Superconducting proximity effect in the strong-coupling limit

William Silvert
Dalhousie University, Halifax, Nova Scotia, B3H 3J5 Canada

(Received 27 May 1975)

Some of the basic results of the theory of the superconducting proximity effect have been generalized to apply to strong-coupling systems. The results agree with Moormann's theory of the proximity effect between weak-coupling superconductors with different Debye frequencies and also indicate that logarithmic frequency averaging is correct. The theoretical results are compared with experimental data on thin films and eutectic alloys, and the agreement is very good.

Previous work on the theory of the proximity effect has assumed weak coupling in both metals, despite the fact that many experiments have been done using strong-coupling superconductors such as lead, tin, and indium. Only one theory, that of Moormann, takes into account the different phonon cutoff frequencies of the two metals.[1] However, since Moormann's theory is developed in the context of weak coupling, it has not been clear that the combined spectra of disparate metals such as lead and copper are correctly averaged by his procedure.[2] In other theories it is assumed that the cutoffs are the same in both metals and that only the strength of the coupling NV varies.[3,4]

The Moormann theory is based on the de Gennes sum rules[3] and can be written in the form[1,2,5]

$$\ln T_c = \langle NV \ln\Theta\rangle/\langle NV\rangle - 1/\langle NV\rangle + \ln 0.85, \tag{1}$$

where Θ is the Debye temperature and NV is the BCS coupling[6]; the weighted averages denoted by $\langle\cdots\rangle$ are defined by

$$\langle A\rangle \equiv \int A(r)\phi(r)\,dr \Big/ \int \phi(r)\,dr, \tag{2}$$

where $\phi(r) \equiv \langle\langle \psi_\uparrow(r)\psi_\downarrow(r)\rangle\rangle$ is the position-dependent Cooper pair correlation amplitude. For a bulk superconductor, Eq. (1) reduces to the BCS expression for the transition temperature $T_c = 0.85\Theta e^{-1/NV}$.[6] In the strong-coupling case we seek to develop an analog to Eq. (1) which reduces for a bulk superconductor to the McMillan formula,

$$T_c = (\Theta/1.45)e^{-1/\lambda^*}, \tag{3a}$$

where

$$\lambda^* = (\lambda - \mu^* - 0.62\lambda\mu^*)/1.04(1+\lambda); \tag{3b}$$

λ is the bare interaction and μ^* is the coulomb pseudopotential.[7] This can be done by observing that the condensation energy of Cooper pairs arises from virtual phonon exchange, so that the basic self-energy term is $\alpha^2 F\phi$, where α is the electron-phonon coupling constant, F is the phonon propagator, and ϕ is the pair correlation amplitude. The average self energy, therefore, involves $\int \alpha^2 F\phi\,dr$, which gives rise to the type of average seen in Eq. (2). In strong-coupling theory the bare interaction is given by $\lambda \equiv 2\int \alpha^2 F\,d\omega/\omega$ (Ref. 7), so the correct generalization to nonhomogeneous systems is to define λ^* in terms of

$$\langle\lambda\rangle = 2\int \frac{\langle\alpha^2 F\rangle\, d\omega}{\omega}. \tag{4a}$$

Similar reasoning can be applied to the averaging of the coulomb term μ^*, but since μ^* does not vary greatly from one metal to another we have used a constant value of $\mu^* = 0.13$. Using a slightly simplified form of Eq. (3b) to calculate the renormalized interaction we obtain

$$\lambda^* \equiv (\langle\lambda\rangle - \mu^*)/(1 + \langle\lambda\rangle). \tag{4b}$$

