Investigations of the Proximity Effect by Electron Tunneling

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We have investigated the proximity effect in the Ag-Pb, Cu-Pb, and Sn-Pb systems by electron tunneling. A well-defined gap structure is induced in the normal metals by contact with the superconductor and, in tin below its transition temperature, the gap is augmented by the proximity of the lead. The results are in reasonable agreement with a theory of McMillan's and indicate electron transmission coefficients at the Ag-Pb, Cu-Pb, and Sn-Pb interfaces of about 0.1, 0.1, and 0.5, respectively.

1. INTRODUCTION

WHEN tunneling occurs between a normal metal and a superconductor, the normalized differential conductance of the junction σ is related to the normalized density of states in the superconductor $n(\epsilon)$ by the well-known result

$$\sigma(V,T)=-\int_{-\infty}^{\infty} n(\epsilon)\frac{\partial}{\partial V}\{f(\epsilon+eV)\}d\epsilon, \qquad (1)$$

where V is the applied voltage, T is the temperature, and f is the Fermi function. At finite temperatures σ is thus a smoothed version of n, the smoothing being about $2kT$, so that from measurements of σ it is possible to infer the nature of n. Such experiments may be used to investigate the proximity effect by tunneling from a normal metal into a layered structure to give the excitation spectrum at the tunneling interface. We have applied the technique to the Ag-Pb, Cu-Pb, and Sn-Pb systems.

2. EXPERIMENTAL DETAILS

A. Sample Preparation

Samples were prepared by evaporation in a conventional vacuum system operating at better than 2.10^{-5} Torr, the substrate being held at room temperature. Attempts to prepare tunneling specimens at ultrahigh vacuum (about 10^{-9} Torr) were unsuccessful, due, at least to some degree, to agglomeration of the metal films deposited under these conditions. This effect would also have rendered interpretation of the proximity results difficult, as it implies local variations in the thicknesses of the deposited layers. Liquid-nitrogen cooling of the substrate during deposition to make the metal layers more continuous and flatter failed because of annealing in the films when they were subsequently raised to room temperature for mounting in the cryostat.

The construction of an experimental specimen is shown in Fig. 1. Aluminum strips about 0.2 mm wide were first evaporated through a mask onto a microscope-slide substrate. An insulating film of collodion or G.E. 7031 varnish was painted on, leaving a small area exposed at the center of each strip. The aluminum was then oxidized in damp air to give tunneling impedances of about 10 Ω. Lower values meant that four-point measurements could not be made to the junction due to the series resistance of the aluminum; higher resistances gave problems of electronic noise. The two metals of the proximity couple, for instance, copper and lead, were finally evaporated through masks using a rotary changer, a period of a few seconds elapsing between evaporations. In this way, several proximity junctions as well as separate reference junctions to the superconductor and normal metal were manufactured. Minor misalignments of the masks and lack of definition of the edges of the proximity sample do not affect the results as the tunneling junction is defined by the insulation.

Film thickness was measured during deposition with a quartz-crystal microbalance, care being taken to ensure that the area of crystal exposed was the same throughout the experiment, that the crystal oscillations were not heavily damped by the deposit, and that a stable oscillation of the correct mode was operating.[1] With these precautions, a sensitivity of 1 Å of evaporated material and accuracies of better than 5% over the range of use were achieved.

B. Choice of Materials

Aluminum was always used as the normal electrode of the tunnel junction and this restricted the temperature range of the experiment somewhat. However, this disadvantage was more than outweighed by the ease of junction formation and the smooth surface presented by

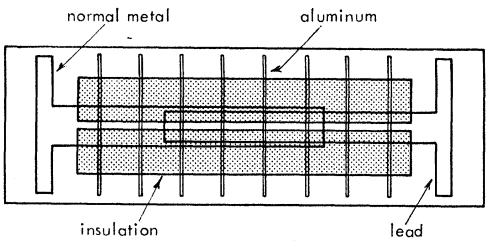

FIG. 1. Details of sample construction.

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[1] B. W. Kington, Marconi Instr. **10**, 81 (1964).

the aluminum as a substrate for the subsequent evaporations.

In the proximity layers it is necessary to ensure that there is as little interdiffusion as possible so that the system approaches an ideal contact between pure metals. Some experimenters[2–4] have achieved this by keeping the substrate at low temperatures through deposition and measurement. However, this results in disordered films with short mean free path, and casts doubt on the interpretation of thickness measurements. We have chosen to minimize interdiffusion by choosing couples of limited solid solubility.[5] On this criterion, and using lead as the superconductor, copper and silver are especially suitable. To these was added tin which, although having a 3% solubility in lead at room temperature, is of interest through becoming superconducting in its own right within the temperature range investigated. Aluminum, although essentially insoluble in lead, is not a particularly good metal for proximity experiments for reasons which we have discussed in an earlier paper.[6]

C. Film Properties

The proximity effect is dependent on the material properties of the deposited layers. It is therefore necessary to establish that these are reproduced on samples prepared at different times and also to attempt to measure them. The most important of these are electron mean free path, degree of continuity of the layers, and the nature of the interface between the two metals. All are dependent on preparation conditions, and thus standard, but otherwise arbitrary rates of deposition were established and the pressure was held between 2.10^{-6} and 2.10^{-5} Torr during evaporation.

