Comment on fluctuation paraconductivity in quasi-one-dimensional systems*

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The results of Allender, Bray, and Bardeen for the paraconductivity above the Peierls transition in a one-dimensional system are modified to include the effects of high-frequency (optical) phonons and interchain coupling. A very good agreement with experiment on tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ) is thus obtained. In particular, it is shown that a mean-field theory based on low-frequency (acoustic) phonons is not consistent with the observed increase and temperature behavior of the conductivity above T_p, while high-frequency phonons ($\omega_{2p_F} \gg T$) fully account for the observed conductivity in the range $T_p \lesssim T \lesssim 2T_p$.

Allender, Bray, and Bardeen[1] (to be referred to as ABB) examined the effect of fluctuations into the Peierls-Fröhlich distorted state on the conductivity of a one-dimensional metal at temperatures above T_p. They applied their calculation to the tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ) crystal and found an enhancement in the conductivity just above T_p, which is in reasonable agreement with typical experimental values.[2-4] They also found a temperature dependence $\sigma(T) \propto (T - T_p)^{-1/2}$, which generally does not agree with experiment. The ABB calculation assumes that the Peierls transition in TTF-TCNQ is driven by acoustical phonons with an unperturbed frequency of $\omega_{2p_F} \simeq 90$ °K. It was suggested independently[5,6] that this transition is rather caused by the interaction of electrons with the propagating intramolecular C≡N bond vibration with a much higher frequency ($\omega_{2p_F} \simeq 2100$ cm^{-1}). It will be shown that the results of the ABB model change considerably when the low-frequency phonons ($\omega_{2p_F} \simeq T_p$) are replaced by high-frequency phonons ($\omega_{2p_F} \gg T_p$).

A second point is that ABB assumed that the observed transition temperature is close to the mean-field T_p. Thereby, they implicitly assumed a sufficiently large interchain coupling which suppresses the thermodynamic fluctuations. We incorporate the interchain coupling into the calculation explicitly and show that a mean-field calculation of the paraconductivity as proposed by ABB can agree with the experiment on TTF-TCNQ only when based on high-frequency phonons. Moreover, the agreement with experiment is in that case better than that obtained by ABB.

Let us start with the strictly one-dimensional calculation of ABB. The fluctuation conductivity is given by Eq. (5.1) of ABB

$$\sigma = \sum_q n_{sq} e^2 \tau / m^*, \tag{1}$$

where τ is the relaxation time of the "superfluid" electrons, m^* is their effective mass, and the "superfluid" charge density n_{sq} is related to the fluctuating gap by

$$n_{sq} = n\langle \Delta_q^2 \rangle 7\zeta(3)/4\pi^2 T^2. \tag{2}$$

In the phenomenological model of ABB, the electrons are assumed to relax rapidly to the propagating lattice waves, and the decay time τ is then equal to the lifetime of the lattice waves, namely,

$$2\tau = -(\mathrm{Im}\,\omega')^{-1}, \tag{3}$$

where ω' is the pole of the phonon propagator $D(2p_F, \omega)$, which for low ω is

$$[D(2p_F, \omega)]^{-1} = -\lambda \left[\frac{-\omega^2}{\lambda \omega_{2p_F}^2} + \ln\left(\frac{T}{T_p}\right) - \frac{i\pi\omega}{8T} + \frac{7\zeta(3)\omega^2}{16\pi^2 T^2} \right]. \tag{4}$$

Assuming $\omega_{2p_F} \simeq T_p$, ABB neglect the last term in the brackets and find $\tau = \pi/16 T_p \epsilon$ for $\epsilon < 0.01$, where $\epsilon \equiv \ln(T/T_p) \simeq (T - T_p)/T_p$, while for the temperature range of interest, $\epsilon > 0.01$, they get a temperature independent τ. If, however, $\omega_{2p_F} \gg T_p$, we can neglect the first term in the brackets of Eq. (4), and obtain

$$\frac{\omega'}{T} = -i \frac{16\epsilon_0}{\pi} \left\{ \left[\frac{1}{\epsilon_0} \ln\left(\frac{T}{T_p}\right) + 1 \right]^{1/2} - 1 \right\}, \tag{5}$$

where $\epsilon_0 = \pi^4/16 \times 7\zeta(3) \simeq 0.8$. Thus, we get

$$\tau = \pi/16 T\epsilon, \quad \epsilon < 0.8, \tag{6}$$

which is exactly the result of ABB just above T_p. However, in our case, this behavior of τ holds over a much wider temperature range. From Eq. (5) we find that the temperature dependence of τ varies gradually from ϵ^{-1} for $\epsilon < 0.8$ to $\epsilon^{-1/2}$ for $\epsilon \gg 0.8$. Actually, the results for $\epsilon > 1$ are not accurate, because then the expansion in Eq. (4) is inadequate, and one has to solve numerically for the poles of $D(2p_F, \omega)$ in the complex ω plane, as was done in Ref. 7.

