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DILUTION OF THE GENERAL SPIN HEISENBERG FERROMAGNET

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The problem of the diluted Heisenberg ferromagnet has been approached via a mean-field approximation for the case of general spin. The Curie temperature versus concentration curves show an upward curvature near the critical concentration which seems to be characteristic of Heisenberg systems. This feature is found to disappear in the limit of classical and Ising spins. The initial slope of the $T_c(x)/T_c(1)$ versus x curves are compared with those derived from experiments on $Mn_xZn_{1-x}F_2$ and the agreement is found to be much better than with a RPA treatment.

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1. *Introduction*

The dilute Ising ferromagnet has been the subject of intensive study for some time. In contrast, the corresponding Heisenberg problem has been attacked far less frequently and then usually for $S = 1/2$ or classical spins. The reason for this is that the mathematically sophisticated methods developed for the study of critical phenomena simply do not work well for the dilute Heisenberg magnet. Series expansions do not converge sufficiently well to allow confident extrapolation [1]. Monte Carlo methods are necessarily limited to the classical spin case [2, 3]. There are the recently developed renormalization methods [4, 5] or the coherent potential approximation [6], and the Green function [7] or mean-field approaches [8]. In this work, we shall adapt the latter to study the spin and concentration dependence of the Curie temperature of a diluted Heisenberg ferromagnet.

2. *The method*

The method we employ in this work is known as the Self-consistent Oguchi Second Approximation (SCOII). In a previous publication [8a] it has been applied to the dilute Ising magnet. To review briefly, the method is based on a trio of lattice sites. In order to

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account for the neglected interactions, an effective field is introduced which is assumed proportional to the number of neglected nearest neighbours. This effective field is then determined by requiring that the average of all three lattice sites be the same. This, of course, is very similar in philosophy to the usual Bethe–Peierls–Weiss approximation.

In performing this calculation, the proper procedure is to do a thermal average for a particular distribution of magnetic sites. Then, a configuration average over all possible distributions should be taken keeping the number of non-magnetic sites constant. Equivalently, one may construct the partition function as the weighted product of the various configurational partition functions.

The dilution problem can be formulated rather succinctly by taking the SCOII Hamiltonian to be

$$-\beta H(\varepsilon_p, \varepsilon_q, \varepsilon_r) = 2j\varepsilon_q\bar{S}_q\cdot(\varepsilon_p\bar{S}_p+\varepsilon_r\bar{S}_r)+\varepsilon_p\lambda_pS_{pz}+\varepsilon_q\lambda_qS_{qz}+\varepsilon_r\lambda_rS_{rz}, \tag{1}$$

where the ε_i are independent random variables with the distribution,

$$\varepsilon_i = \begin{cases} 1 & \text{with probability } x \\ 0 & \text{with probability } (1-x). \end{cases} \tag{2}$$

x is the concentration of magnetic ions.

The ratio of the effective fields will be taken to be proportional to the number of neglected nearest neighbour interactions. However, the number of nearest neighbours depends on the particular configuration of magnetic ions. The effective fields may thus take on any of the values,

$$\begin{gathered} 0 \leqslant \lambda_q \leqslant (n-2)a, \\ 0 \leqslant \lambda_p, \lambda_r \leqslant (n-1)a. \end{gathered} \tag{3}$$

In calculating the thermodynamic properties, a configuration average must include all of these possibilities as well.

For the present calculation the perturbation expansion of Karplus and Schwinger [9] will be used. The idea is to treat the Zeeman term in (1) perturbatively and retain only terms of $O(\lambda^2)$. This will lead to a self-consistency which is correct to linear terms in the effective fields. When the configuration average is performed, the result will be simply to replace n by nx. This follows immediately from the identity

$$\sum_{k=0}^{n} k\binom{n}{k}x^k(1-x)^{n-k} = nx. \tag{4}$$

This results in a great simplification of the computation, since one can now effect the configuration average over the possibilities (3) by making the substitution $n \to nx$. It must be emphasized, however, that this procedure is rigorously correct *only* for the calculation of the high temperature properties, such as the transition temperature.

