Tunneling Study of Impurity Bands in Kondo Superconducting Systems: Cu Alloys Backed by Pb

L. Dumoulin, E. Guyon,* and P. Nedellec
Laboratoire de Physique des Solides,† Université Paris Sud, 91405 Orsay, France
(Received 19 August 1974)

We present tunneling experiments on Cu:X (X stands for Cr, Fe, or Mn) thin alloy films in superconducting proximity with Pb. For cases of Cr and Mn, with Kondo temperatures T_K lower than the critical temperature T_c, we observe an impurity band inside the quasi-BCS gap, in agreement with theoretical predictions. Our results on Cu:Fe ($T_K/T_c \sim 5$) do not show such structure and disagree with theory.

The problem of magnetic impurities in superconductors originally discussed by Abrikosov and Gor'kov (AG)[1] has been theoretically reconsidered to include the Kondo effect.[2] The greater part of the experimental work is devoted to critical temperature T_c measurements, which support this description. Anomalies in the superconducting density of states have also been predicted. Zittartz, Bringer, and Müller-Hartmann (ZBMH)[3] have calculated the density of states at finite concentration c for different alloys characterized by their Kondo temperature T_K. Under certain conditions, an impurity band develops inside the energy gap: At finite c, the wave function of the bound states localized around the impurities overlap and the bound states merge in a band. We present the first (to our knowledge) experimental observation of such localized bands, from tunneling measurements on the normal side of Cu:X-Pb proximity-effect sandwiches (the solute X stands for Mn, Cr, Fe, or Co) with typical results shown in the figures.

Following the pioneering work of Woolf and Reif,[4] several experiments on homogeneous alloys have shown the existence of a density of states in the superconducting gap larger than predicted by AG.

Inducing superconductivity in normal Kondo alloys by proximity effect clearly increases the number of well-studied Kondo-alloy candidates. The previously published tunneling results were done on relatively concentrated alloys and could not resolve any structure[5-7] or were done on systems (Au:Fe-Pb)[8] which are not metallurgically clean. This work follows extensive T_c measurements[9] in the same systems to which we refer for a detailed description of the control measurements on the sandwiches (film thickness d_N and d_S; impurity concentration c; metallurgical controls in particular with respect to the absence of intermetallic diffusion[10]).

The samples are prepared in ultrahigh vacuum ($< 5\times10^{-9}$ Torr during evaporation). We use films of either Mg or Al + 5 at.% Mn as the first normal electrode. The tunneling barriers are formed by glow-discharge oxidation in dry O_2 at low pressure. Each sample consists of four pairs of junctions having the same geometry deposited on a glass plate. The two junctions of a pair are identical and the pairs differ only by the nature or the concentration of impurities in the normal side. There is always also a test Cu-Pb pair of the same d_N. The Cu:Cr and Cu:Fe films are evaporated from a single source and the Cu:Mn films from flash evaporation of small pellets of the alloy (a strong distillation takes place in the evaporation of this alloy). We have checked the excellent homogeneity of the thickness and concentration of the films on single-film test samples. In particular, the Kondo resistive behavior of the alloy films is similar to that of bulk material and is used to determine c.

Our analysis of T_c's in proximity systems was based on a generalization by Kaiser and Zuckermann (KZ)[11] of the McMillan tunneling model of proximity which included the effect of magnetic impurities in the normal-side film. The model implies a constant order parameter in the film and long mean free paths. These conditions are well satisfied here. The Cu:X film thicknesses range from 140 to 750 Å and the electronic mean free path is always larger than d_N. Under these conditions, we were able to interpret the T_c data and in particular to measure the change of depairing as the ratio T_c/T_K varied ($T_K \approx 1000$, 30, 1, and 0.01°K for Co, Fe, Cr, and Mn in Cu, respectively). The McMillan model has also been used successfully in the tunneling experiments of Adkins and Kington[12] on Cu-Pb. Our tunneling results on the same system indicate a similar agree-

ment. The transmission coefficient at the normal-superconducting interface introduced in the McMillan model has a larger value, in the present measurements as well as in our T_c ones, than in the Adkins-Kington case, probably because our samples are prepared in better vacuum.

