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Commensurate-incommensurate conduction in quasi-one-dimensional organic systems

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The commensurability dependence of conduction in one-dimensional systems has been studied. A new umklapp scattering mechanism is proposed in the commensurate phase which causes a quenching of the $2k_F$ phonon flow. It is shown that this quenching mechanism accounts quantitatively for the following observed features: (i) the difference $\Delta\sigma$ between the conductivity of tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ) in the commensurate and incommensurate phase, (ii) the temperature dependence of $\Delta\sigma$, (iii) the pressure dependence of $\Delta\sigma$, which explains why the observed $\Delta\sigma$ for tetraselenofulvalene (TSF)-TCNQ is small, (iv) the commensurability width, and (v) the difference in the effect of commensurability on the conductivity perpendicular to the chains and along the chains. Comparison is made between the present theory and the sliding charge-density-wave contribution to the conductivity.

I. INTRODUCTION

Transport phenomena in quasi-one-dimensional conductors have recently attracted a great deal of interest. The origin of conduction in the metallic phase in these materials above the Peierls transition was one of the main interests in this field. Immediately after the detection of the high conductivity of TTF-TCNQ (tetrathiafulvalene tetracyanoquinodimethane—the prototype of one-dimensional organic conductors) by the Penn Group,[1] many theories were initially suggested[2–6] to explain the features of this high conductivity. Bardeen[2] and independently Lee *et al.*[4] suggested that the high conductivity is due to sliding charge-density waves (SCDW), a mechanism originally proposed by Forhlich[7] to explain superconductivity.

Motivated by this interpretation Salamon *et al.*[8] measured the thermal conductivity. According to the Bardeen theory,[2] the Wiedermann-Franze ratio L/L_0 should be about 10^{-4}. However, the experiment did not support this prediction. The measured ratio L/L_0 was about 1, ruling out the SCDW mechanism as the dominant conduction mechanism. On the other hand, this experiment seemed to indicate that conduction takes place by single-particle mechanisms. Accordingly, many single-particle theories have been proposed.[9–14] On the other hand, it was found that the conductivity depends strongly on the frequency of the applied field (Heeger,[15] Jacobsen[16]). In addition, it was found[17,18] that the conductivity decreases under irradiation by deuterons or by x ray. Neither of these two experiments can be explained by a single-particle mechanism (see a discussion by Heeger[19]).

An important development for the understanding of the origin of conductivity of one-dimensional systems was recently made by the Orsay group.[20] They measured the conductivity as a function of charge transfer Z by applying pressure on TTF-TCNQ at a fixed temperature. They thereby obtained the conductivity for both the incommensurate phase and the commensurate phase.

In this paper we present an explanation for the difference in conduction between the two phases. In particular, we explain the following experimental facts (Andrieux *et al.*,[20] Jerome[21]).

(i) The conductivity in the commensurate phase ($Z = \frac{2}{3}$) is lower by a factor of 2 than the conductivity in the incommensurate phase near the Peierls transition temperature.

(ii) The conductivity perpendicular to the chains σ does *not* change on going from the incommensurate phase.

(iii) The drop in conductivity as a function of pressure ranges over about 5 kbar. It does not occur abruptly at the pressure of 19 kbar, which produces the commensurate charge transfer $Z = \frac{2}{3}$.

(iv) The commensurability dependence occurs only at *low* temperatures ($T < 150$ K), disappearing completely by room temperature.

The Orsay group[20] and later other authors[22] attributed all these results to SCDW, which we denote by σ_{CDW}. The idea that an incommensurate CDW is weakly coupled to its underlying lattice was treated by many authors. A discussion for the possible sliding of a CDW in a incommensurate phase was given by Sacco *et al*.[23,24] The behavior of $\sigma_{\rm CDW}$ near the Peierls transition was already calculated by Patton and Sham.[25,26] They show also that the enhanced conductivity is suppressed in the dirty limit. The enhancement applies only to the incommensurate limit. Both of these results are in accord with the Orsay experiment.[20] However, the temperature dependence of the enhanced conductivity[25,26] $\delta\sigma$ is $(T-T_p)^{-1/2}$ and is not in agreement with the observed temperature dependence $\delta\sigma \propto T^{-3}$ (roughly).

