Normal and Superconducting Heat Capacities of Lanthanum*

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The heat capacities of three samples of lanthanum have been measured in the temperature range 1.6 to to 6.5°K. A four-constant formula was found which represented to high precision the resistance-temperature relation of the carbon composition resistance thermometer from 1.6 to 7.2°K. Two superconducting transitions were found in each sample: one at 4.8°K and the other at 5.9°K. These are associated respectively with the hexagonal close-packed and face-centered cubic modifications of the metal. Below 2.5°K, a magnetic field of 10 000 gauss was found insufficient to quench completely the superconducting phase. The values of the normal heat capacity constants for the purest sample, averaged over the two crystal structures present, were determined by a thermodynamic analysis of the data to be $\gamma=(24.1\pm0.6)\times10^{-4}$ cal/mole (°K)^2, $\Theta=142\pm3$°K. The data are further analyzed for evidence of a law of corresponding states among superconductors.

I. INTRODUCTION

THE properties of superconducting lanthanum are of special interest in two respects. First, even among the samples of relatively high purity, the reported transition temperatures are scattered in the range 4.4 to 6.0°K.[1–4] Second, a study of lanthanum may be expected to cast light on the relationship between superconductivity and crystal structure, since bulk samples of the metal at low temperatures consist of a mixture of hexagonal close-packed and face-centered cubic material.

Among the other elementary superconductors, tin and bismuth exhibit superconductivity in only one of their allotropic forms. White tin (tetragonal) has a transition at 3.74°K whereas gray tin (diamond structure) is not a superconductor at all, at least down to 1.32°K.[5] Bismuth has been shown to be superconducting below 7°K only at pressures greater than 20 000 atmospheres.[6] The onset of superconductivity in this instance is attributed to a transformation of the lattice to a more close-packed structure. In the case of lanthanum both the α (h.c.p.) and β (f.c.c.) phases are close-packed, and, according to an empirical criterion of Born and Cheng,[7] both would be expected to become superconductors. More recently the alloy[8] Bi_4Rh and the alloy[9] Bi_2Pd were shown to have two forms that are superconducting, each form with a distinctive transition temperature. There is also evidence that hexagonal MoC may have a cubic allotropic form with a somewhat higher superconducting transition temperature.[10]

Ziegler, Young, and Floyd[1] have examined lanthanum filings for the relationship between crystal structure and the superconducting transition temperature. X-ray studies showed that annealing caused the filings to transform partially from the hexagonal to the cubic structure. Apparently none of these samples was in one crystal form only. Magnetic measurements to determine the transition temperature of a sample of unannealed filings which were found to be predominantly in the h.c.p. phase both before and after the measurement, gave a value of 3.9°K. This sample was considered however to be highly strained and the transition temperature of the unstrained h.c.p. metal was not determined. Other samples, annealed to produce predominantly f.c.c. material, gave for the purest specimens a transition temperature of approximately 5.4°K.

In the only previously reported heat capacity measurements of lanthanum in the liquid helium range Parkinson, Simon, and Spedding[2] found a single transition at 4.37°K. Their sample, which had a purity greater than 99.94%, showed both h.c.p. and f.c.c. lines on x-ray analysis. They took, however, only 30 measurements below 6°K and no normal data below the transition temperature.

II. EXPERIMENTAL

This report deals with heat capacity measurements made on three samples of lanthanum in the temperature interval from 1.6 to 6.5°K. These samples were all obtained from Professor F. H. Spedding, Director of the Institute for Atomic Research at Ames, Iowa, and

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[1] Ziegler, Young, and Floyd, J. Am. Chem. Soc. **75**, 1215 (1953).
[2] Parkinson, Simon, and Spedding, Proc. Roy. Soc. (London) **A207**, 137 (1951).
[3] James, Legvold, and Spedding, Phys. Rev. **88**, 1092 (1952).
[4] H. M. Rosenberg, Trans. Roy. Soc. (London) **A247**, 441 (1955).
[5] G. Sharvin, J. Phys. (U.S.S.R.) **9**, 350 (1943) and Chem. Abstr. **40**, 3320 (1946).
[6] P. F. Chester and G. O. Jones, Phil. Mag. **44**, 1281 (1953).
[7] M. Born and K. C. Cheng, J. phys. radium **9**, 249 (1948).
[8] Alekseevskii, Zhdanov, and Zhuravlev, J. Exptl. Theoret. Phys. U.S.S.R. **28**, 237 (1955) [translation: Soviet Phys. JETP **1**, 99 (1955)].
[9] Alekseevskii, Zhuravlev, and Lifanov, J. Exptl. Theoret. Phys. **27**, 125 (1954), and Sci. Abstr. **58**, 37 (1955).
[10] B. T. Matthias, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. 2, p. 147.

were the purest specimens available. The specimens were in the form of cylinders $3\frac{1}{2}$ in. long and $\frac{3}{4}$ in. in diameter and contained approximately 1.1 moles. La I was measured as received (La Ia), after annealing in vacuum for 7 hours at 700°C (La Ib), and again after further annealing for 48 hours at 750°C (La Ic). Preliminary measurements were made on La II as received. Further measurements were not made on this specimen because of accidental contamination during annealing. The third sample, La III, was annealed in vacuum for 48 hours at 800°C before the heat capacity was measured. After each annealing the samples were rapidly cooled to room temperature in an atmosphere of helium gas.

