

Nonlocal correlations in the vicinity of the α - γ phase transition in iron within a DMFT plus spin-fermion model approach

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We consider nonlocal correlations in iron in the vicinity of the α - γ phase transition within the spin-rotationally-invariant dynamical mean-field theory (DMFT) approach, combined with the recently proposed spin-fermion model of iron. The obtained nonlocal corrections to DMFT yield a decrease of the Curie temperature of the α phase, leading to an agreement with its experimental value. We show that the corresponding nonlocal corrections to the energy of the α phase are crucially important to obtain the proximity of energies of α and γ phases in the vicinity of the iron α - γ transformation.

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Introduction. Iron is one of the substances known from ancient times. Many technologically important applications of iron and its alloys, such as producing steels, are dealt with the structural transition between the α phase with a body-centered cubic (bcc) lattice and the γ phase with a face-centered cubic (fcc) lattice. In pure iron this transition occurs in the paramagnetic region at 1185 K slightly above the Curie temperature of 1043 K. The theoretical description of this transition is important from both, fundamental and practical points of view.

The ground-state properties of α and γ phases were extensively studied¹ by the density functional theory (DFT) methods, in particular local density approximation (LDA) and generalized gradient approximation (GGA); the disordered local moment (DLM) approach² was applied to simulate the paramagnetic state by randomly distributed magnetic moments. The energies of various phases were compared and the respective correct values of magnetic moments at zero temperature were obtained within these studies^{1,3,4}. The combination of these methods with the Heisenberg model gave a possibility to treat magnetic correlations (also at finite temperature), and provided an accurate value for the Curie temperature of bcc Fe^{5,6}, its thermodynamic properties^{7,8}, and magnon-phonon coupling⁹. This combination also resulted in an accurate value for the alpha-gamma transition temperature as a function of carbon concentration⁸.

Despite these successes, the described methods do not consider important local correlations in iron, and, therefore, do not provide a comprehensive view on the α - γ transition. To treat the effect of local correlations we apply in the present paper the combination of dynamical mean-field theory (DMFT)¹⁰ with density functional theory (DFT) methods, usually called LDA+DMFT¹¹. Previous studies by LDA+DMFT allowed one to obtain the correct values of magnetic moments in α and γ phases¹²⁻¹⁶, the linear behavior of the temperature dependence of the inverse local¹³⁻¹⁶ (α, γ phases) and uniform magnetic^{12,17,18} (α phase) susceptibilities, and revealed the non-monotonic temperature dependence of in-

verse the uniform magnetic susceptibility in the γ phase in a broad temperature range¹⁴.

In most of these studies the Curie temperature of the α phase was found, however, to be substantially overestimated. As a result, the description of the magnetization¹², the temperature of the α - γ transition¹⁹, and the phonon spectra²⁰ was provided in units of the calculated Curie temperature. The overestimation of the Curie temperature mainly comes from the DMFT part and is due to using the approximate (density-density) form of the Coulomb interaction^{16,17} and neglecting nonlocal correlations in DMFT.

To solve the former problem, we apply in the present study the spin-rotationally-invariant DMFT approach¹⁷. Although the nonlocal corrections to DMFT can be taken into account using, e.g., the dynamic vertex approximation²¹, the dual fermion approach²², or cluster methods²³, these approaches are too computationally expensive to be applied to real multiorbital compounds at the moment.

For iron, the nonlocal degrees of freedom can be described within the effective Heisenberg model, which was combined previously with DFT approaches in Refs. 6–9. However, a derivation of this model from microscopic principles, and its combination with a treatment of local correlations within LDA+DMFT was not considered previously. In the present paper we address the microscopic derivation of an effective Heisenberg model in the presence of local moments and calculate the nonlocal correction to the energy of the α phase near the magnetic phase transition. We show that this correction is crucially important to compare the energies of α and γ phases near the structural phase transition without adjustable parameters.

