Temperature dependence of the dc electrical conductivity in low-dimensional metals with strong Kohn anomalies

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The temperature dependence of the dc electrical conductivity $\sigma(T)$ of synthetic metals susceptible to strong Kohn effects is studied by a Kubo-Mori projector scheme in a single-particle approximation. The exponent n in a T^{-n} law of $\sigma(T)$ is reduced with decreasing anisotropy in systems where Fermi-surface nesting is not possible. Nesting also conserves a T^{-2} behavior of $\sigma(T)$ for small anisotropy ratios. Calculated $\sigma(T)$ curves of characteristic synthetic metals are discussed.

The unusual temperature dependence of the dc electrical conductivity in low-dimensional synthetic metals is still a mystery. On the one side this situation is caused by a lack of quantitative theoretical approaches that go beyond phenomenological descriptions. On the other side there also exists a deficit in the evaluation and classification of available experimental measurements. It has been an almost universal trend to assume that the $\sigma(T)$ curves in the synthetic metals follow throughout a T^{-2} law of decay. Such an interpretation is, however, an oversimplification. In Fig. 1 the exponent n in a T^{-n} law of σ is displayed as a function of the room-temperature anisotropy ratio $\sigma_{\parallel}/\sigma_{\perp}$ in the electrical conductivity.[1] $\parallel$ labels the principal axis and $\perp$ the plane perpendicular to $\parallel$. To evaluate the diagram more than 30 synthetic metals have been taken into account. The adopted systems cover all characterized families of highly conducting organic charge-transfer (CT) salts and organometallic representatives. The exponent n has been determined via least-squares fits to the experimental conductivity curves on the basis of a T^{-n} formula for temperatures T larger than the metal-insulator phase transition.

In region 1 n increases linearly with the conductivity anisotropy and reaches a value slightly above 2 in the quasi-one-dimensional (1D) limit. Typical systems belonging to the latter boundary are the different TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane) CT salts.[2] On the extreme left a T^{-2} shape of σ is indicated which is coupled to rather small $\sigma_{\parallel}/\sigma_{\perp}$ ratios. This behavior is found in 2:1 donor-acceptor (DA) systems with an integral CT between both subunits. The respective charge distribution between D and A guarantees the presence of particle-hole symmetry on the Fermi surface of a folded Brillouin zone in the corresponding solids. The topologic prerequisites for the development of a (giant) Kohn anomaly on a nonplanar Fermi surface are thus given for these systems.[3] The potential seen by a phonon with wave vector $(\pi/a,\pi/b,2k_F)$ is effectively flat;[4] a and b are lattice constants and $2k_F$ is twice the Fermi momentum in the principal direction. Experimental investigations of $D_2^+A^-$ or $D^+A_2^-$ metals indeed have shown that the corresponding systems are almost unstable. The formation of a zero-frequency mode leading to an insulating Peierls state[5] is only scarcely suppressed.[6-9] Characterized synthetic metals of this class of low-dimensional solids, e.g., are $(TMTSF)_2X$ (Ref. 6) (tetramethylenetetraselenofulvalene), $(2Y,5Z\text{-}DCNQI)_2Cu$ (Ref. 8), (N,N'-dicyanoquinodiimine) or $(BEDT\text{-}TTF)_2X$ (Refs. 7 and 9) [bis(ethylenedithiolo)tetrathiafulvalene] CT salts with monovalent acceptors X^-. Y and Z are substituents in the organic ring system. The $\sigma_{\parallel}/\sigma_{\perp}$ ratios measured in these compounds are smaller than ~ 20; i.e., the corresponding synthetic metals are far from being quasi-one-dimensional.

It is a challenge of any reliable transport theory to reproduce the T^{-n} dependence of σ schematized in Fig. 1. As the most important result, the display indicates that there must be a functional dependence between the presence of a (giant) Kohn anomaly and an exponent n of

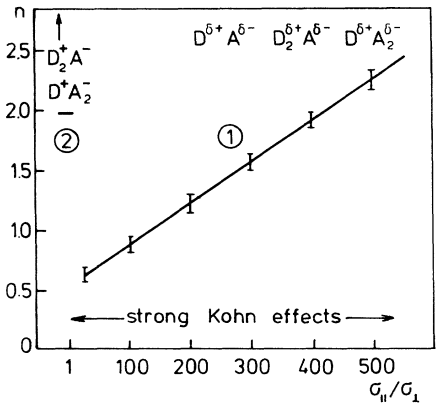

FIG. 1. Schematic display of the exponent n in a T^{-n} law of decay of the electrical conductivity σ as a function of the room-temperature anisotropy $\sigma_{\parallel}/\sigma_{\perp}$ in low-dimensional synthetic metals. In region 1, n increases linearly with $\sigma_{\parallel}/\sigma_{\perp}$. In region 2, an exponent $n \approx 2$ is realized although the $\sigma_{\parallel}/\sigma_{\perp}$ ratios are small. This T^{-n} dependence of $\sigma(T)$ is found in 2:1 donor (D)–acceptor (A) compounds with an integral charge transfer. Possible D-A compositions of the synthetic metals of class 1 are indicated on the top of the figure; $\delta \neq 1.0$. The experimental error bars are indicated by vertical lines.

