Theory of "diffuse" phase transitions

B. Ya. Balagurov and V. G. Vaks

I. V. Kurchatov Institute of Atomic Energy

(Submitted May 11, 1973)
Zh. Eksp. Teor. Fiz. **65**, 1600–1618 (October 1973)

An investigation is made of the influence of randomly distributed pinned impurities present in a low concentration on the singularities of thermodynamic quantities at second-order phase transitions. Two one-dimensional models, exhibiting transitions in a field H at $T=0\,^\circ\mathrm{K}$ in the absence of impurities, and a two-dimensional Ising model are considered. The influence of impurities on the transition in these models can be reduced to the problem of the density of levels of a particle in the field of randomly distributed impurities. It is shown that the presence of impurities results in "diffuseness" of the transition: All the derivatives of the free energy at the transition point are finite. The maxima of the thermodynamic quantities are shifted in the direction of lower temperatures (or in the direction of lower fields in the case of field-induced transitions). The dependence of this shift and of the amplitudes of the maxima on the impurity concentration are deduced. A dimensional analysis, generalizing the results to the three-dimensional case, is given. Some features of field-induced transitions in the presence of magnetic impurities and of transitions in the presence of nonmagnetic impurities in an Ising lattice are considered.

1. INTRODUCTION

A very large amount of experimental work has been done on phase transitions in systems containing impurities and on solid solutions (see, for example, [1-3]). The presence of an additional thermodynamic quantity, which is the impurity concentration c, makes it possible to vary continuously all the parameters of a transition and this is of major theoretical and practical interest. However, little theoretical work has been done on this subject. Obviously, one should distinguish mobile equilibrium impurities whose positions vary with temperature T so as to minimize the thermodynamic potentials and pinned nonequilibrium impurities whose positions are governed only by the method used in the preparation of a mixture and are independent of T (the relaxation times of such impurities are longer than the durations of thermodynamic experiments). Solids contain pinned impurities if the temperature T is not too high.

The thermodynamics of transitions involving interstitial equilibrium impurities has been considered by Syozi[4] and Lushnikov and Shapoval.[5] They have found that nonmagnetic equilibrium impurities reduce the transition temperature and weaken the singularity of the specific heat C(T) but do not affect the kink in the dependence C(T) characterized by an infinite derivative at $T=T_c$. Pinned impurities tend to smooth out the singularities, giving rise to "diffuse" transitions.[1] For example, Mikulinskiĭ[6] shows that the presence of nonmagnetic pinned impurities in a two-dimensional Ising lattice makes all the derivatives of the specific heat finite at $T=T_c$. The same result is obtained rigorously by McCoy and Wu[7] but only for special (linear) impurities and very unusual distribution functions of their interaction. Moreover, Griffiths[8] and Mikulinskiĭ (self-consistent field method)[9] have shown that two nonanalytic points of the free energy F(T) may appear in the Ising model with nonmagnetic pinned impurities. One of these points is associated with the appearance of a spontaneous moment but the significance of the other is not yet clear.

We shall attempt to provide an approach which is more rigorous than that used by Mikulinskiĭ[6,9] and consider the problem of the singularities of phase transitions in systems containing substitutional pinned impurities in a low concentration. The general idea is that, in some cases, particularly in the two-dimensional Ising model, this problem can be linked to the widely discussed[10-16] calculations of the energy spectrum of a particle in a random field of impurities, i.e., it can be reduced to the determination of the density of states $\rho(\epsilon)$. Therefore, using the results on the nature of $\rho(\epsilon)$ near a band edge, we can obtain several results relating to the singularities of F(T) and C(T) at a transition point.

Since explicit equations for the density of states are known only in the one-dimensional case, we shall first consider two one-dimensional Ising-type models subject to a transverse magnetic field $H_x=H$.[17-19] In the absence of impurities, these models predict a phase transition induced by a field H at T = 0 K and the transition field corresponds to the saturation of the moment M_x (in the first model) or of the moment M_z (in the second model).[19] The susceptibility $\chi=-\partial^2F/\partial H^2$ becomes infinite for $H\to H_c$ and the approach to infinity is by a square-root law $\chi\propto(H_c-H)^{-1/2}$ in the first case and by a logarithmic law $\chi\propto\ln|H-H_c|$ in the second case. In the first case, the nature of the singularities of the dependences on H is fully analogous to the singularities in the dependences on T in the two-dimensional Slater model[18] and in the second case it is fully analogous to the two-dimensional Ising model.[19] Thus, the problems in question are quite close to the Slater and Ising models and an explicit solution can be obtained even in the presence of impurities.

In Sec. 4 we shall consider the two-dimensional Ising model. Applying the Vdovichenko method,[20,21] we can express the free energy F at low values of c in terms of the density of states of a particle obeying a two-dimensional equation of the Dirac-Schrödinger type for a random field of impurities. Using the limiting expressions for $\rho(\epsilon)$ near a band edge, we shall show that in the case of weakly magnetic impurities (i.e., impurities whose interaction with the spins of the host crystal J_{21} is less than the interaction of the host spins with one another) a nonanalytic point of F(T) occurs at T_c of a pure crystal and all the derivatives at this point are finite. This is in agreement with the conclusions reached by Mikulinskiĭ.[6] We shall consider the nature of the singularities for strongly magnetic ($J_{21}>J_{11}$) impurities. We shall show that irrespective of the sign of $J_{21}-J_{11}$

the temperature corresponding to the specific heat maximum T_m always shifts (for low values of c) in the direction of low temperatures T and the shift amounts to $T_m - T_c \sim -cT_c \ln(1/c)$. In Sec. 5 we shall give a dimensional analysis of the type used in the similarity hypothesis and apply it to the impurity-concentration dependences of the specific heat maximum C_m and the susceptibility maximum χ_m. This dimensional analysis is supported by the earlier results and is also applicable to the three-dimensional case. According to this analysis, we can express $C_m(c)$ and $\chi_m(c)$ at low values of c in terms of the critical indices of the pure system. We shall conclude by discussing the results obtained and some of the problems in the extrapolation of these results to values of c which are no longer small.

2. CHAIN OF SPINS WITH AN AXIALLY SYMMETRIC INTERACTION IN A TRANSVERSE FIELD

Pikin and Tsukernik[17] obtained the exact solutions for one-dimensional models using the Hamiltonian

$$\mathscr{H} = -\frac{1}{4}\sum_{l=1}^{N} J_{\alpha\beta}(l, l+1)\sigma_l^{\alpha}\sigma_{l+1}^{\beta} - \frac{1}{2}H\sum_{l=1}^{N}\sigma_l^{x}, \tag{1}$$

where σ represents the Pauli matrices and $\alpha, \beta = y, z$. In the case of a pure system considered in [17] the constants $J_{\alpha\beta}$ are independent of l. It is shown in that paper that in the case of axial symmetry of the interaction we have $J_{yz} = 0$ and $J_{yy} = J_{zz} = J$. Moreover, at T = 0 K the moment $M_x = M(H)$ reaches saturation at the point H = J and the susceptibility χ rises as $(J-H)^{-1/2}$ for $H \to J$.

We shall consider the influence of pinned impurities on the thermodynamics of a transition under these conditions. The constants of the interaction of an impurity with spins of the host crystal $J_{21} = J_{12}$ and with other impurities J_{22} will be assumed to be different from $J_{11} = J$, and the magnetic moment of the impurity, i.e., the term with H in Eq. (1), will be assumed (for the sake of simplicity) to be unaffected. If we follow [17] and pass from the spin to the Fermi operators a_l and $\overset{+}{a}_l$, the Hamiltonian (1) becomes

$$\mathscr{H} = -\sum_{l}\left[\frac{1}{2}J_{l,l+1}(a_l^{+}a_{l+1} + \overset{+}{a}_{l+1}a_l) + H\left(\frac{1}{2} - a_l^{+}a_l\right)\right]. \tag{2}$$

The Hamiltonian (2) can be diagonalized by going over from the coordinate representation to an orthonormalized system of functions $\varphi_{\lambda l}$ (analogous to $e^{i\lambda l}$ in the impurity-free case) which diagonalizes single-particle states in $\mathscr{H}$:

$$a_l = \sum_{\lambda} a_\lambda \varphi_{\lambda l}, \quad \sum_{l} \varphi_{\lambda l}\varphi^{*}_{\lambda' l} = \delta_{\lambda\lambda'}, \quad \sum_{\lambda} \varphi_{\lambda l}\varphi^{*}_{\lambda l'} = \delta_{ll'}. \tag{3}$$

The equations for $\varphi_{\lambda l}$ can be obtained, as in [17], by writing out the equations for the operator $\dot{a}_l$ and assuming that $\dot{a}_\lambda = -iE_\lambda a_\lambda$.

