Effect of Magnetic Impurities on the Density of States of Superconductors*

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The technique of electron tunneling has been applied to a systematic study of the density of states in superconductors containing magnetic impurities. Whereas earlier experiments on such superconductors examined the current-voltage tunneling characteristics at 1°K, the present experiments have been refined so as to measure directly the tunneling conductance, and hence the density of states, down to 0.4°K. The present data can therefore be compared with the predictions of the Abrikosov-Gorkov theory worked out in detail by Skalski, Betbeder-Matibet, and Weiss. Qualitatively, the addition of magnetic impurities causes a reduction of the energy gap and a broadening of the peak in the density of states. The detailed shape of the density-of-states curves agrees reasonably well with the theory, at least for a rare-earth impurity system like Gd in lead. The transition-element impurities Fe (in indium) and Mn (in lead) have a more pronounced effect than predicted, the energy gap being substantially more filled in and less well defined than in the Pb-Gd system. Experiments on pure superconducting films with superimposed layers of magnetic metal atoms yield similar marked effects on the density of states. The experiments indicate that it is the presence of strong correlations between electrons rather than the existence of a well defined energy gap which is the essential feature of the superconducting state.

I. INTRODUCTION

EARLY experiments on superconductors containing magnetic impurities showed that a small impurity concentration causes a very large drop in the superconducting transition temperature T_c. The Göttingen group[1] showed that T_c decreases linearly with increasing magnetic impurity concentration in films of such systems. Matthias' systematic study of rare-earth impurities in bulk lanthanum[2] showed further that the lowering of T_c depends on the spin of the impurity atoms rather than on their magnetic moment. This work indicated that the observed effect is due to the exchange interaction between the spins of the impurity atoms and the conduction electrons.

Several theories,[3,4] proposed on the basis of this exchange interaction, predicted that superconductors containing magnetic impurities should have unusual properties. In particular, Abrikosov and Gorkov[4] made the startling prediction that, for concentrations c greater than 0.9 of the critical concentration c_{cr} (that at which T_c becomes zero), the energy gap in the density of states should disappear while the transition temperature is still nonzero. For this range of concentrations, the theory predicts the existence of what has since been termed "gapless superconductivity."

The technique of electron tunneling[5] suggested itself as a direct method for investigating the behavior of the energy gap in these systems. We have previously reported[6] preliminary tunneling experiments on indium films containing Fe impurities. At low concentration ($c \lesssim 0.1c_{cr}$), the energy gap was found to decrease more rapidly than T_c with increasing concentration. At higher concentrations, the tunneling curves became nearly straight, indicating that the energy gap was no longer sharply defined although the resistance of the film went to zero at a well-defined temperature.

In order to obtain more quantitative results, we have now refined the tunneling experiments so as to measure directly the density of states of several superconductor-magnetic impurity systems at low temperature (0.4°K). It is thus possible to compare the data with the predictions of the Abrikosov-Gorkov theory as worked out in detail by Skalski, Betbeder-Matibet, and Weiss.[7]

II. EXPERIMENTAL ASPECTS

Films of superconductors containing magnetic impurities were evaporated *in situ* onto a substrate held near 1°K. Such an alloy film sample separated from a normal reference metal by an insulating oxide barrier formed a tunnel junction whose conductance could be measured at temperatures down to 0.4°K. The resistance of the alloy film itself was measured to determine its transition temperature. Tunneling measurements on such alloy films require the use of some special techniques which will now be described.[8]

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[1] We refer here particularly to R. Hilsch, W. Buckel, G. v. Minnegerode, K. Schwidtal, N. Barth, W. Opitz, and A. Schertel. See K. Schwidtal, Z. Physik **158**, 563 (1960) and references therein.

[2] B. T. Matthias, H. Suhl, and E. Corenzwit, Phys. Rev. Letters **1**, 93 (1958); Phys. Chem. Solids **13**, 156 (1960).

[3] H. Suhl and B. T. Matthias, Phys. Rev. **114**, 977 (1959); W. Baltensperger, Helv. Phys. Acta **32**, 197 (1959); P. Fulde and R. A. Ferrell, Phys. Rev. **135**, 550 (1964); K. Nakamura, Progr. Theoret. Phys. (Kyoto) **21**, 435 (1959); R. Lange, thesis, Harvard University, 1963 (unpublished).

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

[5] I. Giaever and K. Megerle, Phys. Rev. **122**, 1101 (1961).

[6] F. Reif and M. A. Woolf, Phys. Rev. Letters **9**, 315 (1962).

[7] S. Skalski, O. Betbeder-Matibet, and P. T. Weiss (to be published).

[8] A detailed description of the experimental procedures can be found in M. A. Woolf, Ph.D. thesis, University of California, Berkeley, 1964 (unpublished).

