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The Gaussian average method applied to phase transitions in a dilute magnetic alloy

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Abstract. The functional integral formalism which has been applied to the Ising model of ferromagnetism is used here to treat the interaction of the annealing process and magnetization in a dilute magnetic alloy AB (magnetic component A). Only the possibility of 50 : 50 component ordering is considered. A variational principle is derived which leads to an upper limit for the free energy of the model. The approximation obtained by minimizing this upper limit would appear to be an extension of the Horwitz–Callen theory.

Order–disorder and magnetic transition curves are presented for three values of the ratio R of the spin-exchange energy to the mixing energy. Component ordering is found to inhibit the magnetic transition in alloys which are rich in component B.

1. Introduction

Extensions of the Ising model calculations to dilute magnetic alloys have been made for the case of a random distribution of magnetic atoms by Morgan and Rushbrooke (1961), Sato *et al.* (1959) and Bell and Fairbairn (1961), in the latter case calculations also being made for the presence of short-range component ordering. Recently a number of papers have appeared which discuss the interaction of magnetization and long-range component ordering in binary alloys. Let us consider such an alloy AB, for which the crystal structure is body-centred cubic, A being the magnetic component. If the range of the magnetic force is just less than the second-nearest-neighbour separation, then for an alloy of composition 50% A one would expect a magnetic transition to occur at a sufficiently low temperature, provided no 50 : 50 component ordering were present. If the components are ordered on the two equivalent sublattices, then the separation of the magnetic atoms is too great for the magnetic phase transition to occur. This interaction of the annealing process and magnetization is the subject of the present paper. We are not concerned with the effect of variation of atomic magnetic moments with local environment which is the province of crystal-field theory, but only with the statistical mechanics of what is essentially a ternary solution.

Houska (1963) and Bell and Lavis (1965) have attacked the problem using the Bragg–Williams approximation. This work has been extended by Lavis and Fairbairn (1966) to include some short-range correlations using a modification of the Bethe method. Here twelve field parameters are introduced and determined self-consistently. The general features of the temperature–concentration phase diagrams reflect the expected inhibition of magnetization by long-range component ordering. The approximations mentioned above are uncontrolled in the sense that the error committed cannot be estimated or minimized.

Following the work of Muhlschlegel and Zittartz (1963) and Thompson (1965) on the one-component Ising model, we have formulated the alloy problem in terms of a functional integral for the partition function. The virtue of this approach is that one is led to a variational principle for the free energy of the system. As a trial function, we adopt parametrized mean-field expressions which imply the same mathematical mechanism for the second-order phase transitions in the alloy as that of the spherical model of Berlin and Kac (1952).

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2. Formulation

We take over the regular model of an alloy in which the components are distributed over N fixed lattice sites. Let the number of A and B atoms be N_A and N_B respectively. Associated with each lattice site \mathbf{i} there is a variable μ_i such that

$$\mu_i = \begin{cases} +1 & \text{A at site } \mathbf{i} \\ -1 & \text{B at site } \mathbf{i}. \end{cases}$$

The interaction energy of atoms on sites \mathbf{i}, \mathbf{j} may be written as E_{AA}^{ij} , E_{AB}^{ij} or E_{BB}^{ij} according to the pair involved. If we define $U_{ij} = -\frac{1}{4}(E_{AA}^{ij} + E_{BB}^{ij} - 2E_{AB}^{ij})$, the Hamiltonian of the model is

$$H = H_0 - \frac{1}{2} \sum_{ij} U_{ij} \mu_i \mu_j.$$

H_0 is independent of the atomic configuration but depends on composition. For 50 : 50 ordering to be possible it is necessary that $U_{ij} < 0$, where (\mathbf{i}, \mathbf{j}) are nearest neighbours. We incorporate the Ising model of the magnetic interaction by the assumption that the energy of an AA pair is $E_{AA}^{ij} - V_{ij} s_i s_j$, where $s_i = \pm 1$ depending on the spin state. In terms of the quantity $t_i = \frac{1}{2} s_i (1 + \mu_i)$ the Hamiltonian may be written

$$H = H_0 - \frac{1}{2} \sum_{ij} (V_{ij} t_i t_j + U_{ij} \mu_i \mu_j).$$

For a quadratic form such as this, the Boltzmann factor and hence the canonical partition function Z may be written as a functional integral or Gaussian average (Thompson 1965):

$$\exp(-\beta H) = \langle \prod_i \exp(\phi_i \mu_i + \psi_i t_i) \rangle_G$$

where ϕ_i, ψ_i may be termed the ordering and magnetic fields respectively. The average denoted by $\langle \rangle_G$ is over a Gaussian distribution of variables x_α , the fields ϕ_i and ψ_i being linear forms in the set x_α . We define the Fourier expansions

$$V_{ij} = N^{-1} \sum_{\mathbf{k}} v(\mathbf{k}) \exp\{i\mathbf{k} \cdot (\mathbf{i} - \mathbf{j})\}$$

$$U_{ij} = N^{-1} \sum_{\mathbf{k}} u(\mathbf{k}) \exp\{i\mathbf{k} \cdot (\mathbf{i} - \mathbf{j})\}$$

where the vectors \mathbf{k} are the N wave vectors appropriate to a translationally symmetric lattice with periodic boundary conditions. The $\{x_\alpha\}$ are then conveniently chosen as the set of $4N$ variables labelled $\{x_k; y_k; p_k; q_k\}$;

$$\psi_i = \sum_{\mathbf{k}} \{2\beta v(\mathbf{k})\}^{1/2} \{x_k \cos(\mathbf{k} \cdot \mathbf{i}) + y_k \sin(\mathbf{k} \cdot \mathbf{i})\}$$

$$\phi_i = \sum_{\mathbf{k}} \{2\beta u(\mathbf{k})\}^{1/2} \{p_k \cos(\mathbf{k} \cdot \mathbf{i}) + q_k \sin(\mathbf{k} \cdot \mathbf{i})\}.$$

