Phonon drag and the characteristics of the conductivity in one-dimensional metals

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A self-consistent field model that allows the application of the kinetic-equation method to one-dimensional conductors in which the electrons interact with the phonons is formulated. The effects of the phonon drag in very anisotropic metals greatly alter all the temperature dependences of the conductivity even at very high temperatures. In particular, a T^{-2} law is found for the conductivity of TTF–TCNQ. The temperature variation laws for the conductivity of systems that have undergone a slight dimerization (i.e., a lattice-constant doubling) are obtained. The role of the soft mode is investigated, and the laws of critical behavior of the resistance in the chosen model near the structural transition point are found. The dependence of the temperature of the conductivity peak on low defect concentration is found. The theory is not at variance with the experimental data. Finally, it is concluded that the results are fairly general, and depend little on the model.

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1. INTRODUCTION. CHOICE OF THE MODEL

There has thus far been accumulated an enormous amount of experimental data on the transport properties of the quasi-one-dimensional organic conductors. The best studied in this respect are TTF–TCNQ and the related double-chain (two types of carriers) compounds TSF–TCNQ, HMTSF–TCNQ, etc., the single-chain (complete charge transfer) compounds $(TTT)_2I_3$ and $(TMTSF)_2PF_6$, and a number of other compounds.[1)] The theoretical interpretation of the measurement results meets with a number of difficulties. Among them is the difficulty connected with the large number of constants on which the transport properties of highly anisotropic organic conductors clearly depend: the large number of active phonon modes; the three-dimensional effects (the tunneling integrals $t_\perp$), which determine the specific form of the electronic spectrum under conditions of rather complicated symmetry; the constants of the interelectronic interactions both on one chain and between the various chains; the dispersion of the phonon spectrum; the occurrence of the Kohn anomaly (i.e., of a structural transition), and a number of other factors (e.g., defects). The form of the experimental curves, say, for the resistance as a function of temperature clearly cannot furnish enough information. Under these conditions the theory in turn should not pretend to give more than a qualitative insight into the role of the main mechanisms. The situation is aggravated by the fact that the resistance at constant volume ρ_V (which is studied in the theory) and the resistance at constant pressure ρ_P (which is what is measured in experiment) differ significantly from each other, and often have different temperature dependences in these compounds.[8]

The theoretical methods of interpreting the transport properties usually do not fall outside the limits of phenomenological momentum-balance equations based on the kinetic equations for the phonons and electrons (see, for example, Refs. 9–11). At the same time, the kinetic equation is far from being always applicable in the one-dimensional model because of the localization phenomena.[12–15] In equal measure, because of the fluctuations, it is likewise impossible to describe the structural Peierls transition in the one-dimensional model.

An important physical observation is made in Ref. 10 about the transport properties of quasi-one-dimensional conductors. Namely, the Fermi surfaces in them are close in shape to parallel planes the vector $k_\parallel = 2p_F$ apart in the Brillouin zone. Therefore, if this vector is incommensurate with the reciprocal lattice vector, the phonons in the vicinity of the vectors $|k_\parallel - 2p_F| \sim T/v$ cannot give away their momenta, and are strongly coupled to the electrons. Consequently, there occurs in these compounds the so-called phonon drift, i.e., phonon drag by an electric field, and this changes greatly the role of the conventional Bloch mechanism of electron scattering by phonons, and leads, generally speaking, to the appearance of new temperature dependences.

The purpose of the present paper is to formulate for the electron–phonon interactions in one-dimensional conductors a relatively simple model capable of correctly describing the main features of such fundamental phenomenon as the Peierls transition, and then determine the limits of applicability of the kinetic equation in this model. A more detailed investigation of the kinetic equations themselves gives an insight into some qualitative characteristics of the temperature behavior of the resistance, the role of commensurability, the nature of the conductivity peak, and the character of the critical behavior of the resistance in the vicinity of the structural transition point.

As shown in Ref. 16, allowance for the interaction of the electrons on different chains determines the Peierls transition as a three-dimensional transition. The simplest situation (proposed in Refs. 16 and 17), in which the structural transition can be described by means of self-consistent field theories (the fluctuations in the vicinity of the transition point are weak), arises when the elastic properties (i.e., the phonon spectrum) are assumed to be three-dimensional. The electronic spectrum can then be one-dimensional. The "bare" phonon spectrum in the vicinity of $\mathbf{k}=(\pm 2p_F, k_\perp)$ is described by the dispersion law

$$\omega_0^2(\mathbf{k})=\omega_0^2(2p_F,0)\left[1+B(k_\perp/k_{0\perp})^2\right] \quad (k_\perp \ll k_{0\perp}). \tag{1}$$

The renormalization due to the conduction electrons determines a new phonon spectrum:

$$\tilde{\omega}^2(\mathbf{k})=g_{ph}^2\omega_0^2[\ln(T/T_p)+f(\delta v/T)]+\omega_0^2B(k_\perp/k_{0\perp})^2, \tag{1$'$}$$

where $\omega_0^2 \equiv \omega_0^2(2p_F, 0)$, $\delta = k_\parallel - 2p_F$, and g_{ph}^2 is the dimensionless electron–phonon interaction constant that enters into the high-temperature phonon-induced electron relaxation time

$$1/\tau_{e,ph}=2\pi g_{ph}^2 T \tag{2}$$

and in the definition of the Peierls-transition temperature

$$T_p \propto \varepsilon_F \exp(-1/g_{ph}^2). \tag{3}$$

Estimates of g_{ph}^2 from (2) or (3) usually yield g_{ph}^2 values ranging from $\sim\frac{1}{4}$ to $\frac{1}{5}$. In our model we shall consider the interaction to be arbitrarily weak:

$$g_{ph}^2 \ll 1. \tag{4}$$

The function $f(z)$ in (1′) for one-dimensional electrons, i.e., in the flat-Fermi-surface model, could have been computed exactly. The results obtained below depend weakly on the explicit form of $f(z)$. Furthermore, the expression (1′) essentially preserves its form when allowance is made for the small three-dimensional effects (i.e., when the tunneling integral $t_\perp \neq 0$). If the tunneling integral does not destroy the structural transition, then instead of (1′) we have

$$\tilde{\omega}^2(\mathrm{k})=g_{ph}^2\omega_0^2[\ln(T/T_p)+\tilde{f}(\delta v/t_\perp)]+\omega_0^2\tilde{B}(k_\perp/k_{0\perp})^2, \tag{1$''$}$$

where T_p depends on $t_\perp > T_p$, while $\tilde{f}$ is a new function and $\tilde{B}$ is another number. Normally, T_p is comparable to the characteristic phonon frequencies $\omega_0 \approx 50-100$ K. In their turn, the tunneling integrals are estimated in the majority of the compounds to be $t_\perp \lesssim 100-150$ K.

The phonon Green function for the physical frequencies in the neighborhood of the transition point has (for a plane electronic spectrum) the form[17]

$$D^R(\mathrm{k},\omega)=\frac{g_{ph}^2\omega_0^2}{\omega^2-\tilde{\omega}^2(\mathrm{k})+i(\pi/8T_p)g_{ph}^2\omega_0^2\omega}. \tag{5}$$

The imaginary term in the denominator shows that the damping of the "Kohn" phonon is, generally speaking, not weak. Near the transition temperature, and for small $\delta v \ll T$, $t_\perp$, we obtain from (1′) and (1″) the expression

$$\tilde{\omega}^2(\mathrm{k})=g_{ph}^2\omega_0^2[t+a\delta^2+bk_\perp^2], \tag{6}$$

where $t=(T-T_p)/T_p$.

An estimate of the critical fluctuations[16,18] yields the following condition limiting the region of applicability of the model near the transition point T_p:

$$t=|\Delta T/T_p|>g_{ph}^4/B^2. \tag{7}$$

Let us now study the question of the possibility of applying the kinetic equations to the electrons and phonons. For three-dimensional electronic Fermi surfaces the kinetic equation is a consequence of the so-called Migdal theorem (see Ref. 19): The correction depicted in Fig. 1(a), the the electron–phonon interaction vertex is small because of the fact that the denominators of the two electron Green functions differ by an amount of the order of the Fermi energy:

$$1/\tau_{e,ph}\varepsilon_F \ll 1.$$

(This result is another expression of the adiabaticity condition for the electron motion in the field of the ions.)