In this paper we take a different path and present a *single-particle* theory. The conductivity is calculated directly from the Boltzmann equation.[27] The enhancement of the usual single particle conductivity is given through the effect of phonon drag.[14,27–29] We solve the coupled Boltzmann equations[27] for electrons, phonons and librons and calculate explicitly *two* additional conductivities. The first σ_{2k_F} due to the effect of phonon drag[14,27–29] and σ_L due to libron drag.[27] In the commensurate phase we show that the phonon system must remain in thermal equilibrium yielding the usual single-particle conductivity with *no* phonon drag effects. This is achieved due to a new umklapp scattering mechanism which is operative only in the commensurate phase. We also calculate the temperature ($\sigma_{2k_F} \sim T^{-3}$) and pressure dependence of σ_{2k_F} and find excellent agreement with the observed $\delta\sigma$. We account quantitatively for the difference in $\delta\sigma$ between TTF-TCNQ and tetraselenofulvalene (TSF)-TCNQ. In addition, our calculated σ_L offers a solution to the apparent contradiction between the observed collective phenomena[16–18] and the lack of commensurability dependence[20] at room temperature. We show that σ_L does *not* depend on commensurability and remains the same as in the incommensurate phase. However, $\sigma_L \rightarrow 0$ in the "dirty limit" or for high electric field frequencies. Thus, the high-temperature "collective" phenomena are accounted for in our single-particle approach. It should be noted that our results are *unrelated* to the existence of a many-body sliding charge density wave. We argue that σ_{2k_F} dominates over $\sigma_{\rm CDW}$. At temperatures $T \gtrsim 150$ K the dominant enhanced conductivity is σ_L.

The paper is structured as follows. In Sec. II, a phenomena classification is presented; in Sec. III the commensurability dependence of the $2k_F$ phonon drag is discussed. The effect of commensurability dependence of the conductivity perpendicular to the chains is discussed in Sec. IV and its effect on libron drag in Sec. V. A quantitative account for the experiments is given in Secs. VI and VIII and the Summary follows in Sec. IX.

II. PHENOMENA CLASSIFICATION

We can summarize the theoretical situation by writing the conductivity as a sum of two contributions, a single-particle contribution $\sigma_{\rm sp}$ and a collective contribution $\sigma_{\rm coll}$,

$$\sigma = \sigma_{\rm sp} + \sigma_{\rm coll} \quad . \tag{1}$$

Here, we concentrate on $\sigma_{\rm coll}$. We may have a contribution to $\sigma_{\rm coll}$ from sliding charge-density waves (SCDW) proposed by Frohlich[7] and reproposed[22] to account for the experiment.[20] It is denoted here by $\sigma_{\rm CDW}$. However, we must have the experimental constraint that $\sigma_{\rm CDW} < \sigma_{\rm sp}$ since the Wiedemann-Franz law is obeyed.[8] This is in contrast to the first suggestion that almost all the conduction is due to SCDW. In addition to $\sigma_{\rm CDW}$, it was suggested[27–29] that two mechanisms can explain the irradiation[17] and ac experiments.[16] The first mechanism is the $2k_F$ phonon drag, which contributes an extra conductivity σ_{2k_F}. The second mechanism is caused by the unique role of the strong second-order electron-phonon interaction. This interaction is strong[12,14,27,29] because of the coupling of electrons to the rotational modes of the molecules in the one-dimensional organic charge transfer conductors. It was shown[28] that the excess of absorbed momentum in the librational modes causes an increase in the conductivity even at room temperature. This idea is called "libron drag" and we denote its contribution to the conductivity by σ_L. It should be noted that $\sigma_{\rm sp}$, σ_{2k_F}, and σ_L are conductivities caused by the *single-particle* Bloch electron states. σ_{2k_F} and σ_L are extra conductivities caused by the $2k_F$ phonons or by the librational modes which drag the Bloch electrons and cause an additional current. By contrast, $\sigma_{\rm CDW}$ is caused by electron states *not* included in the electron Bloch states.

Thus, we may write $\sigma_{\rm coll}$ as a sum of three contributions:

$$\sigma_{\rm coll} = \sigma_{\rm CDW} + \sigma_{2k_F} + \sigma_L \quad . \tag{2}$$

