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ON PHASE TRANSITIONS OF SECOND ORDER

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It is shown that, subject to certain relations between the parameters, the singularities in the thermodynamic quantities at a second-order transition point in a binary alloy, at which there is a change in the crystal symmetry, are of the same type as in the Ising model, for which a number of results are known from computer calculations. Arguments are presented to show that subsequent terms do not alter these results. A phase transition in a Bose gas is found to be equivalent to a transition in a lattice of plane dipoles.

1. INTRODUCTION

THE thermodynamic theory of phase transitions of second order[1] is based on the possibility of expanding the thermodynamic potential near the transition point $T = T_c$ in a series of powers of $T - T_c$ and of the ordering parameter η. However, as pointed out in[1,2], it is not clear whether such an expansion is possible, and there is every reason to expect that the thermodynamic potential may, as a function of temperature, have a singularity at $T = T_c$. Such a singularity occurs, for example, at the phase transition in an Ising lattice; for the two-dimensional lattice this is known from Onsager's analytic solution[1,3], and in the three-dimensional case this is suggested by computer calculations.[4] In some real systems such a singularity seems to be observed experimentally.[5]

In the present paper second-order phase transitions in binary alloys with changes of crystal symmetry, and in a Bose gas, are studied statistically. Under certain assumptions about the interaction constants it is shown that the singular parts of the thermodynamic quantities are of the same form as in the Ising model or its generalizations. These models can easily be investigated on a computer. Thus a number of results are already available for the three-dimensional Ising lattice,[4] and they may be compared with the behavior of the observed macroscopic quantities near the transition point. Finally we shall discuss what further computer calculations would be desirable to check the validity of the approximations made and for comparison with experiment.

2. TRANSITIONS WITH CHANGE OF CRYSTAL SYMMETRY

Consider second-order phase transitions in which a change in symmetry is caused by the displacement of one of the atoms of the unit cell from a symmetry point to a position of lower symmetry. We assume, for simplicity, that the potential energy of such an atom can be expressed as a sum of the average periodic potential $U(\mathbf{r}_s)$ due to the other atoms, and the interaction potential $V(\mathbf{r}_s - \mathbf{r}_{s'})$ of the given atom with similar atoms in other cells. Consider first the case in which $U(\mathbf{r}_s)$ has two equal minima at two points placed symmetrically with respect to the centre of the cell, at a distance $\pm\mathbf{b}$ from it. At high temperatures, $T \gg V$, when the interaction V is negligible, the atom in each cell will then be with equal probability near either of these minima, and the crystal will be symmetric about the cell center. At low temperatures, $T \ll V$, the interaction V causes an ordering so that all atoms are either near the "right" or near the "left" site. This is a state of lower symmetry. The change in symmetry, i.e., the appearance of a non-zero mean displacement, occurs at some $T_c \sim V$.

For the discussion of the singularities of the thermodynamic quantities at the transition point we consider the partition function of the system

$$Z = \int \prod_s d\mathbf{p}_s \exp\left(-\frac{p_s^2}{2mT}\right) \prod_s d\mathbf{r}_s \exp\left[-\frac{1}{T}\left(\sum_s U(\mathbf{r}_s) + \sum_{ss'} V(\mathbf{r}_s - \mathbf{r}_{s'})\right)\right]. \quad (1)$$

The potential $V(\mathbf{r}_s - \mathbf{r}_{s'})$ decreases rapidly with distance and we take into account only the interactions of atoms in adjacent cells. In addition, we assume that $V \ll U$, and hence near the transition point $T \ll U$.

We may then evaluate the integral (1) by means of the saddle point method, and expand the exponent near the minima of $U(\mathbf{r}_s)$ at the positions

$$\mathbf{r}_{0s} = \sum_{\alpha=1}^{3} s_\alpha \mathbf{a}_\alpha \pm \mathbf{b},$$

where the $\mathbf{a}_\alpha$ are the basic lattice vectors, and the integers s_α indicate the location of the center of the cell. Let

$$\mathbf{r}_s = \mathbf{r}_{0s} + \boldsymbol{\xi}_s. \qquad (2)$$

To the leading order in T/U we may expand $U(\mathbf{r}_s)$ in the exponent of (1) to second order in $\boldsymbol{\xi}_s$, and neglect the dependence of $V(\mathbf{r}_s - \mathbf{r}_{s'})$ on $\boldsymbol{\xi}_s$:

$$\sum_s U(\mathbf{r}_s) + \sum_{ss'} V(\mathbf{r}_s - \mathbf{r}_{s'}) = \sum_s \Big[U(\mathbf{r}_{0s}) + \sum_{\mu,\nu=1}^{3} {}^1\!/_2 U_{\mu\nu} \xi_s{}^\mu \xi_s{}^\nu\Big]$$

$$+ \sum_{ss'} V(\mathbf{r}_{0s} - \mathbf{r}_{0s'}), \quad U_{\mu\nu} = \partial^2 U(\mathbf{r}_0) / \partial x_\mu \partial x_\nu. \qquad (3)$$

The two possible positions of the atom $\mathbf{r}_{0s}$ can conveniently be expressed with the help of an operator $\sigma_\mathbf{r}$ such that the values $\sigma_\mathbf{r} = \pm 1$ correspond to displacements $\pm\mathbf{b}$ in the cell at $\mathbf{r}$:

$$\mathbf{r}_{0s} = \sum_\alpha s_\alpha \mathbf{a}_\alpha + \mathbf{b}\sigma_\mathbf{r} \equiv \mathbf{r} + \mathbf{b}\sigma_\mathbf{r}. \qquad (4)$$

Then the last term of (3) becomes, apart from an additive constant,

$$\sum_{\mathbf{r},\alpha} J_\alpha \sigma_\mathbf{r} \sigma_{\mathbf{r}+\mathbf{a}_\alpha},$$

$$J_\alpha = {}^1\!/_4 [2V(\mathbf{a}_\alpha) - V(\mathbf{a}_\alpha + 2\mathbf{b}) - V(\mathbf{a}_\alpha - 2\mathbf{b})]. \qquad (5)$$

After integrating (1) with respect to $\mathbf{p}_s$ and $\boldsymbol{\xi}_s$, and combining into a quantity $Z_0(T)$ all unimportant factors which vary smoothly with temperature, we obtain

$$Z = Z_0(T) \sum_{(\sigma_\mathbf{r})} \exp\Big(-\frac{1}{T} \sum_{\mathbf{r},\alpha} J_\alpha \sigma_\mathbf{r} \sigma_{\mathbf{r}+\mathbf{a}_\alpha}\Big), \qquad (6)$$

where the summation is over all possible sets of values of the $\sigma_\mathbf{r} = \pm 1$. The sum in (6) is the partition function of a three-dimensional Ising lattice; thus the problem of the phase transition in the crystal is reduced to that of the well-known model. The singularities of the thermodynamic quantities must have the same form as in the Ising lattice. The mean magnetization of the Ising model is proportional to the mean displacement of the atoms from the cell centers. In ferroelectrics this displacement is evidently proportional to the spontaneous electric induction, and the magnetic susceptibility of the Ising lattice is the electric polarizability.

