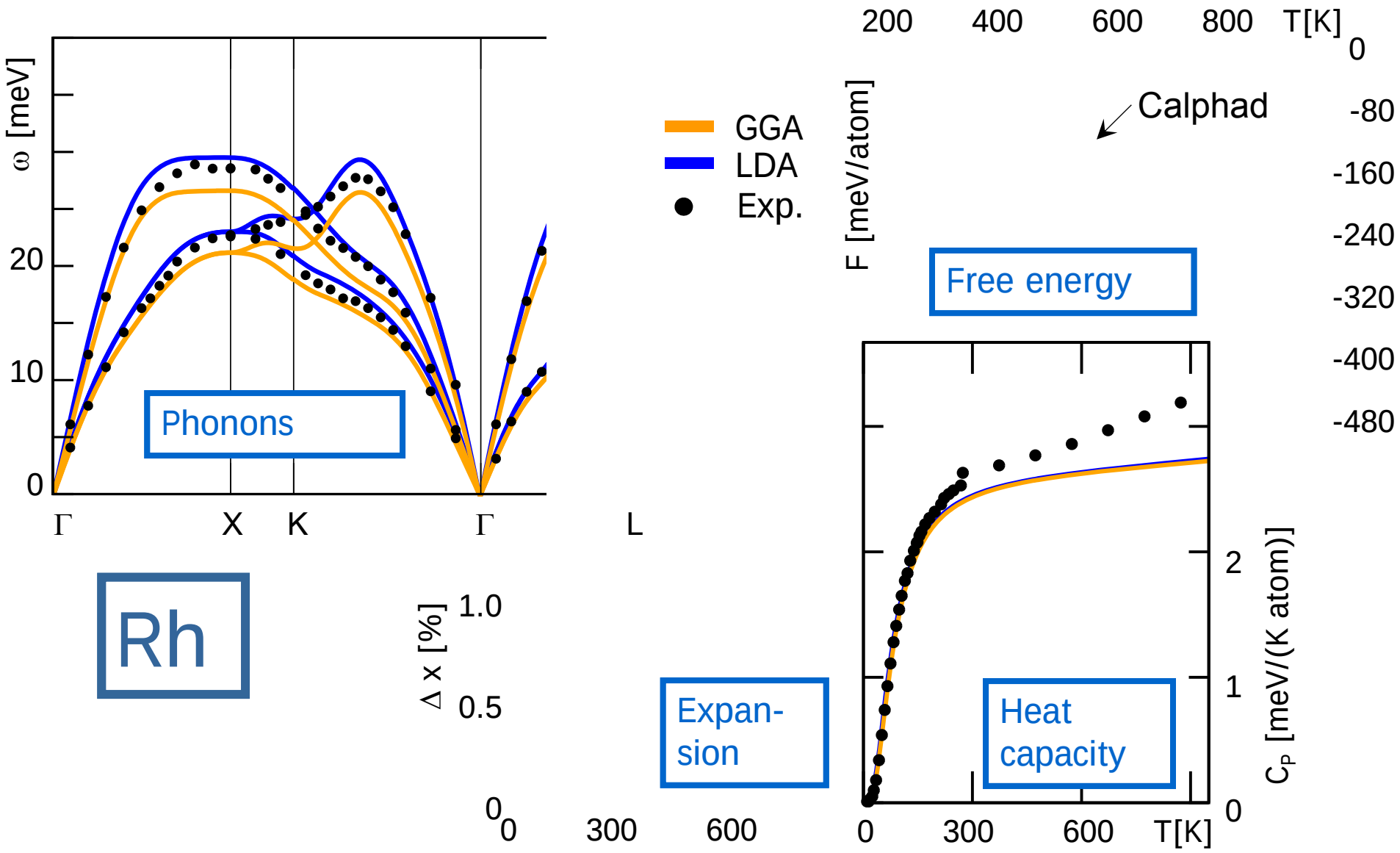


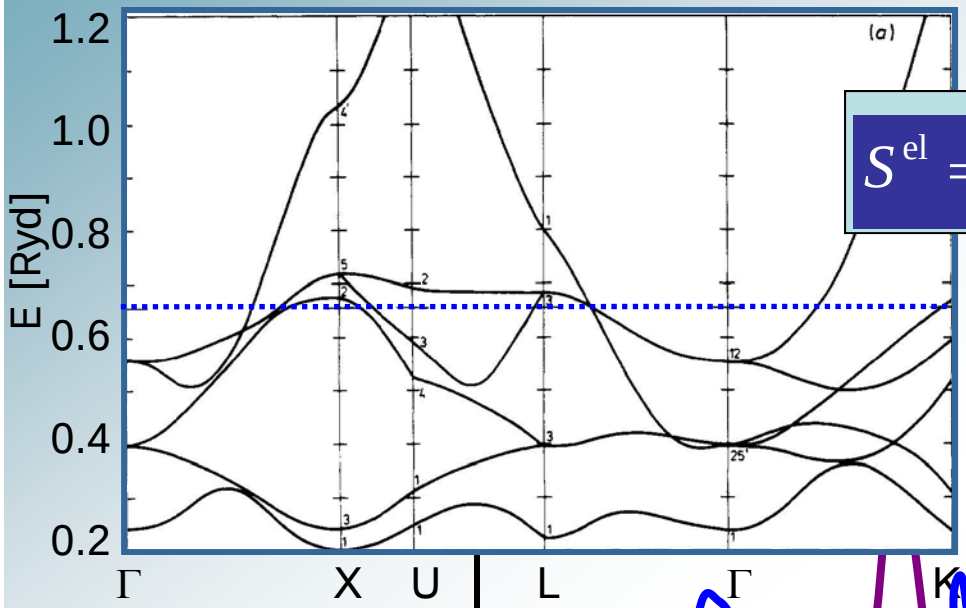
200 400 600 800 T[K]



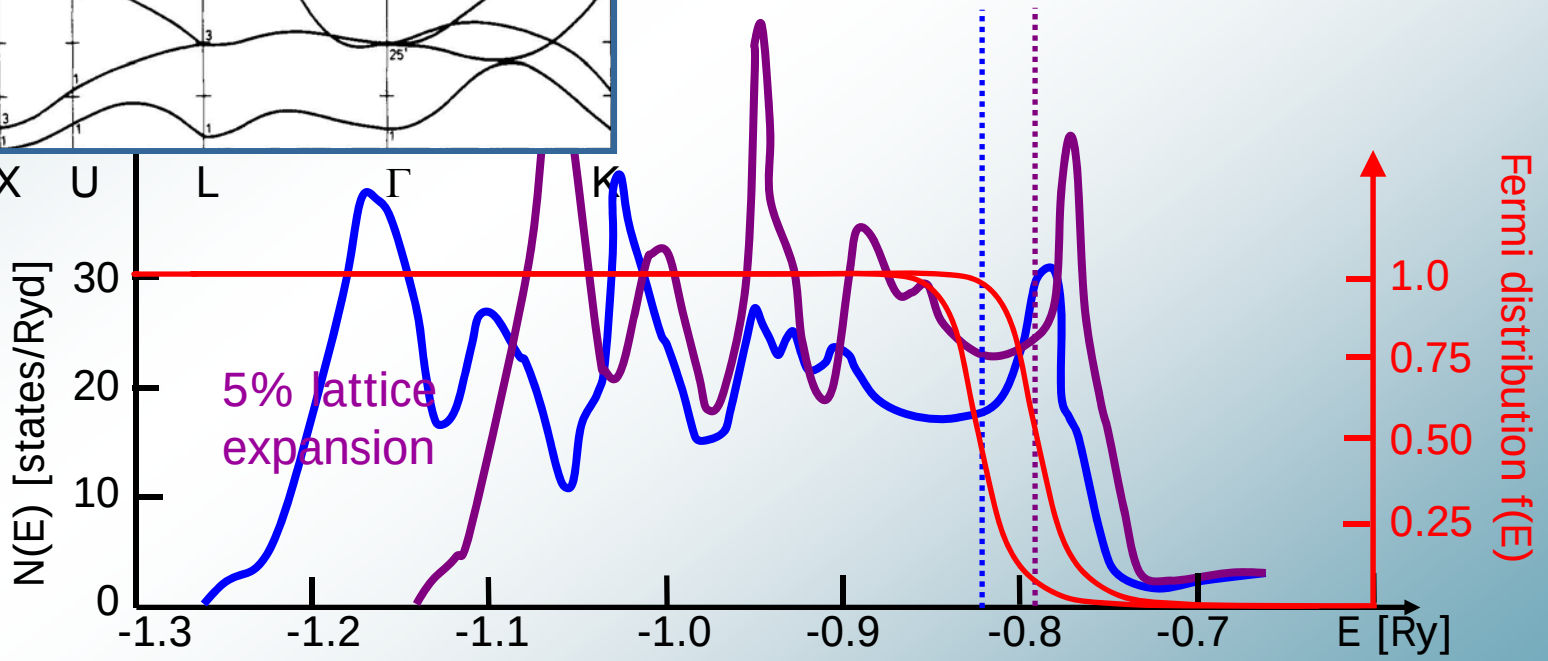

200
400
600
800
T[K]
Δ x [%]
1.0
0.5
0
0
300
600
Expan-
sion
Heat
capacity
0
300
600
T[K]
2
1
0
C_P [meV/(K atom)]

