Metal-insulator transition in PF$_6$ doped polypyrrole: interchain charge transfer versus electronic correlation

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We performed dielectric spectroscopy on polypyrrole near the metal-insulator transition (MIT) down to 2 K. We evaluate the dependence of the plasma frequency ($\omega_p$) and the scattering time ($\tau$) on the distance to the MIT, characterized by the Fermi-level relative to the band-edge of extended states, $E_F - E_c$. Especially the strong decrease of $\tau$ with increasing $E_F - E_c$ is in conflict with the usually applied models for the MIT. Although morphology and disorder are important, the MIT is Mott-Hubbard-like being dominated by the competition of interchain charge transfer and electronic correlation.

In general the occurrence of a metal-insulator transition (MIT) depends on several parameters [1]. In the absence of electron-electron interactions a random potential $W$ localizes charge carriers [2] due to the interference of multiply scattered electronic waves. For this process the scaling-theory of Anderson localization [3] provides a convenient framework. To describe electronic interactions, one usually introduces the on-site interaction energy $U$ and inter-site interaction energy $V$ in the so-called extended Hubbard Hamiltonian [4]. Often the electron-electron interactions suppress the conductivity, e.g. at half-filling for $W = 0$ and $V = 0$, when $U$ becomes comparable to the inter-site charge-transfer integral the so-called Mott-Hubbard metal-insulator transition occurs. As reduced dimensionality enhances the effects of disorder and interactions [5], the geometry of the electronic system plays a profound role as well. For instance, in a strictly one-dimensional system for any amount of disorder all states are localized due to repeated backscattering [6]. Moreover, even in the absence of disorder, one-dimensional systems are insulating due to the Peierls instability and/or finite interactions which, in one dimension, always induce a gap at the Fermi level [7]. In doped conjugated polymers, it is widely recognized that structural disorder drives the MIT [8,9], while recent observations of density wave dynamics points to the importance of electronic correlations [10]. On a microscopic scale charge transport is inevitably anisotropic: the charge transfer perpendicular to the chain is weak compared to that along the chain, which enhances the effects of disorder and electronic correlation. Nonetheless, a positive temperature coefficient of the resistivity [11] and a negative dielectric constant in the microwave and far-infrared regime [12] indicate the presence of a truly metallic state. In a previous study we pointed out a correlation between the plasma frequency $\omega_p$ and scattering time $\tau$ which together characterize the free-carrier dynamics [13]. To explain the required finite density of delocalized states at the Fermi level interchain charge transfer had to be sufficiently strong to overcome the disorder- and interactions-induced localization [13].

In the present work we extend the dielectric measurements as a function of frequency $\omega = 2\pi f$ on PF$_6$ doped polypyrrole (PPy) around the MIT from 300 K to 2 K. The specific $T$- and $\omega$-dependent response enables to characterize the position with respect to the MIT for both insulating and metallic samples. We evaluate the dependence of $\omega_p$ and $\tau$ as a function of this distance. Especially the strong decrease of $\tau$ when going deeper into the metallic phase is in conflict with the usually applied models for the MIT. This discrepancy provides a strong clue for the role of interchain coupling and electronic correlation, indicating that the MIT may be considered as a Mott-Hubbard transition. We suggest a mechanism that explains the influence of structural disorder in this transition.

Free-standing films of PPy-PF$_6$ are prepared by electrochemical polymerization as described in detail elsewhere [14]. Films have been polymerized at different temperatures ($-40^\circ C < T_{pol} < 20^\circ C$). One sample ($D$) has been slightly dedoped after the synthesis. The dc conductivity ($\sigma_{dc}$) of several samples is shown in Fig. 1. The plot of the reduced activation energy $W = d \ln(\sigma_{dc})/d \ln(T)$ versus $T$, Fig. 1a, demonstrates that samples in the metallic ($M2$, $M$), critical ($C$), and insulating ($I$) regime of the MIT are obtained. Sample $M2$ ($T_{pol} = -40^\circ C$) exhibits a conductivity minimum around 13 K, below which $\partial \sigma_{dc}/\partial T < 0$ indicating truly metallic behavior. However, for both $M$ and $M2$, $\partial \sigma_{dc}/\partial T > 0$ at higher $T$ which shows that PPy-PF$_6$ is at best a “bad” metal. For increasing $T_{pol}$ the conductive properties deteriorate and the system goes through the MIT. This can
be attributed to an increase of the structural disorder [7].

