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Atomic forces at finite magnetic temperatures: phonons in paramagnetic iron

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Motivation

- ➢ *Ab initio* methods to predict material properties / phase stabilities of complex materials (steels, magnetic shape memory alloys, etc.)
- ➢ Gibbs free energies provide link to computational thermodynamics (e.g. CALPHAD)
- ➢ Magnetic phases / magnetic excitations often strongly influence results
- ➢ Magnetic entropy plays a key role in free energy considerations, moreover…
- ➢ .. in particular the *atomic forces* sensitively depend on the magnetic state/magnetism

Integration and Impact

- The long term goal is the complete *ab initio* calculation of stable and metastable phase diagrams, which are considered a "road map" of materials design.
- Calculation of free energy surfaces including all relevant excitation mechanisms is a key expertise of the group.
- The methods developed in this group are key tools also for other groups of the CM department.

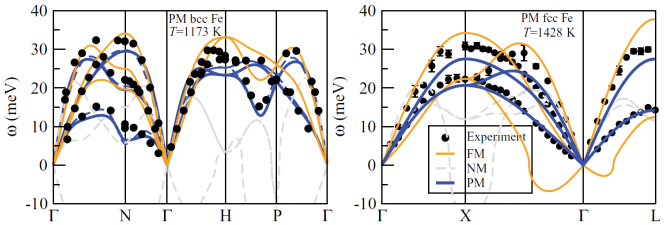
Atomic Forces/Phonons at finite temperatures [1]

Motivation:

- Atomic forces crucial ingredient for various methods (e.g. quasiharmonic approximation, MD simulations, …)
- Coupling magnetic and atomic degree of freedom challenging
- Developing robust and accurate approach to compute forces at finite magnetic temperatures

DFT calculations:

- VASP code [2]
- PAW potentials
- GGA-PBE xc-functional
- Highly converged



NM and FM calculations not sufficient to explain pronounced softening

Magnetic disorder alone guarantees mechanical stability of fcc iron

Adiabatic decoupling (atoms move on pm BOS)

$$\mathcal{F}^{\mathrm{SSA}}_{\{\vec{R}_I\}} = -k_{\mathrm{B}}T \ln Z, \quad Z = \sum_m \exp[-E^{\mathrm{BO}}(\{\vec{R}_I\},\vec{\sigma}_m)/k_{\mathrm{B}}T]$$

Spin-space averaged free energy — *Atomic configuration* — *BO-energy* — *Magnetic configuration*

$$\vec{F}^{\mathrm{SSA}}_{J,\{\vec{R}_I\}} = -\frac{\partial \mathcal{F}^{\mathrm{SSA}}_{\{\vec{R}_I\}}}{\partial R_J} = -\sum_m p_m \frac{\partial E^{\mathrm{BO}}(\{\vec{R}_I\},\vec{\sigma}_m)}{\partial R_J}$$

$$= \sum_m p_m \vec{F}^{\mathrm{HF}}_J(\{\vec{R}_I\},\vec{\sigma}_m). \qquad p_m = \exp[-E^{\mathrm{BO}}(\{\vec{R}_I\},\vec{\sigma}_m)/k_{\mathrm{B}}T]/Z$$

SSA forces — *weights*

Special quasi random structures generated employing ATAT package [3]

More efficient: Employing crystal symmetries

$$\phi^{\mathrm{sym}}_{\alpha\beta} = \sum_\lambda \sum_{\gamma\delta} S^{\beta(\lambda)\delta}_{\alpha\gamma}\, \phi_{\gamma\delta}(\vec{\sigma}_{m_0})$$

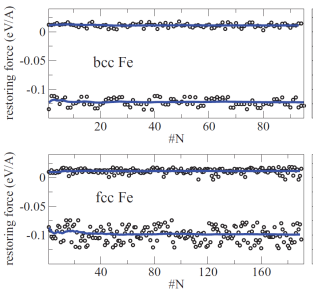
Crystal symmetry operators

$$= \sum_\lambda \phi_{\alpha\beta}(\vec{\sigma}_{\lambda(m_0)}) = \phi^{\mathrm{SSA}}_{\alpha\beta},$$

$$\phi_{\alpha\beta} := -\partial F^{\mathrm{HF}}_\alpha / \partial u_\beta$$

Force constants

Averaging over crystal symmetry equivalent forces improves convergence



Free energy and thermodynamic properties [4-7]