In the quasi-one-dimensional case the corresponding energy difference (for $k_\parallel \approx \pm 2p_F$) is only a phonon frequency, and the condition assumes the form

$$1/\tau_{e,ph}\omega_0 \ll 1, \tag{8}$$

which at high temperatures is, according to (2), possible only when (4) is fulfilled. If the tunneling integral is finite and $t_\perp > \omega_0$, then instead of (8) the condition for the diagram in Fig. 1(a) to be small is the inequality

$$1/\tau_{e,ph}t_\perp \ll 1. \tag{8$'$}$$

The diagram in Fig. 1(b) is the fourth-order anharmonicity for the phonon–phonon interaction. Besides, in the three-dimensional case this anharmonicity makes a small contribution proportional to the mean square of the thermal vibrations $T/\varepsilon_F \ll 1$. For the "quasi-one-dimensional" phonons, i.e., for four phonons with longitudinal momenta $k_{1\parallel} \approx k_{2\parallel} \approx 2p_F$ and $k_{3\parallel} \approx k_{4\parallel} \approx -2p_F$ (the transverse momenta can have any values), all the four Green functions turn out to be "resonant," and the matrix element is small only to the extent that g_{ph}^4 is small. [If $t_\perp > \omega_0$, then there will appear an additional factor equal to $(\omega_0/t_\perp)^2$.] Thus, for the phonons lying near the cross section $|k_\parallel| \approx 2p_F$, the expansion in terms of the anharmonicities corresponds to an expansion in powers of g_{ph}^2 instead of an expansion in powers of T/ε_F. As $\delta = |k_\parallel - 2p_F| \gg T/v$ increases, these amplitudes decrease rapidly to the normal order of magnitude. In the high-temperature region, where the phonon damping is weak (i.e., where $1/\tau_{\text{ph},e} \sim g_{\text{ph}}^2\omega_0^2/T$), not only the electron–phonon collisions, but also the higher-order processes may be important for the phonons with $|k_\parallel| \approx 2p_F$. Thus, it is easy to verify that, for the phonon–phonon scattering vertex shown in Fig. 1(b), the evaluation of the collision integral, defined by the equation

$$\frac{\partial N_\mathbf{k}}{\partial t}=-\frac{1}{\tau_{pp}}\delta N_\mathbf{k},$$

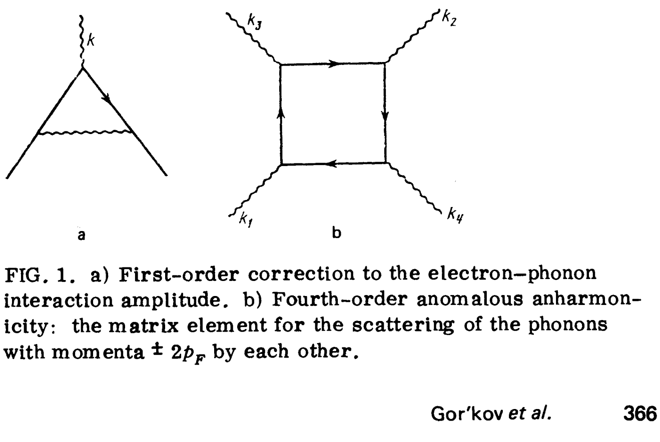

FIG. 1. a) First-order correction to the electron–phonon interaction amplitude. b) Fourth-order anomalous anharmonicity: the matrix element for the scattering of the phonons with momenta ± $2p_F$ by each other.

yields

$$1/\tau_{pp}\sim(g_{ph}^2)^4\omega_0. \tag{9}$$

2. HIGH TEMPERATURES

In this section we shall discuss the case of sufficiently high temperatures, i.e., the case of temperatures $T\gg\omega_0$ (ω_0 is the characteristic frequency of the phonon branch). As asserted above, the effects of the phonon drag in a one-dimensional conductor manifest themselves in the high-temperature region as well. The condition, (8), of applicability of the kinetic equation specifies a model with a weak electron–phonon interaction. The effects due to the slight three-dimensionality of the electronic spectrum will be neglected at first.

Using the standard notation (see, for example, Ref. 20), we shall write the corrections, due to the electric field, to the electron and phonon distribution functions respectively in the form

$$\delta n_p=-\frac{\partial n_0}{\partial\varepsilon}\varphi_p,\quad \delta N_{\mathbf{k}}=-\frac{\partial N_0}{\partial\omega}\chi_{\mathbf{k}}. \tag{10}$$

Let us first investigate the possibility of the normal Bloch mechanism, i.e., of the first-order processes, in which an electron is absorbed or emitted by one phonon. The system of kinetic equations for the electrons and phonons has the form (see, for example, Ref. 20)

$$-e\mathbf{v}_{\mathbf{p}}\mathbf{E}\frac{\partial n_0(\mathbf{p})}{\partial\varepsilon}=I_{e,ph}(\varphi,\chi),\qquad 0=I_{ph,e}(\varphi,\chi)+I_{ph,ph}(\chi). \tag{11}$$

Here $I_{e,\mathrm{ph}}$ is the linearized electron–phonon collision integral:

$$\begin{aligned}I_{e,\,ph}=\delta\Big\{\int\frac{d^3\mathbf{k}}{(2\pi)^3}\,W(\mathbf{p}',\mathbf{k};\mathbf{p})\,[n_{\mathbf{p}'}(1-n_{\mathbf{p}})N_{\mathbf{k}}-n_{\mathbf{p}}(1-n_{\mathbf{p}'})(1+N_{\mathbf{k}})]\\ \times\delta(\varepsilon_{\mathbf{p}}-\varepsilon_{\mathbf{p}'}-\omega_{\mathbf{k}})+(\text{absorption processes})\Big\}\\ =-\int\frac{d^3\mathbf{k}}{(2\pi)^3}\frac{\partial N_0(\mathbf{k})}{\partial\omega}W(n_0'-n_0)\{(\varphi_{\mathbf{p}'}-\varphi_{\mathbf{p}}+\chi_{\mathbf{k}})\,\delta(\varepsilon_{\mathbf{p}}-\varepsilon_{\mathbf{p}'}-\omega_{\mathbf{k}})\\ -(\varphi_{\mathbf{p}'}-\varphi_{\mathbf{p}}-\chi_{-\mathbf{k}})\,\delta(\varepsilon_{\mathbf{p}}-\varepsilon_{\mathbf{p}'}+\omega_{\mathbf{k}})\}\end{aligned} \tag{12}$$

[$W(\mathrm{p}',\mathrm{k};\mathrm{p})$ is the probability for the process; in the second form of the expression we have carried out a natural abridgment of the notation]. The phonon–electron collision integral can be written in a similar form:

$$I_{ph,e}(\chi,e)=2\frac{\partial N_0(\mathbf{k})}{\partial\omega}\int\frac{d^3\mathbf{p}}{(2\pi)^3}\,W(n_0'-n_0)\,(\varphi_{\mathbf{p}'}-\varphi_{\mathbf{p}}+\chi_{\mathbf{k}})\,\delta(\varepsilon_{\mathbf{p}}-\varepsilon_{\mathbf{p}'}-\omega_{\mathbf{k}}) \tag{12'}$$

($\mathrm{p}'=\mathrm{p}-\mathbf{k}$ everywhere). Finally, the term $I_{\mathrm{ph,ph}}(\chi)$ describes the phonon–phonon processes that occur as a result of the third-order anharmonicities, and should of necessity be introduced, since, under conditions in which the electronic umklapp processes are impossible, this is the only mechanism that guarantees the relaxation of the momentum of the electron and phonon system. The term $I_{\mathrm{ph,ph}}$ is the sum of the contribution of the normal three-phonon processes and the umklapp processes:

$$I_{ph,ph}=I^{N}_{ph,ph}+I^{U}_{ph,ph}.$$

The momentum-balance equation yields

$$-e\mathbf{E}n_e=\sum_{g}\int\frac{d^3\mathbf{k}}{(2\pi)^3}\,\mathbf{k}I^{U}_{ph,ph}(\chi). \tag{13}$$

Equation (13) remains valid even when allowance is made for the possible complications of the basis system of equations (11), if, of course, no new umklapp processes are introduced in the process (see below). For the estimates it is convenient to use the relaxation times:

$$\begin{aligned}I_{e,ph}=-\frac{1}{\tau_{e,ph}}\delta n_p=\frac{1}{\tau_{e,ph}}\frac{\partial n_0}{\partial\varepsilon}\varphi_p,\\ I_{ph,e}=-\frac{1}{\tau_{ph,e}}\delta N_{\mathbf{k}},\quad I_{ph,ph}=-\frac{1}{\tau_{ph,ph}}\delta N_{\mathbf{k}},\end{aligned} \tag{14}$$

where at high temperatures we have

$$\frac{1}{\tau_{e,ph}}=2\pi g_{ph}^2T,\quad \frac{1}{\tau_{ph,e}}=\frac{\pi}{8}g_{ph}^2\frac{\omega_0^2}{T}\,\mathrm{ch}^{-2}\left(\frac{v\delta}{4T}\right),\quad \frac{1}{\tau_{ph,ph}}\sim T\frac{\omega_0}{\varepsilon_F}. \tag{14'}$$

