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Percolation conductivity in granular metal films

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Abeles, Pinch, and Gittelman have fitted the conductivity of annealed W-Al_2O_3 granular metal films to a percolation threshold. They find $C^* = 0.47 \pm 0.05$. By numerical simulation of conductivity in resistor networks we demonstrate that these conductivity data can be explained if there is a bias towards the formation of isolated metallic regions.

Abeles, Pinch, and Gittleman (APG) have reported the existence of percolation conductivity[1] in annealed W-Al_2O_2 granular metal films.[2] Their data fit accurately the formula proposed by Kirkpatrick[3]

$$\sigma \propto (C - C^*)^{\beta}, \tag{1}$$

where σ is the conductivity, C is the metallic volume fraction, and C^* is the percolation threshold. They find values of 0.47 ± 0.05 for C^* and 1.9 ± 0.2 for β. They note that "*Existing percolation theories for metal-insulator mixtures predict considerably lower values for* C^*. *Simple-cubic lattices yield*[2] $C^* = 0.25$ *for bond percolation and* $C^* = 0.32$ *for site percolation. The random-lattice percolation model*[4] *predicts* $C^* = 0.3$; *the effective-medium theory*[5] $C^* = 0.33$; *and the Cayley-tree networks*[6] $C^* = 0.20$–0.33. *The values predicted for* β *are 1.5–1.6 for the simple-cubic lattices,*[2] *1 for effective-medium theory, and 2 for the Cayley-tree networks.*[6] *The measured value of* β *in the* W-Al_2O_3 *granular metals agrees with that of the Cayley-tree network. The large discrepancy between the experimental and theoretical values of* C^* *needs yet to be explained.*" The discrepancy between the observed and expected values of C^* is perhaps worse than stated by APG. The films studied by APG were 7000 Å thick. The spacing between the electrodes was much larger, so that the current flowed uniformly throughout the film thickness, apart from an inhomogeneous flow induced by the granular nature of the film. The grain size of the annealed films was reported as 50–100 Å. Because the grains were much smaller than the thickness, the conduction process was three dimensional. For an isotropic continuous random-percolation process, the threshold as mentioned above is 0.145 ± 0.005 in three dimensions[7] and the value of β is 1.4. The discrepancy between the observed and expected threshold is thus a factor of 3. A high value of percolation threshold in the granular metallic films is also indicated by the following experimental evidence.

(a) Recent experimental results on the optical properties of Au–Al_2O_3 and Ag–Al_2O_3 granular films[8] reveal Mie resonance peaks in the absorption spectrum which are neither considerably broadened nor shifted to the red as C is increased up to metallic volume fractions $C = 0.5$–0.6. In contrast, in a random three-dimensional metal insulator composite medium, the Mie resonances should only appear at metallic concentrations below the percolation threhold[9] and should be shifted towards zero frequency as the metallic volume approaches the critical value $C^* = 0.145$.

(b) The electron micrographs of the annealed granular films studied by APG[1] show that the metallic grains are isolated by the dielectric matrix up to $C \cong 0.5$. As the metallic concentration increases above this value most of the metallic phase forms extended channels.

These data lead us to the conclusion that the granular films differ from a continuous random binary medium by being characterized by the formation of noncontacting metallic grains embedded in the dielectric matrix up to high metallic concentrations. In this note, we present a numerical study of the conductivity of a three-dimensional resistor network characterized by a high value of percolation threshold $C^* \lesssim 0.5$, achieved by a bias towards the formation of isolated metallic regions introduced into the network.

The nature of conductivity above percolation threshold in the granular films will be elucidated by confronting the numerical results with the experimental data. In Kirkpatrick's original study[2] of percolation conductivity in random system, one starts with an initial cubic network of nonconducting bonds and then assigns metallic conductance values to a fraction C of the bonds chosen at random. In contrast, in the present model we start

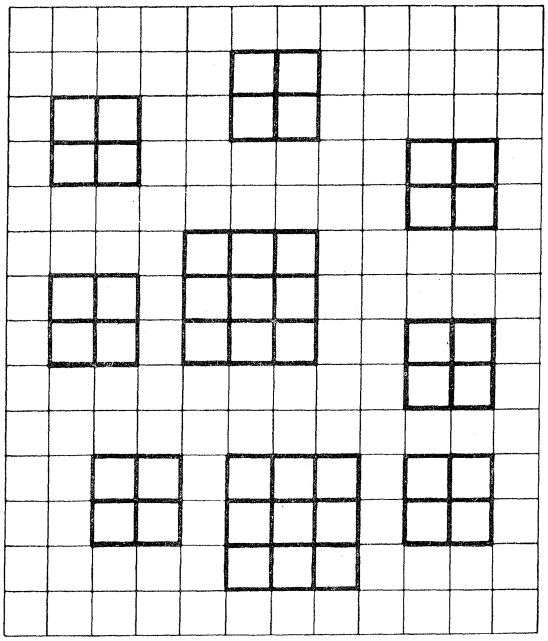

FIG. 1. Schematic description of the cubic network employed for numerical simulations of the conductivity of a granular metal. Heavy lines represent metallic bonds arranged in a configuration of noncontacting metallic regions.

