be considered in looking for unstable transverse deviations from $\bar{\psi}$. Thus we have, in Eq. (C13),

$$\lambda_{-1,q}=-\tfrac{1}{2}\alpha+q^2. \quad \text{(C38)}$$

Let $d_{\max}$ be the largest linear dimension of the sample perpendicular to the direction of the current. The Ginzburg-Landau boundary condition is that ψ have zero gradient normal to a surface through which no supercurrent flows. Thus the smallest allowed q other than zero is $\pi/d_{\max}$, and this mode will be unstable if

$$d_{\max}>\pi(2/\alpha)^{1/2}=\pi\sqrt{2}\xi(T). \quad \text{(C39)}$$

Equation (C39) is our criterion for a superconducting channel to be effectively one-dimensional.

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Electron-Tunneling Measurements on Lanthanum and Lanthanum-Lutetium Alloy Films

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Results of electron-tunneling measurements on evaporated films of fcc lanthanum and dhcp lanthanum-lutetium alloys are presented. The ratio of the zero-temperature energy gap to the temperature at which the energy gap vanishes for both the pure lanthanum and lanthanum-lutetium alloy samples varied from 3.41 to 3.58. If one fits the lowest-temperature data for the energy gap with a curve of the BCS temperature dependence, the values at intermediate temperatures fall below the weak-coupling BCS prediction. The conductance maxima for the (pure La)-Al_2O_3-Al diodes are larger than predicted by the weak-coupling BCS theory. The conductance maxima for the lutetium alloy samples are more nearly equal to the weak-coupling BCS values than are those of the pure samples. They were not significantly altered by the presence of small zero-voltage anomalies. Hence zero-voltage anomalies are not enhanced at temperatures below the superconducting transition temperature. No change in conductance as large as 0.1% was observed which could be associated with the second energy gap predicted by the multiband-superconductor theory of Kuper, Jensen, and Hamilton. Kondo's multiband-superconductor theory is consistent with the experimental results. It is shown that if the f band in Kondo's theory is approximately 20 meV or more higher than the Fermi level, then Kondo's theory reduces to a single-parameter theory having a gap equation identical in form to the BCS gap equation.

I. INTRODUCTION

THERE has been considerable speculation concerning the mechanism for superconductivity in lanthanum.[1–3] Similar elements such as scandium, yttrium, and lutetium are not superconducting down to 0.2°K while lanthanum is superconducting at around 6°K. It has been suggested that the Cooper pairs can make transitions to nearby f states and that these transitions are responsible for lanthanum's relatively high transition temperature.

Electron-tunneling measurements can provide information to test these theories. Previous measurements[4] gave an anomalously low ratio of the zero temperature energy gap $2\Delta(0)$ to transition temperature kT_c of 1.65 ± 0.15. The measurements on face-centered cubic (fcc) lanthanum films and double hexagonal close-packed (dhcp) lanthanum-lutetium alloy films reported here give values for this ratio varying from 3.41 to 3.58. This value is in the range expected on the basis of BCS theory. The difference between the two results is due to sample preparation and will be discussed in Sec. II. Hauser's measurements[5] on evaporated lanthanum films are in reasonable agreement with those reported here, but the values he has obtained for the energy gap are smaller. Recently, Levinstein *et al.*[6] have performed measurements on bulk samples using the technique of point tunneling. Their average value of $2\Delta(0)/kT_c$ was 3.7, though they measured values for the ratio as low as 3.3. Section II describes the method of sample preparation and measuring technique, and gives the experimental results. Section III discusses the results in terms of the multiband-superconductor theories. In particular, it is shown that Kondo's theory reduces to a single-parameter theory (like the BCS theory) if the f band is not too close to the Fermi level.

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[2] C. G. Kuper, M. Anthony Jensen, and D. C. Hamilton, Phys. Rev. **134**, A15 (1964).
[3] D. C. Hamilton and M. Anthony Jensen, Phys. Rev. Letters **11**, 205 (1963).
[4] A. S. Edelstein and A. M. Toxen, Phys. Rev. Letters **17**, 196 (1966).
[5] J. J. Hauser, Phys. Rev. Letters **17**, 921 (1966).
[6] H. J. Levinstein, V. G. Chirba, and J. E. Kunzler, Phys. Letters **24A**, 362 (1967).

