Proximity Effects in Pb-I-$Bi_8Te_7S_5$-I-Pb Sandwiches as Determined by Electron Tunneling*

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Pb-I-$Bi_8Te_7S_5$-I-Pb proximity sandwiches have been produced by evaporating Pb onto both surfaces of atomically smooth films of $Bi_8Te_7S_5$. Tunneling experiments have been performed on these sandwiches and the results are shown to be in agreement with the McMillan tunneling model of the superconducting proximity effect.

I. INTRODUCTION

Proximity effects[1] have been studied extensively by electron-tunneling techniques and recent experiments[2–5] show good agreement with the McMillan tunneling model.[6] In these experiments the films in proximity were produced by vacuum deposition and the decoupling layers were produced either by oxidation or by evaporating insulating films. Vacuum-deposited films have surface roughnesses of the order of a few atoms so that the decoupling between the films is not homogenous and the experimental conductance peaks are smeared. Vrba and Woods[4] attribute their observed discrepancies with the McMillan model to barrier inhomogeneities and they have found that a Gaussian distribution with a standard deviation of 0.5 Å in barrier thickness would produce the observed smearing. Vrba and Woods[4] have calculated both the McMillan densities of states and the smeared McMillan densities of states for Pb-Cu proximity sandwiches. Their calculations show that the smearing of the density of states and the shift in position of the maximum of the peak in the density of states is pronounced when the ratio of the normal metal thickness to that of the superconductor is small, when this ratio approaches unity these effects become small. These experimental and theoretical results indicate that in order to correctly interpret proximity experiments on films with inhomogenous coupling these results must be compared with a smeared McMillan density of states obtained with a computer solution. If a homogenous decoupling on an atomically smooth surface could be obtained, the proxmity parameters could be obtained directly from the experimental curves. In an attempt to produce a more homogenous decoupling we have produced tunneling barriers on both sides of atomically smooth films and in this paper we interpret the tunneling results in terms of the McMillan model.

$Bi_8Te_7S_5$ is a layered compound consisting of quintuple layers of thickness 9.817 Å and having the property that it cleaves in multiples of atomically smooth layers.[7] $Bi_8Te_7S_5$ has a structure similar to that of Bi_2Te_3 which has a remarkably inert cleaved surface. Haneman[8] has studied the cleaved surface of Bi_2Te_3 by electron diffraction and has found that the surface is unaffected by oxygen, nitrogen, and carbon monoxide at room temperature while exposure to water vapor in ambient air extinguishes the surface electron-diffraction pattern. He further found that heating at 110 °C in vacuum for 3 h completely restored the diffraction pattern. If the surface properties of $Bi_8Te_7S_5$ are similar to those of Bi_2Te_3 then it should be possible to produce tunnel junctions by depositing metal films onto the adsorbed water vapor.

Conductivity measurements on bulk $Bi_8Te_7S_5$ in the cleavage plane and in the direction perpendicular to the cleavage plane have been performed by Soonpaa.[9] At room temperature the ratio of these conductivities is $\sigma_{\parallel}/\sigma_{\perp} = 5.95$ with $\sigma_{\parallel} = 1.78 \times 10^3\ \Omega^{-1}\,cm^{-1}$. Grote and Soonpaa[10] have measured the conductivity of thin samples and have found that for thickness from 2 to 9 quintuple layers the conductivity in the clevage plane varies from 0.22×10^3 to $1.25 \times 10^3\ \Omega^{-1}\,cm^{-1}$ with little temperature dependence down to 4.2 °K. Earlier conductivity measurements[11,12] have indicated a semimetal-to-semiconductor transition between five and four quintuple layer thicknesses.

II. EXPERIMENTAL

It was found that depositions onto freshly cleaved surfaces produced Ohmic contacts while depositions onto cleaved surfaces which had been exposed to ambient air for extended periods yielded good tunnel junctions. Typically a 2-week exposure followed by a 15-sec exposure to water-vapor-saturated air yielded a Pb-I-$Bi_8Te_7S_5$ junction having a resistance of 100 Ω for an area of 0.04 mm^2; furthermore, the resistance exhibited a slow increase with time.

