Vol. A55 (1979) ACTA PHYSICA POLONICA No 2

THE EFFECT OF DILUTION ON FERROMAGNETIC CURIE TEMPERATURES

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(*Received June 14, 1978*)

The dependence of the Curie temperature, T_c, of a diluted ferromagnet on the concentration x, is calculated by the constant-coupling approximation in a more rigorous and complete manner than earlier results. The critical concentration, x_c, and the dependence of T_c on x is calculated for various spins and lattices. The procedures and results of this and other calculations are compared, showing considerable divergences is some cases.

1. Introduction

The effect on the Curie temperature, T_c, of a ferromagnet caused by the introduction of non-magnetic ions has been calculated by various means [1–13, 16]. In particular, the constant-coupling approximation has been employed in two quite different and somewhat limited ways [2, 13]. Both of these led to the same behavior of T_c with concentration and the values of the critical concentration, x_c, for which the Curie temperature goes to zero.

It is the aim of this paper to describe the proper and complete approach to the problem within the constant-coupling approximation and to show that, for spin 1/2 at least, this approach does lead to these same results for T_c as a function of the concentration, x, and to some more general results as well.

2. The constant-coupling approximation for dilution

We employ the constant-coupling approximation in the manner described in Ref. [14]. To treat the dilution problem, we consider the entire lattice decomposed into $\frac{1}{2}Nn$ pairs of nearest neighbors. N is the number of lattice sites and n is the coordination number of the lattice. Each of the two sites has $(n-1)$ other neighbors of which $k = 0, 1, 2, \ldots (n-1)$ may be magnetic, the rest not. (When we include the possibility that site 1 has k_1 magnetic neighbors while site 2 has k_2, we find that this has no effect on T_c.)

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The Hamiltonians of the various types of clusters can be written

$$H_2^{(k)} = -2JS_1S_2-\mu kh(S_{1z}+S_{2z}), \quad H_1^{(k)} = 0-\mu khS_{1z}, \quad H_0^{(k)} = 0, \tag{1}$$

when μS is the magnetic moment of the atom, kh is the internal field produced by the k magnetic neighbors, and J is the exchange integral. $H_2^{(k)}$ is the Hamiltonian of a pair of neighboring magnetic sites each of which has k magnetic neighbors; $H_1^{(k)}$ is the Hamiltonian of a pair of sites, the magnetic one with k magnetic neighbors, and $H_0^{(k)}$ is the Hamiltonian of a pair of non-magnetic sites.

In each case,

$$Z_i^{(k)} = \mathrm{tr}\, e^{-\beta H_i^{(k)}}, \tag{2}$$

where $\beta = 1/kT$. The partition function can be written as a product since all the different Hamiltonians commute (not true for an antiferromagnet):

$$Z = \prod_{k=0}^{n-1} (Z_2^{(k)})^{N_2}(Z_1^{(k)})^{N_1}(Z_0^{(k)})^{N_0}. \tag{3}$$

The numbers N_i (actually, $N_i^{(k)}$) refer to the number of ways of having that kind of cluster, assuming random distribution of magnetic and non-magnetic ions. Hence,

$$N_2^{(k)} = \tfrac{1}{2}\, Nnx^2 f_k, \quad N_1^{(k)} = \tfrac{1}{2}\, Nn2x(1-x)f_k, \tag{4}$$

and

$$N_0^{(k)} = \tfrac{1}{2}\, Nn(1-x)^2 f_k,$$

and x is the concentration of magnetic ions and f_k are the binomial coefficients for $(n-1)$ things taken k at a time:

$$f_k = \frac{(n-1)!}{k!(n-1-k)!}\, x^k(1-x)^{n-1-k}. \tag{5}$$

Then

$$\langle \ln Z\rangle = \prod_{k=0}^{n-1} \{N_2^{(k)} \ln Z_2^{(k)} + N_1^{(k)} \ln Z_1^{(k)} + 0\}. \tag{6}$$

The proper procedure [15], having formed the configuration average, $\langle \ln Z\rangle$, by taking the sums over k, is to find the thermal properties by taking the proper derivatives. The Curie temperature will be determined by the magnetization and this is most conveniently found by including an external magnetic field, h_e, by the change $\mu kh \to \mu kh + \mu h_e$, and then taking the derivative of $\ln Z$ with respect to $\beta\mu h_e$. This will give us

$$\overline{m}_2 = \tfrac{1}{2}\frac{1}{\frac{1}{2}Nn}\, \frac{\partial\langle \ln Z\rangle}{\partial(\beta\mu h_e)}\bigg|_{h_e=0}. \tag{7}$$

As explained in Ref. [14], the constant-coupling approximation can be achieved by the use of a one-particle cluster with

$$H_1'^{(k)} = -\mu khS_z. \tag{8}$$

Then

$$\langle \ln Z' \rangle = \sum_{k=0}^{n} Nxf_k'Z_1'^{(k)}, \tag{9}$$

where

$$f_k' = \frac{n!}{k!(n-k)!}x^k(1-x)^{n-k} \tag{10}$$

is the relative probability of finding k magnetic ions on n sites. Then

$$\overline{m}_1 = \frac{1}{N}\frac{\partial\langle \ln Z'\rangle}{\partial(\beta\mu h_e)}\bigg|_{h_e=0}. \tag{11}$$

Now equating $\overline{m}_2$ and $\overline{m}_1$ gives the same results as constant coupling.

