Influence of magnetic excitations on the phase stability of metals and steels

F. Körmann, T. Hickel *, J. Neugebauer

Max-Planck-Institut für Eisenforschung GmbH, Department for Computational Materials Design, 40237 Düsseldorf, Germany

ABSTRACT

Within this article we highlight recent advances in the modeling of magnetic contributions to the finite temperature phase stability of structural materials. A key quantity in this context is the specific heat capacity C_p, since it provides a sensitive link to thermophysical and calorimetric experiments and to established thermodynamic databases. For iron-based materials, the Heisenberg model and its extensions are used as an elegant way for coupling ground-state *ab initio* calculations with concepts of many-body theory to simulate the temperature dependence. Besides analytical concepts to derive the free energy of the Heisenberg model, our work is mainly devoted to numerical approaches such as Monte-Carlo methods. In particular, we highlight the need to go beyond a classical to a fully quantum-mechanical description of magnetic excitations. In order to achieve a quantitative description of C_p, also lattice and electronic degrees of freedom as well as their dependence on magnetism are addressed. Due to the large variety of experimental data, pure iron is best suited to discuss the method developments and to perform evaluations. Nevertheless, the application to other magnetic elements (e.g. Co, Ni) and Fe-based materials (e.g. Fe_3C) will also be addressed.

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1. Introduction

The consideration of magnetic excitations is currently one of the major challenges in Integrated Computational Materials Engineering (ICME). There is no doubt that ICME became over the last decade a dominating topic in materials science and that the need to determine a large variety of reliable data for new, advanced materials has lead to large-scale programmes like the Materials Genome Initiative. A particular attractive approach in this context is the application of *ab initio* methods like density functional theory (DFT) that allow the determination of energies, forces and derived material parameters directly from the fundamental laws of quantum mechanics. Since these methods are free of empirical assumptions or experimental data, they are perfectly suited for design strategies solely based on computer simulations. Accordingly, over the last years *ab initio* methods have proven to be suitable for high-throughput screenings in order to identify optimized compositions for certain applications [1].

For the scientifically interesting as well as technologically decisive class of Fe-based materials, however, *ab initio* techniques are less established. This has several reasons. One of them is the large amount of alloying elements in steels that are in their combination ensuring the complex microstructure and the resulting unique mechanical properties of steels. Since DFT is limited to supercells of a few hundred atoms, the diversity of chemical configurations present in reality can often not be sufficiently captured. Alternative methods, such as CALPHAD (CALculation of PHAse Diagrams, [2]), that use empirical approaches for chemical disorder and are based on extensive calorimetric measurements, are therefore much more common in steel design [3]. This is also due to the fact that many steel properties are determined by a characteristic temperature dependence of microstructure features, such as the phase stability of precipitates, the mobility of grain boundaries, or the value of stacking fault energies.

Ab initio methods are seemingly inadequate for thermodynamic predictions, since they have traditionally been applied to ground state properties only. It is meanwhile well known that also free energies and therefore the temperature dependence of derived quantities such has thermal expansions, heat capacities, or defect concentrations can reliably be determined within DFT, if all thermodynamic processes are respectively simulated with a high accuracy [4]. The reason why this is challenging for Fe-based materials and an important reason for the limited predictive power of *ab initio* methods for steels is the insufficient knowledge regarding the treatment of magnetic excitations. This is particularly harmful due to the strong impact of magnetism on the phase stability of

the different structural phases of Fe. The shortcoming is, however, not only limited to *ab initio* simulations, as the description of the magnetic entropy in the above mentioned CALPHAD approach, for example, is also characterized by rough and unphysical approximations [5]. Furthermore, the impact of magnetic exitations is typically not adequately treated in empirical potentials that are used for molecular dynamics simulations of Fe-based materials.

In the present paper, recent advances in the treatment of the magnetic contributions to free energies of metals are outlined that help to resolve these shortcomings. For this purpose, model Hamiltonians that are derived from *ab initio* investigations are evaluated with different kind of approximations. The considerations are subdivided into two steps: First the magnetic excitations are treated independently of other degrees of freedom (Section 2). Afterwards, also the coupling of degrees of freedom is taken into account (Section 3). The discussion will be focused on heat capacities since they are sensitive descriptors of magnetic excitations and directly accessible by calorimetric measurements.

2. Adiabatic approach to free energies

The adiabatic decoupling of the electronic, vibrational, and magnetic degree of freedom

$$F(T, V) = F^{el}(T, V) + F^{vib}(T, V) + F^{mag}(T, V), \qquad (1)$$

within the Helmholtz free energy is a common approximation to extend ground state DFT calculations to finite temperatures. The separation can be justified by considering the different time scales of the underlying physical excitations (see, e.g. [6–10]). For d-metals the electronic excitations are inherently connected to the d-band width W_d revealing the underlying excitations in the order of $\hbar/W_D \sim 10^{-15}$ s. The characteristic time of spin-waves are inverse proportional to their excitation energy, $1/\omega_{mag} \sim 10^{-13}$ s, and vibronic excitations are characterized by their inverse Debye temperature $\sim 10^{-12}$ s. One should note that the adiabatic decoupling given above does not imply that the individual contributions do not depend on each other. In fact, the contributions due to the coupling of different degrees of freedom (e.g., due to magnon–phonon interactions [11,12]) can be quite substantial and will be discussed in Section 3.

