SUPERCONDUCTIVITY AND THE KONDO EFFECT IN
QUENCH-CONDENSED FILMS CONTAINING CERIUM

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MASTER

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Superconductivity and the Kondo effect in
quench-condensed films containing cerium

by

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Superconductivity and the Kondo effect in
quench-condensed films containing cerium

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The superconducting transition temperature, T_c , and the Kondo resistance anomaly were studied in flash-evaporated quench-condensed thin films of Pb(Ce) and In(Ce). In both alloys, cerium caused a uniform depression of T_c , with a slope of 1 K/at % Ce. Measurements after low temperature annealing and measurements on samples of different residual resistivities, ρ_0 , showed T_c to be relatively insensitive to structural disorder. Approximately half of the samples showed a Kondo effect with a resistivity rise proportional to $\log T$ at low temperatures. For the In(Ce) system the rise in resistivity over one temperature decade, $\Delta\rho$, equalled $.03 \mu\Omega \text{ cm/at \% Ce}$ relatively independent of structural disorder. For the Pb(Ce) system, however, $\Delta\rho = 3 \mu\Omega \text{ cm/at \% Ce}$ for disordered films having $\rho_0 = 400 \mu\Omega \text{ cm}$, but $\Delta\rho = .015 \mu\Omega \text{ cm/at \% Ce}$ for films having $\rho_0 = 100 \mu\Omega \text{ cm}$. Similar decreases of $\Delta\rho$ with ρ_0 were also observed after low temperature annealing of the films. Calculations of the superconducting state scattering time, τ_s , and the normal state Kondo scattering time, τ_m , showed that for In(Ce), τ_m and τ_s were both approximately equal

to 5×10^{-12} seconds. For the Pb(Ce) system, however, τ_s was approximately 8×10^{-12} seconds whereas τ_m ranged from 4×10^{-14} seconds to 8×10^{-12} seconds. The result that $\tau_s \gg \tau_m$ for a sizable fraction of the Pb(Ce) films may signify that the onset of superconductivity greatly depresses the scattering associated with the Kondo effect.

INTRODUCTION

For several years there has been extensive interest in the effects of impurities on both the superconducting transition temperature T_c and the normal state resistivity $\rho(T)$ of metals.^{1,2,3,4,5} Early studies on superconductors showed that the occurrence of magnetism can be very detrimental to superconductivity, and in many cases even small traces of magnetic impurity can completely suppress superconductivity. This behavior of magnetic impurities is to be contrasted with ordinary non-magnetic impurities which normally depresses T_c only slightly. In the case of normal state resistivity, the difference between magnetic and non-magnetic impurities arises primarily at low temperatures where magnetic impurities cause a small low temperature resistivity rise called the Kondo effect. No similar resistance anomaly is seen in metals containing non-magnetic impurities.

The question of whether an impurity atom will be magnetic or non-magnetic in a given host material has been the study of several theoretical investigations.¹ Genuine progress began in this field when Friedel⁶ pointed out that dissolved impurities might lead to the formation of virtual bound states in which resonant scattering of conduction electrons from impurity sites gives a local enhancement of the density of states. The impurity's electrons spend part of their time in the magnetic levels near the impurity, but they also have many free electron characteristics, hence the name "virtual bound" electrons. Friedel's general idea was made more quantitative by the work of Anderson⁷ who

calculated the magnetic properties of the impurities from the amount of free electron-localized level hybridization and from the energy of the magnetic orbitals relative to the Fermi surface. In general, magnetic levels which are near the Fermi surface are most strongly hybridized and are most likely to change from magnetic to non-magnetic.

We see, therefore, that often an impurity atom shows different magnetic characteristics depending on its host. For cases where the magnetic nature of the dissolved impurity cannot be theoretically predicted, examination of ρ vs. T can give insight into the fundamental magnetic properties of the impurities. Theories of the normal state resistivity are developed for a variety of impurity characteristics ranging from non-magnetic resonant state impurities to long-lived paramagnetic impurities.

The first theoretical explanation of the effects of magnetic impurities on the normal state conductivity was given by Kondo.⁸ His theory, which is based on a second Born approximation for conduction electron scattering from magnetic impurities, assumes a long-lived impurity moment, and predicts an excess resistivity proportional to $\ln T$ at low temperatures. Although the theory explained the experimentally observed $\ln T$ dependence, it had an obvious flaw of predicting a singularity at $T = 0$. Modifications of this theory by Nagaoka⁹ removed this singularity by allowing the conduction electrons to form a spin compensating cloud around the impurity, reducing its effective moment to zero, and causing a leveling off of the resistivity.

Hamann¹⁰ subsequently showed that in this case the excess resistivity should obey the expression

$$\Delta\rho = \frac{2\pi C}{ne^2 k_F} \left\{ 1 - \ln(T/T_K) \left[\ln^2(T/T_K) + S(S+1)\pi^2 \right]^{-1/2} \right\}$$

where n is the electronic density, e is the electronic charge, and k_F is the Fermi wave vector. Their result agrees with Kondo's for $T > T_K$, passes smoothly through $T = T_K$, and reaches the unitarity limit at $T \ll T_K$. In this expression the Kondo temperature T_K is the temperature at which many of the conduction electrons are scattering off the impurity and thereby causing the excess resistivity.

Suhl¹¹ and Levine¹² have studied short-lived localized spin fluctuations, and predict that their excess resistivity should follow a $\rho_0 (1 - T^2/T_K^2)$ behavior at low temperatures. The non-magnetic resonant state model of Abrikosov,¹³ Suhl,¹⁴ and Kondo,¹⁵ on the other hand, predicts a peak in the excess resistivity with the resistivity dropping off as $\ln T$ both above and below the peak. Of course, if the impurity has no magnetic properties, then no low temperature anomaly will be present.

An alternate and rather novel explanation of the Kondo resistance rise, developed by Korn,¹⁶ emphasizes scattering of conduction electrons by magnetic impurity-lattice defect pairs. In his theory, the conduction electrons are first polarized by the magnetic impurity and then scattered by the fields of the lattice defect. The scattering is mainly ordinary Coulomb scattering, but Korn includes the magnetic forces arising from

the polarized electrons sensing a magnetic field caused by their motion in the defect's electric field. He predicts a resistivity proportional to $T \ln (\cosh \frac{T_K}{T})$ which agrees reasonably well with his data, but the theory, as yet, has not been critically tested for a wide range of materials.

The presence of an anomaly in the normal state resistivity is only one effect of magnetic or nearly-magnetic impurities. Another important effect is the very rapid depression of the superconducting transition temperature T_c . Just as there is a variety of theories explaining the Kondo resistance anomaly, many theories of impurity-doped superconductors have been developed to cover the whole range of impurity behavior from non-magnetic to magnetic. They predict different concentration dependences of T_c and serve as starting points for interpretation of experimental results.

As mentioned previously, the manner in which an impurity interacts with superconductivity depends on the nature of the impurity state. For long-lived magnetic impurities in superconductors, the basic theory is a first Born approximation calculation by Abrikosov and Gor'kov.¹⁷ It predicts that increasing the impurity concentration causes a rapid decrease in T_c with $d^2 T_c / dC^2 < 0$ (where C is the concentration), and predicts no superconductivity if the concentration exceeds a critical concentration, C_{cr} . One of the theory's basic results is that the transition temperature is related to the concentration C according to the relation

$$\ln \left(\frac{T_c}{T_{cp}} \right) = \psi \left(\frac{1}{2} \right) - \psi \left(\frac{1}{2} + \frac{C T_{cp}}{4 \gamma_e C_{cr} T_c} \right) .$$

Here ψ is the digamma function, T_c and T_{cp} are the transition temperatures of the alloy and the pure host, γ_e is the Euler constant, and C_{cr} is the critical concentration. In the low concentration limit, the equation above reduces to

$$\frac{T_c}{T_{cp}} = 1 - .691 \left(\frac{C}{C_{cr}} \right).$$

An essential feature of the Abrikosov-Gor'kov theory is that magnetic impurities break the superconducting Cooper pairs, giving them a finite lifetime τ_s and an energy broadening $\Gamma_s \sim \frac{\hbar}{\tau_s}$. The mechanism is a spin-flip scattering similar to the scattering causing the Kondo resistance rise in which the impurity exchanges spin angular momentum with the superconducting electrons, and destroys the time reversal invariance necessary for superconductivity. Many experiments have verified the predictions of the theory: tunneling measurements of Wolff and Reif in Pb(Gd),¹⁸ tunneling measurements of Millstein and Tinkham in Sn alloys,¹⁹ heat capacity measurements of Finnemore et al. in La(Gd),²⁰ critical field measurements of Decker and Finnemore on Th(Gd),²¹ and thermal conductivity measurements of Cappelletti and Finnemore in Th(Gd).²²

In contrast to the behavior of magnetic impurities, non-magnetic impurities have a relatively small effect on the transition temperature. At low concentrations they depress T_c slightly as the impurities mix the different portions of the Fermi surface and remove the anisotropy

of the superconducting properties.²³ This lowering of T_c levels off when enough impurity has been added to completely remove the anisotropy. At higher impurity concentrations, valency effects are important.²⁴ These can either raise or lower T_c depending on the details of the band structure, but the effects are typically much smaller than the effects of magnetic impurities.

Intermediate between the magnetic and non-magnetic impurities are the nearly-magnetic or short-lived magnetic impurities. As discussed earlier, often the effect of the host metal is to hybridize the impurity levels so that the impurity's electrons spend part of their time in localized magnetic levels and part of their time in non-magnetic states of the host. The interaction of these special types of states with the superconducting electrons was treated by Zuckermann,²⁵ Bennemann,²⁶ and Rivier and MacLaughlin²⁷ who predict that T_c initially be depressed linearly with concentration and then gradually level off at high concentration. For the case of non-magnetic resonant states, the theory of Kaiser²⁸ predicts

$$T_c = T_{cp} \exp [-(\alpha + \beta) C / \lambda (1 - \beta C)]$$

where λ is the interaction parameter. Measurements by Huber and Maple on Th(Ce)²⁹ and measurements by Watson et al.³⁰ on Th(U) both give excellent agreement with this theory.

An additional complication to the theory of magnetic impurities in superconductors arises from the effects of crystalline fields on the impurity. Fulde, Hirst, and Luther³¹ have shown that in certain

cases magnetic impurities having appropriately placed crystalline field levels can increase T_c by providing an inelastic scattering mechanism that binds the electrons in a Cooper pair. In this theory, the virtual excitation of the crystal field levels replaces the electron-phonon interaction as the mechanism responsible for superconductivity. Another effect of crystalline fields is decreasing T_c by providing additional magnetic scattering levels. This latter effect usually dominates, but it is possible for the magnetic levels to either raise or lower T_c .

So far we have seen that there exists a sizable body of theory for the effects of impurities on the normal state resistivity and on the superconducting transition temperature. These theories, however, consider the depression of T_c and the presence of a Kondo effect as separate independent problems, while actually for many alloys they occur together as two competing effects. From a theoretical point of view this particular problem is especially difficult because it involves the interplay of two competing many-body phenomena. For the Kondo effect there are spin correlations between the impurity atom and the conduction electron cloud around it, and there is rather strong evidence that this cloud extends at most a few atomic spacings.^{32,33,34} The spin correlations in the superconducting ground state, on the other hand, are much longer range and might typically be $100\text{\AA}$ to $1000\text{\AA}$. Each of these is a complicated problem by itself and as yet there has been only limited success in solving them simultaneously.

