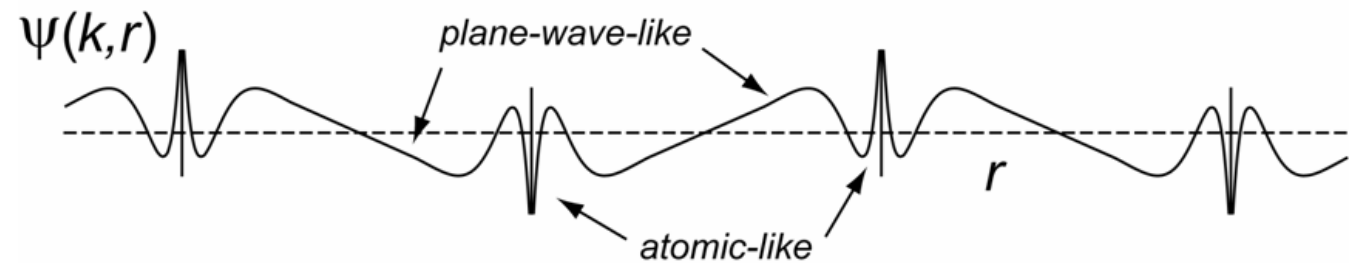


ab initio Thermochemistry

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First principles simulations and standard thermochemical data

Application to the High Temperature Superconductor $YBa_2Cu_3O_{6+x}$

Starting from the beginning: *ab initio*

Aim of Quantum Chemistry: Solution of Schrödinger's Equation

$$\hat{H}\Psi = E\Psi$$

for molecular and crystalline systems

Cannot be solved exactly for systems with more than one electron

→ approximations (e.g. Hartree-Fock, DFT)

Solid state quantum chemistry:

→ **Density functional theory (DFT)**

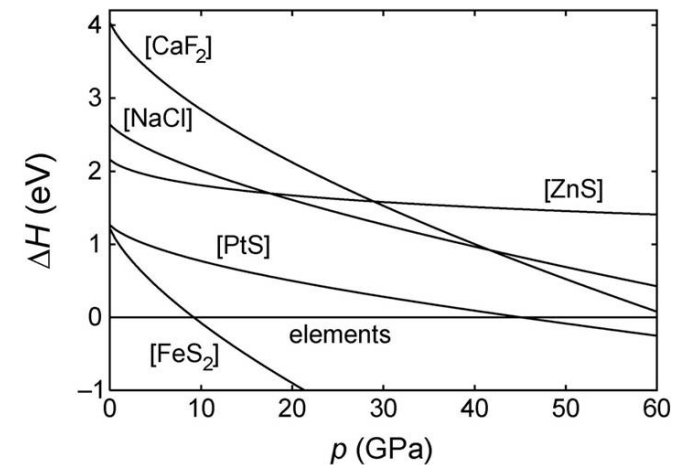
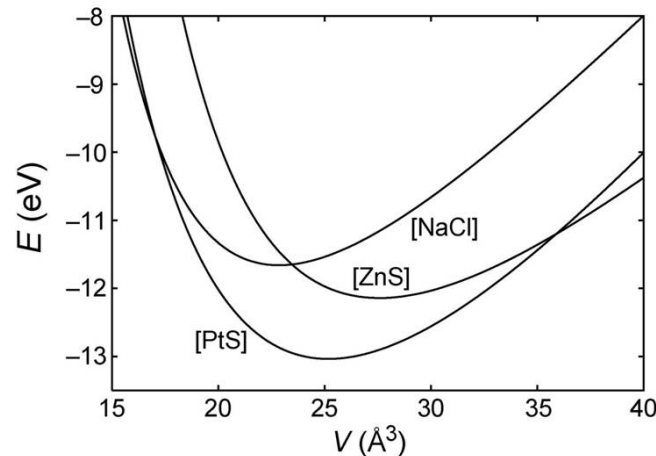
→ electronic band structures and energies, crystal structures, forces etc.

Theoretical Calculation of Enthalpies

Standard density-functional total-energy calculations give access to the total electronic ground state energy at 0 K, $E_{\text{tot}} \approx U$

$$E-V \text{ diagrams} \Rightarrow p = -\frac{\partial E}{\partial V} \Rightarrow H = E + p \cdot V \Rightarrow \Delta H(p)$$

Example:
Platinum Nitride



- stability of solid compounds / different structure types
- prediction of high-pressure phases
- up to this point: *Temperature* neglected

How to deal with temperature?

Main effect of temperature: *Vibrations*

Other contributions: electronic excitations, configurational entropy

ab initio methods involving Temperature:

- Molecular Dynamics (MD), Monte Carlo (MC),
- Simulation of *lattice vibrations* (*Phonons*), assuming harmonic oscillator scenario
 - Mostly used: Direct Method
 - Programs: *PHONON*, *FROPHO* (in combination with electronic structure programs, e.g. *VASP*)

Gibbs free energy from lattice vibrations

Calculations are carried out at const. Volume (relaxed structure)

$$G(p, T) = F(T, V) + pV = F(T, V) - \left(\frac{\partial F}{\partial V} \right)_T \cdot V$$

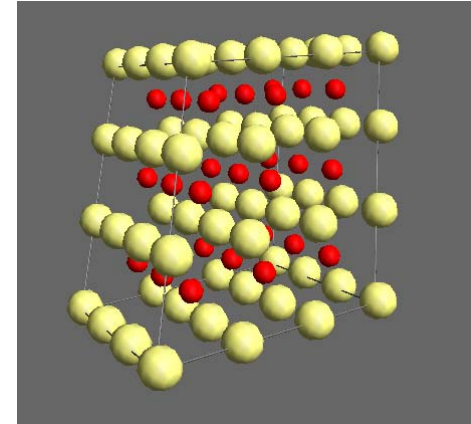
$$F(T, V) = \underbrace{E_{\text{tot}}(V) + F_{\text{ph}}(T, V)}_{\text{main contribution}} + F_{\text{el}}(T, V) + F_{\text{id}} + F_{\text{vib}}^{\text{ah}}(T, V)$$

$F_{\text{ph}}(T, V)$: *phonon free energy* (harmonic vibrational energy)

$$F_{\text{ph}} = \frac{1}{2} \sum_{\vec{k}, \nu} \hbar \omega(\vec{k}, \nu) + k_B T \sum_{\vec{k}, \nu} \ln \left[1 - \exp \left(\frac{-\hbar \omega(\vec{k}, \nu)}{k_B T} \right) \right]$$

we only need to know the *phonon frequencies* ω

Phonon frequencies / Direct Method



supercell method (> 50 atoms, $a > 8 \text{ \AA}$)

