Tunneling Study of the Superconducting Proximity Effect in the Thin-Normal Limit*

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We report the tunneling characteristics of Pb-Zn-oxide-Pb junctions in which the average Zn thickness is approximately one atomic layer. This thin layer is produced either by indirect evaporation of Zn or by dissociation of ZnS upon evaporation. The tunneling characteristics show an added current shoulder just above the gap-edge voltage similar to that frequently reported for Nb junctions and several other systems, but unexplained until recently. We discuss the McMillan theory of the proximity effect in relation to earlier experiments using thicker normal films. We then use the theory to demonstrate that the observed current shoulder results from the proximity effect, involving a much thinner normal layer than in any previous experiments. A similar effect can explain the observations with Nb and other materials.

I. INTRODUCTION

When a superconducting film is placed in contact with another metal film, either a normal or lower-transition-temperature material, electrons can pass from one layer to the other. If one or both of the layers is thin, its superconducting properties are modified by the presence of the other layer. This is called the proximity effect. In particular, superconductivity and a superconducting gap may be induced in the normal film, and the gap may be reduced or disappear for the superconductor. Several tunneling studies of the proximity effect have previously been reported.[1–7] These studies show that the tunneling density of states in either the normal (N) or superconducting (S) layer of the N-S film is qualitatively different from that of a homogeneous superconductor. Most of these previous experiments involved layers of a few hundred to several thousand angstroms thickness. The thinnest reported N layers are 40 Å for the Al-Sn sandwiches of Vrba and Woods.[1] Vrba and Woods[1–3] and Adkins and co-workers[4,5] reported that their observations are matched qualitatively by the McMillan theory.[8]

In the present work, we have studied the proximity effect with Pb-Zn films by use of Pb-Zn-oxide-Pb tunnel junctions, and have compared these with Pb-oxide-Pb junctions. The quantity of Zn corresponds to an average film thickness on the order of one atomic layer, much thinner than the N films of any previous experiments. (We refer to Zn as the N metal even though it is in fact a superconductor, with bulk $T_c = 0.9$ K.[9]) The superconducting tunneling I-V characteristic of the Pb-Zn-insulator-Pb junctions differs from that of ordinary Pb-I-Pb junctions primarily in the presence of a distinct current overshoot which we have shown experimentally is associated with the presence of the Zn layer. This overshoot is similar to that observed in several other tunneling systems, notably in Nb junctions.[10,11] We use the McMillan theory as a means of comparing the density of states implied by our data with those found in proximity junctions with thicker N layers, and thus establish that the physical mechanism producing the current overshoot is the proximity effect.

Section II, describing our samples and their fabrication, is followed by a summary of our experimental observations in Sec. III. In Sec. IV we describe the McMillan theory and compare it with earlier experiments. In Sec. V we use the McMillan theory to relate our observations to those on thicker films. In the Appendix we discuss the configuration of our N layer and of the oxide barrier.

II. EXPERIMENTAL PROCEDURE

The equipment used in these experiments has been described previously.[12] The samples are prepared by vacuum evaporation in an oil-diffusion-pumped system which is equipped so that the samples are not exposed to air until after they are completed. The pressure during and between evaporations, except while oxidizing, does not exceed 10^{-7} Torr. Data are recorded by conventional means with the sample immersed in liquid He at 1.2 K. For normal-state tunneling curves, a magnetic field of around 2 kOe is applied perpendicular to the plane of the sample.

The steps involved in fabrication of the two main types of sample are shown in Figs. 1(a) and 1(b). The junctions are about 0.2 mm^2, with tunneling resistances between 0.1 and 1000 Ω. Nontunneling current is less than 0.1% in all of the junctions described in this paper. In most cases the substrate is mica cleaved in air. The substrate temperature is usually held at around 200 °C during deposition of the first Pb film, resulting in a (111) epitaxial film.[13] During the remainder of the fabrication steps the substrate is between 0 and 50 °C. Several samples are made in sequence in each pumpdown, so that 1 h or more under vacuum

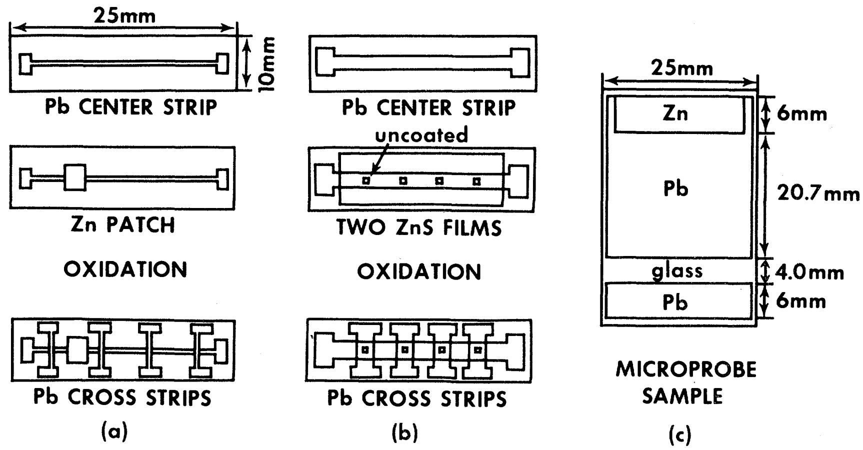

FIG. 1. Geometry of the main sample types. (a) Steps involved in making Pb-Zn-oxide-Pb junctions. Undoped junctions are similar but without the Zn patch. (b) Steps in making Pb-ZnS-oxide-Pb junctions. (c) The sample used for electron microprobe study. The two Pb films were deposited simultaneously, followed by the Zn film. For all junctions, all steps are performed without breaking vacuum.

passes between each step, e.g., between the fabrication of the first Pb film and that of the Zn or ZnS films on a given sample.

