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Magnetic cluster expansion simulations of FeCr alloys

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ABSTRACT

We present a new method for simulating magnetic alloys characterized by configurational disorder, the magnetic cluster expansion. Each atom in an alloy is assigned a discrete variable denoting the atomic species, and the (continuous) magnetic moment. The parameters of the model are determined by matching energies and magnetic moments of atoms found in trial simulations to DFT calculations. Monte Carlo simulations are then performed to investigate magnetic properties of pure iron, and magnetic *and* structural properties of FeCr alloys. We found that the Curie temperature of the ordered FeCr alloy with small concentration of Cr ($Fe_{15}Cr$) increases in comparison with pure Fe and the random mixture of Cr in iron (Fe-6.25% Cr). The method is also applied to the investigation of the correlation functions for the directions of magnetic moments at elevated temperatures.

1. Introduction

It is widely recognized that the central problem with the description of FeCr is the presence of two contributions to the energy of the alloy, where one is a function of the orientations of magnetic moments and the other (configurational) is a function of positions of atoms in the alloy, which are related to each other in a non-trivial way. The existing approaches, such as the cluster expansion (CE) [1,2] or the interatomic potentials-based approaches do not explicitly treat magnetic moments of atoms and hence are not able to distinguish between the two physically distinct contributions to the energy noted above. As a result, to describe a magnetic alloy, such as FeCr, and to fit the DFT data, one has to introduce CE with large (containing up to 5 atoms or more) clusters [1]. The absence of the treatment of magnetic moments in the conventional CE does not make it possible to apply the method to the investigation of magnetic phase transitions occurring in FeCr.

Recently, a model Ising system with antiferromagnetic and ferromagnetic species was applied to the investigation of the immiscibility gap and magnetic properties of FeCr [3]. Here we introduce a new more realistic method for treating the energy and magnetic properties of solid solutions: the magnetic cluster expansion (MCE). The expression for the energy of the system in MCE, in addition to the conventional discrete occupational variables $\sigma_i = \pm 1$ (where in the case of the binary FeCr alloy we take +1 for Fe, -1 for Cr), explicitly includes also the magnetic moments $\mathbf{M}_i$ formed the constituent atoms of the solid solution. These magnetic variables, unlike those used in the Ising (or Heisenberg) models, can take any continuous (vector) values. For pure iron, this allows restricting the range of interactions, in comparison with the conventional CE, to the nearest and the second nearest neighbours only, in good agreement with the DFT analysis of the effective Heisenberg model for ferromagnetic iron [4]. The values of the magnetic moments for each given atomic configuration are found by minimizing the total energy of the system. We present a procedure for the derivation of the MCE interaction parameters, obtained by fitting to the DFT enthalpies of formations and magnetic moments, found for a set of reference structures in binary FeCr system. We then apply the method to the investigation of the energy and the magnetic properties of pure iron and FeCr alloy.

2. Model

The Hamiltonian for the MCE model includes short-range (up to the second nearest neighbour) non-magnetic and the longer-range (up to the fifth nearest neighbour) magnetic interaction terms. This choice of the interaction cut-offs in the current study is made in order to keep the number of Hamiltonian parameters as small as possible. We found that while for pure Fe the first and the second nearest neighbour interactions are generally sufficient for describing the basic properties of the material, in the case of Cr and FeCr alloys one needs to take into account longer-range interactions. The need for introducing effective long-range interactions comes from the fact that low Cr systems have negative heat of formation which becomes positive above 10–12% Cr. In particular, the sign of the heat of formation, according to our DFT calculations, changes if chromium atoms enter the sixth nearest neighbours coordination shell (see below, Table 1). Thus, we introduce the fifth nearest neighbour magnetic interaction that acts only between Cr atoms, still truncating the non-magnetic interactions at short-range,

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Table 1
Comparison between DFT and MCE results for energies of several FeCr configurations.