Proximity sandwiches of Pb-I-$Bi_8Te_7S_5$-I-Pb having junction resistances in the range 1–100 Ω for an area of 0.01 mm^2 were produced by allowing the cleaved surfaces of $Bi_8Te_7S_5$ to be exposed to ambient air for at least 24 h prior to deposition of the lead. The procedure followed was to initially deposit a 0.1-mm strip of lead onto a cleaved surface of $Bi_8Te_7S_5$ and then fasten this surface to a microscope slide with room-temperature-curing epoxy resin. The crystal was later reduced to a thickness in the range 10–500 Å by sucessively applying epoxy resin and cleaving until an area appropriate for tunneling was obtained. The sample was examined by light transimission with an optical comparator and when the $Bi_8Te_7S_5$ appeared continous across the lower lead film, two second lead films 0.1 mm wide were deposited across this film. During both depositions the sample was unheated with the vacuum better than 5×10^{-6} torr. Within minutes after the second lead film had been deposited the $Bi_8Te_7S_5$ was scratched in the neighborhood of the junctions to reduce leakage current, contact was made to the lead with beryllium-copper springs, and the sample was placed in a standard double-Dewar helium cryostat which was cooled to liquid-nitrogen temperature. The total elapsed time between the two lead depositions varied from 1 to 4 weeks with a total of 1000 initial lead depositions resulting in 30 sucessful proximity junctions; the low success rate is attributed to the difficulty in cleaving the $Bi_8Te_7S_5$ to appropriate thickness in the region above the initial lead film. I-V and (dI/dV)-V measurements were obtained by standard four-terminal techniques in the temperature range 4.2–1.5 °K.

III. McMILLAN MODEL

In his model McMillan[6] assumes a layer of superconductor S of thickness d_S separated by a potential barrier from a layer of normal metal N of thickness d_N; d_S and d_N are assumed to be small compared to the coherence length. Electron transmission between the layers is treated as a tunneling process and the solution for these conditions gives the excitation spectrum in each film. For the case of a normal film backed by a superconductor, electrons tunnel into the normal film spending an average time τ_N before tunneling into the superconductor where they spend an average time τ_S.

Two important parameters in the theory are Γ_N and Γ_S which are related to τ_N and τ_S by

$$\Gamma_N = \hbar/\tau_N \ , \tag{1}$$

$$\Gamma_S = \hbar/\tau_S \ , \tag{2}$$

and

$$\frac{\Gamma_S}{\Gamma_N} = \frac{d_N N_N(0)}{d_S N_S(0)} \ , \tag{3}$$

where $N_N(0)$ and $N_S(0)$ are the bulk densities of states (per unit volume) in the normal metal and superconductor, respectively. Γ_N is related to the Fermi velocity v_{FN} and the barrier penetration probability σ by

$$\Gamma_N = \hbar v_{FN}\sigma/2Bd_N \ , \tag{4}$$

where B is a function of the ratio of the mean free path to the film thickness d_N. For the case that there is no pairing interaction in the normal metal ($\Delta_N^{ph}=0$), an energy gap Ω_N is induced in the normal metal such that

$$\Gamma_N = C(\Gamma_S)[(\Delta_S^{ph}+\Omega_N)/(\Delta_S^{ph}-\Omega_N)]^{1/2}\Omega_N \tag{5}$$

(provided $\Gamma_S < \Gamma_N < \Delta_S^{ph}$), where $C(\Gamma_S)$ is of the order of unity,[13] and Δ_S^{ph} is the BCS potential in the superconductor. $\Delta_S^{ph} \neq \Delta_S^{bulk}$ so that Ω_N and Γ_N are related to Δ_S^{bulk} (with $\Delta_N^{ph}=0$) by

$$\Omega_N = \Gamma_N/(1+\Gamma_N/\Delta_S^{bulk}) \ . \tag{6}$$

When $\Gamma_N = 0$, McMillan finds

$$\Delta_S^{ph} = \Delta_S^{bulk}(1-2\Gamma_S/\Delta_S^{bulk})^{1/2} \ . \tag{7}$$

It can be shown that when Γ_N is small, Eq. (7) is still valid.

IV. RESULTS

Figures 1–4 illustrate the dependence of the low-voltage tunneling characteristics upon the thickness of $Bi_8Te_7S_5$ and Table I presents the tunneling proximity-effect parameters as determined from these curves and interpreted in terms of the McMillan model.

