Random-field method in the theory of binary-alloy ferromagnetism

V. I. Belokon' and S. V. Semkin

Far Eastern State University, 690000 Vladivostok, Russia

(Submitted 26 May 1993; revised 30 July 1993)
Zh. Eksp. Teor. Fiz. **104**, 3784–3791 (November 1993)

We use the method of averaging over local fields to examine the magnetic properties of an Ising binary alloy of magnetic and nonmagnetic atoms. The concentration dependence of the Curie temperature is studied for different values of the interatomic interaction potential in the case of hexagonal lattice. We show that magnetic interaction can lead to separation of the system into phases with different concentrations of magnetic atoms.

1. Study of the properties of ferromagnets whose crystal lattice contains nonmagnetic impurities began many years ago.[1–4] In most cases, however, researchers focused on the effect of what became known as "frozen-in" impurities, randomly located at the lattice sites without correlations and not in thermodynamic equilibrium with the lattice. Usually the time it takes thermodynamic equilibrium to set in exceeds the spin-relaxation time and is much longer than the observation time. However, there are phenomena for which the effects related to the setting-in of impurity equilibrium can be significant. For instance, variation of the magnetic properties of a material related to the redistribution of impurities may affect the formation of magnetization in rocks, a process taking place over a long time interval.[5,6]

In our previous paper[7] we described a method for constructing a self-consistent equation for the magnetization of a ferromagnetic with randomly located nonmagnetic impurities. It is worth noting that the results obtained there for a crystalline ferromagnet can be arrived at by employing the method of differential operators.[3,4] Our approach, however, is apparently more universal since it can easily be generalized to include more complicated models of magnetic systems, say, the Heisenberg model of a diluted ferromagnet with any given dependence of the exchange integral on the atom separation.

In this paper we study within the Ising model a ferromagnet with impurities in thermodynamic equilibrium with the lattice by the method of averaging over the exchange-interaction fields.

2. Let us examine a crystal lattice, with a coordination number Z, whose sites can contain magnetic and nonmagnetic atoms (atoms of type 1 and 2, respectively). With each magnetic atom there is associated the Ising spin $S_i = \pm 1$, so that the energy of exchange interaction of two magnetic atoms with spins S_i and S_j is $-JS_iS_j$ if the atoms occupy neighboring lattice sites and zero in all other cases. We assume, as is done when studying binary alloys, that interatomic Coulomb forces act in the system and that their range is limited to the first coordination sphere. We denote the potential of these forces by $U_{\alpha\beta}$, with $\alpha,\beta = 1,2$. By assigning to each lattice site a variable σ_i equal to S_i if the given site contains a magnetic atom and is zero otherwise, we can write the system's exchange energy as

$$E_{\text{exch}} = -\sum_{\langle i,j \rangle} J\sigma_i\sigma_j,$$

and the Coulomb interaction energy as

$$E_{\text{Coul}} = -\sum_{\langle i,j \rangle} \{U_{11}\sigma_i^2\sigma_j^2 + U_{22}(1-\sigma_i^2)(1-\sigma_j^2) + U_{12}[\sigma_i^2(1-\sigma_j^2) + \sigma_j^2(1-\sigma_i^2)]\},$$

or, to within an additive constant, as

$$E_{\text{Coul}} = -\sum_{\langle i,j \rangle} U\sigma_i^2\sigma_j^2 - \sum_i f\sigma_i^2,$$

$$U = U_{11} + U_{22} - 2U_{12},$$

$$f = Z(U_{12} - U_{22})$$

(summation is over all pairs of nearest neighbors).

Allowing for the fact that the number of magnetic atoms in the lattice is $\Sigma_i\sigma_i^2$, we write the grand partition function as

$$\mathscr{Z} = \sum_{\{\sigma\}} \exp\left\{\frac{1}{kT}\left[\sum_{\langle i,j \rangle} (J\sigma_i\sigma_j + U\sigma_2^2\sigma_j^2) + (f+\mu)\sum_i \sigma_i^2\right]\right\}, \qquad (1)$$

where μ is the chemical potential, and summation is over all possible configurations $\{\sigma_i\}$. We denote the mean value of σ_i in the equilibrium state by pm and the probability of σ_i being zero by $1-p$; clearly, these quantities are independent of i since all lattice sites are equivalent (in the thermodynamic limit). The quantities p and m have a simple meaning: p is the probability that the given site is occupied by a magnetic atom (concentration), and m is the mean value of the spin of this atom.

