Magnetic Cluster Expansion Model for High-Temperature Magnetic Properties of Iron and Iron-Chromium alloys

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Abstract

Magnetic Cluster Expansion model is developed for bcc Fe-Cr alloys, and applied to the investigation of magnetic properties of these alloys for a broad interval of concentrations ranging from pure Fe to pure Cr, and for a broad interval of temperatures extending well over 1000 K. Finite-temperature configurations simulated using the Magnetic Cluster Expansion Hamiltonian describe various magnetically ordered ferromagnetic and antiferromagnetic phases, partially magnetically ordered phases, and transitions between them and paramagnetic phases. We investigate the dependence of the Curie and Néel transition temperatures on the composition of the alloy. Analysis of the magnetic specific heat treated as a function of Cr concentration shows that in the low Cr concentration limit the Curie temperature increases as a function of Cr content. We find that for alloys containing high level of Cr the Curie temperature depends sensitively on the degree of Cr precipitation, varying by as much as 150K between random alloy configurations and configurations containing Cr precipitates.

Introduction

Developing computationally efficient predictive models for magnetic properties of Fe-Cr alloys, solid solutions, and nanostructures is necessary for many applications, including the development of radiation-resistant steels for fusion and fission power generation, magneto-electronic devices, and spintronics. It proves particularly challenging to formulate a model for both structural *and* magnetic phase transitions in iron-based alloys, for example the magnetism-driven α-γ bcc-fcc phase transformation occurring in pure iron at 912°C, and the associated high-temperature magnetic fluctuation effects. At present there is still no model describing, at a quantitative level of accuracy, the interplay between the structural and magnetic properties of Fe-Cr alloys for systems containing up to 10^6 atoms.

In this work we describe a new mathematical method for treating magnetic *and* structural degrees of freedom of bcc and fcc Fe-Cr alloys, the Magnetic Cluster Expansion (MCE) [1-3]. In this method, atomic magnetic moments are included in the Hamiltonian *via* the symmetry-breaking Landau formalism, as continuous vector variables, together with the conventional discrete lattice site Cluster Expansion (CE) occupation variables. In MCE, an alloy is characterized by its instantaneous atomic configuration and its instantaneous magnetic state. A Monte Carlo simulation algorithm based on an MCE Hamiltonian, parameterized using *ab initio* calculations, offers an efficient means for modelling structural and magnetic properties of Fe-Cr for a broad range of compositions and structures ranging from ferromagnetic Fe to anti-ferromagnetic Cr, in the temperature interval extending well above 1000 K, and spanning various magnetically ordered, partially ordered, and paramagnetic phases. Monte Carlo simulations performed using an

MCE Hamiltonian allow the evaluation of free energies for competing atomic and magnetic configurations, and modelling the high-temperature phases of iron and Fe-Cr alloys, including bcc-fcc phase transitions, and the γ-loop in the Fe-Cr temperature-composition phase diagram [2].

In this paper we investigate magnetic and thermodynamic properties of random Fe-Cr solutions, as well as magnetic properties of concentrated alloys containing Cr precipitates, with the emphasis on predicted features characterizing the magnetic properties of the alloys, which are accessible to direct experimental observations.

Magnetic Cluster Expansion Hamiltonian

The Magnetic Cluster Expansion approach developed in [1-3] extends and generalizes the classical Cluster Expansion treatment of alloys [4-5] to the case of magnetic alloys. While conventional CE only treats the configurational atomic disorder in alloys, an MCE Hamiltonian explicitly includes continuous magnetic vector variables and describes the magnetic degrees of freedom for the atoms forming the alloy. A simulation algorithm based on an MCE Hamiltonian allows investigating the interplay between structural and magnetic properties for large simulation cell sizes that are well beyond the reach of *ab initio* methods, and can be readily implemented on a million atom scale. The energy of an alloy configuration in MCE depends both on discrete CE site occupational variables σ_i and classical magnetic moments $\mathbf{M}_i$ of atoms. The atomic magnetic moments have variable direction *and* magnitude. The MCE Hamiltonian is a sum of conventional CE terms, the self-energy terms that in a self-consistent local-environment-dependent way determine the magnitude of magnetic moments of atoms, and Heisenberg-like inter-site