Because electrons tunnel from a superconductor into a proximity sandwich the conductance peaks in Fig. 1 occur at $\Delta_{Pb}^{bulk}+\Delta_{Pb}^{ph}$ and $\Delta_{Pb}^{ph}+\Omega_N$ as indicated. The peak at $\Delta_{Pb}^{bulk}+\Delta_{Pb}^{ph}$ is much larger than the peak at $\Delta_{Pb}^{bulk}+\Omega_N$ because the tunneling electrons spend much less time in the normal metal than in the superconductor. This is substantiated by calculating Γ_N from Eq. (6), $C(\Gamma_S)$ from Eq. (5), and Γ_S from McMillan's empirical relation[9]; the re-

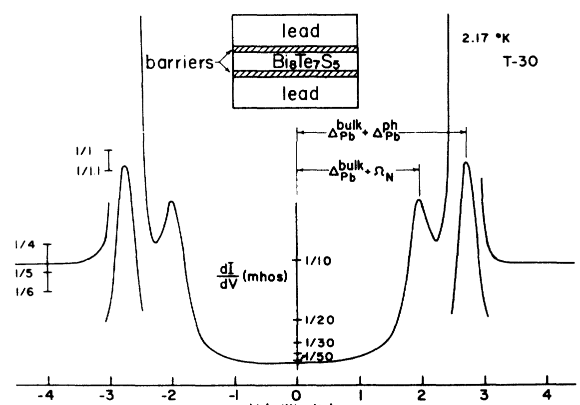

FIG. 1. dI/dV-vs-V characteristics for a Pb-I-$Bi_8Te_7S_5$-I-Pb proximity sandwich in which the thickness of the atomically smooth normal metal is 30 Å.

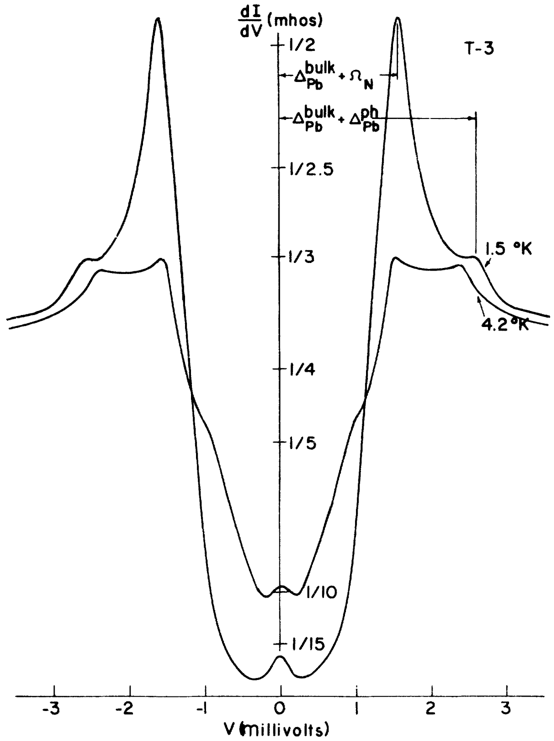

FIG. 2. Temperature dependence of the dI/dV-vs-V characteristics for a superconducting proximity sandwich; the thickness of the normal film is 120 Å.

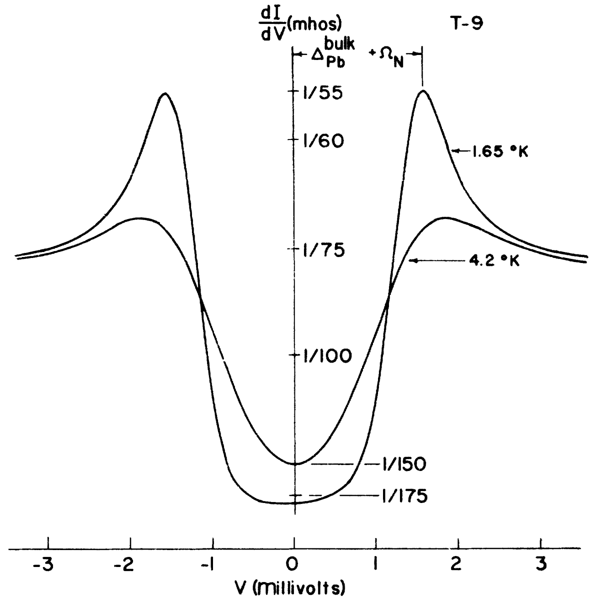

FIG. 3. dI/dV-vs-V characteristics for a tunneling sandwich in which the thickness of the normal film is 100–120 Å.

sult of such a calculation is $\Gamma_S/\Gamma_N = 0.08$. As the thickness of $Bi_8Te_7S_5$ is increased, the electrons spend proportionately more time in the normal film and less time in the superconductor so that the intensity of the peak at $\Delta_{Pb}^{bulk} + \Omega_N$ increases. For these cases Γ_N is obtained from Eq. (6) and Γ_S can be obtained from Eq. (7) (provided Γ_N is small). The experimental and the calculated results for these cases are illustrated in Figs. 2–4 and Table I, respectively, and they exhibit the predicted behavior.

