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ENGINEERING EXPERIMENT STATION
of the Georgia Institute of Technology
Atlanta, Georgia

STATUS REPORT NO. 28

PROJECT NO. 116-18

INVESTIGATION OF FUNDAMENTAL PROPERTIES OF ELEMENTS AND THEIR COMPOUNDS INCLUDING THE RARE METALS AT VERY LOW TEMPERATURES WITH PARTICULAR EMPHASIS UPON SUPERCONDUCTIVITY

by

W. T. KINZER

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NAVY DEPARTMENT, OFFICE OF NAVAL RESEARCH
CONTRACT NO. N6-ori-162, TASK ORDER I
NR 016-406

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MARCH 31, 1953

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I. SUMMARY

Work on the construction of an adiabatic calorimeter for heat capacity studies in the range 15°-360° K. is progressing satisfactorily. A cryostat for the calibration of platinum thermometers to be used in the calorimeter is under construction.

Geiger-counter spectrometer measurements of the relative line intensities of lanthanum nitride (LaN) and β-(f.c.c.) lanthanum have been made which are in general agreement with the results obtained earlier using less accurate film techniques.

A research paper entitled "Crystal Structure and Superconductivity of Lanthanum" has been published in The Journal of the American Chemical Society 75, 1215 (1953).

II. LOW-TEMPERATURE RESEARCH

A. Low-Temperature Calorimeter

Further progress has been made on the construction and instrumentation of the adiabatic shield calorimeter mentioned in earlier status reports.[3,4] This calorimeter is to be used to measure the heat capacities of rare earth compounds, particularly lanthanum oxide (La_2O_3) and neodymium oxide (Nd_2O_3), over the range 15° to 360° K.

A precision platinum thermometer of the Meyer's type,[1] made by Leeds and Northrup Company, has been calibrated for us by the National Bureau of Standards on the International Temperature Scale down to 90° K. and by comparison against the NBS temperature scale from 90° to 10° K. This thermometer will serve as the primary temperature standard for the calorimeter. Three platinum resistance thermometers to serve as secondary standards

are under construction. These will be calibrated by comparison with the primary thermometer at a number of points in a suitable cryostat now under construction.

III. CRYSTAL STRUCTURE STUDIES

X-ray diffraction methods have been, and are being, used* wherever possible to characterize substances under study for superconductivity and heat capacity measurements. Additional measurements which have recently been completed are described below.

A. Crystal Structure of Lanthanum Nitride (LaN) and β-Lanthanum

In a previous publication[2] the intention was announced of using a newly acquired Geiger counter spectrometer to obtain more accurate measurements of relative line intensities than had been obtained with film techniques. Such measurements have now been made. The equipment used was the North American Philips "High and Low Angle Wide Range X-ray Spectrometer-Goniometer," with automatic recording and copper radiation, together with a specially devised specimen holder designed to prevent contact of the powder specimen with air.

The results for lanthanum nitride are in general agreement with those obtained with film techniques, i.e., the pattern observed for $LaN_{0.95}$ (Experiment 25[2]) is more like that calculated for an NaCl-type LaN lattice than for a ZnS or random type. However, the agreement is not as good as might be expected. This lack of agreement may indicate false assumptions in the method of calculating the relative line intensities, or it may

*Such measurements and their analysis have been largely the work of Mr. R. A. Young, who is presently in charge of the X-ray Laboratory of the Engineering Experiment Station.

indicate that the experimental sample was not exactly an NaCl structure, even though it approximated this structure. The lack of agreement could not be accounted for by experimental error in the measurements, but could conceivably, although not probably, result from the superposition of the lines from another compound (not, however, lanthanum metal) upon the lines of LaN.

The agreement obtained between the measured and calculated relative intensities of the lines for β-(f.c.c.) lanthanum was much better than for LaN. However, again, the agreement was not as good as might be expected. The reason for this disagreement is not known.

B. Crystal Structure of Cerium Earth Oxides

The cerium earth oxides of the formula R_2O_3 have been reported to exhibit two different structures, a "hexagonal" type and a "cubic" type. X-ray diffraction experiments designed to aid in the characterization of the La_2O_3 and Nd_2O_3 samples (which are to be studied calorimetrically) have been begun.

