Froehlich collective mode and permittivity of quasi-one-dimensional crystals with charge transfer

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It is shown that in quasi-one-dimensional complexes with charge transfer, of the TTF–TCNQ type, there exist an optically inactive Froehlich mode with a spectrum of the acoustic type and an optically active mode of phase oscillations with a gap in the spectrum; the latter mode is determined by the interaction of the charge-density waves on the neighboring cation and anion chains. An expression is obtained for the permittivity with allowance for the Froehlich mode, and estimates of the corresponding parameters are presented for TTF–TCNQ.

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Lee, Rice, and Anderson[1] have shown that in a one-dimensional system, below the Peierls-transition point, a collective mode, the Froehlich collective mode (FCM) appears and corresponds to oscillations of the phase of the charge density wave (CDW)—. In the case of a noncommensurate CDW in an ideal lattice made up of chains of the same type, without allowance for the Coulomb interaction of the electrons, the spectrum $\omega(q)$ of this mode has an acoustic character in the limit of small momenta $q \ll \Delta/v_F$, i.e., $\omega(q) = v_F q\sqrt{m_e/m^*}$, where Δ is the Peierls gap in the electron spectrum, m^* is the effective mass of the CDW, $m^*/m_e = 1 + 4\Delta^2/\lambda\omega_0^2$, λ is the dimensionless constant of the interaction between the electrons and phonons with quasi-momentum $2k_F$, and ω_0 is the unrenormalized frequency of these phonons. Allowance for the interaction of the CDW between the chains in crystals of conducting chains of one type (crystals of the KCP type) leads only to an additional dependence of the FCM frequency on the excitation momentum $k_\perp$ transverse to the chains, and the acoustic character of the FCM is preserved. Since the oscillations of the CDW phase corresponds to oscillations of the local electron density, allowance for the long-range part of the Coulomb interaction of the electrons is of importance for the FCM, and when the Coulomb forces are taken into account, the FCM spectrum acquires a gap $\lambda\omega_0(\cos\theta)/2$ at $k_\perp$, $q \to 0$ and $m^* \gg m_e$, where $\cos\theta = q/\sqrt{q^2 + k_\perp^2}$.[2] It is also shown in[1] that the FCM is optically active, and in a noncommensurate CDW, without allowance for impurities, the FCM makes a contribution to the dielectric constant which is analogous to the contribution of the free electrons. When this contribution is taken into account, the dielectric constant, for a field directed along the chains at $q = k_\perp = 0$ and $\omega \ll \Delta$ takes the form

$$\epsilon_{\parallel}(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2}\frac{m_e}{m^*}, \qquad \epsilon_\infty = \epsilon_0 + \frac{\omega_p^2}{6\Delta^2}, \tag{1}$$

where ϵ_0 is the contribution of the core, ω_p is the plasma frequency, and the term $\omega_p^2/6\Delta^2$ corresponds to transition of the electrons through the gap. Allowance for the impurities leads to a finite value of $\epsilon_{\parallel}(\omega)$ as $\omega \to 0$.[2]

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We consider in the present paper the FCM in crystals containing chains of anion (A) and cation (C) type (we have in mind crystals of the TTF-TCNQ type). We investigate first the simple structure of a CDW with two chains (A and C) in a unit cell of the superstructure.

We confine ourselves to oscillations of the CDW phase at $T=0$. The changes $\delta\rho$ of the charge density along the chains are connected with the phases of the CDW by the relations $\pi\delta\rho_{1,\mathbf{n}}=-|e|(\partial\phi_{1,\mathbf{n}}/\partial z)$, and $\pi\delta\rho_{2,\mathbf{n}}=|e|(\partial\phi_{2,\mathbf{n}}/\partial z)$ respectively for the anion ($\phi_{1,\mathbf{n}}$) and cation ($\phi_{2,\mathbf{n}}$) chains (the chains are arranged along the z axis, and $\mathbf{n}$ is the two-dimensional coordinate of the chains). The system of equations for the CDW phases is (see, e.g., [3])

$$\mu_1\frac{\partial^2\phi_{1,\mathbf{n}}}{\partial t^2}-\kappa_1\frac{\partial^2\phi_{1,\mathbf{n}}}{\partial z^2}+\beta(2\phi_{1,\mathbf{n}}-\phi_{2,\mathbf{n}}-\phi_{2,\mathbf{n}+1})=\frac{|e|}{\pi}E_z,$$

$$\mu_2\frac{\partial^2\phi_{2,\mathbf{n}}}{\partial t^2}-\kappa_2\frac{\partial^2\phi_{2,\mathbf{n}}}{\partial z^2}+\beta(2\phi_{2,\mathbf{n}}-\phi_{1,\mathbf{n}}-\phi_{1,\mathbf{n}-1})=-\frac{|e|}{\pi}E_z,$$

$$\epsilon_\infty \operatorname{div}\mathbf{E}(z,\mathbf{r})=4\pi|e|\sum_{n,l}\left[\frac{\partial\phi_{2,\mathbf{n}}}{\partial z}\delta(\mathbf{r}-\mathbf{n})-\frac{\partial\phi_{1,\mathbf{n}}}{\partial z}\delta\left(\mathbf{r}-\mathbf{n}-\frac{\mathbf{l}}{2}\right)\right], \tag{2}$$

$$\epsilon_\infty=\epsilon_0+\frac{\omega_{p1}^2}{6\Delta_1^2}+\frac{\omega_{p2}^2}{6\Delta_2^2},$$

