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STATE ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA

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REPORTS

PROJECT NO. 116-18

SUPERCONDUCTIVITY STUDIES

BY

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R. A. YOUNG

NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH
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4	June 16, 1953	Superconductivity Studies.	W. T. Ziegler and R. A. Young

Georgia Institute of Technology
STATE ENGINEERING EXPERIMENT STATION
Atlanta, Georgia

TECHNICAL REPORT NO. 1

PROJECT NO. 116-18

SUPERCONDUCTIVITY OF LANTHANUM, CERIUM,
PRASEODYMIUM, AND NEODYMIUM

BY

W. T. ZIEGLER

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CONTRACT NO. N6-cri-192, TASK ORDER I

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JANUARY 20, 1949

GEORGIA INSTITUTE OF TECHNOLOGY

THE STATE ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

TECHNICAL REPORT NO. 1

PROJECT NO. 116-18

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I. INTRODUCTION

In the fall of 1946 a program of low temperature research was initiated at the Georgia Institute of Technology with the assistance of the Office of Naval Research under Contract No. N6-ori-192, Task Order I. This program had for its immediate objective the testing of certain rare earth metals and their compounds, chiefly the hydrides and nitrides, for superconductivity by electrical and magnetic means. The first efforts under this program were directed toward the construction and assembly of the equipment necessary to carry out such measurements at liquid helium temperatures.

The rare earth metals have been chosen for study because of these fourteen elements only lanthanum and cerium had been tested for superconductivity previously, the results for even these two being somewhat unclear. In addition, the interesting possibility of studying the metals in more than one crystalline modification exists.

The purpose of the present report is to describe the results of some magnetic experiments which have been carried out to test for the possible occurrence of superconductivity in lanthanum, cerium, praseodymium, and neodymium. A short article describing the results for lanthanum and cerium has already been published.¹⁸ A brief description of the low temperature facilities has also appeared.¹⁹

II. SUMMARY

The present report describes some results obtained in a program of research at low temperatures which was initiated at the Georgia Institute of Technology with the assistance of the Office of Naval Research in October, 1946, under Contract No. N6-ori-192, Task Order I. In the present work samples of lanthanum metal from two different sources were investigated and found to be superconducting at $4.85 \pm 0.15^{\circ}\text{K}$ and $4.45 \pm 0.10^{\circ}\text{K}$, respectively. No magnetic transition was found in specimens of cerium, praseodymium, and neodymium down to 2°K , the lowest temperature reached in these experiments. Chemical analysis of the samples studied showed the metals to have the following purities: lanthanum (Cooper), 95.5-98%; lanthanum (Hilger), 99%; cerium, 88-95%; praseodymium, 54.8% (major impurity, 37% La); neodymium, 78.7% (major impurity, 15% Pr.). Samples of lead and tin of high purity were run to check the operation of the apparatus.

Powder X-ray diffraction studies were made of the samples in the "as received" state. These revealed that both lanthanum samples had a predominantly hexagonal close-packed structure, while the cerium had a predominantly face-centered cubic structure. The results for praseodymium and neodymium were inconclusive.

Reprints of two published articles are appended. One of these is a preliminary report of the low temperature studies

herein described on lanthanum and cerium, the other is a brief description of the laboratory and some of its equipment.

III. REVIEW OF WORK BY OTHER INVESTIGATORS

The superconductivity of lanthanum metal has previously been studied by Mendelssohn and Daunt,¹¹ using a magnetic method. These investigators reported a transition temperature of 4.71°K for a sample containing 1% iron. Shoenberg,¹³ also using a magnetic method, has reported that a lanthanum sample (Hilger, Lab. No. 7259), presumably identical with our sample La 3 (which will be discussed below), was superconducting at 4.2°K. On the other hand, McLennan, Allen, and Wilhelm⁸ have measured the electrical conductivity of "pure" samples of lanthanum and cerium from 300 to 1.9°K and reported that neither substance became superconducting. Cerium has been reported to remain in the normal state down to 1.43°K.⁶ Very recently cerium, praseodymium, neodymium, and yttrium have been studied by a magnetic method and found to remain normal down to 1.1°K.¹⁴

McLennan, Howlett, and Wilhelm⁹ have studied the electrical conductivity of "misch" metal down to 2.3°K and found no evidence of superconductivity. The sample was free of iron and had the following composition: cerium-35%, lanthanum-20%, neodymium-20%, samarium-10%, gadolinium-6%, praseodymium-5%, europium-2%, and yttrium-2%.

Lanthanum, cerium, praseodymium, and neodymium all exhibit both hexagonal close-packed and face-centered cubic structures.^{17,20}

There is some evidence that lanthanum may exist in three allotropic modifications⁵ and cerium in four modifications.^{5,16} The rates of transition between the various allotropic modifications are only imperfectly known. In view of this multiplicity of structures, there would seem to be some uncertainty as to actual allotropic modifications of the metals which have been investigated for superconductivity.

IV. EXPERIMENTAL WORK

A. Materials

The samples of lead, tin, lanthanum, cerium, praseodymium, and neodymium studied were obtained from commercial sources. The lead and tin specimens were used to check the behavior of the apparatus with known superconductors. A description of these materials follows.

1. Lead

This material was obtained from Johnson, Matthey, and Co., Ltd., London, England, in the form of rods seven mm. in diameter. It had the designation Lab. No. 1932 and was stated to be 99.998 per cent pure.

2. Tin

The tin metal used was cut from a U. S. Bureau of Standards freezing point standard (Std. Sample 42d) which was marked as freezing at 231.90°C.

3. Lanthanum, Cerium, Praseodymium, and Neodymium

Samples of these rare earth metals were obtained from Cooper Metallurgical Laboratory, Cleveland, Ohio, in the form of irregular pieces from which small cylinders having the approximate dimensions 5 mm. x 20 mm. were cut.

4. Lanthanum (Hilger)

A second sample of lanthanum, obtained from Adam Hilger, Ltd., London, England, and designated by them as Lab. No. 7259, was reported to contain a total of between one-half and one per cent of aluminum, silicon, and tungsten and to be substantially free of other rare earth metals.

The rare earth metals obtained from the Cooper Metallurgical Laboratory were analysed qualitatively using a spectrographic method employing the copper spark technique.² Using the spectrographic results as a guide, the metals were then analysed quantitatively for insoluble matter (reported as silicon), iron, praseodymium, neodymium, and in some instances, lanthanum and cerium. Calcium, aluminum, and traces of other rare earths which also were shown to be present in all samples by spectrographic analysis were not analysed for quantitativity. The results of these analyses are shown in Table I.

Silicon was determined by filtering off the insoluble matter remaining after a sample of the metal was dissolved in dilute hydrochloric acid. This residue was ignited to constant

weight at about 800° C. The resulting residue was assumed to be SiO₂ and the result reported as per cent silicon in the metal.

TABLE I
ANALYSES OF COMMERCIAL RARE EARTH METALS^a

	<u>Lanthanum</u>	<u>Cerium</u>	<u>Praseodymium</u>	<u>Neodymium</u>
La, %	95.5	b	37.0	ca 5
Ce, %	b	88.4	b	b
Pr, %	(<1)	0.4	54.8	15
Nd, %	(<1.5)	1.4	3.5	78.7
Fe, %	0.8	2.5	1.6	2.8
Si, %	0.7	0.5	0.9	1.2
Total	97.0	93.2	97.8	102.7
Unaccounted for	3.0 ^c	6.8 ^c	2.2	-2.7

(a) Obtained from Cooper Metallurgical Laboratory, Cleveland, Ohio.

(b) Not determined.

(c) It is possible that a portion of the unaccounted for balance may have been the parent metal, in which case the lanthanum and cerium contents may have been as high as 98 and 95 per cent, respectively.

Iron was determined by reduction to the ferrous state with zinc in dilute sulfuric acid solution, followed by titration with potassium permanganate.

Praseodymium and neodymium were determined spectrophotometrically by means of a Beckman Model DU quartz spectrophotometer

using the general method of Rodden,¹² care being taken to first reduce the iron to the ferrous state. The salts were present as sulfates. A complete survey of the absorption spectrum of each metal sample was made in the range 380 to 1000 millimicrons. No absorption bands not assignable to neodymium and praseodymium were found.

Lanthanum was determined in the lanthanum metal sample by precipitation as the oxalate in dilute acid solution and the oxalate ignited to the oxide at 850° C. The oxide was presumed to be pure lanthanum oxide since the qualitative spectrographic analysis had indicated that only traces of other rare earths were present in this sample. Due to the appreciable solubility of lanthanum oxalate in dilute acid it is possible that the result reported in Table I is somewhat low.

The lanthanum content of the praseodymium was determined by a spectrographic method soon to be published. It involved the use of the copper spark technique and employed manganese as an internal standard. The result given was checked against a synthetic sample of known praseodymium and lanthanum content. The lanthanum content of the neodymium sample was estimated from the intensity of its spectrum in a similar manner.

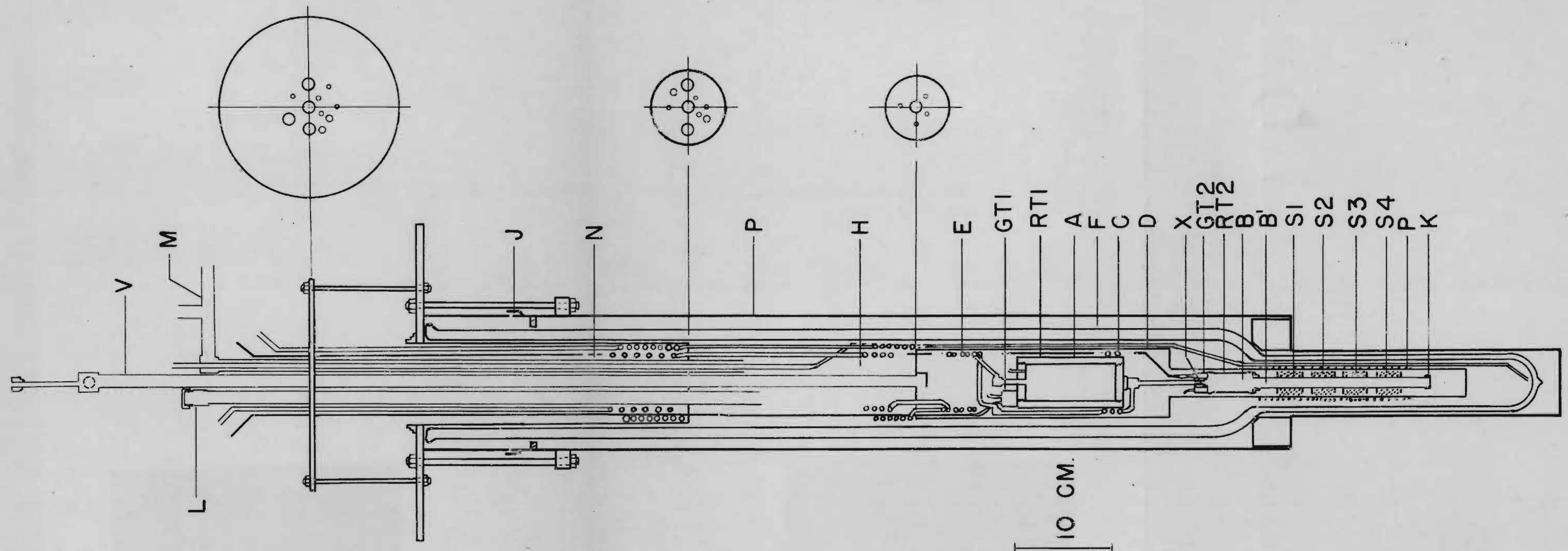
B. The Helium Cryostat

1. General Description

A brief general description of the cryogenic facilities which were utilized in determining the superconductivity data is given in Appendix B.

The helium cryostat which has been constructed is shown schematically in Figure 1. It differs only in detail from one described by Horn³ and Horn and Ziegler.⁴ Liquid helium is produced within the cryostat in two separate processes, the helium produced in one reservoir serving as the thermal dam for the experimental helium chamber.¹⁵ Briefly, the apparatus consists of a heavy-walled copper vessel, A, in which the main charge of liquid helium is produced. Suspended from A is the experimental chamber, consisting of the sections B and B', in which the samples to be studied are located. The experimental chamber and helium reservoir are surrounded by a case, D, which can be evacuated at will. All tubes and wires leading to the helium reservoir and experimental chamber pass first through a liquid nitrogen bath, N, and then through a liquid hydrogen bath, H, which serve as thermal dams. The entire apparatus is surrounded by a glass Dewar vessel, F, supported in the brass case, P. A vacuum tight seal is formed at the joint, J, by means of Apiezon Q putty.

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The main charge of liquid helium is produced in the helium reservoir, A, by the Simon expansion method. This reservoir has a volume of 101 cubic centimeters. Starting from a temperature of 11.5°K, and a pressure of 2,300 psi, a filling of 70-80% can be achieved. The yield of liquid helium produced in this expansion process is the major factor governing the length of time available for experimentation below 11°K. Seventy-five cubic centimeters of liquid helium provide about 2.5 hours for experimentation.

Helium is condensed into the experimental chamber, B and B', by bringing gas at about 20 psi into contact with A in the condensing coil, C. This condensation results in the loss of an equivalent amount of liquid helium from A. The cold gas from A passes through the heat exchanger, E, thus cooling the incoming low pressure helium before it reaches C.

The temperature of the reservoir, A, is measured by means of the gas thermometer, GT1, and the constantan resistance thermometer, RT1.

2. The Experimental Chamber

The all-copper experimental chamber consists of two parts, an upper section, B, having a volume of 12 cubic centimeters, and a lower section, B', having a volume of nine cubic centimeters, in which the samples are placed. The section, B', was constructed by boring and machining a single piece of copper

rod. It has an inside diameter of 5/16 in. (eight mm.) and a wall thickness of 0.047 in. On the outside of B' are wound four secondary coils which are used in the magnetic measurements. It is closed at the bottom end by a cap, K, sealed on with Wood's metal.

The temperature of the experimental chamber is measured by means of the constantan resistance thermometer, RT2, and the gas thermometer, GT2.

The pumping line leading to B contains a constriction, X, 0.50 in. long and 0.029 in. in inside diameter, which is introduced to reduce the "creep" of liquid helium.¹

3. Temperature Measurement and Control

The temperature of the experimental chamber was measured using a gas thermometer of the type described by Mendelssohn,¹⁰ the bulb of which is attached by means of a supernickel capillary (one mm. i.d.) to a bourdon gauge and a closed-end mercury manometer made of two mm. capillary glass tubing. The volume of the gas thermometer bulb is 1.67 cubic centimeters, and the external volume (bourdon gauge and manometer) at room temperature is approximately 20 cubic centimeters. The thermometer system was filled with helium gas at one atmosphere pressure while at room temperature and then sealed off. This system was quite sensitive in the range 3.2 to 8°K, a change of 0.1° being detectable. Below 3°K the gas thermometer acted as a vapor pressure thermometer.

The pressure measurements made with this system were converted to temperatures by assuming that the connecting capillary had a negligible volume. If this be done, it can then be shown that the temperature of the bulb is given by an expression of the form

$$T = \frac{1}{\left[\frac{P_0}{PT_0} (1 + a) - \frac{a}{T'} \right] c}$$

where

T = temperature of the bulb in $^{\circ}\text{K}$

P = observed pressure in mm.

P_0 = filling pressure in mm.

T_0 = filling temperature in $^{\circ}\text{K}$

T' = temperature of external volume at time of experiment in $^{\circ}\text{K}$

a = ratio of external volume, V_e , to volume of bulb, V_b

c = the compressibility factor $c = Pv/RT$

For practical purposes, a can be taken as a parameter to be determined at a known temperature. In our experiment, this parameter was found to be 12.2, using the normal boiling point of helium as a fixed point.

Gas imperfection was taken into account by utilizing P-V-T data from which values of the compressibility factor, c , were either calculated or estimated.⁷

Comparisons of this temperature scale were made against the vapor pressure of helium in the experimental chamber in

the range 4.2 to 3.2°K and agreement to $\pm 0.1^\circ$ was found. Samples of pure lead and tin were run in the apparatus in the manner described later and were found to undergo magnetic transitions at 3.6° and about 7°K, respectively. The transition range in each case was less than 0.1°.

The resistance thermometer, RT2, constructed of No. 40 B and S gauge constantan wire, had a resistance of 1,069 ohms at 4°K and a dR/dT of 0.96 ohm per degree. It could be read to 0.05°. It was found to be useful for interpolation purposes as well as for judging the sharpness of transitions.

The main helium reservoir is fitted with a similar temperature measuring system except that pressures were read with a bourdon gauge only. In this instance, the boiling point and triple point of hydrogen were used to fix the parameter of the gas thermometer.

4. Magnetic Method of Detecting Superconductivity

The system for carrying out the magnetic measurements is shown in Figure 2. It consists of a primary coil, P, wound upon the lower end of the vacuum case, D, and four equally spaced secondary coils S1, S2, S3, and S4, wound on the outside of the experimental chamber, B', co-axial with the primary coil. The primary consists of 1,117 turns of No. 30 B and S single cotton enameled copper wire wound in three layers; the winding, which is 19.7 cm. long, extends 13 mm. beyond the secondaries at each end. Each secondary coil is 22 mm. long

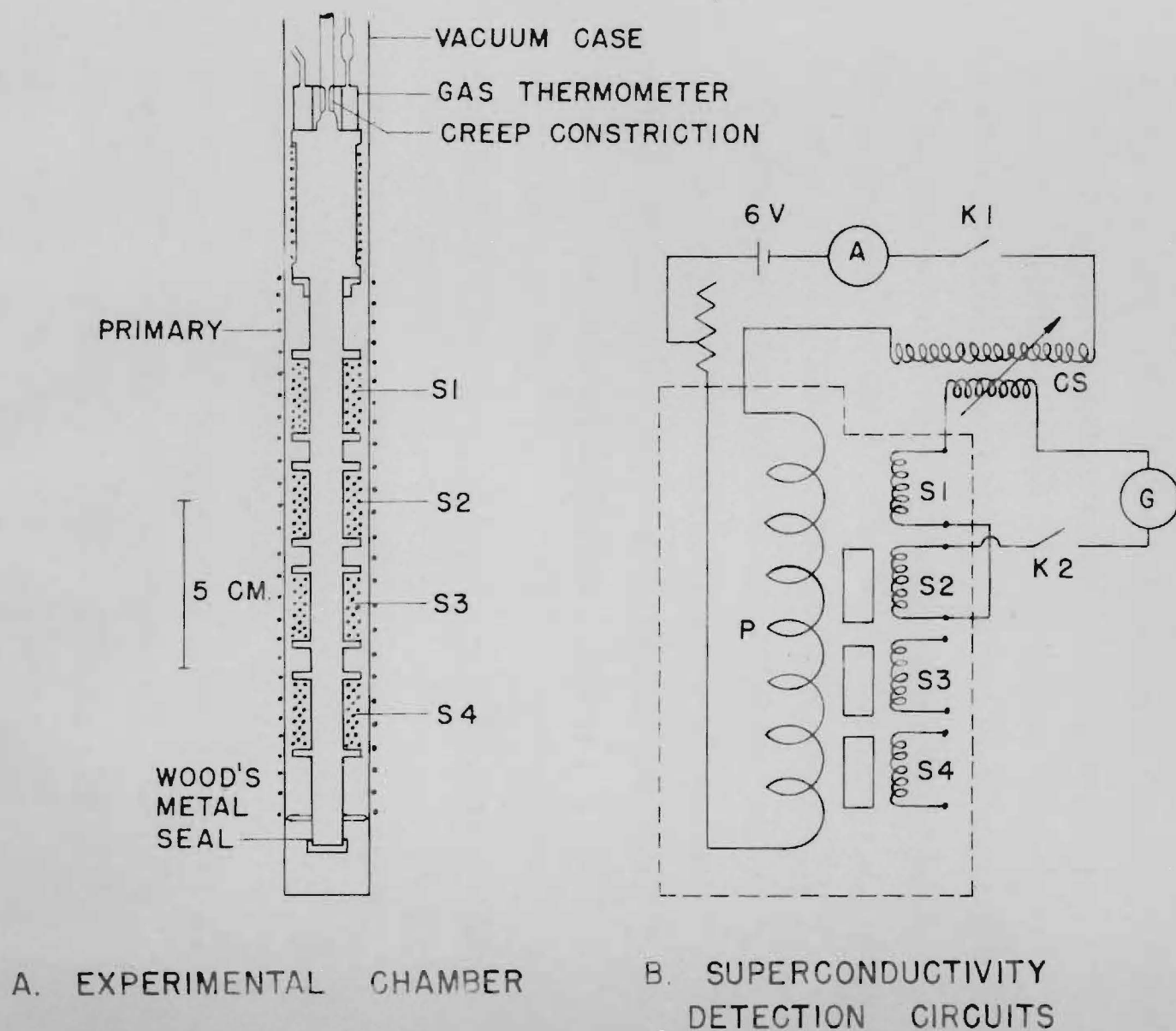


FIGURE 2. MAGNETIC MEASUREMENTS SYSTEM

and consists of about 3,100 turns of No. 40 B and S single cotton enameled copper wire.

In order to prevent air oxidation of the rare earth metals all samples were sealed in small glass capsules, made of seven mm. o. d. pyrex glass tubing, under helium gas at ten cm. Hg pressure. Three capsules were then separated by lucite spacers and the entire assembly held together with cellulose acetate cement. This assembly was then slipped into the experimental chamber, B', after which the cap, K, was soldered on with Wood's metal. The spacers were so made that each sample was properly positioned in the center of its secondary coil.

Figure 2 also includes a diagram of the superconduction detection circuit used. In all experiments described in this paper, coil S1 was always empty, with the samples to be studied contained in coils S2, S3, and S4. The experimental procedure was as follows. With the samples in place and at a fixed temperature, coil S1 (the compensating coil) and another coil, for example, coil S2, were connected by means of a suitable switching arrangement outside the cryostat in such a manner that the voltages induced in them, when the tap key, K1, in the primary circuit was closed, opposed each other. If the tap key, K2, was closed, the galvanometer,^a G, usually showed a

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a The galvanometer used was a Leeds and Northrop type R instrument having the following characteristics: Sensitivity, 0.43 microv./min.; critical damping resistance, 46 ohms; period, 5.0 sec.; coil resistance, 11.6 ohms.

deflection when the primary was energized, due to some unbalance between S1 and S2. (Opening K2 prior to de-energizing the primary was found to be helpful in restoring the galvanometer to its zero position quickly.) This unbalance was removed by adjusting a variable external compensating coil, CS, until the galvanometer showed no deflection. The temperature of the experimental chamber was then lowered (or raised) slowly. With K2 closed, K1 was tapped every few seconds and any unbalance of the coils observed as a galvanometer deflection. In passing from room temperature to a temperature just above the transition a single setting of the compensating coil, CS, usually sufficed, an unbalance corresponding to only one or two mm. galvanometer deflection being observed. The transition of a sample from the normal to the superconducting state was easily recognized by the appearance of a sudden large unbalance. In our experiments a galvanometer deflection of three to seven cm. was observed, depending upon the sample being studied and the magnitude of the current in the primary circuit. For instance, a deflection of 5.0 cm., using a primary current of 260 milliamperes, was obtained when a sample of lanthanum (La 1, Run No. 4) underwent a transition from the normal to the superconducting state.

In a given experiment time-temperature and time-galvanometer deflection measurements were made from which temperature vs. galvanometer deflection data were obtained. Such measurements

were made both on warming and cooling through the transition range, though cooling was usually used since this process was controllable. Measurements were made on warming by allowing the experimental chamber to warm up due to the heat leaks present.

Controlled cooling in the temperature range 8° to 4.2°K was achieved by increasing the pressure of the helium gas in the experimental chamber. This resulted in the condensation of some helium in the condenser coil in contact with the main helium reservoir, with the result that the liquid helium so formed flowed down to the experimental chamber where it re-evaporated, thus cooling the samples. Cooling rates of 0.2 to 0.3° per minute were obtained, and no difficulty was encountered in making deflection measurements once every 20 seconds. However, this method of cooling is not wholly satisfactory, since much depends upon the skill of the operator.

C. Magnetic Measurements

Specimens of tin, lead, lanthanum, cerium, praseodymium, and neodymium have been studied by means of the technique outlined above, the last four metals down to 2°K . Of these, only tin, lead, and lanthanum were found to undergo a magnetic transition into superconductivity, the transition taking place in an interval of 0.1° or less in each instance. Tin and lead were studied, primarily, to observe the behavior of the magnetic circuits, since the transition temperatures of these metals are

well established. Table II summarizes the results obtained, together with other pertinent data.

TABLE II
SUMMARY OF RESULTS OF MAGNETIC MEASUREMENTS

Run	Sample	Source	Dimensions		Coil Used	Transition Temp. (°K)
			Dia. (mm.)	Length (mm.)		
1	Sn 1	a	6.9	22.5	S2	3.6 + 0.05
	Pb 1	b	6.6	22.4	S3	7.0 + 0.2
	La 1	c	4.4	19.0	S4	4.6-5.1
2	Sn 1	a	6.9	22.5	S2	—
	Pb 1	b	6.6	22.4	S3	—
	La 1	c	4.4	19.0	S4	4.85 + 0.15
3	La 2 ^d	c	4.8	20.3	S2	4.75 + 0.10
	Ce 1	c	4.8	21.2	S3	<2.0 ^e
	La 3	f	g	g	S4	4.45 + 0.10
4	Nd 1	c	4.8	20.0	S2	<2.0 ^e
	Pr 1	c	4.8	17.8	S3	<2.0 ^e
	La 1	c	4.4	19.0	S4	4.9 + 0.15

(a) Bureau of Standards, Standard Freezing Point Sample No. 420.

(b) Johnson, Matthey and Co., Ltd., London, England.

(c) Cooper Metallurgical Laboratory, Cleveland, Ohio.

(d) La 1 and La 2 were both cut from same piece of metal.

(e) Lowest temperature reached in these experiments.

(f) Adam Hilger, Ltd., London, England.

(g) A roughly rectangular piece 4 x 11.5 x 2.6 mm.

The experimental results obtained show that the two different lanthanum metal samples studied underwent a magnetic transition in the neighborhood of 4.7°K . The transition temperature of the samples obtained from the Cooper Metallurgical Laboratory (La 1 and La 2) was definitely higher than that of the Hilger sample (La 3). While it is possible to ascribe the observed difference to the existence of a temperature gradient along the experimental chamber, it is felt that the actual experimental conditions largely obviate this possibility. Furthermore, the good agreement obtained from samples La 1 and La 2 in Runs 2 and 3, in which coils S4 and S2, respectively, were used, indicate that the temperature gradient was probably too small to be entirely responsible for the observed difference in transition temperatures for the different samples. These results are in general agreement with those reported by Mendelsohn and Daunt¹¹ and Shoenberg¹³ as discussed previously in this report.

Lanthanum sample La 2 was studied down to 2°K . No further changes were noted in its magnetic behavior once it had become superconducting.

