THE CRYSTAL STRUCTURE AND SUPERCONDUCTIVITY OF LANTHANUM NITRIDE

A THESIS

Presented to

the Faculty of the Division of Graduate Studies

Georgia Institute of Technology

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Physics

by

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December 1950

THE CRYSTAL STRUCTURE AND SUPERCONDUCTIVITY OF

LANTHANUM NITRIDE

Approved:

THESIS ADVISOR

Date Approved by Chairman May 17, 1951

ACKNOWLEDGMENTS

It is with great pleasure that I acknowledge the help and cooperation that I have received from many persons during the course of this research. I wish to extend my particular thanks to Dr. W. T. Ziegler whose patience, diligence, and readiness to discuss any pertinent point in detail until his listener thoroughly understands, as well as his personal mastery of many fields of science, have made the pursuit of this research a most instructive and interesting adventure in science in general as well as in the restricted field of this problem.

I wish to thank George Cook, Francis Lafond, J. Thomas Roberts, and Dr. John Blomeke for their aid to Dr. Ziegler and myself in operating the cryostat. My thanks are also extended to Dr. Joseph H. Howey, Director of the School of Physics, for the use of the x-ray equipment and the darkroom facilities, and to many other members of the School of Physics who were always willing to discuss the various aspects of this problem with me.

This work was carried out in part with the assistance of the Office of Naval Research under contract No. N6-ori-192 with the State Engineering Experiment Station.

ABSTRACT

Lanthanum nitride was prepared by a modification of the direct combination method used by Muthmann and Kraft[1]. The preparation of lanthanum nitride in this research differed from the preparations previously reported in the literature in that the reaction product was characterized by volumetric measurement, as well as gravimetric measurement, of the absorbed nitrogen, and in that air and moisture were kept away from the sample at all times. The product obtained was a black, free-flowing powder which had the formula LaN_x where "x" varied from 0.91 to 0.99. The exact value of "x" depended upon the length of time allowed for the reaction and upon the choice of the volumetric or the gravimetric measurements as a basis for calculation. The volume measuring feature of the apparatus made it possible to follow the progress of the reaction in a qualitative manner by noting the change in volume (at constant pressure) of the nitrogen remaining over the sample. The reaction was found to proceed rapidly at temperatures above 600°C. It proceeded to approximate completion in two to four hours at 750°C and in one to two hours at 900°C. These reaction times are in general agreement with the observations of Muthmann and Kraft[1].

X-ray data on the product were gathered by the powder method of x-ray diffraction. Lanthanum nitride was found to crystallize in a face-centered cubic lattice with a unit cell having an a_0 equal to 5.284 ± 0.004 kx-units (5.295 Å). Consideration of the integrated intensities

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1. Muthmann, W., and Kraft, K., Ann. 325, 261-78 (1902).

of the diffraction lines demonstrated that lanthanum nitride has the same space-group as NaCl (Fm3m in the Hermann-Mauguin system of nomenclature). These crystal structure results are in agreement with those reported by Iandelli and Botti[2] who published the only x-ray data on lanthanum nitride that could be found in the literature up to March, 1950. The x-ray work in this research differs from the data of Iandelli and Botti in that the information leading to the determination of the lattice parameter was obtained from films which had been individually calibrated with a standard substance and in that the detailed evidence for the assignment of the space-group is presented herein.

Iandelli and Botti[2] made the suggestion that, since the a_o's of face-centered cubic lanthanum and lanthanum nitride were the same within experimental error, perhaps the pattern previously ascribed in the literature to face-centered cubic lanthanum might in reality be due to a surface formation of lanthanum nitride, thus explaining the observation by Rossi[3] that the face-centered cubic modification of lanthanum seemed to be only a surface effect. This investigation offers experimental proof that the relative line intensities in the powder patterns of the two substances are detectably different, even though very similar, and that hence both substances do exist.

The lanthanum nitride which had been prepared herein and studied with x-rays was tested for superconductivity, using a magnetic method, down to 1.8°K with negative results. A helium cryostat, using the Simon expansion process, was employed. The nitride had not been previously

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2. Iandelli, A., and Botti, E., Atti accad. nazl. Lincei, Classe sci. fis. mat. nat. 26, 233-8 (1937).

3. Rossi, A., Nature 133, 174 (1934).

tested for superconductivity. One specimen of cerium nitride was prepared in a similar manner for comparison purposes. It was found to have a face-centered cubic crystal lattice with an a_0 equal to 5.014 $\pm$ 0.005 kx-units (5.024 Å) in agreement with the results of Iandelli and Botti[4]. Cerium nitride was also found not to be superconducting down to 1.8°K.

Insofar as could be determined from the literature this is the first investigation in which data on the preparation, the composition, and the x-ray structure have been obtained for the same samples of lanthanum nitride.

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4. Iandelli, A., and Bott, E., Loc. cit.

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CHAPTER I

INTRODUCTION

In the past three years in the low temperature laboratory of the Georgia Tech State Engineering Experiment Station considerable work has been done on the purification of the rare earths and the investigation of their fundamental properties. Johnson[1] and Lafond[2] have studied the application of ion-exchange techniques to the separation of the rare earths. Blomeke[3] has investigated the high temperature heat capacities of lanthanum, praseodymium, and neodymium oxides. Floyd[4] has studied the effect of temperature on the crystal structure of some of the rare earth metals and the relation of crystal structure to superconductivity.

The present thesis, which is partly a continuation of Floyd's work, is concerned with the crystal structure and superconductivity of lanthanum nitride. This study is part of a more general study concerning the properties of rare earth compounds. Lanthanum nitride was chosen for this investigation for the several reasons that follow.

The nitrides of a number of metals are known to be superconductors

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1. Johnson, W. N., Master's Thesis in Chemical Engineering, Georgia Institute of Technology, (1950).

2. LaFond, F. W., Master's Thesis in Chemical Engineering, Georgia Institute of Technology, (1950).

3. Blomeke, J. O., Doctor's Thesis in Chemical Engineering, Georgia Institute of Technology, (1950).

4. Floyd, A. L., Jr., Master's Thesis in Physics, Georgia Institute of Technology, (1949).

(see Chapter IV). The occurrence of superconductivity in lanthanum has been noted several times by magnetic methods[5,6]. Ziegler[7,8,9] and Floyd[10] also found that lanthanum was a superconductor while cerium, praseodymium, and neodymium were not superconducting down to the lowest temperature obtainable with the cryostat in the low temperature laboratory (about 2°K). Thus a lanthanum compound was preferable to a compound of one of the other rare earths mentioned. Lanthanum was also available in a much higher state of purity than any of the other rare earths. Up to March, 1950, no superconductivity measurements on lanthanum nitride had been reported in the literature. However, lanthanum nitride had been prepared several times (see Chapter II) and its crystal structure had been studied once[11]. The crystal structure reported was one that could be determined by the powder method of x-ray diffraction which was available for use in this research. It is the investigation of this crystal structure which constitutes the primary problem of this thesis.

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

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

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

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

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

10. Floyd, A. L., Jr., loc. cit.

11. Iandelli, A., and Botti, E., Atti. accad. nazl. Lincei, Classe sci. fis. mat. e. nat. 25, 129-32 (1937)

The preparation of lanthanum nitride as reported in the literature was relatively easy to carry out. The values for "x" in the formula LaN_x that had been obtained by the different investigators varied from 0.8 to 0.9. This suggested the possibility of carrying out an experiment analogous to that performed by Horn and Ziegler[12] in which the supercon-ducting transition temperatures of niobium and tantalum hydrides were found to be a function of the lattice parameter, which, in turn, was a function of the hydrogen content of the hydride.

With this in mind the nitriding apparatus was built in such a manner that the amount of nitrogen available for the lanthanum-nitrogen reaction could be controlled. In this research attention was centered on an attempt to make "x" as large as possible. This particular phase of the problem was undertaken for several reasons: (1) an excess of ni-trogen sufficient to maintain atmospheric pressure in the reaction volume eliminated the problem of leakage into the reaction chamber during the course of an experiment; (2) atmospheric pressure in the reaction volume readily permitted following the progress of the reaction by manipulation of the containing volume at constant pressure (this measurement is de-scribed in Chapter II); (3) "x" might be ideally unity and the incomplete reaction could be responsible for the fact that all reported values for "x" were less than unity.

The apparatus used for preparing the nitride samples was designed so that the amount of nitrogen absorbed by the metal during the reaction

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

could be measured volumetrically as well as gravimetrically. It was felt that since volumetric measurements had not been previously used in determining the value of "x" in LaN_x such measurements would provide an interesting cross-check. Under ideal conditions volumetric measurements would be more accurate than either gravimetric or chemical analysis. Due to unforseen difficulties, to be discussed later, such was not the case in these experiments. Chemical analysis has not been performed at the present time on the nitrides prepared in this research.

Up to March, 1950, the only study of the crystal structure of lanthanum nitride found in the literature was that of Iandelli and Botti. While preparing the metal prior to making lanthanum hydride, Rossi[13] made the observation that the face-centered cubic modification of lanthanum (hereinafter referred to as fcc lanthanum) appeared to be a surface effect. When Iandelli and Botti subsequently investigated the crystal structure of lanthanum nitride, they found that the x-ray diffraction (hereinafter referred to as XRD) pattern of lanthanum nitride was very like the pattern reported in the literature for fcc lanthanum. This led them to suggest the possibility that the pattern reported as belonging to fcc lanthanum might in reality be due to a surface formation of lanthanum nitride. Two other factors further emphasized Iandelli and Botti's suggestion. In 1902 Muthmann and Kraft[14] reported that lanthanum seemed to have a great affinity for nitrogen, even at room temperature. As the diffracted beam in XRD comes from a relatively thin layer near the surface of the irradi-

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13. Rossi, A., Nature 133, 174 (1934).

14. Muthmann, W., and Kraft, K., Ann. 325, 270 (1902).

ated sample, particularly when the absorption is large as it is in lanthanum, it would be quite possible that a thin layer of nitride on the surface of a lanthanum metal sample could completely mask the character of the metal underneath it. It was therefore decided to study the crystal structure of lanthanum nitride in order to verify and improve upon the measurements of Iandelli and Botti, in order to characterize the samples, and in order to gather enough data to decide whether or not the XRD pattern ascribed in the literature to fcc lanthanum was in reality due to lanthanum nitride.

The following thesis is divided into three chapters.

Chapter II is concerned with the preparation of the nitride samples, observations about the reaction, the purity of the materials used, the analysis of the product, and an attempt to produce a surface nitride at room temperature in order to check the observation of Muthmann and Kraft and to check the feasibility of the suggestion put forth by Iandelli and Botti concerning the formation of a surface nitride.

Chapter III is concerned with all the XRD studies made in connection with this research. This includes the measurement of the lattice parameter, the determination of the relative line intensities in the XRD pattern, and the XRD evidence for and against the formation of a surface nitride.

The final chapter, Chapter IV, is concerned with the general problem of superconductivity of nitrides and the superconductivity measurements of lanthanum nitride that were carried out.

Although this research was primarily on lanthanum nitride, one sample of cerium nitride was also prepared and studied in order that the two metals might be compared with regard to their reaction with nitrogen, the crystalline structure of their nitrides, and the possible superconducting properties of their nitrides. The experiments performed with cerium nitride are summarized in Appendix I.

CHAPTER II

PREPARATION OF LANTHANUM NITRIDE

Several methods have been used by other investigators to prepare lanthanum nitride. Of these various methods, only the one employed by Muthmann and Kraft[1], that of direct combination, supplied a reasonably pure product. Since a modification of this method was used in the present research, the greatest emphasis is given it in the discussion of the various methods in the first part of this chapter.

The remainder of the chapter is devoted to a description of the method found most suitable, the preparation of acceptable nitride samples, attempts to dissociate these samples, and an attempt to produce a surface formation of the nitride on lanthanum metal at room temperature.

Numerous exploratory experiments were performed in order to determine the characteristics of the equipment and the most suitable modification of the method of Muthmann and Kraft for use in this investigation. These experiments are summarized briefly in Appendix II.

Methods Used by Other Investigators to Prepare Lanthanum Nitride

The methods used by previous investigators to prepare lanthanum nitride may be divided into two classes. These are the reduction methods (which are discussed elsewhere*) and the direct combination methods. The reduction methods seem generally unsatisfactory for preparing samples for XRD studies as the nitride cannot be readily separated from the other reaction products. Direct combination, on the other hand, yields a product

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1. Muthmann, W., and Kraft, K., Ann. 325, 262, 274-7 (1902).

* The reduction methods reported in the literature are summarized in Appendix III.

whose purity depends only on the purity of the components and the degree of completion of the reaction.

The method of direct combination was first used by Muthmann and Kraft[2] about 1901. Because of its simplicity and the purity of the product it yields this method was subsequently more widely used than any other. Muthmann and Kraft found that lanthanum nitride formed most readily at 850 to 900°C. The experimenters who have used their general method, and the properties of lanthanum nitride obtained by each, are summarized in Table I. A somewhat more detailed account of the work of Muthmann and Kraft follows.

The lanthanum they used was prepared from material obtained by the recrystallization of a completely cerium-free mixture of the double nitrates of the monazite ores.

Great care was taken by these experimenters in the purification of the nitrogen used. It was obtained from the decomposition of sodium nitrite and was purified by being passed first through a red-hot tube filled half with copper wire and half with piano wire, then through a ferrous sulfate solution, and finally through several drying tubes containing sulfuric acid.

Muthmann and Kraft used the lanthanum metal in the form of fine filings. Copper boats were substituted for the porcelain boats used in the first experiments as it was found that otherwise a certain amount of silicide formation occurred. The boats were pushed into a glass tube and a thermocouple was placed over the central boat. Upon passing a

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2. Muthmann, W., and Kraft, K., Loc. cit.

TABLE I

PREVIOUS PREPARATIONS OF LANTHANUM NITRIDE BY THE DIRECT COMBINATION METHOD

Investigator	Starting Material	Product	Properties Studied
Muthmann and Kraft[3]	Fine filings from lump produced by electrolysis of the chloride	Black mass, easily ground up	Reaction with water and air. Conditions of formation (some at ordinary temperatures)
Kellenberger and Kraft[4]	- - - - - - - - - - - - - -	- - - - - - - - -	Specific heat of the nitride made by Muthmann and Kraft
Tamman[5]	Solid lump, purity not stated	Black layer formed on the lump	Studied velocity of formation at 317-404°C, plotting layer thickness against time and obtaining intersecting straight line isotherms. Noted that color changed, as layer thickened, in order of Newton colors.
Sieverts and Muller-Goldegg[6]	Lanthanum mischmetal La(Nd,Pr,Y,) 84.3%	- - - - - - - - -	Absorbed nitrogen so slowly, up to 800°C, as not to be of interest.

3. Muthmann, W., and Kraft, K., Loc. cit.

4. Kellenberger, F., and Kraft, K., Ann. 325, 280 (1902).

5. Tamman, G., Z. anorg. u. allgem. Chem. 124, 33-4 (1922).

6. Seiverts, A., and Muller-Goldegg, G., Z. anorg. u. allgem. Chem. 131, 77 (1923).

TABLE I (continued)

PREVIOUS PREPARATIONS OF LANTHANUM NITRIDE BY THE DIRECT COMBINATION METHOD

Investigator	Starting Material	Product	Properties Studied
Neumann, Kroger, and Haebler[7]	Filings 97.5% La, magnetically freed of Fe.	Black powder	Decomposition in air, heat of nitriding, nitrogen content
Neumann, Kroger, and Kunz[8]	Same as above	Black powder	Heat of solution in 1:20 HCl, Nitrogen content
Iandelli and Botti[9]	Filings, no data on purity	Black mass, easily powdered	Crystal structure, formula (LaN), inability to form a solid solution

7. Neumann, B., Kroger, C., and Haebler, H., Z. anorg. u. allgem. Chem. 207, 144-8 (1932).

8. Neumann, B., Kroger, C., and Kunz, H., Z. anorg. u. allgem. Chem. 207, 133 (1932).

9. Iandelli, A., and Botti, E., Atti. accad. naz. Lincei, Classe sci. fis. mat. e nat. 25, 129-32 (1937).

stream of nitrogen through the tube and heating at bright red heat (850-900°C) the experimenters noted that the reaction took place gradually without any noticeable glowing of the substance.

The experiment was interrupted several times and weight increases were noted to determine the rate of nitrogen absorption. The filings were cooled in a stream of nitrogen and weighed as quickly as possible. The median of three runs gave a composition of 9.21% nitrogen by weight. They reported that the nitride so obtained was black with very little sheen. It could be easily ground up, and reacted with moist air to give ammonia.

Muthmann and Kraft carried out chemical analysis of their nitride on the assumption that it was decomposed completely with dilute HCl according to the reaction

$$LaN + 4HCl = LaCl_3 + NH_4Cl$$

and by determination of the amount of ammonia thus formed. According to their paper, the agreement was not perfect in that, with each weighing, the weight was increased somewhat by atmospheric moisture. Because of that fact the final total weight increase was considerably more than that calculated for LaN, namely 9.15%. A 9.15% weight increase would correspond to $x = 1$ in LaN_x.

Method, Apparatus, and Materials

A modification of the method of Muthmann and Kraft was chosen as being the method most likely to yield a pure product. Lanthanum filings were prepared from a bulk specimen and placed in a molybdenum reaction boat. The boat was then placed in a closed volume and the gas was exhausted from the volume. A known amount of pure dry nitrogen was admitted, and the boat was heated to the reaction temperature over a period of about two hours. A rough check on the progress of the reaction was kept by noting the change in volume at constant pressure. At the end of the experiment the nitrogen remaining in the closed volume was withdrawn and measured, and the amount of gas that had been absorbed was thus determined. Analysis of the product was also made by determining the weight increase. The entire operation was carried out in the absence of air.

Figure 1 is a schematic diagram of the component parts of the reaction apparatus. Several unimportant details are not shown. The molybdenum boat containing the finely divided metal filings was placed in the quartz furnace tube "D" which made up a part of the closed volume bounded, in Figure 1, by the vacuum system, the Toepler pump, and the gas burette.

Temperatures were determined by means of a platinum-platinum, 10% rhodium thermocouple, indicated by "T.C." in Figure 1, placed in the reentrant well in the furnace tube. With the indicated arrangement of parts the material in the boat could be degassed by evacuating the closed volume while heating the sample to or holding it at any desired temperature. The vacuum system could be closed off from the reaction volume and a sample of nitrogen, measured in the gas burette, could be admitted to the reaction volume, withdrawn by the Toepler pump, and remeasured in the gas burette.

The gas burette was a Burrell Type 6 Premier model, graduated in 0.1 ml divisions, and had a capacity of 100 ml. The burette was equipped with a water jacket and a Petersson compensator. Mercury was used as the confining fluid in both the gas burette and the Toepler pump.

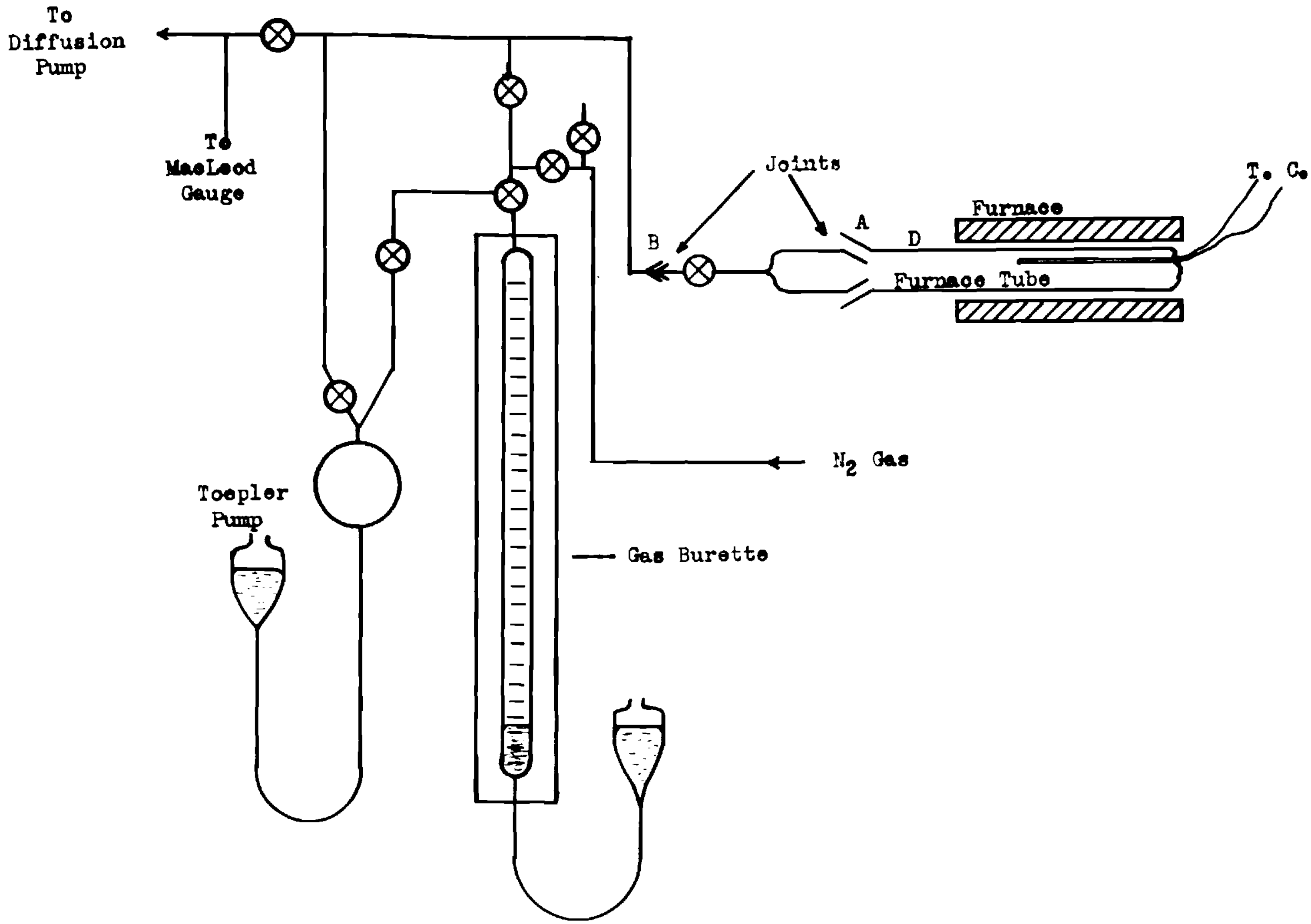

Figure 1. Schematic Diagram of Apparatus Used in Preparation of Lanthanum Nitride

The sample could be completely protected from the atmosphere by removing the furnace tube assembly at joint "B", Figure 1, and placing this assembly in the dry-box before disjointing it at "A". An analogous but smaller assembly was used to prevent the nitride samples from coming into contact with air while being sealed off in glass capsules.

