PHYSICAL REVIEW VOLUME 164, NUMBER 2 10 DECEMBER 1967

Gapless Superconductivity Induced by the Proximity Effect

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(Received 13 June 1967)

Fulde and Maki have calculated the tunneling conductance of a superconducting film in the gapless regime. We have studied the tunneling characteristics of Al-Al_2O_3-Pb-M junctions (where M was respectively Ni, Fe, and Pt) as a function of temperature and of the lead film thickness. In the case of Pb-Ni and Pb-Fe sandwiches, the lead film is gapless and the ratio of the conductances at zero bias in the normal and superconducting states approaches unity linearly as the temperature approaches T_c (the sandwich transition temperature). The slope of this linear portion is proportional to $C(t_c)$, which is a universal function of $t_c = T_c/T_{cs}$, where T_{cs} is the transition temperature of pure lead. In agreement with theory $C(t_c)$ approaches 2 as t_c approaches unity; but sandwiches with $t_c < 1$ are found to be more gapless than predicted by theory. The same conclusions apply to Pb-Pt sandwiches which exhibit quasigapless superconductivity. Finally, Pb-Pt and Pb-Ni sandwiches with the same T_c display the same degree of gapless superconductivity. On the other hand, Josephson tunneling experiments were performed with Cr-Pb-PbO-Pb-Cr junctions. Although the magnitude of the Josephson current seems to decrease with increasing degree of gapless superconductivity, its temperature and field dependences are very similar to those previously observed in superconductors displaying an energy gap.

I. INTRODUCTION

GAPLESS superconductivity induced by the proximity effect of magnetic as well as nonmagnetic films was discussed theoretically by Fulde and Maki[1,2] and de Gennes and Mauro.[3] Experimentally, gapless superconductivity in superimposed films was first reported by Woolf and Reif.[4] A quantitative study of the degree of gapless superconductivity as a function of superconducting film thickness was reported by the author,[5] and some further measurements were recently obtained by Claeson and Gygax.[6] As the conductance at zero bias has been calculated[1] in the Ginzburg-Landau limit as a function of temperature, it would be interesting to compare the theoretical predictions with experimental measurements close to the transition temperature of the sandwich. (Most previous measurements[5,6] were obtained at very low temperatures where the theory[1] does not apply.) Furthermore, in view of the different theoretical predictions of Fulde and Maki[2] and of de Gennes and Mauro,[3] the strength of the depairing by magnetic (Fe, Ni) and nonmagnetic (Pt) elements will be compared in the first part of this paper.

The second part of the paper will describe Josephson tunneling experiments performed between two gapless superconducting films. Such experiments demonstrate that the presence of a Josephson tunneling current only depends on the existence of superconducting electron pairs irrespective of the presence or absence of an energy gap. As very small magnetic fields or electric currents destroy the Josephson current, the state of gapless superconductivity must be attained either by dissolving paramagnetic impurities in the superconductor or by proximity effect with a magnetic element. The alloy method is inconvenient owing to the fact that the insulating barrier is a thermally grown oxide, and during such a treatment, metastable lead or tin magnetic alloys reject the magnetic impurities from solid solution. As a result, the proximity effect method was used and the Josephson tunneling current was measured between two Pb-Cr sandwiches. The degree of gapless superconductivity can be changed by varying the lead film thickness.

II. DEPAIRING BY PROXIMITY EFFECT

A. Experimental Procedure

The details of the apparatus and the technique used in the preparation of the tunnel junctions have already been described elsewhere.[5] In brief, an aluminum film is evaporated and oxidized; subsequently, a Pb-M sandwich (where M is 50 Å of Ni, or 50 Å of Fe, or a platinum film) is deposited at 77°K by getter sputtering. The tunnel junctions were not warmed up above 77°K until measured, in order to avoid spurious diffusion effects. The tunneling experiments were performed on the lead side of the sandwich using derivative apparatus with an ac modulating signal of about 20 μV at a frequency of 10 000 cycles. The transition temperature of the superimposed films is taken as the temperature at which the dV/dI versus V curve is parallel to the V axis.

B. Experimental Results

Figures 1(a) and 1(b) show the dV/dI versus V curve for an Al-Al_2O_3-Pb-Fe tunnel junction. As shown in Fig. 1(b), the dynamic resistance of the junction (dV/dI) around zero bias increases sharply below 1.52°K, the transition temperature of the aluminum film. Simultaneously, one can see around 1.2 mV

