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**ABSTRACT.**

We present a combined experimental and computational study of high-temperature magnetic properties of Fe-Cr alloys with chromium content up to about 20 at.%. Magnetic Cluster Expansion method is applied to model the magnetic properties of random Fe-Cr alloys, and in particular the Curie transition temperature, as functions of alloy composition. We find that at low (3-6 at. %) Cr content the Curie temperature increases as a function of Cr concentration. It is maximum at approximately 6 at. % Cr and then decreases for higher Cr content. The same feature is found in thermo-magnetic measurements performed on model Fe-Cr alloys, where a 5 at.% Cr alloy has a higher Curie temperature than pure Fe. The Curie temperatures of 10 and 15 at.% Cr alloys are found to be lower than the Curie temperature of pure Fe.

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## Abstract

We present a combined experimental and computational study of high-temperature magnetic properties of Fe-Cr alloys with chromium content up to about 20 at.%. Magnetic Cluster Expansion method is applied to model the magnetic properties of random Fe-Cr alloys, and in particular the Curie transition temperature, as functions of alloy composition. We find that at low (3-6 at. %) Cr content the Curie temperature increases as a function of Cr concentration. It is maximum at approximately 6 at. % Cr and then decreases for higher Cr content. The same feature is found in thermo-magnetic measurements performed on model Fe-Cr alloys, where a 5 at.% Cr alloy has a higher Curie temperature than pure Fe. The Curie temperatures of 10 and 15 at.% Cr alloys are found to be lower than the Curie temperature of pure Fe.

## Introduction

Stainless ferritic-martensitic steels based on Fe-Cr alloys and containing several atomic percent of chromium are among candidate materials for the structural components of fusion power plants. Developing mathematical algorithms for modelling effects of irradiation on these steels, as well as on ferritic steels with high Cr content, is one of the objectives of the EU fusion materials programme [1]. Given that these steels are going to be used for constructing tritium breeding modules and components of the divertor in a magnetically confined fusion plasma device operating at high temperatures, the engineering design analysis inevitably requires the investigation of high-temperature magnetic properties of structural steels.

The high temperature magnetic behaviour of Fe-Cr alloys with low chromium content is dominated by the Curie transition between the ferromagnetic and paramagnetic phases. In pure iron, the temperature of this transition is 1043 K. With increasing chromium content, the Curie temperature generally decreases; however, there are indications that at low Cr concentration there is a region of Cr content where the transition temperature actually rises [2]. For example, we found a small increase of the Curie temperature for Fe-3.125 at.% Cr alloy in our earlier simulations [3]. Recently, the specific heat measurements by Xiong *et al.* showed that the Curie temperature of a 3.36 at. % Cr alloy is 11K higher than that of pure Fe [4]. The motivation for the present work is to perform a computational and experimental study of Fe-Cr alloys in the concentration range relevant to applications, and to find out whether at low (several at. %) chromium content the Curie temperature does indeed increase in comparison with pure Fe. In addition, we also performed magnetization measurements for several alloys as a function of Cr content. These experimental observations are compared with predictions derived from simulations.

## Magnetic Cluster Expansion

The Magnetic Cluster Expansion (MCE) model developed in [5-7] extends and generalizes the Cluster Expansion (CE) method [8-9] to the case of magnetic alloys. While CE only treats the configurational disorder effects in alloys, an MCE Hamiltonian explicitly includes magnetic vector

variables and hence describes both the configurational alloy disorder *and* magnetic degrees of freedom of the constituent atoms.

The energy of an alloy configuration in MCE depends both on the discrete CE occupational variables  $\sigma_i$  ( $\sigma_i=+1$  for Fe,  $\sigma_i=-1$  for Cr) and on the classical vector magnetic moments  $M_i$  of the constituent atoms. The magnetic moments of atoms have variable direction *and* magnitude. An MCE Hamiltonian contains the CE terms, the magnetic self-energy terms that determine the magnitude of magnetic moments, and the inter-site Heisenberg-like magnetic interaction terms. The self-energy terms in the Hamiltonian are given by the sums of local atomic-configuration-dependent Landau terms quadratic and quartic in  $M_i$ . In the current implementation, we retain only two-atom clusters in both the non-magnetic and magnetic terms:

$$\begin{aligned}
H(\{\sigma_i\}, \{M_i\}) = & NI^{(0)} + I^{(1)} \sum_i \sigma_i + \sum_{ij} I_{ij}^{(2)} \sigma_i \sigma_j + \sum_i \left( A^{(0)} + A^1 \sigma_i + \sigma_i \sum_j A_{ij}^{(2)} \sigma_j \right) M_i^2 \\
& + \sum_i \left( B^{(0)} + B^{(1)} \sigma_i + \sigma_i \sum_j B_{ij}^{(2)} \sigma_j \right) M_i^4 + \sum_{ij} \left( J_{ij}^{(0)} + J_{ij}^{(1)} (\sigma_i + \sigma_j) + J_{ij}^{(2)} \sigma_i \sigma_j \right) M_i \cdot M_j
\end{aligned} \tag{1}$$

In this Hamiltonian,  $I^{(i)}$  are the non-magnetic CE coefficients, parameters  $A^{(i)}$  and  $B^{(i)}$  enter the configuration-dependent 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  $M_i$  predicted by the model, depend on the local environment of each atom in the alloy. The interaction parameters of the Hamiltonian were found by fitting the energy and the magnetic moments of atoms to density functional theory calculations performed using a  $4 \times 4 \times 4$  bcc 128 atom cell. Several structures with Cr content ranging from 6.25% to 93.75%, as well as pure Fe and Cr, were used. To perform DFT calculations we used the Vienna Ab initio Simulation Package (VASP), where the pseudo-potentials were generated within the projected augmented wave approach from the VASP library [10]. Calculations were performed for spin-polarized configurations in the generalized gradient approximation, and verified by comparison with the exchange-correlation functionals by Perdew and Wang, and by Perdew, Burke and Ernzerhof. Parameters of the MCE Hamiltonian (1) derived from DFT calculations and used in this study are given in Refs. [6-7]. For Fe-Fe interactions, interactions up to the second nearest neighbour were used. This agrees with results by other authors that show that longer-range interactions in iron are much weaker (see, e.g., Table 1 in [11]) than in Cr or Fe-Cr alloys. For Fe-Cr and Cr-Cr interactions, exchange parameters

up to the fourth nearest neighbour (Fe-Cr) and up to the fifth nearest neighbour for Cr-Cr were taken into account.

Monte Carlo simulations reported in this work were performed using a 16000 atom cell (20×20×20 bcc unit cells). The equilibration and accumulation stages of simulations involved 40000 steps per atom each. At each Monte Carlo step, an attempt is made to vary the magnetic moment of a randomly chosen atom. The attempt is accepted or declined according to the Metropolis criteria.

The morphology of distribution of Cr atoms in the iron matrix at low temperatures strongly depends on the alloy composition. It is now well known [12] that below ~10 at. %, chromium atoms prefer to stay apart, whereas above this concentration, chromium clustering occurs. However, at high temperatures studied in this paper, Fe-Cr alloys are above the solubility gap (the top of the solubility gap, the consolute temperature, is about 900 K). This makes it possible to use random distribution of Cr atoms in the configurations explored in simulations. The temperature of the Curie transition is identified with the peak in the magnetic specific heat.

## Experimental

Measurements of magnetisation versus magnetic field were carried out at room temperature using a Vibrating Sample Magnetometer (VSM). The maximum applied field for the magnetic loops was 2 T and a Hall sensor was used to monitor the magnetic field values. The calibration of the VSM was performed using the Standard Reference Materials SRM 762 from the National Institute of Standards & Technology, USA. From the magnetic hysteresis loops the magnetisation measurements were scaled with the scaling factor obtained from the SRM magnetization measurements. In order to obtain the saturation magnetisation,  $M_{sat}$ , we assume that the magnetisation near saturation can be expressed as

$$M = M_{sat} - A/H^2 \quad (2)$$

Thermomagnetic analysis (TMA) was carried out at a Diamond Perkin-Elmer instrument in order to accurately determine the Curie temperature. The TMA measurements were carried out for different cooling/heating rates and the optimum rate, for which the heating and cooling results were the same within the interval of less than 0.1%, was determined as 5 K/min (Fig. 1a). The minimum of the first derivative of the magnetization curve (Fig. 1a) was used for the determination of the Curie temperature (Fig.1b).

