# Temperature-Dependent Pair Breaking in *La*Ce and *La*Gd

P. M. Chaikin*†
*Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania* 19104
and
T. W. Mihalisin‡
*Department of Physics, Temple University, Philadelphia, Pennsylvania* 19122
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Using multiple-pair-breaking theory, we have analyzed our $H_{c2}$ data for pure La and for *La*Ce and *La*Gd alloys. For the *La*Gd samples, we find a deviation from simple-pair-breaking theory, which is caused by the presence of the strong exchange field from the spin-$\frac{7}{2}$ impurities. This deviation implies significant Pauli paramagnetic pair breaking for this type of superconductor where the total internal field is large, even though the (externally applied) critical field is small. The *La*Ce data provide a direct measurement of the spin-flip scattering rate as a function of temperature. The strong temperature dependence observed implied that *La*Ce is a Kondo system with a characteristic temperature much less than 1 K. The $T_c$-vs-concentration study shows that impurity-impurity interactions play a large role.

## I. INTRODUCTION

In this paper we will present a method for studying a certain class of many-body effects using superconductivity and multiple-pair-breaking theory. The many-body effects we are interested in are those which produce spin-flip scattering rates that are temperature dependent. The premise is that superconductivity provides a more sensitive measurement than normal-state properties such as resistance, susceptibility, etc. We have substantiated this with the experimental measurement of the Kondo effect through the temperature dependence of the upper critical field.

Previously, several authors have studied both the impurity concentration dependence of $T_c$ and $H_{c2}$ for *La*Ce and *La*Gd.[1,2] They usually tried to compare their data to the theory of Abrikosov and Gorkov[3] (AG) and found large deviations. The point of emphasis we will take is that these deviations contain a good deal of information about the impurity systems which can be revealed by doing the right experiments.

Specifically we find that previous experiments on *La*Ce have given contradictory results as to $\tau_s^{-1}(T)$ (the temperature-dependent spin-flip scattering time) as measured by the $T_c$-vs-concentration curve and the critical field ($H_{c2}$) curves. We find that $\tau_s^{-1}(T)$ is self-consistently obtained if we attribute the differences to impurity-impurity interactions which modify the Ce concentrations to effective concentrations.

In treating the problem of magnetic impurities in a superconductor,[3] AG showed that the depression in transition temperature should obey the following equation:

$$-\ln\left(\frac{T_c}{T_{c0}}\right)=\sum_n\left(\frac{1}{n+\frac{1}{2}+1/2\pi T_c\tau_s}-\frac{1}{n+\frac{1}{2}}\right)$$

$$=\Psi\left(\frac{1}{2}+\frac{1}{2\pi T_c\tau_s}\right)-\Psi\left(\tfrac{1}{2}\right), \qquad (1)$$

where $\tau_s$ is the spin-flip scattering time and $\Psi$ is the digamma function. For the AG calculation, which is to first order in the Born approximation for the impurities, we have

$$\tau_s^{-1}=nN(0)\,s(s+1)\int[J(\rho-\rho')]^2\,d\Omega\,.$$

Later several theorists[4-6] showed that whenever a strong perturbation breaks time-reversal symmetry (or causes a spatial variation of the order parameter) it tends to depair the time-reversed electron states which couple and condense to form the superconducting state. This pair breaking entails a lifetime effect on the Cooper pairs and the perturbation can be described by the spin-flip scattering rate $\tau_s^{-1}$. In many regions this $\tau_s$ has the same effect on the Green's function, and hence on the thermodynamic properties, as $\tau_s$ derived by AG. Therefore, to calculate the reduction of $T_c$, one can find the effective $\tau_s$ for the particular perturbation and place it in Eq. (1).

In Refs. 4-6, the value of $\tau_s^{-1}$ for several different pair breakers and the constraints on applicability are tabulated. When generalizing Eq. (1) to other perturbations, it is usually written as

$$-\ln\left(\frac{T_c}{T_{c0}}\right)=\Psi\left(\frac{1}{2}+\frac{T_{c0}}{2\pi T_c}\,\frac{\alpha}{\alpha_{cr}}\right)-\Psi\left(\tfrac{1}{2}\right). \qquad (2)$$

Here $\alpha_{cr}$ is the value of the pair breaking necessary to reduce $T_c$ to 0. This transcendental equation defines a universal function relating the re-

duced perturbation strength to the reduced transition temperature:

$$\alpha/\alpha_{cr} = U_n (T_c/T_{c0}) \ . \tag{3}$$

One should not be confused as to what is the dependent variable. For the case of magnetic impurities, we usually describe $T_c$ as a function of $\alpha$ (proportional to concentration), while convention usually describes critical field as a function of temperature.

Since pair breaking involves scattering and is a lifetime effect, we would expect the effect of two or more perturbations to be additive in the reciprocal of the scattering time[5-7]

$$1/\tau_s = 1/\tau_{s1} + 1/\tau_{s2} + \cdots \ , \tag{4}$$

if $\tau_s$ is frequency independent and each pair breaker is independent of all of the others. The addition is not valid, for instance, if the scattering from the impurities is strongly influenced by an applied field. In terms of $\alpha$, Eq. (4) becomes

$$\alpha/\alpha_{cr} = \sum_i (\alpha/\alpha_{cr})_i \ . \tag{5}$$

Conceptually the experiment we have in mind is very simple. We note that the upper critical field is a valid pair breaker in the "dirty" limit ($l \ll \xi$), with the reduced pair-breaking parameter given by $H_{c2}(T)/H_{c2}(0)$. Then we consider two experiments: first a critical-field experiment on a pure "dirty" superconductor, and second a critical-field study of the same superconductor with a small amount of magnetic impurities present. We see from Eq. (3) that for a given $T_c/T_{c0}$ the strength of the pair breaking is the same. For case (i), we have

$$\frac{\alpha}{\alpha_{cr}} = \frac{H_{c2}(T)_{pure}}{H_{c2}(0)_{pure}} = U_n \frac{T}{T_{c0}} \ .$$

For case (ii), we have

$$\frac{\alpha}{\alpha_{cr}} = \frac{H_{c2}(T)_{alloy}}{H_{c2}(0)_{pure}} + \left(\frac{\alpha(T)}{\alpha_{cr}}\right)_{imp} = U_n \frac{T}{T_{c0}} \ .$$

Therefore, we have

$$\left(\frac{\alpha(T)}{\alpha_{cr}}\right)_{imp} = \frac{H_{c2}(T)_{pure}}{H_{c2}(0)_{pure}} - \frac{H_{c2}(T)_{alloy}}{H_{c2}(0)_{pure}} \ . \tag{6}$$

Here $[\alpha(T)/\alpha_{cr}]_{imp}$ is the total pair breaking due to the impurity.

Since there has been some confusion in the published literature as to how to deal with deviations from AG theory, we shall give a general discussion of the relations between $H_{c2}(T)$, $\alpha_{imp}$, and $T_c$ vs concentration.

In the original treatment of AG, the approximations made led to an inverse spin-flip scattering rate ($1/\tau_s = \alpha_{imp}$) which was independent of temperature and linear in concentration. Under these conditions, Eq. (6) shows that the critical field of the alloy is merely that of the pure superconductor minus a constant. This is illustrated in Fig. 1.

There is also the possibility of having temperature-dependent pair breaking. Some instances where this might be a sizable effect would be for magnetic impurities which magnetically order or exhibit the Kondo effect. For temperature-dependent $\tau_s^{-1}$, the deviations from simple multiple pair breaking would show up in the $H_{c2}$ curve as one of the dashed curves ($x$) or ($y$) in Fig. 1. (Here we use the expression "simple multiple pair breaking" to mean the prediction of multiple pair breaking in the case of an AG impurity.)

Using Eq. (6), we can determine $[\alpha(T)/\alpha_{cr}]_{imp}$ from $H_{c2}(T)$. Figure 2(a) shows a schematic plot of $[\alpha(T)/\alpha_{cr}]_{imp}$ for the cases pictured in Fig. 1. If the normalized critical field lies above the AG prediction, the pair breaking is decreasing as temperature is lowered [shown as ($x$)]. Increased pair breaking with lower $T$ is illustrated as ($y$).

In principle a temperature-dependent $\tau_s^{-1}$ can also be measured via studies of $T_c$ vs concentration. Assuming that the total pair breaking can be expressed as a normalized scattering rate per impurity times the number of impurities [i.e., the total pair breaking at a given temperature is linear in concentration, see Eq. (21)] we can use Eq. (2) to find $T_c$ vs $c$. This is shown schematically in Fig. 2(b) for the cases illustrated in Figs. 1 and 2(a).

In order for experimental results to be self-consistent, there must be agreement between $H_{c2}$ data and $T_c$ data. This has not been true in previous studies of the *La*Ce system. Sugawara and Eguchi[1] and Umlauf *et al.*[2] find $H_{c2}$ curves which imply "($y$)-type" behavior and $T_c$-vs-$c$ curves which im-

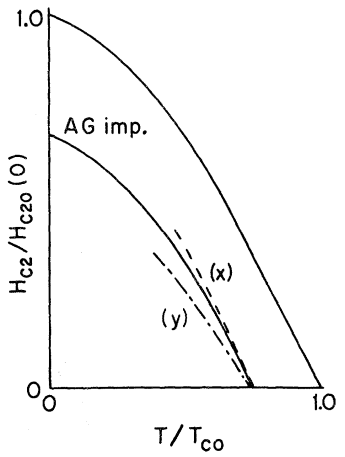


FIG. 1. Normalized critical fields predicted for a pure sample and the same material with magnetic impurities which exhibit temperature-independent (AG) or temperature-dependent ($x$ or $y$) pair breaking.