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[1] P. Fulde and K. Maki, Phys. Condensed Matter **5**, 380 (1966).
[2] P. Fulde and K. Maki, Phys. Rev. Letters **15**, 675 (1965).
[3] P. G. de Gennes and S. Mauro, Solid State Commun. **3**, 381 (1965).
[4] M. A. Woolf and F. Reif, Phys. Rev. **137**, A557 (1965).
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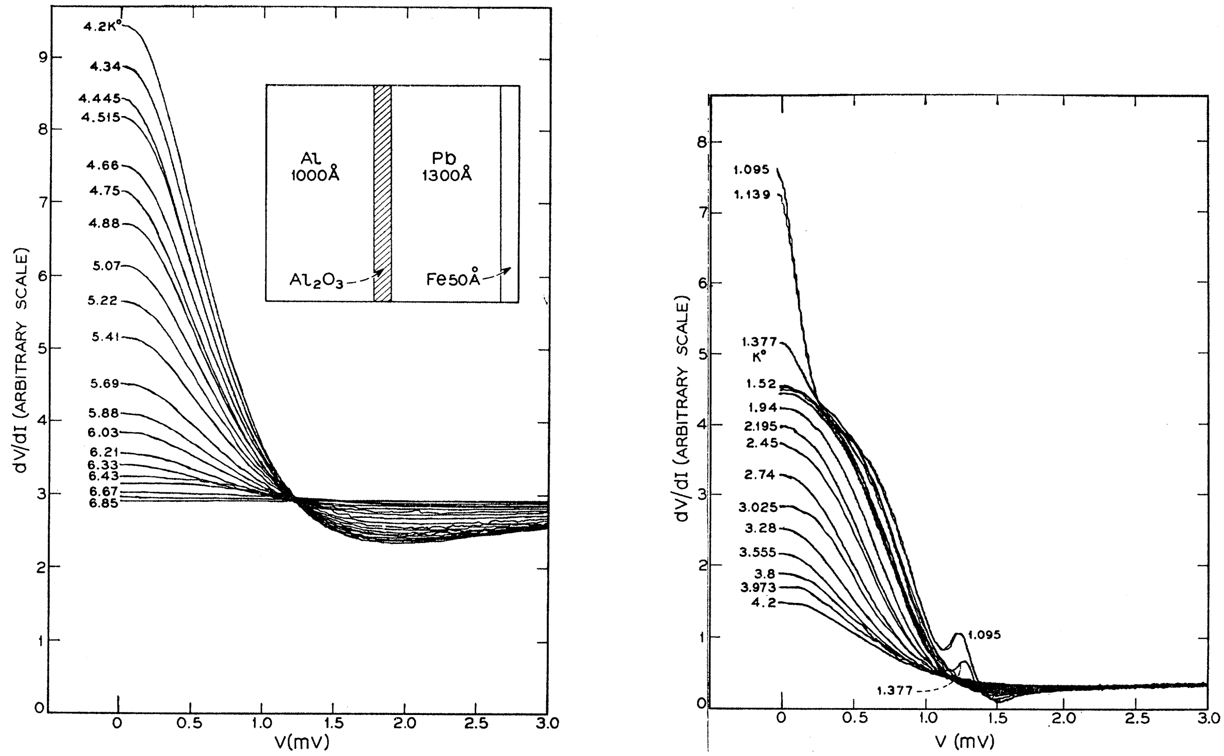

(a) (b)

FIG. 1 (a) and (b) $dV/dI-V$ curve for an Al-Al$_2$O$_3$-Pb-Fe junction as a function of temperature. The dV/dI scale (vertical) corresponds to 2 μV per division at constant current.

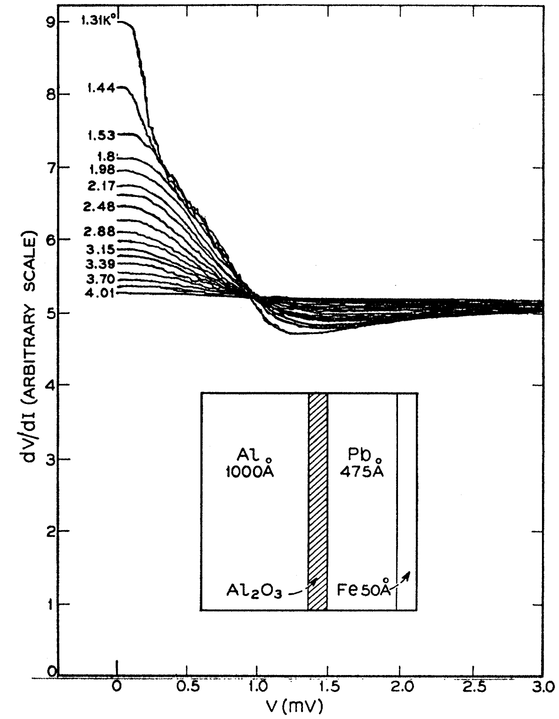

FIG. 2. $dV/dI-V$ curve for an Al-Al$_2$O$_3$-Pb-Fe junction as a function of temperature. The dV/dI scale (vertical) corresponds to 2 μV per division at constant current.

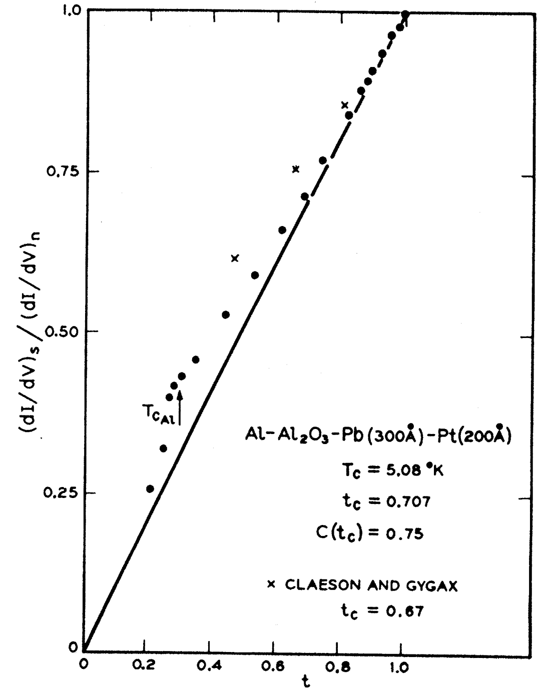

FIG. 3. Relative conductance at zero bias $[(dI/dV)_s/(dI/dV)_n]$ as a function of $t=T/T_c$ for an Al-Al$_2$O$_3$-Pb-Ni junction.

