Weak two-fold commensurability in a one-dimensional Peierls system

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A theory, which describes the properties of *K (def)TCP*-type compounds, is proposed.

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1. It is known that a one-dimensional metal with a half-filled zone is singled out in the Peierls instability problem. As a result, quasi-one-dimensional compounds of the type $K_{1.75}Pt(CN)_4.1.5H_20$, which will be referred to by the usual designation K(*def*)*TCP* below, are of considerable interest. According to available data,[1] a complete transfer of the valence electron charge of a potassium atom to the conducting Pt chain occurs in these substances. As a result, there are 1.75 electrons for each Pt atom. A complete unit cell contains 7 K atoms and four Pt atoms, which are located in three nonequivalent positions; therefore, the true Brillouin zone is half-filled. According to structural data,[1,2] however, the distances a between any neighboring Pt atoms are the same within an accuracy of 0.1%. This feature of the strucutre indicates that the potential of the K^+ ions has a weak influence on the rigid Pt atom chains. If this weak external modulation of the field of the conducting chains is ignored, then the one-dimensional unit cell will contain one Pt atom, and the corresponding Brillouin zone will be 1/8 filled. The charge-density wave with the wave vector $2p_F = \pi/4a$, which is produced as a result of Peierls instability, is eight-fold commensurable and the properties of the system are indistinguishable from the properties of the gel model within an accuracy of $(\Delta/E_F)^3$.[5] When the weak periodic field of the K^+ ions is taken into account, we must expect the appearance of features that are characteristic of systems with a half-filled zone. Analogous effects should also occur in other compounds such as $TTT_2I_3 + \delta$ and $TSeT_2Cl$. In this paper we shall examine the specific case of K(*def*)*TCP*, since the Peierls theory is applicable to this compound.

2. We shall disregard the direct influence of the K^+ ions with wave vectors $4P_F$ and $8p_F$ on the electron spectrum and the interaction of the electrons with $\pm 6p_F$-phonons, since these effects are of the order of $(\Delta/\epsilon_F)^3$ in smallness. We write the Hamiltonian of the system in the form

$$\hat{H} = \sum_p \xi_p C_p^+ C_p + \sum_q \omega_q b_q^+ b_q + \sum_q \left[\frac{U_q}{\sqrt{\omega_q \omega_{q-K/4}}} \phi_q \phi_q^+ - K/4 + \frac{U_q}{\sqrt{\omega_q \omega_{q+K/4}}} \phi_q \phi_{q+K/4}^+ \right] + \sum_{p,q} \frac{g_{pq}}{\sqrt{N}} C_p^+ C_{p-q} \phi_q . \quad (1)$$

Here $C_p^+ (C_p)$ are the creation (annihilation) operators of electrons with quasimomen-

tum p, ξ_p is the electron energy measured from the chemical potential, $b_q^+(b_q)$ are the creation (annililation) operators of phonons with momentum q, ω_q is the bare frequency of the phonons, $\phi_q = (\omega_{q/2})^{1/2}(b_q + b_{-q}^+)$, g_{pq} is a matrix element of the electron–phonon interaction, and U_q is the Fourier component of the potential of the K^+ ions, which, for specificity, we assume to be real and positive. Here $U_q = U_{-q} = U_{q \pm K/4}$, where $K = 2\pi/a$.

Ignoring the long-wave fluctuations, which perturb the long-range order in a one-dimensional system, we can assume that the ground state corresponds to static deformations with wave vectors $\pm 2p_F = \pm K/8$ and $\pm 6p_F = \pm 3K/8$:

$$<\phi_{K/8}> = <\phi^*_{-K/8}> = \phi_1 = |\phi_1| e^{i\chi_1}; \; <\phi_{3K/8}> = \phi_2 = |\phi_2| e^{i\chi_2}. \tag{2}$$