We consider (1) to be the partition function of a system with the Hamiltonian

$$\mathscr{H} = -\sum_{\langle i,j \rangle} (J\sigma_i\sigma_j + U\sigma_i^2\sigma_j^2) - (f+\mu)\sum_i \sigma_i^2 \qquad (2)$$

and use the method developed in Ref. 7 to find m. We define the local exchange field H_i and the crystalline field N_i acting on the given site as sums over all neighboring sites:

1063-7761/93/110815-04$10.00

$$H_i=\sum_j \sigma_j,\quad N_i=\sum_j \sigma_j^2.$$

Hamiltonian (2) can then be written as the sum

$$\mathscr{H}=\sum_i E(\sigma_i),$$

$$E(\sigma_i)=-JH_i\sigma_i-UN_i\sigma_i^2-(f+\mu)\sigma_i^2. \tag{3}$$

We think of all σ_i as being independent and random quantities that assume a zero value with a probability $1-p$, a $+1$ value with a probability $\frac{1}{2}p(1+m)$, and a -1 value with a probability $\frac{1}{2}p(1-m)$. In this approximation the crystalline and exchange fields are also random quantities and independent of the site number. Hamiltonian (2) can be written as a sum of independent terms of type (3), and the partition function (1) can easily be calculated. For given N and H the mean value of spin per site is given by the formula

$$pm=\left[\exp\left\{-\frac{E(+1)}{k_BT}\right\}-\exp\left\{-\frac{E(-1)}{k_BT}\right\}\right]\times\left[\exp\left\{-\frac{E(+1)}{k_BT}\right\}+\exp\left\{-\frac{E(-1)}{k_BT}\right\}+\exp\left\{-\frac{E(0)}{k_BT}\right\}\right]^{-1},$$

and the configurational mean value is

$$\langle pm\rangle=\int pm\,W(H,N)\,dHdN. \tag{4}$$

Here $W(H,N)dHdN$ is the probability that the values of the exchange and crystalline fields acting on the given site lie inside the intervals $(H,H+dH)$ and $(N,N+dN)$. Equation (4) must be supplemented by one more self-consistent equation for the quantity $1-p$:

$$1-p=\int\frac{\exp\{-E(0)/k_BT\}W(H,N)dHdN}{\exp\{-E(+1)/k_BT\}+\exp\{-E(-1)/k_BT\}+\exp\{-E(0)/k_BT\}}. \tag{5}$$

The function $W(H,N)$ for the given system can easily be obtained by simple combinatorial reasoning:

$$W(H,N)=\sum_{k=0}^{z}\binom{z}{k}p^k(1-p)^{z-k}\delta(N-k)\sum_{l=0}^{k}\binom{l}{k}\left(\frac{1+m}{2}\right)^l\left(\frac{1-m}{2}\right)^{k-l}\delta[H-(2l-k)], \tag{6}$$

where $\binom{z}{k}$ and $\binom{k}{l}$ are binomial coefficients, and $\delta(x)$ Dirac's delta function. Using (6) and (3), we obtain from (4) and (5)

$$\sum_{k=1}^{z}\binom{z}{k}p^{k-1}(1-p)^{z-k}\sum_{i=0}^{[(k-1)/2]}A_k^i(t,x)m^{2i}=1,$$

$$\sum_{k=0}^{z}\binom{z}{k}p^k(1-p)^{z-k}\sum_{l=0}^{[k/2]}\frac{(1-m^2)^l}{2^k}\,\frac{x\Sigma_{i=0}^{k-2l}\binom{k-2l}{i}[1+(-1)^i]m^i}{\exp(qk/t)\cosh[(k-2l)/t]+x}=1-p, \tag{7}$$

where $t=k_BT/J$, $q=U/J$, $x=\exp\{-(f+u)/k_BT\}/2$, and

$$A_k^i(t,x)=\begin{cases}0 \quad \text{if } i>[(k-1)/2],\\ \left(\frac{1}{2}\right)^{k-1}\sum\limits_{m=0}^{i}(-1)^m\sum\limits_{l=m}^{[(k-1)/2]-(i-m)}\binom{l}{m}\binom{k}{l}\binom{k+2l}{2(i-m)+1}\dfrac{\exp(qk/t)\sinh((k-2l)/l)}{\exp(qk/t)\cosh((k-2l)/t)+x}.\end{cases}$$

