"THE STUDY OF LOCALIZED MOMENTS, PARTICULARLY IN INSULATORS AND ALLOYS"

by

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A thesis submitted to the University of London for the degree of Doctor of Philosophy in the Faculty of Science.

Imperial College 1967.

Abstract

The Heisenberg Hamiltonian is the basis of the theory of localized moments. A correction to the decoupling procedure of Callen based on this Hamiltonian is presented, which eliminates the erroneous T^3 term in $\langle S^z \rangle$ and improves the critical temperature predicted.

The biquadratic exchange term is included in the Hamiltonian and results for the renormalized spin wave energies are found for both ferromagnets and antiferromagnets. It is concluded that the biquadratic exchange integral j is very small for both types of ordering.

The Molecular Field Theory (MFT) and the Bethe-Peierls-Weiss approximation (B.P.W.) are used to study the properties of binary alloys. These approximations improve on previous theories by using the distribution function $p_{\underline{n}}$ to describe the randomness of the alloy correctly. The basic equation in all the calculations is that for $\sigma_{\underline{n}} = \langle S^z_{\underline{n}} \rangle / S$

$$\sigma_{\underline{k}} = p_{\underline{n}} \Delta_{\underline{n}}(T) \left\{ \bar{H} e^{-i\underline{k}\cdot\underline{n}} + \sum_{\underline{\ell}'} F(\underline{\ell}', T) \sigma_{\underline{n}+\underline{\ell}'} \right\}$$

where only the functions $\Delta_{\underline{n}}$ and F change from theory to theory. This equation is generally solved by iteration, and with the aid of a graphical representation various approximations to $\sigma_{\underline{n}}$ (and therefore $\chi(\underline{k})$) are obtained. Using the condition $1/\chi = 0$, curves for the critical temperature vs. concentration are obtained. Further, expressions for the critical energy and critical entropy are obtained.

The MFT for arbitrary interactions and the B.P.W. approximation using the Heisenberg model give unphysical properties for low concentrations.—However, the Ising

model and the Classical Heisenberg model do not have this failing and are presented for arbitrary interactions.

Acknowledgments

The author wishes to acknowledge the valuable encouragement offered by Professor E.P. Wohlfarth; also the receipt of a S.R.C. grant.

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PART 1

Chapter 1

Exchange Mechanisms and Hamiltonians

The Hamiltonian is the basis of the theory of a magnetic system (and, in fact, of any quantum mechanical theory in Physics) so it is appropriate to begin with a discussion of the Hamiltonians to be used, and by implication the physical mechanisms which determine these Hamiltonians.

In the 1920's the ferromagnetism of iron was not understood in any sense, as Classical Physics had failed to provide a description of the spontaneous magnetization found in this material. Even when Weiss[1] produced his theory of this phenomenon, the origin of the molecular field he proposed was still a problem as magnetic forces are much too small to explain the required molecular fields. The origin was to be found in electrostatic forces. Heisenberg[2] pointed out that ordinary Coulomb interactions among electrons, together with the Pauli principle, could lead to an exchange effect strongly coupling their spins, which might give rise to ferromagnetism. The Pauli exclusion principle implies that parallel spins keep from each other spatially and so the Coulomb repulsion between them is reduced. This can be illustrated by the hydrogen molecule. If ϕ_a and ϕ_b are two wave functions associated with two electrons, and the system of these two electrons is studied, we can construct two types of states according as the two electrons have parallel or antiparallel spins, These states are the symmetric and antisymmetric combinations,

$$\Phi_S(r_1, r_2) = \frac{1}{\sqrt{2}} \left\{ \phi_a(r_1)\phi_b(r_2) + \phi_a(r_2)\phi_b(r_1) \right\}$$

$$\Phi_A(r_1, r_2) = \frac{1}{\sqrt{2}} \left\{ \phi_a(r_1)\phi_b(r_2) - \phi_a(r_2)\phi_b(r_1) \right\} \tag{1.1}$$

Calculating the averages of the Coulomb energy $\frac{e^2}{|r_1 - r_2|}$ in these two states, we find that they differ by an amount

$$J_{12} = \iint \phi_a^*(r_1)\phi_b^*(r_2) \frac{e^2}{|r_1 - r_2|} \phi_a(r_2)\phi_b(r_1) dr_1 dr_2 \tag{1.2}$$

which is the exchange integral. So this exchange effect could give rise to ferromagnetism. Simultaneously, Dirac[3] showed that for the case of orthogonal orbitals the exchange interaction coupling the spins of electrons localized in an assembly of orbitals may be written

$$V_{ex} = -\sum_{i,j} J_{ij}\, \underline{S}_i \cdot \underline{S}_j \tag{1.3}$$

where J_{ij} is given by an expression similar to (1.2) and $\underline{S}_i$ is the spin vector of the i^{th} electron. J_{ij} is necessarily positive because it is the self energy of the charge distribution $\phi_i^*\phi_j$. If we have slightly non-orthogonal orbitals J_{ij} must be replaced by

$$J_{ij} = \iint \phi_i^*(r_1)\phi_j(r_2) \frac{e^2}{|r_1 - r_2|} \phi_i(r_2)\phi_j(r_1) dr_1 dr_2$$
$$-2 \int \phi_i^*(r_1)\phi_j(r_1) dr_1 \int \phi_j^*(r_2) V_i \phi_i(r_2) dr_2 \tag{1.4}$$

where V is some attractive potential between antiparallel electrons in non-orthogonal wave functions (this is the basis of the Heitler-London scheme of chemical binding). Thus the state of the two electrons now depends on the relative magnitudes of the two terms in (1.4).

This type of mechanism would seem ideal for the insulator case where the electrons are well localized and the atoms can be said to have localized moments with a definite spin. Carr[4] applied Löwdin's methods for non-orthogonal arrays to the problem of ferromagnetism and developed the energy in powers of the overlap integral $\int \phi_i(r)\phi_j(r)dr$, where i,j are nearest neighbour sites. With one electron per atom the leading term of the Hamiltonian is the Heisenberg term, but higher terms are of the type

$$\underline{S}_i \cdot \underline{S}_j \; \underline{S}_n \cdot \underline{S}_m$$

Recently, Harris and Owen[5,6] have invoked terms similar to these to describe some of their experimental results. They, in fact, suggest a Hamiltonian which includes the biquadratic exchange term

$$\mathcal{H} = -J \sum_{(i,j)} \underline{S}_i \cdot \underline{S}_j \; - j \sum_{i,j} (\underline{S}_i \cdot \underline{S}_j)^2 \qquad (1.5)$$

where the sums are over nearest neighbour atoms.

It has been suggested that the last term is not entirely due to the exchange forces, but partially to a balance between these and elastic forces.

Mattis[7] has discussed a universal Hamiltonian for the description of various solids. By applying perturbation theory to second order he obtains the effective Hamiltonian for a non-conducting medium as

$$\mathcal{H} = \sum_{i \neq j} \left[\frac{2}{U} H^2(\underline{R}_{ij}) - J(\underline{R}_{ij}) \right] \underline{S}_i \cdot \underline{S}_j$$

where $\underline{S}_i$ are the total atomic spin operators. $H(\underline{R}_{ij})$ comes from the term which represents "hopping" of an electron from site j to site i ; $J(\underline{R}_{ij})$ arises from exchange between nearest neighbour atoms. Thus the total Hamiltonian must

be considered as the sum of two effects; one an anti-ferromagnetic interaction due to virtual "hopping" of an electron from $\underline{R}_i$ to $\underline{R}_j$ (and back), a "one-body" or "kinetic" exchange mechanism, and the second a ferromagnetic interaction arising from the exchange of two electrons not on the same atom. As in the Heitler-London theory the type of interaction found depends on the relative magnitude of these two interactions.

This, however, cannot constitute a general theory of magnetism in insulators as it can not predict the strength of interaction in insulating material such as manganese oxide, MnO. The value of the exchange integrals is, of course, determined in the above by the direct overlap of electron orbitals of electrons on neighbouring atoms; but because in MnO the distance between nearest neighbour Mn atoms is so large these integrals are small, and they cannot account for the strength of interaction needed. Kramer[8] suggested that this discrepancy could be resolved if the mechanism was, in fact, an indirect exchange via the oxygen atoms so increasing the overlap of the electron orbitals of nearest neighbour Mn atoms. Anderson[9,10] has shown in his theory of superexchange (i.e. assuming Kramer's mechanism) that the Hamiltonian is still of the Heisenberg form, as far as the leading term in his perturbation treatment is concerned.

At the present stage, therefore, the Heisenberg Hamiltonian is very fundamental to the theory of localized moments in insulators. There is, however, one exchange mechanism, known as Double exchange, introduced by Zener,[11,12] which does not give a Heisenberg type Hamiltonian. This theory was introduced to explain the rather different properties of mixed valency oxides of the form $(La_{1-x}Ca_x)(Mn^{3+}_{1-x}Mn^{4+}_{x})O_3$. These oxides exhibit

remarkable conductivity variations with the concentration x of Mn^{4+} atoms, while the extreme cases (x = 0 or 1) behave as antiferromagnetic insulators.

The full treatment of the Heisenberg Hamiltonian is impossible for a magnetic crystal and many papers have dealt with approximating this Hamiltonian. One simple way to approximate is, of course, to neglect its diagonal elements, giving,

$$\mathcal{H}_I = -\sum_{(i,j)} J_{ij} S_i^{\gamma} S_j^{\gamma} \qquad (1.6)$$

This new Hamiltonian is called the Ising Hamiltonian and was used by Lenz and Ising[13] to formulate the problem of ferromagnetism in a one dimensional chain before the Heisenberg Hamiltonian was envisaged. This Hamiltonian cannot be an exact description of a ferromagnetic or antiferromagnetic system in two or three dimensions, as it excludes the existence of spin waves (see chapter 2); but it short-circuits the difficult mathematics of the Heisenberg Hamiltonian, and it is a tractable model of a system which should exhibit co-operative phenomena and phase transitions. In this latter sense it is really part of the theory of statistical mechanics and not of solid state theory (it is especially important in the theory of order-disorder transitions).

Another important point is that two ferromagnetic insulators $CuK_2Cl_4.2H_2O$ and $Cu(NH_4)_2Cl_4.2H_2O$[14] seem to provide a good representation of the Heisenberg model's predictions: the zero-field susceptibility near the Curie temperature is proportional to $(1-\frac{T_c}{T})^{-n}$ with n = 1.36, 1.37 respectively, which is reasonably consistent with the theoretical value n = 1.33[15]; also the critical entropy has an experimental value 0.22, which compares well with the theoretical value 0.265[16] (Ising model predicts 0.102

for spin-$\frac{1}{2}$ case). The best agreement with the Ising model is obtained from cobalt tutton salts.[17]

In metals the physical situation is more complicated, because not all the electrons are highly localized as they are in insulators. Some electrons are still core electrons, belonging to filled shells tightly bound to the nucleus, and unaware of the metallic environment. Others in unfilled shells have a range of behaviour intermediate between that of the quasi-free conduction electrons and the tightly bound localized electrons. In devising a model of this situation it is simpler to consider the electrons as either quasi-free or localized. For instance, the electrons in the well-localized magnetic d or f shells could be considered as interacting with each other via a Heisenberg exchange mechanism as in insulators, while the quasi-free conduction electrons account for the metallic properties. This approach, is, however, much too simple and it is certain that the conduction electrons are extremely important in accounting for the magnetic properties, as these electrons alone are capable of sustaining correlations over several interatomic distances.

The indirect exchange theory of magnetism in metals makes use of this mechanism and leads to an effective interatomic Heisenberg Hamiltonian which can be derived by second order perturbation theory. Ruderman and Kittel[18] first invented this theory in connection with nuclear magnetic resonance, where they studied the effective long range interaction between nuclear spins due to the hyperfine coupling with the common sea of conduction electrons. The extension to the s-d or s-f interaction in metals by Yosida[19] permitted the explanation of Zimmerman's[20,21] specific heat measurements on Cu-Mn alloys. The Mn impurity atoms retain part of their Hund's rule

magnetization in the solute and because of this the spins of the conduction electrons are polarized at least in the neighbourhood of the impurities. If the R-K-Y theory is applicable this polarization is not localized, and Mn atoms at fairly large distances away are affected giving an effective interaction between Mn atoms. This interaction can be shown to have the form,

$$\mathcal{H}_{eff.} = -\sum_{(i,j)} J(R_{ij})\, \underline{S}_i \cdot \underline{S}_j$$

$$\text{where} \quad J(R_{ij}) = -G\left[\frac{\sin(2k_F R_{ij}) - 2k_F R_{ij}\cos(2k_F R_{ij})}{(2k_F R_{ij})^4}\right] \tag{1.7}$$

k_F is the Fermi momentum and G depends on this and the square of the exchange coupling between the localized electrons and the conduction electrons.

The most likely application of the indirect exchange theory is to metals containing elements in the gadolinium rare earth series. Generally the f shell radii of the rare earth atoms are so small that even nearest neighbour atoms do not have significant direct overlap and the R-K-Y interaction can be considered the principle interaction (with crystal field anisotropy the main correction). Ordered alloys containing transition elements can also be described by this theory if the magnetic atoms are sufficiently far apart for the d shell overlaps to be unimportant.

The indirect exchange theory would be invalid not only if the exchange coupling between the localized electrons and the conduction electrons could not be treated as a perturbation with respect to the kinetic energy of the conduction electrons, but also if the conduction gas in its ground state exhibited long range order. This last is certainly not true for Cu, but

Overhauser[22,23] has argued that if the correlation energy in an electron gas can be neglected, the Hartree-Fock ground state is not the usual Fermi sea, but a spiral spin configuration, a spin-density-wave. This is different from the ordering caused by polarization of the electron gas by paramagnetic impurity atoms as it would exist even when these atoms were absent. When the impurities are present their effective interaction is similar to the R-K-Y interaction, but the potential $J(R_{ij})$ is of a more complicated form.

This effective interaction is similar to that produced when the effects of the superzone boundaries are included in the R-K-Y interaction.[24]

In all cases quoted, of course, anisotropy, and spin-orbit coupling have been ignored, as they will be in subsequent chapters. Even apart from these the theory of magnetism is not the theory of the Heisenberg Hamiltonian, but in insulators this Hamiltonian is of great importance, and in the theory of alloys it has a definite contribution to make to our understanding of the subject.

Chapter 2

Decoupling Methods and The Spin-Wave Approximation

2.1 The Spin-Wave Approximation for Ferromagnets

The model Hamiltonian being considered is simple in form but it leads to difficult mathematics when it is used to calculate physical properties, such as magnetization, and so some further approximation will be needed. In two temperature regions approximations to the Heisenberg Hamiltonian are well developed; these are at the two extremes, low and high temperatures.

In the low temperature region the spins in a magnetic crystal are very nearly aligned and for ferromagnetic ordering, following Holstein and Primakoff,[25] we can define the usual quantum number m (which corresponds to the z component of the atomic spin S), and hence the spin-deviation quantum number $n = S-m$, which measures the deviation of S^z from its maximum value S. If only one spin deviation is present in a lattice it does not remain localized on any atom, but because of the exchange interaction with other spins it will propagate itself through the lattice. This leads to the definition of an elementary excitation, a spin wave, corresponding to the propagation of a spin deviation with a definite wave-number vector. The basis of the spin-wave approximation, first used by Bloch,[26] is the fact that at sufficiently low temperatures the influence of the interaction between the spin deviations may be neglected or alternatively that the interactions between spin waves can be neglected. Bloch used linear harmonic oscillators[27] to approximate the spin operators, because of the similarity between the

corresponding matrix representations, while Holstein and Primakoff used creation and annihilation operators. From the definition of these operators for spin deviations an exact representation of the spin operators can be found,

$$S_{\underline{\ell}}^{+} = S_{\underline{\ell}}^{x} + i S_{\underline{\ell}}^{y} = (2S)^{1/2}\left(1 - a_{\underline{\ell}}^{*} a_{\underline{\ell}}/2S\right)^{1/2} a_{\underline{\ell}} \quad ; \quad S_{\underline{\ell}}^{z} = S - a_{\underline{\ell}}^{*} a_{\underline{\ell}}$$

$$S_{\underline{\ell}}^{-} = S_{\underline{\ell}}^{x} - i S_{\underline{\ell}}^{y} = (2S)^{1/2} a_{\underline{\ell}}^{*}\left(1 - a_{\underline{\ell}}^{*} a_{\underline{\ell}}/2S\right)^{1/2} \qquad (2.1)$$

and $\quad [a_{\underline{\ell}}, a_{\underline{m}}^{*}] = a_{\underline{\ell}} a_{\underline{m}}^{*} - a_{\underline{m}}^{*} a_{\underline{\ell}} = \delta_{\underline{\ell},\underline{m}}$

where $a_{\underline{\ell}}^{*}$ creates a spin deviation on site l, and $a_{\underline{\ell}}$ is the corresponding destruction operator. The difficulty with this representation is, of course, the operator $(1 - a_{\underline{\ell}}^{*} a_{\underline{\ell}}/2S)^{1/2}$. As a first approximation it can be replaced by 1, as at very low temperatures $\langle a_{\underline{\ell}}^{*} a_{\underline{\ell}} \rangle \ll 2S$, ($\langle A \rangle$ denotes the thermodynamic average of A) and terms $a_{\underline{\ell}}^{*} a_{\underline{\ell}} a_{\underline{m}}^{*} a_{\underline{m}}$ can be neglected (assuming that there is no correlation in the location of the different spin deviations). Using the simplified representation the Heisenberg Hamiltonian is easily transformed into its new form, but a further transformation is needed to diagonalize it. This is provided by transforming the spin deviation operators into the corresponding spin-wave operators,

$$a_{\underline{\lambda}} = \frac{1}{N^{1/2}} \sum_{\underline{\ell}} e^{i \underline{\lambda} \cdot \underline{R}_{\underline{\ell}}} a_{\underline{\ell}} \quad ; \quad a_{\underline{\lambda}}^{*} = \frac{1}{N^{1/2}} \sum_{\underline{\ell}} e^{-i \underline{\lambda} \cdot \underline{R}_{\underline{\ell}}} a_{\underline{\ell}}^{*} \qquad (2.2)$$

In this simple theory the Heisenberg Hamiltonian,

$$\mathcal{H} = -2 \sum_{(\underline{i},\underline{j})} J(\underline{i}-\underline{j})\, \underline{S}_{\underline{i}} \cdot \underline{S}_{\underline{j}} + H \sum_{\underline{j}=1}^{N} S_{\underline{j}}^{z} \qquad (2.3)$$

is finally transformed to,

$$\mathcal{H}^{(0)} = HSN - S^2 J(0) N + \sum_{\underline{\lambda}} \left(-H + 2S\left[J(0) - J(\underline{\lambda})\right]\right) a_{\underline{\lambda}}^{*} a_{\underline{\lambda}} \qquad (2.4)$$

and it gives a result for the temperature dependence of the magnetization identical with that obtained by Bloch, i.e. $M \sim M_0 (1 - AT^{3/2} \rightarrow)$ as well as the well known dependence of the spin wave energy $\epsilon_{\underline{k}} = ak^2$. H is a measure of the applied field, and $J(\underline{\lambda}) = \sum_{(\underline{l}-\underline{m})} J(\underline{l}-\underline{m}) e^{i\underline{\lambda}.(\underline{l}-\underline{m})}$

Oguchi[28] extended the approximation by expanding the operator $(1 - a^*_{\underline{l}} a_{\underline{l}}/2S)^{1/2}$ in powers of $1/2S$ and neglecting all terms in the Hamiltonian which had more than 4 operators or whose coefficient was of order $(1/2S)^2$ or less. This improved treatment allowed the interaction between spin waves, to be examined and the leading correction to the magnetization was found to be $O(T^4)$, while the energy of the excitations was renormalized by a factor $(1 + BT^{5/2} \rightarrow)$. The Hamiltonian in this theory is

$$\mathcal{H} = \mathcal{H}^{(0)} + \frac{1}{2N} \sum_{\underline{\lambda},\underline{\mu},\underline{\nu}} \left[J(\underline{\lambda}) + J(\underline{\nu}) - 2J(\underline{\lambda}-\underline{\nu}) \right] a^*_{\underline{\lambda}} a^*_{\underline{\mu}} a_{\underline{\nu}} a_{\underline{\lambda}+\underline{\mu}-\underline{\nu}} \qquad (2.5)$$

and Oguchi[28] obtained his results using perturbation theory. (This Hamiltonian is the effective one used by other authors; the extra terms treated by Oguchi have their contributions cancelled by 'higher' order terms).

Dyson[29,30] used a different Hamiltonian (still derived from the Heisenberg Hamiltonian) in an earlier paper in which he also obtained the temperature dependences stated above. This Hamiltonian can be found by using the following effective representation of the spin operators[31,32]

$$S^+_{\underline{l}} \simeq (2S)^{1/2} \left(1 - a^*_{\underline{l}} a_{\underline{l}}/2S\right)^{1/2} a_{\underline{l}};$$

$$S^-_{\underline{l}} \simeq (2S)^{1/2} a^*_{\underline{l}} \quad ; \quad S^z_{\underline{l}} = S - a^*_{\underline{l}} a_{\underline{l}} \qquad (2.6)$$

and it is

$$\mathcal{H} = \mathcal{H}^{(0)} + \frac{1}{N} \sum_{\underline{\lambda},\underline{\mu},\underline{\nu}} \left[J(\underline{\lambda}) - J(\underline{\lambda}-\underline{\nu}) \right] a^*_{\underline{\lambda}} a^*_{\underline{\mu}} a_{\underline{\nu}} a_{\underline{\lambda}+\underline{\mu}-\underline{\nu}} \qquad (2.7)$$

The last term is non-Hermitian and gives rise to great difficulties but Dyson's masterly treatment solved these and showed that at all low temperatures the kinematic interaction is negligible. (This arises because the 'exclusion principle' forbids more than (2S) spin deviations to occur on the same site). (2.7) has been used by Tahir-Kheli and Ter Haar[32] using the Green function decoupling method, and this will be considered later.

2.2 The Spin Wave Approximation for Antiferromagnets

The concepts of spin deviation and spin waves can be used in the antiferromagnetic case to study the low temperature properties, but the Néel ground state (which takes the spins as totally aligned in the z direction or -z direction with any spin 'pointing' in the opposite direction to its nearest neighbours) is not the true one as spin deviations still exist when T=0. The problem is also complicated by the need to consider the two sublattices separately (all simple treatments assume that the Néel ground state is, in fact, the true ground state) and so two sets of spin deviation (and spin wave) operators must be used (see Kubo[33] and Oguchi[28]). Following Oguchi the representations of the spin operators are,

(i) for the 'up' spins on the $\underline{l}$ sublattice,

$$S_{\underline{l}}^{+} = (2S)^{1/2}\left(1-a_{\underline{l}}^{*}a_{\underline{l}}/2S\right)^{1/2}a_{\underline{l}};$$

$$S_{\underline{l}}^{-} = (2S)^{1/2}\, a_{\underline{l}}^{*}\left(1-a_{\underline{l}}^{*}a_{\underline{l}}/2S\right)^{1/2} \qquad S_{\underline{l}}^{z} = S-a_{\underline{l}}^{*}a_{\underline{l}}; \qquad (2.8)$$

(ii) for the 'down' spins on the $\underline{m}$ sublattice,

$$S_{\underline{m}}^{+} = (2S)^{1/2}\, b_{\underline{m}}^{*}\left(1-b_{\underline{m}}^{*}b_{\underline{m}}/2S\right)^{1/2};$$

$$S_{\underline{m}}^{-} = (2S)^{1/2}\left(1-b_{\underline{m}}^{*}b_{\underline{m}}/2S\right)^{1/2}b_{\underline{m}}\,; \quad S_{\underline{m}}^{z} = -S+b_{\underline{m}}^{*}b_{\underline{m}} \qquad (2.9)$$

Kubo[33] found a divergence of the fluctuation of magnetization in his spin-wave theory of antiferromagnets, but it can be avoided by introducing anisotropy energy terms into the Hamiltonian. This latter is idealised to,

$$\mathcal{H} = 2|J| \sum_{(\underline{l},\underline{m})} \underline{S}_{\underline{l}} . \underline{S}_{\underline{m}} + h_1 \sum_{\underline{l}} S^{z}_{\underline{l}} + h_2 \sum_{\underline{m}} S^{z}_{\underline{m}} \quad . \tag{2.10}$$

where h_1 is a measure of the field acting on the $\underline{l}$ sublattice; h_2 that acting on the $\underline{m}$ sublattice. Denoting these by different constants enables the sublattice magnetization to be calculated, as well as providing a simple means of introducing some anisotropy. The operator $(1-a^{*}_{\underline{l}} a_{\underline{l}}/2S)^{1/2}$ is treated as previously, and in Oguchi's treatment terms with more than 6 operators are neglected.

As in the ferromagnetic case spin-wave creation and destruction operators can be defined (except that now the sum over lattice sites is restricted to one or other of the sublattices), but here they do not diagonalize the two operator terms and a further transformation is necessary. If the spin-wave operators are $a_{\underline{k}}, b_{\underline{k}}$ etc. and the new operators $\alpha_{\underline{k}}, \beta_{\underline{k}}$ etc. the transformation is defined by

$$\begin{aligned}
a_{\underline{k}} &= \alpha_{\underline{k}} \cosh\theta_{\underline{k}} - \beta^{*}_{\underline{k}} \sinh\theta_{\underline{k}} \\
b_{\underline{k}} &= -\alpha^{*}_{\underline{k}} \sinh\theta_{\underline{k}} + \beta_{\underline{k}} \cosh\theta_{\underline{k}} \\
a^{*}_{\underline{k}} &= \alpha^{*}_{\underline{k}} \cosh\theta_{\underline{k}} - \beta_{\underline{k}} \sinh\theta_{\underline{k}} \\
b^{*}_{\underline{k}} &= -\alpha_{\underline{k}} \sinh\theta_{\underline{k}} + \beta^{*}_{\underline{k}} \cosh\theta_{\underline{k}}
\end{aligned} \tag{2.11}$$

where $\tanh(2\theta_{\underline{k}}) = \gamma_{\underline{k}} / (1 - \tfrac{1}{2}h'_1 + \tfrac{1}{2}h'_2)$

and $h'_1 = h_1/(2z|J|S)$, $h'_2 = h_2/(2z|J|S)$, and $\gamma_{\underline{k}} = \frac{1}{z}\sum_{(\underline{l}-\underline{m})} e^{i\underline{k}.(\underline{l}-\underline{m})}$
(z is the number of nearest neighbours).

The effective Hamiltonian becomes

$$\mathcal{H} = \text{Const.} + \sum_{\underline{k}} \left(A^{-}_{\underline{k}} n_{\underline{k}} + A^{+}_{\underline{k}} n'_{\underline{k}} \right) + \sum_{\underline{k}_1, \underline{k}_2} \left[B^{(1)} (n_1 n_2 + n'_1 n'_2) + B^{(2)} n_1 n'_2 \right] \tag{2.12}$$

where $n_{\underline{k}} = \alpha^{*}_{\underline{k}} \alpha_{\underline{k}}$, $n'_{\underline{k}} = \beta^{*}_{\underline{k}} \beta_{\underline{k}}$ and the coefficients are

$$A^{\pm}_{\underline{k}} = \left[(D^2 - \gamma^2_{\underline{k}})^{1/2} \pm \tfrac{1}{2}(k'_1 + k'_2) - \frac{1}{SN} C_{\underline{k}} \sum_{\underline{k}'} (C_{\underline{k}'} - 1) \right] 2z|J|S$$

$$B^{(1)} = -\frac{z|J|}{N} (C_{\underline{k}_1} C_{\underline{k}_2} - 1) \quad , \quad B^{(2)} = -\frac{2z|J|}{N} (C_{\underline{k}_1} C_{\underline{k}_2} + 1) \tag{2.13}$$

$$C_{\underline{k}} = \frac{D - \gamma^2_{\underline{k}}}{(D^2 - \gamma^2_{\underline{k}})^{1/2}} \quad , \quad D = 1 - \frac{k'_1}{2} + \frac{k'_2}{2}$$

Using this Hamiltonian Oguchi[28] found the low temperature expression for a number of thermodynamic quanties including specific heat, sublattice magnetization and parallel susceptibility. In this expression the spin-wave interactions produced contributions very much smaller than the leading terms and also smaller than terms produced by treating the deviation from linearity of the spin-wave energy spectrum ($\epsilon_{\underline{k}} \sim a|\underline{k}|$). Nevertheless, the smallness of the effect of the spin-wave interactions confirms the usefulness of the first approximation in Holstein and Primakoff's method.

Anderson[34] in an earlier paper treated the simple non-interacting spin-wave approximation to (2.12); and concluded that the 'sublattice' picture of antiferromagnetism is not qualitatively affected by complications in the actual ground state. This is very important as spin wave theories of this type of antiferromagnet have had considerable success in explaining experimental results.[35] Ziman[36,37] treated the antiferromagnet in a similar way but included dipole-dipole interactions in the Hamiltonian.

2.3 The Green Function Method and Decoupling Procedures at Low Temperatures

The method is based on the equation of motion of the operator $a^*_{\underline{\lambda}}(t) = e^{i\mathcal{H}t} a^*_{\underline{\lambda}} e^{-i\mathcal{H}t}$ which is

$$i\frac{dA(t)}{dt} = [A(t), \mathcal{H}] \qquad (2.14)$$

and the definition of the Green function (retarded)

$$\ll a_{\underline{\lambda}}(t);\, a^*_{\underline{\lambda}'} \gg = -i\,\theta(t) \langle [a_{\underline{\lambda}}(t), a_{\underline{\lambda}'}] \rangle \qquad (2.15)$$

where $\mathcal{H}$ is the Hamiltonian of the system; $\theta(t)$ is a step function, unity for positive t and zero for negative t; $[A,B]$ denotes the commutator of the operators A and B and equals AB-BA. The Green function can, of course, be Fourier transformed with respect to time to give $\ll a_{\underline{\lambda}}; a^*_{\underline{\lambda}'} \gg_E$ which satisfies the equation of motion

$$E \ll a_{\underline{\lambda}}; a^*_{\underline{\lambda}'} \gg_E = \frac{\langle [a_{\underline{\lambda}}, a^*_{\underline{\lambda}'}] \rangle}{2\pi} + \ll [a_{\underline{\lambda}}, \mathcal{H}]; a^*_{\underline{\lambda}'} \gg_E \qquad (2.16)$$

where E is the argument of the Fourier transformed Green function. This equation and the relationship between the Green function and the corresponding time-dependent correlation function

$$\langle a^*_{\underline{\lambda}'} a_{\underline{\lambda}}(t) \rangle = \lim_{\epsilon \to 0} i \int_{-\infty}^{\infty} \frac{\ll a_{\underline{\lambda}}; a^*_{\underline{\lambda}'} \gg_{\hbar\omega + i\epsilon} - \ll a_{\underline{\lambda}}; a^*_{\underline{\lambda}'} \gg_{\hbar\omega - i\epsilon}}{\exp(\hbar\omega/kT) - 1} e^{i\omega t}\, d\omega \qquad (2.17)$$

are the only equations required for the application of the Green function method, and so the reader is referred to Zubarev's[38] paper for further information about the theory of the method.

So far the method is exact but in equation (2.16) a new Green function occurs. This function could, of course, be treated by an equation of motion method but this, far from eliminating the difficulty, introduces another Green function. In fact, by repeated use of the equation (2.16) we can produce an infinite set of coupled equations. To approximate the original Green function this set must be terminated at some stage i.e. 'decoupled'.

Tahir-Kheli and Ter Haar[32] used this method in the spin wave approximation and decoupled in the first equation by assuming that,

$$\ll a^*_{\underline{\lambda}_1} a_{\underline{\mu}_1} a_{\underline{k}+\underline{\lambda}_1-\underline{\mu}_1} ; a^*_{\underline{k}'} \gg_E \simeq \delta_{\underline{\lambda}_1,\underline{\mu}_1} \langle a^*_{\underline{\lambda}_1} a_{\underline{\lambda}_1} \rangle \ll a_{\underline{k}} ; a^*_{\underline{k}'} \gg_E + \delta_{\underline{k},\underline{\mu}_1} \langle a^*_{\underline{\lambda}_1} a_{\underline{\lambda}_1} \rangle \ll a_{\underline{k}} ; a^*_{\underline{k}'} \gg_E \tag{2.18}$$

where they were in effect considering the corresponding zero-time correlation function as

$$\langle a^*_{\underline{\lambda}_1} a^*_{\underline{\lambda}_2} a_{\underline{\lambda}_3} a_{\underline{\lambda}_4} \rangle \simeq \langle a^*_{\underline{\lambda}_1} a_{\underline{\lambda}_3} \rangle \langle a^*_{\underline{\lambda}_2} a_{\underline{\lambda}_4} \rangle + \langle a^*_{\underline{\lambda}_1} a_{\underline{\lambda}_4} \rangle \langle a^*_{\underline{\lambda}_2} a_{\underline{\lambda}_3} \rangle \tag{2.19}$$

(i.e. the average is symmetrically decoupled), and $\delta_{\underline{\lambda},\underline{\mu}}$ is the Kronecker delta.

This theory gave results identical with Dyson's except for the coefficients of the first interaction contributions to the magnetization and specific heat, which agree with Dyson's only in the limit $S \to \infty$. These errors could, of course, be corrected by decoupling the second instead of the first equation and Tahir-Kheli and Ter Haar proved this and obtained an expression for the damping of spin waves.

2.4 Decoupling Procedures for Spin Operators

Even though the results from spin wave theory are much more realistic at higher temperatures than the basic assumptions would allow one to hope,[35,39] the properties of the model are less satisfactory in the region very near the critical temperature. The magnetization has a discontinuity at the critical point,[39] and the critical temperatures are only within 10% of the values obtained by using high temperature series expansion (though it must be admitted that some Green function theories have similar or larger errors). Thus, either higher terms must be included in the Hamiltonian, or, what appears to be a more sensible course, a Green function theory using the spin operators themselves must be devised.

A number of authors have taken this latter course, which using the obvious generalisation of the equations of section 2.3 gives the basic equation,

$$E' G_E(\underline{g},\underline{l}) = \frac{2\langle S^z\rangle}{2\pi}\delta_{\underline{g},\underline{l}} - 4\sum_{\underline{f}} J(\underline{g}-\underline{f}) \ll S^z_{\underline{g}} S^+_{\underline{f}} - S^z_{\underline{f}} S^+_{\underline{g}} ; S^-_{\underline{l}} \gg_E \qquad (2.20)$$

where $E'=E-\mu H$, and $G_E(\underline{g},\underline{l}) = \ll S^+_{\underline{g}} ; S^-_{\underline{l}} \gg_E$ with the corresponding form of (2.15) as its definition.

Tyablikov[40] used this equation for the $S=\frac{1}{2}$ case and suggested the decoupling

$$\ll S^z_{\underline{g}} S^+_{\underline{h}} ; S^-_{\underline{l}} \gg_E \xrightarrow[\underline{g}\neq\underline{h}]{} \langle S^z\rangle \ll S^+_{\underline{h}} ; S^-_{\underline{l}} \gg_E \qquad (2.21)$$

This decoupling implies that,

$$\langle [S^z_{\underline{g}} S^+_{\underline{h}}, S^-_{\underline{l}}]\rangle \simeq \langle S^z\rangle \langle [S^+_{\underline{h}}, S^-_{\underline{l}}]\rangle$$

using the definition of the corresponding time-dependent Green function in the limit $t\to 0$.

i.e. $$2\langle S_i^z S_n^z\rangle\delta_{n,i} - \langle S_i^- S_n^+\rangle\delta_{i,n} \simeq 2\langle S^z\rangle\langle S^z\rangle\delta_{n,i} \qquad (2.22)$$

This is obviously a crude relationship as at low temperatures $\langle S_i^- S_n^+\rangle \simeq O(T^{3/2})$ and it is not surprising that the spin-wave energies are renormalised by a factor $(1+AT^{3/2}\rightarrow)$ instead of the factor $(1+BT^{5/2}\rightarrow)$ obtained by Dyson. There is also a spin-wave interaction contribution to the magnetization of $O(T^3)$ only part of which is due to the erroneous renormalisation. The rest is due to the form of the equation used to determine $\langle S^z\rangle$,

$$\langle S^z\rangle = \frac{1/2}{1+2\Phi} \qquad (2.23)$$

where $\Phi = \frac{1}{N}\sum_k \{ e^{\beta E_k} - 1 \}^{-1}$ and E_k is the excitation energy. The corresponding expression for the spin-wave approximation is

$$\langle S^z\rangle = \tfrac{1}{2} - \Phi \qquad (2.24)$$

and as $\Phi \simeq AT^{3/2}$ the difference between the two values of $\langle S^z\rangle$ will be of order T^3.

Tahir-Kheli and Ter Haar[41] generalised this theory to include $S > 1/2$ using the same decoupling. They had to introduce the more complicated Green function $\ll S_i^+; (S_i^-)^n (S_i^+)^{n-1} \gg_E$ because for higher spins $\langle S_i^- S_i^+\rangle \neq S - \langle S^z\rangle$, but,

$$\langle S_i^- S_i^+\rangle = S(S+1) - \langle (S^z)^2\rangle - \langle S^z\rangle \qquad (2.25)$$

and so $\langle (S^z)^2\rangle$ must be calculated as well as $\langle S^z\rangle$. Calculating $\langle (S^z)^2\rangle$ leads to higher powers of S^z being needed and only the fact that $(S^z)^{2S+1}$ is related to smaller

powers of S^z saves the method from failure. Their method becomes laborious very quickly. Callen[42] introduced the Green function $\ll S_f^+ ; e^{\alpha S_i^z} S_i^- \gg_E$ and succeeded by differentiating with respect to the parameter a in obtaining the relationships between $\langle S^z \rangle$ and $\frac{I}{\Phi}$ for general S quite easily.

Callen also changed the decoupling procedure to

$$\ll S_h^- S_f^+ S_k^+ ; A \gg_E \simeq \langle S_h^- S_k^+ \rangle \ll S_f^+ ; A \gg_E - \alpha \langle S_h^- S_f^+ \rangle \ll S_k^+ ; A \gg_E \qquad (2.26)$$

where $\alpha = \langle S^z \rangle / 2S^2$ instead of zero as in (2.21). Instead of (2.22) we have,

$$2\langle S_f^z S_h^z \rangle \delta_{h,l} - \langle S_f^- S_h^+ \rangle \delta_{f,l} \simeq 2\langle S^z \rangle^2 \delta_{h,l} - \alpha \langle S_f^- S_h^+ \rangle \delta_{f,l} \qquad (2.27)$$

a much improved approximation which corrects the renormalisation factor to $(1 + AT^{5/2} + \ldots)$ but still fails to correct the error implied by using (2.23) for $S = 1/2$. We shall return to this in section 2.5.

Identical results to those of Callen can be obtained if α is taken to unity, and this choice seems more satisfactory when the definition of the Green function being decoupled is considered in the limit $t \to o$. Instead of the previous decoupling procedures, the author has tried introducing two 'constants' α, γ

$$\ll S_f^- S_f^+ S_h^+(t) ; S_i^- \gg_E \rightarrow \alpha \langle S_f^- S_f^+ \rangle \ll S_h^+(t) ; S_i^- \gg + \gamma \langle S_f^- S_h^+ \rangle \ll S_f^+(t) S_i^- \gg \qquad (2.28)$$

where α, γ are two functions of temperature. Transforming both sides of this expression to the corresponding correlation functions and allowing $t \to o$ gives,

$$\langle S_{\underline{l}}^- S_{\underline{i}}^- S_{\underline{j}}^+ S_{\underline{n}}^+ \rangle = \alpha \langle S^- S^+ \rangle \langle S_{\underline{l}}^- S_{\underline{n}}^+ \rangle + \gamma \langle S_{\underline{j}}^- S_{\underline{n}}^+ \rangle \langle S_{\underline{i}}^- S_{\underline{j}}^+ \rangle \qquad (2.29)$$

If $l=g$ the left hand side is zero so $\alpha+\gamma=0$ and only one more condition is needed.

When $S=\frac{1}{2}$ the quantity being approximated is,

$$\sum_{\underline{n}} J(\underline{q}-\underline{n}) \ll \left(S_{\underline{g}}^- S_{\underline{g}}^+ S_{\underline{n}}^+(t) - S_{\underline{n}}^- S_{\underline{n}}^+ S_{\underline{g}}^+(t) \right); S_{\underline{\ell}}^- \gg \qquad (2.30)$$

and the other condition is obtained by using the definition of this Green function used and equating this exact quantity at $t=o$ to the approximation found by using the decoupling. A further approximation is used, because as both α and γ are assumed independent of site labels, $\langle S_{\underline{n}}^- S_{\underline{g}}^+ \rangle$ must be replaced by $\frac{1}{N} \sum_{\underline{n}-\underline{g}} \langle S_{\underline{n}}^- S_{\underline{g}}^+ \rangle$. Denoting this last quantity by μ the condition is found to be,

$$\tfrac{1}{2} - \sigma - \mu = 2\alpha\sigma\left(\tfrac{1}{2}-\sigma\right)\frac{1}{2\sigma} + 2\mu\gamma(\mu-\sigma)$$

$$\therefore \quad \alpha = \frac{\tfrac{1}{2}-\sigma-\mu}{\tfrac{1}{2}-\sigma-2\mu(\mu-\sigma)} \qquad (2.31)$$

where $\sigma = \langle S^z \rangle$

Following Callen, the energy of the spin-wave excitations is

$$E(\underline{k}) = \mu H + \left\{1 - 2\alpha\left(\tfrac{1}{2}-\sigma-\mu\right)\right\}\left[J(0)-J(\underline{k})\right] \qquad (2.32)$$

$$\text{and} \quad \frac{1}{2\sigma} = 1 + \frac{2}{N}\sum_{\underline{k}} \phi(\underline{k}) \quad , \quad \frac{\mu}{2\sigma} = \frac{1}{zN}\sum_{\underline{k}} \gamma(\underline{k})\phi(\underline{k}) \tag{2.33}$$

$$\text{where} \quad -\phi(\underline{k}) = \frac{1}{1 - e^{\beta E(\underline{k})}}$$

These expressions give the same low temperature behaviour as Callen's theory and at temperatures near the transition temperature the theory's prediction is unfortunately even less satisfactory. If the sum $\frac{1}{N}\sum_{\underline{k}} \phi(\underline{k})$ is to diverge when $\sigma=0$, as it must, then

$$1 - 2\alpha\left(\tfrac{1}{2} - \sigma - \mu\right) = 0$$

and so $\mu=0$. Thus, $\mu/2\sigma = 1/zN\sum_{\underline{k}} \gamma(\underline{k})\phi(\underline{k})$ cannot be satisfied and the only solution for the Curie temperature is infinity.

This situation may, of course, be improved if some of the dependence of α, γ on lattice sites were included.

2.5 A Correction to Callen's Decoupling Procedure for $S=\frac{1}{2}$

The low temperature error in Callen's theory, as compared with the known spin wave approximation limit, can be rectified. The two Green functions that must be decoupled are

$$\ll S_{\underline{n}}^- S_{\underline{n}}^+ S_{\underline{m}}^+(t) ; S_{\underline{\ell}}^- \gg \quad \text{and} \quad \ll S_{\underline{m}}^+ S_{\underline{n}}^- S_{\underline{n}}^+(t) ; S_{\underline{\ell}}^- \gg$$

Callen decoupled these in the same manner and this is the cause of the error. If the Green functions are considered in the $t \to 0$ limit their values differ:-

$$\lim_{t\to 0} \ll S_{\underline{n}}^- S_{\underline{n}}^+ S_{\underline{m}}^+(t) ; S_{\underline{\ell}}^- \gg = 2\langle S_{\underline{n}}^- S_{\underline{n}}^+ S_{\underline{m}}^z \rangle \delta_{\underline{m},\underline{\ell}} + \langle S_{\underline{n}}^- S_{\underline{m}}^+ \rangle \delta_{\underline{m},\underline{\ell}} \tag{2.34}$$

and $$\lim_{t\to 0} \ll S_{\underline{m}}^+ S_{\underline{n}}^- S_{\underline{n}}^+(t); S_{\underline{\ell}}^- \gg = 2\langle S_{\underline{m}}^z S_{\underline{n}}^- S_{\underline{m}}^+ \rangle \delta_{\underline{m},\underline{\ell}} + \langle S_{\underline{m}}^+ S_{\underline{n}}^- \rangle \delta_{\underline{n},\underline{\ell}}$$

that is, they differ by $2\langle S^z \rangle \delta_{\underline{n},\underline{\ell}} \delta_{\underline{m},\underline{n}}$

Further, we can define at $t=0$ the correlation functions

$$\psi_{(1)}(\underline{k}_1, \underline{k}_2) = \sum_{\substack{\underline{g}-\underline{\ell} \\ \underline{g}-\underline{n}}} e^{i(\underline{g}-\underline{\ell})\underline{k}_1 + i(\underline{g}-\underline{n})\underline{k}_2} \langle S_{\underline{\ell}}^- S_{\underline{g}}^- S_{\underline{g}}^+ S_{\underline{n}}^+ \rangle \tag{2.35}$$

and $$\psi_{(2)}(\underline{k}_1, \underline{k}_2) = \sum_{\substack{\underline{g}-\underline{\ell} \\ \underline{g}-\underline{n}}} e^{i(\underline{g}-\underline{\ell})\underline{k}_1 + i(\underline{g}-\underline{n})\cdot\underline{k}_2} \langle S_{\underline{\ell}}^- S_{\underline{n}}^+ S_{\underline{g}}^- S_{\underline{g}}^+ \rangle \tag{2.36}$$

which differ since

$$\frac{1}{N^2}\sum_{\underline{k}_1,\underline{k}_2} \psi_{(1)}(\underline{k}_1, \underline{k}_2) = 0 \quad \text{and} \quad \frac{1}{N^2}\sum_{\underline{k}_1,\underline{k}_2} \psi_{(2)}(\underline{k}_1, \underline{k}_2) = \langle S_{\underline{g}}^- S_{\underline{g}}^+ \rangle \tag{2.37}$$

The errors introduced into the limits of the Green functions and the correlation function $\psi_{(2)}$ by decoupling 'symmetrically' are only obviously large when all the

sites are equal. Those in $\psi_{(1)}$, however, occur when $l=g$ or $n=g$. We restrict the correction in the procedure to account only for discrepancies in $\psi_{(1)}$ which can be eliminated by adding the correction

$$2\langle S^- S^+\rangle \ll S^+_{\underline{l}} ; S^-_{\underline{l}} \gg_E \delta_{\underline{h},\underline{l}} \tag{2.38}$$

to the decoupled expression for $\ll S^-_{\underline{g}} S^+_{\underline{g}} S^+_{\underline{m}} ; S^-_{\underline{l}} \gg_E$.
The Green function is taken with identical sites for all operators as we wish to mirror the form the correction must take (cf. (2.58)).

Using (2.38) as a correction to the decoupling procedure used by Callen[42] the correction to the equation of motion is

$$-2\left[J(0)-J(\underline{k})\right]\frac{1}{N}\sum_{\underline{k}} G_E(\underline{k})\langle S^- S^+\rangle \tag{2.39}$$

and the complete equation of motion for $G_E(\underline{k})$ is

$$\left[E-E(\underline{k})\right] G_E(\underline{k}) = \frac{2\langle S^z\rangle}{2\pi} - 2\left[J(0)-J(\underline{k})\right]\langle S^- S^+\rangle \frac{1}{N}\sum_{\underline{k}} G_E(\underline{k}) \tag{2.40}$$

As a simple approximation this equation can be iterated to give

$$G_E(\underline{k}) \simeq \frac{2\langle S^z\rangle}{2\pi\left[E-E(\underline{k})\right]} - \frac{2\langle S^- S^+\rangle\left[J(0)-J(\underline{k})\right]}{2\pi\left[E-E(\underline{k})\right]N}\sum_{\underline{k}'} \frac{2\langle S^z\rangle}{E-E(\underline{k}')} \tag{2.41}$$

which transforms to

$$\psi(\underline{k}) \simeq 2\langle S^z\rangle\left[2-2\langle S^z\rangle\right]\phi(\underline{k}) \tag{2.42}$$

Thus

$$\tfrac{1}{2} - \langle S^z \rangle = (1 + A\cdot T^3 + \cdots)\Phi + O(T^4) \qquad (2.43)$$

The error compared with the spin wave approximation of $\langle S^z \rangle$ is now of $O(T^{9/2})$ instead of $O(T^3)$ as found by Callen, and thus the spin wave interactions contribute from $O(T^4)$.