According to (12′), the result $1/\tau_{\mathrm{ph},e}\sim g_{\mathrm{ph}}^2\omega_0^2/T$ pertains to the phonons with longitudinal momentum $|k_{\parallel}|\approx 2p_F$, and is a specific property of flat (or near-flat) Fermi surfaces. If $k_{\parallel}=\pm 2p_F+\delta$, then $I_{\mathrm{ph},e}$ has a large magnitude only in a narrow neighborhood $|\delta|v\sim T$, and exponentially falls off outside this region. But inside this neighborhood $1/\tau_{\mathrm{ph},e}\gg 1/\tau_{\mathrm{ph,ph}}$. This inequality also expresses the physical fact that the phonons effectively interacting with the electrons (i.e., those with $k_{\parallel}\approx\pm 2p_F$) participate in the electron drift: $\chi\approx 2\varphi$ (Ref. 10). When $T\gg\omega_0$, the integrals (12) and (12′) get simplified:

$$I_{e,px}(\mathbf{p})=\frac{2}{(2\pi)^3}\left\langle\frac{\partial N_0(\mathbf{k})}{\partial\omega}\frac{W}{v}\frac{\partial n_0(\mathbf{p})}{\partial\varepsilon}\,\omega(\mathbf{k})\,(2\varphi_p-\chi_{\mathbf{k}})\right\rangle\quad\left(\delta=\frac{2\varepsilon_p}{v}\right),$$

$$I_{ph,e}(\mathbf{k})=-\frac{1}{(2\pi)^3}\left\langle\frac{\partial N_0(\mathbf{k})}{\partial\omega}\frac{W}{v}\frac{\partial n_0(\mathbf{p})}{\partial\varepsilon}\,\omega(\mathbf{k})\,(2\varphi_p-\chi_{\mathbf{k}})\right\rangle\quad\left(p-p_F=\frac{\delta}{2}\right). \tag{15}$$

(where $\langle\cdots\rangle$ denotes integration over the corresponding transverse momentum).

Thus, on the one hand, it follows from the kinetic equation for the phonons that $\chi\approx 2\varphi$ in the region $v|\delta|\sim T$. On the other, using (14) and (15), we see from the two equations of the system (11) that in the region $|k_{\parallel}-2p_F|\sim T/v$

$$\frac{evE}{T}\sim\frac{T}{\tau_{ph,ph}\omega_0^2}\chi_{2p_F},\quad \chi_{2p_F}\sim\frac{eEv\omega_0\varepsilon_F}{T^3}; \tag{16}$$

whence we obtain for the conductivity the law

$$\sigma(T)\propto\frac{ne^2}{m}\frac{\omega_0\varepsilon_F}{T^3}. \tag{17}$$

Let us return to Eq. (13) for the momentum balance. Generally speaking, it contains a contribution from the three-phonon processes of decay and fusion of all the phonons (we are talking about umklapp processes). In other words, we should further estimate the magnitude of $\chi_{\mathbf{k}}$ outside the region of its maximum, which is located in the neighborhood of $|k_{\parallel}|\approx 2p_F$. As stated above, $I_{\mathrm{ph},e}(\mathbf{k})$ falls off rapidly outside this region. For an arbitrary phonon momentum the second of the equations (11) reduces to the equation

$$I_{ph,ph}(\chi)=0.$$

Since all the phonon characteristics (the probabilities for the decay processes and the phonon frequencies) change over the atomic constants, we find from this equations the estimate

$$\chi_{k\|\neq 2p_F}\sim\frac{T}{\varepsilon_F}\chi_{k\|\approx 2p_F}\sim\frac{T}{\varepsilon_F}\varphi.$$

The factor T/ε_F is the relative width of the phase-space region where total phonon drag by the electrons occurs. Since $2\varphi\approx\chi_{2p_F}\propto j/eS$ (where S is the cross-section area of the Brillouin zone and j is the current density), we obtain for the resistance from (13) the final expression, equivalent to (17):

$$E \propto \frac{m}{ne^2}\frac{T^3}{\omega_0\varepsilon_F}j. \qquad (17')$$

In other words, the phonons with $|k_{\parallel}|\approx 2p_F$ can, generally speaking, either participate or not participate in the three-phonon umklapp processes. This is determined by the specific form of the phonon spectrum. But even in the latter case they give up their momentum to other phonons, which in turn transfer the momentum to the lattice. The form of the temperature dependence of the resistance is preserved.

Thus, both the temperature dependence of the conductivity and the physical mechanisms underlying the dissipation in the one-dimensional case turn out to be significantly different. As to the three-phonon mechanisms themselves, it is to be expected that they will have the normal—for dielectrics—character in the organic conductors. The conservation laws corresponding to the phonon decay or fusion processes can, one should think, be fulfilled fairly easily in these media owing to the abundance in them of different phonon modes.

The expressions (17) and (17′) contain the anharmonic parameter T/ε_F, which characterizes the relative intensity of the thermal vibrations of the lattice. This circumstance compels us to investigate the role of another process that is formally of the same order of smallness in the anharmonicity, namely, the process in which an electron interacts simultaneously with two phonons. The corresponding matrix element is depicted in Fig. 2(a). This type of process was first introduced by Gutfreund and Weger[21] for the so-called librational (rotational) vibrations of plane molecules. We shall now show that, if we do not make any special assumptions about the magnitude of the matrix element of such a transition, then the indicated process will make a smaller contribution to the resistance than (17′). As noted in Ref. 21, the conservation laws that obtain in the process depicted in Fig. 2(a) limit only the total longitudinal momentum component $(k_1+k_2)_{\parallel}\approx\pm 2p_F$, and therefore allow umklapp processes that make an additive contribution to the momentum-balance equation (13). We shall not write out the corresponding collision integral $I^{(2)}_{e,\mathrm{ph}}(\chi,\varphi)$ in its explicit form. It is sufficient for what follows to write

$$I^{(2)}_{e,ph}(\varphi)\sim-\frac{1}{\tau^{(2)}_{e,ph}}\delta n_{\mathbf{p}},$$

and estimate the time $\tau^{(2)}_{e,\mathrm{ph}}$ by investigating the imaginary part of the diagram in Fig. 2(b). Let us, without going into details, give the estimate

$$1/\tau^{(2)}_{e,ph}\sim T^2/\varepsilon_F. \qquad (18)$$

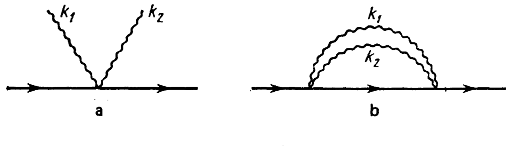

FIG. 2. a) Matrix element for electron scattering accompanied by the emission of two phonons. b) Contribution to the self-energy part of an electron from the two-phonon processes.

Substituting into (13), we obtain in place of (17′) the expression

$$E=\frac{m}{ne^2}\left\{A_1\frac{T^3}{\omega_0\varepsilon_F}+A_2\frac{T^2}{\varepsilon_F}\right\}j \qquad (19)$$

(A_1 and A_2 are numerical coefficients).

If $A_1\sim A_2\sim 1$ in (19), the first term predominates when $T\gg\omega_0$. Let us recall in this connection that the origin of one of the temperature factors in (17′) is connected with the small effective longitudinal width T/ε_F of the momentum region for the phonons actively interacting with the electrons. If it turns out that the electrons cannot be considered to be one-dimensional, i.e., if the magnitude of the interchain tunneling integral $t_\perp$ is large ($t_\perp\gg T$), then the effective width, as is clear from the foregoing, is of the order of $t_\perp/\varepsilon_F$. As a result, both mechanisms in (19) lead to the following temperature dependence for the conductivity: $\sigma\sim T^{-2}$. In the majority of the compounds, the conductivity at room temperature is of the order of $10^{+3}\,\Omega^{-1}\cdot\mathrm{cm}^{-1}$. This is roughly a factor of $\omega_0/\varepsilon_F\sim 10^{-1}-10^{-2}$ smaller than the value that follows from (19). Therefore, it is expressly argued in Ref. 10 that the large sizes of the molecules in the organic conductors are capable of compensating for the indicated smallness, i.e., that the coefficient A_2 in (19) is correspondingly large. It seems to us that the amplitudes of the librational vibrations in this case would be too high for the expansion in powers of the anharmonicity to be applicable. We shall not, however, investigate the last question, since there are other complications in the expounded picture. For example, the condition (8) is no longer fulfilled at high temperatures.

Thus far, the Kohn anomaly of the phonon spectrum has not been mentioned anywhere. Let us, for simplicity, assume that the structural transition temperature $T_p\gtrsim\omega_0$. The phase-space region affected by the softening of the phonon frequency is, according to (1′), of the order of $(\Delta k)^3\sim g_{\mathrm{ph}}^{\,2}ST/v$. If by chance the Kohn phonons do not participate in the umklapp processes, then they do not directly contribute to the momentum-balance equation (13). But they do participate in the normal processes, transferring their momenta to other phonons, and it is difficult to estimate their role in the resistance. Perhaps, the situation is possible in which the conductivity monotonically increases all the way to the transition temperature. The decrease of the conductivity below the transition point is due to the appearance of gaps in the energy spectrum of the electrons. Therefore, in the absence of impurities, the conductivity peak would occur either in the neighborhood of the transition point, in the critical-fluctuation region, which is determined by the condition (7), or even below the transition temperature (see also Sec. 4 below).

