J. Phys.: Condens. Matter 5 (1993) 8569–8578. Printed in the UK

Freezeout of the electrical resistivity in (BEDT-TTF)$_2$I$_3$ below 20 K

M Weger[†][§], M Tittelbach[†], E Balthes[†], D Schweitzer[†] and H J Keller[‡]

[†] 3 Physikalisches Institut, Universität Stuttgart, D-70550 Stuttgart, Federal Republic of Germany

[‡] Chemisches Institut, Universität Heidelberg, 6900 Heidelberg, Federal Republic of Germany

Received 13 May 1993

Abstract. We have measured the temperature (T) dependence of the resistivity ρ of the β and κ phases of (BEDT-TTF)$_2$I$_3$ from 300 K down to T_c (~ 1.3 K and ~ 4 K for the β and κ phases, respectively). Between 100 K and 20 K, $\rho \propto T^2$. Below 20 K, the resistivity falls below the T^2 law. We calculate the resistivity due to electron–electron scattering and find that this contribution is far too small to account for the measured resistivity, besides being inconsistent with the freezeout below 20 K. We suggest that the resistivity is due to electron–phonon scattering, described by a novel mechanism that has been proposed for the high-T_c cuprates. We also suggest that this mechanism accounts for the T^2 law observed in materials such as TiS$_2$, Nb-doped SrTiO$_3$, and intercalated graphite.

1. Introduction

In many organic metals, the electrical resistivity ρ is proportional to T^2. In quasi-1D (Q1D) organic metals, such as TTF-TCNQ [1, 2] and TMTSF$_2$PF$_6$ [3], we are concerned with the resistivity along the chains. In quasi-2D (Q2D) organic metals, such as (BEDT-TTF)$_2$I$_3$, we are concerned with the resistivity in the a–b plane [4, 5]. In some of these materials, the T^2 law holds from temperatures below 20 K to temperatures above 300 K, and over a resistivity range in excess of 100:1 in TMTSF$_2$PF$_6$ [6], and of about 10000:1 in β-(BEDT-TTF)$_2$I$_3$ [4].

A $\rho \propto T^2$ law is also observed in some inorganic systems. In TiS$_2$, it holds up to 400 K, i.e. over nearly four decades of resistivity [7]. In intercalated graphite (for example C$_8$K), $\rho \simeq a + bT + cT^2$, with the T^2 term being rather large [8]. In Nb-doped SrTiO$_3$, the T^2 law holds except for some contribution from optical phonons at high temperatures [9].

The origin of this T^2 law has not yet been definitely established, in spite of considerable work.

Early theories tried to account for this law by electron–electron [10] scattering [7, 11]. For a one-band model, this mechanism requires Umklapp processes in order to deliver momentum to the lattice [12]. In Q1D metals, such processes are impossible if $4k_F < 2\pi/a$, the smallest reciprocal lattice vector. A similar problem exists for Q2D TiS$_2$, because of the small value of k_F [13].

An alternative approach was to try to account for the T^2 law by electron–phonon scattering. For TiS$_2$, a wide distribution of phonon frequencies, with a form that gives a T^2 law from about 10 K to 400 K, was suggested [13]. For TTF-TCNQ, a wide variety of theoretical models was proposed [14–18]. Specifically, one theory proposed a second-order

---

[§] On leave: Racah Institute of Physics, Hebrew University, Jerusalem, Israel.

0953-8984/93/458569+10$07.50

coupling between electrons and librons, suggesting that the first-order coupling is inhibited because of symmetry, and the second-order coupling is particularly strong because it is unscreened, the libron modes being transverse to the chain (conducting) axis [19].

A key factor that can allow us to discriminate between the two types of mechanism is the possibility of freezeout of the electrical resistivity at low temperatures. For electron–electron scattering, there is no freezeout of the $\rho \propto T^2$ behaviour even at the lowest temperatures. For electron–phonon scattering, there is a freezeout at temperatures of about $(\frac{1}{4}-\frac{1}{2})\ \omega_{\mathrm{ph}}$.

Bulaevskii *et al* [20] measured the resistivity of β-(BEDT-TTF)$_2$I$_3$ between 2 K and 20 K, and observed a T^2 law there; on the basis of this finding, Bulaevskii [21] suggested that there is no freezeout, and therefore the resistivity is due to electron–electron scattering. He also carried out theoretical estimates of the magnitude of the resistivity, which suggested that this mechanism is strong enough to account for the observed resistivity. In contrast, in the present work we find experimentally a freezeout at 20 K and also show theoretically that the electron–electron scattering mechanism is far too weak to account for the observed resistivity.

2. Measurement of the resistivity of β and κ-(BEDT-TTF)$_2$I$_3$

The resistivity of the β and κ phases of (BEDT-TTF)$_2$I$_3$ was measured from T_c (which is about 1.4 K for the β phase, and 4 K for the κ phase) up to about 300 K. Some curves of ρ versus T and ρ versus T^2 are shown in figures 1–3.

Single crystals of β-(BEDT-TTF)$_2$I$_3$ and κ-(BEDT-TTF)$_2$I$_3$ were prepared by the usual electrochemical preparation as described in the literature [22, 23]. In the case of the crystals of κ-(BEDT-TTF)$_2$I$_3$ we used only tetra-n-butylammonium triiodide ((BuN$_4$)I$_3$) as electrolyte salt in contrast to the preparation described by Kajita *et al* [24] who used in addition a small amount of (BuN$_4$)AuI$_2$. In our case we obtained high-quality crystals with a ratio for the resistivities ρ(300 K)/ρ(10 K) up to 3×10^3 for the best crystals. The resistivities were measured by the standard four-probe method with DC and lock-in techniques. The contacts were obtained by evaporation of gold with a mask and connected to gold wires with gold paint.

