

or (4) for  $\mathbf{\epsilon}$  in the regions I, II, or III, respectively. It is also interesting to note that there is a finite polarization for  $T > T_c$  in the absence of an external field, again a consequence of the lack of symmetry of the model. The polarizability  $\chi \equiv \partial \mathbf{P} / \partial \mathbf{\epsilon}$  can now be computed exactly. We note only its critical behavior  $\chi \sim (T - T_c)^{-1/2}$

as compared to the  $(T - T_c)^{-1}$  singularity of the Slater KDP model.<sup>4</sup>

#### ACKNOWLEDGMENT

I should like to thank Professor Elliott H. Lieb for useful comments.

## Statistical Effects of Superexchange in Binary Mixtures with One Magnetic Component

G. M. BELL AND D. A. LAVIS

*Department of Mathematics, Chelsea College of Science and Technology, University of London, London, England*

(Received 21 September 1967)

The statistical thermodynamics of a binary solid mixture of a ferromagnetic or antiferromagnetic component  $A$  and a nonmagnetic component  $B$  is developed theoretically. The nearest-neighbor interaction and exchange energies and a superexchange energy between any two  $A$  atoms sharing one  $B$  atom as a nearest neighbor are introduced. In addition to magnetic spin ordering, long-range  $A$ - $B$  sublattice ordering of a type appropriate to a body-centered cubic lattice is considered, using the zeroth-order statistical approximation. The effects of dilution and long-range component ordering on the onset of magnetic ordering are calculated for several sets of parameter values over the whole range of mole fractions. If the superexchange integral is large enough relative to the direct exchange integral, the curves of Curie (or Néel) temperature against mole fraction are convex upwards, and a maximum may be observed. The interaction of long-range ordering with magnetization is considered in both equilibrium (annealed) and frozen (quenched) mixtures.

### I. INTRODUCTION

IN a series of three papers, Bell and Lavis,<sup>1</sup> Lavis and Fairbairn,<sup>2</sup> and Lavis and Bell<sup>3</sup> investigated the effects of long-range component ordering on the occurrence of magnetization in a binary mixture with a magnetic component  $A$  and a nonmagnetic component  $B$ . In Refs. 1 and 2, the lattice was divided into two equivalent sublattices, and in Ref. 3, into four equivalent sublattices. Nonmagnetic pair-interaction energies and direct-exchange-magnetic-interaction energies for  $AA$  pairs were postulated for nearest-neighbor pairs in Ref. 2 and for all pairs (varying with the distance between the two members of the pair) in Refs. 1 and 3. For both the zeroth-order approximation used in Refs. 1 and 3 and the Bethe-pair approximation used in Ref. 2, the Curie temperature was seriously affected by the presence of component order, and in Ref. 1, the sign and magnitude of the exchange interaction between magnetic pairs on the same sublattice were shown to be significant. In all cases, however, the Curie temperature was seen to be a monotonically increasing function of the percentage of magnetic atoms present. In practice, exceptions occur in, for instance, mixtures of ferromagnetic with semiconducting elements.<sup>4</sup>

The present paper introduces superexchange in the form of an exchange interaction between two second-neighbor  $A$  atoms, with a  $B$  atom as a common nearest neighbor. The existence of such an interaction in certain paramagnetic salts was first proposed by Kramers<sup>5</sup> and has since been discussed by many authors, including Anderson,<sup>6</sup> for nonmetallic  $B$ . As far as we know, the statistical consequences of superexchange in an incompletely ordered mixture have not previously been discussed, and we shall use the simplest, or zeroth-order, approximation. While our analysis is not applicable to the face-centered cubic lattice, it is likely that similar results could be obtained.

As in Refs. 1-3, we shall assume that the magnetic moments of the  $A$  atoms are unaffected by the concentration. We shall also assume that the lattice structure of the mixture is unchanged either in dimension or type by redistribution of the atoms upon it. This tends to confine us to limited ranges of concentration when comparing with experiment.

### II. FREE ENERGY AND INTERNAL VARIABLES

We make the following assumptions:

(i) The lattice divides into a pair of equivalent sublattices, and each lattice site has  $z$  nearest neighbors in the other sublattice and none in its own sublattice.

<sup>1</sup> G. M. Bell and D. A. Lavis, *Phil. Mag.* **11**, 937 (1965).

<sup>2</sup> D. A. Lavis and W. M. Fairbairn, *Phil. Mag.* **13**, 477 (1966).

<sup>3</sup> D. A. Lavis and G. M. Bell, *Phil. Mag.* **15**, 587 (1967).

<sup>4</sup> S. Arajs, *Phys. Status Solidi* **11**, 121 (1965).

<sup>5</sup> H. A. Kramers, *Physica* **1**, 182 (1934).

<sup>6</sup> P. W. Anderson, *Solid State Phys.* **14**, 99 (1963).