Summing over configurations of the ternary solution we obtain

$$Z = (2\pi i)^{-1} \oint_C 2^{-N_B \zeta} \zeta^{-N_B - 1} d\zeta \langle \prod_i \{\exp(\phi_i + \psi_i) + \exp(\phi_i - \psi_i) + 2\zeta \exp(-\phi_i)\} \rangle_G$$

in which the ζ integration selects the alloy of fractional composition c_A, c_B by the requirement

$$N^{-1} \sum_i \mu_i = c_A - c_B$$

where $c_A = N_A/N$, $c_B = N_B/N$ and C is a closed curve surrounding the point $\zeta = 0$. This may be written as the Gaussian average of the expression

$$(2\pi i)^{-1} \oint_C 2^{2N - N_B \zeta} \zeta^{2N - N_B} d(\log \zeta) \prod_i (\cosh \psi_i)^{1/2} \cosh\{\phi_i + \frac{1}{2} \log(\zeta^{-1} \cosh \psi_i)\}.$$

By means of the change of variable

$$p_0 - \{8\beta u(0)\}^{-1/2} \log \zeta \rightarrow p_0$$

in the p_0 integration, we obtain

$$Z = (2\pi t)^{-1} \left(\frac{2N}{\pi}\right)^{2N} 2^{-N_B} \int \prod_{\alpha} \exp(-Nx_{\alpha}^2) dx_{\alpha} \prod_i (\cosh \psi_i)^{1/2} \cosh(\phi_i + \frac{1}{2} \ln \cosh \psi_i) \\ \times \oint d p_0 d(\log \zeta) \exp \left\{ -N \left(\left[p_0 + \frac{\log \zeta}{\{8\beta u(0)\}^{1/2}} \right]^2 + \frac{1}{2} (1 - 2c_A) \log \zeta \right) \right\}$$

where x_{α} is used to denote all the random variables except p_0 . The ζ integration may now be effected by the steepest descent method giving

$$\frac{1}{2} (1 - 2c_A) + \{8\beta u(0)\}^{-1/2} [p_0 + \{8\beta u(0)\}^{-1/2} \log \zeta_s] = 0$$

where $\zeta = \zeta_s$ is the saddle point. After a little algebra we obtain

$$Z = \left(\frac{N}{\pi}\right)^{2N} g \int \prod_{\alpha} dx_{\alpha} dp_0 e^{-NF} \quad (1)$$

where

$$F = (1 - 2c_A) p_0 \{2\beta u(0)\}^{1/2} + \sum_{\alpha} x_{\alpha}^2 - N^{-1} \sum_i \frac{1}{2} \ln \cosh \psi_i + \ln \cosh(\phi_i + \frac{1}{2} \ln \cosh \psi_i)$$

and

$$g = \left(\frac{\beta |u(0)|}{2\pi N}\right)^{1/2} 2^{2N - N_B + 1} \exp\{\frac{1}{2} N \beta u(0) (1 - 2c_A)^2\}.$$

If the mixing energy U_{ij} is between nearest-neighbour sites only, then the condition $U_{ij} < 0$ is equivalent to $u(0) < 0$ and the p_0 integration is convergent. For other ranges of interaction we assume that the condition $u(0) < 0$ is still satisfied.

3. Mean-field approximations

A crude approximation to the functional integral (1) is found by replacing the fields ψ_i and ϕ_i by their average values over the whole lattice, thus

$$\bar{\psi} = N^{-1} \sum_i \psi_i = \{2\beta v(0)\}^{1/2} x_0$$

$$\bar{\phi} = N^{-1} \sum_i \phi_i = \{2\beta u(0)\}^{1/2} p_0.$$

Such a substitution will not lead to component ordering which is essentially a nearest-neighbour effect and therefore presumably associated with the \mathbf{k} components of ϕ_i near the edge of the first basic cell of the reciprocal lattice. Integration over the random variables other than x_0 and p_0 is immediate, and from the saddle-point equations for these two variables we obtain

$$2x_0 = \{2\beta v(0)\}^{1/2} c_A \tanh\{2\beta v(0)\}^{1/2} x_0. \quad (2)$$

As shown by Thompson the magnetization is proportional to the value of x_0 . Equation (2) has non-zero solutions if $\beta v(0) c_A > 1$ which is the Curie-Weiss dilution law. The Bell and Lavis solution may be obtained by dividing the lattice sum into two parts $\Sigma_{(1)}$ and $\Sigma_{(2)}$ each representing a summation over a sublattice. The mean values over these sublattices are

$$\bar{\psi}_{(1)} = 2N^{-1} \sum_{(1)} \psi_i = \{2\beta v(0)\}^{1/2} x_0 + \{2\beta v(\kappa)\}^{1/2} x_{\kappa} \\ \bar{\psi}_{(2)} = 2N^{-1} \sum_{(2)} \psi_i = \{2\beta v(0)\}^{1/2} x_0 - \{2\beta v(\kappa)\}^{1/2} x_{\kappa}$$

where κ belongs to the set of vectors κ , for which $\exp(i\kappa \cdot \mathbf{s}) = -1$, \mathbf{s} being the vector displacement of the sublattices (see appendix). There are similar expressions for $\bar{\phi}_{(1)}$ and