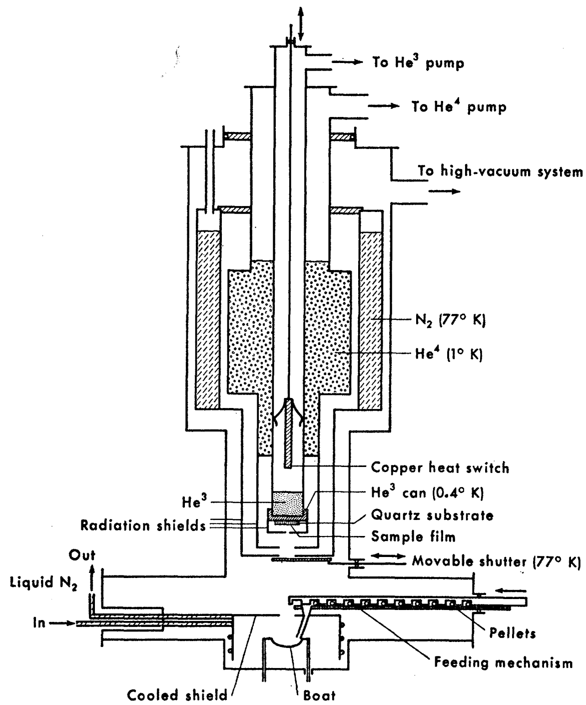

FIG. 1. Dewar for tunneling measurements on alloy films evaporated at low temperatures.

A. Alloy Film Preparation

Three alloy systems have been investigated: Pb-Gd, Pb-Mn, and In-Fe (where the second element indicates the impurity in each case). Although in all of these systems, the two metals are mutually insoluble in equilibrium it is nevertheless possible to deposit good superconducting films[9] by the quench-evaporation technique which was developed and used extensively by the Göttingen group.[1] In this method, small pellets are prepared from an initial macroscopically homogeneous mixture of the component metals. These pellets are then successively evaporated to completion onto a substrate held at a temperature near 1°K. The size of the pellets is such that each contributes only about 10 Å to the final film thickness. Any possible inhomogeneity in the film due to differential evaporation of the component metals extends, therefore, at most over a few atomic spacings. The low temperature of the substrate prevents mutual diffusion which might lead to agglomeration of the components. Thus, as long as the initial mixture is sufficiently homogeneous so that each pellet contains the desired proportions of the components, the resultant film is to good approximation a homogeneous alloy.

The initial mixture of all systems studied was obtained by first roughly blending the component metals together as uniformly as possible and then mixing them thoroughly by mechanical means. To prepare the Pb-Mn and In-Fe alloy samples, the respective impurity metal was evaporated uniformly onto a thin (0.1 mm) sheet of the pure host metal in a high-vacuum bell jar. The sheet was weighed before and after the evaporation to determine the proportions of the two metals. Because Gd oxidizes quite readily, the most satisfactory technique for preparing the Pb-Gd alloy sample was found to be that of Schwidtal.[1] The two metals were melted together in the desired proportions by induction heating in a tantalum crucible in an atmosphere of streaming He gas. The melt was then cooled rapidly to room temperature in order to stabilize the macroscopically uniform dispersal of the Gd brought about by convection currents in the melt.

Mechanical mixing is achieved by repeatedly folding and rolling the composite sheet or the melt about 75 times until a final homogeneously mixed 0.5-mm thick foil is formed. The pellets (0.5 mm in size) for the quench evaporation are cut from this final foil. In all cases the original mixture is prepared to have the highest impurity concentration to be studied. Lower concentrations were then obtained by adding measured amounts of the pure host metal and rerolling.

B. Cryogenics

The Dewar is schematically illustrated in Fig. 1. It is a metal Dewar designed for quench evaporation and capable of cooling the sample to 0.4°K with liquid He^3. The evaporation takes place in the same vacuum which provides thermal insulation. The copper He^3 can is thermally isolated by a section of stainless-steel tubing from the He^4 bath, but may be brought into thermal contact with it by a copper heat switch operated from the top of the Dewar. The quartz sample substrate is mounted on the bottom of the He^3 can and is surrounded by several radiation shields which serve to minimize heat input during evaporation. The bottoms of the shields are slotted to collimate the beam of metal atoms which are evaporated from below. A movable shutter covers the slot in the N_2-temperature shield. In the tail of the Dewar, the feeding mechanism drops one pellet at a time into the resistance-heated tungsten[10] boat.

After the sample is mounted, the Dewar is cooled down; the He^4 bath is then filled and pumped to 1°K so that the He^3 condenses, cooling the sample to this temperature. (An Allen-Bradley and a Speers resistor measure temperatures above 2°K and below 1°K,

[9] The available evidence indicates that such films constitute representative superconducting samples. For example, the effect of magnetic impurities on the transition temperature of superconductors (measured by dT_c/dc) has been shown to be the same for both quenched and annealed films (for the La-Gd system). See R. Hilsch, G. v. Minnegerode, and K. Schwidtal, *Proceedings of the Eighth International Conference on Low Temperature Physics, London, 1962* (Butterworths Scientific Publications, Ltd., London, 1963), p. 155.

