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The localization–interaction model applied to the direct-current conductivity of metallic conducting polymers

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Abstract. The low-temperature DC-transport properties of doped conducting polymers on the metallic side of the metal–insulator transition are analysed with modern localization–interaction theories. The DC conductivity at the lowest temperatures is governed by the 3D electron–electron interaction formula $\sigma = \sigma_0 + mT^{1/2}$, while the magnetoconductance is an interplay between electron–electron interaction and weak-localization contributions. The transition from negative to positive temperature coefficient of resistivity, below 20 K, can be explained by the sign change in the interaction coefficient m . On the basis of experimental data it is shown that the resistivity ratio ρ_r ($\rho_r = \rho(T \cong 1 \text{ K})/\rho(300 \text{ K})$) is a controlling factor in determining the sign and magnitude of these effects. Furthermore, the normalization of relevant coefficients (e.g. m) with σ_0 gives the result that the relative size of the effects is independent of the degree of chain orientation, and therefore the conductivity. However, it is found that the coefficient m crosses from negative to positive values at different values of ρ_r for oriented and non-oriented conducting polymers. The positive magnetoconductance stemming from weak localization is substantial and very anisotropic in highly oriented conducting polymers. It is shown that this positive magnetoconductance exhibits a maximum as a function of ρ_r in the vicinity of the metal–insulator transition. These results are compared with transport in other types of disordered metal.

1. Introduction

The remarkable improvement in recent years in the structural and morphological order achieved in several conducting polymers has provided the opportunity to investigate the metallic properties in the doped state of these systems (Reghu 1997, Reghu *et al* 1998). The room temperature conductivity (σ) of typical isotropic (unoriented) conducting polymer is of the order of 10^2 S cm^{-1} , while for highly oriented polymers the conductivity along the chain axis is of the order of 10^4 S cm^{-1} with an anisotropy of the conductivity of around 100. To date, a metallic state has been observed in six different conducting polymers, listed in table 1. The typical features for these systems are a large finite conductivity at low temperatures, free-carrier absorption in the infrared, a linear temperature dependence of the thermopower, temperature-independent Pauli susceptibility down to 20 K, positive and negative magnetoconductance (MC), and a positive temperature coefficient of W ($W = d \ln \sigma / d \ln T$). The charge carrier density in fully doped metallic conducting polymers is of the order of 10^{21} cm^{-3} (Reghu *et al* 1998). These facts are consistent with a metallic state relatively close to the metal–insulator (M–I) transition. Generally, the

temperature coefficient of resistivity (TCR) is negative, even for metallic samples. The resistivity ratio ρ_r ($\rho_r = \rho(1.3 \text{ K})/\rho(300 \text{ K})$) is then larger than unity, but normally less than 10 in the metallic regime. Furthermore, for the most metallic samples the TCR is positive in the low-temperature limit.

Table 1. Conducting polymers in which a metallic state has been observed in the doped state.

Polymer	Abbreviation	Repeat unit	Orientability	Crystallinity ^a	Conductivity ^b
Polyacetylene	(CH) _x	C ₂ H ₂	High	80%	10 ⁴ –10 ⁵
Poly(p-phenylenevinylene)	PPV	(C ₆ H ₄)C ₂ H ₂	High	80%	10 ⁴
Polyaniline	PANI	(C ₆ H ₄)NH	Low	50%	400
Polypyrrole	PPy	C ₅ H ₂ N	Low	50%	400
Poly(3, 4-ethylenedioxythiophene)	PEDOT	C ₇ H ₄ O ₂ S	Low	40%	300
Poly(3-methylthiophene)	PMT	(C ₅ H ₂ S)CH ₃	Low	40%	400

^a Approximate values for high-quality samples. For references, see Reghu *et al* (1998) ((CH)_x, PPV, PANI, PPy), Aleshin *et al* (1997a, b) (PEDOT), and Masubuchi *et al* (1997) (PMT).

^b In S cm⁻¹. The values give approximately the highest observed values. In the cases of (CH)_x and PPV, the conductivity in the highly oriented state along the direction of the chain alignment is given.

