Infrared-Optical Properties of Gas-Evaporated Gold Blacks: Evidence for Anomalous Conduction on Fractal Structures

G. A. Niklasson and C. G. Granqvist

Physics Department, Chalmers University of Technology, S-41296 Gothenburg, Sweden

(Received 23 September 1985)

We analyze infrared-optical measurements on gas-evaporated gold blacks, performed by Harris many years ago. The data agree quantitatively with recent theories for anomalous conduction on fractal structures. The frequency-dependent conductivity obeys $\sigma \propto \omega^{0.7}$ below the relaxation frequency for electrons in a single particle. This is consistent with the conductivity exponents for percolation clusters and for diffusion-limited aggregates.

PACS numbers: 78.30.Gt, 72.15.Cz, 78.20.−e

The purpose of this Letter is to demonstrate that far-infrared absorption in properly prepared gold blacks, studied by Harris and co-workers[1-3] as far back as the 1940's, shows all the features expected[4,5] for anomalous conduction on fractal structures and, hence, constitutes a striking confirmation of current theoretical notions.

Recently, there has been a lot of theoretical interest in anomalous conduction on percolation clusters and conspicuous dependences on frequency ω have been predicted[4,5] for the dielectric function and the conductivity. Percolation clusters have a fractal (self-similar) geometry for length scales L in the range[6] $a \ll L \ll \xi$, where a is a "microscopic" distance and ξ is the percolation correlation length. At $\omega < \omega_\xi$, where ω_ξ^{-1} is the time it takes the electrons to traverse a distance ξ, the conduction is classical and yields a constant conductivity σ. At $\omega_\xi < \omega < \omega_a$, where ω_a is a frequency determined by the microscopic distance, anomalous conduction occurs and the conductivity follows the power law[4,5]

$$\sigma \sim \omega^{t/(s+t)}, \tag{1}$$

where s describes the divergence of the dielectric constant at the percolation threshold p_c, and t describes the dependence of the dc conductivity above p_c. At $\omega > \omega_a$, the conductivity is determined by the microscopic properties. The frequency range within which Eq. (1) is obeyed is largest at p_c and gradually shrinks when one departs from p_c, as clearly seen in recent[7] model calculations. Computations on another fractal geometry, the so-called Sierpinski gasket, showed qualitatively similar results,[8] which gives credence to the belief that the features outlined above may be universally valid for fractal structures. It should be noted that anomalous diffusion on percolation clusters gives a frequency dependence which is different from the one in Eq. (1). In anomalous diffusion one neglects capacitances on bonds connecting different clusters, as discussed by Gefen, Aharony, and Alexander.[6] We believe that Eq. (1) is pertinent to optical and electrical measurements.

The numerical values of the exponent in Eq. (1) can be estimated for certain fractal structures. For three-dimensional percolation clusters it is known that[9] $s \approx 0.75$ and[10] $t \approx 1.94$, which gives $t/(s+t) \approx 0.72$. For other fractal structures one may use the relations[11,12]

$$t/\nu = 1 + D_{\mathrm{rw}} - D_f, \tag{2}$$

$$s/\nu = (D_f - 1)/2, \tag{3}$$

where ν describes the divergence of ξ at p_c, D_f is the fractal dimension, and D_{rw} is the random walk dimension. Diffusion-limited aggregates[13] are characterized by[14] $D_f \approx 2.4$ and $D_{\mathrm{rw}} \approx 3.33$, which gives $t/(s+t) \approx 0.73$.

Generally, experimental vindication is meager for the theories of anomalous conduction on fractal structures. The work reported[15,16] until now has been confined to frequencies below 10^7 Hz, but ω_a may under certain conditions be sufficiently large that optical measurements, particularly in the infrared, can be used to obtain conclusive results. Below we will prove this point by analyzing data on gold blacks reported by Harris *et al.*[1-3,17]

The gold blacks were produced by evaporation of Au in the presence of 3 Torr of pure N_2 gas.[18] Highly porous coatings, with Au volume fraction f as low as 0.002, were formed. Transmission electron micrographs showed rounded Au particles with radius $r \sim 5$ nm aggregated into chains and clusters. The state of aggregation was dependent on the deposition conditions. We note that gas-evaporated Fe, Zn, and SiO_2 samples have a fractal structure with[19] $1.7 \lesssim D_f \lesssim 1.9$, but it is not clear whether the same D_f applies to Harris's gold blacks.

