Absence of Superconductivity in Metallic Granular Aluminum

M. Kunchur, P. Lindenfeld, and W. L. McLean
Serin Physics Laboratory, Rutgers University, Piscataway, New Jersey 08855

and

J. S. Brooks
Boston University, Boston, Massachusetts 02215, and
Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139
(Received 10 April 1987)

Granular aluminum near the metal-insulator transition has been found to have a range of metal concentrations over which it is metallic (M) but not superconducting (S). For higher concentrations it is superconducting and at lower concentrations insulating (I). There is a striking resemblance of the temperature dependence of resistivity in the S, M, and I ranges of granular aluminum to the temperature dependence of sheet resistance in very thin quench-condensed films. However, there is as yet no theory that gives a satisfactory explanation of this behavior in both two- and three-dimensional systems.

PACS numbers: 74.10.+v, 71.30.+h, 72.15.Rn, 74.70.Mq

Traditionally superconductivity had been associated with metals but as progress was made in understanding the metal-insulator transition in disordered solids it became apparent that the criterion for superconductivity was not necessarily the same as the condition for the system to be metallic.[1] We report here the results of measurements on three-dimensional granular aluminum near the metal-insulator transition that show metallic behavior without superconductivity.

In contrast to the large body of both theoretical and experimental work on two-dimensional films, where there has been the added interest of the study of topological phase transition of the Berezinskii-Kosterlitz-Thouless type,[2] the experimental criteria for the occurrence of superconductivity in highly disordered three-dimensional metals have not been widely explored. Nevertheless, there have been interesting theoretical predictions[1] including the surprising possibility that with increasing disorder superconductivity could persist into the insulating region near the metal-insulator transition.[3] On the other hand, it has been suggested that in a system with strong spin-orbit scattering there will be a nonsuperconducting metallic region (M) lying between the superconducting region (S) and insulating region (I),[4] i.e., with increasing disorder the system should exhibit the S-M-I rather than the S-I transition. A recent scaling treatment for electrons with strong spin-orbit scattering[5] comes to the conclusion that the sequence should be S-M-I in three dimensions but S-I in two.

Additional interest in the present work comes from the suggestion[6] that similar experimental results in two-dimensional discontinuous quench-condensed films comprising superconducting islands are a manifestation of temperature-independent quantum noise effects. There is also considerable debate at present about the relation of the experimental results to macroscopic quantum tunneling.[6-8]

Many of the theoretical results dealing with the metal-insulator transition are based on models of microscopically disordered metals,[9] whereas in practice the interesting region near the metal-insulator transition is accessible only by mixing atoms or molecules of an insulator with a metal. The resulting composite system is not usually a random mixture but can exhibit various degrees of correlation in the spatial arrangement of the different types of atoms with a larger scale of inhomogeneity than is assumed in the theoretical models.[10] Even in granular metals in which there is a well-defined grain size of the order of tens or hundreds of angstroms the qualitative predictions of these models are still useful although an account of the quantitative details may require the granularity to be treated explicitly, as has been done by Imry and Strongin[11] in their discussion of superconductivity in granular metals. There are also cases where the models with only microscopic disorder give a satisfactory account of the measurements as though the granularity can be ignored,[12,13] presumably because the length scales determining the experimentally measured quantities are larger than the scale of the inhomogeneity. This appears to be the case in the results reported here.