~ 2 in a T^{-n} law of σ. In the present contribution the temperature dependence of σ in low-dimensional synthetic metals with remarkable Kohn anomalies is studied by an *ab initio* single-particle theory for one-phonon–one-electron (1ph-1*e*) scattering processes. Subsequently it is shown that this approximation is sufficient in metals with effectively flat Fermi surfaces; the latter lead to a strong "phase-space" control on $\sigma(T)$. The influence of other possible scattering processes is thereby attenuated. Impurity scattering, e.g., has been neglected. The associated temperature-independent resistivity is decisive only for temperatures below the metal-insulator transition.[10] A simple Fröhlich Hamiltonian[11] has been employed for the coupled electron-phonon system. The relaxation time τ for 1ph-1*e* scattering events is evaluated by a Kubo-Mori projector approach.[12,13] The influence of the Kohn anomaly on the relaxation time is explicitly taken into account in the theoretical approach. A first phenomenological single-particle theory showing the formation of high conductivity peaks in metals susceptible to Kohn anomalies has been formulated by Kaveh.[14] Simplified analytic boundary expressions for σ in a Kubo-Mori scheme have been derived previously.[15] Although the influence of a Kohn anomaly has been assigned in this work only a high-temperature expression for $\sigma(T)$ has been discussed explicitly; shifts in the phonon frequency ω_q due to mode softening have been neglected. This simplification unfortunately prevented quantitative comparisons with experimental $\sigma(T)$ curves. Comprehensive numerical calculations of $\sigma(T)/\sigma(298\ \mathrm{K})$ curves of quasi-1D metals with larger $\sigma_{\parallel}/\sigma_{\perp}$ ratios have been reported in Ref. 1. The validity of a single-particle theory for the electrical conductivity has been confirmed in a recent study[16] where it has been shown that the charge fluctuations $\langle(\Delta n_i^2)\rangle$ in the aforementioned low-dimensional metals are "free-electron"-like. The on-site densities in the above materials guarantee the coexistence of stronger electronic correlations and remarkable free-electron-like charge fluctuations even in the localized limit.[17] As a result of the on-site densities in the highly conducting metals the $\langle(\Delta n_i^2)\rangle$ are of an extreme character.

In this work the normalized conductivities $\sigma(T)/\sigma(298\ \mathrm{K})$ of TTF-TCNQ,[18] $(2,5CH_3\text{-}DCNQI)_2Cu$,[19] and β-$(BEDT\text{-}TTF)_2I_3$,[20] respectively, are calculated in a single-particle theory for 1ph-1*e* scattering processes based on a Kubo-Mori projector scheme. The room-temperature $\sigma_{\parallel}/\sigma_{\perp}$ ratio in the TTF-TCNQ CT salt amounts to ~ 500; this number is reduced to ~ 10 and even to 2–3 in the two 2:1 salts of $D^+A_2^-$ and $D_2^+A^-$ stoichiometry.[16] A Peierls transition[5] at ~ 54 K (Ref. 18) has been observed in the quasi-1D TTF-TCNQ system. In the two other CT salts the characteristic lattice modes are only softened, but remain finite also at lowest temperatures.

The electrical conductivity $\sigma(\beta)$ is expressed in Eq. (1) in terms of the relaxation time $\tau(\beta)$ for 1ph-1*e* processes. β stands for $1/k_BT$, with k_B the Boltzmann constant and T the temperature:

$$\sigma(\beta)=(\beta/v_S)C(\beta)\tau(\beta)\ . \tag{1}$$

v_S symbolizes the sound velocity and $C(\beta)$ the scalar product (2) defined for the operator $I(\beta)$ of the electrical current:

$$C(\beta)=\langle I(0)|I(\beta)\rangle\ . \tag{2}$$

The effective flatness of the Fermi surface, which can be either planar or also nonplanar in $D_2^+A^-$ or $D^+A_2^-$ systems, leads to simplifications in the evaluation of the relaxation time $\tau(\beta)$, as only the autocorrelation of the electrical current has to be taken into account.