Harris *et al.* measured spectral optical properties in an extremely wide wavelength range,[1-3,17,20] from the near uv to the far ir. For our comparisons with theory we relied on the transmittance T, reflectance R, and dc conductivity σ_{dc} tabulated in Harris's comprehensive monograph.[3] The overall reproducibility of the data is good, which testifies to the quality of the investigations, particularly since gas evaporation is often a difficult technique with regard to reproducibility. We converted the values of T and R to a frequency-dependent absorption coefficient $\alpha(\omega)$ times a thickness d. This is proportional to the optical conductivity $\sigma(\omega)$ by

$$\alpha(\omega)d = (2\omega d/c)k(\omega) \approx (\epsilon_0 c\rho f)^{-1}(W/A)\sigma(\omega), \tag{4}$$

where $\tilde{n} \approx 1 + ik$ is the complex refractive index, W/A is the weight per area, ρ is the density of the material forming the particles, c is the velocity of light, and ϵ_0 is the permittivity of free space. Figure 1 is a log-log plot of σ versus wavelength λ for a series of gold blacks. The specific values were obtained by use of W/A as stated in the figure, $f = 0.002$, and ρ as for bulk Au. We note that σ joins smothly with σ_{dc} in the long-wavelength limit for the most-conducting samples.

The optical conductivity is consistent with the theories for anomalous conduction on fractal structures, as we will show now. At $\lambda \gtrsim 10$ μm we find that σ falls off with increasing wavelength. The two specimens with lowest σ_{dc} yield an unambiguous power-law dependence according to

$$\sigma(\omega) \sim \lambda^{-p} \sim \omega^p, \tag{5}$$

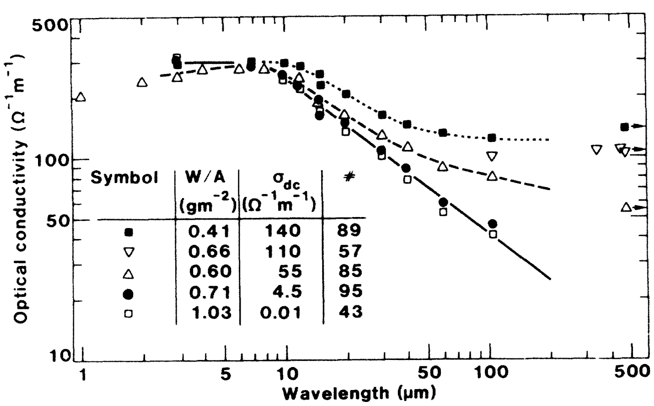

FIG. 1. Optical conductivity as a function of wavelength for gold blacks. The data are based on Harris's measurements (Ref. 3) on a number of samples, referred to by different symbols, with similar weight per area but widely different dc conductivity. The inset table states parameter values together with Harris's sample designation. Arrows at the right-hand part denote σ_{dc} for the most conducting samples. Curves represent free-hand fits to the data points. The results employ Harris's recordings of specular transmittance and reflectance. It can be shown from his results that the diffuse component is not of importance for our arguments. Two data points are given at $\lambda = 15$ μm for some of the samples. This can be explained by the use of different spectrometers at $\lambda \gtrless 15$ μm.

where p was found by linear regression analyses to be 0.703 and 0.717. *This is precisely the expected performance for anomalous conduction on the fractal structures mentioned earlier.* For the samples with higher σ_{dc} we find an initial decrease of σ according to an approximate power law, followed at longer wavelengths by a gradual approach to σ_{dc}. These samples appear to have a crossover to classical dc conductivity at $\lambda_\xi \approx 80$ μm. At $\lambda \lesssim 10$ μm we find $\sigma \approx 300$ Ω^{-1} m^{-1} for all samples.

The high-frequency cutoff of anomalous conduction occurs at ω_a, equal to the inverse relaxation time for electrons in a single metal grain. Assuming diffuse scattering in spherical particles we have[21]

$$\omega_a \approx v_{\text{F}}/r, \tag{6}$$

where v_{F} is the Fermi velocity. Gold particles with $r \approx 5$ nm give a crossover wavelength $\lambda_a \approx 7$ μm, which is in excellent agreement with the results in Fig. 1. As σ_{dc} goes up, the particles tend to be increasingly contiguous, and hence we expect that their "effective radius" becomes larger. This could explain the empirical finding that λ_a seems to shift towards longer wavelengths in the samples with highest σ_{dc}.