In the McMillan theory the parameter Θ is proportional to the mean phonon frequency $\bar\omega$ defined by $\lambda\bar\omega \equiv 2\int \alpha^2 F\,d\omega$. Several recent authors have refined the theory and found that $\bar\omega$ is better defined by $\lambda \ln\bar\omega \equiv 2\int \alpha^2 F \ln\omega\, d\omega/\omega$ (Refs. 8 and 9). With this modification we obtain a generalized expression for the transition temperature,

$$\ln T_c = \langle\lambda \ln\Theta\rangle/\langle\lambda\rangle - 1/\lambda^* - \ln 1.45, \tag{5}$$

with λ^* defined by Eq. (4b) and the averages defined by Eq. (2). For a bulk superconductor this reduces to a slightly simplified form of the generalized McMillan equation,[9] while in the BCS ($\mu^* = 0$) weak-coupling limit $\lambda^* \to \langle\lambda\rangle$ and we recover the Moormann result given in Eq. (1).

Equations (2), (4b), and (5) specify T_c in terms of the correlation amplitude $\phi(r)$, but a general calculation of $\phi(r)$ requires solution of the position-dependent Eliashberg equations.[10] The easiest case to study is the thin-film limit, where both films are thinner than the coherence length, and consequently $\phi(r)/N(r)$, which de Gennes has shown to be continuous,[3] can be considered constant throughout the system.[11] In this limit the required averages take the simplified form

$$\langle\lambda\rangle = (\lambda_S N_S d_S + \lambda_N N_N d_N)/(N_S d_S + N_N d_N)$$
$$= \beta_S \lambda_S + \beta_N \lambda_N \quad (6a)$$

and

$$\langle\lambda \ln\Theta\rangle = \beta_S \lambda_S \ln\Theta_S + \beta_N \lambda_N \ln\Theta_N, \quad (6b)$$

where

$$\beta_s \equiv N_S d_S/(N_S d_S + N_N d_N) = 1 - \beta_N. \quad (7)$$

The dependence of T_C on β_S is shown in Fig. 1 for two typical systems, Pb-Sn and Pb-Cu. As can be seen, the dependence is close to linear for all but the lowest values of T_C.

A number of comparisons with experimental data have been made. The use of the Cooper limit approach restricts consideration to very thin films of at most a few 100 Å in thickness. A general empirical test for the Cooper limit is that T_C depends only on d_S/d_N, and where sufficient data were available this criterion was used, rather than the requirement $d \ll \xi$ which requires that the mean free path be known. This is illustrated by the data of Bergmann, who evaporated varying thicknesses of Pb onto In substrates.[12] The values of T_C obtained for $d_{In} = 440$ Å were appreciably higher than those obtained with $d_{In} = 280$ Å when the ratios of d_{Pb}/d_{In} were the same. Since the value of ξ_{In} is approximately 300 Å, we would expect the 280-Å layers to lie near the upper limit of validity for the Cooper theory. The theoretical values obtained for T_c ran about 0.1 K less than the experimental values, which we consider excellent agreement. Similar results were obtained with the In-Tl data of Migliori and Ginsberg and of Jacobs and Ginsberg, with the theoretical values again running about 0.1 K below the experimental figures.[13] These results are shown in Table I.

TABLE I. Comparison of experimental and theoretical values of T_c.

D_{Pb} (Å)	D_{In} (Å)	β_S	T_c^{expt} (°K)[a]	T_c^{theor} (°K)[b]
0	280	0.00	4.1	4.1
100	280	0.30	5.2	5.1
200	280	0.46	5.8	5.7
300	280	0.56	6.1	6.0
400	280	0.63	6.3	6.2
D_{In} (Å)	D_{Tl} (Å)	β_S	T_c^{expt} (°K)[c]	T_c^{theor} (°K)[b]
350	736	0.38	3.4	3.3
539	804	0.47	3.5	3.4
342	380	0.54	3.6	3.5
619	445	0.65	3.7	3.6
D_{In} (Å)	D_{Tl} (Å)	β_S	t_c^{expt} [d]	t_c^{theor} [b]
175	290	0.44	0.37	0.40
160	210	0.50	0.46	0.46
160	200	0.51	0.48	0.47
175	210	0.52	0.42	0.48
160	160	0.57	0.57	0.53
175	155	0.60	0.48	0.56
160	120	0.64	0.52	0.60
175	110	0.68	0.57	0.68

[a] See Ref. 12.
[b] λ_{In} adjusted to give $T_c = 4.1$ °K for a pure In film.
[c] See Ref. 13 (a).
[d] See Ref. 13 (b). The parameter t_c is defined by $t_c \equiv (T_c - T_{cN})/(T_{cS} - T_{cN})$.