The most successful theory of the coexistence of the Kondo effect and superconductivity is by Muller-Hartmann and Zittartz.³⁵ In their calculation of the depression of T_c by magnetic impurities, the parameter of central interest is the Kondo temperature T_k . At temperatures close to T_k they predict that the impurities are most effective in breaking the superconducting Cooper pairs and causing a very rapid depression of T_c , while far above or below T_k the pair-breaking is reduced. The resulting transition temperature as a function of concentration is very complex, and may have both positive and negative slopes and curvatures. A major accomplishment of the theory was that it correctly predicted the reentrant T_c vs. C curves observed by Maple *et al.*³⁶ in $(\text{La,Ce})\text{Al}_2$.

Recently there has been experimental evidence that the presence of superconductivity can have an important effect on the formation of the Kondo ground state. Measurements by Wollan and Finnemore,³⁷ of the normal state Kondo effect and the superconducting critical field curves of $\text{La}(\text{Ce})$ showed that the scattering times associated with the normal state Kondo effect was at least an order of magnitude shorter than the scattering times associated with the destruction of superconductivity. In addition, the temperature dependence of these times is quite different. Subsequently, specific heat measurements by Bader³⁸ on $(\text{La,Ce})\text{Al}_2$ showed that the presence of superconductivity dramatically decreased the entropy associated with the Kondo state. As yet there is no good model to explain this lowering of the entropy. Both of

these results indicate that there is less spin-flip scattering in the superconducting state than in the normal state. No satisfactory theory explaining the reduced scattering rate has yet been developed.

Motivated by the puzzling results described above, the purpose of this experiment is to study the Kondo effect and superconductivity in $\text{Pb}(\text{Ce})$ and $\text{In}(\text{Ce})$. Both Pb and In have moderately high transition temperatures, making it easy to study the depression of T_c as cerium is added. Cerium was chosen as the impurity because it showed the interesting behavior described above in $\text{La}(\text{Ce})$ and $(\text{La}, \text{Ce})\text{Al}_2$. In addition, other alloys containing cerium show different characteristics ranging from magnetic to non-magnetic and so we might expect to find a Kondo effect in $\text{In}(\text{Ce})$ and $\text{Pb}(\text{Ce})$.

EXPERIMENTAL SYSTEMS

All of the Pb(Ce) and In(Ce) alloys studied were thin films prepared by flash evaporation. Flash evaporation was used because the vapor pressure of cerium is a factor of 10^4 to 10^6 smaller than the vapor pressures of In and Pb,^{39,40,41} as shown in Figure 1. To prepare the film, a series of .020" x .040" pellets were evaporated sequentially so that the film was deposited in 10^8 to 15^8 increments. The relative rates of evaporation of the Pb or In and the Ce for each pellet depends on the degree of entrainment of the Ce in the vapors of the host and on the rate of evaporation, so it is difficult to determine the exact structure of each layer. Because the cerium has the lower vapor pressure, each 10^8 layer is probably deficient in Ce at the substrate side and rich in Ce at the outward-facing side. For the concentrations used here, however, the average distance between the Ce atoms in the plane of the film is about 10^8 , so all we require for homogeneous films is that all of the Ce be evaporated for each pellet.

Another major difficulty of this experiment arises because it is impossible to dissolve more than .1% cerium in either lead or indium.⁴² Therefore, all alloys in this study were evaporated onto a cryogenically cooled substrate, resulting in supersaturated solid solutions. These films could not be warmed without risking cerium precipitation, so they were deposited and measured in the same apparatus. With this equipment,

measurements of the superconducting transition temperature and the normal state resistivity were possible in the temperature interval from 1.3 K to 100 K.

Evaporator-cryostat

The evaporator-cryostat is shown in Figure 2. The evaporator consists of four main parts: 1) A pellet dropper which holds about 200 pellets of the Pb-Ce or In-Ce alloy, 2) A tungsten basket which vaporizes the pellets that drop into it, 3) A movable shutter and an evaporation mask that permit sections of the substrate to be masked off, 4) A substrate fastened to a copper block which is thermally anchored to the bottom of the helium dewar.

The pellet dropper is shown in Figure 3. It is basically a piece of copper that shields and supports a teflon block. Teflon was chosen because of its low friction with the pellets. The chute is a bent tantalum sheet, and the post holding the copper block is clad in tantalum sheet as a shield against the heat. The pellets are loaded into the 11 tubes in the teflon block, with 3 or 4 tubes intended for each section of the film. Eleven drill rods were used to push the pellets out of the tubes, causing them to fall down the chute and into the boat. The drill rods are pushed by a 1/8" rod that passes out of the evaporation manifold through a glass-to-metal vacuum seal. A plate glass window permitted viewing the pellet dropper and controlling the 1/8" rod.

A problem with the pellet dropper, especially after many pellets had been evaporated, was clogging of the chute with pellets partially melted enroute to the basket. The solution to this problem was letting the basket and chute cool for 10 or 20 minutes after evaporating every section of the film. When any unmelted pellets got stuck in the chute, they were freed by tapping the chute with the 1/8" diameter rod operating the pellet dropper.

By operating the 1/8" diameter push rod, it was possible to push the pellets one-at-a-time out of the teflon and into the basket. About 75% of the pellets landed in the boat; the rest hopped out of the chute, missed the basket, and landed underneath it. Approximately 10% of the time, two pellets would stick together and travel together into the basket.

The power supply for the basket was a Kepco KS 30-36 with a large knife switch in its output. Operation of the switch quickly raised the current from a few amperes to the 20 amperes necessary for heating to 1750°C. The temperature rose to 1750°C in less than 1 second. A 0-36 A ammeter on the power supply was used to measure the basket's current.

The evaporation source was .020" diameter tungsten wire spiralled into a conical basket about 7 mm high. In a preliminary experiment, its temperature as a function of current was determined using an optical pyrometer.⁴³ When heated to 1750°C it dissipated 200 watts, at 1930°C it dissipated 375 watts, and at 2050°C it broke while

dissipating 550 watts. The basket was supported by 5 inches of #10 copper wire. The current entered the evaporator through two 3/8" diameter copper feed throughs with viton O-rings. A 3" square of .020" tantalum was placed under the basket to act as a shield against the heat.

Outgassing was typically done at 1930°C, and evaporating the pellets at 1750°C. Preliminary tests showed that at 1750°C a pure cerium pellet of the usual size was completely evaporated in 10 seconds, resulting in an evaporation rate of 1 Å/second. Therefore in the alloys where the host evaporates within a second or two and the cerium should contribute only about 1/2 Å to the total film thickness, an evaporation time of 10 seconds was used to be sure of evaporating all the cerium.

The basket typically was held at 1750°C during the evaporation. This temperature was chosen after evaporations of 4.7% Ce-Pb were made at 8 different temperatures and their superconducting transition temperatures compared (Figure 4). Lower evaporation temperatures caused incomplete cerium evaporation and high transition temperatures. After some evaporations at 1300°C, traces of unevaporated cerium were even found in the basket. This was not surprising because the vapor pressure of cerium is 10^{-5} torr at 1300°C, while lead's vapor pressure is 20 torr at 1300°C. Evaporation temperatures above 1750°C also resulted in slightly higher transition temperatures. This is not well understood but may be associated with thermally activated annealing of the surface of the film. Pure lead films, for example, were driven normal

by the radiated heat from the basket, indicating that the substrate was being warmed above 7 K. Subsequent studies of annealing in the films confirmed that the samples had been heated to 8-12 K during evaporation. The measurements of the transition temperature vs. evaporation temperature (Figure 4) also showed a rather broad minimum near 1600°C where the transition temperature changed only by 0.2 or 0.3 K. Our selection of 1750°C is towards the high temperature side of the minimum, but it was felt better to be a little too hot than too cold in order to insure complete cerium evaporation and avoid the very rapid rise in transition temperatures that would ensue. At temperatures above 2050°C, the basket melted at points where it was strained or weakened.

Each substrate was coated with a w-shaped film of four sections, and each section could be prepared from a different alloy or from the same alloy with different thicknesses, evaporation times, or evaporation temperatures. Figure 5 is a photograph of one film showing the four sections, gold islands, and indium solder. Typically the composition of the sections was different, with all of the sections containing the same host metal. A movable shutter in the liquid nitrogen cooled heat shield about 1 cm in front of the substrate was used to mask sections of the substrate. Before each section was evaporated, the shutter was completely closed, and the basket was heated to 1930°C for 30 seconds in order to clean the basket and outgas its surroundings. The position of the shutter could be observed through the glass window

by using a small glass mirror fastened to the bottom of the nitrogen shield.

A 1/8" thick copper mask with a 'W' shaped slot was placed about 0.3 cm in front of the substrate. This mask was fastened to the substrate support and kept at the temperature of the substrate. It was made relatively thick so that only normally incident vapors from the basket would pass through the slot, but vapors outgassing from the walls would be stopped by the mask. Additional collimation was achieved with a .020" tantalum sheet placed about 3" above the basket. A 1" hole directly above the basket allowed only vapors from the basket to reach the substrate.

The substrate was clamped to the substrate holder with two small beryllium-copper springs. A thin layer of Apiezon N grease on the back of the substrate provided additional thermal contact between the substrate and its support. A germanium resistance thermometer was mounted in a hole in the substrate holder and was used to measure the substrate's temperature during evaporation. During evaporations a liquid helium filled 1/4" diameter tube between the substrate holder and the helium dewar kept the sample near 4.K.

The evaporation manifold was evacuated by a CVC model 20 diffusion pump (Dow Corning 704 oil) isolated from the evaporator by a liquid nitrogen cooled cold trap to prevent oil backstreaming. This pump could produce a vacuum of 10^{-5} torr in the evaporator, and vacuums of 10^{-6} torr with the nitrogen dewar full and 10^{-7} torr with both the

nitrogen and helium dewars full. Pressure was measured by a cold-cathode Philips ionization gauge connected to the evaporator by about a foot of 1" copper pipe.

Thermometry

The film's temperature was measured with a germanium resistance thermometer (GR20601) that was in good thermal contact to the back of the substrate. In addition to having its electrical leads thermally anchored to the substrate holder, the thermometer itself was mounted in a grease-filled, close-fitting hole in the substrate holder. The thermometer was previously calibrated below 18 K against the paramagnetic salt temperature scale of Cetas and Swenson⁴⁴ and between 18 K and 77 K against the NBS 1955 platinum resistance thermometer scale. It was checked against these temperature scales at 96 temperatures between .94 K and 77 K and from these points a fit to $\ln T = \sum_{n=1}^9 A_n (\ln R)^{n-1}$ was made with a rms deviation of less than 1 mK.. Tables based on this polynomial fit were used to determine the temperature from the thermometer's resistance.

During data taking a Leeds and Northrup K-5 potentiometer was used to measure the thermometer's resistance. These measurements were accurate to $\pm .025\%$, which would imply a temperature uncertainty of 2 mK. Self-heating effects were not observed in the thermometer.

