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CONTRIBUTION TO THE THEORY OF SECOND-ORDER PHASE TRANSITIONS AT LOW TEMPERATURES

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Quantum effects are investigated in second-order phase transitions at low temperatures. The temperature dependence of the gap in the spectrum of the critical optical phonons is calculated in first approximation of perturbation theory and in the "parquet" approximation. The results are compared with the experimental data for SnTe and $KTaO_3$. The transition at T = 0 is also investigated.

1. INTRODUCTION

THE purpose of the present paper is to evaluate the influence of quantum effects on the properties of a crystal near a second-order phase transition point. As is well known, the Landau phenomenological theory of phase transitions does not take into account fluctuations in the ordering parameter, which lead to deviations from this theory. Fluctuations with arbitrarily small **k**, which can be regarded as classical, grow at the transition point. Therefore in the immediate vicinity of the transition line there is a region of strong classical fluctuations, which so far could not be fully investigated theoretically. All that could be done was to construct a special type of similarity theory for this region.[1–3]

On the other hand, if the temperature of the phase transition is sufficiently low compared with the characteristic energies of the problem, then besides the "classical similarity region" there is a sufficiently extensive region where quantum effects play an appreciable role.[1] This is the region we shall investigate in the present paper. The limiting case of such a situation is a second-order transition at the absolute zero of temperature, when there are no classical fluctuations at all. (Of course, in this case one can speak of transitions occurring during the change of pressure, during the change of the impurity concentration, etc.).

We shall show later that the situation in the quantum region is much simpler than in the "similarity region," and admits of a sufficiently complete investigation. On the other hand, the results here are apparently more sensitive to the concrete choice of the object and the model. This is connected, in final analysis, with the need for calculating the Green's functions with $\omega_n \gtrsim T$, and not only with $\omega_n = 0$ as in the "similarity region."

We shall consider in this paper the vicinity of a transition with a low-lying critical branch. In this case at the point of second-order phase transition, at some value of the wave vector **k**, the frequency of this branch vanishes. Such transitions are well known in ferroelectrics. Among these we are interested in those revealing a critical branch at low temperatures. We have sufficiently detailed information only on two substances of this type, SnTe[5,6] and $KTaO_3$.[7] The quantum effects were considered also in [8,9].

2. TEMPERATURE DEPENDENCE OF THE SPECTRUM IN THE FIRST ORDERS OF PERTURBATION THEORY

We shall use the Anderson model.[10] At low temperatures, to describe the crystal it is necessary to take into account only the critical low-lying branch and the acoustic branches of the vibrational spectrum. We confine ourselves to the case of one critical branch. The Hamiltonian of such a crystal is

$$\hat{H} = \hat{H}_0 + \hat{H}_{int}.$$

Here $\hat{H}_0$ is the harmonic part. Expressed in terms of normal coordinates of the critical and acoustic phonons, it takes the form[11] ($\hbar = 1$)

$$\hat{H}_0 = -\frac{1}{2}\sum_{\mathbf{k},\alpha}\frac{\partial^2}{\partial\xi_{\mathbf{k}}{}^{\alpha}\partial\xi_{-\mathbf{k}}{}^{\alpha}} + \frac{1}{2}\sum_{\mathbf{k},\alpha}[\omega_0{}^{\alpha}(\mathbf{k})]^2\xi_{\mathbf{k}}{}^{\alpha}\xi_{-\mathbf{k}}{}^{\alpha},$$

The index α(s, a) numbers the coordinates of the critical phonons $\xi_{\mathbf{k}}^{s}$ and of the acoustic ones $\xi_{\mathbf{k}}^{a}$. The polarization indices are omitted.

The term $\hat{H}_{int}$ constitutes anharmonic corrections. For anharmonicity of third and fourth orders we have

$$\hat{H}_{int} = \frac{1}{3!\sqrt{N}}\sum V_3^{\alpha_1\alpha_2\alpha_3}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)\,\xi_{\mathbf{k}_1}{}^{\alpha_1}\xi_{\mathbf{k}_2}{}^{\alpha_2}\xi_{\mathbf{k}_3}{}^{\alpha_3}$$
$$+\frac{1}{4!N}\sum V_4^{\alpha_1\alpha_2\alpha_3\alpha_4}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4)\,\xi_{\mathbf{k}_1}{}^{\alpha_1}\xi_{\mathbf{k}_2}{}^{\alpha_2}\xi_{\mathbf{k}_3}{}^{\alpha_3}\xi_{\mathbf{k}_4}{}^{\alpha_4},$$

where N is the total number of unit cells in the volume of the crystal. The summation is over all α_i and over all $\mathbf{k}_i$ satisfying the condition $\Sigma\mathbf{k}_i = 0$. We do not take Umklapp processes into account here. The nonrenormalized spectrum of the critical phonons at small values of **k** can be taken in the simple form[2]

$$[\omega_0{}^{s}(\mathbf{k})]^2 = \eta + \beta k^2, \quad \beta > 0. \tag{1}$$

We introduce the second-quantization operators

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[1] An important, although untypical, example of such a transition is the superconducting transition in a metal. Classical fluctuations are significant there only in the region $\Delta T/T_c \lesssim (T_c/\epsilon_F)^4$ [4], while quantum effects are significant at $T \lesssim T_c$.