II. EXPERIMENTAL

A. Preparation and General Properties of the Samples

Because the method of sample preparation affects the results, this method will be described in some detail. Microscope slides were used for substrates. First a film of silver 0.25 mm wide and about 10 000 Å thick was evaporated. This film was then covered with an aluminum film 0.50 mm wide and 10 000 Å thick. Usually the aluminum was doped with about 2% of manganese to keep the aluminum from becoming superconducting. The undercoating of silver ensured that the composite film had a low resistance. The substrate was then removed from the evaporator and painted with formvar paint so that only a small area of approximately 0.05 mm^2 was left exposed in the center of the aluminum film. The aluminum was oxidized 15 to 30 min in air before being placed in vacuum. A cross strip 2.3 mm wide of lanthanum was then evaporated so that the center of the lanthanum film was near the unpainted region of the aluminum oxide. Hence, tunneling could occur only between the middle regions of the films. This eliminated possible complications due to edge effects. During the evaporations, the residual pressures varied from 5×10^{-7} to 10^{-5} mm Hg and the substrate was at room temperature. To minimize contamination of the lanthanum film due to the relatively poor vacuum, the lanthanum was evaporated rapidly (100–500 Å/sec) from a tungsten boat. The film thickness was measured to an accuracy of better than 10% by an optical interference technique.

Lanthanum can exist at room temperature in the face-centered cubic and the double hexagonal close-packed phases. Both phases are composed of layers of close-packed molecules, but they differ from one another in the stacking sequence. The stacking sequence in the fcc phase is *ABC* while in the dhcp phase it is *ABAC*. The lanthanum films evaporated in the manner described above were determined by x-ray analysis to be predominantly in the fcc phase. There may have been as much as 5 or 10% dhcp phase present.

Lanthanum-lutetium alloy films were prepared in order to investigate the properties of the dhcp phase. This was done because the addition of a few percent lutetium stabilizes lanthanum into the dhcp phase. At a given temperature lutetium's vapor pressure is about an order of magnitude greater than that of lanthanum. Hence, some caution must be employed in preparing these alloy films in order to minimize concentration variations. The evaporation rate used for the alloys was 600 Å/sec or greater. The substrate was exposed for only 1 to 3 sec near the middle of the evaporation process. For reasons discussed later in connection with the experimental results, it is felt that these films were reasonably homogeneous.

One of the films was analyzed for impurities by spark-source mass spectroscopy. The number of atomic ppm of magnetic and major nonmagnetic impurities detected were: iron 150, nickel 150, chromium 30, neodymium 100, yttrium 80, aluminum 200, silicon 200, chlorine 100. The method was not suitable for detecting the amount of oxygen present.

Typical values for the junction area were about 0.05 mm^2 and the junction resistance was 0.1 to 10 Ω. Considering the long oxidation time of $\frac{1}{2}$ h, the junction resistance was about two or three orders of magnitude smaller than usual for diodes fabricated with another metal[7] in place of the lanthanum. Changes of this magnitude can be expected because the work function of lanthanum is only 3.3 eV.[8] To determine if the insulator thickness was anomalously low, the capacitance of one of the diodes, 73 aA, was measured by pulse techniques. Taking the dielectric constant of Al_2O_3 to be 8.8, the average thickness of the insulation was calculated to be 50 Å. This is a reasonable value for the insulator thickness.

The diodes deteriorate unless stored in vacuum at 77°K. Changes in diode resistance of nearly an order of magnitude have been observed after 10 h at room temperature. From free-energy data[9] on Al_2O_3 and La_2O_3 it is possible that lanthanum will react with the insulation. All samples were either measured immediately after they were prepared or stored in vacuum at 77°K until used.

B. Measurements

The crossed strip geometry of the diodes permitted a four-point measurement of the characteristics. Because of the low resistance of the diodes it was convenient to make measurements at constant current. The current was the sum of a constant dc current and a 1000-cps ac current of constant amplitude. The resulting ac voltage which is proportional to the diode resistance was measured using standard lock-in detection techniques as a function of the dc bias and plotted on an *X-Y* recorder. The magnitude of the constant ac current was adjusted so that the peak to peak voltage modulation was about 20 μV. Changes in resistance of 0.1% could be detected. In order to facilitate comparison with theory the conductance was computed. The solid curve in Fig. 1 shows a normalized conductance curve $g(V)$ taken at 1.22°K. The conductance has been normalized by the limiting large voltage conductance. Theoretically one should normalize by using the normal-state conductance. However, if the normal-state conductance is essentially constant as a function of the applied voltage, then for very low-impedance diodes it is better to use the limiting large voltage super-

[7] Ivar Giaever and Karl Megerle, Phys. Rev. **122**, 1101 (1961).
[8] K. A. Gschneidner, Jr., *Rare Earth Alloys* (D. Van Nostrand, Inc., Princeton, New Jersey, 1961), p. 53.
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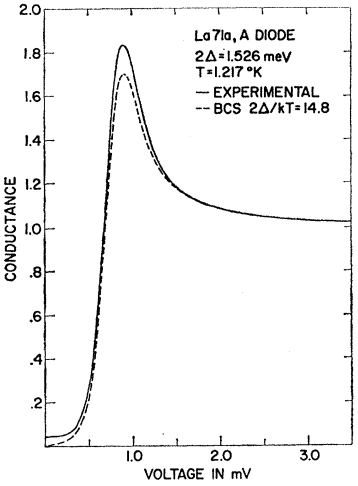