Temperature control was maintained by a 47 Ω carbon radio resistor mounted next to the germanium resistor in the cryostat and measured by a Wheatstone bridge. The off-balance signal of the bridge

was fed into a strip chart recorder that had a switch attached to its pen. When the substrate cooled, the resistance of the carbon resistor would increase, causing the bridge to go off balance and the pen to activate the switch. The switch increased the current to a heater on the substrate holder and tended to restore the bridge balance. Temperature oscillations when using the controller typically amounted to about 5 mK, although near sharp superconducting transitions they were carefully reduced to 1 mK. The heater was a few feet of manganin wire astatically wrapped around the back of the substrate holder, and used for annealing as well as temperature control.

A. C. Resistance Bridge

The resistance of the film was measured using the A. C. resistance bridge shown in Figure 6. Basically the circuit is an A. C. potentiometer in which the voltage across the film is added to a known voltage and a null is obtained when the two are equal and of opposite sign. All four sections of the film are connected in series, and the voltage arising across any one section can be switched into the bridge. The measurements are four terminal potentiometric measurements with no current flowing in the voltage leads to the film at null.

A locally made 400 Hz oscillator, coupled to the circuit by a Gertsch ST248 (1:1) isolation transformer drives the bridge with a primary loop current of 27 mA. Notice that the full 27 mA does not go through the film. All but 10 μ A is shunted around the film by the 73 Ω resistor, so the current through the film is only 10 μ A. The

larger current through the standard resistance and mutual inductance lump was needed to provide ample voltages to the ratio transformers, but it was too much current for the thin film samples. Calculations show that for a $300 \text{ \AA}$ film carrying $10 \text{ \mu A}$, the current density is 20 A/cm^2 . The current was set at $10 \text{ \mu A}$ because it enabled adequate resolution and lowering the current to $1 \text{ \mu A}$ had no measurable effect on the null of the bridge.

The full 27 mA does go through the $10 \text{ \Omega}$ standard resistor and the mutual inductance lump where voltages in-phase and out-of-phase with the primary loop current are developed. Known fractions of these voltages are picked off by the ratio transformers, attenuated by the step-down toroid transformers, and then added in series to the voltage developed across the film. The toroid transformers have several primaries and secondaries, so that by switching it, it is possible to measure resistances from a few ohms to several thousand ohms. A phase-sensitive lock-in detector,⁴⁵ isolated by a Triad G10 (1:35) Geoformer, is used to indicate a null in this secondary loop.

As the resistance of the film changes, it is necessary to adjust the ratio transformers until a null is obtained. The ratio transformer connected to the mutual inductance lump requires very little adjustment because the small voltages that are out-of-phase with the current are almost independent of the film's resistance and temperature. The ratio transformer connected to the standard resistor provides a voltage that is in phase with the primary loop current and is adjusted proportionally to the film's resistance.

A 100 Ω Manganin resistor, surrounded by Dow Corning 200 electronic fluid and immersed in an ice water bath was placed in series with the film and is measured after each data point. Measurements of this resistor, which was stable to 5 ppm, were used to determine the intrinsic drift of the bridge due to changes in lead resistance and changes in room temperature. These effects, as well as anomalies caused by changes in the resistance of the other sections of the film, were somewhat minimized by the presence of the 200 K Ω resistor in series with the film. If a 100 Ω section of the film that was not being measured went superconducting, it would cause a fractional current increase of 100 Ω /200 K or .05% which would show up as a resistance anomaly caused by the bridge design. We could subtract out this anomaly and compensate for any significant bridge drift after measuring the 100 Ω resistor in the ice bath. The 100 Ω resistor also enables us to calibrate the bridge by measuring its known resistance.

The resolution of the bridge is limited by the noise in the circuit and the input noise of the lock-in detector. Calculations by Rhinehart and Mourlam⁴⁶ show that for a 100 Ω film, this noise limits the resolution to 1 - 2 nanovolts --- giving us a resolution of .0001 to .0002 ohms. Measured resolution is about .0002 Ω . Accuracy of the resistance bridge is limited by the accuracy of the standard resistors and is $\pm$ 1%.

SAMPLE PREPARATION AND MEASUREMENT

Preparation of the Substrate

In all of these measurements it is important for the substrate to have high thermal conductivity and a good optical polish so the substrate was made of optically flat, single crystal, 1" x 1" x 1/16" (Z-cut) quartz. To prepare the substrate, the quartz was sequentially cleaned in NaOH, aqua regia, acetone, boiling Decontam detergent, and then rinsed in boiling deionized water. After a final rinse in isopropanol, it was microscopically examined for cleanliness, and any dust remaining was blown off with clean air. One of the substrates had a small crack which did not lie underneath the film and had no effect on the film's resistance.

Gold electrical contacts for the films were then evaporated onto the substrates. The bell jar used for this evaporation could be pumped down to 10^{-5} torr by a cold-trapped diffusion pump and is described by Haskell.⁴⁷ For these electrodes the substrate was masked by a copper sheet with seven appropriately placed holes in it. The mask was taped to the substrate and placed 15 cm above a gold-filled tungsten wire basket. Gold electrodes about 3000 Å thick were laid down at about 2000 Å per minute using an evaporation temperature of 1800°C.

The electrode positions shown in Figure 7 were chosen because they were simple to make and gave a large number of film sections with a minimum number of lead wires. Current enters the film through the large electrode at each end of the "W" and the voltage across each

section is measured by the narrow electrodes at the ends of each section. This electrode pattern has the disadvantages that the potential is measured in the overlap region between two adjacent sections, so that a voltage measurement of section 2 will partially measure the properties of sections 1 and 3 which slightly overlap into section 2. It also causes some uncertainty in the length of each section. The uncertainty in length, however, is less than the 10% - 30% thickness uncertainty, and can be ignored. The effect of measuring the resistivity contributions of adjacent sections at first glance means that the measurement of section 2 is really 94% of section 2 and 3% of sections 1 and 3. Calculations of the worst possible situation, where an adjacent section goes superconducting, shows that there will be a sudden anomalous decrease of a few percent in the measured resistance. Because it depends on the size of the overlap region and on the films' thicknesses and resistivities, this anomaly is difficult to accurately predict and subtract. Fortunately, almost all of the superconducting transitions had widths of less than a few tenths of a Kelvin, and their transition temperatures were low enough so that only the lowest temperature data was affected. Because the Kondo effect typically was seen at temperatures as high as 10 K or 15 K, in almost all cases enough data could be taken at the higher temperatures to accurately characterize the Kondo effect. In actual practice, the anomaly resulting from adjacent sections going superconducting was rarely a problem, but when it occurred, the low temperature data were discarded. A much more common

occurrence was superconducting fluctuations from the same section of the film overpowering a small Kondo effect at low temperatures. In summary, the placement of the gold electrodes used here has some minor disadvantages, but they are not important difficulties.

After the gold was evaporated, the substrate was removed from the bell jar, the mask was unfastened, and nominally 99.99% pure indium was melted onto the edge of the gold electrodes with a soldering pencil. This indium would serve as solder terminals for the wires connecting to the film. These indium solder blobs went superconducting at 3.4 K, but that had no measurable effect on the resistance data.

Preparation of the Pellets

The starting metals for the alloys were nominally 99.9999% pure Pb obtained from Cominco (Lot EM 2287), nominally 99.999% pure In obtained from Cominco (Lot EMS 9803), and 99.99% Ce obtained from Dr. Gschneidner's group of this laboratory (Ce-62073). Surface corrosion is often a problem for Ce, so an electropolish of about 1 minute in a 6% perchloric acid in methanol was used to provide a clean cerium surface which was relatively passive.⁴⁸ The electropolishing was done in a stainless steel beaker held at -50 V. to -100 V. relative to the sample, and with a current density of about 0.5 A/cm^2 . After electropolishing, the cerium was rinsed in methanol.

The lead was cleaned in a 1:3 mixture of 30% hydrogen peroxide and acetic acid, and the indium was cleaned by immersion in concentrated nitric acid. After a final rinse in distilled water, the surfaces of

the samples looked clean and shiny. Gloves and tweezers were used to handle the samples in order to keep clean.

Freshly cleaned and weighed portions each containing about 10 grams of lead or indium and the desired amount of cerium were sealed into outgassed, $3/8$ " diameter tantalum tubes. The sealed tubes of In-Ce were then heated to 1050°C for 3 hours and inverted twice during this time. Finally, the tubes were sealed in outgassed quartz, heated to 1050°C , and rapidly quenched in a salt-ice-water bath at -10°C . The quenching was necessary because we expected the cerium to precipitate into a second phase and the rapid quenching would limit the growth of this cerium-rich second phase. For the Pb-Ce alloys, the procedure was identical except that the samples were heated to 1110°C instead of 1050°C .

After the tantalum was peeled away, small sections from each end of the $3/8$ " diameter ingot were etched and photographed to check for even distribution of the second phase. As shown in Figure 8, the Ce-rich particles shown by the darker areas are about $.0005$ " apart. At 75X the area photographed corresponds to an area of $.060$ " x $.047$ " on the ingot. The ingot will later be cut up into small cylindrical pellets of diameter $.020$ " and length $.040$ ", so the area photographed is 3 times the area of one face of the pellet. Using the average spacing of $.0005$ " between the Ce-rich particles, one calculates about 10^5 such particles in each pellet. Since the distribution of the particles is random, we expect the deviation in the number of particles

in a pellet to be about $\sqrt{105}$, resulting in an error of 0.3% in the cerium concentration. The ingot's surfaces were also examined at 20X and nothing unusual was seen.

The ingots then were electropolished in the 6% perchloric acid solution, rinsed in methanol, dried, and pressed between 2 sheets of clean mylar until they were reduced to approximately 1/4" diameter. After a final electropolishing, rinsing, and drying, the ingots were extruded into a .020" diameter wire in a small hydraulic press. The first few inches of the wire were discarded. The wire was handled with gloves and tweezers, and stored in a vacuum desiccator until it was needed for an evaporation.

A few hours before the quench-condensed film was to be made, the wire was given a final electropolish and cut up into pellets. For this electropolish, approximately 5" of the wire was held by tweezers and partially immersed in the perchloric acid solution. It was then rinsed in methanol, and the other end was similarly electropolished. During electropolishing, the voltage was 50-100 V and the current density was about 1 A/cm². After a final rinse in methanol, the wire was laid on a glass plate and cut into pellets .03" to .05" long with a hardened beryllium-copper knife. Approximately 100 pellets were cut from each wire, and 50 to 70 of them were placed in the pellet dropper. Pellets were randomly selected, with preference to pellets of intermediate (.040") length.

Evaporation Procedure

Evacuation of the evaporator and precooling of the dewars are described below. Within an hour after the pellet dropper was filled, it was loaded into the evaporator and the movable shutter was closed. The evaporator was then evacuated to 500 microns and backfilled with dry nitrogen gas. Subsequently, it was evacuated to about 100 microns, the cold trap was filled, and the diffusion pump was started. After 15-25 hours, depending on how long the evaporator had been contaminated by air, the pressure was reduced to about 8×10^{-5} torr, and the nitrogen dewar was filled with liquid nitrogen. The pressure immediately fell to about 2×10^{-5} torr and after a few hours of additional pumping, the helium dewar also was filled with liquid nitrogen. This further reduced the pressure to 10^{-5} torr after a few hours of pumping.

