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Random walk in the Cu/graphite mixtures

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Transport properties of Cu/graphite composites scanned surfaces were studied by the random walk. The type of random walk used considers the nonzero conductivity of graphite. The obtained results are consistent with the existing scaling theory. The diffusivity composition dependence behavior in two dimensions is in good agreement with the measured electrical conductivity composition dependence behavior of Cu/graphite composites in three dimensions. [S0163-1829(96)05330-1]

I. INTRODUCTION

The Cu/graphite composite material is often used for low-voltage and high-current density applications (for example in welding machines).[1] The nonlinear dependence of electrical conductivity on composition was observed in the range of 0.59–1 volume fraction of copper (see Fig. 1).[2] A percolation theory[3] was used to model this dependence. However, the obtained conductivity critical exponent $t=2.33\pm0.01$ and the percolation threshold for the volume fraction of copper, $p_c=0.10\pm0.05$, differ from the numerically estimated three-dimensional values $t = 1.7$ and $p_c = 0.33$.[4,5] This difference can be attributed to the prolonged nonspherical shape of the copper clusters.[2] Moreover, in the percolation theory the electrical conductivity of graphite is considered as zero. It means that the Cu/graphite composite, from the point of view of the percolation theory, is a mixture of conducting copper regions and nonconducting graphite ones. In reality the Cu/graphite composite is the mixture of two differently conducting regions.

Scanned surface micrographs, prepared from samples with various volume fractions of copper (see Fig. 2), enable one to investigate the Cu/graphite composite system in two dimensions. The direct method to calculate the electrical conductivity for a two-dimensional conductor network[6] (e.g., scanned microphotographs) suffers from the lack of statistical fluctuations. To avoid this, the investigation of diffusion on the random conducting network was proposed (random walk). It allows one to average the large number of walk configurations.[3] The result is an average diffusion coefficient for the given network and the conductivity and diffusivity can be connected by the Nernst-Einstein relation[7]

$$\sigma \sim nD, \tag{1.1}$$

where σ is the electrical conductivity, D is the diffusivity coefficient, and n is the density of the charge carriers.

The typical random walk is usually applied only for one region of the two-component system. But the Cu/graphite composite needs the random walk to be performed on both regions of the two-component system.

The random walk introduced by Hong *et al.*[7] fulfills these requirements. This type of random walk describes the situation when the investigated system is a random mixture of good and poor conducting regions. The random walk is characterized by the conductivity ratio h and for the Cu/graphite mixture it is

