1955

# Some physical-metallurgical properties of scandium, yttrium and the rare earth metals

Kenneth Walter Herrmann
*Iowa State College*

## Recommended Citation

Herrmann, Kenneth Walter, "Some physical-metallurgical properties of scandium, yttrium and the rare earth metals " (1955). *Retrospective Theses and Dissertations*. 13958.
https://lib.dr.iastate.edu/rtd/13958

# SOME PHYSICAL-METALLURGICAL PROPERTIES OF SCANDIUM, YTTRIUM AND THE RARE EARTH METALS

134

by

Kenneth W. Herrmann

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.
In Charge of Major Work

Signature was redacted for privacy.
Head of Major Department

Signature was redacted for privacy.
Dean of Graduate College

Iowa State College
1955

## TABLE OF CONTENTS

## ACKNOWLEDGMENT

The author wishes to acknowledge the direction and helpful criticism given by Dr. F. H. Spedding and Dr. A. H. Daane during the course of this study. Acknowledgment is also made of the assistance of Dr. J. E. Powell who supplied the rare earth oxides, Mr. D. H. Dennison who prepared many of the metals studied, the analytical group for their spectrographic analyses of the rare earths and of the aid given by the mechanical and glass shops in the construction of the equipment used in this study. The advice, assistance and co-operation given by the author's co-workers are also worthy of an expression of appreciation.

# I. INTRODUCTION

It was in the late 1700's that evidence was first obtained for the existence of the elements which are now known as the rare earths. The techniques of inorganic and physical chemistry made great advances during the early 1900's and it was then that the separation of the rare earth elements was begun in earnest. Several methods, both physical and chemical, have been devised since then to obtain these elements in a sufficiently pure state to study their individual properties. Although these metals have acquired the name "rare", it is interesting to note that cerium alone is more abundant than the more common elements such as mercury, tin, antimony, cadmium, bismuth and tungsten.

The understanding of the behavior of the rare earths was furthered considerably by x-ray studies, absorbtion spectroscopy and magnetic investigations on the elements in their condensed states. Spectroscopic studies of the gaseous atoms were also informative, however, there are still several rare earths whose complex spectra have not yet been completely explained. In constructing the electronic configurations of the normal atoms of these elements, experiment and theory require that use be made of the 4f, 5d and 6s orbitals. The addition of two electrons to the 6s subshell, one electron to the 5d orbital and the remainder to the 4f orbital beginning with one electron for cerium on up to fourteen for lutecium, would be the simplest arrangement possible. Experimental investigations have indicated, however, that there are a few discrepancies in the configurations assigned in this manner. Nevertheless, several characteristic properties of the rare earths such as valence, magnetic susceptability, the "lanthanide contraction" and the basicity variation within the group, can be accounted for on this basis.

At present the underlying reasons for the behavior of metals are not completely known. Phase transformations in metals are numerous and usually occur between a few relatively simple structure types. Attempts have been made to predict the stable crystal phases, however, the energy differences between allotropic modifications are small and the inexactness of theoretical calculations of these values makes this approach of little value. Precise experimental investigation has thus been the basis for increased understanding of these phenomena. Such physical properties as crystal structure, magnetic anomalies, electrical resistivity, alloy characteristics, deformation and strength qualities and others must likewise be related to the energies of the metals in a fundamental manner. This implies a direct dependence of their characteristics on the electronic configurations of the respective metallic elements. Precise data on the above properties are indeed necessary before any reliable theoretical explanation of their behavior can be formulated and at present this information is quite limited. The rare earth group represents a series of elements which are remarkably similar in many aspects and which have electronic configurations which differ but slightly. They are, therefore, desirable and convenient to employ for investigations leading to a further understanding of the nature of metals. If one neglects the electrons of these elements located in the 4f, 5d and 6s subshells, the remaining configuration is consistent throughout the series. Thus, if the additional electrons are added uniformly to the 4f, 5d and 6s orbitals the intrinsic properties of the metals should also vary in a uniform manner.

Several characteristic qualities, whose variation within the rare earth group can be correlated, can be obtained from crystal structure studies alone. Crystal structure, metallic radius, atomic volume, density and axial ratio for hexagonal close packed modifications are all pertinent to the formulation of a metal theory. Electrical resistivity studies also are desirable and if examined as a function of temperature they can be used to determine the existence of allotropic phase transformations.

Although previous investigations of the crystal structures, resistivities and phase transformations of the rare earths have been made, the purity of the metals studied and the techniques employed suggest that the data reported be considered with reserved judgment. In many cases the information given is not sufficiently accurate to reveal small differences in behavior among the individual elements. For these reasons the crystal structures of the rare earths as well as scandium and yttrium were determined by x-ray diffraction techniques and precise values of their lattice parameters were obtained. Several of their inherent properties were calculated from these data and correlated graphically. The electrical resistivity values of lanthanum, cerium, praseodymium and neodymium were investigated as a function of temperature and used to determine the phase transformation temperatures of these metals. Metallographic examinations of the distilled metals were also made and revealed interesting structural phenomena.

# II. CRYSTAL STRUCTURES OF THE RARE EARTH METALS

## A. Introduction

Considerable work has been done on the crystal structures of the lighter rare earth elements; however, there is still some controversy over the true normal room temperature structure of lanthanum, cerium, praseodymium and neodymium. The remaining rare earths as well as scandium and yttrium have been previously investigated but only by a few workers. In almost all cases the purity of the metals is questionable especially as concerns their oxygen, nitrogen, hydrogen and carbon content. The lighter rare earths being the most reactive in air, one must consider surface impurities which would not be easily detected. Although the metals were protected from the atmosphere, very little oxide, nitride or hydride would be necessary to give an x-ray diffraction pattern of the impurity since the metal atoms have a relatively high scattering power. This would be especially true if metal filings having large surface areas are used as the diffracting sample.

The techniques and cameras available today also allow for greater precision than was possible for earlier investigations. Most of the previous work had been done with small diameter Debye-Scherrer type powder cameras which in themselves allow only limited accuracy.

For an accurate crystallographic study of alloys one must have precise lattice constants for the metals being investigated. This further emphasizes the need for more accurate values for the unit cell parameters of the rare earths. Although little is being done in this laboratory concerning the alloys of these metals at present, this study will most likely receive increased attention in the near future.

All samples were spectrographically analyzed for other rare earths, tantalum and common impurities; analyses for oxygen, nitrogen and hydrogen were difficult and frequently unreliable. Except for lanthanum, cerium, praseodymium, neodymium and gadolinium, all precision determinations of lattice constants were made with distilled metal which was condensed on tantalum at a relatively low temperature. Metal filings and bulk specimens were used with a Debye-Scherrer camera and a Norelco diffractometer unit to determine the actual crystallographic structure of the metals. When single crystals could be obtained from relatively large quantities of distilled metal, rotation and Weissenberg photographs were obtained for more definite structure assignment. Microscopic examinations of the metals were made for impurity phases as well as for information concerning the microstructure of the various crystallographic forms.

Although scandium and yttrium are not usually classified as rare earths, their properties are very similar and therefore like studies were carried out with them along with the rare earth metals.

## B. Historical

Since a considerable amount of study has been devoted to the structure of cerium, lanthanum, neodymium and praseodymium these will be considered individually whereas the remaining rare earth metals, as well as scandium and yttrium, will be treated as a group. The lattice parameters obtained from literature were given in Angstrom units, however, those reported before 1943 are probably kx units (1 Å = 1.00202 kx).

### 1. Lanthanum

McLennan and McKay,[1] using a modified nonsymmetric back reflecting low temperature camera and a normal powder camera with filtered copper radiation, first studied filings of metallic lanthanum of unspecified purity in 1930. They found its structure to be hexagonal close packed (h.c.p.) with a lattice parameter of $a_o = 3.72$ Å, and a $c_o/a_o$ ratio of 1.63 Å.

In 1932, Quill,[2] using metal received from Kremers of the University of Illinois which had been prepared by the electrolysis of a mixture of lanthanum chloride and sodium chloride or potassium fluoride, also found lanthanum to have an h.c.p. structure. Copper $K_\alpha$ radiation and a 57.4 mm. diameter powder camera were used for the examination of metal filings obtained in a helium atmosphere, the pattern being corrected with silver which was used as an internal standard. The lattice constants obtained were $a_o = 3.75_4 \pm .010$ Å, $c_o = 6.06_3 \pm .03$ Å, $c_o/A_o = 1.613$ and the calculated density of the metal was 6.194 g./cm.$^3$.

Lanthanum, having a purity of 99.6 per cent, prepared by the electrolysis of lanthanum chloride and 15 per cent sodium chloride, was studied by Zintl and Neumayr[3] in 1933. The impurities present were silicon, aluminum, magnesium and carbon, and the metal had a melting point of 812°C. and a measured density of 6.155 g./cm.$^3$. Filtered copper radiation and a 114.6 mm. diameter powder camera were used to examine the metal filings obtained under a nitrogen atmosphere. The unannealed pattern gave broad lines but was indexed as h.c.p. After heating for several days at 350°C. in vacuo, a sharp face centered cubic (f.c.c.) pattern was obtained whose lattice parameter was $5.296 \pm .002$ Å.

Rossi,[4] in 1934, while studying some rare earth hydrides, reported lanthanum as originally h.c.p. but after annealing at 350°C. for several days he found it to be f.c.c. Further investigation led him to report that the f.c.c. structure was only a surface effect. The parameters reported were $a_o = 3.75_7$ Å, $c_o/a_o = 1.61$ for the h.c.p. lanthanum structure and $a_o = 5.62$-$5.63$ Å for f.c.c. lanthanum hydride.

Klemm and Bommer,[5] who are justly acknowledged as the chief workers in this field, prepared lanthanum by reducing the chloride with liquid alkali metal in an argon atmosphere at a temperature of about 350°C. Filtered copper radiation and a 57.3 mm. diameter powder camera were used to examine the reduction mixture of lanthanum metal and potassium chloride, the potassium chloride pattern being used to correct the lanthanum lines. Only the f.c.c. structure was observed which had a lattice constant of $a_o = 5.294$ Å and a calculated density of $6.18_o$ g./cm.$^3$. This f.c.c. structure was again observed by Bommer[6] in 1939.

In 1949, Ziegler,[7] preparing rare earth superconductivity samples observed an initial diffuse pattern of the h.c.p. phase for lanthanum samples of 95.5-98 per cent and 99 per cent purity. After heating at 350° C. for 96 hours a sharp f.c.c. pattern was obtained. Young and Ziegler,[8] in 1952, while studying the structure of lanthanum nitride reported the structure of lanthanum annealed four days at 350°C. as being f.c.c. with a lattice constant of $a_o = 5.291 \pm .003$ kx. Although lanthanum and lanthanum nitride ($a_o = 5.284 \pm .004$ kx) are both f.c.c., they could differentiate between the two structures by their observed line intensities. Copper $K_\alpha$ radiation, a 14.32 cm. diameter powder camera and copper and silver standards were used to investigate the lanthanum filings prepared in dry helium or nitrogen. In 1953 Ziegler, Floyd and Young[9] again reported obtaining a diffuse h.c.p. structure before heating along with additional lines thought due to lanthanum hydride. A pattern containing chiefly f.c.c. lanthanum was found after the sample was annealed at 350°-400°C. for two to four days. The h.c.p. structure had the parameters $a_o = 3.74 \pm .01$ kx, $c_o = 6.06 \pm .02$ kx, $c_o/a_o = 1.62 \pm .01$, and the cubic value was $a_o = 5.285 \pm .005$ kx. In addition to the annealed f.c.c. structure, there were faint lines due to the h.c.p. phase plus a number of weak lines assignable to a second f.c.c. structure having an $a_o$ value .5-1 per cent less than that of the f.c.c. lanthanum. Six samples, varying in purity from 94.8 per cent lanthanum to one containing less than .01 per cent beryllium and traces of aluminum and magnesium received from the Ames Laboratory, were studied using the previously mentioned equipment and techniques. All behaved similarly.

In 1952 James, Legvold and Spedding[10] of this laboratory, while reporting the low temperature resistivity of some rare earth metals, observed lanthanum to have a mixed structure of h.c.p. and f.c.c. phases, the h.c.p. being predominant. Filtered copper radiation was used for the diffraction studies and the samples were in the form of needles of approximately .2 mm. diameter. The metal had been prepared by the reduction of the chloride with calcium under helium or argon with subsequent removal of calcium by melting in a magnesium oxide crucible in a high vacuum. Spectroscopic analysis showed the metal to contain less than 1 per cent magnesium, less than .025 per cent calcium and less than .01 per cent other rare earths, these values being the limits of detection at that time. The fact that the metal was prepared in a magnesia crucible probably accounts for the high magnesium content.

The most recent work on the structure of lanthanum has been reported by Farr, Giorgi and Bowman[11] in 1953. Using copper $K_\alpha$ radiation and a 114.59 mm. powder camera, they examined the mixture resulting from the reduction of lanthanum chloride with potassium vapor. Their results indicated the presence of f.c.c. lanthanum, potassium chloride and lanthanum hydride. The potassium chloride was used as a standard for corrections; the presence of the lanthanum hydride lines could not be explained. Attempts to obtain h.c.p. lanthanum by low temperature reductions (95°C.), slow cooling from 380° to 150°C. and annealing the f.c.c.

lanthanum plus potassium chloride mixture for 28 days at 140°C., all resulted in the f.c.c. phase. By admitting hydrogen to the sample it was found that the lines assigned to lanthanum hydride increased while those of f.c.c. lanthanum decreased in intensity. The parameters reported were $a_o = 5.304 \pm .006$ Å for f.c.c. lanthanum and $a_o = 5.669 \pm .006$ Å for f.c.c. lanthanum hydride.

For easier comparison the literature is summarized in Table 1.

## 2. Cerium

A. W. Hull[12] first studied the crystal structure of cerium in 1921 using filtered molybdenum radiation. He found it to be a mixture of h.c.p. and f.c.c. structures having the respective lattice parameters of $a_o = 3.65$ Å, $c_o/a_o = 1.62$ and $a_o = 5.12$ Å. Although the sample was assumed pure, it had the same diffraction pattern as misch metal (8 per cent iron). The effect of annealing was not studied.

Schumacher and Lucas[13] prepared cerium in 1924 by electrolyzing cerium chloride and remelting it in a magnesia crucible under a flux of pure sodium chloride. The analysis given was 99.9 per cent cerium, .03 per cent carbon and .02 per cent iron. Samples were polished, allowed to air etch

Table 1. Summary of lanthanum literature

| Author | Method of Preparation | Purity | Technique | Results |
|---|---|---|---|---|
| McLennan and McKay[1]<br>(1930) | | | Metal filings powder camera | h.c.p. $a_o = 3.72$ Å<br>$c_o/a_o = 1.63$ Å |
| Quill[2]<br>(1932) | Electrolytic | | Metal filings 57.4 diameter powder camera | h.c.p. $a_o = 3.74$ Å<br>$c_o = 6.06$ Å<br>$c_o/a_o = 1.613$ Å |
| Zintl and Neumayr[3]<br>(1933) | Electrolytic | 99.6% | Metal filings 114.6 mm. diameter powder camera | unannealed: h.c.p.<br>annealed at 350°C.:<br>f.c.c. $a_o = 5.296$ Å |
| Rossi[4]<br>(1934) | | | | originally: h.c.p.<br>$a_o = 3.757$ Å<br>$c_o/a_o = 1.61$<br>annealed at 350°C.: f.c.c.<br>thought a surface effect |
| Klemm and Bommer[5,17]<br>(1937) (1939) | Reduction of $LaCl_3$ with liquid alkali metal | | examined reduction mixture 57.3 mm. diameter powder camera | f.c.c. $a_o = 5.294$ Å |

Table 1. (Continued)

| Author | Method of Preparation | Purity | Technique | Results |
|---|---|---|---|---|
| Ziegler[7] (1949)<br>Ziegler and Young[8] (1952)<br>Ziegler, Floyd and Young[9] (1953) | Several different samples studied | 95.5-99% | Metal filings 14.32 cm. diameter powder camera | originally: h.c.p.<br>$a_o$ = 3.74 kx<br>$c_o$ = 6.06 kx<br>after annealing at 350°C.:<br>f.c.c. $a_o$ = 5.285 kx<br>same $LaH_2$ lines also |
| James, Legvold and Spedding[10] (1952) | Reduction of $LaCl_3$ with Ca | 99% | Metal needles (.2mm. diameter) low temperature camera | Mixture of chiefly h.c.p. and some f.c.c. |
| Farr, Giorgi and Bowman[11] (1953) | Reduction of $LaCl_3$ with K vapor | | Examined reduction mixture 114.59 mm. diameter powder camera | Found f.c.c. La<br>$a_o$ = 5.304 Å,<br>KCl pattern,<br>$LaH_2$, $a_o$ = 5.669 Å<br>f.c.c. |

in a dessicator about seven days and then quickly etched with concentrated nitric acid. From microscopic examinations of these samples they concluded that cerium was of the cubic form.

Using cerium metal obtained from Kremers and prepared by the electrolysis of the chloride, Quill,[2] in 1932, found its structure to be f.c.c. with a unit cell edge of $a_o = 5.143 \pm .004$ Å and a density of 6.799 g./cm.$^3$. No lines due to a h.c.p. phase were observed. The work was done with copper $K_\alpha$ radiation and a 57.4 mm. diameter powder camera.

Rossi[4] in his study of some rare earth hydrides in 1934 reported the structure of cerium as f.c.c. with $a_o = 5.14_6$ Å. Cerium hydride also was f.c.c. with $a_o = 5.61_2$ Å, however, on heating the hydride in vacuo at 530°C. he observed two f.c.c. phases.

Klemm and Bommer[5] in their 1937 article, utilizing the same techniques mentioned earlier, found the structure of cerium to be f.c.c. also, with $a_o = 5.140$ Å and a density of $6.81_6$ g./cm.$^3$.

Lawson and Tang,[14] in 1949, observed a collapsed f.c.c. modification for cerium which was under a pressure of 15,000 atmospheres, the unit cell length being $a_o = 4.84 \pm .03$ Å. Molybdenum $K_\alpha$ radiation was used in conjunction with a camera having a diameter of 7.57 cm. Analysis of the metal showed the presence of .05 per cent magnesium, .03 per cent silicon, .02 per cent iron, .001 per cent copper and .001 per cent silver, no other rare earths being detectable. This structure represents a 16.5 per cent volume decrease over the normal cubic phase and is believed due to the 4f electron being squeezed into the 5d shell. Attempts to induce this transformation in rather impure cerium (approximately .2 per cent iron) having the h.c.p. form at room atmosphere were unsuccessful.

Schuch and Sturdivant[15] observed a similar transition to a collapsed f.c.c. structure with cerium at liquid nitrogen temperatures. The original structure of the metal filings prepared under an atmosphere of argon was f.c.c. with $a_o = 5.140$ Å while the f.c.c. modification observed at 90°K. had a lattice parameter of $a_o = 4.82$ Å. Molybdenum $K_\alpha$ radiation was used. Analysis indicated the presence of .2 per cent calcium, .2 per cent magnesium and .04 per cent beryllium, however, the magnesium and calcium were assumed removed by a subsequent melting in a vacuum.

Ziegler,[7] in 1949, using cerium of 88.4-95 per cent purity, found the metal "as received" to consist of both f.c.c. and h.c.p. phases, their pattern having quite diffuse lines. After annealing at 350°C. for approximately four days the diffraction lines were sharp and indicated a f.c.c.

structure.

James, Legvold and Spedding,[10] in 1952, reported the presence of both f.c.c. and h.c.p. phases existing in approximately 99.9 per cent pure cerium, the former modification being predominant.

The literature cited is summarized in Table 2.

### 3. Praseodymium

Praseodymium also has been found to have more than one crystal structure at room temperature. Rossi,[16] in 1932, examined a 99.4 per cent pure sample obtained by the electrolysis of praseodymium chloride by x-ray diffraction. Small amounts of europium, cerium, neodymium and samarium were present. Filtered copper radiation and a 57.3 mm. diameter powder camera were used to determine its structure as h.c.p. with $a_o = 3.657$ Å, and $c_o/a_o = 1.62$. While investigating the hydrides of cerium, lanthanum and praseodymium in 1934, Rossi[4] again reported the h.c.p. structure but with lattice parameters of $a_o = 3.65_2$ Å and $c_o/a_o = 1.61$. This sample was annealed several days at 350°C. but this treatment did not change its structure.

In 1937, Klemm and Bommer[5] examining their reduction mixture of praseodymium and potassium chloride by methods

Table 2. Summary of cerium literature

| Author | Method of Preparation | Purity | Technique | Results |
|---|---|---|---|---|
| Hull[12] (1921) | | assumed pure | | Mixture of h.c.p. $a_o$ = 3.65 Å $c_o/a_o$ = 1.62 and f.c.c. $a_o$ = 5.12 Å |
| Quill[2] (1932) | Electrolytic | | Metal filings 57.4 mm. diameter powder camera | f.c.c., $a_o$ = 5.143 Å |
| Rossi[4] (1934) | | | | f.c.c., $a_o$ = 5.146 Å (Ce hydride f.c.c. $a_o$ = $5.61_2$ Å) |
| Klemm and Bommer[5] (1937) | Reduction of $CeCl_3$ with liquid alkali metal | | Examined reduction mixture 57.3 mm. diameter camera | f.c.c. $a_o$ = 5.140 Å |
| Lawson and Tang[14] (1949) | | 99% | Under 15,000 atm. pressure 7.57 cm. diameter camera | Collapsed f.c.c. $a_o$ = 4.84 Å |

Table 2. (Continued)

| Author | Method of Preparation | Purity | Technique | Results |
|---|---|---|---|---|
| Schuch and Sturdivant[15] (1950) | Reduction of $CeCl_3$ with Ca | 99% | Studied at room temperature at 90°K. | Room temperature: f.c.c.<br>$a_o = 5.140$ Å<br>90°K.: f.c.c.<br>$a_o = 4.82$ Å |
| Ziegler[7] (1949) | | 88.4-95% | Metal filings | Originally a mixture of h.c.p. and f.c.c. After annealing at 350°C. only f.c.c. ~~La.~~ Ce |
| James, Legvold and Spedding[10] (1952) | Reduction of $CeCl_3$ with Ca | 99.9% | Metal needles low temperature camera | Chiefly f.c.c. but some h.c.p. |

1956

fcc 5.1612

described earlier, found praseodymium to be f.c.c. with $a_o$ = 5.151 Å and having a density of $6.80_5$ g./cm.[3]. Later, in 1939, using a sample of 98-99 per cent purity, they observed with one exception only the h.c.p. modification which could not be transformed to the f.c.c. form by annealing below 300° and 425°C.[17] The lattice parameters reported were $a_o = 3.662 \pm .003$ Å and $c_o = 5.908 \pm .005$ and $c_o/a_o = 1.613$. Irregularities in line intensities between the observed and calculated values were noticed and several additional lines were observed which could be accounted for only if the $c_o$ axis was doubled. The authors evidently did not have enough conviction in their observation to report the structure as having this doubled value.

Using a sample of 54.8 per cent praseodymium, 37 per cent lanthanum, Ziegler,[7] in 1949, observed only a few diffuse lines with the metal in the "as received" state, but after annealing at 350°C. for four days the x-ray diffraction pattern obtained contained several sharp lines due to an unknown structure.

James, Legvold and Spedding[10] reported a mixture of both h.c.p. and f.c.c. phases existing in a sample approximately 99.9 per cent pure in 1952, the former phase predominating.

Table 3 summarizes the literature cited.

Table 3. Summary of praseodymium literature

| Author | Method of Preparation | Purity | Technique | Results |
|---|---|---|---|---|
| Rossi[16,4] (1932) (1934) | Electrolytic | 99.4% | 57.3 mm. diameter powder camera | Annealed at 350°C.:<br>h.c.p., $a_o = 3.657$ Å<br>$c_o/a_o = 1.62$<br>later found h.c.p.,<br>$a_o = 3.652$ Å<br>$c_o/a_o = 1.61$ |
| Klemm and Bommer[5,17] (1937) (1939) | Reduction of $PrCl_3$ with liquid alkali metal | 98-99% | Examined reduction mixture 57.3 mm. diameter powder camera | (1937) f.c.c. $a_o = 5.151$ Å<br>(1939) h.c.p. $a_o = 3.662$<br>$c_o = 5.908$<br>$c_o/a_o = 1.613$<br>($c_o$ value possibly doubled) |
| Ziegler[7] (1949) | - | 54.8% Pr<br>37% La | Metal filings | Annealed at 350°C.:<br>unknwon structure |
| James, Legvold and Spedding[10] (1952) | Reduction of $PrCl_3$ with Ca | 99.9% | Metal needles low temperature camera | Chiefly h.c.p. but some f.c.c. |

## 4. Neodymium

Quill,[2] in 1932, first reported the structure of neodymium as h.c.p. using filings obtained in a helium atmosphere from metal prepared electrolytically by Kremers. Copper $K_\alpha$ radiation and a 57.4 mm. diameter camera were used and a silver standard was added to the filings to correct the diffraction angles. The lattice parameters reported were $a_o = 3.65 \pm .010$ Å, $c_o = 5.88 \pm .030$ Å, $c_o/a_o = 1.608$, and the calculated density was 6.991 g./cm.$^3$.

In 1937, Klemm and Bommer[5] found neodymium to be h.c.p. with $a_o = 3.655$ Å, $c_o = 5.880$ Å, $c_o/a_o = 1.609$ and having a density of $6.99_8$ g./cm.$^3$. Later, in 1939, using purer material (free of all other rare earths) they reported its parameters as $a_o = 3.650 \pm .003$ Å, $c_o = 5.890 \pm .005$ Å, $c_o/a_o = 1.613$ and its density as $7.00_4$ g./cm.$^3$.[17] Again, as with praseodymium, doubling the $c_o$ axis accounted for some additional lines not allowed for with the $c_o$ value reported.

Ziegler,[7] in 1949, using 78 per cent neodymium, 15 per cent praseodymium metal reported, as in the case of praseodymium, a diffuse pattern before annealing at 350°C. for approximately four days and a sharp unidentifiable pattern after heating.

James, Legvold and Spedding[10] found neodymium metal of greater than 99 per cent purity to be entirely h.c.p.

With neodymium containing .03 per cent calcium as its major impurity and less than 30 p.p.m. carbon, Ellinger,[18] in 1955, verified conclusively the suspected structure of Klemm and Bommer. Metal filings were annealed 50 hours at 200°C. in vacuo and were then examined with a 114.6 mm. diameter Straumanis type camera and a 19 cm. diameter Unicam high temperature camera utilizing copper radiation. From the high angle doublets the lattice parameters of the h.c.p. structure were determined as $a_o = 3.655 \pm .001$ Å, $c_o = 11.796 \pm .004$ Å and $c_o/a_o = 3.227$. The calculated density was 7.02 g./cm.$^3$. The space group was given as $P6_3/mmc$ with four atoms of the unit cell at the following positions, (0, 0, 0), (0, 0, 1/2), (1/3, 2/3, 1/4) and (2/3, 1/3, 3/4). This structure was found to be stable to at least 680° ± 10°C.

The doubled $c_o$-axis structure of neodymium has also been verified in this laboratory by Behrendt[19] studying single crystals of neodymium with Weissenberg and precession cameras.

The neodymium literature cited is summarized in Table 4.

