Induced superconductivity in Kondo alloys

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The superconducting proximity effect between thin films of a superconductor and a Kondo alloy is analyzed theoretically, using the McMillan tunneling model to describe the proximity effect and the theory of Müller-Hartmann and Zittartz to describe the effect of Kondo impurities on superconductivity. The calculations are compared to measurements by Dumoulin, Guyon, and Nedellec for *Cu*Cr-Pb and other similar systems. Comparison of the tunneling density of states confirms that the bound state moves up towards the band edge more quickly than predicted by the Müller-Hartmann and Zittartz theory as the Kondo temperature increases. Fitting observed transition temperatures suggests the possibility of reentrant behavior at low temperatures. For both density of states and transition temperature, pair-breaking parameters approximately five times those expected theoretically are required to fit the data, possibly due to orbital degeneracy.

I. INTRODUCTION

Kondo impurities in superconductors are predicted to produce some striking effects.[1] A reentrant behavior of the transition temperature T_c as a function of impurity concentration c was predicted by Müller-Hartmann and Zittartz[2] (referred to hereafter as MZ) and by Ludwig and Zuckermann,[3] and impurity bands within the forbidden gap of the host superconductor, whose location in energy depends on T_c and the Kondo temperature T_K, were predicted by Zittartz, Bringer, and Müller-Hartmann[4] (ZBM). Reentrant T_c behavior has been observed for Ce impurities in several La-based alloys,[5] but many of the most commonly studied Kondo alloys have nonsuperconducting hosts (e.g., Au, Cu). However, superconductivity may be investigated in these alloys by inducing superconductivity in a thin film of the alloy by the proximity of a superconducting film. In a beautiful series of experiments, Dumoulin *et al.*[6,7] observed impurity bands in the gap for induced superconductivity in *Cu*Cr, *Cu*Mn, *Cu*Fe, and *Au*Fe alloys. These experiments appear to be the only specific observations of Kondo impurity bands reported to date. Dumoulin *et al.*[8] have also obtained evidence for temperature-dependent pair breaking in *Cu*Cr (but not reentrant T_c behavior) by transition temperature measurements on *Cu*Cr-Pb sandwiches.

The purpose of this paper is to extend the MZ theory for finite Kondo impurity concentrations to the case of induced superconductivity, using the McMillan tunneling model[9] to describe the superconducting proximity effect between a nonsuperconducting Kondo alloy and a BCS superconductor (a preliminary letter regarding reentrant induced superconductivity has already appeared[10]). The calculations are then used to analyze the experimental tunneling density of states and transition temperature data of Dumoulin *et al.*[7,8] for proximity sandwiches with Kondo alloys. It will be shown that the heuristic "equivalent BCS" model used by Dumoulin *et al.*[7] to describe induced superconductivity in analyzing their density of states data is a good approximation, provided an appropriate effective pair-breaking parameter is defined. Thus our analysis leads to very similar results to those of Dumoulin *et al.* regarding the bound-state location (but not regarding the magnitude of the pair-breaking parameter).

Recently Matsuura *et al.*[11] and Matsuura[12] have proposed an alternative model for Kondo impurities in superconductors which is similar to the pair-breaking MZ theory for $T_K < T_c$, but which introduces an additional repulsive interaction for $T_K > T_c$ where the Nagaoka-Suhl approximation (on which the MZ theory is based) breaks down. Only limited predictions of bound-state locations were made,[12] which will be discussed briefly in relation to the experimental data. Modification of the transition temperature behavior of the MZ theory has been predicted by Schuh and Müller-Hartmann,[13] who extended the MZ theory to include self-consistently the energy and concentration dependence of pair breaking, and by Matsuura *et al.*,[11] although the principal characteristics (including reentrant behavior) are retained. These modifications appear to give rather better agreement with the experimental reentrant T_c data.[13] We suggest that proximity sandwich T_c measurements with Kondo alloys could be used to check these modified theories.

II. THEORY

A. Basic model

We consider a thin film of a nonsuperconducting Kondo alloy (film N) next to a thin film of a BCS superconductor (film S). The treatment follows closely our earlier application (Kaiser and Zuckermann[14]) of the McMillan tunneling model to calculate the properties of induced superconductivity in alloys with magnetic impurities described by the Abrikosov-Gorkov model (in this case, of course, the Kondo effect and impurity states within the gap were excluded). The McMillan model for the superconducting proximity effect has the advantage that it is simple enough to permit a complete solution, yet appears to give a good account of experimental data on clean films.[15] The McMillan model[9] assumes that the film thicknesses are smaller than the superconducting coherence lengths, so that the superconducting properties of the films may be taken as uniform across their thicknesses. The interaction between the films is described by a single-particle tunneling Hamiltonian term.

In second-order self-consistent perturbation theory, the electron self-energies in films S and N in Nambu matrix notation are[9]

$$\Sigma_S(\omega) = \Sigma_S^{\mathrm{BCS}} + T_m^2 \sum_n \tau_3 G_{Nn}(\omega) \tau_3 \ , \tag{1}$$

$$\Sigma_N(\omega) = \Sigma_N^{\mathrm{MZ}} + T_m^2 \sum_{n'} \tau_3 G_{Sn'}(\omega) \tau_3 \ , \tag{2}$$

where T_m is the tunneling matrix element between state n in film N and state n' in film S, taken as the same for all n and n', and $G_{Nn}(\omega)$ and $G_{Sn'}(\omega)$ are the Nambu Green functions in films N and S, respectively. In the usual way, we write

$$\begin{aligned} G_{Nn}^{-1}(\omega) &= \omega\tau_0 - \epsilon_n\tau_3 - \Sigma_N(\omega) \\ &= \omega Z_N(\omega)\tau_0 - \epsilon_n\tau_3 - Z_N(\omega)\Delta_N(\omega)\tau_1 \end{aligned} \tag{3}$$

and similarly for $G_{Sn'}^{-1}(\omega)$. Here ϵ_n is the energy of state n, τ_0 is the 2×2 unit matrix, and τ_1 and τ_3 are the usual Pauli matrices. $\Delta_S(\omega)$ and $\Delta_N(\omega)$ are renormalized gap functions, and $Z_S(\omega)$ and $Z_N(\omega)$ renormalization functions, in films S and N, respectively.

