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Effective-field theory for the magnetic and thermal properties of site- and bond-impure systems

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Abstract. We present different effective-field and cluster-variation treatments of the magnetic spin-$\frac{1}{2}$ Ising model for a fraction x of frozen-in or quenched non-magnetic impurities. The resulting picture for the critical curve, magnetisation, energy, specific heat and susceptibility is simple and compares very well with Monte Carlo and experimental data. Our results can thus be useful in the analysis of 'anomalies' in non-stoichiometric compounds such as metal oxides, mixed alloys and other substances up to the percolation threshold x_c.

1. Introduction

The physical properties in many substances show a rather strong dependence on small deviations from perfect stoichiometry. The analysis of this fact is of great practical interest because deviations from stoichiometry occur commonly in practice and frequently affect materials with a broad spectrum of technological applications. For instance, transition-metal oxides usually show up in Nature as $A_{1-x}O$ and different electronic and magnetic properties are rather frequently observed for different samples, and these presumably correspond to different values of x (see, e.g., McGuire *et al* 1972, de Jongh and Miedema 1974 (and references therein), Seehra and Silinsky 1979, Seehra and Groves 1983, Dominguez *et al* 1984 (and references therein), Hauser and Waszczak 1984). Also, many materials can be prepared in the laboratory as $A_{1-x}B_xC$ compounds, by replacing magnetic A atoms in the pure magnet AC by non-magnetic B impurities, and their magnetic and thermal properties show similar variations with x (Lagendijk and Huiskamp 1972, Birgeneau *et al* 1983, Westerholt and Sobotta 1983, Westerholt *et al* 1984). While the observed dependence on x has sometimes been explained, for instance as a consequence of competing interactions causing spin glass behaviour in MnO (Hauser and Waszczak 1984), the effects are often termed anomalous, thus revealing that they still lack a proper theoretical interpretation (see, e.g., Seehra and Silinsky 1979). It is the purpose of this paper to develop effective-field and cluster-variation treatments, involving simplified models of the above physical situation, which may provide a well defined reference for analysing some of the data that are now available and future experiments on simple materials.

The situation depicted above immediately suggests that the 'anomalous' magnetic and thermal properties when $x \neq 0$ might in principle be analysed through consideration of simple lattice models with defects, say non-magnetic impurities. The basic starting

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model we consider here is the magnetic spin-$\frac{1}{2}$ Ising model with nearest-neighbour (NN) pair interactions defined by the Hamiltonian

$$H = -\sum_{\langle i,j \rangle} J_{ij} s_i s_j \qquad J_{ij} = J \tag{1.1}$$

where the sum extends over all NN pairs in a given lattice of size V and $s_i = \pm 1$. Impurities can then be included in several ways. A site-impure situation is simulated here by setting $s_i = 0$ at xV fixed randomly distributed lattice sites. That is, frozen-in non-magnetic impurities are considered by replacing the spins at randomly chosen sites of the lattice by static ('quenched') impure sites which do not interact with the spins. We also study a bond-impure situation where a fraction x of the interactions in the basic model are broken.

Real materials, of course, exhibit many extra complications that are not included in these models, such as extended interactions, competing ferro–antiferromagnetic bonds, larger numbers of spin components, isotropy and more complex lattice structures and defects. Nevertheless, our results may still give reasonable insight into the phenomena of interest and there are many materials that can in principle be approximated by our models. We shall present evidence to show that our theoretical results do indeed provide good qualitative and semi-qualitative descriptions of the experimental and the Monte Carlo data. This agreement is even more striking given the simplicity of the models we consider here, a simplicity that was dictated by our search for a description covering the behaviour of several quantities over a broad range of values of x and temperature.

An important point is that the random distribution of quenched defects or impurities considered in this paper may represent a rather general situation in practice at low enough temperature, e.g. far below the melting point for the lattice, and that it destroys the regularity of the interactions in the system, so one may in principle expect to observe interesting changes from the 'pure' case ($x = 0$). In fact, similar mathematical models have been used before in order to study both particular physical situations and the overall physical properties in materials including disorder, such as in impure and amorphous systems, spin glasses, dilute magnets and surfaces (see, for instance, the reviews by Mills *et al* 1971, McCoy and Wu 1973, Burkhardt and van Leeuwen 1982, Binder 1979, 1984, Mouritsen 1984). However, neither the theoretical situation concerning impure or disordered systems (Behringer 1957, Grinstein and Luther 1976, Stoll and Schneider 1976, Landau 1980, Newman and Rieder 1982, Dotsenko and Dotsenko 1983, Jug 1983) nor the corresponding experimental situation (Seehra and Silinsky 1979, Cowley and Carneiro 1980, Westerholt and Sobotta 1983, Westerholt *et al* 1984, Birgeneau *et al* 1983, 1984 (and references therein) are clearly understood at present; we refer the reader to the excellent review by Stinchcombe (1983) for further details and references.