The system of equations for determining the Curie temperature can be derived from (7) with $m=0$ and $T=T_C$. Note that at $p=1$ the system (7) has the same solution for $m(t)$ as the equation for magnetization in the case of a random impurity distribution [see Eq. (7) in Ref. 7].

3. We restrict further analysis to the case of $Z=3$ (a hexagonal lattice). Let us examine the behavior of m as a function of p as $t\to 0$. It can easily be demonstrated that, when $q>-1$, the only solution of (7) as $t\to 0$ is $m=1$. The physical interpretation of such a solution is obviously the following: if the Coulomb forces lead to attraction of the magnetic atoms or to repulsion with an effective potential lower than the exchange-interaction energy, the system at a fairly low temperature contains a percolation cluster incorporating, as $T\to 0$, all magnetic atoms. If we put in (7) $q=-1$, the function $m(p)$ behaves in the following manner as $t\to 0$. For $p\in[0,p_{c,1}]$, where $p_{c,1}\simeq 0.451$, $m(p)=0$. For $p>p_{c,1}$ the function increases monotonically with p and reaches a value of unity at $p=1$. This means that when the Coulomb forces lead to repulsion of magnetic atoms with the effective potential equal to the exchange-interaction constant, a percolation cluster forms in the system only for $p>p_{c,1}$. The quantity $p_{c,1}$ should, apparently, be interpreted as the approximate value of the threshold of percolation over the sites of the given lattice, since in this case the state with the lowest energy is independent of the location of the magnetic atoms.

For $-3 \leqslant q < -1$ the function $m(p)$ vanishes at $p=p_{c,2} \simeq 0.539$. For $q < -3$, finite values of m satisfying (7) in the limit as $t \to 0$ exist for $p \in (p_{c,2}, 0.67)$ and for $p \in (p_{c,3}, 1)$, where $p_{c,3} \simeq 0.689$. A solution in the interval $(p_{c,2}, 0.67)$ is physically meaningless because if there is magnetization in the system for a certain value of p, there must be magnetization at all higher values. Hence, $m=0$ should be taken as the true solution in this interval. (A zero solution exists for all p and T; in deriving (7) this solution was discarded.)

Thus, in the adopted approximation, when $q < -1$, there are two values of critical concentration, $p_{c,2}$ and $p_{c,3}$ for $-3 \leqslant q < -1$ and $q < -3$, respectively. At first glance such a solution seems strange, since for $q < -1$ the ground state of the system is independent of q. Indeed, in the ground state the spins of any neighboring atoms are parallel and the energy of this state is $E_0 \sim -(1-q)n_n$, where n_n is the number of neighboring magnetic atoms. Hence, with $q < -1$, the ground state is such that n_n is minimal. Obviously, there is a certain concentration p_c at which a percolation cluster appears in such a state.

However, if the concentration of magnetic atoms exceeds the site-percolation threshold but is lower than p_c, the percolation cluster, which is absent at $T=0$, appears at a certain temperature $T > 0$, and, as $T \to \infty$, the probability of a given magnetic atom belonging to an infinite cluster tends to the respective probability for the site problem. If such a cluster forms at a fairly low temperature, the spins entering into the cluster have no time to become randomized in direction, and at certain values $T > 0$ the system acquires magnetization.