We wanted the substrate to be the last thing cooled, otherwise it might contaminate its clean surface by cryopumping residual gas. During these operations, the 1/4" diameter stainless steel tube connecting the helium dewar and the substrate was evacuated, so the sample remained close to room temperature. When the pressure was below 10^{-5} torr, the 1/4" stainless steel tube was filled with liquid nitrogen, cooling the substrate in less than an hour to 77 K. Quickly, the liquid nitrogen was blown out of the helium dewar and pumped out of the stainless steel tube. This isolated the substrate at 77 K as liquid helium was transferred. The pressure immediately fell below 10^{-6} torr after transferring liquid helium. An hour before the film was to be made, the 1/4" stainless steel tube was filled with liquid helium, cooling the substrate

quickly to 4.2 K. The pressure in the evaporator was now about 10^{-7} torr. The substrate looked clean when viewed through the window in the manifold.

Just a few minutes before the film was made, the basket was outgassed at 1930°C for 30 seconds with the shutter closed. This outgassing typically caused the pressure to rise immediately to 10^{-5} torr and fall back slowly to 10^{-6} torr in a few seconds. The pressure was up to 10^{-5} torr at the end of the 30 second outgassing. The basket was then cooled to 800°C as we waited for 1 to 2 minutes for the pressure to fall below 10^{-6} torr.

The shutter was then opened and, as the basket was viewed through the window, the $1/8''$ push rod operated the pellet dropper. When a pellet fell into the basket, the basket cooled and changed color. Immediately (< 1 second) afterward the temperature of the basket was increased to 1750°C and held there for 10 seconds. At the end of the 10 seconds, as judged by a nearby clock, the current was decreased to enable the basket to cool to 800°C . The cooling was necessary because whenever pellets were dropped into a hot basket their rapid vaporization caused them to immediately bounce out. The $1/8''$ rod was operated to push another pellet into the basket and the steps above were repeated until the 50-70 pellets for a section had been dropped. For the first pellets of each section, the background (800°C basket) pressure was typically 10^{-6} torr; for the last pellets, typically 10^{-5} torr. During the first second of each pellet's evaporation, a sharp pressure spike

of at least an order of magnitude was indicated on the ionization gauge. As the section was being evaporated, the germanium thermometer warmed from 4.2 K before the first pellet to 5.5 K after the last pellet. To prevent overheating of the chute and manifold, the basket was allowed to cool for about 10 or 20 minutes between sections. After this 10 minute period with the basket off, the temperature had fallen again to 4.2 K and the pressure decreased to 5×10^{-7} torr.

As the section was deposited, its resistance was monitored with the a.c. resistance bridge. The sections usually became electrically continuous after 3-6 pellets. Additional pellets caused the film's resistance to decrease with a gradual leveling off after many pellets were dropped. Sections containing high transition temperature superconductors were difficult to monitor because they changed from normal to superconducting depending on whether the basket was hot. Annealing characteristics which were measured later showed that the films were heated to 8 K - 12 K by the radiation and vapors emitted from the basket.

The four sections of the film were evaporated as described above, with a cooling period of 10-20 minutes followed by a 30 second basket outgassing between sections. All sections had approximately the same evaporation characteristics except that plating of the window hindered control of the pellet dropper for the last sections. Also, for about half of the films, the basket became distorted by being heated while strained by its supports, so more pellets missed the basket for section 4 (last made) than for section 1 (first made).

The total time to make a section of the film was about 1/2 hour: 1 minute for outgassing, 1 minute for opening the shutter, 10-15 minutes for evaporating the pellets, 1 minute for closing the shutter, and 10-20 minutes waiting for things to cool off again. It therefore required two hours to make a film containing four sections. During the two hours, liquid helium boil off was increased by about 1 liter per hour.

Electrical Resistivity Measurement Technique

After the pellets were evaporated, the shutter in the heat shield was closed, and the electrical resistance of each section of the film was measured as a function of temperature. The goal was to determine the superconducting transition temperature, the size of any Kondo resistance rise, the temperature dependence of the high temperature resistivity, and the approximate temperature at which the film begins to spontaneously anneal. The data were taken in the following manner. The first resistance measurements were taken near 4.2 K for each of the film's sections. The film was then cooled and data taken at approximately 0.2 K to 0.5 K intervals down to 1.3 K, the lowest temperature that was possible for us to attain. In these data we searched for the superconducting transition and the Kondo effect. Near superconducting transitions the data were taken at smaller temperature intervals in order to accurately determine the width and temperature of the transition. After the low temperature data were taken, the film was warmed above 4.2 K in 0.5 K intervals and again examined for superconducting

transitions and the Kondo effect. Spontaneous annealing usually occurred at about 8 K - 12 K, causing a large unmistakable irreversible decrease in resistance as the film was warmed, and signifying that the film was prepared at 8 K - 12 K. This was not surprising because one expects the film's surface to be warmer than 4.2 K during evaporation because of radiation from the heated tungsten basket and from the energy of the incident vapors.

The onset of spontaneous annealing prevented taking data at higher temperatures, so the film was heated to 20 K to reanneal the film. For this reannealing, a heater quickly heated the film to 20 K and maintained that temperature to a few tenths of a Kelvin. The film's resistance immediately decreased and continued to decrease throughout the anneal. Typically, the annealing would be continued for 2 or 3 hours, during which time the film's resistance would decrease by a few percent. Although no quantitative measurements were made during the annealing, it was noted that the rate of resistance decrease continually diminished during the anneal. When the rate of resistance decrease had slowed to about half its initial rate, the heater was turned off, allowing the film to cool again to liquid helium temperatures. Data could now be taken up to about 17 K without spontaneous annealing occurring. Most of these data were taken in the newly accessible range from 10 K to 17 K, but the superconducting transition temperatures and the Kondo effects also were rechecked.

In order to study the effects of still higher annealing temperatures on superconductivity and the Kondo effect, some of the films were

annealed at 40 K or above. As expected, the annealing at higher temperatures caused a much larger decrease in resistivity.

All resistance measurements were done in a vacuum better than 10^{-6} torr, so oxidation and decomposition of the films were not problems. Measurements were reproducible from day-to-day providing the film was kept far below its previous annealing temperature. Occasionally, the film warmed above its annealing temperature during a liquid helium transfer, resulting in an accidental anneal. Sometimes after a low temperature anneal, the film would spontaneously anneal at a very slow rate even when kept at 4.2 K. This was imperceptible during a single data-taking session, but amounted to a few nano-ohm-cm per day downward shift. Therefore, the data were taken as quickly as possible and a temperature interval of about 10 K was completed during each data taking session. About 4 or 5 temperatures could be examined in one hour.

Film Size Measurements

After all resistance data were taken, the substrate was removed from the cryostat and stored under vacuum until it was photographed. Afterward the substrate was coated with about 500 Å of aluminum, and the film thickness was measured with a Varian Model 980-400 interference microscope. Uncertainties in the thickness determination were ± 50 Å to ± 100 Å arising from irregularities in the film's flatness and the 60 Å resolution of the microscope. This thickness uncertainty caused an error of $\pm 10\%$ to $\pm 30\%$ in the resistivities of the films, and was the major uncertainty in the resistivity.

The length and width of the film's sections were measured with a travelling microscope and also by measuring the photographs of the film. Both methods agreed to a few percent and did not vary by more than 5% between the films. The second major uncertainty in these measurements was the effects of overlapping film sections, and compensating for the curved corners in the sections. Lengths were measured from the center of the overlap regions, and an average length around the corners was used. These approximations could introduce errors of 10% to 15% in the film's length and subsequent resistivity calculations. Sizes of the film's sections and the resulting formulae for ρ are given in Table 1.

Table 1. Lengths and widths of the film's sections

	Length	Width	$\rho = \frac{wt}{L} R$
Sections 1 and 4	1.36 cm	.152 cm	$\rho = (.110) Rt$
Sections 2 and 3	1.60 cm	.170 cm	$\rho = (.106) Rt$

RESULTS AND DISCUSSION

Superconducting Transition Temperatures

The midpoints of the superconducting transitions (T_c) for the films are shown in Figures 9 and 10, and are listed in Tables 2, 3, 4 and 5. The error bars shown on the figure are the transition widths (ΔT_c) which were typically 0.2 to 0.4 K and were independent of cerium concentration and film thickness. Data were included for all films evaporated above 1600°C; lower evaporation temperatures gave incomplete cerium evaporation, as previously discussed in connection with Figure 8. Transition temperatures could be measured down to 1.3 K and if no transition was observed an arrow is used to indicate that it was less than 1.3 K. In the figures the T_c indicated was the one measured after the lowest temperature anneal --- usually a 10 K or 15 K anneal. This should minimize the tendency of high temperature annealing to raise T_c .

The solid lines through the data are the one parameter fits of the Abrikosov-Gor'kov theory of magnetic impurities in superconductors.¹⁷ Critical concentrations of 6.0% for Pb-Ce and 2.4% for In-Ce were chosen on the low side of the data because annealing and incomplete cerium evaporation tend to raise the transition temperature. An important feature of the data is the downward curvature of the T_c vs. impurity concentration curves, with no superconductivity at high concentrations. This signifies that the cerium is behaving as a local moment and not as a short-lived localized spin fluctuation,²⁶ a non-magnetic resonance state,²⁸ or a non-magnetic impurity,²³ but is a well-defined local moment.

Table 2. Summary of the properties of In-Ce films

Film	Percent Ce C	T boat ($^{\circ}\text{C}$)	Thickness ($\text{\AA}$)	T_c (K)	ΔT_c (K)	ρ ($\mu\Omega\text{ cm}$)	$\Delta\rho$ ($\mu\Omega\text{ cm}$)	$\Delta\rho/c$ ($\mu\Omega\text{ cm/at \%}$)
56-1	1.0	1750	413	3.55	0.2	23.0	0 ^a	0 ^a
-2	2.0	1750	610	1.75	0.8	23.3	.03-.30	.015-.150
-3	1.0	1750	295	3.00	0.4	20.9	0 ^a	0 ^a
-4	2.0	1750	244	<1.3	-- ^b	20.0	.02-.20	.01-.10
55-1	4.0	1750	280	<1.3	-- ^b	36.0	.098	.024
-2	3.0	1750	418	<1.3	-- ^b	28.4	.106	.035
-3	0.0	1750	226	4.33	.04	27.2	0 ^a	0 ^a
-4	2.0	1750	189	<1.3	-- ^b	46.0	.05-.50	.025-.250
54-1	2.0	1750	430	1.6	1.6	11.0	.04-.10	.02-.05

^aA reported value of 0 indicates that the quantity was looked for but not found.

^bA dash (--) indicates that no search for the quantity was made.

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Table 3. Detailed summary of the effects of annealing on the properties of In-Ce films

Film	Anneal	ρ ($\mu\Omega\text{cm}$)	$\Delta\rho$ ($\mu\Omega\text{cm}$)	T_c (K)	Anneal	ρ ($\mu\Omega\text{cm}$)	$\Delta\rho$ ($\mu\Omega\text{cm}$)	T_c (K)
56-1	15 K	23.0	0 ^a	3.55				
-2	15 K	23.3	.03-.30	1.75				
-3	15 K	20.9	0 ^a	3.0				
-4	15 K	20.0	.02-.20	<1.3				
55-1	9 K	36.0	.100	<1.3	20 K	34.3	.098	<1.3
-2	9 K	28.4	.108	<1.3	20 K	27.6	.106	<1.3
-3	9 K	27.2	0 ^a	4.333	20 K	24.7	0 ^a	4.324
-4	9 K	46.0	.05-.50	<1.3	20 K	42.8	-- ^b	<1.3
54-1	10 K	11.0	.04-.10	1.60	30 K	10.7	-- ^b	1.95

^aA reported value of 0 indicates that the quantity was looked for but not found.