magnetic interaction terms. The magnetic self-energy part of the Hamiltonian is given by the sum of local atomic-configuration-dependent symmetry-breaking Landau terms, which are quadratic and quartic in $\mathbf{M}_i$. Effects of local atomic environment are included both in the direct Heisenberg magnetic interaction terms and in the Landau coefficients, thus allowing the magnitude and direction of the magnetic moment of each atom to self-consistently adjust to changes in its local environment. In the MCE Hamiltonian parameterized below we retain only two-atom clusters for both the non-magnetic and magnetic terms, namely:

$$E(\{\sigma_i\},\{\mathbf{M}_i\}) = NI^{(0)} + I^{(1)}\sum_i \sigma_i + \sum_{ij} I_{ij}^{(2)}\sigma_i\sigma_j + \sum_i \left(A^{(0)} + A^{(1)}\sigma_i + \sigma_i \sum_j A_{ij}^{(2)}\sigma_j \right)\mathbf{M}_i^2$$

$$+ \sum_i \left(B^{(0)} + B^{(1)}\sigma_i + \sigma_i \sum_j B_{ij}^{(2)}\sigma_j \right)\mathbf{M}_i^4 + \sum_{ij}\left(J_{ij}^{(0)} + J_{ij}^{(1)}\left(\sigma_i + \sigma_j\right) + J_{ij}^{(2)}\sigma_i\sigma_j \right)\mathbf{M}_i \cdot \mathbf{M}_j \qquad (1)$$

Here, $I^{(i)}$ are the non-magnetic CE coefficients, parameters $A^{(i)}$ and $B^{(i)}$ describe the local atom configuration dependence of the Landau coefficients for the magnetic self-energy terms, and $J^{(i)}$ are the inter-site magnetic exchange interaction coefficients. Summation over *i* and *j* involves atoms occupying nearest neighbor coordination shells. The functional form of equation (1) guarantees that the magnetic self-energy terms, and hence the directions and magnitudes of atomic magnetic moments $\mathbf{M}_i$ predicted by the model, depend on the local environment of each atom in the alloy. Numerical coefficients for the MCE Hamiltonian used in this study were derived by fitting the functional form (1) to zero-Kelvin spin-polarized density functional theory (DFT) calculations. These coefficients are given in Ref. [3].

Results and Discussion

Monte Carlo simulations described here were performed for a cell containing 16000 atoms (20×20×20 bcc unit cells). The equilibration and accumulation stages of simulations involved 40000 steps per atom. At each Monte Carlo step, an attempt was made to change the magnetic moment of a randomly chosen atom. The attempt was accepted or declined according to the rules of the Metropolis algorithm.

To illustrate the capabilities of MCE in describing magnetic materials for a broad range of temperatures, in Fig. 1 we show the distribution of magnetic moments of iron atoms *in magnetic moment space* for three different temperatures, starting from a very low temperature (25 K) and reaching the temperature of 1525K well above the Curie point. The distribution of moments in the magnetic moment space is visualised as follows: the vector of magnetic moment for each atom is shown as a dot (assuming that the beginning of the vector is at the origin shown in the figure by an open circle). The resulting distribution of dots represents the distribution of directions *and* magnitudes (i.e. lengths) of magnetic moments for all the atoms in the system. At the low temperature of 25 K, the moments of all the Fe atoms point in the same direction, corresponding to the ferromagnetic phase. The distribution of moments becomes partially ordered at T = 525 K, where the total magnetic moments of the system still remains nonzero. At T=1525 K, which is above the Curie temperature, the magnetic moments are fully disordered and the system is paramagnetic. For the case of pure Cr shown in Fig. 2, the MCE Hamiltonian predicts a partially ordered antiferromagnetic state at low temperature T = 50 K, whereas at T=500 K the system is paramagnetic. Antiferromagnetic ordering vanishes around 350

K [3], which agrees well with the experimentally observed Néel temperature of Cr, which is ~310 K [6].

