Severe discrepancies between experiment and theory in the superconducting proximity effect

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Abstract

The superconducting proximity effect is investigated for SN double layers in a regime where the resulting transition temperature $T_c$ does not depend on the mean free paths of the films and, within limits, not on the transparency of the interface. This regime includes the thin film limit and the normalized initial slope $S_{sn} = (d_s/T_s)|dT_c/dd_n|$. The experimental results for $T_c$ are compared with a numerical simulation which was recently developed in our group. The results for the SN double layers can be divided into three groups: (i) When $N = \text{Cu, Ag, Au, Mg}$ a disagreement between experiment and theory by a factor of the order of three is observed, (ii) When $N = \text{Cd, Zn, Al}$ the disagreement between experiment and theory is reduced to a factor of about 1.5, (iii) When $N = \text{In, Sn}$ a reasonably good agreement between experiment and theory is observed.
1 Introduction

The properties of a superconducting film or thin wire \( S \) are modified when they are in contact with a normal metal \( N \). This phenomenon was first observed in the pioneering experiments by Meissner [1] who explored the properties of superconducting wires covered with normal metals. It is generally called the "superconducting proximity effect" (SPE). It was intensively studied in the 1960’s [2], [3], [4], [5], [6], [7]. During the last decade it has experienced a renewed interest theoretically [8], [9], [10], [11], [12], [13], [14], [15], [16], [17], [18], [19], [20] as well as experimentally [21], [22], [23], [24], [15], [17], [25], [26], [27], [28]. Recently the SPE has been extended to SN-multi layers [29], [30].

A few years ago, our group [27] investigated the proximity effect between Pb and several alkali metals. For a better analysis of these measurements we developed a quantitative numerical method for the calculation of the transition temperature of an SN double layer [31]. Our numerical results show that, when a superconductor \( S \) is covered with a normal metal \( N \), that the initial slope \( \frac{dT_c}{dd_n} \) is independent of the mean free paths of the two metals and the transparency of the interface (if the transmission is not dramatically changed). If one defines a normalized initial slope \( S_{sn} = \frac{d_s T_s}{d_n} \bigg|_{d_n=0} \) then \( S_{sn} \) is independent of the thickness \( d_s \) of the superconductor up to relatively large values of \( d_s \). If the superconductor is very weak coupling \( (2\pi T_s \ll \Theta_D) \), \( \Theta_D=\text{Debye temperature} \) then our result for the initial slope converges towards the results for the thin film Cooper limit [32] (see below).

When we compared our experimental initial slope \( \frac{dT_c}{dd_n} \bigg|_{d_n=0} \) with our numerical calculation we observed that the experimental results were considerably smaller than the theoretical predictions. Surprised by the discrepancy we searched the literature and found early experiments from the 1960s, particularly by Hilsch [2], [3] and Minigerode [7], from which the normalized initial slope can be derived. These measurements showed a similar disagreement in the initial slope with the theory (see ref. [31]).

Since we were rather amazed by the discrepancy between our experiments and theory in the SPE and also by the fact that this discrepancy had not been detected previously, we decided to re-investigate the SPE. In this paper we investigate the SPE in the range, where a minimum of experimental parameters is needed to perform a quantitative comparison with the theory. We focus on the normalized initial slope \( S_{sn} \) of SN sandwiches and the transition
temperature of very thin NS sandwiches in the thin film limit.

2 Experiment and Results

We use thermal evaporation to condense the thin films onto a substrate at liquid helium temperature. To obtain clean films all the evaporation sources are surrounded with liquid N\textsubscript{2} and the vacuum in our system is better than 10\textsuperscript{-11}torr. We first evaporate 10 atomic layers of insulating Sb on a helium cold quartz substrate. The Sb film acts as a fresh substrate and insures that the following quench condensed films are flat and homogeneous.

In a series of experiments a film of the superconductor Pb is first condensed onto the Sb substrate. Afterwards the Pb is covered in several step with an increasing thickness of the normal metal Ag. The thickness of the films is measured with a quartz oscillator. The accuracy of the thickness measurement is about 15\%. After each evaporation the superconducting transition curve, the magnetoresistance and the Hall effect of the double layer are measured. Fig.1 shows a plot of $T_c$ versus the Ag thickness $d_{Ag}$ on top of a 251A thick Pb film. This plot yields graphically the initial slope $dT_c/nd_{n}|_{d_{n}=0}$ and the normalized initial slope $S_{sn}$

$$S_{sn} = \frac{d_{s}}{T_s} \left| \frac{dT_c(d_{n} = 0)}{dd_{n}} \right|$$

where $d_{Pb} = d_{s}$ is the thickness of the Pb films and $T_s = 7.2K$ is the transition temperature for Pb alone.
Fig.1: $T_c$ versus $d_{Ag}$ for an PbAg double layer.