The correction will also affect the coefficient of the first interaction term. The terms that will contribute to order T^4 on the right hand side of (2.43) are

$$\Phi + 2\langle S^- S^+ \rangle \{2F(-1)\} \frac{1}{N} \sum_k \frac{J(0)-J(k)}{J(0)} \phi(k)$$

which, using Callen's notation, gives the first interaction term as

$$-3\pi\nu\, J\left(\tfrac{3}{2}\right) J\left(\tfrac{5}{2}\right) T^4 \left\{1 + \tfrac{4}{3} F(-1)\right\} \qquad (2.44)$$

The corresponding terms in Callen and Dyson are

$$-3\pi\nu\, J\left(\tfrac{3}{2}\right) J\left(\tfrac{5}{2}\right) T^4$$

and $$-3\pi\nu\, J\left(\tfrac{3}{2}\right) J\left(\tfrac{5}{2}\right) T^4 Q \qquad \text{respectively,}$$

where Q depends on spin and the type of lattice. For the simple cubic lattice and $S=\frac{1}{2}$, $Q = 12/3$ whereas the effective Q in this work using (2.44) is 3. This is only an improvement on Callen's result in that the extra interaction contribution is estimated, but the errors are much greater. The results for Q for the cubic lattice are compared with those of Dyson and Callen in Table 2.A. For these Q values we see that the correction is not subtle enough and a further correction is needed with

$\langle S^- S^+ \rangle$ replaced by some average of $O(T^{5/2})$, but it is difficult to see where this error occurs. The error could be occuring in the form of a higher order term in the expansion (2.58).

These results were possible because iteration produced a power series in powers of $\langle S^- S^+ \rangle$ which at low temperatures is of $O(T^{3/2})$. However, at temperatures near the transition temperature this type of approximation is insufficient and the exact equation must be used.

The complete equation can be used to calculate $\frac{1}{N}\sum_k G_E(k)$

$$\frac{1}{N}\sum_k G_E(k) = \frac{\frac{2\langle S^z\rangle}{2\pi N}\sum_{k'} \frac{1}{E-E(k')}}{1 + \frac{2}{N}\sum_{k'} \frac{J(0)-J(k')}{E-E(k')}\left(\frac{1}{2}-\langle S^z\rangle\right)}$$

So,

$$G_E(k) = \frac{2\langle S^z\rangle}{2\pi[E-E(k)]}\left[1 - \frac{(1-2\langle S^z\rangle)(J(0)-J(k))\frac{1}{N}\sum_{k'}\frac{1}{E-E(k')}}{1+\frac{2}{N}\sum_{k'}\frac{J(0)-J(k')}{E-E(k')}\left(\frac{1}{2}-\langle S^z\rangle\right)}\right] \quad (2.45)$$

This equation transforms to

$$\frac{1}{2}-\langle S^z\rangle = 2\langle S^z\rangle \Phi$$

$$-2\frac{\langle S^z\rangle}{N} g \sum_k \left\{\frac{g\,d_1(k)h(k) - 2\left(h(k)+d_1(k)\right)\left(1+g\,d_1(k)\right)}{\left(1+g\,d_1(k)\right)^2 + \frac{J(0)-J(k)}{J(0)}g^2\left(\frac{J(0)-J(k)}{J(0)}+2d_2(k)\right)}\right\}\phi(k) \quad (2.46)$$

where $g = \frac{(1-2\langle S^z\rangle)}{R}$, $d_n(k) = \frac{\mathcal{P}}{N}\sum_{k''}\frac{\left[J(0)-J(k'')\right]\left(J(0)\right)^{n-1}}{\left(J(k'')-J(k)\right)^n}$

and $$h(\underline{k}) = \frac{P}{N}\sum_{\underline{k}''} \frac{J(0)-J(\underline{k})}{J(\underline{k}'')-J(\underline{k})}$$

Assuming that the correction considered above is applied to Callen's[42] decoupling procedure with $E(\underline{k})$ and $\bar{f}$ given by $2\langle S^z\rangle[1+\bar{f}][J(0)-J(\underline{k})]$ and $\frac{\langle S^z\rangle}{S^2 J(0)}\frac{1}{N}\sum_{\underline{k}'} J(\underline{k}')\phi(\underline{k}')$ respectively the equations which provide a solution for the transition temperature are

$$\frac{1}{2} = \frac{kT}{J(0)}(1+\bar{f})^{-1}\left\{F(-1) + \frac{1}{N}\sum_{\underline{k}} \frac{J(0)d_1(\underline{k})}{J(0)-J(\underline{k})}\left[\frac{h(\underline{k})+2d_1(\underline{k})}{d_1^2(\underline{k})+\frac{J(0)-J(\underline{k})}{J(0)}\left[2d_2(\underline{k})+\frac{J(0)-J(\underline{k})}{J(0)}\right]}\right]\right\} \tag{2.47}$$

and $$\bar{f}(1+\bar{f}) = \frac{F(-1)-1}{2S^2 J(0)}kT$$

The only change from Callen's[42] calculation is the integral which corrects the first of these equations, and the sign of this integral is critical in determing whether kT_c is increased or decreased as compared with Callen's values for $S=\frac{1}{2}$. If the integral is positive the value of kT_c will decrease and vice versa.

The integral $d_1(\underline{k})$ is known for certain values of $J(\underline{k})$:

if (i) $J(\underline{k})=0$, $d_1(\underline{k}) = -1$

(ii) $J(\underline{k}) = J(0)$, $d_1(\underline{k}) = -1$

(iii) $J(\underline{k}) = -J(0)$, $d_1(\underline{k}) = -1 + 2F(-1)$

and so we can estimate $d_1(k)$ as a quadratic expression in $J(\underline{k})/J(0)$.

Defining

$$d_1(\underline{k},\alpha) = \frac{1}{N}\sum_{\underline{k}''} \frac{\alpha J(0) - J(\underline{k}'')}{[J(\underline{k}'') - \alpha J(\underline{k})]}$$

$$\text{and} \quad d_2(\underline{k},\alpha) = \frac{1}{N}\sum_{\underline{k}''} \frac{[\alpha J(0) - J(\underline{k}'')]\, J(0)}{[J(\underline{k}'') - \alpha J(\underline{k})]^2} \tag{2.48}$$

we have the relation

$$\frac{\partial}{\partial\alpha}\{d_1(\underline{k},\alpha)\} = \frac{J(0)}{\alpha[J(0)-J(\underline{k})]}\{1+d_1(\underline{k},\alpha)\} + \frac{J(\underline{k})}{J(0)}\, d_2(\underline{k},\alpha) \tag{2.49}$$

and only condition (iii) needs redefinition. If

$$\text{(iii)}' \quad J(\underline{k}) = -J(0) \quad , \quad d_1(\underline{k},\alpha) = -1 + 2F(-1,\alpha)$$

where $$F(-1,\alpha) = \frac{1}{N}\sum_{\underline{k}'} \frac{\alpha J(0)}{\alpha J(0) - J(\underline{k}')}$$

Assuming that $d_1(\underline{k},\alpha)$ is a quadratic expression and using the conditions (i), (ii), (iii)′ we obtain the representation in the limit $\alpha \to 1$

$$d_1(\underline{k}) \simeq F(-1)\,(x^2 - x) - 1$$

$$d_2(\underline{k}) \simeq F(-1) + (1-x)\,[F(-2) - F(-1)] \tag{2.50}$$

where $x = J(\underline{k})/J(0)$

Using these in the correction term to the transition temperature equation the argument of the integrand becomes

$$\frac{2}{1-x} - \frac{2+4F(-2)}{2+2F(-2)} \frac{1-ax+b(x^2-x^3)}{1+dx+ex^2-x^3(2-x)b'}$$

with

$$\begin{aligned} a &= \left[2-4F(-1)+F^2(-1)-4F(-2)\right] / \left[2+4F(-2)\right] \\ b &= \left[F^2(-1)\right] / \left[2+4F(-2)\right] \\ d &= \left[-2+4F(-1)-4F(-2)\right] / \left[1+2F(-2)\right] \\ e &= b-d-\left(1+2F(-1)\right) / \left[1+2F(-2)\right] \\ \text{and} \quad b' &= F^2(-1) / \left[1+2F(-2)\right] \end{aligned} \tag{2.51}$$

For a simple cubic lattice $F(-1) \simeq 1.52$, and $F(-2)$ can be estimated as $\simeq 1.0$ using an expression given by Tikson. The integral of (2.51) can then be approximated by expanding in powers of x first. (This is not very inaccurate as the second term of (2.51) does not diverge). The value of the integral can be expressed as

$$2F(-1)\left[1-.56\right] \tag{2.52}$$

and so finally the first equation of (2.47) becomes,

$$\frac{1}{2} = \frac{kT}{J(0)}\left(1+\bar{f}\right)^{-1} \alpha F(-1) \qquad \text{with } \alpha = 2.00 \tag{2.53}$$

Solving the new equation gives $kT_c/J \simeq 1.03$ as compared with

2.70 found by Callen, and 1.89 by the high temperature expansion method (Rushbrooke and Wood)[43]. This value and those for the other cubic lattice (see Table 2.A) are very much below those of Rushbrooke and Wood, but because of the assumptions made the decrease would seem to have been overestimated. The correction to Callen's theory, is however, at least in the right direction and the errors (with respect to the Rushbrooke results) are marginally smaller than those in Callen's theory.

The form that was assumed for $d_1(\underline{k},\alpha)$ is not a very accurate representation of this function even in the vicinity of the three points fixed accurately and so it is not surprising that the estimated change has been overestimated. For instance, the approximation assumes the following

(i) for $x \simeq 1$

$$d_1(\underline{k},\alpha) = -\left(1 + F(-1,\alpha)(1-x) + \Delta(-2,\alpha)(1-x)^2 + \rightsquigarrow\right)$$

$$\simeq -\left(1 + F(-1,\alpha)(1-x) - F(-1,\alpha)(1-x)^2 + \rightsquigarrow\right)$$

(ii) for $x \simeq -1$

$$d_1(\underline{k},\alpha) = 2F(-1,\alpha) - 1 + \left[2\Delta(-2,\alpha) - F(-1,\alpha)\right](x+1) + \rightsquigarrow$$

$$\simeq 2F(-1,\alpha) - 1 - 3F(-1,\alpha)(x+1) + F(-1,\alpha)(x+1)^2 + \rightsquigarrow$$

where

$$\Delta(-2,\alpha) = \frac{1}{N}\sum_{\underline{k}''} \frac{\alpha^2 J^2(0)}{\left(\alpha J(0) - J(\underline{k}'')\right)^2}$$

From this a correction can be devised for $d_1(\underline{k},\alpha)$ such that

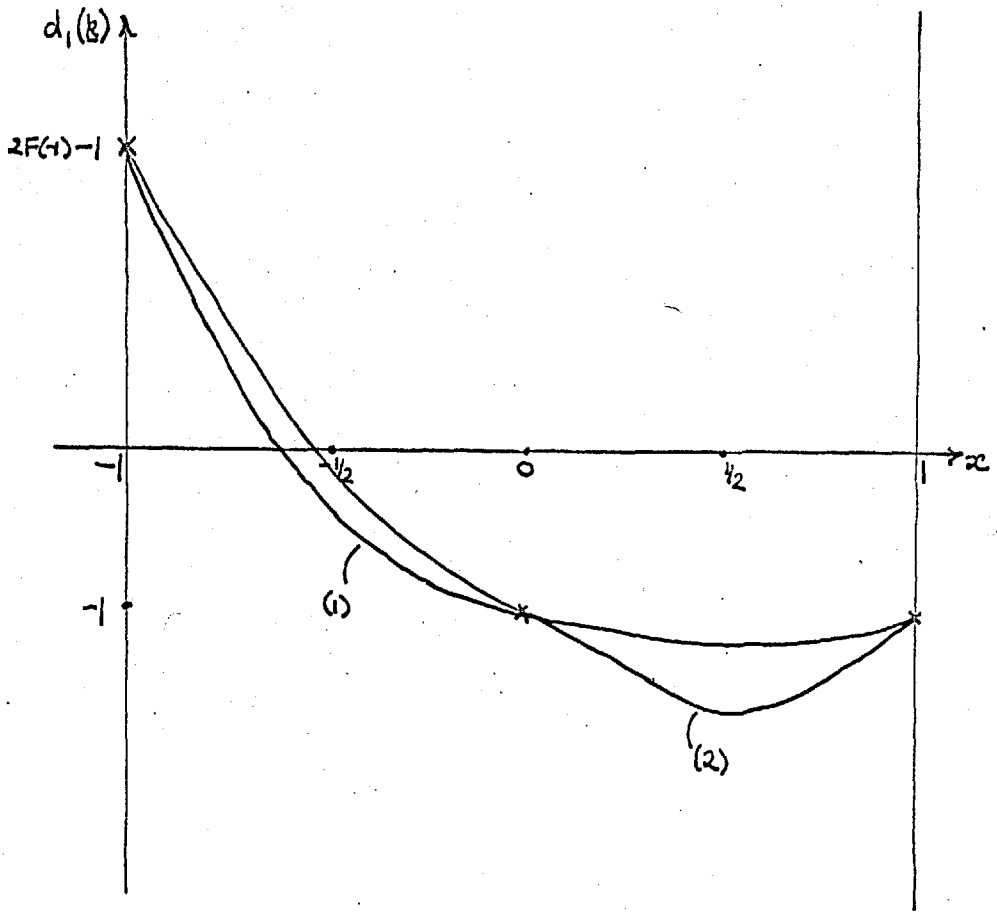
$$d_1(\underline{k},\alpha) = F(-1,\alpha)\,x(x-1) - 1 - \tfrac{1}{2}x(1-x)^2(1+x)\left[F(-1,\alpha) + \Delta(-2,\alpha)\right]$$

Using this together with (2.49) gives the following approximation for $d_1(\underline{k})$ and $d_2(\underline{k})$

$$d_1(\underline{k}) = F(-1)(x^2-x) - 1 - \tfrac{1}{2}(F(-1)+F(-2))\,x(1-x)^2(1+x)$$

$$d_2(\underline{k}) = F(-1) + (1-x)\big(F(-2)-F(-1)\big) + \tfrac{1}{2}\big(F(-1)+F(-2)\big)(1-x)^2 \qquad (2.54)$$

$$+ \tfrac{1}{2}(1-x)(1-x^2)\big[2F(-3)-F(-1)-F(-2)\big]$$



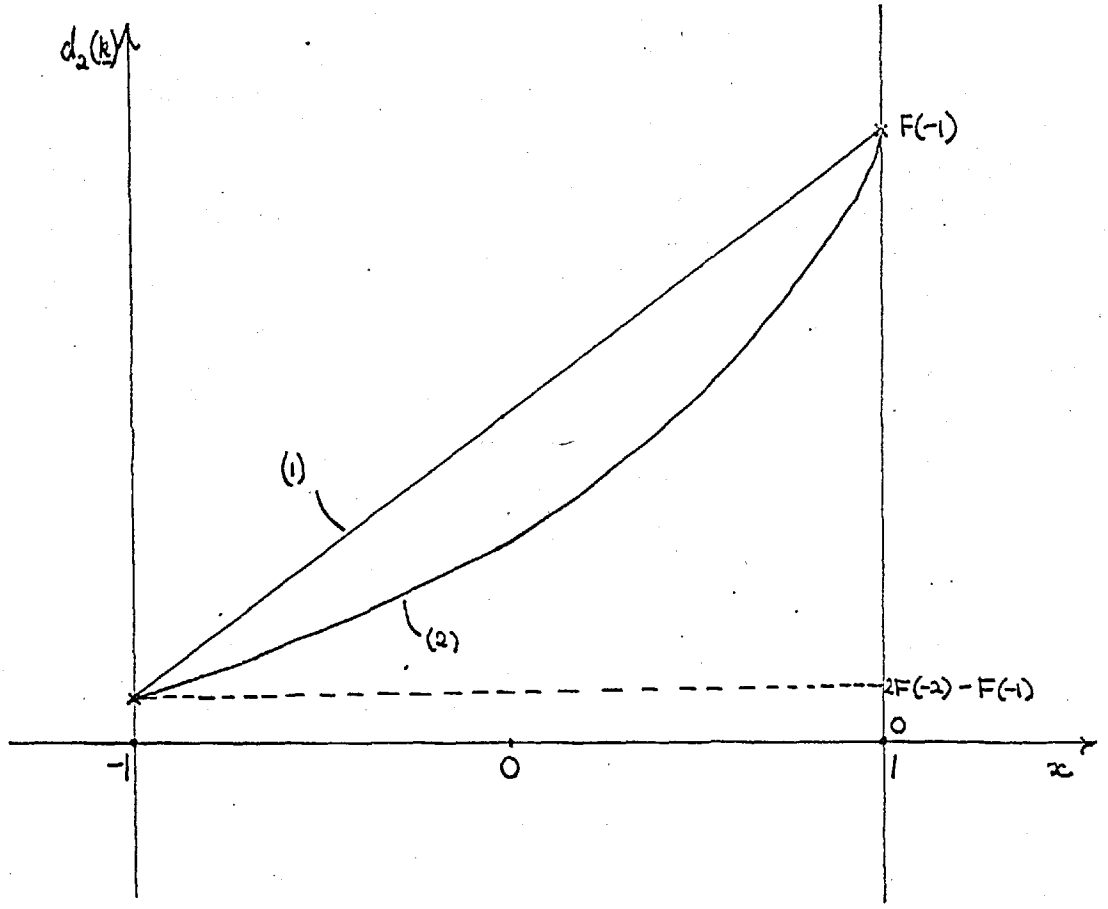
Sketches of $d_1(\underline{k})$ for both approximations

(1) is the curve for first approximation

(2) is the curve for second approximation

x's are actual points for $d_1(\underline{k})$

Treating this as in the previous approximation gives a correction to the first of the two equations (2.47) of the form (2.53), with α now 1.42 for a simple cubic lattice, when $F(-\tilde{\gamma})$ is taken to be approximately 2.0 This gives $kT_c/J \simeq 1.8$ These results are, however, only estimates, but the above suggests that the correction to the Green function decoupling procedure has an importance near the critical temperature as well as eliminating the leading term in the spurious contribution to $\langle S^z \rangle$



Sketches of $d_2(\underline{k})$ for both approximations

(1) is the curve for first approximation

(2) is the curve for second approximation

× are actual points for $d_2(\underline{k})$

The following tables present results for comparison with those of Callen, Dyson, Rushbrooke and Wood, etc.

Table 2.A Comparison of the values of Q

	Dyson	Callen	This Work
simple cubic lattice	1.68	1	3.01
body centred cubic lattice	1.45	1	2.82
face centred cubic lattice	1.35	1	2.78

Table 2.B Comparison of critical temperatures

	Rush-brooke	Callen	T. Kheli et al	This work 1st approx.	This work 2nd approx.
simple cubic lattice	1.89	2.70	2.0	1.03	1.8 †
body centred cubic lattice	2.64	3.70	2.9	1.5 *	2.8 *†
face centred cubic lattice	4.15	5.60	4.5	3.2 *	4.0 *†

* $F(-2)$ was taken as 1.0, a value which may be in error.

† $F(-3)$ was taken as 2.0 which may be in error.

Thus although the major discrepancy is rectified the theory is still far from satisfactory.

2.6 The Correction of the Leading Term of the Spurious Contribution (S=1)

In this case, in a similar manner to that of Tahir-Kheli et al, we consider the pair of Green functions $\ll S_{\underline{g}}^{+}; S_{\underline{\ell}}^{+}(S_{\underline{\ell}}^{-})^{2}\gg_{E}$ and $\ll S_{\underline{g}}^{+}; S_{\underline{\ell}}^{-}\gg_{E}$. The corresponding equations of motion are

$$E\ll S_{\underline{g}}^{+}; S_{\underline{\ell}}^{-}\gg_{E} = \frac{2\langle S^{z}\rangle}{2\pi}\delta_{\underline{g},\underline{\ell}} - \sum_{\underline{f}} J(\underline{g}-\underline{f})\ll \left(S_{\underline{g}}^{z}S_{\underline{f}}^{+}+S_{\underline{f}}^{+}S_{\underline{g}}^{z}-S_{\underline{f}}^{z}S_{\underline{g}}^{+}-S_{\underline{g}}^{+}S_{\underline{f}}^{z}\right); S_{\underline{\ell}}^{-}\gg_{E}$$

$$\text{and } E\ll S_{\underline{g}}^{+}; S_{\underline{\ell}}^{+}S_{\underline{\ell}}^{-}S_{\underline{\ell}}^{-}\gg_{E} = \frac{1}{2\pi}\delta_{\underline{g},\underline{\ell}}\left\{4\left(-1+\tfrac{1}{2}\langle S^{z}\rangle+\tfrac{3}{2}\langle (S^{z})^{2}\rangle\right)\right\} \tag{2.55}$$

$$-\sum_{\underline{f}} J(\underline{g}-\underline{f})\ll \left(S_{\underline{g}}^{z}S_{\underline{f}}^{+}+S_{\underline{f}}^{+}S_{\underline{g}}^{z}-S_{\underline{f}}^{z}S_{\underline{g}}^{+}-S_{\underline{g}}^{+}S_{\underline{f}}^{z}\right); S_{\underline{\ell}}^{+}S_{\underline{\ell}}^{-}S_{\underline{\ell}}^{-}\gg_{E}$$

Decoupling these two Green functions in a manner similar to Callen's procedure ($\alpha=1$) leads to the same error in $\langle S^{z}\rangle$ of order $T^{9/2}$.

Defining the following correlation functions

$$\psi^{(1)}(\underline{k},\underline{k}_{1}) = \sum_{\substack{\underline{g}-\underline{\ell}\\ \underline{f}-\underline{\ell}}} e^{i(\underline{g}-\underline{\ell})\underline{k}+i(\underline{f}-\underline{\ell})\underline{k}_{1}}\langle S_{\underline{\ell}}^{+}S_{\underline{\ell}}^{-}S_{\underline{\ell}}^{-}S_{\underline{g}}^{z}S_{\underline{f}}^{+}\rangle$$

$$\text{and } \psi^{(2)}(\underline{k},\underline{k}_{1}) = \sum_{\substack{\underline{g}-\underline{\ell}\\ \underline{f}-\underline{\ell}}} e^{i(\underline{g}-\underline{\ell})\underline{k}+i(\underline{f}-\underline{\ell})\underline{k}_{1}}\langle S_{\underline{\ell}}^{+}S_{\underline{\ell}}^{-}S_{\underline{\ell}}^{-}S_{\underline{g}}^{+}S_{\underline{f}}^{z}\rangle \tag{2.56}$$

leads to the conditions,

$$\frac{1}{N^{2}}\sum_{\underline{k},\underline{k}_{1}}\psi^{(1)}(\underline{k},\underline{k}_{1}) = \langle S^{+}S^{-}S^{-}S^{+}\rangle \quad , \frac{1}{N^{2}}\sum_{\underline{k},\underline{k}_{1}}\psi^{(2)}(\underline{k},\underline{k}_{1}) = 0$$

Using a "symmetric" decoupling these quantities are both given as $4(1-\langle(S^z)^2\rangle)(2\langle S^z\rangle+\langle(S^z)^2\rangle-2)$.

The error in $\psi^{(1)}$ occurs when $\underline{f}=\underline{g}$ while that in $\psi^{(2)}$ is only obviously important when $\underline{f}=\underline{g}=\underline{l}$ so this is neglected.

The error in $\psi^{(1)}$ can be corrected by assuming a correction to the Green function

$$-4\left(1-\langle(S^z)^2\rangle\right)\left(2\langle S^z\rangle+\langle(S^z)^2\rangle-3\right)\ll S^+_{\underline{l}};S^-_{\underline{l}}\gg_E \qquad (2.57)$$

and this of itself eliminates at least the first spurious term.

This procedure and also that used for $S=\frac{1}{2}$ is perhaps slightly suspect as it cannot be generalized for $S>1$ and therefore, this type of correction is not entirely to be trusted.

2.7 Conclusion

The decoupling procedure method is difficult to apply successfully because there are as yet no formal rules which can be followed. However, if it is to be a standard method which can be relied upon, either such rules must be formulated or any theory based on the method must be backed by studying the higher order Green functions.

For the low temperature boson description a reasonable decoupling can be obtained by decoupling the Green function 'symmetrically'. For instance, the first approximation of T. Kheli et al treats the Green function symmetrically and in the limit $t\to 0$ the correlation function is approximated as

$$\langle a^*_{\underline{k}}a^*_{\underline{\lambda}}a_{\underline{\mu}}a_{\underline{k}}\rangle \simeq \langle a^*_{\underline{k}}a_{\underline{\mu}}\rangle\langle a^*_{\underline{\lambda}}a_{\underline{k}}\rangle+\langle a^*_{\underline{k}}a_{\underline{k}}\rangle\langle a^*_{\underline{\lambda}}a_{\underline{\mu}}\rangle$$

and the Green function in the limit $t \to 0$ is treated exactly:

$$\langle [a^*_{\underline{\lambda}} a_{\underline{\mu}} a_{\underline{k}} , a^*_{\underline{k}'}] \rangle = \langle a^*_{\underline{\lambda}} a_{\underline{\mu}} \rangle \delta_{\underline{k},\underline{k}'} + \langle a^*_{\underline{\lambda}} a_{\underline{k}} \rangle \delta_{\underline{\mu},\underline{k}'}$$

The increased complexity of the commutation rules for the spin operators means that symmetrical decoupling produces errors in the magnetization. The treatment of the errors given previously is not entirely satisfactory, even though the form of the correction becomes even more plausible when we find that the Green function $G(\underline{k})$ (the Fourier transform of $\ll S^+_{\underline{q}}(t) ; S^-_{\underline{\perp}} \gg$) can be expressed as,

$$G(\underline{k}) = \frac{2\langle S^z \rangle}{2\pi \left[E - E^{(0)}(\underline{k})\right]} + \frac{1}{2\pi\left[E - E^{(0)}(\underline{k})\right]} \frac{1}{N} \sum_{\underline{k}'} \frac{J(\underline{k}') - J(\underline{k}'-\underline{k})}{E - E^{(0)}(\underline{k}'-\underline{k})} A(\underline{k}',\underline{k}) \quad (2.58)$$
$$+ \sim$$

where $E^{(0)}(\underline{k})$ are the non-interacting spin-wave energies. So making the assumption that the correction is of the form of the second term, when this equation is restated so that the energies become the interacting spin-wave energies, the obvious choice is that given in (2.38).

The study of (2.58)'s higher term will obviously improve the theory, but there are difficulties in using this expansion because of the vector dependence of $A(\underline{k}',\underline{k})$ and the similar quantities in higher terms. This would come nearer to a more systematic treatment of the problem, and is much preferable to the arbitrary use of decoupling procedures.

Morita[44] et al decoupled the second equation of motion in an attempt to correct the error found by Callen. Their treatment, of course, introduced terms similar to the second term in (2.58). They found difficulties in treating a divergence in the theory which is introduced by the approximation used, and so they could not prove conclusively that no T^3 contribution existed.

The problem has also been treated by using extensions of the perturbation techniques of Quantum Field Theory, but because no simple analogue of Wick's theorem has been found for the spin operators (general S) it is laborious to present even the simplest properties. In this connection the work of Stinchcombe et al[48], Lewis and Stinchcombe[45], Giovannini et al[46], and Wang et al[47] is important.

Chapter 3

The Theory of Biquadratic Exchange in the Spin Wave Region

3.1 Introduction

Coles et al[49] found wide differences between the results of resonance experiments and the predictions of the Molecular-Field theory. They investigated the exchange interactions between neighbouring Mn^{2+} ions present as substitutional impurities in MgO with Mn:Mg ~1:100 These interactions were expected to be similar to those in the antiferromagnetic MnO, as the structures of MgO and MnO are the same, and the difference between their lattice constants is only 5%. The interactions were measured in two cases (a) an isolated nearest neighbour pair of Mn ions. (b) an isolated next nearest neighbour pair. (The structure in this last case is Mn–O–Mn). Assuming that the Hamiltonian for these pairs is

$$2J\,\underline{S}_1.\underline{S}_2$$

Coles et al were able to calculate the values of $2J_{nn}/k$, $2J_{nnn}/k$, and J_{nnn}/J_{nn} from their experimental results. They measured the intensity of transitions (between the Zeeman components) belonging to the S=1 state over a wide temperature range, and compared these with theory. This gave the results,

$$\frac{2J_{nn}}{k} = \frac{2J_{nnn}}{k} \simeq 28 \pm 4^{\circ}K\,; \quad +=\frac{J_{nnn}}{J_{nn}} \simeq 1.0 \pm 0.1$$

The Molecular-Field theory gives, using the measured value of the Curie-Weiss constant and assuming that $\tau = 1.0$

$$\frac{2J_{nn}}{k} \simeq 11.3^{\circ}K$$

Harris et al were able to explain this large difference by introducing a biquadratic exchange term into the Hamiltonian, which becomes (see Chapter I p.9)

$$\mathcal{H} = 2J \sum_{(m,\ell)} \underline{S}_{\ell} \cdot \underline{S}_{m} - 2j \sum_{(m,\ell)} (\underline{S}_{\ell} \cdot \underline{S}_{m})^2$$

Instead of looking only at the state S=1, they considered all those states which were not obscured by other stronger effects, in fact, S=1,2,3,4. Given the normal Hamiltonian the interval rule describing the spacing between adjacent states is,

$$W_{S,S-1} = 2JS \quad \text{(S is the spin of the higher state).}$$

With biquadratic exchange present the interval rule was modified to,

$$W_{S,S-1} = 2JS - 2jS\left[S^2 - S^a(S^a+1) - S^b(S^b+1)\right]$$

where S^a and S^b are both $5/2$ in this case.

They measured these intervals and found that using the normal Hamiltonian 2J varied from $28.0 \pm 3^{\circ}K$ (S=1) to $17.5 \pm 3^{\circ}K$.

Using the ratio $j/J = 0.05$ and $2J/k \simeq 14.6^{\circ}K$ the intervals varied from $26.7^{\circ}K$ (S=1) to $15.7^{\circ}K$ (the values were fitted exactly for S=2).

Thus, allowing for biquadratic exchange in the Hamiltonian and considering the estimate for 2J from the Curie-Weiss constant for MnO (neglecting small differences in structure between MnO and MgO), we have

$$2J \simeq 14.6^{\circ}K \quad (\text{cf. } 11.3^{\circ}K)$$

The value of j obtained by Harris et al is not inconsistent with Anderson's theory of superexchange, which predicts the biquadratic term to be $\sim 1\%$ of the quadratic terms. An effective biquadratic term could also be set up via a mechanism (see Kittel[50]) which produces a balance between elastic and exchange forces. In the case of MnO this latter mechanism seems to give too small an effect to account for Harris et al's results. Other authors have pointed out that biquadratic exchange can correct the sublattice magnetization of rare earth ions (see Will et al)[54].

Nai Li Huang et al[51] considered the terms in the superexchange problem quadratic in $\underline{S}_m.\underline{S}_l$, as Anderson's arguments were qualitative in character. They extended the method of Keffer and Oguchi[52] (which follows the treatment of permutation degeneracy due to Serber and Anderson)[53] to deal with the contribution from terms of order higher than S^4, and obtained expressions for j for various configurations in MnO. Their result for j for the collinear configuration $Mn^{++} - O^{--} - Mn^{++}$ is of order 1% of J, as Anderson predicted.

3.2 The Ferromagnetic Case

The evidence is, of course, for a biquadratic exchange term in the case of antiferromagnets, but as was mentioned in Chapter 1 such terms would appear in the ferromagnet case. Thus, it is of interest to see the effect of the biquadratic exchange term on the low temperature behaviour of ferromagnets.

The Hamiltonian to be considered is

$$\mathcal{H} = -2J\sum_{(n,m)} \underline{S}_n.\underline{S}_m - 2j\sum_{(n,m)} (\underline{S}_n.\underline{S}_m)^2 + h\sum_n S_n^z \qquad (3.1)$$

The extra term will favour neither ferromagnetism nor antiferromagnetism. What is favoured is the maximum projection of one spin either parallel or anti-parallel to another. For this reason the magnetization temperature curve lies above that found in the absence of the term (Rodbell et al).

If $j=0$ and the usual ground state is assumed, the state containing only one spin wave of arbitrary wave vector is an eigenstate of the total Hamiltonian; while those containing more spin waves are only approximately eigenstates (i.e. there are interactions between the spin-wave excitations). The ferromagnetic ground state is defined by

$$S_{\underline{\lambda}}^{-}|0\rangle = 0 \quad , \quad S_{\underline{\lambda}}^{z}|0\rangle = -N^{1/2} S\, \delta_{\underline{\lambda},0}|0\rangle$$

(where $S_{\underline{\lambda}}^{-}$ is the Fourier transform of the spin operator S_j^{-}), and it is still an eigenstate of the Hamiltonian. To prove that the state with only one spin wave present is also an eigenstate we need to show that $[\mathcal{H}, S_{\underline{\lambda}}^{+}] = B S_{\underline{\lambda}}^{+}$ for some constant B. This can, in fact, be proved and so we can confidently apply the spin-wave approximation. Following the usual transformation procedure but retaining only terms with up to four operators the Hamiltonian (3.1) becomes

$$\mathcal{H} = C + h\sum_{\underline{\lambda}} a_{\underline{\lambda}}^{*} a_{\underline{\lambda}} + \sum_{\underline{\lambda}} \Gamma(\underline{\lambda})\, a_{\underline{\lambda}}^{*} a_{\underline{\lambda}} + \sum_{1\ldots4} \delta(1+2-3-4)\,\Gamma(1,2,3)\, a_1^{*} a_2^{*} a_3 a_4 \qquad (3.2)$$

where $$\Gamma(\underline{\lambda}) = 2S\left(J + 2Sj(S-1)\right) z\,(1-\gamma_{\underline{\lambda}})$$

$$\Gamma(1,2,3) = \frac{z}{2N}\left[J + 6jS^2 + 4Sj\left(3-\tfrac{1}{2S}\right)\right](\gamma_1+\gamma_2-\gamma_{1-3}-\gamma_{2-3})$$

$$+ \frac{z}{N}\left(Sj - 2S^2 j\right)(1+\gamma_{1+2}-\gamma_3-\gamma_{1+2-3})$$

and $\gamma_{\underline{\lambda}} = \frac{1}{z} \sum_{\underline{\ell}-\underline{m}} e^{i\underline{\lambda}(\underline{\ell}-\underline{m})}$

In the last term of (3.2) Γ has been put in its symmetric form, so that $\Gamma(1,2,3) = \Gamma(2,1,3) = \Gamma(1,2,1+2-3)$

Using the Hamiltonian (3.2), equation (2.16) becomes

$$(E-h-\Gamma(\underline{k}))\ll a_{\underline{k}} ; a^{*}_{\underline{k}'}\gg = \frac{\delta_{\underline{k},\underline{k}'}}{2\pi} + 2\sum_{1-4}\delta(1+2-3-4)\delta_{\underline{k},1}\Gamma(1,2,3)\ll a_2^{+}a_3a_4 ; a^{+}_{\underline{k}'}\gg$$

and decoupling using approximation (2.18)

$$\ll a_{\underline{k}} ; a^{*}_{\underline{k}'}\gg = \frac{\delta_{\underline{k},\underline{k}'}}{2\pi\,[E-E(\underline{k})]}$$

where $E(\underline{k}) = h + \Gamma(\underline{k}) + 4\sum_{\underline{\lambda}}\Gamma(\underline{\lambda},\underline{k},\underline{k})\bar{n}_{\underline{\lambda}}$

and $\bar{n}_{\underline{\lambda}} = \left\{ e^{\beta E(\underline{k})} - 1 \right\}^{-1}$

The excitation energy can be rewritten, by denoting the energy of the spin waves at zero temperature by $\epsilon_{\underline{k}} = 2Sz\,(J + 2S_j(S-1))(1-\gamma_{\underline{\lambda}})$, as

$$E_{\underline{k}} = h + \epsilon_{\underline{k}}\{1-\Delta(T)\}$$

with $\Delta(T) = \frac{1}{SN}\sum_{\underline{\lambda}}\left\{1 + \frac{16S_j^2 - 4S_j + 6j}{2J + 4S_j^2 - 4S_j}\right\}(1-\gamma_{\underline{\lambda}})\bar{n}_{\underline{\lambda}}$

Obviously

$$\Delta(T) = \left\{1 + \frac{[8S^2-2S+3]j}{J+2S^2j-2S_j}\right\}\Delta_{j=0}(T)$$

and the effect of $j \neq 0$ is to introduce this factor which rises to a value greater than 2 for the spin $S=\frac{1}{2}$ case even if, as seems to be the case for antiferromagnets, $j/J \simeq 0.01$

The power laws for the low temperature expansion of various physical quantities are identical with those where $j=0$, and the introduction of $J_{eff} = J + 2Sj(S-1)$ and the new constant $1 + \frac{[8S^2-2S+3]j}{J+2S^2j-2Sj}$ only change the factors multiplying the powers in temperature. However, even a small value for j/J would affect the results seriously and so the biquadratic exchange type of interactions must be much, much smaller for ferromagnets than for antiferromagnets.

3.3 The Antiferromagnetic Case

The Hamiltonian for the system is

$$\mathcal{H} = 2|J|\sum_{(\underline{l},\underline{m})} \underline{S}_{\underline{l}}.\underline{S}_{\underline{m}} - 2j\sum_{(\underline{l},\underline{m})}(\underline{S}_{\underline{l}}.\underline{S}_{\underline{m}})^2 + h_1\sum_{\underline{l}} S_{\underline{l}}^{z} + h_2\sum_{\underline{m}} S_{\underline{m}}^{z} \qquad (3.3)$$

In the low temperature region the Dyson representation is used to transform this Hamiltonian (the Dyson representation is used for one sublattice, and conjugate representation on the other). A new problem arises when this Hamiltonian has been transformed in this way. The labour involved in performing the next transformation for six and eight operator terms is enormous and so at present these terms which occur with factors jS and j are neglected. This should be quite adequate as these are of $O(1/S)$ or less and are thus of an order neglected by Oguchi in his treatment.

The Hamiltonian can eventually be expressed in the same form as (2.12) by redefining coefficients thus:

$$\mathcal{B}^{(1)} = \mathcal{B}_0^{(1)} - 8jS^2\frac{z}{N}\left(\frac{D-\gamma_1^2}{(D^2-\gamma_1^2)^{1/2}}\right)\left(\frac{D-\gamma_2^2}{(D^2-\gamma_2^2)^{1/2}}\right)$$

$$B^{(2)} = B_0^{(2)} - 16jS^2 \frac{z}{N} \frac{D-\gamma_1^2}{(D^2-\gamma_1^2)^{1/2}} \frac{D-\gamma_2^2}{(D^2-\gamma_2^2)^{1/2}}$$

$$A^{\pm} = A_0^{\pm} - \frac{4jS}{J_{eff}N} \frac{D-\gamma_k^2}{(D^2-\gamma_k^2)^{1/2}} \sum_{k'} \left\{ \frac{2(D-\gamma_{k'}^2)}{(D^2-\gamma_{k'}^2)^{1/2}} - 1 \right\}$$

$$E_h = E_h^{(0)} - \frac{2jS}{J_{eff}N} \left\{ \left[\sum_k \left(\frac{D-\gamma_k^2}{(D^2-\gamma_k^2)^{1/2}} - 1 \right) \right]^2 + \left[\sum_k \frac{D-\gamma_k^2}{(D^2-\gamma_k^2)^{1/2}} \right]^2 \right\}$$

where $B_0^{(1)}, \ldots\ldots E_h^{(0)}$ are the corresponding expressions found by Oguchi, with $|J|$ replaced by $J_{eff} = |J| + 2jS^2$

This theory leads to the same low temperature expansion in powers of kT for the sublattice magnetization and other quantities of interest, as Oguchi found, with only the coefficients changed, a situation similar to the ferromagnetic case. The fact that j is non-zero affects all the properties of the magnetic material; the zero point energy is changed significantly, so the ground state differs from that of the 'normal' antiferromagnet, and the interaction term depends on j, of course.

The zero point energy can be written as

$$E_0 = -zJ_{eff}SN\left(S + c + \frac{c^2}{4S} + \alpha S(2+2c+c^2)\right) \qquad (3.4)$$

From the value of c quoted by Oguchi and the assumption that $\alpha = j/J_{eff}$ is approximately 0.01 it is obvious that the correction produced by the introduction of the biquadratic exchange term can be of the same order of magnitude as the normal deviation from the Néel ground state value. (For example, take $S=\frac{1}{2}$).

At very low temperatures the problem can still be considered in terms of 'non-interacting' spin-waves.

There are again two branches of spin waves, but their energies only differ if some anisotropy energy is present. In zero-field the energy for a 'non-interacting' spin wave is

$$A^0_{\underline{k}} = 2zJ_{eff}S\left(1+\frac{c}{2S}+4\alpha S(2c+1)\right)(1-\gamma^2_{\underline{k}})^{1/2} \qquad (3.5)$$

and again the coefficient is dependent on α. The term depending on α can be smaller or larger than the other correction $c/2S$, and for large S, when this theory is most applicable, it is much larger than $c/2S$.

At higher temperatures this energy will be renormalized by a factor

$$1 - \frac{1+8\alpha S^2}{1+\frac{c}{2S}+4\alpha S(2c+1)}\,\frac{1}{SN}\sum_{\underline{k}}(1-\gamma^2_{\underline{k}})^{1/2}n_{\underline{k}} \qquad (3.6)$$

The actual temperature part is unchanged, but for large S the coefficient can be as much as twice its normal value, $1/(1+\frac{c}{2S})$.

Thus, in both ferromagnets and antiferromagnets the alterations to the normal theories are very similar. The latter case is more complicated, of course, because spin deviations exist in the ground state and probabilities are altered for $\alpha \neq 0$. From consideration of the new coefficients it is certain that α must be extremely small if the theory is to resemble in any way the theory when $\alpha=0$. The calculation of Low suggests that for MnF_2 the theory for $\alpha=0$ is a very good approximation indeed up to 60 °K (The critical temperature is ~ 66°K).

PART 2

Chapter 4

Neutron Scattering and the Wave-vector-dependent Susceptibility

The discovery of the neutron gave to physicists an extremely useful tool in the study of solids (and liquids), as this particle is scattered by nuclear and atomic spins (because it has a magnetic moment) and also by the atoms themselves. Thus neutron experiments can give information as to the arrangement of the spins and atoms in the solid, and about such excitations as spin waves and phonons.

Here we are interested only in the magnetic part of the scattering. The discussion of this is in general difficult, but in certain temperature regions there are simplifications in the processes taking place in the solid, and this leads to simplifications in the discussion. At very low temperatures the spins of a ferromagnetic solid, for instance, are stable in some arrangement, (in this case a parallel arrangement), and so the scattering is mainly elastic and appears as Bragg-scattering peaks. The actual arrangement can be obtained by studying the elastic scattering as described by Bacon[61] (1962). As the temperature increases from 0°K deviations from this arrangement occur, which can be described by using the spin wave approximation (see Chapter 2). The magnetic fluctuations associated with the spin wave excitations interact with the neutrons to produce inelastic scattering, which is in many ways similar to the scattering produced by phonons. Of course, the use of boson-operators instead of the spin operators greatly simplifies the discussion of

the scattering. As the temperature increases further the Bragg scattering decreases till it vanishes at the substance's critical temperature, while excitation of more and more spin waves increases the inelastic scattering.

At very high temperatures the spins in the system have very little effective coupling, and so the neutrons see a system of free spins and the scattering is elastic. As the temperature is lowered the coupling becomes more and more important and the inelastic scattering increases. However, as long as the temperature is still several times the critical temperature the scattering from the paramagnetic spins shows an energy spread which is related to the exchange parameters of the system in a fairly simple manner. This has been discussed by de Gennes (1958)[55] and by Saenz (1960).[56]

The other region where a certain amount of simplification takes place is in the vicinity of the critical point. In this region large fluctuations of spins appear and this gives rise to an increase in the neutron scattering (the 'critical scattering'), which is, in fact, a particular case of the general phenomenon of critical opalescence exhibited when, for instance, light is scattered from a liquid or dense gas near its critical point. From the formula for the scattering cross-section presented below, we see that increase in scattering must be due to changes in the spin correlations.

At high temperatures the static spin correlation $\langle \underline{S}_i(0)\,\underline{S}_j(0)\rangle$ equals $\delta_{ij}\,S(S+1)$, but as the temperature is lowered towards the critical point short range order increases and hence some short range correlations appear, $\langle \underline{S}_i(0)\,\underline{S}_j(0)\rangle \neq 0$ if $\delta_{i,j}=0$. Alternatively we can say that the probability of the formation of large regions of correlated spins increases strongly near the critical

point; hence the maxima in the angular distribution become more pronounced.

The ordering of spins is also time dependent. Away from the critical point there is a strong preference for the spin system to be either ordered or disordered, and so the relaxation time is short. In the critical region, however, the ordered and disordered phases are almost equally stable and only weak restoring forces are involved. Hence the evolution of the fluctuations is slow, and the critical scattering is in general weakly inelastic. Thus we have in the critical region large correlation distances and long relaxation times, and so over a limited range the scattering may be treated as quasi-elastic and discussed in the static approximation.

The scattering of neutrons by atoms possessing magnetic moments requires the use of the Dirac equation for a proper treatment of the interaction between the neutron and the magnetic electrons (Halpern and Johnson, 1939).[57] This leads to the result for the cross-section[94,95]

$$\frac{d^2\sigma}{d\Omega' dE'} = \frac{N}{\hbar}\left(\frac{e^2\gamma}{mc^2}\right)^2 \frac{k'}{k} |F(\underline{K})|^2 \left(\delta_{\alpha,\beta} - \hat{K}_\alpha \hat{K}_\beta\right) \mathcal{S}^{\alpha\beta}(\underline{K},\omega) \qquad (4.1)$$

where the neutron has initial wave vector $\underline{k}$ and initial energy E, and is scattered into a state of wavevector $\underline{k}'$ and energy E'; $\underline{K}$ and $\hbar\omega$ denote the changes in wave vector and energy; $F(\underline{K})$ is the form factor of the magnetic electrons normalized to $F(0)=1$; and

$$\mathcal{S}^{\alpha\beta}(\underline{K},\omega) = \frac{1}{2\pi N}\int_{-\infty}^{\infty} dt\, e^{-i\omega t} \langle S^\alpha(-\underline{K},0) S^\beta(\underline{K},t)\rangle \qquad (4.2)$$

with α,β denoting x,y or z, and $\underline{S}(\underline{K},t) = \sum_{\underline{n}} e^{i\underline{K}\cdot\underline{n}} \underline{S}_{\underline{n}}(t)$

The Bragg scattering contribution in $\mathcal{S}^{\alpha\beta}(\underline{k},\omega)$ is

$$\frac{1}{N}\,\delta(\omega)\,\langle S^{\alpha}(-\underline{k})\rangle\langle S^{\beta}(\underline{k})\rangle \tag{4.3}$$

and the remainder is the "diffuse" contribution

$$\mathcal{S}_{D}^{\alpha\beta}(\underline{k},\omega)=\frac{1}{2\pi N}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\left\{\langle S^{\alpha}(-\underline{k},0)\,S^{\beta}(\underline{k},t)\rangle-\langle S^{\alpha}(-\underline{k})\rangle\langle S^{\beta}(\underline{k})\rangle\right\} \tag{4.4}$$

This expression for the diffuse contribution leads to a generalisation of the susceptibility, because

$$\lim_{\underline{k}\to 0}\int_{-\infty}^{\infty}d\omega\,\mathcal{S}_{D}^{\alpha\beta}(\underline{k},\omega)=\frac{kT\,\chi^{\alpha\beta}}{\mu^{2}g^{2}} \tag{4.5}$$

Following Mori and Kawasaki[58], the wave vector dependent susceptibility can be defined in terms of a relaxation function and shown to be expressed in terms of the "diffuse" contribution to the correlation function as

$$\frac{kT\,\chi^{\alpha\beta}(\underline{k})}{\mu^{2}g^{2}}=\int_{-\infty}^{\infty}d\omega\,\frac{1-e^{-\hbar\omega\beta}}{\hbar\omega\beta}\,\mathcal{S}_{D}^{\alpha\beta}(\underline{k},\omega) \tag{4.6}$$

This is the required generalisation of (4.5). $\chi(\underline{k})$ is the response function for a system with an applied field of the form $He^{i\underline{k}.\underline{r}}$. In the critical region the energy change $\hbar\omega$ during the scattering is small and so $\chi^{\alpha\beta}(\underline{k})$ is related to the static cross section $d\sigma/d\Omega$ directly, as the right hand side of (4.6) reduces to $\int_{-\infty}^{\infty}d\omega\,\mathcal{S}_{D}^{\alpha\beta}(\underline{k},\omega)$. This approximation may not be very accurate for very dilute alloys, but it would be a useful first approximation.

