

# Superconductivity in Silver Induced by the Proximity Effect\*

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The ratio of the thermal conductivities in the normal and superconducting states has been measured for silver made superconducting by the proximity effect. The results lead to measurements of the energy gap and, under certain conditions, of the electron-electron interaction, which is found to be attractive, with  $NV = 0.05 \pm 0.02$ . A second independent determination is based on measurements of the supercooling field and, hence, the saturation temperature. It leads to  $NV = 0.08$ .

## I. INTRODUCTION

The proximity of a superconductor can induce superconducting properties in an otherwise normal metal to a distance of the order of  $10^{-5}$ – $10^{-4}$  cm.<sup>1,2</sup> We have investigated the properties of the layer of induced superconductivity by thermal measurements on multiple-layer thin-film specimens in which the normal metal is silver and the superconductor is a lead-bismuth alloy.<sup>3,4</sup> The measurements lead to values of the energy gap in silver, and, under suitable conditions, also to a value of the electron-electron interaction constant. We find the interaction to be attractive, so that silver must be expected to become an intrinsic superconductor at some sufficiently low temperature.

## II. EXPERIMENTAL PROCEDURES

The specimens consisted of either two or three layers evaporated at room temperature on a substrate of size 00 microscope cover glass. One layer was silver whose thickness  $d_n$  varied from specimen to specimen. For the double-layer specimens the silver was deposited directly on the substrate and followed by a layer of an alloy of lead with 5-at. % bismuth, 1000-Å thick. For the triple-layer specimens there was an alloy layer, 2000-Å thick, on each side of the silver. The method of preparation and the mounting of thermometers ( $\frac{1}{8}$ -W Allen-Bradley resistors) and heater were similar to those which have been used and described before.<sup>5</sup> Table I summarizes the specimen characteristics.

The choice of materials was dictated primarily by the relatively high transition temperature of lead, and by the low mutual solubility of silver and lead. The bismuth was added in order to reduce the electronic mean free path so as to minimize the effects of irregularities or interdiffusion at the interface.

Most of the measurements were made in a He<sup>3</sup> cryostat similar to one which has been described previously.<sup>6</sup> Some modifications were made to isolate the Dewar system mechanically from the

vacuum pumps. The most effective of these was to run the vacuum lines through a 150-lb concrete slab with 12-in. stainless-steel bellows on each side. A NbZr superconducting magnet provided the magnetic field.

## III. DATA ANALYSIS

The nature of the transitions is illustrated on Fig. 1, which shows the difference  $\Delta R$  between the resistances of the two thermometers on the specimen as a function of a magnetic field applied in the same direction as the heat flow. (The exact direction of the field is not critical.)  $\Delta R$  is constant up to some field  $H_s$  of the order of several hundred gauss where it decreases abruptly. The decrease in  $\Delta R$ , corresponding to an increase in the thermal conductivity, is identified with the transition of the silver layer from the superconducting to the normal state. The conductivity then remains constant until the lower critical field  $H_{c1}$  of the PbBi, after which it changes slowly until all parts of the specimen are normal at the upper critical field.

A specimen of PbBi without the silver layer was also measured. In this case  $\Delta R$  remains constant up to  $H_{c1}$ . Above  $H_{c1}$  the behavior of this specimen

TABLE I. Specimen characteristics.  $\epsilon'$  is the energy gap corrected for thickness.

	$d_n$ (Å)	$l_n$ (Å)	$\rho_0$ ( $\mu\Omega$ cm)	$T_i$ (°K)	$\epsilon$ (meV)	$\epsilon'$ (meV)	$\cos\phi$
Double layers	530	13 200	0.21	0.92	0.51		
	650	2 400	0.93	0.75	0.42		
	1000	9 300	0.32	0.54	0.30		
	2000	10 400	0.25	0.25	0.14		
Dirty triple layers	1000	<1000		0.99	0.55		
	1800	1 800	0.70	0.60	0.34		
	2000	1 200	0.91	0.61	0.34		
	2000	2 300	0.58	0.61	0.34		
	5000	4 200	0.28	0.18	0.10		
Clean triple layers	800	2 000	0.64	0.76	0.48	0.48	0.18
	1000	2 000	0.82	0.76	0.42	0.44	0.14
	1300*	1 800	0.78	0.59	0.33	0.34	0.004
	1500	3 200	0.53	0.56	0.31	0.32	0.12
	3000	8 600	0.23	0.29	0.16	0.18	0.09

\*The 1300-Å specimen was not included in the determination of  $NV$  as being too dirty.

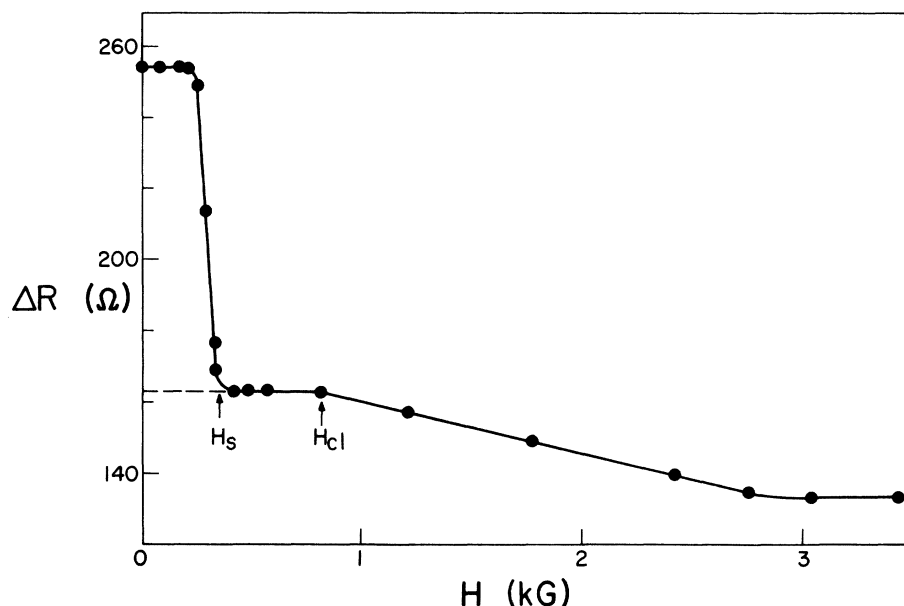


FIG. 1. Difference  $\Delta R$  between the two specimen thermometers as a function of magnetic field. At  $H_s$  the silver layer becomes normal. The lead-alloy layer remains superconducting until  $H_{c1}$ . The dashed line shows the curve for a lead-alloy layer without silver.

is similar to that of the specimens with the silver layer. This shows that the behavior of the PbBi is not appreciably affected by the proximity of the silver. This is to be expected since the coherence length of the PbBi is much smaller than its thickness. (A critical field of 3000 G, as in Fig. 2, corresponds to a coherence length of about 300 Å.)