The most important example is the body-centered cubic for which  $z=8$  and each sublattice is simple cubic. We suppose that the  $N$  lattice sites are occupied by  $N_A=N_{c_A}$   $A$  atoms and  $N_B=N_{c_B}$   $B$  atoms. The symbols  $N_A^{(a)}$  and  $N_A^{(b)}$  denote the number of  $A$  atoms on sublattices  $a$  and  $b$ , respectively, and  $N_B^{(a)}$  and  $N_B^{(b)}$  are similarly defined. The long-range order parameter  $\sigma$  is defined so that

$$\begin{aligned} N_A^{(a)} &= \frac{1}{2}N_{c_A}(1+\sigma), & N_A^{(b)} &= \frac{1}{2}N_{c_A}(1-\sigma), \\ N_B^{(a)} &= \frac{1}{2}N(c_B - c_A\sigma), & N_B^{(b)} &= \frac{1}{2}N(c_B + c_A\sigma). \end{aligned} \quad (2.1)$$

(ii) Apart from the superexchange [see (iii) below], we neglect all interactions beyond nearest-neighbor distance. We write the nearest-neighbor-pair-interaction energy in the form

$$\begin{aligned} E_c^I &= N_{AA}e_{AA} + N_{AB}e_{AB} + N_{BB}e_{BB} - 2J^\phi \sum \mathbf{s}_i \cdot \mathbf{s}_j \\ &= \frac{1}{2}z(N_A e_{AA} + N_B e_{BB}) + N_{AB}w_{AB} - 2J^\phi \sum \mathbf{s}_i \cdot \mathbf{s}_j, \end{aligned} \quad (2.2)$$

where

$$w_{AB} = e_{AB} - \frac{1}{2}(e_{AA} + e_{BB}).$$

Here  $N_{AA}$ ,  $N_{AB}$ , and  $N_{BB}$  are, respectively, the numbers of  $AA$ ,  $AB$ , and  $BB$  nearest-neighbor pairs;  $e_{AA}$ ,  $e_{AB}$ , and  $e_{BB}$  are the corresponding pair-interaction energies, while  $J^\phi$  is the exchange integral, and  $\mathbf{s}_i$  and  $\mathbf{s}_j$  are spin vectors on the members of an  $AA$  nearest-neighbor pair. Using the zeroth-order statistical approximation,

$$\begin{aligned} N_{AB} &= 2z[N_A^{(a)}N_B^{(b)} + N_A^{(b)}N_B^{(a)}]/N \\ &= N_{c_A}z(c_B + c_A\sigma^2), \end{aligned} \quad (2.3)$$

$$\sum \mathbf{s}_i \cdot \mathbf{s}_j = 2z\mathbf{S}^{(a)} \cdot \mathbf{S}^{(b)}/N, \quad (2.4)$$

where  $\mathbf{S}^{(a)}$  and  $\mathbf{S}^{(b)}$  are the vector sums of all the spins on sublattices  $a$  and  $b$ , respectively.

(iii) We introduce a superexchange interaction  $w^\delta - 2J^\delta \mathbf{s}_i \cdot \mathbf{s}_j$  acting between pairs of  $A$  atoms, with a  $B$  atom as common nearest neighbor. In the zeroth-order approximation, the number of such triads of atoms on the lattice is

$$\frac{1}{2}N_B^{(b)} \frac{zN_A^{(a)}(z-1)N_A^{(a)}}{\frac{1}{2}N} + \frac{1}{2}N_B^{(a)} \frac{zN_A^{(b)}(z-1)N_A^{(b)}}{\frac{1}{2}N},$$

which can be written  $N_{c_A}z(z-1)[\frac{1}{2}c_B + (1 - \frac{1}{2}c_B)\sigma^2]$ , and with a random distribution of spins, we can write

$$\begin{aligned} \sum \mathbf{s}_i \cdot \mathbf{s}_j &= \frac{1}{2}N_B^{(b)} \frac{zN_A^{(a)}(z-1)N_A^{(a)}}{\frac{1}{2}N} \frac{\mathbf{S}^{(a)} \cdot \mathbf{S}^{(a)}}{(N_A^{(a)})^2} + \frac{1}{2}N_B^{(a)} \frac{zN_A^{(b)}(z-1)N_A^{(b)}}{\frac{1}{2}N} \frac{\mathbf{S}^{(b)} \cdot \mathbf{S}^{(b)}}{(N_A^{(b)})^2} \\ &= z(z-1)[(c_B + c_A\sigma)\mathbf{S}^{(a)} \cdot \mathbf{S}^{(a)} + (c_B - c_A\sigma)\mathbf{S}^{(b)} \cdot \mathbf{S}^{(b)}]/N. \end{aligned}$$

Hence the superexchange contribution to the energy is

$$E_c^{II} = z(z-1)\{N_{c_A}z[\frac{1}{2}c_B + (1 - \frac{1}{2}c_B)\sigma^2]w^\delta - 2[(c_B + c_A\sigma)\mathbf{S}^{(a)} \cdot \mathbf{S}^{(a)} + (c_B - c_A\sigma)\mathbf{S}^{(b)} \cdot \mathbf{S}^{(b)}]J^\delta\}. \quad (2.5)$$

(iv) We write  $\frac{1}{2}Nm^{(a)}$  and  $\frac{1}{2}Nm^{(b)}$  as the spin components in a given direction of the sublattice spin vector sums  $\mathbf{S}^{(a)}$  and  $\mathbf{S}^{(b)}$ , so that  $m^{(a)}$  and  $m^{(b)}$  are the mean spin components per site. For  $\frac{1}{2}Nm^{(a)}$ ,  $\frac{1}{2}Nm^{(b)} \gg 1$ , we have effectively

$$\mathbf{S}^{(a)} \cdot \mathbf{S}^{(a)} = (\frac{1}{2}N)^2(m^{(a)})^2, \quad \mathbf{S}^{(b)} \cdot \mathbf{S}^{(b)} = (\frac{1}{2}N)^2(m^{(b)})^2, \quad \mathbf{S}^{(a)} \cdot \mathbf{S}^{(b)} = (\frac{1}{2}N)^2m^{(a)}m^{(b)}$$