La III was the purest sample and the most careful measurements were made on it. In an analysis by Spedding the only impurities detected in this sample were 20 ppm of nitrogen and 200 ppm of carbon. The oxygen content was unknown but low. No other rare earths were detected spectrographically on a 21-foot grating using emission spectra. The most likely impurities were considered to be tantalum, calcium, and iron but these were not detected. However the analytical procedure could not detect less than 500 ppm of tantalum and 50 ppm of calcium or iron.

The adiabatic calorimeter, used previously in this laboratory for the measurements on Nb, Ta, and V, has been described in detail elsewhere.[11,12] The temperature of the lanthanum samples was measured by means of half-watt Allen-Bradley carbon resistors. After the insulation was ground off, a coat of Glyptal was baked on and they were then cemented with Glyptal into a transverse hole centrally located in the sample.

For the heat capacity measurements on La I, energy was supplied to the sample with the aid of heaters consisting of about 200 ohms of 3-mil constantan wire wound noninductively on the sample and thermally bonded with Glyptal. Three-foot lengths of B. and S. No. 40 copper wire were used for connecting wires which were attached to separate current and potential leads in the helium bath. For La II and La III the heaters were approximately 4000 ohms of 1-mil constantan wire. This larger resistance made possible the use of higher resistance connecting wires (No. 35 constantan) with a consequent improvement in the thermal isolation of the samples. Current and potential leads of No. 40 constantan were brought directly to the thermometer.

The heating intervals ranged from 0.03 to 0.10 deg with the smaller intervals appropriate to the lower temperatures. The ratio of power input to the background heat leak was at least 10, and for most of the points was considerably greater. To obtain normal data a magnet producing a field of 5000 gauss over the region of the sample was used for La I and La II. A larger magnet was used with La III giving a minimum field of 10 000 gauss.

The thermometer used for the measurements on La III was calibrated against the vapor pressure of helium from 1.6 to 4.8°K, and against the superconducting transition temperature of a specimen of Pb wire of 6-mil diameter and purity 99.999%. The 1955 Leiden scale[13] was used to convert helium vapor pressures into temperatures, and the transition temperature of Pb was taken at 7.22°K. The calibration points were then fitted to the formula

$$\log R = A + B/T - C\log T + DT^2, \qquad (1)$$

where R is the resistance of the carbon resistor, T is the temperature, and A, B, C, and D are constants. These constants were chosen to make the formula fit at 7.22°K, 4.22°K, and at two temperatures below the λ point of helium. The remainder of the 19 experimental points did not deviate by more than 0.0025 deg in the range 1.6 to 4.2°K nor by more than 0.005 deg in the range 4.2 to 4.8°K.

This same thermometer was also used for the measurements on La Ic. The other thermometers used for La I were calibrated only in the range 1.6 to 4.2°K. These points were fitted to the formula of Eq. (1) and this calibration formula was used up to 6.5°K. No attempt was made to improve the accuracy of the thermometry for this sample and the data are used only to show the qualitative effects of annealing. The thermometer used in the measurements on La II was calibrated from 1.6 to 4.8°K and fitted to the same formula.

The molar heat capacity was calculated from the relation

$$C = \tau i^2 R_H/(JN\Delta T), \qquad (2)$$

in which i is the current passing through the heater of resistance R_H for a time τ, J is the mechanical equivalent of heat, N the number of moles in the sample, and ΔT is the increase in temperature brought about by the Joule heating. All quantities except ΔT were measured to 0.1% or better. Errors enter into ΔT in two ways: in deducing the resistance change of the thermometer, ΔR, from the heating curve, and in converting ΔR into a temperature change. The uncertainty in deducing ΔR for La I is 2 to 3%. With improved thermal isolation this was reduced to less than 1% for La II and La III. The uncertainty in converting ΔR to ΔT becomes progressively larger with increasing temperature beyond 4.8°K as the thermometer calibration becomes less certain. The mean value of the transition temperatures reported in the literature for Pb is 7.217°K[14] and the mean deviation is 0.015 deg. Assuming that the cali-

[11] Worley, Zemansky, and Boorse, Phys. Rev. **99**, 447 (1955).
[12] Brown, Zemansky, and Boorse, Phys. Rev. **92**, 52 (1953).
[13] H. van Dijk and M. Durieux, in *Progress in Low Temperature Physics II*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), p. 461. In the region of calibration the 1955 Leiden scale, T_{L55}, differs from the Clement scale, T_{55E}, by less than 0.004 deg.
[14] Boorse, Cook, and Zemansky, Phys. Rev. **78**, 635 (1950).