The basic experimental data consist of curves like that of Fig. 1. From them the specimen conductance was determined in zero field ( $C_0$ ) and in

a field between  $H_s$  and  $H_{c1}$  ( $C_H$ ). The conductances are  $C_0 = C_s^{A\#} + C_s^{PbBi} + C_G$  and  $C_H = C_n^{A\#} + C_s^{PbBi} + C_G$ , where  $C_G$  is the conductance of the substrate and the subscripts  $n$  and  $s$  refer to the normal and superconducting states. The difference  $C_H - C_0$  is therefore equal to the difference  $C_n^{A\#} - C_s^{A\#}$  of the conductances of the silver layer.

Our method of determining the ratio  $(K_s/K_n)^{A\#}$  of the silver layer depends on two remarkable results illustrated in Fig. 2. The first is that for this

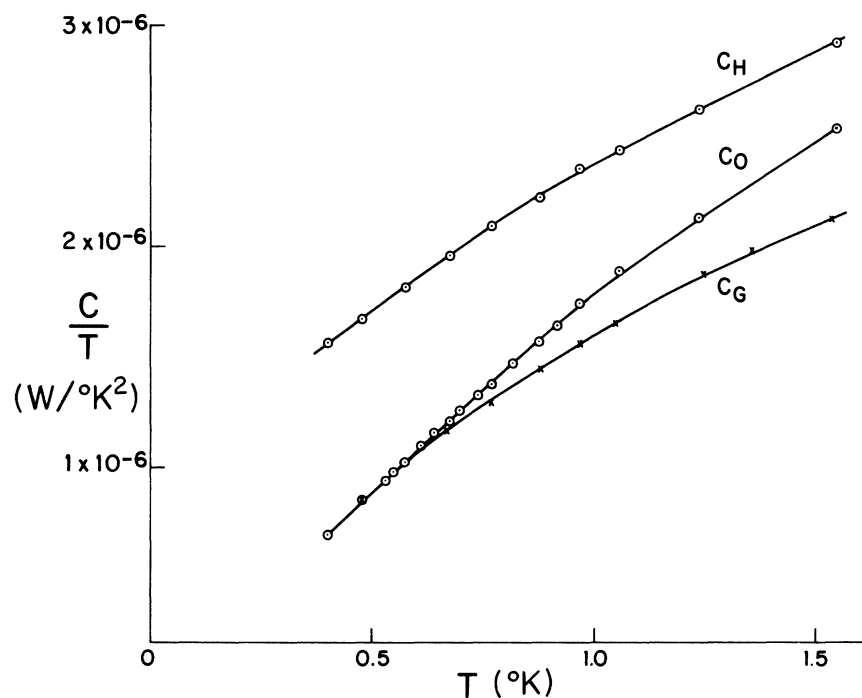


FIG. 2. Thermal conductances plotted as  $C/T$  against  $T$  for the 1500-Å specimen.  $C_0$  and  $C_H$  are the conductances of the specimen assembly in zero field and in a field between  $H_s$  and  $H_{c1}$ , respectively.  $C_G$  is the conductance of the substrate.

film  $C_0$  and  $C_G$  become identical at the lowest temperatures, indicating that  $C_s^{As}$  as well as  $C_s^{PbB1}$  are then negligibly small. Further, the curves of  $C_H/T$  and  $C_G/T$  are parallel, so that their difference ( $C_n^{As}/T + C_s^{PbB1}/T$ ) is independent of temperature. Since  $C_n^{As}/T$  is independent of  $T$ ,  $C_s^{PbB1}/T$  must be also. This is only possible if  $C_s^{PbB1}/T$  remains immeasurably small over the whole temperature range of this measurement.  $(K_s/K_n)^{As}$  can therefore be found directly from the curves of Fig. 2 by

$$\left(\frac{K_s}{K_n}\right)^{As} = \frac{C_0/T - C_G/T}{C_H/T - C_G/T}.$$

The value of  $(K_s/K_n)^{As}$  therefore depends only on the relative values of the conductances illustrated on Fig. 2. The geometrical factor or any other factors which affect the normal and superconducting states equally will not affect this result. We estimate the accuracy of the values of  $(K_s/K_n)^{As}$  to be  $\pm 3\%$ .

An even further simplification now becomes possible: In the absence of a measurement of  $C_G/T$  it can simply be drawn parallel to  $C_H/T$ . For the thinner films (2000-Å Ag or less)  $C_G/T$  becomes equal to  $C_0/T$  at the lowest temperatures. For the thicker films the substrate can be measured in a separate run, or the measured conductance of some other substrate may be used, normalized to take into account the difference in geometrical factors.

The experimentally determined ratios  $(K_s/K_n)^{As}$  for some of the specimens are shown on Fig. 3. The most obvious and important fact that emerges from the curves on this figure is that they go to zero as the temperature is reduced and thus demonstrate the existence of an energy gap in the silver layer when it is superconducting. The ap-

proach to zero is, of course, expected to be exponential although our measurements are not precise enough to show the details of the low-temperature behavior. We have extrapolated the curves to the  $T$  axis linearly, and call the intercept  $T_i$ .

The curve of  $K_s/K_n$  as a function of temperature for ordinary superconductors follows the calculations of Bardeen, Rickayzen, and Tewordt (BRT).<sup>7</sup> The BRT curve is almost linear from  $t = T/T_c = 0.3$  to  $t = 0.7$ , and the linear portion intercepts the  $t$  axis at  $t_i = T_i/T_c = 0.27$ . For the BRT superconductor the energy gap at 0 °K is given by  $\epsilon_0 = 1.76kT_c$  and hence by  $\epsilon_0 = 6.5kT_i$ . We assume that this relation holds for our experimental curves as well, so that the energy gap can be determined directly from the intercept of the curves of  $K_s/K_n$  against  $T$ .

