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Superconductivity and Magnetic Scattering in La-Ce†

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Magnetic impurity scattering for La-Ce has been studied for temperatures well below both the superconducting transition temperature and the Kondo temperature. Two different spin scattering times are involved in this problem. The spin scattering time associated with the breaking of Cooper pairs is found to be approximately 5×10^{-11} sec and to be nearly independent of temperature. The spin scattering time associated with the Kondo effect, however, is found to be on the order of 10^{-14} sec and to have a very strong temperature dependence. These two scattering times appear to be independent of one another. A thorough study of the negative magnetoresistance is presented for several values of impurity concentration to help unravel the effects of impurity-impurity interactions.

I. INTRODUCTION

Magnetic impurity states in metals have been studied[1-4] extensively in the past few years and the experimental evidence seems to confirm the fundamental ideas presented by Anderson[5] for the formation of the impurity ground state. Within this model the formation of a local moment on an impurity site depends on the relative magnitude of the intra-atomic Coulomb repulsion, U, between two electrons of opposite spin, and the broadening Δ caused by the mixing of the impurity state with the conduction band. Large U compared to Δ favors a magnetic ground state, and large Δ compared to U favors a nonmagnetic ground state. Another feature of the model is that the exchange coupling constant of the Heisenberg Hamiltonian, J, is also controlled by the strength of the mixing, V_{kf}.[6] For small V_{kf} the ordinary atomic exchange integral dominates and J is positive (ferromagnetic coupling), whereas for large V_{kf} the mixing term dominates and J is negative (antiferromagnetic coupling).[6] Both the superconducting- and the normal-state properties of the material depend on the values of U, Δ, and V_{kf}, and it is often convenient to categorize the alloy according to the relative magnitude of these parameters.

From a theoretical point of view, the easiest case to solve is that of very weak mixing (small V_{kf}), where $U\gg\Delta$, J is positive, the magnetic impurities are paramagnetic, and the spin scattering time for breaking Cooper pairs, τ_s, is independent of temperature. Abrikosov and Gor'kov[7] have determined the superconducting behavior for this kind of impurity, and the calculations for the free energy and the thermal conductivity[8,9] agree with the experimental work on Th-Gd to an accuracy of a few percent.

For the case of strong mixing (large V_{kf}) the problem is more difficult. Here U is approximately equal to Δ, J is negative, the impurity ground state is nonmagnetic, and localized spin flucuations are an important factor.[10] Experimental work such as the studies of Al-Mn[11] and Th-U[12] seem to confirm the qualitative aspects of localized spin fluctuations,[10] but quantitative verification is not yet available.

La-Ce alloys are a rather special case in that the mixing strength is intermediate between the above two extremes.[6] For these alloys V_{kf} is strong enough to give a negative J and yet weak enough to give a well defined moment ($U/\pi\Delta\sim5$). Hence it is one of the few systems to show a Kondo effect and still have U substantially greater than $\pi\Delta$.

A long series of experimental and theoretical studies have domonstrated the superconducting and Kondo-like properties of La-Ce at temperatures near or above the Kondo temperature. Sugawara and co-workers[13] first reported the presence of a resistance minimum and showed the effect it might have on the superconducting critical-field curves. Soon afterward, Edelstein[14] and Culbert and Edelstein[15] carried out electron tunneling and specific heat measurements to look for magnetic impurity states in the superconducting energy gap. In addition to this work, Maple and co-workers[16] have presented convincing experimental evidence that the position of the $4f$ level and the strength of the interaction parameters can be varied by the application

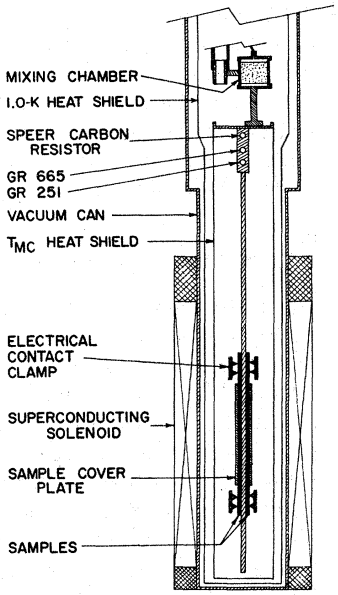

FIG. 1. Sample-holder part of the cryostat.