For the three-dimensional Ising model it has been shown by numerical calculations that the mean magnetization varies near the transition point T_c as $(T_c/T - 1)^\beta$ with $\beta \approx {}^5\!/_{16}$, and that the magnetic susceptibility varies as $(T - T_c)^{-\gamma}$, with $\gamma \approx {}^5\!/_4$[4]; hence the spontaneous polarization and the polarizability of a ferroelectric should vary in the same way. The specific heat of the Ising lattice tends to infinity at $T = T_c$ according to an approximately logarithmic law (possibly more steeply from the high-temperature side)[4]; a similar behavior of the specific heat may therefore also be expected for second-order phase transitions in crystals.

3. THE INFLUENCE OF ATOMIC VIBRATIONS

We must find out whether further terms in the saddle-point calculation may not alter the nature of the singularities of the macroscopic quantities at the transition point. In the next order of the expansion one must take into account the dependence of $V(\mathbf{r}_s - \mathbf{r}_{s'})$ on $\boldsymbol{\xi}_s$ in (1) and (3), and this adds to (3) the term

$$\sum_{\mathbf{r},\alpha} (\xi_\mathbf{r} - \xi_{\mathbf{r}+\mathbf{a}_\alpha}) \nabla V [\mathbf{a}_\alpha + \mathbf{b}(\sigma_\mathbf{r} - \sigma_{\mathbf{r}+\mathbf{a}_\alpha})]$$

$$= \sum_{\mathbf{r},\alpha} (\xi_\mathbf{r} - \xi_{\mathbf{r}+\mathbf{a}_\alpha}) [\mathbf{A}_\alpha + \mathbf{B}_\alpha (\sigma_\mathbf{r} - \sigma_{\mathbf{r}+\mathbf{a}_\alpha}) + \mathbf{C}_\alpha \sigma_\mathbf{r} \sigma_{\mathbf{r}+\mathbf{a}_\alpha}]; \qquad (7)$$

$$\mathbf{A}_\alpha = {}^1\!/_4 \nabla [2V(\mathbf{a}_\alpha) + V(\mathbf{a}_\alpha + 2\mathbf{b}) + V(\mathbf{a}_\alpha - 2\mathbf{b})],$$

$$\mathbf{B}_\alpha = {}^1\!/_2 \nabla [V(\mathbf{a}_\alpha + 2\mathbf{b}) - V(\mathbf{a}_\alpha - 2\mathbf{b})],$$

$$\mathbf{C}_\alpha = {}^1\!/_4 \nabla [2V(\mathbf{A}_\alpha) - V(\mathbf{a}_\alpha + 2\mathbf{b}) - V(\mathbf{a}_\alpha - 2\mathbf{b})]. \qquad (7')$$

For simplicity we shall at first assume that $|2\mathbf{b}| \ll \mathbf{a}_\alpha$. (In not too complicated lattices this condition is probably satisfied. Thus in the ferroelectric KH_2PO_4, whose structure has been determined experimentally, the distance 2b for the movable hydrogen atoms is 2b ~ 0.4 Å, and the distance between hydrogen atoms, which corresponds to $|\mathbf{a}_\alpha|$, is 3.7 Å[6]). The difference in (7′) may then be replaced by derivatives, and the ξ and σ dependent terms in the exponent of (1) take the form

$$-\frac{1}{T} \sum_{\mathbf{r},\mu,\nu} \Big[\frac{1}{2} U_{\mu\nu} \xi_\mathbf{r}{}^\mu \xi_\mathbf{r}{}^\nu$$

$$+ 2 \sum_\alpha b_\mu V_{\mu\nu}(\mathbf{a}_\alpha)(2\sigma_\mathbf{r} - \sigma_{\mathbf{r}+\mathbf{a}_\alpha} - \sigma_{\mathbf{r}-\mathbf{a}_\alpha}) \xi_\mathbf{r}{}^\nu\Big]. \qquad (8)$$

After integration over $\xi_\mathbf{r}$ we find in place of (5) an expression of the form

$$Z = Z_0(T) \sum_{(\sigma)} \exp\Big\{-\frac{1}{T}\Big[\sum_{\mathbf{r},\alpha} J_\alpha \sigma_\mathbf{r} \sigma_{\mathbf{r}+\mathbf{a}_\alpha}$$

$$+ \sum_{\mathbf{r},\alpha,\beta} b_{\alpha\beta} (\sigma_{\mathbf{r}+\mathbf{a}_\alpha} + \sigma_{\mathbf{r}-\mathbf{a}_\alpha})(\sigma_{\mathbf{r}+\mathbf{a}_\beta} + \sigma_{\mathbf{r}-\mathbf{a}_\beta})\Big]\Big\},$$

$$b_{\alpha\beta} = -2 \sum_{\mu\nu\mu'\nu'} b_\mu V_{\mu\nu}(\mathbf{a}_\alpha) U^{-1}_{\nu\nu'} V_{\nu'\mu'}(\mathbf{a}_\beta) b_{\mu'}, \qquad (9)$$

where $U^{-1}_{\nu\nu'}$ is the matrix inverse of $U_{\nu\nu'}$.

In (9) we have omitted all terms which lead merely to a renormalization of the smooth function $Z_0(T)$ and of the constants J_α, in particular the corrections due to higher terms in the expansion of $U(\mathbf{r})$ and $V(\mathbf{r}-\mathbf{r}')$. The sum in (9) is the partition function of a three-dimensional Ising lattice in which there is an interaction not only between nearest neighbors but also between neighbors of neighbors, i.e., those adjacent along a diagonal, and next nearest neighbors along the main lattice axes.

In two dimensions, some exactly soluble Ising models with interactions beyond the nearest neighbors have been investigated. A model of this kind is the so-called "triangular" model, in which, in addition to the usual interaction each spin interacts with its diagonal neighbor in one direction (cf. e.g. ref.[7]). Another is the model in which the sites for which the difference between row and column number is even have interactions along both diagonals.[8] In both cases the singularities of the macroscopic quantities and the form of the correlation functions remain the same as in the simple Ising lattice. This suggests that the interaction with other than nearest neighbors should not alter the character of the singularities in the three-dimensional case either.

With reference to the quoted paper[8] we note that, although the interaction with non-nearest neighbors does not alter the nature of the singularities, it may cause, in addition to the usual transition, an additional transition from the ordered to a disordered state at a lower temperature. In practice such double transitions are rare, but they do occur, for example, in Rochelle salt[1,6]. In two dimensions[8] the existence of such transitions requires special relations between the interactions so that the ordering effect of one is almost cancelled by the other. It is probable that in three dimensions the conditions for the existence of such double transitions will also be rather restrictive, which would explain their rarity.

In higher orders in T/U and b/a there appear, after integration over ξ, interactions between more distant spins. In addition there are many-particle interactions. For example, if one does not use in (7) an expansion in powers of b/a, the exponent in (9) contains already to first order in T/U terms of the form

$$-\frac{1}{T}\sum_{\alpha,\beta,\mu,\nu} B_\alpha^\mu U_{\mu\nu}^{-1} C_\beta^\nu \sum_{\mathbf{r}} \sigma_{\mathbf{r}}(\sigma_{\mathbf{r}+\mathbf{a}_\alpha}+\sigma_{\mathbf{r}-\mathbf{a}_\alpha})(\sigma_{\mathbf{r}+\mathbf{a}_\beta}-\sigma_{\mathbf{r}-\mathbf{a}_\beta}),$$

which describe threefold interactions. To second order in T/U there are fourfold interactions and interactions across two neighbours, etc. These terms correspond to the motion of the atom under consideration near its equilibrium position in the potential $U(\mathbf{r})$, but still leaves out the motion of all the other atoms in the cell, which produce $U(\mathbf{r})$.