(see Van Vleck<sup>7</sup>). We may then add (2.2) and (2.5) to give the configurational energy

$$E_c = E_c^{(0)} + Nz\{c_A^2[w_{AB} + (z-1)(1 - \frac{1}{2}c_B)w^\delta]\sigma^2 - J^\phi m^{(a)}m^{(b)} - \frac{1}{2}J^\delta(z-1)[(c_B + c_A\sigma)m^{(a)2} + (c_B - c_A\sigma)m^{(b)2}]\}. \quad (2.6)$$

For simplicity, we replace the term  $(1 - \frac{1}{2}c_B)w^\delta$ , which varies from  $w^\delta$  to  $\frac{1}{2}w^\delta$ , in the coefficient of  $\sigma^2$  by  $w^\delta$ . If the  $c_B$  dependence were retained, it would introduce a degree of asymmetry in the ordering transition temperature against concentration curves which would depend on the ratio  $w^\delta/w_{AB}$ . In the extreme case when  $w_{AB}=0$ , the maximum would be shifted to  $c_A=0.58$ , while in the case  $w^\delta=0$ , the approximation is negligible. The effect of neglecting the  $c_B$  dependence is, therefore, not likely to be large.

The calculation of entropy is identical to that of Ref. 1, and applying the modification (iv), we can

write the Helmholtz free energy

$$F_c = -kT \ln g(m^{(a)}, m^{(b)}, \sigma) + E_c(m^{(a)}, m^{(b)}, \sigma), \quad (2.7)$$

where

$$g(m^{(a)}, m^{(b)}, \sigma) = \frac{(\frac{1}{2}N)!}{N_A^{(a)}!N_B^{(a)}!} \frac{(\frac{1}{2}N)!}{N_A^{(b)}!N_B^{(b)}!} \gamma^{(a)}\gamma^{(b)}, \quad (2.8)$$

$$\gamma^{(a)} = \left\{ \sum_{i=1}^{2s+1} \exp[\beta_1(i-s-1)] \right\}^{N_A^{(a)}} \exp(-\frac{1}{2}\beta_1 N m^{(a)}),$$

$$\gamma^{(b)} = \left\{ \sum_{i=1}^{2s+1} \exp[\beta_2(i-s-1)] \right\}^{N_A^{(b)}} \exp(-\frac{1}{2}\beta_2 N m^{(b)}), \quad (2.9)$$

<sup>7</sup> J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).

and

$$\begin{aligned} m^{(a)} &= 2(N_A^{(a)}/N) s B_s(\beta_1 s), \\ m^{(b)} &= 2(N_A^{(b)}/N) s B_s(\beta_2 s). \end{aligned} \quad (2.10)$$

$B_s$  is the Brillouin function.<sup>1,7</sup>

### III. EQUILIBRIUM CONDITIONS

We have for equilibrium the stationary-point conditions

$$\partial F_c / \partial m^{(a)} = \frac{1}{2}(kT\beta_1 N) - [3kN/2s(s+1)c_A][T_1^\phi m^{(b)} + T_1^\delta m^{(a)}(c_B + c_A\sigma)] = 0, \quad (3.1)$$

$$\partial F_c / \partial m^{(b)} = \frac{1}{2}(kT\beta_2 N) - [3kN/2s(s+1)c_A][T_1^\phi m^{(a)} + T_1^\delta m^{(b)}(c_B - c_A\sigma)] = 0, \quad (3.2)$$

$$\partial F_c / \partial \sigma = \frac{1}{2}c_A N k T \ln \left\{ \frac{\sum_{i=1}^{2s+1} \exp[\beta_2(i-s-1)](1+\sigma)(c_B + c_A\sigma)}{\sum_{i=1}^{2s+1} \exp[\beta_1(i-s-1)](1-\sigma)(c_B - c_A\sigma)} \right\} - T_2 \frac{c_A N k \sigma}{c_B} - \frac{3NkT_1^\delta (m^{(a)2} - m^{(b)2})}{4s(s+1)} = 0, \quad (3.3)$$

where

$$T_1^\phi = c_A \zeta \tau_1^\phi = 2c_A s(s+1) z J^\phi / 3k, \quad (3.4)$$

$$T_1^\delta = c_A \tau_1^\delta = c_A \kappa \tau_1^\phi = 2c_A s(s+1) z(z-1) J^\delta / 3k, \quad (3.5)$$

$$T_2 = c_A c_B \tau_2 = -2c_A c_B \gamma |J_1^\phi| z / k, \quad (3.6)$$

in which

$$\zeta = J^\phi / |J^\phi|, \quad \kappa = (z-1)J^\delta / |J^\phi|, \quad \gamma = [w_{AB} + (z-1)w^\delta] / |J^\phi|. \quad (3.7)$$

Combining (2.10) with (3.1) and (3.2) gives

$$m^{(a)} = c_A(1+\sigma) s B_s \{ [3\tau_1^\phi / T(s+1)] [\zeta m^{(b)} + \kappa m^{(a)}(c_B + c_A\sigma)] \}, \quad (3.8)$$

$$m^{(b)} = c_A(1-\sigma) s B_s \{ [3\tau_1^\phi / T(s+1)] [\zeta m^{(a)} + \kappa m^{(b)}(c_B - c_A\sigma)] \}. \quad (3.9)$$