In conclusion of this section, let us return to the question of the temperature dependences of the conductivity of compounds of the TTF–TCNQ type (high temperatures). Participating in the conductivity in these materials are two types of carriers: the electrons and holes localized respectively on the acceptor and donor chains. One obvious mechanism that is always present corresponds to the scattering of the electrons and holes by each other on account of the Coulomb interaction of the carriers on different chains. This mechanism will contribute to the resistance a term linear in the temperature (i.e., a term $\rho \propto T$) if the electron–hole spectrum is plane (one-dimensional),[22] or quadratic in T (i.e., a term $\rho \propto T^2/t_\perp$) when $t_\perp \neq 0$ and $T < t_\perp$. The magnitude of the contribution of the electron–hole scattering is determined by the corresponding interaction constant, but we should obtain a reasonable order-of-magnitude estimate for the resistance. As has been mentioned, $\rho_V(T)$ and $\rho_P(T)$ have different temperature variation laws.[8,23]

We should now like to point out that the electron–phonon contribution to the resistance is also changed significantly by the presence of the two types of carriers in, say, TTF–TCNQ. Within the framework of the kinetic equation, this change is due to the fact that the two types of carrier—the electrons and holes—exchange momenta via the phonons. But here again there arise deviations from the three-dimensional picture owing to the unique topology of the almost flat Fermi surfaces. Because of the requirement of electrical neutrality, the two types of carrier always have one and the same Fermi momentum $\pm p_F$ (if we neglect the tunneling effects), but, generally speaking, different velocities in the longitudinal (conducting) direction, i.e., $v^{(e)} \neq v^{(h)}$. Let us take a phonon with vector $\mathbf{k} = (2p_F + \delta, \mathbf{k}_\perp)$ and frequency $\omega(\mathbf{k})$, and write out the δ functions that enter in the electron–phonon and hole–phonon collision integrals and guarantee the conservation laws:

$$\delta(\varepsilon_p - \varepsilon_{p-k} \pm \omega(\mathbf{k})) = \delta(v\delta \pm \omega(\mathbf{k})).$$

It can be seen from this that when $v^{(e)} \neq |v^{(h)}|$ the electrons and holes interact with different phonons,[2)] and, consequently, the mechanism under consideration is by itself not capable of ensuring the relaxation of the momentum. Nevertheless, there is now no need to fall back on the normal three-phonon processes, since, as shown above, the phonons in the neighborhood of $+2p_F$ and $-2p_F$ interrelax by means of the specifically one-dimensional four-phonon mechanism depicted in Fig. 1(b).

Let us return to the kinetic equations (11), (12), and (15). Owing to the two different chains, there are the corresponding collision integrals $I_{e,\mathrm{ph}}$ and $I_{h,\mathrm{ph}}$, which can easily be simplified at high temperatures in the same way as was done in (15). The two types of carriers enter additively into the phonon integral (12′). Adding all the equations together, we obtain for the quantity χ_{2p_F}, as in (16), the estimate

$$\chi_{2p_F} \sim \frac{eEv\omega_0^2}{T^2} \tau_{ph,ph},$$

but with $\tau_{\mathrm{ph,ph}} = \tau_{\mathrm{ph}}$ from (9), i.e., not depending on T.

The next step is to relate χ_{2p_F} with the current. On the one hand, $\chi_{2p_F} \sim \varphi^{(e)} \sim \varphi^{(h)}$; on the other, a current appears only when the electron- and hole-drift velocities $u^{(e)}$ and $u^{(h)}$ respectively are not equal. Assuming that $\chi_{2p_F} \propto u^{(e)} - u^{(h)}$, we obtain for the conductivity the estimate

$$\sigma \sim \frac{ne^2}{m} \left(\frac{1}{g_{ph}^2}\right)^4 \frac{\omega_0}{T^2}. \tag{20}$$

A more correct derivation of (20) would make use of the variational method,[24] in which the trial functions should be chosen with allowance for the strong phonon drag. When the electron and hole velocities are equal, the Bloch mechanism turns out to be adequate for the construction of the equilibrium solution, and the conductivity has the standard form:

$$\sigma = \frac{ne^2}{m} \tau_{e,ph} \propto T^{-1}.$$

In other words, the linear law, which is typical of a metal, arises in the absence of a phonon drag. We shall not discuss this solution, since it corresponds to the physically improbable case of equal velocities for carriers on different chains.

To the foregoing must be added the fact that (20) also provides a reasonable interpretation of the experimental data when $g_{\mathrm{ph}}^2 \sim 1$. All this demonstrates once more the ambiguity in the choice of one or another theoretical description of the experimental data.

3. SINGLE-CHAIN CONDUCTORS AND DIMERIZATION

The phonon-drag phenomena and the conductivity due to the Bloch mechanism can be investigated in greater detail within the framework of the kinetic equation in a number of compounds with one conducting chain, of which $(TTT)_2I_3$ (Ref. 25) and the recently synthesized conductors of the type $(TMTSF)_2X$ (Refs. 5–7) can be considered to be prototypical. In these materials the charge transfer is complete, which corresponds to a quarter-filled band (holes or electrons). Superimposed on this circumstance is the phenomenon of dimerization, which doubles the lattice constant along the conducting chain. Thus, for example, in $(TTT)_2I_3$ the iodine forms, with respect to the TTT chain, I_3^- complexes with a doubled lattice constant.[25] If, as usual, we assume the potential produced by the iodine chain on the conducting (TTT) chains to be sufficiently flat, then the doubled iodine-lattice constant implies a slight structural modulation of the potential in which the conduction electrons move. A slight modulation with a doubled period is also observed in the $(TMTSF)_2PF_6$-type structure.[26]

The difference between the two compounds lies in the fact that the first can, as it turns out, exist in a whole range of nonstoichiometric compositions of the type $(TTT)_2I_{3+\delta}$. (The number of electrons in the conduction band is nonetheless determined by the iodine concentration, and the Fermi momentum is tightly bound with the iodine-lattice constant: $2p_F = \pi/a_i$.) We shall discuss this difference below. Now, however, let us assume that there exists in the system a slight structural (lattice-constant) modulation whose period is equal to $a^* = 2a$. Then since the original band was one-quarter-filled, the new band is now half-filled,[27] and the scattering of a $+p_F$ electron by a $-p_F$ electron, due to the emission of a phonon with momentum $2p_F$, is accompanied by umklapp processes. Otherwise, the momentum $4p_F = \pi/a$ may be given to the lattice owing to the presence in the lattice of the new superstructure. As to the electronic spectrum, the modulation opens a gap in the spectrum of the electrons with momenta $p^* = 2p_F$. But this gap lies far from the Fermi level, and therefore the electronic anharmonicities (the expansions of the various electronic matrix elements in powers of the modulation amplitude) contain the corresponding small quantities. But for the electrically active phonons with momenta $|k_\parallel| \approx 2p_F$ the modulation mixes the $\pm 2p_F$ states. These phonons, as well as the matrix elements for their interaction with the electrons can undergo significant changes.

Let us write out the third-order terms in the expansion of the parent-lattice energy in terms of the anharmonicities in the form

$$H^{(3)} = \sum_{\substack{\alpha\beta\gamma \\ ikl}} \lambda_{ikl}^{(3)\alpha\beta\gamma} u_i^\alpha u_k^\beta u_l^\gamma, \tag{21}$$

where u_i^α is the strain of the i-th "atom." (The Greek index corresponds to the vector component of the displacement. The expansion coefficients λ depend, in particular, on the symmetry, but their actual forms are unimportant for what follows. Below we use in the formulas the simplest model with effective constant $\lambda^{(3)}$.) Let us assume that a structural modulation of the form $e^{\pm i 4 p_F x_n}$ exists in the lattice, and let us characterize its relative magnitude in terms of the lattice constants by the dimensionless parameter α.

The equilibrium positions of the atoms change slightly. Substituting into (21) $u_i = u_{4p_F} + \tilde{u}_i$, where u_{4p_F} is proportional to α and the $\tilde{u}_i$ are small displacements relative to the new equilibrium positions, we see that $H^{(3)}$ generates second-order terms having in the momentum representation the form

$$H_{(2)}^{(3)} = \bar{\lambda}^{(3)} \sum_{\mathbf{k}_1+\mathbf{k}_2+4\mathbf{p}_F=\mathbf{K}} (u_{4\mathbf{p}_F} \tilde{u}_{\mathbf{k}_1} \tilde{u}_{\mathbf{k}_2} + \text{c.c.}). \tag{21'}$$

These terms mix the phonon states with momenta $\mathbf{k}_1$ and $\mathbf{k}_2 = \mathbf{k}_1 \pm \mathbf{Q}$, where

$$\mathbf{Q} = (4p_F, 0, 0) = (\pi/a, 0, 0), \tag{22}$$

and, in particular, make possible the processes depicted in Fig. 3, in which an electron emits (absorbs) a phonon as it gives up momentum to the superstructure. Accordingly, in Fig. 3

$$\mathbf{k}_1 = (2p_F + \delta, k_y, k_z), \quad \bar{\mathbf{k}}_1 = (-2p_F + \delta, k_y, k_z). \tag{22'}$$