[10] A tungsten boat tends to reduce any metal oxides which may form on the pellets. This was shown by K. Schwidtal, Z. Physik **158**, 563 (1960).

respectively.) We perform the quench evaporation of the alloy film by dropping a pellet into the boat, opening the shutter in the N_2-temperature shield, and heating the boat slowly (to prevent the pellet from popping out) until the pellet has evaporated completely. The shutter is then closed and the boat allowed to cool before repeating the operation. During the evaporation, the temperature of the substrate stays below 4°K. Approximately 50 pellets are evaporated in this way to form a film about 500-Å thick.

C. The Tunnel Junction

Aluminum is a good reference metal because it readily forms a thin and coherent oxide layer suitable for tunneling experiments. Since it becomes superconducting below 1.2°K, it is not suitable for direct measurement of the density of states at low temperatures. To obviate this difficulty, we added to the Al a sufficient concentration of Mn (about 1 at.%[11]) to keep it normal down to 0°K.[12] Since the Al-Mn film is oxidized at room temperature and cooled before evaporation of the superconducting alloy, there is the possibility that thermal contraction may lead to cracks in the insulating oxide layer. For this reason it was necessary to make the insulating layer rather thick.[13] (Junction resistances were typically of the order of $10^4\ \Omega$.)

The sample substrate is a 1-mm-thick slab of polished crystal quartz. One side of the quartz is soldered to a copper mounting block with indium to provide thermal contact. Three parallel narrow (0.005 in.) Al-Mn strips are evaporated at room temperature onto the substrate and allowed to oxidize in air for a few minutes. The mounting block is then both screwed down and soldered with gallium to the bottom of the He^3 can of the Dewar. When mounting is complete, the Dewar is assembled, evacuated, and cooled down. The alloy film is deposited across the three oxidized Al-Mn strips to form three tunnel junctions (0.010×0.005 in. in size). In any one run, the tunneling characteristics of all three junctions are found to be the same, demonstrating the reproducible properties of the junctions.

D. Measurements

When electrons tunnel under the influence of an applied voltage V from a normal metal into a superconductor at 0°K, the conductance $G_s(V)$ of the tunnel junction is proportional to the density of states in the superconductor.[14] At nonzero temperatures, $G_s(V)$ measures the density of states broadened by the derivative of the Fermi function. To determine $G_s(V)$ experimentally, we superimpose a small 13 cps modulation on the current I through the junction. The 13-cps voltage component across the junction is proportional to dV/dI. It is measured with a phase sensitive detector and yields on an X-Y recorder a plot of $dV/dI \equiv G_s^{-1}(V)$ versus V. In order to plot the density of states, we calculate the normalized conductance $g(V) \equiv G_s(V)/G_n$, where G_n is the limiting value of $G_s(V)$ for large V (equivalent to the conductance of the junction with the film normal).

The transition temperature is determined for each run by measuring the resistance of the alloy sample film itself using current and potential leads. The resistance of each of the Al-Mn films can also be monitored to see that they stay normal at the lowest temperature.

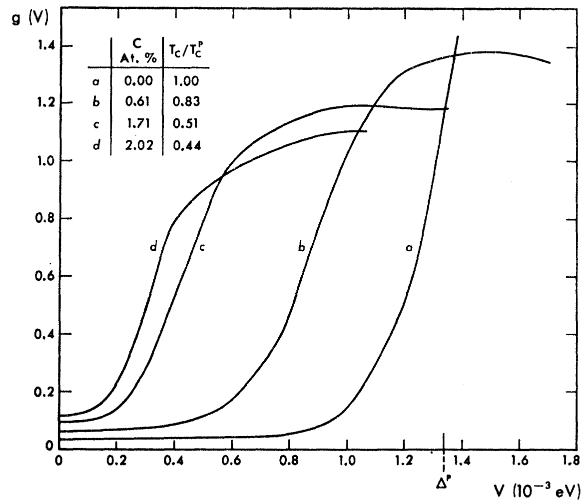

FIG. 2. Measured tunnel conductance $g(V)$ of the Pb-Gd system as a function of energy V for various Gd concentrations c. Curves (a) and (b) were taken at 1.1°K; curves (c) and (d) at 0.4°K. The transition temperature of the pure superconductor is denoted by T_c^P. [The finite values of $g(V)$ near $V=0$ are unreliable; see text.]

III. EXPERIMENTAL RESULTS

The following results were obtained in earlier tunneling experiments[6] on the In-Fe system: For an atomic concentration c of Fe less than 0.2%, an accurate value of the gap in the alloy film could be measured at 1°K. This value was obtained in the usual way from the negative resistance region in the current-voltage characteristics of a tunnel junction when superconducting aluminum was used as the reference metal. The measured gap decreases rapidly with increasing concentration. In the range $0.2\% \lesssim c \lesssim 0.8\%$, the current-voltage

[11] G. Boato, G. Gallinaro, and C. Rizzuto, Rev. Mod. Phys. **36**, 162 (1964).

[12] It was checked that the Al-Mn acts as a normal reference metal by verifying that experiments on pure lead gave the expected density of states. Although we also tried Mg as a normal metal, we found its oxide layer less reliable.