To see the effect of the motion of the other atoms we consider a crystal consisting of two types of atom, 1 and 2, with a potential energy

$$U=\sum_{ss'}[U_{11}(\mathbf{r}_{1s}-\mathbf{r}_{1s'})+U_{12}(\mathbf{r}_{1s}-\mathbf{r}_{2s'})+U_{22}(\mathbf{r}_{2s}-\mathbf{r}_{2s'})]. \tag{10}$$

If we assume $U_{11} \gg U_{12} \gg U_{22}$, the 1 atoms will to the leading order be in the positions $\mathbf{r}_{1s}^0$ at which the potential

$$\sum_{ss'} U_{11}(\mathbf{r}_{1s}-\mathbf{r}_{1s'})$$

is a minimum. The 2 atoms move in a static potential produced by the 1 atoms at rest.

In the next approximation we take into account small displacements of the 1 atoms from their equilibrium positions: $\mathbf{r}_{1s}=\mathbf{r}_{1s}^0+\boldsymbol{\xi}_s$. There now appear new terms in the potential energy, which have not been taken into account above:

$$\delta U=\sum_{ss'} {}^1\!/_2\, U_{11,\mu\nu}(\mathbf{r}_{1s}{}^0-\mathbf{r}_{1s'}{}^0)(\xi_s{}^\mu-\xi_{s'}{}^\mu)(\xi_s{}^\nu-\xi_{s'}{}^\nu)+\boldsymbol{\xi}_s\nabla U_{12}(\mathbf{r}_{1s}{}^0-\mathbf{r}_{2s'}{}^0-\mathbf{b}\sigma_{s'}). \tag{11}$$

The requirement that the points $\mathbf{r}_{2s'}^0 \pm \mathbf{b}$ be equilibrium positions for type 2 atoms gives the relation

$$\sum_s \Delta U_{12}(\mathbf{r}_{1s}{}^0-\mathbf{r}_{2s'}{}^0+\mathbf{b}\sigma_{s'}) \equiv \sum_\rho \nabla U_{12}(\rho+\mathbf{b}\sigma_{s'})=0. \tag{12}$$

We insert (11) in the partition function and evaluate the integral over $\boldsymbol{\xi}_s$ in the momentum representation

$$\xi_{\mathbf{k}}=\sum_s \xi_s \exp(i\mathbf{k}\mathbf{r}_s).$$

Because of (12) the terms linear in σ disappear, so that the $\sigma_{\mathbf{r}}$ dependence of the exponent in the partition function has the form

$$\frac{1}{T}\sum_{\mathbf{r}\mathbf{r}'}\sigma_{\mathbf{r}}\sigma_{\mathbf{r}'}K(\mathbf{r}-\mathbf{r}'). \tag{13}$$

Here

$$K(\mathbf{r}-\mathbf{r}')=\frac{1}{16}\sum_{\mathbf{k}\mu\nu}\exp(i\mathbf{k}(\mathbf{r}-\mathbf{r}'))\lambda_{\mu\nu}{}^{-1}(\mathbf{k})\times\sum_\rho \exp(i\mathbf{k}\rho)\nabla_\mu(U_{12}(\rho+\mathbf{b})-U_{12}(\rho-\mathbf{b}))\times\sum_{\rho'}\exp(-i\mathbf{k}\rho')\nabla_\nu(U_{12}(\rho+\mathbf{b})-U_{12}(\rho-\mathbf{b})), \tag{13'}$$

and λ^{-1} is the inverse matrix to

$$\lambda_{\mu\nu}(\mathbf{k})=\sum_\rho U_{11,\mu\nu}(\rho)(1-\cos\mathbf{k}\rho).$$

Thus the vibrations of the atoms about their equilibrium position cause an additional interaction between the spins because of the exchange of optical and acoustic phonons. As a result one obtains the partition function of an Ising lattice with interactions between other than nearest neighbors and with many-body interactions. In Sec. 6 we shall present arguments to show that the singularities at the transition points of such lattices have the same form as in the ordinary Ising lattice.

We have assumed above that the potential energy has only two equal minima in the unit cell. For higher symmetry the number of such minima may be higher. Thus in a cubic lattice there may be four, six, or eight such minima. If, for example, there are eight of them, so that they lie at the corners of a cube of side $2\beta|\mathbf{a}_\alpha|$, the position of each minimum can be expressed in terms of three operators $\sigma_{1\mathbf{r}}$, $\sigma_{2\mathbf{r}}$, $\sigma_{3\mathbf{r}}$, each of value ± 1 (cf. (4)):

$$\mathbf{r}_{0\mathbf{s}} = \sum_\alpha s_\alpha \mathbf{a}_\alpha + \beta\,(\mathbf{a}_1\sigma_{1\mathbf{r}} + \mathbf{a}_2\sigma_{2\mathbf{r}} + \mathbf{a}_3\sigma_{3\mathbf{r}}). \qquad (14)$$

To the leading order in T/U the problem amounts to the evaluation of the partition function of three interacting Ising lattices. The interaction of these lattices is proportional to higher powers of β, so that for small β the partition function factorizes into the product of three non-interacting Ising lattices:

$$Z = Z_0(T)\,\mathrm{Sp}\exp\Big[-\frac{1}{T}\sum_{\mathbf{r},\,\alpha}(J_{1\alpha}\sigma_{1\mathbf{r}}\sigma_{1\mathbf{r}+\mathbf{a}_\alpha} + J_{2\alpha}\sigma_{2\mathbf{r}}\sigma_{2\mathbf{r}+\mathbf{a}_\alpha}$$
$$+ J_{3\alpha}\sigma_{3\mathbf{r}}\sigma_{3\mathbf{r}+\mathbf{a}_\alpha})\Big]. \qquad (15)$$

For the case of six minima we obtain more cumbersome expressions.

