Finite-Temperature Magnetism of Transition Metals: An *ab initio* Dynamical Mean-Field Theory

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We present an *ab initio* quantum theory of the finite-temperature magnetism of iron and nickel. A recently developed technique which combines dynamical mean-field theory with realistic electronic structure methods successfully describes the many-body features of the one electron spectra and the observed magnetic moments below and above the Curie temperature.

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The theory of itinerant electron ferromagnetism is one of the central problems in condensed matter physics (for reviews, see [1,2]). There is a need for a first principles approach which is able to describe ground state and thermodynamical quantities, as well as the one particle spectral properties of itinerant magnets. These quantities are currently being probed in spin-polarized tunneling as well as spin-polarized photoemission experiments with a view to possible applications as spin valves [3].

Iron and nickel are the oldest and experimentally best studied prototypical systems, and serve as benchmarks for electronic structure methods. At very low temperatures, a bandlike description of Fe and Ni has been very successful. The density functional theory (DFT) in the local density approximations (LDA) gives a quantitatively accurate description of several ground state properties of these materials such as the ordered magnetic moment and the spin wave stiffness [4] as calculated from the spin wave dispersion.

While density functional theory can in principle provide a rigorous description of the finite-temperature thermodynamic properties, at present there is no accurate practical implementing available. As a result the finite-temperature properties of magnetic materials are estimated following a simple suggestion [5], whereby constrained DFT at $T = 0$ is used to extract exchange constants for a classical Heisenberg model, which in turn is solved using approximation methods (e.g., RPA, mean field) from classical statistical mechanics of spin systems [5–8]. The most recent implementation of this approach gives good values for the transition temperature of iron but not of nickel [9]. While these localized spin models give, by construction, at high temperatures a Curie-Weiss-like magnetic susceptibility, as observed experimentally in Fe and Ni, they encountered difficulties in predicting the correct values of the Curie constants [10].

It has been recognized for a long time, that to describe the finite-temperature aspects of itinerant electron magnets, one needs a formalism that takes into account the existence of local magnetic moments present above T_C [11,12]. This is one of the central problems in the physics of strongly correlated electron systems, which forces us to reconcile the dual character of the electron, which as a particle requires a real space description and as a wave requires a momentum space description in a unified framework. A very successful method satisfying these requirements, the dynamical mean-field theory (DMFT) [13], has been recently developed. This many-body scheme can be combined with standard LDA band structure calculations to include the effects of a realistic band structure [14,15]. Such an "LDA + DMFT" approach has been successfully applied for the computations of electronic structure and spin wave spectrum of iron [16,17]. Nevertheless the most difficult and interesting finite-temperature effects were not considered previously and are the subject of this Letter.

Here we present realistic LDA + DMFT calculations of finite-temperature magnetic properties of iron and nickel. A numerically exact quantum Monte Carlo (QMC) scheme is used for the solution of the DMFT equations. We find that a consistent first principles description of the magnetic properties and of the one electron spectra of iron and nickel is possible, within an approach that makes only two essential approximations: the locality of the electron self-energy and of the particle hole irreducible vertex [13].

There have been numerous efforts to construct a many-body theory of these materials, for example, using the T-matrix theory [18], a self-consistent moment method [19], local 3-body equations [20,21], and the GW [22] approximations. The LDA + DMFT approach goes beyond these works in the treatment of a realistic orbitally degenerate band structure, and in the treatment of the many-body interactions.

We start with the LDA Hamiltonian in the tight-binding orthogonal linear muffin-tin orbital representation $H^{\mathrm{LDA}}_{mm'}(\mathbf{k})$ [23], where m describes the orbital basis set containing $3d$, $4s$, and $4p$ states, and $\mathbf{k}$ runs over the Brillouin zone (BZ). The interactions are parametrized by a matrix of screened local Coulomb interactions $U_{mm'}$ and a matrix

of exchange constants $J_{mm'}$, which are expressed in terms of two screened Hubbard parameters U and J, describing the average Coulomb repulsion and the intra-atomic ferromagnetic exchange respectively. We use the values $U = 2.3(3.0)$ eV for Fe (Ni) and the same value of the intra-atomic exchange, $J = 0.9$ eV for both Fe and Ni, a result of constrained LDA calculations [14,15,24,25]. These parameters which are consistent with those of many studies result in a very good description of the physical properties of Fe and Ni.