$$h=\frac{\sigma_{\mathrm{Gr}}}{\sigma_{\mathrm{Cu}}}\sim 10^{-3}, \tag{1.2}$$

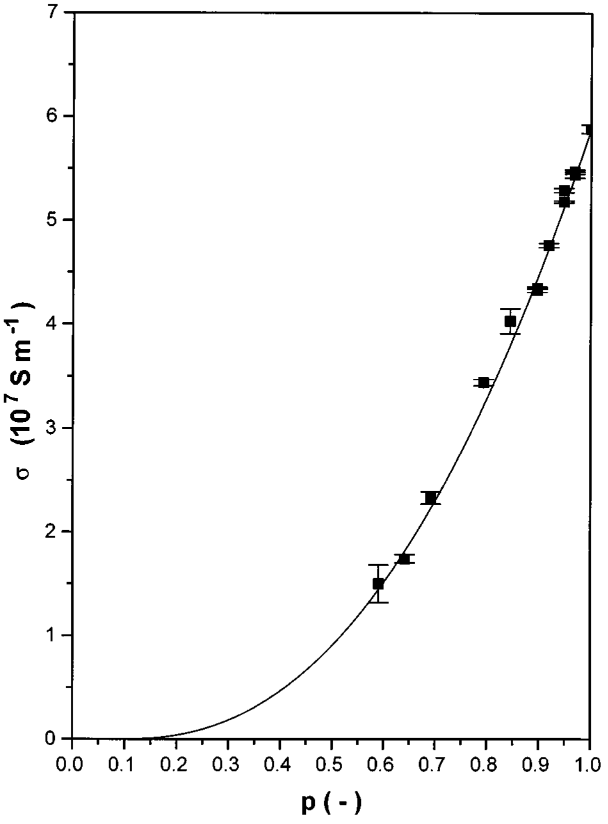
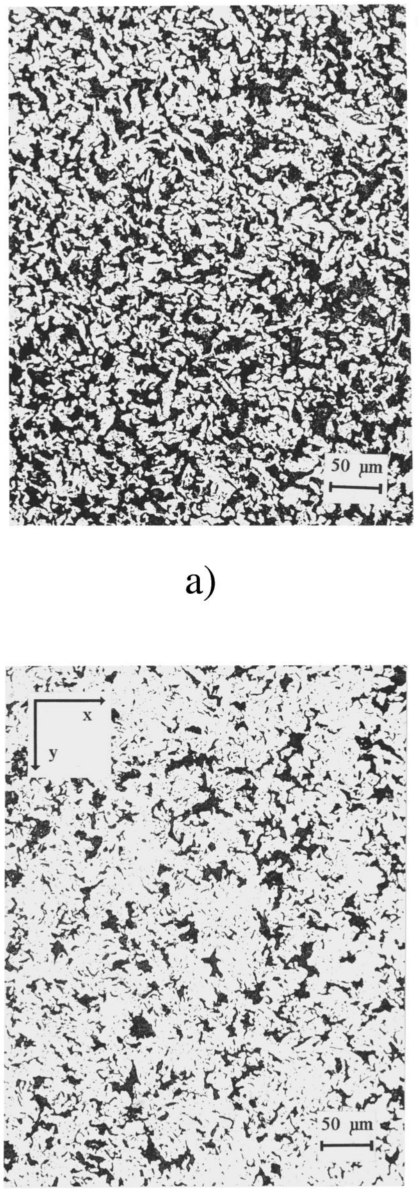


FIG. 1. The electrical conductivity σ of the Cu/graphite material vs volume fraction of copper at 296 K. The plotted line is the result of the percolation theory.



a)

b)

FIG. 2. Cross sections of the Cu/graphite composites for 70% (a) and 85% (b) volume fraction of copper.

where σ_{Gr} is the electrical conductivity of graphite and σ_{Cu} is the electrical conductivity of copper.

Let us assume a random walker placed randomly on the Cu/graphite surface (e.g., Fig. 2). In this case the jump probability A of the random walker to move from copper to graphite is equal to $h = 0.001$ and walker's time in graphite flows $1/h = 1000$ times slower than in copper. The jump probability B for the copper-copper, graphite-copper, and graphite-graphite moves is equal to 1. To describe reality better the probability of the random walker's move from copper to graphite was changed in following way: When a walker chooses the copper-graphite move he moves to graphite with probability $A/(A+B)$ or he stays at a site with probability $B/(A+B)$.

Hong *et al.* also introduced a scaling theory[7] for their computer model of the random walk. Straley,[8] who has been working in this field for a long time,[9,10] presented a slightly different and more general interpretation of this scaling theory.