$\bar{\phi}_{(2)}$. Integration over all variables except $x_0, x_\kappa, p_0, p_\kappa$ is immediate and we may obtain, from the saddle-point equations for the latter,

$$\sigma = \{8\beta u(\kappa)c_A\}^{-1} \log \left\{ \frac{(2c_A\sigma + 1)^2 - (c_A - c_B)^2 \cosh \bar{\psi}_{(1)}}{(2c_A\sigma - 1)^2 - (c_A - c_B)^2 \cosh \bar{\psi}_{(2)}} \right\} \quad (3)$$

$$M^{(a)} = \frac{1}{2}c_A N(1 + \sigma) \tanh \bar{\psi}_{(1)} \quad (4)$$

$$M^{(b)} = \frac{1}{2}c_A N(1 - \sigma) \tanh \bar{\psi}_{(2)} \quad (5)$$

where

$$\sigma = \frac{p_\kappa}{c_A \{2\beta u(\kappa)\}^{1/2}}$$

$$M^{(a)} = \frac{1}{2}N \left[\frac{x_0}{\{2\beta v(0)\}^{1/2}} + \frac{x_\kappa}{\{2\beta v(\kappa)\}^{1/2}} \right]$$

and

$$M^{(b)} = \frac{1}{2}N \left[\frac{x_0}{\{2\beta v(0)\}^{1/2}} - \frac{x_\kappa}{\{2\beta v(\kappa)\}^{1/2}} \right]$$

are the degree of component ordering and magnetization of the two sublattices as defined by Bell and Lavis. A non-zero solution to (3) in the absence of magnetization will only occur when $\beta u(\kappa) > (4c_A c_B)^{-1}$.

4. The root-mean-square field approximation

One way of introducing some short-range spin correlations is to use the r.m.s. field

$$\tilde{\psi} = (N^{-1} \sum_l \psi_l^2)^{1/2} = \left\{ \sum_k \beta v(k) (x_k^2 + x_k x_{-k} + y_k^2 - y_k y_{-k}) \right\}^{1/2}.$$

We also define

$$\bar{\phi} = \{N^{-1} \sum_l (\phi_l - \bar{\phi})^2\}^{1/2} = \left\{ \sum_{k \neq 0} \beta u(k) (p_k^2 + p_k p_{-k} + q_k^2 - q_k q_{-k}) \right\}^{1/2}.$$

In order to evaluate this approximation we introduce continuous variables ψ and ϕ and complex variables z and t , so that the mean-square fields enter the functional integral via Dirac δ functions. The calculation is parallel to earlier work (Thompson 1965) where details of the mechanism of the second-order transition may be found. The saddle-point equations resulting from these calculations are

$$1 - 2c_A + \frac{1}{2} \tanh\left(\frac{1}{2} \ln \cosh \psi + \bar{\phi} - \phi\right) + \frac{1}{2} \tanh\left(\frac{1}{2} \ln \cosh \psi + \bar{\phi} + \phi\right) = 0 \quad (6)$$

$$-2z\psi = c_A \tanh \psi \quad (7)$$

$$2\phi = \frac{1}{2} \ln \left(\frac{c_A - t\phi}{c_A + t\phi} \frac{c_B - t\phi}{c_B + t\phi} \right) \quad (8)$$

$$\psi^2 = (2N)^{-1} \sum_k \frac{2\beta v(k)}{1 + 2\beta z v(k)} \quad (9)$$

$$\phi^2 = (2N)^{-1} \sum_k \frac{2\beta u(k)}{1 + 2\beta t u(k)}. \quad (10)$$

This approximation is clearly unsatisfactory as it contains no coupling of magnetization and component ordering variables. However, $\phi = 0$ is always a solution to (8) corresponding to the absence of component ordering and hence the magnetization equations can be regarded as describing the case of a randomly dilute alloy. The critical temperature for this case is given in figure 1 for a body-centred cubic lattice with nearest-neighbour interactions.

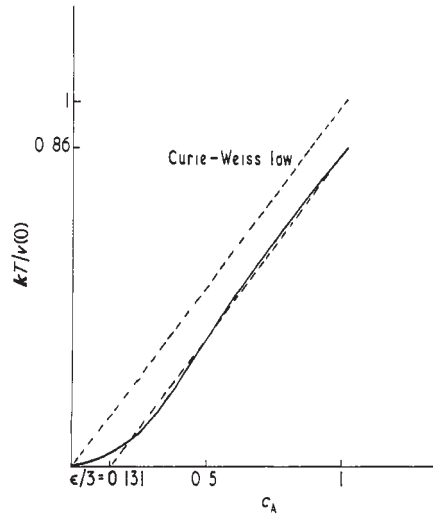


Figure 1. Root-mean-square approximation for the Curie temperature.

5. Variational principle

As the basis of a trial function for the free energy we choose the following parametrized mean-square fields:

$$\begin{aligned} \{\tilde{\psi}^2\} &= 2\beta\tilde{v}(0)(x_0 - a)^2 + \sum_{k \neq 0} \beta\tilde{v}(k)(x_k^2 + y_k^2 + x_k x_{-k} - y_k y_{-k}) \\ \{\tilde{\phi}^2\} &= 2\beta\tilde{u}(k)(p_k - b)^2 + \sum_{k \neq 0, \kappa} \beta\tilde{u}(k)(p_k^2 + q_k^2 + p_k p_{-k} - q_k q_{-k}). \end{aligned}$$

Variable a has the character of the molecular field and by analogy b may be thought of as the 'ordering field' as envisaged by Bragg and Williams (1934).

The functions $\tilde{u}(k)$ and $\tilde{v}(k)$ satisfy

$$\tilde{u}(k) = \tilde{u}(-k), \quad \tilde{v}(k) = \tilde{v}(-k).$$

The partition function in terms of these fields may be written

$$Z_2 = -(2\pi)^2 \left(\frac{N}{\pi}\right)^{2N} g \int \dots \int \prod_{\alpha} dx_{\alpha} dp_0 dz dt d\psi^2 d\phi^2 \exp(-NF_2)$$

where

$$\begin{aligned} F_2 &= \sum_{\alpha} x_{\alpha}^2 - i(1 - 2c_A)p_0\{2\beta|u(0)|\}^{1/2} - \frac{1}{2} \ln \cosh \psi - \frac{1}{2} \ln \cosh(\frac{1}{2} \ln \cosh \psi + \bar{\phi} - \phi) \\ &\quad - \frac{1}{2} \ln \cosh(\frac{1}{2} \ln \cosh \psi + \bar{\phi} + \phi) - z\psi^2 - t\phi^2 + z\{\tilde{\psi}^2\} + t\{\tilde{\phi}^2\}. \end{aligned}$$

