

14. Ginzburg-Landau parameter $\kappa_1(T_c)$:

$$\begin{aligned}\kappa_1(T_c) &= (dH_u/dT)_{T_c} / [\sqrt{2}(dH_c/dT)_{T_c}] \\ &= (6.0\gamma^{1/2})^{-1}(-dH_u/dT)_{T_c},\end{aligned}\quad (\text{A14})$$

assuming, from BCS,⁹⁷ $(dH_c/dT)^2_{T_c} = 18.0\gamma$.

15. Lower critical field ($\xi_0 \gg l$)²⁷:

$$H_{c1}(t) = \sqrt{2}H_c(t) \{ [\ln \kappa_3(t)] / [2\kappa_3(t)] \} \quad (\text{A15})$$

where $\kappa_3(t) = \kappa_3^*(t)/\kappa_G$, $\kappa_3^*(t) \equiv \kappa_3(t)/\kappa_3(t=1)$ is given graphically by Maki, $\kappa_3^*(t=0) = 1.53$, and κ_G is given by Eq. (A13c).

16. Neo-GLAG⁹⁻¹⁴ nonparamagnetically limited upper critical field ($\xi_0 \gg l$, 0°K):

$$\text{a. } H_{c20}^* = \sqrt{2}[\kappa_1(0^\circ\text{K})/\kappa_1(T_c)]\kappa_1(T_c)H_{c0}; \quad (\text{A16a})$$

$$\text{b. } H_{c20}^* \approx 3.06 \times 10^4 \rho_n \gamma T_c G, \quad (\text{A16b})$$

by substitution of¹² $\kappa_1(0^\circ\text{K})/\kappa_1(T_c) = 1.195$, $\kappa_1(T_c) \approx \kappa_l = 7500\rho_n\gamma^{1/2}$, and $H_{c0}(\text{BCS}) = 2.42\gamma^{1/2}T_c$ in Eq. (A16a)].

c. From upper critical field slope^{28,29} [see Eq. (5)],

$$H_{c20}^* = 0.693T_c(-dH_u/dT)_{T_c}. \quad (\text{A16c})$$

17. Clogston upper-critical-field limit (0°K)²³:

$$\frac{1}{2}\chi_P H_{p0}^2 = H_{c0}^2/8\pi = \frac{1}{2}N\Delta_{00}^2; \quad (\text{A17a})$$

$$H_{p0} = \Delta_{00}(\sqrt{2}\mu_B)^{-1} = 1.84 \times 10^4 T_c G, \quad (\text{A17b})$$

substituting $\chi_P = 2\mu_B^2 N$ of Eq. (A6) into Eq. (A17a).

18. Maki paramagnetic limitation parameter²⁸:

$$\text{a. } \alpha \equiv \sqrt{2}H_{c20}^*/H_{p0}; \quad (\text{A18a})$$

$$\text{b. } \alpha = 2.35\rho_n\gamma, \quad (\text{A18b})$$

substituting Eqs. (A16b) and (A17b) into Eq. (A18a), $\xi_0 \gg l$ is assumed;

$$\text{c. } \alpha = 5.33 \times 10^{-5}(-dH_u/dT)_{T_c}, \quad (\text{A18c})$$

substituting Eqs. (A16c) and (A17b) into Eq. (A18a).

19. Spin-flip scattering time²⁹:

$$\tau_{s0} = \hbar(3\pi k_B T_c \lambda_{s0})^{-1} = 8.11 \times 10^{-13} (T_c \lambda_{s0})^{-1} \text{ sec.} \quad (\text{A19})$$

Law of Corresponding States for fcc and d-hcp La*

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The specific heats of fcc and d-hcp La have been measured from 1.0–10.0°K. There is a striking similarity between these two metals, and a law of corresponding states is obeyed for both the superconducting- and normal-state specific heats. An energy-gap parameter determined from both the temperature-dependent electronic specific heat and from the free-energy difference is $3.7kT_c$, in good agreement with the BCS value. No evidence is found for an *f*-band contribution to the superconducting characteristics.

INTRODUCTION

FOR several years theorists have speculated that certain transition-metal superconductors might show substantial deviations from a law of corresponding states. In 1959, Suhl, Matthias, and Walker¹ proposed a two-band model which gives a rather complicated excitation spectrum. In special circumstances it leads to independent energy gaps for each band. Indeed, there is preliminary evidence that Nb may exhibit this two-gap behavior.² In further theoretical work, Kondo³ has shown that exchange coupling between bands enhances superconductivity and he has proposed that this mechanism may be important in determining the relatively high transition temperature T_c of compounds like V₃Ga and the element La. An alternate model

which is especially applicable for La has been proposed by Kuper, Jensen, and Hamilton.⁴ Here it is assumed that there is a narrow *f* band above, but very close to, the Fermi surface and that the coupling comes through an antiferromagnetic exchange. With reasonable approximations for the position of the *f* band and the strength of the coupling, the theory gives two energy gaps and strong deviations from a law of corresponding states.