4. QUANTUM EFFECTS

So far we have considered only the classical expression for the partition function (1). In order to discuss the influence of quantum effects we return to the model of Sec. 2, in which the potential energy U(**r**) has in each cell two deep minima. We shall assume that the distance 2b between these minima is much less than the dimension $|\mathbf{a}_\alpha|$ of the cell, and the penetration probability of the atom from one cell to another is negligible. The potential well U(**r**) has an even and an odd state with energies ϵ_s and ϵ_a; assume all other states to lie so high in energy that their contribution to the partition function is negligible. We expand the potential V in powers of the displacement from the center of the cell

$$V(\mathbf{r}_\mathbf{s} - \mathbf{r}_{\mathbf{s}+\mathbf{e}_\alpha}) = V(\mathbf{a}_\alpha) + (\boldsymbol{\xi}_\mathbf{r} - \boldsymbol{\xi}_{\mathbf{r}+\mathbf{a}_\alpha})\,\nabla V(\mathbf{a}_\alpha)$$
$$+ {}^1/_2\, V_{\mu\nu}(\mathbf{a}_\alpha)\,(\xi_\mathbf{r}^\mu - \xi_{\mathbf{r}+\mathbf{a}_\alpha}^\mu)\,(\xi_\mathbf{r}^\nu - \xi_{\mathbf{r}+\mathbf{a}_\alpha}^\nu) \qquad (16)$$

($\mathbf{e}_\alpha = \mathbf{a}_\alpha/|\mathbf{a}_\alpha|$). In the representation based on the eigenfunctions $\psi_{\mathbf{r}s}$ and $\psi_{\mathbf{r}a}$ of the operator

$$\mathcal{H}_0 = \sum_\mathbf{s}(-\hbar^2\nabla_\mathbf{s}^2/2m + U(\mathbf{r}_\mathbf{s}))$$

the matrix of the quantity V (16) takes the form

$$\hat{V} = A_\alpha + B_\alpha(\sigma_\mathbf{r}^x - \sigma_{\mathbf{r}+\mathbf{a}_\alpha}^x)$$
$$+ C_\alpha(\sigma_\mathbf{r}^z - \sigma_{\mathbf{r}+\mathbf{a}_\alpha}^z) + J_\alpha\sigma_\mathbf{r}^x\sigma_{\mathbf{r}+\mathbf{a}_\alpha}^x. \qquad (17)$$

Here σ^x and σ^z are the Pauli matrices; the coefficients B_α, C_α, J_α (the constant A_α being unimportant) are given by the expressions

$$B_\alpha = \nabla V(\mathbf{a}_\alpha)\,\xi_{sa}, \qquad C_\alpha = \frac{1}{2}\sum_{\mu\nu} V_{\mu\nu}(\mathbf{a}_\alpha)\,[(\xi^\mu\xi^\nu)_{ss} - (\xi^\mu\xi^\nu)_{aa}],$$

$$J_\alpha = -\sum_{\mu\nu} V_{\mu\nu}(\mathbf{a}_\alpha)\,\xi_{sa}{}^\mu\,\xi_{sa}{}^\nu; \qquad (18)$$

the matrix elements of the coordinates are defined in the usual way; for example,

$$\xi_{sa} = \int d^3\xi\,\psi_s(\xi)\,\xi\,\psi_a(\xi). \qquad (19)$$

In this representation the partition function is

$$Z = \mathrm{Sp}\exp\Big(-\frac{\mathcal{H}_0 + V}{T}\Big) = Z_0(T)\sum_{(\sigma)}\exp\Big\{-\frac{1}{T}\Big[\Big(\varepsilon_s - \varepsilon_a$$
$$+ 2\sum_\alpha C_\alpha\Big)\sum_\mathbf{r}\sigma_\mathbf{r}^z + \sum_{\mathbf{r}\alpha} J_\alpha\sigma_\mathbf{r}^x\sigma_{\mathbf{r}+\mathbf{a}_\alpha}^x\Big]\Big\}. \qquad (20)$$

If we now interchange $\sigma_\mathbf{r}^x$ and $\sigma_\mathbf{r}^z$ we see that Z is proportional to the partition function of an Ising lattice in a transverse magnetic field:

$$Z = Z_0(T)\sum_{(\sigma)}\exp\Big[-\frac{1}{T}\Big(H\sum_\mathbf{r}\sigma_\mathbf{r}^x + \sum_{\mathbf{r}\alpha} J_\alpha\sigma_\mathbf{r}^z\sigma_{\mathbf{r}+\mathbf{a}_\alpha}^z\Big)\Big]. \qquad (21)$$

For a very large atomic mass m, which is equivalent to the limit ħ → 0, the quantity H defined by (18) and (20) becomes exponentially small, and (21) reduces to the classical expression (6). Qualitatively the field H has the same effect as the temperature, since it causes an additional mixing between states with different components σ^z. Hence the transitions should take place at lower temperatures for the lighter isotopes. This isotope effect is observed, for example, in the ferroelectrics KH_2PO_4 and KD_2PO_4[6]. For a certain field $H = H_0 \sim J_\alpha$ the transition temperature T_c becomes zero, so that for $H > H_0$ no transition takes place. Whereas, therefore, the quantum effects influence the position of T_c, they evidently do not change the form of the singularities (cf. Sec. 6 below).

5. PHASE TRANSITIONS IN BINARY ALLOYS

Besides cases in which the change in crystal symmetry is due to displacements, there exist also transitions in which the change in symmetry is due to ordering in the crystal. Thus, in the alloy CuZn the Cu and Zn atoms are randomly distributed over the lattice sites above the transition point, and below the transition point they tend to alternate.[1] Let the interaction potential of atoms of type 1 and 2 be

$$U_{12}(\mathbf{r}) = U(\mathbf{r}), \quad U_{11}(\mathbf{r}) = U(\mathbf{r}) + V_1(\mathbf{r}),$$
$$U_{22}(\mathbf{r}) = U(\mathbf{r}) + V_2(\mathbf{r}). \tag{22}$$

Then the interaction energy takes the form

$$W = \sum_{ss'} \{U(\mathbf{r}_s - \mathbf{r}_{s'}) + {}^1/_4 V_1(\mathbf{r}_s - \mathbf{r}_{s'})(1+\sigma_s)(1+\sigma_{s'})$$
$$+ {}^1/_4 V_2(\mathbf{r}_s - \mathbf{r}_{s'})(1-\sigma_s)(1-\sigma_{s'})\}, \tag{23}$$

where $\sigma_\mathbf{s} = \pm 1$, according to whether the site $\mathbf{r_s}$ is occupied by an atom of type 1 or 2.

We shall assume for simplicity that the interaction energies of like and unlike atoms are nearly equal, so that V_1, $V_2 \ll U$ (if one assumes U to be of the order of the melting temperature, and estimates V from the transition temperature, the ratio V/U is of the order 0.1—0.2 for most ordered alloys). Then to the leading order of approximation the atoms form a configuration which minimizes the energy $\sum_{\mathbf{ss}'} U(\mathbf{r_s} - \mathbf{r_s}')$, i.e., they form a lattice.

In the evaluation of the partition function we may again use the saddle point method, and expand the exponent near the minimum of W, which corresponds to a configuration in which all atoms occupy lattice sites $\mathbf{r}_{0\mathbf{s}}$. To the leading order we find

$$Z = Z_0(T) \wr \mathrm{M}$$
$$\times \operatorname{Sp}\exp\left\{-\frac{1}{T}\left[\frac{1}{4}\sum_{ss'}(V_1(\mathbf{r}_{0s} - \mathbf{r}_{0s'}) + V_2(\mathbf{r}_{0s} - \mathbf{r}_{0s'}))\,\sigma_s\sigma_{s'}\right.\right.$$
$$\left.\left. + \frac{1}{2}\sum_s \sigma_s \sum_{s'}(V_1(\mathbf{r}_{0s} - \mathbf{r}_{0s'}) - V_2(\mathbf{r}_{0s} - \mathbf{r}_{0s'}) - \mu)\right]\right\}, \tag{24}$$

where $\mu = \mu_1 - \mu_2$ is the difference in the chemical potentials of the atoms.

