

## Superconductivity in Pure La and La-Gd†

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(Received 24 August 1964)

Superconducting La doped with the magnetic impurity Gd has been investigated to determine whether the thermodynamic properties show evidence for "gapless" superconductivity. The measurements show that the specific heat of pure hcp La closely follows the predictions of the BCS theory. The addition of small amounts of Gd does not appreciably change the normal-state electronic specific heat, but it drastically alters the superconducting characteristics. An increase in the Gd content decreases the rate at which the normalized superconducting specific heat  $C_{es}/\gamma T_c$  approaches zero. This may be due to a diminishing ratio of the energy of the energy gap to the critical temperature, or it may be due to ordering of the Gd ions. The measurements do not extend to low enough temperatures to distinguish between these two possibilities. The magnitude of the specific-heat jump at  $T_c$  is depressed by the Gd somewhat more rapidly than  $1.43\gamma T_c$ , but less rapidly than is suggested by the electron-tunneling energy-gap measurements. These alloys can support current densities greater than  $5 \times 10^4$  A/cm<sup>2</sup>, and they show no latent heat at the transition in a magnetic field. The latter two characteristics are qualitatively similar to behavior of type II superconductors.

ONE of the best established regularities in the properties of superconducting elements is the fact that the energy gap at low temperatures  $2\Delta$  is approximately equal to  $3.5kT_c$ , where  $k$  is the Boltzmann constant and  $T_c$  is the critical temperature. Extensive experimental and theoretical evidence confirms this rule for a wide variety of pure materials.<sup>1</sup> Recent measurements by Leslie and Ginsberg<sup>2,3</sup> indicate that this relation may also hold for superconducting elements doped with nonmagnetic impurities but for this case the evidence is less complete.

If magnetic impurities are added to the material the situation may be quite different. Measurements by Reif and Woolf<sup>4</sup> show that the energy gap of In doped with small amounts of Fe does not follow the  $2\Delta=3.5kT_c$  relationship. They find that  $T_c$  of their thin films as determined by electrical resistance decreases linearly with Fe concentration and extrapolates to zero at approximately 2.0 at. %. This depression is similar to the effect measured for bulk material by Matthias *et al.*<sup>5</sup> In addition, they find that the energy gap determined by electron tunneling decreases more rapidly than  $3.5kT_c$  and extrapolates to zero at approximately 0.9 at. % Fe. This indicates that there is a region of Fe concentration between 0.9 and 2.0 at. % which may show infinite electrical conductivity but no trace of an energy gap in the tunnel characteristic, the so-called region of "gapless" superconductivity.

Theoretical attempts to describe these materials have been only partially successful. Perturbation theory ap-

proaches by Suhl and Matthias<sup>6</sup> and by Baltensperger<sup>7</sup> give a linear depression of  $T_c$  which is close to the measured value, but they also predict a first-order phase transition in zero magnetic field. Failure of specific-heat measurement to detect a latent heat at the transition,<sup>8</sup> however, indicates that further modification of this theory is necessary. A Green's-function approach by Abrikosov and Gorkov,<sup>9</sup> based on the assumption that the magnetic ions are randomly oriented, describes the energy gap and the thermodynamic properties in the limit of small gap (or high magnetic ion concentration). This theory predicts the disappearance of the energy gap at 90% of the concentration necessary to destroy the infinite conductivity. This is in qualitative agreement with the results of Reif and Woolf<sup>4</sup> but quantitatively the discrepancy is large. The theory also predicts a low-temperature electronic specific heat which approaches zero as  $\gamma T$  for high impurity concentration (where  $\gamma$  is normal-state electronic specific heat coefficient). Measurements on La 0.7 at. % Gd by Phillips and Matthias,<sup>10</sup> however, fail to show this  $\gamma T$  behavior, and in fact show a large hump near 0.5°K, which the authors attribute to ordering of the Gd ions. Since the theory assumes no ordering, its applicability to these materials is questionable.

We have set out to determine whether or not the unusual behavior of the electron tunneling energy gap is reflected in corresponding changes in the thermodynamic properties of dilute magnetic alloys. Presented here are measurements on pure La and La-Gd in the 1.5 to 9.0°K temperature range.

† Contribution No. 1555. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

<sup>1</sup> J. Bardeen and J. R. Schrieffer, *Progress in Low Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1961), Vol. III, p. 170.

<sup>2</sup> J. D. Leslie and D. M. Ginsberg, *Phys. Rev.* **133**, A362 (1964).

<sup>3</sup> D. M. Ginsberg and J. D. Leslie, *IBM J. Res. Develop.* **6**, 55 (1962).

<sup>4</sup> F. Reif and M. A. Woolf, *Phys. Rev. Letters* **9**, 315 (1962).

<sup>5</sup> B. T. Matthias, H. Suhl, and E. Corenzwit, *Phys. Rev. Letters* **1**, 93 (1958); *Phys. Chem. Solids* **13**, 156 (1960).

<sup>6</sup> H. Suhl and B. T. Matthias, *Phys. Rev.* **114**, 977 (1959).

