

elaboration of the D. A. model. Such models have been proposed by Lax¹⁷ and by Cowley,⁷ but both appear to involve a considerable number of disposable parameters, and the problem of parameter determination still remains.

¹⁷M. Lax, Phys. Rev. Letters **1**, 133 (1958); and Bull. Am. Phys. Soc. **4**, 181 (1959).

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Statistical Mechanics of Dilute Copper Manganese*†

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The low-temperature specific heat and magnetic susceptibility for dilute concentrations of manganese in copper are studied, using the "statistical model" of Margenau and an expansion of the partition function in a power series of the concentration. An indirect "Ising model" interaction via the conduction electrons is assumed to exist between the magnetic impurities. To find a correction to the statistical model, the two-particle correlation function between impurities is derived in the limit as the temperature approaches zero. It is shown that, in this limit, the system is composed of small clusters of spins that are strongly correlated to each other within a cluster, but various clusters are randomly oriented relative to each other. An impurity within one of these clusters finds itself in an "effective field" arising from the other spins within the cluster and from the random orientation of all spins outside the cluster. This field is a random variable and its probability distribution is easily obtained from the model. The detailed shape of the probability distribution of the field is given for a particular concentration. As the temperature is increased, the internal structure of the clusters is broken up and, at high temperatures, the system exhibits paramagnetic behavior. The theory predicts correctly the experimental low-temperature specific heat and magnetic susceptibility of dilute Cu-Mn.

INTRODUCTION

RECENT experimental studies on dilute concentrations of manganese in copper have revealed several interesting and unusual phenomena. Measurements of the magnetization as a function of temperature¹⁻⁴ have shown a maximum in the low-temperature magnetic susceptibility. This maximum occurs at a temperature approximately proportional to the impurity concentrations and is found at 13 and 40°K for a 1.4 and 5.6 at.% Mn, respectively. The existence of

the susceptibility maximum was interpreted¹ to be a gradual transition to antiferromagnetism as the temperature is lowered; others⁵ suggested that the system may be composed of small ferromagnetic domains aligned antiferromagnetically. The high-temperature paramagnetic susceptibility obeys the Curie-Weiss law with positive temperature intercept characteristic of a ferromagnetic interaction and indicates that the magnetic moment of Mn is close to 5 Bohr magnetons. The system also exhibits remarkable low-temperature specific heat anomalies. Measurements by Zimmerman and Hoare^{6,7} have shown that the alloys exhibit a large excess specific heat compared with that of pure copper, the excess being independent of the Mn concentration and increasing linearly with temperature. To explain

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Zimmerman's results, Overhauser⁸ has postulated a new mechanism for antiferromagnetism involving the concept of a static-spin density wave in the conduction band. Herring⁹ and Marshall¹⁰ suggested that Zimmerman's result can be explained by the well-known interaction derived by Ruderman-Kittel,¹¹ Kasuya,¹² Yosida,¹³ and Blandin and Friedel¹⁴ (in this paper called the Ruderman-Kittel interaction). Marshall¹⁰ has qualitatively explained the specific heat anomaly in terms of the Ruderman-Kittel interaction and has pointed out some objection to the Overhauser mechanism.

In this paper, we show that the Ruderman-Kittel interaction, using the Ising model, accounts for the measured magnetic behavior of dilute Cu-Mn over the temperature range starting from $T=0$ up to and including the high-temperature paramagnetic region.

A brief outline of the paper is as follows. In Sec. 2 we write the form of the partition function for a single spin in terms of the probability distribution of the effective field, $P(H)$, seen by an impurity at some origin due to all other impurities distributed randomly over the volume of the crystal. To find the probability distribution we first neglect all spin correlations between the impurities. In this approximation, following Anderson,¹⁵ we show that the distribution function is a Lorentzian with width proportional to the concentration. Upon properly excluding large fields that come from impurities close to the origin, the distribution function becomes a Gaussian, again with width proportional to the concentration. In order to get a correction to $P(H)$ we wish to obtain the two-particle spin correlation function $\langle \mu_i \mu_j \rangle$. With this in mind in Sec. 3, we expand the partition function diagrammatically in a power series in the impurity concentration, sum the diagrams and perform averages over spins for low enough concentration such that no long-range order is sustained in the solid. The partition function is evaluated exactly up to and including the fourth virial coefficient (3rd power in the concentration), and approximately for higher virial coefficients. It is shown that in a certain approximation the two-particle correlation function $g(r_{12})$, may be expressed as a power series in $cz(r)$, where c is the fractional impurity concentration and $z(r)$ is the number of sites included within some radius $r=R_c$, where R_c is a correlation length to be defined later, and that $g(r_{12})$ decreases rapidly with the radius r_{12} for $cz(r_{12}) < 1$.

Using the cluster expansion method to estimate the function $g(r_{12})$ for $r > R_c$ leads to serious difficulties, since in our approximation $g(r_{12})$ is zero for $r_{12} = R_c$ and

increases proportionally to r^3 for $r_{12} > R_c$, thus increasing indefinitely with r , a result that is a physical absurdity. This difficulty is traced back to the fact that the part of the expansion of the partition function in a power series of the concentration which we have retained has a limited radius of convergence for long-range potentials. To find how the strength of the correlation varies for $r > R_c$, we solve for $g(r_{12})$ by a completely different technique using a self-consistent method which can be linearized for large r_{12} . This is done in Sec. 4.1. Upon extension of this solution to the region inside the correlation radius R_c , we find that the two solutions for the inside and outside regions agree to within a few percent at $r_{12} = R_c$. Thus, we get the important result that impurities are fully or partially correlated to the spin at the origin if they are located within some correlation radius R_c and are approximately randomly oriented if they are located outside of R_c . The field at the origin is, therefore, to a good approximation, the sum of two independent contributions, each of which has its own probability distribution.

Using the corrected probability distribution to evaluate the single-particle partition function, we not only get a much better agreement with the experimental specific heat data,^{15a} but we are also able to derive the variation of the magnetic susceptibility with temperature.

The idea involved in the latter is very simple in terms of the correlation length worked out in Sec. 3, and it involves something that might be termed a random antiferromagnet. The solid is made up of small clusters of impurities (on the average about 3.3) interacting with each other via the Ruderman-Kittel potential. At low temperatures, the spins within a cluster are strongly correlated to the spin at the origin and the impurities within a cluster act in unison to give an effective spin per particle which is smaller than the free ion spin. As the temperature is increased, two competing processes occur. One, the clusters are randomized resulting in a decrease in the susceptibility; two, the internal structure of the clusters breaks up thus increasing the effective spin per impurity and the susceptibility. At low temperatures the second of these is predominant and becomes less important with increasing temperatures when most of the spins in a cluster (i.e., the internal degrees of freedom of the cluster) are already randomized. At very high temperatures all the spins act independently of each other and the susceptibility equals the paramagnetic free gas susceptibility.

Next, we indicate qualitatively what concentrations are necessary for long-range order. It is found that no long-range order exists for concentrations of 0.05 to 5%, the concentrations treated in this paper. Finally, we discuss the validity of some of the approximations used in this work.

^{15a} Note added in proof. Since then one of us (M.W.K.) was able to show that the low-temperature specific heat of Cu-Co and Cu-Fe can also be explained using a Ruderman-Kittel interaction.

⁸ A. W. Overhauser, Phys. Rev. Letters **3**, 414 (1959).

⁹ C. Herring (private communications from R. Brout, 1959).

¹⁰ W. Marshall, Phys. Rev. **118**, 1520 (1960).

¹¹ M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954).

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¹⁵ P. W. Anderson (private communication through R. Brout and Bell Telephone Laboratories).

2. THE FIELD ABOUT AN IMPURITY FROM RANDOMLY ORIENTED SPINS

As mentioned in the introduction, we investigate the thermodynamic functions of a sample containing dilute concentrations of magnetic impurities randomly distributed in a nonmagnetic host lattice where an indirect exchange interaction of the Ruderman-Kittel type is assumed to exist between the impurities. These functions can be obtained by differentiating $\log Z$ with respect to various parameters, where Z is the partition function for the system.

$$Z = \sum_{\text{all states}} \exp(-\beta \mathcal{H}) \quad (2.1)$$

and $\beta = 1/k_B T$, k_B is the Boltzmann factor, T is the temperature in degrees Kelvin, and \mathcal{H} is the Hamiltonian

$$\mathcal{H} = \sum_{i < j} v_{ij} \mu_i \mu_j. \quad (2.2)$$

v_{ij} is the Ruderman-Kittel potential given by Yosida,¹³ μ_i is the spin associated with an impurity at position r_i , and may take values of ± 1 in the Ising model. For convenience we deal with the Ising model rather than the presumably more correct isotropic Heisenberg model. In physical content the latter is different from the former in case it is possible to propagate spin waves. However, at low concentrations there is no long-range order and, therefore, spin waves are not possible. In this model Yosida's expression becomes

$$v_{ij} = |S_i| |S_j| \left(\frac{3n}{N} \right) \frac{2\pi}{E_F} [J(0)]^2 \times \frac{2k_F r_{ij} \cos 2k_F r_{ij} - \sin 2k_F r_{ij}}{r_{ij}^4}. \quad (2.3)$$

(n/N) , E_F , k_F , and $|S_i|$ and $J(0)$ are the number of conduction electrons per atom, the Fermi energy, the Fermi wave vector, the magnitude of the impurity spins and the strength of the s - d interaction, respectively. For Cu-Mn, the smallest value of $2k_F r_{ij}$ is 6.92. We thus drop the $\sin 2k_F r_{ij}$ from (2.3) and we have the approximate expression

$$v_{ij} = a(\cos kr_{ij}/r_{ij}^3), \quad (2.4)$$

where $k = 2k_F$ and $a = 24.8^\circ \text{K} - d^3$, d is the dimensionless lattice constant for copper and r_{ij} is measured in units of the lattice constant. The value of a was calculated using $J(0)$ from Refs. 2 and 13. In principle, we can obtain the partition function by evaluating (2.1) directly, in all probability an impossible task. We therefore adopt the point of view expressed in the introduction and approach the problem in successive stages. We first ignore completely the spin-spin correlation that the interaction (2.2) implies and examine the effective field distribution in a purely random distribution of impurities with random spin orientations; i.e., $\mu_i = \pm 1$ equally

likely. Sections 3 and 4 are devoted to correcting this assumption. In the end, the qualitative results of the random calculation still survive in large measure.

