Evidence for Superlocalization on a Fractal Network in Conductive Carbon-Black–Polymer Composites

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The dc conductivity of carbon-black–polymer composites has been measured as a function of carbon-black concentration from just above the percolation threshold p_c up to $33p_c$, and in the temperature range from 4 to 300 K. To explain the temperature dependence we have modified the Mott-Deutscher model for variable-range hopping between superlocalized states on a fractal by assuming Coulomb-dominated hopping. Our data then yield the first experimental evidence of electron superlocalization, with a superlocalization exponent $\zeta = 1.94 \pm 0.06$, close to theoretical estimates. The derived localization length is of the right order of magnitude.

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Hopping conduction in disordered three-dimensional materials where the wave functions of the electrons at the Fermi level are localized often follows a temperature dependence of the form $\sigma(T) \sim \exp[-(T_0/T)^\gamma]$, with σ the conductivity and T the temperature, and with a fixed exponent $\gamma = 1/4$ [1,2]. However, a value for γ close to 1/2 is observed in systems where Coulomb effects are important [3]. In order to explain $\gamma \approx 1/2$ in systems where Coulomb effects are believed not to play an essential role an extension of Mott's model [1] to variable-range hopping on fractals was proposed by Deutscher, Lévy, and Souillard [4]. It is based on a prediction by Lévy and Souillard [5] that on a fractal network the wave functions of vibrational states and of electronic states (strongly) localized at the Fermi level decay with distance R as $\exp[-(R/L)^\zeta]$, with $\zeta > 1$ and L the localization length, instead of exponentially (Anderson decay, $\zeta = 1$). The exponent ζ has therein been identified with the exponent $d_w/2$ for (half) the dimension of a random walk on a fractal, which in particular has a value of 1.90 on the incipient percolating cluster in three dimensions. However, the value of ζ is still open to controversy [6–9], and an identification with the minimal-path dimension $d_{\min}$ rather than $d_w/2$ gives a value of 1.36 at percolation [9]. The latter value seems to be confirmed by Raman scattering [10] and by simulation [11], while other simulations suggest that superlocalization is absent [12,13]. Superlocalization has implications for the hopping conductivity: Assuming a flat density of states, $\zeta = d_w/2$ and the Alexander-Orbach conjecture $2D/d_w = 4/3$ for the incipient percolating cluster [14], with D the fractal dimension, Deutscher, Lévy, and Souillard [4] derive from their model that near a percolation transition $\gamma = 3/7 \approx 1/2$. Furthermore, and in direct contrast with hopping on three-dimensional networks, T_0 is then independent of concentration. These conclusions hold provided that typical jump distances are smaller than the percolation correlation length ξ_p.

In this Letter we will present experimental evidence of superlocalization in conductive carbon-black–polymer composites with a percolation threshold well below 1 vol.%. From a master batch of well-dispersed carbon black (CB) in a liquid thermosetting polymer, fifteen castings of cross-linked samples were made, with CB concentrations varying up to a factor of 25. The conducting electrical-grade CB consists of semispherical hollow shells with a diameter of about 30 nm. These shells (thickness ≈ 1–1.5 nm) contain 2–4 layers of graphitic planes packed in a turbostratic manner [15].

Measurements of the dc conductivity σ versus CB concentration p at room temperature were made on samples with dimensions $15 \times 3 \times 1$ mm. Gold electrodes were evaporated onto the polished surfaces. Both two-contact and four-contact methods were applied. Except for one sample (see below), no contact resistance could be detected. The experimental data have been fitted by the scaling law $\sigma = \sigma_T |p - p_c|^t$ (Fig. 1). This gives for the critical ex-

