Site-diluted Blume–Capel model for the Fe–Al disordered alloys

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The phase diagram of a site-diluted spin-1 Blume–Capel model on a simple cubic lattice is studied by using the mean-field renormalization group approach in the pair approximation. The critical temperature has been obtained as function of the vacant sites concentration and the crystal-field. Considering exchange and superexchange interactions between Fe atoms we applied this model to the description of the thermodynamic properties of Fe–Al alloys. The experimental phase diagram has been adjusted with the theoretical parameters and compared with previous theoretical results.

Dilute systems exhibit a wide range of phenomena and their study is of great interest to experimentalists and theoreticians [1,2] because it is quite difficult to find completely pure systems in nature. They have been examined by using various techniques, ranging from mean-field, series expansion, renormalization group, and Monte Carlo simulations (see, for instance, Refs. [1,3–5] and references therein).

The magnetic and structural properties of magnetic alloys, in particular the Fe–Al ones, have also been widely studied [6,7]. These alloys are arranged on a bcc structure and can be represented by Fe 1–q Al q, where p is the iron concentration and q the aluminum concentration with p + q = 1. In the range of 0 < q < 0.18 they are ferromagnetic and structurally disordered. When prepared by slow cooling or quenching for T ≥ 800 °C they also are ferromagnetic and structurally disordered. Depending, however, on the treatment and Al concentrations they can be found in a ferromagnetic state but structurally ordered, i.e., if one considers that the bcc lattice can be divided into two interlocking simple cubic sub-lattices, then there are Al atoms only on one of the two sub-lattices.

The structurally ordered alloys exhibit an anomalous behavior in the magnetization and critical temperature. The magnetization as function of Al concentration presents a sharp decrease for 0.3 ≤ q ≤ 0.4 and then slowly goes to zero, while the critical temperature, for small proportions of Al, is almost constant, and it only decays for q ≥ 0.1. This is an unexpected behavior for dilute systems because it is theoretically predicted a finite slope of the transition temperature at q = 0 [1]. Otherwise, the disordered alloys do not present the anomalous behavior in the magnetization, but also exhibit the same unexpected behavior in their critical temperatures.

Theoretical treatments for such a system have to consider Hamiltonians which take into account several contributions coming from different aspects of the involved physics. In general, the Hamiltonian can be written as

\[ H = \mathcal{H}_e + \mathcal{H}_a + \mathcal{H}_z + \mathcal{H}_d, \]  

where \( \mathcal{H}_e \) represents the exchange energy term, \( \mathcal{H}_a \) an anisotropy term, \( \mathcal{H}_z \) is the Zeeman contribution due to an external field, and \( \mathcal{H}_d \) a dipolar interaction. As the last term is very small compared to the others, and the critical behavior occurs at zero external field, for the present system we need only to consider the exchange interaction and the anisotropic energies, the latter one coming from the crystalline structure and is generally given by \( D \sum_i (S_i^z)^2 \), where \( S_i^z \) is the z component of the spin at site i and D is the crystal-field. The exchange term, on the other side, should also present some anisotropies.

Some theoretical \( \mathcal{H}_e \) models, based on a spin-1/2 Ising model [8] and a quantum Heisenberg model [9], have been proposed for these systems, but they were not able to explain the anomalous behavior of the critical temperature \( T_c \) for small concentrations q as well as the critical concentrations \( q_c \) observed experimentally (for \( q > q_c \), one does not expect the system being critical). Some recent works have considered an extra superexchange interaction between second-neighbors Fe atoms, induced by Al atoms. The theoretical curve obtained for the phase diagram in these cases are in better accord with the experimental data, despite the anomalous region being still slightly far from the theoretical curve [11,10].
One must keep in mind that earlier treatments have been done by approximations in the Ising model, whereas the Blume–Capel (BC) model [12,13] has not yet been used to describe this specific alloy. As for spin-1/2 breaking fields, the quadrupole and magnetization per spin are not, thus the probability distribution for proposed previously in the literature and, since Al atoms have no $z$ where

$$H = -J_1 \sum_{\langle \text{nn} \rangle} \epsilon_i \sigma_i \sigma_j - J_2 \sum_{\langle \text{nnn} \rangle} \epsilon_i \sigma_i \sigma_j + D \sum_{i=1}^{N} \epsilon_i \sigma_i^2,$$

