

McMillan Model of the Superconducting Proximity Effect for Dilute Magnetic Alloys

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We extend the tunneling model of McMillan for the proximity effect in normal-superconducting sandwiches to the case when the normal metal film contains magnetic impurities. The excitation spectrum in each film and the superconducting transition temperature of the sandwich are calculated as functions of the impurity concentration and the film thickness. For a large range of impurity concentrations, the calculations predict that the density of states in both films is gapless, although the transition temperature of the sandwich is nonzero. The calculations are considered in relation to experiment, with reference to possible experimental probes for the Kondo effect in alloys which are nonsuperconducting in the bulk.

I. INTRODUCTION

THE literature dealing with the superconducting proximity effect is extensive for both experiment and theory. The major theoretical difficulty is that the superconducting order parameter in a normal-superconducting (NS) sandwich is spatially dependent. It is therefore only possible to perform a detailed calculation based on Gor'kov's equations¹ at temperatures T near the superconducting critical temperature T_c of the sandwich. The de Gennes-Werthamer theory² calculates T_c for "dirty" NS sandwiches from Gor'kov's equations by imposing certain boundary conditions. This calculation explicitly involves the effective coherence length ξ in each film, and it is assumed that in each film the electronic mean free path l is much smaller than ξ and the film thickness. The excitation spectrum in dirty NS sandwiches has been computed only near T_c .³

However, using a tunneling model for the proximity effect, McMillan⁴ has been able to calculate for all temperatures $T < T_c$ the tunneling density of states in each film of "clean" NS sandwiches, for which $l \sim$ film thickness. In this model the electrical contact is replaced by a potential barrier and tunneling through this barrier is described by the transfer Hamiltonian of Cohen *et al.*⁵ For the model to be applicable the thickness of each film must be smaller than the corresponding coherence length, so that the properties of each film may be considered constant across its thickness. Hence calculations for the McMillan model do not involve the coherence lengths.

Experimental measurements made on clean NS sandwiches have yielded at least qualitative agreement

with the McMillan model. Adkins and Kington⁶ have measured the tunneling densities of states for both films in Pb-Cu sandwiches. They find that the McMillan model accounts for the main features of their observations. In addition, reasonable agreement with theory is obtained for the dependence of the induced energy gap on normal film thickness.^{7,8} Finally, we show in Sec. V below that the McMillan model gives a very good fit to Minnigerode's measurements⁹ of the dependence of T_c for Pb-Cu sandwiches on the thicknesses of the Pb and Cu films.

In this paper, we present the extension of McMillan's calculation⁴ to the case when the normal side contains magnetic impurities. The Hamiltonian of the total system therefore is identical to that of McMillan except for the inclusion of an s - d exchange term¹⁰ describing the spin exchange scattering of electrons in the normal film by magnetic impurities. Such s - d scattering is treated in the Born approximation only¹⁰ and therefore does not include the Kondo effect.¹¹ As in McMillan's paper the transfer Hamiltonian is treated self-consistently up to second order in perturbation theory.

The advantage of the superconducting proximity effect as a probe for dilute magnetic alloys is twofold:

(i) Superconductive tunneling is a very sensitive probe and the proximity effect, by inducing superconductivity into normal magnetic alloys, makes possible the experimental investigation of a large range of magnetic alloys which are nonsuperconducting in the bulk, e.g., *AuFe*, *AuV*, *CuFe*, *AuCo*. (See Mihalisin *et al.*¹² for proximity experiments with *AuFe*.)

(ii) Tunneling into a dilute magnetic alloy is complicated by the possibility of tunneling anomalies due to spin scattering of electrons by magnetic impurities near or in the barrier. This is avoided by tunneling into

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¹ L. P. Gor'kov, *Zh. Eksperim. i Teor. Fiz.* **34**, 735 (1958) [English transl.: *Soviet Phys.—JETP* **7**, 505 (1958)].

² P. G. de Gennes and E. Guyon, *Phys. Letters* **3**, 168 (1963); N. R. Werthamer, *Phys. Rev.* **132**, 2440 (1963).

³ P. Fulde and K. Maki, *Phys. Rev. Letters* **15**, 675 (1965); P. G. de Gennes and S. Mauro, *Solid State Commun.* **3**, 381 (1965).

⁴ W. L. McMillan, *Phys. Rev.* **175**, 537 (1968).

⁵ M. H. Cohen, L. M. Falicov, and J. C. Phillips, *Phys. Rev. Letters* **8**, 316 (1962).

⁶ C. J. Adkins and B. Kington, *Phys. Letters* (to be published).

⁷ C. J. Adkins and B. Kington, *Phys. Rev.* **177**, 777 (1969).

⁸ J. J. Hauser, *Physics* **2**, 247 (1966).

⁹ G. v Minnigerode, *Z. Physik.* **192**, 379 (1966).

¹⁰ A. A. Abrikosov and L. P. Gor'kov, *Zh. Eksperim. i Teor. Fiz.* **39**, 1781 (1961) [English transl.: *Soviet Phys.—JETP* **12**, 1243 (1961)]; S. Skalski, O. Betbeder-Matibet, and P. R. Weiss, *Phys. Rev.* **136**, A1500 (1964).

¹¹ J. Kondo, *Progr. Theoret. Phys. (Kyoto)* **32**, 37 (1964).

¹² T. N. Mihalisin, D. P. Snowden, and P. M. Chaikin (unpublished).

the superconducting side of an NS sandwich in which the normal film is a dilute magnetic alloy. Such an experiment may lead to an accurate investigation of gaplessness in superconductors (see Sec. III) and the relation of the Kondo effect to superconductivity (see discussion below).