Cr concentration	E_{DFT} (meV)	E_{MCE} (meV)
0.0625	−6.46	−5.17
0.125	22.21	8.23
0.1875	45.34	17.93
0.25	32.08	39.76
0.5 (layered structure)	38.39	51.63
0.5 (B2 structure)	177.15	155.62
0.75	35.78	42.18
0.875	36.11	44.34
0.9375	26.49	24.08

similarly to the case of pure iron. In the future, extending the range of non-magnetic Cr–Cr interactions beyond the second neighbour, or the magnetic Cr–Cr interactions beyond the fifth neighbour may be used in order to refine the current fit. The Hamiltonian of the magnetic cluster expansion model is:

$$\begin{aligned}E(\sigma_1,\sigma_2,\ldots,\sigma_N,\mathbf{M}_1,\mathbf{M}_2,\ldots,\mathbf{M}_N) &= NJ^{(0)} + J^{(1)}\sum_i \sigma_i + J^{(2)}\sum_{i,j}\sigma_i\sigma_j \\ &+ \sum_i\left(A^{(0)} + A^{(1)} + \sum_{j\neq i} A_{ij}^{(2)}\sigma_i\sigma_j\right)\mathbf{M}_i^2 \\ &+ \sum_i\left(B^{(0)} + B^{(1)} + \sum_{j\neq i} B_{ij}^{(2)}\sigma_i\sigma_j\right)\mathbf{M}_i^4 \\ &- \sum_{i\neq j}\left(J_{ij}^{(0)} + J_{ij}^{(1)}(\sigma_i+\sigma_j) + J_{ij}^{(2)}\sigma_i\sigma_j\right)\mathbf{M}_i\mathbf{M}_j. \qquad (1)\end{aligned}$$

Here, $J^{(n)}$ are the short-range non-magnetic interaction parameters, $A^{(n)}$ and $B^{(n)}$ are the on-site terms that determine the magnitude of the magnetic moment, and $J_{ij}^{(n)}$ are the magnetic interaction parameters. For any given atomic configuration defined by a set of discrete variables $\{\sigma_i, i = 1,\ldots,N\}$, values of the magnetic moments are obtained by minimizing the total energy of the system.

The interaction parameters of the Hamiltonian are found by fitting the energy *and* the magnetic moments of atoms to DFT calculations performed using a 4 × 4 × 4 bcc 128 atom cell. We used several structures with Cr content ranging from 6.25% to 93.75%, as well as pure Fe and Cr. We use the Vienna Ab initio Simulation Package (VASP), where the pseudo-potentials were generated within the projected augmented wave approach (PAW) from the VASP library [5]. The calculations were performed for the spin-polarized configurations using the generalized gradient approximations (GGA), and verified by comparison with the exchange-correlation functionals of Perdew and Wang, and of Perdew, Burke and Ernzerhof. The results of our DFT calculations used for fitting the MCE Hamiltonian are published and discussed in [6]. We preferred to use structures evenly distributed trough the whole concentration range rather than concentrate on low Cr concentration, because knowing Fe–Cr properties for all concentrations is important in order to model the phase diagram of the system. Also, for consistency we decided to use energies and magnetic moments computed within a single calculation. We would like to emphasize that at low Cr concentrations (0–10 at.%), our DFT and exchange Monte Carlo calculations [2,6] have showed consistently that the ordered $\mathrm{Fe_{15}Cr}$ structure (see below, Section 3) is the most stable one with lowest negative enthalpy of mixing. Similar results have been obtained recently by Erhart et al. [7] who also concluded that a stable intermetallic phase at 6.25 at.% Cr (although with a different structure) plays the dominant role in the phase stability between the Fe-rich and the Fe–Cr segregated (>10 at.% Cr) regions.

At finite temperatures, the behaviour of the system was investigated by the Monte Carlo method. Unlike in DFT, in the MCE the magnetic moments on atoms at elevated temperatures were treated as vectors adopting arbitrary non-collinear configurations. At each MC step, a random vector was added to a magnetic moment of a randomly chosen atom and this change was either accepted or rejected according to the Metropolis algorithm. Simulation box included 16 000 atoms (20 × 20 × 20 bcc unit cells). Each Monte Carlo run consisted of 1.28×10^9 attempts to change the magnetic moment of randomly chosen atoms in both the equilibration and accumulation stages (80 000 exchange attempts per atom).