Calculation of the Hellmann-Feynman-forces F_α acting on each atom when the other atoms are slightly dislocated (harmonic oscillator)

$$\begin{aligned} \Phi_{\alpha\beta} &= -\frac{F_\alpha}{u_\beta} \\ D_{\alpha\beta}(jj', \vec{k}) &= \frac{1}{\sqrt{m_j m_{j'}}} \sum \Phi_{\alpha\beta} \exp [i\vec{k} (\vec{r} - \vec{r}')] \\ |D_{\alpha\beta}(jj') - \delta_{\alpha\beta} \delta_{jj'} \omega^2| &= 0 \end{aligned}$$

Vibrational frequencies $\omega(k) \Rightarrow F_{\text{ph}}(T, V)$

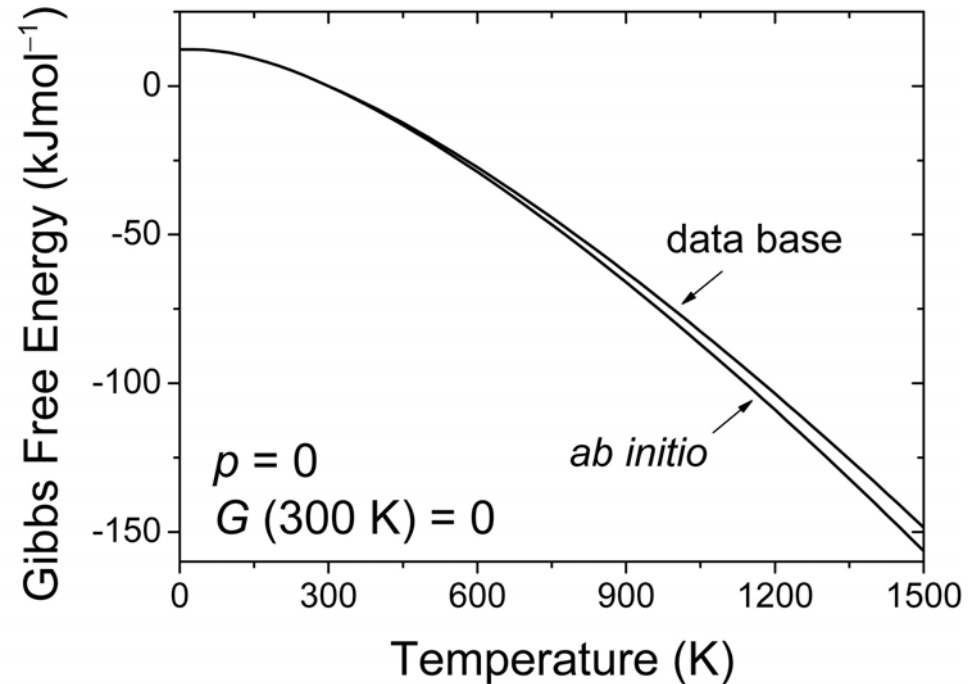
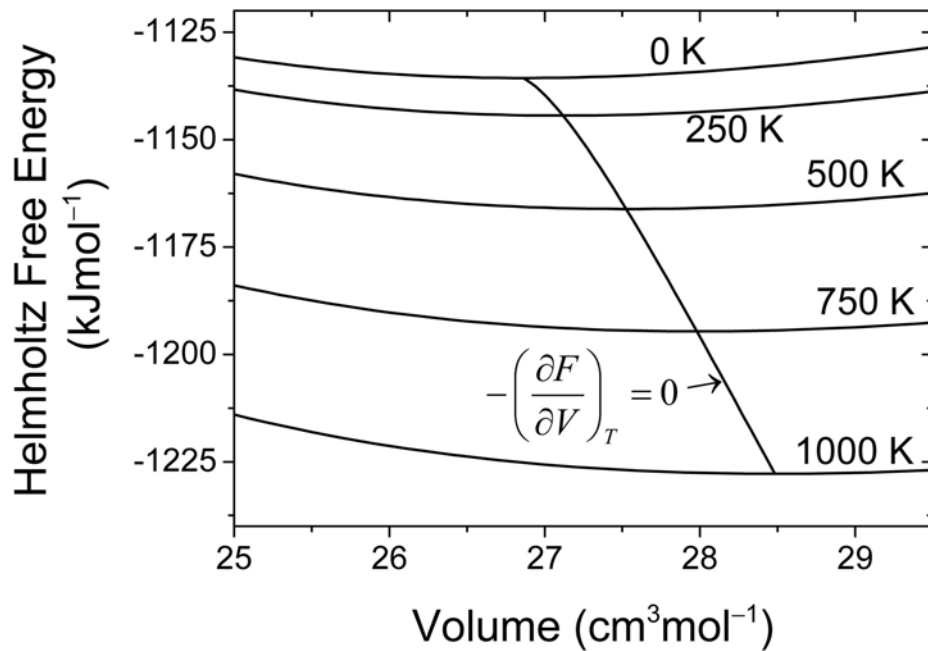
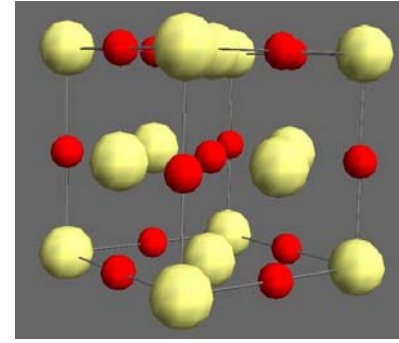
Obtaining the Gibbs Free Energy

(Example: Barium Oxide)

Our calculations result in $F(T)$ at different V

$\Rightarrow F(V)$ at different T

$\Rightarrow G(p, T)$



Handling Pressure & Temperature

Example:

Tantalum oxide nitride:

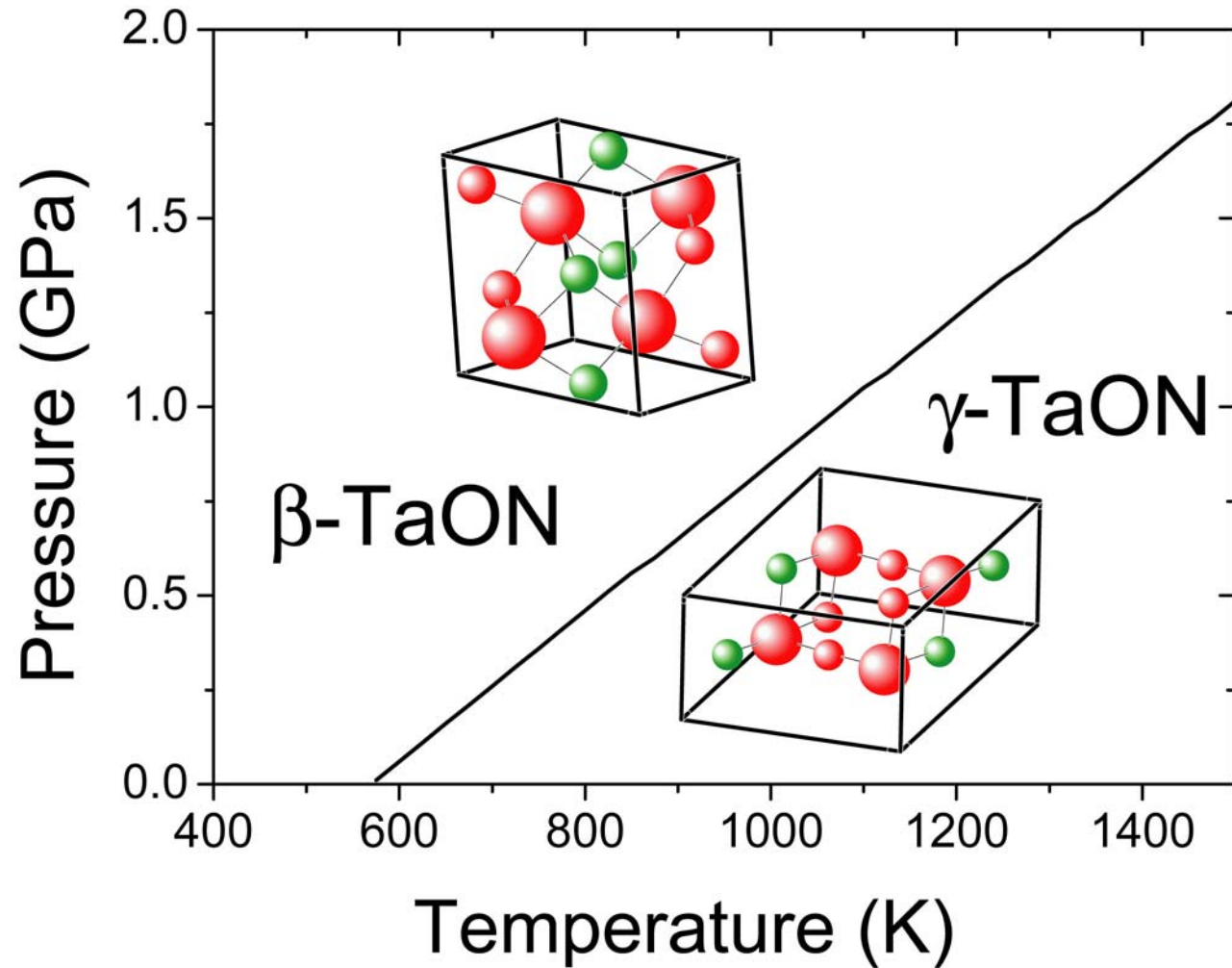
$\beta \rightarrow \gamma$ Phase transition at

higher temperature and
ambient pressure

$$V_m(\gamma) > V_m(\beta)$$

\Rightarrow No pressure-induced
transition

Temperature must be
explicitly included!



Standardized thermochemical data

Numerical calculation of H , S and C_p from the *ab initio* Gibbs Function by the well known relations:

$$S = -\left(\frac{\partial G}{\partial T}\right)_p \quad H = G + T \cdot S \quad C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

Fitting to parametrized Equation ($C_p \Rightarrow S \Rightarrow H \Rightarrow G$)

$$G = C_1 + C_2 T + C_3 T \ln T + C_4 T^2 + C_5 T^3 + \frac{C_6}{T}$$

Gibbs function is not related to the elements but to „absolute“ zero energy
 \Rightarrow pure *ab initio* treatment: no problem with ΔG
 \Rightarrow mixing with exp. data: values must be related to the elements

Cooperation with

Project ELSA: Computational modelling and preparation of the
high temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$

Our „job“: Prediction of thermochemical potentials where there is no experimental data available

First step (done): Comparing properties of simple compounds with known thermochemical data (binary systems, e.g. CuO, BaO)

Recent work: System Y-Ba-Cu-O,
Handling of gaseous compounds (oxygen),
 $\Delta G(p, T)$, Phase transitions

System Ba-Y-O

Binary oxides **BaO** and **Y₂O₃**: well known compounds, reliable thermochemical data available

Ternary Oxides **BaY₂O₄** and **Ba₃Y₄O₉**: wide range of different experimental data

