# Effect of Paramagnetic Atoms on the Energy Gap of Superconductors*

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The presence of paramagnetic impurities in a superconductor introduces spin-dependent interactions which are expected to influence appreciably the correlations between superconducting electrons. Indeed, such impurities are known to have pronounced effects on the observed transition temperature $T_s$ of the metal.[1,2] More recent experiments[3] have also provided evidence that, if the impurity concentration is sufficiently high, such a superconducting metal does not exhibit a well-defined energy gap even though it has zero resistance and a definite transition temperature. The theoretical description of the situation is of considerable interest, but more difficult than that of ordinary nonmagnetic impurities. Several different theories have been proposed. The following paragraphs give a brief review of the present experimental situation.

Most of our experiments have been performed on quenched thin film samples evaporated *in situ* on to quartz substrates at 4°K. Two kinds of measurements can be made on these samples: (a) The dc electrical resistivity of the sample film can be measured to determine the superconducting transition temperature and (b) the tunneling current across a dielectric junction into a reference metal can be measured to determine the energy gap or density of states. Two types of samples have been studied:

(1) Samples of superconducting films containing small amounts of paramagnetic impurities. The advantage of the quenching technique in this case is that good homogeneous film samples can be prepared readily without the requirement of mutual equilibrium solubility of the alloy components.

(2) Samples of pure superconducting films upon whose back surface (i.e., the side opposite the tunneling junction) there is superimposed a film of pure paramagnetic metal. Although the pure superconducting films have been deposited at room temperature in some cases, the paramagnetic films have always been evaporated afterwards *in situ* at 1°K. The advantage of this procedure is that diffusion of the paramagnetic atoms into the pure metal can then be pretty well ruled out.

The superconducting transition temperature $T_s$ of our quenched alloy samples shows the usual rapid linear decrease with increasing impurity concentration $c$ as is found for most bulk alloys.[1] This is in agreement with the observations on thin films of the Göttingen group.[2] Experiments on superconducting lanthanum films containing Gd impurities[4] have also verified that the effect of the Gd impurities, measured by $dT_s/dc$, is the same in such films regardless of whether they are quenched or annealed.

Some experimental details and preliminary results have been reported in an earlier publication.[3] The main alloy system investigated in this work was In containing small concentrations of Fe impurities. Here the data show an initial linear decrease of the energy gap with increasing impurity concentration $c$, this decrease being more rapid than that of the transition temperature $T_s$. At concentrations larger than $c \approx 0.2$ at. %, the tunneling curves no longer indicate the presence of a well-defined energy gap, but suggest an increasing number of states within the gap. Finally, when the concentration $c$ reaches approximately 0.8%, the tunneling curves are essentially straight as though the gap in the impure superconductor had disappeared entirely. Nevertheless, electrical resistivity measurements show that the sample is still superconducting with a transition temperature of about 2.2°K. Indeed, it would require a concentration of about 1.7% to reduce $T_s$ to zero. Measurements on lead containing Gd impurities also showed no noticeable energy gap in the tunneling characteristics despite superconducting behavior with negligible resistance and well-defined transition temperature.

A phenomenological description of the data (which has some theoretical justification in terms of a reduced quasi-particle lifetime $\tau$) can be obtained by considering the density of states $\sigma(\epsilon)$ of the impure superconductor to result from an ordinary BCS density of states where each quasi-particle energy level $\epsilon$

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[1] B. T. Matthias, H. Suhl, and E. Corenzwit, Phys. Rev. Letters **1**, 93 (1958); J. Phys. Chem. Solids **13**, 156 (1960).
[2] See, for example, K. Schwidtal, Z. Physik **158**, 563 (1960).
[3] F. Reif and M. A. Woolf, Phys. Rev. Letters **9**, 315 (1962).
[4] R. Hilsch, G. v. Minnigerode, and K. Schwidtal, *Reprint Program of the Eighth International Congress on Low Temperature Physics* (Butterworths Scientific Publications Ltd., London, 1962), p. 117.

