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Search for maximum metallic resistance in random metal-particle composites

J. C. Garland, W. J. Gully,* and D. B. Tanner
Department of Physics, Ohio State University, Columbus, Ohio 43210
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One-dimensional quantum localization of electronic states has been sought in a composite material consisting of small silver particles randomly embedded in a dielectric KCl medium. Near the conduction threshold, the composite behaves like a filamentary network of interconnected wires. The electrical resistance of this composite material has been measured to below 1 mK. No evidence for quantum localization or other nonmetallic behavior was observed. The present measurements suggest that the temperature scale for localization may be lower than previously believed.

In a recent paper, Thouless[1] has proposed that electronic states in metals should become localized at $T=0$ for wires whose impurity limited resistance exceeds approximately $2\hbar/e^2 \approx 8000\ \Omega$. Similar ideas have also been advanced by Adkins,[2] Licciardello and Thouless,[3] and most recently by Abrahams *et al.*[4] A wire exhibiting one-dimensional quantum localization would at sufficiently low temperatures have an electrical resistance which increased with length in the usual way up to a maximum of about 8000 Ω; the resistance of longer wires would increase exponentially with length.

Associated with the Thouless model is a characteristic localization length l which sets the range of the localized electronic wave functions. For a wire of radius r, l is the length of wire which has a resistance of $2\hbar/e^2$ and is equal to $2r^2\lambda/a^2$, where λ is the electronic mean free path and a is the lattice constant of the metal.

Also associated with the localization phenomenon is a characteristic activation temperature T^*. Far above T^* the wire behaves like an ordinary metal, while below T^* the wire has the temperature-dependent resistance of a nonmetallic activated conductor, with hopping transitions between localized regions induced by phonon or electron scattering, or by thermal fluctuations. The experimental signature of localization would be an increase in the resistance of the wire as the temperature is lowered below T^*. At present, however, there is no theoretical consensus on either the value of T^* of the explicit temperature dependence of the resistance near T^*. Probably the most conservative (i.e., lowest) estimate of T^* can be obtained by supposing that ordinary thermal fluctuations would induce transitions between localized energy levels. According to this view, $T^* \approx \Delta\epsilon/k_B$, where $\Delta\epsilon$ is the energy level spacing of the N electrons confined to a localization volume $\pi r^2 l$. Thus, for a wire whose radius and mean free path λ are 100 Å, we can set an approximate lower limit on T^* of

$$T^* \gtrsim \frac{1}{k_B}\left(\frac{2\epsilon_F}{3N}\right) = \frac{\epsilon_F a^5}{3\pi k_B \lambda r^4} \approx 0.5\ \text{mK}. \qquad (1)$$

For this example, which sets very difficult constraints on the wire dimensions, the value of T^* is about equal to the minimum temperature now attainable.

Other estimates of T^* are not so stringent, however. Thouless[1] defines T^* as the temperature at which the localization length l becomes comparable to a characteristic electronic diffusion length $l_d = D\tau_i$, where D is a diffusion constant and τ_i is an appropriate inelastic scattering time. For impure wires having a diameter of approximately 10^2 Å, this model predicts T^* to be of the order of 1 K. Other models for temperature-induced delocalization[5] suggest characteristic temperatures somewhat below the Thouless prediction but still within the realm of experiment. Regardless of the model one believes, however, the only reasonable hope for observing one-dimensional localization lies in measurements on very thin conductors at the lowest attainable temperatures.

In the experiment reported here, we have searched for maximum metallic resistance in a composite system consisting of 100 Å radius silver particles randomly dispersed throughout a nonconducting KCl medium. As discussed below, this material easily satisfies the geometrical conditions for one-dimensional localization. Our resistance measurements extended down to 0.5 mK, well below the Thouless estimate for T^* but above the estimate given by Eq. (1). At no temperature did we find any evidence of localization or other nonmetallic behavior.

