

ON THE ELECTRON-ELECTRON INTERACTION AS THE SOURCE OF THE
METALLIC RESISTIVITY IN TTF-TCNQ

P. E. Seiden
IBM Thomas J. Watson Research Center
Yorktown Heights, New York 10598

and

P. M. Grant
IBM Research Laboratory
San Jose, California 95193

ABSTRACT

The source of the metallic resistivity in TTF-TCNQ and related compounds has been a subject of much interest and dispute. Many candidates have been suggested but few have been considered extensively. In this contribution we will consider in detail the possibility that the electron-electron interaction is responsible for the resistivity in these compounds.

We have developed a simple relation for the resistivity due to electron-electron scattering based on one-dimensional tight-binding bands along with a three-dimensional treatment of the more isotropic Coulomb scattering potential. The relation includes the temperature and pressure dependence of the lattice parameters, the bandwidths and the charge transfer. The result is an expression for the resistivity that accounts well for both its temperature and pressure dependence as well as for the contribution of the scattering term to the thermopower.

We have also considered the origin of the temperature independent part of the optical resistivity. We show that the observed magnitude can readily arise from electron-molecular vibration interactions.

INTRODUCTION

The source of the resistivity in quasi-one dimensional organic conductors has been a question of much concern for the last few years. The debate is two-fold; firstly, there is a question as to whether the resistivity arises from independent particle scattering or from the existence of a collective mode. Secondly, there is the question of exactly what interaction is involved. As far as the first question is concerned we feel that the evidence is now overwhelmingly in favor of the independent particle picture¹⁻³, although to be sure, some questions remain. In any event, for the purpose of this paper we will assume an independent particle point of view. There have been a number of suggestions put forth to answer the second question. The mechanisms proposed include, electron-phonon⁴, electron-libron⁵, electron-spin wave⁶, and electron-electron³ scattering. For the most part, however, the details and consequences of these mechanisms are just beginning to be worked out. In this paper we will concentrate on the electron-electron interaction with a view to testing its applicability by a careful comparison with the available data. We will also focus on the compound tetrathiafulvalenium-tetracyanoquinodimethanide (TTF-TCNQ) since it has been most extensively investigated so that more data exists for it than for other materials. Although we emphasize the importance of the electron-electron interaction, we do propose that part of the optical resistivity is due to a phonon emission process and will, therefore, also explicitly discuss this process.

ELECTRON-ELECTRON MODEL

The model we will discuss here is a hybrid description of the conduction process in TTF-TCNQ which we hope will be adequate to delineate the functional dependencies of the resistivity on experimental variables such as temperature and pressure. We begin by assuming a two-band, one-dimensional tight-binding model for the conduction bands, which has been shown to give a good representation of the band properties of the system⁷. The electron energy is given by

$$E = B/2 \cos kb \quad (1)$$

"On the Electron-Electron Interaction as the Source of the Metallic Resistivity in TTF-TCNQ," P. E. Seiden and P. M. Grant, Lecture Notes in Physics, Vol. 95, Quasi One-Dimensional Conductors I, (Springer-Verlag, Berlin, 1979), p. 130. (Dubrovnik, 1978)

where k is the electron wave direction.

For the scattering p dimensional representation of the overlap of the electronic directions. The electron-electron Coulomb potential. The band one-dimension this depends that the electron-electron distance roughly quarter filled bands scattering is three-dimensional and assume the same three-dimensional. The electron-electron

where k_f and E_f are the Fermi electron-electron scattering cross section electron scattering cross section who found the important resonance electron scattering over a large equal to two. Therefore, we factor.

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where $a = k_s/2k_f$ and k_s is the

where α is the charge transfer conductivity will then be a function of TCNQ. The main factors to transfer ($\alpha^3 \sin^4 \pi\alpha/2$). It is the deviation of the temperature

The pressure dependence of the charge transfer, but including the pressure dependence is accounted for.

We do not know the pressure dependence of the diffuse X-ray scattering experiment. The interpretation of this line can derive from it the temperature 60 K to 0.55 at 300 K, but the dependence in Eq. (4). We conclude the variation is due to the charge transfer for a lattice that is the range of the temperature result of Eq. (4) including the

where k is the electron wave vector, B the bandwidth, and b the lattice parameter along the conducting direction.