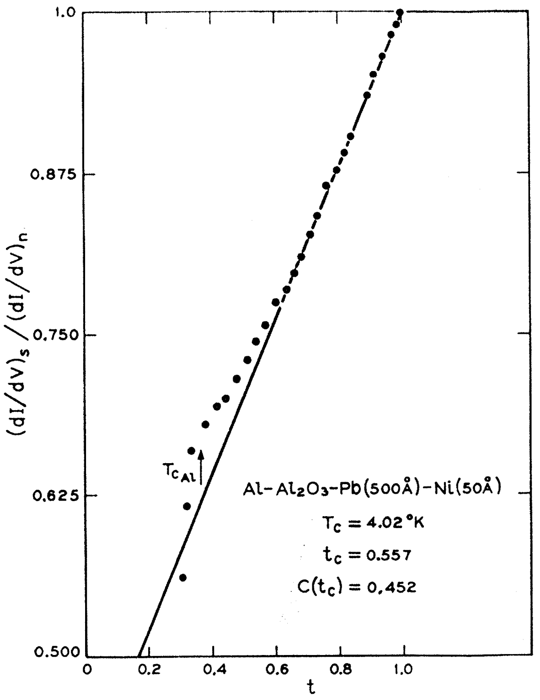

FIG. 4. Relative conductance at zero bias as a function of $t = T/T_c$ for an Al-Al$_2$O$_3$-Pb-Pt junction.

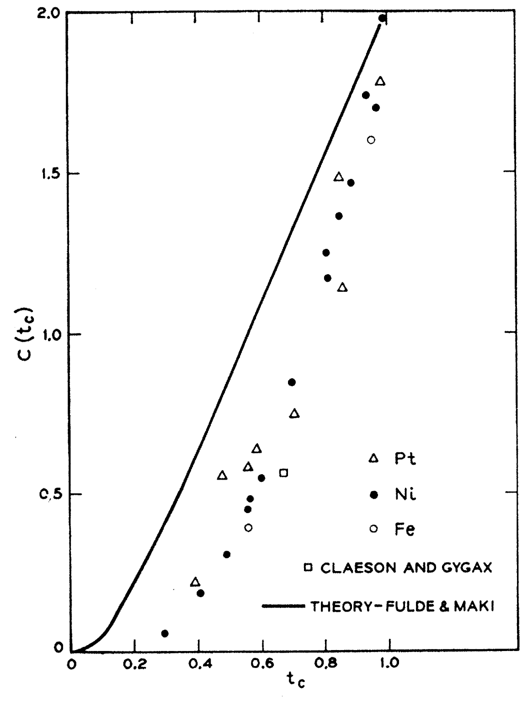

FIG. 5. Plot of $C(t_c)$ as a function of $t_c = T_c = T_c/T_{cs}$ for Pb-Ni, Pb-Fe, and Pb-Pt sandwiches.

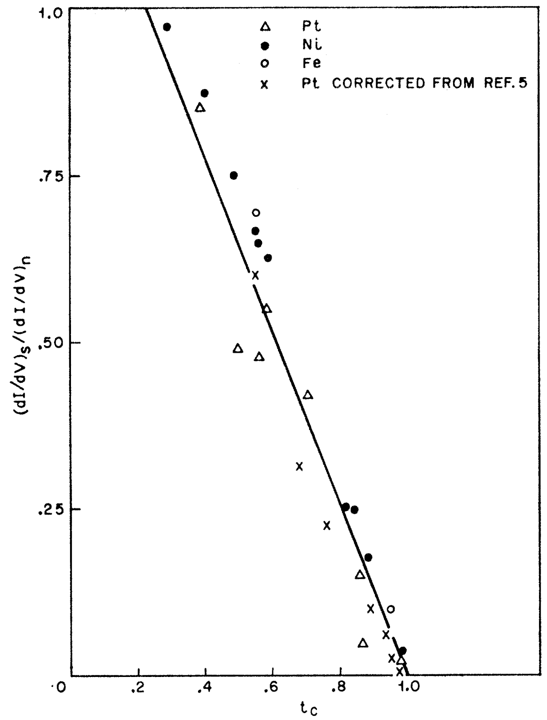

FIG. 6. Relative conductance $(dI/dV)_s/(dI/dV_n)$ measured above but very close to $T_{c\,\mathrm{Al}}$ versus t_c for Pb-Ni, Pb-Fe, and Pb-Pt sandwiches.

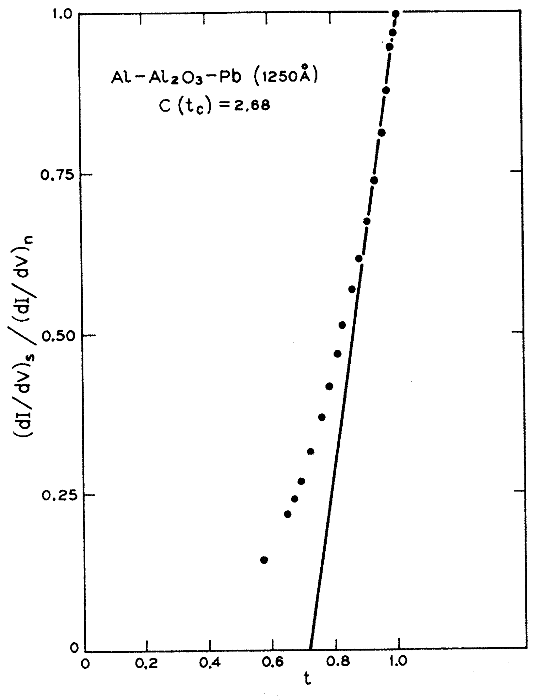

FIG. 7. Relative conductance at zero bias as a function of t for an Al-Al$_2$O$_3$-Pb junction.