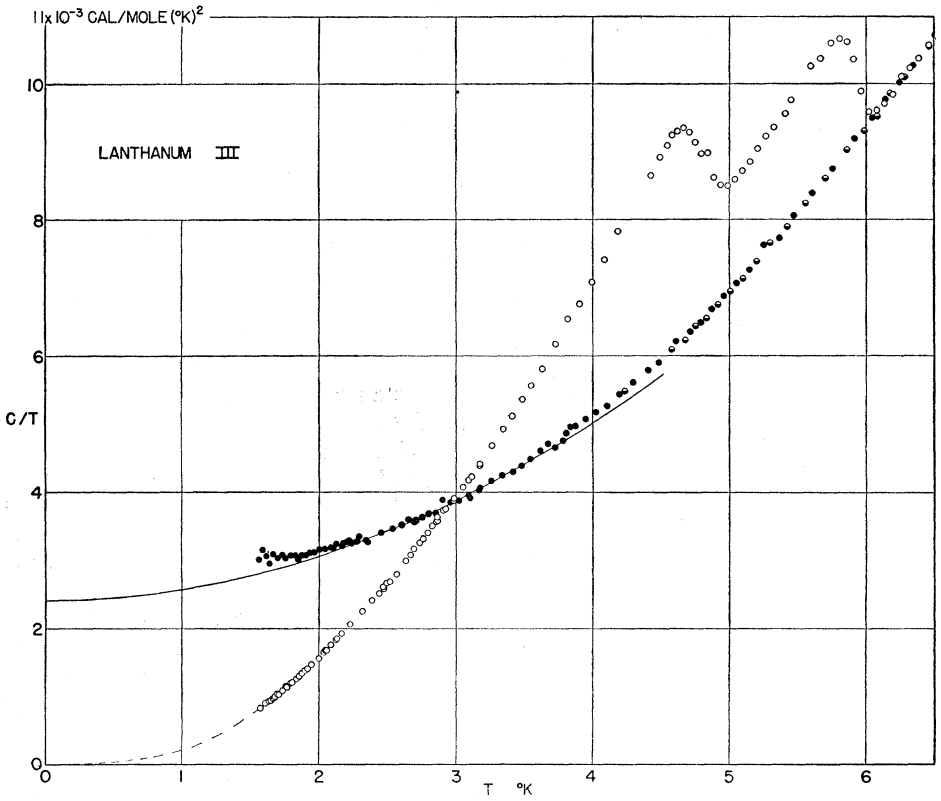

FIG. 1. C/T *versus* T for sample La III. The open circles, half-filled circles, and solid circles represent the results in zero field, in 4000 gauss, and in 10 000 gauss, respectively. The full curve represents the relation

$$C/T = 2.41\times10^{-3} + 464T^2/(142)^3.$$

bration of the La III thermometer is without significant error below 4.6°K, an error in thermometry of 0.03 deg at 7.2°K would lead to a maximum error in the calculated heat capacity no greater than 2% at 6.5°K and about 1% at 6°K. For La I and La II the uncertainty is considerably greater due to the more limited region of thermometer calibration.

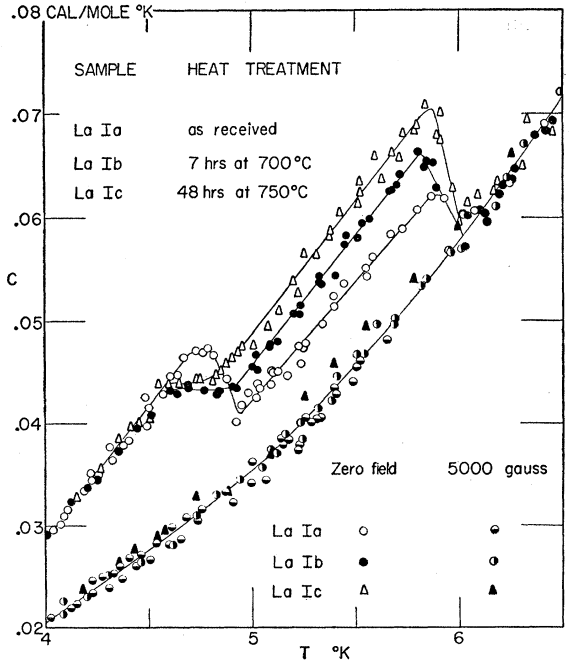

FIG. 2. The effect of heat treatment on the heat capacity of sample La I.

