Magnetoconductivity in doped poly(*p*-phenylenevinylene)

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Abstract. Magnetoconductivity in highly doped (with H_2SO_4 and $FeCl_3$) poly(p-phenylenevinylene) (PPV) has been studied. Oriented samples with different stretching ratios were measured. A room-temperature conductivity of 10^3–10^4 S cm^{-1} is achieved in highly oriented PPV, depending on the dopant. PPV–H_2SO_4 is metallic and has a strong positive magnetoconductance while PPV–$FeCl_3$ is insulating and its magnetoconductance predominantly negative and large. In PPV–H_2SO_4 the magnetoconductance is analysed with the localization-interaction model for disordered metals. The positive magnetoconductance of highly oriented PPV–H_2SO_4 is due to weak localization. Its size, temperature dependence and anisotropy is discussed. With a lower stretching ratio we find negative magnetoconductance.

1. Introduction

Conducting polymers of a sufficiently high quality can nowadays be routinely synthesized to yield a metallic conductivity in the doped state of the polymer. By 'metallic' conductivity we mean a conductivity that stays finite in the zero-temperature limit ($\sigma(T = 0) > 0$). Still, the high disorder in the morphology and large concentration of defects often prevents the formation of a metallic state and results in localized electronic states, i.e. a Fermi glass (Reghu *et al* 1997, Reghu 1997). In this picture, the insulating state is therefore of the Anderson type (Lee and Ramakrishnan 1985). Whether a metallic or an insulating phase is formed can be varied by changing processing conditions or by ageing the doped polymer (Ahlskog *et al* 1997a and references therein). It has been found in such studies of the metal–insulator (M–I) transition in polyacetylene ($(CH)_x$) and PPV that the MC turns from positive to negative roughly coincidentally with the transition (Ahlskog *et al* 1997b, Kaneko *et al* 1993).

Poly(p-phenylenevinylene) (PPV) is a conjugated polymer (conducting polymer) which when oriented and doped with a suitable dopant reaches conductivities of up to 10^4 S cm^{-1} and has a very weak temperature dependence of conductivity (Ohnishi *et al* 1991, Madsen *et al* 1989, Ahlskog *et al* 1996). Typically the resistivity ratio $\rho_r (= \sigma(200\ K)/\sigma(1.3\ K))$ is 1.1–1.3 in oriented, sulphuric-acid- (H_2SO_4-) doped, PPV. The anisotropy ratio between the parallel and perpendicular conductivities ($\sigma_\parallel/\sigma_\perp$) with respect to the chain orientation is approximately 100, making the polymer an anisotropic 3D conductor. This material exhibits the transport properties of a disordered metal. Our recent extensive work on

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the low-temperature transport in PPV–H_2SO_4 showed that the magnetoconductivity (MC) is strongly positive at low fields if the field is perpendicular to the chain orientation, while it is exclusively negative if the field is parallel to the chain orientation. These features were explained as an interplay between electron–electron (e–e) interaction and weak localization (WL), where the latter is responsible for the anisotropic behaviour of the MC.

Of other conducting polymers, only $(CH)_x$ can be oriented equally well. High-quality $(CH)_x$ possesses in the doped state a parallel conductivity of 10^4–10^5 S cm^{-1} and a similar anisotropy ratio, $\sigma_\parallel/\sigma_\perp \cong 100$, as in PPV. Moreover, since the discovery of doped conjugated polymers ('conducting polymers') it has been their prototypical example, and thus many transport studies, including MC experiments, have been undertaken on this conducting polymer (Tsukamoto 1992). A metallic state in $(CH)_x$ has been achieved with several dopants: among these systems are $(CH)_x$–AsF_5 (Kwak *et al* 1979, Gould *et al* 1981) and $(CH)_x$–I_2 (Nogami *et al* 1991, Reghu *et al* 1994). In most of these cases the MC has been positive at low fields. The size of the effect is ∼1% at cryogenic temperatures. As in PPV–H_2SO_4, the anisotropy of the positive MC has been found to be particularly clear in highly oriented $(CH)_x$–I_2 (Reghu *et al* 1994). All these features are consistent with the localization-interaction model of a disordered metal (Lee and Ramakrishnan 1985). However, a thorough systematic investigation of MC in conducting polymers remains to be made since most experiments have dealt with either oriented or non-aligned samples but not both.

It is important to note that very different behaviour of the MC has been found in $FeCl_3$-doped $(CH)_x$ (Kaneko and Ishiguro 1994). This system exhibits positive MC at low temperatures and negative at high temperatures, that is, opposite to the behaviour of the other systems mentioned. This material also shows a very low ρ_r, and is therefore particularly important to understand. The magnetic moment of the Fe atom has been suggested to play a role in the MC properties in this case.