We present results on two κ-phase crystals and one β-phase crystal. Figure 1(*a*) shows the resistivity versus the temperature for a κ-(BEDT-TTF)$_2$I$_3$ crystal. The ratio ρ(300 K)/ρ(10 K) is about 3.5×10^3 for this crystal. Figure 1(*b*) shows a plot of the resistivity versus T^2 up to 100 K. The linear part of the plot is given by $\rho(T) = \rho_0 + aT^2$ with $\rho_0 = 4.1 \times 10^{-4}$ Ω cm and $a = 2.9 \times 10^{-7}$ Ω cm/T^2. In figure 1(*c*) we see an analogous plot but now only in the range up to 20 K. Now the slope is totally different and $\rho_0 = -3 \times 10^{-5}$ Ω cm and $a = 7.3 \times 10^{-7}$ Ω cm/T^2. (Note that the value extrapolated to $T = 0$ is negative!). In figures 2(*a*)–(*c*) and 3(*a*)–(*c*) analogous curves are presented for a second κ-phase crystal (ρ(300 K)/ρ(10 K) $\simeq$ 400) and a β-phase crystal (ρ(300 K)/ρ(10 K) $\simeq$ 300). For the κ-phase crystal, between 20 K and 100 K the resistivity is given by $\rho_0 = 7.1 \times 10^{-5}$ Ω cm, $a = 7.9 \times 10^{-8}$ Ω cm/T^2, and below 20 K $\rho_0 = 1.5 \times 10^{-5}$ Ω cm, $a = 1.8 \times 10^{-7}$ Ω cm/T^2. For the β-phase crystal, between 20 K and 100 K, $\rho_0 = 1.7 \times 10^{-3}$ Ω cm, $a = 1.2 \times 10^{-6}$ Ω cm/T^2, and below 20 K, $\rho_0 = 6 \times 10^{-4}$ Ω cm, $a = 2.6 \times 10^{-6}$ Ω cm/T^2.

The data show clearly that the $\rho \propto T^2$ law is obeyed above 20 K to a rather high accuracy, but below 20 K, the resistivity falls *below* the $\rho \propto T^2$ line, i.e. there is a freezeout of the resistivity below 20 K.

Over the limited temperature range 2–20 K, it is possible to fit the resistivity to a T^2 law, in agreement with the results of Bulaevskii *et al* [20]. But the slope of the curve is much

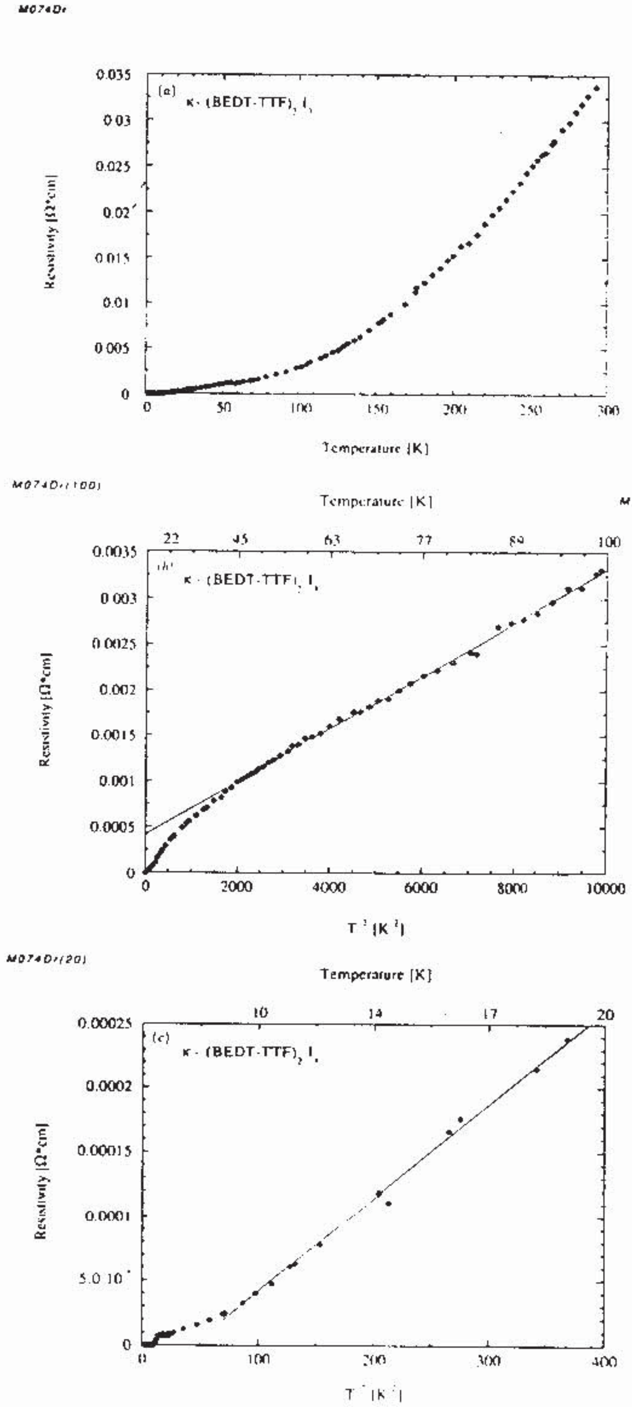

Figure 1. The resistivity of a sample of κ-(BEDT-TTF)$_2$I$_3$, as a function of temperature. (*a*) ρ versus T, up to 300 K; (*b*) ρ versus T^2, up to 100 K; (c) ρ versus T^2, up to 20 K.