An additional source of error is introduced by the heat capacity of the Glyptal. This may be estimated for temperatures above 4°K from the data of Pearlman and Keesom[15] and is at most 0.4% of the heat capacity of the lanthanum. The heat capacity of the thermometer, as estimated from the data of Bergenlid *et al.*[16] for graphite, is everywhere much less than 0.1%.

It is felt that the total uncertainty in the heat capacity of La III is less than 1% of the mean line below 4.8°K, increasing to about 2% at 6°K and 3% at 6.5°K.

III. RESULTS AND DISCUSSION

A. Zero-Field Data

The results for La III are shown in Fig. 1 in which C/T is plotted against T for zero field and for fields of 4000 and 10 000 gauss. Two abrupt changes at 4.8 and 5.9°K are apparent in the zero-field data. It may be seen that the application of a field of 4000 gauss in the temperature range above 4.2°K lowers the heat capacity and completely suppresses the two abrupt changes. Moreover, the application of a field of 10 000 gauss

[15] N. Pearlman and P. H. Keesom, Phys. Rev. **88**, 398 (1952).
[16] Bergenlid, Hill, Webb, and Wilks, Phil. Mag. **45**, 851 (1954).

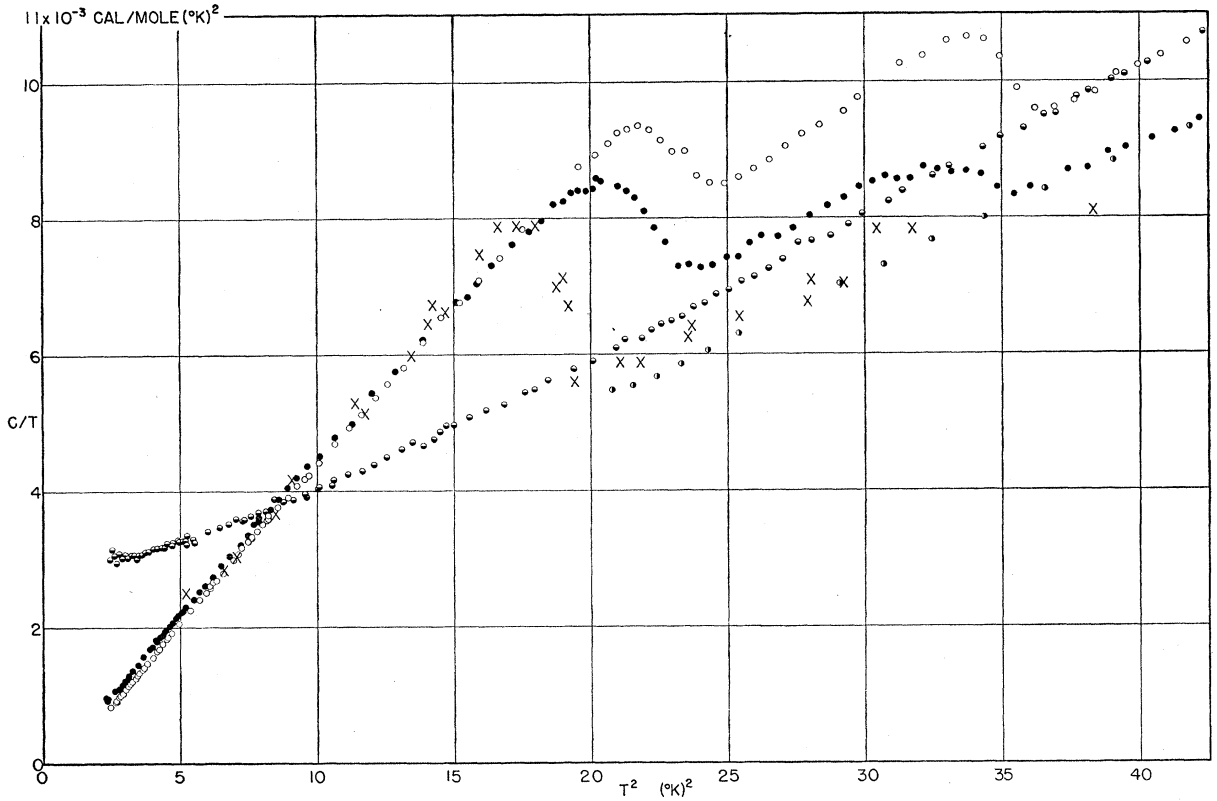

FIG. 3. C/T *versus* T^2 for lanthanum. Open circles—results in zero field for La III; half-filled circles (bottom-half black)—results in 10 000 gauss for La III; solid circles—results in zero field for La II; half-filled circles (right-half black)—results in 5000 gauss for La II; crosses—results in zero field of Parkinson, Simon, and Spedding.

produces no further change. This behavior is uniquely characteristic of superconductivity and allows both anomalies to be identified as superconducting transitions.