Samples of granular aluminum were prepared by electron-beam evaporation of aluminum onto water-cooled substrates in the presence of oxygen at about 10^{-4} Torr.[13,14] Transmission-electron-microscopy studies confirm that the average grain diameter is about 30 Å, as found in earlier work.[14] The metallic behavior reported here was observed in samples near the middle of each of two different sets. Each set had seven or eight samples evaporated at the same time, ranging from just below to just above the metal-insulator transition. In the preparation of the second set particular care was taken to ensure the minimum possible variation of concentration within each sample. Seven coplanar rectangular glass plates, each of which at the end of the preparation procedure had on it three samples, were arranged with their centers on a line perpendicular to the contours of equal metal concentration. The inset in Fig. 1 shows one of the seven substrates and how its three samples (No. 5, No. 6, and No. 7) were oriented with respect to the direction of the concentration gradient, indicated by the dashed line with the arrow. From the geometry it is estimated that the concentration variation within each sample is less than the difference between adjacent samples. As can be seen from the main part of Fig. 1 and in Fig. 2 there is a smooth progression of the characteristics of the samples. The sample thicknesses were between 2000 and 5000 Å for the first set and were 1500 Å for the second. Instead of direct concentration measurements we use the room-temperature resistivity ρ_{RT} to characterize the specimens. Previous measurements[13] have shown that superconductivity disappears near a value of ρ_{RT} of 0.02 Ω cm, corresponding to a metal concentration near 55% found from Rutherford-backscattering experiments.[15]

The resistances of both sets of samples were first measured from 4.2 to 1.2 K in order to decide which samples should be studied later in a dilution refrigerator at the Francis Bitter National Magnet Laboratory. The preliminary results for all samples in the second set are shown in Fig. 1 and indicate that the set extends from superconducting to insulating with no clear indication in the case of samples No. 5 and No. 6 as to what will eventually happen at lower temperatures. A similar range of behavior had been observed earlier in the first set of samples.[16]

The samples chosen from those in Fig. 1 for further measurement to lower temperatures were Nos. 3–7. The first two continued to show a monotonic decrease in resistivity with decreasing temperature until their resistances were below the limit of measurement. There was no evidence in either of these samples of a rise in the resistance at the lowest temperatures, as would be the case if their transitions were of the reentrant type first predicted in granular superconductors by Šimánek.[17] The results for the other three samples are shown in Fig. 2.

Sample 7 is evidently insulating and will be discussed in another publication[18] together with measurements on other insulating samples even further from the metal-insulator transition.

Of main interest here are the results for samples No. 5 and No. 6 and also for sample d of the first set of samples which was found in an earlier experiment in a different dilution refrigerator to behave in a similar way.[16] It is evident from Fig. 2 that these samples are metallic in the sense that their resistivities have become independent of temperature at low temperatures. The metallic behavior of sample No. 5 at low temperatures suggests that samples No. 3 and No. 4, which have still higher metal concentrations than sample No. 5, are also

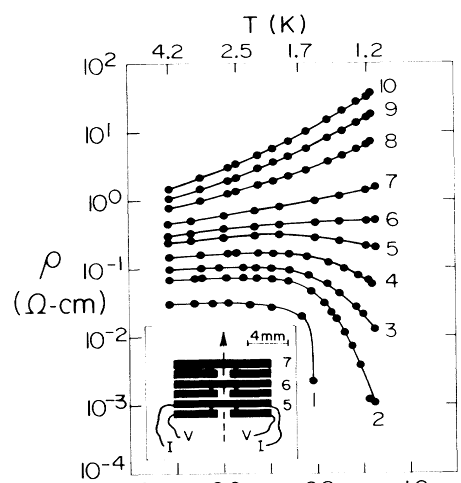

FIG. 1. Logarithm of resistivity vs $T^{-1/2}$ between 1.2 and 4.2 K for a range of granular aluminum samples near the metal-insulator transition. The room-temperature resistivities of samples No. 1–10 are, respectively, 9.1, 13, 16, 20, 25, 28, 34, 37, 40, and 41 mΩ cm. Inset: Relative positions of samples 5, 6, and 7 in the evaporator. The other samples were coplanar and in sequence along the dashed line.