The expression (24) was derived previously (cf. for example,[7]) and represents the partition function of an Ising lattice in a longitudinal magnetic field. This system shows a phase transition of "antiferromagnetic" type if below the transition point the average spins at adjacent sites are opposite. The average of the total magnetic moment of the lattice

$$M = \langle \sum_s \sigma_s \rangle$$

is proportional to the difference between the numbers of atoms $N_1 - N_2$. The case of equal numbers, $N_1 = N_2$, corresponds to zero magnetic field. For $N_1 \neq N_2$ the correlation function $\langle \sigma_{\mathbf{s}_0+\mathbf{s}}\sigma_{\mathbf{s}_0}\rangle$ remains finite as $s \to \infty$ at any temperature, but above the transition point it tends to a unique limit at large s, whereas below there are two limits for like and unlike sites.

The singularities of the thermodynamic functions will evidently be the same for a lattice with different numbers of atoms of each kind, as for equal numbers. This corresponds to the fact that a longitudinal magnetic field, which causes the disappearance of sharp transitions in the "ferromagnetic" case, does not change the nature of an antiferromagnetic transition, but only lowers the transition temperature. This statement agrees, in particular, with the results of numerical calculations[4]. If one assumes the free energy to be of the form

$$F = F_0(T, H^2) + A_\pm[T - T_c(H^2)]^2 \ln|T - T_c(H^2)|$$

(A_+ and A_- for the regions above and below T_C), then one obtains results for the specific heat $C = -T\partial^2F/\partial T^2$ and for the susceptibility $\chi_0 = -\partial^2F/\partial H^2|_{H=0}$ which are compatible with the computed results[4] for $A_-/A_+ \sim 3$.

Besides the specific heat, there may also be a singularity in the electric resistivity ρ, the singular part of which, according to[9,10] decreases in proportion with the square of the number of ordered atoms, so that below the transition point $\rho \approx \rho_0 - \alpha(T_C - T)^{5/8}$.

Consider next what changes are caused in the partition function by the vibrations of the atoms about their equilibrium positions. If we expand the expression (23) in powers of the displacements $\boldsymbol{\xi}_\mathbf{s} = \mathbf{r_s} - \mathbf{r}_{0\mathbf{s}}$, we obtain

$$W - W_0 = \frac{1}{2}\sum_{ss'\mu\nu} U_{\mu\nu}(\mathbf{r}_{0s} - \mathbf{r}_{0s'})(\xi_s^\mu - \xi_{s'}^\mu)(\xi_s^\nu - \xi_{s'}^\nu)$$
$$+ \sum_{ss'}(\xi_s - \xi_{s'})\nabla(V_1(\mathbf{r}_{0s} - \mathbf{r}_{0s'})\sigma_s^+\sigma_{s'}^+$$
$$+ V_2(\mathbf{r}_{0s} - \mathbf{r}_{0s'})\sigma_s^-\sigma_{s'}^-), \tag{25}$$

where $\sigma_\mathbf{s}^\pm = {}^1/_2(1 \pm \sigma_\mathbf{s})$. Insert (25) in the partition function. The resulting Gaussian integral can be evaluated like that in (11) by going over to momentum space. As a result we obtain a contribution to the exponent of (24) which is analogous to (13):

$$\frac{1}{T}\sum_{\substack{\mathbf{rr}'\\ \mu\nu}} \exp[i\mathbf{k}(\mathbf{r} - \mathbf{r}')]\lambda_{\mu\nu}^{-1}(\mathbf{k}) \sum_{\boldsymbol{\rho}} \nabla_\mu [V_1(\rho)\sigma_\mathbf{r}^+\sigma_{\mathbf{r}+\boldsymbol{\rho}}^+$$
$$+ V_2(\rho)\sigma_\mathbf{r}^-\sigma_{\mathbf{r}+\boldsymbol{\rho}}^-] \sum_{\boldsymbol{\rho}'} \nabla_\nu [V_1(\rho')\sigma_{\mathbf{r}'}^+\sigma_{\mathbf{r}'+\boldsymbol{\rho}'}^+$$
$$+ V_2(\rho')\sigma_{\mathbf{r}'}^-\sigma_{\mathbf{r}'+\boldsymbol{\rho}'}^-], \tag{26}$$

where λ^{-1} has the same meaning as in (13), but with U_{11} replaced by U. The expression (26) contains, in addition to terms of the type (24), also three-body and four-body interactions.

6. CLASSICAL-FIELD STATISTICS

One may also approach the calculation of the partition function near the phase transition from a somewhat different angle. The Hamiltonian of the lattice has, according to (11), the form

$$\mathscr{H} = \sum_s [p_s^2/2m + U(\mathbf{r}_s) + V(\mathbf{r}_s - \mathbf{r}_{s'})]. \tag{27}$$

If U and V are expanded in powers of the displacements from the mean positions, up to terms of the second order, the Hamiltonian (27) represents the Hamiltonian of non-interacting phonons,

$$\mathscr{H}_0 = \sum_{\mathbf{k}} a_{\mathbf{k}}^+ a_{\mathbf{k}} \hbar\omega_{\mathbf{k}}, \tag{28}$$

where $a_{\mathbf{k}}^+$ and $a_{\mathbf{k}}$ are phonon creation and annihilation operators. In the general case (27) is the Hamiltonian of interacting phonons. One may then use in the evaluation of the partition function with the Hamiltonian (27) the usual method of diagrams[11], expanding the free energy in powers of the coupling. However, even if the anharmonicity, which is measured in order of magnitude by a parameter g, is small, it turns out that near the transition point T_c, the expansion parameter is $g(T - T_c)^{-1/2}$, and at $T = T_c$ every diagram diverges at small momentum k.

The ordered state, in which the mean displacement of the atoms is non-zero, can be regarded as a Bose condensation of optical phonons. As T approaches T_c the mean occupation numbers $n_{\mathbf{k}}$ for small k increase, so that near $T = T_c$ the $n_{\mathbf{k}}$ for small k are large, and the commutator $[a_{\mathbf{k}}, a_{\mathbf{k}}^+] = 1$ is negligible compared with $\langle a_{\mathbf{k}}^+ a_{\mathbf{k}} \rangle = n_{\mathbf{k}}$ (this argument is due to L. D. Landau). The singularities in the thermodynamic functions are connected with just these small k, i.e., with the long-range correlations near the transition point. For this reason we may, in the investigation of the singularities, treat the phonon field as classical, i.e., treat p and r as classical variables in the evaluation of the partition function (25), as was done above. According to Sec. 2, the partition function for strong coupling then turns out to be proportional to the partition function for an Ising lattice.[1)]

The method presented above may be applied not only to phase transitions in crystals but also to the transition of a Bose gas. The partition function of an imperfect Bose gas is

$$\begin{aligned} Z &= \operatorname{Sp} \exp\left(\frac{\mu\hat{N} - \mathscr{H}}{T}\right) \\ &= \operatorname{Sp} \exp\left\{-\frac{1}{T}\int dV\left[\frac{\hbar^2}{2m}\nabla\psi^+\nabla\psi - \mu\psi^+\psi + \frac{g}{2}(\psi^+\psi)^2\right]\right\}. \end{aligned} \tag{29}$$

