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Citation: Journal of Applied Physics 120, 043902 (2016); doi: 10.1063/1.4958981
View online: http://dx.doi.org/10.1063/1.4958981
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Magnetic cluster expansion model for random and ordered magnetic face-centered cubic Fe-Ni-Cr alloys

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(Received 19 February 2016; accepted 6 July 2016; published online 22 July 2016)

A Magnetic Cluster Expansion model for ternary face-centered cubic Fe-Ni-Cr alloys has been developed, using DFT data spanning binary and ternary alloy configurations. Using this Magnetic Cluster Expansion model Hamiltonian, we perform Monte Carlo simulations and explore magnetic structures of alloys over the entire range of compositions, considering both random and ordered alloy structures. In random alloys, the removal of magnetic collinearity constraint reduces the total magnetic moment but does not affect the predicted range of compositions where the alloys adopt low-temperature ferromagnetic configurations. During alloying of ordered fcc Fe-Ni compounds with Cr, chromium atoms tend to replace nickel rather than iron atoms. Replacement of Ni by Cr in ordered alloys with high iron content increases the Curie temperature of the alloys. This can be explained by strong antiferromagnetic Fe-Cr coupling, similar to that found in bcc Fe-Cr solutions, where the Curie temperature increase, predicted by simulations as a function of Cr concentration, is confirmed by experimental observations. In random alloys, both magnetization and the Curie temperature decrease abruptly with increasing chromium content, in agreement with experiment.

I. INTRODUCTION

Fe-Cr-Ni based austenitic stainless steels retain high mechanical strength at elevated temperatures, making them attractive structural materials for light water and fast breeder fission reactors.1 Because of its robustness, austenitic stainless steel 316L(N) was selected as a structural material for the International Thermonuclear Experimental Reactor (ITER).2 Fe-Ni alloys are good permanent magnets, with high Curie temperature, where ordered Fe-Ni alloy with L10 structure (tetrataenite) appears particularly promising.3,4 Alloying tetrataenite with Cr may help stabilize this alloy entropically and even increase its Curie temperature. Until now, very few comprehensive theoretical investigations of Fe-Cr-Ni ternary alloys were performed, owing to the difficulty of treating the interplay between structural order and magnetism in these alloys. Recently, we have developed an ab initio parameterized Heisenberg–Landau lattice Hamiltonian-based Magnetic Cluster Expansion (MCE) model for binary fcc Fe–Ni.5 To describe the high- and low-spin magnetic configurations of fcc Fe, terms up to the 8th order in atomic magnetic moment were included in the Landau expansion for the on-site terms in the Hamiltonian. Thermodynamic and magnetic properties of the alloys were explored, using configurational and magnetic Monte Carlo simulations, over a broad temperature range extending well over 1000 K. The predicted fcc-bcc coexistence curve; the phase stability of ordered Fe3Ni, FeNi, and FeNi3 intermetallic compounds; and the predicted temperatures of magnetic transitions simulated as functions of alloy compositions were found to agree well with experimental observations. In particular, simulations show that magnetic interactions stabilize fcc phases of binary Fe–Ni alloys. The parameters of an MCE model for Fe-Ni alloys5 were derived from DFT calculations performed for a large number of representative atomic configurations, as well as from DFT data on pure fcc Ni and Fe. The success of the model, together with the availability of DFT data accumulated in the context of a recent comprehensive ab initio investigation of Fe-Ni-Cr alloys,6 makes it possible to extend MCE to ternary fcc Fe-Ni-Cr alloys.

An initial parameterization of the Fe-Ni-Cr MCE Hamiltonian and initial simulations performed using this Hamiltonian are described in Ref. 6. Here, we describe an improved, more accurate, MCE model based on a larger DFT database of structures and magnetic configurations. Monte Carlo simulations, which use the MCE Hamiltonian, span both random and ordered alloy structures. Advantages of MCE include the possibility of simulating a broad range of alloy compositions and a large variety of chemical and magnetic configurations. Also, MCE makes it possible to study magnetic properties of both ferro- and antiferromagnetic alloys. This aspect of the model is particularly significant for fcc Fe-Ni-Cr alloys, since Ni at low temperature is ferromagnetic, whereas pure fcc Fe and Cr, according to ab initio calculations, have vanishingly small magnetic moments.