II. GAP EQUATION

The physical system under consideration is represented in Fig. 1. The superconducting film is usually a Pb film (because of the high transition temperature), of thickness $\sim 1000 \text{ \AA}$. The normal film in contact with the Pb film is taken to be a dilute magnetic alloy with a thickness of the same order of magnitude. Both films must be clean, i.e., the mean free path l is of the same order as the film thickness, and the coherence length ξ is larger than the film thickness. The purpose of this section is to derive self-consistent equations for the renormalized superconducting energy-gap functions in each film. These gap functions determine the nature of the one-electron excitation spectrum in the superconducting state.

The Hamiltonian for such a sandwich in the McMillan tunneling model⁴ is given by

$$H = H_S + H_N + H_T. \quad (1)$$

(a) H_S is the total Hamiltonian of film S and is given by

$$H_S = H_{0S} + H_{SS}^{BCS}. \quad (2a)$$

H_{0S} is the noninteracting Hamiltonian for the superconducting film and H_{SS}^{BCS} is the BCS interaction between superconducting pairs with coupling constant λ_S .

(b) H_N is the total Hamiltonian for the dilute magnetic alloy film and is written

$$H_N = H_{0N} + H_{N'} + H_{N}^{sd}. \quad (2b)$$

H_{0N} is the noninteracting Hamiltonian for the alloy. H_{N}^{sd} is the s - d exchange interaction between the spins of the conduction electrons and the impurities in the alloy film and is written

$$H_{N}^{sd} = -J \sum_{i=1}^N \sum_{n,n',s,s'} (\hat{\sigma} \cdot \mathbf{S}_i)_{ss'} \times \psi_n^*(\mathbf{R}_i) \psi_{n'}(\mathbf{R}_i) a_{ns}^\dagger a_{n's'}, \quad (2c)$$

where $\hat{\sigma}$ is a Pauli-spin matrix, \mathbf{S} is the spin operator for the i th impurity with position \mathbf{R}_i , and J is the coupling constant of the s - d exchange interaction (assumed to be a δ force at the impurity site). a_{ns}^\dagger creates an electron

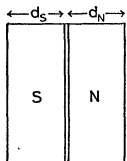


FIG. 1. Geometry of the NS films. Film S is a BCS superconductor, film N is a dilute magnetic alloy. The films have thicknesses d_S and d_N , respectively, and both films have the same area A .

FIG. 2. Self-energy equations in diagrammatic form in films S and N . $G_S(\omega)$ and $G_N(\omega)$ are the full electron propagators in films S and N , respectively; T is the tunneling matrix element; D_S is the BCS electron-phonon interaction in film S ; and the crosses represent scattering from a magnetic impurity.

in a one-electron state (labeled by n) with spin s and with wave function $\psi_n(\mathbf{r})$. The coupling constant of the BCS interaction on the normal side is taken to be zero. $H_{N'}$ is the Hamiltonian describing the nonmagnetic scattering of the magnetic impurities and has coupling constant U .

(c) The electrical contact between these films is described by the transfer Hamiltonian H_T given by

$$H_T = T \sum_{n,n'} (a_n^\dagger b_{n',\uparrow} + b_{-n',\downarrow}^\dagger a_{-n}) + \text{H.c.}, \quad (2d)$$

b_{ns}^\dagger creates an electron in state n and spin s in the superconducting film. T , the transfer matrix element, is assumed independent of n and n' .

The Hamiltonian H in (1) is treated self-consistently to second order in both T and J in the Nambu-Schrieffer formalism for superconductivity.¹³ The equations for the 2×2 matrix self-energies $\hat{\Sigma}_N(\omega)$ and $\hat{\Sigma}_S(\omega)$ of superconducting electrons in the normal and superconducting films are presented in diagrammatic form in Fig. 2. The double lines represent the full matrix propagators $\hat{G}_{Nn}(\omega)$ and $\hat{G}_{Sn'}(\omega)$ for electrons in the normal and superconducting films, respectively, and are given by the ansatz

$$\hat{G}_{Nn}(\omega) = [Z_N(\omega)\omega \mathbf{1} - \epsilon_n \tau_3 - \phi_N(\omega)\tau_1]^{-1}, \quad (3a)$$

$$\hat{G}_{Sn'}(\omega) = [Z_S(\omega)\omega \mathbf{1} - \epsilon_{n'} \tau_3 - \phi_S(\omega)\tau_1]^{-1}, \quad (3b)$$

where $\mathbf{1}$ is the 2×2 unit matrix, τ_1 and τ_3 are Pauli matrices, $Z(\omega)$ is the renormalization function, and $\phi(\omega)$ is the unrenormalized gap function in terms of the frequency ω . The quantity ϵ_n is the energy of the n th one-electron state. Substitution of (3) into the equations represented by the diagrams of Fig. 2 gives, after averaging over impurity sites,¹⁰ the following self-consistent equations for ϕ_S , ϕ_N , Z_S , and Z_N :

$$\phi_S(\omega) = \Delta_S^{ph} + \Gamma_S \phi_N(\omega) [\phi_N^2(\omega) - Z_N^2(\omega)\omega^2]^{-1/2}, \quad (4a)$$

$$Z_S(\omega) = 1 + \Gamma_S Z_N(\omega) [\phi_N^2(\omega) - Z_N^2(\omega)\omega^2]^{-1/2}, \quad (4b)$$

$$\phi_N(\omega) = \Gamma_N \phi_S(\omega) [\phi_S^2(\omega) - Z_S^2(\omega)\omega^2]^{-1/2} + \Gamma_2 \phi_N(\omega) [\phi_N^2(\omega) - Z_N^2(\omega)\omega^2]^{-1/2}, \quad (5a)$$

$$Z_N(\omega) = 1 + \Gamma_N Z_S(\omega) [\phi_S^2(\omega) - Z_S^2(\omega)\omega^2]^{-1/2} + \Gamma_1 Z_N(\omega) [\phi_N^2(\omega) - Z_N^2(\omega)\omega^2]^{-1/2}, \quad (5b)$$

where Δ_S^{ph} is the order parameter of the superconduct-

¹³ J. R. Schrieffer, *Theory of Superconductivity* (W. A. Benjamin, Inc., New York, 1964).