## 5. Scandium, yttrium and the remaining rare earths

The remaining rare earth metals except for element number 61 have been studied chiefly by Klemm and Bommer.[5,6,17]

Table 4. Summary of neodymium literature

| Author | Method of Preparation | Purity | Technique | Results |
|---|---|---|---|---|
| Quill[2] (1932) | Electrolytic | | Metal filings 57.4 mm. diameter powder camera | h.c.p., $a_o = 3.65$ Å<br>$c_o = 5.88$ Å<br>$c_o/a_o = 1.608$ |
| Klemm and Bommer[5,17] (1937) (1939) | Reduction of $NdCl_3$ with liquid alkali metal | 98-99% | Examined reduction mixture 57.3 mm. diameter powder camera | (1937) h.c.p. $a_o = 3.655$ Å<br>$c_o = 5.880$ Å<br>$c_o/a_o = 1.609$<br>(1939) h.c.p. $a_o = 3.650$ Å<br>$c_o = 5.890$<br>$c_o/a_o = 1.613$<br>$c_o$ value possibly doubled |
| Ziegler[7] (1949) | | 78% Nd<br>15% Pr | Metal filings | Annealed at 350°C.: unknown structure |
| Ellinger[18] (1955) | Reduction of $NdCl_3$ with Ca | 99.9% | Metal filings 114.6 mm. diameter Straumanis type camera and Unicam high temperature camera | Annealed at 200°C.:<br>h.c.p. $a_o = 3.655$<br>$c_o = 11.796$<br>$c_o/a_o = 3.227$<br>stable to 680°C. |

Table 4. (Continued)

| Author | Method of Preparation | Purity | Technique | Results |
|---|---|---|---|---|
| Behrendt[19] | Reduction of $NdCl_3$ with Ca | 99% | Single crystals Weissenberg and precession cameras | h.c.p.: $a_0 = 3.69$ Å<br>$c_0 = 11.83$ Å |
| James, Legvold and Spedding[10] (1952) | Reduction of $NdCl_3$ with Ca | 99% | Metal needles low temperature camera | Entirely h.c.p. |

In 1937 they prepared the metals by reducing the chloride with liquid rubidium, cesium or potassium metal at temperatures low enough to eliminate a reversal of reaction. These reduction mixtures were sealed in glass capillaries under argon and examined in a 57.3 mm. diameter powder camera. Filtered copper radiation was used for all metals except ytterbium and europium for which cobalt $K_\alpha$ radiation was employed. In every case the alkali chloride in the mixture was used in correcting the diffraction angles of the rare earth metal. Exact analytical data for the materials were not reported except for samarium which contained .8 per cent europium and .3 per cent gadolinium. The gadolinium oxide had a purity of 99.5 per cent and the europium and ytterbium were reported as being "pure". Lutecium was contaminated with approximately 4 per cent thulium and the purity of the terbium oxide employed was about 85 per cent. Ytterbium oxide (4.7 per cent) and lutecium oxide (5.7 per cent) were the chief impurities in the thulium oxide used. The excess alkali from the reduction process was assumed to have been distilled off in heating to 200°-300°C., but no analyses for these metals were given. Klemm and Bommer found the metals to be f.c.c., h.c.p. or body centered cubic (b.c.c.) in structure type. Their results are given in Table 5. Included are their results obtained in 1939 on praseodymium and neodymium, and Bommer's work on the structure of holmium[20] also reported

Table 5. Klemm and Bommer's x-ray data for the rare earth metals[5,17,20]

| Element | Crystal structure | $a_o$ (Å) | $c_o$ (Å) | $c_o/a_o$ | Density (g./cm.$^3$) |
|---|---|---|---|---|---|
| La | f.c.c. | 5.294 | ----- | ----- | $6.18_0$ |
| Ce | f.c.c. | 5.140 | ----- | ----- | $6.81_0$ |
| Pr | f.c.c. | 5.151 | ----- | ----- | $6.80_5$ |
| Pr | h.c.p. | 3.662 | 5.908 | 1.613 | $6.77_6$ |
| Nd | h.c.p. | 3.655 | 5.880 | 1.609 | $6.99_8$ |
| Nd | h.c.p. | 3.650 | 5.890 | 1.613 | $7.00_4$ |
| Eu | b.c.c. | 4.573 | ----- | ----- | $5.24_4$ |
| Gd | h.c.p. | 3.622 | 5.748 | 1.587 | $7.94_8$ |
| Tb | h.c.p. | 3.585 | 5.664 | 1.580 | $8.33_2$ |
| Dy | h.c.p. | 3.578 | 5.648 | 1.579 | $8.56_2$ |
| Ho | h.c.p. | 3.557 | 5.620 | 1.580 | $8.76_4$ |
| Er | h.c.p. | 3.532 | 5.589 | 1.582 | $9.16_4$ |
| Tm | h.c.p. | 3.523 | 5.564 | 1.580 | $9.34_6$ |
| Yb | f.c.c. | 5.468 | ----- | ----- | $7.01_0$ |
| Lu | h.c.p. | 3.509 | 5.559 | 1.584 | $9.74_0$ |

in 1939. The holmium sample contained 1-2 per cent dysprosium and a few tenths per cent yttrium.

McLennan and Monkman[21] first reported the structure of erbium as h.c.p. with lattice parameters of $a_o = 3.74$ Å, $c_o/a_o = 1.63$ in 1929. They obtained their diffraction pattern with a modified unsymmetric back reflection camera using copper radiation and a standard of copper filings.

Scandium was reported as having the h.c.p. structure by Meisel[22] and Bommer[6] in 1939. Meisel obtained his sample from Fischer who together with Brunger and Grieneisen[23] had determined its density as about 3.1 g./cm.$^3$. They reported its purity as 94-98 per cent scandium containing .3-.5 per cent silicon and .2-.5 per cent iron. It was prepared by the electrolysis of scandium chloride and a potassium chloride-lithium chloride eutectic mixture using a liquid zinc cathode. Meisel's diffraction patterns were not very sharp but he was able to discern both f.c.c. and h.c.p. phases in the metal. Later workers[24] indicated the f.c.c. structure may be due to scandium nitride. The lattice constants given were $a_o = 4.532 \pm .005$ Å and $a_o = 3.30 \pm .01$ Å, $c_o = 5.23 \pm .01$ Å, $c_o/a_o = 1.585$ respectively. Densities of $3.20 \pm .01$ g./cm.$^3$ (f.c.c.) and $3.02 \pm .04$ g./cm.$^3$ (h.c.p.) were calculated for the two structures. Bommer,[6] using metal of an unspecified purity prepared by the reduction of scandium chloride with potassium metal reported only the h.c.p. modification with parameters of $a_o = 3.302 \pm .003$ Å, $c_o = 5.245 \pm .006$ Å and an axial ratio of $c_o/a_o = 1.588$.

The structure of yttrium was first mentioned by Quill[2] in a 1932 article and was more fully reported by him later in the same year.[25a] His metal had been obtained from Kremers who had prepared it by the electrolysis of yttrium chloride and sodium chloride, the original yttrium oxide being approximately 99.5 per cent pure. Copper $K_\alpha$ radiation, a 57.4 mm. diameter powder camera and a silver standard were used to obtain the corrected yttrium diffraction pattern which also contained the strongest yttrium oxide lines. The structure reported was h.c.p. with $a_o = 3.663 \pm .008$ Å, $c_o = 5.814 \pm .012$ Å and $c_o/a_o = 1.588$. The calculated density was 4.34 g./cm.$^3$ and the bulk value measured by Kremers was 4.57 g./cm.$^3$. Bommer,[6] in 1939, verified the h.c.p. structure but reported the lattice parameters as $a_o = 3.629 \pm .004$ Å, $c_o = 5.750 \pm .007$ Å and $c_o/a_o = 1.585$. No analysis for the metal was given.

Banister, Legvold and Spedding,[25b] in 1953, studied the effect of temperature on the lattice parameters of gadolinium, dysprosium and erbium from room temperature down to about 45°K. The purities of the metals investigated were given as 99.9 per cent or greater. Each metal was found to retain its h.c.p. structure over the temperature range studied, their room temperature lattice parameters being: gadolinium, $a_o = 3.635 \pm .002$ Å, $c_o = 5.775 \pm .005$ Å; dysprosium, $a_o = 3.596 \pm .002$ Å, $c_o = 5.653 \pm .004$ Å; erbium, $a_o = 3.562 \pm .002$ Å, $c_o = 5.602 \pm .003$ Å.

From the literature cited one can easily understand why more precise determinations of the structure and lattice constants of pure rare earths, scandium and yttrium metals are desirable.

## C. Equipment

For the structure determination of the rare earth metals a Debye-Scherrer camera, Weissenberg camera and an x-ray diffractometer were employed. The Debye-Scherrer camera, obtained from The North American Phillips Company, had a diameter of 114.59 mm. A Norelco Geiger counter diffractometer unit was used to obtain the diffraction patterns of bulk specimens of the more easily oxidized metals. This camera is based on the Seeman-Bohlin principle where the x-ray source, sample and receiving slits of the Geiger counter all lie on the circumference of a variable diameter circle. When single crystals were available a Weissenberg camera of 57.3 mm. diameter, obtained from the Charles Supper Company, was used in their investigation.

Once the structures were obtained, a Norelco symmetrical focusing precision back reflection camera of 12 cm. diameter was used to obtain patterns for accurate lattice constant determinations. This camera was checked for accuracy by using it to determine the lattice constant of potassium chloride before studying the rare earths.

In all cases copper radiation filtered with nickel foil was used in conjunction with a North American Phillips basic x-ray diffraction unit.

Kodak no-screen x-ray film was employed with the Debye-

Scherrer camera and Ilford high speed industrial film was used with the Weissenberg and back reflection cameras. The recommended film developing and fixing procedures using General Electric chemicals were followed to maintain uniformity.

To measure the diffraction lines on the film a General Electric Illuminator, Model 5-17, with vernier scale was employed. This device reportedly allows line positions to be read to one-twentieth millimeter on a millimeter scale 42 centimeters long.

Microscopic examinations of all bulk and distilled samples were made and photomicrographs were obtained with an American Optical Metallograph, Model 2400.

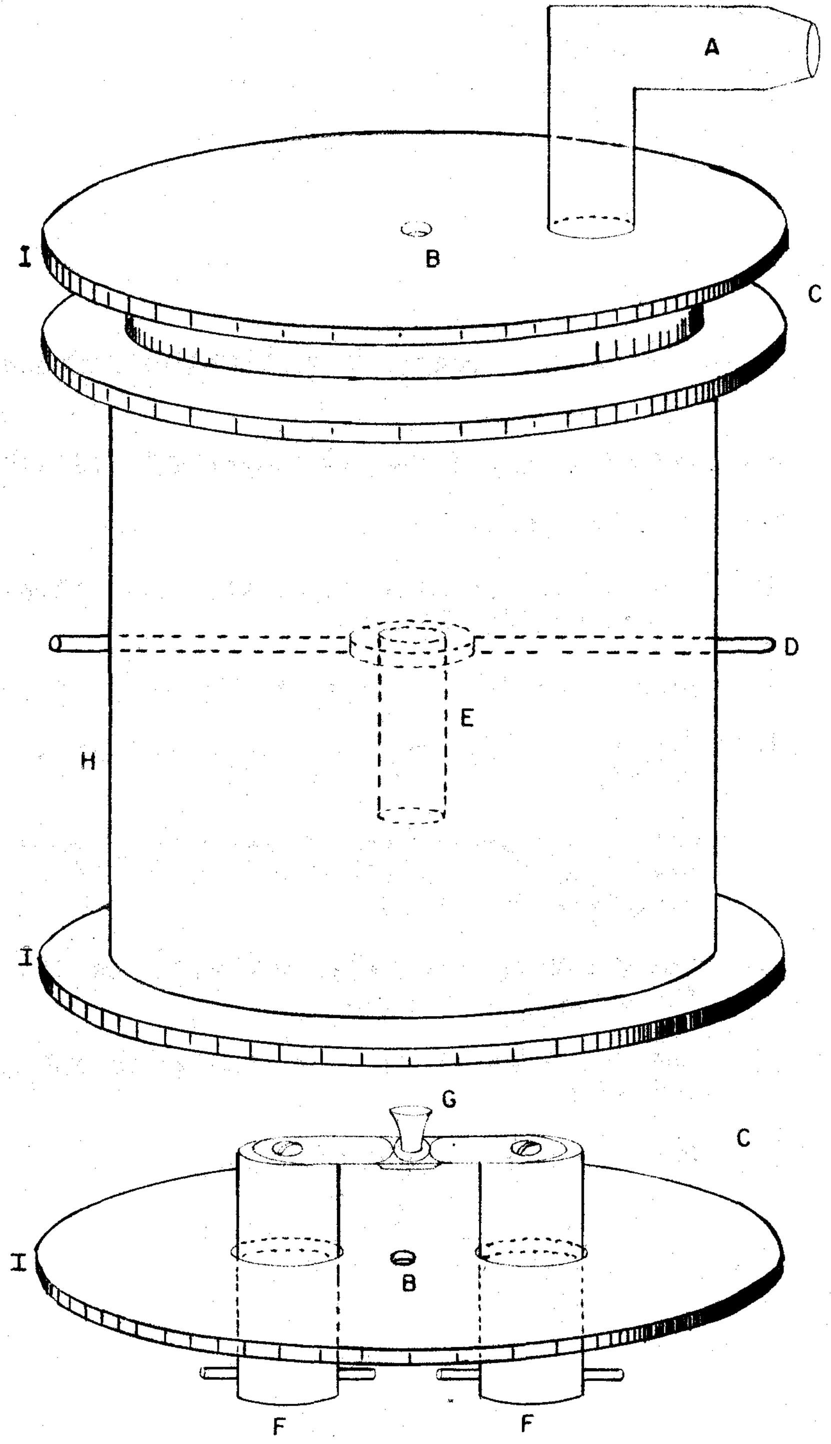
In order to obtain pure metals free of tantalum and atmospheric gases, it was found necessary to distill them in a high vacuum. To do this the apparatus illustrated in Figure 1 was designed and successfully used. Power for the heating element was supplied by a 10 kilowatt stepdown transformer and the vacuum conditions were achieved with an H. S. Martin mercury diffusion pump and a Welch mechanical pump.

## D. Procedure and Techniques

Samples in the form of metal filings were examined with

Fig. 1 High vacuum metal distillation furnace.

| | |
|---|---|
| A. | Tapered connection to mercury diffusion pump |
| B. | Sightglass hole |
| C. | Vacuum seals made with six inch diameter neoprene "O" rings |
| D. | Water cooled condensing cylinder support |
| E. | Tantalum cylinder on which the metal is condensed |
| F. | Water cooled copper electrodes; vacuum sealed and electrically insulated with neoprene "O" rings |
| G. | Tantalum heating element with tantalum distillation bucket |
| H. | Water cooled five inch diameter copper cylinder |
| I. | Water cooled brass flanges |


A
I
B
C
D
E
H
I
G
C
I
B
F
F

the 114.59 mm. diameter powder camera. After obtaining filings which passed through a 200 mesh screen a small, thin-walled pyrex capillary was filled with them and the metal then annealed in high vacuum at about 300°C. for one to three hours. In some cases powdered potassium chloride was added to the filings and used as an internal standard, however, since more precise lattice parameters were obtained by a different technique this practice was not followed in all cases. The annealing procedure allowed adequate relief of stresses in the filings and yet did not result in excessive grain growth. With these samples sharp diffraction patterns could be obtained in which resolution of the $\text{alpha}_1$, $\text{alpha}_2$ radiation occurred in the region of $50°\theta$. An exposure time of approximately 10-11 hours was found necessary to obtain the back reflection lines. The vernier scale illuminator was used to measure the line positions. This powder camera and procedure was used with all metals except lanthanum, cerium, praseodymium and neodymium.

To obtain the diffraction patterns of the four remaining elements the Norelco diffractometer unit was employed. With this unit bulk specimens (which can be more easily protected from the atmosphere) were investigated. The samples of lanthanum, cerium, praseodymium and neodymium were the same specimens whose electrical resistivity variations were studied, and which are considered in a later section. To prepare the diffraction samples the metals were mounted in bakelite, polished and then etched to give a flat, bright metallic surface of approximately two square centimeters area. After applying a thin coat of Krylon (plastic) as protection from oxidation, the specimens were examined in the diffraction region $20^{\circ}$-$160^{\circ}$ $2\theta$. The patterns were automatically recorded on a Brown recorder strip chart from which the angles of the diffraction peaks could easily be determined. Prior to the study of these metals the diffractometer was alligned and calibrated using a silicon standard.

Once the diffraction patterns were obtained, either in film or chart form, their calculated $\sin^2\theta$ values were compared with those calculated from previously reported lattice parameters. In this manner the appropriate Miller indices could be assigned to the proper reflections, and more suitable lattice constants could then be calculated. Irregularities appeared when this procedure was applied to lanthanum, neodymium and praseodymium, therefore, Bunn charts were employed to obtain the correct structure, approximate axial ratio and the proper Miller indices. From this information the correct lattice parameters were calculated.

Although the above procedures gave diffraction patterns of yttrium, scandium and the rare earths from which relatively accurate lattice constants could be obtained, greater accuracy was desired for the study of the individual nature of these metals and for future use in their alloy study. A symmetrical focusing back reflection camera was employed to accomplish this. Samples of gadolinium, neodymium, praseodymium and cerium in the form of slabs having the approximate dimensions 3/4 inch by 1 inch by 1/32-1/16 inch, were shaped to the curvature of the camera by pressing in molds which had the same radius of curvature as the camera's film holder. After forming, the samples were annealed in high vacuum (approximately $10^{-6}$ mm. mercury) at about 300°C. for one to two hours. If discoloration occurred they were etched with a 5 per cent concentrated nitric acid-water solution and rinsed with absolute alcohol.

Specimens of the remaining metals were prepared by distillation and subsequent condensation in high vacuum. Small quantities (1-2 grams) of the various metals were placed in tantalum buckets and vaporized with the apparatus shown in Figure 1. An optical pyrometer was used to determine the very approximate temperature of the specimens and the pressure fluctuation of the system was used as a measure of the degree of vaporization occurring. Since the rare earths and yttrium are extremely good getters for atmospheric gases a rather sudden decrease in pressure occurred when appreciable quantities of metal began distilling. From a knowledge of the vapor pressure of some of the rare earth metals a very approximate vapor pressure of 1-2 mm. mercury was estimated for the metals at the temperature at which the pressure dropped suddenly. In every case the pressure within the system dropped from approximately $1 \times 10^{-5}$ mm. to $5 \times 10^{-7}$ mm. mercury within one to two minutes after the pressure began decreasing. Usually 20 or 30 minutes was sufficient time to obtain a suitable diffraction sample if the metal was held at a temperature approximately 50°-100°C. above its appreciable vaporization temperature. The distilled metal condensed on either the tantalum cylinder walls surrounding the upper lip of the tantalum crucible or on the tantalum baffles spaced within the cylinder. Since the thickness of the tantalum was only .0025 inches and the condensed metal was estimated at approximately .001-.002 inches thick, the samples could easily be formed to the radius of the back reflection camera by means of the sample holder built into the camera.

An internal standard of 200 mesh potassium chloride was used with cerium, ytterbium, praseodymium, neodymium, gadolinium, dysprosium and erbium. The salt was uniformly screened onto the surface of the metal to which a thin coating of collodion had been freshly applied. The standard was necessary in order to determine their lattice parameters by a method devised by Thewlis which is described later.

High speed Ilford x-ray film was used with the back reflection camera to shorten the exposure time, thus minimizing oxidation of the samples by decreasing the time they were exposed to a corroding atmosphere. Although the camera was designed to be used under vacuum or under a dynamic inert atmosphere, indications of attack could be observed with lanthanum and cerium if left in the camera for an hour or more. Filtered copper radiation was used and an exposure time of approximately 20-30 minutes gave satisfactory diffraction patterns. The patterns obtained from the above procedure were measured with the aid of the vernier scale illuminator mentioned previously. Whereas the bulk samples of cerium, praseodymium, neodymium and gadolinium required annealing to produce sharp diffraction lines, the distilled specimens required no such treatment. Undoubtedly the metal condensed at a sufficiently high temperature to relieve any strains or stresses it may have incurred in depositing.

### 1. Parameter determination techniques

Two methods of treating the data were employed to obtain accurate lattice constants of the hexagonal structures and the results were compared and evaluated for accuracy and source of error. Cohen's[26] analytical method involving a least squares treatment and a technique devised by Thewlis[27] were the methods compared. Cohen's evaluation of the data has long been recognized as an approved analysis and can be found in most crystallographic textbooks, while Thewlis' method has not yet been widely accepted.

In Cohen's[26] method errors in theta due to shrinkage, eccentricity and absorption are accounted for by an analytical expression obtained by a Taylor's expansion of Bragg's law:

$$n \lambda = 2d \sin \theta .$$

For the hexagonal system, when using a symmetric back reflection camera, the correct error equation is:

$$\alpha A_o + \gamma C_o + \delta D_o = \sin^2 \theta \qquad (1)$$

where $\alpha = h^2 + hk + k^2$

$\gamma = l^2$ $\qquad A_o = \frac{\lambda^2}{4a^2}$

$\delta = 10 \phi \sin^2 2\phi$ $\qquad C_o = \lambda^2/3c^2$

$\phi = 90^\circ - \theta$ $\qquad D_o =$ exp. drift constant of error

Only three such equations are necessary to obtain a solution of $A_o$, $C_o$ and $D_o$, however, the random errors of measurement can be minimized by applying a least squares treatment to equation (1). The equations resulting from such treatment are:

$$A_0 = \frac{\begin{vmatrix} \sum \alpha \sin^2\theta & \sum \alpha\gamma & \sum \alpha\delta \\ \sum \gamma \sin^2\theta & \sum \gamma^2 & \sum \gamma\delta \\ \sum \delta \sin^2\theta & \sum \gamma\delta & \sum \delta^2 \end{vmatrix}}{\begin{vmatrix} \sum \alpha^2 & \sum \alpha\gamma & \sum \alpha\delta \\ \sum \alpha\gamma & \sum \gamma^2 & \sum \gamma\delta \\ \sum \alpha\delta & \sum \gamma\delta & \sum \delta^2 \end{vmatrix}}$$

$$C_0 = \frac{\begin{vmatrix} \sum \alpha^2 & \sum \alpha \sin^2\theta & \sum \alpha\delta \\ \sum \alpha\gamma & \sum \gamma \sin^2\theta & \sum \gamma\delta \\ \sum \alpha\delta & \sum \delta \sin^2\theta & \sum \delta^2 \end{vmatrix}}{\begin{vmatrix} \sum \alpha^2 & \sum \alpha\gamma & \sum \alpha\delta \\ \sum \alpha\gamma & \sum \gamma^2 & \sum \gamma\delta \\ \sum \alpha\delta & \sum \gamma\delta & \sum \delta^2 \end{vmatrix}}$$

$$D_0 = \frac{\begin{vmatrix} \sum \alpha^2 & \sum \alpha\gamma & \sum \alpha \sin^2\theta \\ \sum \alpha\gamma & \sum \gamma^2 & \sum \gamma \sin^2\theta \\ \sum \alpha\delta & \sum \gamma\delta & \sum \delta \sin^2\theta \end{vmatrix}}{\begin{vmatrix} \sum \alpha^2 & \sum \alpha\gamma & \sum \alpha\delta \\ \sum \alpha\gamma & \sum \gamma^2 & \sum \gamma\delta \\ \sum \alpha\delta & \sum \gamma\delta & \sum \delta^2 \end{vmatrix}}$$

Again only three equations are required for solution, however, the more reflections available the more reliable the results.

Thewlis'[27] method requires prior correction of the usual errors by the addition of an internal standard to the sample studied. It is also necessary to assume an approximate value for the $a_o$ parameter, thus a previous knowledge of the structure is necessary.

The basic equation used in Thewlis'[27] technique for the hexagonal system is:

$$c^{*2}_{obs} = c^{*2} + 8/3 \; \frac{(h^2 + hk + k^2)}{l^2} \; (a^*_{ass.} \delta a^*) \qquad (2)$$

where a and c are the lattice parameters and

$$c^* = \frac{1}{c} \qquad\qquad a^*_{true} = \frac{1}{a}$$

$$c^{*2}_{obs} = \frac{1}{l^2 d^2} - \frac{4}{3} \; \left(\frac{h^2 + hk + k^2}{l^2}\right) \; a^{*2}_{ass.}$$

$$\delta a^* = \frac{3}{8} \; \frac{(\text{slope of plotted line})}{a^*_{assumed}}$$

$$a^*_{true} = a^*_{ass.} + \delta a^*$$

Equation (2) can be derived directly from the geometry of the hexagonal unit cell and the assumption that the square of the error ( $\delta a^*$) in the value of $a^*_{ass.}$ is small enough to be neglected.

As can be observed from equation (2) a plot of $c^{*2}_{obs.}$ against $\frac{(h^2 + kh + K^2)}{l^2}$ should result in a straight line which intersects the former axis at $c^{*2}$ and has a slope of $\frac{8}{3}$ $a^*_{ass.}\,\delta a^*$. From a knowledge of these two values the correct lattice constants can be calculated from the suitable equations.

A graphical extrapolation employing a correction function derived by Nelson and Riley[28] was used to obtain accurate values for the lattice constants of the cubic metals. This technique consists of plotting the calculated $a_o$ values against $\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta} + \frac{\cos^2\theta}{\theta}\right)$ and extrapolating to 90° $\theta$. With this method the high angle diffraction lines which contain less error are weighted somewhat, and since all errors theoretically vanish at 90° $\theta$, the lattice parameters obtained are quite accurate.

The standard errors present in the lattice parameters reported were calculated by a method described by Jette and Foote.[29]

## 2. Metallographic techniques

Photomicrographs of the metals studied were obtained with a metallograph. The distilled samples were examined directly with no polish or etch treatment. Because of the reactive nature of the rare earths it was exceedingly difficult to obtain a well polished, clean and characteristic surface on the bulk metals which would persist during the time required for proper microscopic examination. Of the solutions tried as a suitable etchant, a 5 per cent concentrated nitric acid-water solution gave the best results for lanthanum, cerium, praseodymium and neodymium although even this solution left much to be desired. For the rare earths of greater atomic number a solution of 40 per cent concentrated nitric acid, 60 per cent glacial acetic acid proved of greatest value as an etchant but this, too, was of relatively poor quality. This etching solution could also be used with praseodymium and neodymium. Mechanical polishing wheels employing papers of 320, 500 and 600 grit and 2-8 micron grit diamond compound used in conjunction with a lap wheel were also employed in obtaining proper metallographic surfaces on the metals investigated.

## E. Results

### 1. Analysis of metals

In all cases the metals studied were those prepared by the Ames Laboratory from pure scandium, yttrium and rare earth material obtained by ion exchange separation techniques. Thulium, ytterbium and europium were prepared by reduction of the rare earth oxide with lanthanum metal and subsequently distilled in high vacuum leaving a residue of lanthanum oxide and some excess lanthanum. The remaining metals were prepared by calcium reduction of the fluoride in an atmosphere of helium or argon. Excess calcium remaining in the metal was removed by vaporization from the molten metal in high vacuum. In all cases, tantalum metal was used as the crucible and condensing material. Although there is some attack of tantalum at high temperature by the metals investigated, this was remedied as described earlier by vaporizing the rare earth metals from it.

Spectrographic analysis results of the metals studied are given in Table 6. Metallographic examination of the distilled metals revealed little, if any, presence of a second phase.