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[Published by AIP Publishing. http://dx.doi.org/10.1063/1.4958981]
II. MAGNETIC CLUSTER EXPANSION MODEL FOR A TERNARY ALLOY

MCE has been applied to a variety of binary magnetic alloys, including bcc and fcc Fe-Cr\(^7\) and fcc Fe-Ni.\(^5\) Combining a lattice MCE Hamiltonian model with experimental data on vibrational spectra, we explained the origin of bcc-fcc structural phase transitions in pure Fe and reproduced the occurrence of fcc $\gamma$-loop in the Fe-Cr phase diagram. In the case of Fe-Ni alloys, a phase diagram including both the disordered alloy configurations and ordered FeNi and FeNi\(_{\text{f}}\) compounds was derived in Ref. 5. A large DFT dataset of atomic structures and magnetic configurations accumulated within the framework of a recent investigation on Fe-Ni-Cr alloys\(^6\) makes it possible to extend the Magnetic Cluster Expansion treatment of fcc Fe-Ni system to ternary alloys. Within the MCE formalism,\(^3,9\) an alloy configuration is defined by its discrete chemical ($\sigma_i$) and continuous magnetic ($\mathbf{M}_i$) atomic degrees of freedom. To simplify applications of MCE to a ternary alloy, and to reduce the number of model parameters, the ternary alloy MCE Hamiltonian includes only pairwise interatomic interactions. The energy of an arbitrary structural and magnetic alloy configuration ($\{\sigma_i\}, \{\mathbf{M}_i\}$) in an MCE model has the form

\[
E(\{\sigma_i\}, \{\mathbf{M}_i\}) = \sum_{ij \in \text{NN}} I_{\sigma_i \sigma_j}^{(\text{NN})} + \sum_{ij \in \text{2NN}} I_{\sigma_i \sigma_j}^{(\text{2NN})} + \ldots
\]

\[
+ \sum_i A_{\sigma_i} \mathbf{M}_i^2 + \sum_i B_{\sigma_i} \mathbf{M}_i^4 + \sum_i C_{\sigma_i} \mathbf{M}_i^6
\]

\[
+ \sum_{ij \in \text{NN}} D_{\sigma_i \sigma_j} \mathbf{M}_i \cdot \mathbf{M}_j + \ldots
\]

(1)

where $\sigma_i, \sigma_j = \text{Fe, Cr, or Ni}$, $\mathbf{M}_i$ is the magnetic moment of atom $i$, and the non-magnetic and magnetic interaction parameters ($I_{ij}$ and $Y_{ij}$, respectively) for each set of neighbors in the lattice are $3 \times 3$ matrices defined in the discrete space of atomic species. Parameters $A$, $B$, $C$, and $D$ in (1) are the Landau coefficients for the quadratic, quartic, 6th- and 8th-order magnetic self-energy terms, respectively. To make the model consistent with the MCE Hamiltonian for Fe-Ni alloys, the 29 binary fcc Fe-Ni configurations used in fitting the MCE model for fcc Fe-Ni alloys to DFT data\(^3\) were also used in this study. The magnetic Fe-Fe and Ni-Ni interaction parameters are retained from the earlier Fe-Ni MCE parameterization,\(^5\) whereas the possibility of varying the Fe-Ni interaction parameters is included in the new fit. In addition to binary Fe-Ni configurations, the new parameterization involves DFT data for the 31 ordered ternary Fe-Cr-Ni structures spanning the entire alloy composition triangle, together with the DFT data on pure elements. We derived exchange coupling parameters for the non-collinear MCE Hamiltonian from collinear \textit{ab initio} calculations, following a procedure that proved successful in the context of applications of MCE to a broad range of magnetic metals and alloys.\(^10,11\) Investigations of Fe/Cr interfaces and clusters,\(^12,13\) as well as the MCE prediction of a non-collinear ground state of fcc iron,\(^5\) are in good agreement with experiment as well as with non-collinear \textit{ab initio} calculations, confirming the validity of this approach to parameterizing MCE. A list of ternary structures used for fitting is included in the supplementary material of Ref. 6. No Ni-Cr binary alloy configurations were used as input for the fitting procedure, and hence MCE predictions for alloys with low iron content are expected to be less accurate than those for iron-rich alloys. \textit{Ab initio} calculations were performed using the projector augmented wave method implemented in VASP package. Similarly to the binary Fe-Ni case, MCE model Hamiltonian interaction parameters were assumed to extend up to the fourth nearest neighbors in fcc lattice. In total, the model involves 24 non-magnetic ($I_{ij}$) and 24 magnetic ($Y_{ij}$) interaction parameters. At the initial stage of fitting, the on-site terms $A$, $B$ etc., were fitted using the energy versus magnetic moment curves computed for ferromagnetic pure Fe, Ni, and Cr. For chromium, only the quadratic and quartic terms in the Landau expansion for the energy versus magnetic moment were used, whereas for iron and nickel, the on-site Landau expansion was extended to the 8th order in magnetic moment. The dependence of the on-site energy terms on local atomic environment was neglected to reduce the number of model parameters. Subsequently, using the procedure described in Ref. 5, fitting of interaction terms $I$ and $Y$ was performed for both energies and magnetic moments on each atom in the simulation cell. DFT and MCE energies of mixing for the structures included in the fit are shown in Figure 1. The average error of the fit for energies is 18 meV/atom. A complete list of interatomic MCE interaction parameters for Fe-Cr-Ni alloys is given in Table I. The on-site terms are given in Table II.