One must now evaluate the partition functions corresponding to the various configurations of magnetic ions.

$$Z(\varepsilon_p, \varepsilon_q, \varepsilon_r) = \operatorname{tr}\exp(-\beta H(\varepsilon_p, \varepsilon_q, \varepsilon_r)). \tag{5}$$

If all three of the lattice sites are magnetic, then the partition function to second order in the fields is, for spin S_0, (see Appendix)

$$Z(1,1,1) = \sum_{S_1}\sum_{S} \frac{2S+1}{S(S+1)}\left(S(S+1)+(\lambda_0\sigma_0+\lambda_1\sigma_1)^2/24 + \frac{\sigma_0\sigma_1}{24jS(S+1)}(\lambda_0-\lambda_1)^2\right)e^{j\sigma} + \sum_{S}\delta_{S0}(1-(\lambda_0-\lambda_1)^2 S_0(S_0+1)/6_j) \times \exp(-2jS_0(S_0+1)), \tag{6}$$

where $0 \leqslant S_1 \leqslant 2S_0$, $|S_1-S_0| \leqslant S \leqslant |S_1+S_0|$ and the $S = 0$ term (if it occurs) is to be excluded from the first sum in (6). λ_0 and λ_1 are the effective fields, assumed to be of the form:

$$\lambda_0 = (n-2)xa$$

and

$$\lambda_1 = (n-1)xa$$

with a being the internal field per spin. Finally,

$$\sigma = S(S+1)-S_0(S_0+1)-S_1(S_1+1),$$

$$\sigma_0 = S(S+1)+S_0(S_0+1)-S_1(S_1+1),$$

and

$$\sigma_1 = S(S+1)-S_0(S_0+1)+S_1(S_1+1).$$

Similarly, if either of the end lattice sites are non-magnetic, the partition function will be the same, except that now S_1 takes only the single value, S_0.

$$Z(0,1,1) = Z(1,1,0) = \sum_{S} \frac{2S+1}{S(S+1)}\left(S(S+1)+(\lambda_0\sigma_0+\lambda_1\sigma_1)^2/24 + \frac{\sigma_0\sigma_1}{24jS(S+1)}(\lambda_0-\lambda_1)^2\right)e^{j\sigma} + \sum \delta_{S0}(1-S_0(S_0+1)(\lambda_0-\lambda_1)^2/6_j) \times \exp(-2jS_0(S_0+1)), \tag{7}$$

but since $\sigma_0 = \sigma_1 = S(S+1)$ in this case,

$$Z(0,1,1) = \sum_{S=1}^{2S_0} (2S+1)(1+S(S+1)(\lambda_0+\lambda_1)^2/24+(\lambda_1-\lambda_0)^2/24j)e^{j\sigma} + (1-S_0(S_0+1)(\lambda_0-\lambda_1)^2/24j)\exp(-2jS_0(S_0+1)). \tag{8}$$

If the central lattice site is non-magnetic, then

$$-\beta H(1,0,1) = \lambda_1 S_{1z}. \tag{9}$$

So,

$$Z(1,0,1) = \sum_{S_1=0}^{2S_0} \sum_{m=-S_1}^{S_1} \exp(m\lambda_1) \cong \sum_{S_1=0}^{2S_0} ((2S+1)+S(S+1)(2S+1)\lambda_1^2/6). \quad (10)$$

In obtaining (10), the exponential has been expanded and the M sum evaluated using

$$\sum_{m=-S}^{S} m^2 = \tfrac{1}{3}(2S+1)(S+1)S. \quad (11)$$

Finally, the S_1 sum in (10) can be done explicitly to yield

$$Z(1,0,1) = (2S_0+1)^2(1+S_0(S_0+1)\lambda_1^2/3), \quad (12)$$

where the following identities have been employed.