$S = 1/2$:

For spin 1/2, we can easily find

$$\overline{m}_2 = \frac{x^2 \sinh\lambda}{1+2\cosh\lambda + e^{-2p}} + \tfrac{1}{2}x\tanh\tfrac{1}{2}\lambda, \tag{12}$$

and

$$\overline{m}_1 = \tfrac{1}{2}x\tanh\tfrac{1}{2}\lambda', \tag{13}$$

where

$$\lambda = \beta\mu(n-1)xh, \tag{14}$$

and

$$\lambda' = \beta\mu nxh. \tag{15}$$

If we expand (12) and (13) in powers of h, keep only linear terms, and equate $\overline{m}_1$ and $\overline{m}_2$, we have the Curie temperature equation

$$\frac{4x}{3+e^{-2p_c}} + (1-x) = \frac{n}{n-1}, \tag{16}$$

where

$$p_c = \beta_c J = J/kT_c, \tag{17}$$

which gives the behavior of $T_c(x)$ for a given lattice.

Other ways of obtaining this same result exist. One is to replace the Hamiltonians, $H_i^{(k)}$, of Eq. (1) by simply H_i with k replaced by $(n-1)x$ and by nx in H_1'. Another is to take the Curie temperature equation for the constant-coupling approximation for an undiluted lattice and take a configuration average of this equation. This approach is due to Handrich [13]. Finally, a third approach is to examine an arbitrarily chosen pair of *magnetic* neighbors and follow the constant-coupling procedure (for $T \geqslant T_c$) with $(n-1)$ replaced by $(n-1)x$ in the internal field. This method is due to Elliott [2] and a variation of it has more recently been published by Oguchi and Obokata [12]. All these methods are discussed briefly in Appendix A. We note here that the present procedure is more rigorous than Handrich's and more general than it or the last two.

$S = 1$:

Proceeding in the same way for the spin-1 case, we find the following result for $T_c(x)$:

$$3xf(p_c)+2(1-x) = \frac{2n}{n-1}\,, \tag{18}$$

where

$$f(y) = \frac{e^{2y}+5e^{6y}}{1+3e^{2y}+5e^{6y}}\,. \tag{19}$$

To find the critical concentration, let $p_c \to \infty$ and get

$$x_c = \frac{2}{n-1}\,. \tag{20}$$

$S = \infty$:

Elliott [2] has shown that, in the limit of classical spin,

$$x_c = \frac{1}{n-1}\,.$$

a result which is also found for the Ising model and the Bethe-Peierls-Weiss classical spin approximation. (Consult the Appendices B and A.5).

3. Conclusion

The behavior of T_c vs. x is shown in Fig. 1 for a body-centered cubic lattice ($n = 8$). We note the abrupt descent of T_c to zero for the critical concentrations:

$$\begin{aligned} x_c &= 3/(n-1) && \text{for } S = 1/2 \text{ (Eq. (16))},\\ &= 2/(n-1) && \text{for } S = 1 \text{ (Eq. (18))},\\ &= 1/(n-1) && \text{for } S = \infty \text{ (Eq. (A7))},\\ & && \text{or Ising model (Eq. (B1)).} \end{aligned}$$

All of these (except the Ising model) agree with Elliott's general-spin result given by Eq. (A5) in Appendix A.

The general behavior shown in the figure is as expected from previous observations and calculations (see Ref. [7], for example), viz., a decrease, initially linear, in T_c as x decreases, a more rapid decrease for smaller x (negative curvature), ending with an infinite slope, $dT_c/dx \to \infty$ as $x \to x_c$.

Calculations of x_c by other methods are mostly for the spin $-1/2$ case (or the Ising model). High-temperature expansion methods are used to find expansions of the susceptibility in powers of the concentration [6–8] and give a value for $x_c \approx 2/n$. A similar result is obtained by solutions of the percolation (site) problem [5], the spin-wave theory [9, 20], the coherent potential approximation [21]. This rather common approximate result can be qualitatively justified by the simple argument that, to be ferromagnetic, a minimum requirement is that each magnetic site have at least *two* magnetic neighbors or $nx_c = 2$. Our result, $(n-1)x_c = 3$, requires a lattice of considerably higher concentration.