The tunneling barrier is produced by oxidation of the first Pb film, after deposition of the Zn or ZnS, in a pure-oxygen dc glow discharge, generated by a negative voltage applied to a shielded aluminum electrode. Film thickness is monitored during deposition with a quartz-crystal oscillator and, except for the extremely thin Zn layer, subsequently measured with a two-beam Nomarski-type interferometer[14] to an accuracy of ± 100 Å. Most of our Pb films are about 1000 Å thick. The ZnS films are about 300 Å thick and are electrically insulating, so that in the junctions illustrated in Fig. 1(b) tunneling current is restricted to the central part of the films.

The Zn thickness is much too small to measure using the interferometer. We can estimate from thicker Zn films, assuming a constant sticking coefficient, that the average thickness is 1 Å within a factor of 2 in the rectangle which is directly exposed to the evaporant beam. One expects the sticking coefficient to increase as the amount of deposit increases,[15] so a nonconstant coefficient would tend to make this estimate too high. However, our experience suggests that Zn atoms incident on the bare substrate near a Pb-coated area tend to migrate onto the Pb film before they equilibrate. The widths of the Zn patch and the Pb center strip in Fig. 1(a) are such that a multiplication by up to 20 of the Zn thickness could result from this migration. Thus, we are safe in stating that the Zn thickness in the intentionally covered area of the Pb center strip is no more than about 20 Å, and could be substantially less.

Figure 1(a) indicates that the junctions are not directly on the Zn patch, but are placed at several different distances from it. We find that Zn atoms migrate along the surface of the Pb film, producing a thin layer at least as far from the intentionally covered patch as the farthest junction, 7.5 mm away. We have used an electron microprobe to study the distribution of Zn on the surface of a Pb film in the sample shown in Fig. 1(c). This sample was made on a glass substrate. The Pb thickness was about 1000 Å, and the Zn thickness in the intentionally coated area was 80 Å within a factor of 2, as determined with the Nomarski interferometer, at least four times the Zn thickness in the tunneling samples. The second Pb rectangle is a control area, the uncoated glass between the Pb strips serving as a barrier to Zn migration.

Figure 2 gives the Zn density distribution measured in this study. Each point is the average over an area of 0.008–0.04 mm^2, the error bars representing ± one standard deviation. We find that for this test sample the average Zn thickness at 2 mm from the nominal edge is 5 Å (all Zn thicknesses are estimated to within a factor of 2 due to the difficulty of measuring the 80 Å thickness with a two-beam interferometer), 1.3 Å at 6 mm, 0.4 Å at 10 mm, and zero at 20 mm, the end of the film.

This test sample is considerably different from our tunneling samples, so that this study only allows us to estimate the average thickness in the latter. We can reasonably say that the quantity of Zn must correspond to an average thickness of no more than about two atomic layers for the junction nearest to the intentionally covered patch and no less than a tenth of a layer for the farthest junction, the amount decreasing with distance. Because the layer is so very thin we cannot be certain of its configuration. It is likely that the Zn thickness is highly nonuniform, perhaps several atomic layers in some limited areas and zero in adjacent areas. There is some reason to believe, however, that most of the tunneling current passes through regions which are Zn covered. This problem is discussed in the Appendix.

III. EXPERIMENTAL OBSERVATIONS

Despite the uncertainty in the *N*-layer configuration, we can say without doubt that the quantity of Zn in the junction areas is extremely small, since the total quantity incident in the intentionally covered area is so small. Even this amount, on the order of one atomic layer, has a striking effect upon the tunneling curves. The way in which it appears in current-versus-voltage curves is shown in Fig. 3. Curve (a) is from an ordinary Pb-PbO_x-Pb junction, while (b) is from a similar junction with a ZnS patch masking the center of the junction. The main difference between (a) and (b) is the distinct current shoulder located at the top of the gap-edge current step. In addition to the shoulder itself, we see that the current at somewhat higher voltages is a larger fraction of the normal-state current than it is for the pure-Pb junction. Thus, the main effect of the doping is to add extra current to the ordinary Pb characteristic. On first derivative characteristics, the shoulder appears as a very sharp resistance peak, but the extra current at higher voltage, being a broad function, does not appear at all. Hence, direct current-voltage data are at least as important as derivative data.

