# *Defects in metals and alloys at finite temperatures from DFT*

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ERC CoG project
**Materials 4.0**

Deutsche Forschungsgemeinschaft
German Research Foundation

# Motivation: Defects in metals and alloys

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- defects are always there
- defects modify material properties
- need to control defects
- need to **understand** defects

**Defects:**

**point defects (vacancies)**

**stacking fault energies**

**anti-phase boundaries**

**surfaces**

our most favorite *ab initio* simulations

(mine: periodic, plane-wave density functional theory, mostly VASP)

# Motivation: DFT at finite temperatures

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- typical experiments at **finite** temperatures
- usual applications at **finite** temperatures
- processing often at **high** temperatures (specifically metals)
- need extension from 0K to **finite** T DFT

**energy →** **Helmholtz (free) energy**
**Gibbs energy** (pressure included)

# The free energy surface

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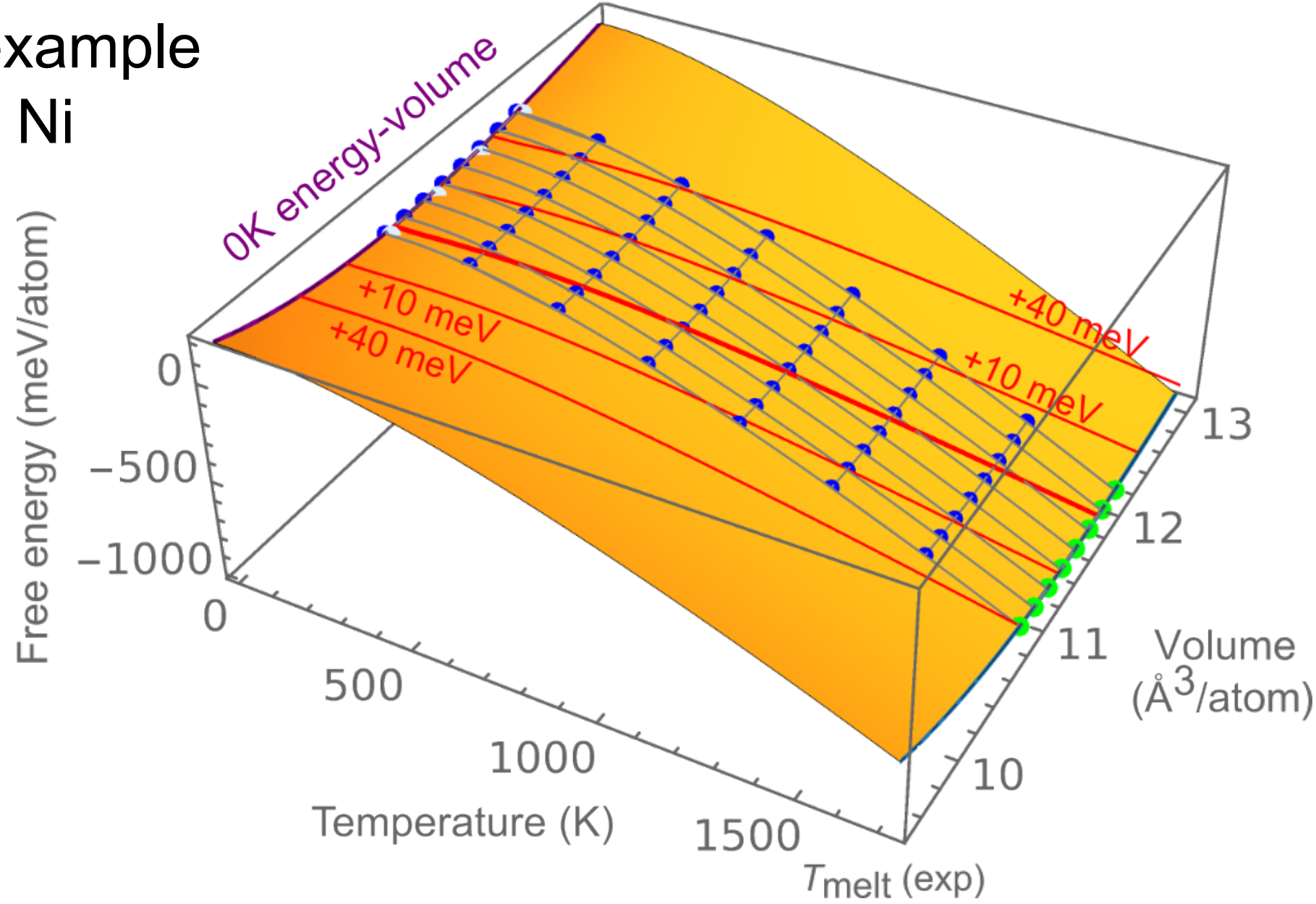
# Real-life example for FM fcc Ni



# The free energy surface

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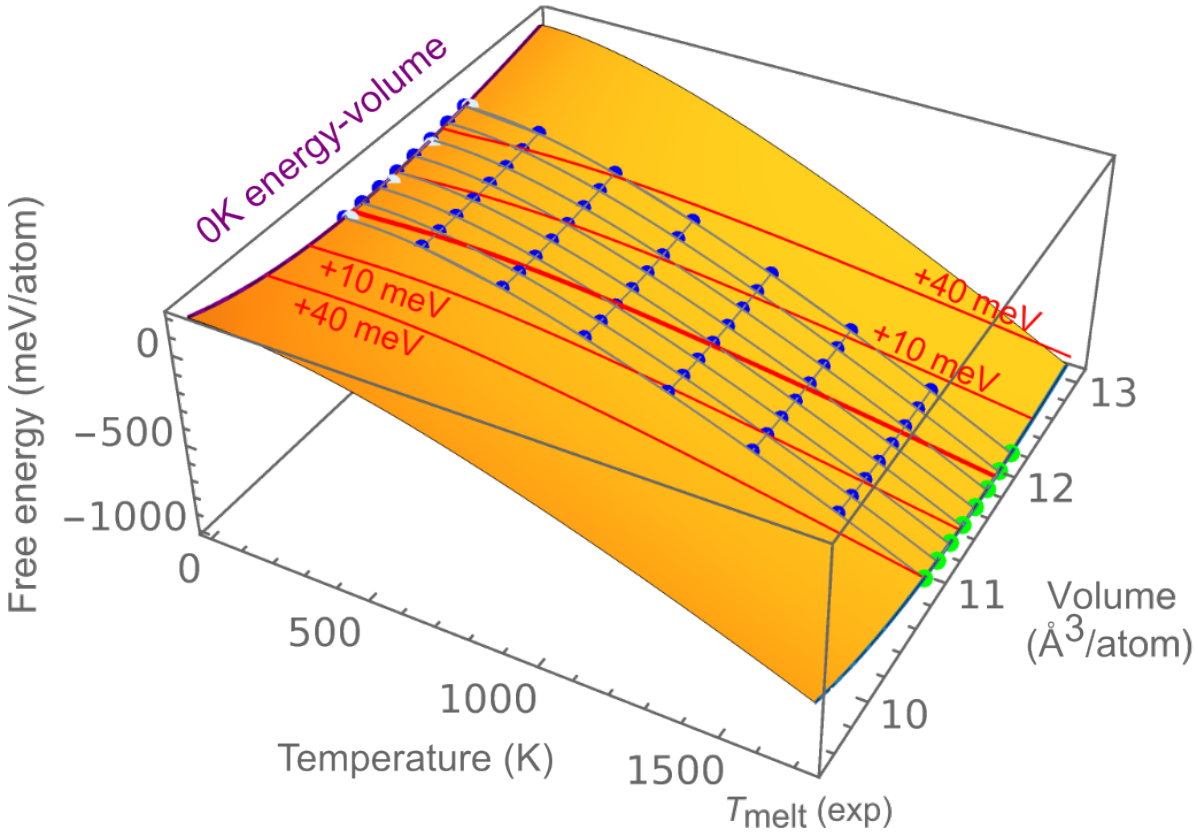
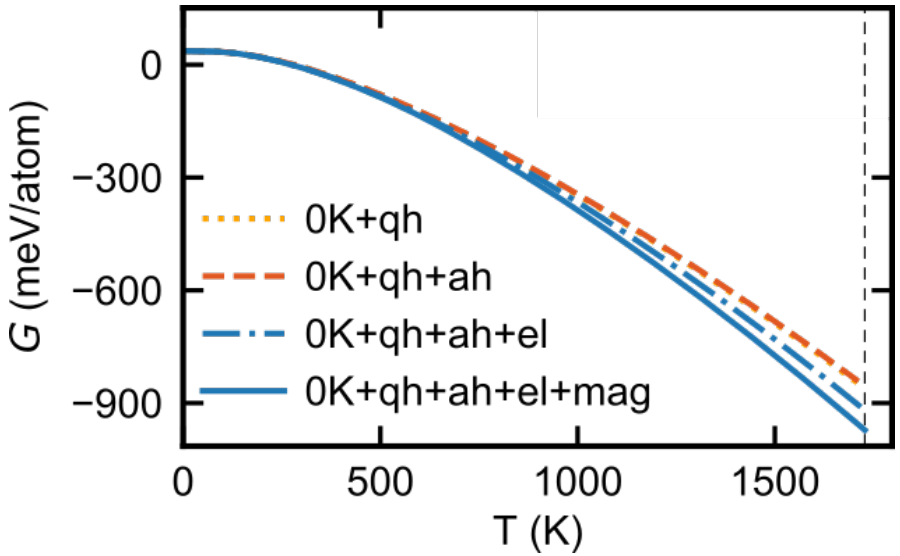
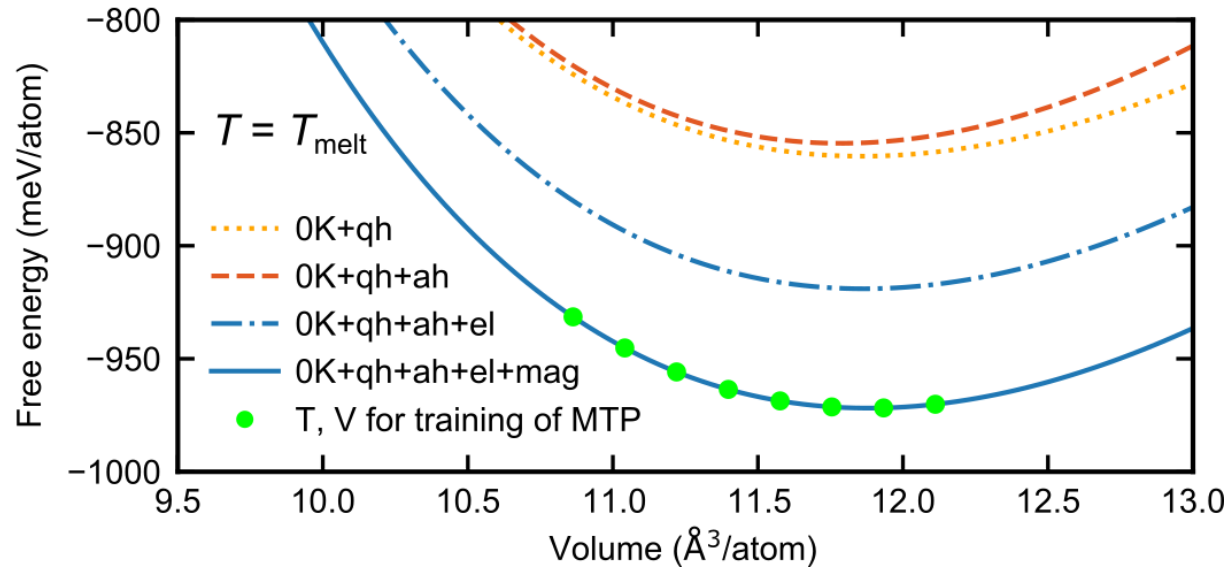
- → largest contribution from (quasiharmonic) vibrations
- → **BUT: other contributions important for phase stability, thermodynamic properties**



# Importance of small free energy changes, example for Al

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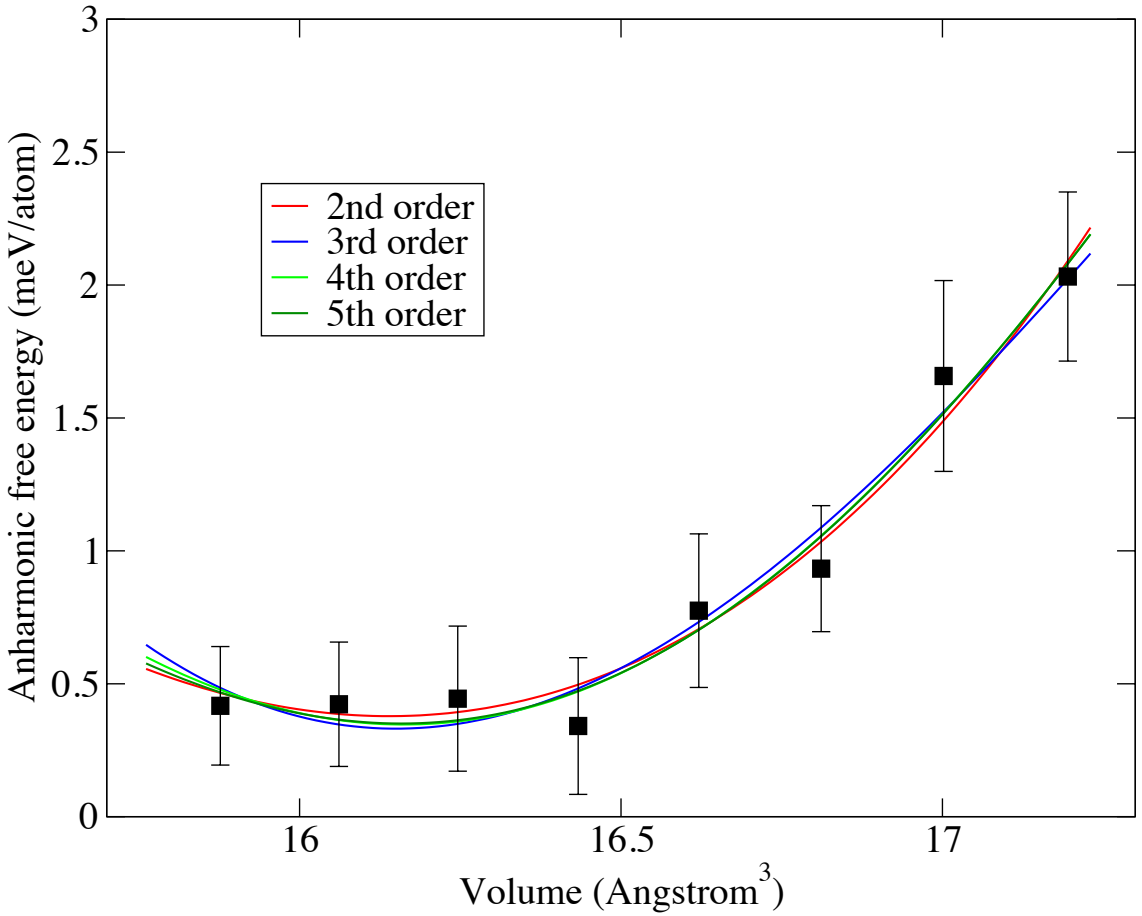
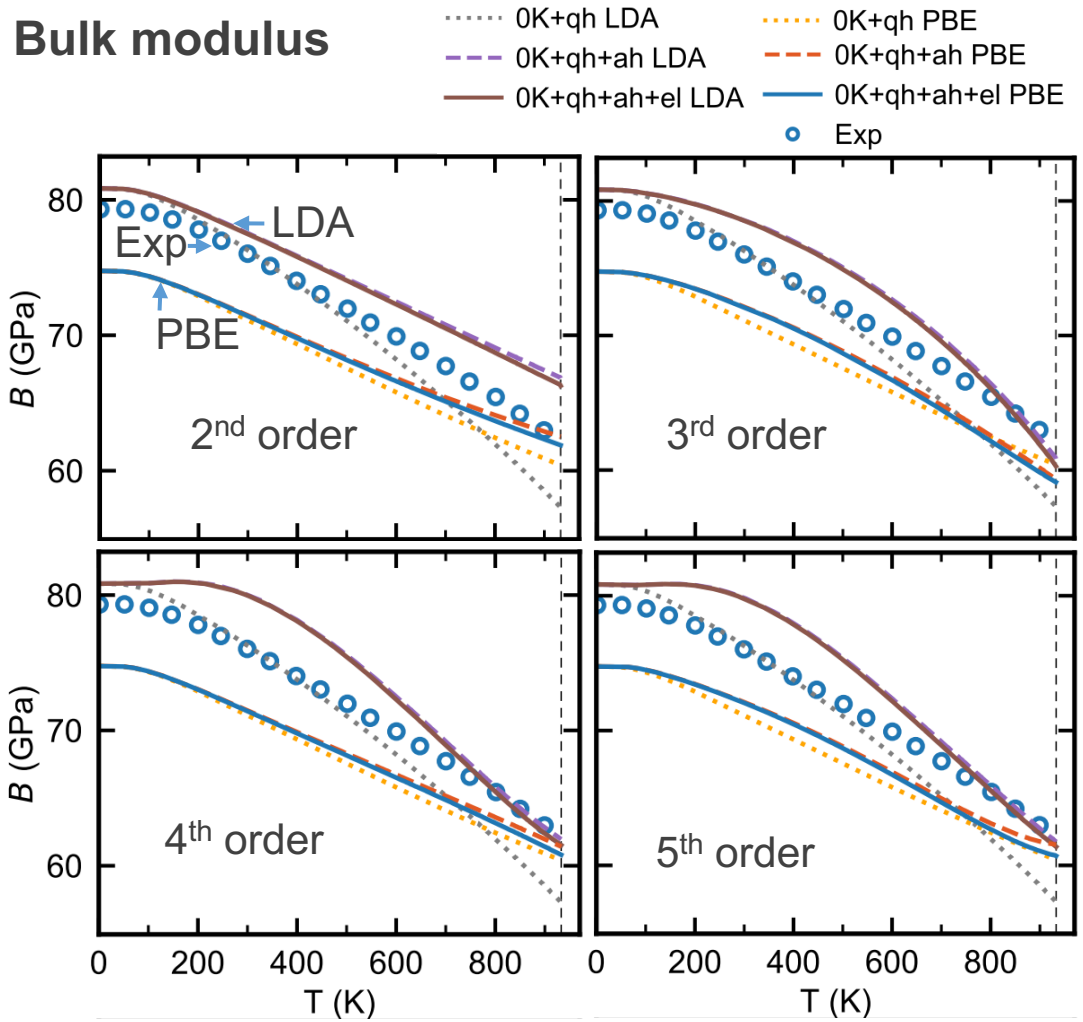
## Anharmonic free energy at 933 K for LDA




## Bulk modulus



# The free energy surface

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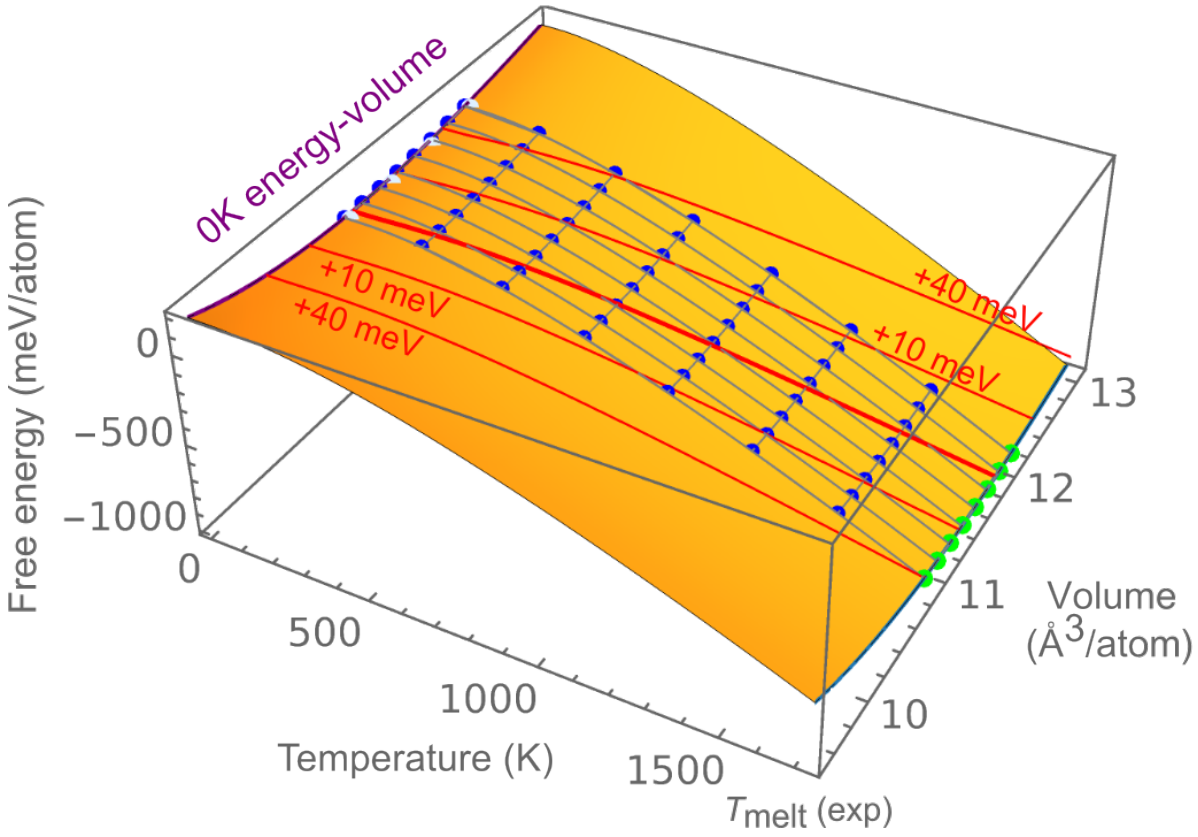