Although some of the metals are reported as containing considerable tantalum, it should be noted that the analytical samples were taken from the cast metal and it has been shown that distillation effectively eliminates this impurity. The vaporized metals were usually prepared in such small quantities that an analytical sample could not easily be obtained. There was insufficient europium metal available for analysis, however, it was prepared from the oxide of about 98 per cent purity, the chief contaminant being gadolinium (approximately 1.3 per cent). This impurity should have been eliminated in

Table 6. Spectrographic analyses of metals %

| Impurity | Sc | Y | La | Ce | Pr | Nd | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Y |  |  |  |  |  |  | .07 | <.03 | <̄.02 | <̄.01 | .03 | <.03 | <̄.01 | .016 |
| La | .03 |  |  | <̄.02 | <̄.005 |  |  |  |  |  |  |  |  |  |
| Ce |  |  | <̄.03 |  | <̄.1 |  |  |  |  |  |  |  |  |  |
| Pr |  |  | <̄.04 | <̄.02 |  | <̄.08 |  |  |  |  |  |  |  |  |
| Nd |  |  | <̄.05 | <̄.02 | <̄.06 |  | <̄.02 |  |  |  |  |  |  |  |
| Sm |  | <̄.1 |  |  |  | <̄.06 | <̄.1 | <.01 |  |  |  |  |  |  |
| Eu |  |  |  |  |  |  | <.03 |  |  |  |  |  |  |  |
| Gd |  | <.05 |  |  |  |  |  | <̄.03 |  |  |  |  |  |  |
| Tb |  | .45 |  |  |  |  | <̄.01 |  | <̄.1 |  |  |  |  |  |
| Dy |  | <.02 |  |  |  |  | <.05 | <̄.05 |  | .2 | <̄.01 |  |  |  |
| Ho |  | <.02 |  |  |  |  | .06 |  | <̄.01 |  | <.01 |  |  |  |
| Er | .1 | <̄.02 |  |  |  |  |  |  | <.05 | .28 |  | <̄.03 | <̄.01 |  |
| Tm | .2 |  |  |  |  |  |  |  |  | <̄.01 | <.01 |  | <.01 | <.02 |
| Yb | <.01 |  |  |  |  |  |  |  | .02 |  | <̄.01 | <̄.03 |  | .08 |
| Lu |  |  |  |  |  |  |  |  |  |  |  | <̄.03 | <̄.01 |  |
| Ca | M. | .04 | <.06 | <.04 | <.04 | <.04 | <.04 |  | <.04 | .04 | <.04 | <.04 | <.04 | vw |
| Ta | v.s. | 1.0 |  | <̄.05 | .01 | .05 | .1 |  | 1.0 | .2 | 1.0 | <.1 | <̄.05 |  |
| Fe |  |  | .04 | <.01 |  | .007 | .006 |  | .01 |  | .006 | <̄.0005 |  |  |
| Si | v.w. | .06 | .05 | <.03 | <.03 | .03 | <̄.03 |  | <.03 | <.02 | <.03 |  | <.02 | vw |
| Mg | <.01 | .01 | <.02 | .04 | <.02 | <.02 | <.03 |  | <.03 | <.03 | <.03 | <.02 | <.02 | vw |

Table 7 gives the meaning of the symbols used in Table 6.

Table 7. Code for Table 6

| Symbol | Meaning |
|---|---|
| $\overline{<}$ | element not detected at stated detection limit |
| — | element not detected |
| $<$ | less than |
| v.w. | very weak (less than .01%) |
| M. | moderate (.01% to 1%) |
| v.s. | very strong (greater than 1%) |

the subsequent distillation of the metal.

## 2. Diffractometer results

Bulk samples of lanthanum, cerium, praseodymium and neodymium, prepared and examined by the techniques stated earlier, were investigated with the Norelco diffractometer unit. Cerium was found to have a f.c.c. structure while the others were h.c.p. with $c_0$ axes approximately double those previously reported, except for Ellinger[18] and Behrendt's[19] findings concerning neodymium. The diffraction data for those metals are given in Table 8.

Since the recorded peaks of the $\alpha_1$, $\alpha_2$ copper radiation

Table 8. X-ray diffractometer data for Ce, La, Pr and Nd

| hkl | La $^{\circ}\theta$ | Pr $^{\circ}\theta$ | Nd $^{\circ}\theta$ | hkl | Ce $^{\circ}\theta$ |
|---|---|---|---|---|---|
| 100 | 13.61 | 13.95 | 14.08 | 111 | 14.99 |
| 101 | 14.11 | 14.48 | 14.54 | 200 | 17.36 |
| 004 | 14.63 | 15.07 | 15.12 | 220 | 24.97 |
| 102 | 15.48 | 15.92 | 15.99 | 311 | 29.65 |
| 103 | 17.54 | 18.07 | 18.17 | 222 | 31.12 |
| 104 | 20.22 | 20.78 | 20.90 | 400 | 36.65 |
| 105 | 23.25 | 23.92 | 23.97 | 331 | 40.55 |
| 110 | 24.07 | 24.79 | 24.86 | 420 | 41.80 |
| 106 | 26.50 | 27.34 | 27.43 | 422 | 46.95 |
| 114 | 28.70 | 29.55 | 29.69 | 333 | 50.80 |
| 202 | 29.20 | ----- | 30.19 | 531 | 61.90 |
| 008 | 30.40 | 31.32 | ----- | 442 | 63.50 |
| 206 | ----- | 38.40 | 38.58 | | |
| 109 | ----- | 39.25 | 39.45 | | |
| 211 | ----- | ----- | 40.25 | | |
| 212 | 39.45 | ----- | 40.95 | | |
| 118 | 40.50 | 41.89 | 42.09 | | |
| 1,0,10 | 42.41 | 43.95 | 44.13 | | |
| 216 | ----- | 48.50 | 48.80 | | |
| 304 | 48.60 | ----- | 50.67 | | |

were not resolved, the weighted value of 1.5418 Å was used for the wavelength of the radiation in all necessary calculations. The calculated lattice constants of the metals investigated are given in Table 9.

Table 9. Lattice parameters of Ce, La, Pr and Nd
(Angstrom units)

| Element | Ce | La | Pr | Nd |
|---|---|---|---|---|
| Structure | f.c.c. | h.c.p. | h.c.p. | h.c.p. |
| $a_o$ | 5.17 | 3.78 | 3.68 | 3.66 |
| $c_o$ | ---- | 12.20 | 11.86 | 11.82 |

### 3. Debye-Scherrer camera results

Metal filings of the remaining elements were obtained from the reduced and cast metals which in some cases contained approximately 1 per cent tantalum. They were considered of sufficient purity, however, for structure determinations and the evaluation of approximate lattice parameters. Copper radiation was employed in all cases and the techniques described previously were used to obtain the diffraction patterns of the respective metals.

Of the metals investigated scandium, yttrium, gadolinium, dysprosium, holmium, erbium, thulium and lutecium were found to be h.c.p. while the structure of europium was b.c.c. and ytterbium exhibited a f.c.c. phase. These structures are in agreement with those previously reported. Tables 10a and 10b give the experimental data and Table 11 lists the approximate lattice constants. Examples of the patterns obtained from the f.c.c., b.c.c. and h.c.p. structures are reproduced in Figure 2.

## 4. Rare earth single crystal results

Rotation and Weissenberg x-ray photographs were obtained for a single crystal of dysprosium which was separated from a massive piece of distilled metal prepared in the Ames Laboratory. Filtered copper radiation was employed and the Weissenberg pattern obtained is reproduced in Figure 3.

The existent and absent reflections were found to satisfy the space group $C_6$/mmc which requires:

a) hkl, all present
b) hhl, present only if $l = 2n$
c) $h\bar{h}l$, all present
d) $h-k = 3n$, only if $l = 2n$.

There are two atoms in the hexagonal unit cell which occupy the positions (1/3, 2/3, 1/4) and (2/3, 1/3, 3/4). The lattice parameters of the dysprosium unit cell were calculated as $a_o = 3.57$ Å, $c_o = 5.62$ Å.

A rotation pattern of a thulium single crystal was obtained, but since it had the same symmetry as dysprosium no

## Table 10a. X-ray diffraction data for rare earths, scandium and yttrium

| hkl | Gd °θ | Tb °θ | Dy °θ | Ho °θ | Er °θ | Tm °θ | Lu °θ | Sc °θ | Y °θ |
|---|---|---|---|---|---|---|---|---|---|
| 100 | 14.18 | 14.29 | 14.36 | 14.36 | 14.44 | 14.54 | 14.68 | 15.48 | 14.06 |
| 002 | 15.44 | 15.60 | 15.83 | 15.84 | 15.94 | 16.05 | 16.04 | 16.89 | 15.53 |
| 101 | 16.16 | 16.26 | 16.41 | 16.43 | 16.55 | 16.65 | 16.76 | 17.71 | 16.18 |
| 102 | 21.21 | 21.36 | 21.61 | 21.61 | 21.78 | 21.92 | 21.99 | 23.24 | 21.19 |
| 110 |  | 25.15 | 25.39 | 25.40 | 25.58 | 25.76 | 25.96 | 27.54 | 24.90 |
| 103 | 27.94 | 28.20 | 28.54 | 28.58 | 28.76 | 28.98 | 29.00 | 30.73 | 27.96 |
| 200 |  |  | 29.66 | 29.68 | 29.91 | 30.13 | 30.31 | 32.32 | 29.06 |
| 112 | 30.04 | 30.21 | 30.54 | 30.54 | 30.76 | 31.00 | 31.13 | 33.08 | 29.89 |
| 201 | 30.46 | 30.60 | 30.89 | 30.93 | 31.13 | 31.36 | 31.60 | 33.64 | 30.28 |
| 004 | 32.16 | 32.58 |  | 33.03 | 33.23 | 33.56 | 33.49 | 35.48 | 32.29 |
| 202 |  | 34.01 | 34.37 | 34.43 | 34.69 | 34.96 | 35.13 | 37.28 | 33.69 |
| 104 |  | 36.28 |  |  | 37.10 | 37.43 | 37.33 | 39.75 | 35.95 |
| 203 | 39.15 | 39.43 | 39.89 | 39.88 | 40.28 | 40.59 | 40.71 | 43.57 | 39.00 |
| 210 |  |  |  | 40.88 | 41.25 | 41.58 | 41.88 |  | 39.98 |
| 211 | 41.31 | 41.56 | 41.97 | 41.90 | 42.31 | 42.70 | 42.88 | 46.07 | 40.99 |
| 114 | 42.87 | 43.31 | 43.37 | 43.95 | 44.29 | 44.70 | 44.76 | 47.99 | 42.86 |
| 212 |  |  | 45.14 | 45.25 | 45.59 | 46.00 | 46.31 | 49.79 | 44.14 |
| 105 | 45.12 | 45.76 | 46.39 | 46.53 | 46.89 | 47.30 | 47.26 | 50.67 | 45.29 |
| 204 |  |  |  | 47.53 | 47.84 | 48.30 | 48.41 |  |  |
| 300 |  |  |  | 48.03 | 48.41 | 48.85 | 49.31 |  | 46.81 |
| 213 | 49.40 | 49.88 | 50.44 |  | 50.99 | 51.50 | 51.81 | 56.07 | 49.26 |
| 302 | 51.35 | 51.66 | 52.17 | 52.33 | 52.76 | 53.30 | 53.76 | 58.19 | 51.01 |
| 205 | 55.70 | 56.41 | 57.19 | 57.53 | 57.99 | 58.65 | 58.76 | 64.59 | 55.84 |
| 220 |  |  |  |  | 59.64 | 60.40 | 61.13 |  |  |
| 222 |  |  | 63.97 | 64.23 | 64.89 | 65.80 | 66.73 |  |  |

Table 10a. (Continued)

| hkl | Gd o θ | Tb o θ | Dy o θ | Ho o θ | Er o θ | Tm o θ | Lu o θ | Sc o θ | Y o θ |
|---|---|---|---|---|---|---|---|---|---|
| 311 | | | | 64.63 | 65.31 | 66.20 | 67.23 | | 62.24 |
| 304 | | | 66.97 | 76.33 | 68.01 | 69.05 | | | |
| 116 | 64.62 | 65.96 | | 67.68 | 68.39 | 69.50 | | | 64.99 |
| 312 | | | | 69.15 | 69.94 | 71.08 | 72.38 | | 66.36 |
| 215 | 68.07 | 69.41 | 70.77 | 71.30 | 72.14 | 73.45 | 74.11 | | 68.06 |
| 206 | | | | | 74.21 | | | | |
| 107 | 74.45 | 77.23 | 79.79 | | | | | | |
| 313 | 75.50 | | 78.82 | 79.75 | 81.49 | | | | 74.61 |

Table 10b. X-ray diffraction data for rare earths, ytterbium and europium

| hkl | Yb<br>° $\theta$ | hkl | Eu<br>° $\theta$ | $a_o$<br>(Å) |
|---|---|---|---|---|
| 111 | 14.11 | 110 | 13.713 | 4.595 |
| 200 | 16.33 | 200 | 19.575 | 4.602 |
| 220 | 23.40 | 211 | 24.200 | 4.606 |
| 311 | 27.76 | 220 | 28.250 | 4.607 |
| 222 | 29.09 | 310 | 31.950 | 4.607 |
| 400 | 34.18 | 222 | 35.430 | 4.607 |
| 331 | 37.71 | 321 | 38.780 | 4.605 |
| 420 | 38.86 | 411 | 45.180 | 4.611 |
| 422 | 43.38 | 420 | 48.455 | 4.606 |
| 333 | 46.76 | 332 | 51.730 | 4.606 |
| 440 | 52.51 | 510 | 58.630 | 4.604 |
| 531 | 56.06 | | | |
| 442 | 57.33 | | | |
| 620 | 62.53 | | | |
| 533 | 66.91 | | | |
| 622 | 68.56 | | | |
| 444 | 76.51 | | | |

Table 11. Lattice parameters of rare earths, scandium and yttrium

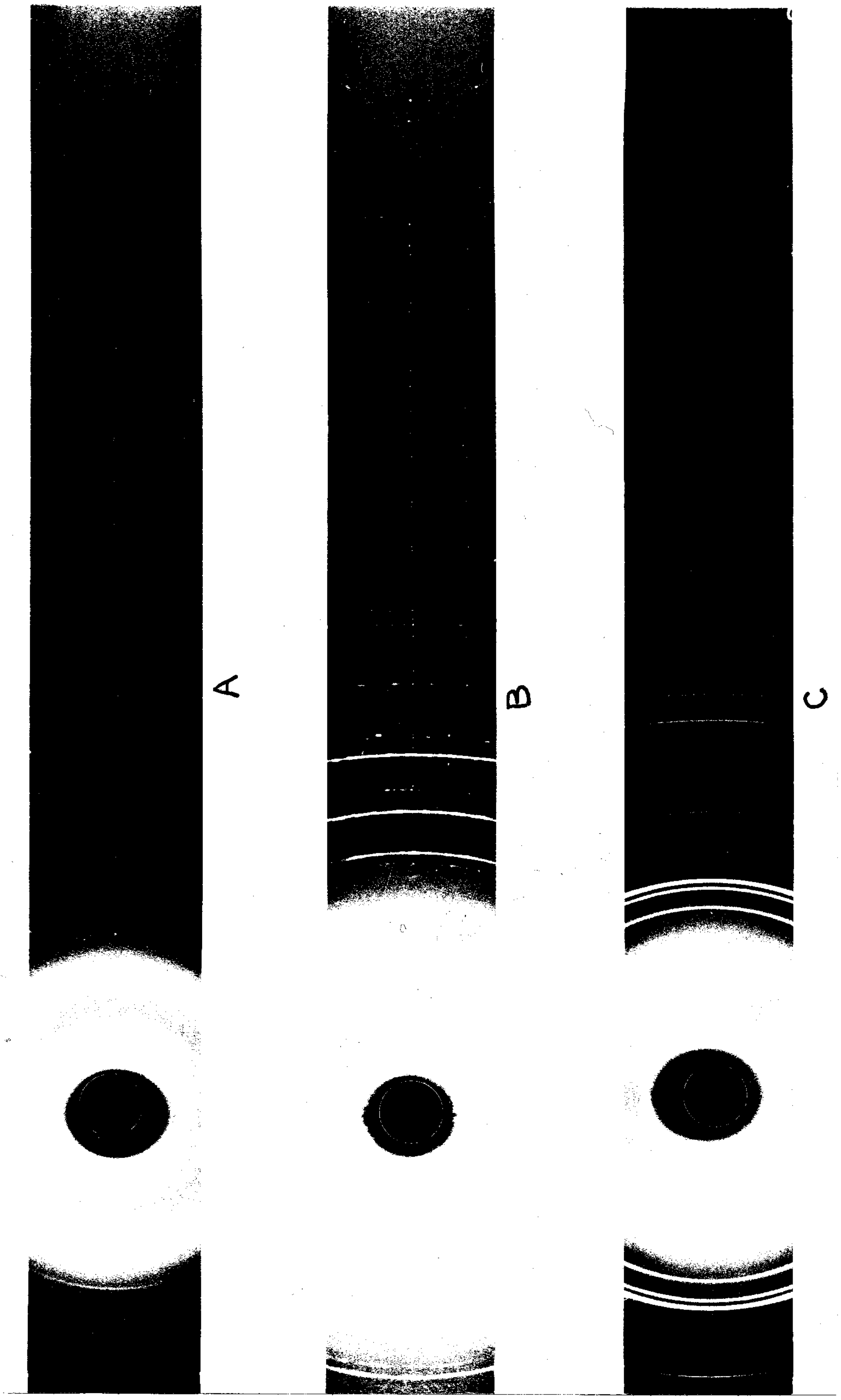
| Element | Structure | (Å) $a_o$ | (Å) $c_o$ |
|---|---|---|---|
| Sc | h.c.p. | 3.33 | 5.30 |
| Y | h.c.p. | 3.66 | 5.77 |
| Eu | b.c.c. | 4.606 | ---- |
| Gd | h.c.p. | 3.63 | 5.78 |
| Tb | h.c.p. | 3.63 | 5.73 |
| Dy | h.c.p. | 3.59 | 5.66 |
| Ho | h.c.p. | 3.59 | 5.65 |
| Er | h.c.p. | 3.57 | 5.61 |
| Tm | h.c.p. | 3.54 | 5.57 |
| Yb | f.c.c. | 5.49 | ---- |
| Lu | h.c.p. | 3.52 | 5.59 |

Fig. 2 Debye-Scherrer x-ray diffraction photographs

A. Europium (b.c.c.)

B. Ytterbium (f.c.c.) plus potassium chloride

C. Erbium (h.c.p.)


A
B
C

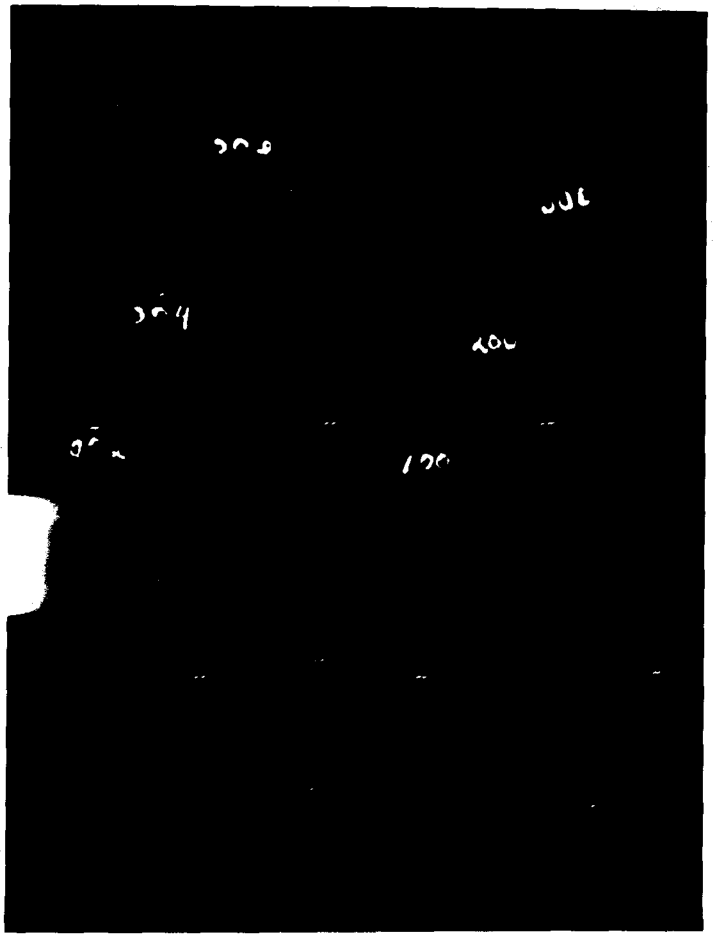


Fig. 3 Weissenberg diffraction photograph of dysprosium

further investigation was made.

Unpublished work on single crystals of neodymium (Figure 4) with a precession camera by Behrendt[19] of this laboratory, indicate neodymium also belongs to the space group $C_6/mmc$. This hexagonal unit cell contains four atoms located at the positions (0, 0, 0), (0, 0, 1/2), (2/3, 1/3, 1/4), (1/3, 2/3, 3/4); and the stacking arrangement is ABAC, ABAC, etc. Ellinger[18] obtained similar results from powder studies.

Since the metals investigated (dysprosium, thulium and neodymium) by single crystal techniques were considered representative of the hexagonal structures no other metals were examined. The diffraction reflections obtained by the powder study of the other metals showed the same hexagonal symmetry as the single crystal data.

### 5. Back reflection camera results

Prior to the investigation of the metals of interest the precision back reflection camera was tested for accuracy by determining the lattice constant of potassium chloride and comparing it with the value reported by the Bureau of Standards. To obtain a sharp diffraction pattern it was found necessary to anneal the finely pulverized salt (200 mesh) at approximately 800°C. The lattice constant of the

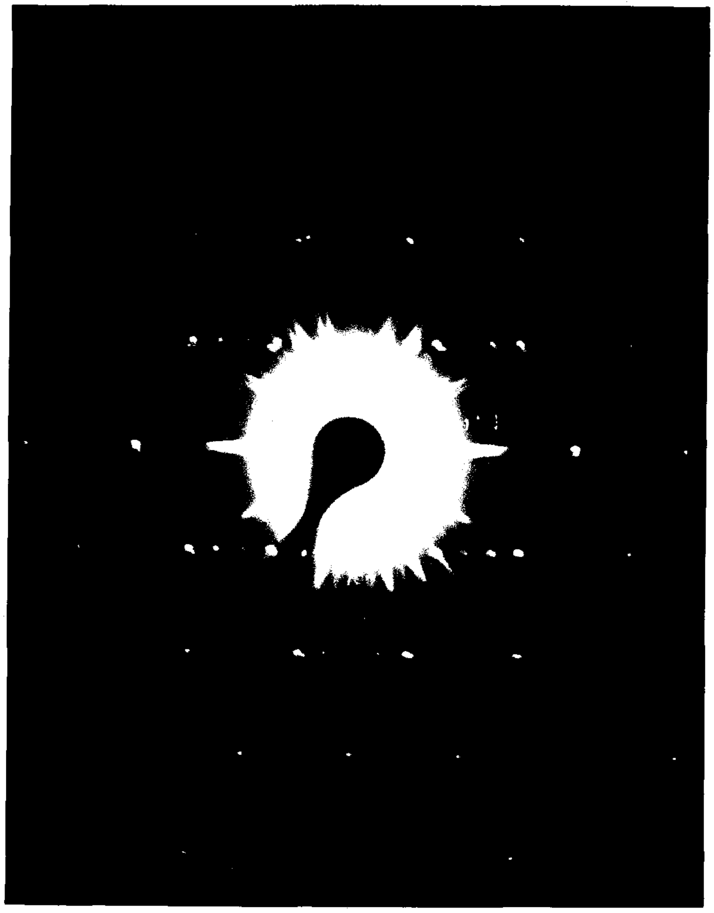


Fig. 4 Precession diffraction photograph of neodymium[19]

cubic material was evaluated by the extrapolation devised by Nelson and Riley[28] which succeeds in minimizing all errors as theta approaches 90° . Excellent agreement was obtained between the experimental (6.2932 Å) and reported (6.2931 Å) values for the potassium chloride lattice parameter.

For the back reflection study of scandium, yttrium and the rare earths, both bulk and distilled samples were used as described earlier. Examples of the diffraction patterns obtained are illustrated in Figure 5. To compare Cohen's[26] and Thewlis'[27] methods of determining lattice constants, the parameters of praseodymium, neodymium, gadolinium, dysprosium and erbium were determined by obth techniques. Only Cohen's method of evaluation was used for the remaining hexagonal metals, while the graphical extrapolation of Nelson and Riley[28] was used to determine the single parameter of the cubic metals. Copper radiation was employed with the values of 1.5405 Å and 1.5443 Å taken as the wavelengths of copper K $_1$, and copper K $_2$, respectively. The diffraction data are given in Tables 12a and 12b and Figure 6 illustrates Nelson and Riley's method of determining lattice constants. Since insufficient europium metal was available for a back reflection sample no precise determination of its parameters was made.