[13] Instead of relying on an oxide, we attempted to deposit the thin insulating layer by evaporation of a dielectric onto the cold substrate. Using Au as the normal metal, such insulators as Ar, LiF, SiO, TlCl, and nylon were tried. In all cases, however, junctions were short-circuited either because the insulating film contained pin-holes or was punctured by the subsequent deposition of superconducting metal.

[14] I. Giaever, Phys. Rev. Letters **5**, 147 (1960); J. Bardeen, *ibid.* **6**, 57 (1961).

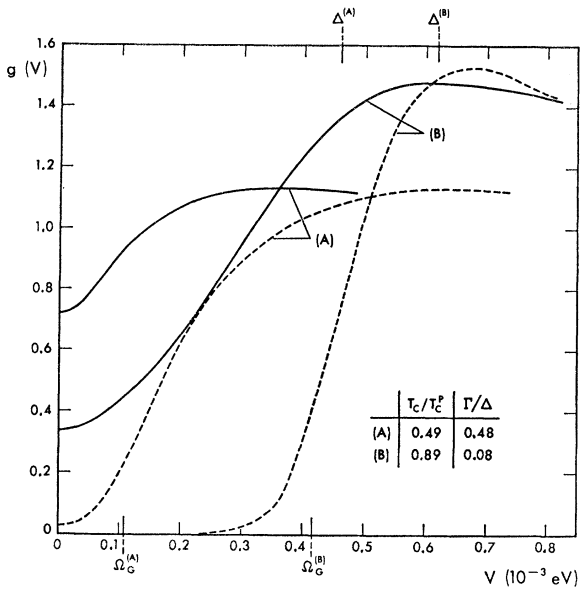

FIG. 3. Conductance curves of the In-Fe system. The experimental data are indicated by solid curves, the theoretical predictions by dashed curves. The Fe concentration is 0.86 at.% for curves (A), 0.18 at.% for curves (B). The theoretical parameter Γ is proportional to concentration; Δ denotes the order parameter and Ω_G the gap width.

curves no longer show a negative resistance region but still have some curvature. This curvature decreases as c is increased until for $c \gtrsim 0.8\%$ the curves are essentially straight, although T_c has dropped to only about half that of the pure indium. The data, then, show that there is initially a well-defined gap and a progressive appearance of states in the gap at higher concentrations.[15]

When the energy gap is not well defined, there is no obvious single parameter which characterizes the superconducting density of states. In order to make detailed comparisons with theory, we decided to measure directly the whole density of states curve at a temperature low compared with the transition temperature. Quench evaporated films of three alloy systems were studied: Pb-Gd, Pb-Mn, and In-Fe. The slope dT_c/dc of the linear decrease of T_c with c of these systems had already been measured in quench-evaporated films of these alloys.[16] We have studied the Pb-Gd system most extensively since the rare-earth atoms are expected to have well-localized spins due to the unfilled $4f$ shell. Lead is also a good candidate for the host superconductor because of its high transition temperature and ease of evaporation.

The transition temperature of all alloy samples studied was found during each run by measuring the resistance $R(T)$ of the film as a function of temperature. (For a film 1 in.×0.010 in.×500 Å thick, a typical value of the normal resistance R_n is 400 Ω.) The value of T_c chosen was the midpoint of the temperature range between which $R(T)$ was 10% and 90% of R_n. (The width of this range was usually of the order of 0.4°K.) In some cases, $R(T)$ had a long low-temperature tail, although tunneling measurements were always made at a temperature well below that at which R went to zero. The values of T_c for a given nominal concentration were consistent with the transition temperature of the pure superconductor and the measured value of dT_c/dc.

In Figs. 2, 3, and 4, we present the normalized tunneling conductances $g(V)$ of the three alloy systems. These curves should be a direct measure[14] of the density of states in the superconducting alloys as a function of energy. Figure 2 shows the $g(V)$ curves for the Pb-Gd system at three concentrations which span the range of concentrations studied. The curve for pure Pb is also shown and reflects the ordinary BCS[17] density of states. The small but nonvanishing values of $g(V)$ at $V=0$ are unreliable because the resistance of the junctions at low voltage is extremely high compared with the impedance of the measuring equipment. The following trends in the data are evident:

(1) Even for small concentrations, the sharp peak in the BCS density of states is drastically rounded off, the peak becoming less pronounced at higher concentration.