The problem now is to express the exact partition function given by (1) in terms of Z_2 . We define the averaging process

$$\langle\langle f \rangle\rangle = -Z_2^{-1} (2\pi)^2 \left(\frac{N}{\pi}\right)^{2N} g \int \dots \int \prod_{\alpha} dx_{\alpha} dp_0 dz dt d\psi^2 d\phi^2 f \exp(-NF_2)$$

and hence may write

$$Z = Z_2 \langle\langle \exp\{N(F_2 - F)\} \rangle\rangle.$$

Therefore

$$\log Z > \log Z_2 + \langle\langle N(F_2 - F) \rangle\rangle$$

and the Helmholtz free energy

$$A < -(\beta N)^{-1} \log Z_2 + \langle\langle F - F_2 \rangle\rangle.$$

The parameters a , b , $\hat{u}(k)$, $\hat{v}(k)$ are determined by requiring that A be stationary with respect to variations.

When evaluating Z_2 we need to diagonalize the quadratic form

$$\sum_{k \neq 0} x_k^2 + y_k^2 + z\{\tilde{\psi}^2\} + \sum_{k \neq 0, \kappa} p_k^2 + q_k^2 + t\{\tilde{\phi}^2\}$$

obtaining the eigenvalues

$$1 + 2\beta z \tilde{v}(k) \equiv \lambda_k \quad (k \neq 0), \quad 1 + 2\beta t \hat{u}(k) \equiv \chi_k \quad (k \neq 0, \kappa), \quad 1 \quad (\sim 2N \text{ times}).$$

The terms of F_2 in x_0 and p_κ are

$$x_0^2 + 2\beta z \tilde{v}(0)(x_0 - a)^2 + p_\kappa^2 + 2\beta t \hat{u}(\kappa)(p_\kappa - b)^2 \quad (11)$$

so that the saddle-point method is exact for integration over these variables. Let

$$\tilde{f}(z) = (2N)^{-1} \sum_k \log\{1 + 2\beta z \tilde{v}(k)\}$$

$$\tilde{g}(t) = (2N)^{-1} \sum_{k \neq 0} \log\{1 + 2\beta t \hat{u}(k)\}.$$

Then

$$\begin{aligned} \tilde{F}_2 = & \tilde{f}(z) + \tilde{g}(t) - z\psi^2 - t\phi^2 - i(1 - 2c_A)p_0\{2\beta|u(0)|\}^{1/2} \\ & - \frac{1}{2} \ln \cosh \psi - \frac{1}{2} \ln \cosh(\frac{1}{2} \ln \cosh \psi + \bar{\phi} - \phi) \\ & - \frac{1}{2} \ln \cosh(\frac{1}{2} \ln \cosh \psi + \bar{\phi} + \phi) + (\lambda_0 - 1)\lambda_0^{-1}a^2 \\ & + (\chi_\kappa - 1)\chi_\kappa^{-1}b^2. \end{aligned}$$

As in the r.m.s. approximation the saddle-point equations for the five variables z , t , ψ , ϕ , p_0 may be written

$$G^{(1)} \equiv (1 - 2c_A) + \frac{1}{2} \tanh(\frac{1}{2} \ln \cosh \psi + \bar{\phi} + \phi) + \frac{1}{2} \tanh(\frac{1}{2} \ln \cosh \psi + \bar{\phi} - \phi) = 0 \quad (12)$$

$$G^{(2)} \equiv \tilde{f}(z) - \psi^2 + 2\beta \tilde{v}(0)a^2\lambda_0^{-2} = 0 \quad (13)$$

$$G^{(3)} \equiv \tilde{g}(t) - \phi^2 + 2\beta \hat{u}(\kappa)b^2\chi_\kappa^{-2} = 0 \quad (14)$$

$$G^{(4)} \equiv 2z\psi + c_A \tanh \psi = 0 \quad (15)$$

$$G^{(5)} \equiv 2\phi - \frac{1}{2} \log\left(\frac{c_A - t\phi}{c_A + t\phi} \frac{c_B - t\phi}{c_B + t\phi}\right) = 0. \quad (16)$$

Details of the calculation of $\langle F \rangle$ involve a straightforward modification of earlier work (Thompson 1965) and so we state the result only:

$$\begin{aligned} \langle F \rangle = & \frac{1}{2} \pi^{-1/2} \int \exp(-X^2) dX \ln \cosh[\sqrt{2\Psi X + \{2\beta v(0)\}^{1/2}x_0}] \\ & + (2\pi)^{-1} \iint \exp\{-(X^2 + P^2)\} dX dP \ln \cosh(\bar{\phi} + \{2\beta u(\kappa)\}^{1/2}p_\kappa + \sqrt{2\Phi P} \\ & + \frac{1}{2} \ln \cosh[\sqrt{2\Psi X + \{2\beta v(0)\}^{1/2}x_0}]) \\ & + (2\pi)^{-1} \iint \exp\{-(X^2 + P^2)\} dX dP \ln \cosh(\bar{\phi} - \{2\beta u(\kappa)\}^{1/2}p_\kappa + \sqrt{2\Phi P} \\ & + \frac{1}{2} \ln \cosh[\sqrt{2\Psi X + \{2\beta v(0)\}^{1/2}x_0}]) \end{aligned}$$

where x_0 , p_κ are at their saddle-point values which from (11) are

$$x_0 = 2\beta z \tilde{v}(0)a\lambda_0^{-1}$$

$$p_\kappa = 2\beta t \hat{u}(\kappa)b\chi_\kappa^{-1}$$

and

$$\Psi^2 = N^{-1} \sum_k \beta v(k)\lambda_k^{-1}, \quad \Phi^2 = N^{-1} \sum_k \beta u(k)\chi_k^{-1}.$$