To verify the accuracy of MCE fit for magnetic moments, we selected several special quasi-random structures (SQS) with Fe content close to 70 at. %, Cr content close to 18 at. %, and Ni content close to 12 at. %. The structures comprised 108 atoms each, corresponding to 27 ($3 \times 3 \times 3$) fcc unit cells. Magnetic moments of atoms in these structures were calculated in the collinear approximation using DFT. Next, MCE simulations were performed in two different ways, with and without imposing the collinearity constraint on the directions of magnetic moments. Table III compares results obtained using the two approaches. For

\[\text{FIG. 1. Comparison between DFT and MCE energies of mixing for alloy configurations used for fitting the MCE Hamiltonian. Data points for Fe-Ni and Fe-Cr-Ni alloys are shown using different colours.}\]
TABLE I. Non-magnetic interaction parameters $I_{ij}$ and magnetic Heisenberg interaction parameters $Y_{ij}$ (meV) derived using a fitting procedure described in Ref. 5.

<table>
<thead>
<tr>
<th></th>
<th>1st NN $I_{ij}$</th>
<th>2nd NN $I_{ij}$</th>
<th>3rd NN $I_{ij}$</th>
<th>4th NN $I_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Fe</td>
<td>1.856364</td>
<td>-0.793072</td>
<td>10.741989</td>
<td>-10.827175</td>
</tr>
<tr>
<td>Fe-Ni</td>
<td>-2.710858</td>
<td>-3.805516</td>
<td>-12.447877</td>
<td>-1.487362</td>
</tr>
<tr>
<td>Fe-Cr</td>
<td>-6.627640</td>
<td>5.778819</td>
<td>-4.571750</td>
<td>0.488416</td>
</tr>
<tr>
<td>Ni-Ni</td>
<td>1.132506</td>
<td>-13.153009</td>
<td>0.006062</td>
<td>7.227536</td>
</tr>
<tr>
<td>Ni-Cr</td>
<td>-0.419121</td>
<td>-5.501130</td>
<td>7.440212</td>
<td>0.692985</td>
</tr>
<tr>
<td>Cr-Cr</td>
<td>-3.933508</td>
<td>-0.741406</td>
<td>-4.550795</td>
<td>-0.01726</td>
</tr>
</tbody>
</table>

TABLE II. Values of on-site Landau expansion terms (in meV units) entering the MCE Hamiltonian (1).

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>-0.99016</td>
<td>30.37460</td>
<td>-3.47938</td>
</tr>
<tr>
<td>$B$</td>
<td>29.05331</td>
<td>455.69</td>
<td>5.226</td>
</tr>
<tr>
<td>$C$</td>
<td>-6.49401</td>
<td>-138.05</td>
<td>18.8</td>
</tr>
<tr>
<td>$D$</td>
<td>0.42817</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

MCE simulations performed in the collinear approximation, the two approaches agree well for the four out of five structures investigated here. Once the collinearity requirement was removed, atomic magnetic moments rotated away from their magnetization axis, and the total magnetic moment of the alloy decreased. Also, the moments of individual atomic species decreased. The non-collinear magnetic configurations were found to be more stable than collinear configurations, although the energy gain associated with the relaxation of collinear magnetic states into non-collinear states was relatively small, varying from 3 to 11 meV/atom, which is within the accuracy of the fit. It was therefore not possible to conclude without ambiguity whether the true ground state was collinear or non-collinear.

Most of the structures used in the parameterization of the MCE Hamiltonian (1) belonged to the Fe-rich area of the ternary phase diagram, and to Fe-Ni solid solutions. Hence, we expect that predictions derived from MCE simulations should be more accurate for alloys where Fe content exceeds 50 at.%, as well as for alloys where Fe and Ni are the dominant components. Almost all the Monte Carlo simulations were performed using 16384 atom simulation cells (containing $16 \times 16 \times 16$ fcc unit cells). Each Monte Carlo run included 80 000 attempts to change magnetic moment per atom at the equilibration stage, and the same number of Monte Carlo attempts at the subsequent accumulation stage. As an example of application of MCE to low-temperature magnetic properties of a ternary alloy, as well as another test of accuracy of the MCE fit for magnetic moments, we investigated the dependence of the total magnetic moment of $(\text{Fe}_{0.5}\text{Ni}_{0.5})_{1-x}\text{Cr}_x$ alloys on Cr content. An ordered Fe-Ni alloy with L1$_0$ structure was used as an initial configuration, and Cr content was then increased by replacing equal numbers of Fe and Ni atoms with Cr atoms in two ways: (i) by keeping the structures ordered and supercell small and (ii) by randomly choosing the atoms to be replaced in a large supercell. Figure 2 shows the total magnetic moments predicted by MCE for the alloys formed in this way. Simulations were performed with and without the collinearity constraint. As Cr content increases, magnetization rapidly decreases, resulting in an almost completely nonmagnetic alloy at $x_{\text{Cr}} = 0.5$, in agreement with ab initio DFT calculations. The experimental data for random $(\text{FeNi})_{1-x}\text{Cr}_x$ alloys ($x = 0, 0.2, 0.25$) by Men’shikov and Teplykh\textsuperscript{14} are also shown in Figure 2 and follow the same trend of rapid decrease with increasing chromium content. The decrease of the magnetization with increasing Cr content was found also by Rode et al.\textsuperscript{15} for $\text{Fe}_{0.6}(\text{Ni}_{1-x}\text{Cr}_x)_{0.4}$, where magnetization disappears completely for $x_{\text{Cr}} > 15$ at. %.