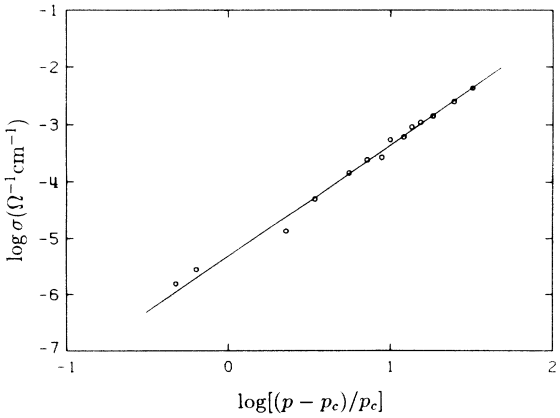

FIG. 1. The dc conductivity σ at room temperature as a function of concentration p for the samples 1 to 14 as listed in Table I.

ponent a value $t=2.0\pm0.2$, which is in perfect agreement with values previously reported ([16], and references cited therein). In Fig. 1, sample 15 as listed in Table I has been omitted. The CB concentration of this sample is very close to p_c. It appeared that the measured conductivity strongly depended on the positioning of the four electrodes on the sample surface. Visual inspection of a slice of sample 15 revealed that the CB distribution was not uniform on a length scale of a few mm.

The temperature dependence of the conductivity was determined on disk-shaped samples of thickness 0.2 mm and diameter 4 mm. The reduction in sample size as compared to that for the concentration-dependence measurements at room temperature (Fig. 1) was found necessary in order to obtain a measurable conductivity at 4 K. The results have been fitted by $\ln[\sigma_p/\sigma(T)]=(T_0/T)^\gamma$. The optimal values for T_0 and γ are listed in Table I. Sample 3 is not represented because of contact problems with the electrodes. To illustrate the accuracy of the data, $\ln[\sigma_p/\sigma(T)]$ for sample 1 is plotted in Fig. 2 as a function of $T^{-\gamma}$. A fit of all curves simultaneously, with γ, T_0, and the σ_p as free parameters, yields as common values $\gamma=0.66\pm0.02$ and $T_0=112\pm15$ K. The resulting values of the prefactors σ_p still obey the scaling law as a function of p, albeit with a much larger scatter compared to Fig. 1. This is most probably caused by the smaller thickness of the samples used for the variable-temperature measurements, which introduces an uncertainty in the local CB concentration.

Both γ and T_0 show no trend with CB concentration p, although p varies a factor of 25. In the context of variable-range hopping, the only model that is known to explain such an independence of the concentration is variable-range hopping on a fractal network [4]. The presence of a fractal structure at small length scales is also inferred from the fact that all our samples are in the scaling regime for the conductivity versus concentration. In an earlier set of samples prepared from the same batch, a hierarchy of structures has been observed with confocal-scanning optical microscopy, standard optical microscopy, and transmission-electron microscopy [16].

We shall adopt the picture of variable-range hopping of electrons between superlocalized states, and relate γ and T_0 to the microscopic properties of the system. (We note in passing that the fluctuation-induced-tunneling model by Sheng, Sichel, and Gittleman [17], specifically proposed for CB-polymer composites, was not able to satisfactorily reproduce our data; this model had been successful in explaining the conductive behavior of composites with much higher percolation thresholds. The random-charging-energy model by Sheng and Klafter [18], which has also been applied to CB-polymer composites [19], could yield a value for γ of the order observed here, but only in its high-temperature limit that hops be much smaller than the grain size. Besides, in that model T_0 is concentration dependent. Large energy splittings due to the quantum size effect can be ruled out because of the large size of the CB particles: An upper limit for the splitting is about 1 K.) In the original variable-range-hopping model by Mott [1], and in the extension by Deutscher, Lévy, and Souillard [4], the conductivity is obtained by optimizing the hopping probability with respect to two competing effects: hopping over large distances in order to arrive at a site with a thermally accessible energy, and the jumping limitation set by the decay of the wave function. The competition leads to optimal values for the distance R and the energy jump E of the hop. The argument focuses solely on hops between single pairs of sites and ignores the statistical aspects of the percolation over the full network. This objection has been

TABLE I. Parameters obtained by fitting the experimental temperature dependence of the dc conductivity σ by $\sigma(T)\sim\exp[-(T_0/T)^\gamma]$.