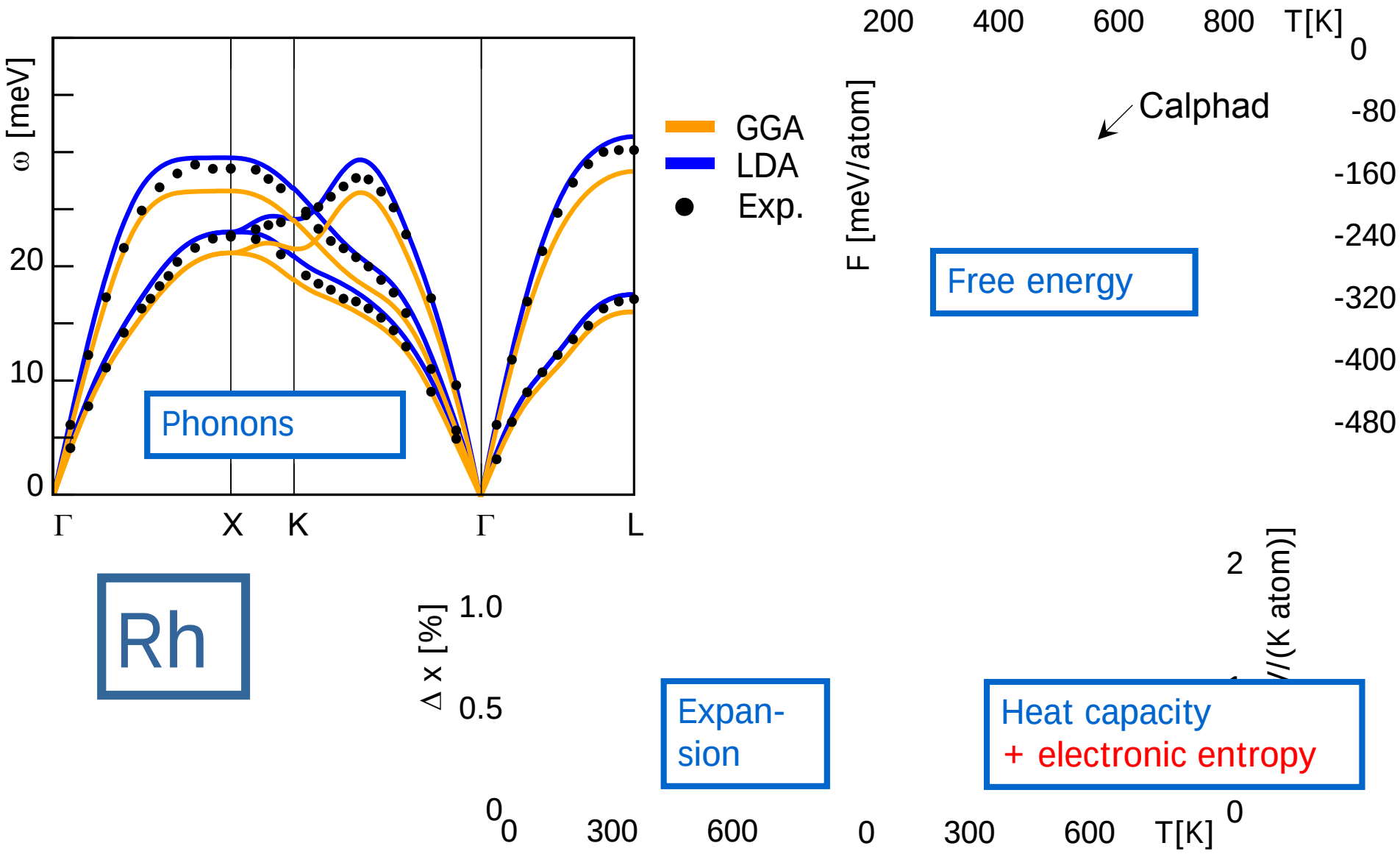

ω [meV]
20
10
0
Γ
X
K
Γ
L
Phonons
GGA
LDA
Exp.
Rh
Δ x [%]
1.0
0.5
0
0
300
600
Expan-
sion
200
400
600
800
T[K]
F [meV/atom]
0
-80
-160
-240
-320
-400
-480
Calphad
Free energy
Heat
capacity
0
300
600
T[K]
2
1
0
C_P [meV/(K atom)]

Contribution of electronic excitations to free energy



$$S^{\mathrm{el}} = -k_{\mathrm{B}} \int N\left[f \ln f + (1-f)\ln(1-f) \right] \mathrm{d}E$$




ω [meV]
20
10
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Γ
X
K
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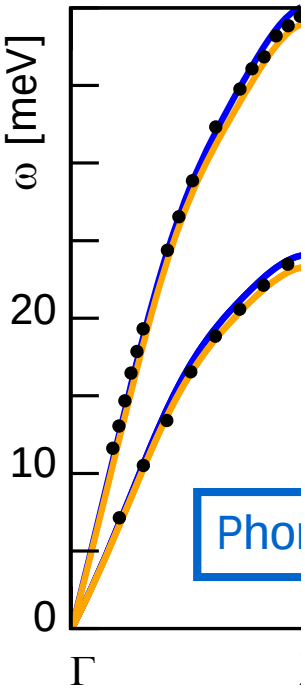
L
Phonons
GGA
LDA
Exp.
Rh
200
400
600
800
T[K]
0
-80
-160
-240
-320
-400
-480
F [meV/atom]
Calphad
Free energy
Δ x [%]
1.0
0.5
0
0
300
600
Expan-
sion
2
/(K atom)]
0
0
300
600
T[K]
Heat capacity
+ electronic entropy

Are contributions beyond quasiharmonic approximation relevant?

Example: Bulk (fcc) Alum



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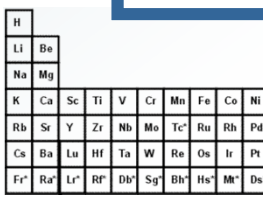
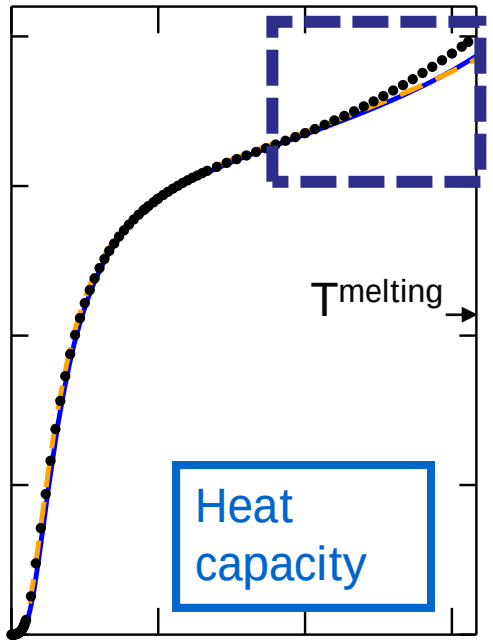


200 400 600 800 T[K]



Specific Heat at High Temperatures

Über die spezifische Wärme fester Körper bei hohen Temperaturen.

Von **M. Born** und **E. Brody** in Göttingen.

(Eingegangen am 9. Juli 1921.)

Einleitung. Nach dem Gesetz von Dulong und Petit bzw. seiner Verallgemeinerung durch Neumann, Regnault und Kopp soll die Atomwärme bei konstantem Volumen C_v im festen Aggregatzustande sich mit wachsender Temperatur dem Grenzwerte

$$C_v = 3R = 5{,}96 \text{ cal grad}^{-1}$$

nähern (R ist die absolute Gaskonstante). Bei vielen Substanzen aber wird dieser Wert merklich überschritten, und zwar um so mehr, je näher die Temperatur dem Schmelzpunkt kommt. Es gibt hauptsächlich zwei Ursachen, auf die man diese Erscheinung zurückführen kann: Einmal das Anwachsen der Schwingungsamplituden der Atome über den Bereich hinaus, in dem Proportionalität zwischen Ausschlag und zurückziehender Kraft besteht; sodann das Auftreten neuer Freiheitsgrade. Besonders bei den Metallen liegt es nahe, an die Freiheitsgrade der Leitungselektronen zu denken, die bei hohen Temperaturen einen Anteil am Wärmeinhalt übernehmen könnten. Aber das Ansteigen der spezifischen Wärme bei der Annäherung an den Schmelzpunkt spricht mehr für die erste Hypothese; denn das Schmelzen muß doch in einem Anwachsen der Atomschwingungen zu solcher Stärke bestehen, daß das Gefüge des Kristallgitters zerstört wird, und es ist wahrscheinlich, daß sich diese heftige Agitation der Atome schon vorher thermisch bemerklich macht.

Question:

→ **origin of additional degrees of freedom at high T**

Assumption:

→ **anharmonicity**

→ **electrons in conduction band**

Present proposals:

→ **vacancies**

→ **di-vacancies and interstitials**

→ **self-critical vacancy conc.**

→ **anharmonicity**

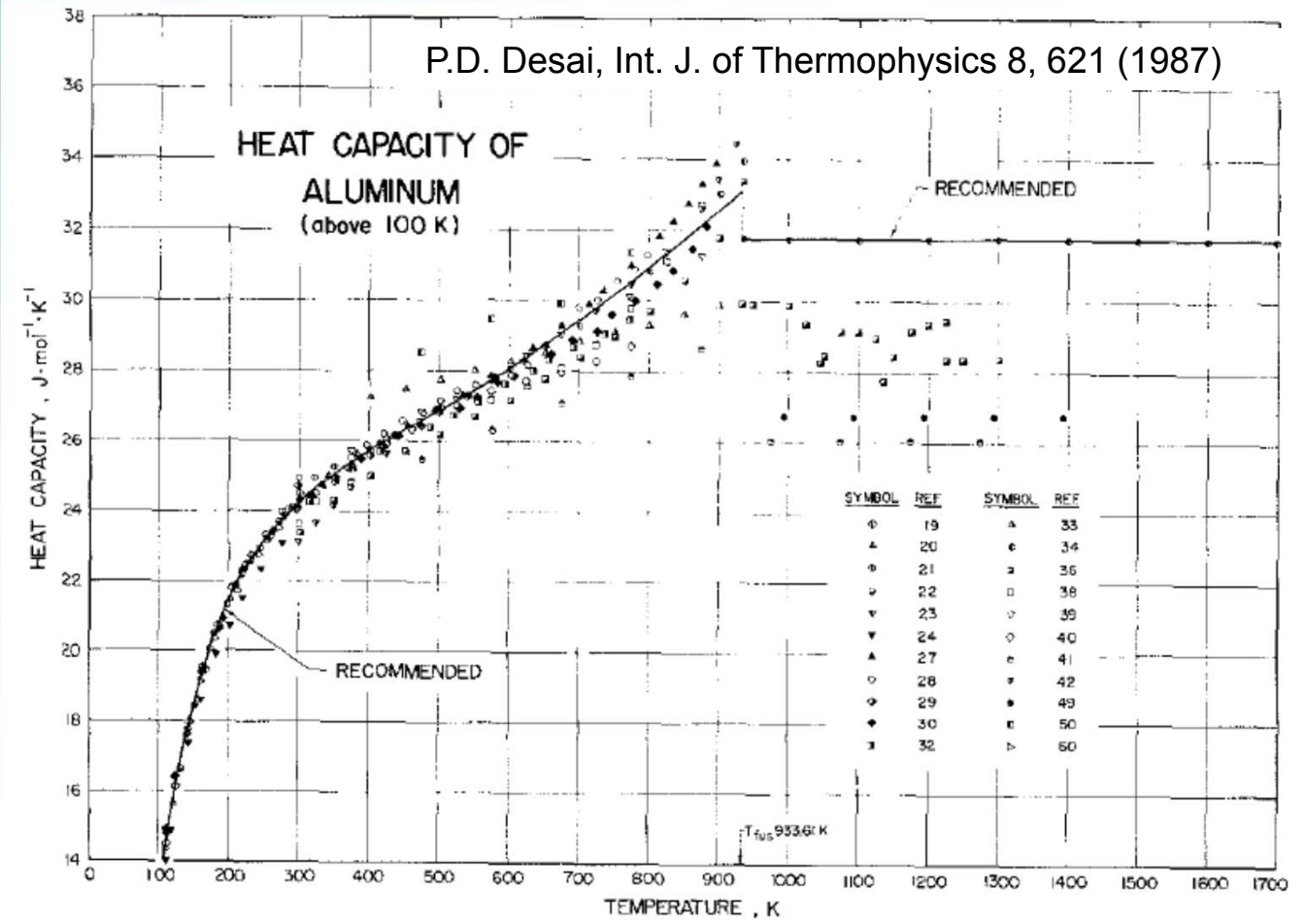
→ **electrons in conduction band**

…

Challenges

Experiment

P.D. Desai, Int. J. of Thermophysics 8, 621 (1987)



Error sources

- **Radiation losses (~T^3)**
- **Defects, imperfections**

How to sample over 10^7 configurations with ab initio accuracy?