For the scattering process, however, we cannot use a one-dimensional representation. The one-dimensional representation for the band parameters is adequate because the bands are primarily determined by the overlap of the electronic wave functions which is much greater along the stacks than in the perpendicular directions. The electron-electron scattering process, however, is dominated by the more slowly varying Coulomb potential. The bare Coulomb field drops off as $1/r$ and since screening is much less effective in one-dimension this dependence is not strongly affected. The intermolecular spacings in TTF-TCNQ are such that the electron-electron distances between the stacks are of the same order as along the stack (for the roughly quarter filled bands) so that fully three-dimensional scattering is important. Even though the scattering is three-dimensional it will certainly be anisotropic. However, we will ignore the anisotropy here and assume the same three-dimensional isotropic scattering used for normal metals.

The electron-electron contribution to the conductivity is given by⁸

$$\sigma = \frac{e^2}{\hbar} \frac{1}{k_f \sigma_f} \left(\frac{E_f}{k_B T} \right)^2 \quad (2)$$

where k_f and E_f are the Fermi wave vector and energy respectively, T is the temperature, and σ_f is the electron-electron scattering cross section for electrons at the Fermi surface. We will calculate the electron-electron scattering cross section in the Born approximation. This has been justified by Kukkonen and Smith⁹ who found the important result that the Born approximation gives an excellent representation of electron-electron scattering over a large range of electron densities to within a multiplicative constant approximately equal to two. Therefore, we will use the Born approximation multiplied by the Kukkonen-Smith correction factor.

$$\sigma_f = \frac{\pi e^2}{16} \frac{Q}{E_f^2}, \quad Q = \frac{1}{a^2(a^2+1)} - \frac{\ln(1-1/a^2)}{2a^2+1}, \quad (3)$$

where $a = k_s/2k_f$ and k_s is the Bohm-Pines screening constant¹⁰. Combining this with Eqs. (1-2) we get

$$\sigma = \frac{\pi^2 b}{2e^2 \hbar k_B^2} \frac{B^4 \alpha^3 \sin^4 \pi \alpha / 2}{QT^2} \quad (4)$$

where α is the charge transfer from the inverted donor band to the normal acceptor band. The total conductivity will then be a sum of two terms of the form of Eq. (4), one for the TTF band and one for TCNQ. The main factors to note are the extremely strong dependencies on bandwidth (B^4) and charge transfer ($\alpha^3 \sin^4 \pi \alpha / 2$). It is just these factors that give the large pressure dependence of the resistivity and the deviation of the temperature dependence from T^2 .

The pressure dependence is shown in Fig. 1. The dashed line is a plot of Eq. (4) with constant charge transfer, but including the pressure dependence of the lattice parameters and bandwidths^{7,11}. About 50% of the pressure dependence is accounted for.

We do not know the pressure (or lattice parameter) dependence of the charge transfer, however, the diffuse X-ray scattering experiments¹² in TTF-TCNQ do show a " $4k_f$ " line over the whole metallic range. The interpretation of this line is still controversial, but if we assume that it really indicates the value of k_f we can derive from it the temperature dependence of the charge transfer. The variation is only from 0.59 at 60 K to 0.55 at 300 K, but even this small change is exceedingly important due to the strong functional dependence in Eq. (4). We convert the temperature dependence to a pressure dependence by assuming that the variation is due to the change in lattice parameter along the stack⁷. This means that we will only know the charge transfer for a lattice parameter variation of 2.4% (corresponding to a pressure of 6 kbar) since that is the range of the temperature variation of the lattice parameter. The solid curve in Fig. 1 shows the result of Eq. (4) including the charge transfer. The agreement with experiment is quite good.

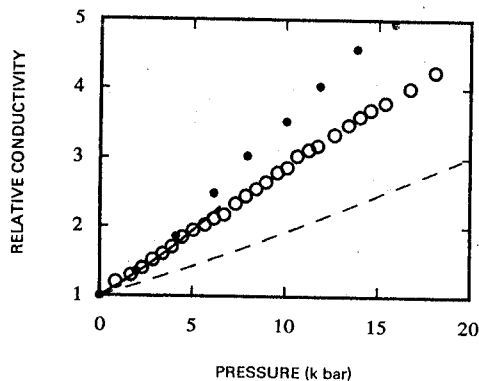


Fig. 1. Conductivity of TTF-TCNQ as a function of pressure. The dashed line is the theory with constant charge transfer and the solid line includes the variation of the charge transfer. (×) are the data of reference 23; (■) are the data of reference 24.

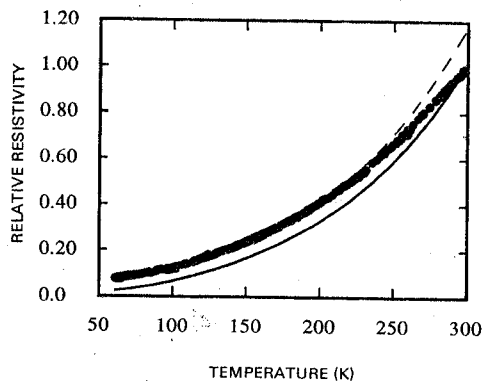


Fig. 2. Resistivity of TTF-TCNQ as a function of temperature. The solid line is theory, and (■) are the data of S. Etemad (private communication). (For dashed line see text.)

