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# Dynamical Mean-Field Theory for Correlated Electron Materials

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## Abstract

A brief introduction into the LDA+DMFT approach for the investigation of correlated electron materials is presented. In this scheme ab initio techniques for the calculation of band structures, such as the local density approximation (LDA) or the generalized gradient approximation (GGA), are supplemented by electronic correlations and solved within dynamical mean-field theory (DMFT). In particular, we address a fundamental question: How does the Coulomb repulsion between electrons influence the lattice stability of solids? Results are presented for elemental Fe above the Curie temperature and the iron chalcogenide FeSe. They show that the structural properties of materials such as transition metals and their compounds can only be explained if correlations between the electrons are explicitly taken into account.

**Keywords:** Electronic correlations; correlated electron materials; dynamical mean-field theory; DMFT; LDA+DMFT

## 1. Introduction

In modern condensed matter physics the concept of *electronic correlations* plays an important role. It refers to electronic interaction effects which cannot be explained within a static mean-field picture and which go beyond factorization approximations such as Hartree or Hartree-Fock theory. Electronic correlations in solids lead to the emergence of complex behavior, resulting in rich phase diagrams. In particular, the interplay between the spin,

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charge, and orbital degrees of freedom of the correlated  $d$  and  $f$  electrons with the lattice degrees of freedom leads to a cornucopia of correlation and ordering phenomena, which are not only of interest for fundamental research but also have a great potential for technological applications. Namely, the great sensitivity of correlated electron materials with respect to changes of external parameters such as temperature, pressure, electromagnetic fields, doping, etc., can be employed to develop materials with useful functionalities. Consequently there is a great need for theoretical investigation techniques which permit a comprehensive, and at the same time reliable, exploration of correlated electron materials.

## 2. Dynamical mean-field theory

For a long time first-principles investigations of correlated materials were out of reach. During that time the electronic properties of solids were investigated by two essentially separate communities, one employing density functional theory (DFT), the other studying model Hamiltonians using many-body techniques. Indeed, the electronic properties of materials can be computed from first principles by DFT, e.g., in the local density approximation (LDA) [1], the generalized gradient approximation (GGA) [2], or using the so-called LDA+U method [3]. These approaches are able to describe the phase diagrams of many simple elements and semiconductors, and even of some insulators, quite accurately. Moreover, they often allow one to correctly predict the magnetic, orbital, and crystal structures of solids where the equilibrium structures are determined by the simultaneous optimization of the electron and lattice systems [4-6]. However, these methods usually fail to describe the correct electronic and structural properties of electronically correlated paramagnetic materials since they miss characteristic features of correlated electron systems, e.g., heavy quasiparticle behavior and Mott physics.

Here the Dynamical Mean-Field Theory (DMFT), whose development started almost 30 years ago [7-13], opened new perspectives. Within DMFT the electronic correlation problem, whose most extreme simplification is provided by the Hubbard model, is mapped onto a self-consistent single-impurity Anderson model [9]. This mapping is exact in the limit of infinite coordination number [7] and allows one to investigate the dynamics of correlated lattice electrons non-perturbatively at all interaction strengths. In contrast to single-particle theories the mean field of the DMFT is energy dependent, i.e., dynamical. Thereby local quantum fluctuations are fully taken into account. The only approximation of the DMFT is the neglect of spatial fluctuations. Thus DMFT provides a comprehensive theoretical framework for the investigation of correlated lattice models and can describe, for example, fluctuating moments and the renormalization of quasiparticles. DMFT also allows one to define electronic correlations in a way that they can be tested by experiments such as electron spectroscopies: correlations lead to the transfer of spectral weight and to a finite lifetime of quasiparticles through the real and imaginary part of the dynamic self-energy, respectively. Most importantly, DMFT is not only useful for the investigation of correlated electron model, but can also be employed to study correlation effects in real materials. Indeed, the computational scheme obtained by merging DFT with DMFT, usually referred to as DFT+DMFT (or more explicitly as LDA+DMFT, GGA+DMFT, etc.) [14-21], provides a powerful new method for the calculation of the electronic, magnetic, and structural properties of correlated materials from first principles. The DFT+DMFT approach is able to describe and explain the effect of finite temperatures, including thermally driven phase transitions, in real materials. By overcoming the limitations of conventional band-structure methods, it opens the way for fully microscopic investigations of the structural properties of strongly correlated systems. It has already led to important insights into the properties of strongly correlated materials, e.g.,  $d$  or  $f$  transition metals and their oxides and Fe-based superconducting materials [18-21]. So far the DFT+DMFT approach has been mainly used to calculate one-particle and local two-particle observables needed to explain experimental results obtained, for example, by photoemission and x-ray absorption spectroscopies.