Although a considerable amount of work on the charge transport and the M–I transition in conducting polymers has been published, the real nature of the metallic state in these systems remains a topic of interest and controversy. The main reasons for the lack of consensus are the difficulties in understanding the roles played by the intrinsic quasi-one-dimensionality of polymeric chains and the inherent presence of disorder in polymeric materials. In a previous generation of conducting polymers (1977–90) the extent of disorder was rather substantial, and the metallic state was rarely observed. The heterogeneous model proposed by Kaiser and Graham (1990) was quite appropriate for such systems. However, in the new generation of conducting polymers the extent of disorder is considerably less and the hidden metallic features of conducting polymers have become more apparent.

Nevertheless, it is argued that the nature of disorder is such that these systems cannot be considered as fairly homogeneous (see Kohlman *et al* (1997) and references therein). A two-fluid model was proposed in which a small fraction of carriers (nearly 1%) are highly delocalized through the crystalline domains, having an extraordinarily large mean free path of the order of a micron (and a relaxation time $\sim 10^{-11}$ s), and the rest of the carriers are localized in the amorphous domains consisting of weakly interacting quasi-one-dimensional chains. In this inhomogeneous model the M–I transition can be described in terms of percolation between metallic islands (i.e. crystalline domains). However, the counter-argument (Reghu 1997, Reghu *et al* 1998) suggests that, if the average correlation length on the metallic side (or the localization length on the insulating side) is larger than or nearly equal to the average crystalline coherence length, then the system can be considered as fairly homogeneous. In other words, if the wavefunctions of the delocalized states overlap rather well (i.e. random fluctuations of the disorder potentials are within the homogeneous limit), then the carrier transport is nearly coherent and the transport properties of the polymer resemble those of a disordered metal. In this disorder-induced-localization model the M–I transition can be described by the Anderson transition (Lee and Ramakrishnan 1985). Moreover, in high-quality conducting polymers, the so-called crystalline and amorphous domains are not really segregated; rather, the long- and short-range-ordered domains form

an interpenetrating ensemble.

In several disordered systems near the M–I transition the transport properties are described by the localization–interaction model (Lee and Ramakrishnan 1985). In early efforts Thummes *et al* (1988) and Nogami *et al* (1991) used this model to interpret the conductivity and MC data for metallic $(\text{CH})_x$. Later, this model was found to be appropriate for other conducting polymer systems near the M–I transition (Reghu 1997, Reghu *et al* 1998), explaining in a consistent manner the temperature dependence of the conductivity, MC, high-frequency behaviour, etc. In this paper we will present the pertinent experimental data on low-temperature DC transport in metallic conducting polymers published to date and present new features and unifying concepts, using the localization–interaction model. It will be shown that the sign and magnitude of the TCR are controlled by the resistivity ratio ρ_r and behave in part differently for oriented and non-oriented samples. The positive MC which is observed in highly oriented polymers is also analysed as a function of ρ_r , and shown to exhibit a maximum close to the M–I transition boundary. We will present our data analysis by making extensive use of normalization with respect to the low-temperature conductivity which will enable us to better compare oriented and non-oriented polymers. Comparison with other disordered metals will also be made.

2. Theoretical background

The localization–interaction model describes electronic transport in homogeneously disordered metals (Lee and Ramakrishnan 1985). The model gives quantum mechanical corrections to the semiclassical Boltzmann conductivity which arise in sufficiently disordered metals at low temperatures. These corrections are weak localization (WL), which is an interference phenomenon which tends to localize the electron wavefunction, and electron–electron interaction (EEI), which follows from the enhanced interaction between partly localized electrons. These effects have been thoroughly investigated for systems like thin metal films, highly doped semiconductors, amorphous alloys, and semiconductor heterostructures. Quasicrystals and highly doped conducting polymers are less familiar systems. Both EEI and WL theories are derived in the weak-disorder limit, $k_F l \gg 1$, where k_F is the Fermi wave vector and l the mean free path. In the approximation usually made, their effects on the conductivity are additive. The MC is especially useful for separating the two effects. The theory of EEI in the 3D case gives the correction to the zero-temperature conductivity as (Lee and Ramakrishnan 1985, Dai *et al* 1992)

$$\sigma = \sigma_0 + mT^{1/2} + BT^{p/2} \quad m = \alpha[(4/3) - \gamma(3F_\sigma/2)] \quad (1)$$