In this work we will present complementary data to our previous papers (Ahlskog *et al* 1996) on transport in doped PPV, in which we studied conductivity and MC at low temperatures in highly oriented (stretching ratio (λ) = 10) PPV–H_2SO_4, this time focusing on the MC. We will discuss the size of the WL effect and its temperature dependence, the anisotropy in oriented PPV and the effects of differing degrees of orientation. We have extended our previous measurements to include MC at higher temperatures (15 K) and lower orientation (λ = 3). H_2SO_4 and $FeCl_3$ doping of PPV results in materials of different conductivities. We have also studied MC in highly oriented $FeCl_3$-doped PPV (λ = 10).

2. Experiment

PPV was synthesized as described earlier according to a precursor route (Ohnishi *et al* 1991). Samples with different stretching ratios were obtained during conversion from the precursor to the final polymer. In this work we have used samples with λ = 3 and 10. Conductivity and MC measurements were made in a helium Dewar equipped with a superconducting 8 Tesla magnet down to temperatures of 1.3 K. The samples were checked to be in good thermal contact with the temperature sensor. The samples were doped with H_2SO_4 and $FeCl_3$ and immediately transferred to the Dewar for conductivity measurements. The doping process is discussed by Ahlskog *et al* (1997c).
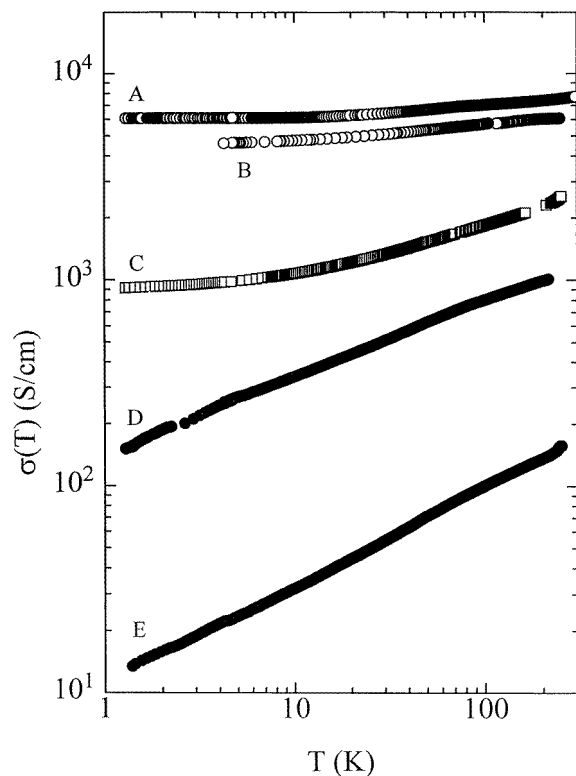
Figure 1. Temperature dependence of conductivity of the samples analysed in this work and presented in table 1. Samples doped with H_2SO_4 are indicated with open labels while those doped with $FeCl_3$ have solid labels.

3. Results

3.1. Temperature dependence of conductivity

Figure 1 shows the temperature dependence of PPV–H_2SO_4 (samples A–C) and PPV–$FeCl_3$ (samples D, E). Table 1 displays the dopant, stretching ratio, conductivity and resistivity ratio for the samples. It is most important to note that the samples doped with H_2SO_4 are metallic while $FeCl_3$-doped samples have a lower room-temperature conductivity and exhibit a power law temperature dependence ($\sigma \propto T^\beta$) with no extrapolated zero-temperature conductivity, that is, they are insulating. This has been verified by plotting $W = d(\ln \sigma)/d(\ln T)$ as a function of the temperature T, which conveniently distinguishes metallic samples from insulating ones (Zabrodskii and Zinovjeva 1984). This technique has been successfully employed to study the M–I transition in several conducting polymers (Ahlskog *et al* 1997a, Reghu *et al* 1997, Reghu 1997). The resistivity ratios ρ_r for the highly oriented H_2SO_4-doped samples (A, B) have values in accord with our previous work (Ahlskog *et al* 1996, 1997b). Sample C ($\lambda = 3$) has a lower conductivity than those with $\lambda = 10$ which is in accord with the general behaviour of conductivity in highly orientable conducting polymers, and to be expected naturally due to the lower degree of chain orientation. However, it also has a significantly higher $\rho_r = 2.7$ which may signify that the sample is closer to the M–I

transition boundary. ρ_r is approximately 10 for both FeCl$_3$-doped samples (D, E). Such a value for the resistivity ratio is typical for weakly insulating samples (Ahlskog *et al* 1997a). The MC of these samples is discussed below.