Dynamical mean-field theory maps the many-body system onto a multiorbital quantum impurity, i.e., a set of local degrees of freedom in a bath described by the Weiss field function $\mathcal{G}$. The impurity action [here $n_{m\sigma} = c^+_{m\sigma} c_{m\sigma}$ and $\mathbf{c}(\tau) = [c_{m\sigma}(\tau)]$ is a vector of Grassman variables] is given by

$$S_{\text{eff}} = -\int_0^\beta d\tau \int_0^\beta d\tau' \, \mathrm{Tr}[\mathbf{c}^+(\tau)\mathcal{G}^{-1}(\tau,\tau')\mathbf{c}(\tau')] + \frac{1}{2}\sum_{m,m',\sigma}\int_0^\beta d\tau\,[U_{mm'}n^m_\sigma n^{m'}_{-\sigma} + (U_{mm'} - J_{mm'})n^m_\sigma n^{m'}_\sigma]. \quad (1)$$

It describes the spin, orbital, energy, and temperature dependent interactions of a particular magnetic $3d$ atom with the rest of the crystal and is used to compute the local Green's function matrix:

$$\mathbf{G}_\sigma(\tau - \tau') = -\frac{1}{Z}\int D[\mathbf{c},\mathbf{c}^+]e^{-S_{\text{eff}}}\mathbf{c}(\tau)\mathbf{c}^+(\tau'), \quad (2)$$

(Z is the partition function) and the impurity self-energy $\mathcal{G}^{-1}_\sigma(\omega_n) - \mathbf{G}^{-1}_\sigma(\omega_n) = \mathbf{\Sigma}_\sigma(\omega_n)$.

The Weiss field function is required to obey the self-consistency condition [14,15], which restores translational invariance to the impurity model description:

$$\mathbf{G}_\sigma(\omega_n) = \sum_{\mathbf{k}}[(i\omega_n + \mu)\mathbf{1} - \mathbf{H}^{\text{LDA}}(\mathbf{k}) - \mathbf{\Sigma}^{\text{dc}}_\sigma(\omega_n)]^{-1}, \quad (3)$$

μ is the chemical potential defined self-consistently through the total number of electrons, $\omega_n = (2n+1)\pi T$ are the Matsubara frequencies for temperature $T \equiv \beta^{-1}$ ($n = 0, \pm 1, \ldots$), and σ is the spin index. The local matrix $\mathbf{\Sigma}^{\text{dc}}_\sigma$ is the sum of two terms, the impurity self-energy and a so-called "double counting" correction, E_{dc} which is meant to substract the average electron-electron interactions already included in the LDA Hamiltonian. For metallic systems we propose the general form of the dc correction: $\mathbf{\Sigma}^{\text{dc}}_\sigma(\omega) = \mathbf{\Sigma}_\sigma(\omega) - \frac{1}{2}\mathrm{Tr}\mathbf{\Sigma}_\sigma(0)$. This is motivated by the fact that the static part of the correlation effects are already well described in the density functional theory. Only the d part of the self-energy is presented in our calculations, therefore $\mathbf{\Sigma}^{\text{dc}}_\sigma = 0$ for s and p states as well as for nondiagonal d-s, p contributions. In order to describe the finite-temperature ferromagnetism of transition metals we use the non-spin-polarized LDA Hamiltonian $\mathbf{H}^{\text{LDA}}(\mathbf{k})$ and accumulate all temperature dependent spin splittings in the self-energy matrix $\mathbf{\Sigma}^{\text{dc}}_\sigma(\omega_n)$.

