Peierls structure transition in quasi-one-dimensional crystals

L. N. Bulaevskiĭ

P. N. Lebedev Physics Institute, USSR Academy of Sciences, Moscow

This review is concerned with the structure, electrical, and optical properties of mixed-valence platinum complexes of the $K_2Pt(CN)_1 Br_{0.30} 3H_2O$ type and of TTF-TCNQ salts. Special attention is paid to the experimental results on the anisotropy of electron motion in these quasi-one-dimensional crystals. The theory of the Peierls metal-insulator transition is considered for a one-dimensional system in the molecular field approximation, allowing for statistical fluctuations of the order parameter. It is shown that the Peierls transition is associated with the appearance of a giant Kohn anomaly in the phonon spectrum. The experimental results confirming the occurrence of the Peierls transition in platinum complexes (structure data, paramagnetic susceptibility, and phonon spectrum) are analyzed from the theoretical point of view. An analysis is also made of the influence of three-dimensional effects and of the disorder in crystals on the Peierls transition. The possibility of the Peierls transition in TTF-TCNQ is considered and the problem of the paraconductivity resulting from this transition is discussed.

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1. INTRODUCTION

Extensive investigations of quasi-one-dimensional systems were stimulated by Little in 1964,[1] who suggested that high-temperature superconductivity could occur in one-dimensional systems. According to Little, one would have to synthesize a long linear conducting molecule (core) with easily polarizable side branches (polarizers). The polarization of the bound electrons in the side branches by the conduction electrons of the core could, under favorable conditions, result in attraction between the conduction electrons and consequently give rise to superconductivity. In this case, the superconductivity would be due to the high-frequency exchange of electron excitations of the polarizers (exciton mechanism) and the temperature of the superconducting transition should be higher than in the conventional phonon mechanism.

In attempts to realize this idea, it was found that it would be difficult to produce a sufficiently long molecular system with metallic conduction: all the polymers produced so far are semiconductors with a fairly wide gap. Therefore, experimenters were attracted to three-dimensional crystals in which the electron motion was almost one-dimensional because of the special nature of the crystal structure. These crystals, known as quasi-one-dimensional, contain parallel conducting filaments and, in principle, specially selected strongly polarizable groups of atoms can be placed between these filaments. Systems of this kind have all the necessary elements of the Little model but their three-dimensional nature makes it possible to investigate them by conventional experimental methods.

Clearly, quasi-one-dimensional crystals needed for the realization of the exciton superconductivity mechanism should have a sufficiently high metallic or near-metallic conductivity and a search for new crystals has been made particularly with this point in mind. However, all the quasi-one-dimensional crystals known so far are insulators at low temperatures. This situation is not accidental.

In fact, theoretical investigations of one-dimensional electron systems, started well before quasi-one-dimensional crystals were prepared experimentally, have demonstrated that the properties of one-dimensional electron systems differ considerably from the properties of crystals with two- or three-dimensional motion. The following three statements describe sufficiently fully all the special features of one-dimensional systems.

a) If the Coulomb interaction between electrons is ignored, a one-dimensional metallic system is found to be unstable in the presence of changes in the crystal lattice period which split a partly filled band into completely filled and empty subbands (see Peierls[2]). In other words, when the temperature is lowered, a one-dimensional metal should exhibit lattice distortions with a wave number equal to twice the Fermi momentum.

b) One-electron excited states in a one-dimensional electron system with a half-filled band are separated from the ground state by a gap, no matter how weak the electron repulsion.[3] This statement has been proved in the case when the interaction between electrons can be described by the Hubbard Hamiltonian. However,

there are no grounds for assuming that this statement is invalid in the case of the real Coulomb interaction between electrons. Thus, even the Coulomb interaction between electrons gives rise to an insulator (Mott transition) when the temperature is lowered.

c) One-electron states in a one-dimensional system are localized no matter how weak the random potential. Therefore, at low temperatures, the conductivity of a one-dimensional electron system in a lattice with defects cannot be metallic. [4,5]

All three statements show that, at least for three reasons, a one-dimensional electron system may be nonmetallic at low temperatures.

The question arises as to what degree all these statements are applicable to quasi-one-dimensional crystals in which electron motion is not strictly one-dimensional. Clearly, in considering any one effect in quasi-one-dimensional crystals, we obtain basically new results typical of one-dimensional systems only if the kinetic energy of the motion of an electron between filaments, $E_\perp$ is much smaller than the energy typical of the effect in question (thus, for example, in the case of the Peierls or Mott transition, the value of $E_\perp$ should be much smaller than the corresponding Peierls or Mott gap). We shall understand quasi-one-dimensional systems to be only those crystals which satisfy this condition because, otherwise, we have a conventional anisotropic three-dimensional system and the statements a)—c) are inapplicable to these systems.

Two classes of compounds with a fairly high (at room temperature) and anisotropic conductivity are being investigated at present: one class represents charge-transfer salts based on tetracyanoquinodimethane (TCNQ) [6] and mixed-valence planar square complexes of transition metals (Pt, Ir), whose typical representative is $K_2Pt(CN)_4Br_{0.30} \cdot 3H_2O$ (KCP). [6,7] The experimental data show that the main low-temperature properties of platinum complexes are related to the Peierls metal-insulator transition, whereas, in the case of TCNQ salts — with the exception of salts with tetrathiafulvalinium (TTF) and tetrathiatetracinium (TTT) — the localization of electrons due to the Coulomb repulsion and disorder in the lattice play the dominant role at low temperatures.

In KCP and TCNQ salts, the condition for quasi-one-dimensional structure is satisfied for almost all the phenomena of physical interest. The current popularity of these systems is due to the fact that we can observe those basically new effects which are associated with the one-dimensional electron motion. One of these effects is the Peierls instability of a metallic one-dimensional system which results in a metal-insulator structure transition when the temperature is lowered. The present review is devoted to the theory of this transition and its experimental manifestation in quasi-one-dimensional crystals. The Peierls nature of the transition in TCNQ with TTF salts is established less reliably than for KCP. Therefore, we shall concentrate our attention on the experimental properties of variable-valence complexes.

We shall conclude the review by considering the problem of the realization of the exciton superconductivity mechanism in quasi-one-dimensional crystals since this is closely associated with the Peierls instability of one-dimensional metallic systems.

2. STRUCTURE AND ANISOTROPY OF PHYSICAL PROPERTIES OF MIXED-VALENCE PLATINUM COMPLEXES

a) Crystal structure of KCP. In the platinum complexes under discussion, a Pt atom and four CN groups form a planar structure, shown in Fig. 1a. In crystals, these planar $Pt(CN)_4$ groups form chains or columns, one of which is shown in Fig. 1b. The relative positions of the $Pt(CN)_4$ chains, alkali atoms (K, Na, Rb), halogens (Br, Cl), and water molecules are shown in Fig. 2. A complete unit cell corresponds to the formula $K_4Pt(CN)_4Br_{0.30} \cdot 3H_2O$. Thus, only 50% of the sites available to K and 60% available to Br are occupied; the positions of both these ions are random (according to x-ray structure data). The Pt ions in KCP crystals are, on the average, equivalent but the electrons of these ions experience a random potential of the disordered distribution of the Br and K ions.

There are ten platinum electrons and two of them participate in the bonds with the CN groups; of the remaining eight electrons, a small fraction (0.30) is transferred to the halogens. Formally, the platinum ions have the Pt^{2+} and Pt^{4+} charge so that the KCP-type materials are known as mixed-valence complexes. The orbital degeneracy of the d levels of platinum is lifted by the crystal field and the new levels correspond to the orbitals which are superpositions of five atomic wave functions of the d level (d_{xy}, d_{xz}, d_{yz}, d_{z^2}, and $d_{x^2-y^2}$), which are the eigenfunctions of the orbital momentum projection operator. According to the data on the magnetic circular dichroism of $K_2Pt(CN)_4$ solutions, [8] the energies of the orbitals can be arranged in the following sequence: $b_{2g}(d_{xy}) < e_g(d_{xy}, d_{yz})$, $a_{1g}(d_{z^2}) < b_{1g}(d_{x^2-y^2})$
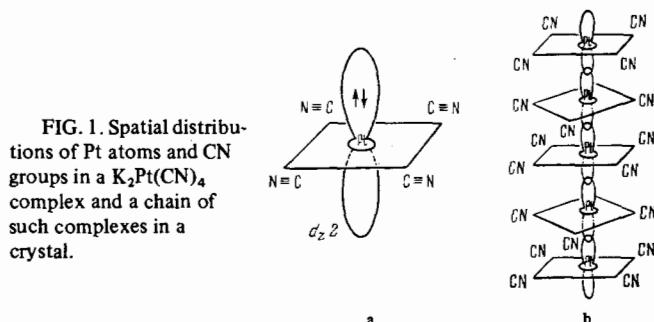

FIG. 1. Spatial distributions of Pt atoms and CN groups in a $K_2Pt(CN)_4$ complex and a chain of such complexes in a crystal.
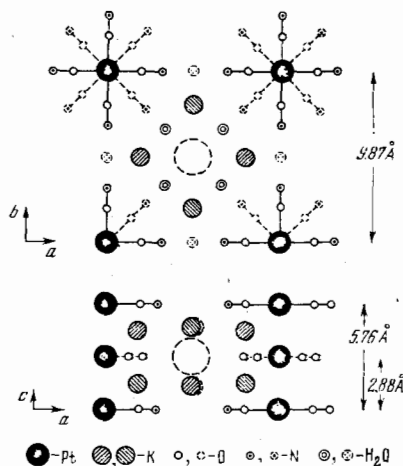

FIG. 2. Unit cell of KCP projected on the c and b axes.

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(the coordinate z is normal to the plane of the complexes and the indices b_{2g}, e_g, etc. indicate which irreducible representations of the symmetry group of the crystal apply to the wave functions which are the orbitals of a given level; the parentheses following the indices show which superpositions of the atomic functions form the orbitals). The loss of some of the electrons from the d_{z^2} band to the halogens gives rise to holes in this band. Above the d_{z^2} band there is another band corresponding to the $6p_z$ orbital of the Pt ion and the band $b_{1g}(d_{x^2-y^2})$. Thus, in mixed-valence complexes, the partial population of the d_{z^2} band may give rise to metallic properties of the investigated crystals. The ESR spectra, which will be discussed in detail later (Chap. 6), confirm that the electron properties of KCP are governed by the carriers in the d_{z^2} band.

The quasi-one-dimensional nature of the motion of holes in the d_{z^2} band is governed by two factors. First of all, the d_{z^2} orbitals (Fig. 1) are directed along the Pt ion chain and they ensure a good overlap of the neighboring ions in the chain but not of the nearest Pt ions in neighboring chains. Secondly, the distance c between the neighboring Pt ions in a chain (c = 2.89 Å) is only slightly greater than the distance between the nearest ions in a metal plate (2.77 Å). On the other hand, the large distance a between the neighboring platinum chains (a = 9.87 Å) results in a very weak overlap of the electron wave functions of the neighboring conducting chains.

It follows from these very simple band representations that KCP should exhibit all the properties of a quasi-one-dimensional metal. Optical measurements indicate that, at frequencies $\hbar\omega > 0.4$ eV, the KCP electrons do behave as a one-dimensional electron gas. The room-temperature electrical conductivity of KCP is fairly high (up to 300 $\Omega^{-1} \cdot$ cm^{-1}) and strongly anisotropic. However, at low temperatures and frequencies, we find that KCP is an insulator.

b) Optical properties of KCP. Measurements of the reflectivity of KCP have been carried out in polarized light at room temperature in the frequency range from $\hbar\omega$ = 0.001 eV to 6 eV. [9–12]. The results of these measurements are plotted in Fig. 3. When light is polarized perpendicularly to the conducting axis, the reflection coefficient is small, constant in the visible range, and represents the phonon spectrum in the infrared range. This behavior of the reflection coefficient is typical of an insulator. The frequency dependence of the coefficient $R_\parallel$ for light polarized along the conducting axis has a characteristic plasma edge in visible light. The $R_\perp(\omega)$ and $R_\parallel(\omega)$ dependences allow us to determine $\epsilon_\perp(\omega)$ and $\epsilon_\parallel(\omega)$. In the range $\hbar\omega > 0.4$ eV, we obtain

$$\varepsilon_\parallel(\omega) = \varepsilon_\infty \left\{ 1 - \frac{\omega_p^2}{\omega[\omega - (i/\tau)]} \right\}, \quad \varepsilon_\perp(\omega) = 2.25, \quad \varepsilon_\infty = 2.1,$$
$$\omega_p^2 = 4\pi e^2 N_e / m_e \varepsilon_\infty, \tag{1}$$

where ω_p is the plasma frequency (2.88 eV); m_e is the mass of a free electron; N_e is the electron density; τ is the collision time approximately equal to 3.2×10^{-15} sec; ϵ_∞ is the contribution of the inner-shell electrons to the permittivity. The value of N_e represents the electron density in the d_{z^2} band, i.e., $N_e = 1.7N_a$, where N_a is the concentration of the Pt atoms. Thus, the d_{z^2} electrons make exactly the same contribution as free electrons. On the other hand, the motion of electrons between the
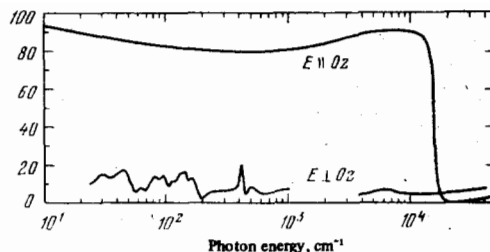

FIG. 3. Reflectivity of KCP for light polarized parallel and perpendicular to the conducting c axis (at room temperature). [12]

chains does not appear up to frequencies corresponding to $\hbar\omega \approx 6$ eV.

