1/*f* noise through the metal–nonmetal transition in percolating composites

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We have measured the $1/f$ noise through the metal–nonmetal transition in carbon black/polymer composites as a function of temperature and doping. At the electronic transition, the resistivity power spectrum S_ρ varies as $S_\rho \sim \rho^Q$, with $Q=2.77$, in agreement with classical three-dimensional percolation. At lower temperatures, a crossover to tunneling-dominated transport occurs with $S_\rho \sim \ln S_\rho/\rho^2$. Our results show that $1/f$ noise can be a more sensitive technique than resistivity itself for probing transport behavior near a percolation-induced electronic transition. © *2000 American Institute of Physics.* [S0003-6951(00)02505-5]

Most systems contain some type of noise that is generated through local fluctuations in energy or charge. Noise power spectrums that vary inversely with frequency. $1/f$ noise are prevalent in disordered materials and are important for understanding materials near a metal–nonmetal transition as noise can readily distinguish between classical and quantum percolation effects. Understanding the nature of transport near such an electronic transition is important to many technologically relevant materials, including semiconducting devices, superconductors, magnetoresistive materials, and polymer composite sensors. In this letter, we present measurements of the $1/f$ noise in a percolating disordered composite driven continuously through the three-dimensional (3D) metal–nonmetal transition with temperature. We show that the electronic transition is driven by classical lattice percolation at finite temperatures with a crossover to quantum tunneling deeper into the metallic state. Our results demonstrate that $1/f$ resistivity noise can be a more sensitive technique than resistivity itself for understanding transport phenomena near a metal–nonmetal transition.

Carbon black–polymer composite systems were chosen for this study since they are the canonical examples of classical percolating systems as well as being important commercial materials for resettable fuses, self-regulating heaters, and electronic noises.[1–3] The samples consist of commercial metallic carbon black nanoparticles on the order of 80 nm in diameter that aggregate to form clusters roughly 200 nm in size. The aggregates are distributed randomly throughout an insulating high density polyethylene polymer of melting point 408 K. When sufficient carbon black is present to form a continuous connected pathway, the sample becomes conducting. This metal–nonmetal electronic transition occurs at a critical volume filling fraction p_c of 0.170 ± 0.001 as predicted for homogenous 3D classical percolation.[1,2] We have studied high-quality samples of metallic concentration p of 0.175, 0.182, and 0.350 with a control over p to within a few tenths of a percent.

For noise measurements, the samples were typically 3 mm by 13 mm and 250 μm thick. The contacts for the true four-probe measurements were made using silver paint on the sample edge to minimize contact noise, and two-probe measurements were taken to verify that sample noise dominated over contact noise. Constant current was sourced using a battery and limiting resistor, and voltage was measured using an electrometer and a low noise preamplifier. The sample was kept inside an Oxford cryostat for temperature stability. The noise power spectrum S_ρ was derived from the time-dependent noise measurements using a Butterworth filter and Fourier transform. Fits to $1/f^\alpha$ in the metallic state yield an α of 1.00 ± 0.12 throughout the entire temperature range, consistent with $1/f$ noise.

Most previous studies of $1/f$ noise near the metal–nonmetal transition have involved two dimensional (2D) samples of a metallic continuum with nonconducting circular gaps dispersed throughout, known as a continuum or Swiss cheese lattice.[4–6] Very few experimental studies exist on either 3D systems or systems consisting of a percolative backbone of conducting spheres in an insulating medium, known as a classical lattice.[7] In addition, the metal–nonmetal transition in previous experiments was driven by changing the concentration of the components. Because of sample to sample variation in morphology, the number of samples required, and the changes in contacts, this method makes it difficult to systematically measure $1/f$ noise through the transition as well as to approach the transition close enough to be in the critical scaling regime.[1] For our experiment, we take a single sample on the metallic side and drive it through the transition as a function of temperature.[8] As a metallic composite is heated, the higher thermal expansion of the polymer matrix causes the overlap of carbon black aggregates to decrease, eventually breaking the percolative pathways and driving the sample insulating. Although this is analogous to changing the concentration of the components, by taking this approach we are able to use a single sample to probe much closer to the transition than previous experiments.

Because more thermal expansion is needed to drive the

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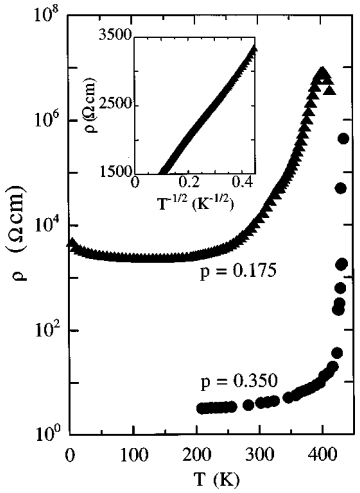

FIG. 1. Resistivity vs temperature for the 0.175 and 0.350 filling fractions of metallic carbon black in an insulating polyethylene host with the metal–nonmetal transitions occurring at 355 and 408 K, respectively. The inset shows $T^{-1/2}$ temperature-dependence characteristic of disordered materials in the presence of electron–electron correlations.