All samples were handled in a dry-box to minimize exposure to moisture and oxygen. The dry-box consisted of a vertical metal cylinder 11 inches high and 20 inches in diameter. The bottom of the cylinder was closed with a metal plate that was soldered in place. The top of the dry-box consisted of a circular piece of plate glass held in air tight contact by Apiezon putty and suitable clamps. Three equally spaced short metal cylinders about four inches in diameter were mounted in the sides of the dry-box to serve as armholes. Obstetrical gloves were lapped over these short cylinders. Gas entry and exit was made through two short pieces of copper tubing soldered into opposing walls near the bottom of the dry-box. A removable section about five inches square was provided in the side of the dry-box for putting objects into or removing them from the apparatus. After the materials of an experiment were in place in the dry-box approximately six cubic feet of helium gas was allowed to flow through the box over a period of about 45 minutes. At the end of this flow it was considered that the atmosphere in the dry-box was essentially helium. A flow of helium through the dry-box was maintained while operations were carried out inside the box.

Sample weights were determined by use of an analytical balance that could be read to 0.1 mg. In order to avoid exposing the samples to air they were placed in a capped weighing bottle while in the dry-box.

The helium-filled bottle was first weighed alone, then with the sample in it. Buoyancy corrections were assumed to cancel out, although it was later found that this assumption was not entirely justified because the temperature of the bottle and also room temperature varied slightly between weighings.

The nitrogen used was commercially available, chemically pure nitrogen. It was stored in iron cylinders and was stated by the supplier, the Air Reduction Sales Co., Birmingham, Alabama, to be 99.5% pure. It was further purified before use by passing it over about nine inches of copper turnings at 550-600°C to remove oxygen and through a trap cooled by liquid air to remove any condensable gases.

The filings used in these experiments were prepared from lanthanum samples which had been previously tested for superconductivity. The metal had been found to undergo a transition to superconductivity at 5°K[10]. These metals may be described as follows, according to analyses carried out by Dr. Ziegler's research group:

Lanthanum (Cooper) This material was obtained from the Cooper Metallurgical Laboratories, Cleveland, Ohio. It was analyzed in the low temperature laboratory by spectographic methods, by direct precipitation of the rare earths as oxalates, and by ion exchange techniques. Consideration of the results of the three methods let to the choice of the figure 97.5% as being representative of the rare earth content in the

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10. 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, March 2, 1950.

sample. The ion-exchange analysis was carried out by Mr. F. W. Lafond, and the result is presented here to shown the distribution of the rare earths.

Lanthanum	94.8%
Cerium	1.1%
Praseodymium	0.2%
Neodymium	0.4%
Other rare earths	0.2%
Silicon	0.7% (est.)
Iron	0.8% (est.)
Carbon and others	present
Total accounted for	98.2%

Lanthanum (Spedding) This material was obtained from Dr. F. H. Spedding, Institute for Atomic Research, Iowa State College, Ames, Iowa. It was shown by spectrographic analysis to contain 0.13% beryllium, 0.1% magneisum, traces of calcium, aluminum and iron, and to be quite free from other rare earths. By direct precipitation as the oxalate the lanthanum content was found to be 97.3%. In view of the high purity of this material the lanthanum content has been taken somewhat arbitrarily to be 100%.

Experiments

Lanthanum nitride was prepared several times by direct combination of the metal with nitrogen at elevated temperatures in a closed reaction volume. The appearance of the products of the more successful experiments was the same as that reported in the literature for lanthanum nitride. The nitride was a black, free-flowing, easily powdered material. It was homogenous to the eye and gave a remarkably clear XRD pattern showing face-centered cubic symmetry.

Exploratory experiments, which are discussed in Appendix II, indicated that a molybdenum boat was preferable to a copper boat, and that it was desirable to maintain atmospheric pressure in the reaction chamber at all times during the course of heating.

The experimental procedure used in experiments 23, 25, 26, and 29 is described below. The procedure was essentially identical in each of the experiments with the exception of the temperatures and times involved, unless otherwise noted.

The molybdenum boat used in the experiment, if not already clean, was washed in CCl_4 to remove grease and then heated in the quartz furnace tube at about 900°C under a pressure of about 1×10^{-5} to 1×10^{-4} mm Hg to remove the oxide. The boat was thereafter protected from air.

Filings of the metal to be nitrided were obtained under a helium atmosphere in the dry-box. They were weighed, placed in the molybdenum boat, and the boat was placed in the furnace tube which was then attached to the rest of the reaction apparatus as shown in Figure 1. The filings were protected from the atmosphere and moisture throughout.

After the sample had been degassed at room temperature by evacuating the closed volume to pressures lower than 1×10^{-5} mm Hg the stopcock leading to the vacuum system was closed. Measured amounts of pure, dry nitrogen, supplied from the gas train, were then let into the reaction volume until atmospheric pressure was attained. The stopcock connecting the closed volume to the burette was left open at this point. The furnace was then turned on with the voltage set for the desired equilibrium temperature (750°C to 900°C, depending upon the experiment). The mercury level in the gas burette was adjusted frequently to keep the pressure in the reaction volume at approximately one atmosphere. The position of the mercury level in the burette and the temperature of the thermocouple were recorded as a function of time to give a running indication of the progress of the reaction.

When the furnace was turned off at the close of the experiment the mercury level in the gas burette was again adjusted frequently to maintain atmospheric pressure in the reaction volume during cooling. When the furnace had cooled to about 300°C the stopcock connecting the burette with the reaction volume was closed. This caused the final nitrogen pressure in the reaction volume at room temperature to be about 4/5 of an atmosphere. The nitrogen remaining at the end of the experiment was then removed and measured in the gas burette. The difference between the volume of nitrogen originally put into the system and the volume removed was assumed to be the amount of gas absorbed by the sample, subject to a correction of about 0.13 cc. This correction arose because (1) the Toepler pump could not produce a pressure less than about 1/2 mm Hg, hence a small amount of nitrogen was left in the reaction volume, and (2) preliminary experiments had indicated that about 0.10 cc of nitrogen was absorbed by the glass walls of the system under experimental conditions.

After the volume measurements had been made the sample was removed and weighed. The weight increase was assumed to be due to the absorption of nitrogen. Capillaries containing some of the sample were then prepared for XRD studies. The operations were all carried out in the absence of air by use of the dry-box.

The formula of the nitride was calculated both from the weight measurements and the volume measurements. The resulting value of "x" in the formula LaN_x is recorded in Table II.

In general, the reaction of lanthanum with nitrogen proceeded rapidly at temperatures above 600°C, contrary to the result reported by Sieverts and Mueller-Goldegg for lanthanum mischmetal[11]. The reaction went to approximate completion in two to four hours at about 750°C and in one to two hours at about 900°C. The better experiments, experiments 23, 25, 26, and 29, are discussed in Appendix IV. These experiments are summarized in Table II.

The reason for the differences between the values of "x" as calculated from volume measurements and those calculated from weight measurements in Table II is not understood.

Numerous experiments were performed to determine the characteristics of the experimental apparatus. These experiments showed that the gas burette could be read to 0.02 ml and that a volume of approximately 50 cc of nitrogen could be measured in the gas burette, admitted to the closed volume, withdrawn with the Toepler pump, and remasured with an accuracy of about 0.1 ml. Since one of the principal possible sources of error was the lack of temperature equilibrium of the gas in the burette, this error should be considered as a percentage error, i.e., 0.2% rather than as an absolute error. Unfortunately this was not fully appreciated until the experiments were completed, hence the volume measurements are less accurate than they were originally believed to be. The usual starting volume was about 250 cc and the residual volume was from 200 to 230

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11. Sieverts, A., and Muller-Goldegg, G., Loc. cit.

TABLE II

NITRIDATION OF LANTHANUM AND CERIUM METAL

Expt. No.	Source	Metal Filings- Wgt. (mg.)	Nitrogen Absorbed (mg.)	Nitrogen Absorbed cc. (NTP) By Weight Increase	Nitrogen Absorbed cc. (NTP) By Volume Meas.	X in MN_x[1] By Wgt. Increase	X in MN_x[1] By Vol. Meas.	Experimental Conditions[2]
23	Lanthanum (Cooper)[3]	333.6	30.0	24.1	21.9	0.92	0.84	5 hrs. at 900°
25	Lanthanum (Cooper)	415.7	38.8	31.0	29.6	0.97	0.93	17 hrs. at 750° 3 hrs. at 920°
26	Lanthanum (Cooper)	424.0	41.3	33.1	31.4	0.99	0.95	20 hrs. at 920°
29	Lanthanum (Spedding)	562.6	55.9	44.7	41.0	0.97	0.91	20 hrs. at 920°
30	Cerium[4] (Cooper)	829.0	68.6	55.0	55.1	0.86	0.86	1.5 hrs. at 700° 18 hrs. at 800°

1. The "M" refers to lanthanum or cerium. The value of x was calculated on the assumption that the original metal samples had the following purities: Cooper, 97% La; Spedding, 100%La; Cerium 95%.

2. Temperatures in degrees Centigrade. Nitrogen pressure one atmosphere.

3. The Cooper lanthanum specimens had the laboratory designation Cooper No. 2.

4. This experiment with cerium is included here only for comparison. The experiment is discussed in Appendix I.

cc. Therefore, then from 450 to 480 cc was measured in the gas burette during the course of an experiment. 0.2% of this amount is 0.90 to 0.96 cc, which represent the maximum error in the measurement of the volume absorbed. Thus, both absolutely and percentagewise, the smaller the absorption, the larger the error.

Because the effect of temperature changes on the bouyancy of the helium-filled weighing bottle was not taken into account during the experiments it is possible that an error of 0.1 to 0.3 mg exists in the reported values of weight increases during the experiments in addition to the error assigned to individual readings. The error assigned during the experiments was determined by taking one half the difference in weight of the helium-filled weighing bottle before and after the sample was weighed in it, and adding this error to the smallest scale reading of the balance, i.e., 0.1 mg. This error was normally 0.2 to 0.3 mg. Thus the total probable error in the weight measurements was on the order of 0.5 mg.

The percentage error in both the volume measurements and the weight measurements could have been substantially reduced, of course, by using larger samples, but only a limited supply of lanthanum was available. Furthermore it was felt that the metal sample should be spread out rather thinly in the reaction boat in order to present the largest possible surface and so that any heat created by the reaction would be dissipated in the boat before causing the sample to sinter.

In comparison to the work of Muthmann and Kraft[12] and to that of

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12. Muthmann, W., and Kraft, K., Ann. 325, 262, 274-7 (1902).

Neumann, Kroeger, and Kunz[13] it is notable that the experiments undertaken in this research indicate that the lanthanum-nitrogen reaction will take place rapidly at temperatures 100°C and more below the temperatures used by those investigators. As also observed by the aforementioned investigators, lanthanum nitride was observed in this research to be black and one of the samples was observed to liberate ammonia upon exposure to air.

Brief Investigation of the Dissociation Pressure of Lanthanum Nitride

Since the values of "x" in LaN_x listed in Table II approach very closely to unity, it might be considered that the dissociation pressure of the nitride was the factor which prevented "x" from being 1. With this in mind experiment 24 was undertaken in which an attempt was made to dissociate a nitride sample. The product of experiment 23 was placed in the quartz furnace tube and degassed at room temperature. The sample was then heated to about 900°C while the surrounding gas pressure was kept between 8×10^{-4} mm Hg and 5×10^{-5} mm Hg for five hours. No weight change, within experimental error, resulted from this treatment of the sample. Thus it was considered proven that the dissociation pressure of lanthanum nitride is extremely small, even at 900°C, and could not be responsible for the observed values of "x" being different from unity.

Attempt to Produce a Surface Formation of Lanthanum Nitride

In view of a remark by Muthmann and Kraft[14] that lanthanum had a

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13. Neumann, B., Kroger, C., and Kunz, H., Z. anorg. u. allgem. Chem. 207, 133 (1932).

14. Muthmann, W., and Kraft, K., Loc. cit.

great affinity for nitrogen even at room temperature, and in view of the suggestion by Iandelli and Botti[15] that the reported face-centered cubic modification of lanthanum might really be a surface formation of lanthanum nitride, an attempt was made to produce such a nitride. In experiment 28 a sample of lanthanum filings weighing 0.5004 grams was obtained under a helium atmosphere. The filings were then placed in the quartz furnace tube and degassed at room temperature. Sufficient nitrogen was metered in to produce atmospheric pressure in the closed volume. After six days at room temperature the nitrogen was withdrawn by means of the Toepler pump and remeasured. No nitrogen absorption was noted within an experimental error of about 0.5 cc. No weight increase of the sample was observed within an experimental error of about 0.5 cc. Thus it was concluded that if a lanthanum-nitrogen reaction does take place at room temperature it is very slight.

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15. Iandelli, A., and Botti, E., Loc. cit.

CHAPTER III

X-RAY DIFFRACTION STUDIES OF LANTHANUM NITRIDE

Prior to this research the XRD pattern of lanthanum nitride had been investigated only once. This was one of the princiapl reasons for undertaking the study of the crystal structure of lanthanum nitride through XRD techniques. The previous investigators, Iandelli and Botti[1], used the powder XRD method and reported that lanthanum nitride was a face-centered cubic crystal of the NaCl type with a unit cell size, a_o, equal to 5.27_5Å.

Both the lattice parameter and the crystal structure type of the lanthanum nitride described in Chapter II were studied. The powder XRD method was used for both determinations. The measurements leading to the lattice parameter were made on films which had been calibrated with a standard substance by the septum technique. The crystal structure type was determined from a study of films which registered only the lines due to lanthanum nitride.

Because the determination of the lattice parameter does not depend upon an accurate knowledge of the crystal structure type (and vice versa, in this case), this chapter has been divided into three parts. Part 1 deals with the equipment used to obtain the XRD photographs and the general procedure involved. In Part 2 the accurate determination of the lattice parameter is discussed. Part 3 is concerned with the determi-

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1. Iandelli, A., and Botti, E., Atti accad. nazl. Lincei, Classe sci. fis. mat. e nat. 25, 129-32 (1937).

nation of the crystal structure type and includes a discussion of the x-ray evidence, derived from the structure determination, against the possibility that the XRD pattern commonly ascribed to fcc lanthanum could in reality be due to lanthanum nitride.

Part 1: Equipment and Procedure for Obtaining the X-ray Diffraction Photographs

A General Electric type XRD-1 machine vertically mounting a two-port, water-cooled, copper anode, Coolidge type x-ray tube, was used with a nickel filter to produce essentially monochromatic x-radiation. Cylindrical cameras of approximately 14.32 cm diameter and 2 inch width were mounted on horizontal, adjustable, stainless steel camera ways located in a vertical plane passing through the x-ray tube. A stainless steel collimator, yielding a beam cross-section of about 4 mm horizontally and 1 mm vertically, was mounted through the wall of each camera in such a manner that the x-ray beam passed through the exact center of the camera and was caught in a beam trap on the far side.

The samples to be irradiated were contained in Pyrex glass capillaries. Each capillary was mounted with its axis coinciding with the axis of the camera and was oscillated through an angle of 20° during the irradiation. For calibration purposes a septum, consisting simply of a flat metal plate with appropriate cut-outs and fittings, was placed with its plane in the plane of the cylindrical camera and in such a manner as to divide the XRD pattern into two halves. This allowed the patterns of two samples which were placed in tandem in the capillary to register simultaneously but independently on the same photographic film.

Eastman Kodak No-screen, Duplitized, Medical X-ray Safety Film was used in strips 1 7/8 inches wide by 12 inches long. These strips were wrapped around the circumference of the cameras and were held in place by light-tight covers. The films were exposed from 1 to 6 hours with a 25 ma plate current under a voltage of approximately 35 kv in the x-ray tube. The films were developed with Eastman Kodak Rapid X-ray Developer at temperatures ranging from 20°C to 27°C. Development time was varied according to the temperature of the developer and the contrast desired but was usually about 5 minutes at 24°C.

The capillaries used to contain the XRD samples were drawn down to 0.4-0.6 mm inside diameter from 15 mm inside diameter Pyrex glass test tubes. The capillaries were loaded in the absence of air by use of the dry-box*.

Those capillaries which were to be used with the septum contained two samples. They were prepared by loading the capillary to a depth of about 1 cm with the nitride sample, then putting a few mm of the standard sample in the capillary on top of the nitride sample. Care was taken to make the interface between the two samples as clearly defined as possible. Because lanthanum nitride reacts readily with water it was not considered advisable to follow the usual technique in filling such capillaries, i.e., that of separating the two samples with some material such as cotton. The open end of each capillary was sealed in a flame within 10 to 30 seconds after it was removed from the helium atmosphere. It was assumed that the hot gases expanding out of the capillary prevented the advent of water vapor.

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* See Chapter II for a description of the dry-box.

The positions of the diffracted lines of the photographic film were measured on a film reader which consisted of a pointer attached to a millimeter vernier scale placed before an illuminated background. The line positions could be measured to about 0.1 mm with this device.

Part 2: The Determination of the Lattice Parameter of Lanthanum Nitride

As previously mentioned, those films used for the determination of the lattice parameter were calibrated by the septum technique. In this technique the pattern of a standard sample and that of the unknown sample are simultaneously registered side by side along the length of the film strip. This is accomplished by placing the standard sample-unknown sample interface of a two sample capillary, such as described above, in the plane of the septum. The result is that the shadow of the septum falls on the longitudinal center of the film strip, the pattern of the standard sample falls on one side of this center, and the pattern of the unknown sample falls on the other side.

The positions of the lines in both patters are then read and translated into terms of the observed Bragg angle. As the diameter of the camera was approximately 14.32 cm, the translation was accomplished by simply multiplying by $4^{\circ}/$ cm the distance in cm from the position of the undeviated beam to the position of the diffracted line in question. Knowing the Miller indices for each line in the standard pattern and the lattice parameters of the standard substance, it is then possible to calculate the theoretically expected Bragg angle. The deviation of the observed Bfagg angle from the theoretically expected value may be plotted as a function of the observed angle, thus providing a calibration curve for the particular film. The correction at any observed Bragg angle may then be read from this curve and applied to the pattern of the unknown. Such a method of calibration corrects for all systematic errors and even, to a large extent, for errors due to non-uniformity in film shrinkage.* It does not correct for errors due to absorption in the sample unless both samples have the same absorption coefficient in the particular physical states in which they exist in the capillary. The accuracy of the result depends also, of course, upon the accuracy with which the lattice parameters of the standard substance are known.

By using both silver and copper filings as standard samples it was shown that, within the limits of accuracy of these measurements, no errors were introduced by the differing absorption coefficients of the samples,** since essentially the same lattice parameter was obtained for lanthanum nitride with either standard. A further check was made on this point by using the septum to register the patterns of copper filings and solid copper (diameter of the samples essentially identical) simultaneously on film #16-229. No difference could be detected in the line positions of the two patterns. Therefore, it was concluded that for the accuracy desired in this research, absorption in the sample did not create a significant error. Copper filings were most frequently used as the standard sample.

The diffraction center of each pattern was determined from the average position of several lines which were registered on both sides of

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* See Appendix V for an example of this calibration.

** For the Cu K radiation used, the linear absorption coefficients for the solid materials are roughly as follows: Ag, 2300; Cu, 454; La (and hence approximately LaN), 2300.

center. All the lines in the patterns measured were well defined and their positions were measured to 0.1 mm.

Although many x-ray diffraction photographs were taken of the nitride samples, all of which were remarkably clear, the four films numbered 16-231, 16-233, 16-235, and 16-237 were considered the best films to use for the determination of lattice parameters because these four films had been calibrated with the septum technique and because the samples used for these films came from the two best nitriding experiments with Cooper lanthanum (experiments 25 and 26).

Only one experiment was carred out with Spedding lanthanum and film #16-245 was the only calibrated photograph made from the product.

In every XRD photograph made of the products of experiments 23, 25, 26, and 29 the lines displayed the 2-1-2-1-2 grouping characteristic of face-centered cubic symmetery. The interplanar spacings of the atomic planes were calculated in each case from the corrected observed Bragg angles according to Bragg's law

$$n\lambda = 2\ d\ \sin\ \theta \tag{1}$$

where n is an integer, λ is the wavelength of the radiation used, d is the interplanar spacing, and θ is the Bragg angle. The lattice parameter, a_o, was then calculated from the d values by the relation

$$a_o = d\ (h^2 + k^2 + l^2)^{1/2} \tag{2}$$

which holds for the cubic system[2], where d is the interplanar spacing of

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2. Bunn, C. W., CHEMICAL CRYSTALLOGRAPHY, Oxford University Press, London, (1945), pp 103-27

the set of planes with the Miller indices h, k, and l, and a_0 is the length of the side of the unit cell.

By formulae (1) and (2) an a_0 (i.e., lattice parameter) was calculated from each line whose Bragg angle fell within the range of angles calibrated by the standard sample used for the particular film. The a_0 values so obtained were arithmetically averaged and this average was called the a_0 of the pattern. The mean deviation of the individual a_0 values from the average value was assigned as the probable error in the average a_0 determined for a given film. A complete sample calculation of this type is carried out in Appendix VI.

The average a_0 values obtained for the five films mentioned are listed in Table III. One film, 16-242, was made with a standard sample and a substance thought to be fcc lanthanum in order that its lattice parameter might be compared with that of lanthanum nitride. The a_0 value obtained from this film is also given in Table III. It will be noted that all of the values reported in Table III are in kx-units. This is the unit suggested by Siegbahn[3]. It is used here in order that strict numerical comparison may be made with the results obtained by others prior to the recent revision of Avogadro's number[4] and reported in units then thought to be Angstroms. One kx-unit is equal to 1.00203 Angstroms.

From Table III it appears that the a_0 of lanthanum nitride might depend to some extent upon the lanthanum used in its preparation. However, since only one calibrated film of the Spedding lanthanum nitride has been

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3. Siegbahn, M., Nature 151, 502 (1943).

