Deviations from mean-field behavior in disordered nanoscale superconductor–normal-metal–superconductor arrays

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We have fabricated quasi-two-dimensional disordered arrays of nanoscale Pb grains coupled by an overlayer of Ag grains. Their temperature-dependent resistive transitions follow predictions for an array of mesoscopic superconductor–normal-metal–superconductor junctions. The decrease of their transition temperatures with Ag overlayer thickness systematically deviates from the Cooper limit theory of the proximity effect as the Pb grain size decreases. The deviations occur when the estimated number of Cooper pairs per grain is \( < 1 \) and suggest the approach to a superconductor-to-metal transition.

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Superconductor (S) normal-metal (N) structures are fundamentally interesting as systems with spatially varying order parameters whose properties can be successfully described using mean-field microscopic theories.\(^{1–3}\) For example, “proximity effect” models account for the upper critical field of SN multilayers,\(^{4}\) the spatial dependence of the tunneling density of states in mesoscopic SN structures,\(^{5}\) and the critical currents of SNS junctions.\(^{6}\) These proximity effects are simplest to describe in the so-called Cooper limit in which the dimensions of the S and N regions are smaller than \( \xi_S \) and \( \xi_N \), the S and N coherence lengths, respectively.\(^{1,3,7}\) In this regime, the Cooper pair density is spatially uniform and the mean-field transition temperature \( T_{co} \) is determined by the volume average of the pairing interaction strength over the N and S regions.\(^{1,3}\) This approximation improves as the N and S dimensions decrease. Studies of nanoscale SN devices\(^{8}\) and isolated ultrasmall superconducting grains,\(^{9}\) however, suggest reasons that a mean-field description of SN composites might eventually break down in the extreme Cooper limit. They demonstrate that mesoscopic fluctuation and energy level quantization effects falling outside the realm of mean-field theory increasingly dominate their behavior as the size of the S and N regions decrease.

Recently, dramatic, non-mean-field behavior has been predicted for two-dimensional (2D) arrays of ultrasmall superconducting grains embedded in a metal.\(^{10,11}\) Spivak, Zyuzin, and Hruska\(^{11}\) presented evidence that these arrays undergo a superconductor-to-metal quantum phase transition (SMT) as the superconducting grain radius \( r \) or concentration \( x_{sc} \) decreases. This prediction deviates strongly from the Cooper limit model which would predict that \( T_{co} \) only exponentially approaches zero as \( r \) and \( x_{sc} \) decrease. We present an investigation of this interesting prediction using disordered 2D arrays of nanoscale Pb grains coupled through an overlayer of Ag. By changing the Ag overlayer thickness \( d_{Ag} \) at fixed Pb layer thickness \( d_{Pb} \), we have been able to tune \( x_{sc} \). By changing \( d_{Pb} \), we have been able to change \( r \). We find that \( T_{co} \) of bilayers with the largest \( r \) decreases exponentially with \( x_{sc} \) in quantitative agreement with theory. Systematic deviations from theory appear and grow as \( r \) decreases. They appear where fluctuations in the order parameter amplitude on the grains are expected to be large and near the estimated critical concentration for the SMT.\(^{11}\)

The nanoscale SNS arrays were fabricated using the structure that spontaneously forms in films that are quench condensed from vapor onto cryogenically cooled substrates. In situ scanning tunneling microscopy (STM) experiments have shown that quench condensed Pb films with bulk equivalent thicknesses \( d_{Pb} \), up to \( \approx 3 \) nm form a 2D disordered array of physically separate nanoscale grains.\(^{12,13}\) At \( d_{Pb} = 3 \) nm, the average grain radius, height, and intergrain gaps are 10, 4, and \( 1.2 \) nm, respectively. In thicker films, an overlayer of grains forms that bridge the intergrain gaps. The SNS “arrays” were made by first depositing Pb (superconductor) followed by a series of Ag (normal) depositions onto fire polished glass substrates held at 8 K. In situ STM on other Pb/Ag structures at 77 K reveal that the Ag forms an overlayer of grains that “bridge” the underlying Pb grains.\(^{14}\) Each series of depositions and measurements was done in the ultrahigh vacuum environment of a dilution refrigerator without breaking vacuum. The equivalent bulk density film thicknesses were determined to an accuracy of 0.01 nm using a quartz-crystal microbalance. Predeposited Au/Ge pads provided electrical contact to the films and film sheet resistances \( R \) were measured in their Ohmic regime using standard four-probe dc or ac techniques. Film homogeneity was checked by comparing the \( R \) of adjacent film regions, which typically agreed to better than 5%. Data from three arrays with \( d_{Pb} = 1.5, 2.2, \) and \( 3.0 \) nm are presented here. They are consistent with less complete data sets on separate arrays with both smaller and larger \( d_{Pb} \).