TABLE III. Magnetic moments per atom computed for several SQS structures using the Magnetic Cluster Expansion model (with and without the collinearity constraint applied) and DFT ($\mu_B$).

<table>
<thead>
<tr>
<th></th>
<th>MCE (non-collinear)</th>
<th>MCE (collinear)</th>
<th>DFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$M_{\text{total}}$</td>
<td>0.674</td>
<td>1.221</td>
</tr>
<tr>
<td></td>
<td>$M_{\text{Fe}}$</td>
<td>1.244</td>
<td>2.202</td>
</tr>
<tr>
<td></td>
<td>$M_{\text{Ni}}$</td>
<td>0.294</td>
<td>0.415</td>
</tr>
<tr>
<td></td>
<td>$M_{\text{Cr}}$</td>
<td>1.372</td>
<td>2.155</td>
</tr>
<tr>
<td>2</td>
<td>$M_{\text{total}}$</td>
<td>0.727</td>
<td>1.154</td>
</tr>
<tr>
<td></td>
<td>$M_{\text{Fe}}$</td>
<td>1.211</td>
<td>2.081</td>
</tr>
<tr>
<td></td>
<td>$M_{\text{Ni}}$</td>
<td>0.331</td>
<td>0.433</td>
</tr>
<tr>
<td></td>
<td>$M_{\text{Cr}}$</td>
<td>0.942</td>
<td>2.060</td>
</tr>
<tr>
<td>3</td>
<td>$M_{\text{total}}$</td>
<td>0.493</td>
<td>0.386</td>
</tr>
<tr>
<td></td>
<td>$M_{\text{Fe}}$</td>
<td>0.919</td>
<td>0.932</td>
</tr>
<tr>
<td></td>
<td>$M_{\text{Ni}}$</td>
<td>0.224</td>
<td>0.041</td>
</tr>
<tr>
<td></td>
<td>$M_{\text{Cr}}$</td>
<td>1.040</td>
<td>1.433</td>
</tr>
<tr>
<td>4</td>
<td>$M_{\text{total}}$</td>
<td>0.836</td>
<td>1.124</td>
</tr>
<tr>
<td></td>
<td>$M_{\text{Fe}}$</td>
<td>1.600</td>
<td>2.111</td>
</tr>
<tr>
<td></td>
<td>$M_{\text{Ni}}$</td>
<td>0.422</td>
<td>0.454</td>
</tr>
<tr>
<td></td>
<td>$M_{\text{Cr}}$</td>
<td>1.748</td>
<td>2.142</td>
</tr>
<tr>
<td>5</td>
<td>$M_{\text{total}}$</td>
<td>0.641</td>
<td>1.200</td>
</tr>
<tr>
<td></td>
<td>$M_{\text{Fe}}$</td>
<td>1.185</td>
<td>2.222</td>
</tr>
<tr>
<td></td>
<td>$M_{\text{Ni}}$</td>
<td>0.332</td>
<td>0.436</td>
</tr>
<tr>
<td></td>
<td>$M_{\text{Cr}}$</td>
<td>1.185</td>
<td>2.136</td>
</tr>
</tbody>
</table>

III. RANDOM Fe-Ni-Cr MIXTURES

Technologically important Fe-Ni-Cr austenitic steels\textsuperscript{1,2,16} are usually produced at high temperatures, 1000°C or higher.\textsuperscript{17} At reactor-relevant operating temperatures of over 0.3 $T_m$, where $T_m$ is the melting temperature, and at a high irradiation dose,\textsuperscript{18} the structure of alloys is...
close to a completely random solid mixture. For example, in almost all the experimentally investigated binary Fe-Cr, Fe-Ni, and ternary Fe-Ni-Cr alloys, the absolute magnitude of Warren-Cowley short-range order parameters does not exceed 0.1 for any of the three pairs of elements. This shows that the completely random ternary solid solution approximation provides a good representation of a real alloy.