By employing a novel implementation of DFT+DMFT in combination with plane-wave pseudopotentials we recently demonstrated that it is possible to compute atomic displacements, to perform structural optimizations, to calculate the lattice dynamics, to explore structural transitions, and to determine the phase stability of correlated materials [22-30]. Thereby the DFT+DMFT approach allows one to study electronic and structural properties of strongly correlated materials on the same footing. In the following we will discuss the results obtained by us within

this approach for two exemplary materials: elemental Fe above the Curie temperature and the iron chalcogenide FeSe.

### 3. Lattice dynamical properties of paramagnetic Fe

Elemental iron (Fe) has been known for its extraordinary magnetic and metallurgical properties for several thousand years already. Iron exhibits a rich phase diagram with at least four allotropic forms; for a discussion see [26]. At ambient conditions it is ferromagnetic and has a bcc crystal structure ( $\alpha$  phase). Upon heating above the Curie temperature  $T_C \sim 1043$  K, iron becomes paramagnetic, but remains in its bcc crystal structure. Only when the temperature is increased above  $T_{\text{struct}} \sim 1185$  K does a structural phase transition to an fcc structure ( $\gamma$  phase) take place.

State-of-the-art band structure methods provide a qualitatively correct description of various electronic and structural properties of iron [31]. For example, these methods provide a good quantitative understanding of the equilibrium crystal structure and the lattice dynamical properties of the ferromagnetic  $\alpha$  phase. However, applications of these techniques to describe, for example, the  $\alpha$ -to- $\gamma$  phase transition in iron, do not lead to satisfactory results. They predict a simultaneous transition of the structure and the magnetic state at the bcc-to-fcc phase transition while, in fact, the bcc-to-fcc phase transition occurs only about 150 K above  $T_C$ . Moreover, the elastic and dynamical stability of the bcc phase is found to depend sensitively on the value of the magnetization. For example, in the absence of the magnetization, standard band-structure methods predict bcc iron to be unstable [32]. We now understand that the stability of paramagnetic bcc iron is due to the presence of local moments above  $T_C$  which cannot be treated realistically by conventional band structure techniques.

This problem has been overcome by employing the DFT+DMFT approach which allows one to study correlated materials both in the long-range ordered and paramagnetic state [24-26,32-36] since it accounts naturally for the existence of local moments above  $T_C$ . In particular, DFT+DMFT studies of the equilibrium crystal structure and phase stability of iron at the  $\alpha$ -to- $\gamma$  phase transition found that the bcc-to-fcc phase transition indeed takes place at a temperature well above the magnetic transition, at about  $1.3 T_C$ , in agreement with experiment [24].

In view of the crucial importance of electronic correlations for the phase stability of iron we also computed the phonon dispersion relations of paramagnetic iron near the bcc-to-fcc phase transition. For this purpose we employed the DFT+DMFT approach implemented with the frozen-phonon method [25, 26]. The calculated phonon dispersions of the bcc phase of iron show the typical behavior of a bcc metal with an effective Debye temperature  $\sim 458$  K. The phonon frequencies are overall positive, implying mechanical stability of the bcc lattice structure at  $\sim 1.2 T_C$ , i.e., well above the Curie temperature, in agreement with experiment. This corrects the results obtained with the non-magnetic GGA which finds the bcc lattice to be dynamically unstable even for the equilibrium lattice constant  $a = 2.883$  Å. Overall, the structural phase stability, equilibrium lattice constant, and phonon frequencies of bcc iron obtained by DFT+DMFT are in remarkably good agreement with the experimental data which were taken at nearly the same reduced temperature  $T/T_C$  [37]; for details we refer to [25].

We also studied the lattice dynamical properties of the paramagnetic fcc phase [25]. The effective Debye temperature was obtained as  $\sim 349$  K. The phonon frequencies were all found to be positive, implying mechanical stability of the fcc lattice structure at  $T \sim 1.4 T_C$ . Although nonmagnetic GGA calculations also find the fcc lattice structure to be mechanically stable (for the GGA equilibrium volume), the GGA energy for fcc iron is *higher* than that for the close-packed hcp structure. By contrast, DFT+DMFT calculations find the simultaneous thermodynamic and lattice dynamical stability of the paramagnetic fcc phase of iron in agreement with experiment [38].

