Ab initio-based mean-field theory of the site occupation in the Fe-Cr σ-phase

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An efficient *first-principles*-based mean-field theory is applied to study the site occupations in the Fe-Cr σ phase. It is based on the expansion of the total energy of a random alloy close to the equiatomic composition in the paramagnetic state in terms of the effective on-site interactions and takes into account longitudinal spin fluctuations at high temperatures. The calculated site occupation is in very good agreement with the existing experimental data.

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The Fe-Cr σ phase was first observed by Bain in 1923 as a hard, nonmagnetic intermediate phase, which has formed after long-term high-temperature annealing for nearly equiatomic composition. In the early 1960s, the σ phase formation has been found in some Ni-based alloys and soon after in many other high-temperature alloys. Nevertheless, the Fe-Cr σ phase is the most investigated due to relevance to different types of steels, where its formation should be avoided because of extreme brittleness. The σ phase has a low-symmetry structure with a disordered distribution of atoms in all crystallographic sites. In particular, it has a tetragonal unit cell (space group $P4_2/mnm$) with 30 atoms divided into five nonequivalent groups of sites or sublattices (A, B, C, D, E).[1] The σ phase structure can be written in a general form as $A_2^{12} B_4^{15} C_8^{14} D_8^{12} E_8^{14}$, where the bottom and top indices denote the site multiplicities and coordination numbers for each sublattice, respectively (see Fig. 1). In Fe$_{1-x}$Cr$_x$ alloys, the σ phase is formed in a quite narrow concentration ($0.462 < x < 0.505$) and temperature range ($700\,\text{K} < T < 1100\,\text{K}$).[1–3] It is paramagnetic at ambient temperatures. However, already at the end of 1960s it was found that the Fe-Cr σ phase has a small magnetic moment at temperatures below the Curie temperature of about 50 K.[4,5] These data were reproduced 35 years later and extended in a broad experimental study of the Fe-Cr system.[6,7]

One of the most difficult issues for theory as well as for experiment is to determine accurately the occupation numbers of the five different crystallographic sites. As has been mentioned, the alloy components are randomly distributed between all the nonequivalent sites or sublattices, but they exhibit certain preferences. Already in 1955, based on a neutron and X-ray diffraction study in Fe-V, Ni-V, and Mn-Cr alloys, Kasper and Waterstrat[8] suggested a general scheme of the ordering for binary σ phases of the first-row transition-metal elements (and those containing Mo). They concluded that the elements to the left of Mn in the periodic table (V, Cr, Mo) predominantly occupy the B sites, the elements to the right of manganese (Fe, Co, Ni) the A and D sites, while Mn appears anomalous in both groups. The C and E sites are mixed with various proportions of the components depending on the specific alloy.

There are a number of first-principles investigations of the site occupation in the Fe-Cr σ phase.[9–13] Although the models and applied methods vary, they are all based on the expansion or analysis of total energies of *ordered* σ phase structures, where the five nonequivalent sublattices (A, B, C, D, E) are occupied exclusively by either Cr or Fe atoms, and disorder and partial site occupations were completely neglected. Such a choice of the site occupation leads to $2^5 = 32$ configurations, but for most of them the Fe (Cr) concentrations are far outside the narrow experimental composition range, which severely limits the accuracy and efficiency of such schemes.

In this Brief Report we suggest a different approach, outlined below, which does not suffer from these shortcomings. It considers the relevant experimental conditions and parameters of the system and thus makes the approach both quantitatively accurate and very efficient. At high temperature the Fe-Cr σ phase forms as an inhomogeneous random alloy with partial site occupations. Such an alloy can be effectively treated in the coherent potential approximation (CPA), which has sufficient accuracy and tremendously simplifies modeling of the system at the atomic scale. It was shown before[14,15] that the CPA and locally self-consistent Green's function technique give basically identical results for Fe-Cr alloys in the bcc structure, and thus CPA should produce reliable results in the present study.

