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Site Occupation Reversal in the Fe-Cr $\sigma$ Phase

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The site occupation in the Fe-Cr $\sigma$ phase is computed as a function of temperature and composition. The calculations suggest that the preferential occupancy of a given type of site can be reversed by a change in temperature or composition. This phenomenon has not been reported previously but may in fact be visible in previously published experimental work.

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In recent years much progress has been made in the first-principles theory of alloy phase stability [1–3]. So far, these studies have been limited to superstructures of simple crystal structures, i.e., superstructures based on fcc, bcc, or hcp. The study of complex phases, where several inequivalent sites exist, is of interest both in its own right and for practical reasons. In many commercial alloys, such as Al-based and Fe-based alloys, age hardening is achieved by precipitation of phases with low crystalline symmetry, and in other alloys the mechanical properties can be very adversely affected by the formation of complex intermetallics. Outside the area of metallurgy there are widespread uses for materials whose properties critically depend on the low symmetry of its crystal structure, such as for transducers. Our theoretical interest in the phase stability of complex phases is motivated by the possibility of new physical phenomena, phenomena that cannot occur in phases based on simple, high-symmetry crystal structures. Here, we report such a new phenomenon found in the FeCr $\sigma$ phase [4]; see Fig. 1. The FeCr $\sigma$ phase was selected because it is an example of a topologically close packed (tcp) phase of which there are many representatives [5], and because, in contrast to many other tcp phases, much experimental work has been done on this material [6–9]. Its unit cell contains 30 atoms that pertain to five crystallographically inequivalent sites $A, B, C, D,$ and $E$, with the occupation numbers 2, 4, 8, 8, and 8, respectively [4,5]. Three types of coordination occur: the $A$ and $D$ sites are icosahedrally coordinated, the $B$ site has 15 nearest neighbors, and the $C$ and $E$ sites are 14-fold coordinated. The $A$ and $D$ sites are preferentially occupied by Fe atoms, and Cr is found mainly on the $B, C,$ and $E$ sites as has been determined from x-ray, synchrotron radiation anomalous scattering, neutron powder diffraction [6], and Mössbauer spectroscopy [8] experiments.

The five inequivalent sites make for 32 possible distributions of Fe and Cr atoms. It should be noted that these configurations are not superstructures of the $\sigma$ phase because they all have the same space group. The total energies of these configurations were computed within the local density approximation with the linear muffin tin orbital (LMTO) method in the atomic sphere approximation (ASA) [10]. The atomic sphere sizes were selected corresponding to the average nearest neighbor distances, given that the $\sigma$ phase is a tcp phase, the smallest and largest sphere radii differed by less than 8%. We found, however, that this size difference could not be ignored. Spin polarization was ignored because actual FeCr is paramagnetic at ambient temperatures [9]. Integrations in reciprocal space were carried out with the tetrahedron method using 52 $k$ points in the irreducible wedge. The von Barth–Hedin exchange correlation parametrization was used. The $a$ and $c$ parameters of the tetragonal $\sigma$ phase, and the cell internal coordinates were held fixed at the experimental values for all configurations [4].
Formation energies $E_{\text{form}}$ were computed from the total energies by subtracting the concentration weighted total energies of pure Fe and Cr with the $\sigma$ structure. Effective interatomic interactions $V_i$ were extracted from the formation energies with the Connolly-Williams method (CWM) [11]. In this method the effective interactions are determined by solving a linear system given by

$$E_{\text{form}}^\alpha = \sum_i \xi_i^\alpha V_i,$$

where $\alpha$ represents a particular ordered atomic configuration (supercell), and $\xi_i$ refers to a correlation function pertaining to cluster $i$. This system of equations here is both underdetermined and overdetermined at the same time. Therefore, a singular value decomposition (SVD) algorithm was used to extract values for 24 effective interactions. The sets of equations corresponding to thermodynamically stable structures were given more weight than the equations pertaining to unstable structures in the SVD procedure. The weighting in the SVD provides an alternative to the linear optimization technique suggested recently [12] for ensuring that the cluster expansion reproduces the proper sequence of the energy of structures. Details will be provided in a forthcoming publication. Here, the word “interactions” will refer to both multisite terms and single-site terms. The interactions reproduced the formation energies with a root mean square error of 0.1 mRy/atom. This error is well within the precision of the LDA calculations, and is much smaller than the smallest difference between the formation energies of any of the 32 configurations used in the CWM (see Fig. 2).