Derivative curves, taken by ac modulation,[12] show that the Pb phonon structure is modified by the presence of Zn or ZnS as follows: (i) All the usual structure[16] appears and is the same size as in Pb-PbO_x-Pb junctions, or larger by as much as 3%. (ii) No structure is added except that the second-derivative peak at 6.1 mV[12,17] is clearly resolved, while without the Zn it is never more than a shoulder. Except for these slight differences,

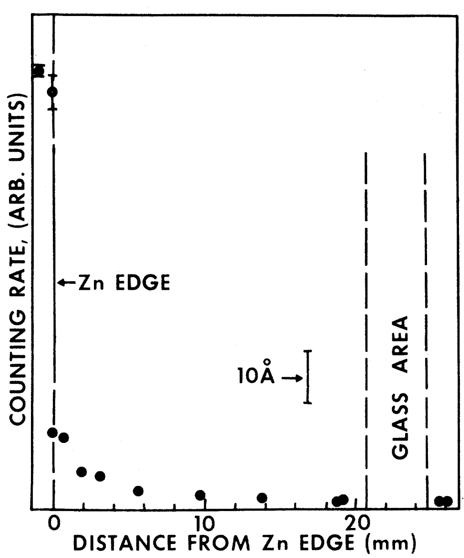

FIG. 2. Zn distribution on the sample of Fig. 1(c) as determined by counting the x rays characteristic of Zn atoms bombarded by the electron microprobe beam. The 10-Å marker is estimated within a factor of 2.

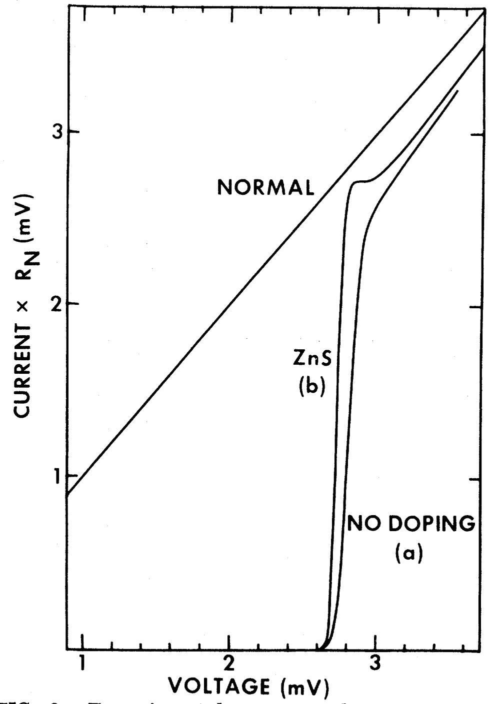

FIG. 3. Experimental current-voltage curves for (a) a Pb-PbO_x-Pb junction and (b) a Pb-ZnS-oxide-Pb junction at $T = 1.2$ K. The characteristics of Zn-doped junctions are similar to (b).

the superconducting structure in the derivative curves beyond about 3.5 mV is the same as for ordinary Pb-PbO_x-Pb junctions.

We find that the superconducting tunneling characteristics of the Zn- and ZnS-doped junctions are the same, although their normal tunneling characteristics are different. Although no microprobe studies have been performed on ZnS-coated Pb films, it is clear that Zn metal is responsible for the current shoulder in both kinds of junction. It is known that ZnS dissociates on evaporation,[18] so one expects to find free Zn on the sample, along with the ZnS and possibly some free S. The latter two materials would simply be incorporated into the tunneling barrier and could not produce the observed effect.

Another effect of the Zn or ZnS is to reduce the energy gap. We use the following working definition of this gap. For most of our thin pure-Pb samples, whether on glass or mica substrate, the resistance minimum is located at 2.78 ± 0.01 mV. We assume that the two films have very nearly the same density of states, and therefore that the gap in all our thin Pb counterelectrodes Δ_c is 1.39 ± 0.01 meV. For thick Pb films the situation is complicated by the existence of multiple gaps,[17,19] but this does not seriously affect our conclusions. We determine the gap of the Pb-Zn sandwich by subtracting Δ_c from the voltage of the resistance minimum. Following this procedure we find values of the Pb-Zn gap in the range 1.26–1.37 meV, with no significant difference between samples with Zn and those with ZnS. The gap tends to be correlated with the current shoulder, and is smaller in junctions with a large shoulder.

The transition temperature, in contrast, does not depend on the presence of Zn or ZnS. For almost all of the samples for which it was measured, T_c lies in the range 7.19 ± 0.03 K,[20] determined from the resistance of a germanium thermometer at the temperature at which all superconducting structure disappears from the tunneling resistance characteristic.

We have never seen the current shoulder in ordinary Pb-PbO_x-Pb junctions. Zn- and ZnS-doped samples always exhibit the shoulder, provided that the first Pb film is less than about 3000 Å thick. This is true for samples made on glass substrates held at room temperature during deposition of the first Pb film, leading to a (111) textured Pb film, as well as for samples made on heated mica substrates with a resulting (111) epitaxial Pb structure.[13]

For Pb films 3000 Å and thicker, the shoulder does not appear in the I-V characteristic, but the current at voltages higher than 2Δ is greater than it is for pure-Pb junctions. This is in accord with the results for samples with thin Pb layers. Tomasch oscillations[21] and multiple gaps[17] are observed with these thick Pb samples. If a small amount of Tl (less than 1 wt.%) is mixed with the Pb in the evaporation source, so that the Pb films are Tl doped, then the current shoulder appears even for thick Pb-Tl films, and Tomasch oscillations do not appear. The amount of Tl is very small, as indicated by negligible reductions in T_c and small reductions (from 150–300 to 30–150) in resistivity ratio.

As noted above, the form of the current shoulder in Fig. 3(b) is as if a current peak were added to the pure-Pb characteristic of Fig. 3(a). The size of this added current varies from sample to sample, but its shape does not. It generally becomes higher and sharper as the first Pb film thickness is decreased. For some thin Pb samples, there is even a negative resistance region on the upper side of the added peak. Our information on the Zn-thickness dependence of the peak is limited to one sample in which all three of the junctions on one side of the Zn patch [see Fig. 1(a)] were good. For that sample, the current shoulder became less distinct and the energy gap increased with increasing distance from the Zn patch, presumably due to decreasing quantity of Zn. This, of course, is the expected result.