The search for magnetic ground states spanned the entire range of alloy compositions. The concentration step for each element was 6.25 at. %. Three-stage magnetic quenching was performed, in the temperature interval from $T = 1000\, \text{K}$ to $T = 1\, \text{K}$ (first stage), then down to $10^{-3}\, \text{K}$ (second stage), and finally to $10^{-6}\, \text{K}$ (third stage). Pure fcc Fe and Cr were found to have vanishing total magnetic moments, in agreement with DFT calculations. Experimental studies of coherent Fe precipitates in fcc Cu matrix show that the magnetic ground state of fcc Fe is non-collinear, whereas for fcc Cr, only a non-magnetic ground state was found in DFT calculations. Our MCE-based simulations predict a non-collinear magnetic ground state for Fe, while for fcc Cr, collinear antiferromagnetic ground state was found, which is only 6 meV/atom more favorable energetically than a non-magnetic ground state. Pure fcc Ni is predicted to be collinear ferromagnetic, also in agreement with experiment. As a result, random alloy structures with non-vanishing total magnetic moment are predominantly found in the Ni-rich part of the alloy composition triangle. Figure 3 shows the total magnetic moment at $T = 0\, \text{K}$ (ground state) as a function of alloy composition found in simulations performed with and without the collinearity constraint. In both cases, the addition of up to 50 at. % of Fe or Cr to pure nickel increases the overall magnetic moment per atom, and alloy remains ferromagnetic. While for Fe-Ni alloys, this agrees well with ab initio data; in the Ni-Cr alloy system, a rapid decrease of the total magnetic moment was found both in DFT and in experimental studies, with the total moment vanishing above 20 at. % Cr concentration. This disagreement of MCE predictions with ab initio and experimental data likely results from the fact that no Ni-Cr binary structures were used in fitting the MCE model Hamiltonian and explains why MCE predictions for alloys with low iron content are less accurate than those for iron-rich compounds. At higher concentration of Fe or Cr, the total moment found in MCE simulations decreases rapidly, and alloys become antiferromagnetic once the concentration of Ni drops below 25 at. %. These results correspond well to the experimental study of Fe$_{80-x}$Ni$_x$Cr$_{20}$ for $x = 14, 17$, and 21. Alloys with small Ni content ($x = 14$ and 17) were found to be antiferromagnetic, while for $x = 21$, ferromagnetic correlation increases, leading to a spin-glass phase. In our simulations, systems with $x = 14$ and 17 have zero total magnetization, and $x = 21$ alloy is at the border between antiferromagnetic and ferromagnetic concentration ranges. Application of a collinearity constraint leads to the overall increase of the average magnetic moment. The predicted areas in the ternary concentration triangle where the total moment is non-zero largely coincide, irrespectively of whether the simulations are performed in the collinear or non-collinear approximation. This includes the Fe-Cr composition line. The occurrence of an interval of concentration where alloys have non-zero total magnetic moment stems from strong antiferromagnetic coupling between Fe and Cr. This gives rise to the

![FIG. 2. Total magnetic moment per atom in (Fe$_{0.5}$Ni$_{0.5}$)$_{1-x}$Cr$_x$ alloys computed assuming ordered and disordered alloy configurations, with (Coll) and without (Ncoll) the collinearity constraint applied. DFT results (black squares) are shown for comparison. Experimental data for completely disordered alloys are from Ref. 14.](https://example.com/figure2)

![FIG. 3. Magnetic moment in the ground state of a random Fe-Ni-Cr mixture ($\mu_B$) without (a) and with (b) collinearity constraint applied.](https://example.com/figure3)
non-compensation of the total moment once the iron content exceeds that of chromium. It is instructive to compare Figure 3 with Figure 9 of Ref. 6, which shows magnetic moments of various ordered Fe-Ni-Cr compounds. The pattern of variation of magnetic moment over the composition triangle is similar, but the magnitude of magnetic moment is higher for the ordered stable structures compared to random structures, reaching almost 2 \( \mu_B \) at the Fe-Ni composition line.

When analysing the energies of Fe-Ni-Cr alloys, it is important to distinguish between the enthalpy of mixing and the enthalpy of formation. The difference between the two entities stems from the fact that in pure Ni, fcc structure has the lowest energy, while in Fe and Cr, the bcc phases are energetically more stable. The enthalpy of mixing of fcc Fe-Ni-Cr is calculated with respect to the enthalpies of constituting elements, assuming that they all have fcc crystal structure. The enthalpy of formation, on the other hand, is calculated with respect to the lowest energy crystal structures of the constituting pure elements, which in the case of Fe and Cr are bcc. A comprehensive \textit{ab initio} study of various structures was performed in Ref. 6, and in the current work, we use the fcc-bcc energy differences derived there, namely, \( E_{\text{fcc}}(\text{Fe}) - E_{\text{bcc}}(\text{Fe}) = 82 \text{ meV/atom} \), \( E_{\text{fcc}}(\text{Cr}) - E_{\text{bcc}}(\text{Cr}) = 405 \text{ meV/atom} \), \( E_{\text{fcc}}(\text{Ni}) - E_{\text{bcc}}(\text{Ni}) = -96 \text{ meV/atom} \). Enthalpies of mixing and formation computed for fcc Fe-Ni-Cr alloys at \( T \rightarrow 0 \text{ K} \) are shown in Figure 4. The mixing enthalpy is negative over the entire range of alloy compositions, with the lowest absolute values corresponding to Ni-Cr binary mixtures (note that these values characterise random mixtures only). The enthalpy of formation is minimum near the pure Ni corner of the composition triangle.