2. The Bethe–Peierls method

Effective-field approaches to magnetism (see, e.g., Smart 1966, Pathria 1977) usually give a poor quantitative description of the data: they fail to reproduce the correct exponents describing the asymptotic behaviour when $T \to T_c$ and the spin wave behaviour at low temperatures and yield only semi-quantitative agreement at best in other cases. This is a consequence of the defective treatment of the short-ranged correlations, symmetries and dimensionality of the systems.

There are in practice many ways of taking account of these effects in the context of

impure Ising models. For instance, one may consider different microscopic arrangements of magnetic ions and impurities around a given lattice site or different relations between a given cluster of spins and its surroundings or one may consider impurity bonds instead of impurity sites. As a consequence, the resulting pictures are varied and their validity is uncertain *a priori* (see, for instance, Behringer 1957, Sato *et al* 1959, McCoy and Wu 1973, Katsura and Matsubara 1974 (and references therein), Stinchcombe 1983, Dotsenko and Dotsenko 1983). We present in this and the following two sections different effective-field treatments yielding a very useful qualitative description of the phenomena of interest. As compared with more sophisticated approaches, the one in this paper is more general in the sense that it allows in principle an economic computation of any physical quantity over a broad range of temperatures and concentrations x, and it also produces semi-quantitative agreement with experimental data, while the mathematical framework is here simpler and transparent.

We shall first consider a given 'central' spin s_0 surrounded by $q' < q$ spins at NN sites; q (=6 for a SC lattice) represents the coordination number of the lattice and $q' = (1 - x)q$. This situation can be handled by the first-order effective-field treatment introduced by Bethe (1935) and Peierls (1936) for the 'pure' case $x = 0$. More specifically, we consider the Hamiltonian H given by

$$-H/k_BT = hs_0 + (h + h')\sum_{j=1}^{q'} s_j + k\sum_{j=1}^{q'} s_0 s_j \tag{2.1}$$

where $k \equiv J/k_BT$, h is proportional to the external field and h' represents an internal 'molecular' magnetic field arising from the spins in the system not included explicitly in (2.1). The system partition function follows immediately:

$$Z = Z_+ + Z_- \qquad Z_\pm = e^{\pm h}[2\cosh(h + h' \pm k)]^{q'}. \tag{2.2}$$

Now we assume self-consistency in the sense that $\langle s_0\rangle = \langle s_j\rangle$, where $j \neq 0$ is any spin in the lattice and $\langle \ldots \rangle$ represents an ensemble average; this implies that the cluster of q' spins being considered is in thermodynamic equilibrium with the rest of the system. It then follows that

$$[\cosh(a_+)/\cosh(a_-)]^{q'-1} = e^{2h'} \tag{2.3}$$

where $a_+ \equiv h + h' + k$, $a_- \equiv h + h' - k$, which can be used to obtain the mean magnetisation per spin (or magnetic ion) in the system:

$$m(T, h; x) \equiv \langle s_0\rangle = \frac{\tanh(a_+) + \tanh(a_-)}{2 + \tanh(a_-) - \tanh(a_+)}. \tag{2.4}$$

The above procedure is a straightforward generalisation of the Bethe–Peierls method for the case $x \neq 0$ and was previously considered by Sato *et al* (1959). We include it here, however, in order to fix the notation for the other two treatments in this paper; moreover, we shall show below how the simple model (2.1)–(2.3) does indeed give a reasonable description of data and so thus can be used with some confidence in the analysis of experiments.

The use of (2.3) for $h = 0$ (zero magnetic field) in (2.4) produces the coexistence curves shown in figure 1 for different values of the impurity concentration x. Also following from (2.3) when $h = 0$ is the critical curve

