PHYSICAL REVIEW B VOLUME 40, NUMBER 1 1 JULY 1989

Local superconducting coupling in the strong-localization limit of ultrathin granular metal films

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(Received 3 April 1989)

The onset of fluctuations into the superconducting state, as identified by the appearance of a local minimum in the resistance versus temperature, is found to be coincident with the characteristic activation energy of normal-state conduction falling to a value the order of the superconducting energy gap of the material at $T=0$. The model of conduction used is variable-range hopping with a Coulomb gap, appropriate to granular metals.

The nature of the onset of superconductivity in ultrathin films has been the subject of numerous investigations on a variety of materials.[1-3] Depending upon the relative size of the length scales of the disorder and the superconducting correlations, paradigms such as percolation[4] or localization[5] may be relevant. The depression of the superconducting transition temperature relative to that of bulk metals has been observed in microscopically disordered, but very *homogeneous,* ultrathin films, and has been attributed to weak-localization effects.[2] Although effects attributable to superconductivity have been observed in high-resistance *granular* films,[6-8] presumably in the strong-localization limit, previous experiments have produced few quantitative results and as a consequence there are few conclusions of a general nature relating to superconductivity in this limit. Although the point should not be belabored, the signatures of superconductivity in insulating and nearly insulating systems are of current interest as a consequence of the view that high-temperature superconductors are doped Mott insulators.

In describing the onset of superconducting behavior it is necessary to distinguish between effects associated with the amplitude and the phase of the order parameter. Quasi-long-range phase coherence is a precondition for the nearly zero electrical resistance usually associated with global superconductivity in ultrathin films. This particular issue has been considered elsewhere.[1] Even in the absence of such phase coherence in relatively high-resistance films, there may be a signature of superconductivity at a well defined temperature in the form of the onset of a more rapid increase of electrical resistance with decreasing temperature. This follows from the opening of the energy gap in the quasiparticle excitation spectrum of isolated grains constituting the film.[6,8] This phenomenon will be described as "local superconductivity" to distinguish it from another phenomenon in which partial phase coherence, or "local superconducting coupling" is established. The latter is characterized by the appearance of a dip or local minimum in $R(T)$. Local superconducting coupling has also been described as quasireentrant superconductivity. This feature might be interpreted as evidence of superconducting fluctuations beginning to extend across the sample, or as the beginning of the phase coupling of the order parameters of many of the superconducting grains constituting the film. Because this local superconducting coupling extends over length scales much less than the sample size, the resistance of the entire sample is dominated by quasiparticle transport, and therefore will eventually increase as the temperature is lowered further. The above phenomena have been found in thin films that are highly disordered, i.e., which have high nominal resistivities, and thus are in the strong-localization limit.

In this Brief Report we present extensive measurements that suggest a condition for the appearance of local superconducting coupling in the form of a fall of the energy characterizing the normal resistance to a value approximately equal to the zero-temperature superconducting energy gap. Furthermore, the appearance of the minimum is uncorrelated with either the thickness or the characteristic resistance of the films. The fact that this condition is found in a variety of superconducting materials suggests that it is a general feature of superconductivity of disordered films in the strong-localization limit.

Films of a number of different soft superconducting metals were deposited in small thickness increments onto glazed alumina substrates. The substrates were held at a temperature of about 16 K during deposition and Knudsen cells were used as evaporation sources. Resistance was measured as a function of temperature using four-probe techniques *in situ* between successive depositions.[1,9] These studies were carried out over the temperature range between 0.60 and 15 K. Warming much above the latter temperature during measurement resulted in irreversible annealing effects. Measurements of sheet resistance were made over 11 orders of magnitude. From the first stages of growth in which there was no measurable conductance, through the onset of global superconducting behavior (zero resistance), the total increase in the nominal thicknesses of the films was the order of 2 Å. The use of shuttered Knudsen cells permitted us to increment the nominal thickness by amounts as small as 0.05 Å, a capability which was essential for the observations reported here.