Can we use empirical potentials to describe anharmonic contributions

Coarse graining configuration space

Main challenge:

Reduce number of (ab initio) configurations by several orders of magnitude

from MD or MC

$$\langle U(T) \rangle = \frac{1}{N} \sum_{i}^{N} E^{BOS}\left(\left\{\vec{R}_I(t_i)\right\}\right)$$

Two major concepts

Thermodynamic integration

Free energy perturbation

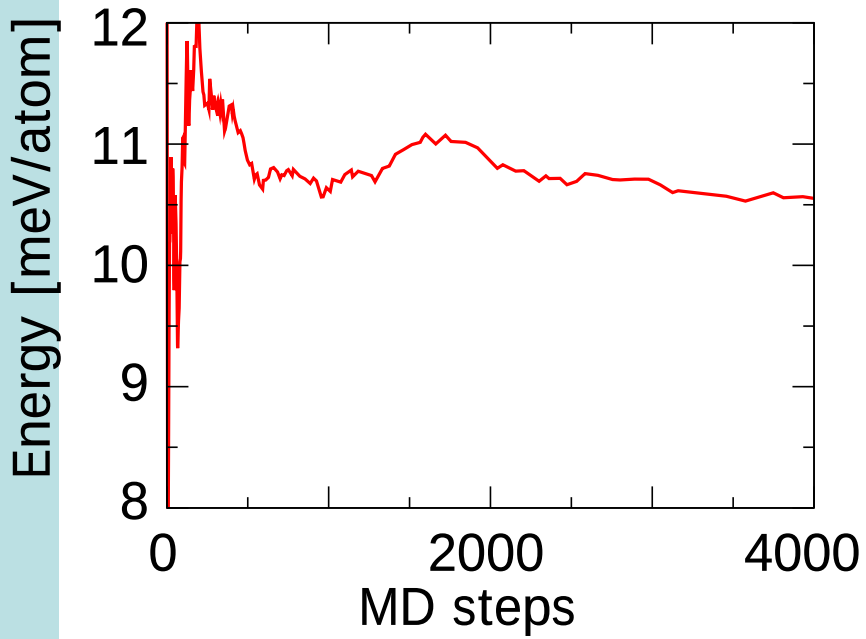
Thermodynamic Integration

Key idea: Compute free energy change between reference system A and real system B

$$\Delta F(A \rightarrow B) = \int_0^1 \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_\lambda d\lambda$$

with $$U(\lambda) = U_A + \lambda (U_B - U_A)$$

MD simulation in TI-step



Application straightforward if good reference is available

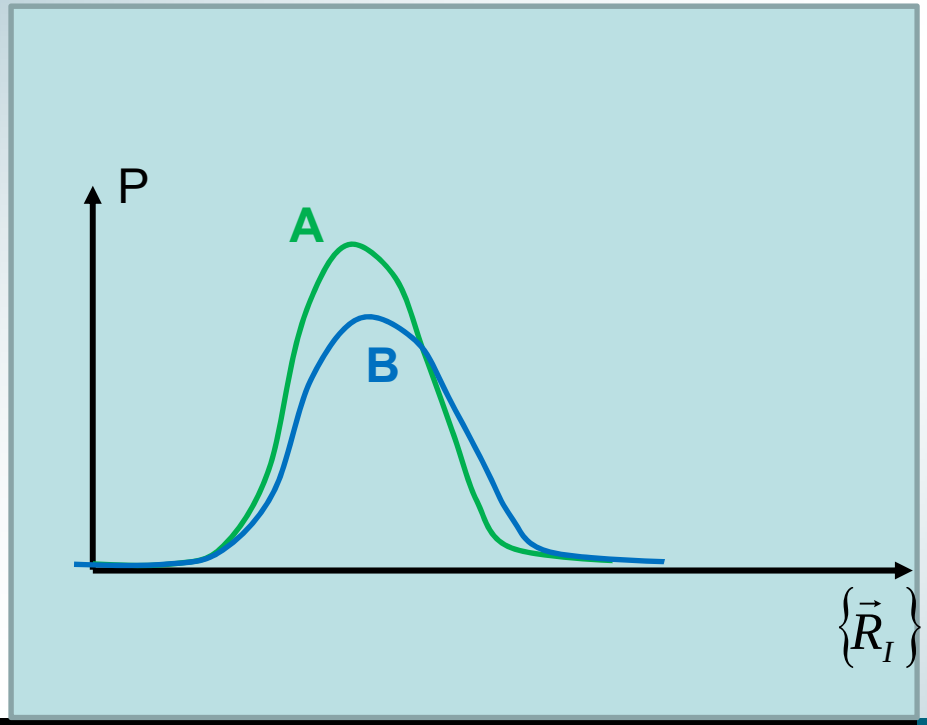
Typically the number of configurations can be reduced by 1-2 orders of magnitude
→ several 10^4 configurations

Not affordable on highest ab initio level

Free energy perturbation

Key idea: Compute free energy change between reference system A and real system B

$$\Delta F(A \rightarrow B) = -k_B T \ln \left\langle \exp\left(-\frac{E_B - E_A}{k_B T} \right) \right\rangle_A$$



Performance increases with quality of reference

For large differences to reference the method becomes inefficient/ fails

For the targeted accuracy less efficient than thermodynamic integration

How to boost coarse graining?

Cycles in thermodynamic integration

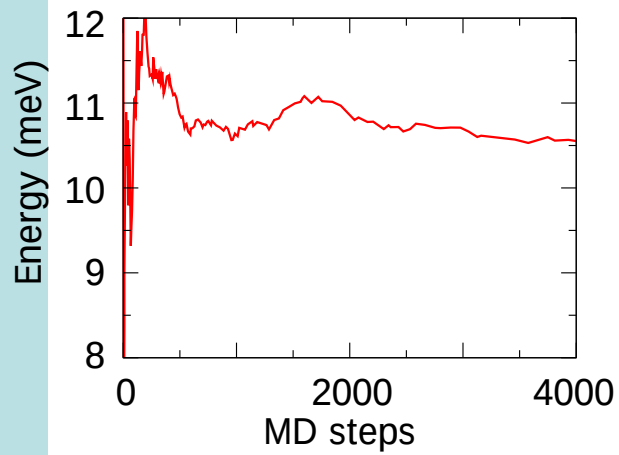
$$\Delta F(A \to B) = \int_0^1 \left\langle \frac{\partial U(\lambda)}{\partial \lambda} \right\rangle_\lambda d\lambda$$

λ integration (2-10 steps)

→ Improved reference reduces step number

Thermodynamic average (10^3…10^4 MD steps)

→ Performance bottleneck



Solution

λ integration (2-10 steps)

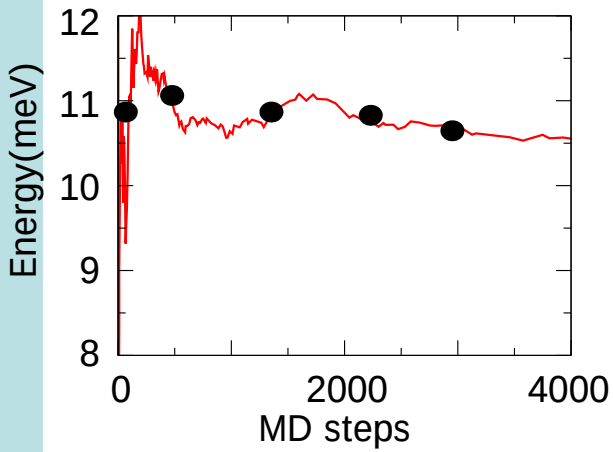
→ Improved reference reduces step number

→ Here: Quasiharmonic reference

Thermodynamic average (10^3…10^4 MD steps)