The matrix element for such a process, computed with the aid of ordinary perturbation theory, would have the form

$$\langle \mathbf{p}_2, \bar{\mathbf{k}}_1 | H | \mathbf{p}_1, 0 \rangle = \frac{\langle \bar{\mathbf{k}}_1 | H_{(2)}^{(3)} | \mathbf{k}_1 \rangle \langle \mathbf{p}_2, \mathbf{k}_1 | H_{e,ph} | \mathbf{p}_1, 0 \rangle}{\varepsilon_{\mathbf{p}_1} - \varepsilon_{\mathbf{p}_2} \pm \omega_0(\mathbf{k}_1)}. \tag{23}$$

In its turn, according to the conservation laws, $\varepsilon_{\mathbf{p}_1} - \varepsilon_{\mathbf{p}_2} = \pm\omega_0(\bar{\mathbf{k}}_1)$. In accordance with (22), the scattering by the regular superstructure does not change the transverse component of the longitudinal momentum. The frequency difference $\omega_0(\mathbf{k}_1) - \omega_0(\bar{\mathbf{k}}_1)$ in (23) may be small, especially in the case of a relatively high crystal symmetry, if $\omega(k_\parallel, \mathbf{k}_\perp) = \omega(-k_\parallel, \mathbf{k}_\perp)$. [The latter is valid for the symmetry of the $(\mathrm{TTT})_2\mathrm{I}_3$ crystal; although such a relation does not exist for the triclinic $(\mathrm{TMTSF})_2\mathrm{X}$, the maximum effect of (23) in the expression for the resistance will, as follows from (1), correspond to small $\mathbf{k}_\perp$. Therefore, the formulas obtained below are applicable at low temperatures to these compounds as well.] Thus, the slight dimerization can be compensated for by the small denominator in (23). Because of this, the phonon spectrum undergoes substantial reconstruction in the vicinity of $k_\parallel = \pm 2p_F$. Figure 4(a) shows the appearance of a gap in the phonon spectrum in the case in which the Kohn anomaly can be neglected (high temperatures), while Fig. 4(b) schematically depicts the splitting of the phonon frequencies in the case of a developed soft phonon mode (in the band of the parent lattice). The effect of the dimerization extents to an entire momentum neighborhood $\Delta k_\parallel = \delta$ around $2p_F$. In its turn, the momentum region that is important for the scattering processes is determined by the Fermi factors $v\delta \sim T$ for the electrons.

In order to illustrate these ideas, we considered the simplest model, in which in $H_{e,\mathrm{ph}}$ the electrons interact with one phonon branch and the strain u_{4p_F} belongs to the same branch. The occurrence of quadratic terms in (21′) indicates that it is necessary to rediagonalize the square matrix for the phonon vibrations. It can also be seen from (23) and Fig. 4(a) that it is necessary to take into consideration the longitudinal dispersion of the phonon branch in the vicinity of $\pm 2p_F$:

$$\omega_0^2(k) = \omega_0^2(\pm 2p_F)\{1 + 2\beta(\delta/p_F)\}$$

(β is a numerical coefficient).

The new phonon creation and annihilation operators (a_δ, a_δ^+) in the presence of dimerization can be expressed in terms of the old operators (a_k, a_k^+) by means of the canonical transformation:

$$a_\delta = a_{2k_F+\delta} \cos\chi_\delta + a_{-2k_F+\delta} \sin\chi_\delta, \quad a_{-\delta} = a_{2k_F-\delta} \cos\chi_\delta - a_{-2k_F-\delta} \sin\chi_\delta, \tag{24}$$

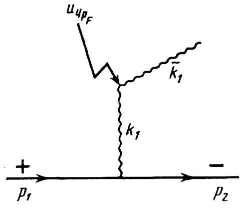

FIG. 3. Umklapp processes in the presence of a slight dimerization: first-order matrix element for electron–u_{4p_F}-superstructure scattering with simultaneous emission of a phonon.

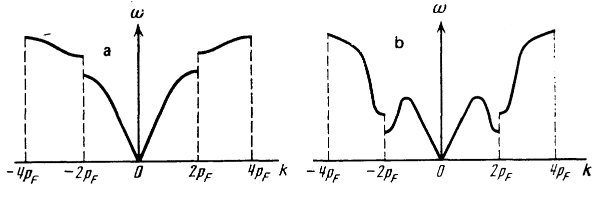

FIG. 4. Formation of a gap in the phonon spectrum in the presence of a mild dimerization structure: a) at high temperatures; b) in the presence of the Kohn anomaly.

where in our model

$$\cos^2\chi_\delta = {}^1/_2\{1+\beta(\delta/p_F)/[\beta^2(\delta/p_F)^2+\alpha^2\gamma^2]^{1/2}\},$$

$$\sin^2\chi_\delta = {}^1/_2\{1-\beta(\delta/p_F)/[\beta^2(\delta/p_F)^2+\alpha^2\gamma^2]^{1/2}\} \tag{24'}$$

[α characterizes the relative magnitude of the modulation, γ is a numerical dimensionless coefficient formed from the constant $\tilde{\lambda}^{(3)}$ in (21′) and the atomic quantities].

The two phonon-frequency branches shown in Fig. 4 are described in the neighborhood of the edge of the new band (i.e., near $k_\parallel = 2p_F = \pi/2a$) by the spectrum

$$\omega^2(\mathbf{k}) \equiv \omega^2(\delta, \mathbf{k}_\perp) = \tilde{\omega}^2(\delta, \mathbf{k}_\perp) \pm 2\omega_0^2[\beta^2(\delta/p_F)^2+\alpha^2\gamma^2]^{1/2}. \tag{25}$$

In (25) $\tilde{\omega}^2(\delta, \mathbf{k}_\perp)$ corresponds to a phonon frequency that has, generally speaking, been renormalized on account of the electronic corrections in accordance with (1′). The Kohn anomaly makes only one of the two branches vanish.

After we have diagonalized the phonons and have found their spectrum, we must substitute the expressions (24) and (25) into $H_{e,\mathrm{ph}}$, expand the displacements in terms of the new modes, and thus obtain the matrix elements for the processes describing the interaction of the electrons with the new phonons. The dissipation of the momentum is due to the umklapp processes, which should have been defined in terms of the new (doubled) band. Since, as explained above in the derivation of (23), the point of the matter is that the electron momentum assumes a modulation structure, we shall call, although somewhat conditionally, those umklapp processes which in the expansion of the deformation in terms of the new modes contain $\cos\chi_\delta$ and $\sin\chi_\delta$ respectively normal umklapp processes. The probability for the "umklapp processes" is thus

$$W(\delta, \mathbf{k}_\perp) = g_{ph}^2 \frac{\omega_0^2}{\omega(\delta, \mathbf{k}_\perp)} \sin^2\chi_\delta, \tag{26}$$

where $\omega(\mathbf{k}_\perp, \delta)$ can be either the "amplitude" or the "phase" mode [the two roots of (25)] [and the choice of $\sin^2\chi_\delta$ ensures the correct passage to the limit in (23)] when $(\delta/p_F)^2 \gg \alpha^2$.

The momentum-balance equation (13) assumes (under the assumption that the dimerization effects predominate) the form

$$eEn = -u\omega_0^2 g_{ph}^2 \int (d^2\mathbf{k}_\perp d\delta) \frac{N_0(\mathbf{k})}{T\omega(\mathbf{k})} n_0\left(\frac{\delta v}{2} - \frac{\omega(\mathbf{k})}{2}\right) \times\left[1 - n_0\left(\frac{\delta v}{2} + \frac{\omega(\mathbf{k})}{2}\right)\right] \sin^2\chi_\delta \tag{27}$$

with $\omega(\mathrm{k})$ from (5). (Here u is the electron drift velocity.) The Fermi factors yield $\delta v \sim T$; substituting this into (24′) and (25), we see that for

$$T/\varepsilon_F \ll \alpha \tag{28}$$

the resistance has the usual order of magnitude, as if the phonon drag did not occur. The smallness of the dimerization drops out from the answer. The condition (28) imples that the shifts in the lattice that are due to the doubling of the lattice constant are greater than the root-mean-square thermal fluctuations.