We believe that these observations result from a modification of the superconducting Pb density of states by the proximity effect, involving a substantially thinner N layer than in any previous experiments. Previous work[1–3] indicates that for N films a few hundred angstroms thick (and thicker S films) the density of states exhibits a double peak, with both the energy gap and the transition temperature smaller than for the homogeneous pure superconductor. It further shows that as the N thickness decreases, both the gap and T_c approach their pure-S values. These observations are qualitatively predicted by the McMillan theory,[8] which we discuss in Sec. IV.

IV. MCMILLAN THEORY

Theories of the proximity effect have been limited by the difficulty of treating inhomogeneous superconductors. The McMillan approach[8] avoids this problem by some simple assumptions. First, it is assumed that both layers are thin enough so that their properties are uniform across their thickness. This requires that they be thin compared to their coherence lengths. Second, it is assumed that the two layers are weakly coupled so that the coupling can be treated in second-order self-consistent perturbation theory. The assumed coupling has the form of a transfer Hamiltonian, commonly used for tunneling problems. Third, the transmission probability of electrons incident on the N-S interface from both sides is assumed to be independent of their energy and direction. Fourth, it is assumed that the electron-electron interaction in each film is BCS-like (or zero for a strictly normal N material). Finally, it is assumed that the films are reasonably clean so that the mean free path is roughly equal to the film thickness.

In this model, each film acts as a perturbation on the electrons of the other, so that the density of states in each is modified. The important parameters of the theory are Γ_S and Γ_N, which are defined as $\hbar/2\tau_S$ and $\hbar/2\tau_N$, respectively, where $\hbar$ is Planck's constant divided by 2π and $\tau_{N(S)}$ is the mean time that an electron spends in the $N(S)$ film before tunneling into the other. Note that the third assumption above implies that τ is the same for all the states of one film. The Γ's can be written as follows[22]:

$$\Gamma_{N(S)} = \hbar v_{FN(S)}\sigma/Bd_{N(S)} ,$$

where v_F is the Fermi velocity, σ is the transmission probability for an electron incident on the N-S interface, d is the film thickness, and B is a function of the ratio of d to the mean free path. According to McMillan[8] the value of B for reasonably clean films is around 2. If v_F is 10^8 cm/sec and B is 2, then Γ is $800\sigma/d$ meV, with d in angstroms. (Throughout this paper the units of Γ are meV.)

We will use the McMillan theory in Sec. V as a means of relating our observations to those of earlier experiments on thicker N layers. We must therefore establish to what degree the theory is confirmed by those experiments. Direct comparison with experiment is difficult, because one does not know the value of σ and therefore the Γ's. One can only assume that with sufficient experimental care, σ is about the same for all samples made the same way. With this qualification in mind, let us consider previous results.

Adkins and Kington[4] have reported measurements of the energy gap of N-Pb sandwiches, using Ag, Cu, and Sn as the N metal. They adjust σ/B_N in the McMillan theory to reproduce gap-versus-d_N curves for d_N between 100 Å and a few thousand Å, and $d_{Pb} = 5000$ Å, much greater than the Pb coherence length (800 Å). From this fit, they estimate that σ is rather large: ~0.1 for Cu and Ag and ~0.5 for Sn. Thus, the range of validity of the theory seems to be exceeded in both these aspects, but they find excellent agreement with experiment for all three N metals. Gilabert *et al.*[6] also find good agreement for the temperature dependence of the gap in Sn-Pb sandwiches.

In addition to the gap, the McMillan theory predicts an excitation spectrum at all energies for each layer of the sandwich. The spectrum is decidedly different from that of a homogeneous superconductor. In particular, it is predicted that the N density of states exhibits a double peak over a wide range of thicknesses for $\Gamma_N > \Gamma_S$. Vrba and Woods[1,3] observed doubly peaked densities of states, the peak positions varying with temperature as predicted, at least for temperatures well below T_c. (See, for example, Fig. 9 of Ref. 1.) The observed peaks are much less sharp than those predicted, however. This is not surprising, since even for homogeneous superconductors some form of gap smearing must be invoked to fit tunneling data. Vrba and Woods[3] point out another source of smearing in the proximity sandwiches: Variation in the Γ's due to variation in the film thickness and especially in the coupling strength over the area of the interface. By assuming an arbitrary distribution of the Γ's they find that the fit can be improved, but is still far from perfect.[3]

Careful consideration of the published data indicates that a quantitative determination of the Γ's for a given sample is difficult. It is important to emphasize, more strongly than previous authors have done, that if different methods are used to determine the Γ's the resulting values differ by as much as a factor of 5 (Table I of Ref. 1 and Tables I and II of Ref. 2). The preceding paragraph suggests that the problem may lie partly in large variations of σ over the sample area. Clearly every effort should be made in experiments to make the interface as uniform as possible, and to make many samples with the same value of σ. While such efforts may improve the comparison of theory and experiments, previous efforts with Γ distributions suggest that a quantitative fit is not possible.