To determine the mean free path, resistance measurements were made on samples of the various films at 4.2°, or, for lead, above the critical temperature. From these, it was estimated that the residual electronic bulk mean free paths were usually in the ranges 400±100 Å for copper, 850±100 Å for silver, 2000±400 Å for tin, and greater than 2000 Å for lead. Sometimes, especially with thinner films, values of resistivity were found which were anomalously high as against what would be expected from the Fuchs-Sondheimer theory.[7] As no anomalies were seen in other measurements (for instance, optical absorption or the tunneling characteristics), these were attributed to gross but localized faults in the film structure. Complete electrical discontinuity of the films occurred at thicknesses much less than those used in the experiments.

To confirm that the films were continuous (and that any superconducting properties observed in a normal material backed by a superconductor were not due to observations of the superconductor through holes in the normal metal), electron microscope studies were made of thin films of the various metals deposited onto oxidized aluminum to simulate the actual experimental conditions. No pores were observed at the minimum thicknesses of the proximity specimens. Furthermore, there was no evidence that alloying on a gross scale occurred in the superimposed films: Films down to 100 Å deposited on the other metal retained the appearance of the isolated metal and electron diffraction of the superimposed films showed the characteristics of the individual components.

At the pressures holding in the vacuum system there is the possibility that an impurity layer has time to form between the two films of the proximity structure. Such a layer would reduce the coupling between the metals and inhibit the proximity effect. The crystal thickness gauge was used to test for such contamination directly by looking for accretion immediately after the deposition of a fresh metallic layer. Absorption of a monolayer of gas would result in a change of frequency of about 4 cps, which is readily observable. After 1 min., no adsorption was observed on copper, silver, and tin, which in general were first deposited and then coated with lead, while lead appeared to have about half a monolayer coverage. Aluminum became covered by a monolayer in the same time, most of the adsorption occurring within about 15 sec. On the evidence of exposing the clean surface to atmospheric pressure and studying the adsorption, silver was the least subject to contamination.

D. Instrumentation

The instrumentation was similar to that described in our earlier work.[6] The tunneling conductance or the I-V characteristics could be plotted directly. The ac signal used to differentiate the characteristic was kept at 90 μV peak to peak, which introduced negligible smoothing at the temperatures of the experiments.

3. EXPERIMENTAL RESULTS

In all of the experiments described here, the normal metal into which the tunneling takes place is backed by some 5000 Å of lead. The lead therefore acts essentially as bulk material, being much thicker than the coherence length, and the experiment measures the density of states in the normal metal at the surface next to the tunneling barrier. We interpret the results by comparing the measured conductances with those calculated for a BCS density of states.[8] This enables a value to be given to the energy gap at the tunneling surface and qualitative remarks to be made about the general shape and

[2] J. J. Hauser, (a) Physics (N. Y.) **2**, 247 (1966); (b) Phys. Rev. **164**, 558 (1967).
[3] P. Hilsch and R. Hilsch, Z. Physik **180**, 20 (1964).
[4] R. Frerichs and J. P. Wilson, Phys. Rev. **142**, 264 (1966).
[5] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Co., New York, 1958).
[6] C. J. Adkins and B. W. Kington, Phil. Mag. **10**, 971 (1966).
[7] E. H. Sondheimer, Advan. Phys. **1**, 1 (1952).
[8] S. Bermon, Technical Report, Department of Physics, University of Illinois (unpublished).