3.2. Magnetoconductance of H$_2$SO$_4$-doped PPV; $\lambda = 3, 10$

The upper part of figure 2 shows the MC with the field perpendicular to the chain direction of PPV–H$_2$SO$_4$ stretched ten times (sample A) at different temperatures from 1.3 to 9 K. The MC is positive at low fields but the differential MC turns negative at high fields, resulting in a maximum of MC. This maximum depends on the temperature since it shifts to higher fields with increasing temperature. The strength of the positive MC at low fields (dσ/dH), where H is the magnetic field intensity, is largely temperature independent within the investigated range of field and temperature. However, the total magnitude of the positive MC saturates at higher temperatures. The positive MC follows approximately an $H^{1/2}$ behaviour at higher fields, before it reaches the maximum. This is shown explicitly in figure 3 for another similar metallic sample of PPV–H$_2$SO$_4$, at a temperature of 7 K. In the lower part of figure 2 is shown the temperature dependence of the conductivity in a $T^{1/2}$ scale between 1.3 and
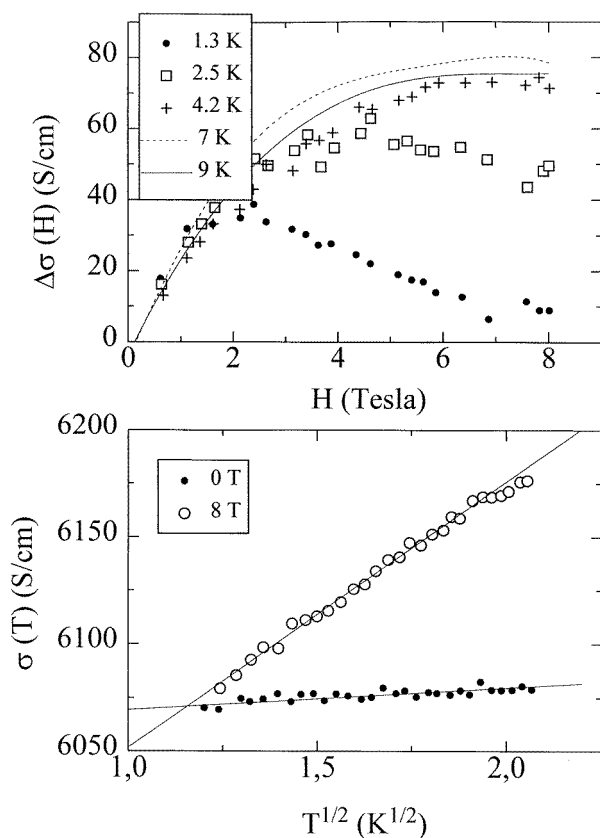

Figure 2. Magnetoconductivity (upper figure, $\Delta\sigma(H) = \sigma(H) - \sigma(H = 0)$) and temperature dependence of conductivity at 0 and 8 Tesla (lower figure) in oriented PPV–H$_2$SO$_4$ with $\lambda = 10$ (sample A). The field is perpendicular to the chain orientation.
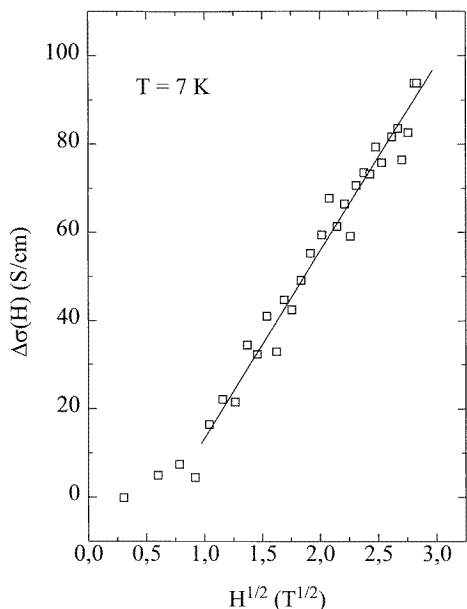
Figure 3. Magnetoconductivity of highly oriented ($\lambda = 10$) PPV–H$_2$SO$_4$ at a higher temperature (7 K), $\rho_r = 1.20$, $\sigma = 10\,000$ S cm^{-1}.

4.2 K at zero magnetic field and at 8 Tesla. The temperature coefficient of resistivity (TCR) is positive in both cases but becomes larger with applied magnetic field.

Figure 4 shows the MC of sample B in the temperature range 1.3–4.2 K, with the field parallel to the chain direction. The difference is clear: the MC is mainly negative with an almost negligible contribution of positive MC. However, the temperature dependence of conductivity, shown in the lower part of figure 4, is similar to that of sample A.

In figure 5 is shown the MC in an H^2 scale, with the field perpendicular to the chain direction, of the less oriented sample C ($\lambda = 3$) in the temperature range 1.3–4.2 K. The MC is clearly negative, even at low fields. We note that the MC follows the H^2 behaviour at low fields. Furthermore, the region of H^2 dependence extends to higher fields with increasing temperature. The lower part of figure 5 shows the temperature dependence of conductivity in a $T^{1/2}$ scale, which again is similar to those of samples A and B.