$$T_c(x) = 2J/k_B \ln[q'/(q' - 2)]. \tag{2.5}$$

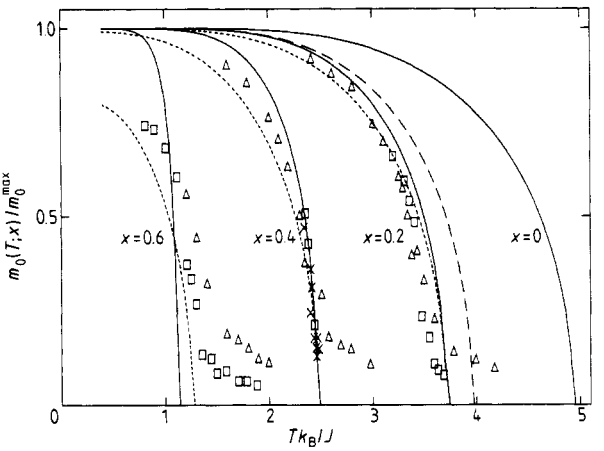

Figure 1. The mean spontaneous magnetisation per magnetic ion, normalised to the maximum value when $T = 0$ and $x = 0$, versus temperature as follows from the models in § 2 (full curves), § 3 (broken curves) and § 4 (dotted curves), for different values of x as indicated, in the case of a SC lattice. The symbols correspond to Monte Carlo data from Landau (1980): △ ($10 \times 10 \times 10$ SC lattice), □ ($20 \times 20 \times 20$) and × ($30 \times 30 \times 30$).

As noted previously by Sato *et al* (1959), this vanishes when $q' = (1 - x)q = 2$; that is, in order to obtain a finite value for T_c one needs enough spins to make, on average, a linear chain throughout the system. Interestingly enough, for the SC lattice ($q = 6$) this predicts that $T_c(x)$ vanishes as $x \to \frac{2}{3}$ and this is very close to the (site) percolative transition threshold $x_c \simeq 0.689$ (Sur *et al* 1976, Stauffer 1979). Note that the spins cannot correlate throughout the entire lattice when $x > x_c$ so one should indeed expect no phase transition for such large concentrations of impurities, in approximate agreement with the first-order mean-field results (2.5). The zeroth-order Bragg–Williams (Pathria 1977) approximation, in contrast, predicts $T_c(x) = \frac{1}{3}s(s + 1)q(1 - x)J/k_B$, where s is the spin number, vanishing as $x \to 1$. The function (2.5) is shown in figure 2 together with $T_c(x)$ obtained under other hypotheses and with some experimental data.

Near T_c, equation (2.3) for $h = 0$ gives $h' \simeq [3(q' - 1)(k_c - k)]^{1/2}$, $k_c \equiv J/k_B T_c$, and the following spontaneous magnetisation per spin:

$$m_0(T;x) \simeq \left[\frac{3}{2}\frac{q'^2}{q' - 1}\ln\left(\frac{q'}{q' - 2}\right)\left(1 - \frac{T}{T_c}\right)\right]^{1/2} \qquad T \to T_c. \tag{2.6}$$

This implies that the critical amplitude characterising the coexistence curve near T_c depends on x while the corresponding critical exponent β has the 'classical' value $\frac{1}{2}$, independently of x; this is an intricate question to which we shall return later in this paper.