where σ_0 is the zero-temperature conductivity, the second term is due to EEI, and the third term is due to WL. For the latter, p is determined by the temperature dependence of the scattering rate of the dominant dephasing mechanism. For EEI, α is inversely proportional to the diffusion coefficient (D), and γ is a parameter dependent on details of the electronic structure. F_σ is a complicated but monotonic function of the screening wave vector K (see Lee and Ramakrishnan (1985), Dai *et al* (1992) and references therein). A small screening length K^{-1} implies a larger F_σ and vice versa. Well inside the metallic regime, where F_σ is large, the expression $((4/3) - \gamma(3F_\sigma/2))$ is negative. As the M–I transition is approached, K^{-1} diverges and F_σ decreases, causing a sign change in m . Since α is proportional to $D^{-1/2}$, and thus to $\sigma_0^{-1/2}$, this gives a contribution to m which increases in magnitude as the M–I transition is approached. A multitude of experimental data on heavily doped semiconductors suggest the following overall behaviour of m as a function of the dopant concentration n (Dai *et al* 1992, Rosenbaum *et al* 1983). Deep in the metallic regime, with

high n , the m -value is negative and grows in magnitude as n decreases. This has been explained as an increase in the magnitude of α . Eventually m will reach a minimum and start increasing. A zero-point crossing will occur and m will attain positive values. This latter behaviour is seen to reflect the divergence of the screening length K^{-1} , causing a sign change in the bracketed factor of m , and thus of m itself. EEI theory (calculated from the particle-hole channel (Lee and Ramakrishnan 1985)) predicts a negative MC, where the low- and high-field limits are separated by the Zeeman splitting energy ($g\mu_B H = k_B T$, where g is the electron gyromagnetic ratio, μ_B the Bohr magneton, and H the magnetic field intensity). Often the EEI contribution to the MC becomes important with respect to the WL contribution only when the high-field condition applies ($H/T > k_B/g\mu_B$).

The WL correction to σ_0 is controlled by the phase-coherence time (Bergmann 1984). Different phase-breaking processes have characteristic phase-coherence (scattering) times, or alternatively scattering lengths, such as the temperature-dependent inelastic scattering time (τ_i) and spin-dependent scattering times. The WL contribution to the temperature dependence of the conductivity is then determined by the temperature dependence of the scattering time (parameter p in equation (1)). However, its contribution to the low-temperature TCR is small for conducting polymers (Ahlskog *et al* 1996). Taking into account only the former, the WL magnetoconductance in 3D is given as (Lee and Ramakrishnan 1985, Kawabata 1980a)

$$\Delta\sigma(H) = \sigma(H) - \sigma(H = 0) = (e^2/2\pi^2\hbar)\sqrt{(eH/\hbar c)}f(x) \quad (2)$$

where $x = \hbar c/(4eHl_i^2)$, l_i is the inelastic scattering length, and $f(x)$ has the asymptotic forms $f(x) = 0.605$, $x \ll 1$, and $f(x) = x^{-3/2}/48$, $x \gg 1$. The asymptotic field dependencies are H^2 for low fields and $H^{1/2}$ for high fields. This basic formula which assumes the absence of spin-dependent scattering processes has been quite successful for many conducting polymers (Reghu 1997, Reghu *et al* 1998). The WL magnetoconductance is then exclusively positive and becomes in the high-field limit

$$\Delta\sigma(H) = B_{WL}H^{1/2} \quad (3)$$

where the prefactor B_{WL} is a constant. It has an estimated value for isotropic material of the order of magnitude of $1 \text{ S cm}^{-1} \text{ T}^{-1/2}$. The case of an anisotropic system has been discussed (Kawabata 1980b) and also applied to conducting polymers. The prefactor has been found to be considerably larger for oriented conducting polymers than when the conductivity is along the direction of the chain alignment. A correction term for the prefactor which takes into consideration the uniaxial symmetry of polymers was introduced by Nogami *et al* (1991): equation (3) is then multiplied by $(D_{\parallel}/D_{\perp})^{2/3}$, where D_{\parallel} and D_{\perp} are the parallel and perpendicular diffusion coefficients, respectively. Another consequence of the chain orientation is the anisotropy of the MC; the positive MC due to WL is much stronger with the field perpendicular to the direction of the chain alignment than with the field parallel to it. This is a general feature due to the orbital character of the WL effect and has been observed in several other systems (Bergmann 1984).