<sup>7</sup> W. Baltensperger, *Helv. Phys. Acta* **32**, 197 (1959).

<sup>8</sup> J. Müller and M. Risi, *Helv. Phys. Acta* **33**, 459 (1960).

<sup>9</sup> A. A. Abrikosov and L. P. Gor'kov, *Zh. Eksperim. i Teor. Fiz.* **39**, 178 (1960) [English transl.—*Soviet Phys.—JETP* **12**, 1243 (1961)].

<sup>10</sup> N. E. Phillips and B. T. Matthias, *Phys. Rev.* **121**, 105 (1961).

## EXPERIMENTAL

Preparation of the fcc modification of La has been described in an earlier publication,<sup>11</sup> so a few comments will suffice here. An anneal at 400°K for 16 h is sufficient to transform a La sample to fcc, but the quench to room temperature must be very rapid or the sample partially reverts to the hcp<sup>12</sup> structure. We find that samples more than  $\frac{1}{8}$  in. thick do not quench rapidly enough. In addition, even a small amount of strain will induce the transformation from fcc to hcp. Therefore we have found it necessary to handle all fcc samples in helium-filled Pyrex tubes.

These severe restrictions on sample thickness and strain make specific heat measurements on fcc very difficult and have led us to use the hcp modification. To prepare these samples we arc melt 0.5 mole of material into a slab approximately  $\frac{1}{4}$  in.  $\times$   $\frac{1}{2}$  in.  $\times$  3 in., anneal for 16 h at 400°C in an outgassed Ta capsule, and quench into water. At this point the sample is approximately 50% hcp. The sample then is removed from the Ta capsule in an argon atmosphere and the copper sheets which hold the heater and thermometer are firmly glued to the large surfaces with a thin layer of undiluted GE-7031 varnish. The cryostat is assembled and the varnish is dried overnight in a vacuum. Final transformation to hcp is induced by strain as the sample cools to 4°K.

The specific-heat measurements are made by a pulse heating technique which employs powers of the order of 100  $\mu$ W for durations of the order of 60 sec. The equilibrium time for transit of heat across the sample and the addenda is less than 1 sec for power levels less than 1 mW.

We have calibrated the secondary thermometer, a Honeywell type II germanium resistor, at 121 points between 4.2 and 20°K by means of a constant-volume gas thermometer. Since similar thermometers have been described many times,<sup>13</sup> we outline here only the statistics pertinent to our measurement. The 135 cc high-purity copper gas bulb has eight deeply recessed holes for the secondary thermometers. All lead wires are thermally anchored to the shield before going to the inner system. A 2 cc vapor-pressure bulb, which is used as the primary thermometer at 4.2°K, extends into the center of the gas bulb. The 0.020-in. i.d. gas bulb capillary has one copper-constantan thermocouple cemented to it at approximately 30°K to assist in the calculation of the dead-volume correction. The maximum dead-volume correction, calculated with the assumption that the thermal conductivity of the capillary varies linearly with temperature, is one part in 900. The filling pressure of 3 Torr/°K gives a maxi-

mum nonideality<sup>14</sup> correction of 0.016°K. The thermomolecular correction is determined from the calculations of Roberts and Sydoriak.<sup>15</sup> If we assume that He<sup>4</sup> has a saturated vapor pressure of 760.00 Torr at 4.215°K, then we measure the temperature of equilibrium hydrogen at a saturated vapor pressure of 760.00 Torr to be  $20.253 \pm 0.03$ °K. This value is within 0.01°K of that derived from work of Moessen *et al.*,<sup>16</sup> but is 0.025°K less than the value given by Hilsenrath *et al.*<sup>17</sup> As an additional check on thermometry we have measured the vapor pressure of He<sup>4</sup> from 4.2 to 5.0°K and confirm the work of Berman and Swenson<sup>18</sup> (and hence the *T*-58 scale)<sup>19</sup> to  $\pm 0.003$ °K.

## RESULTS AND DISCUSSION

## Specific Heat of Pure La

The specific heat results for pure La in zero magnetic field are shown in Fig. 1. There is a distinct jump at the hcp critical temperature 4.9°K but no trace of a jump at the fcc critical temperature 6.0°K. The absence of a jump at 6.0°K, coupled with the absence of fcc lines in an x-ray diffractometer pattern for this sample, leads us to conclude that the sample is at least 95% hcp La. Above 5°K the data lie approximately 5% higher than the measurements of Berman, Boorse, and Zemansky (BBZ)<sup>20</sup> for a mixed fcc and hcp sample. This small discrepancy is not surprising in view of the differences in the lattice of the two samples. Since this small difference has a cubic temperature dependence we tentatively conclude that the discrepancy is caused entirely by changes in the lattice and that the electronic contributions are the same for both measurements. Measurements are underway to confirm this conclusion. In the subsequent analysis we will assume that  $\gamma$  for our sample is 10.0 mJ/mole°K<sup>2</sup>, the value derived by BBZ from their measurements in a field of 10 000 G.

