Tunneling conductance for superconducting alloys with 3d magnetic impurities*

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It is shown that the tunneling conductance curves of Woolf and Reif for quench-condensed In-Fe alloy films do not agree with values which are calculated from the theory of Shiba and Rusinov, which is supposed to describe magnetic impurities that interact strongly with the conduction electrons. Possible reasons for the discrepancy are presented. It is also suggested that the theory should be modified to take strong electron-phonon coupling into account in relating the pair-breaking parameter to the impurity concentration for Pb-Mn alloy films. This would not affect the good agreement between the observed tunneling curves for Pb-Mn films and the theory, which Chaba and Nagi have found previously.

A theory of the influence of magnetic impurities (local moments) on the properties of superconductors was developed by Abrikosov and Gor'kov,[1] and was extended by Skalski *et al.*[2] and others. The theory is in good agreement with the observed properties of alloys in which the magnetic impurity is a rare earth,[3] where the magnetic electrons are in the 4f atomic shell. For magnetic impurities which are 3d elements, the theory of Abrikosov and Gor'kov does not agree well with the data.[4,5] This is thought to result from the inability of that theory, which relies on the first Born approximation, to treat properly the interaction of the conduction electrons with 3d impurity electrons, which is stronger than that with 4f impurity electrons.[4]

A theory which goes beyond the first Born approximation was developed by Shiba[6] and, later but apparently independently, by Rusinov.[7] This theory treats the impurity spin classically; the noncommutativity of the spin operators is ignored. The spin lifetime is assumed to be infinite. The impurity atoms are assumed to be randomly distributed in the sample, and are presumed not to interact with each other.

Chaba and Nagi[8,9] used the Shiba-Rusinov theory to calculate the tunneling curves for Pb-Mn alloy films. Their results agree well with the data of Woolf and Reif.[4] However, the theoretical tunneling curves for In-Fe alloy films, which Woolf and Reif also obtained,[4] were not calculated.[10] We have calculated them, and it is found that the theory is in poor agreement with the data for In-Fe alloys.

Our calculation is based on the same equations as those used by Chaba and Nagi.[8] [Their Eqs. (1), (3), and (4), and their relation between the density of states and the function U are equivalent to Rusinov's Eqs. (38), (36), the equation following his equations (36), and (41), respectively.] The tunneling conductance $g(V)$, normalized to that in the normal state, is related to the density of states $N(E)$ at the voltage V in the usual way,[4]

$$g(V) = \int_{-\infty}^{\infty} N(E)K(E, V, T)\,dE\,, \tag{1}$$

where

$$K(E, V, T) = e^x/(e^x+1)^2kT\,, \tag{2}$$

$$x = (E - eV)/kT\,, \tag{3}$$

and where e is the electron charge, k is Boltzmann's constant, and T is the temperature. As in Ref. 8, the density of states used is that appropriate for $T=0$, since the data were obtained at $T=0.4$ K, which is much less than the transition temperature T_c. Also as in Ref. 8, after $N(E)$ is calculated, the strong electron-phonon coupling in lead and the moderately strong coupling in indium are taken into account by scaling energies up by an amount $\Delta(0)/\Delta_w(0)$, where $\Delta(0)$ is the measured order parameter for lead[8] (1.335 meV) or indium[11] (0.675 meV) at $T=0$ and Δ_w is the weak-coupling BCS value,[12] $1.764kT_c$. For pure indium films,[11] we take $T_c=4.18$ K.

We began by calculating the tunneling curves for the Pb-Mn films, and our results agree perfectly with those of Chaba and Nagi. The tunneling curves for the In-Fe films were then calculated. They are shown in Figs. 1 and 2. For a given ratio of T_c to T_{c0}, the transition temperature of the pure host metal, the pair-breaking parameter $\alpha=\hbar/\tau$ is expected to be smaller for an In-Fe sample than for a Pb-Mn sample, because T_c is smaller in the former case [see Eq. (5)]. The calculated tunneling curves show this effect.