The heat capacity of La I after various heat treatments is shown in Fig. 2. The annealing increases the magnitude of the upper discontinuity at the expense of that of the lower. Evidently 5.9°K is the transition temperature of the β phase and 4.8°K the transition temperature of the α phase of these samples.

It is not surprising that the two transitions were not clearly seen by the earlier magnetic and resistance measurements because of the possibility of magnetic shielding or electrical short circuiting of the normal by the superconducting material in the temperature interval between the two transitions. In the magnetic measurements of Ziegler, Young, and Floyd one transition of width 0.8 deg was observed while all other transition widths were 0.3 deg or less. In the resistance measurements of James, Legvold, and Spedding[3] there were two instances in which transitions were found to be as broad as 0.9 deg. These unusually broad transitions could be explained as the overlapping of two separate transitions in cases in which the magnetic shielding or electrical short circuiting of the normal hexagonal material was incomplete. The results of the calorimetric work of Parkinson, Simon, and Spedding are shown in Fig. 3. A possible higher temperature transition might easily have been overlooked in these data owing to the scarcity of points in the region where it would be expected. These investigators deduced values of the normal heat capacity constants γ and Θ from their data in the range 4.4 to 6.0°K. Since their data in this range may relate to a mixture of superconducting and normal material rather than to the normal state alone, their values of γ and Θ are doubtful.

Within the precision of the data the superconducting heat capacity of La III in millicalories/mole (°K) may be represented by the expression $C_s=-0.36T+0.485T^3$ in the interval from 1.6 to 2.8°K, and by $C_s=-0.08T+0.450T^3$ from 2.8 to 4.5°K. The transition temperature of the α phase, T_α, and of the β phase, T_β, as well as the transition widhts, ΔT_α and ΔT_β, are given in Table I for each of the three samples. The transition temperatures are taken as the midpoints of the transitions.

B. Normal Data

It is expected that at a sufficiently low temperature the normal heat capacity of a metal can be represented by the Debye-Sommerfeld relation,

$$C_n=\gamma T+(464/\Theta^3)T^3.$$

TABLE I. Transition temperatures and transition widths of superconducting lanthanum.

Sample	T_α (°K)	ΔT_α (deg)	T_β (°K)	ΔT_β (deg)
La Ia	4.8	0.2	5.9	...
La Ib	4.7$_5$	0.3	5.9	0.2
La Ic	4.7	0.2	5.9	0.2
La II	4.7	0.4	5.8	0.3
La III	4.80	0.33	5.91	0.26

The first term in this expression represents the electronic heat capacity, and the second term the heat capacity of the lattice. When values of C/T are plotted against T^2, as in Fig. 3, this dependence appears as a straight line. Inspection of the La III data shows a deviation from linearity, as well as excessive scatter at the lowest temperatures. It is presumed that this scatter arises from the appearance of the intermediate state. Previous magnetic measurements[4] have shown that lanthanum is a hard superconductor remaining in the intermediate state in the presence of magnetic fields several times greater than the critical field as deduced thermodynamically from heat capacity measurements. The presence of the intermediate state at the lowest temperatures would be expected to produce a spuriously high heat capacity due to the absorption of latent heat, and has been shown[11] to cause excessive scatter in heat capacity data.

A guide for the extrapolation of the normal line was obtained through the procedure of matching the normal and superconducting entropies above the upper transition. Since in the absence of a magnetic field the transitions take place without latent heat, the third law of thermodynamics requires that these entropies be equal. In order to compare the entropies it is necessary to extrapolate both the normal and superconducting curves to the absolute zero of temperature. The method of extrapolation of the superconducting curve is not critical since the extrapolated portion contributes only 1% to the total entropy.