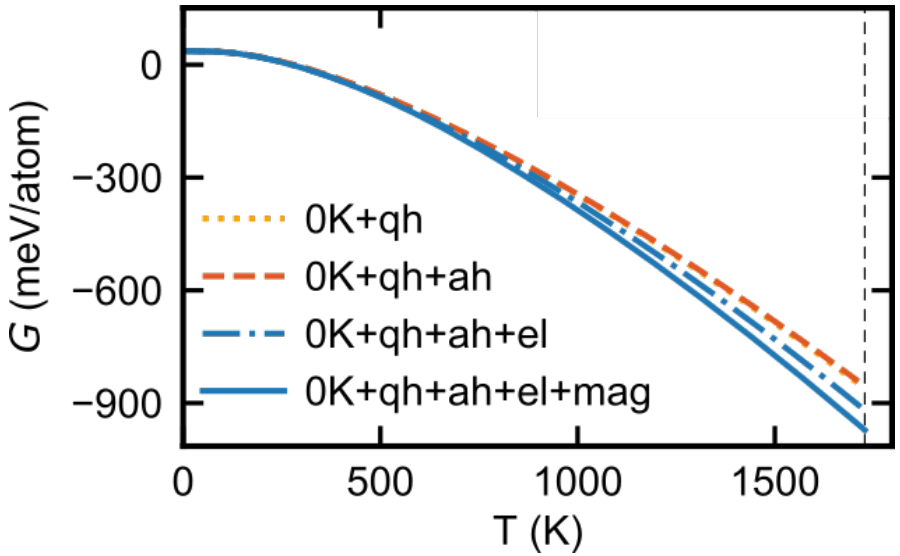


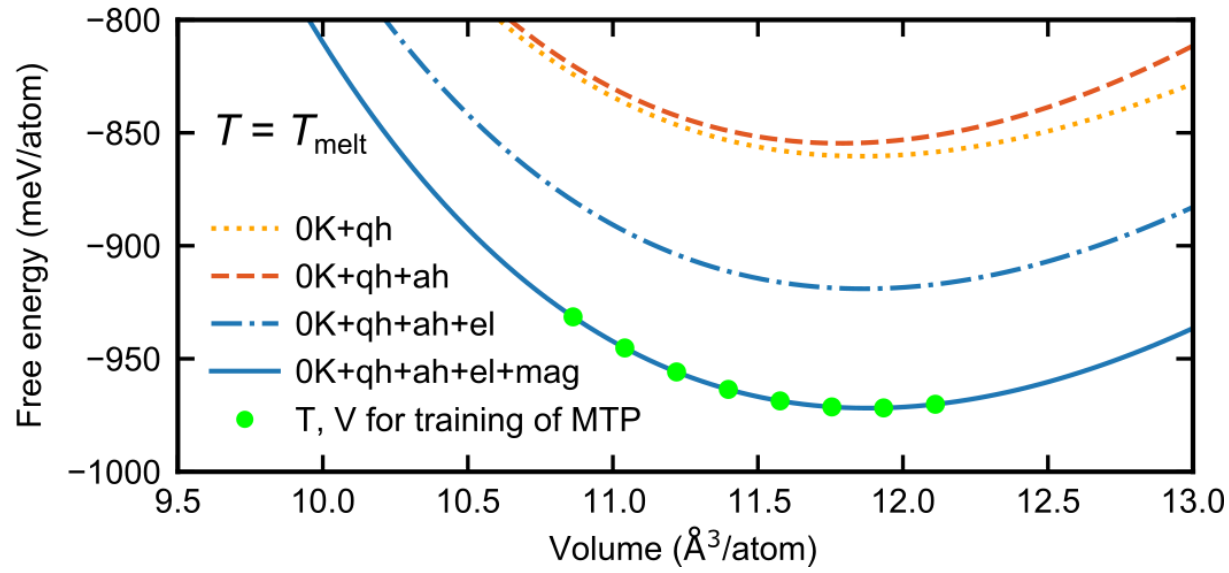

# Quasiharmonic vibrations

# Quasiharmonic approximation

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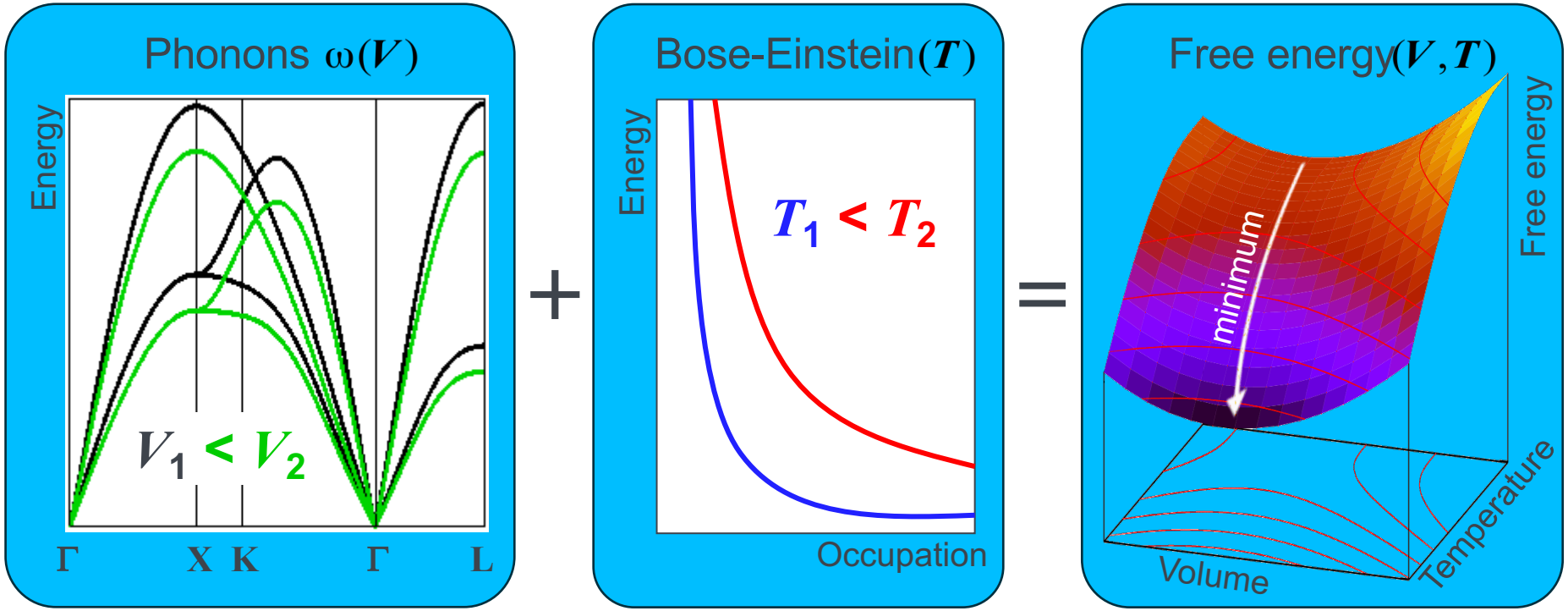
e.g.: Wallace, *Thermodynamics of Crystals* (Dover, 1998).




Combination (DFT + quasiharmonic approximation) since ≈ 1989:
Ref.: Biernacki und Scheffler, *PRL* **63**, 290 (1989).

$$F^{\mathrm{qh}}(T,V) = E_{T=0\mathrm{K}}(V) + \sum_{\mathbf{q}}^{\mathrm{BZ}} \sum_{i}^{3} \left[ \frac{1}{2}\hbar\omega_{\mathbf{q},i}(V) + k_{\mathrm{B}}T \ln\left[ 1 - \exp\left( -\frac{\hbar\omega_{\mathbf{q},i}(V)}{k_{\mathrm{B}}T} \right) \right] \right]$$

# Phonons for fcc metals

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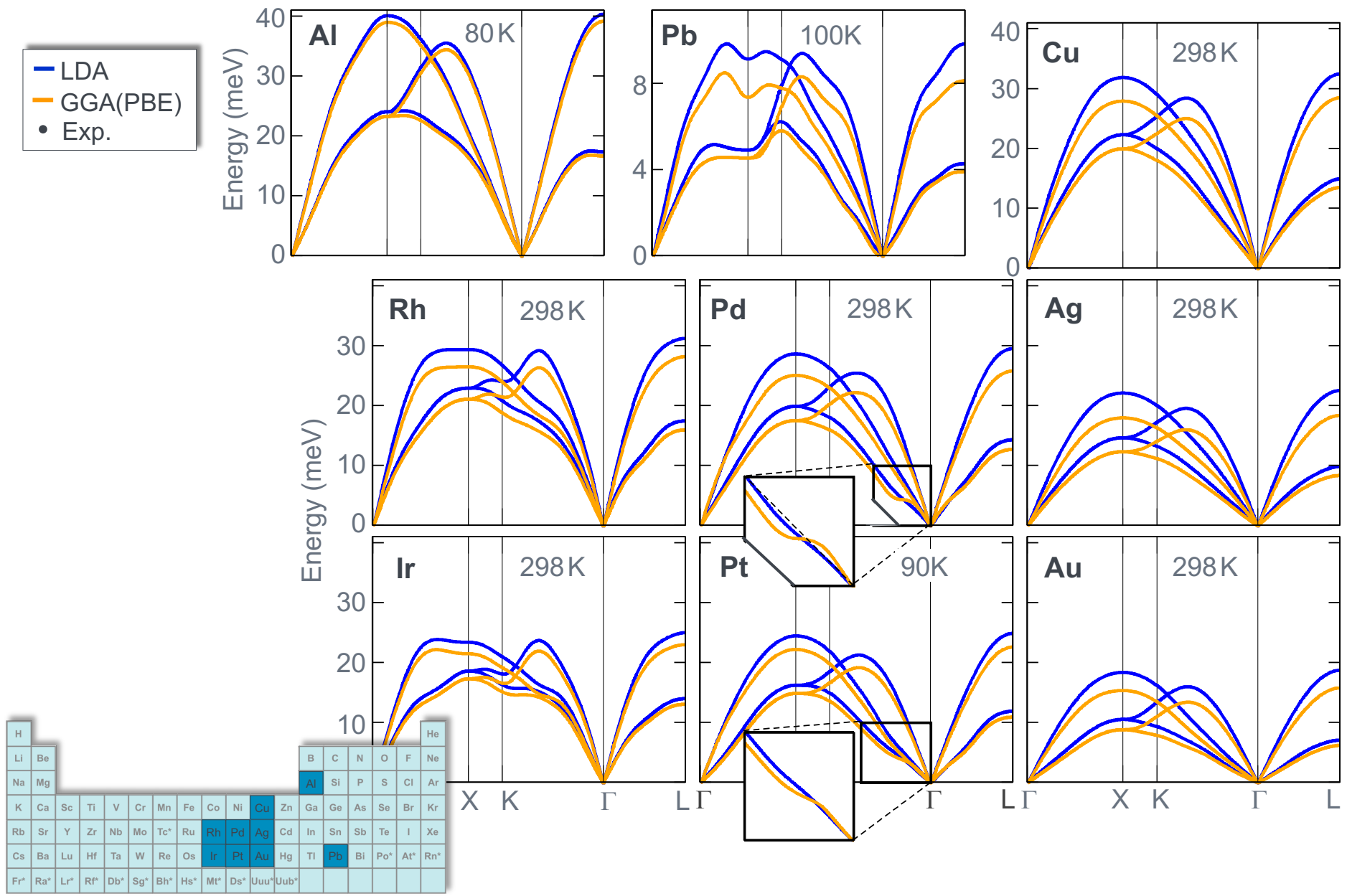


Blazej Grabowski, blazej.grabowski@imw.uni-stuttgart.de

Phys. Rev. B 76 (2007) 024309

# Phonons for fcc metals

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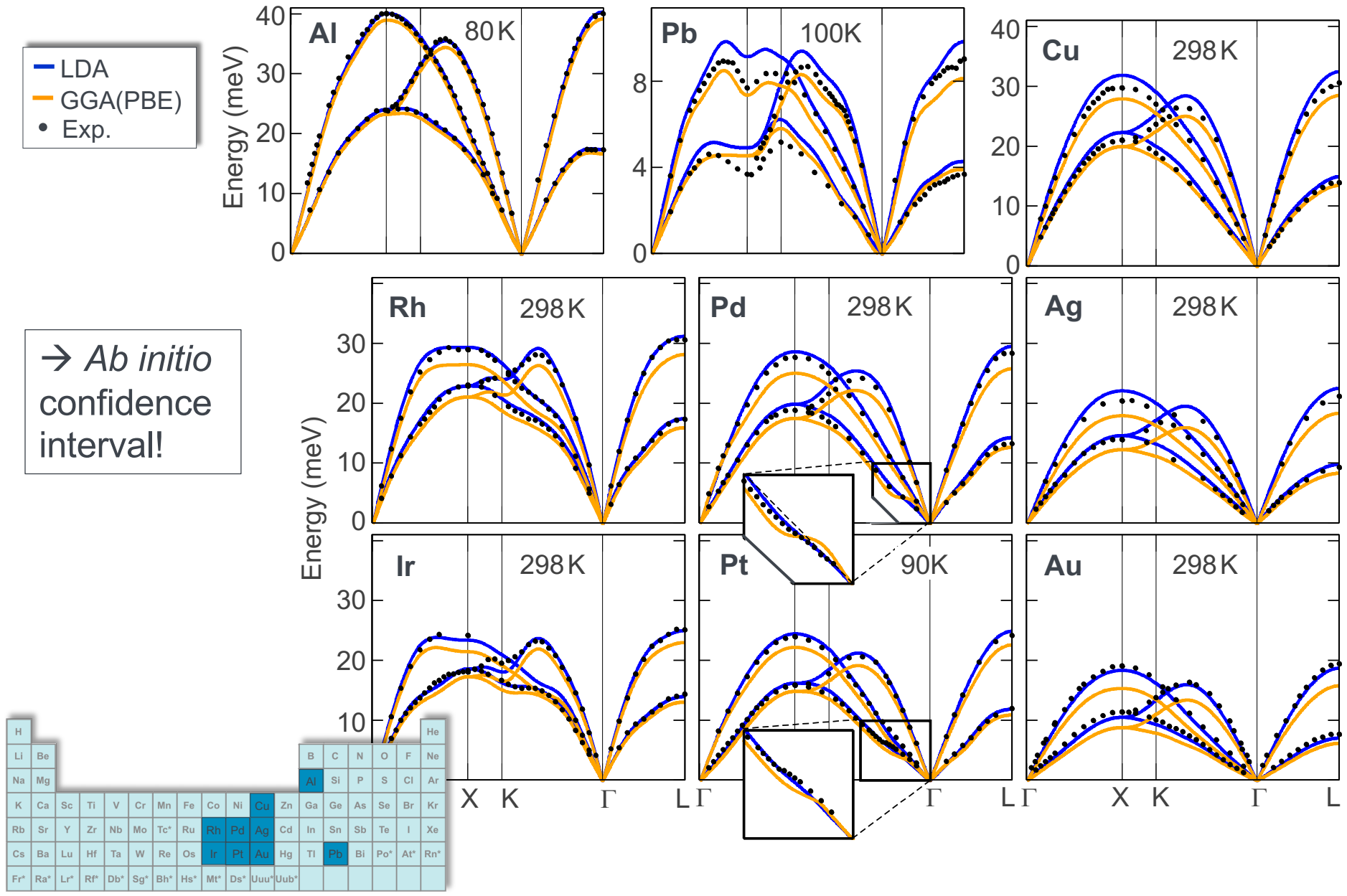


→ *Ab initio* confidence interval!






Phys. Rev. B 76 (2007) 024309

# Electronic excitations

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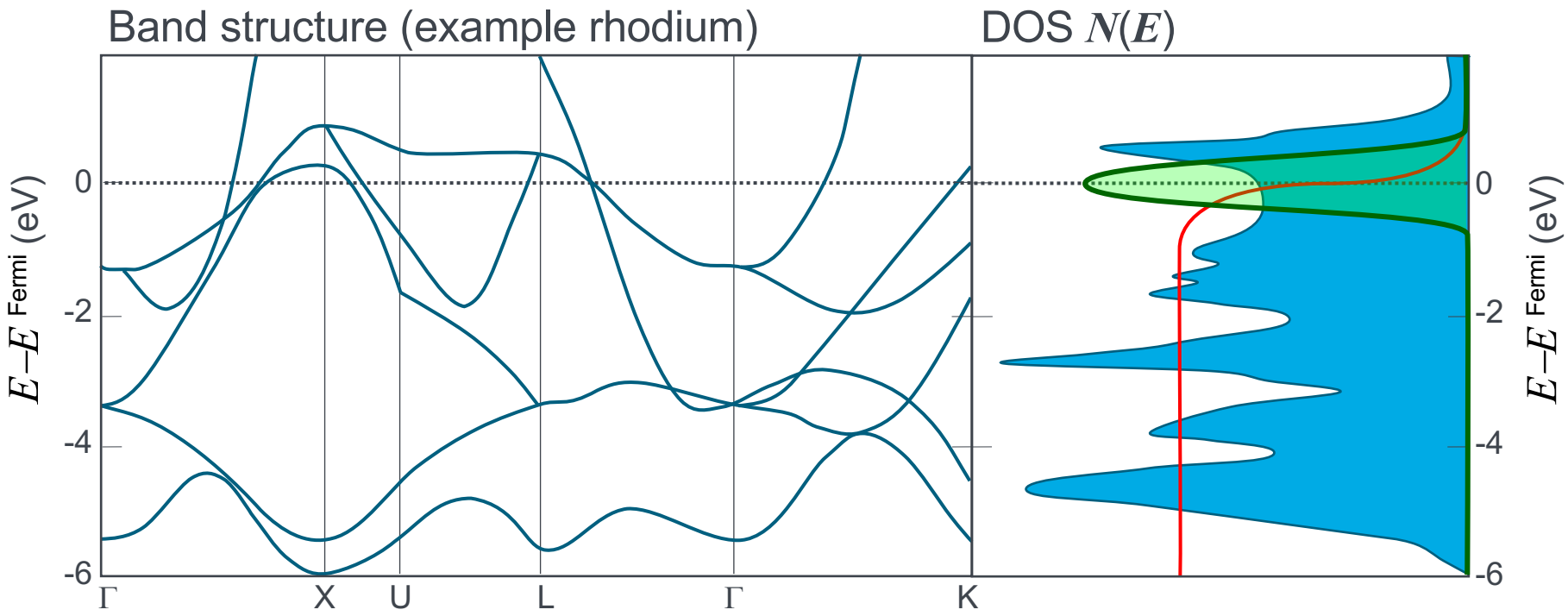
Mermin, Phys. Rev. 137, A1441 (1965)




DOS ↓ Fermi-Dirac ↓

$$F^{\text{el}} = k_{\text{B}}T\int N(E)\left[f\ln f + (1-f)\ln(1-f)\right]dE$$

ideal entropy

# Electronic excitations, wide range study

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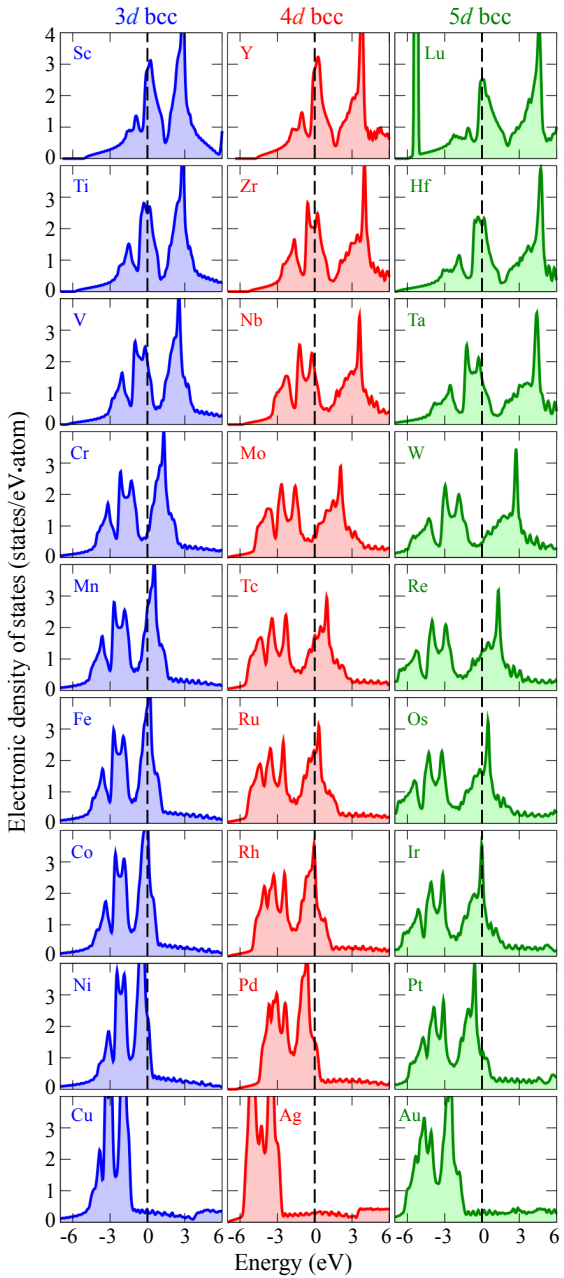