The partition function (2.2) may also be written as

$$Z = Z_{++} + Z_{--} + Z_{+-} \tag{2.7a}$$

where

$$Z_{++} = \exp(2h + h' + k)[2\cosh(a_+)]^{q'-1} \tag{2.7b}$$

$$Z_{--} = \exp(-2h - 3h' + k)[2\cosh(a_+)]^{q'-1} \tag{2.7c}$$

$$Z_{+-} = 2\exp(-h' - k)[2\cosh(a_+)]^{q'-1} \tag{2.7d}$$

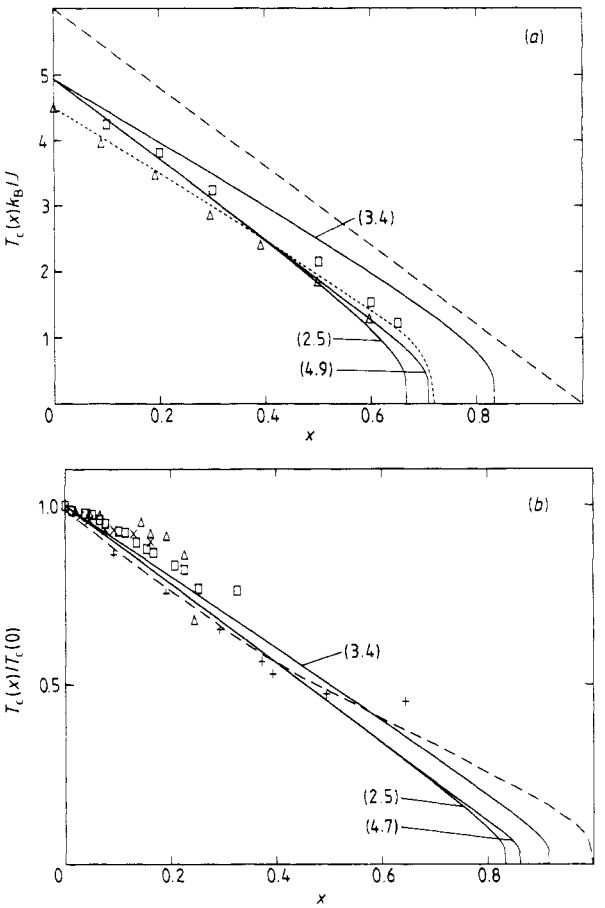

Figure 2. (*a*) The critical curve $T_c(x)$ for a SC lattice as predicted by the three models studied in this paper (full curves, as indicated). The broken curve shows the zeroth-order Bragg–Williams result. The dotted curve is from a renormalisation group computation by Stinchcombe (1979). The triangles correspond to the Monte Carlo data from Landau (1980). The squares represent the experimental data from Lagendijk and Huiskamp (1972). (*b*) $T_c(x)/T_c(0)$ versus x for the same models as in (*a*) but for a FCC lattice. The broken curve is from the computation by Behringer (1957). The symbols correspond to experimental data reported by Behringer as follows: Fe–Si (□), Fe–Al (△) Fe–Zn (×) and Fe_3O_3–Cr_2O_3 (+).

after using the self-consistency condition (2.3). The short-ranged order parameter, $\sigma \equiv N_{++}N_{--}/(N_{+-})^2$ where N_{++}, N_{--} and N_{+-} represent respectively the total number of up–up, down–down and up–down NN pairs of spins averaged over the equilibrium state defined by Z, is then given by

$$\sigma = \tfrac{1}{4}\exp(4k). \tag{2.8}$$

The system energy may be written as

$$E = -\tfrac{1}{2}J(1-x)qN'\langle s_0 s_1\rangle \tag{2.9}$$

where the spin–spin correlation function is

$$\langle s_0 s_1\rangle = [\cosh(2h') - \exp(-2k)]/[\cosh(2h') + \exp(-2k)] \tag{2.10}$$

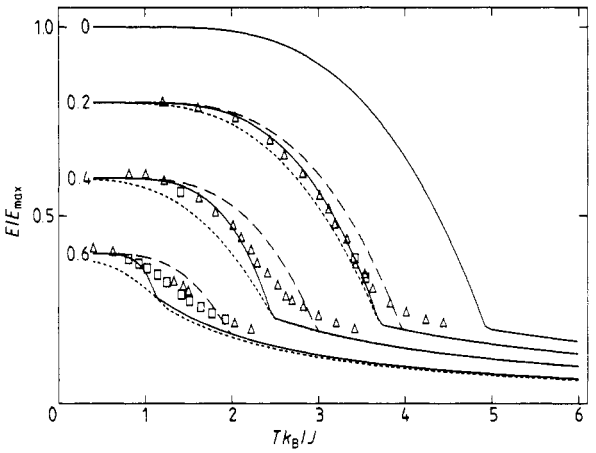

Figure 3. The configurational energy of the system (SC lattice), normalised to its maximum value for $x = 0$, versus temperature at selected values of x, as indicated; the symbols have the same meaning as in figure 1.

at zero field and $N' = (1 - x)N$ is the number of spins; see figure 3 for the explicit behaviour of the energy versus temperature at selected values of x. The corresponding specific heat is shown in figure 4; we avoid giving here the explicit expression which is rather complex. It is interesting to note that the discontinuity of the specific heat at T_c shown by figure 4 behaves in such a way that

$$\frac{\Delta C(T_c)}{(1-x)Nk_B} = \frac{3}{8}\frac{q'^2(q'-2)}{q'-1}\left(\ln\frac{q'}{q'-2}\right)^2 \tag{2.11}$$

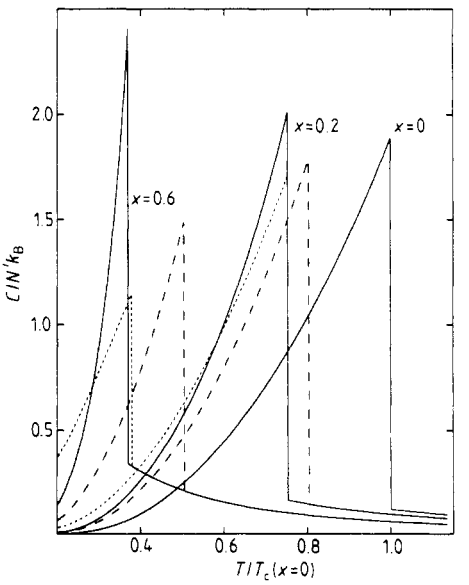

Figure 4. The specific heat per magnetic ion versus temperature for a SC lattice using the same notation as in figure 1. $N' = N(1 - x)$ represents the number of magnetic ions in the system.

