our data on a 3.6-Ω junction at 23.4 GHz. The dashed lines are the value of $|J_N(2\alpha)|$ for the $N = 1, 4$, and 10 steps. The solid lines are computed from Eqs. (2) and (3) using the values $2\Delta = 1.163$ meV and $f = 23.40$ GHz. At this frequency, the 24th Josephson step falls near the gap. Thus we expect to see the largest deviations from the $|J_N(2\alpha)|$ curve in the even numbered steps. Our data strongly support Eq. (3). The close agreement between experiment and theory especially at the unusually large maxima (for instance, those at $N=4$, $2\alpha=42$ and $N=10$, $2\alpha=40$) is strong evidence for the existence of the Riedel peak. Although we have shown the results for only three of the steps, we find similar agreement for all twelve steps measured. This experiment has been performed with several junctions over a range of frequencies with equally good results.

A somewhat more quantitative determination of $I_J(f)$ near the peak may be made. To do this, we choose a series of data points for a fixed N and α and a small range of frequency for which there is a particularly strong and frequency-dependent deviation. For each datum point, we select the one term (n') in the n summation of Eq. (3) which most nearly satisfies Eq. (5), i.e., $n' = 2\Delta/hf + N/2$. Using the datum point, and the theoretical values for the remaining terms of Eq. (3), we solve for $I_J((n'-\frac{1}{2}N)2f)$. A series of points obtained in this way is plotted on the insert of Fig. 1. The error bars indicate the spread which results from selecting different data points at the same frequency. A more complete discussion of these results will be presented elsewhere.

We wish to thank Andrew Longacre, Jr., and Karl Bennemann for many fruitful discussions.

*Work supported by the National Science Foundation under Grant No. GK 10562.

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Kondo Effect in Superconductors*

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(Received 23 November 1970)

A self-consistent treatment of the Kondo scattering of conduction electrons from magnetic impurities is presented in order to treat finite concentrations of such impurities in superconductors. The present theory leads to a concentration dependence for the transition temperature which differs markedly from the Abrikosov-Gor'kov result. The theory appears to account nicely for various experimental results. We also find that superconductivity, under certain circumstances, does not exist at all temperatures below T_c.

In this Letter, we present a theory of the Kondo effect in superconductors with finite concentrations of magnetic impurities. Recently, there has been some progress in extending to superconductors[1-4] the Nagoaka approximation,[5] as well as the Suhl approach,[6] treating the s-d model for magnetic impurities in metals. However, these theories confine themselves to a single impurity alone, i.e., to the lowest order in impurity concentration, while the finite-concentration case has not been seriously attacked in this context. One knows, however, that nonlinear effects can arise for even very low impurity concentrations, so that this case is of considerable interest. There is also an experimental challenge to the existing theory, since a number of systems investigated demonstrate a variation of the transition temperature T_c with impurity concentration which deviates in a characteristic and often inexplicable fashion from the Abrikosov-Gor'kov (AG) prediction.[7]

Our treatment of finite concentrations is based

on earlier results for one impurity[1-3] and is, in fact, a rather straightforward extension of that work. To first order in the impurity concentration c, the conduction electron self-energy is given by

$$\hat{\Sigma}_1(z,\Delta) = cJ\hat{t}(z,\Delta), \tag{1}$$

where $\hat{t}$ is the 2×2 matrix of spin-nonflip scattering amplitudes for the scattering of conduction electrons from one impurity, defined in detail in Ref. 1, with diagonal and nondiagonal components t_1 and t_2, respectively. J is the spin-flip coupling energy which appears above as a result of the particular definition of $\hat{t}$ which was convenient in Ref. 1. As has been shown, since the work of AG,[7] it is inappropriate to use $\hat{\Sigma}_1(z,\Delta)$ as a self-energy, if nonlinear effects due to a finite concentration of impurities are to be described correctly. Instead, one has to calculate the self-energy self-consistently by inserting the exact conduction-electron Green's function wherever one had previously used the unperturbed one. Recalling that the energy z and the order parameter Δ in the self-energy $\hat{\Sigma}_1$ originate from the free Green's function, one immediately sees that this can be accomplished by introducing the renormalized energy $\tilde{z}(z)$ and order parameter $\tilde{\Delta}(z)$ into $\hat{\Sigma}_1$, so that one has a self-consistent self-energy represented[8] by $\hat{\Sigma}_1(\tilde{z},\tilde{\Delta})$. We then obtain for the Dyson equation