ing film given self-consistently by

$$\Delta_S^{ph} = \lambda_S \int_0^{\omega_D} d\omega \operatorname{Re}\{\phi_S(\omega)[\phi_S^2(\omega) - Z_S^2(\omega)\omega^2]^{-1/2}\} \\ \times \tanh[\omega/2kT], \quad (6)$$

where ω_D is the Debye cutoff frequency for the superconducting film.

In these equations, Γ_N and Γ_S are defined in terms of the tunneling matrix element T as follows:

$$\Gamma_N = \pi T^2 A d_S N_S'(0) = \hbar/2\tau_N, \quad (7a)$$

$$\Gamma_S = \pi T^2 A d_N N_N'(0) = \hbar/2\tau_S, \quad (7b)$$

where $N_N'(0)$ and τ_N are the density of states (per unit volume for one spin orientation, at the Fermi level) and the relaxation time in film N of thickness d_N and area A , and similarly for film S . Hence,

$$\Gamma_N/\Gamma_S = d_S N_S'(0)/d_N N_N'(0). \quad (8)$$

This relation implies that the numbers of electrons crossing the barrier in opposite directions are equal, as required.

The relaxation time is given by⁴ $\tau_N = 2Bd_N/(V_{FN}\sigma)$ so that¹⁴

$$\Gamma_N = \hbar V_{FN}\sigma/(4Bd_N), \quad (9)$$

where V_{FN} is the Fermi velocity, σ the probability that an electron incident on the barrier from film N will be transmitted, and $2Bd_N$ the length traveled in film N between successive collisions with the barrier. McMillan⁴ suggests that for clean films B is constant with value ~ 2 . Hence Γ_N is inversely proportional to d_N and similarly Γ_S is inversely proportional to d_S . Thus we may calculate the dependence of the properties of the NS sandwich on film thicknesses d_N and d_S .

Γ_1 and Γ_2 are related to U and J , the coupling constants in the normal film of the nonmagnetic and s - d exchange interactions, respectively, as follows:

$$\frac{1}{2}(\Gamma_1 + \Gamma_2) = n_I \pi N_N(0) u^2, \quad (10a)$$

$$\frac{1}{2}\Gamma = \frac{1}{2}(\Gamma_1 - \Gamma_2) = \frac{1}{4} n_I \pi N_N(0) J^2 S(S+1), \quad (10b)$$

where n_I is the number density of impurities in film N and $N_N(0)$ is the density of states (per atom for one spin orientation, at the Fermi level). We define the renormalized energy-gap functions Δ_N and Δ_S as follows:

$$\Delta_N(\omega) = \phi_N(\omega)/Z_N(\omega), \quad \Delta_S(\omega) = \phi_S(\omega)/Z_S(\omega). \quad (11)$$

From (4)–(6) we obtain the following equations for Δ_N and Δ_S :

$$\Delta_N(\omega) = \Gamma_S \Delta_S(\omega) [\Delta_S^2(\omega) - \omega^2]^{-1/2} \\ \times \{1 + \Gamma_N [\Delta_S^2(\omega) - \omega^2]^{-1/2} \\ + \Gamma [\Delta_N^2(\omega) - \omega^2]^{-1/2}\}^{-1}, \quad (12a)$$

$$\Delta_S(\omega) = \{\Delta_S^{ph} + \Gamma_S \Delta_N(\omega) [\Delta_N^2(\omega) - \omega^2]^{-1/2}\} \\ \times \{1 + \Gamma_S [\Delta_N^2(\omega) - \omega^2]^{-1/2}\}^{-1}, \quad (12b)$$

where $\Gamma = \Gamma_1 - \Gamma_2$ and

$$\Delta_S^{ph} = \lambda_S \int_0^{\omega_D} d\omega \operatorname{Re}\{\Delta_S(\omega)/[\Delta_S^2(\omega) - \omega^2]^{1/2}\} \\ \times \tanh(\omega/2kT). \quad (13)$$

The gap equations (12a) and (12b) are analyzed in the next section.

III. EXCITATION SPECTRUM

Equations (12) have been solved by computer using an iterative procedure, with $\Delta_N(\omega)$, $\Delta_S(\omega)$, Γ_N , Γ_S , Γ , and ω all expressed in terms of the order parameter Δ_S^{ph} . (Note that, in general, Δ_S^{ph} depends on Γ_N , Γ_S , and Γ .) The selection of the sign of the square roots in (12) is not simple. We must choose those square roots which lead to positive real parts in the square roots of (4) and (5). This is done by assuming a sign for the square roots in (12), then calculating $Z_N(\omega)$ and $Z_S(\omega)$ and checking whether the correct choices have been made. When the signs of $\operatorname{Im}\Delta_N$ and $\operatorname{Im}\Delta_S$ are different (see Fig. 3), no solution of (12) is obtained if the positive real square roots are taken.