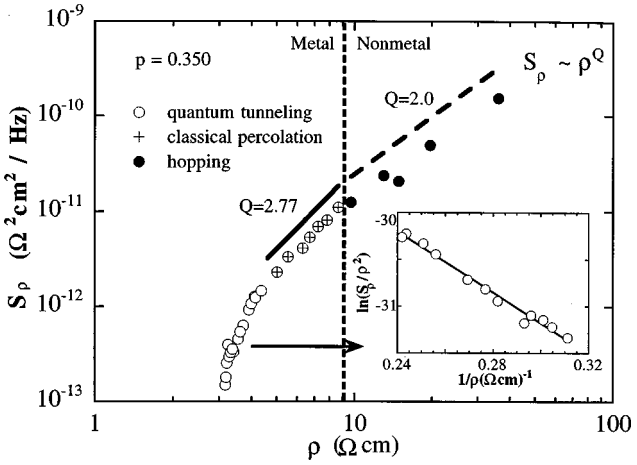

FIG. 2. The resistivity noise power spectrum S_ρ taken at 1 Hz vs the resistivity ρ with the open and closed symbols representing the metallic and nonmetallic states, respectively. The thin dashed line marks the transition from metallic to insulating behavior corresponding to the sharp transition in the resistivity observed in Fig. 1. The lines are theoretical fits to $S_\rho \sim \rho^Q$ for classical percolation (solid line: $Q=2.77$) and hopping transport (dashed line: $Q=2.0$). The inset shows the fit to quantum tunneling forms, $\ln(S_\rho/\rho^2)$ vs $1/\rho$.

transition, the transition temperature increases with increasing carbon black concentration, as shown in Fig. 1. For the sample with 0.175 metallic filling fraction, the broad transition temperature occurs near 355 ± 5 K. For the 0.350 sample, the sharper transition is at the polymer melting point of 408 ± 2 K. Resistivity measurements taken on several concentrations are consistent with classical percolation at finite temperatures.[1] Resistivity measurements taken at lower temperatures ($5\text{ K}<T<50\text{ K}$), however, show features of a correlated metal in the presence of disorder where $\rho\sim T^{-1/2}$ (inset to Fig. 1).

Although resistivity is frequently used as a probe of electron dynamics, interpreting the data is difficult since resistivity is insensitive to the current distribution density, and therefore to the electronic fluctuations. In contrast, $1/f$ resistivity noise, being a higher order measurement, is inherently sensitive to such fluctuations. Theoretical predictions for the dependence of S_ρ on ρ can be used to distinguish between quantum and classical mechanisms for the electronic transport. These predictions vary from exponential divergence for different quantum mechanisms to power laws for various forms of percolation arising from classical effects. Quantum tunneling mechanisms include both quantum percolation and disorder-induced electron localization.[9]

Although no complete microscopic theory of $1/f$ noise currently exists for quantum effects, simple scaling arguments for disorder-induced localization suggest[10] that the normalized noise S_ρ/ρ^2 should diverge exponentially with a form consistent with $\exp[-(2L_\phi/\xi_0)k_f l]$, where L_ϕ is the coherence length for conductance fluctuations and ξ_0 is the correlation length scale factor characteristic of the minimum building blocks of the percolation network. The Fermi wave vector multiplied by the mean free path, $k_f l$, is approximated to vary inversely with resistivity for comparison to theory. A similar exponential dependence is expected for quantum percolation, where it can be approximated that $S_\rho/\rho^2\sim\exp[-c\theta x_c/\rho]$. Here, c is a proportionality constant, θ is a constant in the range of $0<\theta<2$ and $x_c=1-p_c$.[11]

The similarity of these forms makes it difficult for $1/f$ noise to distinguish between the two quantum mechanical mechanisms; however, quantum tunneling is readily distinguished from classical percolation where S_ρ varies as a power law, $S_\rho\sim\rho^Q$, with Q ranging from 2.77 for classical lattice percolation to 4.10 for Swiss cheese percolation in 3D.[12–15] A value of $Q=2$ indicates a region where both the noise and the transport are dominated by thermally activated hopping.