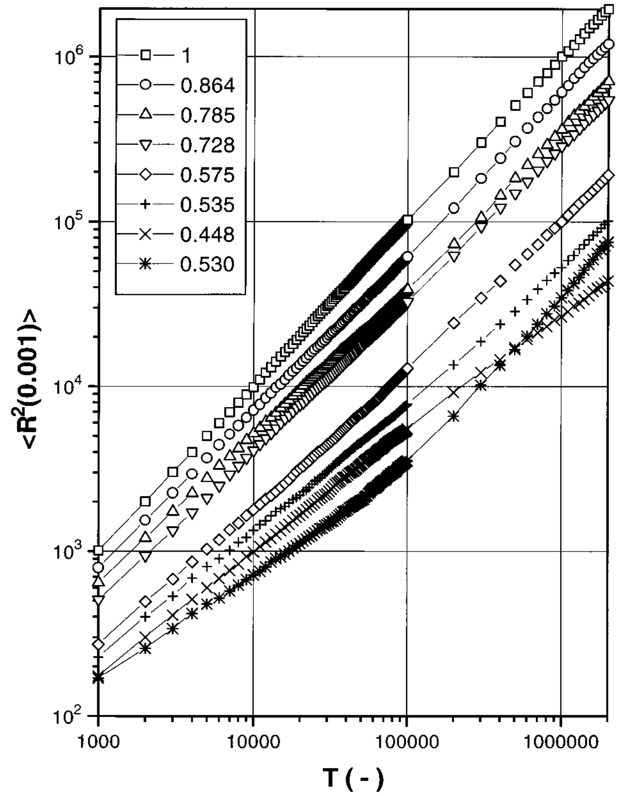


FIG. 3. Log-log plot of $\langle R^2(0.001)\rangle$ as a function of time for various p.

The aim of this work is to prove the suitability of the scaling theory according to Straley for the simulation of the transport properties of Cu/graphite composites. At first, Straley's scaling theory will be briefly mentioned. Then the results of a computer simulation will be presented and compared with the measurement of the electrical conductivity of Cu/graphite composites.

II. SCALING THEORY FOR THE RANDOM WALK

The behavior of the diffusivity coefficient D near the percolation threshold can be considered as the scaling law for the mean square displacement of a random walker, $\langle R^2\rangle$, according to Straley,[8]

$$\begin{aligned}\langle R^2\rangle &\equiv TD(\varepsilon,A,B,T^{-1})\\ &= \mu TD(\varepsilon/\lambda,\lambda^{-s}A/\mu,\lambda^{t}B/\mu,d^2\mu^{-1}\lambda^{\beta-2\nu}T^{-1}),\end{aligned} \tag{2.1}$$

where T is time, A, B are jump probabilities, $\varepsilon = (p-p_c)/p_c$, p is the volume fraction of copper, d is the lattice spacing, λ,μ are arbitrary parameters, and s,t are critical exponents; $s = t$ in two dimensions. Equation (2.1) holds only in a critical region, e.g., ε small, $A \ll B$, and T large. The scaling in μ means a change of units for T. The scaling in λ is nontrivial.

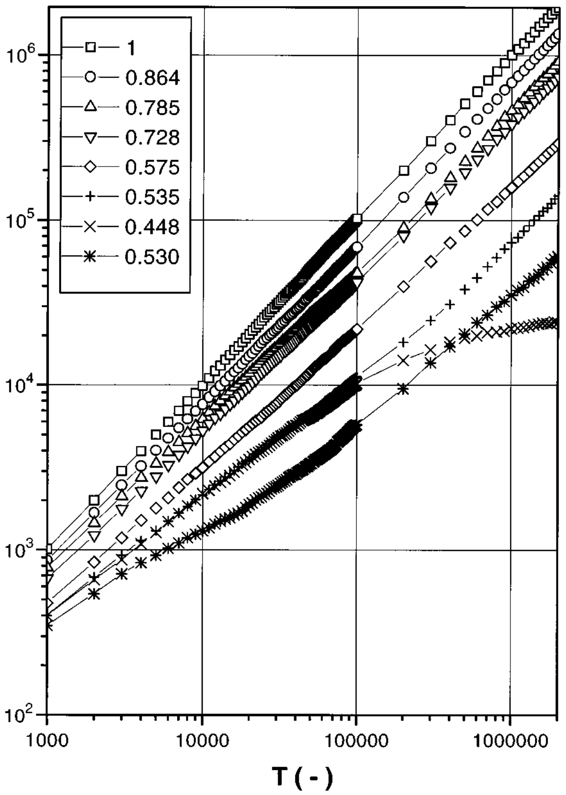


FIG. 4. Log-log plot of $\langle R^2(0)\rangle$ as a function of time for various p.