The density of states $N(\omega)$ corresponding to gap function $\Delta(\omega)$ is

$$N(\omega)/N(0) = \operatorname{Re}\{\omega/[\omega^2 - \Delta^2(\omega)]^{1/2}\}. \quad (14)$$

Typical examples of the gap functions and densities of states are illustrated in Figs. 3 and 4, with the gap edge shown in greater detail in Fig. 5. The curves for $\Gamma = 0$ are for a pure normal metal film, as given by the simple McMillan⁴ model. The energy gap is the value of ω at which Δ_N and Δ_S first become complex. Keeping Γ_S/Δ_S^{ph} and Γ_N/Δ_S^{ph} constant, the energy gap is reduced as the impurity concentration n_I increases.

As Γ increases, at some critical value Γ_c we find that Δ_N and Δ_S are complex right down to $\omega = 0$, the cusp in their real parts disappears, and the density of states is gapless. When Γ is large, the density of states in film N is essentially normal, while the density of states in film S is also gapless but still shows the peak near Δ_S^{ph} and is reduced below unity for small ω . An expression for Γ_c may be obtained by solving (12) analytically at $\omega = 0$:

$$\Delta_N(0) = 0 = \Delta_S(0), \quad \Gamma \geq \Gamma_c. \quad (15a)$$

$$\Delta_N(0) = [\Delta_S^{ph} \Gamma_N - \Gamma(\Delta_S^{ph} + \Gamma_S)] / \\ [\Delta_S^{ph} + \Gamma_S + \Gamma_N], \quad \Gamma \leq \Gamma_c. \quad (15b)$$

The energy gap disappears when $\Delta_N(0)$ first becomes zero. Hence,

$$\Gamma_c = \Gamma_N / (1 + \Gamma_S / \Delta_S^{ph}), \quad (16)$$

for $\Gamma_S = \Gamma_N = 0.3\Delta_S^{ph}$, $\Gamma_c = 0.23\Delta_S^{ph}$ (see Fig. 5).

If film S is thick (i.e., $\Gamma_S \ll \Delta_S^{ph}$), (16) reduces to $\Gamma_c = \Gamma_N$. Hence as d_N is varied, $n_c d_N = \text{const}$, where n_c is the critical impurity concentration corresponding to Γ_c .

¹⁴ Note that this expression for Γ_N differs by a factor of 2 from that of McMillan (Ref. 4) which was used by Adkins and Kingston (Ref. 7). This difference arises because the numerical factors 2 and π in (7) appear to have been omitted in Ref. 4.

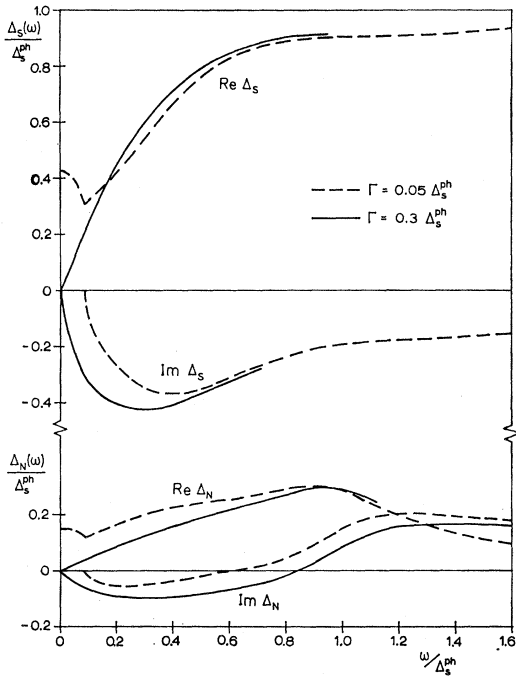


FIG. 3. Gap functions in films S and N for $\Gamma_S = \Gamma_N = 0.3\Delta_S^{ph}$. The density of states if gapless for $\Gamma = 0.3\Delta_S^{ph}$.

Therefore the total number of impurity atoms which must be added to film *N* to eliminate the energy gap is a constant.

To prove that for $\Gamma > \Gamma_c$ the sandwich exhibits gapless superconductivity, we must verify that the order parameter Δ_S^{ph} and transition temperature T_c are nonzero. In Sec. IV it is shown that, provided film *S* is not thin, the magnetic impurities produce only a small reduction in T_c . This is illustrated in Fig. 6 for $\Gamma_S = \Gamma_N$

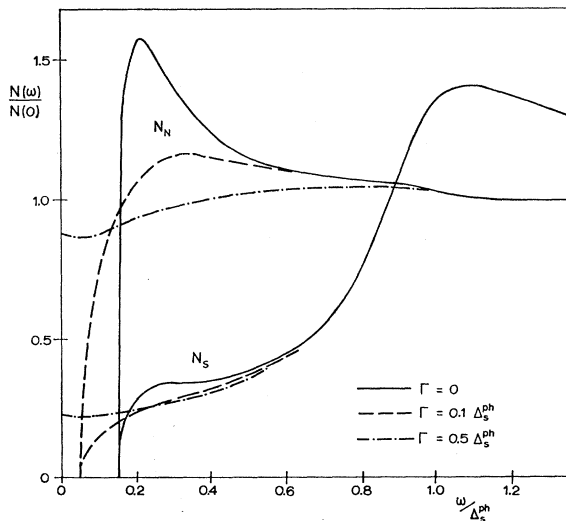


FIG. 4. Effect of magnetic impurities on the density of states for $\Gamma_S = \Gamma_N = 0.3\Delta_S^{ph}$. $N_N(\omega)$ is the density of states for tunneling into film *N*, $N_S(\omega)$ for tunneling into film *S*.

