

TEMPERATURE AND PRESSURE DEPENDENCE OF THE RESISTIVITY OF β -(BEDT-TTF)₂X (X = I₃, I₂Au) AND α_t -(BEDT-TTF)₂I₃

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Abstract

The temperature dependence of the resistivity of the organic metals and superconductors β -(BEDT-TTF)₂I₃, β -(BEDT-TTF)₂I₂Au and α_t -(BEDT-TTF)₂I₃ was measured at ambient and at several isotropic pressures (up to 2.5 kbar). By the application of a relatively low pressure, it is possible to measure the term in the resistivity that is linear in temperature. This term is masked by the larger T^2 term at ambient pressure. It is shown that in the temperature range below 120 K, the external modes are mainly responsible for the resistivity, while above this temperature the flipping of the CH₂ groups becomes important. The linear electron-phonon coupling corresponds to a value of λ between 1 and 1.5.

Introduction

At room temperature organic metals usually have electrical conductivity (σ) values not much larger than $1000 (\Omega \text{ cm})^{-1}$. This value is at least two orders of magnitude smaller than that of good ordinary metals (Cu: $\sigma = 5 \times 10^5 (\Omega \text{ cm})^{-1}$). This difference in conductivity is understandable, since σ can be expressed by

$$\sigma = ne^2l/p_F \quad (1)$$

(n = number of carriers/cm³, e = elementary charge, l = mean free path and p_F = Fermi momentum) and n is about two orders of magnitude smaller for the organic metal ($\approx 10^{21} \text{ cm}^{-3}$), since organic molecules are large compared to metal atoms and every molecule usually provides only about one

conduction electron. In addition, in the organic metals the mean free path l is much shorter. For the quasi-one-dimensional organic metal TTF-TCNQ, with a typical value of $\sigma \approx 500 (\Omega \text{ cm})^{-1}$, the mean free path is $l \approx 3 \text{ \AA}$, while in the quasi-two-dimensional ambient pressure organic superconductors β -(BEDT-TTF) $_2$ I $_3$ (1) ($T_c = 1.3 \text{ K}$, $\sigma \approx 20 - 50 (\Omega \text{ cm})^{-1}$), β -(BEDT-TTF) $_2$ I $_2$ Au (2) ($T_c = 4.5 \text{ K}$, $\sigma \approx 10 - 30 (\Omega \text{ cm})^{-1}$) and α_t -(BEDT-TTF) $_2$ I $_3$ (3) ($T_c = 8 \text{ K}$, $\sigma \approx 10 - 30 (\Omega \text{ cm})^{-1}$) l is only about 0.25 \AA . Since in 1, 2 and 3 the stacking axis of the organic donors is of the order of 3.3 \AA , this means that the mean free path l is less than $1/10$ of the molecular separation. This small value of l would suggest a hopping-type conductivity rather than a metallic one. However, the temperature dependence of the conductivity and of the susceptibility exhibits a metallic behaviour. The susceptibility is temperature independent and has the Pauli value [1, 2]. Thus, the exceedingly small value of l in the metallic state is something of a mystery.

In this paper we want to discuss the following questions, which are important for the theory of the resistivity of organic metals:

(a) What are the phonon modes responsible for the resistivity? Are these external modes, *i.e.*, librations and translations, or internal modes? What is the frequency of these modes?

(b) Is the electron-phonon coupling linear or quadratic in the phonon operators?

(c) How can we account for the extremely high value of the resistivity at ambient pressure and temperature in the organic metals 1, 2 and 3?

Therefore, we have measured the temperature dependence of the resistivity $\rho = 1/\sigma$ at ambient pressure of 1, 2 and 3 as well as of 1 at isotropic pressures between 1.5 and 2.5 kbar.

Experimental and results

Single crystals of 1, 2 and α -(BEDT-TTF) $_2$ I $_3$ were grown by electrochemical methods [3]. Crystals of 3 were prepared by tempering α -(BEDT-TTF) $_2$ I $_3$ crystals at $75 \text{ }^\circ\text{C}$ for several days [4]. The conductivity measurements were done by the usual four-point method in the ab plane of the crystals. The measurements at 1.5, 2 and 2.5 kbar were carried out in a single Cu-Be ice bomb [5].