$$\tilde{z} = z - cJt_1(\tilde{z},\tilde{\Delta}), \tag{2a}$$

$$\tilde{\Delta} = \Delta - cJt_2(\tilde{z},\tilde{\Delta}) \tag{2b}$$

which determines the two functions $\tilde{z}(z,\Delta)$ and $\tilde{\Delta}(z,\Delta)$. This renormalization procedure, which does not require the solution of a new integral equation, appears naturally within the Nagaoka approach. Indeed, it has been employed by Nagoaka[9] in normal metals and by Zuckermann[10] in superconductors. There is, however, a different treatment of renormalization effects by Griffin[11] and Maki.[12] The difference is particularly obvious for normal metals and has been discussed in some detail by Griffin.[13] We definitely disagree with Griffin's preference for the procedure of Refs. 11 and 12 and wish to outline briefly some of the reasons why we do. In formulating the scattering equations in the presence of many impurities, one has to use renormalized wave functions to describe the initial and the final states. This important part of the renormalization, which should also show up in an adequate diagrammatic approach, has not been incorporated in Maki's paper,[12] whereas it is present in our procedure. For the normal metal we are quite positive that Nagaoka's[9] disagreement with experiment is due to his incorrect solution. As is well known, the resistivity calculated from the unrenormalized exact solution does not agree with experiment at low temperatures; we believe that agreement can be improved by the renormalization.

The Dyson equation (2) has to be completed by the self-consistency relation for the order parameter,

$$\ln\frac{T}{T_{c0}} = \frac{2\pi}{\beta}\sum_{\omega_n>0}\left\{\frac{\tilde{\Delta}(i\omega_n,\Delta)/\Delta}{[\tilde{\Delta}^2(i\omega_n,\Delta)+\tilde{z}^2(i\omega_n,\Delta)]^{1/2}} - \frac{1}{\omega_n}\right\} \tag{3}$$

which is supposed to determine Δ as a function of temperature in the presence of the impurities. Equations (2) and (3) are strongly coupled, and a straightforward numerical solution has not been attempted, especially since the scattering amplitudes t_1 and t_2 are not explicitly known.[14] One can give, however, an approximate version of these amplitudes,[3] which yields reasonable results to first order in impurity concentration, where

$$2\pi i J N_0 t_1(z,\Delta) = (y^2-1)^{1/2}\frac{y(1-y_0)}{y^2-y_0^2}, \tag{4a}$$

$$2\pi i J N_0 t_2(z,\Delta) = -(y^2-1)^{1/2}\frac{y_0(1-y_0)}{y^2-y_0^2}, \tag{4b}$$

with $y = z/\Delta$. We will here employ this approximation for t_1 and t_2, although it is only reliable for energies of the order of Δ. The amplitudes (4) are actually identical to those for a classical impurity spin,[15] except that the position y_0 of the pole in the energy gap is temperature dependent here.

The major achievement of Shiba's exact treatment of impurities with a classical spin in superconductors[15] was the appearance of impurity bands within the energy gap (originating from the poles of the scattering amplitudes). A qualitative discussion of these impurity bands in the present context would be very nearly parallel to that of Shiba's and will not be repeated here.