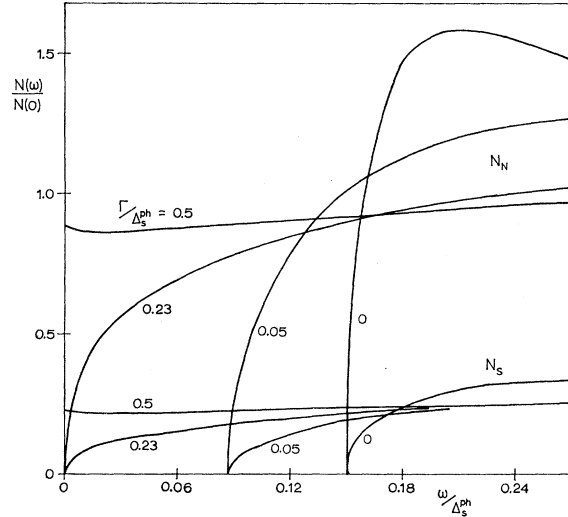


FIG. 5. Detail of gap edge showing production of gaplessness as the magnetic impurity concentration increases. The figures beside the curves are the values of Γ/Δ_S^{ph} . As in Figs. 3 and 4, $\Gamma_S = \Gamma_N = 0.3\Delta_S^{ph}$.

$= 0.23\Delta_B$, where Δ_B is the order parameter of the bulk material of film *S*. (Γ_N , Γ_S , and Γ are expressed in units of Δ_B rather than Δ_S^{ph} in calculating T_c .) For comparison with the reduction of the energy gap, it may therefore be assumed in this case that Δ_S^{ph} is unchanged by the addition of magnetic impurities. In consequence the value $\Delta_S^{ph} = 0.76\Delta_B$ (at $T=0$) from Ref. 4 may be used. Hence $\Gamma_S = \Gamma_N = 0.23\Delta_B = 0.3\Delta_S^{ph}$. In Fig. 6 the reduction of the energy gap ω_g is plotted as a function of Γ for $\Gamma_S = \Gamma_N = 0.3\Delta_S^{ph}$, where ω_g is computed numerically from (12). We see that the addition of magnetic impurities to film *N* has a marked effect on ω_g but a much smaller effect on T_c , i.e., a very large region of gapless superconductivity is obtained.

For comparison we show in Fig. 7 the excitation spectrum for the case where there is no magnetic

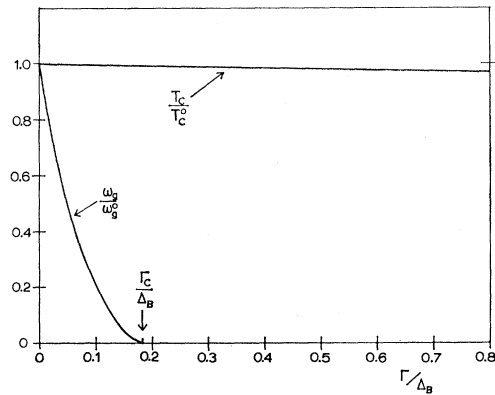


FIG. 6. Reduction of energy gap ω_g at $T=0$ and critical temperature T_c by magnetic impurities for $\Gamma_S = \Gamma_N = 0.3\Delta_S^{ph} = 0.23\Delta_B$. Δ_B is the order parameter of the bulk superconductor; T_c^0 and ω_g^0 are the values of T_c and ω_g when $\Gamma=0$, i.e., when film *N* is a pure normal metal.

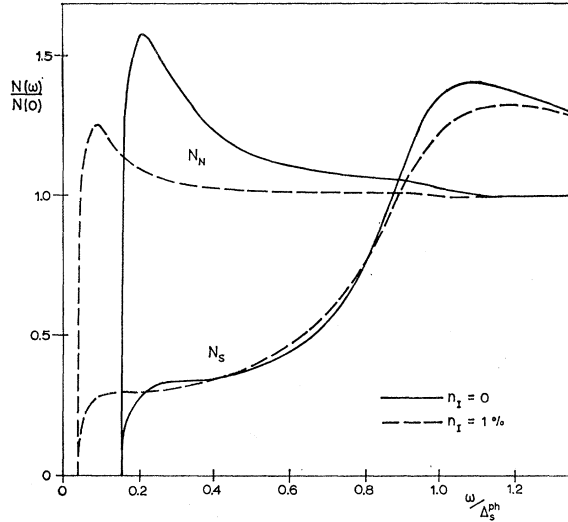


FIG. 7. Reduction of energy gap by resonance scattering and correlation effects for nonmagnetic localized states at impurity sites in film N.

moment associated with the localized states at the impurity sites.¹⁵

IV. TRANSITION TEMPERATURE

A. Pure Normal Metal

This subsection is included in order to obtain values of Γ_N and Γ_S derived from experimental data. This information indicates the order of magnitude of these parameters to be used in the calculations for dilute magnetic alloys.

The McMillan⁴ formula for the transition temperature T_c of an NS sandwich in which the N film is a pure normal metal is

$$\ln(T_c^B/T_c) = \left(\frac{\Gamma_S}{\Gamma_N + \Gamma_S} \right) \Psi \left(\frac{\Gamma_N + \Gamma_S}{\pi k T_c} \right), \quad (17)$$

where $\Psi(x) = \psi(\frac{1}{2} + \frac{1}{2}x) - \psi(\frac{1}{2})$, ψ being the digamma function,⁴ and T_c^B the transition temperature of the bulk material of film S .

