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Theory of phase equilibria in Co-Fe alloys

F. J. Martínez-Herrera and F. Mejía-Lira
Instituto de Física, Universidad Autónoma de San Luis Potosí, 78000 San Luis Potosí, San Luis Potosí, México

F. Aguilera-Granja and J. L. Morán-López*
Institut für Festkörperforschung der Kernforschungsanlage Jülich, D-5170 Jülich, West Germany

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The phase diagram of ferromagnetic Co-Fe alloys is calculated within a mean-field theory that includes chemical and magnetic interactions simultaneously. Short-range-order correlations are included by the calculation of the entropy in the Bethe approximation. A very good agreement with the experimental observations is obtained.

Order-disorder transformations as well as constitutional short- and long-range orders in binary alloys are some of the classical problems in material sciences. Recently, much effort has been devoted to measuring and understanding the alloy phase diagrams. However, only some phase diagrams of paramagnetic systems have been reproduced theoretically.[1-3]

More interesting, and obviously more diffucult to treat, are alloys with magnetic components, where in addition to the spatial order-disorder phenomena, the magnetic phase transformation takes place. An example is the Co_xFe_y ($y=1-x$) system, which is an ordering alloy with a body-centered-cubic crystal structure and with magnetic Curie temperatures higher than the spatial-order-disorder temperatures. The phase diagram reported by Hansen[4] shows a maximum in the Curie temperature ($T_C=1258$ K) at $x=0.465$ and a maximum in the spatial-order-disorder temperature ($T_0=1003$ K) at $x=0.49$. In a more recent experiment,[5] Oyedele and Collins found that $T_0=998.5$ K at $x=0.48$ (see Fig. 1).

Bienenstock and Lewis[6] calculated the phase diagram of an ordering alloy with paramagnetic components by means of the low-temperature series expansion of the Ising model. They obtained a symmetric phase diagram with respect to $x=0.5$. Those results applied to the Co_xFe_y alloy[5] are shown by the short-dashed curve in Fig. 1.

Another attempt to reproduce the concentration dependence of the spatial-order-disorder transition temperature was made by Racz and Collins.[7] Within the real-space renormalization-group theory they found that, in order to get the observed asymmetry in the spatial-order-disorder phase diagram, it is necessary to include three-body interactions. However, as shown by the long-dashed line in Fig. 1, the agreement with the whole phase diagram is not satisfactory. Both studies ignored the magnetic properties of the system.

Here, we present a model that reproduces quite well not only the concentration dependence of the spatial-order-disorder transition temperature but also the concentration dependence of the Curie temperature. It is a mean-field theory in which magnetic and chemical effects are treated on the same footing and short-range-order correlations are taken into account by calculating the configurational entropy in the Bethe approximation. It has been shown[8-12] that in order to describe the phase transitions taking place in binary alloys with magnetic components, it is necessary to take into account chemical and magnetic interactions simultaneously. However, most of the theoretical investigations have been devoted to the study of the spatial and magnetic long-range order. The phase diagram obtained in that approximation[10] is shown by the dash-period line in Fig. 1. Only recently have some authors[12-15] considered short-range-order effects.

To describe the spatial ordering we subdivide the bcc lattice into two equivalent sublattices, α and β, and the magnetic properties are simulated by an $\frac{1}{2}$-spin Ising model. Therefore, 16 different pair probabilities can be defined.

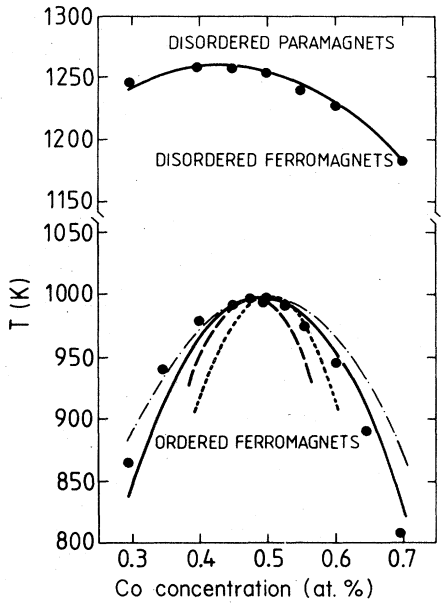

FIG. 1. Phase diagram for Co_xFe_{1-x}. The upper curve is the Curie temperature and the lower one the spatial-order-disorder critical temperature. The experimental values (solid circles) of the Curie temperatures and the spatial-order-disorder transition temperatures were taken from Refs. 4 and 5. The short-dashed curve are the results (Ref. 6) of low-temperatures series expansion of the Ising model. The long-dashed curve are the results (Ref. 7) of the real-space renormalization-group theory with three-body interactions. The period-dashed curves are the results in the Bragg-Williams approximation and the solid lines are our results.

