

## Bragg-Williams model of Fe-Co order-disorder phase transformations in a strong magnetic field

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A modified Bragg-Williams statistical model with nearest-neighbor magnetic exchange and chemical interactions and an additional Zeeman energy term has been used to predict an increase in the critical ordering temperature ( $T_{\text{order}}$ ) of Fe-Co alloys in the presence of a large magnetic field ( $\Delta T_{\text{order}} \sim 20$  K near equiatomic composition for  $H=100$  T). The magnitude of the predicted  $\Delta T_{\text{order}}$  increases with increasing field and is only predicted to be significant ( $\Delta T_{\text{order}} \geq 2-3$  K near equiatomic) for  $H \geq 10$  T. The predicted shift in the ordering temperature is due to the higher average exchange interaction per atom in the ordered phase resulting in a larger theoretical Curie temperature as compared to the disordered phase. The dependence of the average magnetic moment of Fe on the degree of order was neglected in this work, however it is expected to contribute to an additional shift in  $T_{\text{order}}$ . Theoretical magnetization versus temperature curves are also presented for equiatomic FeCo subject to uniform applied magnetic fields. © 2006 American Institute of Physics. [DOI: 10.1063/1.2151821]

Nanocrystalline Fe-Co based alloys are technologically important materials.<sup>1</sup> In the bcc disordered A2 and CsCl-type ordered B2 structures ( $\alpha$  and  $\alpha'$ , respectively), the Curie temperatures are characteristically high, resulting in ferromagnetism persisting up to temperatures approaching 1000 °C. In addition, the largest currently obtainable saturation magnetization can be achieved in Fe-Co alloys and a low magnetocrystalline anisotropy results in low coercivity, high permeability, and low hysteresis losses. Because field annealing offers interesting possibilities for optimizing technical properties by inducing transverse magnetic anisotropy, we have decided to investigate the effects of strong magnetic fields on phase transformations in this alloy system. It is important to note that both chemical and magnetic interactions determine the equilibrium zero-field phase diagram in this system.

The order-disorder phase transformation in the Fe-Co system is a higher-order transformation that has been studied by many authors.<sup>2-5</sup> They have shown that the contribution of the magnetic interactions to the equilibrium phase diagram should not be neglected. A modified Bragg-Williams model has been used in past work<sup>2,3</sup> to predict the critical temperature for chemical ordering ( $T_{\text{order}}$ ) in this system as a function of composition. In this model, magnetic ordering and chemical ordering are taken into account simultaneously. Here we have added a Zeeman energy term to the model to predict how strong magnetic fields affect  $T_{\text{order}}$  in this system. Effects of applied magnetic fields on the equilibrium temperatures for the first-order bcc to fcc ( $\alpha \rightarrow \gamma$ ) phase transformation will be discussed in a future publication.

Following Eguchi *et al.*,<sup>2</sup> five parameters are introduced to describe the degree of long-range chemical and magnetic order in the system using a local moment Ising model in which each atomic moment is oriented either parallel or an-

tiparallel to an applied field. The definitions of various chemical and magnetic exchange energies ( $J_{\text{FeFe}}, J_{\text{CoCo}}, J_{\text{FeCo}}, V$ ) can be found in Ref. 2. The first parameter  $x$  describes the degree of long-range chemical order in the system and the other four parameters  $p, q, r,$  and  $s$  describe the distribution of atomic moment orientations in the sublattices ( $\alpha$  and  $\beta$  sites) of the spin system. The exact relationship between these parameters and the probabilities of site occupation ( $x$ ) or moment orientation ( $p, q, r, s$ ) of atoms on each sublattice are available in Ref. 3. We assumed nearest-neighbor exchange interaction ( $J_{\text{FeFe}}=265$  K,  $J_{\text{CoCo}}=360$  K, and  $J_{\text{FeCo}}=435$  K) and chemical interaction terms ( $V=812$  K) independent of both composition and temperature as estimated in Ref. 3. Note that a value of  $V=812$  K rather than the 820 K of Ref. 3 was used here to obtain better agreement with the experimental value of  $T_{\text{order}}$  for equiatomic composition reported in Ref. 6. The free energy of the system relative to the chemically and magnetically disordered state ( $x=p=q=r=s=0$ ) is calculated as a function of the order parameters, composition, temperature, and applied magnetic field. The free energy expression is detailed in Ref. 2, to which the additional magnetic energy term (1) is added to account for the presence of a uniform external magnetic field,

$$\begin{aligned} \Delta E_{\text{Zeeman}} &= -\vec{M} \cdot \vec{H} = -\frac{1}{V} \sum_i \vec{\mu}_i \cdot \vec{H} \\ &= -\frac{N}{4} [\mu_{\text{Fe}}(p+r) + \mu_{\text{Co}}(q+s)]H. \end{aligned} \quad (1)$$