Fe-Cr samples used for magnetic measurements were cut from rods of model Fe-Cr alloys supplied by European Fusion Development Agreement (EFDA), with Cr content given in Table 1. The samples were heat treated at various temperatures (see Table 1) for one hour under high purity argon atmosphere, followed by cooling in air.

## Comparison of Experimental Results and Simulations

Experimental observations and MCE simulations of the Curie temperature for iron-chromium alloys and pure iron treated as functions of Cr concentration are shown in Fig. 2. The error bars on the experimental points are hardly visible since they are comparable with the size of the points themselves. The Curie transition between the ferromagnetic and paramagnetic states of pure Fe, according to MCE simulations, occurs near 1075 K, which is approximately 30 K higher than the transition temperature observed experimentally. At the same time, both the calculated and experimental curves exhibit the same trend – the Curie temperature increases for small Cr concentrations, and decreases once the concentration of Cr in the alloy exceeds about 6 at. % Cr. The calculated Curie temperatures are systematically 35-45 K higher than the experimentally observed Curie temperatures, and if this constant difference is subtracted from the temperatures found in simulations the curves agree very well. The difference between the calculated and observed Curie temperatures remains almost the same in the entire range of concentrations studied, indicating the occurrence of a small systematic error likely related to the choice of parameterization of the MCE Hamiltonian for pure iron.

The overall trend exhibited by the Curie temperature vs. Cr concentration, with  $T_C$  increasing for small ( $\leq 5-6$  at. % Cr) and decreasing for higher Cr content, is well described by our simulations. This makes it possible to use the data on magnetic coupling obtained when fitting the MCE parameters, to explain the non-monotonic behaviour of the Curie temperature treated as a function of alloy composition. Electronic density of states of Fe-Cr alloys within an interval of small Cr concentrations was investigated by Nguyen-Manh *et al.* [13]. It was shown that the density of states in the minority channel has a minimum for 6.25 at.% Cr composition, resulting in the negative enthalpy of mixing for antiferromagnetic Fe-Cr coupling at low chromium concentrations. We note that a similar low density of states in the minority channel was observed for Fe- and Cr-containing Heusler alloys, which exhibit rich magnetic structure [14,15]. As a result, at small Cr concentrations

the chromium atoms, being antiferromagnetically coupled with their nearest-neighbor Fe atoms [6,16], strengthen *ferromagnetic* ordering of moments in the *iron* subsystem of the alloy. We note that this is only possible if the Fe-Cr magnetic interactions are stronger than Fe-Fe interactions. Only in this case a chromium atom replacing an iron atom in an alloy lowers the total energy and favours the stronger overall magnetic ordering of moments. In our set of MCE parameters [6], the nearest-neighbour and the next-nearest-neighbour Fe-Cr Heisenberg interaction parameters are indeed larger than the corresponding Fe-Fe exchange interactions. As a result, the overall energy of a Fe-Cr alloy, with chromium atom aligned antiferromagnetically with respect to the Fe ferromagnetically ordered sublattice, is lower than the magnetic energy of Fe-Fe interactions, despite the fact that the magnetic moment of Cr is smaller than that of Fe. As Cr concentration increases, Cr atoms more and more often find themselves to be in the nearest and next-nearest neighbour environment of each other. Since Cr-Cr MCE interactions are antiferromagnetic for all the distances [6], in the case of pure Fe environment, where the magnetic moments of chromium atoms are aligned antiferromagnetically to the Fe matrix - and thus ferromagnetically to each other - we find that at relatively large Cr concentrations the total magnetic energy of a ferromagnetic state increases, giving rise to lower  $T_C$ . If we denote the chromium content by  $x$ , the reduction of the energy associated with Fe-Cr interaction is proportional to  $x$ , whereas the increase of the energy due to Cr-Cr interactions is proportional to  $x^2$  (because the probability of finding two chromium atoms in the close proximity to each other is proportional to  $x^2$  for small  $x$ ), resulting in a parabolic energy dependence of the Curie temperature on Cr concentration, with a maximum at relatively low value of Cr concentration, in agreement with experimental observations. A similar behaviour, as a function of Co content, was found in first principles rigid-band calculations of Fe-Co alloys [17]. The authors of Ref. [17] found that the Fermi energy  $E_F$  of iron is located at an ascending point of  $T_C(E_F)$  curve, before the maximum, whereas for Co,  $T_C(E_F)$  is already descending. As a result, an ordered FeCo structure was found to have a higher Curie temperature than pure bcc Fe and Co. For bcc Cr, our previous spin-polarized calculations show that the density of states is rather low for both up and down spins near the Fermi energy  $E_F$  ([18], Fig. 3), explaining the fact that the effect in Fe-Cr is less pronounced, both in simulations and experiment.