It is desirable to separate the lattice and electronic contributions to the specific heat so that direct comparison can be made with existing theoretical models. To analyze these data for the separate terms we make the usual assumptions that (1) the total specific heat  $C_T$  is the sum of the electronic  $C_e$  and lattice  $C_L$  terms, (2) the normal-state electronic term is of the form  $C_{en} = \gamma T$ , (3) the lattice term is of the form  $C_L = \alpha T^3$

<sup>14</sup> J. E. Kilpatrick, W. E. Keller, and E. F. Hammel, *Phys. Rev.* **97**, 9 (1955).

<sup>15</sup> T. R. Roberts and S. G. Sydoriak, *Phys. Rev.* **102**, 304 (1956).

<sup>16</sup> G. W. Moessen, J. G. Aston, and R. G. Asch, *Temperature, Its Measurement and Control in Science and Industry*, edited by C. M. Herzfeld (Reinhold Publishing Corporation, New York, 1962), Vol. III, p. 91.

<sup>17</sup> J. Hilsenrath, C. Beckett, W. Benedict, L. Fano, J. Masi, R. Nuttall, Y. Touloukian, and H. Woolley, *Tables of Thermodynamic and Transport Properties of Air, Argon, Carbon Dioxide, Carbon Monoxide, Hydrogen, Nitrogen, Oxygen, and Steam* (Pergamon Press, Inc., New York, 1960).

<sup>18</sup> R. Berman and C. A. Swenson, *Phys. Rev.* **95**, 311 (1954).

<sup>19</sup> F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, *J. Res. Natl. Bur. Std. (U. S.)* **64A**, 1 (1960).

<sup>20</sup> A. Berman, M. W. Zemansky, and H. A. Boorse, *Phys. Rev.* **109**, 70 (1958).

<sup>11</sup> J. D. Leslie, R. L. Cappelletti, D. M. Ginsberg, D. K. Finnemore, F. H. Spedding, and B. J. Beaudry, *Phys. Rev.* **134**, A309 (1964).

<sup>12</sup> The hexagonal modification of La has an *ABAC* stacking sequence.

<sup>13</sup> J. P. Frank and D. L. Martin, *Can. J. Phys.* **39**, 1320 (1961).

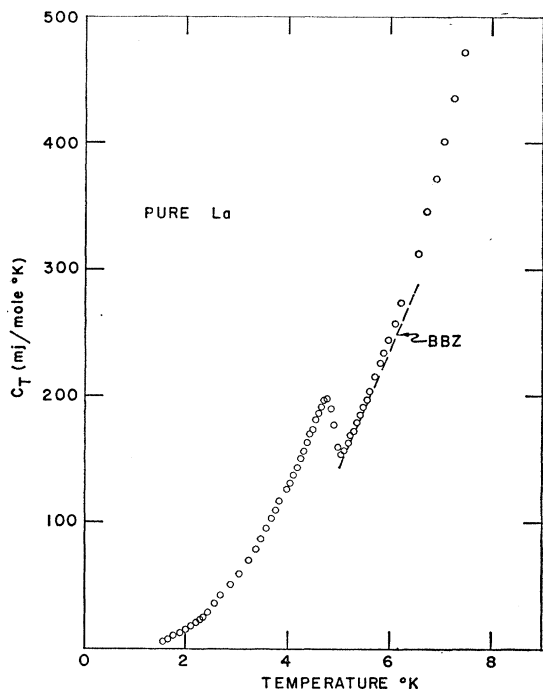


FIG. 1. The total specific heat of pure La.

$+\beta T^5$ , and (4) the lattice term is not changed by the superconducting transition. The lattice term derived from our data with these assumptions is

$$C_L = 0.684T^3 + 0.00522T^5 \text{ mJ/mole}^\circ\text{K}.$$

This gives a Debye temperature of 123°K at 6°K. The electronic term derived by subtracting  $C_L$  from the total is shown in Fig. 2. In this presentation the absence of a jump in the specific heat at 6.0°K shows up even more clearly. The magnitude of the jump at 4.9°K is  $74 \pm 5$  mJ/mole°K or  $1.5\gamma T_c$  in good agreement with the BCS<sup>21</sup> value of  $1.43\gamma T_c$ . At low temperatures the electronic specific heat is of the form  $C_{es} = ae^{-bT_c/T}$ , as

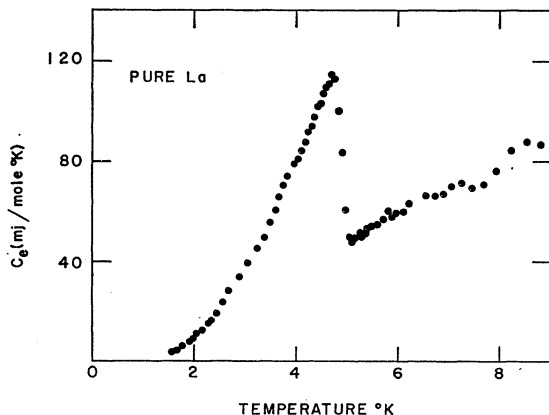


FIG. 2. The electronic specific heat of pure La.

