Crossover in Electrical Frequency Response through an Insulator-Metal Transition

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(Received 2 May 1996)

The insulator-metal transition (IMT) for a model quasi-one-dimensional (quasi-1D) conducting polymer (polyaniline) is probed at room temperature (RT) over an unusually broad frequency range (2 meV–6 eV) and also via T-dependent dc conductivity ($\sigma_{\rm dc}$). We determine that the IMT is not monotonic with increasing $\sigma_{\rm dc}$(RT). The RT far infrared scattering time (τ) becomes unusually long ($\geq 10^{-13}$ s) as $\sigma_{\rm dc}$(RT) increases, even for samples on the insulating side of the IMT. We conclude that the IMT is due to percolation in the presence of inhomogeneous disorder and quasi-1D localization rather than 3D Anderson localization. [S0031-9007(96)01283-5]

PACS numbers: 71.30.+h, 72.30.+q, 72.60.+g, 78.66.Qn

The study of insulator-metal transitions (IMTs) has provided insight into a wide variety of phenomena in heavily doped semiconductors, metal ammonia solutions, and conducting polymers [1–10]. Generally, these studies focused on dc transport properties [1,2,5,8–10], and the effects of pressure [1,2,5,9], magnetic field [1,2,4,5,9], and composition [1,2,4,5]. Systematic probes of the electronic response away from the Fermi level (E_F) would provide new insight into IMTs. High frequency studies are particularly useful for discerning the essential differences between a three-dimensional (3D) Anderson transition and an IMT due to percolation in the presence of inhomogeneous disorder and quasi-1D localization.

A 3D Anderson transition occurs in the presence of large homogeneous (uniform statistical) disorder. A mobility edge (E_C) separates localized from extended states [1–4], and the transport scattering time (τ) varies slowly with energy in the vicinity of E_C [11]. At the IMT, the electronic localization length ($L_{\rm loc}$) diverges. A monotonic development of the transport properties occurs as E_F crosses E_C into the delocalized states [1]. In particular, $\sigma_{\rm dc}$ grows in magnitude and weakens in temperature dependence [1], and the slope of the quantity W [$\equiv d\ln\sigma_{\rm dc}(T)/d\ln T$] [12] vs T changes sign from negative to positive. However, the large disorder required to localize electronic wave functions leads to the slowly varying τ being short (typically $\sim 10^{-15}$ s). The Ioffe-Regel condition [13] requires $k_F\lambda \sim 1$, where k_F is the Fermi wave vector and λ is the mean free path. Approaching the IMT from the metallic side, the optical conductivity [$\sigma(\omega)$] is monotonically suppressed due to the short τ beneath the free carrier $\sigma_{\rm Drude}(\omega)$ at low energy [2,14]. For short τ, localization corrections to the metallic Drude response result in a dielectric function [$\epsilon(\omega)$] that is positive in the far infrared [2,4,11,14], in contrast to the negative low energy $\epsilon_{\rm Drude}(\omega)$ for usual metals [15].

In contrast, a very different IMT is presented by an array of 3D (spatially [16,17] and electronically [18] anisotropic) metallic ellipsoids with an open Fermi surface [6,7,10,19] separated by a disordered quasi-1D medium (inhomogeneous disorder model). Conduction electrons in isolated 1D systems are localized by even small disorder [1] with $L_{\rm loc}$ increasing as the disorder decreases. When $L_{\rm loc}$ in the quasi-1D disordered regions exceeds the separation between metallic ellipsoids for a sufficient fraction of the sample, an IMT occurs [7,20]. As for a 3D Anderson transition, there is a crossover in slope for W vs T as the IMT is achieved, though the IMT is no longer necessarily a monotonic function of the room temperature (RT) $\sigma_{\rm dc}$. Because of an open Fermi surface, a very long τ may be associated with a fraction (δ) of the carriers present at percolation. For this circumstance at 0 K, $\sigma(\omega)$ will increase below an unscreened plasma frequency Ω_p ($= \sqrt{4\pi\delta ne^2/m^*}$ [15], where n is the full carrier density and m^* is the effective mass of the fraction δ of delocalized carriers) and $\epsilon(\omega)$ will become negative below Ω_p. Because of phonon-induced delocalization in the quasi-1D disordered regions, $\sigma(\omega)$ and $\epsilon(\omega)$ can have this behavior at finite T *even for samples that are on the insulator side of the IMT at 0 K.*

