EFFECT OF NONMAGNETIC IMPURITIES ON THE PHASE TRANSITION IN A FERROMAGNET

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The influence of nonmagnetic impurities on the phase transition in a ferromagnet is investigated within the framework of the two-dimensional Ising model. The extent to which the impurities weaken the long-range correlation between spins is shown. This weakening results in a finite value of the specific heat at the Curie point.

1. A large amount of experimental data on the influence of impurities on second-order phase transitions (critical points) exists at the present time.[1-4] A large number of effects have been uncovered which have not hitherto found an explanation. We list some of them:

a) The specific heat curve at the critical point broadens upon increase in the impurity concentration, and the specific heat maximum is finite (in place of a narrow peak tending to infinity in a pure substance).

b) At temperatures slightly above the specific heat maximum, a characteristic "discontinuity" appears. The phase transition point is apparently associated with this discontinuity.

c) As noted in[3], the Curie temperature in ferromagnets having nonmagnetic impurities falls more slowly than is predicted by existing theories, e.g., the self-consistent field method.

The influence of impurities on second-order phase transitions in ferromagnets above the Curie temperature T_c is evaluated in this paper. It is shown that in such systems, the contribution of the long-range correlations to the specific heat ($r_c > 1/c_{im}^{1/3}$, where r_c is the radius of the long-range correlations, and c_{im} is the concentration of nonmagnetic impurities) is strongly reduced in comparison with the pure substance, whereas the contribution of the short-range correlations is only slightly changed. This results in a finite value of the specific heat at the critical point.

Brout[5] has noted that in the study of disordered systems of the type investigated in the present paper, two limiting cases can arise:

a) If the sample is prepared at a temperature much above T_c, and quenched rapidly, so that the impurities cannot achieve thermal equilibrium, but are held to fixed positions, it is necessary to average the thermodynamic potential assuming a random distribution of impurities in the lattice sites.

b) If the same sample is cooled infinitely slowly, so that the ions are in equilibrium at each temperature, one must average a statistical sum.

2. The subsequent calculations are made within the framework of the two-dimensional Ising model, by the method set forth in[6]. For the Ising lattice with impurities, at a temperature $T > T_c$, it is possible to show that the part Φ of the thermodynamic potential which is related to the discontinuities at the critical point can be written

$$\Phi \sim T \sum_{r=1}^{\infty} f_r, \tag{1}$$

where f_r is the number of closed loops of length r, given by

$$f_r = \frac{1}{2r} \operatorname{Sp} \Lambda^r(kl\nu|k'l'\nu'),$$

$$\Lambda(kl\nu|k'l'\nu') = x\Lambda_0(kl\nu|k'l'\nu'), \quad x = \operatorname{th}\frac{J(kl;\, k'l')}{T};$$

the quantity $J(kl;\, k'l')$ is equal to J if magnetic ions occur at the sites kl and $k'l'$, and is equal to zero only if a nonmagnetic impurity is located at one of these sites; Λ_0 is the "transition probability" matrix.[6,7]

We shall examine the case of impurities rigidly held in randomly distributed positions. If only one site with a nonmagnetic impurity falls on a loop, this loop will not contribute to the thermodynamic potential. The probability that all sites of a loop of length r will be occupied by magnetic atoms is equal to c^{r-m}, where c is the concentration of magnetic atoms, and m is the number of self-intersections of the loop; therefore, after averaging, the thermodynamic potential Φ can be written

$$\overline{\Phi} \sim T \sum_r x^r c^r \sum_{m=0} c^{-m} f_{rm}, \tag{2}$$

where f_{rm} is the number of closed graphs with m self-intersections (in the pure material).

Terms with $r \gg 1$, corresponding to the long-range correlations, are the most important near the phase transition point, and in the subsequent evaluation we shall use this condition. We shall call the area of a graph the area bounded by its external lines, and rewrite Eq. (2) as

$$\overline{\Phi} \sim T \sum_r x^r c^r \int \Big(\sum_m f_{rm}(S) c^{-m} \Big) dS; \tag{3}$$

here $f_{rm}(S)dS$ is the number of graphs of length r with m self-intersections, occurring in the interval of area from S to S + dS.

The evaluation of Eq. (3) will be made under the assumption that the function $f_{rm}(S)$ has a narrow peak with maximum at the point $m_0(r, S)$ and decreases with increasing m (for $m > m_0$) more rapidly than $e^{-\kappa(m-m_0)}$, where κ is some arbitrary constant. With this assumption, Eq. (3) can be rewritten in the following form:

$$\overline{\Phi} \sim T \sum_r x^r c^r \int c^{-m_0(r,S)} f_r(S)\, dS, \tag{4}$$

where $f_r(S)dS$ is the number of graphs of length r occurring in the interval of area from S to S + dS.