→ Use free energy perturbation approach

→ Use low/medium converged DFT as reference

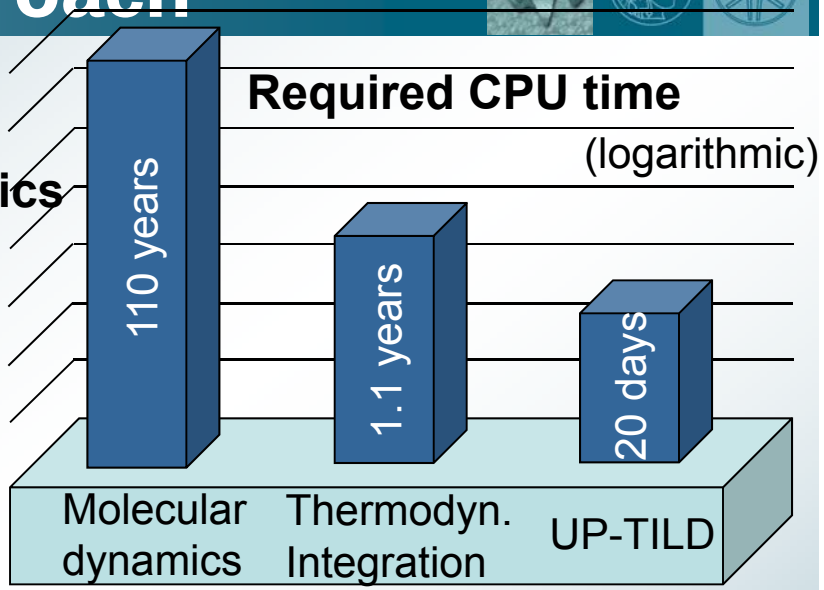


→ **Reduces number of configurations by 10^2**

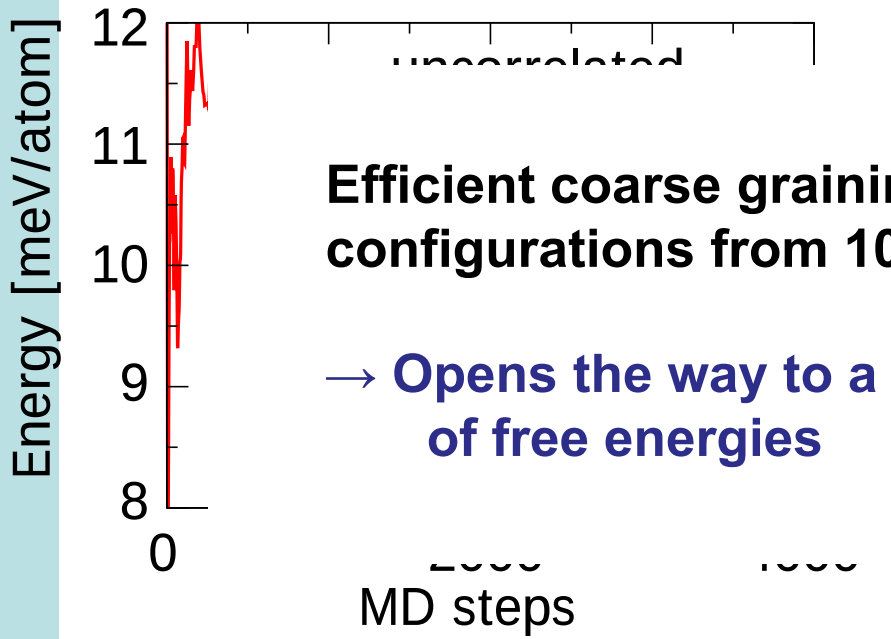
Performance of the new approach

- **Wavefunction extrapolation**
- **Thermodyn. integr. (TI) with Langevin dynamics**
- **Ensemble average instead of time average (parallelization)**
- **Up-sampling in λ–TI step**
- **etc.**

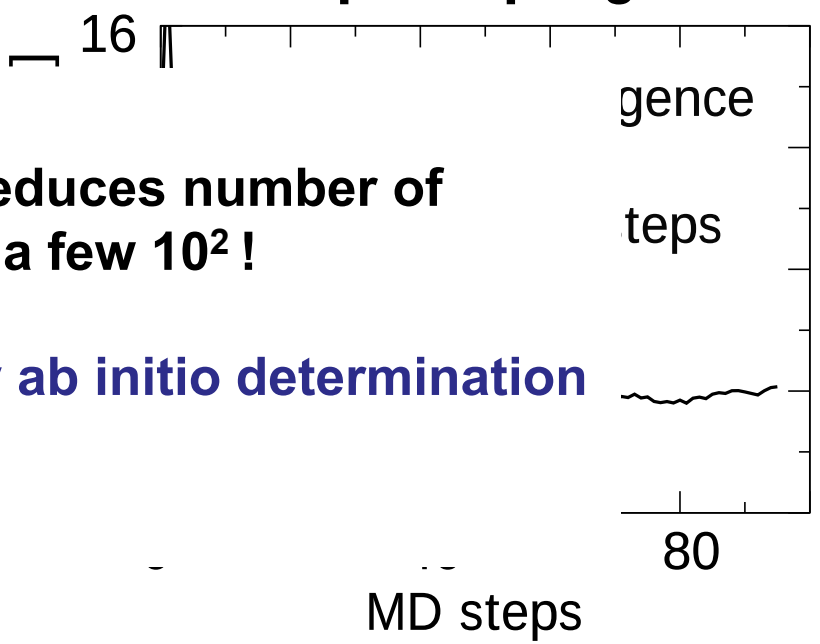
Grabowski et al., Phys. Rev. B79, 134106 (2009).



MD simulation in TI-step



Up-sampling



Efficient coarse graining reduces number of configurations from 10^7 to a few 10^2 !

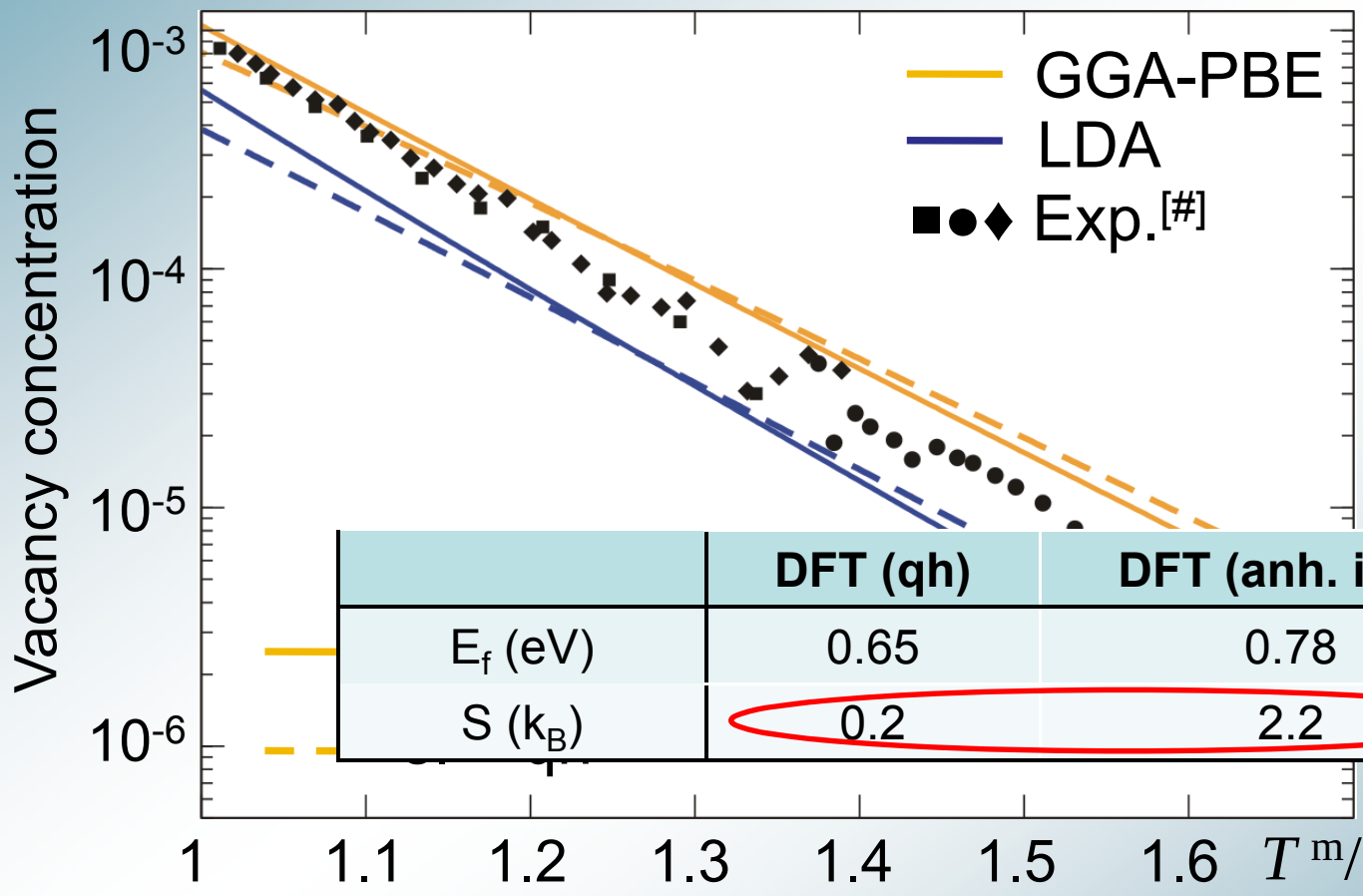
→ Opens the way to a fully ab initio determination of free energies

Benchmark against experiment

Vacancy concentration

[#] R. O. Simmons and R. W. Balluffi, Phys. Rev. 117, 52 1960.
Th. Hehenkamp, J. Phys. Chem. Solids 55, 907 1994.