FIG. 1. Normalized conductance versus applied voltage for sample La71aA. The dashed curve is the weak-coupled BCS prediction for this quantity based upon $2\Delta=1.526$ meV.

conducting-state conductance in normalizing. By driving the film normal with a magnetic field it is possible to eliminate complications which might arise due to the temperature dependence of the characteristics. However, for low-impedance diodes, such as the ones employed in the present study, the strip resistance of the metals comprising the diode will affect the characteristics when the metal is in the normal state. In fact, in Ref. 4, it was suggested that this was the cause of an observed conductance change. Further work at this laboratory and elsewhere[10] confirms the importance of this effect for low-impedance diodes. In the case of tunneling from a normal metal to a superconductor, the normalized conductance is predicted to have the form[11]

$$g(\mathrm{V})=\int_{-\infty}^{\infty} N(V')K(V, V', T)dV', \qquad (1)$$

where

$$K(V, V', T)=ce^{y}/T(e^{y}+1)^2,$$
$$c=11.61,$$
$$y=c(V-V')/T. \qquad (2)$$

The function $N(V)$ is the ratio of the density of states of the superconductor to its density of states above its transition temperature T_c. The variable V is measured from the Fermi level. The constant c has been chosen so that V is expressed in meV and T in °K. In the weak-coupling limit BCS theory predicts that

$$N(V)=|V|/(V^2-\Delta^2)^{1/2} \quad \text{for } |V|>\Delta \qquad (3)$$
$$=0 \quad \text{for } |V|\leq\Delta,$$

where 2Δ is the energy gap. Bermon[12] has tabulated the conductance defined by Eqs. (1) to (3). Using his tabulated values, a dashed theoretical curve is plotted in Fig. 1. The single adjustable parameter Δ is chosen so that the maxima of the two curves occur at the same voltage. The measured zero-voltage conductance is only a few percent of the large voltage limiting conductance. Hence, the "leakage" current is small. This can be regarded as indicating the excellent quality of the diode. The experimental maximum is larger than the theoretical one based on weak-coupling BCS theory. This feature is common to all samples that have small "leakage" currents and has been observed in the strong-coupled superconductor mercury.[13]

Figure 2 shows tunneling characteristics measured at several temperatures near and above T_c. The presence of the anomaly shown in Fig. 2 does not depend on the aluminum being doped with manganese. It was present in an undoped aluminum sample and absent in several doped samples. Its magnitude is similar to that observed by Bermon and Ginsberg[13] for aluminum oxide, but of opposite sign! Wyatt[14] and Rowell[15] have seen such anomalies and Appelbaum[16] has suggested they are due to magnetic states within the oxide. It is perhaps surprising that the anomaly was not always present when the aluminum oxide was formed from the doped aluminum. In the absence of an applied field, Appelbaum has shown that the conductance $g(\mathrm{V})$ due to these states is proportional to $\ln\{(eV+k_\beta T)/E_0\}$. This is the temperature and voltage dependence observed for tunnel junctions composed of two normal metals. The tunneling probability is proportional to the sum of two terms of the form

$$P^{(n)}(\omega)=\int_{\epsilon_F-E_0}^{\epsilon_F+E_0}\frac{\rho^{(n)}(\epsilon)f(\epsilon)\,d\epsilon}{\epsilon-\omega}, \qquad n=a, b, \qquad (4)$$

where a and b refer to the two metals, ρ is the density

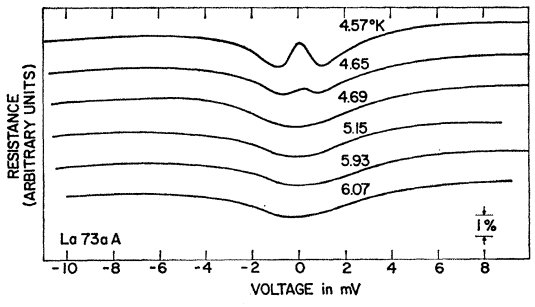

FIG. 2. Curves of resistance of one diode, La73aA, at several temperatures which show the presence of a zero-voltage anomaly.

[10] R. J. Pedersov and F. L. Vernon, Jr., Appl. Phys. Letters **10**, 29 (1967).

[11] This expression can be obtained by differentiating Eq. (4.8) of Ref. 7.

[12] Stuart Bermon, Technical Report No. 1, 1964 (unpublished). Performed under National Science Foundation Grant No. NSF-GP1100, University of Illinois. This report also contains a program which was used to extend Bermon's table.

[13] S. Bermon and D. M. Ginsberg, Phys. Rev. **135**, A306 (1964).

[14] A. F. G. Wyatt, Phys. Rev. Letters **13**, 401 (1964).

[15] J. M. Rowell and L. Y. L. Shen, Phys. Rev. Letters **17**, 15 (1966).