3.3. Magnetoconductance of $FeCl_3$-doped PPV; $\lambda = 10$

Figure 6 shows the MC of the two FeCl$_3$-doped samples, D (a) and E (b), with the field perpendicular to the chain direction. The MC is predominantly negative in both cases, but the more conductive one (D) exhibits at 4.2 K positive MC up to 5.5 T. At lower temperatures the MC is close to zero up to 2 T, after which it becomes strongly negative. For the less conductive sample (E) the MC is not positive anywhere but exhibits again neutral behaviour up to 1–2 T, depending on the temperature. Also, the negative MC is stronger for sample E.
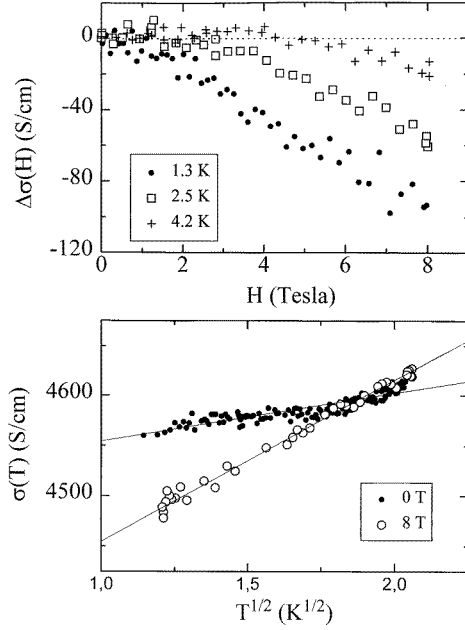
Figure 4. Magnetoconductivity (upper figure) and temperature dependence of conductivity at 0 and 8 Tesla (lower figure) in highly oriented PPV–H$_2$SO$_4$ with $\lambda = 10$ (sample B). The field is parallel to the chain orientation.

4. Discussion

As we will show below, the MC exhibits contributions from both WL and e–e interaction. The theoretical expression for MC in weak localization (Lee and Ramakrishnan 1985) is:

$$\Delta\sigma(H) = (e^2/2\pi^2\hbar)\sqrt{(eH/\hbar)}f(x) \qquad x = \hbar/4eHl_{in}^2 \tag{1}$$

where $\Delta\sigma(H) = \sigma(T, H) - \sigma(T, 0)$, l_{in} is the inelastic scattering length and f a function which in the high-field limit ($x \ll 1$) has the value 0.605. Therefore, at high fields the MC due to WL becomes:

$$\Delta\sigma(H) = B_{WL}\sqrt{H} \tag{2}$$

where the constant $B_{WL} \cong 4.8$ S (cm T$^{1/2}$)$^{-1}$ (Kawabata 1980a). This value has been derived for the isotropic case. At low fields the weak localization MC is proportional to H^2. In the absence of spin–orbit interaction WL gives a positive MC, which we assume to be the case here.

In e–e interaction theory the low- and high-field regimes have the same field dependencies as in WL. However, the interaction effects are separated by the Zeeman splitting energy $g\mu_B H = k_B T$. The low-field MC given by e–e interaction (Dai *et al* 1992b) is:

$$\Delta\sigma(H) = -0.041(g\mu_B/k_B)^2\alpha\gamma F_\sigma T^{-3/2}H^2 = B_{LEE}(T)H^2 \qquad H < k_B T/g\mu_B \tag{3}$$

where α is a parameter dependent on the diffusion constant, γ depends on the band structure and F_σ on the Hartree factor (Dai *et al* 1992a, b, Lee and Ramakrishnan 1985). At high fields the e–e interaction MC becomes:

$$\Delta\sigma(H) = -0.77(g\mu_B/k_B)^{1/2}\alpha\gamma F_\sigma H^{1/2} = B_{EE}H^{1/2} \qquad H > k_B T/g\mu_B. \tag{4}$$
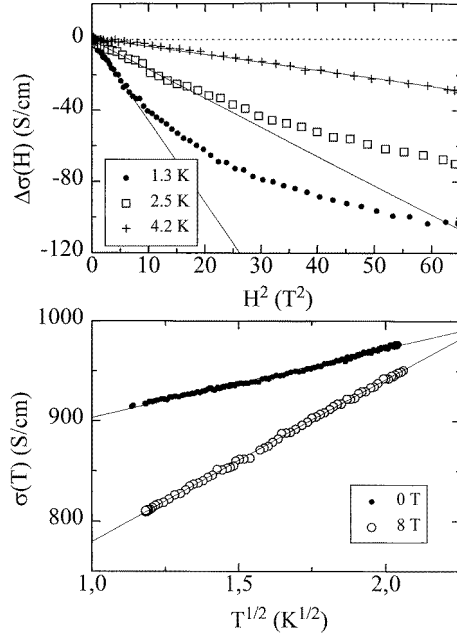
Figure 5. Magnetoconductivity (upper figure) and temperature dependence of conductivity at 0 and 8 Tesla (lower figure) in oriented PPV–H_2SO_4 with $\lambda = 3$ (sample C). The field is perpendicular to the chain orientation.