Figures 1(a), (b) and (c) show the temperature dependence of the resistivity at ambient pressure of 1 (I), 2 and 3 in the temperature range 4 - 300 K. Figure 2(a) shows the temperature dependence of the resistivity for a second sample of 1 (II) at ambient pressure as well as at an isotropic pressure of 2 kbar (measured from high temperature to low temperature and vice versa), while Fig. 2(b) shows the resistivity of a third crystal of 1 (III) in the range 4 - 100 K at ambient pressure as well as at isotropic pressures of 1.5 and 2.5 kbar. In the temperature range 4 - 100 K, the specific resistivity ρ was fitted with the following equation:

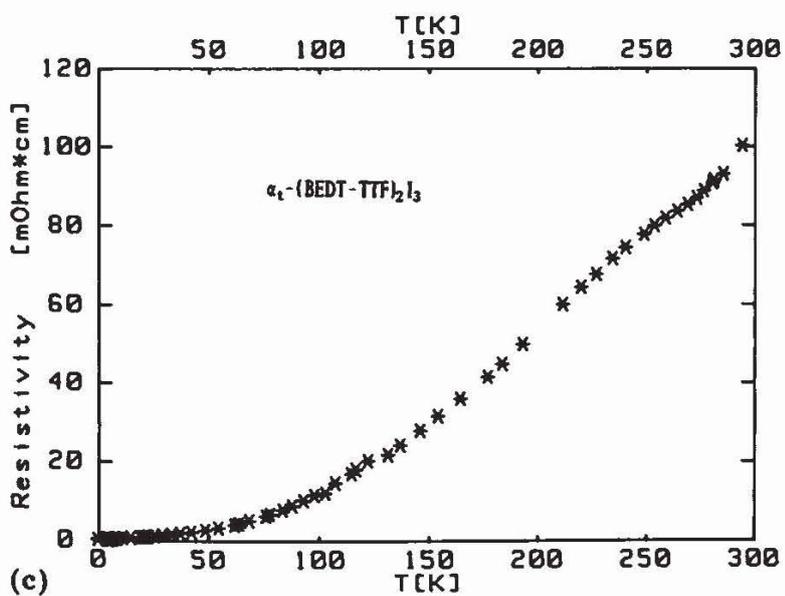
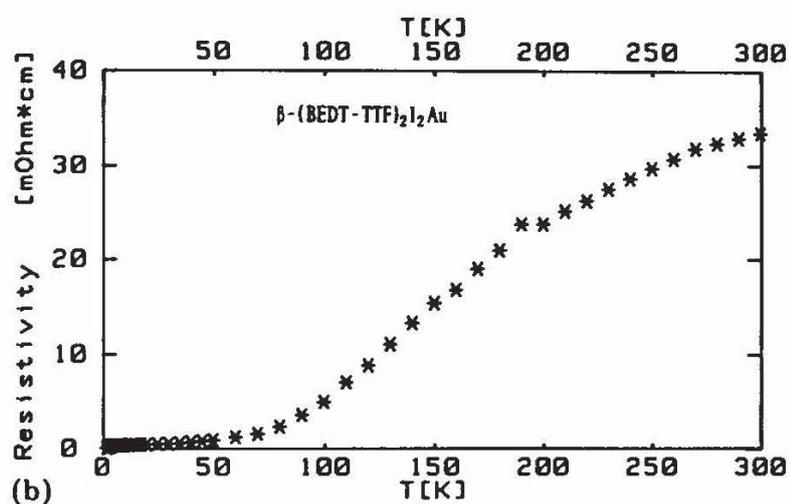
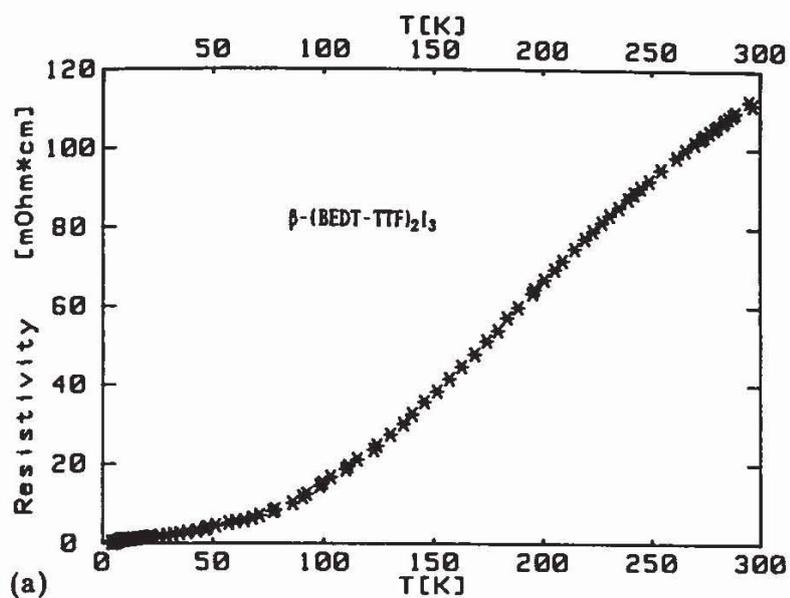
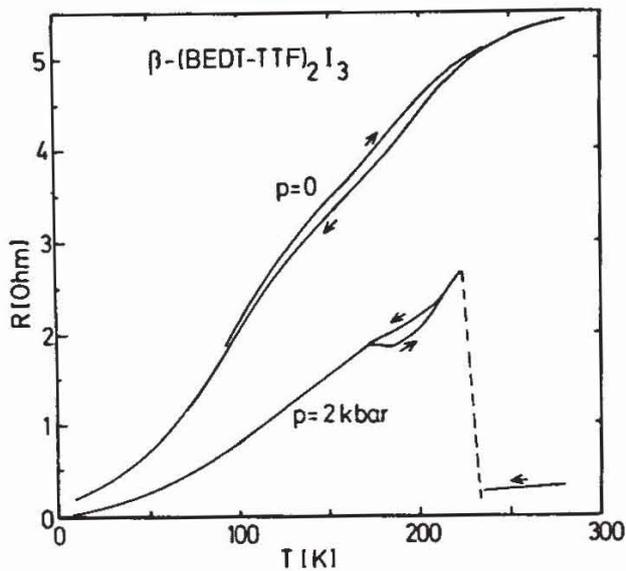
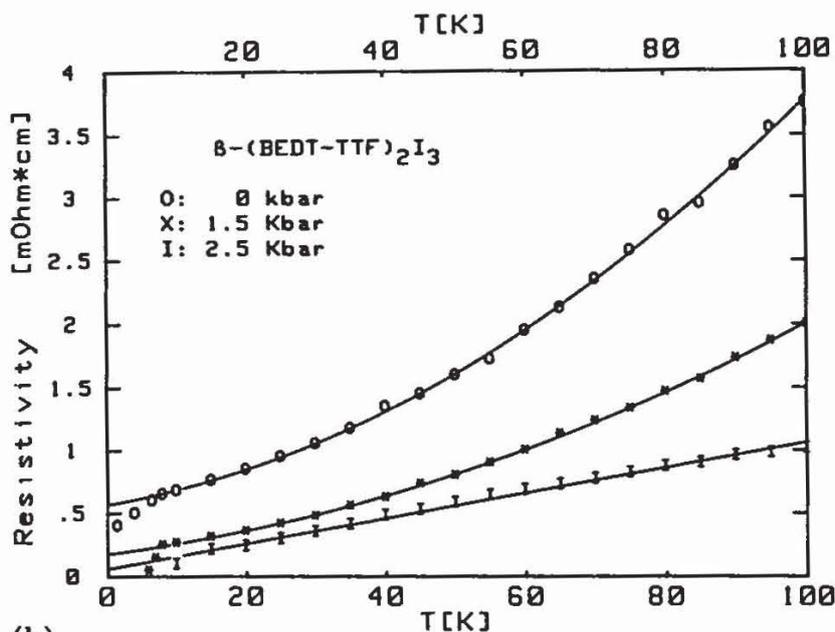