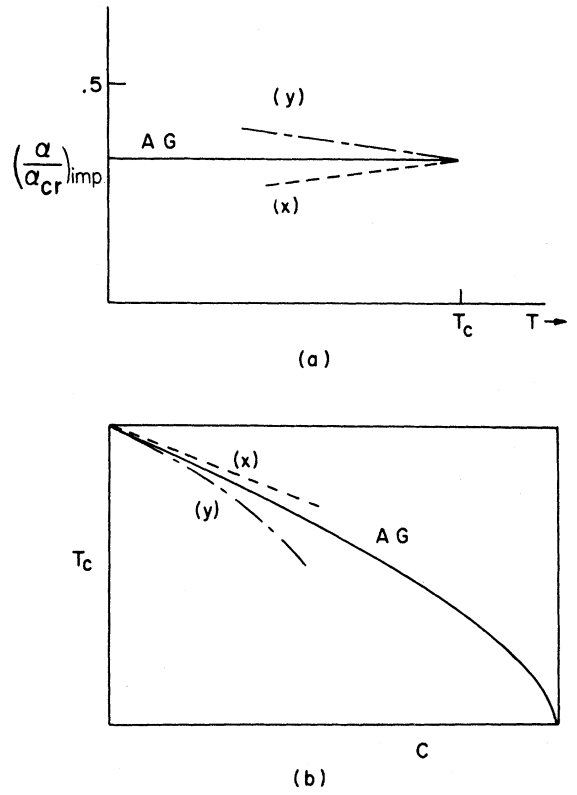


FIG. 2. (a) Total normalized pair-breaking parameter for the impurities shown in Fig. 1. (b) Reduction of $T_c$ for the three types of impurities shown in Figs. 1 and 2 (a).

ply "$(x)$-type" behavior. This is indicative of the presence of an additional effect and is attributable to a nonlinear concentration dependence.

Thus although in the simplest approximation the same information is available from $T_c$ and $H_{c2}$ measurements, in fact the critical-field measurements, done at fixed concentration, are much more useful for determining temperature-dependent effects. However, $T_c$-vs-concentration studies should also be done in order to check for self-consistency. That is to be sure that $(x)$-type behavior [or $(y)$ type] is seen in $H_{c2}(T)$ *and* $T_c$ vs concentration as indicated in Figs. 1 and 2.

There is one more note of caution. The upper critical field is only a "legitimate" pair breaker in the dirty limit. In this region the value of $H_{c2}$ is a very sensitive function of the mean free path $l$; in fact, $H_{c2} \sim 1/l$. Since it is difficult to attain this region ($l \ll \xi_0$) and still keep $H_{c2}(0)$ in the range of a relatively low critical-field superconductor, care must be taken to evaluate $H_{c2}(0)$ as a function of mean free path so that a proper normalization may be obtained.

Most of the previous work has been done on clean samples. In those experiments the sample resistances (hence mean free path) are due almost entirely to the addition of the magnetic impurities themselves. The normalization is then impossible as the impurity resistivity contains two parts, one due to potential scattering and the other from the spin scattering. The potential term tends to decrease $l$ and modified $H_{c2}(0)$. The role of the spin contribution to $l$ is less well understood. Since the separation of the two terms and their respective effects on the resistivity cannot be accomplished (indeed the resistivity due to the impurities is even changing with temperature), the only "out" lies in dominating the scattering with lattice imperfections. We have done this, and hence found a way to normalize our critical-field data so that we may carry out the subtraction in Eq. (6) to determine $[\alpha(T)/\alpha_{cr}]_{imp}$. Previous experiments are not amenable to this analysis.

To illustrate the usefulness of this technique, we have measured the temperature-dependent spin-flip scattering rate $\tau_s^{-1}(T)$ of *La*Ce via the critical-field procedure described above. Resistivity minimum and other anomalies reported indicate that *La*Ce is a Kondo system and should exhibit temperature-dependent depairing in the superconducting state. *La*Gd was also studied for comparison and to see the effects of the large exchange field which leads to ordering at lower temperatures than those studied here.

## II. SAMPLE PREPARATION

The main disadvantage of working with lanthanum alloys is that two phases having different superconducting properties are stable at room temperature.[8] The $\alpha$ phase is hexagonal close packed with a double-layer packing *abac* (dhcp) and is stable below 260 °C. The $\beta$ phase which is fcc exists from 260 to 864 °C. Experiments to stabilize the $\beta$ phase to low temperatures by quenching were tried by several other experimenters, but there always remained approximately 10% of the low-temperature $\alpha$ phase. It was therefore decided to use the $\alpha$ phase for the main body of experiments.

The samples were prepared from 99.9 to 99.99% pure lanthanum, cerium, and gadolinium obtained from Research Chemicals. The ingots were cut, cleaned, weighed to the appropriate concentrations, and then arc melted in an argon arc furnace and turned over six to ten times. The alloys were then cut into smaller chips and extensively cold rolled to a thickness of approximately 0.0015 in. Then the foils were placed in a vacuum furnace at $2 \times 10^{-5}$ Torr and annealed at below 200 °C for from $\frac{1}{2}$ h to a week. The purpose of the cold rolling was threefold. At room temperature any cold working greatly promotes the $\beta$-to-$\alpha$ transformation as the structures are quite close.[9,10] The extensive rolling produces a great deal of imperfections and dis-

locations resulting in a high-resistivity, low-resistivity ratio and short mean free path at low temperatures (bringing the samples close to the "dirty limit"). The thinness of the foils provides a small cross-sectional area and allows us to easily introduce high current densities to determine the upper critical field.

The transition temperature of $\alpha$-La is 4.9 K, whereas that of $\beta$-La is 5.9 K.[10] In all of the $H_{c2}$ experiments described below the runs were made with six samples, two of pure La, two of the same *La*Ce alloys, and two of the same *La*Gd alloys. All the samples used in the same run were arc melted, cold rolled, and, most importantly, annealed in the same manner. The annealing of the six samples for each run was done in one quartz vacuum tube so that the heat treatment would be identical. In the analysis which follows, only $\alpha$-phase samples are included as determined by the $T_c$ of the La foils. This was found to be $4.9 \pm 0.1$ K at very low currents and about 4.6 K for currents of the order of $10^3$ A/cm$^2$ comparable to the current densities used to determine $H_{c2}$. In several cases the annealing temperature was allowed to drift above 200 °C, up to approximately 230 °C. The La foils at high current density were then found to have a $T_c$ of 5.4 K, indicating a sizable percentage of $\beta$ phase present.

The lanthanum-cerium[11] phase diagram shows complete solubility in both the $\alpha$ and $\beta$ phase. The lanthanum-gadolinium[11] system is much more complicated, but a solid solution of up to 58% gadolinium in lanthanum is stable up to 200 °C. Several authors have commented that addition of Gd and Ce tends to stabilize the high-temperature $\beta$ phase. We are dealing with very small concentrations of the magnetic impurities, and the depression of $T_c$ with concentration agrees more with the $\alpha$-phase La alloys in the published literature. We therefore expect that all of the alloys are in the $\alpha$ phase when the pure La treated in the same way shows a $T_c$ of about 4.6 °K.

## III. EXPERIMENTAL PROCEDURE

The La and alloy foils were then cut into strips approximately 1 cm long by 0.5 mm wide, placed on a glass slide. Four wires were indium soldered on for the four-probe resistance measurement to determine the transition. The slide was placed on a copper block, thermally anchored to it with Apiezon N grease, and the low-temperature apparatus with sample, heaters, leads, and germanium temperature resistors was then lowered into a Dewar. The apparatus is so commonly used and the results so little dependent on the design that it will not be described further. For all of the measurements at less than 4.2 K the samples were completely submerged in liquid helium. The temperature was controlled by pumping on the helium bath and regulating the pressure with a Cartesian manistat. The temperature was measured by a Wallace-and-Tiernan gauge or a McLeod gauge monitoring the helium vapor pressure at the top of the Dewar and corroborated with the resistance of a germanium thermometer. The temperature could be measured and controlled to better than 1 mdeg in the range 4.2–1.1 K. For measurements above 4.2 K the helium bath was allowed to fall below the level of the copper block, which would then warm up at a very slow rate in the helium vapor. The temperature was then measured with the germanium resistors. Since the vapor provided cooling for very small amount of power, only transition temperatures were measured above 4.2 K, and to do this minute current densities were used.

The magnetic field was provided by a Varian magnet controlled by a Fieldial magnetic field regulator which features a feedback controller utilizing a Hall probe measurement of the strength of the field. The magnet was rotatable, allowing the field to be positioned parallel or perpendicular to the foils in the Dewar. The accuracy of the setup was better than 1% up to 12 500 G.

The measurements were taken by stabilizing the samples at a fixed temperature, passing a fixed current through a foil, and monitoring the voltage drop as the field was swept through the critical-field region. A typical set of recorded resistance-vs-field plots is shown in Fig. 3. The widths of the resistive transition with field are of the order of 10% (probably owing to the inhomogeneity in distribution of lattice imperfections, rather than impurity concentration, as the widths are also characteristic of the pure lanthanum samples). Note that the critical field for each current density was consistently taken as an extrapolation of the linear part of the transition curve to the value at which the resistance is zero (illustrated in Fig. 3). This tends to favor the lowest $H_c$ and $T_c$ of a smeared transition, and together with the high critical current densities corresponding to the values chosen for $H_{c2}$ (see later discussion) explains why the $T_c$ of our samples of pure lanthanum falls below that in the previously published literature.