In order to extrapolate the normal line, use is made of the Debye-Sommerfeld relation on the assumption that there is an interval of temperature low enough so that the lattice heat capacity follows a T^3 dependence yet high enough to be above the region in which the intermediate state may appear. The crossover temperature ($C_n=C_s$) of 2.95°K was assumed to lie in this interval. Hence the contribution of the normal entropy at 2.95°K is given in terms of the constants γ and Θ by

$$\int_0^{2.95} C_n/T\,dT=\int_0^{2.95}[\gamma+(464/\Theta^3)T^2]dT$$
$$=2.95\gamma+\frac{464}{\Theta^3}\frac{(2.95)^3}{3}, \quad (3)$$

and the remainder of the normal entropy at 6°K is given by $\int_{2.95}^{6}(C_n/T)dT$. This latter value is determined from the data by the use of a planimeter. The total normal entropy at 6°K must be equal to the *superconducting* entropy at 6°K, the value of which is determined by a planimeter measurement of the data. This gives an expression involving only the unknowns γ and Θ:

$$2.95\gamma+\frac{464}{3}(2.95)^3\frac{1}{\Theta^3}=\int_0^{2.95}\frac{C_s}{T}dT+\int_{2.95}^{6}\frac{C_s-C_n}{T}dT. \quad (4)$$

A second relation is obtained by inserting the measured value of the normal heat capacity at 2.95°K in the Debye-Sommerfeld relation. The values of γ and Θ which satisfy these two simultaneous equations are respectively 24.1×10^{-4} cal/mole (°K)^2 and 142°K.

It should be noted that each of these values is an average for the two crystal structures present. Letting x represent the fraction of sample La III which was in the α phase, then at the lowest temperatures the measured normal heat capacity may be expressed by the relation

$$C_n=x\left(\gamma_\alpha T+\frac{464}{\Theta_\alpha{}^3}T^3\right)+(1-x)\left(\gamma_\beta T+\frac{464}{\Theta_\beta{}^3}T^3\right), \quad (5)$$

or

$$\gamma T+\frac{464}{\Theta^3}T^3=[x\gamma_\alpha+(1-x)\gamma_\beta]T+464\left[\frac{x}{\Theta_\alpha{}^3}+\frac{1-x}{\Theta_\beta{}^3}\right]T^3, \quad (6)$$

where the subscripts α and β refer to the crystallographic phases. From Eq. (6) it follows that

$$\gamma=x\gamma_\alpha+(1-x)\gamma_\beta, \quad (7)$$

and

$$\frac{1}{\Theta^3}=\frac{x}{\Theta_\alpha{}^3}+\frac{1-x}{\Theta_\beta{}^3}. \quad (8)$$

The solid line in Fig. 1 is the Debye-Sommerfeld curve for these values of γ and Θ. The fact that this curve fits the data smoothly in an interval including 2.95°K lends confidence to the assumptions made in extrapolating the normal data. The deviation of the data from this curve above 3.8°K or $\Theta/37$ indicates that the Debye Θ value decreases, as is to be expected.[17]

The calculated values of γ and Θ may be shown to be rather insensitive to systematic errors in thermometry. Thus, if T' represents the measured temperature and T the true temperature, then the measured heat capacity C' is related to the true heat capacity C as follows:

$$C'=dU/dT'=(dU/dT)(dT/dT')=CdT/dT'. \quad (9)$$

The measured entropy S' at T_c may be expressed as

[17] M. Blackman, Repts. Progr. in Phys. 8, 11 (1941).

follows:

$$S'=\int_0^{T_c'}(C'/T')dT'=\int_0^{T_c}(C/T)(T/T')dT. \quad (10)$$

The error introduced in the entropy comes from the departure of the ratio T/T' from unity. Since this factor is unity to within less than 0.2% up to 4.8°K as a result of direct calibration against the vapor pressure of helium, and since the error is probably no larger than 0.03 deg at 7.2°K or 0.4% in T/T', the uncertainty in the entropy at T_c due to thermometry may be taken as 0.2%.

The maximum scatter in the data is about 1% from the mean, while the average deviation from the mean line is about 0.3%. An additive error due to the heat capacity of the Glyptal will cancel from the last term in Eq. (4). In the other terms the error from this source is taken as 0.5%. On the basis of these estimates of uncertainties, $\gamma=(24.1\pm0.6)\times10^{-4}$ cal/mole (°K)^2 and $\Theta=142\pm3$°K.

The critical field at absolute zero, H_0, of a *single* superconductor is related to the heat capacities by the formula

$$\frac{vH_0^2}{8\pi}=\int_0^{T_c}(C_s-C_n)dT, \quad (11)$$

where v is the molar volume. A planimeter measurement of the La III data, using the Debye-Sommerfeld low-temperature extrapolation of the normal line, gives, when substituted in Eq. (11), a formal value for H_0 of 910 gauss. However in this case the right-hand side of Eq. (11) may be expressed in terms of the contributions from the two crystal forms, as follows:

$$\int_0^{T_\beta}(C_s-C_n)dT=x\int_0^{T_\alpha}(C_{s\alpha}-C_{n\alpha})dT+(1-x)\int_0^{T_\beta}(C_{s\beta}-C_{n\beta})dT, \quad (12)$$

or

$$\frac{vH_0^2}{8\pi}=x\frac{v_\alpha H_{0\alpha}^2}{8\pi}+(1-x)\frac{v_\beta H_{0\beta}^2}{8\pi}. \quad (13)$$