is broadened by a Lorentzian of width $\gamma = \tau^{-1}$. That is

$$\sigma(\epsilon) \propto \left(\int_{-\infty}^{-\Delta} + \int_{\Delta}^{\infty}\right) \frac{\gamma/\pi}{(\epsilon - \epsilon_0)^2 + \gamma^2} \frac{|\epsilon_0| d\epsilon_0}{(\epsilon_0^2 - \Delta^2)^{\frac{1}{2}}}$$

$$= \frac{1}{\sqrt{2}b} [\gamma(b-a)^{\frac{1}{2}} + |\epsilon|(b+a)^{\frac{1}{2}}], \qquad (1)$$

where $a \equiv (\epsilon^2 - \Delta^2 - \gamma^2)$, $b \equiv (a^2 + 4\gamma^2\epsilon^2)^{\frac{1}{2}}$, and $2\Delta$ is the full energy gap of the superconductor. One can try to represent the tunneling data by first correcting for the broadening caused by the finite temperature and then fitting the data with suitable choices of the two parameters $\Delta$ and $\gamma$. Our actual data on these alloys have, up to now, not been sufficiently accurate to warrant detailed quantitative comparisons with (1). It can be said, however, that the alloys which show no measurable gap must be characterized by $\Delta$ less than 20% that of the pure metal value $\Delta_0$, or by $\gamma$ such that $\gamma/\Delta > 1$.

Quenched alloy films containing *non*paramagnetic impurities behave like ordinary superconductors and confirm that the effects observed in the present experiments are due to the spin-dependent properties of the impurities. Additional experiments involving layers of paramagnetic metals superimposed upon pure superconducting films are of interest intrinsically; they also provide a check that the effects observed in the alloy samples are not due to inhomogeneities. In the first experiments of this kind, the tunneling characteristic of a 500-Å-thick pure In film was found to become nearly straight when a 15-Å-thick layer of Fe was evaporated on its back surface. More recent experiments have used Mn as the backing material since it has the advantage of not being ferromagnetic. It is found that very thin layers of Mn cause a remarkably large amount of broadening of the observed density of states in the superconductor.[5] For example, only 15 Å of Mn quench-evaporated onto a 3000-Å annealed Sn film yield a density of states curve whose best fit to (1) is with $\Delta/\Delta_0 = 0.8$ and $\gamma/\Delta_0 = 0.4$. (The transition temperature is lowered by 0.7°K in this case.) Similar effects are found when quenched Sn or Pb films are backed by Mn; and in all cases no further effect on the density of states is found when the thickness of the superimposed Mn is increased beyond that at which the marked broadening first appears.[6] It has been found that 5000 Å is the limiting thickness of Sn above which the Mn no longer has this pronounced effect; at this Sn thickness, as much as 100 Å of Mn produces only a small broadening.

All these experiments are still rather exploratory in nature and need to be made more quantitative. We are now working on experiments designed to explore in detail the actual density of states in carefully chosen superconducting samples containing paramagnetic atoms. In these experiments we measure directly the derivative of the tunneling current against a normal reference metal at the lowest accessible temperature (0.3°K, if necessary). After numerically correcting for the remaining temperature broadening (by the Fourier convolution theorem or an iteration procedure), these data should yield directly the density of states of the superconductor and can then be compared with an expression of the type (1).

The various theories dealing with superconductors containing paramagnetic impurities all focus attention on the exchange interaction between the paramagnetic atoms and the conduction electrons. The work of Abrikosov and Gorkov[7] treats the case of impurities with static randomly oriented spins and arrives at the remarkable conclusion that, in the region where $c > c'$ (where $c'$ is a concentration about 90% of that necessary to suppress superconductivity entirely) a well-defined energy gap no longer exists. Earlier criticisms of this work[8] have now been withdrawn. This investigation, and extensions thereof,[9,10] predict qualitatively results similar to those observed in the present experiments; they also show that it is possible to have a consistent theoretical model exhibiting a persistent current in the absence of a well-defined energy gap. However, the observed effects are more pronounced than those predicted. Phillips[10] has speculated that magnetic impurity bands may account for the quantitative discrepancy. On the other hand, Suhl and Fredkin[11] have suggested that dynamic effects associated with the reorientation of the impurity spins may be predominant in reducing the lifetime of quasi-particle states and may account for the tunneling results in the region of concentration $c < c'$.