## IV. DETERMINATION OF $H_{c2}$

For an infinite uniform superconductor the upper critical field is the point at which the resistance goes sharply finite and the magnetization goes to zero (with zero slope). Experimentally, this situation is much less clearly defined. The complications involve the existence of surface superconductivity at fields considerably higher than $H_{c2}$, in a region of order the coherence length from the surface, on planes parallel to the applied field. This surface superconductivity is quenched at $H_{c3}$

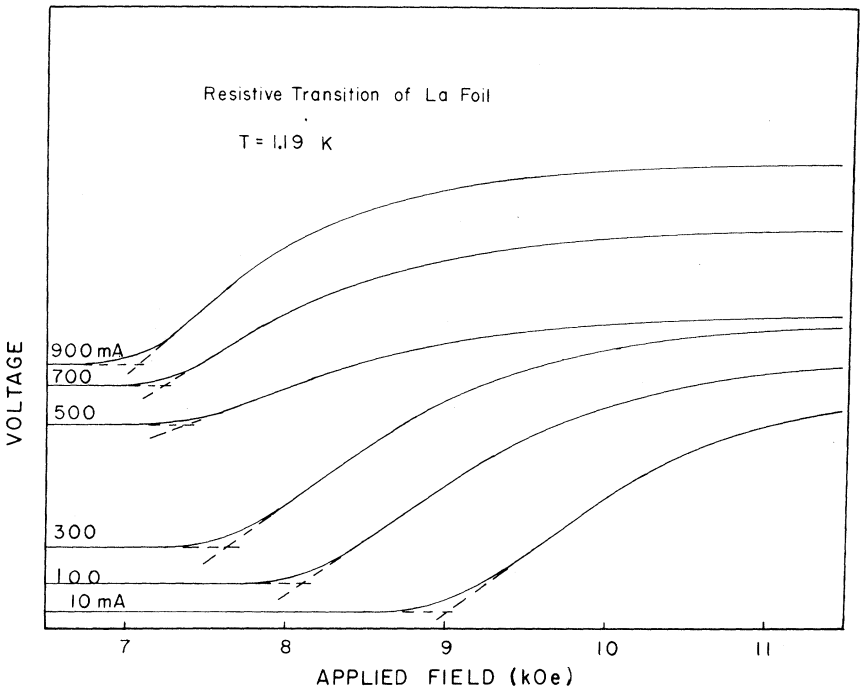


FIG. 3. Resistive transitions of pure La foils (displaced for different currents). The dashed lines exhibit the construction used to determine the critical field at each current.

$\approx 1.69 H_{c2}$.[12] Although $H_{c3}$ is a legitimate pair breaker, it is very difficult to measure experimentally; thus it must be separated out when measuring $H_{c2}$. Two methods are commonly employed [13,14] using high current densities (that cannot be carried with zero resistance in the surface layer) and placing the field perpendicular to the foils so that only the edges can remain superconducting above $H_{c2}$. Unfortunately, for very "dirty" superconductors such as we are dealing with, even this is not enough and studies of current vs $H$ must be taken to unambiguously determine $H_{c2}$.

The first study done was the critical fields in the perpendicular and parallel directions for several alloys, temperatures, and currents. The parallel $H_{c2}$ was consistently found to be 10–15% larger than the perpendicular field as expected. Fortunately, the perpendicular-field measurements showed a definite resistive onset at a reasonable value, indicating the absence of flux-flow resistance. This was due to the great number of imperfections which act as pinning sites for the flux lines. All of the results reported here were taken with the field perpendicular to the foil.

The actual determination of $H_{c2}$ was then taken from the characteristic rapid drop of the critical current at the upper critical field. This method has been shown to be valid by several authors previously (by comparing this criterion with the measurements of magnetization and susceptibility[14,15]). Our plots are most similar to those of the authors of Ref. 15, who have investigated dirty transition-metal foils produced by cold rolling. For several samples the $I$-vs-$H$ plots were taken over a range of current densities from 1 to $10^4$ A/cm$^2$. However, after the initial bendover at high currents the log $I$-vs-$H$ curves were generally straight lines and the great majority of data were thus taken between $10^2$ and $10^4$ A/cm$^2$. In Fig. 4, we have plotted $\log_{10} I$ vs $H$ for a typical set of samples from one run, with constant temperature. Included are the data derived from Fig. 3.

After studying the critical current curves, it was determined that $H_{c2}$ corresponded to a current density of about $10^3$ A/cm$^2$ and that the field could be most consistently measured [with least scatter in the $H_{c2}(T)$] by merely selecting the resistive transition at this current for all temperatures. Using other criteria to determine $H_{c2}$ from the plots resulted in slight proportional shifts in the magnitude of the critical field, without affecting the functional form of the temperature dependence.

## V. REDUCED CRITICAL FIELD OF La MEAN-FREE-PATH DEPENDENCE

The determination of the impurity pair breaking is carried out in terms of reduced parameters as in Eq. (6). It is therefore necessary to normalize the measured $H_{c2}(T)$ by the value at $T=0$. The AG theory is strictly valid only when describing the critical field of a superconductor in the dirty limit ($l \ll \xi_0$). In that case, $H_{c2}(0)$ is inversely proportional to the transport scattering time $\tau_{tr}$. We can measure the relative values of $\tau_{tr}$ by the resistivity

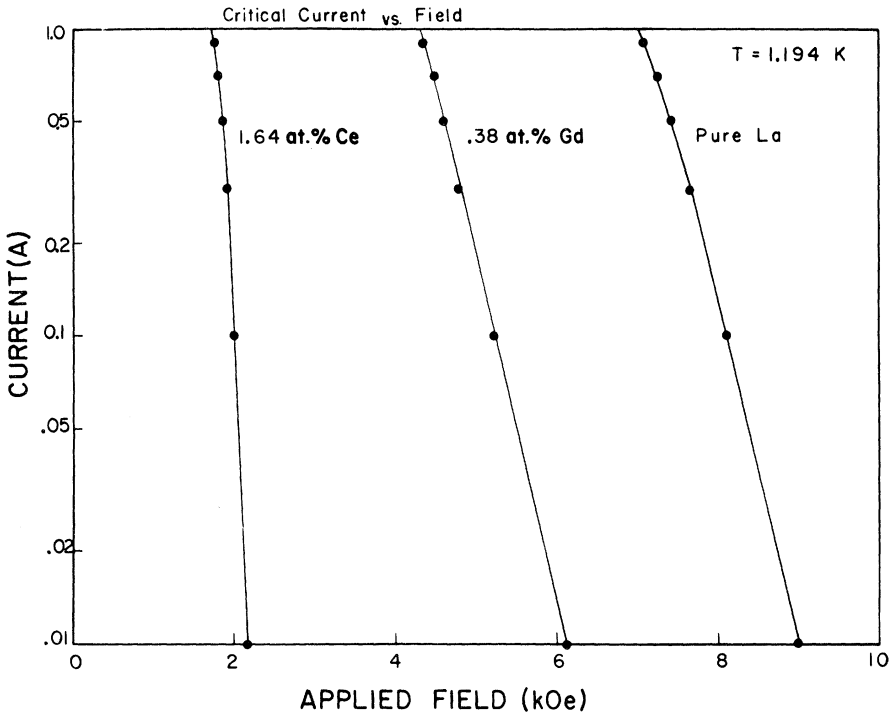


FIG. 4. Log$I$ vs magnetic field for a pure sample and alloys with Gd and Ce impurities. The linear drop of the log of the critical current with applied field, after a less drastic dependence at lower fields, is indicative of the upper critical field of a type-II superconductor.

ratio $\rho$ defined as

$$\rho = (\text{resistance at 300 K})/(\text{resistance at 4.2 K})$$

and we should find $H_{c2}(0)$ proportional to $1/\rho$.

In Fig. 5, we have plotted $H_{c2}(1.4\ \text{K}, \rho)$ vs $\rho$. [Since we are only interested in the relative magnitudes of the curves, we assume that $H_{c2}(T, \rho)$ has the same temperature dependence for different $\rho$ (see Fig. 6 and argument below) and we therefore set

$$H_{c2}(1.4, \rho)_{\text{La}} = 0.8463\ H_{c2}(0, \rho)_{\text{La}},$$

where

$$0.8463 = \frac{U_n(1.4/4.56)}{U_n(0)}$$

and $T_{c0} = 4.56$ K for our pure La samples.] We see that we are not quite in the dirty limit but rather in the region where the mean free path goes from

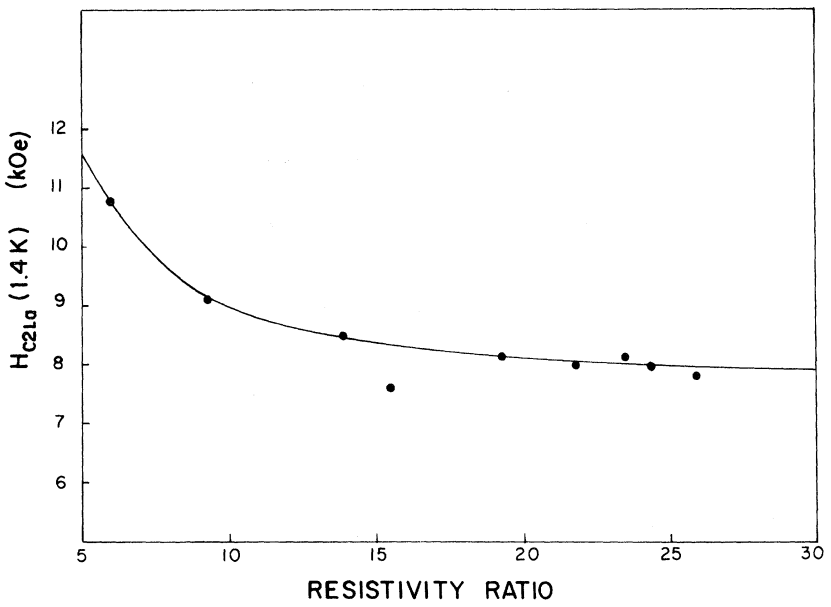


FIG. 5. Measured value of the critical field at 1.4 K for pure lanthanum foils of varied resistivity ratios.