We use the impurity QMC scheme for the solution of the multiband DMFT equation [26]. The Hirsch discrete Hubbard-Stratonovich transformation introduces $(2M-1)M$ auxiliary Ising fields $S^{\sigma\sigma'}_{mm'}$ where M is the orbital degeneracy of the d states, and we calculate $\mathbf{G}_\sigma(\tau)$ by an exact integration of the fermion degrees of freedom in the functional integral [Eq. (2)] [13]. In order to sample efficiently all the spin configurations in the multiband QMC scheme, it is important to use "global" spin flips: $[S^{\sigma\sigma'}_{mm'}] \to [-S^{-\sigma-\sigma'}_{mm'}]$ in addition to the local moves of the auxiliary fields. The number of QMC sweeps was of the order of 10^5. A parallel version of the DMFT program was used to sample the 45 Ising fields for $3d$ orbitals. We used 256 $\mathbf{k}$-points in the irreducible part of the BZ for the k integration. Ten to twenty DMFT iterations were sufficient to achieve convergence far from the Curie point. Because of the cubic symmetry of the bcc-Fe and fcc-Ni lattices the local Green function is diagonal in the basis of real spherical harmonics. The spectral functions for real frequencies were obtained from the QMC data by applying the maximum entropy method [27].

Our results for the local spectral function for iron and nickel are shown in Figs. 1 and 2, respectively. The LDA + DMFT approach describes well all the qualitative features of the density of states (DOS), which is especially nontrivial for nickel. Our QMC results reproduce well the three main correlation effects on the one particle spectra below T_C [28]: the presence of a famous 6 eV satellite, the 30% narrowing of the occupied part of the d band, and the 50% decrease of exchange splittings compared to the LDA results. Note that the satellite in Ni has substantially

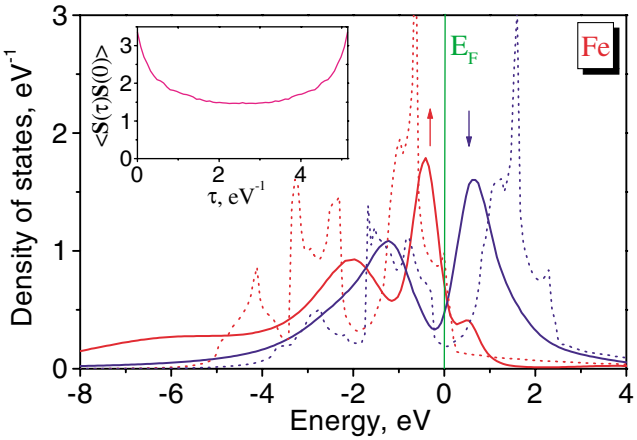

FIG. 1 (color). LDA + DMFT results for ferromagnetic iron ($T = 0.8T_C$). The partial densities of d states (full lines) are compared with the corresponding LSDA results at zero temperature (dashed lines) for the spin-up (red lines, arrow-up) and spin-down (blue lines, arrow-down) states. The inset shows the spin-spin autocorrelation function for $T = 1.2T_C$.

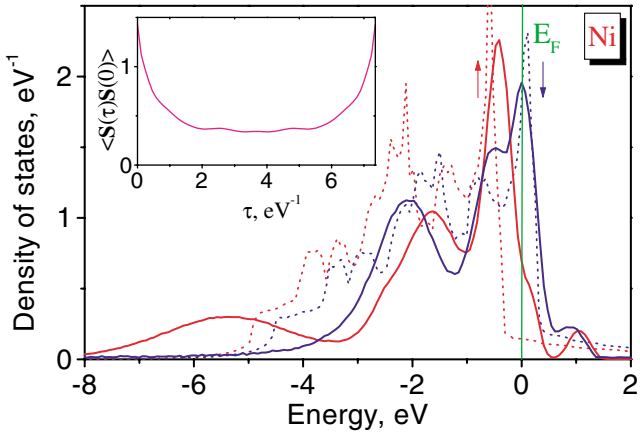

FIG. 2 (color). Same quantities as in Fig. 1 for ferromagnetic nickel ($T = 0.9T_C$). The inset shows the spin-spin autocorrelation function for $T = 1.8T_C$.