3. Results and discussion

Comparison of results for DFT and the MCE energies for the structures used to fit the MCE parameters is given in Table 1. The agreement is very good for the lowest Cr concentration of 6.25%, where both DFT and the MCE give negative energy of mixing, agreeing with each other within 1 meV/atom range. Larger differences between the two calculations are observed at 12.5% and 18.75% Cr, where MCE results underestimate the energies found in DFT calculations. In our opinion, this disagreement results from the difficulty of taking into account the long-range Cr–Cr interactions, which contribute significantly to the energy in this concentration range. At higher chromium concentrations, the agreement improves again, with MCE predicting slightly higher energies in comparison with the DFT data. Note that at 50% Cr, MCE agrees with DFT in predicting the large energy difference between the low-energy layered and the high-energy B2 structures.

It is important to mention here the non-collinearity of some of the resulting magnetic structures. We found that in most cases the magnetic structures are collinear. In particular, the magnetic structures are collinear at both ends of the concentration range, i.e., for pure Fe and pure Cr. At the same time, non-collinear magnetic structures formed in the intermediate range of Cr concentrations, for example at 50% Cr (layered structure) and at 75% Cr. The question of whether there is a relation between the instability of collinear magnetism and the instability of the bcc lattice and the formation of the σ phase in the middle of the Cr concentration range should be investigated in the future.

Turning now to the results of Monte Carlo simulations, the magnetic moment of pure iron as function of temperature $\langle M\rangle$ is shown in Fig. 1(a), and the average length of the magnetic moment on Fe atom $\langle \mathbf{M}^2\rangle^{1/2}$ - in Fig. 1(b). Magnetic moment decreases with temperature, starting from $T = 0$, and the Curie point T_C is found at about 1100 K. This is only slightly higher than the experimentally observed Curie temperature of 1043 K. Note that the parameters of the model were determined only from comparison with DFT results, without fitting to the Curie point or to any other finite temperature data. The average square magnetic moment $\langle \mathbf{M}^2\rangle^{1/2}$ decreases with temperature approximately until T_C, and starts to increase slowly at higher temperatures. Several previous studies failed to predict a definite type of behaviour for $\langle \mathbf{M}^2\rangle^{1/2}$ vs. T. For example, our calculations agree well with the results by Hasegawa et al. [8] in that $\langle \mathbf{M}^2\rangle^{1/2}$ decreases with temperature below the Curie point, and increases above it. At the same time, Rosengaard and Johansson [9] found that the magnetic moment increases for all temperatures between 0 K and 1600 K, while the recent calculations by Ruban et al. [10] show that the $\langle \mathbf{M}^2\rangle^{1/2}$ decreases with temperature both below and above the T_C, albeit with different slopes. This disagreement can be explained by the strong dependence of the predicted behaviour on the choice of parameters of the MCE Hamiltonian. The discrepancy may be clarified and used in order to refine the parameters of the Hamiltonian, if the experimental data on the behaviour of the magnetic moment vs. temperature become available.