IV. OTHER ACTIVITIES

A paper entitled "Crystal Structure and Superconductivity of Lanthanum" by W. T. Ziegler, R. A. Young, and A. L. Floyd, Jr. appeared in the March 5 issue of The Journal of the American Chemical Society 75, 1215 (1953). A copy of this paper is attached to the present report. This paper is a summary and extension of work presented in earlier technical reports.[5,6] Part of the work reported is taken from the theses carried out by Mr. Young (1950) and Mr. Floyd (1949) for the Master's degree in physics.

A paper entitled "Studies of Compounds for Superconductivity" by W. T. Ziegler and R. A. Young is scheduled to appear in the April 1, 1953, issue of The Physical Review.

Notice has been received of the extension of the present contract from July 1, 1953, to July 1, 1955.

V. FUTURE WORK

Construction and testing of the adiabatic calorimeter will be continued. Construction and testing of the cryostat for intercomparison and calibration of platinum thermometers will continue. It is hoped that calibration of the thermometers can be started shortly.

Studies on the crystal structures of the cerium earth oxides will be continued.

Preparation of a technical report of work carried out during the past few years on the chemistry of the rare earths will be continued.

VI. PERSONNEL

The following individuals have been associated with the project during the period covered by this report.

Name	Position	Employment
Dr. W. T. Ziegler	Director	Half-time
Mr. R. A. Young	Research Associate	Part-time
Mr. L. H. Morgan	Research Assistant	Part-time
Mr. H. A. McGee, Jr.	Graduate Assistant	None
Mr. Leigh Ierlan	Machinist	Part-time

Respectfully submitted:

W. T. Ziegler

W. T. Ziegler,
Project Director

Approved:

Herschel H. Cudd

Herschel H. Cudd, Acting Director
Engineering Experiment Station

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(4) Ziegler, W. T., ibid. Status Report No. 26, September 30, 1952.

(5) Ziegler, W. T., Superconductivity of Lanthanum, Cerium, Praseodymium and Neodymium. Technical Report No. 1, Project No. 116-18, ONR Contract No. N6-ori-192, January 20, 1949.

(6) Ziegler, W. T., Floyd, A. L., Jr., and Young, R. A., Crystal Structure and Superconductivity of Lanthanum. Technical Report No. 2, Project No. 116-18, ONR Contract No. N6-ori-192 (NR 016-406), March 2, 1950.

APPENDIX

Crystal Structure and Superconductivity of Lanthanum

By

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

[Reprinted from the Journal of the American Chemical Society, 75, 1215 (1953).]

[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[7-9] (h.c.p.) and face-centered cubic[10,11] (f.c.c.) structure. Measurements of heat capacity,[12] electrical resistance,[13] coefficient of linear expansion[13] and magnetic susceptibility[14] 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.

(2) Taken in part from the Master's theses in Physics of R. A. Young (1950) and A. L. Floyd, Jr. (1949).

(3) G. Sharvin, *J. Phys.* (*U.S.S.R.*), **9**, 350 (1945); *C. A.*, **40**, 3220 (1946).

(4) J. T. Kendall, *Proc. Phys. Soc.* (*London*), **63B**, 821 (1950).

(5) W. T. Ziegler, *Research Engineer*, Georgia Institute of Technology, No. 4, 15 (1946–1947).

(6) B. B. Goodman, *Nature*, **167**, 111 (1951).

(7) J. C. McLennan and R. W. McKay, *Trans. Roy. Soc.* (*Canada*), III, **24**, 33 (1930).

(8) L. L. Quill, *Z. anorg. allgem. Chem.*, **206**, 273 (1932).

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

(10) R. Zintl and S. Neumayr, *Z. Elektrochem.*, **39**, 84 (1933).

(11) W. Klemm and H. Bommer, *Z. anorg. allgem. Chem.*, **231**, 138 (1937).

(12) F. M. Jaeger, J. A. Bottema and B. Rosenbohm, *Rec. trav. chim.*, **57**, 1137 (1938).

(13) F. Trombe and M. Foex, *Compt. rend.*, **217**, 501 (1943).