## Trends in the periodic table

| 1A | | | | | | | | | | | | 3A | 4A | 5A | 6A | 7A | 8A |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 H 1.00794 | 2A | | | | | | | 8B | | | 1B | 2B | | | | | 2 He 4.002602 |
| 3 Li | 4 Be | 3B | 4B | 5B | 6B | 7B | | | | | | | 5 B | 6 C | 7 N 14.0067 | 8 O 15.9994 | 9 F 18.9984032 | 10 Ne 20.1797 |
| 11 Na | 12 Mg | | | | | | | | | | | | 13 Al | 14 Si | 15 P 30.973762 | 16 S 32.065 | 17 Cl 35.453 | 18 Ar 39.948 |
| 19 K | 20 Ca | 21 Sc | 22 Ti | 23 V | 24 Cr | 25 Mn | 26 Fe | 27 Co | 28 Ni | 29 Cu | 30 Zn | | 31 Ga | 32 Ge | 33 As 74.92160 | 34 Se 78.96 | 35 Br 79.904 | 36 Kr 83.798 |
| 37 Rb 85.4678 | 38 Sr 87.62 | 39 Y | 40 Zr | 41 Nb | 42 Mo | 43 Tc | 44 Ru | 45 Rh | 46 Pd | 47 Ag | 48 Cd | | 49 In 114.818 | 50 Sn 118.710 | 51 Sb 121.760 | 52 Te 127.60 | 53 I 126.90447 | 54 Xe 131.293 |
| 55 Cs 132.9054519 | 56 Ba 137.327 | *1 Lu | 72 Hf | 73 Ta | 74 W | 75 Re | 76 Os | 77 Ir | 78 Pt | 79 Au | 80 Hg | | 81 Tl 204.3833 | 82 Pb 207.2 | 83 Bi 208.98040 | 84 Po [209] | 85 At [210] | 86 Rn [222] |
| 87 Fr [223] | 88 Ra [226] | 57-71 Lanthanides | 104 Rf [267] | 105 Db [268] | 106 Sg [271] | 107 Bh [272] | 108 Hs [270] | 109 Mt [276] | 110 Ds [281] | 111 Rg [280] | 112 Cn [285] | | 113 Uut [284] | 114 Fl [289] | 115 Uup [288] | 116 Lv [293] | 117 Uus [294] | 118 Uuo [294] |
| | | 89-103 Actinides | | | | | | | | | | | | | | | | |

Phys. Rev. B 95 (2017) 165126

# Electronic excitations, wide range study

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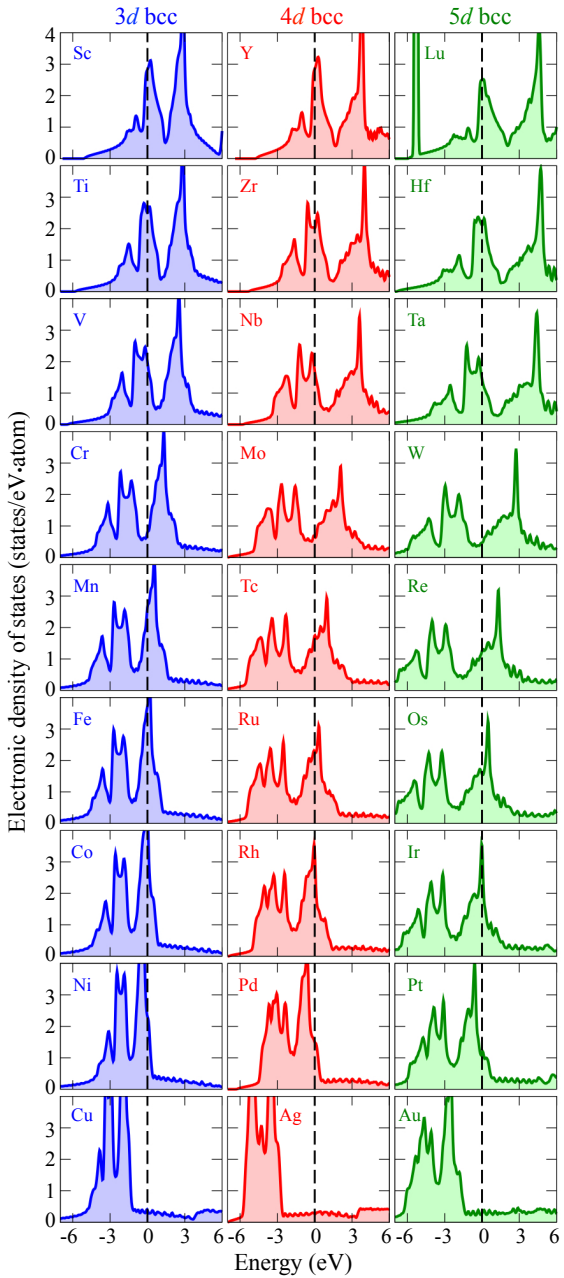
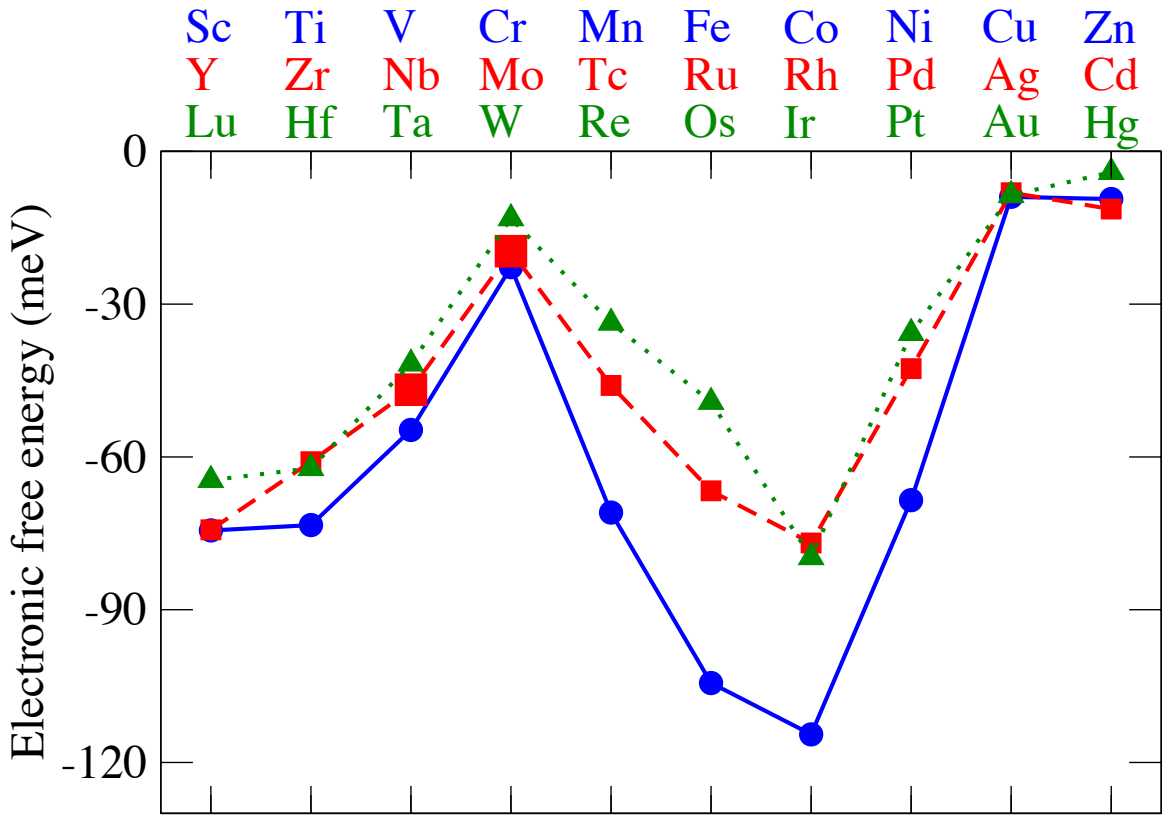



## Electronic free energies at 1500 K




→ **Electronic free energies important for phase stabilities**

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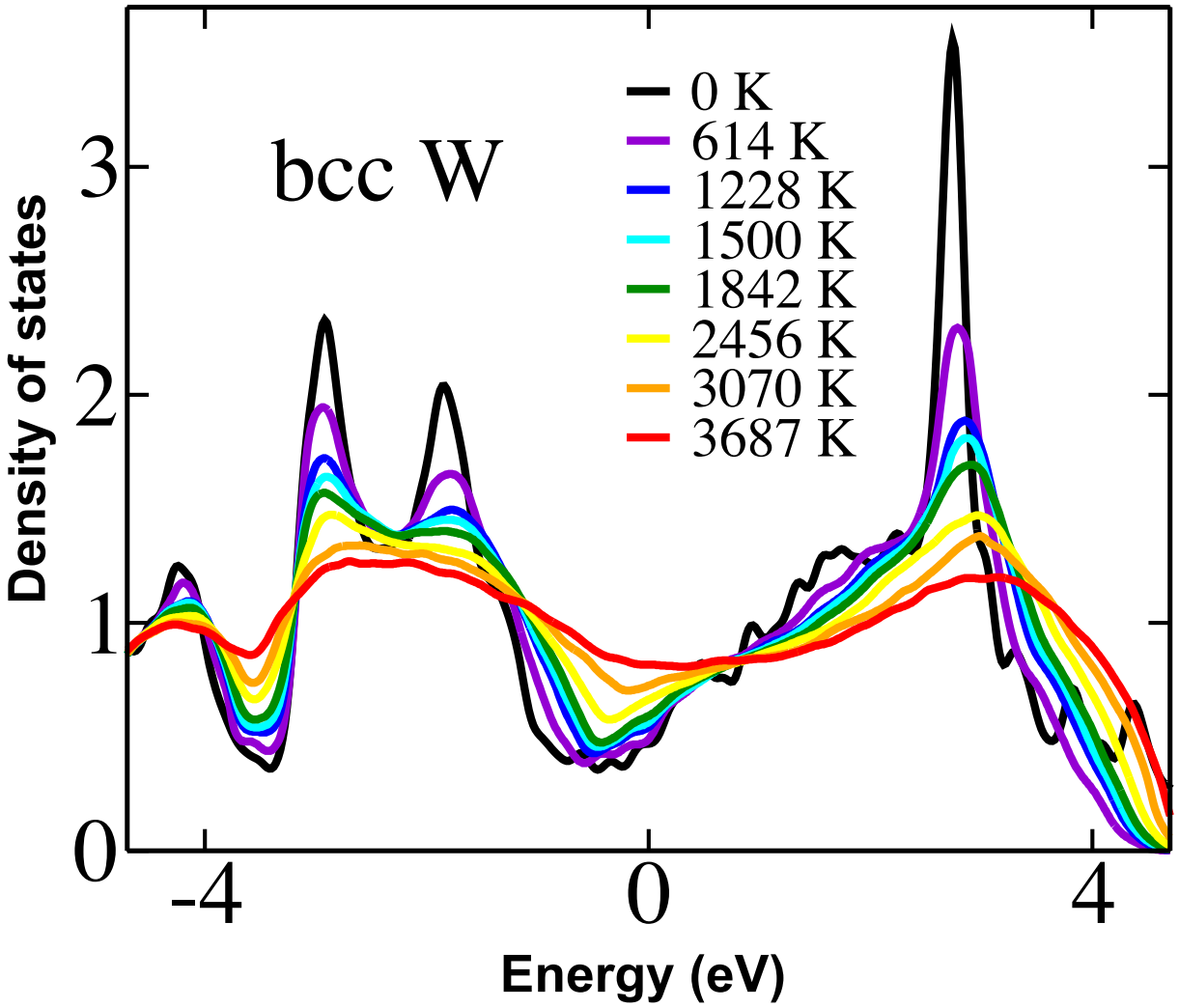
**Example for tungsten**

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→ **Very strong broadening**
→ **Thermal disorder**
→ **Localization**

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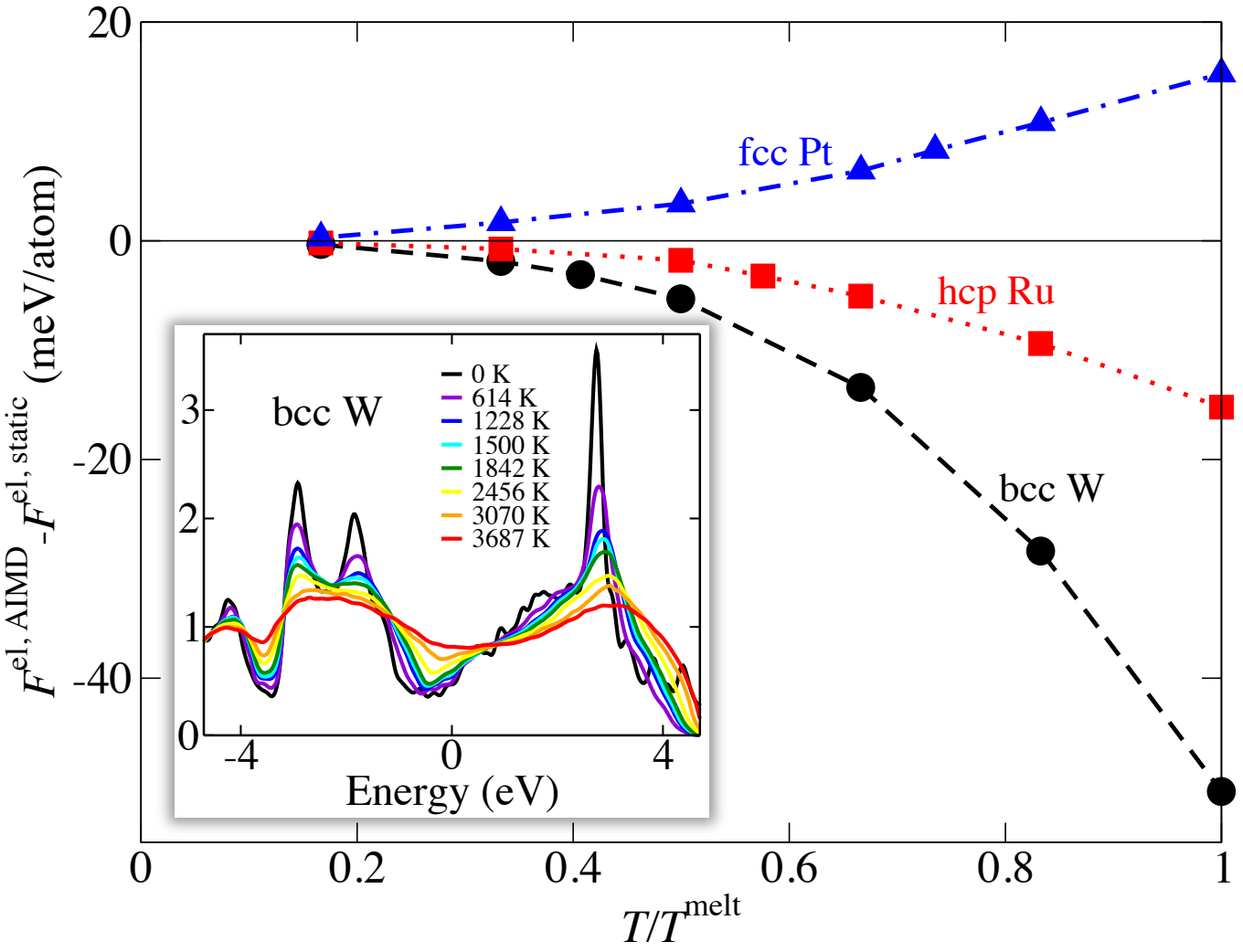
## Impact on electronic free energies




→ **Very strong coupling**

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# Anharmonic vibrations

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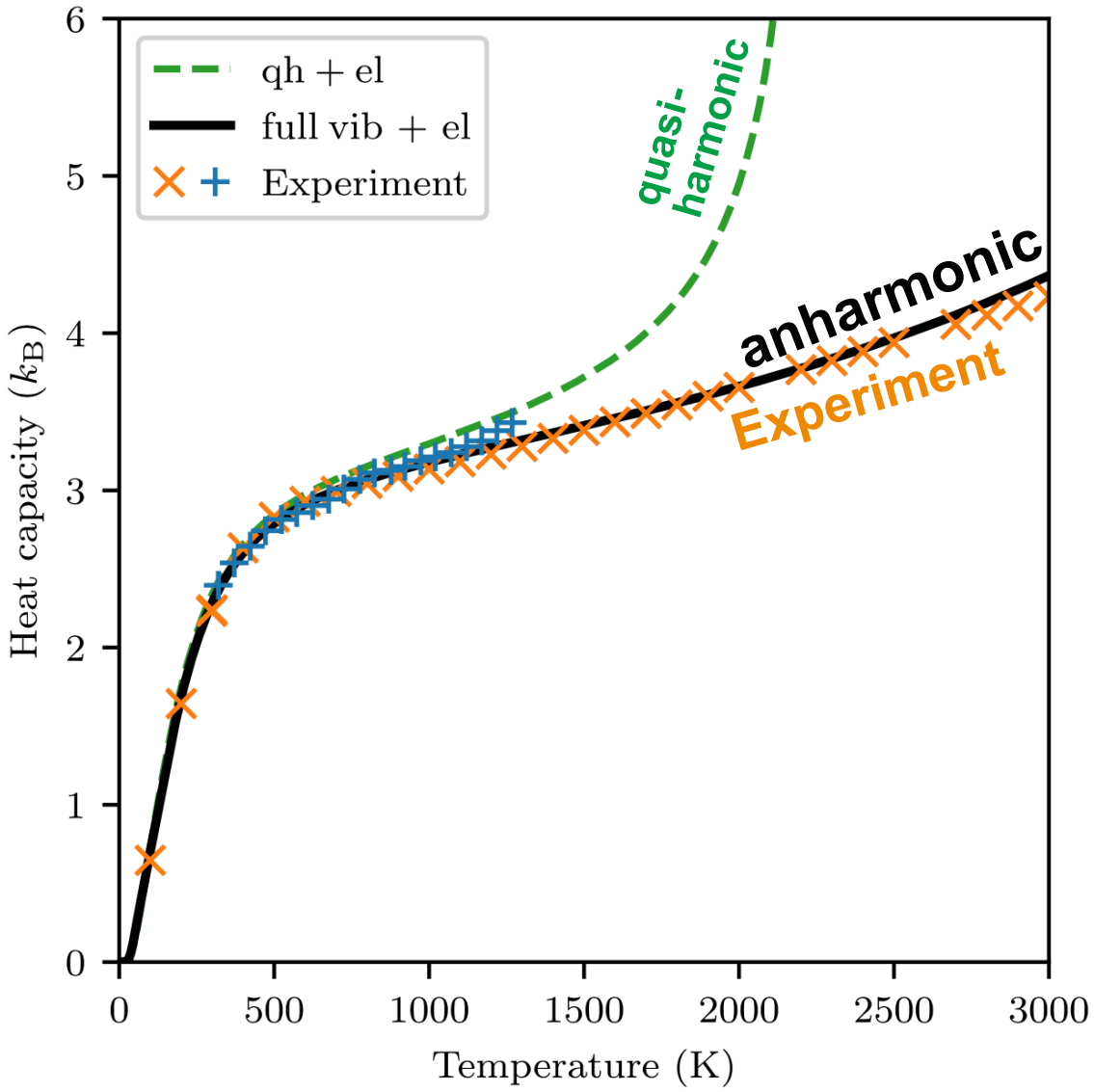
## Example: Heat capacity of TiN




→ anharmonic (phonon-phonon interaction) contribution can be very important

→ many such examples

→ **anharmonicity cannot be neglected in general!**

Reference:
Forslund, Grabowski et al.,
PHYSICAL REVIEW B 103,
195428 (2021)