4. Birge, R. T., Revs. Modern Phys. 13, 233 (1941).

TABLE III

EXPERIMENTAL LATTICE PARAMETERS

Film Number	Standard Sample	Sample* Being Measured	Sample Preparation	Average a_o (kx-unit)	Mean Deviation (Kx-unit)
16-231	Ag	Lanthanum Nitride	Exp. 25	5.282	$\pm$ 0.004
16-233	cu	Lanthanum Nitride	Exp. 25	5.283	$\pm$ 0.004
16-235	cu	Lanthanum Nitride	Exp. 25	5.283	$\pm$ 0.004
16-237	Ag	Lanthanum Nitride	Exp. 25	5.282	$\pm$ 0.004
16-242	cu	Face-centered cubic La	Heated 4 days at 350°C	5.291	$\pm$ 0.003
16-245	cu	Lanthanum Nitride (Spedding)	Exp. 29	5.287	$\pm$ 0.003

* The Lanthanum Nitride used for Film #16-245 was prepared with Lanthanum supplied by F. H. Spedding. All the other Lanthanum was supplied by Cooper Metallurgical Laboratories, Cleveland, Ohio

measured to date, and inasmuch as the various values do overlap within experimental error, this slight discrepancy is not considered significant. It does, however, suggest that several more measurements of the a_0 of lanthanum nitride prepared from Spedding lanthanum be made, along with the measurements of the a_0 of face-centered cubic lanthanum (both Spedding and Cooper) to determine the existence or absence of a correlation between the source of the lanthanum and the size of the fcc lattice and the nitride lattice.

In Table III the value 5.284 ± 0.004 kx-units includes all the measurements of the a_0 of lanthanum nitride. This value is therefore taken to be the best value in this research. This is equivalent to 5.295 ± 0.004 Angstroms.

The value determined here for the lattice parameter of lanthanum nitride agrees well with that of 5.27_5 obtained by Iandelli and Botti[5]. Their value was reported as being in Angstroms, but since their work was published in 1937, i.e., before the revision of Avogadro's number, the assumption is made here that the units are really kx-units.

Table IV compares the lanthanum nitride lattice parameter with those of other rare earths and their nitrides. The lattice parameters of cerium, cerium nitride, and fcc lanthanum were determined in connection with this research* by the method employed with lanthanum nitride. The lattice parameters of all four rare earth nitrides listed are much the same, although cerium seems to be exceptional in that the lattice suffers

5. Iandelli, A., and Botti, E., loc. cit.

* The studies dealing with cerium are discussed in Appendix I.

TABLE IV

LATTICE PARAMETERS OF RARE EARTH

METALS AND NITRIDES

Rare Earth	a_0 of F.C.C. Metal Kx-units	Reference	a_0 of Nitride Kx-units	Reference
La	5.291 ± .003	1	5.284 ± 0.004	1
	5.285 ± 0.005	3	5.27_5	2
Ce	5.13 ± 0.01	1	5.014 ± 0.005	1
			5.01	2
Pr	---		5.15_5	2
Nd	---		5.14	2

1. This research.

2. Iandelli, A., and Botti, E., Att; accad. nazl. Lincei, Classe sci. fis. mat. nat. 26, 233-8, (1937).

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

a marked decrease upon the addition of nitrogen.

In Table IV the value listed for the a_o of fcc lanthanum is that which was determined from film #16-242. This value differs slightly from the value 5.285 ± 0.005 kx-units previously reported[6] for fcc lanthanum, although the two numbers are the same within experimental error. This slight difference may be due to the fact that the value reported in this research was obtained by a single determination, whereas the previous value was the average of several determinations. However it should be pointed out that the previous value was obtained from films calibrated by a different, and perhaps less accurate method.

Part 3: Relative Intensities of the Lines in the XRD Patterns and Deductions Therefrom

Measurements of the relative intensities of the lines in the XRD pattern of lanthanum nitride were desired primarily for the determination of crystal structure type. They have also been used herein to show the distinction between the XRD patterns of the material though to be fcc lanthanum and that known to be lanthanum nitride. Insofar as possible a comparison has been made between the relative line intensities observed in this research in the XRD pattern of lanthanum nitride and those obtained by Iandelli and Botti[7]. The various topics dealing with the relative intensity measurements will be discussed in the sequence: observed relative line intensities, crystal structure determinations, distinction between the XRD patterns of "fcc lanthanum" and lanthanum nitride. The

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

7. Iandelli, A., and Botti, E., Loc. cit.

quotation marks will be used throughout the following discussions to indicate the substance which results from heating lanthanum metal at 350-400°C for several days, and which then gives an XRD pattern showing a face-centered cubic lattice with the same a_o as lanthanum nitride.

Observed Relative Line Intensities

Perhaps the simplest method of obtaining observed relative line intensities is that of assigning an estimated strength to each line in the pattern (e.g., strong, medium, weak, etc.,) upon unaided visual inspection. The most accurate method of determing the relative intensities from a photographic registration of the XRD pattern involves the use of a microphotometer. In this case no microphotometer was available, yet the change in line intensities produced by the introduction of nitrogen into the lanthanum lattice is sufficiently small to render the first mentioned method useless. This is because of the large difference in the scattering power for x-rays of nitrogen atoms and lanthanum atoms. Therefore a method of intermediate accuracy was used, one of approximating the line intensities through the use of visual aids.

The method used yielded a numerical value for the relative intensity of any given line in the XRD pattern. While subject to considerable error, this number was still more useful than a casual visual estimate of the intensity. The number used to represent the intensity of any given line was the product of the width of the line, estimated to 0.1 mm, and a number roughly proportional to the exposure required to produce the density of the line. This second number, which represented the exposure, was the time in seconds required to produce a spot of approximately the same density on a similar piece of film. This standard film strip had been previously prepared by exposing successive portions of it to the x-ray beam for uniformly increasing times, i.e., 1 second, 2 seconds, 3 seconds, etc. As an example of the procedure followed, suppose that the width of the major portion of an XRD line was 0.3 mm and suppose further that, on the average, the density of the line seemed most closely to approximate the density of that portion of the standard film strip which had been exposed to the x-ray beam fro 5 seconds. Then the numerical intensity assigned to this XRD line would be 3 x 5 = 15.

The above process was carried out for three films bearing the lanthanum nitride pattern. These are not the same films that were used for the determination of lattice parameters because it was more convenient to make intensity measurements on films which registered only the pattern of lanthanum nitride. The averaged* results of these observations are presented in Figure 2. The correlation between Miller indices and line number is shown in Table V. The other relative intensities in Figure 2 were calculated for an NaCl type structure of LaN and for fcc lanthanum by the formula**

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* The observed line intensities were averaged by first reducing all three sets of observed intensities to unity at the 620 plane (line 14). The resulting "curve" was fitted to the theoretical "curves" as well as possible by multiplying the entire experimental "curve" by a suitable constant. It was not given the value of unity at the 620 plane because such a procedure would cause the error in this point to be reflected throughout all the other experimental points. The error, shown by the vertical lines, in Figure 2 for each diffracted line other than that from the 620 planes is the mean deviation of the three individual observed intensities for this line from the average. The error shown at the 620 planes (line 14) is the mean of the percentage errors at each of the other lines.

** See Appendix VII for a discussion of this formula and the reasons for its choice.

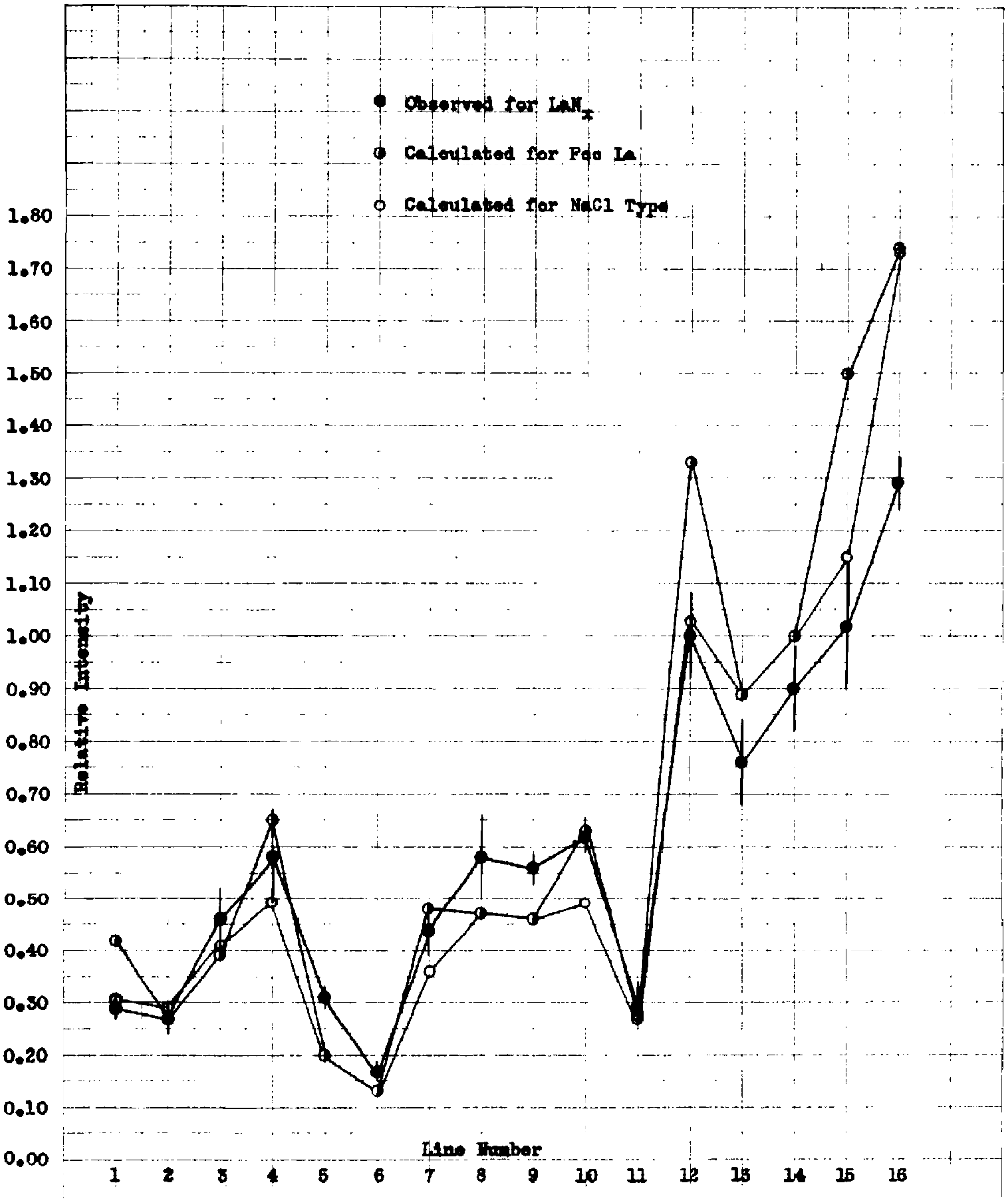

Figure 2
Observed Relative Line Intensities Compared
To Theoretical For Lanthanum Nitride

$$I \sim F^2 \, p \, \frac{1 + \cos^2 2\theta}{\sin 2\theta \sin \theta} \, U \qquad (3)$$

where I = intensity of the diffracted line

F = the crystal structure factor

P = the number of cooperating planes

θ = the Bragg angle of the diffracted line

U = the appropriate absorption factor as obtained from a plot of the values listed by Rusterholtz[8] for the case of large absorption in a cylindrical sample

Insofar as comparison is possible the relative intensities observed here agree well with those reported by Iandelli and Botti[9] for lanthanum nitride, who made the statement that the intensities they observed agreed well with those calculated for the NaCl type structure of LaN. Unfortunately their intensity observations were reported in a purely qualitative fashion. The reason for showing only the relative intensities calculated for the NaCl type structure and the fcc lanthanum structure in Figure 2 will become apparent shortly.

Determination of the Crystal Structure Type of Lanthanum Nitride

Two separate methods were used to compare the observed relative line intensities with the theoretically calculated intensities in order to determine the crystal structure type of lanthanum nitride. The method

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8. Rusterholtz, A., Z. Physik. 63, 1 (1930), see Appendix VIII for a plot and discussion of this factor.

9. Iandelli, A., and Botti, E., Loc. cit.

to be discussed first is semi-quantitative, whereas the second method is purely qualitative. The same result was obtained from both methods, namely that lanthanum nitride has the NaCl type crystal structure.

The formula obtained for the nitride prepared in this research, as shown in Table II, was LaN_x where "x" varied between 0.9 and 1.0. The proximity of this number to unity suggests three possible dispositions, consistent with fcc symmetry, of the nitrogen atoms in the lanthanum metal lattice: (1) a random orientation, (2) the NaCl type structure, and (3) the ZnS type structure. For the purposes of calculating the relative intensities to be expected from each type the formula of the nitride was assumed to be exactly LaN.

As mentioned earlier the theoretical relative intensities were calculated according to formula (3). The values obtained for the above three structure types are listed in Table V and are plotted in Figure 3. All of the calculated relative intensities have been reduced to unity at the 620 plane for ready comparison. A sample calculation of relative line intensities is given in Appendix VII. In the calculation of the intensities expected from the random structure it was assumed that the nitrogen played no part in scattering, hence this calculation is the same as for fcc lanthanum. To facilitate reference to a particular line all the lines have been numbered in the order of increasing Bragg angle. The correspondence between the line numbers and the Miller indices of the diffracting planes is also shown in Table V.

It would seem that all that need be done to determine the crystal structure type would be to plot the observed relative intensities on Figure 3 and to note which of the three assumed structures gives the best

TABLE V

CALCULATED RELATIVE LINE INTENSITIES*

Line No.	Plane (hkl)	Relative Intensity in an LaN Structure of Indicated Type		
		NaCl	ZnS	Random**
1	111	0.298	0.374	0.421
2	200	0.285	0.196	0.273
3	220	0.396	0.396	0.385
4	311	0.489	0.577	0.649
5	222	0.202	0.149	0.198
6	400	0.131	0.131	0.129
7	331	0.364	0.421	0.475
8	420	0.468	0.357	0.467
9	422	0.457	0.456	0.460
10	511 333	0.487	0.561	0.633
11	440	0.274	0.274	0.275
12	531	1.035	1.18	1.33
13	600 442	0.885	0.692	0.892
14	620	1.00	1.00	1.00
15	533	1.150	1.31	1.50
16	622	1.73	1.35	1.74

* All relative intensities are reduced to unity at the 620 plane (line no. 14) for ready comparison.

** The calculations in this column were made on the assumption that the nitrogen atoms were randomly arranged in the metal lattice, hence they would not play any part in the diffraction pattern. Thus the relative intensities calculated in this column also apply to the face-centered cubic lanthanum structure.

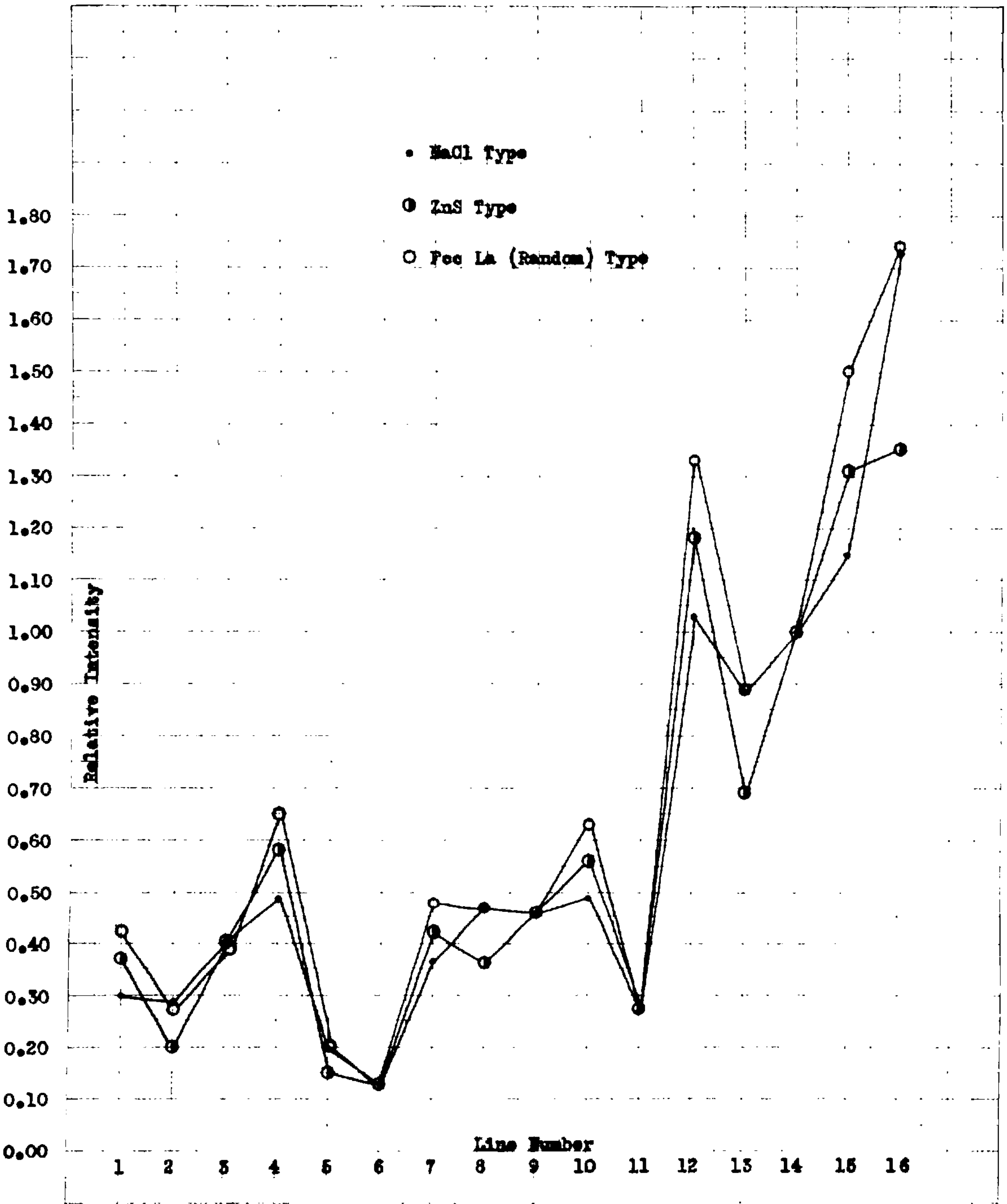

Figure 3

Calculated Relative Line Intensities for LaN agreement with observation. It will be noted, however, that the relative line intensities are actually very little different for the three structures. If was found, as is indicated by Figure 2, that it was impossible to make a clear cut decision between these various possibilities in this manner. Therefore two other methods were used, both of which compared the ratio of the relative intensities of neighboring lines in the various calculated structures with the ratio actually observed for the given lines.

The semi-quantitative method of comparing the intensity ratios of neighboring lines will be discussed first. This method utilized the intensities already observed for lanthanum nitride. The ratios of the intensities of neighboring lines were determined separately for each of the three films that were used to obtain the observed relative line intensities of lanthanum nitride already reported in this chapter. The intensity ratios so obtained were arithmetically averaged for each line pair. The mean deviation of the three indicidual ratios from the average was taken to be the error in the average. The average ratios so obtained, and their errors, are plotted in Figures 4 and 5 against the intensity ratios predicted by Figure 3 for the corresponding line pairs in the three possible structure types. These date are presented in two plots in order to avoid confusion of data on one plot. The abscissas in Figures 4 and 5 are the line pairs and the ordinates are the intensity ratios of the line pairs, i.e., the point above "2/3" on the plots represents the ratio of the intensity of line 2 to line 3. Point by point inspection of Figures 4 and 5 demonstrates that the observed intensity ratios agree better with the NaCl type structure than with either of the other two possible structures. It was therefore tentatively concluded that lanthanum nitride has

