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Random-field-induced rounding of the Ising-type transition in physisorbed $(CO)_{1-x}(N_2)_x$ mixtures: Monte Carlo studies of a simple model

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Abstract. We propose a simple model for $(CO)_{1-x}(N_2)_x$ mixtures adsorbed on graphite, where a lattice site carries a spin $S_i = \pm 1$ representing the orientations of the CO electric dipole moment if the site is occupied by a CO molecule, while the spin $S_i = 0$ if the site is taken by an N_2 molecule, which has a quadrupole moment only. Assuming a bilinear dipole–quadrupole coupling, randomly quenched N_2 impurities then act as random fields would act on an Ising antiferromagnet. For simplicity, a square lattice is treated and the range of all interactions is restricted to nearest neighbours. Monte Carlo studies are performed for a range of lattice linear dimensions L from $L = 24$ to $L = 50$, and the specific heat, order parameter and susceptibility, as well as the fourth-order cumulant, are studied, applying finite-size scaling concepts where appropriate. Our specific heat results display a striking qualitative similarity to the experimental data of Wiechert and Arlt, and provide evidence that the transition is already rounded by arbitrarily small dilution, consistent with theoretical predictions for the two-dimensional random field Ising model. While the experiments needed to rely on the specific heat only, our data for the (strongly rounded) ordering susceptibility and the cumulant (where the common intersection point disappears, consistent with the absence of a transition) provide compelling evidence for this picture. The crossover scaling analysis first proposed by Ferreira *et al* for dilute antiferromagnets in a field also works out reasonably well for the present model.

1. Introduction: overview and motivation for the model

The statistical thermodynamics of systems with randomly quenched disorder is a real challenge for theory (Stinchcombe 1983, Imry 1984, Binder and Young 1986, Villain 1985, Nattermann and Villain 1988, Young *et al* 1992, Binder and Reger 1992). Particularly striking phenomena are predicted in reduced dimensionality, such as the destruction of long-range order of Ising-type systems in $d = 2$ dimensions by arbitrarily weak random fields (Imry and Ma 1975, Morgenstern *et al* 1981, Villain 1982, Grinstein and Ma 1982, Binder 1983); see figure 1: making use of fluctuations of the excess of the random field of one sign in subvolumes of the system, a kind of irregular 'chinese box' pattern with domains inside domains is stabilized, with pronounced roughness of the walls induced by the random field even at zero temperature. This absence of true long-range order also shows up in a rounding of the transition even by very weak random fields (see, e.g., figure 2). While this mechanism had been confirmed by beautiful experiments for dilute quasi-two-dimensional anisotropic antiferromagnets such as $Rb_2Co_{0.85}Mg_{0.15}F_4$ (Ferreira *et*

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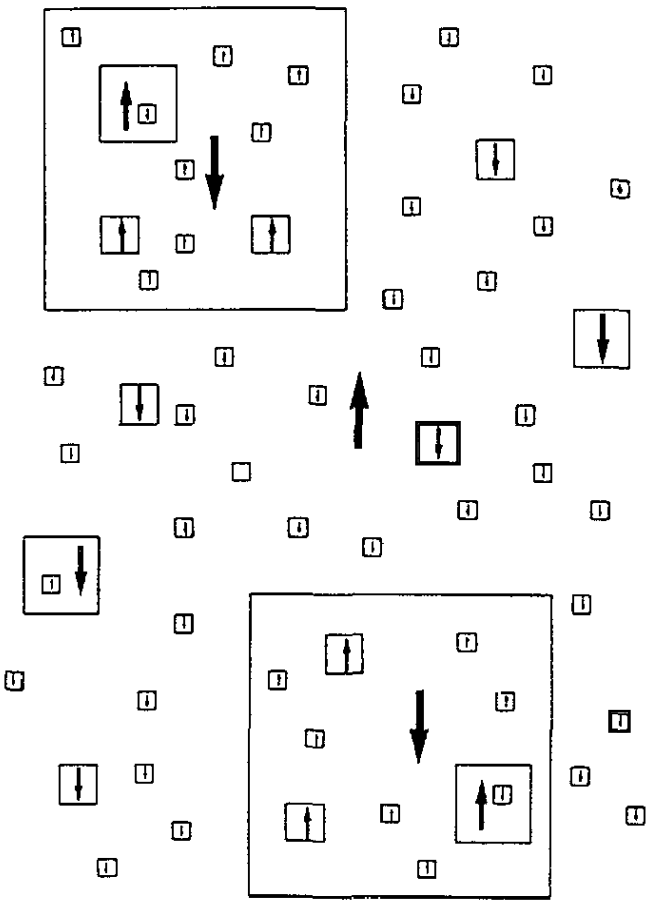


Figure 1. Ground-state domain pattern of the two-dimensional Ising lattice in a small random magnetic field (schematic diagram). Arrows indicate orientations of the domains. Note that in reality the domain walls also exhibit irregular roughness, which is not shown here. From Morgenstern *et al* (1981).

al 1983), it had never been confirmed for genuine real two-dimensional phase transitions such as occur in adsorbed atomic monolayers at surfaces (Dash 1975, Sinha 1980, Dash and Ruvalds 1980, Einstein 1982, Binder 1993), until a recent experiment on $(Co)_{1-x}(N_2)_x$ mixtures (Wiechert and Arlt 1993). Pure CO adsorbed on grafoil at a coverage such that the $\sqrt{3} \times \sqrt{3}$ R30° phase commensurate with the graphite structure occurs undergoes a first transition from the orientationally disordered solid at high temperatures to the herringbone structure ($2\sqrt{3} \times \sqrt{3}$ R30°) at $T_H(CO) \simeq 25$ K (You and Fain 1985) and an analogous transition occurs for N_2 at $T_H(N_2) \simeq 28$ K (Diehl and Fain 1983). Figure 3(*a*) indicates schematically the quadrupolar ordering of this 'herringbone phase'. Now CO also exhibits a small electric dipole moment, and hence one interprets the transition at $T_c \simeq 5.4$ K (Inaba *et al* 1988) or $T_c = 5.18$ K (Wiechert and Arlt 1993) as an (antiferroelectric) head–tail ordering of the electric dipoles of the CO molecules, see figure 3(*b*). We emphasize that this interpretation of the structure shown in figure 3(*b*) is speculative, and that other structures of the electric dipole moments are conceivable as well. In fact, plausible models

for the interactions may lead to ferrielectric structures (Marx *et al* 1993). However, at this point this problem is not solved, and for simplicity we shall only consider an antiferroelectric structure in the following.

Very weak dilution of CO with N_2 molecules (concentrations of 3% or less) produce a strong rounding of the specific heat anomaly of the transition at T_c (Wiechert and Arlt 1993) while the herringbone ordering at higher temperatures should be affected relatively little by dilution: the diatomic molecules CO and N_2 are isoelectronic, and have the same mass, and about the same size; only their quadrupole moments differ (the moment of CO is about a factor of 1.3 larger than that of N_2, see You and Fain 1985). Assuming that the quadrupole moment and dipole moment of the CO molecules are linearly coupled, one would obtain from the quadrupole–quadrupole interaction between N_2 and CO an effective random field acting on the CO dipole moments. Note that we do not imply, of course, that interactions of any electrostatic origin dominate—van der Waals forces between the atoms may lead to pseudodipolar or pseudoquadrupolar terms as well.