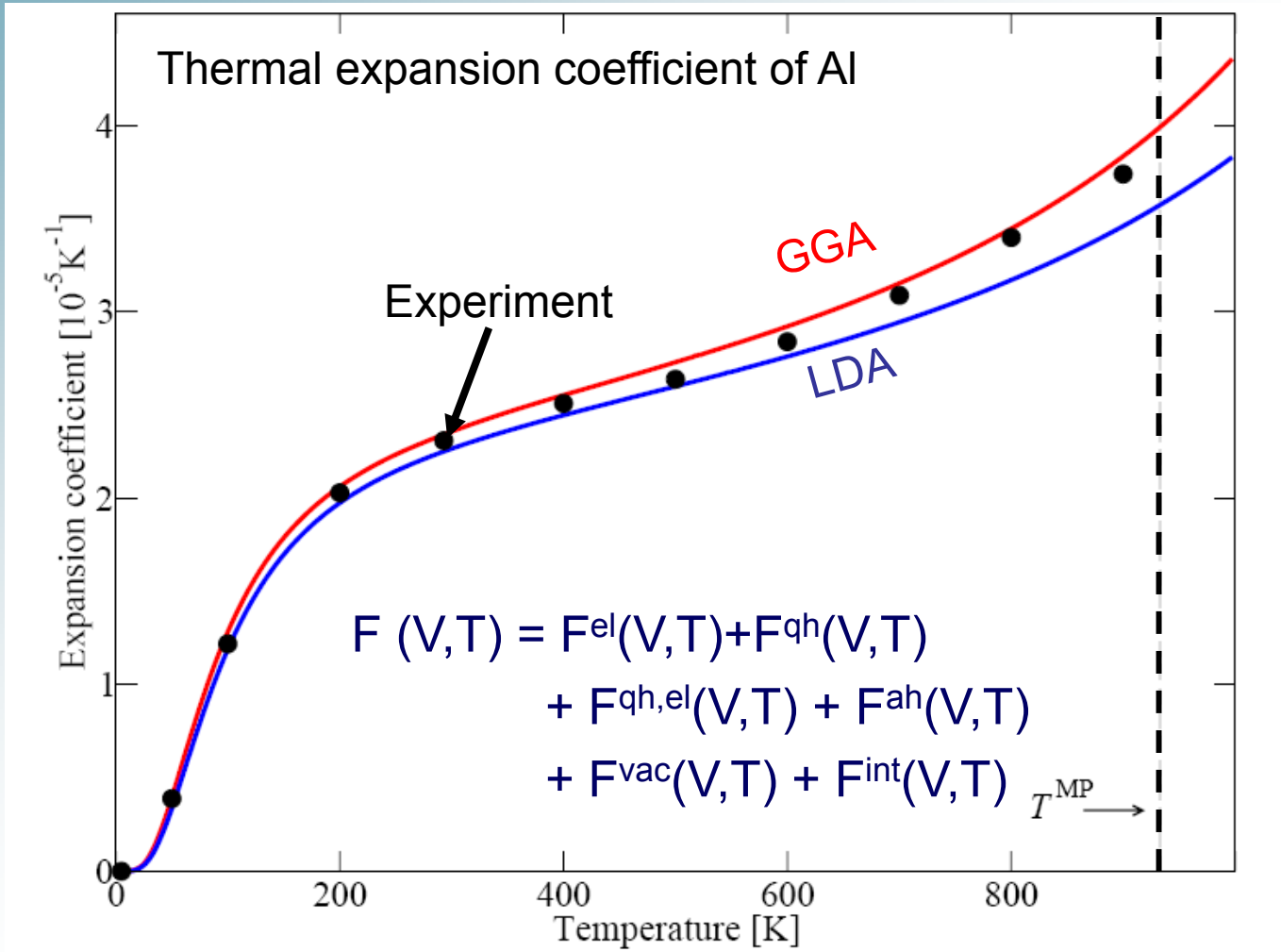
fcc aluminum



	DFT (qh)	DFT (anh. incl.)	Exp.
E_f (eV)	0.65	0.78	0.75
S (k_B)	0.2	2.2	2.4

el: electronic, qh: quasiharmonic,
ah: anharmonic

Thermal expansion coefficient



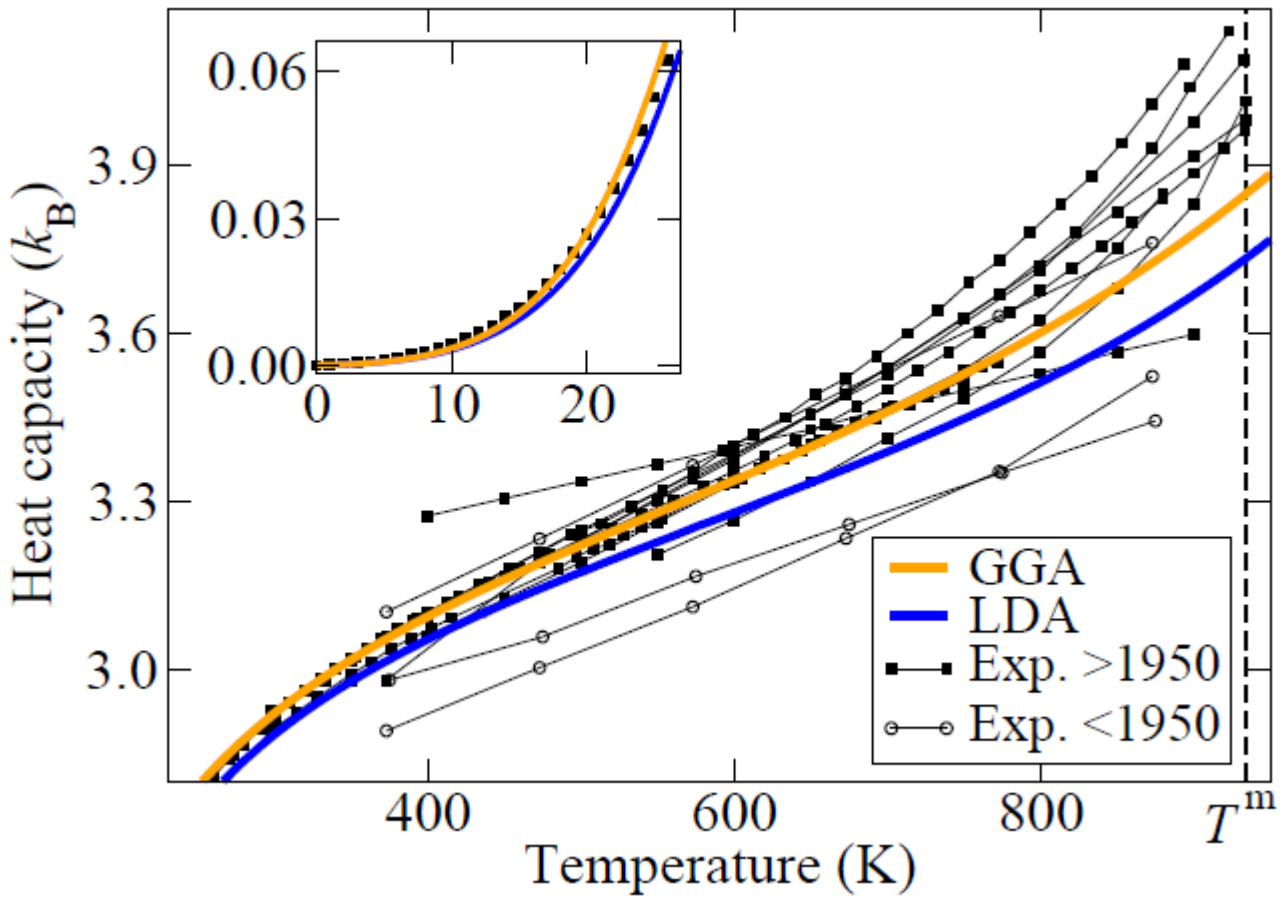
→ Excellent agreement with experiment

→ Systematic trend: LDA and GGA provide approximate measure of error bars

Grabowski, Ismer, Hickel, Neugebauer, Phys. Rev. B 79, 134106 (2009)