For $|\varepsilon|>(A/B)^{1/(s+t)}$ and large T the expanding in the small parameters of Eq. (2.1) gives

$$\langle R^2\rangle \approx \varepsilon^t BTD(\mathrm{sgn}\varepsilon,0,1,0)+\varepsilon^{-s}ATD(\mathrm{sgn}\varepsilon,0',1,0)$$
$$+\varepsilon^{\beta-2\nu}d^2D(\mathrm{sgn}\varepsilon,0,1,0')+\cdots. \tag{2.2}$$

For $\varepsilon>0$ the last term can be neglected and the first term is leading. For $\varepsilon<0$ the first term vanishes. The term ''large T'' is defined relatively to the time scale

$$\tau \approx \varepsilon^{\beta-2\nu-t}d^2/B. \tag{2.3}$$

TABLE I. The results of the random walk for $A=0$ and $A=0.001$.

p	$D_{0.001}$	D_0	$k_{0.001}$	k_0	$\tau_{0.001}$ [a]	$\tau_{0.001}$ [b]	$W^{1/2}$
1.000	0.994	0.996	0.500	0.500	2.3	0	0.996
0.864	0.603	0.679	0.488	0.481	9.4	10	0.892
0.785	0.360	0.459	0.472	0.460	29.3	20	0.805
0.728	0.255	0.346	0.468	0.457	86.6	28	0.756
0.575	0.095	0.026	0.466	0.419	338346.0	80000	0.616
0.535	0.045	-	0.389	0.374	338346.0	200000	-
0.448	0.015	-	0.370	0.325	545.0	300	-
0.530	0.041	-	0.370	0.333	143945.0	50000	-

[a] The time constant calculated by Eq. (2.3).

[b] Experimentally obtained.

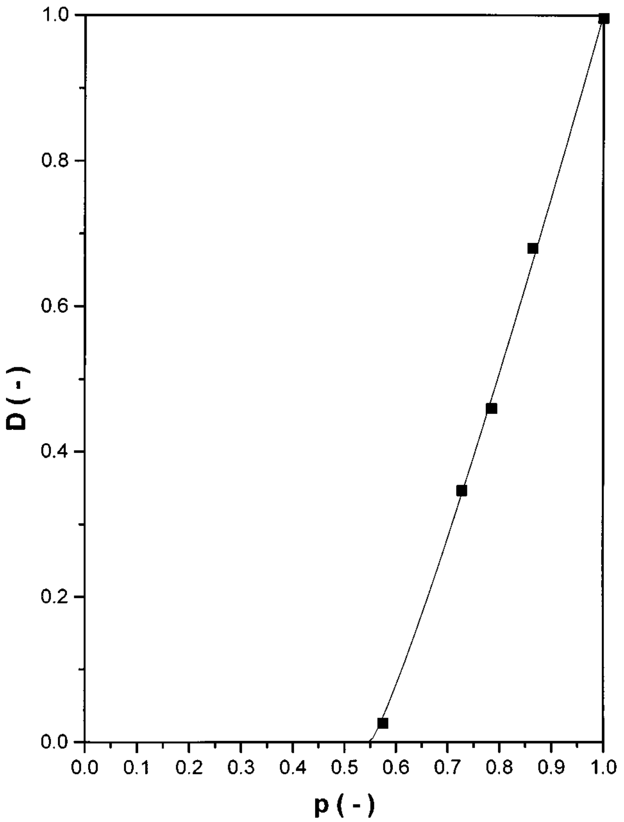


FIG. 5. Diffusivity dependence on the composition for $A=0$. The plotted line is the percolation theory result.

On the contrary, in the scaling theory of Hong *et al.*[7] the second time constant τ_H is defined as

$$\tau_H \approx \varepsilon^{\beta-2\nu+s}d^2/A, \tag{2.4}$$

and Hong *et al.*[7] presented a sketch in which $\langle R^2\rangle$ increases for $T<\tau$, has a plateau for $\tau<T<\tau_H$, and exhibits a linear (diffusive) growth for $\tau_H<T$.