Proceeding with the random spin calculation, we first evaluate the probability distribution $P(H)$ of the field H about an impurity and then calculate the mean free energy per particle according to

$$\ln Z(\beta) = \int_{-\infty}^{\infty} P(H) \ln Z(\beta, H) dH, \quad (2.5)$$

where $P(H)$ is the normalized probability distribution of the field. The method is then that of the molecular field where the molecular field is a random variable. Since there is no long-range order, the average field is zero.

$$\ln Z(\beta, H) = \ln \sum_{\mu = \pm 1} e^{-\beta H \mu} = \ln \cosh \beta H + \ln 2. \quad (2.6)$$

To find $P(H)$ we use the so-called statistical model developed by Margenau¹⁶ and applied to dipole-dipole interactions by Anderson.¹⁵

We consider a crystal having N impurities distributed on N_0 sites such that $N/N_0 = c$, where c is the fractional concentration. The position coordinate, r , of each impurity is an independent random variable uniformly distributed over the volume of the crystal V with probability $1/V$. With each impurity i we have associated a random spin variable μ_i which in the Ising model can take values of ± 1 with a probability that generally is a function of the temperature. However, for the moment, we will assume the spins to be randomly oriented and proceed with the calculation. We define the field at impurity i to be

$$H_i = \sum_j v_{ij} \mu_j, \quad (2.7)$$

and thus calculate the probability distribution of the field $P(H)$ about an impurity i . Without going into details, we quote the results of Anderson¹⁵ as applied to our problem.

$$\begin{aligned} P(H) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\rho H} d\rho \left[\frac{1}{2V} \sum_{\mu = \pm 1} \int_V e^{i\rho v(r)\mu} d^3r \right]^N \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-i\rho H} d\rho \left[1 - \frac{4V'c}{N} \right]^N \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-4V'c} e^{-i\rho H} d\rho, \end{aligned} \quad (2.8)$$

where c is the concentration, there are 4 sites per unit cell in an fcc lattice, hence, the factor of 4 and

$$V' = \frac{4\pi}{V} \int_0^{\infty} \left[1 - \cos \left\{ \frac{\rho a \cos kr}{r^3} \right\} \right] r^2 dr. \quad (2.9)$$

¹⁶ H. Margenau and W. Watson, Rev. Mod. Phys. 8, 22 (1936).

Replacing the value of $a \cos kr$ in the integrand by some average value, α , to be determined later and substituting the result of (2.9) in (2.8) gives

$$P(H) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp(-i\rho H) \exp[-(16\pi/3)c\alpha|\rho|] d\rho$$

$$= -\frac{H_0}{\pi H_0^2 + H^2}, \quad (2.10)$$

where $H_0 = (16\pi^2/6)c\alpha$. We note the important result that the width of the Lorentzian is proportional to the concentration in agreement with the qualitative arguments of Marshall.

In deriving Eq. (2.8) it was assumed that the impurities could take up a continuous range of distances from the one located at the origin. This assumption leads to the wrong conclusion that none of the moments of the distribution function (2.10) exist. This is not the case because the lattice is discrete, the most important consequence of this is that there is a finite "minimum distance" between the impurities resulting in a cutoff of the wings of the distribution function. Again, following Anderson, we may idealize the minimum distance problem by letting the distribution of the impurity distances be continuous, but place upon it the limitation that two impurities cannot approach closer than a minimum distance r_0 , where r_0 will be determined later. Thus, the maximum field from a single impurity is given by $(a \cos kr_0)/(r_0^3)$ where a is the strength of the potential.

All previous equations remain valid, except (2.9) which we modify by excluding the volume close to the origin. The expression for V' in Eq. (2.9) becomes

$$V' = \frac{4\pi}{V} \int_{r_0}^{\infty} \left[1 - \cos \frac{\rho\alpha}{r^2} \right] r^2 dr = \frac{4\pi}{3} \rho\alpha \varphi(Q), \quad (2.11)$$

where $Q = (\rho\alpha/r_0^3)$ and

$$\varphi(Q) = \frac{\cos Q - 1}{Q} + \int_0^Q \frac{\sin Q_0}{Q_0} dQ_0. \quad (2.12)$$

We see that the shape of the distribution function is still not easily obtained and (2.8) must be done by using approximations on (2.12). We let

$$\begin{aligned} \varphi(Q) &= \frac{1}{2}Q; & Q < \frac{3}{4}\pi, \\ \varphi(Q) &= \frac{1}{2}\pi - (1/Q); & Q > \frac{3}{4}\pi. \end{aligned} \quad (2.13)$$

A graphical comparison of the approximation (2.13) with the function $\varphi(Q)$ shows very good agreement between the two. Using (2.13) and (2.11) in (2.8) gives

$$P(H) = \frac{r_0^3}{2\pi s\alpha} \int_{-\frac{3}{4}\pi s}^{\frac{3}{4}\pi s} dx \exp\left(-ix \frac{Hr_0^3}{\alpha s} - \frac{x^2}{2}\right)$$

$$+ \frac{r_0^3}{\pi\Gamma\alpha} \int_{(\frac{3\pi}{4})\Gamma}^{\infty} dx \cos\left[\frac{Hr_0^3 x}{\Gamma s}\right] \exp\left[\frac{2}{\pi}\Gamma - x\right], \quad (2.14)$$

where $s = [(16\pi/3)(cr_0^3)]^{1/2}$ and $\Gamma = (8\pi^2/3)(cr_0^3)$. The parameters r_0 and α still remain to be determined. At this point we choose a cutoff radius r_0 which is determined by our subsequent statistical argument. We will show in Sec. 4 that the proper r_0 to be used in (2.14) is given by $r_0 = R_c = 0.514c^{-1/3}d$, where d is the dimensionless lattice constant and R_c is a correlation length to be derived later. With this value of r_0 the limits on both integrals become independent of the concentration, $\frac{3}{4}\pi s = 3.54$, and the second integral in (2.14) contributes less than $\exp(-5.6)$. The probability distribution becomes

$$P(H) \sim (2\pi\sigma^2)^{-1/2} \exp\left[-\frac{1}{2}(H^2/\sigma^2)\right], \quad (2.15)$$

with $\sigma = [16\pi/3(cr_0^3)]^{1/2}c\alpha$. Equation (2.15) is the central result of this section. The probability distribution is a Gaussian with width proportional to the concentration and the essential point of Herring and Marshall that $P(H=0) \propto 1/c$ is maintained. It remains to discuss the value of α which is the average value of $a \cos kr$ in Eq. (2.9). If the cosine is expanded in (2.9) and we integrate from r_0 to ∞ , we find that convergence is good and $\alpha = a/\sqrt{2}$ is then a good approximation.

We now make a rough calculation of the low-temperature specific heat from a set of randomly oriented impurities whose probability distribution and width is given by (2.15).

$$C_v = -\frac{1}{2} \frac{N_0 c}{k_B T^2} \frac{\partial^2}{\partial \beta^2} \int_{-\infty}^{\infty} P(H) \ln Z(\beta, H) dH$$

$$= \frac{N_0 c}{2(2\pi)^{1/2} k_B T^2 \sigma} \int_{-\infty}^{\infty} H^2 dH \operatorname{sech}^2 \beta H$$

$$\times \exp\left[-\frac{H^2}{2\sigma^2}\right], \quad (2.16)$$

where $\ln Z(\beta, H)$ is given by (2.6) and the factor of $\frac{1}{2}$ arises from the self-consistent field calculation. We evaluate (2.16) for the case of $\beta \gg 1/\sigma$ using an asymptotic expansion. The specific heat is approximately $(C_v/T) = 1.7 \times 10^{-2}$ J/mole-deg. We thus find that the specific heat goes linearly with temperature, is independent of the concentration, and C_v/T has an intercept of 1.7×10^{-2} J or approximately three times the experimental result. At this point we should recall that except for the cutoff r_0 we have neglected correlations between the impurities. We will find that by including the effect of correlation not only do we get closer agreement between the theoretical and experimental specific heats but also obtain the magnetic properties of the system.

3. THE TWO-PARTICLE CORRELATION FUNCTION: CLUSTER METHOD

We wish to expand the free energy of a system of randomly distributed impurities in a power series of the impurity concentration. We associate with each impurity j two random variables, the position coordinates

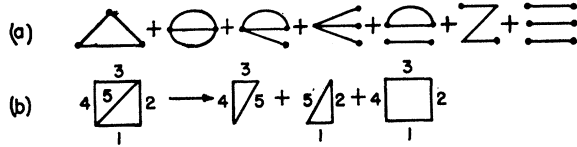


FIG. 1. (a) Diagrams contributing to the third semi-invariant. (b) Rings of ladders arising from the 4 vertex 5 ladder diagram.

r_j and the spin μ_j . To obtain the free energy, averages are performed over spin as well as spatial configurations, and care has to be exercised in the order of which these averages are performed. We are interested in a random sample with frozen-in spatial configurations; i.e., in a specific nonequilibrium situation. It is desired first to calculate the spin sum in the partition function (since the spin system is assumed to be in thermal equilibrium) and then average the logarithm of this quantity over all random spatial configurations. In short, we must calculate the mean free energy averaged over configuration space. The importance of this point is discussed in a previous article by one of us,¹⁷ henceforth called Ref. B, to which we refer the reader. We will use the cluster method of B to evaluate the two-particle correlation function. The important physical effect which we are evaluating is the effect of the screening out of the field of one spin on another by intermediary spins.