(2) As the concentration increases, more and more states spill over into the pure lead gap region. The portion of the $g(V)$ curves with steepest slope seems to

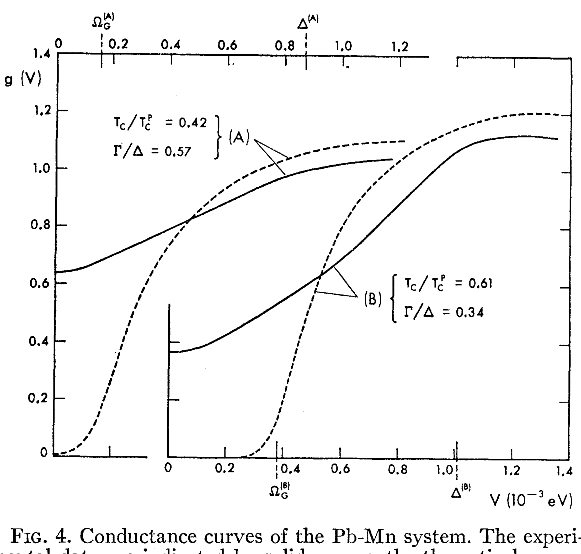

FIG. 4. Conductance curves of the Pb-Mn system. The experimental data are indicated by solid curves, the theoretical curves by dashed curves. The upper scale refers to curves (A), corresponding to a Mn concentration of 0.20 at.%; the lower scale refers to curves (B), corresponding to a Mn concentration of 0.13 at.%.

[15] By contrast, the tunneling characteristics of quenched films of superconductors containing *non*magnetic impurities (e.g., Pb-10%Tl, In-0.5%Zn) exhibit a well-defined gap. See Ref. 6.

[16] Pb-Gd: K. Schwidtal (Ref. 10); Pb-Mn: N. Barth, Z. Physik **148**, 646 (1957); In-Fe: W. Opitz, Z. Physik **141**, 263 (1955).

[17] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

define a gap edge which shifts to progressively lower energies. Nevertheless, the region below this edge remains relatively devoid of states even at higher concentration. This last feature implies that, contrary to our previous suggestion,[18] the curves are incompatible with a Lorentz-broadened BCS density of states.

The qualitative features of the data are consistent with the theoretical curves shown in Fig. 6. A detailed comparison will be made in the next section.

The data for the In-Fe and Pb-Mn systems are shown by the solid curves of Figs. 3 and 4, respectively. Although the curves show the same progressively decreasing peak and shift to lower energy as in Fig. 2, they differ from the Pb-Gd case in that there is considerably more filling in of states in the gap. Note also that this difference is very much more pronounced for Pb-Mn than for In-Fe, even though both sets of data were taken at 0.4°K. Parenthetically, we remark that this filling-in of states in the In-Fe gap is sufficient to account for the nearly straight tunneling characteristics observed in previous experiments[6] at the higher temperature of 1°K.

IV. DISCUSSION

The most satisfactory treatment of magnetic impurities in superconductors is provided by the theory of Abrikosov and Gorkov (AG).[4] This theory has been further developed by several other workers.[19,7] In particular, Skalski, Betbeder-Matibet, and Weiss[7] have made detailed calculations and extensions of the theory. In this section, we shall outline the important parameters and predictions of the theory and compare these with our experimental results.

A. Theoretical Aspects

The AG theory assumes that each impurity spin **S** is localized and is coupled to the spin **s** of a conduction electron by an exchange interaction of the form $J\mathbf{S}\cdot\mathbf{s}$. The model supposes that the impurities are randomly

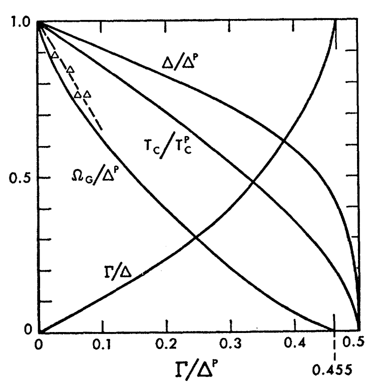

FIG. 5. The transition temperature T_c, the order parameter Δ, the energy gap Ω_G, and the quantity Γ/Δ plotted as a function of the inverse collision time Γ (from Skalski *et al.*, Ref. 7). The quantities Δ^P and T_c^P refer to the pure superconductor. The triangles are experimental points of Ω_G measured in Ref. 6 for the In-Fe system.

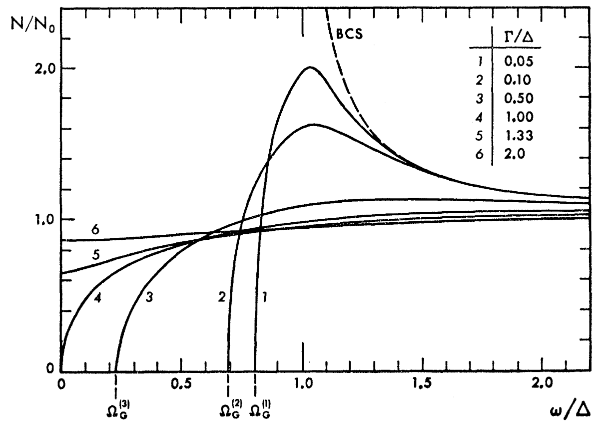

FIG. 6. The normalized density of states N/N_0 plotted as a function of the reduced quasiparticle energy for several values of the reduced inverse collision time Γ/Δ (from Skalski *et al.*, Ref. 7). The corresponding values of the gap Ω_G are indicated.

distributed in space and that their spin orientations are fixed and random. Applying the Green's function formalism of Gorkov[20] to this model, AG are able to predict the observed, initially linear, rapid decrease of T_c with increasing concentration c. As already mentioned, they arrive at the remarkable conclusion that the gap in the excitation energy spectrum becomes zero for a range of impurity concentrations $(0.91c_{cr}\leq c\leq c_{cr})$ below the concentration c_{cr} required to reduce T_c to zero. In this region, the theory predicts that the specific heat has a term linear in T (to be expected if there is no gap), but that there are still pair correlations, persistent currents, and a Meissner effect.

