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Pressure dependence of conductivity and magnetoconductance in ion-irradiated polyimide

A N Aleshin†, M Ahlskog‡ and M Reghu‡

† A F Ioffe Physico-Technical Institute, Russian Academy of Sciences, St Petersburg 194021, Russia

‡ Institute for Polymers and Organic Solids, University of California, Santa Barbara, CA 93106, USA

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Abstract. The effect of pressure (up to 15 kbar) and magnetic field (up to 8 T) on the low-temperature (down to 1.3 K) DC conductivity and magnetoconductance (MC) of ion-irradiated (Ar^+ and Ga^+ ions) polyimide films with a room-temperature conductivity $\sigma(300\ \mathrm{K})$ of 200–400 S cm^{-1} has been investigated. It was shown that for samples on the metal side of the metal–insulator transition with the resistivity ratio $\rho_r \simeq \rho(1.3\ \mathrm{K})/\rho(300\ \mathrm{K}) = 1.8$–$2.3$ the application of pressure increases $\sigma(300\ \mathrm{K})$ by a factor of 2–3 with respect to that at ambient pressure and the value of ρ is slightly reduced. The low-temperature conductivity shows a $T^{1/3}$ dependence. The sign of the MC at ambient pressure is negative at all fields, thus implying that the contribution for the electron–electron interaction is dominant. However, at 15 kbar a positive MC at low fields, in both the transverse and the longitudinal directions to the field, has been observed. This implies that under pressure the system is more metallic with respect to that at ambient pressure, and the positive MC due to the dominance of the weak-localization contribution is enhanced by making the system more metallic under pressure.

1. Introduction

Ion irradiation or ion implantation of organic polymers, both conjugated and non-conjugated, is an effective method to change both the chemical and the physical properties of these materials for various technological applications [1–7]. It is possible to achieve room-temperature conductivities as high as 10^3 S cm^{-1} by this method and these conductivities are relatively stable in air. The surface modification and blackening of yellowish polyimide films during the ion irradiation process are possibly due to some carbonization, which occurs only in a surface layer a few hundreds of Ångstroms in depth; below this the film remains an insulator. Moreover, this technique allows one to fabricate samples with conductivity close to the metal–insulator (M–I) transition and to investigate the features of the M–I transition in such modified materials [4–7]. Recent advances in ion irradiation of thermally stable aromatic polymers such as polyimide show that the DC conductivity at 300 K of modified layers would be enhanced by more than 18 orders of magnitude up to 10^3 S cm^{-1} [4–6].

The ion-irradiated polyimide (IRPi) samples near the M–I transition show a relatively weak negative temperature coefficient of resistivity (TCR), and they have a high finite conductivity at $T \rightarrow 0$ K. Hence they are just on the metallic side of the M–I transition. From previous transport measurements it is known that the electron–electron (e–e) interaction and weak localization (WL) influence the low-temperature conductivity of IRPi samples close to the M–I transition [8, 9]. Usually the external pressure is supposed

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to enhance $\sigma(300\ \mathrm{K})$ and as a result the negative TCR is reduced for systems near the M–I transition. It is well known that application of a high pressure usually increases the conductivity of various conducting polymers [10, 11]. The magnetic field dependence is much more complicated near the M–I transition. Both positive and negative MCs have been observed on the metallic side of M–I transition depending upon the dominant contributions from the e–e interaction and WL to the low-temperature transport. In general for systems on the insulating side of M–I transition the field tends to decrease the conductivity owing to the localization of electronic wavefunctions [12, 13].

In this work an extensive study of the low-temperature (down to 1.3 K) DC conductivity as a function of pressure (up to 15 kbar) and magnetic field (up to 8 T), both parallel and perpendicular to the sample plane and current, has been carried out on IRPi samples near the M–I transition. At high pressures, $\sigma(300\ \mathrm{K})$ increases by a factor of 2–3 and the resistivity ratio $\rho_r \simeq \rho(1.3\ \mathrm{K})/\rho(300\ \mathrm{K})$ is slightly reduced. At low temperatures, $\sigma(T)$ follows a $T^{1/3}$ dependence. The sign of the MC is negative at all fields at ambient pressure. However, at 15 kbar a positive MC has been observed at low fields. This clearly shows that, by making the system more metallic by pressure, it is possible to observe the positive MC due to the WL contribution. Moreover, the subtle interplay of e–e interactions (negative MC) and WL (positive MC) contributions can be observed in this system.