In this way, we obtain

$$(E_\lambda - H)\varphi_{\lambda l} + {}^1/_2 J(\eta_{l-1,l}\varphi_{\lambda,l-1} + \eta_{l,l+1}\varphi_{\lambda,l+1}) = 0. \tag{4}$$

Here, $\eta_{ll'} = J_{ll'}/J$, and E_λ represents the required eigenvalues of $\mathscr{H}$.. Multiplying the left-hand side of Eq. (4) by $\varphi^{*}_{\lambda l}$ and summing over λ and l with the aid of Eq. (3), we find that the sum of E_λ over λ is equal to N(H). Consequently, the Hamiltonian $\mathscr{H}$ and the free energy per unit cell F at T = 0 K become

$$\mathscr{H} = \sum_{\lambda} E_\lambda\left(a_\lambda^{+}a_\lambda - \frac{1}{2}\right), \quad F = -\frac{1}{2N}\sum_{\lambda}|E_\lambda|. \tag{5}$$

The susceptibility χ is given by the formula

$$\chi = \frac{-\partial^2 F}{\partial H^2} = \frac{1}{N}\sum_{\lambda}\delta(E_\lambda) = \rho(E=0), \tag{6}$$

where $\rho(E)$ obviously represents the usual energy density of states.

In the absence of impurities we have $\eta_{ll'} = 1$ and it follows from Eqs. (4)–(6) that

$$\varphi_{\lambda l} = \frac{e^{i\lambda l}}{N^{1/2}}, \quad E_\lambda = H - J\cos\lambda, \quad \chi(H \to J-0) \to \frac{1}{\pi}[2J(J-H)]^{-1/2}. \tag{7}$$

We shall consider only the case of low impurity concentrations $c \ll 1$ and fields H close to $H^{(0)} = J$. If we replace E_λ with a dimensionless energy ϵ_λ and change $\rho(E)$ to the corresponding density of states $\rho(\epsilon)$:

$$E = H - J + J\varepsilon, \quad \varepsilon = \frac{k^2}{2}, \quad \chi = \frac{1}{J}\rho\left(\frac{J-H}{J}\right) \tag{8}$$

(here and later the index λ will be omitted), we find that the values $k \ll 1$ are important in the thermodynamic description of the critical range $|H-J| \ll J$. In this long-wavelength limit we can improve the clarity of the results by going over from a discrete equation (4) to a continuous one. We can see that in the impurity-free case and if $k \ll 1$, Eq. (4) transforms to the free Schrödinger equation and ϵ then represents the dimensionless energy. Clearly, in the presence of impurities Eq. (4) transforms to the Schrödinger equation with a potential energy u(x) which depends on the coordinates of the impurities. It is also clear that distant impurities in a discrete chain may act as isolated scatterers. Therefore, in the case of small values of k considered here, the equivalent potential u(x) in the Schrödinger equation should be of the short-range type, i.e., it can be represented in the delta-function form $g\delta(x)$. The value of g can be determined from the condition that, in the case of small values of k, the scattering by impurities should be the same in the discrete and continuous problems. We shall therefore solve the problem of the scattering of a plane wave $\exp(ikl)$ by a single impurity in a discrete chain.

Let us assume that an impurity is located at a site $l = 0$ so that in Eq. (4) we have

$$\eta_{ll'} = 1 - (1-\eta)(\delta_{l0} + \delta_{l'0}), \qquad \eta = J_{12}/J. \tag{9}$$

We shall now separate from Eq. (4) the term corresponding to the ideal lattice and transfer the inhomogeneity to the right-hand side. Solving the equation obtained in this way by the Fourier transform method, we find that

$$\varphi_l = e^{ikl} + (1-\eta)\delta_{l0}\varphi_0 - \frac{1-\eta^2}{\eta}(E-H)G(l)\varphi_0, \tag{10}$$

where G(l) is the Green's function in the scattering problem:

$$G(l) = \int_{-\pi}^{\pi}\frac{dp}{2\pi}\frac{e^{ipl}}{E-H+J\cos p+i\delta}, \qquad \delta \to +0. \tag{11}$$

Assuming that $l = 0$ in Eq. (10), we can find φ_0. Comparing then φ_l from Eq. (10) for $l \gg 1$, $k \ll 1$ with the solution of the continuous equation

$$\varphi''(x) + k^2\varphi(x) = g\delta(x)\varphi(x), \tag{12}$$

we find that the solutions are identical if

$$g = 2(1-\eta^2)/\eta^2. \tag{13}$$

We must stress that the relationship between k and the distance l to an impurity is now arbitrary: the solutions become identical as soon as l and $1/k$ become much greater than the lattice constant. In the case of low impurity concentrations (in the lowest approximation with respect to c), we may assume that the impurities are sufficiently far apart so that allowance for the configurations with close impurities gives rise to corrections of higher orders in c. Therefore, the transformation from Eqs. (4) and (10) to Eq. (12) can be made for each impurity independently of all the other impurities. In this way, Eq. (4) becomes

$$\varphi''+k^2\varphi=g\sum_i\delta(x-x_i)\varphi, \qquad (14)$$

where the summation is performed over the impurity coordinates x_i, and g is given by Eq. (13). Thus, the problem of the energy spectrum of Eq. (4) in the range of low values of k has been reduced to the problem of an electron in a field of random point impurities, which has been discussed widely in the literature.[10-15]

Equations (8) and (14) are the solutions of the problem and give the susceptibility of the spin system with impurities in terms of the density of states of an electron in a random field. It should be noted that Eqs. (8) and (14) are obtained without imposing restrictions on the nature of the impurity distribution function or on the value of the constant J_{12}.

We shall assume that the impurities are distributed at random and use the well-known results[10-15] for the density of states in the presence of such impurities. We shall first consider the case of weakly magnetic impurities $|J_{12}|<J$, which corresponds, in the continuous problem of Eq. (13), to a repulsive potential $g>0$. Moreover, we shall restrict ourselves to moderate values of g: $g\gg\{c, k\}$. The problem of finding $\rho(\epsilon)$ under these conditions was solved by Bychkov and Dykhne.[12] If we use their results, we find that the susceptibility of one unit cell follows from Eq. (8):

$$\chi(H)=\frac{1}{J}\frac{\pi c^2}{4|\Delta|^{3/2}}\,\mathrm{sh}^{-2}\frac{c\pi}{2|\Delta|^{1/2}}, \qquad (15)$$

where $\Delta=2(H-J)/J$.

If $|\Delta|\gg c^2$, we find that Eq. (15) reduces to Eq. (7) and in the case when $|\Delta|\ll c^2$ the susceptibility χ decreases exponentially:

$$\chi\approx\frac{1}{J}\frac{\pi c^2}{|\Delta|^{3/2}}\exp\left(-\frac{c\pi}{|\Delta|^{1/2}}\right). \qquad (16)$$

If $H>J$ we find that the susceptibility vanishes ($\chi=0$), which corresponds to saturation of the magnetic moment.

Thus, the presence of pinned impurities causes a transition to become diffuse and makes all the derivatives of the susceptibility finite at the transition point $H_c=J$. It follows from Eq. (15) that the maximum of χ shifts in the direction of lower magnetic fields by an amount which is proportional to c^2: $(H_c-H_m)\propto c^2J$ and the maximum value of χ is $\chi_m\sim 1/cJ$. The general nature of the dependence $\chi(H)$ is illustrated in Fig. 1.

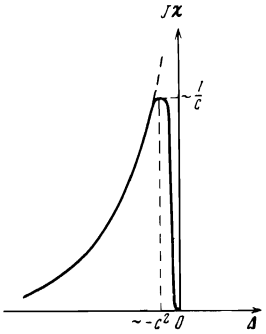

FIG. 1. General nature of the dependence $\chi(\Delta)$ in the case of weakly magnetic impurities; $\Delta=2(H-J)/J$.

The conclusion that χ and all its derivatives are finite at $H=H_c$ is not dependent on the assumption $g\gg c$, which is utilized in [12] to obtain Eq. (15). It follows from other investigations[11,14] that for any value $g>0$ the density of states near a band edge ($k\to 0$) has the form $\rho\propto\exp(-c\pi/k)$ for a Poisson-type distribution of impurities. Therefore, in the case of small values $g<c$ the susceptibility in fields $H\to H_c$ is given with exponential precision by Eq. (16). However, as H_c-H rises, the case $g<c$ begins to differ from the $g\gg c$ case discussed above. Thus, according to Magarill and Éntin,[15] in the $g\ll c$ case, the density of states has its maximum at $\epsilon_m\sim cg$ and $\rho(\epsilon_m)\propto(cg^2)^{-1/3}$. Therefore, in the case of low values of $g\ll c$, we obtain

$$H_c-H_m\propto J_{cg},\quad J\chi_m\propto(cg^2)^{-1/3},$$

so that the influence of impurities on the susceptibility singularity is weaker.

The exponential suppression of the singularity (16) at the transition point has a simple meaning discussed by Mikulinskiĭ.[6] Weakly magnetized impurities reduce that interaction between the spins which confines them to a plane perpendicular to H. Therefore, as $H\to H_c$, the system is close to saturation everywhere except for the regions which, as a result of fluctuations of the Poisson distribution, are free of impurities. In fields $H\to H_c$ the magnetic moment is not saturated only in these regions for which the correlation radius of the pure system $r_c\sim|\Delta|^{-1/2}$ is less than the size of a region l which is free of impurities. Since the probability of the appearance of such a region in the Poisson distribution is exponentially small, being proportional to $\exp(-cl)$, it follows that the thermodynamic contribution of such regions decreases as $\exp(-c|\Delta|^{-1/2})$.