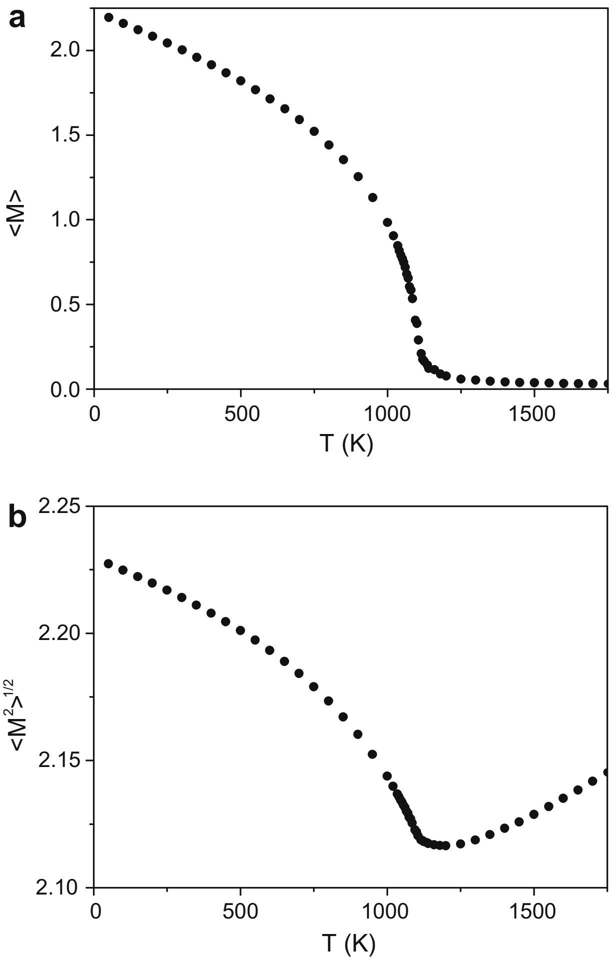

Fig. 1. Magnetic moment of pure iron as function of temperature (a), and the average length of the magnetic moment on Fe (b).

At low Cr concentrations (below 10–15%), the energy of mixing in FeCr system is negative [11]. This can result in the miscibility gap being moved towards higher Cr content and the possible formation of an ordered structure, as discussed in [1]. In that structure, denoted below as $Fe_{15}Cr$, chromium atoms are situated in the vertices of a large cell consisting of 8 ($2 \times 2 \times 2$) unit cells of the bcc structure. It is important to mention here that in the previous, non-magnetic, version of the Cluster Expansion, this structure has the same energy as similar structures that can be obtained by shifting some of Cr layers. As long as the Cr–Cr distance exceeds the radius of the fifth nearest neighbour coordination shell, the CE employed in [1] predicts the same energies for all the structures with the same Cr content. However, in the present magnetic CE, even if Cr–Cr distance is larger than the fifth nearest neighbour chosen here as interaction cutoff, chromium atoms still effectively interact with each other via the magnetic moments of intermediate atoms. The mathematical origin of the effective long-range interaction comes from the minimization procedure intrinsic to an MCE calculation, which determines the magnitude of magnetic moments on all the atoms in a simulation cell. As a result, the *degeneracy of $Fe_{15}Cr$ structures is removed* in MCE. We found that the structure described above does indeed have lower energy than the energy of similar ordered structures with the same Cr content.

In order to study the influence of configurational ordering on the ferromagnetism, we performed Monte Carlo simulations for both the ordered ($Fe_{15}Cr$) system and for a system with the same content of Cr, but for the randomly distributed, in the bcc lattice, chromium atoms (we call this system Fe-6.25% Cr). Of course, the choice of a particular configuration of the random structure influences the results, so the findings obtained for Fe-6.25% Cr differ between different disordered structures. The results for Fe-6.25% Cr can only be considered as indicative, and Monte Carlo study with possibility to exchange positions of Cr and Fe atoms in the course of simulation should be performed.

The magnetic moment $\langle M \rangle$ for both $Fe_{15}Cr$ and Fe-6.25% Cr in the temperature region around the Curie point is shown in Fig. 2, together with the magnetic moment of pure iron shown for comparison. For both FeCr structures, magnetic moment retains its value up to higher temperatures than for pure Fe. In $Fe_{15}Cr$ magnetic moment is more stable at higher temperatures than in random Fe-6.25% Cr alloy. The difference in the Curie temperatures between $Fe_{15}Cr$ and Fe-6.25% Cr is about 50 K.