2. Experimental details

The same polyimide samples were used as in earlier investigations [8, 9]. Polyimide films were irradiated consecutively with 40 keV Ar^+ and 90 keV Ga^+ ions at a dose (for Ga^+) of 5×10^{16} ions cm^{-2}. The thickness of the irradiated layer was estimated by a standard TRIM calculation [14], and it was of the order of 500 A for an ion energy of 90 keV. Samples with a conductivity very close to the M–I transition were chosen for the transport experiments. Electrical contacts to the samples were made in planar geometry by conductive carbon paint. The DC conductivity measurements were carried out within the region of Ohm's law by the standard four-probe method with the help of a computer-controlled measuring system. High-pressure conductivity measurements were carried out in a self-clamped beryllium–copper pressure cell [10, 15]. After pressurizing, the cell was clamped at room temperature and then cooled to 1.3 K in a cryostat containing a superconducting magnet (0–10 T). Fluorinert[a] was used as the hydrostatic pressure-transmitting medium. The temperature was measured with a calibrated Cernox[a] resistor (300–1.3 K). To avoid sample heating at low temperatures, the current source was adjusted at each temperature so that the power dissipated into the sample was less then 1 μW.

3. Results and discussion

A typical pressure dependence of $\sigma(300\ \mathrm{K})$ of an IRPi sample very close to the M–I transition is shown in figure 1. It is seen that the room-temperature conductivity increases from 250 S cm^{-1} at ambient pressure to 450 S cm^{-1} at 15 kbar. The values of the resistivity ratio ρ_r at ambient pressure and 15 kbar are 1.8–2.2 and 1.7–1.9 respectively. A log–log plot of conductivity versus T at ambient pressure and 15 kbar is shown in figure 2. Although the behaviour of $\sigma(T)$ looks nearly identical, the slight reduction in the value of ρ_r at 15 kbar makes the system more metallic with respect to that at ambient pressure. This is consistent with the behaviour observed in doped conjugated polymers under pressure, in which the enhanced interchain coupling makes the system more metallic [10, 11]. However,

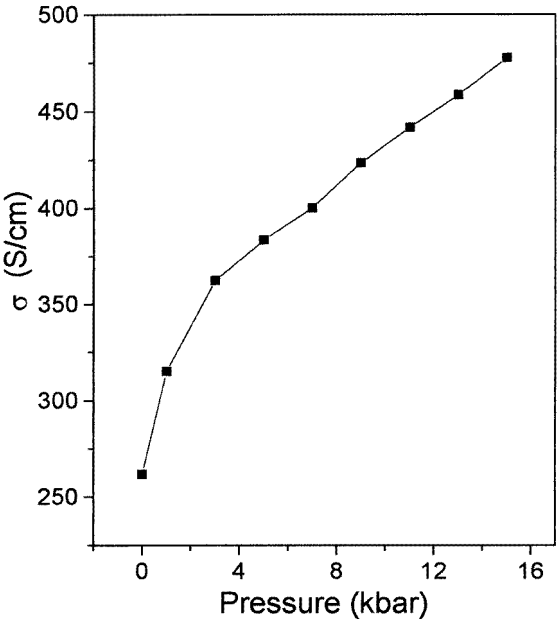

Figure 1. Conductivity versus pressure for IRPi.

even under pressure the system is not metallic enough to show any positive TCR which is usually observed in metallic systems, and still it is on the metallic side of M–I transition.

As has been shown in our previous studies [8, 9], the low-temperature conductivity of the IRPi samples on the metal side of the M–I transition at ambient pressure can be described by the law [12, 13]

$$\sigma(T) = \sigma(0) + mT^{1/2} + BT^{p/2} \tag{1}$$

where m and B are constants; the second and third terms are the corrections to the conductivity due to the e–e interaction and localization effects, respectively, and $p \simeq 1$, typical of the metallic regime of disordered systems near the M–I transition with e–e correlations in three dimensions. A rather similar temperature dependence of $\sigma(T)$ has been observed for doped conjugated polymers [10, 11, 16]. However, a detailed analysis of $\sigma(T)$ for IRPi samples show that a $T^{1/3}$ fit is more appropriate than a $T^{1/2}$ fit, and $\sigma(T)$ is given by

$$\sigma(T) = \sigma(0) + BT^{1/3} \tag{2}$$

This is shown clearly in figure 3. Previously Maliepaard *et al* [17] and Biskupskii *et al* [18] had observed a similar crossover from a $T^{1/2}$ to $T^{1/3}$ dependence as the system approached the M–I transition from the metallic side in inorganic semiconductors. In that case the value of p was around 0.66 rather than 1 near the M–I transition to give a $T^{1/3}$ fit, and this is not very well understood. Nevertheless, since the conductivity near the M–I transition is determined by the shortest length scale, and in this case the interaction length on the metallic side of the transition is the governing length scale, a $T^{1/3}$ fit is appropriate [17, 18]. In our case, even in presence of a magnetic field, this $T^{1/3}$ fit seems to be appropriate (figure 3), although the field reduces the conductivity. However, the slope of the $T^{1/3}$ term changed significantly with field, indicating that the system becomes more insulating in a