For the case of bcc Fe-Cr alloys, we showed earlier that in the limit of small chromium concentration, the presence of randomly distributed Cr atoms gives rise to the increase of the magnetic moment per atom, and the increase of the Curie temperature [3]. This increase is clearly visible as a shift of the peak of magnetic specific heat shown in Fig. 3a. For a random Fe-3.125% Cr alloy, the singularity in the specific heat, corresponding to the Curie transition temperature, is shifted upwards by ~25-30 K.

Another issue, significant for applications of Fe-Cr alloys, is the dependence of their magnetic properties on the presence of Cr precipitates. For example, one may pose a question if the onset of Cr precipitation could be detected experimentally by monitoring the temperature dependent magnetic properties of the alloys. In order to investigate how the precipitation of Cr in Fe-Cr alloys influences the Curie temperature, we calculated the magnetic specific heat for two different atomic configurations of a Fe-25%Cr alloy: one corresponding to a random mixture of Cr in iron, and another where chromium atoms formed a large precipitate. The configuration containing a chromium cluster was produced using an Exchange Monte Carlo algorithm [7-8]. It consists of a single large Cr cluster of 3696 atoms, and 304 individual Cr atoms distributed in the iron matrix in the form of a solid solution. Fig. 3a shows that in the limit where Cr atoms are distributed at random, the predicted Curie temperature is fairly low, and the peak of the specific heat is at about 900K. At the same time, for the alloy containing a Cr cluster, the apparent Curie temperature, corresponding to the position of the peak of the specific heat, is much higher and equals ~1050 K, which is only slightly below its value corresponding to the case of

pure Fe (which in our simulations equals 1075 K). This difference is seen also in the temperature dependence of the total magnetic moment of the system shown in Fig. 3b for both Fe-25% Cr alloys. For the random mixture, the moment vanishes at temperatures that are lower by 150-200K than those characterizing the alloy with a Cr precipitate. Hence we find that magnetic properties of a concentrated alloy containing Cr atoms in the form of precipitates closely resemble those of almost pure iron. In other words, we show that the occurrence of Cr precipitation can be readily detected experimentally by monitoring how the magnetic properties of the material change as a function of alloy microstructure. For example, the effective Curie temperature of a concentrated Fe-Cr alloy is expected to increase significantly as a function of time as the initially random alloy solution decomposes, and Cr precipitates form.

Conclusions

In this paper we illustrate applications of Magnetic Cluster Expansion to modelling bcc Fe-Cr alloys for a broad range of concentrations, from pure Fe to pure Cr, and temperatures. We show that a single Hamiltonian can describe both ferromagnetic and antiferromagnetic phases of the alloy, as well as transitions into a paramagnetic state (Curie and Néel points) at elevated temperatures. A random Fe-Cr alloy containing 3.125% Cr has the Curie temperature higher than that of pure Fe, as illustrated by the shift of the peak in the magnetic specific heat curve simulated for this alloy. Simulations performed for concentrated alloys show that the Curie temperature of the alloys is highly sensitive to the degree of clustering of Cr atoms. This observation offers a possibility of

developing an experimental method for non-destructive monitoring of Cr precipitation in the alloys by means of investigating their temperature-dependent magnetic properties.

Acknowledgement

This work was funded by the RCUK Energy Programme under grant EP/G003955 and the European Communities under the contract of Association between EURATOM and CCFE. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

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Figure captions

Figure 1. Diagrams showing magnetic moments of iron atoms *in magnetic moment space* for temperatures below and above the Curie point: T = 25 K (a), T = 525 K (b), T = 1525 K (c). The diagrams show directions and magnitudes of magnetic moments for all the atoms in the simulation cell. Empty circles denote the origin of the magnetic moment space corresponding to $\mathbf{M} = 0$. Real space view of atoms themselves is not shown.

Figure 2. Magnetic moment diagrams showing moments of chromium atoms below and above the Néel point: T = 50 K (a), T = 500 K (b). Empty circles denote the origin of the spin space corresponding to $\mathbf{M} = 0$.

Figure 3a. Magnetic part of the specific heat plotted as a function of temperature for pure Fe (solid circles), a random Fe-3.125%Cr alloy (empty circles), a random mixture Fe-25%Cr alloy (empty triangles), and a Fe-25%Cr alloy containing a large Cr precipitate (solid triangles).