This very strong anisotropy of the frequency dependence of the permittivity gives rise to characteristic frequency and angular dependences of the reflection coefficient. [13–15] For example, in the case when the conducting chains (filaments) are perpendicular to the surface of a crystal and the electric field vector is parallel to the plane of incidence, the dependence $R(\omega)$ has a peak at the plasma frequency if the direction of the propagation of light does not coincide with the normal to the surface.

At frequencies $\hbar\omega < 0.4$ eV, the dependence $R_\parallel(\omega)$ shows that the behavior of electrons ceases to be metallic. In fact, if we use the Kramers-Kronig dispersion relationship, we can obtain from $R_\parallel(\omega)$ the real and imaginary components of the permittivity $\epsilon_\parallel^{(1)}(\omega)$ and $\epsilon_\parallel^{(2)}(\omega)$. As $\omega \to 0$, the real part of the permittivity tends to a constant value and not to $(-\infty)$, as predicted by the Drude theory of free electrons. Measurements carried out at 4.2°K at 10^{10} Hz give $\epsilon_\parallel^{(1)} \approx 10^3$. [16] In the imaginary part, there is a peak at a frequency of about $\hbar\omega \approx 0.14$ eV and then $\epsilon_\parallel^{(2)}(\omega)$ rises with decreasing ω. This peak is obviously due to a transition from the $5d_{z^2}$ to the $6p_z$ band. If this assumption is valid, the lower edge of the $6p_z$ band lies about 0.14 eV above the Fermi level and at frequencies exceeding 0.4 eV the contribution to ω_p^2 includes transition within the d_{z^2} band and $5d_{z^2} - 6p_z$ interband transitions. If we also assume that the matrix elements of the transitions to all the other bands are small and the excitation energies of the inner electrons exceed 6 eV, this band picture is in agreement with the observation that, in the frequency range $\hbar\omega$ from 0.4 to 6 eV, the optical properties are associated with the d_{z^2}-band electrons and these electrons can be regarded as free. This interpretation of the peak at 0.14 eV is only one of the possible explanations and a detailed discussion of the other interpretations of this peak can be found in the reviews. [8,104]

c) Conductivity anisotropy and metal-insulator. transition. The first investigations yielded the temperature dependence of the electrical conductivity along the chains $\sigma_\parallel$. [8,16] Later, the temperature dependences of $\sigma_\perp$ and the ratio $\sigma_\parallel/\sigma_\perp$ were determined for the same crystal. [17] The results of these measurements are plotted in Fig. 4. The anisotropy $\sigma_\parallel/\sigma_\perp$ varies from 5×10^4 at room temperature to 2.5×10^3 at 30°K. The temperature dependence of the conductivity shows clearly the transition to the insulating state when the temperature is reduced below 200°K. Above 200°K, the electrical conductivity is practically independent of temperature.
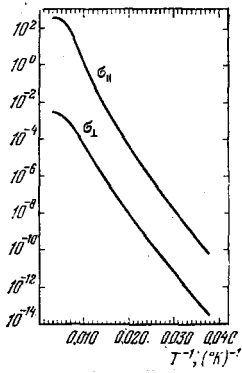
FIG. 4. Electrical conductivity ($\Omega^{-1} \cdot cm^{-1}$) of KCP parallel and perpendicular to the c axis [17].

The temperature dependences of the thermoelectric properties of KCP and $K_2Pt(CN)_4Cl_{0.3} \cdot 2.6H_2O$ are reported in[5,18,19]. Fedutin[19] discovered that these salts exhibited a strong anisotropy in the temperature dependence of the Seebeck effect. Above 200°K, the Seebeck effect along the chains, $\alpha_{||}$, is approximately constant for KCP; it is small (≈ 1 $\mu V/deg$ K) and positive, which indicates p-type conduction, in agreement with the band representations. The coefficient $\alpha_{||}$ changes its sign below 200°K and its absolute value rises strongly when the temperature is lowered. This temperature dependence of $\alpha_{||}$ confirms the existence of the metal-insulator transition in the electron motion along the chains. On the other hand, the Seebeck effect at right-angles to the chains remain small (≈ 3 $\mu V/deg$ K) and positive in the range from 300 to 85°K. This temperature dependence $\alpha_{\perp}$ indicates that the motion of electrons between the chains is of the hopping type.

Thus, electrical and optical measurements show that, at high temperatures and high frequencies, the electrons in KCP do indeed represent the quasi-one-dimensional metallic system. On the other hand, according to these measurements, the crystal is undoubtedly an insulator in the ground state and when the temperature is lowered the metal-insulator transition takes place in KCP.

Investigations of the Mössbauer effect have shown that, at low temperatures, the conduction electrons are delocalized at the Pt ions in such a way that the maximum variations of the electron density between different Pt ions are much smaller than one electron per center.[7] These measurements exclude the possibility of transition to an insulating state with strongly localized electrons (such as the Mott transition[20] or the formation of small-radius polarons). Experiments on the diffuse scattering of x-rays have made it clear that the main low-temperature properties of KCP should be associated with the Peierls transition.[21] These experiments have demonstrated that the Pt chains exhibit the same superstructure as predicted by the Peierls instability theory. Thus, in the case of $K_2Pt(CN)_4Br_{0.30} \cdot 3H_2O$, the superlattice period is equal to six Pt-Pt distances, whereas, in $Rb_2Pt(CN)_4Br_{0.23} \cdot 1.3H_2O$, it is equal to eight c distances. These periods are exactly equal to the value of $2k_F$ (k_F is the Fermi momentum of electrons), since the d_{z^2} electron band is approximately five-sixths full in KCP and seven-eighths full in the Rb salt. We shall analyze in detail these experimental results after considering the Peierls transition theory.

3. THEORY OF PEIERLS TRANSITION IN ONE-DIMENSIONAL SYSTEM IN STATIC APPROXIMATION

a) Molecular-field approximation. As pointed out in the Introduction, if we ignore the Coulomb repulsion between electrons, we find that, at sufficiently low temperatures, a one-dimensional metal is unstable in the presence of such lattice distortions which transform this system to the insulating state, i.e., it is unstable in the presence of distortions with a wave number equal to $2k_F$. Such distortions appear at a temperature T_p, which is a second order phase-transition point. We shall show that this is valid in the molecular field approximation.[22-24] We shall use this approximation to consider the static distortion of the lattice with just one wave number and ignore the rest of the lattice dynamics. In other words, we shall minimize the free energy of the system in respect of the equilibrium coordinates of the ions and ignore the ion vibrations about the equilibrium positions (phonons).

We shall use the tight-binding approximation to describe the motion of electrons in the ion field.[25] The applicability of this model to quasi-one-dimensional systems is justified by the fact that the overlap between the nonnearest neighbors in a chain is always weak. It should be pointed out that the tight-binding approximation automatically allows for the umklapp processes, i.e., for the lattice periodicity. The electron Hamiltonian is then of the form

$$\mathscr{H} = \sum_{n,\sigma} \epsilon_n a_{n\sigma}^+ a_{n\sigma} + b_{n,n+1}(a_{n\sigma}^+ a_{n+1,\sigma} + a_{n+1,\sigma}^+ a_{n\sigma}), \qquad (2)$$

where the first term is the electron energy at the sites n and the second term describes electron transitions to neighboring sites, and $b_{n,n+1}$ is the resonance integral for the sites n and n + 1 (we shall use the single-band approximation). If all the sites are equivalent and the interstitial distances are equal, it follows that $b_{n,n+1} = b$, the quantities ϵ_n can be assumed to vanish (all that changes is the origin from which energy is measured), and the electron spectrum is

$$E(k) = 2b\cos k, \quad k = \frac{2\pi n}{N} \quad \left(n = 0, \pm 1, \ldots, \pm \frac{N}{2}\right), \qquad (3)$$

where N is the number of sites in the lattice.

We shall consider the simplest case when there is one external electron per atom in the lattice. Then, below the temperature T_p, the lattice period should double. The doubling displaces the n-th atom by an amount

$$u_n = (-1)^n u. \qquad (4)$$

The resonance integrals of the lattice displacements given by Eq. (4) are characterized by $b_{n,n-1} = b_1$ and $b_{n,n+1} = b_2$ and the electron spectrum is

$$E_{1,2}(k) = \pm\sqrt{b_1^2 + b_2^2 + 2b_1 b_2 \cos k}, \quad k = \frac{2\pi n}{N} \quad \left(n = 0, \pm 1, \ldots, \pm \frac{N}{4}\right). \qquad (5)$$

If the distortion is small ($\Delta = |b_1 - b_2| \ll b$, $2b = b_1 + b_2$), Eq. (5) can be written in the form

$$E_{1,2}(k) = \pm\sqrt{\Delta^2 + 4b^2 \cos^2 k}, \quad k = \frac{2\pi n}{N} \quad \left(n = 0, \pm 1, \ldots, \pm \frac{N}{4}\right). \qquad (6)$$

In the case of a half-filled band, the chemical potential vanishes since the subbands (1) and (6) are symmetric relative to the energy E = 0 and half the states lie in the

range E < 0. The free energy (per atom) of the electrons and lattice can then be expressed in terms of the parameter u using the relationship

$$F(u, T) = -T \sum_{i=1, 2; k} \ln(1 + e^{-E_i(k)/T}) + \frac{1}{2}\varkappa u^2, \quad (7)$$

where $\varkappa$ is the elasticity constant of the lattice subjected to the displacements (4) and this constant is found ignoring the electron transitions between centers [the contribution of these transitions to the lattice elasticity is governed by the first term in Eq. (7)]. We shall show that below the Peierls transition temperature T_p the free energy minimum is reached for $u \neq 0$. Clearly, T_p is that temperature at which the nontrivial solution $u \neq 0$ is first obtained for the equation

$$\lim_{u \to 0} \frac{\partial F(u, T)}{\partial u} = 0. \quad (8)$$

We shall now find the dependence $F(u, 0)$ at $T = 0$. We obtain from Eq. (7)

$$F(u, 0) = -\frac{1}{N} \sum_k \sqrt{\Delta^2 + 4b^2 \cos^2 k} + \frac{1}{2}\varkappa u^2. \quad (9)$$

We shall assume that N is large and change the summation in Eq. (9) to integration with respect to k. We shall introduce a dimensionless constant g for the electron-lattice interaction by means of the relationship $\varkappa u^2 = \Delta^2/2\pi bg^2$. Then, assuming that the transition parameter is not u but Δ, we obtain

$$F(\Delta, 0) = -\frac{1}{2\pi} \int_0^\pi \sqrt{\Delta^2 + 4b^2 \cos^2 k}\, dk + \frac{\Delta^2}{4\pi bg^2}$$
$$= -\frac{\Delta^2}{4\pi b}\left(\ln \frac{8b}{\Delta} + \frac{1}{2}\right) + \frac{\Delta^2}{4\pi bg^2}. \quad (10)$$

It is clear from Eq. (10) that, in the case of small values of Δ, we have $F(\Delta, 0) < 0$, i.e., a lower free energy is obtained for the nontrivial solution

$$\Delta(0) = 8be^{-1/g^2}. \quad (11)$$

The value of T_p is described by an equation derived from Eq. (8) and this equation is similar to the BCS equation for the critical temperature of a superconductor:[26]

$$g^2 \int_0^{2b} \frac{d\varepsilon}{\sqrt{1 - (\varepsilon/2b)^2}} \cdot \frac{\mathrm{th}(\varepsilon/2T)}{\varepsilon} = 1. \quad (12)$$

Equations (6) and (9)—(12) are valid if $T_p \ll b$, i.e., if $g^2 \ll 1$. We shall confine our attention to the systems which satisfy this condition. Equation (12) differs from the BCS equation by the integration limit with respect to the energy (band half-width 2b and not the Debye frequency ω_D) and by the factor $[1 - (\epsilon/2b)^2]^{-1/2}$. This factor describes the density of electron states in the tight-binding approximation and its appearance in Eq. (12) is due to the fact that the contribution to the Peierls instability is made by the whole electron band, whereas in a superconductor the interaction between electrons and phonons vanishes only in an energy interval of the order of ω_D near the Fermi surface and $\omega_D \ll 2b$. In this narrow interval, the density of states may be assumed to be constant. Since $\omega_D \ll 2b$ and the interaction constants governing the Peierls instability and superconductivity are identical (or approximately identical), the Peierls instability is, generally speaking, a stronger effect than the superconductivity. We find that T_p is given by the following expression derived from Eq. (12):

$$T_p = \frac{8\gamma b}{\pi} e^{-1/g^2}, \quad (13)$$

where $\ln\gamma = C$ is the Euler constant. The ratio $\Delta(0)/T_p$ for the Peierls transition is the same as in the BCS

theory. Similar calculations carried out in the molecular field approximation show that, for an arbitrary band population, the static distortions of the lattice at the Peierls instability point are characterized by a wave number equal to $2k_F$. The formulas for $\Delta(0)$ and T_p in the case of an arbitrary number of p electrons per center ($0 < p < 2$) are obtained from Eqs. (11) and (13) by replacing b with b $\sin(\pi p/2)$ and g^2 with $g^2/2$, provided p is not close to a rational fraction n/m with a small denominator m, i.e., if the Peierls distortion period is not commeasurable with the initial lattice period. For small deviations of p from unity (for $|1 - p| \lesssim T_p/b$), it is more convenient to double the period (this is explained in Sec. 5b; the result was communicated to the author by Yu. P. Kopaev). If $m \geq 2$, the commeasurability effects are less important than in the doubling of the period when $m = 1$.