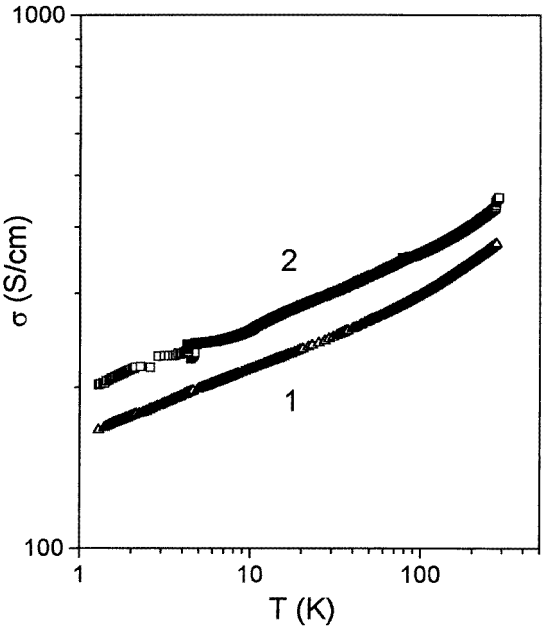

Figure 2. Log–log plot of conductivity versus T at ambient pressure (data 1) and 15 kbar (data 2).

magnetic field. Identical results are obtained when the field is parallel and when the field is perpendicular to the plane of the sample and current direction, and at ambient pressure and 15 kbar. Those similar behaviours of $\sigma(T)$ in directions both parallel and perpendicular to the field suggest that the transport is isotropic in this three-dimensional disordered system. Moreover, the preliminary data tend to show a crossover from $T^{1/3}$ to $T^{1/2}$ dependence by making the system more metallic at 15 kbar. More detailed studies of $\sigma(T)$ at various pressures are required to clarify the exact nature of this crossover.

The behaviours of the MC at ambient pressure and at 15 kbar are shown in figures 4 and 5, respectively. In both cases the MCs at low and high fields follow H^2 and $H^{1/2}$ dependences, respectively. At all temperatures the MC is negative at ambient pressure, and at high fields the slopes of the $H^{1/2}$ dependence at various temperatures are quite parallel. This suggests that at ambient pressure the e–e interaction contribution is dominant with respect to WL.

The contribution to the MC from e–e interactions can be written as $\Delta\Sigma(H,T) = \sigma(H,T) - \sigma(0,T)$ [12, 19–21]:

$$\Delta\Sigma_I(H,T) = \begin{cases} -0.041\alpha(g\mu_B/k_B)^2\gamma F_\sigma T^{-3/2}H^2 & (g\mu_B H \ll k_B T) \quad (3) \\ \alpha\gamma F_\sigma T^{1/2} - 0.77\alpha(g\mu_B/k_B)^{1/2}\gamma F_\sigma H^{1/2} & (g\mu_B H \gg k_B T). \quad (4) \end{cases}$$

Thus, at low and high fields, $\Delta\Sigma_I(H,T)$ is proportional to H^2 and $H^{1/2}$, respectively. This clearly explains the behaviour of the MC at ambient pressure.

Although under pressure the temperature dependence of conductivity is not very different from that at ambient pressure, the behaviour of the MC is rather more interesting and it is not similar to that at ambient pressure. A positive MC at fields below 3 T is shown in figure 5(a) for the sample at 15 kbar. This suggests that by making the sample more