The samples of cerium, praseodymium, and neodymium studied did not exhibit any detectable magnetic anomaly down to 2.0°K , the lowest temperature reached in these experiments. These

results are in agreement with unpublished results already discussed obtained at the University of Cambridge.¹⁴ The failure of cerium to become superconducting is also in agreement with the observations of McLennan, Allen and Wilhelm⁸ of the electrical conductivity of this metal and a report by Justi and Koch.⁶

D. X-Ray Diffraction Studies

Powder X-ray diffraction studies, using copper K α radiation, were made of the metals both in the "as received" state and after heat treatment in a vacuum furnace for about four days at 350°C. The powder samples were prepared by filing the metals in an atmosphere of dry nitrogen and sealing the rather coarse filings so obtained in a Pyrex capillary. Exposure times of three to five hours, with oscillation of the sample, were used.

The results of these studies are shown in Table III. These experiments showed that in the "as received" state the lanthanum metal had the hexagonal close-packed structure, whereas the cerium metal had largely the face-centered cubic structure with a smaller amount of the hexagonal closed-packed structure. The results for praseodymium and neodymium were inconclusive. These experiments also indicate that both lanthanum and cerium can be converted by heat treatment from the hexagonal close-packed to the face-centered cubic structure, which is in agreement with the observations of Zintl and Neumann.²

TABLE III

STRUCTURES OF RARE EARTH SAMPLES AS SHOWN BY X-RAY DIFFRACTION

Metal	Purity (Per Cent)	Major Impurity (Per Cent)	Structure	
			As Received	After Heating at 350°C for 96 Hours
Lanthanum ^a	95.5-98		h.c.p., lines diffuse	f.c.c., lines sharp
Lanthanum ^b	99		h.c.p., lines diffuse	
Cerium ^a	88.4-95		f.c.c., ^c lines diffuse h.c.p., lines diffuse	f.c.c., lines sharp
Praseodymium ^a	54.8	37.0 (La)	Only a few diffuse lines obtained	Many sharp lines of unidentified structure
Neodymium ^a	78.7	15 (Pr)	Similar to Pr	Similar to Pr

(a) Obtained from Cooper Metallurgical Laboratory, Cleveland, Ohio.

(b) Obtained from Adam Hilger, Ltd., London, England (Lab. No. 7259).

(c) Approximately three parts f.c.c. to one part h.c.p.

h.c.p. = hexagonal close-packed; f.c.c. = face-centered cubic

It is interesting to note that the lanthanum samples which became superconducting, were predominately in the hexagonal close-packed structure, whereas the cerium sample, which did not become superconducting down to 2°K, was predominantly face-centered cubic. In view of the several phase transitions possible in these metals and the absence of information as to the rate of transition from one to another, it remains to be seen whether these structural observations apply to the metals in question at low temperatures.

V. FUTURE PROGRAM

Experiments to investigate the structure of lanthanum and cerium metals as a function of temperature are underway. It is hoped that these metals can be investigated for possible superconductivity in both the hexagonal close-packed and the face-centered cubic structures.

VI. ACKNOWLEDGMENT

The writer wishes to express his appreciation to Dr. W. M. Spicer for carrying out many spectrographic analyses and to Mr. J. B. Downs, Jr. for carrying out the spectrophotometric and chemical analyses of the rare earth metals. He wishes also to acknowledge his indebtedness to Mr. A. L. Floyd for carrying out the X-ray diffraction studies, to Messrs. W. A. Phillips and J. M. Ziegler for assistance in making the low

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temperature measurements, and to Mr. George Cook for his careful construction of much of the apparatus.

Respectfully submitted:

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W. T. Ziegler,
Projector Director

Approved:

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✓ Gerald A. Rosselot, Director
State Engineering Experiment Station

VII. APPENDICES

APPENDIX A

Georgia Institute of Technology
STATE ENGINEERING EXPERIMENT STATION

VOL. X, No. 13

AUGUST, 1948

**The Superconductivity of Lanthanum
and Cerium**

W. T. ZIEGLER

Research Professor of Chemical Engineering

REPRINT NO. 27

(From Journal of Chemical Physics, August, 1948)

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1948

APPENDIX B

Georgia Institute of Technology

STATE ENGINEERING EXPERIMENT STATION

VOL. X, NO. 15

REPRINT

NOVEMBER, 1948

Georgia Tech Constructs New Low Temperature Laboratory

WALDEMAR T. ZIEGLER

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REPRINT NO. ²⁹30

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of the American Society of Refrigerating Engineers

ATLANTA, GEORGIA
1948

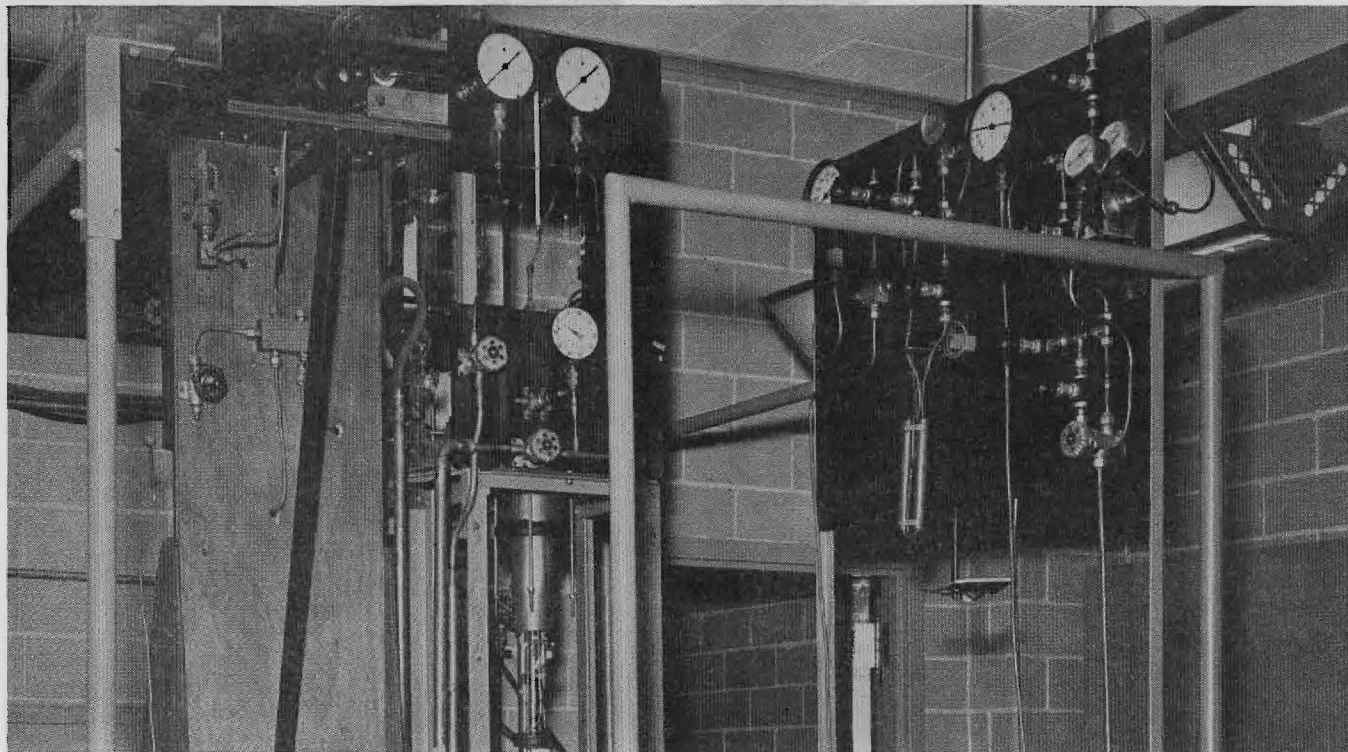


Fig. 1. Helium cryostat and associated apparatus in the new low temperature laboratory at the Georgia Institute of Technology.

Georgia Tech Constructs New Low Temperature Laboratory

Waldemar T. Ziegler

*Research Professor of Chemical Engineering
State Engineering Experiment Station
Georgia Institute of Technology*

RESEARCH at low temperatures is often divided somewhat arbitrarily into work at two temperature ranges—above and below 50 K (-223°C). Temperatures down to about 50 K can be reached rather easily by employing standard refrigeration processes or by using liquid air or nitrogen as a refrigerant. Temperatures below 50 K are usually obtained by employing liquid hydrogen (boiling point = 20.4 K) or liquid helium (boiling point = 4.2 K) as refrigerants, depending upon the temperature range to be studied. Liquid air or nitrogen can usually be purchased from commercial sources, but liquid hydrogen and helium are not available commercially and must be produced in the laboratory.

There is, at present, an increasing technical interest in the properties of matter at low temperatures. The necessity for designing equipment for use in (1) airplanes operating at high altitudes, (2) the low temperature processing of light hydrocarbons, (3) the construction of large liquefaction plants for producing oxygen for use in blast and open hearth furnace operations and in synthetic processes, and (4) the building of portable plants for producing pure oxygen gas for military use, to mention only a few problems, has greatly increased the need for reliable data on the physical properties of materials at low temperatures. Such properties as tensile strength, brittleness, and thermal and electrical conductivity of metals and alloys, as well as the need for data on the thermodynamic properties of many gases and gas mixtures in the temperature range 0 to -190°C (the boiling point of liquid air) are extremely useful to the research worker and the designer.

New experiments are also needed at very low temperatures to aid in the theoretical understanding of the fundamental properties of matter. Two apparently closely related phenomena which, as yet, lack adequate theoretical explanations are the superconductivity of metals and the superfluidity of liquid helium. Both of these effects occur at temperatures below 20 K (-253°C). Superconductivity is characterized by the sudden disappearance of electrical resistance, as well as the appearance of zero permeability to low magnetic fields. This effect, observed only in certain substances, occurs at a characteristic temperature for each substance. It may be thought of as the frictionless flow of electrons.

The superfluidity of helium is characteristic of liquid helium below 2.17 K. Below this temperature, liquid helium has many unusual properties, among them that of possessing an extremely small apparent viscosity. A satisfactory explanation of both superconductivity and superfluidity may require drastic changes in certain of the presently accepted theoretical principles of the fundamental properties of matter.

Georgia Low Temperature Laboratory

Since March 1946 the Engineering Experiment Station of the Georgia Institute of Technology has been actively engaged in creating a laboratory for the performance of research at very low temperatures. Great impetus was given to this effort in October 1946 by a research grant* from the Office of Naval Research.

The properties of a considerable number of the rarer metallic elements, including most of the rare earth metals, have never been studied at very low tempera-

cu ft per minute (measured at 25 C and one atmosphere pressure). When the pressure in the storage cylinders has dropped to about 500 psi, the cylinders are replaced by full ones at 2000 psi.

As yet, no detailed measurements of operating efficiency have been carried out. Present indications are that the average efficiency in the range 1900 to 1200 psi is about 60 percent of theoretical at a flow of 5 cfm.

The Helium Cryostat

The helium cryostat, which contains apparatus for producing liquid helium by the Simon expansion method, is very similar in design and construction to one described by Horn and Ziegler⁴.

This cryostat is shown schematically in Figure 3. Briefly, the apparatus consists of a heavy-walled copper vessel, A, in which the main charge of liquid helium is produced. Suspended from A is the experimental chamber, B, in which the samples to be studied are located. Helium can be condensed into B by bringing helium gas at about 20 psi into contact with A in the condensing coil C. This condensation results in the loss of an equivalent amount of liquid helium from container A. The cold gas from A passes through the heat exchanger, E, thus cooling the incoming low pressure helium before it reaches the condenser. The experimental chamber and helium vessel are surrounded by a

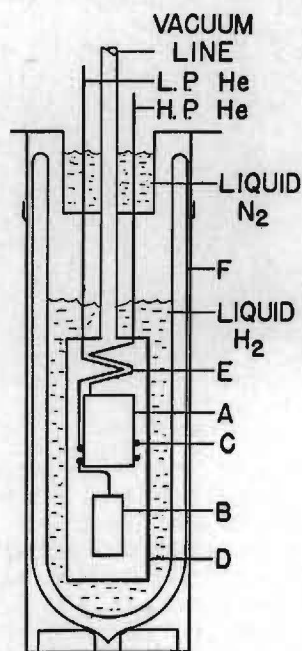


Fig. 3. Schematic view of helium cryostat. This apparatus produces liquid helium by the Simon expansion method. The main charge of the helium is produced in chamber A and test samples are obtained in chamber B.

case, D, which can be evacuated at will. All tubes and wires leading to the helium reservoir and experimental chamber pass first through a liquid nitrogen bath and then through a liquid hydrogen bath which serve as thermal dams. The entire apparatus is surrounded by a glass Dewar vessel, F.

Briefly, the expansion method for producing liquid helium works as follows. Helium gas is compressed in the heavy-walled container, A, and cooled to the temperature of solid hydrogen (about 12 K). The container is then thermally isolated by means of an evacuated space. The cold high-pressure helium gas is then allowed to discharge through a small-bore tube to a low-pressure (1 atm) space outside the cryostat. In so doing, the helium gas in the container does work, thereby reducing its temperature, with the result that a considerable portion of the helium may remain in the container as a liquid.

process is the major factor governing the length of time available for experimentation in the range 4.2 K (normal boiling point of helium) and below. In the present apparatus, the main helium reservoir, A, has a volume of 101 cu cm and can be filled to about 70 percent of this value in a single expansion from a starting pressure of 2300 psi and a starting temperature of 11.5 K. This quantity of liquid helium provides about 2.5 hours for experimentation.

A helium gasometer-compressor cycle for compressing and purifying helium gas at 3000 psi has been constructed to provide the high-pressure helium gas used in the helium expansion process.

Experimental studies using the cryostat have been under way since April 1948. So far, magnetic studies utilizing the Meissner effect have been carried out on commercially available specimens of lanthanum, cerium, praseodymium, and neodymium metals down to 2 K, with a view to ascertaining if these metals exhibit the phenomenon of superconductivity. Only lanthanum has been observed to become superconducting (at about 4.8 K) down to 2 K, the lowest temperature reached in these studies. Further work is in progress.

Liquid Nitrogen Plant

To assure the laboratory an adequate supply of liquid nitrogen (or air), a large liquid oxygen plant, designed for military field use, has been installed and is now being converted to produce liquid nitrogen. The original plant had a capacity of 50 pounds of liquid oxygen per hour. The plant, operating at a top pressure of 300 psi, makes use of both the Joule-Thomson effect and a reciprocating expansion engine to produce the necessary refrigeration. The intake and exhaust conditions of the expansion engine are -101°C (-150°F) and 300 psi, and -168°C (-270°F) and 4 psi, respectively.

The liquid nitrogen distillation column needed has been built in the shops of the Engineering Experiment Station. It is designed to produce liquid nitrogen of 99.5 percent purity, utilizing the newest available data for packed columns. The packed section consists of four copper tubes, 4 inches in diameter and 26 inches long, arranged in parallel. Aluminum shoe eyelets are used as the packing material.

Other Facilities

The low temperature research program on the rare earth metals has necessitated the setting up of a chemical laboratory for the production and analysis of the rare earth materials. In this laboratory, chemical and spectrophotometric methods of analysis of these materials have been carried out, and new methods have been developed as needed. Research on the separation of the rare earths, by means of the new ion exchange techniques employing synthetic resins, is being carried out with a view to obtaining adequate materials of known high purity for use in the preparation of the pure metals.

Science and industry both require a continual flow of new and more accurate scientific data and information on substances and properties little explored. The Georgia Tech Low Temperature Laboratory was created specifically to play its part in this continued effort.

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APPENDIX C

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STATE ENGINEERING EXPERIMENT STATION
Atlanta, Georgia

TECHNICAL REPORT NO. 2

PROJECT NO. 116-18

CRYSTAL STRUCTURE AND SUPERCONDUCTIVITY OF LANTHANUM

By

W. T. ZIEGLER, A. L. FLOYD, JR., AND R. A. YOUNG

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NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH
CONTRACT NO. N6-ori-192, TASK ORDER I
NR 016-406

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MARCH 2, 1950

Georgia Institute of Technology
STATE ENGINEERING EXPERIMENT STATION
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SUMMARY

The data and conclusions included in this report are presented in the form of a paper which will be presented at the ONR sponsored Cryogenics Conference to be held at the Georgia Institute of Technology, Atlanta, Georgia, March 20 and 21, 1950. The paper is divided into two parts. Part I deals with the crystal structure of lanthanum; Part II deals with the superconductivity of lanthanum. These parts are summarized below.

The Crystal Structure of Lanthanum

The reported occurrence of hexagonal close-packed and face-centered cubic structures for lanthanum has been confirmed for this element in the form of filings. It has been shown that the f.c.c. modification is probably not a surface phenomenon and that the rate of transition of filings from the f.c.c. to the h.c.p. structure is very slow at room temperature.

Efforts to prepare bulk lanthanum specimens known to be in the f.c.c. structure, using the same procedures found satisfactory for filings, appear to have failed. This failure could arise from the fact that either (1) the mechanical strains introduced in the filing operation convert the filings to the h.c.p. structure or (2) the rate of transition from f.c.c. to h.c.p. structure on cooling to room temperature in the furnace used is very much more rapid in the bulk specimen than in the filings. The experiments carried out in this research have not served to differentiate between these two possibilities.

There seems to be no published work in which the crystal structure of a bulk specimen of lanthanum has been determined in an unambiguous manner.

The Superconductivity of Lanthanum

Four different samples of lanthanum metal have been examined for superconductivity, both in the as-received state and after heat treatment at 350° C for four days. X-ray examination of filings taken from all four samples, both before and after heat treatment, showed that the filings had the hexagonal close-packed structure. It was found that bulk specimens cut from the four samples exhibited a transition into superconductivity at 5.05 (Cooper No. 1), 5.25 (Spedding), 4.6 (Hilger), and 3.2° K (Cooper No. 2), respectively, before heat treatment, whereas after heat treatment the transition temperature was 5.2, 5.25, 5.45, and 3.2° K, respectively. Filings taken from one of the samples (Cooper No. 1) in the as-received state were found to exhibit a transition into superconductivity at 5.2° K after heat treatment for four days at 350° C. X-ray examination of the filings both before and after the low temperature experiment showed that they have primarily the face-centered cubic structure, with only a small amount of hexagonal close-packed structure being present.

On the basis of these experiments, it has been tentatively concluded that both the hexagonal close-packed and face-centered cubic modifications of lanthanum exhibit superconductivity at about 5.2° K.

THE CRYSTAL STRUCTURE AND SUPERCONDUCTIVITY OF LANTHANUM*

W. T. Ziegler, A. L. Floyd, Jr.** and R. A. Young

INTRODUCTION

The relation between crystal structure and superconductivity in allotropic modifications of the elements has been investigated only for tin. It has been found that while white tin is a typical superconductor, gray tin,^a which differs from it in crystal structure, does not become superconducting down to the lowest temperature tried (1.32°K).¹ Gray tin (the low temperature form) has a diamond crystal structure; white tin has a complex tetragonal structure. These two forms of tin also differ quite markedly in other physical properties.

A search for other elements having allotropic modifications which might be studied for superconductivity revealed that lanthanum, cerium, and praseodymium (see Table I) exhibit both the cubic close-packed (f.c.c.) and hexagonal close-packed (h.c.p.) structures. These structures, which are typical of many superconducting elements, have the advantage of being simple, making theoretical analysis easier. A beginning

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* Part of the work described in this paper has been taken from a Master's Thesis in Physics by Mr. A. L. Floyd, Jr. entitled "Effect of Temperature on the Crystal Structure of Lanthanum, Cerium, Neodymium, and Praseodymium. The Relation Between Crystal Structure and Superconductivity," Georgia Institute of Technology, Atlanta, 1949.

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a) Gray tin is converted into white tin at 292°K .

in the theoretical analysis has been made by Born and Cheng.³

TABLE I

CRYSTAL STRUCTURE OF LANTHANUM, CERIUM, AND PRASEODYMIUM²

Form	Structure	$\frac{a}{\text{\AA}}$	$\frac{c}{\text{\AA}}$	Atomic Radius $\frac{\text{\AA}}{\text{\AA}}$
α -La	h.c.p.	3.754	6.063	1.870
β -La	f.c.c.	5.294		1.872
α -Ce	h.c.p.	3.65	5.96	1.81
β -Ce	f.c.c.	5.140		1.817
α -Pr*	h.c.p.	3.657	5.924	1.824
β -Pr	f.c.c.	5.151		1.821

* α -Pr is distorted somewhat from true h.c.p.

A survey of the literature made at the time the present work was undertaken indicated that only lanthanum and cerium had been studied for superconductivity. No data were reported concerning crystal structure of the materials investigated.²

The present paper is a report of work carried out to examine the relation between the crystal structure and superconductivity of lanthanum. This metal was chosen because of its availability from several sources in reasonably pure form, and because it seemed to give promise of ready conversion from h.c.p. to the f.c.c. form. Consideration of the studies reported here is divided into two parts. Part I deals with the

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- a) Born and Cheng (Ref. 3) list both α -La and β -La as superconductors. Private correspondence with these investigators indicated that these facts were inferred from the structures known for lanthanum, rather than from superconductivity measurements made on lanthanum specimens of known structure.

crystal structure studies on lanthanum and with attempts to produce the f.c.c. form. Part II deals with superconductivity studies carried out on several samples of lanthanum before and after heat treatment.

PART I

THE CRYSTAL STRUCTURE OF LANTHANUM

The determination of the crystal structure of lanthanum by X-ray powder diffraction techniques has been the subject of a number of researches. These researches have shown that lanthanum exists in both the hexagonal close-packed (h.c.p.) and the face-centered cubic (f.c.c.) structures. The temperature of the thermodynamic transition point has not been determined.

Measurements of heat capacity,⁴ electrical resistance,⁴ density,⁵ and magnetic susceptibility⁶ as a function of temperature have revealed anomalies in these properties in several temperature regions. These anomalies suggest that lanthanum may exist in more than two allotropic modifications.

In the present work, a study of the hexagonal close-packed and face-centered cubic modifications of lanthanum has been made using the powder X-ray diffraction method. The effect of various heat treatment conditions on the rate of transition from the hexagonal close-packed to the face-centered cubic structure has also been studied, as well as the rate of transition of the f.c.c. to the h.c.p. structure at room temperature and at liquid helium temperatures.

EXPERIMENTAL

X-ray Diffraction Studies

All but a few of the X-ray diffraction studies reported in this paper have been carried out on lanthanum metal in the form of filings. A General Electric XRD unit equipped with two cylindrical powder cameras was used in all experiments. All pictures were taken with oscillation through an angle of $\pm 10^\circ$. Copper K α radiation was used in all instances unless otherwise stated. A nickel filter, consisting of two sheets of nickel foil each 0.0004 inch thick, was placed over the end of the collimating tube to filter the copper radiation. The power expended across the X-ray tube was about 25 milliamperes at 30,000 volts. Exposure times usually were three hours.

A few diffraction pictures were taken using a molybdenum tube, because of the much smaller absorption coefficient of lanthanum for molybdenum radiation. A zirconium filter, made by spreading a mixture of zirconium oxychloride and beeswax uniformly over a piece of paper was used in these cases.

The samples for the X-ray studies were prepared by filing the bulk specimen of lanthanum under dry nitrogen gas. Care was taken to first remove any oxide coating. This operation was carried out in a dry box having a volume of about two cubic feet. Dry nitrogen was passed through the box at a rate of about 11 cubic feet per hour for at least 45 minutes before beginning the filing operation, and steady flow of nitrogen

was maintained throughout the filing operation and while filling the capillaries. While still in the dry box the filings so obtained were placed in pyrex glass capillaries having an outside diameter 0.6-0.8 mm. Upon removal from the dry box, the capillaries were immediately sealed in an oxygen-gas flame.

All line positions were measured visually to 0.1 mm. Uniform, sharply defined lines were read at their centers. Nonuniform lines were read at their centers of density.

A visual estimate of the density of the lines was made, and an intensity symbol was assigned to each line according to the following plan:

vs = very strong	f = faint
s = strong	vf = very faint
ms = medium strong	vvf = very, very faint (barely discernable)
m = medium	
mf = medium faint	(d) = diffuse

The strongest line on any given photograph was always designated as "very strong," and the intensities of the other lines were then assigned accordingly.

All results were calculated by taking the unresolved $K\alpha$ lines to have a wave length of 1.539 kx-units. Where resolution occurred, the wave length of the $K\alpha_1$ line was taken to be 1.537 kx-units.

Film corrections were applied to all lines on the basis of corrections obtained as an average of a series of photographs taken of capillaries containing pure KCl. This salt (C.P. grade) was heated to dull red heat for 15 minutes and cooled in a desiccator. The salt was then powdered with a

dry mortar and pestle in the dry box, and capillaries were prepared as described above. The a_0 value for KCl was taken to be 6.277 kx-units.

Since the only structures which were likely to be encountered belonged to the cubic or the hexagonal systems, it was possible to index the lines by graphical means.^{7, 8} This method was used in all studies described in this paper.

Description and Purity of Lanthanum Samples

Four different lanthanum samples from three different sources have been used in these studies. The crystal structure of these materials has been determined both in the as-received state and after a variety of different heat treatments.

Chemical and spectrographic analyses were carried out on three of the four samples. Silicon was determined by filtering off the insoluble matter remaining after a sample of the metal was treated with dilute hydrochloric acid.^a The residue was ignited to constant weight at about 800° C; the residue was assumed to be SiO_2 and the result reported as per cent silicon in the metal.

Iron was determined by reduction to the ferrous state with zinc in dilute sulfuric acid solution, followed by titration with potassium permanganate.

Lanthanum was determined by precipitation of the rare

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a) An acetylene-like odor was always noted when the metal was dissolved in acid.

earths present as oxalates at a pH of 3. The precipitate was removed and ignited to the oxide at 850° C. The oxide so obtained was taken to be pure La_2O_3 unless otherwise indicated.

Spectrographic analyses^a were carried out using the copper spark technique.⁹ These analyses were usually qualitative or semi-quantitative in nature. In certain instances, quantitative analyses were made by comparison with standards of known concentration.

1. Lanthanum (Cooper No. 1). This material (30 gm.) was obtained (4/9/47) from the Cooper Metallurgical Laboratory, Division, Acme Aluminum Alloys, Inc. (now Cooper Metallurgical Associates), Cleveland, Ohio. Spectrographic analysis showed that the chief impurities were iron, silicon, and yttrium. In addition, it contained small amounts (estimated to be less than 0.1 per cent each) of many of the rare earths and other elements, including calcium, magnesium, and aluminum. Spectrophotometric analysis of a solution of the metal as chloride by means of a Beckman Model DU quartz spectrophotometer failed to reveal any absorption bands for other rare earths in the range 380 to 1000 m μ . Chemical analysis by the methods described showed the metal to contain 97.1% La, 0.8% Fe, and 0.7% Si.

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a) The spectrographic analyses were carried out by Dr. W. M. Spicer of the School of Chemistry.