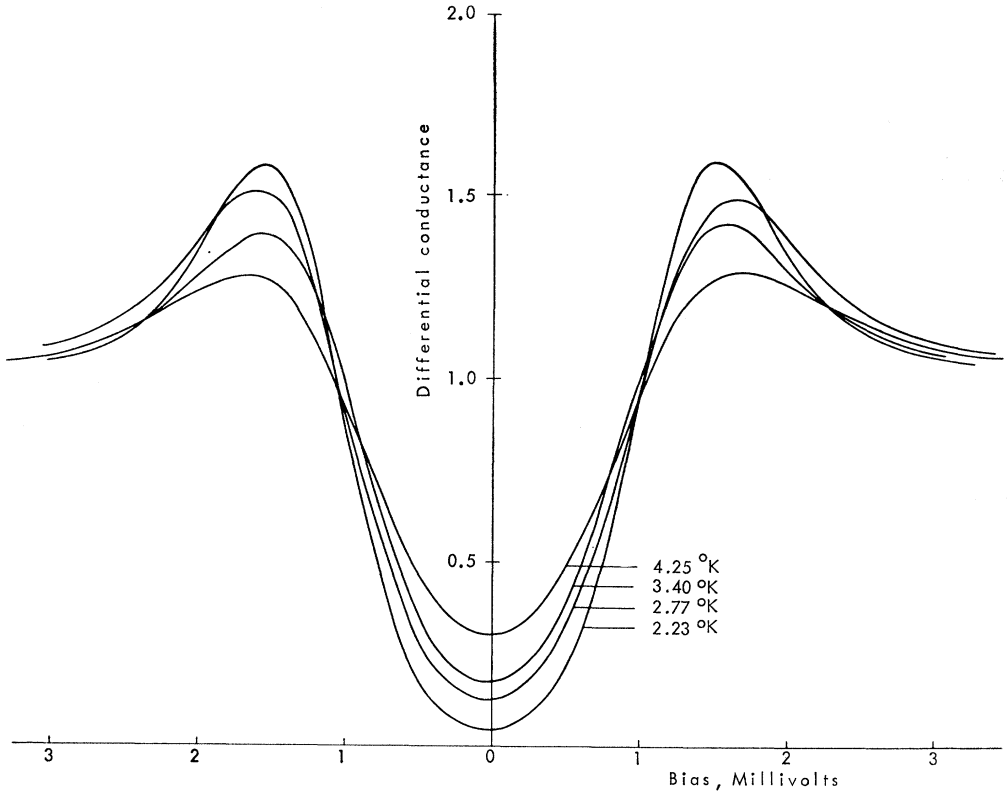

FIG. 2. Differential conductance as a function of bias voltage for tunneling into a 130-Å silver film backed by 5000 Å of lead.

specific features of the density of states. To assist with this comparison, three parameters in the conductance curves have been identified: σ_0, the normalized conductance value at zero bias; V_1, the voltage at which the conductance reaches unity as the bias is increased; and σ_{max}, the maximum value of conductance. Tabulated values of these parameters as a function of material, film thickness, and temperature have been recorded elsewhere.[9]

The experiments showed good reproducibility. We sometimes encountered the leakage currents which have troubled other workers[10]; but their variability showed that they were associated with blemishes in the tunneling junction rather than with any fundamental property of the proximity structure. Rejecting samples in which the leakage currents were large, we achieved a reproducibility in the conductances of $\pm 2\%$ for similar samples which were prepared at the same time and of $\pm 5\%$ for ones prepared at different times.

A. Energy Gap Induced in a Normal Metal by a Thick Superconductor

The outstanding feature of the differential conductance curves is the well-developed gaplike structure (Fig. 2). We shall show that the results are consistent with the presence of a well-defined energy gap.

There are at least three ways of estimating the size of the energy gap: One may simply take the value of V_1 as Frerichs and Wilson[4] did; but reference to the tabulated values for the BCS case[8] shows that V_1 may be very different from the true gap (except, of course, at $T=0$). Correction of V_1 using the BCS model is an improvement; but the value of V_1/Δ is quite sensitive to the form of the density of states just above the gap, and, in fact, one obtains values of V_1/kT in proximity experiments which are impossible for a BCS density of states. The value of σ_0 depends less on the form of the density of states just above the gap, and so appears to offer a better means of estimating the gap, although even this can be misleading if there is a resistive bridge across the barrier or if the excitation spectrum is gapless.

Assuming for the moment that the density of states is not gapless, we use the values of σ_0 from curves like those of Fig. 2 to obtain the energy gap as a function of film thickness and temperature. The results are shown in Fig. 3.

Now if the spectrum *were* gapless, the low-energy states would be most noticeable at low temperatures where they would significantly augment the values of σ_0, and, in our interpretation, give the appearance of a

[9] B. W. Kington, thesis, University of Cambridge, 1967 (unpublished).

[10] T. Claeson, S. Gygax, and K. Maki, Physik Kondensierten Materie **6**, 23 (1967).

decreasing gap. Referring to Fig. 3, we see that there is some tendency for the estimated gap values to decrease at low temperatures. However, this effect could be caused by residual leakage currents or by the presence of a density of states which is not BCS-like. (A gradual rise could produce the same result since we used tables based on the BCS model.) If we calculate the sizes of the extra contributions to σ_0 which would be necessary to account entirely for the apparent decreases, we find (a) that there is no regular variation with the thickness