A simple form for $\chi(\underline{k})$ above T_c is predicted by Molecular Field Theory for a ferromagnet:

$$\chi^{xx}(\underline{K}) = \chi^{zz}(\underline{K}) = \frac{\chi_c}{\gamma_1^2(K_1^2 + q^2)} \qquad (4.7)$$

where $\underline{K} = \underline{\tau} + \underline{q}$ and $\underline{\tau}$ is the nearest reciprocal lattice vector; also

$$\chi_c = \mu^2 g^2 S(S+1)/3kT_c$$

$$\gamma_1^2 = \frac{1}{6} \frac{\sum_{\underline{R}} J(\underline{R}) R^2}{\sum_{\underline{R}} J(\underline{R})}$$

giving a measure of the range of the exchange interaction,

and $\gamma_1^2 K_1^2 = \dfrac{\chi_c}{\chi^{zz}(0)} = \dfrac{T - T_c}{T_c}$ with K_1 being an inverse correlation range.

These "constants" γ_1^2, K_1^2 defined through (4.7) are used to study $\chi(\underline{K})$ conveniently both above and below kT_c (see Elliott and Marshall[60]).

The $\underline{K}$ dependence of the denominator of $\chi(\underline{K})$ also introduces a continuous range of values for the transition temperatures. For any given set of $J(R)$ the actual transition temperature is determined by finding the vector $\underline{K}_0$ which makes the critical temperature a maximum. This is a very great advantage as the transition temperature to any possible type of ordering can be found from $\chi(\underline{K})$ (see Smart[59] p.105).

Therefore, $\chi(\underline{K})$ is an extremely important quantity and in later chapters it will be calculated using two effective field theories.

Chapter 5

An Introduction to the Theory of Alloys

The behaviour of solid solutions of paramagnetic impurities which are exchange coupled in a non-magnetic matrix turns out to yield a considerable body of information with regard to the nature of the exchange coupling, as well as being of interest in itself. In chapter 3 it was mentioned that the need for a biquadratic exchange term in the Hamiltonian in considering the properties of Mn_2O was shown by experiments on a dilute solution of this compound in MgO. Further, Lomer and Marshall[62] in discussing the electronic structure of transition metals drew extensively on results from alloy experiments.

A magnetic alloy is considered as a random arrangement of localized moments on the lattice with the Hamiltonian for the system still the Heisenberg Hamiltonian. Because not all the sites have moments associated with them, the sum over all pairs of sites must be restricted to those pairs which do have moments.

A number of relatively simple approximations have been used to obtain a description of the alloy's properties. The simplest theory is an extension of the Molecular Field Theory mentioned in Chapter 1. In addition to the standard assumption of the theory when applied to the pure substance, it is assumed that the susceptibility is independent of the fluctuations in the distribution of the spins. The results from this theory are equivalent to the Bragg-Williams approximation in the order-disorder problem; the critical temperature is

proportional to the concentration of magnetic atoms, and $1/\chi$ obeys a Curie-Weiss law with the slope giving the magnetic moment of the magnetic atoms.

The extra assumption makes this theory unreasonable as it treats all atoms, no matter what their distance from the 'central atom', with the same weight. Although the defect does not become serious for high concentrations except near the critical temperature, the theory becomes completely meaningless in the case of dilute solutions, leading to the conclusion that co-operative phenomena can occur in a dilute alloy, no matter how dilute!

The approximation is used by many authors because of its simplicity, but using extensions of the Bethe-Peierls-Weiss effective field theory (see Chapter 7). Tomita[63], Hecht[64] and Sato et al[65] have improved on these results. The first of these methods treats an 'average' cluster, hence the name given to it by Sato, the 'averaged co-ordination number method' (ACN). The method shows that the ferromagnetic Curie temperature does not appear until a certain finite concentration, the critical concentration, is reached. This concentration does not depend on the strength of the interaction, but only on its range and the co-ordination number, and has the value $2/z$ for nearest neighbour interactions. The paramagnetic Curie temperature rises linearly with concentration and the slope depends on the strength of the coupling. In this method $1/\chi$ is no longer linear against T, as the interaction term, which for MFT was independent of temperature, now depends on this parameter. Further, in the low concentration region the $1/\chi$ vs. T curves start from zero $1/\chi$ and zero T with a slope which increases with increasing T. Therefore, the magnetic moment calculated from the slope of the curve at all but the high temperature limit is overestimated.

Kaufmann's[66] experimental results for the Fe-Au system for χ vs. concentration are sketched below, and these can be explained by the ACN method (and also by means of MFT) although, of course, the theory is for nearest neighbour interactions while the situation in the alloys is much more complicated. In Cu Mn alloys the interaction is long range, as was mentioned in the first chapter, and may be represented (see Dekker)[67] by a combination of a short range ferromagnetic interaction and a weak longer range antiferromagnetic interaction. The situation in the Fe-Au system seems to be similar in this respect.

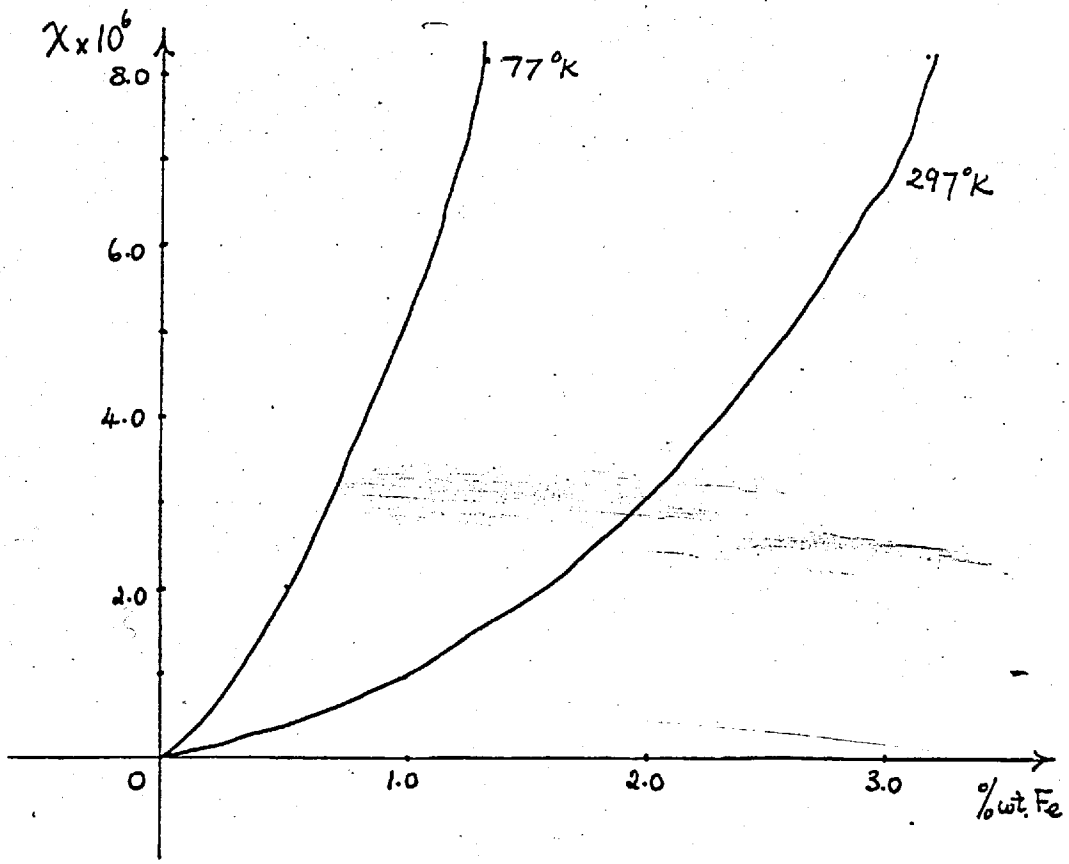


Diagram 5.A Some of Kaufmann's experimental results for the Fe-Au system.

Sato et al reviewed these two previous methods and using the Ising model for $S=\frac{1}{2}$ they used the 'cluster variation' method (CV), after Takagi[69] and Kikuchi,[68] to include some of the fluctuation of the atomic distribution. (Not all pairs of nearest neighbour atoms are equivalent as they may have different atmospheres of spins). The approximation to the fluctuations was obtained by counting the number of possible arrangements of each possible type of pair without any contradiction on the crystal lattice.

The results of the CV method differ from those of the ACN method in two respects: the formula for the critical concentration of a ferromagnet with nearest neighbour interactions is now $c_0=\frac{1}{z-1}$, and the interaction term in $1/\chi$ has a concentration as well as temperature dependence.

Smart[70] used the Classical Heisenberg model for $S=\frac{1}{2}$ and the cluster variation approach to the alloy problem. For a ferromagnet the relationship for the critical temperature leads to the same expression for the critical concentration as for the Ising Model. Elliott[71] considered the Heisenberg model for general spin using the constant coupling approach, but his expression for the critical concentration $c_0=(S+1)/[S(z-1)]$ agrees with Smart's result only for $S\to\infty$. Charap[72] (corrected by Lyons)[73] obtained results identical with those of Smart for the critical concentration.

Apart from the closed form approximations to the solution of the alloy problem, a number of authors have considered series expansion solutions for the critical concentration and the concentration dependence of the critical temperature. Rushbrooke and Morgan,[74,75,76] in particular, in a series of three papers considered expansions in concentration and $1/(\text{temperature})$ for $1/\chi$, and in concentration for χ. In the first two papers the

Ising model gives reasonable agreement for the c_0 values obtained by the two methods (even though one of the values is found by extrapolating the curve from high concentrations), but for the Heisenberg model the extrapolation gives an appreciably higher value for the critical concentration. Using fairly general arguments a number of authors suggest that the critical concentrations obtained by the Ising or Heisenberg models respectively are the same, and this leads Rushbrooke and Morgan in their final paper to suggest that the curve H(i) in diagram 5.B represents the dependence of $kT_c(c)/kT_c(1)$ on concentration. I is the type of curve suggested for the Ising model, and H(ii) is the curve if the extrapolated results are, in fact, correct. There is, of course, also the problem that for [2] lattices c_0 is not unity, and so if the orthodox spin wave theory is correct $c>c_0$ may not imply that ordered behaviour occurs. Some of the results from the third paper by Morgan and Rushbrooke are sketched below and these authors had to state that the low concentration part of the curve of critical temperature versus concentration is still not fully established.

The critical concentration c_0 can be identified with the critical probability for the site percolation problem of the corresponding lattice. This problem has been studied extensively by Frisch et al and other authors.[77,78,79]

Dalton et al[80] listed the value of c_0 for various lattices and found that c_0 seems to tend to the asymptotic limit of about $2.7/z$ as z increases for [3] lattices.

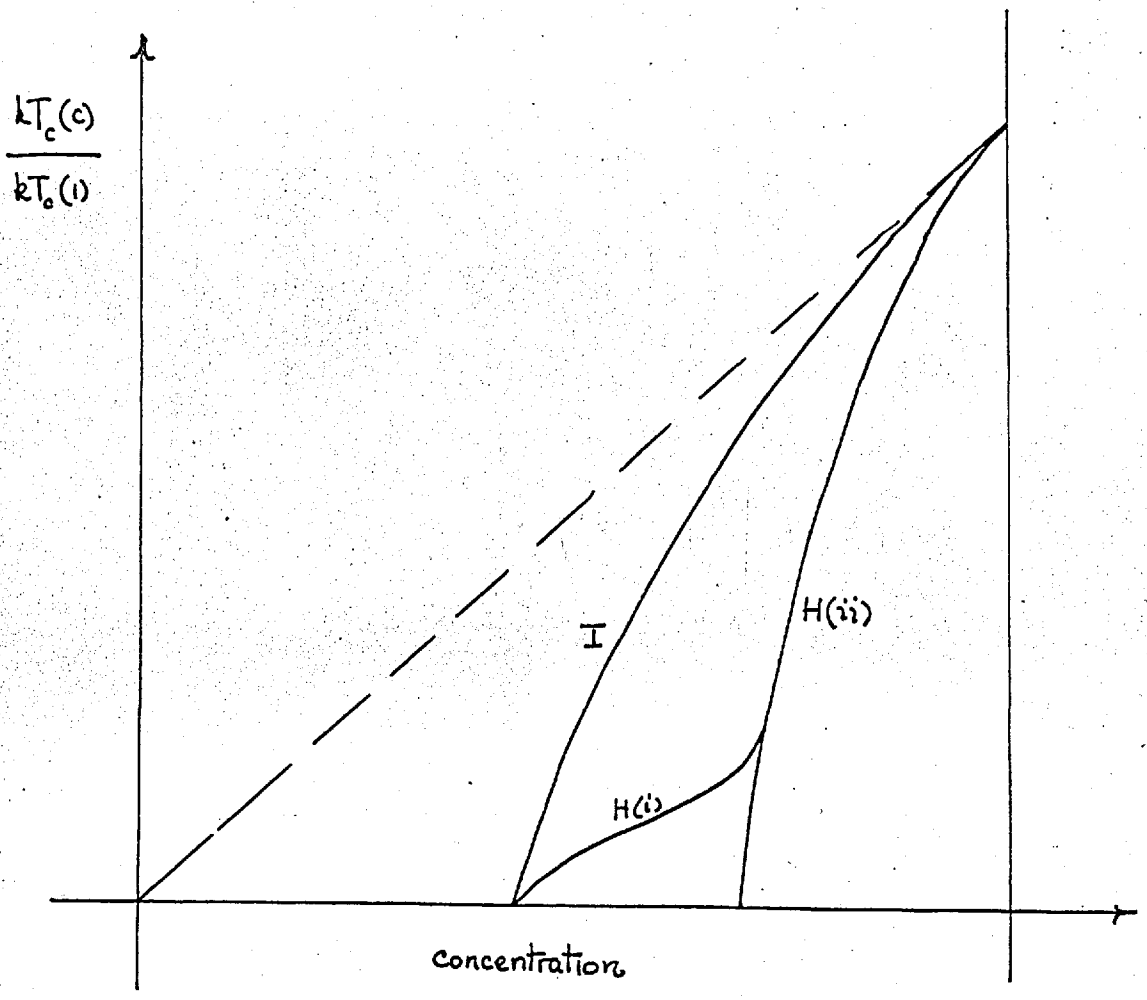


Diagram 5.B Curves suggested by Rushbrooke for the critical temperature vs. concentration.

I denotes Ising model curve ; H(i) , H(ii) denote possible curves for Heisenberg model.

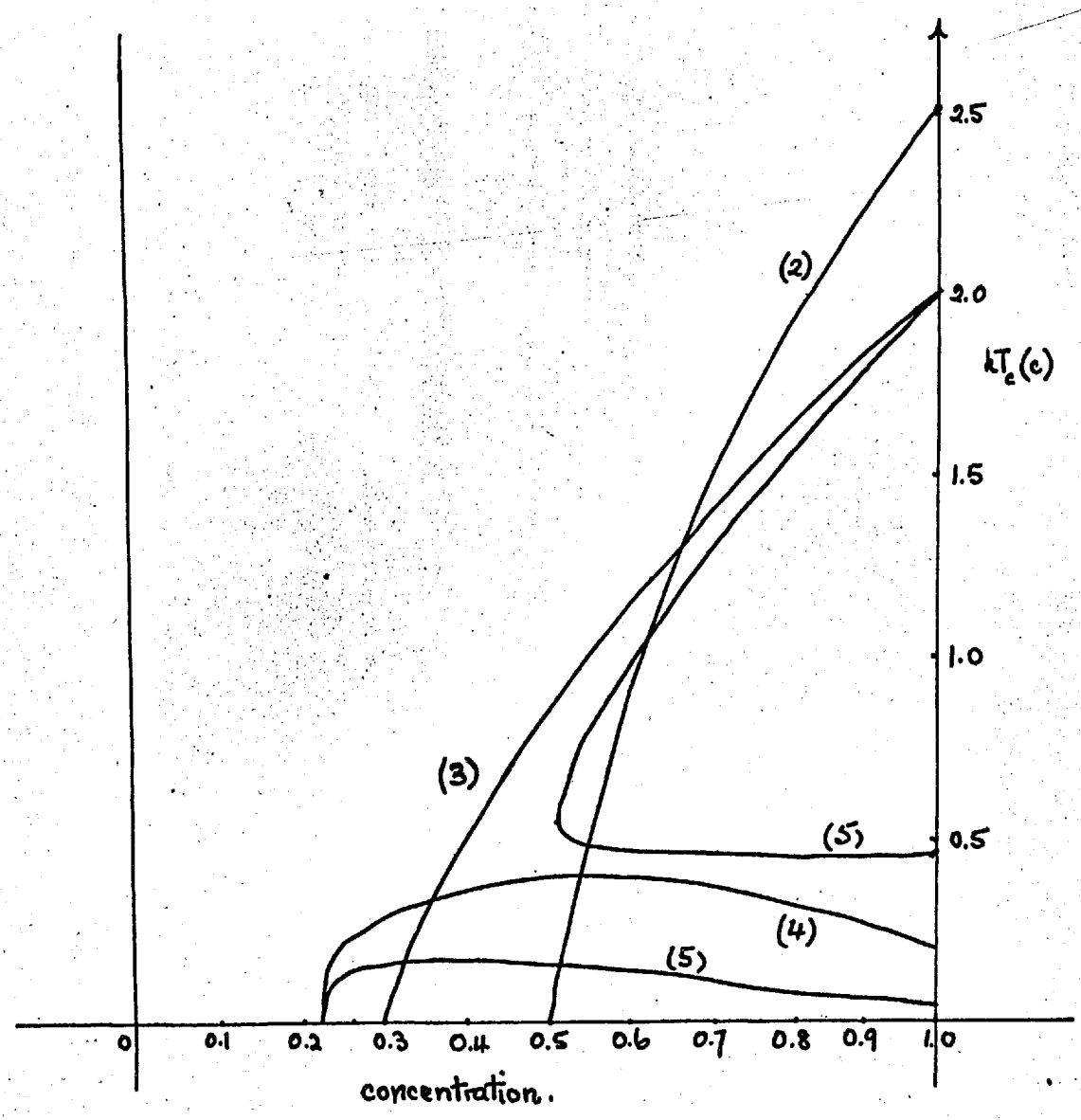


Diagram 5.C Curves of the critical temperature vs. concentration from successive approximate solutions to $1/\chi$, taken from the third paper of Morgan and Rushbrooke.

(2)-(5) denote the second to fifth approximations, respectively.

This may give a reasonable estimate of c_0 for long range interactions, which are very important in the theory of alloys and metals.[81,82] A limit $4.5/z$ was found for [2] lattices.

Elliott and Heap[83] produced similar results to those of Rushbrooke and Morgan and extended the work to anti-ferromagnets. However, the application of their results to $MnZnF_2$ was very unsatisfactory. Brout[84] produced a sophisticated attack on the alloy problem but the simplest approximation which he actually evaluated is only equivalent to the first two terms of the series expansion of χ in powers of c.

Murray[85] studied low-energy spin waves for impure Heisenberg ferromagnets (the alloy consisted of atoms with different spin values) and was able to give low bounds for the critical concentrations of the three cubic lattices. (One of the atoms must have zero spin, of course). These bounds were, in fact, higher than the Ising model results of other authors.

Friedel and co-workers[86,87,88,89] introduced for the study of the behaviour of transition impurities dissolved in normal metals the concept of virtual bound levels, which phenomenon was already known in the scattering of electrons by free atoms. These levels arise because the d-states of the transitional impurities and the conductive states of the matrix have similar energies, and resonance phenomena occur. The properties of the virtual bound states can be simply studied in two rather different models: (i) a free electron model is used for the conduction electrons, while the wave functions of the alloy can be analyzed in spherical harmonics; (ii) Anderson[90] and Wolff[91] postulated a perturbation potential U, introduced by the impurity, which is small and repulsive.

(This seems to be the case for Cu-Mn). These methods have been used to study the conditions which are needed for localized moments to exist.

This is an alternative method to using the R-K-Y interaction and leads to a very similar behaviour for the interaction between impurities. These couplings are both long range and oscillate rapidly with distance, and so the effective field on a given impurity atom depends on its interaction with several other impurity atoms. The distribution function for the internal fields is therefore a quasi-continuous and symmetrical curve. This was discussed by Marshall,[92] who succeeded in explaining the specific heat result of Zimmerman et al using the R-K-Y potential. The distribution function was evaluated by M. W. Klein and R. Brout.[93]

From this brief account we see that the critical concentration is relatively well understood, but the shape of the $kT_c(c)$ vs. concentration curve is not. It would seem sensible, as the series expansion methods are at the moment difficult to apply to sufficient accuracy, to use some approximation to the behaviour of localized moments already used for pure substances so that the problem is reduced to the discussion of the concentration effects. The Green function approach is obviously too difficult an approximation to apply to this problem because the decoupling procedure is still little understood and the introduction of impurities into the theory increases the decoupling difficulties. For instance, even in the MFT approach decoupling of the averages over all possible distributions of impurities is needed (see Chapter 6). The effective field theories have been used to discuss the properties of a random alloy system. The Molecular Field Theory is used in Chapter 6 because it

gives the possibility of studying interactions of arbitrary range. In Chapter 7 the Ising model is used together with the Bethe-Peierls-Weiss effective field theory in order to treat long range interactions in this approximation, while in Chapter 8 the Heisenberg model is discussed for nearest neighbour interactions.

The difference between these theories and those of Smart, Sato et al is the use of ρ_n, a distribution function for the "impurity" spins, and the production of a series of closed form approximations, which will give a much more valuable guide to the behaviour of the models.

Chapter 6

Calculation of the Wavevector-Dependent Susceptibility using the Molecular Field Theory for a Magnetic Alloy

6.1 Introduction

The simplest effective field theory is the Molecular Field Theory (MFT) mentioned in the first chapter. As a first attempt at prediction of the magnetic properties of a pure substance this theory was a major triumph. However, when a detailed comparison is made between theory and experiment it is found that the quantitative agreement is not very good. The low temperature magnetization does not behave as the Molecular Field Theory would predict, that is, it does not decrease from saturation exponentially but much more rapidly and only the inclusion of spin wave excitations in the theory can give the desired power law. The experiments of Heller and Benedik[96] on EuS, an insulating ferromagnet, near its Curie temperature have shown that the magnetization follows a $(T_c - T)^n$ law but their value for n is nearer $\frac{1}{3}$ than the value $\frac{1}{2}$ predicted by MFT. The other major deficiency of the MFT is its prediction that the zero-field specific heat is zero for $T>T_c$, when in fact, experimental data indicates a high temperature tail.

Despite these erroneous results the simplicity of the MFT makes it attractive for a first attempt to approximate the susceptibility for the more difficult alloy problem. The alloy is assumed to be binary with one component consisting of atoms of a magnetic material, and the model chosen is the Heisenberg one for localized

moments; though the range of the interaction is not restricted. Thus, the Hamiltonian is,

$$\mathcal{H} = -2\sum_{\underline{m},\underline{n}} J(\underline{m}-\underline{n})\underline{S}_{\underline{m}}\cdot\underline{S}_{\underline{n}} - \mu g H \sum_{\underline{n}} S_{\underline{n}}^{z} e^{i\underline{k}\cdot\underline{n}} \qquad (6.1)$$

where $\underline{S}_{\underline{m}}$ is the spin operator associated with the magnetic atom on site $\underline{m}$ and the summation is over all sites on which a magnetic atom is present. The exchange parameter $J(\underline{m}-\underline{n})$ is, in fact, quite arbitrary but it will be assumed to be independent of the direction of the vector $\underline{m}-\underline{n}$ and only depend on its magnitude.

The Molecular Field Approximation consists in considering only one magnetic atom and replacing its interaction with the remainder of the crystal by an effective field. From (6.1) we see that the single atom Hamiltonian is,

$$\mathcal{H}_{\underline{n}} = -2\sum_{\underline{m}} J(\underline{m}-\underline{n})\underline{S}_{\underline{m}}\cdot\underline{S}_{\underline{n}} - \mu g H S_{\underline{n}}^{z} e^{i\underline{k}\cdot\underline{n}} \qquad (6.2)$$

This Hamiltonian is to be approximated as,

$$\mathcal{H}_{\underline{n}} \simeq -\mu g \underline{S}_{\underline{n}}\cdot\underline{H}_{\underline{n}} \qquad (6.3)$$

So $$\mu g \underline{H}_{\underline{n}} = 2\sum_{\underline{m}} J(\underline{m}-\underline{n})\underline{S}_{\underline{m}} + \mu g H e^{i\underline{k}\cdot\underline{n}} \qquad (6.4)$$

In the spirit of the Weiss approximation each vector $\underline{S}_{\underline{m}}$ is replaced by its average $\langle \underline{S}_{\underline{m}} \rangle$, and as the applied field is taken along the z-axis, as usual, and defining $\sigma_{\underline{m}} = 2\langle S_{\underline{m}}^{z} \rangle$ we have

$$\mu g \underline{H}_{\underline{n}} \rightarrow \sum_{\underline{m}} J(\underline{m}-\underline{n})\sigma_{\underline{m}} + \mu g H e^{i\underline{k}\cdot\underline{n}} \qquad (6.5)$$

Thus, the standard calculation gives,

$$\sigma_{\underline{n}} = \frac{2S+1}{2S}\coth\left(\frac{2S+1}{2}\cdot\frac{\mu g H_{\underline{n}}}{kT}\right) - \frac{1}{2S}\coth\left(\frac{\mu g H_{\underline{n}}}{2kT}\right) \qquad (6.6)$$

This equation, if it is to be used to calculate the paramagnetic susceptibility, need only be considered in its linearised form,

$$\sigma_{\underline{n}} = \alpha_s\beta\left[\sum_{\underline{m}} J(\underline{m}-\underline{n})\sigma_{\underline{m}} + \mu g H e^{i\underline{k}.\underline{n}}\right] \qquad (6.7)$$

where $\alpha_s = \frac{2}{3}S(S+1)$, $\beta = 1/kT$. Here the sum, as in all the above formulae, is restricted to those sites where a localized moment is situated. To remove this restriction define the following distribution function,

$$p_{\underline{n}} = \begin{cases} 1 & \text{if the atom on site } \underline{n} \text{ is magnetic} \\ 0 & \text{if the atom on site } \underline{n} \text{ is not magnetic} \end{cases}$$

Using this function (6.7) becomes,

$$\sigma_{\underline{n}} = \alpha_s\beta p_{\underline{n}}\left[\sum_{\underline{m}} J(\underline{n}-\underline{m})\sigma_{\underline{m}} + \mu g H e^{i\underline{k}.\underline{n}}\right] \qquad (6.8)$$

where the sum is now over all sites of the lattice.

We now Fourier transform (6.8) using the following transforms,

$$\sigma(\underline{\lambda}) = \sum_{\underline{n}} \sigma_{\underline{n}} e^{-i\underline{\lambda}.\underline{n}} \quad , p(\underline{\lambda}) = \sum_{\underline{n}} p_{\underline{n}} e^{-i\underline{\lambda}.\underline{n}}$$

$$, J(\underline{\lambda}) = \sum_{\underline{n}-\underline{m}} J(\underline{n}-\underline{m}) e^{-i(\underline{n}-\underline{m}).\underline{\lambda}}$$

where $\underline{\lambda}$ is a reciprocal lattice vector, to give,

$$\sigma(\underline{\lambda}) = \mu g H \alpha_s \beta p(\underline{\lambda}-\underline{k}) + \frac{\alpha_s\beta}{N}\sum_{\underline{\xi}} J(\underline{\xi})\sigma(\underline{\xi})p(\underline{\lambda}-\underline{\xi}) \qquad (6.9)$$

Defining $a_{\underline{\lambda}}$ to describe the fluctuations of $\phi(\underline{\lambda})$, that is, $\phi(\underline{\lambda}) = cN\delta_{\underline{\lambda},0} + a_{\underline{\lambda}}$ (c is the concentration of the alloy sample), (6.9) can be written as,

$$\sigma(\underline{\lambda})Q(\underline{\lambda}) = \mu g H \alpha_{s\beta}\left[cN\delta_{\underline{\lambda},\underline{k}} + a_{\underline{\lambda}-\underline{k}}\right] + \frac{\alpha_{s\beta}}{N}\sum_{\underline{t}} J(\underline{t})\sigma(\underline{t})a_{\underline{\lambda}-\underline{t}} \qquad (6.10)$$

where $Q(\underline{\lambda}) = 1 - \alpha_{s\beta}c\,J(\underline{\lambda})$

The wave-length dependent susceptibility is related to $\sigma(\underline{\lambda})$ by the following relationship,

$$\chi(\underline{\lambda}) = \lim_{H\to 0} \frac{\mu g \langle\sigma(\underline{\lambda})\rangle}{2H} \qquad (6.11)$$

where the average of $\sigma(\underline{\lambda})$ is taken over all possible arrangements of spins.

So the problem of determining the response of the system is the problem of solving equation (6.10) for $\sigma(\underline{\lambda})$. An exact solution to (6.10) is, in general, impossible but when $c=1$ the functions $a_{\underline{\lambda}} \equiv 0$ and (6.10) becomes an algebraic equation instead of the integral equation it is in general and,

$$\chi(\underline{\lambda})_{c=1} = \frac{\frac{1}{2}\mu^2 g^2 \alpha_{s\beta} N \delta_{\underline{\lambda},\underline{k}}}{1 - \alpha_{s\beta} J(\underline{\lambda})} \qquad (6.12)$$

6.2 The Decoupling Approach

Averaging (6.10) over all possible arrangements of spins gives a relationship between the two averages $\langle\sigma(\underline{\lambda})\rangle$ and $\langle\sigma(\underline{t})\,a_{\underline{\lambda}-\underline{t}}\rangle$. We could equally have multiplied equation (6.10) by the factor $a_{\underline{t}'-\underline{\lambda}}$ and then averaged to give a relationship between the two averages $\langle\sigma(\underline{\lambda})\,a_{\underline{t}'-\underline{\lambda}}\rangle$ and $\langle\sigma(t)\,a_{\underline{\lambda}-\underline{t}}\,a_{\underline{t}'-\underline{\lambda}}\rangle$; and so on using in succession the

factors 1, $a_{\underline{\lambda}'-\underline{\lambda}}$, $a_{\underline{\lambda}'-\underline{\lambda}}\ a_{\underline{\lambda}''-\underline{\lambda}'}$, $a_{\underline{\lambda}'-\underline{\lambda}}\ a_{\underline{\lambda}''-\underline{\lambda}'}\ a_{\underline{\lambda}'''-\underline{\lambda}''}$ etc. The single equation (6.10) is, thus, represented by a system of integral equations connecting $\sigma(\underline{\lambda})$s various averages (compare Chapter 2). In fact, we have the equations,

$$g(\underline{\lambda})Q(\underline{\lambda}) = \mu g H \alpha_{s\beta} c N \delta_{\underline{\lambda},\underline{k}} + \frac{\alpha_{s\beta}}{N}\sum_{\underline{t}} J(\underline{t})\, g(\underline{t},\underline{\lambda})$$

$$g(\underline{\lambda},\underline{t}')Q(\underline{\lambda}) = \mu g H \alpha_{s\beta} c(1-c) N \delta_{\underline{t}',\underline{k}} + \frac{\alpha_{s\beta}}{N}\sum_{\underline{t}} J(\underline{t})\, g(\underline{t},\underline{\lambda},\underline{t}')$$

$$g(\underline{\lambda},\underline{t}',\underline{t}'')\, Q(\underline{\lambda}) = \mu g H \alpha_{s\beta} c(1-c)\left[c N \delta_{\underline{\lambda},\underline{k}} + (1-2c)\right] N \delta_{\underline{t}'',\underline{k}}$$

$$+ \frac{\alpha_{s\beta}}{N}\sum_{\underline{t}} J(\underline{t})\, g(\underline{t},\underline{\lambda},\underline{t}',\underline{t}'')$$

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where $\langle \sigma(\underline{\lambda})\rangle = g(\underline{\lambda})$; $g(\underline{\lambda},\underline{t}') = \langle \sigma(\underline{\lambda})\, a_{\underline{t}'-\underline{\lambda}}\rangle$

$$g(\underline{\lambda},\underline{t}',\underline{t}'') = \langle \sigma(\underline{\lambda})\, a_{\underline{t}'-\underline{\lambda}}\, a_{\underline{t}''-\underline{t}'}\rangle$$

and $$g(\underline{t},\underline{\lambda},\underline{t}',\underline{t}'') = \langle \sigma(\underline{t})\, a_{\underline{\lambda}-\underline{t}}\, a_{\underline{t}'-\underline{\lambda}}\, a_{\underline{t}''-\underline{t}'}\rangle$$

These equations can be simplified by defining $f(\ldots,\underline{t})$ by the relationship,

$$g(\ldots,\underline{t},\underline{t}') = \mu g H \alpha_{s\beta} c N \delta_{\underline{t}',\underline{k}}\, f(\ldots,\underline{t})$$

They, in fact, become, (see Appendix I),

$$f Q(\underline{k}) = 1 + \frac{\alpha_{s\beta}}{N}\sum_{\underline{t}} J(\underline{t}) f(\underline{t})$$

$$f(\underline{\lambda})Q(\underline{\lambda}) = (1-c) + \frac{\alpha_{s\beta}}{N}\sum_{\underline{t}} J(\underline{t}) f(\underline{t},\underline{\lambda}) \qquad (6.13)$$

$$f(\underline{\lambda},\underline{t}')\, Q(\underline{\lambda}) = c(1-c) N \delta_{\underline{\lambda},\underline{k}} + (1-c)(1-2c) + \frac{\alpha_{s\beta}}{N}\sum_{\underline{t}} J(\underline{t}) f(\underline{t},\underline{\lambda},\underline{t}')$$

Obviously, this system of equations has to be short-circuited in some manner, so we have a decoupling problem to solve. This situation is identical to that found with Green function methods (Chapter 2).

A number of decoupling procedures have been tried and the least effective of these are commented on in Appendix 2, but we deal with the most effective here. Simple iteration of (6.10) is of little use in approximating $\sigma(\underline{\lambda})$, but it shows that $\sigma(\underline{\lambda})$ can be expanded in the following form,

$$\sigma(\underline{\lambda}) = A(\underline{\lambda}) + B(\underline{\lambda}) a_{\underline{\lambda}-\underline{k}} + \frac{1}{N}\sum_{\underline{t}} C(\underline{t},\underline{\lambda}) a_{\underline{\lambda}-\underline{t}} a_{\underline{t}-\underline{k}} + \rightsquigarrow \qquad (6.14)$$

that is, $\sigma(\underline{\lambda})$ is expanded in powers of the $a_{\underline{\lambda}}$ functions. The functions $A(\underline{\lambda}), B(\underline{\lambda})$ etc. are completely arbitrary. For a <u>particular</u> arrangement of spins on the sites this formula is not exact (as there exists a relationship between these functions), but when averages are considered we are, by introducing this arbitrariness, approximating the moments of $\sigma(\underline{\lambda})$ more effectively. (6.14) is, however, not in its most useful form as the $\langle \sigma(\underline{\lambda}) \rangle$ is given by,

$$\langle \sigma(\underline{\lambda}) \rangle = A(\underline{\lambda}) + c(1-c) N \delta_{\underline{\lambda},\underline{k}} \frac{1}{N}\sum_{\underline{t}} C(\underline{t},\underline{\lambda}) + \rightsquigarrow \qquad (6.15)$$

which is an infinite series. Reorganizing the terms so that only $A(\underline{\lambda})$ needs to be calculated, $\sigma(\underline{\lambda})$ becomes,

$$\sigma(\underline{\lambda}) = A(\underline{\lambda}) + B(\underline{\lambda}) a_{\underline{\lambda}-\underline{k}} + \frac{1}{N}\sum_{\underline{t}} C(\underline{t},\underline{\lambda}) \{ a_{\underline{\lambda}-\underline{t}} a_{\underline{t}-\underline{k}} - c(1-c) N \delta_{\underline{\lambda},\underline{k}} - (1-2c) a_{\underline{\lambda}-\underline{k}} \} \qquad (6.16)$$

$$+ \rightsquigarrow$$

where the average $\langle a_{\underline{\lambda}-\underline{t}} a_{\underline{t}-\underline{k}} - c(1-c)N\delta_{\underline{\lambda},\underline{k}} - (1-2c)a_{\underline{\lambda}-\underline{k}} \rangle = 0$ and also the average $\langle a_{\underline{x}} \{ a_{\underline{\lambda}-\underline{t}} a_{\underline{t}-\underline{k}} - c(1-c)N\delta_{\underline{\lambda},\underline{k}} - (1-2c)a_{\underline{\lambda}-\underline{k}} \} \rangle = 0$, for all vectors $\underline{x}$. If this procedure is extended to higher and higher terms each additional term makes one more of the equations of (6.13) necessary to determine the solution, and so decouples the system of equations at a later equation than before; but more important the change in any lower moment due to the addition of the next term comes from the redefinition of the highest equation and the addition of a further equation, but not from a redefinition of all the equations.

Let us now consider the sequence of approximations found by approximating (6.14) by a finite number of terms.

6.3 The First Approximations

The simplest approximation is to assume that

$$\sigma(\underline{\lambda}) \simeq A(\underline{\lambda})$$

so that $\sigma(\underline{\lambda})$ is independent of the fluctuations in concentration. From previous definitions,

$$g(\underline{\lambda}) = A(\underline{\lambda}) ,$$

$$g(\underline{\lambda},\underline{t}) = 0$$

and so the first equation of (6.13) (which is sufficient to determine $A(\underline{\lambda})$), becomes,

$$AQ(\underline{k}) = 1 + \frac{\alpha_s \beta}{N} \sum_{\underline{t}} J(\underline{t}) f(\underline{t})$$

where $f(\underline{t}) \equiv 0$ and $A(\underline{\lambda}) = \mu g H \alpha_s \beta c N \delta_{\underline{\lambda},\underline{k}} A$.

So $$\chi(\underline{\lambda}) = \frac{\frac{1}{2}\mu^2 g^2 \alpha_s \beta c N \delta_{\underline{\lambda},\underline{k}}}{1 - \alpha_s \beta c J(\underline{k})} \tag{6.17}$$

This is the simple Molecular Field Theory result mentioned in Sato. In the limit $c \to 1$ it reduces to (6.12), and in the high temperature limit it gives the correct-leading terms and a Curie-Weiss type law. The critical temperature condition is, of course,

$$kT_c = \alpha_s c J(\underline{k}) \tag{6.18}$$

and so no matter what the type of ordering there is no critical concentration. The critical scattering, if we assume that the quasi-elastic limit is applicable, will, of course, be of the same form as for a pure substance and only the temperature at which the divergence in scattering occurs (for a ferromagnet) will be reduced.

If the next term in (6.14) is allowed to be non-zero the approximation for $\sigma(\underline{\lambda})$ is

$$\sigma(\underline{\lambda}) \simeq A(\underline{\lambda}) + B(\underline{\lambda}) a_{\underline{\lambda}-\underline{k}} \tag{6.19}$$

and this implies that

$$g(\underline{\lambda}) = A(\underline{\lambda})$$

$$g(\underline{\lambda},\underline{t}) = c(1-c) N \delta_{\underline{t},\underline{k}} B(\underline{\lambda})$$

and $$g(\underline{\lambda},\underline{t}',\underline{t}'') = c(1-c) N \delta_{\underline{\lambda},\underline{t}''} A(\underline{\lambda}) + c(1-c)(1-2c) N \delta_{\underline{t}',\underline{t}} B(\underline{\lambda})$$

So the first two equations of (6.13) become

$$AQ(\underline{k}) = 1 + \alpha_s \beta c(1-c) \frac{1}{N} \sum_{\underline{t}} J(\underline{t}) \bar{B}(\underline{t}) \tag{6.20}$$

where $A(\underline{\lambda}) = \mu_g H \alpha_s \beta c N \delta_{\underline{\lambda},\underline{k}} A$,

$$B(\underline{\lambda}) = \mu_g H \alpha_s \beta c \bar{B}(\underline{\lambda})$$

and $$c\bar{B}(\underline{\lambda})Q(\underline{\lambda}) = 1 + \alpha_s \beta c J(\underline{k}) A + \frac{\alpha_s \beta c (1-2c)}{N} \sum_{\underline{k}} J(\underline{k}) \bar{B}(\underline{k}) \tag{6.21}$$

The dependence of these equations is simple enough to allow a complete solution. Multiplying equation (6.21) by a factor $J(\underline{\lambda})/Q(\underline{\lambda})$ and summing over $\underline{\lambda}$ gives an algebraic equation for $c\frac{1}{N}\sum_{\underline{k}} J(\underline{k})\bar{B}(\underline{k})$ in terms of A. Using this condition together with equation (6.20) gives,

$$\chi(\underline{\lambda}) = \frac{\frac{1}{2}\mu^2 g^2 \alpha_s \beta c N \delta_{\underline{\lambda},\underline{k}} \left(1 + \alpha_s \beta c y\right)}{\left(1 - \alpha_s \beta c J(\underline{k})\right)\left(1 - \alpha_s \beta (1-2c) y\right) - \alpha_s^2 \beta^2 c(1-c) y J(\underline{k})} \tag{6.22}$$

where $$y = \frac{1}{N} \sum_{\underline{k}} \frac{J(\underline{k})}{Q(\underline{k})}$$

In the high temperature limit this reduces to (6.17) and the correction is $O(\beta^3)$.

In the high concentration limit (6.22) becomes

$$\frac{\frac{1}{2}\mu^2 g^2 \alpha_s \beta c N \delta_{\underline{\lambda},\underline{k}}}{1 - \alpha_s \beta c J(\underline{k})} + \frac{1}{2}\mu^2 g^2 \alpha_s \beta N \delta_{\underline{\lambda},\underline{k}} (1-c) \left\{ \frac{\alpha_s \beta y_0}{(1 + \alpha_s \beta y_0)(1 - \alpha_s \beta J(\underline{k}))^2} \right\}$$

$$+ O\left[(1-c)^2\right] \tag{6.23}$$

where $y_0 = y(\text{at } c=1)$

As one would expect the corrections vanish when $c=1$.

For small concentrations (6.22) becomes,

$$\frac{\frac{1}{2}\mu^2 g^2 \alpha_s \beta c N \delta_{\underline{\lambda},\underline{k}}}{1-\alpha_s \beta c J(\underline{k})} + \frac{1}{2}\mu^2 g^2 \alpha_s^3 \beta^3 c^2 N \delta_{\underline{\lambda},\underline{k}} \frac{1}{N}\sum_{\underline{t}} J^2(\underline{t}) + O(c^3) \tag{6.24}$$

The correction, of course, vanishes in the limit $c \to 0$, as the leading term is of a higher order.

Consider the condition for the critical temperature given by (6.22). It is,

$$(1-\alpha_s \beta c J(\underline{k}))(1-\alpha_s \beta (1-2c) y) - \alpha_s^2 \beta^2 c(1-c) y J(\underline{k}) = 0 \tag{6.25}$$

As we need the smallest value of β which satisfies this equation the values of $\underline{\lambda}$ allowed are given by the set of equations $\frac{\partial J(\underline{\lambda})}{\partial \lambda_\alpha} = 0$.

Defining $\alpha = \alpha_s \beta c$ (6.25) becomes,

$$\frac{1}{N}\sum_{\underline{t}} \frac{J(\underline{t})}{1-\alpha J(\underline{t})} = \frac{c(1-\alpha J(\underline{\lambda}_0))}{\alpha\left[(1-2c) + \alpha c J(\underline{\lambda}_0)\right]} \tag{6.26}$$

When $\alpha < \frac{1}{J_{max}(\underline{t})}$, $\frac{\partial}{\partial \alpha}\left\{\frac{1}{N}\sum_{\underline{t}} \frac{J(\underline{t})}{1-\alpha J(\underline{t})}\right\} \geq 0$

for all concentrations.

Hence, y is an increasing function.

Also $\frac{c(1-\alpha J(\underline{\lambda}_0))}{\alpha\left[(1-2c) + \alpha c J(\underline{\lambda}_0)\right]} < 0$ if $\alpha > \frac{1}{J(\underline{\lambda}_0)}$

and this function has positive values from ∞ to 0 in the region $0 < \alpha < \frac{1}{J(\lambda_0)}$. So for all concentrations there will be a solution of (6.26), α_0. This is shown graphically in the diagram (6.1)

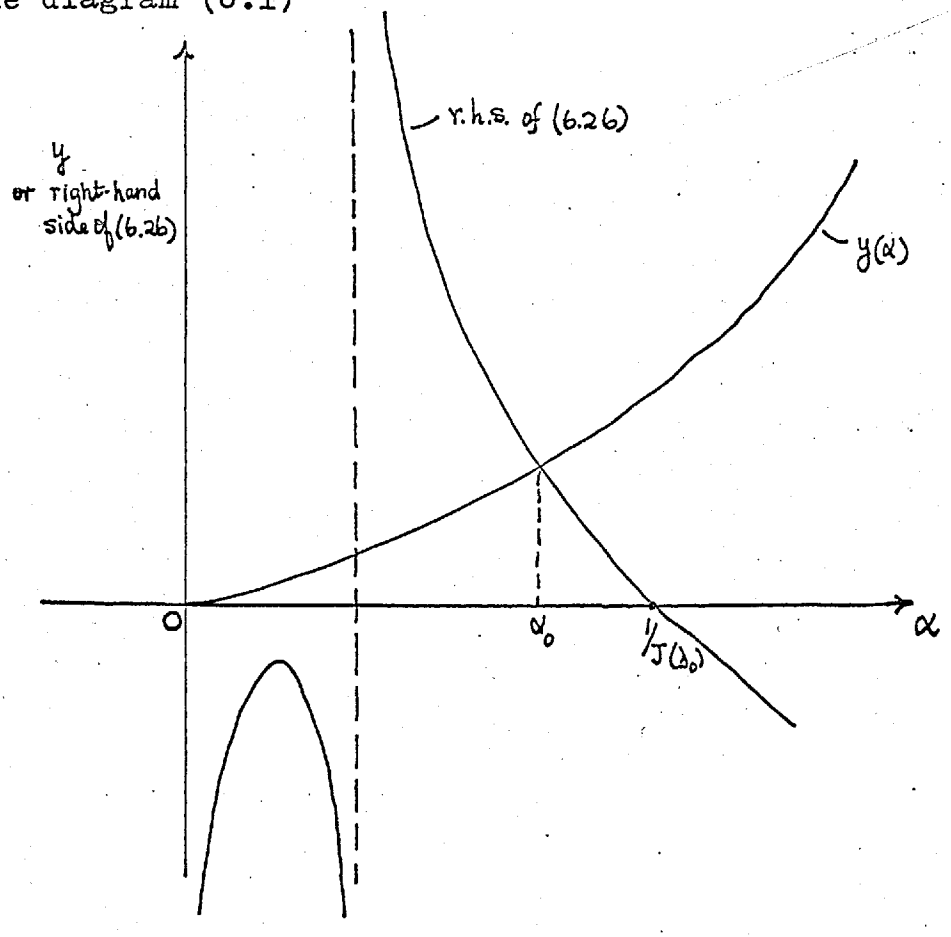


Diagram 6.1 This shows a plot of both sides of (6.26)

It also follows that $\alpha_0 < \frac{1}{J(\lambda_0)}$ and so for all concentrations the critical temperature determined by using (6.26) is always greater than that predicted by the simpler condition (6.17). The graph of kT_c (normalized at $c=1$) as against that calculated from the simple theory is shown in the diagram (6.2).