If we adopt the molecular field approximation, we find that below T_p the electron spectrum acquires a gap in accordance with Eq. (6). The point T_p represents then a second order phase transition. However, it is clear that, since we are dealing with a one-dimensional system, the results of the molecular field approximation are modified greatly if we go outside the range of validity of this approximation and allow for fluctuations of the system. In the Peierls transition case, fluctuations of the order parameter represent displacements of atoms from their equilibrium positions, i.e., essentially, the allowance for fluctuations is the allowance for phonons or, in other words, the allowance for the lattice dynamics.

b) Allowance for fluctuations within the framework of Ginzburg-Landau static approximation. The influence of fluctuations (phonons) on the Peierls transition can be allowed for if the electron energy is calculated in the adiabatic approximation. In this approximation, the phonon frequency is assumed to be zero because the energies of the majority of electrons exceed considerably the phonon energies. Thus, within the adiabatic approximation, we may assume that the displacements of atoms are independent of time and vary only with the coordinates, i.e.,

$$u_n = \sum_q e^{iqn} u_q. \quad (14)$$

Having determined the one-electron energies in the lattice with displacements described by Eq. (14), we can express the free energy in terms of u_q. Confining ourselves, as usual, to the terms of the second and fourth order in u_q and to the second derivatives with respect to the coordinates, we obtain a Ginzburg-Landau functional. If we introduce parameters with the dimensions of energy $\Delta_q = gu_q(2\pi b\varkappa)^{1/2}$, we find that the free energy associated with the distortion of u_q has the following form if $2k_F \neq \pi$:

$$F(\Delta_q) = \alpha(T)|\Delta_q|^2 + \beta|\Delta_q|^4 + \tilde{\gamma}(q - 2k_F)^2|\Delta_q|^2, \quad (15)$$

where the coefficients α, β, and $\tilde{\gamma}$ are calculated in the molecular field approximation and $\alpha(T)$ vanishes at $T = T_p$, in accordance with the Ginzburg-Landau theory. The coefficients of the expansion of the free energy in terms of Δ_q are found in[27] and, to within numerical factors, we have $\alpha(T) \sim (T - T_p)/bT_p^2$, $\beta \sim 1/bT_p^2$, and $\tilde{\gamma} \sim b/T_p^2$.

All the one-dimensional thermodynamic functions can be calculated exactly from the Ginzburg-Landau functional.[28] This procedure was applied to the Peierls transition by Lee, Rice, and Anderson[27] in the model

of an electron band with an initially constant density of states. Their calculations showed that, strictly speaking, there should be no long-range order in the system at any finite temperature because the correlation function should decrease exponentially with distance x:

$$\langle \Delta (x) \, \Delta (0) \rangle = \langle \Delta^2 \rangle \exp [-x \xi^{-1} (T)] \cos 2k_F x. \qquad (16)$$

The result (16) is obtained because the long-range order in a one-dimensional system described by a real order parameter is disturbed if the amplitude of the order parameter vanishes due to fluctuations at just one point. A finite energy is required for the amplitude of the real order parameter to vanish at one point and, if $T \neq 0$, the potential barrier can be overcome simply by thermal fluctuations. However, if $T < T_p/4$, the correlation length becomes very large and rises exponentially with decreasing temperature so that we can assume that a Peierls superlattice appears in the system at temperatures below $T_p/4$. The correlation function (16) can be used to calculate the electron spectrum of the system employing the approximate expression relating the one-electron Green's function with the Fourier transform $D(q)$ of the correlation function $\langle \Delta (x) \Delta (0) \rangle$:

$$G^{-1} (k, \omega) = \omega - E(k) - \sum_q D(q) [\omega$$
$$- E(k+q) + i\delta]^{-1}. \qquad (17)$$

The calculation results show that the system does not have a gap but a density-of-states dip. Only at temperatures $T < T_p/4$ does the density of states approach the value which would be obtained in the molecular field approximation (Fig. 5). Quantitatively, the static Ginzburg-Landau approximation is exact for $\omega_D \ll T_p$ and, as shown below in the case of KCP, this condition is satisfied because $\omega_D/T_p \lesssim 0.25$. However, it is difficult to estimate the precision of the calculation of the one-electron Green's function carried out using the approximation (17). All that we can show is that Eq. (17) becomes exact in the limit $\xi^{-1}(T) \to 0$, i.e., when $T < T_p/4$.

4. INFLUENCE OF THREE-DIMENSIONAL EFFECTS ON PEIERLS TRANSITION IN QUASI-ONE-DIMENSIONAL CRYSTALS

In discussing the Peierls transition above, we have ignored the interaction between displacements of atoms in different chains. Clearly, if this interaction is allowed for, the order parameter of the Peierls transition becomes three-dimensional. The interaction between displacements of atoms in different chains is due to the Coulomb forces and due to the overlap of the electron wave functions of different chains (electron
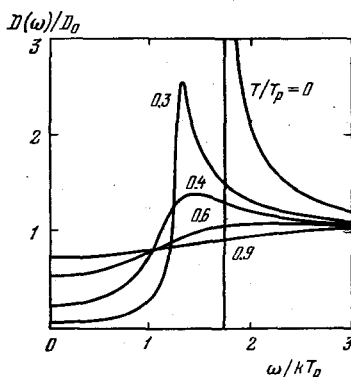

FIG. 5. Density of electron states $D(\omega)$ in the static Ginzburg-Landau approximation, normalized to the metallic density of states D_0. The value of ω is the deviation of the energy from the Fermi value. The $T/T_p = 0$ curve corresponds to the molecular field approximation [27].

transitions take place between the chains); we shall consider these two effects separately.

a) Coulomb interaction between electrons. Since we are assuming that all the sites are equivalent in the original distortion-free lattice, they are all also neutral because the electron density must be the same at all sites. The Coulomb forces appear if the lattice distortion makes the sites inequivalent and redistributes the charges along the chain. As pointed out by Barisic, [25] such redistribution occurs if the displacements of atoms are not exactly equal to twice the lattice period (see Note 1 added in proof at the end of the paper). In fact, the kinetic energy of the interatomic motion of electrons decreases if electrons are transferred partly to the sites which are closer to one another since the resonance integrals of such sites are larger. An excess electron density appears at ions located close to one another and the region where the ion density is higher is charged negatively, whereas the region where the ion density is lower becomes positively charged. The order of magnitude of the variation of the charge density is $\delta\rho/\bar{\rho} \sim \Delta/b$. Thus, the Peierls displacement of the lattice ions with $2k_F \neq \pi$ gives rise to a charge-density wave in the ground state. We shall see later that this effect is responsible for all those features of the behavior of a Peierls insulator in an electric field which distinguish it from ordinary insulators. Since the characteristic electron redistribution time is governed by the plasma frequency, $\omega_p \gg \omega_D$, we may assume that the displacements $u_{m, n}$ of sites n in chains m (the chain lattice is assumed to be two-dimensional and the coordinates of a chain are given by integers $m = m_x, m_y$) result in the instantaneous appearance of charges $\rho_{m, n}$ at sites (m, n).

When this effect occurs in the metallic state of quasi-one-dimensional crystals, it is important to note that, as in the case of one-dimensional crystals (see [28,29]), the Coulomb potential is screened even if we allow for electron transitions between chains. In fact, a redistribution of the charge in a chain in a quasi-one-dimensional crystal and the associated electric field polarize the neighboring chains and this polarization screens the electric field over long distances and reduces the electric field energy due to the Peierls deformation.

Self-consistent calculations of the influence of the Coulomb interaction on the Peierls transition in a quasi-one-dimensional system have not yet been carried out. However, we can point out one qualitative effect which results from the Coulomb interaction. [25,31] The energy of the electric field associated with the Peierls deformation is minimal if the displacements of ions in neighboring chains are in antiphase. Consequently, the interaction of electrons should result in corresponding correlations in the displacements of ions in neighboring chains and such correlations can be observed in studies of the diffuse x-ray scattering and neutron scattering in KCP [31,32] below 120°K (Sec. 6).

Allowance for the Coulomb interaction (and for all other three-dimensional effects) in the static Ginzburg-Landau approximation reduces to the description of the displacement u by a three-dimensional momentum and by the addition of a term allowing for the interaction between charge waves in different chains to the expression for free energy. The interaction energy of charge-density waves in neighboring chains m and m' is $Q_1 \Delta_m \Delta_{m'}/b^2$, where Q_1 is the Coulomb interaction (per

atom) between charge-density waves $e \cos(2k_F n)$ in neighboring chains. The order of magnitude of this interaction is $Q_1 = C_\perp e^2/r_\perp$, where $r_\perp$ is the distance between the chains and the parameter $C_\perp$ depends on $2k_F$, $r_\perp$, and $\epsilon_\perp$ ($C_\perp \to 0$ in the limit $2k_F \to \pi$). If we consider only the interaction between the nearest chains, we obtain the following expression for the free energy

$$F(\Delta_{k,q}) = \alpha(T)|\Delta_{k,q}|^2 + \beta|\Delta_{k,q}|^4 + \tag{18}$$
$$+ [\bar{\gamma}(q - 2k_F)^2 + \delta(2 + \cos k_x + \cos k_y)]|\Delta_{k,q}|^2,$$

where $\delta = \delta_Q \sim Q_1/b^2$.

b) **Electron transitions between chains.** If we allow for the overlap of the electron wave functions of different chains and for the dependence of this overlap on the atomic displacement, we find that the system is really anisotropic and three-dimensional. A structure transition of the Peierls type should be also observed in a three-dimensional crystal if the following symmetry condition is satisfied by the electron spectrum:

$$E(\mathbf{k}) - \varepsilon_F = -E(\mathbf{k} + \mathbf{q}) + \varepsilon_F, \tag{19}$$

where q is a particular vector. When the temperature is lowered, a Peierls deformation with a wave vector q appears in a system with an electron spectrum given by Eq. (19) and a charge-density wave is generated. [25, 33-35] However, in contrast to a purely one-dimensional system, such a deformation of a three-dimensional crystal produces an energy gap on the Fermi surface only for directions perpendicular to the vector q. Therefore, below the structure transition point, a three-dimensional metal remains a metal or becomes a semimetal. [1] In a quasi-one-dimensional crystal, the energy gap on the Fermi surface may also be absent for the motion of electrons between the chains but the weak overlap of the wave functions of the neighboring chains makes the conduction between the chains negligible (in the majority of the currently known quasi-one-dimensional crystals, this conduction is of the hopping type). Therefore, a quasi-one-dimensional crystal becomes an insulator below the Peierls transition point. If allowance is made for transitions of electrons between the nearest platinum ions in neighboring chains, the electron spectrum of KCP becomes

$$E(\mathbf{k}) = 2b \cos q + 2b_1(\cos k_x + \cos k_y), \tag{20}$$

where b_1 is the resonance integral of the transition between the nearest ions in neighboring chains (compare with the structure of KCP shown in Fig. 2). The spectrum (20) has the symmetry properties of Eq. (19) if $q = (\pi, \pi, 2k_F)$. Thus, electron transitions between the chains lead, like the Coulomb interaction of electrons, to three-dimensional correlations of the Peierls distortions of the chains and, in the case of KCP, these correlations are such that the displacements of neighboring chains are shifted in phase by π.

Allowance for the electron transitions between the nonnearest ions in neighboring chains (along the diagonal) violates the condition (19) and such transitions suppress the Peierls instability. [34] If we use b_2 to denote the resonance integral of the interchain transitions violating the condition (10), we find that the Peierls instability temperature decreases with decreasing ratio b_2/T_p (in the molecular field approximation). However, in the case of quasi-one-dimensional crystals, this effect can always be neglected because these crystals satisfy the inequality $b_1 \ll T_p$ (it follows from the definition of quasi-one-dimensional crystals) and we also have $b_2 \lesssim b_1$.

Clearly, in the case of the spectrum (20), the interaction between chains in the Ginzburg-Landau functional has exactly the same form (18) as the Coulomb interaction between the nearest chains but $\delta = \delta_b \sim b_1/T_p^2$. Therefore, these two effects can be included in the functional (18) by introducing $\delta = \delta_Q + \delta_b$.

c) **Influence of chain interaction on type of transition.** We shall now consider the question of the strength of the interaction between the chains at which fluctuations in the system cease to be one-dimensional. This problem can be solved in the static Ginzburg-Landau approximation by calculating the correlation function $\langle \Delta_{m,n} \Delta_\theta, 0 \rangle$ for the order parameter $\Delta_{m,n}$. Taking the Ginzburg-Landau free energy to be given by Eq. (18), retaining terms quadratic in $\Delta_{m,n}$, and making calculations similar to those reported by Rice, [37] we find that, in the temperature range $T < T_p$:

$$\Delta_{m,n} = \Psi_{m,n} e^{i\pi(m_x + m_y)} \cos(2k_F n),$$
$$\langle \Psi_{m,n}^2 \rangle = \Psi_0^2 + \frac{T}{2N} \sum_{k,q} \frac{1}{-2\alpha(T) + \bar{\gamma}q^2 + \delta(2 + \cos k_x + \cos k_y)}, \tag{21}$$

where $\Psi_0^2 = \alpha/\beta$ is the average value of the amplitude of the order parameter $\Delta_{m,n}$ in the molecular field approximation, N is the total number of sites in the system, and $\alpha(T_p) = 0$. The fluctuations are small if

$$\langle \Psi_{m,n}^2 \rangle - \Psi_0^2 \ll \Psi_0^2, \tag{22}$$

and, in this case, we can use the self-consistent field approximation. It follows from Eq. (21) that

$$\langle \Psi_{m,n}^2 \rangle / \Psi_0^2 - 1 = \begin{cases} T\beta/\alpha \sqrt{\alpha\bar{\gamma}} \sim \tau^{-3/2}, & \delta \ll \alpha, \\ T\beta/\alpha \sqrt{\delta\bar{\gamma}} \sim 1/\tau \sqrt{\delta b}, & \delta \gg \alpha, \end{cases} \tag{23}$$

where $\tau = (T_p - T)/T_p$ and T_p is the transition temperature calculated allowing for the interaction between the chains in the molecular field approximation. Since $\delta = \delta_Q + \delta_b$, the parameter δ/α, which governs the role of fluctuations, is of the same order as $Q_1/b + b_1 b/T_p^2$. In the Peierls transition, the Coulomb interaction between the charges within a chain is $Q_0 < b$ (otherwise, the Mott and not the Peierls transition would take place). Since $Q_1 < Q_0$, the degree of suppression of the fluctuations governs primarily the parameter b_1, representing the transitions of electrons between the chains. [2]

In the case of quasi-one-dimensional crystals ($b_1 \ll T_p$) and if $b_1 \gg T_p^2/b$, the fluctuations are important only in a very narrow region near the transition point so that the molecular field approximation is applicable at almost all the other temperatures and the thermodynamics of the Peierls transition is basically three-dimensional. It should be pointed out that the physical interpretation of the condition for the smallness of the fluctuations is fairly simple. In fact, the condition $b_1 \gg T_p^2/b$ reduces to the requirement that, in a characteristic correlation length along a chain $\xi_0 = b/T_p$ (ξ_0 is expressed in interatomic scattering units), the total interaction between the chains $b_1 \xi_0$ is much lower than the temperature in energy units.