The lattice constants of the metals investigated and the

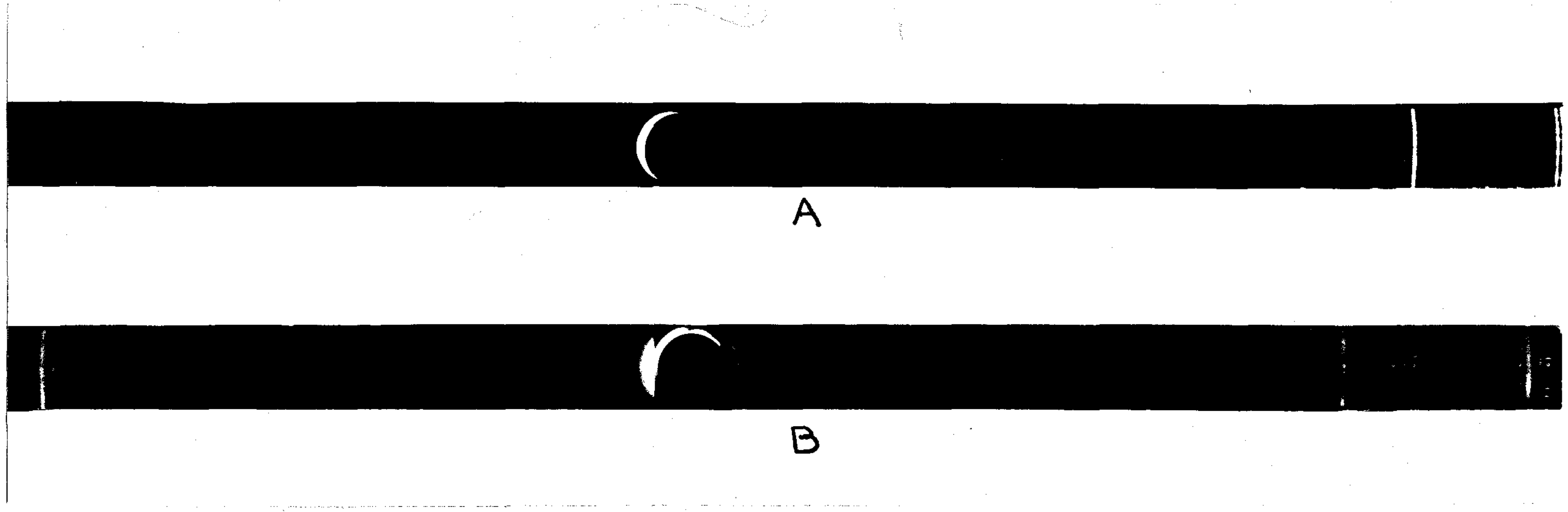


Fig. 5 Back reflection diffraction
Photographs; A. Erbium (h.c.p.), B. Ytterbium (f.c.c.) plus potassium chloride

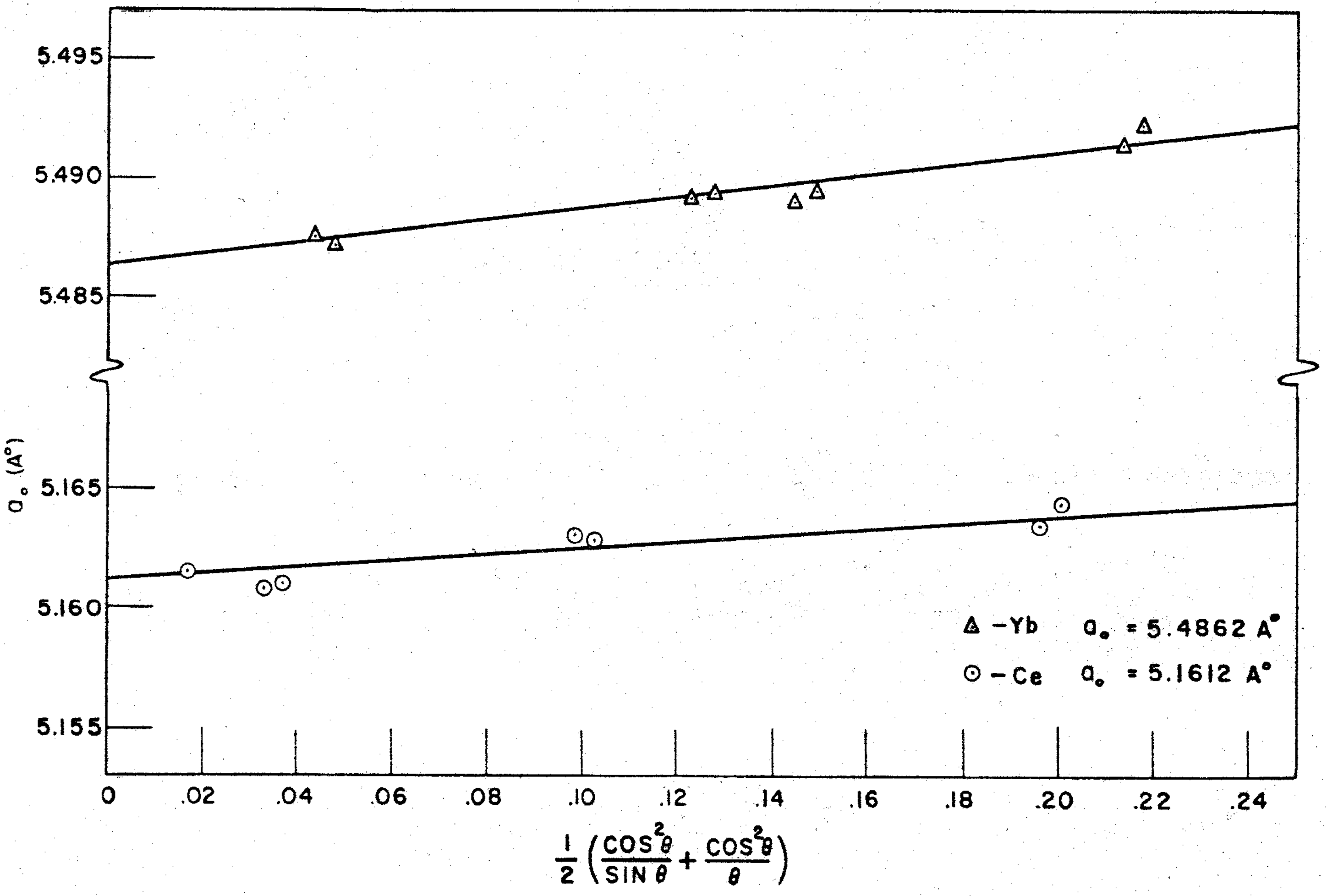
Table 12a. X-ray back reflection data for the rare earths, scandium and yttrium - interplaner spacings (Å)

| hkl | Pr | Nd | hkl | Gd | Tb | Dy | Ho | Er | Tm | Lu |
|---|---|---|---|---|---|---|---|---|---|---|
| 2,0,11 | .89112 | .88856 | 214 | | | | | | .88961 | |
| 2,0,11 | ------ | ------ | 214 | | | | | | .88955 | |
| 219 | | .88438 | 220 | | | | | .88993 | .88465 | .87627 |
| 219 | | ------ | 220 | | | | | .89005 | .88470 | .87615 |
| 1,0,13 | .87495 | | 310 | | .86582 | | | .85503 | .84984 | .84178 |
| | | | | | | | | | | |
| 1,0,13 | ------ | | 310 | | .86572 | | | .85506 | .84977 | .84169 |
| 1,1,12 | .86893 | .86634 | 222 | | | .85589 | .85240 | .84796 | .84287 | .83545 |
| 1,1,12 | .86883 | .86628 | 222 | | | .85589 | .85239 | ------ | ------ | ------ |
| 308 | | .85886 | 311 | | .85589 | .85289 | .84960 | .84519 | .84009 | .83210 |
| 308 | | .85890 | 311 | | .85585 | .85290 | .84954 | .84508 | .84004 | .83209 |
| | | | | | | | | | | |
| 2,1,10 | .84336 | | 304 | | .84017 | | | .82781 | .82284 | |
| 2,1,10 | ------ | | 304 | | .84008 | | | ------ | .82277 | |
| 1,0,14 | .81714 | .81461 | 116 | .85134 | | .83393 | .82945 | | | |
| 1,0,14 | .81707 | .81459 | 116 | .85125 | | .83399 | .82947 | | | |
| 2,1,11 | .80170 | .79905 | 312 | | .82814 | .82500 | .82175 | .81750 | .81259 | .80540 |
| | | | | | | | | | | |
| 2,1,11 | .80179 | ------ | 312 | | .82804 | .82503 | .82168 | .81745 | .81258 | .80531 |
| 2,0,13 | .79005 | .78756 | 215 | .82925 | .81940 | .81461 | .81074 | .80657 | | |
| 2,0,13 | .79013 | ------ | 215 | .82915 | .81930 | .81454 | .81074 | .80651 | | |
| | | | 206 | .82178 | | | | .79703 | | |
| | | | 206 | .82177 | | | | .79702 | | |
| | | | | | | | | | | |
| | | | 213 | .79543 | | .78407 | .78095 | | | |
| | | | 213 | .79542 | | .78405 | .78091 | | | |
| | | | 107 | .79897 | .78720 | | .77663 | | | |
| | | | 107 | .79893 | .78714 | | .77661 | | | |

Table 12b. X-ray back reflection data for scandium and yttrium - interplanar spacings (Å)

| hkl | Ce | Yb | hkl | Sc | hkl | Y |
|---|---|---|---|---|---|---|
| 442 | .86074 | | 115 | .88314 | 222 | .87005 |
| 442 | .86058 | | 115 | .88310 | 222 | .86997 |
| 620 | .81633 | .86839 | 220 | .82753 | 116 | .84675 |
| 620 | .81635 | .86825 | 220 | .82749 | 116 | .84670 |
| 533 | .78704 | .83712 | 310 | .79495 | 215 | .82739 |
| 622 | .77812 | .82756 | 222 | .78939 | 313 | .79674 |
| 622 | ------ | .82753 | 222 | .78937 | 313 | .79669 |
| 444 | | .79202 | 311 | .78599 | 107 | .79262 |
| 444 | | .79202 | 311 | .78594 | 107 | .79260 |

Fig. 6  Nelson and Riley extrapolation for cerium and ytterbium.


5.495
5.490
5.485
5.165
5.160
5.155
$a_o$ (A°)
0
.02
.04
.06
.08
.10
.12
.14
.16
.18
.20
.22
.24
$\frac{1}{2}\left(\frac{\cos^2\theta}{\sin\theta}+\frac{\cos^2\theta}{\theta}\right)$
△ –Yb $a_o$ = 5.4862 A°
⊙ – Ce $a_o$ = 5.1612 A°

standard errors included in the parameters as calculated by the method of Jette and Foote[29] are given in Table 13.

For each element the density, mole-atomic volume, metallic radii and axial ratio (where appropriate) were calculated from the experimental unit cell dimensions and are tabulated in Table 14. The above properties were obtained from the following equations.

a) Unit cell volume $= a_o^3$ (cubic)

$= \sqrt{3}/2 \; c \, a^2$ (h.c.p.)

b) Density $= \dfrac{(\text{At. Wt.})\ (\text{No. atoms/unit cell})}{(\text{Avogodros No.})\ (\text{Unit cell vol.})}$

c) Atomic volume $= \dfrac{\text{At. Wt.}}{\text{Density}}$

d) Metallic radii (Co-ordination number (C.N.) = 12)

$= \dfrac{a}{2\sqrt{2}}$ (f.c.c.)

(C.N. = 8) $= \dfrac{\sqrt{3}\,a}{4}$ (b.c.c.)

(C.N. = 12) = a/2 (in h.c.p. basal plane)

$= \dfrac{\sqrt{a^2/3 + c^2/4}}{2}$ (along $c_o$ axis)

$= \dfrac{\sqrt{a^2/3 + c^2/16}}{2}$ (along $c_o$ axis for La, Nd, and Pr only)

Table 13. Lattice constants of scandium, yttrium and the rare earth metals

| | | Lattice constants (Å) | | Standard error (Å) | |
|---|---|---|---|---|---|
| Element | Crystal structure | $a_o$ | $c_o$ | $a_o$ | $c_o$ |
| Sc | h.c.p. | 3.3090 | 5.2733 | .0001 | .0016 |
| Y | h.c.p. | 3.6474 | 5.7306 | .0007 | .0008 |
| La | h.c.p. | 3.770 | 12.159 | .002 | .008 |
| Ce | f.c.c. | 5.1612 | ----- | .0005 | ----- |
| Pr | h.c.p. | 3.6725 | 11.8354 | .0007 | .0012 |
| Nd | h.c.p. | 3.6579 | 11.7992 | .0003 | .0005 |
| Sm[a] | rhom-h.c.p. | 3.621 | 26.25 | ----- | ----- |
| Eu | b.c.c. | 4.606 | ----- | .001 | ----- |
| Gd | h.c.p. | 3.6360 | 5.7826 | .0009 | .0006 |
| Tb | h.c.p. | 3.6010 | 5.6936 | .0003 | .0002 |
| Dy | h.c.p. | 3.5903 | 5.6475 | .0001 | .0002 |
| Ho | h.c.p. | 3.5773 | 5.6158 | .0001 | .0002 |
| Er | h.c.p. | 3.5588 | 5.5874 | .0003 | .0003 |
| Tm | h.c.p. | 3.5375 | 5.5546 | .0001 | .0004 |
| Yb | f.c.c. | 5.4862 | ----- | .0004 | ----- |
| Lu | h.c.p. | 3.5031 | 5.5509 | .0004 | .0004 |

[a] Values reported by Daane, Rundle, Smith and Spedding.[30]

Table 14. Summations of structure characteristics of the rare earth metals, scandium and yttrium

| Element | Structure | $c_o/a_o$ | Density (g./cm.$^3$) | Mole at. vol. (cm.$^3$) | Metallic radii (Å) | |
|---|---|---|---|---|---|---|
| | | | | | a | b |
| La | h.c.p. | 1.613 | 6.162 | 22.544 | 1.8852 | 1.8694 |
| Ce | f.c.c. | ----- | 6.768 | 20.705 | 1.8248 | ----- |
| Pr | h.c.p. | 1.612[c] | 6.769 | 20.818 | 1.8363 | 1.8201 |
| Nd | h.c.p. | 1.613[c] | 7.007 | 20.590 | 1.8290 | 1.8139 |
| Sm[d] | rhom-h.c.p. | 1.611 | 7.540 | 19.950 | 1.8105 | 1.7943 |
| Eu[e] | b.c.c. | ----- | 5.166 | 29.423 | 1.994[f] | ----- |
| Gd | h.c.p. | 1.590 | 7.868 | 19.941 | 1.8180 | 1.7865 |
| Tb | h.c.p. | 1.581 | 8.253 | 19.258 | 1.8005 | 1.7626 |
| Dy | h.c.p. | 1.573 | 8.556 | 18.989 | 1.7952 | 1.7515 |
| Ho | h.c.p. | 1.570 | 8.799 | 18.745 | 1.7887 | 1.7428 |

[a] Radii calculated from atoms in basal plane

[b] Radii between layers

[c] One-half the actual axial ratio

[d] From data of Daane, Rundle, Smith and Spedding,[30] (calculations based on h.c.p. unit cell)

[e] From Debye-Scherrer camera data

[f] Radii for co-ordination number 8

Table 14. (Continued)

| Element | Structure | $c_o/a_o$ | Density ($g./cm.^3$) | Mole at. vol. ($cm.^3$) | Metallic radii (Å) | |
|---|---|---|---|---|---|---|
| | | | | | a | b |
| Er | h.c.p. | 1.570 | 9.058 | 18.458 | 1.7794 | 1.7340 |
| Tm | h.c.p. | 1.570 | 9.318 | 18.131 | 1.7688 | 1.7237 |
| Yb | f.c.c. | ----- | 6.959 | 24.867 | 1.9397 | ----- |
| Lu | h.c.p. | 1.585 | 9.849 | 17.768 | 1.7516 | 1.7171 |
| Sc | h.c.p. | 1.594 | 2.995 | 15.061 | 1.6545 | 1.6280 |
| Y | h.c.p. | 1.571 | 4.472 | 19.886 | 1.8237 | 1.7780 |

[a] Radii calculated from atoms in basal plane

[b] Radii between layers

The information obtained from this study can be more easily correlated when observed in graphical form as is illustrated in Figures 7, 8, 9, 10 and 11 which show the respective variation of mole-atomic volume, density, axial ratio, metallic radii and average metallic radii with atomic number.

Table 15 gives the results of a brief investigation concerning the effect of tantalum on the lattice parameters of dysprosium and erbium.

The lattice parameters of praseodymium, neodymium, gadolinium and dysprosium as determined by both Cohen's[26] and Thewlis'[27] methods are compared in Table 16.

A very crude indication of the relative vapor pressures of the metals distilled were obtained by noting the temperatures at which the pressure on the distillation apparatus decreased suddenly as was described earlier. The temperature at which the metals have an estimated vapor pressure of 1-2 mm. are given in Table 17.

## 6. Metallographic results

Samples of distilled erbium, yttrium and holmium were examined microscopically to obtain information concerning the condensed metal surface and to observe the presence of

Fig. 7 Mole-atomic volumes of the metals studied.

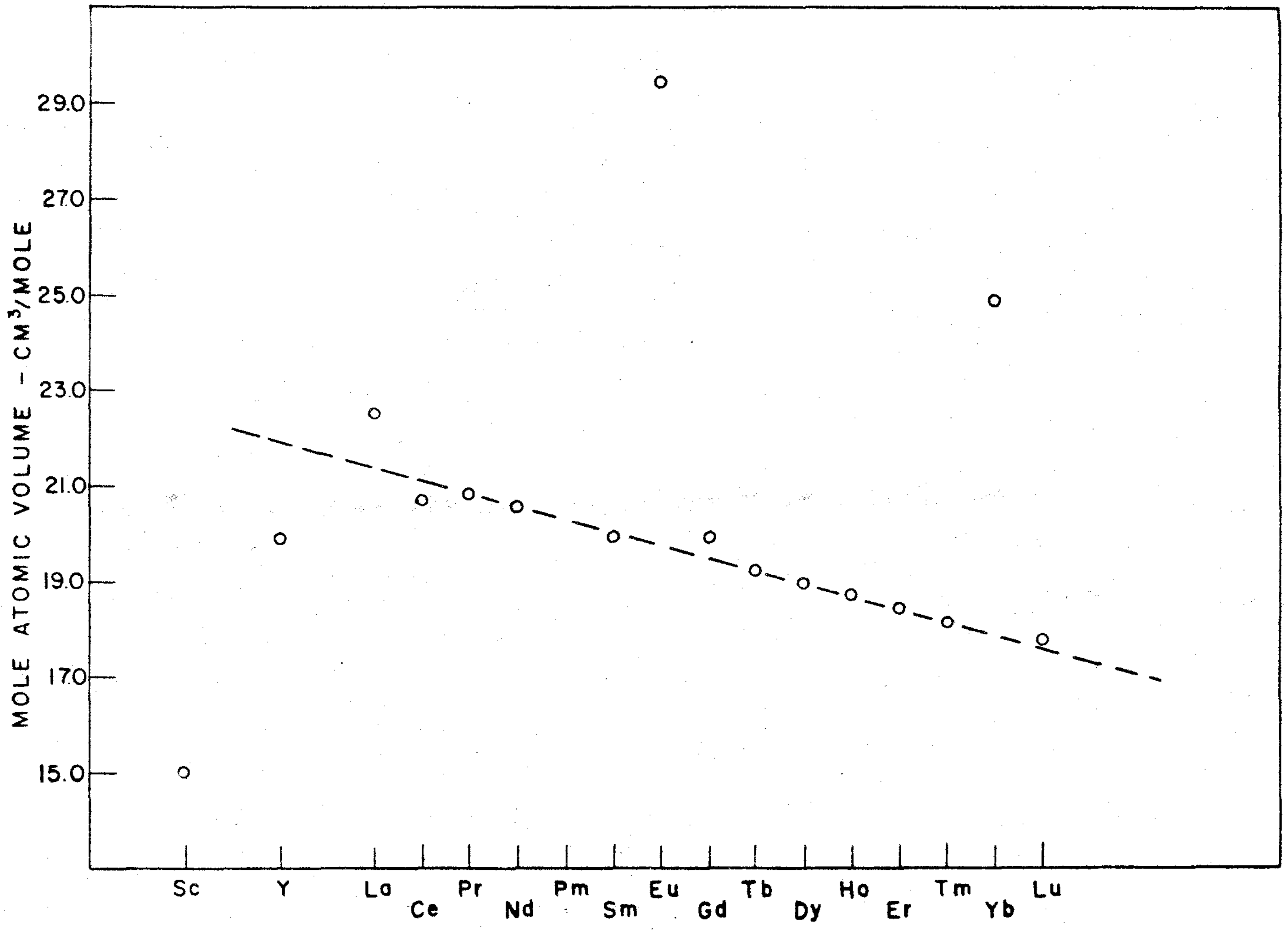

MOLE ATOMIC VOLUME - CM³/MOLE
29.0
27.0
25.0
23.0
21.0
19.0
17.0
15.0
Sc
Y
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

Fig. 8  Densities of the metals studied.

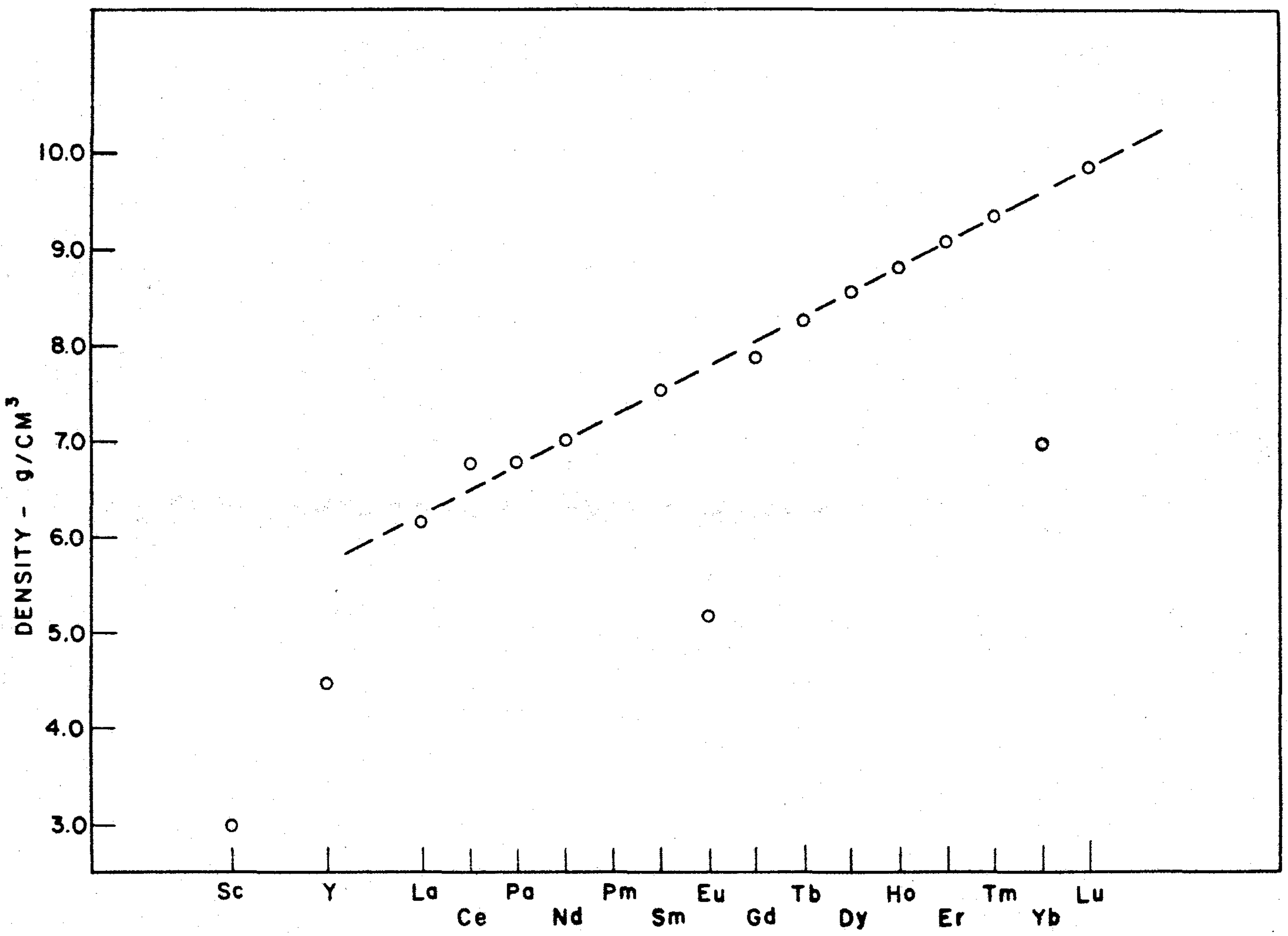

DENSITY - g/CM$^3$
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
Sc
Y
La
Ce
Pa
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

Fig. 9 Axial ratios of the metals studied.

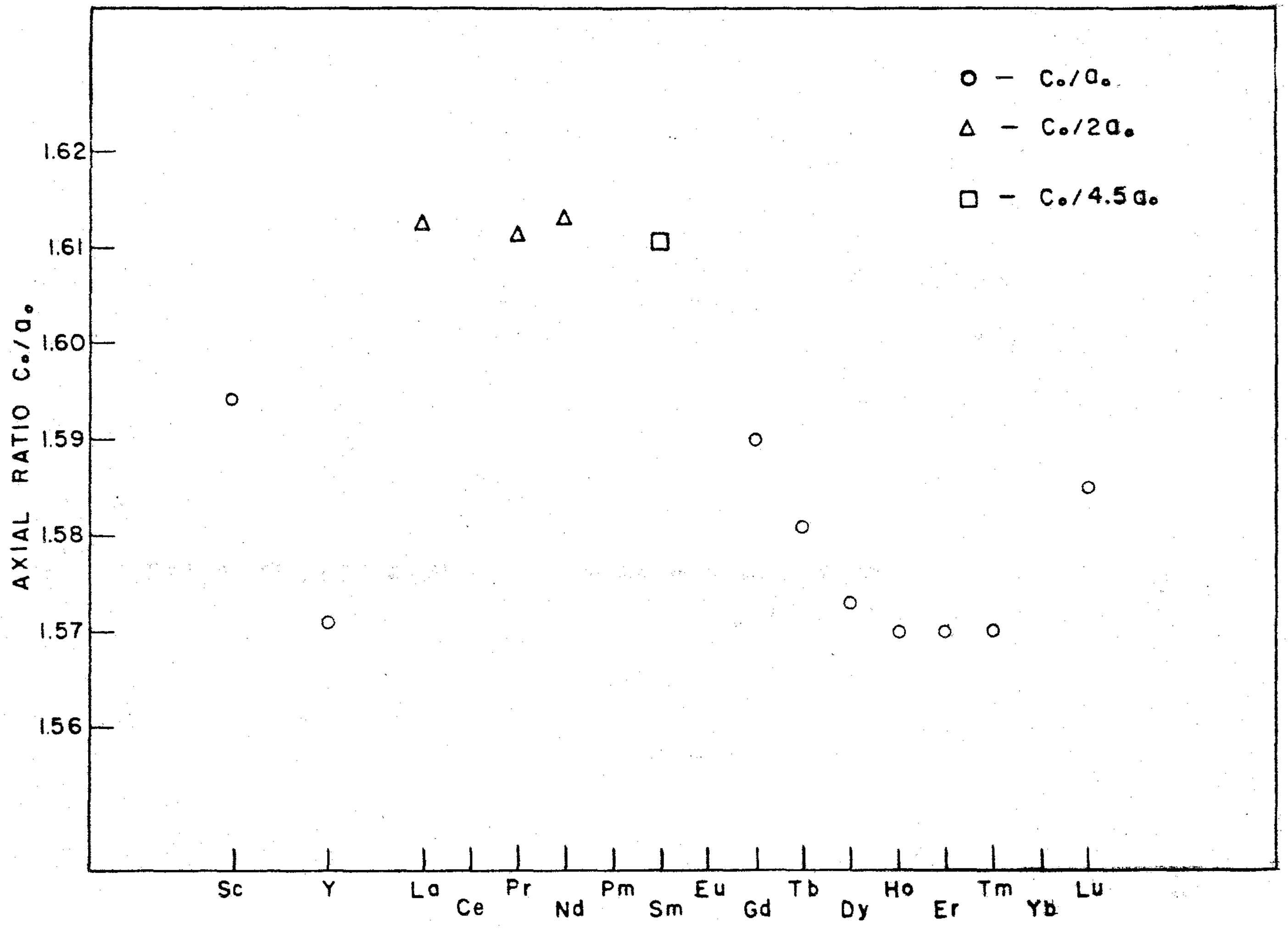
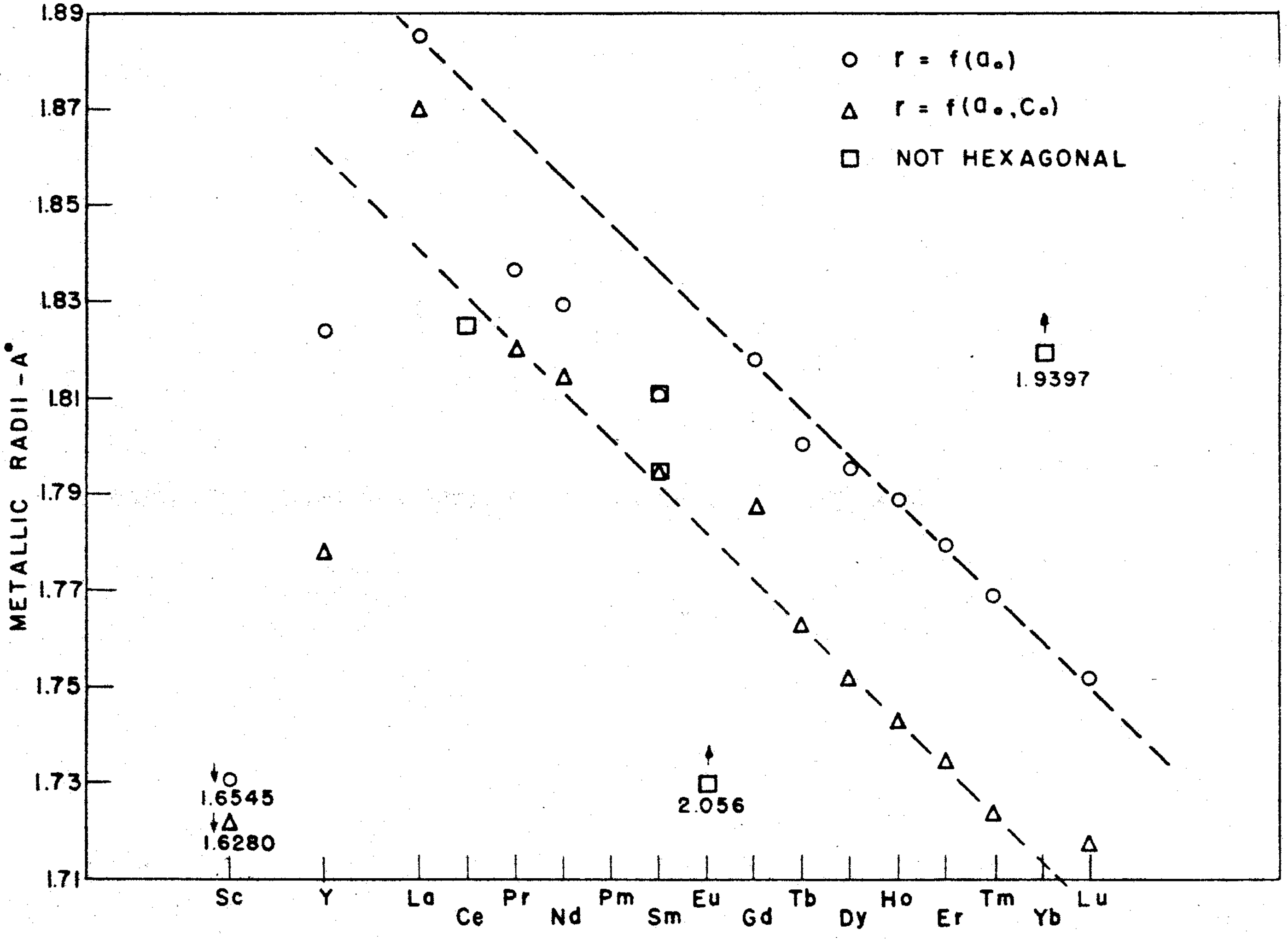

AXIAL RATIO $C_o/a_o$
1.62
1.61
1.60
1.59
1.58
1.57
1.56
○ – $C_o/a_o$
△ – $C_o/2a_o$
□ – $C_o/4.5a_o$
Sc
Y
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

Fig. 10 Metallic radii of the metals studied.