[2] All the results obtained below can be readily generalized to the case of an anisotropic spectrum, and also to the case when the minimum is at $\mathbf{k} = \mathbf{k}_0 \neq 0$:

$$[\omega_0{}^{s}(\mathbf{k})]^2 = \eta + \sum_{i=1}^{3}\beta_i(k_i - k_{i0})^2.$$

$$\xi_{\mathbf{k}}^{\alpha} = \frac{1}{\sqrt{2\omega_0^{\alpha}(\mathbf{k})}}(b_{\mathbf{k}}^{\alpha} + b_{-\mathbf{k}}^{\alpha+}),$$

$$\frac{\partial}{\partial \xi_{\mathbf{k}}^{\alpha}} = -i\sqrt{\frac{\omega_0^{\alpha}(\mathbf{k})}{2}}(b_{\mathbf{k}}^{\alpha} - b_{-\mathbf{k}}^{\alpha+}),$$

and then

$$\hat{H}_0 = \sum_{\mathbf{k},\alpha} \omega_0^{\alpha}(\mathbf{k}) \left(b_{\mathbf{k}}^{\alpha+} b_{\mathbf{k}}^{\alpha} + \frac{1}{2}\right).$$

We shall use for the investigation the method of temperature Green's functions:[12]

$$\mathscr{D}^{\alpha}(\mathbf{k}, \tau) = -\operatorname{Sp}\{e^{-\hat{H}/T} T_{\tau}(\xi_{\mathbf{k}}^{\alpha}(\tau)\, \xi_{-\mathbf{k}}^{\alpha}(0))\},$$

$$\xi_{\mathbf{k}}^{\alpha}(\tau) = e^{\tau\hat{H}} \xi_{\mathbf{k}}^{\alpha} e^{-\tau\hat{H}},$$

$$\mathscr{D}^{\alpha}(\mathbf{k}, \varepsilon_n) = \int_0^{1/T} \mathscr{D}^{\alpha}(\mathbf{k}, \tau)\, e^{i\varepsilon_n\tau}\, d\tau, \quad \varepsilon_n = 2\pi T n, \quad n = 0, \pm 1, \pm 2.$$

We shall also have to carry out the calculations for T = 0. It is then more convenient to use not the temporal but the temperature technique in the limit as T → 0. As is well known,[12] in this case the sums over ϵ_n are replaced by integrals:

$$T \sum_{\varepsilon_n} \to \frac{1}{2\pi} \int_{-\infty}^{+\infty} dz, \quad \varepsilon_n \to z.$$

The anharmonicity is regarded as weak and we use methods of perturbation theory. In the zeroth approximation we get

$$\mathscr{D}_0^{\alpha}(\mathbf{k}, \varepsilon_n) = -\frac{1}{\varepsilon_n^2 + [\omega_0^{\alpha}(\mathbf{k})]^2}. \tag{2}$$

The complete Green's function is expressed in terms of the self-energy part from the Dyson equation:

$$(\mathscr{D}^{\alpha}(\mathbf{k}, \varepsilon_n; T))^{-1} = (\mathscr{D}_0^{\alpha}(\mathbf{k}, \varepsilon_n))^{-1} - \Sigma^{\alpha}(\mathbf{k}, \varepsilon_n; T). \tag{3}$$

The square of the gap in the spectrum of the critical phonons is expressed in terms of the Green's function in the following manner:

$$\Delta^2(T) = -[\mathscr{D}^s(0, 0; T)]^{-1} = \eta + \Sigma^s(0, 0; T). \tag{4}$$

Let us consider the contributions to $\Sigma^S(0, 0; T)$ in the first few orders of perturbation theory. The corresponding terms are shown graphically in Fig. 1. The solid and dashed lines denote respectively the Green's functions of the critical and of the acoustic phonons. The points at the vertices of the graphs denote the corresponding anharmonic potentials. Cubic anharmonicity makes a contribution in the second order of perturbation theory (the diagrams a, b, and c of Fig. 1), while fourth-order anharmonicity contributes in first order (graphs, d, e).

We shall consider crystals in which the principal role is played by fourth-order anharmonicity, i.e., the main contribution is made by diagrams d and e of Fig. 1, and the contributions from diagrams a, b, and c are small. Thus, for example, if in the crystal each of the atoms is an inversion center, then[13,14]

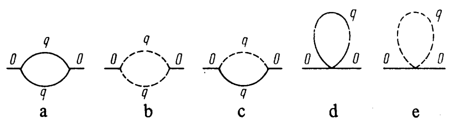

FIG. 1

$$V_3^{\alpha_1\alpha_2\alpha_3}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) = V_3^{\alpha_1\alpha_2\alpha_3}(-\mathbf{k}_1, -\mathbf{k}_2, -\mathbf{k}_3),$$

and since

$$V_3^{\alpha_1\alpha_2\alpha_3}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3) = V_3^{\alpha_1\alpha_2\alpha_3}(\mathbf{k}_1, \mathbf{k}_3, \mathbf{k}_2),$$

it follows that $V_3^{\alpha_1\alpha\alpha}(0, \mathbf{k}, -\mathbf{k}) = 0$, and consequently the contributions of diagrams 1a and 1b to the gap are equal to zero. The diagram 1c is connected with the striction term in $\hat{H}_{\text{int}}$ corresponding to the interaction of two critical phonons and one acoustic phonon. If in such crystals the striction is weak, then the cubic anharmonicity can be neglected.

The anharmonic potentials of the interaction of four critical phonons can be described by one constant $V_4^{ssss}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4) = g_0$, and we assume $g_0 > 0$. Only in this case are the effects of interest to us at present. The interaction potentials of the acoustic and critical phonons are proportional to the momenta of the acoustic phonons.[11] For example,

$$V_4^{ss\alpha\alpha}(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4) \sim k_3 k_4. \tag{5}$$

Such a model of a crystal with a low-lying critical branch and positive anharmonicity of fourth order, stabilizing the lattice, is equivalent to the models considered in the general theory of second-order phase transitions. At the transition point, the Green's function of the critical phonons becomes infinite at zero value of the momentum and frequency, i.e.,

$$\mathscr{D}^{-1}(0, 0; T_c) = 0 \tag{6}$$

(The index s for the critical phonons will henceforth be omitted), meaning, in accord with (4), the vanishing of the frequency of these phonons at **k** = 0. Equation (6) for the transition temperature, using (4), can be written in the form

$$\Delta^2(T_c) = \eta + \Sigma(0, 0; T_c) = 0. \tag{7}$$

We note immediately that allowance for striction causes the transition to become one of first order.[15] However, if the striction is small, then the heat of the transition is also small, and the first-order transition is close to a second-order one. In this case there exists a sufficiently wide region in which the formulas obtained by neglecting striction are valid.

