[6] R. M. Fleming, D. E. Moncton, and D. B. McWhan, Phys. Rev. B 18, 5560 (1978).

[7] P. A. Lee and T. M. Rice, Phys. Rev. B 19, 3970 (1979).

[8] H. Fröhlich, Proc. Roy. Soc. London, Ser. A 223, 296 (1954).

[9] For a review, see V. Emery, in *Chemistry and Physics of One Dimensional Metals*, edited by H. J. Keller (Plenum, New York, 1976), pp. 1–23.

[10] P. A. Lee, T. M. Rice, and P. W. Anderson, Solid State Commun. 14, 703 (1974).

[11] F. J. DiSalvo and J. V. Waszczk, unpublished results.

Inhomogeneous Superconducting Transitions in Granular Al

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(Received 12 May 1980)

Granular Al films have been measured in a microwave cavity at 9.4 GHz together with their dc resistance, $R(T)$. The change in resonant frequency is proportional to the number of superconducting electron pairs which is finite *above* the temperature $T_c{}^\rho$, where $R(T) \simeq 0$. Microwave loss has been identified which appears to be specific to granular materials and vanishes only well below $T_c{}^\rho$. This is shown to be due to normal conduction between grains, which upon cooling becomes progressively more Josephson-like.

PACS numbers: 74.30.Gn, 74.40.+k, 74.50.+r, 74.70.Nr

The interest in granular superconductors has increased considerably over the past years.[1] More recently, Al samples at the high-resistivity end, containing 30- to 50-Å Al grains and more than 30% Al_2O_3, have come under focus. For example, the 100-Å films needed to observe the Kosterlitz-Thouless transition were granular in nature.[2] Earlier studies of the resistive transition used thicker films.[3] These, and the more recent specific heat measurements[4] on similar films, were aimed at understanding how long-range superconductivity in these materials arises. A model with an inhomogeneous distribution of grain coupling, referred to as percolative, accounts for the smeared and shifted specific-heat peak.[5] On the other hand, renormalization-group theory for weak and uncorrelated distributions yields a homogeneous transition.[6] If this is not the case, the experimentally observable transition can be spatially inhomogeneous. The criteria where one or the other situation prevails are not well established.[6]

In the present work we have employed microwave measurements to examine the superconducting transition in a variety of granular Al films. The films were sufficiently thin that the electric fields penetrated the whole sample. Thus the technique is still useful even if a superconducting path is established and dc measurements cease to give information. Our measurements show that there is a temperature range in which *all* the Al metal is superconducting but there does not exist a uniform phase relation between the grains.

The experiments were conducted using a Varian Model-4500 electron-spin-resonance spectrometer. The samples were mounted along the axis of cylindrical TE_{01} microwave cavity operating near 9.4 GHz. To minimize losses the films were positioned with their surfaces parallel to the microwave magnetic vectors. The microwave data were taken by locking the klystron frequency to the cavity. Then the shift in frequency, $\Delta\nu$, due to the superconductivity of the sample was measured by recording the output of an attached Hewlett-Packard spectrum analyzer, as a function of the applied external magnetic field of the spectrometer. Simultaneously, the change in Q of the cavity, due to the microwave loss, was monitored by the change of power reflected from the cavity. For the range of temperatures reported here the available magnetic field of 6500 Oe was sufficient to induce the normal state. Therefore the changes due to the superconducting state would be obtained. The microwave power was kept low enough so that the data were power independent.

The dc conductivity was probed by pressing

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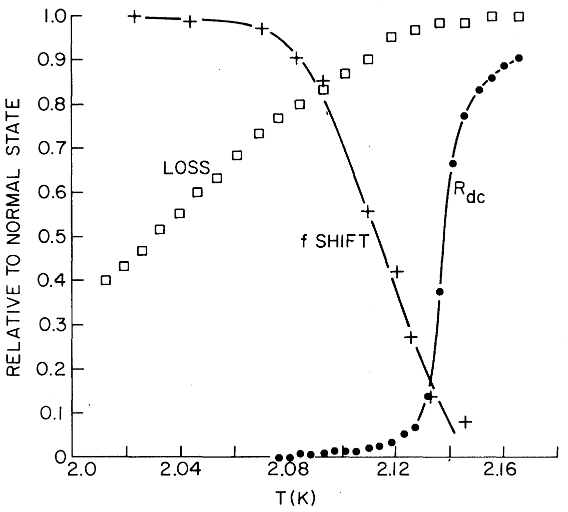