C. Comparison with Theory

These data, which refer to a mixture of two superconductors, do not lend themselves readily to comparison with theoretical prediction because of the ambiguity in separately determining the parameters of the two modifications of lanthanum. Such a comparison may be made however, based on the assumption that the two modifications of lanthanum conform to a law of corresponding states of the form

$$C_{es}=\gamma T_c f(t), \quad (14)$$

where C_{es} is the superconducting electronic heat capacity and $t=T/T_c$ is the reduced temperature.

If C_{es} is expressed in the form

$$C_{es}=C_s-C_n+\gamma T, \quad (15)$$

then at T_c Eq. (14) reduces to

$$\Delta C/(\gamma T_c)=f(1)-1, \quad (16)$$

where $\Delta C=(C_s-C_n)_{T=T_c}$ is the molar discontinuity in the heat capacity at T_c. If ΔC_α and ΔC_β represent the *measured* discontinuities in the zero-field data of La III at T_α and T_β, then the *molar* discontinuities will be $\Delta C_\alpha/x$ and $\Delta C_\beta/(1-x)$. Equation (16) then implies the equalities

$$\frac{\Delta C_\alpha}{x\gamma_\alpha T_\alpha}=\frac{\Delta C_\beta}{(1-x)\gamma_\beta T_\beta}=f(1)-1. \quad (17)$$

Together with Eq. (7), this leads to $x\gamma_\alpha=13.1\times10^{-4}$, $(1-x)\gamma_\beta=11.0\times10^{-4}$, and $f(1)-1=1.80$. This is close to the Koppe value of 1.71 and agrees well with the ratios found for other superconductors.[18] It is somewhat higher than the value 1.32 predicted by the microscopic theory of Bardeen, Cooper, and Schrieffer[19,20] as applied to a rather idealized model of a metal.

Equation (11) may be written, using Eqs. (14) and (15),

$$\frac{vH_0^2}{8\pi}=\int_0^{T_c}[\gamma T_c f(t)-\gamma T]dT=\gamma T_c^2\int_0^1 f(t)dt-\tfrac{1}{2}\gamma T_c^2, \quad (18)$$

or

$$\frac{vH_0^2}{8\pi\gamma T_c^2}=\int_0^1 f(t)dt-\tfrac{1}{2}. \quad (19)$$

Again assuming $f(t)$ to be the same for both forms of lanthanum, we have the equalities

$$\frac{xv_\alpha H_{0\alpha}^2}{8\pi x\gamma_\alpha T_\alpha^2}=\frac{(1-x)V_\beta H_{0\beta}^2}{8\pi(1-x)\gamma_\beta T_\beta^2}=\int_0^1 f(t)dt-\tfrac{1}{2}. \quad (20)$$

Upon using the values for $x\gamma_\alpha$ and $(1-x)\gamma_\beta$ deduced from Eq. (17), the above equation together with Eq. (13) leads to the values $v_\alpha\times H_{0\alpha}^2=8.30\times10^6$, $(1-x)v_\beta\times H_{0\beta}^2=10.56\times10^6$, and $\int_0^1 f(t)dt-\frac{1}{2}=0.259$. The value predicted by the Bardeen, Cooper, and Schrieffer theory is 0.234.

The general form of $f(t)$ predicted by the Bardeen theory, as well as by earlier energy gap models,[21] is, for low values of the reduced temperature,

$$f(t)=ae^{-b/t}. \quad (21)$$

[18] Worley, Zemansky, and Boorse, Phys. Rev. **87**, 1142 (1952). The more recent data available for several of the metals listed here yield essentially the same values of the ratio.

[19] Bardeen, Cooper, and Schrieffer, Phys. Rev. **106**, 162 (1957).

[20] Bardeen, Cooper, and Schrieffer, Office of Ordnance Research Technical Report No. 9, 1957 (unpublished).

[21] W. L. Ginsburg, Fortschr. Physik **1**, 101 (1953); H. Fröhlich, Proc. Roy. Soc. (London) **A223**, 296 (1954); J. Bardeen, Phys. Rev. **97**, 1724 (1955).