The existence of a nonzero $\sigma_{\rm coll}$ is supported by three experiments: (i) the irradiation[17] dependence of σ, (ii) the frequency[15,16] dependence of σ, and (iii) the commensurability[20] dependence of σ. These experiments can be classified as temperature-dependent and temperature-independent phenomena. The commensurability dependence of σ disappears above 150 K in TTF-TCNQ and may be classified as a low temperature phenomena. On the other hand, the irradiation dependence[17] and the frequency dependence[16] of σ do not depend much on temperature. This classification suggests that there are *two* different mechanisms responsible for the two classes of phenomena. We show in the next two sections that among the four sources contributing to σ in Eqs. (1) and (2) only σ_{2k_F} and σ_{CDW} depend on commensurability, σ_{sp} and σ_L do not. Also, we show that σ_{2k_F} is large only below 150 K in agreement with experiment. The fact that σ_L does not depend on commensurability is consistent with the above classification. It was shown[28] that σ_L is a *high-temperature* phenomenon being about the same as σ_{sp} even at room temperature. Moreover, it was recently shown[27] that σ_L vanishes for $\omega \geq 10^{12}\ \text{sec}^{-1}$ in accord with recent experiments.[16] Thus, it is satisfactory to see that the *similar* decrease in σ under irradiation or by increasing the frequency is accounted for by the same quantity σ_L. Moreover, since both of these effects occur at room temperature, they *cannot* be attributed to σ_{CDW}, which is a low-temperature phenomenon. The fact that we find σ_L to be independent of commensurability completes the physical picture. Thus, σ_{CDW} and σ_{2k_F} account for the commensurability experiment[20] whereas σ_L accounts for the room-temperature collective phenomena.[16,17] We concentrate here on σ_{2k_F} and σ_L. The properties of σ_{CDW} can be found in the papers of Heeger,[15] Andrieux *et al.*[20], and Bishop.[22]

III. COMMENSURABILITY DEPENDENCE OF σ_{2k_F}

It was shown[27,28] that the first order electron-phonon interaction in one-dimensional systems is not resistive. This is due to one-dimensional phonon drag. In the presence of an electric field, the steady state requires a $2k_F$ phonon flow in addition to the charge current along the chains. In this view, the extra conductivity σ_{2k_F} is achieved by dragging the k_F electrons via $2k_F$ phonon flow. The k_F electrons and the $2k_F$ phonons form a closed system and the electrons cannot lose their extra momentum (gained by the electric field) via an electron-phonon interaction. The main idea is that in a one-dimensional system the $2k_F$ phonons can interact with *all* the electrons on the *nested* Fermi surface. This gives an effective channel for momentum transfer from the $2k_F$ phonon system *back* to the k_F electrons. This explains the absence of a linear term in the temperature dependence of the conductivity for pure organic systems and its reappearance under irradiation.[27,28]

We argue here that the $2k_F$ phonon drag picture is possible only in the incommensurate phase. In the commensurate phase this picture breaks down. Thus, the lower conductivity in the commensurate phase arises because the $2k_F$ electron-phonon interaction becomes *resistive*.

The quenching mechanism for phonon drag in the commensurate phase can be understood in the following way. Diffuse x-ray scattering shows an enhanced intensity for a momentum change of $2k_F$.[30,31] This "$2k_F$" satellite reflection is appreciably only below 150 K for TTF-TCNQ. Near the Peierls transition temperature, $T_P = 53$ K, there are large dynamical fluctuations to a distorted lattice with periodicity in momentum space, $Q = 2k_F$. The $2k_F$ x-ray intensity increases sharply as the temperature approaches T_P. Thus, there is a tendency to form a super-lattice in addition to the underlying lattice. This tendency to a new order must influence not only the structural properties, measured by *external* scattering but also the *internal* scattering, i.e., the single particle scattering of electrons within the material.

We now show here that there exists a new possibility for umklapp scattering which is possible only via the superlattice. This mechanism is effective, therefore, only below the mean-field temperature T_{MF}. In a one-dimensional system with charge transfer $Z < 1$ the usual electron-phonon umklapp scattering process $2k_F = q + G$ is impossible (where q is the phonon wave vector and G the reciprocal lattice vector). Only a normal electron-phonon scattering process $2k_F = q$ is possible. However, in the commensurate phase, a superlattice with $Q = 2k_F$ is "in phase" with the underlying lattice. Thus, in the commensurate phase there exists the following umklapp scattering process

$$2k_F = q + G' \ , \tag{3}$$

where $G' = G - Q$ is a new reciprocal-lattice vector. Therefore, there are *two* different scattering processes each corresponding to a different phonon, by which an electron in state $-k_F$ can give up its momentum by being scattered to $a + k_F$ state

$$q_N = 2k_F \quad \text{normal scattering}$$
$$q_U = 2k_F - G' \quad \text{umklapp scattering}. \tag{4}$$