Straley[8] on the other hand showed that this sketch is valid only for the two-dimensional square bond problem and for two and three dimensions is not true in general. He concluded that there is only one relevant time scale defined by Eq. (2.3). This time scale characterizes the time required to sample the various environments of the system. On time scales larger than τ the inhomogeneity has been averaged out, allowing the linear-in-T behavior.

For a more complex view on this problem and also on the standard cases of the mentioned scaling theory the reader is referred to the work of Straley.[8]

Introducing $A = 0$ in Eq. (2.1) (random walk on one component of a two-component system) it can be shown[8]

TABLE II. The results of the conductivity critical exponent t.

	$A=0$	$A=0.001$	Analytically obtained [a]
t	1.16±0.04	1.46±0.13	1.30

[a] References 3 and 4.

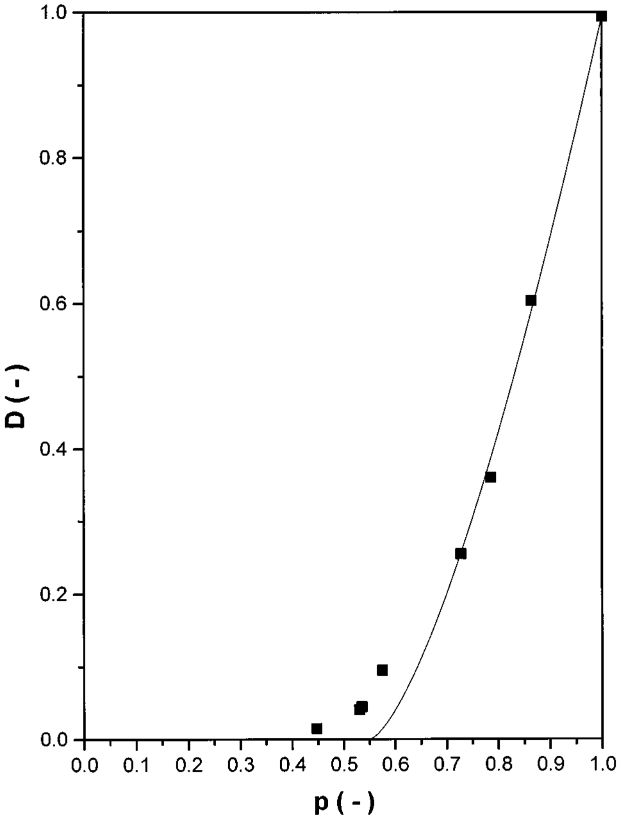


FIG. 6. Diffusivity dependence on the composition for $A = 0.001$. The plotted line is the percolation theory result for $p > p_c$.

that, after simplifications, the percolation scaling theory for the conductor-insulator system is obtained.

In this model for $p = 1$ a diffusion law

$$R^2 = D_0 T \tag{2.5}$$

holds exactly and for $p < 1$ is fulfilled for large T. Here D_0 is the diffusivity and R^2 is the mean square displacement of the random walker. For $p=1$ $D_0 = 1$, and for $p<1$, $D_0 = D_0(p)$.

D_0 tends to zero when p approaches p_c from above according to

$$D_0 \propto (p - p_c)^t, \tag{2.6}$$

and the mean square displacement possesses an anomalous diffusion at p_c

$$R^2 = D_0 T^{2k}, \tag{2.7}$$

where k is an anomalous diffusion exponent; k is about 0.33 in two dimensions.[3]

For $p < p_c$ the diffusion is impossible, $D_0 = 0$, R^2 cannot increase, and for the large T it obeys

$$R^2 \propto (p_c - p)^{\beta - 2\nu}, \tag{2.8}$$

where β and ν are the critical exponents. β is 5/36 and ν is 4/3 in two dimensions.[3,4]