The parameter ϵ_0 which is referred to in Figs. 1 and 2 determines the energies of the states within the BCS energy gap which appear when magnetic impurities are added, according to the Shiba-Rusinov theory. This parameter is given by

$$\epsilon_0 = |(1-\beta^2)/(1+\beta^2)|\,, \tag{4}$$

where $\beta = \frac{1}{2}\pi JSN_0$, N_0 is the electronic density of states at the Fermi level for one spin direction in the normal state, J is the strength of the exchange interaction, and S is the impurity spin. For very small impurity concentrations, the states in the BCS gap are expected to appear at an energy $\epsilon_0\Delta$. For larger impurity concentrations, the impurity states form a band of energies around $\epsilon_0\Delta$. This is clearly indicated by the densities of states from which the curves shown in Figs. 1 and 2 were calculated; also evident is the expected smearing out of the BCS singularity in the density of states. We treat ϵ_0 as an adjustable parameter.

The figures show that the observed tunneling conductance g is best accounted for near $V=0$ if $\epsilon_0 = 0$. For larger values of ϵ_0, the agreement between experiment and theory becomes worse, and no value of ϵ_0 which one can choose in the allowed range from 0 to 1 makes the disagreement between the experimental curve and the theoretical curve acceptably small. If ϵ_0 is allowed to approach 1, corresponding to small values of JSN_0, the Shiba-Rusinov curves approach those of the Abrikosov-Gor'kov theory, which are shown in Ref. 4.

Figures 1 and 2 indicate that the impurities introduce a larger number of states into the BCS energy gap than the theory predicts. Several explanations for this are possible. Perhaps the noncommutativity of the spin operators must be taken into account.[13] Only isotropic scattering is treated here or in Ref. 8. Orbital degeneracy, if it is unquenched, may be playing an important role; it is known that this increases the effect of magnetic impurities.[14,15] However, we do not know why the Pb-Mn films obey the theory and the In-Fe films do not.

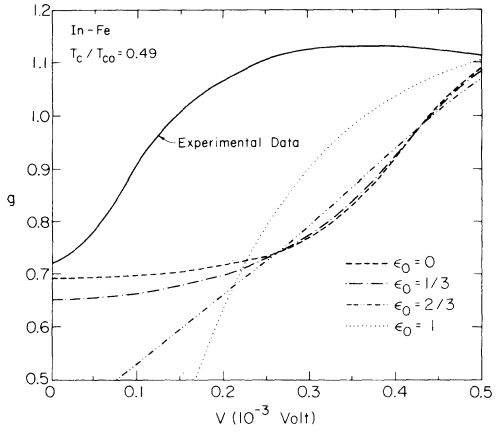

FIG. 1. Experimental and theoretical tunneling curves for a quench-condensed film of indium with 0.86-at.% iron. The parameter ϵ_0 is defined in Eq. (4).

Impurity-impurity interactions would play a role for bulk superconductors with the impurity concentrations of the samples being considered, which are 0.86 at. % for Fig. 1 and 0.18 at. % for Fig. 2. However, in these films the electron mean free path l, estimated[16] from the "typical" normal-state film resistance given by Woolf and Reif, is only about 55 Å. This is much less than a typical distance between nearby impurity atoms in the sample with 0.18-at. % impurities. Interactions between impurity atoms are mediated by the conduction electrons. These interactions are proportional to $e^{-R/l}$, where R is the distance between impurities,[17] and this exponential factor would be very small for that sample. The tunneling curves for the Pb-Mn films, which are in agreement with the theory, are for impurity concentrations of 0.20 and 0.13 at. %. The value of l in these films are estimated[18] to have a typical value of 35 Å, so the interaction between impurity atoms would be even smaller than in the In-Fe films (which have approximately the same average interatomic spacing). However, this conclusion relies on taking the "typical" value of the film resistance, and it is not completely clear from the article of Woolf and Reif or from Woolf's thesis[19] that the same value is in fact typical of the Pb-Mn films and of the In-Fe films.

The tunneling data for the In-Fe films could be easily fitted to the theory if the pair-breaking parameter were an adjustable parameter, rather than being calculated from the measured transition temperature according to Eq. (5). The experimental determination of the transition temperature was made by measuring the electrical resistance of the alloy film. If inhomogeneities are present,