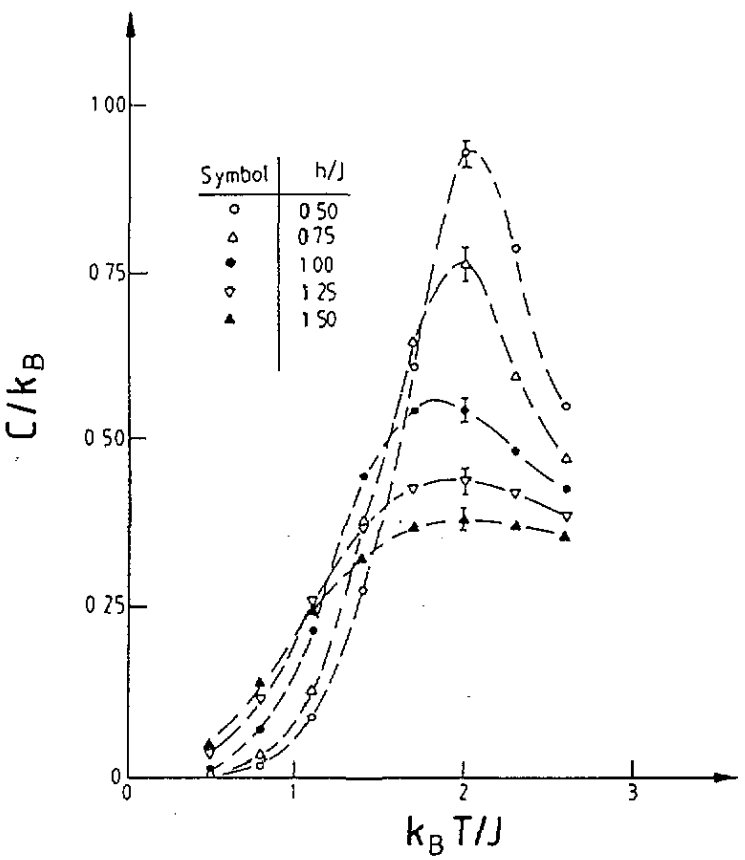


Figure 2. Specific heat plotted versus temperature for the nearest-neighbour Ising square lattice with exchange constant J exposed to random fields $\pm h$, for a 12×12 system averaged over 30 configurations of the random field, using exact transfer matrix methods. Different curves refer to different values of h/J as indicated in the figure. From Morgenstern *et al* (1981).

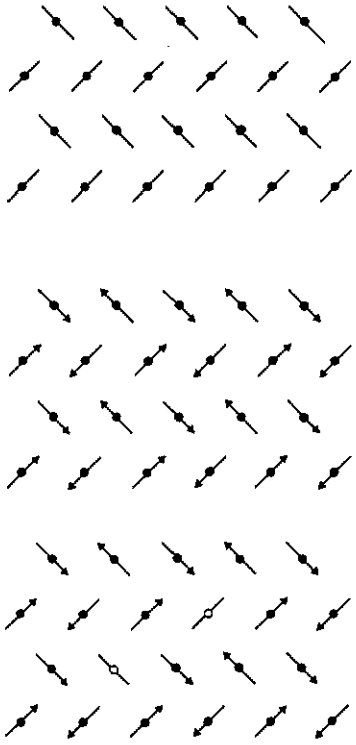


Figure 3. (*a*) Schematic arrangement of the molecule orientations in one domain of the herringbone structure, where the centres of gravity of the molecules form a regular triangular lattice. (*b*) Generalized antiferroelectric structure that may occur in CO physisorbed on graphite and already ordered in the herringbone orientational structure. (*c*) Random dilution of the structure of case (*b*) with N_2 (open circles), which has no dipole moment.

Now the physical origin of such a coupling is not completely clear. If the quadrupolar ordering in the mixed system $(CO)_{1-x}(N_2)_x$ is not at all disturbed by the dilution (figure 3(*c*)), one could also expect that the effect of dilution is simply to randomly remove spins, and then the problem would be equivalent to that of a randomly diluted Ising antiferromagnet (or ferromagnet, respectively) without a random field. In such systems the specific heat sometimes seems to be strongly rounded even if long-range order still occurs (Stichcombe 1983). If the quadrupolar ordering is disturbed by the dilution, one might expect bilinear terms coupling the quadrupole moment tensor $f_i^{\mu\nu}$ of a molecule at site i and the tensor $\epsilon^{\mu\nu}(x)$ of elastic strain (Michel 1987a–c).

Since random elastic strain fields are discussed as a mechanism of creating orientational glasses (Michel 1987a–c, Binder and Reger 1992), it could be that in the diluted system a picture of the type shown in figure 1 should be drawn even for the quadrupolar order at temperatures above T_c in the mixed system. Since, then, the dipolar long-range order established at T_c is limited in range by the typical domain size of the quadrupolar order, the rounding of the specific heat seen at T_c in the experiment would be a kind of finite-size rounding (Fisher 1971, Privman 1990, Binder 1992a, b) by which one indirectly measures the random-field rounding of the orientational transition at $T_H(CO)$.

A first-principles derivation of the effective Hamiltonian of the mixed system $(CO)_{1-x}(N_2)_x$ would be very desirable but is far beyond the scope of the present work. For simplicity, we assume that it is the first mechanism that is operative, and describe the system by a simple square lattice, disregarding the actual sublattice structure of figure 3. Associating an Ising spin $S_i = \pm 1$ with a CO molecule at site i and $S_i = 0$ with an N_2 molecule at the site, we arrive at the following simplified model Hamiltonian:

$$\mathcal{H} = +\sum_{(i,j)} J S_i S_j - \sum_{(i,j)} J' S_i (1 - S_j^2) - \sum_{(i,j)} J'' S_i^2 (1 - S_j^2). \tag{1}$$