^bA dash (--) indicates that no search for the quantity was made.

Anneal	ρ ($\mu\Omega\text{cm}$)	$\Delta\rho$ ($\mu\Omega\text{cm}$)	T_c (K)	Anneal	ρ ($\mu\Omega\text{cm}$)	$\Delta\rho$ ($\mu\Omega\text{cm}$)	T_c (K)	Percent Ce C
								1.0
								2.0
								1.0
								2.0
40 K	30.5	.090	<1.3	293 K	8.07	0 ^a	3.7	4.0
40 K	26.1	.109	<1.3	293 K	9.33	0 ^a	3.2	3.0
40 K	19.0	0 ^a	4.305	293 K	9.32	0 ^a	4.05	0.0
40 K	42.1	-- ^b	<1.3	293 K	25.5	0 ^a	3.9	2.0
110 K	8.5	-- ^b	3.36					2.0

Table 4. Summary of the properties of the Pb-Ce films

Film	Percent Ce C	T boat (°C)	Thickness (Å)	T _c (K)	ΔT _c (K)	ρ (μΩ cm)	Δρ (μΩ cm)	Δρ/c (μΩ cm/at %)
59-1	5.5	1750	300	1.8	0.2	128	.70	.13
-2	7.0	1750	250	<1.3	-- ^a	95	.187	.027
-3	6.0	1750	400	<1.3	-- ^a	105	.218	.036
-4	4.5	1750	600	<1.3	-- ^a	167	.167	.037
58-1 ^b	2.0	1750	250	5.2	0.4	494	5.7	2.8
-2 ^b	5.0	1750	300	2.5	0.6	85	.026-.040	.005-.008
-3 ^b	0	1750	500	6.8	0.2	53	0 ^c	0 ^c
-4 ^b	3.0	1750	360	4.7	0.3	113	0 ^c	0 ^c
57-1	5.0	1750	680	3.3	0.3	154	0 ^c	0 ^c
-2	1.0	1750	1000	6.4	0.2	83	0 ^c	0 ^c
-3	4.0	1750	840	3.9	0.3	145	0 ^c	0 ^c
-4	3.0	1750	750	5.5	0.2	134	0 ^c	0 ^c
53-1	3.9	1750	630	4.1	0.3	162	0 ^c	0 ^c
-4	3.9	1750	671	3.4	0.2	313	0 ^c	0 ^c
49-1	6.0	1600	290	<1.3	-- ^a	139	.15-.25	.025-.142
-2	6.0	1750	340	1.5	1.0	119	.115	.019
-4	7.0	1750	290	<1.3	-- ^a	94	.167	.024
47-3	4.7	1750	540	2.2	0.2	460	0 ^c	0 ^c
-4	4.7	1930	460	3.0	0.2	320	0 ^c	0 ^c
46-2 ^d	4.7	1930	270	3.3	0.8	383	4.0	.85
-3 ^d	4.3	1930	310	3.6	0.3	217	.34	.085

^a A dash (--) indicates that no search for the quantity was made.

^b T_c data taken after 10 K anneal; Kondo effect data taken after 20 K anneal.

^c A reported value of 0 indicates that the quantity was looked for but not found.

^d T_c data and Kondo effect data taken after 30 K anneal.

Table 4. continued

Film	Percent Ce C	T boat ($^{\circ}\text{C}$)	Thickness ($\text{\AA}$)	T_c (K)	ΔT_c (K)	ρ ($\mu\Omega\text{ cm}$)	$\Delta\rho$ ($\mu\Omega\text{ cm}$)	$\Delta\rho/c$ ($\mu\Omega\text{ cm/at \%}$)
45-1	0 ^c	1930	1400	6.5	0.3	308	0 ^c	0 ^c
-2	3.1	1930	1080	4.2	0.3	283	0 ^c	0 ^c
-3	3.9	1930	1000	3.7	0.2	255	0 ^c	0 ^c
-4	4.7	1930	700	1.5	0.4	348	.92	.196
44-2	2.0	1930	960	5.8	0.4	300	0 ^c	0 ^c
-3	4.7	1930	870	2.6	1.0	500	0 ^c	0 ^c
-4	3.9	1930	970	<1.3	-- ^a	600	3.66	.94

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Table 5. Detailed summary of the effects of annealing on the properties of Pb-Ce films. A range of values is indicated for some of the Kondo effect measurements because the onset of superconductivity prevented taking more accurate data

Film	Anneal	ρ ($\mu\Omega\text{cm}$)	$\Delta\rho$ ($\mu\Omega\text{cm}$)	T_c (K)	Anneal	ρ ($\mu\Omega\text{cm}$)	$\Delta\rho$ ($\mu\Omega\text{cm}$)	T_c (K)
59-1	10 K	128.4	.70	1.8	20 K	124.8	.45	<1.95
-2	10 K	95.0	.187	<1.3	20 K	94.5	.192	<1.95
-3	10 K	104.7	.218	<1.3	20 K	104.0	-- ^a	<1.95
-4	10 K	166.8	.167	<1.3	20 K	165.9	.197	<1.95
58-1	10 K	535	+- ^a	5.2	20 K	494	5.1	-- ^a
-2	10 K	86.0	-- ^a	2.5	20 K	85.1	.026-.04	-- ^a
-3	10 K	56.6	0 ^b	6.8	20 K	53.0	0 ^b	-- ^a
-4	10 K	115.1	0 ^b	4.7	20 K	113.3	0 ^b	-- ^a
57-1	10 K	154.5	0 ^b	3.3	20 K	151.9	0 ^b	-- ^a
-2	10 K	83.0	0 ^b	6.4	20 K	69.9	0 ^b	-- ^a
-3	10 K	145.0	0 ^b	3.9	20 K	143.4	0 ^b	-- ^a
-4	10 K	133.6	0 ^b	5.5	20 K	72.0	0 ^b	-- ^a
53-1	8 K	161.6	0 ^b	4.17	21 K	158.8	0 ^b	4.18
-4	8 K	313.5	0 ^b	3.46	21 K	309.9	0 ^b	3.49
49-1	7 K	139.1	.15-.25 ^c	<1.3	20 K	136.9	.14-.24 ^c	<1.3
-2	7 K	119.4	.115	1.50	20 K	118.2	.099	1.58
-4	7 K	93.8	.167	<1.3	20 K	93.2	.150	<1.3
47-3	10 K	460	-- ^a	2.2				
-4	10 K	320	-- ^a	3.0				
46-2	10 K	451	-- ^a	-- ^a	12 K	411	-- ^a	-- ^a
-3	10 K	241	-- ^a	-- ^a	12 K	230	-- ^a	-- ^a
45-1	9 K	308	0 ^b	6.49	20 K	267	0 ^b	6.60
-2	9 K	283	0 ^b	4.24	20 K	279	0 ^b	4.26
-3	9 K	255	0 ^b	3.695	20 K	249	0 ^b	3.70
-4	9 K	348	.92	1.45	20 K	341	.85	1.48
44-2	10 K	300	0 ^b	5.8				
-3	10 K	500	0 ^b	2.6				
-4	10K	600	3.66	<1.3				

^a A dash (--) indicates that no search for the quantity was made.

^b A reported value of 0 indicates that the quantity was looked for but not found.

^c Both 7 K anneal and 20 K anneal measurements show a Kondo effect, but there is too much curvature in the ρ vs. T data to accurately measure $\Delta\rho$. However, in this temperature interval, the 8 K anneal values of $\Delta\rho$ are $11\% \pm 4\%$ greater than the 20 K anneal values of $\Delta\rho$.

Anneal	ρ ($\mu\Omega\text{cm}$)	$\Delta\rho$ ($\mu\Omega\text{cm}$)	T_c (K)	Percent Ce C
41 K	108.5	.25	2.0	5.5
41 K	89.8	.145	2.4	7.0
41 K	98.7	.123	2.5	6.0
41 K	159.6	-- ^a	3.8	4.5
35 K	379	2.4	-- ^a	2.0
35 K	79.9	0 ^b	-- ^a	5.0
35 K	47.4	0 ^b	-- ^a	0.0
35 K	71.5	0 ^b	-- ^a	3.0
				5.0
				1.0
				4.0
				3.0
				3.9
				3.9
77 K	107.3	0 ^b	3.8	6.0
77 K	97.0	0 ^b	4.7	6.0
77 K	79.8	0 ^b	4.6	7.0
				4.7
				4.7
30 K	383	4.0	3.3	4.7
30 K	217	.34	3.6	4.3
77 K	96.3	0 ^b	7.12	0.0
77 K	93.6	0 ^b	6.3	3.1
77 K	85.3	0 ^b	6.2	3.9
77 K	116.8	0 ^b	6.0	4.7
				2.0
				4.7
				3.9

These rates of depression of T_c of $dT_c/dC = 1.0$ K/at % for Pb-Ce and of $dT_c/dC = 1.5$ K/at % for In-Ce are very close to the $dT_c/dC = 1.5$ K/at % measured by Wollan and Finnemore³⁷ in bulk La-Ce and not too different from $dT_c/dC = 2.5$ K/at % in In-Fe and $dT_c/dC = 4.7$ K/at % in Pb-Fe films.^{49,50}

The 6.7 K transition temperatures of the pure lead films is slightly below the 7.1 K - 7.2 K transitions of similarly prepared films of Buckel and Hilsch.⁵¹ Their films go superconducting only slightly below the 7.2 K bulk value, and have a sharper transition with $\Delta T_c \leq 0.1$ K. This discrepancy may be due to the large structural disorder of our films. For example, annealing one of our pure lead films at 77 K decreased its resistivity from 300 $\mu\Omega$ cm to 100 $\mu\Omega$ cm, sharpened its transition, and brought its transition temperature up to Buckel and Hilsch's value.

Indium's 4.4 K transition temperature agrees with the Buckel and Hilsch value of 4.2 K, but it is much greater than the bulk value of 3.4 K. The transition temperature of indium is more sensitive than lead to the amorphous nature of the thin films. As reported by Buckel and Hilsch, the changes in the transition temperatures of quench condensed films depends on the magnitude of the Debye temperature θ_D . Metals with large θ_D show greatly increased T_c ; metals with moderate θ_D show little change in T_c ; metals with low θ_D show a decrease in T_c .

Annealing always increased the transition temperatures of both Pb and In films. Superconducting transitions having characteristic

increases in T_c are shown in Figures 11 and 12. A summary of the shifts in T_c for all Pb-Ce films is given in Figure 13. Notice that the transition temperature changes less than 0.1 K after anneals of 20 K, but that anneals of 40 K usually raise T_c more than 1.0 K. Similar analysis on In-Ce data was performed using the data in Table 3, and the conclusion was drawn that In-Ce can be annealed to 30 K or 40 K without changing T_c by more than a few tenths of a Kelvin. However, annealing In-Ce films to 110 K and 293 K causes increases of a few degrees. Apparently In-Ce behaves like Pb-Ce except that higher annealing temperatures are needed to shift T_c significantly.