The electrodynamic properties have been studied by means of transmission experiments [14] in the frequency range 8–700 GHz (0.27–23 cm$^{-1}$, 0.033–2.9 meV), which overlaps with both the microwave and far-infrared regime. Both amplitude and phase are obtained by means of an ABruu vector network-analyzer. The data are fitted to first principle transmission formulae to derive the complex conductivity $\sigma^*(\omega) = \sigma(\omega) + i\omega\varepsilon(\omega)$, without the use of Kramers-Kronig manipulation [14]. Uncertainty in $\sigma$ and $\varepsilon$ is less than 5% in the range 100–600 GHz at all $T$.

The $T$-dependent $\varepsilon(\omega)$ of $C$ and $M$ are shown in Fig. 2. For $C$ $\varepsilon < 0$ only at high $T$, while for $M$ a negative contribution to $\varepsilon(\omega)$ persists down to low $T$. The negative $\varepsilon$ agrees with the findings of Kohlman and co-workers [8], and establishes the presence of free carriers in PPy-PF$_6$. Solid lines are fits to the Drude model:

$$\varepsilon(\omega) = \varepsilon_b - \frac{\omega_p^2\tau^2}{1 + \omega^2\tau^2},$$

with $\tau$ the free-carrier scattering time, $\varepsilon_b$ the background dielectric constant due to polarization of the lattice and localized carriers, and $\omega_p$ the plasma frequency:

$$\omega_p = \sqrt{\frac{n_f e^2}{\varepsilon_0 m^*}},$$

with $n_f$ the free-carrier density, $e$ electronic charge, $m^*$ the effective mass, and $\varepsilon_0$ the vacuum permittivity. The insets of Fig. 2 show $\sigma(\omega)$ for $C$ and $M$ at the same $T$’s. Note that for $M$, $\partial\sigma/\partial\omega < 0$ at low $\omega$ at all $T$ as expected for free carriers, while for $C$ only at room temperature $\partial\sigma/\partial\omega < 0$ is observed.

By fitting to Eq. (1), the $\varepsilon(\omega, T)$ data lead to $\omega_p(T)$ as shown in Fig. 3a. The $T$-dependent data do not extend to low enough $\omega$ to derive $\tau$ from $\varepsilon(\omega)$. However, according to Drude $\sigma(\omega = 0) = \omega_p^2\varepsilon_0$, which is estimated by $\sigma_{dc} - \sigma(95 \text{ GHz})$ [13]. For metallic $M$ and $M_2$, $\tau(T)$ could thus be obtained, see Fig. 3b.

First we consider the behavior of $\omega_p(T)$ near the MIT. For $M_2$ and $M$, $\omega_p$ decreases when cooling but remains finite at low $T$: for these metallic samples free carriers are present at $T = 0$. For $C$, $I$, and $D$, $\omega_p$ strongly drops when lowering $T$ which shows that the free-carrier density vanishes as $T \rightarrow 0$. In comparison with conventional metals where $\omega_p \sim 1$–10 eV, the $\omega_p$’s in PPy-PF$_6$ are very low. For these systems near the MIT only a fraction of the carriers occupies extended states (0.1% if $m^*$ equals the free electron mass $m_e$; a larger $m^*$ would imply a larger $n_f$) with the majority of the carriers residing in localized states [8][13]. The observed increase of $\omega_p$ with $T$ of both the metallic and insulating samples shows that barely localized carriers can be thermally activated to higher-lying extended states. For given Fermi-level $E_F$ and energetic boundary $E_c$ between localized and extended states, the density of occupied extended states follows from

$$n_f(T) = \int_{E_c}^{\infty} f_{FD}(T) g(E) dE,$$

(3)