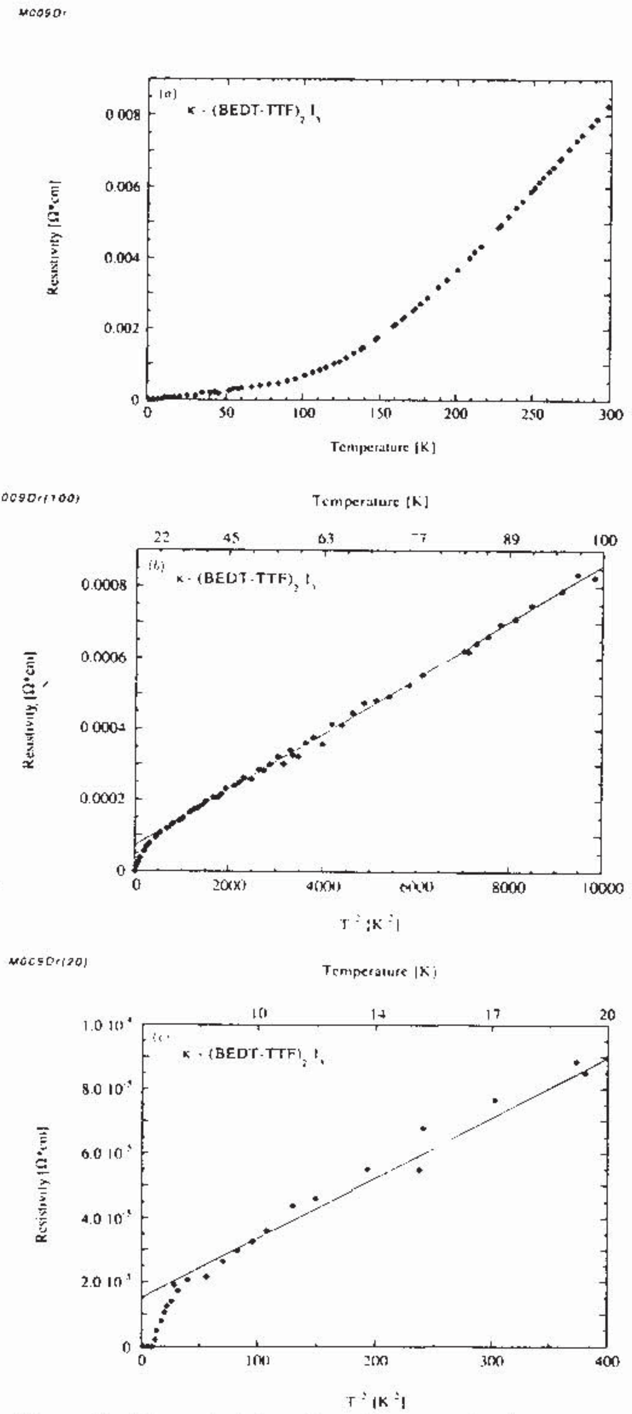

Figure 2. The resistivity of another sample of κ-(BEDT-TTF)$_2$I$_3$ as function of temperature: (*a*), (*b*) and (*c*) as in figure 1.

larger than that of the ρ versus T^2 curve above 20 K. Since the temperature and resistance range of these low-temperature data is small (the resistance range is just 2:1 [20], or at most 5:1 (this work)!), we doubt whether this approximate T^2 fit is an inherent physical law.

3. Difficulties associated with the electron–electron scattering mechanism

A $\rho \propto T^2$ law was originally proposed by Baber [10], based on electron–electron scattering. In that model, s electrons are scattered by d electrons, and deliver their momentum to them;