Normal State Resistivity

Figure 14 demonstrates three common features of the film's resistivity: 1) A very rapid decrease in resistivity at low temperatures, caused by the onset of superconductivity 2) A region with $dR/dT < 0$, often called the Kondo resistance region 3) A rapid increase in resistivity at high temperatures, caused by the electrons scattering off of phonons and off other electrons. Except for high concentration films that did not become superconducting, and for low concentration films that showed no Kondo effect, these features were generally observed. However, sample inhomogeneities and superconducting fluctuations can cause partial superconductivity at $T > T_c$ and complicate the interpretation of the film's resistivity.

At the lowest temperatures, portions of the film that are becoming superconducting will short the other portions and lower the film's

resistance. The ρ vs. T characteristics of these precursors of superconductivity are not of fundamental importance to us here, and often complicated data analysis by concealing the low temperature behavior of the Kondo anomaly.

For high resistivity quench condensed films, superconducting fluctuations can make a substantial contribution to the conductivity even at temperatures well above T_c , as was shown by Glover.⁵² Generally speaking, the experiments are in reasonable agreement with the work of Aslamazov and Larkin.^{53, 54} This theory was used to estimate the magnitude of these superconducting fluctuations. For our film geometry, the theory predicts a decrease in the resistivity $\delta\rho$ given by $\delta\rho = (1.52 \times 10^{-5} \Omega^{-1}) \left(\frac{T_c}{T - T_c} \right) \rho_0^2 / t$ where ρ_0 is the normal-state resistivity and t is the film thickness. Notice that the excess resistivity depends on ρ_0^2 , so the fluctuations are more important for the high resistivity films. Figure 15 shows results of compensating for these fluctuations in such a high resistivity film (Film 58-1) using both $T_c = 6.5$ K and $T_c = 5.2$ K. The actual transition temperature, although not recorded for this anneal, is known to lie in that temperature interval. As expected, assuming these upper and lower limits results in overcompensation and undercompensation of the fluctuations. Thus superconducting fluctuations can have a considerable effect on the resistivity at temperatures as high as $2T_c$ or $3T_c$. Subtracting out the effects of superconducting fluctuations also increases the resistivity's slope in the Kondo effect.

region by 30% to 50% for these high resistivity films. Compensations for a typically lower resistivity film, shown in Figure 16, also show that the fluctuations again are important up to $2T_c$ or $3T_c$, but that their effect on the slope in the Kondo region is less than 10%.

One should keep in mind that fluctuations and sample inhomogeneity work together to broaden the transition, and that in a full calculation of superconductivity far above T_c , both must be considered. Fluctuation theory predicts a smoothly varying $\rho(T)$ dependence, but the data taken sometimes showed small kinks or steps in the transition region within about 0.1 K of T_c . This may be evidence of small inhomogeneities in the sample causing a narrow range of transition temperatures. Inhomogeneity smears the transition so there is no one defined T_c for the film. Because the combined problem of inhomogeneities and fluctuations was too difficult to consider here, no further attempts were made to subtract them from the higher temperature data. Their possible effects will be noted in subsequent discussion of the normal state data. The important thing to remember is that the true Kondo resistivities are always larger than the measured combinations of fluctuations and Kondo resistivity.

Our main attention is given now to the structure of the normal state resistivity at higher temperatures. The normal state resistivity is expected to obey Matthiessen's rule, $\rho = \sum \rho_i$, where we sum over all possible electron scattering mechanisms. The term for the Kondo effect, approximated by $\rho_K = A \log (T/T_K)$ with $A < 0$, is the only temperature

dependent term at low temperatures and increases logarithmically as the temperature is decreased. The other temperature dependent scattering mechanisms give power law terms like αT^2 , βT^3 , and γT^5 . The T^2 term arises from two mechanisms: conduction electrons scattering off spin waves, and conduction electrons of different mass scattering off each other.⁵⁵ The T^3 term arises from interband scattering of electrons,⁵⁶ and the T^5 term results from small angle scattering of electrons from phonons.⁵⁷ For most of these films the data do not warrant several adjustable parameters in the fit, so these terms are approximated by BT^n . Besides, an extensive study by Wollan has shown that La-Ce can be well represented by this form with constant B and n for all cerium concentrations. When added to the Kondo resistivity, this term causes a minimum in the resistivity.

For this study the most important characterization of the Kondo effect was the magnitude of the resistance rise over one temperature decade, $\Delta\rho$ (1 decade), $\Delta\rho$, or A in the equation above. Because the films are very close to linear in $\log T$, $\Delta\rho$ is then accurately proportional to the slope of ρ vs. $\log T$. It is known from other studies^{58,59} that typically the resistance increases logarithmically for 1 to 1 1/2 decades in temperature, so choosing one decade gives a reasonable estimate of the maximum resistivity contribution for Kondo scattering. Because of the onset of superconductivity or because of the low temperature limitations of the cryostat, a full temperature decade with $\rho \propto \log T$ was never seen, but could be accurately extrapolated in most cases from the data.

A rather important and puzzling aspect of the data is that the magnitude of the Kondo effect, $\Delta\rho$, varies substantially from film to film and in many cases it is below our limit of detection. A Kondo resistance minimum was seen in half of the 26 Pb-Ce films, and was seen in 75% of the 8 In-Ce films.

Figure 17 shows measurements for a film with a superconducting transition far below the temperature of the resistance minimum. This gives a large temperature interval where $d\rho/dT < 0$ and facilitates accurate measurements of slopes in that interval. Figures 15 and 18 show typical resistivities for films with high transition temperatures, showing the rapid decrease at low temperatures caused by statistical fluctuations into the superconducting state. Often this partial superconductivity, extending several degrees above the transition temperature, dominates the resistivity and makes it impossible to measure films with a very small Kondo resistance anomaly. Therefore, films with high T_c are less likely to show a measurable Kondo effect, even if one is actually present. In fact, it was almost impossible to measure a Kondo effect in Pb-Ce films if the transition temperature was above 3.6 K, and the concentration was below 4% Ce (Figure 10). Figure 18 shows a 2% Ce-Pb film where partial superconductivity extends up to 12 K and would have concealed a typical Kondo effect with the temperature of its resistance minimum ($T_{\min}$) of 10 K or 15 K. In the In-Ce films, because $T_{\min} = 5$ K, it was difficult to obtain any Kondo effect data if the film went superconducting above 1.3 K. The

only accurate Kondo data for In-Ce was from high concentration films that showed no superconductivity (Figure 9).

The resistance rise on the high temperature side of the minimum is caused by the scattering of the conduction electrons with phonons and other electrons. These scattering mechanisms also occur at lower temperatures, but since their resistivities vary as T^n , at low temperatures they are much smaller than the Kondo resistivity. Hence, if we go to low enough temperatures, we can be assured that the temperature dependence of the resistivity is caused almost entirely by the Kondo spin-flip scattering. In the intermediate temperature range, we can isolate the Kondo effect resistivity by calculating the high-temperature resistivity, and then subtracting it from the total resistivity by using Mattiessen's rule. Fits to BT^n were made to some of the high temperature data and, as expected, it gives only a small resistivity contribution at low temperatures. Figure 19 compares the low temperature resistivity of a film to the BT^n extrapolated from higher temperatures. Notice that in the Kondo effect region, the BT^n term is less than 10% of the Kondo resistance rise, and that in the region where ρ is proportional to $\log T$, the BT^n term is negligible.

Because one of our major goals was to study the Kondo effect, it might seem best to always fit the high temperature data to BT^n , and then subtract the BT^n dependence in the intermediate temperature region. This is typically done in Kondo effect studies of bulk materials in order to isolate the Kondo effect resistance. Here, however,

it is not that simple, because a high temperature anneal is necessary before the data can be gathered at high temperatures, and the high temperature anneal changes the size of the Kondo resistance rise at low temperatures. Naively, one would like to anneal the film at 50 K, take data on the high temperature resistivity between 20 K and 50 K, fit this data to BT^n , and then subtract the extrapolated BT^n from the resistivity below 10 K. However, the 50 K anneal would greatly alter the size of the Kondo effect, reducing it by about 50%.

Examples of the effects of annealing on the Kondo resistance rise are shown in Figures 20 and 21. As the annealing temperature increases, the ρ vs. T curves flatten, with the effect being most pronounced after high temperature anneals. This behavior was observed in over 20 of the films reported here, but for two of the films annealing increased the size of the Kondo effect. We have no sound reason for eliminating these two films in that they were prepared in the usual prescription, but the occurrence of this rise was so rare that we feel it is spurious. The regular decrease was certainly the rule.

Figure 22 summarizes the effects of annealing on the size of the Kondo resistance rise in Pb-Ce. Notice the strong dependence of $\Delta\rho$ on the annealing temperature, and that anneals of 77 K completely eliminated the Kondo resistance minimum. Another important feature is that even after annealing from 10 K to 20 K there is still an appreciable change in $\Delta\rho$. Similar analysis of the effects of annealing in In-Ce alloys is not as conclusive because only two In-Ce films showed

accurately measurable Kondo effects. However, the size of the Kondo effect is less dependent on annealing in the In-Ce films than in the Pb-Ce films, and $\Delta\rho$ changes only by about 10% following a 40 K anneal (Table 3). So we can see that extensive high temperature data cannot be taken without reducing the size of the Kondo effect. For this reason, detailed fits to $\rho = BT^n$ were not very fruitful. Some were made, showing that the BT^n term is less than about 10% of the observed Kondo resistance rise, and that in the region where the resistance is proportional to $\log T$, the BT^n term is negligible small.

A listing of the logarithmic increase in resistivity, $\Delta\rho$, extrapolated over one temperature decade, is given in Tables 2, 3, 4 and 5. In some cases a range of values is given for $\Delta\rho$, signifying that the onset of superconductivity prevented a more accurate determination, as is illustrated in Figure 14. This problem occurred often for the In-Ce alloys because the low cerium concentrations caused a small Kondo effect with a low $T_{\min}$ which was overpowered by the superconductivity. Cerium also had an intrinsically smaller Kondo effect in indium than in lead, as we will discuss later.

Dividing the Kondo resistivity rise by the percentage of cerium in the alloy gives the "effectiveness" of the cerium in causing the Kondo effect. A graph of the quantity, $\Delta\rho/C$, as a function of film resistivity ρ_0 is given in Figure 23. Films showing no Kondo effect were not included on the graph, but they had a range of resistivities that was identical to films shown. Thus a 4.7% Ce-Pb film with a

resistivity of $500 \mu\Omega \text{ cm}$ might show no Kondo effect (Film 44-3), or it might show a large Kondo effect (Film 46-2). But if we consider those Pb-Ce films that do show a Kondo effect we see that there is a correlation between the effectiveness of the cerium in causing a Kondo resistance rise and the residual resistivity of the film. The high resistivity films show larger Kondo effects than the low resistivity films of the same concentration. A rough line through the data shows that $\Delta\rho/C$ is proportional to $(\rho_0)^2$ or $(\rho_0)^3$, suggesting that the correlation cannot be due to errors in determining film thickness or to other similar errors that would effect $\Delta\rho/C$ and ρ_0 equally. The range of two orders of magnitude in $\Delta\rho/C$ is also surprising. The effect of the superconducting fluctuations on $\Delta\rho/C$ is largest for the high resistivity films, and subtracting them out would make $\Delta\rho/C$ even 30% to 50% larger, thus increasing the differences between the Kondo effects in the high and low resistance films.