¹⁵ C. F. Ratto and A. Blandin [Phys. Rev. **156**, 513 (1967)], M. Kiwi and M. J. Zuckermann [*ibid.* **164**, 548 (1968)], and M. J. Zuckermann [*ibid.* **140**, A899 (1965)] have calculated the effect of resonance scattering from localized d states on superconducting properties, including the effect of Coulomb correlations between d electrons at the same impurity site. In a similar way to the magnetic case, we have computed the effect of nonmagnetic localized states in film N on the excitation spectrum in each film (Fig. 7) using the formalism of Kiwi and Zuckermann. If $\Delta_S^{ph} \sim 1.3$ meV (appropriate if film S is lead), the parameter values used correspond to a d level of width 0.1 eV at the Fermi surface, with a d - d Coulomb interaction $U = 10$ eV. As the impurity concentration n_I in film N is increased, the energy gap decreases. However, in contrast to the magnetic impurity case, there is no region of gapless superconductivity. So long as the order parameter Δ_S^{ph} in film S is nonzero, a finite gap ω_g exists. This behavior is expected since nonmagnetic localized states in a bulk superconductor do not produce gapless superconductivity [A. B. Kaiser (unpublished)], in contrast to the Kiwi-Zuckermann result. The postulation of gaplessness in their paper was due to nonself-consistency in the calculation of the order parameter.

Minnigerode⁹ investigated in detail the dependence of T_c on d_S and d_N for Pb-Cu sandwiches in which the electronic mean free paths were of the same order as d_S and d_N , and the coherence length $\xi \sim 1000$ – 2000 Å. He concluded that the de Gennes-Werthamer² theory, which holds in the dirty limit, did not account for the results, although an extension for cleaner films¹⁶ gave good agreement.

Figures 8 and 9 show that the McMillan model (full lines) gives a very good fit to Minnigerode's data. In the McMillan model, from (9),

$$\Delta_B/\Gamma_S = d_S/c_S, \quad \Delta_B/\Gamma_N = d_N/c_N, \quad (18)$$

where c_S and c_N are constants. The data in Fig. 8 show the variation of T_c with d_S for a thick Cu film ($d_N \approx 3100$ Å). For d_N large, Γ_N should be small; for best fit we find $\Gamma_N = 0.15\Delta_B$, $\Gamma_S = \Delta_B \times 160$ Å/ d_S (i.e., $c_S = 160$ Å). As expected, there is some deviation from the McMillan model when d_S is large. The data of Fig. 9 show how T_c varies with d_N for $d_S = 270$ and 350 Å. For these values of d_S , $\Delta_B/\Gamma_S = 1.7$ and 2.2 , respectively (using $c_S = 160$ Å). The choice $c_N = 250$ Å gives a good fit with the McMillan model. The fit is not as good as when d_S is varied, probably because the Cu films are dirtier (bulk mean free path ≈ 200 Å).

From (8) and (18),

$$c_N/c_S = N_S'(0)/N_N'(0). \quad (19)$$

Experimentally, $c_N/c_S = 1.6$, with error up to 15% because the fits in Figs. 8 and 9 are interdependent. The ratio of electronic heat capacities per unit volume is¹⁷ $\gamma_{Pb}/\gamma_{Cu} = N_S'(0)/N_N'(0) = 1.67$, in good agreement with the value of c_N/c_S . Note that $N_S'(0)$ and $N_N'(0)$ include

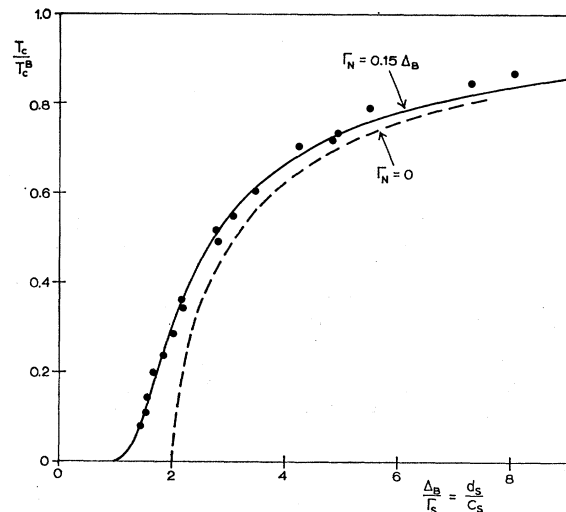


FIG. 8. Critical temperature T_c of sandwich as film thickness d_S is varied. The McMillan theory is compared with experimental data of Minnigerode (Ref. 9) with $c_S = 160$ Å. The normal film thickness is constant at 3100 Å.

¹⁶ W. Moormann, Z. Physik **197**, 136 (1966).

¹⁷ C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, to be published), p. 212, 3rd ed.

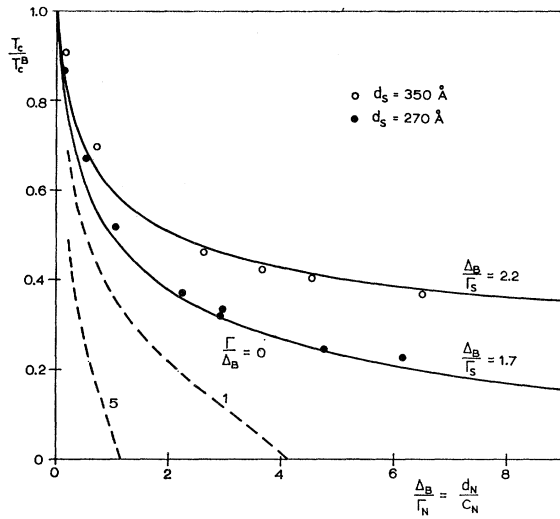


FIG. 9. Critical temperature T_c of sandwich as film thickness d_N is varied. The McMillan theory is compared with experimental data of Minnigerode (Ref. 9) for $d_S=270$ and 350 Å, with $c_N=250$ Å. The dotted lines show the effect of magnetic impurities for $\Delta_B/\Gamma_S=1.7$.