Perhaps a disturbing point is that the thicknesses of the normal films for the junctions T-3 and T-9 are essentially the same but the experimental tunneling characteristics are dissimilar. Evidently there is a nonlinear dependence of Γ on the square of the transmission matrix element, i.e., Γ is not proportional to T^2, so that Eq. (3) is not valid here; this is to be expected because the thicknesses of lead used here are much greater than the coherence length. If τ_N can be predicted theoretically, the ratio τ_S/τ_N does not follow simply, as τ_N and τ_S depend upon the barrier in a complicated way. It should be noted too that the proximity barriers were produced by varied exposure to ambient air and probably arose through an adsorption layer so that sandwiches having the same normal-layer thickness should not necessarily have the same barrier-penetration probability. The essential point is that the values Γ_N and Γ_S are of interest by themselves without having to relate them to the microscopic properties. We do see, however,

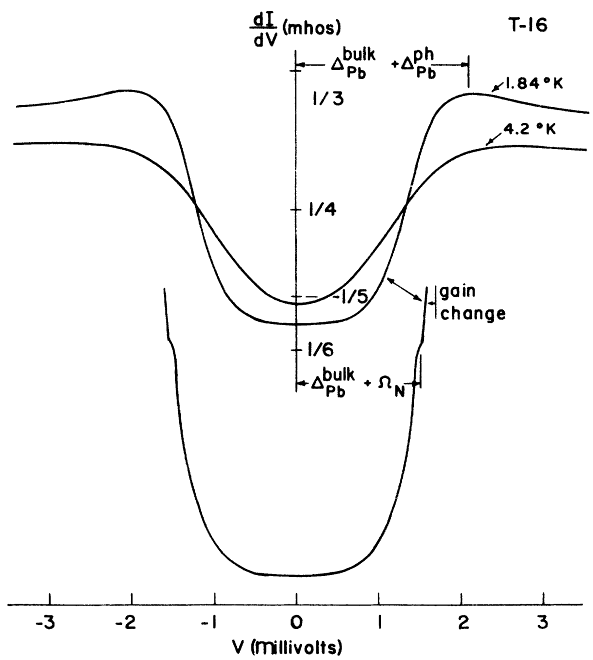

FIG. 4. dI/dV-vs-V characteristics for a tunneling sandwich in which thickness of the normal film is 250–290 Å.

TABLE I. Proximity-effect parameters as determined from the conductance curves of Figs. 1–4 and the McMillan tunneling model.

Sample	d_S (Å)	d_N (Å)[a]	Δ_S^{ph} (mV)	Ω_N (mV)	Γ_N[b] (mV)	Γ_S (mV)	Γ_S/Γ_N
T-30	5700, 4200	30	1.35	0.60	1.06	0.08	0.08
T-3	18 000[c]	120	1.24	0.21	0.25	0.12	0.48
T-9	4300[c]	100–120		0.19	0.22	0.20	0.91
T-16	6100[c]	250–290	0.7	0.12	0.13	0.51	3.92

[a]In some instances it was not possible to determine the thickness of the $Bi_8Te_7S_5$ exactly because on one side of the lower lead film one thickness was measured while on the other side another thickness was measured and it was not possible to determine where the cleavage step occurred.

[b]In calculating Γ_N the value $\Delta_S^{bulk} = 1.38$ mV has been used.

[c]For these films the lower-lead-film thickness was not determined directly by interferometer measurements; however, the depositions were monitored by quartz-crystal microbalance and the thicknesses are within the range 5000 ± 1000 Å, the uncertainty arising because of the deposition geometry.

that Γ_S/Γ_N does increase with increasing thickness of the normal metal and/or decreasing thickness of the superconducting film.

A question arises as to which insulating layer provided the proximity barrier. Because of the observed increase of junction resistance with time at room temperature and because completed proximity sandwiches were cooled to liquid-nitrogen temperature in a short time after deposition, it is assumed that the proximity barrier existed between the $Bi_8Te_7S_5$ and the top Pb films.

In conclusion we have shown how tunneling junctions exhibiting superconducting proximity effects can be fabricated by depositing lead onto atomically smooth films and that these junctions can be described by the McMillan tunneling model so that the ratio Γ_N/Γ_S which is related to the lifetimes of tunneling electrons in the normal metal and in the superconductor can be measured.

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