This experiment is repeated for different thicknesses of the superconductor Pb. In Fig.2 $S_{sn}$ is plotted versus the Pb thickness $d_{Pb}$. It is essentially independent of the Pb thickness. This was the prediction of our numerical results. The value of the normalized initial slope is $S_{PbAg} = 0.66 \pm 0.05$. 

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In the next experimental series we investigate NS double layers in the thin film limit and express the results in terms of the normalized initial slope $S_{sn}$. As an example a thin Ag film ($d_{Ag} = 41.0\text{A}$) is condensed onto the insulating Sb substrate and covered in several steps with increasing thickness of Pb. Fig.3a shows the results. The inverse $T_c$-reduction $1/\Delta T_c = 1/(T_s - T_c)$ is plotted as a function of the Pb thickness. From these plots we extract the value of the normalized initial slope. For the AgPb double layer the value is $S_{Pb,Ag} = 0.66$. This is in excellent agreement with the results from the first experimental series.
Figure 3. The inverse $T_c$ reduction $1/(T_s - T_c)$ versus the Pb thickness $d_{Pb}$ for double layers of N/Pb where N stands for the metals Ag, Mg, Zn and Sn.

We use this much more efficient procedure to investigate sandwiches of Pb with the normal metals Ag, Au, Cu, Mg. Furthermore we included also as "normal metals" superconductors with a transition temperatures $T_n$ which lie below the value of $T_c$ for Pb. These metals are Zn, Cd, Al, In and Sn. Fig.3b-d shows some of the results for Mg, Zn and Sn.
In Table I the experimental data are collected. The first column gives the experimental code; which includes the symbols for the normal metal and the superconductor. The following columns give the thickness of the normal metal (or the superconductor with the lower $T_c$), the transition temperature $T_n$ of $N$ if $N$ is a superconductor, the ratio of the experimental (i.e., phonon enhanced) density of states and the experimental normalized initial slope $S_{\text{exp}}$. The estimated error of $S_{\text{exp}}$ is about 15%. The density of states are taken from Kittel’s book [33]. The theoretical prediction of the normalized initial slope by the Werthamer theory $S_{\text{Wh}}$ and our numerical result $S_{\text{sim}}$ will be discussed below. The transition temperatures for quench condensed Cd and Zn are taken from ref. [34] and [35], the transition temperatures of quench condensed Al, In and Sn are taken from [36] and [37].

| exp.      | $d_n$(A) | $T_n$(K) | $N_n^*/N_s^*$ | $S_{\text{exp}}$ | $S_{\text{Wh}}$ | $S_{\text{sim}}$ | $S_{\text{exp}}/S_{\text{sim}}$ | $S_{\text{sim}}/(N_n^*/N_s^*)$ |
|-----------|----------|----------|----------------|------------------|-----------------|-----------------|-------------------------------|-------------------------------|
| AgPbJB    | 41.2     | 41.2     | 0.387          | 0.66             | 0.95            | 0.38            | 4.5                          |                               |
| CuPbJE    | 32.9     | 32.9     | 0.603          | 0.98             | 1.49            | 2.67            | 0.37                         | 4.43                          |
| AuPbJD    | 29.5     | 29.5     | 0.442          | 0.62             | 1.09            | 1.98            | 0.31                         | 4.48                          |
| MgPbJG    | 28.5     | 28.5     | 0.572          | 0.48             | 1.41            | 2.54            | 0.19                         | 4.44                          |
| CdPbJJ    | 31.4     | 31.4     | 0.329          | 0.39             | 0.40            | 0.528           | 0.74                         | 1.60                          |
| ZnPbUU    | 26.0     | 26.0     | 0.430          | 0.33             | 0.44            | 0.54            | 0.61                         | 1.26                          |
| AlPbUT    | 21.5     | 21.5     | 0.833          | 0.44             | 0.68            | 0.76            | 0.58                         | 0.91                          |
| InPbUP    | 32.1     | 32.1     | 0.663          | 0.30             | 0.31            | 0.354           | 0.85                         | 0.53                          |
| SnPbUN    | 33.0     | 33.0     | 0.664          | 0.29             | 0.25            | 0.283           | 1.02                         | 0.43                          |

Table I: The experimental normalized initial slope $S_{\text{exp}}$ are compared with the theoretical predictions by Werthamer’s theory $S_{\text{Wh}}$ and the author’s numerical calculations $S_{\text{sim}}$. The first four columns give the experimental code (containing the symbols of the normal conductor $N$ and superconductor $S$), the thickness of $N$, the transition temperature of $N$ (if superconducting) and the ratio of the experimental density of states $N_n^*/N_s^*$ (which includes electron-phonon enhancement). The second to last column gives the ratio between the experimental $S_{\text{exp}}$ and the numerical results $S_{\text{sim}}$.