An important parameter for the interpretation of the results is the electronic mean free path of the silver layer. We first attempted to determine it from the electrical resistivity of a silver layer (without the lead alloy) deposited on a second substrate simultaneously with the silver layer of the composite specimen. In the course of the experiment it became clear that the values of the resistivity of the two silver layers could not be relied upon to be the same in spite of their simultaneous deposition. As has also been shown by others<sup>8,9</sup> the resistivity of the film deposited on the alloy layer was usually higher than that of the film deposited directly on the glass substrate.

We therefore used the measured thermal conductance  $C_n^{As} = C_H - C_G$  and the length-to-area ratio  $L/A$  to determine the resistivity  $\rho_0$  from  $\rho_0 L/A = L_0 T/C_n^{As}$ , where  $L_0 = 2.445 \times 10^{-8} \text{ V}^2/\text{°K}^2$ .

The actual electronic mean free path  $l$  can be found from the value of the product  $\rho l$ . We have

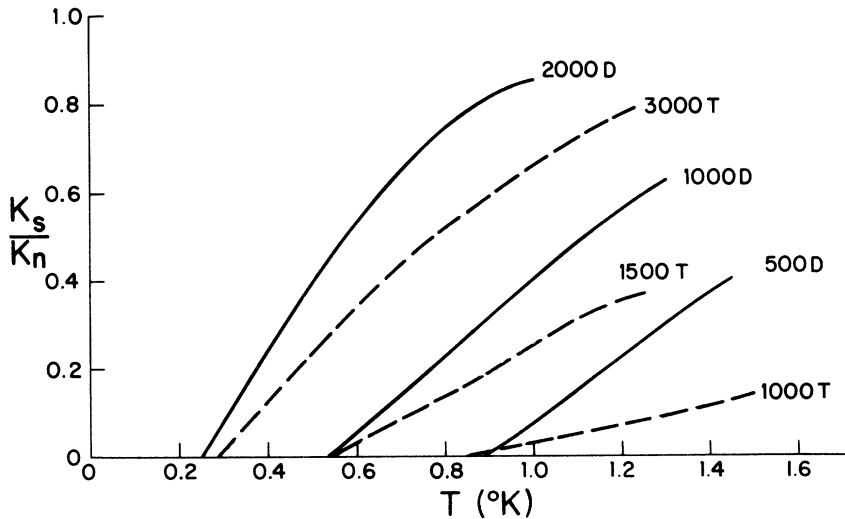


FIG. 3. Ratio of the silver thermal conductivities in the superconducting and normal states for three double-layer specimens (full lines, marked D) and three clean triple-layer specimens (dashed lines, marked T). The thicknesses in Å are indicated on the graph.

used the free-electron value  $\rho l = 0.85 \times 10^{-11} \Omega \text{ cm}^2$ . We have also calculated the bulk electronic mean free path  $l_n$  of an equivalent specimen in which the mean free path is not reduced by boundary scattering. We used the tables of Toxen, Burns, and Quinn<sup>10</sup> with the results shown on Table I.

#### IV. ELECTRON-ELECTRON INTERACTION

It might seem at first that the existence of an energy gap in the silver layer implies an attractive electron-electron interaction. The interpretation would then be straightforward, and it would only be necessary to consider the theorem of de Gennes,<sup>11</sup> which states that in an inhomogeneous structure the energy gap is equal to the minimum value  $\Delta_{\min}$  of the pair potential  $\Delta(r)$ .

For thin specimens, with constant order parameter, the value of  $T_c$  is then thickness independent, while for thicker specimens a correction needs to be made to take into account the variation of the order parameter. At high temperatures (above the saturation temperature, see Sec. VI) the correction is given by

$$\Delta_n = \Delta_{\min} \cosh(\frac{1}{2} K d_n), \quad (1)$$

where  $\Delta_n$  is the value of  $\Delta(r)$  in the silver at the interface, and  $K^{-1}$  is the characteristic distance for the penetration of Cooper pairs into the normal metal.<sup>11</sup> At lower temperatures the appropriate form is

$$\Delta_n = \frac{1}{2} \Delta_{\min} \{1 + [1 + (d_n/2x_0)^2]^{1/2}\}, \quad (1')$$

where  $x_0$  is defined in Sec. VI.

It turns out, however, that the situation is considerably more complicated. In the first place the de Gennes theorem is valid only for the case where  $\Delta_s$  and  $\Delta_n$  have the same sign, while there can be an energy gap also when the signs are opposite. It is possible to show this and to distinguish between the two cases with the help of calculations of the density of states which have been made by Saint-James.<sup>12</sup> Furthermore both the de Gennes theorem and the Saint-James calculations are valid only in the clean limit, i. e., when there is no impurity scattering in the normal layer. Finally the results depend crucially on the nature of the reflections of the quasiparticles at the boundaries of the silver layer. We shall consider the details of these points in Secs. IV A–E.

##### A. Anisotropy of Density of States

The basis for our interpretation is the calculation of the density of states by Saint-James<sup>12</sup> for a double layer of two clean superconductors with specular reflections at the boundaries, thin enough that the pair potential can be considered to be constant in each. Since for our specimens one layer is normal and the other superconducting at the

temperatures of the measurements, we refer to the two values of the pair potential as  $\Delta_n$  and  $\Delta_s$ . We shall show from our results that they do, in fact, have the same sign, so that the material of the “normal” layer is also a superconductor.