Our random composite system undergoes a metal-insulator transition when the metal volume fraction p equals the percolation concentration $p_c \approx 0.18$. For $p < p_c$, the material is nonconducting, while for $p \gtrsim p_c$, the material acquires a con-

ductivity which is initially low but which approaches the conductivity of bulk silver as $p \to 1$. Kirkpatrick,[6] Straley,[7] and others[8-11] have recently carried out extensive studies of the structural and electrical properties of random composite materials of this type. Their studies have shown that for $p \approx p_c$, the metallic current-carrying paths in the composite form a random network of interconnected conducting filaments whose diameters are approximately equal to the diameters of the metal particles which make up the conducting portion of the composite. In addition to the conducting filaments, there are a number of "tag end" strands which are connected to the filamentary network at only one point. These tag end strands do not contribute to the conductivity since they cannot support a current flow.

There are several characteristic lengths associated with the conducting filaments, including a cluster coherence length $\xi(p)$, which is the average separation between nodes which join filaments together, and the average filament length between nodes $\bar{L}(p)$. Each of these lengths diverges near p_c as a power of $(p - p_c)$, with a critical exponent which is independent of the particular properties of the material (except for its dimensionality).[6,7] A similar expression[7] governs the conductivity of the composite, which near p_c is given by

$$\sigma \approx \sigma_0 (p - p_c)^{1.7} \tag{2}$$

(σ_0 is the conductivity of the metallic constituent of the composite). Thus by an appropriate choice of $(p - p_c)$, it is possible to manufacture a composite whose conduting filaments satisfy the requirements for one-dimensional localization.

As the temperature of the composite is lowered below T^*, one would expect those filaments having length L greater than the electron localization length l to cease conducting and the total resistance of the composite to increase; the residual, zero-temperature resistance of the composite would then be determined by the remaining filaments, for which $L < l$. To illustrate a possible temperature dependence to be expected from localization, we can model the composite as a random network of resistors, some of which exhibit localization and some of which do not. Those filaments having $L < l$ do not exhibit localization and are assumed to have a constant, temperature-independent resistance R_L; the remaining filaments are assigned an exponentially activated resistance $R_L e^{T^*/T}$. The effective conductivity of the entire random network can then be estimated from the effective medium approximation.[9,10] In this approximation, the effective conductivity σ_{eff} of a two-component conducting mixture is given by the solution to the following quadratic equation:

$$(1-f)\frac{\sigma_1 - \sigma_{\text{eff}}}{\sigma_1 + 2\sigma_{\text{eff}}} + f\frac{\sigma_2 - \sigma_{\text{eff}}}{\sigma_2 + \sigma_{\text{eff}}} = 0. \tag{3}$$

In the above equation, $\sigma_1 = (R_L \xi)^{-1}$ and $\sigma_2 = (R_L e^{T^*/T} \xi)^{-1}$, where $\xi(p)$ is the percolation cluster coherence length and f is the fraction of links showing an activated resistance. Figure 1 shows the effective resistance $R(T)$ for composite samples having $T^* = 0.2$ K and various values of f, obtained by solving Eq. (3) for σ_{eff}. Even for $f = 0.1$, there is an easily discernible increase in the composite resistance above the residual resistance R_0. Other (nonexponential) types of delocalizing processes lead to qualitatively similar resistance increases at low temperatures. More sophisticated theories of the composite resistance are undoubtedly possible but would not affect our conclusion that localization leads to an increase in the resistance of the composite below the activation temperature.

The silver particles used in our composite samples were prepared by evaporating silver in an inert gas atmosphere containing a small amount of oxygen.[12,13] Particle radii were measured independently with an electron microscope and were determined to obey an approximate log-normal distribution with a mean value of about 250 Å (sample 1) and 100 Å (sample 2). The oxide-coated silver particles were then mixed with micron-sized KCl powder and compressed under vacuum into a solid pellet, using a pressure of 12 kbar. The compacted pellet was then reground into a powder and additional silver was added. Volume fractions of silver were determined by weighing the two constituents of the com-

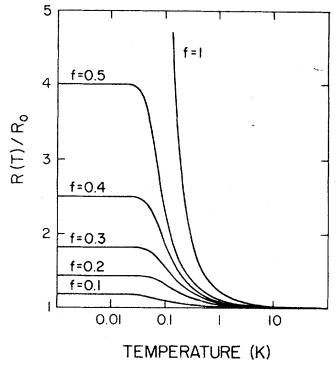

FIG. 1. Fractional increase in resistance to be expected from one-dimensional localization at low temperatures. The various curves correspond to different fractions of filaments undergoing localization. The curves are all based on an exponentially activated delocalization mechanism, with a characteristic temperature $T^* = 0.2$ K, and are normalized to the residual resistance R_0.

posite before each mixing step. This procedure was repeated until the desired volume fraction of silver was reached and the electrical resistance of the pellet had stabilized. Typical samples were compacted and reground about forty times.