Comparison of the theoretically calculated and experimentally determined room temperature magnetization per atom as a function of Cr content is given in Fig. 3. Results of MCE simulations are shown for both experimental (room) temperature and for 0 K. Both in experiment and in simulations magnetization decreases almost linearly with Cr concentration. In absolute terms the experimental data are closer to the low-temperature data, which can be explained by the fact that in MCE the Heisenberg-type Hamiltonian is treated classically. It has long been known (see e.g. [19]),

that the classical treatment of the Heisenberg model predicts linear variation of magnetization as a function of temperature at low temperatures. At the same time, the low temperature behaviour predicted by the quantum Heisenberg model is better described by a higher order power law. The summary of experimental data given by Köbler [20] suggests a  $T^2$  – type temperature variation for the spontaneous magnetization. Due to the difference between the classical and quantum treatment of magnetism, the variation of the average atomic magnetic moment predicted by MCE for zero and room temperatures follows a curve with the slope somewhat higher than that characterizing experimental observations, as shown in Fig. 3.

## Conclusions

We have carried out a combined theoretical and experimental investigation of magnetic properties of Fe-Cr solid solutions in the region of small Cr concentration. Both experimental and computational results show that in the limit of small chromium content (up to ~6 at. %), the Curie temperature of the alloy is slightly higher than that of pure iron. Above that concentration, the Curie temperature decreases as a function of Cr content. The reason for such an unusual behaviour of the transition temperature is the strengthening of magnetic coupling in the iron subsystem in the limit of small Cr concentration due to antiferromagnetic Fe-Cr coupling, whereas at higher Cr content the increasing contribution of Cr-Cr interactions to the total magnetic energy decreases the strength of ferromagnetic ordering in the alloy. Simulations based on Magnetic Cluster Expansion Hamiltonian predict the reduction of the average atomic magnetic moment as a function of Cr content, in agreement with experimental observations.

It is worth noting that in a real alloy, the presence of vacancies and (under irradiation) self-interstitial atom defects influence Fe-Cr interactions and the observed magnetic properties. While a full treatment of defects requires their inclusion into the MCE framework, some insights can be obtained from the DFT investigations of magnetic properties of Cr atoms in Fe matrix in the presence of vacancies and self-interstitial atom defects. For example, an *ab initio* study by Olsson *et al.* [21] shows that near both vacancies and self-interstitials, magnetic moment of chromium atom is substantially reduced in comparison with the case of perfect bcc lattice. This could result in the suppression of Fe-Cr magnetic interactions and the resulting smaller effect of chromium atoms on iron matrix around radiation defects.

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Table 1. Composition and heat treatment temperatures for various Fe-Cr alloys

Sample Code	Cr content (at. %)	Heat treatment temperature (°C)
Fe pure	0	700
Fe-5Cr	5.78	750
Fe-10Cr	10.77	800
Fe-14Cr	15.14	850

## Figure captions

Figure 1. Magnetisation of pure Fe versus temperature during cooling at a rate of 5 K/min (a) and its first derivative versus temperature during cooling and heating (b).

Figure 2. Curie temperatures, measured and computed for several iron-chromium alloys and pure iron, experiment and MCE simulations.

Figure 3. The average atomic magnetic moment shown as a function of Cr concentration.