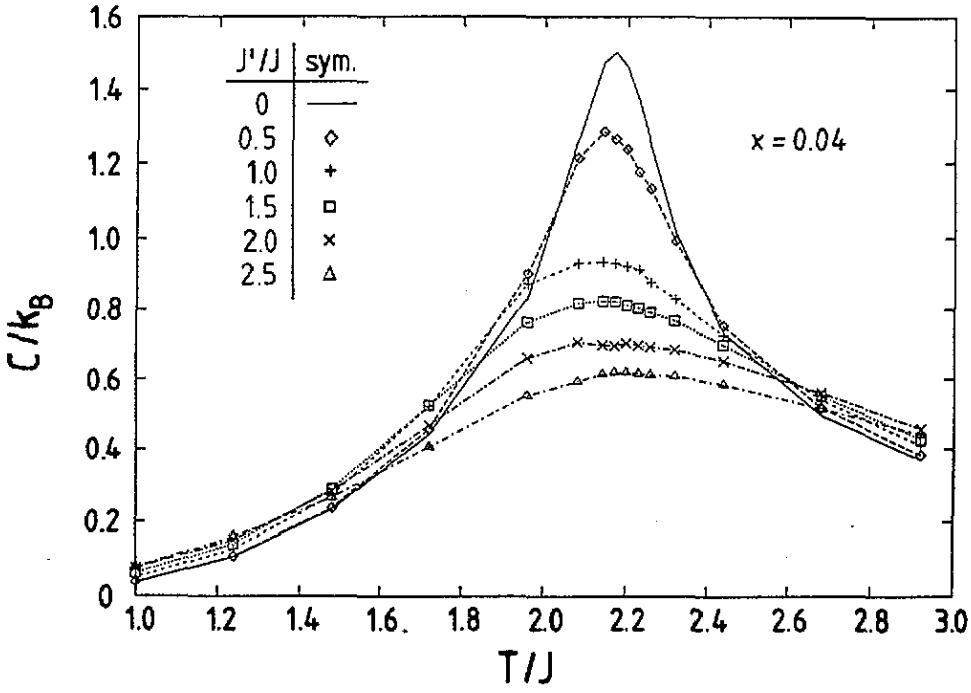


Figure 4. Specific heat C per lattice site plotted versus T/J (choosing $k_B \equiv 1$), for $L = 24$ and various choices of J'/J as indicated in the figure.

Here J is the interaction between the nearest-neighbour pairs of spins (pseudo-dipole–dipole interaction), J' the hypothetical pseudo-dipole–quadrupole interaction, while J'' is a pseudo-quadrupole–quadrupole interaction. For simplicity, we choose $J'' = 0$ in the results presented here, but we have checked by preliminary calculations that the opposite choice $J'' \neq 0$, $J' = 0$ would not yield results similar to the experimental data, and that long-range order remains for small impurity concentrations then, as expected. In the model (1), the sites j taken by N_2 produce a field randomly, sometimes on a site in the sublattice where the spins are up and sometimes on a spin in the sublattice where the spins are down (for $J > 0$ where we have an antiferromagnetic ground state).

This model is studied by Monte Carlo methods as is described in section 2, while section 3 applies a crossover scaling analysis as is appropriate for the Ising problem in a random field (Fishman and Aharony 1979, Ferreira *et al* 1983, Binder 1984). Section 4 summarizes some concluding remarks.

2. Monte Carlo results

We used square lattices of sizes $L = 24$, 32, 40, 50 with periodic boundary conditions and different impurity concentrations x. Averages have been taken over 100–200 different configurations of the impurity distribution over the lattice for each x. Typically, systems were equilibrated with runs of a duration of 2.5×10^4 Monte Carlo steps (MCSs) per site, while 'measurements' were taken over the subsequent period of 2.5×10^4 MCS/spin. With this fairly moderate effort (all calculations were done at IBM RISC 6000/320 workstations)

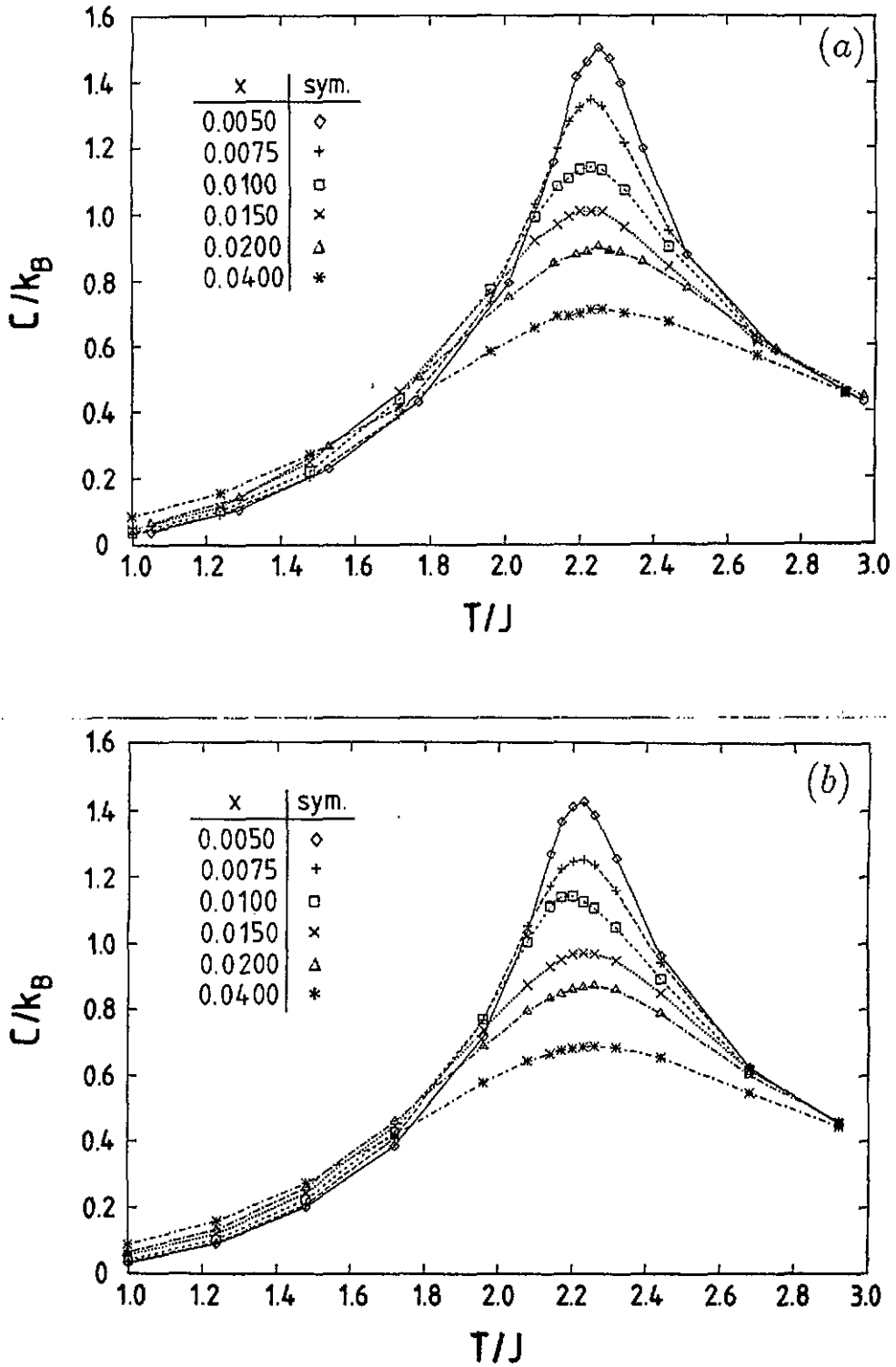


Figure 5. Specific heat C per lattice site plotted versus T/J for $L = 32$ (a) and $L = 50$ (b) and various choices of x as indicated.

