Critical Behavior of the Dielectric Constant of a Random Composite near the Percolation Threshold

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Measurements are reported of a singularity in the dielectric constant of a random metal-insulator composite below the percolation threshold. The composite sample consists of small silver particles randomly dispersed throughout a KCl matrix. The dielectric constant is found to obey a scaling relation with a critical exponent of $s = 0.73 \pm 0.07$.

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It has recently been suggested that the dielectric constant of a metal-insulator mixture might exhibit divergent behavior near the percolation threshold.[1-5] In this Letter we report the observation of a dielectric singularity at percolation in a three-dimensional (3D) granular composite consisting of small metal particles randomly dispersed in a nonconducting host. We have found the dielectric constant to obey a scaling relation, characterized by a critical exponent, which resembles that observed in thermodynamic phase transitions.

The formal resemblance between a percolation transition and a second-order phase transition was recognized in 1972 by Fortuin and Kasteleyn,[6] who pointed out that the percolation fraction p_c could be related to the critical temperature T_c of a classical phase transition. Kirkpatrick,[7] Straley,[8] and others[9] have subsequently extended this analogy to incorporate the idea of scaling. According to the scaling hypothesis, certain properties of a percolating system should exhibit a power-law dependence on $|p - p_c|$, where p is the volume fraction of metal in the material. Each power law is thought to be universal in the sense that its exponent depends primarily on the dimensionality of the system and not upon the details of structure or interactions.

Tests of this scaling hypothesis in real percolating systems are difficult because, in essence, each datum point requires a separate sample. The constituents of each sample must be distributed in a random, uncorrelated manner. Furthermore, to be statistically valid, the size of each sample must approach the thermodynamic limit of an infinite system. Because of these experimental constraints, the strongest support for the scaling hypothesis has come from numerical studies of computer-simulated resistor networks.[7,8] The few experimental studies on real 3D composites have been limited to resistance measurements of granular metal films above percolation[10,11] and are in general agreement with the numerical calculations. There are no prior measurements of the critical behavior of the dielectric constant below percolation.[12]

In our opinion, the samples used in this work were sufficiently well characterized to allow a reasonable test of the scaling hypothesis below percolation. The samples consisted of small spherical Ag particles randomly embedded in a nonconducting KCl host. The volume fraction of metal in the samples could be varied from zero up through the percolation threshold. At percolation, a typical sample contained about 10^{15} particles.

The small metal particles were made by evaporating Ag in the presence of about 1 Torr of argon gas, according to the method of Granqvist and Buhrman.[13] A small amount of oxygen was introduced into the bell jar during the evaporation in order to produce a thin (approximately 10 Å) oxide coating on the metal spheres; this coating prevented the Ag particles from cold-welding together during the evaporation, yet was sufficiently thin to allow metal-to-metal contact under high pressure. As shown in the electron micrograph of Fig. 1, the particles were spherical with

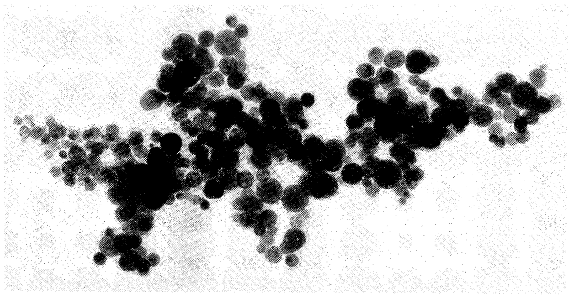

FIG. 1. Electron micrograph of a sample of the spherical silver particles used in the experiment. The mean diameter of the particles was 200 Å.

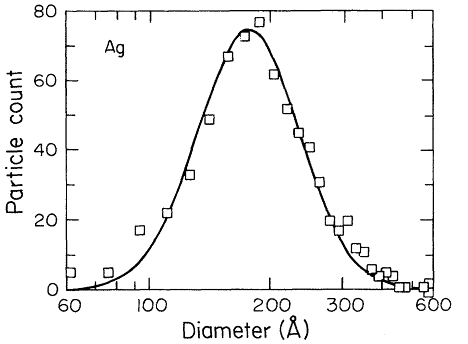

FIG. 2. Size histogram of a sample of 500 silver particles illustrating the log-normal distribution of particle diameters.

a mean diameter of 200 Å. The distribution of particle diameters is shown in Fig. 2 for a sample of 500 particles; the particle diameters followed a log-normal distribution with a geometric standard deviation of 1.5.