# Heat capacity of silver

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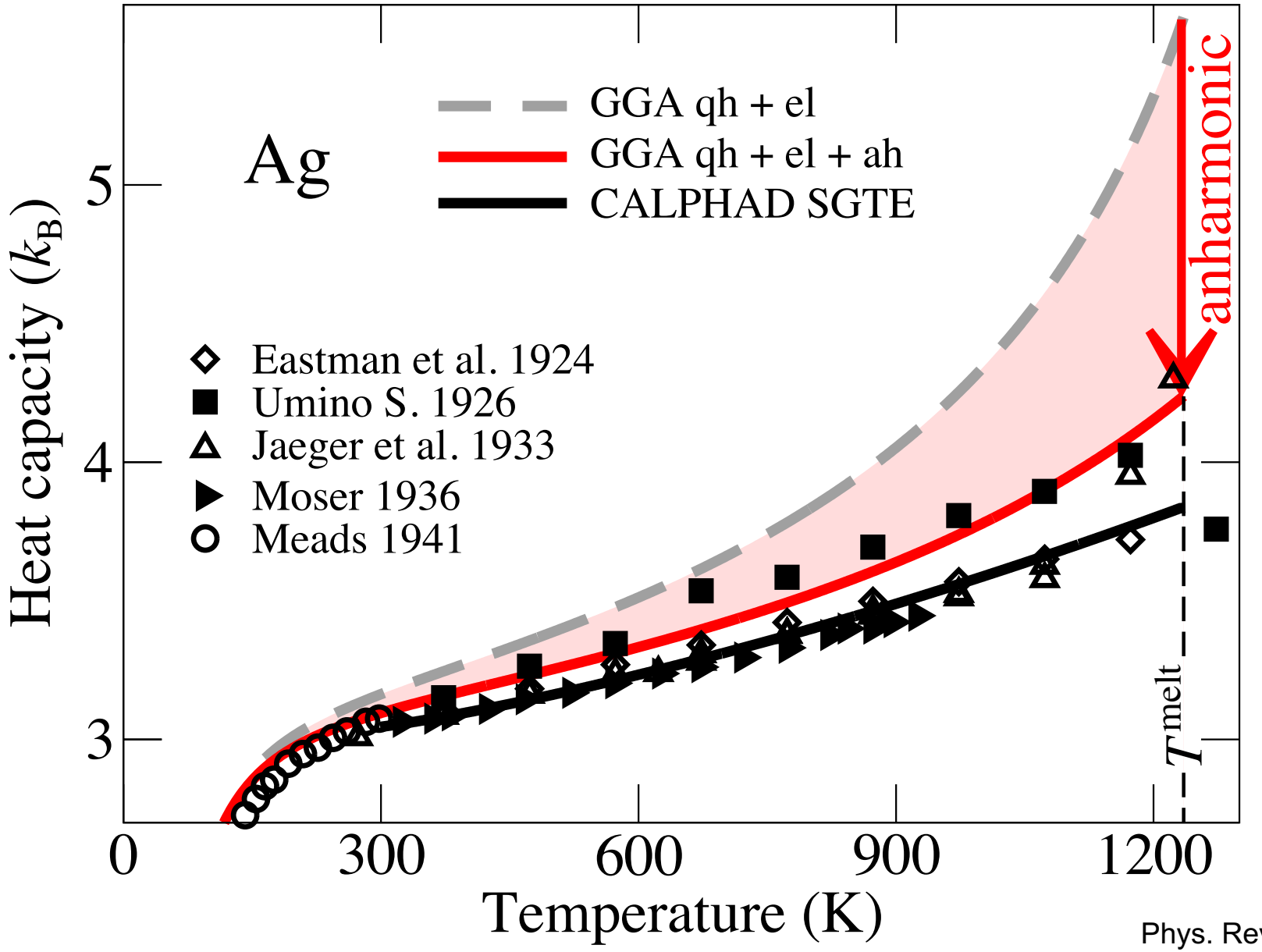


Phys. Rev. Lett. 114 (2015) 195901

# Wide range study of heat capacities

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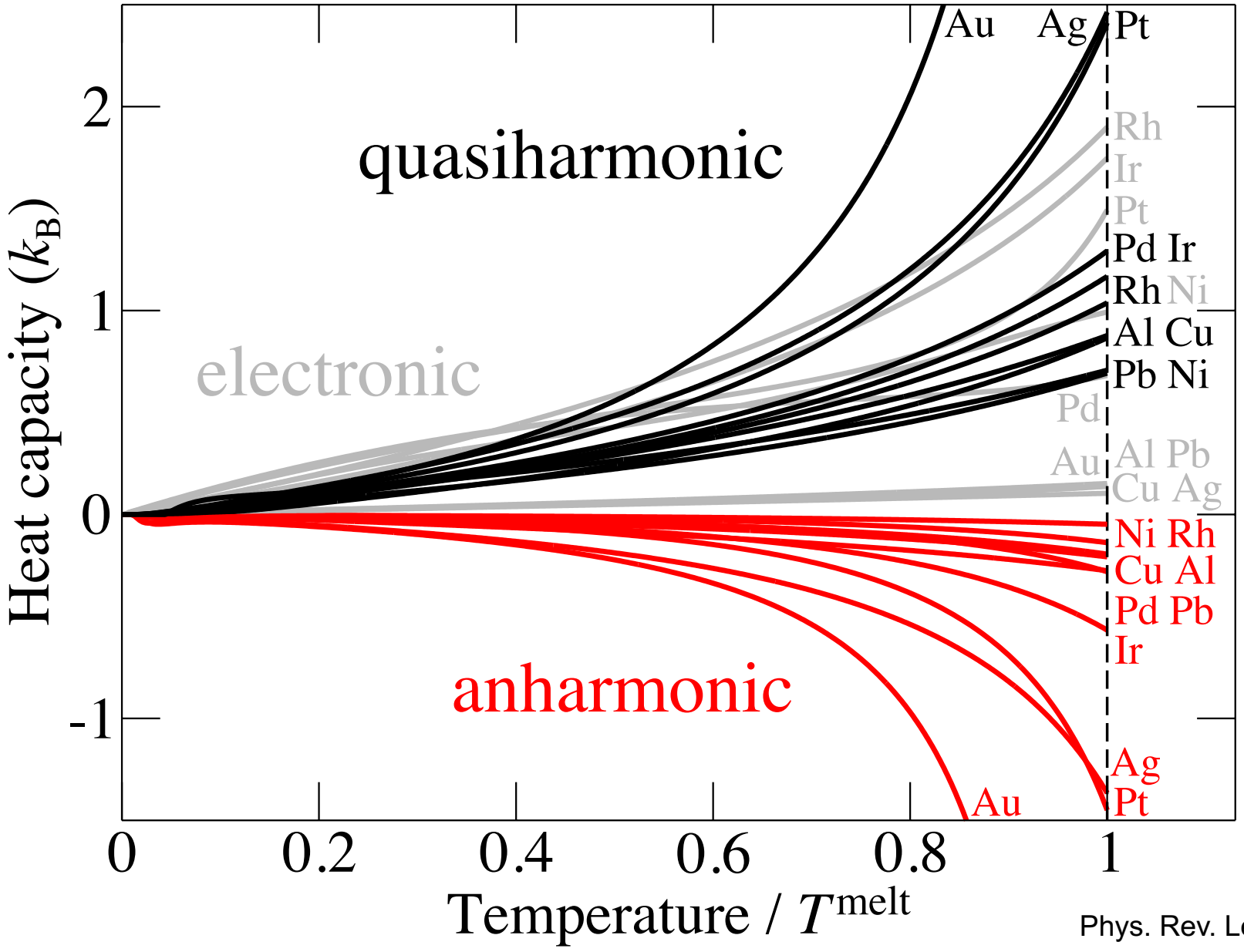


Phys. Rev. Lett. 114 (2015) 195901

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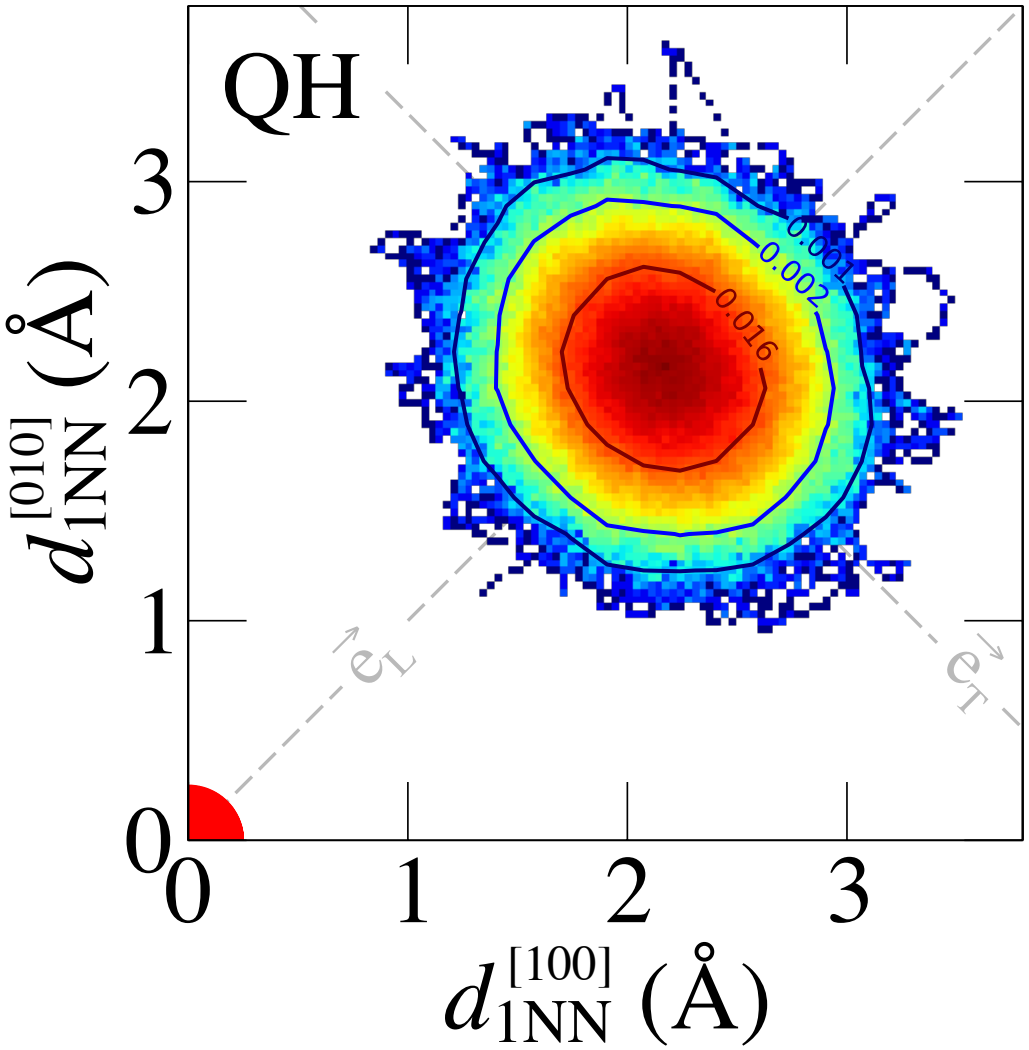


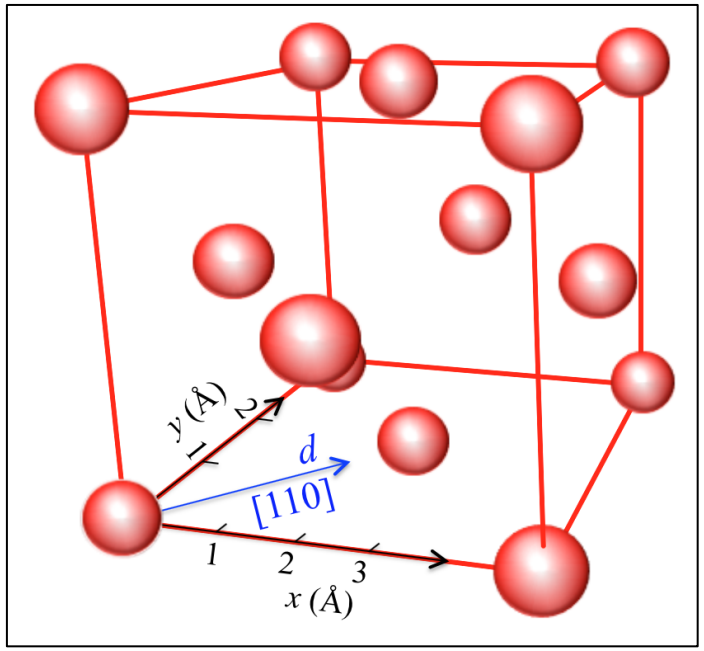


Phys. Rev. Lett. 114 (2015) 195901

# First nearest-neighbor distance distribution

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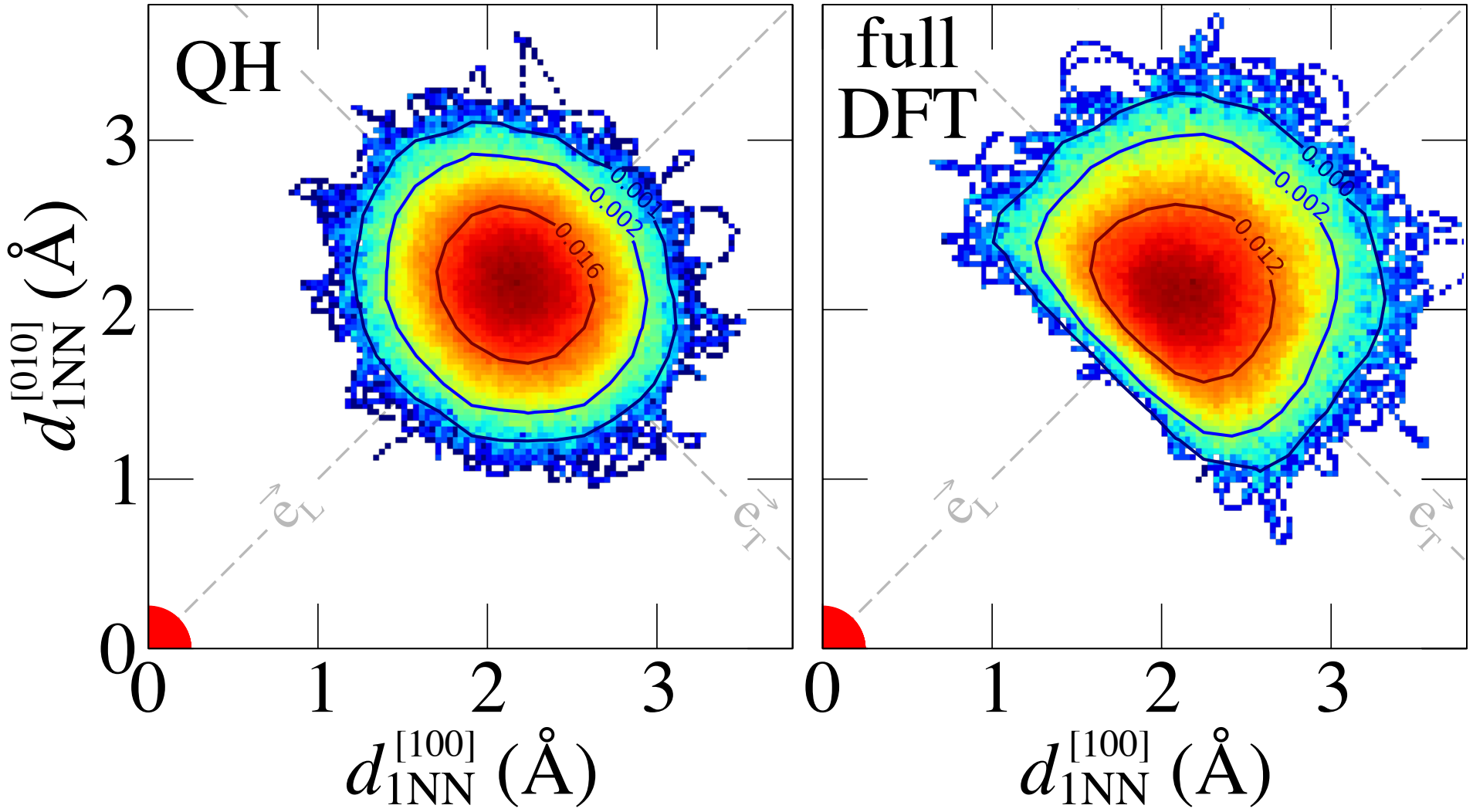


Phys. Rev. Lett. 114 (2015) 195901

# Magnetic excitations

# Magnetic excitations (dreaming of what could be)

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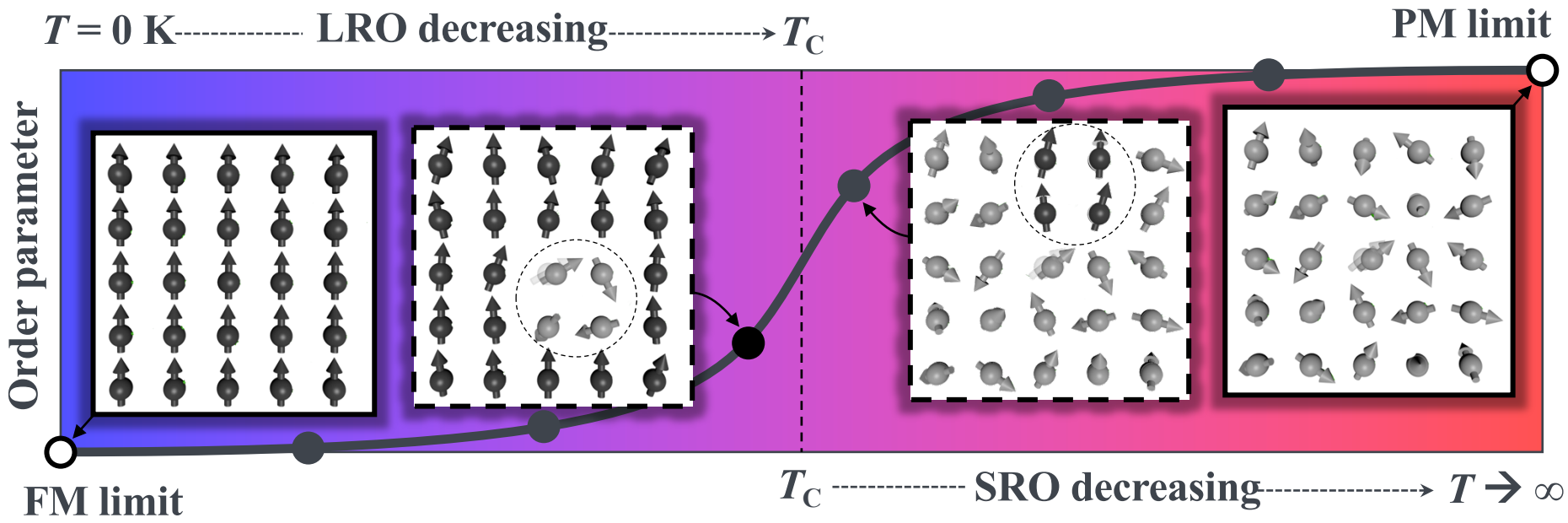


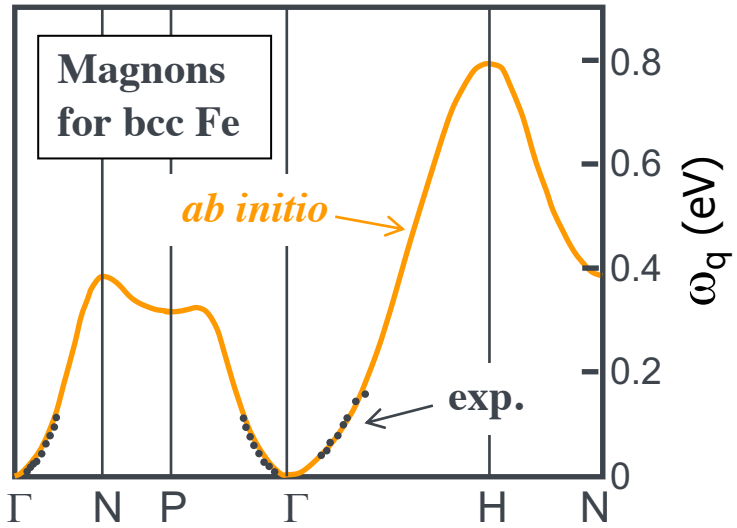


Phys. Rev. B 78 (2008) 033102

- Magnons are bosons
- BUT no simple occupation due to strong interactions
- BETTER mean field theories