Fig. 1. Temperature dependence of the resistivity at ambient pressure of (a) β -(BEDT-TTF)₂I₃ (I); (b) β -(BEDT-TTF)₂I₂Au; (c) α_t -(BEDT-TTF)₂I₃.



(a)



(b)

Fig. 2. Temperature dependence of the resistivity in the range 4 - 100 K of (a) β -(BEDT-TTF) $_2$ I $_3$ (II) at ambient pressure as well as at an isotropic pressure of 2 kbar. (b) β -(BEDT-TTF) $_2$ I $_3$ (III) at ambient as well as of isotropic pressures of 1.5 and 2.5 kbar.

$$\rho = \rho_0 + \rho_1 T + \rho_2 T^2 \quad (2)$$

where ρ_0 is the residual resistivity.

The wide range of measured room-temperature resistivities (20 to 100 m Ω cm) is apparently due to crystal imperfections as well as to imperfections in the contacts (evaporated gold films). In addition, sample 1 (III) may have some cracks, which are responsible for its high resistance (see Fig. 2(a)). On the basis of experience with many more samples of this material, we believe that an inherent room-temperature resistivity of about 50 m Ω cm and a resistivity of about 4 m Ω cm at 100 K are the best values.

TABLE 1

Parameters ρ_0 , ρ_1 and ρ_2 of eqn. (2) for crystals of β -(BEDT-TTF) $_2$ I $_3$, β -(BEDT-TTF) $_2$ I $_2$ -Au and α_t -(BEDT-TTF) $_2$ I $_3$ at ambient pressure and for the temperature range 4 - 100 K (see text)

	β -(BEDT-TTF) $_2$ I $_3$	β -(BEDT-TTF) $_2$ I $_2$ Au	α_t -(BEDT-TTF) $_2$ I $_3$
ρ_0 ($\mu\Omega$ cm)	300 \pm 100	510 \pm 170	730 \pm 180
ρ_1 ($\mu\Omega$ cm/K)	<1	negligible	negligible
ρ_2 ($\mu\Omega$ cm/K 2)	1.0	0.3	1.3

TABLE 2

Parameters ρ_0 , ρ_1 and ρ_2 of eqn. (2) for β -(BEDT-TTF) $_2$ I $_3$ (crystals II and III) at ambient pressure as well as at several isotropic pressures for the temperature range 4 - 100 K

	β -(BEDT-TTF) $_2$ I $_3$ (II)	β -(BEDT-TTF) $_2$ I $_3$ (III)
ρ_0 ($\mu\Omega$ cm)	0 kbar: 1500 \pm 100 2 kbar: 150 \pm 50	0 kbar: 560 \pm 50 1.5 kbar: 180 \pm 10 2.5 kbar: 60 \pm 10
ρ_1 ($\mu\Omega$ cm/K)	0 kbar: 35 2 kbar: 5	0 kbar: 9 1.5 kbar: 7 2.5 kbar: 9
ρ_2 ($\mu\Omega$ cm/K)	0 kbar: 1.9 2 kbar: 1	0 kbar: 0.25 1.5 kbar: 0.1 2.5 kbar: 0

Tables 1 and 2 show the values of ρ_0 , ρ_1 and ρ_2 for 1 (I), 2 and 3 at ambient pressure as well as for 1 (II) and 1 (III) at ambient and several isotropic pressures.