(14) F. Trombe, *ibid.*, **198**, 1591 (1934).

using a zirconium filter became of the smaller absorption coefficient of lanthanum for this radiation.

The lanthanum filings were prepared by filing the bulk specimen of lanthanum in a dry-box under dry nitrogen, care being taken to first remove any surface films. Helium gas was used in a few instances, but gave results identical with those obtained when nitrogen was used. Experiments described elsewhere[15] showed that dry nitrogen reacts slowly (if at all) with lanthanum filings at room temperature. Pyrex glass capillaries were filled in the dry-box and sealed immediately upon removal.

A few studies were made using bulk specimens. The surface was protected from contact with air during the exposure to X-rays by means of paraffin, a hydrocarbon oil, by enclosing the specimen in a gelatin capsule, or by a thin film of aluminum. The first three techniques used were not very satisfactory, largely because of the difficulty of completely preventing surface oxidation. The use of an aluminum film (estimated to be 1000–2000 Å. thick), produced by evaporation in a high vacuum, gave good results, there being no evidence of oxidation during the time required for exposure to X-rays (5–8 hr.).

All line positions were measured visually to 0.1 mm. Line intensities were estimated visually. All results were calculated by taking the unresolved K_α lines and the $K_{\alpha 1}$ line to have wave lengths of 1.539 and 1.537 kx. units, respectively. The observed data were corrected either on the basis of a series of diffraction patterns taken of pure KCl powder or by the septum technique using copper and silver as standards.

Description of Lanthanum Materials.—Six different lanthanum materials were investigated. All were sections cut from cast rods. Three of these, designated as Cooper 1, Cooper 2 and Cooper 3, were obtained at different times from Cooper Metallurgical Associates, Cleveland, Ohio. These were analyzed by spectroscopic and spectrophotometric methods, by direct precipitation as the oxalate and by ion-exchange techniques. The analytical results (in %) for Cooper 1, 2 and 3, respectively, were: La, 95.3, 95.6, 94.8; Ce, 1.3, 1.1, 0.3; Nd, 0.4, 0.4, 0.6; Pr, 0.2, 0.2, < 0.1; other rare earths, 0.3, 0.2, < 0.1; Si, 0.7, 0.7, 0.1; Fe, 0.8, 0.8, 0.8; unaccounted for, 1.0, 1.3, 3.4. Trace amounts of a number of other metals were detected spectrographically.

Two specimens, Spedding 1 and Spedding 2, were obtained at different times from Dr. F. H. Spedding, Iowa State College, Ames, Iowa. Spectrographic analysis of Spedding 1 showed that it contained 0.13% Be, 0.1% Mg, traces (estimated to be a few hundredths of a per cent.) of calcium, aluminum and iron, and was free of other rare earths. Direct precipitation as oxalate gave a lanthanum content of 97.3%. Spectrographic examination of the sample designated as Spedding 2 showed it to be considerably purer than Spedding 1; it contained < 0.01% Be and traces of Al and Mg. The sixth specimen (0.85 g.) was obtained from Adam Hilger, Ltd., and bore the designation Lab. No. 7259. It was reported to contain a total of 0.5–1.0% aluminum, silicon and tungsten and to be substantially free of other rare earths.

No chemical analyses of the specimens for carbon, nitrogen, oxygen or hydrogen were made. The presence of carbon in the Cooper and Spedding specimens was inferred from the acetylene-like odor (more pronounced in the Cooper specimens) given off when the filings were dissolved in dilute hydrochloric acid. X-Ray diffraction analysis of the metal filings from all specimens showed that all except a few faint lines were assignable either to a h.c.p. or f.c.c. lanthanum structure. These faint lines were identified as belonging to lanthanum hydride.

Experimental Results

Hexagonal Close-Packed Lanthanum.—Lanthanum has been reported to exhibit the h.c.p. structure at room temperature by McLennan and McKay,[7] Quill[8] and Rossi.[9] The purity and thermal history of the specimens investigated were not given. Zintl and Neumayr[10] reported that a specimen, containing 99.6% lanthanum (the remainder consisting of silicon, aluminum and carbon) had primarily the h.c.p. structure; the lines obtained were so diffuse that no exact measurements could be made. In all these studies the lanthanum powder investigated was prepared by filing.

