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Materials Design Based on Ab Initio Thermodynamics

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Materials Design Based on Ab Initio Thermodynamics

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and Dierk Raabe

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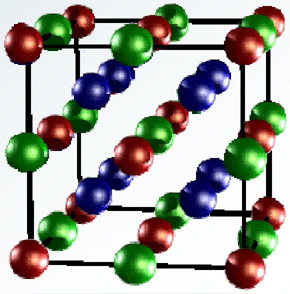
Department: Computational Materials Design

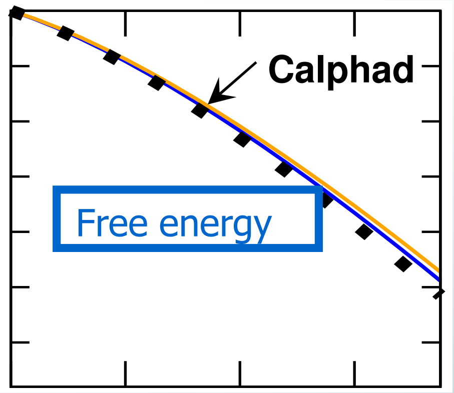
“Genome”



$\left\{\vec{R}_I , Z_I\right\}$

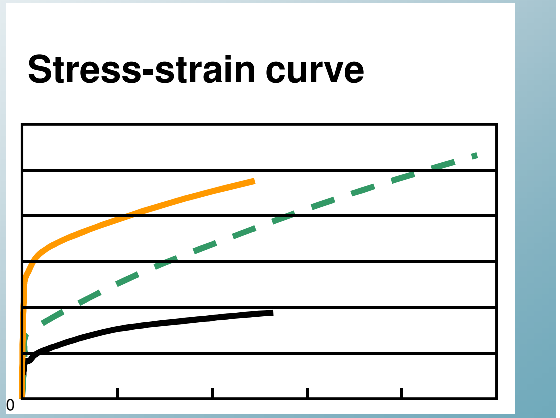
?

Ab initio thermodynamics



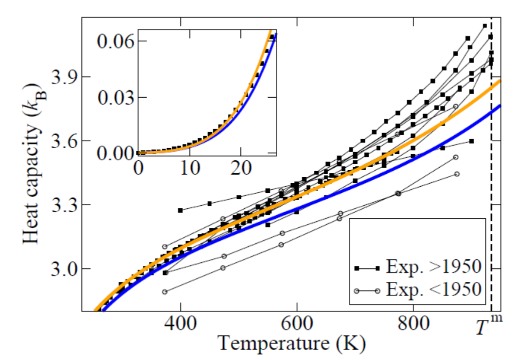
?

Engineering properties

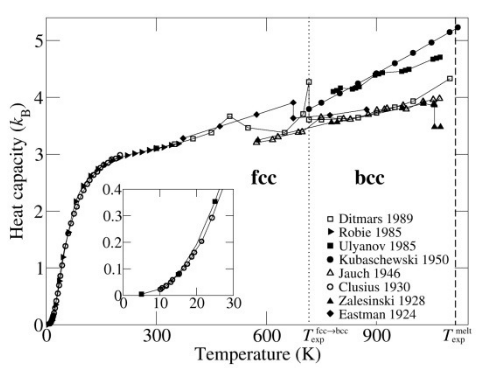


Do we have to go beyond experiment?

Calorimetric measurements



fcc Al



fcc/bcc Ca

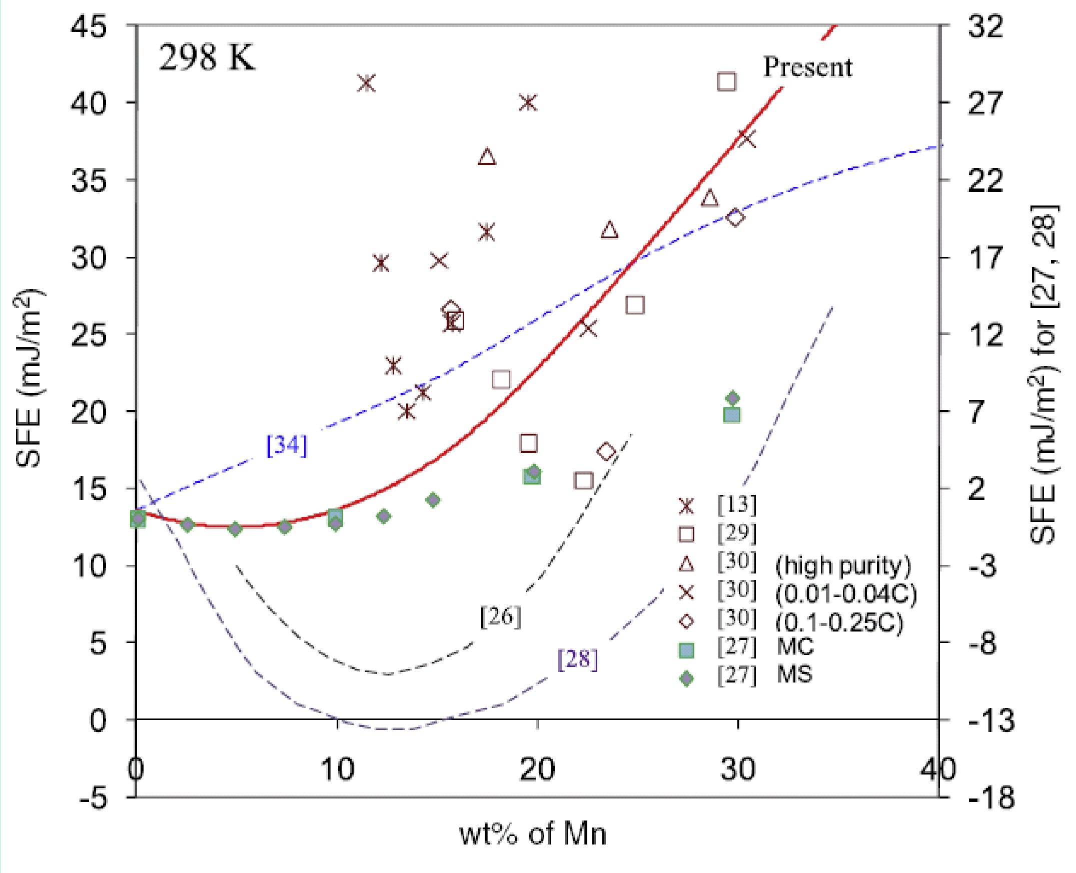
Fundamental input for all thermodynamic databases
→ But: Scatter of ~0.3 … 1 k_B

Point defects (vacancies): Formation energies and entropies

	Al		**Cu**	
	Exp.	DFT	Exp.	DFT
E_f (eV)	0.7	0.6	1.2	0.9
S (k_B)	2.4	0.2	2.3	0.3

Do we have to go beyond experiment?

Stacking fault energies (fcc Fe-Mn)



Key quantity to design novel high-strength steels

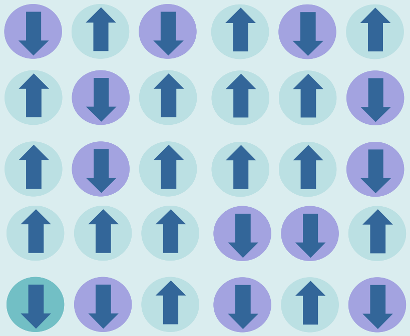
Additional complication
→ magnetism

Even chemical trends are hard to derive from existing data

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, …

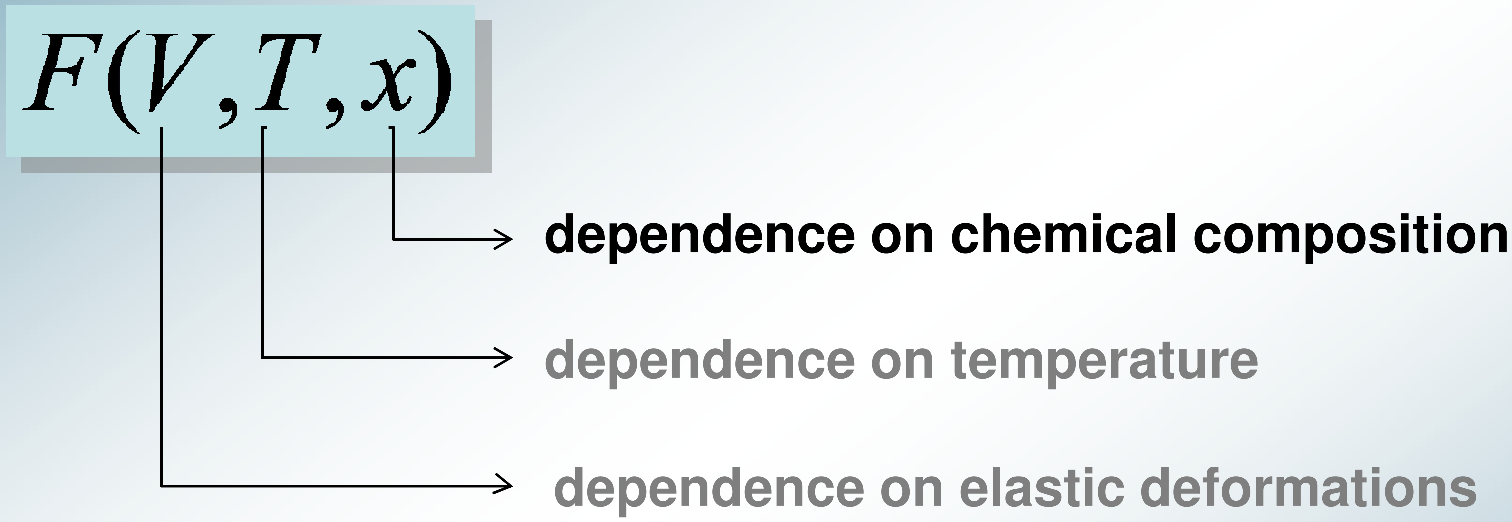
Statistical averages provide thermodynamic quantities:

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

Knowledge of partition function allows to derive any thermodynamic quantity!

Accuracy

Free energy:



$$F(V,T,x)$$

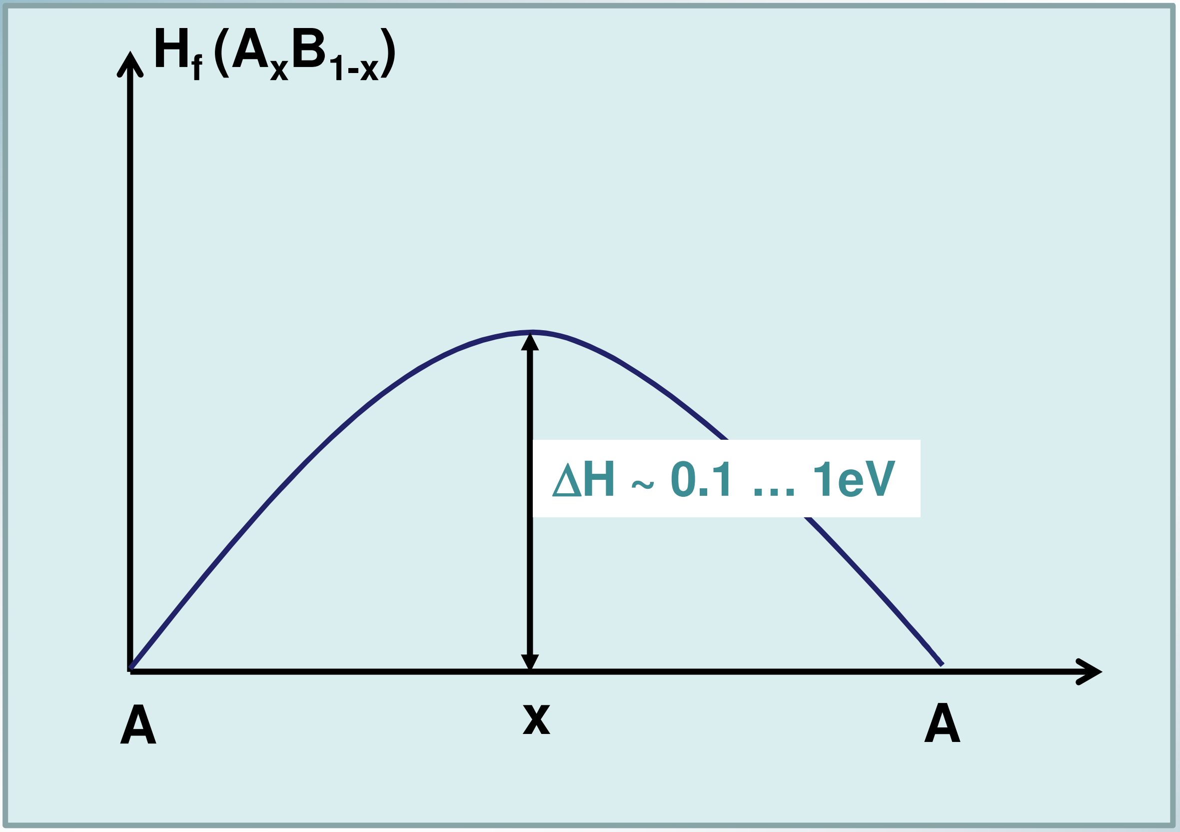
dependence on chemical composition

dependence on temperature

dependence on elastic deformations

Accuracy: Chemical Composition

Alloy formation enthalpy



Errors in the order of 10meV are often acceptable
→ DFT provides reliable results

Accuracy

Free energy:

$$F(V,T,x)$$

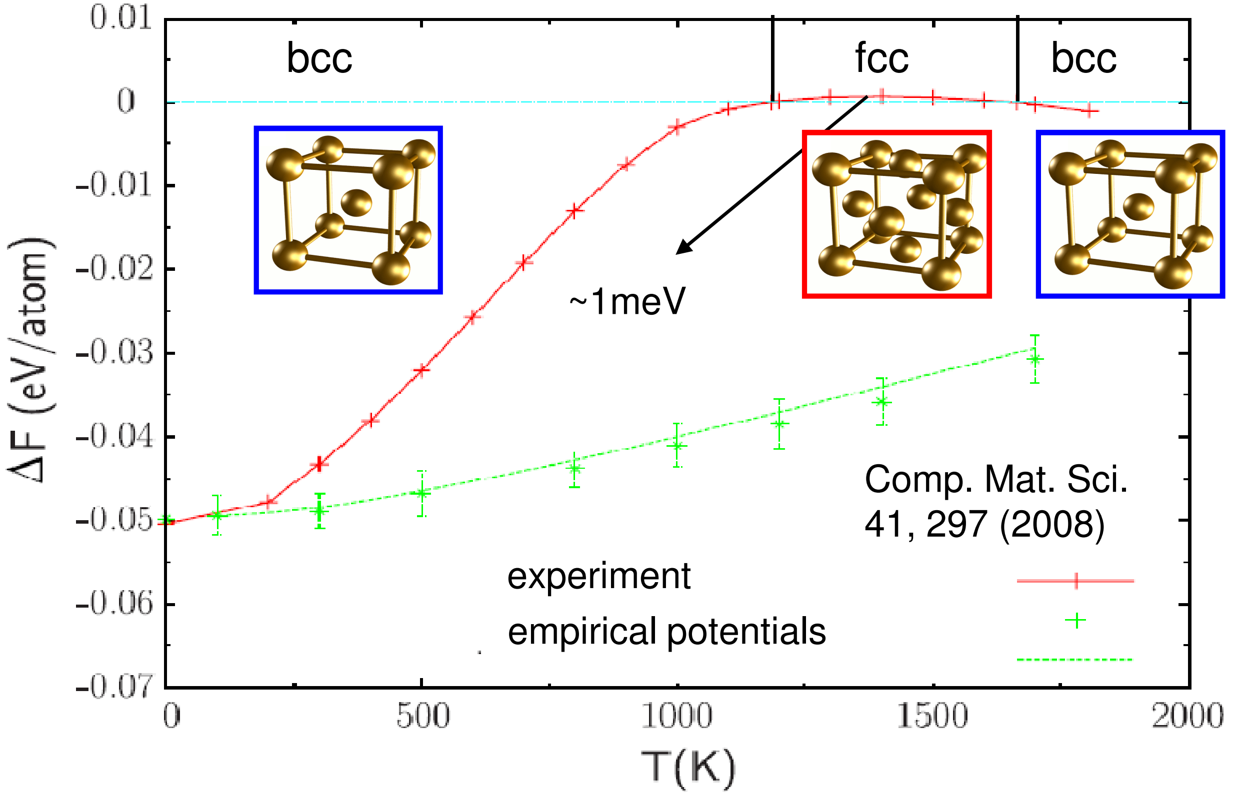
dependence on chemical composition

dependence on temperature

dependence on elastic deformations

Accuracy

Free energy difference between bcc and fcc iron

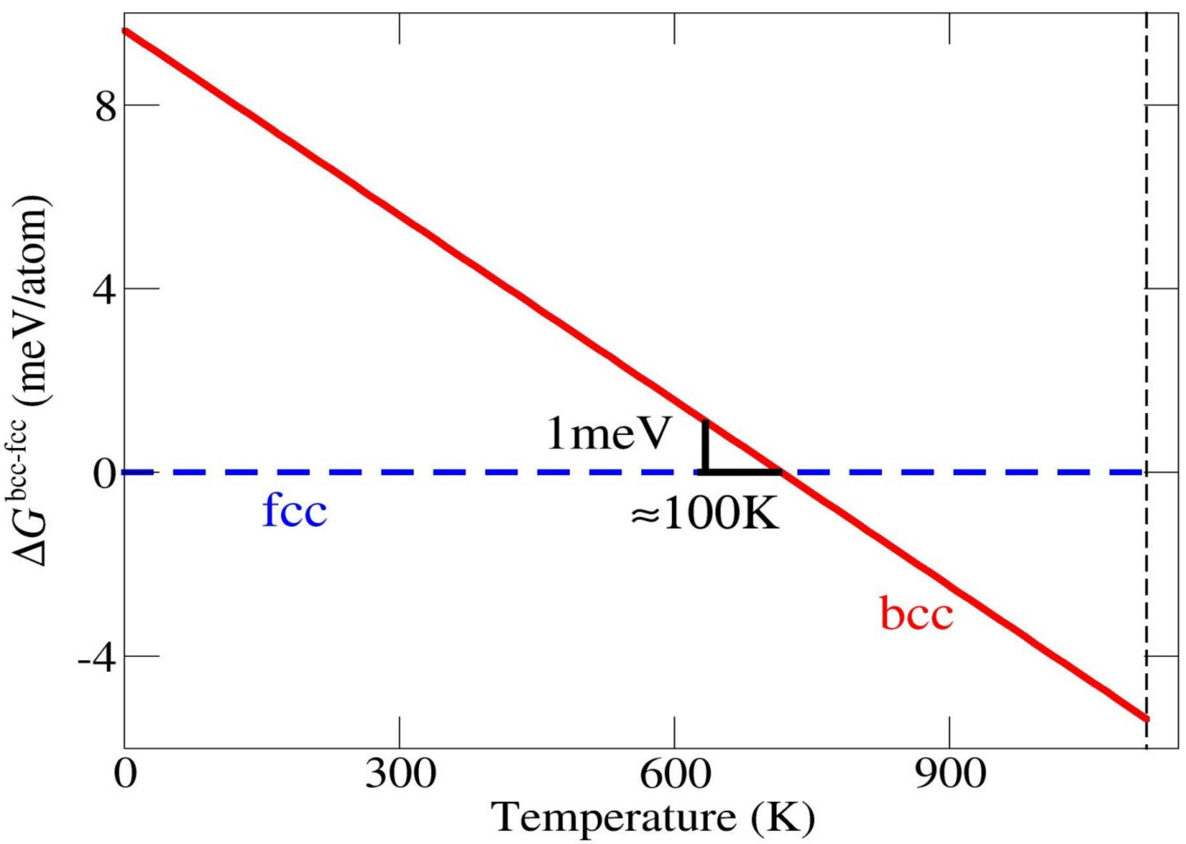


Energy resolution better 1 meV!

→ Can we achieve such accuracy with present day ab initio techniques?

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

Ab initio Thermodynamics

10^7 configurations

a few hours

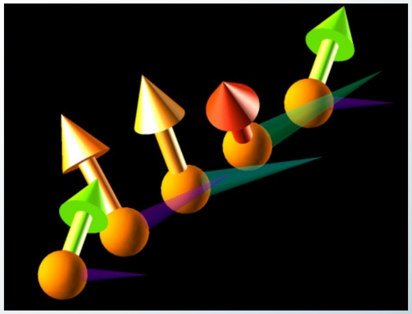
$$Z(\hat{A},T) = \sum_{\{\vec{R}_I\}_{\hat{A}}} e^{-E^{BOS}\left(\{\vec{R}_I, Z_I\}_{\hat{A}}\right)/k_B T}$$

Ab initio Thermodynamics

Approach (schematic)

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

- electronic excitations: E^{el}
- magnetic excitations: E^{mag}
- structural excitations
  - → intrinsic defects: E^{def}
  - → elastic deformations: E^{elast}



+ interactions between these contributions
  - → electron-phonon interaction
  - → magneto-volume effects
  - → …

10^7 configurations

a few hours

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

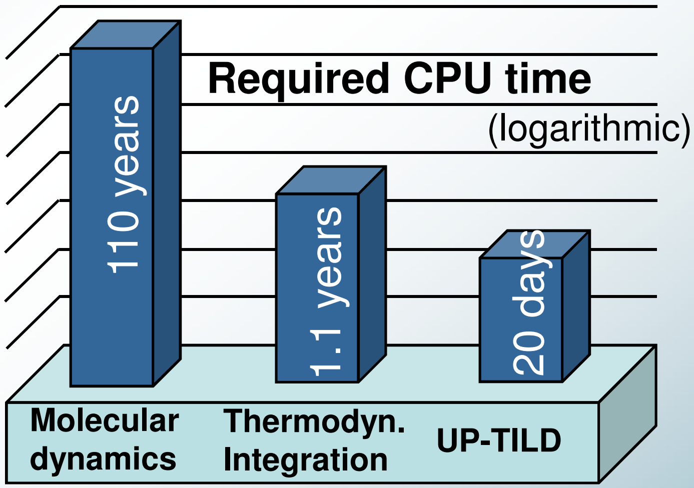
Methodological Approach

Quasiharmonic approximation + electronic excitations

- work horse for free energy studies (typically largest contribution)
- highly sensitive with respect to DFT convergence parameters
- Ref.: Grabowski et al., PRB 76, 024309 (2007).