FIG. 1. The microwave loss, cavity frequency shift, and dc resistance, as functions of temperature. The resistance and loss are normalized to their values in the normal state and are equated to zero at their lowest measured values in the superconducting state. The frequency shift from the normal state is normalized to its largest positive value. The sample parameters are thickness = 10 000 Å, $\rho = 3000$ μΩ cm ($R_\square = 30$ Ω/□).

two contacts on to the film *in the cavity* and recording the resistance with a Keithley Model-616 electrometer. The reliability of the two-probe dc measurements and the current used were checked by comparing such measurements with a four-probe arrangement in separate runs outside the cavity. The cavity and sample were immersed in pumped liquid He. Apertures were provided so that the superfluid He could flow freely in and out of the cavity to improve thermal uniformity. The temperature itself was monitored by a calibrated carbon resistor inside the cavity sited near the sample, but shielded from the microwave field. The films of 10 000 Å thickness were prepared by evaporation of aluminum in an oxygen atmosphere as described in detail previously.[3] The 100-Å-thin films resulted from flash evaporation.[7] The grain size was on the average 30–40 Å in the thick[3] films and somewhat larger in the thin[8] films.

Over a half-dozen different samples were measured. Typical and reproducible data obtained for the 10 000- and 100-Å sheets are shown in Figs. 1 and 2, respectively. Further characterization is given in their figure captions. Their dc resistive transitions are typical of granular material of the kind used here and have been reported for several thousand angstroms thick[3] as well as for very thin films.[2,7] In our samples the microwave absorption drops by no more than 15% over a range where 80% of the change in dc resistance occurs. Thus, over this range the microwave penetration depth is about the same as in the normal state, 30 μm; it is much larger than the thicknesses of all samples. Therefore, in this temperature interval, the microwave electric fields penetrate the films entirely.

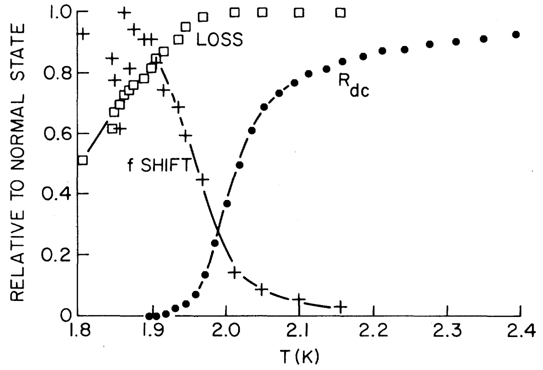

FIG. 2. Same as Fig. 1, except that sample parameters are thickness ≈ 100 Å, $\rho \approx 280$ μΩ cm ($R_\square \approx 280$ Ω/□).

We first discuss the observed inductive frequency shift of the microwave cavity. The extra inductance manifests itself by a frequency drop when, at fixed temperature, the film becomes superconducting upon switching off the magnetic field. It results from the inductive loading of the cavity by the inertia of the superconducting Cooper pairs against the accelerating electric field. According to the first London equation[9] there is a kinetic inductance L_s given by $L_s^{-1} = n_s e^2/m$, where n_s is the density of superconducting pairs. Thus the cavity shift is directly proportional to the total number of superconducting electrons in the sample:

$$\Delta\nu(T) \propto \int_{\text{sample}} n_s(T)\,dv. \tag{1}$$

The shift data of Fig. 1 show a near-linear region in $\Delta\nu(T)$; this has important implications. By Eq. (1) this is what is expected in the high-frequency limit[10] from a system which follows BCS or mean-field behavior,

$$\langle |\psi|^2 \rangle = n_s = c(T_c^{\,0} - T), \tag{2}$$

where the superconducting order parameter is given by $\psi = (n_s)^{1/2}\exp(i\varphi)$. The linear dependence implies that all the metal has the same superconducting transition temperature, $T_c^{\,0}$. A distribution in $T_c^{\,0}$'s over the sample would yield, by Eqs. (1) and (2), a concave upward curve of $\Delta\nu(T)$.

Thus all the aluminum particles have a nonzero Cooper-pair density below T_c^0. However, at this temperature and somewhat below, the sample is still quite resistive. This means that no macroscopic, phase-locked, superconducting paths are yet formed across the sample. Our $n_s(T)$ results confirm directly the assumption of a well-defined particle transition temperature T_c^0 made in a recent theory[5] used to explain specific-heat data by Worthington, Lindenfeld, and Deutscher.[4] Presumably T_c^0 can be associated with clusters containing appreciable numbers of tightly coupled small grains. At lower temperatures, an inverse shift is superposed onto the inductive one causing the latter to level off (Fig. 1). In a forthcoming paper this will be related to the increasing diamagnetic response of the sample to microwave magnetic fields and can be ascribed to progressive phase locking of the clusters below T_c^0.