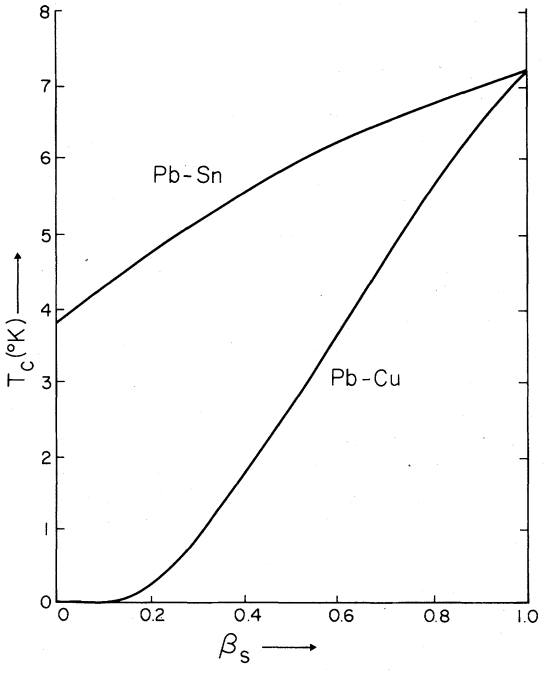

FIG. 1. Dependence of T_c on β_S for the systems Pb-Sn and Pb-Cu.

It would be desirable to apply the theory to systems consisting of a weak-coupling superconductor in contact with a strong-coupling superconductor, in order to test the logarithmic averaging of the frequencies. Some data are available on Pb-Al systems, but the films used were too thick for analysis by the Cooper argument.[14] However, as will be discussed below, results from superconducting normal pairs such as Pb-Cu give useful information even though we know considerably less about the electron-phonon interaction in normal metals than we do in superconductors. Because of this, and because it is always interesting to use the proximity effect to study normal metals, we have also looked at some of the data on systems containing the group-IB metals Cu, Ag, and Au. To obtain information on the pairing interaction in these metals it is important to try to avoid having

TABLE II. Comparison of experiment and theoretical values of T_c with different values of λ and density assumed.

D_{Pb} (Å)	D_{Cu} (Å)	T_c^{theor} (°K)[a]	T_c^{expt} (°K)[b]	T_c^{theor} (°K)[c]
280	264	3.8	3.36	3.32 ± 0.06
334	177	4.9	4.62	4.67 ± 0.05
272	131	4.8	4.80	4.86 ± 0.05
243	39	6.1	6.30	6.35 ± 0.03
229	33	6.0	6.39	6.44 ± 0.02
329	41	6.4	6.50	6.55 ± 0.02

[a] See Ref. 5.
[b] Bulk density assumed for copper, $\Theta_{Cu} = 343$ °K, $\lambda_{Cu} = 0.25$.
[c] Density for copper is $\frac{2}{3}$ of bulk value, $\Theta_{Cu} = (250 \pm 50)$ °K, $\lambda_{Cu} = 0.15$.

$\beta_N\lambda_N$ much smaller than $\beta_S\lambda_S$, since otherwise we end up with $\langle\lambda\rangle \approx \beta_S\lambda_S$, $\langle\lambda \ln\Theta\rangle \approx \beta_S\lambda_S \ln\Theta_S$, and $\ln\Theta = \langle\lambda \ln\Theta\rangle / \langle\lambda\rangle \approx \ln\Theta_S$. If a strong-coupling superconductor is used, it is necessary to have $d_S \ll d_N$ (while still requiring that $d_N \lesssim \xi_N$). Unfortunately, this fairly stringent requirement is not met in the experiments we have reviewed. We shall discuss some experiments for which $\beta_N\lambda_N/\beta_S\lambda_S$ is small, but which still provide information on λ_N, and then we shall mention a possible extension to the theory.