Further proof that these interactions accurately represent the LDA formation energies is provided by an additional set of 10 structures [13], which were not used in the CWM type fitting. Figure 2 shows that their formation energies, too, are accurately predicted within a fraction of a mRy/atom.

The interactions were used to compute the site occupancy, entropy, and Helmholtz free energy of the $\sigma$ phase as a function of temperature and composition within the tetrahedron approximation of the cluster variation method (CVM) [14]. The tetrahedron approximation, a natural choice given that the $\sigma$ phase is tetrahedrally close packed, has 17 tetrahedron maximal clusters and a total of 71 correlation functions.

Figure 2 also shows the site preference at zero temperature. Following the most stable configurations going from pure Fe towards pure Cr composition (right to left in the figure), it is seen that first the $E$ site takes Cr occupancy, followed sequentially by the $C$, $B$, and $A$ sites. Initially the various sites change occupancy from Fe to Cr one by one, but towards the Cr side the $A$ site reverses its occupancy with the $D$ site. This curious composition dependent behavior persists in a weakened form at finite temperatures, as is shown in Fig. 3.

In the context of the Ising-type Hamiltonian it results from competing single-site and multisite interactions. The single-site interactions pertaining to the $A$ and $D$ sites make for a stronger Fe preference of the $D$ site. However, the pair interactions can balance this preference because a $D$ site has a $D$ nearest neighbor, whereas an $A$ site has no $A$ nearest neighbors. If we start with the Cr on each site, and gradually exchange Fe for Cr, it follows that in case the Fe atoms are placed on the $A$ sites only favorable Fe-Cr pairs are formed, whereas if those Fe atoms were placed on the $D$ sites also unfavorable Fe-Fe pairs would result.

Once all the $A$ sites are filled, the $D$ sites must be filled. At that point, the pairwise disadvantage for the $D$ sites disappears because the $A$ site has four $D$ nearest neighbors, whereas the $D$ site has only one $A$ and one $D$ nearest neighbor. Clearly Fe occupation of the $D$ sites leads to fewer Fe-Fe type pairs and thus becomes energetically more favorable than the $A$ site occupation.

![FIG. 2. Energy of formation (in mRy/atom) of atomic configurations with the $\sigma$ structure: configurations used with the CWM, as computed with the LMTO-ASA (circles); as computed from the effective interactions (plusses); configurations not used for the determination of the effective interactions, as computed with the LMTO-ASA (squares); as computed from the effective interactions (crosses). The most stable configurations have been connected with a solid line, and the occupancies of the $A$, $B$, $C$, $D$, and $E$ sites have been indicated.](image)

![FIG. 3. Computed occupancy of the inequivalent sites in the $\sigma$ phase at 500 K as a function of composition; $A$ site (solid), $B$ site (dashed), $C$ site (chain-dotted), $D$ site (chain-dashed), and $E$ site (dotted).](image)
While the $D$ sites get filled with Fe, the $A$ sites are reclaimed by Cr. Only when all the $D$ sites have been filled can Fe occupancy of the $A$ sites increase again.

This description has been verified by computing the site occupation as a function of composition with all the multisite interactions set to zero. In that case, the simple site occupation sequence $D$, $A$, $B$, $C$, and $E$ is found with increasing Fe composition. For the $B$, $C$, and $E$ sites our computations do not show such a frustrated site occupation behavior.