2. Lanthanum (Hilger). This material (0.85 gm.) was obtained (7/10/47) from Adam Hilger, Ltd., London, England. This sample, designated by them as Lab. No. 7259, was reported to contain a total of 0.5-1.0% of aluminum, silicon, and tungsten, and to be substantially free of other rare earths. No analysis of this material was made here.
3. Lanthanum (Cooper No. 2). This material (30 gm.) was obtained (6/30/49) from Cooper Metallurgical Associates, Cleveland, Ohio. Comparison of the copper spark spectrum of this samples with that obtained for Cooper No. 1 on the same film showed that the chief difference between the samples was that Cooper No. 2 contained less yttrium and more cerium than Cooper No. 1.
4. Lanthanum (Spedding). This material (7.3 gm.) was obtained (1/2/50) from Dr. F. H. Spedding, Institute for Atomic Research, Iowa State College, Ames, Iowa, to whom we wish to express our thanks for making this material available. Spectrographic analysis showed that it contained 0.13% Be, 0.1% Mg, and traces (estimated to be a few hundredths of a per cent) of calcium, aluminum, and iron. The sample appeared to be free of other rare earths. The lanthanum content was found to be 97.3 per cent by direct precipitation as oxalate.

EXPERIMENTAL RESULTS

Crystal Structure of Lanthanum

A. Hexagonal Close-Packed Lanthanum

Lanthanum has been reported to exhibit the hexagonal close-packed structure at room temperature by McLennan and McKay,¹⁰ Quill,¹¹ and Rossi.¹² The purity and past history of the specimens investigated were not stated. The crystal parameters obtained by these investigators are given in Table II, together with the results obtained here.

Zintl and Neumayr¹³ have examined filings taken from a sample of lanthanum containing 99.6 per cent lanthanum, the remainder consisting of silicon, aluminum, magnesium, and carbon. They found primarily lines for the h.c.p. structure. However, the lines obtained were so diffuse that no exact measurements could be made.

Filings taken from our four lanthanum specimens in the manner described above showed that all of the specimens in the "as received" condition had the h.c.p. structure. Lines obtained were somewhat diffuse. Actual results agreed reasonably well with those reported by other investigators.

Table III contains a summary of the actual data. These data represent the average of five films, two taken of filings from lanthanum (Cooper No. 1) and three from lanthanum (Cooper No. 2). No systematic differences were noted in the films for the two samples. Detailed comparison of the results given in Table III with those reported by Quill¹¹ shows very good agreement

TABLE II
CRYSTAL PARAMETERS OF H.C.P. LANTHANUM

Observer	$\frac{a}{\text{KX-units}}$	$\frac{c}{\text{KX-units}}$	$\frac{c}{a}$
McLennan and McKay ¹⁰	3.72	6.06	1.63
Quill ¹¹	3.754+0.010	6.061+0.030	1.613
Rossi ¹²	3.757	6.05	1.61
This research	3.74+0.01	6.06+0.02	1.62+0.01

TABLE III
X-RAY DIFFRACTION DATA FOR H.C.P. LANTHANUM

Quill ¹¹	Intensity This re- search	Times line occurred in 5 films	Corrected θ deg.	hkl	$\frac{a}{\text{KX-units}}$
m	mf	5	13.69	100	3.752
vs	vs	5	14.69	002	3.744)
s	m	5	15.64	101	c = 6.068) 3.736
	f	4	22.69	Not identified	
s	s	5	24.25	110	3.748
	vvf	1	25.08	Not identified	
s	m	5	26.76	103	3.729
	f	1	28.31	(200)	(3.748)
vs	vs	5	28.91	112	3.741)
					c = 6.056)
s	ms	5	30.54	004	3.738
f	f	5	37.55	203	3.738
f	f	4	39.79	121	3.747
vs	s	5	40.78	114	3.743
f	vf	2	42.77	105	3.734
				122	
m	mf	4	45.12	300	3.762
f	f	3	47.20	123	3.747
f	f	4	49.15	302	3.740
m	f	3	53.81	124	3.745
				303	

in the relative intensities of the lines. The "a" values were calculated using the c/a ratio obtained from the average "c" and "a" values for the 002, 004, 100, 110, 200, and 300 planes.

In one experiment a capillary containing filings taken from lanthanum (Cooper No. 1) in the "as-received" condition was cooled to liquid helium temperatures and then allowed to warm up again to room temperature. The filings were observed to have h.c.p. structure both before and after cooling.

B. Face-Centered Cubic Lanthanum

The stable structure for lanthanum at room temperature apparently is the hexagonal close-packed structure, the face-centered cubic modification being formed at elevated temperatures.

Zintl and Neumayr¹³ were able to convert finely divided lanthanum from the h.c.p. to the f.c.c. structure by heating in vacuum at 350° C for several days. Klemm and Bommer,² using liquid potassium and cesium, reduced the anhydrous chloride at 350-400° C and obtained finely divided lanthanum having the f.c.c. structure. Klemm and Bommer compared their results with those obtained from preparations made by treating finely divided lanthanum (obtained from bulk lanthanum) with potassium, rubidium, and cesium metals. No differences were observed. The results found by these investigators are given in Table IV.

We have also been able to prepare the f.c.c. modification by heating lanthanum filings at 350 to 400° C for several days.

Sealed pyrex capillaries containing filings of the lanthanum sample known to be in the h.c.p. structure were heated in a vacuum furnace for about four days. Upon removing the capillaries and examining them, the lanthanum was found to have been converted to the f.c.c. structure. The diffraction lines were now quite sharp, as contrasted with the relatively diffuse lines always found by us for the h.c.p. structure. In most films, several faint lines assignable to the h.c.p. were found, indicating that a small amount of the h.c.p. structure was also present. All four lanthanum samples were found to undergo this transition under similar heat treatment.

The value for a_0 obtained in this work is compared with the results of previous investigators in Table IV.

TABLE IV
FACE-CENTERED CUBIC LANTHANUM

Observer*	a_0 kx-units
Zintl and Neumayr ¹³	5.296±0.002
Klemm and Bommer ²	5.294±0.002
This research	5.285±0.005

* Copper K α radiation used in all studies.

Our value for a_0 given in Table IV is an average result obtained from nine films taken of the two Cooper and the Hilger lanthanum samples.

Table V contains a summary of the actual data. The intensities reported by Zintl and Neumayr¹³ are given for

comparison. The intensities found here agree quite well with those reported by Zintl and Neumayr¹³ and Klemm and Bommer.²

TABLE V

X-RAY DIFFRACTION DATA FOR F.C.C. LANTHANUM

Copper K α radiation; $\alpha = 1.539$ kx-units, $\alpha_1 = 1.537$ kx-units

<u>Zintl and Neumayr¹³</u>	<u>Intensity This re- search</u>	<u>Corrected θ deg.</u>	<u>hkl</u>	<u>a_0 kx-units</u>
s	vs	14.65	111	5.271
m	s	16.96	200	5.276
ms	s	24.33	220	5.275
s	vs	28.91	113	5.280
f	m	30.34	222	5.276
vf	mf	35.68	400	5.276
mf	s	39.43	133	5.283
mf	ms	40.66	240	5.282
f	m	45.52	422	5.281
m	ms	49.11*	511) 333)	5.285
vf	mf	55.40	440	5.289
m	vs	59.35*	135	5.285
f	ms	60.74*	600) 244)	5.285
	ms	66.84*	260	5.287
	ms	72.41*	533	5.287
	ms	74.60*	226	5.287

*These lines refer to $K\alpha_1$; all others refer to $K\alpha$.

Thermodynamic Transition Temperature for the System: Hexagonal Close-Packed--Face-Centered Cubic Lanthanum

The experiments of Zintl and Neumayr, Klemm and Bommer, and our research as discussed in the previous section strongly suggest that the thermodynamic transition temperature of this transition is below 350° C. Trombe and Foex⁵ have studied the expansion of lanthanum (99.2% la) over the range -190° to 350° C. These investigators found that the expansion was linear

and uneventful between -190 and 150° C. Between 150° and 375° C, hysteresis developed, the volume at a given temperature depending upon whether the sample was being warmed or cooled. This hysteresis was attributed by Trombe and Foex to the coexistence of face-centered cubic and hexagonal close-packed lanthanum.

We have carried out experiments in which sealed capillaries containing filings from lanthanum (Cooper No. 1), known to be in the hexagonal close-packed structure, were heated for two days in a vacuum furnace at various fixed temperatures. After the heat treatment, the capillaries were again examined by X-ray diffraction and the extent of conversion to the face-centered cubic structure noted. Results obtained, summarized in Table VI, show that conversion to the face-centered cubic structure occurred even at 254° C. The hexagonal close-packed lines were still relatively more diffuse than the lines from face-centered cubic structure.

TABLE VI

CONVERSION OF LANTHANUM TO FACE-CENTERED CUBIC STRUCTURE

<u>Capillary</u>	<u>Temperature</u> $^{\circ}$ C	<u>Length of</u> <u>Heating Period</u> days	<u>Structure after</u> <u>Heat Treatment</u>
S-18	400	2	f.c.c., small amount h.c.p.
S-19	354	2	f.c.c., small amount h.c.p.
S-20	254	2	approx. 1/2 converted to f.c.c.

Another series of experiments was carried out to determine the rate of conversion of the face-centered cubic to the hexagonal close-packed structure at room temperature. Five sealed capillaries containing filings from the two Cooper and the Hilger lanthanum samples were heat treated (three at 350° C, two at 400° C) to convert them to the face-centered cubic structure. Examination of the capillaries immediately after heat treatment showed the filings to be primarily in the f.c.c. structure, with a small amount of h.c.p. structure present. The capillaries were reexamined at intervals over a period of 130 to 160 days to determine if any transition to the h.c.p. structure had taken place. At the end of this period the samples still had primarily the f.c.c. structure; the very weak lines due to the h.c.p. structure had not increased noticeably in intensity.

In a second series of experiments, capillaries containing filings known to be in the face-centered cubic structure were heated for five days at 100° C in a vacuum furnace, on the assumption that this treatment might introduce nuclei having the hexagonal close-packed structure. The capillaries were then repeatedly cooled and warmed^a between -195° C and room temperature by dipping in a liquid nitrogen bath. Examination of the capillaries showed that the structure was still face-centered cubic; no change in the diffraction patterns could be

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a) Trombe and Foex¹⁵ found this method satisfactory for converting cerium from the f.c.c. to the h.c.p. structure.

detected.

Heat Treatment of Bulk Lanthanum Specimens

The experimental studies described above, both by ourselves and others, pertain to the conversion of finely divided lanthanum from the h.c.p. to the f.c.c. structure. The ease with which lanthanum filings could be converted to the f.c.c. modification led us to assume that the bulk specimens needed for the superconductivity studies could easily be prepared by heat treatment in a furnace at 350 to 400° C for four days.

Bulk specimens cut from all four of the lanthanum samples mentioned earlier were heat treated under a variety of conditions. These bulk specimens were generally in the form of cylinders approximately 20 mm. long and having a diameter of about 4.5 mm. Conditions employed included (a) heating for four days at 350° C, (b) heating for four days at 400° C, and (c) heating for two days at 722° C. These heat treatments were carried out either under vacuum or under helium, to prevent oxidation. After cooling to room temperature, filings were obtained under dry nitrogen from all bulk specimens. Upon X-ray examination, in all instances these filings have proved to be entirely or almost entirely in the hexagonal close-packed structure.

These results were definitely contrary to expectations, in view of the ease of converting lanthanum filings to the f.c.c. structure. Several possibilities suggested themselves.

1. The strains set up in the operation of filing may

be sufficient to convert the filings taken from the bulk sample to the h.c.p. structure.

2. Insufficient time was allowed for the transition to occur.
3. The f.c.c. structure is a surface effect.
4. The f.c.c. structure observed in the filings is due to some compound of lanthanum and is not due to lanthanum metal.
5. The rate of transition from the f.c.c. to the h.c.p. structure in the bulk samples is such that essentially complete reconversion to the h.c.p. structure occurs during the 4-5 hours required for the furnace to cool to room temperature.

These possibilities will be discussed briefly in the above order.

One experiment was carried out in which a thin lanthanum chip, cut from lanthanum (Cooper No. 2) under dry nitrogen and having the dimensions 6 x 6 x 1 mm., was heat treated in a vacuum furnace for four days at 400° C. Filings taken from the chip after heat treatment proved to have the h.c.p. structure. The chip was then covered with a thin layer of oil to diminish oxidation, one edge of it placed in the X-ray beam, and a picture was taken with oscillation. The chip was found to consist primarily of the h.c.p. structure. Thus, there is some evidence that the filing operation may decrease the amount of f.c.c. structure.

The length of time required for the transition of filings at 350° C has been shown to be about two days. The fact that the chip was still primarily in the hexagonal close-packed structure after four days at 400° C could be interpreted to mean that the transition in bulk samples is indeed slow. On the other hand, filings taken from a cylindrical specimen 4.5 mm. in diameter and 15 mm. long, after the specimen had been heat treated at 722° C for two days, showed no conversion to f.c.c. structure.

As yet, we have not been able to devise an experiment which shows clearly the effect of the mechanical filing operation on the structure of the filings.

The possibility that the f.c.c. structure is a surface phenomenon has been suggested by Rossi.¹² He stated that after annealing bulk lanthanum specimens^a at 350° C in vacuum for several days, the f.c.c. phase was obtained. However, after removing a very thin outer layer from the annealed specimens the latter then gave again the characteristic h.c.p. structure.

In order to throw some light on this possibility, heat treated lanthanum filings which were determined to be in the f.c.c. modification by using copper K α radiation, were examined by means of molybdenum K α radiation. Since the absorption coefficient of lanthanum for molybdenum radiation is only 1/8

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a) The work of Rossi is the only published investigation known to us in which the structure of annealed bulk specimens of lanthanum is considered.

that for copper radiation, the thickness of the scattering layer being examined should be considerably greater. However, the diffraction pattern obtained with molybdenum radiation was also that for the f.c.c. modification. From a consideration of the particle size of the filings (maximum diameter about 0.005 mm.) and the absorption coefficient for molybdenum radiation, it was concluded that the major fraction of each particle was being examined. The a_0 found for the f.c.c. structure using molybdenum was 5.293 ± 0.005 kx-units.

The possibility that the f.c.c. structure observed in annealed filings might be due to some surface chemical reaction was also considered. The most likely compound seemed to us to be LaN , which also has the f.c.c. structure, with an a_0 of 5.275 inches. However, the X-ray diffraction pattern of the filings was found to be independent of whether the filings were prepared and heat treated in an atmosphere of nitrogen or helium. Furthermore, the intensities of the lines found do not agree with those reported¹⁴ for lanthanum nitride.

The possibility that the rate of transition from the f.c.c. to the h.c.p. structure in the bulk is sufficiently rapid that it occurs during cooling of the specimens in the furnace cannot at present be excluded, and will require further investigation. The observed very slow rate of transition of the filings cooled under identical conditions would seem to oppose this possibility. However, the dilatometric experiments of Trombe and Foex⁵ clearly indicate that an anomalous volume change, presumed by them

to be due to this structure transition, does occur in bulk lanthanum in the range 150 to 375° C. Unfortunately, Trombe and Foex give no information as to the rate conditions under which these measurements were made.

SUMMARY

The reported occurrence of hexagonal close-packed and face-centered cubic structures for lanthanum has been confirmed for this element in the form of filings. It has been shown that the f.c.c. modification is probably not a surface phenomenon, and that the rate of transition of filings from the f.c.c. to the h.c.p. structure is very slow at room temperature.

Efforts to prepare bulk lanthanum specimens known to be in the f.c.c. structure, using the same procedures found satisfactory for filings, appear to have failed. This failure could arise from the fact that either (1) the mechanical strains introduced in the filing operation convert the filings to the h.c.p. structure or (2) the rate of transition from f.c.c. to h.c.p. structure on cooling to room temperature in the furnace used is very much more rapid in the bulk specimen than in the filings. The experiments carried out in this research have not served to differentiate between these two possibilities.

There seems to be no published work in which the crystal structure of a bulk specimen of lanthanum has been determined in an unambiguous manner.

PART II

THE SUPERCONDUCTIVITY OF LANTHANUM

The occurrence of superconductivity in lanthanum has previously been studied by Mendelssohn and Daunt,¹⁶ using a magnetic method. These investigators reported a transition temperature of 4.71° K for a sample reported to contain 98% La, 1% Fe, and traces of C, Si, Al, and Mg. Shoenberg,¹⁷ also using a magnetic method, has reported that a lanthanum specimen (Hilger, Lab. No. 7259), presumably identical with our Hilger lanthanum specimen, was superconducting at 4.2° K. On the other hand, McLennan, Allen and Wilhelm¹⁸ measured the electrical conductivity of a "pure" specimen of lanthanum from 300 to 1.9° K and reported that the specimen did not become superconducting.

A report of some measurements on our Cooper (No. 1) and Hilger lanthanum specimens has already appeared,^{19, 20} in which the occurrence of superconductivity at 4.85 ± 0.15 and $4.45 \pm 0.10^{\circ}$ K, respectively, was noted. Measurements here have since been extended to include two additional samples. It is the purpose of this portion of this paper to summarize the results of tests for superconductivity carried out to date on all four samples of lanthanum.

EXPERIMENTAL

The Cryostat

The helium cryostat used in these measurements has been described elsewhere.²⁰ It differed only in detail from one described by Horn and Ziegler.²¹ Liquid helium was produced

within the cryostat in two separate chambers, the upper of which served as a thermal dam for the experimental chamber which was suspended from it. The main charge of liquid helium was produced in the thermal dam by the Simon expansion method, and in the experimental chamber by condensation.

The all-copper experimental chamber (Figure 1A) consisted of two parts, an upper section to which the resistance and gas thermometers were attached and a lower section in which the specimens to be tested for superconductivity were placed.

The temperature of the experimental chamber was measured by means of a gas thermometer of the type described by Mendelssohn²² and a constantan resistance thermometer. The gas thermometer was filled with helium at one atmosphere pressure while at room temperature and then sealed off. This gas thermometer had a sensitivity of about 0.04° in the range 3 to 5.5° K. Below about 3° K the gas thermometer acted as a vapor pressure thermometer. Gas imperfection was taken into account by utilizing P-V-T data from which the compressibility factor, $C (= PV/RT)$, was either calculated or estimated.²³

The resistance thermometer, constructed of B and S No. 40 constantan wire, had a resistance of 1069 ohms at 4° K and a dR/dT of 0.92 ohm per degree. This thermometer was useful in following the course of the superconducting transition. It had a sensitivity of 0.02° .

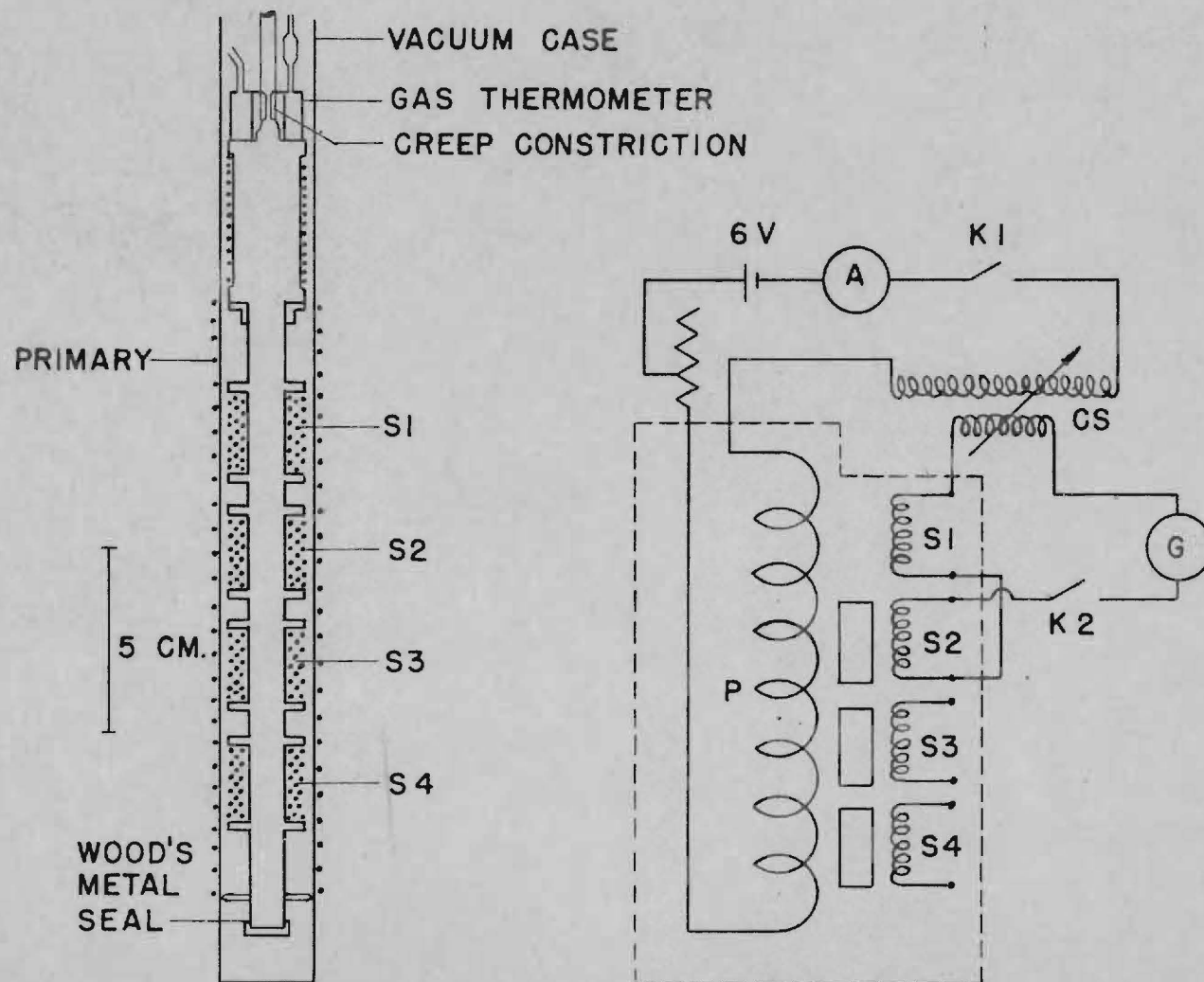
Magnetic Method of Detecting Superconductivity

Superconductivity was detected in the specimens under investigation by observing the change in induction of a coil

containing the specimen as the temperature of the samples was changed. The details of the experimental arrangement are shown in Figure 1A. The system for making the magnetic measurements consisted of a primary coil, wound upon the lower end of the vacuum case, and four equally spaced secondary coils S1, S2, S3, and S4, wound on the outside of the experimental chamber, and co-axial with the primary coil.

In order to prevent air oxidation, each specimen was sealed at room temperature in a small capsule, made of 7 mm. o.d. pyrex glass, under helium gas at about 10 cm. Hg pressure. The capsules were separated by Lucite spacers, and the entire assembly was held together with cellulose acetate cement. The assembly was then slipped into the experimental chamber and the chamber closed with a cap sealed on by Wood's metal. The spacers were so constructed that each specimen was positioned approximately at the center of its secondary coil.

The circuits for detecting superconductivity are shown in Figure 1B. In all experiments, Coil S1 (a compensating coil) was always empty, the specimens under test being located in Coils S2, S3, and S4. The experimental procedure was as follows. With the experimental chamber at a fixed temperature, Coil S1 and another coil, for example Coil S2, were connected by means of a suitable external switching arrangement in such a manner that the voltages induced in them opposed each other when the tap key, K1, in the primary circuit was closed. With the tap key K2 closed, the galvanometer usually showed a deflection



A. EXPERIMENTAL CHAMBER

B. SUPERCONDUCTIVITY
DETECTION CIRCUITS

FIGURE 1. MAGNETIC MEASUREMENTS SYSTEM

when the primary was energized, because of an unbalance between S1 and S2. This unbalance could be reduced to zero by suitably adjusting a variable external compensating coil, CS. With the circuit balanced and K2 closed, K1 was tapped at about 10-15 second intervals during a series of measurements in which the temperature of the experimental chamber was slowly lowered (or raised), and any unbalancing of the coils was observed as a galvanometer deflection.

In passing from room temperature to a temperature just above the transition, a single setting of CS usually sufficed, the observed unbalance corresponding to a few mm. deflection of the galvanometer. The transition of a specimen from the normal to the superconducting state was recognized by the appearance of a considerable galvanometer deflection. In our experiments, deflections of from three to seven centimeters were observed, depending upon the size of the sample being studied and the magnitude of the current in the primary circuit. For instance, a deflection of 5 cm. was obtained, using a primary current of 260 milliamperes, when a specimen of lanthanum (La 2, Run No. 12) underwent a transition from the normal to the superconducting state.

In a given experiment, time-temperature and time-galvanometer deflection measurements were made, from which galvanometer deflection vs. temperature data were obtained. Such measurements were made both on warming and cooling through the transition.

Measurements were made on warming by allowing the experimental chamber to warm up due to heat leak. This heat leak was

due primarily to the copper lead wires to the experimental chamber which were in imperfect contact with the thermal dam.

Cooling was usually achieved in the range 6 to 4.2° K by allowing the pressure of the helium in the experimental chamber to decrease slowly. The decrease in the helium pressure was controlled by an external needle valve in the filling line. Temperature below 4.2° K were, of course, obtained by pumping on the helium in the experimental chamber. The lowest temperature reached in these studies was about 2° K.

The manipulative procedure for controlled warming or cooling depended considerably on the amount and pressure of the helium in the experimental chamber. Warming and cooling rates of 0.1 to 0.2° per minute were usually observed.

SUPERCONDUCTIVITY STUDIES

Tests for superconductivity have been carried out on specimens taken from all four lanthanum samples described in Part I of this report. These studies have been made both on specimens in the "as-received" state and after heat treatment of the specimen under a variety of conditions. Tables VII through XI summarize the experimental results obtained, and Table XII gives a condensed summary of the results. In these tables, the transition range, ΔT , corresponds to the temperature change in which at least 90 per cent of the total galvanometer deflection occurred. The transition temperature given corresponds to the temperature at which one half of the total deflection was noted. In general, the midpoint of the transition

has been computed from the gas thermometer reading. The transition range, as well as warming and cooling rates, however, have been computed from the resistance thermometer by the relation $\Delta T = 1.10 (\Delta R)$, where the constant 1.10 expresses the relation between the gas thermometer and resistance thermometer.

When a specimen underwent a transition, the change in galvanometer deflection observed ranged from 12 to 50 mm., with a primary current of 260 milliamperes, depending upon the size of the specimen. Readings of this deflection were reproducible to about 1 mm. when the specimen was maintained at a fixed temperature.