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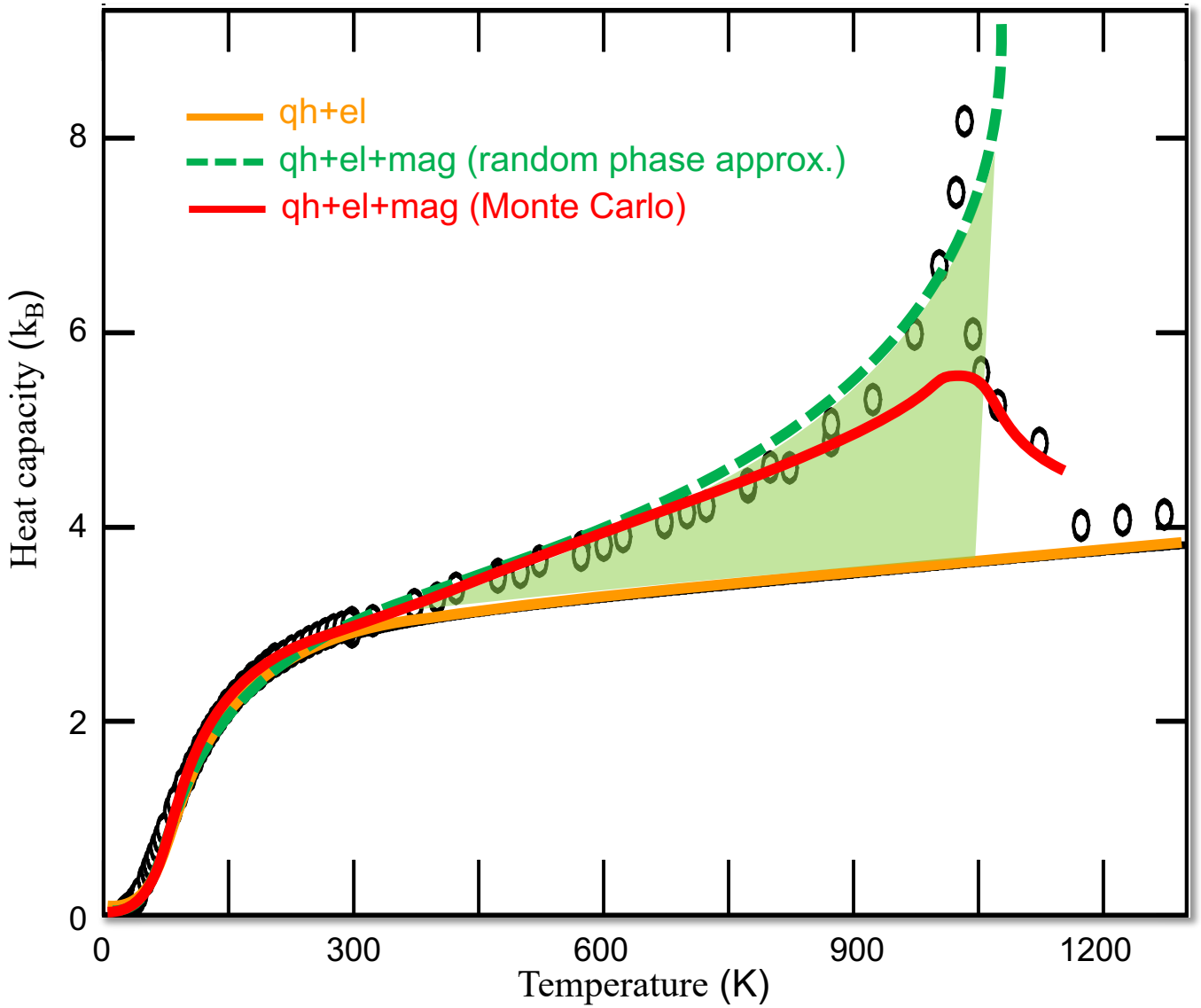
## Example: Heat capacity for iron




Phys. Rev. B
78 (2008)
033102

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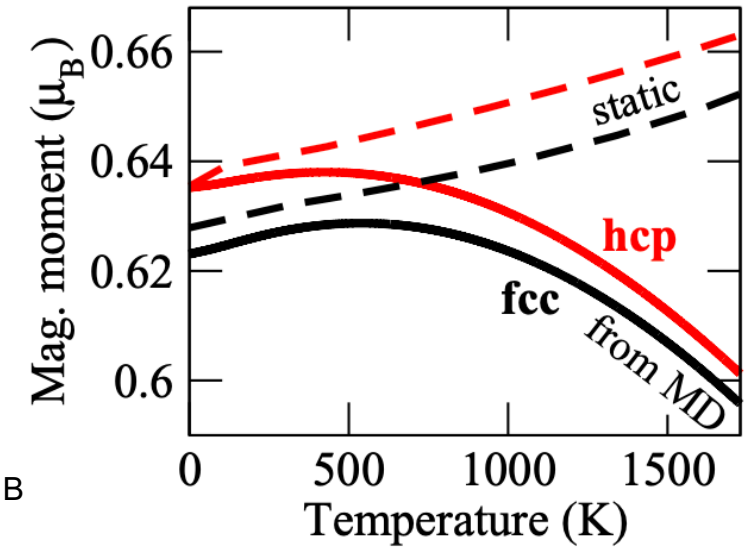
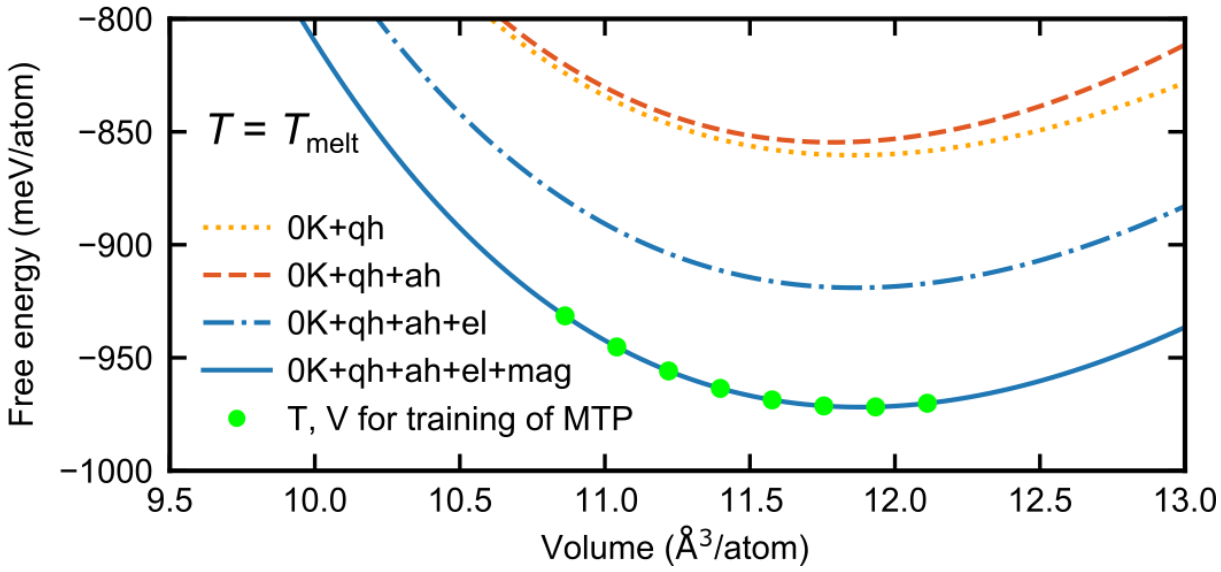
- **mean-field approximation if well above Curie temperature**
- **or empirical approach with DFT/experimental input**

$$C^{\mathrm{mag}}(T) = \begin{cases} k_f(T/T_C)\exp[-4(1-T/T_C)] & T < T_C \\ k_p(T/T_C)\exp[8p(1-T/T_C)] & T > T_C \end{cases}$$

$$S^{\mathrm{mag}} = k_B \ln(m+1)$$




Phys. Rev. B 98 (2018) 224106



# Magnetic excitations (our present real-life practice)

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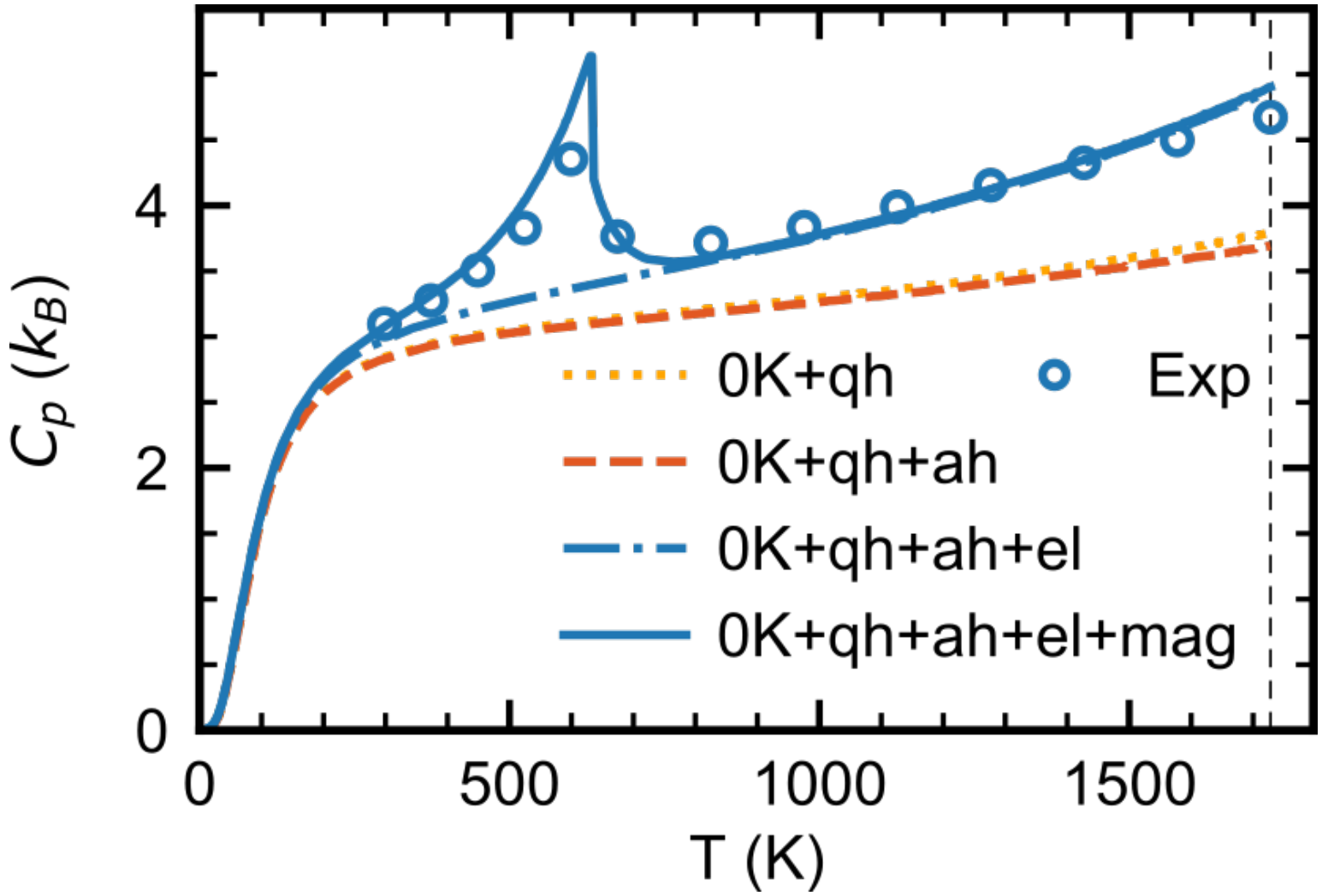
**Example: Heat capacity for nickel**



# Back to defects

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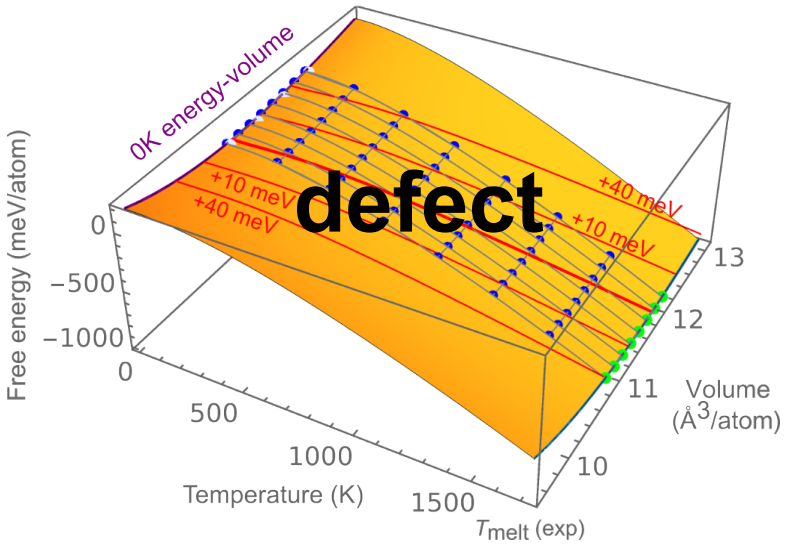
**“master” equation:**

**defect formation free energy** =

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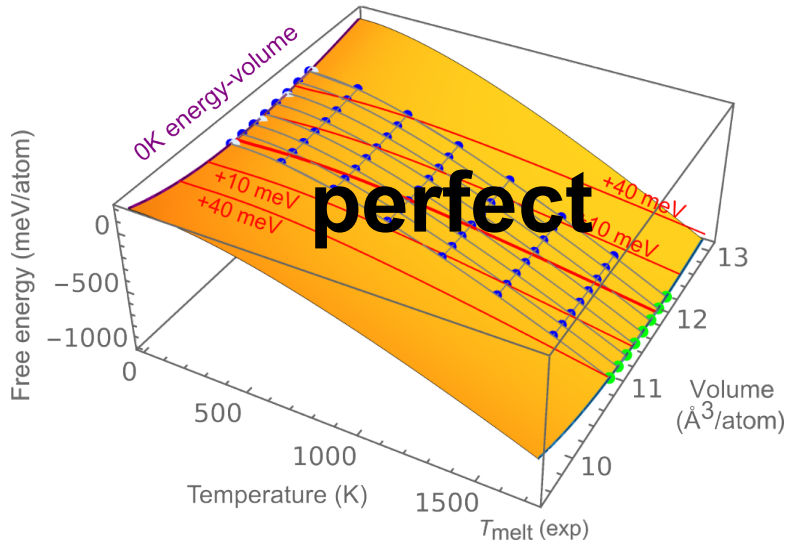


→ **once you have anharmonic vibrations, do not care much about defects**
→ **but supercell size convergence can be tough (error scales with # atoms)**
→ **and sometimes special care necessary, e.g.:**
- stacking plane migration
- vacancy migration

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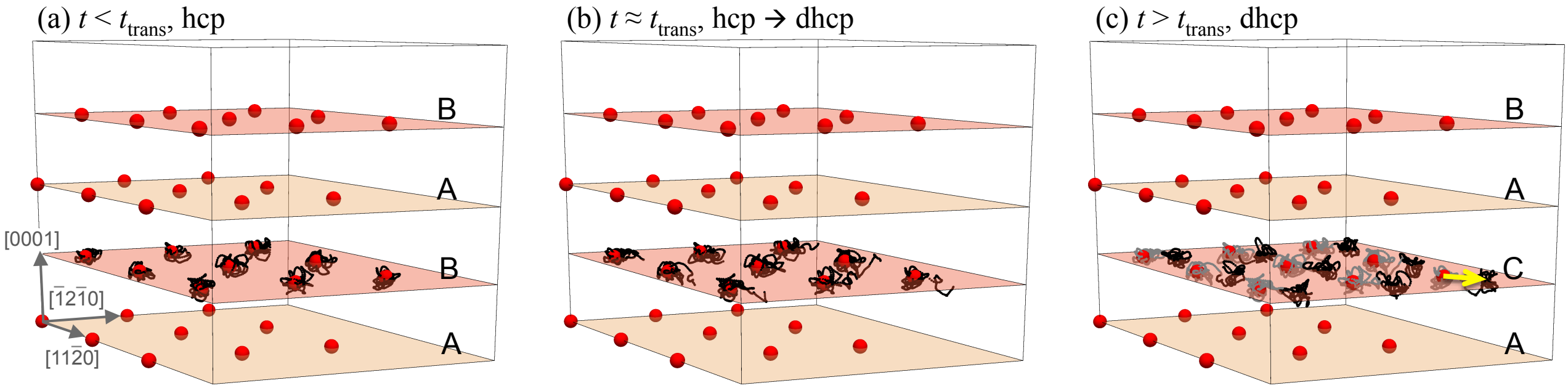
ANNNI = axial-next-nearest- neighbor-Ising

**Example: hcp Ni for ANNNI model (SFE = hcp – fcc)**




Phys. Rev. B 98 (2018) 224106

→ **MD needs to be monitored carefully**
→ **here finite size effects play a role**
→ **supercell size needs to be large enough**

# Most recent method for finite temperature DFT

# Methodology: **Direct upsamling**

(to be published)

1. Run low accuracy DFT molecular dynamics
2. Fit preliminary moment tensor potential (MTP)
3. Optimize MTP on high accuracy DFT snapshots

4. TILD from effective harmonic to MTP for F(V,T)
5. Upsampling from MTP to DFT on snapshots for F(V,T)
6. Parametrize F(V,T) → Legendre transform to G(P,T)

7. Extract thermodynamic properties
   (e.g. heat capacity, expansion coefficient, bulk modulus)

TILD = thermodynamic integration using Langevin dynamics

# Moment tensor potentials (MTPs)

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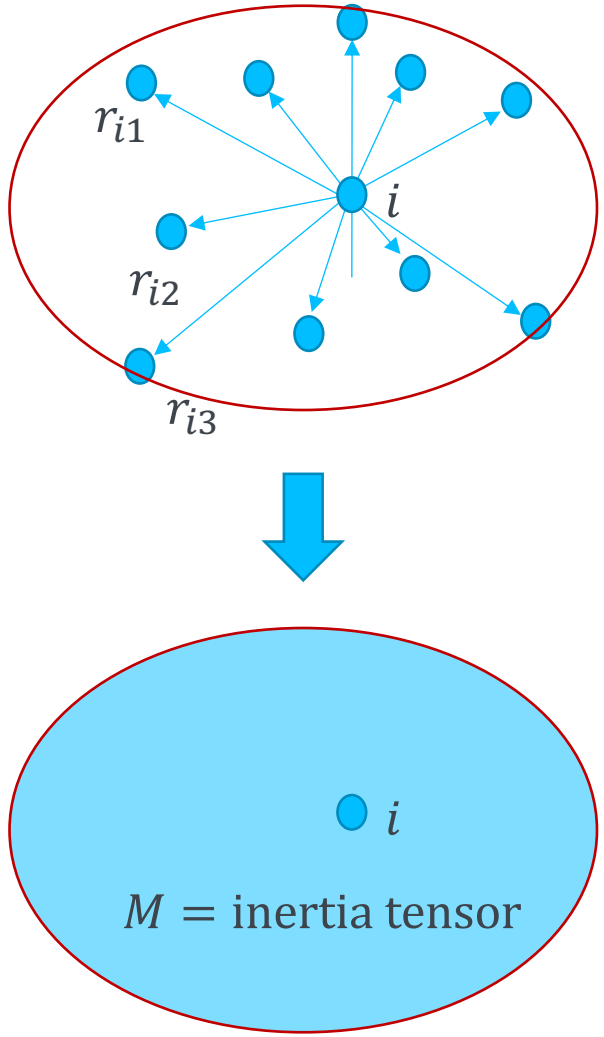
Shapeev, Multiscale Modeling & Simulation 14, 1153 (2016)

Descriptors of atomic environments:

- Moments of inertia of surrounding atoms
- They satisfy the needed symmetries (rotation, permutation, translation, …)
- **Math:**
  - Moments: $M_{n,m}(\boldsymbol{r_i}.) = \sum_j f_n(|r_{ij}|) \underbrace{r_{ij} \otimes \cdots \otimes r_{ij}}_{m \text{ times}}$
  - Basis functions $B_\alpha$ are (all) different multiplications (contractions) of inertia tensors $M_{m,n}$ yielding a scalar
  - Energy: $E = \sum_\alpha \theta_\alpha B_\alpha$
  - Active learning via D-optimality



# Methodology: Direct upsampling (to be published)

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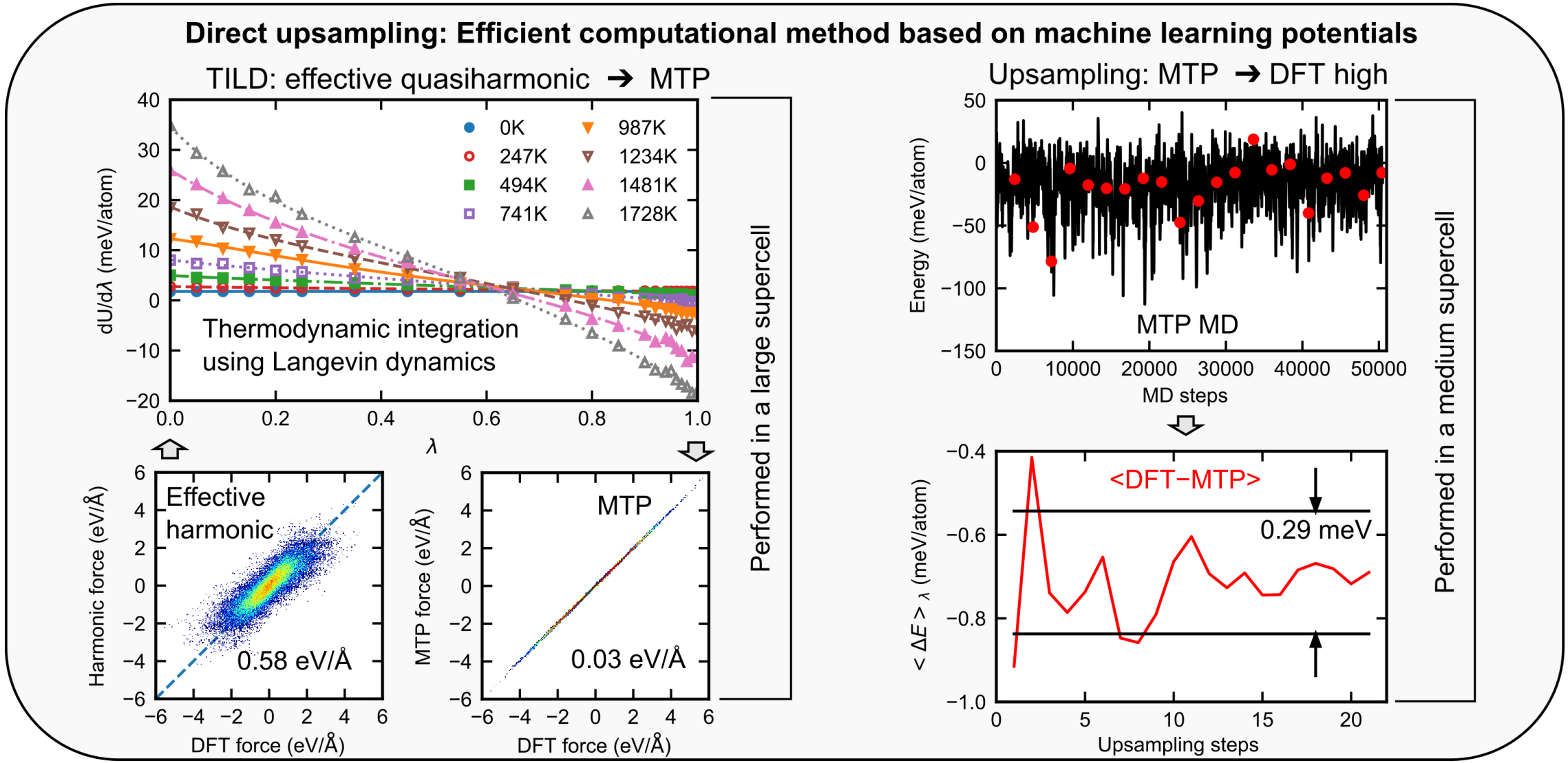