of pressure. The superconducting results correlate very well with the Kondo-effect results, and together they provide confirmation of the Anderson model.[17]

In the present work we extend these measurements to temperatures well below the Kondo temperature and study details of the magnetic field and concentration dependence of the magnetic scattering. The primary objective of the work is to compare the normal-state transport spin scattering time with the spin scattering time associated with the breaking of Cooper pairs[7] for temperatures far below both the superconducting transition temperature T_c, and the Kondo temperature T_K.

II. EXPERIMENTAL

A. Sample Preparations

A series of La-Ce alloys ranging from 0.22 to 3.98% Ce was prepared from ingots of pure La and pure Ce furnished by Professor Spedding's group of this laboratory. (For this paper all impurities will be given as weight percent.) Chemical and spectroscopic analyses of the samples showed that unwanted impurities which might be magnetic were Fe at 20 ppm, Ni at 10 ppm, Pr at 70 ppm, Nd at 12 ppm, and Gd at 20 ppm. All other rare earths were at the 1–2 ppm level. Pure La does not show a resistance minimum, so we have assumed that impurities other than Ce are not an important factor.

Appropriate quantities of La and Ce were arc melted on a water-cooled Cu hearth under an atmosphere of He into a finger-shaped sample $\frac{3}{8}$ in. in diameter and 3 in. long. Each sample was arc melted at 250 A for about 1 min, flipped and remelted 10 times to ensure homogeneity. (The 1% sample was melted only 4 times.) After melting, the 1.03, 2.02, and 3.23% samples were spark cut (the 0.22 and 3.98% were cut with a diamond saw) to parallelopipeds $0.3\times0.3\times6$ cm, lapped, electropolished, and annealed at 250 °C for 60–90 h. Neutron-diffraction powder patterns on the 2.02 and 3.23% samples showed that the samples contained about 7% fcc phase before the anneal. No further neutron-diffraction data were taken after the anneal, but the amount of fcc phase presumably decreased.

B. Cryostat

A He^3-He^4 dilution apparatus was used to provide refrigeration for the measurements. Samples were mounted in a holder, shown in Fig. 1, which was a copper plate $\frac{1}{8}\times\frac{3}{4}\times9$ in. with a $\frac{1}{4}$-in.-thick section at the top for the germanium and carbon resistance thermometers. Removing the thermometers from the applied field eliminated magnetoresistance effects. The samples, mounted two at a time, were held firmly to the holder with a $\frac{1}{16}$-in.-thick copper plate and a series of brass screws. Cigarette paper impregnated with G. E.-7031 varnish was used to provide electrical insulation but still gave thermal contact. Apiezon N grease was also used as a thermal contact agent. To attach the sample holder to the mixing chamber, the copper surfaces were coated with N grease and joined with brass screws.

Electrical leads to both the samples and the thermometers were thermally grounded to the sample holder via terminal strips which were constructed by affixing manganin strips to the copper with epoxy-impregnated cigarette paper. Electrical contacts to the 0.22, 1.03, and 3.98% Ce samples were made with knife-edge copper contacts. For the 2.02 and the 3.23% samples electrical contacts were made by ultrasonically soldering No. 24 copper wires to the sample. Surfaces were first tinned with Indium solder and the wires were attached with pure tin. Surprisingly, the contact resistance for the soldered joints was somewhat higher than the resistance for pressure contacts. This may have been caused by oxidation of the La during the soldering process.

Electrical leads from the samples to room temperature had to have low electrical resistance and yet provide good thermal isolation. Hence it was necessary to use different wires in different temperature regions. From the samples to the top of the vacuum can the leads consisted of 24-in.-long, 0.006-in.-diam, lead-coated manganin wires. No. 32 copper wires then passed through an Epoxy seal into the He^4 bath. Between 4 and 300 K No. 18 manganin wire was used.