[16] Joel Appelbaum, Phys. Rev. **154**, 633 (1967).

of states, and f is the Fermi function. Applebaum's derivation assumed that the density of states is a slowly varying function. Clearly, this assumption is not valid if either of the metals is a superconductor. The tunneling probability as well as the density of states will be singular at Δ. One might expect that the effect will be enhanced for voltages such that $eV \approx \Delta$.

Because of this, some caution must be used in drawing any conclusions from the fact that the measured conductance maximum is larger than predicted by weak-coupling BCS theory. However, there have been samples which did not exhibit a zero-voltage conductance change and yet had conductance maxima larger than predicted by BCS theory. This is illustrated in Fig. 3, which shows a plot of the magnitude of the conductance maxima g_m versus reduced temperature $t = T/T_c$ for several samples of pure lanthanum: La70aA, La71aA, La73aA, and of lanthanum–lutetium alloys: La74aA, La74aB. The temperature at which the gap vanishes was taken as T_c. All the samples of pure lanthanum gave nearly the same results independent of the presence of a zero-voltage anomaly. The insert shows the region near T_c. Above T_c the value of the zero-voltage anomaly is shown. The curve represents the value of g_m one obtains from BCS theory if the ratio $2\Delta(0)/kT_c$ equals 3.52. The points for the pure samples consistently lie above the curve independent of the presence of a zero-voltage anomaly. Evidently the possible enhancement of the zero-voltage anomaly when one of the metals is a superconductor is not large enough to significantly alter the shape of the conductance curve. Included in Fig. 3 are results for two lanthanum–lutetium samples. They will be discussed more fully later. Their values of g_m agree with those predicted by BCS theory.

To within 0.1% there was no reproducible structure which could be associated with the presence of a second energy gap or a phonon spectrum. The former is predicted in one of the multiple band superconductor theories.[2] In light of the strained nature of the evaporated films the absence of a phonon spectrum is not too surprising. Rowell and Kopf[17] observed that strains can wash out the phonon spectrum. Evidence for the strained nature of the films is discussed below. Levinstein *et al.*,[6] in their point tunneling measurements, have reported seeing the phonon spectrum in bulk samples having higher residual resistivity ratios.

Three different determinations were employed for measuring the temperature dependence of the energy gap. They are based on: (1) the voltage at which the maximum in conductance g_{max} occurs; (2) the zero-voltage conductance $g(0)$; (3) the magnitude of g_{max}. The first method is described above and is the most accurate at low temperatures. At high reduced temperatures it becomes very insensitive. Using the tabulated values,[12] the quantities described in 2 and 3 can

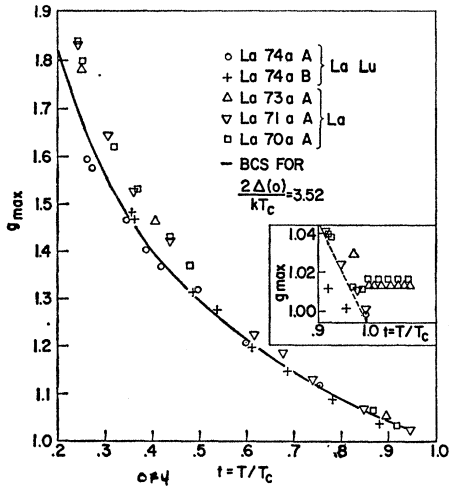

FIG. 3. Plot of the conductance maximum g_{max} versus reduced temperature $t = T/T_c$ for several samples. The solid curve represents the weak-coupling BCS prediction for this quantity. Samples La70aA, La71aA, La73aA are of pure lanthanum. Samples La74aA, La74aB are lanthanum-lutetium alloy samples. The g_m's of the alloy samples follow the BCS prediction while the pure samples have larger values of g_m.

be used to determine the energy gap. There is usually a small "leakage" current present at low voltages in excess of the theoretically predicted one. This implies that the value of the energy gap based on the zero-voltage conductance will be a lower bound on the correct value. If the "leakage" current is small, then this method will be accurate at high reduced temperatures. As discussed earlier, at low reduced temperatures g_{max} is larger than theoretically predicted. Hence, the value of the energy gap based upon the magnitude of g_m will be larger than the one that gives the best fit to the data. It is likely that this method gives an upper bound on the correct energy gap. If a zero-voltage anomaly is present it will tend to lower the value of the lower bound determined by using $g(0)$ and raise the value of the possible upper bound determined by using g_{max}.