In (29) the interactions were taken to be δ-functions, since in the region of small k, which dominates the transition, the details of the interaction are unimportant, and the potential may be replaced by the parameter g[12]. By the same reasoning as the one used in connection with the phase transition based on (27), we may again replace the quantized ψ field by a classical one. We introduce the canonical variables

$$q_{\mathbf{r}} = 2^{-1/2}(\psi_{\mathbf{r}} + \psi_{\mathbf{r}}^+), \qquad p_{\mathbf{r}} = i2^{-1/2}(\psi_{\mathbf{r}}^+ - \psi_{\mathbf{r}})$$

and replace the trace in (29) by an integration over $q_{\mathbf{r}}$, $p_{\mathbf{r}}$:

$$\begin{aligned} Z = \int \prod_{\mathbf{r}} dq_{\mathbf{r}} dp_{\mathbf{r}} \exp\left\{-\frac{1}{2T}\int dV\left[\frac{\hbar^2}{2m}((\nabla p_{\mathbf{r}})^2 + (\nabla q_{\mathbf{r}})^2)\right.\right. \\ \left.\left. - \mu(q_{\mathbf{r}}^2 + p_{\mathbf{r}}^2) + \frac{g}{4}(q_{\mathbf{r}}^2 + p_{\mathbf{r}}^2)^2\right]\right\}. \end{aligned} \tag{30}$$

We evaluate the functional integral (30) by integrating over the values of the field at points **r** which form the corners of a simple cubic lattice with side a. The gradient is then replaced by a finite difference (e.g. $\nabla_\alpha q_{\mathbf{r}} = (q_{\mathbf{r}+\mathbf{n}_\alpha} - q_{\mathbf{r}})a^{-1}$). In the limit $a = 0$ the free energy $F = -T \ln Z$ tends to infinity, reproducing the usual classical divergence of the Rayleigh-Jeans type at large k. In reality this divergence is cut off by quantum effects, so that we may understand a to be a quantity of the order $\hbar(2mT)^{-1/2}$. We are interested in the effects of small k, i.e., smooth long-wave correlations, and for these the assumption of a point structure is unimportant; the quantity a will appear as a parameter in the answer. For example, for a perfect gas, $g = 0$, we find for the number of particles with momentum **k**

$$n_{\mathbf{k}} = T\left[\frac{\hbar^2}{2ma^2}\sum_\alpha(1 - \cos \mathbf{k}a_\alpha) - \mu\right]^{-1}, \qquad -\pi/a \leqslant k_\alpha \leqslant \pi/a \tag{31}$$

in place of the Planck distribution

$$[\exp(\hbar^2k^2/2mT - \mu/T) - 1]^{-1}.$$

For small k and μ the two expressions are identical.

[1)] The possibility of reducing the partition function of a phonon gas to the Ising model was pointed out previously by L. P. Gor'kov and L. P. Pitaevskiĭ.

We define a two-dimensional vector $\boldsymbol{\rho}_{\mathbf{r}}$ with the components $(2^{-1/2}q_{\mathbf{r}}\, a^{3/2},\ 2^{-1/2}p_{\mathbf{r}}\, a^{3/2})$, and rewrite (30) in the form

$$Z = \int \exp\left\{-\frac{1}{T}\sum_{\mathbf{r}}\left[\sum_{\alpha}\frac{\hbar^2}{2ma^2}(\rho_{\mathbf{r}} - \rho_{\mathbf{r}+\mathbf{a}_\alpha})^2 - \mu\rho_{\mathbf{r}}{}^2 + ga^{-3}2^{-1}\rho_{\mathbf{r}}{}^4\right]\right\}\prod_{\mathbf{r}} d\rho_{\mathbf{r}}\, a^{-3N}2^N. \qquad (32)$$

The exponent of (32) can be interpreted as the potential energy of N particles moving in the external potential

$$U(\rho) = -\mu\rho^2 + ga^{-3}2^{-1}\rho^4,$$

with an attraction between nearest neighbors. The energy minimum corresponds to a distribution of the particles near $\rho = \rho_0$, which gives the minimum of U. The temperature tends to spread the particles over all directions of the two-dimensional vector $\boldsymbol{\rho}$, whereas the attraction tends to keep them close to each other, i.e., near some common mean angle φ. The phase transition consists of the fact that for $T < T_c$ the system possesses a mean value $\langle \boldsymbol{\rho} \rangle \neq 0$, so that it loses its isotropy in $\boldsymbol{\rho}$ space. Thus the phase transition is connected essentially with the first term in the exponent of (32), i.e., with the kinetic energy of the helium atoms. If this is neglected, Z splits into a product of independent integrals and has no singularities as a function of T and μ. In that case the transition temperature is zero. (This conclusion was reached in 1958, in joint work with V. M. Galitskiĭ).

As above, consider the case $|U_{\min}(\rho)| \gg T$. We may then again use the saddle-point method to evaluate (32). To zero order, assuming $\rho^2 = \rho_0^2 = \mu a^3 g^{-1}$, we find

$$Z = Z_0(T)\int \exp\left(\frac{J}{T}\sum_{\mathbf{r},\,\alpha}\mathbf{n}_{\mathbf{r}}\mathbf{n}_{\mathbf{r}+\mathbf{a}_\alpha}\right)\prod_{\mathbf{r}} d\mathbf{n}_{\mathbf{r}}, \qquad (33)$$

where $J = \hbar^2\mu a(mg)^{-1}$ and $\mathbf{n}$ is a two-dimensional unit vector. In this way the singular part of the partition function reduces to an expression of the same type as the Ising model, except that the magnetic moment at every site may have any direction in a plane, rather than only two directions, as in the Ising model. Higher terms in the saddle-point method produce, as above, interactions between several moments. The partition function for a ferromagnet has the same form as (33), but the moments can there take any direction in three dimensions.

As in the case of the Ising model, the problem of evaluating the partition function (33) for the Bose gas can be stated as a combinatorial problem:

$$\frac{Z}{Z_0} = I_0^N(x)\sum_{n_1\ldots n_\nu=0} g_{n_1,\, n_2\ldots n_\nu}\,\alpha_1^{n_1}\alpha_2^{n_2}\ldots\alpha_\nu^{n_\nu}, \qquad (34)$$

where $x = J/T$, $a_m = I_m(x)I_0^{-1}(x)$; I_m is the Bessel function of imaginary argument, and $g_{n_1,\,n_2,\ldots n_\nu}$ is the number of ways in which one can draw connected oriented polygons with n_m links which are passed m times in the same direction. In one dimension

$$Z/Z_0 = I_0^N(J/T) \qquad (35)$$

and, as in the one-dimensional Ising model, for which $Z = 2^N \cosh^N(J/T)$, Z has no singularity, indicating that there is no transition. It is not clear to us whether the singularities of the thermodynamic functions for (33) will, in the two and three-dimensional cases, have the same form as in the Ising model.