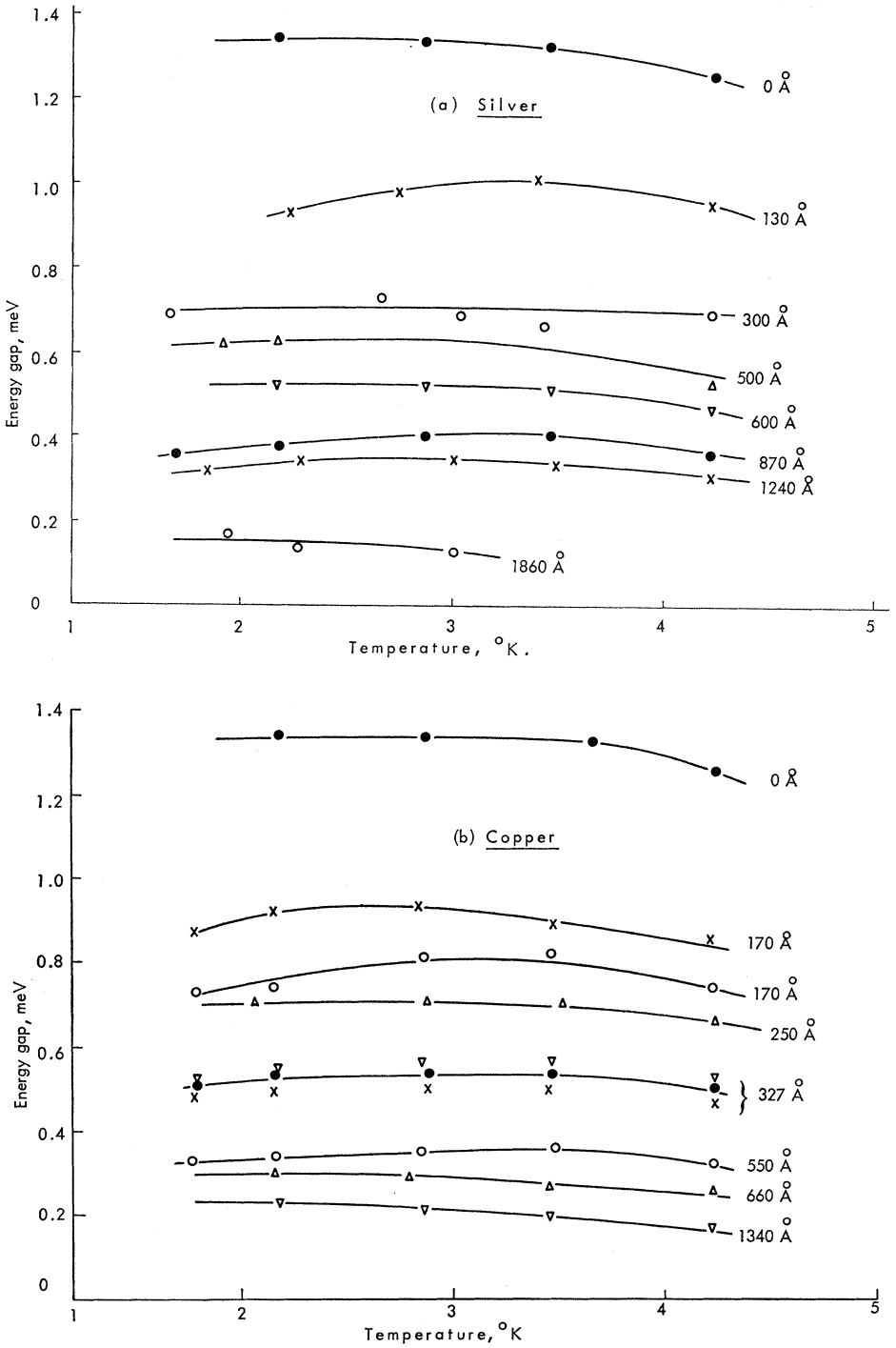

FIG. 3. The energy gaps induced at the surfaces of silver, copper, and tin films backed by 5000 Å of lead as a function of temperature and film thickness.

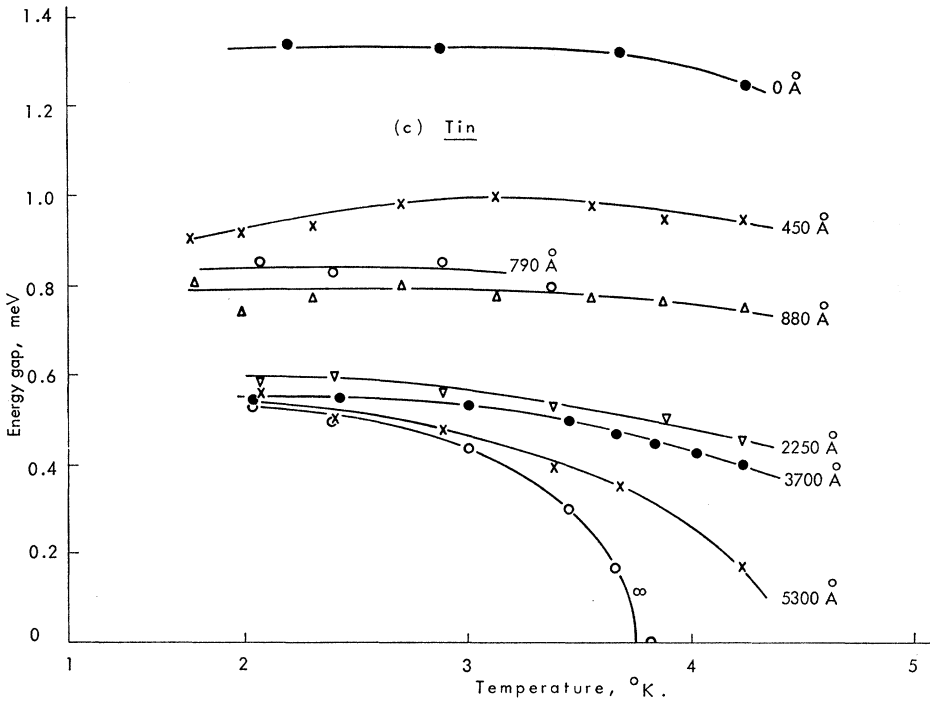

FIG. 3 (*continued*)

of the normal film and (b) that in most cases[11] the extra contribution required is not greater than 0.02. The former property inclines us to the belief that we are observing leakage currents but, in any case, we assert that if states do exist to low energies in our experiments, then their normalized density is certainly less than 0.03.