Figure 4 shows the temperature variation of the energy gap. The points at low temperature are based on the voltage at which the maximum in conductance occurs. Because a small zero-voltage anomaly was present the values of $g(0)$ and g_{max} were corrected before they were used to compute the lower and possible upper bounds. The extrapolated curve through the low-temperature points lies very close to and above the lower bounds based on the zero-voltage conductance. The dashed curve is the temperature variation of the energy gap based on the weak-coupling BCS theory, $2\Delta(0) = 1.526$ meV and $T_c = 4.94$°K. It lies slightly above the upper bound based upon quantity 3. The correct value for the energy gap is probably closer to the lower than to the upper bound. Hence, the experimental temperature variation of the energy gap lies below the theoretical prediction of weak-coupling theory. This effect

[17] J. M. Rowell and L. Kopf, Phys. Rev. **137**, A907 (1965).

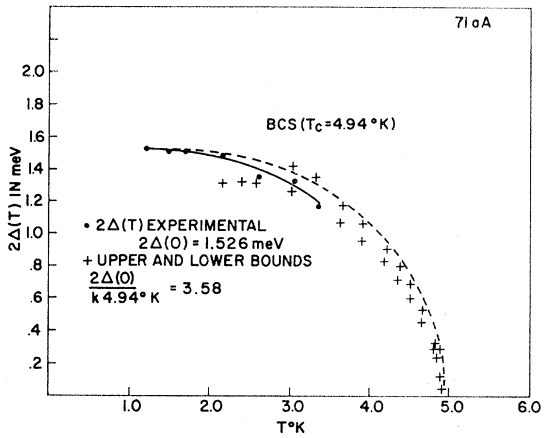

FIG. 4. The temperature variation of the energy gap. The points and crosses represent experimental values and bounds, respectively, on the energy gap. The solid curve is the BCS weak-coupling prediction.

has been seen on several samples, including a lanthanum-lutetium alloy sample, La71aA, containing 9 at.% lutetium. The lutetium concentration was determined by x-ray fluorescence. This sample was determined by x-ray analysis to be in the dhcp phase. Hence this property of $\Delta(T)$ is independent of the phase of the lanthanum film. It is not clear whether this is characteristic of bulk lanthanum or is just a characteristic of lanthanum films prepared under the conditions described above. Energy-gap measurements by Levinstein *et al.*[6] on bulk lanthanum made over a smaller temperature range than that of the present work do not show this deviation from the BCS temperature dependence. Their results imply either an anomalously high transition temperature for each phase or a deviation from the BCS temperature dependence of $\Delta(T)$ in the opposite direction from that reported here.

Table I shows a summary of results for several samples. The last two samples are lanthanum–lutetium alloy films. Under the listing T_{cr} is the range over which the resistive transition occurs. The temperature T_{cg} is the temperature at which the energy gap vanishes. That the leakage currents were small is indicated by the small values listed in Table I of the normalized zero-voltage conductance $g(0)$ at 1.2°K. The conductance has been normalized by the large-voltage limiting conductance. For the alloy sample La74aB, $g(0)$ at 1.2°K is only 0.05 greater than the theoretical prediction. Weak-coupling BCS theory predicts that the ratio $2\Delta(0)/kT_c$ is equal to 3.52. Because the energy gap often vanishes at a temperature T_{cg} slightly below the resistive transition temperature T_{cr}, there is some uncertainty as to which temperature to use in computing the ratio $2\Delta(0)/kT_c$. There are two listings for this ratio. The first is based upon the bottom of the resistive transition temperature T_{cr}. The second, based upon T_{cg}, is likely to be more significant. For some samples, the two ratios are nearly equal. When this occurs the

TABLE I. Results on several samples.

Sample	Composition	Energy gap (meV)	T_{cr} (°K)	T_{cg} (°K)	Residual resistivity ratio	Diode resistance room temperature (ohms)	La film thickness (Å)	$g(0)$, $T=1.2$°K	$(2\Delta/kT_{cr})$	$(2\Delta/kT_{cg})$
71aA	La	1.526	5.13–5.39	4.94	3.63	2.46	11 000	0.045	3.46	3.58
68aA	La	1.512	5.32–5.53±0.05	4.97±0.05	3.70	0.0729	26 000	0.06	3.30	3.54
70aA	La	1.46	5.16–5.40	4.92±0.05	3.50	12.9		0.11	3.28	3.45
73aA	La	1.38	5.06–5.50	4.69		14.1	19 000	0.12	3.17	3.41
74aB	$La_{0.91}Lu_{0.09}$	0.980	3.31–3.39	3.28	1.78	1.55	2 200	0.10	3.43	3.47
74aA	$La_{0.951}Lu_{0.049}$	1.290	4.37–4.43	4.37	1.33	0.975	1 600	0.09	3.43	3.43