If $b_1 \lesssim T_p^2/b$, the fluctuations are important at temperatures well below and above T_p. It is natural to assume that, in this situation, the results of Lee, Rice, and Anderson, [27] obtained for a purely one-dimensional system, are applicable also to those physical properties of quasi-one-dimensional crystals which relate to one

chain and further studies are needed to determine the correlations of displacements in different chains. This is basically correct but some refinements are still necessary.

The point is that the long-range order in a three-dimensional system with a real order parameter is established no matter how small the value of δ (this is not true at any temperature in a one-dimensional system). The dependence of the transition temperature T_3, at which the long-range order is established, on the value of δ can now be obtained using the static Ginzburg-Landau functional and the self-consistent field method to allow for the interaction between the chains (a similar method was used by Efetov and Larkin[38] in considering the temperature of a superconducting transition in quasi-one-dimensional systems for a weak interaction between the chains). We shall use the Ginzburg-Landau functional in the form

$$F(\Delta_{m, n}) = \sum_m [F_m + \sum_{m'} \delta_{m, m'} \Delta_{m, n} \Delta_{m', n}], \qquad (24)$$

where the free energy F_m of a chain m is given by Eq. (18) with $\delta = 0$. We shall calculate the average value of the order parameter

$$\langle \Delta_{m, n} \rangle = \int \Delta_{m, n} \, e^{-F/T} D\Delta_{m, n} / \int e^{-F/T} D\Delta_{m, n}, \qquad (25)$$

using the self-consistent field approximation in respect of the interaction between the chains

$$F(\Delta_{m, n}) = \sum_m [F_m + \sum_{m'} \delta_{m, m'} \Delta_{m, n} \langle \Delta_{m', n} \rangle]. \qquad (26)$$

We then find that Eq. (26) yields the following expression for T_3:

$$\langle \Delta_{0, 0} \rangle = \frac{\delta}{T} \sum_n \langle \Delta_{0, 0} \Delta_{0, n} \rangle \langle \Delta_{0, n} \rangle, \quad \delta = \sum_{m'} \delta_{m, m'}. \qquad (27)$$

Substituting the correlation function of the displacements along a chain, given by Eq. (16), we find that, if $2k_F \neq \pi$ (see Note 2 added in proof)

$$(\delta/2T_3) \langle \Delta^2 \rangle \xi(T_3) = 1. \qquad (28)$$

Since $\xi(T)$ rises exponentially when the temperature T approaches $T_p/4$, the temperature at which the long-range order appears (T_3) is close to $T_p/4$. However, if $b\delta \ll 1$, the fluctuations in the atomic displacements remain large throughout the range $T \lesssim T_p$. This means that, in the correlation function

$$\langle \Psi_{m, n} \Psi_{0, 0} \rangle = \Psi_0^2 + K(m, n) \qquad (29)$$

the ratio is $\Psi_0^2/K(0, 0) \sim 1$ for $b\delta \sim 1$ and $\Psi_0^2/K(0, 0) \ll 1$ for $b\delta \ll 1$. The fall of $K(m, n)$ when $m = 0$ and n rises is no faster than in a purely one-dimensional case and the correlation length of the function $K(m, n)$ along the chains is $\xi_\parallel \gtrsim \xi(T)$. The correlation between the chains, governed by the function $K(m, n)$ with $m \neq 0$, appears — like the long-range order — at a temperature $\sim T_3$. In fact, in this range of temperatures, the interaction between the chains in a distance equal to the correlation length along the chains $\delta \langle \Delta^2 \rangle \xi(T)$ becomes comparable with the temperature T. However, if $b\delta \ll 1$, the correlation length $\xi_\perp$ of the function $K(m, n)$ does not become greater at any temperature (at $T \to 0$, we have to allow for the quantum fluctuation).

Thus, depending on the value of the parameter $b_1 b/T_p^2$, we can either have an almost three-dimensional or almost one-dimensional Peierls transition in quasi-one-dimensional crystals. In the latter case, the energy gap, long-distance correlations of displacements along the

chains, and the correlation between the chains are practically negligible above the point $T_3 \approx T_p/4$ and rise strongly below this temperature. In the former case, we have the usual gradual rise of the characteristics when the temperature is reduced below T_p.

5. CHANGES IN ONE-DIMENSIONAL PHONON AND ELECTRON SYSTEM DURING PEIERLS TRANSITION

a) Fröhlich Hamiltonian. Even if we retain the static molecular field approximation, we find that a Peierls transition causes a considerable change in the phonon spectrum in the range of quasimomentum of the order of $2k_F$, i.e., in the range $q \approx \pi$ for a half-filled band. In fact, the macroscopic displacements of atoms from their equilibrium positions which occur below T_p are equivalent to the condensation of phonons whose wave number is $2k_F$. However, such condensation is possible only if the frequency of phonons with the wave number $2k_F$ tends to zero when the temperature T approaches T_p. Thus, because of the electron-phonon interaction, a Peierls transition not only changes the electron but also the phonon system. Therefore, in a self-consistent analysis of Peierls transitions, we must use a Hamiltonian which describes electrons, phonons, and their interaction, i.e., the Fröhlich Hamiltonian.

In the tight-binding approximation, we may assume that only the resonant integrals $b_{n, n+1}$ are affected when ions are displaced from their equilibrium positions. The electron Hamiltonian derived allowing for the ion motion is then

$$\mathcal{H} = \sum_{n, \sigma} \left\{ [b + b'(u_{n+1} - u_n)] (a_{n+1, \sigma}^+ a_{n\sigma} + a_{n\sigma}^+ a_{n+1, \sigma}) \right. \qquad (30)$$
$$\left. + \frac{1}{8} \varkappa (u_{n+1} - u_n)^2 + \frac{1}{2} M (\dot{u}_n)^2 \right\},$$

where b' is the derivative of the resonance integral with respect to the interatomic distance, and m is the mass of ions. Going over, as usual, to the phonon representation

$$u_n = \sum_q \sqrt{\frac{\hbar}{2NM\omega_q}} (b_q e^{iqn} + b_q^+ e^{-iqn}), \qquad (31)$$

we obtain the Fröhlich Hamiltonian in the tight-binding model [25]

$$\mathcal{H} = \sum_{k\sigma} E(k) a_{k, \sigma}^+ a_{k, \sigma} + \sum_q \hbar\omega_q b_q^+ b_q$$
$$+ N^{-1/2} \sum_{k, q, \sigma} g(k, q) a_{k+q, \sigma}^+ a_{k, \sigma} (b_q - b_{-q}^+), \qquad (32)$$
$$g(k, q) = ib'[\sin(k+q) - \sin k] \sqrt{\frac{2\hbar}{M\omega_q}}, \quad E(k) = 2b\cos k.$$

In the Hamiltonian (32), the frequencies ω_q are calculated ignoring the transitions of electrons between the lattice centers and they correspond to the lattice vibrations in the case when each ion vibrates together with its outer electron. Since such a lattice originally consists of neutral centers, it follows that ω_q, considered in the limit $q \to 0$, gives an acoustic spectrum. The interaction between electrons and phonons in the case under consideration is essentially similar to the interaction between electrons and phonons in the deformed potential model used for semiconductors.

b) Thermal changes in phonon spectrum above transition point. Renormalization of the phonon spectrum in the model under consideration is understood to include allowance for the interatomic motion of electrons on the lattice vibrations. We shall show that such renormal-

ization gives rise to a "soft" mode above T_p with a quasimomentum $2k_F$. We shall allow for the electron-phonon interaction using the random phase approximation. We shall introduce the Green's functions of phonons $D(\omega, q)$ and electrons $G(\omega, k)$ exactly as was done in [26]. The random phase approximation corresponds to allowance only for the polarization loops in the equation for $D(\omega, q)$, i.e.,

$$D(\omega, q) = D_0(\omega, q) - D_0(\omega, q) \Pi(\omega, q) D(\omega, q),$$

$$\Pi(\omega, q) = 2i \int_0^{2\pi} dk \int_{-\infty}^{+\infty} \frac{d\varepsilon}{(2\pi)^2} |g(k, q)|^2 G_0(\varepsilon, k) G_0(\varepsilon - \omega, k - q),$$

$$D_0(\omega, q) = \frac{\omega_q}{2} \left(\frac{1}{\omega - \omega_q + i\delta} - \frac{1}{\omega + \omega_q - i\delta} \right),$$ (33)

$$G_0(\omega, k) = \frac{n_k}{\omega - E(k) + i\delta} + \frac{1 - n_k}{\omega - E(k) - i\delta}, \quad n_k = \frac{1}{1 + \exp[(E(k) - \varepsilon_F)/T]}.$$

It follows from Eq. (21) that the polarization operator is described by

$$\text{Re}\,\Pi(\omega, q) = \frac{\sin^2(q/2)}{2\pi b M \omega_q} \int_0^{2\pi} \frac{n_k - n_{k+q}}{E(k) - E(k+q) + \omega} dk,$$

$$\text{Im}\,\Pi(\omega, q)$$ (34)

$$= \frac{\sin^2(q/2)}{2bM\omega_q} \int_0^{2\pi} dk\, n_k (1 - n_{k+q}) [\delta(E_k - E_{k+q} + \omega) + \delta(E_k - E_{k+q} - \omega)].$$

The polarization operator governs the renormalized frequencies $\Omega(q)$, in accordance with the relationship

$$\Omega^2 = \omega_q^2 [1 - \Pi(\Omega, q)].$$ (35)

We can easily see that the real part of the polarization operator becomes infinitely large for $\omega \to 0$, $T \to 0$, and $2k_F$. In fact, in the one-dimensional case, the momenta k close to k_F satisfy the condition $E(k \pm 2k_F) - \varepsilon_F = -E(k) + \varepsilon_F$ and, at $T = 0$, $\omega = 0$, the integral with respect to k in the expression for $\text{Re}\,\Pi$ has a logarithmic singularity. In the isotropic three-dimensional case, the polarization operator also has a singularity at $q = 2k_F$ (this is the well-known Kohn anomaly in the permittivity and phonon spectrum [39]) but this singularity is weak [only the derivative $\partial\Pi(0, q)/\partial q$ diverges logarithmically for $q \to 2k_F$]. In the one-dimensional case, the same Kohn anomaly results in a logarithmic rise of $\Pi(0, q)$ at $T = 0$ for $q \to 2k_F$ and, according to Eq. (35), it makes the original system unstable because phonons of imaginary frequency are obtained when the temperature is lowered. Thus, the Peierls transition is closely related to the giant Kohn anomaly in the polarization operator of a one-dimensional electron system.

If $\omega = 0$, we find from Eq. (34) that

$$\text{Im}\,\Pi(0, q) = 0, \quad \text{Re}\,\Pi(0, q)$$

$$= \frac{T \sin(q/2)}{4b^2} \int_0^{2b/T} \frac{d\varepsilon\, \text{sh}(\varepsilon \sin q/2)}{\varepsilon \sqrt{1 - (\varepsilon T/2b)^2}} \left\{ \left[\text{ch}\left(\varepsilon \sin\frac{q}{2}\right) \right. \right.$$

$$\left. + \text{ch}\left(\frac{2b}{T}\left(\cos\frac{q}{2}\sqrt{1 - \left(\frac{\varepsilon T}{2b}\right)^2} + \cos k_F \right) \right) \right]^{-1}$$ (36)

$$\left. + \left[\text{ch}\left(\varepsilon \sin\frac{q}{2}\right) + \text{ch}\left(\frac{2b}{T}\left(\cos\frac{q}{2}\sqrt{1 - \left(\frac{\varepsilon T}{2b}\right)^2} - \cos k_F \right) \right) \right]^{-1} \right\}.$$

It follows from Eq. (36) that, in the weak-binding case ($T_p \ll b$), when $\cos k_F \neq 0$, the contribution to $\text{Re}\,\Pi(0, q)$ comes only from one of the two terms in the braces and this contribution is greatest when $q = 2k_F$. In the case of a half-filled band ($\cos k_F = 0$), the same contribution is made by both terms and this explains why the argument of the exponential function in the formula for T_p differs by a factor of two in the cases corresponding to $p = 1$ (half-filled band) and to $|1 - p| \sim 1$ (band population differing strongly from $1/2$). When the degree of population of a band differs slightly from $1/2$, i.e., for

small values of $\cos k_F \lesssim T_p/B$, the quantity $\text{Re}\,\Pi(0, q)$ reaches its maximum at $q = \pi$ (doubling of the period) and not at $q = 2k_F$ (see Note 3 added in proof).