Anharmonic contributions:

- relevant close to the melting temperature
- efficient sampling strategies (UP-TILD) boost efficiency by 4 orders of magnitude
- Ref.: Grabowski et al., PRB 79, 134106 (2009)
  PSS-B 248, 1295 (2011)



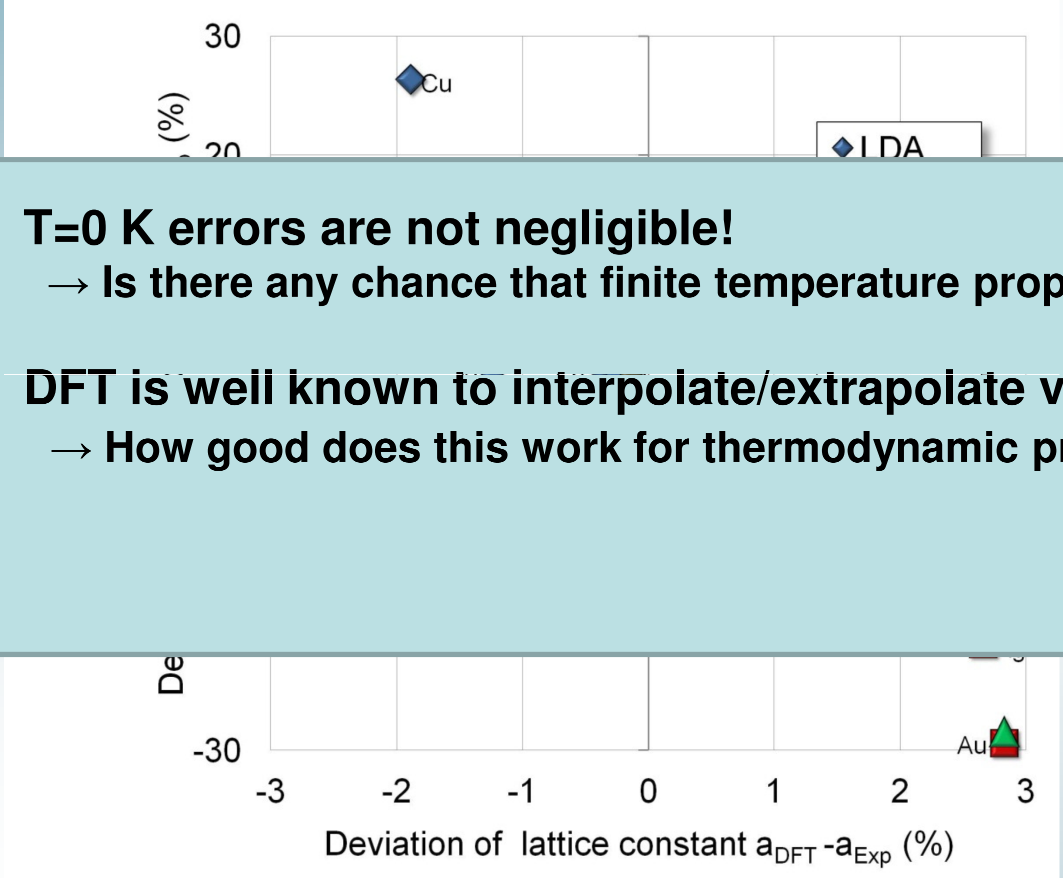
Magnetic contributions:

- relevant for practically all steels
- spin-quantization crucial
- Ref.: Körmann et al., PRB 78, 033102 (2008); PRB 83 (2011)
  Uittjewal et al. PRL 102, 035702 (2009).

Typical numerical precission for free energy: 1 meV
Remaining error: xc-functional (LDA, GGA)

T=0K: Structural and Elastic Properties

Errors in LDA/GGA(PBE)-DFT computed lattice constants and bulk modulus with respect to experiment



→ Fully converged results (basis set, k-sampling, supercell size)

T=0 K errors are not negligible!

→ **Is there any chance that finite temperature properties are accurately predicted?**

DFT is well known to interpolate/extrapolate very well (error cancellation)

→ **How good does this work for thermodynamic properties?**

bounds to exp. data

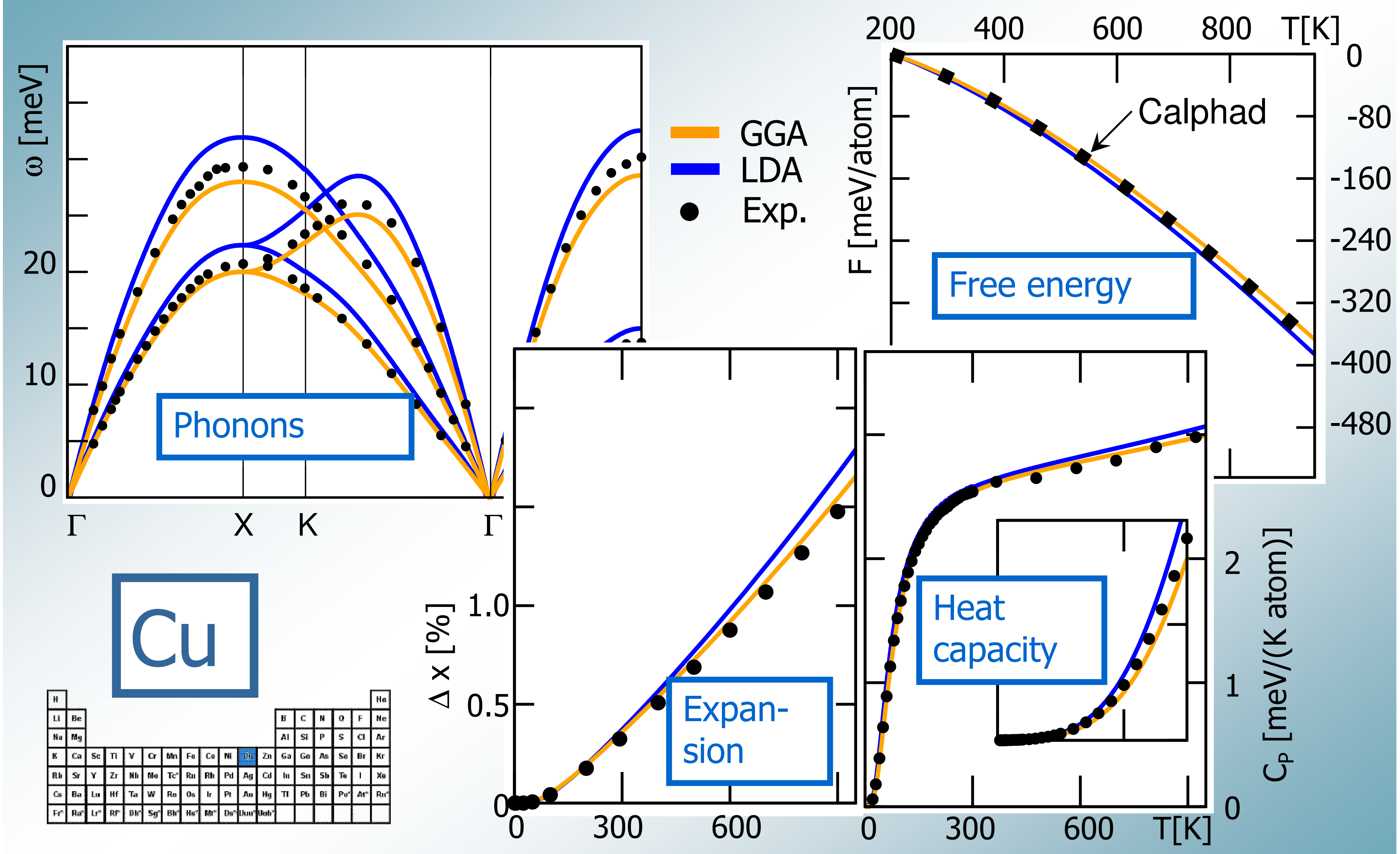
→ provide "ab initio error bars"

⇒ **Inspection of several xc-functionals is critical to estimate predictive power and error bars!**