Let us turn first to the *LDA+DMFT part*. We performed DFT calculations using the full-potential linearized augmented plane-wave method implemented in the ELK code supplemented by the Wannier function projection procedure (Exciting-plus code²⁴). The Perdew-Burke-Ernzerhof form²⁵ of GGA was considered. The calculations were carried out with the experimental

lattice constant $a = 2.91 \text{ \AA}$ for the α phase in the vicinity of the α - γ transition²⁶. The lattice constant for the γ phase was set to keep the experimental volume of the unit cell for the α phase. The integration in the reciprocal space was performed using an $18 \times 18 \times 18$ \mathbf{k} -point mesh. The convergence threshold for the total energy was set to 10^{-6} Ry. From the converged DFT results we constructed effective Hamiltonians in the basis of Wannier functions, which were built as a projection of the original Kohn-Sham states to site-centered localized functions as described in Ref. 27, considering *spd* states. This differentiates the present approach from that of Ref. 19, where only *sd* states were taken into account. The difference of DFT total energies obtained in our non-magnetic calculations for α and γ phases is 0.280 eV/at in agreement with previous DFT studies^{19,28,29} resulting in values from 0.24 to 0.3 eV/at.

The effect of local correlations is considered within the DMFT approach of Ref. 17, applied to the Hamiltonian

$$\hat{H}_{\text{DMFT}} = \hat{H}_{\text{DFT}}^{\text{WF}} + \hat{H}_{\text{Coul}} - \hat{H}_{\text{DC}}, \quad (1)$$

where $\hat{H}_{\text{DFT}}^{\text{WF}}$ is the effective Hamiltonian in the basis of Wannier functions constructed for states near the Fermi level, \hat{H}_{Coul} is the on-site Coulomb interaction Hamiltonian, and \hat{H}_{DC} is the double-counting correction. This correction was considered in the fully localized limit and had the form $\hat{H}_{\text{DC}} = \bar{U}(n_{\text{DMFT}}^{\text{d}} - 1/2)$, where $n_{\text{DMFT}}^{\text{d}}$ is the number of d electrons in DMFT, and \bar{U} is the average Coulomb interaction in the *d* shell. We choose the on-site Coulomb and Hund interaction parameters $U \equiv F^0 = 4 \text{ eV}$ and $J_S \equiv (F^2 + F^4)/14 = 0.9 \text{ eV}$, where F^0 , F^2 , and F^4 are the Slater integrals as obtained in Ref. 30 by the constrained density functional theory (cDFT) in the basis of *spd* Wannier functions.

From the uniform magnetic susceptibility of the α phase, we extracted the effective local moment $\mu_{\text{eff},\alpha}^2 = 2.7\mu_{\text{B}}^2$ and the Curie temperature $T_C^{\alpha,\text{DMFT}} = 1400 \text{ K}$ in agreement with a previous study¹⁷. As in this study, we expect that the Curie temperature is weakly dependent on Hubbard U and is more sensitive to the Hund's coupling. The DMFT results for the energies are shown in Fig. 1. One can see that the energy of the α phase strongly increases with decreasing temperature. Looking at the partial contributions from kinetic and potential energies, one can see that the increase of the energy of the α phase with decreasing T is due to the strong increase of the kinetic energy, while the potential energy expectedly decreases, reflecting the increase of instantaneous magnetic moment $\langle \mathbf{S}_{i,\alpha}^2 \rangle$ (Ref. 14). Although the energy of the γ phase also increases with decreasing T , it saturates in the temperature range 1000 – 1500 K. Moreover, inspection of kinetic and potential energies shows the opposite tendencies to those in the α phase: the mentioned increase of total energy upon cooling is provided by a strong increase of the *potential* energy, and a weaker decrease of the *kinetic* energy. The increase of potential energy reflects a decrease of instantaneous moment $\langle \mathbf{S}_{i,\gamma}^2 \rangle$ (Ref. 14),