The normal-state sheet resistance \( R_N = R(8K) \) of the bilayers evolves with total film thickness in a manner resembling pure granular film systems [Fig. 1(a)].\(^{12,15}\) The bilayer with \( d_{Pb} = 1.5 \) nm became electrically continuous at \( d_{Pb} + d_{Ag} = 4.7 \) nm, which falls between the thicknesses at which pure Ag (2.2 nm) and pure Pb films (5.5 nm) become continuous. All sets of films exhibited proximity effect driven insulator to superconductor transitions [e.g., Fig. 1(b)].\(^{16,17}\) For the highest \( R_N \) in Fig. 1(b) \( R(T) \) shows a dip near 1.3 K, which is a signature of the appearance of local superconductivity and a consequence of the granular morphology of these films.\(^{18}\) The initial superconducting transition is quite broad.
Subsequent transitions become sharper and take place at lower $T$. Each occurs in a single step indicating that the Pb and Ag constituents simultaneously become superconducting.

Strong evidence that these bilayers form nanoscale SNS arrays comes from comparing their $R(T)$ to predictions for an array of mesoscopic SNS junctions. In general, $R(T)/R_N=[I_0(\gamma/2)]^{-2}$ for a junction array, where $I_0$ is the modified Bessel function, $\gamma=hl_\ell(T)/ek_BT$ is the normalized energy barrier to a phase slip across a single junction, $l_\ell(T)$ is the junction critical current, $C \approx 0.1$, and $R_N$ is the normal-state resistance. For junctions with dimensions less than $\xi_N=(hD/k_BT)^{-1/2}$, where $D$ is the electronic diffusivity in the metal, $I_\ell(T)=Ne\Delta/h$, where $N=A/\lambda^2_F$ is the number of transverse modes in the point contact and $\Delta$ is the energy gap. $A$ is the point contact area and $\lambda_F$ is the Fermi wavelength. For the bilayers, $\xi_N \approx 100$ nm at 1 K based on the $R(d_{Pb})$ data, which exceeds the characteristic dimensions of the films. Thus the prediction for $R(T)/R_N$ depends only on $T_{co}$ through $\Delta$ and $N$.

The SNS array model fits the $R(T)$ of bilayers far from the insulator to superconductor transition over more than three decades. This agreement is shown in Fig. 2 for five of the Pb/Ag films shown in Fig. 1 $(d_{Pb}=1.5$ nm and $d_{Ag}=5.6, 7.5, 7.6$ nm). The open circles are a fit to the data using an array of mesoscopic SNS junctions model with $N$ transverse modes per junction.

with increasing $d_{Ag}$ is shown in Fig. 3 for three bilayer sets. The uncertainties are smaller than the size of the symbols. For $d_{Pb}=3.0$ nm, $T_{co}(d_{Ag})$ is exponential over more than a decade. For $d_{Pb}=2.3$ nm and $d_{Pb}=1.5$ nm, $T_{co}$ exhibits a similar exponential decrease at high $T_{co}$, but appears to decrease more rapidly at lower $T_{co}$.

An exponential form of $T_{co}(d_{Ag})$ is expected for SN composites with low resistance SN interfaces and characteristic dimensions that are less than $\xi_S$ and $\xi_N$. In this so-called Cooper limit, the effective superconducting coupling constant, $\lambda$, in the expression $T_{co}=T_c\exp(-1/\lambda)$ becomes the average of the coupling constants in the S and N regions. For the Pb-Ag bilayers $\lambda=\lambda_Pd_{Pb}+\beta\lambda_Agd_{Ag}/(d_{Pb}+\beta d_{Ag})$ where $\lambda_P$ and $\lambda_A$ are the coupling constants in

![Image](https://via.placeholder.com/150)

**FIG. 1.** (a) Sheet resistance at $T=8$ K vs total film thickness, $d_{Pb}+d_{Ag}$, with $d_{Pb}=1.5$ nm. The arrow indicates the thickness of the initial Pb film. (b) Sheet resistance vs temperature for the films in (a).

**FIG. 2.** Normalized sheet resistance vs reduced temperature $T/T_c^*$ of five of the Pb/Ag films shown in Fig. 1 ($d_{Pb}=1.5$ nm and $d_{Ag}=5.5, 7.5, 7.6$ nm). The open circles are a fit to the data using an array of mesoscopic SNS junctions model with $N$ transverse modes per junction.