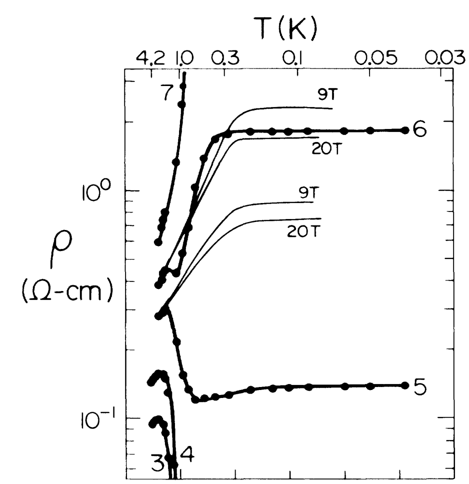

FIG. 2. Logarithm of resistivity vs $T^{-1/2}$ for samples 3, 4, 5, 6, and 7 of Fig. 1 selected for measurement in the dilution refrigerator. Curves labeled 9 T and 20 T: measurements done in fields at that value. Unlabeled curves: zero magnetic field.

metallic. This is consistent with the fact that their superconducting transitions are not of the reentrant type since reentrance is predicted only in samples that are insulators in their nonsuperconducting state.[17]

The nonmonotonic features just above 1 K in Fig. 2 are attributed to small superconducting inclusions. This view is confirmed by the application of magnetic fields sufficiently large to destroy the superconductivity. Previous work[19] has shown that near the metal-insulator transition the bulk critical field of granular aluminum has a maximum value of 3.6 T at temperatures well below T_c. Figure 2 shows the results of applying fields of 9 and 20 T. Two different effects are evident. First the resistivity increases with increasing field because of the destruction of superconducting regions. Second, as shown earlier,[13] there is a negative magnetoresistance in the normal state associated with localization and electron-interaction effects which is clearly evident by comparing the 9- and 20-T curves but which also competes with the positive magnetoresistance caused by destruction of the superconductivity.

The absence of superconductivity in metallic samples and in insulating samples such as No. 7 near the metal-insulator transition in granular aluminum (Al-Al_2O_3) is to be contrasted with the report of a so-called semiconductor-superconductor transition in granular Al-Ge near its metal-insulator transition.[20] Although both systems comprise aluminum grains embedded in an amorphous insulator, the principal difference in their structures is that the average grain diameter in Al-Ge is about 120 Å whereas in granular aluminum it is about 30 Å. We return to a comparison of these two granular systems later.

A principal result of the experiments described in this paper is that as the metal concentration decreases granular aluminum passes through the sequence S-M-I. This sequence has been predicted for a three-dimensional system with strong spin-orbit scattering.[5] At first this seems surprising in view of the small atomic number of aluminum ($Z=13$) since the spin-orbit coupling is expected to vary as Z^4. Here the criterion for the spin-orbit scattering to be strong is that $\hbar \tau_{\text{s.o.}}^{-1} > kT_c$,[5] where $\tau_{\text{s.o.}}$ is the spin-orbit scattering time. For granular aluminum with a T_c of 1.3 K the condition for strong spin-orbit scattering is that $\tau_{\text{s.o.}} < \hbar/kT_c = 6\times10^{-12}$ sec. At present there are no theories that allow a determination of $\tau_{\text{s.o.}}$ from other types of experiment on strongly disordered metals. However, from magnetoresistance measurements in the less-disordered metallic regime for which there are applicable theories, Mui, Lindenfeld, and McLean[21] found an approximately linear dependence of $\log\tau_{\text{s.o.}}$ on $\log\rho_{\text{RT}}$. The smallest value of $\tau_{\text{s.o.}}$ found in those experiments was about 10^{-11} sec. An extrapolation of those results to the value of $\rho_{\text{RT}}=0.03$ Ω cm for sample 5 gives a value of $\tau_{\text{s.o.}}=3\times10^{-12}$ sec. In spite of possible doubts about this extrapolation procedure the result does not seem unreasonable when compared with other determinations of $\tau_{\text{s.o.}}$ in both aluminum[21] and magnesium.[22] It thus appears that the spin-orbit scattering rate in granular aluminum near the metal-insulator transition could be sufficiently strong to allow a range of metallic samples to exist between those that are superconducting and those that are insulating.