If $f_{rm}(S)$ decreases with increasing m as $e^{-\kappa(m-m_0)}$, the region of applicability of this method is $|\ln c| < \kappa$. If $f_{rm}(S)$ decreases more rapidly than $e^{-\kappa(m-m_0)}$ for any κ (for example, $e^{-(m-m_0)^2}$), the proposed method is applicable for any c.

We express the average number of self-intersections, $m_0(r, S)$, in terms of r and S. To estimate it, we assume that the probability of passage of a loop through any site within the area S is the same for all sites. Through each site, a line passes on the average r/S times. We consider two extreme cases. For $r/s \ll 1$, this parameter can be taken as the probability of passage of a line through the given point. The probability of self-intersection at some point is equal to $(r/S)^2$ (three, four, etc., self-intersections can in this case be neglected). The average number of intersections in the whole area is of the order of $(r/S)^2 S$. In the opposite extreme ($r/S \gg 1$), a line passes through a point many times, and one may assume that a line has fallen on all sites, the number of which is of order S, only one time; therefore the number of self-intersections is $m_0 \sim r - S$. Thus

$$\begin{aligned} m_0 &\sim r^2/S \quad \text{for } S \gg r, \\ m_0 &\sim r - S \quad \text{for } S \ll r. \end{aligned} \tag{5}$$

3. We shall compute the number of graphs $f'_r(S)$ of length r located in an area smaller than or of the order of S. (For simplicity we select a square with side $L \sim \sqrt{S}$.) We have

$$f_r'(S) \sim \frac{1}{r} \operatorname{Sp} \Lambda_0^r(kl\nu|kl\nu) = \frac{1}{r} \operatorname{Sp} \Lambda_0^r(pg\nu|pg\nu) = \frac{1}{r} \sum_{ipg} \lambda_i^r(pg), \tag{6}$$

where the $\lambda_i(p, g)$ are the eigenvalues of the matrix Λ_0, and the summations on k, l and p, g go in integer steps from 0 to L − 1:

$$\Lambda_0(pg\nu|p'g'\nu') = \frac{1}{L^2} \sum_{k'l'=0}^{L-1} \exp\left\{ i \frac{2\pi}{L} [(p-p')k' + (g-g')l'] \right\} \cdot \sum_{n=-k'}^{L-k'-1} \sum_{n'=-l'}^{L-l'-1} \exp\left\{ i \frac{2\pi}{L} (pn + gn') \right\} \Lambda_0(n, n'|\nu\nu'). \tag{7}$$

We have used the fact that Λ_0 depends only on the difference of the corresponding coordinates, and have introduced the notation $\Lambda_0(k l\nu|k'l'\nu') = \Lambda_0(n, n'|\nu\nu')$, where $n = k - k'$ and $n' = l - l'$.

Because of the finite ranges of summation, the sums over n and n′ depend upon k′ and l'. Hence the matrix Λ_0 is not diagonal in the indices p and g. Since |n| and |n′| cannot be greater than unity, in the Ising model with nearest-neighbor interactions, we have from Eq. (7)

$$\begin{aligned} \Lambda_0(pg\nu|p'g'\nu') &= e^{i2\pi p/L} \Lambda_0(10|\nu\nu')(\delta_{pp'}\delta_{gg'} - \\ &- L^{-1}\delta_{gg'} \exp\{-i2\pi(p-p')/L\}) + \\ &+ e^{i2\pi g/L} \Lambda_0(01|\nu\nu')(\delta_{pp'}\delta_{gg'} - L^{-1}\delta_{pp'} \exp\{-i2\pi(g-g')/L\}) \\ &+ e^{-i2\pi g/L} \Lambda_0(0-1|\nu\nu')(\delta_{pp'}\delta_{gg'} - L^{-1}\delta_{pp'}) + \\ &+ e^{-i2\pi p/L} \Lambda_0(-10|\nu\nu')(\delta_{pp'}\delta_{gg'} - L^{-1}\delta_{gg'}). \end{aligned} \tag{8}$$

We shall find the eigenvalues of the matrix (8) by perturbation theory (assuming $L^{-1} \ll 1$). In the zeroth approximation, this matrix consists of fourth-order blocks situated along the main diagonal, and the calculation of the eigenvalues reduces to the solution of an algebraic equation of fourth order. It is easy to see that the main contribution to the sum (6) comes from two complex conjugate roots λ_i, for small p/L and g/L (p/L and g/L $\ll 1$), respectively equal to

$$\lambda_{i0} = (\sqrt{2}+1)\left[1 - \frac{\sqrt{2}}{16}\left(\frac{2\pi}{L}\right)^2 (p^2+g^2)\right] \exp\left\{ \pm i \frac{\pi}{L} \sqrt{p^2+g^2} \right\}. \tag{9}$$