Defining $G = \langle F - F_2 \rangle$ we require

$$\delta(F_2 + G) = 0.$$

6. Variational equations

Let e denote one of the four variational parameters; the variational equations simplify with the help of the saddle-point conditions to

$$\frac{\partial F_2}{\partial e} + \frac{\partial G}{\partial e} + \frac{\partial G}{\partial z} \frac{\partial z}{\partial e} + \frac{\partial G}{\partial t} \frac{\partial t}{\partial e} + \frac{\partial G}{\partial \phi} \frac{\partial \phi}{\partial e} + \frac{\partial G}{\partial \psi} \frac{\partial \psi}{\partial e} + \frac{\partial G}{\partial \bar{\phi}} \frac{\partial \bar{\phi}}{\partial e} = 0. \quad (17)$$

But, by the saddle-point equations (15) and (16), t , ϕ depend only on the pair b , $\bar{u}(k)$, and, by (13) and (14), z , ψ depend only on a , $\bar{v}(k)$. Thus in practice (17) has four terms on the right rather than six. The mean field $\bar{\phi}$ is given from the saddle-point equations by

$$\exp(2\bar{\phi}) = \cosh \psi \left\{ \frac{c_B^2 - (t\phi)^2}{c_A^2 - (t\phi)^2} \right\}^{1/2}.$$

We adopt the customary suffix notation for partial derivatives, obtaining

$$\frac{\partial z}{\partial e} = - \frac{G_\psi^{(4)}}{G_z^{(4)}} \frac{\partial \psi}{\partial e} = - \frac{G_e^{(2)} G_\psi^{(4)}}{G_\psi^{(4)} G_z^{(2)} - G_\psi^{(2)} G_z^{(4)}} \quad (18)$$

$$\frac{\partial t}{\partial e} = - \frac{G_\phi^{(5)}}{G_t^{(5)}} \frac{\partial \phi}{\partial e} = - \frac{G_e^{(3)} G_\phi^{(5)}}{G_\phi^{(5)} G_t^{(3)} - G_\phi^{(3)} G_t^{(5)}}. \quad (19)$$

Also, if e is a magnetic parameter,

$$\frac{\partial \bar{\phi}}{\partial e} = - \frac{G_\psi^{(1)}}{G_\phi^{(1)}} \frac{\partial \psi}{\partial e}$$

whereas, if it is an ordering parameter, then

$$\frac{\partial \bar{\phi}}{\partial e} = - \frac{G_\phi^{(1)}}{G_\psi^{(1)}} \frac{\partial \phi}{\partial e}.$$

In the thermodynamic limit the equations (17) reduce to

$$\begin{aligned} \frac{\partial}{\partial a} (F_2 + G) \frac{1}{G_a^{(2)}} &= \frac{\partial}{\partial \bar{v}(k)} (F_2 + G) \frac{1}{G_{\bar{v}(k)}^{(2)}} = \frac{\partial}{\partial \bar{v}(0)} (F_2 + G) \frac{1}{G_{\bar{v}(0)}^{(2)}} \\ \frac{\partial}{\partial b} (F_2 + G) \frac{1}{G_b^{(3)}} &= \frac{\partial}{\partial \bar{u}(k)} (F_2 + G) \frac{1}{G_{\bar{u}(k)}^{(3)}} = \frac{\partial}{\partial \bar{u}(\kappa)} (F_2 + G) \frac{1}{G_{\bar{u}(\kappa)}^{(3)}}. \end{aligned}$$

Before writing these equations explicitly it is convenient to define four double integrals. Using the preliminary definitions

$$\langle f \rangle_E = \pi^{-1} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dX dP \exp\{-(X^2 + P^2)\} f(X, P)$$

$$A^\pm \equiv \frac{1}{2} \tanh(\bar{\phi} \pm \{2\beta u(\kappa)\}^{1/2} p_\kappa + \Phi \sqrt{2P} + \frac{1}{2} \ln \cosh[\sqrt{2\psi} X + \{2\beta v(0)\}^{1/2} x_0])$$

then

$$K_1 = \langle A^+ - A^- \rangle_E$$

$$K_2 = \frac{1}{\sqrt{2}} \langle P(A^+ + A^-) \rangle_E$$

$$H_1 = \frac{1}{2} \langle \tanh[\sqrt{2\psi} X + \{2\beta v(0)\}^{1/2} x_0] (1 + A^+ + A^-) \rangle_E$$

$$H_2 = \frac{1}{2} \langle \sqrt{2X} \tanh[\sqrt{2\psi} X + \{2\beta v(0)\}^{1/2} x_0] (1 + A^+ + A^-) \rangle_E.$$

Hence the variational equations become

$$\frac{2}{\{2\beta v(0)\}^{1/2}} \frac{\lambda_0 - 1}{\lambda_0} a = H_1 \quad (20)$$

$$-2z\beta\tilde{v}(k) = \Psi^{-1}\beta v(k)H_2 \quad (21)$$

$$\frac{2}{\{2\beta u(\kappa)\}^{1/2}} \frac{\chi_\kappa - 1}{\chi_\kappa} b = K_1 \quad (22)$$

$$-2t\beta\tilde{u}(k) = \Phi^{-1}\beta u(k)K_2. \quad (23)$$

In the limit $c_A = 1$, (20) and (21) are the same as those of Horwitz and Callen (1961). Similarly for $v(k) = 0$, all k and $c_A = c_B = \frac{1}{2}$, (22) and (23) represent the corresponding solution for the mathematically identical binary alloy problem.

