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# Site-diluted Ising model for the magnetic properties of $Fe_{1-q}Al_q$, $0 \leq q \leq 0.5$, alloys in the disordered phase

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We present a theoretical study for the magnetic behavior of disordered Fe-Al alloys on the basis of a simple site-diluted Ising spin model. With the assumption that the exchange interaction $J$ depends on the Al concentration $q$, we calculate the thermodynamical properties of the model through a variational method for the free energy, based on Bogoliubov's inequality. An acceptable fit to the experimental phase diagram for Al concentrations in the range $0 \leq q \leq 0.475$ is obtained. A relation between the reduced magnetic hyperfine field and the theoretical magnetization is proposed, and rather good agreement with the experimental results at room temperature is also achieved.

## I. INTRODUCTION

The magnetic properties of Fe-Al alloys have been, experimentally, widely studied.[1-4] These alloys, in the "ordered" phase, present an anomalous magnetic behavior at an Al concentration $q = 0.3$ (Ref. 1). Some theoretical models have been proposed in order to study the magnetic properties of Fe-Al ordered alloys. Sato and Arrott[5] obtained the magnetization by assuming a ferromagnetic exchange between nearest-neighbor Fe atoms and an antiferromagnetic superexchange between two Fe atoms separated by an Al atom. This model, however, predicts an antiferromagnetic phase at low temperatures which was not revealed by neutron scattering experiments.[6] Shukla and Wortis[7] and Grest[8] did their estimates assuming a spin-glass state near the critical Al concentration. In this case, a rather good agreement with experimental data has been achieved.

More recently, an experimental study of Fe-Al alloys in the "disordered" phase has been reported for Al concentrations $q$ in the range $0 \leq q \leq 0.5$ (Ref. 9). It has been shown[9] that this system, at room temperature, undergoes a ferro- to paramagnetic phase transition at a critical Al concentration $q_c = 0.475$. It has also been noted that the critical temperature of the ferro- to paramagnetic transition decreases as the Al concentration increases. Moreover, these alloys are all ferromagnetic and do not show the anomalous behavior of the ordered ones.

In this work we report a possible interpretation for the experimental results of Pérez Alcazar and Galvão da Silva[9] on the basis of a simple-diluted Ising spin model for the magnetic behavior of Fe-Al alloys in the disordered phase.

## II. MODEL SYSTEM

In order to obtain the thermodynamic properties of the Fe-Al disordered alloys we assume a quenched site-diluted Ising model with only the nearest-neighbors ($NN$) interaction. The Hamiltonian for this model can be given by

$$H = -\sum_{\langle ij \rangle} J_{ij} \sigma_i \sigma_j \ , \tag{1}$$

where $J_{ij} > 0$ is the exchange parameter between neighboring spins and $\sigma_i = \pm 1$. For site dilution we have a probability distribution

$$P(\epsilon_i) = p\delta(\epsilon_i - 1) + (1-p)\delta(\epsilon_i) \ , \tag{2}$$

where $p$ is the ferromagnetic site concentration and $J_{ij} = \epsilon_i \epsilon_j J$ with $\epsilon_i = 1$ or 0, depending if the site $i$ is occupied by a magnetic atom or not, respectively. The nonferromagnetic site concentration is given by $q = 1 - p$.

Some experimental evidence reinforces the choice of this model: (1) It was shown experimentally[9] that the alloys are all ferromagnetic and the average magnetic hyperfine field gradually decreases with the increasing of the Al concentration $q$. Also it does not show the anomalous behavior of Fe-Al ordered alloys. In this way, we can assume only one type of exchange parameter, $J_{ij} \geq 0$ for that case. (2) The experimental results indicate that while the alloys are disordered the average Fe magnetic moment is constant. Moreover, theoretical calculations of Fe-Al clusters[10] using the discrete variational method (DVM) have shown that the local Fe magnetic moment presents a weaker dependence upon the number of $NN$ Al atoms. Then, it seems to be reasonable to use a model with constant atomic spin. (3) Because the Al atom behaves like a magnetic hole, the model must be site dilute. (4) Finally, we consider only $NN$ interactions, mainly because the magnetic studies of amorphous alloys[11] show evidence that the exchange parameter between next-nearest neighbors ($NNN$), $J_2$, has a maximum value which is one order of magnitude smaller than that between $NN$, $J_1$. The ferromagnetism of disordered crystalline alloys is similar to that of the amorphous ones. It was also shown[9] that Al atoms substitute Fe atoms with higher probability in the first Fe neighborhood. This was done by using a theoretical estimation of the probability of having different types of configurations for a complete disordered binary alloy and by associating with each arrangement one given magnetic field, by taking $J_1/J_2 = 5$. This model shows rather good agreement with the experimental results and allows us to propose the correct mechanism of substitution of Fe by Al. All these results favor strongly the choice of the Hamiltonian model (1) to describe the magnetic properties of disordered Fe-Al alloys.