The qualitative features of data on films of Al, Ga, Pb, In, and Sn throughout the entire range of sheet resistances were reproducible. A ubiquitous feature of data from these films, which are believed to consist of metal clusters or grains, is evidence for superconducting pairing without zero-electrical resistance being achieved. The earliest evidence in a sequence of films of increasing thickness was the observation of local superconductivity, i.e., an abrupt increase in the characteristic activation energy at the bulk transition temperature.[8] (Note the upper traces of Fig. 1.) At some later point in the film growth, this sharp kink in $R(T)$ developed into a dip or local minimum (lower traces of Fig. 1).

To interpret the data in a more quantitative manner, it is first necessary to note the nature of electrical transport in the limit of strong disorder. The dominant mechanism is believed to be thermally activated hopping of electrons from one localized site to another. There are a number of models of such hopping. In the case of fixed-range hopping the temperature dependence of the resistance is given by[10]

$$R = R_1 \exp(T_1/T)\,, \tag{1}$$

where T_1 is the activation energy in Kelvin. If the overlap of localized states becomes more significant, variable-range hopping becomes relevant and the resistance for a two-dimensional system is of the form[5]

$$R = R_2 \exp[(T_2/T)^{1/3}]\,. \tag{2}$$

Here R_2 and T_2 are constants that depend on various properties of the system. Variable-range hopping however may be affected by a suppression of the density of states near the Fermi level due to the Coulomb interaction, which is not easily screened by the localized electrons. In this case the resistance is given by[5,11]

$$R = R_3 \exp[(T_3/T)^{1/2}]\,, \tag{3}$$

a result valid in both two and three dimensions. The characteristic activation energy in this instance is given by $k_B T_3 = e^2/\kappa\alpha$, where α is the localization length, and κ is the dielectric constant. Equation (3) was also derived by Abeles for a model applicable to granular metal films rather than semiconductors.[12] In this instance $k_B T_3 = (e^2/\kappa d)[s/(s+d/2)]$, where d is the diameter and $s+d$ is the nearest-neighbor separation of metal spheres in a square array used to model a granular film. A general discussion of the applicability of Eqs. (1)–(3) to granular metals has been given by Entin-Wohlman, Gefen, and Shapira[13] and by Nemeth and Mühlschlegel.[14]

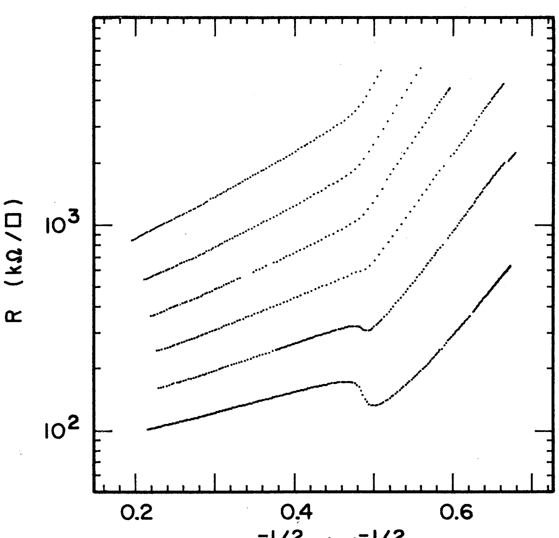

FIG. 1. Plots of log R vs $T^{-1/2}$ for an Sn film made slightly thicker by *in situ* deposition. The thicknesses in Å from top to bottom are 30.0, 30.16, 30.32, 30.44, 30.56, and 30.64. The minimum in $R(T)$ appears when the characteristic activation energy (the slope on this plot) in the normal state becomes the order of the superconducting gap.