If  $(m_0^{(a)}, m_0^{(b)}, \sigma_0)$  is a solution of (3.1)–(3.3) then the condition for a second-order transition from that state at a temperature  $T$  is that the equations

$$\begin{aligned} (\partial^2 F_c / \partial \sigma^2)_0 \delta \sigma + (\partial^2 F_c / \partial \sigma \partial m^{(a)})_0 \delta m^{(a)} + (\partial^2 F_c / \partial \sigma \partial m^{(b)})_0 \delta m^{(b)} &= 0, \\ (\partial^2 F_c / \partial m^{(a)2} \partial \sigma)_0 \delta \sigma + (\partial^2 F_c / \partial m^{(a)2})_0 \delta m^{(a)} + (\partial^2 F_c / \partial m^{(a)} \partial m^{(b)})_0 \delta m^{(b)} &= 0, \\ (\partial^2 F_c / \partial m^{(b)2} \partial \sigma)_0 \delta \sigma + (\partial^2 F_c / \partial m^{(a)} \partial m^{(b)})_0 \delta m^{(a)} + (\partial^2 F_c / \partial m^{(b)2})_0 \delta m^{(b)} &= 0, \end{aligned} \quad (3.10)$$

should have a solution nonzero in some or all of  $\delta\sigma$ ,  $\delta m^{(a)}$ , and  $\delta m^{(b)}$ . This will be the case if the determinant  $D(m^{(a)}, m^{(b)}, \sigma)$  formed from the coefficients of (3.10) is zero.

At high temperatures the only solution to (3.1)–(3.3) is  $m^{(a)} = m^{(b)} = \sigma = 0$  (state I). In this case,

$$\partial^2 F_c / \partial m^{(a)} \partial \sigma = \partial^2 F_c / \partial m^{(b)} \partial \sigma = 0,$$

and  $D(0, 0, 0)$  factorizes into two parts, corresponding to a transition to an ordered nonmagnetic state for which  $\delta m^{(a)} = \delta m^{(b)} = 0$ ,  $\delta\sigma \neq 0$  (state II) and a transition to a disordered magnetized state for which  $\delta\sigma = 0$ ,  $\delta m^{(a)} = \pm \delta m^{(b)} \neq 0$  (state III).

We shall also consider transitions from states II or III to a state which is both ordered and magnetic ( $\delta\sigma$ ,  $\delta m^{(a)}$ ,  $\delta m^{(b)}$  all nonzero) (state IV).

The transition to state II occurs at the temperature given by taking  $m^{(a)} = m^{(b)} = \sigma = 0$  in  $\partial^2 F_c / \partial \sigma^2 = 0$ , namely, at  $T = T_2$ .

When we examine the transition to state III, however, the effects of superexchange are evident. The factor of  $D(0, 0, 0)$  corresponding to the magnetic transition when equated to zero gives

$$(T - c_A c_B \kappa \tau_1^\phi)^2 - c_A^2 \tau_1^{\phi 2} = 0.$$

This equation has solutions

$$T = c_A \tau_1^\phi (c_B \kappa \pm 1). \quad (3.11)$$

The significance of the choice of sign is seen by taking  $\sigma = 0$  in (3.8) and (3.9). These equations then have the solution

$$m^{(b)} = \pm \zeta m^{(a)}, \quad (3.12)$$

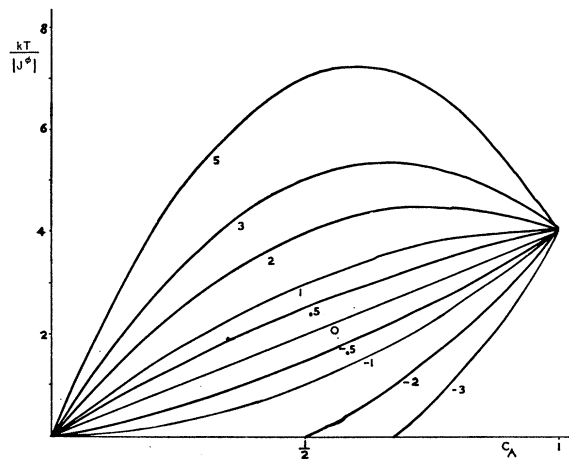


FIG. 1. Curie temperature against mole fraction of magnetic compound ( $s = \frac{1}{2}$ ) in the disordered state for various values of  $\kappa$ .

and as  $m^{(a)} \rightarrow 0$ ,

$$T \rightarrow c_A \tau_1^\phi (c_B \kappa \pm 1). \quad (3.13)$$

Of the two temperatures given by (3.11), the higher temperature

$$T_1 = c_A \tau_1^\phi (c_B \kappa + 1) \quad (3.14)$$

corresponds to a transition, and from (3.12) we see that this is to the ferromagnetic state  $m^{(a)} = m^{(b)}$  if  $J^\phi > 0$ , and to the antiferromagnetic state  $m^{(a)} = -m^{(b)}$  if  $J^\phi < 0$ .

The Curie (or Néel) point  $T_1$  depends significantly on  $\kappa$  (see Fig. 1). If  $\kappa < -1$ , magnetization does not occur for  $c_A \leq c_0$ , where

$$c_0 = (1 + \kappa) / \kappa. \quad (3.15)$$

For  $\kappa < 0$ , the Curie temperature plotted against mole fraction  $c_A$  is convex towards the  $c_A$  axis. For  $\kappa > 0$ , the curve becomes concave, with a maximum appearing at

$$c_A = \frac{1}{2}(1 + \kappa) / \kappa \quad (3.16)$$

for  $\kappa \geq 1$ . This maximum will tend towards  $c_A = \frac{1}{2}$  as  $\kappa$  tends to infinity. This corresponds to the case when direct exchange becomes negligible ( $J^\phi = 0$ ).