The self-energy term Σ_S^{BCS} represents the BCS pairing correlation in film S

$$\Sigma_S^{\mathrm{BCS}} = \Delta_S^{\mathrm{ph}} \tau_1 \ , \tag{4}$$

where Δ_S^{ph} is the usual BCS order parameter, given as a function of temperature T in the usual finite temperature formalism by[14]

$$\Delta_S^{\mathrm{ph}}(T) = \lambda_S \pi k T \sum_{(|\omega_n|<\omega_c)}^{n} \frac{\Delta_S^{\mathrm{ph}}(T)}{[\Delta_S^2(i\omega_n) + \omega_n^2]^{1/2}} \ , \tag{5}$$

where $\omega_n = (2n+1)\pi kT$, λ_S is the BCS coupling constant in film S, ω_c is the BCS cutoff frequency and k Boltzmann's constant.

The self-energy term Σ_N^{MZ} describes the effect of the Kondo impurities on superconductivity. In the MZ theory,[2] the scattering amplitudes of the Kondo impurities are approximated by those for a classical impurity spin,[16] except that the bound-state energy parameter y_0 is a function of transition temperature T_c rather than a constant. The MZ self-energy in our notation is

$$\Sigma_N^{\mathrm{MZ}} = \frac{c(1-y_0)(\Delta_N^2 - \omega^2)^{1/2}(\omega\tau_0 - y_0\Delta_N\tau_1)}{2\pi N_0(\omega^2 - \Delta_N^2 y_0^2)} \ , \tag{6}$$

where N_0 is the density of states at the Fermi level for the Kondo alloy of film N. The appropriate definition of y_0 for our case will be discussed in the next section. Substituting Eq. (6) into Eq. (2), the effect of Kondo impurities can be included in the self-consistency program. The resulting equations for the energy-gap functions are

$$\Delta_S(\omega) = \frac{\Delta_S^{\mathrm{ph}} + \Gamma_S \Delta_N(\omega)/E_N(\omega)}{1 + \Gamma_S/E_N(\omega)} \ , \tag{7}$$

$$\Delta_N(\omega) = \frac{\Gamma_N \Delta_S(\omega)/E_S(\omega)}{1 + \Gamma_N/E_S(\omega) + \Gamma E_N(\omega)/[y_0^2\Delta_N^2(\omega) - \omega^2]} \ , \tag{8}$$

where $E_S(\omega) = [\Delta_S^2(\omega) - \omega^2]^{1/2}$ and $E_N(\omega) = [\Delta_N^2(\omega) - \omega^2]^{1/2}$. The sign of the square roots is chosen so that the real parts of $Z_S(\omega)E_S(\omega)$ and $Z_N(\omega)E_N(\omega)$ are positive.[14] Γ is the pair-breaking parameter

$$\Gamma = c(1-y_0^2)/2\pi N_0 \tag{9}$$

which has maximum value $\Gamma_0 = c/2\pi N_0$. Γ_S and Γ_N are the McMillan tunneling parameters[9] which are inversely proportional to the corresponding film thicknesses d_S and d_N. We write

$$\Gamma_S/\Delta_B = C_S/d_S, \quad \Gamma_N/\Delta_B = C_N/d_N \ , \tag{10}$$

where C_S and C_N are constants, and Δ_B is the order parameter of film S in the absence of a proximity effect. Mohabir and Nagi[17] found that for the McMillan model without magnetic impurities, the primary effect of taking into account higher orders of perturbation theory was to renormalize Γ_S and Γ_N. Thus if C_S and C_N are evaluated from experimental data, the validity of our calculations should not be limited to weakly coupled films.

B. Density of states

The quasiparticle density of states observed by tunneling into film N (normalized by the normal-state density of states at the Fermi level) may be calculat-

ed from

$$N_N(\omega) = \mathrm{Re}\{\omega/[\omega^2 - \Delta_N^2(\omega)]^{1/2}\} \quad (11)$$

and similarly for $N_S(\omega)$ for tunneling into film S, where $\Delta_N(\omega)$ and $\Delta_S(\omega)$ are calculated iteratively by computer from Eqs. (7) and (8). A typical shape of the density of states in each film is illustrated in Fig. 1. An energy gap is induced in film N, with a rounded BCS-like peak above the gap, and a shoulder or second peak at an energy near the value of the order parameter Δ_S^{ph} in film S. The BCS peak in film S is blurred and $N_S(\omega)$ acquires a small tail down to the value of the induced gap in film N. These features are characteristic of the McMillan model.[9] The effect of the Kondo impurities in film N is to introduce a small impurity band into the energy gap in *both* films. As the impurity concentration increases, the impurity bands grow and the density of states soon becomes gapless, giving rise to gapless superconductivity. The densities of states shown in Fig. 1 are essentially equivalent for a given value of y_0 to those of Machida,[18] who extended our[14] McMillan model for magnetic impurities using a treatment equivalent to Shiba's[19] Hartree-Fock analysis of the Anderson model; similarly Shiba's density of states is equivalent to that of ZBM.[4] The key difference when the Kondo effect is included (as in the present calculations or the ZBM theory) is that the bound state changes position as the superconducting order parameter varies.