In the notation of B

$$\begin{aligned} \langle \ln \langle Z \rangle_s \rangle_c &= \langle \ln \langle \exp[-\beta \sum_{i < j} v_{ij} \mu_i \mu_j] \rangle_s \rangle_c \\ &\equiv \sum_{n < 1} \frac{\langle (-\beta v_{ij})^n \rangle_c}{n!} M_n(\mu_j \mu_i), \end{aligned} \quad (3.1)$$

where s and c stand for spin and configurational averages.

$$\begin{aligned} -\beta F_n &= (N^n/n!) \langle \ln \langle \exp[-\beta (v_{ij} \mu_i \mu_j + v_{jk} \mu_j \mu_k + \dots + v_{ni} \mu_n \mu_i)] \rangle_s \rangle_c - \binom{l}{1} \langle \ln \langle \exp[-\beta (\sum_{\substack{l-1 \\ \text{bonds}}} v_{ij})] \rangle_s \rangle_c \\ &\quad + \binom{l}{2} \langle \exp[-\beta \sum_{\substack{l-2 \\ \text{bonds}}} v_{ij}] \rangle_s \rangle_c + \dots + (-1)^{n-1} \binom{l}{l-1} \langle \exp(-\beta v_{ij} \mu_i \mu_j) \rangle_s \rangle_c. \end{aligned} \quad (3.4)$$

The meaning of (3.4) is the following. The contribution to $-\beta F_n$ from an n vertex diagram containing l -ladder bonds is given by the semi-invariant of the sum of all l bonds taken at a time, minus all the semi-invariants formed by erasing one ladder bond at a time, plus all the semi-invariants formed by erasing two ladder bonds at a time, and so on, the last term giving all l semi-invariants only with a single-ladder bond. Equation (3.4) is evaluated in Appendix 1 for the case when $\langle \mu_i \rangle = 0$ giving the result

$$-\beta F_n = \frac{N^{n-1}}{n!} \left\langle \sum_{\substack{\text{all sets that} \\ \text{have rings}}} \ln \left[1 + \sum_{\substack{\text{rings in} \\ \text{the diagram}}} (-1)^m \prod_{\substack{\text{over } m\text{-bonds} \\ \text{in a ring}}} (\tanh \beta v_{m,m+1}) \right] \right\rangle_c, \quad (3.5)$$

where by the sets that have rings we mean all diagrams that close upon themselves; the latter we call ring diagrams. The following example will clarify the point. Consider the diagram with 5 ladder bonds as shown in Fig. 1(b). The ring diagrams arising here have bonds 125, 345, and 1234; i.e., those bonds that close upon themselves.

When any vertex is connected to only *two* other vertices (no cross diagrams), the contributions from all but one

Upon a diagrammatic expansion of (3.1) we find that the n th semi-invariant contains all possible diagrams that can be formed from n bonds, each bond having a strength of v_{ij} and a spin μ_i and μ_j associated with its two ends. Thus, the diagrams contained in the third semi-invariant are shown in Fig. 1.

We now wish to sum the diagrams according to a power series in the concentration and perform the spin averages for the case when no long-range order exists; i.e., the long-range order parameter $R = \langle \mu \rangle = 0$. We will show later that no long-range magnetic order is expected to exist for the dilute impurity concentrations considered in this paper. We should also note that in the Ising model, the model considered here, $\langle \mu_i^{2l+1} \rangle = \langle \mu_i \rangle = 0$, and $\langle \mu_i^{2l} \rangle = \langle \mu_i^2 \rangle = 1$ whenever l is an integer.

We write

$$\sum_{l=2}^{\infty} -N\beta F_l = \langle \ln \langle \exp[-\beta \sum_{i < j} v_{ij} \mu_i \mu_j] \rangle_s \rangle_c, \quad (3.2)$$

where F_l is the free energy per particle from all l vertex diagrams. Since $\langle \mu \rangle = 0$, only irreducible diagrams (and excluded volume diagrams to be discussed later) survive in the spin averaging process. $-\beta F_2$ for $l=2$ is obtained from Eq. (35) Ref. 17 and is

$$-\beta F_2 = -\frac{c}{2} \sum_i \ln \cosh[\beta v(r_{ij})], \quad (3.3)$$

where i is taken with respect to some arbitrary origin. We now define a "ladder bond" to be a bond containing the sum of any number of v_{ij} interactions between two fixed vertices. The contribution to $-\beta F_n$ from the n -vertex irreducibly linked diagram containing l ladder bonds is derived in Appendix 1 and is given by

¹⁷ R. Brout, Phys. Rev. **115**, 824 (1959) (referred to as B throughout the article).

term in (3.5) vanish and the free energy from the n -vertex rings of ladder diagram becomes

$$-\beta F_n = \frac{N^n}{n!} G_n \langle \ln [1 + (-1)^m \prod_{\substack{m\text{-bonds} \\ \text{in ring}}} \tanh \beta v_{ij}] \rangle_c, \tag{3.6}$$

where G_n gives the number of topologically distinct diagrams;

$$G_n = \frac{1}{2}(n-1)!,$$

where m labels the bonds in the ring.

We now show on the basis of the previous paragraph together with the self-consistent method of Sec. 4 that at zero-degrees temperature and for low-impurity concentrations ($c \leq 0.05$) the volume of the crystal about a fixed impurity, i , may be divided into two regions, henceforth, called regions 1 and 2.

Region 1: The volume within some correlation radius R_c , to be defined shortly, from an impurity i fixed at the origin in which a site occupied by an impurity j is strongly correlated to spin i . The strength of the correlation depends upon the distance r_{ij} between spins i and j . R_c itself will be a function of the impurity concentration and temperature.

Region 2: The volume of the crystal for $r_{ij} > R_c$ in which spins i and j will be only weakly correlated.

In order to show the above we examine the two-particle spin correlation function between two impurities i and j located at a distance r_{ij} from each other. We obtain the correlation function from Eq. (3.2)

$$\langle \mu_i \mu_j \rangle = \left\langle -\frac{\partial}{\partial [\frac{1}{2}\beta v_{ij}]} \ln \langle \exp(-\beta \sum_{i < j} v_{ij} \mu_i \mu_j) \rangle_s \right\rangle_c, \tag{3.7}$$

where we should note that the summation over i and j is omitted in the configurational average of (3.7).

Let $\langle \mu_i \mu_j \rangle_l$ be the contribution to $\langle \mu_i \mu_j \rangle$ from a general l vertex diagram and let $\langle \mu_i \mu_j \rangle_l^{\text{ring}}$ be the contribution to $\langle \mu_i \mu_j \rangle$ from the l -vertex ring diagrams.

Note: In all subsequent discussion, unless explicitly stated otherwise, we fix impurity i at the origin with spin up and j occupied with unspecified spin orientation, or

$$\langle \mu_0 \mu_j \rangle \equiv \langle \mu_0 \mu_j | \mu_0^{\text{even}} = +1 \rangle \text{ and site } j \text{ occupied.} \tag{3.8}$$

We thus get for the two vertex diagrams

$$\langle \mu_0 \mu_j \rangle_2 = -\tanh \beta v(r_{0j}). \tag{3.9}$$

The physical meaning of Eq. (3.9) is the following. If we consider the two-particle interaction only, i.e., the first term of the power series expansion of the free energy, we get the result that, at $T=0$, the magnitude of the correlation between μ_0 and any other spin μ_j will be unity. However, we expect that a third particle located between μ_0 and μ_j will screen some of the effect of μ_0 on μ_j . To find the effect of one or more intermediate particles between spins μ_0 and μ_j , we first consider the contribution to $\langle \mu_0 \mu_j \rangle$ from a general ring of ladders, the equation for which is given by (3.6) and will treat the nonring contributions later.

Rewriting Eq. (3.6) gives

$$-\beta F_n^{\text{ring}} = \frac{1}{2n} (c)^{n-1} \sum_{i_2, i_2, \dots, i_n} \ln [1 + (-1)^n \tanh \beta v_{i_1, i_2} \tanh \beta v_{i_2, i_3} \dots], \tag{3.10}$$

where each i_k takes values from one to N_0 , where N_0 is the number of sites in the crystal. Differentiating (3.10) with respect to $-\frac{1}{2}\beta v_{ij}$

$$\langle \mu_{i_1} \mu_{i_2} \rangle_n^{\text{ring}} = -c^{n-2} \sum_{i_3 \dots i_n} \frac{(-1)^n t_{i_2 i_3} t_{i_3 i_4} \dots t_{i_n i_1}}{1 + (-1)^n t_{i_1 i_2} t_{i_2 i_3} \dots t_{i_n i_1}} \frac{\partial}{\partial [\frac{1}{2}\beta v_{i_1 i_2}]} t_{i_1 i_2}, \tag{3.11}$$

where

$$t_{i_k i_{k+1}} = \tanh \beta v_{i_k i_{k+1}}, \tag{3.12}$$

and we eliminated the factor $1/n$ in (3.12) by differentiating with respect to each of the n random variables occurring in the expansion. There will be no loss of generality by letting v_{02} be positive. Thus, we get

$$\langle \mu_0 \mu_2 \rangle_n^{\text{ring}} = \mp 4c^{n-2} \sum_{i_3 \dots i_n} [(t_{02} t_{2i_3} \dots t_{i_n 0})^{-1} \pm 1]^{-1} [e^{2\beta v_{02}} - e^{-2\beta v_{02}}]^{-1} \tag{3.13}$$

where the upper and lower sign belongs to the n =even and n =odd cases, respectively. In the $\lim \beta \rightarrow \infty$ we make the following observations.