first listing based on T_{cr} is large and nearly equal to the average of the second listings. Also, when $2\Delta(0)$ is smaller as in sample La73aA, T_{cg} is also smaller and the ratio $2\Delta(0)/kT_{cg}$ is nearly unchanged, but there is no such correlation with $2\Delta(0)/kT_{cr}$. It is seen that the average of the second listings is close to the weak-coupling BCS prediction of 3.52. These values are larger than those obtained by Hauser,[5] which averaged about 3.2. If one uses the Douglass criterion[18] instead of the one employed by Hauser for determining the energy gap in case both metals comprising the diode are superconductors, the values of $2\Delta(0)/kT_c$ obtained from Hauser's data are still smaller. The measurements[6] of Levinstein *et al.* yield values for $2\Delta(0)/kT_c$ ranging from 3.3 to 3.9, with the average for the dhcp phase being 3.7 and for the fcc phase being 3.9. They interpreted their spread of values as due to anisotropy. Specific-heat measurements[19] yield values for this ratio of around 3.7 for both phases. Thompson's microwave surface-resistance measurements on evaporated films[20] indicate that $2\Delta(0)/kT_c$ increases from 1.64 to 2.87 when the films are annealed. Infrared absorption[21] and thermal conductivity[22] measurements give values for the ratio of 2.85.

The resistive transitions T_{cr} listed in Table I are lower than the measured value[21] of 6.06°K for bulk fcc lanthanum. They are in agreement with the transition temperatures previously reported[4] for evaporated lanthanum films used in electron-tunneling measurements. Thompson[20] has found that a suitable heat treatment raises both the transition temperature and the residual resistance ratio. The annealing process presumably increases the crystalline perfection. Magnetic impurities[23,24] have the effect of washing out the structure in the conductance. The sharp conductance curves, such as the one shown in Fig. 1, make it very unlikely that the depression in transition temperature is due to magnetic impurities.

It is felt that the results on the lanthanum-lutetium alloys indicated these films were reasonably homogeneous. The samples were in the dhcp phase. The temperatures T_{cg} listed in Table I are equal in one case and nearly equal in the other case to the temperature corresponding to the bottom of the resistive transition. Because of its higher vapor pressure the concentration of lutetium might be higher in the first part of the film, i.e., the part nearest the oxide. This part of the film would then have a lower transition temperature and presumably a smaller energy gap. If this were the case one would not expect T_{cg} and the bottom of the resistive transition to be so nearly the same. Further, the large values of $g_{\max}$ and low values of $g(0)$ are consistent with the absence of large concentration variations.

It is appropriate at this point to discuss the difference between the results listed in Table I and those previously reported.[4] The diodes used in the earlier measurements did not have the edges of the lanthanum film masked with formvar paint. These diodes have characteristics less sharp than those reported on here and sometimes the energy gap was absent at 4.2°K. At the time of the earlier measurements these features were not observed due to lack of sensitivity. Evidently the masking of the edges of the lanthanum film has rather a large effect.

It is not certain why covering the edges of the lanthanum film has such a big effect. Thin lanthanum films have low transition temperatures[5] and presumably small energy gaps. The region of a lanthanum film near the edge, being thinner, will have a low transition temperature and a small energy gap. If tunneling occurs over the entire width of the film the tunneling characteristics will be altered by the small gap region near the edge. Clearly, it is desirable to remove this complication. It is possible that the formvar paint masking the lanthanum also affects its properties. The large thermal contraction of the formvar paint may have changed the stress on the lanthanum film; however, the transition temperature and residual resistance ratio of a film evaporated on the formvar paint were in the range shown in Table I.

Recent samples with uncovered edges have smaller energy gaps than those listed in Table I but not as small as those quoted in Ref. 4. Hence, the edge effect probably cannot account entirely for the difference between the past and present measurements. This remaining discrepancy is not understood.

Microwave surface-resistance measurements[20] on films prepared under similar evaporation conditions yield smaller energy gaps than those listed in Table I.

In summary, it is felt that the present measurements represent an improvement over previous ones in that they give more reproducible results and were performed under conditions in which edge effects were eliminated. The results listed in Table I for the ratio $2\Delta(0)/kT_{cg}$ are in approximate agreement with the weak-coupling BCS prediction of 3.52. Recent bulk tunneling[6] and specific-heat measurements[19] give values around 3.7.

III. RELATION TO MULTIPLE BAND THEORIES

As discussed earlier, it has been suggested that the superconductivity in lanthanum was due to multiple band effects. This section will summarize the predictions of some of these multiple band theories[1–3] and compare them with the experimental results of Sec.

[18] D. H. Douglass, Jr. and R. Meservey, Phys. Rev. **135**, A19 (1964).
[19] D. L. Johnson and D. K. Finnemore, Phys. Rev. **158**, 376 (1967).
[20] W. A. Thompson, Phys. Letters **24A**, 353 (1967).
[21] J. D. Leslie, R. L. Capelletti, D. M. Ginsberg, D. K. Finnemore, F. H. Spedding, and B. J. Beaudry, Phys. Rev. **134**, A309 (1964).
[22] T. Mamiya *et al.*, J. Phys. Soc. Japan **20**, 1559 (1965).
[23] M. A. Woolf and F. Reif, Phys. Rev. **137**, A557 (1965).
[24] Preliminary measurements show this occurs in lanthanum–cerium alloys.