The exact point of the magnetic phase transition can be identified by finding the maximum of the specific heat, which is calculated by investigating the fluctuation of the energy of the system [12]:

$$C = \frac{(\langle E^2 \rangle - \langle E \rangle^2)}{k_B T^2}. \tag{2}$$

The specific heat for the alloys investigated in this work is shown in Fig. 3. One can see that the maxima of the specific heat for the ordered $Fe_{15}Cr$ and random Fe-6.25% Cr systems are close to each other, and located at 1250–1300 K, with ordered structure having slightly higher transition temperature. Thus, we find a substantial increase of the Curie temperature compared to pure iron. In our opinion, the reason for the increase of the Curie point in both the ordered and the random structures is associated with the effect of Cr magnetic moments on surrounding Fe atoms. Both DFT and the MCE show antiferromagnetic alignment between chromium and iron atoms. For well separated Cr atoms, like in the ordered structure, this alignment helps preserving ferromagnetic structure in Fe up to higher temperatures than for the random structure, where some of the chromium atoms are closer to each other. So far, we are aware of only one published experimental study in which a slight increase of the Curie point was probably observed [13]. In our opinion, the investigation of the behaviour of the Curie temperature for small Cr content becomes now important, because our results show that the observed variation of the Curie temperature reflects the structure of the alloy and in particular the degree of local configurational order in the alloy.

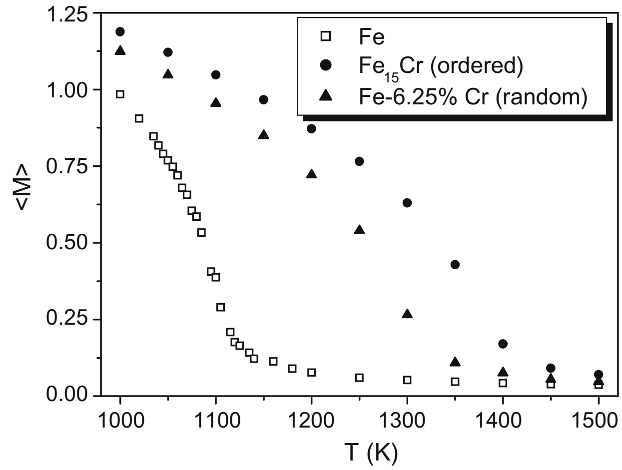

Fig. 2. Magnetic moment of pure iron, the ordered $Fe_{15}Cr$ alloy, and of random Fe-6.25% Cr structures as a function of temperature.

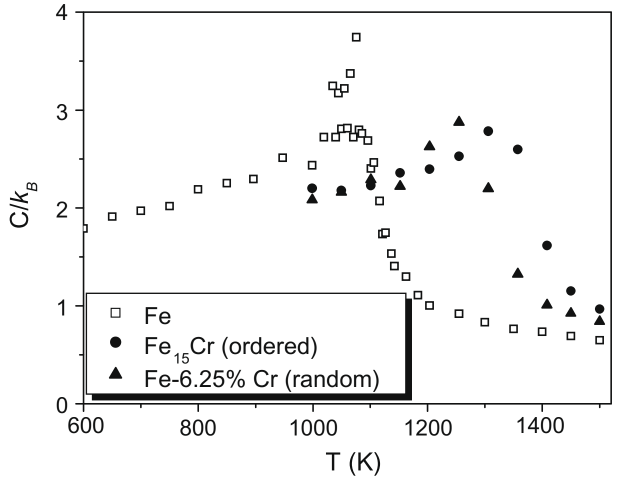

Fig. 3. The specific heat of pure iron, and the ordered and disordered FeCr alloys.