For charge transfer $Z = \frac{2}{3}$, for which $G = 4k_F/Z = 6k_F$, we get

$$q_U = -q_N \quad . \tag{5}$$

This situation is illustrated in Fig. 1(a). A normal process corresponds to scattering from A to B via q_N. An umklapp process corresponds to scattering from C to D via the lattice vectors G, $-Q$, and q_u. The above results lead to the complete quenching of σ_{2k_F} in the commensurate phase. In the incommensurate phase a phonon $q = 2k_F$ may be excited only by a $2k_F$ change in electron momentum. However, in the commensurate phase the $2k_F$ phonon may also be excited by a $-2k_F$ change of electron momentum via umklapp scattering. Thus, in the commensurate phase, we have two possibilities,

$$q = 2k_F \quad ,$$
$$q = (-2k_F) + G' = 2k_F \quad . \tag{6}$$

This implies that there should not be any drag effect, since the $2k_F$ phonons do not absorb any *net* momentum from the electron system. This idea is illustrated in Fig. 1(b) and can be derived from the following phenomenological equation of motion for the $2k_F$ phonons in the commensurate phase

$$\frac{dP_{\mathrm{ph}}(2k_F)}{dt} = \frac{dP_e(k_F)}{dt} + \frac{dP_e(-k_F)}{dt} \quad , \tag{7}$$

where $P_{\mathrm{ph}}(2k_F)$, $P_e(k_F)$, and $P_e(-k_F)$ are, respectively, the net momenta for the $2k_F$ phonons, the k_F electrons, and the $-k_F$ electrons. In the commensurate phase, a $2k_F$ phonon can be excited by a k_F electron and a $-k_F$ electron. Therefore, in the steady state, we get

$$\frac{P_{\mathrm{ph}}(2k_F)}{\tau_{pe}} = \frac{P_e(k_F)}{\tau_N} + \frac{P_e(-k_F)}{\tau_U} \quad , \tag{8}$$

where τ_{pe}, τ_N, and τ_u are, respectively, the phonon-electron scattering relaxation time, the normal electron-phonon scattering relaxation time ($2k_F = q$), and the umklapp electron-phonon scattering relaxation time ($2k_F = q + G'$).

In the incommensurate phase, the umklapp term [second term of (8)] does not exist, leading to a nonzero $P_{\mathrm{ph}}(2k_F)$ which cancels the first-order electron-phonon scattering from the resistivity (see Kaveh and Weger[27]). However, in the commensurate phase the umklapp term is nonzero and exactly cancels out the normal term. Therefore, $P_{\mathrm{ph}}(2k_F) = 0$ in the commensurate phase because τ_U is equal to τ_N in a one-dimensional system. τ_U and τ_N involve the following ingredients: (i) matrix elements between initial state $|k_1\rangle$ and final state $|k_2\rangle$, (ii) $N(\omega_q)$, the number of phonons of wave vector q participating in the scattering event described by Eq. (4), and (iii) the phase space involved in the scattering. In a three-dimensional system, all three of these factors are different for normal and for umklapp scattering. However, in a one-dimensional system, there is only *one* scattering event for normal scattering or for umklapp scattering [see Fig. 1(a)]. Thus $|k_1\rangle = |-k_F\rangle$ and $|k_2\rangle = |k_F\rangle$ for *both* normal and umklapp scattering. This yields the same matrix element (which is a function of $k_2 - k_1 = 2k_F$). Moreover, since $|q|$ is the same in both scattering events, there are the same number of phonons $N(\omega_q)$ available. Finally, the phase space is obviously the same for both scattering events. Thus, it follows that

$$\frac{P_e(-k_F)}{\tau_U} = \frac{P_e(k_F)}{\tau_N} \quad , \tag{9}$$

where we make use of the relation $P_e(-k_F) = -P_e(k_F)$. This yields, from (8), the expected result that $P_{\mathrm{ph}}(2k_F) = 0$. Hence, in the commensurate phase, first-order electron-phonon scattering *does* contribute to the resistivity and the conductivity is accordingly lower.