In the first approximation in L^{-1}, it is necessary to calculate only the corrections to the matrix elements diagonal in p and g. From Eq. (8), we obtain

$$\lambda_{i1} = \lambda_{i0}(1 - L^{-1}). \tag{10}$$

The result (10) is quite reasonable, since the computation of the difference of the transition probability within and on the surface of the area S results in corrections of order L^{-1}. Substituting Eqs. (9) and (10) into (6), we obtain

$$f_r'(S) \sim \frac{1}{r}(\sqrt{2}+1)^r e^{-r/L} \sum_{p,g=0}^{L} \exp\left\{ -\frac{\sqrt{2}}{16}\left(\frac{2\pi}{L}\right)^2 (p^2 + g^2) r \right\} \cos \frac{\pi}{L} \sqrt{p^2+g^2}\, r. \tag{11}$$

The effective range of summation on p and g in this formula is less than L/r.

We shall examine the two extreme cases $L/\sqrt{r} \gg 1$ ($S \gg r$) and $L/\sqrt{r} \ll 1$ ($S \ll r$). In the first case we replace the summation on p and g by integration on $\omega_1 = 2\pi p/L$ and $\omega_2 = 2\pi g/L$. For $r \gg 1$, the resulting integral is easy to estimate:

$$\begin{aligned} f_r'(S) &\sim \frac{S}{r}(\sqrt{2}+1)^r e^{-r/L} \int_0^\infty \omega \exp\left(-\frac{\sqrt{2}}{16}\omega^2 r \right) \cos \frac{1}{2}\omega r\, d\omega = \\ &= \frac{S}{r^2}(\sqrt{2}+1)^r e^{-r/L} \frac{\partial}{\partial \gamma} \int_0^\infty \exp\left(-\frac{\sqrt{2}}{16}\omega^2 r \right) \sin \gamma\omega r\, d\omega \big|_{\gamma=1/2} \sim \\ &\sim -\frac{S}{r^3}(\sqrt{2}+1)^r e^{-r/L}. \end{aligned} \tag{12}$$

In the integration we have made use of the fact that $\exp(-2\omega^2 r/16)$ is a smooth function in comparison with $\sin \gamma\omega r$.

In the opposite extreme, $S \ll r$, the first term (p = g = 0) in the series in Eq. (11) gives the main contribution, and

$$f_r'(S) \sim \frac{1}{r}(\sqrt{2}+1)^r e^{-r/L}. \tag{13}$$

The total number of graphs in the entire lattice of N sites having an area less than S is determined from

$$f_r'(S) \sim -\frac{N}{r^3}(\sqrt{2}+1)^r \exp\left(-\frac{r}{\sqrt{S}} \right), \quad S \gg r, \tag{14a}$$

$$f_r'(S) \sim -\frac{N}{rS}(\sqrt{2}+1)^r \exp\left(-\frac{r}{\sqrt{S}} \right), \quad S \ll r. \tag{14b}$$

In the region $S \sim r$, the two methods of derivation of the limiting values (14a) and (14b) give incorrect factors multiplying the exponentials, since these factors cannot be made continuous in this region. However, as will be seen in the following, the region $S \sim r$ does not make a significant contribution to the specific heat of the system and does not influence the critical temperature.

4. We divide the integral in Eq. (4) into two parts: from zero to r and from r to r^2. Substituting Eqs. (5), (14a), and (14b) into (4), we obtain

$$\bar{\Phi} \sim -NT\sum_r c^r x^r (\sqrt{2}+1)^r \Big[\frac{1}{r^2}\int_r^{r^2} \exp\Big\{-\frac{r}{\sqrt{S}}+|\ln c|\frac{r^2}{S}\Big\}\frac{dS}{S^{3/2}} - \int_0^r \exp\Big\{-\frac{r}{\sqrt{S}}+|\ln c|\,(r-S)\Big\}\frac{dS}{S^{3/2}}\Big]. \quad (15)$$

To estimate these integrals, we note that the exponents have two maxima, at the points $S \sim r^2$ and $S \sim [r/|\ln c|]^{2/3}$. For $r|\ln c|^2 \ll 1$, the first integral gives the main contribution, its integrand having a maximum near $S = r^2$. For $r|\ln c|^2 \gg 1$, the second integral dominates.