The density of states at low energy is characterized at any given temperature by the energy V_1 [such that the conductance $D(V_1)$ is equal to its normal value $D_N = 1$] and by the conductance at zero bias, D_0. A typical experiment on a $d_N = 240$-Å Cu film backed by a 2000-Å thick Pb film indicates the following values: $V_1 = 0.800 \pm 0.010$ mV and $1/D_0 \sim 175$ to 200 at the lowest temperature of our experiments, $T = 0.95$°K. This result is very close to the case of a BCS superconductor: For $\Delta_0 = 0.800$ mV and $T_c = \Delta_0/1.76k_B = 5.3$°K, one expects $1/D_0 = 180$. In the following analysis, we assume that a thin and clean Cu film in proximity behaves as a homogeneous BCS superconductor with a gap Δ obtained from the value of V_1 at the lowest temperature.[13] When dilute impurities are introduced in films of the same thickness prepared under the same conditions, we assume that they experience a characteristic pairing energy equal to the value Δ_0 obtained at zero concentration. We also assume that the magnetic properties (in particular the value of T_K) of the Cu:X alloys are retained.

The tunneling data, given in the figures, indicate structures below the gap Δ_0 in the Cu:Cr and Cu:Mn cases. Before analyzing them, we mention the different tests performed on the junctions as this is the critical part of the experiment: Junctions prepared under similar conditions have resistance of the same order (within 50%). The relative increase of tunneling resistance from room to low temperature was the same (within ±2%) for all "good" junctions. Good junctions on thin Cu-Pb sandwiches have a very low zero-bias conductance, as mentioned above. Finally we have an excellent reproducibility over two junctions of a pair, over different runs when similar proximity samples are prepared, and when using the two different types of barriers. This point also indicates that the effects reported are not due to the barrier or to the first electrode. We estimate the nontunneling current of the good junctions (over 75% of the junctions prepared) to be less than a few percent of D_N.

Cu:Cr-Pb: The Cr concentration ranged between 25 and 300 ppm; the thicknesses were kept constant in all the experiments: $d_N = 240 \pm 10$ Å; $d_S = 2000$ Å. The variation of conductance (Fig. 1)

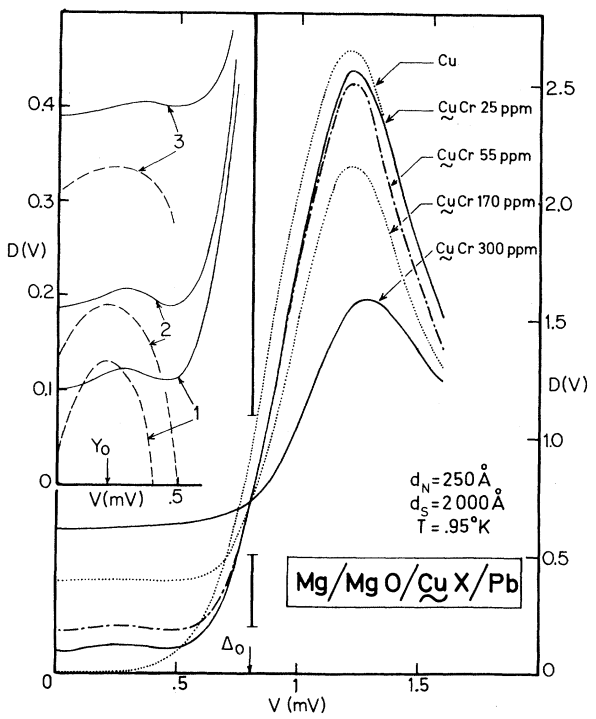

FIG. 1. Experimental normalized conductance of Cu:Cr-Pb sandwiches of variable Cr concentration. Δ_0 is the quasi-BCS gap measured on a Cu-Pb test sample. The inset uses an extended vertical scale. y_0 is the energy of the one-particle bound state. The dashed lines give the corresponding band calculated from the ZBMH model. Curve 1, $c = 25$ ppm, $\bar{c} = 0.033$; curve 2, $c = 55$ ppm, $\bar{c} = 0.070$; curve 3, $c = 170$ ppm, $\bar{c} = 0.225$, where $\bar{c} = c/2\pi N_0 \Delta_0$ with $N_0 = 0.15$ states per atom eV Cu spin.

shows the following behavior: (1) The degree of "gaplessness" (measured by D_0) increases regularly with impurity concentration. (2) The conductances have a maximum inside the gap at an energy $V_M \sim 0.25$ to 0.3 mV between two minima at $V = 0$ and V_m. The width of the structure is also controlled by thermal smearing (~0.4 mV). (3) The voltage V_1, which characterizes the rapid increase of the density of states, moves towards larger energies as c increases. The effect is much larger than that given by the uncertainty in d_N. (4) The variation of shape when c increases suggests a broadening of the band. For larger concentrations, the structure disappears.

