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Percolation Scale Effects in Metal–Insulator Thin Films

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Thin metal films near their continuity threshold and metal–insulator mixture films near their metal–insulator transition are well described by the percolation theory. Here we demonstrate that statement by reviewing some geometrical measurements done on both types of thin films. We then comment on the measurements of the other physical quantities.

KEY WORDS: Percolation; fractal; metal–insulator.

1. INTRODUCTION

Metal–insulator thin films[1,2] were shown recently to exhibit percolation characteristics.[1,3,4] This happens in the case where the metallic grains are large enough to be viewed as "classical."[4] An example is when such a system having a metal concentration p will conduct in a metallic fashion only if $p > p_c$[1–8] where p_c is the percolation threshold.

Much of the current interest in the properties of such systems concentrates on their geometrical structure in the vicinity of the percolation threshold.[1,6–11] As the concentration approaches p_c, the pair connectedness length ξ diverges, $\xi \propto (p - p_c)^{-\nu}$. It is also argued that on large length scales, $L \gg \xi$, the infinite cluster which appears for $p > p_c$, is homogeneous with a density $p_\infty \propto (p - p_c)^{\beta}$.[8]

Two kinds of systems are reported in this review. The first is of thin metal film deposited on an insulating substrate[1,3,4] The second is the case of a mixture of metal and insulator,[1,3,4] immicible in each other. The former will be classified as a two-dimensional system where the percolation threshold is identified as the surface coverage for which conductivity appears for the first time (an infinite metallic cluster which connects the two ends of

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the system exists). The second case is more complicated and involves a crossover from two-dimensional behavior for very thin films to a three-dimensional for very thick films.

In this paper we concentrate on the geometrical *scale effects* for both these systems. This means that we work mainly in the regime where the length scale is smaller than the relevant correlation length.

In the second section we show some results on the geometrical investigation of thin Pb films. We comment there on the validity of our results to other types of metals.

As it is more difficult to investigate geometrical effects in a three-dimensional system, we do it by virtue of the two-dimensional to three-dimensional crossover in the resistivity. This phenomenon involves the two-dimensional correlation length which governs the percolation transition as well as the three-dimensional one which tells us how much we are scale dependent with the thickness. This is discussed in Section 3.

In the last section we conclude with some remarks on the relevance of those geometrical effects to the measurements of physical quantities involving conduction and superconductivity.

2. THIN METAL FILMS (TWO DIMENSIONAL SYSTEMS)

The structural analysis of thin metal films is based on the fact that all the structural information can be interpreted from the electron micrographs. For this purpose, transmission electron microscopy (TEM) is an ideal tool.[1,2] Films were deposited onto microscope grids or alternatively on some colloidon layer that could be removed later and placed onto grids. The type of substrate chosen played a particular role in controlling the internal structure or the basic aggregation size. Nevertheless, as we shall show later, for a certain class of metal films the resultant structure is indeed a percolation like near the films continuity threshold. Such a film of Pb deposited onto an amorphous Ge substrate is shown in Fig. 1. The structure indeed looks random in the scene that loops and clusters of all sizes are present. The basic aggregation here is the Pb crystallite size $\sim$250 Å in diameter. We assume[3] that the *same* structure will occure for all metal–substrate combinations for which the mean diffusion length on the substrate is at most comparable to the crystallite size (providing a low surface tension). The *only effect* that will differentiate all those systems is the crystallite size, D_c, which will cause a different percolation threshold due to short-range correlations (the "universality" concept).[5]

For more complicated films, e.g., Sn deposited SiO, the conditions (static) are so strong that one should take into account also the preparation process. This will result in a modified percolation theory.[4]