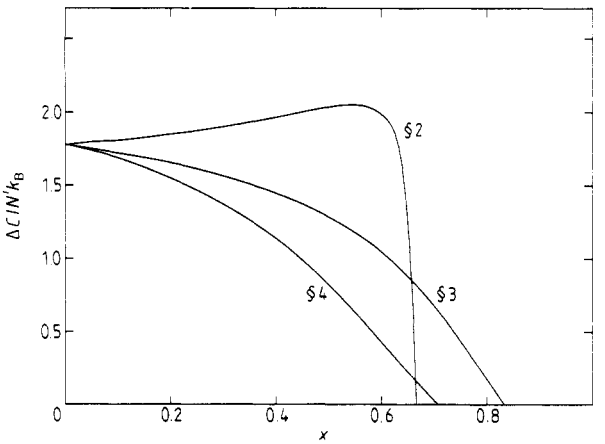

Figure 5. The discontinuity of the specific heat (per magnetic ion) at $T_c(x)$ as a function of x for the three models considered, as indicated; SC lattice.

and the height in such a way that

$$\frac{C(T_c^-)}{(1-x)Nk_B} = \frac{1}{8}\frac{q'^2(q'-2)(3q'-2)}{(q'-1)^2}\left(\ln\frac{q'}{q'-2}\right)^2. \tag{2.12}$$

These functions are represented, respectively, in figures 5 and 6 as functions of x in the case of a SC lattice. Finally, the magnetic susceptibility is given by

$$\chi \equiv \left(\frac{\partial m}{\partial h}\right)_{h=0} = (1-m_0^2)\frac{e^{2k}+\cosh(2h')}{e^{2k}+\cosh(2h')-q'\sinh(2k)}. \tag{2.13}$$

This function is shown in figure 7 together with one obtained using other hypotheses. Section 5 contains a discussion of the behaviour shown by figures 1–7.

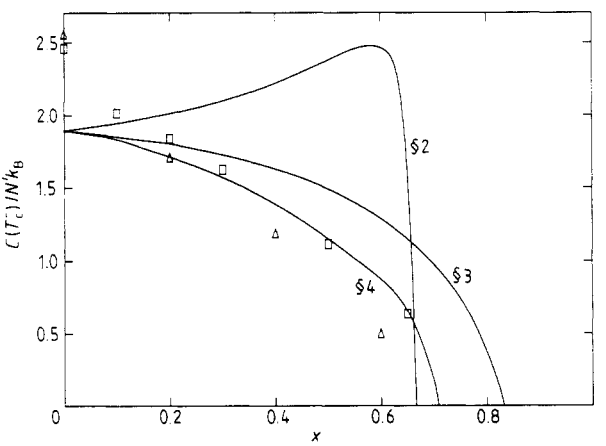

Figure 6. The height of the specific heat at $T_c^-(x)$ as a function of x for different models as indicated. Some experimental data are also shown: △, Landau (1980); □, Lagendijk and Huiskamp (1972).

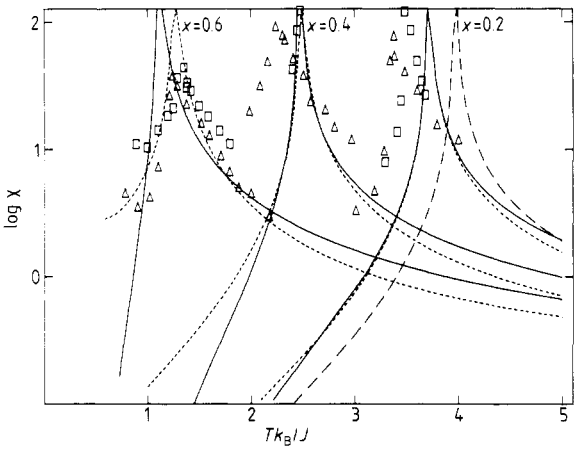

Figure 7. A semilogarithmic plot of the magnetic susceptibility (cf (2.13)), in units of J/k_BT, versus temperature for the three models and different values of x. The notation is the same as in figure 1.

3. Broken bonds

Real impure magnets are normally site-impure, as with the model described above; it would be interesting, however, to extend the above method to the case of bond impurity. In fact, any reasonable theory is expected to distinguish between the two cases; for instance the percolation threshold x_c is known to vary from one case to the other. We consider now the central spin with q NN spins and assume that qx of the bonds (interactions) are broken. That is, the Hamiltonian H is now

$$-H/k_BT = hs_0 + (h + h')\sum_{j=1}^{q} s_j + k\sum_{j=1}^{q'} s_0 s_j \tag{3.1}$$

where $q' = (1 - x)q$ is the number of bonds remaining, and the partition function is $Z = Z_+ + Z_-$ with

$$Z_\pm = e^{\pm h}[2\cosh(h + h' \pm k)]^{q'}[2\cosh(a)]^{qx} \tag{3.2}$$

where $a \equiv h + h'$. Introducing self-consistency as before one has

$$e^{-2h'}\left(\frac{\cosh(a_+)}{\cosh(a_-)}\right)^{q'-1} = \frac{q'\,e^{-k} + qx\cosh(a_-)/\cosh(a)}{q'\,e^{-k} + qx\cosh(a_+)/\cosh(a)} \tag{3.3}$$

and $T_c(x)$ is the solution of

$$1 = \frac{qx\sinh(k_c)}{q'\,e^{-k_c} + qx\cosh(k_c)} + (q' - 1)\tanh(k_c). \tag{3.4}$$