II. It will be shown that a special case of Kondo's theory is compatible with the experimental results. In this special case Kondo's theory reduces to a single-parameter theory with a gap equation identical to the BCS gap equation.

All the multiple band theories use a Hamiltonian of the same form, which in the case of two bands can be written

$$\mathcal{H}=\sum_{ks}(\epsilon_k a_{ks}^{\dagger}a_{ks}+e_k b_{ks}^{\dagger}b_{ks})+\sum_{kk'}(V_{kk'}a_{k\uparrow}^{\dagger}a_{-k\downarrow}^{\dagger}a_{-k'\downarrow}a_{k'\uparrow}+U_{kk'}b_{k\uparrow}^{\dagger}b_{-k\downarrow}^{\dagger}b_{-k'\downarrow}b_{k'\uparrow})+\sum_{kk'}J_{kk'}(a_{k\uparrow}^{\dagger}a_{-k\downarrow}^{\dagger}b_{-k'\downarrow}b_{k'\uparrow}+\text{c.c.}),\quad(5)$$

where ϵ_k and e_k are the single-particle energies of the two bands measured with respect to the Fermi energy. To be explicit we shall consider a conduction band composed of s electrons and a localized f band. Equation (5) has a simple interpretation. The interactions V and U are pairing interactions within each band, whereas J is the interaction of electrons in the different bands. The interaction term has been chosen to describe the simultaneous destruction of a pair in one band and the creation of a pair in the other. One way the various multiple band theories differ from one another is in their choice of the parameters U, V, and J.

The Hamiltonian can be diagonalized by a suitable Bogoliubov transformation. The quasiparticle energies in the two bands which will be denoted as the s and f bands are of the form

$$E_s=(\epsilon_k^2+I^2)^{1/2},\quad(6)$$

$$E_f=(e_k^2+K^2)^{1/2}.\quad(7)$$

Equations (6) and (7) have an important consequence. If, as will turn out to be the case, I and K are constant near the Fermi level, then the density of states in the two bands will have exactly the same form as the BCS density of states Eq. (3). It should be noted that despite this formal similarity with regard to the two bands, Eq. (6) and (7), there will be no singularity in the density of states in the f band if there are no single-particle f band states at the Fermi level. Hence, there will be a singularity in the density of states in the conduction band but none in the f band unless the bands overlap or there is a condensation into the f band. Therefore, the shapes of conductance curves for the s band observed in tunneling measurements are identical to those of the usual BCS superconductor.

In their theory, Kuper *et al.*[2] chose U attractive, i.e., negative. The electrons will condense into lower-energy states in both bands and there will be two energy gaps. As stated earlier, no change in conductance as large as 0.1% was detected which could be associated with a second energy gap. This implies the density of states of f electrons N_f is much less than the density of states of s electrons N_s or that the model is not applicable to lanthanum. If $N_f \ll N_s$, it is difficult for the f band to cause a significant enhancement of T_c, since T_c is of order[25] $N_f U/20N_s$. Further, the ratio $2I/kT_c$ is not expected to equal 3.52. The values listed in Table I are near 3.52.

Kondo, on the other hand, assumed that U is repulsive and constant. In this case there will be no condensation in the f band or second energy gap. In Kondo's theory an empty f band is assumed to lie an energy Γ_1 above the Fermi level. Since the predicted absence of a second energy gap is consistent with the experimental result, it is relevant to consider whether the other predictions of Kondo's model are consistent with the experimental results. Kondo derived an expression for the transition temperature in the case that $\Gamma_1 \gg kT_c$. In this section, the gap equation will be derived subject to this limitation. It will be shown that the gap equation's form is identical to the BCS gap equation.

It is assumed that

$$V_{kk'}=-V \quad \text{for} \quad |\epsilon_k| \text{ and } |\epsilon_{k'}|<\hbar\omega$$
$$=0 \quad \text{otherwise.}\quad(8)$$

Further, it is assumed that the densities of states in the two bands are constant and equal to N_s and N_f over the energy ranges $(-\Delta_1, \Delta_2)$ and (Γ_1, Γ_2), respectively. Outside these energy ranges they are taken to be zero. The simplified form of Kondo's equations for the gap parameters for the case $\Gamma_1 \gg kT_c$ are

$$2I_i=I_i N_s V\int_{-\hbar\omega}^{\hbar\omega}(1-2f)(\epsilon^2+I_i^2)^{-1/2}d\epsilon+2KN_f Ja,\quad(9)$$

$$2I_e=2KN_f Ja,\quad(10)$$

$$2K=-2KN_f Ua+I_i N_s J\int_{-\hbar\omega}^{\hbar\omega}(1-2f)(\epsilon^2+I_i^2)^{-1/2}d\epsilon+2I_e N_s Jb,\quad(11)$$