## III. APPROXIMATION FOR THE MODEL

The free energy of this system may be derived, approximately, via the variational technique based on Bogoliubov's inequality[12]

$$\phi(\gamma)=[F_0(\gamma)]_{\epsilon_i}+[\langle H-H_0\rangle_0]_{\epsilon_i}\geq F\ , \tag{3}$$

where $F$ is the exact free energy associated with the system defined by the Hamiltonian $H$, $F_0(\gamma)$ is the free energy of the trial Hamiltonian $H_0(\gamma)$, with $\gamma$ standing for the variational parameters. In Eq. (3), $\langle\cdots\rangle_0$ is the thermal average in the ensemble defined by $H_0$ and $[\cdots]_{\epsilon_i}$ is the configurational average. Different choices of the trial Hamiltonian $H$ lead to different approximations. In order to obtain results at least comparable to the constant-coupling approximation we will follow the procedure suggested by Ferreira *et al.*[13] In this case, the trial Hamiltonian $H$ is given by

$$H_0=-\sum_P[J_{ij}\sigma_i\sigma_j+\gamma_p(\sigma_i+\sigma_j)]-\sum_S\gamma_s\sigma_i\ , \tag{4}$$

where the first sum runs over $n$ disconnected pairs of linked spins and the second sum runs over $N$-$2n$ free spins, $N$ being the total number of spins. $\gamma_s$ and $\gamma_p$ are variational parameters (molecular fields) to be determined through the minimization of $\phi$ and by imposing the condition that the magnetization is obtained either for a free spin or for a spin belonging to a linked pair.

The partition function for the trial Hamiltonian (4) can then be written as

$$Z_0=Z_p^nZ_s^{N-2n}\ , \tag{5}$$

where

$$\begin{aligned} Z_s&=2\cosh(\beta\gamma_s)\ ;\\ Z_p&=2e^{\beta J_{ij}}\cosh(\beta\gamma_p)+2e^{-2\beta J_{ij}}\ , \end{aligned} \tag{6}$$

with $\beta=1/k_BT$. The thermal average $\langle H-H_0(\gamma)\rangle_0$ can also be easily evaluated once there is no correlation between free spins and spins belonging to linked pairs in the trial Hamiltonian. After averaging over all the configurations we obtain

$$\begin{aligned} \phi(\gamma)=&-nk_BT\ln Z_p(\gamma_p)-2nk_BT(1-p)\ln Z_s(\gamma_p)\\ &-(N-2n)k_BT\ln Z_s(\gamma_s)-pJNzm^2/2\\ &+pJnm^2+2\gamma_pnm+(N-2n)\gamma_sm\ , \end{aligned} \tag{7}$$

where the magnetization $m=[\langle\sigma_i\rangle]_{\epsilon_i}$ is given by

$$\begin{aligned} m&=\tanh(\beta\gamma_s)\\ &=(1-p)\tanh(\beta\gamma_p)+\frac{p\sinh(2\beta\gamma_p)}{\cosh(2\beta\gamma_p)+e^{-2\beta J}}\ . \end{aligned} \tag{8}$$

Minimization of $\phi$ with respect to the variational parameters leads to

$$\gamma_s=z\gamma_p/(z-1)\ , \tag{9}$$

where $z$ is the coordination number of the lattice. We have used for the number of linked pairs of spins the value $n=Nz/2$, obtained from the matching of the first few terms of the high-temperature series expansion for $F$ and $\phi$ in the pure Ising limit $p=1$ (for further details see Refs. 13 and 14). By assuming that $F=\min\phi$, we have from Eqs. (7)–(9) all the approximated thermodynamical properties of the model (1). For instance, close to the transition one has $m\simeq0$, $\gamma_s\simeq0$, and $\gamma_p\simeq0$. Then, from Eqs. (8) and (9) we obtain the following equation for the critical temperature as a function of the concentration:

$$\beta_cJ=\frac{1}{2}\ln\left[\frac{(z-1)p+1}{(z-1)p-1}\right]\ , \tag{10}$$

which is the same result as that obtained through the constant coupling approximation for the diluted Ising model.