In (1),  $N$  is the number of atoms per unit volume and  $\mu_{\text{Fe}}$  and  $\mu_{\text{Co}}$  are the atomic moments of Fe and Co atoms, respectively. The free energy is minimized to yield the equilibrium values of  $x, p, q, r,$  and  $s$ . In doing so, the characteristic equations (2)–(6) are obtained for an  $\text{Fe}_{1-\epsilon}\text{Co}_{1+\epsilon}$  alloy assuming the values of both  $\mu_{\text{Fe}}$  and  $\mu_{\text{Co}}$  are independent of  $x$ :

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$$x = \frac{kT}{8V} \ln \frac{(1 - \varepsilon + x + p)(1 - \varepsilon + x - p)(1 + \varepsilon + x + q)(1 + \varepsilon + x - q)}{(1 - \varepsilon - x + r)(1 - \varepsilon - x - r)(1 + \varepsilon - x + s)(1 + \varepsilon - x - s)}, \quad (2)$$

$$\frac{H}{2} \mu_{\text{Fe}} + J_{\text{FeFe}}r + J_{\text{FeCo}}q = \frac{kT}{4} \ln \frac{1 - \varepsilon + x + p}{1 - \varepsilon + x - p}, \quad (3)$$

$$\frac{H}{2} \mu_{\text{Co}} + J_{\text{CoCo}}s + J_{\text{FeCo}}p = \frac{kT}{4} \ln \frac{1 + \varepsilon + x + q}{1 + \varepsilon + x - q}, \quad (4)$$

$$\frac{H}{2} \mu_{\text{Fe}} + J_{\text{FeFe}}p + J_{\text{FeCo}}s = \frac{kT}{4} \ln \frac{1 - \varepsilon - x + r}{1 - \varepsilon - x - r}, \quad (5)$$

$$\frac{H}{2} \mu_{\text{Co}} + J_{\text{CoCo}}q + J_{\text{FeCo}}r = \frac{kT}{4} \ln \frac{1 + \varepsilon - x + s}{1 + \varepsilon - x - s}. \quad (6)$$

In Eqs. (2)–(6),  $k$  is the Boltzmann constant and  $J_{\text{FeFe}}$ ,  $J_{\text{CoCo}}$ ,  $J_{\text{FeCo}}$ , and  $V$  are expressed in units of energy. Although the moment of Co atoms does not depend significantly on the identity of nearest neighbors, the atomic moment of Fe in Fe-Co alloys is known to be dependent on the number of Co nearest neighbors.<sup>7,8</sup> Consequently, the average value of  $\mu_{\text{Fe}}$  depends on both composition and degree of order while  $\mu_{\text{Co}}$  is relatively constant with a value of  $\sim 1.8\mu_B$ . For the purpose of brevity, the variation of  $\mu_{\text{Fe}}$  with the degree of order is neglected in the present work unless otherwise specified and the average Fe moment for fully disordered FeCo (Ref. 8) is used for  $\mu_{\text{Fe}}$ . The additional complication has been accounted for through generalization of (2) in calculations not presented here. The estimated effect on the external field dependence of  $T_{\text{order}}$  was found to be secondary for most compositions. Nevertheless, these modifications to the model will be discussed in a future publication.

The order parameters were numerically calculated as functions of temperature by solving the characteristic equations (2)–(6). Figure 1 illustrates the plot of  $x$ ,  $p$ ,  $q$ ,  $r$ , and  $s$  for the equiatomic composition in the case of both  $H=0$  (dashed) and  $H=100$  T (solid). At zero field, the relevant ordering temperatures ( $T_{\text{order}}$  and  $T_{\text{Curie}}$ ) predicted by the model for equiatomic composition agree with the original calculations by Eguchi in Ref. 3. The effect of the applied field is to stabilize some degree of magnetic order ( $p, q, r, s \neq 0$ ) at temperatures above the theoretical Curie temperature. It can also be observed that at the equiatomic composition  $T_{\text{order}}$  increases by  $\sim 20$  K in the presence of the 100 T field, indicating that the ordered phase is stabilized relative to the disordered phase. The inset of Fig. 1 illustrates the shift of  $T_{\text{order}}$  as a function of applied field for the equiatomic composition. Notice that while deviations from linearity are observed for relatively small applied fields ( $H \leq 10$ – $20$  T), the shift in the ordering temperature scales approximately linearly with increasing field in the high-field regime.