where f is the Fermi function, $a=\ln(\Gamma_2/\Gamma_1)$, $b=\ln(\Delta/\hbar\omega)$, and $\Delta=(\Delta_1\Delta_2)^{1/2}$,

$$I_k=I_i \quad |\epsilon_k|<\hbar\omega$$
$$=I_e \quad \Delta_2>\epsilon_k>\hbar\omega \text{ and } -\hbar\omega>\epsilon_k>-\Delta_1,\quad(12)$$

$$K_k=K, \quad \text{for all } k.\quad(13)$$

Eliminating, I_e one obtains

$$2(1+N_f JaU-N_f N_s J^2 ab)K=I_i N_s J\int_{-\hbar\omega}^{\hbar\omega}(1-2f)(\epsilon^2+I_i^2)d\epsilon.\quad(14)$$

[25] This bound is obtained by combining Eqs. (28a) and (41) of Ref. 2.

Multiplying Eq. (9) by J and Eq. (14) by V and subtracting one obtains

$$2I_iJ-2KV(1+N_fUa-N_fN_sabJ^2)=KN_fJ^2a \quad (15)$$

or

$$K=JI_i/(V+N_fJ^2a+N_fVaU'), \quad (16)$$

where

$$U'=U-N_sbJ^2. \quad (17)$$

Thus Eq. (9) can be written

$$\frac{1}{N_s[V+J^2\{U'+1/(N_fa)\}^{-1}]}$$

$$=\frac{1}{2}\int_{-\hbar\omega}^{\hbar\omega}(1-2f)(\epsilon^2+I_i^2)^{-1/2}d\epsilon. \quad (18)$$

Equation (18) has exactly the same form as the BCS gap equation where the usual $(N_0V)^{-1}$ is replaced by the left side of Eq. (18). Thus in the weak-coupling limit the ratio of energy gap to transition temperature is unchanged from the value 3.52 and the temperature dependence of the energy gap is the same as predicted by BCS theory. As stated earlier, the density of states predicted by all the multiple band theories is identical to the BCS density of states, Eq. (3). Tunneling measurements of $\Delta(T)$ and conductance curves cannot distinguish between an ordinary superconductor and one described by Kondo's model.

In concluding this discussion of Kondo's model it is worth examining how much greater Γ_1 must be than kT_c for the above to be valid. As the ratio Γ_1/kT_c decreases the parameter a becomes a function of temperature. It was an approximation for

$$a=\int_{\Gamma_1}^{\Gamma_2}(1-2f)(e^2+K^2)^{-1/2}de. \quad (19)$$

Near T_c

$$a=a_0-|\delta a|, \quad (20)$$

where

$$|\delta a|<(2kT_c/\Gamma_1)\exp(-\Gamma_1/kT_c), \quad (21)$$

$$a_0=\ln(\Gamma_1/\Gamma_2). \quad (22)$$

At $T=0$

$$a=a_0-\tfrac{1}{4}K^2\left(\frac{1}{\Gamma_1^2}-\frac{1}{\Gamma_2^2}\right). \quad (23)$$

Since K from Eq. (16) is probably of order I_i or kT_c the correction term to a_0 is small if Γ_1 is appreciably greater than kT_c.

IV. CONCLUSION

The results of tunneling measurements on fcc lanthanum and dhcp lanthanum-lutetium alloy films are, for the most part, in good agreement with BCS theory. For all the samples made with their edges covered the ratio $2\Delta(0)/kT_{cg}$ is close to the value 3.52 predicted by weak-coupling BCS theory. It is not completely clear why covering the edges of the lanthanum film has such a large effect or why the microwave surface resistance measurements give different results. To within 0.1% no second energy gap was observed. In the case of the lanthanum diodes the conductance maxima are consistently larger than predicted by BCS theory and fall on the same curve when plotted as a function of reduced temperature. This may be connected with the possibility that lanthanum is a strongly coupled superconductor. Lanthanum's relatively high transition temperature and low Debye temperature, $T_D\approx 140°$K, suggest lanthanum might be a strongly coupled superconductor. The recent specific-heat and bulk tunneling measurements indicate $2\Delta(0)/kT_c\approx 3.7$ and hence are consistent with this hypothesis. That the values of $g_{\max}$ for the alloy samples were nearly equal to the value predicted by BCS theory may imply that the alloys are weakly coupled superconductors. The measured temperature dependence of the energy gap $2\Delta(T)$ is slightly different than predicted by weak-coupling BCS theory, but this may be due to difficulties in sample preparation.

Of the multiple band superconductor theories, Kondo's appears to be consistent with the experimental results. It has been shown that Kondo's theory reduces to a single-parameter theory which is equivalent to the BCS theory if the f band is not too close to the Fermi level. Hence, it is possible that Kondo's theory is consistent with the experimental results only because the present measurements cannot distinguish between Kondo's theory and the usual BCS theory.

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