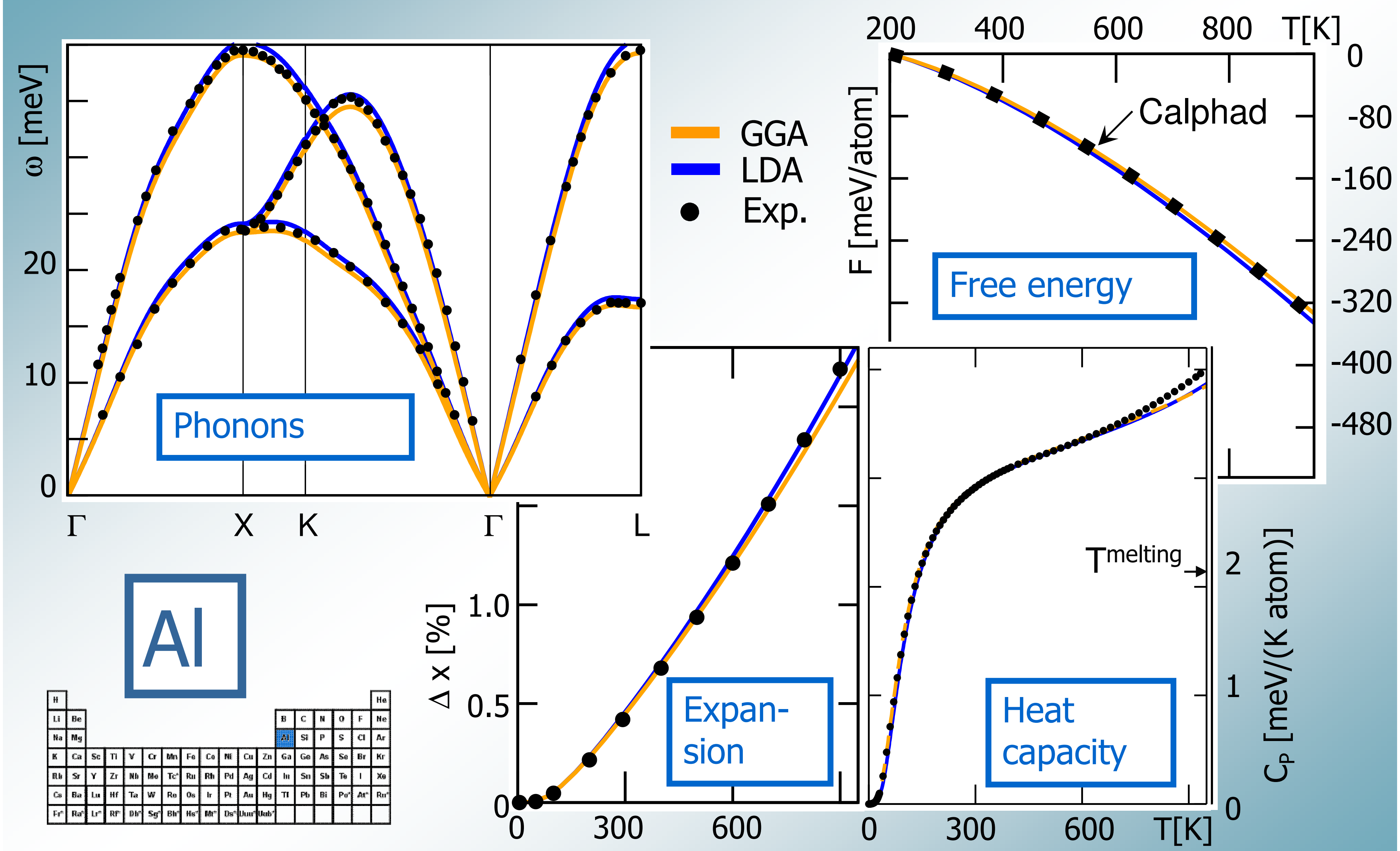
Non-magnetic materials

→ low and medium temperatures

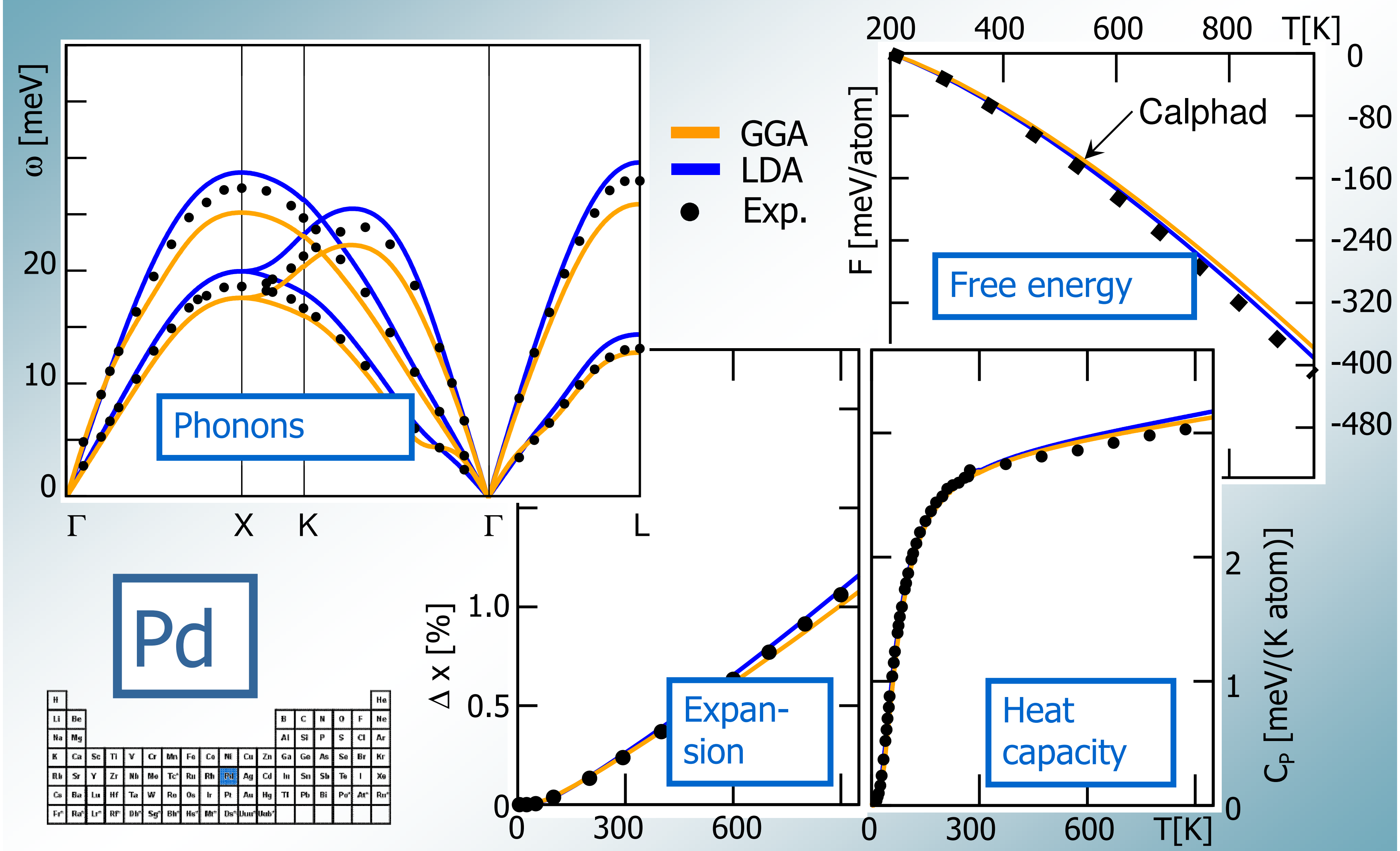
Thermodynamic Properties of Cu



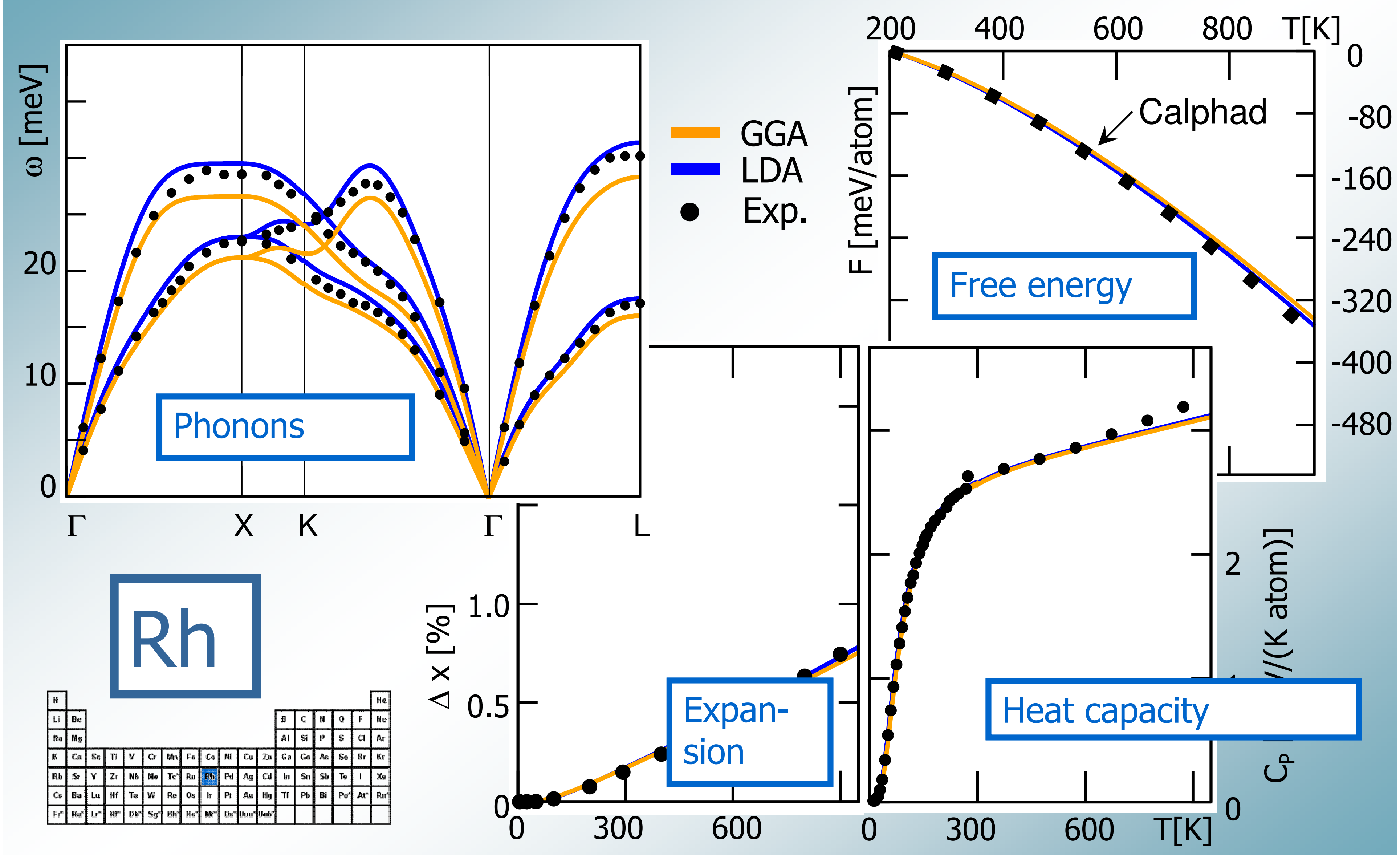
Thermodynamic Properties of Al



Thermodynamic Properties of Pd

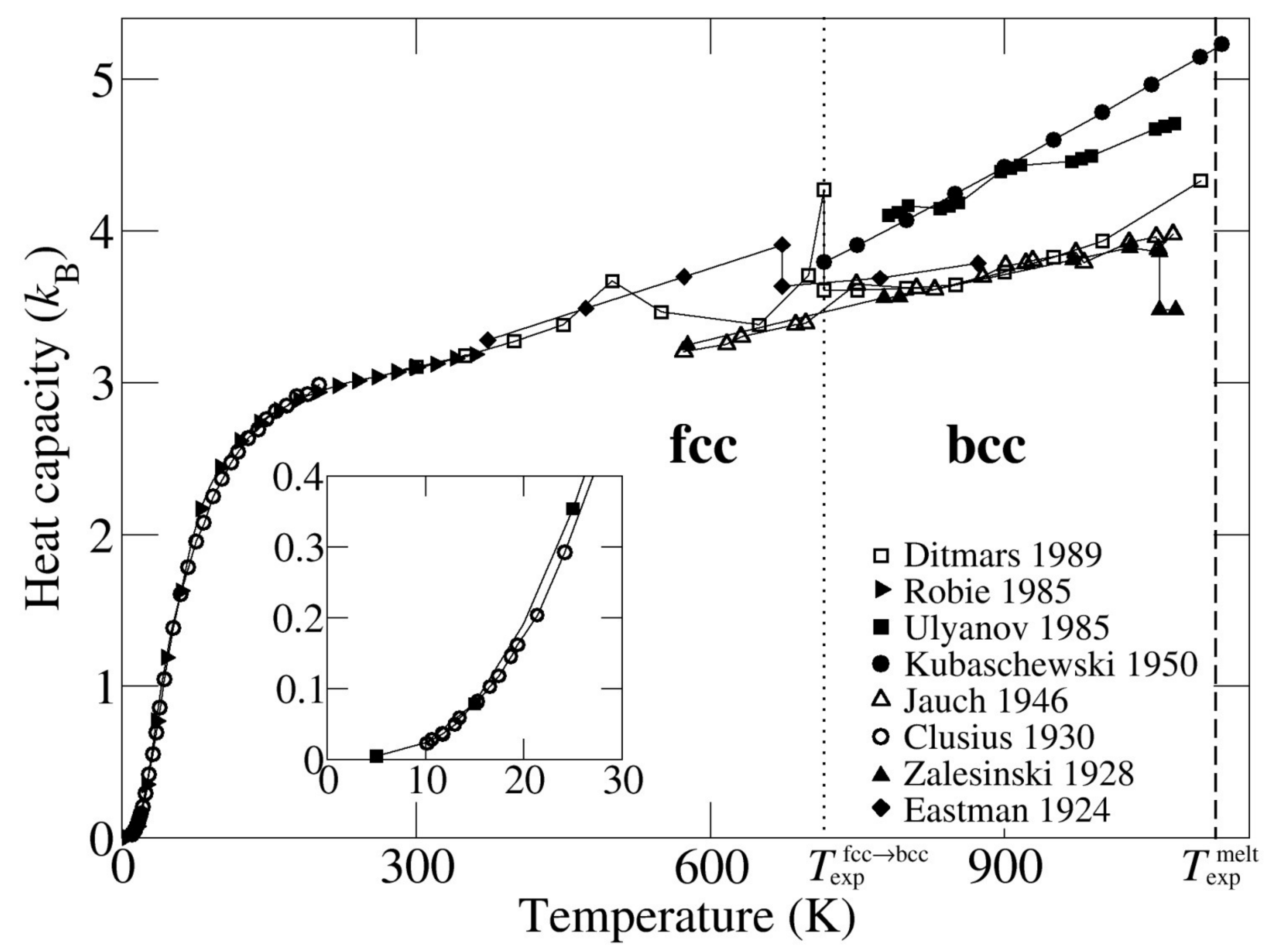


Thermodynamic Properties of Rh

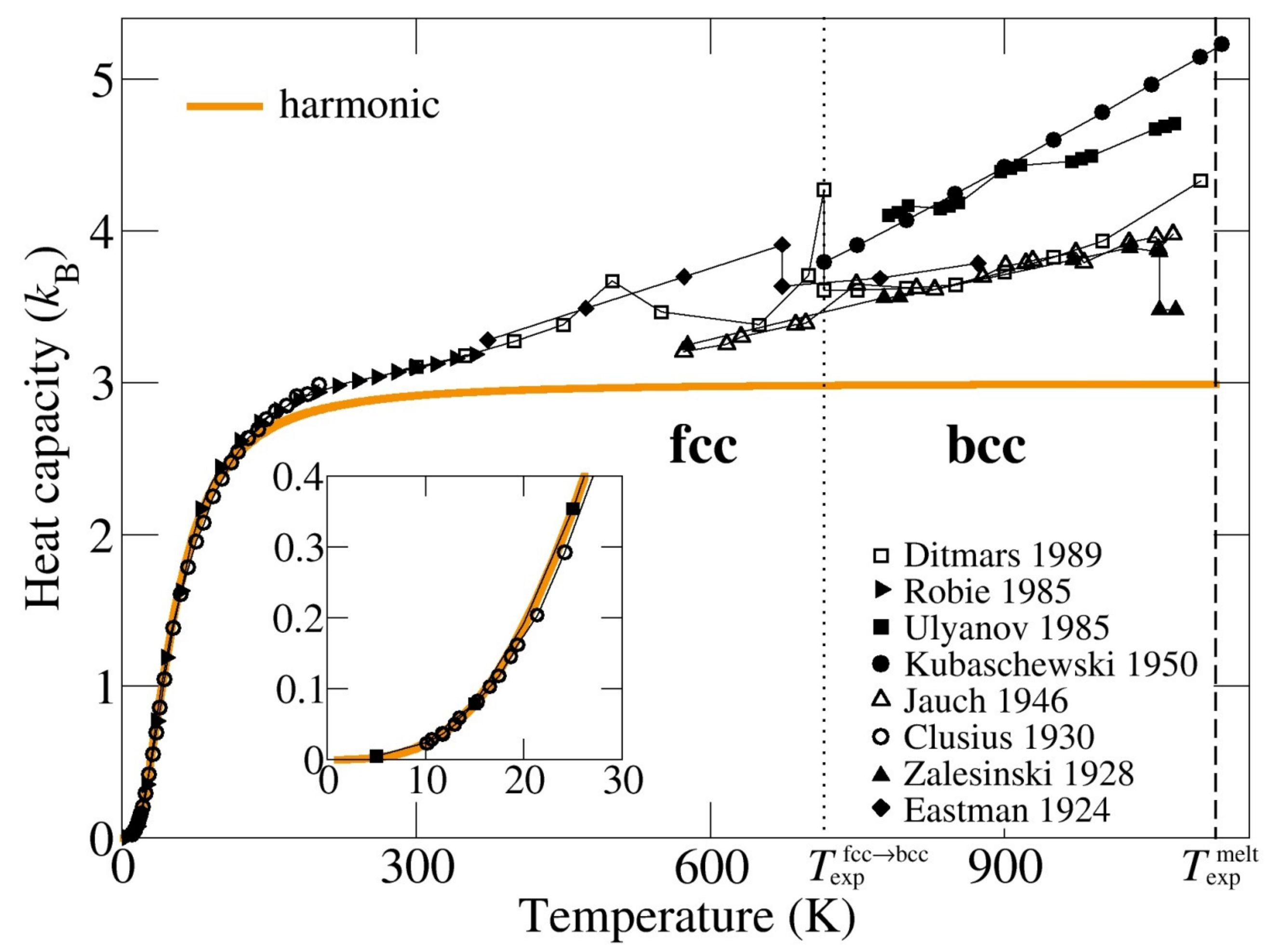


Applications

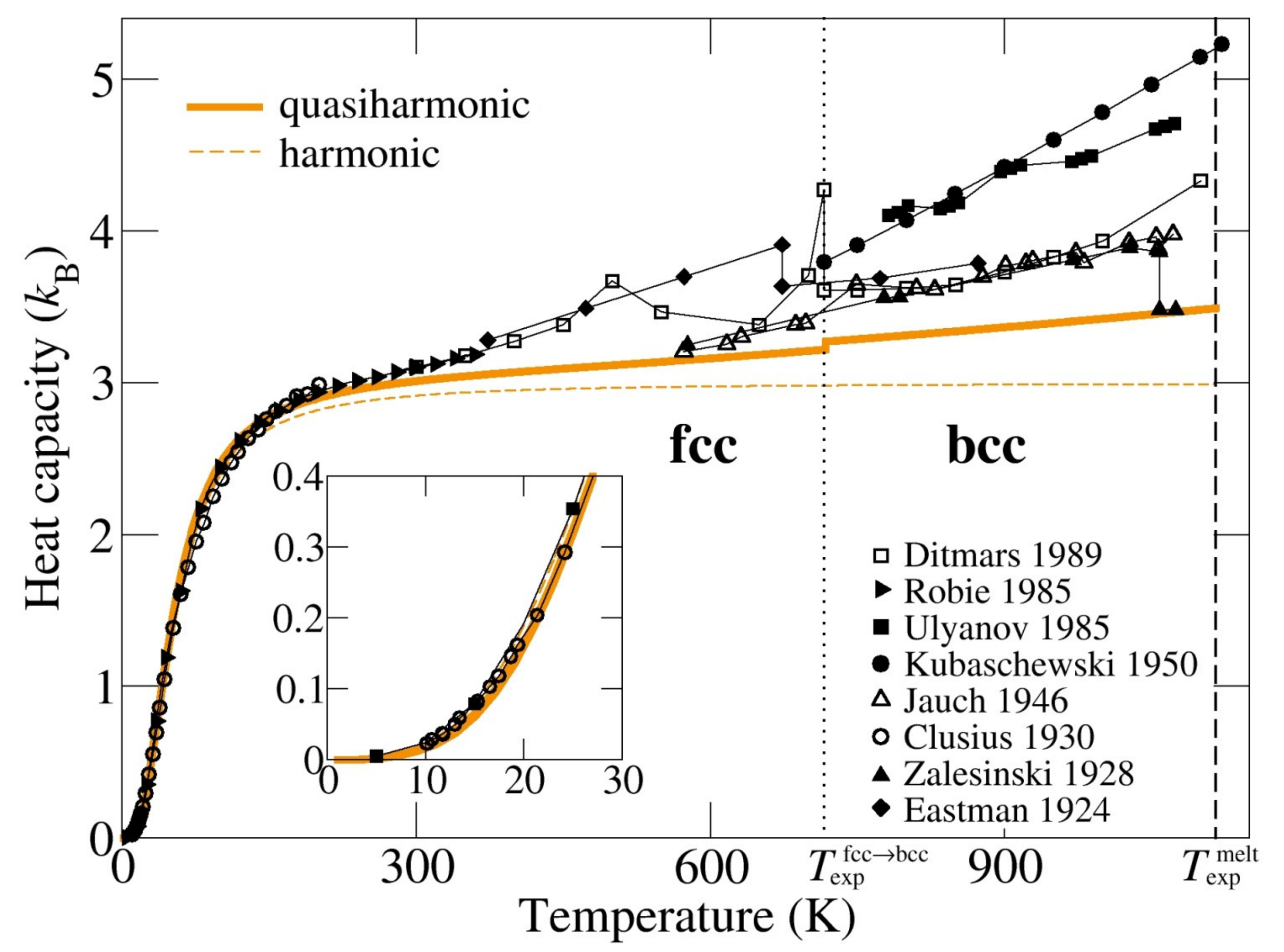
Calcium: Heat capacity



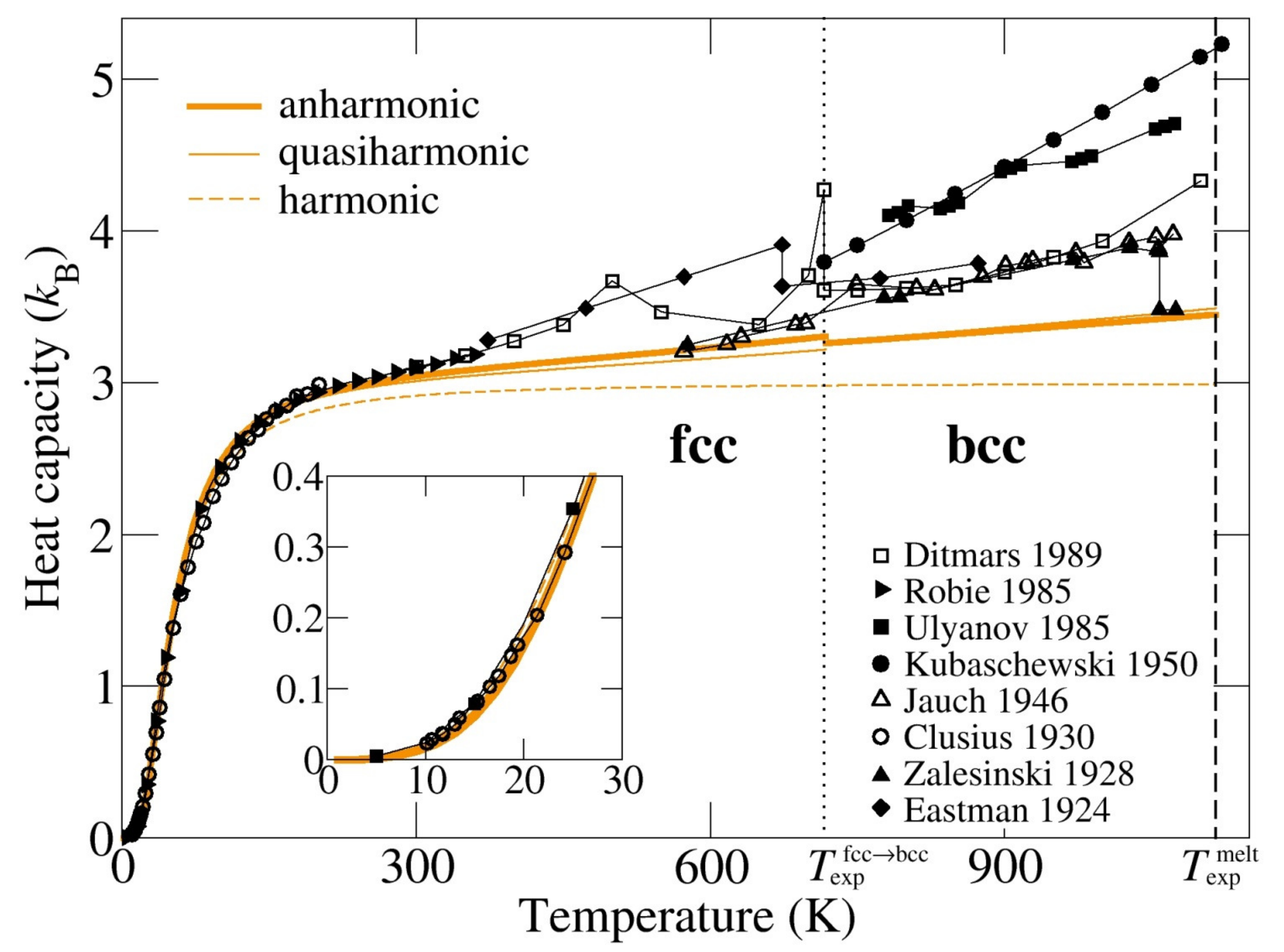
Calcium: Heat capacity



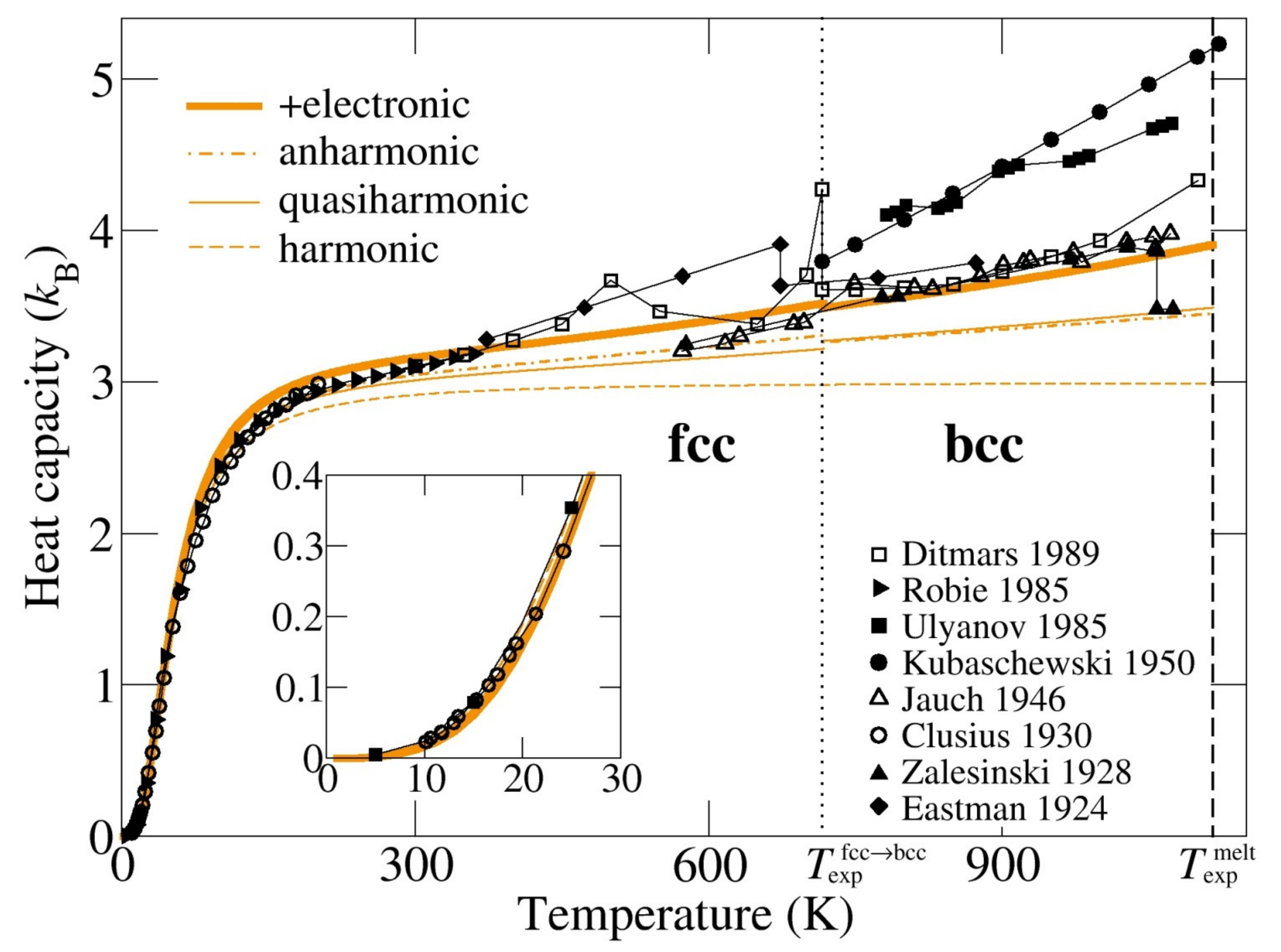
Calcium: Heat capacity



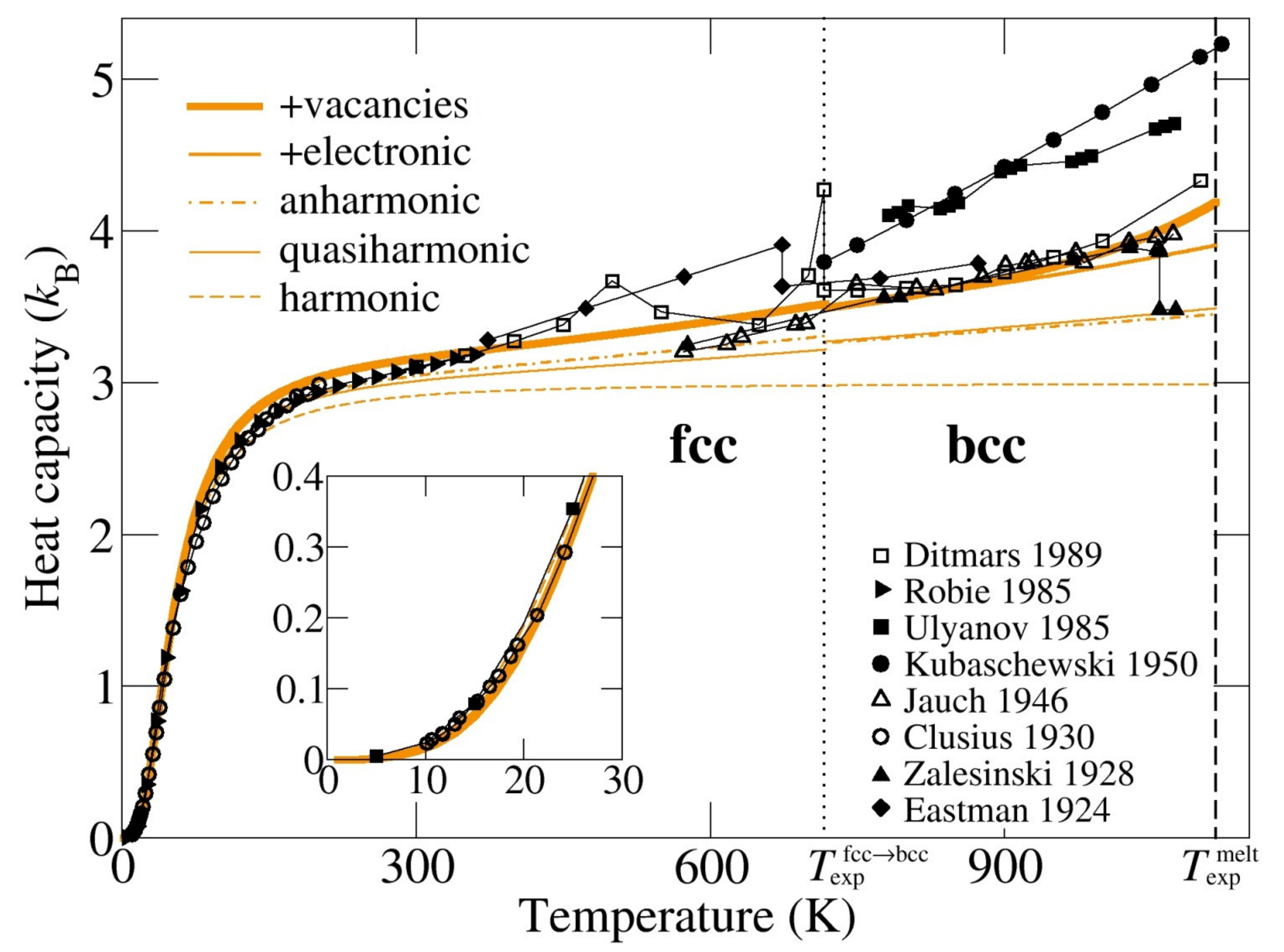
Calcium: Heat capacity



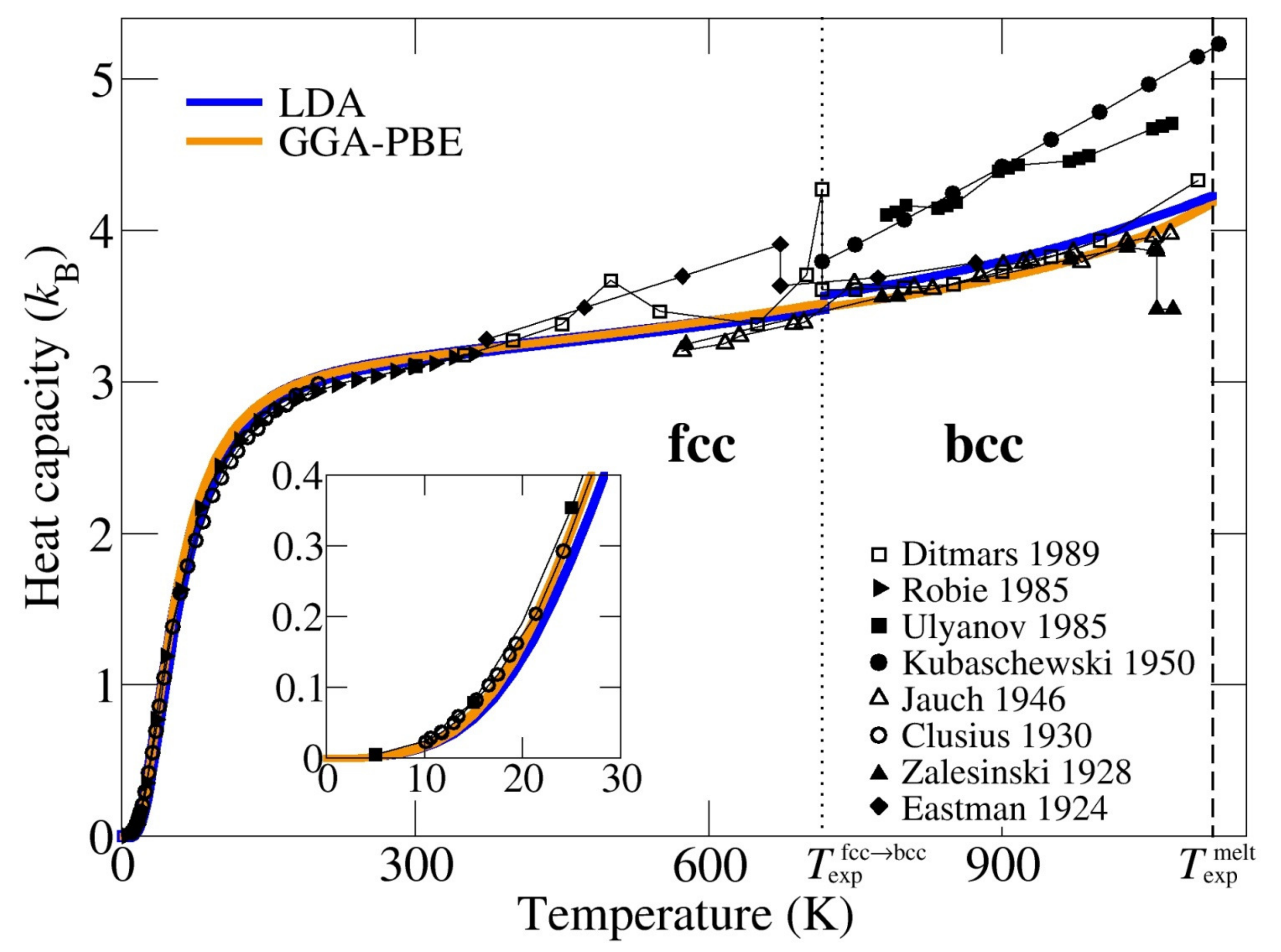
Calcium: Heat capacity



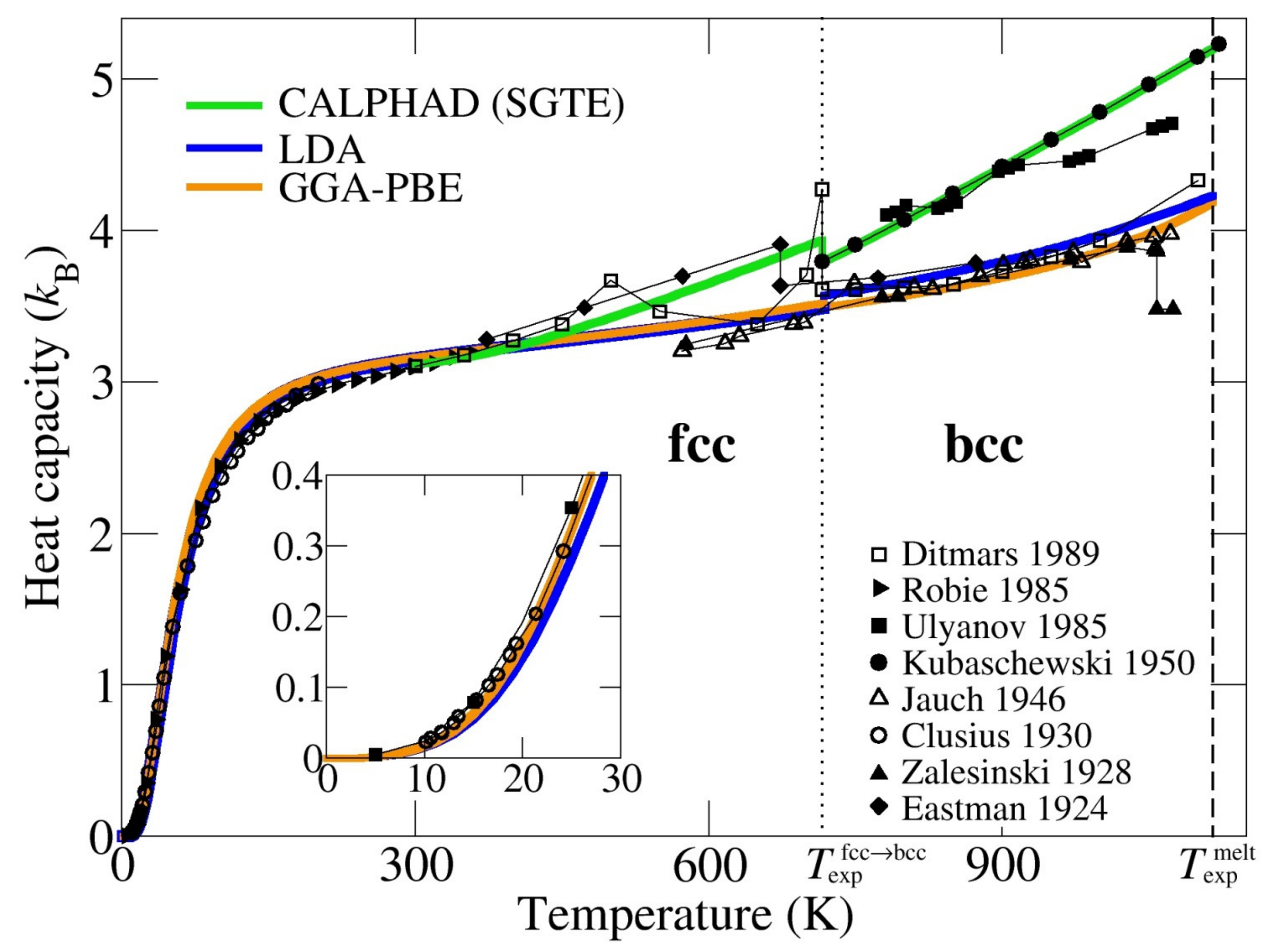
Calcium: Heat capacity



Calcium: Heat capacity

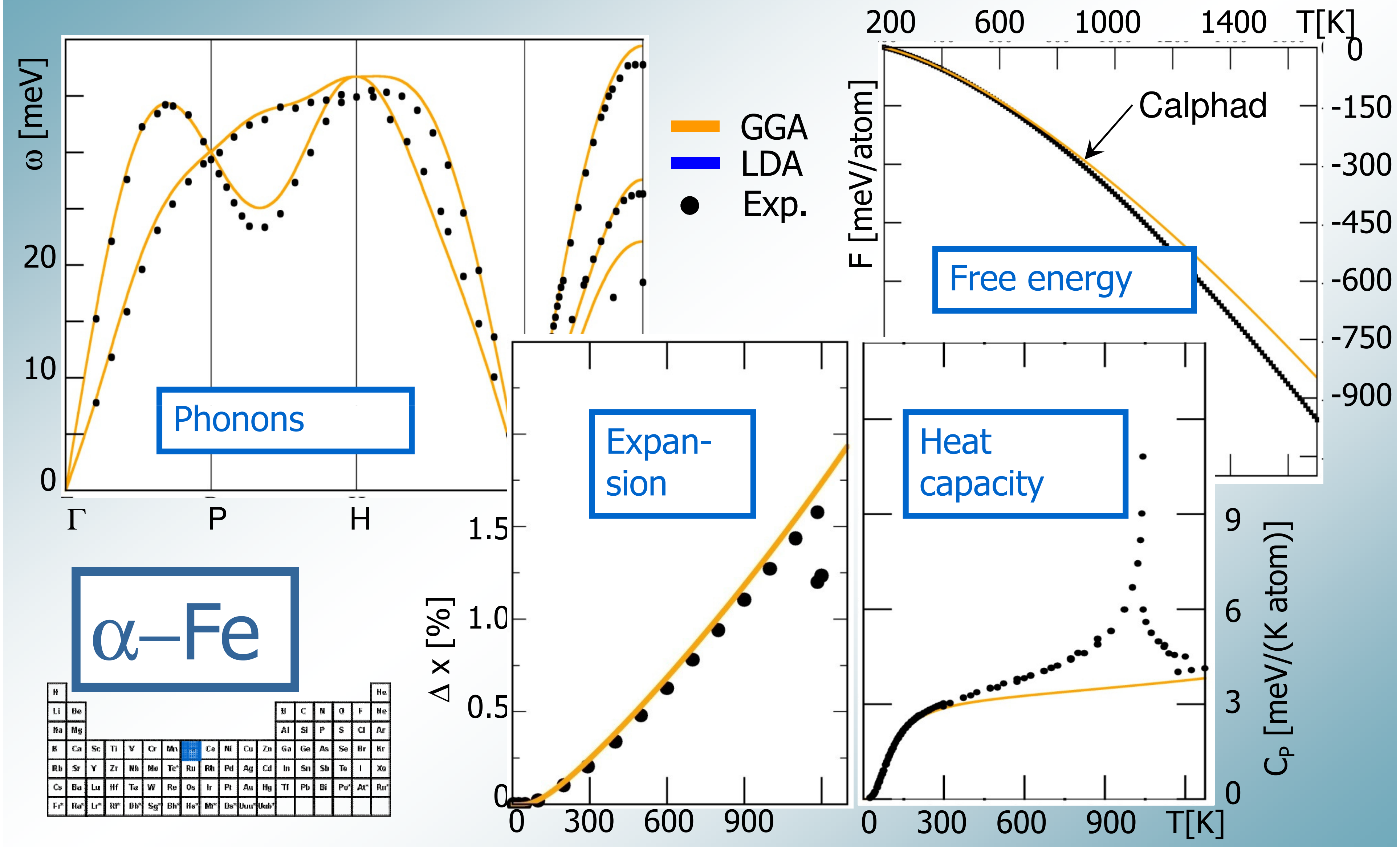


Calcium: Heat capacity



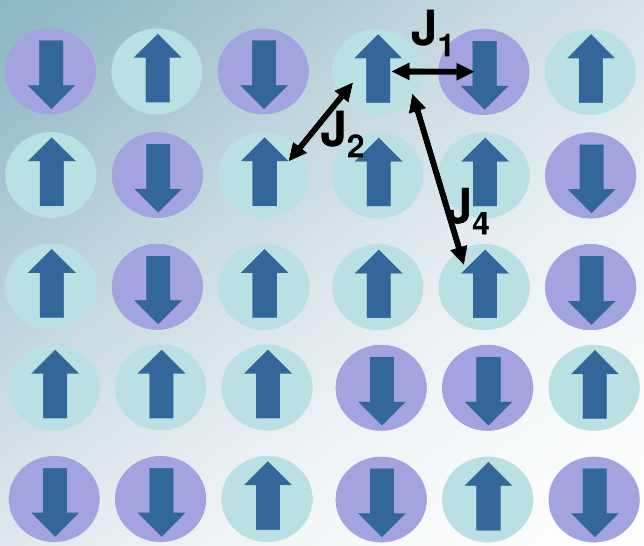
