Structural hcp-fcc phase transition in Fe-Mn alloy from CPA+DMFT approach

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We present a computational scheme for total energy calculations of disordered alloys with strong electron correlations. It employs the coherent potential approximation combined with the dynamical mean-field theory and allows us to study the structural transformations. The Hamiltonians in the Wannier function basis are obtained by density functional theory. The proposed approach is applied to study the hcp-fcc structural transition in Fe0.9Mn0.1 alloy. The hcp-fcc transition temperature is found to be about 600 K, which is in good agreement with the experimental value of about 500 K. We demonstrate that in contrast to the bcc-fcc transition in pure iron, the hcp-fcc transition in Fe0.9Mn0.1 is not driven by the magnetic correlation energy.

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I. INTRODUCTION

Despite the rapid development of computational techniques in last decades, the investigation of disordered alloys from first principles still causes considerable difficulties. Nowadays these alloys are mainly studied within the density functional theory (DFT) by two different approaches. In the first approach, large supercells with randomly distributed atoms are employed. The main drawbacks of this approach are the high computational costs and discrete set of concentrations. The second approach involves the use of the coherent potential approximation (CPA). In the CPA, the effective (coherent) potential is introduced on every site of the lattice. This potential is such as to simulate properties of the actual substitutional alloy. However, the DFT within the commonly used local density approximation (LDA) or generalized gradient approximation (GGA) usually fails to reproduce the properties of the strongly correlated systems. In addition, the paramagnetic state cannot be properly simulated by the nonmagnetic DFT calculations.

To overcome some of these difficulties, various extensions of the CPA have been proposed, e.g., combinations of the CPA with the disordered local moment model and with the static approximation for electron correlations. Moreover, the CPA can be naturally combined with the dynamical mean-field theory (DMFT) which is exact in infinite dimensions. The DMFT allows mapping the lattice problem with many degrees of freedom onto a quantum impurity embedded in a self-consistently determined bath. Both the CPA and DMFT neglect the spatial correlations and belong to the mean-field methods. In the CPA+DMFT approach, the simulation of a disordered system is carried out by iterative solution of several impurity problems supplemented by self-consistency conditions. Calculating the material specific aspects within DFT, the CPA+DMFT method can be applied to real disordered systems and alloys. In particular, the electronic structure and magnetic properties of Na2CoO2 were studied by CPA+DMFT in Ref. 6 In these studies, the on-site potential was introduced to mimic the Na potential. The parameters for a minimal Hamiltonian were calculated within DFT. The CPA+DMFT approach was also implemented and successfully applied within the Korringa-Kohn-Rostoker method with the spin-polarized T-matrix plus fluctuation exchange approximation as an impurity solver. In some sense, the CPA+DMFT can be regarded as a generalization of the well-known LDA+DMFT method for the case of substitutional alloys.

In this paper, we propose a computational scheme for total energy calculations of disordered alloys with strong electron correlations. This scheme is implemented within CPA+DMFT approach and applied to study the hcp-fcc structural transition in Fe1−xMnx alloy at x = 0.1. The Fe-Mn alloys exhibit a variety of unusual properties such as Invar and anti-Invar effects. In addition, these alloys at 15 − 35 at. % were found to possess the improved strength and ductility making them the basis for the transformation- and twinning-induced plasticity (TRIP and TWIP) steels. Due to their wide applications, the Fe-Mn alloys have been intensively studied theoretically and experimentally. On the Fe-rich side of the phase diagram, a metastable phase with the hexagonal close packed (hcp) lattice can be found at low temperatures. Upon heating, a transition from antiferromagnetic to paramagnetic states occurs. Further heating results in a structural transition to the face-centered cubic (fcc) phase. In particular, the structural transition in Fe0.9Mn0.1 alloy is observed at temperature $T_{\text{struct}}^{\exp} \sim 500$ K (Ref. 13). This transition occurs in the paramagnetic region which significantly complicates the use of most electronic structure calculation methods. Even the state-of-the-art LDA+DMFT method only recently was applied to study the structural transitions in paramagnetic iron.

The paper is organized as follows. In Sec. we present...
a computational scheme of the CPA+DMFT method implemented for total energy calculations. In Sec. IV we employ this technique to study the structural and magnetic properties of Fe$_{0.9}$Mn$_{0.1}$ alloy. Finally, conclusions are presented in Sec. V.