In contrast to the theory[5] we have just discussed, which is based on scaling arguments in $2+\epsilon$ dimensions and does not explicitly take into account the granularity of the system, there are other theories that are specifically applicable to granular metals. None of them, however, deals with the effects of spin-orbit scattering. In some cases it may be irrelevant but the theories based on the scaling theory of localization[23] are particularly open to doubt because of this omission. It is expected that in them there should be some manifestation of the antilocalization[22] effect produced in weak localization by spin-orbit scattering.

Two such theoretical discussions are those of Imry and Strongin[11] dealing with the criteria for superconductivity in granular metals and an extension of this approach by Shapira and Deutscher[20] for the semiconductor-superconductor transition in granular Al-Ge. The conclusion reached was that an S-M-I–type transition could occur in a small-grain system such as Al-Al_2O_3, whereas in a large-grain system such as Al-Ge the transition should be S-I. The effect of spin-orbit scattering was not considered.

The similarity of the zero-field temperature dependence in the present results for the resistivity of granular aluminum and in the sheet resistance of quench-condensed films of tin and gallium[24] suggest a common origin of the details, in particular the temperature independence of resistance in a range of samples lying between those that are superconducting and those that behave like insulators at the lowest temperatures of measurement. Although the theory by taking into account strong spin-orbit scattering predicts the possibility in three-dimensional systems of the sequence S-M-I, in two dimensions it allows only the S-I sequence. In the case of the quench-condensed films it has been suggested[6] that the metallic type of behavior is caused by quantum fluctuations between physically unconnected but Josephson-coupled superconducting islands, the counterpart of which in granular aluminum would be the grains or clusters of grains. However, the details of this explanation are based on the Berezinskii-Kosterlitz-Thouless theory which is applicable in two dimensions but not in three. A more general objection to quantum fluctuations as a possible origin of the effect we observe in granular aluminum is that there is evidence[18] that our sample No. 5, sample No. 6, and sample d are above the percolation threshold so that intergrain charging energies are negligible. Therefore it does not appear that explanations based on quantum fluctuations can apply to three-dimensional granular aluminum.

Many recent theoretical discussions of granular metals and granular superconductors are based on the effect of quantum fluctuations in a single small tunnel junction[25] or in an array of Josephson tunnel junctions.[8,26] None of these theories seems to predict the S-M-I–type transition and all are based on the presence of a charging energy between grains that vanishes once percolation occurs, as we believe to be the case in our sample No. 5, sample No. 6, and sample *d*.

In summary, the experimental results presented here clearly show the existence of a narrow range of composition where granular aluminum is metallic without being superconducting. Our analysis shows that the spin-orbit scattering may be sufficiently strong to explain this result. However, the similar behavior in thin quench-condensed films suggests a common origin that has not yet been given theoretical explanation.

We thank L. G. Rubin and the staff of the Francis Bitter National Magnet Laboratory for their help and cooperation and M. Schmiedeschoff for his assistance in the operation of the dilution refrigerator. We are grateful to M. Ma and T. A. L. Ziman for discussions about the effects of spin-orbit scattering on localization. This work was supported by the National Science Foundation through Grant No. DMR-85-11982.

[1]For a recent account and earlier work, see G. Kotliar and A. Kapitulnik, Phys. Rev. B **33**, 3146 (1986), and references therein.

[2]See P. Minnhagen, Phys. Rev. Lett. **54**, 2351 (1985), for references to recent work.

[3]M. Ma and P. A. Lee, Phys. Rev. B **22**, 5658 (1985).

[4]D. J. Bishop, E. G. Spencer, J. P. Garno, and R. C. Dynes, Bull. Am. Phys. Soc. **29**, 343 (1984).