Magnetic Excitations

Vibronic excitations in bcc iron



Magnetic Excitations

T > 0K

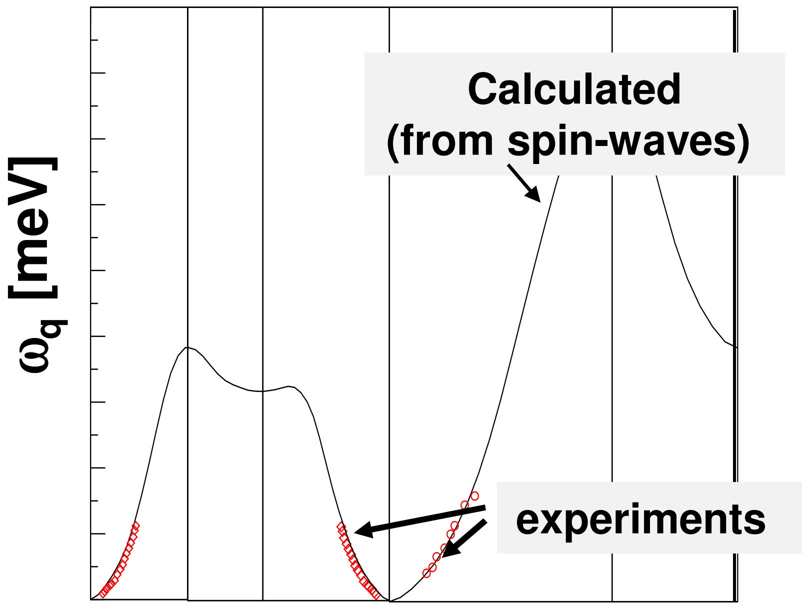


Construct spin Hamiltonian (e.g. Heisenberg model)

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

Typically 30 an more neighbors have to be incl led!

Magnons



Calculated (from spin-waves)

experiments

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

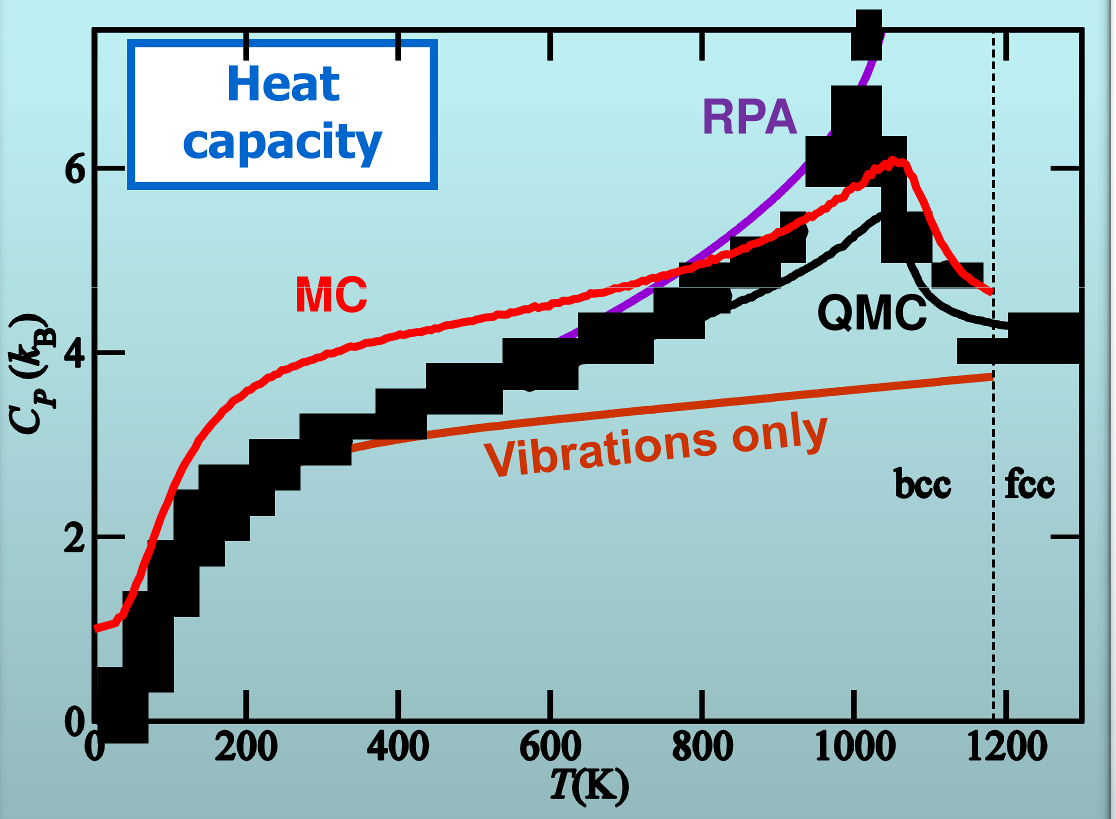
Finite Temperature Magnetism

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

→ from DFT

→ >30 neighbors

Example: Heat capacity of α iron



Hierarchy of approaches:

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

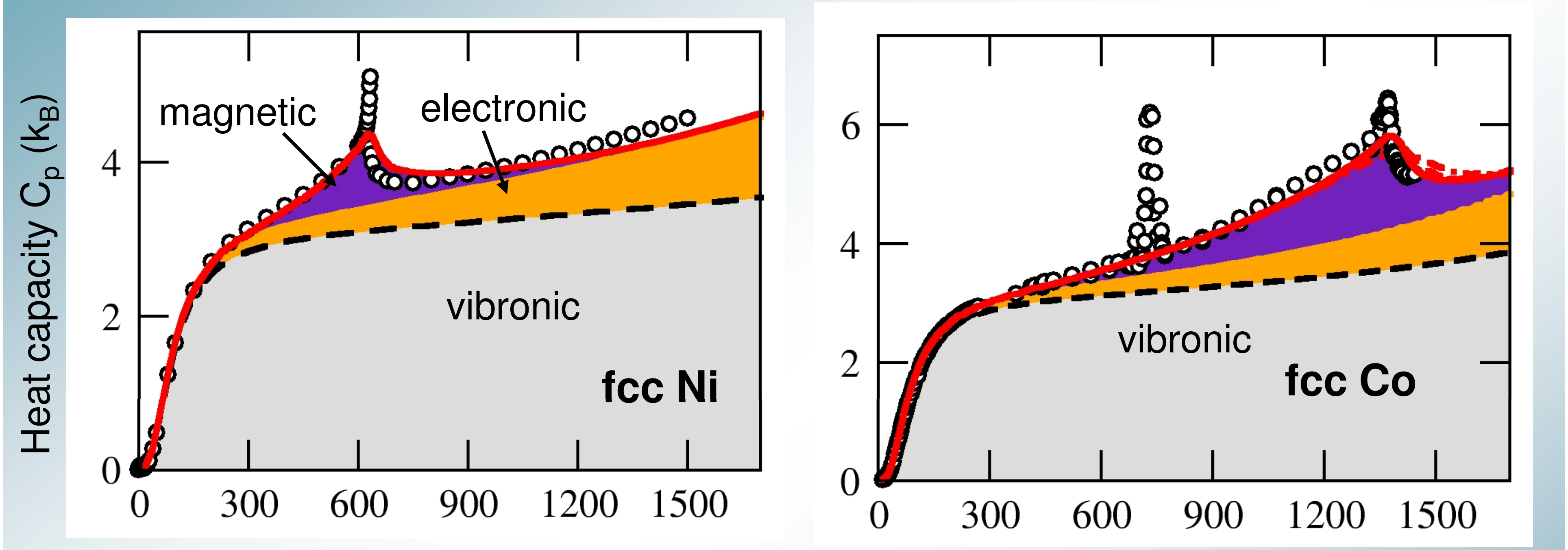
→ analytical approach (**RPA**):
  → only $<T_C$

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

Koermann et al , PRB **78**, 033102 (2008);
PRB **81**, 134425 (2010);
PRB **83** (2011)

