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Noise spectra of three-dimensional random metal-insulator composites

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We report on measurements of low-frequency noise in percolating *Ag*Pt-tetrafluoroethylene metal-insulator composites. For all samples, the excess noise showed a $1/f$ frequency dependence, and the magnitude of the noise scaled with V^2. In addition, the magnitude of this noise was linearly proportional to the sample resistance R far from the percolation threshold, but increased more rapidly as the critical volume fraction was approached, with $S_v(f)$ varying approximately as R^3 near the transition.

INTRODUCTION

The excess electrical conduction noise (commonly called $1/f$ noise) of randomly inhomogeneous materials is known to exceed greatly the noise of homogeneous materials of comparable resistance.[1-3] In this paper we report on a study of this excess noise in a bulk inhomogeneous system prepared by compacting mixtures of fine metal and insulator powders.

All of our samples exhibit orders of magnitude with more excess noise than homogeneous samples (such as thin metal films or wires) of comparable resistance. For metal volume fractions p much larger than the critical percolation fraction p_c, the excess noise power scales linearly with the sample resistance. As the percolation threshold is approached, however, the excess noise increases more rapidly than the resistance, crossing over to an approximate R^3 dependence. This result suggests that the excess noise of percolating composites originates in constrictions in the conducting path.[1,4]

SAMPLE PREPARATION AND CHARACTERIZATION

The composites used in this study were made by compacting a random mixture of metal and insulator powder into rods 3.1 mm in diameter and 2.0 cm in length. The rods showed a sharp metal-insulator transition (percolation threshold) at a metal volume fraction $p_c \approx 0.21$, near the theoretical value of 0.16 for three-dimensional random percolation.[5] Samples with resistances spanning the range from 30 kΩ to 0.5 Ω were prepared by increasing the metal volume fraction up to $p = 0.30$.

The metal powder used in the study was a Ag–10-at.% Pt alloy.[6] When pressed into a pellet, the compacted powder had a resistivity of $\rho_0 = 34\ \mu\Omega$ cm, reasonably close to the bulk resistivity value for the alloy of $\rho(\text{bulk}) = 9.2\ \mu\Omega$ cm.[7] The typical metal-particle dimension, approximately 1 μm, corresponded to a particle count of about $\sim 10^{11}$ metal particles per sample. The individual metal particles were typically oblong in shape, often with protrusions, and appeared to be formed from an agglomeration of much smaller metal spheres.

The insulator used for all samples was tetrafluoroethylene (TFE) spherical powder with a mean particle diameter of 0.5 μm.[8] We found this extremely inert dielectric to be both easier to handle and more stable than the ionic salt dielectrics (e.g., KBr) typically used as a host for optical studies of fine metal powders.[9]

The low resistivity of the pure compacted metal powder indicates that electrical continuity between the pressed metal particles in our samples arises from a metal-to-metal bond rather than by tunneling through an insulating (oxide) barrier. In addition, the resistance/length of the four composities tested (1520, 121, 2.61, and 1.49 Ω/cm) decreased by about 26% as the temperature was lowered from room temperature to 4.2 K. While differential thermal contractions of the constituents could account for part of this decrease, this result also corroborates the idea that the conduction mechanism in these samples is metallic, and not activated tunneling or hopping.

Samples were prepared by first mixing a small volume fraction of metal (as determined from mass and density) into the TFE powder. The powders were then thoroughly stirred in a vortex mixer and then vacuum compacted into a pellet, using a hydraulic press at a pressure of about 20 kpsi. The solid mixture was then ground into a powder of micrometer-sized particles by using a freezer mill at liquid nitrogen temperatures, and then compacted again.

After several of these press-and-grind cycles, additional metal powder was added, and the entire process repeated until the desired volume fraction was reached. A typical sample was cycled 30–70 times. Although the final volume fraction was determined by measuring the mass of each constituent powder, the accuracy of this determination was limited to about one percent because of the large number of processing steps. This figure is consistent with the scatter in the resistivity of samples having nominally identical metal volume fractions.