A fair amount of work has been done on the Pb-Cu system, which is metallurgically nice because of the low mutual solubilities, and interesting to us because Cu has the highest Debye temperature of the IB metals. Von Minnigerode has obtained data that satisfy the thin-film requirements of the Cooper theory, but his lead films are thicker than the copper layers so that $\beta_N/\beta_S \lesssim 1$.[5] Since lead is a strong-coupling superconductor, the ratio $\beta_N\lambda_N/\beta_S\lambda_S$ is small, $\lesssim 0.1$, and the first term in Eq. (5) reduces to $\ln\Theta_{Pb}$. A fairly good fit to the data is obtained if we use $\lambda_{Cu} = 0.25$, corresponding to $(NV)_{Cu} = 0.09$ and to a transition temperature for bulk copper of several millidegrees. This is consistent with other estimates of the strength of the interaction in copper.[15] A lower value for λ_{Cu} leads to theoretical transition temperatures that are too low. These films were deposited at relatively high temperatures (200 °K) so the structure of the films is believed close to that of bulk metal. At present it is customary to rely on low-temperature deposition in the preparation of thin-film systems to avoid diffusion and other interfacial problems. Such films often have structures quite different from that of the bulk material, and copper in particular goes down in a low-density porous form.[16] To see how significant a factor this could be, we repeated the analysis using a density of states appropriate to this reduced density. The result was a reduction of λ_{Cu} to 0.15, or $(NV)_{Cu} = 0.02$ (the results are insensitive to possible changes in Θ_{Cu}). The calculations are shown in Table II. This illustrates how important it is to allow for the structure of thin films in the interpretation of proximity effect data.

A different type of experiment with a weak-coupling superconductor is the work of Blanc, Némoz, and Solecki on Al-Ag eutectic alloys.[17] Their results are shown in Table III. We obtain theoretical agreement with their data for $\lambda_{Ag} = 0.15$, corresponding to $(NV)_{Ag} = 0.02$, but since $\beta_N \lesssim 0.05$, the theoretical values of T_C are quite insensitive to λ_N. They report a value of $\lambda_{Ag} \approx 0.25$ using the unrenormalized form of the Cooper theory, which should be corrected to $\lambda_{Ag} = 0.2$ when phonon corrections to the normal density of states are taken into account [corresponding to $(NV)_{Ag} = 0.05$]. This is fully consistent with our analysis, as are the thermal conductivity data of Deutscher *et al.*[18]

As mentioned previously, a better test of the theory would be to look at systems for which $d_S \ll d_N \lesssim \xi_N$. A possible alternative might be to consider the case of a thin superconducting film on a thick normal substrate. If the penetration of pairs into the normal film can be considered relatively constant, then the value of β_S used previously can be replaced by $\beta_S = N_S d_S / (N_S d_S + N_N d_N')$, where d_N' is an effective penetration depth of the same order of magnitude as ξ_N. For such a theory there would be two basic parameters to be

TABLE III. Comparison of experimental and theoretical values for depression of T_c in Al by Ag precipitate.

at.% Ag	β_S	$-\Delta T_c^{expt}$ (°K)[a]	$-\Delta T_c^{theor}$ (°K)
0.0	1.00	0.00	0.00
4.15	0.98	0.15	0.12
5.02	0.97	0.17	0.14
6.7	0.96	0.20	0.19
10.1	0.94	0.24	0.29

[a] See Ref. 17.