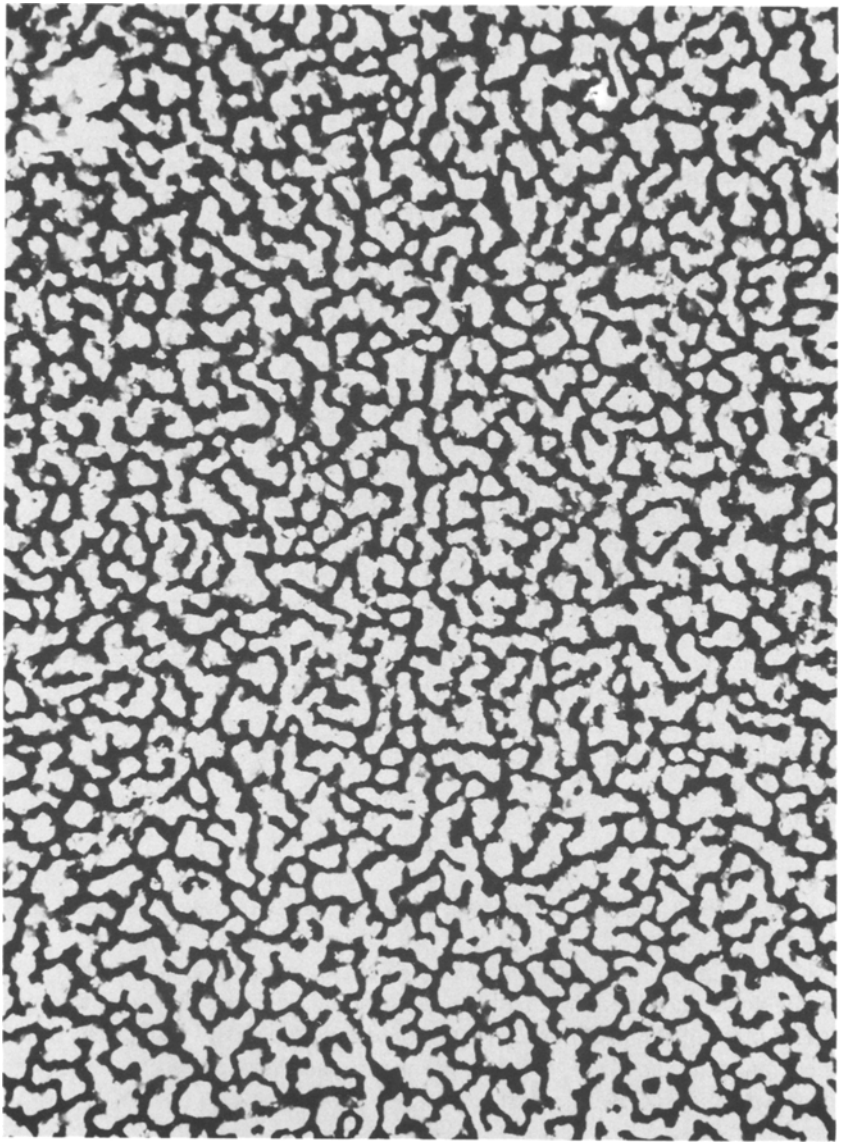

Fig. 1. TEM micrograph of Pb (white areas) deposited onto amorphous Ge; typical width of Pb crystallites: ~250 Å.

Thus, with the restriction of short-range correlations one can rescale, e.g., the crystallite to be the basic lattice site and the intercrystallite distance a to be the basic lattice constant. The short-range surface diffusion provides us with random occupancy of those sites and thus with a percolation type of structure.[6]

To perform quantitative analysis, the pictures were digitized and recovered in the computer very carefully to include the delicate structure of weak connections and weak separation between clusters.[7] We have used different analysis for pictures below the percolation (continuity) threshold and for those above it.

