Influence of collective modes on the order of the phase transition

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It is shown that the contribution made to the system energy by the zero-point oscillations of the order parameter near the phase-transition point determines essentially the order of the phase transition. For example, in the case of a structure phase transition, such an oscillation is a soft phonon mode, with which the lattice instability is connected and which vanishes only at the transition point. This behavior of the branch of the collective excitations leads to a first-order phase transition.

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1. It is known that a structural instability takes place in systems whose electron spectrum $\epsilon(\mathbf{k})$ satisfies the condition $\epsilon(\mathbf{k}) = -\epsilon(\mathbf{k}+\mathbf{q})$ near the Fermi surface. The symmetry of the restructured lattice is determined by the vectors $\mathbf{q}$. In the self-consistent-field approximation, the transition turns out to be second order and is the consequence of the appearance of a soft mode, the oscillation frequency of which at momenta $\mathbf{q}$ vanishes only at the transition point. This nonanalyticity makes the similarity in the total energy near the transition point stronger than the singularity in the self-consistent part of the energy (the Hartree energy). As a result, the structural transformation proceeds via a first-order phase transition. We shall demonstrate this first with the two-band model with hybridization, which was investigated in[1], inasmuch as the phase transition in it can result from a change in the hybridization parameter at $T = 0$.

2. We neglect the Coulomb interaction in comparison with the electron-phonon interaction. Allowance for the Coulomb interaction leads simply to a renormalization of the effective coupling constant. The Hamiltonian of the system can be written in the following form[1]:

$$H = \sum_{\mathbf{k}} \left\{ \epsilon(\mathbf{k}) \left(a^{+}_{1\mathbf{k}} a_{1\mathbf{k}} - a^{+}_{2\mathbf{k}} a_{2\mathbf{k}} \right) + \frac{\hbar}{m_0} \left(\mathbf{p}\mathbf{k}\, a^{+}_{1\mathbf{k}} a_{2\mathbf{k}} + \text{c.c.} \right) \right.$$
$$\left. + g \sum_{\mathbf{k},\mathbf{q}} \left\{ a^{+}_{1\mathbf{k}} a_{2\mathbf{k}+\mathbf{q}} (b^{+}_{\mathbf{q}} + b_{-\mathbf{q}}) + \text{c.c.} \right\} + \hbar\omega_0 \sum_{\mathbf{k}} b^{+}_{\mathbf{k}} b_{\mathbf{k}} \right. . \tag{1}$$

Here ω_0 is the unrenormalized frequency of the unstable phonon mode, g is the electron-phonon coupling constant, and $\mathbf{p}$ is the matrix element of the momentum operator for the interband transition. The interband term $(\hbar/m_0)\mathbf{p}\cdot\mathbf{k} \equiv V$ will for simplicity be regarded as constant in absolute value $|V|$ and as reversing sign at those momenta $\mathbf{k}$ at which the scalar product goes through zero.

Introducing the anomalous electron Green's function $G_{21} = -i\langle Ta_{1k}a^{+}_{2k}\rangle$ and the phonon mean values $\langle b^{+}_0 + b_0\rangle$, [1] we obtain at $T=0$ the following expression for the order parameter Δ, which is proportional to the mean value $b^{+}_0 + b_0$,

$$\Delta = \sqrt{\Delta_o^2 - |V|^2}. \tag{2}$$

where

$$\Delta_o = 2\epsilon_F \exp\left\{ \frac{-1}{4N(0)\, g^2/\omega_o} \right\}$$

and $N(0)$ is the density of state at the Fermi level. It is seen from (2) that a phase transition occurs when a change takes place in the value of V or in the coupling constant g, when $\Delta_0 \gtrsim |V|$.

By directly averaging the Hamiltonian (1) we can obtain the following expression for the change of the energy E_c (in the self-consistent approximation) in the course of the phase transition:

$$E_c = -\Delta^2 + |V|^2 \ln\left(1 + \frac{\Delta^2}{|V|^2}\right). \tag{3}$$

At small Δ ($\Delta \ll |V|$), i.e., near the phase-transition point, we obtain from this

$$E_c \approx -\Delta^4/|V|^2, \tag{4}$$

i.e., the second derivative of E_c with respect to $|V|$ (or with respect to the volume, since V depends on the volume) experiences a discontinuity, as should be the case in a second-order phase transition.

At a fixed level of V (including $V=0$), the discontinuity takes place in the second derivative of the free energy with respect to temperature.

3. We shall show now that inclusion in the energy of a contribution from the zero-point oscillations of the collective modes on top of the self-consistent part (the influence of the quantum oscillations) leads to a first-order phase transition. In a structural transformation, such oscillations are the phonons of the "soft mode." The change of the free energy in the system is the result of the electron-phonon interaction can be expressed in terms of the complete phonon Green's function D [2]:

$$\delta F = T \int_0^g \frac{dg}{g} \sum_{\omega_n} \int \frac{d\mathbf{k}^3}{(2\pi)^3} D_o^{-1}(\omega_n, \mathbf{k})[D(\omega_n, \mathbf{k}) - D_o(\omega_n, \mathbf{k})], \tag{5}$$

where D_0 is the Green's function of the free phonons.