#### IV. MAGNETIZATION TRANSITIONS IN THE ORDERED STATE (STATES II TO IV)

The magnetization transition in the ordered state is given by factorizing  $D(0, 0, \sigma)$  into the form  $D_m \partial^2 F_c / \partial \sigma^2$  and taking the factor  $D_m = 0$ . This gives

$$T_c = c_A \tau_1^\phi [\kappa (c_B + c_A \sigma^2) + (\kappa^2 \sigma^2 + 1 - \sigma^2)^{1/2}]. \quad (4.1)$$

Figure 2 contains graphs of  $T_c$  plotted against  $c_A$  with parameter  $\sigma$  for  $\kappa = 4$ ,  $s = \frac{1}{2}$ . From (3.8) and (3.9) this corresponds to a transition in which the sublattice magnetizations are parallel if  $J^\phi > 0$  and antiparallel if

$J^\phi < 0$ . The magnetization transition temperature for equilibrium ordering is obtained by simultaneous solution of Eqs. (4.1) and (3.3) ( $m^{(a)} = m^{(b)} = 0$ ). For  $\kappa \geq 1$ , (4.1) is a monotonically increasing function of  $\sigma$ , and hence magnetization will be enhanced by ordering. Similarly for  $-1 \leq \kappa < 0$ , (4.1) is monotonically decreasing, and we deduce that magnetization will be decreased by ordering. Outside these ranges (4.1) is no longer monotonic; we may, however, determine the relative behaviors of the Curie temperatures in the presence and absence of ordering near  $P$ , the crossing point of  $T_1$  and  $T_2$ , and at  $T = 0$ . Near  $P$ , the determining factor is the sign of

$$(d^2 T_c / d\sigma^2)_{\sigma=0} = c_p \tau_1^\phi [2\kappa c_p + \kappa^2 - 1],$$

where  $c_p$  is the value of  $c_A$  at  $P$ . Note that

$$(dT_c / d\sigma)_{\sigma=0} = 0,$$

while  $c_p$  is given by

$$c_p = [\tau_2 - \tau_1^\phi (\kappa + 1)] / (\tau_2 - \tau_1^\phi \kappa). \quad (4.2)$$

Hence

$$(d^2 T_c / d\sigma^2)_{\sigma=0} = c_p (\tau_1^\phi)^3 V(\kappa) / (\tau_2 - \tau_1^\phi \kappa)^2, \quad (4.3)$$

where

$$V(\kappa) = [\kappa + 3\gamma / s(s+1)] \{ \kappa^3 + [3\gamma / s(s+1) + 2] \kappa^2 + [6\gamma / s(s+1) + 1] \kappa - 3\gamma / s(s+1) \}.$$

The condition that  $0 < c_p < 1$  implies that

$$\kappa < -[1 + 3\gamma s^{-1}(s+1)^{-1}].$$

Examination of  $V(\kappa)$  reveals the presence of two roots

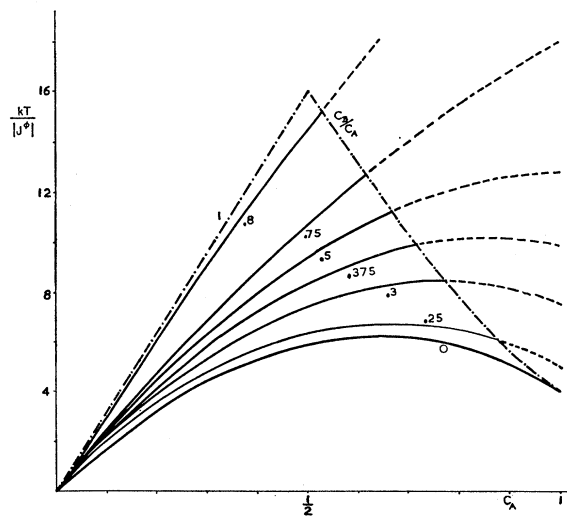


FIG. 2. Curie temperature against mole fraction of magnetic component ( $s = \frac{1}{2}$ ) in the frozen (quenched) state for  $\kappa = 4$  and various values of the (frozen) long-range ordering parameter  $\sigma$ . (---, perfect order; ---, impossible value of  $\sigma$  at given  $c_A$ .)

at values of  $\kappa$  greater than one, another root  $\kappa_1$  between one and zero, and the remaining root  $\kappa_2$  at a value less than minus one. This implies that magnetization will be enhanced by ordering near  $P$  for

$$\kappa_1 < \kappa < -[1 + 3\gamma s^{-1}(s+1)^{-1}],$$

suppressed for  $\kappa_2 < \kappa < \kappa_1$ , and enhanced for  $\kappa < \kappa_2$ , which is in agreement with the monotonic character of (4.1) mentioned above.