Application to magnetic metals

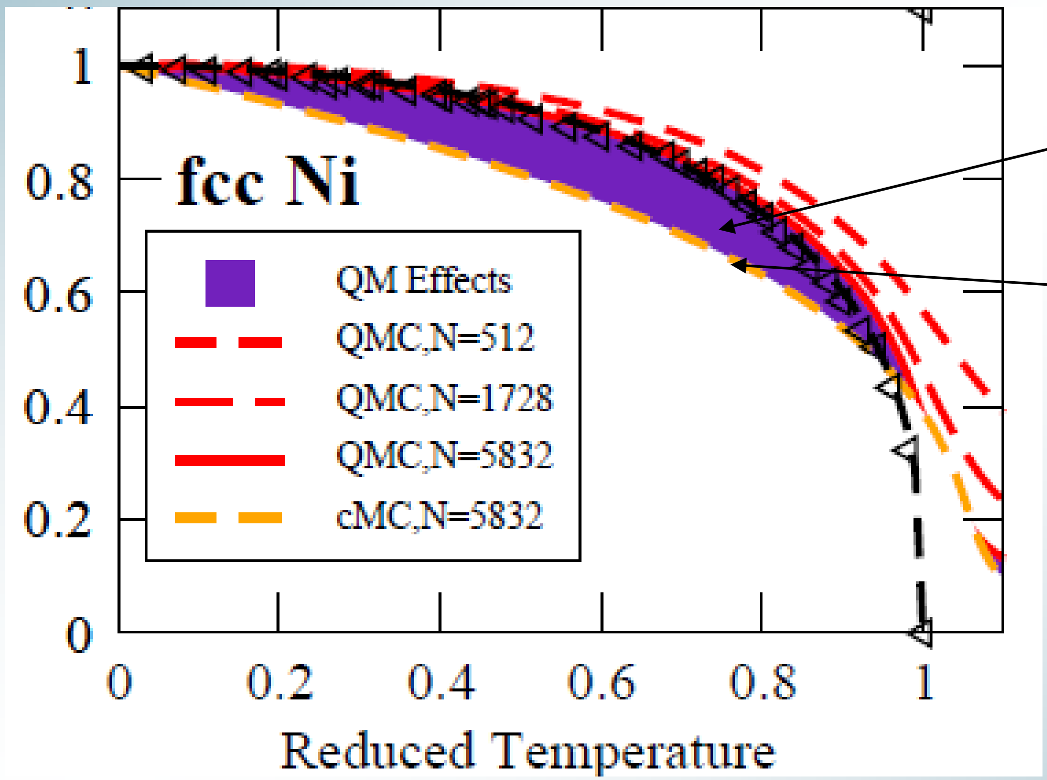
Specific heat



Free energy contributions well captured by PBE-DFT
→ accurate description even of highly sensitive quantities such as c_p

Magnetization curves

Reduced magnetic moment of other transition metals



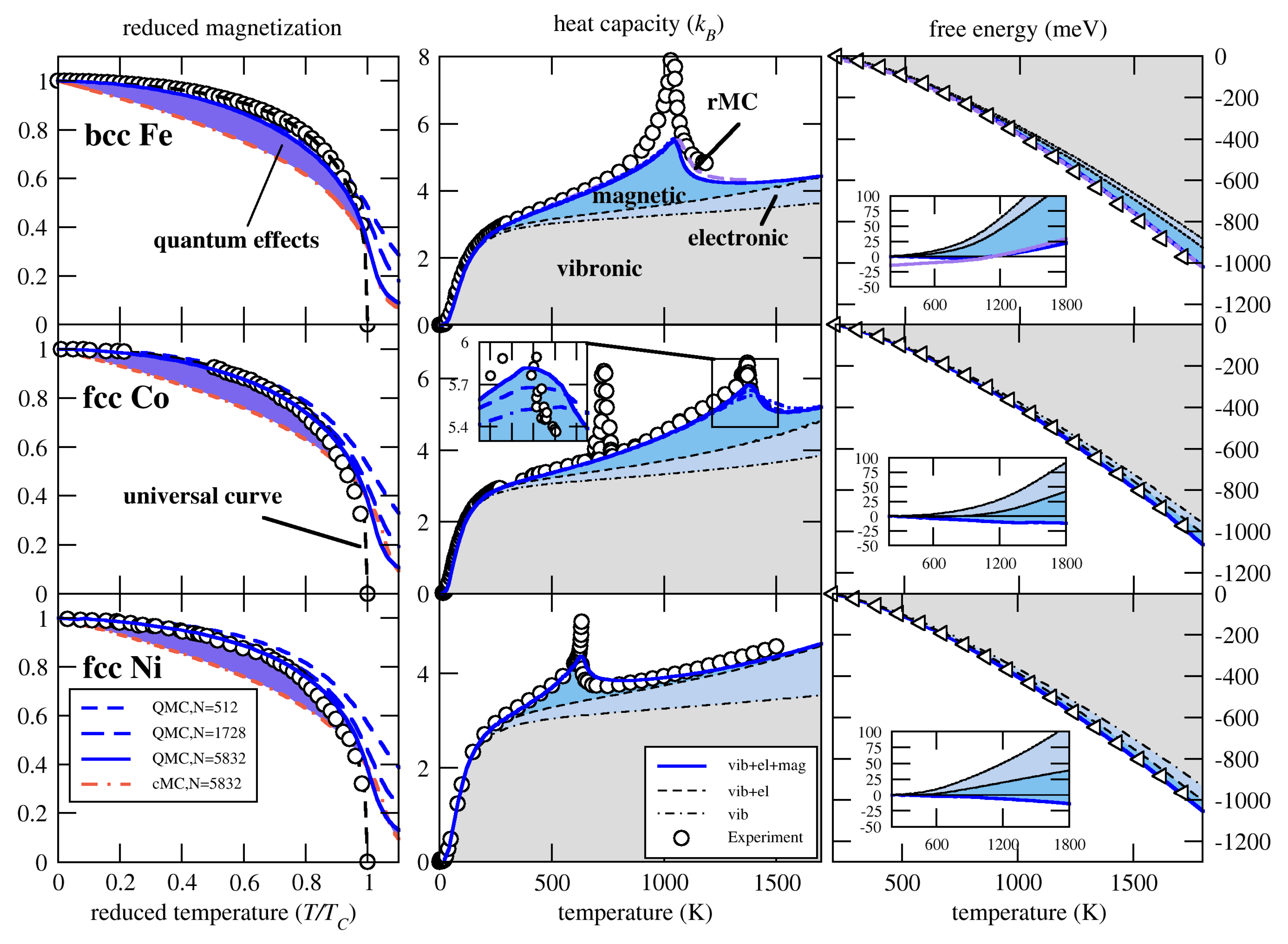
spin quantum effects

classical solution (no spin discretization)

Spin QMC calculations of effective Heisenberg Hamiltonian allow ab initio description of magnetization curves of real materials (long range frustrated interactions)

→ Hitherto achievable only by empirical (fitted) relations

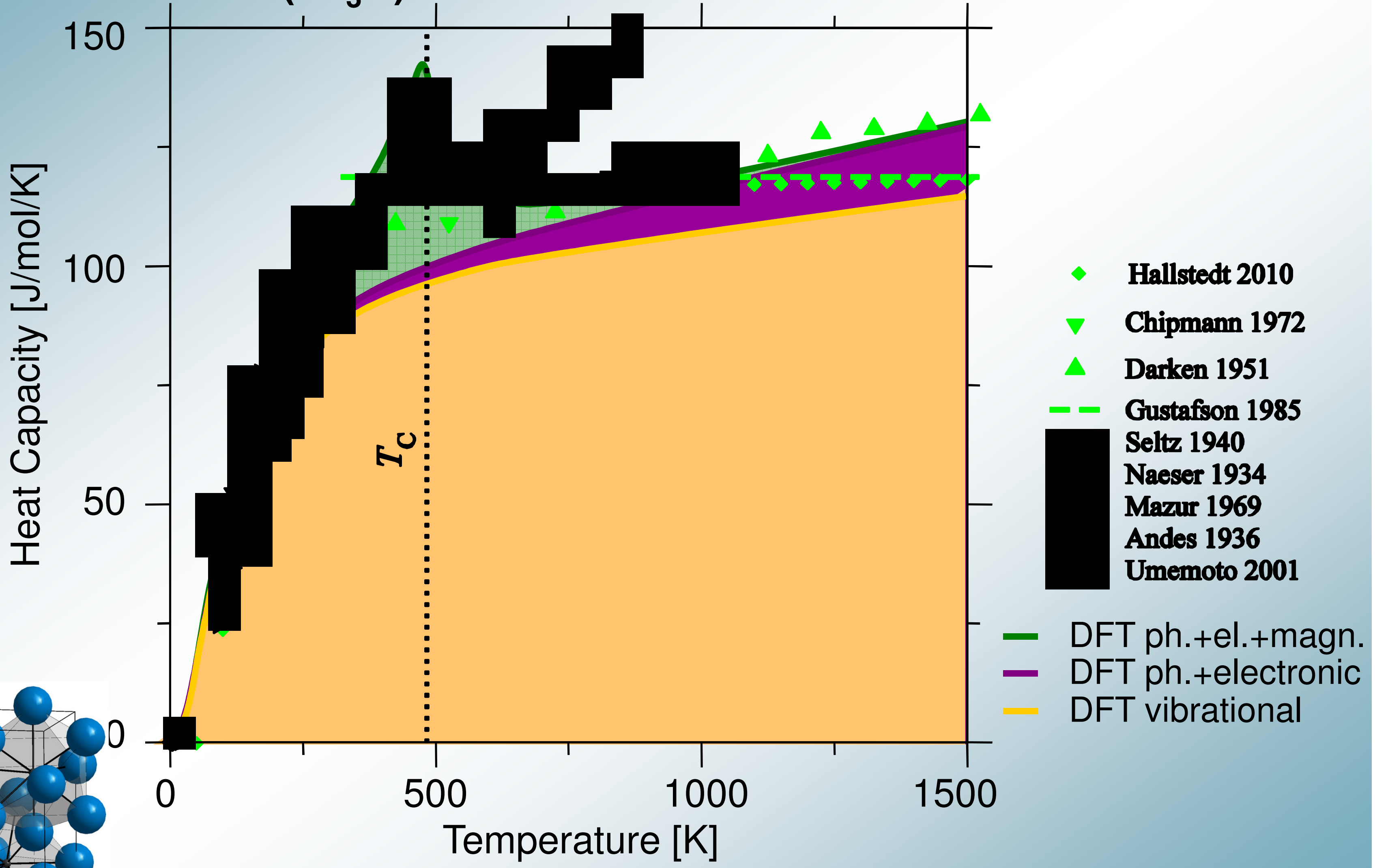
Magnetization, heat capacity, free energies

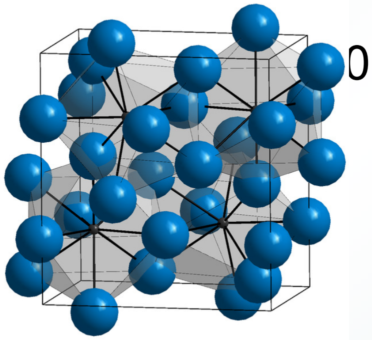


F. Körmann, A. Dick, T. Hickel, and J. Neugebauer, Phys. Rev. B 83, 165114 (2011)

Heat capacity of alloys

Example: Cementite (Fe_3C)





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

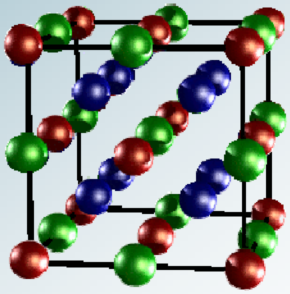
Ab initio thermodynamics

Newly developed approaches allow to systematically improve performance of DFT to describe finite temperature properties

Accuracy often exceeds calorimetric experimental data

→ Provide excellent basis to compute thermodynamic data

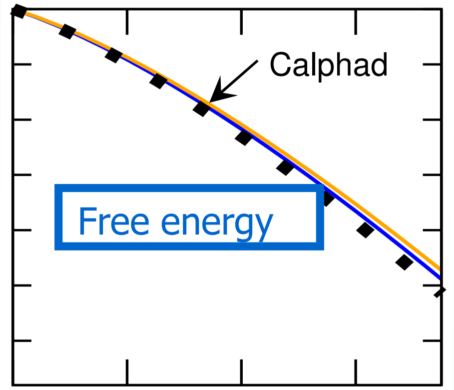
“Genome”



$\left\{\vec{R}_I, Z_I\right\}$

ok

Ab initio thermodynamics



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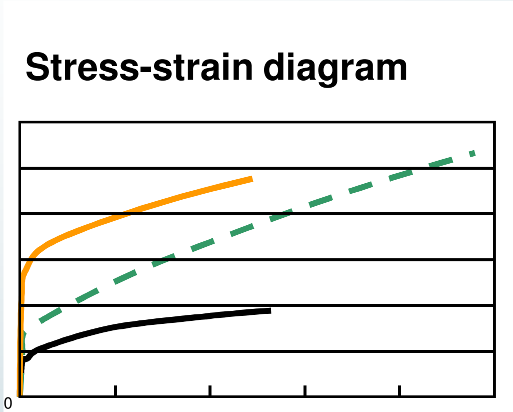
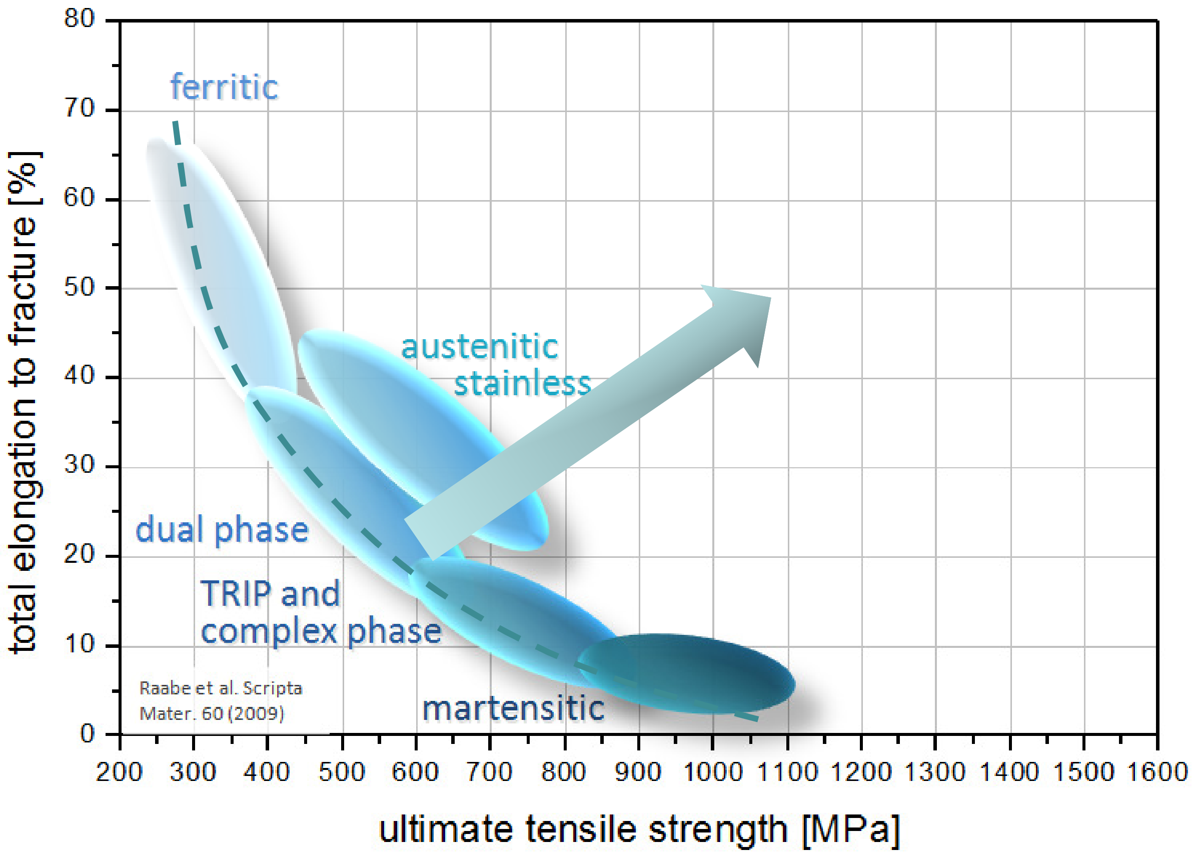
Engineering properties



Applications

Designing high strength steels

Why do we need new steel grades?



Raabe et al. Scripta Mater. 60 (2009)

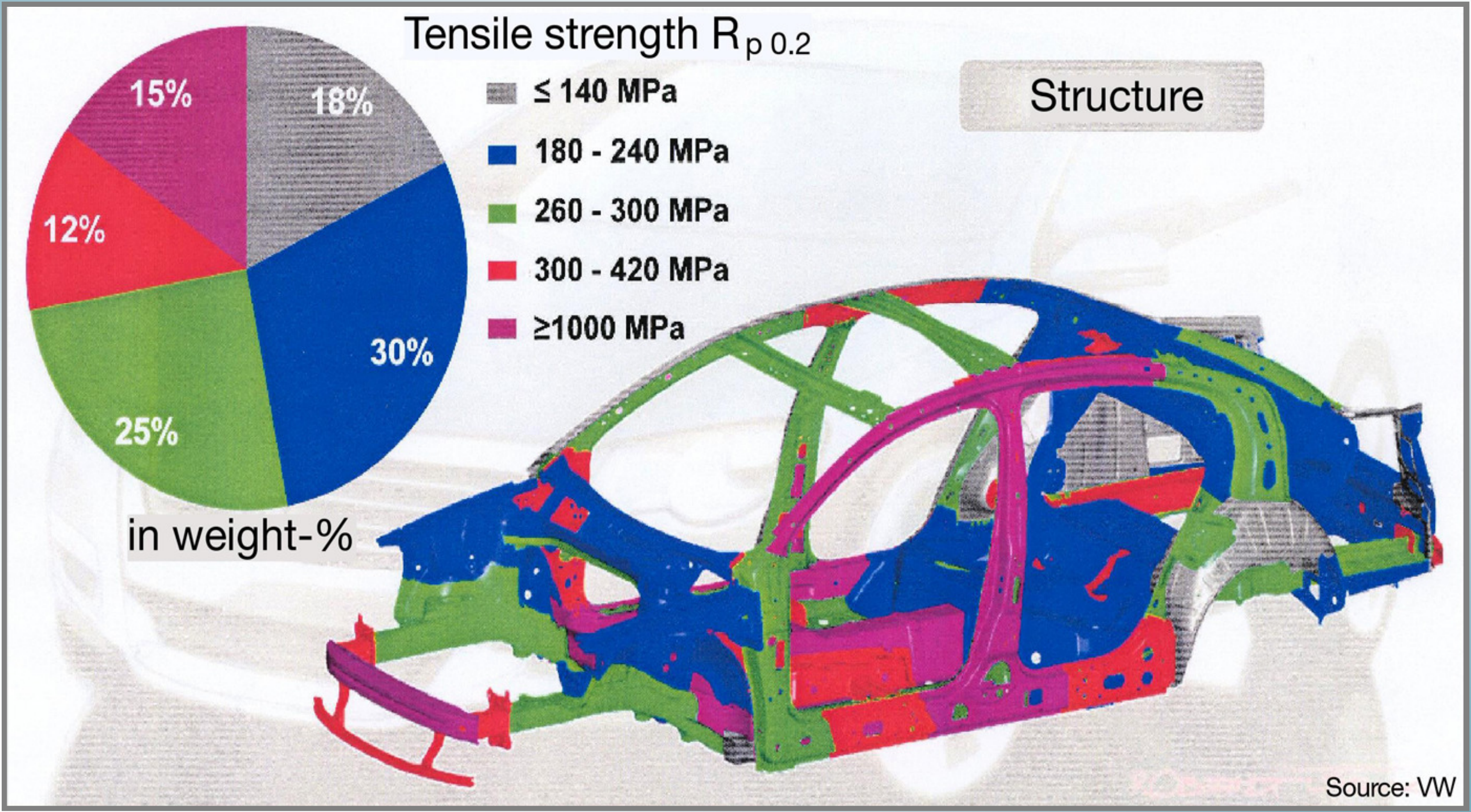
Key challenge of structural materials design:

→ Inverse strength-ductility relation

Development of Novel Steels

Steel Innovations in Cars: The New VW Passat is Leading

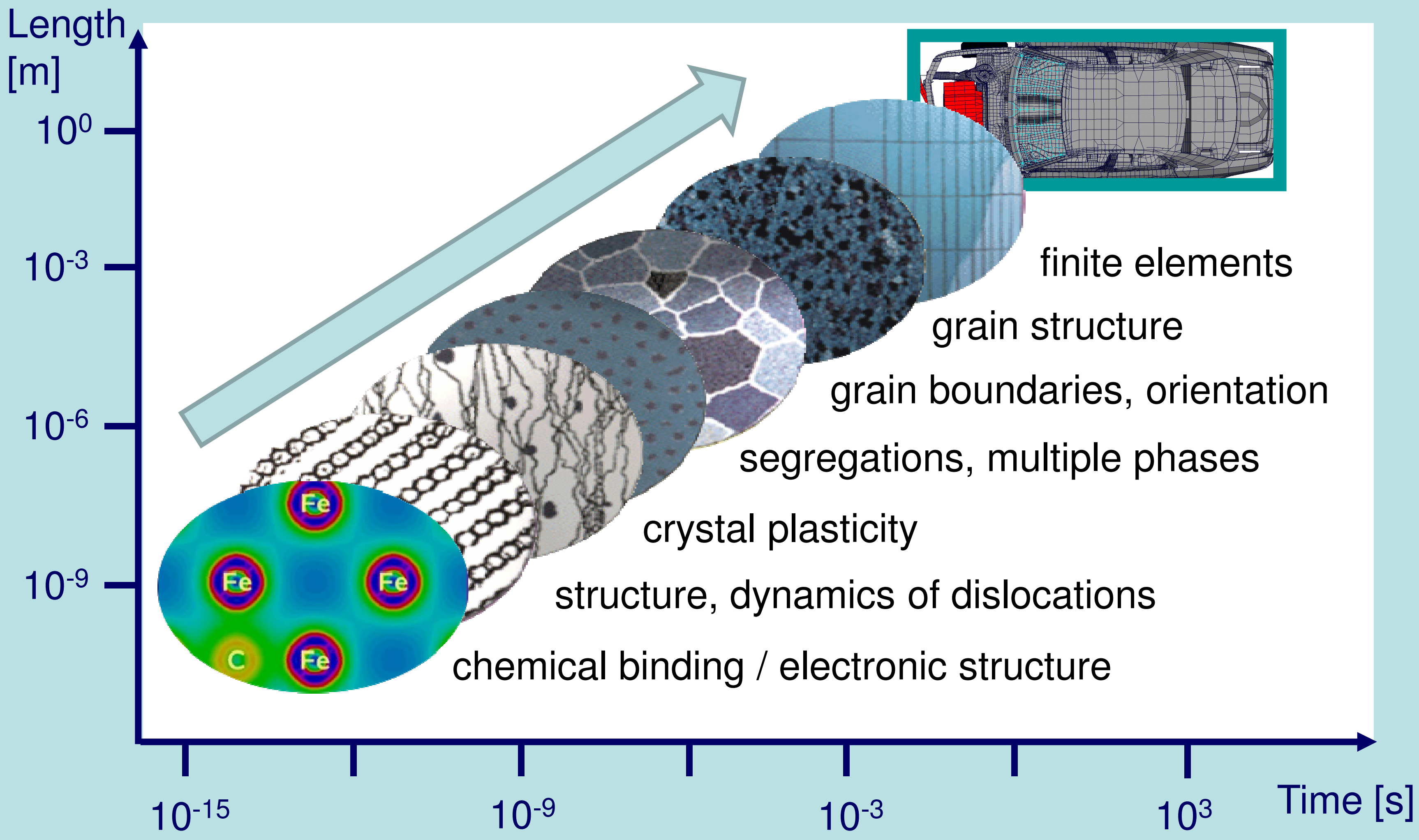
Load optimised use of steel (grades)