The essential feature of the superconducting state is the strong pair correlation between electrons in time-reversed states (BCS pairs in the pure superconductor, Anderson pairs[21] in dirty superconductors). The presence of magnetic impurities introduces, however, spin-dependent interactions which are not invariant under time reversal. The problem is therefore essentially different from that of nonmagnetic impurities. Since collisions preserve time-reversal invariance in the latter case, they do not break up the pairs formed from time-reversed single-particle states; such a pair has, therefore, infinite lifetime. On the other hand, since collisions with magnetic impurities do not preserve time-reversal symmetry, it is not possible to form pairs which are unaffected by such collisions. Such a pair, therefore, has a finite lifetime τ_s. This finite lifetime is responsible for an energy spread $\Gamma=\hbar/\tau_s$ which introduces states into the gap. The quantity Γ, being essentially the collision rate, is proportional to the impurity concentration and is the parameter which characterizes the superconducting alloy. There is an important distinction in the alloy between the order parameter $\Delta(\Gamma)$ and the energy gap

[18] F. Reif and M. A. Woolf, Rev. Mod. Phys. **36**, 238 (1964).
[19] P. G. deGennes and G. Sarma, J. Appl. Phys. **34**, 138 (1963). J. C. Phillips, Phys. Rev. Letters **10**, 96 (1963).
[20] L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. **34**, 735 (1958) [English transl.: Soviet Phys.—JETP **7**, 505 (1958)].
[21] P. W. Anderson, Phys. Chem. Solids **11**, 56 (1959).

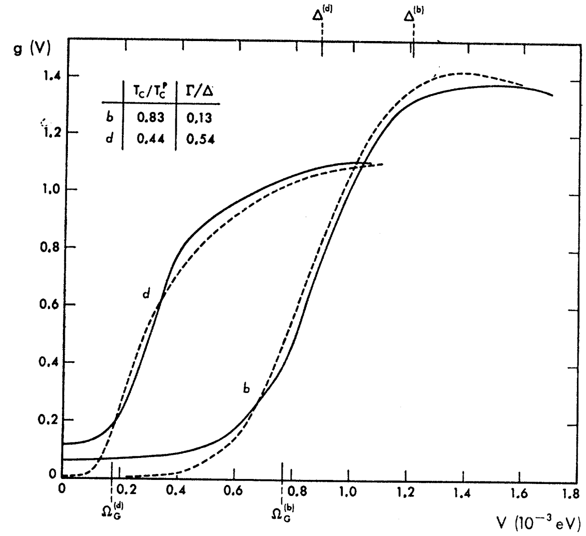

FIG. 7. The conductance curves (b) and (d) (solid lines) of Fig. 2 and the corresponding theoretically predicted conductance (dashed lines) for two concentrations of the Pb-Gd system.

$\Omega_G(\Gamma)$ (we use the notation of Ref. 7). In a pure BCS superconductor, the order parameter and the energy gap are the same [$\Delta(0)=\Omega_G(0)=\Delta^P$, where Δ^P is the order parameter of the pure superconductor]. In the alloy, however, gapless superconductivity arises because Ω_G goes to zero while Δ is still finite; it persists until the concentration reaches the critical value $c_{\rm cr}$ (corresponding to $\Gamma_{\rm cr}$) where the order parameter Δ vanishes so that T_c goes to zero.

These relationships are clearly shown in the theoretical curves of Skalski, Betbeder-Matibet, and Weiss which are reproduced in Figs. 5 and 6. Figure 6 shows the density of states N (divided by the density of states N_0 in the normal metal) as a function of the reduced quasiparticle energy ω/Δ. The sharp cutoff of the density-of-states curves of Fig. 6 defines the quantity Ω_G which is the energy gap for these alloys. The dependence on Γ of Ω_G, Δ, Γ/Δ, and T_c is shown in Fig. 5. Note that $\Omega_G=0$ when $\Gamma/\Delta=1$ (see also curve 4 in Fig. 6). This corresponds to $\Gamma=0.91\Gamma_{\rm cr}(\Gamma_{\rm cr}=0.5\Delta^P)$. The theory also gives the temperature dependence of Δ. The reduced temperature of the present experiments is, however, low enough so that the data can be discussed with negligible error by using the value of Δ at T=0.