The symbol $P_{\alpha\beta}(I,m;J,n)$ denotes the probability of finding an atom of type I (Co,Fe) with spin m ($\uparrow$, $\downarrow$) at a site of the α sublattice with a nearest-neighbor of type J (Co,Fe) with spin n ($\uparrow$, $\downarrow$) at a site of the β sublattice. The single site probabilities are given in terms of the pair probabilities by

$$P_\alpha(I,m)=\sum_{J,n}P_{\alpha\beta}(I,m;J,n)\ . \tag{1}$$

In terms of these probabilities the average concentration of Co atoms can be written as

$$x=\tfrac{1}{2}\sum_{\nu,m}P_\nu(\mathrm{Co},m)\ . \tag{2}$$

An additional constrain to the probabilities is given by the normalization condition

$$\sum_{I,J,m,n}P_{\alpha\beta}(I,m;J,n)=1\ . \tag{3}$$

In order to follow the phase transitions we define five long-range-order parameters; one describes the spatial order,

$$\eta\equiv[P_\alpha(\mathrm{Co},\uparrow)+P_\alpha(\mathrm{Co},\downarrow)]-[P_\beta(\mathrm{Co},\uparrow)+P_\beta(\mathrm{Co},\downarrow)]\ , \tag{4}$$

and four the magnetic transition

$$m_\nu(I)=P_\nu(I,\uparrow)-P_\nu(I,\downarrow)\ . \tag{5}$$

To describe the short-range correlations we define also five short-range-order parameters; the spatial short-range order parameter is defined by

$$\sigma_1\equiv 1-\frac{\sum_{m,n}[P_{\alpha\beta}(\mathrm{Co},m;\mathrm{Fe},n)+P_{\alpha\beta}(\mathrm{Fe},m;\mathrm{Co},n)]}{2x(1-x)}\ , \tag{6}$$

and the magnetic short-range-order parameters are defined by

$$\begin{aligned}
\sigma_2&=P_{\alpha\beta}(\mathrm{Fe},\uparrow;\mathrm{Co},\uparrow)+P_{\alpha\beta}(\mathrm{Fe},\downarrow;\mathrm{Co},\downarrow)-P_{\alpha\beta}(\mathrm{Fe},\uparrow;\mathrm{Co},\downarrow)-P_{\alpha\beta}(\mathrm{Fe},\downarrow;\mathrm{Co},\uparrow)\ ,\\
\sigma_3&=P_{\alpha\beta}(\mathrm{Fe},\uparrow;\mathrm{Fe},\uparrow)+P_{\alpha\beta}(\mathrm{Fe},\downarrow;\mathrm{Fe},\downarrow)-P_{\alpha\beta}(\mathrm{Fe},\uparrow;\mathrm{Fe},\downarrow)-P_{\alpha\beta}(\mathrm{Fe},\downarrow;\mathrm{Fe},\uparrow)\ ,\\
\sigma_4&=P_{\alpha\beta}(\mathrm{Co},\uparrow;\mathrm{Fe},\uparrow)+P_{\alpha\beta}(\mathrm{Co},\downarrow;\mathrm{Fe},\downarrow)-P_{\alpha\beta}(\mathrm{Co},\uparrow;\mathrm{Fe},\downarrow)-P_{\alpha\beta}(\mathrm{Co},\downarrow;\mathrm{Fe},\uparrow)\ ,\\
\sigma_5&=P_{\alpha\beta}(\mathrm{Co},\uparrow;\mathrm{Co},\uparrow)+P_{\alpha\beta}(\mathrm{Co},\downarrow;\mathrm{Co}\downarrow)-P_{\alpha\beta}(\mathrm{Co},\uparrow;\mathrm{Co},\downarrow)-P_{\alpha\beta}(\mathrm{Co},\downarrow;\mathrm{Co},\uparrow)\ .
\end{aligned} \tag{7}$$

