Inverse Proximity Effect in a Strongly Correlated Electron System

Olivier Bourgeois,[1] Aviad Frydman,[2] and R. C. Dynes[1,*]

[1]*Department of Physics, University of California–San Diego, 9500 Gilman Drive, La Jolla, California 92093-0319*

[2]*Departement of Physics, Bar Ilan University, Ramat Gan 52900, Israel*

(Received 13 April 2001; published 23 April 2002)

An anomalous superconducting proximity effect between a strongly correlated electron system and a normal metal is demonstrated. The model system is a 2D ultrathin superconducting quench-condensed Pb film. Such a highly disordered film has a reduced transition temperature ($T_c = 1.7$ K) due to the strong e^--e^- interaction. Instead of weakening the superconductivity, an overlayer of Ag on Pb induces an increase of both the T_c and the gap. The restoration of the electron screening brought about by the quasiparticles from the normal metal can explain this striking inverse proximity effect.

DOI: 10.1103/PhysRevLett.88.186403 PACS numbers: 71.27.+a, 71.30.+h, 73.20.At, 74.50.+r

It is well understood that, when a superconductor and a normal metal are in good electrical contact, the microscopic mechanism of Andreev reflection [1] leads to a leakage of superconducting pairs and phase coherence into the normal metal. At the same time, unpaired electrons from the normal metal diffusing into the superconductor have a strong influence on the properties of the latter. This results in the so-called classic proximity effect, where the superconductivity is weakened in the superconductor and induced in the normal metal. It is well described within the framework of the de Gennes model [2,3]. However, when the superconductor is a strongly correlated electron system, significant deviations from this model could arise from several sources. These include a potential nonconventional pairing symmetry, small coherence length, or strong Coulomb interactions [4–7].

Materials characterized by a strong electron-electron interaction are under study in numerous areas of solid-state physics such as the metal insulator transition, high-T_c superconductors (HTSC), or heavy fermion compounds. In spite of previous studies [6–9], the phenomenon of the superconducting proximity effect between those materials and a normal metal remains unclear. In HTSC and heavy fermion materials, low transparency interfaces and high Fermi wave vector mismatch with normal metals such as Ag or Au can lead to great difficulties in observing and studying such effects. Furthermore, the possibility of non-*s*-wave symmetry for the superconducting gap in those materials makes the interpretation of the results complicated [10].

It is well known that, for an ultrathin uniform homogeneous film, as the sheet resistance, or resistance per square (R_{sq}), decreases, the film encounters an insulator to superconductor transition with a well-defined superconducting critical temperature. The critical temperature, depressed compared to the bulk value, scales with the R_{sq} of the film. Superconductivity in ultrathin films in the 2D limit has been extensively studied [11–13]. It has been argued that the Coulomb interactions in those highly disordered amorphous films can be the explanation for the depression of the superconducting parameters (T_c and Δ_0) [14–16]. In this Letter, we report an inverse proximity effect between quench-condensed ultrathin superconducting Pb films close to the superconductor-insulator transition, where the strongest Coulomb interactions are expected, and Ag is the nonsuperconducting metal.

The system was prepared by low temperature quench condensation. This technique allows evaporations under ultrahigh-vacuum (UHV) conditions at liquid helium temperatures onto a cryocooled substrate [17]. This permits transport measurements to be performed *in situ*. This offers several essential advantages. First, the UHV conditions optimize the electron transmission across the interface which is crucial. Second, the low atom mobility at 4.2 K minimizes intermetallic diffusion, and, hence, negligible alloying. The third advantage comes from the possibility of sequential evaporations *in situ*. A complete experiment can be performed on a single tunnel junction and an identical interface transparency between Pb and Ag.