METALLIC RADII - A°
1.89
1.87
1.85
1.83
1.81
1.79
1.77
1.75
1.73
1.71
○ r = f(a₀)
△ r = f(a₀, c₀)
□ NOT HEXAGONAL
1.9397
1.6545
1.6280
2.056
Sc
Y
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

Fig. 11  Average metallic radii of the metals studied.

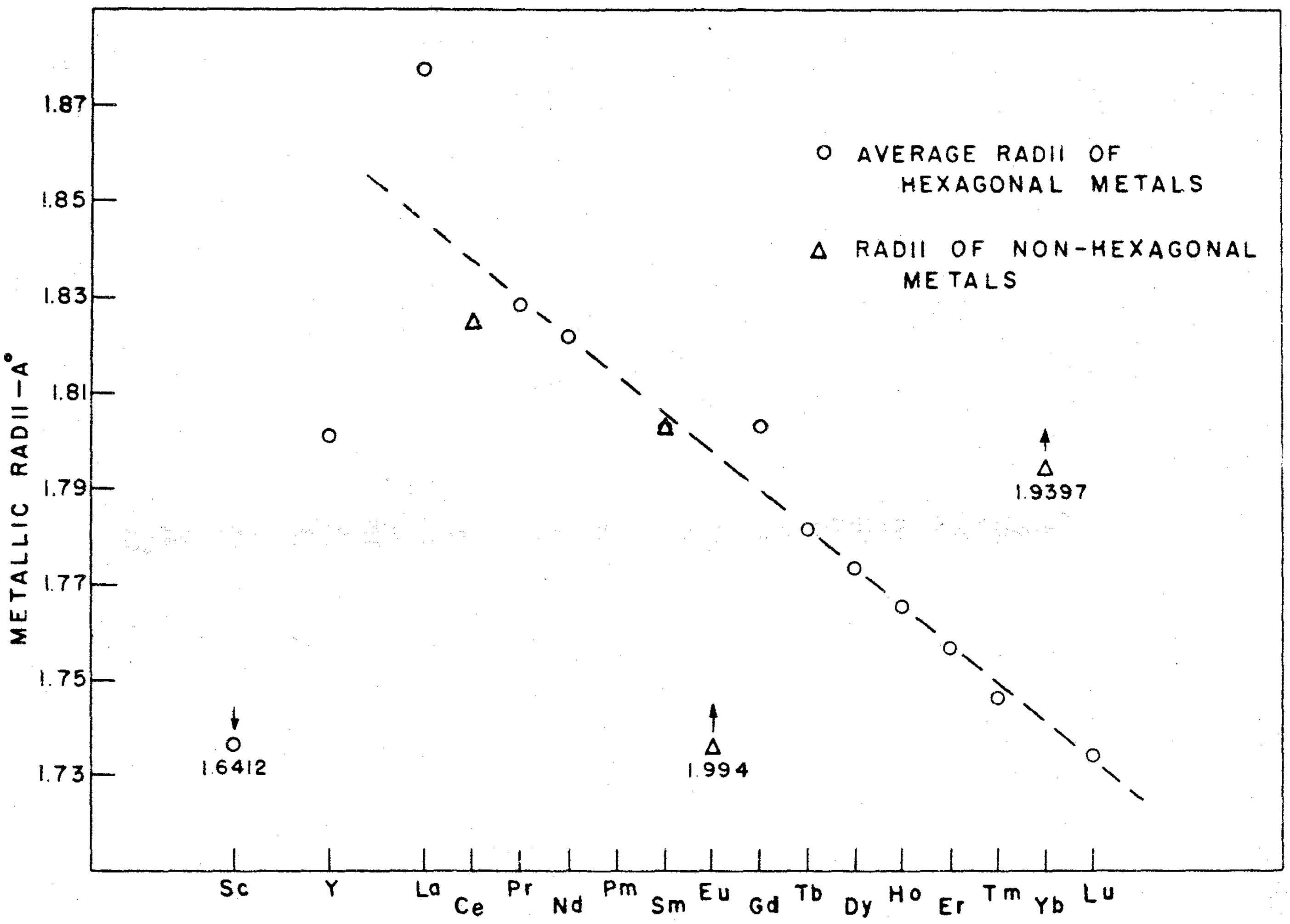

METALLIC RADII—A°
1.87
1.85
1.83
1.81
1.79
1.77
1.75
1.73
○ AVERAGE RADII OF HEXAGONAL METALS
Δ RADII OF NON-HEXAGONAL METALS
1.6412
1.994
1.9397
Sc
Y
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu

Table 15. Lattice parameters of dysprosium and erbium of different tantalum content

| Element | Per cent Ta | $a_o$ (Å) | $c_o$ (Å) | $\Delta a_o$ (Å) | $\Delta c_o$ (Å) |
|---|---|---|---|---|---|
| Dy | 1% | 3.5925 | 5.6538 | | |
| Dy | distilled | 3.5903 | 5.6475 | .0022 | .0063 |
| Er | 1% | 3.5592 | 5.5942 | | |
| Er | distilled | 3.5588 | 5.5874 | .0004 | .0068 |

Table 16. Comparison of lattice parameters determined by Cohen's and Thewlis' techniques

| | | Lattice Parameters (Å) | |
|---|---|---|---|
| Element | Axis | Cohen's | Thewlis' |
| Pr | $a_o$ | 3.6725 | 3.6728 |
| | $c_o$ | 11.8354 | 11.8352 |
| Nd | $a_o$ | 3.6579 | 3.6591 |
| | $c_o$ | 11.7992 | 11.8003 |
| Gd | $a_o$ | 3.6360 | 3.6344 |
| | $c_o$ | 5.7826 | 5.7817 |
| Dy | $a_o$ | 3.5925 | 3.5918 |
| | $c_o$ | 5.6538 | 5.6537 |

Table 17. Approximate temperatures where vaporized metals achieve a vapor pressure of 1-2 mm. Hg

| Element | Temp. °C. | Element | Temp. °C. |
|---|---|---|---|
| La | 1950 | Er | 1500 |
| Tb | 1670 | Tm | 1225 |
| Dy | 1500 | Lu | 1800 |
| Ho | 1600 | Y | 1750 |

impurity phases, if existent. The metals studied were condensed on tantalum cylinder walls which had a temperature gradient estimated as $dT/dl = 400^\circ C./inch$. Figure 12 shows unpolished and unetched holmium metal as it condensed on various regions of the cylinder wall. Metallographic photographs obtained from untreated distilled yttrium are given in Figure 13. To obtain a better understanding of the geometrically straight lines apparent within individual grains of the metal, a distilled sample of erbium was examined both before and after polishing and etching, the results being given in Figure 14. Diamond compound was used with a lap wheel as the final polish and the etchant employed was a solution containing 40 per cent nitric acid and 60 per cent acetic acid. As can be observed, the lines persisted even after the polish and etch treatment.

Fig. 12 Holmium metal condensed tantalum cylinder walls at various temperatures (200X).

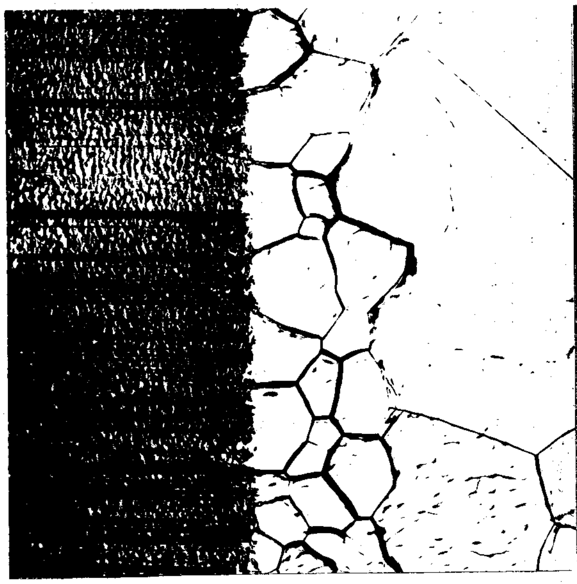
A. Tantalum-holmium interface; hottest region of condensation

B. Colder region of condensation

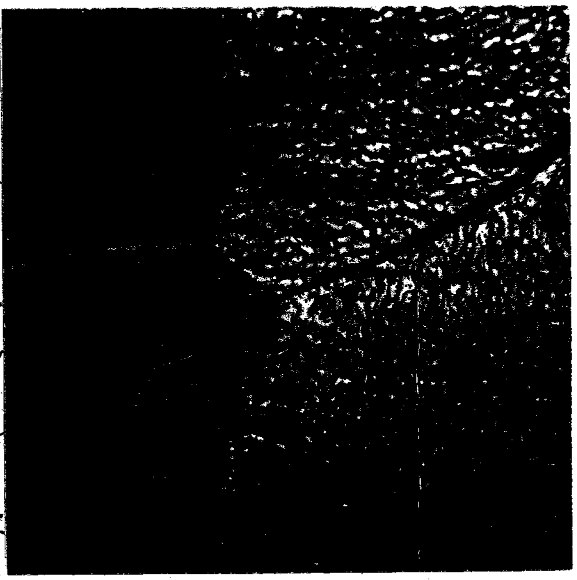
C. Still colder region of condensation

D. Coldest region of condensation; well defined crystals

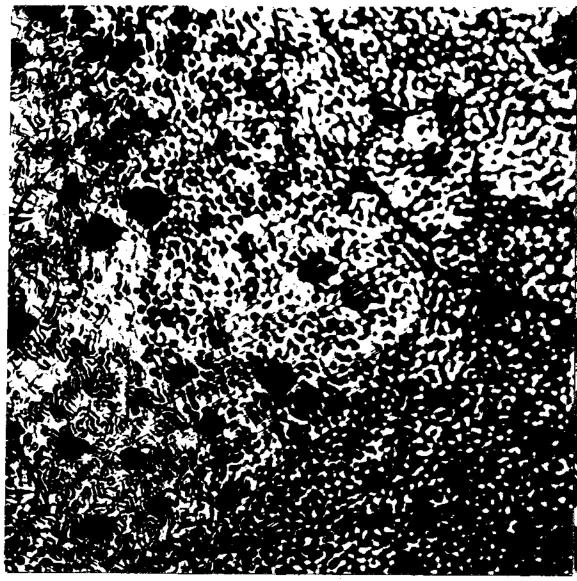
A



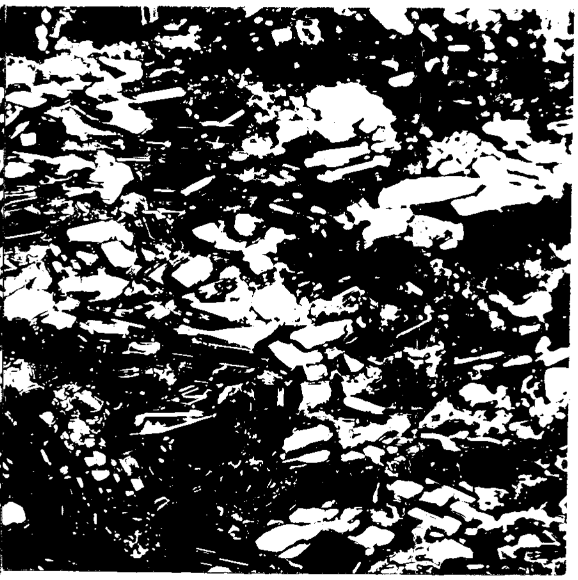
B



C



D



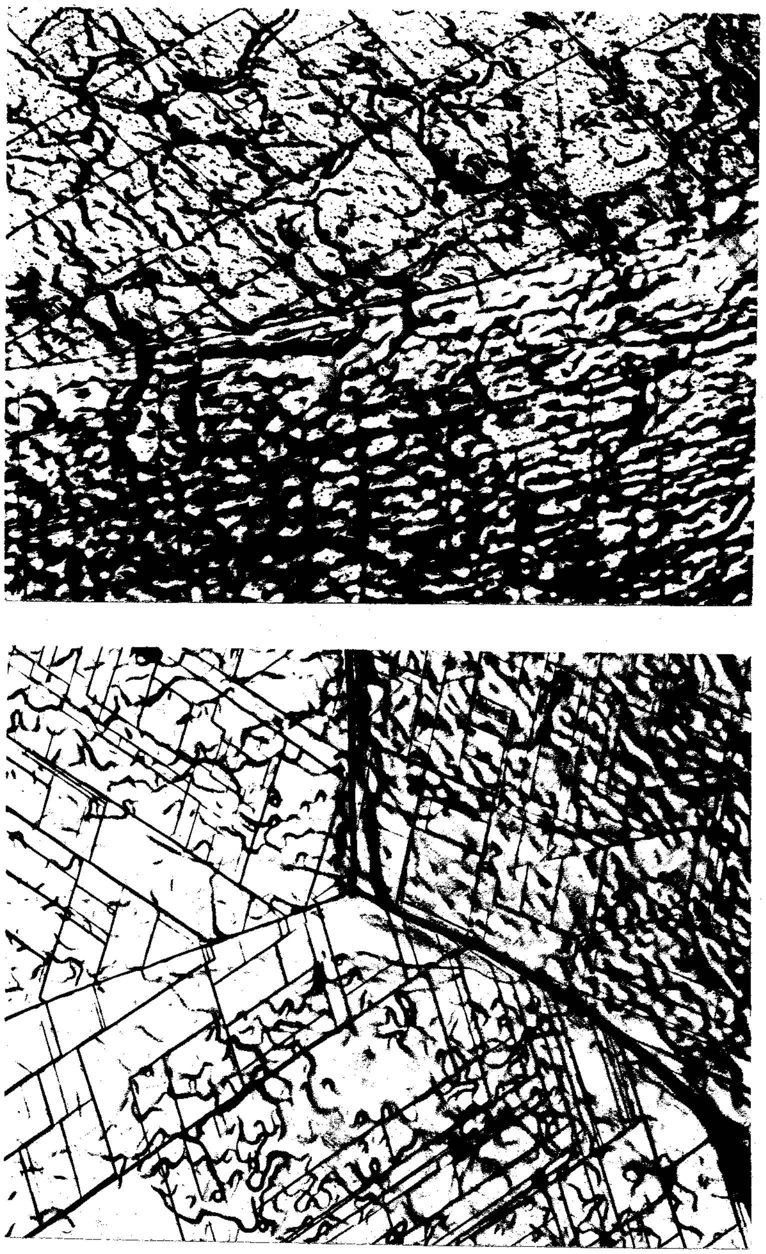
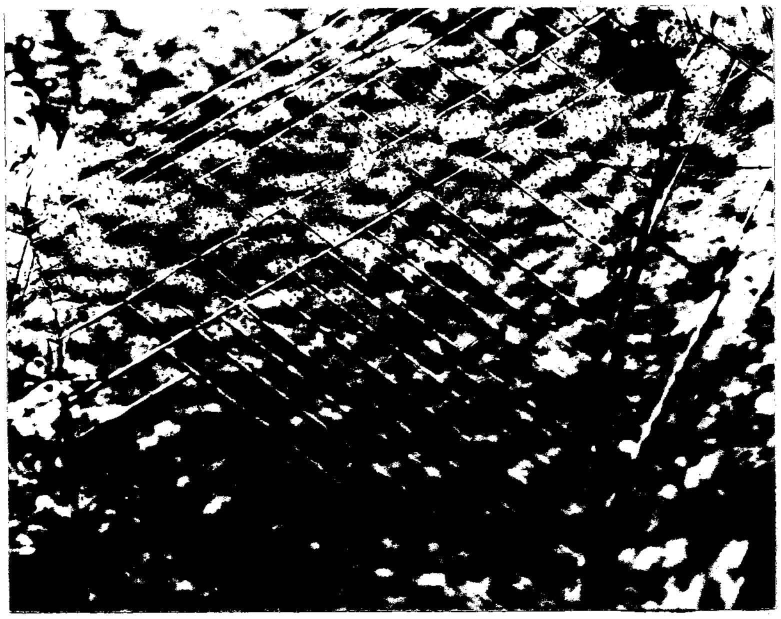


Fig. 13 Yttrium metal condensed on tantalum (200X)

A. As condensed



B. Etched and polished

Fig. 14 Erbium metal condensed on tantalum (200X)

## F. Discussion

### 1. Structure determination

Little discussion of the diffractometer, Weissenberg and Debye-Scherrer camera results is necessary since in most cases the structures found were those expected. It should be noted that this work verifies the structures previously reported for scandium, yttrium and the rare earths, with the exception of lanthanum, praseodymium and neodymium, the latter being consistent with the structure type found recently by Ellinger[18] and Behrendt.[19] These three metals were found to be h.c.p. having $c_0$ axes twice the values reported earlier.

None of the earlier work on lanthanum, cerium, praseodymium and neodymium was performed with bulk metal specimens. The use of filings suggests several reasons why there have been conflicting reports concerning the true structure of these elements, particularly with lanthanum and cerium. These two metals are exceedingly reactive in air and even though precautions are taken to prevent their contamination such action is certainly a possibility. Both lanthanum nitride and lanthanum hydride are f.c.c. and have lattice parameters similar to that reported for the f.c.c. structure of lanthanum. Similar correspondence is true of cerium also. Another explanation is that the strains produced by filing may possibly induce a transformation to the f.c.c. modification.

## 2. Precise lattice parameters

Interesting comparisons can be made among scandium, yttrium and the rare earth metals for several properties calculated from the accurate lattice constants of the elements.

A relatively straight line can be drawn along the rare earth series in the mole-atomic volume v.s. atomic number plot (Figure 7) except for the expected discontinuities due to different structure types. Lanthanum and gadolinium, however, are noticeably displaced from this line. The value for yttrium if displaced along the abcissa would fall just after samarium.

Assuming the atoms exist as hard spheres in the h.c.p. system the calculated axial ratio for this structure is 1.633. Figure 9 shows that the $c_o/a_o$ ratios of the h.c.p. metals studied all fall below this value, lanthanum, praseodymium, neodymium and samarium making the closest approach to it. The variation in axial ratio from gadolinium to lutecium results in a U shaped curve with a rather flat minimum.

The plot of metallic radii v.s. atomic number (Figure 10) indicates that the bonds between metal atoms located in the hexagonal layers are weaker than the bonds between layers. These metals should, therefore, exhibit direction sensitive properties such as thermal expansion, electrical resistivity, compressibility and strength characteristics. Single crystal investigations of these properties would be interesting. Definite deviations are apparent with lanthanum, gadolinium and lutecium in the plot relating the radii calculated for the atoms lying along the $c_o$ axis, while praseodymium, neodymium and samarium show deviations in the plot involving the metallic radii calculated from the $a_o$ value alone.

Undoubtedly the lanthanide contraction accounts for the uniform variation in density, mole-atomic volume and average metallic radii of the elements studied, but the individual radii and axial ratio relationships cannot be interpreted satisfactorily. It is interesting to note that lanthanum, gadolinium and lutecium have unfilled, half-filled or filled 4f shells respectively. It is possible that the spherical symmetry resulting from such electronic configurations may be responsible for their different behavior. The fact that h.c.p. lanthanum, gadolinium and lutecium have axial ratios less than 1.633 suggests the possibility that the 5d and 6s shells influence the symmetry of the metal atoms. The evidence available to date, however, does not permit the postulation of a completely valid interpretation of the data presented.

To obtain a rough indication of the influence of tantalum on the lattice parameters of the rare earth metals, back reflection x-ray diffraction patterns were obtained for samples of dysprosium and erbium known to contain approximately 1 per cent tantalum. The parameters calculated by the previously mentioned techniques are compared in Table 15. It would appear that the tantalum in solid solution preferentially positions itself so as to exert greater influence on the $c_0$ values than on the $a_0$ parameters of the rare earths. However, a more detailed study would be necessary to definitely determine their exact behavior.

### 3. Evaluation of parameter calculation techniques

Values of the lattice parameters of praseodymium, neodymium, gadolinium, dysprosium and erbium obtained from calculations using Cohen's[26] and Thewlis'[27] methods are given in Table 16.

The apparent advantages and disadvantages of Thewlis' evaluation of data are:

1. Somewhat less time required for the determination of the lattice constants.
2. Errors in line measurement and assignment of incorrect Miller indices to the various reflections are readily apparent.
3. An internal standard must be used whose diffraction lines may coincide with some of those of the material of interest.
4. Corrections as determined from the standard may not be linear along the film where interpolations are made.

5. There is a slight difference in the effective camera radii between the metal sample and the thin layer of potassium chloride standard which leads to slightly inaccurate corrections.

6. Although the lattice parameter calculated from the graphical intercept is considered accurate the value calculated from the slope is relatively insensitive when reflections having low h and k values are used in the plot.

7. No weight is given to the high angle reflections which contain less error.

The characteristics inherent in Cohen's[26] method are:

1. No internal standard is required; the errors due to eccentricity, shrinkage and radius discrepancies are accounted for in the analytical extrapolation itself.

2. A least squares refinement of the data is employed to minimize the random errors of measurement.

3. It is necessary to have a definite knowledge of the Miller indices of the reflections used in the calculations, since errors are not readily apparent in this method.

4. The calculations are somewhat cumbersome and time consuming.

5. The more accurate high angle reflections are not weighted.

In view of the above evaluations of the two methods described earlier it is the opinion of the author that Cohen's technique is to be preferred.

## 4. Metallographic observation

The straight lines apparent within the grains in the photomicrographs may be explained as being due to slip, twinning, or both, within the metal. If they are slip lines they should most likely vanish after polishing whereas twin lines would persist after such treatment. Figure 14 thus gives strong evidence for the existence of twinning. When crystals have a definite orientation in common at their junction they are said to be twinned; this phenomena can be induced by deformation or certain grain growth conditions, both of which are likely in the rare earths prepared in the previously mentioned manner. The former mechanism results in Neumann bands, an illustration of which given by Barrett [30, p.377] is quite similar to the lines present in Figures 12, 13 and 14. It is also interesting to note that the acute angles formed by these straight lines are of a fairly constant value ranging from about 69° to 76°.

One can explain the relatively rough background of the photomicrographs as being due to non-uniform condensation of the metal deposit. Figure 12 illustrates the increasingly irregular metal surface as the metal is condensed on the colder regions of the tantalum cylinder.

The small dots in the photomicrographs cannot be satisfactorily explained. Microscope examinations show that they are projections from the metal surface as evidenced by the shadows cast when low angle illumination was employed. One explanation is, of course, that they are a result of impurities. This, however, is not too probable since they were distilled in a vacuum of the order of $1\text{-}5 \times 10^{-7}$ mm. Hg.

# III. ELECTRICAL RESISTIVITY AND ANOMALOUS BEHAVIOR OF LANTHANUM, CERIUM, PRASEODYMIUM AND NEODYMIUM ABOVE ROOM TEMPERATURE

## A. Introduction

In order to help clarify the confused literature as concerns the regions of stability of the reported phases for the light rare earth metals, namely lanthanum, cerium, praseodymium and neodymium, the transformations occurring in these elements above room temperature were investigated. Little information is available concerning these transitions, and what evidence there is must be considered with reserved judgment because of the purity of the metals employed.

There are several experimental techniques useful for the study of phase transitions, for example, thermal analysis (cooling curves and heat capacity), dilatometric analysis, electrical resistivity variations with temperature, and high temperature x-ray diffraction analysis. After a consideration of the advantages and disadvantages of each method the electrical resistance technique was adopted. This being a null method, the effects of the potential leads are eliminated and errors due to galvanometer deflection readings are minimized. Also, since James[10] of this laboratory had investigated the resistivity of lanthanum, cerium, praseodymium and neodymium as a function of temperature from room temperature to approximately 2° K, there was interest in extending this study to elevated temperatures. The pure metals were studied in high vacuum in the temperature region, room temperature to approximately 20°-100°C. below their melting points, depending on how high the melting point of the particular metal was. The apparatus was primarily constructed of Vycor and could not be safely used at temperatures much above 950°C.

Interesting results were obtained from this study and except for lanthanum, the phase transformations found differed considerably from those previously reported by other laboratories.

## B. Historical

Although a considerable amount of material has been published concerning the magnetic, electrical resistivity and structure behavior of the rare earth metals at low temperatures, little work has been done in this field above room temperature. Undoubtedly the scarcity of material and the difficulties encountered when working with these metals at high temperatures had discouraged some investigators and probably accounts for the disagreement in results reported. For simplicity the elements of interest, lanthanum, cerium, praseodymium and neodymium, will be treated individually. The resistivity values and the anomalous behavior of these metals above room temperature will be discussed at length but the low temperature results will be mentioned but briefly.

## 1. Room temperature electrical resistivity

(a) Lanthanum. Benedicks,[32] in 1915, first reported the resistivity of lanthanum as $59.5 \times 10^{-6}$ ohm. cm. at 18°C. Bridgman,[33] in 1921, determined the resistivity ($\rho$) of lanthanum as $\rho = 59 \times 10^{-6}$ ohm. cm. at room temperature. The sample was in the form of an extruded wire and contained 10-20 per cent magnesium and considerable silicon. In 1927, again using an extruded wire but of greater purity, Bridgman[34] found its value to be $\rho = 57.6 \times 10^{-6}$ ohm. cm. at 0°C. McLennan, Allen and Wilhelm,[35] in 1930, studying the electrical conductivity of several metals at low temperatures found for the ratio of the resistance at any temperature (R) to that at 0°C. ($R_o$), the values $R/R_o = .520$ at 1.9°K. and $R/R_o = 1.040$ at 300°K. for what was described as a pure sample of lanthanum. James,[10] in 1952, using both cast and extruded samples found the resistivity value of lanthanum at 300°K. to vary between $64.5 \times 10^{-6}$ and $100 \times 10^{-6}$ ohm. cm. The iron content of the specimens varied from 4200 p.p.m. to 85.5 p.p.m. and the samples were found to exist as a mixture of f.c.c. and h.c.p. phases with a small amount of lanthanum oxide being present. The wide variation in resistivity values was explained as possibly being due to purity differences, crystal allignment on extrusion or because of the presence of varying amounts of the two possible crystal structures.