It should be reiterated that the  $T_{\text{Curie}}$  indicated in Fig. 1 is the theoretical value predicted by the model for thermal equilibrium.

Because  $T_{\text{order}} < T_{\text{Curie}}$  in this system, the equilibrium value of  $T_{\text{Curie}}$  corresponds to that of the disordered phase. In reality, the  $T_{\text{Curie}}$  of Fig. 1 cannot be observed experimentally for equiatomic composition as the bcc (ferromagnetic) to fcc (paramagnetic) phase transformation results in a loss of ferromagnetism and occurs at a temperature below  $T_{\text{Curie}}$  of the disordered  $\alpha$  phase. All theoretical Curie temperatures stated in this work correspond to the  $T_{\text{Curie}}$  that would be observed if the phase under consideration remained stable up to the temperature of interest.

Because the estimated value of  $J_{\text{FeCo}}$  is greater than both  $J_{\text{FeFe}}$  and  $J_{\text{CoCo}}$  in this model, the effective exchange interaction in the chemically ordered state is larger than that of the disordered state ( $J_{\text{eff}} = J_{\text{FeCo}}$  for  $x=1$  as compared to  $J_{\text{eff}} = \frac{1}{4}J_{\text{FeFe}} + \frac{1}{4}J_{\text{CoCo}} + \frac{1}{2}J_{\text{FeCo}}$  for  $x=0$  at equiatomic composition). The theoretical Curie temperature of the fully ordered phase is therefore predicted to be larger than the theoretical Curie temperature of the fully disordered phase ( $\sim 1720$  and  $\sim 1500$  K, respectively) resulting in a greater degree of magnetic order at finite temperatures below the Curie temperature of the maximally ordered alloy in zero field. A larger magnetization is therefore predicted for the ordered phase in the vicinity of the zero-field critical ordering temperature, and the reduction in free energy of the maximally ordered phase due to an applied magnetic field is larger than that of the disordered phase. As a result, the ordered state is stabilized relative to the disordered state and a shift in  $T_{\text{order}}$  to higher temperatures is observed. In support of the previous statements, the difference between the Curie temperature of the ordered and disordered phases disappears entirely for a hypothetical case in which the ordered and disordered states are assigned the same effective exchange interaction per atom ( $J_{\text{FeFe}} = J_{\text{CoCo}} = J_{\text{FeCo}}$ ). In addition, a shift in  $T_{\text{order}}$  cannot be induced through the application of a field.

The critical ordering temperatures were calculated for a range of compositions in order to observe how the order-disorder phase boundary changes as a function of applied field. Figure 2 illustrates the calculated phase boundary for  $H=0$ , 50, and 100 T as well as experimentally measured critical temperatures in the absence of a field.<sup>6</sup> Except for the fact that the peak in the experimental phase boundary does not occur at equiatomic composition, the model reproduces the variation in the ordering temperature reasonably well with composition at zero field, as first shown in Ref. 3. It is observed that the shift in the phase boundary due to an applied field is fairly symmetric and a maximum at the equiatomic composition.

The model presented here has also been used to predict the magnetization behavior of the system in the presence of strong magnetic fields as a function of temperature. The magnetization as a function of temperature can be calculated

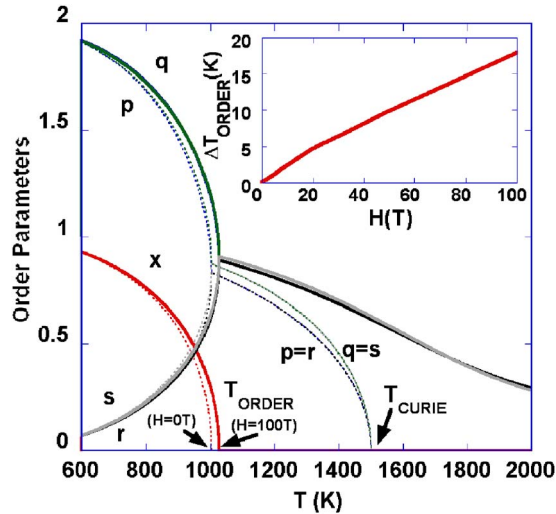


FIG. 1. (Color online) Order parameters  $x$ ,  $p$ ,  $q$ ,  $r$ , and  $s$  as a function of temperature for both  $H=0$  (dotted lines) and  $H=100$  T (solid lines). The inset illustrates the shift in the ordering temperature as a function of  $H$ .