At typical fields and temperatures of 1 Tesla and 1 K the ratio between the low- and high-field expressions for the e–e interaction MC is much less than 1. Therefore the Zeeman energy, which separates the two regimes, is expected to be a significant hallmark in the MC. The equation for the Zeeman energy can be written in the form of a ratio between the field and the temperature:

$$H/T = k_B/g\mu_B = 0.75 \text{ T K}^{-1}. \tag{5}$$

In figure 2, for highly oriented PPV–H_2SO_4 ($\lambda = 10$), sample A, the maxima of MC at 1.3, 2.5 and 4.2 K correspond to H/T ratios of 1.7, 1.8 and 1.8 T K^{-1}, respectively. The ratio is thus rather constant. In the MC of sample C it was noted above that H^2 behaviour is followed at low fields up to a maximum field which increases with increasing temperature. The H/T values for the deviation from H^2 behaviour are for 1.3, 2.5 and 4.2 K (for 4.2 K we simply have to take the maximum field value of 8 Tesla): 2.2, 1.6 and 1.9 T K^{-1}. These values are more scattered but centre around the same value as those of sample A. Similar behaviour can also be observed in the MC of sample B. We thus conclude and base our further analysis on the premise that the observed MC is an interplay between the positive contribution from WL and the negative contribution from e–e interaction.

We can note that at all fields the observed positive MC is roughly temperature independent. It is therefore reasonable to assume that the temperature dependent conductivity below 4.2 K is due to e–e interaction effects. The theory of e–e interaction gives the correction to the zero temperature conductivity σ_0 as:

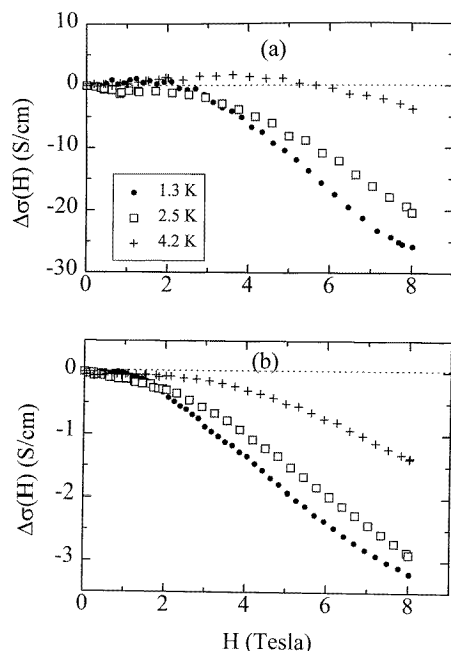$$\sigma(T) = \sigma_0 + mT^{1/2} \qquad g\mu_B H < k_B T. \tag{6a}$$

Figure 6. Magnetoconductivity of two samples (D (a), and E (b)) of highly oriented PPV–FeCl$_3$ with $\lambda = 10$. The field is perpendicular to the chain orientation.

At high fields this becomes:

$$\sigma(T) = 0 + m_H T^{1/2} \qquad g\mu_B H > k_B T. \tag{6b}$$

The parameters m and m_H are:

$$m = \alpha[(4/3) - (3\gamma F_\sigma/2)] \tag{7a}$$

$$m_H = \alpha[(4/3) - (\gamma F_\sigma/2)]. \tag{7b}$$

Depending on γF_σ they can, and have been observed to, attain both positive and negative values. Furthermore, since γF_σ is always a positive value (Lee and Ramakrishnan 1985), the magnetic field makes m_H more positive than m, which is in agreement with our observations. These values are displayed for samples A–C in table 2. The coefficients $B_{LEE}(T)$ and B_{EE} from (3) and (4) can now be expressed as:

$$B_{LEE} = -0.075(m_H - m)T^{-3/2} \ (\text{K T}^{-1})^2 \tag{8a}$$

$$B_{EE} = -0.89(m_H - m) \ (\text{K T}^{-1})^{1/2}. \tag{8b}$$

Therefore we can compare the direct experimental values for B_{LEE} and B_{EE}, which we will call B^*_{LEE} and B^*_{EE}, respectively, and those which theoretically follow from (8), using the data of the temperature dependence $(m_H - m)$ of the conductivity. Since sample A has a strong positive MC also, the experimentally observable B_{WL} (40 S cm^{-1} T$^{-1/2}$) has to be subtracted from B_{EE}. Since B_{EE} and B_{WL} are temperature independent we choose the former (that is, B^*_{EE}) from the 1.3 K and the latter from the 4.2 K data where they can be observed most clearly. Since the other samples (B, C) do not have a measurable positive MC, B^*_{EE} is directly obtained from the high-field MC data at 1.3 K. The values B_{EE} and B^*_{EE} for samples A–C, and B_{LEE} and B^*_{LEE} for sample C, are summarized in tables 2 and 3,

Table 1. Basic properties of the PPV samples studied in this work. Dopant, stretching ratio, room-temperature conductivity and resistivity ratio ($\sigma(200\ \text{K})/\sigma(1.3\ \text{K})$) are given.