Magnetic fields were produced by a supercon-

ducting solenoid with a rated field of 15 kOe at 22.4 A. Magnet current was supplied by a spectromagnetic constant-current supply stable to 1 part in 10^4 for up to 8 h.

C. Measurements

Electrical-resistance measurements were made by a 47-Hz four-terminal ratio transformer bridge at power levels ranging from 10^{-9} to 10^{-7} W. These power levels were within the capacity of the refrigerator, and they permitted four-figure accuracy for the resistance. Several lengths of heavy copper rod were measured by both ac and dc techniques to verify that the bridge worked properly.

D. Thermometry

Temperatures were determined with two different secondary germanium resistance thermometers because neither one of them could cover the entire range. Resistances were determined by both the four-terminal potentiometric method and also by means of a three-terminal, 32-Hz, ac Wheatstone bridge. The dc method was used from 20 to 0.3 K with GR 251 and from 0.8 to 0.14 K with GR 665. From 0.5 to 0.060 K ac measurements on GR 665 were used. Temperature scales for the thermometers were established in separate experiments. Between 20 and 4 K a constant-volume gas thermometer[18] was used as a primary scale. From 4 to 1.2 K the vapor pressure of He^4 was used[19] and from 1.2 to 0.060 K the susceptibility of cerium magnesium nitrates was used. A calibrated Speer carbon resistor verified that the residual applied field had no effect on the germanium calibrations.

III. RESULTS AND ANALYSIS

Electrical-resistivity data for these alloys above 12 K follow the simple resistivity theories[20] rather well. As shown in Fig. 2, all samples can be represented by $\rho = A + BT^{2.25}$ where A and B are constants given in Table I. The values of A increase linearly with Ce concentration so this term can be associated with impurity scattering. Values of B are approximately independent of concentration so this term can be associated with the temperature-dependent scattering of the host. For a transition metal, such as La, a T^3 term is expected for s-d electron scattering by phonons, and a T^2 term is expected for electron-electron scattering.[20] Hence the $T^{2.25}$ term shown by the data is probably an empirical combination of these phonon and electron scattering terms. The data do not cover a sufficiently wide temperature range to warrant more than

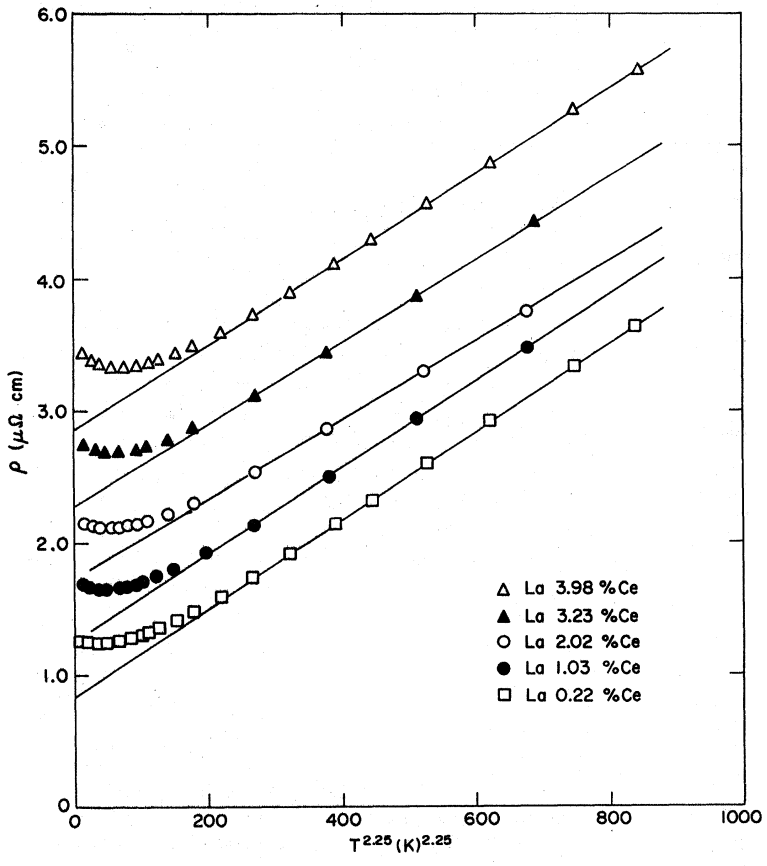

FIG. 2. High-temperature behavior of the resistivity.