The results of the Saint-James calculation show that the energy of a quasiparticle is strongly dependent on the angle  $\theta$  between its trajectory and the normal to the interface. When  $\Delta_n$  and  $\Delta_s$  have the same sign the minimum value of the energy occurs for  $\theta = \frac{1}{2}\pi$  and is equal to  $\Delta_n$ . The density of states exhibits sharp peaks corresponding to  $\theta = 0$ . Their number and position depend primarily on the thickness of the normal layer, and only weakly on  $\Delta_n$ , as long as  $\Delta_n$  is much smaller than  $\Delta_s$ .<sup>13</sup>

The strong angular dependence is the reason for the difficulty of studying the excitation spectrum by tunneling. A tunneling experiment is sensitive mainly to the excitations traveling perpendicular to the junction ( $\theta = 0$ ). The measured gap  $\epsilon_1$  corresponds to this orientation and is therefore strongly thickness dependent and quite insensitive to the value of  $\Delta_n$ .

A thermal-conductivity measurement does not suffer from this limitation and can measure the true minimum gap of the system. The gap cannot, however, be expected to be equal to  $\Delta_n$  unless the normal layer is clean and all reflections at its boundaries are specular.

##### B. Effect of Reflections

The fundamental importance of the specular condition leads to a decisive difference in the behavior of double- and triple-layer specimens.

It is well known that reflections at the boundaries of evaporated specimens are likely to be diffuse except under very special circumstances. This is probably so not because of any lack of crystalline order at the surface, but rather because the surfaces are not perfectly plane.

A reflection at the interface between the normal layer and the substrate or at a free surface will then not preserve the angle  $\theta$  of the trajectory and will wash out the sharp structure of the density of states. Because the original density of states is strongly peaked at energies corresponding to  $\theta = 0$  we can expect the measured gap to be much closer to the value  $\epsilon_1$  corresponding to this orientation than to the value  $\Delta_n$  corresponding to the parallel orientation.

A quite different description applies to the interface between the normal and the superconducting layer. Here the reflections follow the description of Andreev<sup>14</sup>: An electron is reflected along its incident trajectory as a hole and vice versa. The angle  $\theta$  is preserved *regardless* of the local orientation of the interface. The Andreev reflection is

therefore essential for maintaining the conditions of Saint-James's calculations and for observing the effects of the anisotropic density of states which he describes.

In double layers Andreev reflections will take place on only one side, while on the other side the reflections will be diffuse. Only in triple-layer specimens, with the normal layer bounded by a superconductor on each side, can we expect to observe a gap close to the true thickness-independent gap  $\Delta_n$  for the system. Naturally it is also necessary that the material of the normal layer be sufficiently pure to make the electronic mean free path long compared with the thickness.

#### C. Results on Double Layers

In our series of double-layer specimens the silver layer was deposited directly on the glass substrate at room temperature. The bulk electronic mean free path  $l_n$  is then almost always much larger than the thickness  $d_n$ . It can be seen from Fig. 4 that the gap which we observe is very close to and has the same thickness dependence as the tunneling gap observed by Adkins and Kington.<sup>15</sup> The fact that the thermal-conductivity gap is consistently a little smaller may indicate that a weak anisotropy of the gap remains even when the reflections on one side of the normal layer are diffuse.

The results are in accord with the theory of McMillan.<sup>16</sup> They are also in agreement with the Saint-James model if we identify the observed gap with  $\epsilon_1$ . We also note that the slope of the curves of  $K_s/K_n$  against  $t$  is the same as that of ordinary (BCS) superconductors.

#### D. Results on Triple Layers

Only in triple-layer specimens, because of the Andreev reflections at both boundaries of the normal layer, can we expect the Saint-James calculations to apply. Unfortunately, it turned out to be difficult to achieve large values of  $l_n$  when the silver layer was deposited on a layer of lead alloy. Nevertheless the specimens clearly fall into two classes: those with  $l_n \gtrsim d_n$  (dirty) and those with  $l_n > d_n$  (clean).

The dirty specimens behave exactly as do the double layers. When appropriately scaled (the thickness of the triple layers has to be divided by 2) the measured gaps fall on the same curve of gap versus thickness (Fig. 4). As expected the scattering by impurities has the same effect as do the diffuse reflections in eliminating the effect of the anisotropy in the density of states.

The clean triple layers behave differently from the double layers and from the dirty triple layers in three significant ways: For a given value of  $d_n$  the gap is smaller; the variation of the gap with thickness is smaller; and the slopes of the curves of  $K_s/K_n$  against  $t$  are smaller (see Figs. 3 and 5).

Each of these characteristic differences confirms the appropriateness of the results of Saint-James. The observed gap is smaller than  $\epsilon_1$ . In the clean limit the gap would be expected to be equal to  $\Delta_n$  and independent of thickness. Although the specimens are not in this limit it is clear that they show the effects of a distinct gap anisotropy. Finally, again as expected, the smaller slope indicates that the density of states is reduced for energies just above the gap.

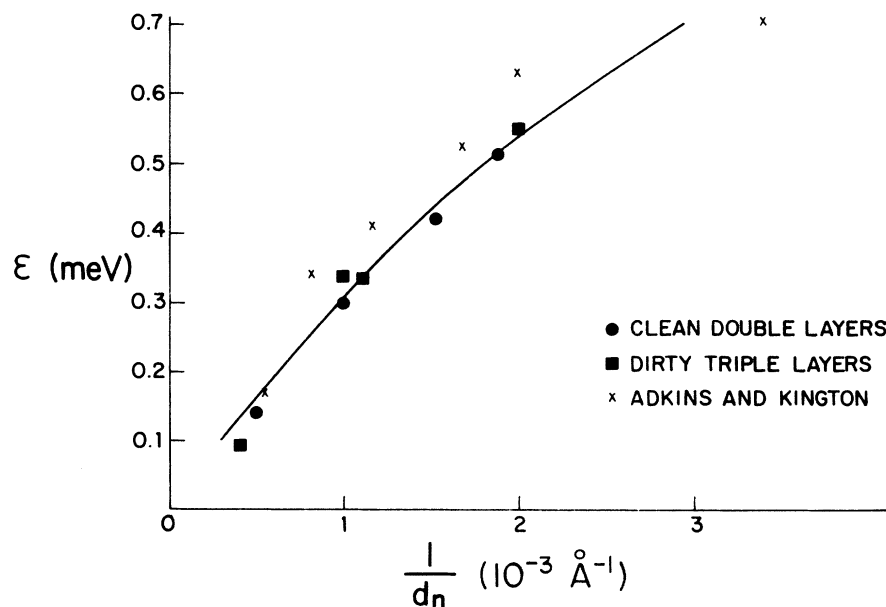


FIG. 4. Energy gap  $\epsilon$  as a function of the reciprocal of the thickness for the double-layer specimens (round points) and the dirty triple-layer specimens (square points). For the triple layers the thickness has been divided by two. The line is calculated from Eq. (1) with  $\cos \theta = 1$ ,  $\cos \psi = 0$ , and  $\xi = 108 \text{ \AA}$ .