Further information on this point should be available from the tunneling current for a voltage V somewhat higher than the sum of the gaps, where the current is no longer changing rapidly with voltage. This quantity is a measure of the total number of states of energy less than $eV - \Delta_c$, that is, the number of states in the peaked part of the proximity density of states. This measure should be insensitive to peak sharpness and to other details of the density of states at low energy. Unfortunately, current-voltage curves for proximity superconductors have not usually been published, as conductance is normally considered to be the quantity of interest. However, graphically integrating Fig. 9 of Ref. 1 suggests that the current at 1.0 mV for the theoretical proximity junction is about 10% larger than for the experimental one, indicating that too many states are predicted to be close above the gap edge. We will discuss this point further in Sec. V.

The above considerations suggest that the McMillan theory gives a good qualitative description of the energy gap and density of states of proximity superconductors. The thin-film and weak-coupling requirements assumed in deriving the theory appear to be relatively unimportant. Attempts to fit the density of states quantitatively, however, indicate substantial differences between theory and experiment. It is not clear at present whether these differences are due to sample nonuniformity or to the fundamentals of the theory. We conclude that while the theoretical basis and some details of the density of states in the McMillan approach are open to question, its predictions provide an acceptable means, the best available, of classifying and comparing experimental observations.

V. COMPARISON OF THEORY AND EXPERIMENT

In this section we use parameters appropriate to our samples in the McMillan theory and compare the results with our experiments. We must first estimate approximate values for the Γ's. We expect d_N to be on the order of 3 Å, corresponding to one atomic layer. Our Pb films are exposed to the vacuum atmosphere for a long time, during part of which they are hot, before deposition of the Zn. Therefore, we expect the coupling to be considerably less than one. We estimate $\sigma = 0.05$. If we further assume $v_F = 10^8$ cm/sec and $B = 2$ (mean free path $\approx d_N$[8]), we find $\Gamma_N = 13$. With the same assumptions and $d_S = 1000$ Å, we find $\Gamma_S = 0.04$. These, of course, are very rough estimates; they express the order of magnitude which we expect may give agreement with our experiments.

We have solved the McMillan equations for several values of Γ in this range and have used the resulting densities of states to calculate current-voltage curves, shown in Fig. 4. Zero temperature is assumed in these calculations, introducing negligible error since at 1.2 K, kT is much less than the energy gap of the proximity sandwich. The counterelectrode in these calculations is assumed to be a superconductor with Δ a complex constant such that $\Delta^2 = 1.39^2 + 0.05i$, and the usual strong-coupling form for the density of states.[23] This amounts to a BCS superconductor with the gap edge smeared by the amount required to fit Pb-PbO_x-Pb tunneling curves. This density of states is not quite normalized, but the error is small and unimportant. A current shoulder similar to that observed experimentally is predicted for Γ_N around 7. The dependence on Γ_S is very weak, consisting of a slight sharpening of the current shoulder and a slight increase in the gap-edge energy as Γ_S is decreased. Variations of Γ_S have no effect on the current above about 3.5 mV. The dependence on Γ_N is very strong, as shown in Fig. 4. As Γ_N is decreased, implying either weaker coupling or thicker N layer, the current shoulder gets larger, the energy gap decreases, and the current at voltages well above the current step increases.

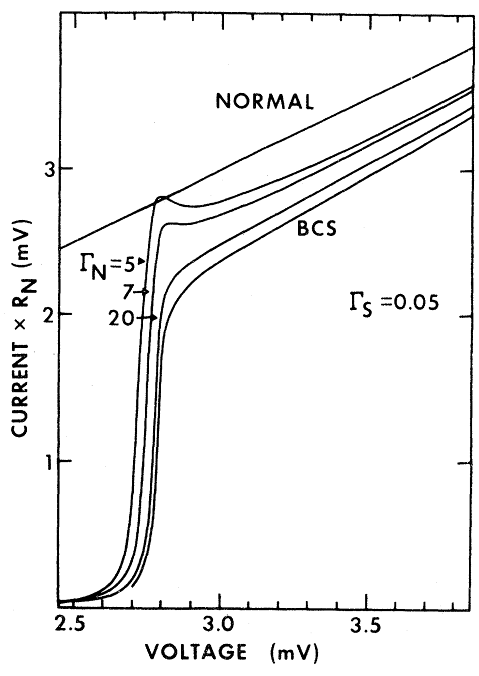

FIG. 4. Predicted current-voltage curves according to the McMillan theory for tunneling between the Zn side of Pb-Zn proximity sandwiches with the parameters shown, and a smeared BCS superconductor at $T = 0$ K. The curve labeled BCS is for tunneling between unsmeared and smeared BCS superconductors. The error inherent in the assumed smearing makes all the curves about 1% too low at the high-voltage side of the figure.