Example: Heat of formation ($\Delta H^{\circ x}$) of BaY₂O₄ from the oxides

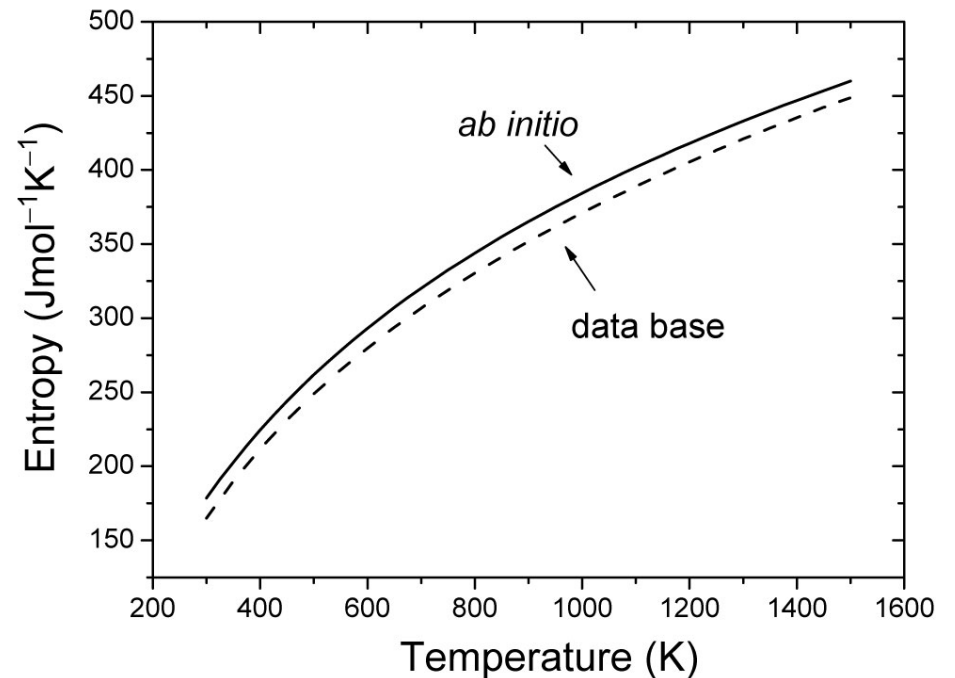
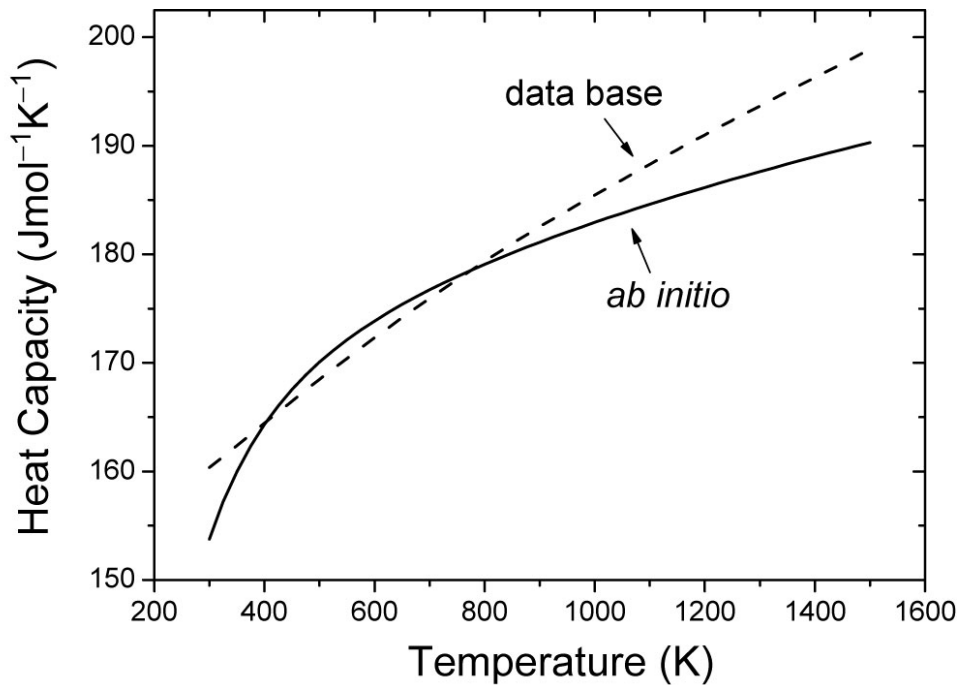
Lit: -113 to +0.4 kJ/mol

GTT: -70.788 kJ/mol

Ab initio: -10.1736 kJ/mol

System Ba-Y-O

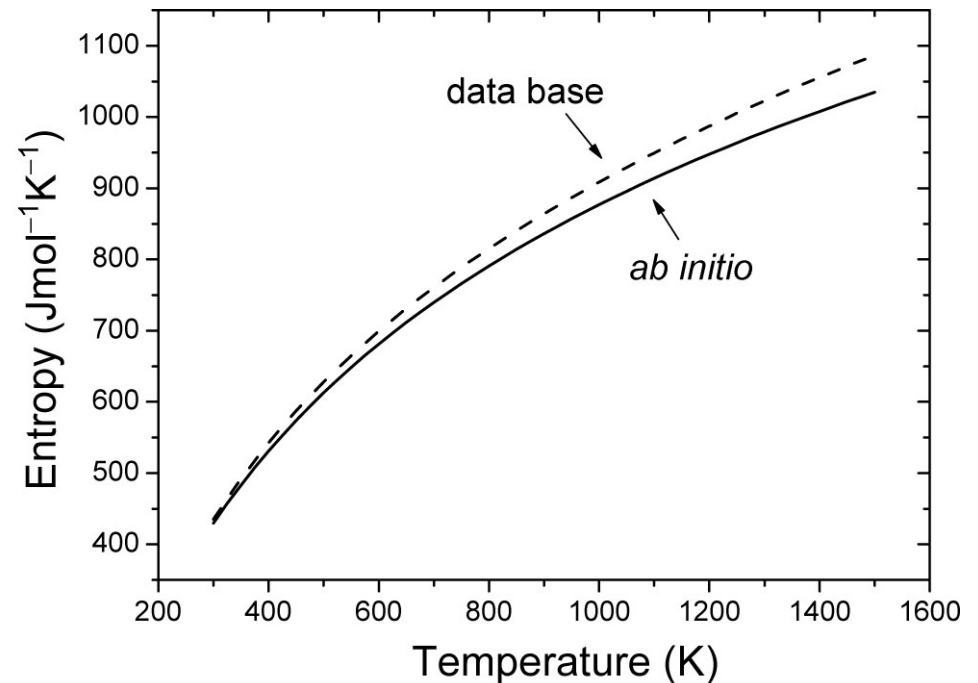
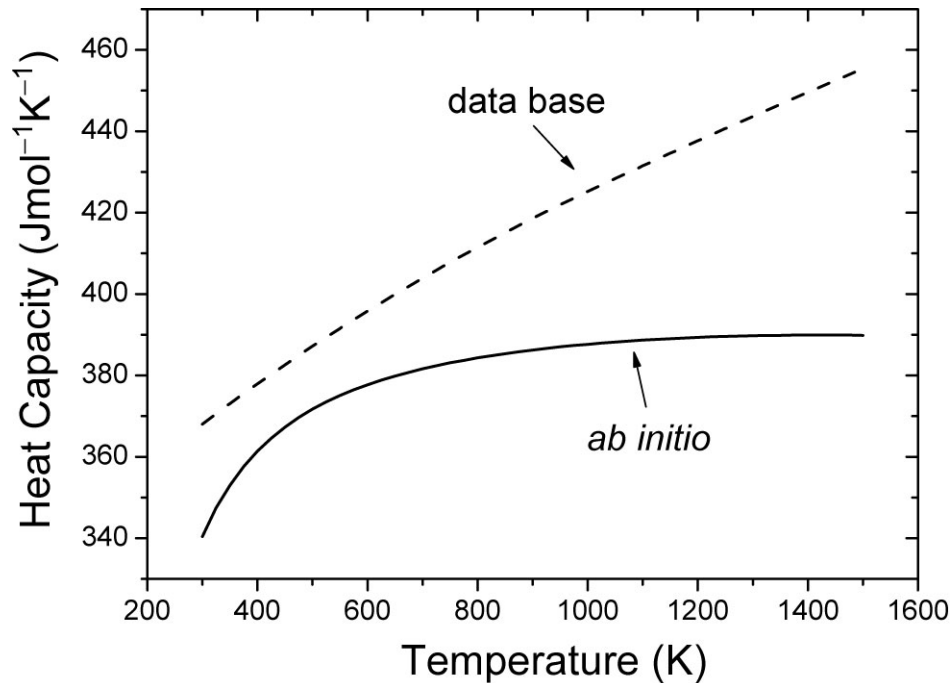
Heat Capacity and Entropy of BaY_2O_4 compared with the data base:



Heat Capacity not linear, Entropy slightly overestimated

System Ba-Y-O

Heat Capacity and Entropy of $\text{Ba}_3\text{Y}_4\text{O}_9$ compared with the data base:

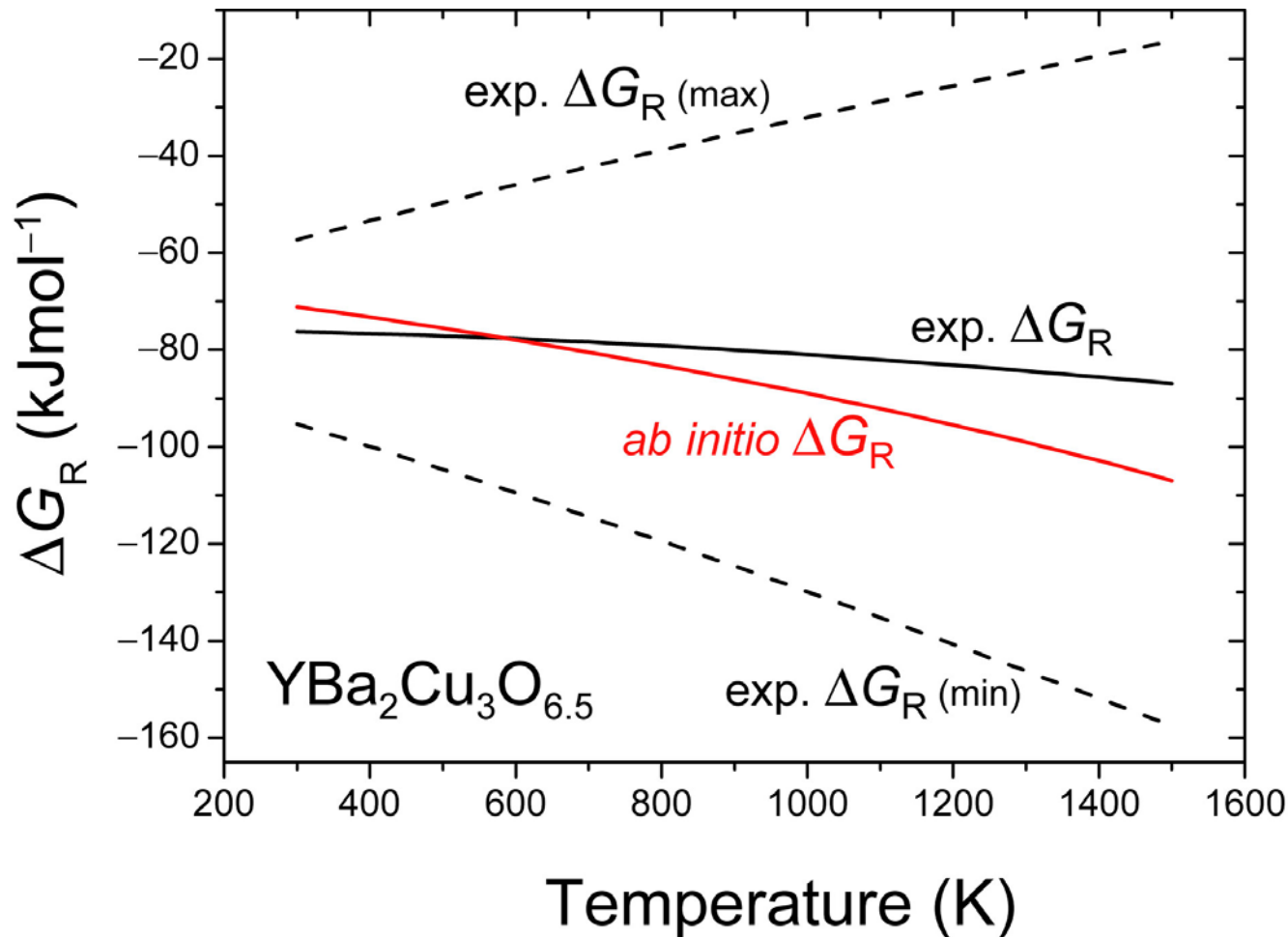


Heat Capacity underestimated,

Entropy also slightly underestimated at higher Temperatures

Gibbs Free Energy of Formation (ΔG_R)

Free energy of formation of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ from the Oxides



- ΔG_R shows correct tendency
- Wide range in exp. function

T - x phase diagram of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$

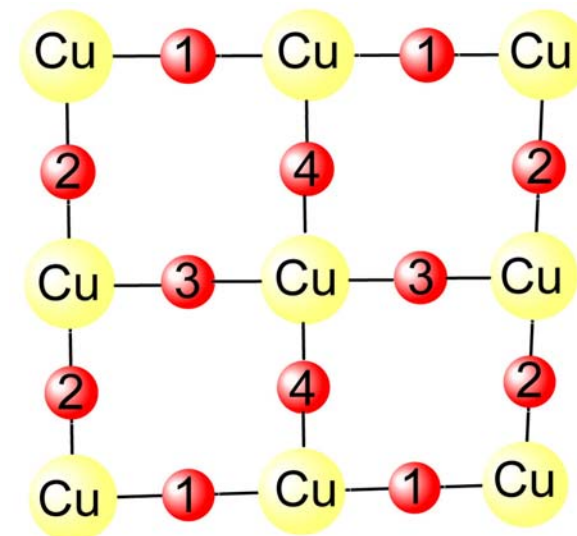
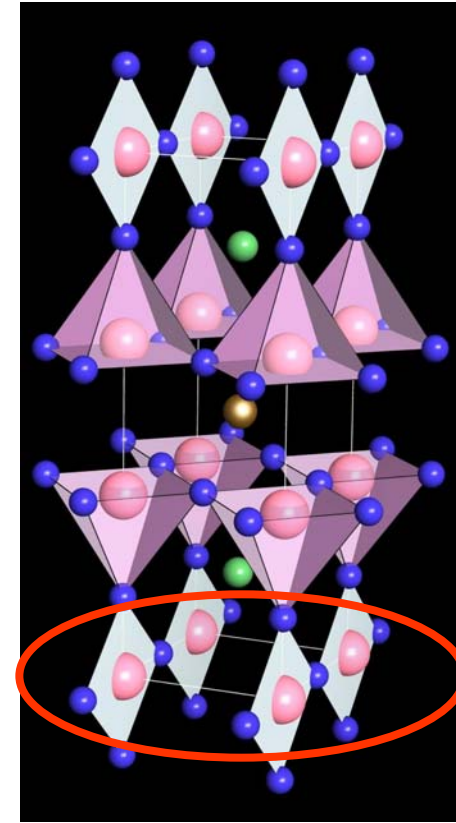
3 possible crystal structures depending on oxygen site fractions in the CuO_x -planes