<sup>21</sup> J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

can be seen from the semilog presentation shown on Fig. 3. The values of  $a$  and  $b$  derived for pure La from this plot,  $7.8\gamma T_c$  and 1.56, respectively, are again close to the BCS values.

The entropy difference between the normal state and the superconducting state and the critical-field curve have been calculated by the standard thermodynamic relationships.<sup>22</sup> If we assume that  $C_{en}$  extrapolates to  $T=0$  as  $\gamma T$  and that  $C_{es}$  extrapolates to  $T=0$  as  $7.8\gamma T_c \exp(1.56T_c/T)$ , then the calculated entropy difference goes to zero as required by the third law. This internal check supports the validity of our analysis. The thermodynamic critical field curve very nearly follows the  $H_c = H_0(1 - T_c^2/T^2)$  relation. At the maximum deviation from this parabolic behavior, the calculated curve is 1.5% lower than the fiducial parabola. The value of  $H_0$  is 808 G and  $T_c = 4.88^\circ\text{K}$ . The value of the energy gap calculated by the BCS relationship,  $\Delta = H_0(\pi k^2 V / 6\gamma)^{1/2}$  is  $1.52 \times 10^{-3}$  eV or  $3.60kT_c$ . Within experimental error, this is just the magnitude of the energy gap of fcc La measured by infrared techniques.<sup>11</sup>

The fact that the infrared gap for fcc La appears to be equal to the specific heat gap for hcp La has led us to an extensive x-ray study of these two samples. By electropolishing 10- $\mu$  layers from the surface of the samples we are able to investigate the structure as a function of depth from the surface. The results of this

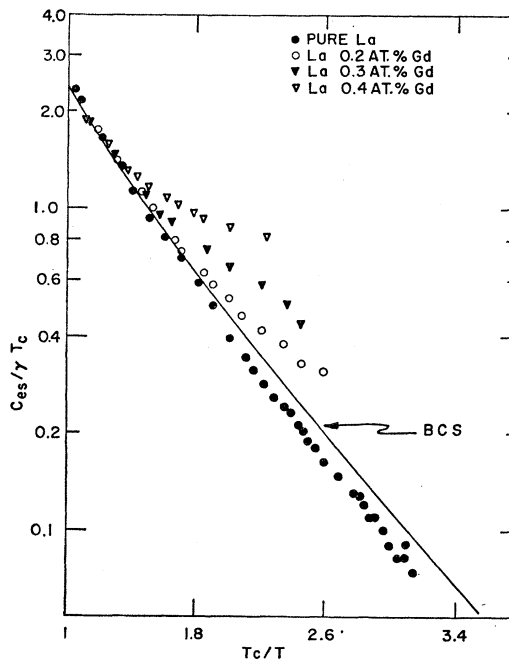


FIG. 3. A comparison of the electronic specific heat of pure La and the La-Gd alloys with the BCS theory. The data for the alloys may contain a contribution from the ordering of the Gd ions.

<sup>22</sup> D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, England, 1952).

study can be briefly summarized as follows: (1) The infrared sample shows no sign of hcp metal at any depth; (2) the infrared sample has a layer of lanthanum hydroxide on the surface which is at most  $100 \mu$  thick; (3) the interior of the infrared specimen has the fcc structure; (4) the specific-heat sample shows no sign of fcc metal; (5) the specific-heat sample has a layer of lanthanum hydroxide on the surface; and (6) the interior of the specific heat specimen has the hcp structure. We do not know why these two energy gaps have the same value.

### Specific Heat of La-Gd

The addition of small amounts of the magnetic impurity Gd has only a small effect on the normal state properties of the material but it has profound effects on the superconducting characteristics. The results of the specific-heat measurements for La-Gd are shown on Fig. 4. Above  $5^\circ\text{K}$  there is a small but measurable depression of the specific heat with increasing Gd content. The predominately cubic nature of the depression leads us to conclude that the shifts are caused primarily by changes in the lattice term. The changes in  $\gamma$ , if present at all, are too small to be resolved by these measurements and almost certainly are less than 20% of  $\gamma$ . The magnitude of  $\gamma T$  is shown for comparison on Fig. 4. We will assume in subsequent analysis that  $\gamma$  is a constant equal to  $10.0 \text{ mJ/mole}^\circ\text{K}^2$  for all samples.