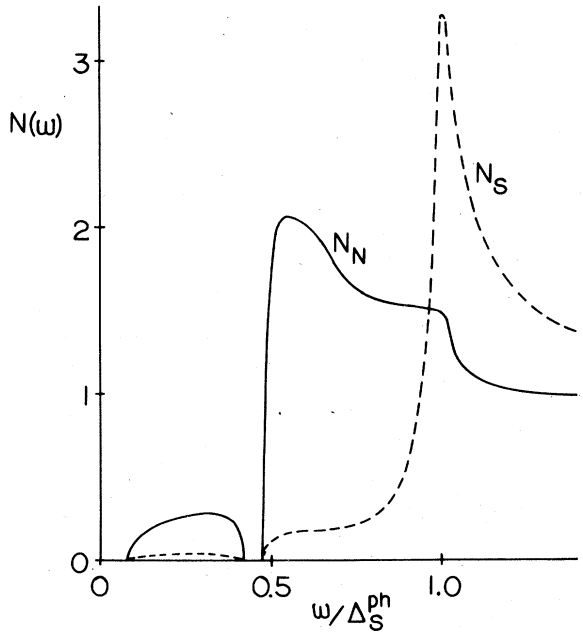

FIG. 1. Normalized tunneling density of states into superconductor film $S(N_S)$ and into Kondo alloy film $N(N_N)$, for proximity tunneling parameters $\Gamma_S = 0.1\Delta_S^{ph}$ and $\Gamma_N = 3\Delta_S^{ph}$, bound-state location parameter $y_0 = 0.5$ and pair-breaking parameter $\Gamma = 0.07\Delta_S^{ph}$.

The density of states $N_N(\omega)$ in film N qualitatively resembles that calculated by ZBM[4] for Kondo impurities placed directly in a BCS superconductor. In interpreting their proximity sandwich tunneling data for Kondo alloys, Dumoulin *et al.*[7] assumed that the ZBM calculations applied to their case with an effective superconducting order parameter taken as the induced energy gap in film N. To investigate the validity of this approximation, we note that Eq. (8) has some similarity to the corresponding equation in the ZBM theory[4] if film N were a Kondo superconductor isolated from film S

$$\Delta_N(\omega) = \frac{\Delta^*}{1 + \Gamma^* E_N(\omega)/[y_0^{*2}\Delta_N^2(\omega) - \omega^2]} \quad , \quad (12)$$

where Δ^* is the order parameter, Γ^* the pair-breaking parameter, and y_0^* the bound-state location parameter. In particular, for $\omega \to 0$ where analytic solutions are possible, Eq. (8) for the proximity case becomes

$$\Delta_N(0) = \frac{\Gamma_N - (1 + \Gamma_S/\Delta_S^{ph})\Gamma/y_0^2}{1 + (\Gamma_N + \Gamma_S)/\Delta_S^{ph}} \quad (13)$$

and Eq. (12) for the ZBM case becomes

$$\Delta_N(0) = \Delta^* - \Gamma^*/y_0^{*2} \quad . \quad (14)$$

These equations are identical if we define the following "effective ZBM parameters" for the proximity case

$$\Delta^* = \Delta_N(0)(\Gamma = 0) = \Gamma_N/[1 + (\Gamma_N + \Gamma_S)/\Delta_S^{ph}] \quad , \quad (15)$$

$$\Gamma^* = \Gamma(1 - \Delta^*/\Delta_S^{ph}) = \frac{\Gamma(1 + \Gamma_S/\Delta_S^{ph})}{1 + (\Gamma_S + \Gamma_N)/\Delta_S^{ph}} \quad , \quad (16)$$

$$y_0^* = y_0 \quad . \quad (17)$$

This equivalence of our proximity effect model to the ZBM theory holds only at the Fermi level ($\omega = 0$), but since $\Delta_N(\omega)$ for the McMillan model without magnetic impurities[9] is reasonably constant up to above the energy of the induced gap, one might expect $\Delta_N(0)$ to be an appropriate effective BCS order parameter for all frequencies of interest. This is indeed the case, as demonstrated in Fig. 2, which shows that the effective ZBM model gives a very good description of the impurity band for two widely different proximity effect cases. The BCS-like peak at around Δ^* is not given quite so well. For a thick superconductor film ($\Gamma_S = 0.1\Delta_S^{ph}$), the upper gap above the impurity band is larger than predicted by the effective ZBM model and the density of states has a second peak at about Δ_S^{ph} (for this case $\Delta_S^{ph} = 1.37\Delta^*$). For a thin superconductor film on the other hand ($\Gamma_S = 3\Delta_S^{ph}$), the upper gap has disappeared earlier than predicted by the effective ZBM model and the BCS-like peak is very blurred; for this case $\Delta_S^{ph} = 2.33\Delta^*$ (i.e., the induced gap is small), so the proximity effect structure in $N_N(\omega)$ around Δ_S^{ph} is