a bump which corresponds to the lead localized states.[5] Another example of a similar junction with a thinner lead film is shown in Fig. 2. In this case, one can only observe the sharp increase in dV/dI around zero bias when the temperature is lowered below 1.8°K. From such curves as shown in Figs. 1 and 2, one can obtain $[dV/dI\ (7.5\ \mathrm{mV})]/[dV/dI\ (0\ \mathrm{mV})]=(dI/dV)_s/(dI/dV)_n$ as a function of temperature. The relative conductance of the junction at zero bias, obtained in such a way, is plotted in Fig. 3 for an Al-Al_2O_3-Pb-Ni junction as a function of the reduced temperature $t=T/T_c$ (where T_c is the transition temperature of the sandwich). For every sandwich with a given lead film thickness and therefore with a certain $t_c=T_c/T_{cs}$ (where T_{cs} is the transition temperature of pure lead), one can experimentally determine the function $C(t_c)=0.75\{d/dt[(dI/dV)_s/(dI/dV)_n]\}_{t=1}$. The slope of the relative conductance versus t as t approaches unity is displayed in Fig. 3 by the solid line. One again notices in Fig. 3 the sharp decrease in the relative conductance as the temperature is reduced below the transition temperature of the measuring aluminum film. If the nickel backing film is replaced by a thick nonmagnetic film, such as platinum, one obtains very similar results (see Fig. 4), i.e., a linear portion close to $t=1$ from which $C(t_c)$ is determined and a sharp decrease of the relative conductance below $T_{c\mathrm{Al}}$. The data can be summarized by plotting $C(t_c)$ as a function of t_c (see Fig. 5) and comparing it with the theoretical calculation of $C(t_c)$ by Fulde and Maki.[1]

The data may be differently summarized by plotting the value of the relative conductance of the junction measured slightly above $T_{c\mathrm{Al}}$ ($T_{c\mathrm{Al}}+0.1$°K) as a function of t_c (see Fig. 6). Figure 7 shows the dependence for the relative conductance of an Al-Al_2O_3-Pb junction on t while Fig. 8 shows the same for an Al-Al_2O_3-Pb-Pt junction in which the platinum film is very thin.

C. Discussion

As previously discussed,[5] the sharp increase in dV/dI around zero bias below $T_{c\mathrm{Al}}\simeq 1.5$°K in Figs. 1(b) and 2 is proof that the lead film is gapless: When the aluminum film becomes superconducting the states present in the gap as a result of the spin depairing by the magnetic film (Ni or Fe) are removed in the energy range of the aluminum gap. This effect is very clearly shown in Fig. 3 by the rapid decrease in relative conductance below $T_{c\mathrm{Al}}$. Consequently, comparing Figs. 3 and 4 would lead us to the conclusion that depairing by a nonmagnetic film such as platinum produces also a gapless state. However, de Gennes and Mauro[3] have predicted theoretically that the proximity effect with a nonmagnetic film does not result in a gapless state even close to the transition temperature of the sandwich. As a matter of fact, we have shown[5] how the energy gap induced by a lead film in a platinum film varies as a function of the lead film thickness. These experiments agreed quite well with McMillan's theory,[6] which predicts a zero energy gap in the platinum film only when its thickness becomes infinite. In the present experiments, the platinum films were 200 Å thick (about five coherence lengths) and, consequently, the gap will be extremely small and, as a result of thermal smearing, undetectable experimentally. The Pb-Pt sandwiches should therefore be referred to as quasigapless: quasi, because the very small gap present in such sandwiches could be detected by tunneling at very low temperatures and gapless because the dependence of the relative conductance on temperature is similar to that of a truly gapless sandwich such as Pb-Ni. The three crosses shown in Fig. 4 were obtained from recent measurements of Claeson and Gygax[6] on an Al-Al_2O_3-Pb(350 Å)-Ag(1000 Å). The agreement with the Pb-Pt data is quite good, especially if one realizes that the technique used in film deposition was completely different in both cases.

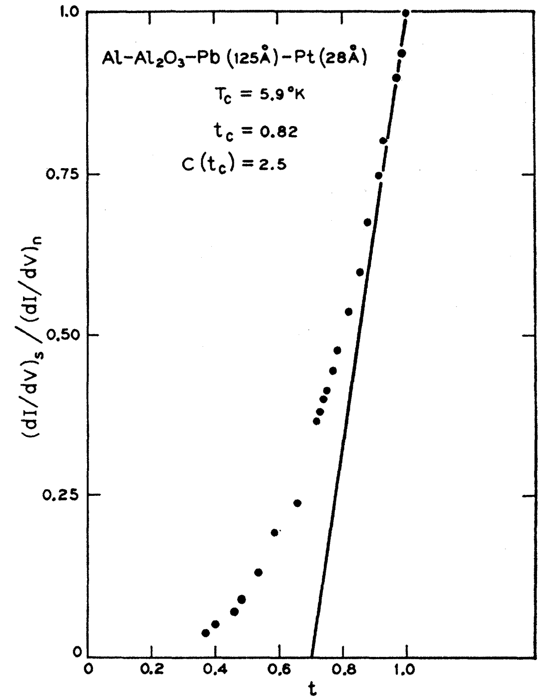

FIG. 8. Relative conductance at zero bias as a function of t for an Al-Al_2O_3-Pb-Pt junction.