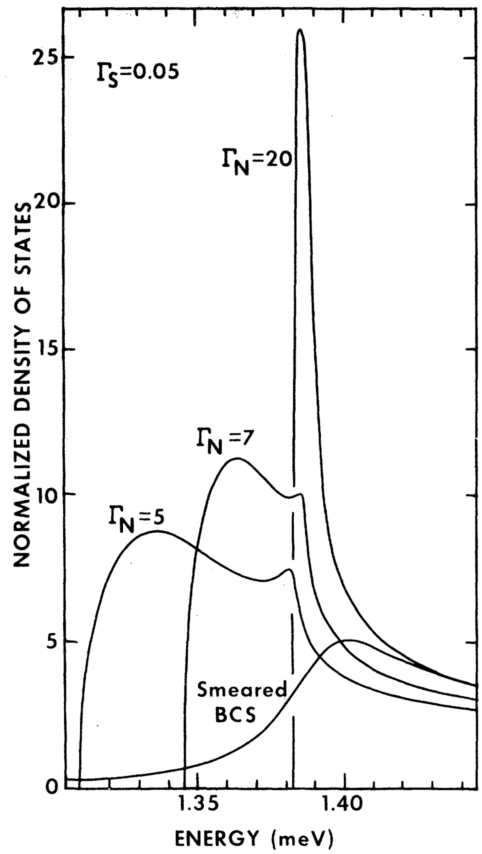

FIG. 5. McMillan and smeared BCS densities of states used to calculate the tunneling curves of Fig. 4.

The proximity densities of states leading to these curves are shown in Fig. 5. A double peak is predicted for some Γ values as in the thicker N case discussed above, but the higher energy peak is so sharp that it is not resolved in the theoretical tunneling characteristic, even though no smearing has been assumed for the proximity superconductor. A smeared BCS density of states, as used for the counterelectrode is also shown in Fig. 5. The important effect of the proximity layer is that the number of states in a narrow energy range above the gap edge is increased relative to the number for an ordinary superconductor. It is this increase which leads to the higher current and the current shoulder observed with the proximity superconductor. The proximity density of states at higher energy is reduced so that normalization is maintained. This reduction is spread over a wide energy range with no apparent structure. Thus, the sharp resistance peak associated with the current overshoot does not indicate a corresponding dip in the density of states as one might expect.

Comparison of Figs. 3 and 4 shows that the size and shape of the current shoulder is well reproduced by $\Gamma_N = 7$. However, the fit is not quantitative; we find the same deviations as in Vrba and Woods's experiments.[1-3] If instead of fitting the current shoulder we fit the energy gap, we find $\Gamma_N = 5$. If we fit the current at a voltage well above the sum of the gaps, say 3.5 mV, we find $\Gamma_N = 20$. These correspond to N thicknesses of 5, 8, and 2 Å, respectively. As noted previously, the dependence on Γ_S is weak; we take $\Gamma_S = 0.05$, corresponding to $d_S = 1000$ Å, $v_F = 1.2 \times 10^8$ cm/sec,[24] $B = 2$, and $\sigma = 0.05$.

If Γ_N is chosen to fit the energy gap, then the predicted current shoulder is much too big. We have noted previously that in order to fit pure-S tunneling data it is necessary to smear the density of states. For the proximity superconductor we expect such smearing to reduce the size of the current shoulder and thus improve the fit in this respect. For a BCS material the smearing is conveniently accomplished by adding a small imaginary part to Δ, which produces only a small and unimportant error in normalization. A similar procedure with a proximity superconductor does not work well. Since in this case $\Delta(E)$ is not constant, the modification due to adding an imaginary constant is highly arbitrary, depending unpredictably on the size of the added constant.

As noted in Sec. IV, Vrba and Woods[3] have smeared their McMillan density of states by assuming a distribution of the Γ's due to a nonuniform σ, a reasonable assumption. In Fig. 6 we have assumed a simplified distribution, with $\Gamma_N = 5$ in 0.9 of the effective tunneling area and no Zn (smeared BCS) in the remaining area. This procedure is no more arbitrary and considerably less tedious than calculation with the smoother distributions of Vrba and Woods.[3] Clearly, the desired result is obtained: The current shoulder is reduced in size without significantly changing the energy gap. It is likely that other, perhaps more realistic, Γ_N distributions could be found to adjust the fit more precisely.

We find, however, that no such distribution can fit the experimental current at higher voltages. Since Pb is not a BCS material, and this is a BCS theory, we must specify exactly what is meant by fitting the current. The current I_S in an ordinary Pb-PbO_x-Pb junction at 3.5 mV is about 92% of the normal value I_N at that voltage, while that of a BCS junction of the same gap is only 86%.

Thus, direct comparison of the current is not possible, and instead we compare the experimental shift produced by Zn in the junction with the corresponding theoretical shift resulting from the McMillan density of states. Implicit in this approach is the assumption that the modification of

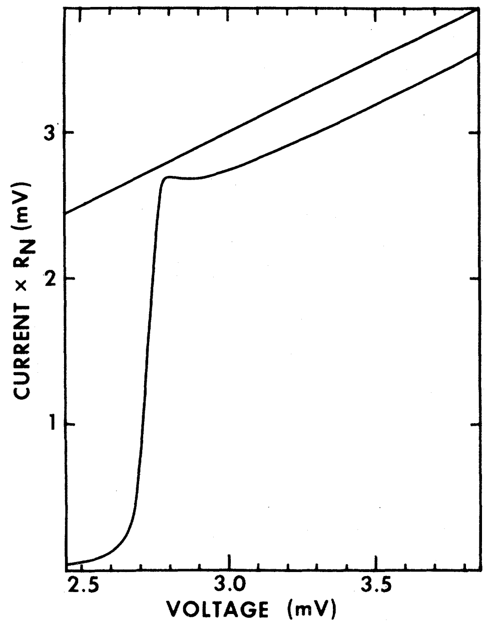

FIG. 6. Calculated current-voltage curve as in Fig. 4, with $\Gamma_N = 5$, $\Gamma_S = 0.05$ for 90% of the current and smeared BCS (i.e., zero N thickness) for the remaining 10%.

the Pb density of states by the Zn layer is about the same as the corresponding modification of a BCS superconductor of the same gap. It is convenient to speak of the difference between the normal and superconducting currents, 8% for pure-Pb junctions and 14% for BCS junctions.