The specific-heat measurements which are reported here were undertaken to look for evidence of this proposed *f* band near the Fermi surface and to look for deviations from a law of corresponding state. Since La occurs in two crystallographic modifications, there are essentially two different metals available for this work and the effects of crystal structure have been studied. Normal-state results have been analyzed in terms of deviations from the Sommerfeld and Debye⁵ theories

* Work performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Contribution No. 2003.

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² L. Shen, N. M. Senozan, and N. E. Phillips, Phys. Rev. Letters **14**, 1025 (1965).

³ J. Kondo, Progr. Theoret. Phys. (Kyoto) **29**, 1 (1963).

⁴ C. G. Kuper, M. A. Jensen, and D. C. Hamilton, Phys. Rev. **134**, A15 (1964).

⁵ C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1966), 3rd ed.

of specific heat; superconducting-state data are compared with the Bardeen, Cooper, Schrieffer⁶ (BCS) theory of superconductivity.

EXPERIMENTAL

Specific heats C were measured by a conventional pulse heating method in which heater power $\dot{Q}$ is supplied to a nearly isolated sample for a time t , thus raising the temperature by ΔT . $\dot{Q}$ ranged from 2×10^{-6} W at 1°K to 7×10^{-4} W at 10°K. The duration of the heating pulse ranged from 10 sec at 1°K to 2 min at 8°K to 8 min at 10°K. Equilibrium times after a pulse for the d-hcp sample were less than 2 sec at 1°K and less than 10 sec at 10°K. For the fcc sample equilibrium times were approximately 5 times longer because the sample was made of laminated slabs rather than one solid piece. Corrections for random heat input were made by extrapolating the drift curves back to the center of the pulse. The magnitude of these corrections was approximately one-tenth of ΔT . A factor of 3 change in ΔT by varying either $\dot{Q}$ or t produced no detectable change in C . Each specific-heat measurement was accurate to approximately 1%.

Cryostat

A schematic diagram of some of the essential features of the cryostat is shown in Fig. 1. Temperatures below 1°K were obtained by pumping on a He⁴ reservoir (A) through a 0.030 in. diam orifice. Thermal contact between this 1°K bath and the sample was made through a mechanical heat switch and a long copper wire. To close the heat switch, the reservoir was lowered, thus forcing a copper sphere (B) against a platform (D) which is thermally connected to the reservoir. All contacts were gold-plated. A taut nylon string positioned the sphere when the heat switch was opened. Less than 20 ergs of heat were developed in the sample by opening the switch.

A 67 000 Ω heater (K) was cemented to a copper sample holder (H) with G. E. 7031 varnish. Contact between the sample (J) and the sample holder was made with N grease so that the exact amount of addenda could be easily controlled. Although N grease is not as good a contact agent as 7031 in this temperature range, it was completely satisfactory for this experiment. The addenda heat capacity over much of the temperature range was approximately 6% of the total normal-state heat capacity.

The germanium resistor (F) used as a secondary thermometer exhibits a large magnetoresistance so it was moved out of the magnetic field of the main solenoid (I) on the end of a long copper rod (G). Fringe fields from solenoid (I) were then cancelled by a smaller solenoid (E) mounted below the 1°K platform. To establish a zero-field condition in the region of the germanium thermometer, the superconducting critical

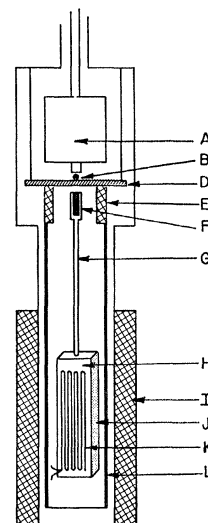


FIG. 1. Cryostat.

field of a Pb sample was measured in both field directions and the average of these two fields was taken to be zero field. All electrical leads were thermally grounded to the sample holder and to the heat shield (L) which surrounds the sample.

Some details of the cryostat such as the Pb wire mentioned above, the nylon support lines for the sample, the electrical leads, and several thermal links are omitted for clarity of the drawing. A Leeds and Northrup type K-3 potentiometer and a Kiethley 150 AR dc amplifier were used to detect voltages.