To determine the equilibrium deformations, we must write the standard expression for the energy of the system (see, for example, Ref. 5); in this case it is a function of both in the gel model case, and of the displacement phases χ_1 and χ_2. Minimization of the energy with respect to $|\phi_1|$, $|\phi_2|$, χ_1 and χ_2 defines the equilibrium values of these quantities

$$\begin{aligned} &g|\phi_{10}| = \Delta = \epsilon_F \exp(-1/\lambda_{\text{eff}}), \; \lambda_{\text{eff}} = \lambda(1 + 2U/\omega_1), \\ &|\phi_{20}| = 2U|\phi_{10}|/(\omega_1\omega_2)^{1/2}, \quad \chi_{10} = \pm\pi/2, \quad \chi_{20} = \mp\pi/2, \end{aligned} \tag{3}$$

where $g = g_{K/16,K/8}$ is real, $\lambda = g^2/\pi v_F$ a dimensionless electron–photon interaction constant, v_F is the Fermi velocity, $U = U_{K/8} = U_{3K/8}$, $\omega_1 = \omega(\pm K/8)$, $\omega_2 = \omega(\pm 3K/8)$, and 2Δ is the gap in the electron spectrum. We draw attention to the fact that the effective interaction constant increases at the same time as the phase of the equilibrium displacements is established—a property known to be characteristic of a metal with a half-filled zone. It can also be seen that in addition to displacements of the Pt atoms with wave vector $K/8 = 2p_F$, strictive displacements ϕ_{20} with wave vector $3K/8$ should be observed; the deformations ϕ_{10} and ϕ_{20} are opposite in phase. The assumption that the influence of the field of the K^+ ions is weak means that the small parameter of the theory is $U/\omega_{1,2} \ll 1$. Below all the values are calculated to first order in $(U/\omega_{1/2})$.

3. To investigate the dynamics of the system, let us consider small-amplitude, long-wave deformations of the ground state:

$$\phi_j = (|\phi_{j0}| + \eta_j(x,t)) \exp[i\chi_j(x,t)]; \; j = 1, 2.$$

The effective Lagrangian for the fields n_j and χ_j has the form

$$\mathcal{L}\{\eta_j, \chi_j\} = \int \frac{dx}{L}\left\{\left[\frac{\dot\eta_1^2}{\omega_1^2} + \frac{\dot\eta_2^2}{\omega_2^2} - \lambda\eta_1^2 - \left(1 - \frac{2U}{\omega_2}\right)\eta_2^2 + \frac{4U}{(\omega_1\omega_2)^{1/2}}\eta_1\eta_2\right.\right.$$

$$-\frac{\lambda v_F^2}{6\Delta^2}(\eta_1')^2\Big]+\Big[\frac{|\phi_{10}|^2}{\omega_1^2}\dot{\chi}_1^2+\frac{|\phi_{20}|^2}{\omega_2^2}\dot{\chi}_2^2-\frac{2U|\phi_{10}|^2}{\omega_1}(1+\cos 2\chi_1)$$

$$-\frac{v_F}{4\pi}(\chi_1')^2-\frac{4U}{(\omega_1\omega_2)^{1/2}}|\phi_{10}\phi_{20}|(1+\cos(\chi_1-\chi_2))$$

$$-\frac{2U|\phi_{20}|^2}{\omega_2}(1+\cos 2\chi_2)\Big]\Big\}. \tag{4}$$

For $U=0$ Eq. (4) becomes the Lagrangian of the Peierls system in the gel model.

If the phase deviations from the equilibrium values $\delta\chi_j=\chi_j-\chi_{j0}$ are small, then the Lagrangian can be diagonalized by introducing the normal coordinates ζ_j and θ_j, and for $\lambda\ll 1$ we have

$$\zeta_1=\frac{1}{\omega_1}\left(\eta_1+\frac{2U}{(\omega_1\omega_2)^{1/2}}\frac{\omega_1^2}{\omega_2^2}\eta_2\right);\ \zeta_2=\frac{1}{\omega_2}\left(\eta_2-\frac{2U}{(\omega_1\omega_2)^{1/2}}\eta_1\right);$$

$$\theta_1=\frac{|\phi_{10}|}{\omega_1}\delta\chi_1;\ \theta_2=\frac{|\phi_{10}|}{\omega_1}\frac{2U}{(\omega_1\omega_2)^{1/2}}\frac{\omega_1}{\omega_2}(\delta\chi_2-\delta\chi_1). \tag{5}$$