In (3) the inverse relaxation time $1/\tau(\beta)$ is given for metals, where strong Kohn effects develop with decreasing temperatures:

$$1/\tau(\beta)=C(\beta)^{-1}\int_0^{\infty}dz\,\langle iL_1I(0)|\exp[iz(L_0+L_1-PL_1)]iL_1I(0)\rangle\ . \tag{3}$$

In this expression the Liouville operator L has been decomposed into a zeroth-order term L_0 associated with the unperturbed electron and phonon parts and the electron-phonon coupling element L_1. P is the projector onto the electrical current at time $t=0$. One key element in the evaluation of Eq. (3) is the explicit consideration of the Kohn anomaly leading to a characteristic shift in the temperature dependence of $\sigma(T)$ from a T^{-1} behavior to a T^{-2} one. By adopting equation-of-motion methods for the electronic and phononic Hamiltonian and inserting the respective thermal expectation values, one derives Eq. (4) for

$$\frac{1}{\tau(\beta)}=\frac{\pi^2e^2}{2m\hbar^2C(\beta)}\int_0^{q_D}\frac{N(-k_0)D(q)|G(q)|^2\exp[\beta\alpha(k_0^2-k_F^2)]q^2K(q,\beta)}{\{1+\exp[\beta\alpha(k_0^2-k_F^2)]\}\{1+\exp[\beta\alpha(-k_0^2-k_F^2)]\}[\exp(\beta\hbar\omega_q)-1]}dq\ . \tag{4}$$

The integration over the phonon wave vector q is from $q=0$ to the Debye vector q_D. $N(-k_0)$ is the electronic density of states and $D(q)$ the phonon one. $G(q)$ stands for an electron-phonon term that contains the dimensionless electron-phonon coupling constant λ. α abbreviates $\hbar/2m$ with m the electron mass; e in Eq. (4) is the electron charge. $K(q,\beta)$ modulates the inverse relaxation time as a function of the phonon-frequency shift accompanying the mode softening. ω_q is the bare frequency and $\hat{\omega}_q$ the softened one. $K(q,\beta)$ is given in Eq. (5):

$$\begin{aligned}K(q,\beta)=&\left[1-\frac{\omega_q}{\hat{\omega}_q}\right]^2[\exp(\beta\hbar\omega_q)+\exp(-\beta\hbar\hat{\omega}_q)]+\left[1+\frac{\omega_q}{\hat{\omega}_q}\right]^2\{1+\exp[\beta\hbar(\omega_q-\hat{\omega}_q)]\}\\&+\left[1-\left[\frac{\omega_q}{\hat{\omega}_q}\right]^2\right][1+\exp(\beta\hbar\omega_q)][1+\exp(-\beta\hbar\hat{\omega}_q)]\frac{\sinh(\beta\hbar\hat{\omega}_q)}{\beta\hbar\hat{\omega}_q}\ .\end{aligned} \tag{5}$$

Vanishing frequency shifts gradually reduce the value of the exponent n in the T^{-n} law for $\sigma(T)$. The parameter k_0 in (4) abbreviates to

$$\pm k_0 = \frac{\alpha q^2 \pm \hbar\omega_q}{2\alpha q} . \tag{6}$$

A Romberg integration has been adopted in the numerical integration of Eq. (4). For the numerical solution the following material constants are necessary: Debye temperature Θ_D, electron-phonon coupling constant λ, width of the conduction band $\Delta\varepsilon$, and the Fermi momentum k_F. The subsequent experimental data have been adopted for the three selected synthetic metals. $\Theta_D = 97, 109, 109$ K; $\lambda = 0.208, 0.138, 0.110$; and $\Delta\varepsilon = 0.5, 1.0, 0.5$ eV. The numbers refer to the above-given sequence of the three model systems. In (7) the pendant to (3) is given for metallic systems with negligible frequency shifts of phonon modes:

$$1/\tilde{\tau}(\beta) = C(\beta)^{-1} \int_0^\infty dz \langle iL_1 I(0) | \exp(izL_0) iL_1 I(0) \rangle . \tag{7}$$