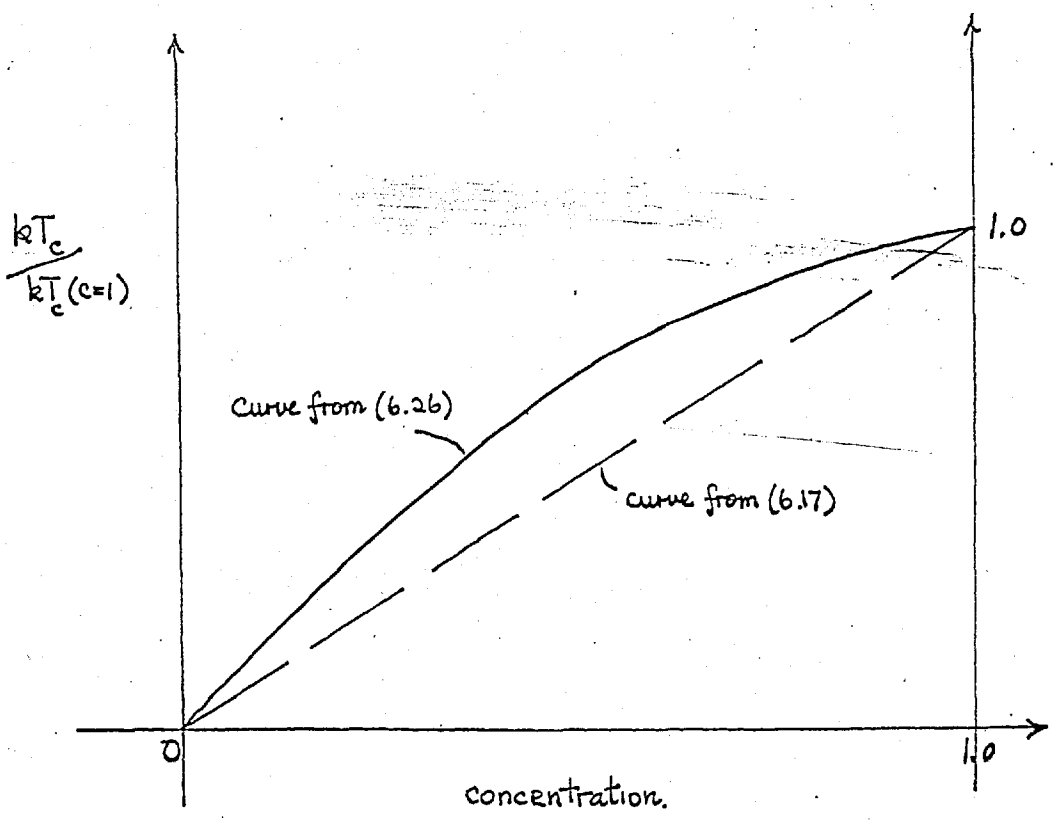


Diagram 6.2 Comparison of first two approximations to the critical temperature.

These preliminary findings are encouraging even though no critical concentration is found. For long range interactions the value of any critical concentration would be very small indeed; and so provided the detailed behaviour is reasonable this theory could be useful for these interactions (RKY etc.).

The corrections to kT_c are in the right direction to explain the results of Popplewell et al[97] and Thoburn et al[98] on the systems Gd-Lu and Gd-Y respectively (see Fig. 6.1). These corrections may also help in some measure to account for the discrepancy in the strength of the

interaction in Mn-Cu alloys. When calculations are made the simple theory gives the coupling constant $J \simeq 0.5$ ev. (errors are obviously made here as nearest neighbour interactions are used), but this is a factor 2 larger than J deduced from Owen et al data on free Mn^{++} ions, which gives $J \simeq 0.22$ ev. If the second approximation is to offer an improvement the graph of the critical temperature against concentration must be linear in concentration for c up to 0.12. However, as the localized moment model can only be regarded as a convenient phenomenological procedure for the Mn-Cu system the rare-earth alloys give the main encouragement.

We now proceed by considering condition (6.26) in more detail. When the concentration is very small we assume that the solution for kT_c is represented by a power law c^{η}.

If $kT_c \simeq A c^{\eta}$, $\alpha = A^{-1}\alpha_s J(\lambda_0) c^{1-\eta}$.

Substituting this into (6.26) and expanding for small values of concentration gives,

$$\left[Ac^{\eta} + \alpha_s c J(k_0)\right]\left[1 - \alpha_s^2 (1-2c) c^{1-2\eta} \frac{\gamma_2}{A^2} + \rightsquigarrow\right] - \alpha_s^3 c^{2(1-\eta)}(1-c)\frac{\gamma_2}{A^2} J(k_0) = 0 \qquad (6.27)$$

Equating coefficients of the leading term in c, we find the result,

$$kT_c = \alpha_s \sqrt{\gamma_2}\, c^{1/2} \qquad (6.28)$$

where $\gamma_2 = \frac{1}{N}\sum_k J^2(k)$, and we assume that η is the smallest exponent possible as we need the highest values of kT_c possible.

As was expected (6.28) gives values greater than those found in the simple theory and the critical

temperature for small concentration does not now depend on the maximum value of $J(\underline{\lambda})$ but on the average γ_2 .

The other limit of interest is when $c \simeq 1$. Following the same procedure as above we define $kT_c \simeq \alpha_s J(\underline{\lambda}_0) + B(1-c)^{\eta} + \cdots$ and expand (6.26) in powers of $(1-c)$, and by considering the coefficients, values for B and η are found.

The result for the critical temperature is,

$$kT_c \simeq \alpha_s J(\underline{\lambda}_0) \left\{ 1 - \frac{(1-c)}{1 + \frac{1}{N}\sum_{\underline{k}} \frac{J(\underline{k})}{J(\underline{\lambda}_0) - J(\underline{k})}} \right\} \qquad (6.29)$$

This expression implies that $kT_c \geq \alpha_s J(\underline{\lambda}_0) c$ as was expected. The linear decrease seems to apply quite well to Gd-Lu and Gd-Y systems.

The concentration behaviour of the simple approximation to the susceptibility has a simple dependence on concentration. There are no extrema and its graph is always above (or below for $\alpha_s J(\underline{\lambda}_0) > 0$) a linear dependence; see diagram (6.3)

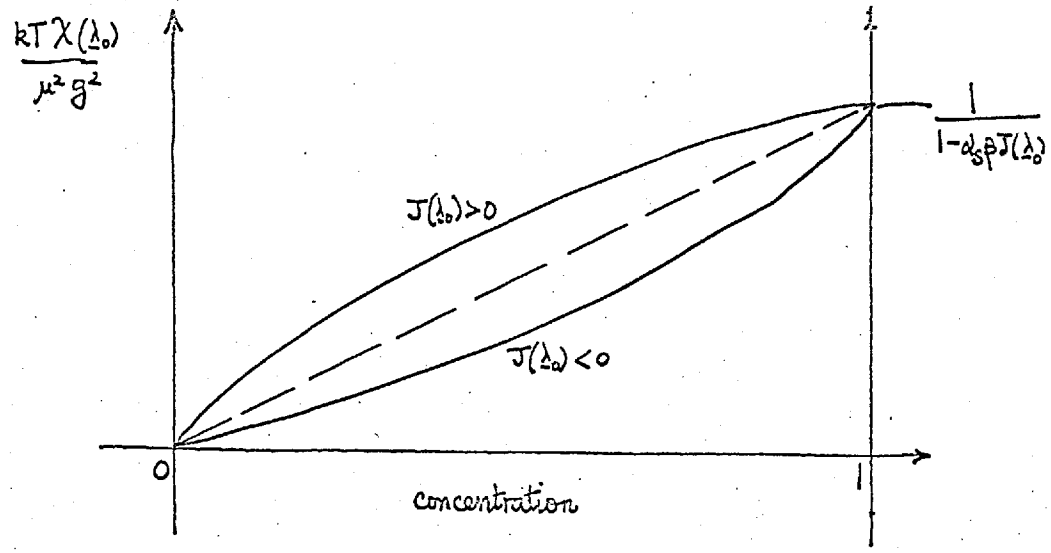


Diagram 6.3 The concentration dependence of the susceptibility (6.17). $(kT > kT_c(c=1))$

The second approximation (6.22) is only equal to (6.17) at $c=0$, or 1 and extremely high temperatures. In fact, if $\chi(\underline{\lambda})$ given by (6.17) is labelled $\chi^{(1)}(\underline{\lambda})$ and that given by (6.22) $\chi^{(2)}(\underline{\lambda})$, we have,

$$\chi^{(2)}(\underline{\lambda}) \geqslant \chi^{(1)}(\underline{\lambda}) \tag{6.30}$$

in the temperature region considered.

$\chi^{(2)}(\underline{\lambda})$ can be compared with the appropriate linear law as was $\chi^{(1)}(\underline{\lambda})$. $\chi^{(2)}$ equals the value of the linear law when

$$J(\underline{\lambda}) = y\left[1 - \alpha_s\beta c J(\underline{\lambda})\right] \tag{6.31}$$

(we are interested in this condition when $\underline{\lambda}$ is the value for which $J(\underline{\lambda})$ is a maximum). For any interaction (6.31) cannot be satisfied.

For (6.22) the condition for stationary points is difficult to deal with. It is

$$1 - \alpha_s\beta y(1-2c) - 2\alpha_s^2\beta^2 c(1-c)y^2 + \alpha_s\beta c(1-c)\frac{dy^*}{dc} = 0 \tag{6.32}$$

Near $c=0$, and $c=1$ it can be shown that there are no stationary points, and, in fact, considering (6.23) and (6.24) the behaviour in terms of power laws is the same although the slopes are altered.

The result (6.30) shows that introducing some of the randomness increases the response of the system over the whole temperature range for all concentrations. Hence, one would expect the inverse susceptibility to be of the form shown in the diagram below.

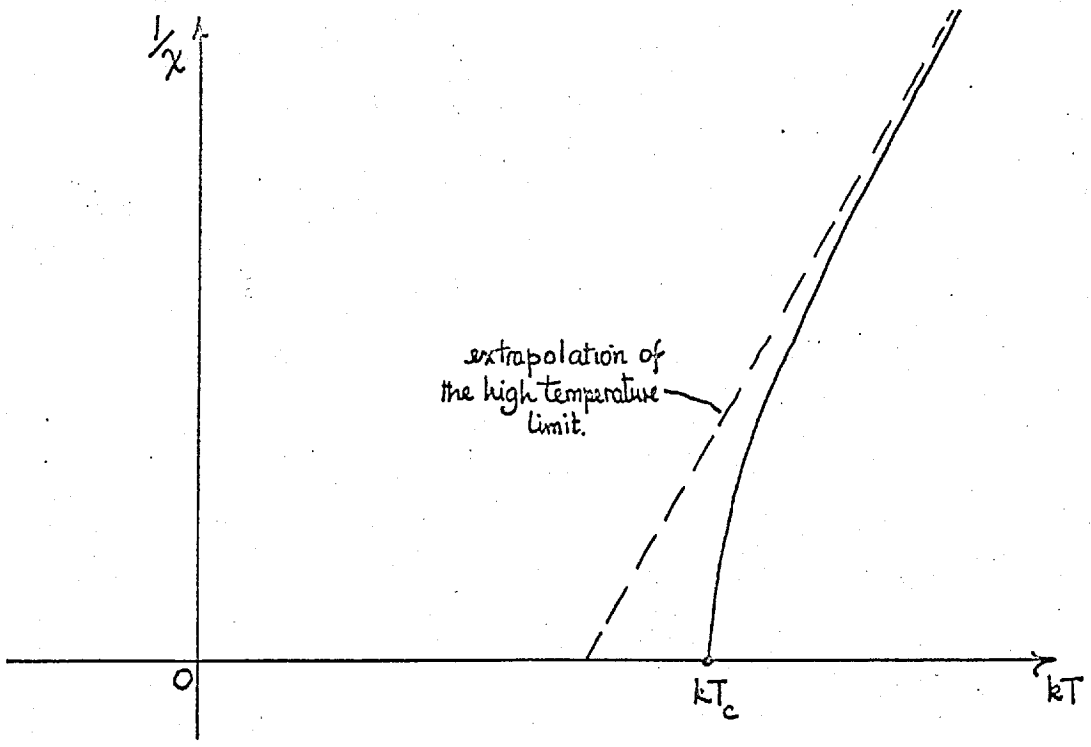


Diagram 6.4 The temperature dependence of the susceptibility (6.22)

To complement these general results, calculations have been carried out for a simple cubic lattice and nearest neighbour interactions. The integral y is only to be evaluated for $0 \leq \alpha \leq 1/J_{max}$ The integrand is regular and only diverges when $\alpha = 1/J_{max}$ and $J(\underline{\lambda})$ has its maximum value. A uniform net of points in $1/48^{th}$ of the Brillouin zone was used and convergence was adequate. The results are presented in graphs 6.1 and 6.2.

Since completion of these calculations, a table of values by Tikson[100] for the integral y has been found. The two sets of values do not differ significantly.

6.4 A Further Approximation

After this prolonged discussion we return to the approximation of (6.16), the expansion of $\sigma(\underline{\lambda})$. Assuming that

$$\sigma(\underline{\lambda}) \cong A(\underline{\lambda}) + B(\underline{\lambda})\, a_{\underline{\lambda}-\underline{k}} + \frac{1}{N}\sum_{\underline{k}} C(\underline{k},\underline{\lambda}) \left\{ a_{\underline{\lambda}-\underline{k}} a_{\underline{k}-\underline{k}} - c(1-c)N\delta_{\underline{\lambda},\underline{k}} - (1-2c)\, a_{\underline{\lambda}-\underline{k}} \right\}$$

the relevant averages can be expressed in terms of A,B,C as follows

$$g(\underline{\lambda}) = A(\underline{\lambda}) \quad ; \quad g(\underline{\lambda},\underline{k}) = c(1-c)N\delta_{\underline{k},\underline{k}} B(\underline{\lambda}) \quad ;$$

$$g(\underline{\lambda},\underline{k}',\underline{k}'') = c(1-c)N\,\delta_{\underline{\lambda},\underline{k}''} A(\underline{\lambda}) + c(1-c)(1-2c)N\,\delta_{\underline{k}'',\underline{k}} B(\underline{\lambda}) + \frac{1}{N}\sum_{\underline{k}} C(\underline{k},\underline{\lambda}) \left\{ c^2(1-c)^2 \left[-2N\,\delta_{\underline{k},\underline{k}''} + N^2 \delta_{\underline{k}'',\underline{k}} \left(\delta_{\underline{k},\underline{k}'} + \delta_{\underline{\lambda}-\underline{k},\underline{k}'-\underline{k}''} \right) \right] \right\}$$

and $g(\underline{\lambda},\underline{k}',\underline{k}'',\underline{k}''') - c(1-c)N\delta_{\underline{k}',\underline{k}'''}\, g(\underline{\lambda},\underline{k}') - (1-2c)\, g(\underline{\lambda},\underline{k}',\underline{k}''')$

$$= c^2(1-c)^2(1-2c)N\,\delta_{\underline{\lambda},\underline{k}''} \frac{1}{N}\sum_{\underline{k}} C(\underline{k},\underline{\lambda}) \left\{ -4 + N\left(\delta_{\underline{k}'',\underline{k}} + \delta_{\underline{k}'''-\underline{k}''+\underline{\lambda}-\underline{k},0} + \delta_{\underline{k}'''-\underline{k}''+\underline{k}'-\underline{k},0} + \delta_{\underline{k}''-\underline{k}'+\underline{\lambda}-\underline{k},0} \right) \right\}$$

This decoupling implies the following three equations

$$A Q(\underline{k}) = 1 + \alpha_s \beta c(1-c) \frac{1}{N}\sum_{\underline{k}} J(\underline{k}) \bar{B}(\underline{k}) \tag{6.33}$$

$$c\bar{B}(\underline{\lambda}) Q(\underline{\lambda}) = 1 + \alpha_s\beta \frac{1}{N}\sum_{\underline{k}} J(\underline{k}) \left\{ cN\delta_{\underline{k},\underline{k}} A + c(1-2c)\bar{B}(\underline{k}) \right\} + \alpha_s\beta c(1-c)\frac{1}{N^2}\sum_{\underline{k},\underline{k}'} J(\underline{k})\, C(\underline{k}',\underline{k}) \left\{ -2 + N\left(\delta_{\underline{\lambda},\underline{k}'} + \delta_{\underline{\lambda}-\underline{k}+\underline{k}'-\underline{k},0} \right) \right\} \tag{6.34}$$

$$\text{and, } \frac{1}{N}\sum_{\underline{k}} C(\underline{k},\underline{\lambda})\left\{-2 + N\left(\delta_{\underline{\lambda}-\underline{k}+\underline{\varkappa},0} + \delta_{\underline{k}-\underline{k}+\underline{\varkappa},0}\right)\right\} c(1-c)\,Q(\underline{\lambda})$$

$$= \alpha_s\beta c^2(1-c)\frac{1}{N}\sum_{\underline{k}} J(\underline{k})\,\bar{B}(\underline{k})\left\{-2 + N\left(\delta_{\underline{\lambda}-\underline{k}+\underline{\varkappa},0} + \delta_{\underline{k}-\underline{k}+\underline{\varkappa},0}\right)\right\} \qquad (6.35)$$

$$+ \alpha_s\beta c(1-c)(1-2c)\frac{1}{N^2}\sum_{\underline{k},\underline{k}'} J(\underline{k})\,C(\underline{k}',\underline{k})\left\{-4 + N\left(\delta_{\underline{k}'-\underline{k}+\underline{\varkappa},0} + \delta_{\underline{\lambda}-\underline{k}+\underline{k}'-\underline{k}+\underline{\varkappa},0} + \delta_{\underline{k}'-\underline{k}+\underline{\varkappa},0} + \delta_{\underline{\lambda}-\underline{k}'+\underline{\varkappa},0}\right)\right\}$$

It obviously becomes increasingly difficult to deal with the set of equations produced as the approximations become more complicated but in this case $C(\underline{k},\underline{k}')$ can be eliminated as follows.

Using equation (6.34) gives

$$\alpha_s\beta c\,(1-c)\frac{1}{N^2}\sum_{\underline{k},\underline{k}'} J(\underline{k})\,C(\underline{k}',\underline{k})\left\{-4 + N\left(\delta_{\underline{\lambda}-\underline{k}'+\underline{\varkappa},0} + \delta_{\underline{\lambda}-\underline{k}+\underline{k}'-\underline{k}+\underline{\varkappa},0} + \delta_{\underline{k}'-\underline{k}+\underline{\varkappa},0} + \delta_{\underline{k}-\underline{k}'+\underline{\varkappa},0}\right)\right\} \qquad (6.36)$$

$$= c\,\bar{B}(\underline{k}-\underline{\varkappa})\,Q(\underline{k}-\underline{\varkappa}) + c\,\bar{B}(\underline{k}+\underline{\varkappa})\,Q(\underline{\lambda}+\underline{\varkappa}) - 2\Delta(\underline{k})$$

where $$\Delta(\underline{k}) = 1 + \alpha_s\beta c\,J(\underline{k})\,A + \alpha_s\beta c(1-2c)\frac{1}{N}\sum_{\underline{k}} J(\underline{k})\,\bar{B}(\underline{k})$$

This equation can be used to re-express (6.35) as

$$\left[-\frac{2}{N}\sum_{\underline{k}} C(\underline{k},\underline{\lambda}) + C(\underline{\lambda}+\underline{\varkappa},\underline{\lambda}) + C(\underline{k}-\underline{\varkappa},\underline{\lambda})\right] Q(\underline{\lambda})$$

$$= \alpha_s\beta c\frac{1}{N}\sum_{\underline{k}} J(\underline{k})\,\bar{B}(\underline{k})\left\{-2 + N\left(\delta_{\underline{\lambda}-\underline{k}+\underline{\varkappa},0} + \delta_{\underline{k}-\underline{k}+\underline{\varkappa},0}\right)\right\} \qquad (6.37)$$

$$+ \frac{(1-2c)}{c(1-c)}\left\{c\,\bar{B}(\underline{k}-\underline{\varkappa})\,Q(\underline{k}-\underline{\varkappa}) + c\,\bar{B}(\underline{\lambda}+\underline{\varkappa})\,Q(\underline{\lambda}+\underline{\varkappa}) - 2\Delta(\underline{k})\right\}$$

Multiplying by $J(\underline{\lambda})/Q(\underline{\lambda})$ and summing over $(\underline{\lambda})$ gives

$$-\frac{2}{N^2}\sum_{\underline{t},\underline{t}'} J(\underline{t}')C(\underline{t},\underline{t}') + \frac{1}{N}\sum_{\underline{t}} J(\underline{t})C(\underline{t}+\underline{x},\underline{t}) + \frac{1}{N}\sum_{\underline{t}} J(\underline{t})C(\underline{k}-\underline{x},\underline{t})$$

$$= -2\left[\alpha_s\beta c\frac{1}{N}\sum_{\underline{t}} J(\underline{t})\bar{B}(\underline{t}) + \frac{1-2c}{c(1-c)}\Delta(\underline{k})\right]y \qquad (6.38)$$

$$+\frac{1}{N}\sum_{\underline{t}}\frac{J(\underline{t}-\underline{x})}{Q(\underline{t}-\underline{x})}R(\underline{t})\bar{B}(\underline{t}) + y\,R(\underline{k}-\underline{x})\bar{B}(\underline{k}-\underline{x})$$

where $$R(\underline{t}) = \frac{(1-2c)}{(1-c)} + \alpha_s\beta c^2 J(\underline{t})\frac{1}{1-c}$$

Choosing $\underline{x}=\underline{k}-\underline{\lambda}$ and using equations (6.38) and (6.34) completesthe elimination of C :-

$$c\bar{B}(\underline{\lambda})Q(\underline{\lambda}) = \Delta(\underline{k}) - 2\alpha_s\beta c(1-c)y\left[\alpha_s\beta c\frac{1}{N}\sum_{\underline{t}} J(\underline{t})\bar{B}(\underline{t}) + \frac{1-2c}{c(1-c)}\Delta(\underline{k})\right]$$

$$+\alpha_s\beta c(1-c)\left[y\,R(\underline{\lambda})\bar{B}(\underline{\lambda}) + \frac{1}{N}\sum_{\underline{t}}\frac{J(\underline{t}+\underline{k}-\underline{\lambda})}{Q(\underline{t}+\underline{k}-\underline{\lambda})}R(\underline{t})\bar{B}(\underline{t})\right] \qquad (6.39)$$

The behaviour of the integrand of the last term makes it impossible to obtain a complete solution for A from equations (6.39), (6.33).
Formally (6.39) can be re-expressed as

$$cP(\underline{\lambda})\bar{B}(\underline{\lambda}) = \Phi(\underline{k}) + \alpha_s\beta c(1-c)\frac{1}{N}\sum_{\underline{t}}\frac{J(\underline{t}+\underline{k}-\underline{\lambda})}{Q(\underline{t}+\underline{k}-\underline{\lambda})}R(\underline{t})\bar{B}(\underline{t}) \qquad (6.40)$$

where $$P(\underline{\lambda}) = Q(\underline{\lambda}) - \alpha_s\beta c(1-c)yR(\underline{\lambda})$$

and $$\Phi(\underline{k}) = \Delta(\underline{k}) - 2y\alpha_s\beta c(1-c)\left[\alpha_s\beta c\frac{1}{N}\sum_{\underline{t}} J(\underline{t})\bar{B}(\underline{t}) + \frac{1-2c}{c(1-c)}\Delta(\underline{k})\right]$$

Comparing this approximation with the last the leading correction to $c\bar{B}(\underline{\lambda})$ for small concentrations is of order c. This is shown by simply iterating (6.40); and using the leading terms in this expansion and equation (6.33), the leading correction to the denominator of $\chi(\underline{k})$ is

$$\alpha_s^3 \beta^3 c \frac{1}{N^2} \sum_{\underline{\lambda},\underline{\xi}} J(\underline{\xi}+\underline{k}-\underline{\lambda}) J(\underline{\xi}) J(\underline{\lambda}) \tag{6.41}$$

So the critical temperature is $kT_c \simeq Ac^{1/3}$ for low concentrations. This throws doubt on the validity of the theory for small concentrations and as we shall see in the next section this doubt is justified.

For concentrations near $c=1$, (6.39) leads to important additions to the susceptibility of $O(1-c)$, as one expects, since most of the terms in the exact high temperature expansion contribute to $O(1-c)$ and the earlier approximation did not include all these contributions. In the limit $c \to 1$, $c\bar{B}(\underline{\lambda})$ satisfies the equation

$$\bar{P}(\underline{\lambda})\, C(\underline{\lambda}) = \chi(\underline{k}) - \alpha_s \beta \frac{1}{N} \sum_{\underline{\xi}} \frac{J(\underline{\xi}+\underline{k}-\underline{\lambda})}{\bar{Q}(\underline{\xi}+\underline{k}-\underline{\lambda})} \bar{Q}(\underline{\xi}) C(\underline{\xi})$$

where $$\bar{P}(\underline{\lambda}) = (1-\alpha_s\beta J(\underline{\lambda}))(1+\alpha_s\beta y_1)$$

$$\chi(\underline{k}) = (1+2\alpha_s\beta y_1)\left[1+\alpha_s\beta J(\underline{\xi}) A - \alpha_s\beta \alpha\right]$$

Obviously, terms proportional to $\frac{1}{N^2}\sum_{\underline{\xi},\underline{\lambda}} J(\underline{\lambda}) J(\underline{\xi}) J(\underline{\xi}+\underline{k}-\underline{\lambda})$ will be included in the terms of $O(1-c)$, but the change in the critical temperature vs. concentration relation near $c=1$ is difficult to determine.

6.5 The High Temperature Expansion

Using the averages considered in Appendix 1 an expansion of the exact solution of equation (6.10) can be obtained. The first five terms of this expansion are

$$\chi(\underline{\lambda}) = \tfrac{1}{2}\mu^2 g^2 \alpha_s \beta c N \delta_{\underline{\lambda},\underline{k}} \Big\{ 1 + \alpha_s\beta c J(\underline{\lambda}) + A(\alpha_s\beta)^2 + B(\alpha_s\beta)^3 + D(\alpha_s\beta)^4 + E(\alpha_s\beta)^5 + \rightsquigarrow \Big\} \tag{6.42}$$

$$A = c^2 J^2(\underline{\lambda}) + c(1-c)\gamma_2$$

$$B = c^3 J^3(\underline{\lambda}) + c^2(1-c)\left[\gamma_3 + 2J(\underline{\lambda})\gamma_2\right] + c(1-c)^2 \frac{1}{N^2}\sum_{\underline{t},\underline{t}_1} J(\underline{t})J(\underline{t}_1)J(\underline{k}-\underline{t}+\underline{t}_1)$$

$$D = c^4 J^4(\underline{\lambda}) + c^3(1-c)\left(\gamma_4 + 2\gamma_3 J(\underline{\lambda}) + 3\gamma_2 J^2(\underline{\lambda})\right) + c^2(1-c)(2-3c)\gamma_2^2 + 2c^2(1-c)^2 J(\underline{\lambda})\frac{1}{N^2}\sum_{\underline{t},\underline{t}_1} J(\underline{t})J(\underline{t}_1)J(\underline{k}+\underline{t}-\underline{t}_1) + c(1-c)^3(1-2c)\frac{1}{N^3}\sum_{\underline{t},\underline{t}_1,\underline{t}_2} J(\underline{t})J(\underline{t}_1)J(\underline{t}_2)J(\underline{t}-\underline{t}_1+\underline{t}_2) + c^2(1-c)^2\frac{1}{N^2}\sum_{\underline{t},\underline{t}_1} J(\underline{t})J(\underline{t}_1)J(\underline{k}-\underline{t}+\underline{t}_1)\left[J(\underline{t})+J(\underline{t}_1)+J(\underline{k}+\underline{t}_1-\underline{t}_1)\right]$$

etc.

where $\gamma_n = \frac{1}{N}\sum_{\underline{t}} J^n(\underline{t})$

It is interesting to compare the high temperature expansions of the approximations considered previously. The simplest approximation (6.17) only mirrors the exact MFT expansion to $O(\beta)$, and the first few terms of the other approximations are respectively

$$\chi(\underline{\lambda}) \simeq \tfrac{1}{2}\mu^2 g^2 \alpha_s \beta c N \delta_{\underline{\lambda},\underline{k}} \Big\{ 1 + \alpha_s\beta c J(\underline{k}) + A_1(\alpha_s\beta)^2 + B_1(\alpha_s\beta)^3 + \rightsquigarrow \Big\}$$

$$A_1 = c^2 J^2(\underline{k}) + c(1-c)\gamma_2$$

$$B_1 = c^3 J^3(\underline{\lambda}) + c^2(1-c)\left(\gamma_3 + 2J(\underline{\lambda})\gamma_2\right)$$

and

$$\chi(\underline{\lambda}) \simeq \tfrac{1}{2}\mu^2 g^2 \alpha_s \beta c N \delta_{\underline{\lambda},\underline{k}} \Big\{ 1 + \alpha_s\beta c J(\underline{k}) + A_2(\alpha_s\beta)^2 + B_2(\alpha_s\beta)^3 + \rightsquigarrow \Big\}$$

$$A_2 = c^2 J^2(\underline{k}) + c(1-c)\gamma_2$$

$$B_2 = c^3 J^3(\underline{k}) + c^2(1-c)\left[\gamma_3 + 2\gamma_2 J(\underline{k})\right] + c(1-c)^2 \frac{1}{N^2}\sum_{\underline{t},\underline{t}_1} J(\underline{t})J(\underline{t}_1)J(\underline{k}-\underline{t}+\underline{t}_1)$$

Thus, the succession of approximations is gradually improving the high temperature expansion's representation.

What is more important than the form of the expansion (6.42) is the infinite series of terms proportional to c, i.e.

$$\alpha_s\beta c J(\underline{\lambda}) + \alpha_s^2\beta^2 c\gamma_2 + \alpha_s^3\beta^3 c \frac{1}{N^2}\sum_{\underline{t},\underline{t}_1} J(\underline{t})J(\underline{t}_1)J(\underline{k}-\underline{t}+\underline{t}_1) + \cdots$$

The n^{th} term of this series can be found using the recursive relation given in Appendix 2. In fact, in the n^{th} term the most important contribution for the low concentration term is

$$\frac{1}{N^n}\sum_{\underline{t}_1,\ldots,\underline{t}_n} J(\underline{t}_1)\ldots J(\underline{t}_n)\langle a_{\underline{\lambda}-\underline{t}_1} a_{\underline{t}_1-\underline{t}_2}\ldots a_{\underline{t}_n-\underline{k}}\rangle$$

When n is odd this gives

$$c^2\frac{1}{N^{n-1}}\sum_{\underline{t}_1,\ldots,\underline{t}_{n-1}} J(\underline{t}_1)J(\underline{t}_2)\ldots J(\underline{k}-\underline{t}_1+\underline{t}_2\ldots+\underline{t}_{n-1})$$

while for n even it gives

$$c^2\frac{1}{N^{n-1}}\sum_{\underline{t}_1\ldots\underline{t}_{n-1}} J(\underline{t}_1)J(\underline{t}_2)\ldots J(\underline{t}_1-\underline{t}_2+\underline{t}_3-\ldots+\underline{t}_{n-1})$$

For nearest neighbour interactions these can be evaluated and the terms to $O(c^2)$ are

$$\chi(\underline{k}) \simeq \tfrac{1}{2}\mu^2 g^2 \alpha_s\beta c N\left\{1 + \frac{\alpha_s\beta c J(\underline{k}) + \alpha_s^2\beta^2 c J J(0)}{1-\alpha_s^2\beta^2 J^2} + O(c^2)\right\}$$

Thus, for small concentrations the critical temperature is $kT_c \simeq \alpha_s J$, which is the reason the approximations listed previously could not give a coherent picture for this concentration region. If the situation is considered as a pure dilution problem the number of nearest neighbours

for low concentrations becomes cz, and when $c \leq \frac{2}{z}$ the effective co-ordination number is ≤ 2. When MFT is used to treat the linear chain for a pure substance it predicts a ferromagnetic state, which is incorrect, so it is perhaps not surprising that for small concentrations the theory gives an unphysical ordered state.

Following a procedure similar to that of Rushbrooke and Wood[99] but including the distribution function p_n, an exact high temperature expansion can be found. The first few terms are

$$\chi(0) = \tfrac{1}{2}\mu^2 g^2 \alpha_s \beta c N \left\{ 1 + \alpha_s \beta J(0) c + \alpha_s^2 \beta^2 c J J(0) \left[c(z-1) - \frac{1}{2\alpha_s} \right] + \rightsquigarrow \right\}$$

The MFT, as in the pure substance case, agrees with the exact expansion to only the first two terms, and what is much more significant is that the largest term for small concentrations of $O(\beta^2)$ has changed sign. It is obviously this error, and others in higher terms, which lead to the unphysical results for low concentrations.

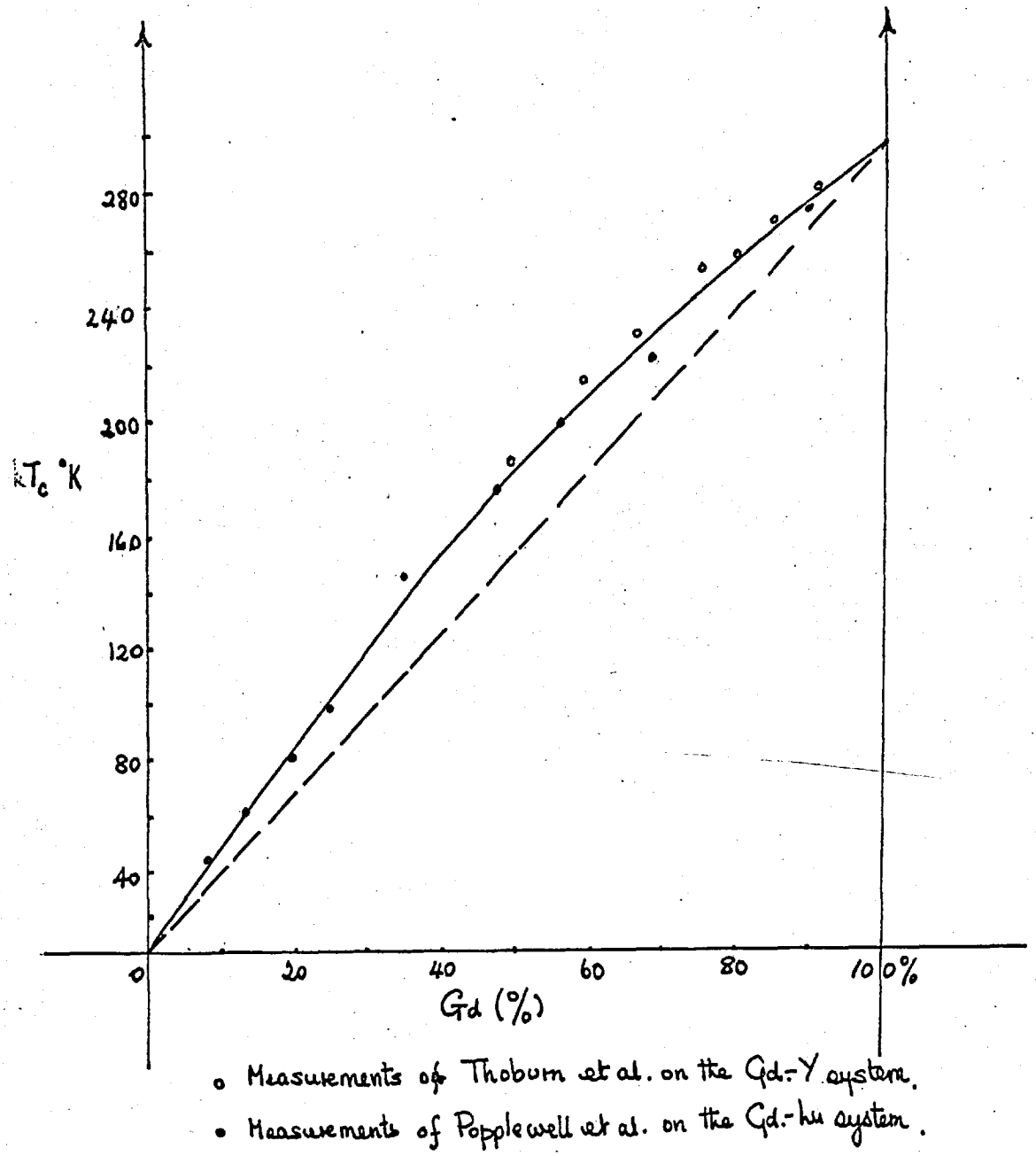


Figure 6.1 The results for the critical temperature vs. concentration curve for the Gd-Lu and Gd-Y systems from Popplewell et al and Thoburn et al.

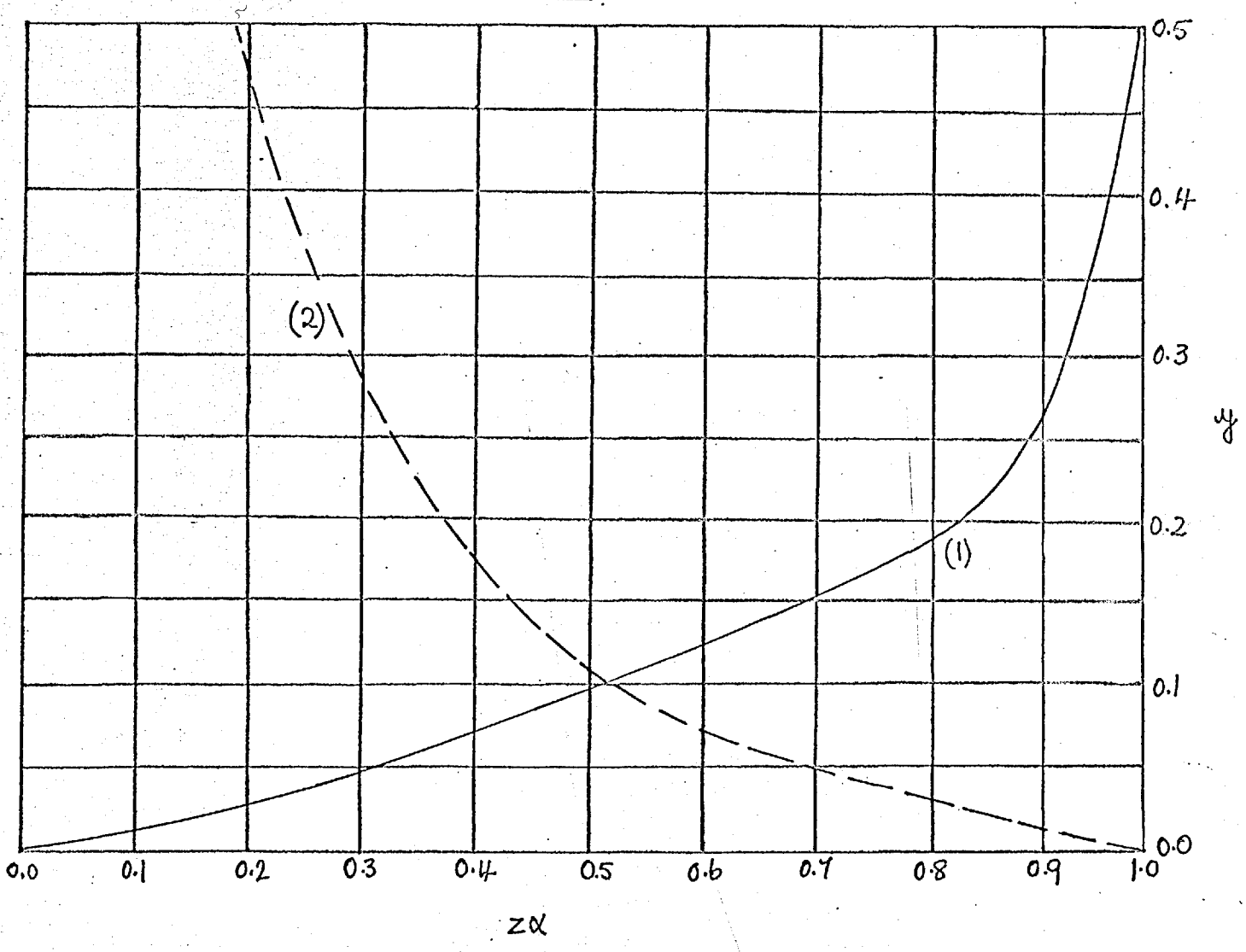
GRAPH 6.1

Curve for the integral y against α compared with the curve of the right hand side of equation (6.26) for concentration, $C = \cdot 1$

(1) denotes the curve of y.

(2) denotes the right hand side of (6.26).

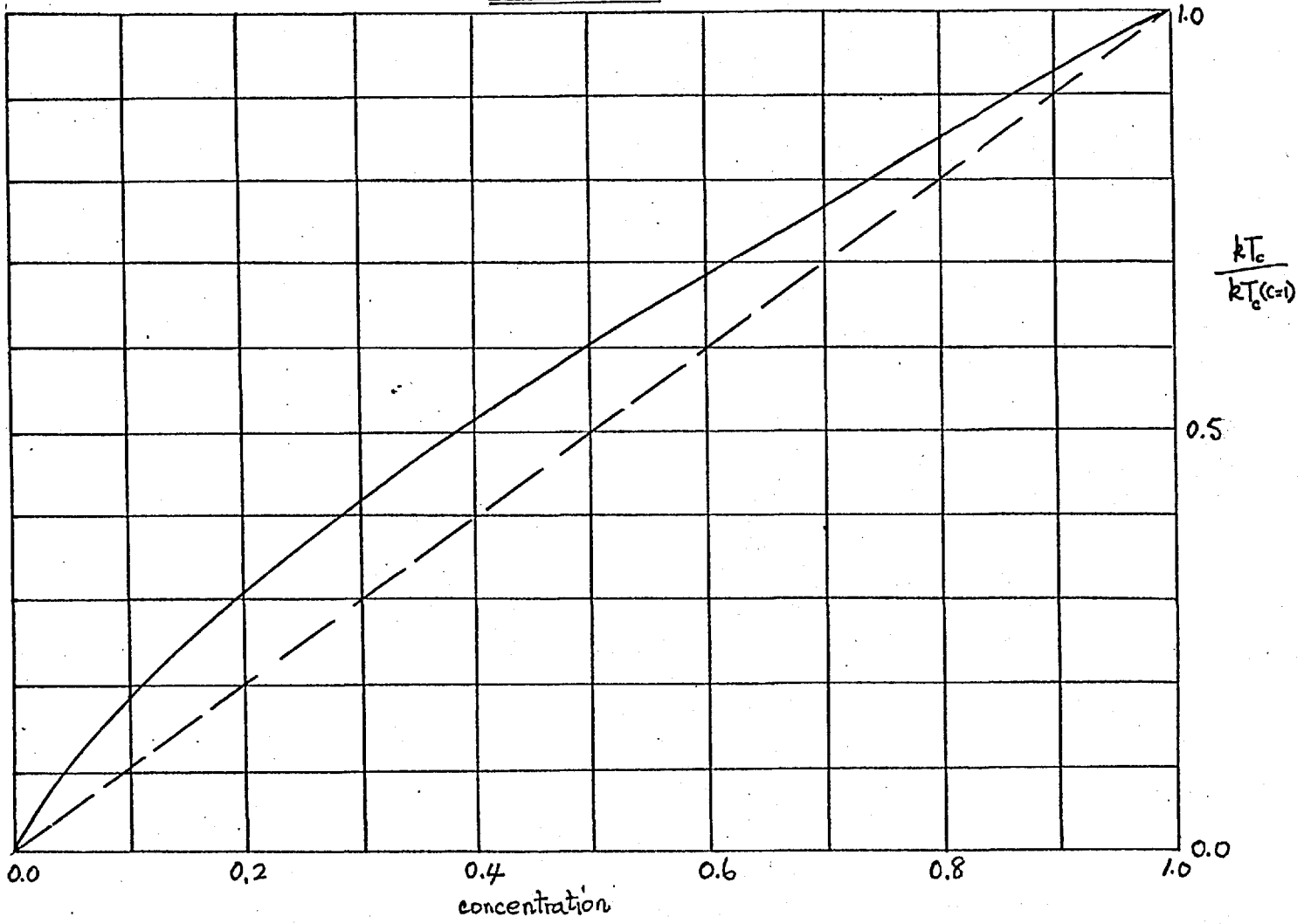
GRAPH 6.1



GRAPH 6.2

Curve of critical temperature against concentration obtained from the condition (6.26).

GRAPH 6.2



Chapter 7

The Bethe-Peierls-Weiss Method for Magnetic Alloys - Ising Model

7.1 Introduction

In the last chapter it was shown that besides the deficiencies of the MFT for the pure substance, this approximation cannot deal with the dilute alloy region and does not give a critical concentration. In fact, the validity of the approximation in the region of $c=1$ is all that can be claimed, and a more sophisticated theory is needed. In looking for an improvement an obvious compromise is to consider some small section of the crystal, treat the exchange interactions within the section exactly, and assume the section to be coupled to the remainder of the crystal by an effective field. For the pure substance, the simplest choice for this small section is a pair of nearest neighbour atoms selected at random; this is the Oguchi method.[101] It would seem impossible to extend such a method to longer range interactions, and more important in the alloy situation, the value of $\langle S_i^z \rangle$ for some site i would depend on the choice of the other site of the cluster, and it can be shown quite easily that the dependence is not trivial. Thus the application of the Oguchi method must be restricted to pure substances with nearest neighbour interactions.

The next improvement would be to consider more than two atoms in order to take several interactions into account exactly, instead of just one. Kikuchi[102] has made such an attempt (for pure substances and nearest neighbour

interactions) using the constant coupling method and has found that the amount of improvement increases rather slowly with increases in the number of atoms considered. Another method, that of Bethe, Peierls and Weiss (BPW) involves much less labour. For nearest neighbour interactions it uses a group of (z+1) atoms and an effective field. This method was originally developed by Bethe to treat the problem of order-disorder in alloys, extended to the Ising Model of ferromagnetism by Peierls,[103] and to the Heisenberg model by P.R. Weiss.[104] The BPW method is an improvement on the MFT as it predicts Curie temperatures for a pure ferromagnet which are very much nearer the values obtained by Rushbrooke and Wood from the exact high temperature expansion of the susceptibility; and also gives a non-zero zero-field specific heat above the transition temperature. Below the transition temperature it has the major deficiency that it predicts an unphysical anti-Curie temperature; and in this respect alone it is inferior to the MFT.

The BFW method does not suffer from the troubles of the Oguchi method and can be extended to longer range interactions and to the alloy situation. The introduction of even next nearest neighbour interactions when considering the Heisenberg model created difficulties and so in the next section we use the Ising model, where interactions of arbitrary range can be formally dealt with. We also restrict the spins to the spin $\frac{1}{2}$ case in the next section to simplify the mathematics still further.

7.2 Ising model, $S=\frac{1}{2}$ Method 1.

The problem of extending the BPW method to long range interactions can be overcome if we relax the restriction on the cluster that we treat all the

interactions between spins in the cluster exactly (as we would in the nearest neighbour interaction case), and attempt instead to treat the interactions of the central spin exactly and those of the other spins in the cluster by means of effective fields. So we first choose a cluster of sites centred on the site $\underline{n}$ such that a spin on $\underline{n}$ would interact with another spin in the crystal if and only if the spin is on a site belonging to the cluster of sites centred on $\underline{n}$. As we are considering an alloy we introduce the same distribution function $p_{\underline{n}}$ as defined in the MFT discussion (Chapter 6 p.69), which enables us to write the Hamiltonian of the cluster of spins as,

$$\mathcal{H}_{\alpha,\underline{n}} = -2\sum_{\underline{\ell}} p_{\underline{n}} p_{\underline{n}+\underline{\ell}} J(\underline{\ell}) S^z_{\underline{n}} S^z_{\underline{n}+\underline{\ell}} - \mu_g \left\{ \sum_{\underline{\ell}} p_{\underline{n}+\underline{\ell}} S^z_{\underline{n}+\underline{\ell}} H_{\underline{n}}(\underline{\ell}) + H p_{\underline{n}} e^{-i\underline{k}.\underline{\Lambda}} S^z_{\underline{k}} \right\} \quad (7.1)$$

where $H_{\underline{n}}(\underline{\ell})$ is the effective field for the spin on site $\underline{n}+\underline{\ell}$ and the sums over $\underline{\ell}$ extend over all $\underline{\ell}$ such that $\underline{\Lambda}+\underline{\ell}$ belongs to the cluster of sites centred on $\underline{n}$.

Some means of obtaining values for the effective fields is, of course, needed and in the light of the MFT discussion we choose,

$$\mu_g H_{\underline{n}}(\underline{\ell}) = \sum_{\underline{m}} J(\underline{n}+\underline{\ell}-\underline{m})\sigma_{\underline{m}} - J(\underline{\ell})\sigma_{\underline{n}} + \mu_g H e^{-i\underline{k}.(\underline{n}+\underline{\ell})} \quad (7.2)$$

where $\sigma_{\underline{m}} = 2\langle S^z_{\underline{m}} \rangle$

Because the Ising Model is being used the eigenfunctions of the cluster Hamiltonian (7.1) are obvious and the eigenvalues are,

$$E(\varepsilon_{\underline{n}}, \varepsilon_{\underline{n}+\underline{\ell}_1}, \ldots, \varepsilon_{\underline{n}+\underline{\ell}_{N_J}}) = -\tfrac{1}{2} p_{\underline{n}} \sum_{\underline{\ell}} J(\underline{\ell}) p_{\underline{n}+\underline{\ell}} \varepsilon_{\underline{n}+\underline{\ell}} \varepsilon_{\underline{n}} - \tfrac{1}{2}\mu g H p_{\underline{n}} \varepsilon_{\underline{n}} e^{-i\underline{k}\cdot\underline{n}} - \tfrac{1}{2}\mu g \sum_{\underline{\ell}} H(\underline{\ell}) p_{\underline{n}+\underline{\ell}} \varepsilon_{\underline{n}+\underline{\ell}} \tag{7.3}$$

where $\varepsilon_{\underline{n}+\underline{\ell}_m} = \begin{cases} +1 & \text{if } S^z_{\underline{n}+\underline{\ell}_m} = 1/2 \\ -1 & \text{if } S^z_{\underline{n}+\underline{\ell}_m} = -\tfrac{1}{2} \end{cases}$, N_J+1 = no. of sites in cluster.