The galvanometer deflection vs. temperature data obtained for the majority of the transitions listed in Tables VII through XI have been plotted in Figures 2 through 10. In a number of instances, the transition curve found on cooling lay about 0.1° degree below that found for warming (see Figures 5, 6, and 9). This difference is about twice the estimated detectable difference. In other instances (Figures 2, 4, and 7), no consistent difference was noted. It is not clear whether these differences represent an actual hysteresis in the transition or only a temperature inequality. However, on the basis of the rapidity of response of the specimen to temperature variation when in the transition, it is believed that much of this difference represents a temperature gradient along the experimental chamber itself.

In general, transition ranges of 0.1 to 0.3° were observed,

TABLE VII

SUPERCONDUCTIVITY OF LANTHANUM (COOPER NO. 1)

Run	Coil Used	Series	Warming	Cooling	Transition	Midpoint of Transition		
			Rate	Rate	Range, ΔT	Gas Therm.	R. Therm.	
			deg./min.	deg./min.	deg.	mm. Hg	°K	ohms
A.	Specimen La 1, as-received condition; cylinder 19 mm. x 4. ^b mm.							
4	S4		0.15		0.11	129	5.0	1070.01
	Specimen La 2, as-received condition; cylinder 20.3 mm. x 4.8 mm.							
5	S4			0.2	0.2	127.5	5.1	1070.0
6	S3		0.2		0.2	128	5.1	
10	S4	I		0.05	0.08	127.5	5.04	1070.05 ^b
		II	0.11		0.16	128	5.06	1070.13
12	S2	I	0.10		0.12	134 ^c	5.02	1070.25 ^d
		II	0.11		0.12	134	5.02	1070.25
		III	0.21		0.15	135	5.05	1070.26
		IV		0.10	a	134.5	5.07	1070.20
B.	Specimen La 1, after heat treatment for 4 days at 350° C							
9	S4		0.15		0.10	132	5.22	1070.41 ^e
			0.16		0.12	132	5.22	1070.38
			0.16		0.12			1070.39

a) Complete transition not covered.

b) Helium boiling point = 4.19° K, R = 1069.24 ohms.

c) Gas thermometer refilled prior to Run No. 12.

d) Helium boiling point = 4.19° K, R = 1069.37 ohms.

e) Helium boiling point = 4.19° K, R = 1069.28 ohms.

TABLE VIII
SUPERCONDUCTIVITY OF LANTHANUM (COOPER NO. 2)

Run	Coil Used	Series	Warming	Cooling	Transition	Midpoint of Transition		
			Rate deg./min.	Rate deg./min.	Range, ΔT deg.	Gas Therm. mm. Hg	R. Therm. °K	ohms
A.	Specimen La 7, as-received condition; cylinder 11.4 mm. x 4.2 mm.							
12	S3	I		0.09	> 0.16	87 ^d	3.06	1068.15 ^b
		II	0.31		a	87	3.06	1068.24
		III		0.25	ca. 0.3	89	3.14	1068.21
B.	Specimen La 6, cylinder 12.3 mm. x 4.1 mm.; heat treated 4 days at 350° C							
11	S3	I		0.45	a	85	3.17	1068.03 ^c
		II	0.26		0.20	86	3.22	1068.19
		III		0.3	a	85	3.17	1068.03
		IV		0.21	0.20	84	3.12	1068.11
		V	0.26		a	86	3.22	1068.22

- a) Complete transition not covered.
b) Helium boiling point = 4.19° K, R = 1069.37 ohms.
c) Helium boiling point = 4.19° K, R = 1069.20 ohms.
d) Gas thermometer refilled prior to Run 12.

TABLE IX
SUPERCONDUCTIVITY OF LANTHANUM (SPEDDING SAMPLE)

Run	Coil Used	Series	Warming	Cooling	Transition	Midpoint of Transition		
			Rate deg./min.	Rate deg./min.	Range, Δ T deg.	Gas Therm. mm. Hg	$^{\circ}$ K	R. Therm. ohms
A. Specimen La 1S, as-received condition, cylinder 9.8 mm. x 4.4 mm.								
12	S4	I	0.16		$>0.17^a$	138.5	5.23	1070.43 ^b
		II	0.12		$>0.15^a$	138.5	5.23	1070.42
		III		0.22	0.25		5.15	1070.37
		IV	0.14		0.17	139	5.26	1070.42
		V		0.62	a			1070.33
		VI	0.20		$>0.13^a$	138.5	5.23	1070.41
		VII		0.16	$>0.16^a$	137.5	5.17	1070.35
B. Specimen La 2S, cylinder 9.9 mm. x 4.4 mm., heat treated 4 days at 350 $^{\circ}$ C								
13	S4	I	0.25		$>0.43^a$	139	5.26	1070.39 ^c
		II		0.25	$>0.49^a$	137.5	5.18	1070.33
		III	0.09		0.76	140.5	5.33	1070.38
		IV		0.19	0.88			1070.40
		V	0.15		0.64			1070.40
		VI		0.16	0.57			1070.34
a) Complete transition not covered.								
b) Helium boiling point = 4.19 $^{\circ}$ K, R = 1069.37 ohms.								
c) Helium boiling point = 4.20 $^{\circ}$ K, R = 1069.41 ohms.								

TABLE X

SUPERCONDUCTIVITY OF LANTHANUM (HILGER LAB. NO. 7259)

Run	Coil Used	Series	Warming	Cooling	Transition	Midpoint of Transition		
			Rate	Rate	Range, ΔT	Gas Therm.	R. Therm.	
			deg./min.	deg./min.	deg.	mm. Hg	OK	ohms
A.	Specimen La 3, as-received state; roughly rectangular piece $4 \times 11.5 \times 2.6$ mm.							
3	S4				ca. 0.1			4.6 ^a
B.	Specimen La 3, heat treated 4 days at 350° C							
9	S3	I	0.18		0.07	136	5.45	1070.63
		V	0.08		0.14	136	5.45	1070.68
		VI	0.09		0.13	137	5.51	1070.66 ^b

a) In this same Run Specimen La 2 showed transition at 4.9° K.

b) Helium boiling point = 4.19° K, R = 1069.29 ohms.

TABLE XI

SUPERCONDUCTIVITY OF LANTHANUM (COOPER NO. 1) POWDER^a

Run	Coil Used	Series	Warming	Cooling	Transition	Midpoint of Transition		
			Rate	Rate	Range, ΔT	Gas Therm.	R. Therm.	
			deg./min.	deg./min.	deg.	mm. Hg	$^{\circ}\text{K}$	ohms
A.	Specimen La ⁴ F, filings, occupying cylindrical volume 12 mm. x 5 mm.							
13	S3	I		0.17	0.33	108	3.90	1069.00 ^b
		II		0.15	0.27	108	3.90	
		III	0.10		0.30	107.5	3.88	1069.04
B.	Specimen La ⁴ F, filings, after heat treatment for 4 days at 350 ^o C							
14	S3	I		0.14	ca. 0.25	139.5	5.22	1070.37 ^d
		II		0.03	> 0.1 ^c	139	5.24	1070.38

a) Prepared from bulk lanthanum by filing under dry helium gas.

b) Helium boiling point = 4.20^o K, R = 1069.41 ohms.

c) Complete transition not covered.

d) Helium boiling point = 4.19^o K, R = 1069.37

TABLE XII

SUMMARY OF DATA ON SUPERCONDUCTING TRANSITION FOR VARIOUS LANTHANUM SAMPLES

<u>Sources of Lanthanum</u>	<u>Specimen Designation</u>	<u>As-received Condition</u>		<u>After Heat Treatment</u>	
		<u>Transition Temperature</u>	<u>Transition Range</u>	<u>Transition Temperature</u>	<u>Transition Range</u>
Cooper No. 1	La 2	5.05	0.15		
	La 1	5.0	0.1	5.2	0.1
	La 4F	3.9	0.3	5.25	0.3
Cooper No. 2	La 6			3.2	0.2
	La 7	3.1	0.3		
Spedding	La 1S	5.25	0.2		
	La 2S			5.3	0.6-0.8
Hilger	La 3	4.6	ca. 0.1	5.45	0.1