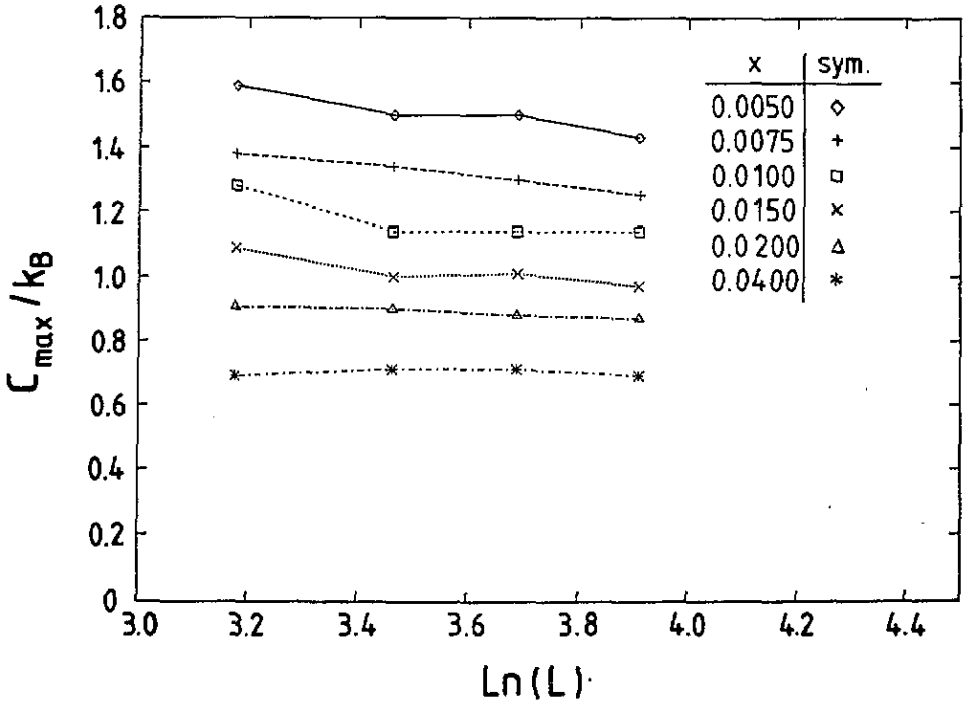
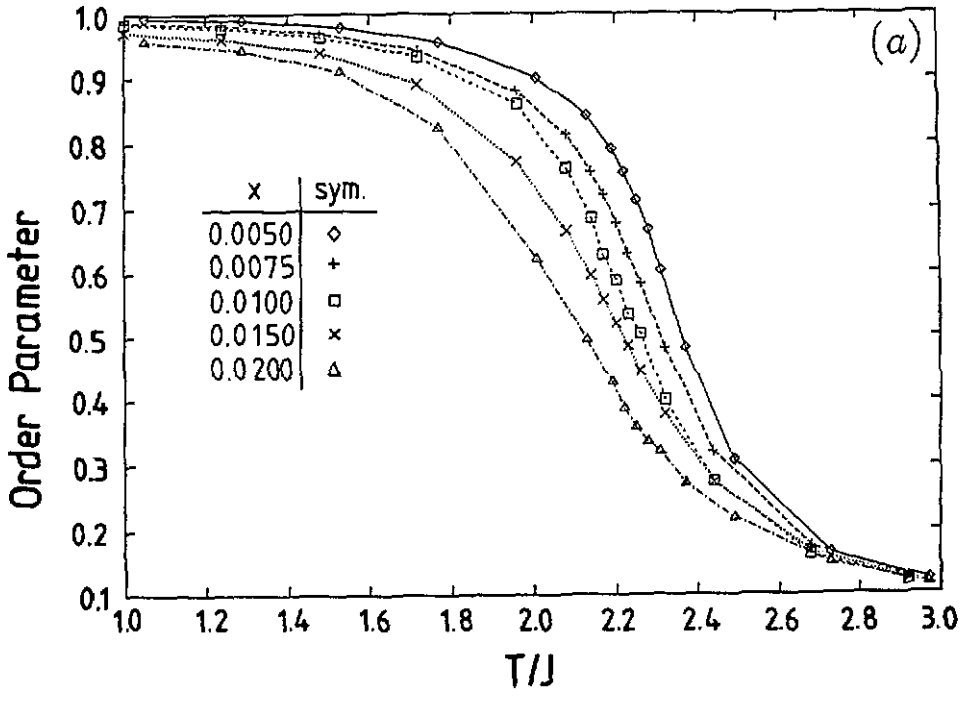


Figure 6. Checking for finite-size effects by a plot of the maximum value of the specific heat C_{max}/k_B versus $\ln L$ for several impurity concentrations.

it would not make any sense to try histogram techniques or other sophisticated simulation analysis methods. Due to the need of averaging over a large sample of configurations of the impurity sites, such techniques are less useful than for pure models (D'Onorio De Meo 1992). We emphasize again that the present work does not aim at a 'high-resolution study' of critical phenomena, but rather at a qualitative exploration of a model that is new and interesting.

Figure 4 shows the effect of varying J'/J for an impurity concentration ($x = 0.04$) where in the experiment strong rounding of the specific heat would already be observed. Due to the choice of a finite lattice size ($L = 24$ here), the data for $J'/J = 0$ are also rounded. For all other values of $J'/J \neq 0$ shown here, however, the rounding due to the random field by far exceeds the finite-size rounding. In order to qualitatively reproduce the experimental trends, we have hence decided to work typically with $J'/J = 2$. Figure 5 shows typical data for various impurity concentrations and lattice sizes. While some finite-size effects are still seen for very small impurity concentrations, no significant effects occur for $x \gtrsim 0.01$ and $L \geqslant 32$. This is also evident from figure 6 where the maximum value of the specific heat is plotted versus $\ln L$ for the various impurity concentrations investigated. Note also the remarkable qualitative similarity of figure 5 and figure 2.

Figure 7 analyses the order parameter for various sizes and impurity concentrations. While for the range of available lattice sizes the system at low temperatures is always well ordered for $x \leqslant 0.010$, we see a distinct decrease of the absolute value of the order parameter with increasing size for $x \geqslant 0.015$. We actually expect, alluding to figure 1, that in a sufficiently large system the order parameter will average to zero, and figure 7 is not incompatible with this hypothesis. In fact, we speculate that the same trend could be