The evidence of a nonuniform transition is supported by our microwave absorption measurements. In the 10 000-Å-thick sample the decrease of the absorption occurs over a temperature range $\gtrsim 0.3$ K below T_c^0, ten times larger than the main resistive change. The microwave loss can arise from either electrons in the Al metal grains or electrons in the oxide barriers between the grains. From the cavity shift $\Delta\nu(T)$ we have just shown that below T_c^0 all the aluminum metal is superconducting. The applied microwave quantum is $h\nu = 0.2kT_c^0$. For this value, comparing with microwave absorption data[11] on bulk clean or dirty Al superconductors, as well as using the Mattis-Bardeen BCS electrodynamic theory,[12] one finds that the microwave loss due to the aluminum should drop in a temperature range of about 0.01 K if it were a uniform superconductor. Therefore, we conclude that the losses are not in the metal grains but are due to the poorly conducting barriers between them. Because the loss is present in the normal state also, this conclusion applies to the normal films as well. This microwave loss mechanism in granular metals seems not to have been discussed before.[1] Electron transmission coefficients computed earlier from H_{c2} measurements led to the conclusion that the dc conductivity is barrier limited. This agrees with the present direct microwave evidence.[13] The reduction in microwave loss upon cooling cannot result from hopping processes becoming slower, because the loss was entirely restored upon switching the films to their normal state. The gradual reduction in loss upon cooling is therefore assigned to lossy junctions which become more Josephson-like, i.e., a phase relation between superconducting patches of grains is established. The 100-Å-thick samples show an even more gradual reduction than the 10 000-Å-thick ones. In the former, the microwave field penetrates the sample in the superconducting state entirely. Thus the reduction in loss cannot result from a reduced skin depth. Although the change in microwave loss cannot be taken to be proportional to the number of superconducting junctions (it depends nonlinearly on barrier width), the mere fact that about 80% of the loss is still present when the film's resistance has vanished suggests that non-phase-locked clusters exist well below T_c^0. Losses arise also from quasiparticle tunneling[14] but these progressively decrease as T decreases. The uniform-state model does not seem capable of explaining the shifted peaks in the specific heat data,[4] whereas the inhomogeneous "percolation" of phase-locked bonds can.[5] Moreover, as required by the inhomogeneous-state model,[5] the loss becomes small at $T \approx 1.7\,^\circ$K where the peak in the specific heat occurs (in samples with $\rho \approx 3000$ $\mu\Omega$ cm).

The 100-Å thin samples (Fig. 2) showed qualitatively similar behavior, but the dc transition is broader and the loss, as already mentioned, more gradual. The frequency shift curve of the particular sample shown is more rounded than that of Fig. 1. However, other thin specimens displayed a more extended linear region. The measurement reproduced here is of interest as there is a distinct tail in $\Delta\nu(T)$ extending nearly 0.1 K above the extrapolated T_c^0. Because the thickness of the sample is less than the coherence length one is tempted to ascribe this tail to low-dimensional fluctuations in n_s. Indeed, the extent of the tail correlates with the gradual change in $R_{\rm dc}$, which has been explained[3,15] by two-dimensional (2D) fluctuations. As $\Delta\nu(T) \propto \langle |\psi|^2\rangle$ and $\psi = \langle\psi\rangle + \delta\psi(t)$, above T_c^0 where $\langle\psi\rangle = 0$ the average $\langle |\psi|^2\rangle = \langle |\delta\psi|^2\rangle$, i.e., fluctuations in n_s are observable. This is analogous to the birefringence measurements of Courtens near the structural phase transition of $\mathrm{SrTiO_3}$, where such a fluctuation-induced tail has been reported.[16] Of course, due to scaling, the fluctuations exist below T_c^0 as well and contribute to the rounded n_s curve. The rounding could also be due to there being a range of T_c^0's. But the grain size distribution in the 100-Å samples was similar to that in the 10 000-Å one where not much rounding near T_c was seen. Thus this explanation is less likely, but it is possible.