In actual Fe-Cr alloys it is not possible to verify the site occupation over such a wide span of composition because the $\sigma$ phase has a narrow range of existence. However, around equiatomic composition extensive studies have been performed [6–9] and the dominant Fe occupation of the $A$ and $D$ sites is well established, as is the strong Cr preference of the $E$ site. Regarding the $B$ and $C$ sites, our calculations are not in complete agreement with experiment. In actual alloys the $B$ sites are found to have higher Cr occupancy than the $C$ sites, in contrast to our results. One possible cause for the discrepancy is inaccuracy in our calculations due to the simplifying assumptions we have made, among which we can mention: (1) it is assumed that the Fe and Cr species are sufficiently similar in size that the relaxation in the $\sigma$ phase is independent of the occupancy of the sites; (2) the ASA sphere sizes are selected according to the average nearest neighbor distances around each site, but selecting different sphere sizes will affect the calculated site preferences somewhat. On the experimental side too, there are complicating factors. For example, impurities can play a crucial role in the formation of the $\sigma$ phase [9].

These issues may not play a role in some of the other $\sigma$ phases. In Fe-V alloys, for example, the $\sigma$ phase occurs over a very wide range of compositions, so that it may actually be possible to observe a compositional site occupation reversal. In other physical systems, too, such as adsorption of a molecular species on specific surface sites, similar frustrations and reversals of surface concentrations with coverage may occur [15].

We have found that the reversal of site occupancy occurs not only as a function of composition, but can also occur as a function of temperature. In Fig. 4 the site occupation of an Fe$_{94}$Cr$_{06}$ alloy is shown. At high temperature the site occupation very slowly approaches the value corresponding to the random configuration. However, this limit is not reached at any finite temperature and, as no symmetry elements are removed in going from the chemically randomized configuration to a configuration with pure Fe and Cr occupancies, no order-disorder transformation takes place [16]. When the temperature is lowered, the fraction of Fe on the $A$, $D$, and $B$ sites increases and, concurrently, a strong Cr preferential occupation develops on the $E$ sites. The $C$ sites display a curious behavior in contrast to the other four sites. Descending from a high temperature, this site exhibits a Cr-type preferential occupation, but at some lower temperature this preference reverses itself, and below this “reversal temperature” the site increases its Fe occupancy until at very low temperature a certain limit value is reached.

The limit occupancy is determined purely by the composition. Figure 3 shows that in a $\sigma$ phase with 60% Fe the $C$ site has the most mixed occupancy, the other sites approaching almost pure Fe and Cr occupancy. In this alloy there are on average 12 Cr atoms per unit cell, eight of which are accommodated on the $E$ sites. The remaining four are placed on the $C$ sites, which makes for a Cr (Fe) occupancy of 50% (50%) at zero temperature. At the reversal temperature of about 1000 K the Fe occupancy is as low as 42%, whereas at very high temperatures it approaches the average Fe concentration, 60%. This apparent reversal of the site occupation is unique to complex phases. Again, it arises from the competition between single-site interactions and multisite interactions. When the calculations are performed with single-site interactions only, the site occupancy is monotonic with temperature, and no reversal occurs. The site occupation reversal is a rather robust feature. CVM computations show that it occurs over a wide range of composition and effective interaction parameter space. Hence, it is likely to occur in actual alloys.

The occupancy reversal phenomenon has not yet been reported in the literature in spite of a large body of experimental work. However, it may in fact already have been observed. In Table 4 of Ref. [6] it appears that the $B$, $C$, $D$, and $E$ sites all exhibit nonmonotonous site occupation as a function of temperature. It should be remarked that our calculations predict that site occupation reversal should be limited to 1 site only for a given composition.

In conclusion, we have shown that the site occupation in a complex phase can be computed from first principles. A new phenomenon is predicted where a particular crystallographic site initially becomes enriched in one elemental species but then at some given temperature or composition reverses itself and becomes enriched in another species. There is an indication that this phenomenon was measured already but went unnoticed.

![Graphical representation of Fe occupancy as a function of temperature.](image-url)
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[13] The 10 additional structures, in contrast to the earlier set of 32 structures, have lower symmetry than the sigma phase and hence are superstructures.
[16] An order-disorder transformation from sigma to some lower symmetry structure is possible. The 10 superstructures considered in this study did not break the convex hull of the ground states. However, there might be other superstructures that do break the convex hull.
FIG. 1. Orthographic projection of the σ unit cell (a) top view, (b) side view. Sites A through E have been marked with spheres of decreasing size.