The temperature dependence of σ for the acous-

tic phonons is determined by that of the fluctuating gap, which is [from Eq. (5.7) of ABB],

$$\sum_q \langle \Delta_q^2 \rangle \propto \epsilon^{-1/2}. \tag{7}$$

For the high-frequency phonons, we would thus get $\sigma(T) \propto \epsilon^{-3/2}$ for $\epsilon < 0.8$ changing to ϵ^{-1} for $\epsilon > 0.8$. This should be compared to $\epsilon^{-1/2}$ for $\epsilon > 0.01$, obtained by ABB. These conclusions, however, depend on the validity of Eq. (7). To examine the temperature range in which this equation is valid we have to take into account the interchain coupling.

Interchain coupling is necessary if one wants to get a real phase transition and, in fact, it has to be rather large if mean-field theory is to be applicable. We adopt a model in which the interchain coupling is represented by an anisotropic electron dispersion of the form

$$\epsilon(p) = \epsilon(p_z) + \eta\epsilon_F(\cos ap_x + \cos ap_y), \tag{8}$$

where a is the distance between two chains. The details of this model are described elsewhere.[8] Here we quote only the pertinent results. The phonon associated with the Peierls transition has a momentum $q = (\pi/a,\ \pi/a,\ 2p_F)$. As η increases, the mean-field-transition temperature is almost independent of η up to very close to $\eta_c \simeq 3(T_p^0/T_F)^{1/2}$, where T_p^0 is the result for $\eta = 0$, and then it rapidly drops to zero at η_c. The value of η_c depends on the nature of $\epsilon(p_z)$, and the result quoted above is obtained for a free-electron dispersion along the chain. There is a characteristic temperature

$$T_0 = \eta T_F/\sqrt{8}\ , \tag{9}$$

which plays an important role in the model. At this temperature, the inverse transversal correlation length $(\xi^0)^{-1}$ crosses the Brillouin-zone boundary. If the mean-field T_p happens to be smaller than T_0, then thermodynamic fluctuations will have a small effect, suppressing the actual transition temperature by at most 20%. In this case, mean-field theory makes a reasonable approximation. If, however, the mean-field T_p exceeds T_0, we expect large fluctuations and mean-field theory is then invalid. For the fluctuating gap above T_p one gets

$$\sum_q \langle \Delta_q^2 \rangle = 4\pi^2 \left(\frac{T^2}{\eta T_F}\right)^2 \left[1 - \left(\frac{\epsilon}{2}\right)^{1/2} \tan^{-1}\left(\frac{2}{\epsilon}\right)^{1/2}\right] \tag{10}$$

for $T < T_0$, and

$$\sum_q \langle \Delta_q^2 \rangle = 4\pi^2 \left(\frac{T^2}{\eta T_F}\right)^2 \left\{\left[\epsilon + \frac{1}{\pi}\left(\frac{\eta T_F}{T}\right)^2\right]^{1/2} - \epsilon^{1/2}\right\} \tag{11}$$

for $T > T_0$. This last equation defines another characteristic temperature $T_1 > T_0$, given by

$$\epsilon_1 \equiv \ln(T_1/T_p) = (1/\pi)(\eta T_F/T_1)^2. \tag{12}$$

For $T > T_1$ one obtains the one-dimensional result of Eq. (7), $\sum \langle \Delta^2 \rangle \propto \epsilon^{-1/2}$, while for $T < T_1$, the interchain coupling dominates, yielding a convergent behavior of $\sum \langle \Delta_q^2 \rangle$.

Let us now discuss TTF-TCNQ, and let us assume that the observed transition temperature $T_p/T_F \simeq 0.02$ is close to its mean-field value. This implies from Eq. (9) that $\eta \lesssim 0.075$. The value of η is crucial for the behavior of the system. If η is small, say $\eta = 0.01$, then T_1 from Eq. (12) is very close to T_p, and the one-dimensional behavior of Eq. (7) persists down to the neighborhood of T_p. In this case, however, the actual three-dimensional-transition temperature T_{3d} is significantly depressed and comparison of mean-field calculation with experimental results slightly above T_{3d} is meaningless. It is possible that this is the case, but we believe that a mean-field theory with $\eta \simeq 0.1$ is consistent with all the experiments on TTF-TCNQ.