The main point of interest, rather, is the variation of the transition temperature with concentration, which in Shiba's work turned out to be identical to that of AG. In our treatment, this

will be quite different. Equations (2)-(4) give

$$\ln T_c/T_{c0} = \psi(\tfrac{1}{2}) - \psi(\tfrac{1}{2}+\rho), \tag{5a}$$

$$\bar{c} \equiv \frac{c}{(2\pi)^2 N_0 T_{c0}} = \frac{T_c}{T_{c0}} \frac{\rho}{1-y_0^2}. \tag{5b}$$

Although it looks like the AG (and Shiba) relation, Eq. (5) differs significantly because the pair-breaking factor $(1-y_0^2)$ itself depends on the transition temperature[1,3] T_c:

$$1-y_0^2 = \frac{\pi^2 S(S+1)}{\ln^2 T_c/T_K + \pi^2 S(S+1)} \tag{6}$$

(where we have assumed antiferromagnetic spin-flip coupling, $J<0$). This additional T_c dependence leads to considerable deviations from the AG results, as may be seen from the plots of Eqs. (5) and (6) illustrated in Fig. 1, for spin-$\frac{1}{2}$ impurities.

Our results differ substantially depending on whether $T_K > T_{c0}$ or $T_K < T_{c0}$. In the former case [Fig. 1(a)], the variation of T_c with impurity concentration has a positive curvature. This can be easily understood qualitatively from the temperature-dependent pair breaking (6), which, for $T_K > T_{c0}$, decreases monotonically with increasing concentration. Since the pair breaking $\to 0$ as $T_c \to 0$ in this theory, there is never a critical concentration above which superconductivity would be suppressed at all temperatures. It is easily verified that for small T_c the curves have a tail of the form

$$\frac{T_c}{T_{c0}} = \frac{T_K}{T_{c0}} \exp\{-[\pi^2 S(S+1)(\alpha\bar{c}-1)]^{1/2}\} \tag{7}$$

($\alpha = 4e^{\gamma} = 7.124\cdots$).

Variations of T_c with impurity concentration as in Fig. 1(a) are actually being observed in several systems.[16] They have been explained by theories which assume nearly nonmagnetic[17,18] or nonmagnetic resonant[19] states for the impurity, and were therefore until now interpreted as evidence of such impurities. Our theory, which is based on a well-defined impurity spin, fits some of these experiments[20] (Fig. 2, Th-U) as well as,[21] e.g., Kaiser's theory.[19] Accordingly, one must use different criteria to decide whether an impurity carries a well-defined spin or not.

In the other case, $T_K < T_{c0}$, depicted in Fig. 1(b), the T_c variation develops a negative curvature as in AG. However, although our results approach those of AG for $T_K/T_{c0} \to 0$, the approach proceeds in a very striking fashion. When T_K is sufficiently small ($T_K/T_{c0} < \sim \frac{1}{10}$), T_c ceases to be a single-valued function of the impurity concentration. Instead, for a certain range of concentrations, three solutions for T_c exist. Although the existence of three solutions for T_c may at first seem peculiar, it is in fact quite understandable in view of the temperature-dependent pair breaking (6). For $T_K < T_{c0}$, the pair break-