See figure 2 for the shape of the function $T_c(x)$; this is seen to vanish in the case of a SC lattice at $x = 0.833$ which can be compared with the series value for bond percolation, $x_c \simeq 0.751$ (Stauffer 1979).

The mean magnetisation per spin is

$$m(T, h; x) = \frac{2qx \tanh(a) + q'[\tanh(a_-) + \tanh(a_+)]}{2q + q'[\tanh(a_-) - \tanh(a_+)]}. \tag{3.5}$$

The case where $h = 0$ is displayed in figure 1. Note that on setting $qx = 0$ and $q = q'$, equation (3.5) formally reduces to (2.4) as one should expect. The short-range order parameter, on the other hand, is now

$$\sigma = \tfrac{1}{4}e^{4k} \frac{q' e^{-k} \cosh(a) + qx \cosh(a_+)}{q' e^{-k} \cosh(a) + qx \cosh(a_-)} \tag{3.6}$$

as compared with the value obtained from (2.8). We also have for the energy at zero field the result (2.9) with

$$\langle s_0 s_1 \rangle = \frac{\{q'[\cosh(2h') - e^{-2k}] + qx[\sinh(2k) + \tanh(h')\sinh(2h')]\}}{\{q'[\cosh(2h') + e^{-2k}] + qx[\cosh(2h') + \cosh(2k)]\}}. \tag{3.7}$$

This is shown in figure 3. The analytic expressions for other quantities are rather complex; we show in figures 4–7 the behaviour of the specific heat $C(T, x)$, the discontinuity $\Delta C(x)$ at T_c, the height $C(T = T_c^-, x)$ of the specific heat and the magnetic susceptibility, respectively.

4. Site impurities

The analytical treatment of the model in § 2 can be generalised along the lines of the cluster-variation method of Kikuchi (1951). Let us consider a given central spin surrounded either by 0, 1, 2, . . . or q vacant sites, each situation weighed by the corresponding binomial probability. The partition function then follows assuming those groups of spins independent from each other but affected by the same mean internal magnetic field due to the rest of the spins. That is, when one considers $q + 1$ situations characterised by having 0, 1, 2, . . . or q non-magnetic ions, one has $m_0 = 1, m_1 = q, \ldots, m_{q-1}, m_q$ as the numbers of different possible realisations of each situation, $n = \Sigma_i m_i$, and

$$Z = \sum_{\{s_{0i}, s_j = \pm 1\}} \exp\left[\sum_{i=1}^{n}\left(hs_{0i} + (h + h')\sum_{j=1}^{q_i} s_{ji} + k\sum_{j=1}^{q_i} s_{0i}s_{ji}\right)\right]$$

$$= \sum_{\{s_{0i} = \pm 1\}} \exp\left(h\sum_{i=1}^{n} s_{0i}\right) \prod_{j=1}^{n} [2\cosh(h + h' + ks_{0i})]^{q_i} \tag{4.1}$$

so it follows that

$$\langle s_{0j} \rangle = Z^{-1}\left[\sum_{\{s_{0i} = \pm 1\}} s_{0j} \exp\left(h\sum_{i=1}^{n} s_{0i}\right) \prod_{j=1}^{n} [2\cosh(h + h' + ks_{0i})]^{q_i}\right] \tag{4.2}$$

and

$$\langle s_0 \rangle \equiv \sum_{j=0}^{q} p_j \langle s_{0j} \rangle \tag{4.3}$$

where

$$p_j \equiv m_j \Big/ \sum_{i=0}^{q} m_i$$

where m_i is the number of different possibilities for each situation considered; that is, for each i one has

$$p_j = \binom{q}{j} x^{q-j}(1-x)^j. \tag{4.4}$$

Assuming self-consistency in the sense that $\langle s_0 \rangle = \langle s_j \rangle$, where

$$\langle s_j \rangle = \sum_{i=1}^{q} p_i \langle s_{ji} \rangle \tag{4.5}$$

it follows after some algebra when $h = 0$ and $h' \to 0$ that

$$\sum_{j=1}^{q} p_j[1 - (q_j' - 1)h' \tanh(k)] \Big/ \sum_{j=1}^{q} p_j[1 + (q_j' - 1)h' \tanh(k)] = \mathrm{e}^{-2h'}. \tag{4.6}$$