Figure 2 shows a log–log plot of $S_\rho(1\text{ Hz})$ vs ρ for the 0.350 sample. Three distinct transport regions are evident. Lower resistivities (occurring for $T<347$ K) exhibit exponential dependence, as shown in the inset to Fig. 2. The linear fit gives a dimensionless slope of -16 ± 2. This is consistent with the localization model assuming that L_ϕ and ξ_0 are roughly the same order of magnitude. Alternatively, the same slope for the quantum percolation model would mean that the constant c would be roughly 19, assuming that $x_c=0.83$ and $\theta=1$. Attempts to fit this region to the form $S_\rho\sim\rho^Q$ yield a nonphysical exponent of $Q>6$.[15] As the transition is approached from the metallic side, a turnover to power law behavior occurs. Fits in this regime give an exponent of $Q=2.90\pm0.09$, in agreement with classical lattice percolation. Above the electronic transition, the slope turns over to a slightly weaker power law, $Q=2.0\pm0.2$, indicating that hopping dominates both the transport and the noise in this insulating region. This turnover is used to determine the location of the metal–nonmetal transition in Fig. 2. Contrary to previous results,[7] we observe no divergence in the normalized noise at the transition that would suggest that tunneling effects are important. The inability to probe very close to the transition when using a series of samples may explain the discrepancy with previous results (see Table I).

Figure 3 shows noise in the metallic region for the 0.175, 0.182, and 0.350 samples. S_ρ and ρ have been scaled by their values at the turnover from quantum to classical metallic behavior. The universal scaling displayed indicates that the transport mechanisms are the same in these samples, regard-

TABLE I. $1/f$ noise in metal–nonmetal transition systems: experiments and theory.

Experimental/Theoretical	Reference	Q value ($S_\rho \sim \rho^Q$)
2 D Pt–Al_2O_3 film	Mantese *et al.*[a]	6.22 ± 0.06
2 D Mo–Al_2O_3 film		4.39 ± 0.04
3 D carbon powder wax composite	Chen *et al.*[b]	3.7 ± 0.2
Various 2D Al, In, and Cr films	Garfunkel *et al.*[c]	5.4–8.1
2 D In_2O_{3-x} and ZnO films	Cohen *et al.*[d]	$\ln S_\rho/\rho^2 \sim 1/\rho$
2 D Au film	Koch *et al.*[e]	4.0 ± 0.1
3 D carbon black–polymer composites	Breeze *et al.* (this letter)	2.86 ± 0.13 crossover to $\ln S_\rho/\rho^2 \sim 1/\rho$
Quantum percolation theory	Snarskii *et al.*[f]	$\ln S_\rho/\rho^2 \sim 1/\rho$
Anderson localization	Cohen *et al.*[d]	$\ln S_\rho/\rho^2 \sim 1/\rho$
Classical lattice percolation	Ramal *et al.*[g] Tremblay *et al.*[h] Wright *et al.*[i]	2.86 (2 D), 2.77 (3 D)
Swiss cheese continuum	Tremblay *et al.*[h] Garfunkel *et al.*[j]	5.2–6.2 (2 D), 4.1 (3 D)

[a]Reference 6.
[b]Reference 7.
[c]Reference 15.
[d]Reference 10.
[e]Reference 5.
[f]Reference 11.
[g]Reference 12.
[h]Reference 13.
[i]Reference 14.
[j]Reference 4.

less of the carbon black filling fraction. The transition from quantum to classical behavior occurs when the length scale for percolation becomes comparable to the length scale of the disorder or when the percolating pathways start to break. The sample becomes insulating when the last of the conducting pathways are broken. With our current measurements, we cannot identify the specific type of quantum tunneling occurring just below the classical region. Quantum percolation would occur if there were tunneling over small gaps in some of the percolation paths; these could be present in the metallic phase in addition to the solid pathways and could dominate the noise mechanism. The temperature dependence of this form of tunneling may result in a crossover to localization at lower temperatures. Alternatively, it is possible that localization dominates over the entire quantum range.

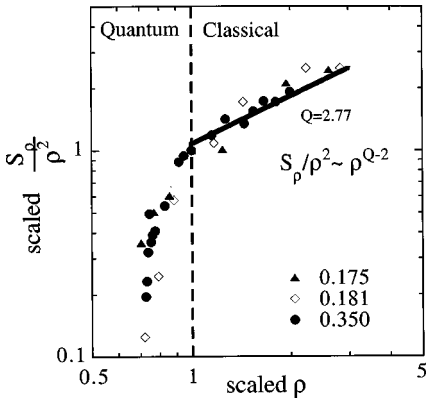

FIG. 3. The scaled normalized resistivity noise power spectrum S_ρ/ρ^2 vs the scaled resistivity ρ demonstrating universality for all three metallic carbon black filling fractions, 0.175, 0.181, and 0.350. The normalized noise and the resistivity have been scaled by their values at the crossover between classical percolation and quantum tunneling. The thin dashed line represents the crossover from classical to quantum behavior.

The transitions from quantum tunneling, classical percolation, and finally to insulating behavior in these disordered composite systems, while clearly marked in the $1/f$ noise, are extremely difficult to observe in the resistivity, indicating that $1/f$ resistivity noise is a more sensitive technique for understanding transport mechanisms in disordered media at finite temperatures. Given the current broad interest in the nature of electronic transitions in two and three dimensions, measurements of $1/f$ noise should prove a critical method for answering questions regarding the mechanisms for quantum and classical phase transitions as well as for understanding transport in more complex composite systems.

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