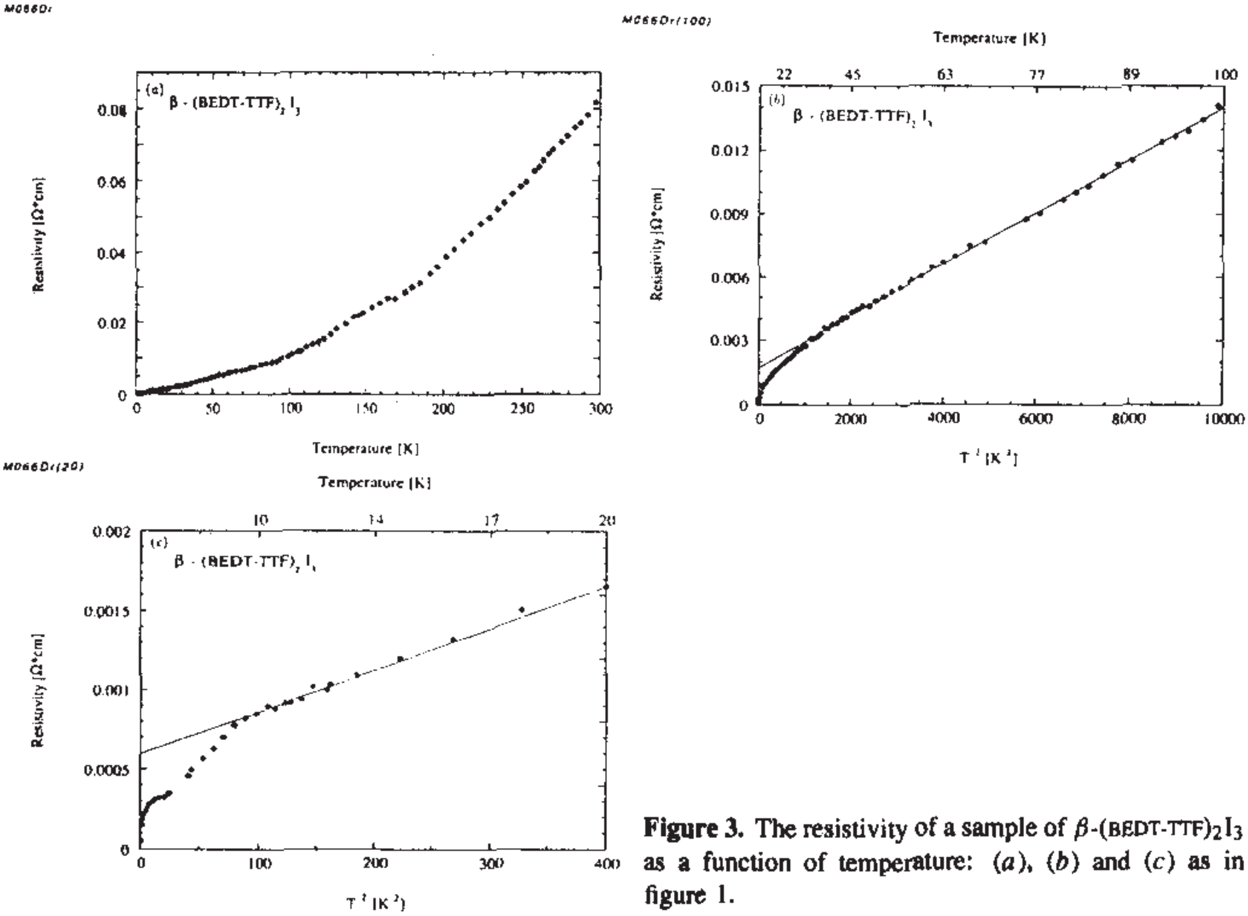

Figure 3. The resistivity of a sample of β-(BEDT-TTF)$_2$I$_3$ as a function of temperature: (*a*), (*b*) and (*c*) as in figure 1.

the d electrons are in turn relaxed very rapidly by the phonons. Therefore, no Umklapp processes must be invoked. Because of the large density of states of the d states, the scattering cross-section is large, and the contribution to the resistivity is significant. This mechanism is discussed in detail by Ziman [12], who also considers a one-band situation where Umklapp processes are essential. This mechanism was proposed to account for the T^2 law in TTF-TCNQ by Seiden and Cabib [11], and more recently, to account for the T^2 law in β-(BEDT-TTF)$_2$I$_3$ by Bulaevskii [21].

The expression for the resistivity by this mechanism is given by Ziman [12]:

$$\rho_{ee}(T) = G^2(k_F a_0)\{[e^2/\varepsilon_0^2(\omega)]/v_F E_F\}(k_B T/E_F)^2$$

where v_F is the Fermi velocity, E_F the Fermi energy, and $\varepsilon_0(\omega)$ is the dielectric constant of the background in which the conduction electrons are immersed (*not* the dielectric constant $\varepsilon(q, \omega)$ of the conduction electrons themselves, $\varepsilon_0 = \varepsilon_{\rm core} + \varepsilon_{\rm interband} + \varepsilon_{\rm lattice}$, but *without* $\varepsilon_{\rm carrier}$ [8]). $G^2(k_F a_0)$ is the Umklapp factor; Umklapp processes are necessary (in a one-band model) for the electrons to deliver momentum to the lattice. For normal d-state metals, $G^2(k_F a_0) \simeq 10^{-3}$–$10^{-2}$.

For (BEDT-TTF)$_2$I$_3$, the dielectric constant of the insulating α-phase is about 15–20 [25]. The Bohr radius a_0 is about 2–3 Å, and $k_F \simeq 2 \times 10^7$ cm^{-1} [26]. Thus, $k_F a_0 \simeq 0.5$, which is close to the value for 'normal' metals and in any case is not smaller than that for d electrons. Therefore, the Umklapp factor is not larger than that for 'normal' d metals, i.e. 10^{-2}–10^{-3}. Thus, for $E_F \simeq 0.2$ eV, $v_F \simeq 10^7$ cm s^{-1} we find: $\rho_{ee} \simeq 10^{-12} \times T^2$ Ω cm K^{-2}, about five orders of magnitude *smaller* than the measured value ($\rho \simeq 2 \times 10^{-7}$ Ω cm K^{-2} [4, 20]). Therefore, we believe that this mechanism cannot account for the resistivity of (BEDT-TTF)$_2$I$_3$.

A different conclusion was reached by Bulaevskii [21], who obtains a value of ρ_{ee} five orders of magnitude larger. The difference lies in the value of $a_0 = \hbar^2\varepsilon_0/m^*e^2$ employed by Bulaevskii. Using his parameters $\varepsilon_0 = 1$, $m^* = 5m_0$, one obtains $a_0 = 0.1$ Å, and thus: $k_F a_0 \simeq 0.02$ (i.e. $r_s \simeq 100$). This value is an order of magnitude beyond the value that gives rise to a Wigner or a Mott transition. When one introduces this value of $k_F a_0$ 'mechanically' into the formulas that apply to the *metallic* state, one obtains highly anomalous results, namely the electron–electron scattering rate is increased by two to three orders of magnitude, and the Umklapp factor is about one (instead of 10^{-2}–10^{-3}), leading to a five-order enhancement of the resistivity.

We believe that the value of $a_0 \simeq 0.1$ Å is inappropriate for several reasons.

(i) a_0 is approximately the size of the molecular orbital, which is the size of the 'heterocyclic' region of the molecule (i.e. the two fivefold rings, without the saturated sixfold rings outside), i.e. about 2–3 Å. This follows from band calculations [26, 27] and is substantiated by measurements of spin density by NMR [28].

(ii) The value of the background dielectric constant $\varepsilon_0(\omega) \simeq 15$–$20$ was determined experimentally [25], leading to the 'appropriate' value of a_0.

(iii) When $a_0 k_F \simeq 0.02$, we are so far into the insulating (Wigner-lattice) state that we cannot use a 'metallic' formalism.

(iv) If $a_0 \simeq 0.1$ Å, and the separation between the electrons is approximately 6 Å, the overlap is so small that the effective mass (even in a one-electron picture) is virtually infinite, and not $5m_0$.