Measurements were made simultaneously on Pb/Ag bilayers and on $Al/Al_2O_3/Pb/Ag$ tunnel junctions using a four point probe technique in a pumped ^{4}He cryostat. The aluminum layer is first thermally evaporated at room temperature on a fire polished glass substrate. The substrate is then transferred to the cryostat-evaporator chamber, and pumped down to below 10^{-5} Torr. The native oxide layer grown on the Al during this process is used as the tunnel barrier. The entire evaporation chamber is then immersed in liquid helium, thus cryopumping to UHV. At 4.2 K a thin (10–12 Å) Ge adhesion layer is first evaporated over the Al layer. It has been shown previously that, with such an appropriate adhesion layer, an evaporation of Pb on Ge is electrically continuous for films as thin as 5 Å (one or two monolayers) [12,14,15]. At two monolayers the conductance of the film corresponds to a uniform slab of metal two monolayers thick. If the film was granular it would not yet percolate. We then proceeded to the first evaporation of lead (around 10 Å), followed by the deposition of silver. Film thicknesses were monitored by a quartz crystal microbalance with a high resolution frequency counter; each evaporation could be measured with an accuracy of approximately 0.02 Å. From the normal state transport results as a function of film thickness, we believe these films to be continuous on an atomic scale.

We have studied different starting thicknesses of Pb ranging from 9 to 40 Å followed by a silver overlayer with a thickness d_{Ag} ranging from 0 to 40 Å. The superconducting critical temperature measurements performed on sample No. 1 (11 Å of Pb) followed by 0 to 7 Å of silver are presented in Fig. 1. Here we show the resistive transition for the Pb layer ($R_{\mathrm{sq}} = 6\ \mathrm{k}\Omega$) and the first nine evaporations of Ag; each evaporation represents an additional Ag layer of approximately 0.25 Å/0.35 Å. Instead of T_c decreasing, as in the classical proximity effect [as in sample No. 3 (14.3 Å of Pb, see Fig. 2)], it appears to increase with the addition of the first few layers of Ag, and, at the same time, the R_{sq} of the bilayer in the normal state decreases as $1/(d_{\mathrm{Ag}} + d_{\mathrm{Pb}})$ with the thickness of the Ag. The inset of Fig. 1 shows the transition for further increases of Ag. It is seen that, after 2.6 Å of Ag, the transition temperature turns around and begins to be depressed.

The broadening of the transition is due to fluctuations in the Pb layer. This is expected and unavoidable for such thin two-dimensional films with high resistance. Qualitatively, the appropriate value for T_c must lie in the vicinity of the midpoint of the transition, meaning around $R_N/2$. Above the T_c, when $T > T_c(1 + 2R_N e^2/16\hbar)$ (Glover criterion) and $T < 2T_c$, the excess conductivity can be described by the Aslamazov-Larkin (AL) model of fluctuation pairing of electrons [18]. In the AL model, the decreasing resistance per square with decreasing T is described in the following form, where T_c is the only free parameter:

$$R_{\mathrm{sq}}(T) = R_N\left(1 - R_N \frac{e^2 T_c}{16\hbar(T - T_c)}\right). \qquad (1)$$

Here R_N is the normal resistance per square at high temperature (above 10 K). The fits of the high temperature part of the $R_{\mathrm{sq}}(T)$ measurements with this formula are shown in Fig. 1 as solid lines. Considering the Glover criterion which allows such fits 20% above T_c in the case of Pb or Ag1 ($R_{\mathrm{sq}} = 7\ \mathrm{k}\Omega$) and 6% for Ag9 ($R_{\mathrm{sq}} = 2\ \mathrm{k}\Omega$), those fits are quite good, and allow us to more accurately determine T_c. The results of this analysis on sample No. 1 and sample No. 3 are shown in Fig. 2. The uncertainty of the T_c extracted from these AL fits is estimated to be at most ± 0.02 K from the range of validity of the fit. Instead of a monotonic decrease as in sample No. 3 (solid squares in Fig. 2), the increase of T_c of up to 15% is very clear in the case of sample No. 1 (solid circles) and reaches a maximum at $d_{\mathrm{Ag}} = 2.5$ Å, before decreasing for higher thicknesses of Ag. Further layers of Ag (more than 4 Å) cause T_c to continue decreasing linearly with thickness as expected for the proximity effect in the Cooper limit, when the thickness of the superconducting bilayer is thinner than the superconducting coherence length. All samples studied in this work are in this limit, since the coherence length in amorphous Pb is approximately 60–70 Å.