Below the threshold we measured the number distribution N_s of clusters of size (area) S. It was found that for large enough clusters, a power law

$$N_s \propto S^{-\tau} \tag{1}$$

exists, and we have found $\tau = 2.1 \pm 0.2$. This value of τ is in agreement with theoretical prediction[8] and other experimental results.[9,10] The saturation for small s is also in accord with theory.[8]

Above the threshold an infinite cluster of metal crystallites that connects the two ends of the sample exists. To analyze it, we note that for length scales below the percolation correlation length, the infinite cluster is a self-similar object having an anomalous mass exponent[11–13]:

$$M(L) \propto L^{\bar{d}}, \qquad a \gg L \gg \xi \tag{2}$$

$\bar{d}$ is the fractal dimensionality, being ~ 1.9 for two-dimensional percolation.[11] Moreover, for length scales above ξ a regular behaviour is expected, thus

$$M(L) \propto P_\infty L^d, \qquad L \gg \xi \tag{3}$$

where d is the spatial dimensionality and P_∞ is the density of the infinite cluster.

The infinite cluster is composed of a backbone through which electrical current flows and dangling bonds hanging on it. Together they give the mass M. The mass of the backbone, $B(L)$, should also scale with a different fractal dimension $\bar{d}_B$ in the short length scales regime and is expected to be constant for large length scales. We thus expect

$$B(L) \propto L^{\bar{d}_B}, \qquad a \ll L \ll \xi \tag{4}$$

$$B(L) \propto B_\infty L^d \qquad L \gg \xi \tag{5}$$

B_∞ is the density of the backbone.

The analysis of the Pb films was in excellent agreement with those predictions. Figure 2 shows log–log plot of $M(L)/L^2 = \bar{\rho}(L)$ and $B(L)/L^2$ for the infinite cluster and the backbone, respectively. The picture chosen was very close to the percolation threshold and thus ξ was large. This prevented us from seeing a crossover like predicted in Eqs. (3) and (5). Nevertheless, the slopes agreed with Eqs. (2) and (4), yielding $\bar{d} = 1.90 \pm 0.02$ and $\bar{d}_B = 1.65 \pm 0.05$, in excellent agreement with theories.[11,14,17,18]

To observe the crossover effect[11] we used micrographs of depositions far from the threshold. Figure 3 shows typical crossover where ξ is identified as the break where the averaged density starts to be flat. Both the crossover length and the plateau level are in agreement with what is expected from ξ and P_∞ for the investigated film.[6,7]

To conclude our geometrical analysis in this two-dimensional system, we have measured the fluctuations of the mass of the infinite cluster in the

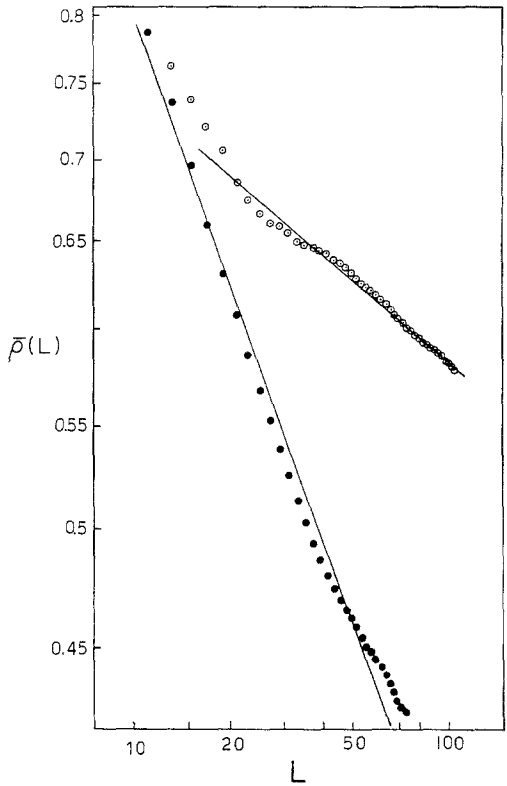

Fig. 2. Log–log plot of the averaged mass density vs. the length scale for the infinite cluster (super curve) and the backbone (lower curve).