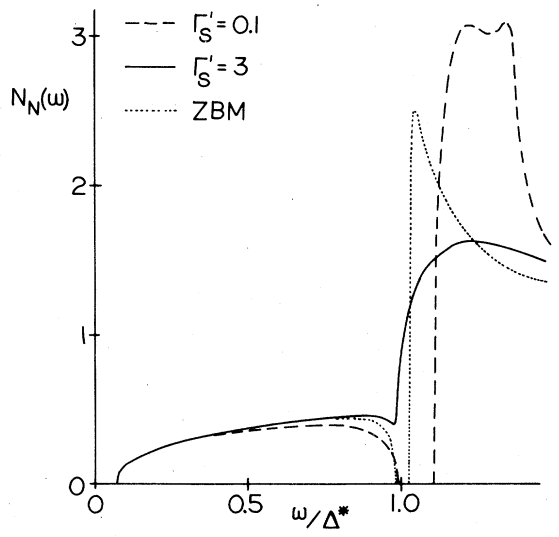

FIG. 2. Comparison of two examples of the tunneling density of states $N_N(\omega)$ into film N of the proximity sandwich with $N(\omega)$ for a superconducting Kondo alloy (ZBM case) for $y_0 = 0.5$ and $\Gamma^* = 0.15\Delta^*$. For the ZBM case, Δ^* is the order parameter of the Kondo superconductor and Γ^* is the pair-breaking parameter Γ; for the proximity case, Δ^* and Γ^* are the corresponding effective ZBM parameters defined by Eqs. (15) and (16). $\Gamma_N' = \Gamma_N/\Delta_S^{ph} = 3$, and $\Gamma_S' = \Gamma_S/\Delta_S^{ph}$ has the value shown.

at much higher energies than the BCS-like peak. Although the peak around Δ_S^{ph} may lead to worse agreement for tunneling conductance for a thick film N, as noted experimentally by Dumoulin *et al.*,[7] the effective ZBM model is still valid for the impurity bands. Since Δ^* is approximately the induced gap in film N, our effective ZBM model defined by Eqs. (15)–(17) is very similar to the "equivalent BCS" model used by Dumoulin *et al.*[7] In particular, the impurity bound state is centered at an energy of approximately $y_0\Delta^*$, as in the analysis of Dumoulin *et al.*[7] However, the effective value Γ^* of the pair-breaking parameter for the proximity case is reduced below Γ, the pair-breaking parameter in the ZBM theory defined by Eq. (9). The physical reason for this is that in the proximity case, much of the pair-breaking effect of the Kondo impurities in film N is exported to film S rather than acting directly to reduce the effective order parameter in film N. Thus the reduction in Γ^* is particularly significant if film N is very thin (Γ_N large) so that electrons spend only a short time in film N before tunneling into film S. The Kondo impurities produce an impurity band in film S as well as in film N.

The effective ZBM model confirms the definition of Dumoulin *et al.*[7] for the bound-state parameter y_0 for the proximity case. Calculations of y_0 at low temperatures for finite impurity concentrations have not been made, but calculations for a single impurity at $T=0$ for $S=\frac{1}{2}$ suggest that y_0 is not too sensitive to temperature for $T_K < T_c$. However, in the proximity case, the effective order parameter Δ^* in film N is not related by the usual BCS relation to the transition temperature T_c of the proximity sandwich. Since y_0 depends on the effective superconducting coupling[1] represented by Δ^*, it is appropriate to define an effective transition temperature by the BCS relation

$$T_c^* = \Delta^*/1.76k \tag{18}$$

and to follow Dumoulin *et al.*[7] in using T_c^* instead of T_c as a measure of Δ^* for the proximity case when the bound-state location at low temperatures is to be estimated. Thus the definition of y_0 from the ZBM theory[4] becomes

$$y_0^2 = \frac{\ln^2(T_c^*/T_K)}{\ln^2(T_c^*/T_K) + \pi^2 S(S+1)} , \tag{19}$$

where S is the impurity spin.

C. Order parameter and transition temperature

In order to compare our calculated densities of states with experiment, it is necessary to evaluate the BCS order parameter Δ_S^{ph} in film S. It is convenient to rewrite Eq. (5) for $\Delta_S^{ph}(T)$ as

$$\frac{\Delta_S^{ph}(T)}{\Delta_B} = \frac{2\gamma_e T/T_c^B}{\ln(T/T_c^B)} \sum_{n\geq 0} \left[\frac{\Delta_S(i\omega_n)}{E_S(i\omega_n)} - \frac{\Delta_S^{ph}(T)}{\omega_n} \right] , \tag{20}$$

where T_c^B and Δ_B are the transition temperature and order parameter (at $T=0$) for film S in the absence of any proximity effect, $\gamma_e = 1.781$, and the cutoff at ω_c need no longer be made. At low temperatures $T \ll T_c$, we have

$$\frac{\Delta_S^{ph}(0)}{\Delta_B} = \exp \int_0^\infty \left[\frac{\Delta_S(i\omega_n)}{\Delta_S^{ph}(0) E_S(i\omega_n)} - \frac{1}{\{[\Delta_S^{ph}(0)]^2 + \omega_n^2\}^{1/2}} \right] d\omega_n . \tag{21}$$

Results for $\Delta_S^{ph}(0)$ for various parameter values are shown in Fig. 3. Note the effect of the impurities in reducing $\Delta_S^{ph}(0)$ as the concentration (and therefore the pair-breaking parameter Γ) are increased. The limit $\Gamma \to \infty$ shown by the dotted curve corresponds to the case where electrons tunneling out of film S lose all superconducting correlation before returning; this limit may also be approached by increasing the thickness of film N ($\Gamma_N \to 0$). Clearly the superconductivity of the proximity sandwich can only be quenched by adding Kondo impurities to film N if $\Gamma_S > 0.5\Delta_B$; if film S is thick (e.g., $\Gamma_S = 0.1\Delta_B$), the

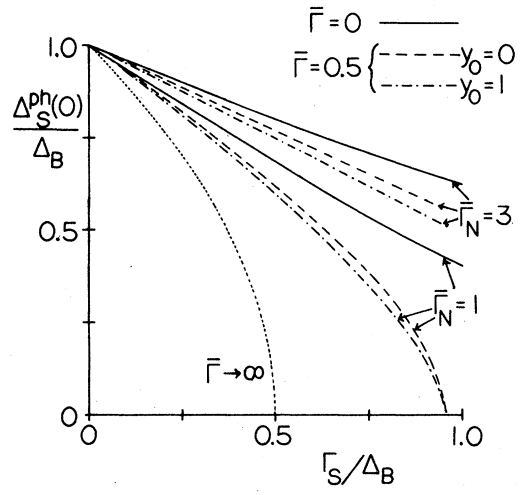

FIG. 3. Order parameter Δ_S^{ph} at temperatures $T \ll T_c$ in film S of the proximity sandwich for various parameter values as shown. Δ_S^{ph}, Γ_N, Γ_S, and Γ are all normalized relative to Δ_B.

impurities are not able to produce a large reduction in $\Delta_S^{ph}(0)$.