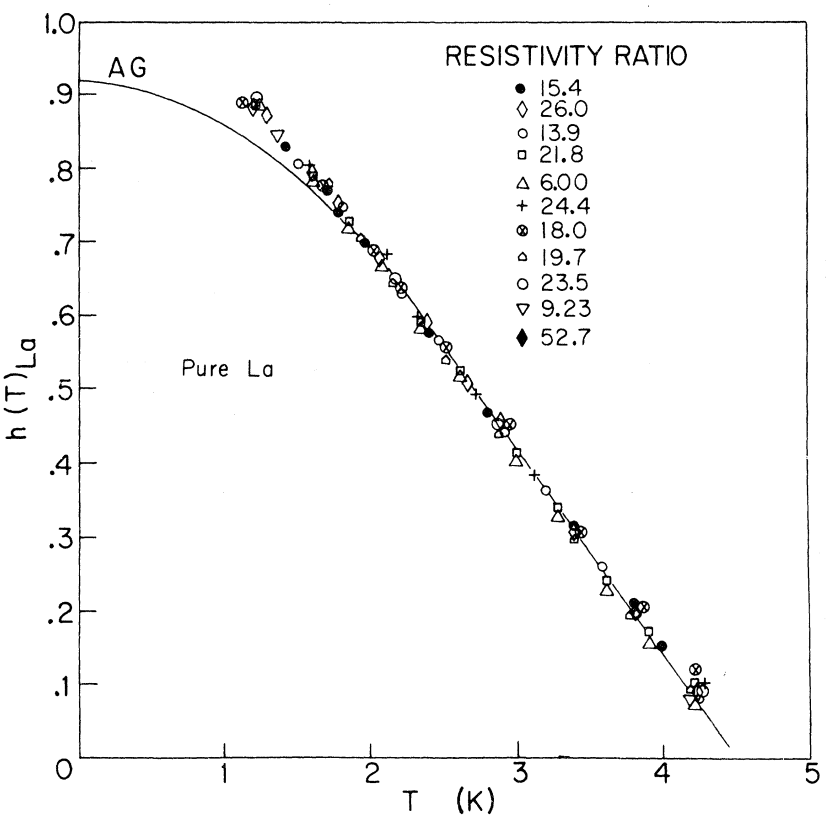


FIG. 6. Reduced critical field of pure La foils for many different values of resistivity ratio as defined in Eq. (7). The solid line is the prediction of the pair breaking or AG equation fit at two points.

longer than the coherence length to shorter. Although we are not strictly in the limit of direct applicability of the AG theory, we are close. Helfand and Werthamer[16] have calculated the *reduced* upper critical field and find that the dependence on $l$ is very slight and that temperature dependence is very near AG-theory behavior.

In Fig. 6, the measured value of the reduced critical field

$$h(T) \equiv \frac{H_{c2}(T,\ \rho)_{\mathrm{La}}}{0.8463\, H_{c2}(1.4\,K,\ \rho)_{\mathrm{La}}} \qquad (7)$$

has been plotted for the experimental range of resistivity ratios. As expected, the critical fields all normalize to the same curve with no systematic dependence on $\rho$. We have thus taken the curve from Fig. 5 as the functional dependence of $H_{c2}(0)$ on $\rho$ and have used these values to normalize the critical fields of the alloys as is required in Eq. (6).

The measured reduced critical field of the pure lanthanum described almost a straight line as temperature was varied, in marked contrast to the pair-breaking curve, plotted as the solid line in Fig. 6. Surawara and Eguchi[1] also found a straight-line behavior (lying above the curve of AG) for the $H_{c2}(T)$ of lanthanum samples with resistivity ratios much higher than ours, as did Umlauf *et al.*[2] (whose work was also in the clean limit). Several other systems tend to remain superconducting at fields higher than that predicted by AG, in particular niobium and vanadium among the elements. The strong-coupling effects seem to give a correction of at most 2%.[17] At present it is assumed that this anomalous behavior, which creates discrepancies of up to 15%, is due to band structure and anisotropy of the Fermi surface.[18] Since we are adding only very small percentages of impurities, it is doubtful that we are significantly changing these effects. *We therefore take Fig.* 6 *to determine a new universal function for the lanthanum system being studied.* This amounts to saying that we may use Eq. (6) directly, rather than attempting to fit the observed pure critical field with an AG curve from which one would subtract $H_{c2\,\mathrm{alloy}}$. The latter procedure is clearly incorrect if one wishes to determine $\tau_s^{-1}(T)$ due to impurities!

## VI. REDUCED CRITICAL FIELD OF *La*Ce AND *La*Gd

Since each of the different alloy foils studied had a different concentration as well as a different resistivity ratio, the normalization procedure was not as direct as that used for the pure La. As mentioned above, the method used was to measure the resistivity ratio and then take the interpolated results from Fig. 5 for $H_{c2}(1.4\ \mathrm{K},\ \rho)$ of pure lanthanum. The reduced critical field of the alloy is

then defined as

$$h(T)_{\text{alloy}}=\frac{H_{c2}(T,\rho)_{\text{alloy}}}{0.8463\,H_{c2}(1.4\,K,\rho)_{\text{La}}} \tag{8}$$

and Eq. (6) then becomes

$$[\alpha(T)/\alpha_{\text{cr}}]_{\text{imp}}=h(T)_{\text{La}}-h(T)_{\text{alloy}}\,. \tag{9}$$

The normalized upper critical fields $h(T)_{\text{alloy}}$ measured and calculated using (8) are shown in Fig. 7 for *La*Ce and Fig. 8 for *La*Gd.

There are two characteristic differences between the sets of data for the Ce and Gd impurities. The *La*Ce curves tend to remain linear in shape throughout the measured range (much as did the pure lanthanum). However, the slope of these straight lines is strongly dependent on concentration with a smaller negative slope for higher concentrations. The *La*Gd curves all exhibit a turnover at low temperatures and have only a small change in slope at the transition temperature of the alloy. Both sets of critical fields differ markedly from the AG prediction illustrated in Fig. 1, implying that neither are "simple" AG-type magnetic impurities. At temperatures close to $T_c$ of the alloy, the behavior of the gadolinium impurities is closer to that expected from a temperature-independent contribution to the spin-flip scattering.

Although *La*Gd was one of the original systems studied and in fact prompted the calculation of AG, it was soon realized that a simple treatment was not sufficient. The source of the difficulty is that the gadolinium impurities magnetically order, presumably via an induced conduction-electron polarization as envisioned by Ruderman-Kittel-Kasuya-Yosida (RKKY).[19] The consequences of the ordering are primarily twofold. First, the electrons see a large effective internal field which can act as a Pauli paramagnetic pair breaker. Second, the ordering of the magnetic impurities reduces some of their degrees of freedom and hence the spin-flip scattering is decreased.

The *In*$La_3$Gd system has been extensively studied by Crow[19] and sheds some light on the *La*Gd data. At low temperatures there is a very large depression of the field with respect to the behavior of an AG impurity, until at concentrations of order 1% the field actually becomes reentrant, having gone through a maximum. Crow finds good qualitative agreement with the calculation of Bennemann, who has treated the effects of ordering and exchange fields in the dirty limit. Bennemann's theory[20] predicts the following behavior:

$$\ln\left(\frac{T_c}{T_{c0}}\right)+\frac{1}{2}\left[\left(1+\frac{b}{(b^2-I^2)^{1/2}}\right)\Psi\left(\tfrac{1}{2}+\rho_-\right)+\left(1-\frac{b}{(b^2-I^2)^{1/2}}\right)\Psi\left(\tfrac{1}{2}+\rho_+\right)\right]-\psi\left(\tfrac{1}{2}\right)=0\,,$$

$$\rho_\pm=(1/2\pi T_c)\left[a\pm(b^2-I^2)^{1/2}\right]\,,$$

$$a=\frac{2(s)(s+1)-sB_s(\beta s\omega_1)(\tanh\tfrac{1}{2}\beta s\omega_1+\coth\tfrac{1}{2}\beta s\omega_1)}{2s^2\tau_{ex2}}+\frac{1}{b\tau_{so}}+\frac{\tau_{tr}V_F^2 e H_{c2}}{3}\,,$$

$$b=\frac{sB_s(\beta s\omega_1)(\tanh\tfrac{1}{2}\beta s\omega_1-\coth\tfrac{1}{2}\beta s\omega_1)}{2s^2\tau_{ex2}}+\frac{1}{b\tau_{so}}\,, \tag{10}$$

$$I=nJ(0)\langle s_z\rangle+H_{c2}=nJ(0)\,sB_s(\beta s\omega_1)+H_{c2}\,,$$

$$\omega_1=g\mu_B H_{c2}+\omega_1'\,,$$

where $\omega_1'$ is the molecular field due to the indirect spin-spin interaction and $\tau_{ex2}$ (the exchange scattering time) and $\tau_{so}$ (the spin orbit scattering time) are given by

$$1/\tau_{ex2}=n\pi N(0)\langle J^2(0)\rangle s^2\,,$$
$$1/\tau_{so}=n_{so}\pi N(0)\int|J_{so}(\theta)|^2\sin\theta\,d\Omega\,. \tag{11}$$

We first note that the equations above are much more complicated and the pair breakers more interdependent than is given by the simple universal function for multiple pair breakers [Eqs. (3) and (5)]. This is due to the strong dependence of both the Pauli paramagnetic term ($I$) and the spin-flip scattering term ($a$) on both temperature and applied field. If we expand in terms of $I^2/b^2$ and keep only the lowest-order contribution (implying the Pauli paramagnetic term is small compared to the others) we find that the pair breakers are additive in this limit and we can write

$$\frac{\alpha}{\alpha_{\text{cr}}}\approx\frac{\tau_{\text{scr}}}{\tau_s(T)}+\frac{H_{c2}(T)}{H_{c2}(0)}+\left(\frac{H_{\text{eff}}}{H_{p0}}\right)^2\,, \tag{12}$$

where $H_{\text{eff}}$ is the total effective internal field seen by the conduction electrons and $H_{p0}$ is the Pauli pair-breaker field which produces $T_c=0$ in the absence of any other perturbations. The Pauli term comes from the antiparallel electron spin pairing in the superconducting state. Clogston[21] and others[22] have pointed out that in the limit of