Heat Capacity

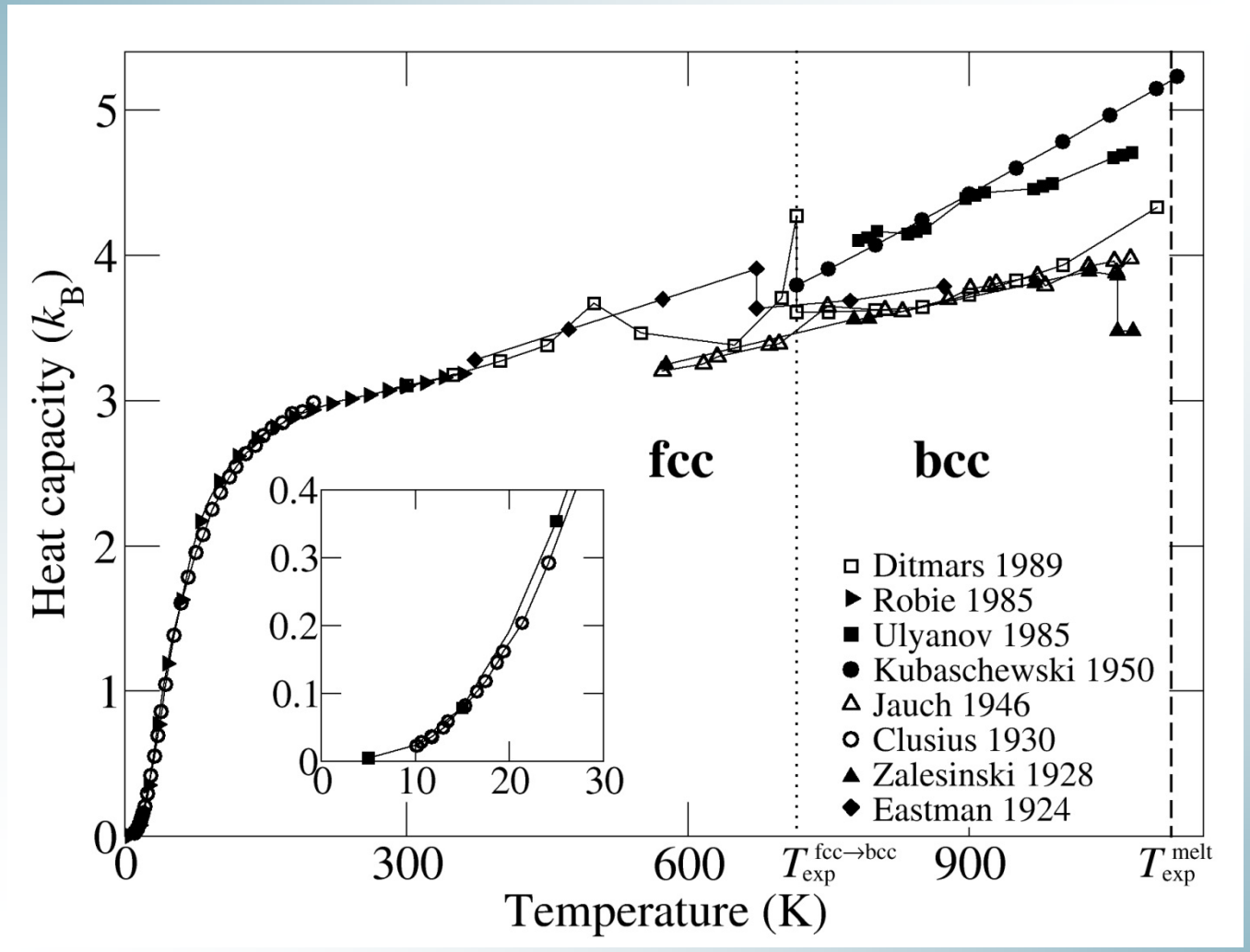
Heat capacity of Al



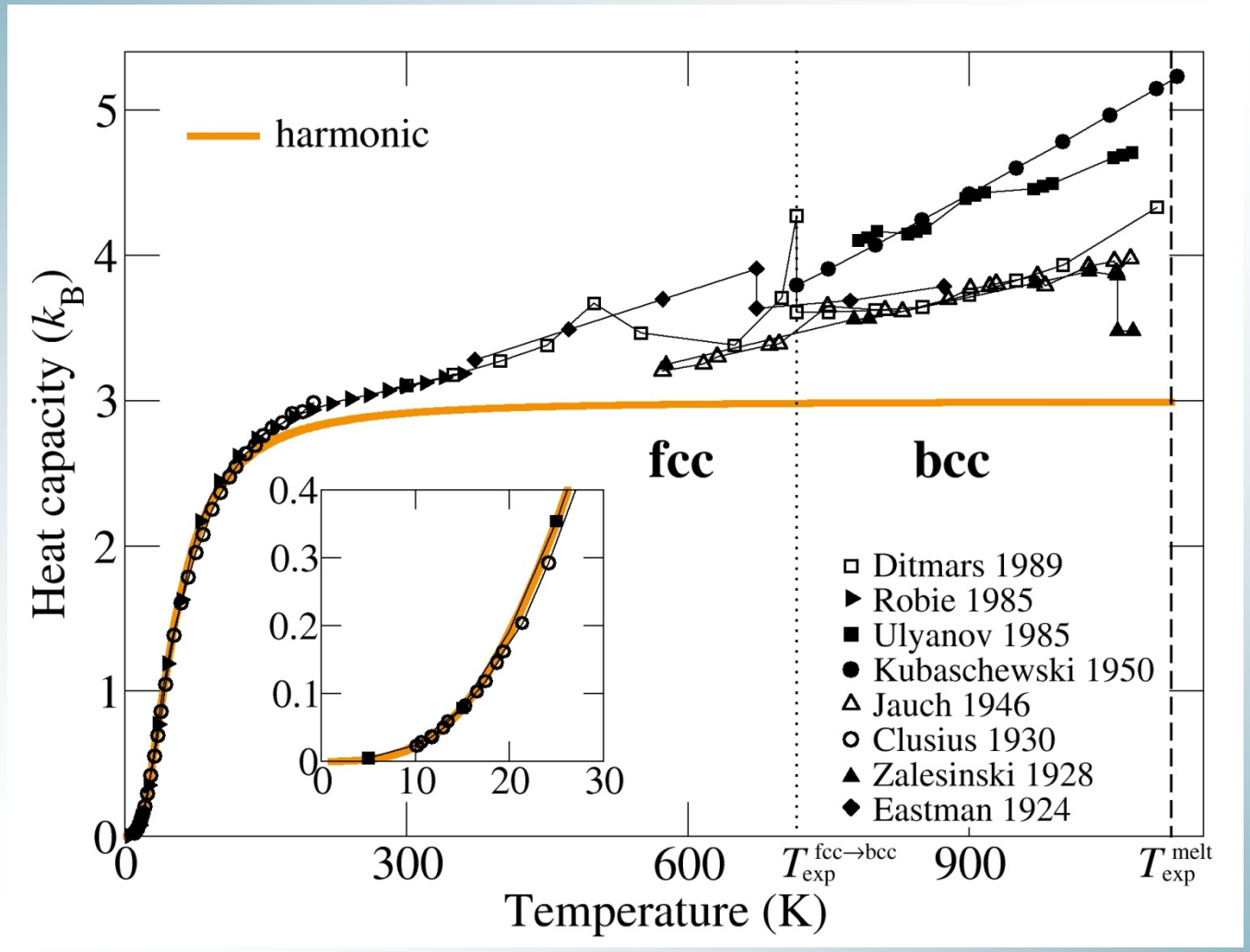
→ DFT gives lower bound to all recent experiments