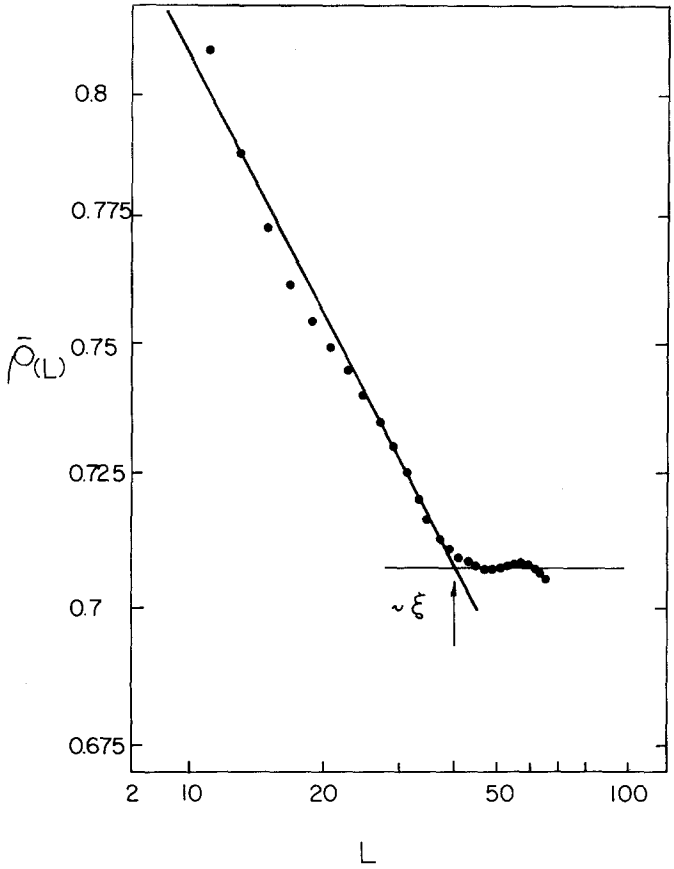

Fig. 3. Log–log plot of the averaged mass density vs. the length scale for a sample far from p_c. The crossover length, identified as ξ is marked.

self-similar regime. Theory, confirmed by Monte Carlo results, predicts that[21,22]

$$\overline{\Delta M(L)^2} \equiv \overline{(M(L) - \overline{M(L)})^2} \propto L^{\bar{d}_f} \tag{6}$$

with $\bar{d}_f = 2\bar{d}$.

We thus measured this effect with the same micrograph shown in Fig. 2. We clearly observed a power law for large enough L with $\bar{d}_f = 3.80 \pm 0.02$. Another expected result is that in the region of small L where the deviations around the straight line in Fig. 2 were big, in the case of the second moment ($\overline{\Delta M^2}$) they were enhanced. This means that, as the statistics become purer the higher moments of the mass distribution cannot be measured.

3. METAL-INSULATOR MIXTURES (THREE-DIMENSIONAL SYSTEMS)

The case of metal–insulator (MI) mixture films is more complicated than the previous one. Also, micrographs of the composite can easily be produced; the observed structure, not being a two-dimensional one, prevent us from direct analysis. Nevertheless, qualitative points can be drawn.

Two types of mixture films are observed when a metal and insulator are co-evaporated or cosputtered in a vaccum chamber.[1,2,3,19,20] They are the granular and the random structure. Each of them is a result of different preparation conditions. The granular material is composed of spherical metallic crystallites, embedded in an insulating amorphous matrix. For this structure the MI transition occurs for very high metallic concentration and the conduction mechanism is rather complicated, being mainly generated by activation of electrons between grains. Percolation effects do exist in such a structure but are very complicated. They are discussed extensively in Refs. 1, 3, and 4.

The random structure is simpler to analyze. It consists of metallic and insulating crystallites, randomly distributed in space to fill it. The simplest case to which we will refer is when both the metallic and the insulator crystallites are of the same size. Rescaling again, the crystallite size to be the basic site in the system, we end up with the random percolation problem.[21–24] Figure 4 shows typical micrograph of Al–Ge thin mixture film. This composite was used by us to study percolation effects.