### 4. Correlation-induced topological Fermi surface transitions in FeSe under expansion and compression

The iron chalcogenide FeSe is the structurally simplest member of Fe-based superconductors. It becomes superconducting below a critical temperature  $T_c \sim 8$  K without applying doping and/or external pressure [39]. In contrast to the iron pnictides, FeSe shows no long-range magnetic order, but displays a strong enhancement of short-range spin fluctuations near  $T_c$ , with a resonance at the  $(\pi, \pi)$  magnetic vector (stripe-type) in the spin excitation spectra [40]. Compression leads to a dramatic increase of the critical temperature  $T_c$  to a maximum of about 37 K at 6 GPa [40, 41]. It has been shown that the electronic and lattice properties of bulk FeSe can be effectively tuned by

the isoelectronic substitution of Se by S and Te, respectively. Namely, S has a smaller ionic radius than Se and hence results in a compression of the unit cell, while Te has a larger ionic radius, leading to an expansion of the lattice. In the expanded lattice  $T_c$  is found to increase up to 14 K [42].

While FeSe is not magnetically long-range ordered, magnetism appears both upon compression (most probably consistent with a stripe-type  $(\pi, \pi)$  wave vector [43]) and upon expansion. For example, the end-member FeTe has a long-range  $(\pi, 0)$  antiferromagnetic order [44]. These findings clearly demonstrate that isoelectronic tuning of the lattice of FeSe, e.g., by doping, can be an effective means to control  $T_c$  in iron chalcogenides. To explore and explain these findings theoretically we employed a fully charge self-consistent implementation of the GGA+DMFT method both for FeSe under expansion [28] and under compression [29]. The results will be discussed in the following.

The results for the Fermi surface of FeSe under expansion (negative pressure) of the lattice reveal a complete reconstruction of the electronic structure, resulting in a dramatic change of the Fermi surface topology (“Lifshitz transition”). This leads to a corresponding change of the magnetic correlations in FeSe; for details see [28]. We find in-plane nesting with wave vector  $(\pi, \pi)$ , connecting hole and electron parts of the Fermi surface, to be dominant in the low-volume phase. Upon expansion of the lattice, the Lifshitz transition sets in, resulting in  $(\pi, 0)$ -type magnetic correlations in the high-volume phase. Our findings suggest that the proximity of a van Hove singularity to the Fermi level strongly influences, or even induces, superconductivity in the chalcogenide  $\text{FeSe}_{1-x}\text{Te}_x$  series [28].

We also performed a full structural optimization of the tetragonal phase of paramagnetic FeSe under compression (positive pressure) at  $T = 290$  K [29]. In agreement with previous studies our results demonstrate that electronic correlations need to be included to determine the correct lattice parameters of FeSe both in the equilibrium and upon compression. Our results for the lattice parameters are in overall good agreement with experimental data; for details see [29]. The spectral properties show only a weak dependence of the bandwidth on the lattice volume, associated with a small change of the Fe-Se hybridization upon a moderate compression of the lattice up to 10 GPa. Most importantly, we again find a drastic reconstruction of the Fermi surface (FS) topology, i.e., a Lifshitz transition, indicating a two-to three-dimensional crossover in the FS. Our results are in good agreement with recent ARPES measurements for the  $\text{FeSe}_{1-x}\text{S}_x$  solid solution, which is regarded as an isoelectronic and isostructural (with a smaller lattice volume due to chemical pressure) counterpart of FeSe. Under pressure, we observe a weak reduction of the quasiparticle mass renormalization  $m^*/m$  by about 5 % for the  $e$  and less than 1 % for the  $t_2$  states, as compared to results at ambient pressure. This implies that  $\text{FeSe}_{1-x}\text{S}_x$  is less correlated than FeSe, in agreement with recent studies [45].

The behavior of the momentum-resolved magnetic susceptibility under pressure shows no topological change of magnetic correlations. This suggests that both FeSe under pressure and  $\text{FeSe}_{1-x}\text{S}_x$  exhibit stripe-type spin excitations. Moreover, an analysis of the FS and magnetic correlations exhibits only a small reduction of the degree of the in-plane  $(\pi, \pi)$  nesting, which implies that magnetic correlations are weakened due to the damping of spin fluctuations under pressure.

Based on these results we conjecture that the anomalous behavior of FeSe upon variation of the lattice volume is associated with a crossover between superconductivity mediated by spin-fluctuations (upon expansion of the lattice) and by phonons (upon compression of the lattice), respectively.

## 5. Conclusions

Within the DFT+DMFT scheme it is possible to calculate the electronic, magnetic, and structural properties of correlated electron materials from first principles. In particular, the approach can be used to compute atomic displacements, to perform full structural optimizations, and to determine the phase stability of correlated materials. Our results obtained for Fe and FeSe described in this paper clearly demonstrate that electronic correlations not only influence the electronic properties of a material but also greatly affect their lattice dynamics and phase stability. In the future further insights can be obtained by combining the DFT+DMFT approach with linear-response techniques to compute the electron-phonon coupling, and by implementing non-equilibrium DFT+DMFT methods in the Keldysh formalism for the electrons with (quantum) molecular dynamics simulation techniques.

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