where $\mu_{1,2}=m^*_{1,2}/\pi^2 n$, n is the concentration of the electrons in the chain C per unit length of chain, $\kappa_{1,2}=v_{F1,2}/2\pi$, $\mathbf{r}$ is the radius vector in the plane perpendicular to the z axis, $\mathbf{l}/2$ are the vectors that connect the chains C and A in this plane, the parameter β characterizes the interaction of the CDW on neighboring chains C and A, and $\mathbf{E}$ is the electric field. Equations (2) are valid for slow changes of the phase with time (frequencies $\omega\ll\Delta_1,\Delta_2$) and in space along the z axis (wave vectors $q_{1,2}\ll\Delta_{1,2}/v_{F1,2}$). It is shown in[4] that the interaction of the CDW of the chains is determined by the tunneling of the electrons between the chains and by the Coulomb interaction of the CDW (for the interaction of the chains A and C, these two contributions to β have opposite signs). Estimates show that the tunnel interaction seems to play the principal role, and if we disregard the Coulomb interaction of the CDW we obtain

$$\beta=\frac{2t_\perp^2}{\pi\hbar\sqrt{v_{F1}v_{F2}}}f\left(\frac{\Delta_1}{\Delta_2},\frac{v_{F1}}{v_{F2}}\right),$$

$$f(x,y)=\frac{2x}{\sqrt{(x^2-1)(x^2y^{-1}-y)}}\ln\frac{\sqrt{x^2-1}+\sqrt{x^2y^2-1}}{y(\sqrt{1-x^{-2}}+\sqrt{y^{-2}-x^{-2}})}, \tag{3}$$

where $t_\perp$ is the matrix element of the transition of the electron between neighboring chains A and C.

In the long-wave limit, Eqs. (2) give a collective mode of the acoustic type (which is optically inactive at $k_\perp$, $q \to 0$)

$$\omega^2 = \frac{\kappa_1 + \kappa_2}{\mu_1 + \mu_2} q^2 + \frac{\beta(\beta + 4e^2\nu\cos^2\theta/\pi\epsilon_\infty)}{(\mu_1 + \mu_2)(2\beta + 4e^2\nu\cos^2\theta/\pi\epsilon_\infty)} k_\perp^2 l^2, \tag{4}$$

where ν is the density of the pairs of chains C and A. Besides (4), there exists a mode that is optically active as $k_\perp$, $q \to 0$ with a gap ω_0 in the spectrum; ω_0 is determined by the Coulomb forces and by the interaction of the CDW of neighboring chains A and C

$$\omega_0^2 = \left(\frac{1}{\mu_1} + \frac{1}{\mu_2}\right)\left(2\beta + \frac{4e^2\nu\cos^2\theta}{\pi\epsilon_\infty}\right). \tag{5}$$

This mode contributes to the dielectric constant, and when this contribution is taken into account we have

$$\epsilon_\parallel(\omega) = \epsilon_0 + \frac{\omega_{p1}^2}{6\Delta_1^2} + \frac{\omega_{p2}^2}{6\Delta_2^2} - \frac{\Omega_p^2}{\omega_F^2 - \omega^2},$$

$$\Omega_p^2 = \frac{4e^2\nu}{\pi}\left(\frac{1}{\mu_1} + \frac{1}{\mu_2}\right)^{-1}, \qquad \omega_F^2 = 2\beta\left(\frac{1}{\mu_1} + \frac{1}{\mu_2}\right)^{-1}. \tag{6}$$

In real compounds the unit cell of the superstructure contains several pairs of chains C and A (four in TTF-TCNQ and two in TSeF-TCNQ). An analysis similar to that described above shows that in this case there exists one optically inactive mode with a spectrum (4) and one optically mode with a gap in the spectrum (5), the parameter β being determined only by the interaction of the CDW of chains C and A. The remaining modes are optically inactive, and their spectra contain gaps that are determined by the interaction of the chains CC and AA. Expression (6) for $\epsilon_\parallel(\omega)$ remains valid, and the parameter β in this expression is determined as before by (3).

Thus, in organic crystals with charge transfer, and the state of a noncommensurate CDW, there is always an optically inactive FCM with a spectrum of the acoustic type, and it can be detected by neutron scattering. In addition, in these crystals the optically active FCM has a gap in the spectrum, and this gap is determined not only by the Coulomb forces but also by the interaction of the CDW of the chains A and C. Therefore the dielectric constant of such complexes is finite as $\omega \to 0$ and in the limit of ideal crystals, and the contribution of the FCM to the dc conductivity is zero. We note that this character of the dependence of $\epsilon_\parallel(\omega)$ on the interaction of the CDW of chains A and C was suggested in[2].

In the case of TTF-TCNQ we know the $\epsilon_{\parallel}(\omega)$ dependence at low temperatures from data on crystal reflection in the far infrared band.[5] According to these data, at frequencies below 100 cm^{-1} ϵ_{∞} does not exceed 100. According to[6] we have $\epsilon_{\parallel}(0) \approx 3500$ at 4.2 K. These values of ϵ_{∞} and $\epsilon_{\parallel}(0)$ lead to a value $\beta \approx 5 \times 10^{-9}$ erg/sec. At $v_{F1} \approx v_{F2} (\approx 2 \times 10^7$ cm/sec[7] we have $f \approx 1$ and it follows from (3) that $t_{\perp} \approx 90$ K at $T = 4.2$ K. The value of $t_{\perp}$ can be estimated independently from data on NMR relaxation for TTF-TCNQ,[7] and this estimate yields $t_{\perp} \approx 30$ K at $T = 300$ K. The agreement of these two values of $t_{\perp}$ can be regarded as satisfactory if allowance is made for the temperature dependence of $t_{\perp}$ and for the errors in the estimates of this quantity from NMR data and from measurements of $\epsilon_{\parallel}(0)$.

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