We must show that the structures reflect a bulk behavior: (1) No structure is observed in isolated Cu:Cr films[14] prepared in similar conditions on normal tunneling barriers. (2) The tunneling structures on the Cu:Cr-Pb sandwiches disappear when superconductivity is quenched by a magnetic field. (3) They also disappear when we

decrease the effective gap Δ_0 by increasing the thickness of the Cu:X film or when the concentration is increased. This feature is difficult to understand in terms of a barrier effect but agrees with the ZBMH model. (4) We have prepared a sandwich Cu(100 Å)-Cu:Cr(150 Å, 50 ppm)-Pb. The structure has the same shape as on the Cu :Cr(250 Å, 50 ppm)-Pb samples but the amplitude is reduced by typically a factor of 1.5 to 2.5. Such three-layer samples can be useful in studying the range of magnetic effects in tunneling and possibly size effects in the Kondo problem.

Points 2 and 3, which differ markedly from the AG predictions, are in qualitative agreement with those of ZBMH. A quantitative comparison can also be made using the parameters $T_K = 1$°K, $T_c = 5.3$°K. With this set of parameters, a one-impurity bound state is predicted at $y_0 = 0.27\Delta_0 \sim 0.215$ mV. Using form (12a) of Ref. 3, valid at low concentration, we calculated quantitatively *without any adjustable parameter* the predicted band expected at finite concentration. The agreement is satisfactory for the lowest concentration, considering the approximation involved.[15] At higher concentrations, exact calculations are needed but at this temperature interactions between the Cr. impurities should be considered.

When T is increased, the inflection in the curve washes out beyond a value dependent upon c and $k_B T/\Delta_0$. This effect can explain in part why such a structure has not been observed in previous works. This takes place above 1.3°K for the c = 25-ppm sample. We can still see the anomaly with respect to the Cu-Pb case, using a first superconducting Al electrode ($T_c = 1.5$°K) but, in this case, a deconvolution of the conductance curve is needed to eliminate the effect of the Al. Using a thinner $d_N = 140$ Å ($\Delta_0 = 1$ mV) film of the same concentration, the structure with a first normal electrode disappears only at 1.7°K. On this sample at 0.95°K the decrease of conductance at V_m is sharp and shows more clearly the upper gap above the bound-state band.

Cu:Fe-Pb: The experimental conditions are the same as the previous case. The concentration ranged from 30 to 300 ppm. The Cu:Fe case is interesting for a comparison as the value of $T_K \sim 30$°K is larger than T_c. Moreover the impurity spin $S = \frac{3}{2}$ is the same as in Cu:Cr. The value of $|\ln T_c/T_K|$ being nearly the same, the ZBMH predicts the same effect in both cases. However, (1) we never observed structures in the gap. (2) For a given value of c, the zero-bias conductance is lower than in the Cu:Cr case. (3) The decrease with V of conductance below the gap edge is slower and, at high concentrations, the increase of conductance at low energy is faster. (4) V_1 is lower than the value in Cu-Pb. It decreases as c increases.

These points are illustrated in Fig. 2. The behavior is reminiscent of the AG one, although in the Cu:Fe case we are farther from the free-spin situation. As pointed out by ZBMH, when the bound-state band is very close to the gap edge, the shape is similar to the AG case.

The ZBMH model is certainly less valid below T_K. In our previous T_c work, we mentioned a disagreement with theory in Cu:Co-Pb sandwiches (in Cu:Co, $T_K \sim 10^3$ °K) but not in Cu:Fe-Pb. The rapid deterioration of the agreement with theory just below T_K observed in superconducting-tunneling experiments is remarkable. Such measurements may provide a sensitive test of the occurrence of strong-coupling effects in Kondo systems.

Cu:Mn-Pb: Preliminary data with concentrations $c = 50$ and 500 ppm were obtained (Fig. 2).