with an initial network which already contains a fraction C_0 of metallic bonds arranged in a configuration of noncontacting metallic regions. The transition to metallic conductivity is now effected by increasing the metallic volume fraction through assigning metallic values at random to bonds in the initially nonconducting extended regions surrounding the metallic regions. This process is now carried out for various C values up to $\sigma/\sigma_0 = 1$ and the conductivity $\sigma(C)$ is evaluated. The transition to metallic conductivity occurs at a critical value of volume fraction $C^* > C_0$, which can be controlled by varying the value of the initial metallic volume fraction C_0. In our model, based on a simple-cubic resistor network, we chose for convenience an initial configuration of an array of cubes of metallic bonds. The size of the cubic networks used for our numerical computation were $30\times30\times30$. The sizes of the cubes of metallic bonds were $2\times2\times2$ and $3\times3\times3$. Large cubes of metallic bonds were not used as these may result in large fluctuations due to edge effects. We have studied the following four initial configurations of metallic regions: (i) array of $2\times2\times2$ cubes centered on an ordered cubic sublattice; (ii) A mixture of $2\times2\times2$ and $3\times3\times3$ cubes, whose centers constitute a random array of lattice points (illustrated in Fig. 1). For the initial configurations (i) and (ii), $C_0 = 0.28$, while in cases

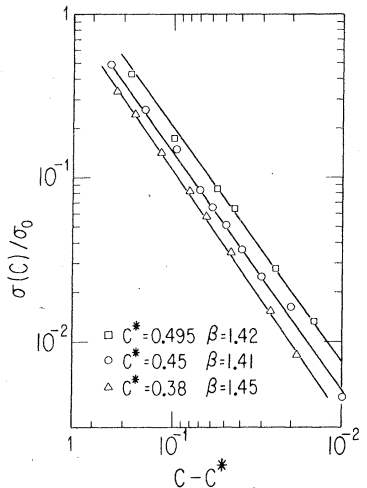

FIG. 2. Log-log plots of σ vs $C-C^*$ for several values, of C_0: □—C_0 0.47, C^*= 0.495, initial configuration (d) ○—C_0 = 0.40, C^*= 0.45, initial configuration (c); △—C_0= 0.28, C^*= 0.38, initial configuration (b).

(iii) and (iv) C_0 can be varied from 0.28 to ~0.5. For all these types of initial configuration the metallic cubes were noncontacting. Log-log plots of σ vs $C-C^*$ for several values of C_0 and of C^* are presented in Fig. 2. A power law $\sigma \propto (C-C^*)^\beta$ holds for all C^* values studied with $\beta = 1.4-1.45$, irrespective of the initial configuration of the metallic regions. These values overlap the value of $\beta = 1.4$ for continuous percolation and are close to the value of $\beta = 1.6 \pm 0.1$ for bond percolation. This result is in agreement with the recent argument of Stinchcombe and Watson[10] that the value of β for a given dimensionality is insensitive to the local statistics and local geometry of the system, and thus also insensitive to the value of C^*. In Fig. 3 we have plotted the numerical results for $\sigma(C)$ evaluated with $C_0 = 0.47$ and $C^* = 0.495$, together with the conductivity data of APG for annealed

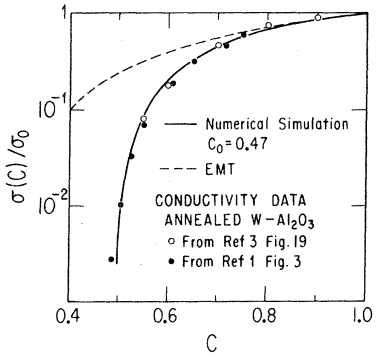

FIG. 3. Analysis of the conductivity data for W-Al_2O_3 granular metals (Refs. 1 and 3) in terms of the results of the numerical simulations (solid curve). The effective-medium-theory result (dashed curve) is shown for comparison.

W-Al_2O_3 films. The fit between the numerical results and the experimental data is good throughout the range $C^* < C < 1$.

It should, however, be noted that the experimental conductivity fit the $\propto (C - C^*)^\beta$ curve with $C^* = 0.47 \pm 0.05$ and $\beta = 1.9 \pm 0.1$, a value which is higher than the exponent obtained from our model. This discrepancy arises from the fact that the part C_0 of the metallic volume fraction C assigned to the separated metallic grains is kept independent of C in our model. Examination of the electron micrographs[1] or consideration of the details of the deposition process strongly suggests that C_0 should increase with C, $C_0 = C_0(C)$. A linear dependence on C is sufficient over the narrow range of C used to establish the value of β:

$$C_0(C) = C_0(C^*) + C_0'(C^*)(C - C^*). \tag{2}$$

Thus, as C increases, so do both C_0 and the value of C^* relevant to Fig. 2. Thus, the actual values of $\sigma(C)/\sigma_0$ follow a line which moves steadily from the lower curve in Fig. 2 towards the upper curve, and the value of β is correspondingly increased. It is apparent that values of the two parameters of the model, $C_0(C^*)$ and $C_0'(C^*)$, can be chosen so as to give agreement with the empirical parameters C^* and β.

In conclusion, while we have not gone into the problem of why the metallic grains in the granular film keep separated up to high C values, we have shown that a percolation process in a medium, which is characterized by such a property, can account for the conductivity data in the metallic region.

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