Consider the right-hand side of the summation in Eq. (3.13). The factor $(e^{2\beta v_{02}} - e^{-2\beta v_{02}})^{-1}$ approaches zero as $\beta \rightarrow \infty$. Thus, we get a contribution to $\langle \mu_0 \mu_2 \rangle_k^{\text{ring}}$ only when the first factor approaches infinity as $\beta \rightarrow \infty$. We now observe that in order to get a contribution to (3.13)

$$(t_{02} t_{2i_3} \cdots t_{i_n 0}) \xrightarrow{\beta \rightarrow \infty} -1 \quad n = \text{even}, \quad (3.14)$$

$$(t_{02} t_{2i_3} \cdots t_{i_n 0}) \xrightarrow{\beta \rightarrow \infty} +1 \quad n = \text{odd}. \quad (3.15)$$

Thus, even vertex diagrams contribute only when an odd number of bonds are negative; odd vertex diagrams, when an even number of bonds are negative. Thus, as $\beta \rightarrow \infty$ we get

$$\langle \mu_0 \mu_2 \rangle_n^{\text{ring}} = \lim_{\beta \rightarrow \infty} [2c^{n-2} \sum_{i_3 \cdots i_n} (1 + \sum_{\substack{k=2,3 \cdots n \\ k \neq 0}} \exp[+2\beta(|v_{02}| - |v_{i_k i_{k+1}}|)])^{-1}] \quad (3.16)$$

with the proviso that *even* vertex diagrams have an *odd* number of negative bonds while *odd* vertex diagrams have an *even* number of negative bonds. Equation (3.16) contains the screening behavior of the correlation function which we have sought. We find that in the limit as $\beta \rightarrow \infty$ whenever $|v_{i_k i_{k+1}}| < |v_{02}|$ (3.16) gives no contribution to $\langle \mu_0 \mu_2 \rangle$; when $|v_{02}| < |v_{i_k i_{k+1}}|$ for all $(k, k+1)$ the summation increases by unity. For the case when some of the potentials $|v_{i_k i_{k+1}}|$ are equal to each other and some others are greater than $|v_{02}|$, the contribution to the summation in (3.16) varies between 1 and $1/n$. We note, however, that the probability for several of the potentials to have the same value decreases rapidly with decreasing concentration. Thus, each summation contributes approximately z , where z is the number of sites within a volume of radius r_{02} . We can now describe the behavior of $\langle \mu_0 \mu_j \rangle$ from both the simple ladders and the rings of ladders. With spin j fixed and occupied the contribution (3.9) is just -1 , while let the n -vertex ring of ladders contribute $\alpha_n (cz)^{n-2}$. The total contribution from these two classes of diagrams is

$$\langle \mu_0 \mu_j \rangle = \lim_{\beta \rightarrow \infty} [-\tanh \beta v_{02} + 2 \sum_{n=3}^{\infty} c^{n-2} \sum_{i_3 \cdots i_n} (1 + \sum_{k=2, \dots, n} \exp[2\beta(|v_{0j}| - |v_{k, k+1}|)])^{-1}] \quad (3.17)$$

$$\equiv -1 + 2 \sum_{n=3}^{\infty} \alpha_n (cz)^{n-2}, \quad (3.18)$$

where α_n is of order unity. The correlation between the spin at the origin and spin j will vanish whenever (3.18) becomes zero indicating a breakdown of the approximations used, a difficulty which we will discuss later.

Let site j be a near neighbor, then z will be of the order of 10, and for low concentrations two near-neighbor spins will be almost completely correlated; i.e., $|\langle \mu_0 \mu_j \rangle| = 1$. As r_{02} increases, so does z until cz is large enough for (3.18) to vanish. The radius at which this occurs we define as the correlation radius R_c already mentioned several times. Since cz , and not z , is the quantity that determines the correlation length, R_c is a function of the concentration as discussed previously.

We have introduced the ring of ladders for two reasons: One, that the ring of ladders very clearly demonstrate the qualitative behavior of the correlation length; two, it becomes very laborious to evaluate the sum of *all* irreducibly linked diagrams for $n \geq 4$. However, we still would like to consider the effect of *all* irreducibly linked diagrams. Therefore, we use the following approximation. We evaluate the 4th virial coefficient (4-vertex diagram) exactly, and compare it to the four-vertex ring of ladders; then using the information obtained from this, predict the qualitative behavior of the higher virial coefficients from the ring of ladder diagrams.

The contribution to the two-particle spin correlation

function from the fourth virial coefficient is evaluated in Appendix 2 in the limit $\beta \rightarrow \infty$. The result is

$$\langle \mu_0 \mu_j \rangle_4 \approx 2c^2 \sum_{i_3, i_4} 1. \quad (3.19)$$

The summation in (3.19) is subject to the condition that each of the six interactions arising in the 4th virial coefficient be equal to or be stronger than v_{0j} . Again, there is a constraint on the sign of the bonds such that, on the average, only half of the diagrams contribute. We note that, except for the restriction that *none* of the four vertices may be separated by a distance greater than r_{02} , the complete 4th virial coefficient gives the same result as the four vertex ring of ladders. For the ring of ladders, only the four external bonds have to be shorter than r_{02} . Because of the additional restriction, it would appear that the contribution of (3.19) to $\langle \mu_0 \mu_j \rangle_4$ is smaller than the ring contribution, but this is not so. The rings are restricted to diagrams with non-crossing paths, whereas crossings are permitted in the complete four-vertex diagram, and there are many more crossing than noncrossing distinct paths on the four-vertex diagram, particularly for low concentrations.

The authors are of the opinion that for the higher virial coefficient the rings of ladder result is correct for $cz < 1$ provided we impose the restriction that none of the vertices in the diagram are separated by a greater

distance than r_{02} . This conjecture is based on the detailed examination of the complete 4th virial coefficient in Ref. 18. It is seen there that for every bond $i-k$ in a diagram, a factor $X_{ik}/X_{02} = \exp[\beta(|v_{02}| - |v_{ik}|)]$ arises in the denominator of $\langle \mu_0 \mu_j \rangle$ and, thus, $\langle \mu_0 \mu_j \rangle$ vanishes unless the strength of each bond v_{ik} is stronger than v_{02} . It is therefore indicated, but not proved, that the same type of terms ($\exp[\beta(|v_{02}| - |v_{ik}|)]$), arise from each bond in the complete n th virial coefficient when $n \geq 5$. Also, it will be shown that the correlation function $\langle \mu_0 \mu_j \rangle$ is insensitive to the contributions from virial coefficients higher than the fourth in the region where the correlation is strong. Thus, little error is made if higher virial coefficients are not evaluated exactly.

We are now ready to find the total contribution to (3.18). The contribution from the three-vertex ring is calculated as follows. We fix a spin at the origin O and another spin at a distance r_{02} from it. Select the third vertex such that the length of each bond is not greater than r_{02} . We are then restricted to the truncated portion of the sphere whose volume, τ_3 , is $\tau_3 = 2(5/24)\pi r_{02}^3$. Let z be the total number of sites within τ_3 , then the contribution of the three vertex diagram to (3.18) is $\langle \mu_0 \mu_j \rangle_3 \approx 2(\frac{1}{2})(cz)$ where the factor of $\frac{1}{2}$ comes from the restriction on the sign of the bonds [see discussion following (3.15)]. Next consider the contribution from a higher-order diagram, and, in particular, the case where the number of vertices becomes large (of order 15 or greater). After r_{02} is fixed, the next vertex may be chosen anywhere in the volume τ_3 . However, any subsequent vertex will be restricted to a volume $\frac{4}{3}\pi(r_{02}/2)^3 = \frac{1}{6}\pi r_{02}^3$, and the total number of sites within this volume is approximately $\frac{2}{5}z$. Then the contribution from the n vertex diagram is

$$\langle \mu_0 \mu_j \rangle_n = cz \left[\frac{2}{5}c(z-1) \right] \left[\frac{2}{5}c(z-2) \right] \cdots \left[\frac{2}{5}c(z-n) \right]; \quad n \ll z. \quad (3.20)$$

Substituting (3.20) in (3.18) yields

$$\langle \mu_0 \mu_j \rangle \approx -1 + (cz) \sum_{n=0}^z \left[\frac{2}{5}c(z-n) \right]^n \approx -1 + \frac{cz}{1 - \frac{2}{5}cz}. \quad (3.21)$$

In the present approximation we choose to define the correlation radius R_c as that radius where $\langle \mu_0 \mu_j \rangle = 0$. Later we will show that this choice of R_c is compatible with the self-consistent linearized theory which is valid for the "tail" of the correlation functions. Setting $\langle \mu_0 \mu_j \rangle = 0$ yields the solution $(cz) = 0.71$. The number of impurities within R_c is $(cz)(\frac{4}{3}\pi R_c^3)/[(5/12)\pi R_c^3] = 2.27$ and, thus,

$$R_c = 0.514c^{-1/3}d, \quad (3.22)$$

where d is the lattice constant.

That one may have confidence in the estimate (3.22) follows from the small contribution of the virial coefficients for $n > 5$ where our calculation is most liable to error. To see this, we evaluate the contribution of V_5 to $\langle \mu_0 \mu_j \rangle$, where V_5 is the 5th virial coefficient.

The third and fourth virial coefficients contribute approximately $cz + \frac{2}{5}(cz)^2$, the fifth contributes $cz[\frac{2}{5}(cz)]^2$, the ratio is

$$\frac{V_5}{V_3 + V_4} \approx \frac{cz(\frac{2}{5}cz)^2}{1 + \frac{2}{5}(cz)^2} \approx \frac{(4/25)(cz)^2}{1 + \frac{2}{5}(cz)} \approx 6.2\%.$$

The reasonably small contribution in the fifth virial coefficient to the two-particle correlation function clearly exhibits the self-consistency of the whole approach to the inside region. This is also seen from the following. We have found that, on the average, there are about two impurities (2.27 to be exact) plus the one at the origin within the correlation length. This shows that two intermediate impurities between a particle located at the edge of the correlation length and the one at the origin are sufficient to destroy the correlation. Thus, contributions from higher virial coefficients having more than four vertices, determined by the location of the four particles, are unimportant. The correlation function $\langle \mu_0 \mu_2 \rangle = g(r_{12})$ as a function of r/R_c is approximated by

$$g(r_{12}) = [1 - (r_{12}/R_c)^3] \text{sgn}(v_{02}), \quad (3.23)$$

where $\text{sgn}v_{02} = +1$ when v_{02} is positive and (-1) when v_{02} is negative.