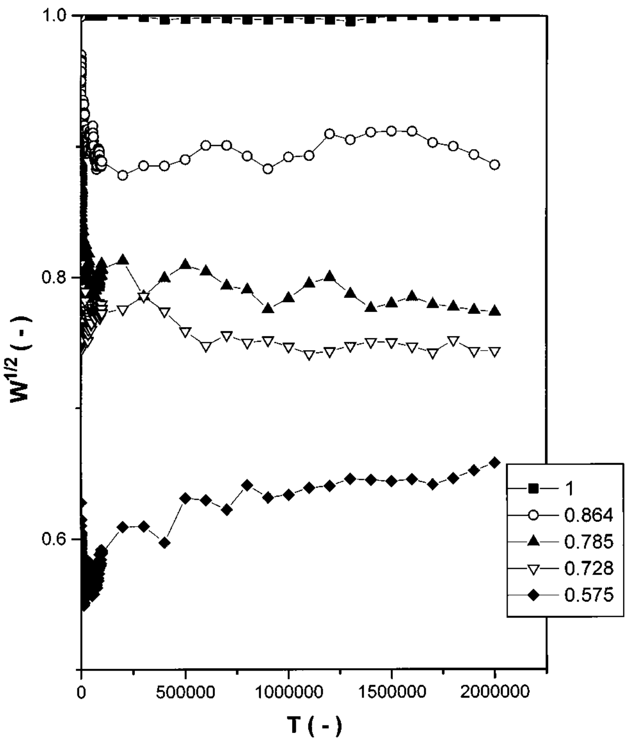


FIG. 7. $W^{1/2}$ as a function of time for $p > p_c$.

III. EXPERIMENTAL RESULTS

A. Cu/graphite composite material

The Cu/graphite composite material was prepared by the powder metallurgical method. The electrolytic Cu powder (particle size <70 μm) was dry mixed with the graphite powder (particle size <3 μm, purity 99.9%) in a tumbler mixer, and then encapsulated and isostatically compacted at 1000 °C for 30 min using an Ar-gas pressure of 100 MPa. The powder mixture was free of any activating sintering additions. The volume fraction of copper in the as-prepared composite varied in the range of 0.59–1.

The composite samples were cut in various directions and polished for metallographic observation. The black and white microphotographs of the prepared surfaces were taken by an optical microscope at the magnification of 200 times. The photographs were scanned by digital scanner with the resolution of 300 dots per inch. The obtained array had a size of about 1800×900 points. The black points were considered as the graphite and the white ones as the copper. One point represents a square with the area of 0.16 μm^2. The computer simulations were done on the set of eight pictures, each from a different sample.

B. Results and discussion

The computer simulation of the random walk was done on the mixture of copper and graphite conducting regions with $A = 0.001$. The random walk on the copper conducting regions was also done for the comparison $(A=0)$.

In the computer simulation, the random walker started randomly from the copper or graphite site within an area of 20% around the center of the rectangular array with the size of about 1800×900 sites (e.g., Fig. 2). The mirror boundary