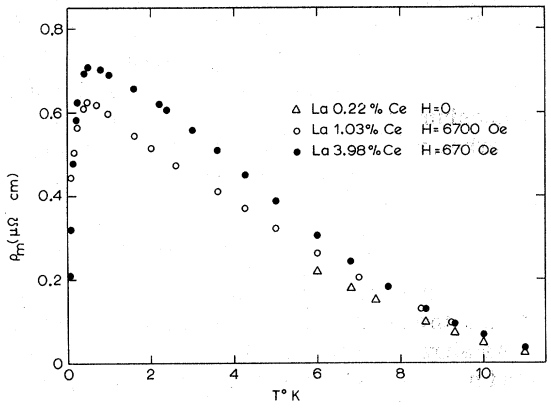

FIG. 3. Temperature dependence of the anomalous scattering on a linear scale. Insufficient field was available to quench superconductivity in the La–0.22%-Ce samples over the entire range.

two adjustable constants in the fitting process.

Below 12 K these alloys show a minimum in the electrical resistivity and a subsequent rise which is reminiscent of the Kondo-like behavior reported in other magnetic impurity systems.[1] To obtain a more detailed view of the results, the additional resistivity caused by the magnetic scattering (ρ_m) has been separated from the total resistivity (ρ) by

$$\rho_m = \rho - \rho_0 ,$$

where

$$\rho_0 = A + BT^{2.25} .$$

Results of this separation for the 0.22, 1.03, and 3.98% Ce samples are shown on a linear plot in Fig. 3. The 2.02 and 3.23% samples show similar behavior. Below T_c a magnetic field has been applied to quench the superconductivity.

Several features of the data are immediately apparent. Both samples show a negative-slope region at high temperatures, a maximum near 0.5 K (T_m), and a distinct positive-slope region below 0.5 K. If the data are cast on a semilogarithmic scale as in Fig. 4, the low-temperature data are very nearly linear over a range where the temperature changes by a factor of eight. Another feature common to all the alloys is that ρ_m goes to zero at about 12 K. It may be a coincidence that 12 K is also the antiferromagnetic temperature of pure Ce,[21] but at least it seems worthy of note.

Another extremely important point to notice is the magnitude of ρ_m. The exchange coupling between the $4f$ level and the conduction band must be very large as evidenced by the ratio of ρ_m to ρ_0. For the 3.98% Ce sample, ρ_m is about 25% of ρ_0 at $T = T_m$, and for the 1.03% Ce sample ρ_m is about 50% of ρ_0 at $T = T_m$. Hence the spin-flip scattering time must be comparable to the potential scattering time in these materials. Changes in resistivity associated with the Kondo effect are about 0.5 μΩ cm, and this corresponds to a spin scattering time of about 10^{-14} sec.

As the magnetic field increases (see Fig. 4), the ln$T$ behavior at low temperatures is retained, but the value of T_m increases by an amount proportional to the applied field. Quantitatively, the shift in

TABLE I. Characteristics of La-Ce alloys.

Sample (wt% Ce)	T_c (K)	$T_m(H=0)$ (K)	A (μΩ cm)	B $\left(\frac{\mu\Omega\,\mathrm{cm}}{(\mathrm{K})^{2.25}}\times 10^{-3}\right)$
0.22	•••	•••	0.841	3.342
1.03	4.49	0.17	1.216	3.362
2.02	3.24	0.23	1.732	2.994
3.23	1.99	0.34	2.245	3.168
3.98	0.91	0.47	2.843	3.256