Sample	Dopant	λ	σ (S cm^{-1})	ρ_r
A	H_2SO_4	10	7700	1.29
B	H_2SO_4	10	6200	1.34
C	H_2SO_4	3	2300	2.7
D	$FeCl_3$	10	1100	10
E	$FeCl_3$	10	160	10

Table 2. Parameters related to the magnetoconductance from e–e interaction of the H_2SO_4-doped samples. These are defined in (3)–(8) and the related text.

Sample	m (S cm^{-1} K$^{-1/2}$)	m_H (S cm^{-1} K$^{-1/2}$)	B_{EE} (S cm^{-1} T$^{-1/2}$)	B_{EE}^* (S cm^{-1} T$^{-1/2}$)
A	7	124	−104	−63
B	48	161	−100	−56
C	69	162	−74	−62

Table 3. Parameters related to the low-field magnetoconductance from e–e interaction for sample C. Definitions are given in (3) and (6)–(8) and related text.

T (K)	B_{LEE} (S cm^{-1} T^{-2})	B_{LEE}^* (S cm^{-1} T^{-2})
1.3	−4.71	−4.59
2.5	−1.76	−1.63
4.2	−0.81	−0.45

respectively. The agreements between theoretically and experimentally obtained values are rather good for sample C. The experimental values (B_{EE}^*) are consistently less negative than expected from (8*b*) for samples A and B. This would point to an underestimation of the positive contribution stemming from WL. A wider range of temperature and field in the experiments would be desirable to obtain more accurate results.

We will now discuss the anisotropy of the MC. The anisotropy of WL which causes the effect particularly clearly in PPV–H_2SO_4 and (CH)$_x$–I_2 has already been discussed by Ahlskog *et al* (1996). The theory behind WL is described for example by Bergmann (1984). Briefly, the weak-localization MC arises when the magnetic flux (Φ) enclosed by the average backscattered electron path becomes comparable to the flux quantum $\Phi_q = h/2e$. In the upper part of figure 7 the conjugate wavefunctions, representing forward (Ψ_f) and reverse (Ψ_b) directions, enclose the shaded area which represents Φ. In such an *isotropic* conductor the area of the backscattered electron path, to which Φ is proportional, is approximately l_{in}^2, or, equivalently, approximately D^2, where D is the diffusion coefficient. On the other hand, in an *anisotropic* conductor the area that encloses the flux depends on the direction of the field. In systems with uniaxial symmetry such as oriented conducting polymers, the material is not represented with a single diffusion coefficient, but instead with one parallel to the chain direction ($D_\parallel$) and one perpendicular to it ($D_\perp$). The lower part of figure 7 illustrates the situation: when the field is parallel to the chain direction the average enclosed flux ($\Phi_\parallel$) is circular and proportional to $D_\perp^2$, while when it is perpendicular to it the flux ($\Phi_\perp$) is elliptical and proportional to $D_\parallel D_\perp$. Now, since $D_\parallel > D_\perp$, it follows that for a
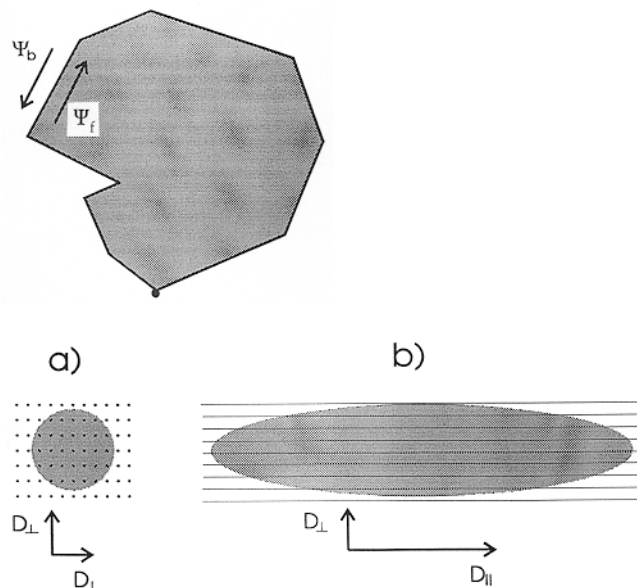
Figure 7. Illustration of the magnetoconductive effect on weak localization in isotropic (upper figure) and anisotropic (lower figures) material. Ψ_f and Ψ_b refer to the conjugate electron wavefunctions in the forward and reverse directions, respectively. The shaded area refers to the magnetic flux enclosed by the electron path. In the lower figures the material represents a highly oriented polymer. In figure (a) the line of view is parallel to the chain orientation (the dots are the polymer chains) while in figure (b) it is perpendicular to the chain axis (the lines are the chains). The anisotropic diffusion coefficients $D_\perp$ and $D_\parallel$ are explained in the text.