These measured values of $\Delta\rho/C$ are not very different from measured values of $\Delta\rho/C$ in other alloy systems. In Cu-Fe alloys,⁵⁸ $\Delta\rho/C = 1.5 \mu\Omega \text{ cm/at \%}$; in La-Ce,³⁷ $\Delta\rho/C = 0.2 \mu\Omega \text{ cm/at \%}$; and in Y-Ce,⁶⁰ $\Delta\rho/C = .45 \mu\Omega \text{ cm/at \%}$. These measurements were on bulk alloys, so scattering mechanisms peculiar to amorphous films were not present. However Knorr and Leslie's⁶¹ study of amorphous Cu-Fe films showed that $\Delta\rho/C = 1.5 \mu\Omega \text{ cm/at \%}$ in a sample with $\rho_0 = 4.7 \mu\Omega \text{ cm}$, and Korn's¹⁶ study of similar films with $\rho_0 = 35 \mu\Omega \text{ cm}$ showed $\Delta\rho/C = 3 \mu\Omega \text{ cm/at \%}$. In these thin films studies, the effect of low temperature annealing was not reported. In passing, it is reassuring to note that our

measured values of $\Delta\rho/C$ do not exceed the unitarity limit of $3.8 \mu\Omega \text{ cm/at } \%$, assuming a spin 1/2 cerium ground state.⁴

For films with sufficient data, Figure 23 also shows the effects of annealing on $\Delta\rho/C$ and ρ_0 . Annealing typically lowers both the residual resistivity and the magnitude of the Kondo resistance rise, but the Kondo resistance rise is lowered the most. One can estimate from Figure 23 that the change in $\Delta\rho/C$ is proportional to the change in ρ_0 raised to the 3rd or 4th power, so the normalized size of the Kondo effect seems correlated with the resistivity of the films when we consider them one-at-a-time as well as in comparisons between different films.

To understand these changes in resistivity in more detail, it is useful to estimate the various lengths and times involved. Electron diffraction studies by Buckel⁶² and Mönch and Sander⁶³ on similarly prepared films show that the grain size is in the range 25 Å to 100 Å, and that the annealing mechanism below 78 K is probably rearrangement of these microcrystals and the elimination of Frenkel defects. Above 100 K grain growth and migration of vacancies and interstitials occurs. Measurements of the size of the residual resistivity ρ_0 can indicate the amount of structural disorder in the films. For the Pb-Ce films, ρ_0 was between 80 and 600 $\mu\Omega \text{ cm}$ at 8 K, compared to the bulk values for pure lead of .02 $\mu\Omega \text{ cm}$ at 8 K and 20 $\mu\Omega \text{ cm}$ at 273 K. For In-Ce we measure $10 \mu\Omega \text{ cm} < \rho_0 < 50 \mu\Omega \text{ cm}$ compared to measured bulk indium values of .0008 to .008 $\mu\Omega \text{ cm}$ at 4.2 K and 8 $\mu\Omega \text{ cm}$ at 273 K.⁶⁴ The

residual resistivities were independent of both cerium concentration and film thickness, indicating that scattering from the cerium and scattering from the surfaces of the film were not important contributions to ρ_0 . A calculation of the mean free path ℓ was made using the expressions for pure lead $\frac{\sigma}{\ell} = 9.4 \times 10^{10} \Omega^{-1} \text{ cm}^{-2}$ determined from Chambers' ⁶⁵ anomalous skin effect measurements, and gave $\ell = 13.5 \text{ \AA}$ for a resistivity of $80 \mu\Omega \text{ cm}$ and $\ell = 1.8 \text{ \AA}$ for a resistivity of $700 \mu\Omega \text{ cm}$. These lengths should be compared to the several hundred angstrom film thickness (t), and to the 10-15 $\text{\AA}$ spacing between the cerium atoms in a perfectly homogeneous 4% Ce-Pb film. Fuchs' ⁶⁶ theory of conductivity in thin films predicts that the thickness dependence of σ will be noticeable only when $t \lesssim \ell$, so size effects should be negligible here where $t \gg \ell$. Similarly, for the In-Ce films, using $\frac{\sigma}{\ell} = 9.0 \times 10^{10} \Omega^{-1} \text{ cm}^{-2}$, gives $\ell = 20 \text{ \AA}$ to $110 \text{ \AA}$ for typical films. ⁶⁷

Superconducting and Normal State Scattering Times

Normal state scattering times

Determination of a scattering relaxation time from the resistivity cannot be exact because Fermi Surface effects in these amorphous materials are not known. Indeed there may be a range of relaxation rates which contribute to the scattering relaxation time τ_m . One can, however, estimate τ_m by calculating the extremes one would expect for a perfect single crystal and for the free electron values.

The scattering time τ_m associated with the low temperature resistivity rise $\Delta\rho$ can be calculated using $\tau = \frac{m}{ne^2 \Delta\rho}$ with free electron

values of the mass, m , and the electron density, n . For Pb, assuming $n = 4$ electrons/atom, one gets $\tau_m = (2.7 \times 10^{-20} \text{ sec } \Omega \text{ cm})/\Delta\rho$; for In, assuming 1 electron/atom, one gets $\tau_m = (9.1 \times 10^{-20} \text{ sec } \Omega \text{ cm})/\Delta\rho$. Because of the amorphous nature of the films, one expects the effects of crystal structure to be small and the electrons to be scattered often enough so that a free electron approximation is sensible. The other extreme, that of a single crystal, gives another value of τ_m that can be compared to the free electron value. Using the previously discussed experimentally determined values of $\frac{\sigma}{\ell}$ from the anomalous skin effect data in single crystal Pb and using $V_F = .50 \times 10^8 \text{ cm/sec}$ one gets that $\tau_m = \frac{\ell}{V_F} = (21.7 \times 10^{-20} \text{ sec } \Omega \text{ cm})/\Delta\rho$. Similarly for In, using the previously discussed anomalous skin effect results for $\frac{\sigma}{\ell}$ and using $V_F = .65 \times 10^8 \text{ cm/sec}$ gives $\tau_m = (12 \times 10^{-20} \text{ sec } \Omega \text{ cm})/\Delta\rho$. Taking an average of the free electron value and the single crystal value for both Pb and In gives approximately $\tau_m = (1.0 \times 10^{-19} \text{ sec } \Omega \text{ cm})/\Delta\rho$. We should remember that this approximate value for τ_m is accurate to about half an order of magnitude.

Let us now consider the normalized scattering time, $\bar{\tau}$, or the scattering time resulting from the addition of one percent cerium. This quantity can be calculated from $\bar{\tau} = \tau \cdot C$ where C is the cerium concentration in atomic percent, and will be useful in making comparisons between films of different concentrations. Scattering times determined from this formula are indicated along the right edge of Figure 23. Notice that for all of the indium alloys, the scattering

times per percent cerium equal $2 - 5 \times 10^{-12}$ seconds. We have also measured several other In-Ce films which have $\bar{\tau}_m \approx 3 \times 10^{-12}$ seconds, but they are not shown because the onset of superconductivity caused a large order of magnitude uncertainty in $\frac{\Delta\rho}{C}$. Therefore, within experimental error, $\bar{\tau}_m$ is constant equal to $2 - 5 \times 10^{-12}$ seconds for the In-Ce films. For Pb-Ce films, $\bar{\tau}_m$ varies over a much wider range from 4×10^{-14} seconds to 8×10^{-12} seconds and it depends on the resistivity ρ_0 . One should remember that half of the films showed no low temperature resistivity rise, and for those $\bar{\tau}_m$ is unknown.

Superconducting scattering time

The scattering time associated with the breaking of Cooper pairs can be determined from the Abrikosov-Gor'kov¹⁷ expression for the energy broadening of a Cooper pair, $\Gamma_S = 1.27 K (T_{cp} - T_c)$ and the Heisenberg uncertainty relation $\tau_S = \frac{\hbar}{\Gamma_S}$. When combined these give $\tau_S = (.60 \times 10^{-11} \text{ sec K}) / (T_{cp} - T_c)$. From Figures 9 and 10 we see that adding an additional 1% Ce to Pb decreases T_c by about 0.8 K. Similarly, adding 1% Ce to In decreases T_c by about 1.3 K. These rates of depression of T_c are approximately constant for all concentrations up to the critical concentration. Therefore, our formula gives $\bar{\tau}_S = 7.5 \times 10^{-12}$ seconds for Pb-Ce, and gives $\bar{\tau}_S = 4.7 \times 10^{-12}$ seconds for In-Ce. These results are almost independent of cerium concentration and film resistivity.

Comparisons of the scattering times

There is good agreement between the values of $\bar{\tau}_m$ and $\bar{\tau}_S$ for the In-Ce films, both being about 5×10^{-12} seconds, and both being

relatively constant. This result is not in disagreement with the widely held assumption that the same spin-flip scattering mechanism is responsible for both the destruction of superconductivity and the low temperature resistivity rise. Agreement between $\bar{\tau}_m$ and $\bar{\tau}_s$ for Pb-Ce, however, films is relatively poor: $\bar{\tau}_s$ is constant and equal to 8×10^{-12} seconds, but $\bar{\tau}_m$ varies from 4×10^{-14} seconds to 8×10^{-12} seconds. It may be significant that none of these films had $\bar{\tau}_m > 8 \times 10^{-12}$ seconds, so the condition $\bar{\tau}_m \leq \bar{\tau}_s$ may set upper limit on the scattering time. However, the inescapable conclusion is that for a large fraction of the Pb-Ce films, the scattering associated with the low temperature rise is occurring much more frequently than the pair breaking scattering. The scattering times were found here to differ by as much as a factor of 200 and this discrepancy is probably not due to the experimental errors or to the uncertainties in the calculations. The differences in scattering times were largest for high resistivity films ($500 \mu\Omega\text{cm}$). For the lowest resistivity Pb-Ce films the difference was less than the errors in the experiment.

Supporting evidence for a fundamental difference between scattering mechanisms in normal and superconducting Pb-Ce films is found from studies of the properties of a particular film when it is annealed. Annealing changes the resistivity of the film, and if the normal state properties $\Delta\rho$ and τ_m are correlated with the resistivity, then they should show changes. Likewise, if the superconducting properties T_c and τ_s are independent of resistivity then they should not change

after slight annealing. Of course one should be careful to avoid high temperature anneals that cause massive cerium precipitation.

The effect of annealing on $\Delta\rho/C$ is shown in Figure 23 by the points which are joined by dashed lines. Basically, the rule that $\Delta\rho/C$ decreases when ρ_0 decreases seems true when considering a film being annealed as well as when considering films of different resistivities. This indicates that whatever is causing the resistivity rise $\Delta\rho$ is becoming less effective as the film is annealed. As seen in Figure 22, this effect is seen even after relatively low temperature anneals of 20 K and seems to be proportional to the annealing temperature up to 40 K or 80 K. This behavior is to be contrasted with the behavior of T_c as shown in Figure 13. T_c is almost unchanged after the low temperature anneals and changes appreciably only after 40 K anneals. This effect cannot be explained by considering the effects of superconducting fluctuations. Both T_c and ρ_0 remain almost unchanged for these low temperature anneals, so the fluctuation conductivity should not change with annealing. Table 6 and Figure 24 summarizes data for all films where both T_c and $\Delta\rho$ could be determined after annealing. Notice that annealing changes τ_s by less than 3%, while changing τ_m by approximately 30%.