Thermometry

The Honeywell Series II germanium resistance thermometer (F) was calibrated at 112 points between 4.2 and 20°K in the same constant volume gas thermometer experiment which was described in earlier publications.^{7,8} Between 4.2 and 1.2°K the resistor was calibrated at 140 points against the vapor pressure of He⁴.⁹ Between 1.2 and 0.9°K the susceptibility of chrome methylamine alum is taken as the primary temperature standard.¹⁰ The data were divided into three overlapping temperature ranges and fitted with an equation of the form

$$\ln T = \sum_{n=0}^{n=6} A_n (\ln R)^n.$$

A very large overlap region was chosen so that the ends of any one fit region were not needed to calculate C . Specific-heat data in the overlap region as determined from the two different fit equations agree within 0.1%.

⁷ D. K. Finnemore, D. L. Johnson, J. E. Ostenson, F. H. Speeding, and B. J. Beaudry, Phys. Rev. **137**, A550 (1965).

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¹⁰ D. K. Finnemore and D. E. Mapother, Phys. Rev. **140**, A507 (1965).

⁶ J. Bardeen, L. N. Cooper, and J. R. Schieffer, Phys. Rev. **108**, 1175 (1957).

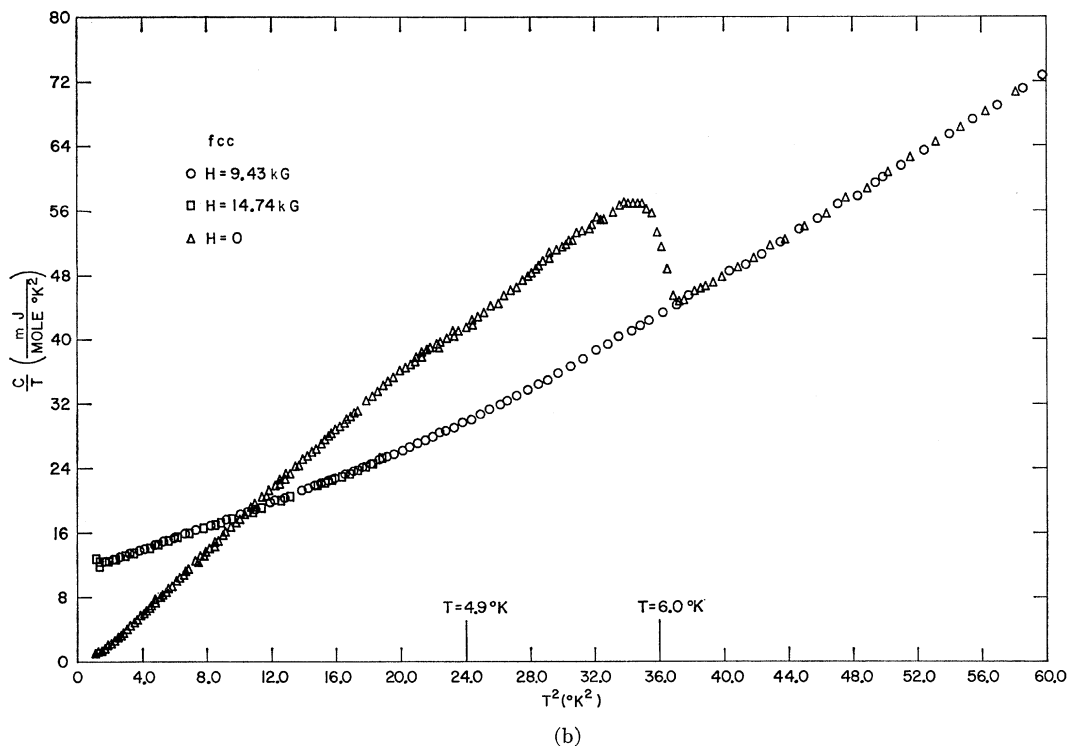
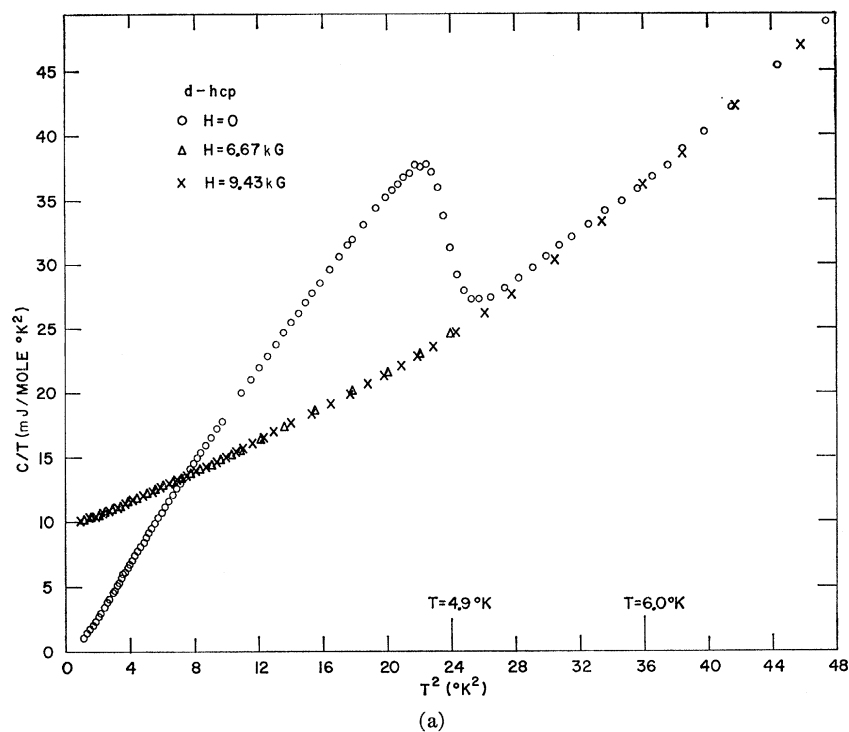