$$\sum_{S=0}^{2S_0} S = S_0(2S_0+1).$$

$$\sum_{S=0}^{2S_0} S^2 = S_0(2S_0+1)(4S_0+1)/3,$$

$$\sum_{S=0}^{2S_0} S^3 = S_0^2(2S_0+1)^2. \quad (13)$$

In like manner,

$$Z(0,0,1) = (2S_0+1)(1+S_0(S_0+1)\lambda_1^2/6), \quad (14)$$

and

$$Z(0,1,0) = (2S_0+1)(1+S_0(S_0+1)\lambda_0^2/6). \quad (15)$$

The configurationally averaged free energy is just

$$\langle -\beta_F \rangle_C = \sum_{\varepsilon} N(\varepsilon_p, \varepsilon_q, \varepsilon_r) \ln Z(\varepsilon_p, \varepsilon_q, \varepsilon_r), \quad (16)$$

where $N(\varepsilon_p, \varepsilon_q, \varepsilon_r)$ is the probability of occurrence.

The condition on the magnetizations to be applied here is

$$\langle\langle S_{0z}\rangle_T\rangle_C = \langle\langle S_{1z}\rangle_T\rangle_C/2, \quad (17)$$

where a subscript $T(C)$ denotes a thermal (configuration) average. This is, of course, consistent with the arguments given in the beginning of this section for a quenched system. From (6), (7), (8), (12), (14), (15) and (16) one obtains the self-consistency condition to first order. From this, the equation determining the transition temperature is found to be

$$x^3(F_1/F_2)+2x^2(1-x)(F_3/F_4)-x^2(1-x)\{S_0(S_0+1)(n-1)/3\}$$
$$-x(1-x)^2\{S_0(S_0+1)/3\} = 0,$$

where

$$F_1 \sum_{S_1} \sum_{S} \frac{2S+1}{S(S+1)} \left[(2\sigma_0 - \sigma_1)(\eta_0\sigma_0 + \eta_1\sigma_1)/24 -- \frac{\sigma_0\sigma_1}{8jS(S+1)} \right] e^{j\sigma_0}$$

$$+ \sum_{S} \delta_{S0} S_0 (S_0+1)/2j,$$

$$F_2 = \sum_{S_1} \sum_{S} (2S+1) e^{j\sigma_0} + \sum_{S} \delta_{S0},$$

$$F_3 = \frac{S_0(S_0+1)}{2_j} + \sum_{S=1}^{2S_0} e^{j(S+1)} (2S+1) \left[S(S+1)(2n-3)/24 - \frac{1}{8j} \right],$$

$$F_4 = \sum_{S=0}^{2S_0} (2S+1) e^{jS(S+1)}. \tag{18}$$

3. Results

The solutions of this last equation are shown as functions of x for several values of spin and the bcc lattice in Figure 1. It was found that the solutions were continuous, implying that the transition was always of second order. (Using the constant-coupling approximation, Kumar and Bhargava [10] find a $T_c(x)$ curve that drops discontinuously to zero at $x_c = 4/n$, i.e., a first-order transition. Their result is unusual.) Furthermore, the present approach does not yield a curve for $T_c(x)/T_c\,(1)$ versus x which is concave downward over the whole range of concentration. This is not the usual result, but it is not unknown. Examples of other results showing similar behavior are reproduced in Figure 2. The

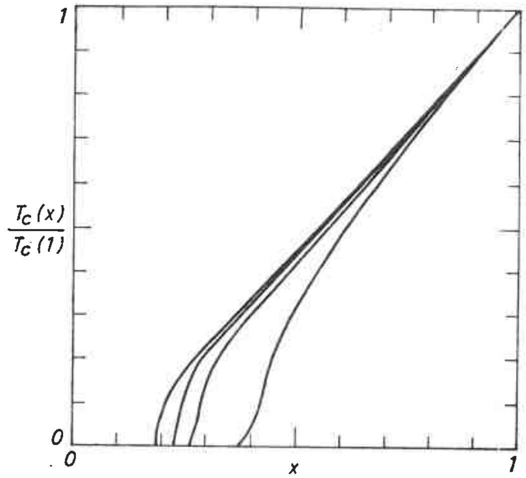

Fig. 1. Concentration dependence of the Curie Temperature for a dilute ferromagnet. The curves shown represent spin values of (right to left) 1/2, 1, 3/2 and 2. Note that the change in curvature disappears for large spin values