The randomness of the particle distribution in the samples was checked using two techniques. The first was to monitor the interim electrical resistance of each sample (above percolation) at the end of each press-and-grind cycle. After adding metal powder to the mixture, we observed that the resistance of the compacted solid decreased rapidly for a few press-and-grind cycles, and then either stabilized or changed slowly with continued cycling. Typically five to eight cycles were needed to stabilize the resistance.

The second test for randomness involved a qualitative elemental x-ray fluorescence mapping of samples as a function of the number of press-and-grind cycles. The mapping showed clear changes from a clustered distribution to a random one (no obvious clustering) over the same number (five to eight) of cycles. Thus, we believe these samples

represent a random three-dimensional percolating system. This conclusion is consistent with the measured value of the percolation threshold, which is near that expected for a truly random system.

EXPERIMENTAL DETAILS

All electrical measurements on the samples were made using a four-point configuration with separate voltage and current electrodes. Low resistance current contacts were made by first wetting the end faces of the sample with a liquid Ga-In eutectic alloy, and then pressing polished copper blocks against the ends. These contacts had resistances typically less than 10% of the total sample resistance. Voltage contacts were made either by attaching point contact electrodes directly to the sample (low-resistance samples) or by bonding electrodes to the sample using either Ga-In or Ag paint (high-resistance samples). The current-voltage characteristics of all the samples were linear (Ohmic) to voltages at least twice the maximum voltage used during the noise measurements. There was no evidence for resistance drift arising from Joule heating in any of our samples.

Extraneous noise from the constant current supply was minimized by using mercury batteries and precision 3-W wire would ballast resistors. The ballast resistors were at least 10 times the sample resistance, and the current was monitored for drift during each measurement. The noise contribution from the current source was checked by comparing the sample noise with that measured on a wire-wound resistor of the same resistance as the sample; no current source noise was found.

Two tests were made to insure that no significant noise was contributed by the current contacts. First, the measured noise did not increase when the voltage probes were moved to include both the sample and the current contacts. Second, the sample noise was found to be independent of the ballast resistance at constant current levels. The large current contact area for these bulk samples apparently prevented contact noise from being a significant problem.

For all noise measurements, the samples and low level electronics were placed in a vibration isolated enclosure fabricated from heliarc welded mumetal. The noise voltage from the sample was amplified by two battery-operated Ithaco 1201 low-noise preamplifiers connected in series. Direct coupling to the input preamplifier was used for sample resistances greater than 100 Ω. For lower-resistance samples, the signal was coupled through a capacitance of 1.5 F to a Princeton Applied Research 190 impedance matching transformer which preceded the first stage of amplification.

The amplified voltage signal was bandwidth limited by an active eight-pole Butterworth filter (Frequency Devices 901F), and then sampled and digitized by a DEC 11/23 minicomputer which performed a fast Fourier transform on the 1024 data points. The resulting power spectra (512 points) were typically averaged 50–200 times at each sample voltage level. The spectra were corrected for the transfer function of the amplification circuitry and the small voltage divider effect of the ballast resistors.[10]

The excess noise spectrum at each voltage level was obtained by subtracting the Johnson and amplifier noise (measured at zero sample current) from the experimental noise spectra. This subtraction removed any current independent noise from the signal. The combined Johnson and amplifier noise power at zero current was always less than 10 times the Johnson limit, even at the lowest frequencies. Noise spectra $S_v(f)$ were measured as a function of applied sample voltage for frequencies between 0.3 Hz and 15 kHz.

EXPERIMENTAL RESULTS

Figure 1 shows the dependence of the excess voltage noise on sample voltage at 10 Hz (with the zero current noise subtracted off) and a 5460-Ω sample. As a reference point, the value of the Johnson noise for this resistance is also shown. The line drawn through the points has a slope of two, and shows that for over three decades of voltage change the noise scales as V^2. This behavior was found for all samples, independent of frequency, with an average exponent of $S_v(f) = V^{2.01 \pm 0.05}$. A V^2 dependence is the expected result for noise generated by resistance fluctuations sampled by an applied current, and is universally found for all "$1/f$" noise systems.