**<u>included</u>: anharmonic vibrations, electronic excitations, coupling, magnetism** (mean field, empirical)

# Defects: Results

# Arrhenius or not Arrhenius

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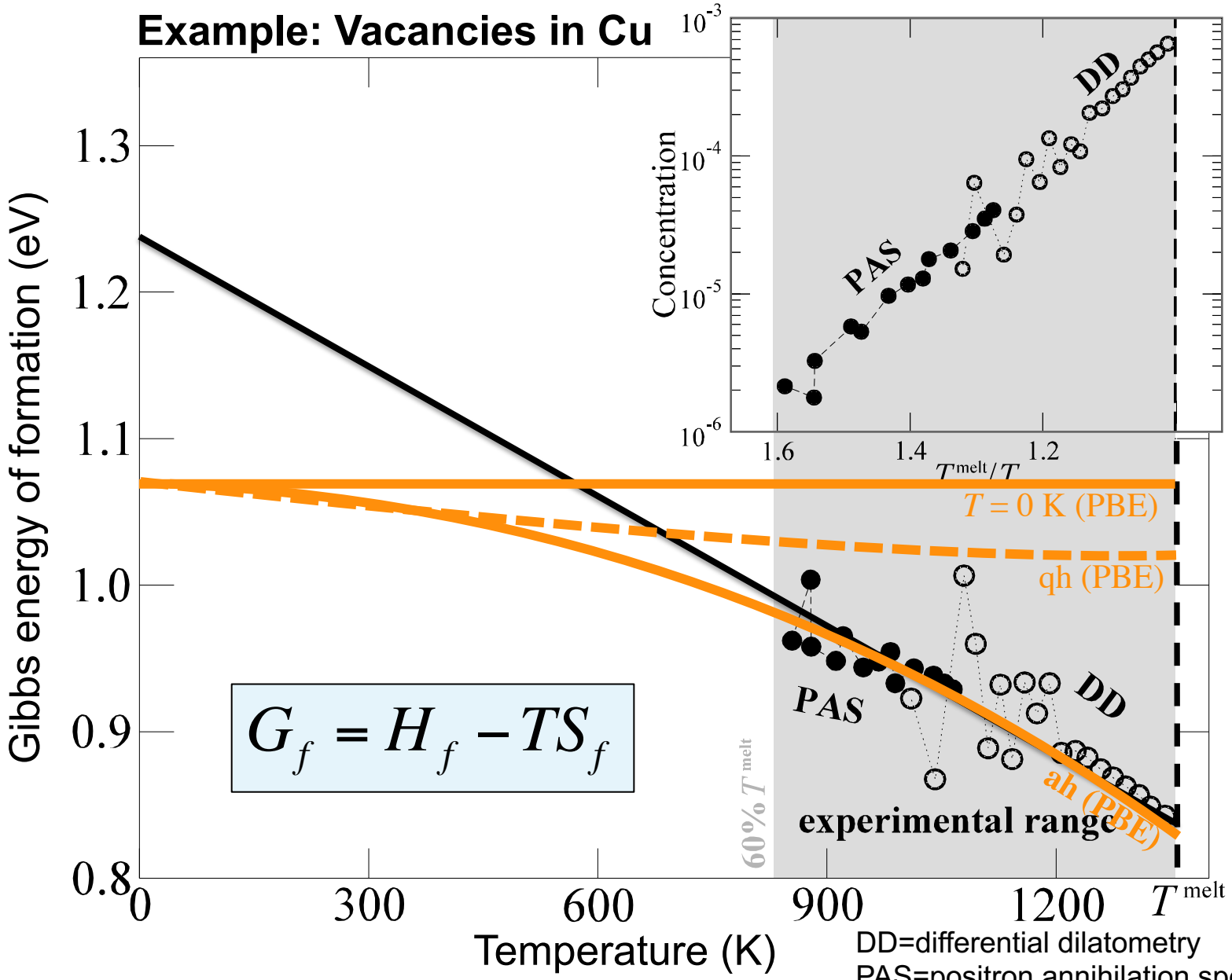


DD=differential dilatometry
PAS=positron annihilation spectroscopy



Phys. Rev. X 4 (2014) 011018

# Arrhenius or not Arrhenius

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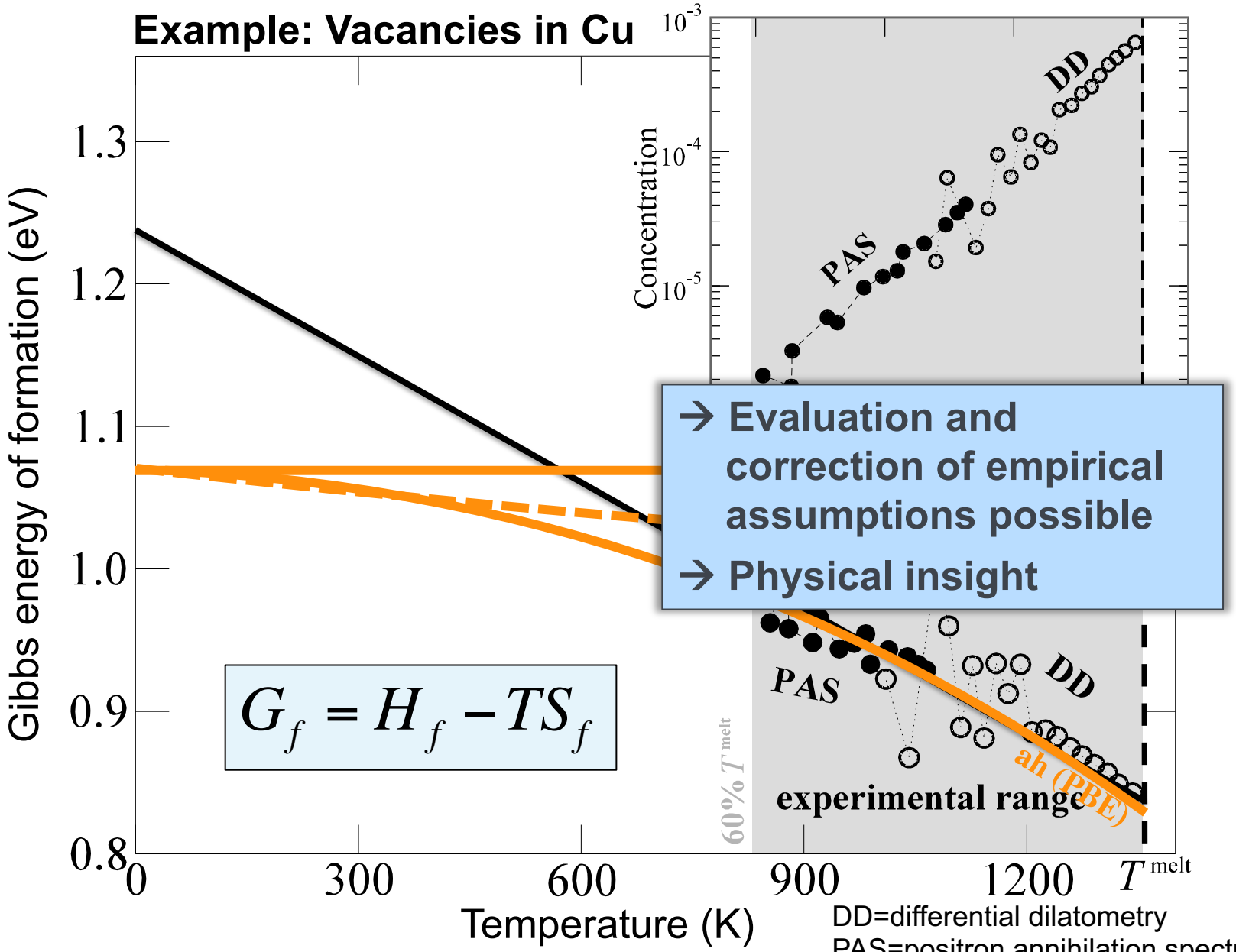


→ Evaluation and correction of empirical assumptions possible

→ Physical insight

DD=differential dilatometry
PAS=positron annihilation spectroscopy



Phys. Rev. X 4 (2014) 011018

# Physical insight

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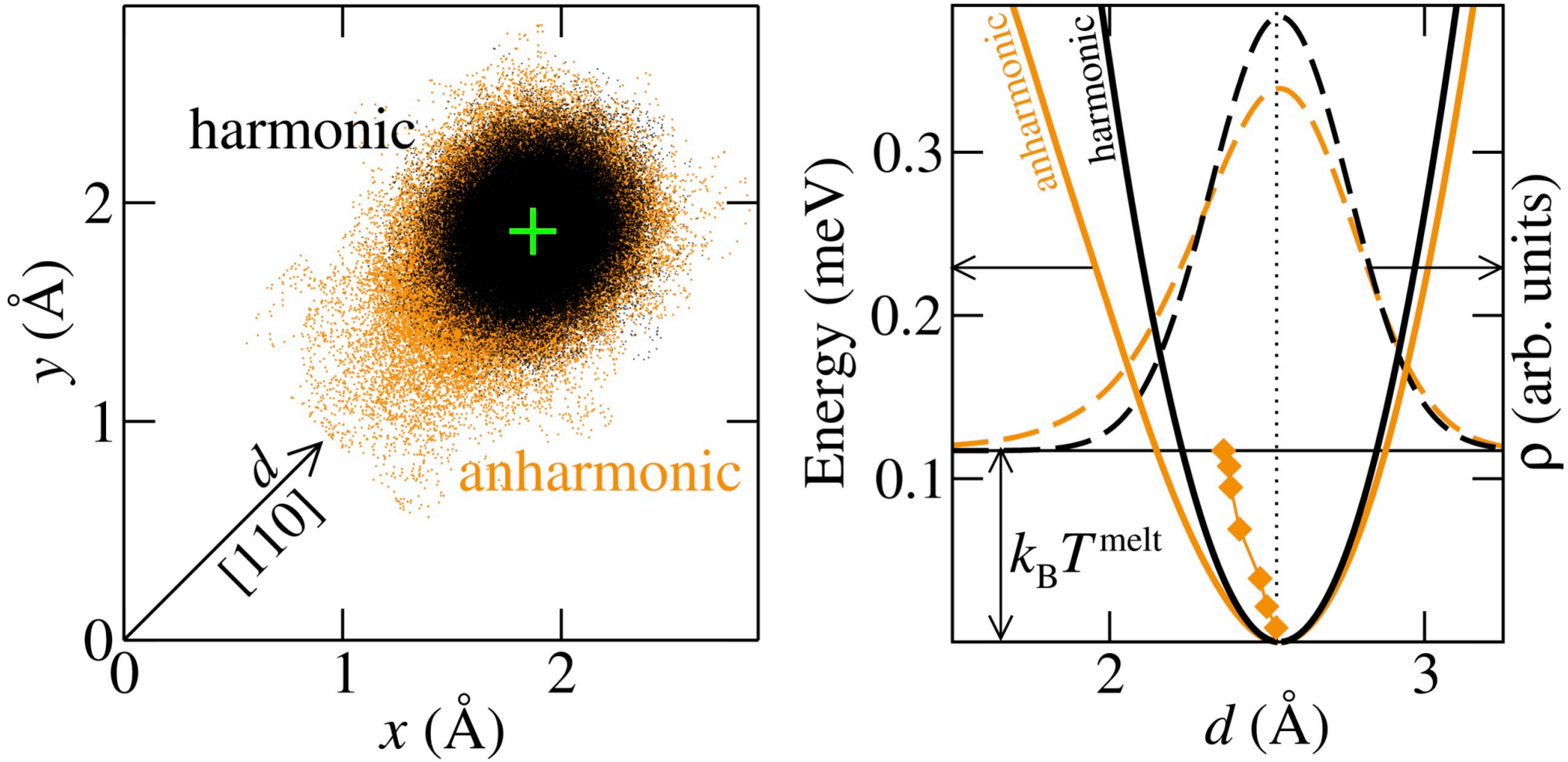
## Nearest neighbor distribution at finite temperatures




→ **Localized interactions around vacancy**



Phys. Rev. X 4 (2014) 011018

# Vacancies in Ni

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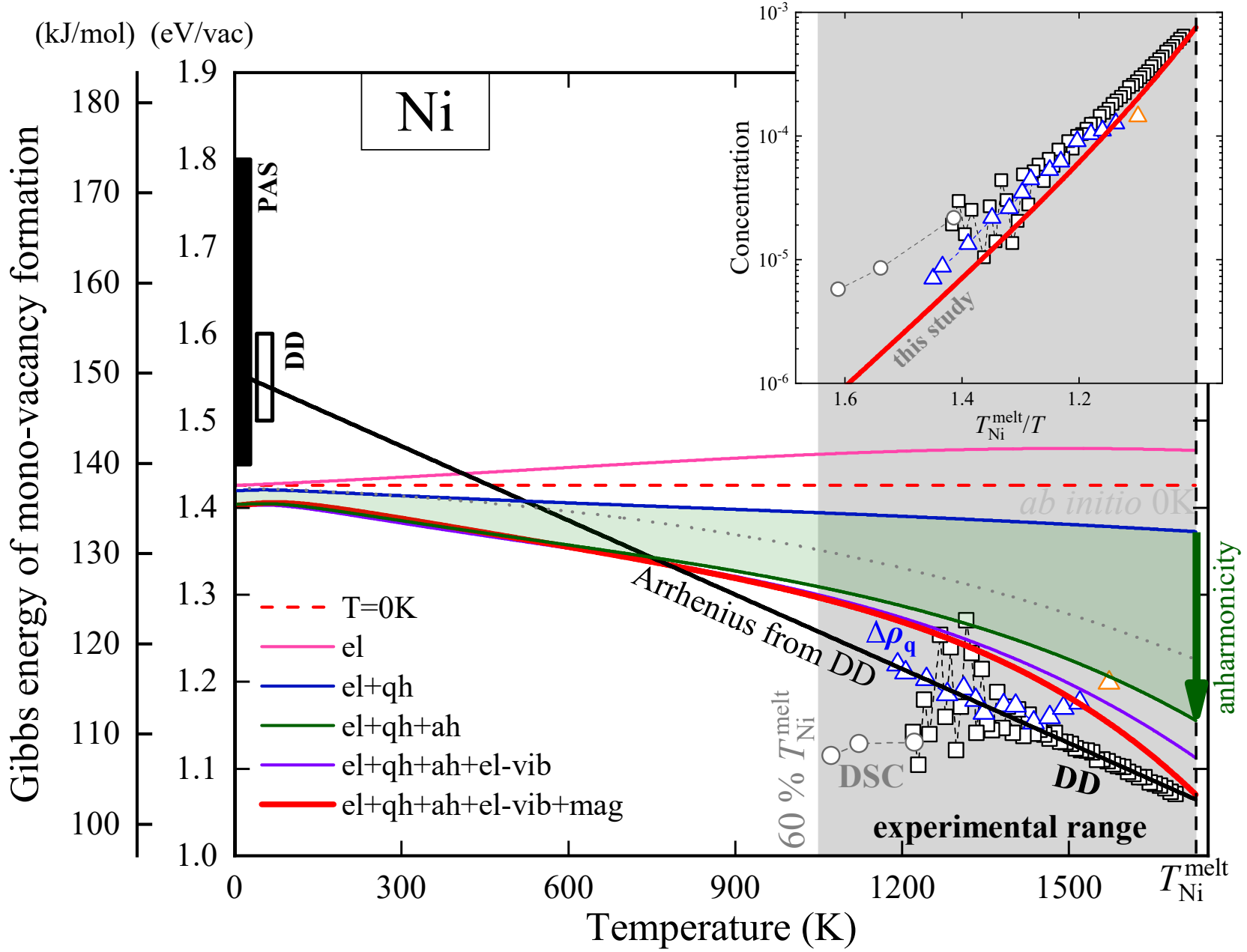




Phys. Rev. B 97 (2018) 214106

# Stacking fault energy for Nickel

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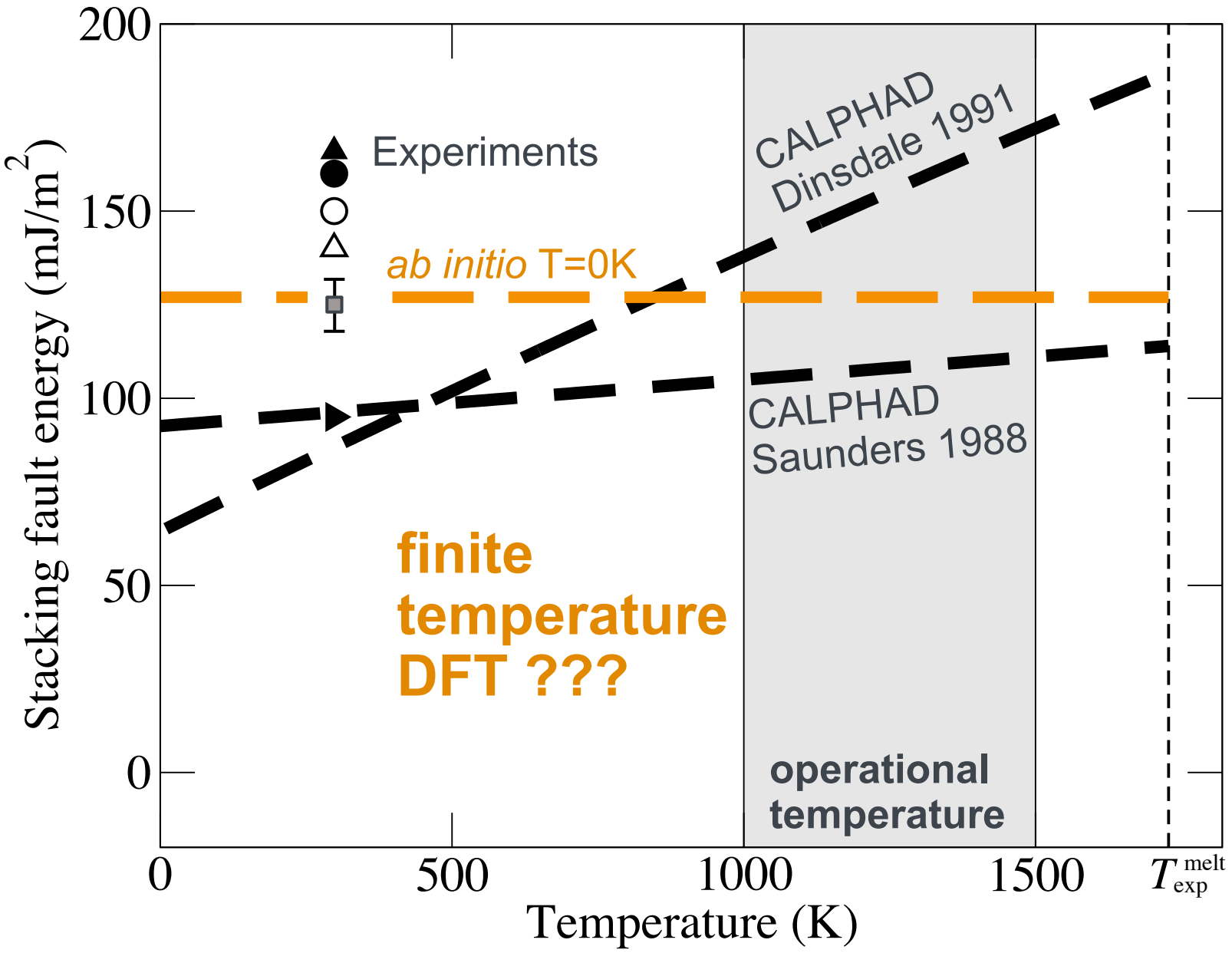