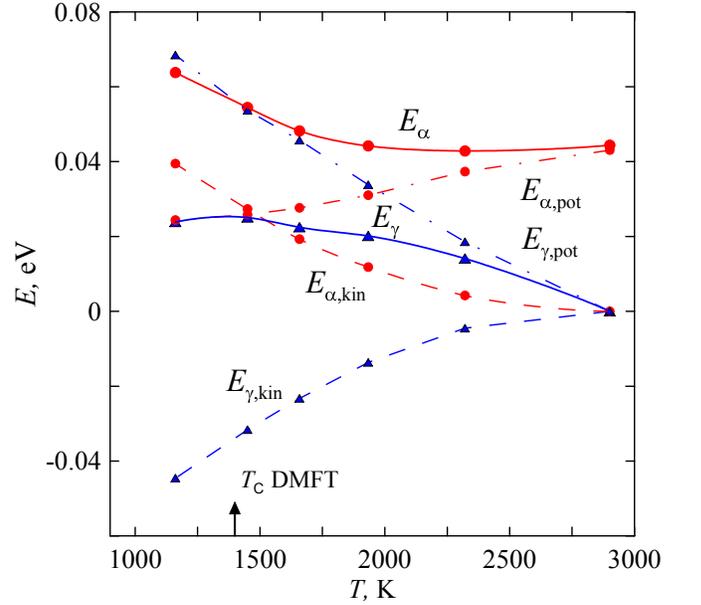


FIG. 1: (Color online) Temperature dependence of total (solid lines), kinetic (dashed lines), and Coulomb (dot-dashed lines) energies per atom obtained by LDA+DMFT for the α (red curves, circles), and the γ (blue curves, triangles) phases of iron. The potential and kinetic energies of the $\alpha(\gamma)$ phase are shifted by $\pm E_{\alpha(\gamma),\text{kin}}(T = 2900\text{K})$ for better view.

and, compared to the opposite tendency of the α phase, provides a mechanism of stabilization of the α phase at low T . However, this mechanism is not the only contribution, and at the level of DMFT the γ phase is "protected" by the respective decrease in kinetic energy in the γ phase and its increase in the α phase.

Non-local corrections. To calculate the nonlocal corrections to the Curie temperature and the energy of the α phase, we treat the effect of local moments on the energy within the spin-fermion model of Ref. 15, supplemented by a soft spin constraint,

$$\begin{aligned} \mathcal{S} = & \sum_{i'l\nu_n\sigma l\nu'} c_{i'l\sigma}^\dagger(i\nu_n) \left[i\nu_n \delta_{ii'} \delta_{ll'} + H_{ll'}^{ii'} - \Sigma_{ll'}(i\nu_n) \right] \\ & \times c_{i'l\sigma}(i\nu_n) + \frac{1}{2} \sum_{i,\omega_n} \chi_S^{-1}(i\omega_n) \mathbf{S}_i(i\omega_n) \mathbf{S}_i(-i\omega_n) \\ & + 2J_K \sum_{i,\omega_n} \mathbf{S}_i(i\omega_n) \mathbf{S}_i(-i\omega_n) + \frac{1}{4} \sum_{i,\omega_n,\omega'_n} \lambda(i\omega_n) \\ & \times \left\{ [\mathbf{S}_i(i\omega_n) \mathbf{S}_i(-i\omega_n + i\omega'_n)]^2 - \delta_{\omega'_n,0} \langle |\mathbf{S}_i(i\omega_n)|^2 \rangle^2 \right\}, \end{aligned} \quad (2)$$

where i, l are site and orbital indices, $H = H_{\text{DFT}}^{\text{WF}}$, $\Sigma_{ll'}$ are the DMFT self-energies, \mathbf{S}_i corresponds to the spin of the local-moment degrees of freedom, $\mathbf{s}_i = \sum_{l\sigma\sigma'} c_{i'l\sigma}^\dagger \boldsymbol{\sigma}_{\sigma\sigma'} c_{i'l\sigma'}$ to the spin of itinerant degrees of freedom, and $\boldsymbol{\sigma}$ are the Pauli matrices. The first and second lines in Eq. (2) describe the propagation of itinerant electrons and the dynamics of the local moments, the third line corresponds to their interaction