One estimate of η can be obtained from the analysis of the conductivity anisotropy by Khana *et al.*[9] Although these authors claim that the interchain motion of the electrons is diffusive, nevertheless their results [in particular, Fig. 15 and Eq. (21)] give an estimate of the overlap integral between two chains, which implies $\eta = 0.07$. This is close to the value assumed here, but significantly larger than the value $\eta = 0.015$ proposed by Berlinsky *et al.*[10] on the grounds of molecular-orbital calculations. It is shown in Ref. 8 that the effective value of η which appears in Eqs. (9)–(11) includes also contributions from other interchain coupling mechanisms like the Coulomb interaction and the anisotropy in the phonon spectrum, and thus may be larger than that implied by the curvature of the Fermi surface alone. For $\eta \simeq 0.1$, $T_0 \simeq 100$ °K and $T_1 \simeq 105$ °K. Note that the interchain coupling does not affect the temperature behavior of the relaxation time τ. In view of Eqs. (1), (2), and (10), a mean-field theory based on acoustic phonons, for which τ does not depend on ϵ, implies that the fluctuation conductivity does not depend on ϵ over a wide temperature range above T_p. This is clearly inconsistent with experiment. For high-frequency phonons $\tau \propto \epsilon^{-1}$ for $\epsilon < 0.8$, and using the same parameters as ABB, we obtain from Eqs. (1), (2), and (10), close to T_p

$$\sigma(T) \simeq 10^3 T/\eta^2 T_F \epsilon \text{ mho/cm}\ . \tag{13}$$

For $T_p = 55$ °K, $\eta = 0.1$ and $\sigma_{RT} = 1000$ mho/cm, we get $\sigma(65\ °)/\sigma_{RT} \simeq 15$, which is consistent with typical experiments.[2-4]

As for the temperature dependence, we find from Eqs. (2), (10), and (11) that n_s varies between $0.4n$ to $0.75n$ over the temperature interval $55 \lesssim T \lesssim 150$ °K, and it is a reasonable approximation to regard it as a constant, equal to $\frac{1}{2}n$. We should point out here that the unusually large value

of n_s poses some difficulties, particularly with regard to the meaning of the Ginzburg criterion for the critical region. However, this is an inherent property of the present model, and we do not see how it can be avoided. This estimate is probably better than a factor of 2 over a temperature range in which $\sigma(T)$ changes by more than an order of magnitude. This assumption leads, on account of Eqs. (1) and (6), to the simple phenomenological formula

$$\sigma(T) \simeq \frac{\pi m e^2}{32 m^*} \frac{T_p}{T(T-T_p)} = \frac{\omega_p^2}{128} \frac{T_p}{T(T-T_p)}, \qquad (14)$$

where ω_p is the plasma frequency. The latter was found by Bright *et al.*[11] from optical reflectivity measurements. Using their value $\omega_p = 1.8 \times 10^{15}$ sec^{-1}, we get $\sigma(65\ ^\circ\text{K}) \simeq 1.7 \times 10^4$ mho/cm, which is close to the result obtained from Eq. (13). As long as T is not too high, the temperature dependence of σ is dominated by the $(T - T_p)$ in the denominator of Eq. (14), which is, in general, consistent with experiment. The results of Cohen *et al.*[2] can be fitted by a form $\sigma(T) \propto \epsilon^{-\gamma}$ with $\gamma = 1$ for $70 \lesssim T \lesssim 120\ ^\circ\text{K}$, as implied by Eq. (14). We should expect a critical region above T_p where Eq. (14) breaks down, so that it is not surprising that the $\sigma(T) \propto \epsilon^{-1}$ behavior starts only around 70 °K. The curves of Groff *et al.*,[4] on the other hand, do not fit so well a form like $\sigma(T) \propto \epsilon^{-\gamma}$, except for their sample with the highest σ/σ_{RT} ratio, for which $\gamma \simeq 1$ gives a reasonably good fit for $80 \lesssim T \lesssim 120\ ^\circ\text{K}$. Equation (14) indicates a transition to a $\sigma(T) \propto T^{-2}$ behavior at higher temperatures, which is consistent with experiment,[12] however a theory of this type cannot be trusted for $\epsilon > 1$, even if other scattering processes are neglected.