Similarly to the Ising model[13], the evaluation of the partition function (32) for the classical field can be reduced to the determination of the lowest eigenvalue of a certain operator. For this purpose we note that (32) may be written in the form

$$Z = \int K^{(N_1)}\{\rho_{N_1\mathbf{l}},\ \rho_{N_1\mathbf{l}}\}\prod_{\mathbf{l}} d\rho_{N_1\mathbf{l}}. \qquad (36)$$

Here N_1 is the number of layers in the z direction, the first subscript on $\boldsymbol{\rho}$ labels the layer, and the second is a two-dimensional vector, $\mathbf{l} = l_1\mathbf{a}_1 + l_2\mathbf{a}_2$, which labels the position of a point in the layer. The symbol $f\{\boldsymbol{\rho}_{\mathbf{l}}\}$ denotes a function of all N_2 variables $\boldsymbol{\rho}_{\mathbf{l}}$, and $K^{(N_1)}\{\boldsymbol{\rho}_{\mathbf{l}}, \boldsymbol{\rho}'_{\mathbf{l}}\}$ is the N_1-th power (N_1-fold iterated kernel) of the integral operator:

$$K\{\rho_{\mathbf{l}},\ \rho_{\mathbf{l}}'\} = \exp\left[-\frac{U\{\rho_{\mathbf{l}}\}}{T} + \sum_{\mathbf{l}}\frac{\hbar^2}{2ma_3{}^2T}(\rho_{\mathbf{l}} - \rho_{\mathbf{l}}')^2\right],$$

$$U\{\rho_{\mathbf{l}}\} = \sum_{\mathbf{l}}\left[\sum_{\alpha=1}^{2}(\rho_{\mathbf{l}} - \rho_{\mathbf{l}+\mathbf{a}_\alpha})^2\frac{\hbar^2}{2ma_1{}^2} - \mu\rho_{\mathbf{l}}{}^2 + \frac{g\rho_{\mathbf{l}}{}^4}{2a_3a_1{}^2}\right]; \qquad (37)$$

a_3 is the spacing between the layers, $a_1 = a_2$ the spacing of points in a layer. In (36) we have made use of a cyclic boundary condition $\boldsymbol{\rho}_{N_1+1\,\mathbf{l}} \equiv \boldsymbol{\rho}_{\mathbf{l}}$ and omitted a constant factor from Z.

Denote by λ_n the eigenvalues of the integral equation

$$\lambda_n f\{\rho_{\mathbf{l}}\} = \int\prod_{\mathbf{l}} d\rho_{\mathbf{l}}' K\{\rho_{\mathbf{l}},\ \rho_{\mathbf{l}}'\} f\{\rho_{\mathbf{l}}'\}. \qquad (38)$$

Then we have from (36) and (38)

$$Z = \sum_n \lambda_n{}^{N_1} \sim \lambda_0{}^{N_1}, \qquad \Omega = -T\ln Z = -TN_1\ln\lambda_0, \qquad (39)$$

where λ_0 is the largest eigenvalue of (38) and N_1 has been assumed macroscopically large.

From what was said earlier one may assume that the nature of the singularities of the thermodynamic functions does not depend on the way in which the lattice structure has been introduced, i.e., on the ratio between a_3 and a_1. If we then choose a_3 much less than a_1 we can convert the integral equation (38) into a differential equation by the Fokker-Planck method (a similar approach was used by Feynman[14] in reducing a functional integral to the Schrödinger equation, cf. also[15]). We may regard the function $f\{\rho_l\} \equiv \exp(\chi\{\rho_l\})$ in (38) as slowly varying compared with the second factor in K (37), and we therefore expand $f\{\rho_l'\}$ on the right-hand side of (38) in powers of $\xi_l = \rho_l' - \rho_l$

$$\exp(\chi\{\rho_l\} + \ln\lambda_0)$$

$$= \exp\left(\chi\{\rho_l\} - \frac{U}{T}\right)\int\prod_l d\xi_l \exp\left(-\frac{\xi_l^2\hbar^2}{2ma_3^2T}\right)$$

$$\times\left[1 - \xi_l\frac{\partial\chi}{\partial\rho_l} + \frac{1}{2}\left(\xi_l\frac{\partial\chi}{\partial\rho_l}\right)^2\right.$$

$$\left. + \frac{1}{2}\sum_{\alpha,\beta=1}^{2}\xi_l^\alpha\sum_{l'}\xi_{l'}^\beta\frac{\partial^2\chi}{\partial\rho_l^\alpha\partial\rho_{l'}^\beta}\right]. \tag{40}$$

For large values of the difference $l - l'$ the derivative $\partial^2\chi/\partial\rho_l^\alpha\partial\rho^\beta$ tends to zero, corresponding to the decrease of correlations at large distances, so that the last term in (40) is of the same order of magnitude as the preceding one. We carry out the integration over ξ_l and take logarithms of both sides; this gives, apart from terms of the order a_3^2:

$$\ln\lambda_0 = -\frac{U}{T} + N_2\ln(2\pi ma_3^2T\hbar^{-2})$$

$$+ \frac{ma_3^2T}{2\hbar^2}\sum_l\left[\left(\frac{\partial\chi}{\partial\rho_l}\right)^2 + \frac{\partial^2\chi}{\partial\rho_l^2}\right] \tag{41}$$

(N_2 is the number of lattice points in a layer). If we multiply (41) by $f = e^\chi$, we are left with the Schrödinger equation for a system of N_2 particles with the potential energy U/T and the mass $\hbar^4(ma_3^2T)^{-1}$:

$$\left[-\frac{ma_3^2T}{2\hbar^2}\sum_l\frac{\partial^2}{\partial\rho_l^2} + \frac{U\{\rho_l\}}{T}\right]f\{\rho_l\} = [N_2\ln(2\pi ma_3^2T\hbar^{-2})$$

$$- \ln\lambda_0]\,f\{\rho_l\}. \tag{42}$$

Thus the task of evaluating the partition function reduces to the determination of the ground state energy of a system with one dimension less. For instance, in the case of a one-dimensional gas, $N_2 = 1$, and (42) becomes the Schrödinger equation of a single two-dimensional anharmonic oscillator[15]. The eigenvalue is then an analytic function of T and there is no phase transition. (The difference between this result and the one obtained in ref[15] is due to the fact that in our case the "potential energy" $U(\rho)$ tends to infinity at large ρ, and this makes the Bose gas stable, as it represents a repulsion for high density, whereas the "potentials" in the models considered in[15] tend to zero at large argument.)