The transition temperature T_c of the proximity sandwich is obtained by letting $\Delta_S^{ph}(T) \to 0$ in Eq. (20)

$$\ln\frac{T_c^B}{T_c} = 2\pi k T_c \Gamma_S \sum_{n\geq 0} \frac{1+\Gamma/\omega_n^c}{(\omega_n^c)^2+(\Gamma+\Gamma_S+\Gamma_N)\omega_n^c+\Gamma\Gamma_S} , \tag{22}$$

where $\omega_n^c=(2n+1)\pi k T_c$, and the T_c dependence of the pair-breaking parameter is given by[2]

$$\Gamma = \frac{c}{2\pi N_0}\frac{\pi^2 S(S+1)}{[\ln^2(T_K^*/T_c)+\pi^2 S(S+1)]} . \tag{23}$$

In order to make the finite concentration calculations reduce to the exact single impurity calculations[1] on T_c depression, T_K has been replaced by[20]

$$T_K^* = T_K/12.9 . \tag{24}$$

It might also be noted that taking account of the energy and concentration dependence of pair breaking, the temperature dependence of Γ (and the degree of reentrance in T_c) are reduced[13] for $S=\frac{1}{2}$.

Examples of T_c given by Eqs. (22) and (23) have been given earlier[10] and so will not be repeated here. The key point was that if film S is thick, the Kondo impurities can produce only a small reduction in T_c. If however film S is thin, the Kondo impurities can quench the superconductivity of the proximity sandwich, and the T_c versus c curve may show reentrant behavior for $T_K < T_c$ as in the original MZ theory[2] for Kondo superconductors.

III. COMPARISON WITH EXPERIMENT

A. Density of states

We now compare our calculations to the experimental data of Dumoulin *et al.*[7] The tunneling conductance $\sigma(V)$ into film N of a proximity sandwich (normalized with respect to the normal-state conductance) is

$$\sigma(V)=\frac{1}{kT}\int_{-\infty}^{+\infty}\frac{N_N(\omega)\exp[(\omega+eV)/kT]}{\{1+\exp[(\omega+eV)/kT]\}^2}d\omega , \tag{25}$$

where V is the voltage applied across the tunneling junction and e is the magnitude of electronic charge.

1. *Cu*Cr

Figure 4 shows the comparison for tunneling into three very different *Cu*Cr alloy films backed with Pb. For the theoretical curves, the values of the McMillan tunneling parameters Γ_S and Γ_N were calculated taking $C_S=225$ Å and $C_N=625$ Å, as determined by Dumoulin *et al.*[8] from T_c measurements on their Pb-Cu sandwiches. Δ_S^{ph} was then determined from Eq. (21). It is pleasing to note that the locations of the large conductance peaks, which are predicted

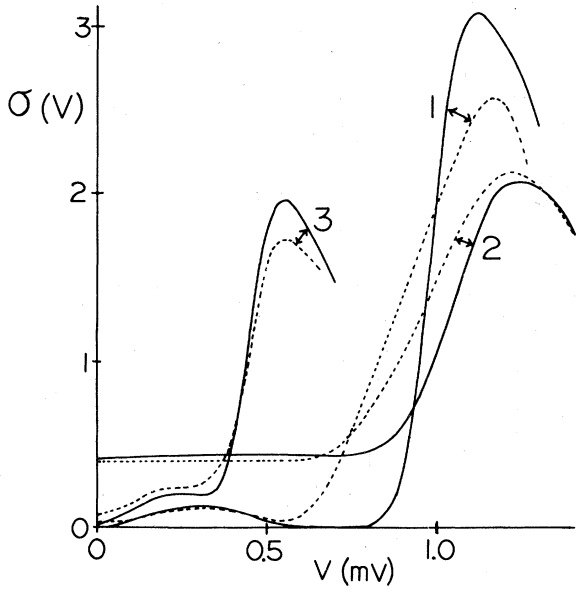

FIG. 4. Experimental normalized tunneling conductance (Ref. 7) into *Cu*Cr alloys backed by Pb (dotted lines) compared to our calculations (full lines), for $d_N=250$ Å and $d_S=2000$ Å, $c=17$ ppm, $T=0.4$ K (curves 1), $d_S=2000$ Å, $c=170$ ppm, $T=0.95$ K (curves 2), $d_S=250$ Å, $c=17$ ppm, $T=0.4$ K (curves 3). For the theoretical curves $C_S=225$ Å, $C_N=625$ Å, $\Gamma_f=5\Gamma$, and y_0 was adjusted to give the observed location of the impurity band maximum.

TABLE I. Comparison of experimental and theoretical locations of the impurity states for the alloy samples with largest values of equivalent critical temperature T_c^*. The arrows indicate the sense of variation of y_0 as T_c^* decreases.