the mass renormalization due to the electron-phonon interaction, which is large for Pb.¹⁸

In addition, we note that the value obtained for c_N is in close agreement with the value deduced by Adkins and Kington⁷ from measurements of the decrease with d_N of the induced energy gap in the Cu film of Pb-Cu sandwiches. From (9) and (18)

$$c_N = \hbar V_{FN} \sigma / (4B\Delta_B). \quad (20)$$

Using¹⁷ $V_{FN} = 1.6 \times 10^8$ cm/sec, we get $\sigma/B = 0.12$, the same value as Adkins and Kington,⁷ taking account of the different formulas used.¹⁴

We conclude that the McMillan model gives a very satisfactory account of Minnigerode's data for Pb-Cu sandwiches, with reasonable values for the adjustable parameters c_N and c_S .

B. Dilute Magnetic Alloy

Next an expression for T_c for an NS sandwich, in which film N is a dilute magnetic alloy, is obtained. It is convenient to make the transformation $\omega \rightarrow i\omega_n$ in (12) and (13), where $\omega_n = (2n+1)\pi kT$, n being an integer. Further, only terms linear in Δ_S and Δ_N are retained in the calculation for T_c . Hence (12) becomes

$$\Delta_N(\omega_n) = \Delta_S(\omega_n) \Gamma_N / (|\omega_n| + \Gamma_N + \Gamma), \quad (21a)$$

$$\Delta_S(\omega_n) = [\Delta_S^{ph} |\omega_n| + \Delta_N(\omega_n) \Gamma_S] / (|\omega_n| + \Gamma_S), \quad (21b)$$

and the integral in (13) becomes a sum:

$$\Delta_S^{ph} = \lambda_S \pi kT \sum_n \frac{\Delta_S(\omega_n)}{|\omega_n|}. \quad (22)$$

The following equation for T_c is obtained from (22):

$$\ln(T_c^B/T_c) = \pi kT_c \sum_n \frac{1}{|\omega_n^c|} \left(\frac{\Delta_S(\omega_n^c)}{\Delta_S^{ph}} - 1 \right), \quad (23)$$

where we have introduced the Debye cutoff at frequency ω_D using

$$\sum_{n, |\omega_n^c| < \omega_D} \frac{1}{|\omega_n^c|} = \ln \left(\frac{1.14\omega_D}{kT_c} \right) \quad (24)$$

and the BCS coupling constant λ_S has been expressed by

$$1/\lambda_S = \ln(1.14\omega_D/T_c^B). \quad (25)$$

In these equations $|\omega_n^c| = (2n+1)\pi kT_c$, and T_c^B is the transition temperature of the bulk material comprising film S .

From (21) an analytic expression for $\Delta_S(\omega_n^c)/\Delta_S^{ph}$ is obtained which, substituted in (23), gives

$$\ln \left(\frac{T_c^B}{T_c} \right) = \pi kT_c \Gamma_S \times \sum_n \frac{1 + \Gamma/|\omega_n^c|}{|\omega_n^c|^2 + (\Gamma + \Gamma_S + \Gamma_N)|\omega_n^c| + \Gamma\Gamma_S}. \quad (26)$$

In terms of digamma functions, (26) becomes

$$\ln \left(\frac{T_c^B}{T_c} \right) = \frac{\Gamma_S}{(A_+ - A_-)} \left[\left(1 - \frac{\Gamma}{A_+} \right) \psi \left(\frac{1}{2} + \frac{A_+}{2\pi kT_c} \right) - \left(1 - \frac{\Gamma}{A_-} \right) \psi \left(\frac{1}{2} + \frac{A_-}{2\pi kT_c} \right) \right] - \psi \left(\frac{1}{2} \right), \quad (27)$$

where

$$A_{\pm} = \frac{1}{2}(\Gamma + \Gamma_N + \Gamma_S) \pm \left[\frac{1}{4}(\Gamma + \Gamma_N + \Gamma_S)^2 - \Gamma\Gamma_S \right]^{1/2}. \quad (28)$$

As $\Gamma \rightarrow 0$, (27) reduces to the McMillan expression (17).

From (27) we obtain an expression for Γ_q , the value of Γ at which the superconductivity of the sandwich is quenched entirely. As $T_c \rightarrow 0$ the asymptotic limit $\psi(x) \rightarrow \ln x$ as $x \rightarrow \infty$ may be used. Then T_c cancels from (27) leaving the following equation for Γ_q :

$$(1 + \Gamma_q/A_+) \ln A_+ - (1 - \Gamma_q/A_-) \ln A_- = \left[(A_+ - A_-) / \Gamma_S \right] \ln \left(\frac{1}{2} \Delta_B \right), \quad (29)$$

where $\Delta_B = 1.76kT_c^B$. In (29) A_+ and A_- are functions of Γ_q via (28), so the equations must be solved numerically by computer.

When $\Gamma \rightarrow \infty$ in (26) the McMillan expression for T_c is obtained with $\Gamma_N = 0$. Thus the dashed curve for $\Gamma_N = 0$ in Fig. 8 is also the curve for $\Gamma \rightarrow \infty$. This limiting curve shows the maximum depression of T_c at different values of d_S ; this maximum depression may be approached by increasing the normal film thickness d_N , or alternatively by adding magnetic impurities to the normal film of constant thickness d_N . Physically, this limiting curve represents the case where electrons leaving film S lose all superconducting correlation in film N .

¹⁸ W. L. McMillan and J. M. Rowell, Phys. Rev. Letters **14**, 108 (1965).