given field intensity $\Phi_\perp > \Phi_\parallel$. Thus, the WL contribution to the MC is much stronger in the perpendicular configuration than in the parallel configuration. This is what is observed in the anisotropic MC of oriented conducting polymers. Hopefully future work will enable a quantitative analysis to be made. Other systems that exhibit anisotropic WL are cylindrical conductors of extremely small diameter (Sharvin and Sharvin 1981, Gijs *et al* 1984), metal thin films (Bergmann 1984) and metal multilayers (Fadnis *et al* 1993). In the first two, the anisotropy is due to geometrical constraints to the electronic motion, where l_{in} is anisotropic but not D, while in the last one the diffusion coefficient is anisotropic, as in our case.

An interesting question is how the MC is affected by chain alignment. We have seen that in highly oriented polymer the perpendicular MC is strongly positive. The perpendicular MC of sample C ($\lambda = 3$) exhibited only negative MC. However, its ρ_r is rather high (table 1). Ahlskog *et al* (1997b) have shown how the positive MC vanishes roughly coincidentally with the M–I transition in highly oriented PPV–H_2SO_4, which in this material occurs at $\rho_r = 2$–4. The available data are not sufficient to analyse how the anisotropy develops as the orientation of the chains increases in PPV. We can again find better answers from the many works on $(CH)_x$. Reghu (1996) has discussed MC in oriented $(CH)_x$–I_2 with $\lambda = 3$, 6 and 14. In the sample with $\lambda = 14$ the MC shows the same strong anisotropy as was discussed above. When $\lambda = 3$ or 6 the MC is positive in both the perpendicular and parallel cases. However, there is still a difference in that the MC with the field parallel is smaller. Unfortunately, the case with $\lambda = 1$ was not studied. There is not much doubt that it will exhibit isotropic MC. The interesting task to be done is to relate quantitatively the observed

anisotropy in MC to the degree of chain alignment which can be obtained, for example, by means of infrared or NMR spectroscopy.

Next we will discuss the size and the temperature dependence of the weak-localization MC. In highly doped oriented PPV–H_2SO_4 the high-field positive contribution from WL, as expressed by the value B_{WL} (2), is roughly 40 S (cm $T^{1/2}$)$^{-1}$ (Ahlskog *et al* 1996). As was noted above, this value is an order of magnitude higher than theoretically predicted. The discrepancy is even more severe for oriented $(CH)_x$–I_2 studied by Nogami *et al* (1991), which has an even higher conductivity. However, in practically all cases of observed positive MC in metallic samples of $(CH)_x$ and PPV the magnitude of the effect is approximately 1%, independent of the value of the conductivity. The relative size of the effect is therefore not very different from, e.g., some heavily doped semiconductors. Nogami *et al* (1991) have discussed this problem and, relying on theoretical results by Kawabata (1980b), suggested that the anisotropic diffusion coefficients may explain the large absolute magnitude of B_{WL}. B_{WL} is in an anisotropic conductor multiplied by a factor containing $D_\parallel$ and $D_\perp$, resulting in an enhanced value in the parallel direction.

We may note in figure 2, as well as in our earlier work (Ahlskog *et al* 1997b), that the contribution from weak localization to MC is rather temperature independent at the range of temperatures at our disposal. This is different for work on $(CH)_x$ that reaches subkelvin temperatures. In samples where ρ_r is small there is a considerable increase in the positive MC with decreasing temperature in the millikelvin regime (Kwak *et al* 1979, Gould *et al* 1981). In the absence of magnetic impurity scattering and in the regimes of either negligible or saturated spin–orbit effects, the low-field weak-localization MC is proportional to l_{in}^3 (Reghu 1997). The inelastic scattering length l_{in} in turn is proportional to T^{-p} (Lee and Ramakrishnan 1985), where p is a positive constant determined by the scattering mechanism. Therefore the MC is expected to be strongly increasing in the low-temperature limit. Future studies in the millikelvin regime of the MC in doped PPV would clearly be very desirable.

Figure 8 shows the ratio $\Delta\sigma(8\,\text{T})/\sigma(H=0)$ as a function of the temperature for three highly oriented PPV–H_2SO_4 ($\lambda = 10$) samples with the ρ_r values below 2 and which are metallic. The positive MC clearly has a tendency to saturate, even to slightly decrease at higher temperatures (>6 K). As the inelastic scattering length, which controls the WL mechanism, decreases with the temperature according to the power law mentioned above, all WL-related effects must eventually vanish (Bergmann 1984). For PPV–H_2SO_4 it was estimated that $p = 3$ (Ahlskog *et al* 1996). This implies a reduction in l_{in} of at least two orders of magnitude within the temperature range presented in figure 8. Accordingly the positive MC stemming from WL will gradually disappear, which is probably what is observed in the figure. The MC at higher temperatures (10–300 K) has to our knowledge not been investigated in conducting polymers. However, in carbon fibres, which show similar transport properties as conducting polymers, it has been shown that a low-temperature positive MC turns negative when the temperature is raised high enough, the negative MC being attributed to classical magnetoresistive effects (Bayot *et al* 1989). Furthermore, it was shown that the negative MC persists to higher temperatures, the lower the conductivity of the sample is. This trend is roughly in agreement with the data of figure 8, though these are insufficient for any firm conclusions.