Alloy	T_K (K)	T_c^* (K)	y_0 (Expt.)	y_0 (Theor.)
*Cu*Mn	0.01	7.5	0.60–0.65↓	0.65↓
*Au*Fe	0.5	6.9	0.23↓	0.40↓
*Cu*Cr	I	6.0	0.30↑	0.28↓
*Cu*Fe	30	6.9	0.77↑	0.23↑

theoretically without adjustable parameters, correspond very well to the experimental locations, even for curve 3 for which the induced gap is much less than the Pb gap. As might be expected the experimental decrease in conductance immediately below the peaks is not as sharp as predicted by the idealized theoretical model.

Regarding the impurity bands below the large peaks, calculations using the theoretical value of the pair-breaking parameter Γ from Eq. (9), with $N_0 = 0.15$ states/eV/atom per spin for Cu, predict impurity bands much smaller than those observed. As seen in Fig. 4, good agreement is obtained only if we take the experimentally fitted value Γ_f as five times the theoretical value Γ. The location of the bound states was matched to the experimental values by adjusting y_0 ($y_0 = 0.30$ for curves 1 and 2, $y_0 = 0.46$ for curve 3), giving values very similar to those of Dumoulin *et al.*[7] using their equivalent ZBM model. As pointed out by Dumoulin *et al.*, the increase of y_0 as Δ^* decreases disagrees strongly with the ZBM theory, which for $S = \frac{3}{2}$ predicts using Eq. (19) a decrease of y_0 from 0.28 for curve 1 to 0.17 for curve 3. Thus *Cu*Cr behaves as though $T_K > T_c^*$ rather than $T_K < T_c^*$. The experimental and theoretical values of y_0 for curve 1 (for which T_c^* is largest) are listed in Table I. Further comparion with the density of states for *Cu*Cr alloys within the Hartree-Fock approximation is given by Machida and Dumoulin[21]; an analysis regarding temperature and concentration dependence in our model would be very similar.

2. *Cu*Mn

Figure 5 shows that the theoretical value $y_0 = 0.65$ (for $S = 2$) gives a good fit to the tunneling conductance data for *Cu*Mn. As for *Cu*Cr the locations of the large conductance peaks (not shown in Fig. 5) are also in good agreement with experiment. We see again that a pair-breaking parameter $\Gamma_f = 5\Gamma$ gives a good fit for the two higher-concentration alloys. The situation for the low-concentration alloy is not so

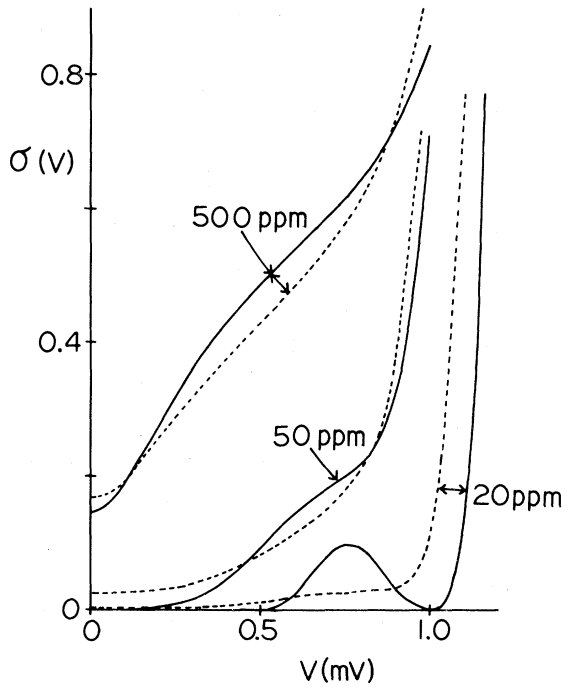

FIG. 5. Experimental conductance into *Cu*Mn alloys (Ref. 7) backed by Pb (dotted lines) compared to our calculations (full lines). For the 20-ppm curves $d_N = 100$ Å, $d_S = 2000$ Å, and $T = 0.4$ K, and for the 50- and 500-ppm curves $d_N = 150$ Å, $d_S = 2000$ Å, and $T = 0.96$ K. For the theoretical curves $C_S = 225$ Å, $C_N = 625$ Å, $\Gamma_f = 5\Gamma$, and $y_0 = 0.65$.

clear, because the impurity band is much less sharp than predicted. The impurity band is also more washed out than predicted at the higher concentrations, but because in these cases the predicted band is broad and the temperature was larger, the overall agreement is good. It would appear therefore that the overall number of impurity states in the gap is best explained with $\Gamma_f = 5\Gamma$, but the states are much more blurred in energy than predicted at low concentrations. Note that Dumoulin *et al.*[7] obtained good agreement using the theoretical value of Γ because their model did not take account of the reduction of effective pair breaking by leakage to film S— see Eq. (16).

If the theoretical impurity-band peak location is matched with the inflection point listed by Dumoulin *et al.*[7] for the 20-ppm alloy in Fig. 5, a fitted value $y_0 = 0.60$ is obtained (Dumoulin *et al.* suggested Fe impurities may also contribute to the impurity band for this alloy.) The fitted value of y_0 is therefore listed as 0.60 to 0.65 in Table I. A similar matching for a 20-ppm alloy with a somewhat smaller value of Δ^* confirms that y_0 decreases as T_c^* decreases, as indicated in Table I.

3. *Au*Fe *and* *Cu*Fe

For these alloys it is difficult to reach any conclusion about the magnitude of the pair-breaking parameter since the experimental impurity bands are very small peaks above a rather diffuse background. Nevertheless, by matching the peak positions with theoretical values, the best-fit values of y_0 can be deduced, as listed in Table I, which also gives theoretical values of y_0 for $S=\frac{3}{2}$. Our use of $C_S=225$ Å and $C_N=625$ Å for the *Au*Fe alloy, although not strictly justified, appears reasonable since the large conductance peak location is given correctly.