In the present paper we shall consider the temperature region above the transition point. Deferring a detailed investigation of the Green's function to the next section, we calculate here the $\Delta^2(T)$ dependence accurate to terms of first order in the anharmonicity.

It will be helpful later if we examine separately the case in which the second-order transition actually does not take place down to the absolute zero of temperature, so that the spectrum has a gap, albeit, a small one, at T = 0. Equation (7) then has no solutions, but such a crystal is close to the phase transition. For example, the "zero" gap may vanish on a pressure change, and this may be followed by the transition at T = 0 that was mentioned in the Introduction. We introduce the quantity

$$\Delta_0^2 = \Delta^2(T = 0) = \eta + \Sigma(0, 0; 0), \tag{8}$$

whereupon we have from (4)

$$\delta\Delta^2(T) = \Delta^2(T) - \Delta_0^2 = \Sigma(0, 0; T) - \Sigma(0, 0; 0). \tag{9}$$

The contribution to $\delta\Delta^2$ from diagram 1d takes the form

$$-\frac{1}{2}g_0 v\int\frac{d^3\mathbf{k}}{(2\pi)^3}\left\{T\sum_{\varepsilon_n}\mathscr{D}(\mathbf{k},\varepsilon_n;T)-\frac{1}{2\pi}\int\mathscr{D}(\mathbf{k},z;0)\,dz\right\},\qquad(10)$$

where $v = V/N$ is the volume of the unit cell. Here we have gone from summation over **k** to integration. We see further that, accurate to terms of first order in the anharmonicity, Σ does not depend on **k** or ϵ_n. We therefore have, with the same degree of accuracy, at small values of **k**

$$\mathscr{D}^{-1}(\mathbf{k},\varepsilon_n;T)=-(\Delta^2(T)+\varepsilon_n^2+\beta\mathbf{k}^2).\qquad(11)$$

Substituting (11) in (10) and carrying out summation and integration with respect to ϵ_n and z, we obtain[3)]

$$\delta\Delta^2=4g\int_0^\Theta\left(\frac{1}{\sqrt{\Delta^2+x^2}}\operatorname{cth}\frac{\sqrt{\Delta^2+x^2}}{2T}-\frac{1}{\sqrt{\Delta_0^2+x^2}}\right)x^2\,dx.\qquad(12)$$

Here $\Theta = \sqrt{\beta}\,k_m$, where k_m characterizes the region of momentum space where the deviations from the quadratic dependence are small:

$$g=\alpha g_0,\qquad \alpha=v\,/\,32\pi^2\beta^{3/2},$$

$g \ll 1$ is the dimensionless anharmonicity constant, in terms of which the expansion is carried out.

Expression (12) constitutes an equation for the determination of Δ^2. At small values of g, it is possible simply to replace Δ^2 by Δ_0^2 in the right-hand side, so that the final answer is

$$\delta\Delta^2(T)=4g\int_0^\Theta\frac{x^2dx}{\sqrt{\Delta_0^2+x^2}}\left(\operatorname{cth}\frac{\sqrt{\Delta_0^2+x^2}}{2T}-1\right).\qquad(13)$$

Were we to determine from (12) the next correction to $\delta\Delta^2$ with respect to g, then it would be of relative order $g\ln(\Theta^2/m^2)$, $m = \max\{\Delta_0, T\}$, so that formula (13) ceases to hold in the vicinity of $g\ln(\Theta^2/m^2) \gtrsim 1$. Similar logarithmic corrections also arise in the next orders of perturbation theory. The approximation (11) for the Green's function does not suffice for a correct calculation of these corrections. The corresponding formula (50) with allowance for the logarithmic corrections is obtained in Sec. 3. Here we confine ourselves to the case $g\ln(\Theta^2/m^2) \ll 1$.

In (13) we can separate three characteristic regions of temperature behavior of the gap:[4)]

a) $\Theta \gg \Delta_0 \gg T$:

$$\delta\Delta^2\approx 4\sqrt{2}\pi\, g\Delta_0^2(T\,/\,\Delta_0)^{3/2}e^{-\Delta_0/T}.\qquad(14)$$

In [9], on the basis of microscopic considerations, a similar exponential dependence was obtained. However, as will be shown below, in this region a large contribution ($\sim T^4$) is made by the diagram 1e, which is connected with the interaction with acoustic phonons.

b) $\Theta \gg T \gg \Delta_0$—quadratic region:

$$\delta\Delta^2\approx 8\zeta(2)gT^2,\qquad(15)$$

$\zeta(2)$ is the Riemann zeta function.

c) $T \gg \Theta$—the Curie-Weiss region:

$$\delta\Delta^2\approx 8g\Theta(T-{}^1\!/_4\Theta).\qquad(16)$$

In this region the critical phonons can be regarded classically and the linear Curie-Weiss law is fulfilled. We emphasize, however, that formula (16) has only a qualitative meaning, for to determine the parameters of the linear part it is necessary to take into account the nonquadratic character of the spectrum at large **k**, and also the interaction with other branches.