The probability of a particular arrangement of spins is $\exp\{-\beta E(\varepsilon_{\underline{n}}, \varepsilon_{\underline{n}+\underline{\ell}_1}, \ldots, \varepsilon_{\underline{n}+\underline{\ell}_{N_J}})\}$ and so,

$$\sigma_{\underline{n}} = 2\langle S^z_{\underline{n}} \rangle = \frac{\sum_{\text{all } E} \varepsilon_{\underline{n}} e^{-\beta E}}{\sum_{\text{all } E} e^{-\beta E}} \tag{7.4}$$

This average can be expanded in powers of the external field, H, and considering the two configurations

$(\varepsilon_{\underline{n}}, \varepsilon_{\underline{n}+\underline{\ell}_1}, \ldots, \varepsilon_{\underline{n}+\underline{\ell}_{N_J}})$ and $(-\varepsilon_{\underline{n}}, -\varepsilon_{\underline{n}+\underline{\ell}_1}, \ldots, -\varepsilon_{\underline{n}+\underline{\ell}_{N_J}})$

together (7.4) becomes,

$$\sigma_{\underline{n}} = \frac{\sum_{\substack{\text{over all} \\ \text{configurations} \\ (\varepsilon_{\underline{n}+\underline{\ell}_1}, \ldots, \varepsilon_{\underline{n}+\underline{\ell}_{N_J}})}} e^{\frac{1}{2}\beta p_{\underline{n}} \sum_{\underline{\ell}} J(\underline{\ell}) p_{\underline{n}+\underline{\ell}} \varepsilon_{\underline{n}+\underline{\ell}}} \left\{ \mu g \beta p_{\underline{n}} \sum_{\underline{\ell}} H_{\underline{n}}(\underline{\ell}) p_{\underline{n}+\underline{\ell}} \varepsilon_{\underline{n}+\underline{\ell}} + \mu g \beta p_{\underline{n}} H e^{-i\underline{k}\cdot\underline{n}} \right\}}{2 \sum_{\substack{\text{over all} \\ \text{configurations} \\ (\varepsilon_{\underline{n}+\underline{\ell}_1}, \ldots, \varepsilon_{\underline{n}+\underline{\ell}_{N_J}})}} e^{\frac{1}{2}\beta p_{\underline{n}} \sum_{\underline{\ell}} J(\underline{\ell}) p_{\underline{n}+\underline{\ell}} \varepsilon_{\underline{n}+\underline{\ell}}}}$$

This is easily reduced to the equation,

$$\sigma_{\underline{n}} = \tfrac{1}{2}\mu g H \beta p_{\underline{n}} e^{-i\underline{k}\cdot\underline{n}} + \tfrac{1}{2}\beta \sum_{\underline{\ell}'} \mu g H_{\underline{n}}(\underline{\ell}') p_{\underline{n}+\underline{\ell}'} \left\{ \frac{1 - e^{-\beta J(\underline{\ell}') p_{\underline{n}}}}{1 + e^{-\beta J(\underline{\ell}') p_{\underline{n}}}} \right\} \tag{7.5}$$

and substituting from (7.2) for $H_{\underline{n}}(\xi)$ into (7.5) gives,

$$\sigma_{\underline{n}} = \tfrac{1}{2}\mu g\beta H p_{\underline{n}}\Big\{ e^{-i\underline{k}.\underline{n}} + \sum_{\underline{m}} p_{\underline{m}} \Phi(\underline{n}-\underline{m}) e^{-i\underline{k}.\underline{m}}\Big\}$$
$$+\tfrac{1}{2}\beta p_{\underline{n}}\Big\{ \sum_{\underline{m}} p_{\underline{m}} \Phi(\underline{n}-\underline{m})\Big[\sum_{\underline{m}'} J(\underline{m}-\underline{m}')\sigma_{\underline{m}'} - J(\underline{n}-\underline{m})\sigma_{\underline{n}}\Big]\Big\} \qquad (7.6)$$

where $\Phi(\underline{m}-\underline{n}) = \{1-e^{-\beta J(\underline{m}-\underline{n})}\}\{1+e^{-\beta J(\underline{m}-\underline{n})}\}^{-1}$

As in the MFT, we Fourier-transform this equation and obtain

$$\sigma(\underline{\lambda}) = \tfrac{1}{2}\mu g\beta H p(\underline{\lambda}-\underline{k}) + \tfrac{1}{2}\mu g\beta H \frac{1}{N}\sum_{\underline{\lambda}_1} \Phi(\underline{\lambda}_1) p(\underline{\lambda}-\underline{\lambda}_1) p(\underline{\lambda}_1-\underline{k})$$
$$+ \tfrac{1}{2}\beta \frac{1}{N^2}\sum_{\underline{\lambda}_2\underline{\lambda}_1} J(\underline{\lambda}_1)\sigma(\underline{\lambda}_1)\Phi(\underline{\lambda}_2) p(\underline{\lambda}_2-\underline{\lambda}_1) p(\underline{\lambda}-\underline{\lambda}_2) \qquad (7.7)$$
$$-\tfrac{1}{2}\beta \frac{1}{N^3}\sum_{\underline{\lambda}_1,\underline{\lambda}_2,\underline{\lambda}_3} J(\underline{\lambda}_1)\sigma(\underline{\lambda}_2)\Phi(\underline{\lambda}_3) p(\underline{\lambda}-\underline{\lambda}_1-\underline{\lambda}_2-\underline{\lambda}_3) p(\underline{\lambda}_1+\underline{\lambda}_3)$$

When $\sigma(\underline{\lambda})$ is assumed to be independent of concentration fluctuations,

$$\chi(\underline{\lambda}) = \frac{\tfrac{1}{4}\mu^2 g^2 \beta\, cN\, \delta_{\underline{\lambda},\underline{k}}\,[1 + c\,\Phi(\underline{k})]}{1 - \tfrac{1}{2}\beta c^2 J(\underline{k})\Phi(\underline{k}) + \tfrac{1}{2}\beta c^2 \frac{1}{N}\sum_{\underline{\lambda}_1} J(\underline{\lambda}_1)\Phi(\underline{\lambda}_1)} \qquad (7.8)$$

In the high temperature limit, therefore,

$$\chi(\underline{\lambda}) \to \frac{\tfrac{1}{4}\beta\mu^2 g^2 cN\, \delta_{\underline{\lambda},\underline{k}}\,[1 + \tfrac{1}{2}\beta c\, J(\underline{k})]}{1 - \tfrac{1}{4}\beta^2 c^2 J^2(\underline{k}) + \tfrac{1}{4}\beta^2 c^2 \frac{1}{N}\sum_{\underline{\lambda}_1} J^2(\underline{\lambda}_1)} \qquad (7.9)$$

and so the first two terms of the high temperature expansion are the correct ones but the form is not that of a Curie-Weiss law, as $\frac{1}{N}\sum_{\underline{\lambda}_1} J^2(\underline{\lambda}_1) \neq 0$.

The susceptibility (7.8) gives the condition for the critical temperature,

$$1 - \tfrac{1}{2}\beta c^2 J(\underline{\lambda})\Phi(\underline{\lambda}) + \tfrac{1}{2}\beta c^2 \frac{1}{N}\sum_{\underline{\lambda}_1} J(\underline{\lambda}_1)\Phi(\underline{\lambda}_1) = 0 \qquad (7.10)$$

Consider this condition, when the only interaction is of nearest neighbour type. Now $J(\underline{\lambda}) = J\gamma(\underline{\lambda})$ and $\Phi(\underline{\lambda}) = \Phi\gamma(\underline{\lambda})$; therefore (7.10) becomes

$$1 - \tfrac{1}{2}\beta c^2 J\Phi\,\gamma^2(\underline{k}) + \tfrac{1}{2}\beta c^2 J\Phi\,\gamma_2 = 0$$

where $\Phi = \dfrac{1-e^{-\beta J}}{1+e^{-\beta J}}$ and $\gamma_2 = \frac{1}{N}\sum_{\underline{\lambda}} \gamma^2(\underline{\lambda})$, and hence,

$$1 - \tfrac{1}{2}\beta c^2 z(z-1) J\Phi = 0$$

Thus the critical temperature $kT_c < \frac{1}{2}z(z-1)c^2 J$ and there can be no finite critical concentration. Comparing this with the MFT result we have the diagram,

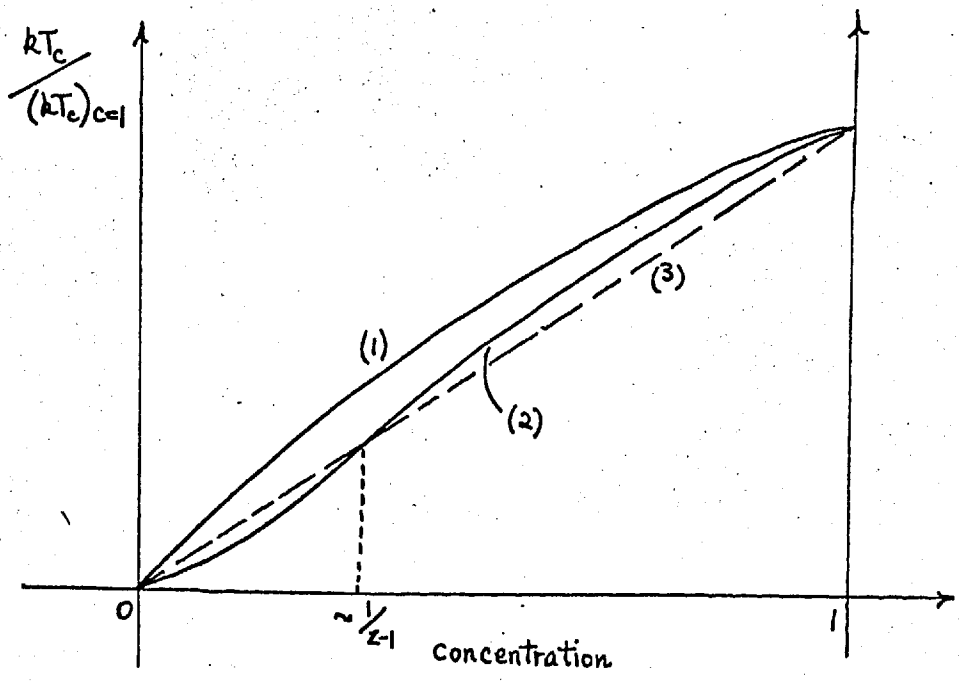


Diagram 7.1 Sketch of kT_c vs. concentration for present method compared with MFT result

Curve (1) is the MFT prediction from the first approximation. Curve (2) is the BPW theory result using condition (7.10). The dotted curve (3) used as reference is the critical temperature curve predicted by (6.17).

The BPW result is an improvement, in this respect, on the type of curve obtained from the MFT approximation.

The condition (7.2) is not fundamental to the calculation. In the next section another method is detailed, which does not use this condition, and gives further improvements.

7.3 Ising Model, $S=\frac{1}{2}$ Method 2

Instead of the condition (7.2) being used to eliminate the effective fields $H_{\underline{n}}(\underline{\varrho})$, these are determined by evaluating $\sigma_{\underline{n}+\underline{\varrho}'}$ for each $\underline{\varrho}'$ which "picks out" a site belonging to the cluster of sites centred on the site $\underline{n}$. By definition,

$$\sigma_{\underline{n}+\underline{\varrho}'} = p_{\underline{n}+\underline{\varrho}'} \frac{\sum_{\text{all } E} \varepsilon_{\underline{n}+\underline{\varrho}'} e^{-\beta E}}{\sum_{\text{all } E} e^{-\beta E}} \tag{7.11}$$

where E's are given by (7.3).

By the same method as used for calculating $\sigma_{\underline{k}}$ (7.11) becomes

$$\sigma_{\underline{n}+\underline{\varrho}'} = \tfrac{1}{2}\mu g \beta p_{\underline{n}+\underline{\varrho}'} \Big\{ H_{\underline{n}}(\underline{\varrho}') + H p_{\underline{n}} e^{-i\underline{k}\cdot\underline{n}} \tanh\left[\tfrac{1}{2}\beta J(\underline{\varrho}')\right] + \tanh\left[\tfrac{1}{2}\beta J(\underline{\varrho}')\right] p_{\underline{n}} \sum_{\underline{\varrho}\neq\underline{\varrho}'} p_{\underline{n}+\underline{\varrho}} H_{\underline{n}}(\underline{\varrho}) \tanh\left[\tfrac{1}{2}\beta J(\underline{\varrho})\right] \Big\} \tag{7.12}$$

These equations together with (7.5) enable us to eliminate $H_{\underline{k}}(\underline{\varrho})$ and obtain,

$$\left[1 + \sum_{\underline{m}} p_{\underline{m}} \Phi_2(\underline{n}-\underline{m})\right] \sigma_{\underline{n}} = \tfrac{1}{2}\mu g \beta H e^{-i\underline{k}\cdot\underline{n}} p_{\underline{n}} + p_{\underline{n}} \sum_{\underline{m}} \Phi_1(\underline{n}-\underline{m}) \sigma_{\underline{m}} \tag{7.13}$$

where $\Phi_2(\underline{n}-\underline{m}) = \dfrac{\tanh^2 \frac{1}{2}\beta J(\underline{n}-\underline{m})}{1-\tanh^2 \frac{1}{2}\beta J(\underline{n}-\underline{m})}$ and $\Phi_1(\underline{n}-\underline{m}) = \dfrac{\tanh \frac{1}{2}\beta J(\underline{n}-\underline{m})}{1-\tanh^2 \frac{1}{2}\beta J(\underline{n}-\underline{m})}$

Fourier transforming this equation gives,

$$\left[1+c\Phi_2(0)-c\Phi_1(\underline{\lambda})\right]\sigma(\underline{\lambda}) = \tfrac{1}{2}\mu g\beta H\{cN\delta_{\underline{\lambda},\underline{k}}+a_{\underline{\lambda}-\underline{k}}\} - \frac{1}{N}\sum_{\underline{\lambda}_1}\left[\Phi_2(\underline{\lambda}-\underline{\lambda}_1)-\Phi_1(\underline{\lambda}_1)\right]\sigma(\underline{\lambda}_1)a_{\underline{\lambda}-\underline{\lambda}_1} \qquad (7.14)$$

The notation here is an obvious extension of that used in the MFT treatment. This equation is very similar to (6.10); only the kernel and $Q(\underline{\lambda})$ have been redefined.

As previously, the simplest approximation is to assume that $\sigma(\underline{\lambda})$ is independent of concentration fluctuations, and under this assumption

$$\chi(\underline{\lambda}) = \frac{\frac{1}{4}\mu^2 g^2 \beta c N \delta_{\underline{\lambda},\underline{k}}}{1+c\left[\Phi_2(0)-\Phi_1(\underline{\lambda})\right]} \qquad (7.15)$$

At high temperatures this becomes,

$$\simeq \frac{\frac{1}{4}\mu^2 g^2 \beta c N \delta_{\underline{\lambda},\underline{k}}}{1+c\left\{\frac{1}{4}\beta^2 \frac{1}{N}\sum_{\underline{\lambda}_1} J^2(\underline{\lambda}_1)-\frac{1}{2}\beta J(\underline{\lambda})\right\}} \longrightarrow \frac{\frac{1}{4}\mu^2 g^2 \beta c N \delta_{\underline{\lambda},\underline{k}}}{1-\frac{1}{2}\beta c J(\underline{\lambda})}$$

and so in this limit it is equivalent to (6.17) obtained using the Heisenberg model (MFT); with a Curie-Weiss behaviour, in contrast to (7.9) obtained using the first method.

The susceptibility (7.15) gives us the following condition for the critical temperature;

$$1-c\left\{\Phi_1(\underline{\lambda})-\Phi_2(0)\right\} = 0 \qquad (7.16)$$

For nearest neighbour interaction the conditions $\frac{\partial \Phi_1(\lambda)}{\partial \lambda_\alpha}=0$ which determine the value of $\underline{\lambda}$ which gives the maximum critical temperature, are entirely equivalent to $\frac{\partial J(\lambda)}{\partial \lambda_\alpha}=0$ and so the two types of ordering are ferromagnetic and antiferromagnetic. Considering the ferromagnetic case, (7.16) is easily proved equivalent to

$$\tanh x = \frac{1}{cz-1} \qquad (7.17)$$

where $x = \frac{1}{2}\beta J$

As $\tanh x$ must by definition be less than unity no solution to (7.17) can be obtained for $c < \frac{2}{z}$, and we have a critical concentration, $c_0 = \frac{2}{z}$. As c increases from c_0, $\tanh x$ decreases and hence the critical temperature increases.

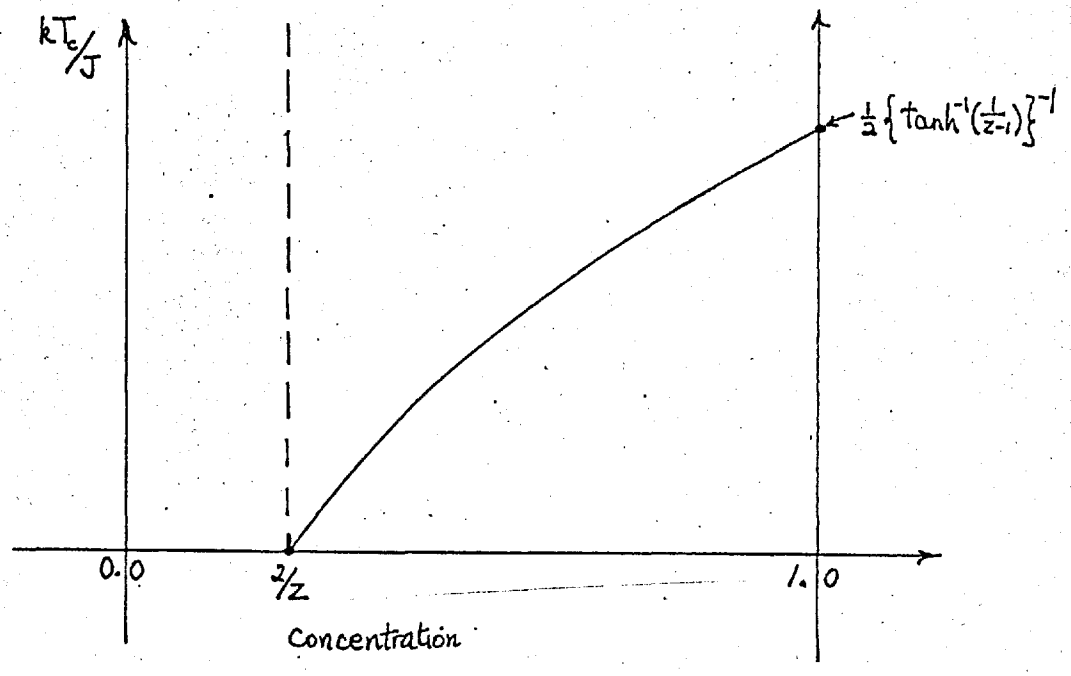


Diagram 7.2 Concentration dependence of critical temperature of nearest neighbour interactions

It is easy to show that exactly the same behaviour is predicted for antiferromagnetic interactions, with J_1, replaced by $|J_1|$.

If the range of the interaction is increased, and the ordering below the critical temperature is ferromagnetic (or some types of antiferromagnetic ordering), the condition (7.16) becomes,

$$1 - c \sum_{m=1}^{n} z_m \frac{\tanh x_m}{1+\tanh x_m} = 0 \qquad (7.18)$$

where $x_m = \frac{1}{2}\beta|J_m|$

As the solution of (7.19) for β tends to ∞, $\tanh x_m \to 1$ and so the critical concentration is

$$c_0 = \frac{2}{\sum_m z_m} \qquad (7.19)$$

Hence, as the range of the interaction increases the critical concentration will decrease as one would expect, but c_0 is independent of the detailed structure of the lattice.

It is very difficult to extend this method to find higher approximations, and this problem will be considered further in a later section.

7.4 Ising Model, $S=\frac{1}{2}$ Calculation of the Free Energy

In previous sections we have considered the calculation of the susceptibility and have found that we can only find approximate solutions, but when the zero-field free energy is considered exact solutions can be found within the limits of the BPW method. Using the

eigenvalues (7.3) and the definition of the Partition function,

$$Z = \sum_{\text{all } E} e^{-\beta E}$$

it is found that

$$Z^{I}_{\alpha,\underline{n}}\left(\begin{smallmatrix}H=0\\T\geq T_c\end{smallmatrix}\right) = \prod_{\underline{\ell}} \cosh\left[\tfrac{1}{2}\beta p_{\underline{n}} p_{\underline{n}+\underline{\ell}} J(\underline{\ell})\right] \qquad (7.20)$$

is the Partition function in the paramagnetic region (suitably normalized to give unity at the high temperature limit).

Using the definition of the distribution function, $p_{\underline{n}}$, this expression can be redefined as,

$$Z^{I}_{\alpha,\underline{n}}\left(\begin{smallmatrix}H=0\\T\geq T_c\end{smallmatrix}\right) = (1-p_{\underline{n}}) + p_{\underline{n}} \prod_{\underline{\ell}} \left\{(1-p_{\underline{n}+\underline{\ell}}) + p_{\underline{n}+\underline{\ell}} \cosh\left(\tfrac{1}{2}\beta J(\underline{\ell})\right)\right\} \qquad (7.21)$$

By definition the free energy is $F=-kT\ln Z$, that is,

$$F = -\tfrac{1}{2}kT \sum_{\underline{n}} \ln\left\{(1-p_{\underline{n}}) + p_{\underline{n}} \prod_{\underline{\ell}} \left[(1-p_{\underline{n}+\underline{\ell}}) + p_{\underline{n}+\underline{\ell}} \cosh\left(\tfrac{1}{2}\beta J(\underline{\ell})\right)\right]\right\} \qquad (7.22)$$

To simplify this expression consider the following function;

$$\gamma^{(k)}_{\underline{n}} = \sum_{\substack{\text{all different sets of different } \underline{\ell}_1,\ldots,\underline{\ell}_m \text{ under condition (1)}}} p_{\underline{n}} \left\{ \prod_{\underline{\ell}_i=\underline{\ell}_1}^{\underline{\ell}_m} p_{\underline{n}+\underline{\ell}_i} \prod_{\underline{\ell}'_i=\underline{\ell}_{m+1}}^{\underline{\ell}_x} (1-p_{\underline{n}+\underline{\ell}'_i}) \right\} \qquad (7.23)$$

where condition (1) states that if $\underline{k}=(k_1,\ldots,k_{k'})$, k_i of the m vectors $\underline{\ell}_1,\ldots,\underline{\ell}_m$ pick out sites in the i^{th} coordination shell of the atom on site $\underline{n}$. The value of x

is, of course, the sum of the co-ordination numbers of the n' shells. This function simply gives the value unity if any arrangement of spins on the cluster of sites centred on the site $\underline{n}$ has k_i spins on the i^{th} co-ordination shell, and zero otherwise. As a simple example the explicit definitions of these functions in the case of a 2 dimensional array of sites (for nearest neighbour interactions only);

$$\tau_{\underline{n}}^{(0)} = p_{\underline{n}}(1-p_{\underline{n}-\underline{e}})(1-p_{\underline{n}+\underline{e}})$$

$$\tau_{\underline{n}}^{(1)} = p_{\underline{n}}p_{\underline{n}+\underline{e}}(1-p_{\underline{n}-\underline{e}}) + p_{\underline{n}}p_{\underline{n}-\underline{e}}(1-p_{\underline{n}+\underline{e}})$$

and $$\tau_{\underline{n}}^{(2)} = p_{\underline{n}}p_{\underline{n}+\underline{e}}p_{\underline{n}-\underline{e}}$$

Using the definition (7.23),

$$p_{\underline{n}}\prod_{\underline{e}}\left\{1-p_{\underline{n}+\underline{e}} + p_{\underline{n}+\underline{e}}\cosh\tfrac{1}{2}\beta J(\underline{e})\right\} = \tau_{\underline{n}}^{(\underline{k})}\prod_{n=1}^{n'}\left(\cosh\left[\tfrac{1}{2}\beta J_n\right]\right)^{k_n}$$

where n' is the number of co-ordination shells and $\underline{k} = (k_1,\ldots,k_{n'})$

Hence,

$$\ln\left\{(1-p_{\underline{n}}) + \sum_{\underline{k}=\underline{0}}^{\underline{z}}\tau_{\underline{n}}^{(\underline{k})}\prod_{n=1}^{n'}\left(\cosh\left[\tfrac{1}{2}\beta J_n\right]\right)^{k_n}\right\}$$

$$= \sum_{\underline{k}=\underline{0}}^{\underline{z}}\tau_{\underline{n}}^{(\underline{k})}\sum_{n=1}^{n'}k_n\ln\left[\cosh\left(\tfrac{1}{2}\beta J_n\right)\right]$$

and therefore,

$$F = -\tfrac{1}{2}kT\sum_{\underline{k}=\underline{0}}^{\underline{z}}\langle\tau_{\underline{n}}^{(\underline{k})}\rangle\sum_{n=1}^{n'}k_n\ln\left[\cosh\left(\tfrac{1}{2}\beta J_n\right)\right] \qquad (7.24)$$

Consider $\tau_{\underline{n}}^{(\underline{k})} = p_{\underline{n}}\tau_{\underline{n},1}^{(k_1)}\tau_{\underline{n},2}^{(k_2)}\ldots\ldots\tau_{\underline{n},n'}^{(k_{n'})}$ with the obvious definition,

$$+^{(k_i)}_{\underline{n},i} = \sum_{\substack{\text{over choices of } k_i \text{ different } \underline{\ell}_x \text{ from the } z_i \\ \underline{\ell}_x \in \text{the } i^{th} \text{ coordination ring}}} p_{\underline{n}+\underline{\ell}_1} p_{\underline{n}+\underline{\ell}_2} \cdots p_{\underline{n}+\underline{\ell}_{k_i}} (1-p_{\underline{n}+\underline{\ell}_{k_i+1}}) \cdots (1-p_{\underline{n}+\underline{\ell}_{z_i}}) \qquad (7.25)$$

Now the average of $\sum_{k_i=0}^{z_i} +^{(k_i)}_{\underline{n},i} = (1-c)^{z_i} + C^{z_i}_1 c(1-c)^{z_i-1} + \cdots + c^{z_i} = 1$

and also that of $\sum_{k_i=0}^{z_i} +^{(k_i)}_{\underline{n},i} k_i = zc$

So

$$\langle F \rangle = -\tfrac{1}{2} c^2 kT \sum_{n=1}^{n'} z_n \ln\left[\cosh\left(\tfrac{1}{2}\beta J_n\right)\right] \qquad (7.26)$$

Using the following relationships,

(i) the entropy, $S = -\dfrac{\partial F}{\partial T}$.

(ii) the critical entropy is $\dfrac{S_\infty - S_c}{k}$.

(iii) the critical energy is $\dfrac{E_\infty - E_a}{kT_c} = \int_1^\infty C_m \, dt$

(C_m is the specific heat, and $t = T/T_c$).

(iv) $C_m = T \dfrac{\partial S}{\partial T}$.

we obtain the following expressions for entropy, critical entropy, and critical energy;

$$\frac{S}{k} = \tfrac{1}{2} c^2 \sum_{n=1}^{n'} z_n \left\{ \ln\left[\cosh \tfrac{1}{2}\beta J_n\right] - \tfrac{1}{2}\beta J_n \tanh\left(\tfrac{1}{2}\beta J_n\right)\right\}$$

$$\frac{S_\infty - S_c}{k} = \tfrac{1}{2} c^2 \sum_{n=1}^{n'} z_n \left\{ \tfrac{1}{2}\beta_c J_n \tanh\left(\tfrac{1}{2}\beta_c J_n\right) - \ln\left[\cosh \tfrac{1}{2}\beta_c J_n\right]\right\} \qquad (7.27)$$

$$\frac{E_\infty - E_c}{kT_c} = \tfrac{1}{2} c^2 \sum_{n=1}^{n'} \tfrac{1}{2}\beta_c z_n J_n \tanh\left(\tfrac{1}{2}\beta_c J_n\right)$$

Looking at the last two of these expressions and considering c=1 we obtain expressions which, when only nearest neighbour and next nearest neighbour forces are allowed, give

$$\frac{S_\infty - S_o}{k} = \tfrac{1}{2}\sum_{n=1}^{2} z_n \left\{ \tfrac{1}{2}\beta_c J_n \tanh\left(\tfrac{1}{2}\beta_c J_n\right) - \ln\left(\cosh \tfrac{1}{2}\beta_c J_n\right)\right\}$$

and $$\frac{E_\infty - E_c}{kT_c} = \tfrac{1}{2}\sum_{n'=1}^{2} \tfrac{1}{2} z_{n'}\beta_c J_{n'} \tanh\left(\tfrac{1}{2}\beta_c J_{n'}\right) \qquad (7.28)$$

and correspond to those given by Dalton.[105]

The expressions above are exact within the BPW approximation, but their numerical accuracy will be limited by errors in kT_c. So their usefulness in interpreting experiments is enhanced if the actual critical temperature is used.

7.5 Critical energy and entropy for nearest neighbour interactions

Consider the critical temperature to be given by (7.16). Then the critical energy can be expressed as

$$\frac{E_\infty - E_c}{kT_c} = \tfrac{1}{2} c^2 z \frac{1}{cz-1} \tanh^{-1}\left(\frac{1}{cz-1}\right) \quad , \; c > \frac{2}{z}$$

$$= \tfrac{1}{2} c^2 z \frac{1}{cz-1} \cdot \tfrac{1}{2} \ln\left(\frac{cz}{cz-2}\right) \qquad (7.29)$$

The critical energy is finite as long as the critical temperature is greater than 0 , but diverges if $kT_c = 0$, ie. if $c < \frac{2}{z}$.

Similarly, the critical entropy can be expressed in terms of logarithms.

$$\frac{S_\infty - S_c}{k} = \frac{1}{4} c^2 z \left\{ \frac{1}{cz-1} \ln\left(\frac{cz}{cz-2}\right) - \ln\left(\frac{(cz-1)^2}{cz(cz-2)}\right) \right\} \qquad (7.30)$$

This tends to $\frac{1}{2}\ln(4)$ as $cz \to 2$.

As an example we calculate the critical energy and entropy for various values of concentration using $z=6$ (i.e. simple cubic lattice).

As one can see from the table (7.1) and the expressions (7.27) the values of these critical quantities could be found, except for the factor , c , by replacing z in the pure substance expressions by cz . The divergence in the critical energy occurs later and the value of the critical entropy as $cz \to 2$ is very much reduced compared with the theory based on mere dilution. This occurs, of course, because of the factor c , which has taken some account of the various possible environments of the central spin of the cluster.

Table 7.1 Critical properties of a ferromagnet with simple cubic lattice (nearest neighbour interactions).

concentration	1.0	.9	.8	.7	.6	.5	.4	.34
$2J/kT_c$	.8110	.9252	1.078	1.293	1.622	2.197	3.584	7.864
$(E_\infty - E_c)/kT_c$	.1217	.1277	.1361	.1486	.1685	.2059	.3071	.6559
$(S_\infty - S_c)/k$	.1094	.1122	.1191	.1251	.1353	.1520	.1848	.2249

7.6 Ising Model, $S=\frac{1}{2}$ A Graphical Method for Susceptibility Calculation

The function $\psi_{\underline{n}}^{(k)}$ defined in the last section can be used in setting up a much more profitable procedure for approximating the susceptibility. Consider equation (7.13),

$$\left(1+\sum_{\underline{m}} p_{\underline{m}} \Phi_2(\underline{n}-\underline{m})\right)\sigma_{\underline{n}} = \tfrac{1}{2}\mu g\beta H e^{-i\underline{k}\cdot\underline{n}} p_{\underline{n}} + p_{\underline{n}} \sum_{\underline{m}} \Phi_1(\underline{n}-\underline{m})\sigma_{\underline{m}} \qquad (7.13)$$

To obtain a solution of this equation it can be iterated and the average over the distribution functions $p_{\underline{n}}$ must be carried out term by term and the series approximated by considering a finite number of terms. Straight iteration, however, leads to averages such as,

$\left\langle \dfrac{p_{\underline{n}}}{1+\sum_{\underline{m}} p_{\underline{m}} \Phi_2(\underline{n}-\underline{m})} \right\rangle$ which are apparently impossible to evaluate as they stand. If $\underline{m}$ is a site which does not belong to the cluster of sites centred on $\underline{n}$, $\Phi_2(\underline{n}-\underline{m}) \equiv 0$ by definition, and so the denominator depends only on the configuration of spins on this cluster of sites, which means that it can be represented as $\sum_{\underline{k}} \psi_{\underline{n}}^{(\underline{k})} Z^{(\underline{k})}$ and averages become much easier to evaluate. Using this (7.13) can now be rewritten as

$$\sigma_{\underline{n}} = \tfrac{1}{2}\mu g\beta H e^{-i\underline{k}\cdot\underline{n}} \sum_{\underline{k}'=0}^{z} \psi_{\underline{n}}^{(\underline{k}')} Z^{(\underline{k}')} + \sum_{\underline{k}'=0}^{z} \psi_{\underline{n}}^{(\underline{k}')} Z^{(\underline{k}')} \sum_{\underline{m}} \Phi_1(\underline{n}-\underline{m})\sigma_{\underline{m}} \qquad (7.31)$$

where $Z^{(\underline{k})} = \left(1+\sum_{m} k'_m \Phi_m^{(2)}\right)^{-1}$, $\Phi_m^{(2)} = \tanh^2 x_m \left(1-\tanh^2 x_m\right)^{-1}$

and the sum over m is over the co-ordination rings of the cluster.

Consider the following changes in notation,

$$\bar{\sigma}_{\underline{n}} = \sigma_{\underline{n}} e^{-i\underline{k}\cdot\underline{n}} \quad , \quad \Phi_1(\underline{\ell},\underline{k}) = \Phi_1(\underline{\ell}) e^{i\underline{\ell}\cdot\underline{k}}$$

Using these (7.31) becomes

$$\bar{\sigma}_{\underline{n}} = \tfrac{1}{2}\mu g\beta H \sum_{\underline{k}'=\underline{0}}^{\underline{z}} t_{\underline{n}}^{(\underline{k}')} Z^{(\underline{k}')} + \sum_{\underline{k}'=\underline{0}}^{\underline{z}} t_{\underline{n}}^{(\underline{k}')} Z^{(\underline{k}')} \sum_{\underline{\ell}} \Phi_1(\underline{\ell},\underline{k})\, \bar{\sigma}_{\underline{n}+\underline{\ell}} \qquad (7.32)$$

Simply iterating this equation gives,

$$\begin{aligned}\bar{\sigma}_{\underline{n}} = \tfrac{1}{2}\mu g\beta H \Big\{ & \sum_{\underline{k}'=\underline{0}}^{\underline{z}} t_{\underline{n}}^{(\underline{k}')} Z^{(\underline{k}')} \\ & + \sum_{\underline{k}',\underline{k}''=\underline{0}}^{\underline{z}} \sum_{\underline{\ell}} \Phi_1(\underline{\ell},\underline{k}) Z^{(\underline{k}')} Z^{(\underline{k}'')} t_{\underline{n}}^{(\underline{k}')} t_{\underline{n}+\underline{\ell}}^{(\underline{k}'')} \\ & + \rightsquigarrow \Big\}\end{aligned} \qquad (7.33)$$

In fact, the n^{th} term is,

$$\sum_{\underline{k}_1,\cdots,\underline{k}_{n+1}=\underline{0}} \sum_{\underline{\ell}_1,\cdots,\underline{\ell}_n} \Phi_1(\underline{\ell}_1,\underline{k})\Phi_1(\underline{\ell}_2,\underline{k})\cdots\Phi_1(\underline{\ell}_{n-1},\underline{k}) Z^{(\underline{k}_1)}\cdots Z^{(\underline{k}_{n+1})} \times t_{\underline{n}}^{(\underline{k}_1)} t_{\underline{n}+\underline{\ell}_1}^{(\underline{k}_2)} \cdots t_{\underline{n}+\underline{\ell}_1+\cdots+\underline{\ell}_n}^{(\underline{k}_{n+1})}$$

and hence the averages which must be studied are

$$\langle t_{\underline{n}}^{(\underline{k}_1)} t_{\underline{n}+\underline{\ell}_1}^{(\underline{k}_2)} \cdots t_{\underline{n}+\underline{\ell}_1+\cdots+\underline{\ell}_n}^{(\underline{k}_{n+1})} \rangle$$

where each $\underline{\ell}_i$ is the vector joining the central atom of the cluster to some site in the cluster.

When $\bar{\sigma}_{\underline{n}}$ is averaged it does not depend on its site label, and so

$$\chi(\underline{\lambda}) = \tfrac{1}{4}\mu g\, \delta_{\underline{\lambda},\underline{k}} N \langle \bar{\sigma}_{\underline{n}} \rangle$$

The averages (which have less than 5 r-factors) needed to calculate $\chi(\underline{\lambda})$ from this series are obtained in Appendix 3, but as is mentioned there some of the infinite series

must be summed to approximate the low concentration behaviour. The scheme of diagrams exhibited in the appendix corresponds to the scheme given below:

A(1)

A(2) B(2)

A(3) B(3) C(3)

A(4) B(4) C(4) D(4)

.....

Each contribution has been divided by the leading term. The columns in the above scheme represent terms whose leading order in concentration is identical: the A(i) are of order c, B(i) of order c^2 etc. Terms in the same row are of the same order in y, that is, those, such as A(n), in the $(n+1)^{th}$ row are $O(y^n)$. The sum of terms in row i will be denoted by S(i), while the sums of terms in the columns will be denoted by SA, SB etc.

In the high concentration limit, c=1, this scheme reduces to a simple geometric series. This suggests that the full scheme near c=1 can be assumed to be a rearranged geometric series, and thus the approximations in the region are

1st order approximation

$$1/\chi \sim 1 - A(1)$$

2nd order approximation

$$1/\chi \sim 1 - S(2) - A(1) + [A(1)]^2$$

3rd order approximation

$$1/\chi \sim 1 - S(2) - S(3) - A(1) + A(1)[A(1) + 2S(2) - [A(1)]^2]$$

These, of course, give the same limiting critical temperature at c=1.

In considering the low concentration behaviour, SA, SB etc., must be calculated. Consider only nearest neighbour interactions. The terms in SA all contain an average over just two clusters and so all factors $\psi_{\underline{n}+\underline{\ell}_1+\cdots+\underline{\ell}_{m'}}$ where m' is an odd integer (these will be termed the odd r-factors), must be contracted with each other, as must the factors where m' is even (these are the even r-factors). Using this fact the first few terms of SA are

$$A(1) \propto \sum_{\underline{\ell}_1} \sum_{\substack{k'=1 \\ k''=1}}^{z} \langle \psi_{\underline{n}}^{(k')} \psi_{\underline{n}+\underline{\ell}_1}^{(k'')} \rangle e^{i\underline{\ell}_1 \cdot \underline{k}} Z^{(k')} Z^{(k'')} \Phi ,$$

$$A(2) \propto \sum_{\underline{\ell}_1} \sum_{\substack{k'=1 \\ k''=1}}^{z} \langle \psi_{\underline{n}}^{(k')} \psi_{\underline{n}+\underline{\ell}_1}^{(k'')} \rangle (Z^{(k')})^2 Z^{(k'')} \Phi^2 ,$$

$$A(3) \propto \sum_{\underline{\ell}_1} \sum_{\substack{k'=1 \\ k''=1}}^{z} \langle \psi_{\underline{n}}^{(k')} \psi_{\underline{n}+\underline{\ell}_1}^{(k'')} \rangle e^{i\underline{\ell}_1 \cdot \underline{k}} (Z^{(k')})^2 (Z^{(k'')})^2 \Phi^3 ,$$

.....

and so the general term A(m) can be expressed as

$$\sum_{\underline{\ell}_1} \sum_{\substack{k'=1 \\ k''=1}}^{z} \langle \psi_{\underline{n}}^{(k')} \psi_{\underline{n}+\underline{\ell}_1}^{(k'')} \rangle A(m, k', k'', \underline{\ell}_1, \underline{k})$$

When m is odd the last r-factor of the average $\langle \psi_{\underline{n}}^{(k')} \cdots\cdots \psi_{\underline{n}+\underline{\ell}_1+\cdots+\underline{\ell}_m}^{(k_m)} \rangle$ is contracted with $\psi_{\underline{n}+\underline{\ell}_1}^{(k')}$ and so $A(m, k', k'', \underline{\ell}_1, \underline{k})$ contains a factor $e^{i\underline{\ell}_1 \cdot \underline{k}}$. When m is even, however, the last r-factor is contracted with $\psi_{\underline{n}}^{(k')}$ and so this factor does not occur. Consider only $A(m, \ldots)$ with m odd. Each successive term in this series arises from an average which has two r-factors more than the preceeding term to be contracted and this leads to an extra factor $Z^{(k')} Z^{(k'')} \Phi^2$ in $A(m, \ldots)$ when compared with $A(m-2, \ldots)$. Therefore,

$$\sum_{m\ \text{odd}} A(m) = \sum_{\underline{\ell}_1} \sum_{\substack{k'=1 \\ k''=1}}^{Z} \langle \psi_{\underline{n}}^{(k')} \psi_{\underline{n}+\underline{\ell}_1}^{(k'')} \rangle e^{i\underline{\ell}_1 \cdot \underline{k}} \frac{Z^{(k')} Z^{(k'')} \Phi}{1 - Z^{(k')} Z^{(k'')} \Phi^2}$$

Similarly,

$$\sum_{m\ \text{even}} A(m) = \sum_{\underline{\ell}_1} \sum_{\substack{k'=1 \\ k''=1}}^{Z} \langle \psi_{\underline{n}}^{(k')} \psi_{\underline{n}+\underline{\ell}_1}^{(k'')} \rangle \frac{(Z^{(k')})^2 Z^{(k'')} \Phi^2}{1 - Z^{(k')} Z^{(k'')} \Phi^2}$$

and thus

$$SA = \sum_{\underline{\ell}_1} \sum_{\substack{k'=1 \\ k''=1}}^{Z} \langle \psi_{\underline{n}}^{(k')} \psi_{\underline{n}+\underline{\ell}_1}^{(k'')} \rangle \left\{ \frac{e^{i\underline{\ell}_1 \cdot \underline{k}} + Z^{(k')} \Phi}{1 - Z^{(k')} Z^{(k'')} \Phi^2} \right\} Z^{(k')} Z^{(k'')} \Phi \qquad (7.34)$$

The denominators in this expression are well behaved. The only possibility of a divergence is when $k'=k''=1$, when the denominator is $1-y^2$, but this cancels with a similar term in the numerator.

The terms summed to give SB contain averages over three r-factors and so either the odd or even r-factors must be partitioned into two groups which are contracted separately. The first few terms of the infinite series SB are

$$B(2) \propto \sum_{\underline{\ell}_1, \underline{\ell}_2} \sum_{\substack{k'=1 \\ k''=1}}^{Z} \sum_{k'''=2} \langle \psi_{\underline{n}}^{(k')} \psi_{\underline{n}+\underline{\ell}_1}^{(k'')} \psi_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}^{(k''')} \rangle (1 - \delta_{\underline{\ell}_1+\underline{\ell}_2,0}) Z^{(k')} Z^{(k'')} Z^{(k''')} \Phi^2 e^{i(\underline{\ell}_1+\underline{\ell}_2)\cdot\underline{k}}$$

$$B(3) \propto \sum_{\underline{\ell}_1, \underline{\ell}_2} \sum_{\substack{k'=1 \\ k''=2}}^{Z} \sum_{k'''=1} \langle \psi_{\underline{n}}^{(k')} \psi_{\underline{n}+\underline{\ell}_1}^{(k'')} \psi_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}^{(k''')} \rangle (1 - \delta_{\underline{\ell}_1+\underline{\ell}_2,0}) Z^{(k')} (Z^{(k'')})^2 Z^{(k''')} \Phi^3 (e^{i\underline{\ell}_1\cdot\underline{k}} + e^{i\underline{\ell}_2\cdot\underline{k}})$$

$$B(4) \propto \sum_{\underline{\ell}_1, \underline{\ell}_2} \sum_{\substack{k'=1 \\ k''=2}}^{Z} \sum_{k'''=1} \langle \psi_{\underline{n}}^{(k')} \psi_{\underline{n}+\underline{\ell}_1}^{(k'')} \psi_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}^{(k''')} \rangle (1 - \delta_{\underline{\ell}_1+\underline{\ell}_2,0}) Z^{(k')} (Z^{(k'')})^2 Z^{(k''')} \Phi^4$$

$$\times \left\{ Z^{(k')} + Z^{(k'')} + (Z^{(k')} + Z^{(k''')}) e^{i(\underline{\ell}_1+\underline{\ell}_2)\cdot\underline{k}} \right\}$$

and so the general term can be written as

$$\mathcal{B}(m) = \sum_{\underline{\ell}_1,\underline{\ell}_2} \sum_{\substack{k'=1 \\ k''=1}}^{Z} \langle \tau_{\underline{n}}^{(k')} \tau_{\underline{n}+\underline{\ell}_1}^{(k'')} \tau_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}^{(k''')} \rangle (1-\delta_{\underline{\ell}_1+\underline{\ell}_2,0}) \mathcal{B}(m,k',\ldots)$$

Consider first the sum over $\mathcal{B}(m)$ when m is odd. To give a contribution to a particular $\mathcal{B}(m)$ the average $\langle \tau_{\underline{n}}^{(k')} \ldots\ldots \tau_{\underline{n}+\underline{\ell}_1+\ldots+\underline{\ell}_m}^{(k_m)} \rangle$ must be contracted so that either all the odd or all the even r-factors are contracted with each other. In the former case $\underline{n}+\underline{\ell}_1+\ldots+\underline{\ell}_m$ must be equivalent to $\underline{n}+\underline{\ell}_1$ and so the contribution to $\mathcal{B}(m,k',\ldots)$ will have a factor $e^{i\underline{\ell}_1\cdot\underline{k}}$. For the contraction of the even r-factors $\underline{n}+\underline{\ell}_1+\ldots+\underline{\ell}_{m-1}$ is equated to $\underline{n}$ so that these terms have a factor $e^{i\underline{\ell}_m\cdot\underline{k}}$ which will transform in each case to $e^{i\underline{\ell}_2\cdot\underline{k}}$. The remaining additional factor in each case depends on the partitioning of the uncontracted set of r-factors into two non-empty groups. As the average being approximated will be over equal numbers of odd and even r-factors, the extra factor in $\mathcal{B}(m,k',\ldots)$ will be the same in both cases. If the factors $\tau_{\underline{n}}$ and $\tau_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}$ are <u>not</u> contracted the extra factor is simply

$$\left(Z^{(k')}+Z^{(k'')}\right)^{m'/2} \Phi^{m'/2}$$

where m' is the number of r-factors in the average being considered. If $\tau_{\underline{n}}$ and $\tau_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}$ are contracted but $\tau_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2+\underline{\ell}_3+\underline{\ell}_4}$ is <u>not</u> contracted with them the extra factor is

$$Z^{(k')}\Phi^{m'/2}\left(Z^{(k')}+Z^{(k'')}\right)^{m'/2-1}$$

Continuing this procedure, the complete factor is found to be

$$\sum_{n'=0}^{n'=m'/2} \left(Z^{(k')}\right)^{n'} \left(Z^{(k')}+Z^{(k'')}\right)^{\frac{m'}{2}-n'} \Phi^{n'/2}$$

Collecting these facts together:

$$\sum_{m\,odd} B(m) = \sum_{\underline{\ell}_1,\underline{\ell}_2} \sum_{\substack{k'=1\\ k''=2\\ k'''=1}}^{z} \langle \psi_{\underline{n}}^{(k')} \psi_{\underline{n}+\underline{\ell}_1}^{(k'')} \psi_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}^{(k''')} \rangle (1-\delta_{\underline{\ell}_1+\underline{\ell}_2,0}) \frac{Z^{(k')}(Z^{(k'')})^2 Z^{(k''')} \left(e^{i\underline{\ell}_1\cdot\underline{k}} + e^{i\underline{\ell}_2\cdot\underline{k}}\right) \Phi^3}{\left[1-Z^{(k')}Z^{(k')}\Phi^2\right]\left[1-Z^{(k'')}\Phi^2\left(Z^{(k')}+Z^{(k''')}\right)\right]}$$

When m is restricted to even values there are again two cases: one when all the odd r-factors are contracted with each other, and the other when all the even r-factors are contracted. In the first case each term will contain a factor $e^{i(\underline{\ell}_1+\underline{\ell}_m)\cdot\underline{k}}$ unless $\psi_{\underline{n}}$ and $\psi_{\underline{n}+\underline{\ell}_1+\cdots+\underline{\ell}_m}$ are contracted, as then $\underline{\ell}_1+\underline{\ell}_m = 0$. Here, of course, $\psi_{\underline{n}+\underline{\ell}_1+\cdots+\underline{\ell}_m}$ is the final r-factor in the average being considered. In the second case, $\psi_{\underline{n}}$ and $\psi_{\underline{n}+\underline{\ell}_1+\cdots+\underline{\ell}_m}$ are contracted and so the corresponding factor is 1 .