Accordingly, the fact that for $q < -1$ there are two values of critical concentration can be interpreted as follows. For small q values $(-3 \leqslant q < -1)$ and for a concentration $p > p_{c,2}$, the magnetization $m(p,T)$ is positive for certain $T > 0$, with the function $m(p,T)$ experiencing a discontinuity at $T=0$. The size of the discontinuity decreases with p and vanishes ar $p=p_{c,2}$. But if $q < -3$ (strong repulsion), the rate of formation of a percolation cluster as T increases is not sufficient and, for each $T > 0$, the spins entering into the cluster are randomized in direction. In this case magnetization with $T \to 0$ appears only for $p > p_c$; thus, we relate the value of p_k to $p_{k,2}$. In other words, the existence of magnetization at low temperatures is due to the balance of two factors: the tendency of a percolation cluster to form as T grows, and the tendency of the spin directions to become disordered. For $-3 \leqslant q < -1$ the first factor prevails, and for $q < -3$ the second.

For finite values of $1/T$ the solution $m(t)$ of (7) decreases as the temperature grows and vanishes at a certain temperature $T=T_c(p)$ known as the Curie temperature. For $q \leqslant -1$ the function $T_C(p)$ vanishes at certain critical values of p.

If $q \leqslant -1$, the chemical potential μ calculated via (7) is a monotonically decreasing function of p at any given temperature. But if $q > -1$, then at temperatures lower than a certain temperature T^*, which is q-dependent, μ ceases to be a monotonic function of p and there is a region where $\partial\mu/\partial p$ is negative. In this case (7) must be supplemented by the well-known Maxwell construction,[8] according to which there is a segment $[p_1, p_2]$ on which $\mu(p)$ should be considered constant, $\mu_p = \mu(p_1) = \mu(p_2)$. Here, at concentrations p such that $p_1 < p < p_2$ the system is a mixture of two phases: a "liquid" with concentration p_2 and magnetization $m_2 = m(p_2, T)$, and a "gas" with concentration p_1 and magnetization $m_1 = m(p_1, T)$. The mean magnetization $\bar{m}$ of the entire system is determined in accordance with the "lever rule"

$$\bar{m} = x m_1 + (1-x) m_2, \quad \text{where } x = \frac{p_2 - p}{p_2 - p_1}.$$

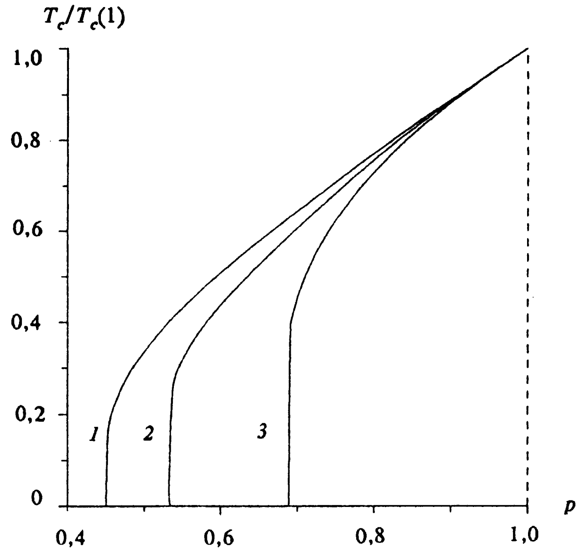

FIG. 1. The p-dependence of the Curie temperature for different values of q: curve *1*, $q=-1$; curve *2*, $q=-2$; curve *3*, $q=-5$.

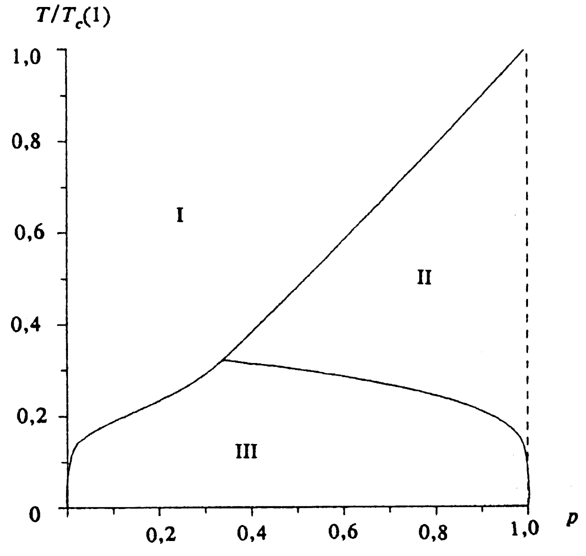

FIG. 2. Phase diagram at $q=0$: I—paramagnetic region; II—ferromagnetic homogeneous region; III—ferromagnetic heterogeneous region.