Fulde and Maki[1] have calculated the relative conductance at zero bias:

$$1-(dI/dV)_s/(dI/dV)_n=\tfrac{4}{3}(1-t)C(t_c), \qquad (1)$$

where $C(t_c)$ is a universal function of the quantity t_c and has been plotted as the solid curve of Fig. 5. Relation (1) predicts that the relative conductance approaches unity linearly as t approaches 1; this fact is verified by the data shown in Figs. 3 and 4. It can be seen from relation (1) that $C(t_c)$ can also be defined as $\frac{3}{4}$ of the experimentally determined slope of the relative conductance versus t at $t=1$. A plot of $C(t_c)$ determined in that manner is shown in Fig. 5.

The agreement with theory is good from the point of view that $C(t_c)$ varies between 0 and 2 as t_c changes from 0 to 1. One the other hand, the experimental points lie systematically below the theoretical curve; in other words, the experiments show a greater degree of gapless superconductivity than predicted by theory. One possible experimental explanation for this discrepancy is that thin lead films may have pinholes, and one would then tunnel partially from the aluminum film directly to the normal film. This additional Ohmic contribution would make the junction look more gapless than it really is. This hypothesis can be ruled out for two reasons. First, in Pb-Ni sandwiches with a $t_c > 0.8$ the lead film thickness is greater than 750 Å; it is unlikely that such thick films would have pinholes and even in that temperature range the data lie already below the theoretical curve. On the other hand, the depairing effect of platinum being much weaker than that of nickel,[5] the lead film in a Pb-Ni sandwich is rather thicker than that of a Pb-Pt sandwich with the same t_c. The agreement shown in Fig. 5 between the Pb-Pt and the Pb-Ni or Pb-Fe data rules out the pinhole hypothesis. Furthermore, this agreement shows that Pb-Pt and Pb-Ni sandwiches with the same T_c display the same degree of gapless superconductivity as measured by the slope of the relative conductance versus T curve near T_c. In conclusion, it is felt that the difference between experiment and theory is significant and must be of theoretical nature.

The degree of gapless superconductivity can also be estimated by measuring the relative conductance at a temperature just above the transition temperature of the measuring aluminum film. Such a plot is shown in Fig. 6. The solid line represents the semiempirical relation previously[5] derived for gapless Pb-Ni sandwiches (see Appendix):

$$(dI/dV)_s/(dI/dV)_n = 1.30(1-t_c). \tag{2}$$

Again, Fig. 6 shows that Pb-Pt and Pb-Ni sandwiches with the same transition temperature have the same degree of gapless superconductivity. The corrected Pb-Pt data from Ref. 5 are also in good agreement with the present data.[7]

Further light may be shed on the difference between the quasigapless and gapless states by reducing the thickness of the platinum film in a Pb-Pt sandwich. The relative conductance for an Al-Al_2O_3-Pb tunnel junction is shown as a function of temperature in Fig. 7. Although the Fulde-Maki theory is not applicable in that case, one can still define for the purpose of comparison $C(t_c)$ as $0.75\{d/dt[(dI/dV)_s/(dI/dV)_n]\}_{t=1}$. The experimental value of $C(t_c)$ is 2.68. Theoretically, using the conductance calculations of Bermon[8] with $2\Delta(0) = 4.3kT_{cs}$ to take into account the strong-coupling nature of lead, one finds $C(t_c) = 2.50$. The difference between the experimental and theoretical values of $C(t_c)$ may be due to the fact that Bermon used a BCS density of states, which is not adequate for lead. The important point is that although in the gapless (Pb-Ni, Pb-Fe) cases and the quasigapless case (Pb-Pt) $C(t_c)$ was always smaller than 2, it is greater than 2 when a measurable gap is present. Figure 8 shows the relative conductance of an Al-Al_2O_3-Pb-Pt junction as a function of temperature. The platinum film is now thin enough to have a measurable gap induced by the lead film.[5] The lead film was chosen thin so that the transition temperature of the sandwich would be below that of pure lead. As shown in Fig. 8, although $t_c = 0.82$, $C(t_c)$ is 2.5, i.e., larger than 2 and would approach 2.68 as the platinum film thickness approaches zero. Consequently, the quasigapless case changes to a gap case as the normal film thickness is reduced, and at this point, $C(t_c)$ exceeds the value of 2; this never happens in the truly gapless case such as Pb-Ni.

III. JOSEPHSON TUNNELING BETWEEN TWO GAPLESS SUPERCONDUCTORS

A. Experimental Procedure

The tunnel junctions consisted of two crossed strips each 0.0125 cm wide. First, a 100 Å Cr film was sublimed from a tungsten filament, followed by the evaporation of a lead film ranging in thickness from 800–2000 Å. This sandwich was then oxidized for 2 h at 40°C in dry oxygen. Finally, a cross-strip sandwich was deposited by first evaporating 800–2000 Å of lead followed by the sublimation of 100 Å of Cr. All the depositions were made on a glass substrate at room temperature.