Conducting polyaniline (PAN), with RT $\sigma_{\rm dc}$ close to the minimum metallic σ ($\sigma_{\rm min} \sim 0.03e^2/\hbar a \sim$ 100 S/cm [1,2,4,9]), is a model anisotropic system to study the origins of an IMT. Its IMT has variously been described by the inhomogeneous disorder model [7,10,19] and the Anderson model [9,14]. Earlier, the IMT was ascribed to charging energy limited tunneling among metallic islands [21] as well as resonant tunneling [22]. In this Letter we report the frequency response over an unusually broad range of frequencies (2 meV–6 eV) of the RT $\sigma(\omega)$ and $\epsilon(\omega)$ for samples of PAN that cross the IMT as probed by $\sigma_{\rm dc}(T)$. These data, which span from near E_F to far from E_F, demonstrate

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that the IMT is due to inhomogeneous disorder and not a homogeneous 3D Anderson transition. In particular, as $\sigma_{dc}(\mathrm{RT})$ increases, the T dependence of σ_{dc} does not weaken monotonically so that some samples with $\sigma_{dc}(\mathrm{RT}) > \sigma_{min}$ become insulating at low T. $\epsilon(\omega)$ shows free carrier dispersion in the far infrared (IR) for PAN samples with $\sigma_{dc}(\mathrm{RT}) \gtrsim 100$ S/cm and associated long $\tau \geq 10^{-13}$ s, much longer than the Ioffe-Regel condition allows. However, only a small fraction (10^{-3}) of the carriers are delocalized with such long τ. Also, as the slope of the low T $W(T)$ plot crosses from insulating to metallic behavior for different samples, the RT Ω_p does not increase monotonically.

The PAN samples for this study were doped with d,1-camphorsulfonic acid (HCSA). Samples C and D were prepared by first mixing the emeraldine base (EB) state of PAN and HCSA separately in *m*-cresol before mixing the solutions, thus doping them in the solution state. The remaining films were prepared by grinding stoichiometric amounts of EB and HCSA powders with mortar and pestle before dissolution in a mixture of *m*-cresol and chloroform. Samples A and B were cast from *m*-cresol [23,24] while E and F were cast, respectively, from 50%/50% and 30%/70% mixtures of *m*-cresol/chloroform [24]. Samples G and H were cast from chloroform [24]. The techniques for measuring $\sigma_{dc}(T)$ [6,7] and reflectance (2 meV–6 eV) [15,19] have been reported separately. $\epsilon(\omega)$ and $\sigma(\omega)$ were determined from the reflectance data via a Kramers-Kronig analysis with suitable extrapolations for high and low frequencies [15,19].

For hopping (insulating) transport $(\sigma_{dc}(T) = \sigma_0 \exp[-(T_0/T)^{\alpha}])$ [1,2,9,12], $\log_{10} W = \text{const} - \alpha \log_{10} T$; therefore the plot of $\log_{10} W$ vs $\log_{10} T$ has a negative slope at low T. W, Fig. 1(a), has a negative slope for samples B–G with α in the range 0.3–0.6. In contrast, $\log_{10} W$ for sample A has a positive slope characteristic of metallic behavior. In addition, $\sigma_{dc} \sim 80$ S/cm was measured for sample A down to ~20 mK [25]. Therefore, sample A displays metallic behavior while B–G display insulating behavior as $T \to 0$. $\sigma_{dc}(T)$ for samples A–E, Fig. 1(b), increases with decreasing T (metallic behavior) near RT, reaches a maximum, and then decreases at low T. This $\sigma_{dc}(T)$ was explained within a model of 3D metallic regions coupled through electronically 1D chains in the presence of quasi-1D localization [7]. Though sample A is metallic at low T, insulating sample C has the highest $\sigma_{dc}(\mathrm{RT})$ ($> \sigma_{min}$); however, sample C becomes insulating at low T. Similar crossover behavior in $\sigma_{dc}(T)$ occurs for samples B and D. Thus the T dependence of σ_{dc} does not weaken monotonically with increasing $\sigma_{dc}(\mathrm{RT})$ as expected for an homogeneous 3D Anderson IMT [1]. For the remaining samples, σ_{dc} decreases monotonically with decreasing T, indicating stronger localization.