In the same manner we can calculate the contribution made to $\delta\Delta^2$ by the diagrams of Fig. 1e. We have

$$\delta\Delta^2=\frac{g_1 v}{8\pi^2c^5}\int_0^{\Theta_1}\left(\operatorname{cth}\frac{x}{2T}-1\right)x^3\,dx.\qquad(17)$$

We have used here for the calculations the isotropic spectrum of the acoustic phonons at small **k**: $\omega^a(\mathbf{k}) = ck$; $\Theta_1 = ck_{m_1}$, k_{m_1} characterizes the region of linearity of the acoustic branch of the spectrum.

In the region of low temperatures $T \ll \Theta_1$, Eq. (17) behaves like

$$\delta\Delta^2\approx\frac{3\zeta(4)}{2\pi^2}\frac{g_1 v}{c^5}T^4.\qquad(18)$$

It is therefore smaller than the contribution from (15). The smallness of the contribution from the interaction with the acoustic phonons is connected with the fact that the corresponding anharmonic potentials are small (see (5)). A similar situation also obtains in the next orders of perturbation theory, so that in the region of low temperatures the decisive role is played by the anharmonicity connected with the interaction of the critical phonons. Only this anharmonicity will be considered in what follows. It is necessary, to be sure, to note that if the critical branch drops sufficiently low, degeneracy of the critical and acoustic oscillations appears in some momentum region. Allowance for the interaction between them causes them to become entangled with one another (we have in mind the branches for which there are no hindrances imposed by symmetry). However, to determine the temperature dependence of the gap these effects can probably be disregarded.

Let us consider now the case of the phase transition. Then Eq. (7) has a solution, and from (4) it follows that

$$\Delta^2=\Sigma(0,0;T)-\Sigma(0,0;T_c).\qquad(19)$$

In the calculation of (19), accurate to terms of first order, it is possible to use the approximation (11). After simple calculations we obtain the following equation for Δ^2:

$$\Delta^2=4g\int_0^\Theta x^2\left(\frac{1}{\sqrt{\Delta^2+x^2}}\operatorname{cth}\frac{\sqrt{\Delta^2+x^2}}{2T}-\frac{1}{x}\operatorname{cth}\frac{x}{2T_c}\right)dx.$$

Neglecting, as before, the logarithmic corrections, we have

$$\Delta^2=8g\left[T^2f\left(\frac{\Theta}{T}\right)-T_c^2f\left(\frac{\Theta}{T_c}\right)\right],\qquad(20)$$

where

$$f(t)=\int_0^t\frac{x\,dx}{e^x-1}.$$

In the region of low temperatures (T, $T_c \ll \Theta$), expression (20) takes the form

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[3)] We write out all the formulas for the quadratic dispersion law, a procedure valid at sufficiently low temperatures, when the main contribution to (10) is made by the region of small k. It is easy to write a general formula for an arbitrary type $\omega_0(\mathbf{k})$.

[4)] It is assumed here that $\Delta_0 \ll \Theta$. If $\Delta_0 \gtrsim \Theta$, then the region b) is missing.

$$\Delta^2 = 8g\zeta(2)(T^2 - T_c^2). \quad (21)$$

A similar formula (51), in which account is taken of the logarithmic corrections, is derived in Sec. 3. In the region $T \gg \Theta$, Δ^2 depends linearly on T, and the Curie-Weiss law holds. Formulas (20) and (21) determine Δ^2 accurate to terms $\sim(gT)^2$. Formula (21) is the equivalent of the Curie-Weiss law at low temperatures.

If $\Delta_0 = 0$ and $T_C = 0$, then formulas (13) and (20) coincide. Moreover, the parameter Δ_0^2 in a real crystal is determined by the force constants and depends on the pressure, impurity concentration, etc. We have already noted that when these quantities change, Δ_0^2 can vanish and then become negative. Then the first case goes over into the second, and a phase transition arises at a nonzero temperature. At small changes of the pressure, the dependence of Δ_0^2 on P is of the form[5]

$$\Delta_0^2 = \sigma(P_0 - P). \quad (22)$$

Then, using (7), (13), and (20) we obtain an equation for the transition curve (in the P, T plane), accurate to terms of third order in g:

$$\sigma(P - P_0) = 8gT^2 f(\Theta / T). \quad (23)$$

Let us compare the formulas obtained in the present section with the results of [5-7]. In [5,7] a neutron-diffraction study was made of the critical oscillations in SnTe and in $KTaO_3$. The temperature dependence of $\Delta^2(T)$, measured in these investigations, deviates from the linear Curie-Weiss law at low temperatures. The alloy SnTe has a simple crystal structure of the NaCl type and is apparently stable down to T = 0. Using the results of [5], we can estimate the constants that enter in our theory. We have $\Delta_0 \approx 21°K$, $g \approx 2.1 \times 10^{-2}$, $\Theta \sim 50°K$, $\beta \sim 1 \times 10^{-11}$ deg^2 cm^2. Formula (13) describes satisfactorily the results of the measurement of $\Delta^2(T)$, see Fig. 2. Unfortunately, in the temperature region of greatest interest to us, only two measurements were made in [5], at T = 6.42°K. More detailed measurements of $\Delta^2(T)$ at low temperatures would make it possible to determine more accurately the anharmonic constants.

It is known also that SnTe forms a continuous series of solid solutions in GeTe in a wide range of concentrations. According to the measurements of [6], a second-order phase transition takes place in this alloy from the cubic structure into a rhombohedral one with decreasing temperature or with increasing GeTe concentration at T = const; the transition temperature depends almost linearly on the GeTe concentration. The authors of [6] extrapolated their measured linear dependence into the region of low temperatures and low concentrations of GeTe, and reached the conclusion that in pure SnTe there occurs a phase transition near T = 0°K; this, however, is in contradiction to the results of [5]. It is possible that this contradiction is connected with the following circumstance: at low temperatures, owing to quantum effects, the transition curve deviates from the linear relation, so that extrapolation of the linear section gives a nonexistent transition point for SnTe. Such an assumption is in good qualitative agreement with formula (23), see Fig. 3.