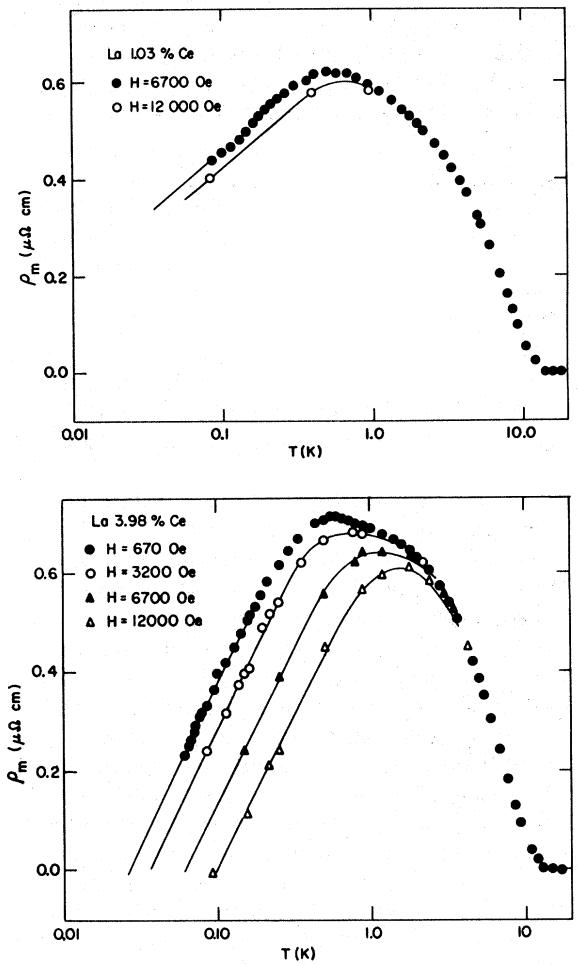

FIG. 4. Semilogarithmic plots to show the ln$T$ behavior and the negative magnetoresistance at low temperatures.

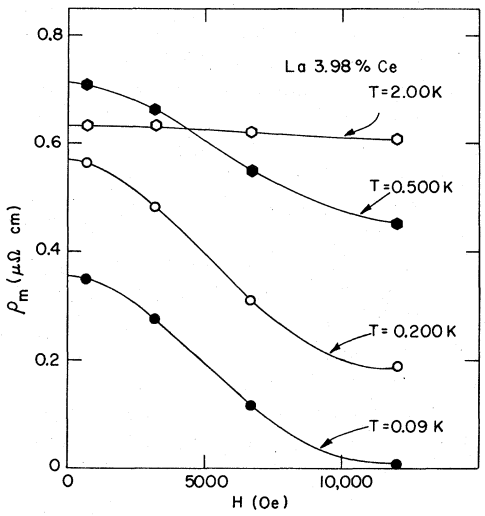

FIG. 5. Conventional magnetoresistance plot of resistivity vs field at constant temperature.

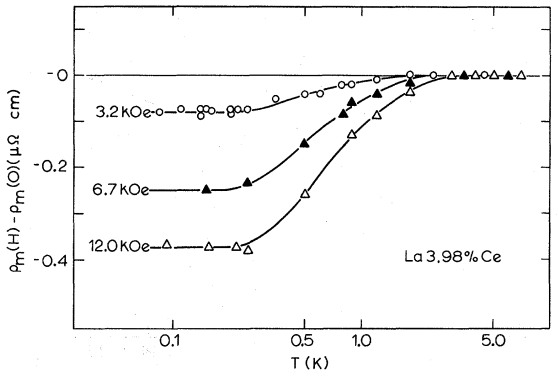

FIG. 6. Negative magnetoresistance of La-Ce vs temperature at constant applied field.

T_m is given by $\mu H/k$, where μ is one Bohr magneton, H is the applied field, and k is the Boltzmann constant. Hence this result would point to a spin-$\frac{1}{2}$ state for the lowest crystal-field level for Ce impurities in La.

If these low-temperature data are cast in the form[1,22] $\rho_m = \alpha \ln(T/T_0)$, where α and T_0 are constants given in Table II, then it would appear that α is independent of magnetic field. On the basis of the simple Kondo expression one expects α to be of the form[1]

$$\alpha = DnJ^3 \ ,$$

where D is a constant, n is the concentration, and J is the exchange coupling constant. Hence the data on Fig. 4 then indicate that J is independent of field, as expected. It is not clear, however, whether this expression applies since α does not scale well with n.