Finally, we studied the behaviour of correlation functions for the directions $\mathbf{s}_i$ of magnetic moments in pure iron, and in ordered $Fe_{15}Cr$ as functions of temperature, considering magnetic moments associated with various pairs of atoms belonging to various coordination shells. The calculated Fe–Fe first and second nearest neighbour correlation functions $\langle \mathbf{s}_i\mathbf{s}_j \rangle$ in Fe are shown in Fig. 4(a). For comparison, the macroscopically averaged normalized value of the magnetic moment $\frac{1}{N|\mathbf{M}|}|\sum_i \mathbf{M}_i|$, where the parameter $|\mathbf{M}|$ in the denominator of this equation is the zero temperature value of magnetic moment, is also shown. Both correlation functions are decreasing functions of temperature, but unlike the magnetic moments, they do not abruptly decrease to near zero value in the vicinity of the Curie temperature. We see that inter-site magnetic correlations persist above the Curie temperature in the paramagnetic region. For the $Fe_{15}Cr$ system, we also show the Fe–Cr correlation functions (Fig. 4(b)). As mentioned above, the negative correlations between Fe and Cr magnetic moments help preserving the ferromagnetic order in the Fe subsystem for higher temperatures than in the case of pure iron. It is interesting to note that in FeCr the nearest neighbour magnetic correlations are weaker than those characterizing the second nearest neighbours correlations for the entire range of temperatures studied here. This can be rationalized if we note that the decay of correlations as a function of interatomic distance is to some extent offset by the increase in the number of interatomic contacts. For example, while each iron atom in the ordered $Fe_{15}Cr$ structure can have no more than one Cr as its nearest neighbour, there are Fe atoms with two chromium atoms as the second nearest neighbours, and there are Fe atoms with four chromium atoms as the third nearest neighbours.

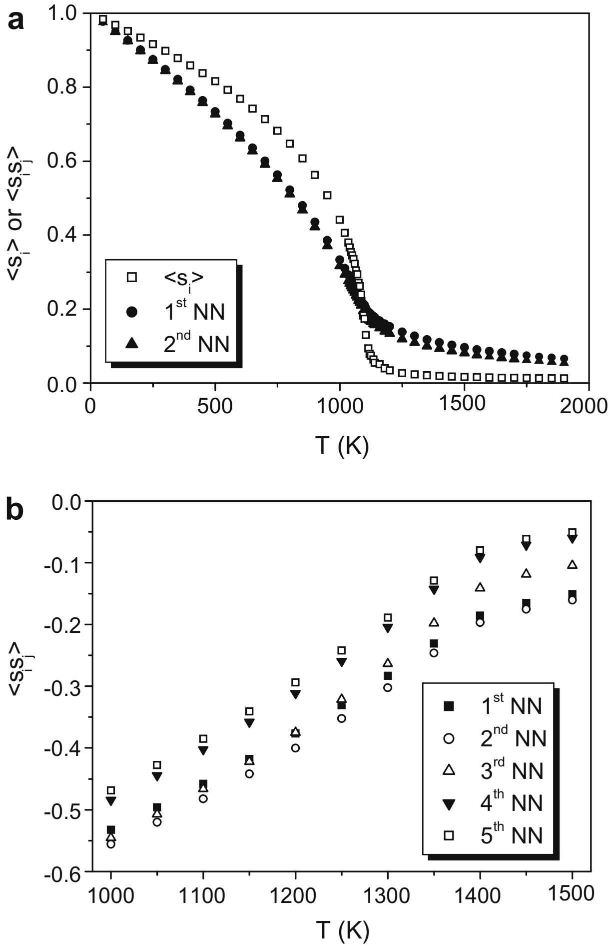

Fig. 4. Fe–Fe correlation functions for directions of magnetic moments in pure iron (a), and Fe–Cr correlation functions for directions of magnetic moments for ordered $Fe_{15}Cr$ (b) shown as functions of temperature. NN denotes the nearest neighbours.

In the future, we intend to extend this work and perform exchange MC simulations, similar to those performed earlier within the cluster expansion method [1,2]. This will allow studying more realistic FeCr configurations including those describing segregation in the immiscibility region of the phase diagram.

4. Conclusions

In this paper we introduced a new method for the study of magnetic systems with configurational disorder – the magnetic cluster expansion. This method allows taking into account the magnetic moments of atoms and studying magnetic properties of the system. The Hamiltonian parameters were found by fitting the MCE results to the DFT data. Monte Carlo simulations of pure iron show that the Fe–Fe correlations persist well above the Curie temperature. MC simulations of the FeCr alloy show that the Curie temperature increases for the ordered and disordered $Fe_{15}Cr$ structure in comparison with pure iron, an effect likely related to the negative magnetic correlations between Cr and Fe atoms.

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