tetragonal: oxygen on every site (statistically)

orthorhombic I: oxygen on two opposite sites (e.g. 1 and 3)

orthorhombic II: oxygen only on one site

Site fraction depends on Temperature T and oxygen content x .



T - x phase diagram of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$

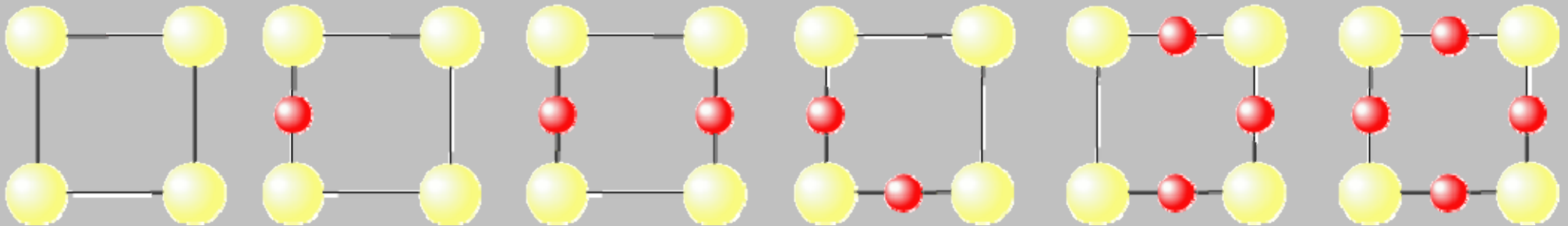
Calculation of the T - x -phase diagram using a sublattice model with four different sites in the CuO_x -planes

All other sites (Y, Ba, Cu, O) are fixed

⇒ 16 different functions, from which some are degenerated

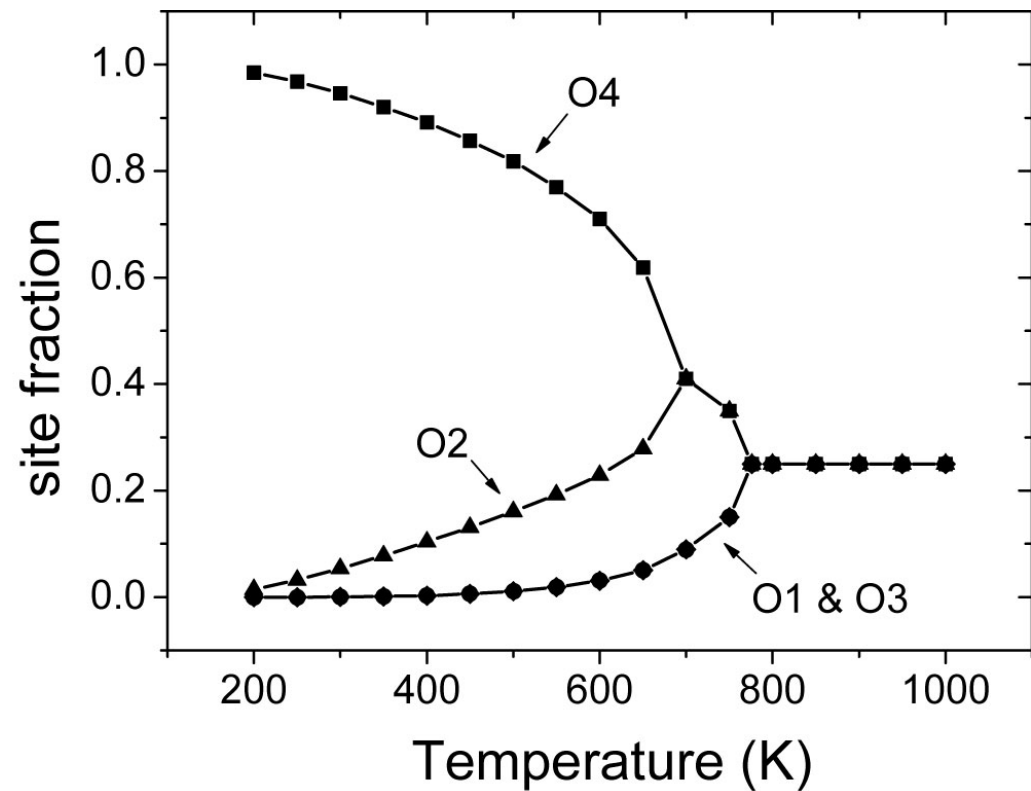
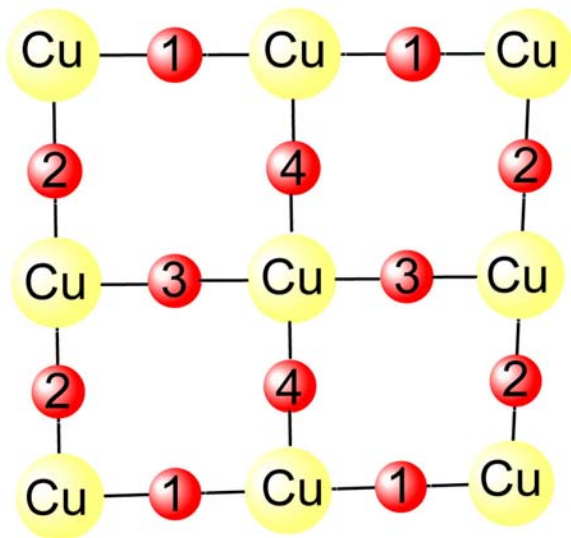
⇒ finally 6 functions