The critical temperature is

$$T_c(x) = 2J/k_B \ln[\overline{q'}/(\overline{q'} - 2p)] \tag{4.7}$$

where

$$\overline{q'} = \sum_{j=0}^{q} p_j q_j' = q(1-x) \tag{4.8}$$

and $p = 1 - x^q$. For a SC lattice this yields

$$T_c(x)/T_c(0) = \ln(\tfrac{3}{2})/\ln[(3 - 3x)/(2 - 3x + x^6)] \tag{4.9}$$

whose behaviour near $x = 0$ (up to x^2) is the same as that described by equation (2.5). At large values of x ($x > 0.4$), equation (4.9) differs from (2.5) as shown by figure 2; for instance, $T_c(x)$ vanishes at $x = 0.709$ for a SC lattice. This is even closer to the series result ($x_c \simeq 0.689$) than the value reported in § 2.

Other quantities are given as averages:

$$Q = \sum_{j=0}^{q} p_j Q_j \tag{4.10}$$

where, as in (4.3) and (4.8), Q_j is the quantity obtained in § 2 from the partition function (2.2) before using any self-consistency condition. See figure 1 and figures 4–7 for the behaviour of the most relevant quantities. Further discussion of the above results is contained in the following section.

5. Discussion

The agreement between the theory and experimental data is well depicted in figure 1 where the model predictions for the magnetisation are compared with the Monte Carlo data given by Landau (1980) at representative values of x in the case of a SC lattice ($q = 6$). Note that most of Landau's data refer to relatively small lattices so the observed discrepancies may partially reflect finite-size effects and anomalous fluctuations. In fact,

the agreement is excellent for $x = 0.4$ where the data refer to a $30 \times 30 \times 30$ lattice; note also that due to finite-size effects one should disregard the data for smaller lattices when $m_0(T; x) < 0.2$, and that the data for $x \geqslant 0.6$, say, are admittedly crude. Also noticeable is the fact that the behaviour of the model (4.1) clearly separates from the behaviour of the other two models; e.g. it predicts a small saturation value for $x \geqslant 0.6$ and a given curvature of the $m_0(T)$ curve. Both facts are in qualitative agreement with the data. Figure 3, comparing the configurational energy for the three models and Monte Carlo data, confirms the situation depicted by figure 1.

The favourable ratio shown by the models studied in this paper between physical relevance and mathematical simplicity can also be demonstrated by comparing their prediction for $T_c(x)$ with that following from more sophisticated computations. Behringer (1957) analysed a magnetically dilute FCC lattice by performing a high-temperature series expansion in an effort to approximate the manner in which $(1 - x)$ paramagnetic ions and x diamagnetic ions distribute themselves. This computation was followed up to fourth order to obtain a crude description of data restricted to the range $0.2 > x \geqslant 0$ (figure 2(*b*)), but even this range of validity is problematical given the slow convergence shown by Behringer's expansion; in fact, the simple examination of the high-temperature series for impure systems is not in principle a valid way of determining the transition temperature (Griffiths 1969, Rushbrooke *et al* 1972). The result from an effective-Hamiltonian approximation (Oguchi and Obokata 1969) also seems less reliable than (2.5), (3.4) or (4.9); e.g. it overestimates experimental values (Lagendijk and Huiskamp 1972) for x_c and $T_c(x)$ by 10% or more. Turning to the behaviour near $x = 0$ where the test is more stringent, we note that (2.5) implies for a SC lattice that

$$T_c(x)/T_c(0) = 1 - 1.233x - 0.021x^2 + \ldots. \tag{5.1}$$

Harris (1974) performed a resummation of perturbation theory, whose validity seems open to question, to obtain a series similar to (5.1) with coefficients -1.060 and -0.085, in that order, and a real-space renormalisation by Stinchcombe (1979), restricted to small cluster sizes however, yields -1.06 for the first coefficient. The latter may also be affected by a relatively large error; e.g. it predicts (probably incorrectly) the same number for site impurities as for bond impurities. The prediction (2.5) seems also to be consistent with experimental data; for instance Lagendijk and Huiskamp (1972) conclude that $x_c > 0.65$ and that the first coefficient in (5.1) is around -1.1.