At high temperatures, magnetic order vanishes for almost all the alloy compositions already at temperatures close to \( T = 500 \text{ K} \) (see Figure 5). Ferromagnetism is retained only in the Ni-rich corner of the composition triangle. This agrees with our previous simulations\(^5\) showing that magnetic order in pure Ni predicted by MCE Hamiltonian based simulations vanishes at 550–600 K (the experimental Curie temperature of nickel is 631 K (Ref. 32)). It is interesting to note that there is also another region where high-temperature magnetic order persists, namely, in random Fe-Cr mixtures with alloy compositions in the range from Fe\(_2\)Cr to Fe\(_3\)Cr (Figure 5). The reason for the occurrence of high-temperature magnetic order here (as well as large magnetic moment at low temperatures, see Figure 3) is related to the strong first nearest-neighbor antiferromagnetic interaction between Fe and Cr (Table 1). This produces an effect similar to the one responsible for the Curie temperature of bcc Fe-Cr alloys being maximum at 6 at. % Cr,\(^3\) with an important difference since in the case of fcc alloys, ferromagnetism emerges in a mixture of two \textit{antiferromagnetic} metals. The occurrence of ferromagnetic order was also noted in DFT studies.\(^6\)

An experimental study where Fe and Ni atoms were replaced with Cr atoms is described in Ref. 34. In that study, disordered fcc (FeNi)\(_{1-x}\)Cr\(_x\) alloys for \( x = 0, 5, 10, \) and 15 at. \% were investigated. A substantial decrease of the Curie temperature as a function of chromium content was discovered. The addition of 5 at. \% chromium results in the Curie temperature decreasing from under 800 K in FeNi to just above 600 K in (FeNi)\(_{0.95}\)Cr\(_{0.05}\). The authors of Ref. 34 also noted further substantial reduction of magnetic ordering temperatures for 10 and 15 at. \% Cr alloys. We have performed simulations on fully disordered systems with the same content. The predicted temperature dependence of the magnetic

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![FIG. 4. Enthalpy of mixing (a) and formation enthalpy (b) in the ground state of random Fe-Ni-Cr mixtures (meV/atom) simulated with no magnetic collinearity constraint applied.](image)

![FIG. 5. Magnetic moment of random Fe-Ni-Cr mixtures (\( \mu_B \)) at T = 500 K.](image)
moment is shown in Figure 6. In simulations performed without and with magnetic collinearity constraint, the Curie temperature decreases with increasing Cr content, in agreement with Ref. 34. The best agreement with experimental temperatures is achieved for the case where magnetic collinearity is imposed on the system. Another experimentally detected property of (FeNi)$_{1-x}$Cr$_x$ alloys that is in agreement with our simulations is the linear decrease of the saturation magnetization with chromium content.

IV. ORDERED Fe-Ni-Cr STRUCTURES

Magnetic properties of several ordered Fe-Ni and Fe-Ni-Cr compounds were investigated using MCE-based Monte Carlo simulations. The phase diagram of binary Fe-Ni alloys involves two, or possibly three, ordered stoichiometric compounds, namely, FeNi with L10 structure, and FeNi$_3$ and Fe$_3$Ni with L12 structure. Whereas FeNi$_3$ is a well-known compound and FeNi (tetrataenite) is found in meteorites, Fe$_3$Ni is an assumed compound since it is less stable, compared to random Fe-Ni alloys, than the two other compounds.

Having completed the investigation of binary Fe-Ni alloys, we now pose a question about how the addition of chromium influences their energy and magnetic properties. For example, it is desirable to clarify which of the two elements, Fe or Ni, is more readily replaced by chromium. To answer this question, we performed Monte Carlo simulations of all the three above stoichiometric compounds with chromium atoms replacing either Fe or Ni, or both Fe and Ni in equal proportion. The fcc lattice sites where Cr atoms replaced Fe or Ni atoms were chosen at random. Figures 7(a)–7(c) show the low-temperature enthalpy of the three compounds plotted as a function of Cr content. Cr concentration varied from 0 to 25 at. % for FeNi$_3$ and Fe$_3$Ni, and from 0 to 50 at. % for FeNi. In all the three cases, chromium atoms clearly prefer Ni sites for replacement, with the enthalpy difference being as high as 50 meV/atom. The bias associated with the preferential replacement of Ni by Cr, rather than Fe by Cr, can be explained by the strong Fe-Cr antiferromagnetic interaction in the first nearest neighbor configuration and by the larger magnetic moment of chromium compared to nickel (note that in Hamiltonian (1) the energy of magnetic interaction is a sum of products of interaction parameters and scalar products of magnetic moments themselves, and not the moment unit vectors).