Figure 2 shows the evolution of the RT $\sigma(\omega)$ for samples crossing the IMT. The oscillations in the vicinity

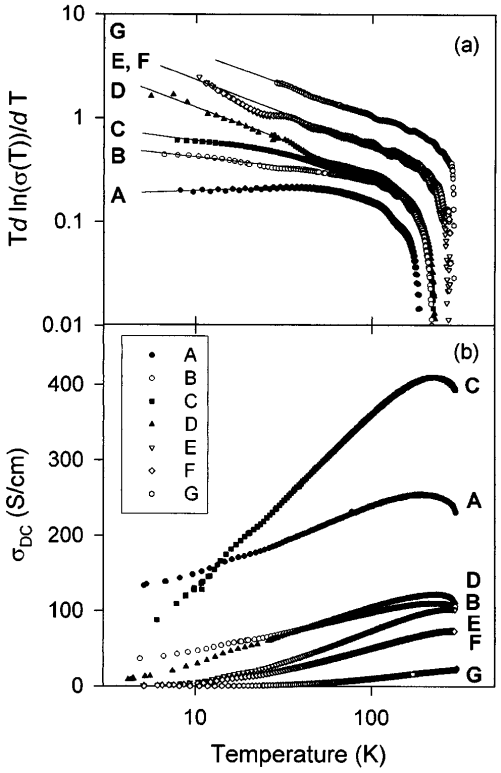

FIG. 1. (a) The logarithmic derivative of the T dependent conductivity, $W = Td\ln[\sigma(T)]/dT$, for PAN-CSA samples. (b) The corresponding $\sigma_{dc}(T)$.

of 0.1 eV are due to phonons. For sample H [$\sigma_{dc} \sim 0.7$ S/cm [6]], $\sigma(\omega)$ is dominated by a peak at ~1.5 eV, previously attributed to very localized charge carriers [24]. As the samples approach the IMT from the insulating side, the 1.5 eV peak is diminished and $\sigma(\omega)$ increases in the IR. An isosbestic point in $\sigma(\omega)$ at ~ 1.3 eV, Fig. 2(a), supports composite behavior in conducting PAN. For samples A–F, $\sigma(\omega)$ shows Drude dispersion for energies below ~2 eV (the full carrier plasma edge, $\Omega_{p1} = \sqrt{4\pi n e^2/m_1^*}$, where m_1^* is an averaged effective mass of the carriers) but is suppressed beneath $\sigma_{\mathrm{Drude}}(\omega)$ in the far IR (below ~0.08–0.4 eV varying with sample). This suppression of $\sigma(\omega)$ in the far IR was previously attributed to strong disorder scattering (localization) within the Anderson model [1–4,14]. The energy below which $\sigma(\omega)$ is suppressed decreases as $\sigma_{dc}(\mathrm{RT})$ increases. Drude formula fits to $\sigma(\omega)$ from ~0.4 to 2 eV for samples A–F [25] indicate that the scattering time for these localized carriers is small, $\tau_1 \sim 10^{-15}$ s, comparable with the Ioffe-Regel criterion. $\sigma(\omega)$ decreases monotonically with decreasing energy in the far IR for all samples except sample C, which has the highest $\sigma_{dc}(\mathrm{RT})$. The increase of $\sigma(\omega)$ in the far IR for sample C is similar to reported $\sigma(\omega)$ for highly conducting polyacetylene [26] and shows the same frequency dependence as percolated metal/insulator composites [27].

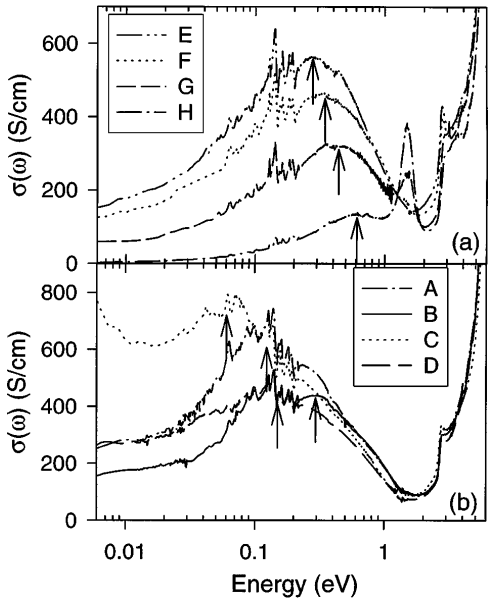

FIG. 2. Room temperature optical conductivity $\sigma(\omega)$ for (a) samples E–H with $\sigma_{\rm dc} < 100$ S/cm and (b) samples A–D with $\sigma_{\rm dc} > 100$ S/cm.