B. Experimental Results and Discussion

In order to ensure that the Josephson current in each junction was not partially caused by microshorts each tunnel junction used in this study displayed an increasing resistance with decreasing temperature (the resistance increased by about a factor of 2 between 77 and 4.2°K). The resistance of all junctions used was approximately $2\times10^{-2}\ \Omega\ \mathrm{mm}^2$. Furthermore, the Josephson current of every junction studied, could be reduced to very nearly zero (a few tens of microamperes) by the application of a very small parallel magnetic field (about 3 G). In the junctions displaying a rather large

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[7] Figure 7 of Ref. 5 showing the relative conductance of Al-Al_2O_3-Pb-Pt junctions as a function of the lead thickness was correct, but the solid curve of Fig. 10 showing the relative conductance as a function of $t_c = T_c/T_{cs}$ was wrong. The reason for this error is that in Ref. 5, T_c was not measured but obtained from the T_c-versus-lead film thickness curve for G-Pt-Pb sandwiches shown in Fig. 3 of Ref. 11. If one correctly uses the curve for G-Pb-Pt instead, which is the order of deposition used in the tunnel junctions, then the solid curve of Fig. 10, Ref. 5, which averages the Pb-Pt data, superimposes on the curve for the Pb-Ni data which can also be seen in Fig. 6 of the present study.

[8] S. Bermon, Physics Department, University of Illinois Technical Report No. 1 on NSFGP 1100, 1964 (unpublished).

TABLE I. Properties of the various Josephson tunneling junctions.

Junction	d_{Pb} (Å)	T_c (°K)	$2\Delta(0°\mathrm{K})$ (mV)	$2\Delta(0°\mathrm{K})/kT_c$	$J_{\mathrm{th}}(0°\mathrm{K})$ (mA)	$J_{\mathrm{expt}}(0°\mathrm{K})$ (mA)	$J_{\mathrm{expt}}/J_{\mathrm{th}}(0°\mathrm{K})$ (%)
Pb-PbO-Pb #30	2500	7.5	2.700	4.2	8.7	5.75	66
Cr-Pb-PbO-Pb-Cr #1	2000	7.3	2.500	4.0	4.35	2.20	51
Cr-Pb-PbO-Pb-Cr #13	1750	7.3	2.55	4.0	5.75	4.0	69.5
Cr-Pb-PbO-Pb-Cr #16	1250	7.1	2.45	4.0	2.2	1.45	66
Cr-Pb-PbO-Pb-Cr #17	1250	7.1	2.50	4.1	2.0	1.22	61
Cr-Pb-PbO-Pb-Cr #15	1000	6.7	2.50	4.3	1.40	0.27	19
Cr-Pb-PbO-Pb-Cr #18	800	6.5	2.28	4.1	0.35	0.094	27

Josephson current, the typical diffraction pattern of current versus magnetic field was obtained; in the case of junction Cr-Pb-PbO-Pb-Cr #1 the period was 2.3 G which, using a penetration depth of 390 Å, corresponds to a flux of 2.3×10^{-7} G cm^2 in the junction. The minima were too poorly defined in the junctions with smaller Josephson current to allow a precise determination of the period.

As shown in Table I, the transition temperature of a Pb-PbO-Pb junction is 7.5°K. This rather high transition temperature for the lead film is believed to be due to strain and was quite reproducible from junction to junction. Therefore, any junction with a transition temperature lower than 7.5°K is composed of two gapless lead films. The fact that the proximity effect with a magnetic film leads to gapless superconductivity has been established in the first part of this paper as well as in previous theoretical[1,2] and experimental studies.[4–6] Another effect of the chromium as shown in Fig. 9 is to reduce the strength of the lead phonon structure in the density of states. If one takes as a definition of the gap the voltage at which the current rises rapidly[9] (after reducing the Josephson current to zero by the application of a few gauss), the temperature dependence of the lead energy gap follows very closely the BCS theory as calculated numerically by Mühlschelegel[10] shown as the upper curve of Fig. 10. For a gapless superconductor, the voltage at which the current rises rapidly corresponds to the value of the order parameter and a plot of this quantity versus temperature is again in good agreement with the BCS theory as shown for sample Cr-Pb-PbO-Cr #13 in Fig. 10. It is clear from Table I that as the lead film thickness is reduced, the critical temperature decreases; the order parameter decreases also, although more erratically, while the ratio $2\Delta(0)/kT_c$ remains approximately constant and equal to 4.15 ± 0.15. The fact that an 800 Å lead film in proximity with chromium has a transition temperature as high as 6.5°K is most probably due to some decoupling occurring between the lead and chromium films as a result of the prolonged exposure to atmosphere.[11] It would have been interesting to study the Josephson effect in more gapless sandwiches, but every attempt to reduce the lead film thickness below 800 Å resulted in shorts.

The question of whether a Josephson tunneling current can flow between two gapless superconductors is clearly answered by the I–V curves shown in Fig. 9. Furthermore, Table I shows that such a Josephson

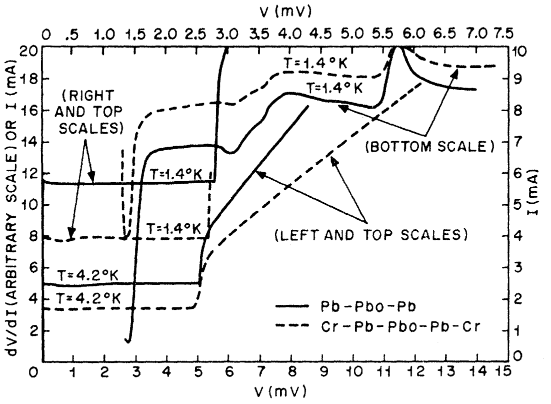

FIG. 9. $dV/dI-V$ curves for tunnel junctions Pb-PbO-Pb #30 and Cr-Pb-PbO-Pb-Cr #13. The dV/dI scale (left) corresponds to 2 μV per division at constant current. The two lower I-V curves were taken on the same junctions at 4.2°K while the two upper I-V curves were obtained at 1.4°K (note the change of scales).