Source: VW

Challenges

Hierarchical nature of structural materials



finite elements

grain structure

grain boundaries, orientation

segregations, multiple phases

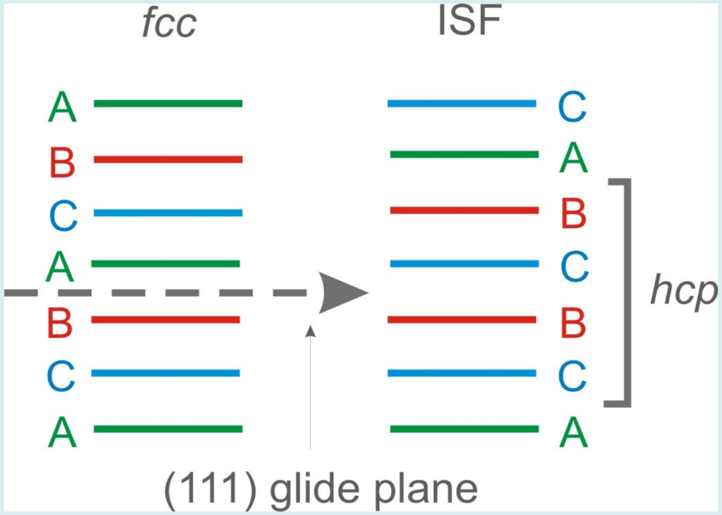
crystal plasticity

structure, dynamics of dislocations

chemical binding / electronic structure

Designing high-strength steels

Stacking Fault Energy



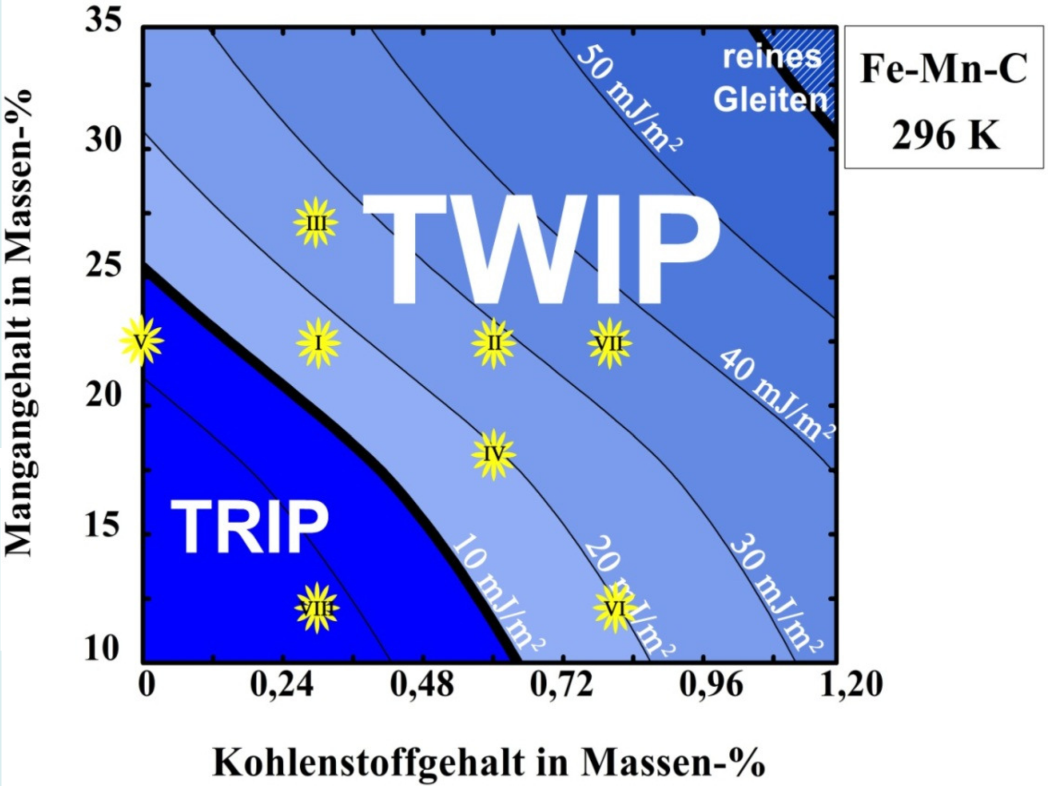
free energy difference fcc/hcp

$$\gamma = 2\rho\Delta G^{\gamma\to\varepsilon} + 2\sigma^{\gamma\to\varepsilon}$$

interface energy

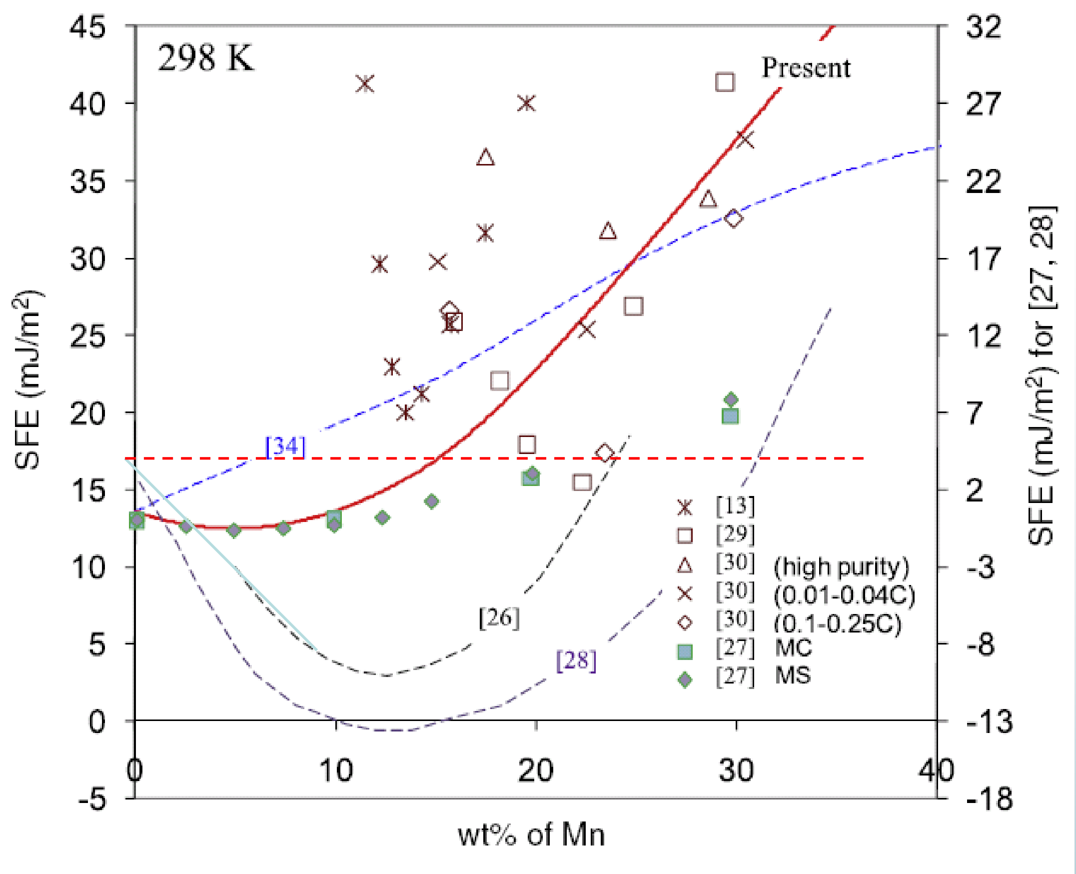
molar surface density

intrinsic SFE



Experiment

Stacking fault energies



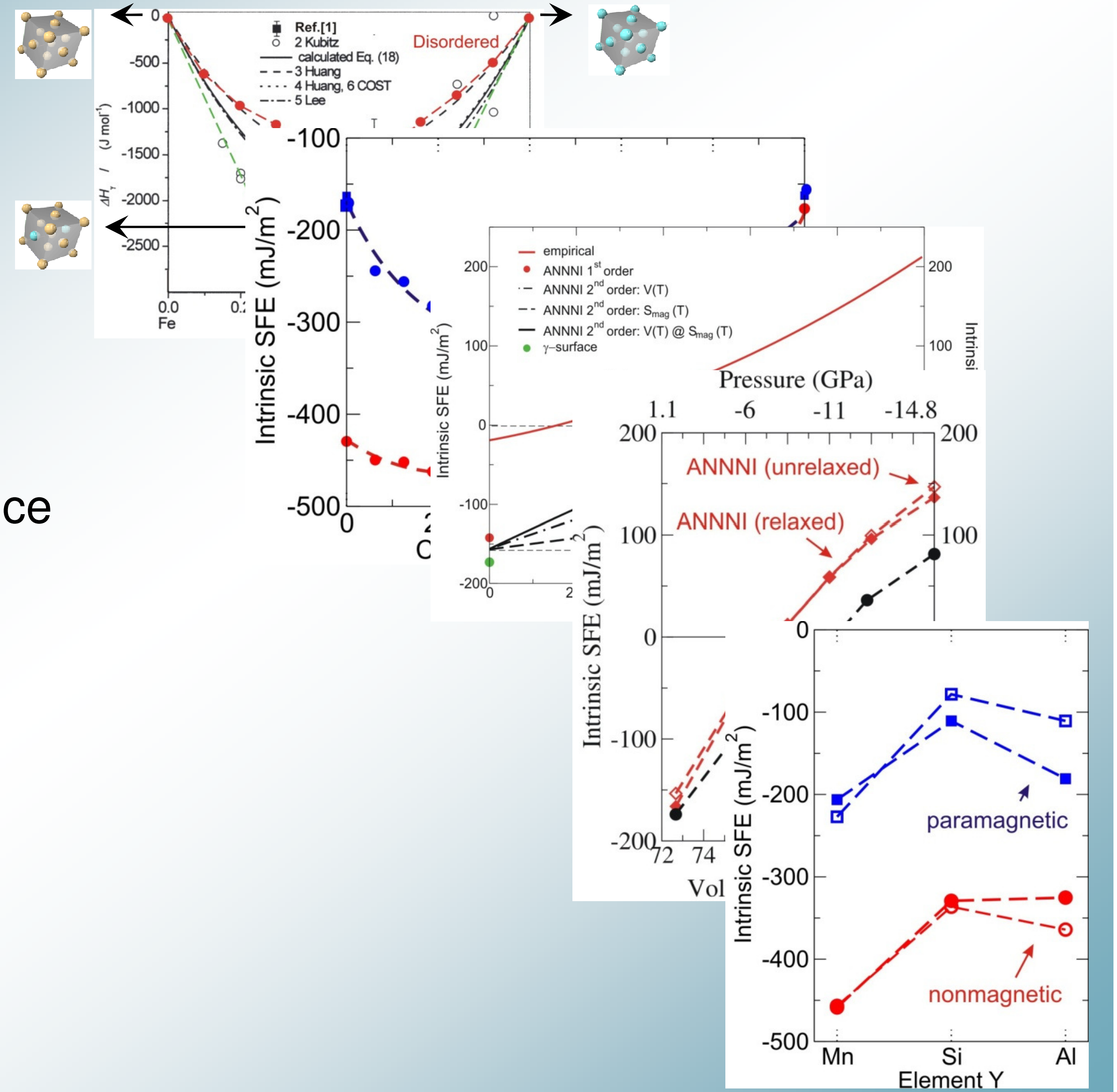
Stacking fault energies are experimentally hard to assess

→ not even qualitative trends can be derived

Figure from: J. Nakano and P. J. Jacques, CALPHAD 34 (2010) 167

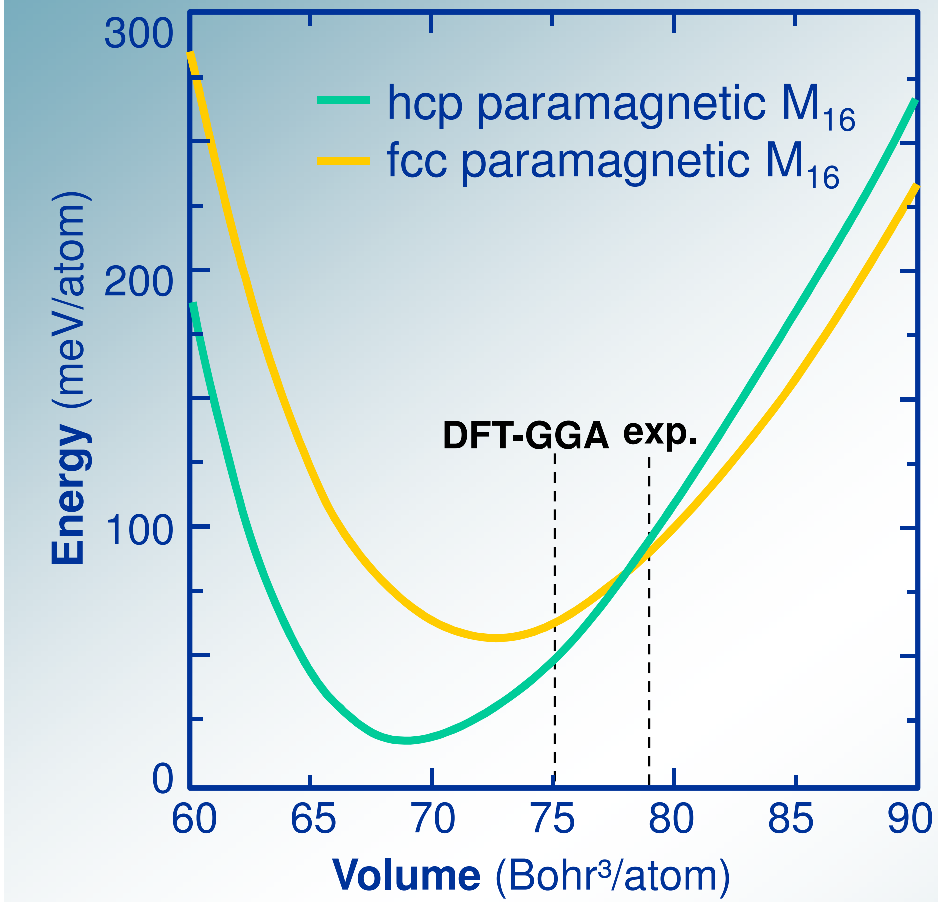
Fully *ab initio* description of the SFE

- → Atomic order/disorder
- → Magnetism
- → Temperature dependence
- → Volume/strain
- → Chemical alloying



Combination of DFT and CALPHAD

Volume dependence for pure iron



Ab initio approach:

$$\gamma = \frac{2\Delta G^{\gamma\to\varepsilon}}{\rho}$$

- ➢ Both phases at *same* volume
- ➢ No empirical parameters

CALPHAD approach to SFE:

$$\gamma = \frac{2\Delta G^{\gamma\to\varepsilon}}{\rho} + 2\sigma^{\gamma\to\varepsilon}$$

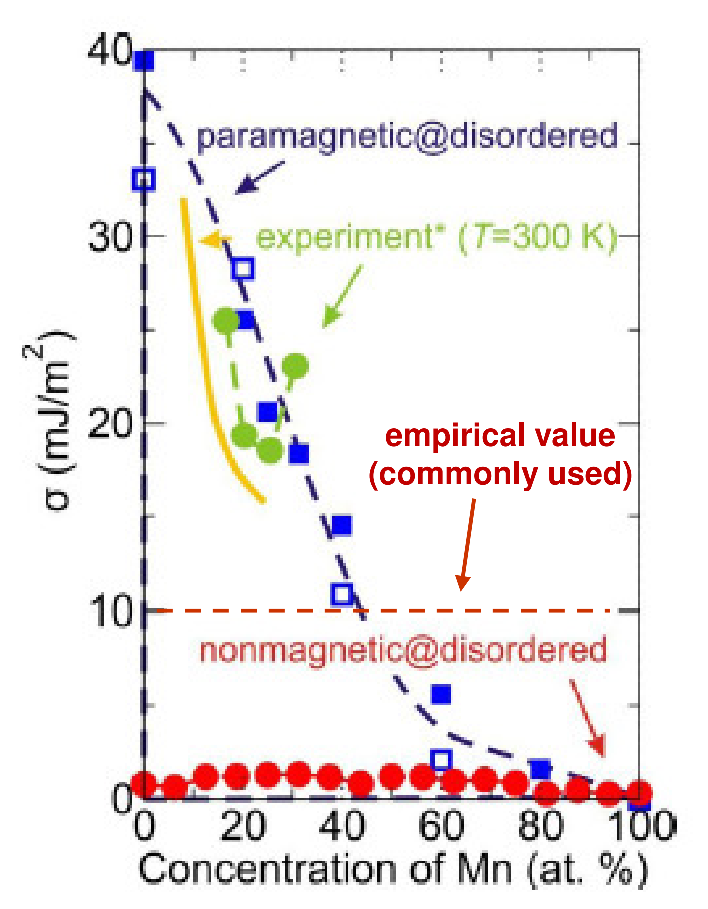
- ➢ Both phases at *equilibrium* volume
- ➢ Unknown empirical parameter σ

Combination:

$$\sigma^{\gamma\to\varepsilon} = \frac{\gamma}{2} - \frac{\Delta G^{\gamma\to\varepsilon}}{\rho}$$

Ab initio determination of the SFE

Determination of the interface energy σ



Conventional approach:

$$\gamma = 2\rho\Delta G^{\gamma\to\varepsilon} + 2\sigma^{\gamma\to\varepsilon}$$

interface energy

→ fitting parameter

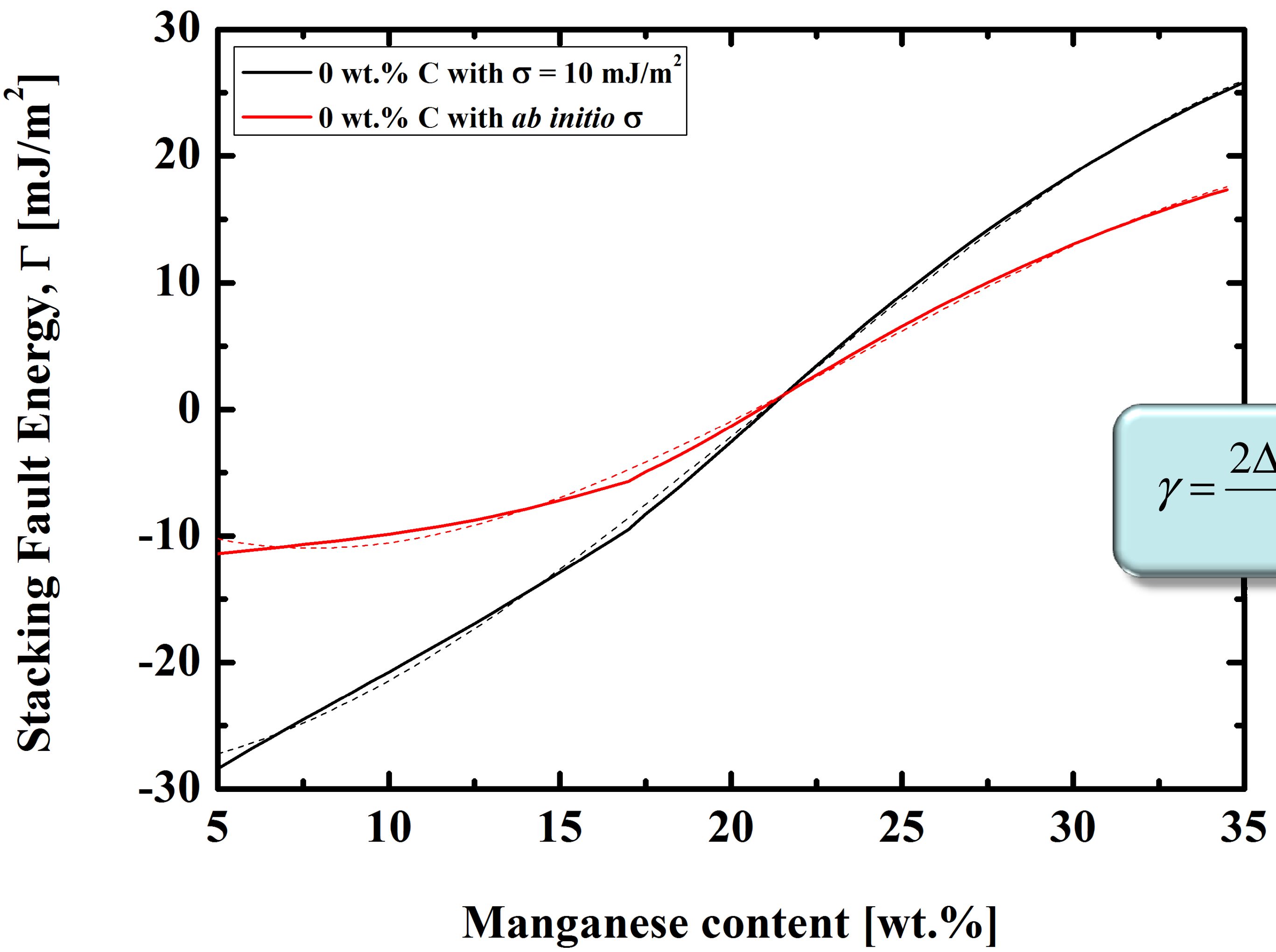
CALPHAD

molar surface density

Ab initio determination

- → **allows assessment of exp. data**
- → **provides insight into relevant mechanisms**
- → **determination of other dependencies, e.g., temperature, pressure, impurities**