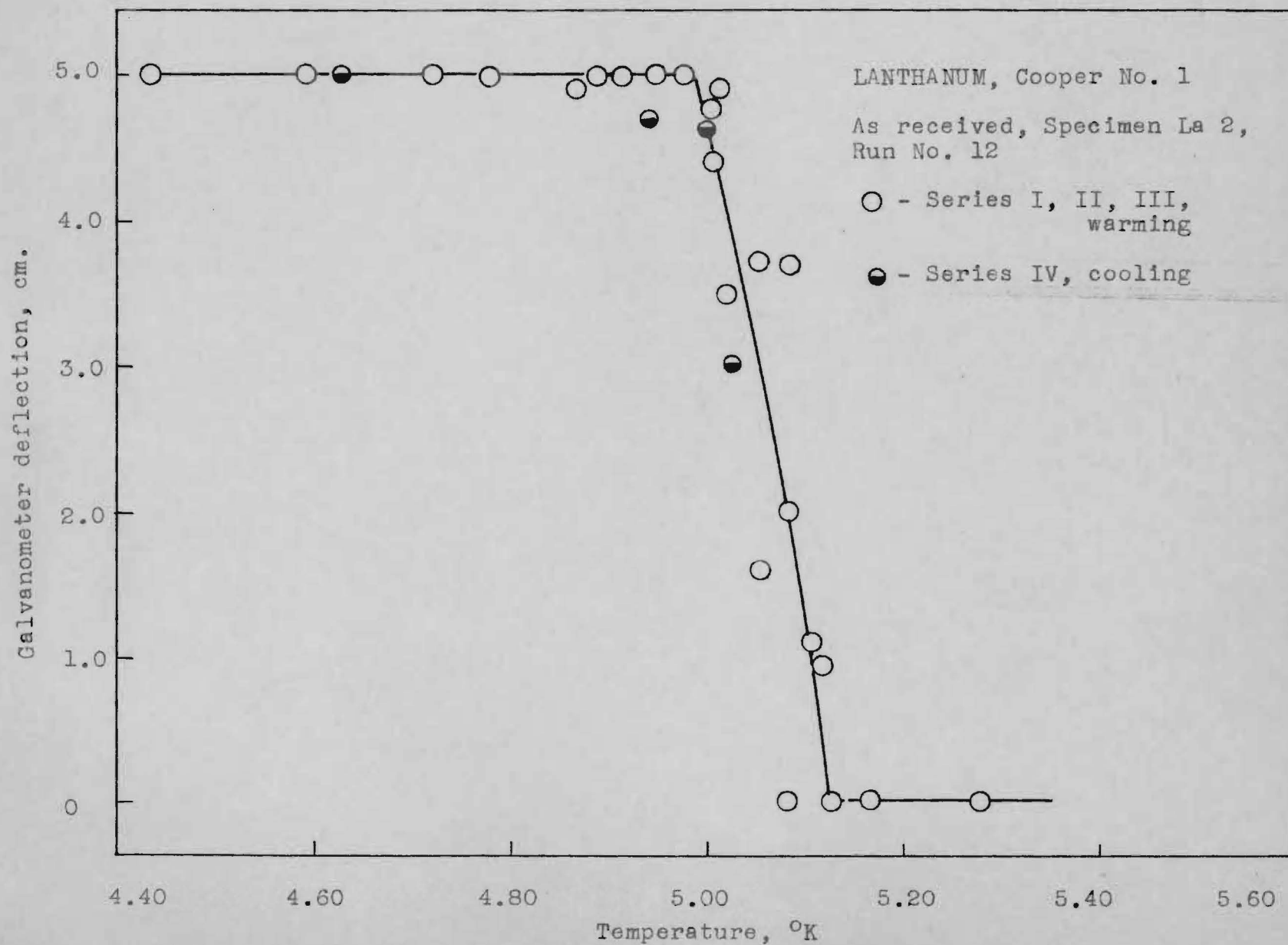


Figure 2. Superconducting Transition of Lanthanum

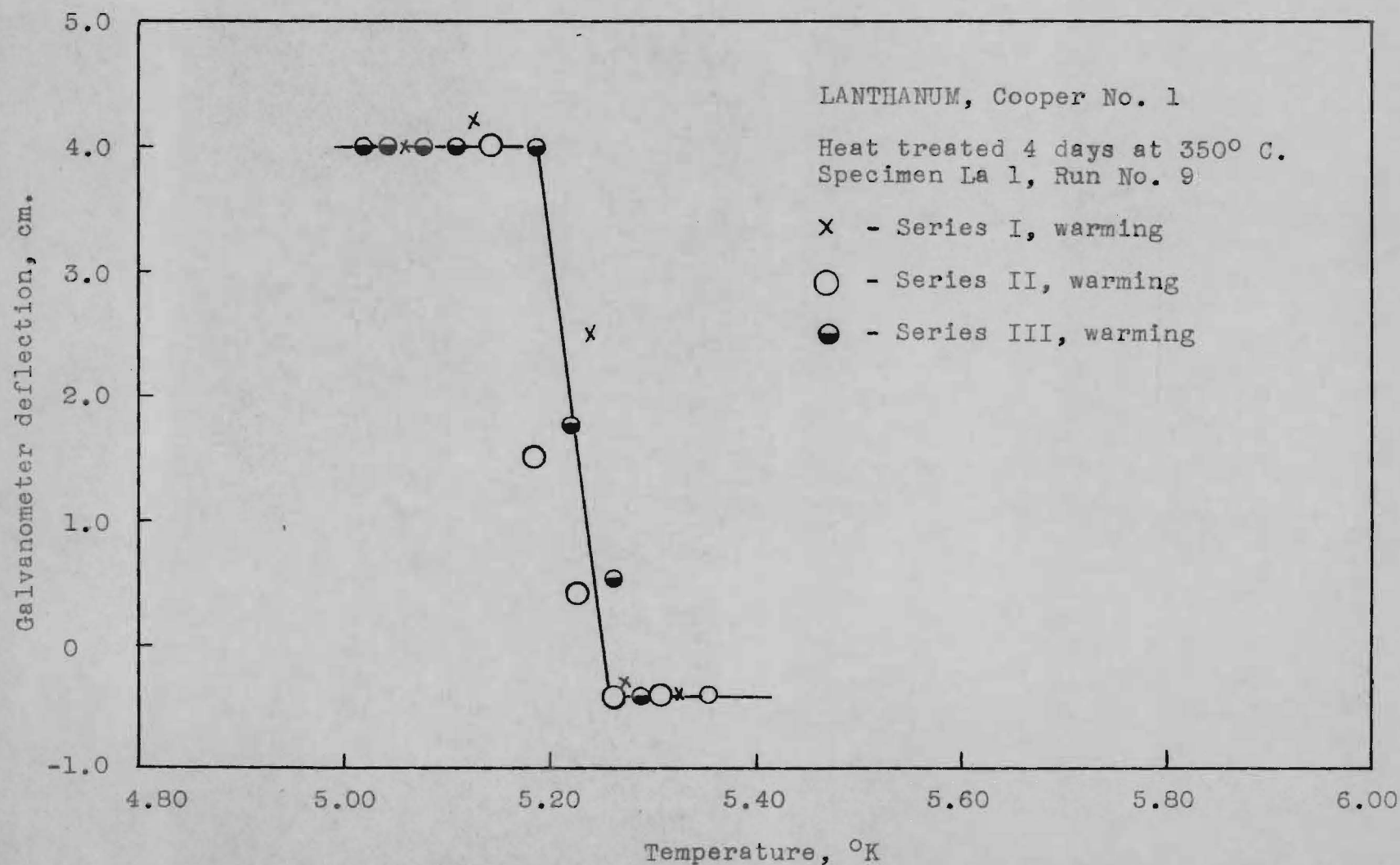


Figure 3. Superconducting Transition of Lanthanum

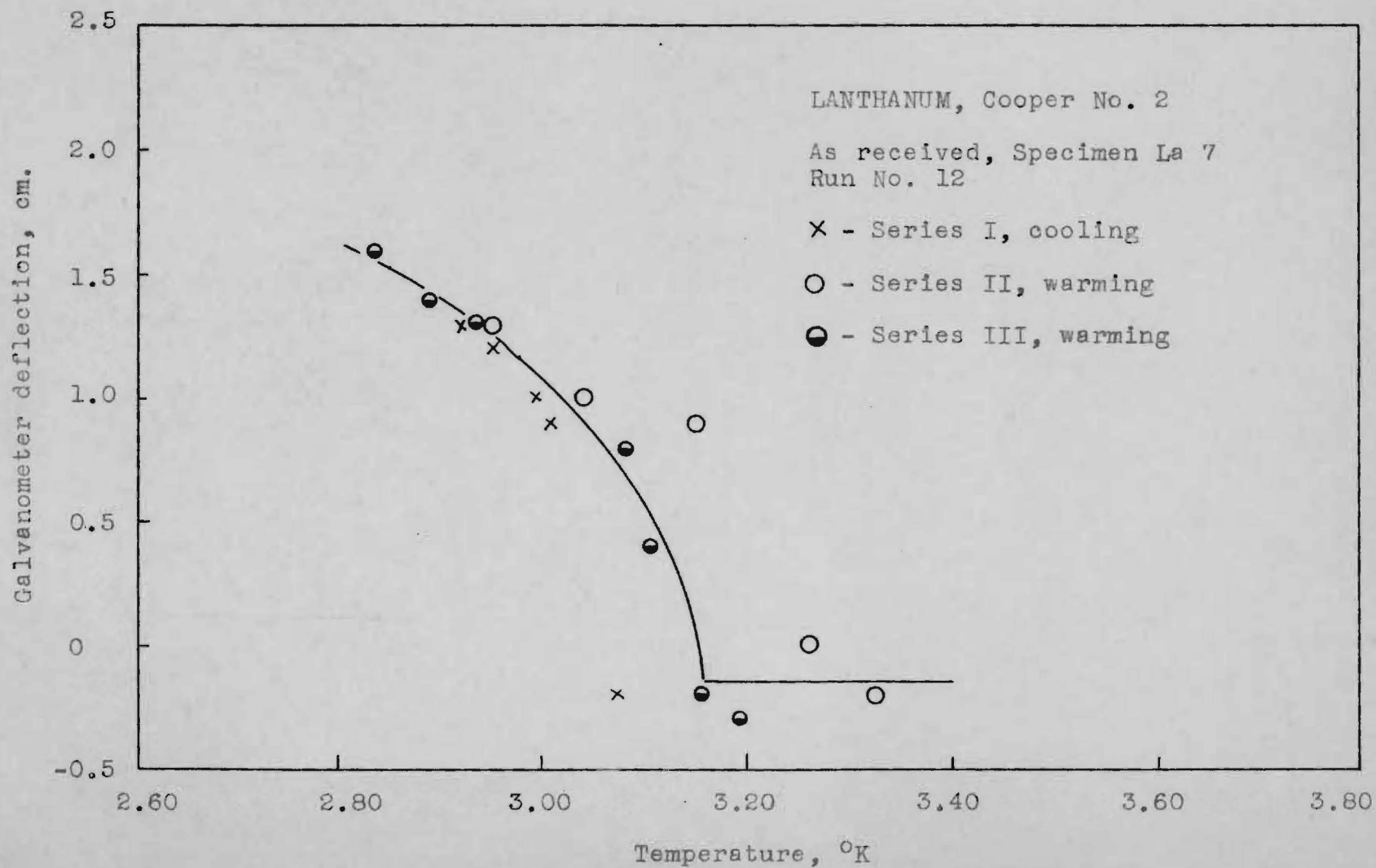


Figure 4. Superconducting Transition of Lanthanum

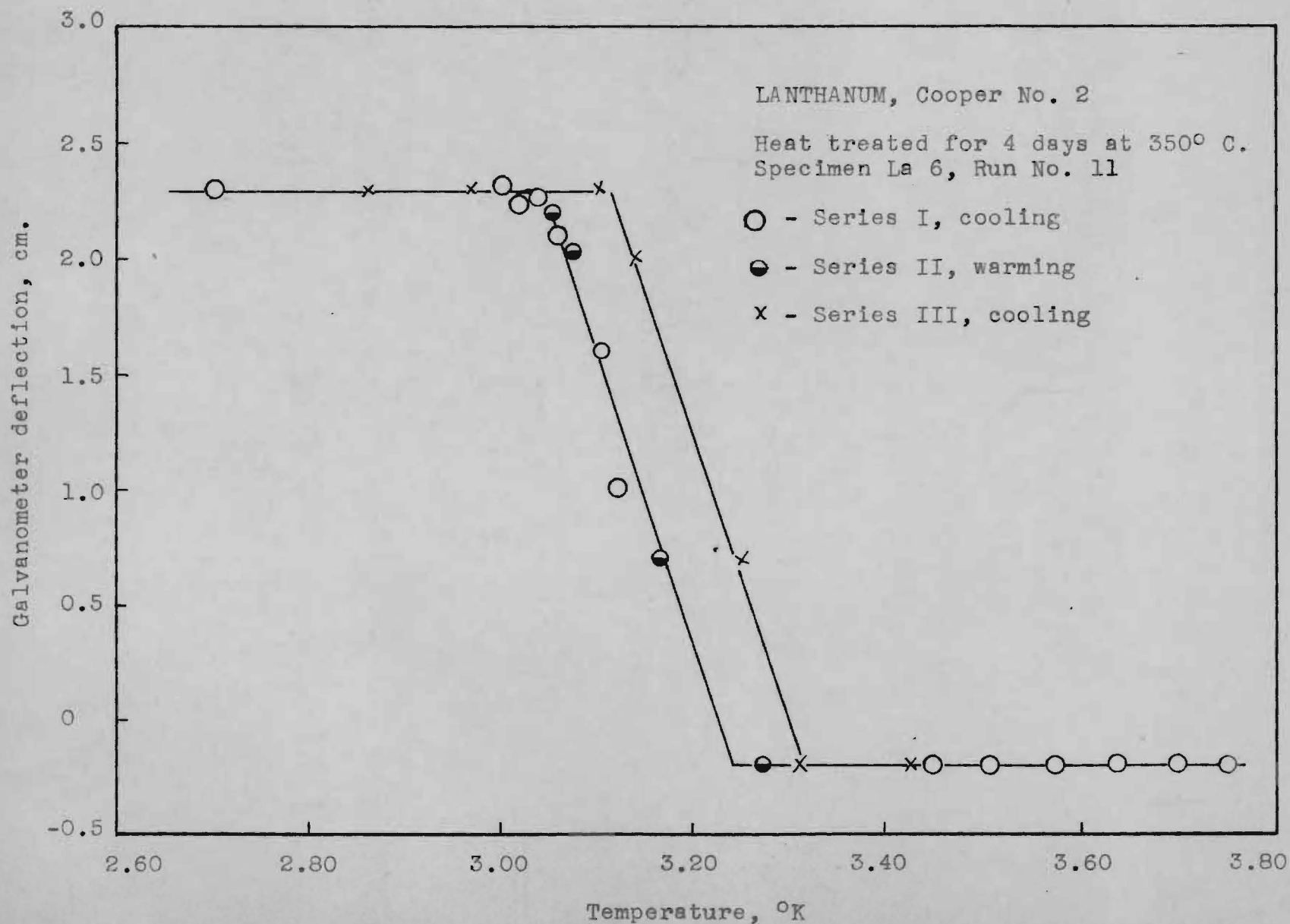


Figure 5. Superconducting Transition of Lanthanum

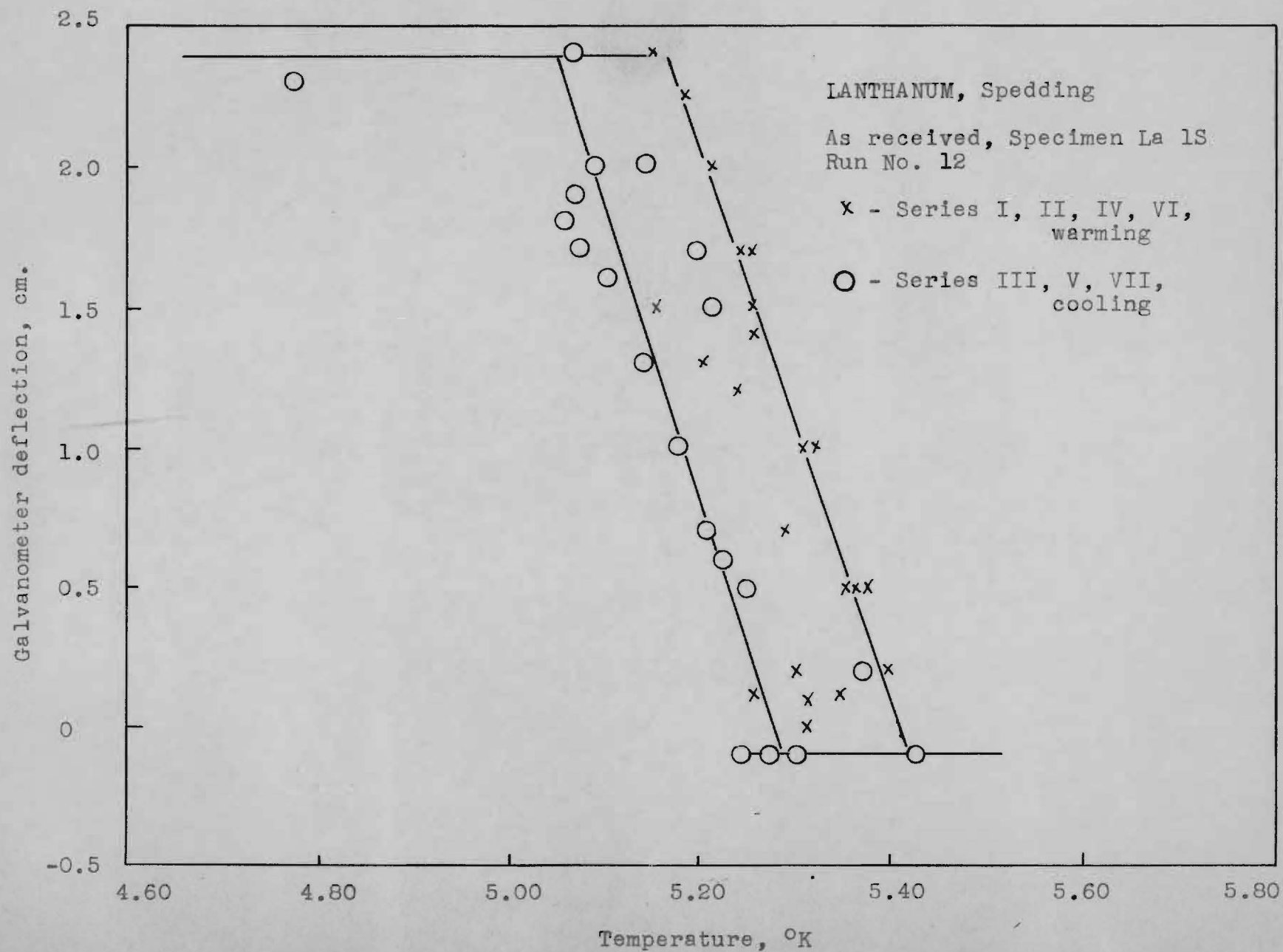


Figure 6. Superconducting Transition of Lanthanum

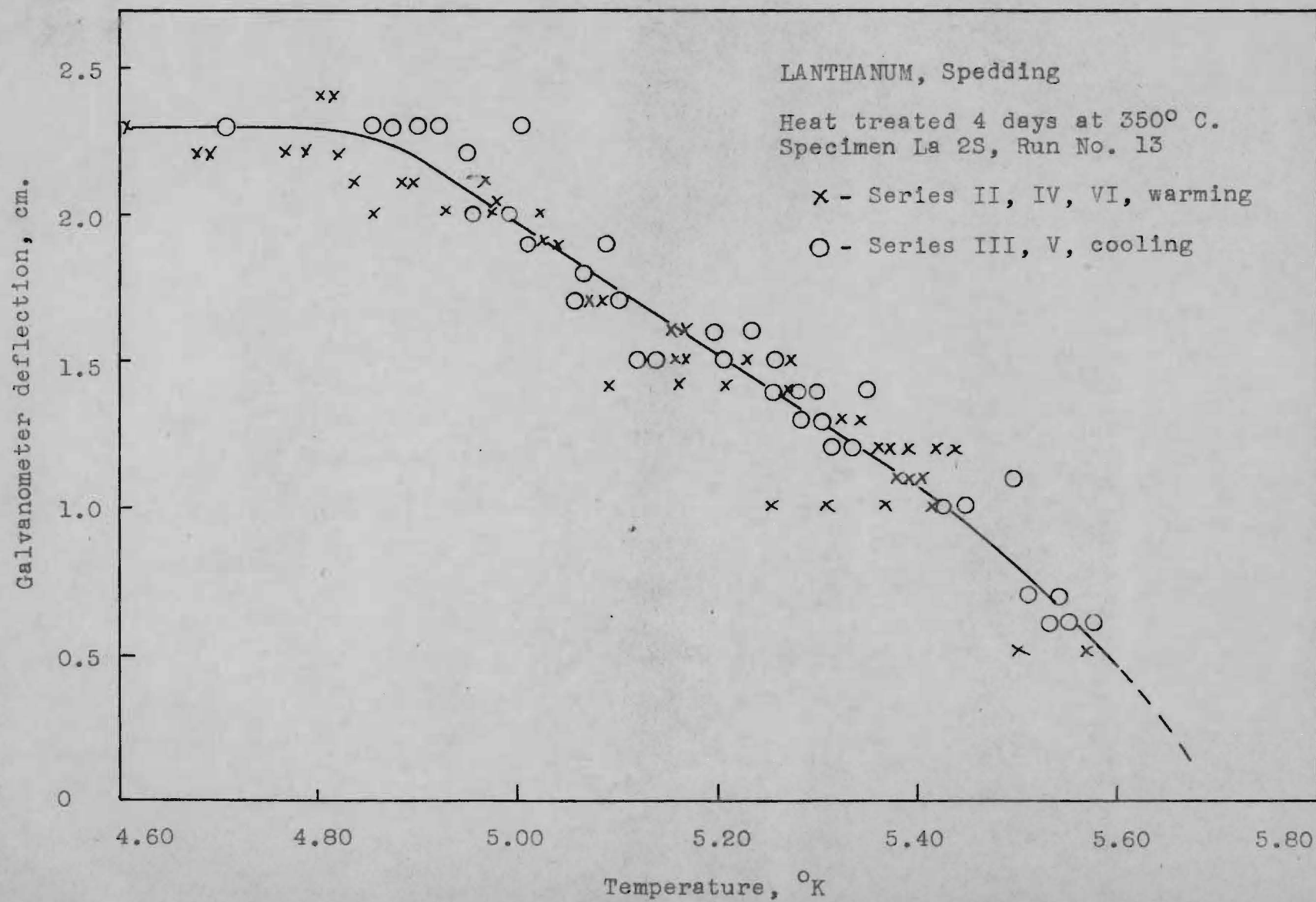


Figure 7. Superconducting Transition of Lanthanum

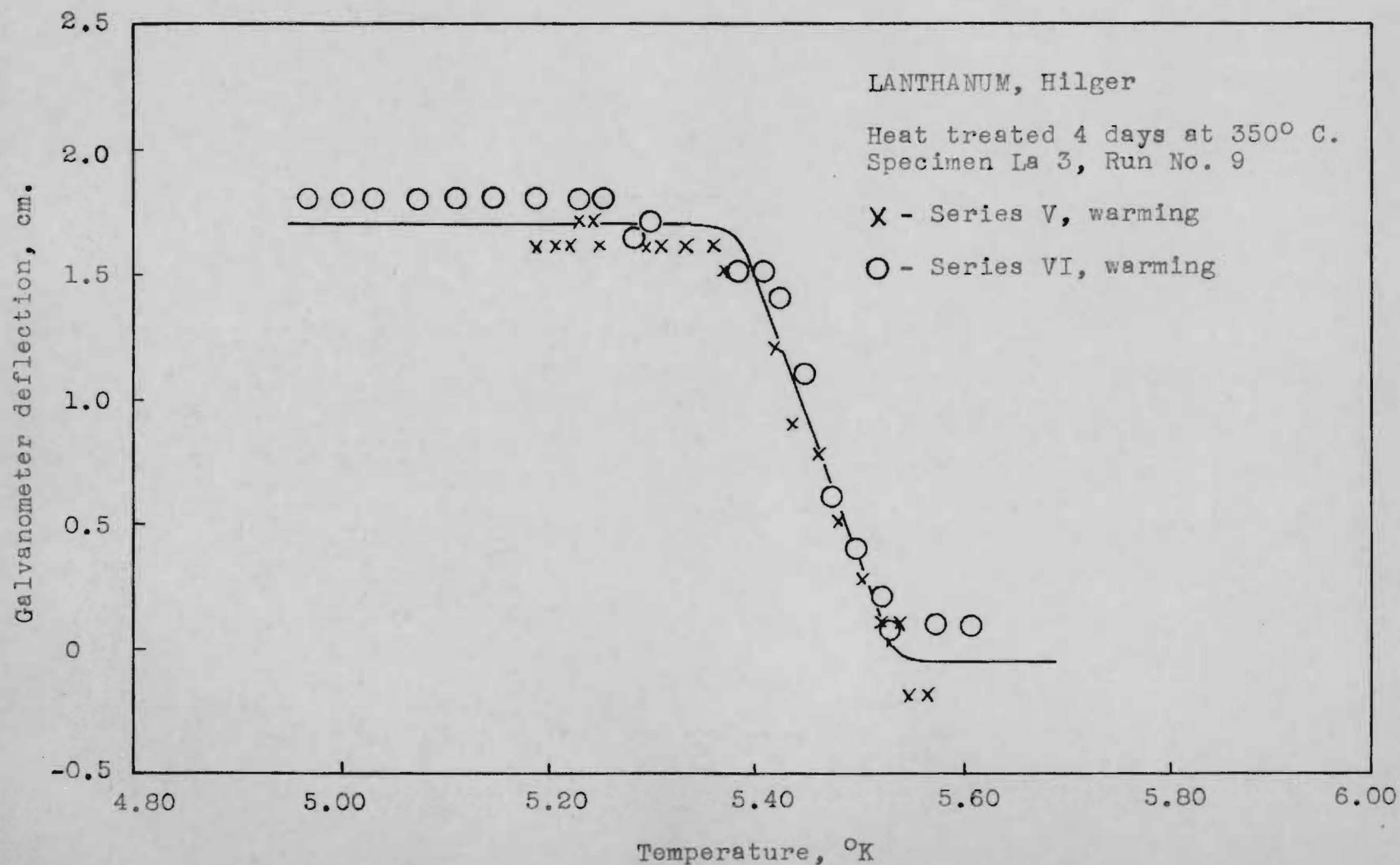


Figure 8. Superconducting Transition of Lanthanum

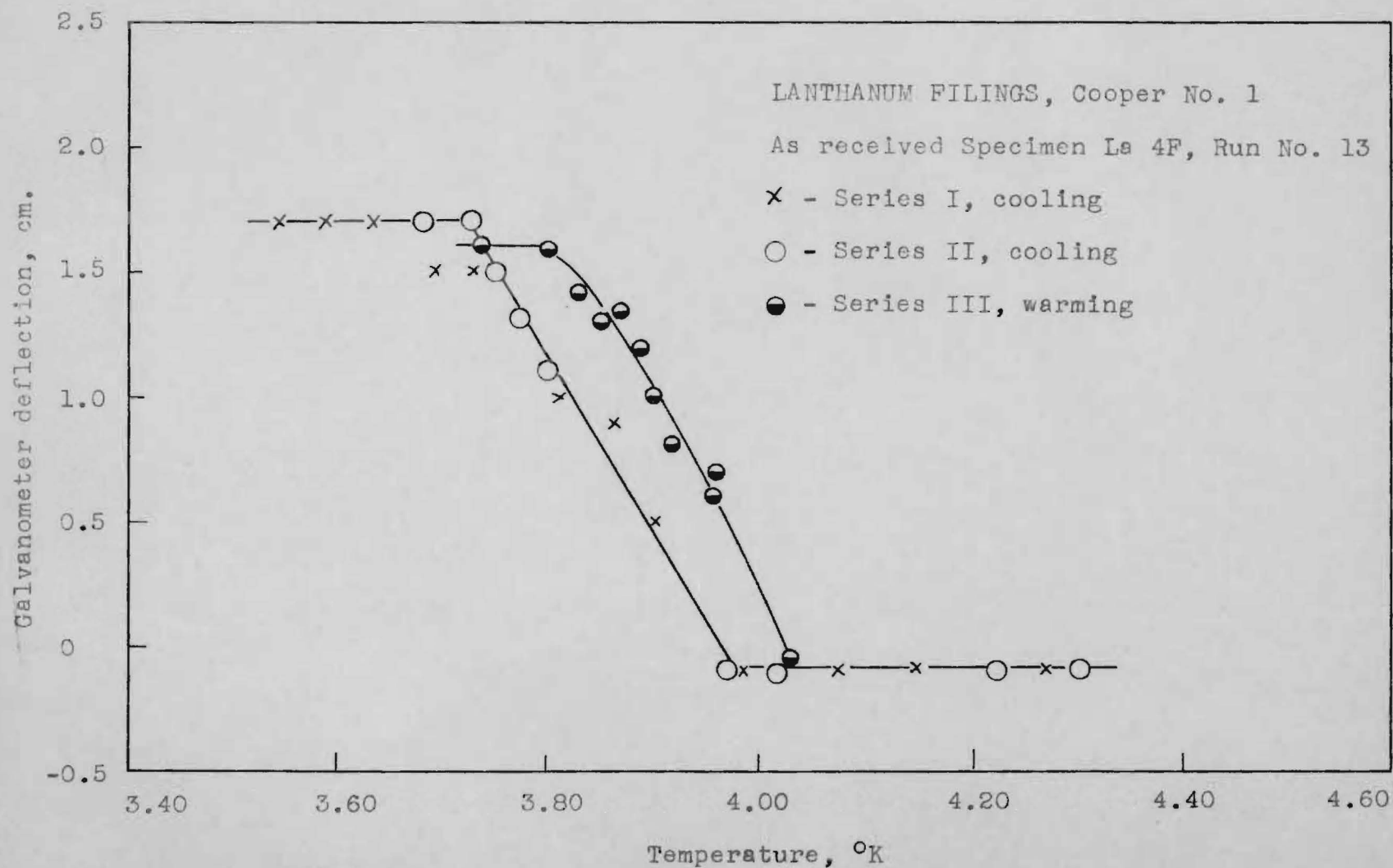


Figure 9. Superconducting Transition in Lanthanum Filings

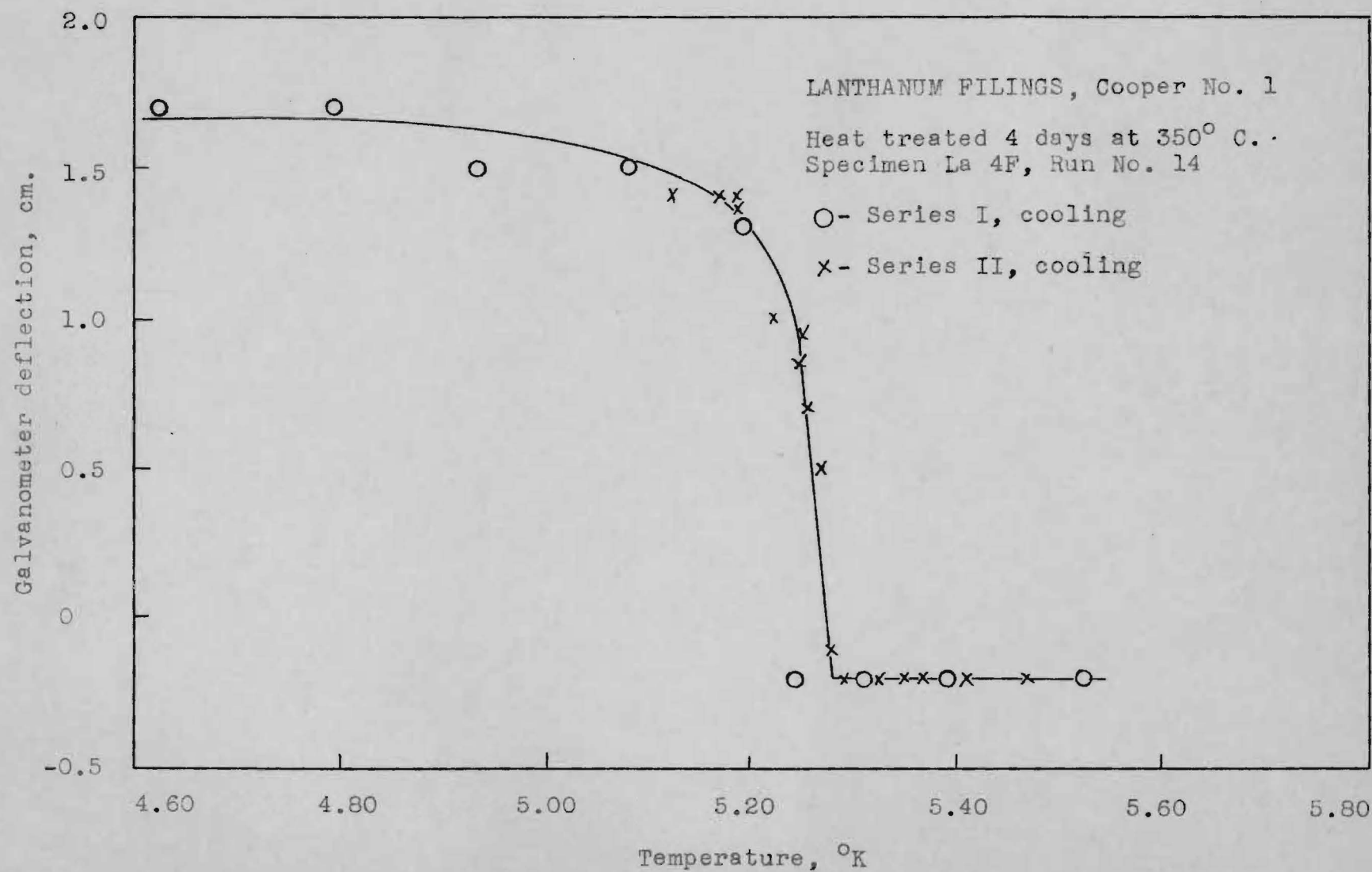


Figure 10. Superconducting Transition of Lanthanum Filings

although the heat-treated Spedding sample exhibited a transition range of 0.6 to 0.8°. Warming and cooling rates of 0.1 to 0.25 degree per minute were ordinarily used.

Hexagonal Close-Packed (3) Lanthanum

As was pointed out in Part I of this paper, filings taken from the four lanthanum samples in the as-received condition all exhibited the hexagonal close-packed structure. It has been assumed, therefore, that the bulk samples also have the hexagonal close-packed structure. Reference to Table XII shows that there is considerable variation in the transition temperatures of these samples. It is believed that these differences are probably due to differences in purity rather than strain. This is certainly true in the case of the Cooper No. 1 and Cooper No. 2 samples, as heat treatment at 350° C for four days changed the transition temperature of specimens of these samples only slightly (Figures 2 and 3).

The effect of strains on the transition temperature seems evident from the fact that the filings (specimen La 4F) taken from the Cooper No. 1 sample in the as-received condition exhibited a transition into superconductivity at 3.9° K (Figure 9), whereas the bulk specimens (La 1 and La 2) exhibited a transition at 5.0° K. After heat treatment the transition temperature of the filings was raised to 5.2° K (Figure 10), identical with that found for the bulk specimen (La 1) after heat treatment.

Face-Centered Cubic Lanthanum

The difficulties encountered in converting lanthanum from

the hexagonal close-packed to the face-centered cubic structure have been discussed in considerable detail in Part I of this paper. It was pointed out that the conversion of lanthanum filings from the hexagonal close-packed to the face-centered cubic structure was readily accomplished by heating the filings for four days at 350° C. Furthermore, once the filings were in the f.c.c. structure the reconversion to the h.c.p. structure took place very slowly. Cooling the filings to liquid helium temperatures did not bring about this reconversion in the course of a typical cryogenic experiment.

On the other hand, filings taken from bulk lanthanum specimens (for instance, La 1, La 3, La 6, La 2S) after heat treatment under identical conditions always exhibited primarily the h.c.p. structure, with only an occasional small amount of the f.c.c. structure.

In order to determine whether the f.c.c. modification of lanthanum is a superconductor, specimen La 4F', consisting of filings obtained from the Cooper No. 1 sample, was heat treated for four days at 350° C to convert it to the f.c.c. modification, and then examined for superconductivity. The filings were found to exhibit a transition into superconductivity at 5.2°. Figure 10 shows the transition curve obtained. X-ray examination showed that the filings had primarily the f.c.c. structure with a small amount of h.c.p. structure both before and after the low temperature experiment.

The magnitude of the galvanometer deflection observed when

the filings became superconducting was very nearly the same as that obtained when bulk specimens of approximately the same mass were studied with the same current in the primary. This suggests that the major portion of the filings became superconducting. It would appear, therefore, that the face-centered cubic modification of lanthanum is a superconductor.^a

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- - - - -

- a) At the ONR Cryogenics Conference held at Berkeley, California, in February, 1949, it was tentatively reported by us that the f.c.c. modification was not a superconductor down to 2° K. The experimental basis for this conclusion has been discussed in another place.^{24, 25} Briefly, it consisted in the fact that bulk specimens La 1 (Cooper No. 1) and La 3 (Hilger), which had been heat treated in sealed capsules containing helium for 4 days at 350° C in a high vacuum furnace, were subjected to tests for superconductivity without reopening. These specimens exhibited no transition into superconductivity down to 2° K. The structure of the bulk specimen was inferred to be f.c.c. from the fact that filings heat treated simultaneously with the bulk specimen had this structure. Later experiments with these same specimens suggested that the failure to observe superconductivity had arisen because of the loss of helium from the capsules during heat treatment, with resultant poor heat transfer. Measurements of the rate of diffusion of helium through pyrex glass indicated that sufficient helium might have been lost during heat treatment to give rise to thermal nonequilibrium.

SUMMARY

Four different samples of lanthanum metal have been examined for superconductivity, both in the as-received state and after heat treatment at 350° C for four days. X-ray examination of filings taken from all four samples, both before and after heat treatment, showed that the filings had the hexagonal close-packed structure. It was found that bulk specimens cut from the four samples exhibited a transition into superconductivity at 5.0 (Cooper No. 1), 5.25 (Spedding), 4.6 (Hilger), and 3.2° K (Cooper No. 2), respectively, before heat treatment, whereas after heat treatment the transition temperature was 5.2, 5.3, 5.45 and .1° K, respectively. Filings taken from one of the samples (Cooper No. 1) in the as-received state were found to exhibit a transition into superconductivity at 5.2° after heat treatment for four days at 350° C. X-ray examination of the filings both before and after the low temperature experiment showed that they have primarily the face-centered cubic structure, with only a small amount of hexagonal close-packed structure being present.

On the basis of these experiments it has been tentatively concluded that both the hexagonal close-packed and face-centered cubic modifications of lanthanum exhibit superconductivity at about 5.2° K.

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TECHNICAL REPORT NO. 3

PROJECT NO. 116-18

STUDIES OF COMPOUNDS FOR SUPERCONDUCTIVITY

By

W. T. ZIEGLER AND R. A. YOUNG

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NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH
CONTRACT NO. N6-ori-192, TASK ORDER I
NR 016-406

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NOVEMBER 28, 1951

Georgia Institute of Technology
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SUMMARY

A number of metal carbides, borides, nitrides, and a hydride, in the form of powders, have been examined for superconductivity down to 1.8° K using a magnetic method.¹⁰ The substances tested included TiC, VC, ZrC, TaC, WC, ZrB₂, NbB₂, TaB₂, WB, MoB, TiB_x, ThB₂, LaN, CeN, NbN, and LaH₂.⁴⁵ All specimens were characterized by X-ray diffraction methods and, in most instances, by chemical analysis. Of these substances only NbN gave evidence for superconductivity. The results for NbN are in general agreement with the work of others.^{1,4,10,24} The results for TiC and VC are in agreement with those found by Meissner et al.,^{18,21} who used an electrical resistance method, while those for TaB₂ and NbB₂ are in agreement with observations recently reported by Hulm and Matthias¹³ using a magnetic method. On the other hand, ZrC, TaC, WC, MoB and zirconium boride had previously been reported to exhibit superconductivity above 1.8° K.^{13,18,21}

Particle size measurements were made on the carbide and boride powders. The particles were large enough that magnetic field penetration effects should cause no difficulty, if a penetration depth of 1×10^{-5} cm, observed for pure metals, is assumed to apply to the present compounds.

The failure to observe superconductivity in the substances ZrC, TaC, WC, MoB and zirconium boride in the present study is discussed in terms of a postulated physical distribution of superconducting impurities of undetermined composition which are assumed to account for the superconductivity observed in these compounds by other investigators.

STUDIES OF COMPOUNDS FOR SUPERCONDUCTIVITY*

INTRODUCTION

The occurrence of superconductivity in binary compounds containing a metal and a nonmetal has been known for more than 20 years as a result of the extensive work of Meissner and his co-workers.^{18,20,21} Most of the compounds found to exhibit the effect are binary compounds between superconducting metals and boron, carbon, or nitrogen. On the other hand, the carbides of tungsten and the carbides, a boride of molybdenum, and two nitrides of molybdenum also show superconducting behavior, even though the pure metals do not become superconducting at the lowest temperatures tried ($< 1^{\circ}\text{K}$).

A survey of the literature has shown that, in almost all instances, the occurrence of superconductivity in compounds has been observed by studying the change of electrical resistance with temperature. In all instances in which the effect was observed by this means, the electrical resistance of the substance was found to decrease with temperature from room temperature to the transition temperature in the manner characteristic of metals.³³

The difficulty of preparing these substances as simple stoichiometric compounds has presented the possibility that the observed superconductivity may arise from superconducting filaments (either of the parent metal or a compound) present in the specimen rather than from the bulk specimen itself.

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*A report of this work was presented in less detail by W. T. Ziegler at the Oxford Conference on Low Temperature Physics, held at Oxford, England, August 22-28, 1951.

This doubt has suggested the re-examination of these substances by means of magnetic methods, since, as Shoenberg has pointed out,³¹ these methods should yield information concerning the behavior of the entire volume of the specimen, rather than of possible superconducting filaments.

Relatively little work has been published on the magnetic transition into superconductivity in compounds and metals which are difficult to purify. Shoenberg³⁰ has examined titanium by an a.c. magnetic induction method and reported it not to be a superconductor down to 1.0° K, whereas electrical resistance measurements by Meissner and others^{19,20} had shown that superconductivity set in below about 1.8° K. A similar anomaly has been reported by Shoenberg for uranium.³¹

Recently Hudson,¹¹ using a magnetic induction method, has reported that Mo_2C was not superconducting down to 1.3° K, whereas Meissner and Franz¹⁸ had reported an extended electrical transition into superconductivity in the range 2.5° to 3.1° K. Darby et al.⁶ have reported PbS, PbSe, and PbTe to become superconductors below 5° K using both electrical resistance and magnetic induction methods. Hudson,¹¹ on the other hand, also using a magnetic induction method, was unable to confirm their results for PbTe and PbS.

Studies are now in progress in our laboratory to re-examine by a magnetic induction method a number of compounds previously found to be superconducting by the electrical resistance method. A number of compounds not previously tested for superconductivity are also being studied.

The present paper deals with the results of studies made during the past year on 16 metal carbides, borides, nitrides, and a hydride. The compounds studied were*: TiC, VC, ZrC, WC, TaC, ZrB₂, NbB₂, TaB₂, WB, MoB, ThB₂, TiB_x, LaN, CeN, NbN, and LaH_{2.45}. Of these substances only NbN exhibited superconductivity above the lowest temperature used, about 1.8° K.

All materials were in the form of rather fine powders. They were examined by X-ray powder diffraction techniques using copper K α radiation. The photographs so obtained were analysed with the aid of published data. Partial chemical analyses were also available for all compounds. Particle size measurements were made on the carbide and boride powders. A detailed description of the materials and the method used, together with a discussion of the results obtained follows.

DESCRIPTION OF COMPOUNDS

A. Metal Carbides

The carbides were obtained through the courtesy of Dr. F. H. Horn, Research Laboratory, General Electric Company. They were prepared by the Carboloy Company, Inc., which provided the analyses shown in Table I. In each instance the value of x in the formula MC_x has been calculated from the principal metal content and the "combined carbon" (i.e., total carbon minus free carbon). Where only the carbon content was given, the remainder was taken to be the metal.

- - - - -
*The formulas used are descriptive rather than exact in that they do not, in general, show the exact chemical composition.

TABLE I
CHEMICAL ANALYSIS OF CARBIDES

Carbide Powder	Total Carbon (%)	Free Carbon (%)	Metal (%)	Others (%)	Calculated x in MC _x
TiC	19.03	0.22	79.01	0.57 Fe	0.948
ZrC	10.32	0.34	88.10	0.83 Ta, Nb	0.860
VC	16.18	0.13	82.8		0.820
WC	6.07	0.01			0.989
TaC	6.32	0.23			0.980

Table II summarizes the X-ray diffraction results obtained. A more detailed discussion of each carbide is given below.

TABLE II
COMPOSITION OF CARBIDES

Metal	Calculated x in MC _x	X-ray Diffraction Analysis		
		Major Constituent	Minor Constituent	Not Identified ^b
Titanium	0.948	TiC	Ti (?) ^a TaC (?)	4-5 f and vf lines
Vanadium	0.820	VC	V	Several m, 15 f lines
Zirconium	0.860	ZrC	Cb and/or Ta Zr (?)	Several m, 15-20 f and vf lines
Tantalum	0.980	TaC	None	No lines
Tungsten	0.989	WC	None identified.	About 20 vf to vvf lines

(a) A question mark (?) implies a few lines corresponding to this structure present.

(b) m = medium; f = faint; vf = very faint, etc.

