ENERGY GAP IN SUPERCONDUCTORS CONTAINING PARAMAGNETIC IMPURITIES*

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The addition of paramagnetic impurities to a superconductor results in a rapid linear decrease of its superconducting transition temperature T_S with increasing impurity concentration.[1,2] Theoretical estimates[3] and systematic experiments with rare earth ions[1] both indicate that the effect is due to exchange (rather than magnetic-dipole) interaction between the paramagnetic impurities and the conduction electrons. Alternative theories based on this mechanism have been proposed[3-5] and suggest that the presence of spin-dependent interactions affecting the Bardeen-Cooper-Schrieffer (BCS) pairs may give rise to superconductors with unusual properties. It seemed, therefore, of interest to study their energy gap and density of states. The present note reports preliminary results of such an investigation by tunneling techniques.[6] Our experiments indicate quite unexpectedly that, for paramagnetic impurity concentrations greater than a relatively small value, the superconductor no longer exhibits any sign of an energy gap in its tunneling characteristics, although resistance measurements show that it has a well-defined transition temperature T_S in accord with the expected concentration dependence.

The experiments were performed on "quenched" alloy films evaporated onto substrates maintained at 4°K. This method yields samples in the form of films convenient for tunneling studies and has the advantage of allowing great flexibility in the choice of alloy components since they need not necessarily be mutually soluble. The superconducting transition temperature T_S of such films, including the alloys used in the present experiments, has been studied by the Göttingen group.[2] They find that T_S decreases rapidly with increasing impurity concentration just as it does in similar experiments on bulk samples.[1] Our technique for preparing the alloy films is similar to that used at Göttingen.[2] The desired amount of paramagnetic impurity is added to the pure metal either by melting the two metals together, or by evaporating the impurity metal onto a thin foil of the pure metal. The resulting mixture is repeatedly folded and rolled until one obtains a foil in which the two components are homogeneously distributed. This foil is then cut into pellets about 1 mm in size. To form the tunneling junction, an Al (or Sn) film is first evaporated onto a thin quartz crystal and is allowed to oxidize. The quartz is then mounted inside the vacuum space of a metal Dewar and cooled by conduction to 4.2°K. Finally, the previously prepared small pellets are successively evaporated in situ onto this substrate. Since diffusion at this low temperature is negligible and since each pellet contributes only about 10 Å to the alloy film thickness, the resulting film is a microscopically homogeneous alloy (irrespective of the mutual solubility of the constituents) as long as the temperature remains low enough to preserve the quenched state. The actual experiment consists of measuring the tunneling current of this junction as a function of the applied voltage, and of measuring the dc resistance of the alloy film.

Figure 1 summarizes results obtained with quenched In films containing Fe impurities. The transition temperature T_S shows the expected linear decrease with increasing Fe concentration c. The energy gap, measured at 1°K, at first also decreases. In the concentration range $0.2 < c \lesssim 0.8$ atomic percent, the characteristics for tunneling into Al no longer exhibit a negative resistance region, although they still display some

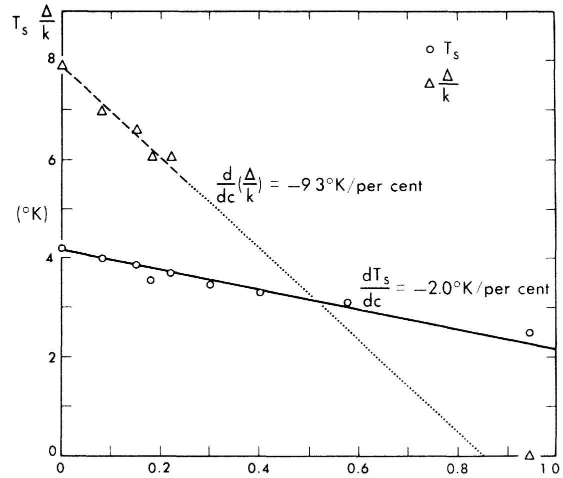

FIG. 1. Transition temperature T_S and energy gap (2Δ) of quenched In films as a function of Fe impurity concentration c. See text for discussion of transition region $0.2 < c \lesssim 0.8$ percent. (Note: T_S for pure quenched In is higher than for bulk In; see Opitz.[2])

curvature which decreases as c increases. The curves suggest a density of states with broadened maxima; these appear to define a gap which continues to decrease (roughly following the dotted line of Fig. 1) while their breadth contributes an increasing number of states within the gap. Finally, for $c \gtrsim 0.8$ percent, the tunneling curves give no evidence for an energy gap in the alloy, i.e., they are essentially straight except for the slight curvature due to the superconducting Al. Since this behavior was surprising, some additional experiments were performed as checks.

(a) Measurements were made on a different alloy system. A quenched Pb film containing 2 atomic percent of Gd had $T_S = 3°\text{K}$, but showed no gap. Pure quenched Pb films, of course, give the expected gap in the tunneling characteristics.

(b) Experiments were done on similarly prepared quenched alloy films containing nonparamagnetic impurities. A sample of In containing 0.5% of Zn and a sample of Pb containing a high concentration (10%) of Tl both showed well-defined energy gaps.

(c) To verify further that the disordered quenched state leads to no unusual properties, we investigated a pure quenched Bi film. Such films become superconducting with $T_S = 6°\text{K}$,[7] although ordinary bulk Bi is not a superconductor. The film showed a well-defined energy gap of 2.15 mV.

(d) A related experiment involving paramagnetic atoms was carried out. Tunneling measurements were made on a pure quenched In film about 500Å thick and gave the usual negative resistance characteristic. When a layer of Fe, about 3% as thick, was subsequently evaporated at 1°K onto the back of the In film (thus forming a sandwich-type superconductor[8]), the negative resistance region disappeared and the tunneling curve became nearly straight; T_S decreased by 0.2°K in the process.

The present experiments thus appear to indicate the disappearance of the energy gap in superconductors containing a sufficient concentration of paramagnetic impurities.[9] They seem to give further evidence that effects, such as the Knight shift, involving spin-dependent interactions of conduction electrons in superconductors are theoretically not well understood.[10] The conclusions of one set of theories[3,4] are inconsistent with our results as well as with heat capacity and critical field measurements.[11] Another calculation[5] does indeed predict the disappearance of the energy gap for a paramagnetic impurity concentration greater than 90% of that required to suppress superconductivity entirely. But since the concentrations used by us have been considerably smaller and since this theory has also been criticized on other grounds,[12] it is doubtful whether it is relevant for the interpretation of the present results.

Experiments are under way to investigate in greater detail the energy gap and density of states of different superconductors with paramagnetic atoms as impurities or in sandwich arrangements. Studies in external magnetic fields and by far-infrared techniques are also contemplated.

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[9] The experimental results possibly might also be explained if the alloy film broke up into distinct normal and superconducting regions, both contributing independently to the observed tunnel current. But such an interpretation of the data seems unlikely, particularly in view of the experimental checks (b) and (d) mentioned above. The impurity concentrations also are too low to expect any ferromagnetic domain formation. [There also is evidence against such domain formation at higher concentrations: N. E. Phillips and B. T. Matthias, Phys. Rev. 121, 105 (1961)].

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