The exponent in (7) is simplified in comparison to (3). Straightforward evaluation of $\tilde{\tau}(\beta)$ gives the approximate proportionality (8) for the dc electrical conductivity in metals with vanishing mode softening:

$$\tilde{\sigma}(\beta) \sim e^{\Theta_D/T} - 1 . \tag{8}$$

In the lowest order of approximation this expression can be expanded to a "conventional" T^{-1} law for $\sigma(T)$. Comparison of the above equations thus shows a continuous transition from a T^{-2} law of σ in metals with remarkable Kohn effects to a T^{-1} behavior in metals where "three dimensionality" prevents stronger frequency shifts. $K(q,\beta)$ in Eq. (5) modulates between the two marginal limits T^{-2} and T^{-1}, respectively. The one-dimensional Kohn anomaly is smeared with a width proportional to the anisotropy ratio $\sqrt{\sigma_\perp/\sigma_\parallel}$. The above 2:1 CT salts with integral CT are an exception, which is caused by particle-hole symmetry on the Fermi surface. Simple interpolation formulas for n as a function of Θ_D and λ can be derived from (3) in the perfect 1D limit:

$$n \approx 1.82 + 3.83 \times 10^{-3} \Theta_D, \quad n \approx 1.82 \lambda^{-0.0715} . \tag{9}$$

The above expressions show the essential T^{-2} dependence of σ in low-dimensional metals with strong Kohn effects. The value of n is controlled here by phase-space effects, i.e., the autocorrelation properties of the electrical current.

The present theory allows for an unambiguous explanation of the T^{-n} behavior schematized in Fig. 1. n values less than 1.0 encountered for very small $\sigma_\parallel/\sigma_\perp$ numbers have their origin in electronic correlations, which are neglected in the present single-particle theory. The influence of many-particle interactions on $\sigma(T)$ is thus retarding.[16] Vanishing mode softening leads then to n numbers less than 1.0.

In Fig. 2 the experimental and theoretically calculated normalized conductivity curves of TTF-TCNQ, $(2,5CH_3\text{-DCNQI})_2Cu$, and β-$(BEDT\text{-}TTF)_2I_3$, respectively, are compared. It is seen that the single-particle *ab initio* theory allows for an almost quantitative reproduction of the experimental $\sigma(T)/\sigma(298\text{ K})$ curves of synthetic metals, which are all susceptible to strong Kohn effects. The experimental $\sigma(T)$ curvature is reproduced with good accuracy in the whole investigated temperature range.

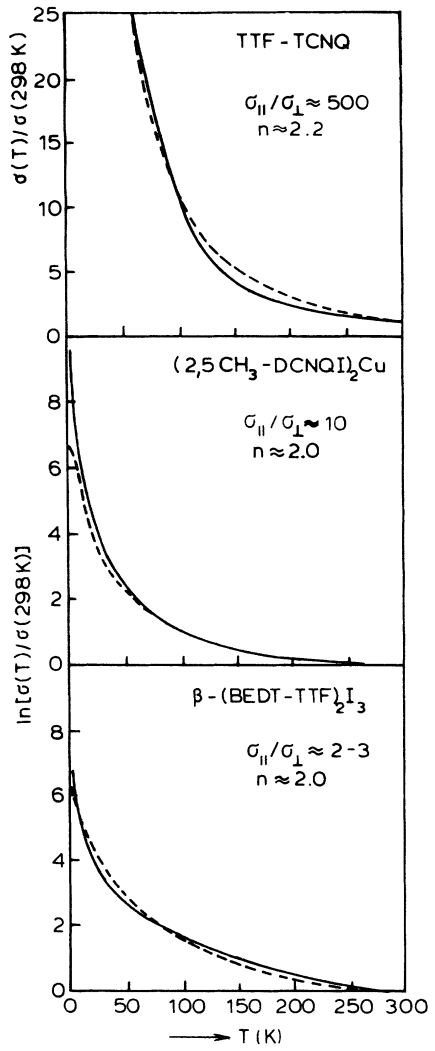

FIG. 2. Normalized conductivity curves of TTF-TCNQ, $(2,5CH_3\text{-DCNQI})_2Cu$, and $(BEDT\text{-}TTF)_2I_3$. Logarithmic scales have been employed in the two lower $\sigma(T)/\sigma(298\text{ K})$ diagrams. The experimental curves (dashed lines) have been adopted from Refs. 18–20. The theoretical results have been represented by solid curves. For convenience we have summarized in the figure the room-temperature anisotropies $\sigma_\parallel/\sigma_\perp$ and the calculated value of the exponent n.

In summary it has been demonstrated that the temperature dependence of the dc electrical conductivity of many synthetic metals can be reproduced with a high degree of accuracy by a single-particle *ab initio* theory based on 1ph-1*e* scattering events. A strong Kohn effect shifts the T dependence of $\sigma(T)$ from the conventional T^{-1} behavior in three-dimensional metals to a T^{-2} law of decay. In metallic systems where Fermi-surface nest-

ing is not possible, the exponent n is reduced with decreasing "three dimensionality." The T^{-2} law of $\sigma(T)$ is conserved in low-dimensional solids, where particle-hole symmetry on the Fermi surface allows for the development of soft modes on nonplanar Fermi surfaces.

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