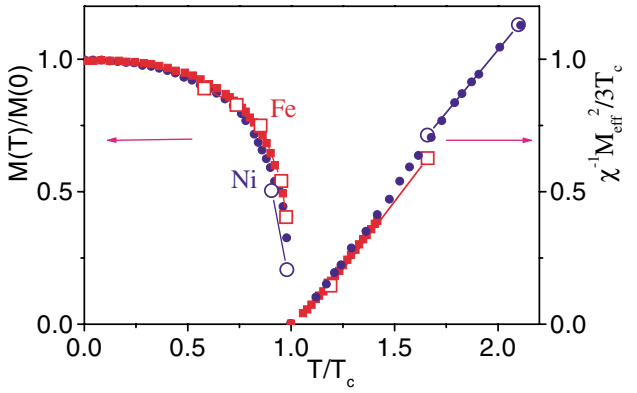

FIG. 3 (color). Temperature dependence of the ordered moment and the inverse ferromagnetic susceptibility for Fe (open squares) and Ni (open circles) compared with experimental results for Fe (squares) and Ni (circles) (from Refs. [1,28]).

more spin-up contributions in agreement with photoemission spectra [28]. The exchange splitting of the d band depends very weakly on temperature from $T = 0.6T_C$ to $T = 0.9T_C$. Correlation effects in Fe are less pronounced than in Ni, due to its large spin splitting and the characteristic bcc-structural dip in the density of states for spin-down states near the Fermi level, which reduces the DOS for particle hole excitations.

The uniform spin susceptibility in the paramagnetic state $\chi_{q=0} = dM/dH$ was extracted from the QMC simulations by measuring the induced magnetic moment in a small external magnetic field. It includes the polarization of the impurity Weiss field by the external field [13]. The dynamical mean-field results account for the Curie-Weiss law which is observed experimentally in Fe and Ni. As the temperature increases above T_C, the atomic character of the system is partially restored resulting in an atomiclike susceptibility with an effective moment:

$$\chi_{q=0} = \frac{\mu_{\text{eff}}^2}{3(T - T_C)}. \tag{4}$$

The temperature dependence of the ordered magnetic moment below the Curie temperature and the inverse of the uniform susceptibility above the Curie point are plotted in Fig. 3 together with the corresponding experimental data for iron and nickel [1,29]. The LDA + DMFT calculations describe the magnetization curve and the slope of the high-temperature Curie-Weiss susceptibility remarkably well. The calculated values of high-temperature magnetic moments extracted from the uniform spin susceptibility are $\mu_{\text{eff}} = 3.09(1.50)\mu_B$ for Fe (Ni), in good agreement with the experimental data $\mu_{\text{eff}} = 3.13(1.62)\mu_B$ for Fe (Ni) [29].

We have estimated the values of the Curie temperatures of Fe and Ni from the disappearance of spin polarization in the self-consistent solution of the DMFT problem and from the Curie-Weiss law in Eq. (4). Our estimates $T_C = 1900\ (700)K$ are in reasonable agreement with experimental values of 1043 (631)K for Fe (Ni), respectively [29], considering the single site nature of the DMFT approach, which is not able to capture the reduction of T_C due to long wavelength spin waves. These effects are governed by the spin wave stiffness. Since the ratio of the spin wave stiffness (D) to T_C, T_C/a^2D is nearly a factor of 3 larger for Fe than for Ni [29] (a is the lattice spacing), we expect the DMFT T_C to be much higher than the observed Curie temperature in Fe than in Ni. Quantitative calculations demonstrating the sizable reduction of T_C due to spin waves in Fe in the framework of a Heisenberg model were performed in Ref. [9].