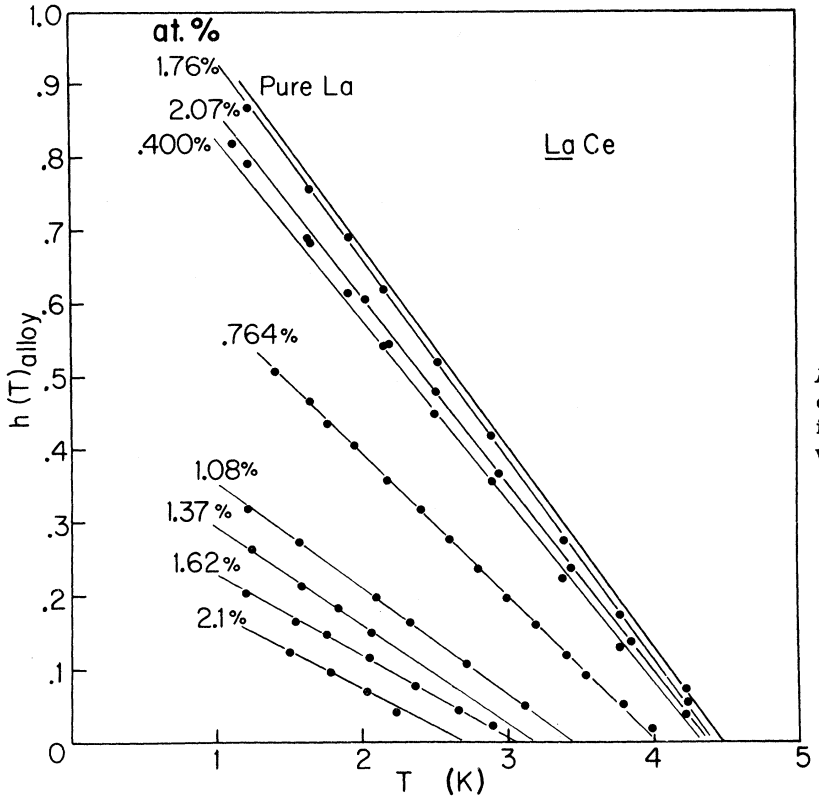


FIG. 7. Reduced critical field of *La*Ce alloys defined by Eq. (8). The concentrations written next to the curves indicate the nominal concentrations to which the alloys were prepared.

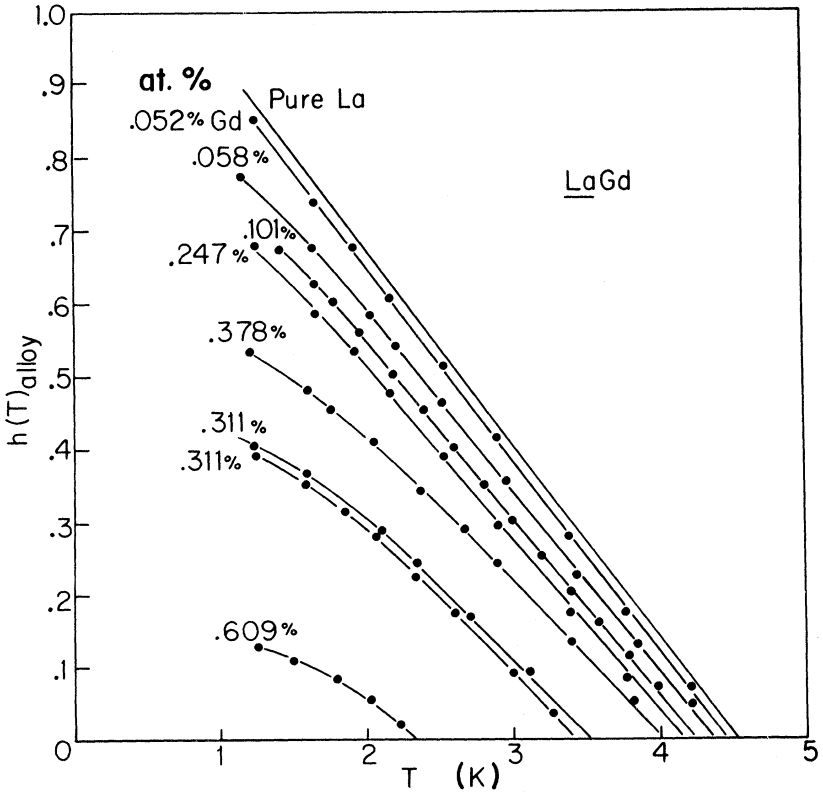


FIG. 8. Reduced critical field of *La*Gd alloys defined by Eq. (8) for several nominal concentrations.

very high $H_{c2}$ the critical field would be determined by the difference in free energy caused by the spin paramagnetism of the normal state which is absent in the superconductor. A simple calculation gives the order of magnitude of the critical value of the Pauli field $H_{p0}$:

$$\tfrac{1}{2}\chi_{\text{Pauli}} H_{p0}^2 = F_N - F_s = \tfrac{1}{2} N(0)\Delta^2 \quad . \tag{13}$$

Since $\chi_{\text{Pauli}} = 2\mu_B^2 N(0)$, and assuming $g=2$, we find

$$(\mu_B H_{p0})^2 = \tfrac{1}{2}\Delta^2 = \tfrac{1}{2}(1.7 s k T_c)^2$$

or

$$H_{p0} \approx 18\,400 T_c \text{ G} . \tag{14}$$

When spin-orbit coupling is considered the time-reversed states are no longer pure-spin eigenstates, but are a combination of spin and orbital angular momentum. In this case the superconducting state can have some Pauli paramagnetism and $H_{p0}$ thus increases as spin-orbit scattering increases, explaining the presence of $\tau_{so}$ in Eq. (10).

Usually the Pauli term is only considered important in very-high-field superconductors, as is seen from the magnitude of $H_{p0}$ in (14) and the fact that the pair breaking goes as $(H/H_{p0})^2$ as in (12). However, in the $La$Gd alloys, because of their large spin ($S=\frac{7}{2}$) the Gd impurities produce a large exchange field even in a modest applied field. This must be taken into account, since $H_{eff}$, which is written as $I$ in Eq. (10), consists of the sum of the applied and exchange fields:

$$H_{eff} = H_{c2} + H_{exc} . \tag{15}$$

For computational purposes we write

$$H_{exc} = (nJs/g\mu_B) B_s(g\mu_B H/K_B T) , \tag{16}$$

where $n$ is impurity concentration and $H$ is the field seen by the impurity atoms. It should be noted that the impurity aligns in the applied field and the field produced by the polarization of the conduction electrons, which is approximately equal to $H_{exc}$ times $J/E_F$. That is, an electron "sees" an exchange field due to one impurity which is proportional to $J$ and becomes polarized to order $N(0)J$ (or $J/E_F$) and hence produces an effective field at a second impurity (via exchange), which is of order $J^2/E_F$. Although this mechanism (actually with the spatial dependence given by RKKY oscillations) produces the magnetic order evident at lower temperatures in $La$Gd, we are high above the ordering temperature so that $(J/E_F)H_{exc}$ is far less than the applied field; hence we take $H \approx H_{c2}$. The highest concentration of Gd used here is 0.6%, which would order at approximately 0.3 K.[19]

Although we are far above the ordering temperatures we still must consider the effect of the applied field on the reduction of the spin-flip scattering. The first term in (12) can be calculated using

$$\tau_s^{-1}(T) \approx (a-b)$$

$$= [s(s+1) - s B_s(\beta s\omega_1)\tanh\tfrac{1}{2}\beta s\omega_1] \times n\pi N(0)\langle J^2(0)\rangle , \tag{17}$$

which comes from the expansion in $I^2/b^2$. This can contribute up to four-percent corrections in our data, but would tend to increase the critical field by decreasing the pair breaking of the impurity. To fit our data, the leading correction to the AG behavior thus must come from the Pauli pair breaking.

Taking the exchange interaction $J$ as 0.048 eV from Sugawara and Eguchi[1] we find for $La$Gd

$$H_{exc} = n(1.45\times 10^4) B_{7/2}(0.470 H_{c2}/T) \text{ kG} , \tag{18}$$

where $H_{c2}$ is in kilogauss and $T$ in degrees Kelvin. Putting in the observed values of $H_{c2}(T)$ for several of the samples we found exchange fields of up to 23 300 G in applied fields of 5340 G. The effective field is then 28 640 G and comparing this to $H_{p0}$ which is 84 kG for our La sample, from Eq. (14), we find that

$$(H_{eff}/H_{p0})^2 \lesssim 0.12 . \tag{19}$$

This shows that the Pauli paramagnetic pair breaking is sizable and of order 10%, in agreement with the departure from linearity of the reduced curves shown in Fig. 8. However, since we are not truly in either the dirty limit or in the limit of very small $I^2/b^2$, the full determination of the critical field of $La$Gd cannot be made from the simple additivity of pair breakers as in (12). The reduced critical field does not contain the information necessary for this analysis as the terms $I$, $a$, and $b$ depend on the actual magnitude of applied field at the transition and in fact even the spin-flip scattering is probably reduced in the presence of the field [see Eq. (17)]. A numerical computer fit to the data might yield quantitative agreement with Eqs. (10) but has not been undertaken.

The main results of the $La$Gd study are that the Pauli paramagnetic effects are sizable even in a low $H_{c2}$ superconductor, but with large exchange fields from magnetic impurities (this has previously not been reported). A quantitative evaluation of the magnitude of these effects is in agreement with theory. We also see that non-Kondo impurities do not strongly effect the slope of the $H_{c2}$ curves at $T_c$.

For the case of $La$Ce we can use the published value of $J$ from Ref. 1 to calculate the exchange field with the result

$$H_{exc} = -n(0.229\times 10^4) B_{1/2}(0.0671 H_{c2}/T) \text{ kG} , \tag{20}$$

$$J = -0.053 \text{ eV} .$$

Putting in the numbers from our data we find that the largest exchange field is $-6200$ G in an applied field of 3520 G, resulting in a total internal effective field of $-2680$ G. This is an order of magnitude below that present in the *La*Gd samples. Since the pair-breaking parameter is proportional to $(H_{\text{eff}})^2$ we are down by better than two orders of magnitude from the *La*Gd case. The Pauli paramagnetic term is thus negligible (about 0.1% effect) for *La*Ce. As can be seen from Eq. (16) the reason for such a small internal field is that the spin of Ce in La is $\frac{1}{2}$, whereas that of Gd is $\frac{7}{2}$. The ordering temperature of our most concentrated sample of *La*Ce is about 0.2 K and we can therefore disregard the freezing out of the Ce spins by magnetic order in the temperature region of our experiments. Using Eq. (17) with our data, we find a correction of less than $\frac{1}{2}\%$, when the combined effects of the internal and applied fields are included.