From a consideration of the chemical analyses and X-ray diffraction results it was concluded that none of the specimens contained more than a trace of free metal. The tantalum carbide sample appeared to be essentially pure TaC. The other carbides all indicated the presence of small amounts of impurities. Both zirconium carbide and vanadium carbide deviated appreciably from the simple stoichiometric formula MC.

a. Titanium Carbide. This material gave an excellent X-ray diffraction photograph with sharp lines. The major constituent was identified as TiC by comparison with the data of Norton and Mowry²⁷ who reported TiC to have the NaCl-type structure with $a_0 = 4.329 \text{ \AA}$. The observed value was $4.34 \pm 0.01 \text{ \AA}$. The presence of a trace of Ti and TaC was also indicated. Four or five faint (f) and very faint (vf) lines could not be identified.

b. Vanadium Carbide. This material gave a fairly good picture with somewhat diffuse lines. The major constituent was identified as VC by comparison with the data of Dawihl and Rix,⁷ who reported VC to have the NaCl-type structure with $a_0 = 4.15 \text{ \AA}$, and the data of Norton and Mowry,²⁷ who found an a_0 of 4.169 \AA . The observed value was $4.17 \pm 0.01 \text{ \AA}$. A trace of vanadium metal was found. Several medium (m) and about 15 f lines were not identified.

c. Zirconium Carbide. This material gave an excellent picture with sharp lines. The major constituent was identified as ZrC by comparison with the data of Norton and Mowry²⁷

who reported ZrC to have the NaCl-type structure with $a_0 = 4.689 \text{ \AA}$. The observed value was $4.70 \pm 0.01 \text{ \AA}$. A trace of niobium and/or tantalum metal was also present. The presence of a trace of zirconium metal was questionable. A small amount of a ZrC-like structure with an a_0 about 0.01 \AA smaller was also noted. Several m, 15-20 f and vf lines were not identified.

d. Tantalum Carbide. This material gave a good picture though all lines were somewhat diffuse, indicating small particle size. The major constituent was identified as TaC by comparison with the data of Norton and Mowry²⁷ who reported TaC to have the NaCl-type structure with $a_0 = 4.457 \text{ \AA}$. The observed value was $4.46 \pm 0.01 \text{ \AA}$. No extraneous lines were present.

e. Tungsten Carbide. This material gave an excellent picture with very sharp lines. The major constituent was identified as WC by comparison with the data of Becker² who reported WC to have a hexagonal structure with $a = 2.94 \text{ \AA}$ and $c = 2.86 \text{ \AA}$. No evidence for the presence of tungsten metal or W_2C was found. About 20 vf and vvf lines were not identified.

B. Metal Borides

The metal borides, obtained from Cooper Metallurgical Associates, Cleveland, Ohio, were made by direct combination at high temperatures between the powdered metal and elemental boron, both of high purity. All specimens were rather finely

divided dark gray powders. Table III summarizes the results of the chemical and X-ray diffraction analyses. The chemical analyses were supplied with the specimens. A more detailed description of each boride is given below:

TABLE III
COMPOSITION OF BORIDES

Metal	Boron (%)	Calc. x in MB _x	X-ray Diffraction Analysis		
			Major Constituent	Minor Constituent	Not Identified ^a
Molybdenum	10.13	0.99	MoB	Mo ₂ B Mo	Few f lines
Tungsten	5.70	1.03	WB	None	No lines
Thorium	8.74	2.04	ThB ₂ (?) ^b	Th ThB ₆ (?)	Many f lines
Titanium	18.33	0.99	TiB _x x = 2-2.5	None identified.	7 f lines
Niobium	18.40	1.94	NbB ₂	Nb (trace)	Many mf, f and vf lines
Zirconium	19.76	2.35	ZrB ₂	None identified.	Few f lines
Tantalum	9.48	1.75	TaB ₂	None identified.	Two vf lines

(a) mf = medium faint; f = faint; vf = very faint.

(b) A question mark implies some lines believed to be due to this substance present.

a. Molybdenum Boride. This material gave an X-ray diffraction photograph with sharp lines which exhibited some spottiness. Comparison of the "d" values from this film with the data given by Kiessling¹⁶ indicated that the major constituent was MoB with the probable presence of traces of Mo₂B

and Mo. Kiessling has assigned a simple tetragonal structure to MoB, with $a = 3.105 \text{ \AA}$ and $c = 16.97 \text{ \AA}$. A few faint lines in the observed pattern could not be identified.

b. Tungsten Boride. This material gave an X-ray diffraction pattern in which all the lines agreed with Kiessling's data¹⁶ for WB. Kiessling assigned a tetragonal structure to WB with $a = 3.115 \text{ \AA}$ and $c = 16.93 \text{ \AA}$. The lines were sharp and showed about the same spottiness as for the molybdenum boride.

c. Thorium Boride. The boride analysis supplied with this material corresponded to the formula $\text{ThB}_{2.04}$. The diffraction pattern from this material contained 69 lines. Of these the 19 strongest lines could be assigned to a face-centered cubic structure having an a_0 of $5.58 \pm 0.01 \text{ \AA}$. A trace of thorium metal was present. Of the remaining lines a few were medium faint, the rest being faint or weaker. Many of these remaining lines could be accounted for by the presence of a small amount of ThB_6 , using the lattice parameter ($a_0 = 4.32 \text{ \AA}$) given by Stackelberg and Neumann.³² However, several of the lines expected to be strongest (as judged by comparison with the published data³² for CaB_6) were absent.

Thorium metal has a face-centered cubic lattice with $a_0 = 5.074 \text{ \AA}$. The unidentified face-centered cubic structure mentioned above may represent the structure of ThB_2 , in which the thorium metal atom lattice has undergone an expansion from $a_0 = 5.074 \text{ \AA}$ to 5.58 \AA because of the introduction of boron.

d. Titanium Boride. The X-ray diffraction pattern of this material was compared with the very detailed study of Ehrlich⁸ who investigated the structure of the TiB_x system over the range $0 \leq x \leq 3$. Detailed comparison of the 23 lines obtained for this material with the work of Ehrlich indicated that the strongest lines corresponded very closely with the pattern given by Ehrlich for TiB_x where x ranges from 2 to 2.5, with a somewhat less satisfactory fit for x over the entire range 1 to 2.5. This latter assignment leaves seven faint lines unidentified. There was no evidence for free titanium. These results suggest that the chemical analysis may be in error since it yields the formula $TiB_{0.99}$.

e. Niobium Boride. The X-ray diffraction pattern given by this material contained 71 lines of which 39 were medium faint or stronger. Comparison with the data of Norton et al.²⁸ for the diboride, NbB_2 , showed that this substance was the major constituent, which is in good agreement with the formula $NbB_{1.94}$ assigned from chemical analysis. These investigators reported NbB_2 to have a hexagonal structure with $a = 3.086 \text{ \AA}$ and $c = 3.306 \text{ \AA}$. A trace of niobium was also present. One ms, several mf, and 30-40 f, vf to vvf lines could not be identified.

f. Zirconium Boride. Comparison of the diffraction pattern given by this material with the data of Norton et al.²⁸ for ZrB_2 showed that the major constituent was ZrB_2 . These investigators reported ZrB_2 to have a hexagonal structure

with $a = 3.170 \text{ \AA}$ and $c = 3.533 \text{ \AA}$. No free zirconium was found. A few faint and diffuse lines remained unidentified.

g. Tantalum Boride. Comparison of the diffraction pattern given by this material with the data of Norton et al.²⁸ for TaB_2 showed that all except two νf lines could be assigned to the diboride. These investigators reported TaB_2 to have a hexagonal structure with $a = 3.088 \text{ \AA}$ and $c = 3.241 \text{ \AA}$.

C. Metal Nitrides

a. Lanthanum and Cerium Nitrides. These nitrides were made by direct combination at $800\text{--}900^\circ \text{C}$ between the rare-earth metal filings and nitrogen gas at one atmosphere pressure. This method differed from that previously used by Muthmann and Kraft,²⁵ Neumann, Kroger and Kunz,²⁶ and Iandelli and Botti¹⁴ in that the nitrogen absorption could be measured volumetrically, as well as gravimetrically. All operations were carried out in a dry, inert (nitrogen or helium) atmosphere to prevent reaction with air or moisture.

The lanthanum nitride samples were prepared using lanthanum metal obtained from two sources. One of the lanthanum samples, designated as "Cooper No. 2," was obtained from Cooper Metallurgical Associates, Cleveland, Ohio, which also supplied the cerium metal. The second, designated as "Spedding," was obtained through the courtesy of Dr. F. H. Spedding, Iowa State College, Ames, Iowa.

The "Cooper No. 2" lanthanum was analysed by spectrographic, spectrophotometric, chemical, and ion exchange techniques. The

results of these analyses gave: La, 94.8%; Ce, 1.1%; Pr, 0.2%; Nd, 0.4%; other rare earths, 0.2%; Si, 0.7% (estimated); Fe, 0.8% (estimated); carbon and others, present; total accounted for 98.2%. On the basis of the overall analysis the total rare earth content, calculated as lanthanum, has been taken as 97%.

Spectrographic analysis of the "Spedding" lanthanum showed that it contained 0.13% Be, 0.1% Mg and traces (estimated to be a few hundredths of one per cent each) of calcium, aluminum, and iron. The sample appeared to be free of other rare earths. The total rare earth content, expressed as lanthanum, was found by direct precipitation as oxalate under carefully controlled conditions to be 97.3%. This low result may arise from the presence of carbon or dissolved gases such as oxygen. In view of the presumed high purity of this material the lanthanum content has been taken somewhat arbitrarily to be 100%.

The Cooper cerium metal was analysed by the same general techniques used for lanthanum. These analyses gave: Ce, 92.2%; La, none; Pr, 0.4%; Nd, 0.6%; other rare earths, none; Si, 0.3%; Fe, 2.5%; carbon and others, present; total accounted for, 96.0%. The total rare earth content, calculated as cerium, was found by direct precipitation as oxalate to be 94.9%. On the basis of all facts concerning the analyses, the total rare earth content, expressed as cerium, has been taken to be 95%.

A summary of the details of preparation of the nitrides is given in Table IV. The two lanthanum nitrides were black free-flowing powders, which appeared to be homogeneous. The formula of these products was LaN_x , $0.91 \leq x \leq 0.99$, where the

value of x depended somewhat upon whether the volumetric or the gravimetric measurement was used in the calculation. Muthmann and Kraft²⁵ and Neumann *et al.*²⁶ had observed $x = 1 \pm 0.08$ and $0.824 \leq x \leq 0.830$, respectively.

TABLE IV
NITRIDATION OF LANTHANUM AND CERIUM METALS

Expt. No.	Metal	Metal Filings Weight (g)	x in LaN_x^a		Experimental Conditions ^b
			Weight Increase	Vol. Meas.	
26	Lanthanum (Cooper No. 2)	0.4240	0.99	0.95	20 hours at 920°
29	Lanthanum (Spedding)	0.5626	0.97	0.91	20 hours at 920°
30	Cerium (Cooper No. 1)	0.8290	0.86	0.86	1.5 hours at 700°, 18 hours at 800°

(a) The value of x was calculated on the assumption that the original metal samples had the following purities: Cooper No. 2, 97% La; Spedding, 100% La, Cooper No. 1, 95% Ce.

(b) Temperatures in °C. Nitrogen pressure, 1 atm.

The cerium nitride was a reddish brown powder with a faint luster. It had the formula CeN_x , $x = 0.86$. Muthmann and Kraft²⁵ found an x of 0.89 as an average of nine experiments; Neumann *et al.*²⁶ reported that x varied from 0.71 to 0.87.

Powder X-ray diffraction studies of the lanthanum nitride products showed no significant difference between them. The structure was found to be of the NaCl-type with $a_0 = 5.284 \pm 0.004$ kx-units, in agreement with the observations of Iandelli and

Bottl¹⁴ who reported the same structure with $a_0 = 5.27$ kx-units. Since the nitride has the same lattice and lattice parameter as face-centered cubic lanthanum metal with $a_0 = 5.285 \pm 0.005$ kx-units, it was impossible to determine whether or not any unreacted lanthanum was present in the products.

The cerium nitride also exhibited a face-centered cubic lattice with $a_0 = 5.014 \pm 0.005$ kx-units. All lines observed could be assigned to this structure. Iandelli and Bottl¹⁴ have reported CeN to have the NaCl-type structure with $a_0 = 5.01$ kx-units.

b. Niobium Nitride. This material was supplied by Dr. F. H. Horn, Research Laboratory, General Electric Company, Schenectady, New York, as part of a cooperative study on Nb-Ta alloys and their nitrides. The nitride was prepared by heating niobium metal powder for 4 to 4-1/2 hours at 1500° C in pure dry nitrogen. The metal was obtained from Fansteel Metallurgical Corporation; it was stated to be 99.9% pure. The nitride was in the form of a coarse gray powder.

X-ray examination of the nitride showed it to be primarily NbN with $a_0 = 4.37 \pm 0.01$ kx-units.¹⁰ A trace of Nb and/or Ta metal appeared to be present. A large number of f to vvf lines could not be identified. These lines did not fit the pattern for Nb₂N reported by Brauer.³

D. Lanthanum Hydride

The lanthanum hydride was prepared by direct combination between lanthanum metal filings (Cooper No. 3) and pure dry hydrogen gas at 210-250° C. The lanthanum metal had a

composition very similar to that reported for the Cooper No. 2 specimen. On the basis of the overall analysis the total rare earth content, calculated as lanthanum, was taken to be 97%. The apparatus used was the same as in the preparation of the rare earth nitrides.

The products were black friable powders. They were handled at all times so as to prevent contact with moisture and air. The details of the preparations are shown in Table V. The resulting products had a composition corresponding approximately to $\text{LaH}_{2.45}$. Muthmann and Kraft²⁵ and Rossi,²⁹ using a similar method, have reported similar products having the approximate formulas LaH_3 and $\text{LaH}_{2.4}$, respectively.

Powder X-ray diffraction photographs gave a pattern corresponding to a f.c.c. lattice with $a_0 = 5.625 \pm 0.007$ kx-units, which is in good agreement with the value of 5.62-3 kx-units reported by Rossi.²⁹ The lines were somewhat diffuse. The pattern of f.c.c. lanthanum ($a_0 = 5.285$ kx-units) was not observed in these products.

TABLE V
PREPARATION OF LANTHANUM HYDRIDE

Expt. No.	Weight of La Metal (g)	x in LaH_x ^b		Experimental Conditions ^c
		Wgt. Inc.	Vol. Meas.	
37 ^a	0.8382	2.40	2.44	Reaction started, ^d 210°; 8 hours at 290° $\pm 10^\circ$.
38	0.9721	2.66	2.47	Reaction started, ^d 225°; 19-1/2 hours at 290° $\pm 10^\circ$.

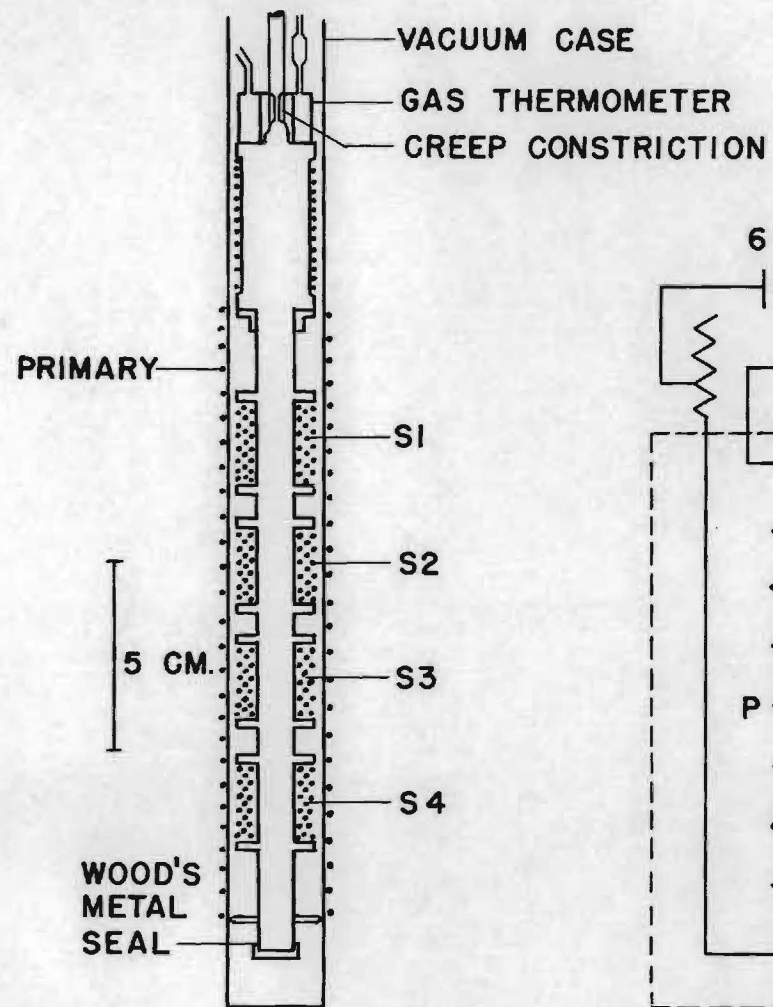
- (a) This product used in superconductivity studies.
 (b) Calculated on basis that metal contained 97% La.
 (c) Temperatures in °C. Hydrogen pressure was 1 atm.
 (d) Reaction took place rapidly at this temperature.

EXPERIMENTAL METHOD

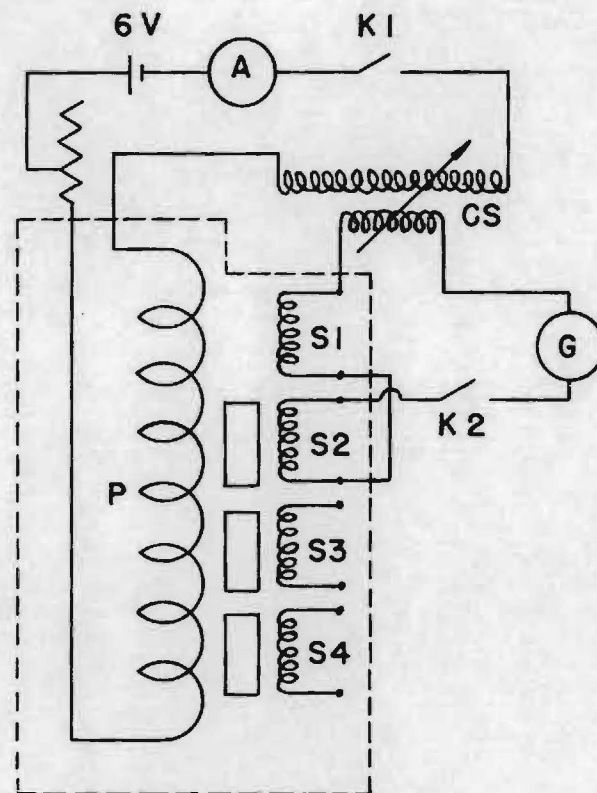
The cryostat used differed in only minor details from one described by Horn and Ziegler.¹⁰ The Simon expansion method was used to produce the liquid helium. From the main helium reservoir was suspended the experimental chamber, into which helium could be condensed at will by bringing low pressure helium gas into contact with the main helium reservoir. The copper experimental chamber (Figure 1A) consisted of two parts, an upper section to which the gas and the constantan resistance thermometers were attached, and a lower section in which the specimens to be tested for superconductivity were located.

The temperature of the experimental chamber was measured by means of a helium gas thermometer. This thermometer was of the type described by Mendelssohn,²² except that helium pressure was measured both by a Bourdon gauge and a capillary mercury manometer. The thermometer was filled with helium gas at one atmosphere pressure while at room temperature and then sealed off.

Temperatures were calculated from the helium pressure on the assumption that the volume of the capillary tubing (0.020 inch i.d. copper-nickel alloy) connecting the manometer and gauge volume, V_r , at room temperature, and the volume of its thermometer bulb proper, V_b , was negligible. Gas imperfection was taken into account by making use of the virial coefficients given by Keesom.¹⁵ The ratio of the two volumes, V_r/V_b , was determined by experiment at the normal boiling point of hydrogen, the triple point of hydrogen and at the normal boiling point of helium. This ratio had a value of 11.9



A. EXPERIMENTAL CHAMBER



B. SUPERCONDUCTIVITY
DETECTION CIRCUITS

Figure 1. Magnetic Measurements System

at the two hydrogen points and a value of 12.4 at the helium point. V_b was equal to 1.6 cc.

The sensitivity of the gas thermometer was about 0.04° per mm. Hg in the range 3 to 5° K and 0.08° per mm. Hg in the range 14- 20° K. Readings were made to 0.5 mm. In the range below about 2.6° K the gas thermometer acted as a vapor pressure thermometer. The vapor pressure of the liquid helium in the experimental chamber was also used to determine the temperature below 4.2° K.

The absolute accuracy of the temperature scale is believed to be about 0.05° in the range below 5° K, 0.1° in the range 5 - 7° K and 14- 20° K and several tenths of a degree in the range between 7° and 14° K.

A resistance thermometer, constructed of B and S No. 40 constantan wire, also was used to follow the temperature changes of the experimental chamber. This thermometer had a resistance of 1069 ohms at 4.2° K and a dR/dT of approximately one ohm per degree over the range 1.8 to 20° K. Temperature changes of 0.01° - 0.02° could be detected with this thermometer.

The system for making the magnetic measurements consisted of a primary coil, wound on the lower end of the brass vacuum case, and four equally spaced secondary coils S1, S2, S3, and S4, wound on the outside of the experimental chamber and coaxial with the primary coil. The primary coil, constructed of 1117 turns of #30 AWG copper wire, was 15.1 cm. long. The secondary coils consisted of about 3000 turns of #40 AWG copper wire. Each coil was 2.2 cm. long. In all experiments

coil S1, a compensating coil, was always empty, the specimens under test being located in coils S2, S3, and S4.

The circuits for detecting superconductivity are shown in Figure 1B. The experimental procedure was as follows: with the experimental chamber at a fixed temperature, coil S1 and another coil, for example coil S2, were connected by means of a suitable external switching arrangement in such a manner that the voltages induced in them opposed each other when the tap key (K1) in the primary circuit was closed. A primary current of 0.27 amperes was usually used. With the tap key (K2) closed, the galvanometer ordinarily showed a deflection when the primary was energized. This unbalance could be reduced to zero by suitably adjusting an external variable inductance, CS. With the circuit balanced and K2 closed, K1 was closed at 10-15 second intervals during a series of measurements in which the temperature of the experimental chamber was slowly lowered (or raised); any unbalancing of the coils was observed as a galvanometer deflection.

The powdered samples were generally mounted in a 7 mm. o.d. pyrex glass tube, partly open at the top end, and were in direct contact with the helium. In a few instances (TiC, VC, $\text{LaH}_{2.45}$, CeN, and LaN), the measurements were made on samples in pyrex capsules sealed at room temperature under 20 cm. Hg pressure of helium. The samples had weights varying from 0.7 to 2.5 gm., and usually had a length of 20-22 mm. and a diameter of 4.5-4.9 mm. The actual volume was determined from the weight of the sample and published or estimated density.

EXPERIMENTAL RESULTS

The experimental results for the various compounds tested are summarized in Table VI, VII, and VIII, in comparison with experimental work of other investigators. In these tables the major constituent given was that found by X-ray diffraction analysis. As mentioned previously, of the substances tested, only NbN was found to exhibit a magnetic transition into superconductivity above about 1.8° K, the lowest temperature used in these studies. Tungsten boride, thorium boride, lanthanum nitride and hydride, and cerium nitride had not previously been tested for superconductivity.

The sensitivity of the magnetic detection system was such that the NbN specimen gave a total galvanometer deflection of 4.2 cm. in passing from the normal to the superconducting state. On the basis of this and other measurements, it was estimated that the occurrence of superconductivity could have been detected in a volume corresponding to five to ten per cent of the volume of the samples used.

Reference to Table VI and VII shows that the failure to observe superconductivity in ZrC, TaC, and WC and zirconium boride is in disagreement with the observations of Meissner et al.,^{18,21} who used the electrical resistance method. The nonappearance of superconductivity in MoB is in disagreement with the recent observations of Hulm and Matthias,¹³ who found a transition at 4.4° K using a magnetic induction method. On the other hand, the magnetic transition observed for NbN is in general agreement with the results found by

TABLE VI
SUPERCONDUCTIVITY OF METAL CARBIDES

Carbide	Major Constituent	Transition Temp. ^a and Range, °K		Method ^c	Observer ^d
		This Research	Lit.		
TiC _{0.95}	TiC	(1.8°) ^b	1.1° (?) (1.31°)	R R	Meissner(1) Meissner(2)
VC _{0.82}	VC	(1.8°)	(1.33°)	R	Meissner(1)
ZrC _{0.86}	ZrC	(1.8°)	3.7°, 3.3°-4.1°	R	Meissner(2)
TaC _{0.98}	TaC	(1.8°)	9.3°, 9.2°-9.4° 7.6°-9.5°	R R	Meissner(1) Meissner(2)
WC _{0.99}	WC	(1.8°)	3.4°, 2.5°-4.0°	R	Meissner(1)

(a) Temperature corresponding to 50 per cent of total resistance change in transition.

(b) Temperatures in parentheses mean substance not superconducting down to this temperature.

(c) R = electrical resistance method.

(d) References: (1) Meissner and Franz, Z. Physik **65**, 30 (1930).

(2) Meissner, Franz, and Westerhoff, ibid., **75**, 521 (1932).

TABLE VII
SUPERCONDUCTIVITY OF METAL BORIDES

Boride	Major Constituent	Transition Temp. and Range, °K		Method ^b	Observer ^c
		This Research	Lit.		
MoB _{0.99}	MoB	(1.74°) ^a	4.4°	M	Hulm(1)
WB _{1.03}	WB	(1.77°)			
ThB _{2.04}	ThB ₂ (?)	(1.77°)			
TiB _{0.99}	TiB _{2-2.5} (?)	(1.8°)	(1.26°)	R	Meissner(2)
NbB _{1.94}	NbB ₂	(1.8°)	(1.27°) (9.5°)	M R	Hulm(1) Aschermann(3)
ZrB _{2.35}	ZrB ₂	(1.8°)	3.1°, 2.9°-3.3°	R	Meissner(2)
TaB _{1.75}	TaB ₂	(1.8°)	(1.32°)	M	Hulm(1)

(a) Temperatures in parentheses mean substance not superconducting down to this temperature.

(b) R = electrical resistance method. M = magnetic induction method.

(c) References: (1) Hulm and Matthias, Phy. Rev. 82, 273 (1951).
(2) Meissner, Franz and Westerhoff, Z. Physik 75, 521 (1932).
(3) Aschermann, Friederich, Justi and Kramer, Physik Z. 42, 349 (1941).

