Evidence for Quasibound States in a Kondo Superconductor

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(Received 16 August 1968)

Contrary to the predictions of the Abrikosov-Gor'kov theory, it is found that a Kondo superconductor (Ce in La) is gapless even at very low concentrations and temperatures. At low impurity (Ce) concentrations in La, the number of states in the gap as determined from electron tunneling measurements is proportional to the Ce concentration. These states are likely to be quasibound states which result from electron scattering from the impurities.

IN a previous paper,[1] results were reported of the first electron tunneling measurements on a Kondo superconductor, a system which exhibits a resistivity minimum in its normal state[2,3] and is a superconductor at lower temperatures. The system that was investigated was Ce in La. The conductance curves indicated that there were many more states at low energy than predicted by the Abrikosov-Gor'kov[4] (AG) theory of gapless superconductivity. Sugawara and Eguchi[5] found AG theory inadequate for fitting their measurements of H_{c2} and T_c for this alloy system. In particular, they found that T_c decreased more rapidly with impurity concentration than predicted by AG. This is consistent with the prediction of Griffin[6] in the case of antiferromagnetic resonant scattering.

It is likely that AG theory is inadequate because of their use of the first Born approximation. The normal-state scattering in this case is independent of energy. Kondo[7] treated the problem in the second Born approximation and found that the scattering probability is singular at the Fermi surface. The superconducting properties are likely to be strongly affected by such a singularity. Several authors[6,8–11] have extended AG theory to include resonant scattering but none of these extensions discusses spatial variations of the order parameter. AG also neglected spin-spin interactions. Susceptibility measurements[12] on Ce in La indicate the validity of the second approximation.

In this paper, direct microscopic evidence is presented which shows for the first time that a Kondo superconductor is gapless even at very low impurity concentrations and temperatures. It is found that the low-temperature zero-energy density of states at low Ce concentrations is proportional to the Ce concentration. This contrasts with the prediction of AG, that there is an energy gap at zero temperature for $n \leq 0.9 n_{cr}$, where n is the concentration of impurities in at.%, and n_{cr} is the concentration which destroys superconductivity. These additional states and the fact that their number is proportional to the Ce concentration provide evidence that quasibound-electron states have been formed.

The method of sample preparation and measuring technique are the same as previously described.[1,13] In general, both the α and β phases of La were present. It is believed that this is not too serious a difficulty for the reasons discussed in Ref. 1. The impurity concentration in the films has been determined by x-ray fluorescence to be equal to within 20% to that of the starting material used in the evaporation. Impurity inhomogeneity was ruled out as an explanation of the effect by determining that successive films evaporated from the same source had nearly the same T_c's and impurity concentration. The latter was determined by x-ray fluorescence. Electron microprobe analysis indicates that the upper half and lower half of the films have the same composition to within 20%.

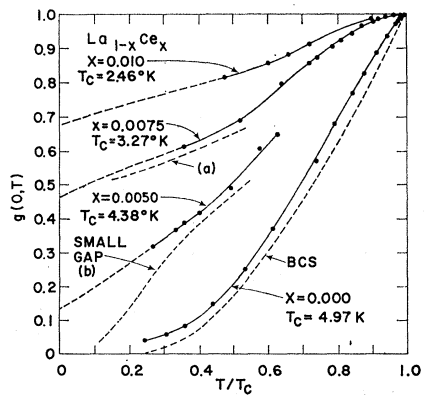

FIG. 1. Plot of the normalized zero-voltage conductance versus reduced temperature for samples containing 0–1.0-at.% Ce. The dashed lines represent theoretical predictions obtained using the BCS density of states and the density of states (a) and (b) shown in Fig. 2.

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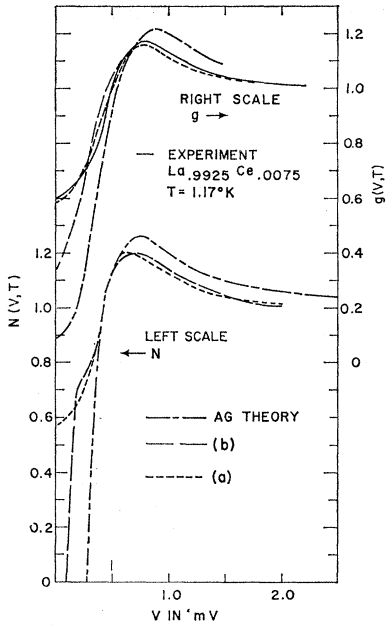

FIG. 2. Lower curves: several trial densities of states. Upper curves: normalized conductances computed from these densities of states using Eq. (1). The solid line represents the experimental results.