3. Results and discussion

3.1. The temperature coefficient of resistivity (TCR) at low temperatures

Figure 1 shows the temperature-dependent conductivity of two samples of highly oriented PPV-H₂SO₄ (H₂SO₄ is the dopant) in which one sample shows a positive TCR below 20 K. The values of ρ_r for samples showing positive and negative TCR are 1.07 and

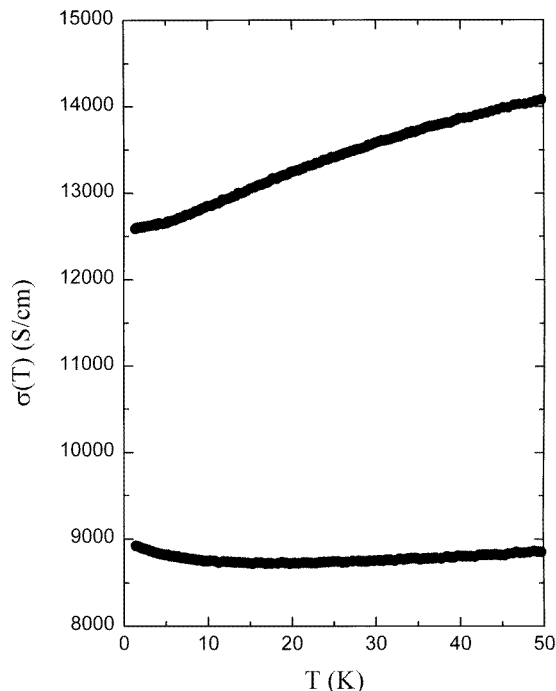


Figure 1. The temperature-dependent conductivity of highly oriented PPV-H₂SO₄ (Ahlskog *et al* 1996). The samples have ρ_r -values of 1.07 (lower curve) and 1.21 (upper curve).

1.21, respectively. The behaviour of $\sigma(T)$ for both samples can be fitted to equation (1), suggesting that both WL and EEI corrections contribute to the low-temperature conductivity. Usually the WL and EEI contributions are dominant at higher and lower temperatures, respectively. The data indicate that the sign change of m (and thus of the TCR) is rather sensitive to the extent of disorder and the associated screening process since the samples are from the same batch and have been measured after identical doping processes. A more detailed discussion on transport in PPV-H₂SO₄ can be found in the work of Ahlskog *et al* (1996). In this section we will discuss the sign and magnitude of the low-temperature TCR for metallic conducting polymers in general.

Figure 2 shows the m -factor (equation (1)) normalized with respect to σ_0 ($m \rightarrow m/\sigma_0$) for several well investigated doped polymer systems. The data have been taken from the relatively few cases in which measurements for several samples of the same polymer have been made at low temperatures ($T < 4.2$ K). The filled symbols indicate unoriented samples of PPy and PEDOT which have been made by the same electrochemical technique (Sato *et al* 1991) using different dopants. The data fall roughly on a common curve. The zero crossing of m occurs at $\rho_r \cong 2.3$. Masubuchi *et al* (1997) presented similar data on PMT-PF₆, which also exhibits metallic conductivity and a positive TCR at low temperatures. The sign change of m occurs at approximately the same value of ρ_r as for PPy and PEDOT. All of these polymers are unoriented. The open symbols indicate data for the highly oriented conducting polymers PPV-H₂SO₄ (Ahlskog *et al* 1996, 1997) and (CH)_x-I₂ (Nogami *et al* 1991). While the magnitudes of the normalized m -values are the same, the difference is obvious; the zero crossing occurs at a distinctly lower value of $\rho_r \cong 1.2$. The zero crossing is observed only for PPV-H₂SO₄ but the behaviour of the data for (CH)_x-I₂ strongly suggests