Voss, Knoedler, and Horn detected white noise at and above the resistive transition of 100-Å thin films.[7] In our 10 000-Å sample such noise, but with considerably smaller amplitude, was found[17] at temperatures where $n_s \propto T_c{}^0 - T$. In this mean-field regime, amplitude fluctuations should not be important. Thus the noise is attributed to phase fluctuations.

For finite 2D films one expects[18] a Kosterlitz-Thouless transition to occur at $T_{2\mathrm{D}} = T_c{}^0/(1 + R_\Box/23.8\ \mathrm{k\Omega})$. For the films we investigated the resistances $R_\Box$ were $\leqslant 300\ \Omega/\Box$. Thus, for a homogeneous sample, $T_{2\mathrm{D}}$ would be less than 0.1 K from $T_c{}^0$. Below $T_{2\mathrm{D}}$ the lossy free-vortex plasma tends to disappear, but since the microwave losses persist to temperatures well below $T_{2\mathrm{D}}$ they cannot be caused by the vortex plasma. On the other hand, in the experiment of Hebard and Fiory,[2] $T_c{}^0 - T_{2\mathrm{D}} = 0.5$ K. For such large temperature differences the inhomogeneities governing the resistive transition should cause minor effects at $T_{2\mathrm{D}}$.

In summary, we have shown that microwave measurements of granular aluminum sheets in a cavity yield directly the number and temperature dependence of superconducting Cooper pairs. The method should be generally applicable to thin films of granular materials or potential molecular superconductors. In all our granular Al films we observed large excess microwave loss which we attribute to lossy oxide barriers between grains in the normal and superconducting state. We conclude from our data that there are important influences of inhomogeneity on resistive superconducting transitions. They proceed by the formation of superconducting regions below a temperature $T_c{}^0$ where all the Al metal becomes superconducting. The locking of phases between grains produces a continuous superconducting path but only after a somewhat lower temperature is reached. At still lower temperatures all resistive paths become superconducting and the microwave loss greatly decreases. In the two-dimensional samples the fluctuations in the density of Cooper pairs may have been observed.

We thank A. A. Baratoff, G. Deutscher, S. Fishmann, D. S. Fisher, G. Grinstein, P. Horn, R. Laibowitz, R. W. Landauer, A. P. Malozemoff, R. Voss, and especially E. Simanek for interesting discussions. One of us (D.A.) received partial support from the U. S.-Israel Binational Science Foundation.

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[1] For a historical introduction, see M. Tinkham, in *Inhomogeneous Superconductors—1979*, edited by D. U. Gubser, T. L. Francavilla, J. R. Laibowitz and S. A. Wolf, AIP Conference Proceedings No. 58 (American Institute of Physics, New York, 1979), p. 1.

[2] A. F. Hebard and A. T. Fiory, Phys. Rev. Lett. 44, 291, 620(E) (1980).

[3] G. Deutscher and S. A. Dodds, Phys. Rev. B 16, 3936 (1977).

[4] T. Worthington, P. Lindenfeld, and G. Deutscher, Phys. Rev. Lett. 41, 316 (1978); R. L. Fibber, P. Lindenfeld, T. Worthington, and G. Deutscher, Phys. Rev. B 21, 5031 (1980).

[5] G. Deutscher, O. Entin-Wohlman, S. Fishman, and Y. Shapira, Phys. Rev. B 21, 5041 (1980).

[6] G. Grinstein and A. Luther, Phys. Rev. B 13, 1329 (1976), and private communication.

[7] R. F. Voss, C. M. Knoedler, and P. M. Horn, Ref. 1, p. 314.

[8] E. Alessandrini, private communication.

[9] A. B. Pippard, Adv. Electron. Electron Phys. 6, 1 (1954).

[10] High frequency means $\nu^{-1} \ll$ time for diffusion of a vortex through a correlation length (cf. Ref. 2).

[11] M. A. Biondi and M. P. Garfunkel, Phys. Rev. 116, 853, 862 (1959); J. R. Waldram, Adv. Phys. 13, 1 (1964).

[12] D. C. Mattis and J. Bardeen, Phys. Rev. 111, 412 (1958).

[13] R. W. Cohen and B. Abeles, Phys. Rev. 168, 444 (1968).

[14] D. E. McCumber, J. Appl. Phys. 39, 2503 (1968).

[15] A. F. Mayadas and R. B. Laibowitz, Phys. Rev. Lett. 28, 156 (1972).

[16] E. Courtens, Phys. Rev. Lett. 29, 1380 (1972).

[17] R. F. Voss, private communication.

[18] B. A. Huberman and S. Doniach, Ref. 1, p. 87, review the theory.