II. METHOD

Let us, for simplicity, consider a binary alloy A$_{1-x}$B$_x$. The atoms of type A (B) will be referred as host (impurity) atoms. In this case, the computational scheme of the CPA+DMFT approach can be constructed in the following steps. First, DFT calculations within LDA or GGA are performed for the lattice containing only host (A) atoms. Second, an effective Hamiltonian $H_A(k)$ in the Wannier functions basis is constructed for states near the Fermi level in the host lattice. Third, a supercell containing one substitutional impurity $B$ embedded in the host lattice is simulated within DFT. From converged DFT results in the Wannier functions basis, one should calculate the impurity level splitting parameters

$$V_n = \varepsilon^B_n - \varepsilon^A_n,$$  

where $\varepsilon^B_n$ and $\varepsilon^A_n$ are the band energies of the impurity and the most distant host atom, respectively. Here, $\alpha$ labels the symmetry of Wannier functions. In the last step, the self-consistent DMFT equations combined with the CPA ideology are iteratively solved. Now we proceed to these equations. Within CPA+DMFT approach the real alloy is replaced by an effective medium with the local Green function

$$G_{\text{med}}(i\omega_n) = \frac{1}{V_{BZ}} \int \frac{d\mathbf{k}}{(\mu + i\omega_n)I - H_A(k) - \Sigma(i\omega_n)},$$  

where $\mu$ is the chemical potential, $\omega_n$ are the fermionic Matsubara frequencies, $I$ is the unit matrix, $H_A(k)$ is the effective Hamiltonian for host lattice in the Wannier functions basis, $\Sigma(i\omega_n)$ is the effective (coherent) potential. The integration is performed over the first Brillouin zone with volume $V_{BZ}$. In contrast to the conventional CPA approach, the effective potential $\Sigma(i\omega_n)$ now contains information not only about disorder but also about electronic correlations. Note that the chemical potential should be adjusted to the average number of electrons per site in alloy. Using the Dyson equation one can obtain the bath Green function

$$G_{0}^{-1}(i\omega_n) = G_{\text{med}}^{-1}(i\omega_n) + \Sigma(i\omega_n),$$  

which is required to calculate the impurity Green functions $G_A(i\omega_n)$ and $G_B(i\omega_n)$. However, the local Green function of effective medium is interpreted as a weighted sum of impurity Green functions:

$$G_{\text{med}}(i\omega_n) = (1 - x)G_A(i\omega_n) + xG_B(i\omega_n).$$  

Having obtained $G_{\text{med}}(i\omega_n)$ by Eq. (4), one can easily compute the new effective potential from the Dyson equation:

$$\Sigma(i\omega_n) = G_{0}^{-1}(i\omega_n) - G_{\text{med}}^{-1}(i\omega_n).$$  

The obtained new effective potential is then used in Eq. (2) to calculate the local Green function of effective medium. The above equations are iteratively solved until the convergence is achieved.

In the orbital space, the above Green functions and effective potential are matrices of the same size as $H_A(k)$. In the uncorrelated subspace (Wannier functions of sp character), the impurity Green function of A (host) type coincides with the bath Green function, while for impurity of B type it can be expressed as

$$G_{B,\alpha}^{-1}(i\omega_n) = G_{0,\alpha}^{-1}(i\omega_n) - V_\alpha,$$  

where $V_\alpha$ are obtained in the supercell calculations for Wannier functions of symmetry $\alpha$ (= s or p). To calculate the impurity Green functions elements in the correlated subspace (Wannier functions of d character), one should solve two single-impurity problems by any quantum impurity solver. Since the on-site Coulomb interaction is already treated in DFT in an average way, a corresponding correction should be introduced to avoid double-counting. This correction can be introduced as a shift of the impurity levels immediately before solving quantum impurity problems. Namely, the diagonal elements of the bath Green function obtained by Eq. (9) can be written in the form

$$G_{0,m}(i\omega_n) = (i\omega_n - \epsilon_m - \Delta_m(i\omega_n))^{-1},$$  

where $\epsilon_m$ is the impurity level for orbital $m$, $\Delta_m(i\omega_n)$ is the hybridization function. Then, the bath Green functions for impurities of type A and B are given by

$$G_A^0(i\omega_n) = (i\omega_n - \epsilon_A - \Delta_A(i\omega_n))^{-1},$$  
$$G_B^0(i\omega_n) = (i\omega_n - \epsilon_B - \Delta_B - V_\alpha - \Delta_A(i\omega_n))^{-1}. $$  

Here, $\epsilon_{dc}^{A(B)}$ is the double-counting correction which was introduced in the form

$$\epsilon_{dc}^{A(B)} = -U^{A(B)}(n_d - \frac{1}{2}),$$  

where $U^{A(B)}$ is the average Coulomb interaction in the d shell for impurity of type A (B), $n_d$ is the number of d electrons per site in effective medium. This form of the double-counting correction is widely used and corresponds to the fully localized limit.