## IV. RESULTS AND DISCUSSION

As was shown by Pérez Alcazar and Galvão da Silva,[9] the increasing of the Al concentration $q$ produces a linear increasing of the lattice parameter, mainly due to the larger atomic size of the Al atoms. This larger distance between interacting spins should reduce the exchange parameter. For amorphous alloys, Kaul[11] has used a dependence of the exchange parameter $J$ with the distance between nearest neighbors $r$ given by

$$J(r)=J_1\exp\{\alpha[(r/a_1)-1]\}\ , \tag{11}$$

where $J_1$ is the maximum value of $J$ (for $r=a_1$) and $\alpha$ is a constant. For Fe-Ni amorphous alloys rich in Ni the $\alpha$ values are in the interval $-5.5\leq\alpha\leq-3.3$.

In a first approximation, (11) can be written as

$$J(r)=J_1[1+\alpha(r-a_1)/a_1]\ . \tag{12}$$

By using the least-square fitted expression for the lattice parameter $r$ as a function of $q$ previously obtained by Pérez Alcazar and Galvão da Silva for Fe-Al alloys,[9] Eq. (12) reads

$$J(q)=J_1(1+\alpha bq/a_1)\ , \tag{13}$$

where $a_1=2.870$ Å and $b=0.154$ Å. This means that the exchange interaction is itself dependent on the Al concentration $q=1-p$. As the $\alpha$ value is not available for the present alloys we can, in general, write (13) as

$$J(q)=J_1-J_0q\ , \tag{14}$$

where $J_0$ and $J_1$ are parameters to be adjusted.

Proceeding now in a similar way as was done in the study of compressible Ising systems,[15] we can introduce the $q$ dependence of $J$ in the present theoretical results by simply assuming $J=J(q)$ given by (14) in Eqs. (7)–(10) of the last section. In this case, the macroscopic magnetization given by (8) takes into account now both effects: dilution of magnetic sites and variation of the exchange parameter $J$ with the Al concentration. Moreover, the critical temperature given by (10) has also now an additional concentration dependence expressed by the fact that $J=J(q)$.

In order to adjust the parameters $J_0$ and $J_1$, we first note that the critical temperature for the pure Fe ($q=0$) is given by $T_c=1040$ K. From Eq. (10) we obtain $J_1=12.846$ meV which is in the range 10–50 meV for

Fe, Co, and Ni (Ref. 11). In that case, $t_c = (\beta_c J)^{-1} = 6.96$ is comparable to the value $t_c = 6.35$ obtained from series expansions on a bcc lattice ($z = 8$) (Ref. 16). As the magnetization, at room temperature, vanishes at a critical Al concentration $q_c = 0.475$ (Ref. 9), we obtain from Eq. (8) $J_0/J_1 = 0.95$. This value implies that $\alpha = -17.75$ which is larger than those obtained for amorphous Fe-Ni (Ref. 11). This discrepancy is due to the larger size of the Al atoms rather than to that of the Ni atoms. In the present case, the exchange $J$ for Fe-Al alloys decreases more rapidly than the exchange for Fe-Ni alloys. Figure 1 shows the critical temperature as a function of $q$ calculated from (10) (with the adjusted parameters above) together with the experimental results reported by Pérez Alcazar and Galvão da Silva.[9] It can be seen that a rather good agreement is achieved for $q > 0.3$, while for $q < 0.3$ the experimental values increase more rapidly than the theoretical ones. This discrepancy, however, may be explained in the present case, as due to the fact that the Mössbauer technique is not adequate for the measurement of large $T_c$ because it takes too long a time to record a good spectrum. As it was shown in Ref. 9, during this time there is an annealing of the sample which induces a phase decomposition with the final phase richer in iron.