Sample	$(p-p_c)/p_c$	T_0 (K)	γ
1	32.7	112	0.65
2	25.2	99	0.66
3	18.7	...	...
4	15.7	135	0.63
5	13.8	108	0.65
6	12.3	134	0.62
7	10.2	90	0.62
8	9.0	127	0.62
9	7.3	154	0.60
10	5.7	111	0.63
11	3.5	116	0.66
12	2.3	104	0.70
13	0.7	159	0.62
14	0.5	129	0.66
15	0.3	151	0.64

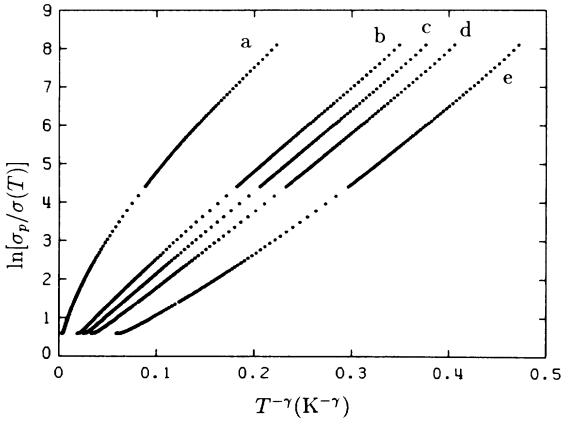

FIG. 2. Temperature dependence of the conductivity of sample 1, plotted in the form of $\ln[\sigma_p/\sigma(T)]$ vs $T^{-\gamma}$, for different values of γ. (a) $\gamma=1.0$, (b) $\gamma=0.70$, (c) $\gamma=0.65$, (d) $\gamma=0.60$, (e) $\gamma=0.50$. It clearly shows that the best fit by a straight line is given by $\gamma=0.65$ (c).

met by Ambegaokar, Halperin, and Langer [2], who consider the network as built of well-conducting regions, linked by critical bonds that determine the temperature-dependent conductivity. The Mott condition on R and E then turns out to be in fact a condition on which bonds are critical at a given temperature. When we apply this critical-path method to our carbon network and assume that the electrons are effectively localized on well-connected clusters of a few CB particles, we have to account for the fractal nature of the latter by incorporating the superlocalization-type decay of the wave function over these well-connected regions; the optimal R then refers to the typical hopping distance between the centers of two such regions, rather than to the jump length over a single critical bond. Since mathematically the critical-path analysis and the single-hop optimization are the same, we will use the original Mott argument, modified for superlocalization.

So we consider quantum hopping for an electron superlocalized at the Fermi level, and optimize the factor

$$\exp[-(R/L)^{\zeta}-\beta E], \tag{1}$$

with $\beta=1/k_BT$, under the constraint that the number of states within distance R and energy E above the Fermi level $E_F=0$ be some constant of order unity:

$$V_0(R/R_0)^D\int_0^E N(E')dE'=c. \tag{2}$$

V_0 is the volume of the CB particle with radius R_0 and $N(E)$ the density of states, given by the general form $N(E)=B|E|^k$ (to be discussed later). We introduce the volume $V_L=V_0(L/R_0)^D$ of a localized state, the exponent $\gamma=\{1+D/[(k+1)\zeta]\}^{-1}$, and the characteristic energy

$$k_BT_0=[(k+1)c/BV_L]^{1/(k+1)}\gamma^{-1}(1-\gamma)^{1-1/\gamma}. \tag{3}$$

Optimization of (1) with (2) then yields for the typical hopping distance R_1 and energy E_1

$$(R_1/L)^{\zeta}=(1-\gamma)(T_0/T)^{\gamma} \tag{4}$$

and

$$E_1/k_BT_0=\gamma(T_0/T)^{\gamma-1}. \tag{5}$$

As a result the conductivity is given by

$$\sigma(T)\sim\exp[-(T_0/T)^{\gamma}]. \tag{6}$$

With $k=0$, $D=3$, $\zeta=1$, the Mott exponent $\gamma=1/4$ is recovered. Variable-range hopping on a fractal network with $D/\zeta=4/3$ and a flat density of states ($k=0$) yields $\gamma=3/7$ [4]. Note that via the Alexander-Orbach conjecture a superlocalization exponent $\zeta>1$ is already presupposed.