The dominant contribution in Eq. (1) is usually the vibronic contribution, F^{vib}, caused by the nuclei motion. A common approach, capturing typically the largest part of F^{vib}, is the quasi-harmonic approximation. It is based on the quantum-mechanical analytic solution of the harmonic oscillator, taking the volume expansion of the crystal self-consistently into account [13]. The inclusion of phonon–phonon interactions, sometimes referred to as *explicit* anharmonic contributions, is possible via *ab initio* molecular-dynamics simulations [14–17]. These typically highly demanding computational methods have become feasible due to a recently developed phase-space coarse-graining procedure [18]. Electron–phonon interactions can be taken into account employing finite electronic temperatures within the DFT simulations [19].

An accurate modeling of the explicit magnetic contribution to the free energy, F^{mag}, implies that not only the magnetic excitations are well captured by the applied magnetic model Hamiltonian, $\mathcal{H}^{mag}$, but also that the (usually unavoidable) approximations when solving the model are well controlled. Once the magnetic inner energy, $\langle \mathcal{H}^{mag} \rangle$, is computed, F^{mag} can be derived via integration [20]. The dominant magnetic excitations in ferromagnets are the single-particle Stoner excitations and the collective spin-wave excitations, which are sometimes referred to as longitudinal and transversal spin fluctuations, respectively. It is well-known that

at low temperatures the spin-waves dominate the magnetic contribution to the thermodynamic properties. A directly related consequence is for instance the famous $T^{3/2}$ Bloch law for the magnetization in ferromagnets as well as a $T^{3/2}$ power law for the specific heat capacity, $C_p(T)$, at low T.

One of the most commonly employed magnetic model Hamiltonians is the Heisenberg model,

$$\mathcal{H}^{mag} = \sum_{ij} J_{ij} \mathbf{S}_i \mathbf{S}_j, \qquad (2)$$

where J_{ij} denote the magnetic exchange between spins localized at lattice sites i and j. The $\mathbf{S}_i$ denote the spin operators obeying the usual commutator rules for orbital moments and having strictly speaking discretized eigenvalues. One of the reasons for the popularity of the above model is that spin waves are naturally included (eigenstates) and that there are nowadays a number of different techniques available that allow one to straightforwardly extract the input parameters from DFT calculations (see, e.g., [21]).

At the same time, the application of the conventional Heisenberg models implies several simplifications. One of them is the neglect of longitudinal spin fluctuations (i.e. variations in the magnitude of the local spin moments). This point will be discussed in detail later. Further, higher-order spin interactions, such as, e.g., biquadratic terms $\widetilde{J}_{ij}(\mathbf{S}_i \mathbf{S}_j)^2$ in Eq. (2) could be of relevance [22–27]. For bcc Fe, such interactions have been explicitly computed in [23,25,26]. It is found that the $\widetilde{J}_{ij}$ are small compared to the bilinear interaction J_{ij} beyond second nearest-neighbors, whereas non-negligible contributions have been identified for nearest-neighbors. Incorporating biquadratic interactions into thermodynamic concepts seems to worsen the prediction of critical temperatures compared to experiment [26]. It has been speculated that the 'better' performance of the conventional Heisenberg model is due to an error cancellation [28] indicating that the inclusion of even higher order interaction terms could cancel the biquadratic ones [26]. For other materials, such as the important class of superconducting ferropnictides, biquadratic interactions turn out to be of crucial importance to resolve a number of different experimentally observed magnetic peculiarities [29]. A more complete mapping of the magnetic energy surface of real materials could be also achieved by the recently proposed spin cluster [22,24,27] or magnetic cluster expansion techniques [30]. However, these techniques are challenged by the long-range nature of magnetic interactions and therefore so far not established.

The employed solution techniques for Eq. (2) can be roughly divided into analytic and numerical approaches. Analytic treatments are often based on different flavors of mean-field (MF) approximations. In the most common form, the spin operator product, $\mathbf{S}_i \mathbf{S}_j$, is simplified by an interaction with an effective field, $\mathbf{S}_i \mathbf{S}_j \rightarrow B_{eff} \mathbf{S}_j$, with $B_{eff} = 2J_0 \langle S_z \rangle$, $J_0 = 1/N \sum_{ij} J_{ij}$, and $\langle S_z \rangle$ is the magnetization. While *physical trends* are typically captured by this method [31], MF based predictions are known to overestimate magnetic ordering quantitatively. One of the reasons for this failure is that collective excitations, i.e. spin waves, are neglected within this approach. In Fig. 1 the MF results for C_p of bcc Fe (dashed[1] orange line) is shown together with the sum of electronic and vibronic contributions (dashed black line) [20]. As expected, the MF prediction for the critical temperature, $T_C^{MF} = 1504$ K, overestimates the experimental value, $T_C^{exp} = 1043$ K, by about 50%. Furthermore, the λ-shaped increase of $C_p(T)$ around the critical temperature as well as the contribution in the short-range order (SRO) regime are not well captured by this approach.

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[1] For interpretation of color in Figs. 1 and 5, the reader is referred to the web version of this article.