In conclusion we have analyzed Harris's old infrared measurements on gas-evaporated gold blacks, comprising particles in electrical contact, and verified that these data provide a striking confirmation of recent theories for conduction on fractal structures. The frequency dependence of the optical conductivity can be understood from the conductivity exponents for percolation clusters and diffusion-limited aggregates. The onset of anomalous conduction coincides with the relaxation frequency for electrons in a single particle. We remark, finally, that particles connected through tunnel barriers are expected to show a behavior analogous to that of the present gold blacks, albeit ω_a should lie at a lower frequency.

This work was financially supported by grants from the Swedish Natural Science Research Council and the National Swedish Board for Technical Development.

[1]L. Harris, R. T. McGinnies, and B. M. Siegel, J. Opt. Soc. Am. **38**, 582 (1948); L. Harris and J. K. Beasley, J. Opt. Soc. Am. **42**, 134 (1952).

[2]L. Harris and A. L. Loeb, J. Opt. Soc. Am. **43**, 1114 (1953); L. Harris, J. Opt. Soc. Am. **51**, 80 (1961).

[3]L. Harris, *The Optical Properties of Metal Blacks and Carbon Blacks,* The Eppley Foundation for Research Monograph Series No. 1 (The Eppley Foundation, Newport, R.I., 1967).

[4]A. L. Efros and B. I. Shklovskii, Phys. Status Solidi (b) **76**, 475 (1976).

[5]D. Stroud and D. J. Bergman, Phys. Rev. B **25**, 2061

(1982).
[6]Y. Gefen, A. Aharony, and S. Alexander, Phys. Rev. Lett. **50**, 77 (1983).
[7]D. Wilkinson, J. S. Langer, and P. N. Sen, Phys. Rev. B **28**, 1081 (1983).
[8]J. P. Clerc, A.-M. S. Tremblay, G. Albinet, and C. D. Mitescu, J. Phys. Lett. **45**, L913 (1984).
[9]H. J. Herrmann, B. Derrida, and J. Vannimenus, Phys. Rev. B **30**, 4080 (1984).
[10]B. Derrida, D. Stauffer, H. J. Herrmann, and J. Vannimenus, J. Phys., Lett. **44**, L701 (1983).
[11]Equation (2) was found for percolation clusters in three dimensions by S. Alexander and R. Orbach, J. Phys. Lett. **43**, L625 (1982).
[12]Equation (3) was suggested to hold in three dimensions by A. Coniglio and H. E. Stanley, Phys. Rev. Lett. **52**, 1068 (1984). The relation is probably only approximate since it does not agree with recent numerical results for percolation clusters; cf. Ref. 9.
[13]T. A. Witten, Jr., and L. M. Sander, Phys. Rev. Lett. **47**, 1400 (1981).
[14]P. Meakin and H. E. Stanley, Phys. Rev. Lett. **51**, 1457 (1983).
[15]G. Giraud, J. M. Laugier, J. Clerc, and J. Roussenq, IEEE Trans. Electr. Insul. **19**, 205 (1984).
[16]R. B. Laibowitz and Y. Gefen, Phys. Rev. Lett. **53**, 380 (1984).
[17]L. Harris, D. Jeffries, and B. M. Siegel, J. Appl. Phys. **19**, 791 (1948).
[18]Gas evaporation in the presence of O_2 gives nonconducting deposits with very different optical properties; cf. data for Au in C. G. Granqvist and O. Hunderi, Phys. Rev. B **16** 3513 (1977). Nonconducting Al deposits, produced by gas evaporation, have enhanced far-infrared absorption as found by C. G. Granqvist, R. A. Buhrman, J. Wyns, and A. J. Sievers, Phys. Rev. Lett. **37**, 625 (1976). This enhancement cannot be explained by anomalous conduction. The gas evaporation technique is discussed in C. G. Granqvist and R. A. Buhrman, J. Appl. Phys. **47**, 2200 (1976).
[19]S. R. Forrest and T. A. Witten, Jr., J. Phys. A **12**, L109 (1979).
[20]L. Harris and K. F. Cuff, J. Opt. Soc. Am. **46**, 160 (1956).
[21]U. Kreibig, Z. Phys. B **31**, 39 (1979).