Finally, we will discuss the $FeCl_3$-doped samples. The magnitude of their negative MC is large, approximately 20% at 1.3 K, much larger than is typically given by localization-interaction phenomena. The temperature dependence in zero field or in a magnetic field is stronger than the $T^{1/2}$ behaviour that applies to metallic samples close to the M–I boundary. Indeed, these samples are insulating as was noted above. We cannot therefore apply the
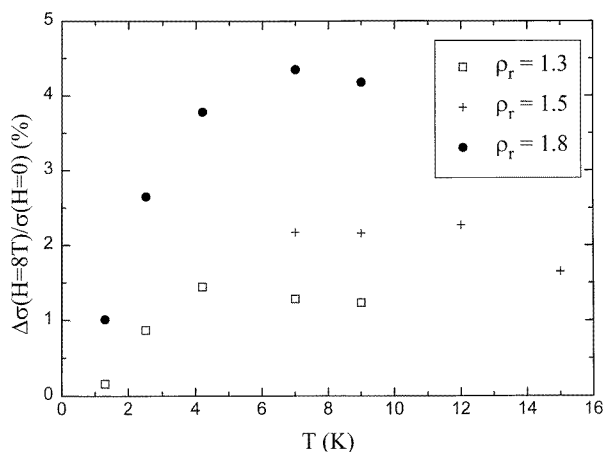
Figure 8. The relative change in conductivity at 8 Tesla ($\Delta\sigma(8\,\mathrm{T})/\sigma(0\,\mathrm{T})$) in three samples of highly oriented PPV–H$_2$SO$_4$ ($\lambda = 10$) as a function of temperature in the interval 1.3–15 K. The change is given in percentages.

same approach to this case as to PPV–H$_2$SO$_4$. However, it seems quite clear that a strong positive component of the MC persists into the insulating side of the M–I transition boundary and gradually vanishes as the material becomes more insulating. Moreover, the behaviour of PPV–FeCl$_3$ is different from PPV–H$_2$SO$_4$ on the insulating side of the transition boundary. Even though the (room-temperature) conductivities of the two samples differ by an order of magnitude, ρ_r and the size of the negative MC are the same. In PPV–H$_2$SO$_4$ these factors increase strongly as the conductivity decreases. In Anderson type insulators the conductivity is due to variable-range hopping in the low-temperature limit. A magnetic field dependence comes from the shrinking of the localized wavefunctions, which decreases the conductivity (Shklovskii and Efros 1984). The size of the effect can be huge and might well explain the negative part of the observed MC in our samples of PPV–FeCl$_3$.

The M–I transition in (CH)$_x$–FeCl$_3$ has been studied by Kaneko and Ishiguro (1994). As was noted above, the MC of this material exhibits differing behaviour in the metallic state. In the insulating side the MC is negative and large at low fields but at higher fields (>2 T) this negative MC peaks and the differential MC becomes positive. These results were explained with field effects on hopping conduction among Anderson localized states when Coulomb correlations are included. In PPV–FeCl$_3$ this peak does not occur. However, since our doping procedure did not yield particularly highly conducting samples (Ahlskog *et al* 1997c), further comparison cannot be made.

5. Conclusions

Our studies on the MC of PPV–H$_2$SO$_4$ and PPV–FeCl$_3$ show that the former is metallic and exhibits a strong positive MC while the latter is insulating and has a large negative MC but also a small positive component. In highly oriented PPV–H$_2$SO$_4$ the positive MC stemming from weak localization is strong and relatively temperature independent in the 1–10 K regime. The magnitude of the positive MC is exceptionally large but might well be explained with WL theory considering the highly anisotropic conductivity. The anisotropy of the positive MC in highly oriented PPV–H$_2$SO$_4$ is also well explained with

WL theory. The unstretched form of this system has not been thoroughly investigated. We have measured the transport properties in a sample with $\lambda = 3$ and found mainly negative MC due to e–e interaction. However, this sample was probably quite close to the insulating regime which might have masked the WL contributions. Generally the MC properties of oriented PPV are similar to those of $(CH)_x$.

In the insulating samples of PPV–FeCl$_3$ the MC is predominantly negative and rather large. The main mechanism is probably the effect of magnetic field on variable-range hopping among localized states in an Anderson type insulator. The interesting magnetoconductance properties of $(CH)_x$–FeCl$_3$ have not been reproduced in PPV, possibly due to differences in the doping conditions of the material.

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