Treating only the terms proportional to $e^{i(\underline{\ell}_1+\underline{\ell}_2)\cdot\underline{k}}$ the extra temperature dependent factor is only

$$\left(Z^{(k')}\right)^{\frac{m-2}{2}} \left(Z^{(k')}+Z^{(k''')}\right)^{\frac{m-2}{2}} \Phi^{m-2}$$

as the two fixed r-factors must be distinct; m is the number of r-factors in the average. So altogether this gives a contribution to $\sum_{m\,even} B(m)$ of

$$\sum_{\underline{\ell}_1,\underline{\ell}_2} \sum_{\substack{k'=1,2\\ k'''=1}}^{z} \langle \psi_{\underline{n}}^{(k')} \psi_{\underline{n}+\underline{\ell}_1}^{(k'')} \psi_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}^{(k''')} \rangle e^{i(\underline{\ell}_1+\underline{\ell}_2)\cdot\underline{k}} (1-\delta_{\underline{\ell}_1+\underline{\ell}_2,0}) \frac{Z^{(k')}Z^{(k'')}Z^{(k''')}\Phi^2}{1-Z^{(k'')}\Phi^2\left(Z^{(k')}+Z^{(k''')}\right)}$$

When the odd r-factors are contracted and so are $\psi_{\underline{n}}^{(k')}$ and $\psi_{\underline{n}+\underline{\ell}_1+\cdots+\underline{\ell}_m}^{(k')}$ the factor for the contribution to $B(m,k',\ldots)$ is found to be

$$Z^{(k'')}Z^{(k')}\left(Z^{(k'')}\right)^{m/2}\Phi^{m}\sum_{n'=1}^{m/2-1}\left(Z^{(k')}\right)^{n'}\left(Z^{(k')}+Z^{(k'')}\right)^{\frac{m}{2}-n'-1}$$

by a similar process to that used previously for odd m. Hence the contribution to $\sum_{m\,\text{even}} B(m)$ is

$$\sum_{\underline{\ell}_1,\underline{\ell}_2}\sum_{\substack{k'=1,k''=2\\ k''=1}}^{z}\langle\psi^{(k')}_{\underline{n}}\psi^{(k'')}_{\underline{n}+\underline{\ell}_1}\psi^{(k''')}_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}\rangle(1-\delta_{\underline{\ell}_1+\underline{\ell}_2,0})\frac{\left(Z^{(k')}Z^{(k'')}\right)^{2}Z^{(k''')}\Phi^{4}}{\left[1-Z^{(k')}Z^{(k'')}\Phi^{2}\right]\left[1-Z^{(k')}\Phi^{2}\left(Z^{(k')}+Z^{(k''')}\right)\right]}$$

Profiting from the previous calculations the remaining contribution can be written down immediately as

$$\sum_{\underline{\ell}_1,\underline{\ell}_2}\sum_{\substack{k'=1,k''=2\\ k'''=1}}^{z}\langle\psi^{(k')}_{\underline{n}}\psi^{(k'')}_{\underline{n}+\underline{\ell}_1}\psi^{(k''')}_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}\rangle(1-\delta_{\underline{\ell}_1+\underline{\ell}_2,0})\frac{Z^{(k')}\left(Z^{(k'')}\right)^{3}Z^{(k''')}\Phi^{4}}{\left[1-Z^{(k')}Z^{(k'')}\Phi^{2}\right]\left[1-Z^{(k'')}\Phi^{2}\left(Z^{(k')}+Z^{(k''')}\right)\right]}$$

Collecting all these expressions together gives

$$SB=\sum_{m}B(m)=\sum_{m}\sum_{\underline{\ell}_1,\underline{\ell}_2}\sum_{\substack{k'=1,k''=2\\ k''=1}}^{z}\langle\psi^{(k')}_{\underline{n}}\psi^{(k'')}_{\underline{n}+\underline{\ell}_1}\psi^{(k''')}_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}\rangle(1-\delta_{\underline{\ell}_1+\underline{\ell}_2,0})B(m,k',\ldots) \quad (7.35)$$

where

$$B(m,k',\ldots)=\frac{Z^{(k')}Z^{(k'')}Z^{(k''')}\Phi^{2}\left\{\left(e^{i\underline{\ell}_1\cdot\underline{k}}+Z^{(k'')}\Phi\right)\left(e^{i\underline{\ell}_2\cdot\underline{k}}+Z^{(k'')}\Phi\right)+Z^{(k')}Z^{(k'')}\Phi^{2}\left(1-e^{i(\underline{\ell}_1+\underline{\ell}_2)\cdot\underline{k}}\right)\right\}}{\left[1-Z^{(k')}Z^{(k'')}\Phi^{2}\right]\left[1-Z^{(k')}\Phi^{2}\left(Z^{(k')}+Z^{(k''')}\right)\right]}$$

As in the case of SA the denominators of each of these terms are well behaved because of the limitation on the values of k', k'', and k'''.

No attempt has been made to calculate SC. The difficulty in this calculation would be the need to partition both the odd r-factors and the even r-factors into two groups. For the contribution where this needs to be done it is not obvious how in general to collect terms with similar dependence on $\underline{k}$.

Formally, the inverse susceptibility can be expressed as being proportional to the infinite series

$$1 + SA + SB + SC + \rightsquigarrow$$

where the $(n+1)^{th}$ term is of $O(c^n)$. This can reasonably be approximated for small concentrations by the following series of approximations:

1st sum approximation $\quad 1/\bar{\chi} \propto 1 - SA$

2nd sum approximation $\quad 1/\bar{\chi} \propto 1 - SA - SB + (SA)^2$

Thus, the problem can be considered using the two types of approximations, the order-type and the sum-type, each very deficient outside its own region of concentration. For instance, when the first order-approximation to $1/\chi$ is expanded, the terms of higher order than $A(1)$ are, in fact, of $O(x^n y^n)$. The approximation is representing the contribution from $B(2)$, $C(3)$, $D(4)$ etc., but is unable to represent the other terms of $O(c)$, $A(2)$, $A(3)$ etc. The other order-approximations will gradually rectify this, but the process will undoubtedly be slow. On the other hand the sum approximations, although representing in some measure all the terms in the scheme being discussed, do not give the correct limit as $c \to 1$. For instance, the first sum approximation for a ferromagnet ($\underline{k}=0$) would give the following condition for the critical temperature (when $Z=6$):

$$1 - \frac{6y}{1+5y^2-y} = 0$$

where $y = \tanh(J/2kT)$, instead of

$$1 - \frac{6y}{1+5y^2} = 0$$

The respective solutions are $y \simeq .17$ and $y = .2$. Again the higher sum approximations should remedy this situation.

In some measure this problem can be alleviated by the following procedure: one of the order-approximations is altered so that account is taken of the terms proportional to c which were not represented: and to keep the critical temperature in the limit $c \to 1$ at its true value the extra term has subtracted from it its limit as $c \to 1$. If the first order approximation is considered this gives

$$1/\chi \propto 1 - A(1) - \left[SA - A(1) - \lim_{c\to 1}(SA - A(1))\right] \qquad (7.36)$$

This procedure can be applied to the other order-approximations, and also used to represent the terms of SB, but the expressions for $1/\chi$ become more complicated. The presence of the factor independent of concentration leads to a tendency to under-estimate the critical temperature, and this means a relatively poor representation for lower concentrations.

7.7 Discussion of the Result found by applying the Graphical Method.

Armed with these approximations, the properties of the solution can be investigated. The unwieldy nature of

the functions used to express the susceptibility made it necessary to use a computer in evaluating the susceptibility and finding its point of divergence.

The results for the calculations which have been completed are represented in the graphs at the end of the chapter. The first three graphs show the curves for the critical value of $\tanh(J/2kT)$ against concentration for the simple cubic lattice for various approximations. The next two are similar graphs but are for the body centred cubic lattice. The final sets of graphs show the susceptibility and the inverse correlation range against temperature for two concentrations, $\cdot 2$ and $\cdot 9$.

In all the approximations the critical temperature for the ferromagnet and the antiferromagnet with nearest neighbour interactions are the same, and so only one set of graphs is needed to deal with the transition points for both types of ordering.

Only the first two order approximations have been studied in detail but preliminary results for the next order approximation have been calculated, which show that the convergence near $c=1$ is better than thought possible when only the first two approximations were known. These two approximations differ in the values they predict for the critical temperature by over 4% even at $c=\cdot 9$. As one would expect at concentrations below $\sim \cdot 6$ the first order approximation gives no solutions, but the improvement shown by the second approximation means that solutions can be obtained at concentrations as low as $c=\cdot 42$. These values cannot be taken, of course, as in anyway estimates of the critical concentration, because the critical temperature does not approach zero as these values are approached; so the theory has become of limited validity for concentrations well above these values.

For the third order approximation values for the critical temperature are only known in the concentration range $[\cdot 5, \cdot 9]$, but although they are within 1% of the second order approximation results down to $c=\cdot 7$, for $c=\cdot 6$ the difference is 3%. The third order approximation curve appears to be in this region between the second order approximation curve and first total approximation curve, which suggests that when the calculation for this order is complete it will give a very good approximation to concentration as low as $c=\cdot 6$.

As was mentioned previously the first sum approximation differs, even at low concentrations, from the first total approximation. They have 'critical concentrations' $\cdot 182$ and $\cdot 184$ respectively, and at $c=\cdot 185$ the results differ by over 1%. Neither approximation gives a solution when $y=1.0$. Because only S_A, S_B etc. have non-zero limits when $y \to 1.0$ both first total and first sum approximation give the same condition for the critical temperature in this limit:-

$$1 - 12c(1-c)^4 = 0 \qquad (7.37)$$

for a simple cubic lattice. The left hand side has it minimum value when $c=\cdot 2$, and this is $0 \cdot 0166$, so there is no solution for physical values of concentration.

Near $c=1$ the first sum approximation is considerably higher than the order approximation, while the first total approximation, of course, follows very closely the values of the second order approximation to concentrations as low as $c=\cdot 6$.

Calculations using the second sum approximation are incomplete but one or two facts about its behaviour can be elucidated. In the limit $y \to 1.0$ the condition corresponding to (7.37) is

$$1-12c(1-c)^4\left[1+\frac{3}{16}(13c-1)c(1-c)^3\right]=0 \qquad (7.38)$$

The new factor is positive for all physical values of c and, in fact, there is a solution with $c\cong .202$. Near $c=1$ this approximation differs from the first sum approximation in that it gives no critical temperature for $c=1$. The condition for a critical temperature for $c=1$ is in this approximation,

$$1-\frac{6y}{1-y+5y^2}\left\{1+\frac{10y}{3}\left(\frac{1+y+5y^2}{(1+5y^2)^2-2y^2}\right)-\frac{6y}{1-y+5y^2}\right\}=0 \qquad (7.39)$$

It is easily shown that the factor in the brackets is less than 1, and so if there is a solution it is for $y>-.16$ the solution for the first sum approximation. Defining $z=y/(1+5y^2)$ the condition can be rewritten as

$$1-8z+21z^2+16z^3-66z^4=0$$

and as $z<\frac{16}{66}$ and $1-8z+21z^2>0$ the left hand side is always positive and there is no critical solution. The results from the order approximations can be represented well by setting

$$y=.2+A(1-c)+B(1-c)^2+D(1-c)^3+E(1-c)^4\rightsquigarrow \qquad (7.40)$$

and, of course, the range of validity of the representation can be increased by adding more terms. The coefficients for a number of representations are listed in table 7.2 together with the concentration c^* above which they are valid to within a 1% error. As can be seen a linear law is reasonable for concentrations above $.9$, but further terms are needed outside this region.

Apart from giving a convenient means for storing the results for these approximations, these representations enable estimates of the critical concentration to be obtained by extrapolation to $y=1.0$. These estimates may not be very realistic, but they give some information about the convergence to the actual value of the critical concentration. As can be seen from the table some representations cannot give a physical solution, but three can, and the results are given in table 7.4 (they are labelled (1)).

The results for $z=8$ can be considered in a similar manner and the coefficients necessary are quoted in table 7.3. For this higher value of z the most interesting point is that the percentage differences between the first and second order approximations, at various concentrations, are smaller than those for the $z=6$ case: at $c=.95$ the percentages are 1% and $1\frac{1}{2}$% respectively, while at $c=.9$ they are $2\frac{1}{4}$% and $3\frac{1}{3}$%. This suggests that for larger values of z the first order approximation may be a good one, at least for high concentrations, and so longer range interactions may not be too difficult to consider. For $z=8$, the first total approximation is still not efficient at low concentrations and so if higher approximations are difficult a more subtle method of combining the low and high concentration behaviour in one curve is needed.

Another possible way to represent the results of the order approximations is

$$y = A c^{-\eta} \tag{7.41}$$

Calculation of the values of η needed to reproduce the values calculated shows that even the best fit could not represent the first order approximation with error less than 1% in the region $c=.7$ to $c=1.0$. Thus, it is inferior

to the series (7.40) in this respect, but it has been used to extrapolate to the critical concentration and the values obtained are given in table 7.4 (they are labelled (2)). The value of η used was obtained by considering the behaviour at $c \simeq .99$.

Table 7.5 gives the critical concentrations calculated from the first and second sum approximations for a selection of lattices, together with, for comparison, the results quoted by Dalton. The values obtained here are not in agreement with those of Dalton, and although the second sum approximation shows an improvement over the first approximation, it is obvious that at least the next approximation is needed before any definite conclusions can be drawn.

When these results are considered in conjunction with the values found by extrapolation it seems certain that the values for the simple cubic and body centred cubic lattices will be less than the values of Dalton et al. One must remember that some of the extrapolation results are suspect, because the values of the coefficients D, E are abnormally large, and that, for $z=6$ at least, the next order approximation is giving high values of the critical value of γ near $c=1.0$.

Further, the values for the critical concentration will be lower than those given by the theory based on simple dilution (approximation A see p.102). So this latter theory underestimates the critical temperature for the whole concentration range.

For all the approximations considered the critical temperature is lower than that predicted by extrapolating the high temperature limit to the theory. This means that the inverse susceptibility vs. temperature curve tends to curve in the opposite manner to that predicted by the MFT (see Chapter 6 p.82). The graphs of $1/\chi$ vs, kT show

changes in curvature not found in any theory of a pure substance, but the changes are less pronounced for higher approximations. The preliminary results of Wolf (unpublished) using the exact high temperature expansion method (using the first 6 terms) do not show these curvature features; so it is concluded that they are, in fact, only an effect of the approximation used, at least at high concentrations.

The $\underline{k}$ dependence of the susceptibility can easily be expressed as follows, for the first 2 order approximations

$$\chi^{(1)}(\underline{k}) = \frac{\frac{1}{2}\mu^2 g^2 \beta \alpha_1}{1 - \gamma(\underline{k})\frac{\alpha_2}{\alpha_1}}$$

and

$$\chi^{(2)}(\underline{k}) = \frac{\frac{1}{2}\mu^2 g^2 \beta \alpha_1}{1-\gamma(\underline{k})\frac{\alpha_2}{\alpha_1} - \gamma^2(\underline{k})\left[\gamma_1 - \left(\frac{\alpha_2}{\alpha_1}\right)^2\right] - \gamma(2\underline{k})C - D}$$

where

$$\alpha_1 = \sum_{k=0}^{z} \langle \uparrow_{\underline{n}}^{(k)} \rangle Z^{(k)} \; ; \quad \alpha_2 = \sum_{k=1,k'=1}^{z} \langle \uparrow_{\underline{n}}^{(k)} \uparrow_{\underline{n}+\underline{\rho}_1}^{(k')} \rangle Z^{(k)} Z^{(k')} \Phi \; ;$$

$$\gamma_1 = \sum_{\substack{k=1,k'=2 \\ k''=1}}^{z} \langle \uparrow_{\underline{n}}^{(k)} \uparrow_{\underline{n}+\underline{\rho}_1}^{(k')} \uparrow_{\underline{n}+\underline{\rho}_1+\underline{\rho}_2}^{(k'')} \rangle (1-\delta_{\underline{\rho}_1+\underline{\rho}_2,0} - \delta_{\underline{\rho}_1,\underline{\rho}_2}) Z^{(k)} Z^{(k')} Z^{(k'')} \Phi^2 \; ;$$

$$\gamma_2 = \sum_{\substack{k=1,k'=2 \\ k''=1}}^{z} \langle \uparrow_{\underline{n}}^{(k)} \uparrow_{\underline{n}+\underline{\rho}_1}^{(k')} \uparrow_{\underline{n}+2\underline{\rho}_1}^{(k'')} \rangle Z^{(k')} Z^{(k'')} Z^{(k)} \Phi^2 \; ;$$

$$\gamma_3 = \sum_{\substack{k=1, \\ k'=1}}^{z} \langle \uparrow_{\underline{n}}^{(k)} \uparrow_{\underline{n}+\underline{\rho}_1}^{(k')} \rangle (Z^{(k)})^2 Z^{(k')} \Phi^2 \; ;$$

$$C = \gamma_2 - \gamma_1 \; ; \quad D = z(\gamma_3 - \gamma_1) \; ; \quad \gamma(\underline{k}) = \sum_{\underline{\rho}_1} e^{i\underline{\rho}_1 \cdot \underline{k}}$$

In general, the susceptibility will depend on $\gamma(n\underline{k})$, and $\gamma^n(\underline{k})$. The expression $\chi^{(1)}(\underline{k})$ is very similar to that for simple MFT; only the fact that α_1, α_2/α_1 have more complicated concentration and temperature behaviour makes the theories different. The dependence of $\chi^{(2)}(\underline{k})$ is obviously more complicated.

In the limit of low $\underline{k}$ these formulae for $\chi(\underline{k})$ can obviously be expressed as

$$\chi(\underline{k}) \sim \frac{\frac{1}{2}\mu^2 g^2 \beta c A(T,c)}{K_1^2 + q^2}$$

(see Chapter 4)
and as in the critical region the scattering cross-section is related directly to $\chi(\underline{k})$ (see Chapter 4), K_1^2 is the effective inverse correlation range (see Fisher and Burford for the definition of true inverse correlation range). As distinct from the simple MFT the function A depends on temperature and concentration.

For the first two order approximations

$$K_1^2(1) = \frac{\alpha_1}{\alpha_2} - z$$

and
$$K_1^2(2) = \left\{ 1 - \frac{z\alpha_2}{\alpha_1} - z^2\left[\gamma_1 - \left(\frac{\alpha_2}{\alpha_1}\right)^2\right] - z(\gamma_2+\gamma_3-2\gamma_1)\right\} \Big/ \left[\frac{\alpha_2}{\alpha_1} + 4c\right]$$

These are plotted against temperature in graph 7.8 for $c=.9$ and they both differ significantly from the curve from approximation A. The curves are almost linear. For $c=.2$ the first sum approximation and the first total approximation have been plotted and here the curvature is more pronounced.

In conclusion, the following are representations of the critical temperature equivalent to the three simplest

ones given in table 7.2 :-

first order approximation

$$kT_c/kT_c(c=1) = 1 - 1.25\ (1-c) \quad ;$$

second order approximation

$$kT_c/kT_c(c=1) = 1 - 1.04\ (1-c) \quad ;$$

first total approximation

$$kT_c/kT_c(c=1) = 1 - 1.11\ (1-c) \quad ;$$

These are all valid to within 1% in the region, $[.9\ ,\ 1.]$.

Table 7.2 Coefficients used with (7.40) to represent the order approximations (z=6)

	1st order approx. (1)	1st order approx. (2)	2nd order approx. (1)	2nd order approx. (2)	2nd order approx. (3)	1st total approx. (1)	1st total approx. (2)	1st total approx. (3)
A	2.8	.256	.22	.207	.208	.225	.207	.207
B	-	.344	-	.228	.254	-	.296	.301
D	-	1.11	-	.310	-.154	-	.139	.025
E	-	-	-	-	1.59	-	-	.642
C*	.9	.75	.9	.8	.7	.9	.6	.5

C* denotes the lowest concentration where error is less than 1%

Table 7.3 Coefficients used with (7.40) to represent the order approximations (z=8)

	1st order approx. (1)	1st order approx. (2)	2nd order approx. (1)	2nd order approx. (2)	1st total approx. (1)	1st total approx. (2)	1st total approx. (3)
A	.185	.177	.163	.156	.163	.143	.133
B	-	.339	-	.501	-	.146	.342
D	-	−2.08	-	−5.62	-	.289	−.257
E	-	7.05	-	14.5	-	-	1.17
C*	.9	.7	.9	.7	.9	.7	.6

C* denotes the lowest concentration where error is less than 1%

Table 7.4 Critical concentrations found by extrapolating the order approximations.

Lattice	z	1st order approx. (1)	1st order approx. (2)	2nd order approx. (1)	2nd order approx. (2)	1st total approx.	Approx. A
Simple cubic	6	.270	.290	.229	.215	.128	·333
Body centred cubic	8	.301	.229	.440	.173	.140	·25

Table 7.5 Critical Concentrations calculated from the sum approximations compared with values given by Dalton et.al.

Lattice	z	Dalton et.al.	1st sum approx.	2nd sum approx.
Linear chain	2	-	0.25	none
Square	4	0.590	0.19	none
Triangular	6	0.500	0.101	0.502
Simple cubic	6	0.307	none	0.202
Body centred cubic	8	0.243	none	0.092
Face centred cubic	12	0.195	0.061	-
Simple cubic (1,2)	18	0.136	0.042	-

(1,2) denotes that next nearest neighbour interactions are present as well as the nearest neighbour ones.

Curves for the critical value of γ against concentration for nearest neighbour interactions and a simple cubic lattice.

GRAPH 7.1 For concentrations between c=.4 and c=1.

(1) denotes the first order approximation.
(2) denotes the second order approximation.
(3) denotes the first approximation designed for the whole concentration range (the first total approximation).
(4) denotes the approximation found by assuming that is independent of concentration fluctuations (approximation A).
(5) denotes the first sum approximation.

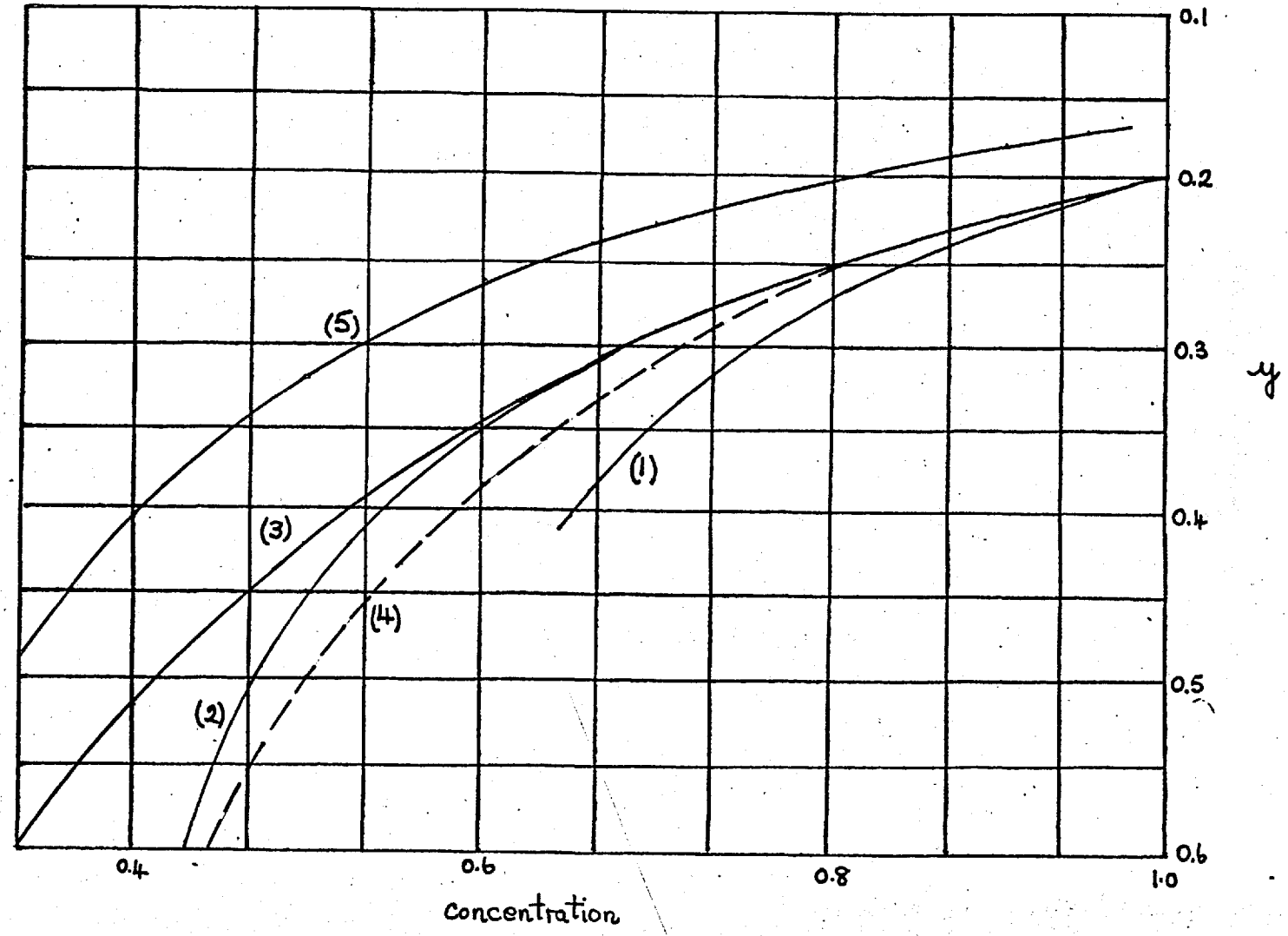
GRAPH 7.2 For small concentrations

(1) denotes the first total approximation.
(2) denotes the first sum approximation.
(3) denotes approximation A.

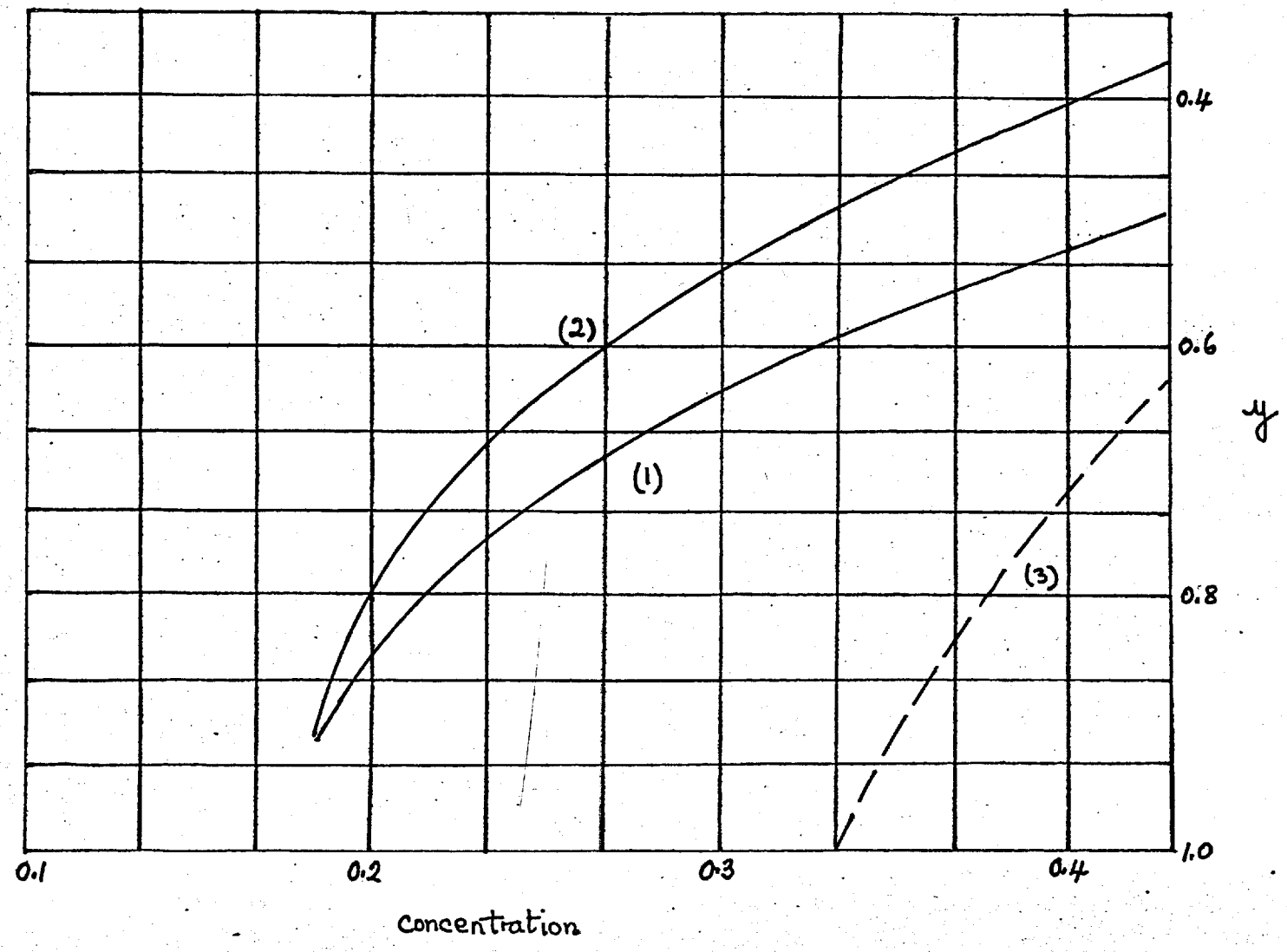
GRAPH 7.3 For all concentrations

(1), (2), (3) are the same as those for graph 7.2.

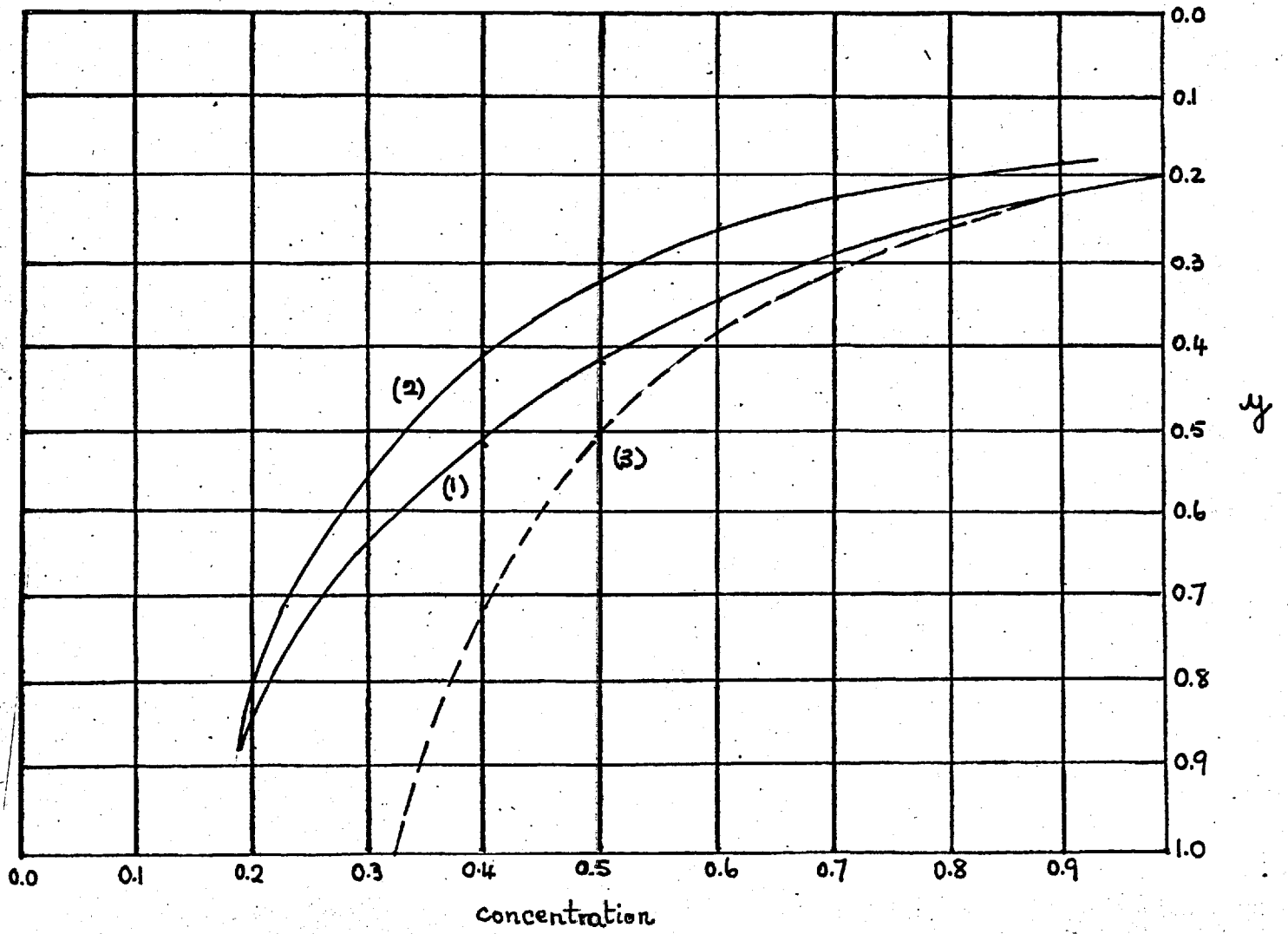
GRAPH 7.1



GRAPH 7.2



GRAPH 7.3


0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
y
(1)
(2)
(3)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
concentration

Curves for the critical value of y against concentration for nearest neighbour interactions and a body centred cubic lattice.

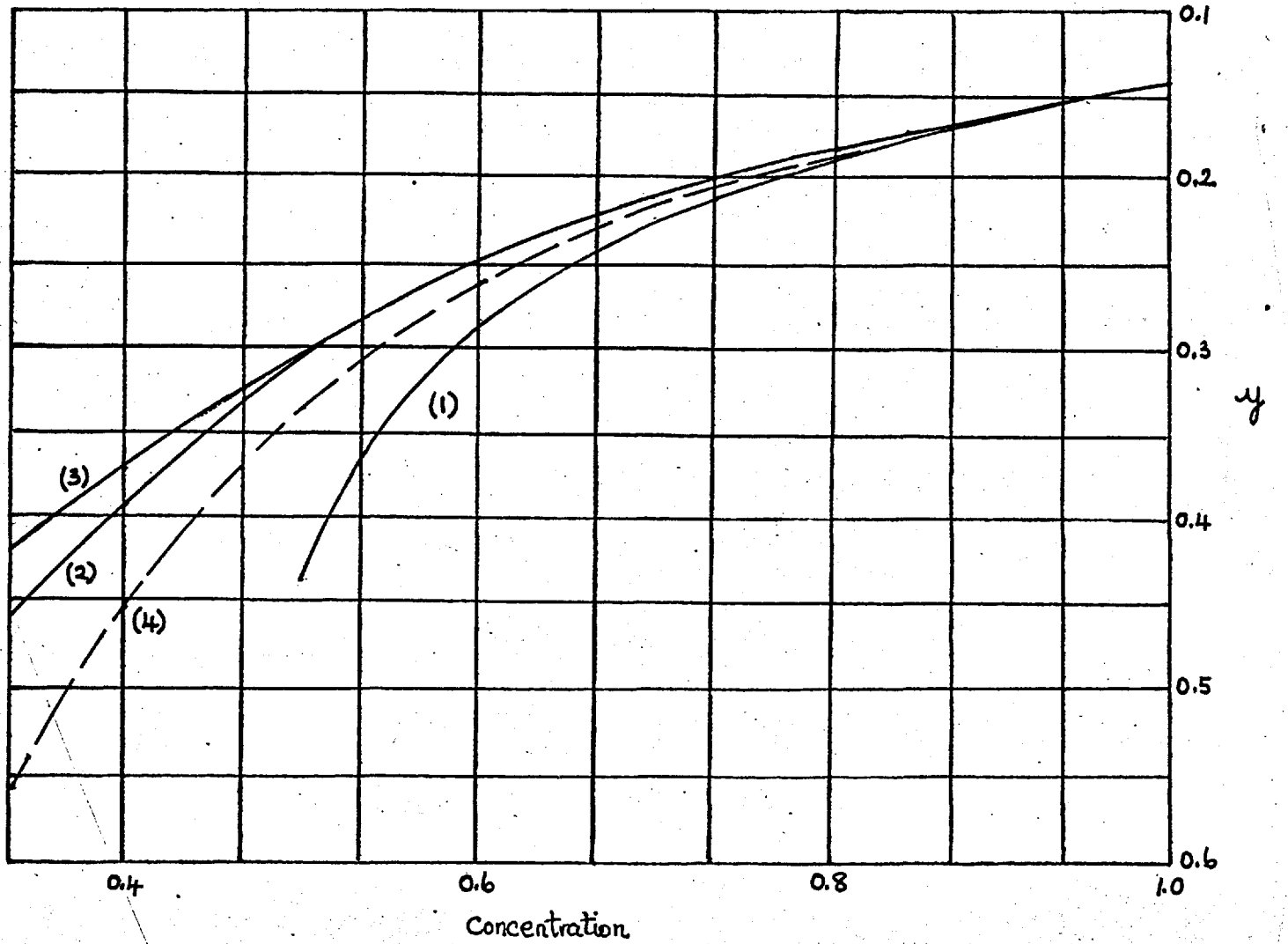
GRAPH 7.4 For concentrations between c= ·4 and c=1.

(1) denotes the first order approximation.
(2) denotes the second order approximation.
(3) denotes the first total approximation.
(4) denotes approximation A.

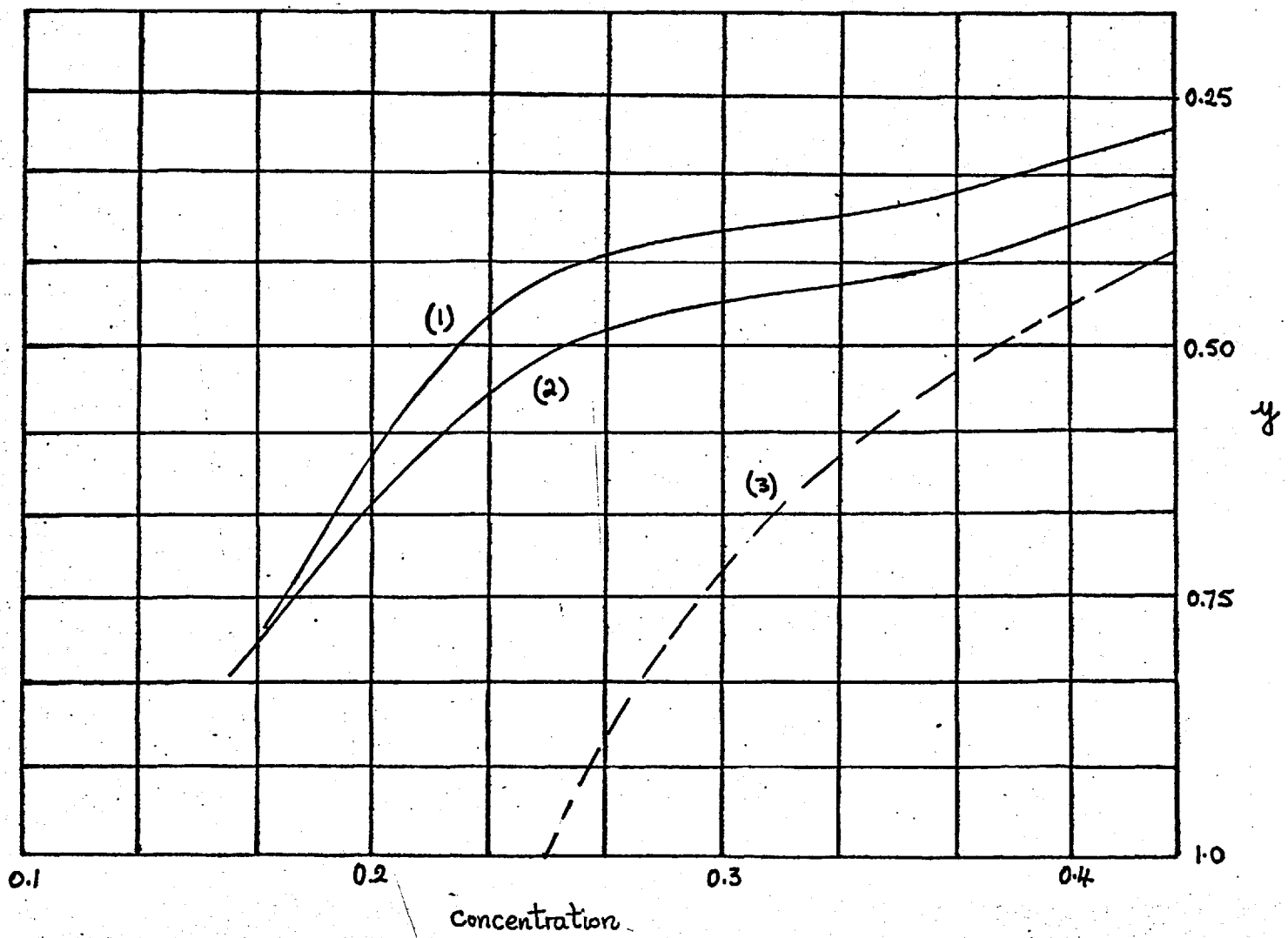
GRAPH 7.5 For low concentrations

(1) denotes the first sum approximation.
(2) denotes the first order approximation.
(3) denotes approximation A.

GRAPH 7.4



GRAPH 7.5



Curves for the inverse susceptibility against temperature for a ferromagnet (nearest neighbour interactions and a simple cubic lattice).

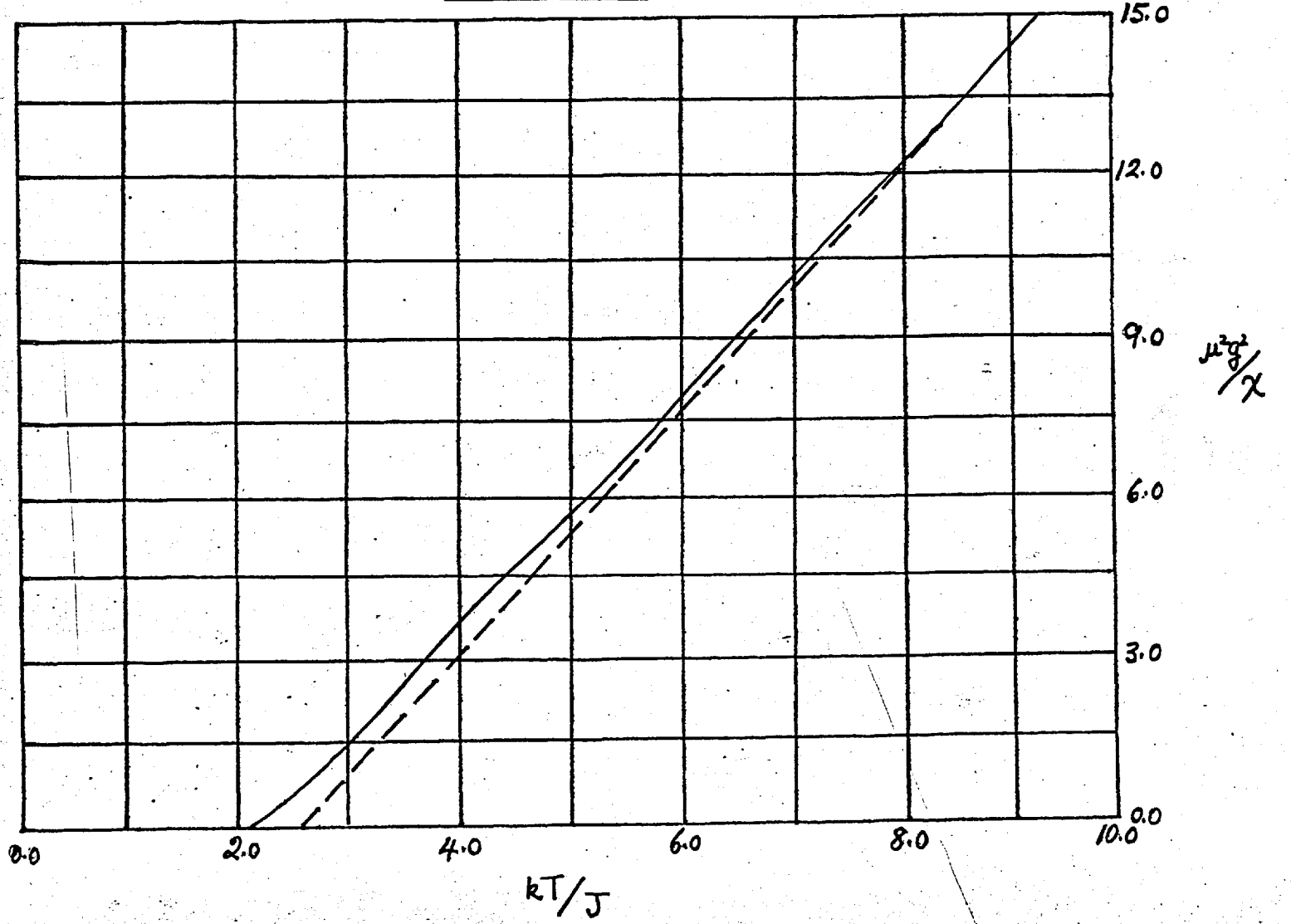
GRAPH 7.6 For concentration $c = .9$

(1) denotes the first order approximation.
(2) denotes the high temperature limit

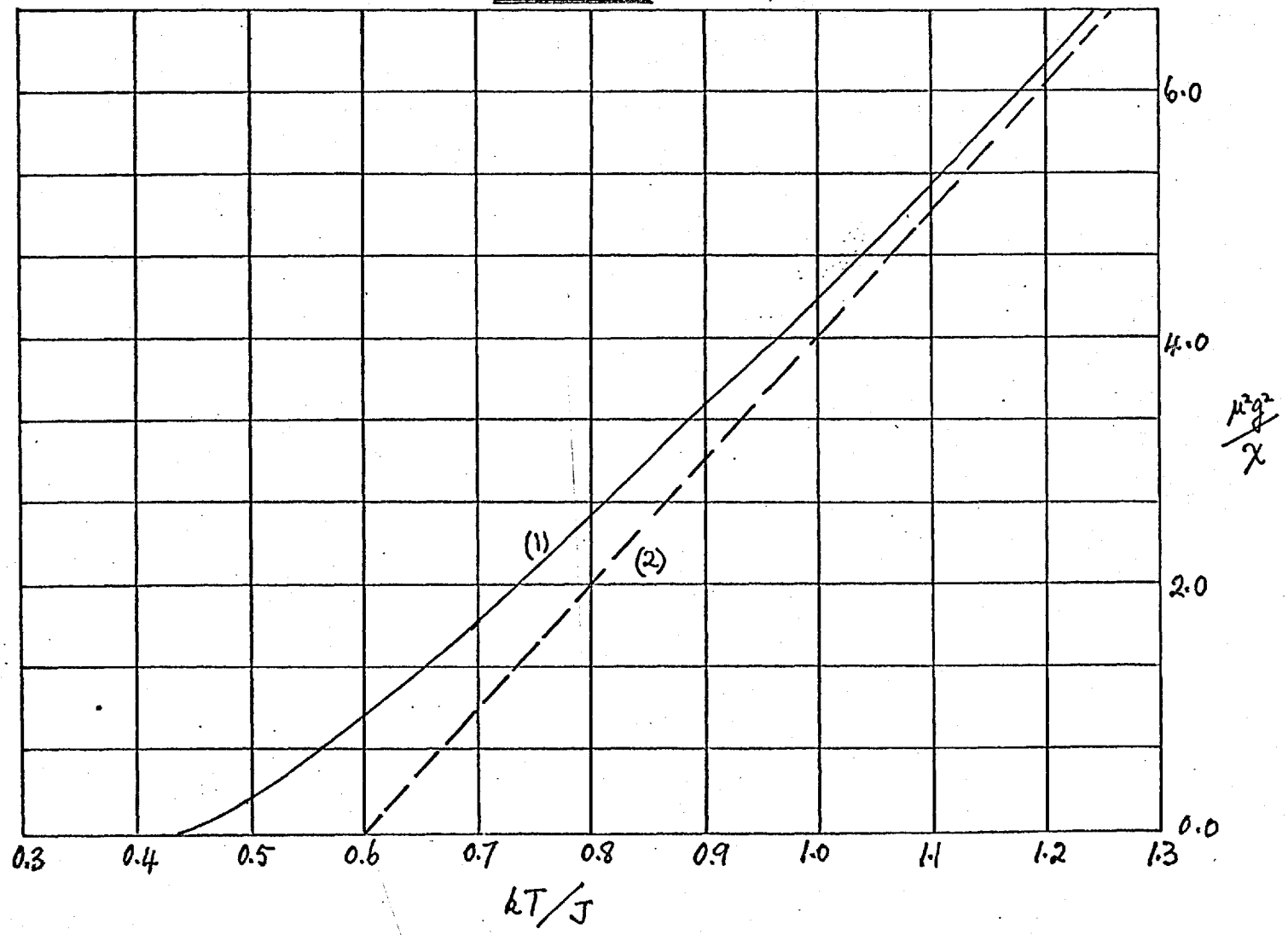
GRAPH 7.7 For concentration $c = .2$

(1) denotes the first sum approximation.
(2) denotes the high temperature limit.