Tin differs from silver and copper in that it is a superconductor in its own right in the temperature range investigated, and the observed gap tends towards that for the bulk metal at large thicknesses. The large penetration in tin, even above its critical temperature, should be noted.

Assuming that we are correct in attributing the apparent decrease in the gaps at low temperatures to leakage currents, we may estimate the size of the induced gaps in the low-temperature limit from the maxima of the curves of Fig. 3. The results are shown in Fig. 4.

B. Excitation Spectrum in a Normal Material Backed by a Thick Superconductor

Superficially the conductance curves are similar to those which would be obtained by tunneling into a BCS superconductor. However, a detailed comparison with the conductances calculated for the BCS case[8] shows that there are marked differences. In the copper-lead and silver-lead cases they are

(i) the much higher value of $\sigma_{\max}$,

(ii) the more rapid return to unity conductance above the gap.

The differences are illustrated in Fig. 5 for the case of copper. The differences are similar in the case of silver, but less marked. (If the BCS curve is fitted at V_1 instead of at σ_0, the same characteristics emerge.) Properties (i) and (ii) indicate that there are more states close above the gap than in a BCS superconductor and correspondingly fewer states at higher energies. They are also evidence against faults in the films or nonuniformities in the specimens which would produce a smearing of the density of states.

These deductions are consistent with the observed V_1 values: In the proximity samples, V_1 usually occurs closer to the gap as estimated from σ_0 than it does for a BCS superconductor. σ_0 is more sensitive to the *lowest* energy at which the density of states becomes comparable with unity, while V_1 is more dependent on the form of the density of states *above* the gap. The closeness of V_1 and the calculated gap in the proximity samples therefore supports the deduction that the density of states is enhanced immediately above the gap and depressed at higher energies.

In the case of the tin-lead system, $\sigma_{\max}$ is very close to the BCS value while V_1 is always greater, indicating that the density of states is more BCS-like in this case but rather more smeared out. This last property may

[11] In four of the twenty-two cases, the observed values required larger contributions. These were 0.04 (330 Å copper), 0.06 (550 Å copper), 0.07 (870 Å silver), and 0.06 (1240 Å silver). As no correlation was observed with increasing thickness of normal metal, we attribute these to high leakage currents through the tunneling junction.

be a result of the sample structure, tin being more liable to agglomerate than copper or silver. This would result in variations in the thickness of the tin film and a less-well-defined energy gap.

In some samples at low temperatures, a dip appeared above the energy gap (Fig. 6). This seems similar to an observation of Hauser[2a] and has also been seen in measurements similar to our own but made below