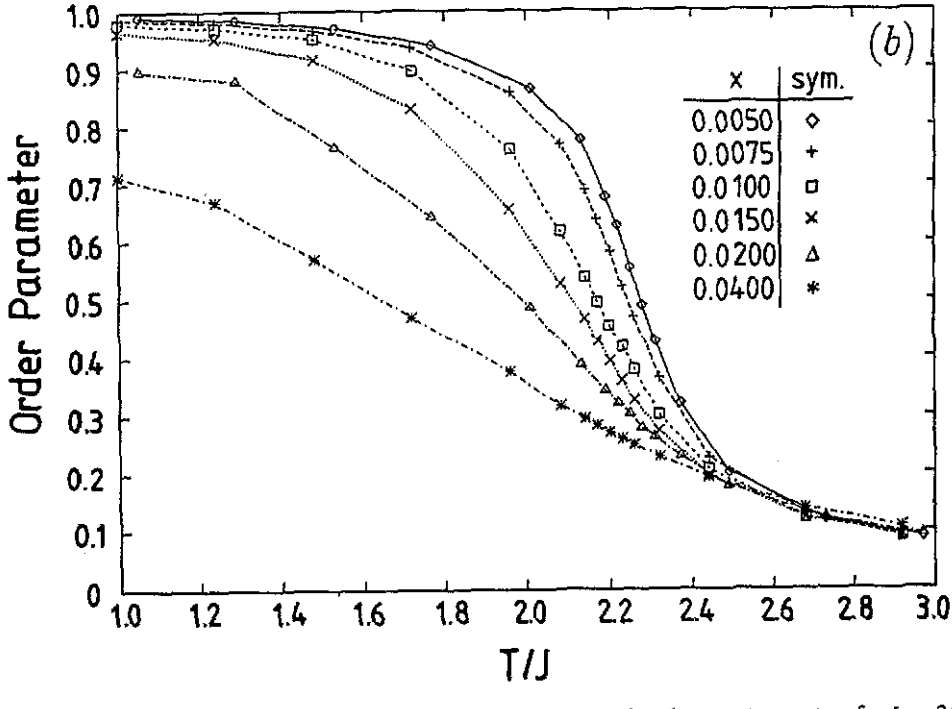
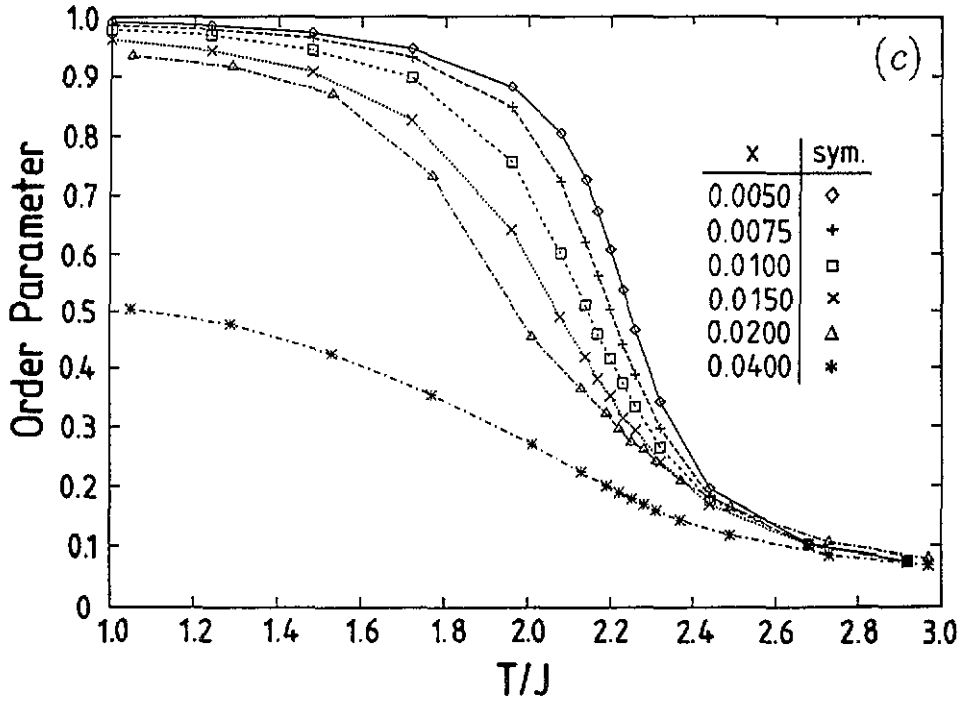
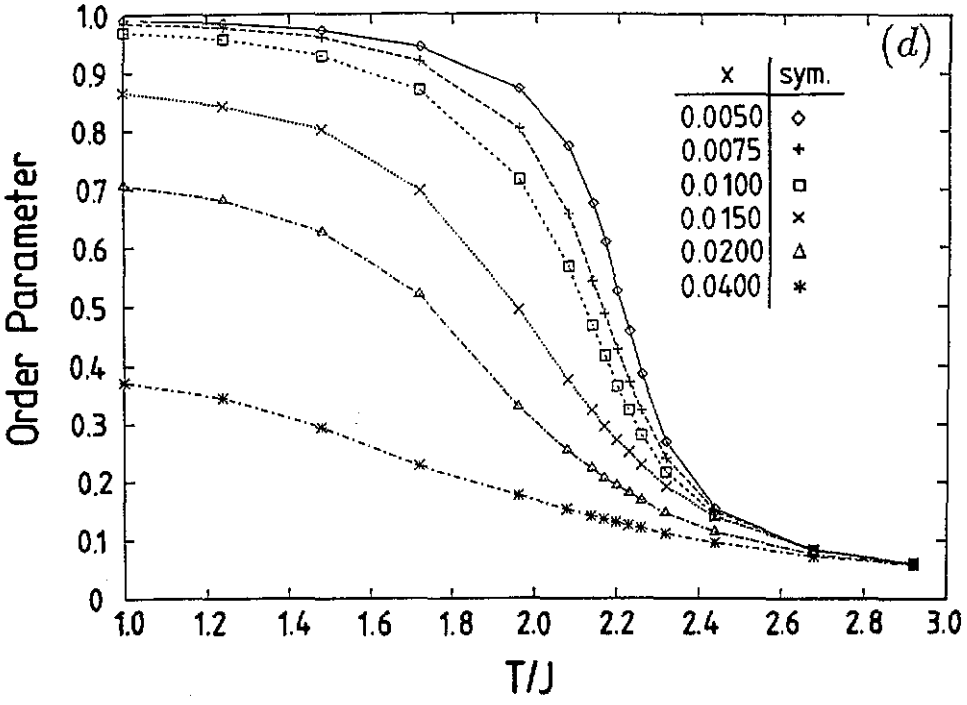


Figure 7. Absolute value of the order parameter plotted versus temperature for $L = 24$ (*a*), 32 (*b*), 40 (*c*) and 50 (*d*). Different symbols denote various impurity concentrations x as indicated.