As  $T$  tends to zero, the Curie temperature in the presence of ordering will approach that for complete ordering tangentially. A consideration of (3.3) reveals that complete ordering for  $c_A \leq \frac{1}{2}$  is given by  $\sigma = 1$ , and for  $c_A \geq \frac{1}{2}$  by  $\sigma = c_B/c_A$ . Substitution in (4.1) gives

$$T_c = c_A \tau_1^\phi [\kappa + |\kappa|], \quad c_A \leq \frac{1}{2} \quad (4.4)$$

$$T_c = \tau_1^\phi [\kappa c_B + (\kappa^2 c_B^2 + c_A^2 - c_B^2)^{1/2}]. \quad (4.5)$$

This indicates that for  $\kappa > 0$ , the Curie temperature will approach  $T = 0$  at  $c_A = 0$ , and for  $\kappa \leq 0$ , at  $c_A = \frac{1}{2}$ . For  $\kappa > 0$ , we have  $dT_c/dc_A = 2\tau_1^\phi \kappa$  as compared with  $dT_1/dc_A = \tau_1^\phi (\kappa + 1)$ , which indicates that ordering will enhance magnetization for  $\kappa > 1$  and decrease it for  $0 < \kappa < 1$ . For  $\kappa \leq 0$ , we see that no magnetization can occur for  $c_A \leq \frac{1}{2}$ , and hence from (3.15) ordering must decrease magnetization for  $0 > \kappa \geq -2$  and enhance it for  $-2 \geq \kappa$ . It may be shown that there is the possibility of at most one crossing point of the Curie temperature in the ordered state with  $T_1$ . We can therefore catalog the following types of behavior for the case  $\gamma = -2$ ,  $s = \frac{1}{2}$  ( $\kappa_1 = 0.456$ ,  $\kappa_2 = -2.286$ ,  $\kappa < 7$ ).

$7 > \kappa > 1$ : Magnetization is enhanced by ordering for all concentrations.

$1 \geq \kappa > 0.456$ : Magnetization is enhanced by ordering near  $P$  and suppressed near  $T = 0$ .

$0.456 > \kappa \geq -2$ : Magnetization is decreased by ordering at all concentrations, there being a critical concentration at  $c_A = \frac{1}{2}$  when  $\kappa \leq 0$ .

$-2 > \kappa > -2.286$ : Magnetization is decreased by ordering near  $P$  and enhanced near  $T = 0$ .

$-2.286 > \kappa$ : Magnetization is enhanced by ordering for all concentrations.

Figures 3-7 are, respectively, illustrations of these types of behavior.

### V. ORDERING TRANSITIONS IN THE MAGNETIZED STATE (STATES III AND IV)

For the disordered magnetized state III, we write  $m^{(a)} = \zeta m^{(b)} = m$ , and (3.8) and (3.9) become

$$m = c_A s B_s [3\tau_1^\phi m (1 + \kappa c_B) (s+1)^{-1} T^{-1}] \quad (5.1)$$

for  $m \neq 0$ ,  $\partial^2 F_c / \partial \sigma \partial m^{(a)} = \partial^2 F_c / \partial \sigma \partial m^{(b)} \neq 0$ , and in the relation

$$D(m, m, 0) = 0, \quad (5.2)$$

the Jacobian determinant does not factorize into two parts; instead we must obtain a solution to (3.10) in which none of  $\delta\sigma$ ,  $\delta m^{(a)}$ ,  $\delta m^{(b)}$  is zero. This may be called a mixed transition (see Ref. 3). After some simplification (5.2) becomes

$$\begin{vmatrix} -\frac{m^2 T}{c_A} - c_A X \left( \frac{T}{c_B} - c_A \tau_2 \right), & m \left( \frac{T}{c_A} + \frac{3c_A \kappa \tau_1^\phi X}{s(s+1)} \right), & -m \left( \frac{T}{c_A} + \frac{3c_A \kappa \tau_1^\phi X}{s(s+1)} \right) \\ m \left( \frac{T}{c_A} + \frac{3c_A \kappa \tau_1^\phi X}{s(s+1)} \right), & 2 \left( \frac{3c_B \kappa \tau_1^\phi X}{s(s+1)} - \frac{T}{c_A} \right), & \frac{6\tau_1^\phi X}{s(s+1)} \\ -m \left( \frac{T}{c_A} + \frac{3c_A \kappa \tau_1^\phi X}{s(s+1)} \right), & \frac{6\tau_1^\phi X}{s(s+1)}, & 2 \left( \frac{3c_B \kappa \tau_1^\phi X}{s(s+1)} - \frac{T}{c_A} \right) \end{vmatrix} = 0, \quad (5.3)$$

where

$$\beta_1 = \zeta \beta_2 = \beta \quad \text{and} \quad X = \partial [s B_s(\beta s)] / \partial \beta. \quad (5.4)$$

By selecting the root of (5.3) which reduces to  $T = T_2$  when  $m = 0$ , we obtain

$$T = T_2 - U(m) \left\{ 1 - \left[ 1 + \frac{3\tau_1^\phi c_B m^2}{U^2(m) c_A s (s+1)} \left( \tau_2 (c_A \kappa + \kappa - 1) + \frac{3c_A^2 \kappa^2 \tau_1^\phi X}{s(s+1)} \right) \right]^{1/2} \right\}, \quad (5.5)$$

where

$$2U(m) = T_2 + 3\tau_1^\phi s^{-1} (s+1)^{-1} [2c_A^3 X \kappa + (1 - \kappa - c_A \kappa) (m^2 c_B + X c_A^2)]. \quad (5.6)$$