We shall now discuss the case of strongly magnetic impurities $\eta^2>1$, which corresponds to attraction in the continuous problem of Eq. (13), and we shall again restrict ourselves to small values $c\ll|g|$. The density of states corresponding to this case has been investigated earlier[11,13] and is plotted in Fig. 2. If $J-H\gg Jc^2$, the values of ρ and χ are still given by Eq. (15). For lower values $|\Delta|<c^2$, the exponential terms $\sim\exp(-c|\Delta|^{-1/2})$ can be ignored and the expression for ρ can be found by expanding the Frisch-Lloyd equation[10] in powers of E/c^2 and c/g. At still lower energies, corresponding to $E>c^2$, the influence of many impurities decreases exponentially and the levels appear only when impurities approach each other closely (mainly in the form of pairs if the concentration c is low).

The corresponding "pair" contribution to $\rho(\epsilon)$ can be found quite easily by calculating the dependence of the energy $\epsilon(l)$ on the distance l between impurities and then replacing the Poisson distribution over the distance $c\exp(-cl)$ with the distribution of ϵ:

$$J\chi(H)=\rho(\varepsilon)=c\left[\frac{d}{d\varepsilon}\left(1-\frac{2\varkappa}{|g|}\right)^{c/\varkappa}\right|,\quad \varkappa=(-2\varepsilon)^{1/2}=\Delta^{1/2}. \qquad (17)$$

In the direct vicinity of an impurity level

$$|1-2\varkappa/|g||<\exp(-|g|/c)$$

Eq. (17) becomes invalid because of the appearance of contributions of many distant impurities. However, the

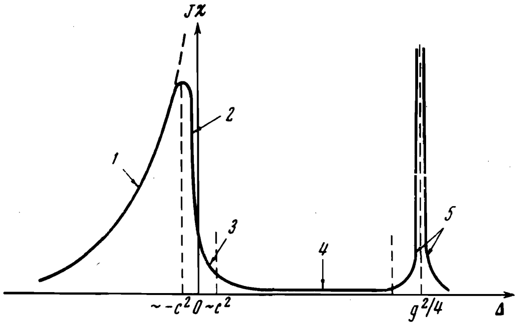

FIG. 2. General nature of the dependence $\chi(\Delta)$ in the case of weakly magnetic impurities: $\Delta = 2(H - J)/J$; $1 - J\chi = 1/\pi\sqrt{|\Delta|}$; $2 - J\chi = \pi c^2 |\Delta|^{-3/2} e^{-c\pi/\sqrt{|\Delta|}}$; $3 - J\chi = {}^4/_3 c g^{-2}(1 - 4\Delta/5c^2)$; $4 - J\chi = 2c^2 g^{-2}/\sqrt{\Delta}$; $5 - J\chi = 8c^2 |g|^{-3} |1 - 2\sqrt{\Delta}/|g||^{2c/|g|-1}$

refined result of Bychkov and Dykhne[13] for this region differs from Eq. (17) only by a numerical factor of the order of unity.

Subject to this stipulation, Eq. (17) describes ρ for $c < \kappa < |g|$. In the case of greater values of κ, the contribution to ρ is made only by impurity triplets proportional to c^3, and so on. We must also mention that the contributions to ρ corresponding to the approach of impurities to distances shorter than or of the order of the lattice constant give an incorrect quantitative description of the discrete problem (4). However, these contributions are proportional to c^2 and higher powers of c, so that refinement of these contributions does not alter the general nature of the dependence $\chi(H)$ given in Fig. 2.

We can see that, in this case, the point of transition in a pure system, $H = J$, is not a singularity and $\chi(H)$ varies continuously at this point. True, the terms $\sim\exp(-c|\Delta|^{-1/2})$, which arise because of expressions such as Eq. (15) and which correspond, as above, to the exponentially small contribution of the impurity-free regions, may give rise to a nonanalyticity of χ at $H = J$; however, the moment $M(H)$ does not become saturated. As in the case of weakly magnetic impurities, the maximum of $\chi(H)$ is shifted to the left. This result is not universally valid: according to Magarill and Éntin,[15] in the case of a weak attraction $g < 0$, $|g| \ll c$, the maximum of χ shifts to the right $(H_m - J) \sim Jc|g|$.

In this case, the most interesting features are the rise and singularity of $\chi(H)$ which occur in accordance with Eq. (17) at the point corresponding to an impurity level $2\kappa = |g|$, which is confirmed by a more rigorous discussion. This feature of χ and the corresponding step-like rise of $M(H)$ can be explained quite simply. Strongly magnetic impurities result in an undersaturation of the magnetic moment and give rise to local moments which are not oriented along the field even if $H > J$. At the point $\Delta = g^2/4$, the energy E of these states vanishes in accordance with Eq. (8). Therefore, in strong fields H the existence of these local moments is not favored by the energy considerations and they disappear. Consequently, the average moment increases by an amount $\sim c$ and this change is discontinuous (to within the concentration broadening). Thus, a characteristic "impurity" phase transition occurs in an external field. Similar phenomena should also occur in three-dimensional systems, but this point will be discussed in a separate paper.

In the next approximations with respect to c we should encounter local levels corresponding to bound states in the fields of impurity pairs, triplets, etc. (in a discrete lattice). This may give rise to singularities in $\chi(H)$ similar to that shown in Fig. 2, but these singularities increase in intensity in proportion to c^2, c^3, etc.[16] The total saturation point of $M(H)$, i.e., the "true" phase transition, corresponds to the coalescence of strongly magnetic impurities into continuous "macrochains," whose probability (for low values of c), is exponentially small, being proportional to $\exp(-1/c)$.

We shall conclude this section by noting that it follows from Eq. (13) that the constant g is independent of the sign of η. In particular, in the case of purely antiferromagnetic impurities, we have $J_{12} = -J$ and $g = 0$, so that in the lowest approximation with respect to c these impurities do not affect the thermodynamics of the system. In this case, the contribution to F is made only by pairs, triplets, and similar configurations if $J_{22} = \tilde{\eta}J \neq J$. In this case, the main results are the same as those given above if c is replaced with the concentration of impurity pairs c^2. Similar considerations apply also to antiferromagnetic impurities in the models considered in Secs. 3 and 4, but this point will not be discussed for lack of space.

3. ISING CHAIN IN A TRANSVERSE FIELD

We shall now consider the case when only the spins σ_l^z interact in the Hamiltonian (1): $J_{zz} = 2J$, $J_{yy} = J_{zy} = 0$ (case a in [17]). If we go over to the Fermi operators,[17] we can replace Eq. (2) with

$$\mathscr{H} = -\frac{1}{2}\sum_l J_{l,l+1}[a_{l+1}a_l + a_l^+ a_{l+1}^+ + a_{l+1}^+ a_l + a_l^+ a_{l+1}] - H\sum_l\left(\frac{1}{2} - a_l^+ a_l\right) \tag{18}$$

We shall now diagonalize the Hamiltonian (18) by the transformation which combines the treatment given in [17] with Eq. (3):

$$a_l = \sum_\lambda (\varphi_{\lambda l} a_\lambda + \chi_{\lambda l}^* a_\lambda^+), \quad a_l^+ = \sum_\lambda (\varphi_{\lambda l}^* a_\lambda^+ + \chi_{\lambda l} a_\lambda), \tag{19}$$

where the number of states λ is, as before, equal to the number of spins N. The functions φ and χ should satisfy the following relationships:

$$\sum_\lambda (\varphi_{\lambda l}\varphi_{\lambda l'}^* + \chi_{\lambda l}^* \chi_{\lambda l'}) = \delta_{ll'}, \quad \sum_\lambda (\varphi_{\lambda l}\chi_{\lambda l'}^* + \varphi_{\lambda l'}\chi_{\lambda l}^*) = 0, \tag{20a}$$

$$\sum_l (\varphi_{\lambda l}^* \varphi_{\nu l} + \chi_{\lambda l}^* \chi_{\nu l}) = \delta_{\lambda\nu}. \tag{20b}$$

The conditions (20a) follow from the commutation relationships for a_l and a_l^+; the condition (20b) follows from the orthogonality requirement, i.e., from the diagonality of the Hamiltonian expressed in the operators a_λ and a_λ^+.

As before, we shall perform the diagonalization operation with the aid of the "equations of motion" for a_l. This gives a system of two equations for the functions $\varphi_{\lambda l}$ and $\chi_{\lambda l}$, which can be written conveniently in the spinor form (the index λ is omitted):

$$(E - H\hat{\sigma}_z)\psi_l + {}^1/_2 J[\eta_{l-1,l}(\hat{\sigma}_z - i\hat{\sigma}_y)\psi_{l-1} + \eta_{l,l+1}(\hat{\sigma}_z + i\hat{\sigma}_y)\psi_{l+1}] = 0. \tag{21}$$

Here, $E = E_\lambda$ are single-particle eigenvalues of the Hamiltonian; $\psi_l = (\varphi_l, \chi_l)$ is a two-component "wave function"; σ_y and σ_z are the second and third Pauli matrices acting on the components of ψ; $\eta_{ll'} = J_{ll'}/J$. For each distribution of impurities Eq. (21) has eigenvalues E of two signs: E_λ with an eigenfunction ψ_λ and $E' = -E_\lambda$ with $\psi_\lambda' = \sigma_x\psi_\lambda$. In order to diagonalize the Hamiltonian (18) it is sufficient to consider, as in [17], only the states with $E_\lambda > 0$ (the selection of $E_\lambda < 0$ corresponds simply to a redefinition of the operators $a_\lambda \rightleftharpoons a_\lambda^+$).