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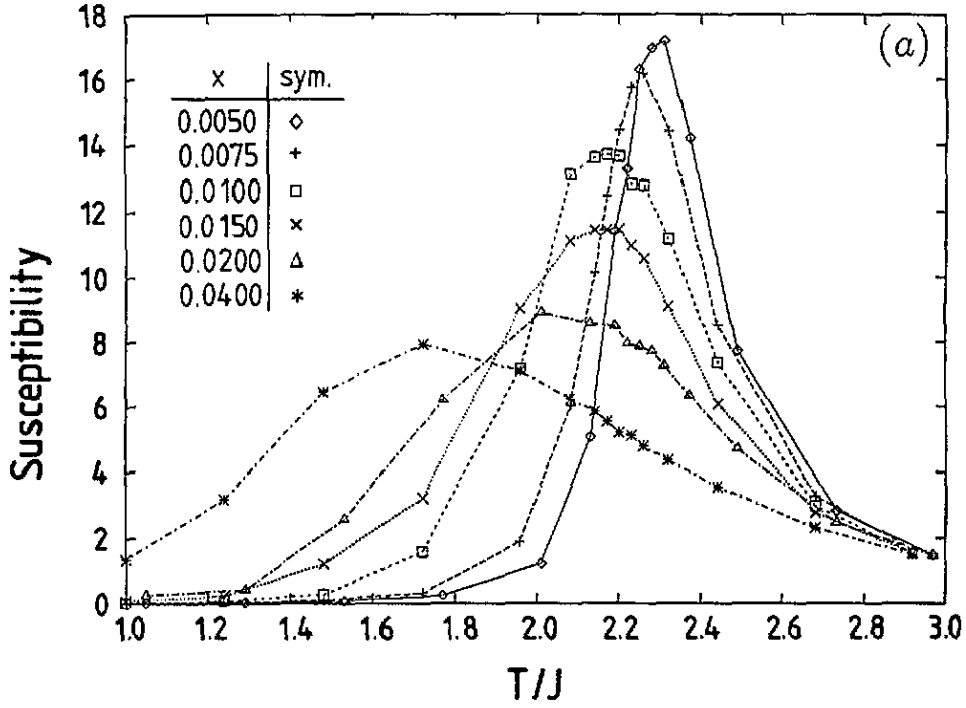


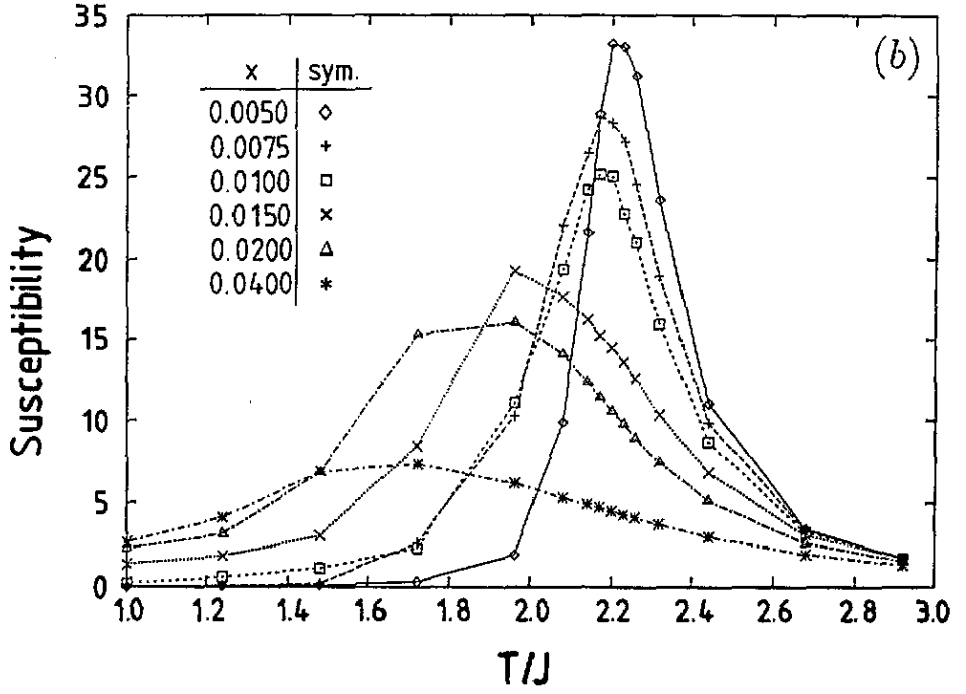


Figure 8. Ordering susceptibility $\chi = L^2(\langle\psi^2\rangle - \langle|\psi|\rangle^2)/T$ plotted versus temperature for $L = 32$ (a) and $L = 50$ (b). Different symbols show various values of x as indicated.

seen for the smaller values of x as well, if we were to study larger system there, which would require huge computer time since then much longer runs would be needed because of critical slowing down.

This interpretation is also corroborated by the behaviour of the ordering susceptibility (figure 8) and the fourth-order cumulant (figure 9). One can clearly recognize that the susceptibility peak becomes more rounded and shifts to lower temperatures as x increases. There are some irregularities in these curves, indicating that due to the huge statistical fluctuations the desired accuracy has not quite been reached. The cumulants (figure 9) no longer exhibit any unique size-independent intersection point, unlike the well known behaviour of pure systems (Binder 1992a, b). Sometimes there seems to be an intersection point for small sizes, but it should not be mistaken as an estimate for T_c, since for larger sizes the cumulants become smaller with increasing size. These findings all are mutually consistent with each other and with the interpretation that the transition present in the pure system is rounded by the random field.

3. Crossover scaling analysis

Following Fishman and Aharony (1979) the crossover from the critical behaviour of the pure system ($x = 0$) to the new behaviour can be described by a scaling theory. Just as there is a scaling behaviour with a uniform ordering field H in a pure system

$$C = |t|^{-\alpha}\tilde{C}_H(tH^{-\Delta}) \qquad \Delta = \gamma + \beta \tag{2}$$

where $t = 1 - T/T_c$, and α, β, and γ are the standard critical exponents of specific heat, order parameter, and susceptibility, there is a similar scaling with the random field amplitude h in the random field Ising model (one considers the case where the configurational average $[h_i]_{av} = 0$ while $[h_i^2]_{av} = h^2$), namely

$$C = |t|^{-\alpha}\tilde{C}_h(th^{-2/\phi}) \tag{3}$$

where the crossover exponent $\phi = \gamma$, the susceptibility exponent of the pure system. By our notation $\tilde{C}_H$, $\tilde{C}_h$ for the scaling functions we have expressed the fact that these are different functions, of course. For the two-dimensional Ising model, all exponents are exactly known (Baxter 1982): $\alpha = 0$, $\beta = \frac{1}{8}$, $\gamma = \frac{7}{4}$. The logarithmic specific heat divergence implied by $\alpha = 0$ actually means that (2) and (3) also need modifications by logarithmic terms, namely

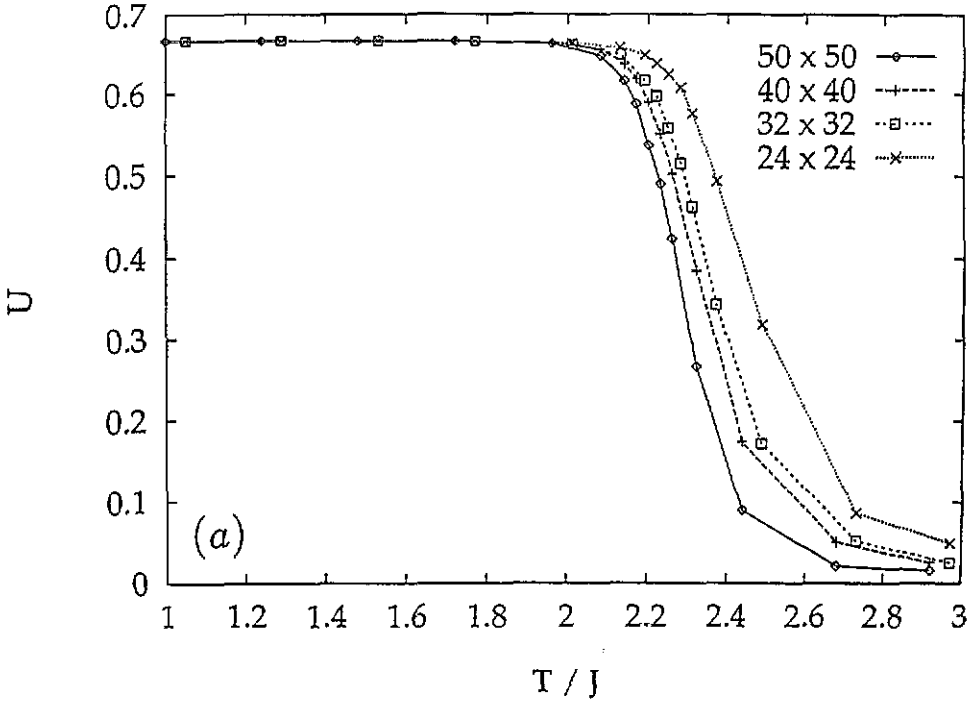
$$C = \tilde{C}_H(tH^{-\Delta}) - (A/\Delta)\ln H \qquad t \to 0 \qquad H \to 0 \qquad |t|H^{-\Delta} \text{ finite} \tag{4}$$