Details of the superconducting state results are most easily seen if the large lattice term is subtracted from the total. This difference, shown on Fig. 5, is then pre-

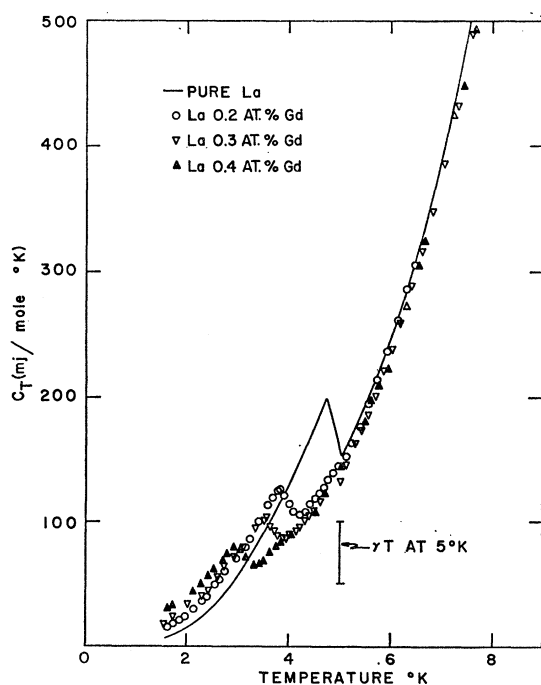


FIG. 4. The total specific heat of La-Gd.

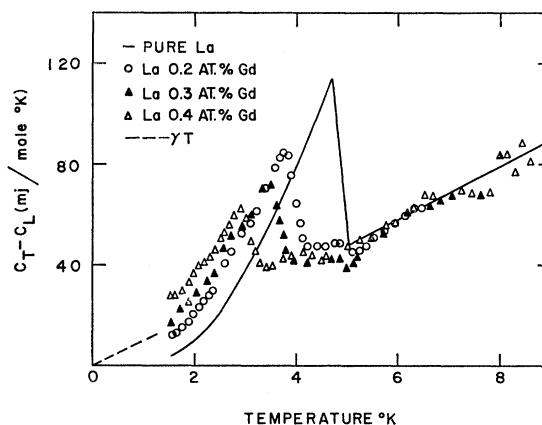


FIG. 5. The difference between the total specific heat and the lattice specific heat for the La-Gd alloys.

sumably the electronic term plus any contribution which might come from ordering of the Gd ions. For each of the alloy samples there is a sharp jump at the hcp transition but unfortunately there is also a shoulder at the fcc transition. From the relative magnitudes of the jump at each transition we estimate that the La 0.2 at. % Gd, La 0.3 at. % Gd, and La 0.4 at. % Gd samples are about 80% hcp. Two La 0.5 at. % Gd samples which we have measured do not even approach complete transformation to hcp, so that their specific-heat results are not presented. X-ray diffractometer measurements of the interior of the samples as exposed by electropolishing corroborate these estimates.

Values of the transition temperature determined from the midpoint of the specific heat jump are shown for the fcc (open circles) and hcp (solid circles) modifications on Fig. 6. The fcc point for pure La is taken from BBZ. Previous measurements by Matthias *et al.*<sup>5</sup> (solid line) for "as arc-cast" alloys lie between the fcc and hcp transitions shown by a specific-heat measurement. We have obtained results for "as arc-cast" alloys which compare favorably with those of Matthias by a 33-cycle mutual-inductance measurement (crosses in Fig. 6). However, x-ray diffractometer measurements show that these samples are not fcc but a mixture of fcc and hcp. We feel that these 33-cycle measurements do not reflect the bulk properties of the material as well as specific heat measurements and should be viewed with some skepticism.

Another view of the low temperature specific heat data for these alloys can be seen from the semi-log plot of  $C_{es}/\gamma T_c$  versus  $T_c/T$  in Fig. 3. If the low-temperature data are fit to  $C_{es} = ae^{-bT_c/T}$ , the value of  $b$  decreases very rapidly with increasing Gd concentration and appears to go to zero at a concentration about half that needed to depress  $T_c$  to zero. A plot of the reduced parameters  $b/b_0$  versus  $T_c/T_{c0}$  (where  $b_0$  and  $T_{c0}$  are the values for pure La) is shown by the open circles in Fig. 7. The rate of depression of  $b$  is very close to rate of depression of the reduced energy gap (dashed line)

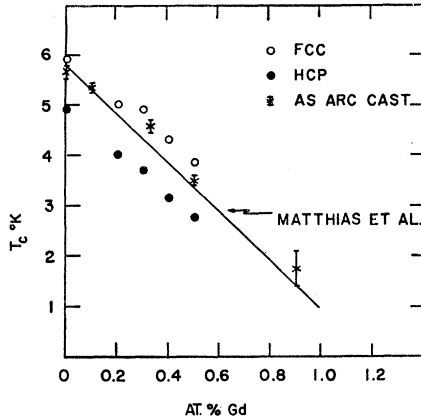


FIG. 6. The critical temperature of La-Gd as determined from the specific heat jump (open and solid circles) and from 33-cycle mutual-inductance measurements (crosses).

derived from electron tunneling measurements by Reif and Woolf.<sup>4</sup> If  $b$  is interpreted as a measure of the energy gap, the agreement is excellent. This is, however, not the only possible interpretation. The apparent rapid fall of  $b$  might be due to ordering of the Gd ions rather than a diminishing gap. Indeed, the low-temperature electronic specific heat of La 0.4 at. % Gd as shown by open triangles of Fig. 5 appears to approach zero well above the  $\gamma T$  line. Additional evidence that the Gd may order comes from the specific heat measurements on an alloy of higher Gd concentration by Phillips and Matthias.<sup>10</sup> Their results are for a 0.7 at. % sample so they, of course, give only a clue concerning the behavior of a 0.4 at. % sample. The indication of ordering, however, is quite clear. Measurements must be extended to lower temperatures before a definitive statement can be made concerning these concentrations.