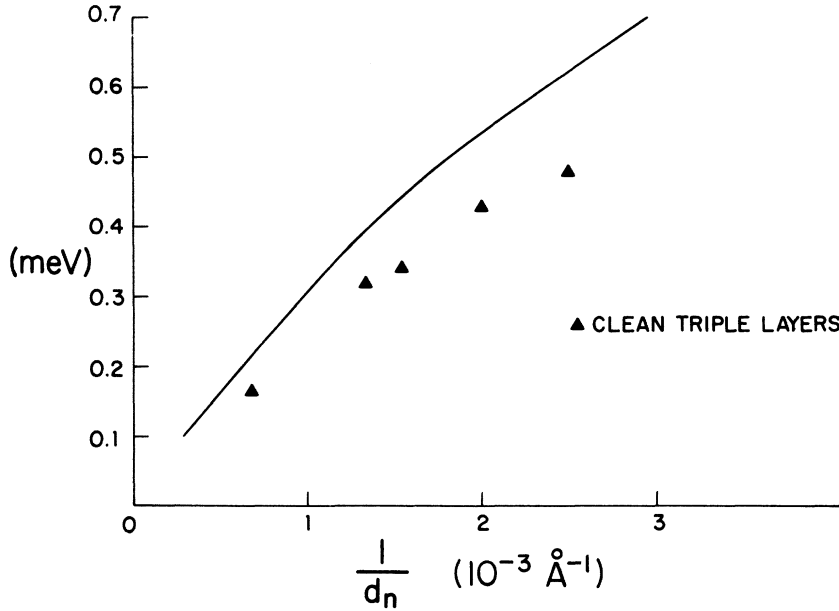


FIG. 5. Energy gap as a function of the reciprocal of the thickness of the clean triple-layer specimens. The line is the same as in Fig. 4.

In order to analyze the results for the clean triple layers more quantitatively, and to attempt to obtain a value for  $\Delta_n$ , we can make a rough correction for the fact that the specimens are not in the clean limit. We assume that the energy of the low-lying excitations is equal to that computed by Saint-James for values of  $\theta$  between 0 and a limiting angle  $\theta_l$  given by  $\cos \theta_l = d_n/l_n$  and that as a result of impurity-scattering states corresponding to angles between  $\theta_l$  and  $\frac{1}{2}\pi$  will not be observed. In other words we take the observed gap to be equal to the energy corresponding to the cutoff angle  $\theta_l$ .

The gap  $\epsilon$  corresponding to an angle  $\theta$  is given by Eq. (18) of Ref. 12, which may be written as

$$\frac{d_n}{\pi \xi \cos \theta} = \arctan \left[ \frac{\sin \phi (\cos^2 \phi - \cos^2 \psi)^{1/2}}{(\cos^2 \phi - \cos^2 \psi)} \right] \times (\cos^2 \phi - \cos^2 \psi)^{-1/2}, \quad (2)$$

where  $\cos \phi = \epsilon/\Delta_s$ ,  $\cos \psi = \Delta_n/\Delta_s$ , and  $\xi$  is the coherence length in the superconducting layer.

We first use Eq. (2) to fit the experimental curve of  $\epsilon$  against  $d_n$ . For this case  $\cos \theta = 1$ . Because of the insensitivity of the result to the value of  $\Delta_n$  we also let  $\cos \psi = 0$ . The only remaining parameter is  $\xi$ . An excellent fit is obtained for a value of  $\xi$  of 108 Å (see Fig. 4). This is certainly too small for a realistic value of  $\xi$ . We suggest that the apparent value of  $\xi$  is affected by the properties of the interface. The parameter  $\xi$  then becomes the counterpart of McMillan's transmission coefficient, which has to be assumed to be about 0.1 to fit the experimental results.<sup>15</sup>

We can now use this value of  $\xi$  with the experimental values of  $d_n$ ,  $\theta_l$ , and  $\epsilon$  for the clean triple-layer specimens to find the corresponding values of  $\cos \psi$ . We first correct the measured value of  $\epsilon (= \Delta_{\min})$  for the thickness dependence of the order parameter in accordance with Eq. (1'). Since  $\Delta_n/(NV)_n = \Delta_s(NV)_s$ , we can find  $(NV)_n$  from  $(NV)_n = (NV)_s \cos \psi$ . With  $(NV)_s = 0.39$ <sup>17</sup> and the values for the four clean specimens shown in Table I we find  $(NV)_n = 0.05 \pm 0.02$ .

The value of  $(NV)_n$  is very sensitive to the value of  $l_n$ , and hence to the value of  $\rho l$  which is used in the calculations. We have used the free-electron value  $0.85 \times 10^{-11} \Omega \text{ cm}^2$ , which is close to the value  $0.84 \times 10^{-11} \Omega \text{ cm}^2$  determined by Reynolds and Stilwell.<sup>18</sup> If instead one uses the value  $0.73 \times 10^{-11} \Omega \text{ cm}^2$  of Boulesteix<sup>19</sup> the value of  $(NV)_n$  is reduced to about 0.03.

#### E. Sign of Electron-Electron Interaction

According to Saint-James the gap goes to zero as  $\Delta_n$  goes to zero. The smallest energies correspond to the values of the angle  $\theta$  closest to the parallel orientation. In the presence of impurity scattering, however, the states with the smallest energies will be eliminated, and a gap will still be observed.