After the substitution of Eqs. (19)–(21) into Eq. (18), the Hamiltonian and the free energy are again given by Eq. (5). In the absence of impurities, it follows from Eqs. (21) and (20) that[17]

$$\begin{gathered}\varphi_{\lambda l}=N^{-1/2}e^{i\lambda l}u_\lambda,\quad \chi_{\lambda l}=N^{-1/2}e^{i\lambda l}v_\lambda,\quad |u_\lambda|^2+|v_\lambda|^2=1,\\ u_\lambda v_{-\lambda}^*+u_{-\lambda}v_\lambda^*=0,\quad E_\lambda=[(J-H)^2+2JH(1-\cos\lambda)]^{1/2},\end{gathered}\tag{22}$$

and after the substitution of E_λ in Eq. (5) we find that the susceptibility at $H \to H_c^{(0)} = J$ has a logarithmic singularity: $\chi \propto \ln|H-J|$.

In general, it is convenient to express Eq. (5) for F in terms of the energy density of states $\rho(E)$:

$$F=-\frac{1}{2}\int E\rho(E)\,dE,\quad \rho(E)=\frac{1}{N}\sum_\lambda \delta(E-E_\lambda).\tag{23}$$

Thus, in this model the problem of calculation of F and χ reduces to the determination of the density of levels of a particle described by Eq. (21) and located in a field of randomly distributed impurities.

As before, we shall assume that the impurity concentration is low and we shall discuss the range near $H=H_c$, i.e., $|J-H| \ll J$. Once again, it is convenient to go over from the discrete equation (21) to the continuous form, having first solved the problem of the scattering on a single impurity in the discrete equation (21). Applying, as in the preceding section, the Fourier transform method, we obtain the following expression instead of Eq. (10):

$$\psi_l=\mathbf{u}(k)e^{ikl}+(1-\eta)\delta_{l0}\psi_0-\frac{1-\eta^2}{\eta}\hat{G}(l)(E_k-H\hat{\sigma}_z)\psi_0.\tag{24}$$

Here, the first term describes an incident plane wave; $\mathbf{u}(k)$ is a normalized spinor, which is the solution of the impurity-free equation (21) with the energy

$$E=E_k=[(J-H)^2+2JH(1-\cos k)]^{1/2};\tag{25}$$

η has the same meaning as in Eq. (9) and $\hat{G}(l)$ is the Green's function of the impurity-free equation (21) for the scattering problem:

$$\begin{aligned}\hat{G}(l)&=\int_{-\pi}^{\pi}\frac{dp}{2\pi}e^{ipl}[E_k+(J\cos p-H)\hat{\sigma}_z-J\sin p\hat{\sigma}_y+i\delta]^{-1}\\ &=-\frac{i}{2JH\sin k}[E_k-(J\cos k-H)\hat{\sigma}_z+J\sin k\hat{\sigma}_y\operatorname{sgn} l)]e^{ik|l|}-\delta_{l0}\frac{1}{2H}(\hat{\sigma}_z-i\hat{\sigma}_y).\end{aligned}\tag{26}$$

If we write the transmitted wave in the form $Au(k)e^{ikl}$ for $l > 0$, we find that Eqs. (24)–(26) subject to the conditions $k \ll 1$, $|J-H| \ll J$ give the amplitude A:

$$A=\frac{2\eta^2}{1+\eta^4-imk^{-1}(1-\eta^4)},\quad m=\frac{J-H}{J}.\tag{27}$$

It should be noted that a comparison of Eq. (27) with the usual quantum-mechanical expression for the amplitude (see, for example, [22]) shows that the case $m(1-\eta^4) > 0$ corresponds to the attraction to an impurity and the presence of bound states, whereas the case $m(1-\eta^4) < 0$ corresponds to the repulsion.

The continuous equation corresponding to Eq. (1) can be found as follows. At points far from an impurity this equation can be obtained from Eq. (21) by an expansion in terms of gradients. The short-range influence of an impurity can be described, by analogy with Eq. (12), applying the boundary condition to ψ at the point where the impurity is located ($x=0$). It follows from the nature of Eq. (21) and from parity considerations [the corresponding transformation is of the form $\psi'(x)=\sigma_z\psi(-x)$] that this boundary condition should be of the form

$$i\hat{\sigma}_y[\psi(+0)-\psi(-0)]=\gamma\hat{\sigma}_z[\psi(+0)+\psi(-0)],\quad \gamma=(1-\eta^2)/(1+\eta^2).\tag{28}$$

The quantity γ in Eq. (28) is selected to give the correct value of the amplitude of the transmitted wave (27).

The condition (28) can be combined with the equation for ψ corresponding to small values of k and the results can be written in a form similar to Eq. (12):

$$(\varepsilon+m\hat{\sigma}_z)\psi+i\hat{\sigma}_y\frac{d\psi}{dx}=2\gamma\hat{\sigma}_z\psi_0\delta(x),\quad \psi_0\equiv\frac{1}{2}[\psi(+0)+\psi(-0)].\tag{29}$$

Equation (28) is obtained from Eq. (29) by integration in the direct vicinity of an impurity. The quantity $\epsilon = E/J$ in Eq. (29) is the dimensionless energy. In the impurity-free case we find that $\psi \propto \exp(ikx)$ and $\epsilon = (m^2+k^2)^{1/2}$ and we can see that the quantity m in Eq. (27) has the properties of mass.

At the low impurity concentrations considered here, each impurity scatters independently. Therefore, the complete equation for the spectrum, analogous to Eq. (14), is of the form

$$\begin{gathered}(\varepsilon+m\hat{\sigma}_z)\psi+i\hat{\sigma}_y\frac{d\psi}{dx}=2\gamma\hat{\sigma}_z\sum_i\psi_i\delta(x-x_i),\\ \psi_i=\tfrac{1}{2}[\psi(x_i+0)+\psi(x_i-0)].\end{gathered}\tag{30}$$

Since the density of the levels corresponding to Eq. (30) has not yet been investigated, we shall first consider the simplest case of nonmagnetic impurities $\eta \ll 1$. Then, in the zeroth approximation a chain can be divided into segments of length l with the Poisson distribution function $c\exp(-cl)$. The boundary conditions for finding the energy in accordance with Eq. (28) are $(\sigma_z + i\sigma_y)\psi = 0$ at the right end and $(\sigma_z - i\sigma_y)\psi = 0$ at the left end. This yields the following equation for the levels ϵ in the continuous spectrum:

$$k/m=\operatorname{tg} kl,\quad k^2=\varepsilon^2-m^2>0.\tag{31}$$

Moreover, if $m > 0$, there are bound states $\epsilon < m$ whose energies are given by

$$\varkappa/m=\operatorname{th}\varkappa l,\quad \varkappa^2=m^2-\varepsilon^2>0.\tag{32}$$

The density of states $\rho(\epsilon)$ can be found from Eqs. (31) and (32) by going over from the Poisson distribution of the lengths $c\exp(-cl)$ to the energy distribution. In this way, the density of states in the continuous ρ_1 and discrete ρ_2 spectra is given by

$$\begin{gathered}\rho_1(\varepsilon)=c\frac{dk}{d\varepsilon}\frac{d}{dk}\left[\frac{1}{2}\exp\left(\frac{c}{k}\operatorname{arctg}\frac{m}{k}\right)\operatorname{sh}^{-1}\frac{c\pi}{2k}\right],\\ \rho_2(\varepsilon)=c\theta(m)\frac{d}{d\varepsilon}\exp\left(-\frac{c}{\varkappa}\operatorname{Arth}\frac{\varkappa}{m}\right),\end{gathered}\tag{33}$$

where $\theta(x)$ is equal to unity for $x > 0$ and to zero for $x < 0$.

We shall now give some asymptotic forms of $\rho(\epsilon)$:

$$c\gg k\gg|m|:\quad \rho_1^+(\varepsilon)=\rho_1^-(\varepsilon)=\frac{\pi c^2}{2k^2}\exp\left(-\frac{c\pi}{2k}\right);\tag{34a}$$

$$k\ll m:\quad \rho_1^+(\varepsilon)\to\frac{2}{3}\frac{c^2}{m^2}\exp\left(-\frac{c}{m}\right)=\rho_2(\varepsilon=m);\tag{34b}$$

$$k\ll|m|:\quad \rho_1^-(\varepsilon)\to\frac{\pi c^2}{4k^3}\operatorname{sh}^{-2}\frac{c\pi}{2k};\tag{34c}$$

$$0<\varepsilon\ll m:\quad \rho_2(\varepsilon)=\frac{c^2}{2m^2}\left(\frac{\varepsilon}{2m}\right)^{c/m-1}.\tag{34d}$$

Here, $\rho_1^+ = \rho_1(m > 0)$ and $\rho_1^- = \rho_1(m < 0)$.