corresponding to $x = 0, 0.5, 1$ (2 different), 1.5, 2



Oxygen site fraction $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$

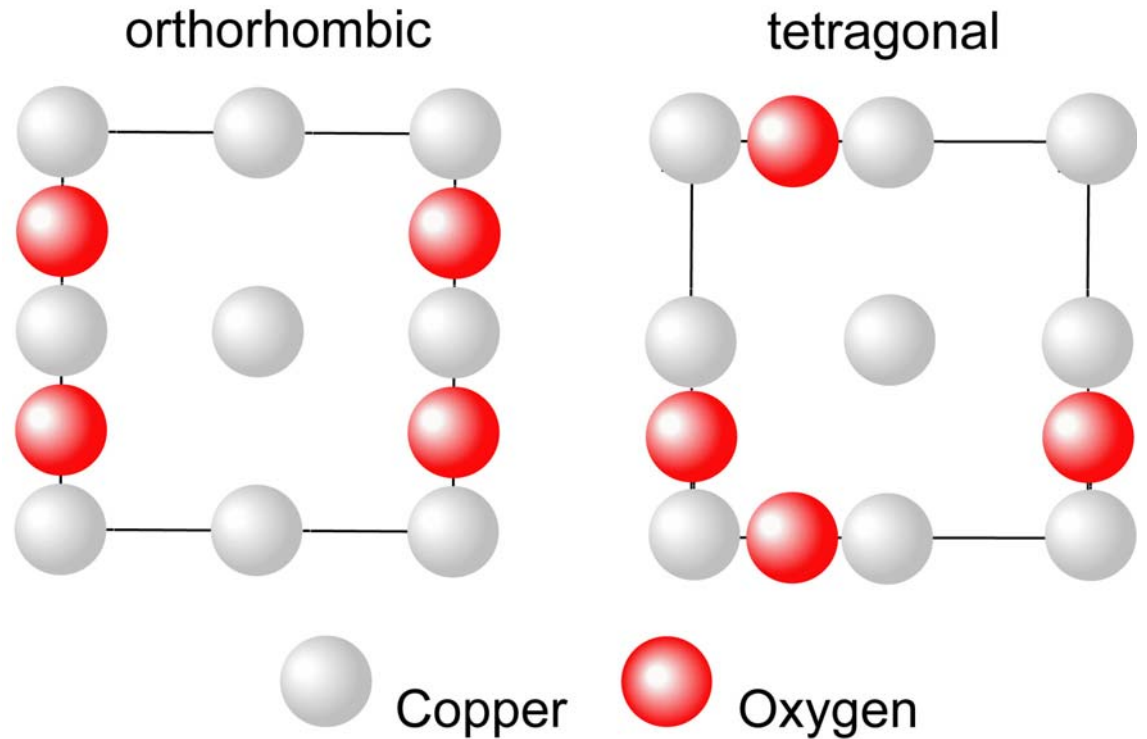
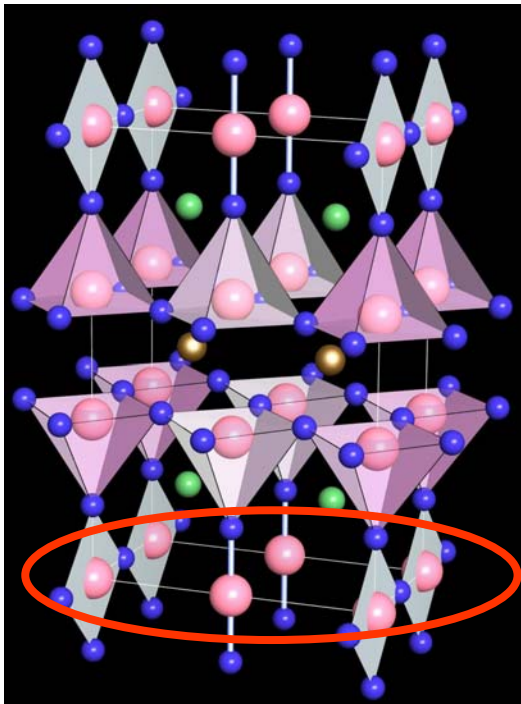
Site fraction of oxygen atoms in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ calculated by Klaus Hack (GTT) from the data base



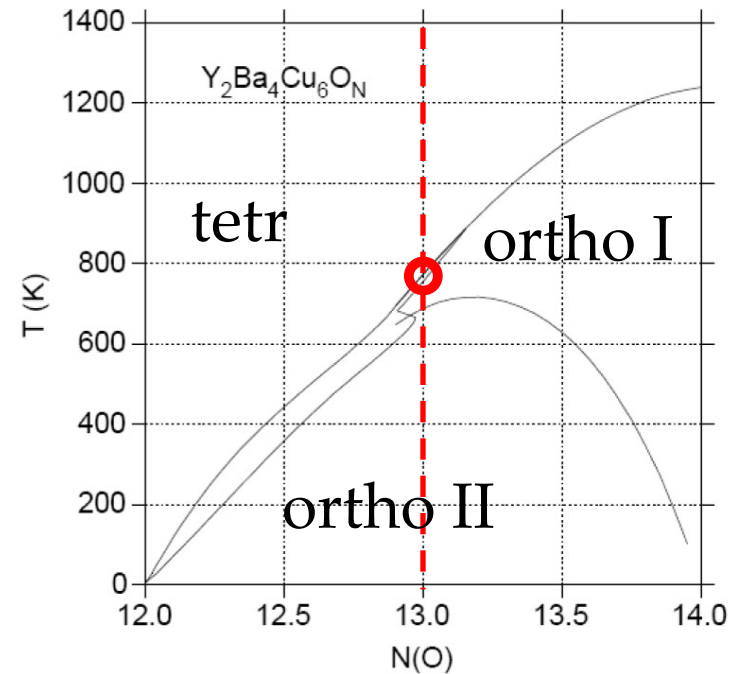
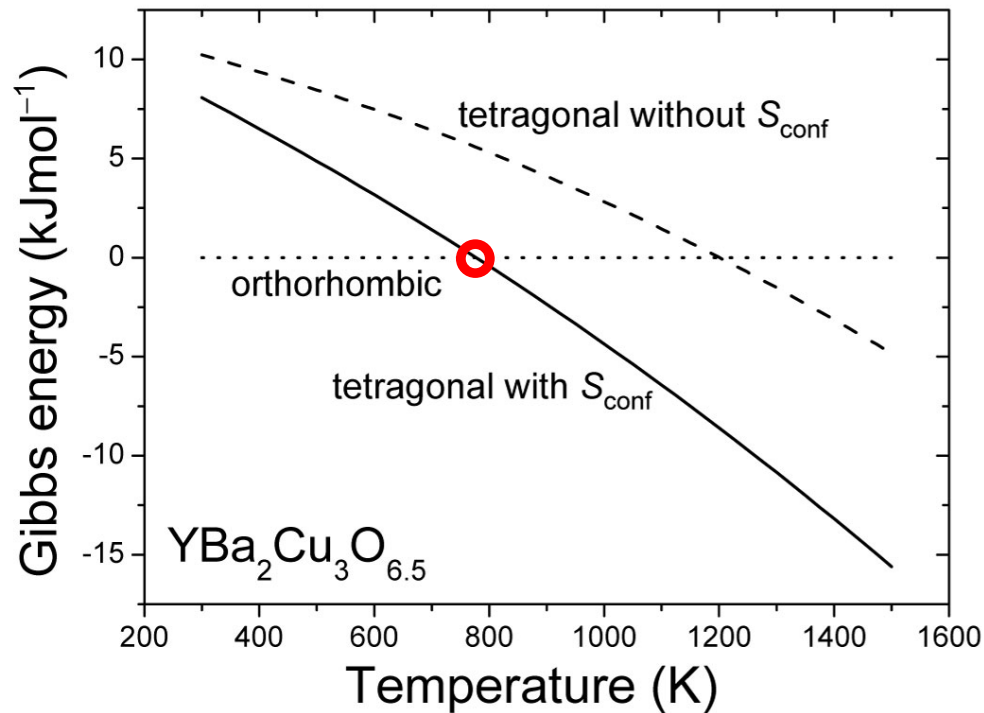
Phase transition of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$