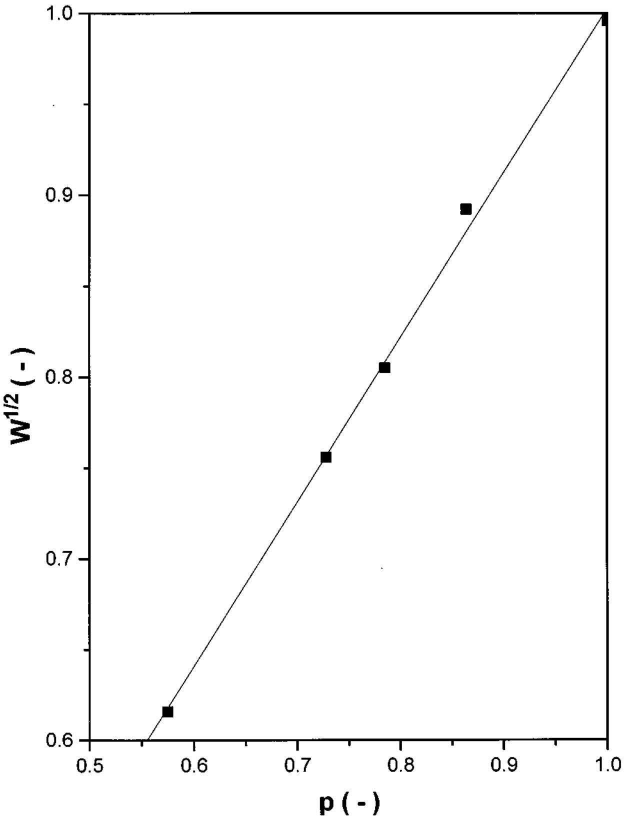


FIG. 8. Composition dependence of $W^{1/2}$ for $p > p_c$.

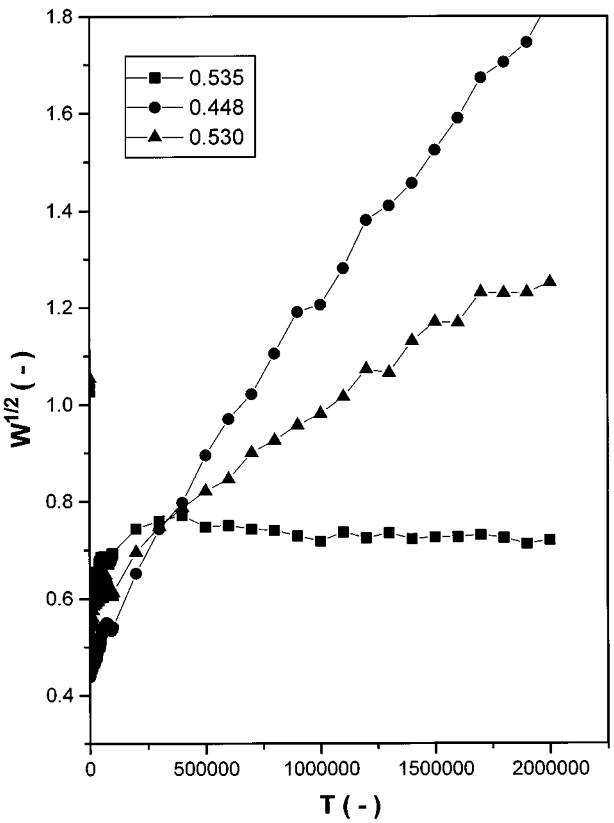


FIG. 9. $W^{1/2}$ as a function of time for $p < p_c$.

conditions were applied. Five thousand walks, with 2×10^6 time steps for each walk, were done on every scanned section.

The obtained two-dimensional percolation threshold for copper, $p_c = 0.55 \pm 0.02$, for the cross sections[11] is consistent with the analytically obtained value of 0.5 for the two-dimensional site percolation problem.[3,4]

Figure 3 displays the results of $\langle R^2\rangle^{1/2}$ for the various p from the range of 0.448–1 and for $A=0.001$. Only the curve with $p = 0.530$ exhibits a plateau. Figure 4 shows almost the same situation for $A = 0$. The time constant $\tau_{0.001}$ (determined from the onset of the linear growth of $\langle R^2\rangle^{1/2}$) is for all other curves very small (see $\tau^a_{0.001}$ in Table I). The calculated time constant $\tau_{0.001}$ (see $\tau^b_{0.001}$ in Table I) and the experimentally obtained values for various p showed that $\tau_{0.001}$ seems to be overestimated by a factor of 10–100. It seems to be true that there is only one relevant time scale.

The conductivity critical exponent t can be determined from data in Table I and Eq. (2.6) by the least squares minimization method. The results for both types of walk are shown in Table II. Figures 5 and 6 show the obtained diffusivity coefficient dependence on composition.