We will now elaborate on the correct density of states of the CB-polymer composites. The flat density of states normally employed in hopping-conduction models is not appropriate for carbon black. The density of states of a two-dimensional graphite lattice is given by $N(E)=B|E|$ [20], i.e., $k=1$. In three-dimensional hexagonal graphite $N(E)$ is not zero at the Fermi energy E_F, and one has to add a constant term to $N(E)$ [20]; this would effectively lower the value of k. However, we ignore the interaction between the graphitic planes and apply the two-dimensional density of states to the carbon black, of which the shell consists of only two to four layers. With a mass density of 2 $\mathrm{g\,cm^{-3}}$ for CB we get $B=3.7\times10^{21}$ $\mathrm{cm^{-3}eV^{-2}}$. Inserting in Eq. (3) $k=1$, $c=1$, and the optimal experimental values $T_0=112$ K and $\gamma=0.66$, we then obtain a characteristic localization length $V_L^{1/3}$ of about 35 nm, which is of the right order of magnitude compared to the diameter of the CB particles. The measured values of γ (0.60–0.70) imply $0.86<D/\zeta<1.33$, indicating the existence of superlocalization ($\zeta>1$), unless D would be of order unity. Note that the Alexander-Orbach conjecture $D/\zeta=4/3$ corresponds to $\gamma=3/5$.

Let us now estimate the effect of Coulomb interactions between the charge carriers. Following Efros and Shklovskii [3] we consider the electron-hole energy $U_1=e^2/4\pi\epsilon R_1$ that has to be overcome in a typical hop, and make an order-of-magnitude estimate of U_1/k_BT. In view of (4) and the values of the temperatures and exponents at hand, we put $R_1=O(L)=O(R_0)$. Since at distances a few times R_0 the charges will be screened by the polymer, we take $\epsilon_r=4$, the room-temperature dielectric constant of the polymer. With $T=T_0=112$ K we then get $U_1/k_BT\approx1$. So, we conclude that at least at the lower temperatures the Coulomb effect is dominant, i.e., $E_1\approx U_1\sim R_1^{-1}$, and a pseudogap is induced. From (2) the density of states in the gap is determined self-consistently, and in particular leads to $k=D-1$. As a result, both k and D drop out of the expression for the exponent γ, and we simply get $\gamma=\zeta/(\zeta+1)$, which is a generalization of the Efros-Shklovskii expression to fractal media. The exponent γ thus becomes a direct measure of the superlocalization exponent ζ. Inserting the best-fit value $\gamma=0.66\pm0.02$ it is found that $\zeta=1.94\pm0.06$, in excellent agreement with the value put forward by Lévy and Souillard [5]. If we impose the Coulomb relation on R_1 (4) and E_1 (5), we obtain instead of (3)

$$k_BT_0=(e^2/4\pi\epsilon L)\gamma^{-1}(1-\gamma)^{1-1/\gamma}. \tag{7}$$

As a more precise estimate for the localization length this gives $L=100$ nm, in good agreement with the size of the CB particles. A possible crossover from Coulomb-dominated hopping at low temperatures to hopping determined by the density of states of two-dimensional graphite cannot be observed because the γ values for both mechanisms are too close to each other.