Consider now the possibility of a negative value of  $\Delta_n$ . For a given value of  $\theta$  the energy will depend on both  $\Delta_s$  and  $\Delta_n$ , and a value of  $\Delta_n$  which is sufficiently negative will lead to a cancellation and consequent disappearance of the gap. Interestingly enough, with a large negative  $\Delta_n$  there may be a gap even in the clean case.<sup>20</sup> We can reproduce

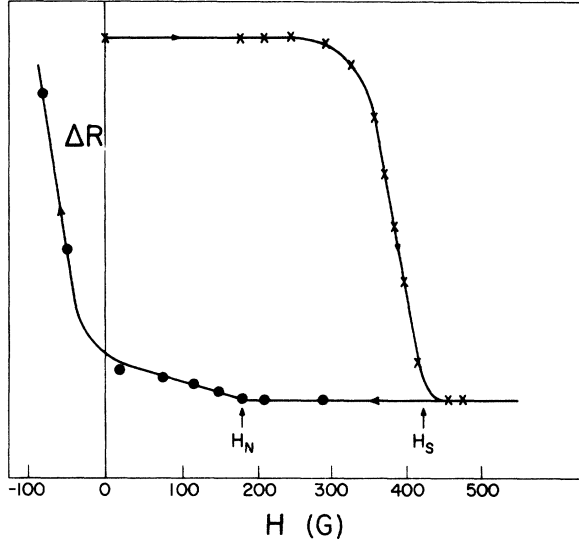


FIG. 6. Hysteresis of the thermal conductivity of a 2000-Å clean triple-layer specimen.

the main features of the exact result and give some physical insight with the aid of a simplified model.

The model consists of averaging over two layers with pair potentials  $\Delta_n$  and  $\Delta_s$  in accordance with the prescription first used by Cooper<sup>21</sup> and extended by de Gennes,<sup>11</sup> so that the energy is given by

$$E(\theta) = \left| \frac{d_n}{\cos \theta} \Delta_n + \xi_s \Delta_s \right| / \left( \frac{d_n}{\cos \theta} + \xi_s \right).$$

When  $\Delta_n$  and  $\Delta_s$  have the same sign  $E(\theta)$  varies monotonically between the values  $\epsilon_{||} = \Delta_n$  and

$$\epsilon_{\perp} = (d_n \Delta_n + \xi_s \Delta_s) / (d_n + \xi_s).$$

On the other hand, when  $\Delta_s > 0$  and  $\Delta_n < 0$  there are two possibilities: for  $d_n |\Delta_n| < \xi_s \Delta_s$  there is always some critical angle  $\theta_c$  for which  $E(\theta_c) = 0$ , and there is no energy gap. In the converse case there will be a gap varying between  $\epsilon_{||} = |\Delta_n|$  and

$$\epsilon = (\xi_s \Delta_s - d_n |\Delta_n|) / (d_n + \xi_s).$$

We can now show that this last possibility may be ruled out. For a specimen for which  $d_n \leq \xi_s$  there can be a gap only when  $|\Delta_n| \geq \Delta_s$ . If we use for  $\Delta_s$  the value for lead this means that  $\Delta_n$  would have to be less than  $-0.4$ . Such a large repulsive interaction in silver is most unlikely, and we conclude that the interaction is attractive.

The presence of impurity scattering eliminates the states with the lowest energy and an even more negative value of  $\Delta_n$  would then be necessary.

### V. HYSTERESIS

If a curve like that of Fig. 1 is taken past  $H_S$  and the field is then reduced, the thermal conductivity remains constant down to a nucleation field  $H_N$  below which the silver layer again becomes superconducting. In some cases the original zero-field conductivity is not reached until a small field is applied in the opposite direction. Figure 6 illustrates this situation. The presence of the hysteresis indicates that the transition is of first order, with  $H_N$  playing the role of a supercooling field.

As the temperature is raised the hysteresis decreases until it disappears at a temperature  $T^*$  (see Fig. 7). The hysteresis effects and the temperature  $T^*$  have been investigated previously, both theoretically and experimentally, at Orsay.<sup>22,23</sup> A preliminary account of some of our results has

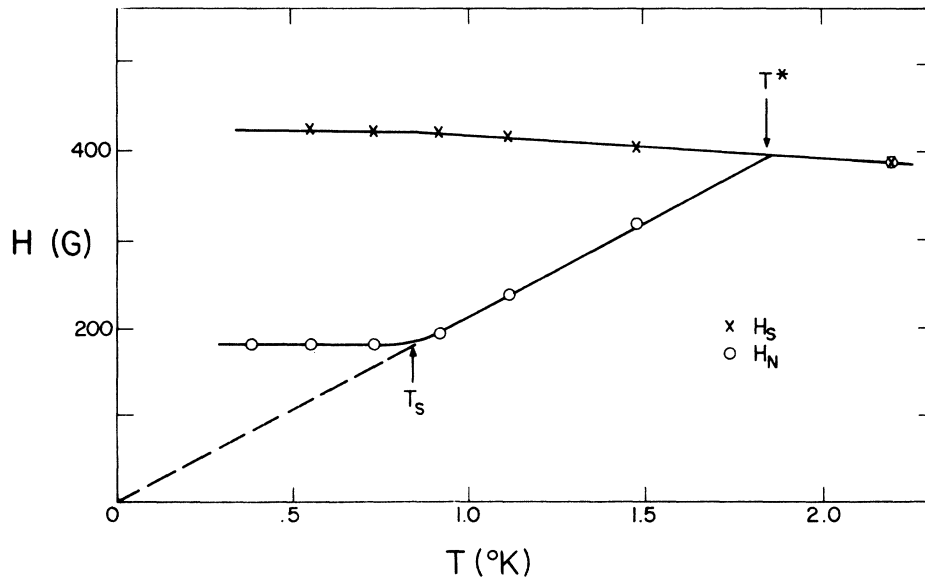


FIG. 7. Critical fields for the same specimen as that of Fig. 6. In increasing field the specimen becomes normal at  $H_S$ .  $T_S$  is the saturation temperature.

also been published.<sup>24</sup>

The behavior below  $T^*$  can be described with the help of the characteristic length  $K^{-1}$  in the normal metal, the position-dependent penetration depth  $\lambda(x, T)$ , and their ratio  $\kappa(x, T) = \lambda/K^{-1}$ .