Filings taken from the six lanthanum specimens in the "as-received" condition all had the h.c.p. structure. The h.c.p. lines obtained were somewhat diffuse, making exact measurements impossible.[16] The results of the present research are compared with the work of other investigators in Table I. The relative intensities of the lines agreed closely with those reported by Quill.[8]

TABLE I

LATTICE PARAMETERS OF H.C.P. LANTHANUM

Observer	a_0, kx. units	c_0, kx. units	c/a
McLennan and McKay[7]	5.72	(5.06)	1.64
Quill[8]	3.754 ± 0.010	6.061 ± 0.030	1.613
Rossi[9]	3.757	6.05	1.61
This research	3.74 ± 0.01	6.06 ± 0.02	1.62 ± 0.01

Face-centered Cubic Lanthanum.—Zintl and Neumayr[10] have been able to convert finely divided lanthanum from the h.c.p. to the f.c.c. structure by heating in a vacuum furnace at 350° for several days. Klemm and Bommer,[11] using liquid potassium and cesium, reduced the anhydrous chloride at 350–400° to obtain finely divided lanthanum having the f.c.c. structure. Klemm and Bommer compared these results with those they obtained from preparations made at similar temperatures by treating finely divided lanthanum (obtained from bulk lanthanum) with potassium, rubidium and cesium metals. No differences were observed in the various preparations.

We also have been able to prepare the f.c.c. modification by heating lanthanum filings for two to four days at 350–400°. Sealed Pyrex capillaries containing the filings were examined before and after heat treatment. Whereas before heat treatment the filings always gave a h.c.p. pattern with relatively diffuse lines, after heat treatment the diffraction lines were quite sharp, the principal lines always corresponding to a f.c.c. structure. The a_0 calculated for this structure and the observed relative intensities of the lines agree quite well with those reported by Zintl and Neumayr and Klemm and Bommer (see Table II).

In addition to the principal f.c.c. pattern most films showed several faint to medium faint lines assignable to the h.c.p. structure, a number of weak lines assignable to the "hydride"[16] and a pattern of faint lines (referred to hereafter as the "y" structure) assignable to a second f.c.c. structure having an a_0 0.5–1% less than that assigned to f.c.c. lanthanum.

All six lanthanum samples behaved similarly.

TABLE II

LATTICE PARAMETER OF FACE-CENTERED CUBIC LANTHANUM

Observer	a_0, kx. units
Zintl and Neumayr[10]	5.296 ± 0.002
Klemm and Bommer[11]	5.294 ± .002
This research	5.285 ± .005

Rossi[9] has noted that the f.c.c. modification of lanthanum seemed to be only a surface effect, since annealed specimens gave the h.c.p. pattern after removal of a very thin outer layer. Iandelli and Botti[17] suggested, in view of Rossi's observation, that the pattern previously ascribed to f.c.c. lanthanum might, in fact, be due to a surface formation of lanthanum nitride, since the lattice parameters of these two substances are the same. It has been shown by us[15] that the X-ray diffraction patterns of f.c.c. lanthanum and lanthanum nitride powders are detectably different. Fur-

(15) R. A. Young and W. T. Ziegler, THIS JOURNAL, 74, 5251 (1952).

(16) Most films showed a number of additional rather weak lines the positions of which agreed closely with the f.c.c. pattern to be expected for lanthanum hydride as reported by Rossi.[9] The prominence of this "hydride" pattern varied from sample to sample, being somewhat stronger in the Cooper specimens. Unpublished work by us has confirmed the observations of Rossi, and has shown that the a_0 of LaH_x increased from 5.62 to 5.65 kx. units as x decreased from 2.45 to 0.8. The lattice parameter of the "hydride" patterns observed in the various specimens fell within these limits. The presence of the "hydride" pattern made the identification of the h.c.p. pattern difficult especially if the f.c.c. pattern was also present.

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

thermore, filings carefully prepared and handled under helium gas to minimize lanthanum nitride formation gave the 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. → F.C.C.—The experiments of Zintl and Neumayr[10] and Klemm and Bommer[11] suggest that the temperature for this transition is below 350°. Trombe and Foex[18] 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°, 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° 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° confirming the observations of Trombe and Foex,[18] 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. → 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° 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 temperature 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 Foex[18] 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° 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°. 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°) specimen was examined both before and after roughening the surface by

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

filing. It was found that, whereas before filing the structure was predominantly f.c.c., after filing the surface showed a predominantly h.c.p. structure.