The total energy of random alloys at $T = 0$ K was determined by the exact muffin-tin orbital (EMTO) method within the full charge density formalism.[16] The CPA[17] was used to get the electronic structure of the σ phase with a random distribution of Fe and Cr on the nonequivalent sites. The exchange-correlation functional was evaluated within the generalized gradient approximation.[18] In order to check the accuracy of the EMTO method, the ground-state structure of the equiatomic Fe-Cr σ phase in the ferromagnetic state has been determined by both the EMTO and full-potential linear augmented plane wave + local orbitals method (LAPW+lo),[19] as implemented in the WIEN2K code.[20] For this purpose we have started from some initial arrangement (guided by experiment)[1,3] of Fe and Cr atoms in the 30-atom unit cell and exchanged Fe and Cr atoms between the sites of the (A, B, C, D, E) sublattices in order to find the minimum of the total energy
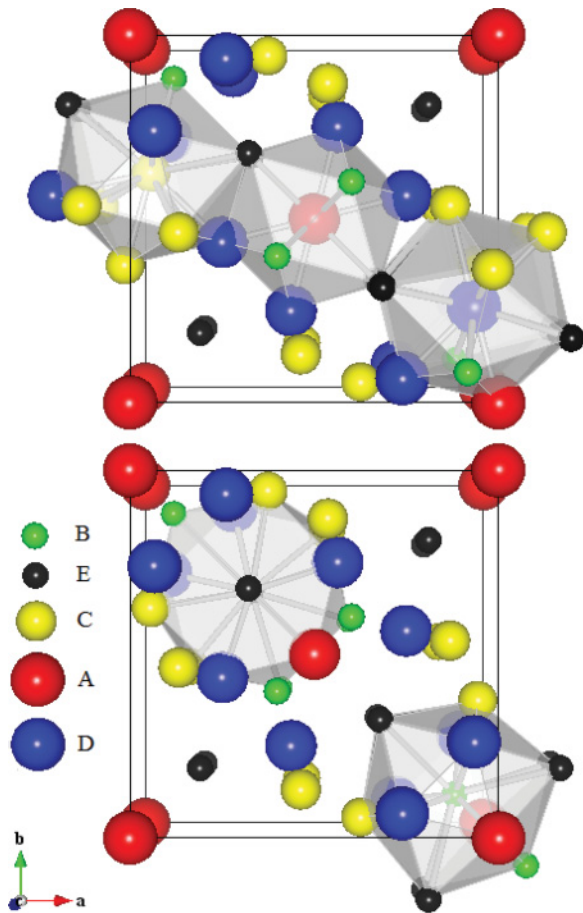
FIG. 1. (Color online) The tetragonal unit cell of the Fe-Cr σ phase structure with five crystallographically inequivalent sites (A, B, C, D, E).

by both WIEN2K and EMTO methods. Both methods obtain the same atomic configuration with the lowest total energy. In this configuration, only the C sublattice is occupied by both Fe and Cr atoms, while the other sublattices are occupied solely by one particular type. Specifically, Fe atoms occupy the icosahedrally coordinated (A, D) sites, while the Cr atoms prefer the (B, E) sites, which have the high coordination numbers. These results are in agreement with the general scheme suggested by Kasper and Waterstrat.[8]

Using the WIEN2K code we have also fully optimized the structure and calculated the formation enthalpy of the σ phase with the optimized atomic distribution. It has a positive value of 5 kJ/mol, which agrees well with the calorimetrically determined enthalpy of formation of 6.5 kJ/mol.[21] The calculated equilibrium structure parameters of the $Fe_{1-x}Cr_x$ σ phase are $a = 0.86433$ nm, $c/a = 0.518$ for $x = 0.50$. The value of the average magnetic moment per atom is $m = 0.53\mu_B$. These results agree well with the experimental room-temperature lattice parameters $a = 0.87968(5)$ nm and $c/a = 0.518$ (Ref. [1]) and reasonably with the experimental magnetic moments $m = 0.20\mu_B$ measured for $x = 0.49$ at 4 K.[4] The local atomic site relaxations calculated during the structural optimization are small and have an effect on the formation enthalpy not greater than 0.1 kJ/mol. The latter is due to the similar atomic sizes of Fe and Cr.