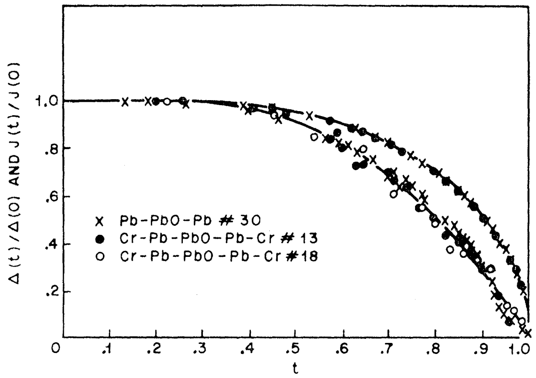

FIG. 10. Reduced energy gap (or reduced order parameter) and reduced Josephson tunneling current (lower curve) as a function of reduced temperature for two gapless junctions (Cr-Pb-PbO-Pb-Cr #13 and 18) and for a regular junction (Pb-PbO-Pb #30).

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[9] R. F. Gasparovic, B. N. Taylor, and R. E. Eck, Solid State Commun. **4**, 59 (1966).

[10] B. Mühlschlegel, Z. Physik **155**, 313 (1959).

[11] J. J. Hauser, H. C. Theuerer, and N. R. Werthamer, Phys. Rev. **136**, A637 (1964).

current is still present between two lead films with transition temperatures as low as 6.5°K. The theoretical value of the Josephson current at 0°K was taken as $J(0°\mathrm{K})=(\pi/2)R_n^{-1}\Delta(0°\mathrm{K})$,[12] where R_n is the normal resistance of the junction. It is difficult to make statements about the absolute value of the Josephson current, as even under identical experimental procedures the Josephson current of a Pb-PbO-Pb junction scatters within broad limits. Nevertheless, Table I seems to indicate that the ratio of experimentally measured to theoretically predicted Josephson current decreases with increasing degree of gapless superconductivity. On the other hand, the temperature dependence of the Josephson current between two identical superconductors is given by[12]:

$$J(T)=(\pi/2)R_n^{-1}\Delta(T)\ \tanh\Delta(T)/2kT. \tag{1}$$

The temperature dependence of the gap parameter $\Delta(T)$ can be very closely approximated (within 1%) by the expression given by Thouless:

$$\Delta(t)/\Delta(0)=\tanh[\Delta(t)/\Delta(0)t], \tag{2}$$

where $t=T/T_c$. Equation (1) can be written as

$$J(t)/J(0)=[\Delta(t)/\Delta(0)]\ \tanh[C\Delta(t)/4t\Delta(0)], \tag{3}$$

where C is defined by

$$2\Delta(0)=CkT_c. \tag{4}$$

If one choses $C=4$, which is approximately true for all junctions used here (see Table I), Eq. (3) becomes, after taking relation (2) into account,

$$J(t)/J(0)=[\Delta(t)/\Delta(0)]^2. \tag{5}$$

Equation (5) has been plotted as the lower curve of Fig. 10 using for $\Delta(t)/\Delta(0)$ versus t the numerically calculated values of Mühlschlegel.[10] The experimental data even for the most gapless junction (Cr-Pb-PbO-Pb-Cr #18) agree quite well with the theoretical predictions.

In conclusion, a Josephson current has been shown to flow between two gapless superconductors thus demonstrating that its presence depends only on the existence of superconducting electron pairs and not on the existence of an energy gap. This Josephson current has the same temperature and field dependence as the Josephson current between two superconductors displaying an energy gap. The theory of the Josephson effect can be used in the gapless regime, as long as $\Delta(t)$ is now interpreted as the order parameter.

ACKNOWLEDGMENTS

I wish to thank W. H. Haemmerle for his technical assistance both in preparing the junctions and in obtaining the data. I also would like to acknowledge helpful discussions with N. R. Werthamer and W. L. McMillan.

APPENDIX

The three equations which give an implicit solution for the transition temperature of the sandwich as a function of the thickness d_s and d_n, of the superconducting and normal paramagnetic films, respectively, are[13]

$$\ln T_{cs}/T_c=\chi(\xi_s^2k_s^2), \tag{A1}$$

$$\ln T_{cn}/T_c=\chi(-\xi_n^2k_n^2+\alpha/t_c), \tag{A2}$$

$$[N\xi^2k\ \tan kd]_s=[N\xi^2k\ \tanh kd]_n, \tag{A3}$$

where all the terms have been previously defined[13] and α measures the strength of the spin depairing. The question of interest is what value of d_s corresponds to $T_c=T_{cn}$. The problem can be considered in two different cases.