The temperature dependence of the resistivity is known to be close to T^2 , although with significant deviations¹³. Probably the most important source of the deviations is the large change in lattice parameter with temperature as pointed out by Cooper^{14,24}. Fig 2 shows the temperature dependence of the resistivity given by Eq. (4) including the variation of the bandwidths and the charge transfer with temperature. The theory and the data are normalized at 300 K since it is at the highest temperature that the impurity or defect contribution is least significant. As can be seen, the theoretical and experimental curves are parallel to each other up to about 230K (separated by an impurity contribution of 0.045), after which the experimental resistivity increases more slowly than the theory. We do not understand the reason for this discrepancy but one possibility will be suggested later. The dashed curve is the theoretical curve which has been normalized at 60 K after an impurity contribution of 0.045 was added. This curve shows quite clearly the agreement up to 230 K. The discrepancy at room temperature is about 20%.

THERMOELECTRIC POWER

The thermoelectric power in a metal is

$$S = - \frac{\pi^2 k_B^2 T}{3 |e|} \left(\frac{d \ln \sigma}{dE} \right)_{E_f} \quad (5)$$

and for the two-band case the total thermopower can be written as¹⁵

$$S = \frac{S_D \sigma_D + S_A \sigma_A}{\sigma_D + \sigma_A} \quad (6)$$

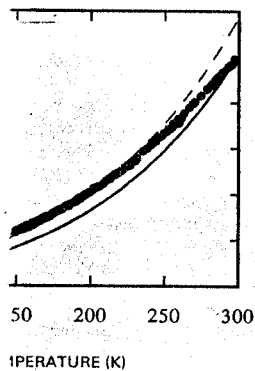
where D and A refer to the respectively. Since we have conductivity we can directly thermopower from Eq. (4). The temperature dependence is shown in interesting points to note. The pressure derivative of the thermopower is not clear whether or not the charge transfer we also show the result for the bandwidths for each stack in TSeF-TCNQ the cancellation of thermopower is small. The bandwidths are such that they change sign at about 5 kbar with constant charge transfer is not seen for TSeF-TCNQ. This does not obviate the result since in TCNQ, a small increase in pressure in TSeF-TCNQ will change in the pressure derivative. The pressure dependence of the thermopower has not been measured for either material present, compare with experiment.

The inclusion of the usual metallic linear temperature dependence from linear is small, amounting to about 20% enough to check this point.

Seiden and Cabib³ have shown the same as for the dc resistivity. However, the temperature dependence is different in case^{3,16,17}. We propose that the temperature dependence of the resistivity is greater than the frequency of dealing with the temperature dependence of the phonons or molecular vibrations. The frequency of electrons and molecular vibrations is greater for the highest temperature for the highest temperature. The Holstein expression made by Holstein expression made by Holstein expression when applied to

Here τ_0^{-1} is the scattering rate of phonon coupling constant for TCNQ⁻, we obtain $\tau_0 = 3$ sec. Considering that we have a satisfactory result. We conclude that the scattering is a major factor d

We have taken serious interaction and have used a



of TTF-TCNQ as a function of temperature. The solid line represents the data of S with constant charge transfer (for communication). (For communication.)

2, although with significant change in lattice parameter dependence of the resistivity with temperature. The curves are parallel to each other which the experimental data for this discrepancy but which has been normalized at clearly the agreement up to

(5)

(6)

where D and A refer to the donor and acceptor bands respectively. Since we have an explicit result for the conductivity we can directly calculate the complete thermopower from Eq. (4). The result for the pressure dependence is shown in Fig. 3. There are two interesting points to note. Firstly, the sign of the pressure derivative of the thermopower depends on whether or not the charge transfer varies. Secondly, we also show the result for TSeF-TCNQ. Since the bandwidths for each stack are more nearly equal for TSeF-TCNQ the cancellation is large and the resulting thermopower is small. The pressure dependence of the bandwidths are such that the thermopower should change sign at about 5 kbar. This result is obtained with constant charge transfer since the $4k_F$ scattering is not seen for TSeF-TCNQ. Nevertheless, this should not obviate the result since, in contrast to TTF-TCNQ, a small increase in the charge transfer with pressure in TSeF-TCNQ will not result in a large change in the pressure derivative of the thermopower. The pressure dependence of the thermopower has not been measured for either material so we cannot, at present, compare with experiment.