It is clear from the formulas (34) that ρ_1 and ρ_2 have the usual properties of the density of states in the presence of impurities. Thus, Eq. (34c), which corresponds to the nonrelativistic limit of the repulsive interaction, is identical with the results given in [12]. The expression (34a), corresponding to the ultrarelativistic case, has the exponential form usual for $k \ll c$ but with a somewhat modified value of the argument of the exponential function ($\pi/2$ instead of π), which is due to the modified boundary conditions. The formula (34b) shows that in the attraction case the distribution $\rho(\epsilon)$ is continuous at $\epsilon = m$. Finally, it follows from Eq. (34d) that $\rho_2(\epsilon)$, corresponding to $c < m$, has an integrable singularity at the point of location of an impurity level (in the case considered $\eta = 0$ lying at $\epsilon = 0$), which is similar to corresponding singularities in the nonrelativistic problem.[11,13]

The substitution of Eq. (33) into Eq. (23) alters the free energy to

$$F=F_1+F_2=-J\int_0^{k_0}(m^2+k^2)^{1/2}\rho_1(\varepsilon)\frac{d\varepsilon}{dk}dk-J\int_0^m\varepsilon\rho_2(\varepsilon)\,d\varepsilon, \tag{35}$$

where $k_0 \sim 1$. It is clear from Eqs. (33)–(35) that in the case of small values of m and c considered here, the main logarithmic contribution to the susceptibility χ comes from the continuous spectrum:

$$\chi\approx\chi_1=-\frac{\partial^2F_1}{\partial H^2}=\frac{1}{2\pi J}\begin{cases}\ln\left|\dfrac{J}{J-H}\right| & \text{for } |m|=\left|\dfrac{J-H}{J}\right|\gg c, & (36\text{a})\\[2ex] \ln\dfrac{1}{c} & \text{for } \left|\dfrac{J-H}{J}\right|\ll c. & (36\text{b})\end{cases}$$

As expected, Eq. (36a) is identical with the result of Pikin and Tsukernik[17] for the impurity-free case. Furthermore, we can show that $\chi' = \partial\chi/\partial H$ is negative for $m = 0$ and is of the order of $(cJ)^{-1}$, so that the maximum of χ lies in the $m > 0$ range, i.e., $H_m < H_c = J$. Equating $\chi'(H)$ to zero, we find that the maximum of χ is located at $n \sim c$, i.e., $(H_m - H_c) \sim -cJ$, and the order of amplitude is given by $\chi_m \sim \ln(1/c)$. Thus, in contrast to Sec. 2, the shift of the maximum is linear and not quadratic in respect of c. Another difference is the relative smallness of the contribution of the bound states. We can easily see from Eqs. (35) and (34) that this contribution to the susceptibility χ_2 is of the order of $-c^3/m^3$ for $m \gg c$, whereas for $m \ll c$ it is given by

$$\chi_2\sim(c/m)^3\exp(-c/m).$$

We can also show that at the nonanalytic point $m = 0$ the expression (35), like Eq. (15) in Sec. 2, is infinitely differentiable with respect to H.

We shall now consider the general case $\eta \neq 0$. In a comprehensive study of the density of states, it would be necessary to use Eq. (30) and derive an equation for $\rho(\epsilon)$ similar to the equation of Frisch and Lloyd[10] for Eq. (14) and then study the behavior of this equation in the case of small values of k and m, as has been done in [13–15] and in Sec. 2.

We shall confine ourselves to the following comments. The general expression for F is always of the form given by Eq. (35) and the general properties of the density of states ρ remain the same as in Eqs. (33)–(34). Variation of η alters only the position of an impurity level so that, for example, the formula analogous to Eqs. (17) and (34d) becomes

$$\rho_2(\varepsilon)=c\left|\frac{d}{d\varepsilon}\left(\frac{\varkappa-\varkappa_0}{\zeta\varepsilon}\right)^{c/\varkappa}\right|,\quad \zeta=\frac{1-\eta^4}{1+\eta^4},\quad \varkappa_0=m\zeta, \tag{34e}$$

where the dependence $\kappa(\epsilon)$ is given by Eq. (32). In particular, in the case of strongly magnetic impurities with $\eta^2 > 1$, the contribution of the bound states corresponds to $H > J$ and not $H < J$, as in the foregoing discussion. The susceptibility χ is obtained by differentiating Eq. (35) with respect to m. It follows clearly from the form and meaning of Eqs. (30) and (27) that the singularity along the m scale in Eq. (35) or in $\rho(\epsilon, m)$ can only occur at the point $m = 0$. Any other value of m is not physically distinguishable and for each $m \neq 0$ the quantity $\rho(\epsilon, m, c)$ is a smooth function of ϵ and c [with an integrable singularity of ϵ of the Eq. (34e) type at the point of location of an impurity level: this singularity does not give rise to singularities in F and χ]. However, it can easily be shown that even at $m = 0$ the density of states $\rho(\epsilon)$ corresponding to Eq. (30) is also a smooth function which falls at small values of k, like Eq. (34a). In fact, if $k \ll c$, a particle experiences, in the first approximation, the average potential of the right-hand side of Eq. (30), which gives a term with $\sim\gamma c\sigma_z$ instead of the term containing the mass. Therefore, the states with small values of $\epsilon = k \ll c\gamma$ can only appear in impurity-free regions of length $l \gtrsim 1/k \gg 1/c$ and averaging over the Poisson distribution of these regions should give a result of the Eq. (34a) type (with a possible substitution $c \to c\gamma$). It therefore follows from Eqs. (30) and (35) that F(H) and χ(H) are infinitely differentiable with respect to H at the point $H = J$; in the case of weakly magnetic impurities, this point is also the transition point.

4. TWO-DIMENSIONAL ISING MODEL

We shall now consider a square Ising lattice with substitutional impurities. The constants of the interaction of neighboring spins of different kinds will still be denoted by $J_{11} = J$, J_{12}, and J_{22}. Well-known methods [20,21,6] can be used to reduce the partition function to the form

$$Z=2^N(\operatorname{ch}\beta J_{11})^{N_{11}}(\operatorname{ch}\beta J_{12})^{2N_{12}}(\operatorname{ch}\beta J_{22})^{N_{22}}\left[\prod_i(1-x\lambda_i)\right]^{1/2}. \tag{37}$$

Here, N is the total number of sites; $N_{kl} = 2Nc_kc_l$ is the total number of bonds of type J_{kl} ($c_k = N_k/N$ is the concentration of spins of type k); $x = \operatorname{th}\beta J$; λ_i are the eigenvalues of the transition matrix $\hat{\Lambda}(\mathbf{r}, \mathbf{r}') = \eta(\mathbf{r}, \mathbf{r}')\hat{\Lambda}_0(\mathbf{r}, \mathbf{r}')$, where $\hat{\Lambda}_0$ is the transition matrix for the impurity-free case;[20,21] the quantity $\eta(\mathbf{r}, \mathbf{r}') = \operatorname{th}\beta J(\mathbf{r}, \mathbf{r}')/\operatorname{th}\beta J$ represents the change in the interaction because of the presence of impurities; and $\mathbf{r}$ are the coordinates of the lattice sites.

The equations which define the eigenvalues λ_i can be found by introducing, as in the book of Landau and Lifshitz,[20] the random walk amplitudes $W_\alpha(\mathbf{r})$ ($\alpha = 1, 2, 3, 4$). Instead of $W_\alpha(\mathbf{r})$, we can conveniently use a four-component function $\boldsymbol{\psi}(\mathbf{r})$ related to W_α by

$$\psi_{1,3}=W_1-W_3\mp i(W_2-W_4),\qquad \psi_{2,4}=-W_1-W_3\mp(W_2+W_4),$$
$$\psi=\begin{pmatrix}\varphi\\ \chi\end{pmatrix},\quad \varphi_1=\psi_1,\quad \varphi_2=\psi_2\quad \chi_1=\psi_3,\quad \chi_2=\psi_4. \tag{38}$$

Then, the equations for $\boldsymbol{\psi}$ and λ_i, similar to Eq. (141.8) in [20], can be written in the form

$$\begin{aligned}\lambda(-1+\sqrt{2}\hat{s}_z)\psi(\mathbf{r})={}&{}^1/_4[\eta_{\mathbf{r},\,\mathbf{r}+\mathbf{a}_1}(1+\hat{\sigma}_x)(1+\hat{s}_x)\psi(\mathbf{r}+\mathbf{a}_1)\\ &+\eta_{\mathbf{r},\,\mathbf{r}-\mathbf{a}_1}(1-\hat{\sigma}_x)(1+\hat{s}_x)\psi(\mathbf{r}-\mathbf{a}_1)\\ &+\eta_{\mathbf{r},\,\mathbf{r}+\mathbf{a}_2}(1+\hat{\sigma}_y)(1-\hat{s}_x)\psi(\mathbf{r}+\mathbf{a}_2)+\eta_{\mathbf{r},\,\mathbf{r}-\mathbf{a}_2}(1-\hat{\sigma}_y)(1-\hat{s}_x)\psi(\mathbf{r}-\mathbf{a}_2)].\end{aligned} \tag{39}$$

Here, $\mathbf{r} \pm \mathbf{a}_1$ are the coordinates of the nearest cells to the right and left of $\mathbf{r}$; $\mathbf{r} \pm \mathbf{a}_2$ are the corresponding coordinates of the nearest upper and lower cells ($|\mathbf{a}_1| = |\mathbf{a}_2| = 1$). The four-row matrices acting on ψ are direct products of the two-row Pauli matrices $\hat{\mathbf{s}}$ and $\hat{\sigma}$, where $\hat{\mathbf{s}}$ acts on a column composed of φ and χ, whereas $\hat{\sigma}$ acts on a column composed of the components of φ or of the components of χ.