Adiabatic approximation: $F \approx F^{\mathrm{vib}} + F^{\mathrm{el}} + F^{\mathrm{mag}}$

Electronic contribution:

- finite temperature DFT yields $F^{\mathrm{el}}(T) = E^{\mathrm{tot}}(T) - TS^{\mathrm{el}}$

Vibrational contribution:

- phonon frequency derived from dynamical matrix
- vibronic free energy using quasiharmonic approximation

$$F^{\mathrm{vib}}(T) = \frac{1}{N}\sum_i^{3N}\left\{\frac{1}{2}\hbar\omega_i + k_B T \ln[1-\exp(-\frac{\hbar\omega_i}{k_B T})]\right\}$$

Incorporation of PM phonons planned…

Magnetic free energy contribution F^{mag}

- strong local moment systems: relevant magnetic excitations are **spin waves** = natural solutions of the **Heisenberg model** $H = \sum_{i,j} J_{ij}\hat{S}_i\hat{S}_j$

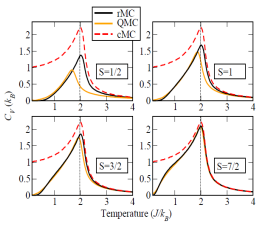
Rescaling MC approach [5]

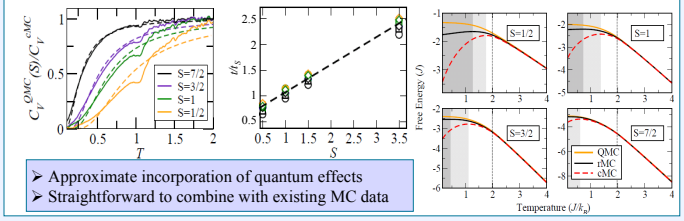
Motivation:

- QMC is numerically exact, but for realistic systems (e.g. *bcc* iron) not feasible (negative sign problem)
- MC is an efficient tool, but fails at low temperatures
- Exploit QMC/MC ratio systematically (ALPS [9])

$$C_V^{\mathrm{QMC}}(t,S) \Big/ C_V^{\mathrm{cMC}}(t) \longleftrightarrow f(t,S) = [t/t_S \sinh(t_S/t)]^{-2}$$

- Rescaled classical MC calculations





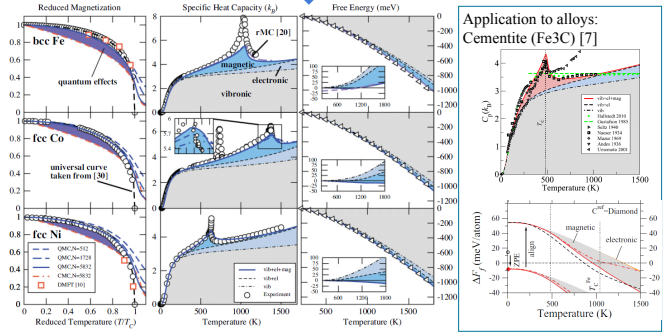
- ➢ Approximate incorporation of quantum effects
- ➢ Straightforward to combine with existing MC data

Nearest-neighbor approach [6,7]

- ➢ Universal behavior found in [7]
- ➢ QMC for nn. Heisenberg very efficient

***Ab initio* or experimental T_C**

Nearest-neighbor model solved quantum-mechanically and numerically exact



Application to alloys:
Cementite (Fe3C) [7]

References

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[2] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
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[5] Körmann, Dick, Hickel, Neugebauer, Phys. Rev. B **81**, 134425 (2010).
[6] Körmann, Dick, Hickel, Neugebauer, Phys. Rev. B **83**, 165114 (2011)..
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[8] Algorithms & Libraries for Physics Sim. (ALPS), alps.comp-phys.org.

Conclusions and Outlook

- ✓ New approach for computing atomic forces and phonons at finite magnetic temeraptures: successful application to bcc and fcc Fe
- ✓ Magnetic excitations strongly affect materials properties
- ✓ Quantum effects significant even close to critical temperature
- ✓ Next step: Combining paramagnetic forces/phonons with quasiharmonic approximation

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