We now show that this quenching mechanism is in fact a low-temperature phenomenon in agreement with experiment.[20] The mechanism for quenching σ_{2k_F} is ultimately based on (3), which is exact only

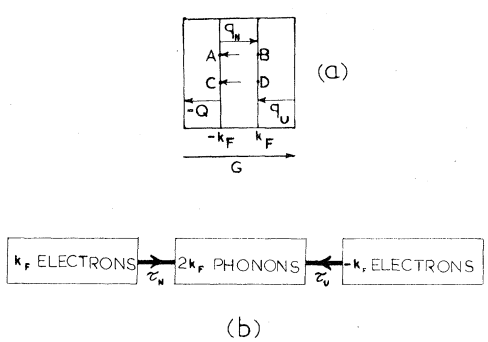

FIG. 1. (a) Normal and umklapp electron-phonon scatterings. The definitions of q_N, q_U, Q, and G are given in the text. (b) Momentum transfer for $2k_F$ phonons in the commensurate phase from k_F and $-k_F$ electrons via relaxation times τ_N and τ_U.

if the $2k_F$ superlattice is static. The dynamical character of the superlattice "smears out" the momentum conservation law (3), because of a *finite* coherence length. Thus, we must replace the momentum delta function for the electron phonon scattering by a Lorentzian function.

$$\delta(2k_F-(q+G-Q)) \rightarrow \frac{(2/\pi)\xi}{1/\xi^2+[2k_F-(q+G-Q)^2} , \qquad (10)$$

where ξ is the coherence length for the fluctuations to the superlattice structure. We see from (10) that (3) is valid only for large ξ. The magnitude of ξ may be deduced from the half-width of the intensity peak of the $2k_F$ x-ray scattering. In this way, the experimental $\xi(T)$ as a function of temperature was obtained.[19,31] It was found that $\xi(T)$ increases sharply below 150 K. For TTF-TCNQ, $\xi(150)=2b$ (b is the lattice spacing) whereas $\xi(58)=50b$. Inserting these values for $\xi(T)$ into (10) shows that only below 150 K is the momentum law in (3) valid, whereas above 150 K, it is smeared out. In other words, the quenching mechanism for σ_{2k_F} proposed here is effective only when the coherence length is large. Therefore, the difference between the conductivities in the incommensurate and commensurate phase vanishes above 150 K. This is in agreement with experiment.[20] We see that σ_{2k_F} possesses the same properties as σ_{CDW}. Namely, it is nonzero only in the incommensurate phase. In addition, *both* conductivites almost disappear for irradiated (or impure) samples.[20,28]

IV. EFFECT OF COMMENSURABILITY ON $\sigma_\perp$

The conduction perpendicular to the chains is related to the *single-particle* conductivity along the chains.[32,33] Therefore, the proposal that commensurability affects *only* σ_{2k_F} is consistent[21] with the experimental fact that $\sigma_\perp$ does not depend on commensurability. The $2k_F$ electron-phonon scattering is not resistive in the incommensurate phase because of phonon drag. However, this scattering does destroy the phase correlations *between* the chains and therefore *does* contribute to $\sigma_\perp$ even in the incommensurate phase.[33] Thus, the commensurate phase affects only the conductivity along the chains by suppressing phonon drag. This idea receives further support[18,34] from the recent experiments on the effect of irradiation on $\sigma_\perp$. The experiments clearly indicate that the effect of irradiation on $\sigma_\perp$ is an order of magnitude less than the effect on the conductivity along the chains. This fact is consistent with the present idea that phonon drag is a one-dimensional effect. Irradiation quenches phonon drag[28] and so the conductivity along the chains decreases *without* an accompanying effect on $\sigma_\perp$. This is very similar to the effect of commensurability for which we propose a similar explanation. Note that quenching of phonon drag by irradiation is already achieved by relatively *small* doses of irradiation.[18] The behavior of the conductivity for higher doses of irradiation was recently extensively studied by the Fontenay-aux-Roses group.[35]

Turning now to σ_{sp}, the experimental fact that $\sigma_\perp$ is independent of commensurability is strong evidence[21] that σ_{sp} is also commensurability independent,[33] since $\sigma_\perp \propto \sigma_{\mathrm{sp}}$.

V. EFFECT OF COMMENSURABILITY ON σ_L

The origin[28] of σ_L is related to the effectiveness of the *second*-order electron-phonon (or libron) interaction, which conserves momentum. It was shown[28] that processes for which

$$2k_F=q_1+q_2 , \qquad (11)$$

are not resistive. We see that unlike first-order scattering we now have *two* phonon wave vectors.