The roots λ_i of Eq. (39) are generally complex quantities but since the partition function (37) is real, it follows that for each $\lambda = \lambda_i$ there is a conjugate $\lambda = \lambda_i^*$. This also follows from Eq. (39). If we examine the equation which is the complex conjugate of Eq. (39), we find that the function $\psi' = \sigma_x\psi^*$ is the solution of Eq. (39) corresponding to the eigenvalue $\lambda' = \lambda^*$.

In regions free of impurities all the components ψ_α can be expressed in terms of any one component and then Eq. (39) becomes

$$4\psi(\mathbf{r})-\psi(\mathbf{r}+\mathbf{a}_1)-\psi(\mathbf{r}-\mathbf{a}_1)-\psi(\mathbf{r}+\mathbf{a}_2)-\psi(\mathbf{r}-\mathbf{a}_2)=2\varepsilon\psi(\mathbf{r}), \tag{40a}$$

$$\varepsilon=-\frac{(\lambda^2-2\lambda-1)^2}{2\lambda(\lambda^2-1)}=-\frac{(\lambda-\lambda_0)^2(\lambda+1/\lambda_0)^2}{2\lambda(\lambda^2-1)}, \tag{40b}$$

where $\lambda_0 = 1 + \sqrt{2}$.

In the absence of impurities the expressions (40) are valid throughout all space. Then, the Fourier transformation of Eq. (40a) with respect to $\mathbf{r}$ gives $\epsilon = 2 - \cos k_x - \cos k_y$ and the substitution of this expression in Eq. (40b) yields four branches $\lambda_\nu(\epsilon)$ for the impurity-free case.

As before, we shall confine ourselves to low impurity concentrations $c_2 = c \ll 1$ and to the vicinity of the transition point of a pure system T_c defined by (see [20]) $\lambda_0 x_0 = \lambda_0 \operatorname{th} J/T_c = 1$. It is clear from Eq. (37) that a singular contribution to F and C(T) now comes from the values of λ close to λ_0, i.e., from small values of ϵ in Eq. (40b). According to Eq. (40a), this corresponds to the functions ψ which vary slowly in the space between the impurities so that in these impurity-free regions Eq. (40a) can be expanded, as before, in terms of gradients. Then, the left-hand side of Eq. (40a) is replaced with $-\Delta\psi$ and once again we go over from the discrete to the continuous problem of the eigenvalues of ϵ in which the impurities that govern the difference between $\eta(\mathbf{r}, \mathbf{r}')$ and unity in Eq. (39) act as isolated scatterers.

The continuous equation corresponding to Eq. (39) can be obtained by solving (as in Secs. 2 and 3) the problem of the scattering of a plane wave by an isolated impurity in a discrete lattice. In accordance with the above discussion, we shall confine ourselves to values of λ close to $\lambda_0 = 1 + \sqrt{2}$. It follows from Eq. (39) that in the corresponding function ψ we have $\chi \ll \varphi$ for the impurity-free regions so that it is convenient to use a two-component equation for φ. Solving the scattering problem for a single impurity by applying, as before, the Fourier transform method and the Green's functions, we find that the wave function in the $r \gg 1$, $k = (2\epsilon)^{1/2} \ll 1$ region is

$$\varphi(\mathbf{r})=\frac{1}{k\sqrt{2}}\begin{pmatrix} k \\ k_+ \end{pmatrix}e^{i\mathbf{kr}}-\frac{g/4}{1+{}^1\!/_2 g(1+\sqrt{2}/\pi)}\begin{pmatrix} kH_0^{(1)}(kr)+in_-k_+H_1^{(1)}(kr) \\ k_+H_0^{(1)}(kr)+in_+kH_1^{(1)}(kr) \end{pmatrix}. \tag{41}$$

Here, $\mathbf{r} = (x, y)$ is the two-dimensional radius vector; $g = (1-\eta^2)/\eta^2$; $k_+ = k_x + ik_y$; $n_\pm = (x \pm iy)/r$; $H_n^{(1)}$ is a Hankel function of the first kind.

The continuous equation for φ can be obtained from Eq. (39) by the usual expansion in terms of gradients and by introducing the potential $V(\mathbf{r})$, which gives the result (41) for a single impurity subject to $r \gg 1$ and $k \ll 1$. It is then clear from Eqs. (39) and (40b) that this "potential" should be purely imaginary, which corresponds to a fall of the wave function in the region of the potential:

$$[-i\hat{\sigma}\nabla+k-iV(\mathbf{r})]\varphi(\mathbf{r})=0. \tag{42}$$

The potential $V(\mathbf{r})$ can be selected in the form of, say, a centrally symmetric barrier of radius a and height V_0. The identity with Eq. (41) subject to $k \ll |V_0|$ gives one condition for the two constants a and V_0. For the sake of simplicity we may assume that the barrier is impermeable: $V_0 \to \pm\infty$. This gives the minimum value of the radius a for a given amplitude (41):

$$a \operatorname{sgn} V_0=\frac{1}{\pi\sqrt{2}}\,\frac{g}{1+{}^1\!/_2 g(1+\sqrt{2}/\pi)}, \qquad g=\frac{1-\eta^2}{\eta^2}. \tag{43}$$

Thus, in the case of nonmagnetic impurities $\eta = 0$, $g = \infty$, and the radius is $a = 0.31$.

The presence of such a barrier can be formulated also as the boundary condition applicable to φ at $r = a$. Assuming, in accordance with Eq. (42), that both components of $\varphi = (\varphi_1, \varphi_2)$ are continuous at $r = a$ and postulating that $V_0 \to \pm\infty$, we obtain the following expression for $\varphi(\mathbf{r})$ in the limit $r \to a + 0$:

$$[n_+\varphi_1(\mathbf{r})+\varphi_2(\mathbf{r})\operatorname{sgn} V_0]_{r=a+0}=0, \tag{44}$$

where n_+ and a have the same meaning as in Eqs. (41) and (43).

The most important qualitative difference between Eq. (42) and Eqs. (12) and (29) considered earlier is the complex nature of the potential, i.e., the non-Hermitian nature of the effective Hamiltonian $\mathscr{H}$; it follows that the eigenvalues of k are imaginary. Moreover, it is clear from Eq. (43) that the sign of V_0, which is identical with the sign of $1-\eta^2$, governs the sign of the scattering length, which is the coefficient of the second term of Eq. (41) divided by k. Therefore, in the nonrelativistic case the transition from weakly magnetic impurities $\eta^2 < 1$ to strongly magnetic impurities $\eta^2 > 1$ should correspond, as in Secs. 2 and 3, to the transition from repulsion to attraction. However, in the case of the imaginary potential in the "ultrarelativistic" equation (42) the interpretation is more complex: in the range of action of V the function φ falls for both signs of V and this basically corresponds to repulsion.

For the same reasons we find that, in contrast to the results in Secs. 2 and 3, there are no bound impurity states with real and negative values $\epsilon = k^2/2 < 0$. In fact, Eq. (41) for the scattering length does not have poles [in contrast to, for example, Eq. (27)] which might be associated with bound states.[22] This can also be demonstrated with the aid of Eqs. (42) and (44). True, all these expressions are valid only for small values of $k^2 = 2\epsilon$. However, if we increase η^2 smoothly from unity to large values, we find that as $-g$ rises a level (pole) appears first and has a low binding energy $-\epsilon \to 0$ and only if η^2 is increased still further can this level deepen to $-\epsilon \gtrsim 1$, whereas Eqs. (43) and (41) do not have a pole even for $\eta \to \infty$ and $g \to -1$.