For the case where the electronic mean free path is small compared to  $K^{-1}$  and where  $(NV)_n$  is zero,  $K^{-1} = (\hbar v_F l / 6\pi k T)^{1/2}$ .<sup>11</sup> It has also been shown theoretically and experimentally that for a case similar to ours, with  $l < K^{-1}$ , the penetration depth  $\lambda$  varies as  $T^{1/2}$ ,<sup>25</sup> so that the parameter  $\kappa$  can be expected to be proportional to  $T$ .

We identify  $H_s$  with the thermodynamic critical field (that is, we assume that there is no superheating) so that  $H_N/H_s = \kappa(T)/\kappa(T^*)$ . Since  $H_s$  is nearly independent of  $T$  we then expect  $H_N$  to be proportional to  $T$ . Figure 7 shows the excellent agreement with this prediction.

In Ref. 24 we went so far as to calculate  $T^*$  from  $K^{-1}$  and  $\lambda$ , with the help of the appropriate relations from Refs. 23 and 25 and got very good agreement, surprisingly so in view of the approximate nature of the theoretical relations for  $K^{-1}$  and  $\lambda$ .

There is a further feature of the hysteresis which must be taken into account: If a hysteresis loop like that of Fig. 6 is traversed a second time, without increasing the field too far beyond  $H_s$ , it repeats. If, however, the field is increased beyond the lower critical field of the lead-bismuth layer, subsequent traversals follow a narrower loop, like that shown on Fig. 8 by dashed lines. The original loop can then only be recovered if the specimen is warmed above the PbBi transition temperature.

It is likely that some flux is trapped in the PbBi

when the field is reduced, and that some of this flux extends into the silver layer. The external field at which the silver becomes normal in increasing fields would then be smaller. In decreasing fields the trapped flux can provide nucleation centers which will reduce the amount of supercooling.

For measurements of  $H_s$  and  $H_N$  it is obviously important to measure virgin curves like that of Fig. 6. For such measurements the specimen was therefore warmed above 8 °K before each curve.

## VI. SATURATION

Figure 7 shows that the linear variation of  $H_N$  continues only to a temperature  $T_s$  below which  $H_N$  remains constant. We have identified the behavior below  $T_s$  with the phenomenon of "saturation" which previously had been thought to be important only in the vicinity of  $T_{cn}$ , the transition temperature of the "normal" layer.<sup>22</sup>

As shown by Falk,<sup>26</sup> and discussed in Refs. 22 and 23, saturation occurs when the cubic term in the Ginzburg-Landau equation,  $C\Delta'' = A\Delta + B\Delta^3$ , dominates. A recent discussion, closely relevant to our experimental situation is that of Deutscher and Valette.<sup>27</sup>

When a saturated region exists in the normal metal the pair potential varies according to  $\Delta = \Delta_n x_0 / (x + x_0)$  up to a distance  $x_c$  from the interface (where  $\Delta = \Delta_c$ ), beyond which the linear term in the Ginzburg-Landau equation dominates, so that  $\Delta = \Delta_c e^{-Kx}$ . Up to  $x_c$ ,  $\kappa$  has the Gorkov-Goodman value  $\kappa_{GG}$  and for  $x > x_c$  it increases exponentially according to  $\kappa = \kappa_{GG} e^{Kx} / e^{Kx_c}$ . By matching the two solutions for  $\Delta$  and their derivatives at  $x_c$  we find the relation  $x_c = K^{-1} - x_0$ .

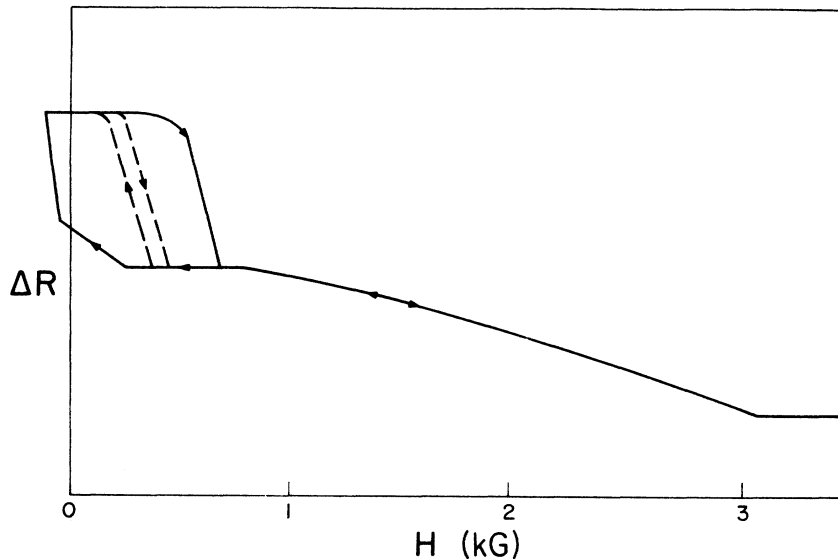


FIG. 8. Hysteresis loop taken to the field where the lead-alloy layer becomes normal. There is very little hysteresis above  $H_s$ . The dashed lines are followed after the first traversal.



A saturated region first appears at the temperature  $T_s^0$  defined by  $K^{-1}(T_s^0) = x_0$ . This temperature is called the saturation temperature by Deutscher and Valette.<sup>27</sup> In our experiment, however, saturation effects will only become evident when the saturated region extends throughout the normal layer, i. e., at a temperature  $T_s$  corresponding to  $x_c = \frac{1}{2}d_n$ . The two temperatures are related by  $\frac{1}{2}d_n = K^{-1}(T_s) - K^{-1}(T_s^0)$ .

For the specimen of Fig. 7,  $T_s = 0.83^\circ\text{K}$ ,  $K^{-1} = 2290/T^{1/2} \text{ \AA}$ , and  $d_n = 2000 \text{ \AA}$ , from which we find  $T_s^0 = 2.3^\circ\text{K}$ . We have shown in Ref. 24 that the saturation temperature is a function of  $(NV)_n$ . A more exact calculation of this function has been made by Deutscher and Valette,<sup>27</sup> who present their result as a graph of  $(NV)_n$  vs  $T_s^0$ . From their graph we find for  $T_s^0 = 2.3^\circ\text{K}$  the value of 0.08 for  $(NV)_n$ .