The libron drag mechanism is caused by excess of net momentum for *every* phonon state. Thus, the momentum absorbed by the q_2 phonon is $2k_F-q_1$. The following question arises: Is it possible to find *another* process in which the q_2 phonon may absorb momentum of $-(2k_F-q_1)$? In that case there would *not* be any excess momentum for the state q_2. We now show that such a possibility exists only for a *few* q_2 states. These are

$$\begin{aligned} q_2 &= 2k_F-q_1 , \\ q_2 &= -(2k_F-q_1)\pm Q\pm G . \end{aligned} \qquad (12)$$

This leads to $q_2=\frac{1}{2}(+-Q\pm G)$. For TTF-TCNQ, this gives,

$$q_2=\pm 2k_F \text{ and } q_2=\pm k_F . \qquad (13)$$

Therefore, only four events for $0<q_2<G/2$ are possible (and in *both* phases). We see that since a second-order electron-phonon interaction involves a general phonon wave vector $q\neq 2k_F$, commensurability does not affect σ_L.

VI. QUANTITATIVE STUDY OF COMMENSURABILITY

We have so far established that among the four contributions to the conductivity, $\sigma_{\rm CDW}$ (as given quantitatively by Bishop[22] and references therein) and σ_{2k_F} depend on commensurability, whereas $\sigma_{\rm sp}$ and σ_L do not depend on commensurability. It has already been pointed out by Heeger *et al.*[19] that it is difficult to distinguish between σ_{2k_F} and $\sigma_{\rm CDW}$ in the temperature dependence of σ in the incommensurate phase. The new common property, commensurability dependence, makes it even more difficult. The properties of $\sigma_{\rm CDW}$ were already studied.[22] We here calculate σ_{2k_F} and its commensurability dependence.

We introduce the notation $\Delta\sigma$ to denote the difference between the conductivity in the incommensurate phase $\sigma_{\rm IC}$ and the conductivity in the commensurate phase $\sigma_{\rm C}$. Thus,

$$\Delta\sigma = \sigma_{\rm IC} - \sigma_{\rm C} \ , \tag{14}$$

where both $\sigma_{\rm IC}$ and $\sigma_{\rm C}$ refer to the conductivity measured at a pressure of 19 kbar. Pressures $P < 19$ kbar correspond to a charge transfer[20] of $Z < \frac{2}{3}$ for TTF-TCNQ (see also Conwell[36]). This means that extrapolating the measured conductivity from below 19 kbar to $P = 19$ kbar yields $\sigma_{\rm IC}$, the conductivity in the *in*commensurate phase at $P = 19$ kbar (see Fig. 2). The measured conductivity minimum gives $\sigma_{\rm C}$, the conductivity at 19 kbar in the commensurate phase (see Fig. 2). In Fig. 3, we plot the temperature dependence of $\Delta\sigma$ by drawing a smooth curve through the seven experimental points. We see that $\Delta\sigma$ decreases very rapidly as a function of temperature. For $80 < T < 150$ K, $\Delta\sigma \sim T^{-3}$ (roughly) with $\Delta\sigma$ decreasing even faster above 150 K.

In the phonon-drag picture, the conductivity in the commensurate phase is lower than the conductivity in the incommensurate phase because of an additional *resistive* mechanism. (This is in contrast to the SCDW mechanism which freezes out a *conductivity* in the commensurate phase.) Thus, one may express σ_{2k_F} as

$$\sigma_{2k_F} = \frac{1}{\rho_{\rm IC}} - \frac{1}{\rho_1 + \rho_{\rm IC}} \ , \tag{16}$$

where ρ_1 and $\rho_{\rm IC}$ are, respectively, the resistivity due to the first order electron-phonon interaction and the resistivity in the incommensurate phase.

We now calculate σ_{2k_F} by using[28,33] the Hopfield expression[37] for ρ_1 and taking $\rho_{\rm IC}$ from experiment.[20] This leads to $\sigma_{2k_F} \propto T^{-3.2}$ in accord with the data for $\Delta\sigma$ below 150 K. The more rapid decrease of $\Delta\sigma$ above 150 K is due to two reasons. First, (16) is not valid above 150 K because the quenching mechanism for σ_{2k_F} in the commensurate phase breaks down, as already explained, leading to $\Delta\sigma < \sigma_{2k_F}$. Second, σ_{2k_F} is quenched above 150 K even in the *in*commensurate phase,[28] because in this temperature range the damping of a phonon via interaction with another phonon is comparable to the damping constant via phonon-electron interaction.