B. Transition temperature

Dumoulin *et al.*[8] measured the transition temperature T_c for proximity sandwiches of *Cu*Cr, *Cu*Mn, *Cu*Fe, and *Cu*Co alloys backed by Pb. As expected, the Co impurities at low concentrations gave no noticeable magnetic depairing, while the *Cu*Mn alloys appeared to be complicated by inhomogeneity and antiferromagnetic ordering. Their data for *Cu*Cr alloys are shown in Fig. 6, together with fits to our Eqs. (22)–(24) for $S=\frac{3}{2}$. The method of analysis used in the original paper by Dumoulin *et al.*[8] was to extract the value of the pair-breaking parameter Γ using the T_c expression from our earlier Abrikosov-Gorkov treatment,[14] then to compare Γ to the predictions of the MZ theory.[1] This method of analysis is perfectly valid since our new T_c expression (22) is exactly the same as our earlier expression,[14] apart from the definition of Γ. Dumoulin *et al.* found evidence that Γ increased as T_c decreased towards T_K^*, as predicted qualitatively by the MZ theory. Our fits for cases 2 and 3 support this result in that the fits with Γ defined by Eq. (23) are better than similar fits made with Γ constant. This is not so for case 1, however, apparently because at this higher concentration the coherence length is shortened sufficiently so that the superconducting properties of film N are not uniform across its thickness for $d_N=970$ Å (i.e., the effective d_N is smaller, as found for some cases by Dumoulin *et al.*[8]).

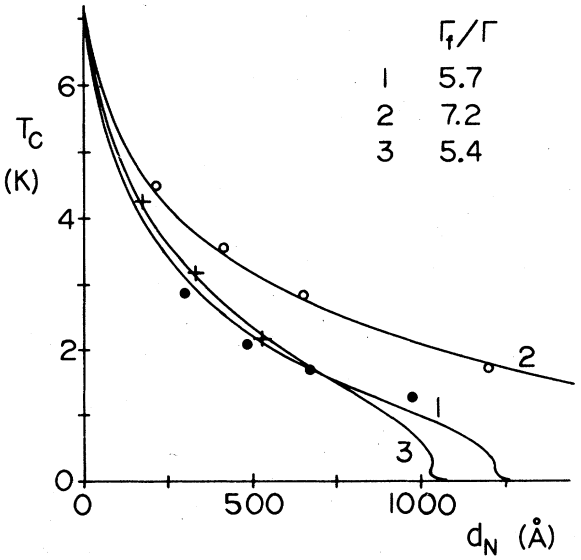

FIG. 6. Experimental measurements of the transition temperature T_c of *Cu*Cr-Pb sandwiches [Dumoulin *et al.* (Ref. 8)] compared to our calculations (full lines) for $d_S=400$ Å, $c=600$ ppm (curve 1), $d_S=372$ Å, $c=110$ ppm (curve 2), and $d_S=295$ Å, $c=110$ ppm (curve 3). For the theoretical calculations, $S=1.5$, $T_K=1$ K, $C_S=225$ Å, $C_N=625$ Å and the fitted values of Γ_f/Γ are listed for each curve.

One point of interest regarding our fits 2 and 3 in Fig. 6 is that reentrant behavior is predicted below 0.3 K since the pair-breaking reaches its maximum at $T_c\sim T_K/12.9$. (Note reentrance occurs as a function of d_N as well as a function of c.) Especially for case 3, for which film S is thinnest, this possible region of reentrant behavior should be accessible experimentally. Of course, recent theoretical refinements mentioned earlier[11,13] may lessen or eliminate reentrance (although results for $S=\frac{3}{2}$ are not given explicitly).

The other point of interest regarding the fits is that the fitted values Γ_f of the pair-breaking parameter are approximately six times the theoretical values Γ, a result similar to that in fitting the densities of states, although it should be noted that Γ_f derived from the T_c data is much more sensitive to the film parameters and to the assumed values of S and T_K. These large pair-breaking values do not appear to be an artifact of the proximity model, since Ginsberg[22] has pointed out that four superconducting Kondo alloys show an initial decrease in T_c which is larger than the maximum permitted by Eq. (9) of the MZ theory.

For *Cu*Fe-Pb sandwiches, Dumoulin *et al.*[8] found $\Gamma_f/c=3.7$ μeV/ppm with little evidence of any T_c dependence between 1.5 and 4 K. The lack of any clear T_c dependence over this range is in agreement[8] with the MZ theory since $T_K^*\sim 2.3$ K, but the pair breaking is again much larger than expected ($\Gamma_f\sim 3.5\Gamma_0$).

IV. DISCUSSION

Our extension of the MZ theory to the proximity effect gives a good qualitative description of the experiments of Dumoulin *et al.*[7,8] for induced superconductivity in *Cu*Cr, *Cu*Mn, *Cu*Fe, and *Au*Fe alloys. The observed experimental features in the density of states are typically less sharp than those predicted, for example some of the peaks in Figs. 4

and 5. This blurring effect would of course be expected if the alloys were not perfectly homogeneous with uniform superconducting parameters across their thickness as assumed in our model. The main discrepancies of interest are those between the values of the best-fit parameters y_0 and Γ_f and the values expected theoretically.