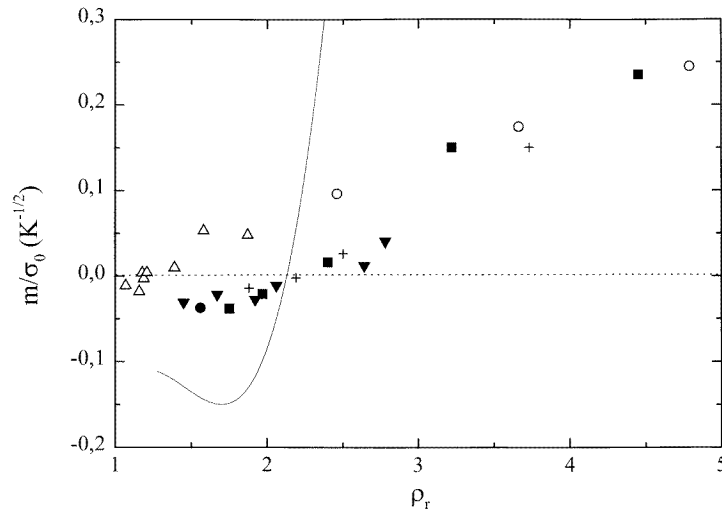


Figure 2. The temperature coefficient of resistivity m obtained from the EEI formula (see equation (1)) normalized with respect to the zero-temperature conductivity σ_0 as a function of the resistivity ratio ρ_r for different doped conducting polymers: (Δ) PPV- H_2SO_4 (Ahlskog *et al* 1996, 1997), (\circ) $(\text{CH})_x\text{-I}_2$ (Nogami *et al* 1991), (\blacksquare) PPy- PF_6 (Yoon *et al* 1994), (\blacktriangledown) PEDOT- PF_6 (Aleshin *et al* 1997b), (+) PEDOT- BF_4 (Aleshin *et al* 1997a), (\bullet) PEDOT- CF_3SO_3 (Aleshin *et al* 1997a). The solid line is a fit to corresponding data for heavily boron-doped silicon (Si:B) from the work of Dai *et al* (1992).

that a zero crossing would also occur for this compound at a low value of ρ_r . Madsen *et al* (1989) presented data on the temperature-dependent conductivities of a series of samples of oriented PPV- AsF_5 . While the data extend down to only 4.2 K, accurate values of m cannot be obtained, but it is clear that the zero crossing occurs at $\rho_r \cong 1.7$.

The solid line shows comparable data for heavily boron-doped silicon, Si:B, which is among the more intensively studied doped semiconductor materials. It exhibits both of the characteristic features of m in the metallic regime: the increase of the negative magnitude of m as the M-I transition is approached and the subsequent drastic change in its sign. The sign change occurs at a value of ρ_r close to the one for unoriented polymers. The magnitude of the normalized value m/σ_0 for conducting polymers is limited to a narrower range, -0.1 – $0.2 \text{ K}^{-1/2}$, than the values for doped semiconductors, -0.5 – $1.0 \text{ K}^{-1/2}$. It is notable that there are no obvious differences in magnitude between oriented and unoriented conducting polymers, even though the former have a conductivity two orders of magnitude higher. A major difference between conducting polymers and doped semiconductors is the substantially higher carrier density in the former (three orders of magnitude higher). It is interesting to compare m/σ_0 further with the values for isotropic materials which have a similar carrier density and value of ρ_r , such as amorphous alloys and quasicrystals. The normalized negative m given by Klein *et al* (1992) for the quasicrystal $\text{i-Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$ is $-0.037 \text{ K}^{-1/2}$, while for amorphous $\text{Ni}_x\text{Si}_{1-x}$ alloys (Rosenbaum *et al* 1997) positive values in the range 0.01 – $0.1 \text{ K}^{-1/2}$ (with x in the range 0.25 – 0.39) can be found[†]. These values are in the same range as for most of the conducting polymers discussed in this work,

[†] Very systematic studies on the m -values for quasicrystals are not available yet, to our knowledge. According to Rosenbaum *et al* (1997), $\text{Ni}_x\text{Si}_{1-x}$ is a representative example of an amorphous alloy for which superconductivity and inhomogeneity do not complicate the transport near the M-I transition boundary.

supporting the assumption that the carrier density plays a role in determining the magnitude of m/σ_0 . It also seems quite clear from the data on the unoriented polymers that a maximum in the magnitude of m (or m/σ_0) on the negative side is reached at $\rho_r \cong 1.5$, which is to be expected in view of the well documented behaviour of doped semiconductors.