Both of our samples were intentionally "tuned" to be as close to p_c as possible. The value of $(p-p_c)$ was measured directly (by weighing the relative amounts of metal and nonmetal in the composite) and also was inferred from the conductivity ratio σ/σ_0, according to Eq. (2). On the basis of the conductivity ratio $\sigma/\sigma_0 \approx 10^{-7}$, we estimate $(p-p_c) \approx 10^{-4}$–10^{-3}, the uncertainty arising from some ambiguity in the appropriate choice of σ_0. This range of values for $(p-p_c)$ is consistent with the measured volume fraction of silver in the composite, which could be determined to an accuracy of 0.1%.

The value of the conductivity exponent $t=1.7$, appearing in Eq. (2), is the one calculated by Straley.[7] Recent low-temperature experiments by Deutscher and Rappaport[14] on random composites of Al in Ge have found a value for this exponent of $t=1.75$. Table I lists the relevant percolation parameters, the localization length l, the lower estimate for T^* [based on Eq. (1)], and other sample properties.

The structural length scale $2r$ which appears in Table I is the diameter of the conducting filaments which is taken to be the particle diameter. Although supported by the computer simulation studies of Kirkpatrick,[6] this assumption has not been tested experimentally in real material. In our experiment, however, we are able to estimate the diameter of the conducting filaments from the measured resistivity ratio. According to the Fuchs[15]-Sondheimer[16] theory for boundary scattering in thin wires, the mean free path in the wire obeys

$$1/\lambda = 1/\lambda_\infty + 3/(8r)\,, \tag{4}$$

where λ_∞ is the mean free path in the bulk material and r is the wire radius. The bulk mean free path in pure Ag at 300 K is approximately $\lambda_\infty(300\,\mathrm{K}) = 310$ Å while at very low temperatures it is several hundred times larger (and much larger than the filament diameter). The residual resistance ratio (R_r) of the filaments can be shown

TABLE I. Sample properties.

Symbol	Description	Expression	Sample 1	Sample 2
t	sample thickness		0.029 cm	0.16 cm
p	volume fraction of Ag		0.18	0.18
r	average particle radius		250 Å	100 Å
ρ_{300}	sample resistivity (300 K)		16.7 Ω cm	13.7 Ω cm
R_r	residual resistance ratio		2.44	1.89
λ	mean free path (4.2 K)		440 Å	280 Å
$p-p_c$	p = vol. fraction; p_c = critical vol. fraction		10^{-3}–10^{-4}	10^{-3}–10^{-4}
$\xi(p)$	cluster coherence length [a]	$2r(p-p_c)^{-0.8}$	12–80 μm	5–30 μm
$\bar{L}(p)$	average length of filament [a]	$2r(p-p_c)^{-1}$	50–500 μm	20–200 μm
R_L	average filament resistance [b]	$\frac{\rho_{Ag}\bar{L}}{r^2}$	900–9000 Ω	4000–40 000 Ω
l	electron localization length	$\frac{2r^2\lambda}{a^2}$	400 μm	40 μm
f	fraction of localized lengths ($T=0$)		≲0.1	~0.5
T^*	activation temperature [based on Eq. (1)]	$\frac{\epsilon_F a^5}{3\pi k_B \lambda r^4}$	0.004 mK	0.23 mK

[a] Exponents taken from Ref. 6.

[b] The residual resistivites were $\rho_{Ag} = 1.1$ μΩ cm for sample 1 and $\rho_{Ag} = 1.8$ μΩ cm for sample 2.

to be

$$R_r = \frac{3\lambda_\infty(300\ \mathrm{K}) + 8r}{3\lambda_\infty(300\ \mathrm{K})} . \quad (5)$$

The observed residual resistivity ratios of 2.44 for sample 1 and 1.89 for sample 2 lead to estimates of filament radii of $r_1 \simeq 170$ Å and $r_2 \simeq 100$ Å. These values are very close to the observed median particle radii of 250 Å and 100 Å, respectively, and support the use of the particle diameter as the structural length scale.