It is reasonable to expect that strong magnetic Fe-Cr interaction might influence the Curie temperature of the alloy.
To investigate this, finite-temperature Monte Carlo simulations were performed for all the compounds, with 1024 Cr atoms (6.25 at. %) added to the simulation cell, again randomly replacing Fe, Ni, or both Fe and Ni (512 atoms of each species). Figure 8 shows the temperature dependence of the total magnetic moment. For all the three compounds, the addition of Cr results in reduction of the total magnetic moment. Cr also changes the Curie temperature of all the alloys, but it is in Fe$_3$Ni where this change is most dramatic. In the Fe$_3$Ni compound, the replacement of Ni by randomly placed Cr atoms increases the temperature of the magnetic transition from ~500 K to well over 700 K. The replacement of both Fe and Ni atoms with Cr also increases the $T_C$, whereas the replacement of Fe alone by Cr does not have such an effect (Figure 8(a)). In the L1$_0$ FeNi compound, the replacement of Ni by Cr results in the Curie temperature increase of less than 100 K, whereas in FeNi$_3$, all the possible substitutions of atoms with Cr result in the decrease of the $T_C$. We interpret this finding as related to the ferromagnetic first, third, and fourth nearest neighbor Ni-Cr interactions (see Table I), which are weaker than ferromagnetic Ni-Ni interactions. As a result, in Ni-rich alloys, the replacement of Ni with Cr results in the decrease of the $T_C$, as opposed to the case of Fe-rich alloys. We note that the effect of Curie temperature increase has already been found experimentally in bcc Fe-Cr alloys with small (below 10 at. %) chromium content, and it was explained by strong antiferromagnetic Fe-Cr interactions. In view of the observation that the change of magnetization and the Curie temperature depends on which species (Fe or Ni) is replaced by chromium atom, it may be worthwhile investigating the magnetic properties of ordered Fe-Ni systems with controlled Cr replacement of one or the other alloy components, or both of them.

We also explored magnetic properties of ternary ordered compound Fe$_2$NiCr. The crystal structure of Fe$_2$NiCr is similar to L1$_0$ FeNi, where one of the Ni atoms in a unit cell is replaced by Cr. This structure was extensively studied using ab initio methods in Ref. 6 and was found to have a lower value of the enthalpy of mixing than all the experimentally known intermetallic phases of fcc Fe-Ni-Cr alloys. An initial MCE investigation of this alloy was performed in Ref. 6. Because of its significance, we simulated its properties again using the improved MCE model developed here. Results of simulations of magnetic ground states of random and ordered Fe$_2$NiCr are summarized in Table IV, together with results of DFT calculations. Ordered Fe$_2$NiCr intermetallic was found to have an almost exactly collinear magnetic structure. While our simulations show that a random mixture with atomic content Fe$_{50}$Ni$_{25}$Cr$_{25}$ is almost completely antiferromagnetic (the average magnetic moment is predicted to be 0.025 $\mu_B$ per atom with no collinearity constraint applied, and 0.206 $\mu_B$ per atom if simulations are constrained to be collinear), an ordered structure with the same composition has large nonzero total magnetic moment, with Cr moments
The alloy remains magnetic until fairly high temperatures. Simulations performed using the current MCE Hamiltonian predict the Curie temperature close to 1050–1100 K, which is slightly higher than the value of ~1000 K found using an earlier parameterization. The effect of transition temperature increase compared to pure Ni and binary FeNi and FeNi3 alloys is similar to the one observed in fcc Fe-Ni, where the chemically ordered FeNi3 compound has higher Curie temperature than pure Ni. In relation to the ternary Fe2CrNi alloy, we again attribute the high stability of its magnetically ordered configuration to strong antiferromagnetic coupling between Fe and Cr atoms.

Structural imperfections in ordered Fe2NiCr intermetallic compound were studied by exchanging atoms of different species situated far apart. The resulting antisite defects have magnetic moments that strongly differ from those characterizing the structurally perfect compound. Data for the moments are summarized in Table V. Negative sign of the magnetic moment in the Table corresponds to antiparallel orientation of the moment in relation to the average moment in the compound. All the antisite defects studied have their magnetic moments aligned collinearly with respect to the neighboring atoms. Variation of the moment is largest for the Fe atom, for which strong decrease of the moment was found for the case of Fe ↔ Ni exchange and even change of sign for the Fe ↔ Cr exchange. Moments of Ni and Cr atoms change less in the antisite positions. For each pair of exchanging atoms, the total magnetic moment of the compound decreases.

We showed earlier that interplay between structural and magnetic order in Fe-Ni is strongly pronounced. Here, we focus primarily on the fully ordered and fully disordered Fe-Ni-Cr alloys, but in order to study the transition between these two limiting cases, we have also studied the magnetic behavior of partially ordered Fe50Ni25Cr25 alloys. To do this, several intermediate alloys of the same composition but with different degrees of disorder were generated, starting from the ordered Fe2CrNi alloy, we again attribute the high stability of its magnetically ordered configuration to strong antiferromagnetic coupling between Fe and Cr atoms.

![Fig. 9. Temperature dependence of the total magnetic moment of ordered Fe2CrNi alloy, and the moments of atoms forming the alloy.](image)

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ordered lattice positions, the low-temperature magnetic moment and its temperature behavior are almost the same as for the completely disordered Fe$_{50}$Ni$_{25}$Cr$_{25}$ alloy. This behavior illustrates a fundamental link between chemical and magnetic order in magnetic alloys.