Up to now we have considered the situation in which the number of sites enclosed within the range of correlation is less than $1/c$. However, if we choose an impurity at a radius r_{02} such that the number of sites enclosed within the range of correlation is greater than $1/c$, the terms contributing to the summation in (3.18) become greater than unity and $g(r_{12})$ increases indefinitely. This is a physical absurdity. The difficulty appears to be even more serious if we consider that the validity of Sec. 3, which is of central importance in explaining the thermodynamic functions of the system, hinges upon the fact that $g(r_{12})$ vanishes for large r_{12} . However, it is for these large radii that our series evaluation of $g(r_{12})$ breaks down completely. The difficulty is traced to the fact that in the limit $\beta \rightarrow \infty$ the part of the free energy from $r_{12} > R_c$ yields a power series in the concentration which appears to diverge. It is probable, however, that excluded volume effects which we have not included will eliminate the divergence. Rather than pursue the cluster approach at large distances, we have adopted a self-consistent method for $r > R_c$, and match this solution with that of the inside region, a region for which the results obtained in this section are presumably valid.

Before completing this section we now briefly digress to the question of the excluded volume effects mentioned previously. In Ref. 17 it was shown that dotted line diagrams arise from the constraint that no multiple occupancy of sites is permitted. Hence, by summing over unrestricted intermediate indices, we have overcounted the contribution to the free energy and must subtract out such extra terms. The important point is

that each dotted line diagram introduces a $-\delta_{ij}$ in coordinate space and reduces the contribution by $1/z$ where z is the effective number of sites within the range of correlation and $z=O(2/c)$. Thus, the dotted line contribution will become important only for diagrams with a large number of vertices, where the number of dotted lines in a graph increased very rapidly. We may conjecture that these dotted line diagrams make the total free energy convergent.

4.1 Self-Consistent Solution of the Field for the Outside Region

We found in the previous section that the approximate value of the two-particle correlation function goes to zero at $r=R_c$ which indicates a mathematical difficulty in our method of approach. We now find the two-particle correlation function for $r>R_c$ by a self-consistent method. This approach will be very useful in the treatment of the problem of the threshold concentration to maintain long-range order. We assume that the probability distribution of the field is simple enough, so that it can be specified by two parameters, the mean field H which is not zero since in finding the correlation function we will fix a spin to be say $+1$ at the origin, and the dispersion $\sigma^2=\langle H^2\rangle-\langle H\rangle^2$. Since we are interested in long-distance correlations, most spins entering into this calculation are for large values of r_{0j} . For asymptotically large r_{0j} , it is sufficient to describe all of these spins by the same single-particle distribution function and, hence, the same σ . The dispersion σ is given by Eq. (2.15).

In the Ising model we may have spin orientations of ± 1 . We perform the self-consistent field calculation at $T=0$ when a spin will be oriented up if the field is positive and down if it is negative. Let $p(H_j)$ be the probability distribution of the field at spin μ_j and let p_j^\pm be the total probability that the field at μ_j is up (+) or down (-),

$$\begin{aligned} \langle \mu_0 \mu_j \rangle &= \int_{-\infty}^{\infty} +\mu(H_j) p(H_j) dH_j \\ &= \int_{-\infty}^0 (-1) p(H_j) dH_j + \int_0^{\infty} (+1) p(H_j) dH_j \\ &= p_j^+ - p_j^- \equiv f[\langle H_j \rangle / \sigma]. \end{aligned} \quad (4.1)$$

We can get an idea of the behavior of $f[\langle H_j \rangle / \sigma]$ as follows: For an impurity j very close to the origin we will have $|\langle H_j \rangle| \gg \sigma$ and $f[\langle H_j \rangle / \sigma]$ will be ± 1 depending upon whether v_{0j} is negative or positive. For an impurity j far from the origin $|\langle H_j \rangle| < \sigma$ and we may linearize $f[\langle H_j \rangle / \sigma]$ to be approximately $\langle H_j \rangle / \sigma$. Thus, $f[\langle H_j \rangle / \sigma]$ has the form shown in Fig. 2. With this introduction we are ready to find the self-consistent field for the outside region, using the information obtained about the inside region in Sec. 3. The trick is to

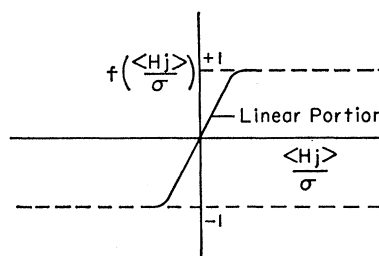


FIG. 2. The form of $f[\langle H_j \rangle / \sigma]$ as a function of $\langle H_j \rangle / \sigma$.

average over an ensemble of systems in which an impurity with spin up is located at the origin and site j is definitely occupied with unspecified spin direction. j is taken to be asymptotically far from the origin. Using the relation $p_j^+ + p_j^- = 1$, we get

$$p_j^\pm = \frac{1}{2}(1 \pm \langle \mu_0 \mu_j \rangle). \quad (4.2)$$

The average field at impurity j is defined by

$$\langle H_j \rangle = v_{0j} + c \sum_k v_{jk} \langle \mu_0 \mu_k \rangle, \quad (4.3)$$

where the average is performed over an ensemble of systems in which the spin at the origin is up and spin j is occupied with unspecified orientation. Thus,

$$\begin{aligned} \langle \mu_0 \mu_k \rangle &= p_j^+ f_k^+ + p_j^- f_k^-, \\ f_k^\pm &= f[(v_{0k} \pm v_{jk} + c \sum_l v_{kl} \langle \mu_k \mu_l \rangle) / \sigma]. \end{aligned} \quad (4.4)$$

Using (4.4) in (4.2) gives

$$\langle H_j \rangle = v_{0j} + \frac{c}{2} \sum_k v_{jk} \{ (f_k^+ + f_k^-) + \langle \mu_0 \mu_j \rangle [f_k^+ - f_k^-] \}. \quad (4.5)$$

Since two impurities will be strongly correlated only if they are within a correlation distance R_c from each other, it is convenient to separate the summation over k into three parts: part A, when $r_{ik} < R_c$; part B, when $r_{0k} < R_c$; part C, the rest of the crystal.

For the case when $r_{jk} < R_c$ a spin k close to j is strongly coupled to j and weakly to all other spins; thus,

$$f_k^\pm \approx \pm \langle \mu_j \mu_k \rangle \sim - \lim_{\beta \rightarrow \infty} \frac{\partial \ln Z}{\partial [\frac{1}{2} \beta v_{jk}]}$$

and $f_k^+ \approx -f_k^-$. Using this expression for f_k in (4.4) gives

$$\begin{aligned} \langle H_j \rangle &= v_{0j} + c \langle \mu_0 \mu_j \rangle \sum_{r_{jk} < R_c} |v_{jk}| |\langle \mu_j \mu_k \rangle| \\ &+ \frac{c}{2} \sum_{r_{jk} < R_c} v_{jk} \{ f_k^+ + f_k^- + \langle \mu_0 \mu_j \rangle (f_k^+ - f_k^-) \}. \end{aligned} \quad (4.6)$$

Now we make the observation that

$$\sum_{r_{jk} < R_c} |v_{jk}| |\langle \mu_j \mu_k \rangle| \approx -E$$

where $-E$ is the energy per particle. Furthermore, since

$r_{0j} \gg R_c$, by hypothesis, $|\langle \mu_0 \mu_j \rangle| \ll 1$ and, hence, we will be in the linear region of the function f . Thus, $\langle \mu_0 \mu_j \rangle = \langle H_j \rangle / \sigma$. We also note that the other terms containing $\langle \mu_0 \mu_j \rangle$ on the right-hand side of (4.6) have a value much smaller than E and, hence, can be neglected. Thus, we lump these three terms together and transpose to the left to get

$$\langle H_j \rangle \left[1 + \frac{cE}{\sigma} \right] = \frac{c}{2} \sum_{r_{jk} < R_c} v_{jk} \{ f_k^+ + f_k^- \} + v_{0j}. \quad (4.7)$$

When k is in region B, f_k^+ and f_k^- are again determined by the strength of the interaction v_{0k} , and again $f_k^+ \approx -f_k^-$. The contribution over this domain vanishes on the average.

The remaining task is to evaluate the sum in (4.7) in region C (far from site 0 and j). We linearize (4.4) and get $f_k^+ + f_k^- \approx 2(\langle H_k \rangle / \sigma)$,

$$\langle H_j \rangle = \left(1 + \frac{cE}{\sigma} \right)^{-1} \left[v_{0j} + c \sum_{r_{jk} < R_c} v_{jk} \langle H_k \rangle \right]. \quad (4.8)$$

We assume for the moment that the second term on the right-hand side of (4.8) is negligible. This is valid for small c as shown below. We then get $\langle H_j \rangle \approx (1 + cE/\sigma)^{-1} v_{0j}$. Using this relation in (4.8) gives

$$\langle H_j \rangle = \left(1 + \frac{cE}{\sigma} \right)^{-1} \left[v_{0j} + \left\{ \frac{c}{\left(1 + \frac{cE}{\sigma} \right)} \right\}_{\substack{r_{jk} > R_c \\ r_{k0} > R_c}} \sum v_{jk} v_{0k} \right]. \quad (4.9)$$

Consider the second term on the right hand of (4.9). Since r_{jk} and r_{k0} are random variables, v_{jk} and v_{k0} are likely to be negative as positive, this second term is negligible in the absence of long-range order [also note that this term is of $O(c^2)$ compared to v_{0j}]. Thus $\langle \mu_0 \mu_j \rangle \approx [v_{0j} / (\sigma + cE)]$ where σ is given by Eq. (2.15).