Regarding (ii), the dielectric constant is measured at microwave frequencies. At optical frequencies, we expect the dielectric constant to be much smaller. in particular, the measured plasma frequency of 0.6 eV [29] corresponds to a dielectric constant of $\varepsilon_0(\omega) \simeq 1$ at this frequency. The formula for the resistivity ρ_{ee} assumes that the electrons can be described by Fermi liquid theory; thus the relevant frequency for the electron–electron scattering is $k_B T$, i.e. not too far above the microwave frequency; thus the dielectric constant measured at microwave (rather than optical) frequencies is the relevant one.

In addition to these considerations, we believe that by invoking the electron–electron scattering mechanism to account for the resistivity of the BEDT-TTF radical salts (and other, similar organic metals), we encounter the following difficulties.

(a) This mechanism requires Umklapp processes to give rise to a resistivity. In 1D metals such as $TMTSF_2PF_6$ where $k_F = \frac{1}{4}\pi/a$, Umklapp processes are impossible. Yet the resistivity follows the T^2 law and is comparable to that of the BEDT-TTF radical salts.

(b) Experimentally, the resistivity of organic metals is extremely strongly pressure dependent [30]. The dependence of the electronic band width, plasma frequency, etc on pressure is far too weak to account for this strong pressure dependence. Also, under a pressure of 2.5 kbar, the $\rho \propto T^2$ law changes into a linear dependence $\rho \propto T$ in β-(BEDT-TTF)$_2$I$_3$ [5]. The pressure dependence was also invoked by Klipstein *et al* [13] to reject the electron–electron scattering mechanism for TiS_2, where there is also a T^2 law.

(c) There is a freezeout of the resistivity below 20 K (which corresponds to the measured phonon frequencies). This freezeout, the data for which we present in the present work, is inconsistent with the electron–electron scattering process.

4. Resistivity due to electron–phonon scattering

Electron–phonon scattering was proposed as the dominant mechanism for the resistivity of organic metals a long time ago [14, 19, 15]. The dilemma with this mechanism is the T^2 law.

Cooper suggested that the resistivity should be measured at constant volume, rather than at constant pressure; but the T^2 law is also observed below 100 K, where the constant-volume and constant-pressure resistivities are nearly identical. (Also, the constant-volume resistivity is in general *not* linear in T [31].) Gutfreund and Weger [19] suggested an inherent second-order mechanism involving the molecular librations. However, the T^2 law is observed in several other systems, such as TiS_2 [13], $NbSe_2$ (below 50 K) [32], intercalated graphite [8], Nb-doped $SrTiO_3$ [9], etc where we cannot invoke molecular librations.

One of the features favouring the electron–phonon scattering mechanism is the strong pressure dependence of the resistivity. Phonon frequencies of organic molecular crystals depend strongly on pressure, and the resistivity due to the 'standard' electron–phonon mechanism is proportional to $1/\omega_{\mathrm{ph}}^2$. Early measurements on TTF-TCNQ showed that the pressure dependence of the resistivity at ambient temperature is about twice as strong as that expected from $\rho \propto \omega_{\mathrm{ph}}^{-2}$ [30]. However, at low temperature ($T = 100$ K) the pressure dependence is considerably weaker. It was suggested that $\rho \propto \omega_{\mathrm{ph}}^{-4}$ for the second-order process. If we attribute the resistivity to a first-order electron–phonon process, we must invoke some other (i.e. electronic) mechanism that increases the pressure dependence of the resistivity at ambient temperature, and reduces it at low temperatures.

Recently, a novel mechanism involving an anomalous density of states with a minimum at E_F (that takes into account electron–electron interactions) was invoked to account for the resistivity of the cuprates as well as that of organic metals [33]. We present a heuristic description of this model in section 5. In this mechanism, $n(E) \propto |E|$ (E measured from E_F), therefore $1/\tau(E) \propto |E|$, the velocity $v(E) \propto 1/|E|$ and therefore the mean free path $l(E)$ has a sharp maximum at $E = 0$, leading to $\rho = A + BT$ for *elastic* scattering by impurities and defects (where the matrix element is temperature independent). For scattering by phonons, where (for $T > \frac{1}{2}\omega_{\mathrm{ph}}$, roughly) the *number* of scatterers is proportional to T, we obtain $\rho = CT^2$. Thus, when both defect and electron–phonon scattering are present, $\rho = A+BT+CT^2$, as observed in intercalated graphite [8], in the cuprates, and in irradiated or 'low-quality' $(\text{BEDT-TTF})_2I_3$ [34]. In good crystals of the organic compound, A and B are particularly small because of the high quality of the sample, and we obtain the T^2 law.

The magnitude of the resistivity is also in accord with a *reduction* in the scattering below the 'normal' elastic scattering or electron–phonon (i.e. Bloch) process, in accord with experiment.

Concerning the absolute value of the resistivity, at ambient temperature the measured resistivity (of the κ-phase sample of figure 2, i.e. 0.008 Ω cm) is not too far from the 'standard' theoretical value $\rho = m^*/ne^2\tau$, where $1/\tau = 2\pi\lambda k_B T/\hbar$, with the electron–phonon coupling constant $\lambda \simeq 1$–2. However, since $\rho \propto T^2$, the measured resistivity at low temperatures falls considerably below this standard theoretical value. (Since the lowest phonon frequency in BEDT-TTF radical salts is approximately 4 meV [35], the standard theoretical formula should hold down to about 20 K.)

A test for this novel mechanism is that the hopping resistivity ρ_c in the c direction, *increases* with increasing temperature, and the anisotropy $\rho_c/\rho_{ab} \simeq 1/T^\alpha$, with α being between 0.5 and 1, approximately. This behaviour is observed in cuprates, in TTF-TCNQ [36, 33], in C_8K [8] and $C_{24}BF_4$ [37], and in β-$(\text{BEDT-TTF})_2I_3$.