In terms of the σ's, the internal energy can be written in a very simple form:

$$\frac{U}{N}=4xyW_c\sigma_1-(\sigma_2+\sigma_4)J_{\mathrm{CoFe}}-\sigma_3J_{\mathrm{FeFe}}-\sigma_5J_{\mathrm{CoCo}}\ , \tag{8}$$

where N is the total number of sites; $W_c=U_{\mathrm{CoCo}}+U_{\mathrm{FeFE}}-2U_{\mathrm{CoFe}}$ contains the information of the chemical interactions and all the exchange integrals J_{IJ} are assumed positive.

To take correlations between pairs of atoms we calculate the entropy in the Bethe approximation, which in our problem is given by

$$\frac{S}{kN}=\tfrac{7}{2}\sum_{\nu,I,m}P_\nu(I,m)\ln P_\nu(I,m)-4\sum_{I,J,m,n}P_{\alpha\beta}(I,m;J,n)\ln P_{\alpha\beta}(I,m;J,n)\ . \tag{9}$$

The equilibrium values of all the parameters are obtained by minimizing the free-energy subject to the constraints (3) and (4):

$$F=U-TS+\lambda\left[x-\tfrac{1}{2}\sum_{\nu,m}P_\nu(\mathrm{Co},m)\right]+\lambda_2\left[1-\sum_{I,J,m,n}P_{\alpha\beta}(I,m;J,n)\right]\ . \tag{10}$$

The minimization of the free energy was carried out by the natural iteration method.[16]

We applied the theory described above to the $\mathrm{Co}_x\mathrm{Fe}_y$ system. The coupling constant J_{FeFe} was estimated from pure iron and the three parameters J_{CoCo}, J_{CoFe}, and W_c were obtained by fitting two experimental values of the Curie temperature and one experimental value of the spatial-order-disorder transition temperature. In absolute temperature units they are $J_{\mathrm{FeFe}}=148$, $J_{\mathrm{CoCo}}=120.13$, $J_{\mathrm{CoFe}}=219.8$, and $W_c=449$.

In Fig. 1 we present our results for the whole phase diagram (solid lines). The agreement with the experimental observations is remarkably good. The observed asymmetry in the phase diagram is obtained in a natural way. It is driven by the magnetic interactions.

The temperature dependence of the long- and short-range-order parameters for $\mathrm{Co}_{0.3}\mathrm{Fe}_{0.7}$ is shown in Fig. 2. The order parameter η takes its maximum value

$$\eta_{\max}=\begin{cases}2x & 0\le x\le 0.5\ ,\\ 2y & 0.5\le x\le 1.0\ ,\end{cases} \tag{11}$$

at $T=0$. As the temperature increases η decreases and the spatial-order-disorder transformation takes place at the lowest temperature T_0 where $\eta=0$. The magnetic parameters are proportional to the magnetization of Co and Fe at the different sublattices. Above T_0, $m_\alpha(\mathrm{Fe})=m_\beta(\mathrm{Fe})=m(\mathrm{Fe})$, $m_\alpha(\mathrm{Co})=m_\beta(\mathrm{Co})=m(\mathrm{Co})$, and the Curie temperature T_C is reached when $m(\mathrm{Co})=m(\mathrm{Fe})=0$.

The short-range correlations are described by the parameters σ. The spatial short-range-order parameter σ_1 takes only negative values and at $T=0$ takes its minimum value (corresponding to the highest spatial ordering):

$$\sigma_{1,\min}=\begin{cases}-\dfrac{x}{y}, & 0\le x\le 0.5\ ,\\ -\dfrac{y}{x}, & 0.5\le x\le 1.0\ .\end{cases} \tag{12}$$

At $T=T_0$, σ_1 remains finite and goes to zero when $T\to\infty$. This means that above T_0 the system still retains some local order. The short-range-order spin correlations are given by σ_2, σ_3, σ_4, and σ_5. They also remain finite through the whole temperature range and present discontinuities in their first derivative at T_0 and T_C. It is worth noticing the high values of σ_1, σ_2, and σ_3 in the range of temperatures of the phase transformations. Lastly, we calculated the temperature dependence of the specific heat C. The results for $\mathrm{Co}_{0.5}\mathrm{Fe}_{0.5}$ are shown in Fig. 3 (solid curve). The experi-