A dozen different samples were measured in this study. The three samples with the smallest thickness [9 Å, 9.35 Å (sample No. 2), and 11 Å (sample No. 1)] exhibit such an anomalous proximity effect with different but consistent magnitudes. We have observed that samples with a higher R_{sq} exhibit a larger increase of the transition temperature.

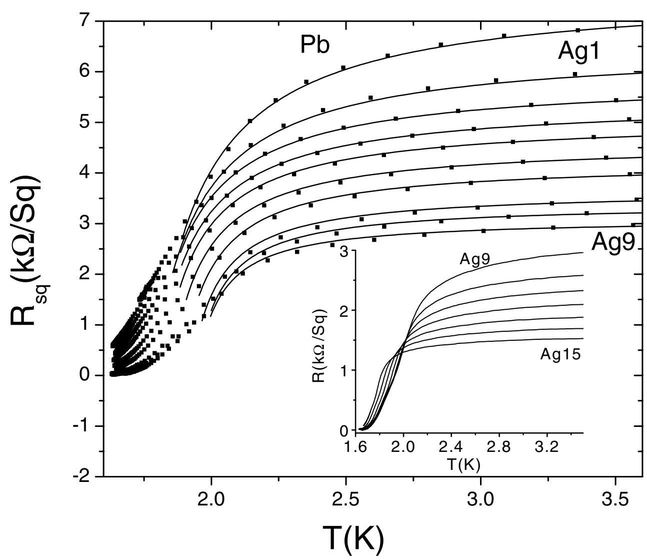

FIG. 1. Resistance per square versus temperature measurements ([$R_{\mathrm{sq}}(T)$]) of a series of Pb/Ag bilayers (sample No. 1). The thickness of Ag varies from 0 Å (Pb) to 2.56 Å (Ag9) in Fig. 1. The solid lines represent the AL fit (see text). The inset represents the $R_{\mathrm{sq}}(T)$ measurements for the ninth to the fifteenth (Ag9–Ag15) evaporations of Ag with additional thicknesses ranging from 0.3 to 2 Å each depending of the evaporation, from Ag thickness range 2.56 to 11.0 Å on sample No. 1.

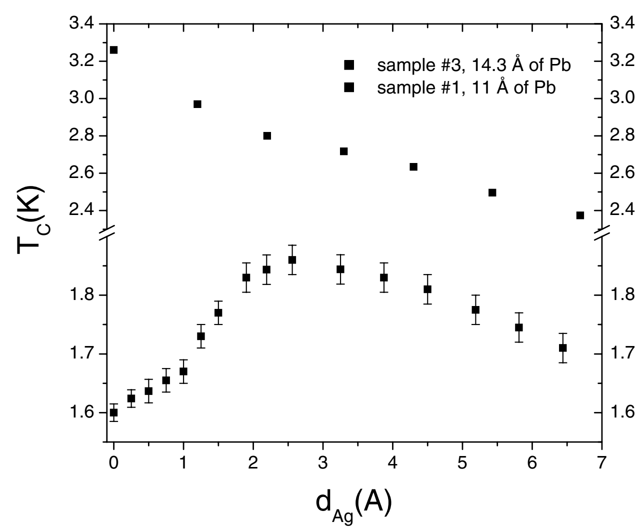

FIG. 2. Critical temperature of the Pb/Ag bilayer versus the thickness of Ag of sample No. 1 (solid circles) and sample No. 3 (solid squares) extracted from the AL fit (see text). The T_c exhibits an unusual increase before reaching a maximum at $d_{\mathrm{Ag}} = 2.56$ Å for sample No. 1, while sample No. 3 exhibits a usual linear decrease as the normal metal is added on top of Pb.