In general it is possible to show that the magnetization m per magnetic atom A is given by

$$m = \frac{2x_0}{\{2\beta v(0)\}^{1/2}} \frac{1}{c_A} = \frac{2}{\{2\beta v(0)\}^{1/2}} \frac{\lambda_0 - 1}{\lambda_0} \frac{a}{c_A}.$$

Also, from the stationarity of the free energy upper limit and the saddle-point equations it follows that the degree of component ordering σ is given by

$$\sigma = \frac{p_\kappa}{\{2\beta u(\kappa)\}^{1/2}} \frac{1}{c_A} = \frac{1}{\{2\beta u(\kappa)\}^{1/2}} \frac{\chi_\kappa - 1}{\chi_\kappa} \frac{b}{c_A}.$$

We see that (20) and (22) are analogous to the Curie-Weiss magnetization equation and the Bragg-Williams ordering equation respectively. By expanding the right-hand sides of (20) and (22) in powers of a and b respectively and cancelling the trivial solutions, we obtain, after linearization, equations defining the appropriate phase transition temperatures. The equations may also be derived from (21) and (23) upon setting $\lambda_0 = 0$ and $\chi_\kappa = 0$ respectively. Whether or not the magnetic transition occurs at a higher temperature than the order-disorder transition depends on the composition of the alloy and the ratio R of the spin-exchange energy to the mixing energy, viz. $R = u(\kappa)/v(0)$. In the z plane the saddle point moves towards the branch point $z = -\{2\beta\tilde{v}(0)\}^{-1}$ and $a = 0$ as the temperature decreases to the critical value when the saddle point and branch point coincide. With further decrease in temperature the saddle point moves away from the branch point but now we have $a \neq 0$. A parallel mechanism for ordering may be described on the t plane. The four possible phases may be denoted by

$$\text{I : } a = b = 0$$

$$\text{II : } a = 0, b \neq 0$$

$$\text{III : } a \neq 0, b = 0$$

$$\text{IV : } a \neq 0, b \neq 0.$$

7. Phase diagrams

7.1. Randomly diluted alloy

The case is obtained by setting $U_{ij} = 0$ in the Hamiltonian, so that in the absence of a magnetic interaction no atomic configuration is preferred. The variational principle gives two equations for a and $\tilde{v}(k)$:

$$\begin{aligned} c_A m &= \frac{1}{2} \langle \tanh\{\sqrt{2\Psi X + \beta v(0)c_A m}\} \\ &\quad \times (1 + \tanh[\bar{\phi} + \frac{1}{2} \log \cosh\{\sqrt{2\Psi X + \beta v(0)c_A m}\}]) \rangle_E \\ -2\beta z\tilde{v}(0) &= \Psi^{-1}\beta v(0) \frac{1}{\sqrt{2}} \langle X \tanh\{\sqrt{2\Psi X + \beta v(0)c_A m}\} \\ &\quad \times 1 + (\tanh[\bar{\phi} + \frac{1}{2} \ln \cosh\{\sqrt{2\Psi X + \beta v(0)c_A m}\}]) \rangle_E. \end{aligned}$$

To find the critical temperature T_c we set $m = \lambda_0 = 0$ in the second equation. The result is

$$1 = \beta_c v(0) \pi^{-1/2} \int dX \exp(-X^2) \frac{1 + (c_B/c_A) \cosh \psi_c \cosh(\sqrt{2}\Psi_c X)}{\{\cosh(\sqrt{2}X\Psi_c) + (c_B/c_A) \cosh \psi_c\}^2} \quad (24)$$

For nearest-neighbour interactions we have $\Psi_c^2 = \beta_c v(0)\epsilon$ which for the body-centred cubic lattice gives

$$\Psi_c^2 = 0.3932\beta_c v(0)$$

and, from the saddle-point equations, ψ_c satisfies

$$c_A \psi_c \tanh \psi_c = 0.3932.$$

Solutions of (24) over the range of concentrations are shown in figure 2. Starting from $c_A = 1$ where $kT_c/v(0) = 0.709$ (the Horwitz-Callen critical temperature) an approximate

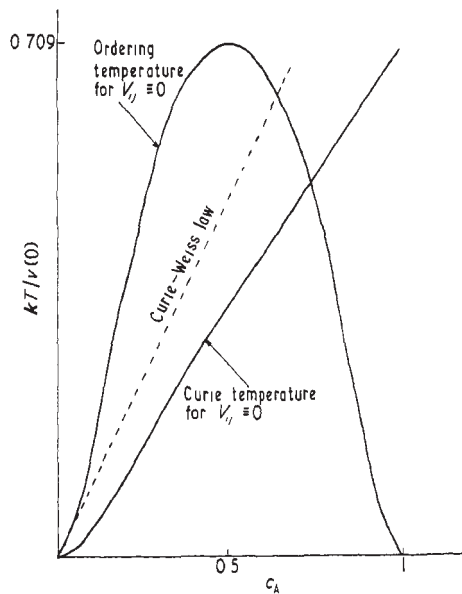


Figure 2. Variational approximation for non-magnetic alloy and for randomly diluted magnetic alloy ($R = 1$).

linear dependence of critical temperature on concentration results, representing the well-known dilution effect. No critical concentration is predicted in this case, and it can be shown that the equation of the curve near to $c_A = 0$ is asymptotic to

$$\frac{0.3932}{c_A^2} = \frac{v(0)}{kT_c} \ln \left(\frac{v(0)}{kT_c} \right).$$

Similarly we may set $V_{ij} = 0$, $\tilde{u}(k) \neq 0$ all k , thus eliminating all magnetization effects. In this situation an ordering transition occurs and is included in figure 2.