An important feature of Fig. 3 is the convergence of the data for all samples near the critical temperature

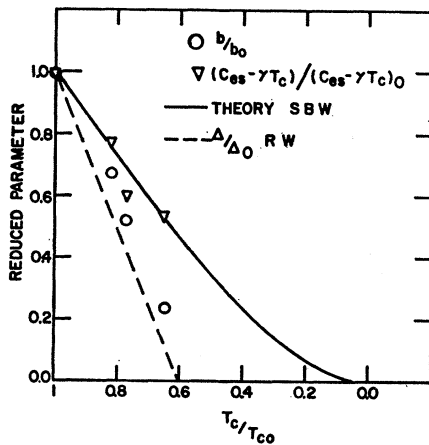


FIG. 7. A comparison of the exponential coefficient  $b$  with the electron tunneling results of Reif and Woolf, and a comparison of the specific heat jump at  $T_c$  with the calculations of Skalski, Betbeder-Matibet, and Weiss.

$T_c/T=1$ . An expanded view of this region is shown in Fig. 8. The magnitude of  $C_{es}/\gamma T_c$  at  $T=T_c$  is between 2.2 and 2.5 for all Gd concentrations measured. The jump in specific heat divided by the jump for pure La  $[(C_{es}-\gamma T_c)/(C_{es}-\gamma T_c)_0]_{T=T_c}$  is shown by the open triangles of Fig. 7. For comparison we have shown the recent theoretical work of Skalski, Betbeder-Matibet, and Weiss<sup>23</sup> (SBW) by the solid line. The agreement between this theory and our experimental values is easily within the experimental uncertainties. The depression of the specific-heat jump is less rapid than the depression of the exponential coefficient  $b$  or the electron tunneling energy gap determined by Reif and Woolf.

### Critical Current of La-Gd

If superconductivity in the presence of magnetic impurities is different in any fundamental way from superconductivity in pure materials, it is of interest to

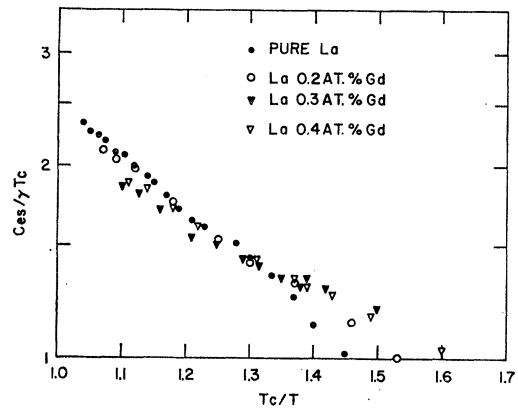


FIG. 8. An expanded view of the reduced specific heat of La-Gd near  $T=T_c$ .

know the magnitude of the electrical current which can be supported with zero power dissipation. We have measured this quantity, the so-called critical current, for La 0.3 at. % Gd and La 0.5 at. % Gd. The alloys are swaged inside a copper sleeve to a diameter of approximately 0.010 in., and the electrical leads are soldered directly to the sleeve. The swaging process transforms most of the material to the hcp structure, although some fcc material is present. Results in zero magnetic field for La 0.5 at. % Gd shown in Fig. 9 are similar to results obtained for La 0.3 at. % Gd. In the temperature range where the fcc material is superconducting but the hcp material is normal (i.e., between 3.85 and 2.75°K) the critical current is less than 10 mA, a value too small to show up on this plot. This very low value is probably due to the fact that only a small fraction of the material is superconducting. Below

<sup>23</sup> S. Skalski, O. Betbeder-Matibet, and P. R. Weiss, Phys. Rev. 136, A1500 (1964).

2.75°K the critical current rises sharply to 35 A with a voltage drop across the sample of less than  $0.1 \mu\text{V}$ . This gives a current density greater than  $5 \times 10^4 \text{ A/cm}^2$  with a resistivity less than  $3 \times 10^{-13} \Omega\text{-cm}$ . These current densities approach the highest current densities known for any superconductor. As far as we can tell, these alloys behave much the same as PbBi or NbZr.<sup>24</sup>