Only in the case of the thinnest and most resistive films of a sequence did the simple T^{-1} activation form [Eq. (1)] best describe $R(T)$. As more material is added to a film, the $T^{-1/2}$ form [Eq. (3)] is expected to be better fit than T^{-1} for granular metal films. It is generally argued from previous experimental work, that this form, which is based on the existence of a Coulomb gap, accounts for the temperature dependence of the resistance of granular films.[8,12,13,15] Indeed, for all of our data, in the range of film thicknesses where the local minimum first appeared, the $T^{-1/2}$ form [Eq. (3)] provides an excellent fit. However it should be noted that on a basis of our measurements alone, one cannot absolutely rule out the $T^{-1/3}$ form [Eq. (2)] due to the limited range of temperatures studied. For films with low T_c (Al and Sn) where fits could be made over a large range of temperature, the variances associated with the fit of the $T^{-1/2}$ form were slightly smaller than those for the $T^{-1/3}$ form. Because both the experimental and theoretical literature on granular metal films support the $T^{-1/2}$ form, it was used for all of our films to extract the parameters of the strong-localization limit, which in turn were used to construct Fig. 2, as discussed below. Figure 1 shows a plot of log R vs $T^{-1/2}$ for data taken on a Sn film near the onset of local superconducting coupling.

There is no apparent correlation of the appearance of local superconducting coupling with either the resistances or thicknesses of the various metal films studied. There is a correlation with the characteristic energy of the normal-state electrical transport falling to a value approximately equal to the superconducting gap Δ_0. The latter was determined using published values[16] for the ratio $2\Delta_0/k_B T_c$ where T_c is taken as the temperature where the minimum in $R(T)$ first appeared. It is important to note that the temperatures at which the features in $R(T)$ are observed remain essentially unchanged in value, from their first observation in the thinnest films as an abrupt change in the activation energy, to their evolution into a full transition to zero resistance in much thicker films. [The values of T_c determined in this manner were consistent with recent estimates[17] for enhancements (Sn, In, and Al) or degradations (Pb and Ga) of T_c of bulk material if reasonable intracluster resistivities are assumed.] The characteristic energy $k_B T_3$ was determined by fitting data for $T > T_c$ to Eq. (3). Figure 2 shows the ratio $k_B T_3/\Delta_0$ plotted versus R_3 determined from data, as shown in Fig. 1. Eight different films of five different metals are presented in Fig. 2. The upper points (open symbols) of the pairs of data points are given by the parame-

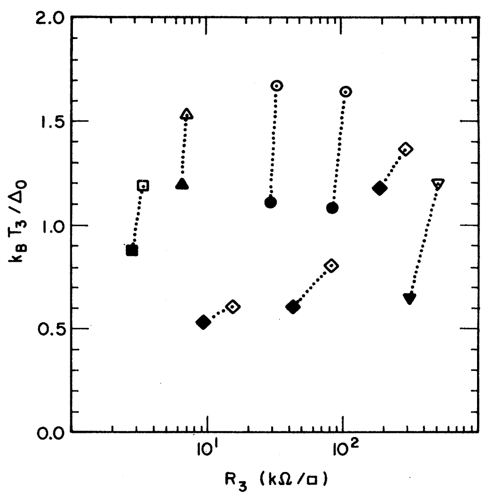

FIG. 2. The ratio of the characteristic activation energy to the superconducting gap $k_B T_3/\Delta_0$ is plotted vs the characteristic resistance R_3 for successive films of several different deposition sequences. The parameters T_3 and R_3 are determined from fits of Eq. (3) to data, as displayed in Fig. 1. The upper point (open symbol) corresponds to parameters determined from the last film in a sequence for which $R(T)$ does not exhibit a minimum, whereas the lower point (filled symbol) connected to the upper one by a dotted line, corresponds to the trace of the next film in the same sequence, which exhibits a minimum. In all materials studied [Al(□), Ga(△), In(◇), Sn(○), and Pb(▽)] the dip appears when $k_B T_3 \approx \Delta_0$, independent of resistance R_3.

ters of the last film in a sequence for which no minimum in $R(T)$ was observed. Slightly incrementing the thickness produced films with minima in $R(T)$, represented by the lower points (filled symbols). For all materials studied, Ga, Sn, Al, Pb, and In, the dip appears when $k_B T_3/\Delta_0 \approx 1 \pm 0.5$, independent of the film thickness or the characteristic resistance R_3. It should be noted that when Eq. (1) rather than Eq. (3) was used to construct a graph like that of Fig. 2, a correlation length between the superconducting gap and the characteristic activation energy was also found.