In this novel mechanism, the minimum in $n(E)$ at E_F (which was clearly seen by spectroscopic methods in some 1D organic metals [38]) is caused by a *maximum* in the velocity there. This sharp maximum is due to an anomalously high background dielectric constant $\varepsilon_0(q, \omega)$ at $q = 0$, $\omega = 0$. This background dielectric constant is due to states *excluding* the conduction band [39]. The sharp maximum of $\varepsilon_0(q, \omega)$ is expected to broaden under pressure, when the material becomes more metallic (i.e. further away from the Mott transition). This gives rise to a pressure dependence of the resistivity in addition to that caused by the pressure- dependence of the phonon frequencies. We illustrate this effect in figure 4. At low temperatures, i.e. temperatures below the width of the velocity peak, broadening of the peak as a result of pressure *lowers* the velocity v, thus the conductivity (which is proportional to v^2) is lower than we would expect for constant (i.e. pressure-independent) velocity. However, pressure increases the phonon frequencies, and thus decreases the scattering matrix element which is proportional to $1/\omega_{\mathrm{ph}}^2$. Thus, $\sigma \propto v^2\omega_{\mathrm{ph}}^2$ and may either increase or decrease under pressure, depending on whether the decrease of v^2 is larger, or smaller, than the increase of ω_{ph}^2. In any case, because of the partial cancellation of these two factors, the effect of pressure on σ at low temperatures is reduced. At high temperatures, i.e. temperatures higher than the width of the velocity peak, the broadening of the velocity peak under pressure *increases* v^2, thus the increase in v^2 and in ω_{ph}^2 under pressure reinforce each other, giving rise to a very large pressure dependence of the resistivity, as observed experimentally.

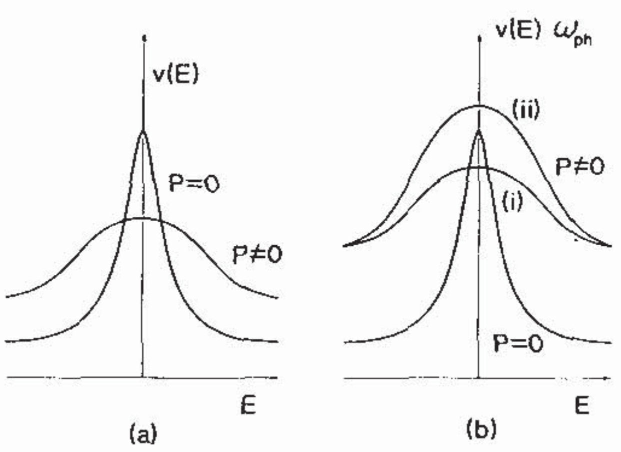

Figure 4. Carrier velocity $v(E)$ (where E is measured from the Fermi level) (*a*) and $v(E)\omega_{\mathrm{ph}}$ (ω_{ph} is the phonon frequency) (*b*) at ambient pressure ($P = 0$) and under pressure ($P \neq 0$) (schematic). The pressure dependence of $v(0)$ may be stronger (curve i) or weaker (curve ii) than that of ω_{ph}, thus the low-T resistivity may either increase or decrease under pressure, but in any case, the effect is weak. The ambient-temperature resistivity falls with increasing pressure much faster than the increase of ω_{ph}^2.

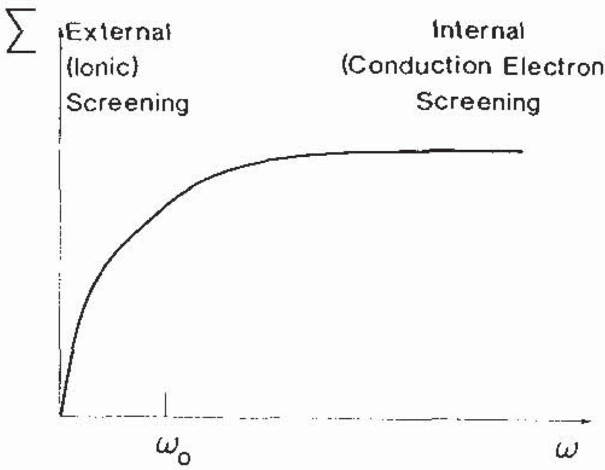

Figure 5. Illustration of the energy dependence of the Coulomb self-energy Σ for an electron gas imbedded in a background with a dielectric function $\varepsilon_0(\omega)$ that falls significantly at a frequency ω_0 ($\omega_0 \ll E_{\mathrm{F}}$). There is a cross-over from screening by the ionic polarization ($\omega < \omega_0$), to screening by the conduction electrons ($\omega > \omega_0$).

When the peak becomes broad, the resistivity changes from a T^2 to a T law, as observed in β-(BEDT-TTF)$_2$I$_3$ at a pressure exceeding 2.5 kbar [5].

For these reasons, we believe that the 'anomalous' electron–phonon mechanism can account for the following observations:

(1) the $\rho \propto T^2$ law;

(2) the freezeout of the resistivity below 20 K (which is about half the lowest optical phonon frequency);

(3) the magnitude of the resistivity;

(4) the extremely strong pressure dependence;

(5) the changeover to a $\rho \propto T$ law under pressure;

(6) analogy with several inorganic systems; and

(7) no need to invoke Umklapp processes.

5. Physical origin of the dip in the density of states

In a normal metal, scattering of electrons by phonons gives rise to a $\rho \propto T$ law. Here we suggest that in several systems, scattering by phonons gives rise to a $\rho \propto T^2$ law. This rather different behaviour is attributed to a deep and sharp minimum of the electronic density of states at the Fermi level. This dip is in turn attributed to a sharp maximum of the velocity at the Fermi surface (FS) (figure 4). Such a velocity maximum was predicted by Hartree–Fock theory for an unscreened electron gas [40], but was shown (using the RPA) to be absent when screening is taken into account [41]. We claim that in organic metals, as well as in several other systems, this velocity peak is present even if screening is taken into account.