FIG. 2(a) Specific heat of nominally pure-phase d-hcp. (b) Specific heat of nominally pure-phase fcc La.

Samples

The preparation of single phase La has proved rather difficult and as yet we have not obtained a sample which is either 100% d-hcp or 100% fcc. At room

temperature the d-hcp structure is stable but unfortunately the phase transition is rather sluggish for our most pure samples. Even after several months there is a few percent of fcc phase left in the material. The relative sluggishness of the transition seems to be

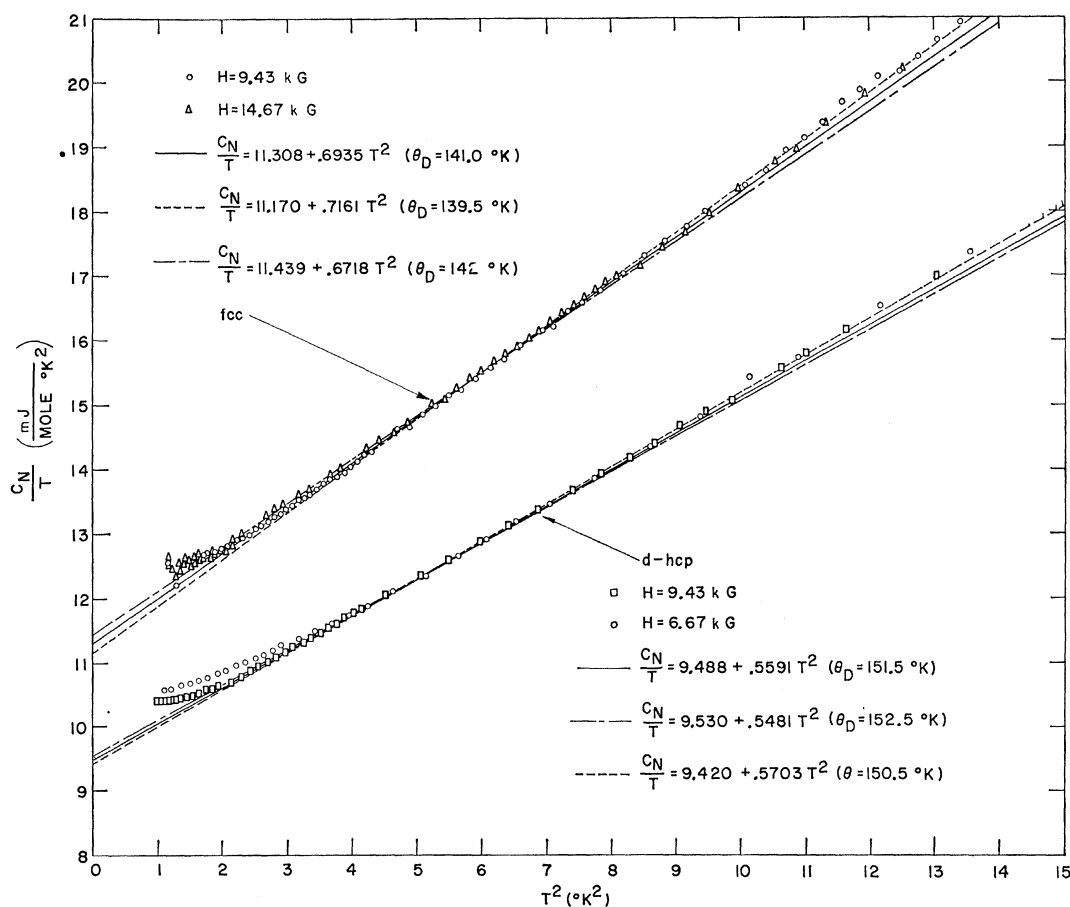


Fig. 3. Low-temperature specific-heat results. Deviations below $T^2=2$ are caused by onset of superconductivity.

closely related to the amount of cold work. Hence, the d-hcp samples were not machined to any particular shape but were measured in the loaf-like shape (3 by $\frac{3}{4}$ by $\frac{1}{4}$ in.) which resulted from the arc melting. After arc melting, the sample was sealed under He in a Ta envelope, annealed at 400°C for 16 h, quenched into water and annealed at room temperature for one month. Grain size for this sample was approximately 100 μ .