Figure 2 shows the normalized excess noise $S_v(f)/V^2$ as a function of frequency for three samples spanning the entire resistance range studied. The resistances have been normalized by the sample length to account for slight differences in sample dimensions. The noise has a power-law dependence on frequency that is approximately the same for all samples at all voltages: $S_v(f) \propto f^{-\alpha}$ with $\alpha = 1.30 \pm 0.15$. This value of α is slightly larger than that usually found in excess noise systems, but is still within the range generically referred to as "$1/f$" noise, i.e., $0.8 < \alpha < 1.4$. The scatter in the values of α is small, and there is no apparent correlation between α and either sample resistance or voltage.

The variation of $S_v(f)$ with sample resistance is illustrated in Fig. 3, where the fully normalized noise $S_v(f)f/V^2$ for all samples is plotted as a function of the sample resistance/length. The dashed line has a slope of one and shows that the noise increases more rapidly than the resistance as the percolation threshold is approached, with $S_v(f)$ varying roughly as R^3 near the transition. This result

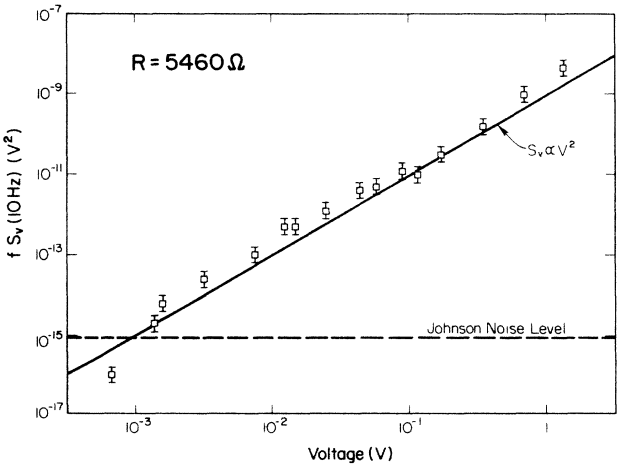

FIG. 1. The excess voltage noise as a function of sample voltage. The data were taken at 10 Hz and the zero current noise has been subtracted from each measurement. The solid line of slope 2 is drawn through the points as a guide. The dashed line is the calculated Johnson noise level for this resistance.

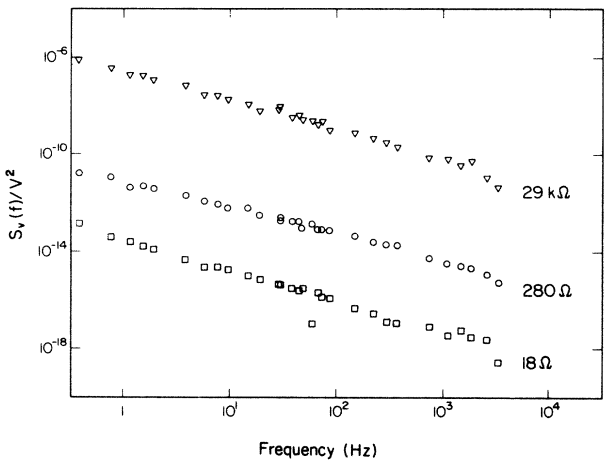

FIG. 2. The normalized excess noise $S_v(f)/V^2$ as a function of frequency for three samples. The sample voltages for this data are 5 mV (26-kΩ sample), 300 mV (260-Ω sample), and 220 mV (18-Ω sample).

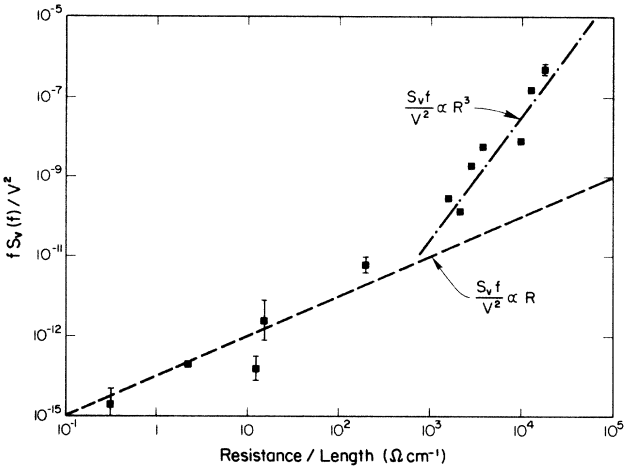

FIG. 3. The normalized noise $S(f)f/V^2$ at 10 Hz as a function of sample resistance/unit length for all samples. The metal volume fractions ranged from approximately 0.29 to 0.23. The dashed and dashed-dotted lines have slopes of one and three.

differs from recent work on carbon-wax composites by Chen and Chou[11] that shows an exponent for the dependence of $S_v(f)$ on resistance of 1.7 over the entire range of sample resistances.