The temperature dependence of the resistance has its simplest form in the limit (28), and we can also investigate the role of the soft mode in this limit, assuming that the Peierls transition temperature T_p satisfies the condition

$$g_{ph}\omega_0 \ll T_p \lesssim \omega_0.$$

For $T \gg T_p$ the usual linear law $\rho \propto T$ follows from (27). In a broad range of $T \sim T_p$ the frequency of the "soft" mode is, according to (1′), given by the expression

$$\omega^2(\delta, \mathbf{k}_\perp) \sim g_{ph}^2\omega_0^2 f\left(\frac{\delta v}{T}, \frac{T}{T_p}\right) + B\omega_0^2 \frac{k_\perp^2}{k_{0\perp}^2}$$

and, in order of magnitude, the function $f \sim 1(\delta v \sim T)$. The integration over $\mathrm{k}_\perp$ in (27) has a logarithmic region when $Bk_\perp^2/k_{0\perp}^2 \gg g_{\mathrm{ph}}^2$, which yields

$$\rho \propto T \ln(T/\omega_0 g_{ph}). \tag{29}$$

The above-presented formulas admit of a large number of different limiting cases, depending on the relationships among the parameters. In practice, we usually have $T_p \sim \omega_0$, while the quantity g_{ph}^2 is not at all small. Therefore, of all the possibilities allowed by (26) we shall investigate only one other limiting case, namely, the one that is the opposite of (28):

$$T/\varepsilon_F \gg \alpha. \tag{30}$$

In the indicated limit, the integration over the longitudinal momentum in (26) gets truncated at $\delta \sim \alpha p_F$ on account of the presence of the factor $\sin^2\chi_\delta$. Instead of (29), we now obtain

$$eEn \sim \alpha \frac{u\omega_0^2}{T} \int (d^2\mathbf{k}_\perp) \frac{N_0(\mathbf{k})}{T\omega(\mathbf{k})} \mathrm{ch}^{-2}\left(\frac{\omega(\mathbf{k})}{4T}\right).$$

From this relation we obtain in the high-temperature region a temperature-independent resistance $\rho \propto \alpha$. In the so-called broad range of temperatures $T \sim T_p$, proceeding in the same way as in the derivation of (29), we obtain in place of (29) the expression

$$\rho \propto \alpha \ln(T/g_{ph}\omega_0 \ln^{1/2}(T/T_p)). \tag{31}$$

This behavior resembles the observed flat temperature dependence of the conductivity in stoichiometric $(\mathrm{TTT})_2\mathrm{I}_3$ (Ref. 25). Such a similarity immediately raises the question whether, in their turn, the characteristics of the conductivity in the case of nonstoichiometric composition of the compound can be understood. According to Kaminskii *et al.*,[25] the compounds $(\mathrm{TTT})_2\mathrm{I}_{3+\delta}$ with $\delta = 0.08$; 0.10 have higher conductivities at low temperatures, the transition in them and their conductivity peak occurring at lower temperatures. A probable answer is that, in the absence of stoichiometry, the iodine chains are not ordered, and their relative disposition is random. In this case the modulating potential varies from chain to chain, although, as has already been noted above, the modulation period is tightly bound with the population.

Let us return to the formulas (21)–(23) of this section. If the modulating potential has a three-dimensional periodicity, then in the matrix element (23) the transverse components of the vectors k_1 and $\bar{\mathrm{k}}_1$ coincide by definition [see (22)]. But if the component u_{4p_F} in (21′) varies from chain to chain, then (21′) is responsible for the phonon scattering involving a change in the transverse component of the momentum. Therefore, the resonance denominators in (23) do not play any role, since the frequencies $\omega(\mathbf{k}_1)$ and $\omega(\bar{\mathbf{k}}_1)$ are completely independent. In other words, it is necessary to average the resistance over the amplitude of the random potential of the iodine chains, which is equivalent to additional integration over $\mathbf{k}_{1\perp}$ in the expression (23) for the square of the modulus. It follows from the foregoing that the temperature dependence of the resistance is almost linear (corrected by the logarithmic term at $T \sim T_p$), but the resistance contains a small factor in comparison with (29), since the resistance is proportional to the square of the magnitude of the modulating potential. This result qualitatively coincides with what is observed for the resistance in nonstoichiometric $(TTT)_2I_{3+\delta}$ (Ref. 25). At the same time, it should be noted that the temperature dependence of the resistance $\rho_p(T)$ in $(TMTSF)_2PF_6$ has been found to be quadratic right down to quite low temperatures. Probably, the transition from $\rho_p(T)$ to $\rho_V(T)$ (allowance for the thermal expansion of the lattice[8,23]) will give a dependence closer to the linear law, which would imply that the scattering on the dimerization of the parent lattice plays the decisive role, i.e., that the limiting case (28) obtains. But we cannot exclude the possibility that other mechanisms are responsible for the conductivity in this material.[2] Whether or not the dimerization effects considered in this section are important in the region of the dielectric-transition temperature is quite difficult to say both because of the insufficient width of the temperature range [the transition temperature $T_c \sim 15$ K (Ref. 5)] and because of the fact that the dielectric transition in this compound has a different character.

4. THE PEAK IN THE CONDUCTIVITY. CRITICAL BEHAVIOR OF THE RESISTANCE

The question of the conductivity due to the contribution from the Fröhlich mode fluctuationally generated in the vicinity of the transition has been repeatedly raised in connection with the study of the transport properties of the one-dimensional conductors.[1,28] With the exception of the phenomenological theory of Ref. 28, the majority of the published papers are devoted to the investigation of the contribution of the diagrams shown in Fig. 5. Similar diagrams are responsible for the paraconductivity in the theory of superconductivity.[29] The diagrams in Fig. 5 are studied either in the purely one-dimensional model[30,31] (which does not have a region of applicability at all), or with allowance for the three-dimensional properties of the phonons.[17] It became clear after the publication of Ref. 10 that the diagrams in Fig. 5 describe the phonon-drag effect, and that they have nothing to do with the question of critical fluctuations. A more correct formulation of the question is contained in Refs. 32 and 33, where it is pointed out that, since the transition is due to the softening of definite phonon frequencies, the critical behavior of the resistance in the vicinity of the transition temperature is determined by the fluctuations of the order parameter of the structural transition. In Ref. 33 the contribution of these fluctuations is studied without allowance for the effects of the drag, and there is an unfortunate mix-up with the dimensionality of the fluctuations.

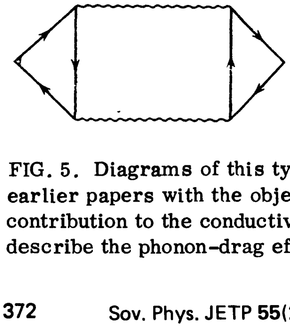

FIG. 5. Diagrams of this type, which were investigated in earlier papers with the object of obtaining the fluctuation contribution to the conductivity from the Fröhlich mechanism, describe the phonon-drag effect in first orders.

Singularities occur in the resistance even within the framework of our model (1′), which is equivalent to the self-consistent field approximation, the singularities occurring even in the dominant terms, which determine the temperature dependence of the resistance. The region of applicability of the results obtained below is naturally limited by the inequality (7), i.e., $\Delta T/T_p > g_{\text{ph}}/B^2$. We shall investigate these singularities in detail[33] within the framework of the kinetic equation and in the relaxation-time approximation with allowance for those modifications which, according to the above-performed analysis, are due to the strong phonon-drag effect. In the neighborhood of the transition point the phonon branch has a large damping constant (5), and the applicability of the approach based on the kinetic equation seems to be doubtful, even with all the approximations noted in Sec. 1. We specifically verified the fact that the analysis of the requisite diagrams with the use of the appropriate expressions for the Green functions (5) leads to equivalent results. The diagrammatic computational method is therefore not presented in order to avoid tedious computations.

Examining the formulas of the preceding sections, e.g., (15), we see that they contain the structural soft-mode factor $T/\tilde{\omega}^2(\mathbf{k})$, which enters into an integral of the form

$$\frac{1}{\tau} \propto T \int \frac{dk_\parallel d^2\mathbf{k}_\perp}{\tilde{\omega}^2(\mathbf{k})} \overline{W} \delta(\ldots), \tag{32}$$

where $\overline{W}$ contains all the other factors figuring in the process, while $\delta(\ldots)$ is the delta function expressing the conservation laws, which depend on the process under investigation (thus, for example, this may be the three-phonon umklapp process considered in Sec. 2 if it is possible for the soft phonon). Let the behavior of $\overline{W}$ limit the quantity $|k_\parallel \pm 2p_F| \sim T/v$. The integration over $\mathbf{k}_\perp$ in this case yields a contribution of the order of unity from the momentum region $k_\perp^2 \sim g_{\text{ph}}^2 k_{0\perp}^2$. [If there is a region where $T \gg \omega_0 g_{\text{ph}}$, then, like (29), the corresponding contribution contains $\ln(T/g_{\text{ph}}\omega_0)$.] The more detailed information about the temperature dependence of the resistance at $T \sim T_p$ depends on the specific form of the function $f(\delta v/T)$ in (1′) and (1″), i.e., on the model for the Kohn anomaly. The softening of the phonon frequency increases the amplitude of the scattering on the soft phonon as the temperature $T \to T_p$ from above. But the temperature dependence of the population factors for the other phonons can compensate for this effect.

The question whether the conductivity possesses a maximum above the transition point cannot (as discussed in part in Sec. 2) be answered unequivocally if, of course, the phonon spectrum in (1) does not possess additional two- or even one-dimensional properties (i.e., if the coefficient B of the transverse phonon dispersion is not small in one or two dimensions). In principle, the peak could be located below the transition point (i.e., in the new phase), owing to the different temperature-variation laws for the mobility and the number of carriers.