The samples were prepared by mixing predetermined amounts of Ag particles and KCl powder and by compressing the mixture into a solid pellet under high pressure. Two series of samples were made, containing 23 and 6 samples, respectively, with metal volume fractions ranging between zero and the percolation fraction. The initial step in the preparation of a series was to grind a pure crystal of KCl into micron-sized particles. A small quantity (no more than 2% by volume) of Ag was stirred into the KCl powder, and the mixture was then compressed in an evacuated die into a solid at a compaction pressure of about 100 000 psi. In order to improve the uniformity of the particle distribution, the compacted solid was then reground and recompacted at least six times. At this stage, the solid was reground again and the powdered mixture was baked overnight at 100 °C to remove moisture absorbed by the KCl. A small portion of the dried powder was then compressed into a cylindrical pellet which, after the attachment of gold electrodes, constituted one of the samples in the series. Additional Ag was then added to the remaining powder and the compaction/grinding/drying cycle was repeated. After each drying step, material was extracted from the mixture to prepare a sample with metal volume fraction slightly greater than that of the previous sample in the series. Near the percolation threshold, metal was added in 0.4% increments in order to resolve more closely the details of the divergence of the dielectric constant.

Several tests were made to insure that the preparation procedure was systematic enough to minimize unwanted sample-to-sample differences within each series. We were particularly concerned about the possibility of water contamination of the KCl, of voids in the compacted pellets, and of clumping or other nonrandom structural correlations among the particles. (Structural correlations would be expected to shift the percolation concentration p_c from the value expected for a perfectly random system but should not otherwise affect the critical behavior of the composite; sample-to-sample variations in particle correlation, however, would increase the scatter in the data.) Small amounts of water were observed in spectrophotometer recordings of unbaked compactions of KCl powder and, in fact, nonreproducibility in some of our early data was traced to water contamination of samples. These problems disappeared after instituting the drying phase in our sample-preparation cycle. The measured dielectric constant of compacted, dried KCl powder could not be distinguished from that of crystalline KCl.

To test for voids, we used a high-precision flotation technique to determine that the density of compressed KCl powder was within 0.1% of the density of a pure KCl crystal. This result suggests that the micron-sized KCl particles fractured under the pressure of the compaction process and fused together, effectively filling in the voids in the loosely packed mixture.

To determine that the repeated grinding and compaction steps in our sample preparation procedure resulted in a homogeneous distribution of Ag particles in the KCl host, we scanned the surface of several samples with an electron beam and mapped the distribution of x rays emitted from the sample surface. To within the resolution of this technique, about 2000 Å, no clumping of Ag particles could be discerned. This observation is supported by measurements of the dielectric constant of several samples with the same metal volume fraction. In all cases, the spread of the values of the measurements was within our overall measurement uncertainty of 1.5%. Furthermore, each sample could be reground and recompacted with no resolvable change in the dielectric constant.

The room-temperature dielectric constant of each sample was measured using a General Radio capacitance bridge operated at 1 kHz with a peak-to-peak voltage amplitude of 40 mV, a value well below the dielectric breakdown voltage of all sam-

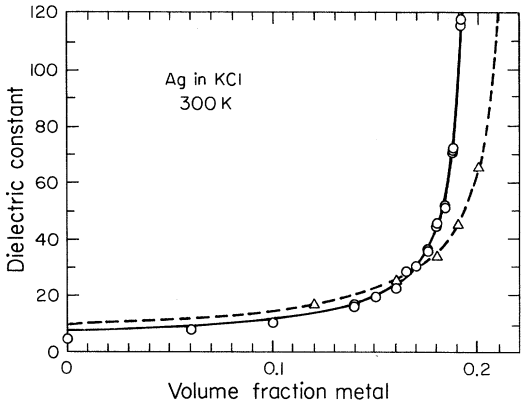

FIG. 3. The dielectric constant K of two series of Ag-KCl composite samples as a function of metal volume fraction p. Series A data are shown as circles and series B data as triangles. The solid lines are the best fits to Eq. (1). These fits were made to the data for $p > 0.11$.