The normalized conductance $g(E,T)$ and the density of states $N(E,T)$ are related via

$$g(E,T)=\frac{dI/dV}{(dI/dV)_{\text{normal}}}$$

$$=\frac{2.90}{T}\int_{-\infty}^{\infty}N(E',T)\cosh^{-2}\left(5.80\frac{E-E'}{T}\right)dE', \quad (1)$$

where the energy E is expressed in meV, and T is the temperature in °K. Equation (1) has the property that in the limit $T\rightarrow 0$, $g(E,T)\rightarrow N(E,T)$. This property is utilized in Fig. 1 to obtain estimates of $N(0,0)$. In Fig. 1, $g(0,T)$ is plotted as a function of T/T_c for several samples containing 0–1-at.% Ce. The values of g are normalized using the large voltage-limiting conductance.[13] The temperature at which $g(0,T)$ is constant was used at T_c. This T_c is sometimes a few tenths of a degree less than the resistive T_c of the film. If the density of states is a weak function of temperature, one may extrapolate the data to $T/T_c=0$ to obtain an estimate of $N(0,0)$. Alternatively, this procedure can be considered to yield an estimate of $N(0,1.2)$. Since a linear interpolation neglects the upward curvature, this estimate is probably a lower bound. The data for the undoped sample extrapolate to zero, i.e., $N(0,0)=0$, and there is an energy gap. The data for the doped samples extrapolate to nonzero values. There is no energy gap.

Figure 2 shows several trial $N(E, 1.18)$'s and the resulting $g(E, 1.18)$'s that were obtained using Eq. (1). The density of states (a), which is an estimate of the correct $N(E, 1.18)$, was found by optimizing the agreement between trial g's and the experimental curve for a sample containing 0.75% Ce. This N is gapless. Further, $g(0,T)$ was calculated from (a) and is plotted in Fig. 1. It agrees with the data for the 0.75-at.% Ce sample both in magnitude and curvature. In Fig. 2, one sees that the N representing AG theory gives a very poor fit to the data. The density of states (b) was used to test whether the data could be fitted using a very small energy gap. The conductance curve found from (b) does not agree with experiment. The conductance $g(0,T)$ was calculated from (b) and is plotted in Fig. 1. It extrapolates to zero as it should, and has the opposite curvature for $0.2<T/T_c<0.5$ from the experimental data. It does not fit the $g(0,T)$ data for the 0.75-at.% Ce sample.

Figure 3(a) shows a plot of $g(0, 1.20)$ for several samples versus T_c/T_{cp}, where T_c is the transition temperature of the sample determined by the method described above and $T_{cp}=5.0$°K is the tunneling transition temperature of the pure material. The agreement with the predictions of AG also shown in the figure is poor. Because the amount of thermal smearing is small at this temperature, these samples are gapless. This property is illustrated more clearly in Fig. 3(b), where $N(0,T)$ is plotted versus T_c/T_{cp}. The values were obtained by the methods of extrapolating $g(0,T)$ and of curve fitting $g(E, 1.2)$ using Eq. (1) as described above. The first method should be a lower bound on $N(0,1.2)$ and the second method an approximate upper bound. The initial departure of T_c/T_{cp} from unity is predicted[4] to be proportional to n, and experiments on this system[5] and others[14] bear this out. For the tunneling T_c of the films $d(T_c/T_{cp})=(0.30\pm0.06)dn$. Sugawara and Eguchi[5] obtained a value of 0.250. Using the number obtained for the films and the data shown in Fig. 3(b), one finds $N(0,1.2)=(0.51\pm0.17)n$ for small n. This is in great contrast to the prediction of AG theory which is discussed above and shown in Fig. 3(b).

The fact that the number of states in the gap is proportional to the Ce concentration suggests that one is observing a single-impurity effect. This leads one to consider the possibility that the density of states is a function of position. One might suppose that each impurity is surrounded by a radius r_0 where the energy gap is zero and the density of states has approximately its normal-state value. Since approximately 2% Ce is sufficient to fill in all the states, one can estimate r_0 from

$$0.02\times\tfrac{4}{3}\pi(r_0)^3=\text{vol/atom}. \quad (2)$$

Using 3.74×10^{-23} cm^3 as the volume per atom in the solid, one finds $r_0=7.6$ Å.