Phys. Rev. B 98 (2018) 224106

# Stacking fault energy for Nickel

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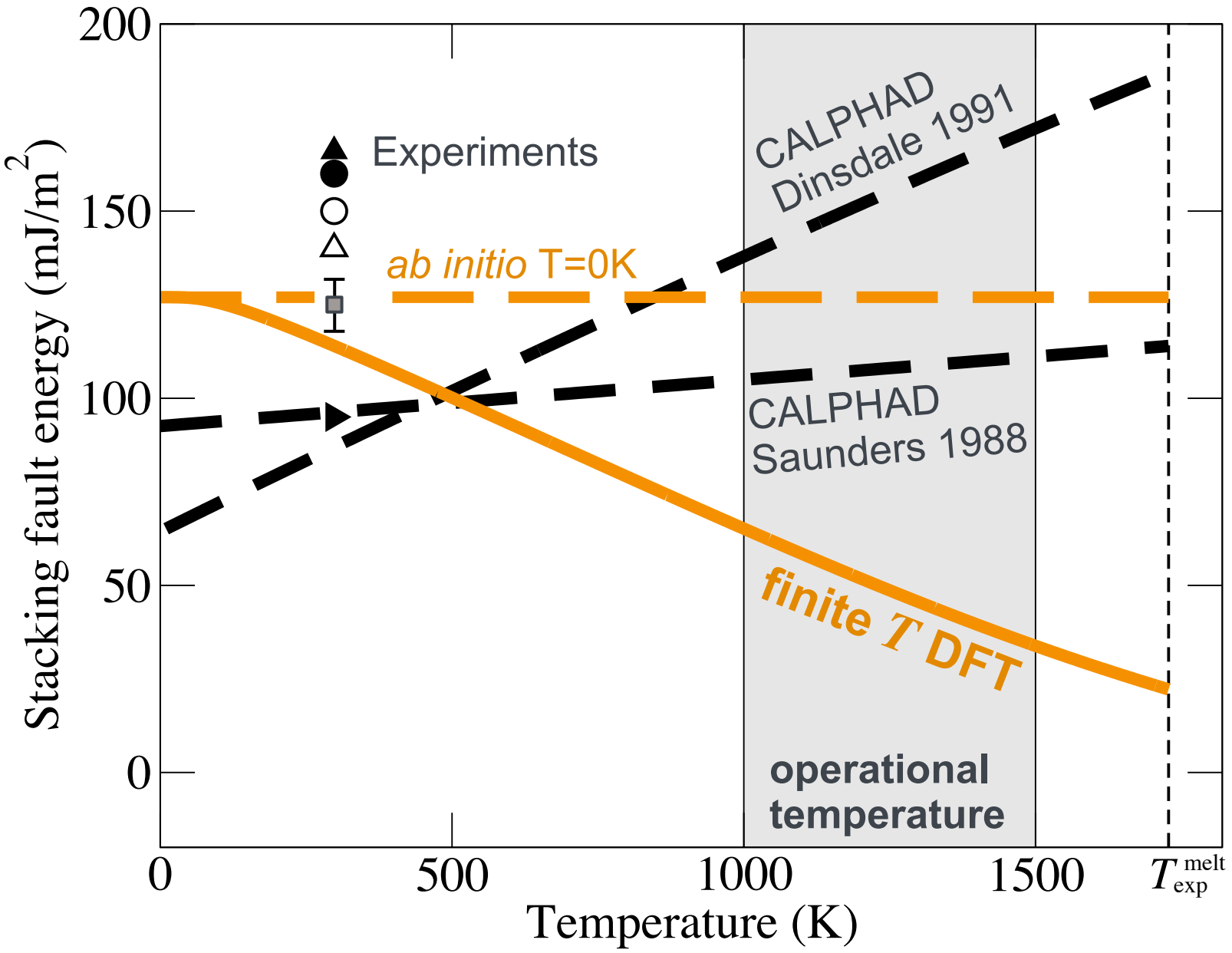




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# Extension to anti-phase boundaries (APB)

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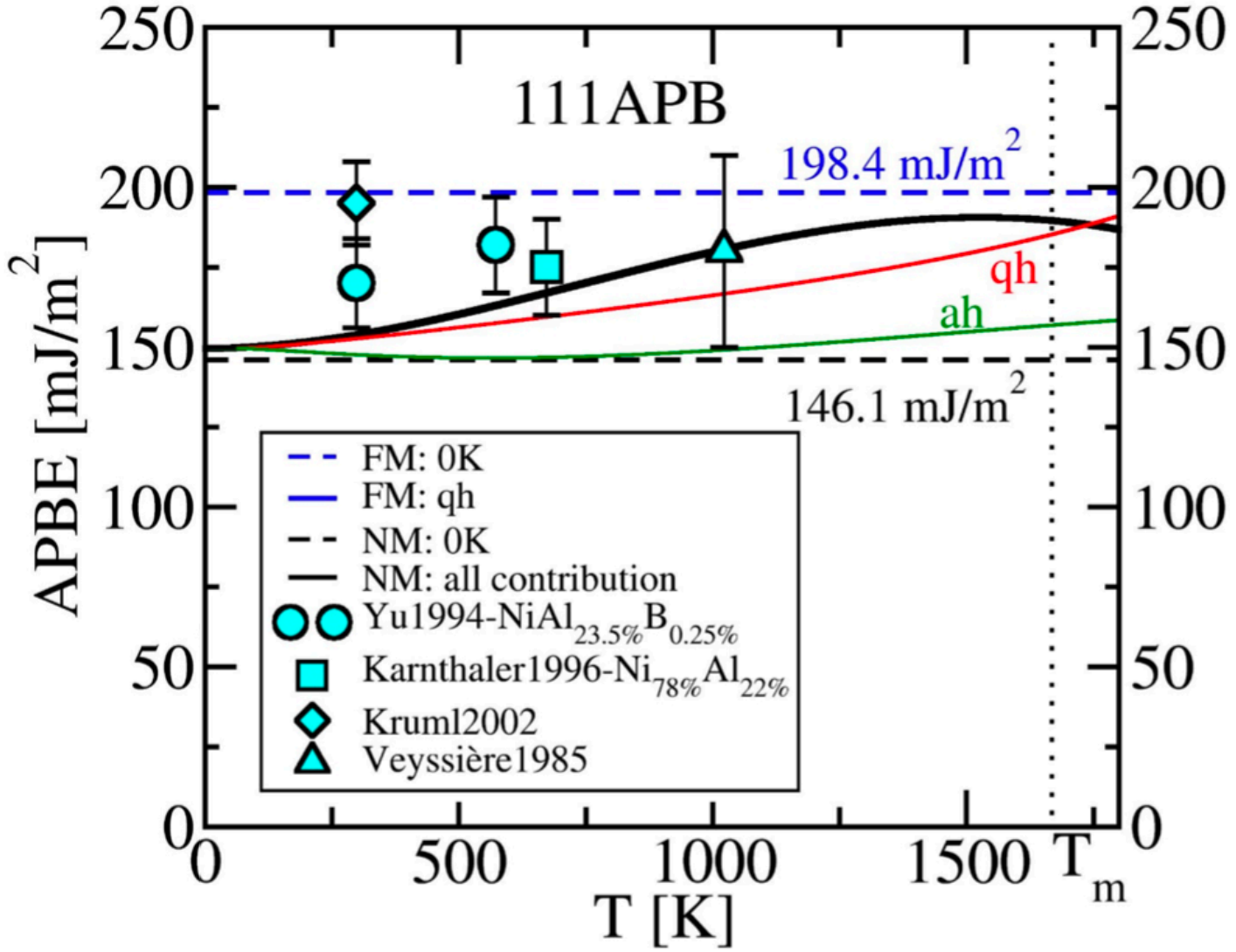
$Ni_3Al$
APB important
for Ni-superalloys
(to be published)



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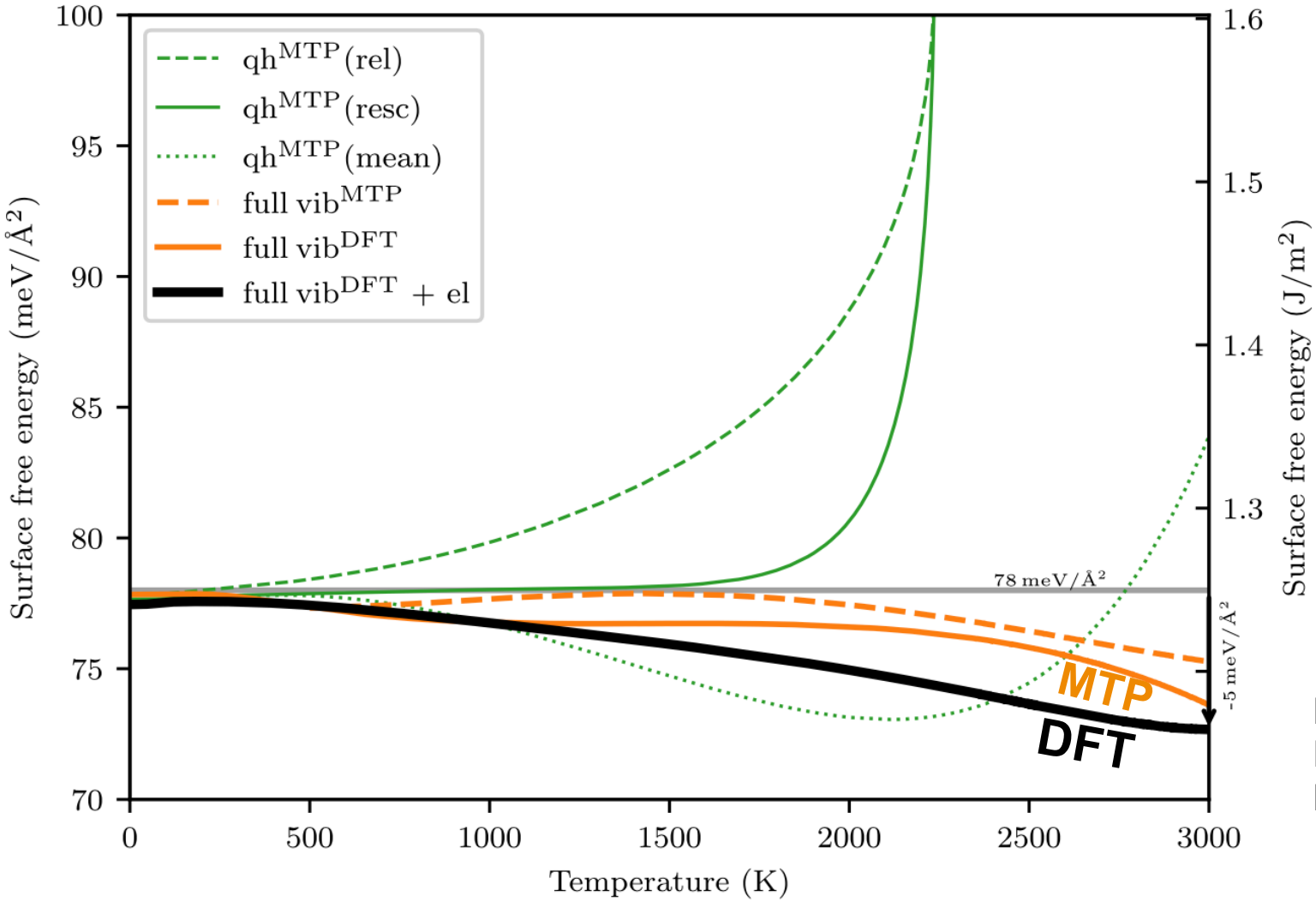
## **Surface free energy of TiN** (very important for coatings)




Reference:
Forslund, Grabowski et al.,
PHYSICAL REVIEW B 103,
195428 (2021)

→ high **accuracy** surface properties possible

# Alloys

# Unaries → Alloys

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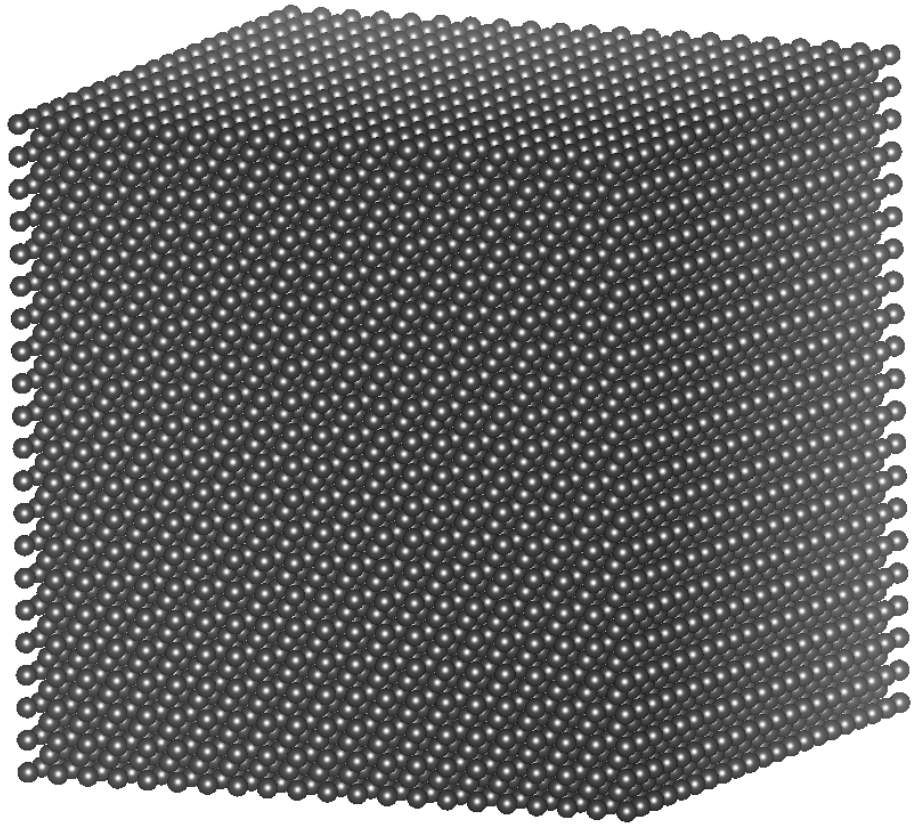
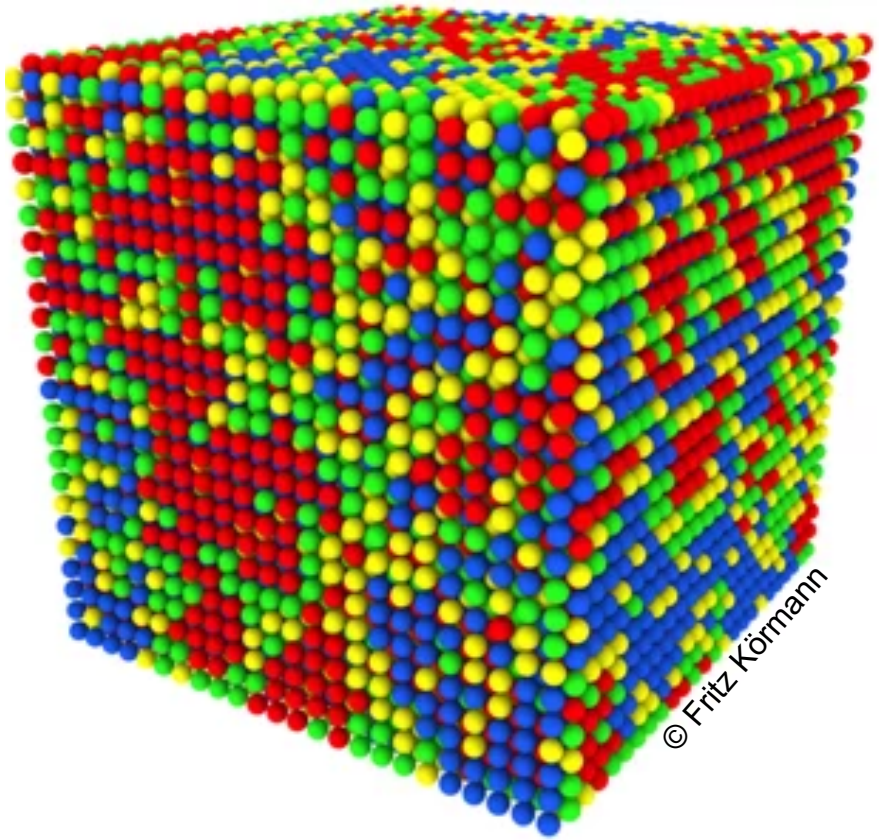
Unary system (single element)



→ **single defect formation energy**

Chemically complex system
High entropy alloy VNbMoTaW




→ **MANY defect formation energies (distribution)**
→ **highly challenging already at 0K**

# Vacancy energetics from unaries to alloys

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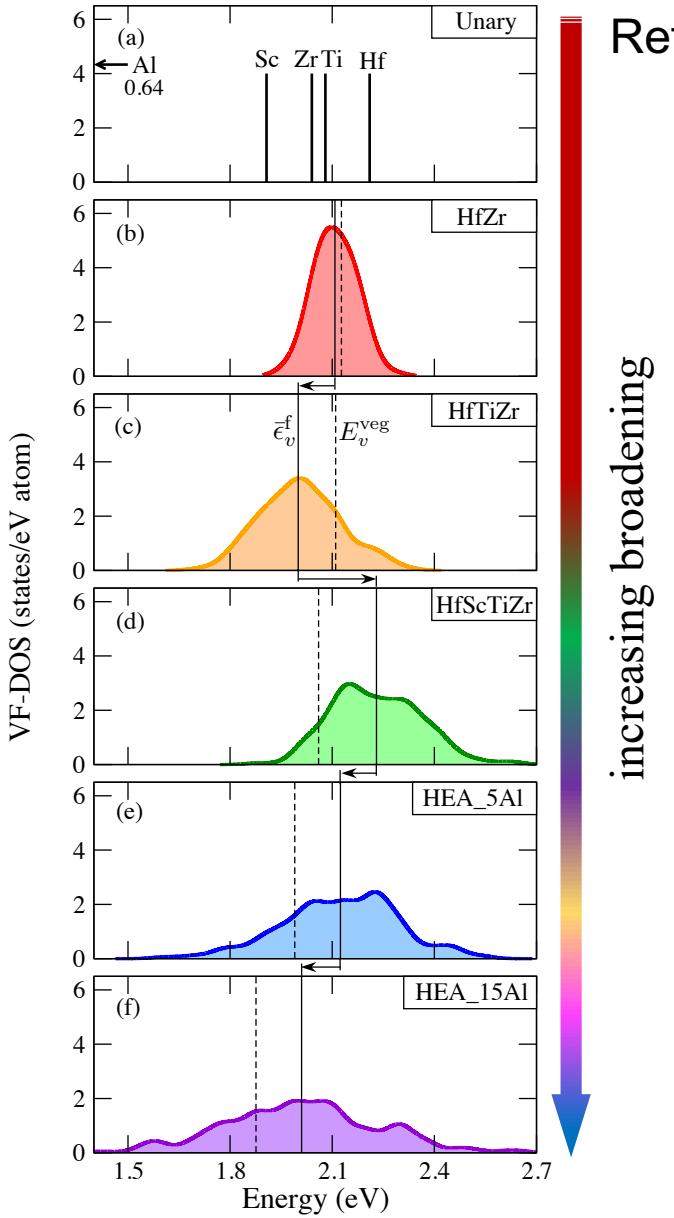
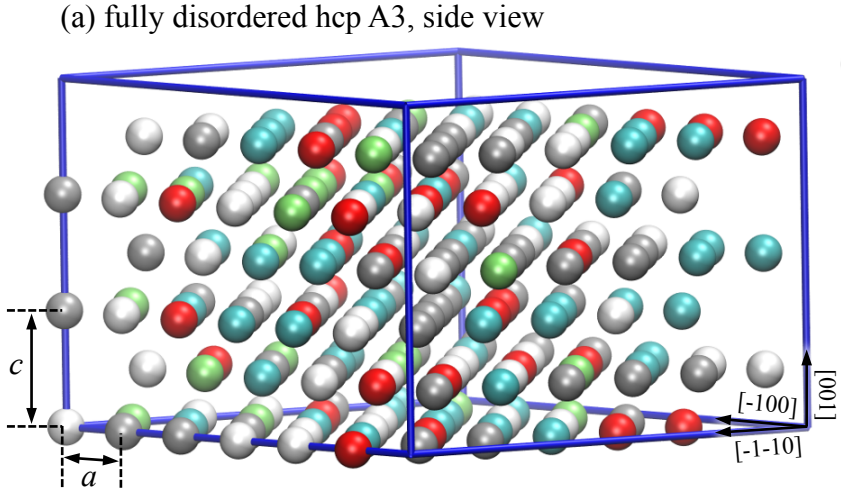
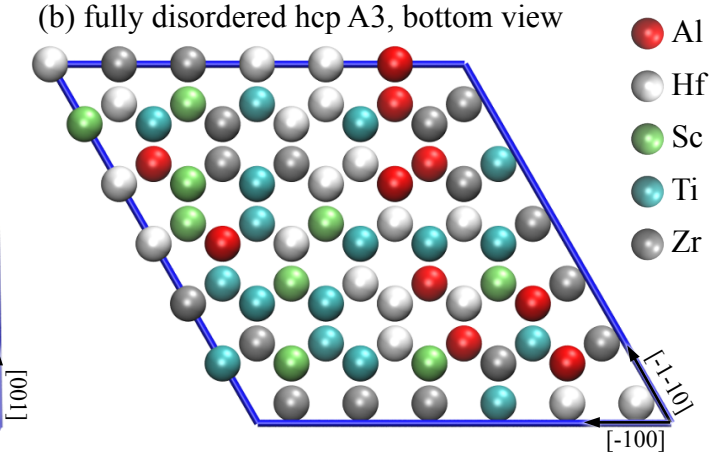
Ref: Xi Zhang, B. Grabowski (under review)