To stabilize the fcc phase, a thin slab of La was heavily cold worked, annealed at 400°C for 16 h, and quenched into room temperature water. The procedure was exactly the same as that used to prepare samples for infrared measurements¹¹ so details will not be repeated here. A typical grain size for this fcc sample was 1 to 10 μ .

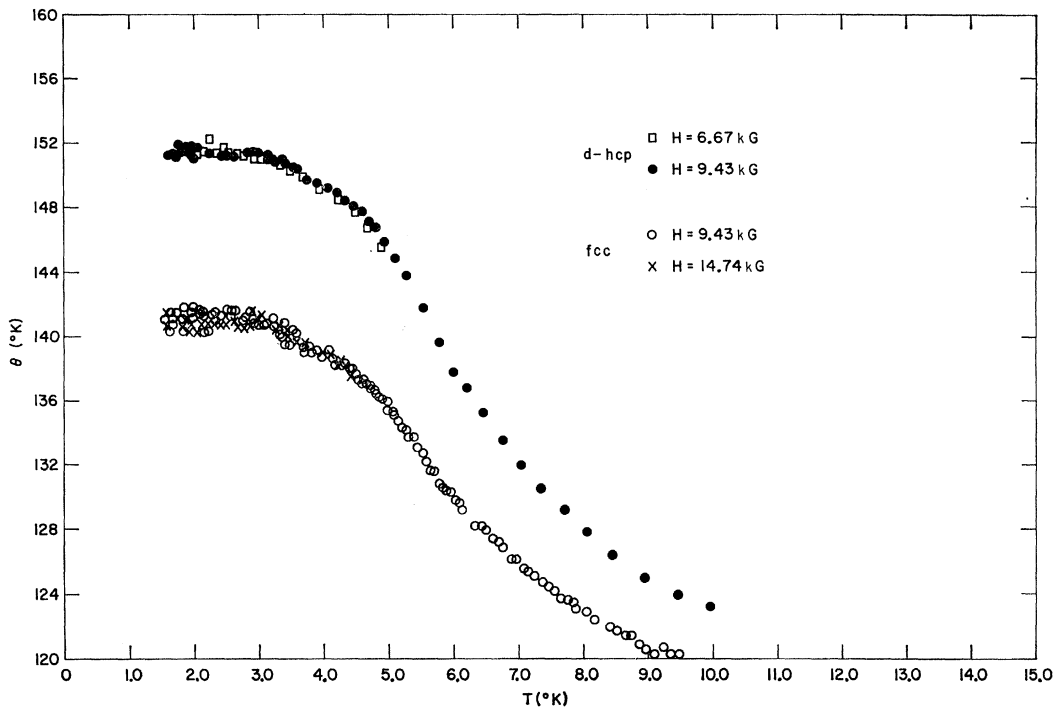
RESULTS AND ANALYSIS

Specific-heat data for the nominally pure phase d-hcp and fcc samples are shown in Fig. 2. For the d-hcp sample of Fig. 2(a) there is a sharp rise in the zero-field specific heat at 4.87°K ($T^2=23.7^\circ\text{K}^2$) indicating the transition of the bulk of the material to the super-

conducting state. Unfortunately, at 6°K, ($T=36^\circ\text{K}^2$), there is also a small shoulder which can be associated with a few percent fcc material in this sample. A similar situation prevails for the nominally pure fcc sample of Fig. 2(b). Here the main transition takes place at 6°K and there is a small shoulder at 4.9°K. The information of primary interest, of course, is the specific heat of a pure-phase sample. In order to analyze the data for these results, it is assumed that the sample is composed of two separate pieces, a d-hcp piece and an fcc piece, in good thermal equilibrium and it is further assumed that the relative amount of each phase present is proportional to the jump in specific heat at T_c . With these assumptions, it is found that the nominally pure d-hcp sample is 96% d-hcp and 4% fcc. The nominally pure fcc sample is 91% fcc and 9% d-hcp. Specific heats for pure-phase samples can then be calculated on this basis. The corrections are only a few percent and the nominally pure-phase sample provides a good first approximation for making the correction. In addition, the specific heats of the two phases are rather close to one another. All of these factors tend to minimize the effect of second phase but it remains the dominant uncertainty in the experiment.