Discussion

The resistivity of 1, 2 and 3 in the ab plane as a function of temperature at ambient pressure has an S-like shape (Fig. 1). We can distinguish three regions:

(i) $T < 120$ K. In this region eqn. (2) is valid. The values of ρ_0 , ρ_1 and ρ_2 are given in the Tables. ρ_2 is seen to decrease drastically under pressure, being essentially zero at $P = 2.5$ kbar. ρ_0 also decreases significantly under pressure. At ambient pressure, ρ_1 of samples 1 (I), 2 and 3 is essentially zero, while ρ_1 of samples 1 (II) and 1 (III) is unreliable because of the large value of ρ_0 . This result is in accord with measurements of other groups [6, 7]. ρ_1 of sample 1 (III) under pressure, namely about 10 $\mu\Omega$ cm/K, seems to be the most reliable value for this parameter.

(ii) $120 \text{ K} < T < 200 \text{ K}$. In this region ρ increases steeply. The rise of ρ with T is faster than can be described by a T^2 law.

(iii) $200 \text{ K} < T$. ρ approaches saturation and in particular above 300 K ρ saturates as a function of T . Yet the pressure dependence of ρ is very strong, $d \ln \rho / dP = -30\% / \text{kbar}$.

From our experience with other organic metals [8], the temperature dependence of the resistivity by itself is not sufficient to provide an adequate theoretical interpretation. Additional sources of information are provided by Raman investigations [9], n.m.r. data about the relaxation time of the protons and carbons as a function of temperature [10, 11] and point contact spectroscopy data [12] providing the Eliashberg function $\alpha^2(\omega)F(\omega)$. A recent determination of the electronic band structure [13] is also of some value for the understanding of the mechanism of the resistivity and the electron-phonon coupling [14] in organic metals.

(a) *The soft mode*

Direct information about the frequency of the phonons responsible for the electrical resistivity is provided by the point-contact spectroscopy data [12] on crystals of 1. These provide the Eliashberg function $\alpha^2(\omega)F(\omega)$ as a function of ω . A very high peak in this function is observed at 1 mV , a shoulder is observed at 4 mV , and a broad peak is observed around 15 mV . Above 25 mV , $\alpha^2 F$ is essentially zero. Thus, the frequency range is that of the *external* modes, though around 15 mV there should be some admixture of internal modes as well (I_3^- -stretching mode [9]). In particular, the low-frequency contribution is to a large extent due to low-frequency librations. The mode at 1 mV is particularly soft, and such soft modes have not yet been observed in organic metals.

Since the mode at 1 mV is so soft, the amplitude of thermal motion

$$\langle \delta R^2 \rangle \simeq k_B T / M \omega^2$$

should be extremely large (M being the mass of the molecule and ω the phonon frequency). This should give rise to anharmonic forces, and the amplitude $\langle \delta R^2 \rangle$ should tend to saturate at high temperature. Also, the large value of $\langle \delta R^2 \rangle$ causes the quadratic interaction of this mode to be particularly strong. Pressure should also have a dramatic effect on the frequency of this soft mode. In this way we can account for the strong reduction of the quadratic term ρ_2 at low pressures, and also account (in part) for the saturation of the resistivity at high temperatures.

We should note that saturation of the resistivity is observed in TTF-TCNQ under *constant volume* conditions [15] and is accounted for by lattice anharmonicities. Here, because of the softness of the mode, lattice anharmonicities are much larger and may account for the saturation observed already under *constant pressure* conditions.

(b) The flipping of the CH₂ group

N.m.r. data in the temperature region 4 - 300 K [10, 11] show that the CH₂ groups at the ends of the BEDT-TTF molecules are frozen below 120 K and become free above this temperature, with an activation energy of about 0.1 eV. The sharp rise of the resistivity in this temperature region may thus be attributed to these internal modes. Once the CH₂ groups flip freely between the two stable positions (chair and boat), the amplitude becomes temperature independent, and thus the contribution to the resistivity should saturate. This may be another factor accounting for the observed saturation of the resistivity.

The frequency of phonons (at low temperatures, where the configurations are frozen in) corresponding to flipping of a CH₂ group in cyclohexane is around 300 - 400 cm⁻¹; in this frequency range, $\alpha^2 F$ was found to be negligibly small. Perhaps the frequency of these modes in BEDT-TTF is lower than in cyclohexane, or perhaps the coupling of these modes with the electrons is quadratic and thus does not show up in the point-contact spectroscopy data.