The typical jump distance R_1 (4) between two well-connected regions varies from $1.8L$ to $0.4L$ between 4 and 300 K. We have to compare these values with the corre-

lation length ξ_p. A rough estimate whether $R_1 < \xi_p$ can be made by calculating the latter from the scaling law $\xi_p = \xi_0 |p - p_c|^{-\nu}$, with $\nu = 0.88$ and $\xi_0 = O(R_0)$. We then find that for the sample with the highest CB concentration ξ_p is still at least 1 order of magnitude larger than the diameter of the CB particle. The condition that the jump distance is smaller than the percolation correlation length is thus satisfied.

In conclusion, we have presented experimental evidence that on the percolating network of carbon-black particles dispersed in an insulating matrix the electronic wave functions are superlocalized. The evidence is provided by the fact that for the system, which for all concentrations is in the dc scaling regime above the percolation threshold, (a) a fit of the temperature-dependent conductivity by the variable-range-hopping expression yields a temperature exponent γ and a reduction temperature T_0 that show no trend with concentration, and (b) excellent agreement is obtained with a theory in terms of Coulomb-dominated hopping between superlocalized states on a fractal. The major result is that the exponent γ is a direct measure for the superlocalization exponent ζ. Our data yield $\zeta = 1.94 \pm 0.06$, in full agreement with the original prediction of Lévy and Souillard [5]. A crossover from Coulomb-dominated hopping at low temperatures to hopping without Coulomb interactions at higher temperatures cannot be ruled out. We have shown that in this case the electronic wave functions are superlocalized as well.

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[1] N. F. Mott, Philos. Mag. **19**, 835 (1969).
[2] V. Ambegaokar, B. I. Halperin, and J. S. Langer, Phys. Rev. B **4**, 2612 (1971).
[3] A. L. Efros and B. I. Shklovskii, J. Phys. C **8**, 49 (1975).
[4] G. Deutscher, Y.-E. Lévy, and B. Souillard, Europhys. Lett. **4**, 577 (1987).
[5] Y.-E. Lévy and B. Souillard, Europhys. Lett. **4**, 233 (1987).
[6] O. Entin-Wohlman, S. Alexander, and R. Orbach, Phys. Rev. B **32**, 8007 (1985).
[7] A. Aharony, S. Alexander, O. Entin-Wohlman, and R. Orbach, Phys. Rev. Lett. **58**, 132 (1987).
[8] A. Brooks-Harris and A. Aharony, Europhys. Lett. **4**, 1355 (1987).
[9] A. Aharony and A. Brooks-Harris, Physica (Amsterdam) **163A**, 38 (1990).
[10] Y. Tsujimi, E. Courtens, J. Pelous, and R. Vacher, Phys. Rev. Lett. **60**, 2757 (1988).
[11] C. J. Lambert and G. D. Hughes, Phys. Rev. Lett. **66**, 1074 (1991).
[12] P. de Vries, H. De Raedt, and A. Lagendijk, Phys. Rev. Lett. **62**, 2515 (1989).
[13] Quiming Li, C. M. Soukoulis, and G. S. Grest, Phys. Rev. B **41**, 11713 (1990).
[14] S. Alexander and R. Orbach, J. Phys. (Paris), Lett. **43**, 625 (1982).
[15] A. I. Medalia, in *Carbon Black-Polymer Composites*, edited by E. K. Sichel (Dekker, New York, 1982), p. 1.
[16] M. A. J. Michels, J. C. M. Brokken-Zijp, W. M. Groenewoud, and A. Knoester, Physica (Amsterdam) **157A**, 529 (1989).
[17] Ping Sheng, E. K. Sichel, and J. I. Gittleman, Phys. Rev. Lett. **40**, 1197 (1978).
[18] Ping Sheng and J. Klafter, Phys. Rev. B **27**, 2583 (1983).
[19] M. Mehbod, P. Wyder, R. Deltour, C. Pierre, and G. Geuskens, Phys. Rev. B **36**, 7627 (1987).
[20] J. W. McClure, Phys. Rev. **108**, 612 (1957).