via Hund exchange $J_K \simeq (5/7)J_S$ in Kanamori parameterization, and the fourth line adds a spin constraint on the local moments, which restricts the size of the moment. This model can be considered as a simplified version of the multiorbital model, studied by LDA+DMFT, where the major effect of correlations – formation of the local moments – is incorporated in the local variables \mathbf{S} . The bare local moment propagator $\chi_S^{-1}(i\omega_n) = 4\mu_B^2\chi_{\text{loc}}^{-1}(i\omega_n) + (J_K/\mu_B)^2\bar{\chi}^{\text{irr}}$ was obtained in Ref. 15; $\chi_{\text{loc}}(i\omega_n)$ is the dynamic local susceptibility and $\bar{\chi}^{\text{irr}} \approx 2\mu_B^2/eV$ is the static local two-particle irreducible susceptibility in the α phase. Decoupling the four-spin interaction in the soft constraint part in Eq. (2) within bosonic mean-field theory (which implies neglecting critical fluctuations near T_C^α), we obtain:

$$\begin{aligned} \mathcal{S} = & \frac{1}{2} \sum_{i,\omega_n} \{ [\chi_S^{-1}(i\omega_n) + \Lambda(T, i\omega_n)] \mathbf{S}_i(i\omega_n) \mathbf{S}_i(-i\omega_n) \\ & - \Lambda(T, i\omega_n) \langle |\mathbf{S}_i(i\omega_n)|^2 \rangle \} + 2J_K \sum_{i,\omega_n} \mathbf{S}_i(i\omega_n) \mathbf{s}_i(-i\omega_n) \\ & + \sum_{ii',\nu_n\sigma\ell\ell'} c_{i\ell\sigma}^\dagger(i\nu_n) \left[i\nu_n \delta_{ii'} \delta_{\ell\ell'} + H_{\ell\ell'}^{ii'} - \Sigma_{\ell\ell'}(i\nu_n) \right] c_{i'\ell'\sigma}(i\nu_n), \end{aligned} \quad (3)$$

where $\Lambda(T, i\omega_n) = \lambda(i\omega_n) \langle |\mathbf{S}_i(i\omega_n)|^2 \rangle$. In the second order in J_K we find the corresponding effective model for spin degrees of freedom (cf. Ref. 15)

$$\begin{aligned} \mathcal{S}_{\text{eff}} = & \frac{1}{2} \sum_{\mathbf{q},\omega_n} \left[\chi^{-1}(\mathbf{q}, i\omega_n) \mathbf{S}_{\mathbf{q}}(i\omega_n) \mathbf{S}_{-\mathbf{q}}(-i\omega_n) \right. \\ & \left. - \Lambda(T, i\omega_n) \langle |\mathbf{S}_{\mathbf{q}}(i\omega_n)|^2 \rangle \right], \end{aligned} \quad (4)$$

where

$$\chi^{-1}(\mathbf{q}, i\omega_n) = 4\mu_B^2\chi_{\text{loc}}^{-1}(i\omega_n) + \Lambda(T, i\omega_n) - J_{\mathbf{q}}, \quad (5)$$

$J_{\mathbf{q}} = (J_K/\mu_B)^2(\chi_{\mathbf{q}}^{\text{irr}} - \bar{\chi}^{\text{irr}})$ is the exchange interaction, $\chi_{\mathbf{q}}^{\text{irr}}$ is the static two-particle irreducible susceptibility, which can be calculated as a bubble, constructed from itinerant Green functions¹⁵. The determination of the function $\Lambda(T, i\omega_n)$ is a rather complicated problem, since it requires knowledge of the $\langle \mathbf{S}^2 \rangle^2$ interaction potential in Eq. (2). We fix its static component by the equality of the obtained static part of the on-site spin correlation function to that, obtained in DMFT $\mu_{\text{eff},\alpha}^2 = 3T\chi_{\text{loc}}(0)$; the latter is found to be almost temperature independent (contrary to the instantaneous moment $\langle \mathbf{S}_i^2 \rangle$) in a broad temperature range¹⁴. The corresponding condition reads

$$3T \sum_{\mathbf{q}} \frac{1}{\lambda_0 - J_{\mathbf{q}}} = \frac{\mu_{\text{eff},\alpha}^2}{4\mu_B^2}, \quad (6)$$

where $\lambda_0 = 4\mu_B^2\chi_{\text{loc}}^{-1}(0) + \Lambda(T, 0)$. The equation (6) is analogous to the one, obtained in the (static) spherical approximation to the classical Heisenberg model

$$H_{\text{Heis}} = -\frac{1}{2} \sum_{ij} J_{ij} \mathbf{S}_i \mathbf{S}_j. \quad (7)$$