7.2. Interaction of magnetization and annealing

The equations to be solved for the four types of transition are listed below, critical values of the variables being specified by a suffix. Let

$$\xi = \{-2\beta z\tilde{v}(0)\}^{-1}, \quad \eta = \{-2\beta t\tilde{u}(\kappa)\}^{-1}.$$

(i) I \rightarrow III:

$$1 = \Psi_c^{-1} \beta_c v(0) \iint \frac{dX dP}{\pi} \exp\{-(X^2 + P^2)\} \frac{\sqrt{2}X \sinh(\sqrt{2}\Psi_c X)}{\cosh(\sqrt{2}\Psi_c X) + \exp\{-2(\bar{\phi}_c + \sqrt{2}\Phi_c P)\}}$$

$$\eta^{-1} = \Phi^{-1} \beta u(\kappa) \iint \frac{dX dP}{\pi} \exp\{-(X^2 + P^2)\} \sqrt{2}P \frac{\exp\{2(\bar{\phi} + \sqrt{2}\Phi P)\} \cosh(\sqrt{2}\Psi X) - 1}{\exp\{2(\bar{\phi} + \sqrt{2}\Phi P)\} \cosh(\sqrt{2}\Psi X) + 1}$$

(ii) I → II:

$$1 = \beta u(\kappa) \iint \frac{dX dP}{\pi} \exp\{-(X^2 + P^2)\} \operatorname{sech}^2\{\bar{\phi} + \Phi\sqrt{2P} + \frac{1}{2} \ln \cosh(\sqrt{2\Psi X})\}$$

$$\xi^{-1} = \Psi^{-1}\beta v(0) \iint \frac{dX dP}{\pi} \exp\{-(X^2 + P^2)\} \frac{\sqrt{2X} \sinh(\sqrt{2\Psi X})}{\cosh(\sqrt{2\Psi X}) + \exp\{-2(\bar{\phi} + \sqrt{2\Phi P})\}}$$

(iii) II → IV:

$$1 = \Psi^{-1}\frac{1}{2}\beta v(0) \iint \frac{dX dP}{\pi} \exp\{-(X^2 + P^2)\} \sqrt{2X} \tanh(\sqrt{2\Psi X})$$

$$\times \left\{ 1 + \frac{1}{2} \frac{\cosh(\sqrt{2\Psi X}) - \exp(-2[\bar{\phi} + \sqrt{2\Phi P} + \{2\beta v(0)R\}^{1/2} p_\kappa b])}{\cosh(\sqrt{2\Psi X}) + \exp(-2[\bar{\phi} + \sqrt{2\Phi P} + \{2\beta v(0)R\}^{1/2} p_\kappa b])} \right.$$

$$\left. + \frac{1}{2} \frac{\cosh(\sqrt{2\Psi X}) - \exp(-2[\bar{\phi} + \sqrt{2\Phi P} - \{2\beta v(0)R\}^{1/2} p_\kappa b])}{\cosh(\sqrt{2\Psi X}) + \exp(-2[\bar{\phi} + \sqrt{2\Phi P} - \{2\beta v(0)R\}^{1/2} p_\kappa b])} \right\}$$

$$\eta^{-1} = \Phi^{-1}\beta u(\kappa) K_2(a = 0)$$

$$\frac{2b}{\{2\beta v(0)R\}^{1/2}} \frac{\chi_\kappa - 1}{\chi_\kappa} = K_1(a = 0).$$

(iv) III → IV:

$$1 = \beta v(0)R \iint \frac{dX dP}{\pi} \exp\{-(X^2 + P^2)\}$$

$$\times \operatorname{sech}^2\{\bar{\phi} + \Phi\sqrt{2P} + \frac{1}{2} \log \cosh[\sqrt{2\Psi X} + \{2\beta v(0)\}^{1/2} x_0]\}$$

$$\xi^{-1} = \Psi^{-1}\beta v(0) H_2(b = 0)$$

$$\frac{2}{\{2\beta v(0)\}^{1/2}} \frac{\lambda_0 - 1}{\lambda_0} a = H_2(b = 0).$$

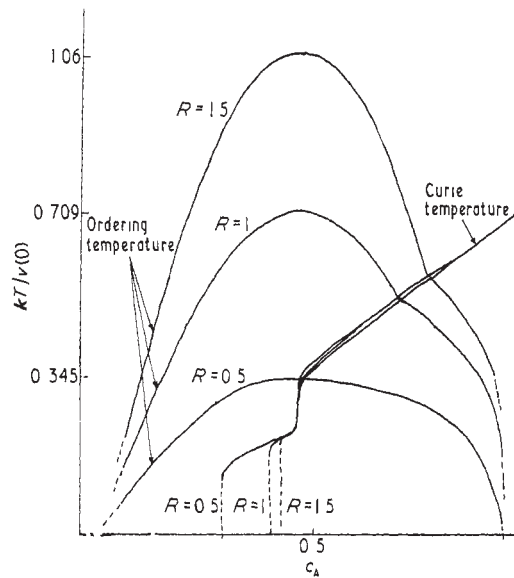


Figure 3. Variational approximation for magnetic alloy with equilibrium distribution.

We have solved these equations for the case of nearest-neighbour interactions in the body-centred cubic lattice. In this case we have from the saddle-point equations

$$\begin{aligned} \tilde{f}'(z) &= \beta\tilde{v}(0)\{\xi^2 F(\xi) - \xi\} \\ \tilde{g}'(t) &= \beta\tilde{v}(0)R\{\eta^2 F(\eta) - \eta\} \end{aligned}$$

where

$$F(z) \equiv \pi^{-3} \int_0^\pi \int_0^\pi \int_0^\pi \frac{du dv dw}{z - \cos u \cos v \cos w}$$

is the function appearing in the work of Lax. Where appropriate we have used Lax's asymptotic expansion of $F(z)$ in our calculations. The four systems of non-linear equations in two and three unknowns were dealt with by the Newton-Rapheson method in conjunction with a repeated Gauss-Hermite quadrature formula (see e.g. Kopal 1961). Phase diagrams are presented for $R = 0.5, 1$ and 1.5 (figure 3).