For junctions exhibiting a current shoulder, I_S is 6 or 7% less than I_N at 3.5 mV, with no clear correlation with the size of the current shoulder. Thus, the shift in current at 3.5 mV with addition of Zn or ZnS is an increase of 1 or 2%, small but significant. The shift in current predicted by the McMillan theory, however, is very large. Figures 4 and 6 show that the current for $\Gamma_N = 5$, which approximately fits the energy gap, is 92% of I_N, a shift of 6%, very much larger than is experimentally observed. Even if we make Γ_N so large that the current shoulder does not appear at all, the shift in current is still too big. Thus, it is quite clear that no gap smearing or Γ distribution which fits the energy gap and current shoulder can simultaneously fit the current level at higher voltage.

The current at voltage V gives a measure of the total number of states of energy less than $eV - \Delta_c$, where Δ_c is the gap of the counterelectrode. Unless V is very close to $\Delta + \Delta_c$, in the range of rapid current change, this quantity is only weakly dependent on the details of the density of states in the peaked region. Therefore, this deviation between theory and experiment is an important one, suggesting that the theoretical predictions are incorrect not only in the sharpness and relative heights of the peaks as noted by Vrba and Woods,[1,3] but also in over-all distribution of states. The prediction is for too many states close above the gap edge, and hence, too few at higher energy. We noted in Sec. IV that other investigators have not reported tunneling-current data, but only derivatives, so that a check of the McMillan theory on this point for the thicker film samples is difficult. Integration of one pair of conductor curves suggests that for that one case the predicted current is too high (see Sec. IV).

The theory predicts that the current overshoot should sharpen with decreasing Γ_S, that is with increasing d_S, while the opposite is observed experimentally. For these thicker films, several thousand angstroms, d_S is large compared with the coherence length (800 Å), so the assumption of the McMillan theory is not satisfied, and this divergence is perhaps not surprising. Junctions made with Pb-Tl alloy films and ZnS doping show a small overshoot which is independent of the S film thickness. Again the divergence from theory is not surprising, since the mean free path in Tl-doped films is shorter than the film thickness.

With regard to the transition temperature, the McMillan theory for $\Gamma_N/\Gamma_S = 100$ and the other parameters appropriate to our samples predicts a reduction in T_c of 0.5%. Experimentally, no difference in T_c between samples with and without Zn is observed, with an experimental scatter between samples of $\pm 0.5\%$. Thus, if a reduction of 0.5% existed, it should be just observable. However, it is likely that the average N thickness of our samples, which we expect to determine T_c, is less than that in the areas involved in tunneling (see Appendix), so that the average $\Gamma_N/\Gamma_S > 100$ and the shift in T_c is reduced. Therefore, there is no deviation between theory and experiment on this point.

VI. CONCLUSIONS

We have demonstrated that the observed current shoulder is produced by the presence of the Zn layer. It may be understood as the result of the proximity effect in the limit of an extremely thin N layer, substantially thinner than in any previous experiments. Using the results of earlier experiments involving thicker N layers, in which the mechanism involved is clearly the proximity effect, we have elucidated the degree of validity of the predictions of the McMillan theory. We find that the predicted behavior of the energy gap and the qualitative nature of the density of states agree rather well with the available experimental data. However, the details of the predicted density of states, and especially the total number of states in the energy range of rapid change, do not agree well with experiment. It is not clear whether this deviation is due to nonuniformity or other imperfection of the samples, or to some fundamentally incorrect factor in the theory.

The next step is to apply the McMillan theory to our samples. We find that in broad terms agreement is qualitatively good just as in the thicker N experiments. In particular, a current overshoot of the right general shape is predicted. One deviation, the size of the predicted overshoot, can be explained by the presence of either thickness or coupling nonuniformity, both of which are likely. The other deviation, the current at higher voltage, which is roughly a measure of the number of states close to the gap edge, cannot be explained by such smearing. However, this deviation appears to be similar to one observed in the thicker N samples. Thus, to the extent that the McMillan theory is confirmed by earlier experiments, the theory agrees with our observations, and the principal deviation between our observations and the theory also seems to occur in the thicker N samples. We therefore conclude that the features observed in our experiments and those of the earlier ones result from the same physical mechanism, the proximity effect.

Current shoulders similar to the one reported here have been seen in junctions made with Nb,[10,11,25,26] La,[27] and Pb-In[28] alloys. In all of these systems we can reasonably suppose the existence of a surface layer of material which, if isolated, would have a lower transition temperature than the underlying material. The most common observation of the shoulder has been with Nb-NbO_x-superconductor junctions, both with bulk and film Nb. This was first reported in 1961[10] and repeatedly since then, but has only recently been explained by the authors[29] and independently by two other investigators.[25,26] The current shoulder for Nb is explained in terms of the proximity effect between an oxygen-rich surface layer and the underlying pure Nb. However, as there were no calculations to support this explanation, there were some points in the earlier work which can be clarified by comparison with the theory and experiment presented here.

