Contribution to the electron theory of ferroelectricity

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It is shown that in a system of two-level molecules (the Dicke model), a phase transition to the ferroelectric state, due to electron-phonon interaction, takes place in semiconductors and semimetals.

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1. It was observed in [1] (see also [2]) that in a system of two-level molecules interacting with an electromagnetic field (the so called Dicke model) a phase transition to a state with a photon Bose condensate is possible if the constant of the interaction with the field exceeds the distance between levels. As shown by one of us,[3] an analogous phase transition takes place in semiconductors and at arbitrarily small interaction constant in semimetals. A gap (proportional to the condensate density) is produced in the electron spectrum and leads to a transition of the semimetal into a dielectric. The equation for the gap is of the same form as the equations in the BCS theory and in the exciton-insulator theory.[4]

It should be noted that the question of the frequency and momentum of the photons of the condensate remains unanswered. In most papers devoted to this problem it is not discussed, and in some it is stated that the photons condense at a frequency equal to the distance between the molecule levels.

We show in this paper that in the systems under consideration the frequency and momentum of the photons of the Bose condensate is equal to zero (we will recall that we are dealing with systems in thermodynamic equilibrium). This means that the phase transition gives rise to a spontaneous electric field that

is constant in space and in time, i.e., a transition to the ferroelectirc state takes place.

We call attention to the fact that this mechanism producing the spontaneous electric field and due to the electron-phonon interaction can play an essential role in the formation of the ferroelectric state in crystals. As to molecular systems, this mechanism can be responsible for the orientation ordering and for the ferroelectric properties in a number of liquid crystals.

2. The equation of motion for the photon operator c_k^+ with the Dicke Hamiltonian

$$H = \omega_k^0 c_k^+ c_k + \frac{\epsilon}{2}\sigma^z + \frac{M_k}{2N^{1/2}}(c_k^+ + c_{-k})(\sigma^+ + \sigma^-), \quad \sigma^{\pm,z} = \sum_{j=1}^{N} \sigma_j^{\pm,z} \tag{1}$$

is of the form

$$i\frac{\partial c_k^+}{\partial t} = -\omega_k^0 c_k^+ - \frac{M_k}{2N^{1/2}}(\sigma^+ + \sigma^-), \quad M_k^2 = \frac{2\pi N}{V}\omega_k^0 (\mathrm{ed})^2 = \gamma\omega_k^0 . \tag{2}$$

Here $\omega_k^0 = ck$ is the bare frequency of a photon with momentum $\mathbf{k}$, $\sigma^{\pm,z}$ are Pauli operators summed over all the molecules, ϵ is the distance between the molecule levels, $\mathbf{e}$ is the field polarization vector, $\mathbf{d}$ is the dipole moment of the electron-phonon interaction, and V is the volume.

Averaging (2) and calculating $\langle\sigma^+ + \sigma^-\rangle$ with the aid of the partition function (see, e.g., [2]), we obtain

$$i\frac{\partial}{\partial t} < c_{-k} - c_k^+ > = \Omega < c_{-k} + c_k^+ >$$

$$= < c_{-k} + c_k^+ > \left[\omega_k^0 - \frac{2M_k^2}{\sqrt{\frac{\epsilon^2}{4} + \lambda^2}} \mathrm{th} \frac{\sqrt{\frac{\epsilon^2}{4} + \lambda^2}}{T} \right],$$

$$\lambda^2 = 4M_k^2 < c_k^+ c_k > /N . \tag{3}$$

Owing to the condition imposed on the density of the Bose-condensate photons, the expression in the square brackets of (3) vanishes. The condensate photon frequency is therefore equal to zero.

Starting from considerations of maximum instability in the non-restructured phase (most favorable energy), the wave vector must also be set equal to zero. (This statement will be explained below with semimetals as an example.) The number of condensate photons ($T = 0$)

$$< \frac{c_k^+ c_k}{N} > = \frac{1}{16\gamma\omega_k^0}(\gamma^2 - \epsilon^2), \quad \gamma > \epsilon \tag{4}$$

then tends to infinity as $\mathbf{k} \to 0$, and the finite quantity is an electric field that is uniform in space and constant in time

$$\mathbf{E} = \mathbf{e} \lim_{k \to 0} (\omega_k^0 < c_k^+ c_k >)^{1/2}, \quad \hbar = 1. \tag{5}$$

3. A similar situation arises in semiconductors and in semimetals. In this case the system is described by the Hamiltonian [3]

$$H = \omega_k^0 c_k^+ c_k + \sum_p E_p (a_p^+ a_p + b_p^+ b_p - 1)$$

$$+ \sum_p \frac{M_k}{\sqrt{N}} (a_p^+ b_{p+k}^+ + b_{p-k} a_p)(c_k^+ + c_{-k}), \quad E_p = p^2/2m + E_g/2. \tag{6}$$

Here a_p^+ and b_p^+ are the electron and hole creation operators, E_g is the width of the forbidden band of the semiconductor ($E_g < 0$ in a semimetal). Just as in Sec. 2, we can show that the condensate photon frequency is equal to zero. To find the momentum we consider the case of a semimetal in which the phase transition takes place at a low interaction constant. From Dyson's equation we find that the photon frequency ω_k of the initial system is pure imaginary

$$\omega_k = i\lambda\left(1 - \frac{1}{6}\left(\frac{v_0 k}{\lambda}\right)^2\right), \qquad \lambda = 2\epsilon_0 \exp(-1/g),$$

$$g = \gamma \rho(v_0), \qquad \rho(v_0) = \frac{p_0 mV}{2\pi^2 N} \tag{7}$$

(ϵ_0 and v_0 are the Fermi energy and velocity on the Fermi surface respectively). As seen from (7), maximum instability is reached at $k=0$. Consequently just as in superconductivity theory, a Bose condensate with zero momentum corresponds to the energywise most favored state, and the equation for the condensate density λ takes the form

$$1 = g\frac{N}{\rho(V_0)} \sum_p \frac{\operatorname{th}\frac{1}{2T}(E_p^2 + \lambda^2)^{1/2}}{2(E_p^2 + \lambda^2)^{1/2}}. \tag{8}$$

At zero temperature, $T=0$, the solution of (8) coincides with λ in (7). The condensate density determines the spontaneous electric field (the polarization)[1)]

$$E = e\frac{\lambda}{2\pi(ed)}. \tag{9}$$

4. As shown above, a ferroelectric transition is realized if account is taken of only the electron-photon interaction. It is well known, however, that exciton [4] and phonon [5] instabilities take place in the systems under consideration, and lead to a restructuring of the electron spectrum and of the crystal lattice. The constant g in (8) must therefore be replaced by an effective constant that depends on the electron-photon, electron-phonon, and Coulomb constants. The foregoing effects yield the electron contribution to the polarization of the ferroelectric. Naturally, the complete polarization will be determined by the aforementioned electron polarization and by the polarization connected with the displacement of the dipole-active ions.

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[1)]In the case of systems with finite dimensions, the electric field should be replaced by the electric induction.

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