We now evaluate the strength of the correlation $\langle \mu_0 \mu_j \rangle$ at $r = R_c$. Using (3.22) and the expression for σ , we sum E for the first two shells about the impurity at the origin and integrate from there to R_c . This gives

$$[\langle \mu_0 \mu_j \rangle]_{r=R_c} = 0.0942 [1 - b(c)], \quad (4.10)$$

where $b(c)$ is a number that decreases with concentration, $b(c) \cong 0$ for $c = 0.05$, $b(c) = 0.15$ for $c = 0.005$, and $b(c) \rightarrow 1$ in the limit as $c \rightarrow 0$. Now we compare the self-consistent solution of the correlation function from the outside region with the result obtained from the inside region. The solution from the inside region gives the result that a spin μ_{R_c} , located at R_c , is just as likely to be up as down; whereas the outside region gives the result that the probability is approximately 54% that μ_{R_c} is up (in case the potential is negative) and 46% that it is down. For spins located at $r > R_c$ the probability $P\{\mu_{r^\pm}\} \approx \frac{1}{2} \pm 0.04(R_c/r)^3$. It is gratifying that the self-consistent method gives a very small correlation at R_c ,

as predicted from the cluster development. Still, we should get a qualitative estimate of the correction introduced due to the slight correlation at $r > R_c$. This is done in Appendix 3 of Ref. 18, where it is shown that 4% correlation at $r = R_c$ shifts the center of the distribution function from $H = 0$ to $H = -0.04H_0$, but otherwise everything goes through as before.

4.2 Probability Distribution of the Total Field

In Sec. 4.1 we have shown that, at zero degrees Kelvin, the field experienced by a spin at the origin is given by the contribution from two approximately independent regions. The region $r > R_c$ from which the field is approximately a Gaussian and $r < R_c$ for which we now obtain the probability distribution.

The average number of impurities within the correlated region is given by $\frac{4}{3}\pi R_c^3 c = 2.27$. We observe the important result that the number of impurities within a correlated region is independent of the concentration. We now fix the number of sites, z , within the correlation radius to be $2.27/c$ and permit any number of impurities from zero to z to be located within the correlated volume. We let $p(z, m)$ be the probability that m impurities are found on z sites. Thus, $p(z, m) \approx e^{-2.27} (2.27)^m / m!$

Let z_i be the number of sites on the i th shell from the origin (sites that are equidistant from the origin are defined to be in the same shell) and let the probability that an impurity within the z sites is on the i th shell by $p(i)$, then $p(i) = z_i / \sum z_i$. Let H_i be the field at the origin due to an impurity with specified spin orientation on the i th shell. We restrict ourselves first to a *single* impurity within the correlation length. We observe that if the orientation of spin j is the same as the sign of $v_{0j}[\text{sgn}(v_{0j})]$ spin j will contribute a positive field at the origin, whereas if spin j has orientation of $-\text{sgn}(v_{0j})$ it will contribute a negative field at the origin. Using (4.2) and the result $\langle \mu_0 \mu_j \rangle \sim (1 - r_{0j}^3 / R_c^3) \cdot \text{sgn}(v_{0j})$ we obtain $H_i^\pm = \pm a |\cos kr_i| / r_i^3$ with probability

$$t_i^\pm = \frac{1}{2} \{ 1 \pm [1 - (r_i/R_c)^3] \},$$

when $r_i < R_c$

$$\text{and } H_i^\pm = \pm a \frac{|\cos kr_i|}{r_i^3} \quad (4.11)$$

with probability $t_i^\pm = \frac{1}{2}$ when $r_i > R_c$.

For a single impurity within the correlation length there will be $2i$ discrete values of H for the field from the inside region, where i is the number of shells within the correlation length, and the probability $P(H_i)$ that the field at the origin is H_i is given by $p(H_i) = p(i_1) t(i_1) \equiv b_{i_1}$. When there are m impurities within the correlated volume, the probability that the field is $\sum_{n=1}^m H_{i_n}$ is in

¹⁸ M. W. Klein, Ph.D. thesis, Cornell University, 1962 (unpublished).

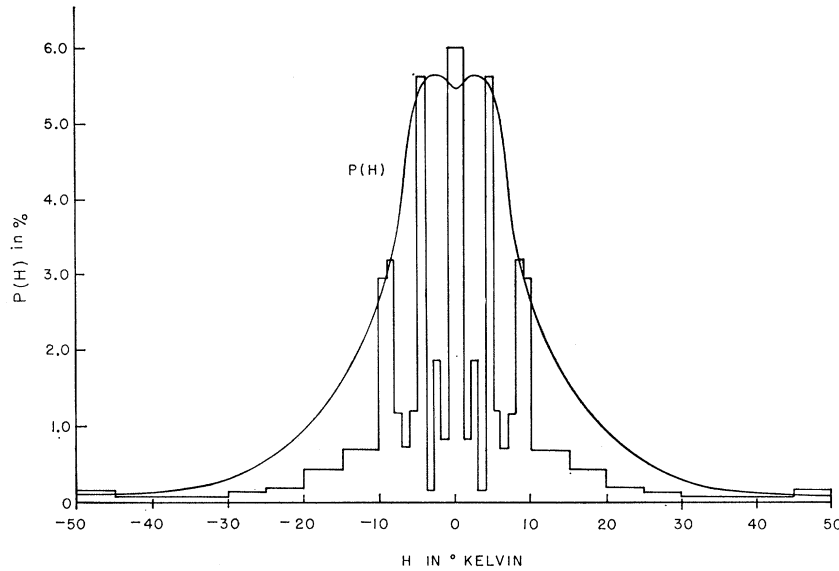


FIG. 3. The histogram shows the probability distribution of the field from the "inside region" for a 1.4% concentration of Mn in Cu. The smooth curve shows the probability distribution of the total field. $P(H)$ is symmetric, because the spin at the origin is just as likely to be up as down.

the two-particle correlation approximation

$$P(H = \sum_{n=1}^m H_{i_n}) = \prod_{n=1}^m b_{i_n}.$$

With this introduction we are able to find the probability from the "inside region" for any given concentration. We calculated the probabilities for a 1.8% concentration of manganese in copper, summed the probabilities for the field in each 1° K interval (the field is measured in units of $\mu H = k_B T$, where μ is taken to be unity) and obtained the histogram shown in Fig. 3.

The probability distribution of the total field is given by the convolution of the distribution from the inside region with that from the outside region given by Eq. (2.15). We thus obtain

$$P(H) = [2\pi\sigma^2]^{-1/2} \sum_{m, j_1, j_2, \dots, j_m} \exp[-\frac{1}{2}(H - H_{j_1, \dots, j_m})^2] \times p(z, m) b_{j_1} b_{j_2} \dots b_{j_m}. \quad (4.12)$$

Equation (4.12) was evaluated with the help of a computer for a 1.8% concentration and the probability distribution obtained is shown by the smooth curve in Fig. 3. We find that for a 1.8% concentration of manganese in copper

$$P(H=0) \approx (2\pi\sigma)^{-1/2}(0.25), \quad (4.13)$$

where σ is given by Eq. (2.15). Thus, the qualitative arguments of Herring and Marshall that $P(H=0)$ is inversely proportional to the concentration is confirmed by our more precise calculation. It is also interesting to note that there is a slight dip in the distribution function about $H=0$ in agreement with the qualitative argument of Marshall on the shape of the distribution function.

At this point we digress to make an interesting remark about the probability that the field is zero; i.e., $P(H=0)$. Using Eq. (2.10) and convolving it with the probability

distribution for the inside region given by Fig. 3 gives that

$$P(H=0) = 0.52/\Delta, \quad \Delta = \frac{2}{3}\pi^2 c \alpha.$$

The ratio, of $P(H=0)$ with a cutoff of the field at the correlation length to that with no cutoff is 0.77 showing that the probability that $H=0$ is not very sensitive to the cut-off radius. We expect this from the consideration that the distant spins contribute primarily small fields.

5. THE SPECIFIC HEAT AND MAGNETIZATION

We calculate the correction to the low-temperature specific heat from the effect of the spin correlations. The specific heat may be found using (2.16) and (4.12). Again we evaluate C_v using an asymptotic expansion of (2.16) and we get for the $T=0$ intercept of the specific heat, $\lim_{T \rightarrow 0} C_v/T = 4.3(10^{-3})$ J/mole-deg in agreement with experimental results.

Next we find the magnetization as a function of temperature and compare with the results of Owen *et al.*² and Schmidt and Jacobs,⁴ who find that the magnetization increases (nearly) linearly with the magnetic field and also increases with concentration and temperature at low temperature. The susceptibility goes through a maximum as a function of temperature and the susceptibility maximum is approximately proportional to the concentration. The susceptibility maximum is now explained in terms of the correlated regions or "clusters" derived on the previous sections. The physical picture is as follows. At low temperatures, the spins within a cluster are strongly correlated to each other and the impurities within a cluster interact with the Ruderman-Kittel potential and the effective spin per impurity is smaller than the free ion spin. As the temperature is increased, two competing processes occur; one, the clusters are randomized, resulting in a decrease in the susceptibility; two, the internal structure of the clusters

is breaking up, thus increasing the effective spin per impurity and the susceptibility. At low temperatures the second of these is predominant and becomes less important with increasing temperatures when most of the spins in a cluster are already randomized. At very high temperatures all spins act independently of each other and the susceptibility equals the paramagnetic free-gas susceptibility.