Another example, illustrating a significant difference between magnetic properties of chemically random and partially ordered Fe-Ni-Cr alloys, is the case of Fe$_{50}$Ni$_{30}$Cr$_{20}$ alloys studied in Ref. 41. The authors found that the highest magnetization can be achieved using the alloy of about 45 emu/g, which corresponds to $\mu_B/\text{atom} \approx 0.46$. Similar Curie temperature of about 100 K was reported for Fe$_{50}$Ni$_{30}$Cr$_{20}$ in Ref. 43. These temperatures are much lower than the Curie temperatures calculated for any of the ordered alloys, see Figures 8 and 9. In order to investigate the origin of this difference, we performed a new set of simulations. The total magnetic moment as a function of temperature was calculated for two cases. In the first (partially ordered system), all the Fe atoms were in their crystallographic positions corresponding to the L1$_0$ structure, while Ni and Cr atoms were disordered. In the second case, a completely random distribution of atoms in Fe$_{50}$Ni$_{30}$Cr$_{20}$ was generated. Results of simulations are shown in Figure 11. In a completely randomly disordered Fe$_{50}$Ni$_{30}$Cr$_{20}$ alloy, magnetic moment at low temperature was found to be $\approx 0.47 \mu_B/\text{atom}$, close to the experimental results of Ref. 41, and much lower than for a partially ordered alloy, where we found magnetization of $1.1 \mu_B/\text{atom}$. Further, partially ordered and random alloys also have very different Curie temperatures. While in a partially ordered system, the Curie temperature is 1000 K; in a disordered alloy, magnetization vanishes at 150 K, which is close to experimentally found values. This shows that our simulations agree with experimental observations of magnetism in fully disordered Fe$_{50}$Ni$_{30}$Cr$_{20}$. Also, an alloy of very similar content Fe$_{40}$Ni$_{25}$Cr$_{25}$ was recently found to have $T_C$ of 125 K (Ref. 44) (note further decrease of the Curie temperature with increasing Cr content).

V. CONCLUSIONS

This paper describes a new Magnetic Cluster Expansion model and its application to a technologically relevant ternary magnetic Fe-Ni-Cr fcc alloy. Despite the fact that the MCE formalism involves several approximations, for example, the model neglects the environmental dependence of the Landau on-site terms, the low temperature predictions derived from the model agree well with DFT data. We are also able to explore high temperature magnetic properties of the alloys, by performing Monte Carlo simulations for both random and ordered alloy configurations. Strong antiferromagnetic Fe-Cr interaction is responsible for that during alloying with Cr, chromium atoms prefer replacing Ni atoms in all the ordered Fe-Ni compounds. Controlled replacement of Ni atoms by Cr also increases the Curie temperature of Fe-rich ordered alloys. The interplay between chemical and magnetic degrees of freedom is responsible for the very high Curie temperature of ordered Fe$_2$CrNi alloys, somewhat similar to the case of bcc Fe-Cr alloys where the Curie temperature is maximum at 6 at. % Cr. In random alloys, both magnetization and the Curie temperature decrease abruptly with increasing chromium content, in agreement with experiment. MCE predictions agree very well with the available experimental data and ab initio calculations performed in the collinear magnetic approximation. This shows that MCE
Hamiltonian-based Monte Carlo simulations can be successfully applied to ternary magnetic alloys exhibiting ferromagnetic and antiferromagnetic properties. Further improvement in the accuracy of MCE models for multi-component magnetic alloys can likely be achieved through the use of larger \textit{ab initio} DFT databases generated using a constrained non-collinear magnetic methodology.\textsuperscript{35,46}

ACKNOWLEDGMENTS

This work was part-funded by the EuroFusion Consortium and has received funding from Euratom research and training programme 2014–2018 under Grant Agreement No. 633053, and funding from the RCUK Energy Programme (Grant No. EP/S01045). The views and opinions expressed herein do not necessarily reflect those of the European Commission. To obtain further information on the data and models underlying this paper, please contact PublicationsManager@ccfe.ac.uk. This work was also part-funded by the United Kingdom Engineering and Physical Sciences Research Council via a programme grant EP/G050031. This work was also partly funded by the European Commission in the 7th Framework programme grant EP/I501045. The views and opinions expressed herein do not necessarily reflect those of the European Commission. To obtain further information on the data and models underlying this paper, please contact PublicationsManager@ccfe.ac.uk. This work was also partly funded by the EuroFusion Consortium and has received funding from Euratom research and training programme 2014–2018 under Grant Agreement No. 633053, and funding from the RCUK Energy Programme (Grant No. EP/S01045). The views and opinions expressed herein do not necessarily reflect those of the European Commission. To obtain further information on the data and models underlying this paper, please contact PublicationsManager@ccfe.ac.uk. This work was also partly funded by the EuroFusion Consortium and has received funding from Euratom research and training programme 2014–2018 under Grant Agreement No. 633053, and funding from the RCUK Energy Programme (Grant No. EP/S01045). The views and opinions expressed herein do not necessarily reflect those of the European Commission. To obtain further information on the data and models underlying this paper, please contact PublicationsManager@ccfe.ac.uk.