Indeed, this model, treated in the spherical approximation, yields the action

$$\mathcal{S} = \frac{1}{2} \sum_{\mathbf{q}} (\lambda_0 - J_{\mathbf{q}}) |\mathbf{S}_{\mathbf{q}}|^2 - \frac{\lambda_0}{2} \langle \mathbf{S}_i^2 \rangle_{\text{Heis}} \quad (8)$$

and the corresponding condition, Eq. (6), with $\mu_{\text{eff},\alpha}^2 = 4\mu_B^2 \langle \mathbf{S}_i^2 \rangle_{\text{Heis}}$. Equation (8) is also essentially equivalent to the static limit of Eq. (4) up to the local contribution, which does not depend on $\mathbf{S}_{\mathbf{q}}$.

The Curie temperature is determined by vanishing of the gap of the paramagnon spectrum, and in the same static approximation reads:

$$3T_C^\alpha \sum_{\mathbf{q}} \frac{1}{J_0 - J_{\mathbf{q}}} = \frac{\mu_{\text{eff},\alpha}^2}{4\mu_B^2}. \quad (9)$$

In the following we assume the nearest-neighbor approximation $J_{\mathbf{q}} = 8J \cos(q_x/2) \cos(q_y/2) \cos(q_z/2)$, as justified in Refs. 15,29. The exchange integral J can be extracted from the Curie temperature without nonlocal corrections (i.e. in DMFT, cf. Refs. 14,15),

$$T_C^{\alpha,\text{DMFT}} = \frac{J_0 \mu_{\text{eff},\alpha}^2}{3 \cdot 4\mu_B^2}. \quad (10)$$

Using this, we find $T_C^\alpha < T_C^{\alpha,\text{DMFT}}$ and $\Lambda(T_C^\alpha, 0) = 3(2\mu_B/\mu_{\text{eff},\alpha})^2(T_C^{\alpha,\text{DMFT}} - T_C^\alpha) > 0$. The corresponding

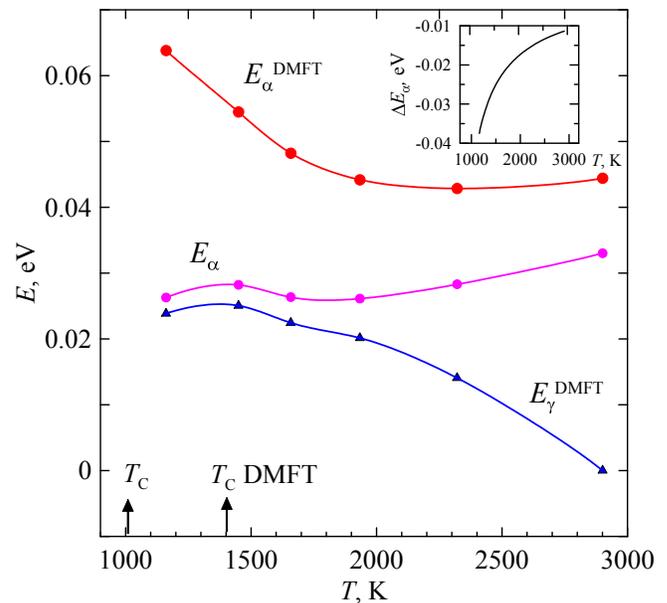


FIG. 2: (Color online) Temperature dependence of total energies per atom of α (upper, red curve, circles) and γ (blue curve, triangles) phases obtained by LDA+DMFT, and the energy of the α phase with the nonlocal correction (middle, magenta curve). Inset shows the nonlocal correction to the energy of the α phase, $\Delta E_\alpha = E_\alpha - E_\alpha^{\text{DMFT}}$, calculated from Eq. (11).