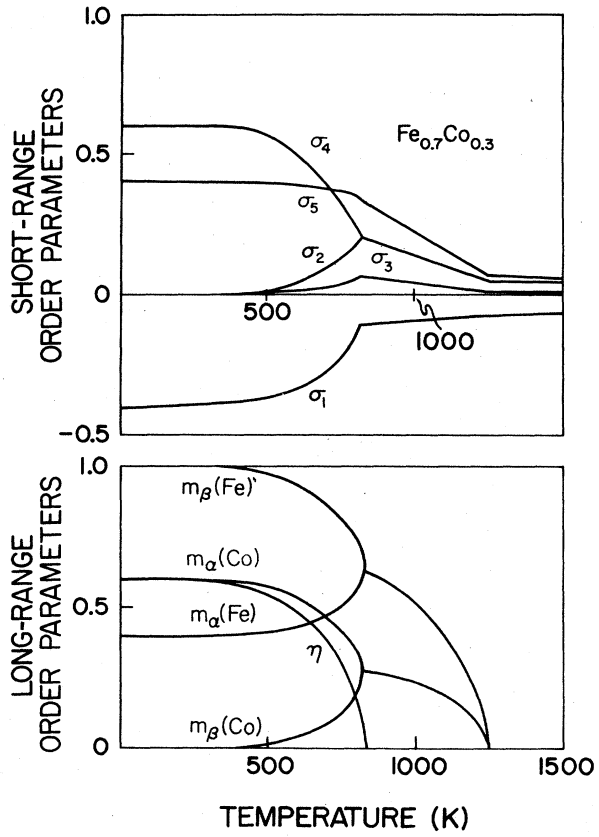

FIG. 2. Temperature dependence of the long- and short-range-order parameters for the $Co_{0.3}Fe_{0.7}$ alloy.

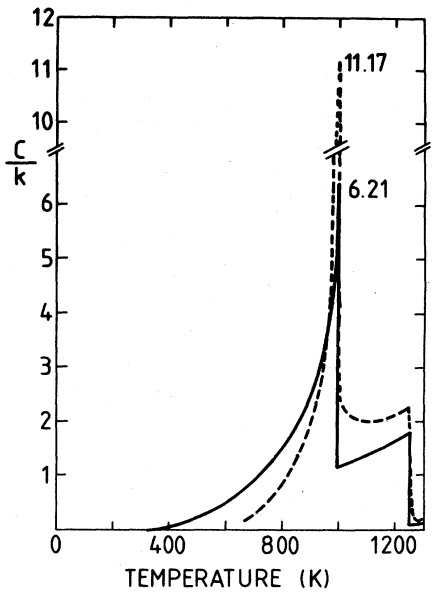

FIG. 3. Temperature dependence of the specific heat for a $Co_{0.5}Fe_{0.5}$ alloy. The short-dashed lines are the experimental results, and the solid lines are our results.

mental observations[17] are given by the short-dashed curve. Here, we subtracted the lattice and electronic contribution to C and we did not plot the observed anomaly in C due to the first-order lattice phase transition at T_C. Our calculation agrees better with the experiment, mainly above T_0. However, the value $C^-(T_0)$ is still small (6.21) as compared with the one observed (11.17).

In conclusion, we have shown that, in contrast to more sophisticated models, this simple-mean-field theory with two kinds of interactions can reproduce to a very good extend the whole phase diagram of Co_xFe_y alloys. This is a clear proof that in binary alloys with magnetic components one cannot ignore one or the other interaction. Here, we assumed that T_C coincides with the temperature where the system becomes unstable towards a crystal structure transformation. Some extrapolation shows a T_C larger than the one adopted here.[18] However, additional experiments are needed in order to determine more accurately the concentration dependence of T_C.

We calculated the short-range correlations and showed that they are big in the range of temperatures of the phase transition. However, local order has been examined[14] only in dilute $Fe_{0.02}Co_{0.98}$. Experiments in concentrated alloys would be desirable to check our theory. The weakest result is the temperature dependence of the specific heat. However, to our knowledge this is the best calculation reported for this system.

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*On leave from Departamento de Física, Centro de Investigación y Estudios Avanzados del Instituto Politécnico Nacional, Apartado Postal 14-740, 07000 México DF, Mexico.

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