It is interesting to note that all the above results could be obtained without any assumption of the specific relation between the experimental Mössbauer magnetic hyperfine field $\bar{H}$ and the theoretical magnetization $m$ given by (8). However, for a further quantitative comparison of the present theoretical results with the experimental data of the hyperfine field, it is necessary to propose a suitable relation between $\bar{H}$ and $m$. In order to do that, we first note that the theoretical magnetization $m$ is a function of the *NN* magnetic atoms (expressed by the dilution $q$) as well as a function of the distance among them (expressed by the variation of the exchange parameter with $q$). On the other hand, $\bar{H}$ is essentially a local parameter which depends mainly on the effective number of magnetic *NN* as well as on the mean value of the local magnetic moment. In addition, as was shown by theoretical calculations of Fe-Al clusters using the DVM method,[10] the magnetic hyperfine field is not sensible to the expansion of the lattice. If we assume that the mean value of the local magnetic moment is proportional to the magnetization $m$, it is then reasonable to propose that

$$H \propto z n_{\text{eff}} m \,, \tag{15}$$

where $z = 8$ and

$$n_{\text{eff}} = \left[ \sum_{n=1}^{z} P(n,p) n \right] / z \,, \tag{16}$$

where $P(n,p)$ is the probability of finding $n$ magnetic *NN* for a concentration $p$ and $z n_{\text{eff}}$ gives the effective number of magnetic *NN*. The mean reduced magnetic field can then be expressed as

$$\bar{H} / \bar{H}(T=0, p=1) = n_{\text{eff}} m \,, \tag{17}$$

where both sides of Eq. (17) are now dimensionless quantities.

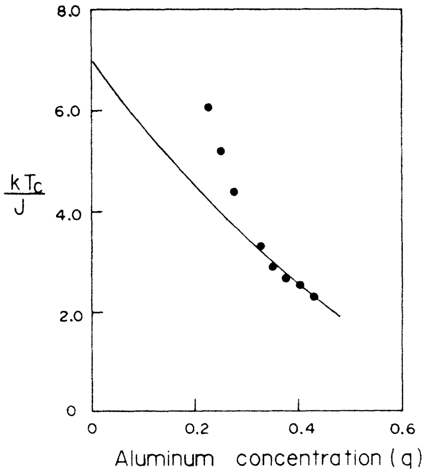

FIG. 1. Critical temperature as a function of the Al concentration obtained from Eq. (10) and the parameters given in the text (solid line). The data (dots) were taken from Ref. 9.

Figure 2 shows the reduced average magnetic Hf field as a function of the Al concentration obtained from Eq. (17) at room temperature and using the values of $J_0$ and $J_1$ given above. It is also shown in that figure the experimental data, obtained by Mössbauer spectroscopy, of the reduced average magnetic hyperfine field $\bar{H}/\bar{H}(T=0, p=1)$, where $\bar{H}(T=0, p=1) = 340$ KOe (Ref. 9). One clearly sees that a rather good fit to the experimental data at room temperature has also been achieved in that case. This agreement certainly reinforces the assumption expressed by Eqs. (15) and (17).

In conclusion, we can see that the present model, although simple, can give a satisfactory description of Fe-Al alloys in the disordered phase. Moreover, from the theoretical point of view, it is surprising that, with just two parameters ($J_0$ and $J_1$), the present model system can account for the main magnetic properties of these disordered alloys. We believe that the present discussion may also be extended to disordered or amorphous ferromagnetic binary alloys in which a nonmagnetic atom substitutes for a magnetic one and dilutes the direct exchange of magnetic nearest neighbors.

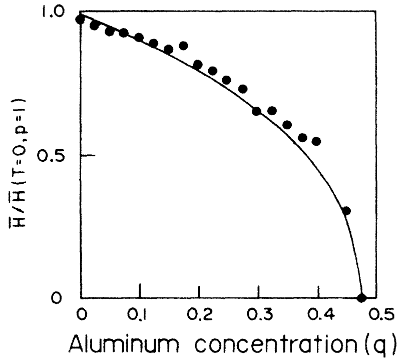

FIG. 2. Reduced magnetic hyperfine field as a function of Al concentration at room temperature obtained from Eq. (17) and the parameters given in the text (solid line). The data (dots) were taken from Ref. 9.

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