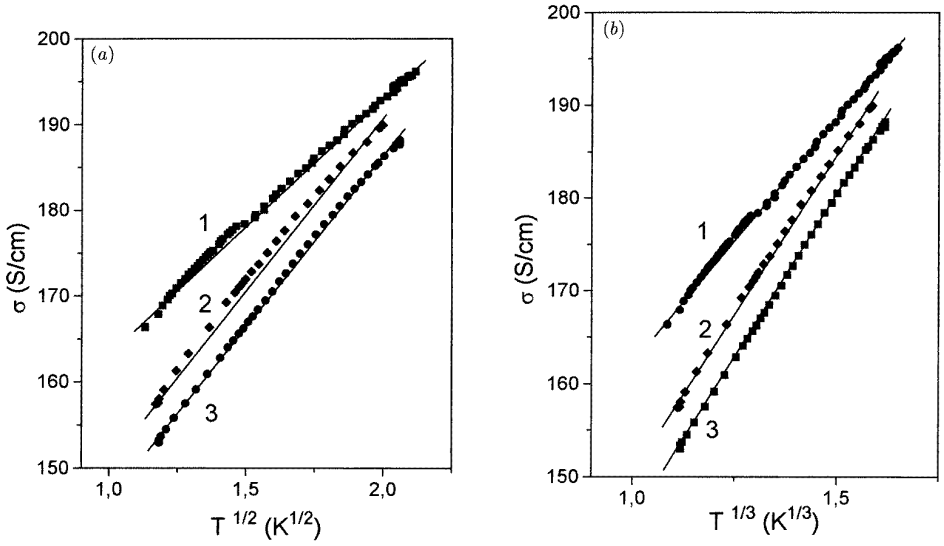

Figure 3. Conductivity versus T showing (a) the $T^{1/2}$ and (b) the $T^{1/3}$ fit at ambient pressure at various magnetic fields H: data 1, 0T; data 2, 5T; data 3, 8T.

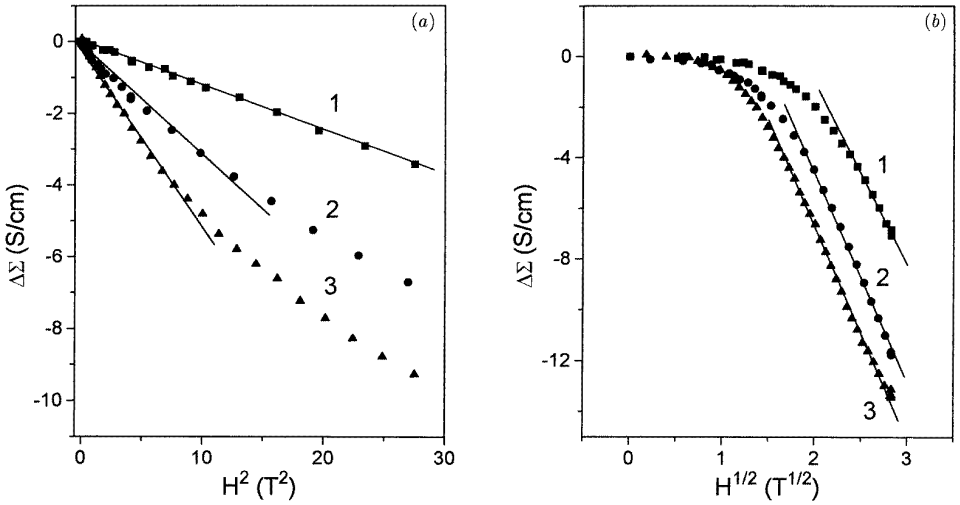

Figure 4. MC $\Delta\Sigma$ versus field at ambient pressure for (a) a H^2 fit at a low field and (b) a $H^{1/2}$ fit at a high field, at various temperatures T data 1, 4.2 K; data 2, 2.5 K; data 3, 1.3 K.

metallic by moving the position of the mobility edge with respect to the Fermi level at 15 kbar it is possible to observe the WL contribution to the MC. This indicates that the WL contribution becomes stronger at 15 kbar with respect to the e–e interaction contribution and this leads to the positive MC at low fields. On decreasing the temperature from 4.2 to 1.3 K, the field at the maximum of the positive MC shifts to lower values, as shown in figure 5. This suggests that the e–e interaction contribution begins to dominate at temperatures below 4.2 K. Moreover, at fields above 3 T the sign of the MC is negative owing to the dominant