TABLE VIII
SUPERCONDUCTIVITY OF NITRIDES AND HYDRIDE

Compound	Transition Temp. and Range, °K		Method ^c	Observer ^d
	This Research	Lit.		
NbN	16.0°			
	14.6°-16.8°			
		14.7°	M, R	Horn(1)
		13.9°-15.3°		
		15°-16.5° ^b	R	Aschermann(2)
		14°-15°	R	Milton(3)
		15.2°	M	Cook(4)
		13.5°-16.2°	M	Cook(4)

LaN_{0.97} (1.8°)^a
(Cooper No. 2)

LaN_{0.94} (1.8°)
(Spedding)

CeN_{0.86} (1.8°)
(Cooper)

LaH_{2.45} (1.8°)
(Cooper No. 3)

(a) Temperatures in parentheses mean substance not superconducting down to this temperature.

(b) On warming only. On cooling, temperatures as high as 23° K obtained.

(c) M = magnetic induction method. R = electrical resistance method.

(d) References: (1) Horn, Dissertation, Johns Hopkins Univ., Baltimore, Md., 1942; Horn and Ziegler, J. Am. Chem. Soc. **69**, 2762 (1947).
(2) Aschermann, Friedrich, Justi and Kramer, Physik. Z. **42**, 349 (1941). Warming curves only.
(3) Milton, Chem. Rev. **39**, 419 (1946).
(4) Cook, Zemansky and Boorse, Phys. Rev. **79**, 1021 (1950).

both electrical resistance and magnetic induction methods.^{1,4,9,10,24}

The failure to observe superconductivity in the lanthanum nitrides and hydride is interesting since the transition temperatures of the three lanthanum metal specimens had previously been found to be³⁴: Cooper No. 2, 3.2°; Cooper No. 3, 3.5°; Spedding, 5.2°. The cerium metal from which the nitride was prepared was not superconducting down to 1.8° K.

Several reasons for the failure to observe superconductivity in ZrC, TaC, WC, and MoB suggested themselves. One of these was that the apparatus was not functioning properly, possibly due to thermal nonequilibrium. However, the detection of superconductivity in bulk specimens of lanthanum, lead, and tin metals, lanthanum filings and powdered NbN with the apparatus seemed to exclude this possibility.

The apparatus was further checked by studying a tin powder which consisted of spheres having a size range of approximately 15 to 50 microns. This material was obtained through the courtesy of Dr. M. C. Steele of the Naval Research Laboratory, Washington, D. C. The powder was free-flowing; it had a yellowish appearance indicating the presence of some oxide on the surface of the tin particles. Tests of this powder gave a magnetic transition into superconductivity over the range 3.63° to 3.49° K. This is somewhat lower than the generally accepted transition temperature (3.7° K) for bulk tin. However, the calculated maximum field generated by the measuring primary was 27 oersteds, which could be expected to produce a lowering as great as 0.15°.

The measurements on LaN, CeN, LaH_{2.45}, TiC, and VC were made on samples sealed in capsules under 20 cm. Hg helium pressure at room temperature. The possibility that the helium gas was adsorbed at low temperatures, thus resulting in poor heat transfer, is not entirely excluded. However, experiments with lanthanum metal filings sealed under similar conditions showed no significant hysteresis in the transition at 4° K. In general, specimens were kept below 4.2° K for as long as an hour, and below the lambda point (2.19° K) for times ranging from 3 to 18 minutes.

In order to obtain some information on the possible magnitude of field penetration effects, the particle size distribution of the carbide and boride powders was determined by measuring microscopically the linear dimensions of 100 particles which had been suitably dispersed on a glass slide.⁵ The particle size distribution observed was expressed in terms of the smallest diameter, d_v , possessed by those particles whose mass constituted 50 per cent of the total mass of the sample.⁵ The appearance of the particles of all powders examined could best be described as roughly spherical. Table IX summarizes the results obtained. It will be noted that the MoB, ZrC, and WC specimens consisted of relatively large particles. Electron-microscopic examination of the TaC powder showed that it contained a considerable fraction below one micron in size.

The field penetration depth in powders of alloy systems such as the carbides and borides has apparently not been investigated. If one takes for the penetration depth, λ , the

rough value of 1×10^{-5} cm. observed in metals,¹⁷ it would appear that the values of d_v for all substances studied was sufficiently large so that field penetration would not be expected to play a significant role in the present measurements.

TABLE IX
PARTICLE SIZE MEASUREMENTS

Borides		Carbides	
Substance	Particle Size ^a d_v (microns)	Substance	Particle Size d_v (microns)
WB	1.3	TaC	1.1
ThB ₂	1.3	TiC	2.3
NbN	1.8	VC	3.7
TaB ₂	1.8	ZrC	6.2
TiB _x	2.0	WC	11.2
MoB	3.2		
ZrB ₂	3.4		

(a) d_v = smallest diameter of those particles whose mass constituted 50 per cent of the total mass of the sample.

The disagreement between the results of Meissner and co-workers^{18,21} and the present work regarding the occurrence of superconductivity in TaC, WC, and ZrC, might be explained, as Shoenberg^{30,31} has suggested for titanium and uranium, by assuming the presence of superconducting filaments in Meissner's specimens of these carbides. A similar explanation would resolve the conflicting observations of Hudson¹¹ and Meissner and Franz¹⁸ regarding the superconductivity of Mo₂C. Unfortunately, no specimens of these substances appear to have been studied by both electrical and magnetic methods.

Hudson,¹² using the magnetic induction method, has made an interesting study of two Sn-Ge "alloys" containing 2.3 and

9.3 atomic per cent of tin, respectively, in which the tin is concentrated along the grain boundaries. He observed a rather broad diamagnetic transition beginning at 4° K. Hudson attributed this behavior to the presence of superconducting filaments of tin. Calculations by him indicated that approximately 50 per cent of the volume of the alloy of lower tin content and the entire volume of the alloy of higher tin content participated in the magnetic transition.

In view of these observations of Hudson on the Sn-Ge alloys, it would appear that the precise physical structure of the "superconducting filaments" might be an important variable. Thus, if the filaments are thread-like, superconductivity might be observed electrically but not magnetically. On the other hand, if the superconducting filaments possess a sponge-like structure²³ with the bulk material in the holes of the sponge, as in the Ge-Sn alloy experiments of Hudson,¹² then both an electrical and a magnetic transition might be observed. The physical structure of such filamentous inclusions might be expected to depend considerably on the method of preparation.

The disagreement between the results of Hulm and Matthias¹³ and the present work regarding the superconductivity of MoB may be due to some such difference in the arrangement of a superconducting inclusion. The conflicting observations of Darby et al.⁶ and Hudson¹¹ on the superconductivity of PbTe and PbS, mentioned earlier, might be explained in a similar fashion.

The possibility that superconductivity in many compounds may be due to rather specific amounts of trace impurities, distributed in a homogeneous manner through the bulk material and which make possible a superconducting, state has not been excluded.

ACKNOWLEDGMENTS

The authors are indebted to F. W. Lafond, J. T. Roberts, Jr., G. Cook, and M. T. Gordon for assistance in carrying out the low temperature measurements, to Dr. W. M. Spicer for the spectrographic analyses, and to C. Orr and Dr. J. M. DallaValle for assistance in the particle size measurements. The help and interest of Dr. F. H. Horn, General Electric Company, in securing the carbides and niobium nitride are greatly appreciated.

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TECHNICAL REPORT NO. 4

PROJECT NO. 116-18

SUPERCONDUCTIVITY STUDIES

By

W. T. ZIEGLER AND R. A. YOUNG

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NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH
CONTRACT NO. N6-ori-192, TASK ORDER I
NR 016-406

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JUNE 16, 1953

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SUMMARY

This Technical Report contains reprints of three papers published during the past eight months. These are:

1. "The Crystal Structure and Superconductivity of Lanthanum," W. T. Ziegler, R. A. Young and A. L. Floyd, Jr., J. Am. Chem. Soc. 75, 1215-21 (1953).
2. "Studies of Compounds for Superconductivity," W. T. Ziegler and R. A. Young, Phys. Rev. 90, 115-19 (1953).
3. "Crystal Structure of Lanthanum Nitride," R. A. Young and W. T. Ziegler, J. Am. Chem. Soc. 74, 5251-3 (1952).

The first paper presents a summary of the work carried out on this subject through September, 1952. It represents an extension of two earlier reports.^{1,2} The results given in this paper were summarized very briefly at the Schenectady Cryogenics Conference.³ More recent x-ray diffraction studies of the f.c.c. and h.c.p. modifications of lanthanum metal using a Geiger-counter spectrometer indicate that the h.c.p. modification may contain stacking faults. This may explain, in part, the variations observed in the superconducting transition of the h.c.p. modification.

The second paper represents an extension of a paper presented at the International Conference on Low Temperature Physics⁴ (held at Oxford, England, in August, 1951) and of a later technical report.⁵

The work reported in the third paper is largely taken from a thesis⁶ submitted by Mr. R. A. Young for the M. S. degree in Physics at the Georgia Institute of Technology. Some of the results have been described in an earlier technical report.⁵ Subsequent powder diffraction studies made of the LaN preparations, using a Geiger-counter spectrometer to obtain more accurate relative line intensities than those previously obtained using film techniques, were in general agreement with the earlier results.

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Respectfully submitted:

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Herschel H. Cudd, Acting Director
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[CONTRIBUTION FROM THE GEORGIA INSTITUTE OF TECHNOLOGY]

The Crystal Structure and Superconductivity of Lanthanum^{1,2}

By W. T. ZIEGLER, R. A. YOUNG AND A. L. FLOYD, JR.

RECEIVED OCTOBER 3, 1952

The crystal structure of lanthanum has been studied by powder X-ray diffraction techniques at room temperature and the existence of the hexagonal close-packed (h.c.p.) and face-centered cubic (f.c.c.) modifications confirmed. The rate of interconversion of these crystal forms has been found to be slow. However, it has been shown that the f.c.c. modification can readily be converted to the h.c.p. structure at room temperature by severe deformation such as results when filings are produced from a massive specimen. The crystal structure of lanthanum filings in the h.c.p. form was not affected by cooling to liquid helium temperatures; the same result (with one possible exception) was noted with filings having the f.c.c. structure.

Six different samples of lanthanum have been examined for superconductivity by a magnetic method. It was found that bulk specimens cut from the six samples in the as-received state each exhibited a transition into superconductivity in the range 3.1° to 5.45°K. Heat treatment for four days at 350° raised the transition temperatures somewhat. The three purest samples all gave a transition temperature of very nearly 5.4°K. From X-ray diffraction studies made of the bulk specimens, together with studies made on filings, it was concluded that both the f.c.c. and h.c.p. modifications of lanthanum are superconductors, the f.c.c. modification having a transition temperature near 5.4°K., while the h.c.p. modification (in a strained state) has a transition temperature of 3.9°K. or greater.

Introduction

The relation between crystal structure and superconductivity in allotropic modifications of the elements has been investigated only for tin. As is well known, white tin is a typical superconductor, whereas gray tin (the stable form below 18°) is not a superconductor down to the lowest temperature tried (1.32°K.).³ These two forms of tin differ quite markedly in crystal structure, electrical conductivity, and in other physical properties. In particular, white tin is a typical metallic conductor; gray tin, on the other hand, is a semiconductor, its conductivity decreasing with decreasing temperature.⁴ As far as the authors are aware no semiconductor has been shown to exhibit superconductivity.⁵

A search for other elements having allotropic modifications which might be suitable for such a study revealed that lanthanum, cerium and praseodymium are reported to exist in both the cubic close-packed (f.c.c.) and hexagonal close-packed (h.c.p.) structures. Both of these structures would be expected to be good electrical conductors.

A survey of the literature made at the time the present work was begun showed that both lanthanum and cerium had been examined for superconductivity, of which only lanthanum was reported to be a superconductor (4.2–4.7°K.). The crystal structure of the materials investigated was not given. Recently cerium and praseodymium have been shown not to exhibit superconductivity down to 0.25°K.⁶ The crystal structure of the specimens investigated was not given.

The present paper is a report of work carried out to examine the relation between the crystal structure and superconductivity of lanthanum. This metal was chosen because of its availability from several sources in reasonably pure form and because it seemed to give promise of ready conversion from the

h.c.p. to the f.c.c. modification. The studies which have been made are presented in two parts. Part I deals with studies made of the crystal structure of lanthanum, particularly with the interconversion of the h.c.p. and f.c.c. modifications. Part II deals with the superconductivity studies made of the lanthanum specimens. The primary purpose of the structure studies was to aid in the characterization of the specimens tested for superconductivity.

Part I. Crystal Structure of Lanthanum

Lanthanum has been shown by powder X-ray diffraction techniques to exist in the hexagonal close-packed^{7,8,9} (h.c.p.) and face-centered cubic^{10,11} (f.c.c.) structure. Measurements of heat capacity,¹² electrical resistance,¹² coefficient of linear expansion¹³ and magnetic susceptibility¹⁴ as a function of temperature have revealed anomalies in these properties in several temperature regions. These anomalies suggest that lanthanum may exist in more than two allotropic modifications.

In the present work a study of the h.c.p. and f.c.c. modifications of lanthanum has been made using the powder X-ray diffraction method at room temperature. The studies made include the effect of various heat treatment conditions on the rate of transition from the h.c.p. to f.c.c. structure, the rate of transition of the f.c.c. to the h.c.p. structure at room temperature, and the effect of cooling to liquid nitrogen and helium temperatures.

Experimental

All but a few of the X-ray diffraction studies were carried out on lanthanum in the form of filings. A General Electric XRD-1 unit equipped with 14.32 cm. diameter powder cameras was used in all experiments. Filtered Cu K α radiation was generally used. Exposure times were 3–5 hours with 25 ma. and 35 kilovolts across the tube. A few diffraction pictures were taken with molybdenum radiation

(1) Carried out with the assistance of the Office of Naval Research under Contract N6-ori-192.

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thermore, filings carefully prepared and handled under helium gas to minimize lanthanum nitride formation gave the same results as those prepared under dry nitrogen. X-Ray diffraction photographs taken of the heat treated filings using molybdenum radiation, which is much less strongly absorbed than copper radiation, gave the same f.c.c. structure as did copper radiation. It has therefore been concluded that the f.c.c. modification is not a surface effect.

Interconversion of H.C.P. and F.C.C. Lanthanum. A. The Transition H.C.P. \rightarrow F.C.C.—The experiments of Zintl and Neumayr¹⁰ and Klemm and Bommer¹¹ suggest that the temperature for this transition is below 350°. Trombe and Foex¹² have measured the coefficient of linear expansion of lanthanum (99.2% La) over the range -190° to 650° . They found that the expansion was linear between -190° and 150° . Between 150° and 375° hysteresis developed, the volume at a given temperature depending upon whether the sample was being warmed or cooled. This hysteresis was attributed by them to the coexistence of the h.c.p. and f.c.c. forms, the h.c.p. being assumed to exist in the range -190° to 150° and the f.c.c. above 375° .

We have heated sealed Pyrex capillaries containing lanthanum filings (Cooper 1), known to be in the h.c.p. form, for two days in a vacuum furnace at 254° , 354° and 400° . The capillaries were cooled to room temperature in the furnace over a period of several hours. After heat treatment the capillaries were again examined by X-ray diffraction and the extent of the conversion to the f.c.c. structure noted. It was found that the filings heated at 254° consisted of the f.c.c. and h.c.p. forms in about equal amount, while those heated at 354° and 400° were predominantly f.c.c. with only a small amount of h.c.p. form. The h.c.p. lines were still relatively more diffuse than the lines for the f.c.c. structure. In a second series of experiments filings (Cooper 2) having the h.c.p. structure showed no noticeable change in diffraction pattern after four days at 150° , but showed almost complete conversion in two days at 400° .

Lanthanum filings heated in a molybdenum boat under high vacuum for four hours (Cooper 1) and 13 hours (Cooper 2) at 700° gave diffraction patterns very similar to those obtained with filings heated at $350-400^{\circ}$, except that no h.c.p. lanthanum appeared to be present. The "y" structure was still present.

In another experiment lanthanum filings (Spedding 2) having the h.c.p. structure were heated slowly to 290° over a period of 3.5 hours, held at $290-302^{\circ}$ for three hours and then cooled to room temperature in the course of several hours. X-Ray diffraction showed that the primary structure was still h.c.p. with a small amount of the f.c.c. modification now present.

From the experiments it was concluded that the transition from h.c.p. to f.c.c. structure begins in the range $150-254^{\circ}$ confirming the observations of Trombe and Foex,¹² proceeds rather slowly at 300° and even after four days at 400° a trace of h.c.p. may still be evident.

B. The Transition F.C.C. \rightarrow H.C.P.—The presence of a small amount of the h.c.p. modification in the predominantly f.c.c. filings after heat treatment at $350-400^{\circ}$ was thought possibly to be due to a small amount of conversion during the rather slow cooling in the furnace. However, no differences were noted between Cooper 2 filings cooled to room temperature rapidly (in a few seconds) and over a period of several hours. In each instance the filings had primarily the f.c.c. structure with a trace of the h.c.p. structure also present.

In order to examine the rate of change of the f.c.c. to the h.c.p. structure at room temperature capillaries containing filings from Cooper 1, Cooper 2 and the Hilger specimen were heat treated at 350° for four days, cooled to room tempera-

ture and powder X-ray diffraction photographs taken. All filings were f.c.c. with traces of h.c.p. and the "y" structure. The capillaries were stored at room temperature and examined at intervals over a period of a year. No noticeable changes occurred in the Cooper specimens, while the Hilger filings showed at most only a slight increase in the amount of the h.c.p. modification. No change could be detected in the "y" structure lines. Filings from Cooper 3, Spedding 1 and Spedding 2, heat treated in a similar manner, showed no change after 19, 31 and 9 months, respectively. Another set of capillaries containing Cooper 1, Cooper 2 and Hilger lanthanum, heat treated at 400° for four days, showed no changes over a 6-month period.

In another series of experiments capillaries containing Cooper 1 lanthanum filings known to be in the f.c.c. modification were heated for five days at 100° on the assumption that this treatment might introduce nuclei having the h.c.p. structure. The capillaries were then repeatedly cooled and warmed between -195° and room temperature by dipping in a liquid nitrogen bath. (Trombe and Foex¹² found this method satisfactory for converting cerium from the f.c.c. to the h.c.p. structure). Examination of the capillaries showed no change in the crystal structure of the filings. Similar results were obtained with filings heat treated at 200° and 250° .

These experiments all lead to the conclusion that the rate of transition of the f.c.c. to the h.c.p. modification is slow. On the other hand, severe deformation, such as filing, produced rapid transformation (see below).

Crystal Structure of Massive Lanthanum Specimens.—The structure studies so far described were primarily concerned with lanthanum filings. Experiments were also performed with massive lanthanum specimens in the form of small cylinders (approx. 5×20 mm.) since these were to be examined for superconductivity.

Examination of the literature reveals no instance in which the crystal structure of massive lanthanum has been determined. In our earlier experiments it was assumed that the structure of massive lanthanum specimens could be inferred from that of filings taken from the specimen in the "as-received" state and from filings heat treated simultaneously with the massive specimen. However, later experience showed that filings taken from massive specimens of all six lanthanum samples after heat treatment for four days at $350-400^{\circ}$ always gave primarily the h.c.p. structure with an occasional trace of the f.c.c. modification, whereas filings heat treated simultaneously with the specimen were predominantly f.c.c. A massive specimen (Cooper 1) cooled rapidly from 400° to room temperature gave the same results.

Efforts made to examine the end of a lanthanum piece in the form of a cylinder were not very successful, due to difficulties encountered in protecting the lanthanum surface from reaction with air. However, sufficiently satisfactory results were obtained to show that massive lanthanum specimens from all six samples were predominantly in the f.c.c. form after heat treatment at $350-400^{\circ}$. The surfaces examined were not mechanically strained by filing, etc., between the heat treatment and the X-ray examination. However, filings taken from these specimens or from specimens heat treated in a similar manner were always predominantly h.c.p.

In two instances (Specimen La 12, Cooper 3; and Specimen La 14, Spedding 2) the surface of a heat treated ($350-400^{\circ}$) specimen was examined both before and after roughening the surface by

(18) F. Trombe and M. Foex, *Ann. chim.*, **19**, 417 (1944).

TABLE III
 CRYSTAL STRUCTURE OF LANTHANUM SPECIMENS

Source	Specimen	Specimen dimensions, mm.	As-received condition	Crystal structure		Heat treatment	
				After heat treatment ^d		Days	Temp., °C.
Cooper 1	La 2	Cyl. 20.3 × 4.8	h.c.p. ^a				
	La 1	Cyl. 19 × 4.4	h.c.p. ^a	f.c.c. ^{b,c}		4	350
	La 4F	Powder	h.c.p.	f.c.c.		4	350
Cooper 2	La 6	Cyl. 12.3 × 4.1	h.c.p. ^a	f.c.c. ^{b,e}		4	350
	La 7	Cyl. 11.4 × 4.2	h.c.p. ^a	f.c.c. ^e		4	700
Cooper 3	La 10	Cyl. 19 × 4.4	h.c.p. ^a	f.c.c. ^{b,f}		4	350
Spedding 1	La 1S	Cyl. 9.8 × 4.4	h.c.p. ^a	f.c.c. ^{b,f}		4	350
	La 2S	Cyl. 9.9 × 4.4		f.c.c. ^b		4	350
Spedding 2	La 15	Cyl. 20 × 4.4	h.c.p. ^{a,f}				
	La 14	Cyl. 25 × 4.4		f.c.c. and some h.c.p. ^{b,f}		4	350
Hilger	La 3	Rect. piece 4 × 11.5 × 2.6	h.c.p. ^a	f.c.c. ^{b,e}		4	350

^a Structure of filings taken from specimen before low temperature experiment. ^b Structure of filings heat treated simultaneously with specimen. ^c Structure of massive specimen from same source heat treated in similar manner but at a different time. ^d Filings taken from massive specimens after heat treatment always had h.c.p. structure, due, it is believed, to the conversion of f.c.c. to h.c.p. modification as result of the filing operation. ^e Structure after cooling to 2°K.; another unidentified structure, presumably the result of surface oxidation, also present. ^f Structure of massive specimen after cooling to 4.2°K. ^g Structure of massive specimen before cooling.

temperature, coil S1 and the coil surrounding the specimen (for example S2) were connected externally in such a manner that on closing the primary circuit the voltages induced in the coils opposed each other. A galvanometer in the secondary circuit ordinarily gave a deflection when the primary was energized. This deflection could be reduced to zero by suitable adjustment of an external variable inductance in the secondary circuit.

With the secondary circuit balanced, the primary circuit was energized at 10–15-second intervals during a series of measurements in which the temperature of the experimental chamber was slowly lowered (or raised); any unbalancing of the coils arising from the occurrence of superconductivity in the specimen was observed as a galvanometer deflection. From the variation of deflection with temperature the course of the transition could be followed. The maximum deflection depended upon the magnitude of the primary current and the volume of the specimen. With the primary current (0.26–0.27 amp.) and the specimen size (1.2–1.8 g.) usually used, galvanometer deflections of 3–5 cm. were observed when a specimen became superconducting.

In the range 6 to 4.2°K. cooling of the specimen was achieved by allowing the helium pressure in the experimental chamber to decrease slowly to atmospheric pressure. Temperatures below 4.2°K. were obtained by pumping on the experimental chamber. Warming was achieved by allowing the experimental chamber to warm up as a result of heat leak or, in later experiments, by means of a heater wound on the lower end of the experimental chamber. This heat leak was due primarily to the copper lead wires leading to the experimental chamber which were in imperfect contact with the main helium reservoir. The heat leak was largely eliminated in the later experiments by a rearrangement of the copper leads.

The lanthanum specimens usually were approximately cylindrical in shape. They had weights varying from 0.7 to 2.5 g., and usually had a length of 20–22 mm. and a diameter of 4.5–4.9 mm. To prevent air oxidation each specimen was sealed at room temperature in a small capsule (made of 7 mm. Pyrex glass tubing) under helium gas at 10–20 cm. pressure. The capsules (usually three) were separated by Lucite spacers, and the entire assembly held together with cellulose acetate cement. The spacers were so constructed that each specimen was positioned approximately at the center of its secondary coil.

Experimental Results

The physical dimensions and heat treatment of the various specimens tested for superconductivity are summarized in Table III. Table IV summarizes the results of the tests for superconductivity. The transition range given in Table IV corresponds to the temperature interval in which at least 95% of the total galvanometer deflection arising from the magnetic transition occurred. The transition temperature given corresponds to the temperature at which one-half of the total deflection was noted. Readings of the deflection

 TABLE IV
 SUPERCONDUCTIVITY OF LANTHANUM SPECIMENS

Source of lanthanum	Specimen designation	As-received condition		After heat treatment	
		Transition temp., °K.	Transition range (deg.)	Transition temp., °K.	Transition range (deg.)
Cooper 1	La 2	5.05	0.15		
	La 1	5.0	.1	5.2	0.1
	La 4F	3.9	.3	5.25	.3
Cooper 2	La 6			3.2	.2
	La 7	3.1	.3	3.2	.2
Cooper 3	La 10	3.55	.22	4.2	.07
Spedding 1	La 1S	5.2	.2	5.4	.15
	La 2S			5.3	0.6–0.8
Spedding 2	La 15	5.45	.3		
	La 14			5.5	.25
Hilger	La 3	4.6	ca. .1	5.4	.1

were reproducible to about 1 mm. when the specimen was maintained at a fixed temperature. In general, the midpoint of the transition has been computed from the gas thermometer reading. The transition range, as well as the warming and cooling rates, were computed from the resistance thermometer readings. Warming and cooling rates of 0.1–0.25° per minute were usually employed.

Figures 1 and 2 show typical transition curves. In these plots the fraction of the total galvanometer reflection resulting from the transition into superconductivity has been expressed as a per cent. change in magnetic induction. In a number of instances the transition curve found on cooling lay 0.05–0.1° below that obtained on warming. In other instances no consistent differences were noted. It is not clear whether these differences represent an actual hysteresis in the transition or resulted from temperature inequalities. However, on the basis of the rapidity of response of the specimen to temperature variation when in the transition, it is believed that much of this difference represents a temperature gradient between the thermometers and the specimen.

Discussion of Results

The occurrence of superconductivity in lanthanum was first observed by Mendelssohn and Daunt²⁴ using a magnetic method. These investigators reported a transition temperature of 4.71°K. for a specimen reported to contain 98% La, 1% Fe, and traces of C, Si, Al and Mg. Shoenberg,²⁵ also using a magnetic method, has reported that a

(24) K. Mendelssohn and J. G. Daunt, *Nature*, **139**, 473 (1937).