As before, we may consider in (40) the case of a very deep potential well. The particles will then be mostly near the minimum of the "external potential"

$$U_0(\rho) = -\mu\rho^2/T + g\rho^4/2a_1^2a_3T,$$

i.e. they will have a practically constant value of the radius $\rho = \rho_0 = (\mu a_3a_1^2g^{-1})^{1/2}$. Replacing to zero order ρ by ρ_0, we are left with the problem of finding the ground state of a two-dimensional lattice of plane rotors with the Hamiltonian

$$H = \sum_l\left[-\frac{\partial^2}{\partial\varphi_l^2} - J\sum_{\alpha=1}^{2}\cos(\varphi_l - \varphi_{l+a_\alpha})\right],$$

$$J = 2\left(\frac{\hbar^2\mu a_1}{mgT}\right)^2. \tag{43}$$

Finally, if we let the parameter a_1 in the potential in (42) tend to zero, the problem of finding Ω becomes equivalent with the determination of the vacuum energy of a two-dimensional relativistic Bose gas with the Lagrangian

$$L = \int d^2r\left[\frac{2\hbar^2}{mTa_3^2}\frac{\partial\psi^+}{\partial t}\frac{\partial\psi}{\partial t} - \frac{\hbar^2}{2mT}\frac{\partial\psi^+}{\partial\mathbf{r}}\frac{\partial\psi}{\partial\mathbf{r}} + \frac{\mu}{T}\psi^+\psi\right.$$

$$\left. - \frac{g}{Ta_3}(\psi^+\psi)^2\right]. \tag{44}$$

Patashinskiĭ and Pokrovskiĭ[12] consider the phase transition of the Bose gas by means of the method of graphs. The starting point of their paper is the fact that the correlation function $G(k, T)$ in the momentum representation has no singularity as a function of $\tau = T/T_c - 1$. The method and the results of[12] are applicable also to the phonon gas, and in two dimensions give for G in the region $k \gg \tau$ a behavior of the type $G(k, \tau) = ak + b\tau$ (a, b are constants). We have shown above that for certain relations between the constants the phonon gas is equivalent to the Ising model. In the two-dimensional Ising model the correlation function takes, for $1 \gg k \gg \tau$ the form[8]

$$G^{-1}(k, \tau) = k^{7/4}\left(a + b\frac{\tau}{k}\ln\frac{k}{|\tau|}\right). \tag{45}$$

The results of Patashinskiĭ and Pokrovskiĭ therefore seem to us unconvincing.

Nevertheless the method of graphs is useful for studying phase transitions since it allows one to assert that the complications of the Ising model found in Secs. 3—5 do not seem to change the nature of the singularity. In the first place, as we pointed out above, one can see from the method of graphs that the quantum effects influence only the values of the parameters, such as the transition temperature, but not the form of the singularity.

Taken together with the results of Sec. 4 this means that a transverse field will only lower T_c in the Ising model, but not change the form of the singularity. In addition, one can see from the method of graphs that the interaction between other than nearest neighbors also should not change the results. Assume, for example, that the interaction between the atoms in Eq. (1) is of the form

$$\sum_{\mathbf{s},\,\mathbf{s}_1} f(\mathbf{s})\,(\mathbf{r}_{\mathbf{s}_1}-\mathbf{r}_{\mathbf{s}+\mathbf{s}_1})^2,$$

where f(s) is any function which decreases sufficiently rapidly with increasing s. In momentum space this term then takes the form

$$\sum_{\mathbf{k}} \mathbf{r}_{\mathbf{k}}\mathbf{r}_{-\mathbf{k}}\cdot 4\sum_{\rho} f(\rho)\sin^2\frac{\mathbf{k}\rho}{2}.$$

Evidently, according to the method of graphs, the important point is that this "zero-order energy" which appears in the zero-order Green's function is for small k proportional to k, so that the interaction of other than nearest neighbors corresponds simply to a "mass renormalization" in the method of graphs.

The effect of many-body interactions in the Ising model can be evaluated similarly. Assume, for example, that the interaction between phonons in (1) contains terms of the form

$$\sum_{\mathbf{s}_1\mathbf{s}_2\mathbf{s}_3\mathbf{s}_4} x_{\mathbf{s}_1}x_{\mathbf{s}_2}x_{\mathbf{s}_3}x_{\mathbf{s}_4}f_{\mathbf{s}_1\mathbf{s}_2\mathbf{s}_3\mathbf{s}_4}, \tag{46}$$

where the x axis is in the direction of the vector **b** introduced in Sec. 2. As we pointed out in the discussion of (29) the application of the method of graphs shows that non-local interactions give in the important region of small k the same result as local interactions with an averaged value of the constant. If we use the saddle-point method of Sec. 2, on the other hand, expression (46) leads already in zero order to an Ising model with four-body interactions. One may expect, therefore, that the presence of such many-body interactions does not affect the nature of the singularity at the transition point.

7. CONCLUSIONS

Although the considerations presented above seem to us convincing, they do not constitute a rigorous proof. It would therefore be interesting to verify by numerical calculation, if only in the simpler two-dimensional case, that the form of the singularities in the macroscopic quantities in the Ising model are not changed by the inclusion of a transverse magnetic field, by interactions between other than nearest neighbors, or by many-body interactions, for example of the form

$$J\sum_{ik}\sigma_{ik}\,\sigma_{ik+1}\,\sigma_{i+1k}\,\sigma_{i+1\,k+1}.$$

It would also be interesting to carry out numerical calculations for a model of the phase transitions of a Bose gas, i.e., to find the form of the singularity at the transition point for the lattice of plane dipoles, (33), or (if that is simpler) the singularity in the ground-state energy of the two-dimensional system (43). It would also be desirable to find the temperature dependence of $\chi = \partial M/\partial H$ below T_c in the Ising model, so as to compare it with the behavior of the dielectric susceptibility of ferroelectrics below the transition point.

For the study of correlation effects, such as the scattering of electromagnetic or sound waves in crystals near the transition point it would also be interesting to have calculations of the correlation function $G(\rho) = \langle\sigma_{\mathbf{r}}\sigma_{\mathbf{r}+\rho}\rangle$ at large ρ for the Ising model. (The hypothesis that $G(\rho, \tau)$ behaves for $|\tau| \ll 1$, $1 \ll \rho$ as $\rho^{\beta}f(\rho\tau)$[16] cannot simultaneously be reconciled with the results for the susceptibility $\chi_0(\tau) \sim \sum_{\rho} G(\rho, \tau) \sim \tau^{-5/4}$ for positive τ, and for the spontaneous magnetization, $G^{1/2}(\infty, \tau) \sim |\tau|^{5/16}$, for negative τ, unlike the situation in the two-dimensional case.)

In conclusion we list those results of our present discussion which can be compared with experiment. The specific heat of crystals should behave near the transition point as in the Ising model. Numerical calculations[4] give for this quantity a variation of the form $C = A_{\pm}\ln|T - T_c|$, where A_+ and A_- are constants, applicable for $T > T_c$ and $T < T_c$, respectively, with $A_+ < A_-$. If one assumes the mean displacement of the ions in a ferroelectric crystal to be proportional to the dipole moment, the polarizability of ferroelectrics should vary above T_c as $(T - T_c)^{-5/4}$ and the spontaneous polarization below T_c as $(T_c - T)^{5/16}$. The resistivity ρ of binary alloys below the transition point should follow the law $\rho = \rho_0 - a(T_c - T)^{5/8}$. The behavior of other quantities near the transition point can be discussed by arguments similar to those presented.

The available experimental data[6,10] are in qualitative agreement with these results. Thus in all cases known to us the specific heat shows a λ point, in which the curve is steeper on the disordered side. The polarizability and the spontaneous polarization of ferroelectrics rise sharply towards the Curie point, although an exact determination of the power law would apparently require an increase in the experimental accuracy; the same applies to the measurements of the resistance of binary alloys near T_c. It has also been suggested that in some materials the size of the region in which the various quantities show an anomalous behavior might be numerically smaller[2], and therefore the comparison with experiment needs a detailed discussion in each case.

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