[5]M. Ma and E. Fradkin, Phys. Rev. Lett. **56**, 1416 (1986).

[6]A. M. Goldman, Bull. Am. Phys. Soc. **32**, 625 (1987).

[7]B. G. Orr, H. M. Jaeger, A. M. Goldman, and C. G. Kuper, Phys. Rev. Lett. **56**, 378 (1986).

[8]S. Chakravarty, G.-L.Ingold, S. Kivelson, and A. Luther, Phys. Rev. Lett. **56**, 2303 (1986); M. P. A. Fisher, Phys. Rev. Lett. **57**, 895 (1986).

[9]See, for example, G. Bergmann, Phys. Rep. **107**, 1 (1984).

[10]G. Deutscher, in *Percolation, Localization, and Superconductivity,* edited by A. M. Goldman and S. A. Wolf, NATO Advanced Studies Institute Series B, Vol. 109 (Plenum, New York, 1984), p. 95.

[11]Y. Imry and M. Strongin, Phys. Rev. B **24**, 6353 (1981).

[12]R. C. Dynes, J. P. Garno, G. B. Hertel, and T. P. Orlando, Phys. Rev. Lett. **53**, 2437 (1984); R. C. Dynes and J. P. Garno, Phys. Rev. Lett. **46**, 137 (1981).

[13]T. Chui, P. Lindenfeld, W. L. McLean, and K. Mui, Phys. Rev. Lett. **47**, 1617 (1981); T. Chui, G. Deutscher, P. Lindenfeld, and W. L. McLean, Phys. Rev. B **23**, 6172 (1981); K. C. Mui, P. Lindenfeld, and W. L. McLean, Phys. Rev. B **30**, 2951 (1984); H. K. Sin, P. Lindenfeld, and W. L. McLean, Phys. Rev. B **30**, 4067 (1984).

[14]G. Deutscher, H. Fenichel, M. Gershenson, E. Grunbaum, and Z. Ovadyahu, J. Low Temp. Phys. **10**, 231 (1973).

[15]A. Lieberich, unpublished.

[16]Y. Z. Zhang, M. Kunchur, T. Miller, S. T. Lu, R. Ruel, H. Kojima, P. Lindenfeld, and W. L. McLean, Bull. Am. Phys. Soc. **31**, 635 (1985).

[17]E. Šimánek, Solid State Commun. **31**, 419 (1979), and Phys. Rev. B **23**, 5762 (1981).

[18]G. Deutscher, M. Kunchur, Y. Z. Zhang, P. Lindenfeld, and W. L. McLean, to be published.

[19]T. Chui, P. Lindenfeld, W. L. McLean, and K. Mui, Phys. Rev. B **24**, 6728 (1981).

[20]Y. Shapira and G. Deutscher, Phys. Rev. B **27**, 4463 (1983).

[21]K. C. Mui, P. Lindenfeld, and W. L. McLean, in *Proceedings of the Conference on Localization, Interaction, and Transport Phenomena in Impure Metals,* Suppl. PTB-PG-1 (Physikalisch-Technische Bundesanstalt, Braunschweig, Germany, 1984), p. 78.

[22]G. Bergmann, Phys. Rev. B **28**, 515 (1983).

[23]E. Abrahams, P. W. Anderson, D. C. Licciardello, and T. V. Ramakrishnan, Phys. Rev. Lett. **42**, 673 (1979).

[24]B. G. Orr, H. M. Jaeger, and A. M. Goldman, Phys. Rev. B **32**, 7586 (1985); H. M. Jaeger, D. B. Haviland, A. M. Goldman, and B. G. Orr, Phys. Rev. B **34**, 4920 (1986).

[25]R. Brown and E. Šimánek, Phys. Rev. B **34**, 2957 (1986).

[26]E. Šimánek and R. Brown, Phys. Rev. B **34**, 3495 (1986).