At zero degrees the average spin at position r we found to be from (3.23); $\langle \mu_0 \mu_j \rangle = (1 - r^3/R_c^3) \text{sgn} v_{0j}$, where $\text{sgn} v_{0j}$ is the sign of v_{0j} . The magnitude of the correlation function depends upon the "screening" of the spins that are located between impurity j and the origin, and since these spins find themselves in a strong effective field, we assume that $|\langle \mu_0 \mu_j \rangle|$ does not change appreciably as we depart slightly from $T=0$. However, the orientation of spin j close to edge of the correlation region will be strongly affected by temperature. We recall that the position of the spins is not affected by the minimization of the free energy, but their spin orientation is. Thus, when we depart from $T=0$, the spin average, in a Weiss field approximation, will be $\tanh \beta v_{0j}$ instead of $\text{sgn} v_{0j}$. Thus, we let

$$\langle \mu_0 \mu_j(T) \rangle = (1 - r^3/R_c^3) \tanh \beta v_{0j}. \quad (5.1)$$

We now let the spins be uniformly distributed over the correlated volume with spin density $\rho = (4/d^3) \cdot (2.3)$.

Let the average spin per cluster be μ_{cl}^{av} ;

$$\mu_{cl}^{av} = 1 + \left[\int_0^{R_c} \rho(r) \left(1 - \frac{r^3}{R_c^3} \right) \tanh \beta v(r) d^3r \right] \times \left[\int_0^{R_c} \rho(r) \left(1 - \frac{r^3}{R_c^3} \right) d^3r \right]^{-1} \quad (5.2)$$

and at $T=0$ we get that

$$(1 - 2.3/R_c^2) > \mu_{cl}^{av} > (1 + 2.3/R_c^2)$$

giving an average μ_{cl} of about 1.

The susceptibility, χ , of an average cluster at temperature T is given by

$$\chi(T) = B \beta S_{cl}^2(T), \quad (5.3)$$

where $B = (N_0/3.3)c[(2)(5/2)]^2$ where $\frac{5}{2}$ is the spin of the manganese atom. $S_{cl}^2(T)$ is the number of free spins in a cluster. This is equal to the average spin of all clusters plus the difference in the number of spins that are correlated within a cluster at temperature zero and T . Thus,

$$\begin{aligned} S_{cl}^2 &= [n(0) - n(T)] + S_{cl}^2(0) \\ &= S_{cl}^2(0) + \frac{2.3}{(R_c^3/6)} \int_0^{R_c} (1 - r^3/R_c^3) \\ &\quad \times [1 - |\tanh \beta v(r)|] r^2 dr, \quad (5.4) \end{aligned}$$

where $S_{cl}^2(0)$ is the average spin per particle at $T=0$.

The value of $S_{cl}^2(0)$ is calculated from the magnetization data of Ref. 4, and is found to be approximately zero near $T=0$. $n(0)$ and $n(T)$ are the number of spins that are correlated within a cluster at temperatures zero and T , respectively. The factor $(6/R_c^3)$ comes from the normalization of the spin density. In (5.4) we let $\beta v(r) = \beta \alpha / r^3$, $b = \beta \alpha / R_c^3$, and differentiating (5.3) with respect to T and substituting (5.4) into (5.3) we get the condition for the maximum in the susceptibility,

$$\begin{aligned} \frac{\partial \chi}{\partial T} &\approx - \frac{Bb(3.3)}{3kT^2} \int_b^\infty \left(1 - \frac{b}{z} \right) \\ &\quad \times \left\{ \frac{1 - \tanh z}{z^2} - \frac{\text{sech}^2 z}{z} \right\} dz \equiv 0. \quad (5.5) \end{aligned}$$

Equation (5.5) has a solution when b is approximately 0.3. Thus, we get that the temperature at which the susceptibility is a maximum is approximately $T_{\max} = 660c^\circ\text{K}$ giving the values of 9.2 and 37°K for a 1.4 and 5.6% concentration, respectively. The experimental values are 13 and 40°K showing reasonable agreement between theory and experiment. (See conclusion for an additional discussion of this point.)

Critical Concentration for Long Range Order

We now wish to inquire at what impurity concentrations, if any, long range order will be sustained throughout the crystal. In particular, we want to show that the spin average $\langle \mu_i \rangle$ equals zero for concentrations treated in this paper. For this purpose the self-consistent field method gives an appropriate tool of analysis since, in its linearized form, one may look for singularities in the homogeneous part in the limit of $r_{0j} \rightarrow \infty$, such a singularity would indicate long-range order. Writing (4.3) in the form

$$\langle H_j \rangle = v_{0j} + c \sum_{r_{jk} < R_c} v_{jk} \langle \mu_k \rangle + c \sum_{r_{jk} < R_c} \frac{v_{jk} \langle H_k \rangle}{\sigma}, \quad (5.6)$$

and transforming into crystal Fourier space and using the translation symmetry of v_{jk} , (5.6) becomes

$$\langle H(q) \rangle = v(q) + cF(q) + (c/\sigma) \bar{v}(q) \langle H(q) \rangle, \quad (5.7)$$

where $F(q)$ is the crystal Fourier sum of the second term in (5.6) and $v(q)$ is the truncated Fourier sum

$$\bar{v}(q) = \sum_{r_{jk} < R_c} v(r_{jk}) \exp[i\mathbf{q} \cdot \mathbf{r}_{jk}] \quad (5.8)$$

and σ is given in (2.15). Transposing and rearranging (5.7) gives

$$\langle H(q) \rangle = \frac{v(q) + cF(q)}{1 - c\bar{v}(q)/\sigma} \equiv \frac{S(q)}{1 - c\bar{v}(q)/\sigma}. \quad (5.9)$$

It is seen from (5.9) that, for a fixed correlation radius R_c , $H(q)$ becomes infinite when $c\bar{v}(q)/\sigma = 1$. This divergence shows that a certain q component of H , say

for $q=q_0$, will be much greater than any other component (in the final result the linear theory must be discarded and an ordered phase postulated and no actual divergence will arise). This indicates that a field with wavevector q will be observed throughout the volume of the crystal; i.e., the existence of long-range order with periodicity $2\pi/q_0$ in real space. Next we examine the function $\bar{v}(q)$ for Cu-Mn. We recall that the Fourier sum for $\bar{v}(q)$ is restricted to $R>R_c$; therefore, for concentrations of the order of 0.15 or less, the lattice sites for $R>R_c$ are dense enough so that we may integrate (5.8). Using Eq. (2.3) we have

$$\bar{v}(q) = \frac{(a)}{k} \int_0^\pi \int_0^{2\pi} \int_{R_c}^\infty \frac{kr \cos kr - \sin kr}{r^4} \times e^{i q \cdot r} \sin \theta d\theta d\Phi dr, \quad (5.10)$$

where a is the strength of the interaction and $k=2k_F$. Performing the integration we find the maximum value of $v(q)$ to be

$$\bar{v}(q)_{\max} \approx \bar{v}(0) = -16\pi a (\sin kR_c/kR_c). \quad (5.11)$$

Thus, $[c\bar{v}(q)/\sigma]<1$ for the concentrations treated in this paper, and no long-range order. We should note, however, that it is wrong to use (5.11) for concentrations that approach unity for two reasons. One, the linearization procedure of Sec. 4 is no longer valid; two, the discreteness of the lattice becomes important and the difference between the integral (5.10) and the discrete sum of the potential becomes large. Indeed, the integral of $v(q)$ from $r=0$ to infinity differs in sign from the sum over discrete sites.

DISCUSSION

We briefly discuss the validity of some of the approximations used in this paper. In Sec. 4 it was assumed that the probability distribution of the outside and inside regions are independent of each other. This is actually not the case (even in the two-particle correlation approximation) for there is a slight correlation between

the two regions at $r=R_c$. However, it is shown in Appendix 4 of Ref. 18 that this correlation only shifts the center of the distribution slightly and effects the low-temperature specific heat very little.

In calculating T_{\max} , the temperature at which the susceptibility is a maximum it was assumed that the average value of $|\cos 2k_F r|$ is unity. This is not unreasonable in view of the fact that we are considering the strongly correlated inside region. If a spin at the edge of the correlation length is correlated to the origin, so will be a spin closer to the origin. The result for T_{\max} may be off by at most a factor of the average value of $|\cos 2k_F r|$, which is $2/\pi$, and still remaining in reasonable agreement with experiment.

This model predicts that dilute substances of cobalt and nickel or other magnetic impurities should have a behavior similar to Cu-Mn. The question arises why Cu-Co should behave so differently from Cu-Mn. The low-temperature specific heat of Cu-Co was found by Crane and Zimmerman¹⁹ to vary linearly with temperature and proportional to the square of the concentration. However, if we use Overhauser's²⁰ argument on the non-localization of Co impurities in Cu, it may be that the Ruderman-Kittel potential is not effective in Cu-Co. This argument goes as follows: Since Co is two atomic numbers closer to Cu than Mn, it is expected that the d orbitals of Co in Cu are less localized than those of Mn in Cu. (Where the solute atomic number two units higher than Co, the d orbitals would be completely nonlocalized.) Therefore, the orbitals of Co extend over a lattice constant or more, the periodicity of the Ruderman-Kittel potential is of the lattice constant, and hence the average field over the Co orbital is cancelled out.

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APPENDIX 1

In this appendix we prove two useful lemmas. First, we introduce some definitions.

Definition 1: We define the *subsets* of a diagram as all possible subdiagrams formed by stripping it of one or more bonds. Example: The subsets of the three-vertex ring are shown in Fig. 4a.

Definition 2: We define a skeleton diagram as one which contains none of its subsets except the identity.

Statement of Lemma 1: The semi-invariant of a skeleton diagram is given by the semi-invariant containing all bonds in the skeleton diagram, minus the semi-invariants of all subsets formed by deleting an odd number, plus the semi-invariants of all subsets formed by deleting an even number of bonds in the skeleton diagram.