To understand the rather sharp drop in the resistivity ρ_m at temperatures below T_m, it is important to study the magnetic field dependence of the resistivity. The question of central interest here is whether the drop in ρ_m is caused by ordering of the Ce impurities. A surprising aspect of the data is that the negative magnetoresistance, shown in Fig. 5, is independent of temperatures below 0.30 K. If the drop in ρ_m were caused by ordering among the Ce ions, one would expect the negative magnetoresistance to change as the ordering takes place. No change is observed. Figure 6 shows that the negative magnetoresistance is independent of temperature and, indeed, is very similar to the results for dilute (28 ppm) solutions of Cr in Cu.[23] The resistivity of Fig. 4 drops very rapidly in a temperature range where the negative magnetoresistance of Fig. 6 is large and independent of temperature. This suggests that some other mechanisms must be found.

At higher temperatures ($T > T_m$) the negative magnetoresistance rapidly decreases and goes over to a small positive magnetoresistance. The magnitude of the normal positive term is only about 5% of the negative magnetoresistance so no correction is made for it. In the temperature range where they overlap, these La-Ce results are in good agreement with the Cu-Mn[24] and Cu-Fe[25] results. Unfortunately, magnetization data are not available so a detailed comparison with the theory of Yosida[26] is not possible.

The concentration dependence of the resistivity is also of interest. To investigate this point we have plotted the concentration dependence of T_m on Fig. 7. A fit to the data shows that

$$T_m = 0.15 + 0.19n^2 \ ,$$

so there appears to be a large concentration-independent term as well as a significant term proportional to the square of the concentration. Any

TABLE II. Low-temperature fit constants for $\rho_m = \alpha \ln(T/T_0)$.

Sample (wt% Ce)	Field (Oe)	T_0 (K)	α (μΩ cm)
1.03	6700	0.002	0.12
1.03	12000	0.003	0.12
2.02	3200	0.0007	0.13
2.02	6700	0.008	0.13
2.02	12000	0.019	0.13
3.23	3200	0.015	0.21
3.23	6700	0.032	0.21
3.23	1200	0.044	0.21
3.98	670	0.026	0.27
3.98	3200	0.036	0.27
3.98	6700	0.060	0.27
3.98	12000	0.098	0.27

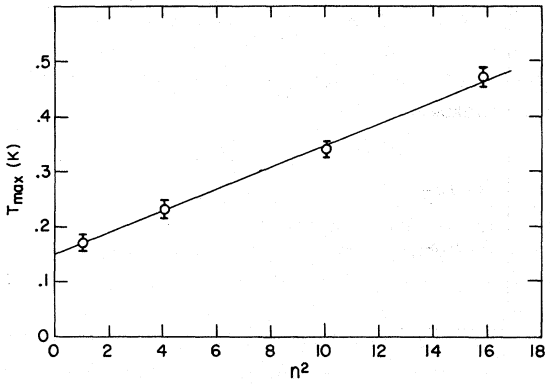

FIG. 7. Concentration dependence of T_m. Solid line represents $T_m = 0.15 + 0.019n^2$.

pairing interaction will show an n^2 dependence, and at concentrations of the order of a few percent there is a high probability that each Ce atom will have at least one other Ce near neighbor. Hence there may be significant impurity-impurity interactions. In the limit of low concentration, however, the resistance maximum persists and appears to have a characteristic temperature of 0.15 K. Presumably this temperature represents the residual splitting of the Ce Kramers doublet.

The normal-state spin scattering time is strongly temperature dependent. This observation holds even though the drop in resistivity for $T < T_m$ is not well understood. Figure 4 shows that there are changes of about 0.5 $\mu\Omega$ cm associated with the spin scattering, and these correspond to changes in the normal-state spin scattering time of about 10^{-14} sec.