B. Comparison with Experiment

In the previous experiments[6] on the In-Fe system, the negative resistance region in the current-voltage tunneling characteristics yielded an accurate value for the energy gap only at low concentration. According to the theory, the gap measured in such an experiment is Ω_G. As predicted, this gap decreases with concentration more rapidly than T_c. The data points are plotted in Fig. 5. It can be seen that in the small accessible low concentration range, the points lie reasonably close to the theoretical curve of Ω_G. The negative resistance region in the current-voltage tunneling curves is due to the sharp peaks in the density of states on both sides of the barrier. Figure 6 shows that these peaks broaden at higher concentration so that the negative resistance region is expected to disappear, as is found experimentally.

We now turn to a comparison of the results of the present experiments with predictions of the theory. It is possible to make this comparison without involving any adjustable parameters, even though the constant of proportionality relating Γ to the concentration is unknown. Using the measured value of T_c for a given sample, we obtain from the theoretical curve of Fig. 5 the corresponding value of Γ/Δ. The predicted density of states curve (see Fig. 6) characterized by this value of Γ/Δ is then chosen for comparison with $g(V)$. Since the conductance $g(V)$ is measured at finite temperatures, it is not equal to the density of states N/N_0, but is related to it by

$$g_{\rm th}=\int_{-\infty}^{\infty}\frac{N(\omega')}{N_0}f'\left(\frac{\omega'-V}{kT}\right)d\omega', \qquad (1)$$

where $\omega'\equiv\omega/\Delta$ and where $f'(x)\equiv(e^x+1)^{-1}(e^{-x}+1)^{-1}$ is essentially the derivative of the Fermi function. The temperature broadening in (1) is calculated on a computer to obtain the theoretical conductance $g_{\rm th}(V)$ at the temperature of the experiment. Direct comparison with the experimentally measured conductance $g(V)$ can then be made. Figure 7 shows the results for the Pb-Gd system. The experimental curves (solid lines) are seen to agree quite well with the theoretical curves (dotted lines). Thus, the AG theory seems to account for the data, at least for a rare-earth impurity like gadolinium. The fit with the theory in this case is sufficiently good not to require invoking any dynamic spin model of the type proposed by Suhl and Fredkin.[22]

The theoretical conductances for the In-Fe and Pb-Mn systems are shown by the dotted curves in Figs. 3 and 4, respectively. The agreement with experiment (solid curves) is not very good, particularly in the case of the Pb-Mn system. The spins of these transition element impurities are expected to be highly localized since they have a large effect on the superconducting transition temperature.[23] The observed discrepancy with the AG theory may, however, arise from the fact that in many alloys the magnetic moments of transition element impurities are thought to be associated with the existence of electrons in virtual bound states in the conduction band.[24] This contrast with the strictly local-

[22] H. Suhl and D. R. Fredkin, Phys. Rev. Letters **10**, 131 (1963).
[23] See, for example, B. Matthias, M. Peter, H. Williams, A. Clogston, E. Corenzwit, and R. Sherwood, Phys. Rev. Letters **5**, 542 (1960).
[24] J. Friedel, Nuovo Cimento Suppl. **2**, 287 (1958); also P. W. Anderson, Phys. Rev. **124**, 41 (1961).

ized inner 4*f* electrons of the rare earths may be responsible for a more complicated coupling with the conduction electrons. In noting the difference between these two impurities themselves, it should parenthetically be pointed out that the Mn impurity concentration is very much less than that of Fe (since dT_c/dc for Mn in Pb is -2100, whereas for Fe in In it is -250).

V. SUPERIMPOSED FILMS

The proximity effect experiments of Smith, Shapiro, *et al.*[25] showed that the tunneling characteristics of a pure superconducting film are altered when a normal film is evaporated onto it. We have performed such experiments where the normal film is a thin layer of magnetic metal atoms evaporated onto the back of a pure superconductor film maintained at 1°K. Because of this low temperature, mutual diffusion of the two metals is eliminated.[26] the *in situ* evaporation allowed us to measure successively during the same run the tunneling characteristics of both the superconductor alone and of the superimposed films. The pure superconducting films were either quenched films evaporated at low temperature, or annealed films evaporated at room temperature. (The difference between the two lies only in the fact that the quenched films, being highly disordered, should have the shorter mean free path.) In addition to their inherent interest, these experiments with superimposed films have the virtue that the junction region always consists of pure superconducting metal. Any positive effects observed cannot, therefore, be attributed to gross inhomogeneities (inclusions of normal material) near the junction.

Early experiments[6] showed that the nonlinear tunneling characteristic of a 500-Å-thick quenched indium film became nearly straight when a 15-Å-thick layer of iron was superimposed on it. Although no very systematic studies of superimposed films were undertaken, further experiments were performed to elucidate the general nature of the effects. In these experiments, we used Mn as the backing metal since it is not ferromagnetic. The effect on the density of states of a thin layer of this metal is drastic, and recalls the pronounced effects of Mn used as an impurity. For example, a 15-Å Mn layer superimposed on an annealed tin film 3000 Å thick is sufficient to smear out the density of states considerably. The same thickness of Mn deposited on quenched lead and tin films (up to 1500 Å thick) has qualitatively the same effect. The Mn appears to act like a surface layer of magnetic atoms since there is no further effect on the density of states when the thickness of the superimposed Mn is increased beyond the 15 Å at which the marked broadening first occurs. We find that the effect decreases rapidly as the thickness of the superconductor film increases. For a 5000-Å-thick annealed tin film, no effect is observed for a superimposed layer of Mn as much as 100 Å thick.