The inclusion of the explicit lattice-dependent variation of the parameters of Eq. (4) will destroy the usual metallic linear temperature dependence of the thermopower. However, in the present case the deviation from linear is small, amounting to only 1-2 $\mu\text{V}/\text{K}$. The presently available experimental data¹⁵ are not precise enough to check this point.

OPTICAL RESISTIVITY

Seiden and Cabib³ have shown that the temperature dependent part of the optical resistivity is exactly the same as for the dc resistivity, therefore, all the preceding analysis should also apply directly to the optical resistivity. However, the temperature independent part of the resistivity is much greater for the optical case^{3,16,17}. We propose that the source of this excess resistivity is a phonon emission process. For the dc resistivity the electron-phonon interaction is limited to phonon absorption. However, when the frequency is greater than the frequency of the appropriate phonons a phonon emission process is allowed. Since we are dealing with the temperature independent part of the resistivity, these phonons are of necessity optical phonons or molecular vibrations. Rice et al.¹⁸ and Torrance et al.¹⁹ have examined the interaction between electrons and molecular vibrations in TTF-TCNQ. In the temperature range of interest; $T \leq \theta_E$, the Einstein temperature for the highest frequency mode. Under these conditions, the one-dimensional analysis of the Holstein expression made by Bright et al.¹⁷ for electron acoustic phonon scattering yields the following expression when applied to our case,

$$\tau_0^{-1} = 2\pi^2 \sum_i \lambda_i \nu_i \quad (7)$$

Here τ_0^{-1} is the scattering rate for electron-molecular vibration interactions, λ_i is the dimensionless electron-phonon coupling constant for mode i , and ν_i is its frequency. Using the values of λ_i calculated by Rice et al.¹⁸ for TCNQ⁻, we obtain $\tau_0 = 3.8 \times 10^{-15}$ sec which is to be compared to experimental values of $3 - 5 \times 10^{-15}$ sec. Considering that we have not considered the scattering rate of the cation chain, the agreement is very satisfactory. We conclude that electron-molecular vibration scattering, rather than impurity or defect scattering, is a major factor determining the optical resistivity.

CONCLUSIONS

We have taken seriously the proposal that the resistivity of TTF-TCNQ is due to the electron-electron interaction and have used a simple model to try to account for the observed experimental data. The model

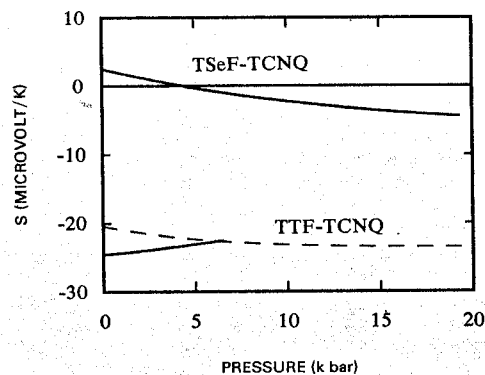


Fig. 3. Thermopower as a function of pressure for TTF-TCNQ and TSeF-TCNQ. For TTF-TCNQ the dashed line has constant charge transfer and the solid line includes the variation of charge transfer.

gives a good account of both the pressure and temperature dependence of the resistivity. The zero pressure thermopower is given approximately correctly and a prediction is made for its pressure dependence.

The present theory, however, suffers from three shortcomings. Firstly, it is an ad-hoc merging of a one-dimensional band model with a three-dimensional isotropic scattering model. This should be reexamined and an attempt at a self-consistent theory should be made. Secondly, there is a question as to the intrinsic temperature dependence of the electron-electron interaction. In three dimensions the proper dependence is T^2 , however, a truly one-dimensional treatment²⁰ gives T . The one-dimensional criterion is that the transverse transfer integral be much smaller than kT . The estimate for this transfer integral²¹ is about 70 K, a value which is neither much less nor much greater than the temperatures of interest. Therefore, the exact temperature dependence is still in question. Thirdly, we have not examined the question of momentum conservation. In order to have a finite contribution to the resistivity from the electron-electron interaction we must have either umklapp or interband scattering. In a really one-dimensional system with flat bands momentum cannot be conserved for an umklapp process so that the resistivity would be zero. Therefore, either the bands must have some curvature or the scattering must be interband, i.e., electron-hole scattering between the TTF and TCNQ bands. Recent work by Shitzkovsky et al.²² indicates that the actual bands in TTF-TCNQ may deviate strongly from the ideal one-dimensional flat bands.

All three of these questions must be examined. The good agreement found between experiment and the present electron-electron model should provide encouragement to examine these points further.

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