The cause for this unusual behaviour is the dielectric function $\varepsilon_0(\omega)$ of the background (i.e. not considering the dielectric function of the conduction-band electrons). For several ionic crystals, $\varepsilon_0/\varepsilon_\infty$ is very large. (ε_∞ refers to a frequency substantially higher than the phonon frequencies.) This large value is due to the Coulomb forces beween the ions [42]. In metals, $\varepsilon_0/\varepsilon_\infty$ is usually close to one, because the Coulomb forces are screened by the electron gas. In several systems that are metallic, but very close to the Mott transition, it is found that $\varepsilon_0/\varepsilon_\infty$ is large; the density of the conduction electrons is not sufficient to effectively screen out the ionic potential. Specifically, in α-(BEDT-TTF)$_2$I$_3$, $\varepsilon_0 \simeq 20$ [22], while $\varepsilon_\infty \simeq 1$ [29]. ε_0 is apparently not much smaller in the other phases of (BEDT-TTF)$_2$X, which are metallic at low temperatures [43].

For electronic states very close to the FS, the Coulomb interaction is given by $e^2/\varepsilon_0 r_{12}$, which is very small because of the large value of ε_0. Thus, these states are very effectively screened by the background ionic polarization. Therefore, they behave like a non-interacting electron gas. In contrast, states that are removed from the FS by an energy $\hbar\omega$ in excess of the frequency ω_0 at which $\varepsilon_0(\omega)$ falls significantly, are not screened by the background (since the ionic polarization is unable to follow the high frequency), therefore the Coulomb interaction between these states is given by $e^2/\varepsilon_\infty r_{12}$, which is very large; since we are near the Mott transition, the Coulomb energy is comparable with the kinetic energy E_F. We illustrate the self-energy Σ due to the Coulomb interaction, as function of the distance $\hbar\omega$ from the Fermi level, in figure 5. We plot $\Sigma(k, \omega)$ along the physical line $\omega = \omega(k)$, i.e. we vary k as well as ω. We see that $\Sigma(\omega) - \Sigma(0)$ (for ω larger than the phonon frequencies, at which $\varepsilon_0(\omega)$ falls sharply) is large; it is somewhat smaller than, but of the order of, E_F. Therefore the slope $d\Sigma/d\omega$ at the origin is very large, of the order of E_F/ω_{ph}. This slope may be as large as 10. The electronic energy is given by $\hbar\omega = \hbar v_F^0(k - k_F) + \Sigma$ (v_F^0 is the unrenormalized Fermi velocity, i.e. the velocity obtained when the Coulomb interaction is neglected). Thus, the electronic group velocity $\partial\omega/\partial k$ is enhanced over v_F^0 by a factor of the order of 10. An explicit calculation shows that the width of this velocity maximum is about a factor of four less than the frequency ω_0 at which the background dielectric function falls by a factor of two [44]. This frequency in β-(BEDT-TTF)$_2$I$_3$ is about 4 meV [43], therefore the width of the velocity peak is expected to be about 1 meV, i.e. considerably less than the temperature of 20 K where the resistivity starts to freeze out.

6. Conclusion

We find experimentally that the resistivity of β- and κ-(BEDT-TTF)$_2$I$_3$ follows a $\rho \propto T^2$ law between 100 K and 20 K; below 20 K the resistivity falls below the T^2 law (freezes out). This behaviour contradicts the theoretical behaviour expected from the electron–electron scattering mechanism, but is in accord with scattering of electrons by phonons, possessing a frequency of about 4 meV.

We also consider the theory of the resistivity due to electron–electron scattering, and point out that the background dielectric constant ε_0 must be introduced into the appropriate formula, and the scattering rate is proportional to ε_0^{-2}. This dielectric constant was measured and found to be about 20. This reduces the scattering rate, as well as the Umklapp factor, by two to three orders of magnitude, giving a total effect about five orders of magnitude smaller than necessary to explain the observed T^2 behaviour.

Resistivity due to scattering of electrons by phonons accounts for the freezeout below 20 K, the pressure dependence of the resisitivity, and its value at 300 K; but would predict a linear $\rho \propto T$ law. A novel theory that takes into account electron–electron interactions predicts a modification of the dispersion $E(k)$ of the electrons very near the Fermi surface. This modifies the density of states $n(E)$ very close to E_F and accounts for the change from a $\rho \propto T$ to a $\rho \propto T^2$ law. This modification also causes the effective mass m^* to possess anomalously low values close to the Fermi level; such anomalous values were found recently by de Haas–van Alphen measurements [45], and indeed attributed to electron–electron interactions.

We point out analogous behaviour in several other systems, such as dichalcogenides, intercalated graphite, Nb-doped $SrTiO_3$, and in some respects, high-T_c cuprates.

Acknowledgments

The similarity between Nb-doped $SrTiO_3$ and the cuprates, as well as radical salts of BEDT-TTF, was pointed out to us by K A Muller.

The stay of M Weger in Stuttgart was supported by the Minerva Foundation.