Martin and Tinkham[15] in their infrared-absorption study of field-induced gaplessness have seen similar large departures from AG. They believe these de-

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partures are due to difficulties in aligning the field parallel to the film. No such explanation is applicable here.

The value of the Kondo temperature T_K is not yet well established for Ce in La. Resistivity measurements[3] on high-concentration samples gave a value of 10°K but Sugawara[16] believes T_K is considerably lower. Suppose[17] $T_K > T_c$. In this case the ground-state theory of Hone[11] predicts the formation of bound or quasibound states near the impurities. This ground-state theory is not adequate for determining the density of states. The discrete levels within the energy gap predicted by Fowler and Maki[9] for $T_K > T_c$ appear to be rather different from the present experimental results, which show a continuous distribution of states. Soda *et al.*[8] discuss how the sharp levels broaden with increasing impurity concentration for $T_K < T_c$. Their arguments seem equally applicable for $T_K > T_c$. Another possible explanation for the difference is that Fowler and Maki employ the BCS density of states in their analysis. This should be correct at sufficiently dilute concentrations if the density of states were homogeneous. However, this might not be correct even at very dilute concentrations if the density of states were a function of position.

By the above interpretation, the density of states is a function of position and a quasibound state is formed near each impurity. The size of this state is 7.6 Å by the estimate made above. This is much smaller than the supposed size of the Kondo state when the metal is normal, which is of order $\hbar v_F/kT_K \approx 10^4$ Å, where v_F is the Fermi velocity. This small size is not unreasonable, since the quasibound state competes against the formation of Cooper pairs. The energy gained by forming the quasibound Kondo state is less in the superconductor because superconducting pairing energy is lost.[11]

In summary, these experiments provide evidence for the inadequacy of the first Born approximation for treating a Kondo superconductor. Results of specific-heat measurements[18] at lower reduced temperatures on bulk samples are in agreement with the gaplessness reported here and yield approximately the same values for $N(0,1.2)$. Hence the tunneling data have been substantiated by another technique and may be considered to be well established. The fact that $N(0,1.2)$ is proportional to impurity concentration suggests it is a single-impurity effect. Since this system also exhibits a Kondo effect, it is extremely tempting to consider the states $N(0,1.2)$ as representing quasibound states located near each Kondo impurity. If this interpretation is correct, the tunneling measurements have provided the first direct microscopic observation of such states. Thermal conductivity experiments are in progress to determine the spatial extent of the gapless region. If these experiments show that the gapless region is localized around each impurity, the result will support the interpretation presented here.

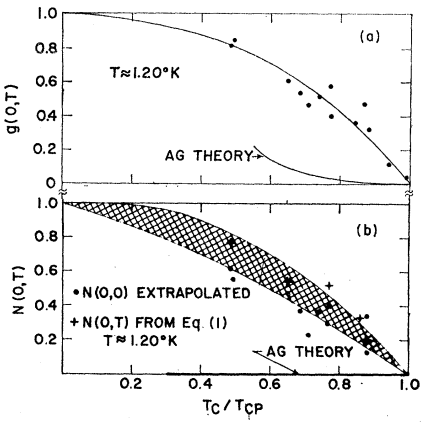

FIG. 3. (a) Plot of $g(0,T)$ versus T_c/T_{cp} for several samples at the lowest available temperature $T \simeq 1.2$°K. $T_{cp} = 5.0$°K. The prediction of AG theory is shown. (b) Plot of $N(0,T)$ versus T_c/T_{cp} for several samples. The data were obtained by extrapolation as illustrated in Fig. 1 or by curve fitting using Eq. (1). The values should be approximately equal to the zero-temperature values. The prediction of AG theory is shown. The correct values for $N(0,0)$ are believed to lie in the shaded area.

The author would like to thank P. C. Kwok and T. D. Schultz for several helpful discussions. The alloys used in making the evaporations were prepared by R. J. Gambino. G. J. Padilla and W. G. Thorn, Jr., provided technical assistance.

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[17] Even if T_K is lower than T_c, this result would not modify the basic idea that the effects reported here are due to the Kondo state. Kondo-state properties (Refs. 2, 3, 5, 12) have been observed up to 10°K.

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