determined, λ_N and d_N'/ξ_N. This would require quite extensive data, and one would be dealing with very low transition temperatures, since β_S would be small. It should be mentioned that recent variational calculations have shown that the variation of the order parameter in the superconducting film is greater than that predicted by diffusion theory[3,4] (i.e., it changes over distances small compared with the Ginzburg-Landau coherence length), so that the restriction that d_S be small may be quite stringent.[2]

For the data that have been analyzed so far, the agreement between theory and experiment has been remarkably good. For some of the data that may be approaching the upper thicknesses for which the Cooper theory applies ($d \sim \xi$) the theoretical values run about 0.1 K less than the experimental transition temperatures. This is well within the expected accuracy of the results, since thickness measurements on these very thin films are difficult, the bulk values of λ are not known exactly, and we have used a simplified form of the strong-coupling theory in which the Debye temperature, rather than a correctly averaged frequency, is used to characterize the cutoff. It should be noted that in the weak-coupling theory it has been rigorously proved that the Cooper theory always provides a lower bound to the correct transition temperature.[2,19] The variational method of Silvert and Cooper[2] has recently been extended to strong-coupling superconductivity by Allen and Dynes,[9] and we feel that the generalized Cooper theory presented here also provides firm lower bounds to the transition temperature, even for thicker films.

A final comment should be made about the logarithmic frequency averaging advocated in recent work on strong-coupling superconductors used in this paper.[8,9] We have repeated some of our calculations using the first and second moments of the frequency distribution and find that the increase in the average value of Θ when a strong-coupling superconductor is in contact with a normal metal having a high value of Θ (such as Pb-Cu) is so marked that as β_N increases the transition temperature actually rises before eventually falling to zero. This effect has not been experimentally observed and provides evidence that logarithmic averaging is indeed an improvement on the McMillan theory.

[1] W. Moormann, Z. Phys. 197, 136 (1966).
[2] W. Silvert, J. Low Temp. Phys. 20, 437 (1975).
[3] P. G. de Gennes, Rev. Mod. Phys. 36, 225 (1964).
[4] N. R. Werthamer, Phys. Rev. 132, 2440 (1963).
[5] G. von Minnigerode, Z. Phys. 192, 379 (1966).
[6] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).
[7] W. L. McMillan, Phys. Rev. 167, 331 (1968).
[8] D. A. Kirzhnits, E. G. Maksimov, and D. I. Khomskii, J. Low Temp. Phys. 10, 79 (1973); P. B. Allen, Bull. Am. Phys. Soc. 20, 459 (1975).
[9] P. B. Allen and R. C. Dynes, Phys. Rev. B 12, 905 (1975).
[10] D. J. Scalapino, in *Superconductivity*, edited by R. D. Parks (Dekker, New York, 1969), Vol. 1, pp. 489 ff.
[11] L. N. Cooper, Phys. Rev. Lett. 6, 689 (1961).
[12] G. Bergmann, Z. Phys. 187, 395 (1965).
[13] (a) A. Migliori and D. M. Ginsberg, Phys. Rev. B 8, 5065 (1973); (b) A. E. Jacobs and D. M. Ginsberg, Phys. Rev. 175, 569 (1968).
[14] J. J. Hauser and H. C. Theuerer, Phys. Lett. 14, 270 (1965); R. Frerichs and J. P. Wilson, Phys. Rev. 142, 264 (1966).
[15] E. Krätzig, Solid State Commun. 9, 1205 (1971).
[16] A. von Bassewitz and G. von Minnigerode, Z. Phys. 181, 368 (1964).
[17] J. Blanc, A. Nêmoz, and J. C. Solecki, in *Proceedings of the Twelfth International Conference on Low Temperature Physics*, edited by E. Kanda (Academic, Kyoto, 1971), p. 297.
[18] G. Deutscher, S. Y. Hsieh, P. Lindenfeld, and S. Wolf, Phys. Rev. B 8, 5055 (1973).
[19] W. Silvert and L. N. Cooper, Phys. Rev. 141, 336 (1966).