(b) Cerium. Benedicks,[36] in 1915, reported the resistivity of cerium as 78 x $10^{-6}$ ohm. cm. and later in 1917[32] gave it as 75 x $10^{-6}$ ohm. cm. at 18°C. Bridgman[34] in his 1927 article reported the resistivity of an extruded cerium sample as $\rho = 74.8 \times 10^{-6}$ ohm. cm. at 30°C. McLennan, Allen and Wilhelm[35] gave for the resistance ratios of "pure" cerium the values $R/R_o = .535$ at 1.9°K. and $R/R_o = 1.025$ at 300°K. deHaas and Voogd,[37] in 1932, found for this same ratio the value of $R/R_o = .697$ at 1.43°K. for cerium.

Four samples of cerium both cast and extruded, were studied by James[10] in 1952 and varied in iron content from 291 p.p.m. to 2835 p.p.m. All were annealed 19 hours at 600°C. but were cooled at different rates. It was found that both f.c.c. and h.c.p. phases coexisted, the latter increasing with successive cycling between room temperature and 40°K. The lowest value of the resistivity at 300°K. was about 81 x $10^{-6}$ ohm. cm.

(c) Praseodymium. In 1915 and 1917 Benedicks[32, 36] reported the resistivity of praseodymium as 88 x $10^{-6}$ ohm. cm. at 18°C. The electrical resistivity of an extruded wire of

99.7 per cent pure praseodymium having an unknown structure was found by Bridgman,[34] in 1927, to have the value of $\rho = 69 \times 10^{-6}$ ohm. cm. at 30°C. James[10] employed an annealed, cast sample of praseodymium for her low temperature resistance study whose iron content was 315 p.p.m. After the third series of measurements the specimen was found to be 75 per cent h.c.p. and 25 per cent f.c.c. with some oxide being present. This metal was found to have $\rho = 76 \times 10^{-6}$ ohm. cm. as its lowest value at 300°K.

(d) Neodymium. Benedicks[32, 36] (1915 and 1917) also was the first to report the resistivity of neodymium. He found it to have the value of $79 \times 10^{-6}$ ohm. cm. at 18°C. but added that this value was somewhat unreliable due to an inhomogeneous sample. Bridgman,[33] in 1921, reported the value of $\rho = 107 \times 10^{-6}$ ohm. cm. for the resistivity of an extruded sample of neodymium containing a large amount of magnesium and considerable silicon. James, in 1952, found the resistivity of an annealed, cast specimen of neodymium to be approximately $72 \times 10^{-6}$ ohm. cm. at 300°K. This material existed exclusively as the h.c.p. structure with a small amount of oxide being present.

## 2. Allotropic phase transformations

(a) Lanthanum. Jaeger, Bottema and Rosenbohm[38] studied the specific heat and electrical resistance of lanthanum over the temperature range -170° to 720°C. Impurities in the 98.8 per cent lanthanum sample consisted of one per cent iron and traces of carbon, silicon, aluminum and magnesium. The graphical representation of results indicates anomalies occurring at 420°-436°C., 560°C. and 709°-715°C., however, no statement of the phases existing at these temperatures is given. Preliminary heating to 700°C. completely altered the shape of the resistance-temperature curve. This was attributed to a complete change of "inner structure" of the metal. Anomalies in the specific heat-temperature curve occurred at 548°, 655° and 709°C. and were found to be independent of previous heating but were lowered somewhat on cooling. In this study of lanthanum, cerium and neodymium it was concluded that all exhibit four reversible allotropic states and that the "inner state" of these metals was complicated and varied with temperature, the state at any one temperature being a mixture of two or more phases.

Trombe,[39] in 1934, noted an anomaly in the magnetic susceptability behavior of lanthanum, containing .05 per cent silicon and .02-.005 per cent iron, at approximately 110°K. In the 1943 dilatometric studies of Trombe and Foex[40] on 99.2 per cent lanthanum a transformation between 425°-600°K. was indicated by a .19 per cent contraction in volume. The investigation was performed in an atmosphere of argon from room temperature to 925°K., however, the sample began to collapse between 650° and 925°K. The results indicated an alpha state from 78°-425°K., a beta state above 625°K., and coexistence of the two phases between 425° and 625°K.

* Bridgman,[41] in 1948, investigating the compressibility of lanthanum of unstated purity, found a transition at 23,400 kg./cm.$^2$ indicated by a volume change of .26 per cent.

The lanthanum-magnesium phase diagram reported by Vogel and Heumann[42] in 1947 indicates a transformation in pure lanthanum at about 830°C. which decreases in temperature to 530°C. at 6.3 per cent magnesium. The melting point of lanthanum is given as 915°C. This transition was believed due to a third allotropic modification in addition to the f.c.c. and h.c.p. phases.

Massenhausen,[43] in 1952, investigated the lanthanum-sodium and lanthanum-calcium systems by thermal analysis. The "contaminated" lanthanum melted at 863°C. and a second arrest was noted at 812°C.

In 1954 Vogel and Klose[44] studied the cerium-lanthanum system. The cooling curve of 97 per cent lanthanum, containing 1.4 per cent iron, .3 per cent silicon and .3 per cent magnesium indicated 865°C. as the melting point of the metal and showed a transformation occurring at 775°C. An indefinite break in the curve was observed at approximately 300°-350°C. and was believed due to the h.c.p. - f.c.c. transition.

Spedding and Daane,[45] in a 1954 review of the rare earth metals, reported the possible existence of a phase transformation occurring at 868°C. as determined by cooling curve studies of the metal.

(b) Cerium. Cerium has been found to exhibit anomalous behavior at low temperatures and under high pressures which has been explained as being due to the shifting of a 4f electron into the 5d shell. This phase transition results in an appreciable decrease in the size of the f.c.c. unit cell.

Hanaman,[46] in 1915, first noted a discontinuity in the cooling curve of 96.7 per cent cerium at 490°C. and Vogel,[47] in 1917, substantiated this finding by observing a similar phenomenon at 497°C. in the cooling curve of a cerium-magnesium alloy (93.5 per cent cerium).

Jaeger, Bottema and Rosenbohm,[38] in 1938, investigated the allotropic behavior of 98.8 per cent cerium found to contain one per cent iron and traces of silicon, carbon, aluminum and magnesium. Reproducible results could be obtained only if the metal was heated above 500°-540oC. The graphical results indicate the existence of three modifications up to 393°C., $\beta$ (h.c.p.), $\gamma$ (f.c.c.) and $\delta$ (unknown). The $\gamma$ form exists between 393° and 440°C., and the $\delta$ phase above 440°C. Differential heat capacity studies revealed transitions at approximately 362°C. and 503°C., the former value being irreproducible and dependent on previous heat treatment.

Trombe and Foex,[40] in 1943, found the dilatometric study of 99.6 per cent cerium to be quite complex, the metal exhibiting three states. The $\gamma$ state existed at high temperatures (above 500°C.) and was preserved by rapid cooling to room temperature; the $\alpha$ state could be obtained from the $\gamma$ state at low temperatures and was characterized by a strong volume contraction. Slow cooling from the $\gamma$ state yielded the $\beta$ form, the latter being unable to give the $\alpha$ state. Also, it was impossible to convert the $\alpha$ modification to the $\beta$ phase at low temperatures. The subsequent magnetic measurements of Trombe[48] (1944) and the electrical resistance investigation of Foex[49] (1944) substantiated their earlier low temperature dilatometric results.

In 1947 Vogel and Heumann[42] reported the phase diagram of the cerium-magnesium system. This indicated a transition in pure cerium at approximately 630°C. which decreased to 490°C. at four per cent magnesium content. Trombe,[50] in 1954, while dilatometrically investigating the cerium-magnesium system between 0° and 600°C. gave the temperature of the $\gamma - \delta$ transition as approximately 500°C.

Loriers,[51] in 1948, investigated samples of cerium metal of approximately 99.6 per cent purity containing .0005 to .22 per cent iron, by differential thermal analysis over the temperature range 20°C. to the melting point of the metal (815°C.). Maxima were noted in the experimental curve at 710° and 740°C. and were found independent of specimen purity. Another maximum was observed at 540° or 640°C. depending on the iron content of the metal examined, the latter value being obtained from iron free cerium. It was suggested that the anomaly observed by Jaeger, Bottema and Rosenbohm[38] at 362°C. was due to the presence of iron in the metal.

Ahmann,[52] of this laboratory, in 1953 observed a solid transformation in cerium at 703° ± 10°C. The metal studied contained .1-.2 per cent calcium and .05-.2 per cent magnesium, and had a melting point of about 793°C. Spedding and Daane[45] (1954) later gave the melting point of cerium as 804°C. and the possible transition temperature as 754°C.

Vogel and Klose[44] investigated the cerium-lanthanum system in 1954. Thermal analysis gave the melting point of 99.5 per cent cerium as 800°C. and showed a transition at 720°C. An h.c.p. - f.c.c. transition was believed to occur at 300°-350°C. but a definite break in the cooling curve was not observed.

(c) Praseodymium. No irregularities have been found in low temperature studies of praseodymium which could be attributed to a phase transformation. It has been observed, as was noted earlier, that praseodymium exhibits both a f.c.c. and h.c.p. structure. Spedding and Daane,[45] in 1954, noted briefly the existence of a possible transition at 798°C. as indicated by a thermal arrest in cooling curve studies of praseodymium metal.

(d) Neodymium. The electrical resistance results of Jaeger, Bottema and Rosenbohm[38] on 99.5 per cent neodymium were rather inconclusive and were affected somewhat by the acknowledged existence of a thermoelectric effect attributed to the inhomogeneity of the metal sample. There was evidence of a discontinuity occurring at about 550°C. in the resistance-temperature curve which was ascribed to the transition of the normal h.c.p. phase to a f.c.c. modification. No structure evidence was given for the f.c.c. phase. Anomalies also occurred at approximately 515°, 655° and 710°C. in the heat capacity curves which were reproducible only after considerable thermal cycling. A transition was thought to occur at about 500°C. Trombe and Foex,[53] in 1951, investigated the behavior of neodymium containing several tenths per cent impurities, chiefly silicon, with a Chevenard micro-dilatometer over the temperature range -195° to 650°C. The study was carried out in an atmosphere of argon at high temperatures and in hydrogen at low temperatures. A slight anomaly was noted at approximately 600°-650°C. which was believed due to the h.c.p.-f.c.c. transformation reported by Jaeger, Bottema and Rosenbohm[38] as occurring at 500°C. Spedding and Daane,[45] in 1954, reported a thermal arrest for neodymium occurring at 868°C. in a cooling curve investigation in addition to the melting point (1024°C.). (Cooling rates of 10°/minute were employed.) An earlier report from this laboratory (Ahmann,[52] 1953) did not reveal a solid transformation in neodymium containing one per cent magnesium and .5 per cent calcium.

Bates, Leach, Loasby and Stevens,[54] in 1955, investigated the magnetic susceptibility behavior of neodymium from 290°K. to 1000°K. No indications of a phase transition were observed with a sample of 98.81 per cent purity containing chiefly .1 per cent lithium, .07 per cent iron.

### 3. Correlation of crystal structure with resistance

A survey was made of all metals known to exist in more than one phase and for which resistance data were available. Although the structures of metals are limited to a relatively few types, it was hoped that it would be possible to predict the structure of a new phase knowing the original structure of the rare earth metals and the relative resistance change occurring at the transformation. The data reviewed are given in Table 18. As can be observed there is somewhat contradictory evidence between the results of iron and thorium. It should be realized that there are insufficient data available at present to draw any definite conclusions, however, a correlation of this type is believed desirable and should be fairly effective in predicting structure types. Undoubtedly there would be exceptions to any generalizations but the existing evidence indicates a definite relationship between structure and resistance.

Table 18. Structure and resistance data

| Metal | Transition | Resistance Change |
|---|---|---|
| Cr, Ti, Zr | h.c.p. to b.c.c. | decrease |
| Sn | f.c.c. to tetragonal | decrease |
| Mn | b.c.c. to cubic | decrease |
| Mn | cubic to tetragonal | decrease |
| U | orthorhombic to tetragonal | decrease |
| U | tetragonal to b.c.c. | decrease |
| Co, Ni | h.c.p. to f.c.c. | increase |
| Fe | b.c.c. to f.c.c. | increase |
| Th | f.c.c. to b.c.c. | increase |
| Po | cubic to rhombohedral | increase |

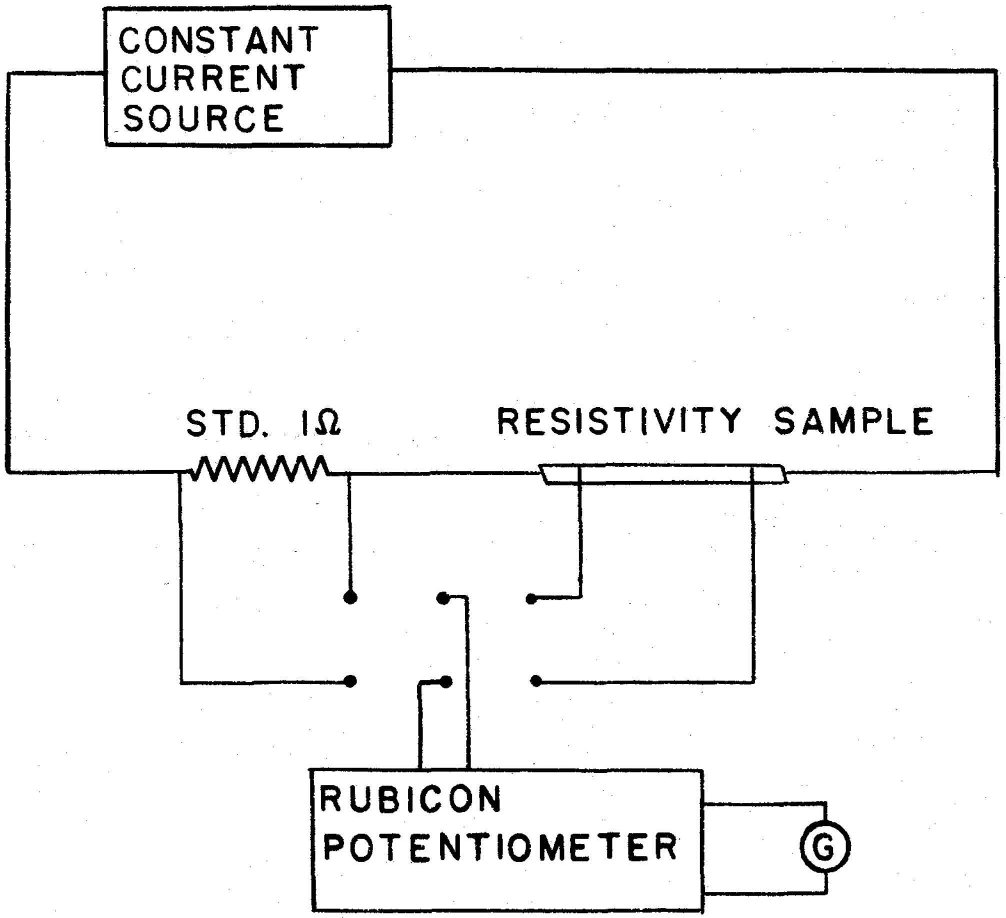
It would appear from the data assembled that the order of decreasing resistance as concerns crystal structure is f.c.c. > tetragonal — h.c.p. > b.c.c.

## C. Equipment

The electrical circuit employed for the potentiometric method of studying the electrical resistivity variation of the rare earth metals with temperature is shown in Figure 15. A Rubicon Type B potentiometer was used with a Rubicon Model 3411 external galvanometer for the E.M. F. measurements. To determine the actual current passing through the resistivity sample the potential across a Rubicon standard one ohm resistance was measured. A constant current source was employed which furnished 50, 100, 150 or 200 milliamps current with a variation of less than ± .01 per cent at 100 milliamps. All electrical leads to the rare earth metal specimen were of .020 inch tantalum wire, the E.M.F. contacts themselves employing .010 inch tantalum. Connections between the rare earth metal and the tantalum leads were made by either crimping or tightly winding the wire around the specimen.

The specimen was supported vertically by tantalum connections in a Vycor sample holder (illustrated in Figure 16) which was placed inside a three inch diameter, 2 1/2 foot long Vycor tube. This tube extended into a well insulated, 25 inch long, Kanthal wound resistance furnace whose heating

Fig. 15 Electrical resistivity circuit.


CONSTANT CURRENT SOURCE
STD. 1Ω
RESISTIVITY SAMPLE
RUBICON POTENTIOMETER
G

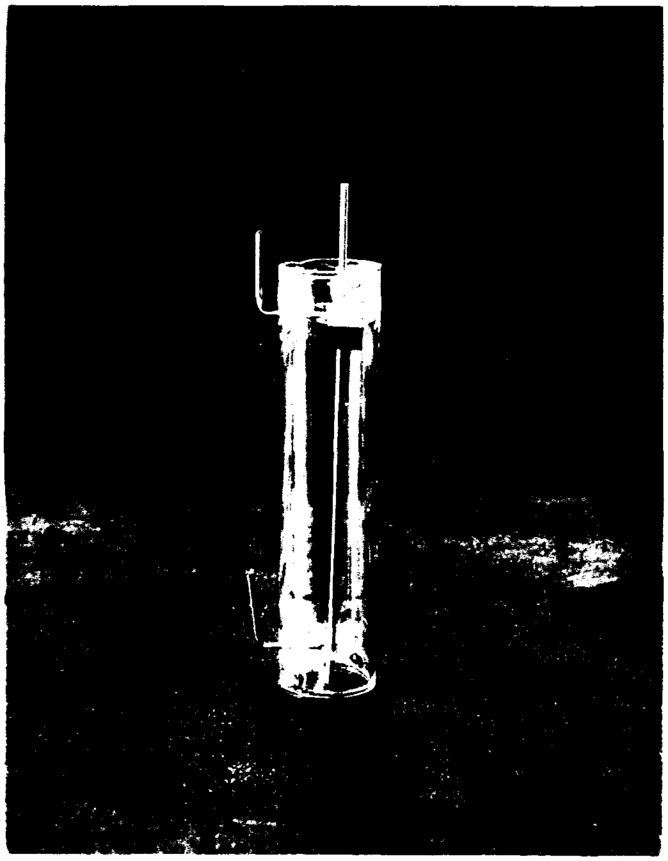


Fig. 16 Electrical resistivity sample holder

and cooling rates were controlled by either a hand or gear driven Powerstat. A chromel-alumel thermocouple positioned at the center of the sample was used to determine the temperature. All electrical and thermocouple leads entered and left the vacuum system through Stupokoff metal-through-glass seals soldered into a water cooled brass head which was sealed to the Vycor tube with Apieyon W wax.

Vacuum conditions were achieved with an H. S. Martin mercury diffusion pump and a Welch mechanical pump; the diffusion pump was trapped with a liquid nitrogen filled Dewar flask.

To measure the length and diameter of the resistivity specimens the General Electric vernier scale illuminator mentioned earlier and a metric micrometer were used respectively.

Bureau of Standard specimens of tin, zinc, aluminum and copper were used to calibrate the chromel-alumel thermocouple and from the data obtained a correction curve was plotted. This was subsequently used in determining the true values of the temperatures measured by the Rubicon potentiometer.

### D. Procedure and technique

All metal samples employed in this investigation were prepared in the Ames Laboratory by the reduction of the rare earth fluoride with calcium in an inert atmosphere. The excess calcium remaining in the rare earth metal was subsequently removed by melting in vacuo. Both of the above processes were carried out in tantalum crucibles. In order to obtain specimens suitable for resistivity investigation the metals were cast in 3/8 inch diameter tantalum crucibles after which the tantalum was machined off. To further reduce the size of the samples they were rolled and finally swaged to the proper dimensions. This was accomplished at room temperature and without the use of a lubricant in order to minimize contamination. A five per cent nitric acid-water solution was used to clean the metals before and after each size reduction and the specimens were annealed in vacuo at approximately 300°-400°C. for about one to two hours between each treatment to relieve the strains incurred. The final dimensions of the rod-shaped specimens were approximately five inches and 1/16-1/8 inches for the length and diameter respectively. At least five measurements of the distance between potential probes were made with the vernier scale illuminator and the values were averaged. These values were estimated to be accurate within ± .1 per cent. A metric micrometer was used to measure the diameter of the specimens, five sets of three measurements each being taken along the length of the specimen between the potential probes. An average for each set of three values was determined and the average of the five sets was taken as the most probable value for the diameter of the specimen. An inaccuracy of approximately ± .4 per cent was estimated for the diameters of the individual resistivity samples. The average values, thus determined, were used in the calculation of the electrical resistivities of the rare earth elements at the various temperatures. No correction was made for the variation of the sample dimensions with temperature.

After placing the sample in the previously outgassed system, all electrical connections were checked and the system was pumped down to about $1 \times 10^{-5}$ mm. mercury before heating was begun. Heating and cooling rates of approximately 2°C./minute were maintained by either a hand or automatically driven Powerstat which furnished power to the resistance furnace. Measurements on the E.M.F. across the potential probes were taken every 20°-25°C., with smaller intervals employed when approaching a suspected anomaly. The temperature was determined before and after each E.M.F. measurement and the average taken as the correct value, while the current passing through the sample was checked each time by measuring the E.M.F. across the standard one ohm resistance. A current of .1 amp was found sufficient to produce an easily measured E.M.F. and is believed incapable of generating significant electrical heat within the sample. Also, the current supplied was sufficiently constant throughout the investigation to allow the value of .100 amp to be used in all calculations.

Although a single thermocouple positioned at the center of the sample was used to evaluate the temperature of the specimen, the furnace was considered sufficiently insulated and of adequate size to insure little, if any, temperature variation within the sample, especially since low heating and cooling rates were employed.

In every case the electrical resistivity as a function of temperature was investigated over the temperature region room temperature to as near the melting point of the individual metals as one could safely approach without causing the sample to sag. At least two heating and cooling cycles were made with each element, the first heating cycle usually being necessary to relieve the strains incurred by the metal in the rolling and swaging processes. The pressure within the vacuum system never exceeded $5 \times 10^{-5}$ mm. mercury and was usually in the $10^{-6}$ mm. mercury region.

From the experimentally measured potential (E) across the metal sample and the current (I) found to be flowing through the specimen, the resistance (R) was easily calculated from Ohm's law.

$$R = E/I$$

Knowing the cross-sectional area (A) and the length (L) of the specimen the electrical resistivity ($\rho$), which is characteristic of the individual metals, was determined from the equation

$$\rho = \frac{R\,A}{L} \text{ ohm. cm.}$$

The calculated resistivity values reported were estimated to be accurate within ± one per cent, with greater accuracy achieved in most cases.

After the completion of each investigation the metal sample was cut into approximately 3/4 inch lengths, mounted in bakelite and examined in the x-ray diffractometer unit. The crystallographic results were given in Table 5 of the previous section. Also, each specimen was spectrographically analyzed for other rare earths, tantalum and common impurities.

## E. Results

All metal samples received essentially identical treatment in their preparation and fabrication as was described earlier. The only varying conditions would have been slight differences in the temperature and time of annealing between the rolling and swaging processes. Table 19 gives the impurities found present in the metals as determined by spectrographic analyses. As was stated earlier, x-ray crystallographic studies at room temperature revealed the

Table 19. Spectrographic analyses data for lanthanum, cerium, praseodymium and neodymium [a,b]

| Impurity | La | Ce | Pr | Nd |
|---|---|---|---|---|
| Ca | $< .04$ | $< .05$ | $< .05$ | $< .05$ |
| Fe | .07 | $< .005$ | $< .005$ | $< .005$ |
| Ta | $\overline{<} .05$ | | | |
| Mg | $< .02$ | $< .02$ | $< .02$ | $< .02$ |
| Si | .02 | $< .01$ | $< .02$ | $< .03$ |
| Pr | .03 | $\overline{<} .03$ | | $\overline{<} .08$ |
| Nd | $\overline{<} .02$ | $\overline{<} .02$ | $\overline{<} .02$ | |
| Ce | $\overline{<} .02$ | | $\overline{<} .1$ | |
| Sm | | | | $< .06$ |
| La | | $\overline{<} .02$ | $\overline{<} .005$ | |

[a] The results of the common impurities are reported with an accuracy of ± 50 per cent while the rare earth values are within ± 100 per cent of the amount reported.

[b] Table 7 gives the meanings of the various symbols.

structure of cerium as being f.c.c. while lanthanum praseodymium and neodymium were found to be h.c.p. with $c_o$ lattice parameters double those values previously reported. No extra diffraction lines were observed which could be attributed to a second allotropic phase.

## 1. Electrical resistivity values

The resistivity values for lanthanum, cerium, praseodymium and neodymium at 25°C. are given in Table 20 along with the experimental data from which they were calculated.

Table 20. Electrical resistivity data and values at 25°C.

| Element | Length (cm.) | Diameter (cm.) | $\rho$ 25°C. x $10^{-6}$ ohm.-cm. | $\rho$ 300°K.[a] x $10^{-6}$ ohm.-cm. |
|---|---|---|---|---|
| La | 9.813 | .2488 | 56.8 | 64.5 |
| Ce | 9.735 | .2161 | 75.3 | 81 |
| Pr | 10.045 | .1796 | 68.0 | 76 |
| Nd | 10.136 | .1873 | 64.3 | 72 |

[a] Values taken from the graphical results of James[10] of this laboratory.

These values are lower than those previously reported which can be interpreted as being due to greater purity of specimen, greater relief of strain through high temperature annealing, or possibly a preferred orientation of the metal crystals resulting in less opposition to electron movement. The first possibility appears to be the more probable.

## 2. Resistivity as a function of temperature

The data showing the variation of electrical resistivity with temperature have been graphically presented in Figures 17 - 27 for lanthanum, cerium, praseodymium and neodymium. Except for lanthanum, the data can be represented by a smooth curve from room temperature to a temperature relatively near the melting points of the respective elements. At this point each metal (lanthanum, cerium, praseodymium and neodymium) exhibits an abrupt increase in resistance over a short temperature interval of approximately 5°-10°C. Enlarged representations of these anomalies are given in Figures 19, 21, 24 and 27 for the individual elements. None of these high temperature irregularities have been previously reported by other laboratories, presumably because they exist beyond the maximum temperature of earlier investigations. Dennison, whose results were reported by Spedding and Daane,[45] in cooling curve studies of the rare earth metals has observed similar irregularities at temperatures which agree with those obtained from the resistivity studies of lanthanum, cerium, praseodymium and neodymium.