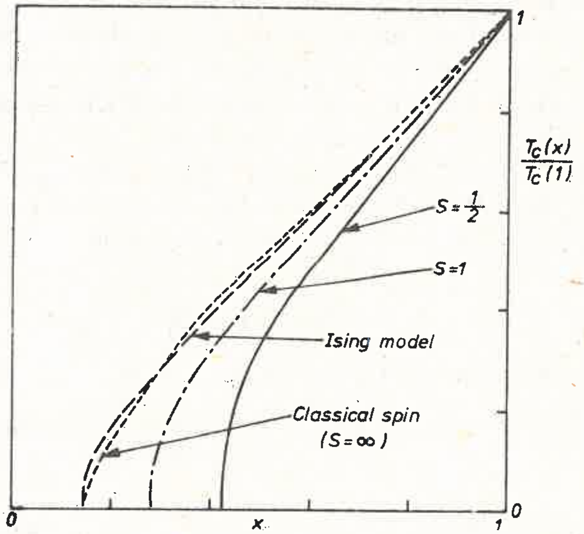

Fig. 1. The reduced Curie temperature vs concentration for a body-centered cubic lattice ($n = 8$), calculated by the constant-coupling approximation

For the Ising model, our result $(n-1)x_c = 1$ appears unreasonably low. It is, however, exactly the result found in Ref. [1] by what was referred to as the cluster variation method, and it is not far from the percolation (bond) problem result of Ref. [5] which is $x_c \approx 1/(n-2)$. One would expect, instead, a result closer to that of the site problem, $2/n$. That result, again, is obtained by the Bethe-Peierls-Weiss second approximation [11] (using an enlarged cluster including next-nearest neighbors) for Ising systems. The lower critical concentration for the Ising model (compared to the Heisenberg spin $-1/2$ case) was suggested in Ref. [6] III.

We find that x_c is the same for the classical-spin as the Ising model and that, as seen in Fig. 1, the two curves of T_c vs. x almost coincide. The only comparison with other work here is with the Bethe-Peierls-Weiss classical-spin result [3] which is identical with ours. (See Appendix A (v)).

The $T_c(x)$ curve for $S = 1$ falls, as might be expected, about midway between those for $S = 1/2$ and classical spin. The rather large spin-dependence of $T_c(x)$ is surprising since one intuitively expects that the problem should be more dependent on lattice topology than spin.

Whether the constant-coupling method is a good approximation for the dilution problem remains an open question in view of all the above. The argument that the two-site Hamiltonian used refers to a cluster too small to describe dilution properly does not bear close scrutiny. There are, after all, $2(n-1)$ neighbors included in the internal field term so that, in all, $2n$ sites are considered and this should be enough for a reasonable description. The series and cluster expansions of Rushbrooke and Morgan [6] and Elliott and Heap [7, 8] include only sets of 5 or 6 sites respectively and the percolation calculations of Domb and Sykes [4] and Sykes and Essam [5] a similar number (larger for simpler lattices) while the Bethe-Peierls-Weiss method [3] uses just $n+1$ sites. The lack of better agreement among all these methods remains unexplained.

APPENDIX A

(*i*) If we replace equations (1) and (4) by

$$H_2 = -2JS_1S_2-\mu h(n-1)x(S_{1z}+S_{2z}), \quad H_1 = 0-\mu h(n-1)xS_{1z}, \quad H_0 = 0, \tag{A1}$$

and

$$N_2 = \tfrac{1}{2}Nnx^2, \quad N_1 = Nnx(1-x), \quad N_0 = \tfrac{1}{2}Nn(1-x)^2, \tag{A2}$$

then, despite obvious modifications to (2) and (6), the same value of $\overline{m}_2$ results. Similarly, for a one-particle cluster, there is no change in $\overline{m}_1$, so equating $\overline{m}_2$ and $\overline{m}_1$ gives Eq. (16) again. Thus, we see that the separate consideration of the different cluster $H_i^{(k)}$ for $k = 0, 1, 2 \ldots n-1$ has no effect on the thermodynamic properties of the system and (A1) can replace (1). (We note that the second term on the l.h.s. of (16) is the contribution of $Z_1 = \operatorname{tr} e^{-\beta H_1}$ see note (*iii*) below.)

(*ii*) Handrich [13] considers dilution by configuration-averaging the Curie-temperature equation. For constant coupling this equation is (take $x = 1$ in (16)):

$$\frac{4}{3+e^{-2p_c}} = g(p_c) = \frac{1}{n-1}\,. \tag{A3}$$

From this, the configuration average is taken by simply setting

$$\langle g(p_c)\rangle = g(p_c)x+g(0)(1-x), \tag{A4}$$

which again leads to (16). The fact that this procedure works in the present case implies that the operations of configuration averaging and taking the derivatives as in (7) and (11) commute. The validity of this procedure will be discussed again below and in a subsequent paper.