It should be pointed out, however, that for lower temperatures the "freezing out" of the spin-flip scattering and of the Kondo effect becomes increasingly important. In the experiments of Umlauf *et al.*[2] and Wollan and Finnemore[23] where $H_{c2}$ of *La*Ce is measured well below 1 K the Kondo effect is swamped by this reduction of $\tau_s^{-1}$, preventing the field from becoming reentrant and also preventing any simple analysis.

Thus for *La*Ce above 1 K, the complicating effects predicted by Bennemann are very small and we should be able to evaluate our data in terms of simple-multiple-pair-breaking theory as in Eq. (9). Unfortunately, the scattering time for a Kondo impurity is energy as well as temperature dependent and the additivity does not strictly hold. However, it is still useful to define an effective spin-flip scattering time averaged over frequencies (but with more weight at low frequencies) which when normalized is defined equal to $[\alpha(T)/\alpha_{\text{cr}}]_{\text{imp}}$ in Eq. (9) and is almost the same effective pair breaker which would appear if the Kondo impurity were the only perturbation. Our preliminary analysis and results have been published elsewhere.[24]

## VII. EVALUATION OF SPIN-FLIP SCATTERING TIME $\tau_s^{-1}(T)$

Since the impurity-impurity interactions which could cause magnetic ordering are negligible in the *La*Ce, we would expect $(\alpha(T)/\alpha_{\text{cr}})_{\text{imp}}$ to be directly proportional to the Ce concentration. We then define

$$[\alpha(T)/\alpha_{\text{cr}}]_{\text{imp}} \simeq nF(T)\,, \tag{21}$$

where $F(T)$ is the pair breaking per impurity and contains the temperature dependence that we wish to measure. Carrying out the subtraction in Eq. (9) we then match the values of $[\alpha(T)/\alpha_{\text{cr}}]_{\text{imp}}$ at 1.4 K for the different samples. This normalization defines our effective relative concentrations $n_{\text{eff}}$, which are only meaningful if the data for different concentrations then fall on the same curve. (The absolute value of $n_{\text{eff}}$ is then fixed by matching $n_{\text{eff}}$ and $n_{\text{nom}}$ at the 0.764% point, but this is arbitrary, as we will be interested only in the functional form of $T_c$ vs concentration.) $F(T)$ is plotted in Fig. 9 and there is no systematic deviation with effective concentration (note that normalizing to one $T$ value does not ensure this).

The resistivity anomalies observed in Kondo systems are the result of temperature-dependent scattering[25] from both spin-flip and non-spin-flip channels (see Ref. 26). The result is an impurity resistivity which monotonically increases as temperature is decreased.[27] The spin-flip scattering rate (which is what we measure) is not monotonic with temperature, having a maximum at $T_K$ (see Fig. 10). Therefore, if $T_{\text{co}} < T_K$, $\tau_s^{-1}(T)$ should decrease as $T$ is reduced, whereas if we are always in the region above $T_K$, $\tau_s^{-1}(T)$ should increase for lower $T$. Since the basic feature of Fig. 9 is the sharp increase in pair breaking as $T$ goes from 4.2 to 1.2 K, we are obviously well above the Kondo temperature. In this region ($T \gg T_K$) the magnetic resistivity is mostly due to the spin-flip channel. The resistivity of *La*Ce alloys is, in fact, rapidly increasing as temperature is lowered from 4.2 to 1.2 K for our concentration range.[23,28,29]

Experimentally determining $\tau_s^{-1}(T)$ from the resistivity data is essentially impossible, especially in the *La*Ce system where the scattering is dominated by a large contribution from lattice imperfections and phonons. To get the spin-flip scattering rate there, other contributions must be subtracted out. Usually this is done by merely taking the difference between $R(T)$ and $R$ at a specific temperature. Thus the resistivity can give a qualitative picture of $\tau_s^{-1}(T)$ but cannot produce the functional form that can be obtained directly from the $H_{c2}$ measurements. From the resistivity we can see that the scattering is rapidly increasing, in agreement with our data on $[\alpha(T)/\alpha_{\text{cr}}]_{\text{imp}}$. Sugawara and Eguchi[28] claim that the resistance curves imply $T_K$ lower than 0.4 K. Hence $T_{\text{co}} > T_K$, as mentioned above.

Most of the theoretical treatments of the effect of Kondo impurities on superconductivity deal with the relationship between $T_c$ and impurity concentration. The Kondo scattering is included in $\tau_s^{-1}(T)$ and the general form of the AG equation is retained by most authors. In terms of our notation [from Eqs. (21) and (2)]

$$-\ln\left(\frac{T_c}{T_{c0}}\right) = \Psi\left(\frac{1}{2} + \frac{nF(T_c)\,T_{c0}}{2\pi T_c}\right) - \Psi\left(\tfrac{1}{2}\right)\,. \tag{22}$$

The largest effect one would expect from superconductivity on the Kondo scattering is the presence

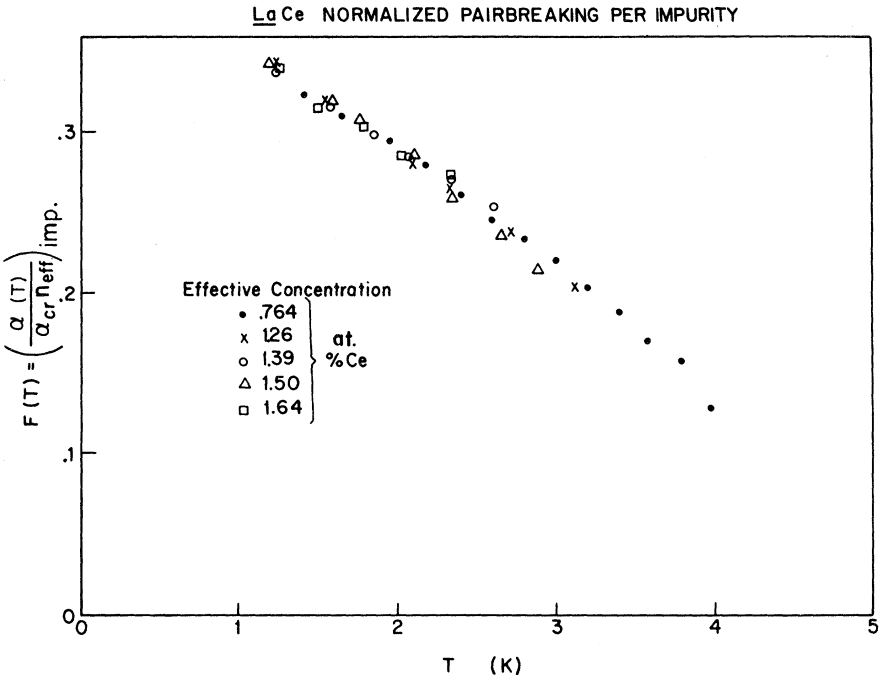


FIG. 9. Normalized pair breaking per impurity of Ce in La for several concentrations. It directly measures the temperature dependence of the spin-flip scattering rate of the cerium impurities.

of the energy gap at the Fermi surface. However, since we have made measurements at the normal-superconducting boundary (either $T_c$ or $H_{c2}$) we are in the highly gapless regime. The temperature-dependent spin-flip scattering should thus be unaffected and the expressions used for $F(T)$ are essentially the same as for the Kondo effect in a normal metal.

The following are some of the functional forms for $F(T)$ which can be found in the literature and which are matched at two points with our experimentally determined $F(T)$ (from Fig. 9). The plots for the different theoretical expressions applied to our data are shown in Fig. 11.

First we try the original Kondo result from second-order Born scattering[30]:

$$F_K(T) \propto [\ln(T/T_K)]^{-1}, \quad T_K \approx 0.23\ \mathrm{K}. \tag{23}$$

Second is the result of a calculation on resonant scattering by Abrikosov[31] which was used in the

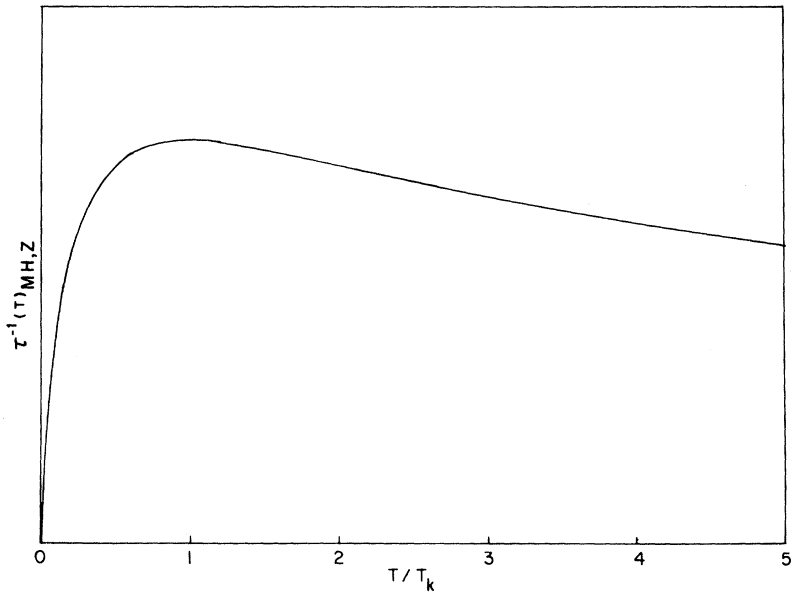


FIG. 10. Functional form of the spin-flip scattering rate at the Fermi energy as a function of temperature from Eq. (26). Plotted vs $\log_{10}T$ the curve would be symmetric about $T_K$.