Finally, we note that the essential reason for the difference between the values of ρ_r for the examples presented of oriented and non-oriented conducting polymers at the sign change of m remains unknown. Still, *the data presented show clearly that the m -value is a characteristic function of ρ_r for different classes of conducting polymers, that m changes sign from positive to negative as ρ_r decreases, and that the degree of chain orientation is likely to play a significant role in determining this behaviour.*

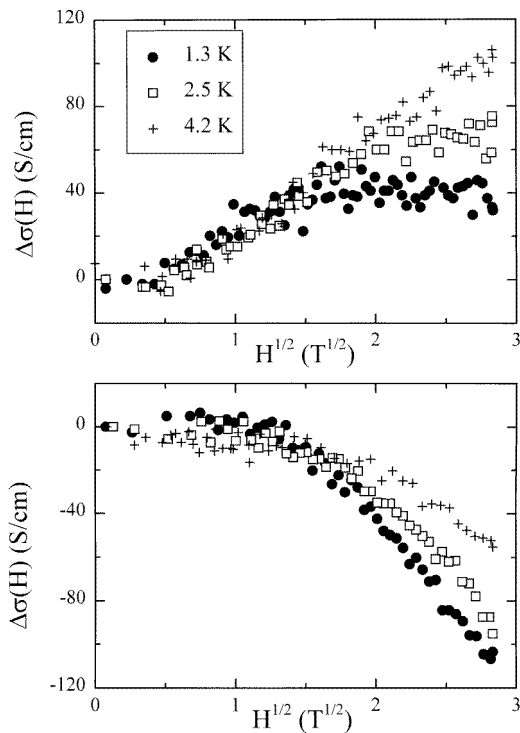


Figure 3. The magnetoconductances of two samples of highly oriented PPV-H₂SO₄, with the magnetic field perpendicular to the chain axis (upper panel, $\rho_r = 1.07$), and parallel to the chain axis (lower panel, $\rho_r = 1.25$).

3.2. Positive magnetoconductance in oriented conducting polymers

The MC is a sensitive local probe for investigating the validity of using the localization–interaction model for any type of disordered electronic system (Lee and Ramakrishnan 1985, Bergmann 1984). Detailed studies of the MC in several conducting polymers have been reported. There is a clear difference between the MC properties of oriented and unoriented conducting polymers. The former exhibit strong positive MC due to WL (with the magnetic field perpendicular to the direction of the chain alignment) at temperatures of a few degrees Kelvin while, consistently, the MC has been found to be negative in unoriented polymers at these temperatures. As has been discussed before, MC in conducting polymers is an

interplay between WL and EEI, and, in the case of these materials, with the simplifying feature that the positive MC stems from WL while the negative MC arises exclusively from EEI (in the absence of spin-orbit interaction). However, for oriented conducting polymers the sign of the MC depends on the angle between the magnetic field and the chain axis. This anisotropic MC in oriented samples is due to the anisotropy of the WL, since the positive MC due to WL is maximized with the field perpendicular to the chain axis (Ahlskog *et al* 1996, Reghu *et al* 1994, Ahlskog and Reghu 1998). This is clearly seen in figure 3, where the MC of highly oriented metallic samples of PPV-H₂SO₄ is plotted on an $H^{1/2}$ -scale. In the upper (lower) figure the MC is positive (negative) when the magnetic field is perpendicular (parallel) to the chain axis. The WL magnetoconductance is difficult to analyse accurately with the available data. Using the low-field formula, equation (2), one obtains an estimate of 10^{-5} cm for the inelastic scattering length. Using the relation $\sigma = e^2 N(E_F) D$, where $N(E_F)$ is the density of states at the Fermi surface, the low-temperature diffusion coefficient becomes $1-10$ cm² s⁻¹ in the parallel direction for oriented polymers ($D = D_{\parallel}$). One then obtains (from the formula $\tau_i = \sqrt{l_i^2/D}$) the value $10^{-10}-10^{-11}$ s for τ_i . Similar values have been observed also for PANI (Reghu *et al* 1993) and (CH)_x-I₂ (Reghu *et al* 1994); they are quite typical for amorphous alloys and quasicrystals. At temperatures above 1 K (up to ~ 10 K) the positive MC is rather temperature independent (Ahlskog and Reghu 1998). The high-field positive MC shown in figure 3 (upper figure) follows well the $H^{1/2}$ -behaviour predicted by equation (3), which also implies a temperature-independent behaviour of the high-field WL contribution to the MC. In the following, the experimentally observable positive MC in highly oriented conducting polymers will be discussed in relation to ρ_r in a similar manner to the low-temperature TCR.