Figure3b. The total magnetic moment of a random Fe-25%Cr alloy (empty triangles), and a Fe-25%Cr alloy containing a large Cr precipitate (solid triangles).

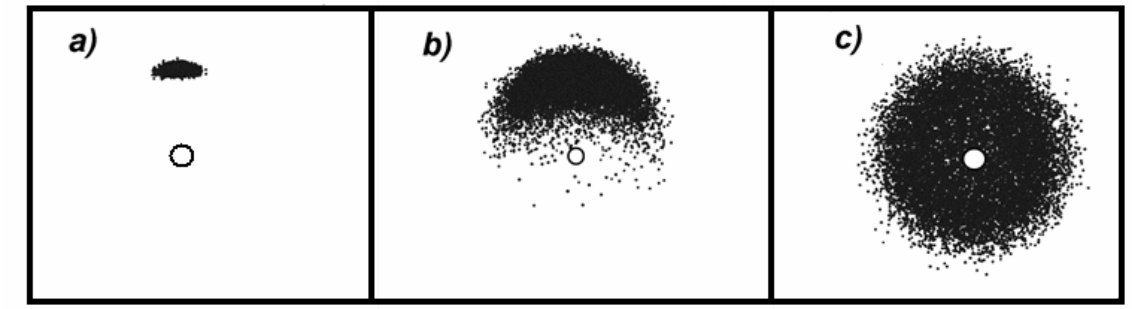

Figure 1.

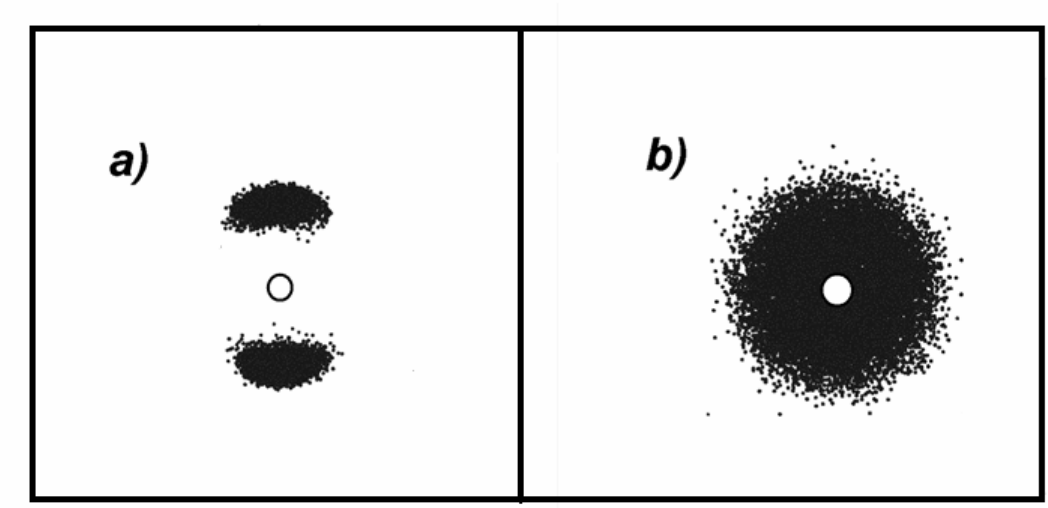

Figure 2.