In $KTaO_3$ the situation is more complicated. Here at $T \approx 10°K$ there apparently occurs a first-order phase transition close to a second-order transition.[7] A circumstance of importance to us here is that $\Delta^2(T)$, as measured in [7], reveals no anomalies connected with this transition. Its temperature variation above the transition is in good agreement with formula (13), see Fig. 4. We present estimates for the constants entering in formula (13): $\Delta_0 \approx 31°K$, $g \approx 8 \times 10^{-2}$, $\Theta \sim 100°K$, $\beta \sim 2.7 \times 10^{-11}$ deg^{2}cm^2. We emphasize that the constant g for SnTe and $KTaO_3$ was estimated only from the nonlinear low-temperature part of the measurements of [5,7].

3. THEORY IN THE "PARQUET" APPROXIMATION

We have already mentioned that the applicability of the formulas derived in the preceding section is limited by the condition

$$g \ln \frac{\Theta^2}{m^2} \ll 1.$$

We now derive formulas free of this limitation. In SnTe and $KTaO_3$, the constant g is quite small and the logarithmic corrections are significant in the unattainable vicinity of the phase-transition point and at very low temperatures. However, it is possible that substances with large values of g also exist. Regardless of this, the complete solution of the problem is of considerable theoretical interest. As usual, the presence of logarithmic terms makes it possible to separate principal diagrams in each order of perturbation theory. These diagrams form a "parquet".[16] The problem of the second-order phase transition at T = 0 turns out to be formally equivalent to the problem of the phase transition in systems with dipole-dipole interaction, solved by Larkin

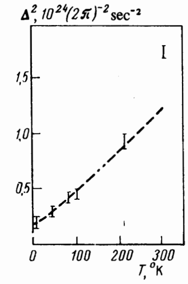

FIG. 2

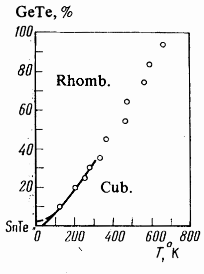

FIG. 3

FIG. 2. $\Delta^2(T)$ plot for SnTe [5]. The dashed curve was calculated from formula (13).

FIG. 3. Transition curve (concentration vs. temperature) for the alloy SnTe-GeTe [6].

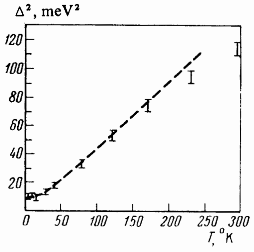

FIG. 4. Plot of $\Delta^2(T)$ for $KTaO_2$ [7]. The dashed curve was calculated from formula (13).

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[5] Actually the bare gap in the Hamiltonian η depends linearly on P. It will be shown in Sec. 3, however, that expression (22) is valid if logarithmic corrections are neglected. By P we can also mean the concentration of the impurities. We do not specify here concretely $\sigma \gtrless 0$.

and Khmel'nitskiĭ at a finite temperature within the framework of classical statistics.[17]

A. Let us investigate the Green's function. We begin with the case T = 0. From (3) we have

$$\mathcal{D}^{-1}(k,\eta) = -\{\eta + k^2 + \Sigma(k,\eta)\}.$$

Here, to simplify the notation, we have introduced the four-vector $k = \{\sqrt{\beta}\,\mathbf{k}, z\}$ (not to be confused with $|\bar{\mathbf{k}}|$),

$$k^2 = z^2 + \beta\mathbf{k}^2.$$

If η is regarded as a parameter, then the physical singularity corresponding to the transition of first order is realized for $\eta = \eta_c$ as determined from (7) at $T_c = 0$. When we are near such a singularity, it is convenient to use as the origin for η the point $\eta = \eta_c$. This corresponds to representation of the Green's function in the form

$$\mathcal{D}^{-1}(k,\tau) = -\{\tau + k^2 + \Sigma(k,\tau) - \Sigma(0,0)\}, \tag{24}$$

where $\tau = \eta - \eta_c > 0$. The self-energy part Σ can be expressed in terms of the complete vertex[12]

$$\Sigma(k) = -\frac{g_0}{2}\int \mathcal{D}(q)\frac{d^4q}{(2\pi)^4} + \frac{g_0}{6}\int \mathcal{D}(q_1)\mathcal{D}(q_2)\mathcal{D}(q_1+q_2-k) \times \Gamma(q_1, q_2, q_1+q_2-k, k)\frac{d^4q_1 d^4q_2}{(2\pi)^8}.$$

The complete vertex part Γ is expressed in the form of an infinite aggregate of diagrams with increasing powers of g, expressed in terms of the complete Green's functions,[12] Fig. 5.

The result is a very complicated, unclosed (since the number of diagrams is infinite) integral equation. We shall investigate it by the iteration method. As the zeroth approximation we choose a Green's function in the form

$$\mathcal{D}_{(0)}^{-1}(k,\tau) = -(\tau + k^2). \tag{25}$$

We first separate in (24) that part of Σ which does not depend on k; we have

$$\mathcal{D}^{-1}(k,\tau) = -\{\Delta_0^2(\tau) + k^2 + \Pi(k,\tau)\}, \tag{26}$$

where

$$\Delta_0^2(\tau) = \tau + \Sigma(0,\tau) - \Sigma(0,0), \tag{27}$$

$$\Pi(k,\tau) = \Sigma(k,\tau) - \Sigma(0,\tau). \tag{28}$$

We consider first the expression for Π. The first nonzero contribution to Π is made by the diagram of Fig. 6. As a result of a calculation of this diagram we obtain

$$\Pi_2 = {}^1\!/_3 k^2 g^2 \ln(\Theta^2/\mu^2), \quad \mu^2 = \max\{k^2, \tau\}.$$