3 Discussion

Let us consider a double layer with the superconducting transition temperature $T_c$. This transition temperature defines a characteristic time $\tau_{T_c} = \tau_c =$
$\hbar / (\pi k_B T_c)$. The superconducting coherence length is the distance that an electron propagates during this time $\tau_c$. In a clean metal this is equal to $\xi_0 = v_F \tau_c$ and in a dirty metal one has $\xi = \sqrt{D\tau_c}$ where $D$ is the diffusion constant of the dirty metal.

When, during the time $\tau_c$, an arbitrary conduction electron propagates through the whole thickness range of the double layer with roughly equal probability then the superconducting properties of the system are averaged over both films. In this case the mean free paths of the individual metal have no bearing on the superconducting transition temperature $T_c$. (However, the mean free paths determine whether the system is in this limit). A well-known example is the thin film or "Cooper" limit of a double layer when both films are much thinner than their coherence lengths and the "transmission time" through the interface is much shorter than $\tau_c$. In the limit that $T_c$ is much smaller than the Debye temperature, $T_c << \Theta_D$, the transition temperature of such a double layer is given by the BCS-Cooper formula

$$T_c = 1.14\Theta_D \exp \left(-\frac{1}{(NV)_{ef}}\right) \tag{2}$$

where the effective BCS interaction $(NV)_{ef}$ of the double layer is

$$(NV)_{ef} = \frac{d_s N_s (NV)_s + d_n N_n (NV)_n}{d_s N_s + d_n N_n}$$

and $(NV)_{s,n}$ are the BCS interactions in the super- and normal conductor.

Using the BCS-Cooper formula for an SN double layer yields for the normalized initial slope

$$S_{Cp} = \frac{d_s}{T_s} \left| \frac{dT_c}{dd_n} \right| = d_s \left| \frac{d (\ln (T_c))}{dd_n} \right| = \frac{N_n (NV)_n - (NV)_n}{N_s ((NV)_s)^2} \tag{3}$$

The predictions of equation (3) for the normalized initial slope (which is derived from equation (2)) has two problems, (i) Pb is not a superconductor with $T_c << \Theta_D$ and therefore the equation (2) does not yield a good representation of Pb, (ii) equation (2) uses the same Debye temperature for both metals and this is generally not fulfilled in the experiment. One can replace the BCS-Cooper formula for $T_c$ by an (implicit) expression

$$\frac{1}{(VN)_{ef}} = \sum_{n=0}^{n_c} \frac{1}{(n + \frac{1}{2})} \tag{4}$$
where $n_c = \Theta_D/(2\pi T_c)$. We do not evaluate equation (4) here because its results are in included in our numerical procedure as a limiting case.

Werthamer [38] derived a set of equations for the transition temperature of a double layer of a super- and a normal conductor in the dirty limit, using de Gennes’ interface boundary condition [39]. In this theory the gap parameter is approximated as a cosine and hyperbolic cosine function in the superconductor and normal conductor respectively. (This is sometimes called the single mode expansion). This theory agrees quite well with the experimental results for double layers of two superconductors [6]. The normalized initial slope can be expressed as

$$S_{Wh} = \frac{N_n}{N_s} \frac{\pi^2}{4} \chi^{-1}(-\ln(T_s/T_n))$$

(5)

here $\chi^{-1}(y)$ is the inverse function of $\chi(x) = \Psi\left(\frac{1}{2} + \frac{1}{2}x\right) - \Psi\left(\frac{1}{2}\right)$ and $\Psi(z)$ is the digamma function. If we assume that the transition temperature $T_n$ for the normal metals Cu, Ag, Au and Mg is infinitely small, then $\chi^{-1}(-\ln(T_s/T_n))$ takes the value one. The values of $S_{Wh}$ according to Werthamer’s theory are included in table I. The values of $S_{Wh}$ don’t show a good agreement for the normal metals Cu, Ag, Au and Mg.

Finally we compare the experimental values $S_{exp}$ with our numerical calculation. This numerical calculation derives the transition temperature of a double or multi layer of a superconductor and a normal conductor. The equivalence in the propagation of the superconducting pair amplitude and a single electron in Gorkov’s linear gap equation is used. The single electrons act as messengers which carry the information about the superconducting gap $\langle N_s \Delta(r')/\tau_T \rangle$ from one position-time $(r', t' < 0)$ to another position-time $(r, t = 0)$. This message which decays thermally with time as $\eta_T(t) = \sum_{|\omega_n|<\Omega_D} \exp(-2 |\omega_n| |t'|)$, is integrated at $(r,t = 0)$ over all starting position-times $(r', t')$ and, after multiplication with the BCS interaction $V_s$, yields the new gap function $\Delta(r)$. At the transition temperature the procedure has to be self-consistent, i.e. the initial and final gap function have to be identical. The propagation of the single electrons is then quasi-classically simulated. The frame work of the calculation is the weak coupling theory of superconductivity.