8. Discussion of results and conclusions

The most striking aspect of our results is the rapid fall in Curie temperature of the alloy in the vicinity of $c_A = \frac{1}{2}$. The magnitude of the temperature change, namely

$$T_c \sim 0.1v(0)/k$$

for a change of approximately 2% in concentration is understood in terms of the high degree of component ordering realized at $c_A = \frac{1}{2}$. For the cases $R = 1, 1.5$, this is about 99% when the magnetic transition occurs. Magnetization in B-rich alloys is possible only for values of c_A greater than some critical value which depends on R . No physically meaningful solutions of the equations were found for smaller concentrations.

Long-range component ordering is enhanced when magnetization has occurred. This effect cannot be understood on energy considerations alone and is presumably an entropy effect

The transition curves (i) and (ii) differ from the curves of the 'decoupled' case only slightly ($\sim \frac{1}{2}\%$ for $R = 1$). However, at $c_A = \frac{1}{2}$ the ratio of the ordering transition temperatures for $R = 1$ and 0.5 (exactly 2 for the 'decoupled' case) has the value 2.06. Unlike the component ordering curves of the Lavis-Fairbairn method, the present approximation does not predict critical concentrations; this is a defect of the approximation.

A better approximation for the transition curves (iii) and (iv) is to be expected if one chooses a slightly different 'trial function' $\{\tilde{\psi}^2\}$ in § 5. Just as parameter a explicitly takes account of the average magnetic field, the addition of a parameter a' to x_k implies differing magnetic fields on the two sublattices. Use of the form

$$\{\tilde{\psi}^2\} = 2\beta\tilde{v}(0)(x_0 - a)^2 + 2\beta\tilde{v}(\kappa)(x_\kappa - a')^2 + \sum_{k \neq 0, \kappa} \beta\tilde{v}(k)(x_k^2 + x_k x_{-k} + y_k^2 - y_k y_{-k})$$

will generate an approximation which describes magnetization on the sublattices more accurately than at present. In fact the difference of the magnetic moments of the two sublattices should be proportional to a' . The variational calculation proceeds as before, with necessary changes of detail, yielding an extra equation for parameter a' .

In another direction, an alternative theory may be derived from the one described here by 'sphericalization', i.e. the variational calculation is performed subject to the constraints $\sum \mu_i^2 = N$, $\sum t_i^2 = N_A$. Muhlschlegel and Zittartz describe a technique for incorporating sum rules of this type.

A discussion of the experimental data for the Fe-Al alloy (see Taylor and Jones 1958) is given by Bell and Lavis and Lavis and Fairbairn. In writing this paper we have attempted to provide an alternative approximation to the ones given by those authors. Inclusion of the effects of 25 : 75 ordering in this scheme has not yet been tried.

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Appendix. Mean field over a sublattice

A basic result of lattice theory is

$$\sum_{\mathbf{l}} \exp(i\mathbf{k} \cdot \mathbf{l}) = ND(\mathbf{k}) \quad (25)$$

(see e.g. Peierls 1955) where $D(\mathbf{k}) = 1$ if \mathbf{k} is zero or any vector of the reciprocal lattice \mathbf{G} , and zero otherwise. Let the vector displacement of the two sublattices be \mathbf{s} . Then

$$\sum_{(1)} e^{i\mathbf{k} \cdot \mathbf{l}} = e^{i\mathbf{k} \cdot \mathbf{s}} \sum_{(2)} e^{i\mathbf{k} \cdot \mathbf{l}}$$

and hence from (25)

$$ND(\mathbf{k}) = \sum_{(1)} e^{i\mathbf{k} \cdot \mathbf{l}} (1 + e^{-i\mathbf{k} \cdot \mathbf{s}}).$$

The factor $\sum_{(1)} e^{i\mathbf{k} \cdot \mathbf{l}}$ vanishes unless $\mathbf{k} = 0 \pmod{\mathbf{G}}$ or \mathbf{k} satisfies

$$\exp(i\mathbf{k} \cdot \mathbf{s}) = -1. \quad (26)$$

Let the set of vectors satisfying (26) which lie in the first Brillouin zone be denoted by $\{\kappa_i\}$. It follows immediately that $2\kappa_i$, or $\kappa_i + \kappa_j$, are vectors of the reciprocal lattice, i.e.

$$\kappa_i + \kappa_j \equiv 0 \pmod{\mathbf{G}}.$$

The set $\{\kappa_i\}$ are half reciprocal lattice vectors. For the body-centred cubic lattice the lattice vectors are

$$\mathbf{l} = \frac{a}{2} [n_1, n_2, n_3]$$

where n_1, n_2 and n_3 have the same parity. In this notation we have

$$\mathbf{s} = \frac{a}{2} [1, 1, 1].$$

The vectors of the reciprocal lattice are

$$\mathbf{G} = \frac{2\pi}{a} [m_1, m_2, m_3]$$

where

$$m_1 + m_2 + m_3 \equiv 0 \pmod{2}.$$

Hence with suitable restrictions on the integers m we have

$$\{\kappa_i\} = \frac{\pi}{a} [m_1, m_2, m_3].$$

Wave vectors are deemed equivalent if they differ by any vector \mathbf{G} . This limits us to the choice of any one vector from the set

$$\begin{array}{ll} \pm \frac{\pi}{a} [2, 0, 0] & \pm \frac{\pi}{a} [1, 1, 0] \\ \pm \frac{\pi}{a} [0, 2, 0] & \pm \frac{\pi}{a} [0, 1, 1] \\ \pm \frac{\pi}{a} [0, 0, 2] & \pm \frac{\pi}{a} [1, 0, 1] \end{array}$$

provided it also satisfies

$$\exp(i\kappa \cdot \mathbf{s}) = -1$$

thence

$$\sum_{(1)(2)} e^{i\mathbf{k} \cdot \mathbf{l}} = \frac{1}{2} ND(\mathbf{k}) \pm \frac{1}{2} ND(\kappa - \mathbf{k})$$

or

$$\frac{2}{N} \sum_{(1)(2)} \cos(\mathbf{k} \cdot \mathbf{l}) = D(\mathbf{k}) \pm D(\kappa - \mathbf{k}).$$

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