ples. The overall uncertainty in our measurements was limited by irregularities in the thickness of the samples, resulting in a standard deviation of about 1.5%. Figure 3 shows the dielectric constants of both series of samples as a function of the metal volume fraction. The solid and dashed lines in the figure are best fits of the data to the scaling relation

$$K = c\epsilon^{-s}, \tag{1}$$

where K is the dielectric constant, c is a constant prefactor, $\epsilon = (p_c - p)/p_c$ is the reduced volume fraction, and s is the critical exponent. In fitting our data to this expression, we have used s, p_c, and c as adjustable parameters. Figure 4 is a logarithmic plot of the same data shown in Fig. 3, now plotted versus ϵ, illustrating the range over which the dielectric constant exhibits power-law behavior. For series A, ϵ spanned the range 0.021–0.282, while for series B, ϵ spanned 0.046–0.441. To within the resolution of the data, there is no curvature apparent in the dielectric constant over either of these ranges. The mean value of s for both series of samples is $\bar{s} = 0.73 \pm 0.07$, the uncertainty reflecting the influence on s of variations in the choice of p_c. Our best fits were obtained with $p_c = 0.20$ for series A and 0.22 for series B. The value of p_c for each series was also determined experimentally by measuring the conductivity of the samples. The value of p corresponding to the onset of conduction was the same, to within the experimental uncertainty of ± 0.002, as the fitted value of p_c.

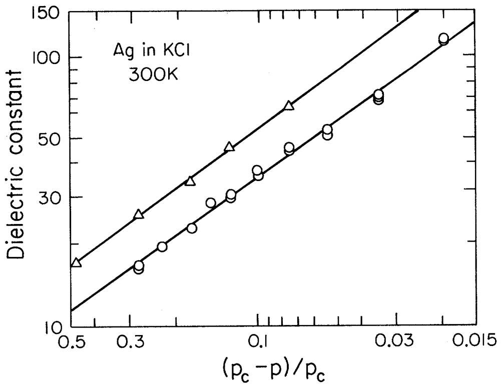

FIG. 4. Logarithmic plot of the dielectric constant as a function of reduced metal volume fraction for the data of Fig. 3. For series A the critical exponent $s = 0.72$, while for series B, $s = 0.74$. The solid lines are fits to Eq. (1).

These values are slightly larger than theoretical estimates, which give $p_c \approx 0.15$ for a perfectly random 3D system.[14,15]

Our measurement of the critical exponent s is consistent with recent suggestions[3-5,8] that the dielectric constant should exhibit the same power-law dependence on volume fraction as the conductivity below p_c of a random system having two conducting constituents. Straley[8,16] has recently modeled such a random system as a cubic lattice of resistors. In this model, the resistors could take on two possible values of resistance, with a probability p and $(1-p)$, respectively. Numerical calculations for a lattice of $39 \times 39 \times 39$ resistors produced a critical exponent of 0.70 ± 0.05 for the variation of effective conductivity with ϵ. We believe that the agreement between the exponents of our measurements and of these numerical simulations is strong support for the universality of the critical exponents.

It is also interesting to note that Eq. (1) is obeyed for our data over a relatively large range in ϵ. We are aware of no theoretical basis for such an extended critical region. In fact, Bernasconi[17] has recently proposed, on the basis of a renormalization-group argument, that the critical exponent s in 3D systems should slowly decrease with increasing ϵ. If such a decrease exists, it is below the resolution of our measurements.

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On page 1904, the following acknowledgment should be added to the final paragraph: This work was supported in part by the National Science Foundation under Grant No. PHY 78-09619.

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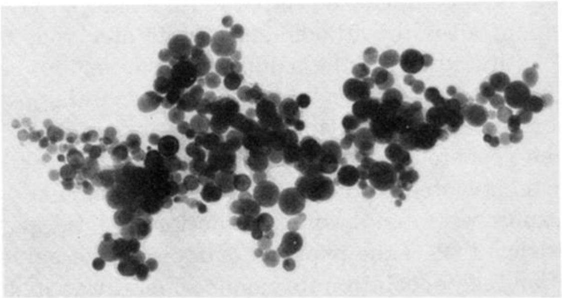
On page 2051 in the first term of the right-hand side of the first equation in (2), $(\pi^2+k^2)V$, should read $(\pi^2+k^2)^2V$.

On the next to the last line on page 2051, the numerator, $(\pi^2+k^2)^2$, of the inequality should read (π^2+k^2).

In Eq. (15) the number on the right-hand side should be preceded by a minus sign.



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