Samples with a thick layer of Pb (35 Å not shown) show a linear decrease of T_c versus d_{Ag}, while the variation of T_c in samples with intermediate thicknesses [14.3 Å (sample No. 3), 15 Å, and 15.5 Å] appears to be nonlinearly decreasing with a kink around 2 Å of Ag. This can be interpreted as a precursor signature of the anomalous effect, but in that intermediate regime the classical proximity effect is still stronger and dominates the entire process.

To further investigate, the density of states (DOS) was measured to determine if the superconducting gap followed the same behavior. The tunneling conductance measurements of the $Al/Al_2O_3/Pb/Ag$ junction were also performed using an ac technique at 1.65 K. The use of the native grown aluminum oxide layer (Al_2O_3) as a tunnel barrier assures that the tunneling is a single step process; hence, the measurement of $dI/dV(V)$ gives directly the DOS of the Pb/Ag sandwich. From previous results, we know that the ultrathin Pb layer behaves similar to a strong coupled Bardeen-Cooper-Schrieffer (BCS) superconductor [15]. The dI/dV measurements show a classical BCS gap feature which can be fitted for every thickness of Pb and Ag evaporated using the finite temperature BCS form of the DOS. We determined the value of the gap (Δ) at 1.65 K extracted from BCS fits of the dI/dV measurements. The only fitting parameter we used is Δ at 1.65 K. The actual T_c does not play a part in these fits. We show in Fig. 3 the value of Δ at 1.65 K for two samples with different thicknesses of Pb (sample No. 2: 9.35 Å; sample No. 3: 14.3 Å) as we vary the thickness of Ag. The inset of Fig. 3 shows the normalized conductance [$(dI/dV)_N(V)$ measurements] for the Pb without Ag and for two different thicknesses of Ag (1.1 and 1.75 Å) at the same temperature (1.65 K) on sample No. 2. The conductance measured at 1.65 K is normalized by the conductance measured above T_c at 2.05 K. We note that, with the addition of Ag, the zero bias conductance *decreases,* consistent with an increasing energy gap Δ. While our normalization procedure could be sensitive to a temperature dependent Coulomb gap, the addition of a Ag layer would tend to reduce this effect, not enhance it. Thus, the observation of a reduced zero bias conductance with the addition of Ag clearly indicates an enhanced energy gap Δ. In contrast, sample No. 3 ($R_{sq} = 2$ kΩ) shows a classical decrease of the superconducting gap with the addition of silver, while sample No. 2 ($R_{sq} = 3$ kΩ) exhibits the inverse proximity effect shown in Fig. 2. Here the superconducting gap is seen to be increasing (20%) with increasing d_{Ag}, before decreasing at high thicknesses of Ag. The evolution of the ratio $2\Delta(0)/k_B T_c$ shows a change from a strong coupling value >4 to a BCS value of 3.5 as Ag is added and T_c is reduced. This result is similar to earlier granular Pb/Ag experiments [19].

We stress that this effect is not to be confused with a similar increase of the transition temperature in granular Pb coated by Ag [19]. In that case, the evaporation of a Ag film over the grains couples the superconducting granular Pb and increases the macroscopic superconducting behavior by restoring the electrical contact between isolated superconducting islands and, hence, the quantum phase coherence over a large length scale. When the Ag thickness is too large the classical proximity effect takes over, and the T_c is depressed. Although apparently similar, the physics underlying the effect described in this paper is very different essentially because, in the current case, samples are continuous and statistically uniform and not granular. Furthermore, with no low temperature solubility the bilayer Pb/Ag is a metallurgically very clean system and, hence, we do not expect the appearance of surface superconductivity due to alloying between Ge, Pb, and Ag. It has been suggested that, in ultrathin Pb films, superconductivity is depressed because the disorder in these amorphous quench-condensed films is high [15]. This disorder suppresses electron screening, reestablishing the strong Coulomb repulsion as the R_{sq} increases. As a normal metal is added, the resistance decreases and electron screening is improved. The Pb/Ag bilayer has a global e^--e^- interaction which is less pronounced. This scenario is strongly supported by the increase of the "normal state" density of states at the Fermi energy, as measured by tunneling and shown in Fig. 4. Here the DOS at 2.05 K—normalized by the DOS of the uncoated Pb measured at $V = 20$ mV (σ_{Pb})—are reported for different thicknesses of Ag, from Pb to Ag9. We chose to normalize the data at a bias of 20 V. This choice of normalization affects any quantitative comparison, but the