where $f_{FD}$ denotes the Fermi-Dirac distribution function, $g(E)$ is the density of states, and the Fermi level is defined as the zero of energy. Using Eqs. (2) and (3) and assuming that $m^*$ is independent of $T$ and $g$ independent of $E$, the $\omega_p(T)$ data sets for each sample can be excellently reproduced (solid lines in Fig. 3a) with only two free parameters: $E_F - E_c$ and $g/m^*$. The $T$-dependence of $\omega_p$ is fixed by $E_F - E_c$; the absolute value is fixed by both. For samples $M_2$, $M$, $C$, $I$, and $D$ $E_F - E_c$ is found to be: $100 \pm 50$ K, $25 \pm 10$ K, $-70 \pm 15$ K, $-120 \pm 20$ K, and $-350 \pm 150$ K respectively; values for $g/m^*$ are presented in Fig. 4. Analysis of the PPy-PF$_6$
data given in Ref. [8] gives $E_F - E_c = 200 \pm 100$ K. As expected, for metallic samples $E_F > E_c$, while for $C$, $I$, and $D$, $E_F < E_c$. While previous studies resorted to the so-called resistivity-ratio to characterize conducting polymers [9], the above results provide an experimental characterization of the conductive state with respect to the MIT in terms of a physical quantity. To our knowledge, for conducting polymers a comparable quantitative analysis has not been reported, and, as demonstrated below, provides a new perspective on the mechanisms behind the MIT.

Let us now turn to the derived $\tau$‘s, see Fig. 3c. In view of commonly reported $\tau \sim 10^{-14}$ s values in normal metals, the scattering times in the disordered PPY-PF$_6$ are extremely long. Following Ref. [8], if all carriers were delocalized in a three-dimensional band, and hence $v \approx \sqrt{2E_F/m^*} \approx 5 \times 10^3$ m/s, these long $\tau$’s lead to anomalously long mean free-paths $\ell \approx 0.2$ $\mu$m and $2$ $\mu$m for M2 and M respectively. However, only above $E_c$ carriers are mobile, hence the free-carrier velocity does not depend on the total carrier density but only on the density of free carriers above $E_c$ [11]. If $k_BT < (E_F - E_c)$ then $v \approx \sqrt{(E_F - E_c)/m^*}$, while $v \approx \sqrt{k_BT/m^*}$ for $k_BT > (E_F - E_c)$. The dotted lines in Fig. 3c) indicate $\tau \propto 1/\sqrt{T}$ for $M$ for $T > 20$ K. Since in this range $k_BT > (E_F - E_c)$ and $v \propto 1/\sqrt{T}$, this suggests that $\ell$ is $T$-independent. The increase of $\tau$ when cooling could indicate an electron-phonon scattering mechanism. However, the $T$-independence of $\ell$ does not support such a scenario, but indicates that scattering is dominated by static disorder. Assuming constant $\ell$ and taking into account the $T$-dependence of the carrier velocity expressed by $v = n_f^{-1} \int_{E_c}^{\infty} f_{FD} \sqrt{(E - E_c)/m^*} dE$, $\tau(T)$ can be excellently reproduced using the $(E_F - E_c)$ derived from $\omega_p(T)$ $(E_F - E_c$ fixes the $T$-dependence of $\tau$). For M2 due to the errorbars we can not be conclusive on the $T$-dependence of $\tau$. Taking $m^* = m_e$, $\ell = 200$ nm and $\ell = 200$ nm for M2 and M respectively; larger $m^*$ would give shorter $\ell$. The reason for $\ell$ to appear longer for the “less metallic” $M$ is discussed below.

Fig. 4 shows the derived values of $\omega_p$ and $\tau$ versus $E_F - E_c$ at 300 K and 4 K and the ratio $g/m^*$ versus $E_F - E_c$, and is the main result of our study. First, consider the dependence of $\omega_p$ on $E_F - E_c$. As discussed above, the finite $\omega_p$ for $T = 300$ K in the insulating regime $(E_F < E_c)$ reflects the thermal activation of barely localized carriers to higher-lying extended states. In the metallic regime for $T \rightarrow 0$ the density of free-carriers $n_f \approx g \times (E_F - E_c)$ and, for constant $g/m^*$, $\omega_p$ would increase according to $\omega_p \propto \sqrt{E_F - E_c}$. However, as $g/m^*$ increases strongly in the metallic regime, a much stronger increase of $\omega_p$ results.

