Aluminum cluster size effects in the phase diagram of disordered Fe-Al alloys

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Abstract. A spin-1/2 Ising model, with nearest-neighbor exchange and next-nearest-neighbor superexchange interactions, is proposed to describe the phase diagram of disordered Fe\textsubscript{p}-Al\textsubscript{q} (p + q = 1) alloys in the body centered cubic lattice. The size of the aluminum clusters have been taken into account in order to induce a superexchange interaction among the Fe atoms. Extensive Monte Carlo simulations have been employed by using a hybrid algorithm consisting of Metropolis spin flip and Wolff cluster algorithm, together with single histograms techniques. A good fit to the experimental phase diagram has been achieved, including the anomalous region for Al concentration in the range q ≤ 0.2.

1. Introduction
The magnetic and thermodynamic properties of Fe\textsubscript{p}-Al\textsubscript{q} alloys, with p + q = 1, have now been studied for almost a century. For p = 1, the pure iron system has a second-order ferromagnetic to paramagnetic phase transition at 1040 K. It has been shown that for low concentrations of Al content (q < 0.2) the critical transition temperature is almost constant and has a steep decreasing behavior for q > 0.3, eventually disappearing about q = 0.7 (see, for example, references [1] and [2]). This behavior is not expected, since theoretical calculations on simple disordered magnets show a finite and negative slope of the critical transition line as the concentration of dilution goes to zero [3]. Several models, with different theoretical approaches, have been proposed to try to understand the underlying physics in this anomalous region of the phase diagram (among them we can cite references [4]-[16]).

In all of the previous theoretical works on these Fe-Al alloys, one basic and common feature is the dependence of the nearest-neighbor exchange interaction on the Al concentration q. This is indeed expected because Al atoms are larger than Fe ones and there is a corresponding increase of the lattice spacing as q increases. Most of the previous works also assumed a superexchange interaction, between nearest-neighbor Fe atoms, which is induced by the aluminum. This latter
assumption has been in fact a crucial ingredient to reproduce the slow variation of the critical temperature as a function of $q$ in the anomalous region.

In the present paper, we consider further that the superexchange interaction is also dependent on the size of the aluminum cluster atoms. In order to pursue these cluster size effects on the thermodynamic properties of the alloys, we employ extensive Monte Carlo simulations allied with single histograms techniques. In the next section we present the model and give some details of the computer simulations. The results are presented in section 3 and some final comments are addressed in the last section.

2. Model and simulations

The Ising like Hamiltonian suitable for these alloys can be defined by

$$
H = -J_1(q) \sum_{\langle mn \rangle} \epsilon_i \epsilon_j S_i S_j - J_2 \sum_{\langle nnn \rangle} \delta_{ij} \epsilon_i \epsilon_j S_i S_j,
$$

where $J_1(q)$ is the nearest-neighbor interaction given by

$$
J_1(q) = J(1 - Aq),
$$

with $A > 0$ being a theoretical parameter that simulates the decrease of the exchange interaction due to the increase of the lattice parameter as the larger Al atoms concentration $q$ increases. $J$ is the Fe-Fe exchange interaction in the pure undiluted system. The next-nearest-neighbor superexchange interaction $J_2$, induced by the Al atoms, is given by

$$
J_2 = BJ,
$$

with the parameter $B$ simply giving the strength of $J_2$ in units of $J$. The first sum in the above equation is over nearest-neighbors $\langle mn \rangle$ pairs and the second sum over next-nearest-neighbors $\langle nnn \rangle$ pairs. $S_i = \pm 1$ represents an Ising spin-1/2 variable at the sites of a body centered cubic (bcc) lattice. In Eq. (1), $\epsilon_i$ are quenched, uncorrelated random variables, representing the existence of two kinds of particles in the system, namely the magnetic ones (Fe) with $\epsilon_i = 1$, and non-magnetic ones (Al) with $\epsilon_i = 0$. The variable $\epsilon_i$ is chosen according to the bimodal probability distribution

$$
P(\epsilon_i) = p\delta(\epsilon_i - 1) + q\delta(\epsilon_i).
$$

The extra variables $\delta_{ij}$ in the second sum of Eq.(1) represent the existence of superexchange interaction between sites $i$ and $j$. However, this new interaction between iron atoms is now induced only by aluminum atoms on small clusters. The cluster size $\xi$ that induces superexchange interaction between the next-nearest-neighbors is thus another adjustable parameter of the model and is given by just the number of Al atoms, independent of the cluster shape. In this way, $\delta_{ij} = 1$ for next-nearest-neighbors $i$ and $j$ adjacent to the border of the cluster, if the cluster size is smaller than $\xi$, and $\delta_{ij} = 0$ otherwise. Fig. 1 depicts a situation where $\xi = 6$ on a two-dimensional lattice. Note that with this assumption, $J_2$ now actually depends on $q$ as well, since in a quenched dilution, the increase in concentration $q$ leads to the formation of larger Al clusters. In this way, as the probability of finding a cluster with size $\xi$ depends of $q$, the parameter $\xi$ will indirectly connect $J_2$ to the concentration $q$.