from the equilibrium values of  $p$ ,  $q$ ,  $r$ , and  $s$  (see Fig. 1 for equiatomic) according to the following expression:

$$M = \frac{N}{4} [\mu_{\text{Fe}}(p+r) + \mu_{\text{Co}}(q+s)]. \quad (7)$$

Figure 3 shows the theoretical magnetization curves for an equiatomic alloy in thermal equilibrium with applied fields of  $H=0, 1, 10, 50$ , and  $100$  T. A kink in the magnetization curve is observed at the  $T_{\text{order}}$  due to the larger magnetization of the chemically ordered phase ( $x=1$ ). The kink is observed to shift to higher temperatures with increasing applied field as  $T_{\text{order}}$  increases. Although the variation of the average atomic moment of Fe with degree of order was neglected in the previous discussion, the magnetization curves of Fig. 3 do account for both the higher theoretical Curie temperature and higher average Fe moment of the ordered phase.

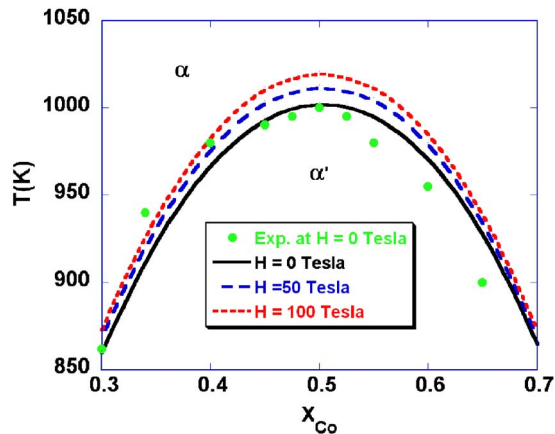


FIG. 2. (Color online) Theoretically predicted order-disorder phase boundary as a function of applied magnetic field and comparison with experimental data (Ref. 6).

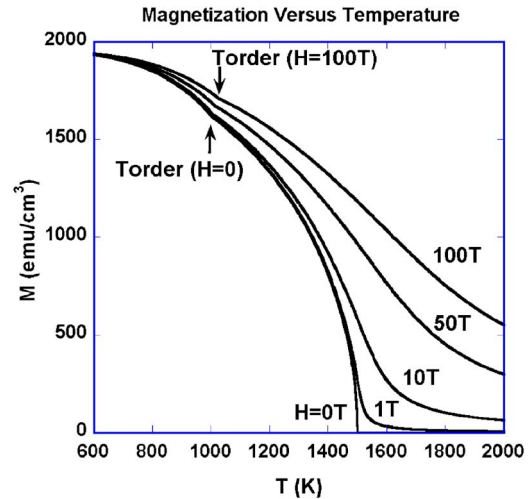


FIG. 3. (Color online) Theoretically predicted magnetization curves of equiatomic FeCo as a function of temperature for several applied magnetic fields.

A modified Bragg-Williams model was used to predict the critical ordering temperatures for the bcc to CsCl-type phase transformation in binary FeCo alloys taking into account nearest-neighbor chemical interactions, magnetic exchange interactions, and the Zeeman energy of the system in uniform external fields. A shift of the order-disorder equilibrium phase boundary was observed in strong applied fields resulting in stabilization of the ordered phase relative to the disordered phase. Because the dependence of Fe moment on degree of order was neglected, the shift calculated here is due entirely to the larger effective exchange interaction per atom resulting in a larger theoretical Curie temperature of the ordered phase relative to the disordered phase. Even though short-range-order effects and the variation of  $\mu_{\text{Fe}}$  as a function of the degree of order were neglected in this work, it is believed that the qualitative features of the predictions (stabilization of chemical order in the presence of strong applied magnetic fields) remain valid when these additional complications are taken into account.

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