(2)

where $J_1$ is the exchange interaction, $J_2$ is the superexchange interaction mediated by an Al atom, $D$ is the crystal-field, the spin variables $\sigma_i = \pm 1, 0$, and $\epsilon_i$ is 1 or 0, whether the site is occupied or not by a Fe atom, respectively. The first sum runs over nearest-neighbor (nn) pairs, the second one over next-nearest-neighbor (nnn) pairs, and the third runs over all $N$ sites of the lattice. It is also assumed that any site can independently be occupied, or not, thus the probability distribution for $\epsilon_i$

$$P(\epsilon_i) = \rho \delta(\epsilon_i - 1) + q \delta(\epsilon_i),$$

(3)

where $p$ is the occupied sites concentration, and $q = 1 - p$ is the vacant sites concentration.

In order to apply the MFRG method we consider systems with one- and two-spin clusters in its improved version [22]. Thus the Hamiltonian for one-site cluster is given by

$$H_1 = -\epsilon_1 \sigma_1 \left( J_1 \sum_{j=1}^{z} \epsilon_j b_1 + J_2 \sum_{j=1}^{z'} \epsilon_j b_1 \right) + \epsilon_1 \sigma_1^2 (D - \delta_1 z_2 p),$$

(4)

where $z$ is the coordination number and $z'$ is the number of next-nearest-neighbors of the lattice. $b_1$ and $\delta_1$ are the symmetry-breaking fields. The quadrupole and magnetization per spin are given by

$$q_1 = \langle \langle \sigma_1^2 \rangle \rangle_{\text{c}} = \int \frac{N}{i=1} d\epsilon_i P(\epsilon_i) \frac{\text{Tr} \sigma_1 e^{-\beta H_1}}{Z_1},$$

(5)

where $\langle \langle \cdot \rangle \rangle_{\text{c}}$ denote thermal and configurational averages, respectively. When $T \to T_c$, $m_1 \to 0$ as well as $b_1 \to 0$, therefore

$$m_1 = \frac{2z p^2 \epsilon_1 e^{-\beta (D - \delta_1 z_2 p)} (K_1 + \alpha q K_2) b_1}{1 + 2e^{-\beta (D - \delta_1 z_2 p)}},$$

(6)

$$q_1 = \frac{2p e^{-\beta (D - \delta_1 z_2 p)}}{1 + 2e^{-\beta (D - \delta_1 z_2 p)}},$$

(7)

where $K_1 = \beta J_1$, $K_2 = \beta J_2$, $\beta = (k_B T)^{-1}$ and $\alpha$ is the number of next-nearest-neighbor pairs which have the same occupied site as neighbor. This parameter $\alpha$ should not be confused with the next-nearest-neighbors $z'$. Next-nearest-neighbors interactions between pairs of Fe atoms are considered only when they have a common nearest-neighbor Al. For instance, on a square lattice, when a Fe has an Al nearest atom, the latter can induce a superexchange interaction with the most $\alpha = 2$ another Fe atoms. On a simple cubic lattice, one has $\alpha = 3$ and so on for other topologies (in general, for hypercubic lattices one has $\alpha = d$). For the bcc lattice it also happens to have $\alpha = 3$.

In the same way, for the two-sites cluster we have

$$H_2 = (\epsilon_1 \sigma_1^2 + \epsilon_2 \sigma_2^2) (D - \delta_2 (z - 1) \rho - J_1 \epsilon_1 \sigma_1 \sigma_2 - \epsilon_1 \sigma_1 \sigma_2) + (\epsilon_1 \sigma_1 \sigma_2) \left( \sum_{j=1}^{z-1} J_1 \epsilon_j b_2 + J_2 \sum_{j=1}^{z'} \epsilon_j b_2 \right),$$

(8)

and we get

$$q_2 = \frac{2p \epsilon_1 e^{-\beta (D - \delta_2 (z - 1) \rho)} + 2e^{-2\beta (D - \delta_2 (z - 1) \rho)} \cosh K_1}{1 + 4e^{-\beta (D - \delta_2 (z - 1) \rho)} + 4e^{-2\beta (D - \delta_2 (z - 1) \rho)} \cosh K_1} + \frac{2pe^{-\beta (D - \delta_2 (z - 1) \rho)}}{1 + 2e^{-\beta (D - \delta_2 (z - 1) \rho)}},$$