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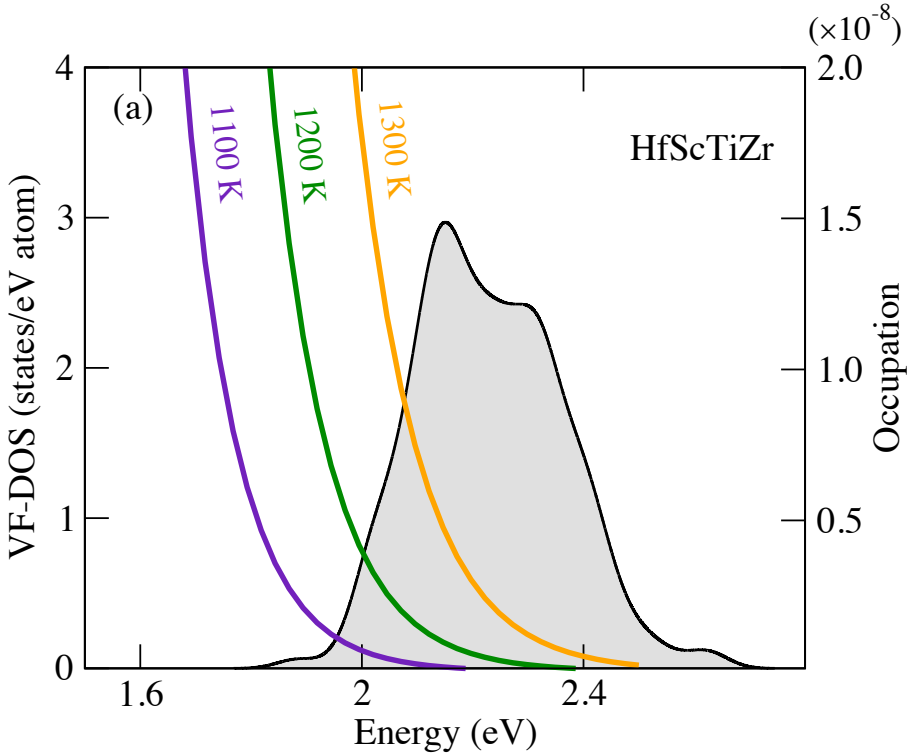
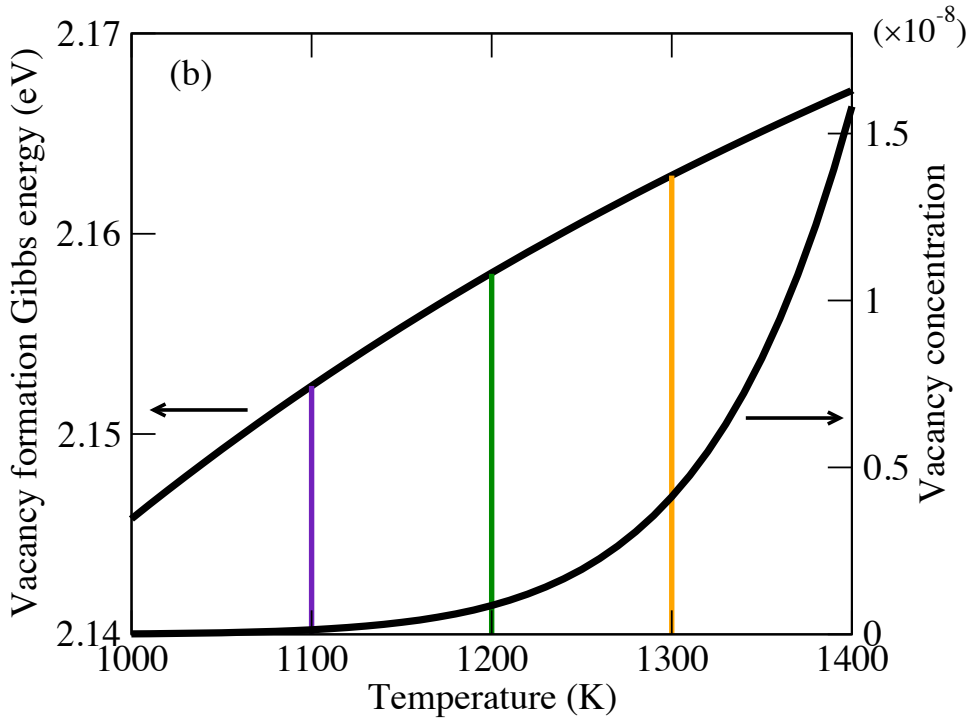
$$x_v^{\mathrm{tot}}(T) = \sum_i x_{v_i} = \sum_i \tilde{D}(\epsilon^{\mathrm{f}}_{v_i}) \exp(-\beta \epsilon^{\mathrm{f}}_{v_i})$$

occupation function



# Equilibrium vacancy concentration

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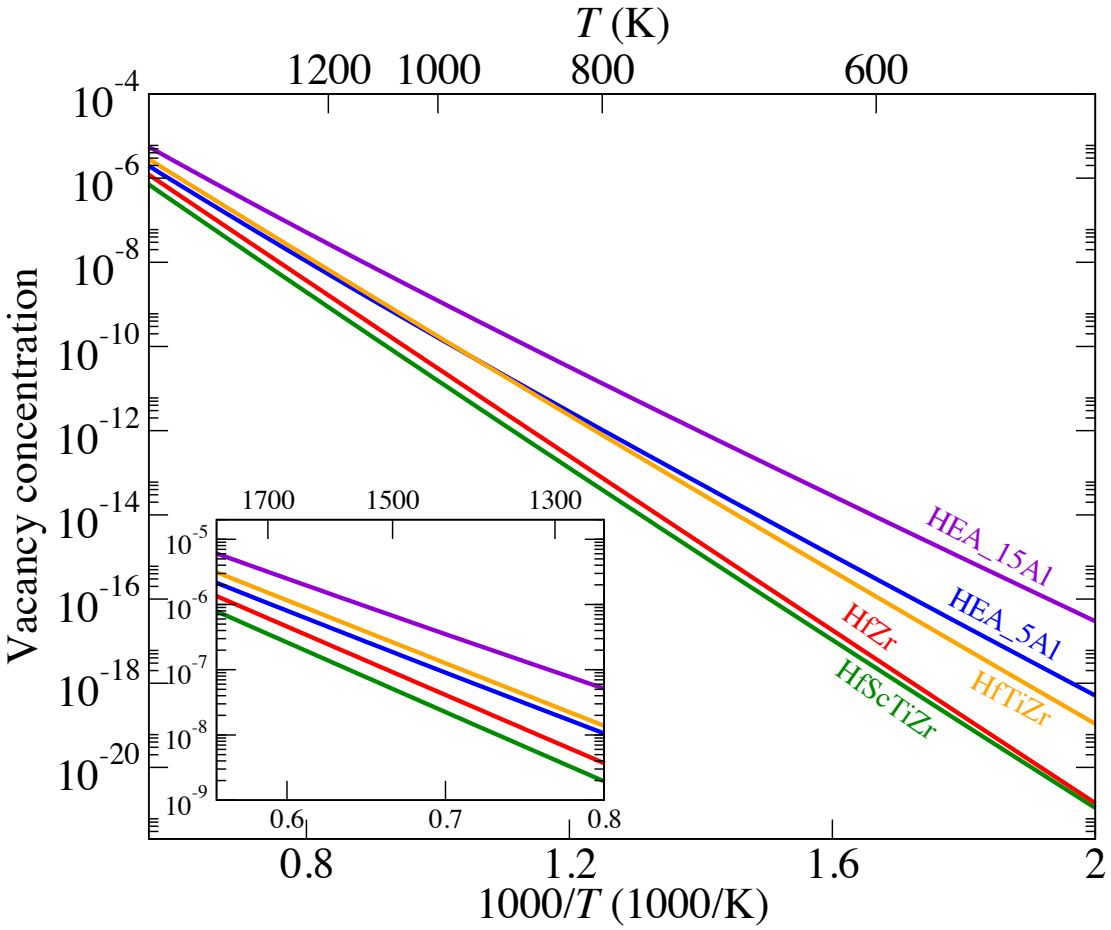
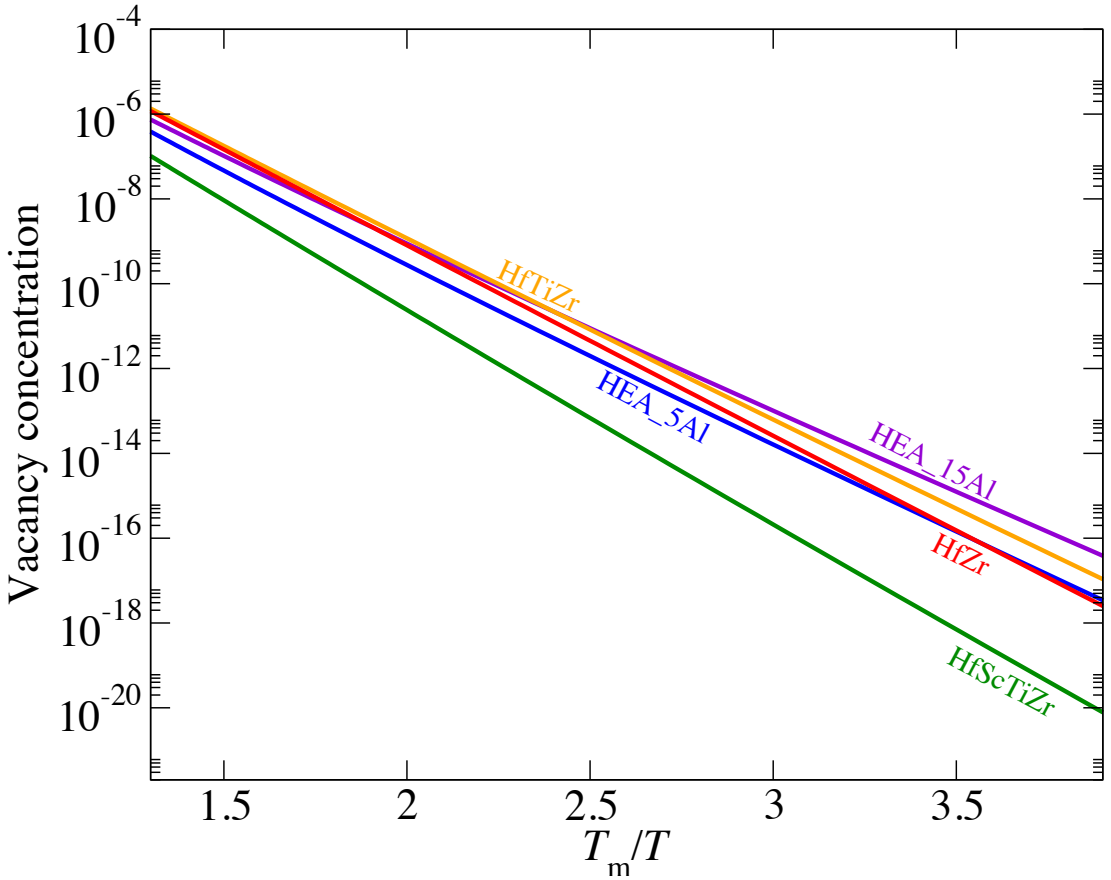
$$x_v^{\mathrm{tot}}(T) = \sum_i x_{v_i} = \sum_i \tilde{D}(\epsilon^{\mathrm{f}}_{v_i}) \exp(-\beta \epsilon^{\mathrm{f}}_{v_i})$$

**non-Arrhenius dependence**




Ref: Xi Zhang, B. Grabowski (under review)

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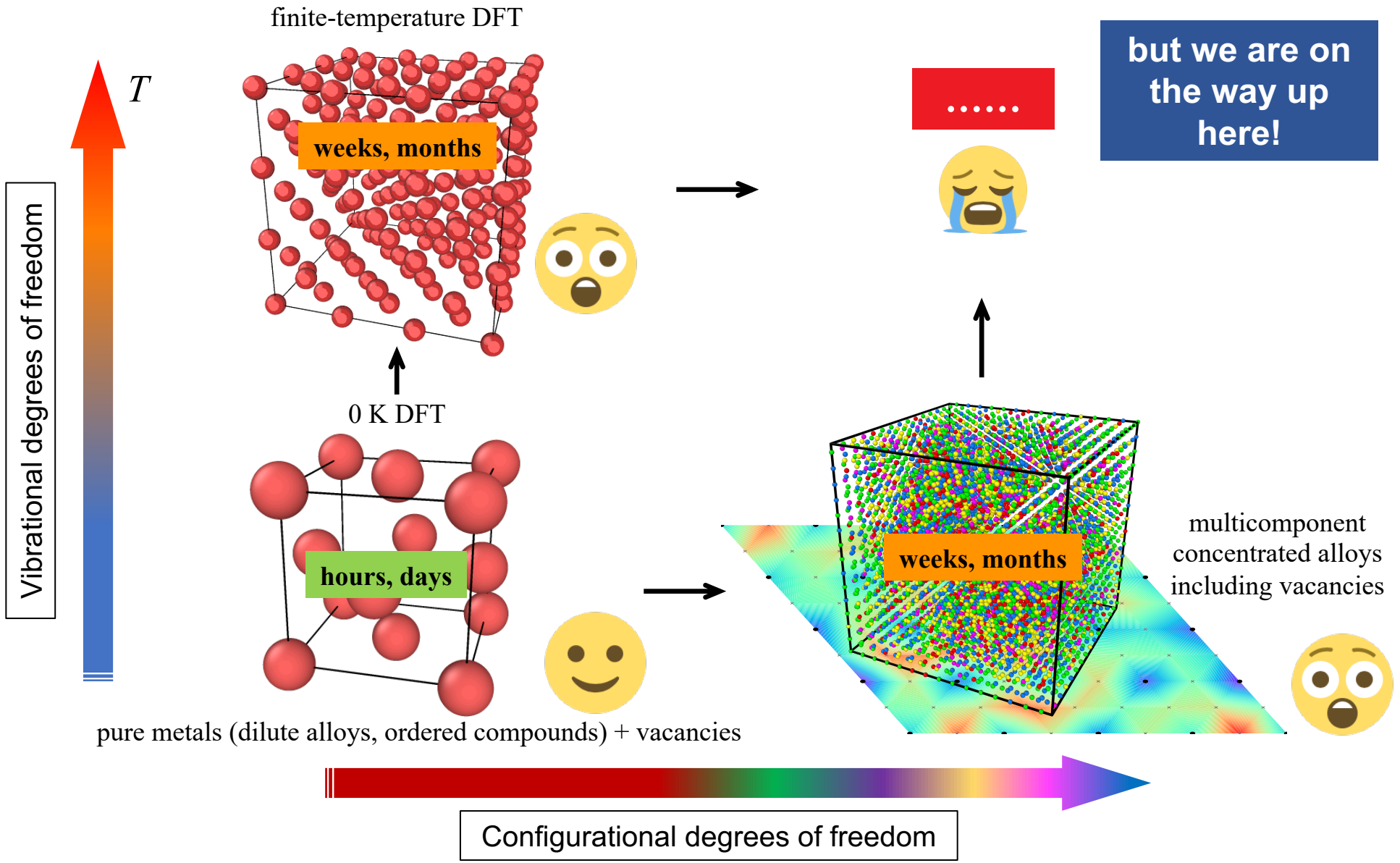


[1] Xi Zhang et al., Comp. Mater. Sci.148 (2018) 249–259

# Summary

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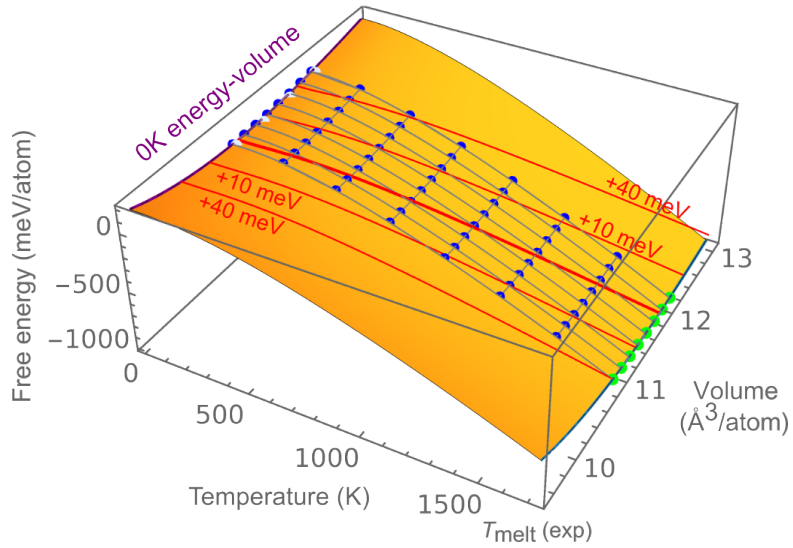
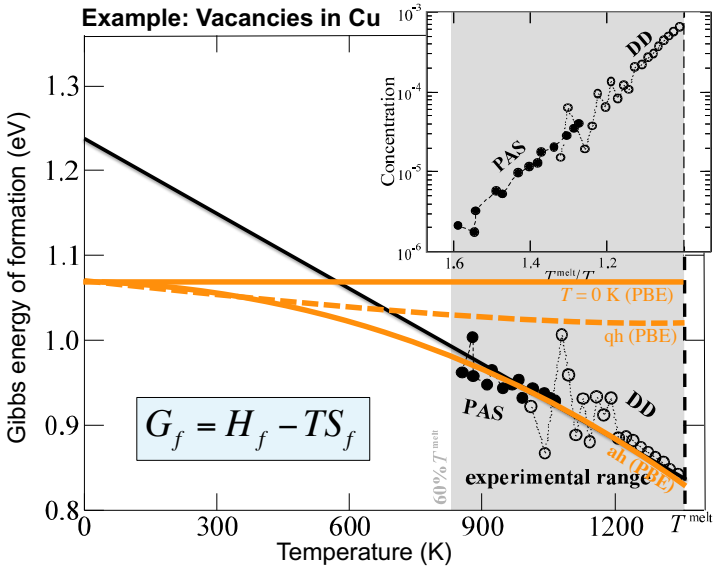
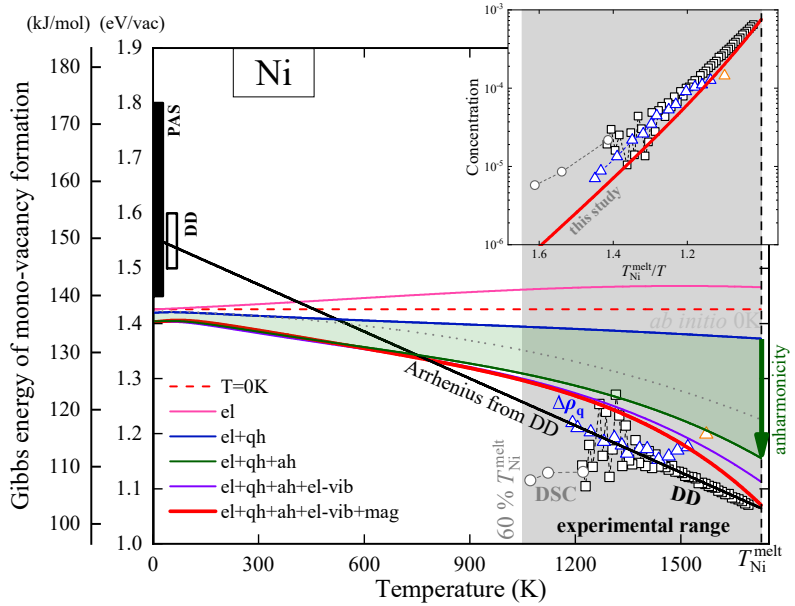
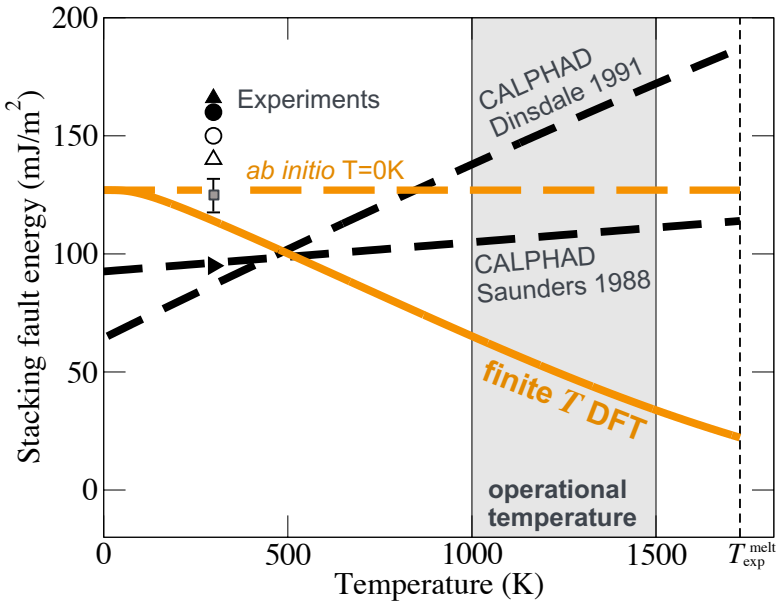
- key: free energy surface, for bulk & defects
- various excitations (qh, ah, el, mag, coupling)
- explicit anharmonic vibrations crucial
- efficient methodology: direct upsampling
- utilizes machine learning potentials
- generally good agreement with experiment
- predictions possible, understanding possible





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