It follows from Eq. (36) that, if a band is half-filled, then

$$\text{Re}\,\Pi(0, \pi) = g^2 \int_0^{2b} \frac{d\varepsilon\, \text{th}(\varepsilon/2T)}{\varepsilon \sqrt{1 - (\varepsilon/2b)^2}}.$$ (37)

According to Eq. (35), the frequency of renormalized phonons with a quasimomentum $2k_F$ vanishes at $\Pi(0, \pi) = 1$ and we again have Eq. (12) for the Peierls transition temperature. Thus, the random phase approximation shows that, when the temperature approaches T_p from above, we obtain soft phonon modes with a quasimomentum close to π; at $T = T_p$, the phonon frequency with $q = \pi$ vanishes, and below T_p we should observe macroscopic displacements of ions from their equilibrium positions, corresponding to the condensation of phonons with $q = \pi$, in accordance with the relationship

$$\langle u_n \rangle = \sqrt{\frac{\hbar}{MN\omega(\pi)}} \langle (b_\pi) + (b_\pi^+) \rangle e^{i\pi n}.$$ (38)

The qualitative temperature dependences of the phonon spectrum above T_p are shown in Fig. 6 (see Note 4 added in proof).

c) Phonons in Peierls insulating phase. Below the transition point, the lattice becomes statically distorted in accordance with Eq. (38), the lattice period changes, and the phonon spectrum becomes more complex because a unit cell of the new structure now contains several atoms. It follows that the Brillouin zone has not only an acoustic branch but also one (if the period is doubled) or several (if $2k_F \neq \pi$) optical branches. [40-43] If a band is half-filled, both acoustic and optical branches appear below T_p and at $T = 0$ the optical mode frequency for $g \ll 1$ is $g\omega(\pi)$ in the model with constant density of states (Fig. 6d).

If $p \neq 1$ (or, more exactly, if $2k_F \neq \pi$), we find that there are several optical branches below T_p. In this
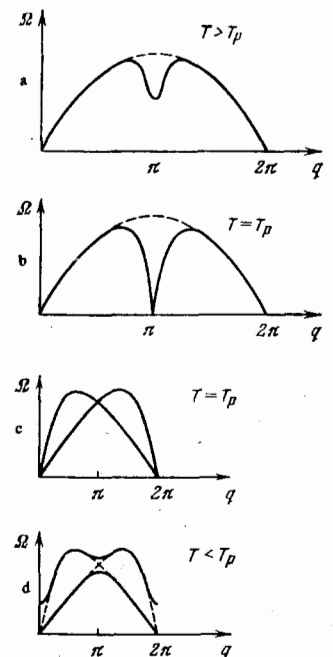

FIG. 6. Qualitative temperature dependences of the phonon spectra in the Peierls transition case: a–b) extended zone scheme (one atom per unit cell); c–d) reduced zone scheme (two atoms per unit cell).

case, the frequencies of two optical modes are equal to zero at $T = T_p$ in the reduced zone scheme. It is important to note that one of them, corresponding in the limit $q \to 0$ to the motion of a charge-density wave along the chains, retains its low frequency in the long-wavelength limit at all temperatures below T_p. The frequency of the second mode (corresponding to the oscillations of the amplitude of the charge-density wave) rises with decreasing temperature and approaches $g\omega(2k_F)$. These conclusions follow from the calculations of Lee, Rice, and Anderson.[43] They consider collective modes in the jellium model below T_p (in the molecular field approximation for the Fröhlich Hamiltonian with a constant density of states) and find the frequencies of two modes $\Omega_+(q)$, corresponding to oscillations of the amplitude and phase of a charge-density wave. The mode $\Omega_-(q)$ corresponds, in the $q \to 0$ limit, to the glide of a charge-density wave along the chains. Since the phase of this wave in the jellium model is not locked in space, it follows that $\Omega_-(0) \to 0$ for all temperatures below T_p and at T_p we have

$$\Omega_-^2(q) = \frac{m}{m^*} v_F^2 q^2, \quad \Omega_+^2 = g^2\omega^2(2k_F) + \frac{4}{3}\frac{m}{m^*} v_F^2 q^2, \quad \frac{m^*}{m} = 1 + \frac{4\Delta^2}{g^2\omega^2(2k_F)},$$
(39)

where v_F is the Fermi velocity and g is the dimensionless electron-phonon interaction constant in the Fröhlich Hamiltonian. The $\Omega_-(q)$ mode in the jellium model is of the Goldstone type, i.e., its appearance is a consequence of the breaking of the symmetry of the original system with respect to a continuous group of translations through any distance (above T_p, the system is homogeneous, whereas, below T_p a charge-density wave with a period $2k_F$ appears in the system). Naturally, the frequency of this wave in the $q \neq 0$ case in Eq. (39) is governed by the characteristics of the ion and electron systems because the propagation of this wave displaces ions and redistributes the electron density.

In a real lattice, where p is a rational fraction n/m, the frequency of the corresponding collective mode differs from zero below T_p for $q \to 0$ because the symmetry of the continuous group is no longer broken (in other words, a charge-density wave is pinned to the sites in the original lattice). However, the value of $\omega_T = \Omega_-(0)$ decreases with increasing noncommeasurability index m between $2k_F$ and the period of the original lattice 2π, and $\omega_T \approx gm (\Delta/b)^{m/2-1} \omega(2k_F)$. The origin of the modes Ω_+ is explained in Fig. 7 with the aid of the temperature dependences of the phonon spectrum in the case of quadrupling of the period.

The finite value of ω_T also results from the Coulomb interaction of charge-density waves in neighboring chains and structure defects or impurities. A defect or impurity is an obstacle to the free glide, along the chains, of a Peierls wave of ion displacements and either of them can pin a charge-density wave in space.

It is important to note that a low-frequency optical mode Ω_- is electrically active and may be excited by an electromagnetic wave even when $q \to 0$. This is due to the fact that oscillations of the charge-density wave reduce to a redistribution of charge within one unit cell in the low-temperature phase of the crystal. Therefore, the interaction of the mode Ω_- with an electromagnetic field is of dipole nature and the corresponding dipole moment is governed by the characteristics of the electron and ion systems. If $\omega \ll \Delta$ and $T = 0$, the per-
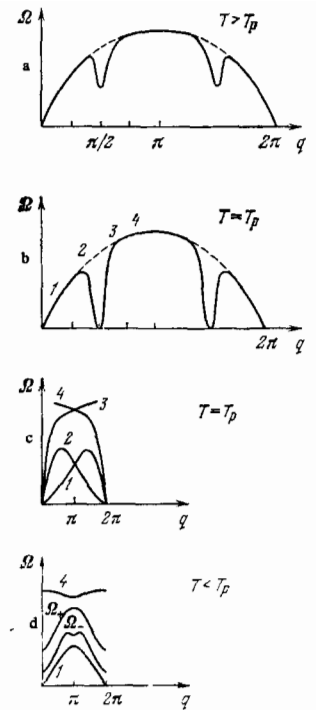

FIG. 7. Qualitative temperature dependences of the phonon spectrum in the Peierls transition with quadrupled period: a–b) extended zone scheme (one atom per unit cell); c–d) reduced zone scheme (four atoms per unit cell). Modes: 1) acoustic; 2) Ω_-; 3) Ω_+; 4) optical.

mittivity $\epsilon_{||}(\omega)$ found allowing for the mode Ω_- and electron transitions across the gap is of the form:[43]

$$\epsilon_{||}(\omega) = 1 + \frac{\omega_p^2}{6\Delta^2} + \frac{\omega_p^2 m/m^*}{\omega_T^2 - \omega^2}, \quad \omega_p^2 = \frac{4\pi e^2 N_e}{m_e}.$$
(40)

The expression (40) gives rise to large values of the static permittivity because of the mode Ω_- and it also gives rise to a peak in the absorption spectrum at a frequency near ω_T.

Since all the conclusions relating to the mode Ω_- are obtained in the molecular field approximation, they apply to a purely one-dimensional system and quasione-dimensional crystals with $b_\perp \ll T_p^2/b$ only at temperatures below T_3.

We must stress once again that the appearance of the mode Ω_- is associated with a charge-density wave below T_p. These two effects are specific to the Peierls metal-insulator structure transition. Essentially, the low-temperature phase of a Peierls insulator with $2k_F \neq \pi$ is, in many respects, similar to ferroelectrics, the dipole moment is due to ions and collective-state electrons.

d) Changes in electron spectrum and accuracy of random-phase approximation. The interaction of electrons with low-frequency phonons whose quasimomentum is about $2k_F$ has almost the same effect as the scattering of electrons by steady-state lattice distortions with wave numbers $\approx 2k_F$. Thus, even above T_p, the electron spectrum should exhibit a dip (pseudogap) in the density of states near the Fermi surface.[41] Below the transition point, the changes in the electron spectrum are due to the scattering of electrons by static ion displacements of Eq. (38) and by low-frequency phonons. Therefore, a pseudogap exists in the electron spectrum also below T_p and approaches a true gap when the temperature is lowered. Qualitatively, the electron spectrum is similar to that obtained by Lee, Rice, and Anderson in the static Ginzburg-Landau approximation.

Thus, using the random phase approximation, we find that a pseudogap, a soft optical mode with $q = 2k_F$, and

a charge-density wave with $2k_F \neq \pi$ all appear at the transition point T_p. When the temperature is lowered, the amplitude of the charge-density wave grows, an energy gap appears, and an optically active mode with a low-frequency remains even at $T \to 0$ if $q \to 0$ (provided $2k_F \neq \pi$). If the period is doubled, the charge-density wave and optically active low-frequency mode are absent (see Note 5 added in proof).

All these results for a system of electrons and phonons are obtained by applying the random phase approximation to the electron-phonon interaction. The perturbation-theory series diagrams corresponding to this approximation are not small for $g^2 \ll 1$ because they diverge logarithmically at $T \to 0$. However, in the one-dimensional case, we find that, in contrast to the three-dimensional systems, [24] the logarithmic divergence affects not only the polarization branches included in the random phase approximation but also the corrections to the vertex part of the electron-phonon interaction. [33] For example, a correction of the first order in g^2, shown in Fig. 8, diverges logarithmically if the difference between the phonon momentum q and $2k_F$, i.e., $q' = q - 2k_F$, approaches ω/v_F. However, this correction is small for $\omega \ll v_F q'$. Since the range of momenta $q' \lesssim \omega/v_F$ is very narrow, inclusion of the corrections to the vertex part is not very important in the Peierls instability.

The diagrams leading to the superconducting instability are also divergent. If the temperature of the Peierls instability lies below ω_D, we have to allow simultaneously for the diagrams containing the Peierls and superconducting instabilities. [44-46] In a system with $\omega_D \gtrsim T_p$, we can have states in which the Peierls deformations and superconducting pairings are present simultaneously. In this case, the equations are very complex and can only be investiged in the "parquet" approximation, corresponding to the self-consistent method. The situation in the $\omega_D \gtrsim T_p$ situation is far from clear but there is little doubt that this case is of greatest interest from the point of view of superconductivity.

If $\omega_D \ll T_p$, the situation is much simpler (in the case of KCP, we have $\omega_D/T_p \approx 0.25$ because, according to [47] the displacements along the chain correspond to $\omega_D = 90°$K and, as shown later, $T_p \approx 400-500°$K). In this case, the thermodynamic functions (including the transition temperature T_p), electron characteristics, and ion displacements can be found in the static approximation discussed above. However, the temperature at which a strong Kohn anomaly is observed can be found only by considering the system of electrons and phonons. If $\omega_D \ll T_p$, the superconducting-type diagrams are unimportant [46] and the Peierls transition can be described simply by considering only those terms in the perturbation theory series in g^2 which correspond to the polarization loops of the phonon Green's function $D(\omega, q)$. However, a quantitative description of the transition requires a self-consistent solution of the equations for the electron and phonon Green's functions. The need for a self-consistent solution follows from the calculations of
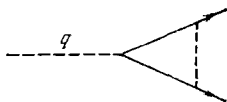
Rice and Strässler. [41] These authors calculated the electron Green's function allowing for the soft mode and then used this function to find the polarization operator and instability temperature from the condition $\Pi(0, 2k_F) = 1$. The temperature found in this way was $0.28T_p$. This result shows that in order to calculate the polarization operator in the logarithmic approximation, we can use zeroth Green's functions but allowance for non-logarithmic corrections requires a self-consistent solution of the equations for G and D.

The author of this review is not aware of any such calculations. Therefore, the temperature of the appearance of a strong Kohn anomaly T_k cannot be found more accurately even in the case when $\omega_D \ll T_p$ (the order of magnitude of T_k is clearly the same as that of T_p).

6. EXPERIMENTAL CONFIRMATION OF PEIERLS TRANSITION IN KCP CRYSTALS

a) Structural changes and appearance of giant Kohn anomaly. An investigation of the diffuse x-ray scattering was carried out at room temperature on KCP and $Rb_2Pt(CN)_4Br_{0.23} \cdot 1.3H_2O$ crystals. [21] X-rays were scattered in these crystals elastically or almost elastically and the change in the momentum was $2k_F$ (in dimensionless units, $2k_F$ is equal to $\pi p/c$, where p is the number of electrons per platinum atom in a chain). The calculation demonstrated the sinusoidal nature of the atom displacements, resulting in the appearance of a superlattice (with a period 6c in KCP and 8c in the Rb salt). The sinusoidal dependence of the displacements confirmed the Peierls nature of the distortions and excluded the possibility of a structure with charge alternation of the type $(5/6)Pt^{2+}$ and $(1/6)Pt^{4+}$. The diffuse nature of the scattering indicated that there was no correlation between the displacements of ions in different chains. On the other hand, the thickness of the diffuse-scattering layer indicated that the correlation length of displacements along a chain was quite considerable (about 400 Å). The diffuse x-ray scattering failed to distinguish the elastic from the almost elastic process and, therefore, the results of these experiments failed to indicate whether the displacement wave with the momentum $2k_F$ was static and corresponded to the long-range order within a chain or whether it was due to low-frequency phonons with momenta close to $2k_F$.

Studies involving inelastic scattering of neutrons [47] clearly indicated that a giant Kohn anomaly was observed in the phonon spectrum at room temperature. The experimentally determined dependence of the phonon frequency on the quasi-momentum is plotted in Fig. 9, which shows clearly the "softening" of phonons with momenta of about $2k_F$. On the other hand, there is also a room-temperature peak in the almost elastic scattering of neutrons involving a change in the momentum

FIG. 8. Graph showing a correction of the first order in respect of g^2 to the vertex part of the electron-phonon interaction.
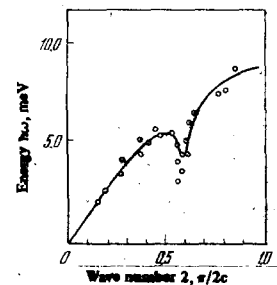
FIG. 9. Dependence of the phonon frequency on the quasimomentum in KCP at room temperature, deduced from inelastic neutron scattering data [47].