One might wonder what role the acoustic phonons play in this model. It turns out that in the Fröhlich Hamiltonian the coupling, in the tight-binding approximation, between electrons and acoustic (intermolecular) phonons vanishes for a half-filled band. This follows from the fact that the linear contribution to this energy is proportional to $(u_{i+1} - u_i) + (u_i - u_{i-1})$, where u_i is the displacement of the ith molecule (only nearest neighbors are considered in the tight-binding limit) and this quantity vanishes when $q = 2p_F = \pi/a$. This no longer holds when the band is not exactly half-filled, when the momentum distribution is smeared out due to finite temperature, when interband matrix elements are considered, etc. Nevertheless, we may expect g_{2p_F} to be small for intermolecular phonons, as long as the deviation from a half- filled band is not too large. This argument clearly does not apply to intramolecular phonons. If the transition in TTF-TCNQ is indeed driven by intramolecular phonons, this would account for the failure to observe any distortion by x rays. Intramolecular phonons should give rise to a much smaller distortion ($u^2 \sim T_p^2 / E_F M \omega_{2p_F}^2$, where M is the reduced mass of the CN pair), than intermolecular phonons. For the latter, $M\omega_{2p_F}^2$ is by an order of magnitude smaller, and the scattering element (the whole molecule), by an order of magnitude bigger. This accounts, in part, for the great difference between TTF-TCNQ and KCP $[K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O]$ where no conductivity maximum is observed but there is a large Peierls distortion. In KCP the band is $\frac{5}{6}$ filled, and thus the coupling with acoustic phonons should be strong.

Regarding the intramolecular C≡N bond vibrations, there still remains the question of the strength of their coupling to the electrons. The assumption that the observed T_p is close to its mean-field value implies that $\lambda \simeq 0.18$. An independent estimate of this coupling constant may be obtained from the observed difference between the C≡N bond lengths in TCNQ and $TCNQ^-$, which is rather large—about 0.05 Å. This was done in Ref. 5, and it was shown there that λ is indeed of the order of 0.15 (in the notation of Ref. 5, $\lambda = s/2$). Actually, these intramolecular vibrations are quite localized and their dispersion relation is expected to be very flat. They are coupled from one molecule to the next via the electrons. It is due to their strong coupling to the electrons that these vibrations may support a collective excitation with a large coherence length.

There is one other characteristic difference between the low-frequency and the high-frequency phonons. ABB define a parameter m_L which is an effective mass associated with the lattice waves, and they find [Eq. (4.20) in ABB] that $m_L/m^* \gg 1$. However, when $\omega_{2p_F} \gg T_p$, we get from the same equation $m_L/m^* \ll 1$. The ratio m_L/m^* plays an important role in the justification of Eq. (1) in the ABB model (Sec. 5 of ABB), since it determines how the change in the crystal momentum, induced by an electric field, is divided between the electrons and the lattice waves. To justify Eq. (1), ABB assume that the lattice momentum is transferred to the electrons in a time much shorter than τ. If m_L/m^* is small, most of the crystal-momentum change goes immediately to the electrons.

We should point out that alternative explanations for the temperature dependence of the conductivity in TTF-TCNQ exist: (a) Pairing-superconductivity fluctuations have been suggested.[2,5] (b) An exponential dependence of the form $\sigma \propto Te^{\Delta/T}$ with $\Delta \simeq 550\ ^\circ\text{K}$ was proposed,[12,13] based on the assumption of a mean-field value of $T_p = 550\ ^\circ\text{K}$ with very strong fluctuations in the investigated temperature range. (c) A resistivity of the form $\rho = \rho_0 + \rho_1 T^2$, possibly due to electron-electron or electron-hole scattering has been suggested.[12,14] (d) A conduc-

tivity dependence $\sigma(T) \propto T^{-2.33\pm0.14}$ was proposed[4] for $60 \leq T \leq 300$ °K.

In the last two models, the increase in the conductivity is not related to the Peierls transition at $T_p = 55$ °K, and it is just interrupted by it. All these entirely different models are consistent with experiment at ambient pressure. However, the pressure dependence of the resistivity[6,15] being strong at 300 °K and weak at 65 °K seems to exclude (b). The exponential factor in (b) is about e^8 at 65 °K and is thus extremely sensitive to changes of T_p with pressure. On the other hand, a power law $\sigma(T) \propto \epsilon^{-\gamma}$ is expected to give a weak-pressure dependence (if T_p depends weakly on pressure), in agreement with experiment.[6,15]

In conclusion, we have shown that the mean-field treatment of the fluctuation conductivity proposed by ABB is consistent with experiments on TTF-TCNQ if one assumes an interchain coupling of $\eta \simeq 0.1$ and if the Peierls-Fröhlich transition is driven by high-frequency phonons.

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