Applications

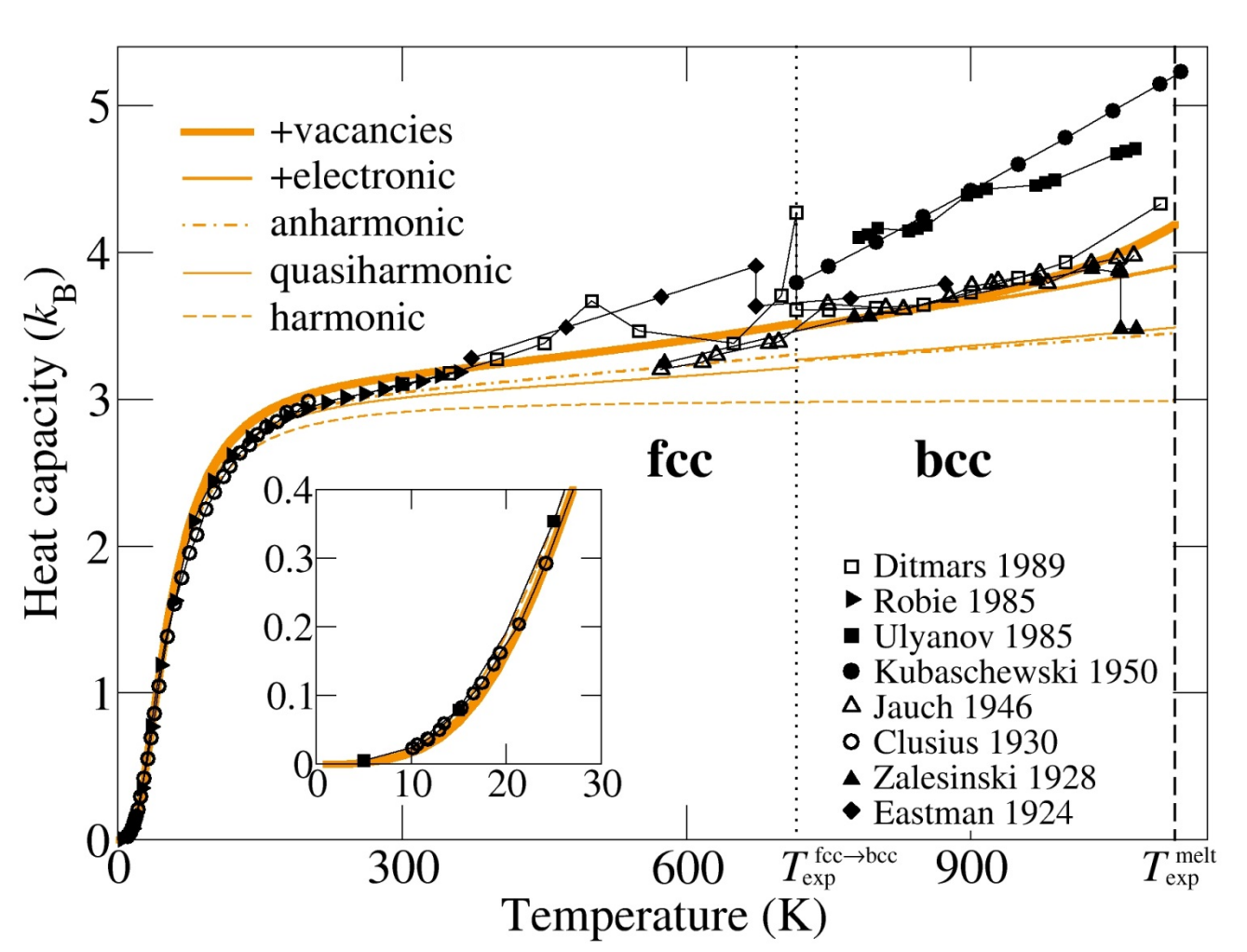
Calcium: Heat capacity



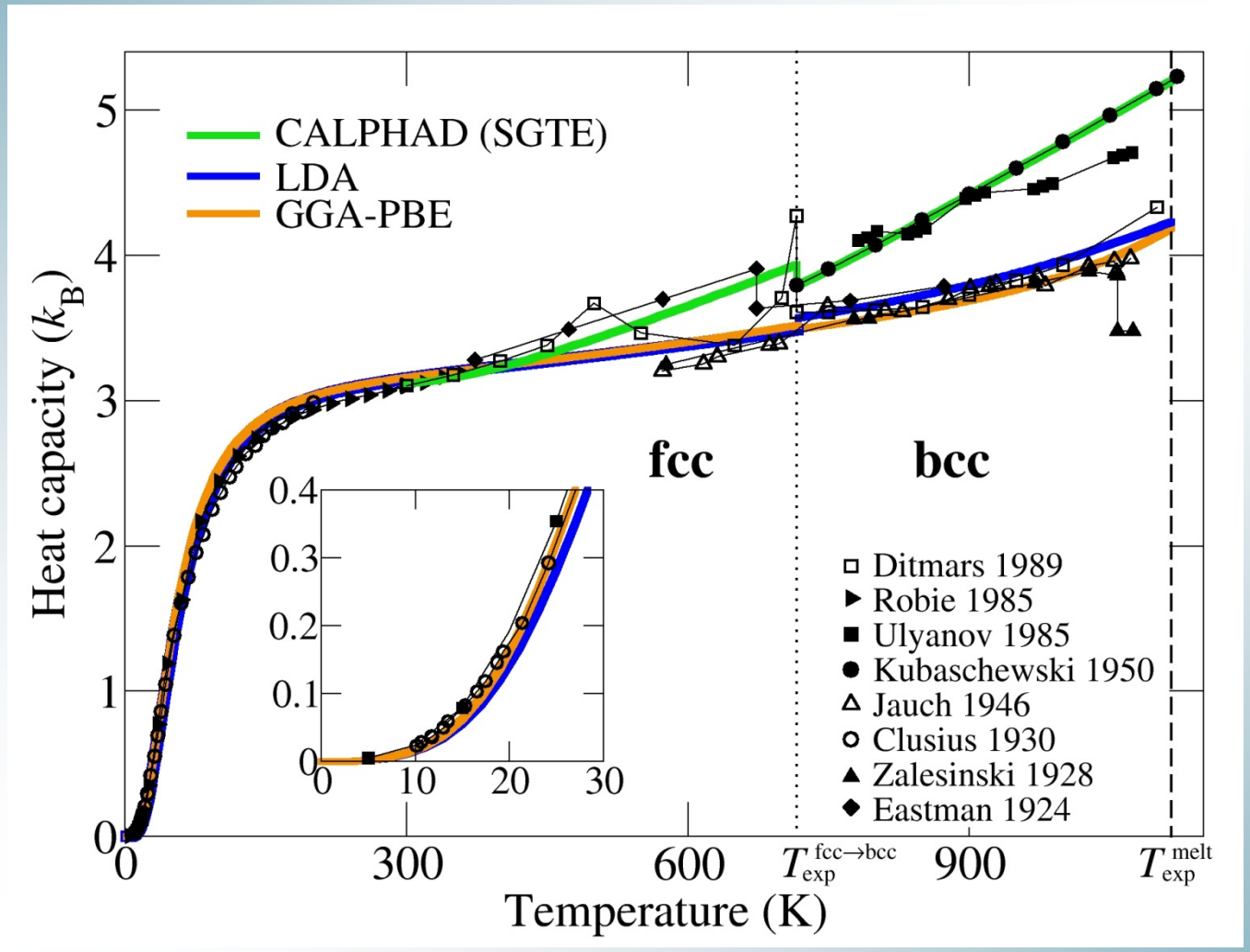
Calcium: Heat capacity



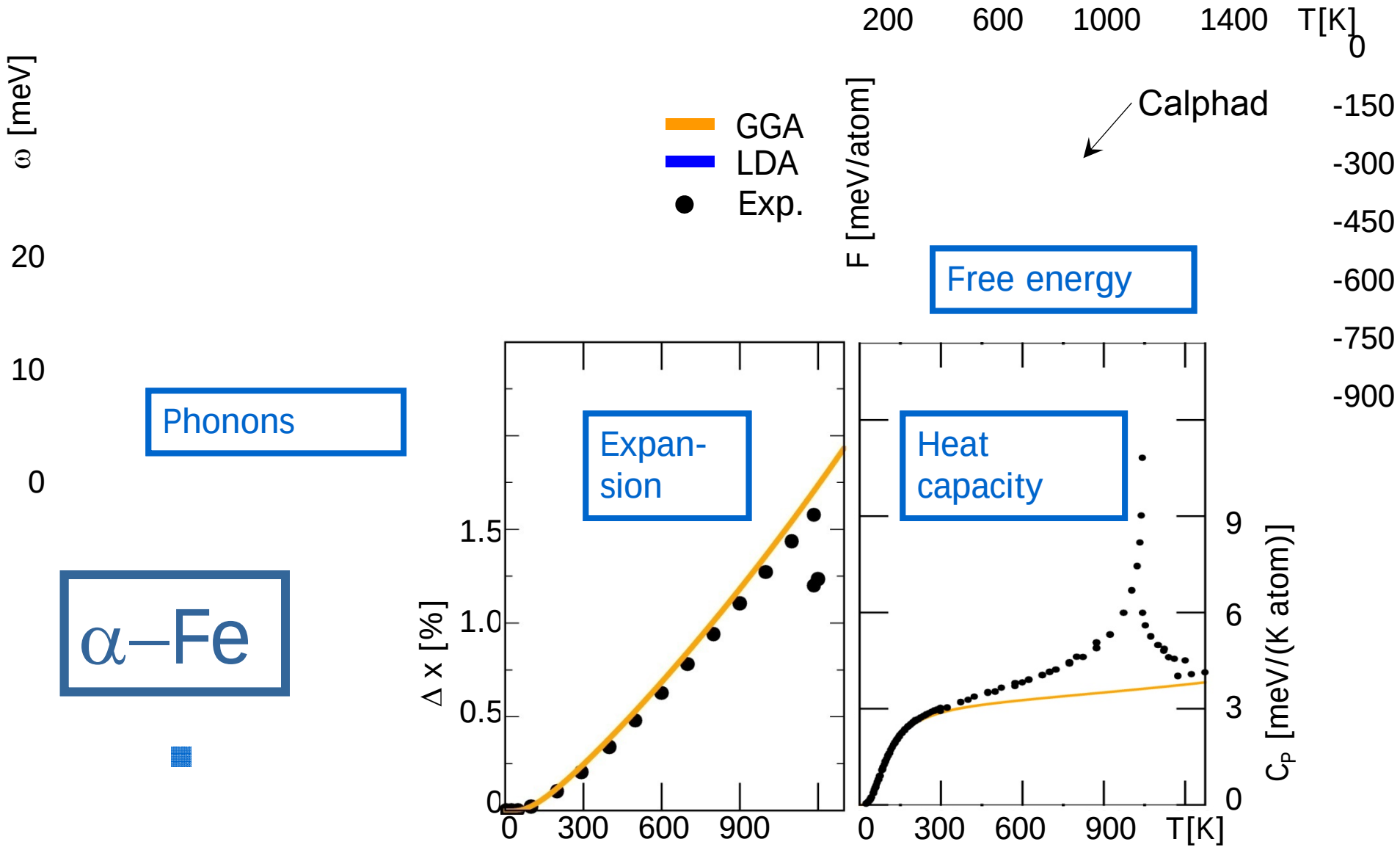
Calcium: Heat capacity



Calcium: Heat capacity

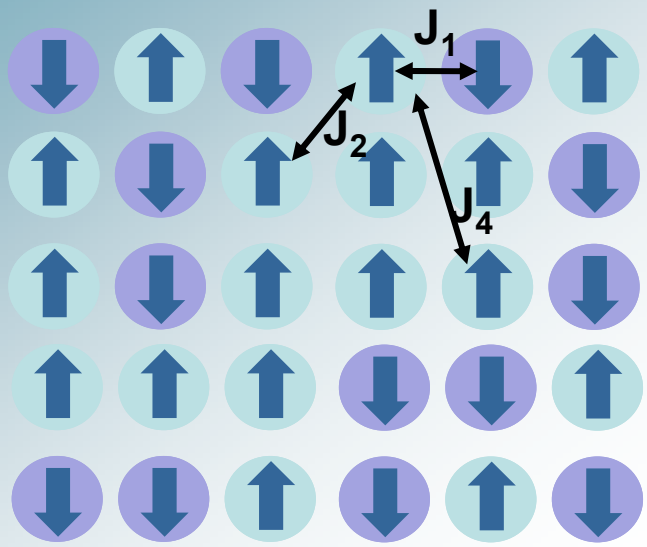


Magnetic Excitations


ω [meV]
20
10
0
Phonons
α–Fe
GGA
LDA
Exp.
200
600
1000
1400
T[K]
F [meV/atom]
0
-150
-300
-450
-600
-750
-900
Calphad
Free energy
Expan-
sion
Δ x [%]
1.5
1.0
0.5
0
0
300
600
900
Heat
capacity
9
6
3
0
0
300
600
900
T[K]
C_P [meV/(K atom)]

Magnetic Excitations

T > 0K

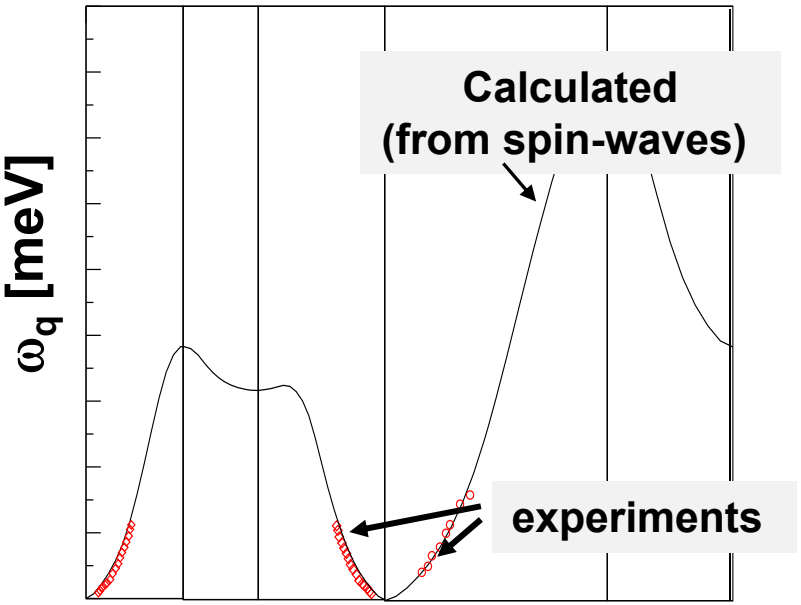


Construct spin Hamiltonian (e.g. Heisenberg model)

$$H = -\sum_{i,j} J_{i,j}\, \mathbf{S}_i \cdot \mathbf{S}_j$$

Typically 30 and more neighbors have to be included!

Magnons



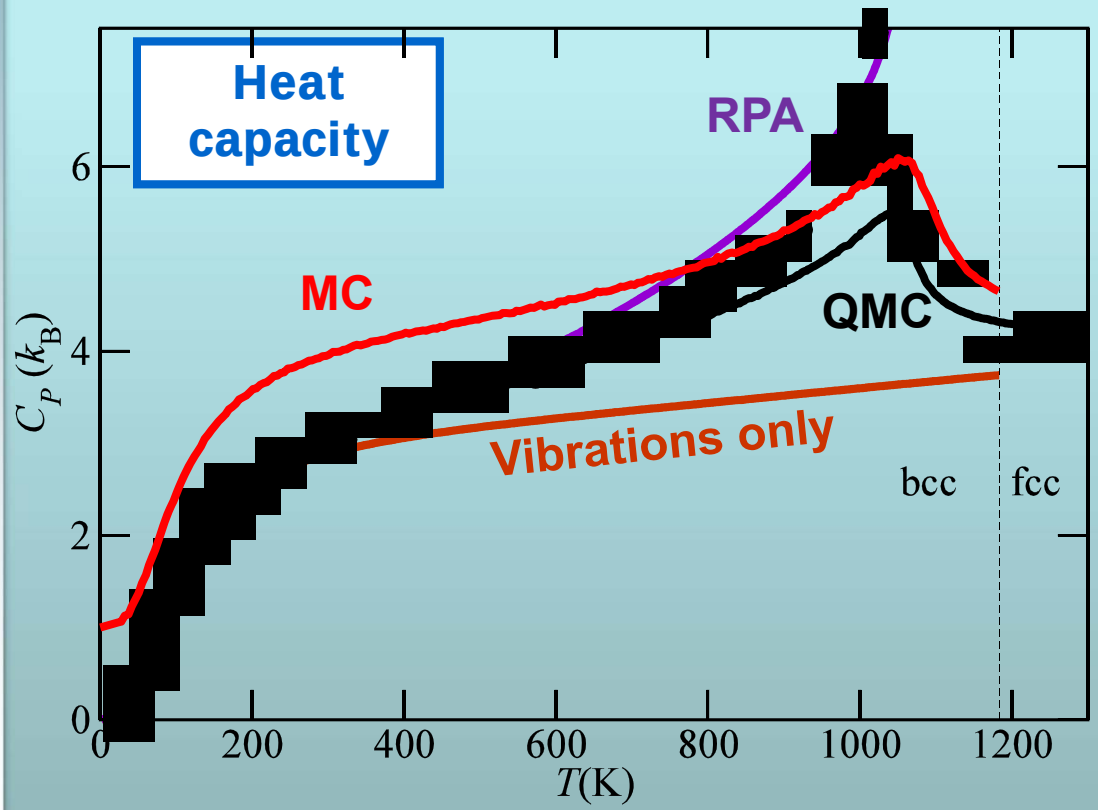
Koermann, et al., PRB 78, 033102 (2008)

Finite Temperature Magnetism

Construct and solve magnetic Hamiltonian: $H^{mag} = -\sum_{i,j} J_{i,j}\, \mathbf{S}_i \cdot \mathbf{S}_j$