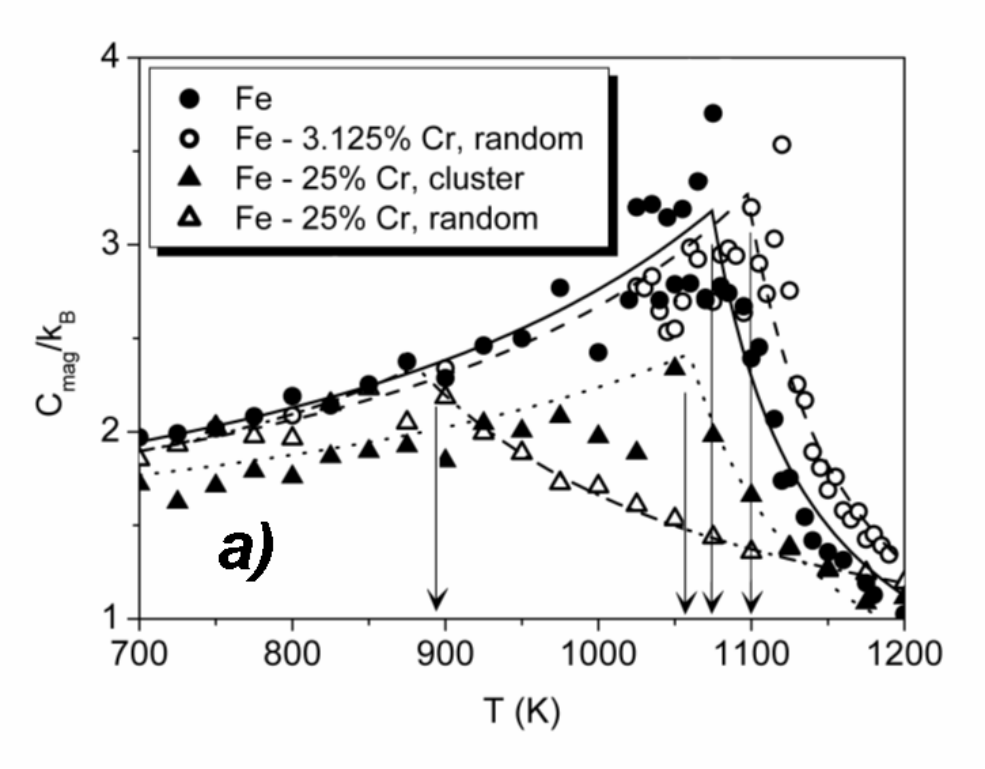

Figure 3a.

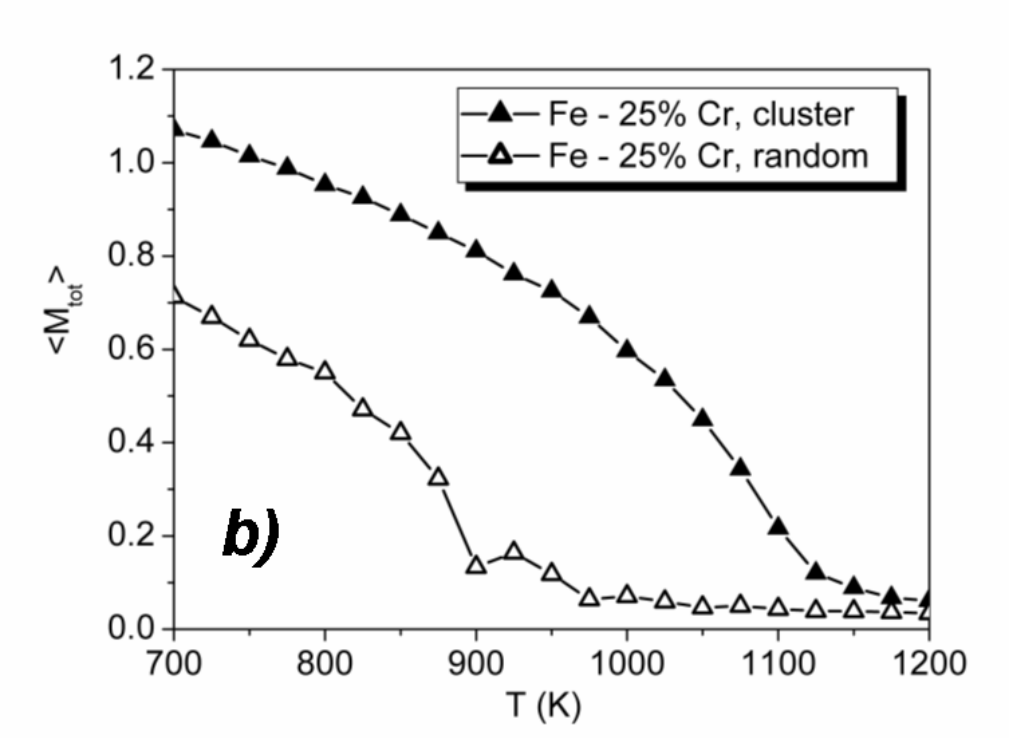

Figure 3b.