As noted in Sec. IV, the McMillan theory predicts two peaks in the density of states, the higher-energy one located very close to the gap of the unperturbed S material. Shen[25] has suggested that this peak appears as a specific feature in the I-V curve. Careful consideration of Figs. 3–5 shows that this is not the case, probably because the peak is very small and narrow (Fig. 5), even without the gap smearing which surely exists in real samples. Our experiments indicate that this higher-energy peak is not resolved in resistance-voltage data either.

The current shoulder appears in derivative data as a very sharp resistance peak located just above the gap-edge resistance minimum. Schwidtal[26] has suggested that this peak results from a dip in the density of states at the corresponding energy. The present work shows that this is not the case. The current shoulder results from states added to the gap-edge peak, not from states removed at slightly higher energy.

It appears[25,26] that Nb junctions always have a current of several percent of the normal-state value at voltages between the counterelectrode gap and the sum of the gaps. This large excess current has been attributed[26] to a gapless density of states resulting from the proximity effect. In our experiments, however, the current shoulder is about the same size as in the Nb junctions, indicating a comparable proximity effect, but negligible excess current is observed. (This current is less than 0.1% in many junctions, both with and without Zn. As in the Nb case, the current is much larger above the counterelectrode gap than below.) Further, gaplessness is not to be expected for extremely thin layers from the McMillan theory. For both these reasons we believe that the excess current does not arise from the same source as the current shoulder.

This work clearly shows that the current shoulder results from the proximity effect, as suggested earlier.[25,26,29] We suppose that the La observation[27] can be explained in the same way as the Nb ones. As for the Pb-In alloy films[28] we suggest that an In-rich surface layer may be present, playing the role of the Zn in the present work.

Our experiments show that superconducting tunneling, making use of the proximity effect, provides an extremely sensitive test for the presence of an inhomogeneous metallic surface layer. The previous observations given above are examples of this application, which might be particularly useful for alloy films.

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APPENDIX: *N*-LAYER CONFIGURATION

Because the *N* layer and the insulating barrier are so thin, their properties are difficult to study other than by tunneling. We discuss in this Appendix the available evidence on the structure of these layers. Further normal-state tunneling data and discussion of the barrier are given elsewhere.[30]

We can estimate from the microprobe data of Sec. II the Zn distribution on a scale comparable with junction dimensions, but no method is readily available for measuring it on a much finer scale. We can imagine many different configurations, including (i) a uniform Zn film covering the entire surface, (ii) Zn mixed with the first layer or two of Pb atoms to form a surface alloy, or (iii) isolated islands of Zn perhaps located at grain boundaries of the underlying Pb. The first of these possibilities is very unlikely, since for the junctions farthest from the Zn patch we believe that there is not enough Zn to make a uniform layer. The second possibility cannot be completely ignored even though the solubility of Zn in bulk Pb is very low ($\lesssim 0.1$ wt.% at 318 °C),[31] since the behavior of the first layers of Pb might be very different from the bulk. However, a uniform $\dot{N}$ layer is still unlikely, and we expect the third possibility to be closer to reality, with the provision that the islands may not be pure Zn.

These islands could be several atoms thick, implying the presence of substantial areas with much less, perhaps zero, Zn coverage. In this situation it is likely that most of the tunneling current passes through the Zn-covered areas due to variation in the oxide thickness. Our experience is that if a thick Zn film on top of Pb is oxidized with the same glow discharge parameters normally used for Pb, a barrier is not formed—the junctions are completely shorted. This suggests that Zn oxide is not as readily formed under these conditions as is Pb oxide. This assertion is supported by physical-chemical data, showing that near their melting points Pb oxidizes about 100 times faster than Zn,[32] although of course the conditions are much different in those experiments. Also, in the one Pb-Zn-oxide-Pb sample with all three good junctions (see Sec. III), the junction resistance increased substantially with distance from the Zn patch, that is, with decreasing quantity of Zn. These observations suggest that the barrier in Zn-coated areas is probably thinner than in uncoated areas. Because tunneling current is extremely sensitive to the barrier thickness, we therefore believe that even if the *N* layer does not completely cover the surface, most of the current passes through *N*-coated areas.

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Magnetic Properties of Vanadium and Niobium at $T = 0\,^\circ$K

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The boson method in superconductivity is applied to the study of the mixed state of pure vanadium and niobium at zero temperature. The magnetization curves around H_{c1} are presented and are in good agreement with experimental data. The results depend on the constant $\alpha = \frac{1}{18}\pi^2 N(0)V$, which plays an important role in the boson method. Although the transition at H_{c1} is of the second order, the magnetization curve is very similar to what one would expect for a first-order transition.

I. INTRODUCTION

In one of our preceding articles[1] we studied the problem of vortices in type-II superconductors by making use of the boson method in superconductivity. There we were able to calculate the distributions of current and magnetic field, not only outside the core, but also *inside the core*. The purpose of this paper is to apply these results to the study of the magnetic properties of pure type-II superconductors. (Impurity effects will be considered in a future publication.) Although the boson method has been formulated so as to be applicable to superconductors at any temperature, in this paper we shall concentrate on cases at zero temperature, because the magnetic properties at T close to T_c have been studied extensively by use of the Ginzburg–Landau equation.[2] In the case $T = 0$ one meets the hard problem of solving the Gor'kov equation or the Bogoliubov equation. A study of type-II superconductors along this line of approach has been attempted by Bardeen *et al.*[3]

The derivation of the boson method has been presented in a series of papers.[1,4,5] In this approach one begins with the case of a position-in-