The A1 and Ge were co-evaporated onto heated glass substrates from two electron beam guns through a mask with slits to combined thickness between 600 and 4000 Å. On each substrate, up to 18 samples were obtained, with different metal concentrations due to different distances of the slits from the sources. The combined evaporation rate on all substrates was ~ 20 Å in a pressure of $\sim 5 \times 10^{-6}$ Torr.

Electrical measurements were performed using the four-terminal method. The resistivity of all those films was observed to diverge at some critical concentration of metal p_c. Typical log–log plot of the resistivity ρ versus the distance from the threshold concentration, $p - p_c$, shown in Fig. 5. It shows a break in slope between two regions that can be fitted to

$$\rho = \rho_0 (p - p_c)^{-\mu} \tag{7}$$

Close to the MI threshold, p_c is that threshold and we measured $\mu = 0.9 \pm 0.25$ averaged over all samples. Far from that threshold the film should have a three-dimensional behavior and thus we chose $p_c = 0.15$,[3] as the

[3] This is not expected to hold when the metal and the insulator crystallite sizes are very different.

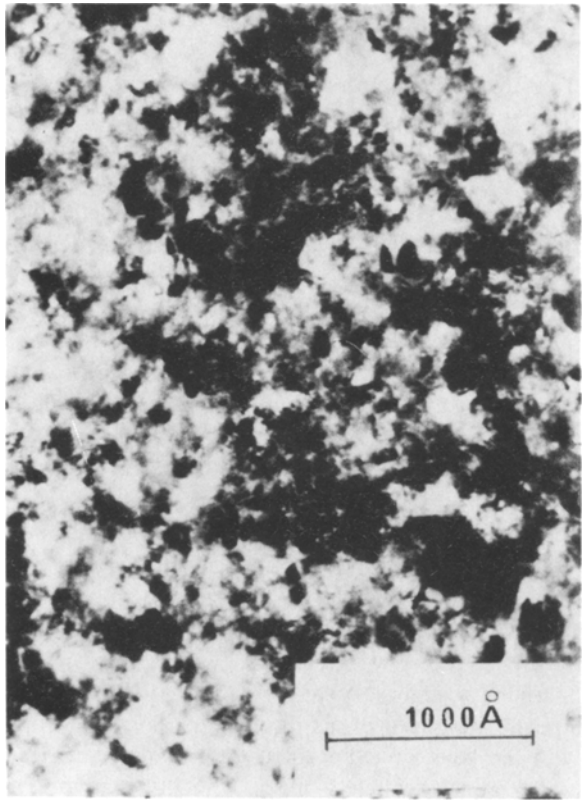

Fig. 4. TEM micrograph of Al–Ge thin mixture film with ~30% vol. Al. "Blacks and whites" do not refer to the different constituents but to different orientations.

three-dimensional value for random percolation.[23,27] We then measured $\mu = 2.1 \pm 0.5$, again in excellent agreement with recent theories of percolation.[28,31]

The crossover is expected to occur when the three-dimensional (3D) correlation length $\xi_{3D}(P)$ is of the same order as the film thickness, t. From the measured values of t, $p - p_c$, and the equation

$$\xi_{3D} = \xi_0(p - p_c)^{-\nu_3} \tag{8}$$

where $\nu_3 \simeq 0.9$, we obtained $\xi_0 = 240 \pm 100$. This is in agreement with the expectation that ξ_0 should be equal to the crystallite size (in the case of Al–Ge is $D_c \cong 250$ Å) times a multiplicative constant b of order unity.[30]