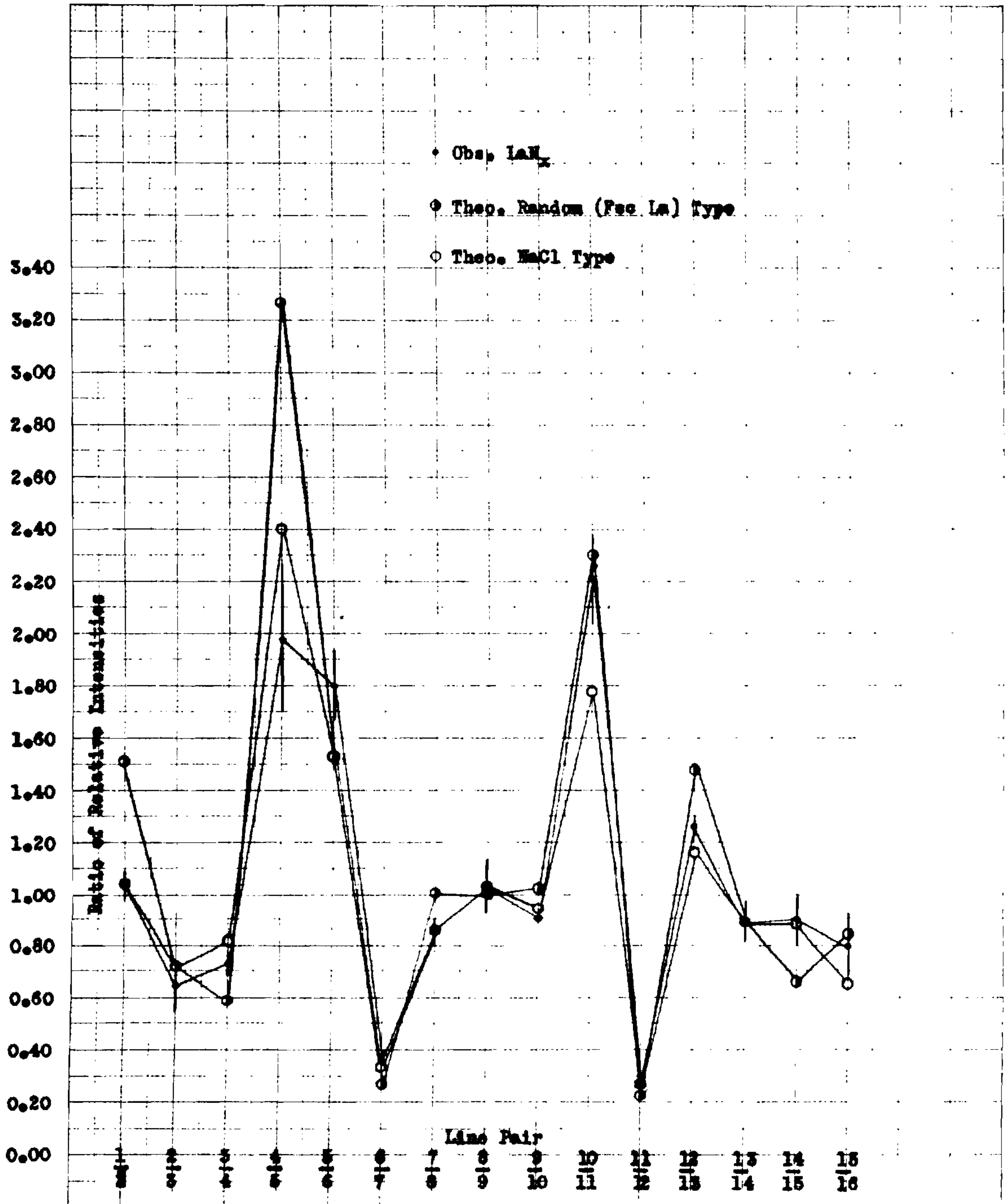

Figure 4
Intensity Ratios of Line Pairs
Obs. LaH$_x$ vs. Random and NaCl Types

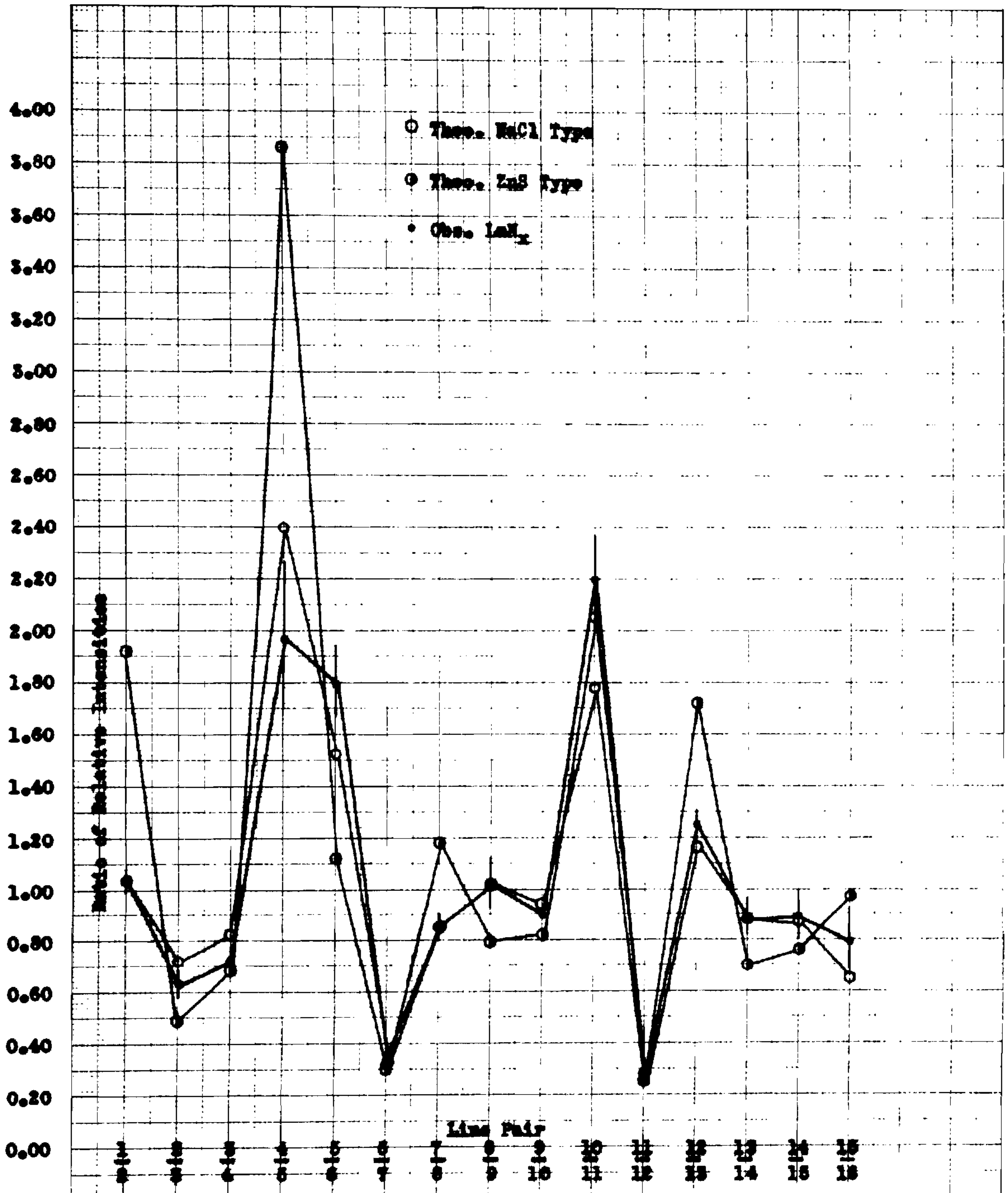

Figure 5
Intensity Ratios of Line Pairs
Obs. LaH$_x$ vs. ZnS and NaCl Types

the NaCl type of crystal structure.

The second, more qualitative, method of determining the crystal structure type of lanthanum nitride did not make use of the intensities already observed for the lines in the XRD pattern. Instead a visual comparison was made directly between the XRD patterns of the substance known to be lanthanum nitride and that thought to be fcc lanthanum, i.e., "fcc lanthanum". Comparison of these observations with Figure 3 was then used to make the determination.

There were a large number of films registering the XRD pattern of "fcc lanthanum" available from previous work[10] in the low temperature laboratory*. It was found by comparing** the apparent ratio of the intensity of one line to the next line in a pattern with the same observation on another pattern that all the films, both those bearing lanthanum nitride patterns and those bearing "fcc lanthanum" patterns, could be divided into two groups. A given group contained only the patterns from one of the two substances, and within each group the individual patterns were indistinguishable from each other. After several intercomparisons

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

* The lanthanum referred to here has been heat-treated as indicated in Table VI while reduced to filings and sealed in glass capillaries. Some of the capillaries contained nitrogen and others contained helium.

** In this special case in which the two structures have the same a_o, the same absorption coefficients, and the same crystal symmetry the line positions and line broadening were the same for both patterns, hence direct comparison of the apparent densities of the lines is justifiable.

TABLE VI

FILMS EXAMINED AND RESULT OF COMPARISONS

Film No.	Sample* Designation	Heat Treatment	Experiment in which obtained	Exposure Time, hrs.	Pattern like typical film No.
16-174	La VI	400°-4 days		3	16-174
16-172	La VI	350°-4 days		3	16-174
16-234	La VI	350°-4 days		5	16-174
16-173	La III	350°-4 days		3	16-174
16-236	La III	350°-4 days		5	16-174
16-232	La I	350°-4 days		5-1/4	16-174
16-238	La IV	350°-4 days		2-1/4	16-174
16-241	La IV	350°-4 days		2	16-174
16-242	La IV	400°-2 days		5	16-174
16-228	LaN		25	5	16-253
16-240	LaN		25	2	16-253
16-245	LaN		29	3-1/2	16-253
16-235	LaN		26	5	16-253
16-226	LaN		23	5	16-253
16-239	LaN		25	2-1/4	16-253

* The lanthanum used to prepare La I and La IV came from the first sample obtained from Cooper Metallurgical Laboratories, that used for La III was obtained from Adam Hilger, Ltd., London, England; and that used to prepare La VI and the LaN in experiments 23, 25, and 26 came from the second sample obtained from Cooper. The lanthanum used in experiment 29 was supplied by F. H. Spedding.

of the various films, one film in each group was chosen as being typical of that group and further comparison was made on that basis. The films examined, their origin and exposure times, and the results of the comparisons are listed in Table VI. The data are presented in detail here because they will be referred to later in the discussion of the distinction between "fcc lanthanum" and lanthanum nitride.

It being established by Table VI that the films bore two different patterns, it was reasonable to suppose that the theoretical relative intensities for both patterns were represented in Figure 3. That is to say, if the "fcc lanthanum" were in reality lanthanum nitride instead of true fcc lanthanum, (and because of the observed a_o value it was not reasonable to suppose that it was a third substance) then it too should have one of the three most probable structures for lanthanum nitride, even though it might be a different structure from that possessed by the lanthanum nitride prepared in this research. Furthermore, if it were actually fcc lanthanum, then the relative intensities should correspond to the relative intensities for the random orientation of nitrogen in the metal lattice.

Accordingly, the intensity relationships of line pairs in the two typical films 16-174 and 16-253 were compared visually with Figure 3. In every case in which the relationships were detectably different in the two films, the film 16-253 compared with the film 16-174 in the same manner as the plot of the values for the NaCl type structure of LaN compared with the plot of either the ZnS structure or the random orientation (fcc lanthanum). The details of this comparison are listed in Table VII. These data indicate that lanthanum nitride, as prepared in this research,

TABLE VII

COMPARISON OF TYPICAL FILMS WITH FIGURE 3

Line Pair	Intensity Relationship of second line of the pair relative to the first in lanthanum nitride as compared to same relationship for fcc lanthanum*	
	Indicated by Plate II No change vs	Observed in films 16-253 and 16-174 No change vs
1-2	Large decrease	Large decrease
3-4	Smaller increase	Smaller increase
4-5	Smaller decrease	Smaller decrease
6-7	Smaller increase	Smaller increase
9-10	Little change vs increase	No change vs increase
10-11	Smaller decrease	Smaller decrease
11-12	Smaller increase	Slightly smaller increase
12-13	Much smaller decrease	Smaller increase
14-15	Much less increase	No change vs. increase

* Assuming the NaCl type structure for lanthanum nitride and assuming that film 16-174 shows an fcc lanthanum pattern. Film 16-253 is used as the film typical of the lanthanum nitride patterns.

has the NaCl type structure.

Inasmuch as both the semi-quantitative method and the qualitative method of determing the crystal structure yielded the same result, it was concluded that lanthanum nitride, as prepared in this work had the NaCl type crystal structure.

Distinction Between Fcc Lanthanum and Lanthanum Nitride

It was shown in the previous section, principally by Table VI, that the XRD patterns of the substance thought to be fcc lanthanum and the substance known to be lanthanum nitride were found to be detectably different upon a detailed investigation of the relative intensities of the lines. It was further concluded that the substance known to be lanthanum nitride had the NaCl type crystal structure. Therefore the possibilities left for the "fcc lanthanum" were a ZnS type structure of lanthanum nitride, a lanthanum nitride structure in which the nitrogen atoms were randomly oriented in the metal lattice, or the true fcc lanthanum structure.

Two pieces of evidence suggest the improbability that "fcc lanthanum" is the ZnS type structure of lanthanum nitride. The first of these is presented in Figure 6 in which the observed intensity ratios of line pairs in the XRD patterns of "fcc lanthanum" have been plotted against theoretical values in the same manner in which Figures 4 and 5 were plotted. In this case the observed intensity ratios were obtained from relative intensity measurements on the four films 16-174, 16-232,

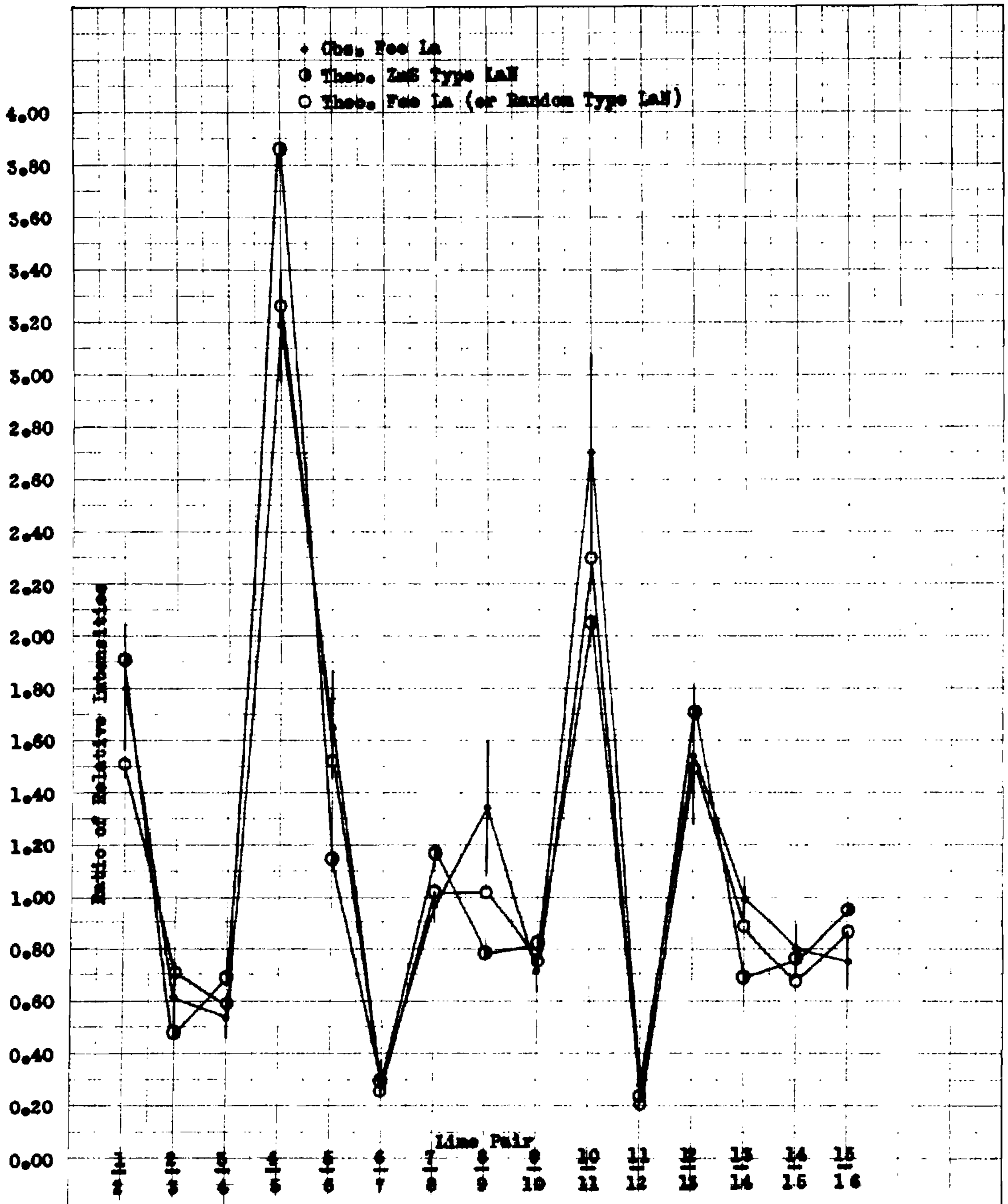

Figure 6
Intensity Ratios of Line Pairs
Obs. Fcc La vs. Theo. Fcc La (or Random Type LaN) and Theo. ZnS Type LaN

16-234, and 16-236*.

The observed relative intensities were obtained in the same manner for these patters as for the lanthanum nitride patterns, with the exception that in this case the density of each line was compared with two different film strips having portions of varying density**. Thus from the four films a total of eight sets of observed relative intensities was obtained. The resulting eight relative intensity ratios for each line pair were averaged together as previously, and it is these average values, with the mean deviation of the eight individual values from the average, that are plotted in Figure 6.

Point by point inspection of Figure 6 indicates that the observed relative intensity ratios are more like those predicted by the random orientation (or fcc lanthanum) structure than like those predicted by the ZnS type structure. It was tentatively concluded from this that "fcc lanthanum" is not the ZnS type structure of lanthanum nitride.

The second piece of evidence indicating the improbability of the occurrence of a ZnS type structure of lanthanum nitride, and hence the improbability that "fcc lanthanum" could be such a structure, is brought forth by a consideration of the accepted atomic radii of the lanthanum and nitrogen atoms. Remembering that it is an experimentally established fact that the a_o of the "fcc lanthanum" structure is approximately 5.284 Å

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* Film 16-174 had been exposed for 3 hours and the other three films had been exposed for five hours. There was no detectable differences in the relative intensities noted on these films and the relative intensities noted on the other films in Table VI.

** See Appendix IX for a comparison of the observed intensities as observed with the aid of the two different film strips.

then if the radius of the neutral lanthanum atom be taken as 1.87 Å (the radius it has in the metal, see Chapter IV) the ZnS type structure would require that the nitrogen atom have a radius no larger than 0.42 Å, whereas the usual radius assumed for the neutral nitrogen atom is 0.71 Å. On the other hand, if ionic radii be taken, the ionic radius of the tri-positive lanthanum ion is usually taken to be approximately 1.15 to 1.22 Å which would require that the nitrogen radius be not larger than 1.14 Å, whereas the radius usually assumed for the tri-negative nitrogen atom is 1.71 Å. Thus the existence of a ZnS type structure of lanthanum nitride with the observed a_o seems improbable.

From the two pieces of evidence bearing on the improbability that "fcc lanthanum" could be a ZnS type structure of lanthanum nitride, and from the fact that the XRD patterns of "fcc lanthanum" and lanthanum nitride (which was concluded to have the NaCl type structure) are different, it was concluded that "fcc lanthanum" was either a random orientation of the nitrogen atoms in the metal lattice or actually fcc lanthanum.

Again two pieces of evidence are available to indicate the proper choice. The first of these is the experiment discussed at the close of Chapter II in which an unsuccessful attempt was made to note any absorption of nitrogen by lanthanum at room temperature. The second piece of evidence is the fact that if the atomic radius of the neutral lanthanum tom is taken to be about 1.87 Å, as it is in the metal, thenthe maximum allowable radius for the nitrogen atom, in order that it might fit into a hole in the metal lattice without expanding the lattice is 0.78 Å. This is very close to the radius normally accepted for the neutral nitrogen atom of 0.71 Å. This means that the nitrogen atom would fit a hole in the metal lattice in such a way as to fill the hole almost exactly, hence its position would be relatively well determined in the lattice, corresponding to an NaCl type and not the random type structure. This same consideration of the atomic radii also could explain why both fcc lanthanum and lanthanum nitride have the same a_o.

From the above considerations it was concluded that "fcc lanthanum" was indeed the face-centered cubic modification of lanthanum, and not a surface formation of lanthanum nitride as suggested by Iandelli and Botti[11].

Summary of the Conclusions Made From the Relative Intensity Measurements

From the measurement of the relative intensities of the lines in the XRD patterns of "fcc lanthanum" and lanthanum nitride several conclusions have been reached.

The lanthanum nitride prepared in this research yields an XRD pattern in which the relative line intensities agree much better with those predicted by an NaCl type structure than those predicted by either a ZnS type structure or a random orientation of the nitrogen atoms in the metal lattice.

From a consideration of (1) the difference of the relative line intensities observed in the XRD patterns known to be due to lanthanum nitride and the relative line intensities in the XRD patterns thought to be due to fcc lanthanum, (2) the comparison of the observed relative line intensities in the "fcc lanthanum" pattern with those predicted by the ZnS type structure and those predicted by a random orientation of nitrogen atoms in the metal lattice, and (3) the atomic and ionic radii of

11. Iandelli, A., and Botti, E., Loc. cit.

the atoms involved, it was concluded that the XRD pattern commonly ascribed to fcc lanthanum in the literature and referred to herein as the pattern of "fcc lanthanum" is in reality due to fcc lanthanum and not to a surface formation of lanthanum nitride, as suggested by Iandelli and Botti.

This would mean that if the fcc modification of lanthanum is actually only a surface phenomenon overlaying the hexagonal close-packed structure of the bulk, as reported by Rossi[12], then a given piece of lanthanum metal need not be composed of a single crystalline phase. Further studies are being directed toward an investigation of the extent to which the fcc modification occurs in the bulk lanthanum metal.

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12. Rossi, A., Nature 133, 174 (1934).

CHAPTER IV

INVESTIGATION OF THE POSSIBLE SUPERCONDUCTIVITY OF LANTHANUM NITRIDE

This chapter is divided into two sections. The first section discusses the relation of some of the rare earth nitrides to certain other nitrides, many of which are superconducting, with regard to atomic radii and thermodynamic data. The purpose of the discussion is to show the reasoning that led to the selection of lanthanum nitride as a substance likely to exhibit superconductivity. On the other hand, the discussion also attempts to point out any differences between the nitrides that might explain why lanthanum nitride was found not to be superconducting down to 2°K.

The second section of this chapter describes the equipment, already in use in the low temperature laboratory prior to this research, which was used to test lanthanum nitride for superconductivity by the magnetic method. The superconductivity tests made and their results are also discussed in the second part of this chapter.

Relationship of Rare Earth Nitrides to Other Nitrides

The occurrence of superconductivity in compounds, including the nitrides, has been summarized by Ziegler[1]. In an unpublished report Ziegler[2] has analyzed the relationships of the rare earth nitrides to

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1. Ziegler, W. T., Research Engineer 9, No. 1, 15-18 (1947).

2. Ziegler, W. T., Investigation of Fundamental Properties of Elements and Their Compounds Including the Rare Earths at Very Low Temperatures With Particular Emphasis Upon Superconductivity. Status Report No. 18, Project 116-18, ONR Contract No. N6-ori-192, September 30, 1950.

other nitrides that were of interest in this investigation. The following discussion of these relationships is taken largely from his report.

The published data on the superconducting transition temperatures, the crystal structures, and the atomic radii of those transition elements which exhibit superconductivity and which form nitrides are summarized in Table VIII. Aluminum, scandium, and yttrium are included for comparison. Sources of the data are listed at the end of the table. Unless otherwise noted the data on the transition temperatures and the crystal structures of the metals have been taken from Shoenberg and Evans, respectively. The data on the rare earth metals were taken from Yost, Russell, and Garner. The nitrogen radii listed in Table VIII have been calculated, with the exception of that for cerium, upon the assumption that the metal atom has the same radius in the nitride as in the metal. In all the nitrides listed except the rare earth nitrides it is found that the face-centered cubic metal lattice has expanded slightly to accomodate the nitrogen atoms.

For the rare earths lanthanum, praseodymium, and neodymium the lattice constants of the face-centered cubic modification of the metal and the corresponding nitride are nearly the same. For cerium nitride, however, the a_0 of the nitride is considerably less than that of the face-centered cubic modification of the metal. If it be assumed that the metal atoms are in contact in CeN, the values 1.77 Å and 0.74 Å are obtained for the radii of the cerium and nitrogen atoms, respectively. It is not known whether this decrease in atomic radius for cerium is in any way associated with the phenomenon responsible for the large decrease

TABLE VIII

SUPERCONDUCTIVITY OF NITRIDES*

Element	Metal				Nitride, MN			
	Transition Temp., °K	Crystal Structure Symmetry	a_o Å	Atomic Radius Å	Transition Temp., °K	Crystal Structure Type	a_o Å	Atomic Radius of N atom Å
Al	1.14	f.c.c.		1.43		ZnO		
Sc				1.51	(1.4)**	NaCl	4.44[a]	0.71
Ti	1.81	h.c.p.		1.45	3.2 1.5	NaCl	4.40[a]	0.75
V	4.3	b.c.c.		1.32	2.3	NaCl	4.28[a]	0.82
Y	(1)[e]	h.c.p.		1.81				
Zr	0.70	h.c.p.		1.585	9.5	NaCl	4.63[a]	0.73
Nb	9.22	b.c.c.		1.430	14-16[b]	NaCl	4.38[b]	0.76
La	5.3	h.c.p. f.c.c.	 5.29	1.870 1.872		NaCl	5.27[c]	0.78
Ce	(1)[e]	h.c.p. f.c.c.	 5.14	1.81 1.817		NaCl	5.01[c]	0.74
Pr	(1)[e]	h.c.p. f.c.c.	 5.15	1.824 1.821		NaCl	5.14[c]	0.75
Nd	(1)[e]	h.c.p.		1.818		NaCl	5.14[d]	0.75

TABLE VIII (continued)

SUPERCONDUCTIVITY OF NITRIDES*

Element	Metal: Transition Temp., °K	Metal: Crystal Structure Symmetry	Metal: a_o Å	Metal: Atomic Radius Å	Nitride, MN: Transition Temp., °K	Nitride, MN: Crystal Structure Type	Nitride, MN: a_o Å	Nitride, MN: Atomic Radius of N atom Å
Hf	0.35	h.c.p.		1.58				
Ta	4.38	b.c.c.		1.43	(1.88)[b]	ZnO		

* This table compiled from information available prior to this research.