GRAPH 7.6



GRAPH 7.7



Curves for the inverse correlation range against temperature for a ferromagnet (nearest neighbour interactions and a simple cubic lattice).

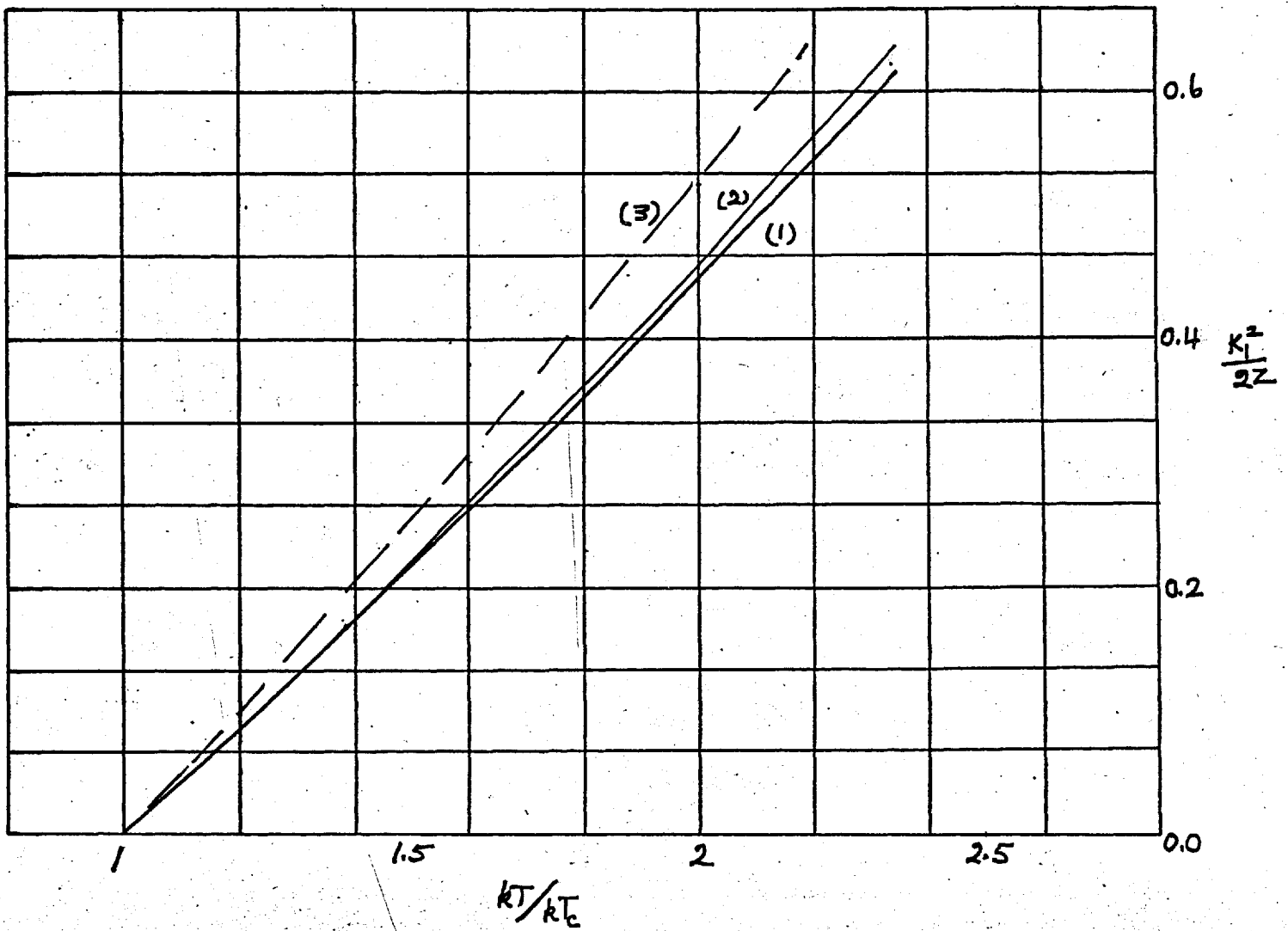
GRAPH 7.8 For concentration $c = .9$

(1) denotes the first order approximation.
(2) denotes the second order approximation.
(3) denotes approximation A.

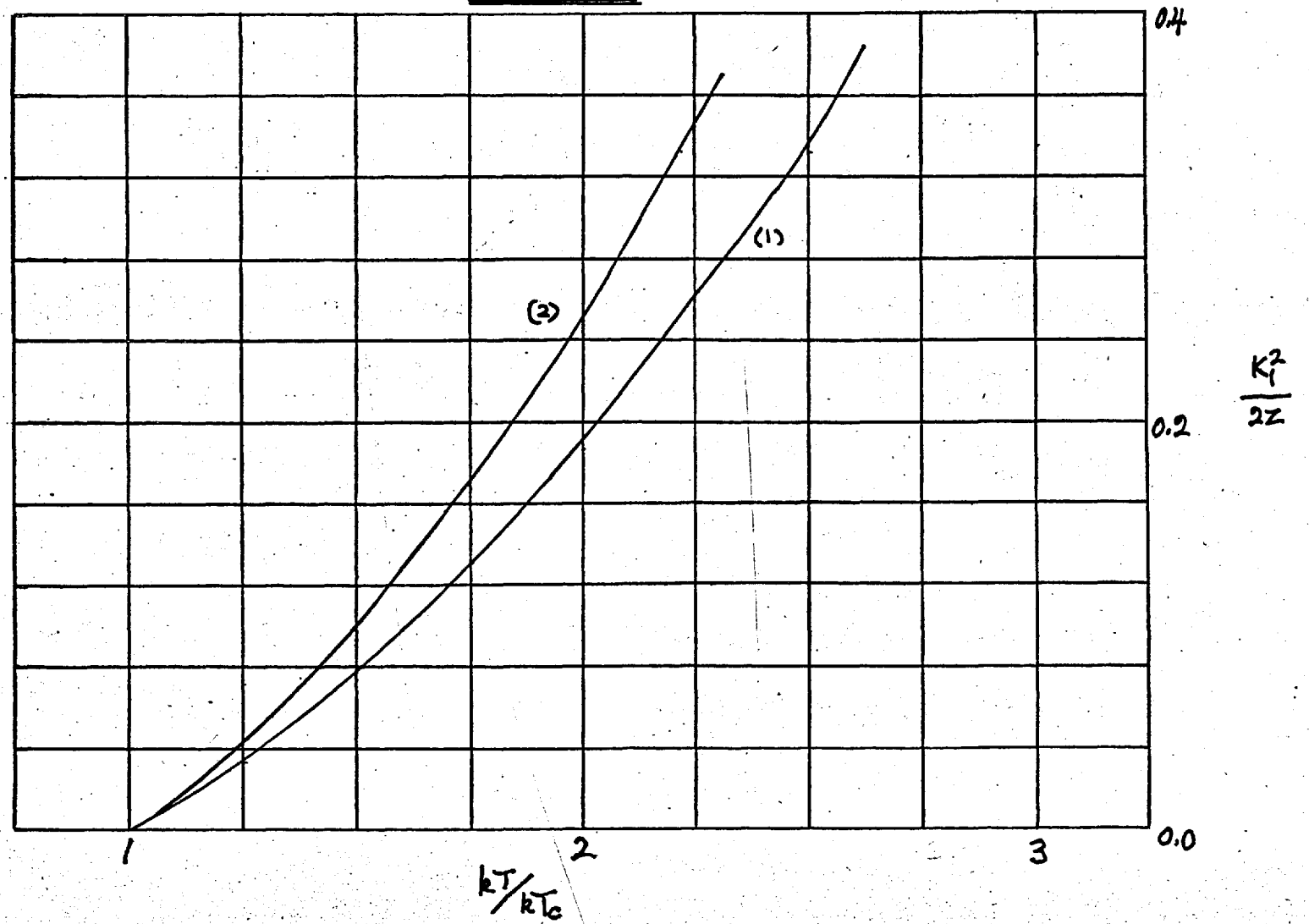
GRAPH 7.9 For concentration $c = .2$

(1) denotes the first sum approximation.
(2) denotes the first total approximation.

GRAPH 7.8



GRAPH 7.9

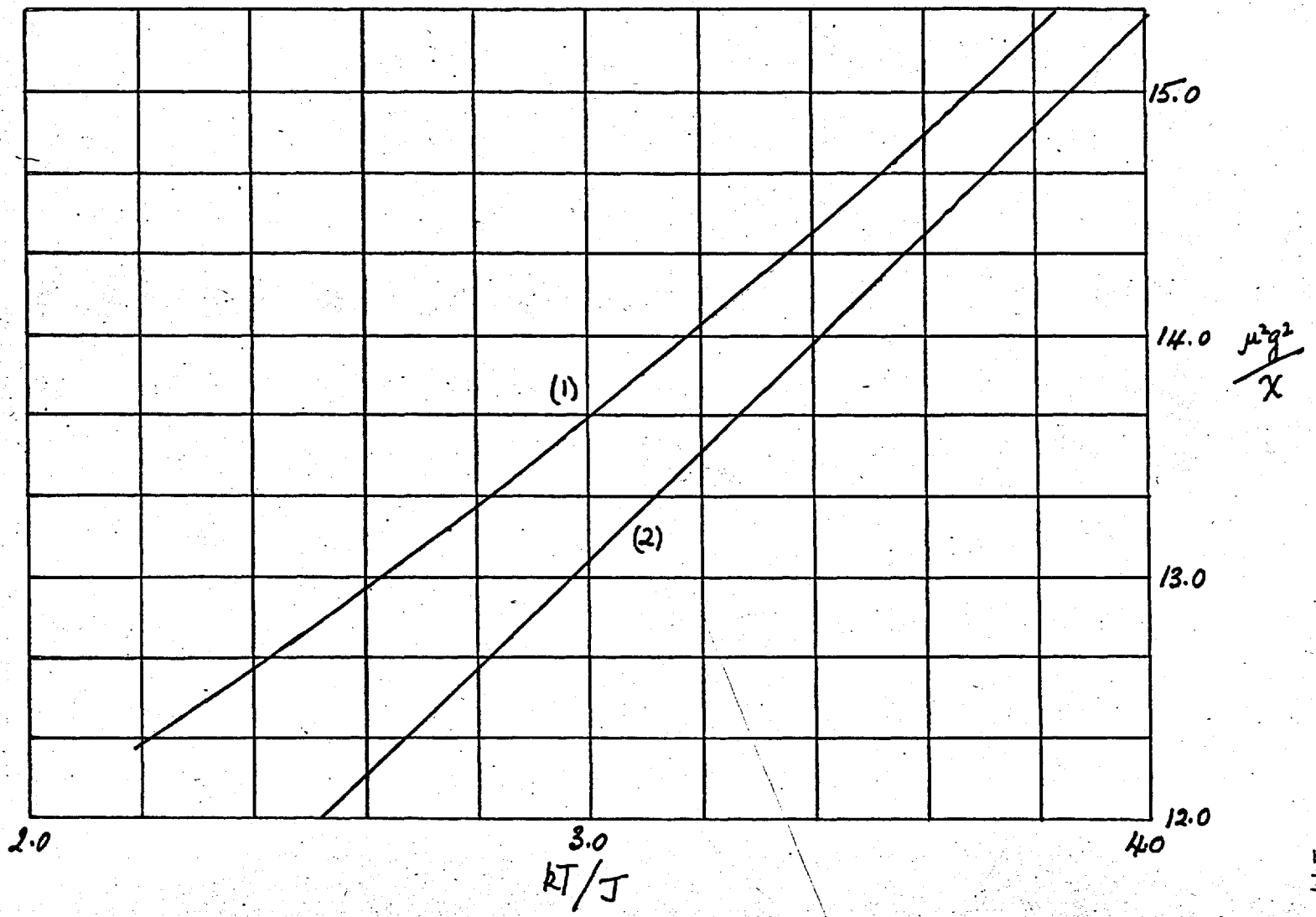


GRAPH 7.10

Curve for the inverse susceptibility vs. temperature compared with the extrapolation of its high temperature limit.

(1) denotes the inverse susceptibility at $c = .9$.
(2) denotes the high temperature limit.

GRAPH 7.10



Chapter 8

The Bethe-Peierls-Weiss Method for Magnetic Alloys Heisenberg Model

8.1 Nearest neighbour interactions theory

As has been mentioned it is difficult to consider long range interactions within the Heisenberg model, and so in this section the discussion is restricted to nearest neighbour interactions. The cluster of sites considered is the central site $\underline{n}$ together with its nearest neighbours. In the alloy case we have the added difficulty that the effective field should vary with the environment of the neighbour that is being considered, but because of the same difficulties that restrict us to using only nearest neighbour interactions, a single effective field has to be used which depends only on the central site of the cluster. Under these restrictions the cluster Hamiltonian is

$$\mathcal{H}_{\alpha,\underline{n}} = -2J\sum_{\underline{\ell}} p_{\underline{n}} p_{\underline{n}+\underline{\ell}}\, \underline{S}_{\underline{n}}\cdot\underline{S}_{\underline{n}+\underline{\ell}} - \mu g h_{1,\underline{n}} \sum_{\underline{\ell}} p_{\underline{n}+\underline{\ell}} S^{z}_{\underline{n}+\underline{\ell}} - \mu g h_{0,\underline{n}} p_{\underline{n}} S^{z}_{\underline{n}} \qquad (8.1)$$

where $h_{0,\underline{n}} = H e^{-i\underline{k}.\underline{n}}$

Of course, we still have the difficulty of dealing with the distribution functions in some simple way; but it is obvious that for some arrangement of spins on the cluster of sites the Partition function is that for a pure substance with a lattice having the given number of nearest neighbour spins. So using the functions defined in the last chapter,

$$Z_{cl,\underline{n}} = \sum_{k=0}^{z} \left\{ \uparrow_{\underline{n}}^{(k)} Z_{\underline{n}}^{(k+)} + q_{\underline{n}}^{(k)} Z_{\underline{n}}^{(k-)} \right\} \qquad (8.2)$$

where $$\uparrow_{\underline{n}}^{(k)} = p_{\underline{n}} \sum_{\substack{\text{all different} \\ \text{sets of different} \\ \underline{\ell}_1 \ldots \underline{\ell}_k}} \left\{ \prod_{\ell_m=\ell_1}^{\underline{\ell}_k} p_{\underline{n}+\underline{\ell}_m} \prod_{\underline{\ell}_x=\underline{\ell}_{k+1}}^{\underline{\ell}_z} (1-p_{\underline{n}+\underline{\ell}_x}) \right\},$$

$q_{\underline{n}}^{(k)}$ is $\uparrow_{\underline{n}}^{(k)}$ with $p_{\underline{n}}$ replaced by $(1-p_{\underline{n}})$

$Z_{\underline{n}}^{(k+)}$ is the Partition function for a cluster with a spin on the central atom and k neighbours, and $Z_{\underline{n}}^{(k-)}$ is the Partition function for a cluster without a spin on the central atom, and k neighbours.

When the atom on site $\underline{n}$ is magnetic and the number of nearest neighbour spins $k>0$, the eigenvalues of $\mathcal{H}_{cl,\underline{n}}(S=\frac{1}{2})$ are specified by,

$$S_1 = \begin{cases} 0, 1, \ldots \tfrac{1}{2}k & \text{, if } k \text{ is even.} \\ \tfrac{1}{2}, \tfrac{3}{2}, \ldots \tfrac{1}{2}k & \text{, if } k \text{ is odd.} \end{cases}$$

$$S' = S_1 \pm \tfrac{1}{2} \qquad (\text{when } S_1 = 0 \text{ , } S' = \tfrac{1}{2} \text{ only})$$

$$M' = S', S'-1, \ldots\ldots, -S'$$

It follows that the eigenvalues of $\mathcal{H}_{cl,\underline{n}}$ are

$$E_{cl,\underline{n}}(S_1, S', M') = \tfrac{1}{2}J \left\{ 1 - 2M' \hat{h}_{1,\underline{n}} \mp \left[(2S_1+1)^2 - 4M' (\hat{h}_{1,\underline{n}} - \hat{h}_{0,\underline{n}}) + (\hat{h}_{1,\underline{n}} - \hat{h}_{0,\underline{n}})^2 \right]^{1/2} \right\}$$

with $\hat{h}_{0,\underline{n}} = \mu g h_{0,\underline{n}}/J$, and similarly for $\hat{h}_{1,\underline{n}}$, and the $\mp$ sign corresponding to $S' = S_1 \pm \tfrac{1}{2}$.

Hence, for $k>0$,

$$Z^{(k+)}_{\alpha,\underline{n}} = \sum_{S_1,S',M'} \exp\left\{-\beta E_{\alpha,\underline{n}}(S_1,S',M')\right.$$

In the paramagnetic region it is assumed that $\hat{h}_{0,\underline{n}}$ and $\hat{h}_{1,\underline{n}}$ are small quantities, and so

$$Z^{(k+)}_{\alpha,\underline{n}}(\hat{h}_{0,\underline{n}},\hat{h}_{1,\underline{n}},j) \cong Z^{(k+)}_{00}(j) + Z^{(k+)}_{20}(j)\,\hat{h}^2_{0,\underline{n}} + Z^{(k+)}_{11}(j)\,\hat{h}_{0,n}\hat{h}_{1,\underline{n}} + Z^{(k+)}_{02}(j)\,\hat{h}^2_{1,n} + \cdots$$

where $j = J/kT$.

Therefore

$$Z^{(k+)}_{00}(j) = \sum_{S_1=0\,or\,1/2}^{k/2} \omega_k(S_1)\,2e^j\left\{\sinh\frac{Rj}{2} + R\cosh\frac{Rj}{2}\right\},$$

$$Z^{(k+)}_{20}(j) = \sum_{S_1=0\,or\,1/2}^{k/2} \omega_k(S_1)\frac{e^j}{12}\left\{j^2\left[3R\sinh\frac{Rj}{2} + (R^2+2)\cosh\frac{Rj}{2}\right] + \frac{4j}{R^2}(R^2-1)\sinh\frac{Rj}{2}\right\},$$

$$Z^{(k+)}_{11}(j) = \sum_{S_1=0\,or\,1/2}^{k/2} \omega_k(S_1)\frac{e^j}{12}\left\{-8j\,\frac{R^2-1}{R^2}\sinh\frac{Rj}{2} + j^2\,\frac{2(R^2-1)}{R}\left[R\sinh\frac{Rj}{2} + 2\cosh\frac{Rj}{2}\right]\right\}, \quad (8.3)$$

and $$Z^{(k+)}_{02}(j) = \sum_{S_1=0\,or\,1/2}^{k/2} \omega_k(S_1)\frac{e^j}{12}\left\{4j\,\frac{R^2-1}{R^2}\sinh\frac{Rj}{2} + j^2\,\frac{R^2-1}{R}\left[R\sinh\frac{Rj}{2} + (R^2-2)\cosh\frac{Rj}{2}\right]\right\}$$

where $R = 2S_1+1$, and $\omega_k(S_1)$ is the number of ways of forming spin S_1, from k spins of $S=\frac{1}{2}$. (see Smart)[59].

Consider the construction of $Z^{(k-)}_{\alpha,\underline{n}}$ for $k>0$. The eigenvalues of $\mathcal{H}_{\alpha,\underline{n}}$ are specified by

$$S_1 = \begin{cases} 0,1,\ldots k/2 & \text{if } k \text{ is even.} \\ 1/2, 3/2, \ldots k/2 & \text{if } k \text{ is odd.} \end{cases}$$

and $$M' = S_1, S_1-1, \ldots, -S_1 .$$

and the eigenvalues are

$$E_{\alpha,\underline{n}}(S_1, M') = J\hat{h}_{1,\underline{n}} M'$$

and hence in the paramagnetic region

$$Z^{(k-)}_{\alpha,\underline{n}}(\hat{h}_{1,\underline{n}}, \hat{h}_{0,\underline{n}}, j) = Z^{(k-)}_{00}(j) + Z^{(k-)}_{20}(j)\hat{h}^2_{0,\underline{n}} + Z^{(k-)}_{11}(j)\hat{h}_{h,\underline{n}}\hat{h}_{0,\underline{n}} + Z^{(k-)}_{02}(j)\hat{h}^2_{1,\underline{n}} + \rightarrow$$

with $$Z^{(k-)}_{20}(j) = Z^{(k-)}_{11}(j) = 0 ,$$

$$Z^{(k-)}_{00}(j) = \sum_{S_1=0,\,or\,1/2}^{k/2} \omega_k(S_1) R , \qquad (8.4)$$

and $$Z^{(k-)}_{02}(j) = \sum_{S_1=0,\,or\,1/2}^{k/2} \omega_k(S_1) \frac{j^2}{24} R(R^2-1)$$

Consider $Z^{(0+)}_{\alpha,\underline{n}}$. It is easily shown that,

$$Z^{(0+)}_{11}(j) = Z^{(0+)}_{02}(j) = 0, \quad Z^{(0+)}_{00}(j) = 2 \quad , \text{and } Z^{(0+)}_{20}(j) = \tfrac{1}{4}j^2 \qquad (8.5)$$

Similarly for $Z^{(0-)}_{\alpha,\underline{n}}$ only $Z^{(0-)}_{00}(j)$ is non-zero, and has the value unity.

We define, in general,

$$Z_{\alpha,\underline{n}} = Z_{00}(j) + Z_{20}(j)\hat{h}^2_{0,\underline{n}} + Z_{11}(j)\hat{h}_{0,\underline{n}}\hat{h}_{1,\underline{n}} + Z_{02}(j)\hat{h}^2_{1,\underline{n}} \qquad (8.6)$$

$$+ \rightarrow$$

where

$$Z_{mn}(j) = \sum_{k=0}^{z} \left\{ +_{\underline{n}}^{(k)} Z_{mn}^{(k+)}(j) + q_{\underline{n}}^{(k)} Z_{mn}^{(k-)}(j) \right\}$$

The average magnetic moment of the central atom in the cluster is

$$\mu_{\underline{n}} = \tfrac{1}{2}\mu g \sigma_{\underline{n}} = kT \frac{\partial \ln Z_{ca,\underline{n}}}{\partial h_{0,\underline{n}}}$$

and that for a nearest neighbour atom is (8.7)

$$\tfrac{1}{z}\sum_{\underline{e}} \mu_{\underline{n}+\underline{e}} = \sum_{\underline{e}} \tfrac{1}{2z}\mu g \sigma_{\underline{n}+\underline{e}} = kT \tfrac{1}{z} \frac{\partial \ln Z_{ca,\underline{n}}}{\partial h_{1,\underline{n}}}$$

Using equations (8.3) to (8.7) and eliminating $\hat{h}_{1,\underline{n}}$ gives,

$$jZ_{00}\left\{ Z_{02}\sigma_{\underline{n}} - \tfrac{1}{2} Z_{11} \sum_{\underline{e}} \sigma_{\underline{n}+\underline{e}} \right\} = \left\{ 4Z_{20}Z_{02} - Z_{11}^2 \right\} \hat{h}_{0,\underline{n}} \qquad (8.8)$$

As previously, we can solve this if we assume that $\sigma_{\underline{k}}$ is independent of fluctuations in concentration, and then,

$$\chi(\underline{\lambda}) = \frac{\tfrac{1}{4}\mu^2 g^2 \bar{c} N \delta_{\underline{\lambda},\underline{k}}}{\bar{a} + \bar{b}\gamma(\underline{\lambda})} \qquad (8.9)$$

with

$$\bar{a} = j\langle Z_{00}Z_{02}\rangle \quad , \quad \bar{b} = -\tfrac{1}{2}j\langle Z_{00}Z_{11}\rangle$$

and

$$\bar{c} = \langle 4Z_{20}Z_{02} - Z_{11}^2 \rangle$$

From previous results we know that this result will only be useful for high temperatures and concentrations

near $c=1$, so a much better treatment is needed.

Consider the following definitions,

$$j Z_{00} Z_{02} = \sum_{k=0}^{z} \left\{ \dagger_{\underline{n}}^{(k)} P_1^{(k)} + q_{\underline{n}}^{(k)} Q_1^{(k)} \right\}$$

$$4 Z_{20} Z_{02} - Z_{11}^2 = \sum_{k=0}^{z} \left\{ \dagger_{\underline{n}}^{(k)} P_2^{(k)} + q_{\underline{n}}^{(k)} Q_2^{(k)} \right\}$$

$$\tfrac{1}{2} j Z_{00} Z_{11} = \sum_{k=0}^{z} \left\{ \dagger_{\underline{n}}^{(k)} P_3^{(k)} + q_{\underline{n}}^{(k)} Q_3^{(k)} \right\}$$

It is clear that $Q_2^{(k)} = Q_3^{(k)} = 0 \ \forall k$ because of the definitions of $Z_{\underline{\ell},\underline{n}}^{(k\pm)}$

Using these definitions and (8.8) the following equation is found for $\sigma_{\underline{n}}$

$$\sigma_{\underline{n}} = \sum_{k=0}^{z} \dagger_{\underline{n}}^{(k)} \frac{P_2^{(k)}}{P_1^{(k)}} \hat{h}_{0,\underline{n}} + \sum_{k=0}^{z} \dagger_{\underline{n}}^{(k)} \frac{P_3^{(k)}}{P_1^{(k)}} \sum_{\underline{\ell}} \sigma_{\underline{n}+\underline{\ell}} \qquad (8.10)$$

which is very similar to the equation (7.13) found when considering the Ising model except that the 'coefficients' need new definitions. We note that $P_2^{(0)}/P_1^{(0)}$ is replaced in the above by $\frac{1}{2} j$.

As in chapter 7, (8.10) can be iterated,

$$\sigma_{\underline{n}} = \sum_{k=0}^{z} \dagger_{\underline{n}}^{(k)} \frac{P_2^{(k)}}{P_1^{(k)}} \hat{h}_{0,\underline{n}} + \sum_{\substack{k=0 \\ k'=0}}^{z} \sum_{\underline{\ell}} \dagger_{\underline{n}}^{(k)} \dagger_{\underline{n}+\underline{\ell}}^{(k')} \frac{P_2^{(k)} P_3^{(k')}}{P_1^{(k)} P_1^{(k')}} \hat{h}_{0,\underline{n}+\underline{\ell}}$$

$$+ \cdots + \sum_{\substack{k_1=0 \\ \cdots \\ k_m=0}}^{z} \sum_{\underline{\ell}_1 \cdots \underline{\ell}_{m-1}} \dagger_{\underline{n}}^{(k_1)} \dagger_{\underline{n}+\underline{\ell}_1}^{(k_2)} \cdots \dagger_{\underline{n}+\underline{\ell}_1+\cdots+\underline{\ell}_{m-1}}^{(k_m)} \frac{P_2^{(k_1)} \cdots P_3^{(k_m)}}{P_1^{(k_1)} \cdots P_1^{(k_m)}} \hat{h}_{0,\underline{n}+\underline{\ell}_1+\cdots+\underline{\ell}_{m-1}} \qquad (8.11)$$

$$+ \rightsquigarrow$$

From this equation it can be seen that the only difference when compared with the Ising model equation, is the more

complicated nature of the temperature functions. The averages needed to calculate $\chi(\underline{\lambda})$ are those used in Chapter 7 and calculated in Appendix 3. In fact, the whole discussion on the approximations to $\chi(\underline{\lambda})$ and the calculation of SA and SB can be carried over to the present case. For this theory

$$SA = \sum_{\underline{\ell}_1} \sum_{\substack{k'=1 \\ k''=1}}^{z} \langle \tau_{\underline{n}}^{(k')} \tau_{\underline{n}+\underline{\ell}_1}^{(k'')} \rangle \left\{ \frac{e^{i\underline{\ell}_1 \cdot \underline{k}} + \bar{P}_3^{(k')}}{1 - \bar{P}_3^{(k')} \bar{P}_3^{(k'')}} \right\} \bar{P}_2^{(k')} \bar{P}_3^{(k'')} \qquad (8.12)$$

where $\bar{P}_3^{(k')} = P_3^{(k')} / P_1^{(k')}$ and $\bar{P}_2^{(k')} = P_2^{(k')} / P_1^{(k')}$

and

$$SB = \sum_{\underline{\ell}_1, \underline{\ell}_2} \sum_{\substack{k'=1 \\ k''=2 \\ k'''=1}}^{z} (1 - \delta_{\underline{\ell}_1 + \underline{\ell}_2, 0}) \langle \tau_{\underline{n}}^{(k')} \tau_{\underline{n}+\underline{\ell}_1}^{(k'')} \tau_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}^{(k''')} \rangle A(k', k'', k''', \underline{\ell}_1, \underline{\ell}_2), \qquad (8.13)$$

with $$A(k', k'', k''', \underline{\ell}_1, \underline{\ell}_2) = \frac{\bar{P}_2^{(k')} \bar{P}_3^{(k'')} \bar{P}_3^{(k''')} \left\{ (e^{i\underline{\ell}_1 \cdot \underline{k}} + \bar{P}_3^{(k'')})(e^{i\underline{\ell}_2 \cdot \underline{k}} + \bar{P}_3^{(k''')}) + \bar{P}_3^{(k')} \bar{P}_3^{(k''')} (1 - e^{i(\underline{\ell}_1 + \underline{\ell}_2) \cdot \underline{k}}) \right\}}{\left[1 - \bar{P}_3^{(k')} \bar{P}_3^{(k'')} \right] \left[1 - \bar{P}_3^{(k'')} (\bar{P}_3^{(k')} + \bar{P}_3^{(k''')}) \right]}$$

8.2 Discussion of the results

As in the Ising model case, convergence seems to be quite good in the region of $c=1$, but for other concentrations, as can be seen from graph 8.1, this is far from true. The first order approximation gives solutions until $y \sim .9$, but the second order approximation gives no solutions below $c=.6$ and at $c=.7$ gives a critical value of $y \sim .6$. This is a reversal of the Ising model case. The sum approximation and the total approximation presented in graph 8.1 give results down to $c=.05$ and appear to always give a solution. The reason for this can

be seen if the limits of S_A, S_B are considered as $kT \to 0$. From the definition of $\bar{P}_3^{(k)}$

$$\lim_{kT\to 0} \bar{P}_3^{(k)} = \frac{1}{k} \tag{8.14}$$

Thus, the denominators of the terms of S_A are $(kk'-1)$, which is zero when $k=k'=1$. So there will always be a non-zero critical temperature until $c=0$. Similarly, for S_B the denominators are $(k'k''-1)$ $(k'k''k'''-k'-k''')$, and the last factor is zero when $k'=k'''=1$, and $k''=2$,

This is a serious failing in this method of approaching the calculation of the susceptibility. This failure may be due to the incorrect use of the sums S_A, S_B, and the sequence of order approximations may eventually give the true behaviour in this limit. However, the convergence will be a very slow process and until an easier way of finding the averages necessary can be discovered, the calculation will be too lengthy.

The results for the critical temperature are again lower than those predicted from extrapolation of the high temperature limit, and the inverse susceptibility against temperature curve is similar to that found in the Ising model case.

8.3 The Classical Heisenberg Model

As the Heisenberg model is important and it is so difficult to extend to long range interactions, it is important to consider the limit of infinite spin, where the spin operators of the quantum-mechanical Hamiltonian may be replaced by classical spin vectors of fixed length. This is the Classical Heisenberg model and it has been argued (Stanley and Kaplan (1966)[106]) that for large spins ($S>2$, say)

this model is a good approximation to the quantum mechanical model. This model is also very important in the context of this present work because of the low concentration behaviour of the Heisenberg model itself.

The energy arising from the central atom of the cluster and that on $\underline{n}+\underline{\ell}$ is given by

$$\mathcal{H}_{\underline{n}} = -p_{\underline{n}} m_c \underline{H} \cdot \frac{\underline{S}_{\underline{n}}}{S} e^{-i\underline{k}\cdot\underline{n}} - m_c \underline{H}_{\underline{n}+\underline{\ell}} \cdot \frac{\underline{S}_{\underline{n}+\underline{\ell}}}{S} p_{\underline{n}+\underline{\ell}} - 2J(\underline{\ell}) \frac{\underline{S}_{\underline{n}} \cdot \underline{S}_{\underline{n}+\underline{\ell}}}{S^2} p_{\underline{n}} p_{\underline{n}+\underline{\ell}} \quad (8.15)$$

where $\underline{S}_{\underline{n}}$, and $\underline{S}_{\underline{n}+\underline{\ell}}$ are classical vectors of fixed length $\sqrt{S(S+1)}$; $\underline{H}$ is assumed parallel to $\underline{H}_{\underline{n}+\underline{\ell}}$; m_c is the classical magnetic moment. The problem is treated using the same cluster used for the Ising model and a similar method is followed.

The evaluation of the partition function for the cluster being considered involves an integral over the phase space defined by the solid angles $d\Omega$ available to each spin vector. This partition function is, using the energies (8.15)

$$Z_{\alpha,\underline{n}} = \int \exp\left(\beta m_c p_{\underline{n}} \frac{\bar{\underline{H}} \cdot \underline{S}_{\underline{n}}}{S}\right) \prod_{\underline{\ell}} \left\{ \int \exp\left[\beta\left(m_c \underline{H}_{\underline{n}+\underline{\ell}} + 2J(\underline{\ell}) p_{\underline{n}} \frac{\underline{S}_{\underline{n}}}{S}\right) \cdot \frac{\underline{S}_{\underline{n}+\underline{\ell}}}{S} p_{\underline{n}+\underline{\ell}}\right] \frac{d\Omega_{\underline{\ell}}}{4\pi} \right\} \quad (8.16)$$

$\bar{H} = H e^{-i\underline{k}\cdot\underline{n}}$

As in the other calculations this must be expanded in powers of $\underline{H}$ and $\underline{H}_{\underline{n}+\underline{\ell}}$ as otherwise the problem is intractable, but as these quantities are small in the paramagnetic region this is no disadvantage for the calculation in hand. The terms to order H^2 can be evaluated using the following expansion quoted by Dalton

$$\int \exp\left\{\beta\left(m_c p_{\underline{n}\underline{\varrho}} H_{\underline{n}+\underline{\varrho}} + 2J(\underline{\varrho}) p_{\underline{n}} \frac{\underline{S}_{\underline{n}}}{S}\right)\cdot \frac{\underline{S}_{\underline{n}+\underline{\varrho}}}{S} p_{\underline{n}+\underline{\varrho}}\right\} \frac{d\Omega_{\underline{\varrho}}}{4\pi}$$

$$= \frac{1}{2}\sum_{r=0}^{\infty} \frac{(\beta m_c \sqrt{X}\, H_{\underline{n}+\underline{\varrho}})^r}{r!} \int_{-1}^{+1} \exp\left(\frac{2\beta X J(\underline{\varrho})\, x}{S^2}\right) f_r(\eta, x)\, dx \qquad (8.17)$$

with $$f_r(\eta, x) = \sum_{p=0}^{[\frac{r}{2}]} \frac{r!}{2^{2p}(r-2p)!\,p!} (\cos\eta)^{r-2p} (\sin\eta)^{2p} x^{r-2p} (1-x^2)^p$$

η is the angle between $\underline{H}$ and $\underline{S}_{\underline{n}}$,

and $H_{\underline{n}+\underline{\varrho}}$ the magnitude of $\underline{H}_{\underline{n}+\underline{\varrho}}$

The expansion of the partition function is

$$Z_{\alpha,\underline{n}} = p_{\underline{n}} \prod_{\underline{\varrho}} \left\{(1-p_{\underline{n}+\underline{\varrho}}) + p_{\underline{n}+\underline{\varrho}} Z(\underline{\varrho})\right\} \left\{1 + \frac{\alpha^2 X}{6} \sum_{\underline{\varrho}'} p_{\underline{n}+\underline{\varrho}'} H^2_{\underline{n}+\underline{\varrho}'}\right.$$

$$+ \frac{\alpha^2 X}{3} \sum_{\underline{\varrho}'\neq\underline{\varrho}''} p_{\underline{n}+\underline{\varrho}'} p_{\underline{n}+\underline{\varrho}''} \tau(\underline{\varrho}')\tau(\underline{\varrho}'') H_{\underline{n}+\underline{\varrho}'} H_{\underline{n}+\underline{\varrho}''} + \frac{\alpha^2 X}{6} \bar{H}^2 \qquad (8.18)$$

$$\left. + \frac{\alpha^2 X}{3} \bar{H} \sum_{\underline{\varrho}'} p_{\underline{n}+\underline{\varrho}'} H_{\underline{n}+\underline{\varrho}'} \tau(\underline{\varrho}')\right\} + (1-p_{\underline{n}})\left[1 + \frac{\alpha^2}{6} X \sum_{\underline{\varrho}'} \prod_{\underline{\varrho}\neq\underline{\varrho}'} (1-p_{\underline{n}+\underline{\varrho}}) p_{\underline{n}+\underline{\varrho}'} \cdot H^2_{\underline{n}+\underline{\varrho}'}\right]$$

with $$Z(\underline{\varrho}) = \frac{\sinh(\beta_{\underline{\varrho}})}{\beta_{\underline{\varrho}}}, \quad \beta_{\underline{\varrho}} = \frac{2\beta X J(\underline{\varrho})}{S^2},$$

$$\tau(\underline{\varrho}) = \frac{1}{Z(\underline{\varrho})} \frac{\partial Z(\underline{\varrho})}{\partial \beta_{\underline{\varrho}}} = \lim_{S\to\infty} B_S(\beta_{\underline{\varrho}}), \quad \alpha = \frac{m_o \beta}{S}.$$

Using the definitions

$$\mu_{\underline{n}+\underline{\varrho}} = \frac{m_c}{S} \langle S^z_{\underline{n}+\underline{\varrho}} \rangle = kT \frac{\partial \ln Z_{\alpha,\underline{n}}}{\partial H_{\underline{n}+\underline{\varrho}}} \qquad (8.19)$$

the following expression for $\sigma_{\underline{n}}, \sigma_{\underline{n}+\underline{\varrho}}$ can be found:

$$\sigma_{\underline{n}+\underline{\ell}} = \frac{\langle S^z_{\underline{n}+\underline{\ell}} \rangle}{S} = \frac{X\alpha}{3S}\Big\{ p_{\underline{n}+\underline{\ell}'} H_{\underline{n}+\underline{\ell}'} \Big[(1-p_{\underline{n}}) \prod_{\underline{\ell}\neq\underline{\ell}'} (1-p_{\underline{n}+\underline{\ell}}) + p_{\underline{n}} \Big] + p_{\underline{n}} p_{\underline{n}+\underline{\ell}'} \tau(\underline{\ell}') \sum_{\underline{\ell}''\neq\underline{\ell}'} p_{\underline{n}+\underline{\ell}''} \tau(\underline{\ell}'') H_{\underline{n}+\underline{\ell}''} + p_{\underline{n}} \bar{H} \tau(\underline{\ell}') p_{\underline{n}+\underline{\ell}'} \Big\} \tag{8.20}$$

and

$$\sigma_{\underline{n}} = p_{\underline{n}} \frac{\alpha X}{3S}\Big\{ \sum_{\underline{\ell}'} p_{\underline{n}+\underline{\ell}'} H_{\underline{n}+\underline{\ell}'} \tau(\underline{\ell}') + \bar{H} \Big\} \tag{8.21}$$

Eliminating $H_{\underline{n}+\underline{\ell}'}$ from the last of these equations gives,

$$\sigma_{\underline{n}} = \frac{p_{\underline{n}}}{1+\sum_{\underline{\ell}'} p_{\underline{n}+\underline{\ell}'} \Phi(\underline{\ell}')}\Big\{ \frac{\alpha X}{3S} H e^{-i\underline{k}\cdot\underline{n}} + \sum_{\underline{\ell}'} \frac{\tau(\underline{\ell}')}{\Theta(\underline{\ell}')} \sigma_{\underline{n}+\underline{\ell}'} \Big\} \tag{8.22}$$

where $\Theta(\underline{\ell}') = 1-\tau^2(\underline{\ell}')$; $\Phi(\underline{\ell}') = \tau^2(\underline{\ell}')/\Theta(\underline{\ell}')$

When the concentration $c=1$, this equation leads to the result

$$\frac{kT}{m_c^2}\chi(0) = \frac{X}{3S^2}\Big\{ 1 - \sum_{\underline{\ell}} \frac{\tau(\underline{\ell})}{1+\tau(\underline{\ell})} \Big\}^{-1} \tag{8.23}$$

which is identical to that obtained by Dalton.
Following the procedure used in both the previous cases (8.22) can be iterated to give,

$$\bar{\sigma}_{\underline{n}} = \frac{\alpha X H}{3S}\Big\{ \sum_{\underline{k}=0}^{z} P_2^{(\underline{k})} \psi_{\underline{n}}^{(\underline{k})} + \sum_{\underline{\varrho}'} \sum_{\underline{k}=0}^{z} \sum_{\underline{k}'=0} \psi_{\underline{n}}^{(\underline{k})} \psi_{\underline{n}+\underline{\varrho}_j}^{(\underline{k}')} P_2^{(\underline{k})} P_3^{(\underline{k}')} e^{i\underline{\varrho}'.\underline{k}} + \rightsquigarrow \Big\} \qquad (8.24)$$

where $P_2^{(\underline{k})} = \dfrac{1}{1+\sum_{i=1}^{n'} k_i \Phi_i}$, $P_3^{(\underline{k})} = \dfrac{\tau(\underline{\varrho}')}{1-\tau^2(\underline{\varrho}')}\left\{\dfrac{1}{1+\sum_{j=1}^{n'} k_j' \Phi_j}\right\}$

and the temperature functions are identical with the Ising case if $\tanh\left(J(\underline{\varrho})/2kT\right)$ is replaced by $\tau(\underline{\varrho})$. These functions also have the same type of behaviour in the limits $kT=0$ and $kT=\infty$. This implies that the equivalent of the sum approximations will for this model give identical critical concentrations to those obtained using the Ising model! Further, the results for the critical value of y for the Ising model are identical with the results for the critical value of τ and this Classical model will be very useful in discussing the binary alloy situation. It becomes very important when one considers that the quantum mechanical Heisenberg model fails to give a reasonable description.

8.4 The Zero-Field Critical Properties of the Heisenberg Models

For both of these models the zero-field critical energy and entropy can be evaluated exactly for the B.P.W. approximation. For the Classical Heisenberg model the expressions are,

$$\frac{E_\infty - E_c}{kT_c} = \frac{1}{2}c^2 \sum_{i=1}^{n'} z_i \beta_i \tau_i \qquad (8.25)$$

$$\frac{S_\infty - S_c}{k} = \frac{1}{2}c^2 \sum_{i=1}^{n'} z_i \left\{ \beta_i \tau_i - \ln Z_i \right\} \tag{8.26}$$

where $\beta_i = \frac{2xJ_i\beta}{S^2}$, $Z_i = \frac{\sinh \beta_i}{\beta_i}$

and $\tau_i = \frac{1}{Z_i} \frac{dZ_i}{d\beta_i}$

These expressions are similar to Ising model expressions.

For the quantum mechanical model the expressions show a much more complicated concentration dependence:

$$\frac{E_\infty - E_c}{kT_c} = \frac{1}{2kT_c} \sum_{k=0}^{z} \langle \gamma_{\underline{n}}^{(k)} \rangle \frac{\partial}{\partial T} \left[\ln \left(Z_{oo}^{(k)}(j) \right) \right] \Bigg|_{T=T_c}^{T=\infty} \tag{8.27}$$

and

$$\frac{S_\infty - S_c}{k} = \frac{1}{2} \sum_{k=0}^{z} \langle \gamma_{\underline{n}}^{(k)} \rangle \left\{ \frac{1}{k} \frac{\partial}{\partial T} \left[\ln \left(Z_{oo}^{(k)}(j) \right) \right] \Bigg|_{T=T_c}^{T=\infty} - \ln \left(Z_{oo}^{(k)}(j_c) \right) \right\} \tag{8.28}$$

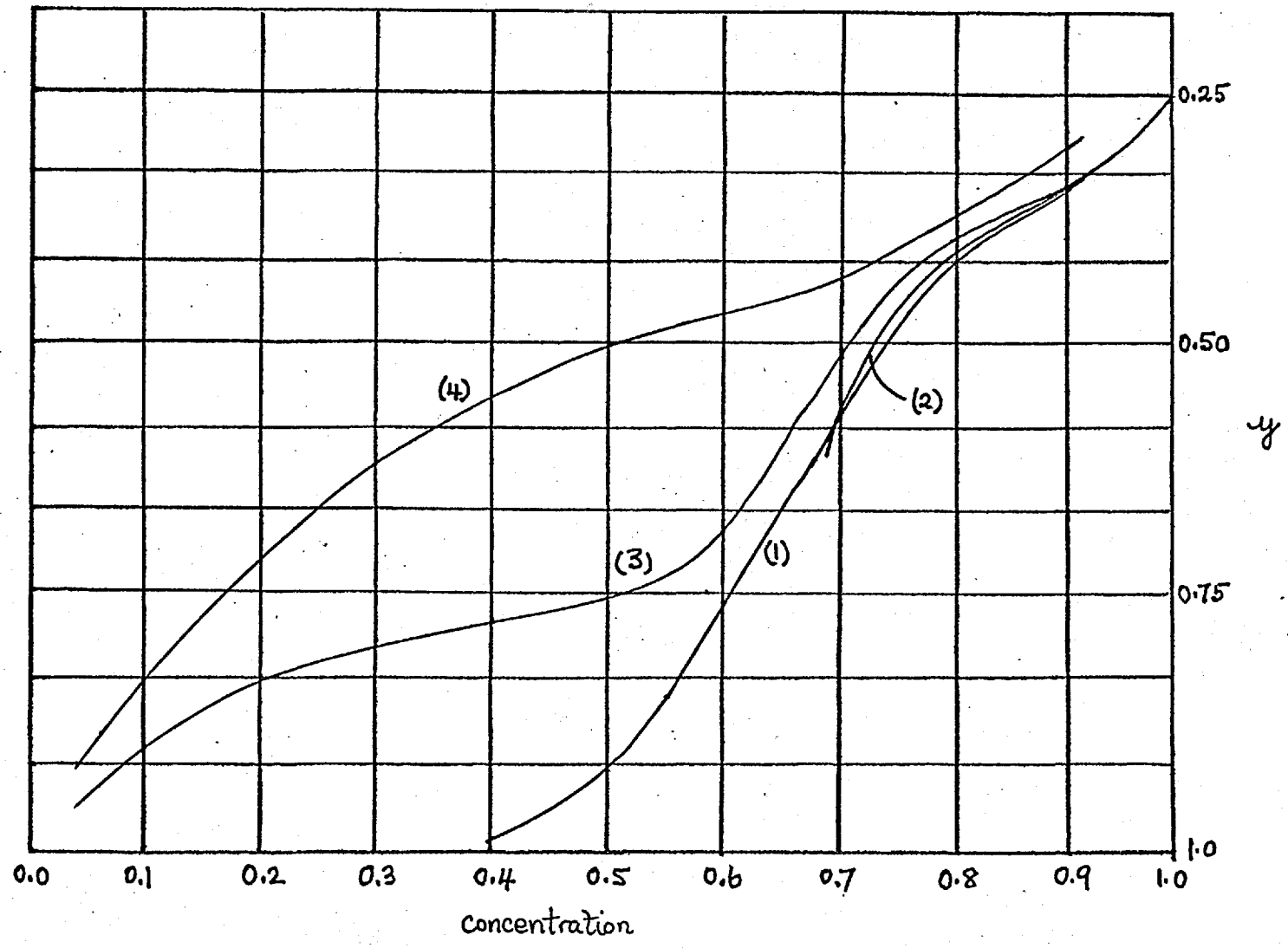
These results are useful for comparing experimental results with the predictions of the three models.