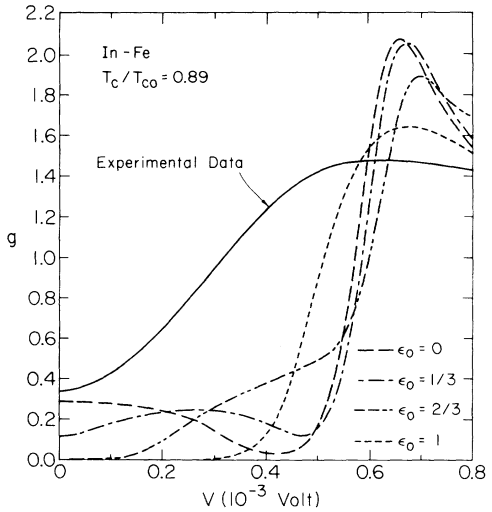

FIG. 2. Experimental and theoretical tunneling curves for a quench-condensed film of indium with 0.18-at.% iron.

the electrical resistance would tend to disappear at a temperature which is higher than the true transition temperature of the alloy; superconducting regions would short-circuit the resistance. On the other hand, the region of the tunneling sample which is near the oxide junction might have a higher-than-average concentration of magnetic impurities. In either of these two cases, the pair-breaking parameter would be larger than the calculated value, and this would explain the discrepancy between the data and the theory. (I am indebted to W. L. McMillan for this suggestion.) However, this explanation seems unlikely, since the samples were made in a manner which is thought to promote great uniformity in composition. Of course, the tunneling barriers in the In-Fe samples may have been faulty.

In summary, the theory of Shiba and Rusinov, which is in good agreement with the tunneling curves for Pb-Mn films, disagrees with those for In-Fe films, possibly because of the noncommutativity of the spin operators or because of orbital degeneracy.

We conclude by making an observation about the analysis of the Pb-Mn data. In the course of calculating the theoretical density of states, one computes the value of the pair-breaking parameter $\alpha = \hbar/\tau$ from the observed transition temperature of the alloy T_c by using the following relation[9]:

$$\ln(T_c/T_{c0}) = \psi(\tfrac{1}{2}) - \psi(\tfrac{1}{2} + \hbar/2\pi kT_c\tau), \quad (5)$$

where ψ is the digamma function. According to the Shiba-Rusinov theory, the spin-flip lifetime τ of the electrons, owing to the impurities, should be given in terms of N_0, ϵ_0, and the impurity concentration n_i by the relation

$$\tau = 2\pi N_0 \hbar / n_i(1 - \epsilon_0^2). \quad (6)$$

In the Shiba-Rusinov theory, $N_0 = mp_F/2\pi^2\hbar^3$, where m is the electron mass and p_F is the Fermi momentum. Thus N_0 is the electronic density of states for one spin direction in the normal state, according to the free-electron model. For a real metal, N_0 should presumably be the band-theory density of states. It is of interest to see whether the values of τ calculated from Eq. (5) for the Pb-Mn films agree with those calculated from Eq. (6). We do this, using Chaba and Nagi's value $\epsilon_0 = 0.55$ and the "observed band-theory density of states" for one spin direction, which has been given by McMillan[20] as 0.276 states/eV atom. Chaba and Nagi do not present their values of τ, but we have found, in repeating their calculations for the Pb-Mn films, that Eq. (5) yields the values $\tau = 1.64\times10^{-12}$ and 2.3×10^{-12} sec for the two samples in question. According to Eq. (6), these values should be 0.82×10^{-12} and 1.26×10^{-12} sec, respectively. Thus the values of τ which are calculated from Eq. (5) disagree with those calculated from Eq. (6). We suggest that this disagreement should be resolved by replacing N_0 in Eq. (6) by $N_0(1+\lambda)$, where λ is McMillan's effective electron-phonon coupling parameter,[20] so that

$$\tau = 2\pi N_0(1+\lambda)\hbar / n_i(1 - \epsilon_0^2). \quad (7)$$

The replacement of N_0 by $N_0(1+\lambda)$ is the usual result of applying strong-coupling theory to superconductors.[21] For lead, $\lambda = 1.12$, according to McMillan,[20] and the resulting values of τ are 1.7×10^{-12} and 2.7×10^{-12} sec for the two samples. A more recent and more reliable value[11] of λ for Pb is 1.55; with this value, Eq. (7) indicates that $\tau = 2.1\times10^{-12}$ and 3.2×10^{-12} sec. For either value of λ, the values of τ calculated from Eq. (7) are in better agreement with those from Eq. (5) than are those from Eq. (6); thus the replacement of N_0 by $N_0(1+\lambda)$ appears to be advisable.

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