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Site-bond correlated model for disordered magnets: Mean-field theory

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A site-bond correlated model for randomly diluted magnetic systems is presented. The model Hamiltonian takes into account that the strength of the exchange interaction between two nearest-neighbor magnetic atoms is also dependent upon the magnetic occupancy of their own nearest neighbors, along the line joining the two atoms. An effective-field theory is used to obtain the critical curves in temperature-concentration space.

Randomly diluted magnetic systems have been extensively investigated in both their theoretical and experimental aspects.[1,2] Particular attention has been given to the way in which the transition temperature is reduced as one decreases the concentration of magnetic atoms. Also, the critical concentration at which magnetic order ceases to exist at finite temperature is of considerable interest.

The shape of the critical curve (transition temperature versus concentration of magnetic atoms) depends upon the lattice structure and the symmetry of the interaction Hamiltonian.[3-5] On the other hand, a well-known result of Elliott and Heap[3,5] and of Rushbrooke and Morgan[3,4] demonstrates that for three-dimensional ferromagnetic lattices with only nearest-neighbor interactions, the critical concentration at which the transition temperature vanishes is independent of the symmetry of the Hamiltonian or the spin value. That is, the critical concentration seems to be a topological property and coincides with the percolation concentration of the lattice.

Recent NMR studies[6] of the randomly diluted Heisenberg magnet $KNi_pMg_{1-p}F_3$ show striking differences in the behavior of this system compared to that of $KMn_pMg_{1-p}F_3$. As the concentration is reduced, the transition temperature decreases faster for $KNi_pMg_{1-p}F_3$ than for the isostructural system containing Mn^{2+} ions. In addition, the critical curve for $KNi_pMg_{1-p}F_3$ exhibits an upward curvature, whereas the opposite is observed in $KMn_pMg_{1-p}F_3$.

Attempting to explain these differences, de Aguiar, Engelsberg, and Guggenheim[6] proposed a dilution model which is quite different from the usual site-dilution percolation scheme. In this model, which is expected to be more appropriate for $KNi_pMg_{1-p}F_3$, the coupling between two nearest-neighbor magnetic atoms is assumed to be dependent upon the occupancy of the other nearest-neighbor sites.

To understand this dilution effect, we first consider the exchange paths in the pure compounds. In Mn^{2+} with a $3d^5$ electron configuration, all five of the one-electron orbitals are half filled ($L=0$), having the unpaired spins available to form both σ and π bonds with the fluorine ligands. However, in Ni^{2+}, with a $3d^8$ configuration, the orbitals d_{xy}, d_{xz}, d_{yz} are completely filled while the $d_{x^2-y^2}$ and d_{z^2} orbitals are half filled; these unpaired electrons can only form σ bonds. In fact, as suggested by Anderson's theory of superexchange,[7] this is the reason why Ni^{2+} has a stronger exchange coupling in this system. On the other hand, in the related randomly diluted magnets, the directionality of the σ bonds suggests that the substitution of a Ni^{2+} ion by a nonmagnetic species has a stronger effect on the exchange coupling of a nearest-neighbor magnetic pair situated along the line joining the three atoms. For Mn^{2+} the directionality of this effect should be less and the overall perturbation of the coupling weaker.

In this paper we introduce a model Hamiltonian which explicitly takes these ideas into account. For the nearest-neighbor Ising model the proposed Hamiltonian is

$$H=-\tfrac{1}{2}\sum_{i,\delta} J_{i,i+\delta}\sigma_i\sigma_{i+\delta} \ , \tag{1}$$

where δ is the lattice vector and $J_{i,i+\delta}$ denotes the exchange interaction between the ions at site i and $i+\delta$, and is given by ($J>0$)

$$J_{i,i+\delta}=J\epsilon_i\epsilon_{i+\delta}[(1-\alpha)\epsilon_{i-\delta}+\alpha] \ . \tag{2}$$

The parameter α ($0<\alpha<1$) correlates the interaction between site i and $i+\delta$ with the occupancy of site $i-\delta$. The limiting cases of $\alpha=1$ and 0 correspond, respectively, to the usual site dilution and to what we call a completely correlated site-bond model. The random variables ϵ_i can take the values one, with probability p, and zero, with probability $1-p$, where p is the concentration of magnetic atoms.

We next treat the Hamiltonian (1) within the scope of mean-field theory. Using the Callen identity,[8] the magnetization can be written as

$$\langle\langle\sigma_i\rangle_T\rangle_{cc}=\langle\langle\tanh(\beta E_i)\rangle_T\rangle_{cc} \ , \tag{3}$$

where $\beta=1/K_BT$, $\langle\cdots\rangle_T$ denotes the canonical thermal average, $\langle\cdots\rangle_{cc}$ the conditional configurational average and

$$E_i=\sum_{\delta} J_{i,i+\delta}\sigma_{i+\delta} \ . \tag{4}$$

First, we consider the standard mean-field treatment, which consists of taking the averages in Eq. (3) as

$$m=\tanh\langle\langle\beta E_i\rangle_T\rangle_{cc}=\tanh(\beta\bar{J}m) \ , \tag{5}$$

where $\bar{J}=zJp[(1-\alpha)p+\alpha]$, and z denotes the coordination number of the lattice.