References

[1] Groff R P, Suna A and Merrifield R P 1974 *Phys. Rev. Lett.* **33** 418
[2] Cooper J R, Jerome D, Weger M and Etemad S 1975 *J. Phys. Lett.* **36** L219
[3] Bechgaard K, Jacobsen C S, Mortensen K, Pedersen H J and Thorup H 1980 *Solid State Commun.* **33** 1119
[4] Kahlich S, Schweitzer D and Keller H J 1990 *Solid State Commun.* **76** 933
[5] Weger M, Bender K, Klutz T, Schweitzer D, Gross F, Heidmann C P, Probst Ch and Andres K 1988 *Synth. Met.* **25** 49
[6] Weger M, Kaveh M and Gutfreund H 1981 *Solid State Commun.* **37** 421
[7] Thompson A H 1975 *Phys. Rev. Lett.* **35** 1786
[8] Dresselhaus M S and Dresselhaus G 1981 *Adv. Phys.* **30** 139
Murray J J and Ubbelohde A R 1969 *Proc. R. Soc.* A **312** 371
[9] Baratoff A and Binnig G 1981 *Physica* B **108** 1335
[10] Baber W G 1937 *Proc. R. Soc.* A **158** 383
[11] Seiden P E and Cabib D 1976 *Phys. Rev.* B **13** 1846
[12] Ziman J M 1962 *Electrons and Phonons* (Oxford: Clarendon)
[13] Klipstein P C, Bagnall A, Liang W Y, Marseglia E A and Friend R H 1981 *J. Phys. C: Solid State Phys.* **14** 4067
[14] Cooper J R 1979 *Phys. Rev.* B **19** 2404
[15] Conwell E M 1980 *Phys. Rev.* B **22** 1761
[16] Rashba E I, Gogolin A A and Melnikov V I 1977 *Organic Conductors and Semiconductors (Lecture Notes in Physics 65)* (Berlin: Springer) p 265
[17] Cohen M H 1977 *Organic Conductors and Semiconductors (Lecture Notes in Physics 65)* (Berlin: Springer) p 225
[18] Staib A G and Bohm M C 1989 *J. Chem. Phys.* **91** 4961

[19] Gutfreund H and Weger M 1977 *Phys. Rev.* B **16** 1753
Gutfreund H, Hartzstein C and Weger M 1980 *Solid State Commun.* **36** 647

[20] Bulaevskii L N, Ginodman V B, Gudenko A B, Karkovnik M V, Kononovich P A, Laukhin V N and Schegolev I F 1987 *Zh. Eksp. Teor. Fiz.* **94** 285 (Engl. Transl. *Sov. Phys.–JETP* **67** 810)

[21] Bulaevskii L N 1988 *Adv. Phys.* **37** 443

[22] Bender K, Heinen I, Schweitzer D, Dietz K, Enders H and Keller H J 1984 *Mol. Cryst. Liq. Cryst.* **108** 359

[23] Balthes E, Breining A, Kahlich S, Moldenhauer J, Schweitzer D, Bele P, Brunner H, Heinen I, Nuber B and Keller H J 1993 *Synth. Met.* **56** 2859

[24] Kajita K, Nishio Y, Moriyama S and Sasaki W 1987 *Solid State Commun.* **64** 1279

[25] Bender K, Dietz K, Enders H, Helberg H W, Hennig I, Keller H J, Schaffer H W and Schweitzer D 1984 *Mol. Cryst. Liq. Cryst.* **107** 45

[26] Mori T, Kobayashi A, Sachi Y, Kobayashi H, Saito G and Inokuchi H 1984 *Chem. Lett.* 957

[27] Kubler J, Weger M and Sommers C B 1987 *Solid State Commun.* **62** 801

[28] Klutz T, Hennig I, Haeberlen U and Schweitzer D 1991 *Appl. Magn. Resonance* **2** 441

[29] Nucker N, Fink J, Schweitzer D and Keller H J 1986 *Physica* B **143** 482

[30] Gutfreund H, Weger M and Kaveh M 1978 *Solid State Commun.* **27** 53

[31] Kaveh M and Weger M 1979/1980 *Synth. Met.* **1** 385

[32] Edwards J and Frindt R F 1971 *J. Chem. Phys. Solids* **32** 2217

[33] Weger M and Wohlleben D 1992 *Z. Phys.* **B 87** 143
Weger M 1991 *Physics and Material Science of High Temperature Superconductors II (NATO ASI E 209)* ed R Kossowsky (Dordrecht: Kluwer)
Weger M and Burlachkov L 1993 *Physics of Transition Metals* ed P M Oppeneer and J Kubler (Singapore: World Scientific) p 87

[34] Dolanski-Babic B, Biskup N, Tomic N and Schweitzer D 1992 *Phys. Rev.* B **46** 11 765

[35] Pokhodnia K I, Graja A, Weger M and Schweitzer D 1993 *Z. Phys.* B **90** 127

[36] Weger M 1978 *J. Physique* **39** C6 1456

[37] Brusilovsky D, Selig H, Vaknin D, Ohana I and Davidov D 1988 *Synth. Met.* **23** 377

[38] Grobman W D, Pollak R A, Eastman D E, Maas E T and Scott B A 1974 *Phys. Rev. Lett.* **32** 534
Nielsen P, Epstein A J and Sandman D J 1974 *Solid State Commun.* **15** 53
Dardel B, Maltere D, Grioni M, Weibel P, Baer Y and Levy F 1991 *Phys. Rev. Lett.* **67** 3144

[39] Weger M, Burlachkov L and Kaveh M 1992 *Europhys. Lett.* **19** 505
Burlachkov L and Weger M 1993 *Physica* B **183** 283
Weger M and Burlachkov L 1993 *Physica* C **209** 129

[40] Lindhard J 1954 *K. Danske Viedensk. Selsk. Mat.-Fys. Meddr. (Skr.)* **28** No 8

[41] Ashkroft N W and Mermin N D 1976 *Solid State Physics* (Philadelphia, PA: Holt Saunders) ch 17

[42] Born M and Huang K 1954 *Dynamical Theory of Crystal Lattices* (Oxford: Clarendon)

[43] Dressel M, Gruner G, Pouget J P, Brening A, Schweitzer D *J. Physique* submitted

[44] Weger M and Burlachkov L *Physica* B submitted

[45] Toyota N, Fenton E W, Sasaki T and Tachiki M 1989 *Solid State Commun.* **72** 859
Singleton J, Pratt F L, Doporto M, Janssen T J B M, Hayes W, Perenboom J A A J, Kurmoo M and Day P 1992 *Phys. Rev. Lett.* **68** 2500