Expression (4) contains a sum of the correlation energy and the exchange energy. It does not contain the Hartree energy [see (3)]. In the high-density approximation, the polarization operator in the Dyson equation for the D functions expressed in terms of the loop diagrams on the normal and anomalous electron functions with zero vertices. For low-wave oscillations of the soft optical mode we obtain from the pole of the D function

$$\omega(\mathbf{k}) = \sqrt{\omega^2(0) + c^2\mathbf{k}^2}; \tag{6}$$

$$\omega^2(0) \simeq 4g^2N(0)\omega_0|\eta|, \qquad \eta = \frac{|V| - \Delta_0}{\Delta_0}. \tag{7}$$

Thus, it is seen from (6) and (7) that the frequency $\omega(\mathbf{k})$ of the mode decreases as the transition point is approached, vanishes at $\mathbf{k}=0$ at the transition point, and begins to increase from zero below the transition point. A similar behavior is observed also when the temperature is varied. Only at the transition point this mode becomes acoustic, this being a consequence of the fixation of the phase of the order parameter, both because of the hybridization term in (1) and of the electron-phonon interaction.[1] In the jellium model, or in the case when the periods of the lattice and of the displacement wave are incommensurate, the phase of the order parameter is arbitrary[3] and therefore two modes appear below the transition point. One behaves in analogy with (7) and the other is acoustic everywhere below the transition point.

Formula (5) for δF can be transformed in analogy with plasma theory[4] into

$$\delta F = \int \frac{d\mathbf{k}^3}{(2\pi)^3}[F(\omega_{(\mathbf{k})}) - F(\omega_0)], \quad F(x) = \frac{\hbar x}{2} + T\ln(1 - e^{-\hbar x/T}), \tag{8}$$

i.e., it reduces to summation, over $\mathbf{k}$, of the difference of the free energies of harmonic oscillators of the renormalized and nonrenormalized frequencies.

Substituting in (8) at $T=0$ expressions (6) and (7) for $\omega(\mathbf{k})$ we see readily that δF, and consequently also the total energy, behaves in the vicinity of the transition point in nonanalytic manner as a function of η (and consequently also of the volume) (see the figure). The first derivative of the energy with respect to η, which is proportional to the pressure, has a discontinuity at the transition point, i.e., a first-order transition takes place. Therefore, the result obtained in[5], namely that the phase transition in the model of the excitonic insulator is of first order if account is taken of the annihilation interaction, is in fact due to the singular [of the type (6)] behavior of the collective exciton mode. In the case of phase degeneracy, if a mode of the type (6) is present in addition to the acoustic mode of the collective excitations (as in the one-dimensional jellium model[3]), the transition is of first order.

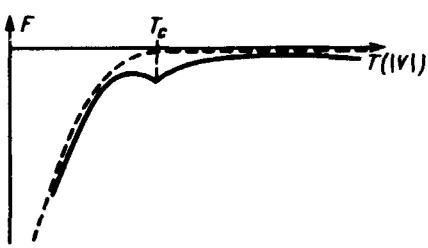

FIG. The dashed line represents the dependence of the free energy on T (or $|V|$) in the self-consistent-field approximation. The solid curve is the same but with allowance for the contribution from the collective oscillations.

4. We present now a phenomenological analysis of the influence of the quantum fluctuations of the order parameter near the critical temperature T_c on the type of the phase transition in the general case. We must find the temperature dependence of the oscillation frequencies, and then use expression (8) for the free energy. We introduce to this end a Schrödinger equation in which the role of the potential energy is played by the Landau expansion for the free energy.[6] At a fixed phase it is possible to choose the order parameter Δ real. In the phase-degenerate case both the real and imaginary parts (u and v) of the order parameter can vary independently. In the limit $\mathbf{k}=0$, the kinetic energy operator $\hat{T}$ takes the form $\hat{T}=(\hbar^2/2M)(\partial^2/\partial\Delta^2)$ in the first case and

$$\hat{T} = -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial u^2} + \frac{\partial^2}{\partial v^2}\right)$$

in the second case. Here M is the effective mass corresponding to the quantum motion of the order parameter. At $T > T_c$, the equilibrium value Δ_p of the order parameter is equal to zero. It is then possible to retain in the Schrödinger equation for the potential energy the terms quadratic in Δ [$\alpha\Delta^2$ in the first case and $\alpha(u^2+v^2)$ in the second case, $\alpha \propto T - T_c$]. In both cases we then obtain the equations of harmonic oscillators whose oscillation frequencies decrease like $\sqrt{T-T_c}$ when T approaches T_c from above.

Similar calculations for $T < T_c$ show that between the case with fixed phase and the case with degeneracy in phase there are significant differences. In the former case there exists one oscillation, the frequency of which (at $\mathbf{k}=0$) is proportional to the equilibrium order parameter, $\Delta_p \propto \sqrt{T_c - T}$. In the second case there are two types of oscillations. The frequency of one of them, which is in phase with Δ_p is proportional to $\sqrt{T_c - T}$. On the other hand the frequency of the other, which is shifted $\pi/2$ in phase, is lower than T_c everywhere and has zero frequency at $\mathbf{k}=0$.

The presence, in both cases, of oscillations whose frequencies squared are proportional to $|T-T_c|$ near T_c lead, in accordance with (8), to the appearance of a single term proportional to $-|T-T_c|$, in the free energy N. Therefore, the entropy at the point T_c changes jumpwise, i.e., a first-order phase transition takes place. Owing to the interaction of the fluctuations, this singularity of T_c may turn out to be "smeared out," but the singular term of δF leads already in the region of Gaussian fluctuations to violation of the theorem that the thermodynamic potential is convex, thus ensuring the fact that the transition is of first order.

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