Case 1. $\alpha=0$ This case corresponds to a normal film without magnetic impurities. The only solution of Eq. (A2) for $T_c=T_{cn}$ is $k_n=0$, which means that k_n^{-1} (the distance that superconducting pairs penetrate on the normal side) is infinite, which is obvious as the "normal" film is now superconducting. Substituting $k_n=0$ in (A3) yields the trivial solution $d_s=0$. An experimental verification of this case was made with the Pb-Al system.[14]

Case 2. $\alpha\neq0$ The solution of Eq. (A2) corresponding to $T_c=T_{cn}$ is

$$k_n^{-1}=\xi_{ns}/(\alpha)^{1,2}, \tag{A4}$$

where $\xi_n=\xi_{ns}/(t_c)^{1/2}$ and $\xi_{ns}=\xi_n(T_c=T_{cs})$. Substitution of (A4) into (A3), combined with Eq. (A1), will yield a nonzero value for d_s. This result was demonstrated experimentally by the horizontal portion of the curve near T_{cn} in Fig. 8 of Ref. 13. It was also pointed out[13] that in the limit of large α and $T_{cn}=0$, Eq. (A4) is valid at any temperature.

In the limit of α infinite, i.e., for strong magnetism, Eq. (A4) yields the well-known result[13] that electron pairs do not penetrate the magnetic film ($k_n^{-1}=0$). The three equations (A1), (A2), and (A3) are then replaced by the single following equation:

$$\ln T_{cs}/T_c=\chi(\pi^2\xi_s^2/4d_s^2). \tag{A5}$$

If one uses the simplifying assumption

$$\chi(z)\simeq\ln[1+\pi^2/4z],$$

which is valid for $z\geq0$, and gives the correct slope of 2.44 for $\chi(z)$ at $z=0$, (A5) reduces to

$$t_c=1-\pi^4\xi_{ss}^2/16d_s^2. \tag{A6}$$

Relation 2 in the text is obtained by combining (A6) with the empirical relation[5]

$$(dI/dV)_s/(dI/dV)_n=(400/d_s)^2. \tag{A7}$$

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From Eq. (A6), setting $T_c=T_{cn}=0$°K, we find

$$d_s=(\pi/2)^2\xi_{ss}. \tag{A8}$$

The meaning of relation (A8) is that a film with the order parameter fixed at zero on one of its boundaries will not be superconducting when its thickness is inferior to the critical thickness given by (A8). Recently, Werthamer[15] solved exactly the Ginzburg-Landau equations for a film of thickness d with the order parameter fixed at zero on both boundaries and found that the film would not be superconducting unless its thickness is greater than $d_c=\pi\delta/\kappa\simeq\pi\xi_0$ (δ is the weak field penetration depth and κ the G-L parameter). Consequently, superconductivity would disappear in a film thinner than $(\pi/2)\xi_0$ when the order parameter is fixed at zero on only one of its boundaries. Equation (A8) is therefore a very general result of the G-L theory; the discrepancy between the two numerical results is most probably due to the fact that (A8) is derived from Eqs. (A1) through (A3), which are only valid in the dirty limit ($l<\xi_0$), while the Ginzburg-Landau result was derived for pure films ($l>\xi_0$).

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PHYSICAL REVIEW VOLUME 164, NUMBER 2 10 DECEMBER 1967

Superconducting Transitions of Isotopes of Zinc*

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(Received 6 March 1967)

The effect of isotopic mass on the superconducting transition temperature T_c of Zn has been investigated in three highly purified samples with average isotopic masses of 63.96, 65.91, and 67.94. By extrapolating critical magnetic field curves to zero field, values of 0.855, 0.846, and 0.836°K were obtained for T_c of Zn^{64}, Zn^{66}, and Zn^{68}, respectively. These values were found to satisfy the relation $T_c \propto M^{-z}=M^{-0.5(1-\zeta)}$ with z taken as 0.37 and ζ as 0.25. Critical field curves measured between 0.39°K and T_c were found to have a maximum deviation from a parabola of about 5.7%. Specific heats calculated from these critical field curves are compared with direct measurements made by others. The superconducting-to-normal transition of a sample was observed to broaden as the applied magnetic field was reduced below some small value. Ratios of transition widths in "zero" field and in the earth's field ranged from about 2 to over 30, depending on the sample.

I. INTRODUCTION

The transition temperatures T_c of superconducting elements have been found to follow the relation $T_c=kM^{-z}=kM^{-0.5(1-\zeta)}$, in which k is a constant different for each element and M is the average isotopic mass of the specimen. The value of z found from the original work[1] with Hg and predicted by the simple model of Bardeen, Cooper, and Schrieffer[2] (BCS) is 0.5. ζ is the deviation from $z=0.5$. Various authors,[3–6] using more detailed models, have made predictions of values for ζ for different elements. The value of ζ predicted for Zn is among the largest made for any nontransition element.

The previous measurement of the isotope effect in Zn by Geballe and Matthias[7] suggested that the normal isotope effect of $z=0.5$ occurs in zinc. The work to be reported here gives a value of 0.37 for z. A slightly lower value was given in previous reports.[8,9] Since then a systematic error was found in the routine for establishing the temperature scale.

II. EXPERIMENTAL TECHNIQUES

Sample Preparation

The three samples used were obtained from the Oak Ridge National Laboratory and had average isotopic masses of 63.96 (99.85% Zn^{64}), 65.91(98.8% Zn^{66}), and 67.94(99.3% Zn^{68}). As received, the samples had residual resistivity ratios r of about 1/10, where $r=\rho(4°\text{K})/\rho(297°\text{K})$. A preliminary run showed that the superconducting-to-normal (S-N) transition of one of these samples in the earth's magnetic field was about 20 times as broad as that of a reasonably pure single crystal of natural Zn. The large values of r and the broad transition indicated that the samples were not adequate for studies of the isotope effect.

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* Work supported by the U.S. Atomic Energy Commission and the Wisconsin Alumni Research Foundation.

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