The calculation of total energy in the LDA+DMFT method has been discussed in Ref. 10. Following the same way, the total energy in the CPA+DMFT approach can be defined as

$$E_{\text{tot}} = E_A^{\text{DFT}} + E_{\text{kin}}^{\text{CPA+DMFT}} + E_{\text{Coul}}^{\text{CPA+DMFT}} - E_0^{\text{kin}} - E_0^{\text{Coul}}. $$  

Here, the first term is the total energy for the host lattice obtained in self-consistent DFT calculations. The second term is the CPA+DMFT kinetic energy which can be defined as

$$E_{\text{kin}}^{\text{CPA+DMFT}} = T \sum_{k,n} \text{Tr}[H_A(k)G_{\text{med}}(k, i\omega_n)]e^{i\omega_n 0^+}$$  
$$+ x \sum_{\alpha} n_{\alpha} B V_\alpha,$$  

where $n_{\alpha}$ is the number of impurities of type $\alpha$. The obtained results for the energy per one impurity $E_{\text{tot}}^{\text{CPA+DMFT}}$ are given in Table I.
where $T$ is the temperature, $n_B^\alpha$ is the occupancy of states with symmetry $\alpha$ for impurity B, $G_{\text{med}}(k, i\omega_n)$ is the lattice Green function of the effective medium defined as

$$G_{\text{med}}(k, i\omega_n) = [(\mu + i\omega_n)I - H_A(k) - \Sigma(i\omega_n)]^{-1}. \quad (13)$$

The necessity of the last term in Eq. (12) becomes apparent in the atomic limit. The third term in Eq. (11) corresponds to the Coulomb energy in CPA+DMFT and can be expressed via double occupancies:

$$E_{\text{Coul}}^{\text{CPA+DMFT}} = (1 - x) \sum_{m'm'\sigma'\sigma} U_{m'm'\sigma'\sigma}^A \langle \hat{n}_{m'\sigma'}^A \hat{n}_{m'\sigma'}^A \rangle + x \sum_{m'm'\sigma'\sigma} U_{m'm'\sigma'\sigma}^B \langle \hat{n}_{m'\sigma'}^B \hat{n}_{m'\sigma'}^B \rangle. \quad (14)$$

where $\hat{n}_{m\sigma}^A$ is the number operator for electrons with spin $\sigma$ at orbital $m$ of impurity A, $U_{m'm'\sigma'\sigma}^A$ is the element of the Coulomb interaction matrix for impurity A. The fourth term is Eq. (11) is the kinetic energy for the host lattice in the absence of effective potential:

$$E_{\text{kin}}^0 = T \sum_{k,n} \text{Tr}[H_A(k)G_{\text{med}}^0(k, i\omega_n)]e^{i\omega_n 0^+}, \quad (15)$$

where

$$G_{\text{med}}^0(k, i\omega_n) = [(\mu + i\omega_n)I - H_A(k)]^{-1}. \quad (16)$$

The last term in Eq. (11) corresponds to the double-counting energy which in the fully localized limit can be written as

$$E_{\text{Coul}}^0 = \frac{(1 - x)\bar{U}^A + x\bar{U}^B}{2} n_{d}\langle \hat{n}_{d} \rangle (n_{d} - 1). \quad (17)$$

### III. RESULTS AND DISCUSSION

To perform calculations within DFT, we employed the full-potential linearized augmented-plane wave method implemented in the Exciting-plus code (a fork of ELK FF-LAPW code\textsuperscript{15}). The exchange-correlation potential was considered in the Perdew-Burke-Ernzerhof form\textsuperscript{23} of the generalized gradient approximations (GGA). The calculations were carried out with the experimental lattice constants $a_{\text{bcc}} = 3.5812$ Å for fcc phase; $a_{\text{hcp}} = 2.5273$ Å and $c_{\text{hcp}} = 4.0857$ Å for hcp phase.\textsuperscript{24} The convergence threshold of $10^{-6}$ Ry was used for total energy. Integration in the reciprocal space was performed using 18 × 18 × 18 and 16 × 16 × 10 k-point meshes for fcc and hcp phases, respectively. The muffin-tin radii were set to 2.2 a.u. for all atoms. In nonmagnetic calculations the ground state of hcp Fe is found to be 101 meV/at. lower in energy than the ground state of fcc Fe. From converged DFT results we constructed effective Hamiltonians in the basis of Wannier functions of spd character. In figure [1] we present the obtained nonmagnetic band structures of fcc Fe and hcp iron in comparison with the bands corresponding to the constructed effective Hamiltonians. Differences of band energies of Mn atom and

![Figure 1](image-url)

**FIG. 1.** (Color online) Nonmagnetic band structures of fcc Fe (upper panel) and hcp Fe (lower panel) obtained within GGA (solid lines) and bands corresponding to the constructed effective Hamiltonians in the spd Wannier functions basis (dotes). The Fermi level is at zero energy.