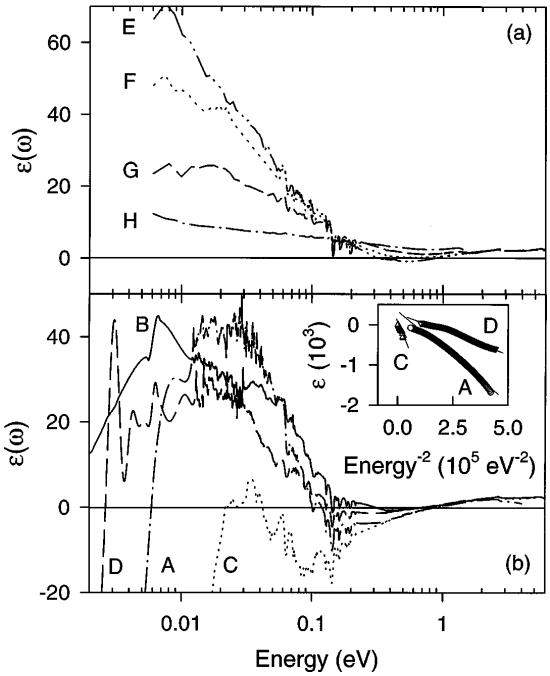

FIG. 3. Room temperature dielectric function $\epsilon(\omega)$ for (a) samples E–H with $\sigma_{\rm dc} < 100$ S/cm and (b) samples A–D with $\sigma_{\rm dc} > 100$ S/cm.

The evolution of the RT $\epsilon(\omega)$ as the PAN samples cross the IMT is presented in Fig. 3. For PAN-CSA sample H, $\epsilon(\omega)$ is small and positive at low energy, with no zero crossings, indicating that the plasma response is overdamped ($\Omega_{p1}\tau_1 < 1$). As the samples approach the IMT from the insulating side, $\epsilon(\omega)$ shows two different behaviors. For samples A–G, Fig. 3, a zero crossing of $\epsilon(\omega)$ develops at $\sim$1 eV as τ_1 grows from $\sim 0.6 \times 10^{-15}$ to 1.3×10^{-15} s. However, $\epsilon(\omega)$ becomes positive in the far IR due to localization effects (small τ_1). For insulating samples C and D and metallic sample A (and likely for insulating sample B), $\epsilon(\omega)$ has three zero crossings, Fig. 3(b), similar to the behavior reported for metallic polyacetylene [26] and polypyrrole [19]. The two higher energy zero crossings are attributed to localized carriers. The third crossing occurs in the far IR, below which energy $\epsilon(\omega)$ remains negative, as expected for free carriers [6,15]. Measurements at 6.5 GHz confirm that $\epsilon(\omega)$ is negative even at microwave frequencies [6,10,25].

Within the Drude model for free electrons with long mean free times ($\tau \gg 1/\omega$) [15], $\epsilon(\omega) = \epsilon_b - \Omega_p^2/\omega^2$, where ϵ_b is the background dielectric function. The slope of $\epsilon(\omega)$ versus $1/\omega^2$, Fig. 3(b) inset, yields $\Omega_p \sim 0.07$, 0.11, and 0.04 eV, respectively, for samples A, C, and D, small values compared to $\Omega_{p1} \sim 2$ eV. The fraction (δ) of carriers with a long τ is estimated as

$$\delta = (m^*/m_1^*)\,(\Omega_p/\Omega_{p1})^2 \sim 10^{-3}, \qquad (1)$$

assuming $m^* \simeq m_1^*$. It is noted that m^* may be larger than m_1^* due to band narrowing in the disordered regions. This small δ resembles the case for metal/insulator composites close to the metallic percolation threshold [27]. In addition, Ω_p scales with $\sigma_{\rm dc}$(RT) and not the low temperature W plot. Therefore, the Ω_p of sample C, for which the 0 K E_F lies in the region of localized states is larger than the Ω_p of sample A, for which the 0 K E_F lies in the region of extended (Drude) states. This is in direct contradiction with 3D Anderson model predictions but is in accord with the inhomogeneous disorder model.