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along a chain by $2k_F$,[32] which is in agreement with the results of the diffuse x-ray scattering.

Even these experiments carried out at room temperature show that a "one-dimensional" Peierls transition (i.e., $b_1 \ll T_p^2/b$) occurs in KCP and that the transition temperature found in the molecular field approximation is $T_p > 300°K$. In fact, according to the results given in Sec. 3 for $b_1 \gg T_p^2/b$, the transition is practically three-dimensional and the existence of a considerable correlation length along the chains is incompatible with the total absence of correlations between the chains. If $b_1 \ll T_p^2/b$, this situation is possible in the temperature range between T_3 and T_p.

The x-ray and neutron measurements below room temperature confirmed the validity of this hypothesis. At temperatures below $120°K$ (the measurements were carried out down to $77°$), the x-ray scattering became less diffuse and the nature of this change indicated the appearance of such three-dimensional correlations for which the ion displacements in neighboring chains were in antiphase.[31] However, these measurements did not yield the temperature dependence of the correlation length across the chains but this dependence was obtained from a study of the almost elastic scattering of neutrons carried out in[32] at temperatures from 300 to $6°K$. Figure 10 shows the experimental results reported in[32] for the intensity of the elastic (or almost elastic) scattering of neutrons involving the transfer of a momentum **Q**. At room temperature, the strongest scattering involved the transfer of a momentum $2k_F$ along the chains. When the temperature was lowered, this scattering became weaker but a peak appeared at **Q** = $(\pi/a, \pi/a, 2k_F)$, which corresponded to such a three-dimensional correlation of displacements in which atoms in neighboring chains moved in antiphase. However, even at $6°K$ the scattering with **Q** = $(0, 0, 2k_F)$ remained sufficiently strong, i.e., the long-range three-dimensional order was not established down to $6°K$. A comparison of the intensities for $(0, 0, 2k_F)$ and $(\pi/a, \pi/a, 2k_F)$ indicated that the correlation length of the displacements in different chains rose strongly at $120°K$ to $3a$ (a is the distance between the Pt chains) and then remained practically constant when the temperature was lowered down to $6°K$. The neutron measurements gave the correlation length along the chains at room temperature, whose lower limit was $20c$.

Thus, low-temperature structure studies indicated clearly that a "one-dimensional" Peierls transition with $b_1 \ll T_p^2/b$ occurred in KCP and the appearance of three-dimensional correlations near $120°K$ corresponded to $T_3 \approx 120°K$ and $T_p \approx 4T_3 \approx 400-500°K$. According to the theoretical estimates given in[27], the correlation length at $T = 300°K$ along the chains $\xi_\parallel$ should amount to about $7c$ for static distortions. The x-ray data indicated that $\xi_\parallel > 140c$ and the neutron-diffraction data gave $\xi_\parallel > 20c$. This discrepancy could be explained by the fact that the theoretical estimates gave $\xi_\parallel$ in the static approximation and this parameter governed only the elastic scattering. The diffuse x-ray scattering could not distinguish the elastic from the almost elastic process and in the neutron measurements the precision of the simultaneous determination of the momentum and energy was insufficient for small energy transfers. Therefore, the structure studies carried out at room temperature probably gave information not on the static ion displacements but on the critical scattering by phonons with $q \approx 2k_F$, characterized by low fre-
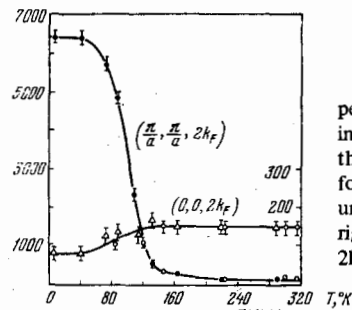

FIG. 10. Temperature dependences of the critical scattering in KCP [32] The abscissa on the left gives the intensity scale for $(\pi/a, \pi/a, 2k_F)$ in arbitrary units and the abscissa on the right gives the intensity for $(0, 0, 2k_F)$.

quencies and strong damping. Such phonons should occur in the phonon spectrum due to the strong Kohn anomaly at $T = 300°K$ (Fig. 10). Clearly, the temperature of this Kohn anomaly T_k agreed approximately with T_p even in the "one-dimensional" transition case.

b) Change in electron state density. The appearance of a gap in the Peierls transition could be deduced from the temperature dependences of the optical properties. In a brief communication,[48] Zeller reported that KCP had a low-temperature energy gap $2\Delta(0) \approx 0.18$ eV. Since $\Delta(0) = 1.76T_p$, it follows that T_p is about $500°K$, which is in full agreement with estimates of this quantity deduced from the structure data.

The temperature dependence of the electrical conductivity $\sigma_\parallel$ (Fig. 4) shows that the activation energy is about $0.08-0.09$ eV between 40 and $100°K$. This value is also in good agreement with the value of $\Delta(0)$ obtained above [it should be noted that the gap is practically independent of temperature and equal to $\Delta(0)$ below $T_3 \approx T_p/4$].

According to theoretical ideas,[27] a "one-dimensional" transition below T_p produces a dip in the density of states on the Fermi surface; this dip becomes significant only when the temperature is lowered to T_3 and an energy gap appears in the region of T_3. Information on the appearance of a dip in the density of states near ϵ_F (appearance of a pseudogap) can be obtained by measuring those quantities which are governed directly by the density of electron states on the Fermi surface. These quantities include the paramagnetic susceptibility and electronic specific heat.

Measurements of the electronic specific heat are possible only at low temperatures (the lattice contribution to the specific heat cannot be separated at high temperatures). Measurements of the specific heat were carried out in the range $1.5-6.5°K$ by Greene and Little on a crystal of $K_2Pt(CN)Cl_{0.3} \cdot xH_2O$.[49] According to the diffuse x-ray scattering data, the Peierls transition should occur in crystals of this compound.[21] Greene and Little failed to find any electronic contribution to the specific heat and the precision of their experiments indicated that the low-temperature density of states on the Fermi surface $\rho(0)$ did not exceed $\approx 10^{34}$ erg$^{-1} \cdot$ mole^{-1}.

Measurements of the paramagnetic susceptibility χ_p can give full information on the temperature dependence of $\rho(0)$ because

$$\chi_p = \frac{1}{2} g^2 \mu_B^2 \rho(0). \qquad (41)$$

Rupp[50] found a small room-temperature shift of the NMR frequency of the Pt^{195} nuclei relative to the NMR frequency of the insulating salt $K_2Pt(CN)_4 \cdot 3H_2O$ and he attributed this shift to the Knight effect. According to the reports in[7,27,109], this shift disappeared in the range $100-200°K$ and the NMR spectrum was inde-

pendent of temperature in the range 1.5–110°K. A somewhat different temperature dependence of 1.5–110°K was deduced from ESR measurements on KCP crystals.[51] Measurements of the resonance frequency indicated that the anisotropy of the g factor was typical of the d_{z^2} band. According to Fig. 11, the intensity of the signal, proportional to the paramagnetic susceptibility, fell when the temperature was lowered from 130 to 65°K (measurements at higher and lower temperatures were impossible because of the resonance line broadening). These results made it possible to reconstruct the temperature dependence of the density of states $\rho(0)$ in the investigated range (at 85°K the intensity of the signal corresponded to 10^{20} spins/cm^3, i.e., to a paramagnetic susceptibility $\chi_p \approx 1.2 \times 10^{-4}$ mole^{-1}). The conversion of the signal intensity to the value of $\rho(0)$ indicated that the density of states fell from 1.3 $\times 10^{36}$ erg^{-1}·mole^{-1} at 130°K to 0.4 $\times 10^{36}$ erg^{-1}·mole^{-1} at 65°K. In the tight-binding model, the density of states in the original band could be expressed in terms of the total band width (4b) with the aid of the relationship

$$\rho(0) = \frac{N_{aT}}{\pi b \sin \pi p_i/2} \qquad (42)$$

and for $\rho(0) \approx 1.3 \times 10^{36}$ we found that $4b \approx 0.6$ eV. Since the dip in the density of states was significant even at 130°K, this value provided only a lower limit and, in fact, the value of 4b could be 1.5–2 times greater. The total band width in metallic platinum was 5 eV and it should be of the order of 1–2 eV in KCP. The ESR data were in good agreement with this estimate.

However, direct measurements of the paramagnetic susceptibility did not agree with the ESR data. According to the experiments reported in [52, 53], only a strongly anisotropic paramagnetic contribution was observed for KCP. To within $\approx 10^{-5}$ mole^{-1}, the susceptibility at right-angles to the chains was negligible and the parallel susceptibility increased in accordance with the Curie law with decreasing temperature and it was $\approx 10^{-4}$ mole^{-1} at room temperature. Measurements of the susceptibility reported in [52, 53] were probably carried out not on freshly prepared KCP crystals (these crystals were known to lose water eventually and this would have affected their structure: according to [51], the ESR signal decreased with time). Undoubtedly, it would be desirable to carry out additional measurements of the paramagnetic susceptibility because this quantity should give direct and unambiguous information on the appearance of a pseudogap in the Peierls transition.

c) "Soft" optical mode Ω_-. Zeller[48] found that KCP had a low-temperature absorption peak in the range 0.002–0.003 eV and he attributed this peak to the excitation of the Ω_- mode. If we adopt this interpretation, we find that $\omega_T \approx 0.002$–0.003 eV. This low value of the excitation energy of the optically active mode explains the high value of the low-temperature permit-

FIG. 11. Temperature dependence of the intensity of the ESR signal of KCP (arbitrary units) [51].

tivity[43] (according to [6], the permittivity is $\epsilon_\| \approx 1200$ at 4.2°K). In fact, it follows from Eqs. (39) and (40) that if $\omega(2k_F) \approx 0.006$ eV (Fig. 9), $g^2 \approx 0.5$, and $\epsilon_\| \approx 1200$, we obtain $\omega_T \approx 0.002$ eV, in agreement with the observations reported in [48] (see Note 6 added in proof).

Thus, the existence of the Peierls transition in variable-valence platinum complexes is not only supported qualitatively by numerous experimental results but, in the case of KCP, these results are in good quantitative agreement with the theory of "one-dimensional" Peierls transitions. However, the temperature dependence of the paramagnetic susceptibility is not yet clear. Very interesting information on the phonon spectrum in the Peierls insulating phase should be obtained from studies of the inelastic neutron scattering at low temperatures.

## 7. INFLUENCE OF LATTICE DISORDER ON PEIERLS TRANSITION

The Peierls instability and associated Kohn anomaly in the phonon spectrum are due to the existence of a Fermi step in the electron momentum distribution. Hence, it is clear that disorder in the lattice, which smears out the step in the momentum (but not in the energy) space, should suppress the Peierls instability. All the quasi-one-dimensional crystals investigated so far, with the exception of the TTF-TCNQ[54, 55] and TTT(TCNQ)$_2$ salts, are characterized by an internal disorder. As pointed out in Sec. 1, the disorder in mixed-valence platinum complexes is due to the random distribution of rare-earth ions and halogens. In highly conducting TCNQ salts, the disorder is due to the random orientations of asymmetric cations.[6] Only in the complexes formed by TCNQ with TTF and TTT are the TTF and TTT cations fully symmetric. The lattice disorder can only be due to structure defects. We shall see later that the influence of disorder on the Peierls transition is as strong as the influence of magnetic impurities on the superconducting transition.[56-58] Clearly, the Peierls transition is not observed in highly conducting TCNQ salts with asymmetric cations because of the disorder. However, the disorder can also alter greatly the Peierls transition itself, if it occurs at all.

a) Influence of disorder on Peierls transition temperature in molecular-field approximation. We shall consider the influence of the lattice disorder on the Peierls transition in the molecular field approximation in the special case when a band is half-filled. There is then no redistribution of charge and the transition temperature T_p can be calculated simply from the dependence of the density of electron states $\rho(u, E)$ on the displacements of the lattice atoms u and the degree of disorder of the lattice since the free energy can be expressed in terms of u using an expression which is a generalization of Eq. (7):

$$F(u, T) = -T \int_{-\infty}^{+\infty} dE\, \rho(u, E) \ln(1 + e^{-E/T}) + \frac{1}{2}\varkappa u^2. \qquad (43)$$

The problem is to determine the density of electron states $\rho(u, E)$ in a disordered lattice. There are doubts about using approximate methods in the determination of the density of states in a one-dimensional system so that we shall consider only those disorder models which allow us to determine the density of states exactly. We shall consider the Lloyd[59] and interrupted-strand[60] models.
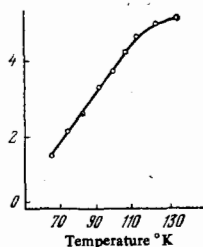
In the Lloyd model, it is assumed that the resonance integral $b_{n, \, n+1}$ in the Hamiltonian (2) is not a random quantity but the potentials ϵ_n are distributed at random between the sites n. It is assumed that the distributions of ϵ_n between different sites are independent and are all described by the Lorentz distribution

$$P(\epsilon) = \frac{\epsilon_1}{\epsilon^2 + \epsilon_1^2}. \qquad (44)$$

Clearly, this model is qualitatively adequate in the case of platinum complexes because the disorder in the distribution of the K and Br ions gives rise to a random potential acting on the conduction electrons in the chains. In the case of the distribution given by Eq. (44), the density of states $\rho(u, E)$ in a disordered lattice ($\epsilon_1 \neq 0$) is expressed in terms of the density of states $\rho_0(u, E)$ in an ideal lattice ($\epsilon_1 = 0$) using the relationship

$$\rho(u, E) = \frac{\epsilon_1}{\pi} \int_{-\infty}^{+\infty} dx \, \frac{\rho_0(u, x)}{(E-x)^2 + \epsilon_1^2} \qquad (45)$$

and the density of states $\rho_0(u, E)$ in a lattice with a doubled period is known from Eqs. (5) and (16). In the Lloyd model, the free energy of electrons is infinite because of the weak fall of the Lorentzian distribution function (44) in the limit $\epsilon \to \infty$. However, this divergence is unimportant because that part of the free electron energy which depends on the displacement u, i.e., $\partial F / \partial u$, if finite. The divergence observed at high values of E in Eq. (43) can be removed physically by allowing for the ion energy in the same potential field ϵ_n. Calculations similar to those given in Sec. 2 yield the following equation for the transition temperature [compare with Eq. (12)]

$$g^2 \int_0^{2b} \frac{d\epsilon}{\sqrt{1-(\epsilon/2b)^2}} \, \frac{\epsilon \, \mathrm{th}\,(\epsilon/2T)}{\epsilon^2 + \epsilon_1^2} = 1. \qquad (46)$$

Equation (46) can be transformed to the digamma function $\psi(x)$

$$\ln \frac{T_{p0}}{T} = \psi\left(\frac{1}{2} + \frac{\epsilon_1}{2\pi T}\right) - \psi\left(\frac{1}{2}\right), \qquad T_{p0} = \frac{8\gamma b}{\pi} e^{-1/g^2}, \qquad (47)$$

which demonstrates the full analogy between the influence of the lattice disorder on the Peierls transition and the influence of magnetic impurities on the superconducting transition. [61] When ϵ_1 increases, the transition temperature T_p falls and the Peierls instability disappears when $\epsilon_1 = \epsilon_{1c} = \Delta_0/2$, where Δ_0 is the Peierls gap in an ideal crystal at T = 0, which is equal to $\pi T_{p0}/\gamma$.