(9)

$$m_2 = \frac{(2z - 1) \rho^2 e^{-\beta (D - \delta_2 (z - 1) \rho)} + 2e^{-2\beta (D - \delta_2 (z - 1) \rho)} \cosh K_1}{1 + 4e^{-\beta (D - \delta_2 (z - 1) \rho)} + 4e^{-2\beta (D - \delta_2 (z - 1) \rho)} \cosh K_1} \times (K_1 + \alpha q K_2) b_2 + \frac{2z - 1 \rho^2 e^{-\beta (D - \delta_2 (z - 1) \rho)}}{1 + 2e^{-\beta (D - \delta_2 (z - 1) \rho)}},$$

(10)

By imposing the scaling relations $m_1 = \ell^\alpha m_2$, $b_1 = \ell^\beta b_2$, and $q_1 = q_2$, $\delta_1 = \delta_2 = \delta$, where $\theta$ is the anomalous dimension, we obtain (see also [16,22])

$$\frac{z}{1 + 2e^{-\beta (D - \delta_2 z_2 p)}} \frac{Z_2}{Z_1} + \frac{p \epsilon_1 e^{-\beta (D - \delta_2 (z - 1) \rho)} + 2e^{-2\beta (D - \delta_2 (z - 1) \rho)} \cosh K_1}{1 + 4e^{-\beta (D - \delta_2 (z - 1) \rho)} + 4e^{-2\beta (D - \delta_2 (z - 1) \rho)} \cosh K_1} \cosh K_2 + \frac{q \epsilon_1 e^{-\beta (D - \delta_2 (z - 1) \rho)}}{1 + 2e^{-\beta (D - \delta_2 (z - 1) \rho)}}$$

(11)

$$\frac{z}{1 + 2e^{-\beta (D - \delta_2 z_2 p)}} \frac{Z_2}{Z_1} + \frac{p \epsilon_1 e^{-\beta (D - \delta_2 (z - 1) \rho)} + 2e^{-2\beta (D - \delta_2 (z - 1) \rho)} \cosh K_1}{1 + 4e^{-\beta (D - \delta_2 (z - 1) \rho)} + 4e^{-2\beta (D - \delta_2 (z - 1) \rho)} \cosh K_1} \cosh K_2 + \frac{q \epsilon_1 e^{-\beta (D - \delta_2 (z - 1) \rho)}}{1 + 2e^{-\beta (D - \delta_2 (z - 1) \rho)}},$$

(12)

where $\eta = J_2 / J_1$. Note that the dimension and topology of the lattice depend, for the present clusters, only on the values of $z$. 

on a simple cubic lattice where to study the phase diagram of the site diluted spin-1 BC model Ref. [8] whereas for this latter limit, when we take this limit, as a result of the superexchange interaction between next-nearest-neighbors induced by Al atoms. Only when the non-magnetic ions concentration is high enough the critical temperature decreases since the dilution tends to disorder the system. As a result, the tricritical point is a decreasing function of $\eta$. However, for $0.789 < q < 0.8$ a rather different behavior is observed. The reduced critical temperature, for some value of $d$, starts increasing with $d$ and afterwards decreases reaching the tricritical point. This behavior implies in a reentrant phenomenon when plotting the reduced temperature against the vacancy concentration. This is clearly seen in Fig. 2, where the reentrant behavior occurs in the region $D \sim -1.2 \leq d < 0$. Such reentrancy has been previously observed in spin-3/2 models [3,5]. We would like to say that at $d = -50$, on the scale of Fig. 2, the curve for the critical temperature is almost equal to that given by Eq. (13).

The corresponding results for $\eta = 0.5$ are depicted in Figs. 3 and 4. Fig. 3 is similar to Fig. 1. The main qualitative difference is for small values of $q$, where the temperature increases. The limit $d \to -\infty$ now goes to the spin-1/2 case treated in Ref. [10]. So, in general, one can see that as the non-magnetic ion concentration increases from zero, the critical temperature also increases in this case, as a result of the superexchange interaction between next-nearest-neighbors induced by Al atoms. Only when the non-magnetic ions concentration is high enough the critical temperature gets lower. This is apparent in Fig. 4. However, apart from this enhancement of $T_c$, the general behavior is similar to that obtained for $\eta = 0$, mainly regarding the reentrance close to the critical concentration (which, for the sake of clarity, is not shown in Fig. 4).