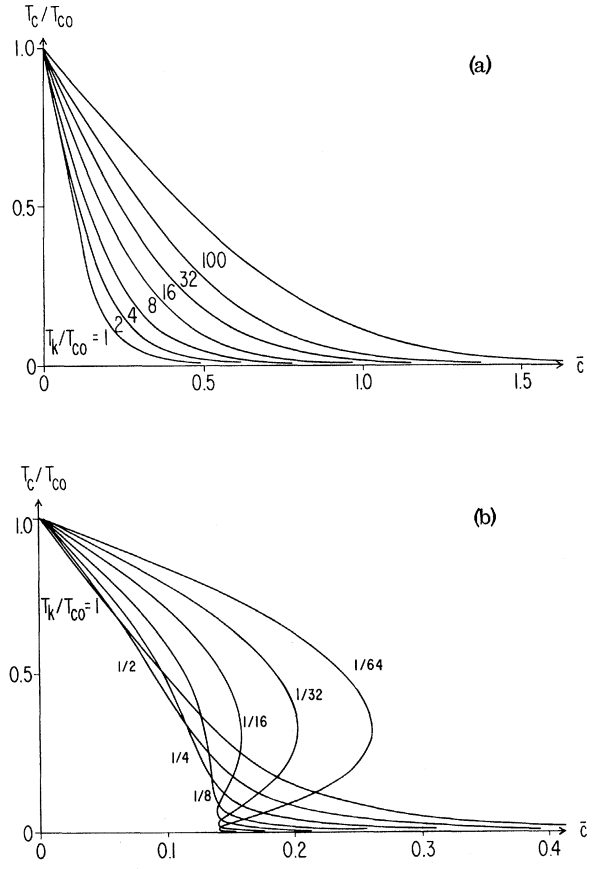

FIG. 1. Transition temperature versus impurity concentration, $c/(2\pi)^2 N_0 T_{c0} \equiv \bar{c}$, for spin $\frac{1}{2}$: (a) $T_K > T_{c0}$, (b) $T_K < T_{c0}$.

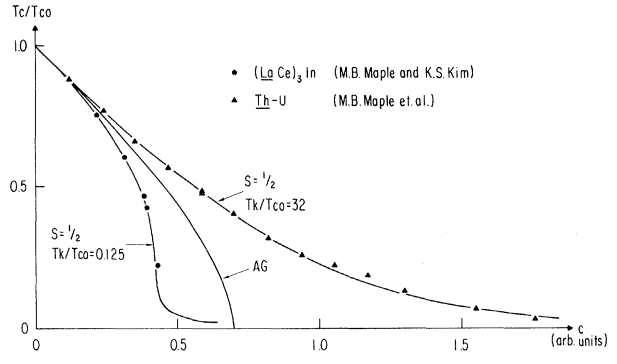

FIG. 2. AG theory and present theory compared with two experimental results. The slopes of all the curves at $\bar{c}=0$ are the same.

ing first increases towards its maximum at $T_c = T_K$, before decreasing again. If T_K is only moderately small compared to T_{c0}, this simply leads to a more sudden drop in T_c than in the AG theory [see $T_K/T_{c0} = \frac{1}{8}$, in Fig. 1(b)]. If, however, T_K is considerably lower than T_{c0}, the alloy becomes superconducting at an upper transition temperature well above T_K, where the pair breaking is still small. When the temperature is further lowered, the pair breaking increases strongly as soon as the Kondo temperature is approached, and superconductivity is again suppressed. It finally reappears at temperatures below T_K, when the pair breaking has passed through its maximum value. Since these temperatures are hardly accessible experimentally, the exponential tail (7) will now be unobservable, and thus a critical impurity concentration effectively does exist. The transition temperature, however, is not zero when this concentration is reached; but the two temperatures between which the superconducting state exists tend to a finite temperature $T_{cr}(T_K)$ instead. When $T_K/T_{c0} \to 0$ AG is recovered, because T_{cr} then goes to zero, too.

The effect, as discussed above, that superconductivity—once it has set in at a certain temperature—does not extend to exist at all lower temperatures, is a striking evidence of the Kondo effect in superconductors. It has not been observed experimentally until now. This might be due to experimental difficulties in investigating the appropriate alloys at low enough temperatures. The system (La, Ce)$_3$In appears to have a Kondo temperature just slightly too high to show the effect discussed. Our curve for $T_K/T_{c0} = \frac{1}{8}$ provides a remarkably good fit to experiments[22] on (La, Ce)$_3$In (Fig. 2), which also shows a marked deviation from the AG predictions.

In view of the excellent agreement of our results with various experiments, and of the striking effect for $T_K \ll T_{c0}$, it seems worthwhile to improve the present theory in order not to have to rely on the approximate scattering amplitudes (4). Solving Eqs. (2) and (3) in the limit $T \to T_c$ is in fact some orders of magnitude less difficult than solving the full problem, since some algebraic steps can be performed analytically. Taking the limit $\Delta \to 0$ of Eqs. (2), one finds for Eq. (3)

$$\ln \frac{T_c}{T_{c0}} = \sum_{n=0}^{\infty} \left[\frac{1}{n+\frac{1}{2}+a(\tilde{\omega}_n, T_c)} - \frac{1}{n+\frac{1}{2}} \right], \tag{8a}$$

$$a(\tilde{\omega}_n, T_c) = \frac{\bar{c}}{T_c/T_{c0}} \left[\frac{\varphi_0(0)}{\varphi_0(i\tilde{\omega}_n)} \left(1 - \frac{X_0(i\tilde{\omega}_n)}{\pi} \int_{-\infty}^{\infty} \frac{\tilde{\omega}_n dx}{\tilde{\omega}_n^2 + x^2} \frac{X_0(x)}{K_0(x)} \right) \right]_{T=T_c} \tag{8b}$$