→ from DFT
→ >30 neighbors

Example: Heat capacity of α iron



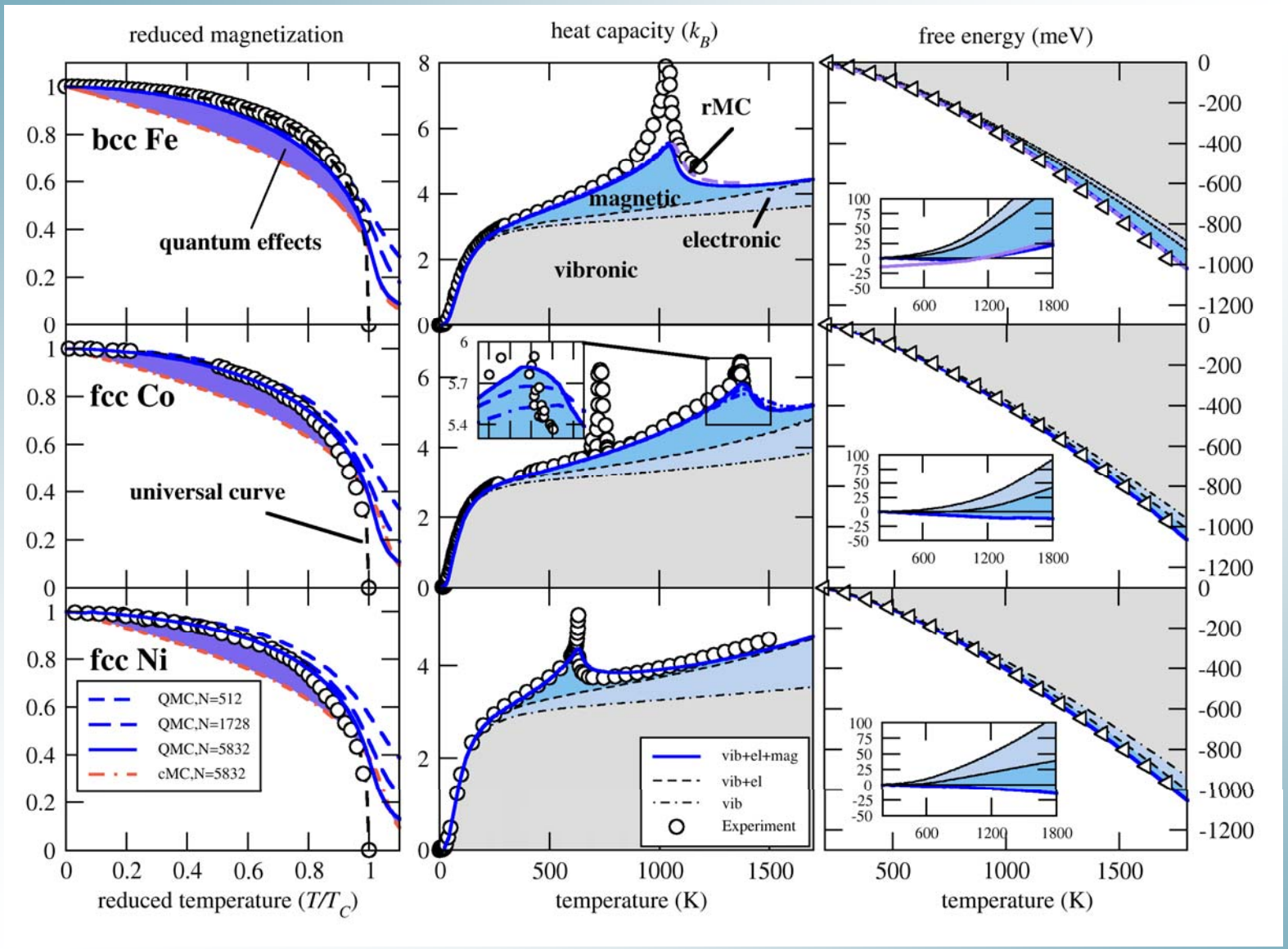
Hierarchy of approaches:

→ classical Monte-Carlo (**MC**):
→ fails below T_C

→ analytical approach (**RPA**):
→ only $<T_C$

→ quantum Monte-Carlo (**QMC**):
→ map on eff. H^{mag}
→ works everywhere

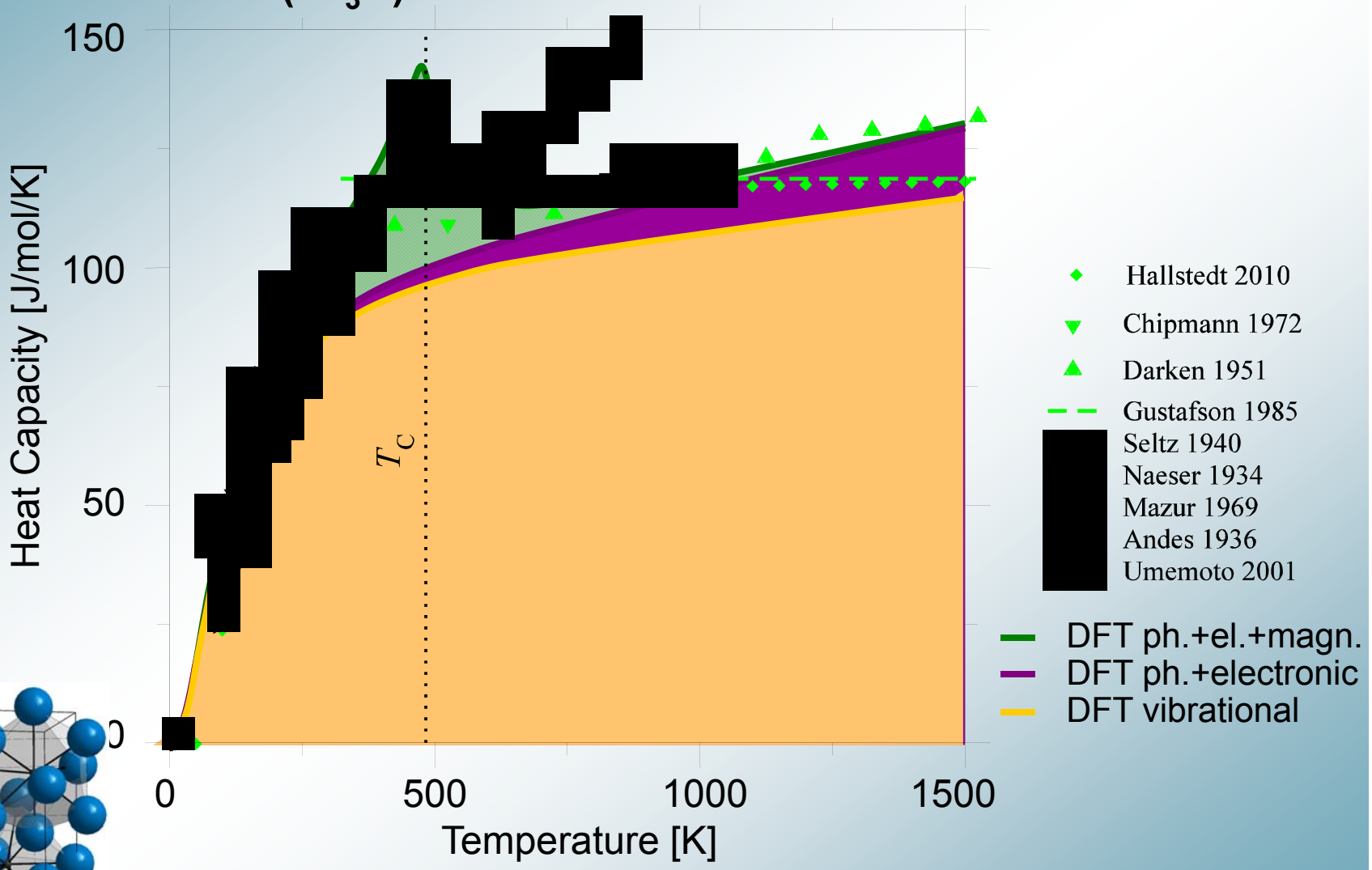
Magnetization, heat capacity, free energies

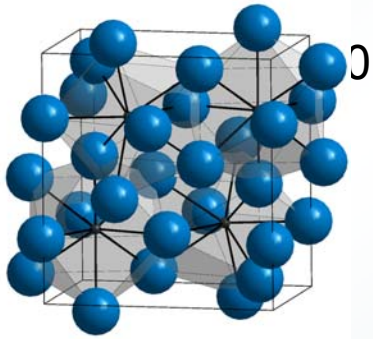


F. Körmann, A. Dick, T. Hickel, and J. Neugebauer, Phys. Rev. B 83, 165114 (2011)

Heat capacity of alloys

Example: Cementite (Fe_3C)



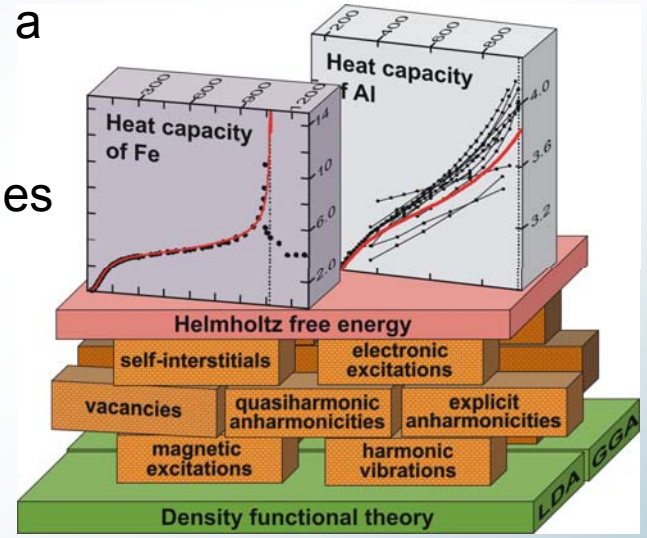


- G. Naeser, Mitt. Kais.-Wilh.-Inst. Eisenforschg. 16 (1934) 207210.

Conclusions

Description of T-dependent materials properties by DFT

- Toolset to compute all free energy contributions with a numerical accuracy of ~1 meV
- Partitioning into various excitation mechanism provides new insight (e.g. dominating entropy contributions close to melting)
- Accuracy in finite temperature effects often close to or even beyond experiment



Powerful basis to design multiscale approaches for real-world materials

- Steel design, understanding/overcoming failure mechanisms (e.g H embrittlement)
- predicting experimentally not accessible phase transitions
- Other materials systems: Lightweight alloys, semiconductor surfaces, phase change and shape memory alloys, biological nanocomposites etc.