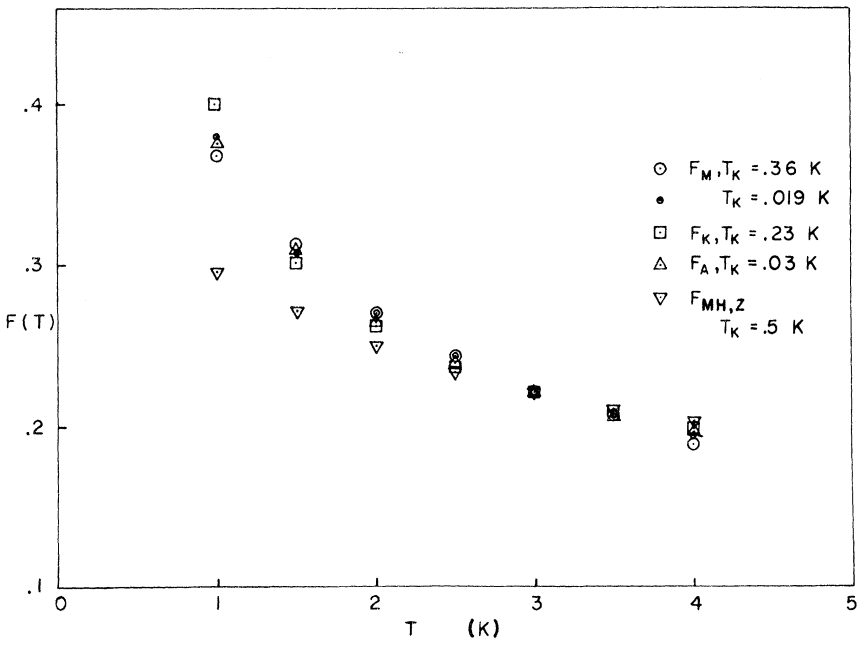


FIG. 11. Different functional forms for the temperature dependence of the spin-flip scattering from theoretical calculations. The different theoretical predictions are given in Eqs. (23)–(26) and are fit to our data (Fig. 10) at 3.0 and 1.2 K.

analysis of some resistivity data on *La*Ce[29] and applied to the superconducting critical field curves of *La*Ce and *La*Gd alloys by Sugawara[1]

$$F_A(T) \propto \frac{1}{[1 - N(0)J\ln(T/T_F)]^2} \propto \ln^{-2}\left(\frac{T}{T_K}\right), \qquad (24)$$

$$T_K \approx 0.03 \text{ K}.$$

Abrikosov's calculation, however, has since been shown to be incorrect.[27] The form used by Maki[32] and Griffin[33] comes from the solution of Suhl's equations and should be valid only for temperatures ranging above $T_K$:

$$F_{M,G}(T) \propto \frac{1}{[\ln^2(T/T_K) + \pi^2(s)(s+1)]^{3/2}}, \qquad (25)$$

$$T_K \approx 0.36,\ 0.02 \text{ K}.$$

The final expression is from the work of Mueller-Hartmann and Zittartz[34] and seems to be the present state of the art of Kondo calculations. It is illustrated in Fig. 10:

$$F_{MH,z} \propto \frac{1}{\ln^2(T/T_K) + \pi^2 s(s+1)}. \qquad (26)$$

Note that this expression cannot be solved for a $T_K$ which produces a rapid enough change in $F$ from 4 to 1 K to do a two-point fit to our data. It is fixed instead to the value at 3 K and $T_K$ is taken as 0.5 K, which produces a maximum slope to the curve in the region of interest.

The theoretical curves do not produce a good qualitative representation of our data. However, the magnitude of the change is fit by Eqs. (23) and (25) with $T_K'$ in the region 0.2–0.4 K, in good agreement with the previous resistivity work.[27] One might try to explain the difference in terms of the effect of the magnetic field on the scattering. Taking $\gamma\mu_B H = KT_K$ or $\gamma\mu_B H = KT$, we find that fields of the order of 2–4 kG in the former or 12 kG in the latter case are necessary to sizably alter the Kondo effect. The field we actually apply is up to 9 kG. Resistivity studies of *La*Ce samples of even higher concentrations than ours remain unchanged in fields up to 12 kG for temperatures greater than 1 deg.[28] Also, if $\tau_s^{-1}(T)$ were strongly field dependent we would not have such consistent results for the different samples (and very different $H_{c2}$) which appear in Fig. 9.

Coqblin and Schrieffer[35] have pointed out that the $s$-$f$ Hamiltonian usually used for calculations relating to *La*Ce is not necessarily valid. The orbital momentum of the cerium atoms may not be quenched and conduction electrons scattering from the total angular momentum $j$ must be considered. They show that there is at least a quantitative difference between their more precise interaction Hamiltonian and the $s$-$f$ exchange model, but that the spin-flip scattering is still strongly temperature dependent. The exact functional form of $\tau_s^{-1}(T)$ has not yet been calculated within the framework of their model.

Recently a great deal of interest has centered on the problem of crystalline-field effects in *La*Ce. It is possible that some of the temperature-dependent spin-flip scattering we have measured is due to the increased population of a low-lying level as temperature is decreased. However, the dominant effect is probably still the Kondo scattering over

this small range of $T$.[36]

## VIII. EXPERIMENTAL SELF-CONSISTENCY OF $\tau_s^{-1}(T)$ DATA, $T_c$ VS CONCENTRATION

If we have truly measured $\tau_s^{-1}(T)$ using the critical field, then the temperature-dependent pair breaking is defined and we can use Eq. (22) to predict the concentration dependence of the critical temperature. Using the experimentally determined functional form of $F(T)$ as shown in Fig. 9, we find the $T_c$-vs-$c$ curve which appears as the solid line in Fig. 12. The effective concentration as calculated from Eq. (21) is also plotted, as are the nominal concentrations. The fact that the effective concentrations (as taken from the magnitude of the scattering measured by $H_{c2}$ and $T_c$) are very close to the predicted concentrations [taken from the temperature dependence of $\tau_s^{-1}(T)$ measured by $H_{c2}$] makes the picture self-consistent and *implies that the pair breaking is additive to the accuracy of the experiment.*

The nominal concentrations plotted are in agreement with the previously published $T_c$-vs-concentration curves,[1,9] and fit a straight line fairly well. In the small temperature region we have used, this behavior is close to that of a typical AG impurity. However, as Sugawara and Eguchi pointed out,[1] the strong depression of $T_c$ by the cerium impurities is not consistent with the accepted value of $J$ ($-0.053$ eV) and spin ($\frac{1}{2}$). At the time of their publication, theorists had only produced a calculation of the initial slope of $T_c$ vs $c$ for a Kondo superconductor. This showed an enhanced depression and Sugawara and Eguchi thus concluded that $La$Ce was a Kondo system. More recent theory[32–34] shows that for $T_{co} \gg T_K$ there is a large deviation from linearity as $T_c$ is reduced. In fact, our results for $N_{eff}$ in Fig. 13 are in good qualitative agreement with the calculation of Mueller-Hartmann and Zittartz for $T_K/T_{co} = \frac{1}{8}$.[34]

The problem which remains is the discrepancy between the nominal concentrations and $n_{eff}$. Unfortunately, a confirming analysis of the concentration in the samples used was not possible, due to the lack of a good microprobe facility. However, the fact that our $T_c$-vs-*nominal*-concentration results agree with Sugawara and Umlauf's data suggests that the reduction of $n_{nom}$ to $n_{eff}$ is a real effect. The probable explanation is impurity interaction. We are at high enough concentration that there is considerable probability of finding cerium impurities as nearest neighbors.

If we assume that when two Ce atoms are situated as nearest neighbors the pair is "frozen out" of the spin-flip scattering process, we will find a highly nonlinear relationship between $n_{eff}$ and $n_{nom}$. We can then write

$$n_{eff} = n_{nom}\,[1 - P(n_{nom})]\,, \tag{27}$$

where $P(n_{nom})$ is the probability of finding a Ce with a Ce nearest neighbor at the concentration $n_{nom}$. Since we have only five points on the $n_{eff}$ and the scatter is large on the $n_{nom}$ data, a detailed evaluation of $P(n_{nom})$ is not necessary. However, we can estimate $P(n_{nom})$ for the lanthanum host easily. The number of nearest neighbors each Ce host has is

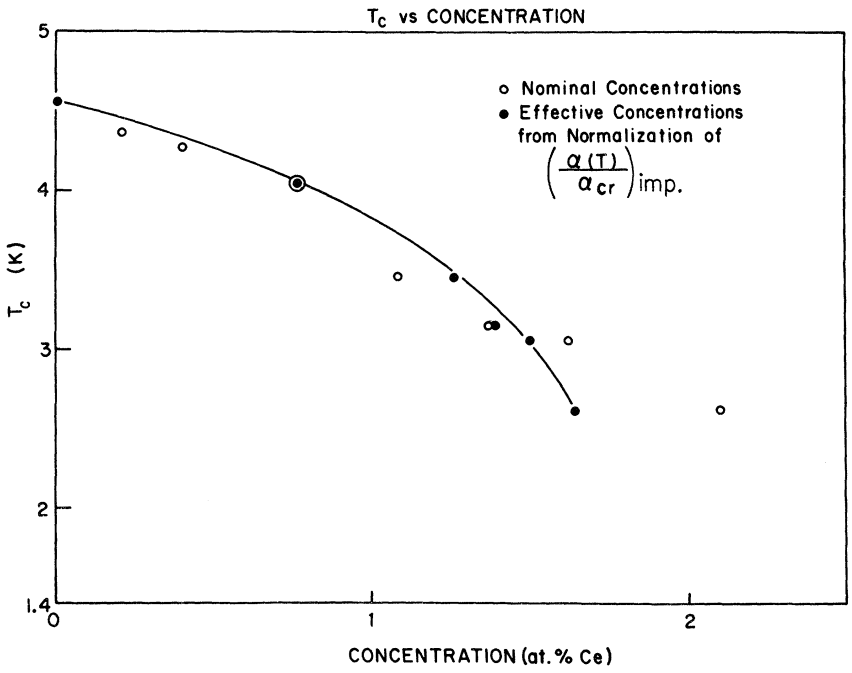


FIG. 12. Transition temperature of the $La$Ce alloys vs Ce concentration. The open circles represent the nominal concentrations. The dots are the effective concentrations determined by matching $F(1.4\ \mathrm{K})$ for the sample, using Eq. (21). The solid line is the prediction for the $T_c$-vs-concentration relationship using the temperature dependence of the spin-flip scattering experimentally determined and illustrated in Fig. 10.

twelve, so

$$P(n_{\text{nom}})_{LaCe} \approx 12\, n_{\text{nom}} ;$$

for the highest $n_{\text{nom}}$ of cerium (2.1 at. %) this is about a 25% effect, as is observed. The reason that these impurity-impurity interaction effects are not seen in $LaAl_2Ce$ is that the number of nearest-neighbor La sites about each Ce impurity is smaller so that a much higher concentration of Ce would be necessary to make a difference between $n_{\text{eff}}$ and $n_{\text{nom}}$. Edelstein *et al.*[37] claim there are no interaction effects up to higher concentrations, but they are measuring susceptibility which seems to reflect different properties than $T_c$, $H_{c2}$, or resistivity (see discussion below).