curves (*a*), (*b*), and (*c*) are theoretical results of (*a*) Heap [11] using a power series (in x) approximation to the susceptibility, (*b*) Mano [12] using a cluster approach, and (*c*) Tahir-Kheli et al. [6] using the coherent potential approximation. These results all apply to the Heisenberg model, spin-1/2, for the body-centered cubic lattice. The curves (*d*) and (e) are both experimental and theoretical results or *anti*-ferromagnets, (*d*) from Heikens and van Bruggen's [13] data on $Mn_xMg_{1-x}S$ and is similar in appearance to data of Breed et al. [14] on $KMn_xMg_{1-x}F_3$ and (*e*) is the theory (CPA-RPA) of McGurn and Tahir-Kheli [15] compared with data of Baker et al. [16] on $Mn_xZn_{1-x}F_2$. In every case we note the presence of the upward curvature in the T_c–x curves. So, although the concave downward behaviour appears to be more common and is intuitively expected (see Refs. [1] and [8]), the concave upward result found here (Fig. 1) does have some precedents. Finally, it is observed that results for the Heisenberg model are often considerably different from those of the Ising model.

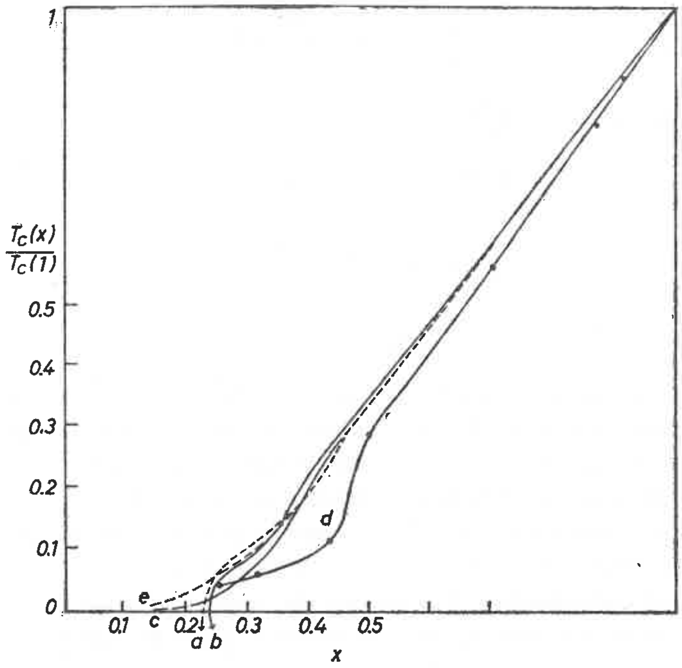

Fig. 2. Various results for the Curie temperature vs concentration. Curves *a*, *b*, and *c* are theoretical results for body-centered ferromagnets for spin 1/2. Also shown (*d* and *e*) are experimental and theoretical results for antiferromagnets. See text for references. Note the presence of the upward concavities

The critical concentration is that value of x for which $j \to \infty$ ($T_c \to 0$). It can be found by taking that limit in (18). A straightforward, though tedious, computation gives the following value for the critical concentration.

$$x_c = \frac{2(S_0+1)}{2S_0(n-1)+1} \,. \tag{19}$$

This value exhibits a somewhat larger spin dependence than one might intuitively expect, but it is not unreasonable. A similar result has been reported by Elliott [17] who used the constant coupling approach. $\left(\text{Actually, his result was } x_c = \dfrac{S_0+1}{S_0(n-1)}.\right)$

Another quantity of interest is the slope of the $T_c(x)\,T_c(1)$ versus concentration curve at $x = 1$. For the bcc lattice, the SCOII method predicts a value of 1.25 which compares well with the value of 1.33 for $Mn_xZn_{(1-x)}F_2$. The RPA [7] yields a value of 1.51 for this quantity.

APPENDIX

Perhaps the simplest way to find the partition functions corresponding to various configurations of magnetic ions is to utilize a representation in which one first couples $\bar{S}_p$ and $\bar{S}_r$. That is, let $\bar{S}_1 = \varepsilon_p\bar{S}_p + \varepsilon_r\bar{S}_r$. Similarly, $\bar{S}_0 = \varepsilon_q\bar{S}_q$. The advantage of this approach is that the effect of particular combination of ε's can be accounted for by simply adjusting the ranges of these coupled spins.