It is of interest to examine the consequences of $k_B T_3$ being the order of the energy gap of a superconductor with a 2-K transition temperature. This implies, assuming a dielectric constant of unity, a value of a the order of 4.7 μm, which would be a very large localization length. On the other hand, taking $k_B T_3 = (e^2/\kappa d)[s/(s+d)/2)]$, a form appropriate to a granular metal, the condition is satisfied with 0.1 μm size grains separated by gaps of the order of 10^{-9} m, which are very reasonable numbers for a granular metal film.

Although there have been a number of efforts directed at explaining the minimum in $R(T)$ found in granular films, none of them accounts for a threshold condition like that shown in Fig. 2. The theories, which include those based on the percolation model,[18,19] and the X-Y model including quantum-phase fluctuations[20-22] treat the films as arrays of tunneling junctions. Unfortunately all of these approaches provide only qualitative results which can only be weakly correlated with experiment. In the event that the modeling of granular films by arrays of small tunneling junction is correct, then it is possible that the work of Iansiti, Johnson, Lobb, and Tinkham,[23] on the crossover between Josephson tunneling and the Coulomb blockade may be relevant to the observations reported here. A generalization of their single-junction picture to an array would be required.

There have been a number of theories which find a condition for some aspect of superconductivity similar to the one found here. Ma and Lee[24] have obtained a requirement for the appearance of superconductivity in homogeneous, but strongly localized systems. They find superconductivity to be possible, i.e., Anderson's theorem to be valid, even below the mobility edge of a localized system, provided $ga^d\Delta_0 > 1$, where g is the density of states per unit energy at the Fermi level. If a Coulomb gap[11] suppresses the density of states at the Fermi level then the condition $k_B T_3 < \Delta_0$ follows as an extension of their argument. This threshold may not correspond to a threshold for reduced resistance as the latter would require a full calculation of fluctuation conductivity. Earlier, Strongin *et al.*[25] suggested a similar threshold for superconductivity which involves the activation energy falling to a value the order of the zero-temperature superconducting gap. They were not able to find in their data as detailed a correlation between these quantities as reported here.

The experimental results presented here and the above discussion are not related in any obvious way to the interpretation of the onset of superconductivity found in the work of White, Dynes, and Garno[3] on granular Pb and Sn films. Their studies of the evolution of $R(T)$ with thickness nevertheless have some features which are qualitatively similar to the present results. In particular, there is no significant reduction of the superconducting transition temperature. However, their tunneling studies are interpreted as evidence for an increase with sheet resistance of an intrinsic lifetime broadening of the density of states. This broadening is associated with inelastic scattering. With increasing disorder, the broadening, upon becoming comparable to the energy gap, results in the disappearance of superconductivity.

It is also interesting to note differences between the present results on granular films and the studies in homogeneous ultrathin films of the suppression of the transition temperature[2] which has been attributed to an enhancement of the Coulomb interaction.[26-28] The Coulomb effects in the granular films described here, although possibly resulting in the same temperature dependence of the normal-state conduction, appear to be of a different character, as no T_c suppression is observed. Possibly the distinctively different behavior of the transition temperatures with thickness of the two classes of materials follows from differences in the length scale of the disorder.

In conclusion, we have found that the appearance of local superconducting coupling in ultrathin granular superconducting films is correlated with the activation energy characterizing the normal resistance falling to a value roughly equal to the superconducting energy gap. This result would appear to provide a feature of superconducting effects in the strong-localization limit of granular films which could serve to test models of this regime.

This work was supported by the Low Temperature Physics Program of the National Science Foundation under Grant No. NSF/DMR-85-03087 and by the Central Administration of the University of Minnesota.

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