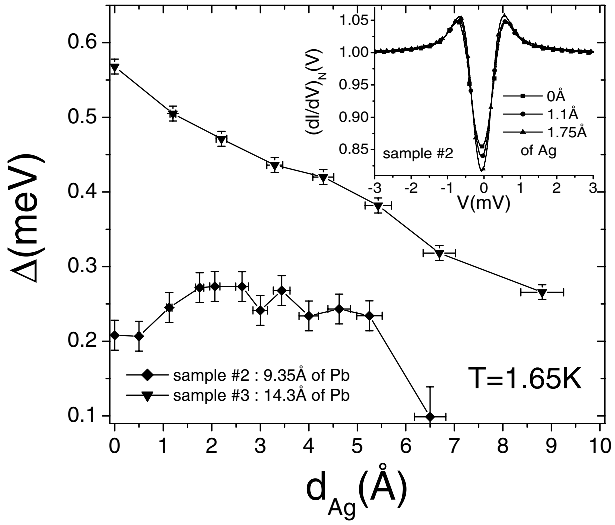

FIG. 3. Variation of the superconducting gap measured at 1.65 K versus the thickness of Ag for samples No. 2 and No. 3 (respectively, 9.3 and 14.3 Å of Pb). Δ(meV) decreases linearly for the thick layer of Pb (sample No. 3, solid upside-down triangles), but increases initially in the case of the thinner layer (sample No. 2, solid diamonds). The enhancement of superconductivity in the Pb/Ag bilayer at 1.65 K with increasing silver thickness is illustrated in the normalized DOS (see text) of Pb/Ag in the case of three different thicknesses of Ag, as shown in the inset.

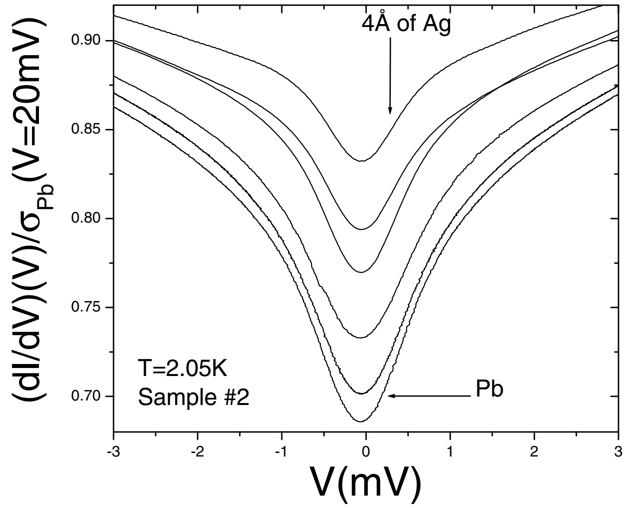

FIG. 4. Normalized density of states at 2.05 K for sample No. 2 normalized by the value of the DOS of the uncoated Pb at $V = 20$ mV. The number of state at the Fermi level increases strongly between the Pb only (bottom curve) and the Pb/Ag (4 Å) (upper curve). Intermediate curves correspond to the evaporations Ag1, Ag3, Ag7, and Ag9 (4 Å). The addition of the Ag results in a reduction of Coulomb effect.

relative changes in Fig. 4 remain for any normalization criterion and these data highlight the variation of the Coulomb gap with thickness of Ag. Clearly, the Coulomb gap is progressively vanishing with increasing Ag.