Handling the phase transition with *ab initio* data:

Simple model: 1x2x1 unit cell



Phase transition of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$



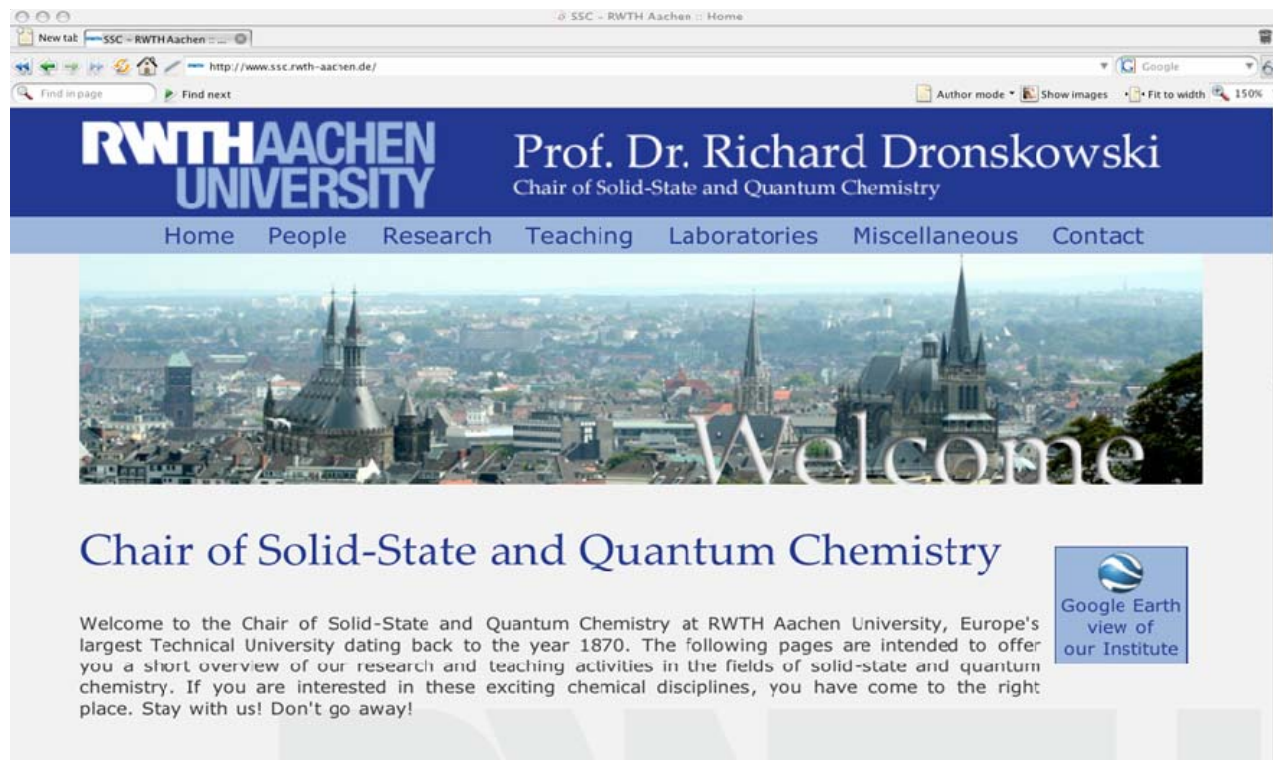
Configurational entropy S_{conf} has to be taken into account

⇒ Good estimation of the phase transition temperature

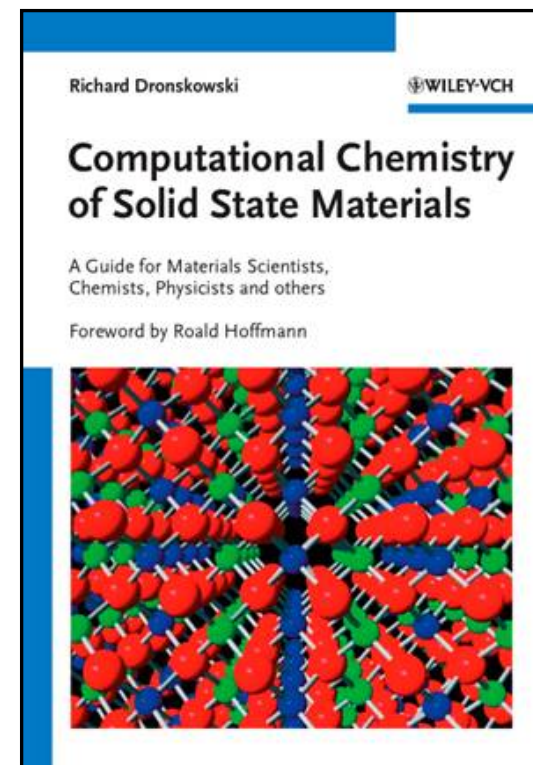
Summary

- Standard *ab initio* calculations: many properties available from Density Functional total energy calculations
- Involving Temperature by the simulation of lattice vibrations
- Good reproduction of temperature dependent potentials like the Heat Capacity and the Entropy
- Prediction of Temperature- and Pressure-induced phase transitions possible via ΔG

Further information:



www.ssc.rwth-aachen.de



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