Regarding the location of the bound state, our values for y_0 (summarized in Table I) differ by no more than about 10% from the values obtained by Dumoulin *et al.*[7] using their equivalent BCS model for film *N*. Although Dumoulin *et al.*[7] regarded their model as an approximation and considered it highly desirable to obtain tunneling results on Kondo alloy superconductors without using the proximity effect, we have shown that their model (with an appropriate effective pair-breaking parameter) is in fact a very good approximation within the context of the McMillan model. The use of the proximity effect to induce superconductivity is of greater interest because it enables the effective order parameter Δ^* and transition temperature T_c^* to be varied[7]; changes in the bound-state parameter y_0 as T_c^* varies confirm the validity of the Kondo theory compared to the Hartree-Fock theory[19] (which gives static bound states). Our Table I confirms the conclusion of Dumoulin *et al.*[7] that the experimental value of y_0 agrees with the ZBM theory[4] for $T_K \ll T_c^*$, but the agreement becomes steadily worse as T_K increases. This conclusion is not sensitive to the use of T_c^* as an effective transition temperature in place of T_c. Nor does the use of y_0 values for $T=0$ rather than $T \lesssim T_c$ offer much hope in resolving the discrepancy: for $S=\frac{1}{2}$, the single-impurity y_0 values for $T=0$ are decreased for $T_K > T_c$ rather than increased. Thus it seems likely that the discrepancy for $T_K \gtrsim T_c^*$ could be related to the breakdown of the Nagaoka-Suhl approximation for this regime. Although no detailed predictions of bound-state location have been made for the interpolation model of Matsuura *et al.*,[11] some results have been given[12] for a half-filled *d* state in the single-impurity limit away from the crossover region $T_K \sim T_c$. The symmetry in the MZ theory of y_0 as a function of $\ln(T_K/T_c)$ as T_K increases is lost in Matsuura's calculation[12]: for $T_K > T_c$, where the Coulomb repulsion pair-weakening effect is dominant, the bound state appears to move up towards the band edge more quickly than it descends for $T_K < T_c$. Once the impurity can be treated in the nonmagnetic Hartree-Fock approximation, the bound state has disappeared into the band.[23] This faster disappearance of the bound state into the band edge as T_K increases is qualitatively consistent with the experimental data. It is interesting to note that Daybell[24] found that the resistivity of Kondo alloys changed to the $T=0$ limit more quickly than predicted by the Suhl-Nagaoka expression, and that *Th*U ($T_K \sim 100$ K) has a specific-heat change at T_c equal to the BCS value[5] (as expected in the nonmagnetic limit[23]). Thus the y_0 values agree with these results in indicating that the Suhl-Nagaoka approximation fails to give correctly the transition to the limit of large T_K.

The other main discrepancy between experimental and theoretical parameter values is the fact that for fitting both the density of states and the transition temperature data, pair-breaking parameters Γ_f approximately five times the theoretical values calculated from Eq. (9) are required. In their T_c measurements, Dumoulin *et al.*[8] noted that pair-breaking parameters larger than those given by the Abrikosov-Gorkov theory were required. Following Blandin[25] and Caroli,[26] they suggested that the inclusion of orbital degeneracy and angular dependence would increase the theoretical values by a factor of $(2l+1)$ and resolve the discrepancy. Shiba (quoted by Ginsberg[22]) has also suggested an additional orbital degeneracy factor $(2l+1)$ in the T_c depression formula of the MZ theory; Shiba showed that the $(2l+1)$ factor, absent in his ealier treatment[16] of the classical limit of the usual *s-d* interaction Hamiltonian, was present in his Hartree-Fock treatment[19] of the Anderson model including orbital degeneracy, with $S=\frac{1}{2}$ (i.e., each orbital is acting approximately independently). Our analysis of the experimental data is certainly very suggestive of the presence of the $(2l+1)$ factor. The use of $S=\frac{1}{2}$ to calculate theoretical y_0 values would mean that the disagreement of the MZ theory with experiment would extend to $T_K \ll T_c^*$ as well: Kondo temperatures an order of magnitude larger than the accepted values listed in Table I would be needed for all the alloys to account for the experimental y_0 values [note that the disagreement would be worse by another order of magnitude if $T_K^* = T_K/12.9$ were used in place of T_K in Eq. (19) for y_0, as used in Eq. (23) in calculating T_c]. Interestingly, Daybell[24] finds that explanation of the temperature dependence of Kondo anomalies requires $S=\frac{1}{2}$ rather than the value determined from high-temperature susceptibility. It should be mentioned that the difference between Γ_f and Γ might also be explained if the density of states N_0 in Eq. (9), the effective density of states for superconducting electrons, is a factor of 5 smaller than the usually accepted density of states at the Fermi level.

Figure 6 shows that the T_c data for *Cu*Cr are consistent with our model for $S=\frac{3}{2}$. For $S=\frac{1}{2}$, curves 2 and 3 give a slightly better fit, curve 1 a slightly worse fit to the anomalous point for $d_N = 970$ Å, and the degree of reentrance is greatly increased. To observe clearly the temperature dependence of pair-breaking, and to check whether reentrant superconductivity occurs, data at lower temperatures are needed for thin films $S(d_S < 300$ K). Data for *Cu*Mn (with $T_K \sim 0.01$ K) as well as *Cu*Cr would be of in-

terest. Values of the effective pair breaking Γ_f could be extracted as a function of T_c from the proximity effect Eq. (22), as in Dumoulin *et al.*,[8] then compared directly to theoretical predictions for Γ as a function of T_c for the MZ theory[2] and its extension by Schuh and Müller-Hartmann.[13] For the theory of Matsuura *et al.*,[11] a similar comparison could be made if the T_c depression is expressed in terms of an effective pair-breaking parameter which includes the pair-weakening Coulomb repulsion effect. It would be interesting to see whether the T_c dependence of the experimental pair breaking Γ_f is that expected for $S = \frac{1}{2}$, or a slower variation corresponding to a larger value of S.

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