or

$$C = \tilde{C}_h(th^{-2/\phi}) - (2A/\phi)\ln h \qquad t \to 0 \qquad h \to 0 \qquad |t|h^{-2/\phi} \text{ finite} \tag{5}$$

where $A \cong 0.4945$ is the exactly known specific heat amplitude of the pure system (Onsager 1944).

Now the problem arises of how we can translate the randomness of our Hamiltonian (1) to the 'random field' considered in the theory. The standard assumption is that one simply equates the configurationally averaged moments, noting that for an antiferromagnet we need to consider a random staggered field rather than a random uniform field. Due to the phase



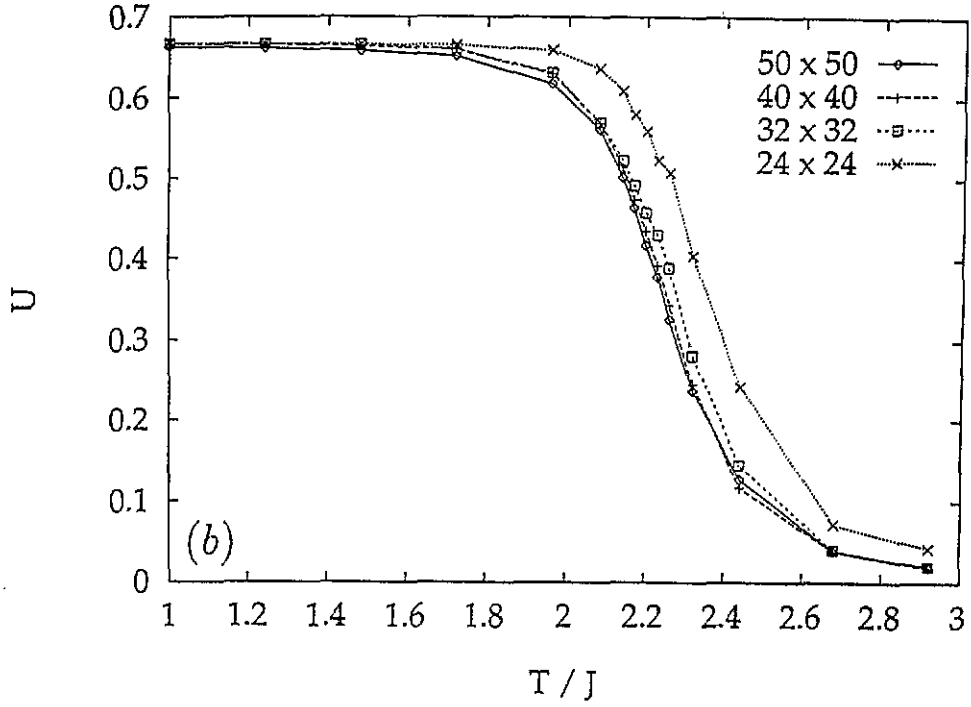
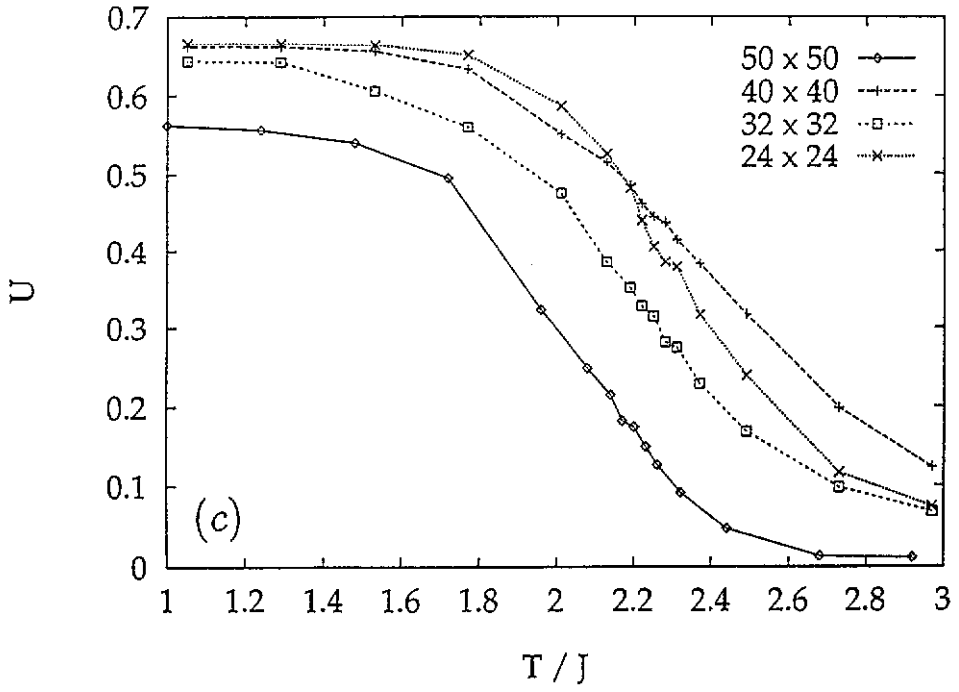


Figure 9. Reduced fourth-order cumulant defined as $U = 1-[\langle(\psi-\langle\psi\rangle)^4\rangle]/[3[\langle(\psi-\langle\psi\rangle)^2\rangle]^2]$ plotted versus temperature for $x = 0.005$ (*a*), 0.010 (*b*) and 0.020 (*c*). Four different lattice sizes are included as indicated.