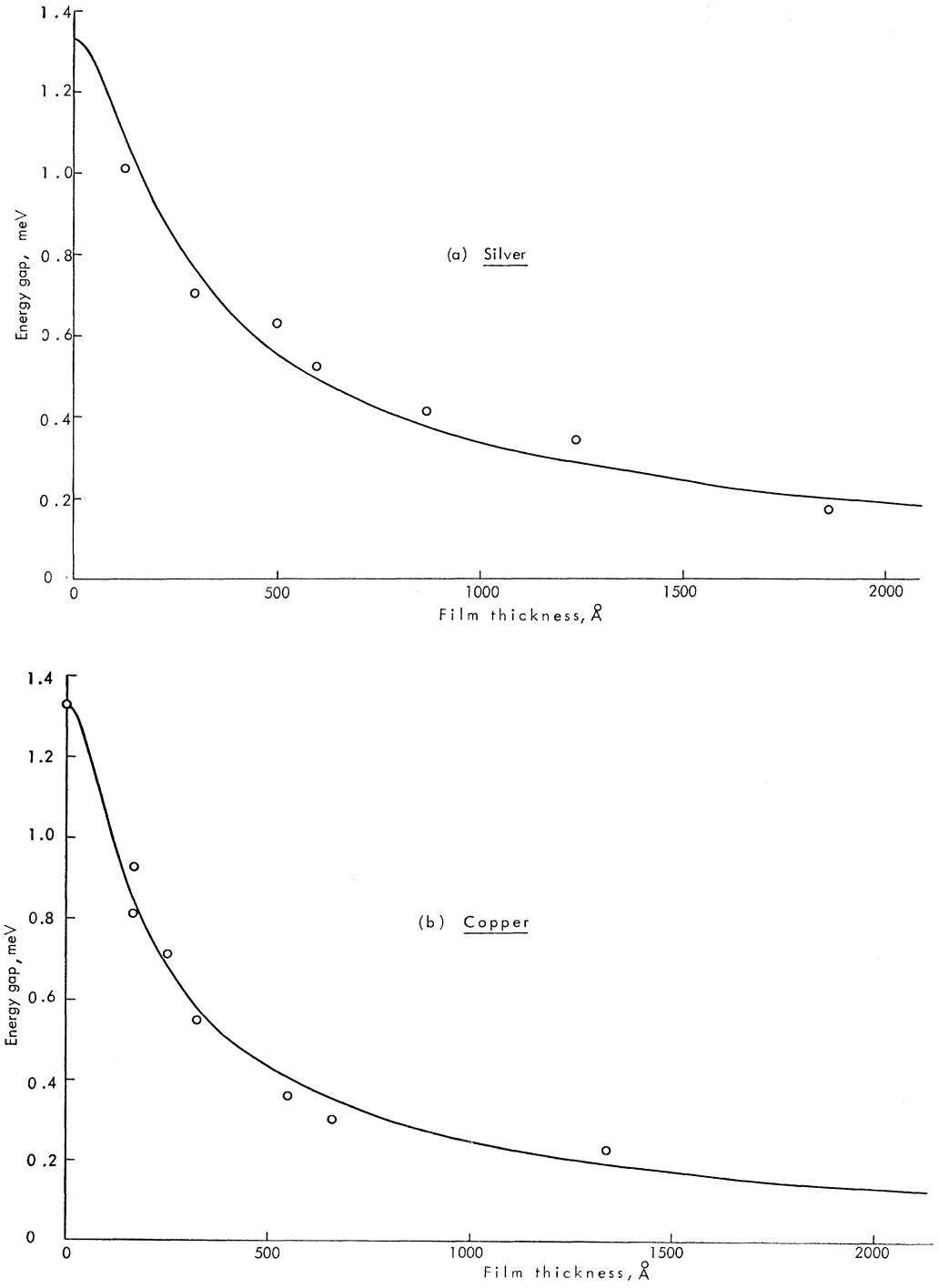

FIG. 4. The points show the low-temperature values of the energy gap induced at the surfaces of silver, copper, and tin films backed by 5000 Å of lead as estimated from our measurements. The curves are calculated from the McMillan theory with $p/B=0.062$ for silver and copper, and $p/B=0.23$ for tin.

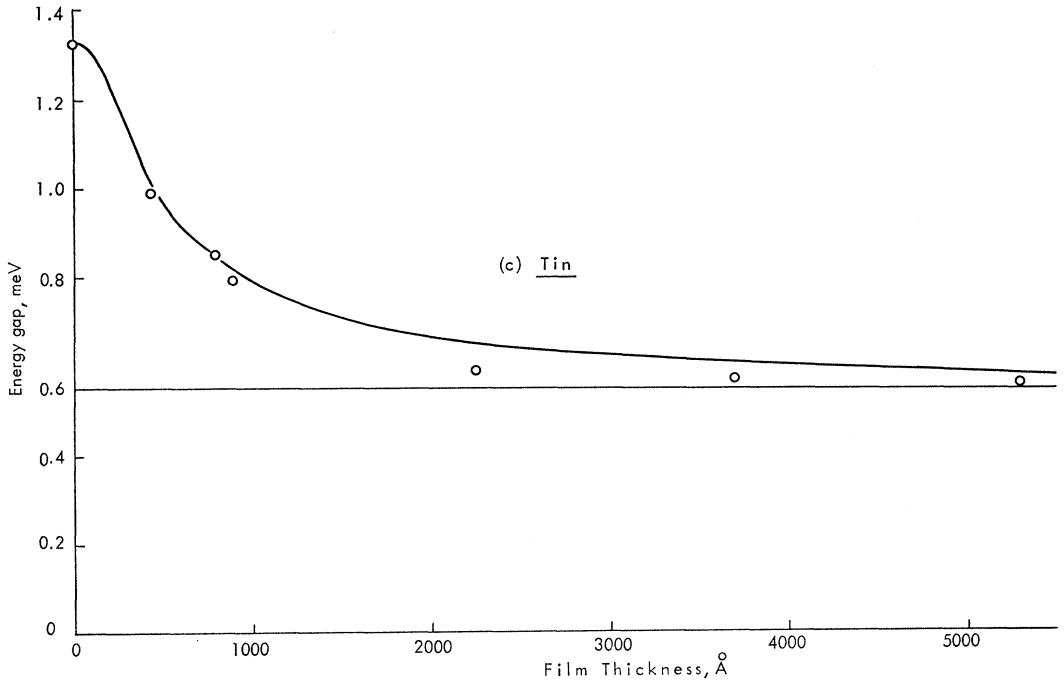

FIG. 4 (*continued*)

0.1°K.[12] In these latter, the normal metal of the tunneling junction was magnesium, so that the effect cannot be associated with the aluminum we have used. The explanation of this feature is not apparent.

4. COMPARISON WITH THEORY

Some experimenters[10,13] using electron tunneling have reported gaplessness in proximity experiments with nonmagnetic films, but their arguments seem to be based on the gradual suppression of the structure in σ and, in particular, on the increased value of σ_0, both of which, as we have pointed out, are consistent with a diminishing but well-defined gap. The near constancy at low temperatures of the gaps calculated from our values of σ_0 (see Fig. 3) indicates that the reduced density of states at low energies is certainly less than 0.03. This would agree with the calculations of de Gennes and Mauro[14] which only predict gaplessness in the limit that the normal layer becomes infinitely thick. The states down to zero energy which are predicted by some theories[15] correspond to quasiparticles propagating along the normal material. In any real system, there would be sufficient scattering to suppress such states; and, in any case, they could not contribute to the tunneling current in which states with **k** vectors within about 15° of the barrier normal dominate.