Within dynamical mean-field theory one can also compute the local spin susceptibility defined by

$$\chi_{\text{loc}} = \frac{g_s^2}{3}\int_0^\beta d\tau\, \langle \mathbf{S}(\tau)\mathbf{S}(0)\rangle, \tag{5}$$

where $g_s = 2$ is the gyromagnetic ratio, $\mathbf{S} = \frac{1}{2}\sum_{m,\sigma,\sigma'} c_{m\sigma}^\dagger \boldsymbol{\sigma}_{\sigma\sigma'} c_{m\sigma'}$ is the single-site spin operator, and $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ are Pauli matrices. It differs from the $q = 0$ susceptibility, by the absence of spin polarization in the Weiss field of the impurity model. Equation (5) cannot be probed directly in experiments but it is easily computed in DMFT-QMC. Its behavior as a function of temperature gives a very intuitive picture of the degree of correlations in the system. In a weakly correlated system we expect Eq. (5) to be nearly temperature independent, while in a strongly correlated system we expect a leading Curie-Weiss behavior at high temperatures $\chi_{\text{local}} = \mu_{\text{loc}}^2/(3T + \text{const})$ where μ_{loc} is an effective local magnetic moment. In the Heisenberg model with spin S, $\mu_{\text{loc}}^2 = S(S+1)g_s^2$, and for well-defined local magnetic moments (e.g., for rare earth magnets) this quantity should be temperature independent. For the itinerant electron magnets μ_{loc} is temperature dependent, due to a variety of competing many-body effects such as Kondo screening, the induction of local magnetic moment by temperature [12], and thermal fluctuations which disorder the moments [30]. All these effects are included in the DMFT calculations. The τ dependence of the correlation function

$\langle \mathbf{S}(\tau)\mathbf{S}(0)\rangle$ results in the temperature dependence of μ_{loc} and is displayed in the insets of Figs. 1 and 2. Iron can be considered as a magnet with very well-defined local moments above T_C (the τ dependence of the correlation function is relatively weak), whereas nickel is more itinerant electron magnet (stronger τ dependence of the local spin-spin autocorrelation function).

The comparison of the values of the local and the $q = 0$ susceptibilities gives a crude measure of the degree of short range order which is present above T_C. As expected, the moments extracted from the local susceptibility Eq. (5) are a bit smaller ($2.8\mu_B$ for iron and $1.3\mu_B$ for nickel) than those extracted from the uniform magnetic susceptibility. This reflects the small degree of the short range correlations which remain well above T_C [31]. The high-temperature LDA + DMFT clearly shows the presence of a local moment above T_C. This moment is correlated with the presence of high-energy features (of the order of the Coulomb energies) in the photoemission. This is also true below T_C, where the spin dependence of the spectra is more pronounced for the satellite region in nickel than for that of the quasiparticle bands near the Fermi level (Fig. 2). This can explain the apparent discrepancies between different experimental determinations of the high-temperature magnetic splittings [11,32,33] as being the result of probing different energy regions. The resonant photoemission experiments [32] reflect the presence of local-moment polarization in the high-energy spectrum above Curie temperature in nickel, while the low-energy angle-resolved photoemission spectroscopy investigations [33] result in nonmagnetic bands near the Fermi level. This is exactly the DMFT view on the electronic structure of transition metals above T_C. Fluctuating moments and atomiclike configurations are large at short times, which results in correlation effects in the high-energy spectra such as spin-multiplet splittings. The moment is reduced at longer time scales, corresponding to a more bandlike, less correlated electronic structure near the Fermi level.

To conclude, we presented the first results of *ab initio* LDA + DMFT calculations of finite-temperature magnetic properties for Fe and Ni and showed that many-body effects which incorporate the local atomic character of the electrons and which are ignored in the standard LDA based scheme are essential for a simultaneous description of the magnetic properties and the one electron spectra of itinerant electron magnets. DMFT gives a satisfactory semiquantitative description of the physical properties of Fe and Ni, far from the Curie point, indicating that the critical fluctuations, which are not included in the DMFT approximation, do not play a crucial role, except for the immediate vicinity of the transition, and many aspects of the physics of this system can be understood within an approach which stresses local physics. It would be interesting to extend this study to other itinerant magnetic systems with more atoms per unit cell, such as $SrRuO_3$ which is also well described by band theory at very low temperatures but has anomalous properties above its Curie point [34].

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