The complete equation for the calculation of ϵ, similar to Eqs. (14) and (30), is obtained from Eq. (42) by the summation of the potentials of all impurities:

$$(-i\sigma\nabla+k)\varphi(\mathbf{r})=i\sum_l V(\mathbf{r}-\mathbf{r}_l)\varphi(\mathbf{r}), \qquad k^2=2\varepsilon. \tag{45}$$

In this case, the potentials V in the range $|k|a \ll 1$ of interest to us are indeed governed by the scattering length (43) or by the boundary condition (44). The values of $\lambda(k)$ are found from Eq. (40b) by expansion in ϵ up to linear terms inclusive. It is clear from Eq. (40b) that the solutions of this equation are $\lambda_1 = \lambda(k)$ and $\lambda_2 = \lambda(-k)$. Moreover, as mentioned earlier, there are also solutions $\lambda_3 = \lambda_1^*$ and $\lambda_4 = \lambda_2^*$. The substitution of these values of λ into Eq. (37) yields the following expression for F_c which represents the contribution of small values of k and $\lambda - \lambda_0$ to the free energy:

$$-\beta F_c = \frac{1}{4}\sum_i \ln|(1-x\lambda_{1i})(1-x\lambda_{2i})|^2$$

$$= \frac{1}{4}\int_0^{E_0}\int_{-\pi}^{\pi} \ln\{[(1-x\lambda_0)^2+\nu Ex(1-x)\cos 2\alpha]^2 \tag{46}$$

$$+2\nu^2 Ex^3(\sqrt{2}-\lambda_0 x)\sin^2 2\alpha\}\rho(E,\alpha)\,dE\,d\alpha,$$

$$E=|\varepsilon|=|k|^2/2; \quad \alpha=\arg k; \quad \nu=\lambda_0^2\cdot 2^{-3/2}; \quad E_0\sim 1.$$

Here, $\rho(E, \alpha)$ is the density of states deduced from Eq. (45):

$$\rho(E,\alpha) = \frac{1}{N}\sum_i \delta(E-E_i)\delta(\alpha-\alpha_i). \tag{47}$$

Thus, once again the problem of the determination of the singular part of F reduces to the problem of finding the density of the levels of a particle in a field of impurities.

The exact solution of this problem is not available. Therefore, we shall confine ourselves to a quantitative discussion similar to that given by I. M. Lifshits[11] for the three-dimensional case and we shall assume, as before, that the impurity concentration is low: $c \ll a^{-2}$. We shall first consider the range of the lowest energies $E \ll c$. It follows from Eqs. (41)–(45) that, in accordance with the above discussion, in the present case the impurities have the same influence on the spectrum as the repulsive impurities in the nonrelativistic problem. In fact, in the case of states with the minimum energy and, consequently, minimum momentum the condition (44) leads to the following behavior of the wave function in the vicinity of the point located by an impurity ($r \gtrsim a$):

$$\begin{aligned} \varphi_1(\mathbf{r}) &= \text{const}[J_0(kr)+{}^1\!/_2 i\pi ka N_0(kr)], \\ \varphi_2(\mathbf{r}) &= -in_+\,\text{const}[J_1(kr)+{}^1\!/_2 i\pi ka N_1(kr)], \end{aligned} \tag{48}$$

where J_n and N_n are the Bessel and Neumann functions.

If another impurity is located at a distance $l \ll 1/|k|$ from the one being considered, we can use the expansions of $J_n(x)$ and $N_n(x)$ at low values of x to show that the condition (44) is not satisfied in the vicinity of the second impurity. Therefore, one or several waves can be fitted between these impurities, $|k| \gtrsim 1/l$ so that small values $|k| \ll c^{1/2} \sim 1/\bar{l}$ may be encountered only in impurity-free regions of size $l \gtrsim 1/|k|$ and it follows from the Poisson distribution that the probability of the appearance of such regions is exponentially small.

We shall estimate quantitatively the minimum value of $k(l)$ by applying the method of I. M. Lifshits.[11] We shall consider a circular region of radius $R \gg \bar{l} \sim c^{-1/2}$, which is free of impurities. Solving Eq. (42) subject to the condition (44) at the boundary of this region, we obtain the following relationship for the determination of the required values of k

$$J_{n+1}(kR) + iJ_n(kR)\,\mathrm{sgn}\,V_0 = 0. \tag{49}$$

If $V_0 > 0$ the solutions of Eq. (49) with the minimum modulus of k corresponding to $n=-1$ and $n=0$ are $k_1R \approx 2.9 - i1.3$ and $k_2R = -2.9 - i1.3$. Moreover, as mentioned earlier, there are roots $k_2 = k_1^*$ and $k_4 = k_2^*$ and the corresponding equation is derived from Eq. (49) by the substitution $k \to -k$.

The density of states can be found from Eq. (47) by averaging over the Poisson distribution. In the case of large values of $E \gg c$, the function $\rho(E, \alpha)$ should have the value $(1/2\pi)\delta(\alpha)$ corresponding to the impurity-free case. Therefore, it is natural to expect that in the range $c \ll a^{-2}$ considered here, the function $\rho(E, \alpha)$ for all the values $E \ll 1$ can be represented in the form $\rho = \rho(E/c, \alpha)$ with the following asymptotes:

$$\begin{gathered} E \ll c: \qquad \rho(E,\alpha) \\ \propto \exp(-Ac/E)\,\delta(\alpha-\alpha_0), \\ A \approx 16, \quad \mathrm{tg}\,\alpha_0 \approx 0{,}46; \end{gathered} \tag{50a}$$

$$E \gg c, \quad \rho(E,\alpha) \to \delta(\alpha)/2\pi. \tag{50b}$$

It follows from Eq. (50) that in both limiting cases $E \ll c$ and $E \gg c$ the angle α_0 is determined unambiguously by the value of E: $\alpha_0 = \alpha_0(E/c)$. It is possible that this property of $\rho(E, \alpha)$ is also retained at intermediate values of E. However, this can be proved only by a separate investigation and it is irrelevant to the estimates given below.

We shall now consider the dependence of the free energy (46) and the corresponding specific heat C on the temperature T and the impurity concentration c. Applying Eqs. (46) and (50), we obtain the specific heat (with logarithmic precision):

$$\begin{gathered} \tau = \left|\frac{T-T_c}{T_c}\right| \gg c^{1/2}: \quad C = \frac{8}{\pi}\left(\frac{J}{T_c}\right)^2 \ln\frac{1}{\tau} = 0.49\ln\frac{1}{\tau}; \\ \tau \ll c^{1/2}: \quad C = 0.49\ln c^{-1/2}, \end{gathered} \tag{51}$$

where T_c is the transition point of a pure system (for weakly magnetic impurities this point is identical with the transition point of a mixture). Next, calculating with the same precision the derivative $C'(T)$ at $T = T_c$, we find that

$$JC'(T_c) = -0.013\ln(1/c) < 0,$$

so that the specific heat maximum C_m shifts in the direction of lower temperatures: $T_m < T_c$. Finally, equating $C'(T)$ to zero, we can find the temperature T_m: $(T_c - T_m) \sim 0.1 T_c c \ln(1/c)$.

The general nature of the dependence of C on T is plotted in Fig. 3. It follows from Eqs. (46) and (50a) that all the derivatives of the specific heat with respect to T are finite at $T = T_c$.

5. DIMENSIONAL ANALYSIS OF THE DEPENDENCE OF SPECIFIC HEAT AND SUSCEPTIBILITY MAXIMA ON IMPURITY CONCENTRATION

The results obtained in the preceding section for weakly magnetic impurities have a simple physical meaning. The correlation radius r_c in the impurity-free two-dimensional Ising model increases on approach to T_c as $1/\tau$ (see, for example, [23]). If r_c is less than the average distance between the impurities, $\bar{r} \propto c^{-1/2}$, i.e., if $\tau > c^{1/2}$, the influence of impurities is weak and the specific heat varies mainly as $\ln 1/\tau$. If $r_c > \bar{r}$ ($\tau < c^{1/2}$) the correlation radius is $\bar{r}$ and the singularity of τ is cut off at $\tau \sim c^{1/2}$.

This reasoning can also be used in estimating the influence of impurities on the magnetic susceptibility χ.

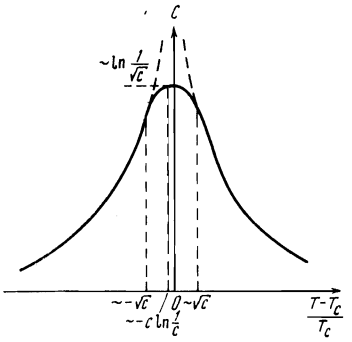

FIG. 3

In the case of an impurity-free two-dimensional Ising lattice, the susceptibility rises as $\chi \propto \tau^{-7/4}$ at $T \to T_c$.[23] Clearly, if $\tau \gg c^{1/2}$, this result also applies in the presence of impurities. If we make the natural assumption that for $\tau \to 0$ the susceptibility χ is a power law of c and if we match χ at $\tau \sim c^{1/2}$, we obtain for $\tau \ll c^{1/2}$:

$$\chi \propto c^{-7/8}.$$

The same approach can be used in the three-dimensional Ising model for which $r_c \propto \tau^{-\mu}$, $\mu \approx 0.64$,[23] and $\bar{r} \propto c^{-1/3}$. In the range $\tau \gg c^{1/\sigma}$ $(\sigma = 3\mu)$ the influence of impurities should be unimportant and we obtain $C \propto \tau^{-\alpha}$ and $\chi \propto \tau^{-\gamma}$.[23]