nonlocal contribution to the energy of the α phase is obtained from the Eq. (4) in the static approximation or from Eq. (8),

$$\begin{aligned} E_\alpha &= E_\alpha^{\text{DMFT}} - \frac{3T}{2} \sum_{\mathbf{q}} \frac{J_{\mathbf{q}}}{\lambda_0 - J_{\mathbf{q}}} \\ &= E_\alpha^{\text{DMFT}} - \frac{\Lambda(T, 0) \mu_{\text{eff}, \alpha}^2}{2 \cdot 4\mu_{\text{B}}^2}. \end{aligned} \quad (11)$$

Since $0 < \Lambda(T, 0) < \Lambda(T_C^\alpha, 0)$ at $T > T_C^\alpha$, the obtained correction is negative, decreasing the energy; the decrease is maximal at T_C^α .

In principle, the same calculation could be applied to obtain the nonlocal correction to the energy of the γ phase. However, since the corresponding Neel temperature is much lower, than T_C^α (see, e.g., Ref. 14), and pronounced corrections are obtained only in the vicinity of the magnetic transition temperature, we do not expect a substantial correction in that case.

Using Eq. (10) we find $J_0 = 0.20$ eV, which is close to the estimates of Refs. 29 and 15. The corresponding Curie temperature with account of nonlocal correlations $T_C^\alpha = 1005$ K is in a good agreement with the experimental data. The resulting temperature dependence of the energy of the α phase is shown in Fig. 2, together with the energies of α and γ phases, obtained in DMFT. One can see, that the obtained nonlocal correction to the energy of the α phase compensates the increase of its kinetic energy upon cooling and makes the energies of α and γ phases very close in the vicinity of the α - γ transition. This demonstrates from one side, that the non-local corrections are crucially important for the description of this transition, and from the other side, the proposed methods are capable of describing adequately the effect of nonlocal correlations. The description of the alpha-gamma transition can be further improved by, e.g., using a more advanced rotationally-invariant quantum impurity solver than in our study (see, e.g., Ref. 16). Another improvement can be made by considering free energies. However, at the moment such calculations are too computationally expensive and beyond the scope of the present paper.

We note that our results considerably differ from those of Leonov *et al.*¹⁹, where the α - γ transition was captured

by LDA+DMFT with density-density interaction in units of the overestimated Curie temperature (1600 K). Aside from using the rotationally-invariant interaction and considering the absolute temperature dependencies, there are some computational details that differ in our study. In particular, (i) we use the all-electron full-potential LAPW method implemented in the ELK code resulting in a difference of DFT total energies of 0.280 eV, while Leonov *et al.* used the pseudopotential Quantum ESPRESSO package leading to 0.244 eV. (ii) We use the *spd* Wannier function basis, while only *sd* states were included by Leonov *et al.* (iii) We use Hubbard $U = 4$ eV, while a much smaller value $U = 1.8$ eV was employed by Leonov *et al.*

Within the above-mentioned methods we found the energy of the γ phase to be at least 0.044 eV below the α phase in the paramagnetic region for the density-density interaction, yielding a Curie temperature ~ 2150 K, which is larger than the 1600 K value obtained by Leonov *et al.* and is close to 1900 K obtained by Lichtenstein *et al.*¹² Previous LDA+DMFT studies of iron indicated that the Curie temperature is weakly dependent on Hubbard U (Ref. 30). Therefore we expect that this discrepancy is mainly due to different Wannier function basis. This is supported by the fact that the DMFT calculations by Lichtenstein *et al.* were performed with *3d*, *4s*, and *4p* states included in the basis set (not Wannier functions). Since the total energy is a subtle quantity, we suppose that the discrepancy between our and Leonov *et al.* results can be further influenced by the above mentioned computational differences (i)-(iii), but consider our calculation to be more accurate in these respects. To shed light on this point, further studies are required.

In conclusion, we have presented a method to evaluate the nonlocal correction to the Curie temperature and energy, obtained in DMFT in the presence of local moments by deriving the spherical approximation results for the effective Heisenberg model from the spin-fermion model. We have shown that the obtained results yield the energies of α and γ phases, which are very close in the vicinity of the α - γ transition, which is necessary to describe the structural phase transition in iron.

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