The over-all behavior of the normal-state specific heat of both phases of La is similar to other nonmag-

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

FIG. 4. Temperature dependence of θ .

netic metals so the results have been cast as deviations from

$$C = \gamma T + \alpha T^3. \quad (1)$$

Here γ is interpreted as the Sommerfeld electronic specific heat coefficient and α is proportional to the inverse cube of the Debye temperature Θ . Values of γ determined by extrapolating the data to $T=0$ are $\gamma = 9.49 \pm 0.05$ mJ/mole $^\circ\text{K}^2$ for the nominally pure-phase d-hcp sample and 11.3 ± 0.1 mJ/mole $^\circ\text{K}^2$ for the nominally pure-phase fcc sample. Corresponding values after corrections have been made for the presence of the second phase are 9.4 ± 0.1 mJ/mole $^\circ\text{K}^2$ for d-hcp La and 11.5 ± 0.3 mJ/mole $^\circ\text{K}^2$ for fcc La (see Table I). An expanded view of the low-temperature data (Fig. 3), shows how these extrapolations were made and it permits an assessment of some of the errors. The small upturn at the lowest temperatures decreases with increasing magnetic field, so it probably reflects the onset of superconductivity. Consequently these lowest-temperature data have been ignored in the extrapolation. At higher temperatures the normal-state data are independent of magnetic field.

Above 3°K the specific heat deviates above the T^3 line indicating an effective drop in the Debye temperature. These results are shown quantitatively in Fig. 4 where Θ is plotted as a function of temperature. Below 3°K, or approximately $\Theta/50$, the Debye temperature is rather constant. In the range $\Theta/50$ to $\Theta/15$, the Debye temperature drops by approximately 20%. This behavior is common for nonmagnetic metals and it

has some theoretical foundation.^{12,13} The over-all behavior of these data is consistent with earlier measurement on La samples with a large fraction of both fcc and d-hcp phases.^{14,15} There is no evidence in any of these results for a Schottky-like anomaly which might result from thermal excitation of electrons into a narrow f band just above the Fermi surface.

TABLE I. Superconducting- and normal-state parameters for La.

Parameter	d-hcp La	fcc La
γ (mJ/mole $^\circ\text{K}^2$)	9.4 ± 0.1	11.5 ± 0.3
Θ ($^\circ\text{K}$)	152 ± 2	140 ± 2
T_c ($^\circ\text{K}$)	4.87 ± 0.02	6.00 ± 0.02
T_c/Θ	0.032	0.043
$C_{es}/\gamma T_c$	1.71	1.73
v (cm ³ /mole)	22.5	22.4
H_0 (Oe)	798 ± 12	1096 ± 15
$2\Delta/kT_c = (2\pi V H_0^3 / 3\gamma T_c^2)^{1/2}$	3.67 ± 0.22	3.69 ± 0.25
$N(\gamma)$ (states per eV per molecule)	2.00	2.44
V (eV)	0.14	0.125

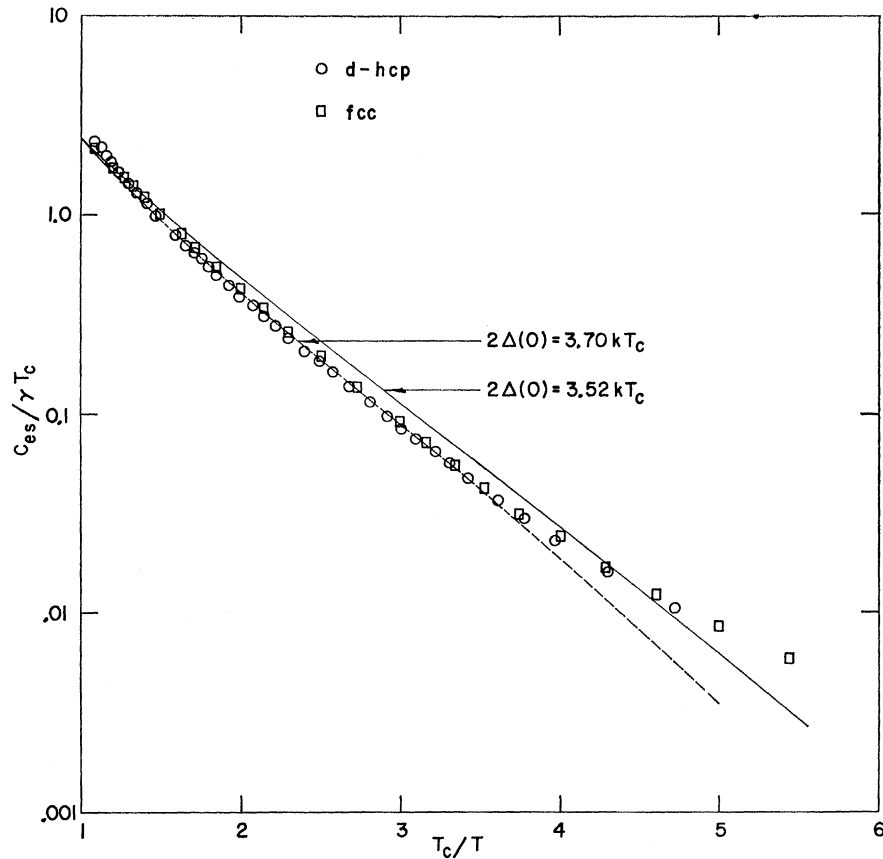
¹² M. Blackman, Proc. Roy. Soc. (London) **A148**, 365 (1935).