Since $\epsilon(\omega)$ does not saturate down to 10 cm^{-1}, inset Fig. 3(b), $\tau > 1/10$ cm$^{-1} \sim 5 \times 10^{-13}$ s, similar to the τ reported for conducting polyacetylene [26]. By comparing Ω_p(RT) with $\sigma_{\rm dc}$(RT) for samples A, C, and D and using the Drude expression $\sigma_{\rm dc} = \Omega_p^2\tau/4\pi$, a scattering time $\tau \sim 10^{-13}$ s is also obtained, indicating that the metallic $\sigma_{\rm dc}$ may be due to only these delocalized carriers. This τ is much longer than allowed by the Ioffe-Regel condition. Since τ varies slowly with energy for 3D Anderson localization, even thermal population of states above E_c is not expected to lead to large τ. On the other hand, phonon-induced delocalization in the quasi-1D disordered regions will lead to large τs consistent with the inhomogeneous disorder model.

Estimating the Fermi velocity as $v_F \sim 5 \times 10^7$ cm/s using a fit of $\sigma(\omega)$ by a localization corrected Drude model [2] (consistent with $v_F \sim \hbar k_F/m_e \sim 2 \times 10^7$ cm/s, where $k_F = \pi/2c$ since E_F lies in the center of a polaron band [28] and $c = 10.2$ Å [16]), the mean free path $\lambda \sim 10^3$ Å for the free electrons. A larger m^* will, of course, reduce this estimate of λ. This λ is much larger than the crystalline domain size for these materials ($\sim$40 Å [6,16]), indicating that the small fraction (δ) of free carriers diffuse among many crystalline regions, consistent with percolation. For conducting polymers,

the percolation is unique because individual polymer chains can be part of both ordered metallic ellipsoids and disordered quasi-1D regions where localization effects are stronger. For PAN-CSA samples B–D, Ω_p is observed at RT even though they become insulating at low T. This is attributed to the importance of phonon-induced delocalization within the disordered regions [7,10,19], as the carriers must transit disordered regions while crossing the sample. At low T when the phonon scattering is weak, the disordered regions provide strong localization, resulting in the strong T dependence of σ_{dc} for the insulating samples [10]. T dependent far IR studies show that $\Omega_p \rightarrow 0$ for insulating samples at low T [25]. In contrast to the large λ for the delocalized carriers, the large majority of the carriers have $\tau \sim 10^{-15}$ s leading to $\lambda \sim 5$ Å, shorter than the $\lambda \sim 40$ Å expected for confinement to the crystalline regions. This difference may be accounted for by averaging over the inhomogeneous disorder and chain orientations.

In summary, with improved processing, PAN-CSA, a model quasi-1D conductor, shows a transition from localized hopping to metallic transport. At RT, a small fraction (10^{-3}) of carriers are delocalized with $\tau > 10^{-13}$ s, inconsistent with the Ioffe-Regel condition, while the large majority of carriers are localized with $\tau \sim 10^{-15}$ s. Also, because the T dependence of σ_{dc} does not monotonically weaken with increasing $\sigma_{\mathrm{dc}}(\mathrm{RT})$ and $\Omega_p(\mathrm{RT})$ scales with $\sigma_{\mathrm{dc}}(\mathrm{RT})$ and not the low T W plot, a homogeneous Anderson transition is not appropriate for conducting polymers. $\sigma_{\mathrm{dc}}(T)$ as well as $\sigma(\omega)$ and $\epsilon(\omega)$ are consistent with the behavior of percolating composite systems. Therefore, a unique percolating composite with inhomogeneous disorder is proposed which accounts for quasi-1D localization and phonon-induced delocalization in disordered regions between fuzzy crystalline regions.

We wish to thank V. N. Prigodin for useful discussions and T. Lemberger and R. Rochlin for experimental assistance. This work was supported by NIST ATP 1993-01-0149 and NSF DMR-9508723.

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