Examination of massive specimens of the different lanthanum samples in the "as-received" state was complicated by the fact that the specimens were always coated with a layer of oxide which had to be removed by filing. The two specimens examined (Hilger, Cooper 3) gave predominantly h.c.p. structures both as massive specimens and as filings.

Attempts were made to obtain a surface which was free of strain or surface contamination by the use of various etching and electropolishing techniques. Many combinations were tried. With a number of etching solutions, particularly those containing acids, a black film or deposit formed on the lanthanum even when used as the anode. This deposit was found by X-ray diffraction to be lanthanum hydride.[16]

The experiments on massive specimens lead to the conclusion that the mechanical strains set up in filing are sufficient to transform f.c.c. lanthanum to h.c.p. lanthanum at room temperature. This may be related to the fact that lanthanum is a relatively soft metal having a hardness approximately that of zinc. It also appears that the massive lanthanum specimens probably are converted to the f.c.c. form by the same heat treatment used to convert the filings (*i.e.*, several days at 350–400°). Finally, none of the massive specimens of lanthanum examined was definitely shown to have wholly the h.c.p. structure.

The general behavior of lanthanum as regards the h.c.p. ⇆ f.c.c. transition observed in this research has some similarity to the corresponding transition in cobalt studied by Troiano and Tokich.[19] In particular, the ready conversion of the f.c.c. to the h.c.p. modification by deformation such as filing is observed for both metals.

Low Temperature Modification of Lanthanum.—Trombe[14] has observed an anomaly in the magnetic susceptibility of lanthanum at 110°K. which indicated the possible existence of a structure transition. However, subsequent dilatometric measurements by Trombe and Foex[18] and specific heat measurements by Parkinson, *et al.*,[20] have revealed no anomaly in this region.

In the present work lanthanum filings in the h.c.p. modification (Cooper 1, Spedding 1) and f.c.c. modifications (Cooper 1, Cooper 3, Spedding 1, and Spedding 2) were examined before and after cooling to 2°K. (The capillaries were placed in the experimental chamber of the helium cryostat. The rate of cooling the cryostat to liquid helium temperatures varied somewhat from run to run.) The h.c.p. filings showed no changes as a result of cooling. The f.c.c. filings, in general, also showed no change in structure. However, in one experiment f.c.c. filings of Spedding 1 showed some conversion to the h.c.p. structure. This was not observed in a subsequent experiment.

Massive specimens of Cooper 3, Spedding 1 and Spedding 2, presumed to have the f.c.c. structure as a result of heat treatment at 350°, were examined after cooling to 2°K. in the helium cryostat. The Cooper 3 and Spedding 1 specimens had the f.c.c. structure with no evidence for any h.c.p. structure, while the Spedding 2 specimen appeared to be a mixture of the two structures. One massive specimen (La 7, Cooper 1) presumed to be in the f.c.c. structure as a result of heat treatment at 350° was examined 17 months after being cooled at 2°K. and found still to have the f.c.c. structure. Thus, there was some evidence that the f.c.c. → h.c.p. transition occurred partially in the purest specimens (Spedding 1 and 2) as a result of cooling to helium temperatures.

Part II. Superconductivity Studies

The six different lanthanum samples were examined for superconductivity in the "as-received" condition and after heat treatment. The purity of these materials, together with the method of heat treatment and the X-ray diffraction analysis have been discussed in Part I of this paper.

Apparatus and Experimental Techniques.—The cryostat used was similar to one described by Horn and Ziegler.[21] The Simon expansion method was used to produce liquid helium in an upper helium reservoir. Below the 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 helium reservoir. The copper experimental chamber consisted of two parts, an upper section to which the gas and the constantan resistance thermometers were attached, and a lower section (machined from a solid copper rod) in which the specimens to be tested for superconductivity were located.