The disorder of the CH₂ groups may contribute to the residual resistivity ρ_0 ; it may be reduced by the hydrostatic pressure, and this may account for the decrease of ρ_0 with pressure.

(c) The electronic band structure and its relationship to the electrical resistivity

An electronic band structure calculation [13] indicates that several bands overlap near the Fermi level. Some of these bands are broad (~ 1 eV) and some are very narrow (~ 0.1 eV).

This feature may account for the large electronic contribution to the McMillan's electron-phonon coupling constant λ , where λ is given by

$$\lambda = \langle I^2 \rangle n(E_F) / M\omega^2$$

with I the electronic matrix element, and $n(E_F)$ is the electronic density of states. For narrow bands, I is usually small (of the order of the electronic bandwidth divided by the atomic size) and therefore $\langle I^2 \rangle n(E_F)$ is small, although $n(E_F)$ is large. For broad bands $n(E_F)$ is small. However, several overlapping bands, some of which are broad, can give rise to a high value of $n(E_F)$, together with a large value of $\langle I^2 \rangle$.

The same argument applies to the quadratic electron-phonon interaction. For this the electronic factor can also be large for several overlapping bands. Thus, we can account for a resistivity about an order larger than in TTF-TCNQ and in the Bechgaard salts.

In addition, the stacking of the molecules gives rise to an electronic band structure that is approximately two dimensional [16]. As a result, symmetry allows linear coupling of librations and transverse phonons with the electrons [17]. Consequently λ is significantly larger than in the one-dimensional TTF-TCNQ and TMTSF₂X materials.

The electronic band structure [13] shows the presence of a narrow (~ 0.1 eV wide) virtual state just above E_F . Scattering of electrons from the itinerant states (*i.e.*, those with a large value of v_F) into the narrow, virtual state (for which v_F is very small) may account for the very high value of the resistivity at ambient temperature and pressure by a mechanism similar to Mott's two-band model. Such scattering may reduce the mean-free path l by a factor $n_1(E_F)/n_2(E_F)$, where $n_1(E_F)$ is the density of states of the itinerant band and $n_2(E_F)$ is the density of states of the nearly localized state [18]. From the preliminary band calculation, we estimate $n_1(E_F)/n_2(E_F) \approx 0.1$ to 0.2 . This may in part account for the small value of l (about 0.25 Å), which is much smaller than the lattice constant.

Returning to the questions presented at the beginning, we can say that the phonons responsible for the resistivity below 120 K are mainly the external modes; above this temperature, flipping of the CH_2 groups becomes important. Also, tunnelling experiments indicate that phonons in the frequency range 15 - 25 meV interact with the electrons. Such phonons give rise to a sharp increase of ρ with T above 100 K; however, the value of the measured Eliashberg function α^2F is not sufficient to account for the observed rise in resistivity. It is possible that phonons in this frequency range also interact quadratically with the electrons, and that this quadratic interaction is responsible for the sharp increase of ρ with T . The linear electron-phonon coupling corresponds to $\lambda \approx 1$ to 1.5 ; this value is estimated from the ρ_1 term of the resistivity, from the integral

$$\lambda = 2 \int \alpha^2(\omega) F(\omega) \omega^{-1} d\omega$$

over the Eliashberg function, and from the value of T_c . This value λ is about an order stronger than in the one-dimensional organic metals, and we understand the cause of this larger value. The quadratic electron-phonon coupling gives rise to the ρ_2 term in the resistivity, which is also stronger at ambient pressure than in the one-dimensional organic metals. As for the flipping of the CH_2 groups, we cannot say whether this mode couples with the electrons linearly or quadratically. Around 100 K, the amplitude of thermal motion $\langle \delta R^2 \rangle^{1/2}$ corresponding to a frequency of order 400 cm^{-1} is about $0.03 - 0.05$ Å, while when the motion becomes free, the amplitude of motion is of order 1 Å, and such a large increase in amplitude can easily account for the increase in resistivity for both linear and quadratic coupling. The very high resistivity at ambient temperature and pressure can be accounted for by phonon-assisted scattering into a nearly localized state, which has a sharp resonance close to the Fermi level.