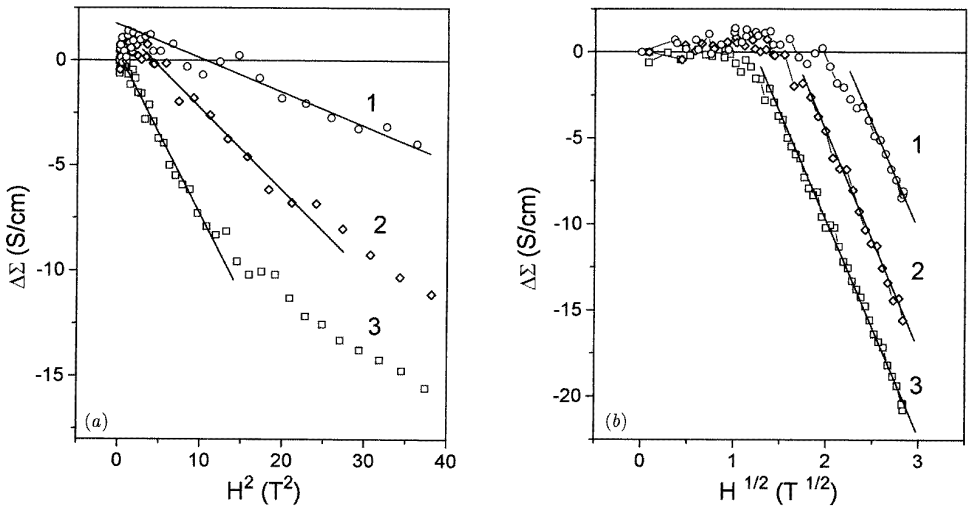

Figure 5. MC $\Delta\Sigma$ versus field at 15 kbar for (a) a H^2 fit at a low field and (b) a $H^{1/2}$ fit at a high field, at various temperatures T data 1, 4.2 K; data 2, 2.5 K; data 3, 1.3 K.

contribution from the e–e interaction. This field-induced crossover at low fields has been observed both for the field transverse and for the field longitudinal to the sample plane and current direction.

This field-induced crossover from a positive to negative MC indicates the subtle interplay of the WL and e–e interaction contributions to the MC. In general the WL contribution dominates at high temperatures and at low fields whereas the e–e interaction contribution dominates at low temperatures and high fields. This is consistent with the data in the case of IRPi samples. This type of subtle interplay of the WL and e–e interaction contributions to the MC has been observed in cases of doped oriented polyacetylene [11] and poly(p-phenylenevinylene) [22], ion-implanted polyaniline (but only at $T < 1$ K) [23], etc. The e–e interaction contributions to the MC are usually negative (positive magnetoresistance) and this is mainly due to the Zeeman splitting of the spin-up and spin-down bands. The MC at a higher field follows the $H^{1/2}$ dependence as expected owing to the e–e interaction contribution.

The contribution to the MC from WL at low fields is given by

$$\Delta\Sigma(H,T) - K\pi^2(e/c\bar{h})^2 G_0(l_{in}^3)H^2 \tag{5}$$

where $K = +1/24$ in the case of weak and $K = -1/48$ in the case of strong spin–orbit scattering [21]. The low-field H^2 dependence, as in figure 5(a), is consistent with equation (5).

At low magnetic fields, according to [19, 20, 24] we assume that the contributions to the total MC which arise from the e–e interaction and WL are additive. Thus the total low-field ($g\mu_B H \ll k_B T$) MC is given by

$$\Delta\Sigma(H,T) = -0.041\alpha(g\mu_B/K_B)^2\gamma F_\sigma T^{-3/2}H^2 + (1/12\pi^2)(e/c\bar{h})^2 G_0(l_{in}^3)H^2 \tag{6}$$

where $G_0 = e^2/\bar{h}$ and l_{in} is the inelastic scattering length. The first term on the right-hand side is the contribution from the e–e interaction (negative MC) and the second term is the contribution from WL (positive MC). The values of the constants $\alpha\gamma F_\sigma$ can be estimated from the plot of $\sigma(H,T)$ versus $H^{1/2}$ in strong magnetic fields, where the e–e interaction

contribution is dominant [11, 19, 20]. Thus at ambient pressure at low H the contributions due to WL and e–e interaction nearly cancel each other and the MC is negligible, and then at larger H the negative MC due to the e–e interaction dominates, since the WL contribution is weak. However, at high pressures the WL contribution is larger than that at ambient pressure and it can be easily observed in the positive MC. This very subtle tuning of both contributions by pressure is very interesting. More detailed study on various IRPi samples near the M–I transition as a function of pressure can shed more light on this interplay of WL and e–e interaction contributions to the charge transport at very low temperatures.

4. Conclusion

The conductivity and MC of IRPi samples close the M–I transition have been investigated as functions of pressure, temperature and magnetic field. At high pressures, $\sigma(300\ \mathrm{K})$ increases by a factor of 2–3 with respect to that at ambient pressure and the value of the resistivity ratio $\rho_r \cong (1.3\ \mathrm{K})/\rho(300\ \mathrm{K})$ is slightly reduced. At ambient pressure the sign of the MC is negative at all fields, indicating that the e–e interaction contribution is dominant. At 15 kbar a positive MC due to the dominant contribution from WL has been observed. This is an interesting example to show that by tuning the position of the mobility edge with respect to the Fermi level it is possible to tune the WL and e–e interaction contributions to low-temperature transport.

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