## VII. COMPARISON WITH OTHER EXPERIMENTS: SUMMARY AND OUTLOOK

In his review of 1969, Clarke<sup>2</sup> described a number of proximity effect experiments which can in principle give information of  $(NV)_n$ . They were based on measurements of transition temperature, critical current and tunneling, all of them with copper as the normal metal. He concluded that in spite of the considerable experimental and theoretical efforts it was possible to conclude only that  $NV$  for copper was between  $-0.1$  and  $+0.1$ . We would like to reexamine this conclusion in the light of the recent experiments of Krätzig,<sup>28</sup> Valette,<sup>8,31</sup> and Gray,<sup>29</sup> as well as our own.

Krätzig measured the attenuation of ultrasonic surface waves on copper-lead and silver-lead double layers. His data give  $K^{-1}(T)$ , which he uses, together with the theoretical expressions of de Gennes,<sup>11</sup> to find  $(NV)_n$ . He finds the values 0.064 for copper and 0.072 for silver, with an experimental error of about  $\pm 10\%$ . The theoretical expressions assume that the specimen is in the dirty limit ( $l \ll K^{-1}$ ) and that the temperature is reasonably close to the transition temperature  $T_{cs}$  of the superconducting metal. Both of these conditions are only approximately fulfilled for his specimens.

The experiment of Valette<sup>8</sup> measures the screening length  $\rho$ , which is the distance from the interface to which a magnetic field penetrates in the normal metal. From the data a value of  $(NV)_n$  can be obtained in two independent ways. A calculation of  $\rho(T)$  made by Deutscher<sup>30</sup> fits at temperatures above  $2.5^\circ$  and leads to a value of  $NV$  for copper and silver of  $0.06 \pm 0.04$ .<sup>31</sup>

At lower temperatures the dependence of  $\rho$  on  $T$  changes as a result of the phenomenon of saturation described in Sec. VI. In the saturated region  $\rho T^{1/2}$  is constant<sup>27</sup> and the saturation temperature  $T_s^0$  can be determined from a graph of  $\rho T^{1/2}$  against

$T$ . From the measurement of  $T_s^0$ , Deutscher and Valette find  $NV = 0.05 \pm 0.02$  for both copper and silver.<sup>27</sup> The determination of  $(NV)_n$  from the saturation temperature is relatively straightforward and, moreover, does not depend on measurements of thickness or electronic mean free path.

In the tunneling experiments of Gray<sup>29</sup> several angstroms of aluminum oxide are evaporated at the NS interface to reduce the transmission of electrons between the two metals. The theory of McMillan<sup>16</sup> can then be used to give a value of  $(NV)_n$ . A possible difficulty with the interpretation is that it uses a relation between the transmission coefficient and the difference  $T_{cs} - T_{cns}$  (where  $T_{cns}$  is the transition temperature of the composite specimen) which assumes that  $(NV)_n = 0$ , and therefore neglects the effect of  $(NV)_n$  on  $T_{cns}$ .

Gray has so far published results only on a gold film for which he found  $NV = 0.072 \pm 0.004$ . Preliminary results on silver and copper lead to values which are smaller, and "perhaps as low as 0.05."<sup>32</sup>

Like the work of Valette our thermal-conductivity measurements lead to two independent results for  $(NV)_n$ , one from the energy gaps, the other from the saturation temperature. The energy-gap measurements are more tedious to carry out and although their principle is perhaps the most straightforward of all, the necessary corrections cause the interpretation to be less direct; on the other hand we have accumulated a considerable amount of data. The theory of the saturation temperature was developed only after the measurements were completed. Otherwise we might have exploited this method more fully. Our results for  $NV$  of silver, of 0.05 and 0.08, respectively, are seen to be in moderately good accord with the other determinations.

We have also made some measurements on copper films. Unfortunately it turned out to be even more difficult to make clean triple layers with copper. The dirty triple layers and the double layers confirmed the results for silver shown on Fig. 4. A single clean triple-layer specimen ( $d_n = 2250 \text{ \AA}$ ,  $\rho_0 = 0.32 \times 10^{-6} \Omega \text{ cm}$ ,  $l_n = 4600 \text{ \AA}$ , using  $\rho l = 0.767 \times 10^{-11} \Omega \text{ cm}^2$ ,<sup>18</sup>  $T_f = 0.24^\circ\text{K}$ ) indicated a value of  $NV$  close to zero.

A new method to determine  $(NV)_n$  has been described by Clarke, Freake, Rappaport, and Thorp.<sup>33</sup> It depends on a measurement of the transverse resistance of SNS sandwiches, and promises to be particularly sensitive.

Although each of the experiments has its particular disadvantages it seems clear that decisive progress has been made since Clarke's review. There can hardly remain any doubt that  $NV$  is positive, particularly for silver and gold. Even the quantitative agreement is quite good, in view of the widely different experimental approaches. Whenever a

difference is reported among the three metals it indicates that  $NV$  is biggest for gold and smallest for copper.

A direct observation of superconductivity may, however, well be elusive. Gold would seem to be the best candidate if the indications that  $(NV)_n$  is largest for it are substantiated. Since a value of 0.07 for  $NV$  corresponds to a transition temperature of about  $10^{-4}$  °K and a value of 0.06 to about  $10^{-5}$  °K it is clear that the experimental difficulties are considerable.

In the nuclear-cooling experiments of Kurti *et al.*<sup>34</sup> temperatures of about  $10^{-6}$  °K are reported for copper. These are not, however, equilibrium temperatures. Only the alignment of the nuclear spin system corresponds to such low temperatures, while the lattice is likely to remain at temperatures in the millidegree region. In a search for superconductivity, it would, of course, be important to use specimens without any traces of magnetic impurities. It is known that these are particularly difficult to remove in copper. An additional difficulty which may be nontrivial in a magnetic-cooling experiment is that the critical fields must be expected to be quite minute.

Finally we mention that the experiments of Luo

and Andres<sup>35</sup> suggest that if it is possible to prepare gold in the hcp phase it is likely to be superconducting at a much higher temperature.

We conclude that the outlook for observation of superconductivity in copper, silver, or gold in the absence of the proximity effect is poor, but that the indirect evidence that these metals are intrinsic superconductors is now so strong as to leave little doubt.

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