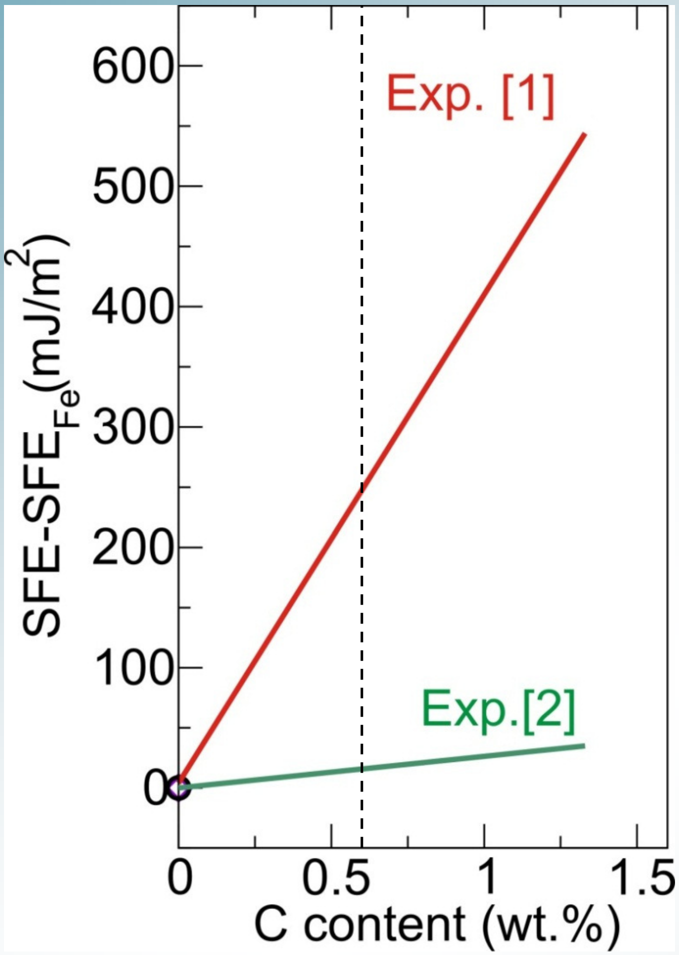
Consequences for SFE



$$\gamma = \frac{2\Delta G^{\gamma\rightarrow\varepsilon}}{\rho} + 2\sigma^{\gamma\rightarrow\varepsilon}$$

Alireza Saeed-Akbari (RWTH Aachen IEHK)

Effect of C on the SFE



- Discrepancy between experiments

[1] R.E. Schramm and R.P. Reed, Metall. Mater. Trans. A **6**, 1345 (1975)
[2] P.J. Brofman and G.S. Ansell, Metall. Trans. A **9**, 879 (1978)

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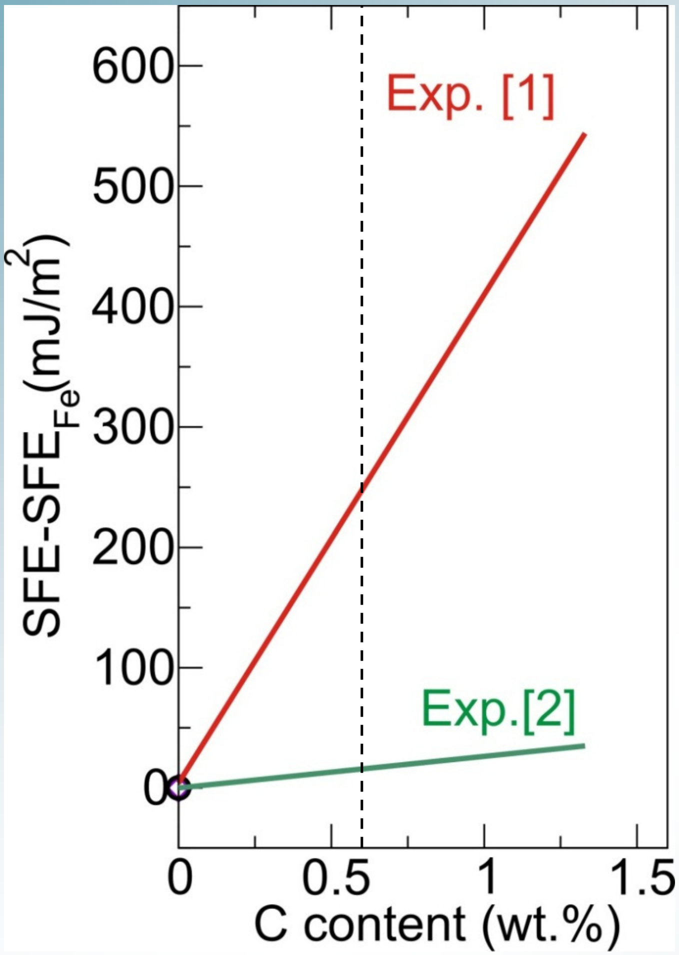

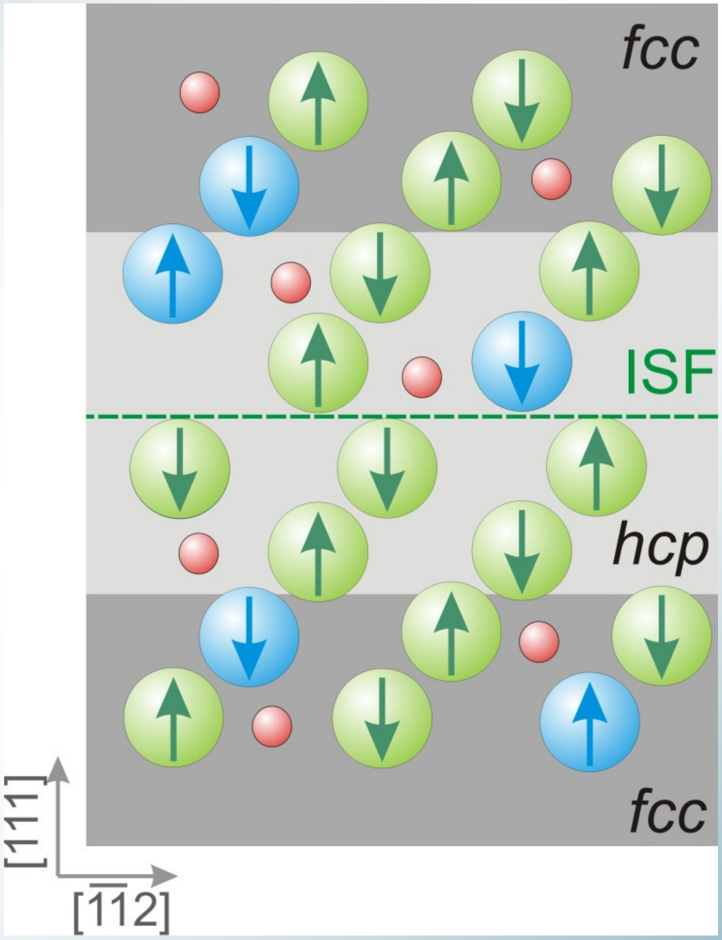

- Discrepancy between experiments
- Simulate different scenario

[1] R.E. Schramm and R.P. Reed, Metall. Mater. Trans. A **6**, 1345 (1975)
[2] P.J. Brofman and G.S. Ansell, Metall. Trans. A **9**, 879 (1978)

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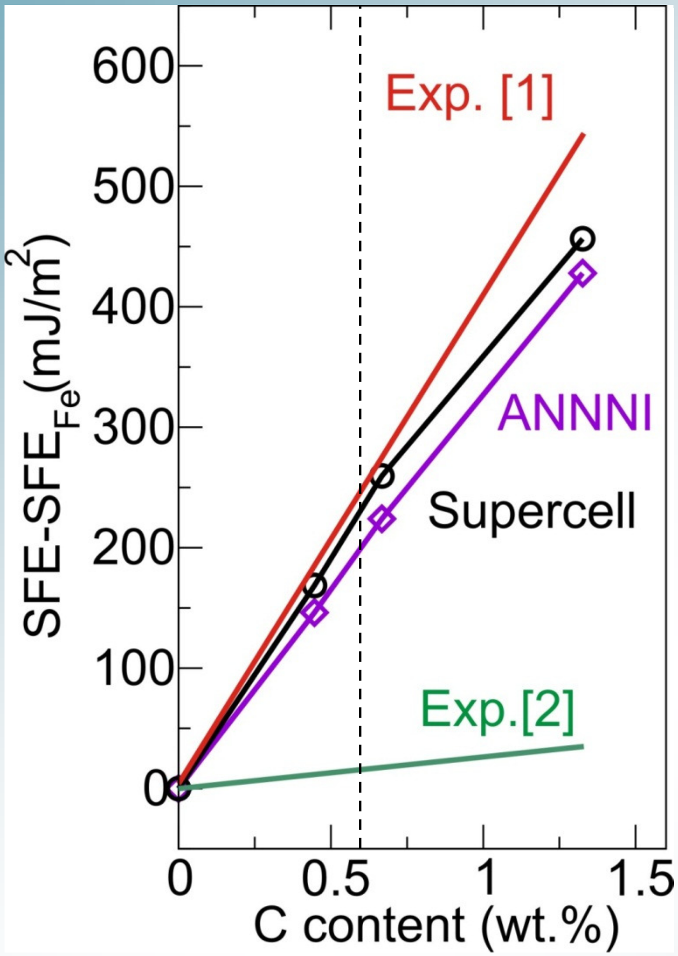

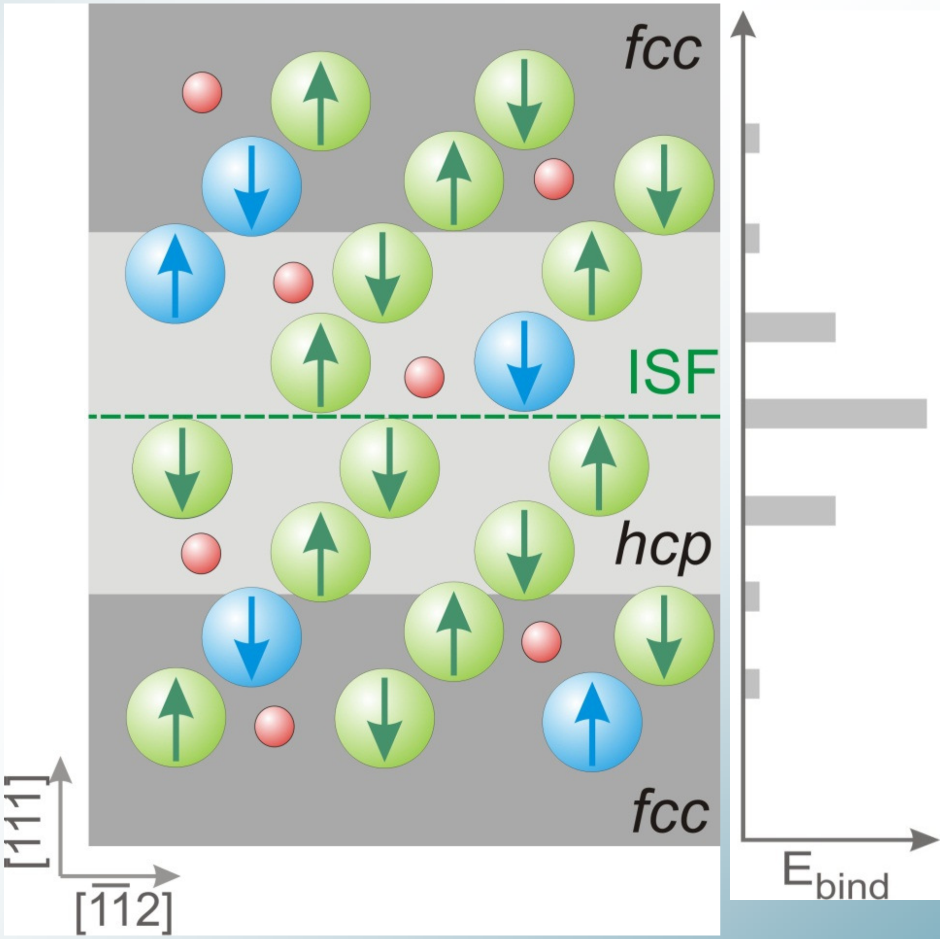

- Case one – homogeneous distribution of C-atoms
- Reproduce Exp.[1] (XRD-experiments)

[1] R.E. Schramm and R.P. Reed, Metall. Mater. Trans. A **6**, 1345 (1975)
[2] P.J. Brofman and G.S. Ansell, Metall. Trans. A **9**, 879 (1978)

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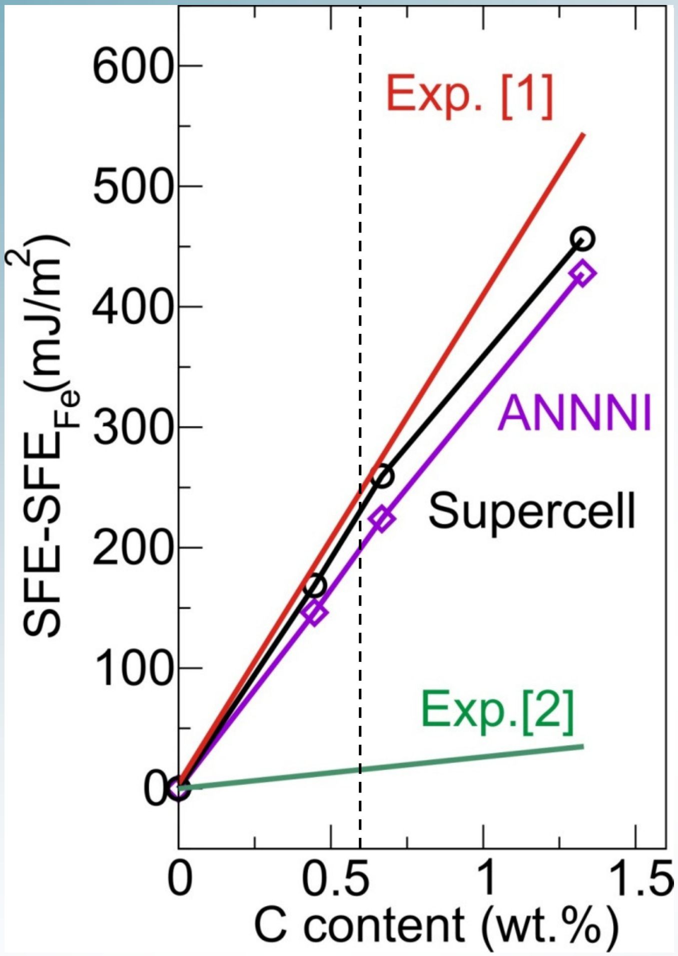

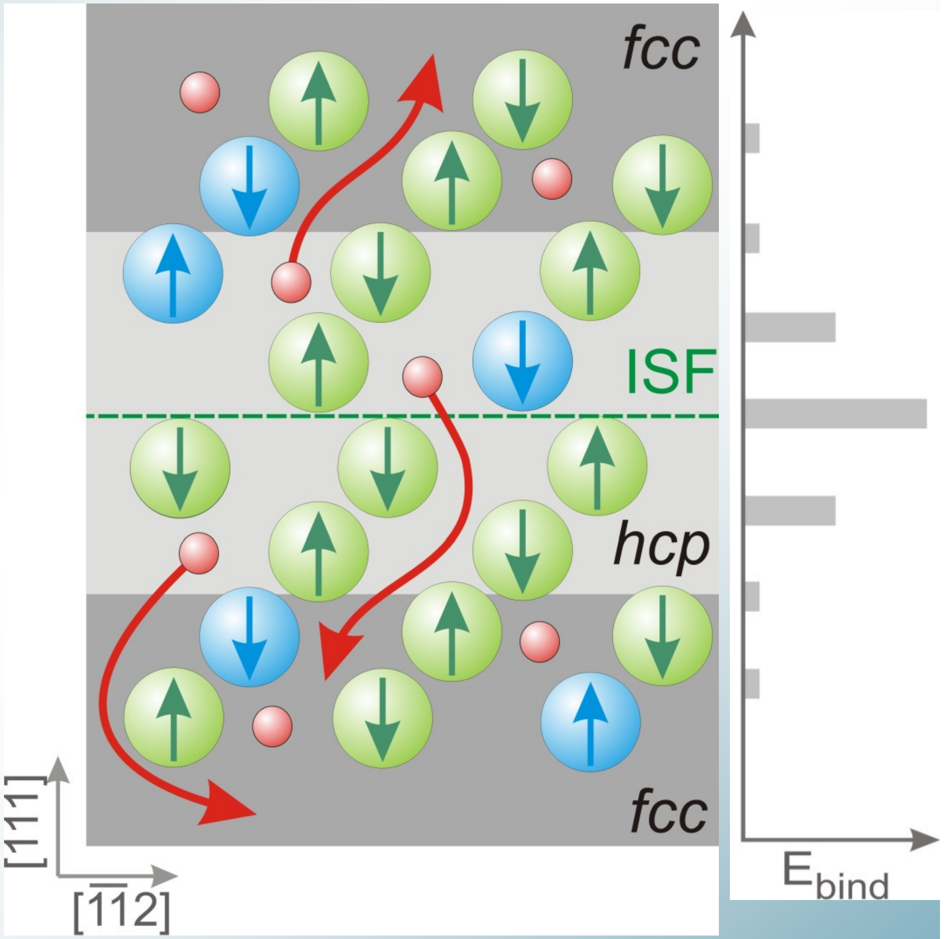

- Case one – homogeneous distribution of C-atoms
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A. Abbasi, A. Dick, T. Hickel, and J. Neugebauer, Acta Mat., (2011) accepted

[1] R.E. Schramm and R.P. Reed, Metall. Mater. Trans. A **6**, 1345 (1975)
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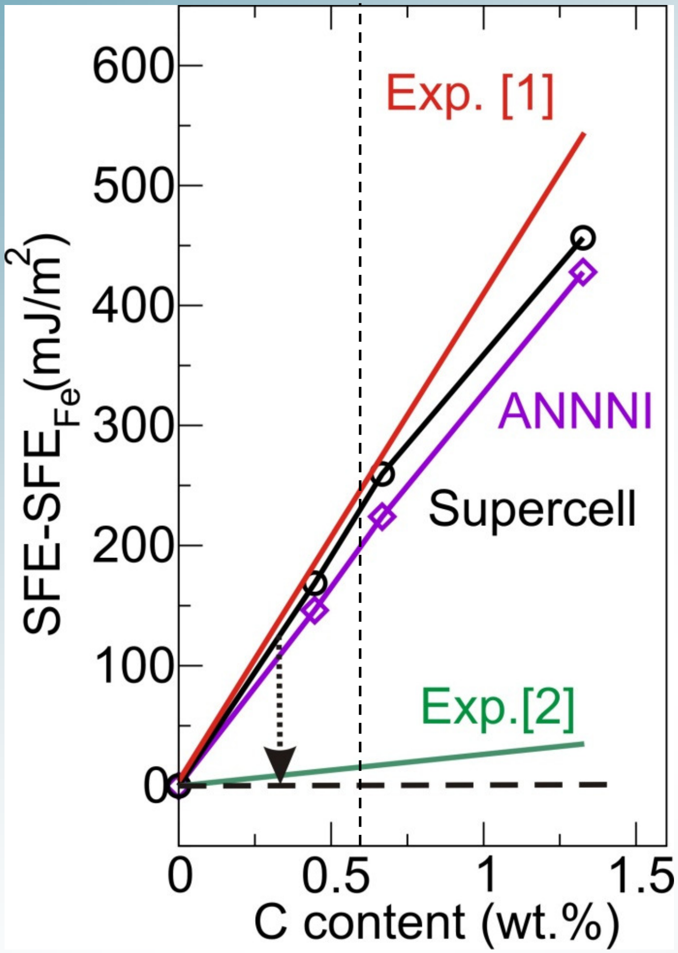
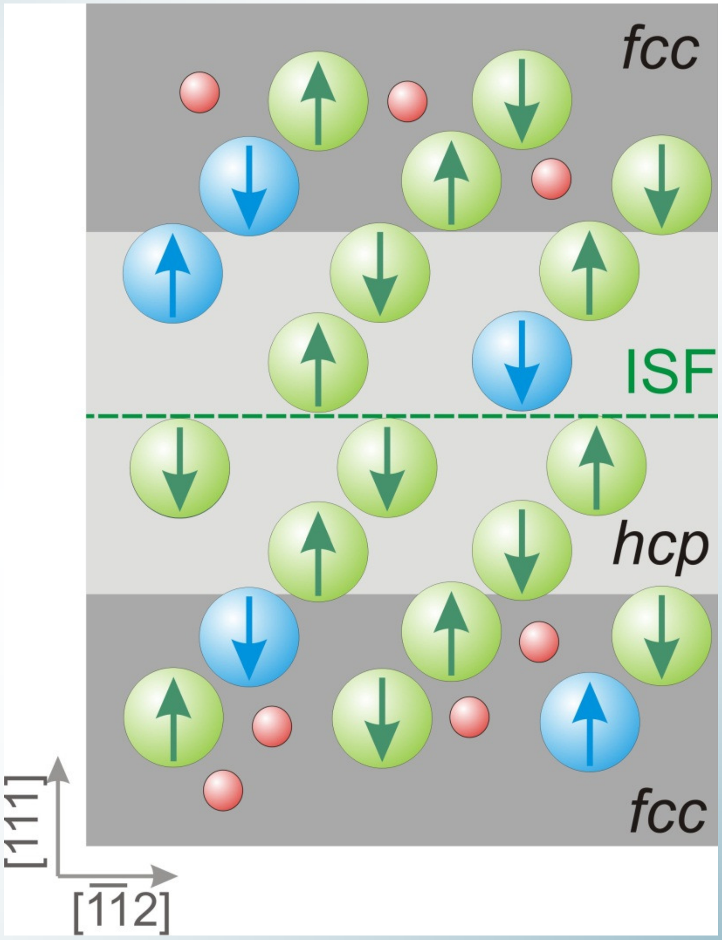
Effect of C on the SFE