The difference between $t=1.16\pm0.04$ for $A=0$ and the analytically obtained two-dimensional value $t=1.3$ is caused by the only one realization of scanned sections for each composition. The large uncertainty in $t = 1.46 \pm 0.13$ for $A = 0.001$ can be the result of using the percolation approach, which was developed for the case of $A = 0$. In this case, the S-shaped curve for the diffusivity coefficient composition dependence can be possibly the better solution.[12] The obtained conductivity critical exponent $t = 1.46 \pm 0.13$ is greater than the analytically obtained value 1.3[3] in two dimensions. This is consistent with the measured electrical conductivity critical exponent $t = 2.33 \pm 0.01$[2] which is also greater than the numerically estimated value 1.7[3] in three dimensions.

It can be pointed out from Figs. 5 and 6 that one can approximately determine the value of percolation threshold p_c in the range of 0.535–0.575 (see the values of D_0 and $D_{0.001}$ in Table I).

The influence of the nonzero value of the jump probability A on the behavior of a computer-simulated random walk is shown in Figs. 7–9.

When the results of the mean square displacement in the random walk with $A = 0.001$ are divided with the results for $A = 0$ we obtain the scale-independent ratio W. It can be shown that this ratio is time independent for $p > p_c$ and large T, and from Eq. (2.2) and Eq. (2.5) we have

$$W = \frac{\langle R^2(0.001)\rangle}{\langle R^2(0)\rangle} \propto \text{const} < 1. \tag{3.1}$$

The obtained values for $W^{1/2}$ are given in Table I. This time independence is also confirmed by Fig. 7. The linear composition dependence of $W^{1/2}$, $W^{1/2} = (0.098 \pm 0.021) + (0.905 \pm 0.027)\,p$ with correlation coefficient $r = 0.9987$, can be found (see Fig. 8). This dependence decreases with increasing graphite volume fraction in the composite.

When $p < p_c$ the second term in Eq. 2.2 becomes the most important, and since Eq. 2.8 is constant, the ratio $W^{1/2}$ for large T tends to infinity (see Fig. 9).

We have demonstrated that the jump probability A influences the random walk results. The changes are obvious especially for large T. In the vicinity of the percolation threshold, the value of the anomalous diffusion exponent k (see k_0 and $k_{0.001}$ in Table I) increases a little bit with the nonzero A. The nonzero A also lowers the rate of the diffusivity coefficient, falling to zero near percolation threshold. It is caused by the ability of the random walker (e.g., charge carrier) to leave a closed copper cluster and walk through graphite. On the other hand, this ability affects the reduction of the diffusivity coefficient for p going to 1 and nonzero A. The reason is the deceleration of the random walker time flow when he occasionally enters the graphite cluster (e.g., dissipation of the current energy due to the presence of the graphite particles in the copper matrix). This behavior of the diffusivity coefficient is obviously similar to the behavior of the measured electrical conductivity as a function of composition.

IV. CONCLUSION

This work proved that Straley's scaling theory[8] can be a suitable tool for the study of the transport properties of Cu/graphite composites.

The two-dimensional diffusion on the cross sections of the Cu/graphite composites was studied by computer simulation of the random walk of Hong *et al.*[7]

The only one characteristic time scale of random walk in the investigated Cu/graphite system was found and our simulation results appear to be consistent with the scaling of Straley,[8] but we cannot rule out the possibility of the existence of the second time scale discussed by Hong *et al.*[7]

The obtained conductivity critical exponent $t = 1.46 \pm 0.13$ is greater than the analytically obtained value 1.3[3] in two dimensions. This is consistent with the measured electrical conductivity critical exponent $t = 2.33 \pm 0.01$[2] which is also greater than the numerically estimated value 1.7[3] in three dimensions.

Due the nonzero jump probability A, the behavior of the diffusivity coefficient as a function of the composition is obviously similar to the behavior of the measured electrical conductivity as a function of the composition.

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