The superconducting electronic heat capacities of V^{22} and Sn^{23} have been shown to exhibit such an exponential temperature dependence for $t<0.7$ with the values $a=9.17$ and $b=1.50$. The superconducting heat capacity of lanthanum goes nearly as T^3 at the lowest temperatures but with a negative intercept. In order to remain positive down to the absolute zero it must fall less rapidly, in a manner suggestive of Eq. (21). An attempt to fit the data of La III to the corresponding relation,

$$C_{es}=x\gamma_\alpha T_\alpha a e^{-bT_\alpha/T}+(1-x)\gamma_\beta T_\beta a e^{-bT_\beta/T}, \quad (22)$$

discloses small but systematic deviations. An approximate fit from 1.6 to 3.4°K, using the values $a=9.20$ and $b=1.58$, deviates by as much as 5% from the data.

[22] Corak, Goodman, Satterthwaite, and Wexler, Phys. Rev. **102**, 656 (1956).
[23] W. S. Corak and C. B. Satterthwaite, Phys. Rev. **102**, 662 (1956).

IV. ACKNOWLEDGMENTS

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Double Electron Capture and Loss by Helium Ions Traversing Gases*

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A beam of pure He^{++} ions was passed through a cell in which the gas pressure could be varied, and the emergent beam was examined for its He^0 and He^+ content. With helium and air in the cell, it was observed that He^0 persists to pressures so low that it could not have been formed except by double electron capture by He^{++} in a single collision. In hydrogen the double capture event is much less probable.

The analogous experiment was performed with a helium atomic beam, and at 250 kev and 450 kev in air He^{++}, formed by double electron loss, was detected. In hydrogen and helium only upper limits for double electron loss could be established.

These results, with values of the sums $(\sigma_{20}+\sigma_{21})$ and $(\sigma_{01}+\sigma_{02})$ measured in previous researches, made it possible to compute values of σ_{20} and σ_{02}, as in the following table.

Cross sections in units of 10^{-17} cm² per atom

kev	Hydrogen σ_{20}	Hydrogen σ_{20}/σ_{21}	Helium σ_{20}	Helium σ_{20}/σ_{21}	Air σ_{20}	Air σ_{20}/σ_{21}
			Double electron capture			
150	1.1	0.04	5.7	0.30	11.8	0.24
250	0.87	0.06	2.7	0.19	5.2	0.15
350	0.20	0.03	1.1	0.10	2.1	0.09
450	0.12	0.05	1.1	0.15	1.3	0.08
			Double electron loss			
	σ_{02}	σ_{02}/σ_{01}	σ_{02}	σ_{02}/σ_{01}	σ_{02}	σ_{02}/σ_{01}
250	0.1±0.1	~0.02	0.2±0.2	~0.02	0.5±0.4	0.02
450	<0.1	<0.01	<0.2	<0.01	1.3±0.4	0.06

A table of the six charge-changing collision cross sections for helium ions is presented. The equations needed to compute the change in the charge composition of a helium ion beam due to passage through a gas film are given.

I. INTRODUCTION

THIS paper reports measurements of cross sections for charge-changing collisions of moving helium ions in gases. A kinetic energy range from 150 to 450 kev is covered, the corresponding velocities ranging between 1.22 and 2.12 times the Bohr electron velocity in the hydrogen atom, 2.18×10^8 cm/sec. In this region the charge-equilibrated helium beam must be considered at least a three-component system; the charge states He^0, He^+, He^{++} all appear in the beam in fractions greater than 1%. For He^0 the most probable charge-changing events are $He^0\rightarrow He^+$ and $He^0\rightarrow He^{++}$, the cross sections for which are called σ_{01} and σ_{02}. For the other charge states the most probable charge changes on collision correspond to the cross sections σ_{10}, σ_{12}, σ_{20}, σ_{21}.

The capture of two electrons by He^+ in a single collision, leading to a negative helium ion, has been observed at kinetic energies as high as 160 kev, with σ_{1I} ranging from 0.01×10^{-19} cm² in helium gas to 0.6×10^{-19} cm² in krypton,[1] but such events occur with a probability of the order of 0.10% of that of the others mentioned. No attempt was made in these experiments to observe negative helium ions.

Charge-changing cross-section measurements for helium beams have been described in two prior publications from this laboratory[2,3] and the equipment used

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[1] Dukel'skii, Afrosimov, and Fedorenko, Zhur. Eksptl. i Teort. Fiz. (U.S.S.R.) **30**, 792 (1956) [translation: Soviet Phys. JETP **3**, 764 (1956)]. The phenomenon of double electron capture had previously been observed in the case of protons, Ya. M. Fogel' and R. V. Mitlin, Zhur. Eksptl. i Teort. Fiz. (U.S.S.R.) **30**, 450 (1956) [translation: Soviet Phys. JETP **3**, 334 (1956)].
[2] S. Krasner, Phys. Rev. **99**, 520 (1955).
[3] Allison, Cuevas, and Murphy, Phys. Rev. **102**, 1041 (1956); this will be referred to as ACM.