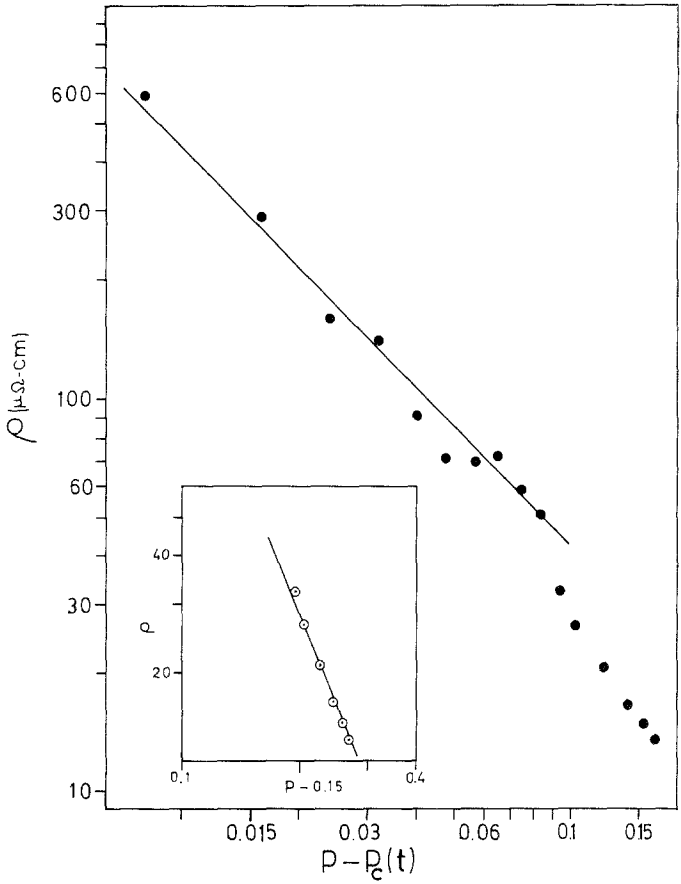

Fig. 5. Log–log plot of the resistivity vs. the distance from the true percolation threshold for Al–Ge film of thickness ~1200 Å. Insert shows the power law behavior in the far region where three-dimensional power law is observed.

The above observation suggests another check for the two-dimensional to three-dimensional crossover, namely, to study the thickness dependence of p_c.[23–32]

Finite size scaling suggests that[31]

$$p_c(t) = p_{c\infty} + \left(\frac{t_0}{t}\right)^{1/\nu_3} \tag{9}$$

The data, as presented in Fig. 6, are consistent with Eq. (9). For this case $P_{c\infty} = 0.15$, again in excellent agreement with random percolation, indicating that for large thickness we approach the three-dimensional regime of this problem. The length t_0 which should satisfy $t_0 = b^{\nu_3} \cdot D_c$ is found

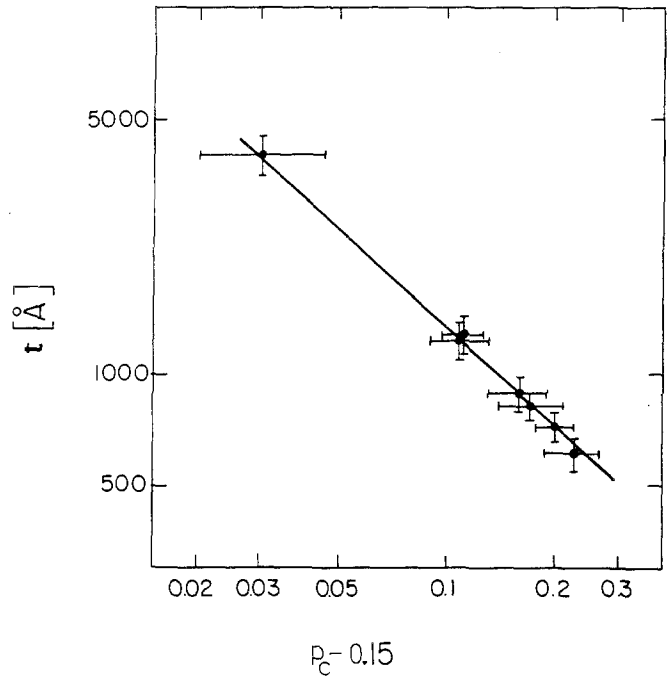

Fig. 6. Thickness vs. critical concentration for Al–Ge mixture films. Power law yields ν_3.