(25) D. Shoenberg, *Proc. Camb. Phil. Soc.*, **33**, 577 (1937).

due to the differing purities of the materials. The occurrence of lanthanum hydride in these samples (as indicated both by X-ray diffraction and from the method of preparation of the metal) suggested that the lower transition temperature of the Cooper 2 sample might be due to the presence of hydrogen, since it has been shown that lanthanum hydride ($\text{LaH}_{2.45}$) is not a superconductor down to 1.8°K .²⁹ However, heat treatment of La 7 in high vacuum for four days at 700° resulted in no marked change in the superconducting transition temperature or the width of the transition, although this treatment has been found adequate

(29) W. T. Ziegler and R. A. Young, *Proc. Int. Conf. on Low Temperature Physics*, Oxford, England, August, 1951, p. 124.

to convert lanthanum hydride to lanthanum metal.³⁰

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Studies of Compounds for Superconductivity*†

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A number of metal carbides, borides, nitrides, and a hydride, in the form of powders, have been examined for superconductivity down to 1.8°K using a magnetic method. The substances tested were TiC, VC, ZrC, TaC, WC, ZrB₂, NbB₂, TaB₂, WB, MoB, TiB₂, ThB₂, LaN, CeN, NbN, and LaH_{2.45}. All specimens were characterized by x-ray diffraction methods and, in most instances, by chemical analysis. Of these substances only NbN gave evidence for superconductivity. The results for NbN are in general agreement with the work of others. The results for TiC and VC are in agreement with those found by Meissner *et al.*, using an electrical resistance method, while those for TaB₂, NbB₂, WC, and WB are in agreement with observations made by Matthias and Hulm using a magnetic method. On the other hand, ZrC, TaC, WC, and "zirconium boride" had previously been observed to exhibit superconductivity above 1.8°K by the electrical resistance

method. The results for WC and MoB have recently been confirmed by Matthias and Hulm. The substances ThB₂, LaN, CeN, and LaH_{2.45} had not previously been examined for superconductivity.

Particle size measurements were made on the carbide and boride powders. The particles were large enough that magnetic field penetration effects should have caused no difficulty, if a penetration depth of 1×10^{-6} cm, observed for pure metal, is assumed to apply to the present compounds.

The failure to observe superconductivity in the substances ZrC, TaC, WC, and MoB in the present study is discussed in terms of a postulated physical distribution of superconducting impurities of undetermined composition which are assumed to account for the superconductivity observed in these compounds by other investigators.

INTRODUCTION

THE occurrence of superconductivity in binary compounds containing a metal and a nonmetal has been known for more than twenty years as a result of the extensive work of Meissner and his co-workers.¹⁻³ A survey of the literature has shown that in many instances the occurrence of superconductivity in compounds has been observed by studying the change of electrical resistance with temperature. In all instances in which superconductivity was observed by this means, the electrical resistance of the substance was found to decrease with temperature from room temperature to the transition temperature in the manner characteristic of metals.^{4,5} Most of the compounds found to exhibit superconductivity are binary compounds between superconducting metals and boron, carbon, or nitrogen. On the other hand, the carbides of tungsten and the carbides, a boride, and two nitrides of molybdenum also show superconducting behavior, even though the pure metals do not become superconducting at the lowest temperature tried ($< 1^\circ\text{K}$).

The difficulty of preparing these compounds in pure form has presented the possibility that the observed superconductivity may arise from superconducting filaments (either of the parent metal or a compound) present in the specimen rather than from the bulk specimen itself. This doubt has suggested the re-examination of these substances by means of magnetic

methods, since, as Shoenberg has pointed out,⁶ these methods should yield information concerning the behavior of the entire volume of the specimen, rather than of possible superconducting filaments.

Relatively little work has been published on the magnetic transition into superconductivity in compounds and in certain metals which are difficult to purify. Titanium specimens of various purities have been reported to have transition temperatures ranging from 1.13° to 1.77°^{2,7,8} when examined by the electrical resistance method, whereas other specimens of titanium of high purity, examined by magnetic methods, have either failed to exhibit superconductivity down to 1°K⁹ or exhibited superconductivity only at much lower temperatures (0.53°K).¹⁰ A similar situation has been reported for uranium.^{6,11}

Recently Matthias and Hulm,⁵ in an extensive survey of the occurrence of superconductivity in compounds examined by the magnetic method, have confirmed the occurrence of superconductivity in a number of compounds in which it has previously been observed using the electrical resistance test, but failed to find the effect in WC in which it had previously been observed by the resistance method.

Studies have been in progress in this laboratory for some time to re-examine by a magnetic induction method a number of compounds previously examined for superconductivity by the electrical resistance method. A number of compounds not previously tested for superconductivity are also being studied. The present paper deals with the results of studies made on fifteen metal carbides, borides, nitrides, and a hydride.

* Carried out with the assistance of the U. S. Office of Naval Research.

† Based on a paper presented at the International Conference on Low Temperature Physics, Oxford, England, August 22-28 (1951).

¹ W. Meissner and H. Franz, Z. Physik 65, 30 (1930).

² Meissner, Franz, and Westerhoff, Ann. Physik (5) 13, 555 (1932).

³ Meissner, Franz, and Westerhoff, Z. Physik 75, 521 (1932).

⁴ W. T. Ziegler, Research Engr. IX, No. 1, 15 (1947).

⁵ B. T. Matthias and J. K. Hulm, Phys. Rev. 87, 799 (1952).

⁶ D. Shoenberg, Nature 159, 303 (1947).

⁷ W. Meissner, Z. Physik 60, 181 (1930).

⁸ W. J. de Haas and P. M. van Alphen, Proc. Acad. Sci. Amsterdam 34, 70 (1931).

⁹ D. Shoenberg, Proc. Cambridge Phil. Soc. 36, 84 (1940).

¹⁰ J. G. Daunt and C. V. Heer, Phys. Rev. 76, 715 (1949).

¹¹ B. B. Goodman and D. Shoenberg, Nature 165, 441 (1950).

ties of these materials is given in another place.¹⁹ The nitrides examined had the approximate formula $\text{LaN}_{0.97}$ (Cooper 2, Expt. 26), $\text{LaN}_{0.94}$ (Spedding 1, Expt. 29), and $\text{CeN}_{0.87}$.

The niobium nitride²⁰ was prepared by heating niobium metal powder (Fansteel, 99.9 percent Nb) for 4 to 4½ hours at 1500°C in pure dry nitrogen. X-ray examination showed it to be primarily NbN with $a_0 = 4.37 \pm 0.01$ kx-units.²¹ A trace of Nb and/or Ta metal appeared to be present. A large number of faint to very faint lines could not be identified. These lines did not fit the pattern for Nb₂N reported by Brauer.²²

The lanthanum hydride was prepared by direct combination between lanthanum metal filings and pure dry hydrogen gas at 210–290°C. The method used was similar to that employed for the nitride. The product examined for superconductivity had the composition $\text{LaH}_{2.45}$. Muthmann and Kraft²³ and Rossi,²⁴ using a similar method, have reported similar products having the approximate formulas LaH_3 and $\text{LaH}_{2.4}$, respectively. The hydride had an fcc lattice with $a_0 = 5.625 \pm 0.007$ kx units in good agreement with the value of 5.62–3 kx units reported by Rossi.²⁴

EXPERIMENTAL METHOD

The cryostat and measuring apparatus used was similar to that described by Horn and Ziegler.²¹ The apparatus, the temperature scale and the magnetic method employed to detect superconductivity have been described elsewhere.²⁵ Briefly, the apparatus consisted of a heavy walled copper vessel in which liquid helium was produced by the Simon expansion method. From the main helium reservoir was suspended the experimental chamber, into which helium could be condensed at will by bringing low pressure helium into contact with the main helium reservoir. The copper experimental chamber consisted of two parts, an upper section to which the thermometers were attached, and a lower section in which the specimens to be tested for superconductivity were located and on the outside of which the coils for detecting superconductivity were wound.

The temperature of the experimental chamber was measured by means of a helium gas thermometer of the type described by Mendelssohn,²⁶ except that the helium pressure was measured both by a Bourdon gauge and a capillary mercury manometer. The thermometer was

TABLE III. Superconductivity of metal carbides.

Carbide	Major constituent	Transition temp. ^a and range, °K		Method ^c
		This research	Lit.	
TiC _{0.95}	TiC	(1.8) ^b	1.1 (?) (1.31)	R ^d R ^e
VC _{0.92}	VC	(1.8)	(1.33)	R ^d
ZrC _{0.86}	ZrC	(1.8)	3.7 3.3–4.1	R ^e
TaC _{0.98}	TaC	(1.8)	9.3, 9.2–9.4 7.6–9.5	R ^d R ^e
WC _{0.99}	WC	(1.8)	3.4, 2.5–4.0 (1.28)	R ^d M ^f

^a Temperature corresponding to 50 percent of total resistance change in transition.

^b Temperature in parentheses means substance not superconducting down to this temperature.

^c R = electrical resistance method; M = magnetic method.

^d See reference 1.

^e See reference 3.

^f See reference 5.

calibrated by using the boiling points of hydrogen and helium and the triple point of hydrogen as fixed points. Gas imperfection was taken into account by making use of the virial coefficients given by Keesom.²⁷ The absolute accuracy of the temperature scale is believed to be about 0.05° in the range below 5°K, 0.1° in the range 5–7°K and 14–20°K, and a few tenths of a degree in the range between 7° and 14°K.

A constantan resistance thermometer, having a sensitivity of 0.01–0.02°, also was used to follow the temperature changes of the experimental chamber.

The magnetic system used for detecting superconductivity essentially measured the change in inductance produced when the specimen became superconducting. This change in inductance was measured as a galvanometer deflection produced when the primary circuit was momentarily energized. The circuits were so arranged that the galvanometer deflection could be reduced to zero at will by the suitable adjustment of a compensating inductance.

The powdered samples were generally mounted in a 7 mm o.d. Pyrex glass tube, partly open at the top end, and were in direct contact with the helium. In a few instances (TiC, VC, $\text{LaH}_{2.45}$, CeN, and LaN), the measurements were made on samples in Pyrex capsules sealed at room temperature under 20 cm Hg pressure of helium. The samples had weights varying from 0.7 to 2.5 g, and usually had a length of 20–22 mm and a diameter of 4.5–4.9 mm.

EXPERIMENTAL RESULTS

The experimental results for the various compounds tested are summarized in Tables III and IV, together with the results of other investigators.^{1,3,5,28,29} In these tables the major constituent given is that found by

¹⁹ R. A. Young and W. T. Ziegler, J. Am. Chem. Soc. 74, 5251 (1952).

²⁰ This material was prepared by Dr. F. H. Horn, General Electric Co., Schenectady, N. Y., as part of a cooperative study on Nb-Ta alloys and their nitrides.

²¹ F. H. Horn and W. T. Ziegler, J. Am. Chem. Soc. 69, 2762 (1947).

²² G. Brauer, Z. Elektrochem. 46, 397 (1940).

²³ W. Muthmann and K. Kraft, Ann. Chem., Justus Liebig 325, 266 (1902).

²⁴ A. Rossi, Nature 133, 174 (1934).

²⁵ W. T. Ziegler and R. A. Young, J. Am. Chem. Soc. March, 1953.

²⁶ K. Mendelssohn, Z. Physik 73, 482 (1931).

²⁷ W. H. Keesom, Helium (Elsevier Publishing Company, New York, 1942), p. 49.

²⁸ J. K. Hulm and B. T. Matthias, Phys. Rev. 82, 273 (1951).

²⁹ Aschermann, Friederich, Justi, and Kramer, Physik. Z. 42, 349 (1941).

as roughly spherical. The particle size distribution observed is expressed in Table V in terms of the median diameter, d_g , and the geometric standard deviation, σ_g .³⁴ Calculations show that at least 50 percent of the total volume of all boride and carbide powders consisted of particles having diameters greater than one micron. It will be noted that the MoB, ZrC, and WC specimens consisted of relatively large particles. Electron-microscopic examination of the TaC powder showed that it contained a considerable fraction below one micron in size. Microscopic examination of the NbN powder showed that it was considerably coarser than the carbide and boride powders, at least 50 percent of all particles having a diameter greater than 15 microns.

The field penetration depth in powders of alloy systems such as the carbides and borides has apparently not been investigated. If one takes for the penetration depth the rough value of 1×10^{-5} cm observed in metals,³⁵ it would appear that the values of d_g for all substances studied was sufficiently large so that field penetration would not be expected to play a significant role in the present measurements.

The disagreement between the results of the present work and those of Meissner and co-workers^{1,3} regarding the occurrence of superconductivity in TaC, WC, and ZrC might be explained, as Shoenberg^{6,9} has suggested for titanium and uranium, by assuming the presence of superconducting filaments in Meissner's specimens of these carbides. Another possibility is that the transition temperatures of our carbide specimens were lowered by strain to a temperature below that reached in our experiments (1.8°).³⁶

Hudson,³⁷ using the magnetic induction method, has made an interesting study of two Sn—Ge "alloys" containing 2.3 and 9.3 atomic percent of tin, respectively, in which the tin was concentrated along the grain boundaries. These materials gave a rather broad diamagnetic transition beginning at 4°K. Hudson attributed this behavior to the presence of superconducting filaments of tin. Calculations by him indicated that approximately 50 percent of the volume of the alloy of lower tin content and the entire volume of the alloy of higher tin content participated in the magnetic transition.

In view of these observations of Hudson on the Sn—Ge alloys, it would appear that the precise physical structure of the "superconducting filaments" might be an important variable. Thus, if the filaments are thread-

TABLE V. Particle size measurements.

Substance	Borides		Substance	Carbides	
	d_g^a microns	σ_g^b		d_g microns	σ_g
NbB ₂	0.8	2.0	TaC	0.8	1.6
ThB ₂	1.1	1.4	TiC	1.3	1.9
WB	1.2	1.4	VC	1.6	2.1
TaB ₂	1.4	1.5	ZrC	2.1	2.4
TiB ₂	1.5	1.6	WC	2.6	2.7
ZrB ₂	1.5	2.1			
MoB	1.7	1.9			

^a d_g = median diameter.

^b σ_g = geometric standard deviation.

like, superconductivity might be observed electrically but not magnetically. On the other hand, if the superconducting filaments possess a sponge-like structure,³⁸ with the bulk material in the holes of the sponge, as in the Ge—Sn alloy experiments of Hudson, then both an electrical and a magnetic transition might be observed. The physical structure of such filamentous inclusions might be expected to depend considerably on the method of preparation of the compound and the nature of the impurity.

The disagreement between the earlier magnetic results of Hulm and Matthias²⁸ and the present work regarding the superconductivity of MoB appears to have been due to some such sponge-like distribution of a superconducting inclusion (Mo₂B).⁵ A similar explanation has been advanced³⁹⁻⁴¹ to account for the conflicting magnetic observations of Darby *et al.*⁴² and Hudson^{39,40} regarding the superconductivity of PbS.⁴³

The possibility that superconductivity in many compounds may be due to rather specific amounts of trace impurities, distributed in a homogeneous manner through the bulk material, which makes possible a superconducting state has not been excluded.

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³⁸ K. Mendelssohn, Proc. Roy. Soc. (London) A152, 36 (1935).

³⁹ R. P. Hudson, Proc. NBS Semicentennial Symposium on Low Temperature Physics, Natl. Bur. Standards, Washington, D. C. March 27-29, 1951 [National Bureau of Standards Circular 519 (1952), p. 61].

⁴⁰ R. P. Hudson, Proc. Phys. Soc. (London) A64, 751 (1951).

⁴¹ Hatton, Rollin, and Seymour, Proc. Phys. Soc. (London) A64, 667 (1951).

⁴² Darby, Hatton, and Rollin, Proc. Phys. Soc. (London) A63, 1181 (1950).

⁴³ This explanation came to our attention after the presentation of our paper at the Oxford Conference.

³⁴ J. M. DallaValle, *Micromeritics: The Technology of Fine Particles* (Pitman Publishing Company, New York, 1948), Chapter 3.

³⁵ F. London, *Superfluids* (John Wiley and Sons, Inc., New York, 1950), Vol. I, pp. 46, 89.

³⁶ The crystallite size may be a more important factor than the particle size in determining the effects of field penetration. The lines of the x-ray diffraction pattern for TaC were all quite diffuse indicating a small crystallite size; on the other hand, those for WC and ZrC were quite sharp.

³⁷ R. P. Hudson, Phys. Rev. 79, 883 (1950).

[CONTRIBUTION FROM STATE ENGINEERING EXPERIMENT STATION, GEORGIA INSTITUTE OF TECHNOLOGY]

Crystal Structure of Lanthanum Nitride^{1,2}

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Lanthanum nitride has been prepared by direct combination between lanthanum metal and nitrogen to yield a product having approximately the composition LaN. The crystal structure of LaN has been shown to be of the NaCl type, confirming the earlier work of Iandelli and Botti.³ The powder X-ray diffraction patterns of LaN and face-centered cubic lanthanum metal have been shown to be demonstrably different. The dissociation pressure of LaN was found to be very small at 900°. The lanthanum nitride specimens gave no evidence of superconductivity down to 1.8°K.

During the course of a study of the occurrence of superconductivity in compounds it became of interest to examine lanthanum nitride for possible superconductivity. This substance has been reported³ to have the NaCl-type structure, but no data were given for the chemical composition of the substance examined. It is the purpose of the present paper to report on the crystal structure of several specimens prepared under carefully controlled conditions. Two different specimens were examined for superconductivity, using a magnetic method similar to that employed by Horn and Ziegler.⁴ No evidence of superconductivity was found down to 1.8° K., the lowest temperature used. The details of the low temperature experiments will be reported in another place.

Preparation of Lanthanum Nitride

The lanthanum nitride specimens were prepared by a modification of the direct combination-method described by Muthmann and Kraft,⁵ since this method appeared most likely to yield a pure product.

The nitriding apparatus consisted of a quartz tube vacuum furnace, connected to a high vacuum oil diffusion pump. The apparatus was also equipped with a 100-ml. water-jacketed mercury-filled gas buret, by means of which a known amount of dry nitrogen could be introduced into the system. Proper manipulation of the buret permitted the pressure of the nitrogen in the furnace to be maintained at about one atmosphere during nitrogen absorption, and also permitted the rate of nitrogen absorption to be followed. The nitrogen remaining after completion of the reaction could be removed by means of a Toepler pump and its volume determined.

The reaction was carried out using several tenths of a gram of lanthanum-filings prepared from the bulk metal by filing in a dry helium or nitrogen atmosphere. In a preliminary experiment it was ascertained that filings exposed for six days to dry nitrogen at room temperature showed no weight increase within experimental error (equivalent to 1.5 atomic % nitrogen). Molybdenum combustion boats were used, copper boats having been found to be unsatisfactory. The dry nitrogen used was a special grade obtained from the Air Reduction Company stated to contain 0.10% oxygen. It was passed over copper at 600° and through a liquid nitrogen trap before being metered into the furnace.

The lanthanum used was obtained from two sources. Specimen A (Table I) was obtained from Cooper Metallurgical Associates, Cleveland, Ohio. It was analyzed by spectrographic and spectrophotometric methods, by direct precipitation as the oxalate and by ion-exchange techniques. Consideration of the results obtained by these methods led to the figure 97.5% lanthanum as being representative of the rare earth content; of this 1.1% was cerium, 0.4% neodymium, 0.2% praseodymium and 0.2% other rare earths. The metal also contained about 0.7% silicon, 0.8% iron and some carbon.

Specimen B was obtained from Dr. F. H. Spedding, Iowa State College, Ames, Iowa. Spectrographic analysis showed that it contained 0.13% beryllium, 0.1% magnesium, traces of calcium, aluminum, and iron and was free of other rare earths. Direct precipitation as the oxalate gave a lanthanum content of 97.3%. However, in view of the high purity of this material the lanthanum content has been arbitrarily taken to be 100%.

No chemical analyses of the lanthanum specimens for carbon, nitrogen, oxygen or hydrogen were made. The presence of carbon was inferred from the acetylene-like odor (more pronounced in the Cooper specimen) given off when the filings were dissolved in dilute hydrochloric acid. However, X-ray diffraction analysis of the metal filings showed that all except a few very faint lines were assignable to either a cubic close-packed or hexagonal close-packed lanthanum structure.

The calculation of x in the formula LaN_x was based on these lanthanum contents. Cerium, praseodymium and neodymium have also been reported to form nitrides with the approximate formula $\text{MN}_{0.8}$.⁶

The reaction was carried out as follows. A weighed amount of filings was degassed by pumping at 10^{-6} mm. for several hours at room temperature. The nitrogen gas was then admitted, and the electric furnace turned on. After about one hour the furnace temperature had risen to 600° at which temperature the reaction began. The reaction proceeded to approximate completion in two to four hours at 750° and in one to two hours at 900°. The reaction chamber was usually kept at 900° for about 20 hours to ensure complete reaction. After cooling to room temperature (the pressure being maintained at approximately one atmosphere by suitable manipulation of the mercury level in the buret) the nitrogen remaining was determined volumetrically and the reaction product was weighed.

The lanthanum filings and nitride products were always handled in such a manner as to protect them from contact with air, since both materials react with moist air.

The details of the several preparations are shown in Table I. The results corresponded rather closely to the formula LaN , although the value of x in the formula LaN_x was in all instances somewhat less than unity. The presence of several per cent. of lanthanum carbide, oxide, nitride or hydride in the metal could account in part for this discrepancy.

The over-all accuracy of the volume measurements was estimated to be about 1%, based on separate control experiments. Weights were reproducible to ± 0.3 mg. It will be noted that the values of x calculated from the volumetric measurements were 4 to 8% smaller than the gravimetric values. The reason for this is not clear. Desorption of gases from the specimen and the apparatus would appear to be ruled out since in Expt. 25 the metal filings were heated in a high vacuum for four hours at 600°, cooled in helium and reweighed before nitriding. The observed change in weight was 0.1 mg. The evolution of hydrogen gas at 900° from any lanthanum hydride present in the metal filings might account for the discrepancy, since the hydride is known (unpublished results by us) to decompose at 700° in a high vacuum.

The lanthanum nitride products were loose black powders which liberated ammonia on exposure to air, in agreement with the observations of Muthmann and Kraft⁵ and Neumann, *et al.*⁷ However, the nitridation reaction was found

(1) This work was carried out with the assistance of the Office of Naval Research under Contract N6-ori-192.

(2) From the M.S. thesis in physics of R. A. Young, December, 1950.

(3) A. Iandelli and E. Botti, *Atti accad. nazl. Lincei. Classe sci. fis. mat. e nat.*, **25**, 129 (1937).

(4) F. H. Horn and W. T. Ziegler, *THIS JOURNAL*, **69**, 2762 (1947).

(5) W. Muthmann and K. Kraft, *Ann.*, **325**, 262 (1902).

(6) A. Iandelli and E. Botti, *Atti accad. nazl. Lincei. Classe sci. fis. mat. e nat.*, **25**, 638 (1937).

(7) B. Neumann, C. Kroeger and H. Kunz, *Z. anorg. u. allgem. Chem.*, **207**, 133 (1932).

somewhat better than for the other two types. In order to examine this agreement more critically the relative intensities were replotted as ratios of the intensity of each line in a set to the intensity of the line with next larger θ . These data are given in Table III.

TABLE III
INTENSITY RATIOS

Miller indices of lines involved	Theoretical ratios of LaN			Average observed ratios		
	NaCl type	ZnS type	Random type ^a	LaN ratio	LaN mean deviation	f.c.c. La ^b
111/200	1.05	1.91	1.51	1.06	0.04	1.80
200/220	0.72	0.49	0.71	0.65	.10	0.61
220/311	0.81	0.69	0.59	0.74	.02	.54
311/222	2.42	3.86	3.27	1.99	.28	3.19
222/400	1.54	1.13	1.53	1.81	.13	1.66
400/331	0.36	0.31	0.27	0.39	.01	0.31
331/420	0.78	1.18	1.02	0.78	.05	0.97
420/422	1.03	0.78	1.01	1.03	.10	1.34
422/ $\left(\begin{smallmatrix} 511 \\ 333 \end{smallmatrix}\right)$	0.94	0.81	0.73	0.90	.01	0.71
$\left(\begin{smallmatrix} 511 \\ 333 \end{smallmatrix}\right)$ /440	1.78	2.05	2.30	2.21	.17	2.70
440/531	0.26	0.23	0.21	0.28	.02	0.28
531/ $\left(\begin{smallmatrix} 600 \\ 442 \end{smallmatrix}\right)$	1.17	1.71	1.49	1.26	.04	1.53
$\left(\begin{smallmatrix} 600 \\ 442 \end{smallmatrix}\right)$ /620	0.89	0.69	0.89	0.88	.08	0.98
620/533	.87	.76	.67	.89	.10	.80
533/622	.66	.97	.86	.80	.10	.75

^a Same as f.c.c. lanthanum metal. ^b Observed for f.c.c. modification of lanthanum metal.

Examination of the data in Table III shows that the observed intensity ratios are most nearly in agreement with those calculated for the NaCl type. It was concluded, therefore, that lanthanum nitride has this crystal structure. This is in agreement with the result reported by Iandelli and Botti.^{3,11} However, these investigators did not consider any random types, and seemingly made a slight error in the calculation of the relative intensities for the ZnS type.¹²

It is interesting to note that, as Iandelli and

(11) A preliminary study of a sample of cerium nitride prepared under similar conditions and having the formula CeN_{0.87} showed this nitride to have a f.c.c. structure with $a_0 = 5.01$ kx. units, in good agreement with the observation of Iandelli and Botti.³

(12) A. Iandelli and E. Botti, *Atti accad. nazl. Lincei. Classe sci. fis. mat. e nat.*, **24**, 465 (1936).

Botti³ have pointed out, lanthanum nitride and the f.c.c. modification of lanthanum have very nearly identical values of a_0 . Thus, a specimen of f.c.c. lanthanum prepared by heat treatment¹³ at 350° for four days showed an a_0 of 5.291 ± 0.003 kx. units, compared to 5.284 ± 0.004 kx. units for the nitride. Because of this fact the X-ray method used here can give no information about the presence of free lanthanum metal in the lanthanum nitride. More precise measurements are planned with a Geiger counter spectrometer.

Rossi¹⁴ noted that the f.c.c. modification of lanthanum seemed to be only a surface effect. Iandelli and Botti³ suggested that, since the lattice parameters were the same, the pattern previously ascribed to f.c.c. lanthanum might actually be due to a surface formation of lanthanum nitride. These suggestions were investigated (1) by visually comparing a large number of films registering the pattern from a material believed to be f.c.c. lanthanum with the films from the nitride samples and (2) by measuring and comparing the observed relative intensities of the f.c.c. lanthanum films in the same way that comparisons were made for the nitride. The data for the quantitative comparisons are also listed in Table III. The comparisons showed that f.c.c. lanthanum yields a powder diffraction pattern having relative line intensities that are detectably, although slightly, different from those of the nitride pattern. The most obvious difference, which may be seen at a glance, occurs in the relative intensities of the first two lines of the patterns. The data also show that the observed relative intensities for f.c.c. lanthanum agree better with those calculated for f.c.c. lanthanum than with those calculated for either NaCl or the ZnS-type nitride.

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(13) See E. Zintl and S. Neumayr, *Z. Elektrochem.*, **39**, 84 (1933).

(14) A. Rossi, *Nature*, **133**, 174 (1934).

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