The only calculation of the excitation spectrum in proximity systems valid for temperatures well below the critical is that of McMillan.[16] He takes a *tunneling model* in which the metals perturb one another by the tunneling of electrons across the interface. If the films are not too thick, the gap parameter may be taken as constant in each metal, and if the coupling is not too great, a solution may be obtained for the excitation spectrum in each film. An important quantity in the theory is the inverse of the time before an electron is lost from one of the metals by transmission across the interface:

$$\Gamma = (\hbar v_F p/2Bd),$$

where $\hbar$ is Planck's constant, v_F is the Fermi velocity, d is the thickness of the film, p is the penetration probability at the interface, and B is a universal function of the ratio of the mean free path to the film thickness. If one film (S) is very thick (a limit in which the theory is not strictly valid) and the other (N) thin, as in our

TABLE I. The transmission probabilities p for electrons incident from silver, copper, and tin at an interface with lead. The values are obtained by fitting the McMillan theory to the measured energy gaps.

	Ag	Cu	Sn
$v_F(10^8$ cm sec$^{-1})$[a]	1.4	1.6	0.65
p	0.1	0.1	0.5

[a] Reference 17.

[12] S. M. Freake (private communication).
[13] H. Tsuya, J. Phys. Soc. Japan **23**, 975 (1967).
[14] P. G. de Gennes and S. Mauro, Solid State Commun. **3**, 381 (1966).
[15] See, for example, D. Saint-James, J. Phys. Radium **25**, 899 (1964).
[16] W. L. McMillan (private communication).

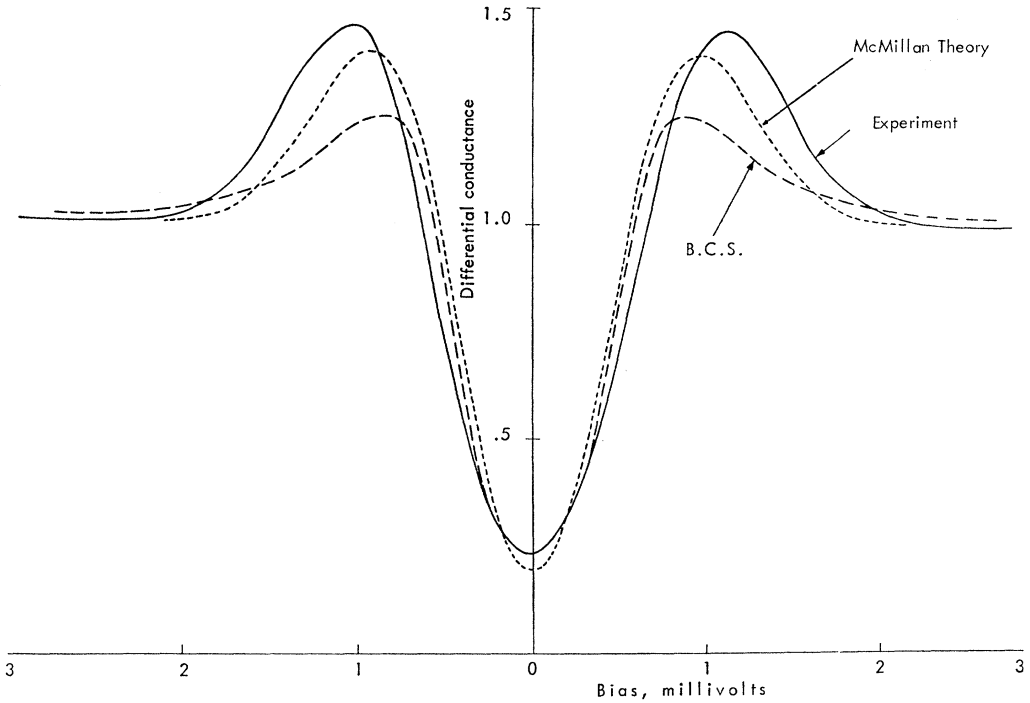

FIG. 5. The differential conductance at 2.18°K for 330 Å of copper backed by 5000 Å of lead compared with the BCS curve fitted at σ_0 (long dashes) and the McMillan theory with $\Gamma_N=1$, $\Gamma_S=0.27$, $\Delta_N{}^0=0$, $\Delta_S{}^0=1.33$ meV (short dashes).