### Magnetization Curves

The magnetic properties of pure La, La 0.3 at. % Gd, and La 0.5 at. % Gd have been investigated by pulling samples through a uniform field between two counter-wound coils. Unfortunately all of our attempts to produce samples which exhibit reversible magnetic behavior at the superconducting transition have been unsuccessful. Every sample which we have prepared shows at least 10% trapped flux. The magnetization curve for fcc La 0.5 at. % Gd at 4°K, shown on Fig. 10, is similar to the results we obtain for the 0.3 at. % Gd alloy. The initial negative slope in low magnetic field indicates the diamagnetic shielding characteristic of superconductivity. At a certain applied field (100 G for this curve) the shielding currents become unstable and the flux collapses into the sample. Further increases of the field bring further diamagnetic shielding and subsequent flux collapses. At a sufficiently high field (300 G for this curve) the diamagnetic property completely disappears and the sample exhibits a paramagnetic susceptibility which is, within experimental error, the value calculated for a random spatial distribution of Gd ions. This indicates that there is no interaction between Gd ions at this temperature. Similar behavior for La doped with magnetic impurities has previously been reported by Bozorth *et al.*<sup>25</sup>

The instabilities shown on Fig. 10 are not well understood at present but we have determined a few of their general characteristics. Pure La, La 0.3 at. % Gd, and La 0.5 at. % Gd all show this behavior although there are quantitative differences. The shielding currents are never unstable at magnetic fields less than  $\frac{1}{10}H_m$ , the field necessary to completely quench the superconductivity, but they are usually unstable for fields above  $\frac{1}{2}H_m$ . In the unstable region, a change in magnetic field of 10 G/sec will usually bring a flux collapse. This feature indicates that eddy current heating may be important. One of the fcc pure La specimens we have prepared will trace an almost ideal "soft" superconductor magnetization curve for increasing field if the rate of increase is less than 0.1 G/sec. This same sample, however, exhibits the instabilities if the rate of increase is greater than 10 G/sec. The only feature of Fig. 10 on which we can base reasonably certain conclusions is the paramagnetic region at high fields.

We have searched for some sign of a Meissner effect

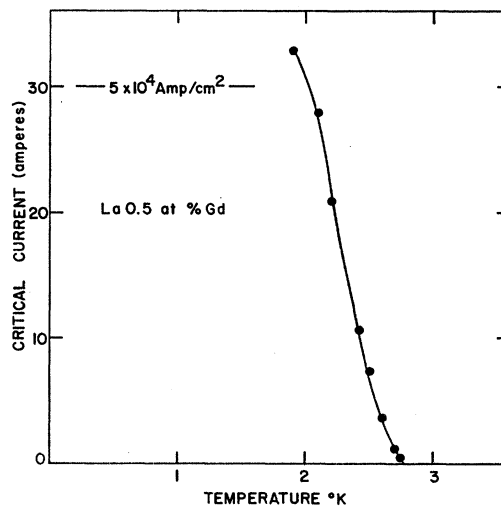


FIG. 9. The critical current of La 0.5 at. % Gd in zero magnetic field.

in the La 0.5 at. % Gd sample by cooling it in the presence of a constant magnetic field. Our equipment can easily detect 1 part in  $10^4$  flux expulsion in a field of 100 G. No trace of a Meissner effect is observed down to 1.1°K. The samples of pure La tested by this same technique all show at least 10% flux expulsion. A similar effect has been reported by Morin *et al.* for  $\text{V}_3\text{Ga}$ .<sup>26</sup> They attribute this behavior to the filamentary nature of the sample. It is a little surprising that the addition of 0.5 at. % Gd, an atom very similar to La except for its magnetic moment, transforms the sample to such a perfect multiply-connected material.

### Critical-Field Curves

The highly irreversible character of the magnetization curves for these materials makes the derivation of a thermodynamic critical-field curve from them im-

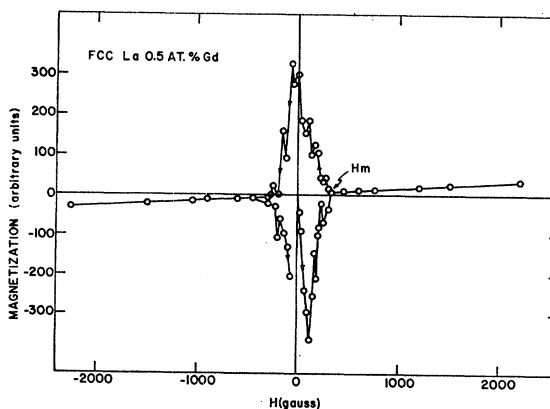


FIG. 10. Magnetization curve for fcc La 0.5 at. % Gd at 4.0°K.

<sup>24</sup> J. E. Kunzler, *Rev. Mod. Phys.* **33**, 501 (1961).

<sup>25</sup> R. M. Bozorth, D. D. Davis, and A. J. Williams, *Phys. Rev.* **119**, 1570 (1960).

<sup>26</sup> F. J. Morin, J. P. Maita, H. J. Williams, R. C. Sherwood, J. H. Wernick, and J. E. Kunzler, *Phys. Rev. Letters* **8**, 275 (1962).