GRAPH 8.1

Curves of the critical value of $y = \tanh (J/2kT)$ against concentration for the Heisenberg model ($S = \frac{1}{2}$, nearest neighbour interactions and a simple cubic lattice).

(1) denotes the first order approximation.
(2) denotes the second order approximation.
(3) denotes the first total approximation.
(4) denotes the second sum approximation.

GRAPH 8.1


0.25
0.50
0.75
1.0
y
(1)
(2)
(3)
(4)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
concentration

Chapter 9

Conclusions

The erroneous results given by the MFT for the alloy situation are a direct consequence of the theory's shortcomings in the limit $c=1$. In this limit the MFT predicts that a linear chain of spins can have an ordered state, which cannot be true if spin-wave theory is valid. In a crude approximation the alloy case can be treated by replacing the co-ordination number z by an effective one cz, and so when $c=2/z$ the MFT treatment gives unphysical results (see Chapter 6). This argument can be extended to consider any range of interactions, and for all cases the low concentration behaviour is found to be unphysical. It seems certain that the MFT is only valid for low concentrations in the limit of infinitesimal interactions of infinite range. (This is the limit in which the theory gives a correct description of the Heisenberg model's properties.)

The MFT does not include the short range order which a valid description must include. In the limit $c=1$ the inclusion of short range order reduces the value of the critical temperature from the MFT value. The MFT curves for the critical temperature against concentration lie above the curve predicted by extrapolating the high temperature limit, denoted by A in diagram 9.1, and hence the theory predicts the erroneous curve shape mentioned in chapter 6.

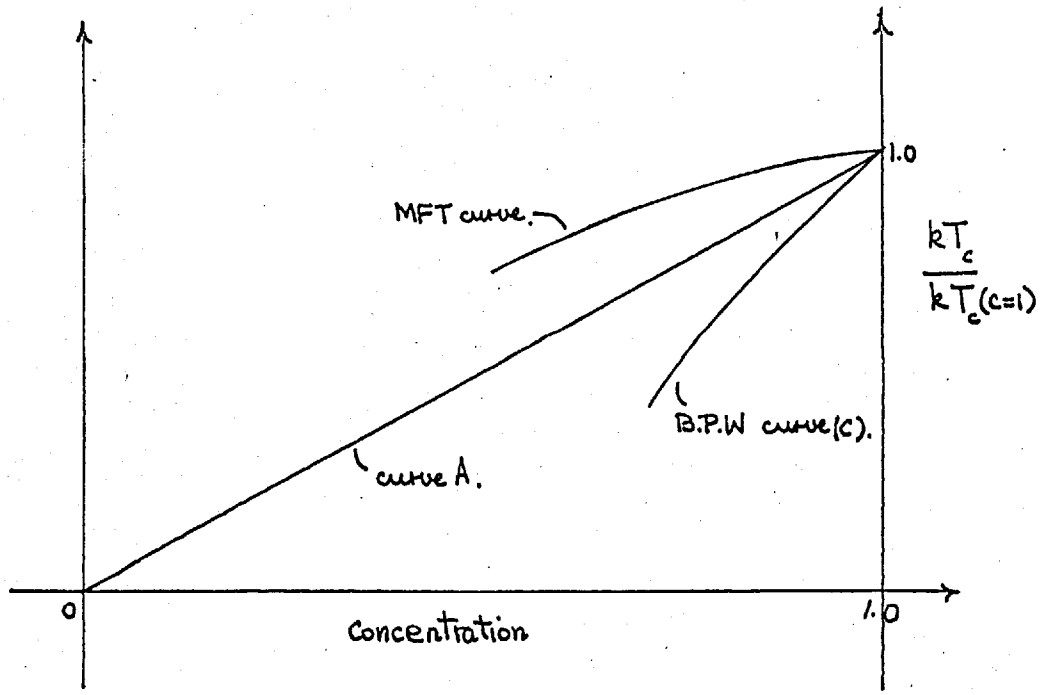


Diagram 9.1 Comparison of the critical temperature vs. concentration curves for the various theories.

When short range order is included the curve A is no longer that predicted by using the high temperature limit and the curvature will be in the correct direction.

The B.P.W. theory of the Ising model case gives curves of the type C, and the evidence so far available suggests that each successive approximation brings the slope near $c=1$ nearer to that of curve A. In fact, the convergence of the successive approximations suggests that the combination of the next order and sum approximations will be sufficient to give an accurate picture of the theory's predictions. It is obvious from the results obtained so far that the properties cannot be predicted correctly by considering the problem merely in terms of

dilution. The critical temperature will be higher than that predicted on the basis of a dilution approximation (see chapter 7).

The B.P.W. theory of the quantum mechanical Heisenberg model has failed (for $S=\frac{1}{2}$) to give a critical concentration, because of the more complicated nature of the temperature functions used. The Classical Heisenberg model does not have this failing as the temperature functions used are as well behaved as those used for the Ising model. In fact, both the theories predict the same critical concentrations for corresponding approximations, though the critical temperatures predicted at $c=1$ differ, of course. This suggests that the Heisenberg and Ising models have identical critical concentrations. The high concentration behaviour of the critical temperature for the Classical Heisenberg model can be represented by the following equations :-

first order approximation

$$kT_c/kT_c(c=1) \simeq 1 - 1.23\,(1-c) \quad ;$$

second order approximation

$$kT_c/kT_c(c=1) \simeq 1 - 1.04\,(1-c) \quad ;$$

first total approximation

$$kT_c/kT_c(c=1) \simeq 1 - 1.07\,(1-c) \quad ;$$

and so the initial slopes are approximately the same as those for corresponding Ising model approximations. Thus, the shape of the critical temperature versus concentration curve may be similar to that of either of the curves H(i) and H(ii) suggested by Morgan and Rushbrooke, and the results for higher approximations are needed to clarify this point.

The closed-form approximations used in the preceeding chapters cannot give the asymptotic power laws for the susceptibility, so no study of these was attempted. For

instance, Domb[107] has shown that closed-form approximations give

$$\chi \propto \left(1 - \frac{T}{T_c}\right)^{\eta}$$

with $\eta = -1$, and the correct exponents are found by considering the exact high temperature expansion of χ using as many terms as can be calculated (usually from six to twelve). The high temperature expansion in the case of the B.P.W. theory of the Ising model (or the Classical Heisenberg model) could be used to estimate the exponents. The calculation of the series is, however, by no means an easy matter.

Despite the preliminary nature of some of the results this simple approach to approximating the properties of a binary alloy seems to have much to recommend it.

Appendix 1

Calculation of the Averages needed in the Molecular Field Approximation

The averages needed in the Molecular Field Approximation are averages of products of the functions $a_{\underline{\lambda}}$, i.e. $\langle a_{\underline{d}_1} \ldots\ldots a_{\underline{d}_n} \rangle$. From the definition of $a_{\underline{\lambda}}$ this average can be expressed as

$$\langle a_{\underline{d}_1} \ldots\ldots a_{\underline{d}_n} \rangle = \sum_{\underline{m}_1 \ldots \underline{m}_n} \langle (p_{\underline{m}_1} - c)(p_{\underline{m}_2} - c) \ldots\ldots (p_{\underline{m}_n} - c) \rangle \, e^{i(\underline{d}_1 \cdot \underline{m}_1 + \ldots + \underline{d}_n \cdot \underline{m}_n)}$$

If in a particular term of this sum a particular $\underline{m}_i$ is not equal to any of the other $\underline{m}_j$ the term can give no contribution as $\langle (p_{\underline{m}} - c) \rangle = 0$. If, however, in this term each $\underline{m}_i$ is equal to some other, say $\underline{m}_i = \underline{m}_j \neq$ any other $\underline{m}$, then $\langle (p_{\underline{i}} - c)(p_{\underline{j}} - c) \rangle = \langle p_{\underline{i}}(1 - 2c) + c^2 \rangle$ as $p_{\underline{i}}^2 = p_{\underline{i}}$ (by definition). So $\langle (p_{\underline{i}} - c)(p_{\underline{j}} - c) \rangle = c(1-c)\, \delta_{i,j}$ and the term has in general a non zero contribution. Thus we only have contributions when each $\underline{m}_i$ is equal to at least one other $\underline{m}$.

Defining the "contraction" of two factors $p_{\underline{i}} - c$ and $p_{\underline{j}} - c$ to equal $(p_{\underline{i}} - c)(p_{\underline{i}} - c)$, the calculation of the average $\langle a_{\underline{d}_1} \ldots\ldots a_{\underline{d}_n} \rangle$ reduces to the calculation of the contributions from each possible contraction of $\langle (p_{\underline{m}_1} - c)(p_{\underline{m}_2} - c) \ldots\ldots (p_{\underline{m}_n} - c) \rangle$. Introducing the diagram ○ to represent one $p_{\underline{m}} - c$ factor and representing the contraction of two such factors as ○—○ allows the various contributions to be represented, as follows,

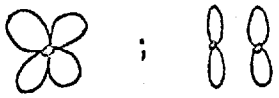
(i) with two factors the possible diagram(s) are



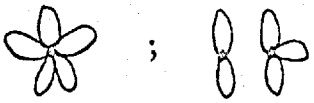
(ii) with three factors the possible diagram(s) are



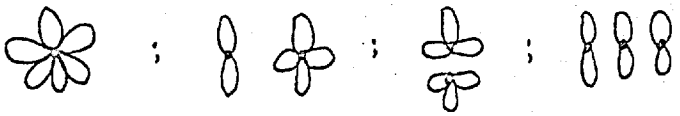
(iii) with four factors the possible diagram(s) are



(iv) with five factors the possible diagram(s) are



(v) with six factors the possible diagram(s) are



and so on, the number of possibilities rapidly increasing.

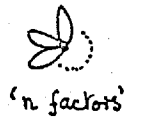
The contributions from the diagrams on the left are easy to calculate as all the factors are contracted with one another, so for example,

$$\langle (p_{\underline{i}} - c)^2 \rangle = c(1-c)\left[(1-c)^3 + c^3\right]$$

and so the contribution to $\langle a_{\underline{d}_1} \ldots a_{\underline{d}_4} \rangle$ from this is

$$c(1-c)\left[(1-c)^3 + c^3\right] N \delta_{\underline{d}_1 + \cdots + \underline{d}_4, 0}$$

In general, if there are n factors, the contribution is



$$\longrightarrow c(1-c)\left[(1-c)^{n-1} + (-1)^n c^{n-1}\right] N \delta_{\underline{d}_1 + \cdots + \underline{d}_n, 0}$$

The other diagrams arise when the set of $\underline{m}$'s, $\{\underline{m}_i\}$, is divided into subsets, where the members of a particular subset are equal to one another but are not equal to m's

belonging to any other subset. Consider the contribution obtained from the diagram ⧓⧓ : the terms to be considered are,

$$\langle (p_{\underline{m}_1}-c)(p_{\underline{m}_2}-c)(p_{\underline{m}_3}-c)(p_{\underline{m}_4}-c)\rangle \{ \delta_{\underline{m}_1,\underline{m}_2}\delta_{\underline{m}_3,\underline{m}_4} + \delta_{\underline{m}_1,\underline{m}_3}\delta_{\underline{m}_2,\underline{m}_4} + \delta_{\underline{m}_1,\underline{m}_4}\delta_{\underline{m}_2,\underline{m}_3} \}$$

$$= c^2(1-c)^2 \{ \delta_{\underline{m}_1,\underline{m}_2}\delta_{\underline{m}_3,\underline{m}_4} + \delta_{\underline{m}_1,\underline{m}_3}\delta_{\underline{m}_2,\underline{m}_4} + \delta_{\underline{m}_1,\underline{m}_4}\delta_{\underline{m}_2,\underline{m}_3} \}$$

The summation over the $\underline{m}$'s must, however, be restricted as all the $\underline{m}$'s cannot be equal, so the contribution becomes

$$⧓⧓ \rightarrow \sum_{\underline{m}_1 \cdots \underline{m}_4} c^2(1-c)^2 e^{i(\underline{d}_1\cdot\underline{m}_1 + \cdots + \underline{d}_4\cdot\underline{m}_4)} \{ \delta_{\underline{m}_1,\underline{m}_2}\delta_{\underline{m}_3,\underline{m}_4}(1-\delta_{\underline{m}_1,\underline{m}_3})$$
$$+ \delta_{\underline{m}_1,\underline{m}_3}\delta_{\underline{m}_2,\underline{m}_4}(1-\delta_{\underline{m}_1,\underline{m}_2})$$
$$+ \delta_{\underline{m}_1,\underline{m}_4}\delta_{\underline{m}_2,\underline{m}_3}(1-\delta_{\underline{m}_1,\underline{m}_2}) \}$$

$$= c^2(1-c)^2 N^2 \cdot \delta_{\underline{d}_1+\cdots+\underline{d}_4,0}(\delta_{\underline{d}_1+\underline{d}_2,0} + \delta_{\underline{d}_1+\underline{d}_3,0} + \delta_{\underline{d}_1+\underline{d}_4,0})$$
$$- 3c^2(1-c)^2 N \delta_{\underline{d}_1+\underline{d}_2+\cdots+\underline{d}_4,0}$$

This procedure enables all the diagrams to be evaluated, but the calculation rapidly becomes tedious. The evaluation of the diagrams for up to six factors has been completed and the results are listed below for the averages $\langle a_{\underline{k}-\underline{t}_1} a_{\underline{t}_1-\underline{t}_2} a_{\underline{t}_2-\underline{t}_3} \cdots\cdots a_{\underline{t}_n-\underline{l}}\rangle$


$$\rightarrow c(1-c)N\delta_{\underline{l},\underline{k}}$$


$$\rightarrow c(1-c)(1-2c)N\delta_{\underline{l},\underline{k}}$$


$$\rightarrow c(1-c)\left[(1-c)^3 + c^3\right]N\delta_{\underline{l},\underline{k}}$$



$$\to c^2(1-c)^2 N^2 \delta_{\underline{\lambda},\underline{k}} \left(\delta_{\underline{k},\underline{t}_1} + \delta_{\underline{k}+\underline{t}_2-\underline{t}_3-\underline{t}_1,0} + \delta_{\underline{k}-\underline{t}_1+\underline{t}_3,\underline{k}} \right)$$

$$-3c^2(1-c)^2 N \delta_{\underline{\lambda},\underline{k}}$$



$$\to c(1-c)\left[(1-c)^4 - c^4\right] N \delta_{\underline{\lambda},\underline{k}}$$



$$\to c^2(1-c)^2(1-2c) N^2 \delta_{\underline{\lambda},\underline{k}} \Big\{ \delta_{\underline{k},\underline{t}_2} + \delta_{\underline{k},\underline{t}_3} + \delta_{\underline{t}_1,\underline{t}_3} + \delta_{\underline{t}_1,\underline{t}_4}$$

$$+ \delta_{\underline{t}_2,\underline{t}_4} + \delta_{\underline{k}-\underline{t}_1+\underline{t}_2,\underline{t}_3} + \delta_{\underline{k}-\underline{t}_1+\underline{t}_3,\underline{t}_4}$$

$$+ \delta_{\underline{t}_2,\underline{t}_3+\underline{k}-\underline{t}_4} + \delta_{\underline{k}+\underline{t}_2-\underline{t}_1,\underline{t}_4} + \delta_{\underline{t}_1-\underline{t}_2,\underline{t}_4-\underline{t}_3} \Big\}$$

$$-10c^2(1-c)^2(1-2c) N \delta_{\underline{\lambda},\underline{k}}$$

Appendix 2

Some other approximations to the Molecular Field Theory Solution for $\chi(k)$

A2.1 Solution by Iteration

The integral equation (6.10) can, of course, be iterated to give the following expression,

$$\sigma(\underline{\lambda}) = \mu g H \alpha_{S\beta} \left\{ \frac{cN\delta_{\underline{\lambda},\underline{k}} + a_{\underline{\lambda}-\underline{k}}}{Q(\underline{\lambda})} + \sum_{n=1}^{\infty} \left(\frac{\alpha_{S\beta}}{N}\right)^n \sum_{\underline{t}_1 \ldots \underline{t}_n} \prod_{i=1}^{n} F(\underline{t}_i) \frac{(cN\delta_{\underline{k},\underline{t}_1} + a_{\underline{t}_1-\underline{k}})(a_{\underline{\lambda}-\underline{t}_n} \ldots a_{\underline{t}_2-\underline{t}_1})}{Q(\underline{\lambda})} \right\} \tag{A2.1}$$

where $$F(\underline{\lambda}) = \frac{J(\underline{\lambda})}{1 - \alpha_{S\beta} c J(\underline{\lambda})}$$

This expansion in itself is of little use, but by rearranging it the reason for making the choice (6.14) in the decoupling approach becomes apparent. The rearrangement gives,

$$\sigma(\underline{\lambda}) = \frac{\mu g H \alpha_{S\beta}}{Q(\underline{\lambda})} \left\{ cN\delta_{\underline{\lambda},\underline{k}} + \frac{a_{\underline{\lambda}-\underline{k}}}{Q(\underline{k})} + \frac{1}{Q(\underline{k})} \sum_{n=1}^{\infty} \left(\frac{\alpha_{S\beta}}{N}\right)^n \sum_{\underline{t}_1 \ldots \underline{t}_n} \prod_{i=1}^{n} F(\underline{t}_i) a_{\underline{\lambda}-\underline{t}_1} \ldots a_{\underline{t}_n-\underline{k}} \right\} \tag{A2.2}$$

Using the averages obtained in the previous Appendix, this equation can be used to calculate the high temperature expansion of the susceptibility.

An alternative way to calculate this expansion is to assume that

$$\sigma(\underline{\lambda}) = \frac{H}{\mu g} \sum_{n=1}^{\infty} (\alpha_{S\beta})^n a_n(\underline{\lambda}) \tag{A2.3}$$

and use the equation

$$a_n(\underline{\lambda}) = c J(\underline{\lambda})\, a_{n-1}(\underline{\lambda}) + \frac{1}{N}\sum_{\underline{\xi}} J(\underline{\xi})\, a_{\underline{\lambda}-\underline{\xi}}\, a_{n-1}(\underline{\xi}) + \begin{cases} 0 & \text{if } n \neq 1 \\ \mu^2 g^2 \left[cN\delta_{\underline{\lambda},\underline{k}} + a_{\underline{\lambda}-\underline{k}} \right] & \text{if } n = 1 \end{cases} \qquad \text{(A2.4)}$$

to obtain successive terms.

Both ways have been used to calculate the expansion (6.42) quoted in the text so as to give some check on the higher terms.

A2.2 A Further Decoupling Approach

The decoupling method was also considered when the functions $A(\underline{\xi}), B(\underline{\xi}), C(\underline{\lambda},\underline{\xi})$ (see Chapter 6 p.72) were not independent. The interdependence occurs because $\sigma_{\underline{n}}$ only has a non zero value for $\underline{n}$ with $p_{\underline{n}} = 1$, and so

$$(1-c)\,\sigma(\underline{\lambda}) = \frac{1}{N}\sum_{\underline{\xi}} \sigma(\underline{\xi})\, a_{\underline{\lambda}-\underline{\xi}}$$

for a particular distribution of spins. This can be rearranged to give

$$\sigma(\underline{\lambda}) = \frac{1}{N}\sum_{\underline{\xi}} \left(cN\delta_{\underline{\lambda},\underline{\xi}} + a_{\underline{\lambda}-\underline{\xi}} \right) A(\underline{\xi}) \qquad \text{(A2.5)}$$

where $A(\underline{\xi})$ is, in fact, equal to $\sigma(\underline{\xi})$. But treating $A(\underline{\xi})$ as an arbitrary function and approximating it by an infinite series in powers of the functions $a_{\underline{\xi}}$, $\sigma(\underline{\lambda})$ can be approximated and a solution found to equation (6.10). If $A(\underline{\xi}) \cong \bar{A}(\underline{\xi}) + \bar{B}(\underline{\xi})\, a_{\underline{\xi}-\underline{k}}$ the problem reduces to the following pair of coupled equations:

$$Z(\underline{\xi})\, Q(\underline{\xi}) = \frac{1}{N}\sum_{\underline{\xi}'} Z(\underline{\xi}') - \alpha_{s\beta}\, c \frac{1}{N}\sum_{\underline{\xi}'} J(\underline{\xi}') Z(\underline{\xi}') + \alpha_{s\beta}(1-c)\frac{1}{N}\sum_{\underline{\xi}'} J(\underline{\xi}+\underline{\xi}'-\underline{k}) Z(\underline{\xi}') \qquad \text{(A2.6)}$$

and $\frac{1}{N}\sum_{\underline{t}} Z(\underline{t})Q(\underline{k}) = \mu g H \alpha_{s\beta} + \alpha_{s\beta}(1-c)\frac{1}{N}\sum_{\underline{t}} J(\underline{t})Z(\underline{t})$

with $Z(\underline{t}) = \frac{1}{N}\sum_{\underline{\lambda}} \bar{\lambda}(\underline{\lambda}) + (1-2c)\frac{1}{N}\sum_{\underline{\lambda}} \bar{B}(\underline{\lambda}) + c\bar{B}(\underline{t})$

From this definition of $Z(\underline{t})$ and the 'definition' of $\sigma(\underline{\lambda})$ by equation (A2.5) it is obvious that $\chi(\underline{\lambda}) = \frac{1}{2}N\delta_{\underline{\lambda},\underline{t}}\mu^2 g^2 \lim_{H\to 0}\frac{1}{H}\frac{1}{N}\sum_{\underline{t}}\frac{Z(\underline{t})}{\mu g}$
This can be used to simplify equations (A2.6) further to give

$$\chi(\underline{\lambda})Q(\underline{k}) = \tfrac{1}{2}\mu^2 g^2 \alpha_{s\beta} c N \delta_{\underline{\lambda},\underline{k}} + \frac{(1-c)}{c}\chi(\underline{\lambda})\left\{\frac{\frac{1}{N}\sum_{\underline{t}}\Delta(\underline{t}) - 1}{\frac{1}{N}\sum_{\underline{t}}\Delta(\underline{t})}\right\} \qquad (A2.7)$$

and $\Delta(\underline{\lambda})Q(\underline{\lambda}) = 1 + \alpha_{s\beta}c(1-c)\frac{1}{N}\sum_{\underline{t}} J(\underline{\lambda}+\underline{t}-\underline{k})\Delta(\underline{t})$; $\Delta(\underline{t}) = \dfrac{Z(\underline{t})}{\frac{1}{N}\sum_{\underline{t}} Z(\underline{t}) - \alpha_{s\beta}c\frac{1}{N}\sum_{\underline{t}} J(\underline{t})Z(\underline{t})}$

The situation is much easier now as only $\frac{1}{N}\sum_{\underline{t}}\Delta(\underline{t})$ is needed to evaluate $\chi(\underline{\lambda})$. The second equation of this set is by no means easy to solve approximately. A variational method can be used successfully, as follows:
Consider the functional,

$$\mathcal{D}(\Delta) = \frac{1}{N^2}\sum_{\underline{t},\underline{t}'}\Delta(\underline{t})\left[2 - Q(\underline{t})\Delta(\underline{t}) + \alpha_{s\beta}(1-c)J(\underline{t}+\underline{t}'-\underline{k})\Delta(\underline{t}')\right] \qquad (A2.8)$$

If the trial function is $\tilde{\Delta}(\underline{t}) = \Delta(\underline{t}) + \delta\Delta(\underline{t})$ (where $\Delta(\underline{t})$ is the actual solution) and we can interchange the orders of integration, $\mathcal{D}(\tilde{\Delta})$ is given by

$$\mathcal{D}(\tilde{\Delta}) = \frac{1}{N}\sum_{\underline{t}}\Delta(\underline{t}) + \frac{1}{N^2}\sum_{\underline{t},\underline{t}'}\delta\Delta(\underline{t})\left[-Q(\underline{t})\delta\Delta(\underline{t}) + \alpha_{s\beta}(1-c)J(\underline{t}+\underline{t}'-\underline{k})\delta\Delta(\underline{t}')\right]$$

If certain conditions of convergence are satisfied by the various integrals involving $\Delta(\underline{t})$ and $\delta\Delta(\underline{t})$

$$\max \mathcal{D}(\tilde{\Delta}) = \frac{1}{N}\sum_{\underline{t}}\Delta(\underline{t}) \qquad (A2.9)$$

and the error in this factor is 0 (square of the error in $\Delta(\underline{t})$)

The simplest trial function for $\Delta(\underline{k})$ would be $\bar{A}/Q(\underline{\lambda})$ which on maximising the functional $\mathcal{D}(\Delta)$ with respect to the constant $\bar{A}$ gives

$$\bar{A} = \frac{\frac{1}{N}\sum_{\underline{k}} \frac{1}{Q(\underline{k})}}{\frac{1}{N}\sum_{\underline{k}} \frac{1}{Q(\underline{k})} - \alpha_s\beta(1-c)\frac{1}{N^2}\sum_{\underline{k},\underline{k}'} \frac{J(\underline{k}+\underline{k}'-\underline{k})}{Q(\underline{k})\,Q(\underline{k}')}}$$

Thus

$$\frac{1}{N}\sum_{\underline{k}}\Delta(\underline{k}) = \frac{\left(\frac{1}{N}\sum_{\underline{k}} \frac{1}{Q(\underline{k})}\right)^2}{\frac{1}{N}\sum_{\underline{k}} \frac{1}{Q(\underline{k})} - \alpha_s\beta(1-c)\frac{1}{N^2}\sum_{\underline{k},\underline{k}'} \frac{J(\underline{k}+\underline{k}'-\underline{k})}{Q(\underline{k})\,Q(\underline{k}')}} \qquad \text{(A2.10)}$$

Using this in the first equation of (A2.7), the correction to the denominator of $\chi(\underline{\lambda})$ caused by including the fluctuations is approximately

$$-\left[\alpha_s^2\beta^2 c\,\frac{1}{N}\sum_{\underline{k}} J^2(\underline{k}) + \alpha_s^3\beta^3 c\,\frac{1}{N^2}\sum_{\underline{k},\underline{k}'} J(\underline{k}+\underline{k}'-\underline{k})\,J(\underline{k})\,J(\underline{k}')\right]$$

for small concentrations. The terms arise when using the first and second methods in the text, respectively.

Appendix 3

Calculation of the Averages needed in the B.P.W. method

In the B.P.W. method, if the graphical approach is used, the averages needed are of the form

$$\left\langle \tau_{\underline{n}}^{(k)} \tau_{\underline{n}+\underline{\ell}_1}^{(k_1)} \tau_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}^{(k_2)} \cdots\cdots \tau_{\underline{n}+\underline{\ell}_1+\cdots+\underline{\ell}_n}^{(k_n)} \right\rangle$$

where

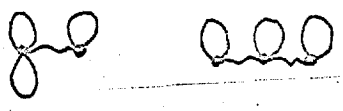
$$\tau_{\underline{n}}^{(k)} = p_{\underline{n}} \sum_{\substack{\text{over all} \\ \text{choices} \\ \underline{\ell}_1 \cdots \underline{\ell}_m \\ m=\sum_i k_i \,;\, z=\sum_i z_i}} \prod_{\underline{\ell}_i=\underline{\ell}_1}^{\underline{\ell}_m} p_{\underline{n}+\underline{\ell}_i} \prod_{\underline{\ell}_{i'}=\underline{\ell}_{m+1}}^{\underline{\ell}_z} (1-p_{\underline{n}+\underline{\ell}_{i'}})$$

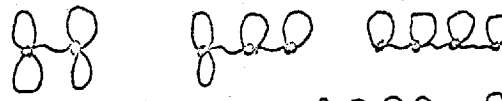
and the m values $\underline{\ell}_1 \ldots \underline{\ell}_m$ are partitioned so that k_j of the site labels $\underline{n}+\underline{\ell}_i$ belong to the j^{th} co-ordination shell.

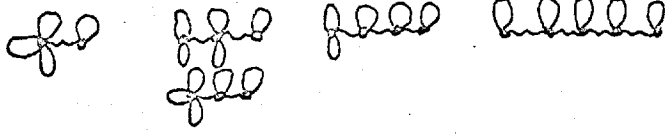
The various contributions to the above average can be represented by the following diagrams. Any of the factors $\tau_{\underline{n}}^{(k)}$ are represented by ○ and if two τ-factors are described by the same site value they are said to have been contracted and are represented as 8 . Any two sets of factors which are not contracted are joined in the diagrams by a bond ∼∼. The number of τ-factors is the order of the average. The diagrams for the first few orders are:

1st order, 

2nd order, 

3rd order, 

4th order 

5th order 

etc.

The importance of this representation is that the leading power in concentration is equal to the number of bonds in the diagram. So for a small-concentration theory we must sum vertically i.e. summing the series of all diagrams with 1 bond, then 2 bonds etc. Near $c=1$ we must improve the approximation by increasing the number of orders of averages taken into account exactly; and the way of summing these orders is to treat them as a rearranged geometric series

A3.1 Nearest Neighbour Interactions

We now consider first the calculation of the first few orders of averages for the simple cubic lattice, and nearest neighbour interactions.

The first order average is easy to evaluate. As there are k nearest neighbour spins the number of p-factors is $k+1$, and the number of $(1-p)$-factors is $z-k$. Hence the concentration factor is $c^{k+1}(1-c)^{z-k}$ and as there are $\frac{z!}{k!\,(z-k)!}$ such terms in the definition of $\Phi_{\underline{m}}^{(k)}$ the first order average is

$$\frac{z!}{k!\,(z-k)!}\; c^{k+1}\,(1-c)^{z-k}$$

The second order average is also easily evaluated, as only the central atoms of the cluster overlap. It has the value,

$$\frac{(z-1)!}{(k-1)!\,(z-k)!}\,\frac{(z-1)!}{(k'-1)!\,(z-k')!}\,c^{k+k'}(1-c)^{2z-k-k'}$$

where k,k' are the number of nearest neighbour spins in the 1^{st}, 2^{nd} clusters respectively.
The exponent of c is only $k+k'$ because two spins overlap.

In the third order we have two diagrams and  is considered first.
The two contracted ψ-factors must have the same number of nearest neighbour spins. So the contribution from

$$\langle \psi_{\underline{n}}^{(k)} \psi_{\underline{n}+\underline{\ell}_1}^{(k')} \psi_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}^{(k'')} \rangle \quad \text{is} \quad \delta_{\underline{\ell}_1+\underline{\ell}_2,0}\,\delta_{k,k''} \langle \psi_{\underline{n}}^{(k)} \psi_{\underline{n}+\underline{\ell}_1}^{(k')} \rangle :$$

thus the contribution from the diagram  is

$$\delta_{\underline{\ell}_1+\underline{\ell}_2,0}\,\delta_{k,k''}\,\frac{(z-1)!}{(k-1)!\,(z-k)!}\,\frac{(z-1)!}{(k'-1)!\,(z-k')!}\,c^{k+k'}(1-c)^{2z-k-k'}$$

The other third order diagram is . The contribution from this diagram can be separated for the simple cubic lattice into two contributions, depending on whether $\underline{\ell}_1 = \underline{\ell}_2$ or $\underline{\ell}_1 \neq \underline{\ell}_2$. When $\underline{\ell}_1 = \underline{\ell}_2$ the contribution to $\langle \psi_{\underline{n}}^{(k)} \psi_{\underline{n}+\underline{\ell}_1}^{(k')} \psi_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}^{(k'')} \rangle$ is,

$$(1-\delta_{\underline{\ell}_1+\underline{\ell}_2,0})\,\delta_{\underline{\ell}_1,\underline{\ell}_2}\,\frac{(z-1)!}{(k-1)!\,(z-k)!}\,\frac{(z-2)!}{(k'-2)!\,(z-k')!}\,\frac{(z-1)!}{(k''-1)!\,(z-k'')!}\,c^{k+k'+k''-1}(1-c)^{3z-k-k'-k''}$$

as only sites with spins on them overlap.
The remaining contribution $(\underline{\ell}_1 \neq \underline{\ell}_2)$ is slightly more difficult to evaluate, as two of the clusters overlap at site A (see Diagram A3.1)

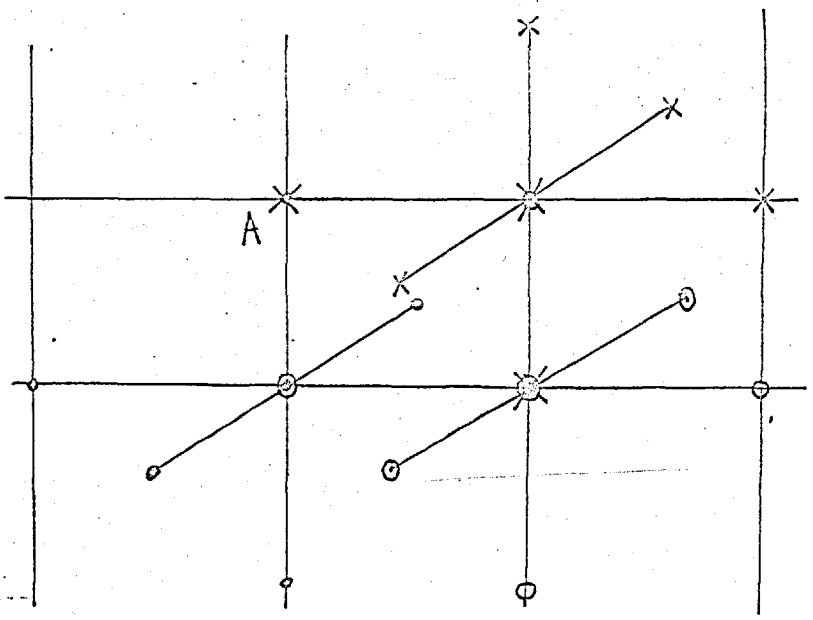


Diagram A3.1 The overlap of three clusters for the simple cubic lattice.

If C_k^z denotes $\frac{z!}{k!\,(z-k)!}$ the contribution from $\sum\sum(\underline{\ell}_1 \neq \underline{\ell}_2)$ is, in fact,

$$(1-\delta_{\underline{\ell}_1,\underline{\ell}_2}-\delta_{\underline{\ell}_1+\underline{\ell}_2,0})\Big\{ C_{k-2}^{z-2} C_{k'-2}^{z-2} C_{k''-2}^{z-2}\, c^{k+k'+k''-2}(1-c)^{3z-k-k'-k''} + C_{k-1}^{z-2} C_{k'-2}^{z-2} C_{k''-1}^{z-2}\, c^{k+k'+k''-1}(1-c)^{3z-k-k'-k''-1}\Big\}$$

The first of these expressions gives the value when a factor $(1-p_A)$ is associated with site A, the second when a factor p_A is associated with site A .

Now consider the even more difficult case of the four factor average $\langle \psi_{\underline{n}}^{(k)} \psi_{\underline{\ell}+\underline{\ell}_1}^{(k_1)} \psi_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}^{(k_2)} \psi_{\underline{\ell}+\underline{\ell}_1+\underline{\ell}_2+\underline{\ell}_3}^{(k_3)} \rangle$. The contribution from $\sum\sum\sum$ is, obviously,

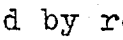
$$\delta_{\underline{\ell}_1+\underline{\ell}_2,0}\delta_{\underline{\ell}_2+\underline{\ell}_3,0}\delta_{k_1,k_2}\delta_{k_1,k_3}\langle \psi_{\underline{n}}^{(k)} \psi_{\underline{n}+\underline{\ell}_1}^{(k_1)} \rangle$$

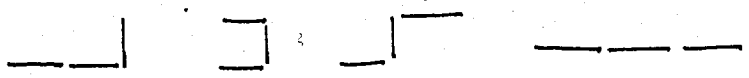
and that from $\sum\sum\sum\sum$ is

$$\delta_{\underline{\ell}_1+\underline{\ell}_2,0}\,\delta_{k_1,k_2}\langle \tau_{\underline{n}}^{(k)}\tau_{\underline{n}+\underline{\ell}_1}^{(k_1)}\tau_{\underline{n}+\underline{\ell}_3}^{(k_3)}\rangle + \delta_{\underline{\ell}_1+\underline{\ell}_2+\underline{\ell}_3,0}\,\delta_{k_1,k_3}\langle \tau_{\underline{n}}^{(k)}\tau_{\underline{n}+\underline{\ell}_1}^{(k_1)}\tau_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}^{(k_2)}\rangle$$

$$+\ \delta_{\underline{\ell}_2+\underline{\ell}_3,0}\,\delta_{k_1,k_3}\langle \tau_{\underline{n}}^{(k)}\tau_{\underline{n}+\underline{\ell}_1}^{(k_1)}\tau_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}^{(k_2)}\rangle$$

In the simple cubic lattice $\underline{\ell}_1+\underline{\ell}_2+\underline{\ell}_3=0$ is impossible for nearest neighbour vectors and so the central term is zero. The first term is apparently a new average but it is identical in value to $\langle \tau_{\underline{n}}^{(k_2)}\tau_{\underline{n}-\underline{\ell}_2}^{(k)}\tau_{\underline{n}+\underline{\ell}_1-\underline{\ell}_3}^{(k_1)}\rangle$ since the sites can be translated by the vector $\underline{\ell}_3$.

The contribution from the diagram  can be further separated by representing the different choices of the nearest neighbour vectors by new diagrams as follows:-



These occur $\delta_{,k},12,1$ times respectively. The directions of the bonds with respect to each other represent the relative directions of $\underline{\ell}_1, \underline{\ell}_2, \underline{\ell}_3$. Defining the following functions, the contributions from the diagrams can be obtained:-

$$A(1,\underline{k}) = a(k)\,C_{k-1}^{z-1}\ ;\ A(2,k) = a(k)\,C_{k-3}^{z-3}\ ;\ A(3,k) = a(k)\,C_{k-2}^{z-3}\ ;$$
$$A(4,k) = a(k)\,C_{k-2}^{z-2}\ ;\ A(5,k) = a(k)\,C_{k-1}^{z-2}\ ;\ a_{4,k}) = c^{k+1}(1-c)^{z-k}$$

 $\rightarrow A(1,k)\,A(4,k'')\left[A(2,k')\,A(4,k''')/c + A(3,k')\,A(5,k''')/(1-c)\right]c^{-b}$

 $\rightarrow A(4,k)\,A(4,k')\,A(4,k'')\,A(4,k''')/c^8$

 $\rightarrow A(1,k)\,A(4,k')\,A(4,k'')\,A(1,k''')/c^6$

 $\rightarrow \left[A(4,k)\,A(2,k'')/c + A(5,k)\,A(3,k'')/(1-c)\right]$

$$\times\left[A(4,k''')\,A(2,k')/c + A(5,k''')\,A(3,k')/(1-c)\right]/c^6$$

For other lattices these types of averages can also be calculated. For the body centred cubic lattice ($z=8$) the first two orders have formulae identical to those of the simple cubic lattice case, but $\langle \tau_{\underline{n}}^{(k)} \tau_{\underline{n}+\underline{\ell}_1}^{(k')} \tau_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}^{(k'')} \rangle$ is changed. In the simple cubic case the diagrams for this average are of three types, for $\underline{\ell}_1=\underline{\ell}_2$, $\underline{\ell}_1+\underline{\ell}_2=0$ and other combinations. For the body centred cubic lattice this last group must be further divided because the choices $\underline{\ell}_2=(-1,1,1)$ and $\underline{\ell}_2=(-1,-1,1)$ give different overlaps between the clusters centred on $\underline{n}$ and $\underline{n}+\underline{\ell}_1+\underline{\ell}_2$ (we assume $\underline{\ell}_1=(1,1,1)$). The first of these choices would mean an overlap of only two sites, while the second would mean an overlap of 4 sites. The corresponding contributions are,

$$\sum_{\alpha=0}^{2} c^{k+k'+k''-1-\alpha}(1-c)^{3z-k-k'-k''-2-\alpha} C_{\alpha}^{2} C_{k-1-\alpha}^{z-3} C_{k'-2}^{z-2} C_{k''-1-\alpha}^{z-3}$$

and

$$\sum_{\alpha=0}^{4} c^{k+k'+k''-1-\alpha}(1-c)^{3z-k-k'-k''-4-\alpha} C_{\alpha}^{4} C_{k-1-\alpha}^{z-5} C_{k'-2}^{z-2} C_{k''-1-\alpha}^{z-5}$$

where the sums over α account for the various distributions of spins over the sites common to the 1^{ST} and 3^{RD} clusters.

The higher order averages are also much changed and because of the added complication these have not been treated yet.

For the face centred cubic lattice even the second order diagram gives a complicated contribution,

$$\sum_{\alpha=0}^{4} c^{k+k'-\alpha}(1-c)^{2z-k-k'-4+\alpha} C_{\alpha}^{4} C_{k-1-\alpha}^{z-5} C_{k'-1-\alpha}^{z-5}$$

as the two clusters overlap at four sites other than the central atoms. The higher orders have not been considered.

A3.2 Longer Range Interactions

One of the reasons for using this approximate theory was to introduce longer range interactions. This has formally been done in Chapter 7, but the calculation of the averages for such a theory is very difficult. As can be seen from the evaluation of the previous averages a description of the overlaps between clusters must be found. The average over just two clusters can be characterised by a two dimensional array of numbers for each co-ordination ring in one of the clusters, and so the difficulties increase rapidly with the range of the interaction.

Further, when the average is over three clusters we also need three dimensional arrays of numbers to represent the number and type of sites common to all three clusters; and the number of two dimensional arrays needed becomes greater than the number of co-ordination rings in a cluster. As an example we consider the simple cubic lattice and next nearest neighbour interactions:

When the 2^{nd} order diagram is considered two cases occur; one when $\underline{\ell}_1$ is a nearest neighbour vector, and the second when $\underline{\ell}_1$ is a next nearest neighbour vector. In each case we define an array of numbers $\{x_{nm}\}$ where n,m vary from 1 to 3, and these are

$$X = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 4 \\ 0 & 4 & 0 \end{pmatrix} \qquad Y = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 2 & 0 \\ 1 & 0 & 4 \end{pmatrix}$$

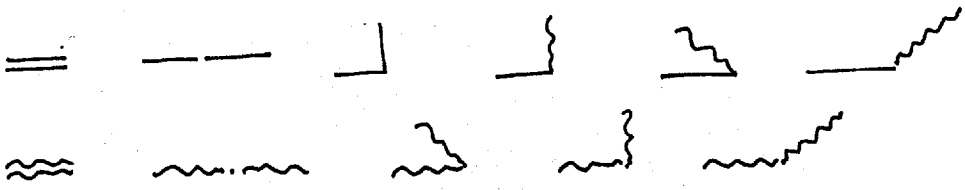
The sum of the numbers in the n^{th} row is the total number of sites in the $(n-1)^{th}$ co-ordination ring of the 1^{st} cluster which are common to the 2^{nd} cluster. Similarly the m^{th} column is concerned with the $(m-1)^{th}$ co-ordination ring of the 2^{nd} cluster. Thus, the element x_{nm} is the

number of sites common to the $(n-1)^{th}$ co-ordination ring of the 1^{st} cluster, and the $(m-1)^{th}$ co-ordination ring of the 2^{nd} cluster. Each of the numbers x_{nm} (if it is non-zero) denotes a region of sites which must be considered separately and will give rise to a sum over α of the type found previously in dealing with the body-centred and face-centred cubic lattices. Therefore, the contribution from $\langle \tau_n^{(k)} \tau_{n+\underline{\ell}_1}^{(k')} \rangle$ when $\underline{\ell}_1$ is a nearest neighbour vector is

$$\sum_{\alpha=0}^{4}\sum_{\gamma=0}^{4} c^{k_1+k_2+k_1'+k_2'-1-\alpha-\gamma}(1-c)^{2z_1+2z_2-k_1-k_2-k_1'-k_2'-8+\alpha+\gamma} \times C_\alpha^4 C_\gamma^4 C_{k_1-1-\alpha}^{z_1-4+\alpha-1} C_{k_1'-1-\gamma}^{z_1-4+\gamma-1} C_{k_2'-\alpha}^{z_2-4+\alpha} C_{k_2-\gamma}^{z_2-4+\gamma}$$

For the general case, for each x_{nm} with $n\neq 1$ and $m\neq 1$ a summation will be introduced, so we denote the variable for this summation by α_{nm} and then the weight for each term is constructed by introducing $C_{\alpha_{nm}}^{x_{nm}}$ for each x_{nm} if $n\neq 1, m\neq 1$ and $C_{k_{m-1}-\sum_n' \alpha_{mn}}^{z_{m-1}-\sum_n'(x_{mn}-\alpha_{mn})-\alpha_{m1}}$ for each co-ordination ring of each cluster $(m>1)$. The summation $\sum_n'$ excludes $n=1$ from the summation $\sum_n$ and a single suffix n denotes that the quantity is associated with the n^{th} co-ordination ring of one of the clusters. The concentration factor is $c^{\Delta}(1-c)^{\Phi}$ where $\Phi = \sum_{m=1}^{M}\left(2z_m - k_m - k_m' - \sum_{n=2}^{M}(x_{mn}-\alpha_{mn})\right)$, $\Delta = \sum_{m=1}^{M}\left(k_m+k_m'-\sum_n \alpha_{mn}\right)-1$ and M is the number of co-ordination rings in the cluster. M such combinations would have to be used and it is easy to see that the evaluation of even this average could become unwieldy. Using the diagrams introduced to deal with the 4^{th} order average for nearest neighbour interactions, the second order average for next nearest neighbour interactions would be represented by —— and ~~~; the second diagram's bond represents $\underline{\ell}_1$ as a next nearest neighbour vector. Similarly, the third order

average would be represented by the eleven diagrams



For each of these diagrams we need the arrays X and Y as well as a two dimensional array to describe the overlap between the 1ST and 3RD clusters and a three dimensional array to describe the sites common to all three clusters. As an example, consider the last of these diagrams. The clusters are centred on $(0,0,0)$, $(1,1,0)$,and $(2,1,1)$ respectively. The first and third clusters have two sites in common, $(1,0,1)$ and $(1,1,0)$. The overlap of all clusters can be represented by two arrays: the first represents the number and type of sites common to the first and second clusters which are nearest neighbour sites in the third cluster; the second represents those sites which are next nearest neighbours in the third cluster. The arrays for the last diagram are

$$X_1 = \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \quad , X_2 = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}$$

as only the site $(1,0,1)$ is common to all clusters and it is a next nearest neighbour site in all the clusters. Thus, the contribution to $\langle \uparrow_{\underline{n}}^{(k)} \uparrow_{\underline{n}+\underline{\ell}_1}^{(k')} \uparrow_{\underline{n}+\underline{\ell}_1+\underline{\ell}_2}^{(k'')} \rangle$ from ~~~ is the rather complicated expression

$$\sum_{\substack{\alpha,\gamma,\alpha',\alpha'' \\ \gamma',\gamma''}} C_\gamma^3 C_\alpha^2 C_{\alpha'}^2 C_{\gamma'}^3 C_{\alpha''}^1 C_{\gamma''}^1 C_{k_1-\alpha}^{z_1-2-\alpha} C_{k_1'-\alpha-\alpha'}^{z_1-4+\alpha+\alpha'} C_{k_1''-\alpha'}^{z_1-2-\alpha'}$$

$$\times C_{k_2'-\gamma_1-\gamma'-\gamma''-2}^{z_2-8+\gamma+\gamma'+\gamma''} C_{k_2-\gamma-\gamma''-1-\alpha''}^{z_2-6+\gamma+\gamma''+\alpha''} C_{k_2''-\gamma'-\gamma''-\alpha''-1}^{z_2-6+\gamma'+\gamma''+\alpha''}$$

$$\times C^4 (1-c)^{\Phi}$$

with $$\Delta = k_1+k_1'+k_1''+k_2+k_2'+k_2''-1-\alpha-\alpha'-\alpha''-\gamma-\gamma'-2\gamma''$$

$$\oplus = 3z_1+3z_2-k_1-k_1'-k_1''-k_2-k_2'-k_2''-13+\alpha+\alpha'+\alpha''+\gamma+\gamma'+2\gamma''$$

It would seem possible to evaluate the contribution from the other diagrams without great difficulty, but for any other long range interaction the number of diagrams will increase rapidly. The dimension of the arrays will also increase and thus make their evaluation much more difficult.

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