Let us determine the approximation in which we shall solve the problem. We include in the consideration τ so small that $g\ln(\Theta^2/\tau) \gtrsim 1$, assuming at the same time that $g^2\ln(\Theta^2/\tau) \ll 1$. In this case it is necessary to take into account diagrams that yield corrections of the type $(g\ln(\Theta^2/\tau))^n$, and neglect corrections of the type $g^m(g\ln(\Theta^2/\tau))^n$. The resultant problem of separating and summing the required diagrams is called the "parquet" problem,[16] since the diagrams for the vertex part, which must be taken into account, form a parquet. The next-higher corrections to Π result from allowance for the corrections to the vertex. As will be seen below, in the "parquet" approximation, accurate to the logarithmic functions, we have $\Gamma \sim g_0$. Consequently, in our approximation $\Pi(k,\tau) \ll k^2$.

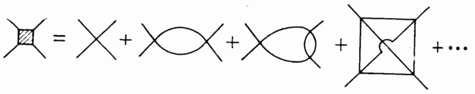

FIG. 5

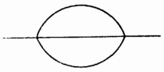

FIG. 6

The complete vertex Γ in the "parquet" approximation was calculated in many papers. This was done most brilliantly, in our opinion, in [18] using a summation method proposed by Sudakov.[16] Without dwelling on the details of the calculations, we present only an equation for Γ obtained by summation of the "parquet" diagrams, and its solution in our case (see Fig. 7):

$$\Gamma(\xi,\zeta,\nu) = g_0 - 3\alpha\int_0^\xi \Gamma^2(x,x,x)\,dx - \alpha\int_\xi^\zeta \Gamma(\xi,x,x)\Gamma(x,x,x)\,dx - \alpha\int_\zeta^\nu \Gamma(\xi,x,x)\Gamma(\zeta,x,x)\,dx,$$
$$\Theta^2 \gg k^2 \gg q^2 \gg p^2 \gg \tau. \tag{29}$$

We have introduced here the logarithmic variables

$$\xi = \ln\frac{\Theta^2}{k^2}, \quad \zeta = \ln\frac{\Theta^2}{q^2}, \quad \nu = \ln\frac{\Theta^2}{p^2}, \quad x = \ln\frac{\Theta^2}{q_1^2}, \quad l = \ln\frac{\Theta^2}{\tau},$$
$$0 \lesssim \xi \lesssim \zeta \lesssim \nu \lesssim l,$$

$$\Gamma(\xi,\zeta,\nu) = \frac{2g_0}{(1+3g\xi)^{2/3}(1+3g\zeta)^{1/3}} - \frac{g_0(1+3g\nu)^{1/3}}{(1+3g\xi)^{2/3}(1+3g\zeta)^{2/3}} \tag{30}$$

We now calculate $\Delta_0^2(\tau)$. Differentiating (27) with respect to τ, we get

$$\frac{\partial\Delta_0^2}{\partial\tau} = 1 + \frac{\partial\Sigma(0,\tau)}{\partial\tau}.$$

We use the Ward identity

$$\frac{\partial\mathcal{D}^{-1}(k,\tau)}{\partial\tau} = -1 - \frac{\partial\Sigma(k,\tau)}{\partial\tau} = \mathcal{T}(k,\tau), \tag{31}$$

$$\mathcal{T}(k,\tau) = -1 + \frac{1}{2}\int \Gamma(k,q)\mathcal{D}^2(q)\frac{d^4q}{(2\pi)^4}. \tag{32}$$

Using (30), we easily obtain

$$\mathcal{T}(\xi,l) = -\left[\frac{2}{(1+3g\xi)^{1/3}} - \frac{(1+3gl)^{1/3}}{(1+3g\xi)^{2/3}}\right] \tag{33}$$

Then, at our accuracy,

$$\partial\Delta_0^2(\tau)/\partial\tau = -\mathcal{T}(0,\tau) = -\mathcal{T}(l,l) = (1+3gl)^{-1/3}$$

or with allowance for the boundary condition

$$\Delta_0^2(0) = 0. \tag{34}$$

we obtain ultimately

$$\Delta_0^2(\tau) = \tau\left(1 + 3g\ln\frac{\Theta^2}{\tau}\right)^{-1/3}. \tag{35}$$

Thus, in the "parquet" approximation the Green's function takes the form

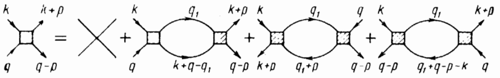

FIG. 7

$$\mathscr{D}^{-1}(k,\tau) = -\left[\tau\left(1+3g\ln\frac{\Theta^2}{\tau}\right)^{-1/3} + k^2\right]. \tag{36}$$

B. We consider a second-order phase transition at T = 0 with change of pressure. As noted in Sec. 2, in this case6)

$$\tau = \sigma(P_0 - P) > 0. \tag{37}$$

An anomalous behavior should be observed in such a transition in the susceptibility and in the compressibility. The static susceptibility is expressed in terms of the Green's function at k = 0:[12,19] 7)

$$\chi_{\alpha\beta} = -\lambda_{\alpha\beta}\mathscr{D}(0,\tau). \tag{38}$$

Using (36)–(38), we obtain

$$\chi_{\alpha\beta} = \frac{\lambda_{\alpha\beta}}{\sigma(P_0-P)}\left[1+3g\ln\frac{\Theta^2}{\sigma(P_0-P)}\right]^{1/3}. \tag{39}$$