The dependence of $\tau$ on $E_F - E_c$ near the MIT seems peculiar: when coming from the insulating regime and crossing the MIT $\tau$ drops sharply. This behavior persists in both the degenerate, $(E_F - E_c) > k_BT$, and non-degenerate, $(E_F - E_c) < k_BT$, regimes. We note that this decrease of $\tau$ with $E_F - E_c$ agrees with a recently pointed out empirical correlation $\tau \propto \omega_p^{x}$ ($x \sim 1.3$) over two orders of magnitude $\omega$-range [3]. According to the scaling theory of Anderson-localization [3], $E_F - E_c$ increases when the amplitude of the disorder potential decreases, and $\ell \propto (E_F - E_c)^{p}$ with $p > 0.5$ [10], becomes larger. Hence, Anderson theory gives $\tau = \ell/v \propto (E_F - E_c)^{p-1/2}$ which is a monotonically increasing function for $E_F > E_c$, and is therefore in conflict with our experimental observations, see Fig. 4. It has been proposed that the MIT in conducting polymers is better viewed in terms of percolation of metallic islands [5][6]. Then $E_F - E_c$ characterizes the barrier heights between the metallic domains, and $E_F = E_c$ is the percolation threshold. In a percolating metallic network $\tau$ corresponds to either the intrinsic free-carrier scattering time in the metallic islands, or reflects the carrier scattering due to finite-size effects of the metallic network. In the first case $\tau$ should be independent of $E_F - E_c$, in the latter case $\tau$ should increase with increasing $E_F - E_c$. Clearly, also this model for the MIT in conducting polymers can not account for our experimental results. Hence, the decrease of $\tau$ in the metallic regime can not be understood in terms of the schemes usually applied to the MIT in conducting polymers [3][10], which only consider effects of disorder. However, even in the absence of disorder, to obtain a macroscopically conducting state interchain charge-transfer $t_c$ is a prerequisite: in the limit of vanishing $t_c$ carriers are bound to individual polymer-chains giving rise to an insulating state. Hence a poor $t_c$ will impede the formation of a metallic state and determine the low-frequency conductive properties (only for $\hbar \omega > t_c$ the interchain transport dominates).

To explain the effect of $t_c$ on the charge transport properties of conducting polymers, a tight-binding picture is illustrative. The bandwidth for interchain transport is directly proportional to $t_c$, while the effective mass for interchain transport is inversely proportional to $t_c$. However, for small $t_c$ this band becomes unstable for electronic interactions. Since optimally doped PPY-PF$_6$ is quarter-filled, the inter-site interaction $V$ will be most important. When $t_c$ lies below $V$ the interchain transfer can not overcome the Coulomb repulsion and the car-
riers remain localized to the chains: the system is an insulator. For $t_c > V$ wavefunctions are delocalized over adjacent chains and the system becomes a metal. Such a mechanism has been demonstrated to drive the MIT e.g. in quasi-one-dimensional, crystalline Bechgaard salts; only for $t_c$ exceeding the correlation energy a three-dimensional metallic state is formed [3]. The analogy goes even further, as in these Bechgaard salts the metallic state is characterized by a small $\omega_p$ (spectral weight 1%) as well [7]. The essential ingredient for this transition, a small value of $t_c$, is illustrated by the following simple calculation. The interchain charge transfer is typically $t_c \sim 0.01 - 0.1$ eV [15], and $V = e^2/(4\pi\varepsilon_0\delta_0 r)$, with $r$ the separation between charges. For optimal doping of 1 charge per 4 monomers $r$ is a few nm and $V \approx 0.1$ eV ($U$ will be even larger). Since $t_c$ and $V$ are of the same order of magnitude the competition between interchain charge transfer and electron-electron correlations may play a dominant role in the occurrence of the MIT in conducting polymers. These conclusions are in agreement with a recent numerical finding of a strong dependence of the MIT on interchain interactions in polyacetylene [18].