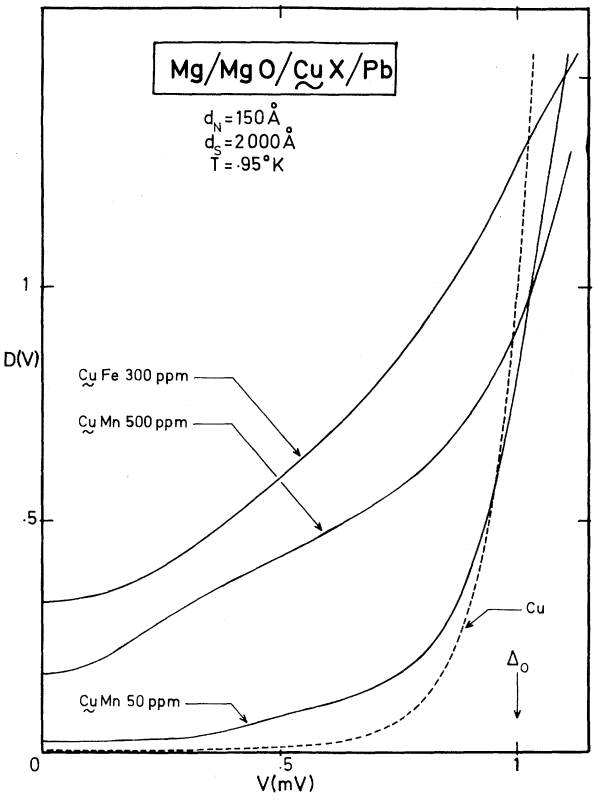

FIG. 2. Tunneling conductance of Cu:Fe-Pb and Cu:Mn-Pb. The gap Δ_0 was obtained from the Cu-Pb test sample.

Here $d_N = 150$ Å and $\Delta_0 = 1$ mV. The behavior is different from the AG case and we see the existence of an inflection in the conductance whose energy decreases as c increases. We tentatively relate the structure to the lower edge of an impurity band which broadens when c becomes larger. Let us also note that the voltage V_1 is larger than the Cu-Pb value. Using $T_K = 0.01$°K and $S = \frac{5}{2}$ for Mn in Cu, we get, from the ZBMH model, an impurity-band state centered at $y_0 = 0.57\Delta_0 \simeq 0.57$ mV, in qualitative agreement with these results. We also studied the upper limit of $k_B T/\Delta_0$ beyond which the inflection structure disappears. For a thicker film $d_N = 240$ Å, this takes place above $T = 0.95$°K.

We will develop these studies to lower temperatures to obtain a better resolution of the structures. It will also become possible to decrease the value of Δ_0 and of the ratio T_c/T_K with sufficient resolution.

We thank J. P. Burger, K. Maki, P. Monod, and R. Orbach for useful discussions and E. Müller-Hartmann for detailed information on his work.

*Also at Physics Department, University of California, Los Angeles, Los Angeles, Calif. 90024.

†Laboratoire Associé au Centre National de la Recherche Scientifique.

[1]A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. 39, 781 (1960) [Sov. Phys. JETP 12, 1243 (1961)].

[2]E. Müller-Hartmann and J. Zittartz, Z. Phys. 232, 11 (1970).

[3]J. Zittartz, A. Bringer, and E. Müller-Hartmann, Solid State Commun. 10, 513 (1972).

[4]M. A. Woolf and F. Reif, Phys. Rev. 137, A557 (1965).

[5]See, for example, A. S. Edelstein, Phys. Rev. Lett. 19, 1184 (1967).

[6]J. J. Hauser, D. R. Hamann, and G. W. Kammlott, Phys. Rev. B 3, 2211 (1971).

[7]E. E. H. Shin, in *Proceedings of the Twelfth International Conference on Low-Temperature Physics, Kyoto, Japan, 1970,* edited by E. Kanda (Keigaku Publishing Co., Tokyo, 1971), p. 201.

[8]T. W. Mihalisin, D. P. Snowden, and P. M. Chaikin, Bull. Amer. Phys. Soc. 13, 1668 (1968).

[9]L. Dumoulin, E. Guyon, and P. Nedellec, J. Phys. (Paris) 34, 1021 (1973).

[10]In particular, no aging effects at room temperature for several-day periods were found. The tunneling structures were unchanged after such cycling to room temperature.

[11]W. L. McMillan, Phys. Rev. 175, 537 (1968); A. B. Kaiser and M. J. Zuckermann, Phys. Rev. B 1, 229 (1969).

[12]C. J. Adkins and B. W. Kington, Phys. Rev. 177, 777 (1969).

[13]This is a rather strong approximation also done in Ref. 12 and deviations from the BCS case take place at energies of the order of the bulk lead gap, ~1.4 mV. However, we are concerned here with structure at lower energies below Δ_0. Calculations involving the effect of the bound-state band in the KZ proximity model are in progress.

[14]G. I. Rochlin, L. Dumoulin, and E. Guyon, Solid State Commun. 8, 287 (1970).

[15]The quantitative agreement in the nonhomogeneous system is not too surprising as the value $T_c = 5.3$°K is not far from the bulk T_c of the sandwich, $\simeq 6.5$ K. In addition, the predicted position of the bound states does not vary rapidly with the choice of T_c/T_K.