The dependence of the reduced critical temperature $T_c(p)/T_c(1)$ upon magnetic concentration p is plotted in Fig. 1, for several values of the parameter α. It is worth noticing that the upward curvature of the critical curve is already apparent, even within the framework of simple mean-field theory, provided site-bond correlation is included

($\alpha < 1$). The curves for $\alpha < 0$ show that this model can also exhibit to some degree the effect of frustration.

In order to improve the above results we next consider the effective-field theory developed by Honmura and Kaneyoshi,[9] which has been applied to a great variety of disordered magnetic systems.[10] By applying the differential operator technique, namely, $e^{\lambda D} f(x) = f(x+\lambda)$, where $D = \partial/\partial x$ is the differential operator, to Eq. (3) we get

$$\langle\langle \sigma_i \rangle_T\rangle_{cc} = \langle\langle \exp(\beta E_i D)\rangle_T\rangle_{cc} \tanh x|_{x=0} \ , \tag{6}$$

substituting (4) into (6), expanding the exponential, and using the following identities: $(\sigma_i)^{2n} = 1$, $(\sigma_i)^{2n+1} = \sigma_i$, $(\epsilon_i)^n = \epsilon_i$, and $(\epsilon_i \epsilon_j)^n = \epsilon_i \epsilon_j$, for all n, one obtains the exact relation

$$\langle\langle \sigma_i \rangle_T\rangle_{cc} = \left\langle\left\langle \prod_{\delta} \{[1+\epsilon_i\epsilon_{i+\delta}(f_1+\sigma_{i+\delta}S_1)][1+\epsilon_i\epsilon_{i-\delta}\epsilon_{i+\delta}(f_2+\sigma_{i+\delta}S_2)]\}\right\rangle_T\right\rangle_{cc} \tanh x|_{x=0} \ . \tag{7}$$

Here we used the notation $f_l = -1+\cosh(K_l D)$ and $S_l = \sinh(K_l D)$ with $K_1 = \alpha\beta J$ and $K_2 = (1-\alpha)\beta J$.

In what follows we shall consider the application of (7) to a square lattice with periodic boundary conditions. For a cluster with five sites, where we need to consider only those configurations for which the central site is occupied by a magnetic atom, we get

$$\langle\langle \sigma_0 \rangle_T\rangle_{cc} = \left\langle\left\langle \prod_{i=1}^{4} [1+\epsilon_0\epsilon_i(f_1+\sigma_i S_1)][1+\epsilon_0\epsilon_i\epsilon_{i+2}(f_2+\sigma_i S_2)]\right\rangle_T\right\rangle_{cc} \tanh x|_{x=0} \ . \tag{8}$$

Performing the thermal and conditional configurational (i.e., $\langle\epsilon_0\rangle_{cc} = 1$) averages, neglecting multispin correlations, and using the fact that $\langle\epsilon_i\rangle_{cc} = p$ for $i \neq 0$, one can obtain the phase diagram displayed in Fig. 2.

The results of Fig. 2 show some of the characteristic features of the site-bond correlated Hamiltonian (1). For instance, even for the Ising model considered here we observe for $\alpha \neq 1, 0$ an upward curvature of the $T_c(p)$ curves, whereas for the usual site-dilution problem ($\alpha = 1$) this is expected only for the Heisenberg model.[2,4] Furthermore, the initial slope of the critical curve $S = (1/T_c)(dT_c/dp)|_{p=1}$ increases continuously as one increases the degree of correlation, taking the values $S_1 = 1.345$ for $\alpha = 1$ and $S_0 = 2.483$ for $\alpha = 0$. The present approximation gives a critical concentration $p_{c1} = 0.428$ for $\alpha = 1$, and $p_{c0} = 0.765$ for $\alpha = 0$. The above results should be compared with the known exact values $S_1 = 1.329$ (Ref. 11) and $p_{c1} = 0.5$ for bond dilution. In fact, in performing the conditional configurational average in Eq. (8) the concentration of connected bonds must be interpreted as the concentration of magnetic atoms. Indeed, within the framework of the percolation problem only two different values p_{c0} and p_{c1} corresponding to $\alpha = 0$ and 1 should be expected. The value $p_c^* = 0.381$ somewhat below p_{c1} (Fig. 2), obtained here for intermediate values of α, should then be considered as a spurious result. Also, the numerical values obtained for T_c in the $p = 1$ case are dependent upon the parameter α ($0 < \alpha < 1$). This result is certainly not expected from the starting Hamiltonian [Eq. (1)] and should be attributed, as should the spurious p_c^*, to the neglect of spin-spin correlations within the differential operator technique.