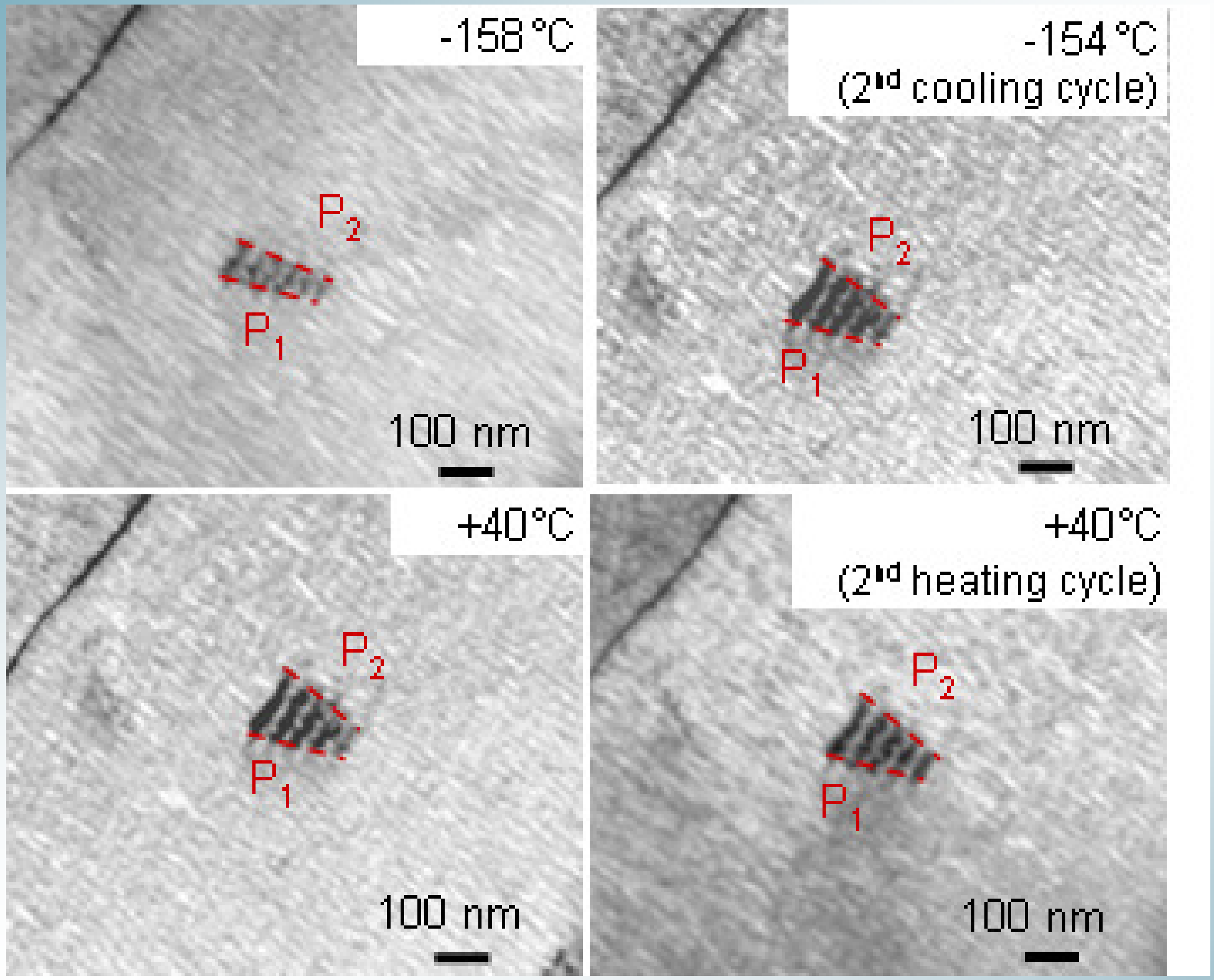
- Case two – defect region is depleted of C-atoms
- Close to Exp.[2] (TEM-experiments)

[1] R.E. Schramm and R.P. Reed, Metall. Mater. Trans. A **6**, 1345 (1975)
[2] P.J. Brofman and G.S. Ansell, Metall. Trans. A **9**, 879 (1978)

A. Abbasi, A. Dick, T. Hickel, and J. Neugebauer, Acta Mat. (2011) accepted

Experimental validation: SFE measurements

Verification by TEM (S. Sandlöbes and D. Raabe):



Sample:

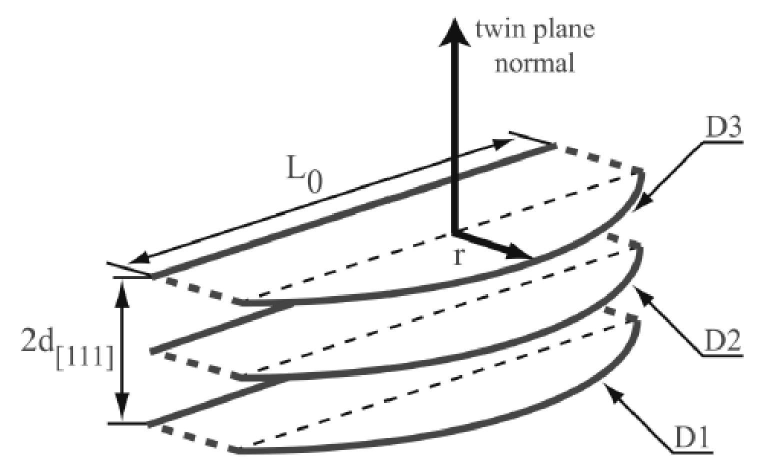
Fe-22Mn-0.6C

From ab initio SFEs to hardening curves

Constitutive model [1]:

→ twin volume and three kinds of vacancies used as state variables

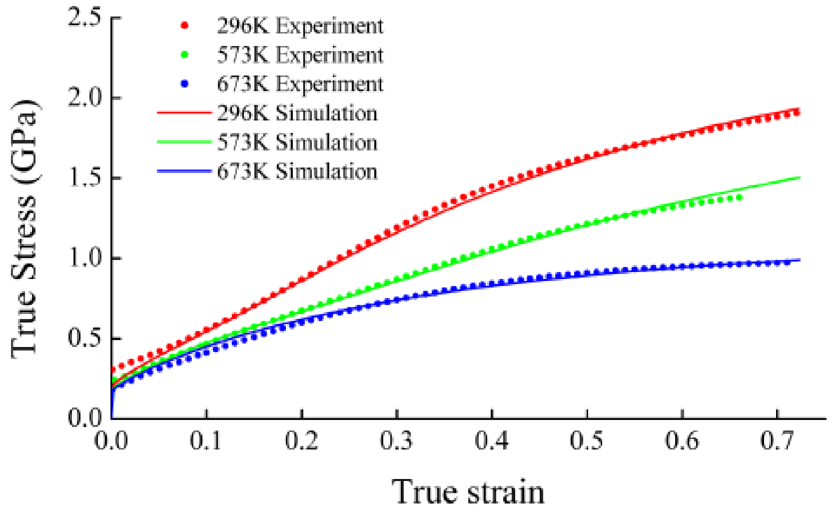
→Twin-nucleation model according to Mahajan and Chin



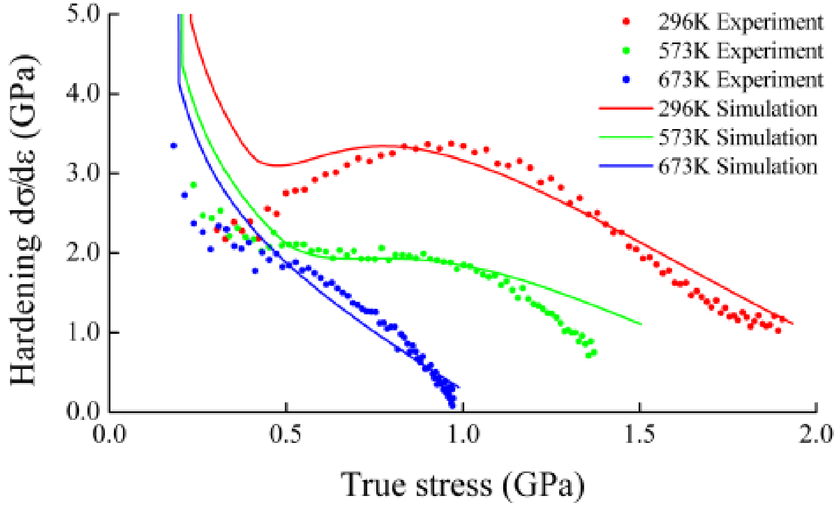
→ Critical twinning stress

$$\tau_{tw} = \frac{\gamma}{3b_s} + \frac{3Gb_s}{L_0}$$

stress-strain curve



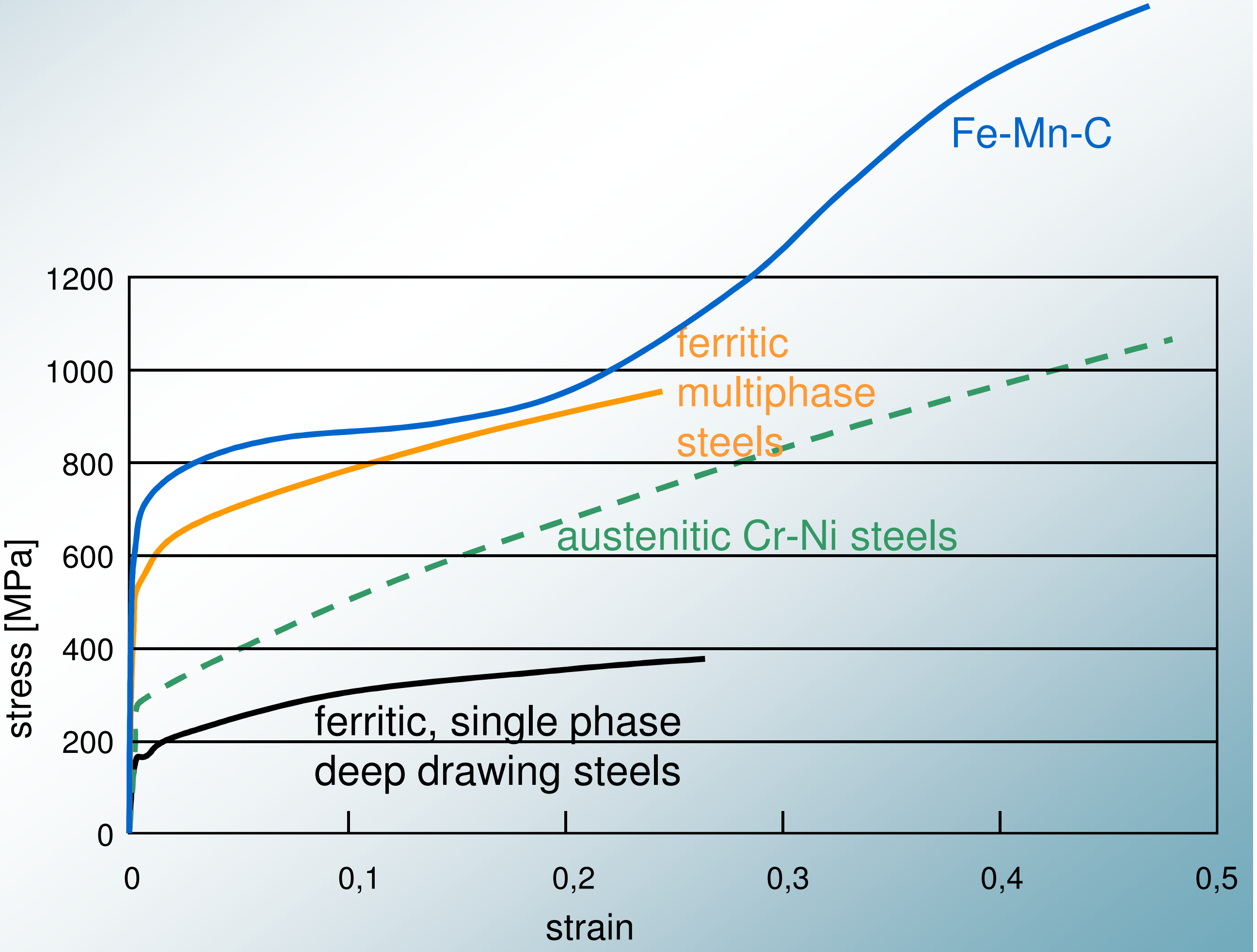
strain-hardening



[1] Steinmetz, Roters, Raabe, et. al. 2011

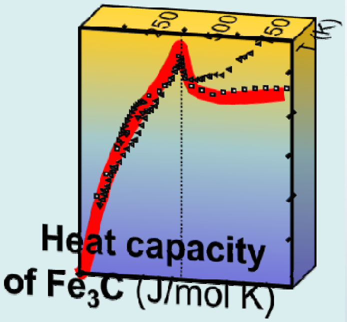
Application of these concepts

Development of a new generation of high-strength steels:



Conclusions

Modern ab initio calculations are no longer restricted to T=0K and ground states

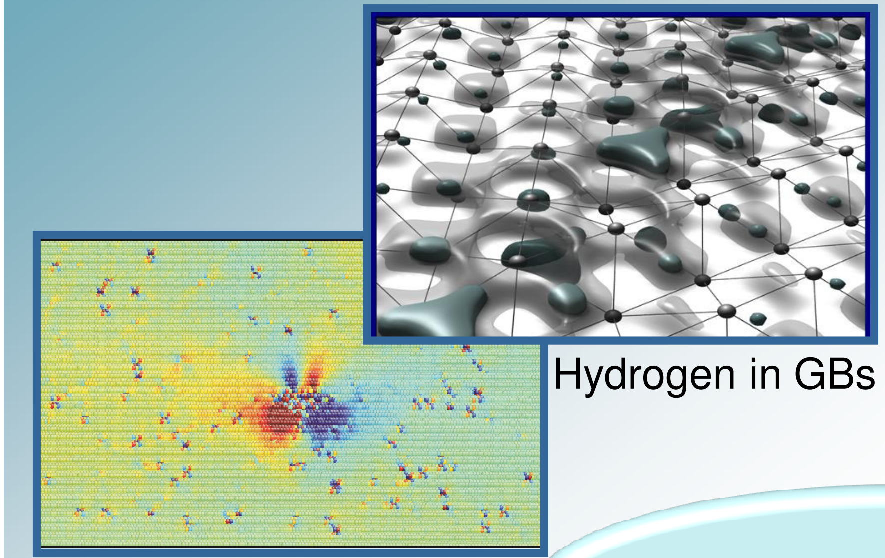


→ **Newly developed approaches allow accurate computation of excitation mechanisms, free energies, heat capacities, phase transitions**

→ **DFT calorimetric data often provide accuracy that is higher then exp.**

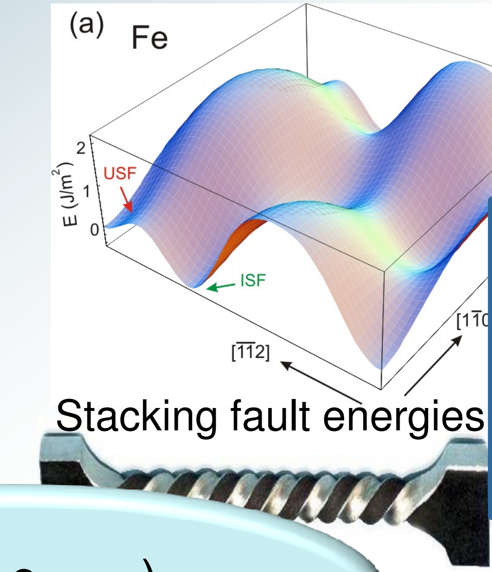
→ **provide important first step to relate fully ab initio the materials genome to macroscopic properties**

Conclusions

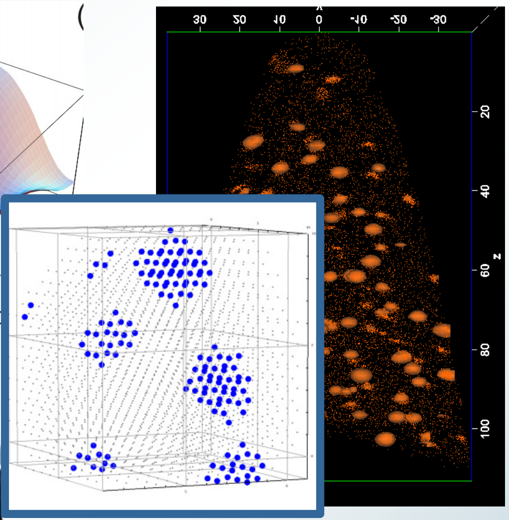


Hydrogen in GBs

Hydrogen embrittlement

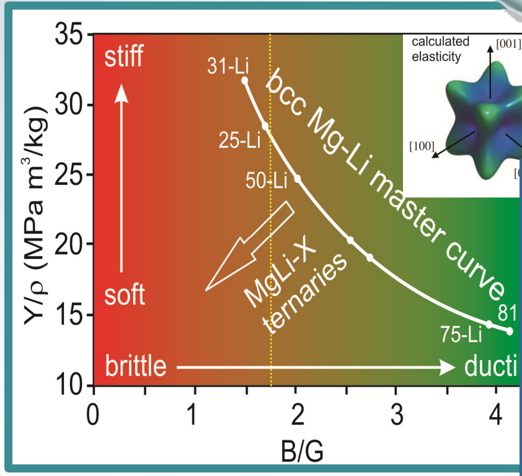


Stacking fault energies

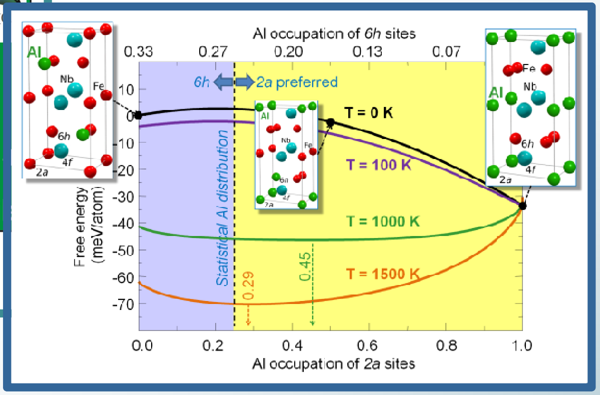


Precipitation kinetics

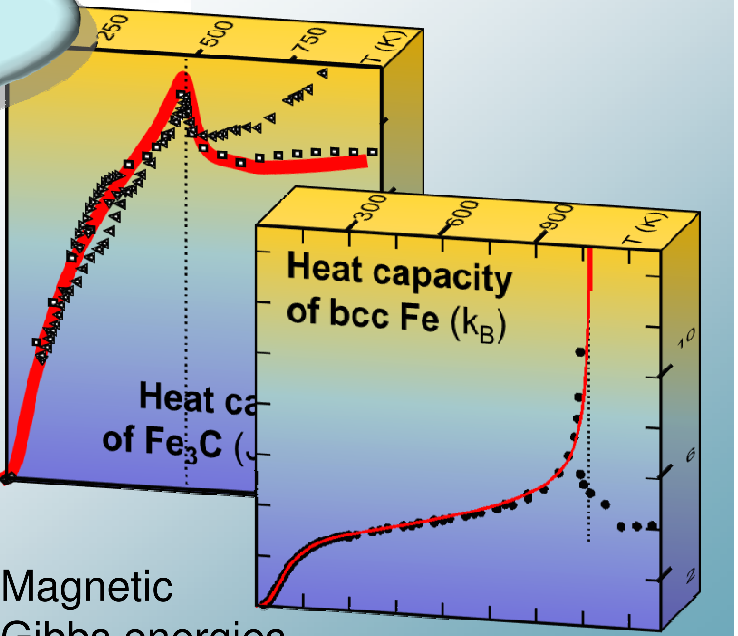
$F(V,T,c_{\alpha}, \ldots)$



Alloy design



High-temperature steels



Magnetic Gibbs energies

Thanks to the department


CM Department (2011)

Thanks for your attention