The temperature of the experimental chamber was determined by means of a helium gas thermometer of the type described by Mendelssohn,[22] the helium pressure being measured both by a Bourdon gage 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 thermometric system consisted of two volumes, one at room temperature (V_r) and the other at low temperature (the thermometer bulb, V_b) connected by a capillary tube of negligible volume. Gas imperfection was taken into account by making use of the virial coefficients for helium given by Keesom.[23] The maximum correction arising from gas imperfection was 0.15°. The ratio of the two volumes was determined by experiment at the normal boiling point of liquid helium to be 12.4. V_b was 1.6 cc.

The sensitivity of the gas thermometer was about 0.04° per mm. in the range 3 to 5.5°K. Readings were made to 0.5 mm. Below 2.6°K. the gas thermometer acted as a vapor pressure thermometer. The vapor pressure of liquid helium in the experimental chamber was also used to determine the temperature below 4.3°K.

The absolute accuracy of the temperature scale is believed to be about 0.05° in the range 3 to 4.5°K. decreasing to 0.1° at 5.5°K.

The constantan resistance thermometer was used to follow the temperature changes of the experimental chamber, particularly during the actual transitions. 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 the magnetic detection of superconductivity[21] 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 No. 30 AWG copper wire, was 15.1 cm. long. The secondary coils consisted of approximately 3000 turns of No. 40 AWG single cotton enameled copper wire. Each coil was 2.2 cm. long. In all experiments coil S1 was empty, the specimens under test being located in coils S2, S3 and S4.

The experimental procedure for detecting superconductivity was as follows: with the experimental chamber at a fixed temperature somewhat above the expected transition

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

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(23) W. H. Keesom, "Helium," Elsevier Publishing Co., New York, N. Y., 1942, p. 49.

TABLE III

CRYSTAL STRUCTURE OF LANTHANUM SPECIMENS

Source	Specimen	Specimen dimensions, mm.	Crystal structure: As-received condition	Crystal structure: After heat treatment[d]	Heat treatment: Days	Heat treatment: 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.[e]	f.c.c.[b,c]	4	350
	La 7	Cyl. 11.4 × 4.2	h.c.p.[e]	f.c.c.[c]	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,c]	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 (1.2–1.3 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: Transition temp., °K.	As-received condition: Transition range (deg.)	After heat treatment: Transition temp., °K.	After heat treatment: 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 Daunt[24] 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).

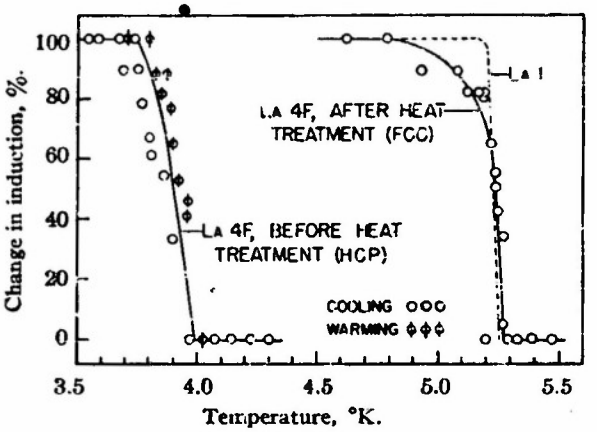

Fig. 1.—Superconductivity of lanthanum filings (Cooper 1) before and after heat treatment for 4 days at 350°. Dotted curve shows transition in bulk specimen after same heat treatment.

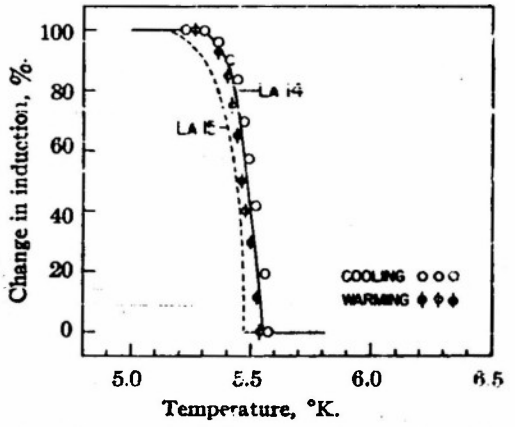

Fig. 2.—Superconductivity of lanthanum (Spedding 2) after heat treatment for 4 days at 350°. Dotted curve shows transition before heat treatment (La 15).

lanthanum specimen (Hilger, Lab. No. 7259), presumably similar to our Hilger specimen, was superconducting at 4.2°K. On the other hand, McLennan, Allen and Wilhelm,[26] using the electrical resistance method, observed no superconductivity in a "pure" specimen of lanthanum over the range 300 to 1.9°K. The crystal structure of these specimens was not given.