Lanthanum, in addition to the high temperature anomaly, also exhibits a slight hysterysis loop between 300° and 450°C. This anomalous effect is more appreciable in the heating cycle than in cooling and appears to become less pronounced with successive cycling but still remains real

Fig. 17 Electrical resistivity of lanthanum: Trial 1

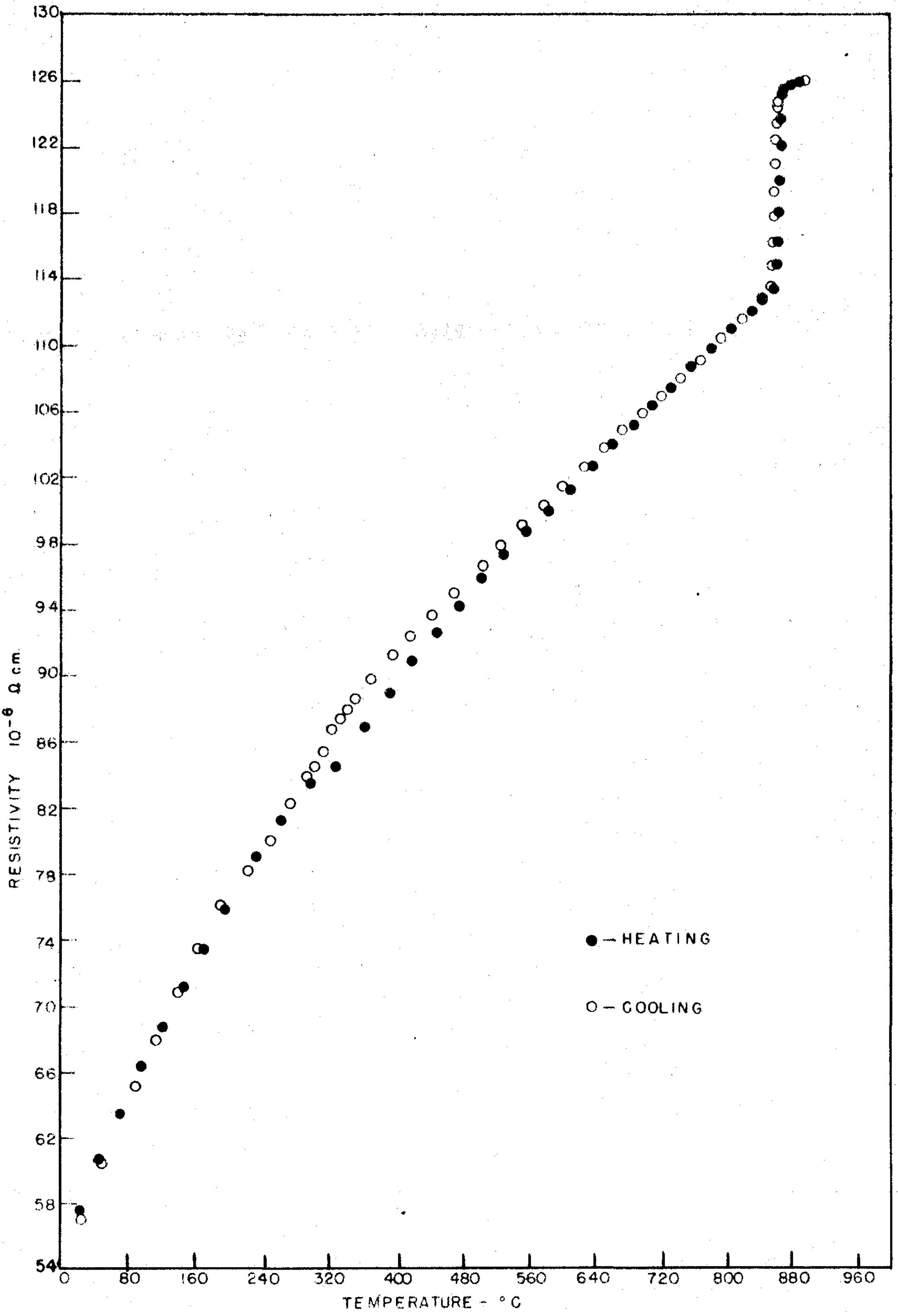

RESISTIVITY 10⁻⁶ Ω cm
130
126
122
118
114
110
106
102
98
94
90
86
82
78
74
70
66
62
58
54
0
80
160
240
320
400
480
560
640
720
800
880
960
TEMPERATURE - °C
● — HEATING
○ — COOLING

Fig. 18 Electrical resistivity of lanthanum: Trial 2

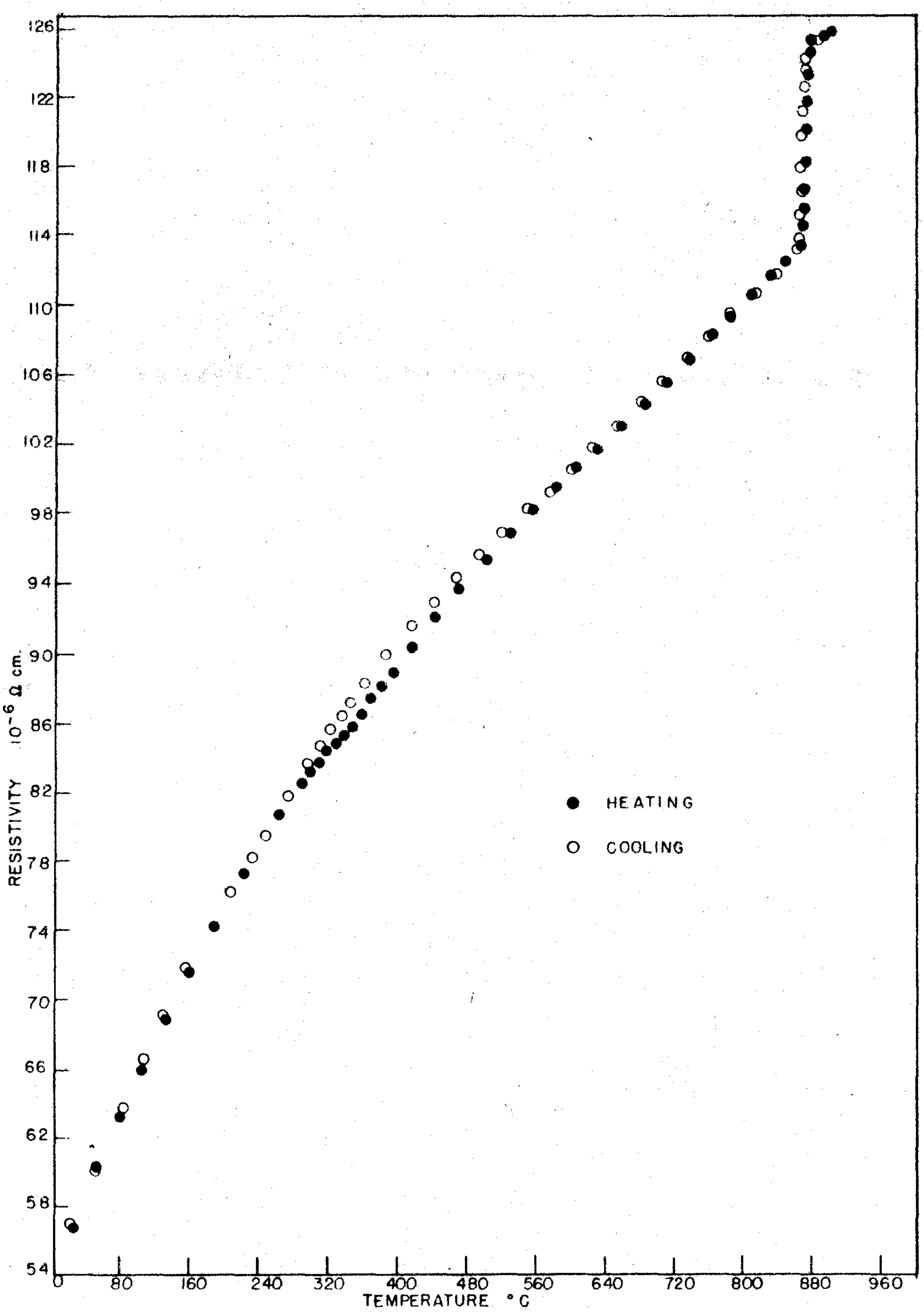

RESISTIVITY $10^{-6}$ Ω cm.
126
122
118
114
110
106
102
98
94
90
86
82
78
74
70
66
62
58
54
0
80
160
240
320
400
480
560
640
720
800
880
960
TEMPERATURE °C
● HEATING
○ COOLING

Fig. 19 Electrical resistivity of lanthanum.

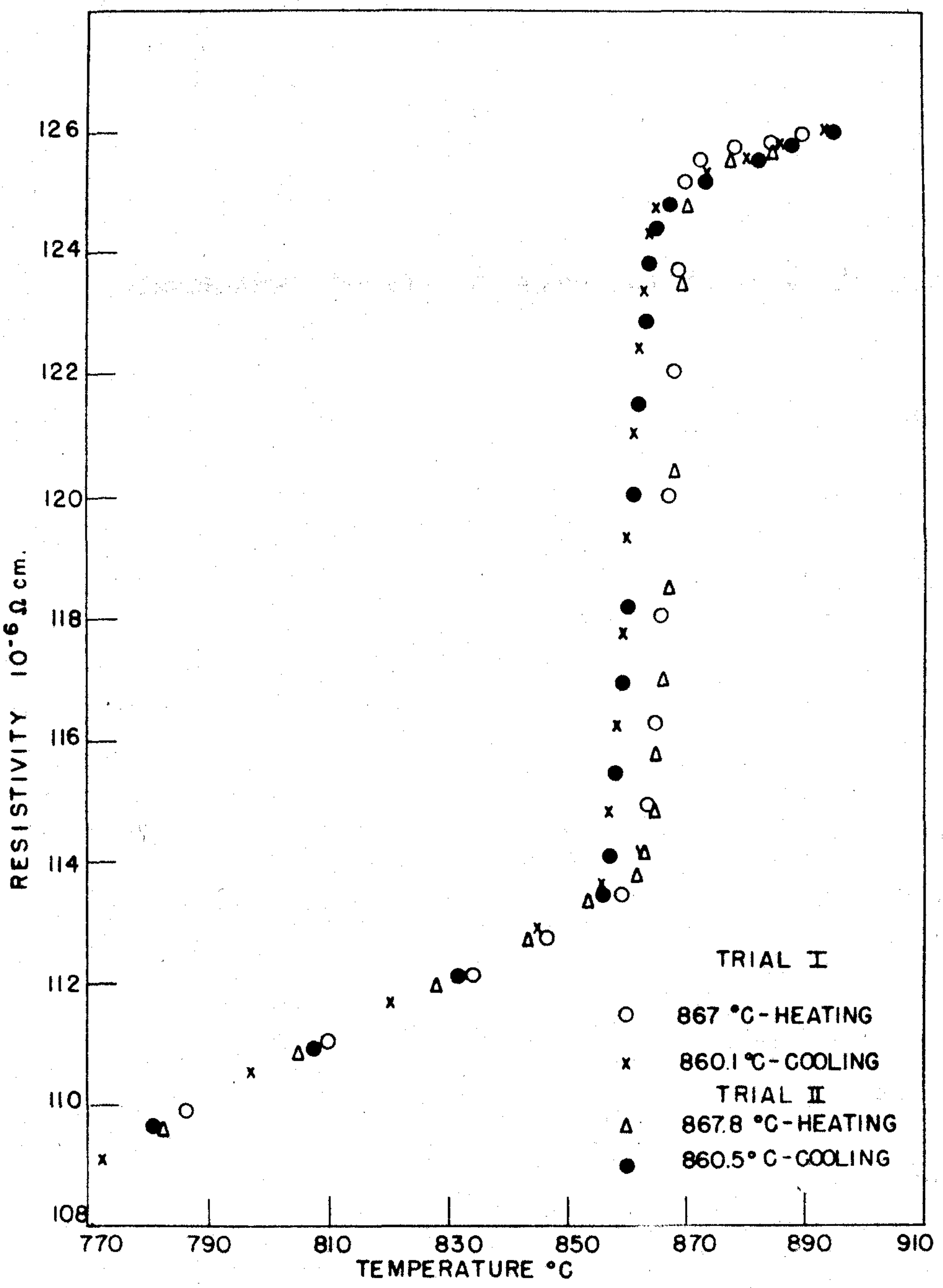

RESISTIVITY 10⁻⁶ Ω cm.
126
124
122
120
118
116
114
112
110
108
770
790
810
830
850
870
890
910
TEMPERATURE °C
TRIAL I
○ 867 °C-HEATING
x 860.1 °C-COOLING
TRIAL II
Δ 867.8 °C-HEATING
● 860.5° C-COOLING

Fig. 20 Electrical resistivity of cerium: Trial 1.

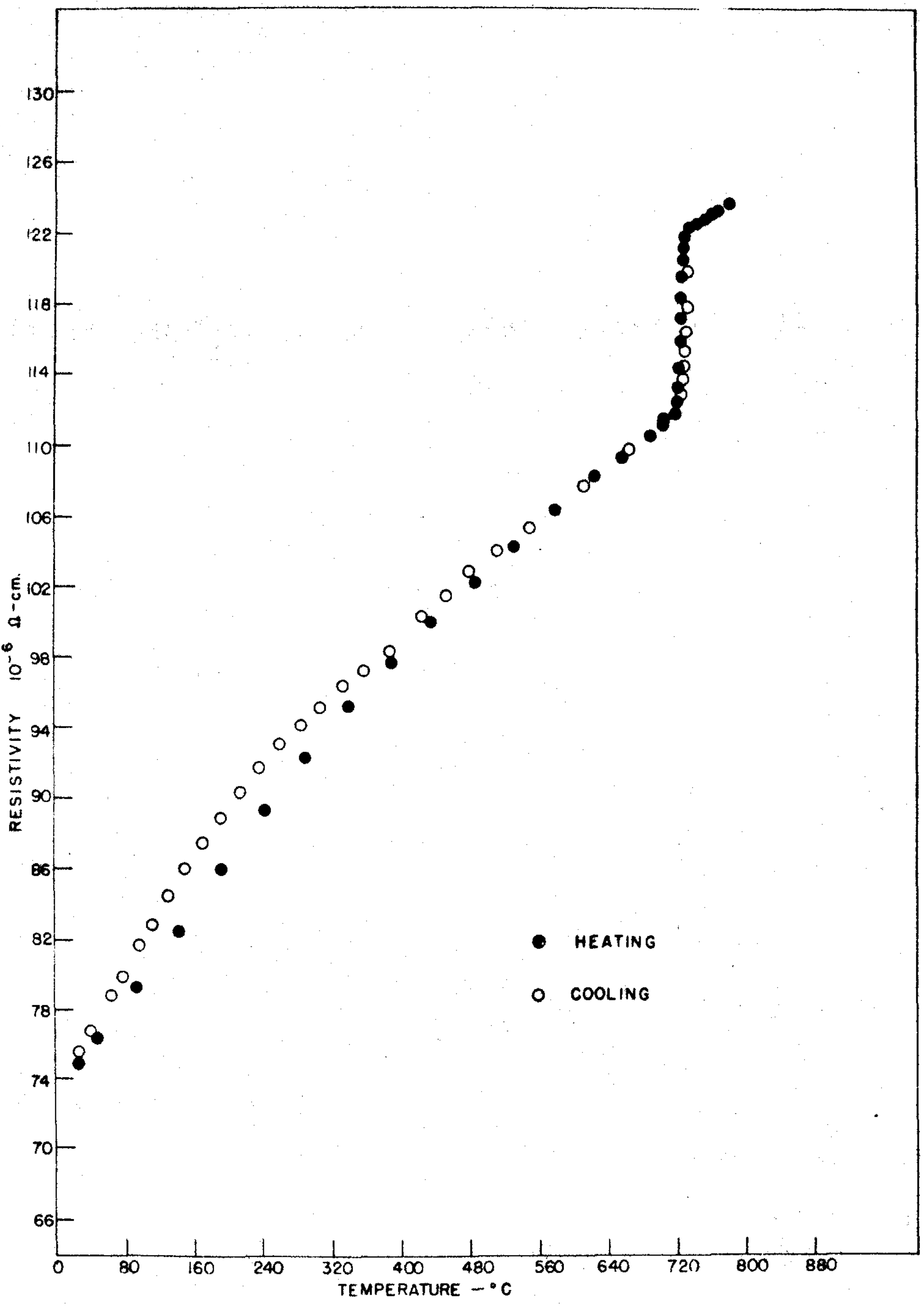

RESISTIVITY $10^{-6}$ Ω-cm.
130
126
122
118
114
110
106
102
98
94
90
86
82
78
74
70
66
0
80
160
240
320
400
480
560
640
720
800
880
TEMPERATURE — °C
● HEATING
○ COOLING

Fig. 21 Electrical resistivity of cerium.

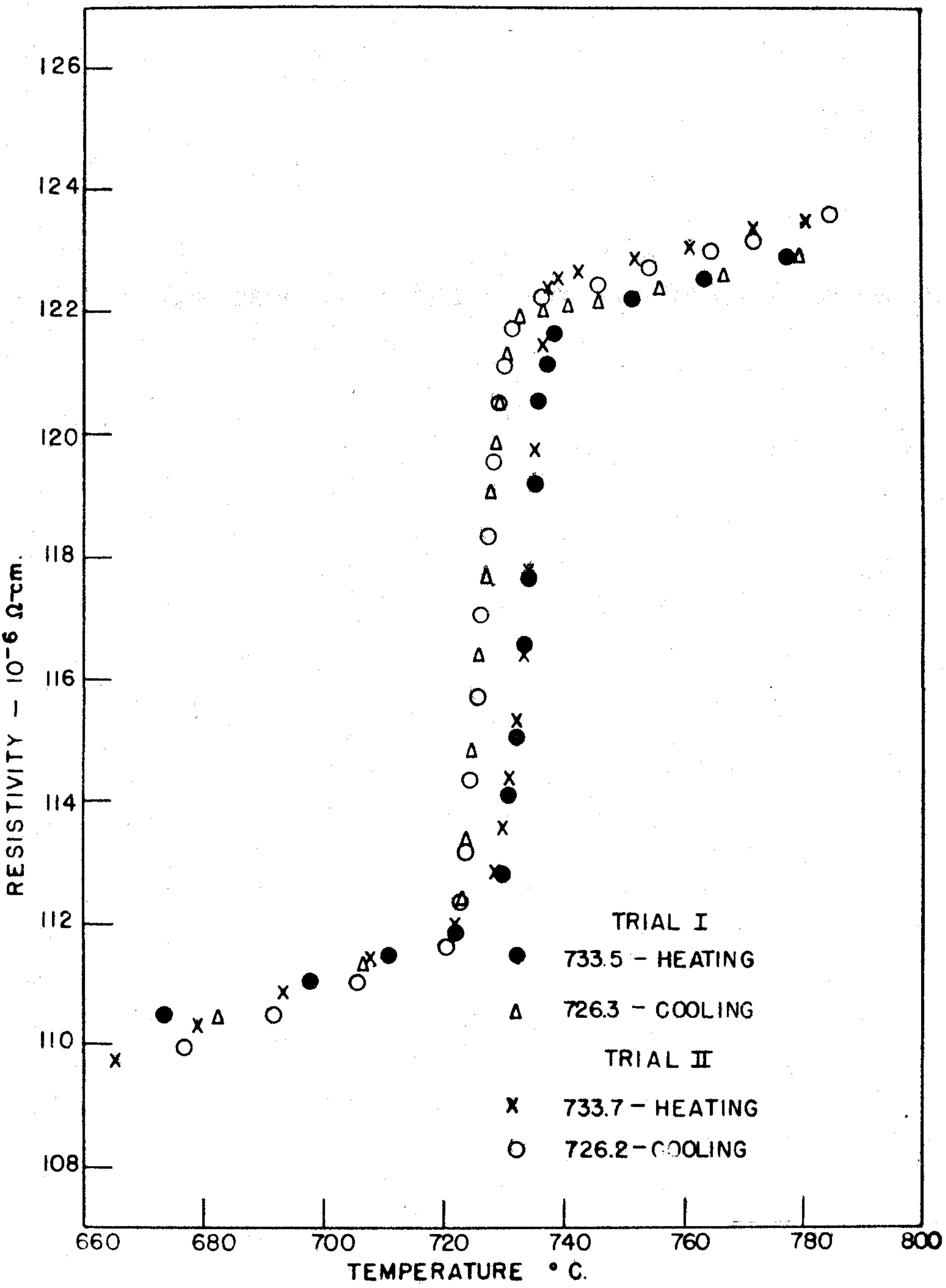

RESISTIVITY — $10^{-6}$ Ω-cm.
126
124
122
120
118
116
114
112
110
108
660
680
700
720
740
760
780
800
TEMPERATURE °C.
TRIAL I
● 733.5 - HEATING
Δ 726.3 - COOLING
TRIAL II
X 733.7 - HEATING
O 726.2 - COOLING

Fig. 22 Electrical resistivity of praseodymium: Trial 1.

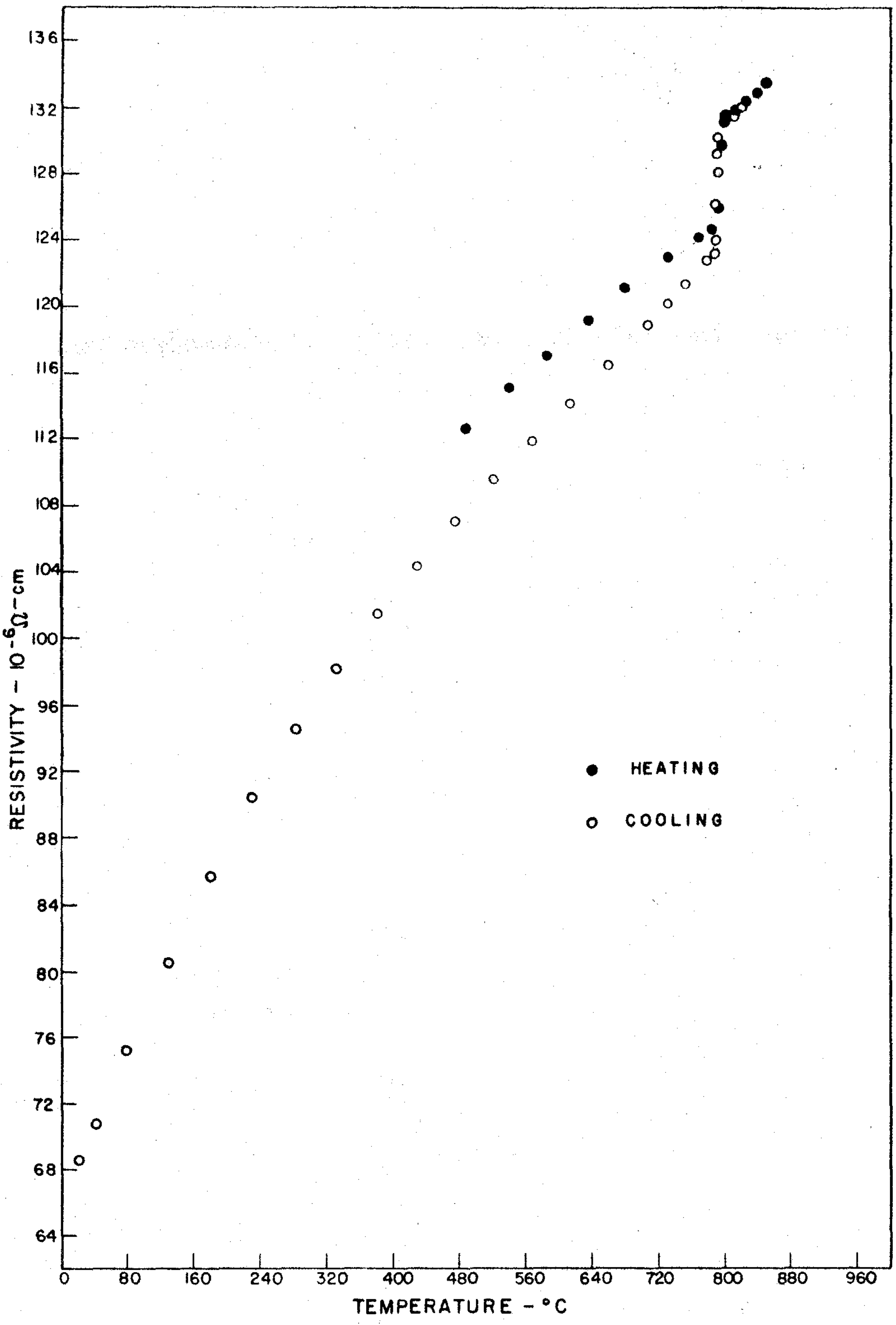

RESISTIVITY - 10⁻⁶ Ω-cm
136
132
128
124
120
116
112
108
104
100
96
92
88
84
80
76
72
68
64
0
80
160
240
320
400
480
560
640
720
800
880
960
TEMPERATURE - °C
● HEATING
○ COOLING

Fig. 23 Electrical resistivity of praseodymium: Trial 2.

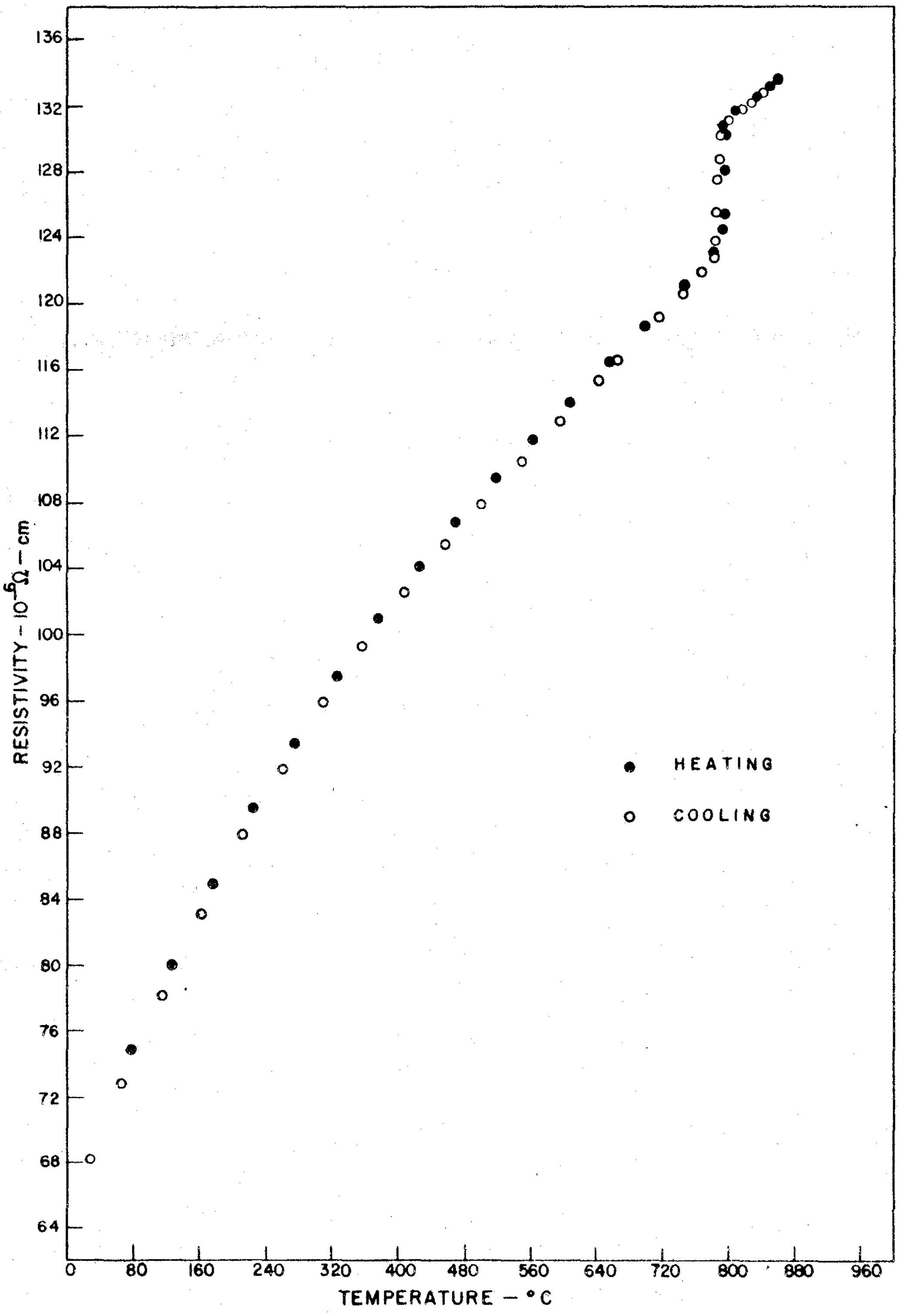

RESISTIVITY - $10^{-6}\Omega$ - cm
136
132
128
124
120
116
112
108
104
100
96
92
88
84
80
76
72
68
64
0
80
160
240
320
400
480
560
640
720
800
880
960
TEMPERATURE — °C
● HEATING
○ COOLING

Fig. 24 Electrical resistivity of praseodymium.