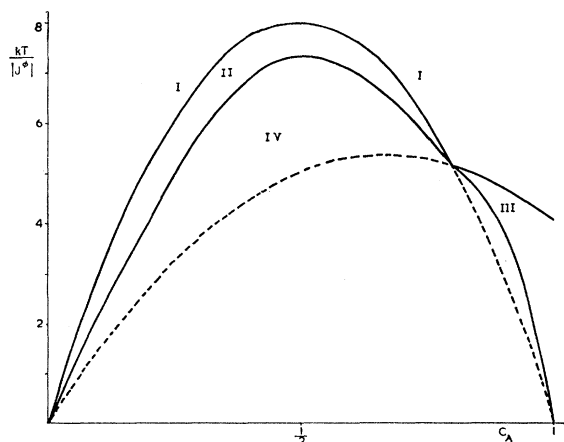


FIG. 3. Transition temperature against mole fraction of magnetic component ( $s = \frac{1}{2}$ ) in the equilibrium state for  $\kappa = 3, \gamma = -2$ . (---, undisturbed I-II and I-III transitions.)

In assessing the behavior of the ordering transition in the presence of magnetization, we may adopt the same procedures as those used in IV, namely, to determine the sign of  $(d^2T/dm^2)_{m=0}$  near  $P$  and to note that the transition curve for equilibrium magnetization will approach its counterpart for complete magnetization as  $T$  tends to zero. We obtain

$$d^2T/dm^2 = [3\tau_1^{\phi^3}(1-c_p)V(\kappa)/2c_p s(s+1)(\tau_2 - \tau_1^{\phi\kappa})^2]$$

and

$$T = T_2 - [3\tau_1^{\phi^3} s^2 c_B c_A^2 / s(s+1)][1 - \kappa(1+c_A)]$$

for complete magnetization. We may therefore classify the following cases (again for  $\gamma = -2, s = \frac{1}{2}$ ).

$7 > \kappa > 0.5$ : Ordering is enhanced by magnetization for all concentrations.

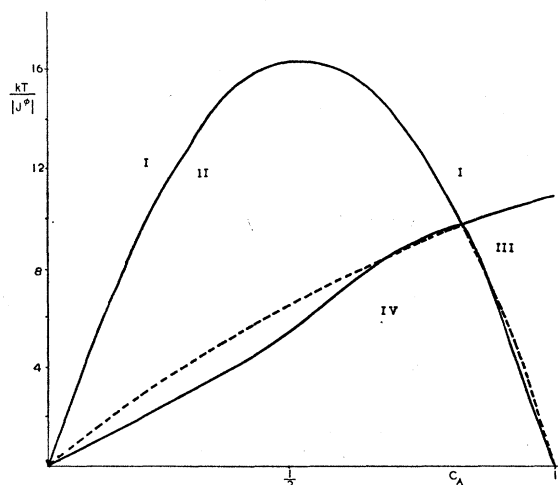


FIG. 4. Transition temperature against mole fraction of magnetic component ( $s = \frac{1}{2}$ ) in the equilibrium state for  $\kappa = 0.5, \gamma = -4$ . (---, undisturbed I-II and I-III transitions.)

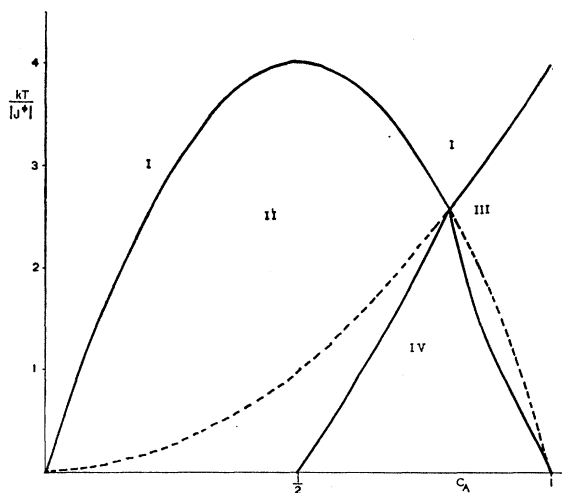


FIG. 5. Transition temperature against mole fraction of magnetic component ( $s = \frac{1}{2}$ ) in the equilibrium state for  $\kappa = -1, \gamma = -1$ . (---, undisturbed I-II and I-III transitions.)

$0.5 \geq \kappa > 0.456$ : Ordering is enhanced by magnetization near  $P$  and suppressed near  $T = 0$ .

$0.456 > \kappa > -2.286$ : Ordering is decreased by magnetization at all concentrations.

$-2.286 > \kappa$ : Ordering is enhanced by magnetization near  $P$  and decreased near  $T = 0$ .

### VI. CONCLUSION

With direct exchange only, the zeroth-order approximation (sometimes termed the "molecular-field method") gives a linear dependence of Curie temperature on mole fraction of the magnetic component. (See the  $\kappa = 0$  curve in Fig. 1.) When short-range ordering effects are taken into account, the

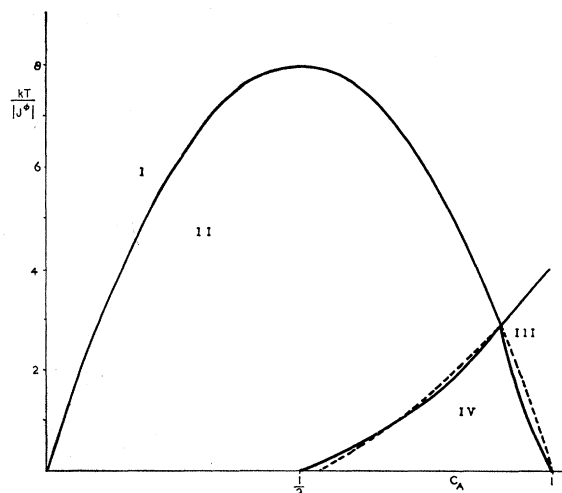


FIG. 6. Transition temperature against mole fraction of magnetic component ( $s = \frac{1}{2}$ ) in the equilibrium state for  $\kappa = -2.1, \gamma = -2$ . (---, undisturbed I-II and I-III transitions.)