Proof: Let $\sum_k v_{ij\mu_i\mu_j}$ be the sum of all k bonds in the skeleton diagram. By the definition of the semi-invariant $M_n(\sum_k v_{ij\mu_i\mu_j})$ contains the skeleton diagrams plus all its subsets. Therefore,

$$M_n^{\sum_k v_{ij\mu_i\mu_j}} = M_n^{(k \text{ bond, skeleton})} + \binom{k}{1} M_n^{(k-1 \text{ bond, skeleton})} + \binom{k}{2} M_n^{(k-2 \text{ bond, skeleton})} + \dots + \binom{k}{k-1} M_n^{(1 \text{ bond, skeleton})}, \quad (\text{A1.1})$$

¹⁹ L. T. Crane and J. E. Zimmerman, Phys. Rev. **123**, 113 (1961).

²⁰ A. W. Overhauser, J. Phys. Chem. Solids **13**, 71 (1960).

$$M_n^{\sum_{k-l} v_{ij}\mu_i\mu_j} = M_n^{(k-l \text{ bond, skeleton})} + \binom{k-l}{1} M_n^{(k-l-1 \text{ bond, skeleton})} + \dots + \binom{k-l}{k-l-1} M_n^{(1 \text{ bond, skeleton})}. \quad (\text{A1.2})$$

Adding all semi-invariants gives

$$\begin{aligned} M_n^{\sum_k v_{ij}\mu_i\mu_j} - \binom{k}{1} M_n^{\sum_{k-1} v_{ij}\mu_i\mu_j} + \dots + (-1)^s \binom{k}{s} M_n^{\sum_{k-s} v_{ij}\mu_i\mu_j} &= M_n^{(k \text{ bond, skeleton})} + \left[\binom{k}{1} - \binom{k}{1} \right] M_n^{(k-1 \text{ bond, skeleton})} \\ &+ \left[\binom{k}{2} - \binom{k-1}{1} \binom{k}{1} + \binom{k}{2} \right] M_n^{(k-2 \text{ bond, skeleton})} + \dots + M_n^{(k \text{ bond, skeleton})}. \end{aligned} \quad (\text{A1.3})$$

This is exactly what we set out to prove. We should note that the proof is general and not restricted to rings of ladders only.

Lemma 2: A k vertex skeleton diagram of ladders gives a contribution to the free energy

$$\langle \ln \langle Z_k \rangle_s \rangle_c = \frac{N^k}{k!} \sum_{\text{subsets}} \langle \ln \langle \prod_{\text{bonds, subsets}} (1 - \mu_i \mu_j \tanh \beta v_{ij}) \rangle_s \rangle_c, \quad (\text{A1.4})$$

and when $\langle \mu_i \rangle = 0$, i.e., no long-range order, the contribution is

$$\langle \ln \langle Z_k \rangle_s \rangle_c = \frac{N^k}{k!} \sum_{\text{closed loops only}} \langle \ln (1 + (-1)^m \prod_{\text{closed loops}} \tanh \beta v_{ij}) \rangle_c, \quad (\text{A1.5})$$

where m is the number of bonds in the closed loop. In case there are no closed loops the contribution is zero. The closed loops of the 5 bond 4 vertex diagram is shown in Fig. 4(b).

Using the definition of the semi-invariant

$$\langle \ln \langle Z_k \rangle_s \rangle_c = \frac{N^k}{k!} \sum_{n=k}^{\infty} (-\beta)^n (M_n^{(k \text{ bond, skeleton})} / n!), \quad (\text{A1.6})$$

and Eq. (A1.3) we get

$$\langle \ln \langle Z_k \rangle_s \rangle_c = \frac{N^k}{k!} \left\{ \sum_{l=0}^{k-1} \binom{k}{l} (-1)^l \langle \ln \prod_{\substack{k-l \\ \text{bonds}}} e^{-\beta v_{ij} \mu_i \mu_j} \rangle_s \right\}_c. \quad (\text{A1.7})$$

Expanding the exponentials on resumming, each exponential becomes $\cosh \beta v_{ij} - \mu_i \mu_j \sinh \beta v_{ij}$, then factoring out a $\cosh \beta v_{ij}$ from each exponential in (A1.7) we get

$$\langle \ln \langle Z_k \rangle_s \rangle_c = \frac{N^k}{k!} \sum_{l=0}^{k-1} (-1)^l \binom{k}{l} \sum_{k-l} \langle \ln \cosh \beta v_{ij} \rangle_c + \frac{N^k}{k!} \sum_{l=0}^{k-1} (-1)^l \binom{k}{l} \langle \ln \langle \prod_{\substack{k-l \\ \text{bonds}}} (1 - \mu_i \mu_j \tanh \beta v_{ij}) \rangle_s \rangle_c. \quad (\text{A1.8})$$

We now show that the first summation in (A1.8) equals zero. Let $\ln \cosh \beta v_{ij} = Y_i$, then

$$\begin{aligned} \sum_{l=0}^{k-1} (-1)^l \binom{k}{l} \sum_{k-l} Y_i &= \binom{k}{0} \sum_k Y_i - \left[\binom{k}{1} \sum_k Y_i - \sum_k Y_i \right] + \left[\binom{k}{2} \sum_k Y_i - \binom{k-1}{1} \sum_k Y_i \right] + \sum_{l=3}^{k-1} \left\{ \binom{k}{l} - \binom{k-1}{l-1} \right\} \sum_k Y_i \\ &= \sum_{l=0}^{k-1} (-1)^l \left[\binom{k}{l} - \binom{k-1}{l-1} \right] \sum_k Y_i = \sum_k Y_i \sum_{l=0}^{k-1} \frac{(k-1)!}{l!(k-l-1)!} (-1)^l = 0. \end{aligned}$$

This is exactly what we proposed to prove in Eq. (A1.4). Next we prove Eq. (A1.5). Consider the product $\langle \prod_{k \text{ bonds}} [1 - \mu_i \mu_j \tanh \beta v_{ij}] \rangle_s$ in (A1.8). The spin average of μ_i^k equals 1 when k is even, and zero when k is odd. For this reason we get a contribution only when an even number of (ladder) bonds emanate from each vertex, i.e., whenever a closed loop is formed by the bonds thus giving (A1.5).

APPENDIX 2

Evaluation of the 4th Virial Coefficient

The evaluation of the 4th virial coefficient becomes quite laborious algebraically; therefore, we use diagrams whenever possible. Every bond in the diagram is a ladder bond. The diagrams which contribute to the 4th virial coefficient V_4 are shown in Fig. 5(a), where for each of the three diagrams A, B, and C, the semi-invariants of all

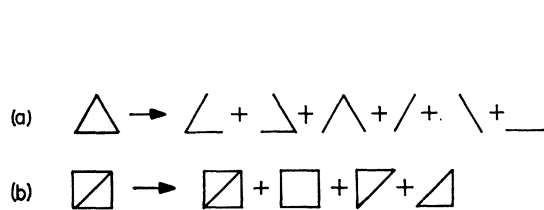


FIG. 4. (a) The 3-vertex ring and its subsets. (b) The closed loops of the 5 bond 4 vertex ladder diagram.

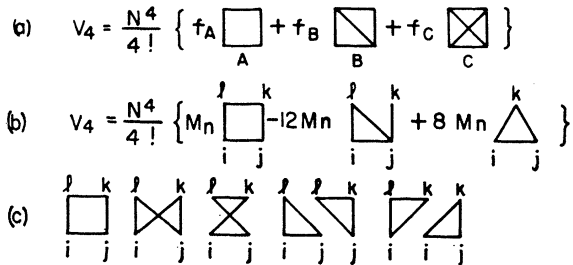


FIG. 5. (a) Contributions to the 4th virial coefficient. (b) The net contribution to the 4th virial coefficient after the appropriate subsets have been subtracted. (c) The total contribution of the first term in Eq. A2.1.

possible subsets are subtracted as discussed in Appendix 1, and $f_A=3$; $f_B=6$; $f_C=1$. Subtracting the proper subsets of V_4 we obtain a contribution as shown in Fig. 5(b).

Using the definition of the semi-invariants (3.1) and letting $\tanh\beta v_{ij} \equiv t_{ij}$, and averaging over the spins with the condition $\langle \mu_i^{2n+1} \rangle = \langle \mu_i \rangle = 0$, $\langle \mu_i^{2n} \rangle = 1$, after performing some simple but laborious algebra we get

$$V_4 = \frac{N^4}{4!} \{ \langle \ln(1 + 3t_{ij}t_{jl}t_{lk}t_{ki} + 4t_{ij}t_{jk}t_{kl}t_{li}) \rangle_c - 4 \langle \ln(1 + t_{ij}t_{jk}t_{kl}t_{li}) \rangle_c \}, \tag{A2.1}$$

where again i, j are random variables ranging from 1 to N . Note: The first term of (A2.1) contains the diagrams shown in Fig. 5(c). The contribution of the fourth virial coefficient to the two-particle correlation functions is obtained by differentiating (A2.1) with respect to $\frac{1}{2}\beta v_{ij}$. For convenience, we let $t_{ij}=1, t_{jk}=2, t_{kl}=3, t_{li}=4, t_{ik}=5, t_{il}=6$, we thus get

$$\langle \mu_i \mu_j \rangle_4 = \frac{N^4}{4} \left\langle \left[\frac{-[(1234) + (1356) + (2456)] + (126) + (145)}{1 + (1234) + (1356) + (2456) - (126) - (145) - (235) - (346)} - \frac{(126)}{1 - (126)} - \frac{(145)}{1 - (145)} \right] \times \left[\frac{1}{e^{2\beta v_{ij}} - e^{-2\beta v_{ij}}} \right] \right\rangle_c. \tag{A2.2}$$

In the limit as $\beta \rightarrow \infty$, $(e^{2\beta v_{ij}} - e^{-2\beta v_{ij}}) \rightarrow \infty$ and each of the terms in (A2.2) contributes only when its denominator vanishes. The reader is referred to Ref. 18 for the evaluation of (A2.2). The result is

$$\langle \mu_0 \mu_j \rangle_4 = 2c^2 \sum_{i_3, i_4} 1. \tag{A2.3}$$

The summation is subject to the conditions discussed immediately following Eq. (3.19) in the text.