(*iii*) Elliott [2] considers the constant-coupling approximation for general spin but only for temperatures above T_c. Dilution is introduced by considering (quoting Elliott), "only pairs where both atoms are magnetic and the coordination number around such a pair reduced from" $(n-1)$ to $x(n-1)$. His result is, again, Eq. (16) which we can find by using his Eqs (11) and (12) (the latter being the transformation whereby the results of the Ising model change over to those of the Heisenberg model for $S = 1/2$ in the constant-coupling approximation) and Eq. (6) from Ref. [1]. (The result of what is called the cluster-variation method for the Ising model.) Elliott's general-spin result for the critical concentration is

$$x_c = \frac{S+1}{S(n-1)}, \tag{A5}$$

which we note goes to $1/(n-1)$ for classical spin and $3/(n-1)$ (Eq. (17)) for $S = 1/2$. The fact that Elliott arrives at Eq. (16) is surprising in view of the fact that he considers only the Hamiltonian H_2 in (A1). The classical-spin model shows $T_c(x)$ to be the same as the Bethe-Peierls-Weiss classical spin result (see (A7) below) and is shown in Fig. 1.

(*iv*) Oguchi and Obokata [12] also use a pair of magnetic neighbors each with $(n-1)x$ magnetic neighbors. This factor replaces $(n-1)$ in the internal field term in the Hamiltonian. When they consider the one-site Hamiltonian, the internal field is replaced by $(1+(n-1)x)h$. The first term in the parenthesis is to account for the fact that one neighbor (the other of the pair) is certainly magnetic. This is, like Elliott's, an obviously incomplete procedure since only pairs of neighboring *magnetic* sites are considered.

(*v*) Finally, we note some results of the Bethe-Peierls-Weiss method for classical spin, using methods similar to those discussed above. If done in the proper way (by taking the configuration average of $\ln Z$), it is found [3] that

$$x_c = \frac{1}{n-1}, \tag{A6}$$

and

$$L(b_c) = \frac{1}{x(n-1)}, \tag{A7}$$

where L is the Langevin function,

$$L(b) = \coth b - 1/b, \tag{A8}$$

and

$$b = 2JS^2/kT. \tag{A9}$$

The Curie temperature equation for the undiluted lattice is

$$L(b_c) = \frac{1}{n-1}. \tag{A10}$$

If we follow Handrich's procedure and take a configuration average of this equation, we find

$$\langle L(b_c)\rangle = L(b_c)x + L(0)(1-x) = L(b_c)x, \tag{A11}$$

and

$$L(b_c) = \frac{1}{x(n-1)},$$

with $x_c = 1/(n-1)$ again, just as in the "correct" result, (A6).

If, on the other hand, we take the most naive approach and replace n by nx in the Hamiltonian, we find [16]

$$L(b_c) = \frac{1}{nx-1}, \tag{A12}$$

and

$$x_c = \frac{2}{n}. \tag{A13}$$

Thus, in this case, the three procedures do not lead to the same result. Handrich's configuration average of the Curie temperature gives the same answer as Smart's more rigorous method, but the third and crudest approach gives what is probably a better value for x_c.

From Elliott [2], Eq. (10), we see that the constant-coupling method in the limit of classical spin gives exactly the result (A7).

APPENDIX B

Here we consider constant coupling for dilution using the Ising model. Changing S_1S_2 to $\frac{1}{4}\sigma_1\sigma_2$ and S_z to $\frac{1}{2}\sigma$ in (A1), we obtain, instead of (A8),

$$\frac{2x}{1+e^{-p_c}} + (1-x) = \frac{n}{n-1}, \tag{B1}$$

which is shown in Fig. 1.

We note that

$$x_c = \frac{1}{n-1}. \tag{B2}$$

Following Handrich's procedure, the Curie temperature equation for the undiluted lattice, viz.

$$\frac{2}{1+e^{-p_c}} = \frac{n}{n-1}, \tag{B3}$$

is used and its configuration average taken as above, leading immediately to (B1) and (B2).

We note that if we were to express (B3) in the simpler, but equivalent form;

$$e^{-p_c} = \frac{n-2}{n}, \tag{B4}$$

and then take the configuration average, we obtain

$$\langle e^{-p_c}\rangle = xe^{-p_c}+(1-x) = \frac{n-2}{n}, \tag{B5}$$

which is quite different from (B1). Also,

$$x_c = \frac{2}{n} \quad \text{instead of (B2).} \tag{B6}$$

In general, when employing Handrich's method, the Curie temperature equation, obtained by equating two magnetizations, must be configuration-averaged without changing it by any further algebraic operations.

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