In order to determine the equilibrium site occupations as function of temperature and concentration we minimize the Helmholtz free energy F with respect to the site occupations for a given x and T, which is defined by $F(\{c_i\}) = E_{\text{tot}}(\{c_i\}) - T(S_{\text{conf}} + S_{\text{magn}})$. Here $E_{\text{tot}}(c_i)$ is the total energy of the $Fe_{1-x}Cr_x$ σ phase for the corresponding site occupations c_i, where c_i is the concentration of Cr in site i ($i =$ A, B, C, D, E). Temperature effects are described by the second term, which takes the configurational and magnetic entropy into account. We neglect contributions from lattice vibrations, assuming that they do not play a decisive role in the distribution of the components between the sublattices. Since the relevant temperatures are relatively high, and there is no experimental evidence of being close to any kind of phase transition (ordering or magnetic), we also neglect short-range order effects in the configurational part of the problem.

In order to describe the free energy $F(c_i)$, we first expand the total energy $E_{\text{tot}}(c_i)$ near the equiatomic composition in terms of on-site effective interactions $V_i^{(1)}$: $E_{\text{tot}}(c_i) = \sum_{i=A,D} V_i^{(1)} c_i$, where $V_i^{(1)} = [\partial E_{\text{tot}}/\partial c_i - \partial E_{\text{tot}}/\partial c_E]|_{c_{\text{alloy}}=\text{const}}$. They are (at a fixed x) the relative effective chemical potentials, which describe the preference of Cr atoms to occupy site i relative to that of site E and were defined by the EMTO-CPA method. The configurational entropy (per unit cell) is $S_{\text{conf}} = k_B \sum_i n_i [c_i \ln c_i + (1 - c_i) \ln(1 - c_i)]$, where n_i is the number of atoms at site i.

The importance of magnetism in the Fe-Cr σ phase, even at the relevant high temperatures, has been recognized first by Korzhavyi et al.,[11] who considered a spin-polarized paramagnetic state of this phase as described by the disordered local moment (DLM) model.[22] It has been shown that the local magnetic moments do not disappear on the Fe atoms at these temperatures, but give an important contribution to the energetics of the σ phase. However, since the Fe-Cr σ phase is a weak itinerant magnet, another magnetic contribution should also appear at high temperatures, namely, thermal Stoner-like excitations leading to fluctuations of the magnitude of the local magnetic moments of Fe and Cr (longitudinal spin fluctuations). To calculate these high-temperature magnetic excitations by accurate first-principles schemes is extremely complicated and time consuming. Therefore we adopt a simple model,[23] which accounts for an additional magnetic entropy contribution to the paramagnetic state due to longitudinal spin fluctuations (LSFs). In particular, LSFs induce modified spin magnetic moments on Fe and Cr atoms and allow Cr magnetic moments, which do not vanish in contrast to the DLM state. The corresponding magnetic entropy is given by the following expression: $S_{\text{magn}} = -k_B \sum_i n_i [c_i \ln(1 + \mu_i^{\text{Cr}}) + (1 - c_i) \ln(1 + \mu_i^{\text{Fe}})]$, where the local magnetic moments are found by minimization of the corresponding magnetic free energy in the first-principles calculations at a given temperature.