Let us differentiate (32) near the transition point with respect to the temperature, using for $\tilde{\omega}(\mathbf{k})$ the expression (1). The singularity of the resistance has the form

$$\frac{d\rho(T)}{dT} \sim -\frac{\rho(T_p)}{T_p}\frac{1}{t^{1/2}}, \tag{33}$$

where $t = (T - T_p)/T_p$. Let us recall that the applicability of (33) is limited by the condition (7); therefore, the factor $t^{1/2}$ cannot be too small. It is interesting, however, that (33) does not contain an additional g_{ph}^2 coefficient, proportional to the weak electron-phonon interaction. [Two opposite effects act below the transition point: the hardness of the phonon mode is restored [an effect which is the opposite of (33)], and the number of carriers decreases like[34] $\Delta/T_p \propto |t|^{1/2}$. Therefore, although the singularity is a root singularity, the sign of the effect is not apparent.]

Let us return to the question of the peak. If $T_p \sim \omega_0 \gg g_{\text{ph}}\omega_0$, then $\ln(T_p/g_{\text{ph}}\omega_0)$ can be considered to be a large number. In that case the peak exists: instead of (33), we obtain

$$\left.\frac{d\rho}{dT}\right|_{T=T_p} \sim -\frac{\rho(T_p)}{T_p}\frac{1}{\ln(T_p/\omega_0 g_{ph})}\frac{1}{t^{1/2}}.$$

Hence for the determination of the position of the peak we have the relation

$$(T_m - T_p)/T_p \sim \ln^{-2}(T_p/g_{ph}\omega_0). \tag{34}$$

Horn and Guidotti[33] have experimentally found that the exponent ϑ for the derivative $|d\rho/dT| \propto t^{-\vartheta}$ of the resistance in the compounds TTF–TCNQ and TSeF–TCNQ below the transition point is indeed close to $\vartheta = \frac{1}{2}$. But above T_p the exponent ϑ is significantly higher than $\frac{1}{2}$ ($\vartheta \approx 1.0$ for TTF–TCNQ and $\vartheta \approx 1.5$ for TSeF–TCNQ). Strictly speaking, these values were obtained in the region of very small t, where (33) is probably no longer applicable. As to Horn and Guidotti's[33] dR/dT curves themselves, the $|dR/dT| = At^{-1/2} - B$ plot can be fitted to them in the region further away from T_p.

Figure 6 shows the experimental $d\log R/d(1/T)$ curves[3)] for $(\text{TTT})_2\text{I}_{3+\delta}$ ($\delta = 0.10$ and 0.08) in the critical region together with the indicated interpolation dependences. Clearly the agreement is quite good. It should be borne in mind that Kaminskii *et al.*[25] measured the derivative of the resistance directly (Horn and Guidotti[33] obtained the corresponding curves by means of a numerical differentiation of the resistance). Therefore, the stoichiometric composition of $(\text{TTT})_2\text{I}_3$, which is characterized by a smooth conductivity law,[25] does not provide reliable data. Let us also note that, as in the derivation of (31), when the dimerization is slight, the dependence of all the expressions in (32) on the longitudinal momentum has another scale [it is necessary to compare $(T - T_p)/T_p$ and α]. This observation undoubtedly pertains also to TTF–TCNQ; for although no dimerization occurs in this compound, there is interaction between several phonon branches, which get complexly reconstructed in the course of the development of the Kohn anomaly. We have not, however, investigated this question quantitatively.

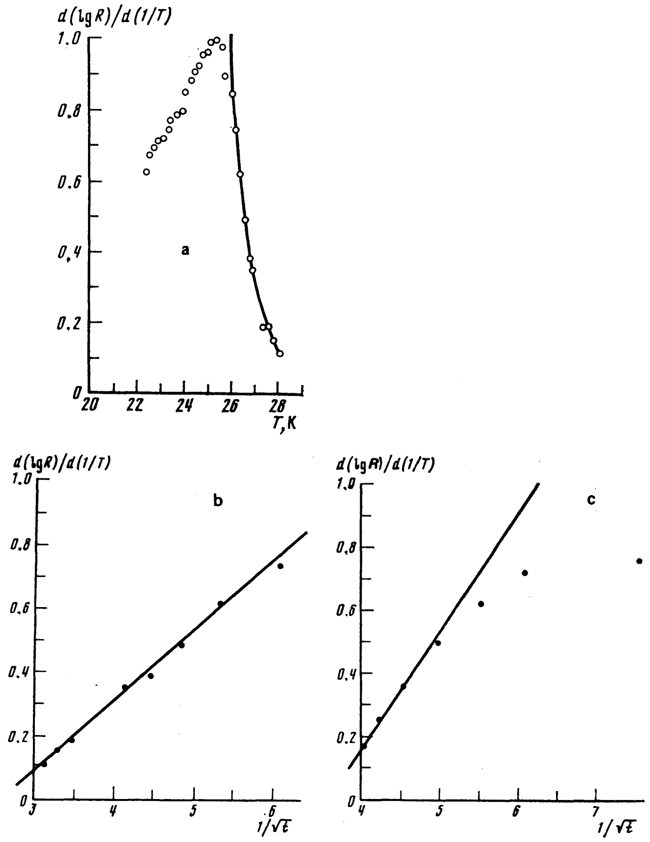

FIG. 6. The $d\log R(T)/d(1/T)$ experimental curves (in arbitrary units) obtained by Kaminskii *et al.*[25] for $(\text{TTT})_2\text{I}_{3+\delta}$ near the transition point. a) $\delta = 0.08$; the general shape of the derivative near T_p. The continuous curve is the result of the theoretical analysis (see the text). b) Dependence of $d\log R(T)/d(1/T)$ on $t^{-1/2}$, where $t = (T - T_p)/T_p$. The straight line is the plot of $d[\log R(T)]/d(1/T) = 0.22t^{-1/2} - 0.57$ (for $\delta = 0.08$). c) Same plots as in b), but for $\delta = 0.1$; the straight line is the plot of $d[\log R(T)]/d(1/T) = 0.37t^{-1/2} - 1.33$.

The low-temperature conductivity curves, the conductivity-peak values, and the corresponding temperatures for one-dimensional conductors are very sensitive to impurities and defects. In the kinetic-equation approximation, and at low defect concentrations c, the scattering by the impurities make an additive contribution to the resistance:

$$\rho(T) = \rho_0(T) + \rho_{imp}(T), \tag{35}$$

where the second term $\rho_{\text{imp}}(T)$ describes the elastic scattering by the static defects, which is, however, temperature dependent also in the region above the transition point.[22] In the model chosen by us, the amplitude $V^*(q)$ of the scattering, involving a $q_\parallel = \pm 2p_F$ momentum transfer, of an electron by an impurity is, as shown in Fig. 7, higher because of the fact that the impurity easily deforms the lattice if the corresponding

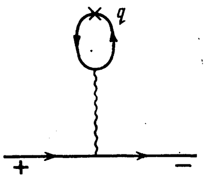

FIG. 7. Schematic representation of the mechanism underlying the increase in the amplitude of the electron scattering by a static defect as a result of the presence of a soft phonon branch.

phonon mode is a soft mode:

$$1/\tau^*_{imp}(T)\propto c\int d^3\mathbf{q}\,|V^*(\mathbf{q})|^2\delta(\varepsilon_\mathbf{p}-\varepsilon_{\mathbf{p}-\mathbf{q}}), \tag{36}$$

where $|V^*(\mathbf{q})|^2$ is connected with the scattering amplitude $|V(\mathbf{q})|^2$ by, when the Kohn anomaly is neglected, the relation

$$|V^*(\mathbf{q})|^2=(\omega_0^2/\tilde{\omega}^2(\mathbf{q},T))^2|V(\mathbf{q})|^2.$$

Using for $\tilde{\omega}^2(\mathbf{q})$ at $T\sim T_p$ the expression (1′), we see that $1/\tau^*_{\text{imp}}(T)\sim 1/g_{\text{ph}}{}^2\tau_{\text{imp}}$, and strongly depends on temperature, since the integral over $\mathbf{q}_\perp$ in (36) converges at small $q_\perp\sim g_{\text{ph}}q_{0\perp}$. The temperature dependence $\rho_{\text{imp}}(T)$, however, depends on the model. The critical behavior of the resistance near T_p is determined by the derivative

$$\left.\frac{d\rho_{imp}}{dT}\right|_{T=T_p}\sim-\frac{\rho_{imp}}{T_p}\frac{1}{t^{1/2}}. \tag{37}$$

It follows from this, in particular, that at low impurity concentrations c the point at which the conductivity attains its maximum value shifts according to the law

$$(T_m-T_p)/T_p\propto c^{2/3}. \tag{38}$$

In Fig. 8 we have plotted the difference T_m-T_p as a function of $c^{2/3}$ for irradiated TTF–TCNQ crystals.[35] As can be seen, the experimental picture is reproduced by the dependence (38) quite well. It is possible that the high critical exponent $\vartheta\approx 1.45$ found for TSeF–TCNQ by Horn and Guidotti[33] is due to the presence of impurities in the investigated samples.