More recently Parkinson, Simon and Spedding[20] have observed a rather sharp specific heat anomaly at 4.37°K. in a specimen of lanthanum having a purity similar to our Spedding 2 specimen. They interpreted this anomaly as arising from a superconducting transition. These investigators reported that a check on the crystal structure of their lanthanum at room temperature showed lines corresponding to both hexagonal close-packed and cubic close-packed forms. They attributed the lack of sharpness of the thermal transition to the known presence of both phases in the specimen.

In the present work the superconducting transition temperature of massive specimens of the six different lanthanum samples tested ranged from 3.1° to 5.5°K. (Table IV). A preliminary report on two of these specimens has been made elsewhere.[27] Heat treatment, which presumably converted the specimens to the f.c.c. form and at the same time removed strains, raised the transition temperature somewhat, while at the same time (with one exception, La 2S) the transition range was narrowed somewhat or remained essentially unchanged.

The crystal structure of the massive specimens studied for superconductivity in the "as-received" state is not known with certainty, though filings taken from the specimen in all cases had primarily the h.c.p. structure. The attempts to fix the structure of these massive specimens have been discussed in Part I of this paper. However, the specimen La 4F (Cooper 1 in the form of filings) which became superconducting at 3.9°K. was shown to have the h.c.p. structure both before and after cooling to 2°K. Thus, it appears that the h.c.p. form of lanthanum (presumably in a strained state) is a superconductor; the transition temperature of h.c.p. lanthanum in the strain-free state remains to be determined.

The structure studies made of massive specimens, as well as filings, of Cooper 1 (La 1), Cooper 2 (La 6) and Hilger (La 3) lanthanum, heat treated as described in Table IV, showed that these specimens very probably had predominantly the f.c.c. structure before cooling to 2°K. None of these specimens was examined immediately after cooling. However, filings from these samples, known to be f.c.c. before cooling, showed no change in structure as a result of being cooled to 2°K. Massive specimens of Cooper 2 (La 7), Cooper 3 (La 10) and Spedding 1 (La 1S) were found to have the f.c.c. structure after cooling to helium temperatures. The specimen La 4F (Cooper 1 filings) was shown to have the f.c.c. structure both before and after cooling to 2°K. All of these specimens were superconductors, the two purest (Hilger and Spedding 1) having the highest transition temperatures (*ca.* 5.4°K.). We conclude, therefore, that f.c.c. lanthanum is a superconductor with a transition temperature near 5.4°K.

The occurrence of superconductivity in both the h.c.p. and f.c.c. modifications of lanthanum is in agreement with an empirical observation relating structure and superconductivity made by Born and Cheng.[28]

There was some evidence that one of the heat treated Spedding 1 specimens (La 2S) may have been a mixture of the h.c.p. and f.c.c. modifications. This may account for the broad transition (0.6–0.8°) observed with this specimen. On the other hand, the specimen La 14 (Spedding 2), which contained a considerable amount of the h.c.p. modification, had a small transition range (0.25°) and the highest transition temperature (5.5°K.).

While there was little difference in behavior between the three Cooper samples as regards the h.c.p.–f.c.c. transition, there was considerable difference in their superconducting transition temperatures both before and after heat treatment. Much of this difference in behavior was probably

(26) J. C. McLennan, J. F. Allen and J. O. Wilhelm, *Phil. Mag.*, [7] 10, 500 (1930).

(27) W. T. Ziegler, *J. Chem. Phys.*, 16, 838 (1948).

(28) M. Born and K. C. Cheng, *J. phys. radium*, [8] 9, 249 (1948).

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 ($LaH_{2.8}$) 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 to convert lanthanum hydride to lanthanum metal.[30]

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

(30) Unpublished work in this Laboratory.

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