Another aspect of this research was to study the spin scattering time associated with the breaking of Cooper pairs, τ_s. To obtain the concentration dependence of τ_s one can use[7]

$$\frac{h}{\tau_s} = \frac{\pi}{8} k (T_{cp} - T_c) ,$$

where T_{cp} is the transition temperature of pure d-hcp La. For the 3.98% Ce sample the measured values of T_{cp} and T_c give $\tau_s = 5 \times 10^{-11}$ sec. To investigate the temperature dependence of τ_s one can use the measurements of the upper critical field H_{c2}. In Fig. 8 the H_{c2} curves for La-Ce are compared with the critical-field curves of a sample for which τ_s is known (from thermal-conductivity measurements)[27] to be temperature independent, La-Lu-Tb. The Tb alloy, which has positive J and shows no Kondo effect, has a critical field curve nearly identical to La-Ce. The H_{c2} curve for La-Lu-Tb has a slightly different shape from La-Ce, but over all the curves are amazingly similar to one another and have almost identical ratios of H_{c2} ($T = 0$) to T_c. In addition to this the La-Ce curves are very similar to the predictions of the multipair breaking theory.[28] For the La-3.98%-Ce sample τ_s determined from these critical-field curves has a magnitude of about 5×10^{-11} sec and it is nearly independent of temperature. Similar results apply for the other alloys.

At present there is no simple theory to relate the spin scattering time associated with the Kondo effect (τ_m) to the spin scattering time associated with Cooper pair breaking (τ_s). Indeed these measurements seem to imply that they are not related for the case of La-Ce. It may be that the free-electron picture is not adequate to describe these alloys and that one must consider details of the band structure. In a metal such as La the Fermi surface has both s and d character and it is possible that different pieces of the Fermi surface make the dominant contribution to the Kondo and superconducting features. Pieces of the Fermi surface with s-like character have a large Fermi velocity and dominate the normal-state conductivity. Hence an s-f interaction would dominate the Kondo problem and control τ_m. It is possible then that pieces of the Fermi surface with d-like character have the strong electron-phonon interaction and dominate the formation of Cooper pairs. Hence a d-f interaction would determine τ_s. With this kind of two-band model[29] the discrepancy between τ_s and τ_m can be understood rather easily. Other explanations, of course, are also possible.

IV. SUMMARY

There is a large discrepancy, both in magnitude

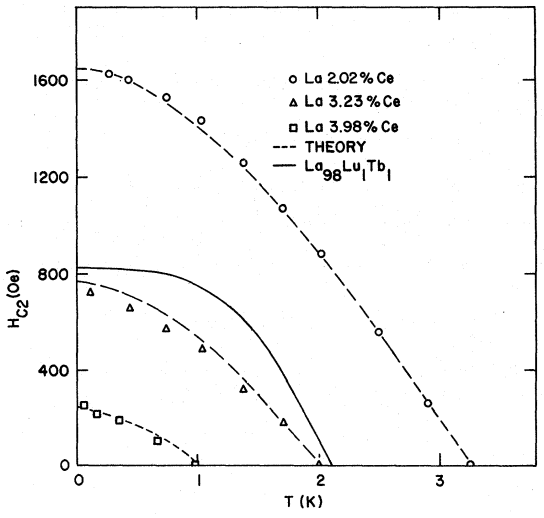

FIG. 8. Critical-field curves for La-Ce and La-Lu-Tb alloys. The dashed lines show the predictions of the multiple-pair-breaking theory with $T_{cp} = 4.87$ K for pure d-hcp La. The adjustable parameter in the theory, the critical field of pure La at $T = 0$, was chosen to fit the experimental slope of the 2% Ce sample at T_c.

and in temperature dependence, between the pair-breaking (τ_s) and normal-state (τ_m) spin scattering times. As yet there is no satisfactory theory relating these two quantities so the results have been interpreted in terms of separate s- and d-band behavior. With this two-band interpretation, the data give strong evidence that superconductivity in these alloys is predominantly a d-band phenomenon.

For temperatures well below the Kondo temperature the resistivity (ρ_m) has a logarithmic temperature dependence with positive slope over a temperature interval of about a factor of eight. One obvious explanation for the drop in resistivity for $T \ll T_K$ is to interpret it in terms of ordering of the Ce ions. If this is true, however, then it must be a very special ordering which gives a negative magnetoresistance which is independent of temperature.

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