It is also noted that, in this case, $q_c$ is dependent on the $J_2$ interaction. In fact, taking the zero temperature limit we get from the above equations

$$q_c = \frac{a\eta - 1 + \sqrt{(a\eta + 1)^2 - 4a\eta/(z - 1)}}{2a\eta}.$$  

It is interesting to notice that $q_c$ is independent of the crystal-field. Despite the crystal being related to the chemical potential controlling the zero state of the spins, it is a local field, and only...
the pair exchange interactions between next-neighbors is relevant for the critical concentration.

Now, in order to describe the magnetic properties of the Fe–Al alloy we can apply this method and model where \( z = 8 \) and \( \alpha = 3 \). Since the increasing of Al concentration \( q \) produces a linear increasing of the lattice parameter, mainly due to the larger atomic size of the Al atom, the spin interaction should decrease. Thus, as in previous works, we consider [10]

\[
J_1(q) = J(1 - Lq),
\]

and

\[
J_2(q) = J(A - Bq)(C - q),
\]

where \( L, A, B, \) and \( C \) are theoretical parameters to be adjusted, as well as the crystal-field \( d \).

The experimental (dots) and calculated phase diagram (full line) for the Fe–Al alloy, using \( d = -10 \), \( L = 0.85 \), \( A = 2.33 \), \( B = 2.9 \) and \( C = 0.35 \), are plotted in Fig. 5. For comparison, we also have plotted in this figure, by dashed and dotted lines, the previous theoretical fittings reported in [8] and [10], respectively. By using these theoretical parameters we find \( t_c = 6.3441 \) when \( q = 0 \), which is in a good agreement with the one obtained from series expansions on a bcc lattice \( t_c = 6.35 \). As \( k_B g = 8.617 \times 10^{-5} \) eV/K and the experimental result for the pure system is \( T_c = 1040 \) K, we also obtain \( J = 0.014 \) eV.

Apart from \( L \) and \( A \), which are different from the values of the theoretical parameters used in the previous fittings of Ref. [10], namely \( L = 0.95 \) and \( A = 2.2 \), the present ones are comparable, as are the value of \( J \), namely \( J = 0.013 \) eV. The present values of \( B \) and \( C \) are the same as in the previous fitting. As can be noted from the figure, the phase diagrams are almost of the same quality when compared to the approximations in the Ising and BC models. However, the agreement now for high values of the vacancy occupation is better than in previous studies. For a clearer picture of the phase diagram, we have not plotted in Fig. 5 the results from Refs. [8] and [10] for \( q > 0.8 \). In fact, in this range of \( q \) the lattice structure in not more bcc, so such approaches are not suitable in this region. The critical concentration from the previous procedures goes to \( q_c = 0.83 \) without superexchange and \( q_c = 0.98 \) with superexchange interactions.

In summary, we have used the renormalization group with mean-field approximations in the study of the diluted spin-1 Blume–Capel model. This system is a generalization of the Ising model in the presence of a crystal-field. We believe we have obtained a satisfactory picture of the thermodynamic behavior of the model as a function of its parameters, where the crystal-field brings an important contribution to the critical behavior.

This approach was in addition applied to the Fe–Al alloy, considering exchange and superexchange interactions, which are dependent of the Al concentration. This approximation provided us with data that were adjusted to a experimental curve in the phase diagram.

One could have, in principle, good expectations in applying the present model to these alloys, since this approach was recently applied in Fe–Ni–Mn and Fe–Al–Mn alloys [21] and a much better experimental agreement were obtained when compared to the Ising model. Despite the results being quite better than those from Ref. [8], they were just comparable to those from Ref. [10] since the anomalous behavior for \( 0.1 < q < 0.25 \) has not yet been successfully explained. In fact, besides the use of several adjustable parameters the low concentration region of the phase diagram still remains puzzling.

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**References**