First we will address the question of how to represent the positive MC due to WL. A simple and rather effective way is to obtain the quantity $\Delta\sigma(H, T)/\sigma(H = 0, T)$ at a value of T such that EEI effects are negligible ($g\mu_B H < k_B T$), and with H such that one is in the high-field-regime (equation (3)). However, the positive MC saturates at different points at different temperatures and variably from sample to sample, depending largely on ρ_r . The temperature-independent behaviour of the WL component of the MC means, more to the point, that B_{WL} in equation (3) exhibits only a small temperature dependence. This behaviour has been observed for both PPV-H₂SO₄ and (CH)_x-I₂. The single parameter B_{WL} thus represents the magnitude of the positive MC due to WL. Furthermore, since the conductivity of oriented polymers varies by at least one order of magnitude, we will normalize B_{WL} with respect to the conductivity, for similar reasons to those for normalizing the interaction parameter m in the previous section. We will analyse B_{WL} as a function of ρ_r .

In figure 4, normalized values of B_{WL} , B_{WL}/σ , are shown for highly oriented samples of PPV-H₂SO₄ and (CH)_x-I₂ (Nogami *et al* 1991, Ahlskog *et al* 1997, Ahlskog 1995). The normalization is carried out with respect to the conductivity at the temperature at which B_{WL} has been taken[†]. B_{WL}/σ for PPV-H₂SO₄ clearly shows a strongly increasing behaviour as the M-I transition is approached, while the data for (CH)_x-I₂ show decreasing behaviour at higher values of ρ_r . For the samples of (CH)_x-I₂, it is not clear whether the one with the highest ρ_r was metallic, but certainly it is very close to the M-I transition boundary. For PPV-H₂SO₄ the M-I transition occurs in the interval $2 < \rho_r < 5$. Beyond this, on the insulating side of the M-I transition the MC is negative and huge in magnitude for both PPV-H₂SO₄ and (CH)_x-I₂ (Reghu 1997, Reghu *et al* 1998). In

[†] The data were taken at 4.2 K for PPV-H₂SO₄ and 7 K for (CH)_x-I₂, and below 8 T. The magnetic field was perpendicular to the direction of the chain alignment.

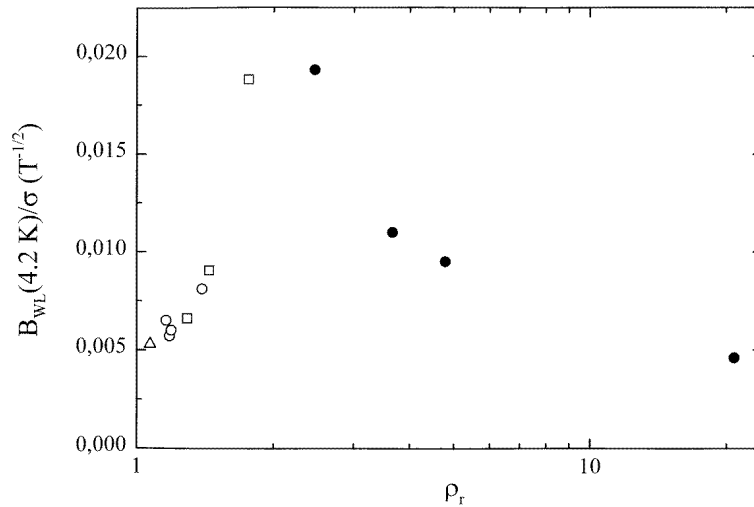


Figure 4. The coefficient of the high-field positive MC, B_{WL} (see equation (3)), normalized with respect to the conductivity as a function of the resistivity ratio ρ_r , for PPV-H₂SO₄ (open symbols) (Ahlskog *et al* 1996, 1997) and (CH)_x-I₂ (solid symbols) (Nogami *et al* 1991). For PPV-H₂SO₄ different symbols identify separate samples, while for (CH)_x-I₂ the symbols are all for separate samples.