As the classical proximity effect can be seen as a leakage of Cooper pairs into the normal metal, this inverse proximity effect has to be seen as an addition of quasiparticles from the normal metal, thus enhancing the screening in the bilayer and suppressing the Coulomb effects. For Pb film thicknesses greater than 12–14 Å ($R_{sq} < 2$ kΩ), the correlation effects are not strong enough for this inverse proximity effect to occur. Hence, we are observing a competition between two effects: With increasing Ag thickness, Coulomb effects are reduced which tends to increase the T_c and superconducting gap. The classical proximity effect which has the opposite effect tends to reduce T_c. When the classical proximity effect does not dominate, T_c and the superconducting gap in a strongly correlated electron system can be significantly enhanced by proximity with a normal metal. We believe that such an effect could be difficult to observe in other strongly correlated electron systems. Though point contact experiments on heavy fermion metals have shown that Andreev reflection processes can occur [20], and an anomalous negative proximity effect has been found for a non-s-wave pairing of the superconducting state [6], no such inverse proximity effect has been observed. Studies of a proximity effect with a normal metal and a HTSC compound are at an early stage and no clear answer has yet emerged [8,9]. The recurrent problems of interface quality, high Fermi wave vector mismatch, as well as incompatible wave function symmetry with a BCS s wave could be a major limitation in observing such an inverse proximity effect either in HTSC or in heavy fermion compounds.

The authors thank O. Naaman and W. Teizer for fruitful discussions. This work was supported by DOE Grant No. DE-FG03-00ER45853, and by NSF Grant No. DMR9705180. One of the authors (A. F.) wants to acknowledge the Israel-U.S. Binational Foundation for financial support.

*Email address: rcd@physics.ucsd.edu

[1] A. F. Andreev, J. Exp. Theor. Phys. **19**, 1228 (1964).
[2] P. G. de Gennes, Rev. Mod. Phys. **36**, 225 (1964).
[3] G. Deutscher and P. G. de Gennes, in *Superconductivity,* edited by R. D. Parks (Dekker, New York, 1969), Vol. 2.
[4] M. Covington *et al.,* Phys. Rev. Lett. **79**, 277 (1997).
[5] D. Rainer, H. Burkhardt, M. Fogelström, and J. A. Sauls, J. Phys. Chem. Solids **59**, 2040 (1998).
[6] Siyuan Han *et al.,* Phys. Rev. Lett. **57**, 238 (1986).
[7] S. Shibata, A. Sumiyama, Y. Oda, Y. Haga, and Y. Onuki, Phys. Rev. B **60**, 3076 (1999).
[8] V. M. Svitsunov, V. Y. Tarenkov, A. I. D'yachenko, O. I. Chernyak, and R. Aoki, Physica (Amsterdam) **303C**, 177 (1998).
[9] V. M. Pan *et al.,* Physica (Amsterdam) **284B–288B**, 915 (2000).
[10] E. W. Fenton, Solid State Commun. **54**, 709 (1985).
[11] J. M. Graybeal and M. R. Beasley, Phys. Rev. B **29**, 4167 (1984).
[12] A. White, R. C. Dynes, and J. P. Garno, Phys. Rev. B **33**, 3549 (1986).
[13] A. M. Goldman and N. Markovic, Phys. Today **51**, 39 (1998), and references therein.
[14] J. M. Valles, Jr., R. C. Dynes, and J. P. Garno, Phys. Rev. B **40**, 6680 (1989).
[15] J. M. Valles, Jr., Shih-Ying Hsu, R. C. Dynes, and J. P. Garno, Physica (Amsterdam) **197B**, 522 (1994).
[16] P. A. Lee and T. V. Ramakrishnan, Rev. Mod. Phys. **57**, 287 (1985).
[17] J. P. Garno, Rev. Sci. Instrum. **49**, 1218 (1978).
[18] L. G. Aslamazov and A. I. Larkin, Phys. Lett. **26A**, 238 (1968).
[19] L. Merchant, J. Ostrick, R. P. Barber, and R. C. Dynes, Phys. Rev. B **63**, 134508 (2001).
[20] M. Jourdan *et al.,* Physica (Amsterdam) **230B**, 335 (1997).