The interrupted-strand model is applicable if a quasi-one-dimensional crystal contains structure defects or impurity atoms which stop the conduction electrons of energies lying close to the Fermi surface (for example, impurity molecules with filled shells). In the Hamiltonian (2), this situation corresponds to the case when $\epsilon_n = 0$ but the resonance integral is a random quantity which assumes the value 0 for some neighboring atoms n and n + 1, whereas, for other neighbors its value is the same as in an ideal lattice. A linear system of atoms then splits into a number of pieces and the Peierls transition in each of these pieces occurs independently at a temperature T_p which depends on the number of atoms in that piece. In a piece with N atoms, the electron spectrum considered in the tight-binding approximation is given by Eq. (6) after the doubling of the period. For a finite value of n, the discrete nature of the spectrum weakens the Peierls instability and when N is reduced, the transition temperature falls and tends to zero. Next, taking N equal to a doubled odd number (when $\epsilon_F = 0$), we find that Eqs. (6) and (7) give an equa-

tion which governs the dependence of the parameter Δ on T:

$$g^2 \sum_{n=-N/2}^{N/2} \mathrm{th} \, \frac{\sqrt{\Delta^2 + 4b^2 \cos^2(2\pi n/N)}}{2T} \, \frac{1}{\sqrt{\Delta^2 + 4b^2 \cos^2(2\pi n/N)}} = 1. \qquad (48)$$

We can find the transition temperature and gap as a function of N from Eq. (48) by applying the Poisson summation formula. [57] The Peierls transition does not occur in the interrupted-strand model if $N < N_c = 2b/T_{p0}$.

The models discussed above are different in respect of the nature of the disorder. To compare the results which follow from these models and, particularly, the Peierls transition criteria, we shall introduce a universal quantity for one-dimensional disordered systems such as the electron localization length, which can be calculated if we know the density of states. [62] In the one-dimensional case, this quantity replaces the concept of the mean free path. Clearly, the localization length l, expressed in units of the interatomic distance c, is identical with N in the interrupted-strand model. The localization length in the Lloyd model is calculated by Thouless [62] and this length at the center of the original band is $2b/\epsilon_1$ when the electron energy is E = 0 and $\epsilon_1 \ll 2b$. The parameters ϵ_1 and $\epsilon_N = 2b/N$, expressed in terms of the localization length l and representing the disorder in the Lloyd and interrupted-strand models, are the same for both models and equal to $2b/T_{p0}$. The critical localization length in these models has very similar values $4\gamma b/\pi T_{p0} = 1.13(2b/T_{p0})$ and $2b/T_{p0}$, respectively. Thus, the Peierls transition criterion, expressed in terms of the localization length,

$$l > l_c \approx \frac{2b}{T_{p0}}, \qquad (49)$$

is applicable to any disorder. On the other hand, the ratio Δ/T_p may differ in either direction from the value π/γ, depending on the nature of the disorder.

Experimental data indicate that the disorder has a weak influence on the Peierls transition in KCP. This means that, in the case of KCP, we have $l \gg 15$ ($2b > 0.3$ eV, $T_{p0} \approx 500°$K) and the fluctuation potential of the K and Br ions is much less than 0.05 eV. This smallness of the fluctuation potential is very surprising because the external Pt electrons cannot screen the charge of the K and Br ions over distances of the order of the interatomic spacing. However, such screening may be due to the dipoles of the water molecules. A strong influence of these molecules on the screening of the K and halogen ion potentials was observed by Butler and Guggenheim [63] in a study of the nuclear magnetic resonance of the water molecules in $K_2Pt(CN)_4Cl_{0.3} \cdot xH_2O$ crystals. The screening role of the water molecules explains why the properties of the crystals of variable-valence platinum complexes change very greatly when water is lost (the conductivity falls strongly and the ESR signal disappears; [51] the paramagnetic susceptibility in a field parallel to the chains begins to rise with decreasing temperature, in accordance with the Curie law [52,53]). In fact, the screening action of the water molecules shows why, when these molecules are lost, the electrons may be localized spatially because of an increase in the random potential of the K and halogen ions. Such localization causes those changes in the properties of crystals which are found experimentally after dehydration of the samples (see Note 7 added in proof).

b) Influence of disorder on low-temperature elec-

trical and magnetic properties of crystals. It is important to note that the Peierls transition in a disordered system does not produce a gap in the electron spectrum even at very low temperatures because the density of states does not vanish due to the disorder even in the Peierls gap range from $-\Delta_0$ to Δ_0, where only a dip in the density of states $\rho(E)$ (pseudogap) is observed. For example, at the center of the original band in the Lloyd model at $T = 0$, we have $\rho_0(0) = \epsilon_1/b\Delta_0 < \rho_0(0)$. The reduction in the transition temperature T_p is essentially due to the appearance of electron states in the Peierls gap region.

Electron levels inside the pseudogap govern the conductivity $\sigma(T)$ at low temperatures and, therefore, the conductivity at $T < T_3$ does not decrease exponentially with decreasing temperature, in contrast to the opposite behavior of the Peierls transition in an ideal lattice. Since levels inside the pseudogap correspond to localized states, the conduction may be of the hopping type. Theoretical analyses of the hopping conduction in quasi-one-dimensional systems at low temperatures have predicted the following temperature dependence of the electrical conductivity: [64-66]

$$\sigma_{\parallel,\perp} \sim e^{-T_0/4T}, \tag{50}$$

where T_0 is a constant; the values of $\sigma_{\parallel,\perp}$ are calculated allowing for the electron hops between the chains.[3] The dependence (50) indeed describes well the low-temperature data on the electrical conductivities $\sigma_{\parallel}$ and $\sigma_{\perp}$ of KCP below 90°K.[65] However, at low temperatures, the conductivity of KCP at frequencies of 10^{10} Hz or higher is from three to five orders of magnitude higher than the dc conductivity[6] (this is also true of other quasi-one-dimensional crystals with a higher permittivity). The cause of this very strong frequency dispersion at relatively low frequencies is not yet clear.

The levels inside the pseudogap correspond to spatially localized states. The Coulomb repulsion between electrons with opposite spins in such states may give rise to unpaired localized electrons at low temperatures. The appearance of such unpaired electrons implies the appearance of a Mott gap for one-electron excitations. The Peierls transition, which reduces the density of states at the Fermi surface, enhances the role of the Coulomb repulsion of electrons and favors the Mott transition at low temperatures. If the interaction between such unpaired spins is weak, the transition to the Mott insulating state should increase the low-temperature paramagnetic susceptibility in accordance with the Curie law[67] (interaction between localized spins is responsible for the slower rise of the susceptibility[68]). Therefore, measurements of the paramagnetic susceptibility of KCP at low temperatures should help in understanding the role of the disorder in these crystals.

Thus, a deviation of the fall in conductivity with temperature from the exponential law, observed at the lowest temperatures (below $\approx 40°$K), is an indirect indication that the disorder in the distribution of the K and Br ions still influences the physical properties of KCP but the influence is weak. Therefore, additional experimental studies of this influence are needed and these can be made, for example, by measuring the paramagnetic susceptibility at low temperatures. Undoubtedly, the most interesting information on the influence of disorder on the Peierls transition in KCP can be obtained by a controlled introduction of impurities or

structure defects and simultaneous investigation of the characteristics of the Peierls transition.

8. PROBLEM OF EXISTENCE OF PEIERLS TRANSITIONS IN TCNQ SALTS

a) Highly conducting TCNQ salts with asymmetric cations. One-dimensional motion of electrons in these compounds is possible because of electron transitions between TCNQ molecules which form parallel piles separated by cations with completely filled electron shells. A detailed discussion of the properties of such crystals is given in Shchegolev's review[6] and we shall only consider the new experimental results which support the occurrence of the metal-insulator transition in compounds of this type. Sufficiently convincing data are now available which demonstrate that this metal-insulator transition occurs at temperatures below $\sim 20°$K in TCNQ salts with N-methylphenazine (NMP), quinoline (Qn), and acridine (Ad) cations. A jump in the specific heat at $T_0 = 7$ and $14°$K is observed in the NMP and Qn salts, respectively.[69] Measurements of the far infrared absorption in the NMP and Qn salts indicate that an energy gap exists in these compounds at low temperatures. For example, the gap in NMP-TCNQ at $4.2°$K is ≈ 50 cm^{-1} and gradually disappears at temperatures above $\approx 15°$K[70,71] [the gap in Qn(TCNQ)$_2$ is about 60 cm^{-1}].

The metal-insulator transition is also supported by measurements of the magnetic susceptibility of the NMP, Qn, and Ad salts,[68,72] whose temperature dependence changes near T_0. The susceptibility χ_p of these salts below T_0 rises in accordance with the law $\chi_p \propto T^{-\alpha}$ with $0 < \alpha < 1$. The dependence $\chi_p(T)$, dependence of the the magnetic moment on the field and temperature, and temperature dependence of the electronic specific heat in the range $T < T_0$[69] can all be described quite accurately by the model of localized spins with the Heisenberg antiferromagnetic interaction if the parameter of this interaction J is a random quantity and we can assume arbitrarily small values with a probability density W such that $W(J) \to 0$ when $J \to 0$. The random nature of the interaction may be primarily due to the disorder in the distribution of the cations because the low-temperature properties of the crystals are practically independent of the preparation method [these properties are the same for Qn(TCNQ)$_2$ and Ad(TCNQ)$_2$ crystals prepared and investigated by different groups of authors[68,73]]. The monotonic rise of the susceptibility below T_0 exhibited by these salts excludes the possibility of the Peierls transition at the point T_0 and supports the hypothesis of a transition to a Mott disordered insulator state.

In the Mott-Hubbard ordered insulator state, a one-dimensional electron system is unstable in the presence of lattice distortions, which make the ground state diamagnetic. In fact, the ground state and all the excited magnetic states of a one-dimensional electron system with a half-filled band can be described in the Mott-Hubbard insulator phase by the Heisenberg Hamiltonian for a linear chain of spins 1/2. Such a spin system, like a one-dimensional system of free electrons with a half-filled band, is unstable when the period is doubled and this gives rise to a gap in the triplet-state spectrum.[74] If the band is initially not half-filled, the situation is more complex. However, theoretical calculations[46] suggest that, in this case, the Peierls

transition is associated with the Mott localization of electrons due to their Coulomb repulsion. Therefore, it is not surprising that the majority of moderately conducting TCNQ complexes are Mott insulators with Peierls distortions [6] (the activation energy of conduction of these complexes is much higher than the gap in the magnetic excitation spectrum). The absence of a Peierls instability of this type in highly conducting TCNQ salts with asymmetric cations can be explained by the disorder of the cation orientation, in agreement with the results presented in Sec. 7.

b) TCNQ salts with symmetric cations. Two TCNQ salts with symmetric cations are known: TTF-TCNQ [54, 55] and TTT(TCNQ)$_2$. [75] These salts differ from the TCNQ salts with asymmetric cations not only by the cation symmetry but also by the presence of outer electrons in the anion and cation chains. The results of x-ray structure analyses indicate that cations and anions in TTF-TCNQ [76] and TTT(TCNQ)$_2$ crystals form piles along which electrons can move. There are two outer electrons per molecule in these compounds, governed by the chemical formula, and these electrons are distributed between both chains. Experimental studies of the photoelectric emission indicate that some of the electrons are transferred from TTF to TCNQ and less than one electron is transferred per one TCNQ molecule. [77, 78]

The room-temperature conductivity of TTF-TCNQ has a record value for quasi-one-dimensional compounds (up to 1000 $\Omega^{-1}.cm^{-1}$ according to [54, 79]). When the temperature is lowered from the room value to 60°K, the conductivity of typical crystals rises by a factor of 10—35 [54, 55, 74] but some samples investigated by the Pennsylvania group [54] are reported to exhibit a rise by a factor of 500. Further cooling below 60°K strongly reduces the conductivity, i.e., the metal-insulator transition occurs at T = 60°K. The hypothesis of the Peierls nature of this transition is put forward in [54] and the giant rise in conductivity before the Peierls transition is attributed to superconducting fluctuations.[4] The conductivity investigations indicate that the ordinary contact measurements may give rise to errors in the case of strongly anisotropic systems [80] and the giant rise in conductivity reported in [54] is doubtful. Contactless microwave measurements of the conductivity indicate that the $\sigma(60°K)/\sigma(300°K)$ ratio is 10—25, depending on the sample. [81] However, one cannot exclude the possibility that the Pennsylvania group workers [54] have been able to grow purer crystals which do indeed exhibit a rise in conductivity by a factor of several hundreds. [82, 83]

The anisotropy of the conductivity of TTF-TCNQ reaches ≈ 100 at room temperature and rises to 10^3—10^4 at about 60°K. [80, 82, 83] The quasi-one-dimensional nature of the electron motion is also supported by the optical data. [84, 85] At frequencies above 0.4 eV, the electrons in TTF-TCNQ behave as if they were free and give rise to a metallic plasma reflection edge (plasma frequency $\hbar\omega_p \approx 1.4$ eV).