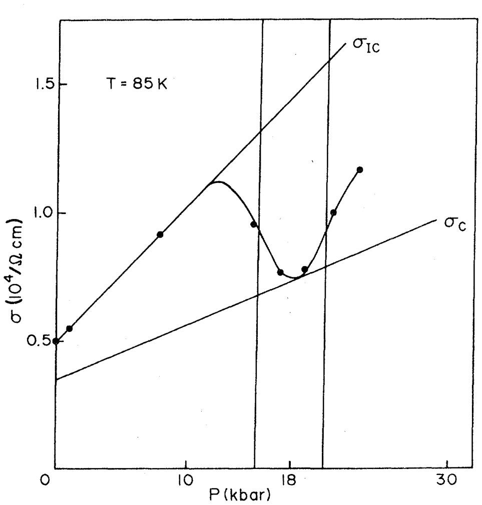

FIG. 2. Pressure dependence of $\sigma_{\rm IC}$ and $\sigma_{\rm C}$ at 85 K. The vertical lines define the range of "pressure commensurability" due to thermal smearing.

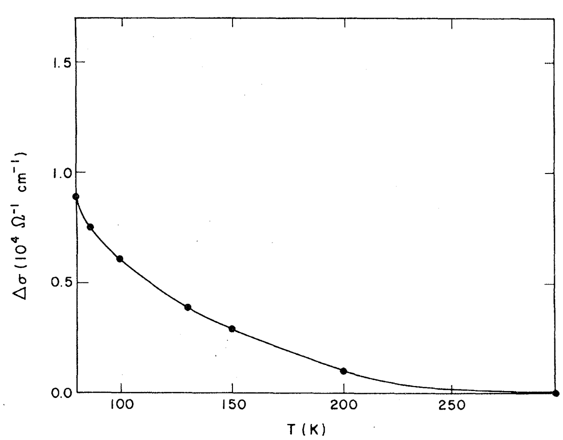

FIG. 3. Temperature dependence of $\Delta\sigma$ at $P = 19$ kbar.

In summary, we have a complete explanation for the temperature dependence of $\Delta\sigma$.

VII. COMMENSURABILITY WIDTH

In Fig. 2 we plot the measured conductivity as a function of pressure at $T = 85$ K. One sees that the "commensurability width" (the range of pressures for which the conductivity is decreased) is about 5 kbar. This is a large width in view of the fact that a pressure of 19 kbar is required to change Z from 0.590 (at $P = 0$) to $Z = \frac{2}{3}$. It will be demonstrated that this width can be accounted for within the framework of the present theory.

The quenching mechanism we have proposed is closely connected with the *commensurate* value of $\pm k_F$, namely $\pm k_F = \pm\frac{1}{6}G$. We now argue that the commensurate width is a manifestation of the fact that the metallic phase in TTF-TCNQ occurs at relatively high temperatures. Since the degeneracy energy ϵ_F for TTF-TCNQ is low, about 0.1 eV, the electron thermal energy "smears out" the sharpness of the commensurability decrease of σ. Therefore, we attribute to k_F a thermal width δk_F in the momentum conservation argument of Sec. III for quenching σ_{2k_F} in the commensurate phase. This modifies (4) into the following equations,

$$\begin{aligned} q_N &= 2k_F \pm 2\delta k_F \ , \\ q_U &= 4k_F - G \pm 4\delta k_F \ . \end{aligned} \tag{17}$$

Thus, we may satisfy the quenching condition, $q_U = -q_N$, even for

$$k_F(Z = \tfrac{2}{3}) \pm \delta k_F \ .$$

We may approximate δk_F from the thermal energy to get

$$\delta k_F = \frac{k_B T}{2\epsilon_F} k_F \tag{18}$$

which gives $\delta k_F \simeq 0.03 k_F$. Using the relation between pressure and charge transfer (see also Conwell[36]) leads to

$$\frac{\delta k_F}{k_F} \simeq \frac{\delta P}{P} \frac{\frac{2}{3} - 0.590}{\frac{2}{3}} \ . \tag{19}$$

For $P = 18$ kbar (commensurability pressure at 85 K) we get a commensurability width $\delta P \simeq 5$ kbar in agreement with experiment.