The corresponding frequencies are

$$\omega_{\zeta_1}(k)=(\lambda\omega_1^2+(2/3)u^2k^2)^{1/2};\ \omega_{\zeta_2}=\omega_2\left(1-\frac{U}{\omega_2}\right);$$

$$\omega_{\theta_1}(k)=(4U\omega_1+u^2k^2)^{1/2};\ \omega_{\theta_2}=\omega_2\left(1+\frac{2U}{\omega_2}\right); \tag{6}$$

where $u/v_F^2=\lambda\omega_1^2/4\Delta^2$.

Thus, two low-lying modes ζ_1 and θ_1 exist in the system, where relative value, determined by the ratio of the two small parameters U/ω_1 and λ of the theory, can be arbitrary. It can also be seen that the mode θ_2, like the Fröhlich mode θ_1, is optically active. However, the oscillator strengths for θ_2 are a factor of $(U/\omega)^2$ smaller than those for θ_1.

4. Let us examine the nonlinear excitations for large deviations of the phase from the equilibrium values. Since the ground state of the system is degenerate with respect to the sign of the phases (3), it may be possible to excite solutions in the system, which connect the two equilibrium positions. The important part of the energy functional has the form

$$E\{\chi_1\}=\frac{|\phi_{10}|^2u^2}{\omega_1^2}\int(\kappa^2\cos^2\chi_1+\chi_1'^2)\,dx;\ \kappa^2=4U\omega_1/u^2. \tag{7}$$

The extremum of the functional (7) satisfies the equation

$$2\chi_1'' + \kappa^2 \sin 2\chi_1 = 0,$$

where solution is

$$\chi_1 = -\pi/2 + 2 \arctan (e^{\kappa x}).$$

The soliton energy E_s and its mass M_s are

$$\frac{E_s}{\Delta} = \frac{2}{\pi} \frac{\omega_{\theta_1}}{\zeta_1}; \quad M_s = E_s / u^2. \tag{8}$$

The phase change in the soliton is $\pm\pi$ and, consequently, it is a charged formation having a charge of $\pm e$.

We note the following important fact. The applicability of the phase soliton theory is restricted by the condition $E_s \sim \kappa v_F \ll \Delta$ (large radius) and by the adiabatic criterion $n^2 u/v_F \ll 1$, where n is the commensurability index. If we use the data of Ref. 3, which identify the two low-lying modes with θ_1 and ζ_1, specifically, $\omega_{\theta_1} = 21$ cm^{-1} and $\omega_{\zeta_1} = 40$ cm^{-1}, then it follows from (8) that $E_s/\Delta \approx 1/3$ (in this case $U/\omega_1 = \lambda/16$) and the soliton radius is rather large. Assuming that the adiabatic criterion is satisfied ($n = 2$), we can say that for now K(*def*)*TCP* is apparently the only compound in which the solitons are not destroyed by quantum fluctuations and inhomogeneity and, therefore, are able to contribute to the conductivity. The conclusion acounts for the two activation regimes with activation energies of E_s and Δ in the temperature dependence of the conductivity $\sigma(T)$.[4] Here the ratio $\Delta/E_s \approx 3$, in accordance with the previous estimate. At temperatures $T < 80$ K σ is determined by the activation of solitons. In the slow rise region 80 K $< T <$ 200 K the soliton conductivity which is saturated is the Fröhlich conductivity with stripped pinning, while for $T > 200$ K the conductivity is determined by electron activation through the gap. The two-order-of-magnitude change in σ in the region 200 K $< T <$ 350 K indicates that the mobility of soliton is low compared with electrons.

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