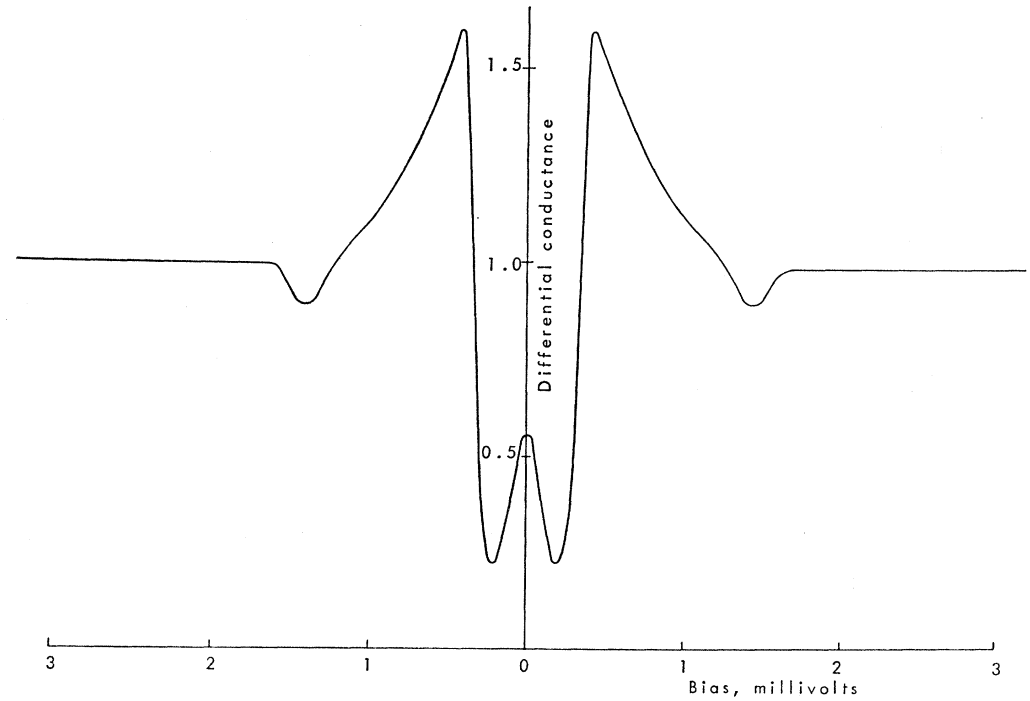

FIG. 6. Differential conductance at about 1.25°K of a specimen of 1340 Å of copper backed by 5000 Å of lead, showing the unexplained dip in the density of states above the gap, and also structure at zero voltage, which we attribute to superconducting bridges.

experiments, then an approximate expression may be obtained for the energy gap in the thinner film, Δ_N, in terms of Γ_N and the natural gaps of the two metals, Δ_N^0 and Δ_S^0:

$$\Gamma_N \ln\frac{\Delta_S^0+\Gamma_N}{\Delta_N^0}=\Delta_N\left(\frac{\Delta_S^0+\Delta_N}{\Delta_S^0-\Delta_N}\right)^{1/2}\ln\frac{\Delta_N}{\Delta_N^0}. \quad (2)$$

If the thin film is of a normal metal ($\Delta_N^0=0$), then this reduces to

$$\Gamma_N=\Delta_N\left(\frac{\Delta_S^0+\Delta_N}{\Delta_S^0-\Delta_N}\right)^{1/2}. \quad (3)$$

If the N film is not too thick, the mean free path will be dominated by boundary scattering, and B will be constant with a value of about 2. Equations (2) and (3) may then be fitted to the results by choosing a suitable value of p/B constant for each system. The calculated curves are shown in Fig. 4. The greater gaps predicted by the theory for the thicker tin films are almost certainly due to the fact that the mean free path is no longer determined by boundary scattering so that B is no longer constant. Taking $B=2$, the transmission probabilities at the interfaces are obtained. These are given in Table I, together with the values taken for the Fermi velocities.[17]

The calculation of the excitation spectrum on the McMillan theory requires a computer calculation. The conductance curve derived from such a calculation is compared with the measured conductances for one sample in Fig. 5. It may be seen that the theoretical curve reproduces the features in which our results are qualitatively different from those which would be obtained for a BCS density of states; namely, there is an increased peaking just above the gap and σ returns to unity more quickly at higher energies. Quantitatively, however, the fit is not particularly good and suggests that the experimental density of states differs from that predicted by the theory in that the rise is more gradual (the spectrum extends to lower energies giving a higher value of σ_0) and the maximum occurs at a higher energy.

The disagreements between theory and experiment here and in Fig. 4 do not constitute a serious challenge to the theory, which applies strictly only to the case of weak coupling between two thin films. Our films are rather strongly coupled and the lead is always thick, so that closer agreement could scarcely be expected.

5. CONCLUSIONS

Within the sensitivity of the experiment a well-defined gap structure has been found to be induced in thin normal films in contact with a superconductor. While lower-temperature measurements are needed for an accurate measurement of the excitation spectrum, it is clear that the density of states at the normal metal surface shows features which are very different from the BCS case. While the McMillan theory is based on a model which is not entirely appropriate to the conditions of our experiments, it does generate the features we find and gives reasonable quantitative agreement with our observed gaps and densities of states.

ACKNOWLEDGMENTS

We have benefited on many occasions from conversations with colleagues in the Mond Laboratory and are also especially grateful to Dr. W. L. McMillan and Dr. J. M. Rowell for making available to us details of the theory and for numerous helpful discussions about the proximity effect. One of us (BWK) also wishes to acknowledge the support of an IBM Studentship for the duration of the research.

[17] The Fermi velocities for copper and silver are taken from C. Kittel, *Introduction to Solid State Physics* (McGraw-Hill Book Co., New York, 1967), p. 208. The Fermi velocity for tin is from J. Bardeen and J. R. Schrieffer, Progr. Low Temp. Phys. 3, 243 (1961).