Let us calculate the contribution made to the compressibility by the critical oscillations. The contribution of the critical phonons to the energy of the crystal is

$$E_{sph} = \langle\Psi|\hat{H}_0 + \hat{H}_{int}|\Psi\rangle.$$

The averaging here is over the ground state of the interacting critical phonons. E_{sph} can be regarded as a small correction to the energy of the entire crystal. Then, using the theorem that small corrections to all the thermodynamic potentials, expressed in terms of their variables, are identical,[20] we obtain for the contribution to the compressibility

$$(\partial V/\partial P)_{sph} = \partial^2 E_{sph}/\partial P^2.$$

Let us calculate $\partial E_{sph}/\partial P$:

$$\frac{\partial E_{sph}}{\partial P} = \left\langle\frac{\partial\Psi}{\partial P}|\hat{H}|\Psi\right\rangle + \left\langle\Psi|\hat{H}|\frac{\partial\Psi}{\partial P}\right\rangle + \left\langle\Psi\left|\frac{\partial\hat{H}}{\partial P}\right|\Psi\right\rangle.$$

The sum of the first two terms is equal to zero,[21] and then

$$\frac{\partial E_{sph}}{\partial P} = -\frac{\sigma}{2}\sum_{\mathbf{k}}\langle\xi_{\mathbf{k}}\xi_{-\mathbf{k}}\rangle = \frac{\sigma V}{2}\int\mathscr{D}(q)\frac{d^4q}{(2\pi)^4}. \tag{40}$$

We differentiate (40) once more with respect to P and use the Ward identity (31) and (32). We have

$$\left(\frac{\partial V}{\partial P}\right)_{sph} = \frac{\sigma^2 V}{2}\int\mathscr{D}^2(q)\mathscr{T}(q)\frac{d^4q}{(2\pi)^4}$$

Substituting (33) for $\mathscr{T}$, we obtain after simple manipulation

$$\left(\frac{\partial V}{\partial P}\right)_{sph} = -\frac{\sigma^2 N}{g_0}\left[\left(1+3g\ln\frac{\Theta^2}{\sigma(P_0-P)}\right)^{1/3} - 1\right]. \tag{41}$$

We note once more the similarity of formulas (36), (39), and (41) to the formulas of [17].

C. Let us consider the case of nonzero temperatures. We shall carry out the investigation in accordance with the same scheme as in Item A, but now in the calculation of the diagrams the integrals with respect to Z are replaced by sums over ω_n. The Green's function is written in the form (26)–(28), but now $k = \{\sqrt{\beta}\,\mathbf{k}, \epsilon_n\}$, $k^2 = \epsilon_n^2 + \beta\mathbf{k}^2$, and $\Delta^2(T)$, $\Sigma(k;T)$, $\Pi(k;T)$ depend also on the temperature. As before, let us estimate the region in which we can neglect Π compared with k^2 and use expression (11) for the Green's function. A study of the first nonzero correction to Π using (11) shows that there are two principal contributions to Π_2 (Fig. 6). The first has the same form as when T = 0:

$$\Pi_2 = {}^1\!/_3\, k^2 g^2 \ln\frac{\Theta^2}{\mu^2}, \quad \mu^2 = \max\{k^2, \Delta^2, T^2\}.$$

It is due to integration and summation over the internal momenta and frequencies in the region $q^2 \gg \mu^2$ in which the summation over ω_n can be replaced by integration. The second principal term is connected with the term in which all the frequencies are equal to zero. Calculation yields for it the following estimate:

$$\Pi_2(k) \ll \beta k^2 \text{ in the region } \Delta^2 \gg {}^{32}\!/_3\pi^2(gT)^2. \tag{42}$$

Let us consider now the corrections to the vertex. In each order of perturbation theory the major role is assumed here by the logarithmic corrections and by the corrections due to the terms with zero frequencies. The former are of the order of $(g\ln(\Theta^2/m^2))^n$, $m^2 = \max\{\Delta^2, T^2\}$, and the latter $(2\pi Tg/\Delta)^n$. We shall henceforth consider $\Delta \gg 2\pi gT$, which coincides with the condition (42) and corresponds to smallness of the classical fluctuations connected with the terms having zero frequencies. As to the logarithmic corrections, they will be taken into account, just as at T = 0, in the "parquet" approximation.

We now calculate $\Delta^2(T)$ with allowance for the logarithmic corrections. We note that to this end it is no longer possible to use differentiation with respect to τ using the Ward identity, as was done in the calculation of Δ_0^2. The point is that we do not have a boundary condition of the type (34) for $\Delta^2(T)$. We shall therefore use another method here.

We note first that as a result of variation of the self-energy part with respect to the complete Green's function, we obtain the relation

$$\delta\Sigma(k;T) = -\frac{1}{2}T\sum_{\omega_n}\int\tilde{\Gamma}(k,q;T)\,\delta\mathscr{D}(q;T)\frac{d^3q}{(2\pi)^3} \tag{43}$$

where $\tilde{\Gamma}(k,q;T)$ differs from the complete vertex part $\Gamma(k,q;T)$ in that it contains no diagrams that can be cut along two lines in such a way that we have on the left the momenta k, k and on the right q, q, or vice versa (for example, the diagram of Fig. 8 8)). To prove (43) it is necessary to vary the diagrams for Σ, expressed in terms of the complete Green's functions, i.e., in all the diagrams for Σ it is necessary to cut up each Green's function, denoting each time its momentum and frequency by q and ω_n, and then sum the vertices obtained in this manner.

The vertex $\tilde{\Gamma}(k,q;T)$ can be calculated in the "parquet" approximation. Just as in Item A, in calculating

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6)The dependence of τ on the pressure is connected with striction effects. We, however, will not stop to discuss this question, deferring it to a detailed study of striction effects.