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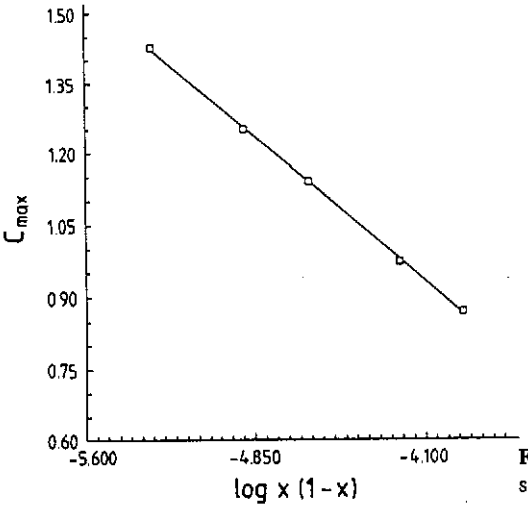

Figure 10. Plot of C_{max} versus $\ln[x(1-x)]$. From the slope one extracts a constant $A^* = (A/\phi)_{eff} = 0.4062$.

factor $(-1)^{l+k}$, where l, k are the x, y coordinates of the lattice site i, the random staggered field acting on site i due to the second term on the right-hand side of (1) is

$$h_i = (-1)^{l+k} J' \sum_j (1 - S_j^2) \qquad [h_i]_{av} = (-1)^{l+k} J' z x \tag{6}$$

z being the coordination number of the lattice, remembering that the sum over j in (6) runs over the nearest neighbours only. If we average (6) over the lattice sites, $[h_i]_{av}$ vanishes

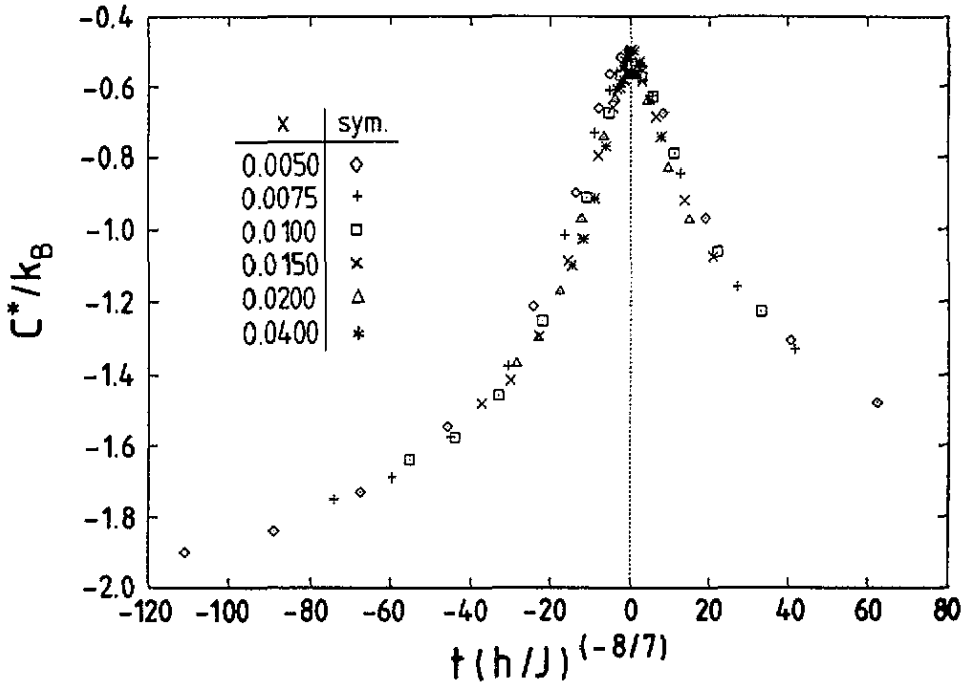

Figure 11. Scaling plot of C^* (9) versus the scaling variable $t(h/J)^{-8/7}$, using the effective amplitude A^* extracted from figure 10 rather than the theoretical one. Different symbols show various values of x. All data are for linear lattice dimension $L = 50$.

due to the phase factor. However, for h_i^2 we find

$$h_i^2 = J'^2 \sum_j (1 - S_j^2) \sum_{j'} (1 - S_{j'}^2) \qquad [h_i^2]_{\text{av}} - [h_i]_{\text{av}}^2 = J'^2 z^2 x(1-x). \quad (7)$$

From this consideration one may identify the random field amplitude h as $zJ'\sqrt{x(1-x)}$. For $x = 0.01$ we thus have $h \simeq 0.4J'$, and comparing figures 2 and 4 this is not unreasonable, considering that this mapping is clearly approximate because it disregards the disorder effects on the Ising exchange term. From (5) and (7) we thus expect

$$C_{\max} = \text{constant} - (A/\phi) \ln[x(1-x)] \quad (8)$$

and this relation is tested in figure 10. While the data are nicely compatible with a logarithmic variation, the constant in front of the logarithm is a factor of about 1.5 too large. In the direct study of the two-dimensional random field Ising problem the theoretical constant could roughly be verified, however, (Binder 1984), and also in the experiment the correctness of (8) was verifed (Wiechert and Arlt 1993). Probably in our case the discrepancy is due to the fact that we work at somewhat too high concentrations, such that non-critical background terms affect our estimates.

In figure 11 we present a full crossover scaling plot of our specific heat data, in order to test (5) more directly. Here we redefine t as $(T/T_m - 1)$, where T_m is the temperature of the specific heat maximum, following previous practice (Ferreira *et al* 1983, Binder 1984,

Wiechert and Arlt 1993). Thus the scaling function $C^*[t(h/J)^{-8/7}]$ plotted in figure 11 is defined as ($k_B \equiv 1$)

$$C^* = C + A^* \ln(h/J) \tag{9}$$

where we simply take $h/J = \sqrt{x(1-x)}$ here, omitting the constant zJ'/J which is 0.8 in our case. It is seen that a reasonable confirmation of crossover scaling is obtained, of similar quality as in the recent experiment of Wiechert and Arlt (1993), and over a somewhat wider range of fields than in the direct study of the random field Ising model (Binder 1984). This is understandable since here we use distinctly larger lattices.

4. Concluding remarks

In the present work, we have postulated a simple model of the random field Ising model type, in order to model the rounding of the phase transition from the paraelectric phase to the antiferroelectric phase in $(CO)_{1-x}(N_2)_x$ monolayers physisorbed on graphite. Our choice of model Hamiltonian is strongly motivated by the corresponding experimental results of Wiechert and Arlt (1993), while a more rigorous justification for this type of model is still lacking. Given our model, the experimental findings of Wiechert and Arlt (1993) are qualitatively reproduced. From the construction of our model it is extremely likely that it must satisfy the crossover scaling behaviour predicted by Ferreira *et al* (1983) along the lines of Fishman and Aharony (1979). Apart from the problem that we must use an effective critical amplitude A^* instead of the theoretically predicted one, the crossover scaling description is reasonably well verified. We attribute this problem to our numerical limitations (critical slowing down and finite-size effects prevented us from the study of somewhat smaller x) rather than to any fundamental effects.

Of course, it would be very interesting if one could justify (1)—or another suitable effective Hamiltonian—from a more realistic treatment of the interactions, perhaps following the line of the lattice dynamical methods of Michel (1987a–c), or by a Monte Carlo study of a fully atomistic model based on suitable pair potentials. Also a study of the analogous problem in $d = 3$ dimensions, where a sharp phase transition should remain for weak dilution, might be rewarding. We hope to report on such extensions in future work.

Acknowledgments

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