The most distant Fe atom in a supercell of 8 atoms is presented in Table 1.

Our CPA+DMFT calculations were carried out with $U = 4$ eV and $J = 0.9$ eV obtained by the constrained density functional theory calculations in the basis of spd Wannier functions.\textsuperscript{23} To solve the auxiliary impurity problems, we employed the hybridization expansion continuous-time quantum Monte Carlo (CT-QMC) method.\textsuperscript{24} The energy cut-off on Matsubara frequencies was set to 600 eV in all calculations.

In figure 2 we present the obtained CPA+DMFT total energy of Fe$_{0.9}$Mn$_{0.1}$ alloy in fcc and hcp phases as a function of temperature. One can clearly see that the hcp-fcc structural transition occurs at temperature about 600 K, which is in good agreement with the experimental value of about 500 K (Ref. 13).

As shown by Leonov et al. using LDA+DMFT ap-

| Phase | $V_e$ (eV) | $V_p$ (eV) | $V_d$ (eV) |
|-------|-----------|-----------|-----------|
| fcc   | 0.943     | 1.964     | 0.352     |
| hcp   | 1.015     | 1.986     | 0.401     |

**TABLE I.** Differences of band energies of Mn atom and the most distant Fe atom in a supercell of 8 atoms calculated within GGA.
FIG. 2. (Color online) Total energy of Fe$_{0.9}$Mn$_{0.1}$ alloy in fcc and hcp phases as a function of temperature obtained by CPA+DMFT.

approach, the bcc-fcc structural transition in pure iron is accompanied by different temperature dependence of local moments in bcc and fcc phases. It was argued that the Coulomb energy can be approximately decomposed into two contributions, one of which is proportional to the square of the local moment, while the other is proportional to the square of the average number of d-electrons per site. Since the average number of d-electrons is almost the same in both phases and only weakly depends on temperature, it was concluded that the magnetic correlation energy is an essential driving force behind the bcc-fcc transition in iron. To verify this conclusion for the case of Fe$_{0.9}$Mn$_{0.1}$ alloy, in figure 3 we present average squared local moments of Fe and Mn atoms calculated as

$$
\langle m^2 \rangle = \sum_{m \sigma} \left( \langle n_{m \sigma} n_{m' \sigma} \rangle - \langle n_{m \sigma} \rangle \langle n_{m' \sigma} \rangle \right).
$$

The obtained squared local moments in both phases gradually increase with temperature maintaining almost the same difference in values. This indicates that in contrast to the bcc-fcc transition in pure iron, the hcp-fcc transition in Fe$_{0.9}$Mn$_{0.1}$ is not driven by the magnetic correlation energy. However, electron correlation effects play an important role in this alloy. In particular, our calculations with the same effective Hamiltonians by the CPA method result in hcp phase being about 60 meV lower in energy than the fcc phase.

FIG. 3. (Color online) Average squared local magnetic moments of Fe and Mn in Fe$_{0.9}$Mn$_{0.1}$ alloy in fcc and hcp phases obtained by CPA+DMFT.

IV. CONCLUSIONS

We presented a computational scheme for total energy calculations of disordered alloys with strong electron correlations. It employs the CPA+DMFT approach treating electron correlations and disorder on the same footing. The material specific Hamiltonians in the Wannier function basis are obtained by density functional theory. The proposed computational scheme can be used to study correlation-induced structural and magnetic transitions as well as related properties in both paramagnetic and magnetically ordered phases. In particular, we applied it to study the hcp-fcc structural transition in Fe$_{0.9}$Mn$_{0.1}$ alloy. The hcp-fcc transition temperature was found to be about 600 K, which is in good agreement with the experimental value of about 500 K. We also demonstrated that in contrast to the bcc-fcc transition in pure iron, the hcp-fcc transition in Fe$_{0.9}$Mn$_{0.1}$ is not driven by the magnetic correlation energy.

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