** Parentheses mean substance is not superconducting down to temperature indicated.

Evans, R. C., Crystal Chemistry. Cambridge University Press, Cambridge, 1939, p. 92, 104.

Shoenberg, D., Superconductivity. Cambridge University Press, Cambridge, 1938, p. 106.

Yost, D. M., Russell, H., and Garner, C. S., The Rare Earth Elements and Their Compounds, John Wiley and Sons, New York, 1947, p. 52.

Ziegler, W. T., "Some Properties of Matter at Low Temperatures," Research Engineer 9, No. 1, 15-18 (1947).

(a) Becker, K., and Ebert, F., Z. f. physik. Chem. 31, 268 (1925).

(b) Horn, F. H., and Ziegler, W. T., J. Am. Chem. Soc. 69, 2762 (1947); Milton, R. M., Chem. Revs. 39, 421 (1946).

TABLE VIII (continued)

SUPERCONDUCTIVITY OF NITRIDES

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

(d) Ibid., 638

(e) Shoenberg, D., Proceedings of the International Conference on the Physics of Very Low Temperatures. Mass. Inst. Technology, Sept. 6-10, 1949, p. 87.

in atomic radius observed by Schuch and Sturdivant[3] in face-centered cubic cerium at 90°K.

But even though cerium nitride seems to differ from the other rare earth nitrides in Table VII, still all the rare earth nitrides listed differ from the other nitrides in that the metal lattice does not expand when the nitride is formed.

The standard free energy, heat and entropy of formation, and reactivity with water of the various nitrides is summarized in Table IX. All data in the table are based upon the assumption that the formula of the nitride is MN in each instance. The thermodynamic data listed do not show any striking differences between the rare earth nitrides and the superconducting nitrides. However, the reaction of the rare earth nitrides with water, as compared with TiN, VN, ZrN, and NbN, all of which exhibit superconductivity, suggests that there may be a difference in electronic structure which could be reflected in the electrical properties of the nitrides.

Inasmuch as no measurements had been made on the possible superconducting properties of either lanthanum nitride or cerium nitride, and since the above considerations seemed to indicate that such superconductivity might occur, measurements were undertaken with the magnetic method upon nitride samples prepared in this research. The preparation and crystal structure of the cerium nitride sample investigated is discussed in Appendix I. This is the sample of cerium nitride that was prepared in Experiment 30 and is listed in Table II.

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3. Schuch, A. F., and Sturdivant, H. H., J. Chem. Phys. 18, 145 (1950).

TABLE IX

THERMODYNAMIC DATA AND REACTIVITY

OF METAL NITRIDES[a]

Nitride MN	Transition Temp., °K	ΔF^{o}_{298} (kcal)	ΔH^{o}_{298} (kcal)	ΔS^{o}_{298} (kcal)	Reaction With Water
Al		-56.3	-64.0	-25.8	Decomposes
Sc	(1.4)[b]	-60.5	-68		Decomposes
Ti	3.2	-73.5	-80.3	-22.9	Insoluble
V	2.3	-34.5	-40.8	-21.0	Insoluble
Y		-64	-71.5		Decomposes
Zr	9.5	-75.3	-82.2	-23.2	Insoluble
Nb	14-16	-53	-59		Insoluble
La		-64.7	-72.1	-25.0	Decomposes
Ce		-70-6	-78.0	-25.0	Decomposes
Pr					Decomposes
Nd					Decomposes
Hf		-72	-78.3		
Ta	(1.88)	-52.2	-58.1	-19.9	Insoluble

(a) Data of Brewer, L. et al., Chemistry and Metallurgy of Miscellaneous Materials. Thermodynamics. McGraw-Hill Book Co., Inc., New York, 1950, p. 42.

(b) Parentheses mean nitride is not superconducting down to temperature indicated.

Note: This table was compiled from information available before this research was carried out.

A discussion of the equipment used in these measurements and the experimental results follows:

Equipment Used and Experimental Results Obtained in Superconductivity Tests

The low temperature measurements were carried out by Dr. W. T. Ziegler and the author with the assistance of several other members of Dr. Ziegler's research group. The equipment used was that which was already in operation in the low temperature laboratory. It consisted of a helium cryostat equipped with a gas thermometer and a resistance thermometer, and provided with suitable means for measuring the change in the magnetic permeability of the samples as a function of temperature.

The helium cryostat is shown in a simplified schematic diagram in Figure 7. A detailed description of this apparatus has been given by Ziegler recently[4] and he has also given a less complete description elsewhere[5]. A complete description of a very similar cryostat has been given by Horn and Ziegler[6]. The main charge of liquid helium is produced in the heavy walled vessel "A", from which the experimental chamber "B" is suspended. Liquid helium is produced in A by the adiabatic expansion of helium gas at a pressure of 2,300 pounds per square inch against atmospheric pressure at the temperature of solid hydrogen (12°K). Helium in-

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

5. Ziegler, W. T., Refrig. Eng. 56, 402 (1948).

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

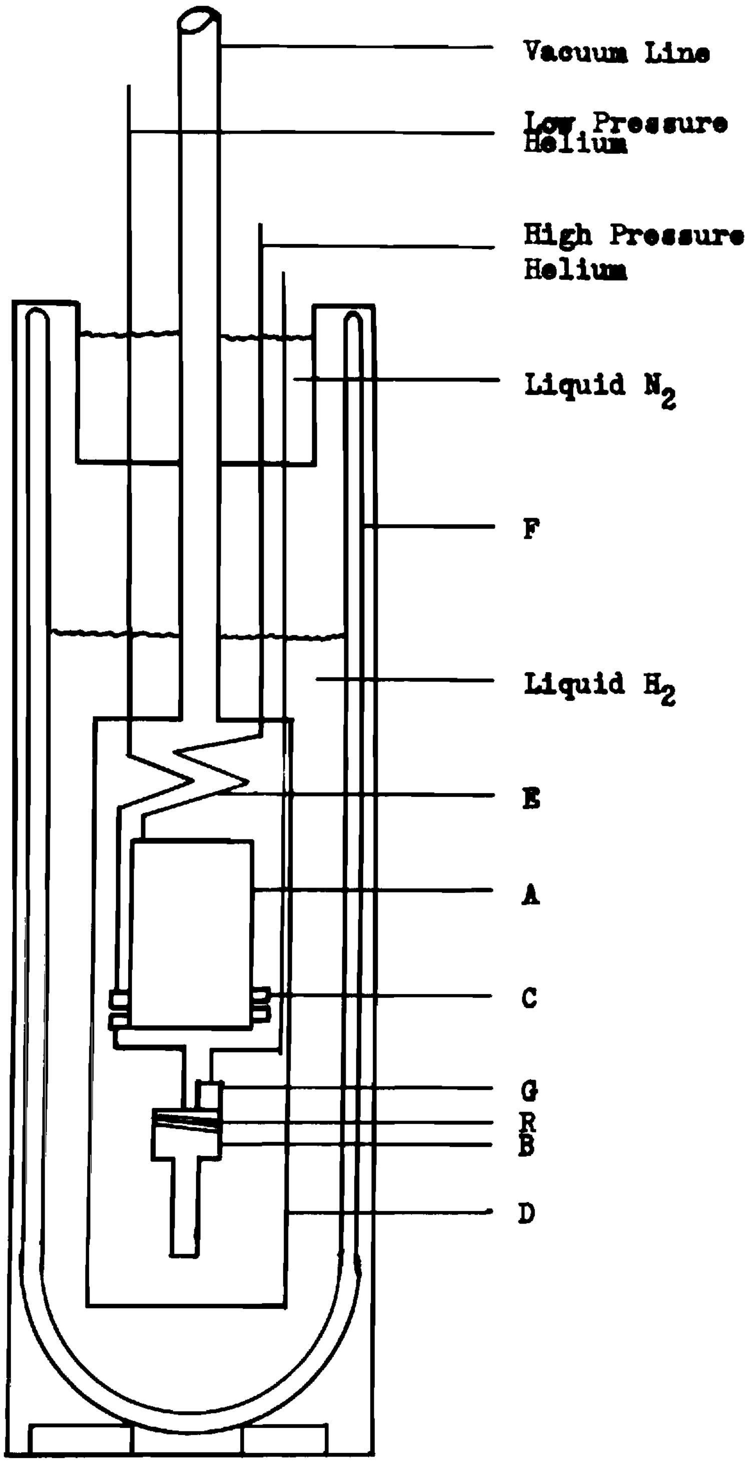

Figure 7. Schematic Diagram of Cryostat

troduced at about 20 pounds per square inch gauge pressure through the coils "C" is cooled by contact with "A" and condenses into the experimental chamber "B". Cold gas from "A" passes upward through the heat exchanger "E" to cool incoming gas. "D" is a vacuum-tight case and is surrounded by liquid hydrogen contained in the glass Dewar vessel "F". The liquid hydrogen and liquid nitrogen baths serve as thermal dams through which all incoming connections to the experimental chamber pass.

The gas thermometer "G" and the resistance thermometer "R" are both located at the upper end of the experimental chamber. The gas thermometer, which is of the type described by Mendelssohn[7], consists of a large bulb connected externally to a bourdon gauge and a mercury manometer by a supernickel capillary tube. If the volume of the capillary is assumed to be negligible then the relation between temperature and pressure in this system is

$$T = \frac{1}{\left[\frac{P_o}{PT_o}(1+a) - \frac{a}{T^1}\right] \quad C} \tag{1}$$

where

T = temperature of the bulb in ^oK

P = observed pressure in mm

P_o= filling pressure in mm

T_o= filling temperature in ^oK

T'= temperature in ^oK of the external volume at the time of the experiment

7. Mendelssohn, K., Z. Physik. 73, 482 (19321).

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

c = the compressibility factor, $\frac{PV}{RT}$

For practical purposes "a" can be considered a parameter and is determined at a known point such as the normal boiling point of helium. The compressibility factor, "c", was calculated or estimated from tabulated P-V-T data[8]. This thermometer could be read to about 0.04°.

The resistance thermometer "R" was constructed of No. 40 B and S gauge constantan wire and had a resistance of 1,069 ohms and a dR/dT of 0.92 ohms per degree at 4°K. A change of about 0.02° could be noted with this instrument, thus making it useful for interpolation between gas thermometer points.

The superconductivity measurements were made by placing the cylindrical samples inside of small cylindrical inductance coils which acted as secondaries of a transformer. Four such small coils, arranged vertically on the outside surface of the lower portion of the experimental chamber, were surrounded by a single primary coil. Each of the four coils had separate electrical connections. Samples were placed in three of the coils, the fourth was left empty. The coil holding the particular sample to be tested was then connected, outside the cryostat, in electrical opposition to the empty coil. A variable inductance, physically outside the cryostat, was placed electrically in the circuit of the empty coil and was excited by the same direct current pulse that excited the primary in the cryostat. By manipulation of the variable inductance

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8. Landolt-Bornstein Tabellen, Erg. I, 59 (1929).

the voltages were balanced so that at room temperature no current flowed in the circuit containing the two small coils, even though a current pulse was sent through the primary by a tap-key arrangement. This condition of balance was usually maintained down to the temperature of liquid helium unless the sample became superconducting. In this event the magnitude of the unbalance was indicated by a ballistic galvanometer in the circuit. For a sample of lanthanum metal of roughly 2 grams the unbalance caused by the superconductivity of the sample resulted in a galvanometer scale deflection of about 5 cm.

In two separate runs, 15 and 16, the samples of lanthanum nitride prepared in experiments 25 and 29, and the cerium nitride sample prepared in experiment 30, were tested for superconductivity down to 1.80°K with negative results. In run 15 a sample of lanthanum metal, designated in the laboratory as La 2, was also placed in the cryostat to check its operation. This sample was found to go superconducting at the same temperature as it had many times before[9,10], thus indicating that the equipment was operating properly. In run 16 a sample of the cerium metal used in preparing the nitride was also included because it was expected that this run would produce the lowest temperature yet reached with this equipment. The results were negative for the cerium metal as well as for the nitrides. Table X summarizes the superconductivity measurements made.

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

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

TABLE X

TESTS OF NITRIDES FOR SUPERCONDUCTIVITY

Run No.	Sample* Designation	Description	Dia. (mm)	Dimensions Length (mm)	Weight (gm.)	Transition Temp., °K
15	La 2	Lanthanum metal (Cooper No. 1)	4.8	20.3	2.3	4.88 (gas thermometer) 5.00 (resistance thermometer)
	LaN 1	LaN_x from Expt. 26 (Cooper No. 2)	5	12.5	0.4	Not superconducting down to 1.80°
	LaN 2	LaN_x from Expt. 29 (Spedding)	5	14	0.6	Not superconducting down to 1.80°
16	Ce 1	Cerium metal (Cooper No. 1)	4.5	20	2.2	Not superconducting down to 1.80°
	LaN 2	LaN_x from Expt. 29 (Spedding)	5	14	0.6	Not superconducting down to 1.80°
	CeN 1	CeN_x from Expt. 30 (Cooper No. 1)	5	25	0.9	Not superconducting down to 1.80°

* The lanthanum and cerium metal samples were solid cylinders; all nitrides were loosely packed powders.

All the samples used had been sealed off in glass capsules under helium at a pressure of about 20 cm Hg at room temperature. The metal samples were in the form of cylinders, while the nitride samples were loosely packed powders held by the containing glass capsules in cylindrical form of about the same size as the metal samples. Heat transfer seems well established by the superconductivity of the La 2 sample and by the fact that in a previous experiment[10], not a part of this research, lanthanum metal filings had been placed in a capsule in the same manner as the nitrides, yet they had been found to be superconducting at the same temperature as the bulk metal. In view of these considerations and the fact that in both runs the temperature of the experimental chamber was below the liquid helium point (4.22°K) for more than half an hour it seems probable that the samples were in thermal equilibrium with their surroundings and that the samples are therefore not superconducting down to 1.8°K.

In reference to the discussion of Table IX, it was found there that the reaction of the rare earth nitrides with water differed from that of the superconducting nitrides and it was suggested that this difference might be ascribed to a basic difference in electronic structure. This view seems to be supported to some extent by the negative results obtained here for superconductivity of the lanthanum and cerium nitrides. However the possibility remains that these nitrides might be superconducting at temperatures lower than those reached in this research. If

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

this were to occur it would not be the first case in which the transition point for the nitride was lower than that for the metal, as is demonstrated by the case VN in Table IX. The possibility also remains that electrical measurements might reveal superconductivity in these nitrides.

BIBLIOGRAPHY

BIBLIOGRAPHY

Becker, K., and Ebert, F., Zeitschrift fur physikalische Chemie. 31, 268 (1925)

Birge, R. T., Reviews of Modern Physics. 13, 233 (1941)

Blake, F. C., Reviews of Modern Physics. 5, 174 (1933)

Brewer, L., et al., Chemistry and Metallurgy of Miscellaneous Materials. Thermodynamics. McGraw-Hill Book Co., Inc., New York, 1950, p. 42.

Bunn, C. W., Chemical Crystallography. Oxford University Press, London, 1945, pp.103-27.

Compton, A. H., and Allison, S. K., X-rays in Theory and Experiment. D. Van Nostrand Co. Inc., New York, 1935, 2nd. ed., p. 417

Debye and Scherrer, Physikalische Zeitschrift vereinigt mit dem Jahrbuch der Radioaktivitat und Elektronik. 19, 481 (1919)

Evans, R. C., Crystal Chemistry. Cambridge University Press, Cambridge, 1939, p.92, 104.

Friederich, E., and Sittig, L., Zeitschrift fur anorganische und allgemeine Chemie. 143, 314 (1925)

Greenwood, G., The London, Edinburgh, & Dublin Philosophical Magazine and Journal of Science. 3, 968 (1927)

Horn, F. H., and Ziegler, W. T., The Journal of the American Chemical Society 60, 2762 (1947)

Iandelli, A., and Botti, E., Atti della accademia nazionale dei Lincei. Rendiconti, Classe di science fisiche, matematiche e naturali. 24, 465 (1936), 25, 129-32 (1937)

Iandelli, A., and Botti, E., Atti della accademia nazionale dei Lincei. Rendiconti, Classe di science fisiche, matematiche e naturali. 26, 233-8 (1937)

Internationale Tabelen Zur Determination Von Kristallstrukturen, Zweiter Band, Mathematische und Physikalische Tabelen, Gebrueder Borntraeger, Berlin, 1935, p. 567

Kellenberger, F., and Kraft, K., Justus Liebigs Annalen der Chemie. 325, 280 (1902)

Landolt-Bornstein Tabellen, Erg. I, 59 (1929)

Matignon, C., Comptes rendus hebdomadaires des seances de l'academie des sciences. 131, 837 (1900)

Mendelssohn, K., Zeitschrift fur Physik. 73, 482 (1931)

______, and Daunt, J. G., Nature 139, 473 (1937)

Muthmann, W., and Kraft, K., Justus Liebig's Annalen der Chemie, 325, 262-77 (1902)

Neumann, B., Kroger, C., and Haebler, H., Zeitschrift fur anorganische und allgemeine Chemie. 207, 144-8 (1932)

______, and Kunz, H., Zeitschrift fur anorganische und allgemeine Chemie. 207, 133 (1932)

Peret, A., and Banderet, A., Comptes rendus hebdomadaires des seances de l'academie des sciences. 204, 586-8 (1937)

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

Rusterholtz, A., Zeitschrift fur Physik. 63, 1 (1930)

Schuch, A. F., and Sturdivant, H. H., The Journal of Chemical Physics. 18, 145 (1950)

Shoenberg, D., Proceedings of the Cambridge Philosophical Society 33, 577 (1937)

______, Proceedings of the International Conference on the Physics of Very Low Temperatures. Massachusetts Institute of Technology, September 6-10, 1949, p. 87.

______, Superconductivity. Cambridge University Press, Cambridge, 1948, p. 106

Siegbahn, M., Nature 151, 502 (1943)

Sieverts, A., and Muller-Goldegg, G., Zeitschrift fur anorganische und Chemie. 131, 77 (1923)

Sproull, Wayne T., X-rays In Practice. McGraw-Hill Book Co., Inc., New York, 1946, p. 576

Tamman, G., Zeitschrift fur anorganische und allgemeine Chemie. 124, 33-4 (1922)

Vournasos, A. C., Bulletin de la societe chimique de France. 9 512 (1912)

Yost, D. M., Russell, H., and Garner, C. S., The Rare Earth Elements and Their Compounds. John Wiley and Sons, New York, 1947, p. 52

Ziegler, W. T., Georgia School of Technology, State Engineering Experiment Station, Research Engineer. 9, No. 1, 15-18 (1947)

_______, Investigation of Fundamental Properties of Elements and Their Compounds Including the Rare Earths at Very Low Temperatures With Particular Emphasis Upon Superconductivity. Status Report No. 18, Project 116-18, ONR Contract No. N6-ori-192, September 30, 1950

_______, Refrigerating Engineering. 56, 402 (1948)

_______, The Journal of Chemical Physics 16, 838 (1948)

_______, Superconductivity of Lanthanum, Cerium, Praseodymium, and Neodymium. Technical Report No. 1, Project 116-18, ONR Contract No. N6-ori-192, January 20, 1949

_______, Floyd, A. L., Jr., and Young, R. A., Crystal Structure and Superconductivity of Lanthanum. Technical Report No. 2, Project 116-18, ONR Contract No. N6-ori-192, March 2, 1950

APPENDICES

APPENDIX I

STUDIES INVOLVING CERIUM

Although this research was primarily concerned with lanthanum nitride, one sample of cerium nitride was also prepared in order that the two metals might be compared with respect to their reaction with nitrogen, the crystalline form of their nitrides, and the possible superconducting properties of their nitrides.

The cerium used was obtained from the Cooper Metallurgical Laboratories, Cleveland, Ohio. Spectrographic, ion-exchange, and direct precipitation analyses were made on this product by the personnel of the low-temperature laboratory. Consideration of the three results led to the choice of 95% as being representative of the total rare earth content of the material. The distribution indicated by the ion-exchange method is as follows:

Cerium	92.2%
Lanthanum	None
Praseodymium	0.4%
Neodymium	0.6%
Other rare earths	None
Silicon	(0.3% by chem. method)
Iron	(2.5% by chem. method)

Total accounted for.... 96.0%

The experiment in which cerium nitride was produced, experiment 30, is listed in Table II with the experiments which produced lanthanum nitride. In so far as possible the same technique was used for the preparation of cerium nitride as for the preparation of lanthanum nitride. Slightly lower temperatures were used in the case of cerium in order to reduce the expected violence of the reaction.

The reaction of cerium with nitrogen, a plot of which is given in Figure 12 which is included with the other reaction plots in Appendix IV, was observed to start at about 525°C. The reaction rate increased during the first fifteen minutes and then remained approximately constant for the ensuing half-hour. At the end of this time the temperature was about 625°C and the reaction was about 2/3 completed. The rate then decreased to nearly zero during the next three hours. The temperature at this time, about three hours and forty-five minutes after the reaction had started, was 710°C. The temperature was deliberately kept lower in this experiment than in the lanthanum nitride experiments because Muthmann and Kraft[1] noted that at 850-900°C the cerium-nitrogen reaction was so strongly exothermic that if fused the wires of their thermocouple. No such violent reaction was noted in this experiment, perhaps because the temperature was raised very gradually.

The cerium nitride obtained was of a light brown color with a slight red tinge. It was homogeneous to the eye and was not sintered. Muthmann and Kraft[1], on the other hand, described their cerium nitride as bronze to yellow in color underneath a black surface coating. Neuman, Kroeger, and Kunz[2] who also prepared cerium nitride by direct combination methods, reported an appearance similar to that observed by Muthmann and Kraft.