Therefore, we consider the function,

$$F(X) = \exp\,[X(A+B)], \tag{A1}$$

where $A = 2j\,\bar{S}_0 \cdot \bar{S}_1$ and $B = \lambda_1 S_{1z} + \lambda_0 S_{0z}$. It is our intention here to treat A as the unperturbed Hamiltonian and B as the perturbation term. This will ultimately lead to a power series in the effective fields.

$F(X)$ will obey the following differential equation [9]:

$$\frac{d}{dX}\left[e^{-AX}F(X)\right] = e^{-AX}BF(X) \tag{A2}$$

with $F(0) = 1$. It also follows that

$$F(X) = e^{AX} + \int_0^X e^{A(X-X')}BF(X')\,dX'. \tag{A3}$$

This latter integral equation can be expanded into the usual Neumann series. We retain here only the first two terms.

$$\begin{aligned} F(1) &= e^A + \int_0^1 e^{(1-X)A}Be^{XA}dX + \int_0^1\int_0^{X'} e^{(1-X)A}Be^{(X-X')A}Be^{X'A}dX\,dX' \\ &= e^A + \int_0^1 e^{(1-X)A}Be^{XA}dX + \tfrac{1}{3}\int_0^1 \bar{B}e^{(1-u)A}\cdot\bar{B}e^{uA}du. \end{aligned} \tag{A4}$$

If one now defines $\bar{S} = \bar{S}_0 + \bar{S}_1$, A will be diagonal in an $|S_0S_1SM\rangle$ representation. Now,

$$\begin{aligned} \operatorname{tr} F(1) &= \sum_{S_1}\sum_{S}\sum_{M}\langle S_0S_1SM|F(1)|S_0S_1SM\rangle = \sum_{S_1}\sum_{S}(2S+1)e^{j\sigma} \\ &+\int_0^1 \sum_{S_1}\sum_{S}\sum_{M} e^{(1-x\sigma)}\langle S_0S_1SM|B|S_0S_1SM\rangle e^{x\sigma}dx + \tfrac{1}{3}\int_0^1 \operatorname{tr}\bar{B}e^{(1-u)A}\cdot\bar{B}e^{uA}du, \end{aligned} \tag{A5}$$

where $\sigma = S(S+1) - S_0(S_0+1) - S_1(S_1+1)$.

Since the first integral in A5 is an odd function of M, its trace will be identically zero. Finally, one needs to calculate

$$\mathrm{tr}\, \bar{B}e^{(1-u)A} \cdot \bar{B}e^{uA} = \sum_{S_1} \sum_{SM} \sum_{S'M'} |\langle SM|B|S'M'\rangle|^2 e^{j(1-\mu)\sigma'} e^{ju\sigma}. \tag{A7}$$

The Wigner–Eckert theorem can be used to determine the M and M' dependence of the above matrix element. The M, S' and M' sums can then be evaluated using straightforward angular momentum techniques. (See also equation (13[3]1′) of Condon and Shortley). The integral can then be evaluated, taking care to treat the $S = 0$ term separately. Finally, one obtains

$$\mathrm{tr}\, F(1) = \sum_{S_1} \sum_{S} (2S+1)e^{j\sigma} + \sum_{S_1} \sum_{S} \frac{2S+1}{24S(S+1)} (\lambda_0\sigma_0 + \lambda_1\sigma_1)^2$$

$$+ \frac{\sigma_0\sigma_1}{jS(S+1)} (\lambda_0 - \lambda_1)^2 e^{j\sigma} + \sum_{S} \delta_{S0}[1 - S_0(S_0+1)\,(\lambda_0-\lambda_1)^2/6_j] \exp\,[-2jS_0(S_0+1)], \tag{A8}$$

where the definitions are those used in the text. Equations (6) and (7) can be inferred directly from the above.

Editorial note: This article was proofread by the editors only, not by the authors.

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