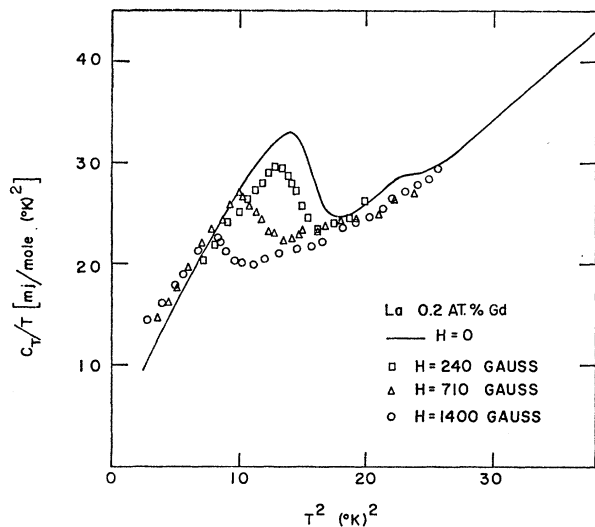


FIG. 11. The specific heat of La 0.2 at. % Gd in the presence of an applied magnetic field.

possible. There is, however, a reversible specific-heat curve with a well-defined jump at the transition temperature if the sample is cooled and warmed in the presence of a magnetic field. The series of specific heat curves for La 0.2 at. % Gd shown on Fig. 11 illustrates qualitatively the behavior shown by all the samples. The normal-state specific heat remains practically unchanged, the transition temperature is depressed, and the samples show no evidence for a latent heat at the

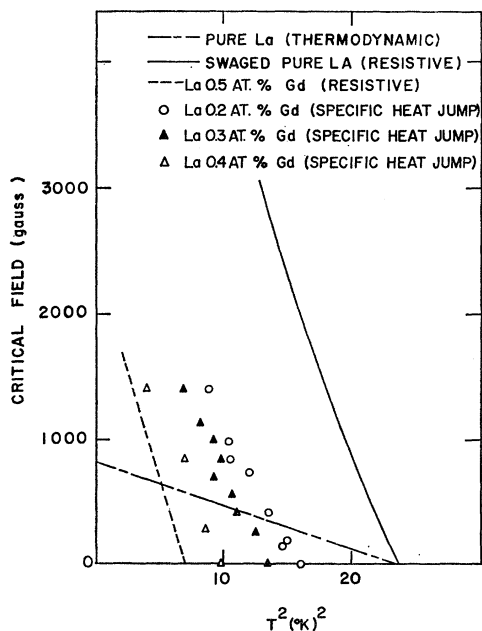


FIG. 12. A comparison of the specific-heat jump critical-field curves to the resistive and thermodynamic critical-field curves.

transition. These features are similar to behavior reported for  $V_3Ga^{26}$  and  $V\ 5\%Ta^{27}$  except that the magnetic fields involved are much smaller. If the midpoint of the specific-heat jump is used to define a critical field curve, the results shown on Fig. 12 are obtained. The curves are roughly linear on an  $H$  versus  $T^2$  plot and have a slope approximately equal to the slope of the resistive-transition curves. The thermodynamic critical field curve derived from the specific-heat measurements is shown for comparison. The slope of the specific-heat jump critical-field curves is about eight times the slope of the thermodynamic critical-field curve. These general characteristics are again similar to behavior reported for  $V_3Ga^{25}$  and  $V\ 5\ at. \% Ta^{26}$

CONCLUSIONS

The experimental evidence presented here indicates that the specific heat of pure hcp La is described very well by the BCS theory. The jump at  $T_c$  is  $1.5\gamma T_c$  and the low-temperature specific heat is given by  $C_{es} = 7.8\gamma T_c \exp(-1.56T_c/T)$ . The addition of small amounts of the magnetic impurity Gd leaves  $\gamma$  essentially unchanged. This indicates that the drastic changes in the superconducting properties are mainly due to the magnetic scattering, and not to changes in the density of states. The value of the exponential coefficient of the low-temperature specific heat,  $b$ , decreases very rapidly with increasing Gd content and extrapolates to zero at about  $\frac{1}{2}$  the concentration required to quench the infinite conductivity. If  $b$  can be interpreted as a measure of the energy gap, then these data show a clear violation of the  $2\Delta = 3.5kT_c$  rule and support the electron tunneling evidence for "gapless" superconductivity. It is possible, however, that the apparent decrease in  $b$  is caused by ordering of the Gd ions. Measurements are now underway to clarify this point.

The behavior of the critical current and the specific heat in a magnetic field are qualitatively similar to corresponding parameters in materials with nonmagnetic impurities. These similarities coupled with the fact that the magnitude of the reduced specific-heat jump at  $T_c$ ,  $(C_{es} - \gamma T_c)/\gamma T_c$ , is very nearly constant seems to indicate that superconductivity in the presence of magnetic scattering may not be fundamentally different from superconductivity in the presence of nonmagnetic scattering.

ACKNOWLEDGMENTS

We are indebted to D. T. Peterson for electropolishing the samples, to T. F. Stromberg for assistance in the constant volume gas thermometry, to W. R. Decker for analyzing part of the data, and to C. A. Swensen and D. M. Ginsberg for helpful conversations.

<sup>27</sup>R. R. Hake and W. C. Brammer, Phys. Rev. **133**, A719 (1964).