The electrical resistance of each composite sample was measured between room temperature and approximately 0.5 mK, the lowest temperatures being achieved by a nuclear demagnetization stage precooled with a dilution refrigerator. Electrical contact to the samples was made by vacuum depositing gold electrodes onto the faces of the pellet. The data reported here were made using 800 Hz ac currents of 1 μA rms maximum; no frequency dependence of the resistance was observed between 100 Hz and 30 kHz. ac voltages across the sample were amplified by a PAR 113 preamplifier and detected using a lock-in amplifier with an integration time of 10 sec. Typical voltage resolution was about 10 nV and the maximum electric field strength in the samples was about 20 μV/cm.

At temperatures below 1mK, we estimate that Joule heating in the sample, about 10^{-12} W, raised the interior temperature of the sample about 0.5–1.0 mK above the temperature of the sample surface. Each surface of the sample was thermally anchored to a sintered copper heat exchanger which was immersed in liquid ^{3}He. Because of the large surface area of these heat exchangers, we estimate the temperature difference between the sample surface and the ^{3}He bath to be only about 0.01 mK.

Resistance data over a six decade range of temperatures are shown in Fig. 2 for two samples.[17] The localization criteria are best satisfied with sample 2 for which $L/l \approx 1$ and for which the average filament resistance approaches 10 000 Ω. For this sample, approximately half of the filaments would be expected to exhibit localization ($f \approx \frac{1}{2}$). In both samples, however, we estimate that a measurable fraction of filaments would satisfy the condition $L > l$. Neither sample showed any unusual low-temperature behavior of the resistance; the resistance increase above 40 K reflected emergence of ordinary electron-phonon scattering. The current-voltage relationship of sample 2 was checked at 20 mK between 0.1 μA and 1 mA. The relationship was linear over the entire current range, as expected for an ordinary metallic conductor.

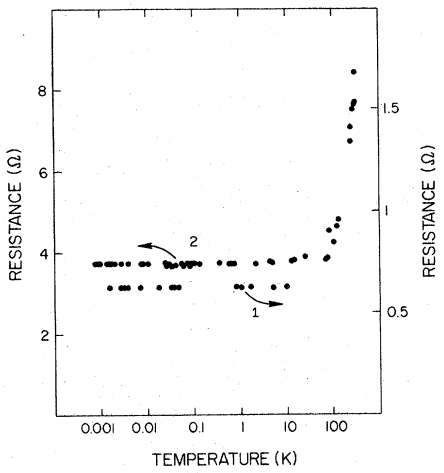

FIG. 2. Temperature dependence of the electrical resistance of composite samples 1 (right scale) and 2 (left scale), illustrating the absence of localization effects.

An unresolved question about the experiments reported here has to do with the influence of the tag ends or noncurrent-carrying strands on the energy level spacing of the electron states in the silver. In our opinion, these tag ends do not affect the level spacing of the relevant states. The tag ends are connected to the current-carrying strands at only one grain. Because they are open-circuited, current cannot flow into the tag ends without incurring a large charging energy. Because of this charging energy, the tag ends are effectively inaccessible to wave functions of interest.

It is possible that this view is incorrect and that tag ends would contribute a reservoir of electrons which would lower the characteristic temperature T^* below the value cited in Table I. In that case, the temperature scale would be reduced from the value in Table I by a factor of perhaps 10, and the localization length would increase by a somewhat smaller amount. However, one should keep in mind that the temperature given by Eq. (1) is not the delocalization temperature proposed by Thouless,[1] Licciardello *et. al*,[3] or Adkins[2]; the temperatures suggested by these authors are all much greater than $\Delta\epsilon/k_B$. The appropriate temperature scale for delocalization and the associated temperature dependence of the resistance are major unanswered questions in this field.

In summary, we have found no evidence for low-temperature electron localization in a material which satisfied the criteria for the effect. Our results suggest that the Thouless criterion for the activation temperature T^* may be too optimistic and that a lower value, based on a different de-

localization process, may be more appropriate.

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*Present address: Department of Physics, University of Massachusetts Amherst, MA 01002.

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