terms of $\Delta\sigma(H = 8T)/\sigma(H = 0)$, for both PPV-H₂SO₄ and (CH)_x-I₂, low values of B_{WL}/σ correspond to a change in conductivity at 8 T of less than 1%, while the highest values correspond to a change $\cong 4\%$. Thus we conclude that a maximum in the positive MC and a subsequent decrease as a function of the resistivity ratio occur in the vicinity of the M-I transition. The (CH)_x-I₂ samples had higher absolute values of B_{WL} than those of PPV-H₂SO₄, with a factor which varies in the range 1.5–10, which clearly follows from the similarly higher conductivity. However, the normalized values are in the same range. This again shows that the interesting quantity is the normalized value of B_{WL} .

In the case of the (CH)_x-I₂ samples for which results are shown in figure 4, Nogami *et al* (1991) also measured the MC with the field parallel to the direction of the chain alignment. The high values for ρ_r , and the high positive magnitude of m/σ_0 along with the decrease of the positive MC show that these samples are very near to the M-I transition where the WL mechanism breaks down. As was mentioned above and shown by Ahlskog *et al* (1996), the anisotropy of highly oriented polymers directly affects the WL mechanism, giving stronger positive perpendicular MC than parallel MC. It is then expected that this anisotropy also vanishes. This is roughly observed for the four (CH)_x-I₂ samples presented here. For the sample with the highest ρ_r , there is hardly any anisotropy observable. As was mentioned in the theory section, in the anisotropic WL mechanism the perpendicular MC is quantitatively enhanced by the factor $(D_{\parallel}/D_{\perp})^{2/3}$. The decrease of the anisotropy would then imply a faster decrease of the parallel diffusion coefficient (D_{\parallel}) compared to that of the perpendicular one (D_{\perp}) as the M-I transition is approached.

Observations of extremal behaviour in the MC in the vicinity of the M-I transition have rarely been made previously. Other examples are a maximum in the negative MC for Ni_xSi_{1-x} (Abkemeier *et al* 1992), attributed to both EEI and WL, and a maximum in the positive MC for In₂O_{3-x} thin films (Faran and Ovadyahu 1988). The latter was interpreted similarly to the case presented here: WL controlled by the inelastic scattering length. The

size of the effect at the maximum, about 6%, is roughly the same as that presented in this work. Furthermore, an analogous anisotropy in the WL mechanism (with respect to the plane of the film) giving the positive MC was observed to develop as a function of the distance to the boundary between the weak- and strong-localization regimes, which corresponds to the M–I transition boundary in 3D systems. As was pointed out by Rosenbaum *et al* (1997), theoretically this behaviour is not well understood, since WL theories are, if strictly interpreted, applicable only in the weak-disorder limit. The phenomena described here occur in materials where $k_F l \cong 1$ —that is, not in the limit of weak disorder.

4. Conclusions

Several metallic conducting polymers have been studied in recent years. The behaviour of the conductivity at low temperatures can be well explained by the localization–interaction model for these materials. A very prominent feature is the sign change in the TCR below 20 K which can be explained by the sign change in the electron–electron interaction parameter m , and is likely to be associated with the subtle variations in the underlying screening process due to disorder. We have shown that the sign change is intimately connected with the value of ρ_r , and in this respect differentiates between oriented and non-oriented conducting polymers. In the highly oriented polymers a strong positive and anisotropic MC is observed which is attributed to WL. It was shown that this positive MC is also a function of ρ_r and exhibits a maximum close to the M–I transition boundary. Due to the possibility of chain alignment in some conducting polymers, the values of the conductivity vary significantly. We introduced in our analysis a normalization of some key parameters (m , B_{WL}) with respect to the low-temperature conductivity, which enabled us to treat the DC transport in oriented and non-oriented polymers in a more unified manner.

All of the essential features of the DC-transport properties in the metallic regime of conducting polymers can be found in other disordered metallic systems, perhaps with the exception of the differences between oriented and non-oriented polymers. However, some of these are not well understood theoretically, since they occur near the M–I transition which is difficult to treat in current theory. On the experimental side, future progress is most likely to be made by extending the measurements to the region below 1 K.

Acknowledgments

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