¹³ J. de Launay, *Solid State Physics* (Academic Press Inc., New York, 1956), Vol. 2.

¹⁴ A. Berman, M. W. Zemansky, and H. A. Boorse, Phys. Rev. **109**, 70 (1958).

¹⁵ D. H. Parkinson, F. E. Simon, and F. H. Spedding, Proc. Roy. Soc. (London) **A207**, 137 (1951).

FIG. 5. Electronic contribution to the superconducting specific heat of d-hcp and fcc La. Corrections have been made for the presence of second phase in the sample.



Both d-hcp and fcc La show a superconducting specific heat which is similar to tin, niobium, or lead. The phase transitions in zero field are several hundredths of a degree Kelvin wide but this is not uncommon for transition-metal superconductors of this purity.¹⁶ If the critical temperature T_c is defined as the midpoint of the transition, then T_c is $4.87 \pm 0.03^\circ\text{K}$ for d-hcp La and $T_c = 6.00 \pm 0.02^\circ\text{K}$ for fcc La.

To determine the electronic contribution to the superconducting specific heat, C_{es} , it is assumed that the lattice contribution, C_{gs} , is the same in both states and that $C_s = C_{es} + C_{gs}$. Once the lattice term in the normal state has been determined, C_{es} is found by a simple subtraction. If there is an energy gap in the excitation spectrum there should be an exponential term in C_{es} at low temperatures. Hence the results are plotted in Fig. 5 on a semilogarithmic scale with $C_{es}/\gamma T_c$ as ordinate and $T_c/T = t^{-1}$ as abscissa. For both crystal modifications, the slope of the curves is slightly steeper than the BCS prediction indicating an energy gap, 2Δ , larger than the BCS value of $3.53 kT_c$ where k is the Boltzmann constant. The dashed line on the figures shows an attempt to fit the data to a BCS-like specific heat where the temperature-dependent energy gap has been scaled by a constant factor.¹⁰ For d-hcp La, $2\Delta(0)/kT_c = 3.73$ gives the best fit to the data between

3.5 and 1.5°K ; for fcc La, $2\Delta(0)/kT_c = 3.77$ gives the best fit in a comparable reduced temperature range. At the lowest temperatures both samples show significant deviations above the exponential curve. Anisotropy effects or impurity states in the gap might cause this sort of behavior but at present the real cause is unknown. Near T_c ($t^{-1} = 1$) the data again rise above the theoretical curve and the jump in specific heat at T_c is $1.71 \gamma T_c$ for d-hcp and $1.73 \gamma T_c$ for fcc, compared with the BCS value of $1.43 \gamma T_c$. These rather large jumps are characteristic of intermediate or strong coupling superconductors.^{10,16,17} On a reduced scale the two phases of La are very similar to one another and they appear to obey a law of corresponding states.

The entropy difference between the superconducting and normal states and the critical field curve, H_c versus T , were calculated from these data using standard thermodynamic relations.¹⁸ Within the accuracy of the measurement, the entropy difference for both samples extrapolates to $T=0$ as γT in accord with the third law of thermodynamics. This provides a check against certain systematic errors in the measurement. The critical-field curve is nearly parabolic in temperature so the results have been displayed in terms of a devia-

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¹⁸ A. B. Pippard, *Classical Thermodynamics* (Cambridge University Press, Cambridge, England, 1957).