The transition to the insulating state at temperatures below 60°K is confirmed by measurements of the specific heat [86] and thermoelectric power [87] (the low-temperature specific heat has no linear term and the thermoelectric power changes its sign at 60°K, becoming negative at temperatures T < 60°K). In the region of 60°K, there is also a jump in the specific heat, [88]

whose value is not in conflict with the Peierls nature of the transition.

The paramagnetic susceptibility of TTF-TCNQ falls monotonically when the temperature is lowered and between 360 and 70°K this fall is slow, [89] whereas it becomes exponential below 60°K. [90] This temperature dependence of the susceptibility excludes the possibility of the Mott transition at 60°K and supports the Peierls mechanism. The Peierls rather than the Mott transition follows also from the pressure dependence of the transition temperature [91] (T_p rises with increasing pressure).[5] Infrared optical data obtained at low temperatures can also be interpreted by assuming the Peierls transition. [92]

However, the interpretation of the experimental data for TTF-TCNQ is complicated by the fact that there are two conducting chains (TTF and TCNQ) in crystals of this compound. The relative contributions of these chains to the physical properties of the system are not known and theoretical models used to explain the measurements results are far from unambiguous (in a system with two types of conducting chain, we can have metal—insulator transitions which are neither of the Mott nor of the Peierls type [93]). Recent experimental results contain information on the state of electrons in the TTF and TCNQ chains. A simultaneous analysis of the ESR data for the temperature dependence of the g factor and of the static magnetic susceptibility shows that the TCNQ chains are in the Mott insulating state with Peierls distortions throughout the investigated temperature range T $\leq$ 300°K and only the TTF chains are metallic above 60°K. [94] (The same conclusion was drawn earlier in [89] from the magnetic susceptibility data). Unambiguous confirmation of the Peierls nature of the transition at 60°K could be obtained from structure studies of these crystals below and above 60°K. However, the x-ray data available so far show no changes in the structure at 60°K [95] (TTF-TCNQ crystals are small, 2 × 0.2 × 0.3 mm, and this makes it difficult to carry out sufficiently precise structure studies). A strong influence of impurities and lattice defects on the transition temperature would be an indication of the Peierls transition in TTF-TCNQ. However, the replacement of TTF with the asymmetric ATTF cations [54, 81] has hardly any influence on the transition temperature. This temperature is practically constant for all the TTF-TCNQ samples obtained so far (see Note 8 added in proof).

The properties of TTT(TCNQ)$_2$ are, in many respects, similar to the properties of TTF-TCNQ. According to [115] a conductivity peak (in the region of 90°K) is also exhibited by TTT(TCNQ)$_2$ and the peak conductivity exceeds the room-temperature value by a factor of about 3.5. However, the rapid fall in the susceptibility of this compound occurs not in the vicinity of 90°K but near 55°K (the susceptibility falls slowly between 300 and 55°K).

9. EXISTENCE OF PARACONDUCTIVITY ABOVE PEIERLS TRANSITION

In the ground state of a Peierls insulator, the total electrical current is naturally zero. The question as to whether metastable current states can exist in a one-dimensional system of electrons and phonons below T_p was raised by Fröhlich. [22] He showed that, in the jellium model, there could be states in which electrons

would have a nonzero total momentum and, at the same time, all the one-electron excitations would be separated from these states by the Peierls gap. In these metastable states, the electrons should move together with a displacement wave so that the transition parameter Δ should depend on time, i.e.,

$$\Delta(n, t) = |\Delta| e^{2ik_F(n - v_s t/c)}, \qquad (51)$$

where v_s is the electron velocity. The presence of a gap in the one-particle spectrum prevents the scattering of electrons by impurities and the current in these states does not decay.

Calculations reported in[41] confirm essentially the correctness of these representations for the jellium model, and the collective mode Ω_- found by Lee, Rice, and Anderson, should correspond to metastable current states. We have $\omega_T = 0$ in the jellium model and the conductivity $\sigma(\omega)$, according to Eq. (40) for $\epsilon_\parallel(\omega)$, has the form of the delta function at $\omega = 0$. In a real lattice, the pinning of charge-density waves (Sec. 4) tends to shift the frequency of the Ω_- mode to $\omega_T \neq 0$ in the limit $q \to 0$ and a nondecaying constant current does not appear in the system.

Bardeen[96] suggested using the Fröhlich model in the explanation of the appearance of a conductivity of TTF-TCNQ before the Peierls transition. His arguments can be summarized as follows. In a real crystal, the Fröhlich current states decay. Therefore, the true superconductivity is impossible in the Peierls system. However, the current states which appear due to fluctuations near T_p may increase considerably the conductivity at temperatures above T_p. Estimates based on the molecular field approximation obtained by Allender, Bray, and Bardeen[97] indicate that, in the case of TTF-TCNQ, this paraconducting contribution to σ increases approximately by a factor of six between room temperature and 60°K and this can explain the "typical" increase of σ by a factor of 10—20. Patton and Sham[98] and Strässler and Toombs[99] estimated the corrections to the normal conductivity on approach to T_p from above and they did this using the diagram technique similar to that employed by Aslamazov and Larkin[100] in the calculation of the fluctuation conductivity of superconductors above T_c. Their calculations demonstrated that the increase in σ in the limit $T \to T_p$ should occur when the band is not half-filled. However, there is as yet no microscopic theory of the Peierls transition analogous to the BCS theory for superconductors. Therefore, we are always left with the question of the magnitude of the terms which are ignored in the calculations reported in[97-99]. We must also point out that KCP shows no increase in the conductivity on approach to T_3 although the Ω_- mode does exist in this crystal, according to[48]. Therefore, the question of the distance and magnitude of the paraconductivity in the Peierls transition is far from clear in the experimental and theoretical aspects (see Note 9 added in proof).

10. CONCLUSIONS

There are still many theoretical and experimental aspects of the Peierls transition which are not clear and this also applies to the properties of mixed-valence platinum-group transition-metal complexes. The outstanding questions include:

a) The theoretical problem of the influence of the Coulomb repulsion of electrons on the Peierls transi-

tion and of the relationship between the Peierls instability and the Mott transition (the first steps in investigating these problems can be found in[25, 44-46, 101]).

b) Theoretical and experimental problems of the paraconductivity above the Peierls transition temperature (see Note 9 added in proof).

c) Experimental aspects of the paramagnetic susceptibility of KCP.

d) Experimental aspects of the influence of the disorder in crystals on the Peierls transition.

e) The theoretical question of the cause of the strong dispersion of the conductivity of KCP (and other highly conducting quasi-one-dimensional compounds) at frequencies below 10^{10} Hz.

There is no doubt that the properties of mixed-valence platinum complexes are associated mainly with the Peierls transition.

In the case of TCNQ complexes with symmetric cations, the situation is less definite. It is possible that the transition which occurs in these compounds is not of the Peierls type.

The possibility of superconductivity in quasi-one-dimensional systems still remains open in the theoretical (and, naturally, experimental) sense. Generally speaking, the Peierls instability is a stronger effect than the Cooper instability because the Peierls transition is governed by the whole electron band, whereas the superconductivity is due to a range of energies of the order of ω_D near the Fermi surface. Therefore, in systems with $\omega_D \ll T_p$, the superconductivity is clearly impossible and one can hope for the superconductivity (including the high-temperature effect) only in the case of quasi-one-dimensional crystals for which $\omega_D \gtrsim T_p$. In this case, the Peierls transition may be either completely suppressed or may cooperate with the superconducting transition.[44-46]

The suppression of the Peierls instability in favor of the superconducting transition may be caused by electron transitions between chains, which violate the condition (19), by the presence of many bands on the Fermi surface with different values of k_F,[38] and, possibly, by the disorder in a crystal. The first possibility applies to systems in which electron transitions between chains are fairly rapid ($b_2 \sim T_p$; see Sec. 3b) and this leads to the consideration of anisotropic three-dimensional systems (see Note 10 added in proof).

The many-band case raises no theoretical doubts but the question remains as to whether it can be realized experimentally. In the case of the simplest method of suppressing the Peierls instability by introducing impurities or structure defects, it is not clear to what extent there is still a chance of the superconductivity because the disorder in one-dimensional systems (which distinguishes them from the three-dimensional case) results in the localization of electrons. If the Peierls instability is in some way suppressed, one may expect a high value of the critical superconducting temperature T_c in the case of quasi-one-dimensional compounds with the phonon mechanism of the superconductivity associated with some features of the density of states typical of the electron spectra of one-dimensional systems (see, for example,[102]).

There is another way of approaching the supercon-

ducting state in quasi-one-dimensional systems which involves an increase in the frequency of excitations, whose exchange attracts the conduction electrons. Clearly, it is unlikely that the value of ω_D can be increased significantly (for almost all the quasi-one-dimensional crystals we have $\omega_D < 100°K$). In this sense, the exciton superconductivity mechanism presents a unique opportunity.[103] However, this mechanism can be effective only in systems in which the attraction of conduction electrons, because of the exchange of electron excitations, is not weaker than the attraction due to phonons. The difficulties in attempting to achieve this situation in the Little model are basically similar to those which arise in the case of layered compounds with molecules.[30]

However, we must point out that the rapid development of the physics of quasi-one-dimensional crystals is stimulated primarily by the exciton superconductivity ideas. There is little doubt that this approach will be fruitful also in future.

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NOTES ADDED IN PROOF

1. Strictly speaking, a redistribution of the charge also occurs when the period is doubled,[105] but it is weak because of the smallness of the overlap of the Wannier functions $w_n(r)$ of neighboring sites, i.e., because of the smallness of the product $w_n(r)w_{n+1}(r)$ compared with $|w_n(0)|^2$.

2. Dieterich[106] obtained by a somewhat different method an equation for T_3 similar to Eq. (28).

3. Similar results were obtained in the tight-binding model by Leung.[107] A detailed description of the behavior of a one-dimensional system of electrons with a half-filled band is given in[107].

4. The dynamics of phonons in the Peierls transition in quasi-one-dimensional crystals is discussed in detail in[108].

5. In a quasi-one-dimensional system of molecules, the Peierls instability may be a consequence of the interaction of electrons with intramolecular vibrations. In this case, a charge-density wave appears below T_p even when the period is doubled and an optical mode frequency $g\omega(\pi)$ is optically active.[105]

6. More detailed results on the Fröhlich collective mode Ω_- are given in[110].

7. According to[111,112], the K ions are distributed at random and a unit cell of KCP contains one K atom and two Pt atoms at inequivalent sites. This inequivalence is weak and hardly alters the interpretation which follows from a unit cell with one Pt atom.

8. It is possible that the Peierls instability in TTF-TCNQ is not due to displacements of the TTF or TCNQ molecules along the walls but to a libration mode[113,114] or intramolecular TTF or TCNQ vibrations.[115]

9. The inclusion of the diagrams corresponding to the pinning of the Ω_- collective mode by impurities predicts a fall in the fluctuation conductivity on approach of T_c to T_p from above.[116] Further experimental information on the magnitude and origin of the peak in the dependence $\sigma(T)$ is reported for TTF-TCNQ in[117].

10. The superconductivity in crystals exhibiting charge transfer from large organic molecules (such as TCNQ or TTF⁺) is more likely in the non-Peierls instability case ($b_2 > T_p$) than in the quasi-one-dimensional situation. It follows that, to obtain organic superconductors, one should try to reduce rather than increase the "one-dimensional nature" of the crystals. In organic systems with metallic conduction and free of Peierls instability, the superconducting state may be prevented only by the Coulomb repulsion of electrons. However, in the case of TTF-TCNQ, even when the band width is ≈ 0.1 eV, the Coulomb repulsion is unimportant (because of the large dimensions of the molecules and their strong polarization by conduction electrons). Therefore, it is quite realistic to expect the superconductivity of crystals made up from molecules of this type and characterized by $b_2 > T_p$. A strong interaction between conduction electrons and intramolecular vibrations (whose frequencies reach 0.1 eV) may give rise to fairly high values of T_c of such systems.

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[1] It should be noted that structure transitions of this type have been observed in layered dichalcogenide compounds [36].

[2] In the case of the hopping motion of electrons between the chains, the parameter b_1 should be replaced with $\hbar/\tau_\perp$, where $\tau_\perp$ is the time for an electron jump between neighboring chains.

[3] The following simple considerations lead to the dependence of Eq. (50). If an electron hop occurs between centers separated from one another by a distance R, it follows that $\sigma \propto \exp\{-\alpha R - (\Delta E/T)\}$, where ΔE is the difference between the energy levels of these centers. The greater the distance R, the more likely we are to find two levels with similar energies and $\Delta E \propto R^{-3}$ in the three-dimensional case. The optimization of σ with respect to R gives Eq. (50).

[4] Subsequent theoretical calculations failed to confirm this hypothesis.

[5] In the Mott transition, the paramagnetic susceptibility tends to a constant value or rises when the temperature is lowered [68] and T_p decreases with rising pressure.

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