In order to estimate contributions of the magnetic entropy and thermal expansion, we simulate different magnetic states (nonmagnetic, DLM with or without LSFs) and slightly increase the lattice parameters. From these investigations we conclude that the distribution of Fe and Cr atoms among the sublattices in the Fe-Cr σ phase can be described by several factors. The integer site occupation at 0 K (except for the C sublattice) is clearly defined by the total energy and described by the effective on-site interactions $V_i^{(1)}$. On the

TABLE I. Effective on-site interactions $V_i^{(1)}$ (mRy/cell) and local magnetic moments of Fe and Cr atom μ_i^{Fe} and μ_i^{Cr} on different sublattices for $x = 0.50$ at $T = 1000$ K (including LSFs).

Site i	$V_i^{(1)}$ (mRy/cell)	$\mu_i^{Fe}(\mu_B)$	$\mu_i^{Cr}(\mu_B)$
A	12.937	1.046	0.306
B	−0.656	1.773	0.481
C	0.656	1.626	0.380
D	10.969	1.236	0.350
E	0.0	1.478	0.358

other hand, the partial site occupation at finite T is mainly driven by the configurational entropy. The contribution of the magnetic entropy corrects in particular the Cr occupancies in the (A, D) and B sites due to a proper account of magnetism (Fe magnetic moments due to the DLM description and Cr magnetic moments due to additional LSFs). Volume expansion corrects slightly the Cr content in the (A, D) sites, because it increases the available space (see Fig. 1) around these sublattices and thus favors accumulating more of the bigger Cr atoms. The Cr redistribution in the (C, E) sites with respect to the other sites depends on the c/a ratio. With expansion of c/a the average volume of the C site increases, while it decreases for the E site. The resulting effective cluster interactions and the local magnetic moments of Fe and Cr at different sublattices are given in Table I for 1000 K, but are temperature dependent in the present work. A positive sign of the effective interaction means a stronger site preference for Fe in the particular site relative to that of the E site.

Now we can calculate the site occupancies c_i as a function of temperature and composition x using these effective (T-dependent) interaction parameters $V_i^{(1)}$. Our mean-field simulations yield the Cr site occupation as function of x at a fixed $T_{calc} = 950$ K shown in Fig. 2(a). The temperature dependence of the site occupation for $x = 0.5$ is shown in Fig. 2(b). The calculated site occupancies agree with the experimental data, which are available for alloy compositions $0.453 < x < 0.505$ at $T_{exp} = 873$, 923, and 973 K.[1,3] As can be seen from Fig. 2(a), the Cr site preference increases linearly with the Cr concentration in accordance with the experimental data, which are slightly scattered due to different alloy preparations. In fact the temperature dependence of the site occupation is relatively moderate [see Fig. 2(b)]. At very low T the Fe atoms occupy predominantly the icosahedral (A, D) sites, and the Cr atoms prefer the (B, E) sites, which have high coordination numbers, while the C site has a mixed occupation. Up to about 700 K the Cr content on the A and D sites remains very low, while the other three sites show a significant redistribution. The occupation of the C sublattice exhibits a rather unusual behavior. The Cr content on this site increases with T up to a maximum around 700 K and then decreases slowly. In the relevant temperature range, where the Fe-Cr sigma phase exists [indicated by vertical lines in Fig. 2(b)], the Cr occupation of the A and D sites start to increase significantly and thus decreases at the other sites. At extremely high T the configurational entropy would drive the system to a fairly homogeneous distribution of Fe and Cr on all five nonequivalent sites. It should be noted that the unusual
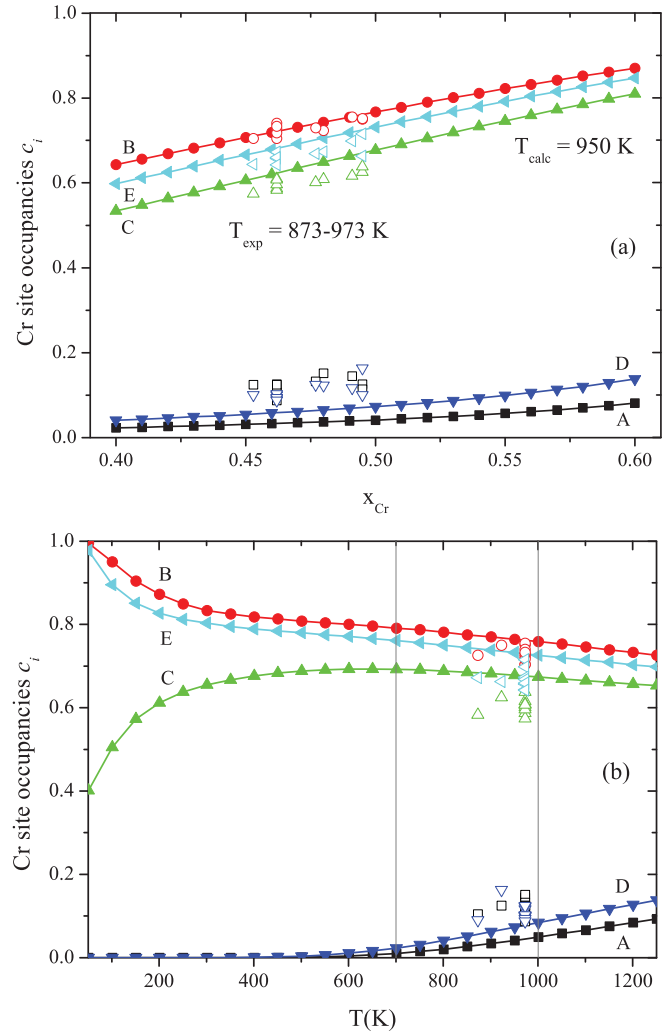