This numerical procedure to calculate the transition temperature of double or multi-layers consisting of thin films of superconductors and normal conductors is very flexible. It uses the following input parameters of the
individual metal films (i) thickness, (ii) density of states and Fermi velocity, (iii) transition temperature, (iv) Debye temperature, (v) mean free path and (vi) transmission through the interface between the films.

An important outcome of the numerical simulation is the result that the normalized initial slope of an SN double layer as a function of $d_n$ at $d_n = 0$ does not depend on (i) the mean free paths of the two metals, (ii) the thickness of the superconductor and (iii) a finite (but not too large) barrier between the two metals.

We include the numerical results $S_{\text{sim}}$ in table I. For the double layers with the normal conducting metals Cu, Ag, Au and Mg the discrepancy between experiment and theory is very large, of the order of 3. It is remarkable that the deviation is considerably smaller when the "normal metal" is really a superconductor with a smaller transition temperature although the deviation is still factor of about 1.5. For In and Sn, however, there is a good agreement between theory and experiment.

It is surprising that this disagreement between experiment and theory has not been noticed in the past. The main reason is that the majority of the experimental and the theoretical work focused on NS sandwiches with thick normal metal films. Then superconductivity is only obtained for a finite thickness of the superconductor. In this case a comparison between experiment and theory requires many fit parameters such as the transparency of the interface and the mean free paths of the superconductor and the normal conductor. Therefore it is quite possible to fit the experimental data by using the wrong parameters that can’t be checked otherwise.

The physical origin of this disagreement between experiment and theory is not understood. Our theoretical simulation of the SPE uses the framework of weak coupling superconductivity. Quench condensed Pb, In and Sn are not weak coupling. The ratios of $2\Delta_0 / (k_B T_s)$ for quench condensed films are 4.6 for Pb, 3.9 for In and 4.0 for Sn [37], [40]. An obvious proposal would be to solve the superconducting proximity effect for strong coupling superconductors. This means to develop and solve a series of equations for the energy and position dependent gap function $\Delta (\mathbf{r}, \omega_l)$. This would be an extremely demanding job. As a start, we considered the thin film limit for the SPE of strong superconductors. This consideration, which will be published elsewhere, does not remove the discrepancy between experiment and theory.

The fact that the Werthamer result $S_{\text{Wh}}$ disagrees less with the experimental data $S_{\text{exp}}$ for Cu, Ag, Au and Mg than our numerical result might be
accidental. The single mode expansion of $\Delta(r)$ in the Werthamer theory is surely less appropriate than a self-consistant gap function.

The experimental normalized initial slope is proportional to the density of states ratio. Although the density of states can be modified in quench condensed films it is inconceivable that this explains a factor of three in the initial slope. Let us return to Fig.1 where the reduction of $T_c$ of Pb by a thin layer of Ag is plotted.

4 Conclusion

In this paper, the superconducting proximity effect is investigated for SN double layers in a regime where the resulting $T_c$ does not depend on the mean free path of the films and, within limits, not on the transparency of the interface. This regime includes the thin film limit and the normalized initial slope $S_{sn} = (d_s/T_s)|dT_c/dd_n|$. While the layer S is always Pb the layer N is either a non-superconducting metal such as Cu, Ag, Au and Mg or a superconductor with a $T_c$ below the transition temperature of Pb. The experimental results for the transition temperature $T_c$ are compared with a numerical calculation which was recently developed in our group. The results for the SN double layers can be divided into three groups:

- When N represents a non-superconducting metal film (N=Cu, Ag, Au and Mg) we observe grave deviations between experiment and theory by a factor of the order of three.

- When N represents a superconductor with a low $T_c$ (N=Cd, Zn, Al) the deviation between experiment and theory is still there but reduced by a factor of two.

- When N represents a superconductor with a $T_c$ which is about half the $T_c$ of Pb (N=In, Sn) then we observe a reasonably good agreement between experiment and theory.

Prior to our recent experiments we believed that the proximity effect between a superconductor and a normal conductor represented an intensively studied phenomenon with a good theoretical understanding. We are deeply puzzled by the large observed discrepancy between experiment and theory. It would be very desirable if other theoretical approaches would give quantitative predictions for the normalized initial slope in SN double layers. There
have been a number of theoretical papers published which extended the proximity effect to more complex systems, for example between a superconductor and a ferromagnet but which include implicitly the simpler case of an SN double layer. These authors would be able to calculate quantitatively the normalized initial slope from their theory.

Experimentally it would be desirable to extend the measurements to SN layers where S is a weak coupling superconductor. This requires lower temperatures but permits the use of thicker films because the coherence lengths are larger at lower temperatures. Aluminum would be a good candidate for the superconductor if evaporated in ultra-high vacuum so that the Al is not granular.
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