What should be expected for the carrier dynamics near the MIT in case of a Mott-Hubbard transition? Starting in the metallic regime, when decreasing $t_c$, the effective mass increases and it has even been suggested that $m^*$ diverges near the critical point [3], while the density of delocalized states vanishes near the MIT [14]. This implies a strong increase of $g/m^*$ with increasing $E_F - E_c$ in qualitative agreement with our experimental findings, see Fig. 4. To our knowledge, a relation between $g/m^*$ and distance to the MIT is not available. Note that, given the values $g \sim 1-10$ states/(eV ring) reported in literature [7,19], Fig. 4 suggests $m^*$ to be in the 1–10 times $m_e$ range. The increase of $m^*$ in the Mott-Hubbard scenario leads to a strongly decreasing free-carrier velocity $v \propto \sqrt{(E_F - E_c)/m^*}$ near the critical point. Since the scattering probability is proportional to the density of states available for scattering, i.e. $g$ [13], we expect $\tau \propto g^{-1}\sqrt{m^*/(E_F - E_c)}$, which decreases for increasing $E_F - E_c$. Hence the unusual decrease of $\tau$, and seemingly shorter $\ell$, in the metallic regime supports our arguments that the MIT is driven by the interplay between $t_c$ and $V$ which gives decreasing $g$ and increasing $m^*$ near the critical regime.

How can we reconcile this picture with the observations that structural disorder drives the MIT? The interchain $\pi$-electronic overlap $t_c$ depends exponentially on separation and orientation of adjacent chain(segment)s and is therefore particularly sensitive to the local ordering of polymer chains. Deviations from the optimal packing make the allowed bandwidth exponentially narrow and the effective mass exponentially large. Due to this extreme sensitivity, the increase of $t_c$ with respect to $U, V$ may be the dominant driving mechanism for the MIT instead of disorder-induced localization. Also X-ray diffraction studies [20] demonstrate that a high conductivity in PPy-PF$_6$ in the vicinity of the MIT. The specific $T$-dependence allows to characterize the position of the samples with respect to the MIT. It is demonstrated that $\omega_p$ increases, and, unexpectedly that $\tau$ strongly drops in better conducting samples. These results are inconsistent with models which only consider the effect of disorder-induced localization. Instead, we have argued that the behavior in the vicinity of the MIT can be explained in terms of a Mott-Hubbard transition due to the competition between electronic correlation and interchain charge transfer. Structural disorder could induce such a Mott-Hubbard transition via the strong sensitivity of $t_c$ on the packing of individual chains.

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[1] M. J. Hirsch, Comments Cond. Mat. Phys. 13, 249 (1987).
[2] P. W. Anderson, Phys. Rev. 109, 1492 (1958).
[3] P. A. Lee and T. V. Ramakrishnan, Rev. Mod. Phys. 57, 287 (1985).
[4] J. Hubbard, Proc. Roy. Soc. A (London) 277, 237 (1964).
[5] N. F. Mott and W. D. Twose, Adv. Phys. 10, 107 (1961).
[6] N. H. March, Electron Correlation in Molecules and Condensed Phases, (Plenum Press, New York, 1996).
[7] C. O. Yoon, Reghu M., D. Moses, and A. J. Heeger, Phys. Rev. B 49, 10851 (1994).
[8] R. S. Kohlman et al., Phys. Rev. Lett. 78, 3915 (1997).
[9] K. Lee, R. Menon, C. O. Yoon, and A. J. Heeger, Phys. Rev. B 52, 4779 (1995).
[10] J. Joo et al., Phys. Rev. B 57, 9567 (1998).
[11] K. Lee et al., Phys. Rev. B 61, 1635 (2000).
[12] T. Hagiwara, M. Hirasaki, K. Sato and M. Yamaura, Synth. Met. 40 35 (1990).
[13] H. C. F. Martens et al., cond-mat/0005512; accepted for Phys. Rev. B.
[14] J. A. Reedijk et al., Rev. Sci. Instrum. 71, 478 (2000).
[15] R. Menon, C. O. Yoon, D. Moses, and A. J. Heeger, Handbook of Conducting Polymers, Second Edition (Marcel Dekker, New York, 1998).
[16] T. G. Castner, Phys. Rev. Lett. 84, 1539 (2000).
[17] V. Vescoli et al., Science 281, 1181 (1998).
[18] M. Paulsson and S. Stafström, Phys. Rev. B 60, 7939 (1999).
[19] A. Raghunathan et al., Phys. Rev. B 57, 9567 (1998).
[20] Y. Nogami, J.-P. Pouget, T. Ishiguro, Synth. Met. 62, 257 (1994).
[21] K. Väkiparta et al., Phys. Rev. B 47, 9977 (1993).