**FIG. 3.** Mean-field transition temperature of three Pb/Ag bilayer sets [$d_{Pb}=3.0$-nm (circles), 2.3 nm (squares), 1.5 nm (triangles)] as a function of Ag thickness. The $d_{Pb}=3$-nm data are fit to proximity effect theory in the Cooper limit with $\lambda_N=\lambda_A=0$ (solid line) and $-0.017$ (dashed line). The other solid lines are fits to the higher $T_{co}$ points of the $d_{Pb}=2.2$ and 1.5 nm bilayers by adjusting $T_c$ (see text). Inset: Fractional deviation of the data from the fits, $(T_{co,fit}-T_{co})/T_{co,fit}$.
the Pb and Ag regions, respectively, and $\beta$ is the ratio of the
densities of states at the Fermi level of the Ag and Pb, $\beta = \nu_{Ag}/\nu_{Pb}$. If $\lambda_{Ag} = 0$ then,

$$T_{co} = T_o \exp\left(-\frac{d_{Pb} + \beta d_{Ag}}{\lambda_{Pb} d_{Pb}}\right) \tag{1}$$

and $T_{co}$ decreases exponentially with $d_{Ag}$.\textsuperscript{1,3,7} For a nonzero
$\lambda_{N}$, small deviations from a simple exponential form should be apparent.\textsuperscript{1}

Equation (1) fits $T_{co}(d_{Ag})$ for $d_{Pb} = 3$ nm if we assume
$\lambda_{Pb} = 0.57$ as appropriate for quenched condensed Pb films,\textsuperscript{24}
set $\beta$ to 0.30 and $T_o$ to 30.1 K. This value of $\beta$ lies between
that derived from a free-electron model and that obtained
from heat-capacity measurements.\textsuperscript{25} Physically, $T_{co}(d_{Ag} = 0)$, which is set by $T_o$, is the temperature at which strong
pairing correlations on an isolated Pb grain appear. It should
decrease with decreasing Pb grain radius due to finite-size
effects,\textsuperscript{26,27} and thus it is less than the bulk Pb value.
The high quality of the fit is expected, in so far as these bilayers
fall in the Cooper limit. The quench condensation technique
ensures the SN interfaces are clean. Also, $(d_{Pb} + d_{Ag}) < 20$
nm, which does not exceed either $\xi_s = 60$ nm (Ref. 23) for
quenched condensed Pb, or $\xi_N$. We hasten to add that $T_{co}(d_{Ag})$
for $d_{Pb} = 3$ nm does have a slight downward curvature,
which can be fit by including a small repulsive interaction in
the Ag, $\lambda_{Ag} = -0.017 \pm 0.004$ and setting $T_o = 28.7$ K and
$\beta = 0.277$ [see Fig. 3].\textsuperscript{1}

Surprisingly, $T_{co}(d_{Ag})$ of the thinner bilayers, $d_{Pb} = 2.3$
and 1.5 nm, which should be deeper in the Cooper limit,
systematically deviates from the exponential dependence at small $T_{co}$.\textsuperscript{28} It is possible to roughly fit the data at the higher
$T_{co}$ by adjusting $T_o$ and setting $\lambda_{Pb}$, $\lambda_{Ag}$, and $\beta$ to the
values used for $d_{Pb} = 3$ nm (solid lines in Fig. 3). The re-
quired changes in $T_o$ with $d_{Pb}$, $T_o(d_{Pb} = 2.3$ nm) = 27.6 K,
and $T_o(d_{Pb} = 1.5$ nm) = 23.5 K can easily be ascribed to a
reduction in $T_{co}$ of the individual Pb grains as they
shrink.\textsuperscript{26,27} The data at lower $T_{co}$, however, fall faster than
exponentially. This characteristic is brought out in the inset
of Fig. 3, where the fractional deviation of the data from the
fits is shown. For the bilayer with the thinnest Pb layer, the
deviation becomes greater than 50%.

Some possible explanations for the deviations can be ruled
out. The deviations are significantly larger than the
breath of the $R(T)$ and thus variations in the definition of
$T_{co}$ cannot account for them. They also appear at large
enough $d_{Ag}$ that they cannot be attributed to changes occurring
at the Pb-Ag interface that could influence $T_{co}$ (e.g.,
alloying). Finally, one might argue that Eq. (1) only holds for
smooth continuous bilayers and deviations might be ex-
pected for more complicated geometries such as nanoscale
arrays. The high quality of the fit to the $d_{Pb} = 3$ nm data,
however, counters this argument.