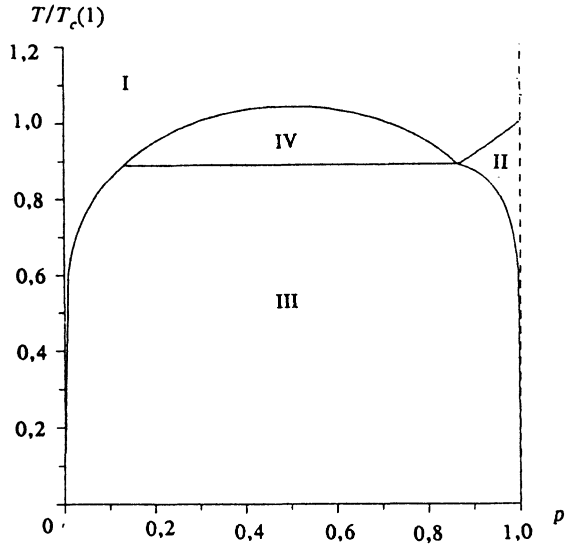

FIG. 3. Phase diagram at $q=4$: I, paramagnetic homogeneous region; II, ferromagnetic homogeneous region; III, ferromagnetic heterogeneous region; IV, paramagnetic heterogeneous region.

It can easily be demonstrated that μ_p is determined via the "equal-areas" principle.

As the temperature grows, the difference p_2-p_1 decreases, and $p_2=p_1=p^*$ at $T=T^*(q)$. For instance, $p^*\simeq0.312$ and $T^*\simeq0.322T_C(1)$ at $q=0$, where $T_C(1)$ is the Curie temperature of the system at $p=1$.

Thus, the properties of the system under investigation are determined by the value of parameter q, that is, the ratio of the effective Coulomb potential U equal to $U_{11}+U_{22}-2U_{12}$ to the value of the exchange integral J.

If $q\leqslant-1$, the system does not separate into phases with different number densities of magnetic atoms, but the Curie temperature as a function of concentration vanishes at different critical values of p depending on the value of q (Fig. 1).

But if $q>-1$, within a certain range of temperatures and concentrations the system is a mixture of two phases with different number densities of magnetic atoms. At moderate values of q the separation into phases occurs primarily owing to exchange interaction (Fig. 2). At large values of q the separation into phases may begin earlier than the emergence of spontaneous magnetization, and the phase diagram has the appearance of Fig. 3

4. Thus, the method suggested in Ref. 7 makes it possible to obtain reasonable results as applied to systems of nonmagnetic impurities that are in equilibrium with the lattice. This, in turn, offers the possibility of estimating the effects of magnetic memory in disordered crystalline magnetic substances.

The work was partially supported by the Russian Ministry of Science, Higher Learning, and Technology Policy under Grant Number 2-122-16-31 and the "Geocosmos" program.

[1] D. C. Rapoport, J. Phys. C **5**, 1830 (1972).
[2] T. C. Lubensky, Phys. Rev. B **15**, 311 (1976).
[3] T. Balcerzak, A. Bobak, J. Mielnicki, and V. H. Truong, Phys. Status Solidi B **130**, 183 (1985).
[4] T. Kaneyosi, I. P. Fittipaldi, and H. Beyer, Phys. Status Solidi B **102**, 393 (1980).
[5] A. A. Lepishchev, Yu. D. Tropin, and É. K. Yakubaĭlik, Izv. Akad. Nauk SSSR, Fiz. Zemli No. 12, 79 (1971).
[6] Yu. D. Tropin, Izv. Akad. Nauk SSSR, Fiz. Zemli No. 6, 100 (1969).
[7] V. I. Belokon' and S. V. Semkin, Zh. Eksp. Teor. Fiz. **102**, 1254 (1992) [Sov. Phys. JETP **75**, 680 (1992)].
[8] K. Huang, *Statistical Mechanics*, Wiley, New York (1966).

Translated by Eugene Yankovsky

This article was translated in Russia and is reproduced here the way it was submitted by the translator, except for stylistic changes by the Translation Editor.