In Table II it is stated that the value obtained for "x" in the formula CeN_x was 0.86 both by measurement of the weight increase of the sample and by measurement of the volume of nitrogen absorbed. It is

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1. Muthmann, W., and Kraft, K., Ann. Chem. 325, 262-77 (1902).

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

notable that Experiment 30 is the only experiment in which the same value for "x" was obtained by both methods. It is not known whether this indicates a fundamental difference in the impurities in the two metals, lanthanum and cerium, or whether the fact that "x" is the same by both methods in the cerium case is coincidental. The value of "x" reported in Table II for CeN_x was calculated on the assumption that the metal sample was 95% cerium.

From nine experiments Muthmann and Kraft obtained an average value of 0.89 for "x". Neumann, et al., reported values ranging from 0.71 to 0.87. Thus the value of "x" = 0.86 obtained in this experiment agrees well with those values obtained by other investigators.

The lattice parameters of both cerium metal and cerium nitride were measured by the same techniques used to measure the lattice parameter of lanthanum nitride. Both the cerium metal and the cerium nitride yielded XRD patterns exhibiting face-centered cubic crystal symmetry. The measurements, made from a single film in each case, yielded the following values for the size of the unit cell, a_o:

Cerium $a_o = 5.130 \pm 0.014$ kx-units

Cerium nitride $a_o = 5.014 \pm 0.005$ kx-units

These values agree well with the values reported by Iandelli and Botti[3] of 5.14 and 5.01 kx-units, respectively. No attempt was made to use the relative intensities of the lines in the XRD pattern of cerium nitride to determine its crystal structure type.

3. Iandelli, A., and Botti, E., Atti. accad. nazl. Lincei, Classe sci. fis. mat. e nat. 25, 129-32 (1937).

As mentioned in Chapter IV, superconductivity tests using the magnetic method were conducted on the cerium nitride down to $1.8^{\circ}K$ with negative results.

APPENDIX II

EXPLORATORY EXPERIMENTS

Exploratory experiments using filings from a lanthanum sample having about the same purity as the Cooper lanthanum sample described in the text indicated that a copper reaction boat was attacked at elevated temperatures, (in this case, 600-700°C). This attack was perhaps due to impurities in the lanthanum because, as previously mentioned, Muthmann and Kraft reported no such difficulty in using copper boats. In addition to the attack on the boat, an unfamiliar but reproducible structure appeared as the major structure in the XRD patterns ofthe lanthanum samples that had been degassed at elevated temperatures in the copper boats. Subsequent heating of one of these samples in nitrogen caused the unfamiliar structure to diasppear and be replaced by the lanthanum nitride structure in the XRD patterns.

The decomposition of stop-cock grease in joint "A" (Figure 1) due to radiated heat from the furnace was considered a possible explanation of the appearance of the unfamiliar structure, even though the joint was continuously cooled by a water-soaked cloth. Hence the cooling of the joint was improved and the furance was moved a few centimeters farther away from it. In addition to this molybdenum boats were substituted for copper boats in the more successful experiments.

Experiments 19, 20, and 22 employed a molybdenum boat that was not thoroughly cleaned, but even so they were able to show that the unfamiliar structure which appeared in the XRD patterns of the earlier experiments no longer occurred. The nitriding experiment of this series, experiment 20, produced some lanthanum nitride but also some lanthanum oxide. In experiment 22, in which the sample of experiment 20 was heated in the evacuated, closed off reaction volume, indicated that the dissociation pressure of the nitride was probably quite low, even at 900°C. Experiment 22 also indicated that the combined effects of the diffusion and leakage of atmospheric gases into the hot furnace tube were very likely responsible for the formation of lanthanum oxide in experiment 20, which had been carried out with a nitrogen pressure of about one-half of an atmosphere in the reaction volume.

The more successful experiments 23, 25, 26, and 29 employed a molybdenum boat which was shiningly clean and the experimental procedure was changed to eliminate a pressure differential across the hot furnace tube.

APPENDIX III

REDUCTION METHODS WHICH HAVE BEEN USED TO PREPARE LANTHANUM NITRIDE

This appendix consists of a chronological review of the various preparations of lanthanum nitride by reduction methods.

Lanthanum nitride was first prepared by Matignon[1] in 1900. His method consisted of reducing lanthanum oxide by heating it as an intimate mixture with powdered magnesium in a closed volume.

Chronologically the next preparation of lanthanum nitride was that carried out by Muthmann and Kraft. This method has been discussed in the text.

In 1911 Vournasos[2] prepared lanthanum nitride by the reduction of KCN with dried, powdered lanthanum metal through heating for 15 minutes at 650°C. Vournasos reported that the lanthanum nitride so obtained was white. If he washed off the excess KCN with water in this experiment, as he did in some other experiments reported in the same paper, this would explain why he reported the color of lanthanum nitride as white whereas all other investigators found it to be of a dark color.

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1. Matignon, C., Comp. rend. 131, 837 (1900).
2. Vournasos, A. C., Bull. Soc. Chim. France. 9, 512 (1912).

Friederich and Sittig[3] prepared lanthanum nitride in 1925 by the reduction of the oxide with carbon in a strem of pure dry nitrogen at 1,300°C. They reported that the lanthanum nitride so obtained was granular, easily soluble in acids, the color of graphite, and probably melts below 1,700°C.

In 1937 Peret and Banderet[4] reported the formation of lanthanum nitride upon using too high a temperature in the preparation of the cyanamide. Using iron as a catalyst the following reactions were obtained at temperatures of 300°C and above:

$$LaCl_3 + 3\ NaCN = La(CN)_3 + 3NaCl \qquad (1)$$

$$2\ La(CN)_3 = La_2(NCN)_3 + 3C \qquad (2)$$

$$La_2(NCN)_3 = 2\ LaN + 3C + 2N_2 \qquad (3)$$

The maximum yield of cyanamide occurred at 500°C. Above this temperature equation (3) became more and more predominant until at 700°C no cyanamide remained. The purity of the resulting lanthanum nitride was not discussed.

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3. Friederich, E., and Sittig, L., Z. anorg. u. allgem. Chem. 143, 314 (1925).

4. Peret, A., and Banderet, A., Compt. rend. 204, 586-8 (1937).

APPENDIX IV

DISCUSSION OF THE MORE SUCCESSFUL EXPERIMENTS IN WHICH LANTHANUM NITRIDE WAS PREPARED

In this appendix the plots of the reactions involved follow a discussion of the experiments. The plot of the cerium-nitrogen reaction of experiment 30 is included here for comparison.

After the lanthanum filings of experiment 23 (see Table II, Chapter II) were degassed at room temperature nitrogen was added. The sample was heated to about 900°C and kept at that temperature for 5 hours. Consecutive observations of the mercury level in the gas burette and of the thermocouple temperature indicated that the reaction started slowly at about 600°C. The reaction rate increased after several minutes, then decreased after about 30 minutes and continued to decrease until the reaction had apparently stopped about one hour after it had started. The temperature had reached 800°C by this time. The product of this experiment was uniformly black, free-flowing particles and yielded very clear XRD patterns which exhibited no lines not attributable to the nitride.

As the sample in experiment 23 had been degassed at room temperature it was decided to degas a sample at an elevated temperature to see if any weight change would result. Consequently the sample of experiment 25 was first degassed at room temperature, then heated to 600°C and degassed for four hours more. The sample was then cooled and reweighed. Since no weight change was noted it was decided to use this sample to

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* See Table I, page 9.

study the effect of temperature upon the rapidity and the degree of completion of the lanthanum-nitrogen reaction. The sample was again degassed at room temperature and after the nitrogen had been added the furnace control was set for an equilibrium temperature of about 750°C. The reaction again started slowly at about 600°C, as in experiment 23. However, within 10 to 15 minutes the reaction rate increased to a more or less constant value which was maintained for about 2 hours before decreasing assymptotically to zero. Even after 17 hours some doubt existed as to whether the reaction was completed.

At this point, however, the nitrogen was removed, measured, and replaced while the sample was kept at the 750°C temperature. The temperature was then raised to about 900°C to find out if the reaction could be driven to a greater degree of completion by the increased temperature. No further absorption was noted by following the reaction with the burette level. Upon cooling the system and removing the nitrogen it was found that about 1 cc more gas was apparently present at the end of the experiment than had been admitted at the 750°C temperature. This anomaly is still not satisfactorily explained. Experiment 24, described in the text, indicated that it could not be due to evolution of gas from the sample. In any event, it would be expected that any gas evolved in passing from the 750° temperature to the 900° temperature would surely be re-absorbed upon cooling the sample to room temperature in the nitrogen atmosphere. The most convincing argument yet advanced to explain this apparent anomaly is that the radiated heat from the furnace, which was located about two feet from the gas burette, set up a non-equilibrium temperature condition in the water jacket of the gas burette. Thus an error would be introduced into the volume measurement made when the furnace was at the 750° temperature. The value of "x" reported for this experiment in Table II is that which was calculated from the volume measurements made at the beginning and the end of the experiment, which were both at room temperature. The measurements made at 750°C were not used for this calculation.

Although experiment 25 apparently resulted in a more complete reaction than did experiment 23, the comparatively slower reaction rate at 750°C suggested the possibility that the reaction might be driven to a slightly greater degree of completion by heating the sample directly to 900°C and holding it there for a very long time. Accordingly the sample of experiment 26 was heated to 900°C (over a period of about two hours, which is the heating time of the furnace with the control set for an equilibrium temperature of 900°C) and maintained at this temperature for 20 hours. Following the reaction with the mercury level in the gas burette indicated that the reaction started at about 575°C, followed much the same pattern as the reaction of experiment 23, and was apparently completed within 1-1/2 hours after it had started. The temperature at this time had reached 850°C. However, the experiment was continued for a total time of 20 hours at the 900° temperature in order to be certain that any slow reaction that might be going on would have an opportunity to reach completion. As is observed from Table II the long time at the high temperature apparently did have some success in driving the reaction to a greater degree of completion than did either of the two previous experiments. However, when it is considered that the error in the tabulated value of "x" is probably 1% to 2% the differences between the values found in experiment 25 and those found in experiment 26 lose significance.

Inasmuch as the Spedding lanthanum sample came from an entirely different source it afforded an opportunity to investigate any correlation between the source of the lanthanum and the resulting nitride. Consequently, in experiment 29, a nitride sample was prepared from the Spedding lanthanum in exactly the same manner as the nitride was prepared from the Cooper lanthanum in experiment 26. Some slight differences were noted. The reaction of the Spedding lanthanum with nitrogen occurred more slowly, although it started at about the same temperature (600°C). The reaction proceeded to approximate completion in about 2 hours, but even after 4 hours had elapsed the reaction still seemed to be going very slowly, after the manner of the reaction of the Cooper lanthanum at 750°C in experiment 25. There was no difference in the appearance of the Spedding lanthanum nitride from that of the Cooper lanthanum nitride. There did seem to be a slight difference in the value of "x" obtained in Table II for the two nitrides, and there also seemed to be a slight difference in their lattice parameters, as noted in Chapter III of this thesis. Again, however, these slight differences in the measured values may be accounted for by experimental error.

In the following figures the temperature plotted is that which was read from the thermocouple. The variable which indicates the progress of the reaction is the burette reading. The value plotted for the burette reading is the actual reading minus the reading when the reaction volume was filled with nitrogen at room temperature and atmospheric pressure, i.e., the burette reading at the start of the experiment.

If no reaction were to take place it would be expected that, because of the expansion of the gas in the furnace upon heating, the burette reading would continuously increase with temperature. On the other hand, chemical reaction resulting in the absorption of nitrogen would result in a decrease in the burette reading. Thus the point at which the burette reading curve ceases to increase with temperature indicates the point at which the two effects exactly balance each other. A decrease in the burette reading indicates an absorption of nitrogen by the metal sample.

No points are shown in the plots. This is partly because the curves are intended to give only qualitative information, and partly because the points taken were too numerous to show individually. This is particularly true in the region at the start of the reaction where points were taken as frequently as every minute. No point of the temperature plots fell off the curves by more than 10° and no point of the burette reading plots fell off the curves by more than 0.5 cc.

In Experiment 23 no data were taken of the burette reading until the reaction had started. Hence the plot for this reaction is incomplete. In this case the burette reading plotted is the true burette reading, no arbitrary zero point being subtracted.

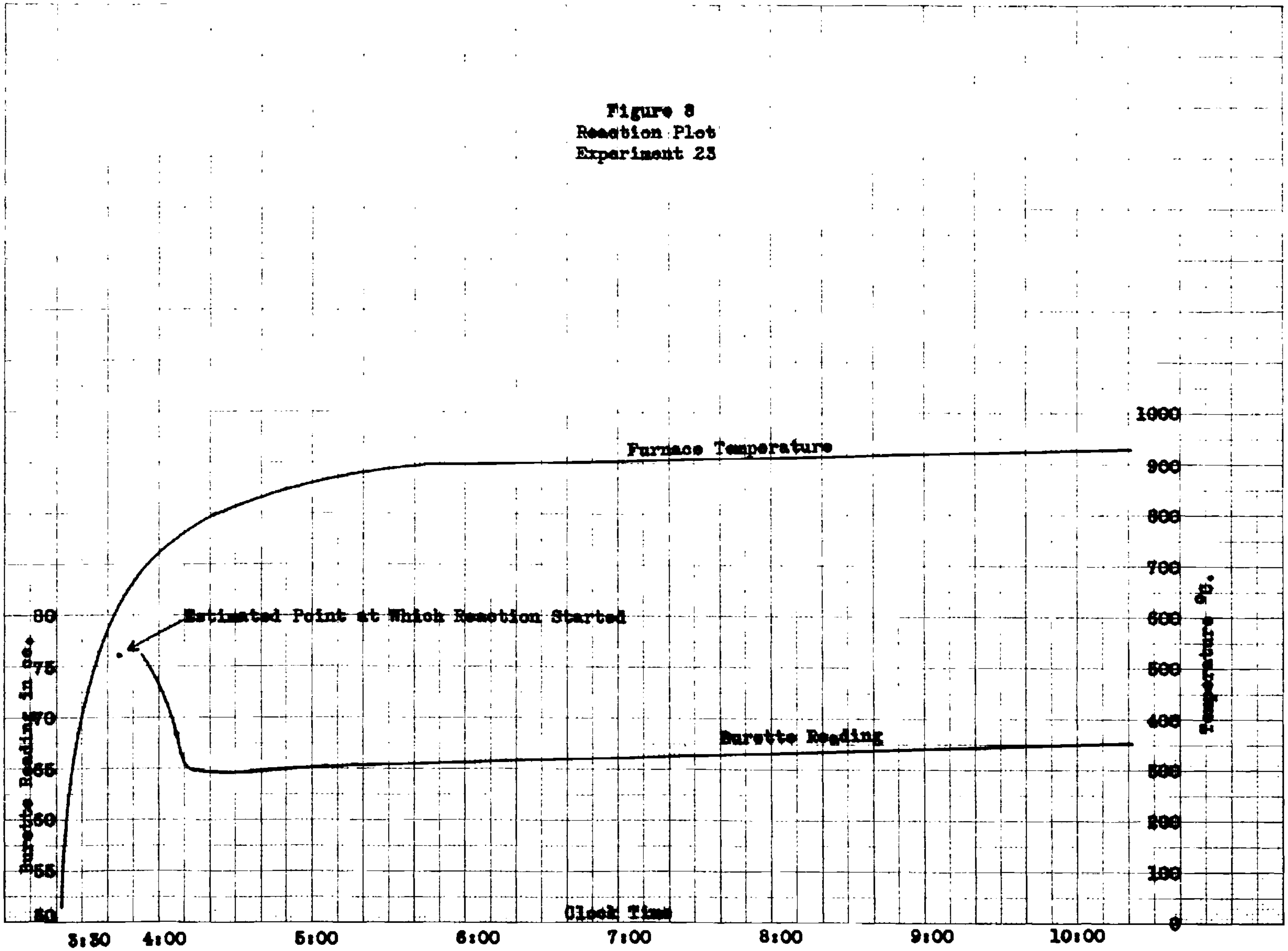
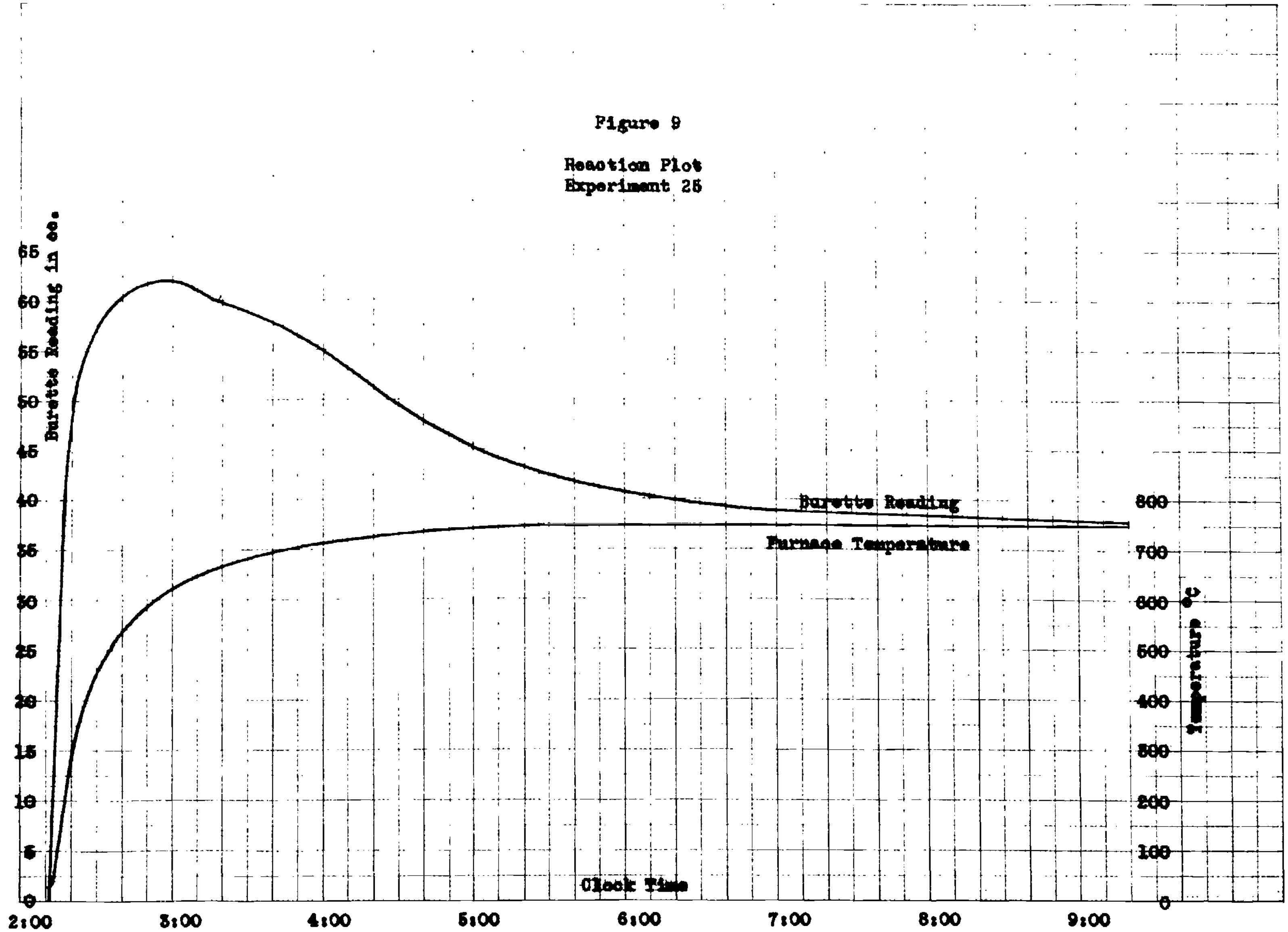


Figure 8
Reaction Plot
Experiment 23

Figure 9

Reaction Plot
Experiment 25



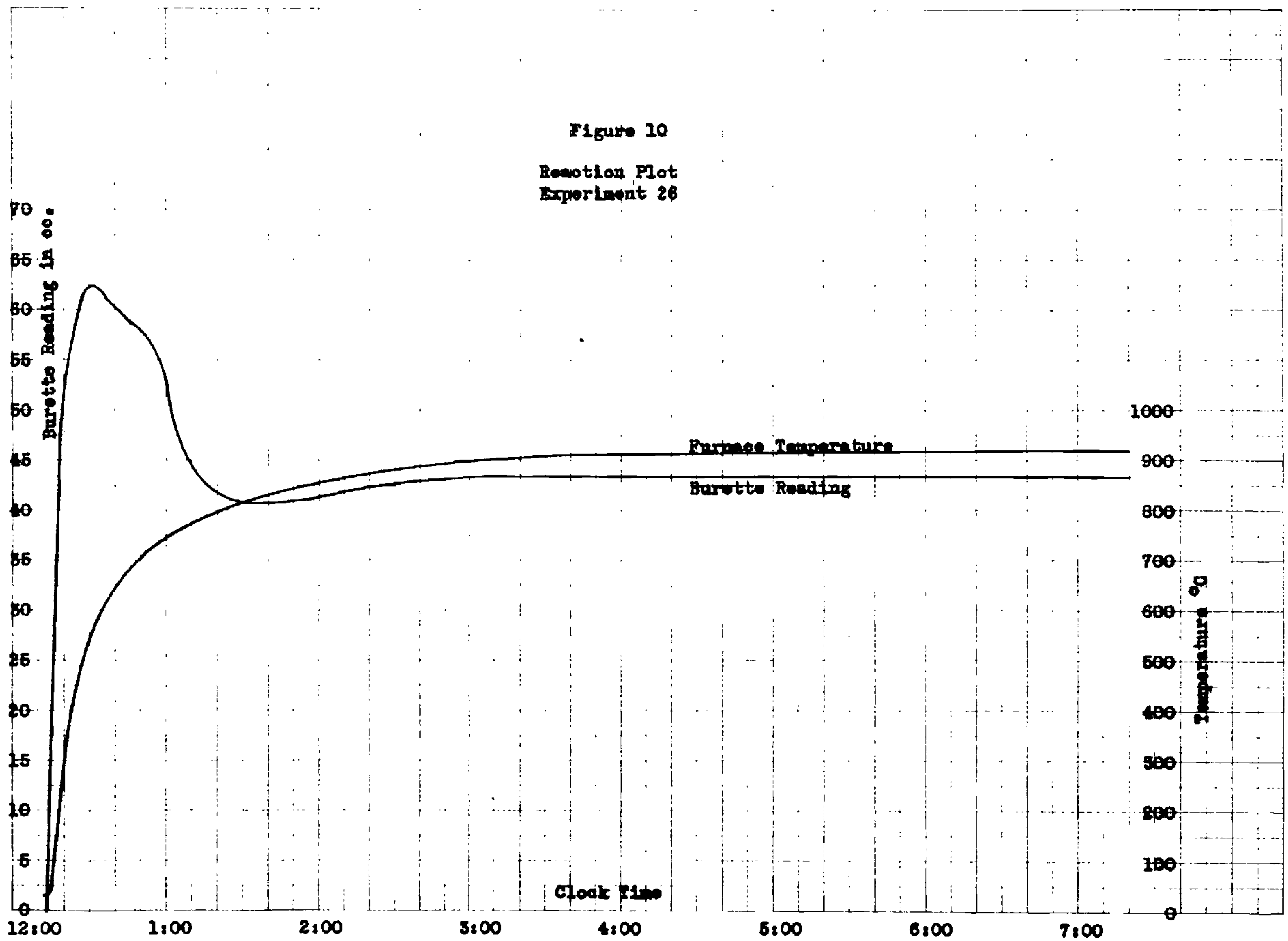


Figure 10
Reaction Plot
Experiment 26
Burette Reading in cc.
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
Furnace Temperature
Burette Reading
Temperature °C
1000
900
800
700
600
500
400
300
200
100
0
Clock Time
12:00
1:00
2:00
3:00
4:00
5:00
6:00
7:00