Curie-temperature curve lies below this line at large values of  $c_A$  for all parameter values, though at lower values of  $c_A$ , the behavior depends on the value of  $\gamma^2$  (see also Bell and Fairbairn<sup>8</sup>). Some mixtures conform to this pattern, but others do not, as can be clearly seen in Ref. 4, Fig. 2. When long-range component order is introduced into the molecular-field model, the Curie-temperature curve remains linear outside the ordered region (including for all  $T > 0$  the region near  $c_A = 1$ ), and inside it the curvature can be upward or downward, depending on the values of the parameters. However, the Curie-temperature curves are monotonically increasing with  $c_A$  in all circumstances. The superexchange effect introduced here makes a considerable difference to this situation, even in the zeroth-order approximation used in this paper. Figure 1 shows the Curie-temperature curves in the absence of long-range order, and it can be seen that the curvature is upwards for  $\kappa > 0$ , while for  $\kappa > 1$  a maximum is observed. For negative values of  $\kappa$ , there is a critical concentration below which magnetization does not occur. When long-range component ordering is introduced as in Figs. 3-7, the effect is more complicated. In Fig. 3, with a value of  $\kappa$  giving a maximum in the disordered state, the upward curvature is enhanced by ordering and the maximum shifted to a lower value of  $c_A$ . In Fig. 4, where there is upward curvature but

no maximum in the disordered state, the upward curvature is increased for high values of  $c_A$  but reversed for lower  $c_A$ . In Fig. 5, where there is downward curvature but no critical concentration in the disordered state, a critical concentration at  $c_A = \frac{1}{2}$  is produced by ordering. In Figs. 6 and 7, we see the effect of ordering when there is already a critical concentration in the disordered state. In most cases (though not in Fig. 6), whatever effects are produced by the superexchange in the disordered state are enhanced by component ordering. Figure 2 shows the situation in quenched mixtures where the ordering parameter is held fixed independent of temperature.

All the curves given in the figures were computed with the aid of an electronic machine, those in Figs. 3-7 being derived by the Newton-Raphson method applied to the pairs of equations [(4.1) (3.3),  $m^{(a)} = m^{(b)} = 0$ ] and [(5.1), (5.5)].

It is now known that in real magnetic materials, a number of exchange mechanisms are likely to operate, including direct exchange, superexchange through solvent atoms and indirect exchange, through electron bands (see Martin<sup>9</sup> and Mattis<sup>10</sup>). Also, in real alloys, the alloying element may considerably affect the electronic structure of the ferromagnetic element. Hence it would be rash to assert that the mechanism of the present paper in fact underlies the phenomena of upward curvature and maxima in Curie-temperature curves in all observed situations. However, what has been shown is that such phenomena can be explained by a combination of direct exchange and superexchange through the alloying atoms, together with the statistical effects of dilution and long-range ordering. It would be valuable to also include short-range order effects by using a better statistical approximation along the lines of Ref. 2 or of Thompson and Lavis.<sup>11</sup> The authors hope to do this in the future, but it seems unlikely that this will modify the basic conclusions reached.

#### ACKNOWLEDGMENTS

Part of this work was performed while one of us (D.A.L.) was a teacher at the University of Manchester Institute of Science and Technology. The calculations were performed on the Atlas computer of that University.

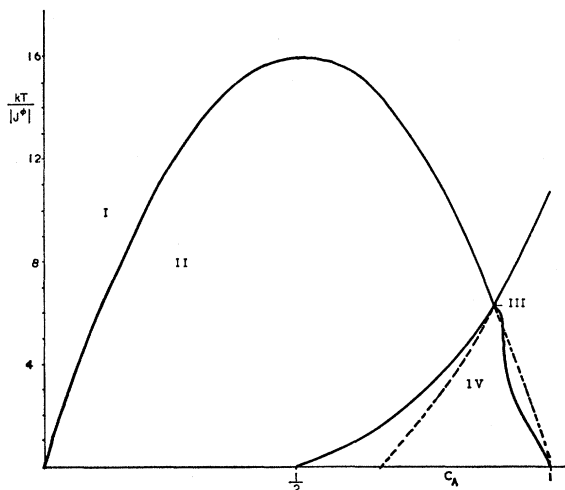


FIG. 7. Transition temperature against mole fraction of magnetic component ( $s=1$ ) in the equilibrium state for  $\kappa=-3$ ,  $\gamma=-4$  (---, undisturbed I-II and I-III transitions.)

<sup>8</sup> G. M. Bell and W. M. Fairbairn, *Phil. Mag.* **6**, 907 (1961).

<sup>9</sup> D. H. Martin, *Magnetism in Solids* (Iliffe, London, 1967).

<sup>10</sup> D. C. Mattis, *The Theory of Magnetism* (Harper and Row, New York, 1965).

<sup>11</sup> B. V. Thompson and D. A. Lavis, *Proc. Phys. Soc. (London)* **91**, 645 (1967).