FIG. 2. (Color online) The Cr site occupancies of the (A, B, C, D, E) sublattices versus (a) the alloy composition at a fixed $T = 950$ K, (b) temperature for a fixed $x = 0.50$. Full symbols denote calculated results and empty symbols available experimental data.[1,3] Vertical lines indicate the temperature range of the σ phase formation.

temperature dependence of the C site occupation has already been found in the theoretical calculations by Sluiter *et al.*,[9] but their results are in strong disagreement with ours as well as with experiment,[1,3] as will be shown below.

In Table II we compare our results with the calculations by Sluiter *et al.*[9] and experimental data for an equiatomic composition. In particular, the previous calculations predict that the B site is occupied mainly by Fe atoms (for the alloy

TABLE II. The calculated and experimental Cr site occupancies of the (A, B, C, D, E) sites for the alloy composition $x = 0.50$.

Reference	T (K)	A	B	C	D	E
Ref. 9	500	0.0	0.080	0.850	0.0	0.985
Present work	500	0.001	0.833	0.682	0.004	0.772
Present work	950	0.041	0.767	0.677	0.073	0.731
Ref. 1 (exp.)	923	0.125	0.750	0.625	0.163	0.663
Ref. 3 (exp.)	973	0.113	0.751	0.638	0.100	0.715

composition $x = 0.50$ at $T = 500$ K), and only the E site has preferential Cr occupancies at low T, while we (and experiment) find that the B site is predominately occupied by Cr. The failure of their model can have several reasons: the use of the linear muffin-tin orbital method in the atomic sphere approximation, the neglect of magnetism, as well as the use of only full site occupations for their cluster expansion, including a range that is not relevant for the experimental situation. From a comparison with experiment it is clear that the present theoretical approach provides a more accurate description of the site preference in the Fe-Cr σ phase and is extremely efficient and lucid.

In the present work we propose a simple and powerful approach to calculate the site occupations in binary σ phases as a function of temperature and composition. It is based on the single-site mean-field description of the free energy, where the total energy is expanded in terms of on-site effective cluster interactions. The calculated site occupations in the Fe-Cr σ phase are in very good agreement with the experimental data. The present results are important for understanding which factors determine the atomic site distribution in the σ phase and for further first-principles investigations of the Fe-Cr phase diagram. The method can easily be generalized to multicomponent systems, which are of great importance for materials science.

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