[5] The effectiveness of Mn impurities in reducing the superconducting transition temperature is also very large: W. Optiz, Z. Physik **141**, 263 (1955).

[6] As a check on these results, it was found that the tunneling characteristics of a 3000-Å Sn film are only slightly affected by the superposition of a 40-Å Au layer. However, an additional 15-Å layer of Mn deposited behind this Au has a pronounced effect.

[7] A. A. Abrikosov and L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. **39**, 1781 (1960) [English transl.: Soviet Phys.—JETP **12**, 1243 (1961)].

[8] P. W. Anderson, in *Proceedings of the Seventh International Conference on Low Temperature Physics* (University of Toronto Press, Toronto, Canada, 1960), p. 306.

[9] P. G. de Gennes and G. Sarma, J. Appl. Phys. **34**, 1380 (1963).

[10] J. C. Phillips, Phys. Rev. Letters **10**, 96 (1963).

[11] H. Suhl and D. R. Fredkin, Phys. Rev. Letters **10**, 131, 268 (1963).

## Discussion 36

FERRELL: To what extent can you establish the abruptness of the drop in the apparent gap and to what extent do these various theories predict any abruptness?

F. REIF, *University of California:* At the present time I cannot establish the abruptness too well. One thing I can say is that the negative resistance region disappears at a rather small concentration range. Beyond this it just seems to broaden out. In order to get better information we would have to plot in detail the density of states. The Suhl theory, if I understand it correctly, would not predict anything terribly sudden. I think the other theory predicts something more sudden.

MEISSNER: I would like to caution that even if you evaporate at low temperatures, you may during the evaporation of the second film actually shoot atoms into the first film. The atoms are coming from a fairly high temperature source and if the metal underneath is something as soft as indium, then the atoms could penetrate for quite some distance.

G. v. MINNIGERODE, *University of Göttingen:* We did an experiment superimposing two films of tin and indium. In such a system of indium and tin, an alloy of the two components has a higher transition temperature than either of the components. These films were superimposed at helium temperature and the transition temperature of the sandwich was between pure tin and pure indium. There was no alloying effect. If we warmed up this sandwich to a temperature of about 200°K, suddenly the alloying process starts and then we found a transition temperature of about 5.6°. We are sure in the low-temperature region there is no alloying effect. We tried another system too–lead and bismuth.

# THEORY

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# The Existence of a Superconducting State in Semiconductors

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Despite the scarcity of published work on superconductivity in semiconductors, degenerate semiconductors have been examined for superconducting properties both experimentally and theoretically. The results of these investigations have not on the whole been encouraging.

The main reason for finding a degenerate semiconductor with superconducting properties is to use this semiconductor as a tool for investigating electron–electron and electron–phonon interactions in both the normal and the superconducting states. A semiconductor of this type could also be used to give further information about the band structure of semiconductors and might possibly yield new insight into the phenomenon of superconductivity.

The band structures of many semiconductors have been determined quite accurately, and the effects on the band structure arising from uniaxial strain, hydrostatic pressure, and alloying are also known. By using these methods, the band structure of a semiconductor can be changed for a fixed concentration of impurities, and if the small effects of the doping on the band structure are neglected, the number of carriers can be changed for a given band structure by changing the doping. The carrier concentration and band structure of a degenerate semiconductor can therefore be varied independently of one another and, if a semiconductor were in a superconducting state, the superconductivity could then be observed as a function of band-structure changes and changes in the number of carriers alone.

The band-structure model used for previous theoretical investigations was that of a single-valley conduction band and valence band. Because this model

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