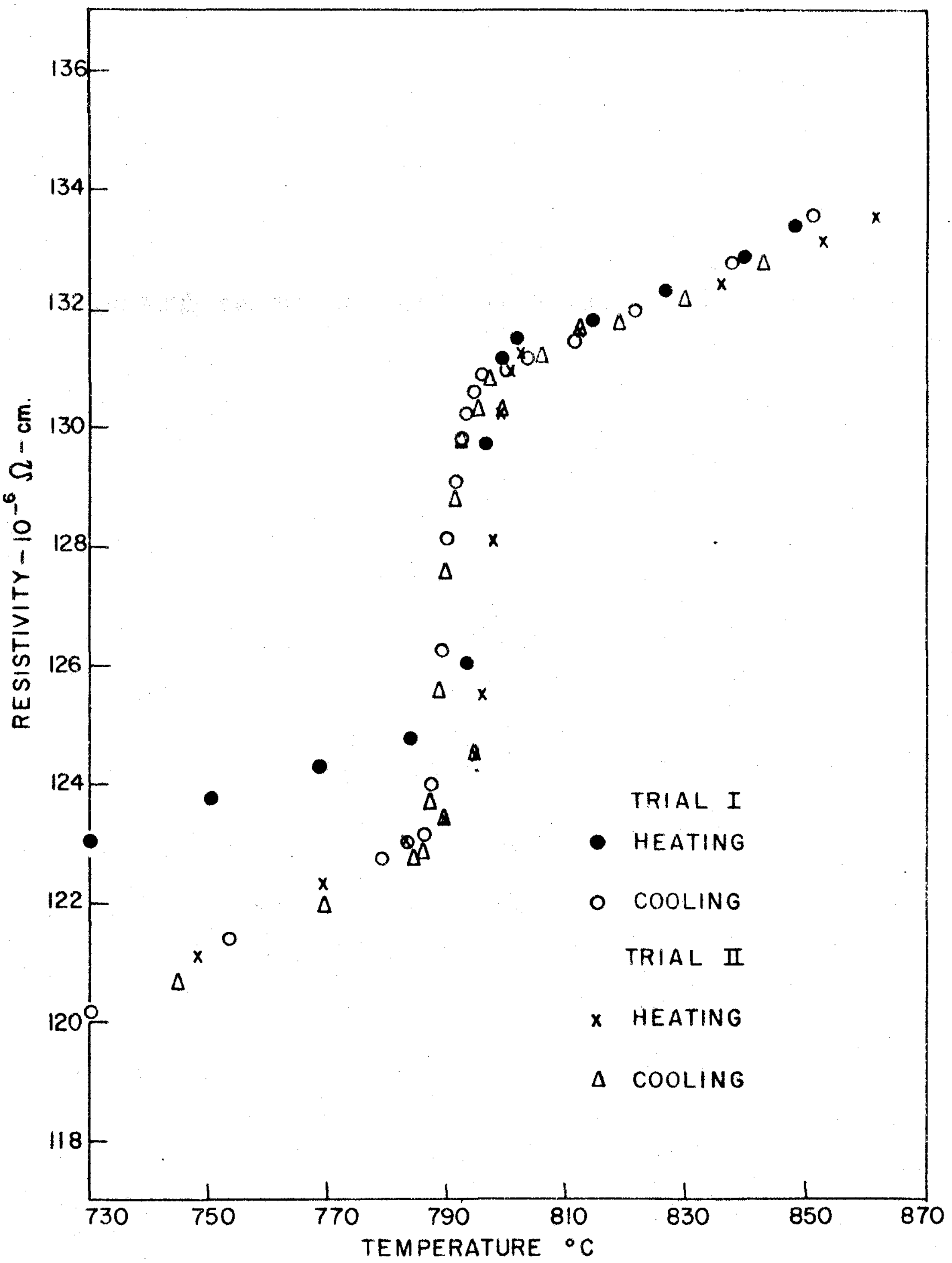

RESISTIVITY - $10^{-6}$ Ω - cm.
TEMPERATURE °C
136
134
132
130
128
126
124
122
120
118
730
750
770
790
810
830
850
870
TRIAL I
● HEATING
○ COOLING
TRIAL II
x HEATING
Δ COOLING

Fig. 25 Electrical resistivity of neodymium: Trial 1.

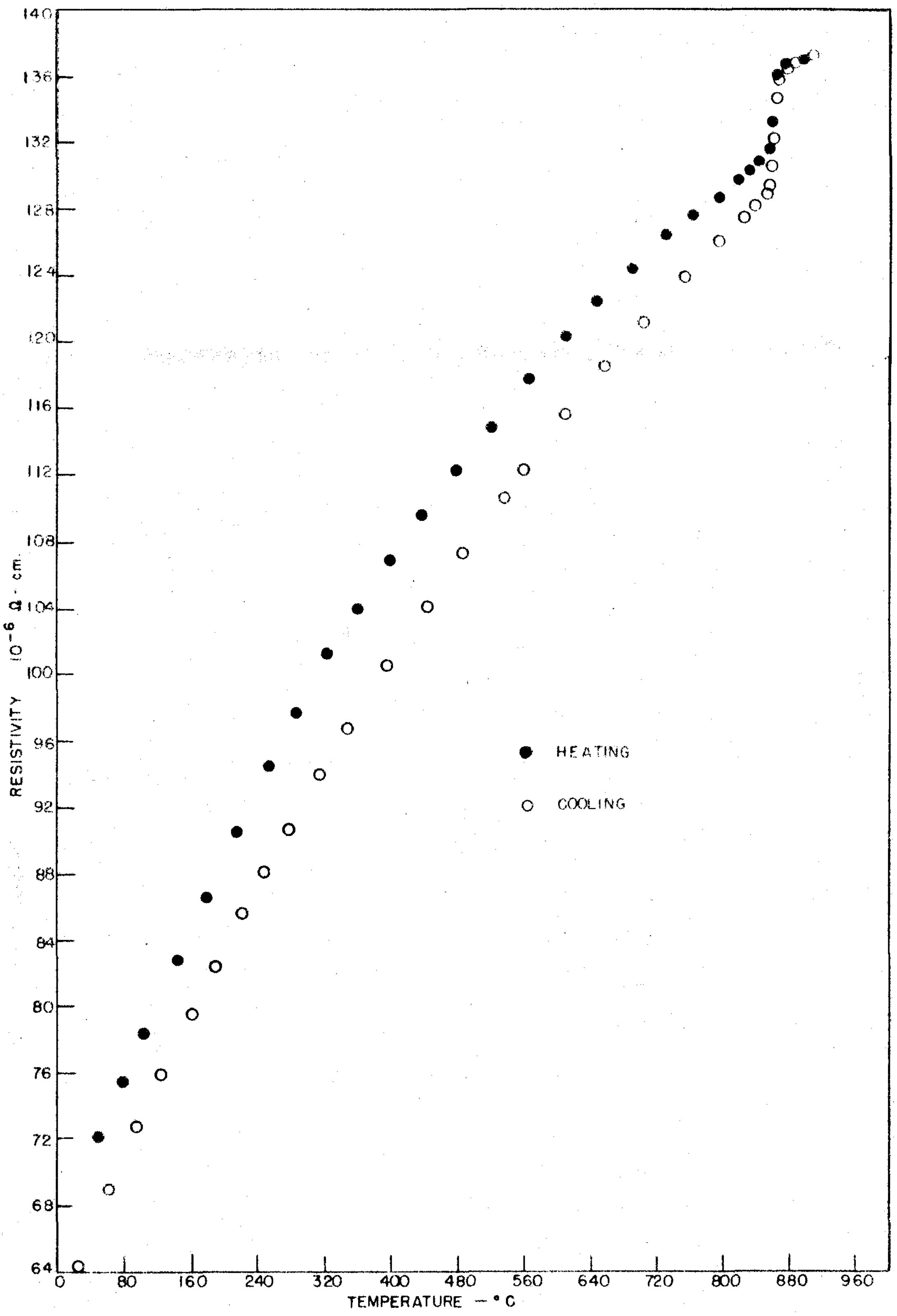

RESISTIVITY $10^{-6}$ Ω · cm
140
136
132
128
124
120
116
112
108
104
100
96
92
88
84
80
76
72
68
64
0
80
160
240
320
400
480
560
640
720
800
880
960
TEMPERATURE — °C
● HEATING
○ COOLING

Fig. 26 Electrical resistivity of neodymium: Trial 2.

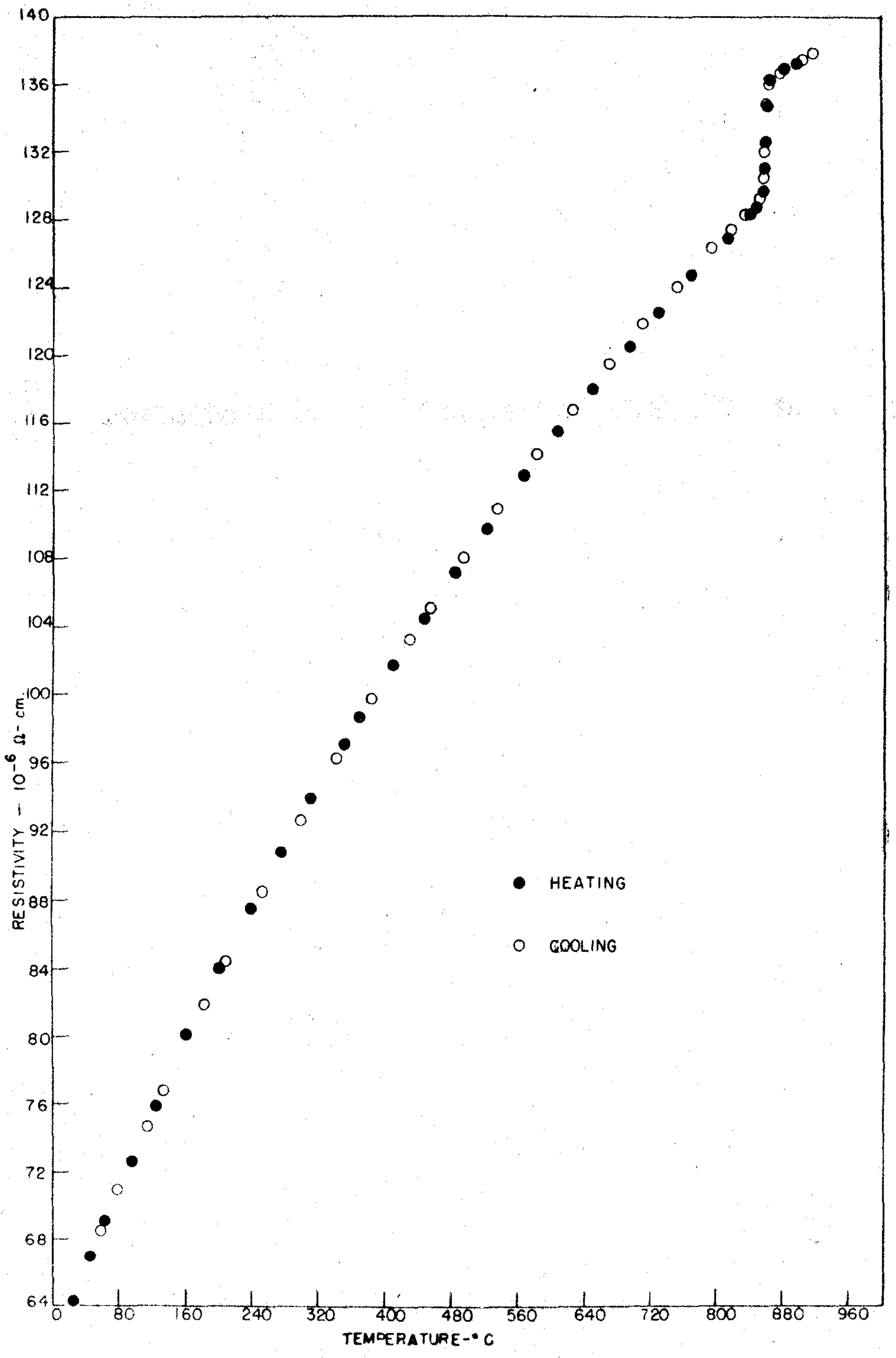
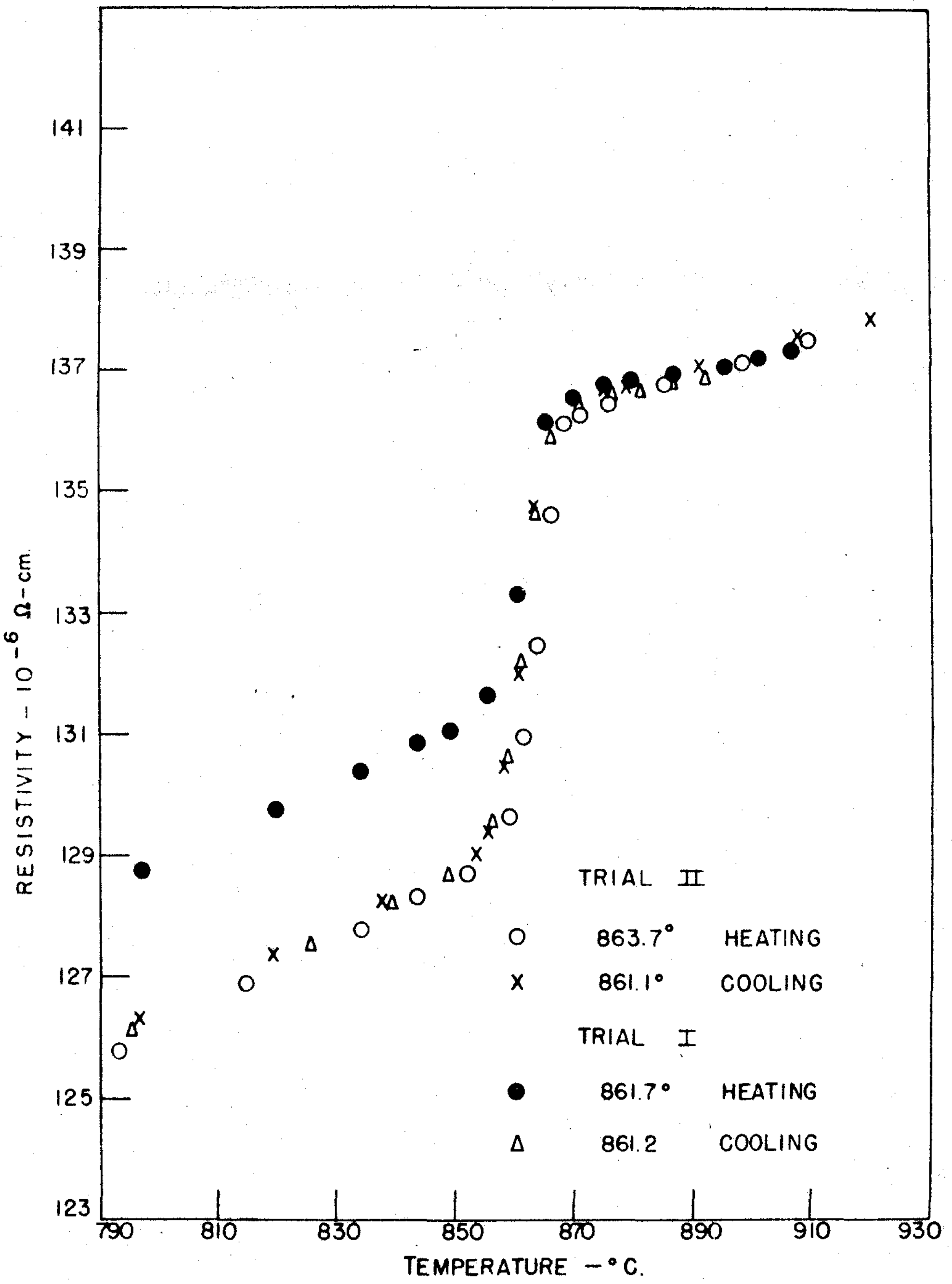

RESISTIVITY — $10^{-6}$ Ω- cm.
140
136
132
128
124
120
116
112
108
104
100
96
92
88
84
80
76
72
68
64
0
80
160
240
320
400
480
560
640
720
800
880
960
TEMPERATURE-°C
● HEATING
○ COOLING

Fig. 27 Electrical resistivity of neodymium.


141
139
137
135
133
131
129
127
125
123
RESISTIVITY - 10$^{-6}$ Ω-cm
790
810
830
850
870
890
910
930
TEMPERATURE -°C.
TRIAL II
○ 863.7° HEATING
X 861.1° COOLING
TRIAL I
● 861.7° HEATING
Δ 861.2 COOLING

after the third heating trial. This peculiarity was not observed in Dennison's[45] cooling curve investigation of lanthanum, however, this method is relatively insensitive to small heat variations. Table 21 lists the temperatures at which lanthanum, cerium, praseodymium and neodymium show anomalous behavior in their resistivity versus temperature plots and also gives the relative resistivity change occurring at the respective transitions.

In the case of praseodymium and neodymium the resistivity values of the first heating trial are appreciably greater than those of subsequent trials. This can be attributed to strains incurred in the fabrication of the samples and their relief on annealing. The cerium and lanthanum specimens had been previously annealed and thus show no such variation.

## F. Discussion

It is difficult to make any definite comparisons or correlations between the resistivity values at 25°C. reported for lanthanum, cerium, praseodymium and neodymium. Of the metals having the same structure type, the resistivity value of lanthanum (56.8 micro-ohm.-cm.) is considerably lower than the closely related values of praseodymium (68.0 micro-ohm.-cm.) and neodymium (64.3 micro-ohm.-cm.). The more open structure of lanthanum may possibly

Table 21. Transformation temperatures of lanthanum, cerium, praseodymium and neodymium

| Element | Trial number | Transition Temperature (°C.) cooling | heating | $R/R_T$[a] |
|---|---|---|---|---|
| La | 1 | 340 | 320 | negligible |
| La | 2 | 340 | 320 | negligible |
| La | 1 | 860.1 | 867.0 | .101 |
| La | 2 | 860.5 | 867.8 | |
| Ce | 1 | 726.3 | 733.5 | .085 |
| Ce | 2 | 726.2 | 733.7 | |
| Pr | 1 | 789.0 | 794.7 | .057 |
| Pr | 2 | 789.0 | 794.7 | |
| Nd | 1 | 861.1 | 863.7 | .054 |
| Nd | 2 | 861.2 | 861.7 | |

[a] $R/R_T$ is the ratio of the resistivity change occurring at the transition to the average resistivity value at the transition temperature observed on heating.

explain this relationship but this is a rather naive interpretation. Cerium has a f.c.c. structure and was observed to have a much higher resistivity value (75.3 micro-ohm.-cm.) even though its atomic volume is very similar to that of praseodymium and neodymium. The high resistivity value for the f.c.c. phase as compared to the h.c.p. form is in agreement with the literature survey involving the relationship of structure type to electrical resistivity.

It would appear at first consideration that the high temperature anomalies exhibited by lanthanum, cerium, praseodymium and neodymium are due to allotropic transformations occurring within the metals, however, no conclusive crystallographic evidence at these temperatures is available to substantiate this interpretation. Assuming these anomalies are due to phase transitions, it is apparent that the transformations are rapid and involve considerable resistance differences, the differences being quite similar for praseodymium and neodymium. The structures usually associated with these rare earths are the irregular h.c.p. and f.c.c. modifications, with which a transition from one to the other can be accomplished by slipping layers from the ABAC, ABAC... pattern to form the ABC, ABC... stacking sequence. This seemingly would involve only a slight energy difference between the two structures and would hardly account for the pronounced irregularities observed in both the resistivity and cooling curve studies, the latter giving a transition phenomena similar in magnitude to that of the melting point. From the literature survey of the resistance changes occurring at the phase transformation temperature of several metals, it was indicated that there is an increase in resistance on the transformation of a h.c.p. phase to the f.c.c. form, and that the order of decreasing resistance as concerns structure type appears to be f.c.c. > tetragonal — h.c.p. > b.c.c.

Undoubtedly there are exceptions to the above order and it should be recognized that there may be considerable resistance variations within structures of the same type. Nevertheless, the survey suggests the possibility of a f.c.c. or tetragonal phase for the high temperature modification.

The lower temperature anomaly of lanthanum is much less pronounced than that occurring at the higher temperature, indicating a relatively slight deviation from the original structure. Crystallographic studies at elevated temperatures, which are still in progress, give evidence that this phenomena is due to a transition of the h.c.p. phase to a f.c.c. modification.

Comparison of the transformation temperatures with those previously reported by other laboratories for lanthanum, cerium, praseodymium and neodymium reveals little agreement. Although the high temperature anomalies occur at temperatures greater than what were attained in the earlier investigations, no evidence was found in this study for those transitions reported at lower temperatures except in the case of lanthanum. The lower transition temperature (300°-450°C.) agrees reasonably well with that reported by Jaeger, Bottema and Rosenbohm[38] (393°-440°C.) and Trombe and Foex[40] (300°-350°C. on heating). Impurities would seem to be the most likely explanation for these disagreeing results, although annealing temperatures, heating and cooling rates and other factors also would be influential.

## IV. SUMMARY

The normal room temperature crystal structures of scandium, yttrium and the rare earth metals were determined by x-ray diffraction methods. Many of the structures previously reported were verified and those of lanthanum and praseodymium were corrected to satisfy the requirements of the data. This necessitated a doubling of the $c_o$ axis reported earlier for the h.c.p. structures of these metals.

With the single exception of europium, each metal studied was examined by back reflection x-ray diffraction techniques. Accurate values for their lattice parameters were calculated by both Cohen's[25] and Thewlis'[26] methods of determining lattice constants, the former being preferred for stated reasons.

From the values of the unit cell dimensions of the metals their mole-atomic volumes, densities, axial ratios (where appropriate) and metallic radii were calculated and compared in graphical form. Microscopic examination of the distilled metals showed strong evidence for the existence of twinning.

To ascertain the regions of stability for the various phases reported for lanthanum, cerium, praseodymium and neodymium, the electrical resistivity of these metals was studied as a function of temperature over the range 20°C. to approximately 20°-100°C. below their melting points. The resistivity values of these elements at 25°C. are tabulated and their transformations are illustrated in their resistivity versus temperature plots.

## V. LITERATURE CITED

1. McLennan, J. C. and McKay, R. W., Trans. Roy. Soc. Can. Sect. III, <u>24</u>, 33 (1930).
2. Quill, L. L., Z. anorg. u. allgem. Chem., <u>208</u>, 273 (1932).
3. Zintl, E. and Neumayr, S., Z. Elektrochem., <u>39</u>, 84 (1933).
4. Rossi, A., Nature (London), <u>133</u>, 174 (1934).
5. Klemm, W. and Bommer, H., Z. anorg. u. allgem. Chem., <u>231</u>, 138 (1937).
6. Bommer, H., Z. Elektrochem., <u>45</u>, 357 (1939).
7. Ziegler, W. T., O.N.R. Tech. Report No. 1, Georgia Inst. Tech., State Eng. Exp. Station (1949).
8. Young, R. A. and Ziegler, W. T., J. Am. Chem. Soc., <u>74</u>, 5251 (1952).
9. Ziegler, W. T., Young, R. A. and Floyd, A. L. Jr., J. Am. Chem. Soc., <u>75</u>, 1215 (1953).
10. James, N. R., Legvold, S. and Spedding, F. H., Phys. Rev., <u>88</u>, 1092 (1952).
11. Farr, J. D., Giorgi, A. L. and Bowman, M. G., U. S. Atomic Energy Commission Report LA-1545 (1953).
12. Hull, A. W., Phys. Rev. Ser. 2, <u>18</u>, 88 (1921).
13. Schumacher, E. E. and Lucas, F. F., J. Am. Chem. Soc., <u>46</u>, 1167 (1924).
14. Lawson, A. W. and Tang, T., Phys. Rev. Ser. 2, <u>76</u>, 301 (1949).
15. Schuch, A. F. and Sturdivant, J. H., J. Chem. Phys., <u>18</u>, 145 (1950).
16. Rossi, A., Atti accad. nazl. Lincei, <u>15</u>, 298 (1932).

17. Klemm, W. and Bommer, H., Z. anorg. u. allgem. Chem., 241, 264 (1939).

18. Ellinger, F. H., J. Metals, 7, 411 (1955).

19. Behrendt, D., Iowa State College, private communication, (1954).

20. Bommer, H., Z. anorg. u. allgem. Chem., 242, 277 (1939).

21. McLennan, J. C. and Monkman, R. J., Trans. Roy. Soc. Can. Sect. III, 23, 255 (1929).

22. Meisel, K., Naturwiss., 27, 230 (1939).

23. Fischer, W., Brunger, K. and Grieneisen, H., Z. anorg. u. allgem. Chem., 231, 54 (1937).

24. Klemm, W., "Anorganische Chemie." Vol. I., p. 48. Wiesbaden, Dieterich, 1949.

25a. Quill, L. L., Z. anorg. u. allgem. Chem., 208, 59 (1932).

25b. Banister, J. R., Legvold, S., and Spedding, F. H., Phys. Rev., 94, 1140 (1954).

26. Cohen, M. V., Rev. Sci. Instr., 6, 68 (1935).

27. Thewlis, J., Acta Cryst., 5, 849 (1952).

28. Nelson, J. B. and Riley, D. P., Proc. Phys. Soc. (London), 57, 164 (1945).

29. Jette, E. R. and Foote, F., J. Chem. Phys., 3, 605 (1935).

30. Daane, A. H., Rundle, R. E., Smith, H. G. and Spedding, F. H., Acta Cryst., 7, 532 (1954).

31. Barrett, C. S., "Structure of Metals." 2d ed. N. Y., McGraw-Hill Book Co., Inc., 1952.

32. Benedicks, C., Svensk Kem. Tid., 27, 136 (1915).

33. Bridgman, P. W. Proc. Am. Acad. Arts Sci., 56, 59 (1921).

34. Bridgman, P. W., Proc. Am. Acad. Arts Sci., 62, 207 (1927).

35. McLennan, J. C., Allen, J. F. and Wilhelm, J. O., Phil. Mag. Ser. 7, 10, 500 (1930).

36. Benedicks, C., Z. Metallkunde, 7, 228 (1915).

37. de Haas, W. J. and Voogd, J., Leiden Comm., 20, Supp. 73b, 22 (1932).

38. Jaeger, F. M., Bottema, J. A. and Rosenbohm, E., Rec. Trav. Chim. Pays-Bas, 57, 1137 (1938).

39. Trombe, F., Compt. rend., 198, 1591 (1934).

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

41. Bridgman, P. W., Proc. Am. Acad. Arts Sci., 76, 55 (1948).

42. Vogel, R. and Heumann, T., Z. Metallkunde, 38, 1 (1947).

43. Massenhausen, W., Z. Metallkunde, 43, 53 (1952).

44. Vogel, R. and Klose, H., Z. Metallkunde, 45, 633 (1954).

45. Spedding, F. H. and Daane, A. H., J. Metals, 6, 504 (1954).

46. Hanaman (1915) Original not available for examination; cited in Loriers, J., Compt. rend., 226, 1018 (1948).

47. Vogel, R., Z. anorg. u. allgem. Chem., 91, 277 (1918).

48. Trombe, F., Compt. rend., 219, 90 (1944).

49. Foex, M., Compt. rend., 219, 117 (1944).

50. Trombe, F., J. recherches centre nat. recherche sci., 29, 65 (1954).

51. Loriers, J., Compt. rend., 226, 1018 (1948).

52. Ahmann, D. H., Iowa State College J. Sci., 27, 120 (1953).

53. Trombe, F. and Foex, M., Compt. rend., 232, 63 (1951).

54. Bates, L. F., Leach, S. J., Loasby, R. G. and Stevens, K. W. H., Proc. Phys. Soc. (London), 68, 181 (1955).