It should be noted that Mueller-Hartmann and Zittartz predict that for certain concentrations and $T_K/T_{co}$ ratios the alloy will go superconducting and then normal again as temperature is lowered. This will occur if $[\alpha(T)/\alpha_{cr}]_{imp}$ increases first slower and then faster than the universal function, Eq. (3). Our measurements indicate this is not the case for *La*Ce. Recently, however, Riblet and Winger have observed the two transitions for the $(LaCe_x)Al_2$ system.[38] Measurement of critical fields would facilitate finding the right system, as with a pure sample and an alloy one could determine $[\alpha(T)/\alpha_{cr}]_{imp}$ and compare it with $U_n(T)$ instead of investigating many alloys and $T_c$'s. Also, interaction effects may be masking an even stronger curvature in the $T_c$-vs-$c$ curves for $(LaCe)Al_2$ and other intermetallics with La + Ce (such as the work of Maple and Kim[39]) as they masked the $\tau_s^{-1}(T)$ for *La*Ce in the concentration study.

## IX. COMPARISON WITH PREVIOUS WORK

Sugawara and Eguchi[1] have measured the upper critical field of *La*Ce and *La*Gd alloys which are much cleaner than ours, having resistivity ratios of about 150. They also observe a change in slope with concentration for the *La*Ce curves, but of smaller magnitude than we see, and they fail to analyze their data in terms of using the differences in $h(T)_{La}$ and $h(T)_{alloy}$ to directly determine $\tau_s^{-1}(T)$. The *La*Gd curves in their study tend to lie above the prediction of multiple-pair-breaking theory. They attribute this to a "Kondo effect with positive $J$," a notion which is inconsistent with present theory. The difference between their data and ours is probably due to the method of analysis. Sugawara and Eguchi try to fit an AG curve to the $H_{c2}$ curve for La (in fact, they are further from the dirty limit than we are and AG theory is even less applicable) and then compare the alloy critical fields to the AG curve. On the other hand, we compare the alloy data to the actual La data using $h(T)_{La}$ as the definition for a new universal function for the system. We have assumed that whatever causes $h(T)_{La}$ to deviate from $U_n(T)$ will also effect $h(T)_{alloy}$.

In plotting the reduced critical field we have normalized by the experimentally determined $H_{c2La}(T=0,\rho)$ for the appropriate resistivity ratio $\rho$. Sugawara and Eguchi do not take into account the change of mean free path on adding impurities, claiming that the magnetic scattering does not enter $\tau_{tr}$ and neglecting the potential scattering. It must be admitted that for their samples the resistivity was mainly due to the magnetic impurities themselves (see the discussion in the Introduction) and hence our type of analysis was impossible. The scattering in our samples was purposely dominated by lattice imperfections. This made possible the normalization procedure used. The $h(T)$ curves for *La*Gd which we obtain by this method are much closer to what is predicted from Crow's work[19] on $LaIn_3Gd$ than the *La*Gd curves of Sugawara. Both the inclusion of the resistivity change with impurities and the use of $h(T)_{La}$ instead of $U_n(T)$ tend to bring Sugawara's data closer to ours.

When theorists first became interested in the problem of combining the Kondo effect with superconductivity, there were several papers[40,41] which predicted the existence of bound states within the superconducting gap for single magnetic impurities and certain ratios of $T_K/T_{co}$. For reasonable concentrations the bound states would form a band and spread out and the effect would manifest itself as a higher degree of gaplessness in the tunneling density of states. Such an effect was observed by Edelstein[42,43] by extrapolation to $T=0$ of his tunneling curves for *La*Ce and also from specific-heat measurements.

More recent theoretical calculations show[44,45] that there are always two bound states located symmetrically with respect to the middle of the gap. For $T_K \gg T_{co}$ or $T_K \ll T_{co}$ the bound states are very close to the gap edges but for $T_K \approx T_{co}$ (actually $T_K$ about an order of magnitude higher[46]) the bound states move toward the center of the gap, $\omega = 0$. Unfortunately, Edelstein's curves show no sharp structure to indicate where the bound states are located experimentally. Since the position depends on $T_K/T_{co}$ approximately logarithmically it is impossible to determine $T_K$ from the tunneling measurements. They do, however, strongly suggest that *La*Ce is a Kondo superconductor.

In several later papers[37,47,48] Edelstein *et al.* investigated the normal-state properties of *La*Ce. His results tend to show that *La*Ce is a Kondo system over a very wide range of cerium concentrations. In his latest paper,[37] he has measured the susceptibility of the cerium impurities with the following results:

$$\chi = \mu^2/3K_B(T+\theta) ,$$

$$\mu = 2.5\,\mu_B , \qquad \theta = 27 \pm 5\ \text{K} , \qquad T > 20\ \text{K}$$

$$= 5.8 \times 10^{-4}\, T^{-1/2}, \quad 1.4\ K \leq T \leq 30\ \text{K} \qquad (28)$$

with concentrations in the range 2–20 at.%.

For $T > T_K$, the perturbation treatments of the susceptibility should hold. Golibersuch and Heeger[49] have shown that an expression due to Scalapino[50] can be closely approximated by

$$\chi = \frac{\mu^2/1.22}{3K_B(T + 4.5\,T_K)}, \quad 7 \leq T/T_K \leq 100 \qquad (29)$$

explaining the general Curie-Weiss behavior of all Kondo systems for large $T$. This theory and comparison of the *La*Ce data to those of *Cu* Fe suggest[51,52] that $T_K \approx 6$ K for the cerium impurities although Edelstein does not commit himself to a value for $T_K$ in Ref. (37). It should also be mentioned that the concentration *independence* of the susceptibility is in marked contrast with Edelstein's own measurements of the resistivity anomaly in concentrated alloys.[47] The resistance begins to show deviation from low-concentration curves at about 6 at.% Ce at 4 K and at 20 at.% the alloys appear to be ordering at 2–4 K. (Edelstein says 40 at.% Ce in La has a Néel temperature of 4 K.)

The sharp disagreement in both concentration dependence and predicted $T_K$ between the susceptibility data and the resistivity has so far been unexplained. It is possible that the susceptibility is reflecting both the crystalline field and Kondo effects in different ways from the other measurements. Our measurements of $\tau_s^{-1}(T)$ definitely imply that $T_K < 1$ K and are in good agreement with the resistivity measurements. Since we are always at low concentration (less than 2.1 at.% Ce) for the superconducting measurements we cannot say much about high-concentration effects. However, we do see that the functional form of the spin-flip scattering is not affected in our range (see Fig. 9), while the magnitude of $\tau_s^{-1}(T)$ per impurity appears to be decreasing (Fig. 12) as more impurities are added.

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†Present address: Department of Physics, University of California, Los Angeles, California 90024.

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PHYSICAL REVIEW B VOLUME 6, NUMBER 3 1 AUGUST 1972

# Quantum Interference Properties of Double Josephson Junctions

T. A. Fulton, L. N. Dunkleberger, and R. C. Dynes
*Bell Telephone Laboratories, Murray Hill, New Jersey* 07974
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The dependence of the critical current $I_c$ on magnetic field $B$ in double Josephson tunnel junctions is discussed in a model which includes the dependence of junction critical currents, magnetic self-screening, and asymmetry. Account is taken both of static (zero-voltage) and dynamic (nonzero-voltage) behavior, the former controlling the over-all shape of $I_c(B)$ and the latter being important in nonadiabatic transitions between multiple states of the junction. The experimental $I_c(B)$ of double Sn-Sn tunnel junctions are interpreted in this model, and display effects of both static and dynamic origin.

## I. INTRODUCTION

A well-known aspect of the Josephson effect[1-4] is quantum interference,[5-7] the oscillatory dependence on magnetic field $B$ of the supercurrent flow and of the maximum supercurrent $I_c$ that can be supported by single or multiple Josephson junctions. One of the simplest and most revealing geometries in which quantum interference can be observed is the double junction,[7-9] two individual weak-link junctions operated in parallel. Under certain assumptions, it is possible to interpret fully the $I_c(B)$ for this system,[10] taking exact account of the loop self-inductance and magnetic asymmetry and allowing a more general form for the supercurrent-phase relation of the junction than the usual sinusoid, first predicted for tunnel junctions by Josephson. The interpretation is thus sufficiently general to make contact with experiment and has been previously employed to interpret the $I_c(B)$ for Ta-Ta and Nb-Nb point-contact double junctions[10] and for Sn Anderson-Dayem bridges,[11,12] providing in these cases a simple relatively accurate determination of the supercurrent-phase relations. In this paper we describe effects occurring in the $I_c(B)$ of double junctions fabricated using superconductor-insulator-superconductor tunnel junctions,[7] the junctions originally discussed by Josephson.[1] Interpretation of the observed behavior requires that the dynamical aspects of the supercurrent flow in the double junction be taken into account, and we extend our previous treatment[10] of the static aspects of the supercurrent flow to include these.

Section II analyzes the properties of the steady-state supercurrent flow and describes a mechanical analog (the double pendulum). Section III discusses the dynamical effects. Section IV describes and interprets experiments on the $I_c(B)$ of double Josephson tunnel junctions.

## II. SUPERCURRENT FLOW IN SMALL DOUBLE JUNCTIONS

In this section we review our approach to the analysis of the double junctions. We also describe an exact mechanical analog (the double pendulum) whose behavior simplifies the qualitative understanding of double junction behavior.