In view of the above discussion, our interpretation of Fig. 2 is as follows. There are *two* conductivities as a function of pressure, $\sigma_{\rm IC}$ and $\sigma_{\rm C}$. Values for $\sigma_{\rm IC}$ at $P > 10$ kbar may be obtained by extrapolating the results from $P < 10$ kbar. This gives the straight line denoted as $\sigma_{\rm IC}$ in Fig. 2. In the next section $\sigma_{\rm C}$ at $P = 0$ will be shown to be smaller than $\sigma_{\rm IC}(P = 0)$ by a factor of 1.4. At the minimum, at $P = 18$ kbar, the measured conductivity is associated with $\sigma_{\rm C}$. Therefore, we may use the straight line passing through $\sigma_{\rm C}(0)$ and $\sigma_{\rm C}(18)$ to estimate the pressure dependence of $\sigma_{\rm C}$.

The two parallel lines in Fig. 2 correspond, roughly, to the thermal smearing width discussed above. Our interpretation is that the measured[20] conductivity as a function of pressure undergoes a transition from $\sigma_{\rm IC}(P)$ to $\sigma_{\rm C}(P)$ over the region of thermal smearing.

VIII. DIFFERENCE BETWEEN TTF-TCNQ AND TSF-TCNQ

It was found[21] that the change in conductivity for TSF-TCNQ in the commensurate phase is much smaller than for TTF-TCNQ. This is somewhat surprising since both compounds become $\frac{2}{3}$ commensurate under pressure. Moreover, the transport and structural properties of these compounds are essentially the same. Although no "$4k_F$" reflection has been observed in TSF-TCNQ, we may assume that "$4k_F$" reflections are absent in both compounds at commensurability, since the $4k_F$ reflection is believed[38] to disappear under pressure in TTF-TCNQ.

We now attempt to account for the difference between these compounds within the framework of the present theory. Since the quenching mechanisms proposed here should apply equally for both compounds, we believe that the experimental difference is a quantitative effect and not a qualitative one. For TSF-TCNQ, the linear electron-phonon term ρ_1, which contributes only in the commensurate phase, is small compared to the quadratic term. An important difference between TTF-TCNQ and TSF-TCNQ is the pressure at which commensurability is achieved. For TTF-TCNQ a pressure of 19 kbar is needed, whereas for TSF-TCNQ, only a few kbars are needed for commensurability since Z is already close to commensurate. The fractional change in the resisitivity $\rho_1/\rho_{\rm IC}$ *increases* with pressure. From irradition experiments,[17] Kaveh *et al.*[28] obtained $(\rho_1/\rho_{\rm IC})_{P=0} \simeq 0.3$ for TTF-TCNQ. This estimate was consistent with the value derived[28,33] from the Hopfield[37] expression for ρ_1 ($P = 0$), using

$\lambda = 0.2$ for the electron-phonon coupling constant deduced from T_P.

We obtain the pressure dependence of ρ_1 from estimates[39-42] of the pressure dependence of the phonon frequency ω, using $\rho_1 \propto \omega^{-2}$. This yields $(\rho_1/\rho_{IC})_{P=19}/(\rho_1/\rho_{IC})_{P=0} \simeq 2$. Therefore, $\rho_1(P=19) \simeq \rho_{IC}(P=19)$, in agreement with the experiment[20] which indicates that ρ_C is higher than ρ_{IC} by a factor of 2. Therefore, the pressure at which commensurability is achieved is important. The fact that $\Delta\sigma$ is larger when the commensurate pressure is larger is thus seen to account for the difference in behavior between TTF-TCNQ and TSF-TCNQ. We take this as a support for the dominance of σ_{2k_F} over σ_{CDW} in explaining the difference in conduction between the commensurate and incommensurate phase.

IX. SUMMARY

An analysis has been presented of the affect of commensurability on the various contributions to the conductivity. It is shown that $2k_F$ phonon drag accounts for the following commensurability features: (i) the difference $\Delta\sigma$ between the conductivities in the incommensurate phase, (ii) the temperature dependence of $\Delta\sigma$, (iii) the pressure dependence of $\Delta\sigma$, which leads to a difference in the effect for TSF-TCNQ relative to TTF-TCNQ, (iv) the commensurability width, and (v) the difference in the effect of commensurability on the conductivity perpendicular to the chains and along the chains. Thus, we have demonstrated that σ_{2k_F} may by *itself* account for *all* the experimental observation. The correlation between σ_{2k_F} and σ_{CDW} was discussed. In particular, we have shown that the various contributions to σ can be classified as either low-temperature contributions or as high-temperature contributions. Both σ_{2k_F} and σ_{CDW} are shown to be low-temperature contributions. The irradiation dependence and frequency dependence of σ at room temperature are accounted for by σ_L, which contributes even at high temperatures. Finally, we have shown that σ_L does not depend on commensurability.

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