DISCUSSION

Previous measurements of noise in percolating systems have primarily emphasized thin discontinuous metal films or cermet films.[2,12,13] For these systems, S_v/V^2 is found to vary as R^2, a result frequently explained by a tunneling conduction mechanism.[2] Very recently, a similar power-law dependence was found for three-dimensional carbon-wax composites and, again, the authors invoked a tunneling picture to account for the data.[11] The conduction mechanism in our samples appears to be metallic, however, so the tunneling model is probably not applicable to our measurements.

An alternative to the tunneling view has recently been advanced that models a composite as a percolating lattice of resistors, with each resistor r having a small fluctuating part δr. Numerical calculations of the noise in this system have found a new critical exponent, κ, that satisfies the relation $\langle \delta R^2 \rangle / R^2 \propto (p - p_c)^{-\kappa}$.[14-17] Limits on κ on three dimensions for a discrete lattice system are given[15,17] as $1.01 \leq \kappa \leq 1.56$. Since $R \propto (p - p_c)^{-t}$ then S_v/V^2 should be proportional to $R^{\kappa/t}$ with values for κ/t between 0.5 and 0.8, using $t = 1.9$. This value is reasonably consistent with the value of $\kappa/t \approx 1$ found in our low-resistance samples.

Near percolation, however, our samples exhibit $\kappa/t \approx 3$, a result predicted by none of the above lattice models. Recently, however, it has been suggested that some critical exponents for certain classes of continuum percolation systems are larger than the corresponding exponents in discrete lattice systems.[18,19] In particular, the continuum percolation system consisting of a conducting medium with randomly placed voids, commonly referred to as a "Swiss Cheese" model, is predicted to have values of t and κ larger than the values given by calculations on resistor lattices. For example, in three dimensions a calculation based on the so-called nodes-links-blobs model gives $t = 2.38$ and $\kappa = 5.14$, yielding $\kappa/t = 2.2$.[20] The increase in κ/t for this system over the discrete lattice value has been verified recently for two dimensions,[21] and has also been suggested[20] as the explanation for the values of the exponents measured by Chen and Chou.

The enhancement of exponents in continuum systems is attributed to the dependence of the total resistance on the few largest individual resistances in the conducting backbone. In the random-void system, for example, these large resistances are determined by the minimum width of the "necks" between adjacent voids. In other continuum models, however, other distributions of resistances, or "bond strengths," can give different results.

Thus the disagreement between the random-void value of $\kappa/t = 2.2$ and our measured values is not intrinsically surprising inasmuch as our samples consist essentially of metal spheres in an insulating host. In an effort to analyze our data with a more realistic model, therefore, we have performed a straightforward modification of the random-void system, in which the random voids in a conducting matrix are replaced by interpenetrating conducting spheres in an insulating matrix. For this case, we find that the nodes-links-blobs picture gives $t = 1.88$ and $\kappa = 5.64$, which yields $\kappa/t = 3$ and is consistent with our results for the higher-resistance samples.[22]

We do not have a detailed explanation for the apparent crossover between the R and an R^3 dependence for S_v/V^2 in our samples. It is possible, however, that this effect arises from volume-fraction-dependent changes in the distribution of interparticle resistances. Such changes could arise from our method of sample preparation in which powders are compacted under hydrostatic pressure. Far above percolation, where the pellets have significant metal content, metal-to-metal bonds could be stronger and more uniform than in the barely percolating high-resistance samples, where there are few parallel conducting paths and the composite is primarily a compressible dielectric.

In conclusion, we have measured the low-frequency noise on pressed pellets of Ag-Pt and TFE. The noise has a $1/f$ frequency dependence and is proportional to the square of the applied sample voltage. The normalized noise power

(S_v/V^2) is proportional to the sample resistance (R) far from the critical metal volume fraction, but is proportional approximately to R^3 close to p_c.

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