Assuming, as before, a power-law dependence of C and χ on the concentration for $\tau \to 0$, we find from the matching condition in the intermediate region $\tau \sim c^{1/\sigma}$ that, in the case of $\tau \ll c^{1/\sigma}$:

$$C \propto c^{-\alpha/\sigma}, \qquad \chi \propto c^{-\gamma/\sigma}.$$

For example, if we assume that $\alpha \approx 1/8$, $\gamma \approx 5/4$, $\mu \approx 5/8$,[23] we find that

$$C \propto c^{-1/15}, \qquad \chi \propto c^{-2/3}.$$

The same estimates can be obtained by a somewhat different method. By analogy with the similarity theory in the impurity-free case,[23] we may expect the free energy in the Ising model with impurities in the absence of a magnetic field to be described by expressions of the type

$$F \propto \tau^{\sigma} f(c/\tau^{\sigma}). \tag{52}$$

Here, $\sigma = \mu d$, d is the spatial dimension, μ is the critical index in r_c $(r_c \propto \tau^{-\mu})$, and f(x) can be expanded in terms of x (or c) in the range $x \ll 1$. If $x \gg 1$ $(\tau \to 0)$ it follows from the finite nature of F and of its derivatives that f(x) is of the form

$$f(x) = x[a_0 + a_1 x^{-1/\sigma} + a_2 x^{-2/\sigma} + \ldots + a_s x^{-s/\sigma} + \ldots], \qquad x \gg 1. \tag{53}$$

Using Eqs. (52) and (53), we can easily show that the specific heat is $C \propto \tau^{\sigma-2}$ in the range $c \ll \tau^{\sigma}$ and $C \propto c^{1-2/\sigma}$ in the range $c \gg \tau^{\sigma}$, which is in agreement with the earlier estimates if we use one of the similarity relationships $\mu d = 2 - \alpha$.[23] The susceptibility χ and the dependences of C and χ on the magnetic field can be analyzed in a similar manner.

In order to avoid misunderstanding, we must stress that these considerations are applicable only to pinned nonequilibrium impurities. No new indices are introduced in the similarity theory because there is no correlation between impurities and $\bar{r}$ is a single-valued function of c and independent of T.

6. CONCLUSIONS

The models discussed above demonstrate that the presence of pinned impurities influences a phase transition in the following way. First of all, such impurities result in a completely "diffuse" transition: all the derivatives of free energy F become finite. Consequently, the specific heat and susceptibility maxima are smooth, whereas in the case of mobile impurities, these quantities have a kink with an infinite derivative at the point $T = T_c$.[4,5] Secondly, the maximum of the specific heat C does not coincide with T_c. In all the models considered the maximum for systems with low impurity concentrations c is shifted in the direction of lower temperatures $T < T_c$ (or lower fields $H < H_c$ in the case of susceptibility discussed in Secs. 2 and 3), irrespective of the nature of the impurities. The shift of the maximum, $T_c = T_m$, increases with the impurity concentration and the maximum value of C decreases. Thirdly, the nonanalytic point in the dependence of F on T coincides with T_c of a pure system and it corresponds to the contribution of exponentially rare impurity-free regions; there are no other singularities near T_c in the case of low values of c. It is natural to assume that, in the case of weakly magnetic impurities, this point coincides with the point of appearance of the spontaneous moment, i.e., it is also the transition point of a system with impurities. In the case of strongly magnetic impurities, the spontaneous moment M should appear at higher values of T as a result of accumulation of impurities (due to fluctuations) into more or less dense regions, although at low values of c the probability of such accumulation and its contribution to F and M should be extremely small, so that they should not affect the lowest approximation with respect to c.

In view of this, it is interesting to consider Griffiths's ideas[8] on the possibility of the existence of two phase transition points in systems with nonmagnetic impurities. His main argument is that at sufficiently high impurity concentrations $c \sim 1$ we may expect phase transitions as such a system is very likely to split into noninteracting regions separated by nonmagnetic impurities. In view of this, Griffiths suggests that the point of appearance of the magnetic moment $T_c(c)$ decreases smoothly with increasing c (dashed curve in Fig. 4), vanishing at some value $c = c_0$. On the other hand, in agreement with Mikulinskiĭ[6] and our results, he points out that the point T_c corresponding to $c = 0$ is a singularity of the free energy and hence he concludes that two transition points are possible.

Extrapolation of the results obtained above, particularly those for nonmagnetic impurities, to higher values of c is outside the scope of the present paper. Clearly, when impurity-impurity distances become of the order of the lattice constant, the assumptions used above (particularly those in the case of nonmagnetic impurities) become invalid. However, in the range of small values of c there is no physical mechanism which could alter basically the results obtained and give rise to a second singularity of F. Consequently, it seems more likely that the dependence of T_c on c does not have the smooth nature predicted by Griffiths but at low values of c the value of T_c does not vary with c and begins to fall only in the range $c \geq c_1$, following curve 1 or curve 2 in Fig. 4, which would correspond to a transition of the first or second (or higher) kind with respect to the im-

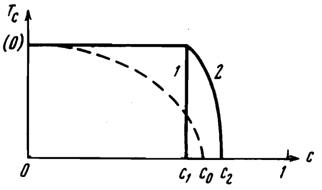

FIG. 4

purity concentration. It would be interesting to apply the method developed above to the calculation of the spontaneous magnetic moment to check and refine these ideas.

The authors are deeply grateful to A. I. Larkin and M. A. Mikulinskiĭ for their interest and valuable comments.

---

[1] V. A. Isupov, Zh. Tekh. Fiz. **26**, 1912 (1956) [Sov. Phys.-Tech. Phys. 1, 1846 (1957); Fiz. Tverd. Tela **5**, 187 (1963) [Sov. Phys.-Solid State **5**, 136 (1963)]; Dissertatsiya (Dissertation), Institute of Semiconductors, Academy of Sciences of the USSR, Leningrad, 1971.

[2] A. V. Voronel', S. R. Garber, and V. M. Mamnitskiĭ, Zh. Eksp. Teor. Fiz. **55**, 2017 (1968) [Sov. Phys.-JETP **28**, 1065 (1969)].

[3] S. Arajs, Phys. Status Solidi **11**, 121 (1965).

[4] I. Syozi, Progr. Theor. Phys. **34**, 189 (1965).

[5] A. A. Lushnikov, Zh. Eksp. Teor. Fiz. **56**, 215 (1969) [Sov. Phys.-JETP **29**, 120 (1969)]; E. A. Shapoval, ZhETF Pis. Red. **8**, 36 (1968) [JETP Lett. **8**, 20 (1968)].

[6] M. A. Mikulinskiĭ, Zh. Eksp. Teor. Fiz. **53**, 1071 (1967) [Sov. Phys.-JETP **26**, 637 (1968)].

[7] V. M. McCoy and T. T. Wu, Phys. Rev. **176**, 631 (1968); **188**, 785 (1969).

[8] R. B. Griffiths, Phys. Rev. Lett. **23**, 17 (1969).

[9] M. A. Mikulinskiĭ, Zh. Eksp. Teor. Fiz. **55**, 2376 (1968) [Sov. Phys.-JETP **28**, 1261 (1969)].

[10] H. L. Frisch and S. P. Lloyd, Phys. Rev. **120**, 1175 (1960).

[11] I. M. Lifshitz, Usp. Fiz. Nauk **83**, 617 (1964) [Sov. Phys.-Usp. **7**, 549 (1965)].

[12] Yu. A. Bychkov and A. M. Dykhne, ZhETF Pis. Red. **3**, 313 (1966) [JETP Lett. **3**, 202 (1966)].

[13] Yu. A. Bychkov and A. M. Dykhne, Zh. Eksp. Teor. Fiz. **51**, 1923 (1966) [Sov. Phys.-JETP **24**, 1290 (1967)].

[14] G. M. Zaslavskiĭ and V. L. Pokrovskiĭ, Zh. Eksp. Teor. Fiz. **51**, 449 (1966) [Sov. Phys.-JETP **24**, 303 (1967)].

[15] L. I. Magarill and M. V. Éntin, Zh. Eksp. Teor. Fiz. **51**, 1852 (1966) [Sov. Phys.-JETP **24**, 1248 (1967)].

[16] A. A. Maradudin, E. W. Montroll, and G. H. Weiss, Theory of Lattice Dynamics in the Harmonic Approximation, Suppl. 3 to Solid State Phys., Academic Press, New York (1963) (Russ. Transl., Mir, M., 1965).

[17] S. A. Pikin and V. M. Tsukernik, Zh. Eksp. Teor. Fiz. **50**, 1377 (1966) [Sov. Phys.-JETP **23**, 914 (1966)].

[18] B. Sutherland, Phys. Rev. Lett. **19**, 103 (1967).

[19] E. Barouch and B. M. McCoy, Phys. Rev. A **3**, 786 (1971).

[20] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika, Fizmatgiz, M., 1964 (Statistical Physics, 2nd ed., Pergamon Press, Oxford, 1969), Sec. 141.

[21] G. V. Ryazanov, Zh. Eksp. Teor. Fiz. **54**, 1010 (1968) [Sov. Phys.-JETP **27**, 538 (1968)].

[22] L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika, Fizmatgiz, M., 1963 (Quantum Mechanics: Non-Relativistic Theory, 2nd ed., Pergamon Press, Oxford, 1965), Sec. 128.

[23] V. L. Pokrovskiĭ, Usp. Fiz. Nauk **94**, 127 (1968) [Sov. Phys.-Usp. **11**, 66 (1968)].

Translated by A. Tybulewicz
167