More evidence in favour of (2.5) concerns its shape near percolation:

$$\exp(-2J/k_BT) \sim (x - x_c)^{\varphi} \qquad x \to x_c \tag{5.2}$$

where φ is the so-called crossover exponent. Wallace and Young (1978) and Stinchcombe (1979) concluded that φ is near unity; from (2.5) it does indeed follow proportionality for any value of x, as can easily be confirmed. Equation (3.4) cannot be solved analytically in the limit (5.2) but a numerical analysis shows that φ is near unity in this case; on the other hand, $\varphi = 1$ for the model § 4, independently of q, as can be seen from (4.7) by computing the ratio $(-2J/k_BT_c)/\ln(x - x_c)$ as $x \to x_c$.

Also interesting is the fact mentioned before that the models make reasonable predictions concerning x_c, the percolation threshold; namely

$$x_c = 1 - 2/q \tag{5.3a}$$

$$x_c = (q - 1)/q \tag{5.3b}$$

$$q(1 - x_c) = 2(1 - x_c^q) \tag{5.3c}$$

for the models in §§ 2, 3 and 4, respectively. These behaviours are plotted in figure 8 together with the results reported by Stauffer (1979). This figure shows how the site-impure models, particularly (5.3*c*), produce a description that is valid overall although, as expected, they do not predict a change of x_c with symmetry; e.g. they predict reasonable values for square and SC lattices while they cannot distinguish between the square and diamond structures ($q = 4$).

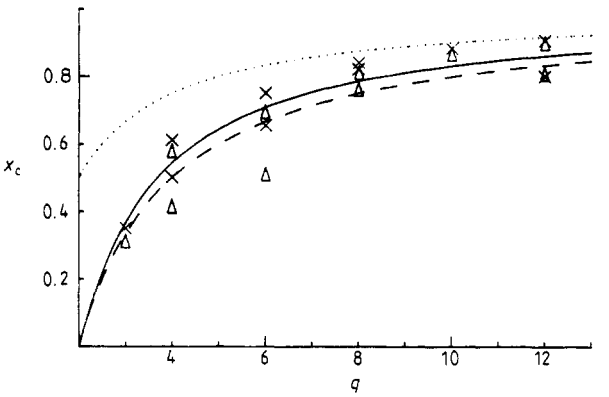

Figure 8. The critical concentration for percolation as predicted by the three models: (5.3*a*), broken curve; (5.3*b*), dotted curve; (5.3*c*), full curve. The symbols correspond to the values reported by Stauffer (1979) for bond (×) and site (△) percolation.

Figures 4–6 compare the behaviour of the specific heat shown by our models. The agreement with experimental data in this case is also good; cf figure 6. Note, however, that effective-field treatments cannot reproduce the divergences at T_c that one should expect in the light of a more detailed analysis of the Ising model (figure 4) and that, for different reasons, the transition is usually rounded in the case of real materials and Monte Carlo computations for small lattices (figure 6).

The critical behaviour of the magnetic susceptibility is again reasonably described by our models. This is shown in figure 7 where one can see that the predictions from the model in § 3 do indeed lie very close to the Monte Carlo data corresponding to the larger lattice; the apparent disagreement shown by figure 7 when $x = 0.2$ is only due to different predictions for $T_c(x)$ when x is small, i.e. when making comparisons between our equations and experimental data one should always normalise to the true T_c.

Summing up, the overall conclusion is that our models give a useful description of the magnetic and thermal properties of impure systems and that our formulae in § 4 provide an economic and reliable way to analyse experimental data over a broad range of values of temperature and x; the resulting description is general and globally accurate as compared with more sophisticated approaches providing partial descriptions whose validity is sometimes open to question.

Finally, we make a few comments about critical behaviour, one of the most interesting and difficult problems associated with impure systems. The effective-field models above show critical amplitudes changing with x and critical exponents independent of x; this can be seen directly in equations such as (2.6) and (4.10) or can be checked numerically. While the first result is in agreement with most observations, the second one is contrary

to some theoretical work (see, e.g., Harris 1974, Grinstein and Luther 1976, Newman and Rieder 1982, Jug 1983, Dotsenko and Dotsenko 1983) and recent experiments (Birgeneau *et al* 1984, Westerholt and Sobotta 1983, Westerholt *et al* 1984). Although our mean-field type of theory cannot be relied upon, of course, to determine critical behaviour it seems of interest to check its predictions more closely. By studying numerically functions such as $m_0 = m_0(T - T_c(x))$ when $T \to T_c(x)$ we thus find that the 'corrections to scaling' change with x in such a way that one may define in practice an *effective* critical exponent near T_c (but not so near that the limit (2.6) holds) different from the classical value (e.g. $\beta = \frac{1}{2}$) and varying continuously with x. This is indeed interesting because it resembles the situation in a recent Monte Carlo analysis (Marro *et al* 1986) where critical exponents are observed to change with dilution in a three-dimensional NN ferromagnetic Ising model.

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