[for notations in (8b), see Ref. 2], where the renormalized energies $\tilde{\omega}_n$ have to be determined from

$$\tilde{\omega}_n = \omega_n + icJt_1(i\tilde{\omega}_n, 0)_{T=T_c}. \tag{9}$$

Here $t_1(z, 0)$ is, nota bene, the well-known spin-nonflip scattering amplitude for the normal metal.[23,24] The initial slope of the depression of T_c which has been calculated earlier[2] is immediately recovered from (8). One obtains from (8) the "semiclassical" approximation (5) and (6) discussed in this Letter by inserting $\tilde{\omega}_n \equiv 0$. According to Griffin[11] the use of a pair breaking with correct energy dependence tends to mute the strong effects of a resonance on the variation of T_c with impurity concentration. We therefore might expect some modification of our present results due to the energy dependence of the pair breaking. A numerical analysis of Eqs. (8) and (9) is in progress and will be reported elsewhere.

One of us (E.M.-H.) gratefully acknowledges discussions with M. B. Maple on experiments related to this work; the other (J.Z.) would like to thank Professor H. Suhl for the kind hospitality extended to him during his visit.

*Work supported by the U. S. Air Force Office of Scientific Research, Office of Aerospace Research under Grant No. AF-AFOSR-67-0610A.

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4*f* Electronic States in the Metals Nd, Sm, Dy, and Er Studied by X-Ray Photoemission

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(Received 16 November 1970)

Photoelectron spectra excited by x radiation are reported for the band-structure part on clean films of the rare-earth metals Nd, Sm, Dy, and Er. The dominant part of the spectra is due to excitation of 4*f* electrons. The spectra exhibit a complex and extended structure which is interpreted in terms of multiplet splitting of the final state in the photoemission process.

In this Letter we wish to report on x-ray photoemission studies of the rare-earth metals Nd, Sm, Dy, and Er. In particular we have studied the location and structure of the 4*f* electrons. We have previously reported[1,2] on similar studies of Eu and Yb. In contrast to these results the present spectra for rare earths with a 4*f* shell which is not filled or half-filled show a much more complicated and widened structure. An interpretation of this in terms of multiplet splitting is given.

The technique of x-ray photoemission spectroscopy (XPS) or electron spectroscopy for chemical analysis has been described elsewhere.[3] Here only some details pertinent to the present experiments will be discussed. The electron spectrometer is of the electrostatic type with direct analysis of the photoelectrons without any retardation. With Al $K\alpha$ radiation for excitation, a resolution of 1.6 eV full width at half-maximum is obtained using a gold sample. As a measure of the sensitivity of the spectrometer one can use the maximum counting rate of the Au 4*f* electron line at a given resolution. In the present instrument this figure is 2000 counts/sec at the above resolution. The vacuum system is an all-metal-gasket chamber. All samples were prepared by repeated evaporation in situ from 99.9% pure ingots in tungsten baskets at a working pressure of 5×10^{-7} Torr or better. The cleanliness of the sample surface was checked by monitoring the appearance of the oxygen photoelectron line. To maintain an oxide-free sample a new evaporation had to be made every 5 min. The energy scale of the spectrometer was calibrated using a Pd sample for which the Fermi level is located at the inflection point of the steep high-energy edge of the 4*d* band. The calibration was also checked by comparing with uv photoemission measurements (UPS).

The metals studied in this investigation all belong to the so-called normal rare earths. The crystal structures are dhcp (double hexagonal close packed) for Nd, rhombic for Sm, and hcp