7)The contribution made to the Hamiltonian by the interaction of the critical oscillations with the electric field E is of the form $-\sqrt{N}\xi_0 sE$, with $\lambda_{\alpha\beta} = v^{-1}s_\alpha s_\beta$, and the vector s can be readily expressed in terms of the polarization vectors at k = 0, and also the masses and charges of the ions of the unit cell [19].

8)In [12] (pp. 224 and 228) there is an error. It is assumed there that the complete vertex part enters in (43).

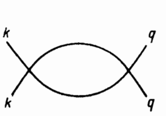

FIG. 8

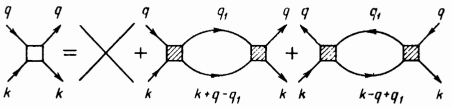

FIG. 9

the total vertex Γ we write down the equation for $\tilde{\Gamma}(k, q, T)$, using the Sudakov method in the summation of the diagrams (see Fig. 9). We have

$$\tilde{\Gamma}(y) = g_0 - 2\alpha \int_0^y \Gamma^2(x, x, x)\,dx, \tag{44}$$

where

$$y = \ln(\Theta^2 / \mu^2), \quad \mu^2 = \max(k^2, q^2, \Delta^2, T^2\}, \quad x = \ln(\Theta^2 / q_1^2).$$

Using (30), we obtain from (44)

$$\tilde{\Gamma}(y) = g_0 \frac{1 + gy}{1 + 3gy}. \tag{45}$$

Just as in Sec. 2, we consider first the case when the crystal is close to the transition, but remains stable down to T = 0.

We introduce the function

$$f(k; T) = \Sigma(k; T) - \Sigma(k; 0), \tag{46}$$

we then have from (9)

$$\delta\Delta^2(T) = f(0; T).$$

Using (43), we can represent (46) at low temperatures in the form

$$f(k; T) \approx -\frac{1}{2} T \sum_{\omega_n} \int \frac{d^3q}{(2\pi)^3} \tilde{\Gamma}(k, q; 0) \{\mathscr{D}(q; T) - \mathscr{D}(q; 0)\}$$
$$- \frac{1}{2} \int \frac{d^3q}{(2\pi)^3} \Big\{ T \sum_{\omega_n} - \frac{1}{2\pi} \int dz \Big\} \tilde{\Gamma}(k, q; 0) \mathscr{D}(q; 0). \tag{47}$$

In the first term of (47), the main contribution is made by the logarithmic region

$$q^2 = \omega_n^2 + \beta \mathbf{q}^2 \gg m^2 = \max\{\Delta^2,\ T^2\}.$$

The integral with respect to q in the second term converges rapidly after summation over ω_n and integration with respect to z, and therefore the slow function $\tilde{\Gamma}$ can be taken outside the integral sign. As a result we obtain the following equation for f:

$$f(\xi, l) = -\alpha \int_0^l \tilde{\Gamma}(\xi, x) f(x, l)\,dx + \frac{1 + g\xi}{1 + 3g\xi} J, \tag{48}$$

where

$$\xi = \ln \frac{\Theta^2}{k^2}, \quad l = \ln \frac{\Theta^2}{m^2}, \quad x = \ln \frac{\Theta^2}{q^2}$$

and it is assumed that $0 < \xi \lesssim l$, and J is determined by formula (13). The integral equation (48) can be reduced to a differential equation. Differentiating it twice with respect to ξ, we obtain

$$(1 + 3g\xi)^2 \frac{\partial^2 f(\xi, l)}{\partial \xi^2} + 6g(1 + 3g\xi) \frac{\partial f(\xi, l)}{\partial \xi} + 2g^2 f(\xi, l) = 0 \tag{49}$$

with boundary conditions

$$f(l, l) = -\alpha \int_0^l \tilde{\Gamma}(l, x) f(x, l) + \frac{1 + gl}{1 + 3gl} J,$$
$$\left. \frac{\partial f(\xi, l)}{\partial \xi} \right|_{\xi = l} = -\frac{2gJ}{(1 + 3gl)^2}.$$

The solution of Eq. (49) with allowance for the boundary conditions takes the form

$$f(\xi, l) = \frac{J}{(1 + 3g\xi)^{2/3} (1 + 3gl)^{1/3}}.$$

It is easy to see that

$$f(0; T) = f(l, l) = J(1 + 3gl)^{-1}.$$

Thus, we ultimately obtain[9)]

$$\delta\Delta^2(T) = \frac{4g}{1 + 3g \ln(\Theta^2/m^2)} \int_0^\Theta \frac{x^2\,dx}{\sqrt{\Delta_0^2 + x^2}} \left(\operatorname{cth} \frac{\sqrt{\Delta_0^2 + x^2}}{2T} - 1 \right), \tag{50}$$
$$m^2 = \max\{\Delta_0^2, T^2\}.$$

Omitting analogous calculations, we present a formula for the temperature dependence of the square of the gap in the case of a phase transition in the low-temperature region:

$$\Delta^2(T) = 8g\zeta(2) \frac{T^2 - T_c^2}{1 + 3g \ln(\Theta^2/T^2)}, \quad T, T_c \ll \Theta. \tag{51}$$

Using (38), we obtain immediately for the static susceptibility in this case the formula

$$\chi_{\alpha\beta}(T) = \frac{\lambda_{\alpha\beta}}{8g\zeta(2)} \frac{1 + 3g \ln(\Theta^2/T^2)}{T^2 - T_c^2}. \tag{52}$$

In conclusion, I am deeply grateful to L. P. Pitaevskiĭ for suggesting the problem and for numerous discussions, and also to A. I. Larkin and D. E. Khmel'nitskiĭ for useful discussions.

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9) By way of illustration it is useful to obtain formula (35) for Δ_0^2 by the method employed here.

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