We see from Fig. 8 that, if the normal film is thick, addition of magnetic impurities can produce little additional decrease in T_c (except if Δ_B/Γ_S is slightly less than 2, as illustrated in Fig. 9 for $\Delta_B/\Gamma_S=1.7$). When the normal film is thin, as in Fig. 10, the addition of impurities produces a much larger decrease in T_c . The superconductivity of the sandwich cannot be destroyed unless d_S is smaller than some critical thickness defined by $\Delta_B/\Gamma_S=2$; (29) has no solution for $\Gamma_S < 0.5\Delta_B$.

The depression of T_c shown in Fig. 10 is qualitatively very similar to that produced by magnetic impurities in the de Gennes-Werthamer theory and observed experimentally for dirty films.¹⁹ However (27) derived in the McMillan model is valid only for clean films (mean free path \sim film thickness).

V. CONCLUSION

In this paper we have investigated the induction of superconductivity in a dilute magnetic alloy by the proximity effect using the McMillan model.⁴ The excitation spectrum falls into two categories: (a) with a finite energy gap and (b) with no energy gap (i.e., gapless superconductivity). The gapless regime is given by $\Gamma_c < \Gamma < \Gamma_q$, where Γ_c and Γ_q are defined in (16) and (29), respectively. In order to quench superconductivity in the NS sandwich, the superconducting film must be quite thin ($\Delta_B/\Gamma_S < 2$). For example in Pb-Cu sandwiches $d_S < 300 \text{ \AA}$ (see Sec. IV). When $\Delta_B/\Gamma_S > 2$ the superconductivity cannot be quenched by adding magnetic impurities to the normal film, i.e., gapless superconductivity occurs for all impurity concentrations for which $\Gamma > \Gamma_c$ (see Fig. 6). However the model breaks down when the impurity concentration is large enough to reduce the electronic mean free path drastically. In contrast, in the case of the bulk superconducting magnetic alloys, the Abrikosov-Gor'kov model¹⁰ predicts gapless superconductivity for only a small range of concentrations, i.e., for $0.46 < \Gamma/\Delta_B < 0.5$, where Δ_B is the order parameter of the pure superconductor.

Mihalisin *et al.*¹² have made tunneling measurements into NS sandwiches, in which the N side is Au-Fe and the S side is Pb, with temperature range from 1.4 to 4.2°K. Their results for the excitation spectrum indicate that the region of gapless superconductivity is large in terms of Fe concentration, as predicted by our calculations. More detailed comparisons with experiment require the experimental curves for the excitation spectra at lower temperatures and at more values of magnetic impurity concentration.

Mihalisin *et al.*¹² observe an anomalous peak in the superconducting density of states for a concentration of 1500 ppm of Fe in Au at 4.2°K, the zero bias con-

¹⁹ J. J. Hauser, H. C. Theuerer, and N. R. Werthamer, *Phys. Rev.* **142**, 118 (1966).

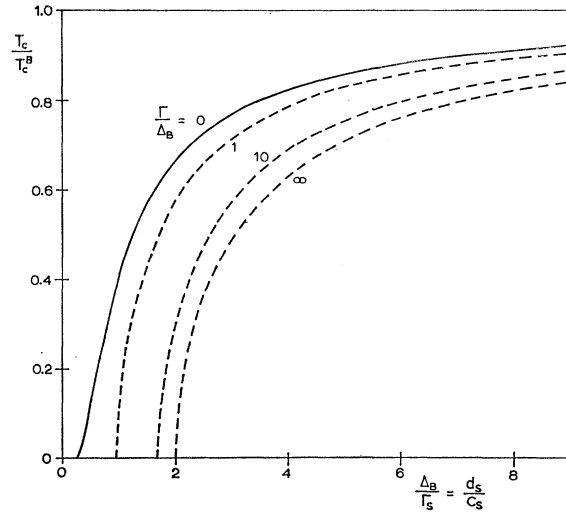


FIG. 10. Effect of magnetic impurities on T_c as d_S is varied, for $\Gamma_N=2\Delta_B$, i.e., the normal film is thinner than for the case illustrated in Fig. 8.

ductance being greater than the normal state value. These authors suggest that this peak may be a manifestation of the Nagaoka singlet bound state^{20,21} at the Fe impurity site. Such a bound state may occur in a superconducting magnetic alloy when $T_c < T_K$, where T_K is the Kondo temperature¹¹ and T_c the transition temperature of the alloy. Mihalisin *et al.* take T_K to be 7°K for Au-Fe. However, recent measurements of resistivity by Ford *et al.*²² show that $T_K=0.27$ °K for Au-Fe, and also that interaction effects dominate over Kondo-like behavior in Au-Fe at 4°K and 1500 ppm. In consequence, this anomalous peak may not be due to the Nagaoka bound state. To determine the conditions in which the Nagaoka bound state may be observed for the regime of induced superconductivity, the work reported in the present paper is being extended to the Kondo problem.

Gapless superconductivity in NS sandwiches has also been observed by Woolf and Reif²³ and by Hauser.²⁴ However, our analysis cannot be directly compared with their results since the normal film was a pure ferromagnetic metal rather than a dilute magnetic alloy.

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²⁰ M. Fowler and K. Maki, *Phys. Rev.* **164**, 484 (1967).

²¹ T. Soda, T. Matsuura, and Y. Nagaoka, *Progr. Theoret. Phys. (Kyoto)* **38**, 551 (1967).

²² P. J. Ford and J. W. Loram (unpublished).

²³ M. A. Woolf and F. Reif, *Phys. Rev.* **137**, A557 (1965).

²⁴ J. J. Hauser, *Phys. Rev.* **144**, 558 (1967).