5. CONCLUSION

The most convincing experimental evidence for the important role played by the phonon-drag effect in the materials under discussion is the strong frequency dispersion of the conductivity that has been found to occur mainly in TTF–TCNQ. The most recent measurements[36] allow us to construct the frequency dependence of the conductivity in the high-frequency region extending right up to $\vartheta = 7$ cm^{-1}. These data clearly show that the conductivity has a sharp peak at zero frequency (in the metallic regime), and falls off rapidly at $\vartheta\lesssim 10$–20 cm^{-1}. We should expect a linear law for the resistance at high temperatures and high frequencies [i.e., the law $\sigma\propto ne^2\tau/m$ with τ given by (2)]. Comparing this with our expressions (19) and (20), we see that the expected decrease of the conductivity with increasing frequency can be very rapid. The frequency scale responsible for the phonon-drag mechanism is clearly determined by the time (14′) characterizing the interaction of the phonons (with $|k_\parallel|\approx 2p_F$) with the electrons. Taking for the frequency of the Kohn phonon at high temperatures the value $\omega_0 = 70$ K (Ref. 37), we obtain for $1/\tau_{\text{ph},e}$ at $T = 160$ K the reasonable estimate $1/\tau_{\text{ph},e}\sim 10$ K. As has been observed by Tanner *et al.*,[36] $1/\tau_{\text{ph},e}$ decreases with increasing temperature.

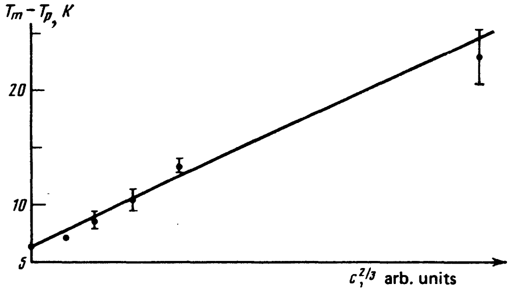

FIG. 8. Results of the measurements of the defect-concentration dependence of the temperature at which the conductivity of irradiated TTF-TCNQ samples attains its maximum[35] in accordance with the theoretical expression (38) of the text.

In conclusion, let us note that our results are fairly general, and do not depend too much on the model, at least in that part which concerns the three-phonon processes. Indeed, the drag effect only indicates that the electrons and the phonons with $|k_\parallel|\approx 2p_F$ are strongly coupled, since the adiabatic approximation is not applicable to them. They give their momentum to the phonons (or the $4p_F$-modulation of the lattice) that do not participate in the development of the structural instability. These phonons and the three-phonon processes corresponding to them are well defined. As to the strong-coupling region (i.e., the subsystem: the electrons and the phonons with $|k_\parallel|\approx 2p_F$), it plays the role of a momentum source with a characteristic width in momentum space of $\Delta k_\parallel\sim T/v$.

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1) For a fairly complete bibliography, see Refs. 1 and 2 and the proceedings of the conferences on one-dimensional conductors[3,4]; see also the references in Refs. 5–7.

2) The same conclusion holds true for the exchange of acoustic phonons. One of the present authros (L.G.) is indebted to R. Curci for this remark.

3) The authors thank I. F. Shchegolev for kindly making the detailed graphs, shown in Fig. 6, of his measurements of the derivative of the resistance in $(\text{TTT})_2\text{I}_3$ available to them.

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[1] J. T. Devreese, R. P. Evrard, and V. E. van Doren (editors), Highly Conducting One-Dimensional Solids, Plenum Press, New York, 1979.

[2] M. Weger, Theory of the Electrical Conductivity of Organic Metals, Paper Presented at the Tomar Conference on Small-

Sized Materials, Tomar, 1979.

[3] S. Barisic (editor), Lecture Notes in Physics, Vol. 95, Springer Verlag, Berlin, 1979, p. 96.

[4] J. Bernasconti (editor), Physics in One Dimension, Springer Verlag, Berlin, 1980.

[5] K. Bechgaard, C. S. Jacobsen, K. Mortensen, H. J. Pedersen, and N. Thorup, Solid State Commun. **33**, 1119 (1980).

[6] H. J. Schulz, D. Jerome, M. Ribault, A. Mazaud, and K. Bechgaard, J. Phys. Lett. **42**, L-51 (1981).

[7] K. Bechgaard, K. Garneiro, M. Olsen, F. B. Rasmussen, and C. S. Jacobsen, Phys. Rev. Lett. **46**, 852 (1981).

[8] J. R. Cooper, Phys. Rev. B **19**, 2404 (1979).

[9] M. Kaveh and M. Weger, Phys. Rev. B **20**, 2264 (1979).

[10] M. Weger and H. Gutfreund, Comments on Solid State Phys. **8**, 135 (1978).

[11] E. M. Conwell, Phys. Rev. Lett. **39**, 777 (1977); Solid State Commun. **33**, 17 (1980).

[12] N. F. Mott and W. D. Twose, Adv. Phys. **10**, 107 (1961).

[13] V. L. Berezinskiĭ, Zh. Eksp. Teor. Fiz. **65**, 1251 (1973) [Sov. Phys. JETP **38**, 620 (1974)].

[14] A. A. Gogolin, V. I. Mel'nikov, and É. I. Rashba, Zh. Eksp. Teor. Fiz. **69**, 327 (1975) [Sov. Phys. JETP **42**, 168 (1975)].

[15] A. A. Abrikosov and I. A. Ryzkin, Adv. Phys. **27**, 147 (1978).

[16] L. P. Gor'kov and I. E. Dzyaloshinskiĭ, Zh. Eksp. Teor. Fiz. **67**, 397 (1974) [Sov. Phys. JETP **40**, 198 (1975)].

[17] L. P. Gor'kov and I. E. Dzyaloshinskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **20**, 37 (1974) [JETP Lett. **20**, 16 (1974)].

[18] S. Barisic and M. Marcelja, Solid State Commun. **7**, 1395 (1969).

[19] A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinskiĭ, Metody kvantovoĭ teorii polya v statisticheskoĭ fizike (Methods of Quantum Field Theory in Statistical Physics), Fizmatgiz, Moscow, 1962 (Eng. Transl., Prentice-Hall, Englewood Cliffs, N.J., 1963).

[20] E. M. Lifshitz and L. P. Pitaevskiĭ, Fizicheskaya kinetika (Physical Kinetics), Nauka, Moscow, 1979 (Eng. Transl., Pergamon Press, Oxford, 1981).

[21] H. Gutfreund and M. Weger, Phys. Rev. B **16**, 1753 (1977).

[22] L. P. Gor'kov and I. E. Dzyaloshinskiĭ, Pis'ma Zh. Eksp. Teor Fiz. **18**, 686 (1973) [JETP Lett. **18**, 401 (1973)].

[23] R. H. Friend, M. Miljak, D. Jerome, D. L. Decker, and D. Debray, J. Physique Lett. **39**, L-134 (1978).

[24] J. Ziman, Electrons and Phonons, Clarendon Press, Oxford, 1960 (Russ. Transl., IIL, Moscow, 1962).

[25] V. F. Kaminskii, M. L. Khidekel, R. B. Lyubovskii, I. F. Shchegolev, R. P. Shibaeva, E. B. Jagubskii, A. V. Zvarykina, and G. L. Zvereva, Phys. Status Solidi A **44**, 77 (1977).

[26] N. Thorup, G. Rindorf, H. Soling, and K. Bechgaard, Acta Crystallogr. B **37**, 1236 (1981).

[27] S. A. Brasovskiĭ and S. A. Gordyunin, Pis'ma Zh. Eksp. Teor. Fiz. **31**, 399 (1980) [JETP Lett. **31**, 371 (1980)].

[28] D. Allender, J. W. Bray, and J. Bardeen, Phys. Rev. B **9**, 119 (1974).

[29] L. G. Aslamazov and A. I. Larkin, Fiz. Tverd. Tela (Leningrad) **10**, 1104 (1968) [Sov. Phys. Solid State **10**, 875 (1968)].

[30] B. R. Patton and L. J. Sham, Phys. Rev. Lett. **31**, 631 (1973); Phys. Lett. **47A**, 133 (1974); Phys. Rev. Lett. **33**, 638 (1974).

[31] S. Takada and E. Sakai, Prog. Theor. Phys. **59**, 1802 (1978); Phys. Rev. B **20**, 2676 (1979).

[32] S. Takada, Prog. Theor. Phys. **46**, 15 (1971).

[33] P. M. Horn and D. Guidotti, Phys. Rev. B **16**, 491 (1977).

[34] L. P. Gor'kov and E. N. Dolgov, Zh. Eksp. Teor. Fiz. **77**, 396 (1979) [Sov. Phys. JETP **50**, 203 (1979)]; J. Low Temp. Phys. **42**, 101 (1981).

[35] C. K. Chang, M. J. Cohen, P. R. Newman, and A. J. Heeger, Phys. Rev. B **16**, 5163 (1977).

[36] D. B. Tanner, K. D. Cummings, and C. S. Jacobsen, Phys. Rev. Lett. **47**, 597 (1981).

[37] G. Shirane, S. M. Shapiro, R. Comes, A. F. Garito, and A. J. Heeger, Phys. Rev. B **14**, 2325 (1976); S. M. Shapiro, G. Shirane, A. F. Garito, and A. J. Heeger, Phys. Rev. B **15**, 2413 (1977).

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