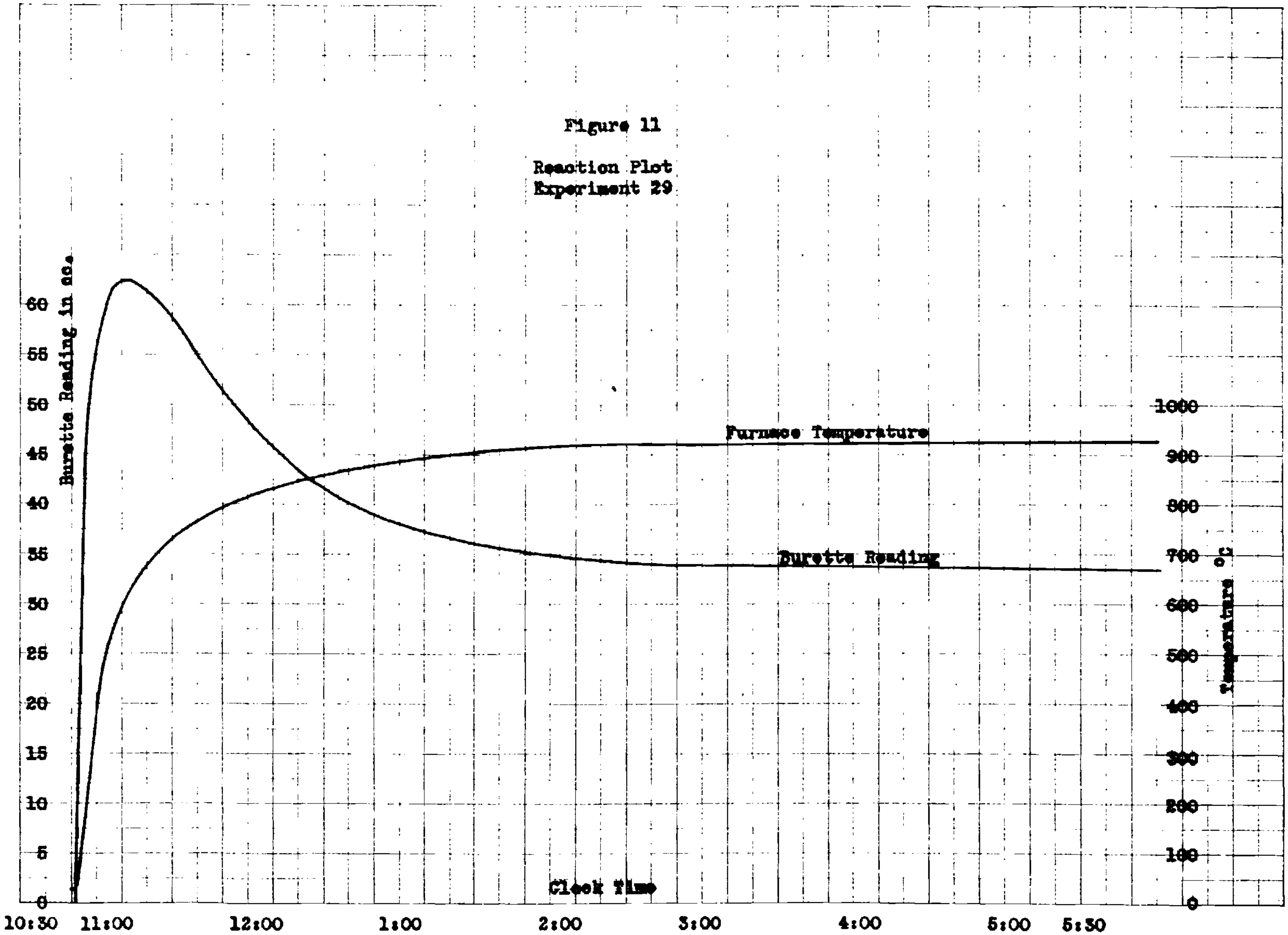


Figure 11

Reaction Plot
Experiment 29

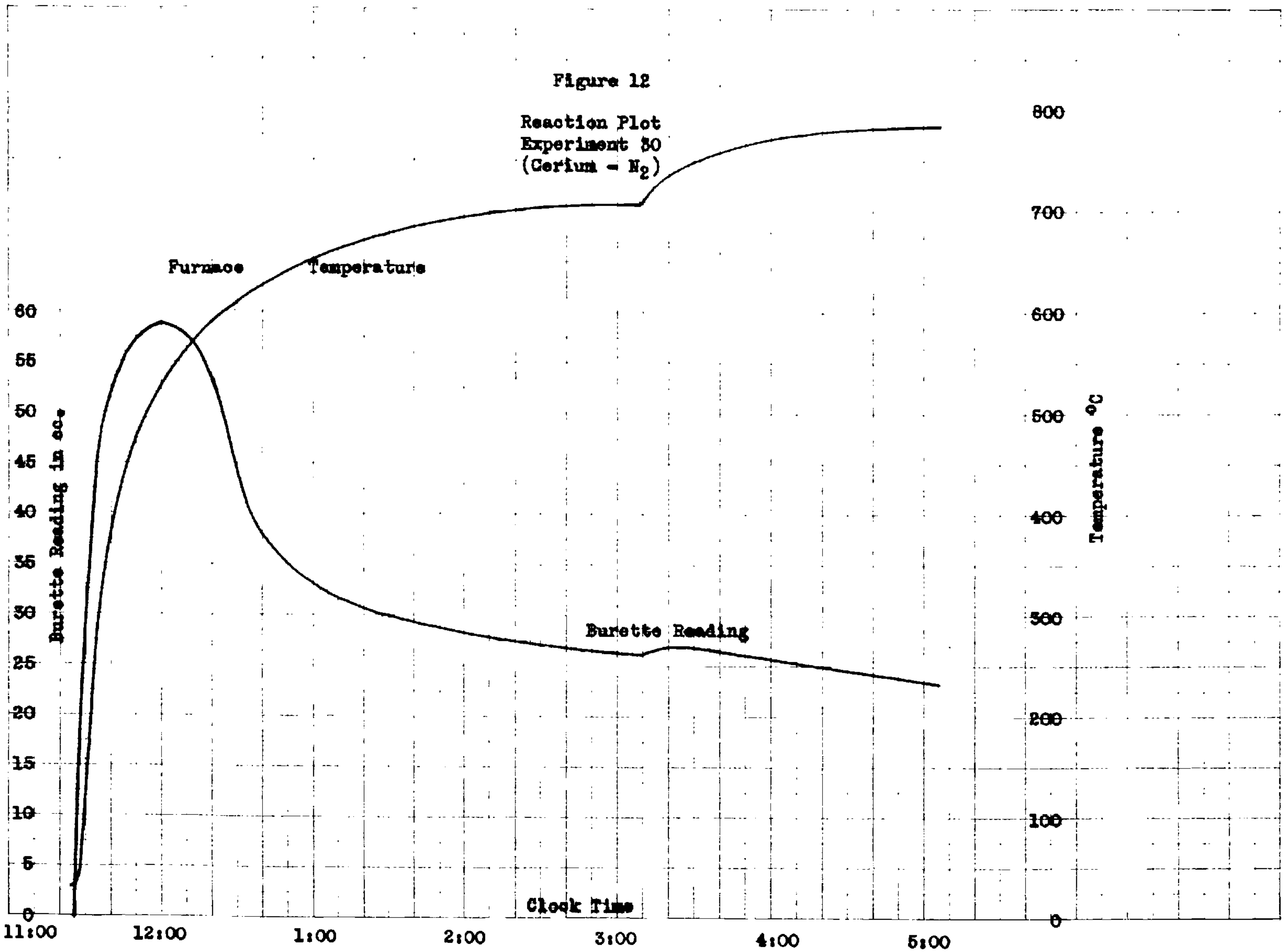


Figure 12
Reaction Plot
Experiment 30
(Cerium - N_2)
Furnace Temperature
Burette Reading
Burette Reading in cc.
Temperature °C
Clock Time
60
55
50
45
40
35
30
25
20
15
10
5
0
800
700
600
500
400
300
200
100
0
11:00
12:00
1:00
2:00
3:00
4:00
5:00

APPENDIX V

TYPICAL CALCULATION OF THEORETICAL BRAGG ANGLES FOR A STANDARD SAMPLE AND A TYPICAL CALIBRATION CURVE

Consider film #16-233 on which is registered the XRD pattern from copper filings and the pattern from a sample of the nitride prepared in experiment 25.

Copper has a face-centered cubic structure, and its a_o is accurately known. In these calculations the value taken for the a_o of copper is 3.608 kx-units and that for silver is 4.0776 kx-units*. Copper radiation was used for all the photographs. The values used for the wavelengths are 1.539 kx-units and 1.537 for the unresolved $K\alpha$ doublet and for the $K\alpha_1$ wavelength, respectively.

From the relation for the cubic crystal system

$$a_o = d\ (h^2 + k^2 + l^2)^{1/2} \qquad (1)$$

the value of d, the interplanar spacing, may be found as a function of the Miller indices, h, k, and l, of the set of planes in question. For the face-centered cubic structure, h, k, and l must be either all even or all odd. Thus the possible values to be substituted in relation (1) are limited to certain choices.

After the value of d is found for each of the various possible h, k, and l combinations, it may then be related to the Bragg angle at which

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* Sproull, Wayne T., X-RAYS IN PRACTICE, McGraw-Hill Book Co., Inc., New York, 1946, p 567.

the diffracted line would be expected to appear by Bragg's law

$$n\lambda = 2\ d \sin \theta, \tag{2}$$

where λ is the wavelength of the copper radiation used. It was found in practice that the $K\alpha_1$, and $K\alpha_2$ components became resolved for θ greater than about 50°. Thus λ = 1.539 kx-units was used for the calculations giving angles less than about 50° and λ = 1.537 kx-units was used for the calculation giving angles greater than about 50°. As the exact line in which the resolution became apparent varied from film to film, depending upon the general quality of the film and the developing conditions, it was necessary to calculate a θ for both the resolved and the unresolved cases in the neighborhood of 50°. The results of the calculations carried out by relations (1) and (2) appear in Table XI below.

TABLE XI

CALCULATION OF THEORETICAL θ VALUES FOR COPPER

Miller indices h k l	$h^2+k^2+l^2$	d	(kx-units)	sin θ x 10^4	θ
1 1 1	1.7321	2.083	1.539	3694	21.68
200	2.0000	1.804	1.539	4266	25.25
2 2 0	2.8284	1.276	1.539	6031	37.09
311	3.3166	1.088	1.539	7073	45.01
2 2 2	3.4641	1.042	1.539	7385	47.60
4 0 0	4.0000	0.9020	1.539	8532	58.56
			1.537	8520	58.43
3 3 1	4.3589	0.8277	1.537	9285	68.20
4 2 0	4.4721	0.8068	1.537	9525	72.27

A calibration curve was then made for each film by plotting θ (observed) - θ (theoretical) vs. θ (observed) for the standard sample used. The appropriate correction to be applied to the abserved θ for the "unknown" pattern was then read off this plot, and the result was θ (corrected) for the "unknown" pattern. Table XII gives the data used in film 16-233 and the resultant θ (observed for the nitride pattern). Figure 13 is the calibration curve drawn from the data and used to obtain the final values.

TABLE XII

OBSERVED BRAGG ANGLES

Copper Pattern				Lanthanum Nitride Pattern			
Miller Indices h k l	θ (observed) (degrees)	θ (theoretical) (degrees)	θ (obs.) θ (theo) (degrees) (degrees)	Miller Indices h k l	θ*(observed) (degrees)	θ(correction) (degrees)	θ Corrected (degrees)
				111	14.88	-0.26	14.62
				200	17.24	-0.26	16.98
111	21.96	21.68	0.28				
				220	2464	-0.28	24.36
200	25.52	25.25	0.27				
				311	29.20	-0.30	28.90
				222	30.64	-0.30	30.34
				400	36.00	-0.32	35.68
220	37.40	37.09	0.31				
				331	39.72	-0.33	39.39
				420	40.96	-0.33	40.63
311	45.32	45.01	0.31				
				422	45.88	-0.34	45.54
222	47.96	47.60	0.36				
				511	49.52	-0.35	49.17
				333			
				440	55.84	-0.37	55.47
400	58.84	58.43	0.41				
				531	59.68	-0.38	59.30
				620	61.12	-0.39	60.73
				533	67.24	-0.40	66.84
331	68.60	68.20	0.40				
420	confused with nitride pattern	--	--	622	74.92	-0.42	74.50

NOTE: Only those θ values of the nitride pattern which fell within the range of θ values for the standard pattern were used for the calculation of lattice parameters.

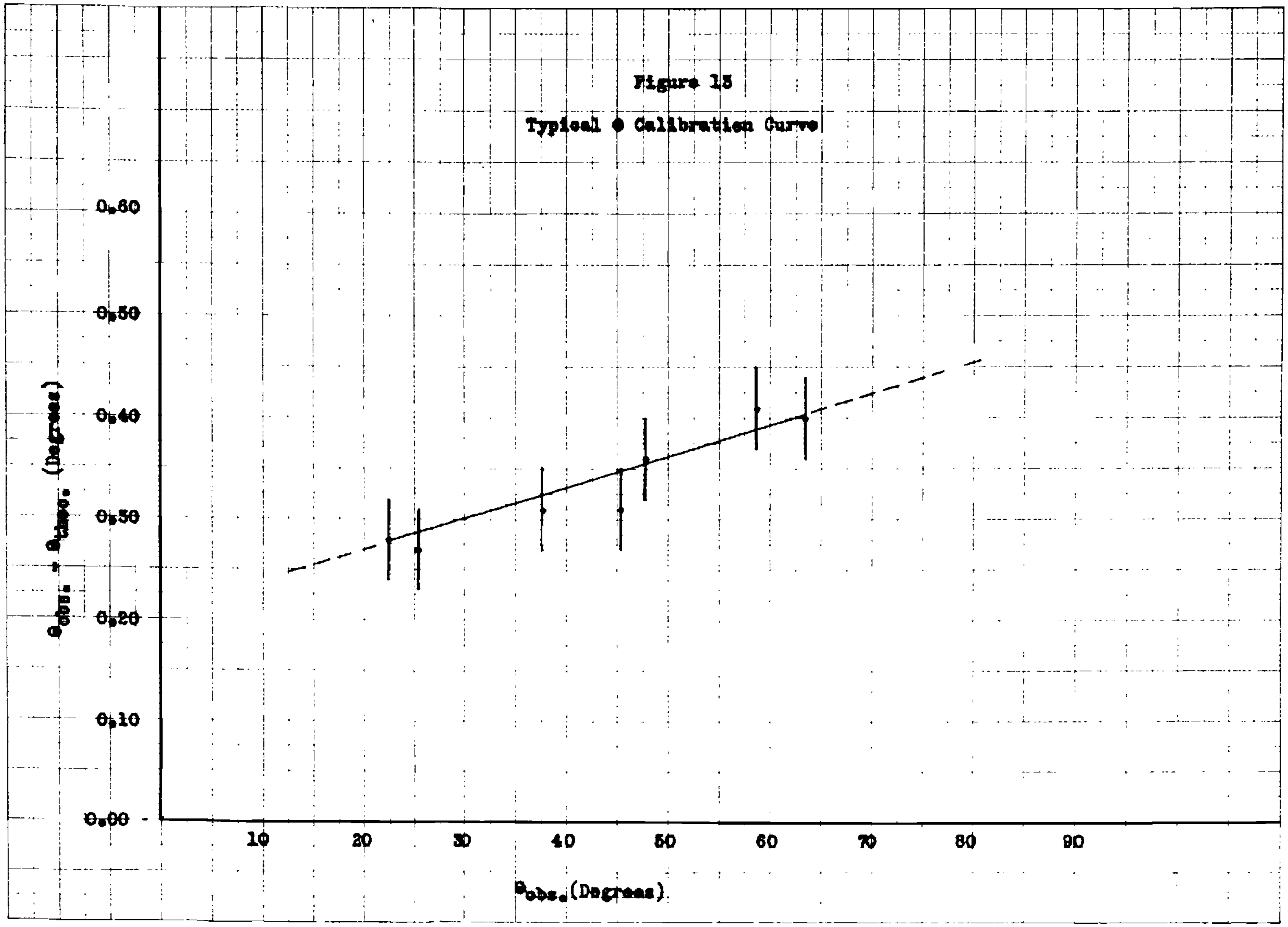
Figure 15
Typical θ Calibration Curve
0.60
0.50
0.40
0.30
0.20
0.10
0.00
$\theta_{obs.} - \theta_{true.}$ (Degrees)
10
20
30
40
50
60
70
80
90
$\theta_{obs.}$(Degrees)

APPENDIX VI

SAMPLE CALCULATION OF LATTICE PARAMETER

After the corrected values of the observed Bragg angles were obtained, as discussed in Appendix V, the values of d, the interplanar spacing of the set of planes giving rise to a given line, were calculated according to Bragg's law

$$n \lambda = 2 d \sin \theta \qquad (1)$$

It then remained to correlate the observed "d" values with the Miller indices of the set of planes with spacing "d". In the general case this correlation is a process of trial and error. However, with only a very little experience, certain crystal systems may be recognized by the grouping of the lines in the x-ray diffraction pattern. The face-centered cubic system is one of these, having a characteristic 2-1-2-1-2 grouping of the lines in a powder x-ray diffraction pattern. In any case, the criterion for the proper assignment of the Miller indices is that when the Miller indices are all assigned to the lines in the pattern (i.e., to the "d" values calculated from the observed line positions) with no lines missing and none left over, then if the correct assignment has been made the individual values of the lattice parameter, as calculated for each "d" value, will be approximately the same.

All the patterns encountered in this research happened to be face-centered cubic, hence the proper Miller indices could be assigned to the lines in the pattern by merely looking at the pattern. The lattice parameter, a_o, was then calculated from the relation

$$a_o = d\ (h^2+k^2+l^2)^{1/2} \tag{2}$$

For easy reference the lines in the X-ray diffraction patterns were numbered in the order of increasing θ (Bragg angle). It happened that certain of the lines of each of the "unknown" patterns had θ values outside the range of θ values observed in the pattern of the standard sample. In such cases the correction to be applied to the observed θ for the "unknown" pattern could only be obtained by an extrapolation of the calibration curve. Hence these lines were not used in the calculation of the lattice parameters. In the case of lanthanum nitride and a copper standard sample the lines not used were lines 1, 2, 15, and 16.

As stated in the text, the value of a_o finally assigned to a pattern was the average value of the various a_o's being calculated from the individual lines falling within the calibration range. Again in the case of lanthanum nitride and a copper standard sample, these lines were lines 3-14.

Table XIII presents the data taken and calculated from film number 16-235, which was calibrated by a copper standard and also registered the pattern of the lanthanum nitride prepared in Experiment 25. The value of θ (corrected) in the table is taken from Appendix V, Table XII.

TABLE XIII

DATA* LEADING TO THE LATTICE PARAMETER, a_o

Line	θ(corrected) (degree)	sin θ x 10^4	λ (kx-units)	d kx-units)	Miller Indices h k l	a_o
1	14.62	2524	1.539	3.049	111	5.281
2	16.98	2920		2.635	200	5.270
3	24.36	4125		1.865	220	5.275
4	28.90	4833		1.592	311	5.280
5	30.34	5051		1.523	222	5.276
6	35.68	5833		1.319	400	5.276
7	39.39	6346		1.213	331	5.287
8	40.63	6512		1.182	420	5.286
9	45.54	7137		1.078	422	5.281
10	49.17	5467		1.017	511 333	5.285
11	55.47	8238		0.9341	440	5.284
12	59.30	8599	1.537	0.8937	531	5.287
13	60.73	8723		0.8810	600 442	5.286
14	66.84	9194		0.8359	620	5.287
15	confused with cu pattern				533	
16	74.50	9636		0.7975	622	5.290

Average a_o from lines 3-14, a_o=5.283 kx-units mean deviation from average - $\pm$ 0.004 kx-units

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* Data from film no. 16-235

APPENDIX VII

CALCULATION OF RELATIVE LINE INTENSITIES

Since the specimens used to obtain the XRD photographs consisted of metal filings or reacted metal filings contained in glass capillaries, and since the capillaries were oscillated during exposure, it was assumed that the samples met the conditions for a cylindrical powder sample. Two different expressions appear to be used to calculate the intensities of the diffracted lines in this case. They are

$$I \sim F^2 p \frac{(1 + \cos^2 2\theta)}{\sin 2\theta \sin\theta} \quad U \tag{1}$$

$$I \sim F^2 p \frac{\cos\theta\,(1 + \cos^2 2\theta)}{\sin 2\theta} \quad U \tag{2}$$

where

I = the intensity of the diffracted line

F = the crystal structure factor, and is to be discussed further

p = the number of cooperating planes and is equal to the number of possible permutations of the Miller indices, both positive and negative, of the set of planes being considered

θ = the Bragg angle of the diffraction line being considered, and is obtained from observed data

U = is the appropirate absorption factor obtained from a plot of the values listed by Rusterholtz[1] for the case of large absorption*. This is the factor which Rusterholtz tabulates as $\frac{u}{R^2} A(\phi)$.