from the data to be 170 ± 90, which means that $t_0 \approx \xi$. As expected, the slope of Fig. 6 gives $\nu_3 = 0.9 \pm 0.2$, one of the best experimental measurements to our knowledge of the three-dimensional percolation correlation length.[4]

We thus used in this case the crossover in resistivity to study geometrical effects in the self-similar regime $L \lesssim \xi$.

4. CONCLUSIONS AND RELEVANCE TO PHYSICAL PROPERTIES

Percolation, while being a geometrical problem, controls a number of physical properties. The first is, of course, the conductivity. We showed that the resistivity of the thin mixture films diverges at the transition in a percolation fashion. As for the thin metal films, recently, using a novel technique with thin Au films, Palevski *et al.*[33] showed that Eq. (7) is satisfied for the two-dimensional system with the result $\mu = 1.25 \pm 0.08$ both, the accuracy of the technique and the result are compatible with numerical or analytical methods.[28,29]

[4] Another important measurement used the critical current experiment to measure ν_3: see Ref. 35.

The existance of large clusters slightly below p_c results in the divergence of the dielectric[7] constant.[34] Measurements in Ag–KCl[34] have confirmed it experimentally with the covert exponent.[34]

The study of superconductivity in percolating films is of special interest because we are dealing here with a macroscopic quantum phenomenon in a system with a well-defined disordered structure. Detailed considerations of the critical field problem,[36–38] the critical current,[36,38] and the superconducting transition[37] were observed in experiments.[38,39] The study of superconductivity in the presence of localization effects in such systems was shown also to exhibit scale effects due to the complicated structure.[40]

Thus, we hope that this paper, which has dealt mainly with the geometry of those systems, stimulated the reader to see that those scale effects can reveal a variety of rich phenomena.

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REFERENCES

1. B. Abels, *Adv. Phys.* **24**:407 (1975); *Appl. Solid State Sci.* **6**:1 (1976), R. Wolfe, ed., Academic Press, New York.
2. K. Chopra, *Thin Film Phenomena* (McGraw-Hill, New York, 1969), p. 167.
3. A. Kapitulnik, Ph.D. thesis, Tel Aviv University, 1983.
4. G. Deutscher, A. Kapitulnik, and M. L. Rappaport, in *Percolation, Structures, and Processes* (Vol. 5 of the Ann. of the Israel Physical Society) 1983, p. 207.
5. A. Aharony, in *Phase Transitions and Optical Phenomena*, Vol. 6, C. Domb and M. S. Green, eds. (Academic Press, New York, 1976).
6. A. Kapitulnik and G. Deutscher, *Phys. Rev. Lett.* **49**:1444 (1982).
7. A. Kapitulnik and G. Deutscher, *Thin Solid Films*, to be published.
8. D. Stauffer, *Phys. Rep.* **54**:1 (1979).
9. R. B. Laibowitz, E. I. Alessandrini, and G. Deutscher, *Phys. Rev. B* **25**:2965 (1982).
10. R. F. Voss, R. B. Labowitz, and E. I. Alessandrini, *Phys. Rev. Lett.* **49**:1441 (1982).
11. A. Kapitulnik, A. Aharony, G. Deutscher, and D. Stauffer, *J. Phys. A.* **16**:L269 (1983).
12. A. Kapitulnik, Y. Gefen, and A. Aharony, *J. Stat. Phys.*, this issue.
13. A. Aharony, Y. Gefen, and A. Kapitulnik, *J. Phys. A* **17**:L197 (1984).
14. H. E. Stanley, in *Proceedings of the International Conference on Disordered Systems and Localization*, C. Dicastro, ed. (Springer-Verlag, Berlin, 1981).
15. H. E. Stanley and A. Coniglio, in *Percolation Structures and Processes, Ann. Israel Phys. Soc.*, Vol. 5 (1983).