It is perhaps not surprising that the effect persists in annealed films up to a thickness of about 3000 Å. Although the phenomenon is not yet well understood, the influence of a superimposed film is expected to extend into the superconductor a distance comparable to the coherence length.

VI. CONCLUDING REMARKS

These experiments show that the addition of magnetic impurities to superconductors can radically alter the density of states in such systems. The impurities bring about a reduction of the energy gap and a broadening of the peak in the density of states. Rare-earth impurities, because of their localized spins, should most nearly satisfy the assumptions of the theory. Indeed, the Abrikosov-Gorkov theory accounts quite well for the observed density of states of lead containing various concentrations of Gd. Agreement with the theory is less satisfactory in the case of the transition element impurities studied, the observed effects being more pronounced than predicted.

Tunneling experiments with other rare earths would be desirable to check the general applicability of the theory to these systems. The discrepancies observed in transition element impurity systems also indicate the need for further work, both experimentally and theoretically. Furthermore, it appears that intrinsically interesting and unambiguous experiments should be possible with quenched superimposed superconductor-magnetic metal films; however, it would be helpful to have a more complete theoretical framework to guide future experiments with such systems. Techniques other than tunneling could also be advantageously applied to the study of magnetic impurities in superconductors. For example, far-infrared transmission experiments on films of these systems are already under way, and measurements of thermal conductivity and ultrasonic attenuation would be of interest. Some preliminary heat capacity measurements on the La-Gd system have been reported by Finnemore[27] and give results which are consistent with the conclusions of the tunneling experiments.

Our experiments indicate that the essential feature of superconductivity is not necessarily the existence of a well-defined energy gap, but rather the presence of correlations between electrons. Indeed, there are theoretical indications that the effects observed in these experiments are not unique to the case of magnetic impurities in superconductors. For example, Maki[28] has

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predicted that gapless superconductivity can occur in superconductors with short mean free path in the presence of persistent currents or magnetic fields. In fact, Fulde[29] has calculated the density of states for different values of supercurrents and magnetic fields, and has found them to be identical to those calculated for different concentrations of magnetic impurities (Fig. 6). Thus, it seems that gapless superconductivity is by no means an exceptional phenomenon, but may occur in superconductors with short mean free path in many cases where there exist interactions which do not preserve time-reversal symmetry.

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Effect of Hydrostatic Pressure on the Néel Temperature in Chromium*

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The electrical resistivity of high-purity chromium polycrystal was measured as a function of temperature in the range of hydrostatic pressure from atmospheric pressure to 8 kbar. The Néel temperature, which manifests itself as the resistivity minimum, was observed to decrease linearly with pressure at a rate of 5.1±0.2°K/kbar. The relative resistivity anomaly in the neighborhood of the Néel temperature was found to be pressure-insensitive. Attempts have been made to interpret the results in terms of the spin-density-wave theory.

THE spin-density-wave (SDW) theory proposed by Overhauser[1] has been successful in interpreting the magnetic properties of chromium. In his theory the electric resistivity and specific heat are explained semiquantitatively as a consequence of the magnetic energy gaps at the Fermi surface for an SDW ground state. It would then appear that the change in the Néel temperature T_N with pressure is primarily due to the effects of changes in the Fermi energy and in the pseudoexchange interaction with decreasing volume. Some information on the pressure dependence of T_N of Cr is available from Bridgman's data[2] on electric resistivity versus pressure. These data, however, do not provide sufficient information, since the measurement covered only six temperatures between 75 and −80°C.

A more precise measurement of the pressure effect on T_N was undertaken in order to elucidate further the magnetic behavior of Cr. Electric resistivity was employed as a measure for T_N because of its convenience for high-pressure measurements and because of its sensitivity in determining T_N. This latter fact is shown in the work of Arajs *et al.*[3] and of Marcinkowski and Lipsitt.[4]

The chromium specimen, supplied by Professor R. Street of Monash University in Melbourne, consisted of polycrystalline chromium of approximate dimensions 58 mm by 0.5 mm by 0.5 mm. It was manufactured from ARL chromium ingots which contained 0.08 wt % nitrogen and 0.03 wt % oxygen. Other impurities were below the limit of spectrographic detection. After being ground and formed the specimen was annealed and recrystallized at 1250°C for approximately two hours in order to remove excess dislocations. The high pressure system used was similar to the system used by Emrick.[5] The pressure vessel made of Cu-Be alloy was mounted inside an oil or dry ice bath. Dow Corning 200 fluid was used as a pressure medium. Current and potential leads (copper) were spot-welded to the chromium specimen which was mounted to a specimen holder attached to a Cu-Be plug fitted with electrical lead-ins. The electric resistivity was measured by the standard dc potentiometric techniques. The voltages were determined with an accuracy of ±0.05 μV. Temperature was controlled

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