The Monte Carlo (MC) simulations of the above Hamiltonian have been done on bcc lattices of linear sizes $L = 10, 15, 20, 25$ and $30$, for Al concentrations ranging from $q = 0$ to $q = 0.7$ with steps of 0.1. For each sample of size $L$ and concentration $q$, the clusters have been measured and the superexchange interaction has been switched on only for those next-nearest-neighbor Fe sites on the border of clusters smaller than $\xi$. Then, we used a hybrid MC algorithm consisting of one
Figure 1. Illustration of a two-dimensional lattice with the induced superexchange interaction by the aluminum cluster for $\xi = 6$. Connected circles are Fe atoms linked by the exchange interaction $J_1$. Larger disconnected circles are Al atoms. In (a) we have two clusters, one with six Al atoms and another with just one Al atom, in such a way that they are able to generate the next-nearest-neighbor superexchange interactions. In (b), a cluster of seven Al atoms is not capable of inducing any next-nearest-neighbor interactions.

The simulation runs comprised $1 \times 10^4$ MCS per spin for equilibration and the measurements were made over more $1 \times 10^4$ MCS at different temperatures, in order to locate the temperature at which the maximum susceptibility occurs or the cumulants cross. Then, a new simulation is performed at this temperature with $3 \times 10^4$ MCS per spin for equilibration and new measurements of the corresponding thermodynamic quantities have been made by using single histogram techniques [19, 20] with $1 \times 10^5$ additional configurations. For each value of the concentration $q$, this whole process is repeated by constructing 50 different randomly diluted samples.

3. Results

The present model for the Fe$_{p}$Al$_{q}$ alloys has in fact just three adjustable parameters: parameter $A$ that quantifies the variations of the exchange interaction with the lattice constant; parameter $B$ that quantifies the intensity of the induced superexchange interaction; and parameter $\xi$ that limits the superexchange interaction to small Al cluster. Note that the parameter $J$ is obtained from the critical temperature of pure iron at $q = 0$, namely 1040 K. Before presenting the fits of the phase diagram, it is worthwhile to see how one gets the corresponding results from the simulations.

Fig. 2 shows, as an example, the magnetization fourth-order cumulant $U_4$ as a function of the reduced temperature $T$, measured in units of $J/k_B$, with $k_B$ the Boltzmann constant, for the case

\[ m = \frac{1}{N} \sum_{i=1}^{N} S_i, \quad \chi = N \frac{\langle m^2 \rangle - \langle m \rangle^2}{T}, \quad U_4 = 1 - \frac{\langle m^4 \rangle}{3\langle m^2 \rangle^2}. \]
q = 0 and several lattice sizes. The crossing of the cumulants gives the transition temperature, and is independent on any critical exponent. This a suitable quantity to be used to get the transition temperature, since for this model any finite-size scaling relation for the thermodynamic limit will depend on critical exponents that will vary as one considers different values of the dilution q [21]. However, we can still notice the presence of residual corrections to finite size scaling. Nevertheless, we can extrapolate the results by doing the limit $1/\ln(L/L') \to 0$, as has been discussed in Ref. [22]. This procedure is shown in the inset of Fig. 2 for $L' = 10$. From there we obtain $T_c = 6.3542(3)$. This critical temperature for $q = 0$ agrees very well with the high-temperature series expansion estimate by Butera and Comi $T_c = 6.35435(3)$ [23] and with other Monte Carlo results $T_c = 6.35441(5)$ [24], and $T_c = 6.3544(6)$ [14].

![Figure 2.](color online) Fourth-order Binder cumulant $U_4$ as a function of the reduced temperature $T$, for $q = 0$ and lattice sizes ranging from $L = 10$ to $L = 30$. The inset in the figure shows $T_L$ (the crossing of the cumulant of lattice size $L$ with the smaller lattice $L' = 10$) plotted versus the inverse of the logarithm of the scale factor $L/L'$. The dashed line is the corresponding linear fit.

The same procedure above has been used to get the transition temperature for $q = 0.3$ and $q = 0.7$, while for the other values of Al concentrations only the cumulant crossing of lattices $L = 20$ and $L' = 10$ have been considered. It should be stressed that the use of only these two lattice sizes can be done, in this case, because the scale of the temperature in the phase diagram does not require a great precision, and also because the error in the simulation results coming from these two lattices alone, when compared to the finite-size extrapolation with larger systems, are smaller than the corresponding symbol sizes used for the experimental and simulational data. Fig. 3 shows the best fit of the phase diagram so obtained with $\xi = 60$, $A = 1.25$ and $B = 0.75$ and the experimental data from references [1] and [2].

4. Final comments
It is clear from Fig. 3 that the present fits to the experimental results are indeed quite good and even better than that obtained in reference [15], where the latter approach did not take into account the superexchange interaction induced by Al atoms. Our procedure of getting simulation data for adjusting experimental results, although not so usual due to the computational time demand required for computing the corresponding thermodynamic properties, is very close to a recent study of the three-dimensional diluted ferromagnetic XY model [25] applied to the experimental data of the insulating pentacoordinate iron(III) molecular ferromagnet Fe[DSC]$_2$Cl.

In the present procedure we have noted that the results are in fact dependent on the size of the aluminum cluster, with the best fit for clusters smaller than 60 atoms. This is in reasonable agreement with a study showing that clusters of only 102 gold atoms behave as a giant molecule, while clusters with 144 atoms exhibit in fact a metallic behavior [26].
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