Alternatively, we suggest that as $T_{co}$ decreases and the
order-parameter amplitude on the Pb grains decreases ampli-
itude fluctuations grow and lead to deviations from mean-
field behavior. These fluctuations reduce the average pairing
interactions. In more detail, we estimate the order-parameter
amplitude by the average number of Cooper pairs per grain,
$N_{cp} = \nu_{Pb} V \Delta$, where $V$ is the grain volume.\textsuperscript{9} For $N_{cp} \geq 1$ the
probability, $P_{AS}$, that an electron entering a Pb grain has a
pairing interaction with another electron within $\Delta$ of $E_F$ or,
equivalently, Andreev scatters from the grain, is close to 1.\textsuperscript{13}

Mean-field treatments of the proximity effect implicitly pre-
sume $P_{AS} = 1$ through the use of the factor $d_{Pb}/(d_{Pb} + \beta d_{Ag})$
to account for the reduction of the pairing interaction
induced by the metal. As $T_{co}$ and $\Delta$ decrease and $N_{cp}$
approaches and falls below 1, fluctuations in $N_{cp}$ are
expected and reduce $P_{AS}$ below 1. Consequently, the volume
for pairing interactions falls faster with $d_{Ag}$ than the factor
$d_{Pb}/(d_{Pb} + \beta d_{Ag})$ would imply, leading to a more rapid
decrease in $T_{co}(d_{Ag})$.\textsuperscript{32}

Simple estimates reveal that the nanoarrays with the lowest
$T_{co}$’s fall in this fluctuation dominated regime. Using $V$
for the $d_{Pb} = 3$ nm film and $\Delta = \Delta_{bulk} T_{co}/T_{co.bulk}$, we find
that $N_{cp} = 1$ for the lowest $T_{co}$ film ($T_{co} = 0.2$ K). This film
lies close to the mean-field prediction. At comparable $T_{co}$,
the $d_{Pb} = 1.5$- and 2.3-nm films which have smaller grains
and thus smaller $N_{cp}$ deviate from the Cooper limit theory.
Presumably these films are firmly in the fluctuation domi-
nated regime. For a rough measure of the fluctuations, the
data point for the $d_{Pb} = 1.5$ nm film at $d_{Ag} = 7.5$ nm must be
shifted to 9.0 nm or by about 20% for it to fall on the mean-
field prediction. In other words, fluctuations prevent 20% of
the Pb volume in this film from promoting pairing interac-
tions.

It is interesting, in the light of recent predictions of a
quantum SMT,\textsuperscript{10,11} that the fluctuation effects tend to drive the
arrays more rapidly toward a metallic state (i.e., $T_{co} = 0$). Spivak, Zyuzin, and Hruska\textsuperscript{11} predicted a critical $x_c$
$\sim |\lambda_N| \ln[(1 + (r_c - r)/r)/2 \pi]$ (Ref. 34) for the SMT where $r_c$
$\approx \xi_s$. By identifying $x_c = d_{Pb}/(d_{Pb} + d_{Ag})$ and using $\lambda_{Ag}$
$= -0.017$, as obtained from the fit in Fig. 3, we can estimate the
critical value $(d_{Ag}/d_{Pb})_c$ for the SMT. For the
$d_{Pb} = 3$-nm film, $r = 7.5$ nm = $(V)^{1/3}$, $(d_{Ag}/d_{Pb}) = 14$. Pres-
suming that $r$ scales as $d_{Pb}$, $(d_{Ag}/d_{Pb})_c \approx 10$ for the $d_{Pb}$
$= 1.5$-nm film. The predicted $(d_{Ag}/d_{Pb})$ is higher than the
$(d_{Ag}/d_{Pb})$ at which strong downward curvature emerges in the
data. This discrepancy may arise because the theory pre-
sumes that the superconducting grain spacing is much larger
than $r$ and $r \approx \xi_{bulk}$. In the experiments, $r \ll \xi_{bulk}$, which
may lead to stronger fluctuation effects than expected.

In summary, quench condensation of ultrathin bilayer
films of Pb and Ag has been used to fabricate arrays of SNS
junctions with nanoscale dimensions. The array $T_{co}$’s
decrease as the Pb grain concentration decreases in a manner
quantitatively consistent with the Cooper limit theory of the
proximity effect until the average number of Cooper pairs
per Pb grain approaches 1. The ensuing, more rapid decrease
in $T_{co}$ with decreasing Pb grain concentration is qualitatively
consistent with the arrays approaching a superconductor-to-
metal transition.

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