The conclusions to be drawn from this approach are

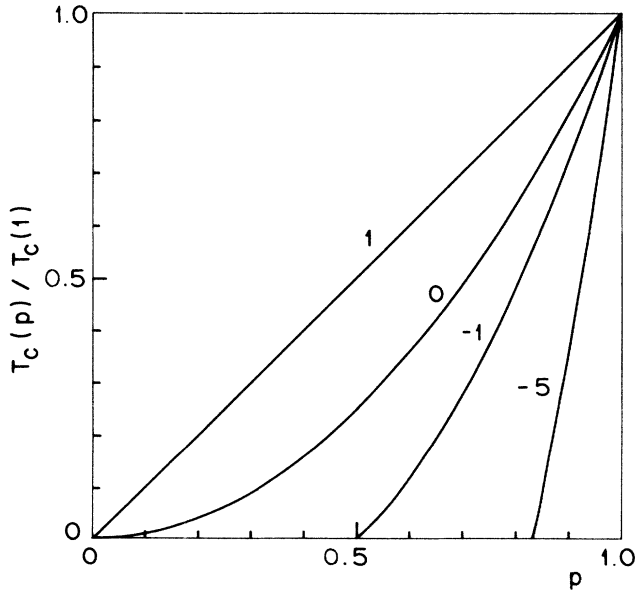

FIG. 1. Reduced temperature vs concentration for different values of α, obtained by standard mean-field theory.

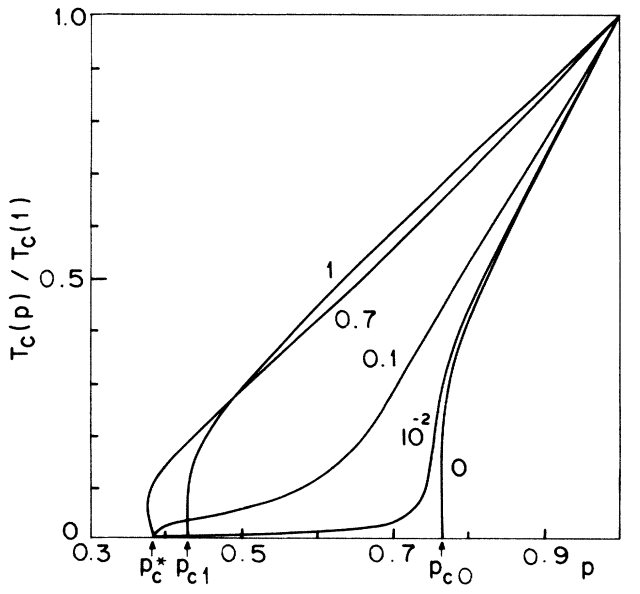

FIG. 2. Transition temperature as a function of concentration of magnetic atoms for different values of α, obtained by the effective-field theory of Honmura and Kaneyoshi.

mainly of qualitative value. Nevertheless, they are believed to be general. Although our calculations were restricted to the spin-$\frac{1}{2}$ Ising model in a square lattice, we expect that the effect of site-bond correlation is to increase the initial slope of the critical curve and eventually also yield an upward curvature in more general cases. In particular, the three-dimensional Heisenberg magnets $KNi_pMg_{1-p}F_3$ and $KMn_pMg_{1-p}F_3$ may be examples of systems which could be described by a Hamiltonian similar to the one employed here [Eq. (1)], with α near zero and one, respectively.

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[1]R. B. Stinchcombe, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. L. Lebowitz (Academic, New York, 1983), Vol. 7, p. 151.

[2]L. J. de Jongh, in *Magnetic Phase Transitions,* Proceedings of a Summer School at the Ettore Majorana Center, Erice, Italy, July 1983, edited by M. Ausloos and R. J. Elliott, Springer Series in Solid State Sciences, Vol. 48 (Springer, New York, 1983), p. 172.

[3]R. J. Elliott, B. R. Heap, D. J. Morgan, and G. S. Rushbrooke, Phys. Rev. Lett. **5**, 366 (1963).

[4]D. J. Morgan and G. S. Rushbrooke, Mol. Phys. **4**, 1 (1961); **4**, 291 (1961); **6**, 477 (1963).

[5]R. J. Elliott and B. R. Heap, Proc. R. Soc. London, Ser. A **265**, 264 (1962).

[6]J. Albino O. de Aguiar, M. Engelsberg, and H. J. Guggenheim, in Proceedings of the ICM, 1985 (unpublished).

[7]P. W. Anderson, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1963), Vol. 14, p. 99.

[8]H. B. Callen, Phys. Lett. **4**, 161 (1963).

[9]R. Honmura and T. Kaneyoshi, J. Phys. C **12**, 3979 (1979); **11**, L973 (1978).

[10]See, e.g., A. F. Siqueira and I. P. Fittipaldi, Phys. Rev. B **31**, 6092 (1985), and references therein.

[11]A. B. Harris, J. Phys. C **7**, 1671 (1974).