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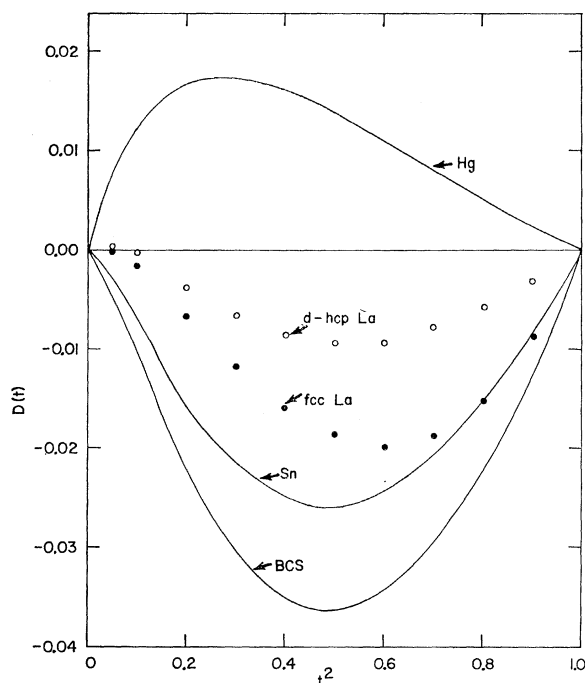


FIG. 6. Deviation function, $D(t) = H_c/H_0 - (1-t^2)$, for d-hcp and fcc La.

tion function

$$D(t) = H_c/H_0 - (1-t^2). \quad (2)$$

H_0 , which is the value of H_c at $T=0$, is found to be 798 ± 12 Oe for d-hcp La and 1096 ± 15 Oe for fcc La. Figure 6 shows that $D(t)$ for both crystal structures lies between a weak coupling superconductor like Sn and a strong coupler like Hg. In addition, the T_c/θ values for La lie between Sn and Hg so La might be classified as an intermediate coupling superconductor.

An energy gap can be calculated from the free energy through the relation

$$2\Delta(0)/kT_c = (2\pi v H_0^2 / 3\gamma T_c^2)^{1/2}, \quad (3)$$

where v is the molar volume.¹⁹ For d-hcp La this gives $(2\Delta(0)/kT_c) = 3.67$ and for fcc La $(2\Delta(0)/kT_c) = 3.69$ in rather good agreement with the fit of the $C_{es}/\gamma T_c$ curves of Fig. 5. These two different ways of determining an equivalent energy gap are not independent, of course, but they emphasize quite different aspects of the data.

Direct measurements of the energy gap with infrared and tunneling techniques have given a variety of values. Infrared results of Leslie *et al.*¹¹ give $2\Delta/kT_c =$

2.85 for fcc La. Tunneling results vary somewhat depending on details for the measurement and $2\Delta(0)$ ranges from 1.65^{20} – $3.2kT_c$.²¹ La surfaces are extremely difficult to prepare so the $3.2kT_c$ results for samples prepared by getter-evaporation are probably the most reliable. The agreement here between specific heat and tunneling results is fairly good.

Table I summarizes the normal and superconducting state parameters for both modifications of La. All the results presented here have been corrected for the presence of second phase. The change in crystal structure from d-hcp to fcc causes an increase of γ and T_c by approximately 20% and a decrease in θ of approximately 10%. If the expression^{6,22}

$$kT_c = 1.14k\theta \exp[-1/N(\gamma)V] \quad (4)$$

is used to calculate $N(\gamma)V$ where $N(\gamma)$ is the specific-heat density of states, then the interaction parameter V decreases only about 10% from 0.14–0.125 eV. These equations are probably not adequate to describe La but they give a clue that the V is nearly constant. If there were an f band very close to the Fermi surface in La, and if this f band were a major factor influencing V , it seems reasonable that a change in crystal structure would alter the position of the f band and bring a large change in V . No large change is observed.

CONCLUSIONS

The specific heats of both phases of La closely follow a law of corresponding states and results are in good agreement with the BCS theory. Bulk thermodynamic properties, of course, are an average over many detailed characteristics of a superconductor so these data do not absolutely rule out the possibility that the mechanism responsible for superconductivity in La differs from that in other pure metals. It would appear, however, that any alternative theory for La, such as that of Kondo or Kuper *et al.*, must give essentially the BCS result for the free energy.

ACKNOWLEDGMENTS

We would like to thank Professor F. H. Spedding and Professor D. T. Peterson for helpful discussions concerning metallurgical problems. Samples were prepared in Professor Spedding's group by B. J. Beaudry and P. E. Palmer. The metallography and electropolishing were done in Professor Peterson's group by H. H. Baker.

²⁰ A. S. Edelstein and A. M. Toxen, Phys. Rev. Letters **17**, 196 (1966).

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¹⁹ K. A. Gschneidner, Jr., *Rare Earth Alloys* (D. Van Nostrand, Inc., Princeton, New Jersey, 1961).