In the first case ($r|\ln c|^2 \ll 1$), we have

$$\int_r^{r^2} \exp\Big\{-\frac{r}{\sqrt{S}}+|\ln c|\frac{r^2}{S}\Big\}\frac{dS}{S^{3/2}} \approx \int_r^{r^2} e^{-r/\sqrt{S}}\frac{dS}{S^{3/2}} \approx \frac{1}{r}. \quad (16a)$$

In the second case ($r|\ln c|^2 \gg 1$), we obtain, except for the factor multiplying the exponential, which does not affect the subsequent results,

$$\int_0^r \exp\Big\{-\frac{r}{\sqrt{S}}+|\ln c|\,(r-S)\Big\}\frac{dS}{S^{3/2}} \sim \exp\{|\ln c|r - 2r^{3/2}|\ln c|^{1/2}\}. \quad (16b)$$

Considering Eqs. (16), we rewrite Eq. (15) as

$$\bar{\Phi} \sim -NT\Big[\sum_{r=4}^{1/|\ln c|^2} \frac{c^r x^r (\sqrt{2}+1)^r}{r^3} - \sum_{r=1/|\ln c|^2}^{\infty} x^r(\sqrt{2}+1)^r \times \exp\{-2r^{3/2}|\ln c|^{1/2}\}. \quad (17)$$

The radius of convergence of the series (17) is determined by the condition $x_c(\sqrt{2}+1) = 1$, from which the critical temperature is found as the singular point of the thermodynamic potential. Thus, for rigidly held impurities the critical temperature does not depend on impurity concentration. From Eq. (17) it is seen that the derivative of the thermodynamic potential with respect to temperature is finite at the critical point.

For small concentrations of nonmagnetic impurities ($1 - c \ll 1$), the second sum is exponentially small relative to the first.

These results can be understood intuitively by recognizing that for any concentration, the finite, although exponentially small, probability of occurrence of an arbitrarily large compact region composed wholly of magnetic atoms, plays a fundamental role in the existence of the phase transition point. A phase transition with a temperature equal to that of the pure substance is possible in such regions, although the contribution of such regions to the integral is exponentially small, in agreement with Eq. (17).

There remains unexplained the question of whether T_c, for small concentrations of magnetic material, corresponds to the formation of a finite magnetic moment per atom, or whether this point represents the onset of infinite correlations in regions consisting of magnetic atoms, for infinitely small magnetic moment per site.

The effective range of summation in the first sum in Eq. (17) is $r \lesssim 1/|\ln c| \ll 1/|\ln c|^2$; therefore the sum on r can be extended to infinity, and the series then summed. We thus obtain the heat capacity at small deviations from the critical temperature:

$$C \sim Nc^2 \ln\Big(1 - c + (\sqrt{2}+1)\frac{T-T_c}{T}\Big). \quad (18)$$

This formula agrees with the empirical expression found by Voronel' and Giterman.[8]

As is seen from Eq. (15), the region $S \sim r$ can give a significant contribution only in the terms of the series for which $r \sim 1/|\ln c|^2$. But these terms do not change the heat capacity, since the effective range of summation in the first sum (which gives the main contribution to the specific heat) is of order $r \ll 1/|\ln c|^2$. Further, the terms for which $r \sim 1/|\ln c|^2$ do not affect the critical temperature. Thus in the region $S \sim r$, the factors multiplying the exponentials in Eqs. (14) do not affect the results.

In the opposite limiting case, $c \ll 1$, the terms with $r \sim 1$ give the principal contribution to the specific heat, as is seen from Eq. (17). This corresponds to a greatly weakened long-range correlation in the specific heat. We have no rule for calculating the specific heat in this limiting case, since all preceding calculations have been made under the assumption that $r \gg 1$.

If the ions are in thermal equilibrium, it is possible to use very rough qualitative considerations showing that the phase transition temperature decreases with increase in concentration of nonmagnetic impurities. For a qualitative estimate, we assume that the deviation from a random distribution is small, even in this case. In the zeroth approximation, making a statistical average over the random distribution of impurities, we obtain in place of Eq. (2),

$$\bar{Z} = \sum_r c^r x^r \sum_m g_{rm} c^{-m}, \quad (19)$$

where g_{rm} is the number of graphs of length r with m self-intersections. Since graphs cannot traverse the same line twice, the number of self-intersections cannot exceed r/2. On the average, $\sum_m g_{rm}c^{-m} = g_r c^{-\bar{m}(r)}$ and $\bar{m}(r) < r/2$. For large r, the quantity $\bar{m}(r)$ can be written as $\bar{m}(r) = \alpha r - \beta(r)r$, where $0 < \alpha < 1/2$, and $\beta(r) \to 0$ as $r \to \infty$. With these considerations, one can write Eq. (19) as

$$\bar{Z} = \sum_r (c^{1-\alpha}x)^r c^{\beta(r)} g_r. \quad (20)$$

The critical point is determined from the relation $c^{1-\alpha}x_c = \sqrt{2}-1$; that is, with a decrease in concentration of magnetic impurities, the transition temperature decreases. The Curie point falls more slowly than according to the self-consistent field theory, in which $T_c = cT_c^0$, where T_c^0 is the Curie temperature of the pure substance. This is in qualitative agreement with experiment.[3]

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