16. B. B. Mandelbrot, *Fractals: Form, Chance, and Dimension* (Freeman, San Francisco, 1977); *The Fractal Geometry of Nature* (Feeman, San Francisco, 1983).
17. S. Kirkpatrick, in *Electrical Transport and Optical Properties of Intomogeneous Media*, 1977, J. C. Garland and D. B. Tanner, eds., *AIP Conference Proceedings*, No. 40 (American Institute of Physics, New York, 1977).
18. D. Stauffer, *Z. Phys. B.* **37**:89 (1980).
19. G. Deutscher, M. L. Rappaport, and Z. Ovadyahu, *Solid State Commun.* **28**:593 (1978).
20. A. Kapitulnik, M. L. Rappaport, and G. Deutscher, Phase diagram and the metal–insulator transition in Al–Ge mixture films, to be published.
21. A. Kapitulnik, N. Frid, and G. Deutscher, Fluctuations of the mass of the infinite cluster in percolation, *J. Phys. (Paris) Lett.* **45**:L401 (1984).
22. A. Kapitulnik, Y. Gefen, and A. Aharony, *J. Stat. Phys.*, this issue.
23. H. Scher and R. Zallen, *J. Chem. Phys.* **53**:3759 (1970).
24. A. Kapitulnik, M. L. Rappaport, and G. Deutscher, *J. Phys. (Paris) Lett.* **42**:L541 (1981).
25. A. Kapitulnik and G. Deutscher, *J. Phys. A* **16**:L255 (1983).
26. M. L. Rappaport and O. Entim-Wohman, *Phys. Rev. B* **27**:6152 (1982).
27. S. A. Solla and N. W. Ashcroft, Percolative conductivity in thin films, to be published.
28. B. Derida and J. Vannimenus, *J. Phys. A.* **15**:L557 (1982); B. Derrida, D. Stauffer, H. J. Herrmann, and J. Vannimenus, *J. Phys. A.* (1983).
29. D. Bergman, Interdimensional scalling laws for the critical exponents of the percolation threshold, *J. Phys. A* **16**:3149 (1983).
30. J. Hoshen, R. Kopelman, and E. M. Monberg, *J. Stat. Phys.* **19**:219 (1978).
31. Y. Imry, G. Deutscher, D. J. Bergman, and S. Alexander, *Phys. Rev. A* **7**:744 (1973).
32. J. P. Clerk, G. Girand, S. Alexander, and E. Guyon, *Phys. Rev. B* **22**:2489 (1980).
33. A. Palevski, M. L. Rappaport, A. Kapitulnik, A. Fried, and G. Deutscher, Hall coefficient and condition in a 2D percolation system, *J. Phys. (Paris) Lett.* **45**:L367 (1984).
34. D. M. Grannan, J. C. Garland, and D. B. Tanner, *Phys. Rev. Lett.* **46**:375 (1981).
35. G. Deutcher and M. L. Rappaport, *J. Phys. Lett.* **40**:L-219 (1979).
36. S. Alexander, *Phys. Rev. B*, in press; S. Alexander and E. Halevi, Superconductivity on networks II. The London approach, *J. Phys. (Paris)*, in press.
37. R. Rammal, T. C. Lubensky, and G. Toulouse, *Phys. Rev. B* **27**:2820 (1983).
38. O. Entin-Wohlman, A. Kapitulnik, G. Deutscher, and S. Alexander, The critical current of a percolating network, unpublished.
39. G. Deutscher, I. Grave, and S. Alexander, *Phys. Rev. Lett.* **48**:1497 (1982).
40. A. Kapitulnik, A. Palevski, and G. Deutscher, Inhomogeneity effects on the magneto resistance and the ghost critical field above Tc in thin mixture Films of In–Ge, *J. Phys. C.*, to be published.