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1. Rusterholtz, A., <u>Z. Physik.</u>, <u>63</u> 1 (1930)

* See Appendix VIII for aplot of this factor

A sample calculation by formula (1) will be considered first since this formula was ultimately used in all calculations. The reasons for its choice will appear in what follows. The method used to obtain the crystal structure factor, F, requires some discussion before the sample calculation is carried out. It is given by

$$F = \sum f_j \, e^{2\pi i(hx_j + ky_j + lz_j)} \qquad (3)$$

where

$i = \sqrt{-1}$

f = atomic structure factor of the jth atom in the unit cell, and is obtained from a plot of the values tabulated by Sproull[2] unless Z (atomic number) is greater than 55, in which case the proper value of "f" for cesium was obtained from a plot of Sproull's values and multiplied by $\frac{Z}{55}$.

e = natural logarithm base.

h, k, and l = Miller indices of the set of planes giving rise to the diffracted line for which the intensity is being calculated.

x_j, y_j, and z_j = the coordinates in the unit cell of the jth atom in the unit cell.

$\sum$ = summation to be taken over all the atoms whose coordinates must be specified in order to describe the structure type.

For the NaCl type structure of lanthanum nitride the coordinates of the lanthanum atoms in the unit cell would be 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, and $0\frac{1}{2}\frac{1}{2}$. The coordinates of the nitrogen atoms would be $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, $00\frac{1}{2}$, $0\frac{1}{2}0$, and $\frac{1}{2}00$.

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2. Sproull, _op. cit._, p 356.

It can then be shown that if the Miller indices are all even, $F = 4 (f_{La} + f_N)$, if the Miller indices are all odd, $F = 4 (f_{La} - F_N)$, and F is 0 for all other cases.

In the ZnS type structure the coordinates of the lanthanum atoms would be the same as in the NaCl type structure, but the coordinates of the nitrogen atoms would be 1/4, 1/4, 1/4; 1/4, 3/4, 3/4; 3/4, 1/4, 3/4; and 3/4, 3/4, 1/4. In this case it can be shown that unless the Miller indices are either all even or all odd F is again 0, but for those cases for which they either all even or all odd, then the following rules apply:

$$1/2\ (h + k + 1) = \text{even},\ F = 4(f_{La} + f_N)$$

$$1/2\ (h + k + 1) = \text{odd},\ F = 4(f_{La} - f_N)$$

$$1/2\ (h + k + 1) = \text{not an integer},\ F\ 4(f_{La} \pm i\ f_N),$$

in which case the magnitude of F is the absolute magnitude of $4\ (f_{La} \pm i\ f_N)$, i.e., $4\ \ f^2_{La} + f^2_N$

The values of the atomic structure factor, "f", are a function of $\frac{\sin \Theta}{\lambda}$, where Θ is again the Bragg angle of the reflection and λ is the wave-length of the radiation used, in this case 1.539 kx-units. The correlation of the proper Miller indices with a line diffracted at a given Bragg angle was, of course, obtained in the process of determining that the crystal had face-centered cubic symmetry.

Table XIV, showing the component values used and the results, is a detailed example of the calculations as carried out by formula (1). The results of this example are those given in Table V in the text for the NaCl type structure of LaN.

TABLE XIV

CALCULATION OF EXPECTED RELATIVE LINE INTENSITIES FROM AN NaCL TYPE STRUCTURE OF LaN

(ACCORDING TO $I \sim F^2 p \dfrac{1 + \cos^2 2\theta}{\sin 2\theta \sin \theta}$ A)

Line	h k l plane	$\frac{p}{2}$	θ degrees	$\frac{\sin \theta}{2}$ x 10^{-8} Å	Relative Value of $\frac{1 + \cos^2 2\theta}{\sin 2\theta \sin \theta}$	f_{La}	f_N	Sign of Combination of f_{La} and f_N	$\frac{F}{4}$	$\frac{F^2}{4}$	U	I x 10^{-3}	Rel. Value of I Reduced to 1.00 ar the 620 plane
1	111	4	14.62	0.16	28.4	48.2	4.9	—	43.3	1875	0.044	9.37	0.298
2	200	3	16.97	0.19	20.4	46.1	4.4	+	50.5	2550	0.058	8.95	0.285
3	220	6	24.38	0.27	9.15	40.9	3.3	+	44.2	1954	0.116	12.45	0.396
4	311	12	28.92	0.31	6.27	38.3	2.9	—	35.4	1253	0.163	15.36	0.489
5	222	4	30.36	0.33	5.53	37.3	2.8	+	40.1	1608	0.178	6.33	0.202
6	400	3	35.65	0.38	4.01	34.6	2.5	+	37.1	1376	0.247	4.10	0.131
7	331	12	39.44	0.41	3.33	33.2	2.3	—	30.9	955	0.294	11.42	0.364
8	420	12	40.67	0.42	3.17	32.8	2.2	+	35.0	1225	0.315	14.70	0.468
9	422	12	45.57	0.46	2.80	31.3	2.1	+	33.4	1116	0.383	14.35	0.457
10	511 333	16	49.20	0.49	2.72	30.1	2.0	—	28.1	790	0.445	15.30	0.487
11	440	6	55.38	0.54	2.91	28.5	1.8	+	30.3	918	0.536	8.61	0.274
12	531	24	59.32	0.56	3.24	27.9	1.7	—	26.2	686	0.61	32.5	1.035
13	600 442	15	60.79	0.57	3.43	27.6	1.7	+	29.3	858	0.63	27.8	0.885
14	620	12	66.89	0.60	4.44	26.7	1.7	+	28.4	807	0.73	31.4	1.00
15	533	12	72.43	0.62	6.12	26.1	1.6	—	24.5	600	0.82	36.1	1.150
16	622	12	74.62	0.63	7.10	25.8	1.6	+	27.4	751	0.85	54.3	1.73

Since the two formulae differ only by the Lorentz factor used, the choice between the formulae was a choice of the form of this factor.

The Lorentz factor, $\frac{1}{\sin 2\theta \sin \theta}$, in formula (1) is recommended by Compton and Allison[2], Debye and Scherrer[3], Blake[4], Greenwood[5], and by the 1935 edition of the International Tables[6] for use with the powder method of XRD. The Lorentz factor in formula (2), $\frac{\cos \theta}{\sin 2\theta}$, was recommended more recently by Sproull[7].

In order to determine the effect of using the differing Lorentz factors, and at the same time attempt to discover the exact form of the formula used by Iandelli and Botti* , who report calculated values only for PrN[8], the relative line intensities to be expected from an NaCl type

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2. Compton, A. H., and Allison, S. K., X-rays in Theory and Experiment, D. Van Nostrand Co., Inc., New York, 1935, 2nd. ed. p 417.

3. Debye, P., and Scherrer, P., Physik. Z. 19, 481 (1919).

4. Blake, F. C., Revs. Modern Phys. 5, 174 (1933).

5. Greenwood, G., Phil. Mag. 3, 968 (1927).

6. Internationale Tabelen Zur Determination Von Kristallstruckturen, Zweiter Band, Mathematische un Physikalische Tabelen, Gebruder Bormtrager, Berlin, 1935, p 567.

7. Sproull, W. T., X-rays in Practice, McGraw-Hill Book Co., Inc., New York, 1946, p 414.

*. The general form of this formula is stated in a separate article by Iandelli and Botti, Atti. accad. nazl. Lincei, Classe sci. fis. mat. e nat. 24, 465 (1936).

8. Iandelli, A., and Botti, E., Atti. accad. nazl. Lincei, Classe sci. fis. mat. e nat. 25, 129-32 (1937)

structure of PrN were calculated from both formula (1) and formula (2). The results of the calculations are presented in Figure 14 along with the values calculated by Iandelli and Botti, all values in the Figure being reduced to unity at line 14 (the 620 plane) for ready comparison. Inspection of the Figure demonstrates that (a) the exact form of the Lorentz factor used has little effect on the general run of the relative intensities, and (b) formula (1) was the formula most likely used by Iandelli and Botti. Inasmuch as the different Lorentz factors did not affect the general run of intensities greatly, and since the majority of investigators seemed to favor it, formula (1) was used for the calculation of relative intensities in this research.

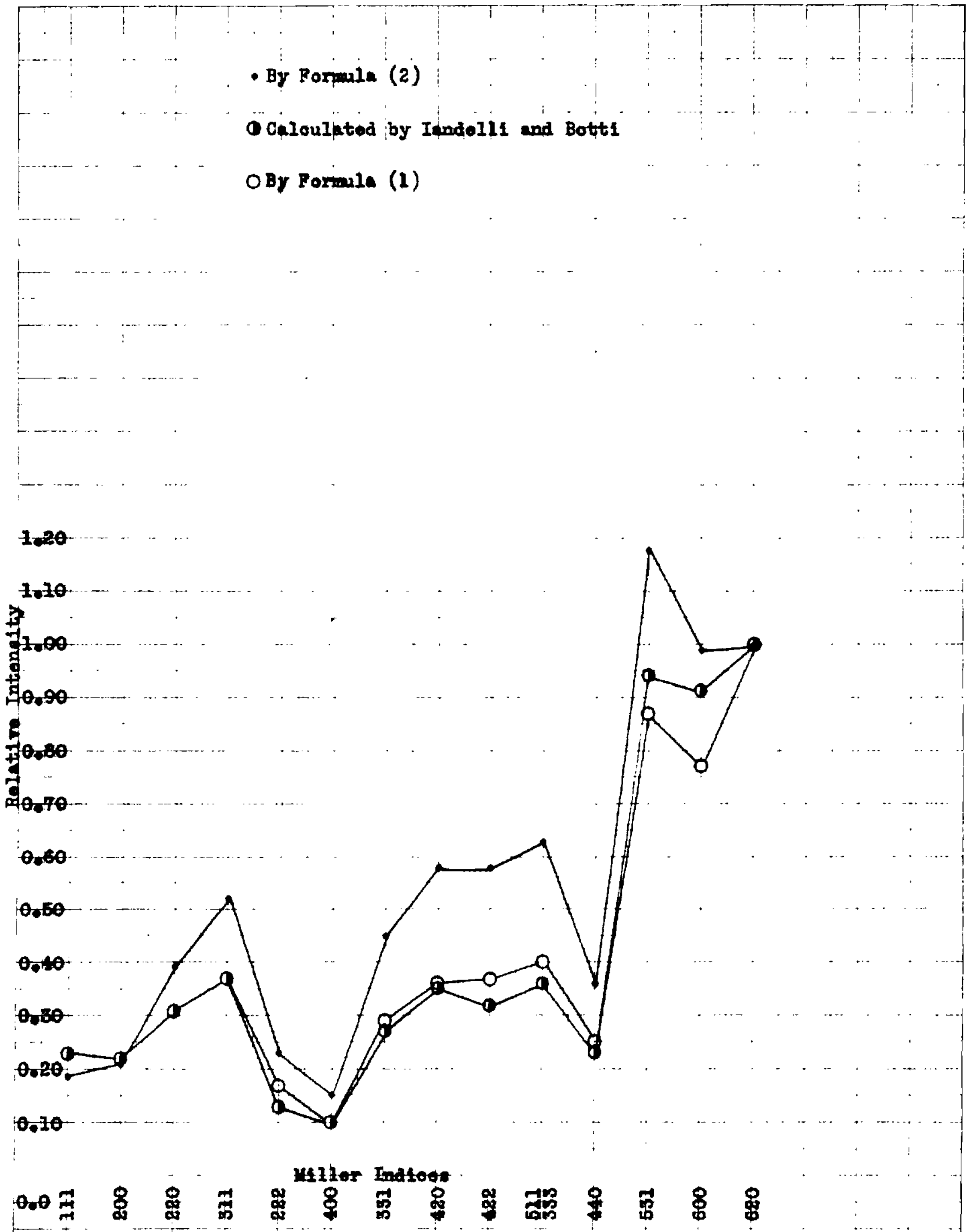

Figure 14

Calculated Relative Line Intensities for PrN

APPENDIX VIII

RUSTERHOLTZ'S DATA ON ABSORPTION IN A CYLINDRICAL SAMPLE

Rusterholtz* has investigated the effect of absorption in a cylindrical powder sample upon the relative intensities of the diffracted maximas. He concluded that the absorption factor, a function of the Bragg angle of the reflection, may be represented by

$$A\ (\phi) = \frac{R^2}{M} \left\{ \frac{1 + \cos^2 \frac{\phi}{2}}{2 \sin \frac{\phi}{2}} \cdot \ln \left[\frac{\cos \phi + \sin \frac{\phi}{2}}{(1 + \sin \frac{\phi}{2})(1 + 2 \sin \frac{\phi}{2})} \right] \right\}$$

where $A(\phi)$ is the absorption factor, ϕ is twice the Bragg angle of the reflection, R is the radius of the cylindrical sample, and u is the linear coefficient of absorption in the sample material for the radiation used. Thus $A(180^\circ) = \frac{R^2}{u}$. Rusterholtz further showed that $A(\phi)$ was very little different for $uR = 8.5$ and $uR = \infty$, by calculating a number of values and plotting them. Since the radius of the sample used was of the order of 0.03 to 0.04 cm, and u for lanthanum, with Cu K_α radiation, is ~ 2300 (i.e. $uR \sim 70$) the values for $uR = \infty$ were assumed to apply to this case. These values were then plotted as shown on the next page, and the u used in the equations for calculating the relative line intensities was the value of $\frac{u}{R^2}\ A(\phi)$ taken from the plot.

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* Rusterholtz, A. A., Z. Physik., 63, 1, 1930.

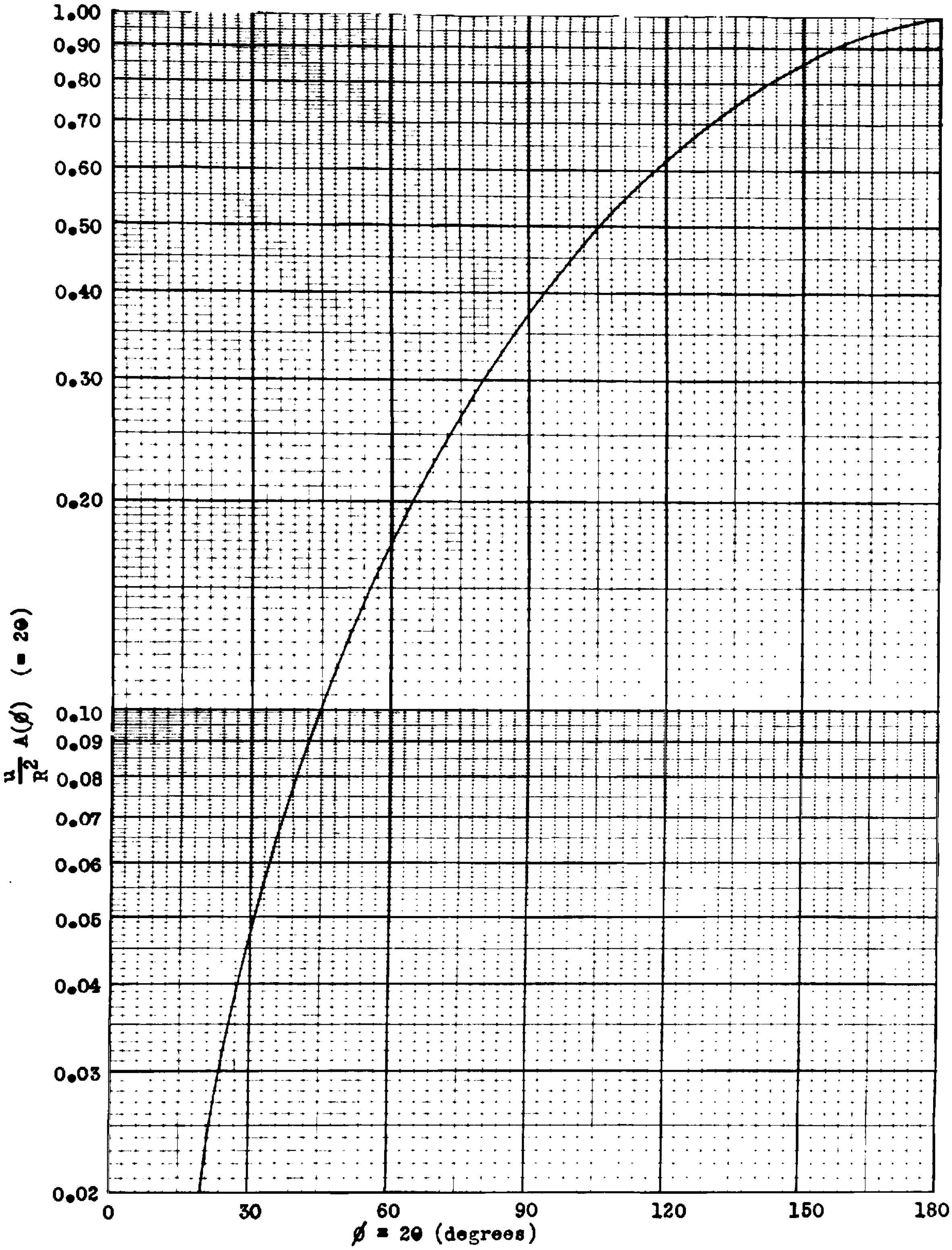

Figure 15

Rusterholtz' Absorption Factor

APPENDIX IX

OBSERVED RELATIVE LINE INTENSITIES FOR FCC LANTHANUM

As stated in Chapter III, two strips were used as aids in estimating the intensity of the lines in the powder XRD patterns of the fcc lanthanum. One of these strips, referred to herein as "Oct. 1950" strip, was the one used in estimating the relative intensities in the lanthanum nitride patterns. The second strip, referred to herein as strip 284, was prepared in the same manner as the first with the exception that more absorber was placed between the tube target and the film, hence the spots were less dense for the same exposure time, and that the spots were restricted to a smaller size (about 0.4 mm wide as compared to about 2 mm in theOct. 1950 strip). The purpose of making and using the second strip was twofold. First, it was considered desirable to demonstrate that the intensities observed with such a strip were roughtly reproducible independently of the particular strip used; Second, the absolute intensities of the lines in the fcc lanthanum patterns were much less than the absolute intensities of the lines in the lanthanum nitride patterns (in general), and thus it happened that the film strip which adequately covered the range of densities observed in the lanthanum nitride patterns did not have a wide enough range of low density spots to give good coverage of the fcc lanthanum patterns.

The film strip 284 did not have any spots of great enough density to cover the density range of lines 1, 3, and 4 in most of the fcc lanthanum patterns. However, in film 16-174, which had been exposed for only 3 hours, the density of all the lines fell within the range of film strip 284. For this reason film 16-174 was chosen for the following plot of observed intensities as observed with the aid of the two different strips. Similar plots have been made of the observed intensities of the other three fcc lanthanum films used in the identification of fcc lanthanum and it was found that approximately the same agreement existed between the two types of measurements for those lines (i.e., all the lines except 1, 3, and 4) whose density fell within the range of both strip 284 and the Oct. 1950 strip. The observed relative intensities have been reduced to unity at line 14 in the figure. The correlation between Miller indices and line numbers is given in both Table V and Table XIV.

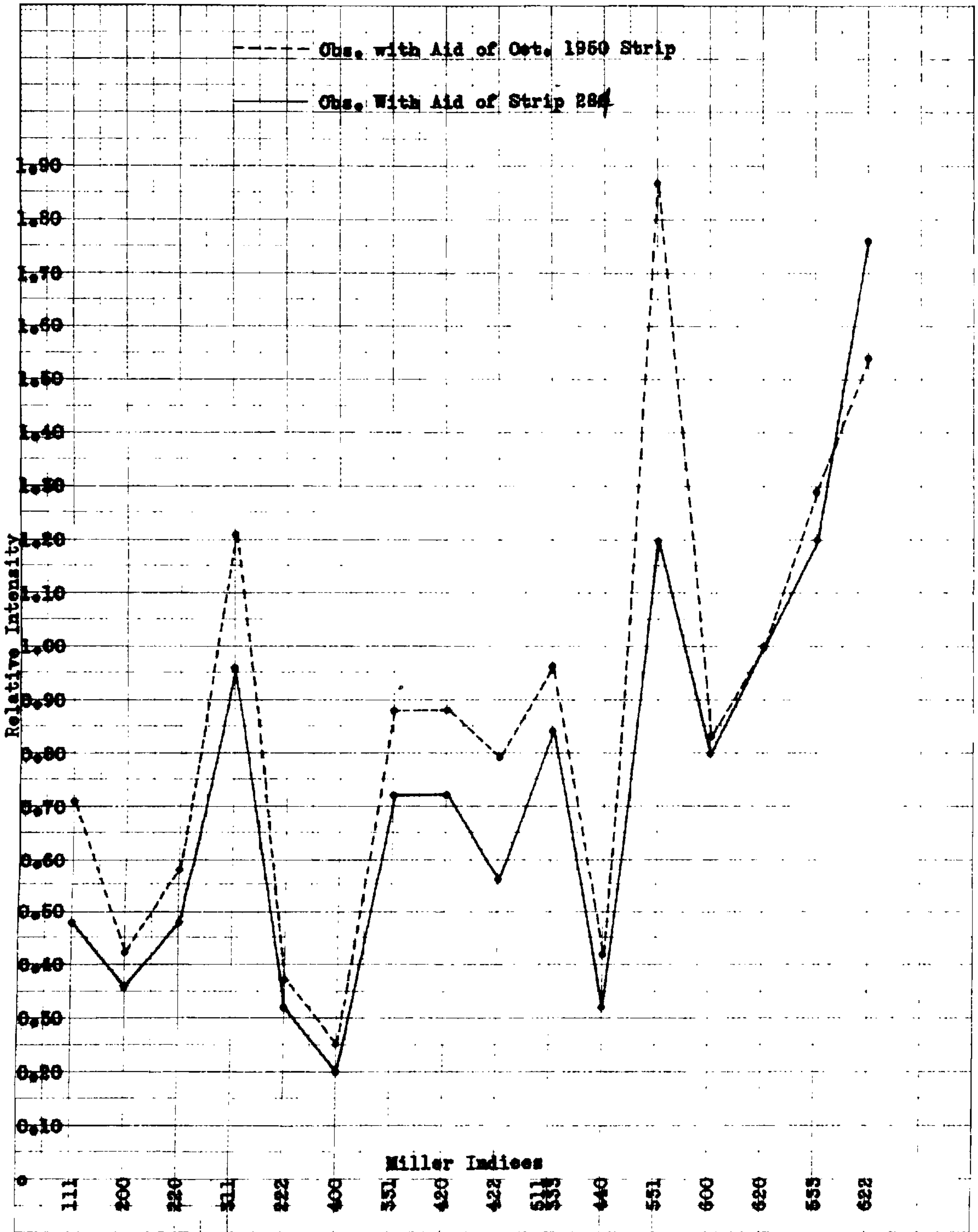

Figure 16

Observed Relative Line Intensities for Fcc Lanthanum