A possible explanation for the relative constancy of τ_s , when compared with τ_m , may be found in the nature of the superconducting state. Superconducting electrons are bound together in a many-body state of dimension equal to the coherence length ξ . The superconducting

Table 6. Summary of τ_s and τ_m for all films where they could be determined after several anneals. Notice that the percentage changes in τ_m are an order of magnitude larger than the changes in τ_s

Film	Percent Ce C	T _{anneal}	ρ ($\mu\Omega$ cm)	$\Delta\rho$ ($\mu\Omega$ cm)	T _c (K)	τ_s (sec)	τ_m (sec)
59-1	5.5%	10 K	128.4	.70	1.8	1.22×10^{-12}	1.43×10^{-11}
59-1	5.5%	20 K	124.8	.45	<1.95	$(1.22-1.28) \times 10^{-12}$	2.23×10^{-11}
59-1	5.5%	41 K	108.5	.25	2.0	1.28×10^{-12}	4.00×10^{-11}
49-2	6.0%	7 K	119.4	.115	1.50	1.15×10^{-12}	8.70×10^{-11}
49-2	6.0%	20 K	118.2	.099	1.58	1.17×10^{-12}	11.1×10^{-11}
49-2	6.0%	77 K	97.0	0	4.7	3.0×10^{-12}	∞
45-4	4.7%	9 K	348	.92	1.45	1.14×10^{-12}	1.09×10^{-11}
45-4	4.7%	20 K	341	.85	1.48	1.15×10^{-12}	1.17×10^{-11}
45-4	4.7%	77 K	117	0	6.0	8.56×10^{-12}	∞

electrons, unlike the normal state electrons, are affected by the average of the sample's properties over a relatively large volume $\frac{4}{3} \pi \xi^3$. For our films we use the Ginsberg-Landau⁶⁸ coherence length $\xi = \sqrt{\xi_0 \ell}$, where ξ_0 is the intrinsic coherence length of a pure bulk sample and ℓ is the mean free path for the electrons. Using this formula with the accepted values $\xi_0(\text{Pb}) = 830 \text{ \AA}$ and $\xi_0(\text{In}) = 2600 \text{ \AA}$, and the measured values of ℓ from the normal state resistivity, we get $\xi = 40 \text{ \AA}$ to $100 \text{ \AA}$ for the Pb-Ce alloys, and get $\xi = 200 \text{ \AA}$ to $500 \text{ \AA}$ for the In-Ce alloys. Thus the superconducting electrons average the scattering mechanisms over relatively large distances. This behavior should be contrasted with the behavior of the normal state electrons participating in Kondo scattering. As mentioned earlier, at low temperatures these electrons can be thought of as being in a virtually bound state centered at the cerium impurity. The size of this state can be estimated from the magnetic proximity work of Hauser³² who reports its dimensions to be $10 - 30 \text{ \AA}$ in Pd-Fe and Pd-Cr. In Cu Fe, Stassis and Shull³³ and Boyce and Slichter³⁴ find the dimensions to be under $8 \text{ \AA}$. Therefore the normal electrons participating in spin-flip scattering while being in this virtual bound state are very sensitive to sample properties relatively near the cerium and do not average sample properties over a large volume. If annealing acted to change the cerium's local environment, such as by causing a migration of cerium atoms towards each other or by removing crystal defects typically found near the cerium atoms, the result might be to greatly

influence the nature of the bound state and thereby change $\bar{\tau}_m$. On the other hand, the superconducting electrons in their larger bound state average more of the sample volume and might not be affected as much. Although we are not sure what is causing the variability of $\bar{\tau}_m$, we offer this as a possible clue to its explanation.

SUMMARY

Within experimental uncertainty, the superconducting transition temperatures of both In-Ce and Pb-Ce films show typical Abrikosov-Gor'kov concentration dependence with a rate of depression $\frac{dT_c}{dc} \sim -1 \text{ K/at \% Ce}$, indicating that the cerium is a magnetic impurity in In and Pb. As one expects for a well-behaved magnetic impurity doped superconductor, the measured T_c were also independent of the film's resistivity and essentially unchanged by low temperature annealing. However, high temperature annealing, probably causing cerium precipitation, resulted in substantial increases in T_c .

A Kondo resistance minimum could be observed in only 50% of the Pb-Ce films and 75% of the In-Ce films, probably because the onset of superconductivity hindered measurements on low cerium concentration films. For the higher concentration films where extensive normal state data could be taken at low temperatures, the resistivity was proportional to $\log T$ even at 1.3 K, although a full temperature decade with ρ proportional to $\log T$ could never be observed because temperatures below 1.3 K were inaccessible with this apparatus.

Extrapolation of the observed ρ vs. $\log T$ behavior over one temperature decade shows a resistivity rise per percent cerium $\Delta\rho/C$ of approximately $.03 \mu\Omega \text{ cm/at \% Ce}$ for all the In-Ce films. For the Pb-Ce films, however, $\Delta\rho/C$ ranged from 0.015 to $3.0 \mu\Omega \text{ cm/at \% Ce}$, scaling with the film's resistivity according to $(\Delta\rho/C) \propto (\rho_0)^2$ or $(\rho_0)^3$. This correlation between $\Delta\rho/C$ and ρ_0 was found true for

resistivity changes caused by annealing as well as between films of different resistivities which were made in different evaporations. Except for two atypical films, both high and low temperature annealing reduced $\Delta\rho/C$, with the amount of reduction greater for the high temperature anneals.

Calculations based on the T_c and $\Delta\rho/C$ measurements show that the superconducting scattering time $\bar{\tau}_s$ and the normal state scattering times $\bar{\tau}_m$ are approximately equal in In-Ce films, both being about 5×10^{-12} sec. For the Pb-Ce films, the superconducting scattering time is about 8×10^{-12} sec, but the normal state scattering time varies from 4×10^{-14} sec to 8×10^{-12} sec. Therefore for a large fraction of the Pb-Ce films there is either too little pair-breaking, or there is too much Kondo scattering.

There are now at least three experiments which show that the onset of superconductivity can cause profound changes in the formation of a Kondo-like many body state. Wollan and Finnemore³⁷ first showed that $\bar{\tau}_s$ was much greater than $\bar{\tau}_m$ for La-Ce alloys and to explain these data the Kondo temperature in the superconducting state would have to be at least a factor of 10 smaller than the normal state Kondo temperature. Bader³⁸ then showed via specific heat measurements that the peak in the Kondo specific heat in $(\text{La,Ce})\text{Al}_2$ is lowered by about a factor of 10 by the onset of superconductivity. In the experiment reported here, the results confirm that the phenomena is quite general in that it occurs in s-p band metals like Pb and In as well as the d-band

metals like La and LaAl_2 , and in addition it shows that amorphous quench condensed films behave in much the same way as crystalline bulk samples. The spin correlations associated with superconductivity markedly suppress spin correlations associated with the Kondo scattering.

FIGURES

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Figure 1. Vapor pressures of the metals used in the evaporation^{39,40,41}

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Figure 2. Evaporator-cryostat

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Figure 3. Pellet dropper

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Figure 4. Superconducting transition temperatures of 4.7% Ce-Pb films evaporated from baskets held at different temperatures

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Figure 5. Photograph of typical film showing the four sections, gold electrodes, and indium solder blobs. Figure 7 shows the dimensions of the film in more detail

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Figure 6. 400 Hz resistance bridge used for measuring the film's resistivity

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Figure 7. Electrode positions on substrate

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Figure 8. Photograph of etched ingots at magnification of 75X. Top photograph is of 1.0 % Ce-In; bottom photograph is of 2.0 % Ce-Pb. The dark regions are the cerium-rich second phase

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Figure 9. Superconducting transition temperatures of In-Ce alloys as a function of cerium concentration. The line through the data is a fit to the Abrikosov-Gor'kov theory of magnetic impurities in superconductors. The solid data points represent films that showed a measurable Kondo effect

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Figure 10. Superconducting transition temperatures of Pb-Ce alloys as a function of cerium concentration. The line through the data is a fit to the Abrikosov-Gor'kov theory of magnetic impurities in superconductors. The solid data points represent films that showed a measurable Kondo effect. If no error is indicated, the width of the transition was less than 0.4 K

Figure 11. Superconducting transition of a 4.7% Ce-Pb film after anneals of 9 K and 20 K, showing the increase in T_c after high temperature annealing.

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Figure 12. Superconducting transition of a 6.0% Ce-Pb film after anneals of 7 K and 20 K, showing the increase in T_c after annealing

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Figure 13. Summary of the influence of annealing at $T = T_{\text{anneal}}$ on the superconducting transition temperature of Pb-Ce films. It shows that low temperature anneals have very little effect on T_c

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Figure 14. Typical In(Ce) film resistivity

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Figure 15. Compensating for superconducting fluctuations in a high resistivity film far above the transition temperature. Points marked with ● are uncompensated. Points marked with □ have been compensated assuming $T_c = 5.2$ K. Points marked with △ have been compensated assuming $T_c = 6.5$ K

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Figure 16. Compensating for superconducting fluctuations in a moderate resistivity film. Points marked with ● are uncompensated. Points marked with ○ are compensated with the measured $T_c = 1.8$ K.

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Figure 17. A film which shows a very large temperature interval where $\rho \propto \log T$ because $T_c \ll 1.3$ K

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Figure 18. A film showing superconducting fluctuations interfering with Kondo effect measurements below 18 K. T_c is approximately 6 K for this film

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Figure 19. Measured resistivity of film 59-3 (10 K anneal) compared to the extrapolated ρ from a 20 K anneal. Points marked $\square$ are extrapolated from $\rho = (1.5 \times 10^{-10} \Omega \text{ cm/K}^2) T^{2.0}$ derived from a fit to data in the range $14 \text{ K} < T < 17 \text{ K}$. Points marked $\bullet$ are data of 5/11/74. Points marked $\circ$ are data of 5/14/74

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Figure 20. Example of annealing lowering $\Delta\rho$ in Pb-Ce films

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Figure 2]. Typical resistivity data after several anneals

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Figure 22. The effects of high temperature annealing of Pb-Ce films on lowering the size of the Kondo effect Δ_0 . Even 20 K anneals have an appreciable effect on Δ_0 , in contrast to behavior of T_c shown in Figure 13

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Figure 23. The Kondo resistance rise over 1 temperature decade per percent cerium concentration in Pb-Ce films ● and in In-Ce films □. The dashed lines are for data that was taken on one film after several anneals. Data is included only for films showing a Kondo effect. The scattering times τ_m were calculated using $\tau_m = (1.0 \times 10^{-19} \Omega \text{ cm sec/at \%}) / (\Delta\rho/C)$ derived in text

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Figure 24. Superconducting scattering time τ_s and Kondo scattering time τ_m for all Pb-Ce films where both could be determined after annealing. Solid lines connect measurements on the same films for different anneals. Notice that the changes in τ_s are about an order of magnitude smaller than the changes in τ_m

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