Conclusion

We have shown that by application of a low pressure, it is possible to measure the term in the resistivity that is linear in temperature. This term

is masked by the larger T^2 term at ambient pressure. This linear term is considerably stronger in the BEDT-TTF₂X salts than in TTF-TCNQ and the TMTSF₂X salts. This correlates with the higher superconducting transition temperature of β -(BEDT-TTF)₂I₃, β -(BEDT-TTF)₂I₂Au and α_t -(BEDT-TTF)₂I₃.

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Note added in proof

We present here a derivation of an approximate expression for the conductivity of ET.

Consider a stack of molecules a distance d apart, with an average transfer integral t between atoms of neighbouring molecules, and several molecular states in the vicinity of the Fermi level, with a scattering time τ_{int} between these molecular states. Then, the hopping time between molecules is given by [10, 14] $\hbar/\tau_{\text{hop}} = t^2 \tau_{\text{int}}/\hbar$, leading to a diffusion constant $D = d^2/\tau_{\text{hop}}$, a mobility $\mu = eDn(E_F)$ and a conductivity $\sigma = n_{\text{int}}e\mu = n_{\text{int}}e^2d^2n(E_F)t^2\tau_{\text{int}}/\hbar^2$, where n_{int} is the density of electrons, taking into account the several molecular states within \hbar/τ_{int} from E_F . Defining

$$m_{\text{ext}}^{-1} = d^2n(E_F)t^2/\hbar^2$$

(an average effective mass for motion between the molecules), we get

$$\sigma = n_{\text{int}}e^2\tau_{\text{int}}/m_{\text{ext}}$$

Defining

$$l_{\text{int}} = \tau_{\text{int}}v_{\text{int}}$$

and

$$m_{\text{int}}v_{\text{int}} = p_{\text{int}}$$

where v_{int} and m_{int} are the velocity and effective mass for motion inside the molecule, we obtain

$$\sigma = (n_{\text{int}}e^2l_{\text{int}}/p_{\text{int}})(m_{\text{int}}/m_{\text{ext}})$$

Estimating $n_{\text{int}}/n_{\text{ext}}$, $l_{\text{ext}}/l_{\text{int}}$, $p_{\text{int}}/p_{\text{ext}}$ and $m_{\text{ext}}/m_{\text{int}}$ all to be about three to five (for molecules like BEDT-TTF, possessing approximately 26 atoms), we find that σ is about 10 to 25 times smaller than $n_{\text{ext}}e^2l_{\text{ext}}/p_{\text{ext}}$, $l_{\text{ext}} \simeq d$, the minimum value predicted by Mott and the Ioffe-Regel rules. Moreover, the saturation of l_{int} by the Ioffe-Regel rule leads to a saturation of σ , in accord with experiment. Also, since n_{int} involves several electrons per molecule, the Pauli principle applies and gives rise to a Pauli spin susceptibility. For smaller molecules like TTF and TCNQ (about half the size of BEDT-TTF), there is apparently only one molecular state in the vicinity of E_F , consequently intra-molecular scattering can be ignored and this analysis does not apply; the resistivity does not saturate and the susceptibility approaches a Curie value, as shown in ref. 14.

This derivation does not apply at low temperatures, where only one molecular state is within distance \hbar/τ from E_F . Above 100 K, there is a sharp rise in the resistivity, above the extrapolated T^2 behaviour. This rise may be due to a transition from the low-temperature $\sigma = n_{\text{ext}}e^2l_{\text{ext}}/p_{\text{ext}}$ behaviour to the high-temperature behaviour with the much lower value of the conductivity. (This is an alternative explanation to the one attributing the sharp rise to flips of the CH_2 groups.)